THE TRANSVERSE ZEEMAN EFFECT IN CRYSTALS

* * *

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by

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STATEMENT

The studies described in this thesis were carried out while I was a full-time research scholar at the Australian National University, Canberra, ACT.

Except where mentioned in the text, the research described in this thesis is my own.

This thesis has never been submitted to another university or similar institution.

Z.U. Noor

May 1977
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ABSTRACT

The transverse Zeeman effect in uniaxial crystals has been studied. Anisotropies in the Zeeman spectra have been observed in the hexagonal crystal, LaES:Er, and the tetragonal crystal, ZrSiO$_4$:U$^{5+}$, when the crystals are rotated about their principal axes. The LaES:Er spectrum exhibited a sixfold periodicity and a fourfold periodicity is observed for the ZrSiO$_4$:U$^{5+}$. This periodic oscillation in the intensity occurs due to the change in selection rules as the crystal is rotated and reaches its maximum polarization when the field is along the high symmetry directions in the crystal. These fluctuations in intensity are explained in terms of the theoretical development of Judd and Runciman (1976).

The transverse Zeeman effect on the line at 12,428 cm$^{-1}$ in LaES:Er has been investigated in detail. It is established that there are two levels at this energy - a $\Gamma_7$ and $\Gamma_9$ level (in the $^4I_{9/2}$) within 0.5 cm$^{-1}$. The intensities of the transitions to these two interacting levels exhibit a wide fluctuation in intensity characteristic of a type B$\rightarrow$B transition. The Zeeman energies and intensities are calculated and give firm agreement with experiment.

Another line studied is a transition at 6,700 cm$^{-1}$ in ZrSiO$_4$:U$^{5+}$. The intensity variation of this line is in excellent agreement with that expected for a type B$\rightarrow$B transition.
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CHAPTER 1: Introduction

1.1. General Introduction

Optical studies of transition metal and rare-earth ions in crystals have been used to obtain information both about the ion and about its surroundings. When, for example, an ion with an incomplete shell is placed in a crystal field its energy levels are split due to the electric field produced by the surrounding ions in the crystal (Stark splitting). The location of the various electronic levels of the ion in the crystal can be established by recording the absorption spectrum. The transitions are normally induced by an interaction of the electromagnetic radiation with the electric or magnetic moment of the ion. When the centre has inversion symmetry the electric dipole transitions within the unfilled shell configuration are forbidden as both the initial and final wavefunctions have the same parity and the electric dipole operator has odd parity. When the centre lacks inversion symmetry the wavefunctions can have an admixture of opposite parity states and hence the transitions are no longer forbidden by parity.

In transition metal ions where the unfilled 3d and 4d shells lie outside the closed shells, the influence of the crystal field on the energy levels is very strong. For the rare-earths the unfilled 4f shells are screened by the outer 5s^2 and 5p^6 closed shells. Thus the influence of the crystal field on their energy levels is not as strong as in the d^n metal ions. There is also less interaction with the lattice and hence line broadening or vibrational coupling effects are not so pronounced. This accounts for the
characteristic sharp transitions observed in the spectra of crystals containing rare-earth ions in contrast with the $d^n$ ion spectra. When the crystals are placed in a magnetic field the crystal field states are further split (Zeeman effect). Zeeman absorption studies can give additional data for interpreting the rare-earth spectra and understanding the magnetic properties of the ion under study and provide one of the best ways of determining the site symmetry of an ion in a crystal and the $J$ and $g$ values of the various states. Various geometries are possible, for example, the magnetic field may be applied in a direction perpendicular to the optic axis (the perpendicular Zeeman effect) or parallel to the optic axis (the parallel Zeeman effect). The direction of the incident light could be along the direction of the magnetic field or perpendicular to it. The former case is known as the longitudinal Zeeman effect, while the latter as the transverse Zeeman effect. As well as splitting the states, a strong magnetic field can cause neighbouring crystal field states to be mixed and more transitions to be observed. In this way the position of further excited levels can be established.

1.2. Present Work

The origin of the present project starts from an experiment done by Spedding et al [1] on erbium ethylsulphate and erbium ethylsulphate in yttrium ethylsulphate. They observed variations of intensities and spectral line positions when the crystal was rotated in a magnetic field about the principal crystal axis. A series of four papers [2-5] was published based on this Zeeman rotation experiment. Recently Judd and Runciman [6] reinvestigated the above types
of intensity and energy variation and greatly simplified the
theory. In light of their work further experimental work
was considered justified.

The present work deals with the experimental
observation of the angular variation of certain lines of
erbium ethylsulphate in lanthanum ethylsulphate and \( U^{5+} \)
in zircon in a transverse magnetic field. The intensity vari­
tions of the spectral lines have been explained on the basis
of the theory developed by Judd and Runciman.

The theoretical treatment of the rare-earth ions
has been developed in Chapter 2. Chapter 3 deals with the
experimental techniques used in this project. In the next
chapter a review of the work on \( \text{Er}^{3+} \) is given together with
both the earlier theory of Zeeman effect and the more recent
theory developed by Judd and Runciman. The experimental work
and results, as well as some theoretical calculations, have
been presented in Chapters 5 and 6.
References to Chapter 1.


CHAPTER 2: Theoretical Treatment of the Rare-earth Ions

2.1. Introduction

Most atoms having incomplete electron shells absorb in the visible and infra-red region. It is mainly for this reason that such atoms have considerable importance in the field of spectroscopic studies. Atoms with incomplete shells may be classified into two groups - the transition metal ions and the rare-earth ions. Transition metal ions have incomplete d shells (3d, 4d or 5d), while the rare-earths have incomplete f shells (4f or 5f). In the rare-earth group, atoms with partly filled 4f shells are known as lanthanides, while the actinides are characterised by the filling of the 5f shell. The trivalent lanthanides have the xenon-like structure of 54 electrons in common and in addition to that contain N 4f electrons. N ranges from zero (La³⁺) to 14(Lu³⁺). The lanthanide ions are chiefly trivalent and in some cases may be divalent or tetravalent. The 4f shells in the lanthanides are electrically shielded by the outer 5s² and 5p⁶ shells while in the transition metal ions the effect of shielding is much less. Due to this shielding, the effect of the crystal field on the energy levels of a rare-earth ion is very small and this gives rise to very sharp lines in the spectrum. The crystal field also acts as a small perturbation relative to the spin-orbit interaction. This forms an ideal case to study the direct physical influence of the crystal forces. The availability of 13 different elements with very similar chemical properties has also added to the importance of their study.
2.2. Classification of many electron states

The electrons of the unfilled shell in the free ion are subject to two kinds of perturbations. One is the mutual repulsion of the electrons and the other is the interaction between the electron spin and orbital angular momenta through the spin-orbit coupling. These interactions give rise to a number of separate quantum states which are designated by their $LS$ values.

The electron repulsion splits the energy levels of a given configuration (which is the $nl$ value of an electron) into a number of terms. A term is symbolised by $2S+1L$ where $S$ and $L$ are the total spin and orbital angular momentum respectively. The degeneracy of a term is $(2S+1)(2L+1)$. A typical separation between the adjacent terms is $10,000 \text{ cm}^{-1}$. The number of terms arising from a given configuration depends on the number of electrons in the unfilled shell. For systems with more than two electrons there may be two or more terms with the same $L$ and $S$ values. In such cases additional quantum numbers are required to distinguish between them.

Spin-orbit interaction couples the spin angular momentum of every term with the corresponding orbital angular momentum causing the term to split into a number of levels called states. A state is $(2J+1)$-fold degenerate and is characterised by its $LSJ$ value where $J$ is the total orbital quantum number.

Various methods of coupling the spin and orbital angular momenta are possible. For the lighter elements the Russell-Saunders coupling scheme is the most common. Such coupling is possible when the spin-orbit coupling is considered
as a small perturbation on the terms formed by Coulomb repulsion. Here the orbital angular momenta of all the electrons are added together to give a resultant angular momenta $L$. Similarly the spins of the electrons are added together giving the resultant spin angular momentum $S$. $L$ and $S$ are then coupled together forming the total angular momentum $J$.

Another coupling scheme known as j-j coupling occurs when the spin-orbit interaction is very large compared to the electrostatic repulsion between the electrons of a configuration. In j-j coupling the spin and orbital angular momenta of each individual electron are coupled together to give the angular momentum $j$. The vector sum of all $j$ gives the total angular momentum $J$. For heavy elements a coupling scheme intermediate between the j-j and the Russell-Saunders coupling known as intermediate coupling is applicable. Here the magnitude of the spin-orbit coupling is such that it cannot be treated as a small perturbation.

The energy matrix is formed by adding the electrostatic and spin-orbit interactions of different terms occurring in the configuration.

There are seven f orbitals and two spin states available, giving a total of fourteen different spin-orbitals. If we consider the case of Pr$^{3+}$ which has two electrons in the 4f we find according to Pauli's exclusion principle that only singlet and triplet terms will be allowed. For Er$^{3+}$ with a configuration 4f$^{11}$ there will be terms with half integral spin which implies that there will be quartets and doublets. In Pr$^{3+}$ the terms arising out of electrostatic repulsion are $^3\text{H}$, $^3\text{F}$, $^3\text{P}$, $^1\text{G}$, $^1\text{I}$, $^1\text{D}$ and $^1\text{S}$. The spin and orbital angular
momenta of these terms will be coupled together to give rise to the LSJ states of \(3_{H6}, 3_{H5}, 3_{H4}, 3_{F4}, 3_{F3}, 3_{F2}, 3_{P2}, 3_{P1}, 1_{D2}, 3_{P0}, 1_{G4}, 1_{I6}, \text{ and } 1_{S0}\). From here we find (taking into consideration the spin multiplicity and the orbital angular momentum multiplicity; (2S+1)(2L+1)) that there are 91 different basis states (quantum states) into which the two electrons can distribute themselves.

In \(\text{Er}^{3+}\) the terms arising out of electrostatic repulsion would be \(4_{D}, 4_{S}, 4_{I}, 4_{F}, 4_{G}, 2_{K}, 2_{H(a)}, 2_{H(b)}, 2_{G(a)}, 2_{G(b)}, 2_{F(a)}, 2_{F(b)}, 2_{D(a)}, 2_{D(b)}, 2_{L}, 2_{K}, 2_{I}\) where (a) and (b) are used to distinguish the two equivalent LS states arising from a configuration. The number of possible ways to distribute the \(4f^{11}\) electrons in \(\text{Er}^{3+}\) (which is equivalent to three holes) following the same principle as before, will be 364. A simpler way of finding these quantum states is by considering that the total number of ways in which the two \(4f\) electrons can be distributed into 14 spin-orbitals is \(14.13/1.2 = 91\) and similarly for a system of three \(4f\) electrons it is \(14.13.12/1.2.3 = 364\).

The ground state according to Hund's rule [1] is \(3_{H4}\) for \(\text{Pr}^{3+}\) and \(4_{I15/2}\) for \(\text{Er}^{3+}\).

Calculation of these energy levels from the basis states using the determinantal method involves the solution of a secular determinant. This often becomes tedious. However, the tensor operator technique devised by Racah [2] is a powerful tool in calculating the term levels in a precise form.
2.3. Free ion Hamiltonian [3]

For a system possessing \( N \) electrons and a nuclear charge \( Z \), the Hamiltonian may be written as

\[
H_{\text{free ion}} = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \frac{Ze^2}{r_i} + \sum_{i<j}^{N} \frac{e^2}{r_{ij}} + \sum_{i=1}^{N} \xi(r_i)(S_i \cdot L_i)
\]

(2.3.1)

where \( \xi(r_i) = \frac{\hbar^2}{2m^2 c^2 r_i} \frac{dU(r_i)}{dr_i} \) .

(2.3.2)

In equations (2.3.1) and (2.3.2) \( r_i \) denotes the distance between the \( i \)-th electron and the nucleus, \( r_{ij} \) is the distance between two electrons, \( Z \) the nuclear charge and the other terms have their usual meaning. The first term in equation (2.3.1) is the sum of the kinetic energy of all the electrons; the second term is the potential energy of all the electrons in the field of the nucleus; the third term represents the interelectronic repulsive Coulomb potential energy. The last term represents the spin-orbit interaction with \( S_i \) denoting the spin and \( L_i \) the orbital angular momentum of the \( i \)-th electron.

The variables in (2.3.1) cannot be separated due to the presence of the Coulomb term so an approximation is used. The usual approximation used in solving the Schrödinger equation for a system containing more than one electron is the central field approximation. In this approximation each electron is assumed to move independently in a spherically symmetric potential \( -U(r_i)/e \) round the nucleus. With this approximation (2.3.1) may be rewritten as

\[
H_{\text{free ion}} = \sum_{i=1}^{N} \left[ \frac{\hbar^2}{2m} \nabla_i^2 + U(r_i) \right] + \sum_{i<j}^{N} \frac{e^2}{r_{ij}} + \sum_{i=1}^{N} \left( \frac{Ze^2}{r_i} + U(r_i) \right) + \sum_{i=1}^{N} \xi(r_i) S_i \cdot L_i
\]
where $H'_C$ is the Hamiltonian for the central field and

$$H_{COUL} = \sum_{i<j} \frac{e^2}{r_{ij}} - \sum_{i=1}^{N} \left( \frac{Ze^2}{r_i} + U(r_i) \right).$$

The Schrödinger equation for the central field is

$$\sum_{i=1}^{N} \left[ - \frac{\hbar^2}{2m} \nabla_i^2 + U(r_i) \right] \psi_0 = E_{CF}^0 \psi_0.$$  \hspace{1cm} (2.3.5)

Eqn (2.3.5) can be solved by choosing a solution such that

$$\psi_0 = \prod_{i=1}^{N} \chi_i(a^i)$$

and

$$E_{CF}^0 = \sum_{i=1}^{N} E_{i}^0 (a^i).$$

Each electron moving in the central field $U(r_i)$ satisfies equations of the type

$$\left[ - \frac{\hbar^2}{2m} \nabla^2 + U(r) \right] \chi(a^i) = E^0(a^i) \chi(a^i)$$

where $(a^i)$ represents a set of quantum numbers $(n^\ell m_\ell)$ which specify the state of motion of the single electron in the central field.

Using polar coordinates and separating the radial and angular parts, the normalised solutions for the bound states may be expressed as

$$\chi(a^i) = r^{-\frac{1}{2}} R_{n^\ell}(r) Y_{m_\ell}^\ell(\theta, \phi).$$

The radial function $R_{n^\ell}(r)$ depends on the central field potential energy function $U(r)$ and the spherical harmonics as defined by Condon and Shortley [4] are
\[
\psi_{m_{\ell},m_s}^\ell(\theta,\phi) = (-1)^m \left[ \frac{(2\ell+1)(\ell-|m|)!}{4\pi (\ell+|m|)!} \right]^{1/2} P_{m\ell}^m(\cos \theta)e^{i m \phi}
\]  

(2.3.10)

and

\[
P_{m\ell}(w) = \frac{(1-w^2)^{m/2}}{2^{\ell+1} \ell!} \frac{d^{m+\ell}}{dw^{m+\ell}} (w^2-1)^\ell.
\]

(2.3.11)

The radial part is dependent on the central field and can be evaluated only approximately while an exact value of the angular part can be calculated.

In order to take the spin of the electron into consideration a spin coordinate \( \sigma \) having a value of \( \pm \frac{1}{2} \) and a spin function \( \delta(m_s, \sigma) \) are introduced. \( m_s \) is the one electron quantum number which may have a value of \( \pm \frac{1}{2} \) corresponding to two possible orientations along the z axis. Eqn (2.3.9) now becomes

\[
\chi(n^l m_{\ell} m_s) = \delta(m_s, \sigma) r^{-1} R_{\ell}(r) Y_{m_{\ell}}^{(\ell)}(\theta,\phi).
\]

(2.3.12)

The solution of eqn (2.3.5) taking the spin into consideration is

\[
\psi = \sum_{i=1}^{N} \chi(\alpha^i)
\]

(2.3.13)

where \( \alpha^i \) represents the quantum numbers \( (n^l m_{\ell} m_s) \) of the ith electron. For a system of \( N \) electrons the solution should be so chosen that the wavefunctions are antisymmetric with respect to the simultaneous interchange of spin and spatial coordinates of any pair of electrons. The resulting antisymmetric solution for the central field wave equation may then be written as

\[
\psi_0 = \frac{1}{\sqrt{N!}} \sum_{P} (-1)^P \chi_1(\alpha^1) \chi_2(\alpha^2) \ldots \chi_N(\alpha^N).
\]

(2.3.14)

This is the wavefunction of the ith electron taking the spin
into consideration. \( P \) represents a permutation of the electrons and \( p \) the parity of the permutation which is +1 if the permutation is even and -1 if it is odd. \((N!)^{-\frac{1}{2}}\) is the normalisation factor. Eqn (2.3.14) may be written in determinantal form as

\[
\psi_0 = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\chi_1(\alpha^1) & \chi_2(\alpha^1) & \ldots & \chi_N(\alpha^1) \\
\chi_1(\alpha^2) & \chi_2(\alpha^2) & \ldots & \chi_N(\alpha^2) \\
\vdots & \vdots & \ddots & \vdots \\
\chi_1(\alpha^N) & \chi_2(\alpha^N) & \ldots & \chi_N(\alpha^N)
\end{vmatrix}
\]

The energy levels of a particular configuration can be obtained by solving the Schrödinger equation.

Several methods can be used to evaluate the Coulomb interaction and these have been discussed in detail in various books [3,4,5,6].

2.4. The tensor operator formalism of Racah

The tensor operator method developed by Racah [2] is a powerful tool for calculating various types of matrix elements which are required to be evaluated for a many-electron system.

Racah [2] defined an irreducible tensor operator \( T^{(k)} \) of rank \( k \) whose \( 2k+1 \) components \( T^{(k)}_{q} \) (\( q = -k,-k+1,\ldots,k \)) satisfy the same commutation rules with respect to the angular momentum operator \( \mathbf{J} \) as the spherical-harmonic operators \( Y_{kq} \).

