CRYSTAL-FIELD SPLITTING OF $Er^{3+}$ IN ZnO AND EXPERIMENTAL OBSERVATIONS

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Chapter 1

Introduction

Rare-earth doped semiconductors have long been studied because of their prominent optical and magnetic properties. With 4f-electrons deeply buried in some Xe-like closed outer shells, trivalent rare-earth elements give a wide range of stable emissions which are insensitive to the host environment.

As GaN being studied intensively as a promising wide band gap semiconductor, some research has been done on doping GaN with rare-earth elements. However, the emission of rare-earth doped ZnO, a promising substrate for the growth of GaN film, has not been studied so far. This thesis attempts to show how to calculate the Stark splitting of the atomic levels of Er$^{3+}$ in the electrostatic field of ZnO crystal by the semi-classical crystal field theory.

When a magnetic ion is doped into a crystal, some of the spatial degeneracy of its angular momentum will be removed by the surrounding electrostatic field of the crystal. In 1929, Bethe [1] first studied the problem using group theory. Koster and others generalized the previous works in crystalline groups and made his monograph [14] a must read for the workers in this field. In 1950's Stevens [2] introduced "operator equivalent" techniques that greatly simplified the calculations of crystal field by interpreting the electrostatic energy terms into angular momentum operators. The number of terms of operators are
fortunately limited to the fourth degree for d-electron wave functions of transition metals and to the sixth degree for f-electrons of rare-earth elements by both symmetry and the finite value of angular momentum. Thus by applying crystal field theory, the splitting of the energy levels of rare-earth elements can be derived by diagonalizing trivial matrices with small dimensions.

In comparison to the strictly derived symmetry of the terms, that is, the angular dependence of the terms and the terms that are required to be zero by symmetry, researchers find it very hard to estimate the radius related integral, which is the constant corresponding to each order of the expansion from electrostatic potential into spherical harmonics. So the widely accepted method is to find these values experimentally by fitting them with respect to some well resolved lines and then these values are used to predict the positions of other emissions.

According to my experience in exploring the problem, I found that several references were exceptionally helpful. The book of Abragam and Bleaney [3] is very instructive for the understanding of elementary theory necessary for these calculations. The textbook by T. Inui et al. [20] introduces group theory with a concentration in its applications in physics, while E. P. Wigner's book [4] gives more systematic and strict discussion. Also I found that the paper by M. T. Hutchings [6] provides a good tutorial for the crystal field theory calculations. The most complete reference which covers the problem is Prather's Monograph [21]. References [3][14][9][21] give an almost complete set of standard tables.

In Chapter 2, some background knowledge is given in a detailed fashion because the intention of this work is to help other peer graduate students like me to start their research in this field. The well developed and widely accepted algorithm to calculate splitting by
crystal field theory is introduced in Chapter 3. In Chapter 4, the result of the splitting of \( \text{Er}^{3+} \) in ZnO is compared with the experimental data of Dr. H. Lozykowski’s group. The last part of the thesis will include some discussions and conclusions. In Appendix, some source codes are included for the convenience of the readers.
Chapter 2

Theory

The calculation of the energy level splitting of magnetic ions in crystalline fields involves group theory and crystal field theory other than the knowledge about the ion and the crystal. We will take the energy level of free ions as a basis for calculation and treat the electrostatic crystal field as the perturbation. In the following sections, we will try to make some basic sense in these fields respectively.

2.1 Group Theory

The section will follow the framework and definitions of the group theory part of Abragam and Bleaney’s book [3, Chapter 12-14] because of its conciseness. But we will interpret the topic in a less complete but more example-oriented style. Also for the theorems that are given without proof in this book, we will specify where you can find them.

2.1.1 Definition

In mathematics a group is defined as in [4]:

**Definition 1** A group is a set of elements, among which one kind of operation is defined, called multiplication. This multiplication specifies, for every two elements of the group, a third element of the group, the product. This group multiplication, which is considered to be an inherent property of group elements, must also exhibit the following characteristics.
1. The associative law: \((AB)C = A(BC)\).

2. Identity element \((E)\) exist: \(EA = AE = A\)

3. Every element has a reciprocal: For every element \(A\), there exist another element \(B\), so that \(AB = BA = E\). The reciprocal of \(A\) is denoted by \(A^{-1}\).

