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1989 J. Phys.: Condens. Matter 1 2331

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The peculiarities of electron–nuclear and pseudo-Zeeman interactions of ^{19}F nuclei in $\text{KZnF}_3:\text{Er}^{3+}$

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Received 16 August 1988

Abstract. The investigation of Er^{3+} ($4f^{11}$) ions in a KZnF_3 crystal is carried out by means of electron–nuclear double resonance. The parameters of the interaction of Er^{3+} with F^- ions of the nearest environment are determined. The microscopic calculation of these parameters is carried out. Also, the microscopic calculation of the pseudo-Zeeman interaction parameters is carried out for the first time.

1. Introduction

The paramagnetic atoms having a Γ_8 quartet ground state are very informative in the investigation of electron–nuclear interactions in crystal. This paper contains a report of the continuation of work presented by Falin *et al* (1987) and is concerned with the experimental and theoretical investigation of the interaction of Er^{3+} ($4f^{11} 4I_{15/2}$) ions with fluorine nuclei of the nearest environment in a KZnF_3 crystal. The choice of KZnF_3 crystal is determined by the fact that for the $\text{KZnF}_3:\text{Er}^{3+}$ system the Stark structure of levels and the wavefunctions of the ground state are determined experimentally (Antipin *et al* 1976).

The spin Hamiltonian has five independent parameters differing from that for Kramers ions in a cubic crystal field which have two parameters. Thus it is possible to control the developing theory more rigidly. It is known that the interaction of rare-earth ions with fluorine nuclei differs considerably from a purely dipole–dipole interaction.

We hope to clarify the reasons for such a difference by a more thorough investigation of the $\text{KZnF}_3:\text{Er}^{3+}$ crystal. In particular, in this paper, we study the effects of spin polarisation of the outer 5s and 5p shells in more detail than was done previously in the papers by Anikeenok *et al* (1982, 1984, 1986). Previously the effects of spin polarisation have been used only for the analysis of rare-earth ions in the S state (Watson and Freeman 1961, Casas-Gonzales *et al* 1986). Clarification of their influence on ions with a non-zero orbital moment presents an additional stimulus to develop the theory.

2. Experiment

The present investigation has shown that Er^{3+} in KZnF_3 substitutes Zn^{2+} isomorphically and the charge compensation occurs non-locally (figure 1). In the octahedral crystal field

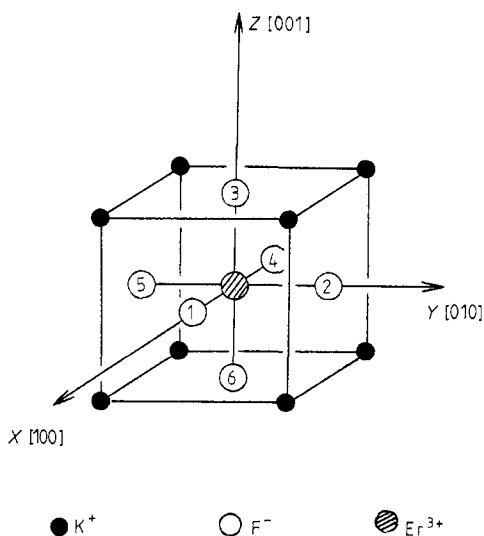


Figure 1. Structure of the admixture centre $(\text{ErF}_6)^{3-}$.

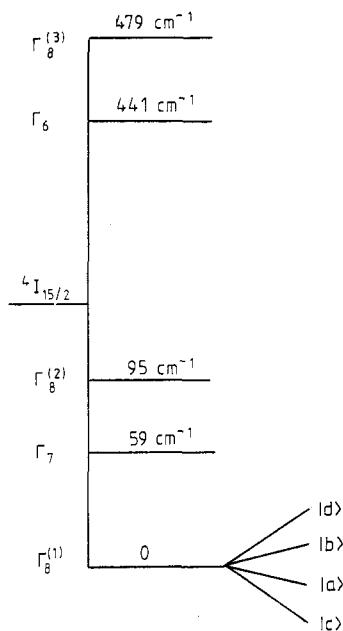


Figure 2. The splitting of the ${}^4I_{15/2}$ term of the Er^{3+} ion in the cubic field of KZnF_3 (Antipin *et al* 1976).

the ground term ${}^4I_{15/2}$ splits into two doublets Γ_6, Γ_7 and three quartets $\Gamma_8^{(1)}, \Gamma_8^{(2)}, \Gamma_8^{(3)}$, one of which is the lowest (figure 2).

The experimental study was carried out by means of ENDOR. The experimental conditions are analogous to those used by Falin *et al* (1987).