These commutation rules are

\[
[(J_x + iJ_y), \, T^{(k)}_{q}] = ((k^2 - q)(k + q + 1))^{\frac{1}{2}} T^{(k)}_{q+1}
\]
and \[ [J_z, T_q^{(k)}] = q T_q^{(k)}. \] (2.4.1)

For \( k=1 \), Eqn (2.4.1) becomes

\[ T_{\pm 1}^{(1)} = \frac{\pm 1}{\sqrt{2}} (T_x \pm i T_y), \quad T_{0}^{(1)} = T_z. \] (2.4.2)

The Wigner-Eckart theorem gives the \( m \) dependence of the matrix elements of \( T_q^{(k)} \) in the \( jm \) scheme as

\[ < a j m | T_q^{(k)} | a' j' m' > = (-1)^{j-m} < a j | T_q^{(k)} | a' j' > \begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix}. \] (2.4.3)

The last factor in the above equation is known as the 3-\( j \) symbol and the double barred factor is called the reduced matrix element.

2.5. Evaluation of spin-orbit interaction by tensor operator technique.

The spin-orbit coupling plays a dominant role in the theory of \( 4f^n \) configurations. Its magnitude is of the order of one to two thousand wavenumbers. The LS coupling scheme is not valid for this case. One then has to use intermediate coupling. In this coupling scheme states of same \( J \) but different \( L \) and \( S \) are mixed appreciably.

The spin-orbit Hamiltonian is given by

\[ H_{so} = \sum_{i=1}^{N} \xi(r_i) (s_i \cdot l_i) \] (2.5.1)

with \( \xi(r_i) = \frac{\hbar^2}{2mc^2r_i} \frac{du(r_i)}{dr_i} \) (2.5.2)

\( H_{so} \) is diagonal in \( J \) and independent of \( M_J \). It commutes with \( J^2 \) and \( M_J \) but not with \( L^2 \) or \( S^2 \).

The energy matrix is formed by adding the
electrostatic energy for the different terms to the spin-orbit interaction. The entire matrix for different LS states is then separated into smaller matrices each having a different value of J. The number of spin-orbit matrices will be equal to the number of different J's occurring in the spin-orbit interaction. The rank of these matrices will vary and is equal to the number of terms occurring with the same value of J. Each of these matrices when diagonalised would give a set of eigenvalues which correspond to the theoretical spin-orbit levels. From the eigenvectors for each matrices we get the different admixtures of the basis states of the well-defined coupling scheme used in constructing the matrices.

For an \( \ell^N \) configuration the spin-orbit matrix elements are obtained by operating with the spin-orbit operators \( \sim \) between two states \( SLJM \) and \( S'L'JM \) in the following way:

\[
< \ell^N a_{SLJM} | \zeta_{n\ell} \sum_{i=1}^{N} (s_i \cdot \ell_i) | \ell^N a'S'L'JM >
\]

\[
= \zeta_{n\ell} (-1)^{J+L+S'} \begin{pmatrix} L & L' & 1 \\ S' & S & J \end{pmatrix} < \ell^N a_{SL} \sum_{i=1}^{N} (s_i \cdot \ell_i) | \ell^N a'S'L' > \quad (2.5.3)
\]

where \( \zeta_{n\ell} \) is the spin-orbit radial integral given by

\[
\zeta_{n\ell} = \int_{0}^{\infty} \frac{2}{n_{\ell}^2} \xi(r) dr \quad (2.5.4)
\]

and \( a, a' \) are additional quantum numbers. The matrix element on the right-hand side of Eqn (2.5.3) may be evaluated to give

\[
< \ell^N a_{SL} \sum_{i=1}^{N} (s_i \cdot \ell_i) | \ell^N a'S'L' > = [\ell (\ell+1) (2\ell+1)]^{\frac{1}{2}} \times
\]

\[
< \ell^N a_{SL} \sum_{i=1}^{N} (s_i \cdot \ell_i) | \ell^N a'S'L' >. \quad (2.5.5)
\]

We then have the final spin-orbit matrix elements as
\[ <\ell^N a\ell^S l^M J|\ell^N a\ell^S l^M J> \]

\[ = \zeta_{\ell a} (-1)^{J+L+S'} \left[ \ell(\ell+1)(2\ell+1) \right]^{1/2} \binom{\ell}{L} \binom{\ell}{L'} \binom{\ell}{S} \binom{\ell}{S'} \binom{\ell}{J} \times <\ell^N a\ell^S l^M|V^{(11)}|\ell^N a\ell^S l^M> \]  

(2.5.6)

The 6-j symbol may be evaluated from the tables of Rotenberg et al [7]. The \( V^{(11)} \) matrix elements for \( p^N, d^N, f^N \) configurations are tabulated in the tables of Neilson and Koster [8].

For \( f^N \) configurations with \( N > 7 \) the coefficients of the electrostatic matrix elements will be the same for the \( f^{14-N} \) configuration. The spin-orbit coupling is also the same in magnitude but has the opposite sign. The electrostatic and spin-orbit matrices for all \( f^N \) configurations have been calculated by various people. In the case of \( f^5, f^6 \) and \( f^7 \) configurations the electrostatic as well as spin-orbit matrices become large. It is only possible to obtain the energy levels by solving with a high speed computer.

2.6. Wavefunction calculation

As a result of mixing of the states in the intermediate coupling, the wavefunction of a definite state is not a pure one. It is a mixture of other terms having the same \( J \) value. The percentage of the contribution from various states may be considered in the following way:

We consider the \( ^4 I_{9/2} \) level of \( Er^{3+} \). In \( Er^{3+} \) the LS states occurring with \( J = 9/2 \) are \( ^4 I, ^4 F, ^2 H(a), ^2 G(a), ^4 G, ^2 H(b), ^2 G(b) \). If the unperturbed (LS coupling) wavefunction of the \( ^4 I_{9/2} \) is denoted by \( | ^4 I_{9/2} > \) and the state with intermediate coupling by \( | ^4 I_{9/2} > \) then the composition of \( | ^4 I_{9/2} > \) is given by
\[ [^{4}\text{I}_{9/2}] = a_{1}[^{4}\text{I}] + a_{2}[^{4}\text{F}] + a_{3}[^{2}\text{H(a)}] + a_{4}[^{2}\text{G(a)}] + \]
\[ a_{5}[^{4}\text{G}] + a_{6}[^{2}\text{H(b)}] + a_{7}[^{2}\text{G(b)}] \]  \hspace{1cm} (2.6.1)

where \( a_{1}, a_{2}, a_{3}, a_{4}, a_{5}, a_{6}, a_{7} \) are the normalised coefficients and the square of these coefficients gives the percentage composition for the respective states.

The coefficients as calculated by Wybourne [9] are given below

\[ [^{4}\text{I}_{9/2}] = -0.672[^{4}\text{I}] + 0.567[^{4}\text{F}] - 0.20[^{2}\text{H(a)}] + \]
\[ 0.004[^{2}\text{G(a)}] - 0.235[^{4}\text{G}] - 0.035[^{2}\text{H(b)}] + \]
\[ 0.360[^{2}\text{G(b)}]. \]  \hspace{1cm} (2.6.2)

From the above Eqn (2.6.2) we find that for the \(^{4}\text{I}_{9/2}\) the composition of the \(^{4}\text{I}_{9/2}\) is 45.1\% of \(^{4}\text{I}\), 32.1\% of \(^{4}\text{F}_{9/2}\), 4\% of \(^{2}\text{H(a)}\), 5.5\% of \(^{4}\text{G}\), 1.2\% of \(^{2}\text{H(b)}\), 13\% of \(^{2}\text{G(b)}\) and about 0.01\% of \(^{2}\text{G(a)}\). Although the contribution from \(^{4}\text{I}_{9/2}\) itself is small the major contribution comes from this state and so it is labelled by \(^{4}\text{I}_{9/2}\). This method of identifying the LSJ levels holds good in small perturbation but for higher perturbation when there is enough mixing of the LS states this process of identifying the levels is not very accurate.

The composition of the ground state of Er\(^{3+}\) has been given by

\[ [^{4}\text{I}_{15/2}] = 0.983[^{4}\text{I}] + 0.177[^{2}\text{K}] - 0.027[^{2}\text{L}] \]  \hspace{1cm} (2.6.3)

which indicates that the ground term in Er\(^{3+}\) has 96.6\% of \(^{4}\text{I}_{15/2}\) with 3.61\% and 0.07\% admixture of \(^{2}\text{K}_{15/2}\) and \(^{2}\text{L}_{15/2}\).
2.7. **Crystal field interactions**

We have seen that the spin-orbit interaction reduces the degeneracy of a term to \((2J+1)\). This degeneracy can be further lifted by the application of an external magnetic field or by the crystal field interaction. The concept of the crystal field was first discussed by Bethe [10].

When a metal ion is incorporated into a crystal, the spherical symmetry is destroyed and the \((2J+1)\)-fold degeneracy is lifted. The extent to which this degeneracy is lifted will depend on the symmetry of the crystal field and the number of electrons in the unfilled shell. For ions with an even number of electrons, a crystal field of low symmetry can remove all the degeneracy. The situation is different for ions with odd number of electrons. According to Kramers' theorem [11] each energy level of a system with an odd number of electrons has a twofold degeneracy which cannot be removed by any electric field. This twofold degeneracy can be removed only by the application of a magnetic field or by exchange interaction between paramagnetic ions.

The influence of the crystal field environment on the electronic properties of complexes of the rare-earths is very small. It produces a splitting of the order of 100 cm\(^{-1}\). The reason for this is the shielding of the 4f orbitals by the outer \(5s^25p^6\) electrons.

In the classical picture the lanthanide crystal field was regarded to be basically due to the electrostatic field originating from the ions in the crystal lattice [12]. It has been observed that this is not exactly the case [13]. Other electronic effects like the overlap, covalency and configuration interaction influence the observed lanthanide
crystal field parameters [14].

The potential energy of the electrons in an unfilled shell of paramagnetic ion in a crystal may be expressed as [14]

\[ V = \sum_{i=1}^{n} v_i = \sum_{i=1}^{n} \sum_{k,q} A_{kq} t^{(k)}_q(i) = \sum_{kq} A_{kq} t^{(k)}_q \]  

(2.7.1)

where \( A_{kq} \) is a set of parameters that describe the system, \( i \) refers to the electrons in the unfilled shell, \( t^{(k)}_q(i) \) is a tensor operator acting on the coordinates of the electrons \( i \) and

\[ t^{(k)}_q = \sum_i t^{(k)}_q(i). \]

The \( A_{kq} \) are independent of \( i \). The crystal field potential expressed in this form does not assume that it is of purely electrostatic origin. This formalism takes into consideration [14] contributions from other effects like the configuration interaction and covalency. The form of Eqn (2.7.1) also implies that \( V \) is a one-particle potential and that it is a function only of the angular coordinates of the electrons so that all the wavefunctions of electrons in the unfilled shell are supposed to have the same radial dependence.

Various ways of expressing the crystal field parameters exist. Some workers [12] express it as the product of a constant term and the expectation value of \( r \) like

\[ A^q_k < r^k >. \]

Making the appropriate choice of tensor operators in (2.7.1) we may express \( V \) in the form given in [3] as

\[ V = \sum_{ikq} B^k_q (C^k_q)_i \]  

(2.7.2)

where the \( C^k_q \) are defined by the relation
The form (2.7.2) is convenient in the sense that it is in an appropriate form for the theory developed in terms of the tensor operator.

The relation between the two parameters \( B_k^q \) and \( B_k^q = \Lambda_k^q < r^k > \) has been given by Dieke [12, Table 8] and Wybourne [3, Table 6.1]. Kassman [15] has provided an erratum for the values with \( q = 2,4 \) in Wybourne's [3] table.

In Eqn (2.7.2) and consequently similar other expressions for crystal field potential there exists a rule limiting the values of \( k \) and \( q \). The value of \( k \) is limited to \( k \leq 2\ell \) which follows directly from group theory as the direct product of \( D^{(\ell)} \otimes D^{(\ell)} = D^{(2\ell)} + D^{(2\ell-1)} + \ldots + D^{(0)} \).

For equivalent electrons, terms with odd \( k \) will have odd parity which means that the matrix element between states of the same \( \ell \) will vanish. Thus for unfilled f shell the value of \( k \) will be restricted to 0,2,4 and 6. The value of \( q \) is restricted by the symmetry of the system under consideration. The higher the symmetry the fewer terms appear in the crystal field potential. Several other rules limiting the number of terms occurring in the crystal field potential have been given by some authors [16,17].

The crystal field potentials for some symmetries are given below

\[
V_{D_{3h}} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_6^6 C_6^6 + B_6^6 (C_6^6 + C_{-6}^6) + i B_{-6}^6 (C_6^6 - C_{-6}^6)
\]

\[
V_{C_{3h}} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_6^6 C_6^6 + B_6^6 (C_6^6 + C_{-6}^6) + i B_{-6}^6 (C_6^6 - C_{-6}^6)
\]

(where the last term can be removed by an appropriate coordinate transformation)
An alternative way of expressing the crystal field potential is by means of the Stevens [18] operator-equivalent notation. This formalism is involved in finding an operator consisting of standard angular momentum operators which act on the angular part of the wavefunction of the rare-earth ion described in the \( |LSJJ_z> \) representation. The operator equivalent method may also be used when \( J \) is not a good quantum number. In such a case the crystal field Hamiltonian is expressed as a polynomial in \( L \). Formulation of the equivalent operator is accomplished by using the Wigner-Eckart theorem, according to which the tensorial operator can be expressed in a power series of angular momentum operators.

In Stevens' notation the crystal field potential is expressed as

$$V_c = \sum_k \sum_{q=-k}^k B_k^q O_k^q(J).$$

(2.7.5)

The \( B_k^q \) are crystal field parameters as defined by Eqn (2.7.4). \( O_k^q(J) \) represent polynomials of angular momentum operators \( J_z, J^2, J_+ \) and \( J_- \). These polynomials as well as the matrix elements associated with the several operators for various \( J \)'s have been tabulated by Hutchings [16]. A few examples of these operators are given below:
\[ [3J^2 Z^2 - J(J+1)] = O_0^0 \]
\[ \frac{1}{2} [J^4_+ + J^4_-] = O_4^4 \]
\[ [23J^6 Z^6 - 315J(J+1)J^4 Z^4 + 735J^4 Z^4 + 105J^2 Z^2 (J+1)^2 J^2 Z^2 - 
525J(J+1)Z^2 + 294J^2 - 5J^3 (J+1)^3 + 40J^2 (J+1)^2 - 
60J(J+1)] = O_6^6 \] (2.7.6)

2.8. Evaluation of the crystal field potential by the tensor operator method.

The crystal field potential as expressed by Eqns. (2.7.1) and (2.7.2) is in tensorial form. It is very convenient to evaluate the potential in terms of the reduced tensor operator.

The matrix element \( V \) for \( f^N \) configuration in terms of the reduced tensor operator may be expressed as

\[
< f^N aSJJ_z | V | f^N a'SL'J' J_z' >
= \sum_{k,q} B^k_{q} < f^N aSJJ_z | U^{(k)}_{q} | f^N a'SL'J' J_z' > < f^N | C^{(k)} | f >
\]

(2.8.1)

with \( < f^N | C^{(k)} | f > = (-1)^3 7 \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix} \). (2.8.2)

Using the Wigner-Eckart theorem the matrix element of the tensor operator \( U^{(k)}_{q} \) may be evaluated to give

\[
< f^N aSJJ_z | U^{(k)}_{q} | f^N a'SL'J' J_z' >
= (-1)^{J-J_z} \begin{pmatrix} J & k & J' \\ -J_z & q & J_z \end{pmatrix} \times < f^N aSJJ | U^{(k)}_{q} | f^N a'SL'J' >
\]

(2.8.3)

where
\[ < f^{N\alpha}n_{SLJ}} \| U^{(k)} \| f^{N\alpha'}n_{SL}'J' \> = (-1)^{S+L'+J+K} [(2J+1)(2J'+1)]^{1/2} \]
\[ \times \left\{ \begin{array}{ccc} J & J' & K \\ L' & L & S \end{array} \right\} < f^{N\alpha}n_{SL} \| U^{(k)} \| f^{N\alpha'}n_{SL'} >. \]

Eqn. (2.8.1) reduces to
\[ < f^{N\alpha}n_{SL}J_z \| V \| f^{N\alpha'}n_{SL}'J'z' \> = \sum_{k,q} B^k_q (-1)^{J-J_z} \left( \begin{array}{ccc} J & k & J' \\ J_z & q & J_z' \end{array} \right) \]
\[ \times (-1)^{S+L'+J+K} [(2J+1)(2J'+1)]^{1/2} \left\{ \begin{array}{ccc} J & J' & K \\ L' & L & S \end{array} \right\} \]
\[ \times < f^{N\alpha}n_{SL} \| U^{(k)} \| f^{N\alpha'}n_{SL'} > (-1)^3 \left( \begin{array}{ccc} 3 & k & 3 \\ 0 & 0 & 0 \end{array} \right). \]

The value of \( U^{(k)} \) matrix elements may be directly calculated from the tables of Neilson and Koster [8].

2.9. Notation and selection rules

In a crystal the states of different \( J_z \) are mixed by the crystal field so that \( J_z \) is no longer an exact quantum number to designate such states. A new quantum number introduced by Hellwege [19] known as the crystal quantum number denoted by \( \tilde{\mu} \) is used for labelling the crystal field states. \( \tilde{\mu} \) is a linear combination of certain \( J_z \) states occurring in a definite multiplet. Hellwege defined the crystal quantum number \( \tilde{\mu} \) as \( J_z = \tilde{\mu} (\text{mod} \ q) \) where \( q \) is the crystal class.