Example 1 One example of a group is the set of matrices and the multiplication is the matrix multiplication.

\[
\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \text{ and } \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}
\] (2.1)

2.1.2 Symmetry and Degeneracy

It is a well known in Quantum Mechanics that the degeneracy relates to the symmetry. Symmetry can be defined as the invariance of the system Hamiltonian \(H\) under certain operations on the space or the wavefunction. It can be proved [3, pp. 601] that non-commuting symmetry induces degeneracy. For example, for an electron in a central potential, the commutators \([\mathcal{L}_\alpha, H] = 0\), while \([\mathcal{L}_\alpha, \mathcal{L}_\beta] \neq 0\) \((\alpha, \beta = x, y, z)\). This is the reason of the \(2L + 1\)-fold degeneracy.

2.1.3 Linear representation, equivalence, irreducibility, characters, and classes

Now we will define several important definitions.

**Linear representation** We define \(S\) to be an element of a transformation group \(G\) and \(\Psi_1, \Psi_2, ..., \Psi_p\) to be a set of basis (Basis is defined as a set of orthonormal vectors that span the space) of a \(p\)-fold degenerate space. If the Hamiltonian of the system
\( \mathcal{H} \) is invariant to the transformations of \( G \), any basis function after transformation is also in the same space, i.e.

\[
\mathcal{S}\Psi_i = \sum_{k=1}^{p} \Psi_k D_{ki}(S)
\]  

(2.2)

The equation sets up a correspondence between each abstract transformation with a matrix. It is easy to prove that the set of matrices also forms a group under the standard matrix multiplication. The matrix group is called a linear representation of group \( G \). For example, the matrix group in Example 1 can be a linear representation of the group of 2-D rotation by 0\(^\circ\), 90\(^\circ\), 180\(^\circ\), and 270\(^\circ\). Note that the linear representation of a group depends on the choice of basis.

It is trivial to show that the isomorphism condition holds

\[
D(S_1S_2) = D(S_1)D(S_2)
\]  

(2.3)

Equivalent Similarity transformation is defined as: if \( X = \mathcal{T}X' \), \( Y = \mathcal{T}Y' \), and

\[
Y = D(S)X,
\]

\[
Y' = D'(S)X' = \mathcal{T}^{-1}D(S)\mathcal{T}X'
\]  

(2.4)

In this case, we say that \( D \) and \( D' \) are equivalent. In general equivalent representations are always considered the same. Also it can be proved that any representation of matrices with nonvanishing determinants can be transformed into a representation of unitary matrices through a similarity transformation. \[4, \text{pp. 74} \] So we will not lose generality by considering unitary representations only.
Reducible A unitary representation \( D \) is said to be reducible if through a similarity transformation all its matrices \( D \) can be transformed to the quasi-diagonal form

\[
\begin{pmatrix}
D_1 & 0 \\
0 & D_2
\end{pmatrix}
\]  

(2.5)

The irreducibility is related to the existence of invariant orthogonal subgroups in the group.

Characters The traces of the matrices of a linear representation are called its characters and are denoted by \( \chi \).

Class Two elements \( A \) and \( B \) of a group belong to the same class if the group contains a third element \( C \) such that

\[
B = CAC^{-1}.
\]  

(2.6)

Elements in a same class has the same characters.

Projection operator The operator

\[
\mathcal{P}_\nu^k = \frac{l_k}{g} \sum_{S \in G} A_{\nu\nu}^{k*}(S) \cdot S
\]  

(2.7)

is defined as “projection operator” because of the fact that \( \mathcal{P}_\nu^{k^2} = \mathcal{P}_\nu^k \). In the expression, \( l_k \) is the dimension of the irreducible representation, \( g \) is the order of the point group, \( A_{\nu\nu}^{k*}(S) \) is the conjugate of the \( \nu\nu \)-th element of the \( k \)-th irreducible representation for operation \( S \), and the summation is carried over all the elements of the point group. For the calculation we are concerned, we can use a simplified “projection operator” by summing over the subscript \( \nu \) [4, pp. 118].

\[
\mathcal{P}^k = \frac{l_k}{g} \sum_{S \in G} \chi^{k*}(S) \cdot S
\]  

(2.8)
where $\chi(S)$ is the character of the operation $S$ in the $k$-th irreducible representation.