The local symmetry of each of the six F_i^- ions ($i = 1, \dots, 6$) corresponds to the D_{4h} group; the Hamiltonian describing the interaction of the central ion and F_i^- in the x, y, z coordinate system has the form

$$\begin{aligned}
 \mathcal{H} = & g\beta\mathbf{H} \cdot \mathbf{S} + g'\beta[4H_z O_3^0 - 3(H_x O_3^1 + H_y \Omega_3^1) + 5(H_x O_3^3 - H_y \Omega_3^3)] \\
 & + a\beta^2 \sum_{k=x,y,z} S_k^2 H_k^2 + b\beta^2 \sum_{\substack{k,l=x,y,z \\ k \neq l}} (S_k S_l + S_l S_k) H_k H_l \\
 & - g_n^F \beta_n \mathbf{H} \cdot \mathbf{I} + \sum_{i=3,6} [A_{\parallel} S_z I_z^i + A_{\perp} (S_x I_x^i + S_y I_y^i)] \\
 & + A_1 O_3^0 I_z^i + A_2 (O_3^1 I_x^i + \Omega_3^1 I_y^i) + A_3 (O_3^3 I_x^i - \Omega_3^3 I_y^i) \\
 & - \beta_n \{ [g_{n1} H_z I_z^i + g_{n2} (H_x I_x^i + H_y I_y^i)] O_2^0 \\
 & + g_{n3} H_z (O_2^1 I_x^i + \Omega_2^1 I_y^i) + g_{n4} (O_2^1 H_x + \Omega_2^1 H_y) I_z^i \\
 & + g_{n5} (H_x I_x^i - H_y I_y^i) O_2^2 + g_{n6} (H_x I_y^i + H_y I_x^i) \Omega_2^2 \} \\
 & + \sum_{i=1,y} [A_{\parallel} S_x I_x^i + A_{\perp} (S_z I_z^i + S_y I_y^i) + \frac{1}{4} \{ A_1 (5O_3^3 - 3O_3^1) I_x^i \\
 & + A_2 [(5\Omega_3^3 - \Omega_3^1) I_y^i + 2(5O_3^2 - O_3^0) I_z^i]
 \end{aligned}$$

$$\begin{aligned}
 & - A_3[(\Omega_3^3 + 3\Omega_3^1)I_y^i - 2(3O_3^2 + O_3^0)I_z^i] \\
 & - \beta_n \{-\frac{1}{2}[g_{n1}H_x I_x^i + g_{n2}(H_y I_y^i + H_z I_z^i)](O_2^0 - 3O_2^2) \\
 & + \frac{1}{2}g_{n3}H_x(2O_2^1 I_z^i + \Omega_2^2 I_y^i) + \frac{1}{2}g_{n4}(2O_2^1 H_z + \Omega_2^2 H_y)I_x^i \\
 & - \frac{1}{2}g_{n5}(H_y I_y^i - H_z I_z^i)(O_2^0 + O_2^2) + 2g_{n6}(H_y I_z^i + H_z I_y^i)\Omega_2^1\} \\
 & + \sum_{i=2,5} [A_{\parallel}S_y I_y^i + A_{\perp}(S_z I_z^i + S_x I_x^i) \\
 & - \frac{1}{4}\{A_1(5\Omega_3^3 + 3\Omega_3^1)I_y^i + A_2[2(5O_3^2 + O_3^0)I_z^i \\
 & + (5O_3^3 + O_3^1)I_x^i] + A_3[2(3O_3^2 - O_3^0)I_z^i - (O_3^3 - 3O_3^1)I_x^i\} \\
 & - \beta_n \{-\frac{1}{2}[g_{n1}H_y I_y^i + g_{n2}(H_z I_z^i + H_x I_x^i)](O_2^0 + 3O_2^2) \\
 & + \frac{1}{2}g_{n3}H_y(\Omega_2^2 I_x^i + 2\Omega_2^1 I_z^i) + \frac{1}{2}g_{n4}(\Omega_2^2 H_x + 2\Omega_2^1 H_z)I_y^i \\
 & + \frac{1}{2}g_{n5}(H_z I_z^i - H_x I_x^i)(O_2^0 - O_2^2) + 2g_{n6}(H_z I_x^i + H_x I_z^i)O_2^2\}
 \end{aligned} \tag{1}$$

where O_m^n and Ω_m^n are spin operators (Altshuler and Kozyrev 1972); $A_{\parallel}, A_{\perp}, A_1, A_2$ and A_3 are the components of transferred hyperfine interaction (THFI); g_{n1}, \dots, g_{n6} are the parameters characterising the nuclear pseudo-Zeeman interaction. The Hamiltonians of the interaction of Er^{3+} with F^- situated in x, y axes have been obtained by means of transformation of the corresponding local axes to the general coordinate system.

The total Hamiltonian of the complex (the central ion and the atoms of the nearest environment) were averaged on the electron states with accuracy up to second order of the perturbation theory in the usual THFI and up to first order in the other terms in (1) using the approximation of the usual strong electron Zeeman interaction. Then the expressions for the frequencies of ENDOR transition for all F_{1-6}^- ions were obtained from the operator containing nuclear variables.