For crystals possessing \( D_{3h} \) symmetry \( \tilde{\mu} \) may have values \( \pm \frac{1}{2}, \pm \frac{3}{2} \) and \( \pm \frac{5}{2} \) for an odd number of electrons and \( 0, \pm 1, \pm 2 \) and \( 3 \) for an even number of electrons. In \( D_{2d} \) symmetry it can have values corresponding to \( \pm \frac{1}{2} \) and \( \pm \frac{3}{2} \) for systems
containing an odd number of electrons and 0, ±1, 2 for a system having an even number of electrons.

The crystal quantum numbers used by different workers vary slightly in their definition. For convenience the correspondence between the numbers used by various workers are given in Table 2.1. We have used the same labelling system as Erath [20]. The most convenient way of designating crystal quantum numbers to definite states is by performing a crystal field calculation. This directly gives the \( \mu \) values of a definite state (we have performed this in Chapter 5). The relation between Hellwege's [19] crystal quantum number and \( M \) is \( M = \bar{\mu} + 3 \) where \( M \) is a linear combination of the different \( J_z \) occurring for a definite state. The linear combination of \( J_z \) for a definite value of \( \mu \) is given in Table 2.1. The irreducible representations corresponding to each \( \mu \) value have been given and we have followed the notations of Koster et al [21].

The transition intensity between two states \( |i\rangle \) and \( |j\rangle \) depends on \( <i|k|j> \). Here \( k \) is an operator which induces transitions between states \( |i\rangle \) and \( |j\rangle \). Some of these matrix elements may be zero [17]. If \( |i\rangle \) and \( |j\rangle \) belong to the irreducible representations \( \Gamma_\alpha \) and \( \Gamma_\beta \) of the symmetry group under consideration, and if \( k \) transforms as \( \Gamma_r \), then the matrix element \( <i|k|j> \) will be zero unless the direct product \( \Gamma_\alpha^* \otimes \Gamma_r \otimes \Gamma_\beta \) contains the identity representation. \( \Gamma_\alpha^* \) is the complex conjugate of \( \Gamma_\alpha \). The alternative condition is that \( \Gamma_r \otimes \Gamma_\beta \) should contain \( \Gamma_\alpha^* \).

In Tables (2.2) and (2.3) the polarisation selection rules for electric-dipole transitions for \( D_{3h} \) and \( D_{2d} \) symmetries in a system containing an odd number of electrons
Table 2.1. Correspondence between the different crystal quantum numbers used by various workers.

<table>
<thead>
<tr>
<th>Linear combinations</th>
<th>μ (M) of Murao, Spedding &amp; Good</th>
<th>μ of Judd &amp; Runciman, Erath and in this work</th>
<th>Irreducible representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-\frac{15}{2}, -\frac{3}{2}, \frac{9}{2})</td>
<td>(\frac{3}{2})</td>
<td>(0)</td>
<td>(\frac{3}{2})</td>
</tr>
<tr>
<td>(-\frac{9}{2}, \frac{3}{2}, \frac{15}{2})</td>
<td>(-\frac{3}{2})</td>
<td>(3)</td>
<td>(-\frac{3}{2})</td>
</tr>
<tr>
<td>(-\frac{13}{2}, -\frac{1}{2}, \frac{11}{2})</td>
<td>(\frac{5}{2})</td>
<td>(1)</td>
<td>(\frac{1}{2})</td>
</tr>
<tr>
<td>(-\frac{11}{2}, \frac{1}{2}, \frac{13}{2})</td>
<td>(-\frac{5}{2})</td>
<td>(2)</td>
<td>(-\frac{1}{2})</td>
</tr>
<tr>
<td>(-\frac{17}{2}, -\frac{5}{2}, \frac{7}{2})</td>
<td>(\frac{1}{2})</td>
<td>(-1)</td>
<td>(\frac{5}{2})</td>
</tr>
<tr>
<td>(-\frac{7}{2}, \frac{5}{2}, \frac{17}{2})</td>
<td>(-\frac{1}{2})</td>
<td>(-2)</td>
<td>(-\frac{5}{2})</td>
</tr>
</tbody>
</table>
Table 2.2. Selection rules (electric dipole) for ions with odd numbers of electrons and having $D_{3h}$ symmetry.

<table>
<thead>
<tr>
<th>Excited states</th>
<th>$\Gamma_7$</th>
<th>$\Gamma_8$</th>
<th>$\Gamma_9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_7$</td>
<td>-</td>
<td>$\pi \sigma$</td>
<td>$\sigma$</td>
</tr>
<tr>
<td>$\Gamma_8$</td>
<td>$\pi \sigma$</td>
<td>-</td>
<td>$\sigma$</td>
</tr>
<tr>
<td>$\Gamma_9$</td>
<td>$\sigma$</td>
<td>$\sigma$</td>
<td>$\pi$</td>
</tr>
</tbody>
</table>

Table 2.3. Selection rules (electric dipole) for ions with odd numbers of electrons and having $D_{2d}$ symmetry.

<table>
<thead>
<tr>
<th>Excited states</th>
<th>$\Gamma_7$</th>
<th>$\Gamma_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_7$</td>
<td>$\sigma$</td>
<td>$\pi \sigma$</td>
</tr>
<tr>
<td>$\Gamma_6$</td>
<td>$\pi \sigma$</td>
<td>$\sigma$</td>
</tr>
</tbody>
</table>
have been given. The electric vector of the incident light may be parallel or perpendicular to the c axis of the crystal. The former case is referred to as \( \pi \) polarisation and the latter as \( \sigma \) polarization.

2.10. **Zeeman effect**

When an external magnetic field is applied to a crystal the Hamiltonian for the ion in the crystal field may be written as

\[
H = H_{\text{Free ion}} + V_{\text{cryst}} + \mathcal{H}(L+2S) \tag{2.10.1}
\]

where the first and the second terms have been described in sections (2.3) and (2.7). Usually the perturbation produced by the magnetic field is smaller than the crystal field perturbation. The matrix elements of \( (L+2S) \) are generally calculated by first diagonalizing the crystal energy matrix. The resulting eigenvectors are then used as the basis functions for calculating the Zeeman splitting.

In the first order theory of Zeeman effect, the Hamiltonian, \( H_{\text{Zeeman}} \) for a system of \( N \) electrons interacting with an external magnetic field \( \mathcal{H} \) is given by

\[
H_{\text{Zeeman}} = \beta \sum_{i=1}^{N} (L_i + g_S S_i) \cdot \mathcal{H} \tag{2.10.2}
\]

where \( \beta = \frac{e\hbar}{2mc} \) is the Bohr magneton (in spectroscopy, the convenient unit of \( \beta \) is 0.467 cm\(^{-1}\) per tesla). \( g_S \) is the gyromagnetic ratio of an electron and has the value 2.00232, i.e. \( \sim 2 \). For transverse Zeeman effect the Hamiltonian is given by
\[
H_{\text{Zeeman}} = \mathcal{H}_x (L_x + 2S_x) \quad \text{where we have substituted} \quad g_s = 2,
\]
\[
= \mathcal{H}_x (J_x + S_x)
\]
\[
= g\beta (J_x + S_x) \cdot H_x
\]
\[
(2.10.3)
\]

where \( g \) is the Lande splitting factor and is given by
\[
g = 1 + (g_s - 1) \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}
\]
\[
(2.10.4)
\]

and for the longitudinal Zeeman effect
\[
H_{\text{Zeeman}} = \mathcal{H}_z (L_z + 2S_z)
\]
\[
= g\beta (J_z + S_z) \cdot H_z
\]
\[
(2.10.5)
\]

The matrix element to be considered for the transverse Zeeman effect is of the form
\[
< f^N aSLJM_J | L_x + 2S_x | f^N aSLJ'M'_{J'} >
\]

and for longitudinal effect it is
\[
< f^N aSLJM_J | L_z + 2S_z | f^N aSLJ'M'_{J'} >.
\]

The matrix element for the transverse case is diagonal in \( S \) and \( L \). This may be evaluated using Eqn. (2.4.2) to yield a matrix element diagonal in \( J \) and this is given by
\[
< f^N aSLJM_J | L_x + 2S_x | f^N aSLJ'M_{J+1} >
\]
\[
= \pm \frac{g}{2} [(J^t M_J)(J^t M_{J+1})]^{1/2}.
\]
\[
(2.10.6)
\]

From the above Eqn. (2.10.6) it is obvious that the first order Zeeman splitting can only be induced between states whose \( M_J \) or \( J_z \) values differ by \( \pm 1 \). For an ion possessing
$D_{3h}$ symmetry the crystal quantum numbers are $\mu = \pm \frac{1}{2}, \pm \frac{3}{2}$ and $\pm \frac{5}{2}$. First order splitting is possible for states with $\mu = \pm \frac{1}{2}$ as it contains $M_J = \pm \frac{1}{2}$. The crystal field states corresponding to $\mu = \pm \frac{5}{2}$ comes from $M_J = \pm \frac{5}{2}$ and $M_J = \pm \frac{7}{2}$ which also differ in $M_J$ by $\pm 1$. $\mu = \pm \frac{3}{2}$ has contribution from states with $M_J = \pm \frac{3}{2}$ and $M_J = \pm \frac{9}{2}$ which has $\Delta \mu = 3$ and will not split in the first order.
References for Chapter 2


CHAPTER 3: Experimental Techniques

3.1. Choice of Crystals

The successful study of the spectroscopic properties of an ion in a crystal field depends to a large extent on the choice of a suitable host lattice. The optical spectrum of a rare-earth ion in a crystalline host generally appears in the same spectral region as that of the free ion. The host crystal then provides a comparatively small perturbation. Inspite of this, several important factors have to be taken into account when choosing a suitable host lattice. In pure crystals the absorption bands are very strong and there are many lines due to pair interaction or vibration of the lattice. Diluting the crystal, i.e. doping it into another crystal, can help in eliminating some of these undesired effects.

The following factors are to be taken into consideration in making the present choice of the host crystal.

1. There should be no absorption band in the range of our interest.

2. It is best to have the ionic charge, the mass and the radius of the host lattice similar to that of the impurity ion. If the radius of the impurity ion is too large, it may cause distortion of the host crystal. On the other hand, an ion with a smaller radius will have enough space to move around in the lattice site and set up its own localised mode of vibration.

3. For rotation experiments, crystals of 3 mm x 3 mm cross sectional area are required. A host lattice should be
chosen which will readily grow to a reasonable size.

In accordance with the above considerations, lanthanum ethylsulphate is transparent in the visible. The La and Er have both a charge of +3 so no charge compensation is required. The ionic radii of La\(^{3+}\) and Er\(^{3+}\) are 1.061 Å and 0.881 Å respectively and the host ion and impurity are reasonably close in size. With the technique described below crystals between 2 mm x 3 mm x 2 mm and 8 mm x 8 mm x 4 mm were grown and these were adequate for our experiments.

It has been used as the host lattice for the study of absorption and Zeeman effect of various rare-earth ion impurities and in many cases the electronic transitions and vibrational sidebands for many of these impurity ions have already been reported. Anisotropic Zeeman patterns where both the energy and intensity vary in the H \perp c spectra have been reported for Er\(^{3+}\), Dy\(^{3+}\) and Ho\(^{3+}\) ethylsulphates. Since our interest lies in observing such intensity variation we decided to reinvestigate one of these crystals.

3.2. **Crystal Structure of Rare-earth Ethylsulphates**

The rare-earth ethylsulphates with the chemical formula \(R(C_2H_5SO_4)_3.9H_2O\) (where R stands for the rare-earth and where from now on \(R(C_2H_5SO_4)_3.9H_2O\) will be abbreviated to RES) crystallize in the hexagonal form with two molecules per unit cell. Its crystal structure has been investigated by Ketelaar [1] and Fitzwater and Rundle [2]. The space group is \(C_{6h}^2\). The overall symmetry of the molecule is \(C_{3h}^9\), but the complex containing the rare-earth ion and the water molecules has pseudo-symmetry \(D_{3h}^9\). Nine water molecules
surround the magnetic ion, three of which lie in the same plane as the rare-earth ion. Of the other six, three lie above and three below the plane forming a triangular prism. The arrangement of the water molecules round the metal ion is shown in Figure (3.1). The sulphate group consists of a regular tetrahedron of four oxygen atoms round the sulphur atom. The sulphate groups are lying with their sulphur and two of their oxygen atoms in the reflection planes at right angles to the c axis. Three groups surrounding each metal ion are situated in the plane in such a way that, from each group, one of the two oxygen atoms lying in the symmetry plane points to the metal ion at a shortest distance of 2.90 Å.

3.3. Crystal Growth

Crystals of lanthanum and erbium ethylsulphate were grown. The starting materials used were the oxides of the corresponding rare-earths. 50% diluted $\text{H}_2\text{SO}_4$ was added to the oxide. The chemical reactions of the acid on the oxides of the metal ions are very slow so the solution was left for a few hours for the reaction to take place. Excess $\text{H}_2\text{SO}_4$ was driven off by heating the solution in a sand bath maintained at a constant temperature of 350°C.

The sulphate so formed was then weighed and the required quantity of barium ethylsulphate was added to it. The two salts were first mixed dry and then water was added to dissolve the products of the reaction. Highly insoluble $\text{BaSO}_4$ was precipitated out. The $\text{BaSO}_4$ was filtered off and
Figure (3.1). Arrangement of the water molecules in lanthanum ethylsulphate as seen along the crystallographic c axis. Ln$^{3+}$ represents the lanthanum ion.
the remaining solution of RES left to evaporate at room
temperature. Crystals of RES appeared within seven days.

The percentages of yield of lanthanum and
erbium ethylsulphate were 20, and 44 per cent respectively
of the theoretically calculated value. This poor yield in
quantity may be due to the fact that all the rare-earth
sulphate had not gone into solution or, in other words,
because of their low solubility they had not been all dissolved.
To obtain a better yield with lanthanum a certain quantity of
the sulphate of this salt was fully dissolved in ice cold
water (as La$_2$(SO$_4$)$_3$ is more soluble in cold water) and then
added the BaES to it. The precipitate of BaSO$_4$ was filtered
off and the solution of LaES was saturated by heating and then
left to crystallize at room temperature. The yield in this
case was 10 per cent higher than the previous one.

Doping:

The pure ErES was then mixed with LaES to
produce 10 per cent doping of the erbium. The crystals
were crushed into powders and then dissolved in distilled
water. Dilute crystals appeared within a few days.

3.4. Experimental Techniques

The zero field absorption spectra for pure
ErES and dilute ErES were recorded on Kodak 1-F (4000 Å -
6800 Å) and 1-N (6000 Å - 9000 Å) photographic plates. In
this way it is possible to observe a wide spectral range
(~700 Å) simultaneously and the sample conditions are the
same over the entire wavelength region. The bubbling
of the liquid in which the sample is immersed is not an
inconvenience in the photographic technique.
For spectra consisting of sharp lines this technique is good for accurate determination of wavelength. A standard iron arc and a zinc/cadmium/mercury spectral lamp were used for calibration. A tungsten filament lamp of 150 watts operating at 22 volts was used as a white light source.

Initially, the transverse Zeeman spectra for erbium ethylsulphate from 10,200 to 22,800 cm\(^{-1}\) were also recorded photographically. As the dispersion was 8.2 \(\AA/\text{mm}\) and the majority of the Zeeman splittings were of the order of \(\frac{1}{10}\) mm on the plate it was difficult to resolve these. In particular the change in intensity of the lines with the rotation of the crystal could not be distinguished from the plates. Thus, for the major part of the experiment photoelectric techniques were employed and the details are given in the next section.

3.5. Jarrell-Ash

The block diagram of the apparatus used is shown in Figure 3.2 and the details of the individual components are given below.

The 1.0 meter Czerny-Turner scanning spectrometer made by the Jarrell-Ash Co. was used for all the experiments. Its effective aperture ratio is f/8.7. With the gratings available spectra could be recorded from 24,000 cm\(^{-1}\) to 5,500 cm\(^{-1}\). In the region 22,500 cm\(^{-1}\) to 11,000 cm\(^{-1}\) a grating having 1180 lines/mm and blazed for 7,500 \(\AA\) was used. In the first order this gave a dispersion of 8.2 \(\AA/\text{mm}\). For recording spectra in the infra-red region a grating with
Figure (3.2). Schematic diagram of the transverse Zeeman effect.
590 lines/mm and blazed for 1.3 μm was used. This gave a dispersion of 16.4 Å/mm in the first order. A resolution of ~1 cm⁻¹ in the visible and ~1.5 cm⁻¹ in the infra-red region could be obtained. This instrument has a cosecant drive and hence is linear in energy and the dial reads directly in wavenumbers.

3.6. Detectors

3.6.1. EMI 9658 B:

The EMI 9658B has a cathode of S-20 trialkali type. The dynodes have a high stable CsSb secondary emitting surface. It provides a high quantum efficiency in the visible with a maximum at 400 nm [3]. It however has an extended infra-red response. This is achieved by having an internally corrugated end window which makes multiple reflection of the incident light.

The signal from the photomultiplier was measured using a H.P. model 510A voltmeter and the output was displayed on a Honeywell model chart recorder.

3.6.2. PbS Cell

In the infra-red 1μm to 3μm an Infra-Red Industries PbS photoconductive cell cooled to dry ice temperature (-78°C) was used. The cell has a sensitive area of 1 mm x 3 mm and is contained within a glass dewar with a hold time of 8 hours.

The light beam was mechanically chopped at 750 Hz and the signal from the PbS cell was then detected using a PAR model 180 lock-in amplifier. The output was again displayed on a chart recorder.
3.7. **Magnet**

For Zeeman measurements a superconducting magnet made by the Oxford Instrument Co. was used (Fig. 3.3). At 4.2K the maximum field strength is 5 tesla and by the use of a superconducting switch it may be run in a persistent mode.

The magnet had four optical windows. The two used were transverse to the magnetic field direction.

3.8. **Glass Dewar**

A glass dewar (Fig. 3.4) was available where the sample could be directly immersed in liquid helium or nitrogen. It was of conventional design, consisting of an inner and outer evacuated glass dewar. The inner vessel is filled with liquid helium and the outer chamber is filled with liquid nitrogen.