A very important application of the operator is generating the basis functions of the irreducible representations. If we write the basis functions of the $k$-th irreducible representation as $\Phi^k$, then it can be proved [3, pp. 637] that

$$D^k_{\nu}|jm\rangle = C\Phi^k_{\nu}. \tag{2.9}$$

One thing to note is that we may get $C = 0$. As a consequence, we can not get the basis function for this irreducible representation from this specific $|jm\rangle$. We can get all the basis functions for this representation by applying the projection operator to all the functions $|jm\rangle$ for $m = [-j,j]$.

### 2.1.4 Relevant theorems

- If a matrix $M$ commutes with all the matrices of an irreducible representation, it is a multiple of the unit matrix. The interested readers can find the proof from [4, pp. 75]

- For two irreducible non-equivalent representations $\mathcal{D}_1$ and $\mathcal{D}_2$ of a finite group $G$, the following orthogonality relation holds for any indices $i$, $j$, $k$, and $l$,

$$\sum_{S \in G} D_{1,ik}(S)D_{2,jl}^*(S) = 0. \tag{2.10}$$

The instant lemma of this relation can be obtained by setting $\mathcal{D}_2$ to be unit representation

$$\sum_{S \in G} D_{1,ik}(S) = 0. \tag{2.11}$$
For every irreducible representation $\mathcal{D}$ of order $p$ of a finite group, the following holds:

$$
\sum_{S \in G} D_{ik}(S)D_{jl}^*(S) = \frac{m}{p} \delta_{ij}\delta_{kl},
$$

(2.12)

where $m$ is the order of the group, i.e., the number of elements of the group.

As a direct result, we can also get from the definition of characters of a group,

$$
\sum_{S \in G} \chi_1(S)\chi_2^*(S) = 0,
$$

(2.13)

$$
\sum_{S \in G} \chi_1(S)\chi_1^*(S) = m.
$$

(2.14)

The proof of the theorem is at [4, pp. 79]. These orthogonal relations are the cornerstones of the representation theory.

- It can be shown [3, pp.604] that the number of non-equivalent irreducible representations of a finite group $G$ equals the number of classes it contains. This theorem is useful since if we can identify the number of the classes in a given group, we can get the number of irreducible representations of the group.

- Let $l_1, l_2, \ldots, l_r$ be the dimensions of the $r$ irreducible representations of a group of order $m$, then

$$
\sum_{i=1}^{r} l_i^2 = m
$$

(2.15)

This is a very important theorem because if we know the number of irreducible representations $r$ and the order $m$ of a group, we can derive the dimension $l_1, l_2, \ldots, l_r$ from equation 2.15 in most of the cases.
Example 2 For example, we know that the cubic group \( O \) contains 24 elements and 5 classes. From equation 2.15, we have

\[
l_1^2 + l_2^2 + l_3^2 + l_4^2 + l_5^2 = 24
\]  

(2.16)

Because \( l_i \)'s have to be an integer, the only solution is the set of integers 1, 1, 2, 3, 3. Thus we have derived the dimensions of the irreducible representations of the cubic group \( O \).

- Let \( \mathcal{D} \) be the reducible representation of a group \( G \). For each operation \( S \) of \( G \), the characters of the representation of \( S \) is \( \chi(S) \). Also we assume that we know all the irreducible representations \( \mathcal{D}_i \) and the characters \( \chi_i(S) \) for each operation \( S \). Then we can get the numbers of times \( a_i \) that the irreducible representation \( \mathcal{D}_i \) is contained in \( \mathcal{D} \) from

\[
a_i = \frac{1}{m} \sum_{S \in G} \chi(S)\chi_i^*(S)
\]  

(2.17)

where \( m \) is the order of group \( G \). The proof can be derived from the definition of reducibility and Equation 2.13 and Equation 2.14.

This theorem is very useful in getting the number of times a reducible representation is decomposed into a specific irreducible representation.