$$\nu_{3,6}^2 = (P - C_1)^2 \cos^2 \vartheta + (Q - C_2)^2 \sin^2 \vartheta + C_3^2 \tag{2}$$

where

$$P = MA_{\parallel} - \mu(M)A_{\perp}^2 - \nu_L$$

$$Q = MA_{\perp} - \mu(M)A_{\parallel}A_{\perp} - \nu_L$$

$$C_1 = \frac{1}{2}\{A_1(3 - 5 \cos^2 \vartheta)O_3^0 + \beta_n[-g_{n1}(1 - 3 \cos^2 \vartheta) + g_{n4} \sin^2 \vartheta]O_2^0 H\}$$

$$\begin{aligned}
 C_2 = \frac{1}{2}\{ & A_2(1 - 5 \cos^2 \vartheta) - A_3 \cos 4\varphi \sin^2 \vartheta\}O_3^0 + \beta_n[-g_{n2}(1 - 3 \cos^2 \vartheta) \\
 & + g_{n3} \cos^2 \vartheta + (g_{n5} \cos^2 2\varphi + g_{n6} \sin^2 2\varphi) \sin^2 \vartheta]O_2^0 H\}
 \end{aligned}$$

$$C_3 = -\frac{1}{2}\{A_3 O_3^0 + \frac{1}{2}\beta_n(g_{n6} - g_{n5})O_2^0 H\} \sin 4\varphi \sin^3 \vartheta.$$

$$\begin{aligned}
 \nu_{1,4}^2 = & (P - C_1')^2 \cos^2 \varphi \sin^2 \vartheta + (Q - C_2')^2 \sin^2 \varphi \sin^2 \vartheta \\
 & + (Q - C_2' - C_3')^2 \cos^2 \vartheta
 \end{aligned} \tag{3}$$

where

$$\begin{aligned}
 C_1' = \frac{1}{2}\{ & A_1(3 - 5 \cos^2 \varphi \sin^2 \vartheta)O_3^0 - \frac{1}{2}\beta_n[g_{n1}(3 \cos^2 \vartheta - 3 \cos 2\varphi \sin^2 \vartheta - 1) \\
 & - 2g_{n4}(1 - \cos^2 \varphi \sin^2 \vartheta)]O_2^0 H\}
 \end{aligned}$$

Table 1. Spin Hamiltonian parameters. The following values were taken from the work of Korableva (1978): $g = 3.990(5)$; $g' = -0.035(5)$; $a = -0.081 \text{ cm}^{-1}$; $b, g_{n3}, g_{n4}, g_{n5} = 0$.

Fluorine shell	A_{\parallel} (MHz)	A_{\perp} (MHz)	A_1 (MHz)	A_2 (MHz)	A_3 (MHz)	g_{n1}	g_{n2}	g_{n6}
1	25.16(5)	-22.56(5)	0.58(5)	-0.42(5)	-0.11(5)	0.03(1)	0.02(1)	0.03(1)
2	3.28(3)	-1.63(3)						
3	1.35(2)	-0.65(2)						

$$\begin{aligned}
 C'_2 &= \frac{1}{2}\{A_2(1 - 5 \cos^2 \varphi \sin^2 \vartheta) + A_3[3 - (4 - \cos^2 \varphi) \sin^2 \vartheta]\}O_3^0 \\
 &\quad - \frac{1}{4}\beta_n[g_{n2}(3 \cos^2 \vartheta - 3 \cos 2\varphi \sin^2 \vartheta - 1) - 2g_{n3} \cos^2 \varphi \sin^2 \vartheta \\
 &\quad - g_{n5}(1 - \cos 2\varphi \sin^2 \vartheta - 3 \cos^2 \vartheta) - g_{n6} \cos^2 \vartheta]O_2^0 H \\
 C'_3 &= -\frac{1}{4}\{5A_2 \cos 2\varphi \sin^2 \vartheta + A_3[8 - (19 - 14 \cos^2 \varphi) \sin^2 \vartheta]\}O_3^0 \\
 &\quad + \frac{1}{2}\beta_n[g_{n5}(\cos 2\varphi \sin^2 \vartheta + 3 \cos^2 \vartheta - 1) - 2g_{n6}(\cos 2\vartheta \\
 &\quad + \cos^2 \varphi \sin^2 \vartheta)]O_2^0 H. \\
 \nu_{2,5}^2 &= (P - C''_1)^2 \sin^2 \varphi \sin^2 \vartheta + (Q - C''_2)^2 \cos^2 \varphi \sin^2 \vartheta \\
 &\quad + (Q - C''_2 - C''_3)^2 \cos^2 \vartheta \tag{4}
 \end{aligned}$$

where

$$\begin{aligned}
 C''_1 &= \frac{1}{2}A_1(3 - 5 \sin^2 \varphi \sin^2 \vartheta)O_3^0 - \frac{1}{4}\beta_n[g_{n1}(3 \cos 2\varphi \sin^2 \vartheta \\
 &\quad + 3 \cos^2 \vartheta - 1) - 2g_{n4}(1 - \sin^2 \varphi \sin^2 \vartheta)]O_2^0 H \\
 C''_2 &= \frac{1}{2}\{A_2(1 - 5 \sin^2 \varphi \sin^2 \vartheta) + A_3[3 - (4 - \sin^2 \varphi) \sin^2 \vartheta]\}O_3^0 \\
 &\quad - \frac{1}{4}\beta_n[g_{n2}(3 \cos^2 \vartheta + 3 \cos 2\varphi \sin^2 \vartheta - 1) \\
 &\quad - 2g_{n3} \sin^2 \varphi \sin^2 \vartheta - g_{n5}(1 + \cos 2\varphi \sin^2 \vartheta - 3 \cos^2 \vartheta) \\
 &\quad - g_{n6} \cos^2 \vartheta]O_2^0 H \\
 C''_3 &= -\frac{1}{4}\{-5A_2 \cos 2\varphi \sin^2 \vartheta + A_3[8 - (19 - 14 \sin^2 \varphi) \sin^2 \vartheta]\}O_3^0 \\
 &\quad + \frac{1}{2}\beta_n[g_{n5}(-\cos 2\varphi \sin^2 \vartheta + 3 \cos^2 \vartheta - 1) \\
 &\quad - 2g_{n6}(\cos 2\vartheta + \sin^2 \varphi \sin^2 \vartheta)]O_2^0 H.
 \end{aligned}$$

M is the projection of the electron spin on the direction of the constant magnetic field H , $\mu(M) = [S(S+1) - M^2]/2g\beta H$ and $\nu_L = g_n^F \beta_n H$.