3.9. **Flow Tube**

With the help of a "flow tube" spectroscopic measurements from room temperature down to 6K can be made. The liquid helium is deliberately boiled by placing a heater in a 25-litre helium dewar. The boil-off gas flows up a quartz tube over the crystal. A second quartz tube surrounds the sample tube and the intervening space is evacuated.

3.10. **Sample Holders**

For recording the spectra in the glass dewar, a simple stainless steel rod with a copper plate at the bottom was all that was necessary. The sample was glued to the flat plate and light passed through a hole in the plate.
Figure (3.3). Schematic diagram of the superconducting magnet.
Figure (3.4). Glass helium dewar.
A special sample holder was made for the rotation experiment using the magnet. Two circular discs made out of copper were screwed to the end of a long stainless steel tube and the sample glued on a rectangular copper block was held between these discs. This avoided any pressure being exerted on the sample. A pointer screwed at the top was used to read the rotation of the crystal from a circular disc graduated into 360 degrees at intervals of 5 degrees (as shown in Figure 3.5a). In this device the sample (ErES) was rotated in the horizontal plane. Light could pass through the crystal when it was rotated through 60 degrees on either side of the principal axis of the crystal.

Spectra for zircon were recorded by rotating the sample in a vertical plane as shown in Figure (3.5b).

The sample was cooled by means of a helium exchange gas and the temperature could be read from a calibrated carbon resistor. The lowest temperature attained in this was 5.5K ± 1K. A wire wound heater also mounted on the sample block could then be used if higher temperatures were required.
Figure (3.5). Sample Holders (a) for ErES, (b) for zircon.
References for Chapter 3.


CHAPTER 4: Zeeman Effect in Erbium Ethylsulphate

4.1. Introduction

The main objective of this chapter is to discuss the classification of the different states in ErES. The rotation of the crystal in a transverse magnetic field causes large fluctuations in intensity of certain lines while the intensity of others are relatively unchanged. To distinguish between these states a new "quantum number" was introduced and the states classified into two types [2,3,4]. More recently this problem has been treated by Judd and Runciman [5]. They have simplified the formulation and extended the treatment to different classes of crystals with odd and even number of electrons at various site symmetries. The second and third sections of this chapter provide a brief review of the previous work on various Er\(^{3+}\) systems, particularly YES:Er and ErES. The fourth section gives a review of the theory of Zeeman rotation in rare-earth ions with C\(_{3h}\) symmetry as examined by Murao et al [1,2], Syme et al [3] and Kambara et al [4] in a series of four papers. In section 5 the theory developed in reference 5 is discussed for hexagonal crystals with a D\(_{3h}\) site symmetry.

4.2. Erbium

Erbium has been studied in a number of crystals. A detailed study of Er\(^{3+}\) in LaCl\(_3\) has been reported by Dieke and Singh [6]. Carnall et al [7] investigated the optical absorption spectra of Er\(^{3+}\):LaF\(_3\) and ErCl\(_3\):6H\(_2\)O at 4.2K in the visible and ultraviolet regions.
A good report of the work on Er$^{3+}$ in various lattice sites has been given by Dieke [8].

4.3. Erbium Ethylsulphate (ErES)

The absorption spectrum of ErES has been observed by Hufner [9] from 26,000 cm$^{-1}$ to 38,800 cm$^{-1}$.

Hellwege, Hufner and Kahle [10] were the first to observe the $\pi$ and $\sigma$ absorption spectra of YES:Er at 4.2 and 85K in the visible region. Zeeman spectra for $H \perp$ and $H \parallel$ to the c-axis of the crystal were also photographed. They obtained the $g$ and $J$ values for various levels.

Erath [11] investigated the spectra of ErES from 2$\mu$ to 2,200 $\mu$. His results agree with those of Hellwege except for three levels at $\mu = \pm \frac{5}{2}$, $\mu = \pm \frac{5}{2}$ and $\mu = \pm \frac{5}{2}$ in the group of $^2H_{11/2}$, $^4F_{7/2}$ and $^2G_{9/2}$ respectively.

The absorption spectra of ErES at 77 and 4.2K in the region 0.9 to 1.1$\mu$ were reported by Wong [12]. Transitions between the Zeeman split Stark components of the ground $J$-manifold in ErES have been studied by Wheeler and Hill [13].

4.4. Effect of Zeeman Rotation on Rare-earth Ions in Crystals with $C_{3h}$ Symmetry.

Spedding et al [14] studied the absorption spectra of YES:Er and pure ErES when the crystal is rotated in a fixed magnetic field. They recorded the $\pi$ and $\sigma$ absorption spectra for $H \parallel$ and $H \perp$ to the c-axis of the crystal.

The spectra for $H \perp c$ were found to have a 60° periodicity in energy and intensity for a rotation about the c-axis of the crystal. The maximum or minimum energy of every line occurred at $\phi_m = 0^\circ + n60^\circ$ while the intensities of the lines, although having the same periodicity, did not all
have the maximum or minimum values at the same angle.
Here $\phi_m$ is the angle between the x axis of the crystal and
the applied magnetic field and $0^\circ = \phi_e - \phi$, $\phi_e$ being the angle
of rotation of the crystal about its c-axis and $\phi$ (the phase
angle) is a measure of the angle between a and x axes of
the crystal. The z axis was chosen in the c direction. The
x axis was determined in such a way that the term $i(C_6^6 - C_{-6}^6)$
appearing in the crystal field potential was zero.

For high magnetic fields in the $H \perp c$ alignment
more lines appeared. This was because $\mu$ is no longer a good
quantum number when the Zeeman energy and the crystal field
energy are similar in magnitude. The appearance of some
"forbidden" lines at high magnetic field helps in identifying
excited levels in the ion under study.

In the first paper [1] on the theory of Zeeman
effect for rare-earth ions with $C_{3h}$ symmetry, Murao et al [1]
gave a theoretical interpretation of the Zeeman spectra for
the rare-earth ions in a crystal field of $C_{3h}$ symmetry, based
on the experimental results of Spedding et al [14]. Murao
et al [1] calculated the selection rules for the electric and
the magnetic dipole transitions, the intensities, the energy
levels and the eigenfunctions for odd and even numbers of
electrons.

In the second of these papers [2], Murao et al
calculated the transition probabilities. They looked for a
probable theory to support the fact that the symmetry of the
rare-earth ion in the ethylsulphate crystals is $D_{3h}$, but
concluded that it cannot be so. According to them the aniso-
tropy in intensity of these is due to the odd parity part
of the crystal field potential. They considered that the odd terms in the crystal field potential must consist of \( Y_{3\pm3}, Y_{5\pm3} \) and \( Y_{7\pm3} \) spherical harmonics. The sixfold periodicity with maxima and minima at certain points of the pattern of the spectrum led them to introduce a new quantum number \( \xi = \pm 1 \). \( \xi \) depends on the choice of the \( x \) axis. States which are independent of the choice of the \( x \) axis are called type A. For the type B, \( \xi \) depends on the choice of the \( x \) axis and is opposite for \( x \) axes \( 30^\circ \) apart. The \( D_{3h} \) symmetry also requires the intensity of transitions to be symmetric about \( \phi_m = 0^\circ, 30^\circ, 60^\circ, \ldots \) in addition to the \( 60^\circ \) periodicity.

In the third paper of the series Syme et al [3] considered the transitions to three different line groups in \( 42E_{\text{ES}} \). The first of these are to the \( ^4I_{9/2} \) and \( ^2G_{9/2} \) multiplets and correspond to states with \( \mu = \pm \frac{5}{2} \) and \( \mu = \pm \frac{3}{2} \). The separation between the two states was small. In the second case he considered transitions to the \( ^4S_{3/2} \) multiplet with crystal field states having \( \mu = \pm \frac{3}{2} \) and \( \mu = \pm \frac{1}{2} \). The third case considered was a set of three states of \( ^4G_{11/2} \) with \( \mu = \pm \frac{5}{2}, \pm \frac{3}{2}, \pm \frac{1}{2} \). From a theoretical study of these cases they predicted that the transitions considered in the first and third cases corresponded to a \( B + B \) type. The intensity of these transitions exhibited a \( \frac{\pi}{3} \) periodicity with rotation. The transition in the second case was shown to be a \( B + A \) type and its intensity remained unchanged with rotation. The possibility of an effective \( D_{3h} \) symmetry for the rare-earth ion have been examined.

Kambara et al [4] related A and B types in a different way than those in the previous paper. They...
approached the problem of classification of the levels by the application of group theory. A potential containing the terms $Y_{20}, Y_{40}, Y_{60}, Y_{66} + Y_{6-6}$ has a symmetry higher than $C_{3h}$. $D_{6h}$ is taken to be the approximate symmetry. $C_{2h}$ is a subgroup of $D_{6h}$. The operations of $C_{2h}$ consist of inversion, reflection in the yz plane and a twofold rotation about the x axis. The irreducible representations of $C_{2h}$ for a system having an odd number of electrons are $\Gamma_3^-$ and $\Gamma_4^-$. From the selection rule it follows that for light polarised along the direction of the field the allowed transitions are $\Gamma_3^- \rightarrow \Gamma_3^-$ and $\Gamma_4^- \rightarrow \Gamma_4^-$. For $A \rightarrow B$ and $B \rightarrow A$ they observed a periodic variation in intensity as the direction of $H$ relative to the crystal axis was changed. Transitions were allowed at certain $x$ axes and forbidden at others $\frac{\pi}{6}$ apart. These transitions depend strongly on the direction of the field.

4.5. Classification of States as Type A and Type B according to Judd and Runciman [5]

The classification of states as type A and type B as made in the above reference differs from those made previously. It does not require the choice of an x axis. The states are labelled by the irreducible representations of $C_{2h}^{1'}$ and $C_{2h}^{1''}$ when the magnetic field is along one of these directions. In a hexagonal crystal with $D_{3h}$ symmetry the even parity terms of the crystal field possess an approximate symmetry of $D_{6h}$. The $C_{2h}^{1'}$ and $C_{2h}^{1''}$ are the two twofold axes in the plane perpendicular to the sixfold axis. They are
separated by $\frac{n}{6}$ from each other. Classification of the states is only possible with the field along one of these directions. No classification is possible when the magnetic field is between $C'_{2h}$ and $C''_{2h}$. If during the rotation of the crystal from $C'_{2h}$ to $C''_{2h}$ representations $\Gamma_3^-$ and $\Gamma_4^-$ remain unchanged, the states are called type A, while for type B the representations would be interchanged.

In crystals having $D_{3h}$ symmetry the three kinds of doublets are designated by the crystal quantum numbers $\mu = \pm \frac{1}{2}, \pm \frac{3}{2}, \pm \frac{5}{2}$ corresponding to $\Gamma_8$, $\Gamma_9$ and $\Gamma_7$ respectively. The classification of $\Gamma_7$ and $\Gamma_9$ has been done in the following section. $\Gamma_9$ does not split in the first order and hence cannot be classified as any type.

In tetragonal systems the $C'_{2h}$ and $C''_{2h}$ axes are the two, twofold axes perpendicular to the fourfold symmetry plane.

4.5.1. **Intensity Sensitive Transitions**

The intensity of transition between two states $i$ and $j$ is given by square of the matrix element $<i|V_0Ey|j>$. Here $V_0$ is the odd part of the crystal field potential that makes transitions between the different crystal field states allowed and $E$ is the magnitude of the incident electromagnetic radiation applied along the $y$ direction. The intensity sensitive transitions in different types of crystals can be obtained by working out how the product $V_0 Ey$ transforms. For $D_{3h}$ symmetry the leading term in $V_0$ is given by
\[ v_0(D_{3h}) = i \{(x+iy)^3 - (x-iy)^3\} \]

With the magnetic field along the y axis (say \( C'_{2h} \) axis) the symmetry of the system is reduced to \( C_{2h} \). If now we perform the operations of \( C_{2h} \) group we find that \( E_y \) transforms as \( \Gamma^-_1 \) and \( V_0 \) transforms as \( \Gamma^-_1 \). The direct product of \( \Gamma^-_1 \) and \( \Gamma^-_1 \) is \( \Gamma^+_1 \). \( V_0 E_y \) thus transforms as \( \Gamma^+_1 \). Rotating the crystal by \( \frac{\pi}{6} \) will make the field lie along a \( C''_{2h} \) axis. The operations of the \( C_{2h} \) group on \( V_0 \) with \( H \) along \( C''_{2h} \) gives characters which correspond to \( \Gamma^-_2 \). The direct product \( \Gamma^-_1 \otimes \Gamma^-_2 \) yields \( \Gamma^+_2 \). The representation for \( V_0 E_y \) along \( C''_{2h} \) is \( \Gamma^+_2 \). Thus the selection rules for \( H \) along \( C_{2h} \) and \( C''_{2h} \) are different.

When the electric dipole operator, i.e. \( V_0 E_y \), transforms as \( \Gamma^+_1 \) for \( H \) along both \( C'_{2h} \) and \( C''_{2h} \), an \( A \rightarrow A \) or \( B \rightarrow B \) transition will remain unchanged. With the operator transforming in a different way along the two directions, transitions between same types of doublets, i.e. \( A \rightarrow A \) or \( B \rightarrow B \), will undergo a change in intensity. Thus the intensity sensitive transitions are \( B \rightarrow B \) and \( A \rightarrow A \) in \( D_{3h} \) symmetry. This corresponds to \( \Gamma^-_7 \rightarrow \Gamma^-_7 \) and \( \Gamma^+_8 \rightarrow \Gamma^-_8 \).

4.5.2. Classification of the States in \( \text{Er}^{3+} \)

We will classify the states of \( \text{Er}^{3+} \) by the irreducible representations of \( D_{3h} \). We consider first the case of a doublet for which \( J = \frac{9}{2} \) and \( \mu = \pm \frac{5}{2} \) (\( \Gamma^-_7 \)). Applying
the rule for constructing the Kramers doublet we have the two components of the above representation as [15]

\[
|1\rangle = a |\frac{5}{2}\rangle + b |\frac{-7}{2}\rangle \\
|2\rangle = -a |\frac{-5}{2}\rangle - b |\frac{7}{2}\rangle.
\]

(4.5.1)

When the magnetic field is applied parallel to the \(C_{2h}'\) axis, the \(y\) axis, the Zeeman matrix element between the states \(|1\rangle\) and \(|2\rangle\) is given by operating by \(J_y\) between the states \(|1\rangle\) and \(|2\rangle\).

\[
\langle 1| J_y |2\rangle = \frac{i}{2} \langle 1| J_- - J_+ |2\rangle
\]

\[
= \frac{i}{2} \left[ (a <\frac{5}{2}| + b <\frac{-7}{2}|) \langle J_- - J_+ | (a |\frac{-5}{2}\rangle - b |\frac{7}{2}\rangle) \right]
\]

\[
= \frac{i}{2} \left[ -ab <\frac{5}{2}| J_- - J_+ |\frac{7}{2}\rangle - ab <\frac{-7}{2}| J_- - J_+ |\frac{-5}{2}\rangle \right]
\]

\[
= -4 abi
\]

(4.5.2)

\[
\langle 2| J_y |1\rangle = \frac{i}{2} \langle 2| J_- - J_+ |1\rangle
\]

\[
= \frac{i}{2} \left[ (-a <\frac{-5}{2}| - b <\frac{7}{2}|) \langle J_- - J_+ | (a |\frac{5}{2}\rangle + b |\frac{-7}{2}\rangle) \right]
\]

\[
= \frac{i}{2} \left[ -ab <\frac{-5}{2}| J_- - J_+ |\frac{-7}{2}\rangle - ab <\frac{7}{2}| J_- - J_+ |\frac{5}{2}\rangle \right]
\]

\[
= 4 abi
\]

(4.5.3)

The Zeeman matrix for the states \(|1\rangle\) and \(|2\rangle\) is given by

\[
|1\rangle \quad |2\rangle
\]

\[
|1\rangle = \begin{pmatrix} 0 & -4 abi \\ 4 abi & 0 \end{pmatrix}.
\]

Diagonalizing this matrix gives \(\lambda = \pm 4 ab\). The Zeeman energies
are thus $-4\text{abg}\beta H$ and $4\text{abg}\beta H$. Diagonalizing the Zeeman Hamiltonian gives the resulting states as

$$
|1'\rangle = x_1 |1\rangle - ix_2 |2\rangle \\
|2'\rangle = x_1 |1\rangle + ix_2 |2\rangle .
$$

Choosing $x_1 = x_2 = \frac{1}{\sqrt{2}}$ we have

$$
|1'\rangle = \frac{1}{\sqrt{2}} |1\rangle - \frac{i}{\sqrt{2}} |2\rangle \\
|2'\rangle = \frac{1}{\sqrt{2}} |1\rangle + \frac{i}{\sqrt{2}} |2\rangle \\
$$

(4.5.4)

where $|1'\rangle$ and $|2'\rangle$ correspond to the energies $4\text{abg}\beta H$ and $-4\text{abg}\beta H$ respectively. For a rotation of $\pi$ about the $y$ axis \(R|J,M\rangle = (-1)^{J+M} |J,-M\rangle\)

thus \(R|1'\rangle = R\left[\frac{1}{\sqrt{2}} |1\rangle - \frac{i}{\sqrt{2}} |2\rangle\right]\)

$$
= \frac{R}{\sqrt{2}} \left[ a \left| \frac{5}{2} \right> + b \left| \frac{-7}{2} \right> - i(-a \left| \frac{-5}{2} \right> - b \left| \frac{7}{2} \right>) \right] \\
= \frac{1}{\sqrt{2}} \left[ a \left| \frac{-5}{2} \right> - b \left| \frac{7}{2} \right> - i(-a \left| \frac{5}{2} \right> - b \left| \frac{-7}{2} \right>) \right] \\
= \frac{1}{\sqrt{2}} \left[ |2\rangle + i|1\rangle \right] \\
= \frac{1}{\sqrt{2}} \left[ |1\rangle - i|2\rangle \right] = i|1'\rangle .
$$

The character table for $C_{2h}$ tells us that this transforms as $\Gamma_3^-$. Performing the same operation on $|2'\rangle$ we have

$$
R|2'\rangle = \frac{R}{\sqrt{2}} \left[ |1\rangle + i|2\rangle \right] \\
= \frac{R}{\sqrt{2}} \left[ a \left| \frac{5}{2} \right> + b \left| \frac{-7}{2} \right> + i(-a \left| \frac{-5}{2} \right> - b \left| \frac{7}{2} \right>) \right] \\
= \frac{1}{\sqrt{2}} \left[ a \left| \frac{-5}{2} \right> - b \left| \frac{7}{2} \right> + i(-a \left| \frac{5}{2} \right> - b \left| \frac{-7}{2} \right>) \right] .
$$
Thus for a rotation of \( \pi \) about the \( y \) axis \(|2'> \) becomes \(-i|2'>\) and the character table for \( C_{2h} \) shows that this belongs to the irreducible representation \( \Gamma_4^- \).