2.1.5 The rotation group and angular momentum

The total angular momentum of an electron in central potential is the sum of two factors, namely the orbital angular momentum and the spin of the electron. When the ion with the electron is placed into an electrostatic crystal field, the relative strength of the spin-orbital coupling and the crystal field have to be taken into consideration. For transition
metal ions, the spin-orbital coupling is smaller than the effect of the crystal field. In this case, the crystal field splitting have to be calculated before we take into account the spin-orbital coupling. However, for the rare-earth elements, the spin-orbit coupling is stronger than the crystal field. Thus we will have all our work based on the results of spin-orbital coupling effects, i.e. we will assume we know the energy levels for each of the total angular momentum \( J \), and all the \( 2J + 1 \) eigenfunctions for each degenerate level. Then we "turn on" the crystal field adiabatically and treat it as a perturbation to the free ion Hamiltonian including the spin-orbit coupling term.

The angular momentum operator \( \mathcal{J} \) and its components on a cartesian coordinate \( \mathcal{J}_x \), \( \mathcal{J}_y \), and \( \mathcal{J}_z \) have the following relations:

\[
\mathcal{J}^2 = \mathcal{J}_x^2 + \mathcal{J}_y^2 + \mathcal{J}_z^2,
\]
\[
[J, J_{\alpha}] = 0, \text{ where } \alpha = x, y, z
\]
\[
[J_x, J_y] = i\hbar J_z; [J_y, J_z] = i\hbar J_x; [J_z, J_x] = i\hbar J_y.
\]

Let \( |jm\rangle \) denote the eigenfunctions of \( J \) and \( J_z \) with eigenvalues \( j \) and \( m \) respectively.

\[
\mathcal{J}^2|jm\rangle = j(j + 1)|jm\rangle
\]
\[
\mathcal{J}_z|jm\rangle = m|jm\rangle
\]

If we define \( \mathcal{J}_\pm = \mathcal{J}_x \pm i\mathcal{J}_y \)

\[
\mathcal{J}_+|jm\rangle = \begin{cases} 
\sqrt{(j + m + 1)(j - m)}|jm + 1\rangle, & \text{for } m < j, \\
0, & \text{for } m = j 
\end{cases}
\]
\[
\mathcal{J}_-|jm\rangle = \begin{cases} 
\sqrt{(j - m + 1)(j + m)}|jm - 1\rangle, & \text{for } m > -j, \\
0, & \text{for } m = -j 
\end{cases}
\]
It can be proved [5, pp.55] that a finite rotation described by Euler angles ($\alpha$, $\beta$, and $\gamma$) can be represented by the operator

$$S(\alpha, \beta, \gamma) = e^{-iaJ_x}e^{-ibJ_y}e^{-igJ_z}$$

(2.25)

It is obvious from equation 2.19 that $[J, S(\alpha, \beta, \gamma)] = 0$. That is, the finite rotation operator will not change the total angular momentum $j$. Then given a set of basis $|jm\rangle$, the operator can have a matrix representation $d_{m'=-j}^{(j)}m\rangle^1(2j+1\times(2j+1))$.

$$S(\alpha, \beta, \gamma)|jm\rangle = \sum_{m'=-j}^{j} d_{m'=-j}^{(j)}|jm\rangle$$

(2.26)

The main reason why we need to discuss angular momentum and spin is that our base in the calculations are the eigenfunctions of angular momentum operators $J$ and $J_z$. And also all the energy levels we will apply the perturbation to, are the energy levels decided by the spin-orbit coupling. Another fact is that if the total number of 4f-electrons is odd, $J$ will be a half-integer. In this case, double crystalline point group has to be used instead of the normal one. The reason is that if the angular momentum number is a half integer, which happens when the number of electrons is odd, a 360° rotation will not bring the system back into itself and an operation of inverting the “spinor” must be included into the group. We will revisit this topic in more detail in later discussions.

**Theorem 1** Given the total angular momentum $j$, the characters of a linear representation of a rotation of angle $\varphi$ are [3, pp. 620]

$$\chi^j(\varphi) = \frac{\sin(j + \frac{1}{2})\varphi}{\sin(\frac{1}{2}\varphi)}$$

(2.27)
2.1.6 The crystalline point groups

All the symmetric point operations of a certain crystal form a group called point group. The reason we are only concerned with the point group of a specific site in the crystal other than the space group of the crystal is that for an ion doped in the crystal randomly, we do not expect a translational symmetry. Now we will try to explore all the point operations that leave a cube invariant, and partition them by the classes they belong to. Note that by point operation we mean the operation that leaves at least one point (the doped ion) invariant, that is, the operations of rotation, inversion, and reflection.