In the experiments, H changed in the x - y plane and made an angle φ with the x axis ($\vartheta = 90^\circ$ (figure 1)). The investigation and analysis of ENDOR spectra are similar to those given by Falin *et al* (1987). The experimental values of the parameters of the spin Hamiltonian and the data on the interaction of Er^{3+} with ^{19}F nuclei forming the second and third coordination spheres of the environment are given in table 1.

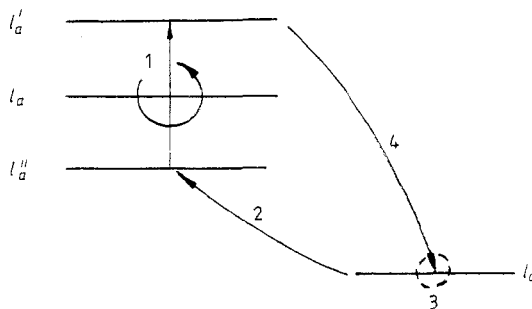


Figure 3. A schematic diagram of the appearance of the local field on the ligand nucleus due to the polarisation of the filled l_a'' shell of the rare-earth ion.

3. Theory

According to Anikeenok *et al* (1986) the A_i components of the THFI tensor are obtained by averaging the Hamiltonian of electron–nuclear interactions of the general form

$$\mathcal{H}_1 = \sum b^{(j)k} [(R^{(j)} I^{(1)})^{(k)} C^{(k)}] \quad (5)$$

where $R^{(j)}$ are irreducible tensor operators, $I^{(1)}$ the spherical components of the nuclear spin I , $b^{(j)k}$ the combinations of the transfer integrals and $C^{(k)}$ the spherical tensors of the angles ϑ and φ . In our case, $C^{(k)} = 1$. The reduced matrix elements of the operators $W^{(1k)j}$ and $V^{(j)}$ for the ground state $|4f^{11} 4I_{15/2}\rangle Er^{3+}$ have been given by Anikeenok *et al* (1984). The effects of the spin polarisation of the outer filled 5s and 5p shells of the rare-earth ions are accounted for by means of the configurational interaction method. A diagram of the virtual electron transfer is given in figure 3. The line labelled 1 corresponds to the Coulomb interaction of the electrons. l_a'' , l_a and l_a' denote the orbital quantum numbers of the filled, non-filled (4f) and empty shells, respectively. l_c is the quantum number of the ligand shells. The broken circle in figure 3 corresponds to the hyperfine interaction of ligand electrons from shell l_c with nuclear spin I . Lines 2 and 4 correspond to the electron jumps.

The matrix elements of the irreducible tensor operators $R^{(j)}$ are determined by

$$(JM|R^{(j)}|JM) = (-1)^{J-M} \begin{pmatrix} J & j & J \\ -M & m & M \end{pmatrix}. \quad (6)$$

Here $I^{(1)}$ are spherical components of the ligand nuclear spin. The quantities $b^{(j)k}$ are determined by the expression

$$\begin{aligned} b^{(j)k} = & -\sqrt{\frac{2j+1}{2}} J^{(0)k} (\bar{\psi}J \| W^{(1k)j} \| \bar{\psi}J) g^{(k)} \\ & - 15 \sqrt{\frac{2j+1}{2}} \sum_{k_1} \left\{ \begin{matrix} k_1 & j & 1 \\ 1 & 2 & k \end{matrix} \right\} (\bar{\psi}J \| W^{(1k_1)j} \| \bar{\psi}J) g^{(k_1)} J_2^{(2k_1)k} \\ & + 5 \sqrt{\frac{3}{2}} (\bar{\psi}J \| V^{(j)} \| \bar{\psi}J) g^{(j)} J^{(1)k} \end{aligned} \quad (7)$$

$$J^{(0k)k} = (-1)^{l'_a} \begin{pmatrix} l'_a & k & l''_a \\ 0 & 0 & 0 \end{pmatrix} \sum \lambda_{ns} a_{s,s'} \lambda_{n's'} \quad (8)$$

$$j^{(2k_1)k} = \sum_{qm'm'} (-1)^{2+k_1+q} \sqrt{2k+1} \begin{pmatrix} 2 & k_1 & k \\ -q & q & 0 \end{pmatrix} (-1)^{l'_a-m'} \\ \times \sqrt{2k_2+1} \begin{pmatrix} l'_a & k_1 & l''_a \\ -m' & q & m'' \end{pmatrix} (-1)^{l'_c-m'} \begin{pmatrix} l'_c & 2 & l'_c \\ -m' & q & m'' \end{pmatrix} \\ \times \lambda_{l'_a m'} a_p \lambda_{l''_a m''} \quad (9)$$