When the crystal is rotated by \( \frac{\pi}{6} \) about the principal axis (the \( z \) axis) from the direction the magnetic field \( H \) will lie along the axis of \( C_{2h}'' \). The states are now given by

\[
|3'> = a|\frac{5}{2}> - b|\frac{-7}{2}> \\
|4'> = -a|\frac{-5}{2}> + b|\frac{7}{2}>
\]

The Zeeman matrix elements are

\[
<3|J_y|4'> = \frac{1}{2} \left[ (a\frac{5}{2} - b\frac{-7}{2}) |J_-J_+| (-a|\frac{-5}{2}> + b|\frac{7}{2}>) \right] \\
= \frac{1}{2} \left[ ab\frac{5}{2}|J_-J_+|\frac{7}{2} > + ab\frac{-7}{2}|J_-J_+|\frac{-5}{2} > \right] \\
= 4ab_i
\]

\[
<4|J_y|3'> = \frac{1}{2} \left[ (-a\frac{5}{2} + b\frac{7}{2}) |J_-J_+| (a|\frac{5}{2}> - b|\frac{-7}{2}>) \right] \\
= \frac{1}{2} \left[ ab\frac{-5}{2}|J_-J_+|\frac{-7}{2} > + ab\frac{7}{2}|J_-J_+|\frac{5}{2} > \right] \\
= -4ab_i
\]

The Zeeman energy levels obtained in the same way as before are now \( 4ab\beta H \) and \(-4ab\beta H \). Comparing this with the previous case we see that the energy levels are reversed.

The resulting states are now given by

\[
|3'> = \frac{1}{\sqrt{2}} |3> - \frac{i}{\sqrt{2}} |4> \\
|4'> = \frac{1}{\sqrt{2}} |3> + \frac{i}{\sqrt{2}} |4>
\]

(4.5.6)
where \( |3'\rangle \) corresponds to the energy \(-4\alpha\beta g\beta H\) and \(|4'\rangle\) to \(+4\alpha\beta g\beta H\).

\[
R|3'\rangle = \frac{R}{\sqrt{2}} \left[ a|\frac{5}{2}\rangle - b|\frac{7}{2}\rangle \right]
= \frac{1}{\sqrt{2}} \left[ -a|\frac{5}{2}\rangle + b|\frac{7}{2}\rangle - i(-a|\frac{5}{2}\rangle + b|\frac{7}{2}\rangle) \right]
= \frac{1}{\sqrt{2}} \left[ |4\rangle + i|3\rangle \right] = \frac{1}{\sqrt{2}} \left[ |3\rangle - i|4\rangle \right] = i|3'\rangle
\]

\[
R|4'\rangle = \frac{R}{\sqrt{2}} \left[ a|\frac{5}{2}\rangle - b|\frac{7}{2}\rangle + i(-a|\frac{5}{2}\rangle + b|\frac{7}{2}\rangle) \right]
= \frac{1}{\sqrt{2}} \left[ -a|\frac{5}{2}\rangle + b|\frac{7}{2}\rangle + i(-a|\frac{5}{2}\rangle + b|\frac{7}{2}\rangle) \right]
= \frac{1}{\sqrt{2}} \left[ |4\rangle - i|3\rangle \right]
= -\frac{i}{\sqrt{2}} \left[ |3\rangle + i|4\rangle \right] = -i|4'\rangle .
\]

\(R|3'\rangle\) belongs to the irreducible representation \(\Gamma_3^-\) and \(R|4'\rangle\) to \(\Gamma_4^-\) of the \(C_{2h}\) group.

We find that in going from \(C_{2h}'\) to \(C_{2h}''\) the labels of the doublets are still \(\Gamma_3^-\) and \(\Gamma_4^-\) but their energies are reversed. The Kramers' doublet corresponding to \(\mu = \pm \frac{5}{2}\) thus transforms as type B.

If now we consider the ground doublet of \(\text{Er}^{3+}\) with \(J = \frac{15}{2}\) and \(\mu = \pm \frac{5}{2}\) (mod 6) the Zeeman components are

\[
\begin{align*}
|1\rangle &= a|\frac{5}{2}\rangle + b|\frac{7}{2}\rangle \\
|2\rangle &= a|\frac{-5}{2}\rangle + b|\frac{7}{2}\rangle
\end{align*}
\]

Operating by \(J_y\) between these two states would give the energies of the two states as \(\sqrt{55}\alpha\beta g\beta H\) and \(-\sqrt{55}\alpha\beta g\beta H\). The resulting states would be the same as equation (4.5.4) which means that one of the energy levels would transform as \(\Gamma_3^-\) and the other as \(\Gamma_4^-\) of the \(C_{2h}\) character group.
Rotating the crystal by $\frac{\pi}{6}$ about the c axis makes the components

$$
\begin{align*}
|3> &= a |\frac{5}{2} > - b |\frac{-7}{2} > \\
|4> &= a |\frac{-5}{2} > - b |\frac{7}{2} > .
\end{align*}
$$

(4.5.8)

The change in sign of $b$ for the component $|3>$ and $|4>$ in equations (4.5.7) and (4.5.8) with the other values unchanged indicates that the energies of the two components are still the same, but they are now reversed. This again transforms as a $B$ type. The $\mu = \pm \frac{1}{2}$ (mod 6) of the ground state ($J = \frac{15}{2}$) have the components of the Kramers' doublets represented by

$$
\begin{align*}
|1> &= a |\frac{-11}{2} > + b |\frac{1}{2} > + c |\frac{13}{2} > \\
|2> &= a |\frac{11}{2} > + b |\frac{-1}{2} > + c |\frac{-13}{2} > .
\end{align*}
$$

(4.5.9)

The Zeeman energies of the two components are found to be $4\sqrt{7}acg\beta H$ and $-4\sqrt{7}acg\beta H$. Under rotation these states transform in the same way as equation (4.5.1). This implies that the $C'_{2h}$ representations for these doublets are $\Gamma^-_3$ and $\Gamma^-_4$. Rotating the crystal by $\frac{\pi}{6}$ to bring it along $C''_{2h}$ gives the states

$$
\begin{align*}
|1'> &= a |\frac{-11}{2} > + b |\frac{1}{2} > + c |\frac{13}{2} > \\
|2'> &= a |\frac{11}{2} > + b |\frac{-1}{2} > + c |\frac{-13}{2} >
\end{align*}
$$

which is the same as equation (4.5.9). The energy levels thus remain unchanged. This is the characteristic of an $A$-type level. From these results we can generalize that for all odd electron systems a state with $\mu = \pm \frac{5}{2}$ is type $B$ and a state with $\mu = \pm \frac{1}{2}$ is type $A$. 
References to Chapter 4

   Ions in Crystals" (Interscience, New York, 1968).
   A218, 553 (1953).
5.1. Introduction

In this chapter we deal with the experimental measurements on LaES:Er and ErES. Our main interest lies in observing the angular variation of the Zeeman spectra. As discussed in Chapter 4, pronounced angular variation is predicted for certain types of transitions, and in a system of $D_{3h}$ symmetry the transitions of interest are forbidden in zero field. A strong magnetic field which mixes the crystal field states is required to induce these transitions, but zero field measurements are required to identify the various transitions and these are presented first.

The low temperature $\pi$ and $\sigma$ spectra for the region between 12,400 cm$^{-1}$ and 22,700 cm$^{-1}$ have been observed in pure ErES and 10 per cent ErES in LaES. The spectra of the concentrated ErES sample consisted of more lines than the number of transitions allowed for a single $D_{3h}$ Er$^{3+}$ site. This presumably is due to cooperative effects and so to eliminate these we studied dilute LaES:Er samples. They show fewer lines and the number is never greater than the number of group theoretically allowed transitions. The spectra were taken at 4.2K and only the lowest level was populated (Boltzmann distribution) since the first Stark level of ErES is 44 cm$^{-1}$ above the ground state. Zeeman measurements to be reported in this chapter were also carried out, but the detailed work is concentrated on the $^4I_{9/2}$ band at 12,400 cm$^{-1}$ and the $^4F_{9/2}$ at 15,300 cm$^{-1}$ as definite orientation effects were observed in these cases. Consequently, in discussion of the zero field absorption we also pay most
attention to these bands.

The optical absorption lines of LaES:Er measured at 4.2K are listed in Table 5.1. The first column in the table gives the term assignment according to Wybourne [1] and Hellwege [2]. Hellwege has not observed transitions to the \( ^4I_9/2 \) and this band has been assigned according to Wybourne [1]. The bands at 12,400 cm\(^{-1}\) and 15,300 cm\(^{-1}\) have been assigned by Wybourne to be transitions to \( ^4I_9/2 \) and \( ^4F_9/2 \) respectively. Erath's [3] assignments to these two LSJ levels are opposite to those of Wybourne. However, it is clearly indicated from Wybourne's calculation of the eigenvectors that Erath's assignments to these two LSJ levels should be reversed. The second column in Table 5.1 gives the crystal quantum number of the excited state. The polarizations in which the transitions appear are listed in column 3. The irreducible representation corresponding to each crystal quantum number is given in column 4 and the positions of the energy levels are listed in column 5.

5.1.1. \( ^4I_{15/2} \rightarrow ^4I_{9/2} \)

Before considering the details of \( ^4I_{15/2} \rightarrow ^4I_{9/2} \) transitions we consider the Stark splitting of the \( ^4I_{15/2} \) ground manifold. The \( D_{3h} \) crystal field splits a level with \( J = \frac{15}{2} \) into eight states, two \( \mu = \pm \frac{5}{2} \), three \( \mu = \pm \frac{1}{2} \), three \( \mu = \pm \frac{3}{2} \). Crystal field calculations including those presented here predict that the lowest Stark level of LaES:Er has \( \mu = \pm \frac{5}{2} \) and the first excited state has \( \mu = \pm \frac{3}{2} \) lying about 44 cm\(^{-1}\) above the ground state (see calculations in Section 5.2 and Table 5.3). These assignments of \( \mu \) values give good agreement with those of previous workers [2,3].

In a crystal field of \( D_{3h} \) symmetry a level with
<table>
<thead>
<tr>
<th>Term assignment</th>
<th>Crystal quantum number $\mu$</th>
<th>Polarization</th>
<th>Irreducible represenation</th>
<th>Energy levels $\text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4I_{9/2}$</td>
<td>$\pm \frac{3'}{2}$</td>
<td>$\sigma$</td>
<td>$\Gamma_9$</td>
<td>12,428.2</td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{3}{2}$</td>
<td>$\sigma$</td>
<td></td>
<td>12,539.4*</td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{1}{2}$</td>
<td>$\pi\sigma$</td>
<td></td>
<td>12,570.3*</td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{3}{2}$</td>
<td>$\sigma$</td>
<td></td>
<td>12,594.2*</td>
</tr>
<tr>
<td>$^4F_{9/2}$</td>
<td>$\pm \frac{3'}{2}$</td>
<td>$\sigma$</td>
<td>$\Gamma_9$</td>
<td>15,309.7</td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{1}{2}$</td>
<td>$\pi\sigma$</td>
<td>$\Gamma_8$</td>
<td>15,339.1</td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{3}{2}$</td>
<td>$\sigma$</td>
<td>$\Gamma_9$</td>
<td>15,377.2</td>
</tr>
<tr>
<td>$^4S_{3/2}$</td>
<td>$\pm \frac{3}{2}$</td>
<td>$\sigma$</td>
<td>$\Gamma_9$</td>
<td>18,460.7</td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{1}{2}$</td>
<td>$\pi\sigma$</td>
<td>$\Gamma_8$</td>
<td>18,488.8</td>
</tr>
<tr>
<td>$^2H_{11/2}$</td>
<td>$\pm \frac{3'}{2}$</td>
<td>$\sigma$</td>
<td>$\Gamma_9$</td>
<td>19,221.8</td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{1}{2}$</td>
<td>$\pi\sigma$</td>
<td>$\Gamma_8$</td>
<td>19,250.5</td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{3}{2}$</td>
<td>$\sigma$</td>
<td>$\Gamma_9$</td>
<td>19,263.7</td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{1}{2}$</td>
<td>$\pi\sigma$</td>
<td>$\Gamma_8$</td>
<td>19,293.6</td>
</tr>
<tr>
<td>$^4F_{7/2}$</td>
<td>$\pm \frac{3}{2}$</td>
<td>$\sigma$</td>
<td>$\Gamma_9$</td>
<td>20,588.9</td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{1}{2}$</td>
<td>$\pi\sigma$</td>
<td>$\Gamma_8$</td>
<td>20,651.8</td>
</tr>
<tr>
<td>$^4F_{5/2}$</td>
<td>$\pm \frac{3}{2}$</td>
<td>$\sigma$</td>
<td>$\Gamma_9$</td>
<td>22,257.1</td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{1}{2}$</td>
<td>$\pi\sigma$</td>
<td>$\Gamma_8$</td>
<td>22,280.6</td>
</tr>
<tr>
<td>$^4F_{3/2}$</td>
<td>$\pm \frac{3}{2}$</td>
<td>$\sigma$</td>
<td>$\Gamma_9$</td>
<td>22,588.6</td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{1}{2}$</td>
<td>$\pi\sigma$</td>
<td>$\Gamma_8$</td>
<td>22,638.6</td>
</tr>
</tbody>
</table>

* Impurity lines associated with low $g$ value (see) discussion on Zeeman effect in Section 5.6.)
$J = \frac{9}{2}$ will split into five states, two $\mu = \pm \frac{5}{2}$, two $\mu = \pm \frac{3}{2}$ and one $\mu = \pm \frac{1}{2}$. Selection rules from Table 2.2 predict that at 4.2K three transitions from a ground state of $\mu = \pm \frac{5}{2}$ are allowed. Transitions to $\mu = \pm \frac{3}{2}$ will be only $\sigma$ polarized and other transitions to $\mu = \pm \frac{1}{2}$ will be both $\sigma$ and $\pi$ polarized. The line at 12,428.2 cm$^{-1}$ was observed in $\sigma$ only and thus assigned to $\mu = \pm \frac{3}{2}$. Two further lines were reported by Erath [3] lying at 12,525 cm$^{-1}$ and 12,540 cm$^{-1}$ from measurements of the concentrated crystals. However, these two transitions may have been masked by very strong additional lines in this energy region at 12,539.4 cm$^{-1}$, 12,570.3 cm$^{-1}$ and 12,594.2 cm$^{-1}$. These strong lines have been established from Zeeman measurements to be associated with a different centre (see later discussion on the Zeeman effect).

5.1.2. $\frac{4}{1}I_{15/2} \rightarrow \frac{4}{1}F_{9/2}$

The $\frac{4}{1}F_{9/2}$ will split in a crystal field of D$_{3h}$ symmetry into the same number of levels as the $\frac{4}{1}I_{9/2}$ and hence three transitions are allowed from the lowest Stark level of the ground manifold. We observed these three allowed transitions. The lines at 15,309.7 cm$^{-1}$ and 15,377.2 cm$^{-1}$ were observed only in the $\sigma$ spectrum and they were therefore assigned to $\mu = \pm \frac{3}{2}$. To distinguish between the two $\mu = \pm \frac{3}{2}$ a prime is used in the tables. The transition at 15,339.1 cm$^{-1}$ was observed in both the $\pi$ and $\sigma$ polarizations and consequently attributed to the $\mu = \pm \frac{1}{2}$ state.
The polarized absorption spectra associated with the crystal field levels of \( ^{4}S_{3/2}, ^{2}H_{11/2}, ^{4}I_{15/2}, ^{4}F_{7/2} \) were observed for a sample temperature of 4.2K and by applying the selection rules of Table 2.2 assignments of the crystal quantum numbers were made (Table 5.1). Good agreement with Hellwege [2] and Erath [3] were obtained for all the LSJ levels. The largest variation was 3 to 5 cm\(^{-1}\) with exact agreement for the majority of the lines.

The Zeeman spectra of many of the lines in the above bands were not resolved. In some cases the Zeeman spectra did not show a pronounced angular dependence. In other cases the lines were weak in zero field and could not be followed when split by a field into several components.

5.2. Crystal Field Calculations of \( ^{4}I_{15/2}, ^{4}F_{9/2} \) and \( ^{4}I_{9/2} \) of LaES:Er.

Crystal field calculations were undertaken to compare with the experimental splittings and to verify our assignments of the crystal quantum numbers. The crystal quantum number of the ground state (which can be determined from a knowledge of the crystal field) taken in conjunction with the selection rules for polarized light allows us to determine the crystal quantum numbers for the excited states.

The crystal field interaction mixes states of the same total spin \( S \) and different total angular momentum \( J \). Calculation of crystal field splitting by means of the operator equivalent method automatically takes intermediate coupling
into account. The crystal field splittings of $^4I_{15/2}$, $^4I_{9/2}$ and $^4F_{9/2}$ levels of ErES were calculated by making use of operator equivalents.