<table>
<thead>
<tr>
<th>Class</th>
<th>Description</th>
<th>Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>the identity operation</td>
<td>1</td>
</tr>
<tr>
<td>$C_2$</td>
<td>rotations of an angle $\pi$ about the 3 axes perpendicular to the faces of the cube</td>
<td>3</td>
</tr>
<tr>
<td>$C_4$</td>
<td>rotations of an angle $\pm \frac{\pi}{2}$ about the same axes of $C_2$</td>
<td>6</td>
</tr>
<tr>
<td>$C_3$</td>
<td>rotation of an angle $\pi$ through the 6 axes connecting the center point of the opposite edges</td>
<td>6</td>
</tr>
<tr>
<td>$C_3$</td>
<td>rotations of angles $\pm \frac{2\pi}{3}$ around the four body diagonals</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 2.1: Classes of operations of group $O$.

We have 5 classes and 24 elements in the cubic symmetry group. From Example 2 we know that these five classes can only have two classes of one dimension, one class of two dimensions, and two classes of three dimensions.

When the ion has odd number of electrons, the quantum number $j$ is a half-integer. In this case, we have to deal with the double group $O^*$ rather than the normal one $O$ we just studied. The reason is we have to consider the operation to flip the spinor of the electrons, which is denoted by $\mathcal{R}$. The operator commutes with all the other operators and so it can be represented by a factor times the unit matrix. Because $\mathcal{R}^2 = \mathcal{E}$, and
\[ R \neq \mathcal{E}, \text{ we get } R = -\mathcal{E}. \] To be more specific, if \( j \) and \( m \) are integers, a 360° rotation will change \( |jm\rangle \) back into itself. If \( j \) and \( m \) are half-integers, a 360° rotation will change \( |jm\rangle \) into \( e^{2\pi i m}|jm\rangle \), that is, \( -|jm\rangle \). In this case, only a rotation of \( 720^\circ \) can turn the function \( |jm\rangle \) back into itself.

In cubic symmetry, we apply \( R \) to each of the 24 elements of the single group and 24 new elements can be derived. So the cubic double group contains 48 elements. Now the question is: Does the number of classes double too? The answer is no. It is true that we can construct five classes, namely \( R E, RC_2, RC'_2, RC_3, \) and \( RC_4 \). However, it can be shown [3, pp. 634] that \( C_2 = RC_2 \) and \( C' = RC'_2 \). So there would be three new classes \( \Gamma_6, \Gamma_7, \) and \( \Gamma_8 \) with characters \( \chi_6, \chi_7, \) and \( \chi_8 \) and 24 new elements other than those of the group \( O \). It is easy to find the only solution for equation

\[ l_6^2 + l_7^2 + l_8^2 = 24 \]  

is

\[ l_6 = 2, \ l_7 = 2, \ l_8 = 4 \]  

\[ (2.28) \]

\[ (2.29) \]

### 2.2 The crystal field theory

The crystal field theory assumes that the crystal field is weak and can be regarded as a perturbation to the 4f-electron system. Now the problem is how to find the perturbation Hamiltonian and the corresponding matrix elements. To get an approximate Hamiltonian, we assume that all the ions are the point charges and then derive the electrostatic energy by classical approach.
The most direct and brute force approach is to use

\[ V(r, \theta, \phi) = \sum_i \frac{q_i}{|\mathbf{R}_i - \mathbf{r}|} \]  

(2.30)

where \( \mathbf{R}_i \) are the positions of the ions in the crystal, \( \mathbf{r} \) is the position of the electron we are studying. The summation goes over all the surrounding ions.

The second approach is to use spherical harmonics and express \( V \) as a linear combination of spherical harmonics

\[ V(r, \theta, \phi) = \sum_{j} q_j \sum_{n=0}^{\infty} \frac{r^n}{R_j^{(n+1)}} \frac{4\pi}{(2n+1)} \sum_{m=-n}^{n} (-1)^m Y_{n}^{-m}(\theta_j, \phi_j) Y_{n}^m(\theta, \phi) \]  

(2.31)

That is,

\[ V(r, \theta, \phi) = \sum_n \sum_{m=-n}^{n} r^n \gamma'_{nm} Y_{n}^m(\theta, \phi), \]  