$$j^{(1k_1)k} = \sum_{qm'm'} (-1)^{1+k_1+q} \sqrt{2k+1} \begin{pmatrix} 1 & k_1 & k \\ -q & q & 0 \end{pmatrix} (-1)^{l'_a-m'} \\ \times \sqrt{2k_1+1} \begin{pmatrix} l'_a & k_1 & l''_a \\ -m' & q & m'' \end{pmatrix} (-1)^{l'_c-m'} \begin{pmatrix} l'_c & 1 & l'_c \\ -m' & q & m'' \end{pmatrix} \\ \times \lambda_{l'_a m'} a_p \lambda_{l''_a m''} \quad (10)$$

$$g^{(j)} = 2 \sum_{k_2} (-1)^{j+k_2+1} (l'_a \| C^{k_2} \| l_a) (l_a \| C^{k_2} \| l''_a) \\ \times \left\{ \begin{matrix} l'_a & l''_a & j \\ l_a & l_a & k_2 \end{matrix} \right\} \frac{R^{(k_2)}(l_a, l'_a; l''_a, l_a)}{|\Delta_{l'_a l''_a}|} \quad (11)$$

$$\bar{g}^{(j)} = \frac{2}{|\Delta_{l'_a l''_a}|} \left(\frac{2\Theta_1^{(j)}}{2j+1} + \sum_{k_2} (-1)^{j+k_2+1} \left\{ \begin{matrix} l'_a & l''_a & j \\ l_a & l_a & k_2 \end{matrix} \right\} \Theta_2^{(k_2)} \right). \quad (12)$$

The quantities $\Theta_1^{(j)}$ and $\Theta_2^{(k_2)}$ are well known in the theory of crystal-field shielding of 4f electrons (Rajnak and Wybourne 1964).

The pseudo-nuclear Zeeman interaction is calculated easily based on operator (5). The effective operator of the interaction of F⁻ nuclei with a magnetic field has the form

$$\mathcal{H}_{\text{eff}} = [\langle \psi_0 | \sum b^{(j)k} (\{R^{(j)} I^{(1)}\}^{(k)} C^{(k)}) | \psi_n \rangle \langle \psi_n | g_j \beta H J | \psi_0 \rangle + \text{CC}] (E_n - E_0)^{-1} \quad (13)$$

where g_j is the Lande factor.

The values of the transfer integrals obtained may be used to estimate the intrinsic parameters of the crystal field. The crystal-field operator may be written in the form

$$\mathcal{H}_{\text{cr}} = \sum_{k,q} a^{(k)}(R_b) (-1)^q C_q^k(r_a) C_{-q}^k(\vartheta_b, \varphi_b) = \sum_{k,q} B_q^k C_q^k \quad (14)$$

where $C_{-q}^k(\vartheta_b, \varphi_b)$ are spherical tensors of the angles ϑ_b, φ_b , fixing the direction of the axis of the metal-ligand pair relative to the chosen coordinate system, C_q^k are spherical tensors operating within the states of the 4f shell and $a^{(k)}(R_b)$ are the intrinsic potentials of the crystal field (Newman 1971). According to Eremin (1988), $a^{(k)}$ are determined by the following expressions:

$$a^{(2)} = -Z'_c e^2 (\langle r^2 \rangle / R_c^3) (1 - \sigma_2) + (5/4\pi) (R_{4f}^2 C_0^2 | V_c) \\ + \frac{1}{2} (T_\sigma S_{4f\sigma} + T_s S_{4f2s} + \frac{3}{2} T_\pi S_{4f\pi}) \\ - \frac{5}{2} (\varepsilon_{4f} - \varepsilon_a - \varepsilon_c + e^2/R + \alpha) (S_{4f\sigma}^2 + S_{4f2s}^2 + \frac{3}{2} S_{4f\pi}^2)$$

$$\begin{aligned}
 & -\frac{5}{7}[\epsilon_{2p}(S_{4f\sigma}^2 + \frac{3}{2}S_{4f\pi}^2) + \epsilon_{2s}S_{4f2s}^2] + \frac{5}{7}[\Delta_{2p4f}(\gamma_{4f\sigma}^2 + \frac{3}{2}\gamma_{4f\pi}^2) \\
 & + \Delta_{2s4f}\gamma_{4fs}^2] + [\frac{4}{3}F^{(2)}(f, d) - \frac{1}{8}G^{(1)}(f, d) \\
 & + \frac{1}{14}G^{(3)}(f, d) - \frac{1}{16}G^{(5)}(f, d)](\gamma_{5d\sigma}^2 + \gamma_{5d\pi}^2)
 \end{aligned} \tag{15}$$