The reduced matrix elements of Eqn. (2.8.4) in terms of operator equivalents between states of the same $J$ are given by [4],

$$< \tau SLJ|\alpha_J|\tau' SL'J' > = -8\sqrt{\frac{7(2J-2)!}{15(2J+3)!}} < \tau SLJ|U^2|\tau' SL'J' > $$

(5.2.1)

$$< \tau SLJ|\beta_J|\tau' SL'J' > = 16\sqrt{\frac{14(2J-4)!}{11(2J+5)!}} < \tau SLJ|U^4|\tau' SL'J' > $$

(5.2.2)

$$< \tau SLJ|\gamma_J|\tau' SL'J' > = -640\sqrt{\frac{7(2J-6)!}{429(2J+7)!}} < \tau SLJ|U^6|\tau' SL'J' > $$

(5.2.3)

where the quantum numbers $\tau$ here corresponds to $a$ in Eqn. (2.8.4). $\alpha_J$, $\beta_J$ and $\gamma_J$ are the Stevens [5] operator equivalents.

The reduced matrix elements for $U^2$, $U^4$, $U^6$ were determined by using Eqns. (5.2.1), (5.2.2) and (5.2.3).

For ions with an odd number of electrons it is not possible to distinguish between $C_{3h}$ and $D_{3h}$ symmetry either on the basis of polarization selection rules or a crystal field calculation [6]. The crystal fields differ by an imaginary non-cylindrical part. By making proper choice of axes this term vanishes. The crystal field potential for $D_{3h}$ symmetry as given by Eqn. (2.7.4) is

$$V_{D_{3h}} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_0^6 C_0^6 + B_6^6 (C_6^6 + C_{-6}^6) .$$

The matrix elements of $V$ given by the above equation were calculated. Diagonalizing the matrix gave the crystal field splittings of a definite multiplet. The splittings of the $^4I_{9/2}$, $^4F_{9/2}$ are given in Table (5.2) and the ground state
Table 5.2. Crystal field splittings for $^4I_{9/2}$ and $^4F_{9/2}$ of ErES.

<table>
<thead>
<tr>
<th>Term</th>
<th>Crystal quantum number $\mu$</th>
<th>Splittings (cm$^{-1}$)</th>
<th>This calculation</th>
<th>Erath's calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^4I_{9/2}$</td>
<td>$\pm \frac{3'}{2}$</td>
<td>-87.70</td>
<td>-87.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{5'}{2}$</td>
<td>-71.63</td>
<td>-71.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{3}{2}$</td>
<td>8.81</td>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{1}{2}$</td>
<td>25.46</td>
<td>25.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{5}{2}$</td>
<td>125.13</td>
<td>125.1</td>
<td></td>
</tr>
<tr>
<td>$^4F_{9/2}$</td>
<td>$\pm \frac{3'}{2}$</td>
<td>-46.73</td>
<td>-46.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{1}{2}$</td>
<td>-18.03</td>
<td>-18.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{5'}{2}$</td>
<td>-1.69</td>
<td>-1.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{3}{2}$</td>
<td>18.93</td>
<td>18.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pm \frac{5}{2}$</td>
<td>47.47</td>
<td>47.5</td>
<td></td>
</tr>
</tbody>
</table>

The crystal field parameters are:

- $A_2^0 < r^2 > = 125.80$
- $A_4^0 < r^4 > = -81.19$
- $A_6^0 < r^6 > = -31.06$
- $A_6^6 < r^6 > = 387.19$
Table 5.3. Ground state splitting of ErES.

<table>
<thead>
<tr>
<th>Crystal quantum number $\mu$</th>
<th>Splittings (cm$^{-1}$)</th>
<th>This calculation</th>
<th>Erath's calculation</th>
<th>Calculated without mixing</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pm \frac{5'}{2}$</td>
<td>-147.31</td>
<td>-147.3</td>
<td>-151.78</td>
<td></td>
</tr>
<tr>
<td>$\pm \frac{3''}{2}$</td>
<td>-104.46</td>
<td>-104.5</td>
<td>-107.48</td>
<td></td>
</tr>
<tr>
<td>$\pm \frac{3'}{2}$</td>
<td>-72.12</td>
<td>-72.2</td>
<td>-74.86</td>
<td></td>
</tr>
<tr>
<td>$\pm \frac{1''}{2}$</td>
<td>-36.65</td>
<td>-36.7</td>
<td>-35.50</td>
<td></td>
</tr>
<tr>
<td>$\pm \frac{5}{2}$</td>
<td>26.36</td>
<td>26.4</td>
<td>28.02</td>
<td></td>
</tr>
<tr>
<td>$\pm \frac{3}{2}$</td>
<td>62.49</td>
<td>62.5</td>
<td>65.02</td>
<td></td>
</tr>
<tr>
<td>$\pm \frac{1'}{2}$</td>
<td>113.34</td>
<td>113.5</td>
<td>114.85</td>
<td></td>
</tr>
<tr>
<td>$\pm \frac{1}{2}$</td>
<td>158.13</td>
<td>158.3</td>
<td>161.71</td>
<td></td>
</tr>
</tbody>
</table>
splitting in Table (5.3). Erath's crystal field parameters were used in making this calculation.

As can be seen from these tables, the above calculation gives exact agreement with those of Erath.

The ground state splitting was included in the above operator equivalent calculations. However a second calculation which does not allow for the mixing due to intermediate coupling was also made. V was evaluated in terms of the reduced matrix elements of \( U^2 \), \( U^4 \) and \( U^6 \) whose values were obtained from the tables of Neilson and Koster [7]. Wybourne [1] has shown that this state, the \( ^4I_{15/2} \), is not appreciably mixed with other states and consequently a comparison of the ground state splitting with those of our previous (operator equivalent method) shows little difference in the predicted splittings.

The calculation of the splitting in the \( ^4I_{9/2} \) band using operator equivalents gave satisfactory agreement with the experimentally observed levels as can be seen from Table (5.4). In this table Erath's data is compared with calculation and it can be seen that there is agreement to within 2 cm\(^{-1}\) between experimental and calculated values. However, although we have only been able to determine two energy levels in this band one of these, i.e. the \( \Gamma_7 \) lying within 1 cm\(^{-1}\) of the \( \Gamma_9 \), has a substantially different energy from the one used by Erath. This indicates that the agreement is slightly fortuitous. The parameters used in the calculation could presumably be changed to give better agreement with the new set of data. However, it would seem advisable first to confirm the other assignments made by Erath. The line at 12,439.9 cm\(^{-1}\) assigned by Erath to the \( \Gamma_7 \) and shown to be incorrect is obtained from concentrated materials (ErES). To avoid this source of error it would be better to confirm the other lines for dilute samples. However, even when
Table 5.4. Comparison with Erath's work on the transitions to the $^4I_{9/2}$ band of Er:LaES.

<table>
<thead>
<tr>
<th>Irreducible representation</th>
<th>Erath's observation cm$^{-1}$</th>
<th>Present observation cm$^{-1}$</th>
<th>Present calculation cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_9$</td>
<td>12,426.2</td>
<td>12,428.2</td>
<td>12,426.1</td>
</tr>
<tr>
<td>$\Gamma_7$</td>
<td>12,439.9*</td>
<td>12,428.7</td>
<td>12,442.2</td>
</tr>
<tr>
<td>$\Gamma_9$</td>
<td>12,525.0</td>
<td></td>
<td>12,522.6</td>
</tr>
<tr>
<td>$\Gamma_8$</td>
<td>12,540.2</td>
<td></td>
<td>12,539.3</td>
</tr>
<tr>
<td>$\Gamma_7$</td>
<td>12,637.7</td>
<td></td>
<td>12,638.9</td>
</tr>
</tbody>
</table>

* Zeeman data to be presented in the next section shows the lower energy $\Gamma_9$ and $\Gamma_7$ levels to be nearly degenerate (separation $< 1$ cm$^{-1}$). Hence Erath's identification of the line at 12,439.9 must be incorrect.

Table 5.5. Comparison with Erath's work on the transition to the $^4F_{9/2}$ band.

<table>
<thead>
<tr>
<th>Irreducible representation</th>
<th>Erath's observation cm$^{-1}$</th>
<th>Present observation cm$^{-1}$</th>
<th>Present calculation cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_9$</td>
<td>15,307.2</td>
<td>15,309.7</td>
<td>15,307.8</td>
</tr>
<tr>
<td>$\Gamma_8$</td>
<td>15,339.8</td>
<td>15,339.1</td>
<td>15,336.5</td>
</tr>
<tr>
<td>$\Gamma_7$</td>
<td>15,346.9</td>
<td></td>
<td>15,352.8</td>
</tr>
<tr>
<td>$\Gamma_9$</td>
<td>15,377.7</td>
<td>15,377.2</td>
<td>15,373.5</td>
</tr>
<tr>
<td>$\Gamma_7$</td>
<td>15,402.1</td>
<td></td>
<td>15,402.0</td>
</tr>
</tbody>
</table>
using thick samples (>4 mm) and various temperatures (2.2K to 77K) no indication of these levels was obtained in our spectrum. Without being able to confirm this line it was considered that further calculations were not justified.

In the case of $^4P_{9/2}$ our experimental energy levels and assignments agree with those of Erath's experimental values. There is also good agreement between the calculated value and the experimental values as can be seen from Table (5.5).

5.3. **Zeeman Effect**

5.3.1. $^4I_{15/2} \rightarrow ^4I_{9/2}$

The field dependence of the transverse Zeeman spectra of the 12428.2 cm$^{-1}$ line in this band is shown in Figure (5.1) and the splittings in Figure (5.2). The spectra were recorded with the electric vector of the incident light and the direction of the field parallel to a twofold axes which is referred (zero rotation) to a $C_{2h}$ axis.

With the magnetic field applied along the $C_{2h}$ axis the symmetry of the Er$^{3+}$ site is lowered from $D_{3h}$ to $C_{2h}$. In this lower symmetry group the $\Gamma_7$, $\Gamma_8$ and $\Gamma_9$ representations of the $D_{3h}$ group transform as $\Gamma_3^-$ and $\Gamma_4^-$. For light polarized along the principal crystal axis ($H \perp E$) the allowed transitions are $\Gamma_3^- \rightarrow \Gamma_4^-$ while for light polarized along the crystal $Y$ axis ($H \parallel E$) the allowed transitions are $\Gamma_3^- \rightarrow \Gamma_3^-$ and $\Gamma_4^- \rightarrow \Gamma_4^-$. For an off-axis direction all transitions are allowed.

Our Zeeman measurements of the Er$^{3+}$ lines and the line at 12,428.2 cm$^{-1}$ in particular show that the ground state splitting is large and at 5T the splitting is ~20 cm$^{-1}$. This ground state splitting corresponds to a g-value of about 8.6 and this is consistent with the EPR measurements [8] which give
Figure (5.1). Field dependence of the transition at 12428.2 cm\(^{-1}\). Solid line joins the allowed transitions and broken lines join the transitions from other polarization.
Figure (5.2). Zeeman splitting of the $\Gamma_7$ and $\Gamma_9$ level in $^{4}_{1}I_{9/2}$. 
a $g_\perp$ value of $8.85 \pm 0.2$.

For an off-axis field direction a four-line Zeeman pattern from the lower Zeeman component of the ground state can arise only when there are two neighbouring levels in the excited state. The above field measurements indicate that this is the situation and that there is enough interaction between two levels to make all lines clearly visible (lines 1, 2, 3, and 4).

For a field along a $C_{2h}'$ axis (Figure 5.1) the lines 1 and 3 are strong corresponding to the allowed transitions $\Gamma_4^- \rightarrow \Gamma_4^-$. The strongest transition in the spectrum is line 3 and must correspond to the transition $\Gamma_4^- \rightarrow \Gamma_4^-$, where the excited $\Gamma_4^-$ is associated with the larger $\Gamma_9$ contribution; as $\Gamma_7 \rightarrow \Gamma_9$ is allowed in zero field. Line 1 corresponds to an allowed transition $\Gamma_4^+ \rightarrow \Gamma_4^-$ where in the excited state the component of $\Gamma_9$ is smaller and consequently that of $\Gamma_7$ larger. These intensities will vary with field as the mixing changes. The field induced transitions (lines 1 and 3) have been observed at 1 tesla which indicates that there is enough mixing between the two excited states even at this field strength. This arises because the separation between the two levels is very small. The two weak lines at 2 and 4 are group theoretically forbidden in this polarization ($E \parallel H$ or $H \parallel C_{2h}$ axis) and their appearance is presumably due to a slight misalignment of the crystal. Lines 6 and 5 are the respective hot components of lines 1 and 3. As is seen, their intensity gradually decreases with the increase of field strength. The energy level diagram is shown in Figure (5.3).

The field measurements (Figure 5.1) show that the splittings are linear and extrapolate to zero field. It
Figure (5.3). Energy level diagram for transitions to \( \Gamma_7 \) and \( \Gamma_9 \) degenerate levels of the \( ^4I_{9/2} \). Solid lines correspond to allowed transitions.
indicates that the \( \Gamma_7 \) level lies within 0.5 cm\(^{-1}\) (Figure 5.2) of the \( \Gamma_9 \) level at 12,428.2 cm\(^{-1}\). According to our crystal field calculation, the separation between the \( \Gamma_7 \) and \( \Gamma_9 \) level is 16 cm\(^{-1}\) and Erath's experimental measurement gives 14 cm\(^{-1}\). If this was the case, then an entirely different Zeeman pattern would be obtained. The \( \Gamma_9 \) does not split in a magnetic field and hence with a separation of \( \sim 16 \) cm\(^{-1}\) between \( \Gamma_7 \) and \( \Gamma_9 \) line at 12,428.2 cm\(^{-1}\) would only show a small splitting, a shift to lower energy and a loss in intensity. The lost intensity would appear 16 cm\(^{-1}\) high in energy corresponding in transition to the \( \Gamma_7 \) state. This is not observed and consequently we conclude that Erath's assignment of a level at 12,439.9 cm\(^{-1}\) to the \( \Gamma_7 \) level is incorrect. As he used a concentrated sample, this line may be due to a cooperative effect.

To confirm the position of \( \Gamma_7 \) the spectra was recorded at 50K. At this temperature the first excited level which has \( \mu = \pm \frac{3}{2} \) is populated and transition from this level to an excited \( \Gamma_7 \) (\( \mu = \pm \frac{5}{2} \)) is allowed in \( \sigma \). Again a transition from \( \Gamma_9 \) to \( \Gamma_9 \) is allowed in \( \pi \). The \( \pi \) and \( \sigma \) spectra at 50K were recorded and the position of \( \Gamma_7 \) was confirmed to be within 0.5 cm\(^{-1}\) of the \( \Gamma_9 \) level.

5.3.2. \[ ^4I_{15/2} \rightarrow ^4F_{9/2} \]

The Zeeman effects for the transitions at 15,339.1 cm\(^{-1}\) (\( \Gamma_8 \)) and 15,377.2 cm\(^{-1}\) (\( \Gamma_9 \)) have been observed and are shown in Figure (5.4) for a temperature of \( \sim 12K \). The line at 15,377.2 cm\(^{-1}\) (\( \Gamma_9 \)) is split into two lines and the separation is consistent with the ground state splitting.
Figure (5.4). Field dependence of the levels in $^{4}F_{9/2}$.
This is what is expected because the \( \Gamma_9 \) state is not split in a field in first order. The two-line spectrum merely reflects the splitting of the ground state.

A four-line pattern was obtained from the \( \Gamma_7 \rightarrow \Gamma_8 \) transition at 15,339.1 cm\(^{-1}\) (\( \Gamma_8 \)). Line 3 (Figures 5.4 and 5.5) is the strongest and must correspond to an allowed transition. Line 1 is the corresponding transition from the upper component of the ground state and loses intensity as the Zeeman separation is increased. Line 4 and line 2 are transitions from the lower and upper ground component to the upper component of \( \Gamma_8 \) (Figure 5.5). The transitions 1 and 4 are group theoretically forbidden for a field along \( C_{2h} \) axis, but they have been observed as the alignment of the crystal with respect to the field is not perfect. The band showed little intensity variation in accordance with that predicted for \( \Gamma_7 \rightarrow \Gamma_8 \) and \( \Gamma_7 \rightarrow \Gamma_9 \) transitions.
5.4. Angular Variation of the Transition at 12,428.2 cm\(^{-1}\)

It has been established above that a \(\Gamma_7\) level lies 0.5 cm\(^{-1}\) from the \(\Gamma_9\) line at 12,428.2 cm\(^{-1}\) and that there is appreciable magnetic field mixing between the two states. It is expected that since the \(\Gamma_7\) transforms as a B type the \(\sigma\) transition to this level from the ground state would show a periodic fluctuation in intensity with the rotation of the crystal in a transverse magnetic field. To observe this angular variation, spectra were recorded for a fixed magnetic field while the crystal was rotated at small intervals about the principal crystal axis.