(2.32)

where

\[ \gamma'_{nm} = \sum_j \frac{4\pi}{(2n+1)} \frac{q_j}{R_j^{(n+1)}} (-1)^m Y_{n}^{-m}(\theta_j, \phi_j). \]  

(2.33)

The problem with spherical harmonic expansion is that the functions are complex. The standard method is to use the real "tesseral harmonics", which are defined as

\[ C_n^m = \frac{1}{\sqrt{2}} \left[ (-1)^m Y_n^m + Y_n^{-m} \right] \]  

(2.34)

\[ S_n^m = \frac{1}{\sqrt{2}i} \left[ (-1)^m Y_n^m - Y_n^{-m} \right] \]  

(2.35)

Then we can write

\[ V(r, \theta, \phi) = \sum_{n=0}^{\infty} \sum_{m=0}^{n} (c_n^m C_n^m + s_n^m S_n^m) \]  

(2.36)

where
Prather's book [21, pp. 4-5] gives a very complete set of tesseral harmonics up to \( n = 6 \) in both cartesian coordinates and spherical coordinates.

Then symmetry properties are used to predict zero terms. Also the finite value of the angular momentum of the system also cut off the higher order terms. Reference [21, pp. 10] gives the non-vanishing terms in the tesseral harmonic expansion predicted by symmetry properties of various point groups. Then the coefficients \( \gamma_{nm} \) or \( C_n^m, S_n^m \) are calculated.

Hopefully, some of them will happen to be zero too. Although the first method can give the same results in many cases [6], the latter method is much more popular because of the concise procedure of calculations.

After the electrostatic potential \( V \) is derived, the hamiltonian can be calculated

\[
H_{\text{crystal field}} = \sum_\alpha eV(R_\alpha)
\]

(2.39)

Where the summation is carried out over all the 4-\( f \) electrons of the ion. If the electrostatic potential is expressed in the cartesian coordinates, the Hamiltonian can be quantized into its "operator equivalent" easily by Stevens' rules [2]:

- \( x \rightarrow J_x, y \rightarrow J_y, \) and \( z \rightarrow J_z. \)

- Always allow for the noncommutation of \( J_x, J_y, \) and \( J_z. \) That is, change any multiplication of \( x, y, \) and \( z \) by the sum of all possible permutations divided by the total number of possible permutations.
• Drop the summation sign.

Example 3

\[ \sum_{\alpha} z^{A} \rightarrow \mathcal{J}_{z}^{A} \]  
\[ \sum_{\alpha} xy \rightarrow \frac{1}{2}( \mathcal{J}_{z}\mathcal{J}_{y} + \mathcal{J}_{y}\mathcal{J}_{z} ) \]

By following Stevens' procedure, we can translate all the tesseral harmonics into its "operator equivalents",

\[ O_{n}^{m} \rightarrow \frac{K_{n}^{m}}{r^{n}} \mathcal{O}_{n}^{m} \]

where \( K_{n}^{m} \) is a constant, and \( \mathcal{O}_{n}^{m} \) are the corresponding operator equivalent. Lea et al. [9] tabulated most of the important \( \mathcal{O}_{n}^{m} \)'s and also the matrix elements of these operators in the angular momentum basis functions.

Then we can get a general result for the 4f-electron systems for the specific point group of the location of the ion in the crystal. For example, for the cubic group,

\[ \mathcal{H}_{CF} = B_{4}(\mathcal{O}_{4}^{0} + 5\mathcal{O}_{4}^{4}) + B_{6}(\mathcal{O}_{6}^{0} - 21\mathcal{O}_{6}^{4}) \]

Where operators \( \mathcal{O}_{n}^{m} \) can be easily found in various standard tables. [6][9] Because the \( \mathcal{H}_{CF} \) is expressed by angular momentum operators in the tables, the calculation of the matrix elements is straightforward, since the basis functions are the linear combinations of the eigenfunctions of the angular momentum. Of course, if the matrix elements are tabulated by other researchers, we can look it up easily. However, the biggest problem is to find the two factors \( B_{4} \) and \( B_{6} \), which involves intractable integrals and shielding factors. The popular method is to leave the factors as variables through all the calculations. Then derive the two factors by fitting the resultant energy levels to the observed emissions.
If we know all the matrix elements of the perturbation Hamiltonian, we can find the energy levels by perturbation theory. Based on the perturbation theory, the energy levels can be calculated easily. The algorithm is introduced in the next chapter.
Chapter 3
Algorithms

Figure 3.1 shows a general flow chart to calculate the energy levels using group theory. The main steps are,

1. From standard tables, find a specific energy level with angular momentum $j$.

2. Reduce the symmetry into the local symmetry of the dopant. Find from standard tables, for this representation of angular momentum of $j$, how many times it will reduce into the each irreducible representation.