$$\begin{aligned}
 a^{(4)} = & -Z'_c e^2 \langle r^4 \rangle / R_c^5 + (9/4\pi)(R_{4f}^2 C_0^4 | V_c) + \frac{1}{7} (T_\sigma S_{4f\sigma} \\
 & + T_s S_{4f2s} + \frac{1}{3} T_\pi S_{4f\pi}) - \frac{9}{7} (\epsilon_{4f} - \epsilon_a - \epsilon_c + e^2/R + \alpha) \\
 & \times (S_{4f\sigma}^2 + S_{4f2s}^2 + \frac{1}{3} S_{4f\pi}^2) - \frac{9}{7} [\epsilon_{2p}(S_{4f\sigma}^2 + \frac{1}{3} S_{4f\pi}^2) \\
 & + \epsilon_{2s} S_{4f2s}^2] + \frac{9}{7} [\Delta_{2p4f}(\gamma_{4f\sigma}^2 + \frac{1}{3} \gamma_{4f\pi}^2) + \Delta_{2s4f} \gamma_{4fs}^2] \\
 & + [\frac{4}{3} F^{(4)}(f, d) - \frac{9}{24} G^{(1)}(f, d) - \frac{1}{135} G^{(3)}(f, d) \\
 & - \frac{5}{39} G^{(5)}(f, d)] (\gamma_{5d\sigma}^2 - \frac{1}{3} \gamma_{5d\pi}^2)
 \end{aligned} \tag{16}$$

$$\begin{aligned}
 a^{(6)} = & -Z'_c e^2 \langle r^6 \rangle / R_c^7 + (13/4\pi)(R_{4f}^2 C_0^6 | V_c) + \frac{2}{7} (T_\sigma S_{4f\sigma} \\
 & + T_s S_{4f2s} + \frac{2}{3} T_\pi S_{4f\pi}) - \frac{13}{7} (\epsilon_{4f} - \epsilon_a - \epsilon_c + e^2/R + \alpha) \\
 & \times (S_{4f\sigma}^2 + S_{4f2s}^2 - \frac{2}{3} S_{4f\pi}^2) - \frac{13}{7} [\epsilon_{2p}(S_{4f\sigma}^2 - \frac{2}{3} S_{4f\pi}^2) + \epsilon_{2s} S_{4f2s}^2] \\
 & + \frac{13}{7} [\Delta_{2p4f}(\gamma_{4f\sigma}^2 - \frac{2}{3} \gamma_{4f\pi}^2) + \Delta_{2s4f} \gamma_{4fs}^2].
 \end{aligned} \tag{17}$$

Here Z'_c is the charge of the ligand ion and σ_2 the shielding constant (Gupta and Sen 1973); the second terms in (15)–(17) are due to electron overlap of the density–density type. These terms have been studied recently in detail (Garcia and Faucher 1984). T_σ , T_π and T_s denote the kinetic energy integrals and S_{4f2s} , $S_{4f\sigma}$ and $S_{4f\pi}$ the overlap integrals via s, σ and π bonds in the metal–ligand pair. It is assumed that the z axes are parallel and directed along the pair axis. ϵ_{4f} is the Hartree–Fock energy for 4f electrons; ϵ_a and ϵ_c are the lattice energies of electrons in the a and c positions (the Madelung energies); α is the approximation factor for exchange two-centre integrals of Coulomb repulsion via overlap integrals, i.e. $(4f\sigma, 2p\sigma|e^2/r_{12}|2p\sigma, 4f\sigma) = \alpha S_\sigma^2$ and so on. According to the estimates of Newman and Curtis (1969) this factor is equal to 0.43 for rare-earth fluorides. ϵ_{2p} and ϵ_{2s} denote Hartree–Fock energies of ligand electrons. $F^k(4f, 5d)$ and $G^k(f, d)$ are direct and exchange integrals of the Coulomb interaction of 4f and 5d rare-earth ion electrons.

4. Discussion of results

The wavefunctions of the Er^{3+} ground state have the form given by Antipin *et al* (1976):

$$\Gamma_8^{(1)} \begin{cases} \psi_{1,2} = 0.0444 | \mp \frac{1}{2} \rangle + 0.4896 | \mp \frac{7}{2} \rangle \\ \quad - 0.4584 | \pm \frac{1}{2} \rangle + 0.7404 | \pm \frac{9}{2} \rangle \\ \psi_{3,4} = 0.0511 | \mp \frac{1}{2} \rangle + 0.1772 | \mp \frac{5}{2} \rangle \\ \quad - 0.2095 | \pm \frac{3}{2} \rangle + 0.9603 | \pm \frac{1}{2} \rangle. \end{cases}$$

The wavefunctions of the nearest excited states necessary for the calculation of the pseudo-Zeeman interaction are the following (Antipin *et al* 1976):

Table 2. The overlap integrals for the 4f, 5s, 5p, 5d, 6s and 6p shells.