With the magnetic field along the y direction, i.e. when there is no rotation the spectrum consists of four lines. At this position the magnetic field is along one of the \(C_{2h}'\) axes of the crystal. As seen from Figure 5.6a (0° rotation) line 2 and 4 are relatively weak. Line 1 is strong and line 3 is the strongest. On rotating the crystal the intensity of the two weak lines gradually increases with simultaneous decrease in intensity of the other two. For example, in the spectra recorded with the crystal rotated +20° (positive: anticlockwise) the intensity of the lines 1 and 2 are nearly the same. The intensity of line 3 has dropped 30% with a corresponding increase in the intensity of line 4. At +24° the lines are equally prominent (factor of 2.5 between the strongest line 2 and the weakest line 1). The pattern of the +30° spectra is just the complement of what it was with \(H\) along \(C_{2h}'\). Lines 2 and 4 are strongest while 1 and 3 are weak (Figures 5.6a and 5.6b). Rotating the crystal further anticlockwise the intensity of 1 and 3 gradually increases
again and the corresponding decrease in 2 and 4 take place. At +60° the intensity of lines 2 and 4 have dropped although the ratios of the intensities of the four lines are not the same as they were with H along \( C_{2h}^1 \) axis (no rotation). Rotating the crystal by 60° should orient the field along another \( C_{2h}^1 \) axis and the spectral pattern should be the same as for zero rotation. In the present experiment the pattern did not repeat exactly. There could be many reasons for the slight discrepancy. Primarily the crystal could be slightly misaligned and we know that this can be critical for these experiments. For example, if the crystal is not perfectly aligned some of the forbidden transitions do not exactly go to zero [9] and indeed in zero rotation we did not have the forbidden transitions exactly zero. A slight change in orientation of the crystal did not alter the situation appreciably. This could be due to the use of a finite cone of light. There could also be irregularities in the mechanical rotation which cause an inaccuracy of the rotating angle. This would give a misleading idea of the expected pattern for that angle. Also in the experimental arrangement, with the rotation of a flat crystal plate the percentage transmission is reduced due to the light having to traverse a thicker cross section of the crystal and the aperture is reduced. Furthermore, the crystals grown had bubbles and cloudy patches in some region so that there was an uneven distribution of transmitted light and this varied with rotation. In spite of these drawbacks it is evident on comparing the spectra for the positive and negative rotation (Figures 5.6a and 5.6b) that there is nearly 60° periodicity in accordance with theory.

A summary of the transitions observed with the
Figure (5.6a). Angular variation of the transition at 12428.2 cm⁻¹ (positive rotation).
Figure (5.6b). Angular variation of the transition at 12428.2 cm$^{-1}$ (negative rotation).
rotation of the crystal is shown in Figure (5.7). With H along $C'_{2h}$ the allowed transitions are $\Gamma_3^- \rightarrow \Gamma_3^-$ and $\Gamma_4^- \rightarrow \Gamma_4^-$ while for H along $C''_{2h}$, $\Gamma_3^- \leftrightarrow \Gamma_4^-$ is allowed. From theory we know that the ground state (a $\Gamma_7$) transforms as a B type and in going from $C'_{2h}$ to $C''_{2h}$ the labels of $\Gamma_3^-$ and $\Gamma_4^-$ should change. It is evident from experimental assignments that all upper states also change their labels $\Gamma_3^- \leftrightarrow \Gamma_4^-$. This will be explained in the following section.

Figure (5.7). Transitions for magnetic field along (a) $C'_{2h}$ axis, (b) midway between $C'_{2h}$ and $C''_{2h}$, (c) $C''_{2h}$ axis.
5.5. Calculation of the Zeeman Energies

Experimental observations (Figure 5.1) indicate that the magnetic field splitting of the nearly degenerate \( \Gamma_7 \) and \( \Gamma_9 \) levels of the \( ^4I_{9/2} \) state is linear with field and that the splittings in both cases are large. The following calculation can explain these observations.

The eigenfunctions for the longitudinal Zeeman components of \( \Gamma_7 \) can be expressed as

\[
\begin{align*}
\Gamma_7' &= a \mid \frac{5}{2} \rangle + c \mid -\frac{7}{2} \rangle \\
&= 0.91 \mid \frac{5}{2} \rangle - 0.41 \mid -\frac{7}{2} \rangle \\
\Gamma_7'' &= -a \mid -\frac{5}{2} \rangle - c \mid \frac{7}{2} \rangle \\
&= -0.91 \mid -\frac{5}{2} \rangle + 0.41 \mid \frac{7}{2} \rangle 
\end{align*}
\]

(5.5.1)

and of \( \Gamma_9 \) as

\[
\begin{align*}
\Gamma_9' &= b \mid \frac{3}{2} \rangle + d \mid -\frac{9}{2} \rangle \\
&= -0.70 \mid \frac{3}{2} \rangle + 0.70 \mid -\frac{9}{2} \rangle \\
\Gamma_9'' &= b \mid -\frac{3}{2} \rangle + d \mid \frac{9}{2} \rangle \\
&= -0.70 \mid -\frac{3}{2} \rangle + 0.70 \mid \frac{9}{2} \rangle 
\end{align*}
\]

(5.5.2)

The numerical values of the coefficients \( a, b, c, d \) have been determined from crystal field calculations in section 5.2.

The Hamiltonian for the Zeeman effect according to Eqn. (2.10.2) is given by

\[
H_{\text{Zeeman}} = \beta (L + 2S) \cdot \hat{H}
\]

and the Zeeman matrix elements for the transverse effect are then given by
\[ < \text{SLJJ}_z | \text{L}_x + 2 \text{S}_x | \alpha \text{SLJJ}_z \pm 1 > = < \alpha \text{SLJJ}_z | g_J \text{J}_x | \alpha \text{SLJJ}_z \pm 1 > \]  

(5.5.3)

\( g_J \) is the \( g \) value of the \( ^4I_{9/2} \) considering intermediate coupling and is given by

\[ g_J(^4I_{9/2}) = \sum_i a_i \rho_i \]  

(5.5.4)

where \( a_i \) is the eigenvector of the states with \( J = \frac{9}{2} \) or, in other words, the states involved in intermediate coupling and \( g_i \) is the respective \( g \)-value (defined by Eqn. (2.10.4)). The value of \( g_J \) was calculated to be 1.0041 using the eigenvectors of Wybourne [1].

Using the above wavefunctions the transverse Zeeman matrix between the components of \( \Gamma_7 \) and \( \Gamma_9 \) is

\[
\begin{bmatrix}
\Gamma_7' & \Gamma_7'' & \Gamma_9' & \Gamma_9'' \\
\Gamma_7' & E & G_1 & G_2 & 0 \\
\Gamma_7'' & G_1 & E & 0 & -G_2 \\
\Gamma_9' & G_2 & 0 & 0 & 0 \\
\Gamma_9'' & 0 & -G_2 & 0 & 0 \\
\end{bmatrix}
\]

where \( G_1 = -4acg_J^2H \)

\[ G_2 = -\frac{g_J^2H}{2} (\sqrt{2} \text{lab} + 3 \text{cd}) . \]  

(5.5.5)

Diagonalizing the matrix for \( \Gamma_7 \) we obtain a secular matrix for \( \Gamma_7 \) and \( \Gamma_9 \) in the form
The solution of the secular determinant gives the energy eigenvalues of the Zeeman components and the eigenvectors will enable us to obtain a comparative intensity of the allowed transitions.

The secular determinant for the $\Gamma_3^-$ component is

\[
\begin{pmatrix}
\Gamma_3^- & \Gamma_4^- & \Gamma_4^- & \Gamma_3^-
\end{pmatrix}
\begin{pmatrix}
-G_1 + E - \lambda & 0 & 0 & G_2 \\
0 & G_1 + E - \lambda & G_2 & 0 \\
0 & G_2 & 0 - \lambda & 0 \\
G_2 & 0 & 0 & 0 - \lambda
\end{pmatrix} = 0
\]

(5.5.6)

which yields

\[
\lambda_{\Gamma_3^-} = \frac{-(-E + G_1)}{2} \pm \frac{1}{2} \sqrt{(E - G_1)^2 + 4G_2^2}.
\]

When the separation between $\Gamma_7$ and $\Gamma_9$ is very small, i.e.

$E \to 0$

\[
\lambda_{\Gamma_3^-} = - \frac{G_1}{2} \pm \frac{1}{2} \sqrt{G_1^2 + 4G_2^2}.
\]

(5.5.8)

The secular determinant for $\Gamma_4^-$ is
\[ \begin{align*} G_1 + E - \lambda & \quad G_2 \\ G_2 & \quad 0 - \lambda \end{align*} \] 

(5.5.9)

The solutions for this part with \( E \to 0 \) are

\[ \lambda_{\Gamma_4} = \frac{G_1}{2} \pm \frac{1}{2} \sqrt{G_1^2 + 4G_2^2} \] 

(5.5.10)

Substitution of the values of \( a, b, c, d \) from (5.5.1) and (5.5.2) in Eqns. (5.5.5) shows that \( G_2 > G_1 \) and the splitting pattern would be given by the following:

\[ \begin{align*} \Gamma_4 & \quad \Gamma_3 \\ \Gamma_4 \text{ pair} & \quad \Gamma_3 \text{ pair} \\ \Gamma_4 & \quad \Gamma_3 \\ \Gamma_4 & \quad \Gamma_3 \\ \Gamma_4 & \quad \Gamma_3 \\ \Gamma_4 & \quad \Gamma_3 \end{align*} \]

Substituting for \( g \) and \( B \) the eigenvalues for a field of 5T are given on the right-hand column.

The overall splitting is found to be 12.4 cm\(^{-1}\) as compared to the experimental splitting of \((11.5 \pm 0.5)\) cm\(^{-1}\). The Zeeman shifts for the \( \Gamma_7 \) and \( \Gamma_9 \) are calculated for various
field values and are compared with the experimentally observed splittings in Table 5.6. As can be seen from this table, there is not exact agreement between the two. This discrepancy may be due to the fact that crystal field mixing between states of different J has been neglected. A full calculation would involve the crystal field calculation of all levels of ErES and has not been attempted here.

Now each of the $\Gamma_3^-$ and $\Gamma_4^-$ (in $C_{2h}$) contains an admixture from the $\Gamma_7$ and $\Gamma_9$ (in $D_{3h}$) levels. The composition of a definite Zeeman level (either $\Gamma_3^-$ or $\Gamma_4^-$) may be expressed as $x\Gamma_7 + y\Gamma_9$ where the coefficients $x$ and $y$ are the eigenvectors. The value for the $\Gamma_3^-$ and $\Gamma_4^-$ component may be obtained in the following way.

The eigenvalue equation for the $\Gamma_3^-$ irreducible representation is given by

$$
\begin{align*}
\Gamma_7 & \quad \Gamma_9 \\
\Gamma_7 & \quad \begin{bmatrix} -G_1 & G_2 \\ G_2 & 0 \end{bmatrix} \\
\Gamma_9 & \quad 0
\end{align*}
$$

This yields

$$
\begin{align*}
-xG_1 + yG_2 &= \lambda x \\
xG_2 &= \lambda y
\end{align*}
$$

Substituting $x/y = x$ we obtain from the above two equations

$$
\begin{align*}
x^2 + \frac{G_1}{G_2} x - 1 &= 0 \\
x &= -\frac{G_1}{2G_2} \pm \frac{1}{2} \sqrt{\left(\frac{G_1}{G_2}\right)^2 + 4}
\end{align*}
$$
Table 5.6. Zeeman splitting for the $\Gamma_7$ and $\Gamma_9$ level of $^4I_{9/2}$.

<table>
<thead>
<tr>
<th>Magnetic field</th>
<th>Line position cm$^{-1}$</th>
<th>Splitting (lines 1-4) cm$^{-1}$</th>
<th>Splitting (lines 2-3) cm$^{-1}$</th>
<th>Splitting (lines 2-3) cm$^{-1}$</th>
<th>Splitting (lines 2-3) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1T</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4)</td>
<td>12429</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3)</td>
<td>12429.8</td>
<td>3.2</td>
<td>2.5</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td>(2)</td>
<td>12431.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1)</td>
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<td></td>
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</tr>
<tr>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>5.0</td>
<td>5.0</td>
<td>2.4</td>
<td>2.2</td>
</tr>
<tr>
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<td></td>
<td></td>
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<tr>
<td>(2)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
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<tr>
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<td>12441.9</td>
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<td>12.4</td>
<td>5.2</td>
<td>5.4</td>
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<tr>
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<tr>
<td>(4)</td>
<td>12445.5</td>
<td></td>
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</tbody>
</table>
\[ -\frac{1}{2} G_1 \pm \frac{1}{2\sqrt{G_1^2 + 4G_2^2}} \]
\[ \frac{A}{G_2} \]  

(5.5.12)

where \( A \) is the eigenvalue.

Substituting the numerical value gives

\[ X = -1.46 \quad \text{(from negative eigenvalue)} \]
\[ = 0.68 \quad \text{(from positive eigenvalue)}. \]

From the normalization condition \( x^2 + y^2 = 1 \) and from the above values of \( \frac{x}{y} \), the coefficients of \( \Gamma_7 \) and \( \Gamma_9 \) are evaluated. In the same manner, by considering the eigenvalue equation for the \( \Gamma_4 \) part, the value of \( x \) and \( y \) is calculated. Following this calculation, contributions from the two interacting crystal field states in each of \( \Gamma_3^- \) and \( \Gamma_4^- \) are given in Table 5.7. The relative shifts in the magnetic field are also given in this table. The square of the coefficients of the \( \mid \Gamma_9 \rangle \) wavefunction give a measure of the relative intensities.

For example, the allowed \( \sigma \) transition, \( \Gamma_4^- \rightarrow \Gamma_4^- \) for the \( C_{2h}^1 \) orientation arises from the allowed zero field \( \Gamma_7 \rightarrow \Gamma_9 \) transition. Hence, the intensity is proportional to the square of (0.83). The other allowed \( \sigma \) transition being to the highest level (line 1 in Fig. 5.3) and again the intensity of this line is proportional to the square of (0.57). Therefore for a field along \( C_{2h}^1 \) axis only two transitions are allowed (lines 3 and 1). The relative intensity is in the ratio 1:0.3.

When the crystal is rotated so that the field is along a \( C_{2h}^2 \) axis, splitting of the \( \Gamma_7 \) level is reversed; \( \Gamma_4^- \) lowered and \( \Gamma_3^- \) raised. This can be achieved by reversing the sign of the terms involving \( G_1 \) and the same secular determinant results. The solutions are then
Table 5.7. The relative splittings (for 5T) of the $\Gamma_7$ and $\Gamma_9$ level with $H$ along $C'_{2h}$ and $C''_{2h}$ axis of the crystal.

<table>
<thead>
<tr>
<th>Irreducible Representation</th>
<th>Field along $C'_{2h}$</th>
<th>Field along $C''_{2h}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Relative splittings cm$^{-1}$</td>
<td>Wave functions</td>
</tr>
<tr>
<td>$\Gamma_3^-$</td>
<td>-6.2</td>
<td>$-0.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.57</td>
</tr>
<tr>
<td>$\Gamma_4^-$</td>
<td>-2.7</td>
<td>$-0.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.83</td>
</tr>
<tr>
<td>$\Gamma_3^-$</td>
<td>2.7</td>
<td>$0.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.83</td>
</tr>
<tr>
<td>$\Gamma_4^-$</td>
<td>6.2</td>
<td>$0.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.57</td>
</tr>
</tbody>
</table>
\[
\lambda_{\Gamma_3^-} = \frac{G_1}{2} + \frac{1}{2\sqrt{G_1^2 + 4G_2^2}} \]
\[
\lambda_{\Gamma_4^-} = -\frac{G_1}{2} + \frac{1}{2\sqrt{G_1^2 + 4G_2^2}}
\]

It is thus obvious that the positions of the \( \Gamma_3^- \) and \( \Gamma_4^- \) levels are all interchanged.

The wavefunctions and the relative splittings for this field direction are also given in Table 5.7. The labellings for the ground components is also reversed with \( \Gamma_3^- \) becoming the lowest component and the relevant allowed transition is \( \Gamma_3^- \rightarrow \Gamma_4^- \). Again it is the coefficient of \( \Gamma_9 \) which gives a measure of the intensity and for lines 4 and 2 the intensity ratio is 1:0.3. So when the field is along the \( C_{2h}^2 \) axes, the line 2 at 2.7 cm\(^{-1}\) and line 4 at -6.2 cm\(^{-1}\) should be strong. This reversal of intensity is in keeping with our observations (Figs. 5.6a and 5.6b).

Clearly the energy and intensity predictions are not exact. With the field along the \( C_{2h}^1 \) axis the lines 3 and 1 are in the ratio 1:0.3 (Fig. 5.6a, 30° rotation) which is in good agreement with the calculated values. However, lines 2 and 4, although weak, are still apparent in this spectrum. When the crystal is rotated so that the field is directed along a twofold axis, the lines 2 and 4 gain intensity and are stronger than lines 1 and 3, but the ratio is 1:0.8. This is only in poor agreement with the calculated value of 1:0.3. This must arise from the crystal being less well aligned in comparison to the zero rotation position. The misorientation also gives rise to appreciable intensities in lines 1 and 3 as can be seen from the spectrum for 30° rotation. Again, the experimental energies are accurate to within ± 0.5 cm\(^{-1}\). There is then a disagreement of the order of 5%. 

Overall, it is concluded that although the numerical agreement is only fair, variations in the spectra due to a rotation of the crystal are correctly predicted by the theoretical treatment of the transverse Zeeman effect.

5.6. Zeeman effect of the transition observed at 12,570.3 cm$^{-1}$

Three prominent lines were observed when recording the $^4I_{15/2} \rightarrow ^4I_{9/2}$ band. The strongest line at 12,570.3 cm$^{-1}$ absorbed 50% of the light for crystals of thickness 3 mm. The line was sharp with a half-width of $\approx 2$ cm$^{-1}$. The higher energy line at 12594.2 cm$^{-1}$ was weaker (halfwidth 3 cm$^{-1}$) and at the peak the absorption corresponded to $\approx 25\%$ of the radiation. The lower energy line was about a factor of 3 weaker again, but was sharp (halfwidth 3.5 cm$^{-1}$).

None of these lines corresponded in position to those reported by Erath [3] (for the concentrated samples). This indicates they may arise from impurities and the Zeeman measurements reported below support this view.

The Zeeman spectrum of the intense sharp line at 12,570.3 cm$^{-1}$ is shown for $\sigma$ polarization in Fig. (5.8) for field strengths from zero to 5T. The line splits linearly into four components and at 8K the centre of gravity of these lines is approximately equal to that in zero field. This implies that the ground state may be split, but the Boltzmann distribution over the ground state components is fairly even which would correspond to the situation of a small g-value. In contrast it was shown in the case of the 12428.2 cm$^{-1}$ line for the Er$^{3+}$ centre that at the same temperature the upper Zeeman level was depopulated and the centre of gravity of the observed lines was shifted $\approx 10$ cm$^{-1}$ to higher energy.
Figure (5.8). Field dependence of the transition at 12570.3 cm$^{-1}$ in LaES:Er.
Measurements were therefore recorded with the temperature of the crystal reduced to 2.2K. The lines 2 and 4 in Fig. 5.8 are then substantially reduced and lines 1 and 3 gain in intensity. Assuming that these transitions arise from two Kramers doublets, the separation between 1 and 3 must correspond to the excited state Zeeman splittings. The separation between 3 and 4 or 2 and 1 are equal and they correspond to a ground state splitting of 4 cm$^{-1}$ at 5T (Fig. 5.9). The intensity dependence is also consistent with this value of the ground state splitting. Having confirmed the g-value of the Er$^{3+}$ ground state splitting from several transitions it can be concluded from these Zeeman measurements that this line does not arise from the Er$^{3+}$ ion at the D$_{3h}$ site.

In our observation the relative intensity of the π and σ transition of 1 and 4 lines to that of 3 and 2 were sample and orientation dependent. This is attributed to the slight misorientation and to crystal cracks. It is concluded that the lines 4 and 1 are π allowed and 3 and 2 are σ allowed, all these lines appear in σ because of the above experimental factors. If the centre involved a D$_{3h}$ site the observed selection rules indicate that the lines are from a $\Gamma_7 \rightarrow \Gamma_9$, $\Gamma_7 \rightarrow \Gamma_8$ transition (see Table 5.1).

It has been noted that the line position and g-value of the above transitions are very close to that reported by Dieke and Heroux [10,11] for NdES. Furthermore, the ground state of NdES has $\mu = \pm \frac{5}{2}$ and the excited state is attributed to $\mu = \pm \frac{1}{2}$ [11] and this is wholly consistent with the line at 12,570.3 cm$^{-1}$ corresponding to the $\Gamma_7 \rightarrow \Gamma_8$ transition. The line at 12,594.2 cm$^{-1}$ corresponds to a $\Gamma_7 \rightarrow \Gamma_9$ transition.

It is not known how the Nd could have entered the
Figure (5.9). Energy level diagram for the transition observed at 12570.3 cm$^{-1}$ in LaES:Er at 5T.
samples. The line at 12,570.3 cm\(^{-1}\) shown by Dieke and Heroux [10] is very broad. In their spectrum the line was totally absorbing and consequently distorted in shape. There is the possibility that the present absorption corresponds to very low dopant levels. Further crystal growth is necessary to establish this point.

The lines at 12,539.4 cm\(^{-1}\) and 12,594.2 cm\(^{-1}\) were broader on the one hand and much weaker on the other. The Zeeman pattern was not clearly resolved. However in the 8K spectra the centre of gravity did not move to higher energy. This suggest that these lines are also associated with a "low \(g\) value" site.

For the \(^4I_{15/2} \rightarrow ^4I_{9/2}\) band, Erath has reported transitions in the concentrated ErES samples. The transitions at 12,525.0 cm\(^{-1}\) and 12,540.2 cm\(^{-1}\) which are group theoretically allowed at zero field have not been found in the 10% Er samples. Possibly they have been partially masked by the above impurity lines.

5.7. Conclusion

A good agreement with theory has been obtained for the transition at 12,428.2 cm\(^{-1}\) in the \(^4I_{9/2}\) band. The spectrum showed a sixfold periodicity for a rotation of the crystal about the \(c\) axis in a transverse magnetic field. It was shown that two levels are almost degenerate at this energy. One transforms as a \(\Gamma_7\) irreducible representation and a spectrum corresponding to a type \(B \leftrightarrow B\) transition is anticipated. The second state is a \(\Gamma_9\). Without any interaction with the \(\Gamma_7\) state this level will not split in a field (in first order). However, the very strong interaction with the \(\Gamma_7\) state has
caused this state to split linearly in a field and possess a type B character. Hence the spectrum arises from two type B→B transitions. Although the numerical calculations do not give exact agreement with experimental results, they support the analysis qualitatively. A situation similar to this occurs in the ground doublet of Co\(^{2+}\) in CoCs\(_3\)Cl\(_5\) [12,13]. There is strong interaction between the ground doublet which transforms as type A (\(\Gamma_6\)) and another doublet 8 cm\(^{-1}\) above it transforming as type B (\(\Gamma_7\)). This interaction makes both the doublets transform as type B and a transition to an excited \(\Gamma_7\) shows fluctuation in intensity as is expected in a crystal with D\(_{2d}\) symmetry.

In accordance with the present investigation the anisotropic Zeeman effects for ions at D\(_6\), C\(_{6v}\) and D\(_{3h}\) site symmetries can be observed when there is an appreciable mixing between the crystal field levels. Here we have only reported rotational effects for one line. Other lines do show some anisotropies, but we are unable to obtain satisfactory data with the present field (5T) and spectral resolution (~1 cm\(^{-1}\)). Work with higher magnetic fields and improved resolutions should be able to provide further examples of anisotropic spectra which should be useful in a better understanding of the transverse Zeeman spectra.
References for Chapter 5


CHAPTER 6: Angular Variation of U$^{5+}$ in Zircon

6.1. Introduction

This chapter deals with the anisotropies in the Zeeman spectra of U$^{5+}$ in zircon. The crystal is tetragonal and Judd and Runciman [1] have extended the treatment of the anisotropic transverse Zeeman patterns to cover crystals of this type. Variations in intensities have been previously observed in tetragonal crystals Cs$_3$CoCl$_5$ and Cs$_3$CoBr$_5$ [2,3]. Vance and Mackey [4] have also observed a fourfold periodicity in the Zeeman spectrum of U$^{5+}$ in zircon, but attributed this to the existence of a near degeneracy in the ground state. Judd and Runciman pointed out that this could be a B\rightarrow B type transition and hence a periodic fluctuation in the intensity of the Zeeman spectra is expected and the present experiments were undertaken to establish if this was the correct explanation of the variations observed by Vance and Mackey [4].

We have studied the angular dependence of the transition at 6,700 cm$^{-1}$ in a field of 5T with higher resolution than was achieved by the original work of Vance and Mackey.

6.2. Structure of Zircon

Zircon, ZrSiO$_4$, has a tetragonal structure with space group D$_{4h}^{+}$. There are four molecules per unit cell which are magnetically equivalent [5]. The impurity ions replace Zr$^{4+}$ in the lattice. Each zirconium atom is surrounded by four atoms of oxygen at 2.15 Å and by another four at 2.29 Å [6]. The distribution of oxygen atoms round zirconium is regular. The silicon atoms are at the centres of the small
tetrahedra and oxygen atoms are at the corner points of these tetrahedra. The Si-O distance within the SiO$_4$ tetrahedra is 1.62 Å [7]. The arrangement of the different atoms in ZrSiO$_4$ is shown in Figure (6.1) and the crystal faces are shown in Figure (6.2).

6.3. $^{5+}$ in Zircon

In an optical study of natural and synthetic zircon, Vance and Mackey [8] obtained an 'extra' spectrum in addition to the expected spectrum of $^{4+}$ [9]. Two strong σ polarized lines were observed at 9,026 cm$^{-1}$ (1,107 nm) and 6,700 cm$^{-1}$ (1,492.5 nm). The lines were enhanced when the crystal was simultaneously doped with a trivalent ion such as Al$^{3+}$ and consequently the lines were attributed to $^{5+}$ with the trivalent ion necessary for charge compensation. A study of the π,σ and axial spectra revealed that the 'extra' lines were electric dipole transitions. The point group of the metal ion in zircon is non-centrosymmetric D$_{2d}$ so that the f→f electronic transitions are not parity forbidden. Although Vance and Mackey established the origin of these lines using synthetic crystals, the $^{5+}$ lines are also strong in natural zircon and since larger samples were available natural zircon was used. By using an improved version of the detector used by Vance and Mackey a resolution of 1 cm$^{-1}$ was obtained as opposed to 3 cm$^{-1}$ in the case of Vance and Mackey.

The electronic configuration of $^{5+}$ is (Rn)5f$^1$. Its ground state is $^2$F$_{5/2}$ and the only excited level is $^2$F$_{7/2}$. The lowest Stark level with $J_z = \pm \frac{3}{2}$ corresponds to an irreducible representation of $\Gamma_6$. In D$_{2d}$ symmetry a state with $J = \frac{7}{2}$ splits into two $\Gamma_6$ and two $\Gamma_7$ levels. Selection rules for D$_{2d}$
Figure (6.1). Structure of zircon. Circles represent zirconium atoms, silicon atoms are at the centres of the small tetrahedra whose corners mark the positions of the oxygen atoms.
Figure (6.2). Crystal faces of zircon.
(Table 2.3) predict that transitions to all four levels are allowed. A $\Gamma_6 \rightarrow \Gamma_6$ transition is allowed in $\sigma$ only, while a $\Gamma_6 \rightarrow \Gamma_7$ is allowed both in $\pi$ and $\sigma$. The transitions at 6,700 cm$^{-1}$ and 9,026 cm$^{-1}$ correspond to $\Gamma_6 \rightarrow \Gamma_6$ transition. The classification of states by Judd and Runciman [1] shows that $\Gamma_6$ transforms as type B. Hence these transitions will correspond to a B $\rightarrow$ B type transition. These transitions will exhibit variation with respect to changes in the angle between $H$ (the magnetic field) and $E$ (the electric vector of the incident light). For a system having $D_{3h}$ symmetry mixing between the Zeeman levels is required to observe the anisotropy in the spectra. In $D_{2d}$ symmetry the A $\rightarrow$ A and B $\rightarrow$ B transitions are allowed in zero field and no field mixing is required to observe intensity variation.

The $C'_{2h}$ and $C''_{2h}$ axes for a system of tetragonal crystals are separated by $\frac{\pi}{4}$. Thus these two axes occur every 90° in the crystal. When rotating the crystal the magnetic field will be directed along a given twofold crystallographic direction every 90° and hence the pattern of the spectrum will have a fourfold periodicity.

The experiment was carried out at 5T with the sample at 8K and the c-axis of the crystal along the direction of propagation of light. When the magnetic field is applied along a $<100>$ axis of the crystal the $D_{2d}$ symmetry is reduced to $C_2$. Since we are dealing with an odd electron system, the irreducible representations in this lower symmetry group are $\Gamma^-$ and $\Gamma^-_4$.

With $H$ along $C'_{2h}$, the product $V_0^\pi E_y$ transforms as $\Gamma_1^+$ for $E \parallel H$ and as $\Gamma_2^+$ for $E \perp H$. Hence the selection rules with $H$ along $C'_{2h}$ are $\Gamma^-_3 \rightarrow \Gamma^-_3$ and $\Gamma^-_4 \rightarrow \Gamma^-_4$ for $H \parallel E$. With $H \perp E$ the
transitions $\Gamma_3^- \leftrightarrow \Gamma_4^-$ are allowed (Figure 6.4a). The selection rules with $H$ along $C_{2h}$ are $\Gamma_3^- \rightarrow \Gamma_3^-$ and $\Gamma_4^- \rightarrow \Gamma_4^-$ in $H \parallel E$ and for $H \parallel E$ the transitions corresponding to $\Gamma_3^- \leftrightarrow \Gamma_4^-$ can occur (Figure 6.4c).

The Zeeman measurements of Vance and Mackey [2] show that the ground state splitting at fields of 5T is still small (~2 cm$^{-1}$) and this is consistent with our analysis. This small splitting of the ground state implies that both the Zeeman components of the ground state will be appreciably populated at 8K. The selection rules indicate that transitions between the Zeeman components of the ground state and excited $\Gamma_6$ state are all allowed but are strongly polarized.

The spectra are shown in Figures (6.3a) and (6.3b). It is apparent that the line at 6,700 cm$^{-1}$ is resolved into four components rather than two as seen by Vance and Mackey [3] and hence significant new experimental data can be obtained. This is reported below. In the case of the line at 9,026 cm$^{-1}$ no improvement was obtained and will not be reported further.

6.4. Angular Variation

Figs. (6.3) and (6.4) show the angular dependence spectra and the energy level diagram for U$^{5+}$ in zircon with $E \parallel H$ and $E \perp H$. When the magnetic field is along a $<100>$ axis of the crystal the two transitions corresponding to $\Gamma_3^- \rightarrow \Gamma_3^-$ and $\Gamma_4^- \rightarrow \Gamma_4^-$ are allowed for $E \parallel H$. With $E \perp H$, transitions corresponding to $\Gamma_3^- \rightarrow \Gamma_4^-$ and $\Gamma_4^- \rightarrow \Gamma_3^-$ can occur. From Figures (6.3a) and (6.3b) of $H \parallel <100>$ we find that for $E \parallel H$ the two lines are separated by 8 cm$^{-1}$ and for $E \perp H$ the only two lines seen have a separation of 4.5 cm$^{-1}$. As the crystal is rotated about the c-axis four lines are seen in both polarizations ($H$ at 16° from $<100>$). With $E \parallel H$, the
Figure (6.3a). Angular variation of zircon:U$^{5+}$ for E $\parallel$ H.
Figure (6.3b). Angular variation of zircon:U$^{5+}$ for $E \perp H$. 
Figure (6.4). Energy level diagram for the angular variation in zircon: (a) $H \parallel <100>$, (b) $H$ at $22.5^\circ$ to $<100>$, (c) $H$ at $45^\circ$ to $<100>$. Solid lines for $H \parallel E$ and broken lines for $H \perp E$. 
two inner components corresponding to the above $\Gamma_3^- \rightarrow \Gamma_4^-$ and $\Gamma_4^- \rightarrow \Gamma_3^-$ transitions are just resolved. With $E \perp H$ the two outer components corresponding to the previous $\Gamma_3^- + \Gamma_3^-$ and $\Gamma_4^- + \Gamma_4^-$ gain some intensity. With further rotation of the crystal in the same direction it is found that these new components gain further in intensity until at an angle of $22\frac{1}{4}\degree$ from $H \parallel <100>$ four lines are roughly equally prominent in both the polarizations. At this angle all four transitions between the two levels are allowed. The transition from the upper Zeeman component is slightly weaker (a factor of 0.8) than the corresponding transition from the lower component corresponding to a slight thermal population difference between the two components.

Rotating to an angle of $45\degree$ (i.e. $H \parallel <110>$) from the $<100>$ the spectra for $E \parallel H$ and $E \perp H$ should have interchanged. The field is then along a $C_{2h}^n$ axis and the selection rules, as well as the labelling of the two components of the doublet, have been interchanged. $\Gamma_3^- \rightarrow \Gamma_3^-$ and $\Gamma_4^- \rightarrow \Gamma_4^-$ are allowed for $H \perp E$ whereas $\Gamma_3^- \rightarrow \Gamma_4^-$ and $\Gamma_4^- \rightarrow \Gamma_3^-$ are allowed in $H \parallel E$. The two outer components should appear in $H \perp E$ and the inner ones in $E \parallel H$. Experimentally two strong lines with a separation of $4.5 \text{ cm}^{-1}$ were obtained and the lower energy line is weaker by a factor of 0.8 in contrast to the spectrum for $H \parallel <100>$. Lines 1 and 2 which are group theoretically forbidden in this polarization ($E \parallel H$) appeared as weak shoulders. This is due to slight misalignment of the crystal axis with respect to the field. For $E \perp H$ two lines are observed, but they are significantly broader than in the spectrum with $H$ along the $<100>$ direction.
On rotating the crystal through 90° from its original position the spectra for both the polarizations repeated the 0° pattern. Further rotation confirmed that the pattern was repeated at intervals of \( \frac{\pi}{2} \) although throughout the \( E \parallel H \) spectrum gave better and sharper lines than those for \( E \perp H \).

The main reason for not obtaining totally polarized lines for the field along symmetry directions presumably arises because the crystal was not aligned with its axes along the field and rotation axes.

The spectra and its intensity variation is however satisfactory to confirm that the fourfold variation in the spectrum involves changes of intensity as suggested by Judd and Runciman [1]. Clearly the explanation will also cover the other \( U^{5+} \) line at 9,026 cm\(^{-1} \), although in this case because the lines are broader the intensity variations cannot be so elegantly demonstrated.

This experiment gives the ground state splitting of \( U^{5+} \) in zircon as 1.8 cm\(^{-1} \) at 5T and this corresponds to a \( g_\perp \) value of 0.8. The \( g_\parallel \) value given by Vance and Mackey is 0.2. This explains why no paramagnetic resonance signal was obtained for this sample by previous workers [5,10]. To observe magnetic resonances corresponding to such small \( g \)-values would require a field strength of \(~3T\) in the Q band.

At a magnetic field of 5T the splitting of the \( \Gamma_6 \) level at 6,700 cm\(^{-1} \) is 6.3 cm\(^{-1} \). This gives a \( g_\perp \) value for this level as 2.7 ± 0.1. Analyzing the 9,026 cm\(^{-1} \) Zeeman effect in the same way gives an excited state \( g \)-value of \( g_\perp = 2.3 \pm 0.3 \), where the larger error arises because the spectrum is not so well resolved as for the 6,700 cm\(^{-1} \) line.
6.5. Conclusion

The transverse Zeeman spectra displayed here for the 6,700 cm\(^{-1}\) line in ZrSiO\(_4\):U\(^{5+}\) is in agreement with that predicted for a type B \(\rightarrow\) B transition at a site of D\(_{2d}\) symmetry. It is noted that in contrast to the trigonal case presented earlier these effects do not require field mixing. This also applies to type A \(\rightarrow\) A and type B \(\rightarrow\) B transitions in site symmetries D\(_4\), C\(_{4v}\), S\(_4\) and D\(_{2d}\) and studies of such transitions should prove fruitful.

In conclusion, it is clear that rotation experiments in the transverse Zeeman geometry give valuable information about the interaction of a magnetic field with ions in crystals.
References to Chapter 6.