Overlap integral designation	Value of the overlap integral		Overlap integral designation	Value of the overlap integral	
	R = 4.063 au	R = 4.278 au		R = 4.063 au	R = 4.278 au
S_{4f1s}	0.0007	0.0009	S_{5d1s}	0.022	0.0189
S_{4f2s}	0.0123	0.0134	S_{5d2s}	0.1973	0.1913
$S_{4f\sigma}$	-0.0171	-0.018	$S_{5d\sigma}$	-0.1772	-0.1814
$S_{4f\pi}$	0.0109	0.0117	$S_{5d\pi}$	0.1235	0.12
S_{5s1s}	0.0005	0.0004	S_{6s1s}	0.0224	0.0193
S_{5s2s}	0.0335	0.0294	S_{6s2s}	0.2099	0.1986
$S_{5s\sigma}$	-0.1159	-0.1069	$S_{6s\sigma}$	-0.1511	-0.1489
S_{5p1s}	0.0024	0.0021	S_{6p1s}	0.0436	0.0374
S_{5p2s}	0.0665	0.0599	S_{6p2s}	0.2628	0.2446
$S_{5p\sigma}$	-0.1329	-0.1269	$S_{6p\sigma}$	-0.084	-0.082
$S_{5p\pi}$	0.0417	0.0381	$S_{6p\pi}$	0.1511	0.1427

$$\Gamma_7 \begin{cases} \psi_{5,6} = 0.6332 |\pm \frac{1}{2}\rangle + 0.5819 |\pm \frac{3}{2}\rangle \\ -0.4507 |\mp \frac{3}{2}\rangle - 0.2393 |\mp \frac{1}{2}\rangle \end{cases}$$

$$\Gamma_8^{(2)} \begin{cases} \psi_{7,8} = -0.0845 |\mp \frac{1}{2}\rangle - 0.7309 |\mp \frac{3}{2}\rangle \\ + 0.2363 |\pm \frac{1}{2}\rangle + 0.6347 |\pm \frac{3}{2}\rangle \\ \psi_{9,10} = 0.7712 |\pm \frac{1}{2}\rangle - 0.4556 |\pm \frac{3}{2}\rangle \\ + 0.4235 |\mp \frac{3}{2}\rangle + 0.1354 |\mp \frac{1}{2}\rangle. \end{cases}$$

The calculation of the components of A_i and g_{ni} parameters was carried out accounting for all the mechanisms proposed by Anikeenok *et al* (1984) and in the present paper. The values of the overlap integrals are given in table 2. They have been calculated with the Hartree-Fock wavefunctions of Er^{3+} (Eremin *et al* 1977) and the fluorine functions (Clementi and Roetti 1974). The distance from Er^{3+} to F^- was taken to be equal to 2.15 Å (4.063 au) (the expansion of the crystal lattice due to the difference between the ionic radii of Zn^{2+} (0.75 Å) and Er^{3+} (0.881 Å) (Shannon and Prewitt 1969) was taken into account. The radial 5s and 5p functions were taken from Van Piggelen *et al* (1980) and the 5d, 6s and 6p functions from Rajnak (1963) for Tm^{3+} . The mixing of 1s and 2s shells of F^- was taken into account. The transfer integrals were taken from Anikeenok *et al* (1984). They had the following values: $\gamma_{4fs} = 0.013$; $\gamma_{4f\sigma} = -0.04$; $\gamma_{4f\pi} = 0.05$; $\gamma_{5ds} = 0.02$; $\gamma_{5d\sigma} = -0.13$; $\gamma_{5d\pi} = 0.09$; $\gamma_{5ps} = 0.04$; $\gamma_{5p\sigma} = -0.15$; $\gamma_{5p\pi} = 0.09$.

The covalency parameters for 6s and 6p shells which are very uncertain in the crystal are considered to be equal to γ_{5d} .

The energies of electron transfer were estimated by the same method used by Anikeenok *et al* (1984): $\Delta_{2p4f} \approx 8.5 \times 10^4 \text{ cm}^{-1}$; $\Delta_{2s4f} \approx 26.5 \times 10^4 \text{ cm}^{-1}$; $\Delta_{2p5d} \approx 1.5 \times 10^5 \text{ cm}^{-1}$; $\Delta_{2s5d} \approx 3.3 \times 10^5 \text{ cm}^{-1}$; $\Delta_{5s5d} \approx 3.2 \times 10^5 \text{ cm}^{-1}$; $\Delta_{5s6s} \approx 3.5 \times 10^5 \text{ cm}^{-1}$; $\Delta_{5p6p} \approx 1.9 \times 10^5 \text{ cm}^{-1}$.

The radial integrals are as follows: $R^{(3)}(5s, 4f; 6s, 4f) = -0.0303 \text{ au}$; $R^{(3)}(5s, 4f; 5d, 4f) = 0.0571 \text{ au}$; $R^{(2)}(5p, 4f; 6p, 4f) = -0.0291 \text{ au}$; $R^{(4)}(5p, 4f; 6p, 4f) = -0.0249 \text{ au}$.

The f-5d interaction parameters G_1 , G_3 , G_5 were taken from Starostin *et al* (1975) for Er^{2+} and f-6s interaction parameter $G^{(3)}$ was taken to be equal to 2205 cm^{-1} from

Table 3. Calculated and experimental values of A_i and g_{ni} for $KZnF_3:Er^{3+}$.

	H_{d-d}	H_{4f}	H_{5d}	H_{6s}	H_d	$H_{5s \rightarrow 5d}$	$H_{5s \rightarrow 6s}$	$H_{5p \rightarrow 6p}$	Total	Experimental
$A_{ }$ (MHz)	29.92	2.00	-2.86	-0.40	0.34	0.01	1.65	-4.92	25.74	25.16
A_{\perp} (MHz)	-0.06	0.39	-0.01	0	0.11	-0.01	0	0.02	0.45	0.58
A_1 (MHz)	-14.91	-5.29	0.93	-0.61	-2.39	0.04	1.25	-1.39	-22.36	-22.56
A_2 (MHz)	-0.01	-0.14	0.04	0	-0.08	0	0	0	-0.19	-0.42
A_3 (MHz)	0.04	-0.09	0.01	0	-0.04	0	-0.01	0	-0.09	-0.11
g_{n1}	0.05	0	0	0	0	0	0	-0.01	0.04	0.03
g_{n2}	0.01	0	0	0	0	0	0	0	0.01	0.02
g_{n6}	0.01	0.01	0	0	0	0	0	0	0.02	0.03

Table 4. Calculated and experimental values of A_s and A_p for $CsCaF_3:Gd^{3+}$. The experimental values of $A_s = -3.86$ MHz and $A_p = 5.8$ MHz were taken from the work of Casas-Gonzales *et al* (1986) and the experimental values of $A_s = -3.869$ MHz and $A_p = 5.729$ MHz from the work of Allsopp *et al* (1987).

	H_{d-d}	H_{4f}	H_{5d}	H_{6s}	H_d	H_{5s-6s}	H_{5p-6p}	Total	Experimental
A_s (MHz)	0	2.48	-3.13	-1.85	0.51	3.12	-5.02	-3.89	-3.86 -3.869
A_p (MHz)	6.40	0.08	-0.70	-0.22	0.09	0.59	-0.44	5.80	5.8 5.729

Goldschmidt (1978). The results of the theoretical calculations are compared with the experimental results in table 3. The values of the separate calculations are given in the second to ninth columns, respectively: the dipole-dipole contribution H_{d-d} accounting for multipole corrections; the contribution H_{4f} due to the effect of overlap and covalency of 4f shells; the contribution $H_{5d,6s}$ due to the electron transfer to the empty 5d and 6s shells; the contribution H_d due to the mixing of 4f and 5d states by the field of virtual hole in F^- ; the contributions $H_{5s \rightarrow 6s}$, $H_{5s \rightarrow 5d}$ and $H_{5p \rightarrow 6p}$ due to the spin polarisation of 5s and 5p shells. The summary and experimental values of THFI are given in the last two columns.

On the basis of the theory developed, it is interesting to calculate the parameters for Gd^{3+} in $CsCaF_3$ (Casas-Gonzales *et al* 1986, Allsopp *et al* 1987). Casas-Gonzales *et al* (1986) gave an analysis of THFI based only on the spin polarisation. The distance $Gd^{3+}-F^-$ was taken to be equal to 4.278 (Casas-Gonzales *et al* 1986). In table 4 the results of the theoretical calculation, together with the experimental results and calculated values of Casas-Gonzales *et al* (1986), are presented. The columns in table 4 are analogous to those of table 3. The values of the overlap integrals are given in table 2. The radial integrals and γ parameters were similar to those for Er^{3+} . The energies of the electron transfer were as follows: $\Delta_{2p4f} \approx 10^5 \text{ cm}^{-1}$; $\Delta_{2s4f} \approx 2.8 \times 10^5 \text{ cm}^{-1}$; $\Delta_{2p5d} \approx 1.9 \times 10^5 \text{ cm}^{-1}$; $\Delta_{2s5d} \approx 3.7 \times 10^5 \text{ cm}^{-1}$; $\Delta_{5p6p} \approx 1.9 \times 10^5 \text{ cm}^{-1}$; $\Delta_{5s6s} \approx 3 \times 10^5 \text{ cm}^{-1}$.

It is obvious from a comparison of the results presented in table 4 that our calculations are in better agreement with the experiment than those of Casas-Gonzales *et al* (1986) and have more apparent physical sense.

In conclusion, let us calculate the crystal-field parameters B_4^0 and B_6^0 which in octahedral environment are connected with parameters $a^{(4)}$ and $a^{(6)}$ by the following relations: $B_4^0 = \frac{7}{16} a^{(4)}$; $B_6^0 = \frac{3}{64} a^{(6)}$ using equations (16) and (17). The following calculated values were used in the calculation: $T_\sigma = -0.0094$; $T_s = -0.0002$; $T_\pi = 0.002$; $\varepsilon_a = 0.8243$ au; $\varepsilon_c = -0.43$ au; $\varepsilon_{4f}(\text{Er}^{3+}) = -1.97378$ au (Van Piggelen *et al* 1980); $\varepsilon_{2p}(\text{F}^-) = -0.1808$ au (Fuchikami 1970); $\varepsilon_{2s}(\text{F}^-) = -1.0744$ au (Fuchikami 1970). As a result the contributions calculated according to equations (16) and (17) are as follows: $B_4^0 = 319 \text{ cm}^{-1}$; $B_6^0 = 13 \text{ cm}^{-1}$. According to Antipin *et al* (1977) the corresponding values are $B_4^0 = 302 \text{ cm}^{-1}$ and $B_6^0 = 13 \text{ cm}^{-1}$.

As can be seen from tables 3 and 4 and the values of the calculated parameters B_4^0 and B_6^0 , the theory developed for the mechanisms of the rare-earth ion–ligand bonding explains without contradiction the THFI parameters including the pseudo-Zeeman interaction of rare-earth ions in the various parameters as well as in the crystal-field parameters.

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