3. Make the following judgement for each irreducible representation. Is the irreducible representation is only repeated once?

- If yes, the first-order energy is

$$E^{(1)} = \frac{1}{t_i} \sum_{i=1}^{t_i} \langle f_i|V|f_i \rangle$$

where $f_i$ is the basis for the irreducible representation.

- If no, and the the irreducible representation is repeated $n$ times, then the first order energy $E^1$ is the solution of

$$
\begin{vmatrix}
\langle f_1|V|f_1 \rangle - E^{(1)} & \langle f_1|V|f_2 \rangle & \ldots & \langle f_1|V|f_n \rangle \\
\langle f_2|V|f_1 \rangle & \langle f_2|V|f_2 \rangle - E^{(1)} & \ldots & \langle f_2|V|f_n \rangle \\
\vdots & \vdots & \ddots & \vdots \\
\langle f_n|V|f_1 \rangle & \langle f_n|V|f_2 \rangle & \ldots & \langle f_n|V|f_n \rangle - E^{(1)}
\end{vmatrix} = 0
$$

(3.2)
where $f_n$ are the first basis function of each irreducible representation. The $n$
roots of the equation give a $n$-fold splitting in energy. For the basis functions,
it is always preferred to express them by angular momentum basis functions.

4. Go to step 1 to work on another energy level to have another set of splitted energy
   levels. Then apply selection rules to find possible emissions.

5. Fit the unknown factors with respect to the observed emissions.

6. Use the derived factors to predict other emissions.
2J+1 fold degenerate level, irreducible representation

Apply the lower symmetry of the crystalline field

Representation can be reduced into the linear combination of the irreducible representations of the crystalline group

For each irreducible representation, Does it occur once?

Yes

The functions corresponding to the irreducible representation are the 'right' zeroth-order wavefunction
New emission is at SUM(<f|W|f>)/dimension

No

The irreducible representation occurs p times (Assume p=2)

f, g are the functions that span the two representations

\[ \begin{vmatrix} <f|W|f> & <f|W|g> \\ <g|W|f> & <g|W|g> \end{vmatrix} = 0 \]

for p splitted levels and p set of eigenfunctions

Figure 3.1: The flow chart for the calculation of crystal field splitting.
Chapter 4

Calculations of the atomic level splitting of $Er^{3+}$ in ZnO

4.1 Characteristics of $Er^{3+}$ and ZnO

$Er^{3+}$ has a strong photoluminescence emission at the wavelength around 550nm. It can be assigned to the angular momentum transition $^4S_{\frac{3}{2}} \rightarrow ^4 I_{\frac{11}{2}}$. We observed very strong emission from the $Er$-doped ZnO samples and well resolved splittings. So we will try to calculate on this transition.

Our host crystal ZnO has a Wurtzite structure, its space group belongs to the Number 186 space group, which can be denoted as $P6_3mc(186)$ and has a crystal constant of $3.2495 \pm 0.0005 \AA$[19, P-B212]. From the space group, we can derive that the crystal class is Hexagonal and the point group is $C_{3v}$ in Schoenfiles' notation and $3m$ in international notation when the $Er^{3+}$ ion take the substitutional place of $Zn^{2+}$ [22, pp. 293]. An illustration of the symmetry of $C_{3v}$ point group is given as Figure 4.1.

By studying the classes of operations, we can find how the rotation group decompose into the irreducible representations of point group $C_{3v}$. 
Figure 4.1: An illustration of the symmetry of $C_{3v}$ point group.

<table>
<thead>
<tr>
<th>Class</th>
<th>Description</th>
<th>Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>Identity Operation</td>
<td>1</td>
</tr>
<tr>
<td>$C_3$</td>
<td>three-fold rotation about the hexagonal axis</td>
<td>2</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>reflection about the plane of the symmetric axis</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 4.1: Irreducible representations of group $C_{3v}$.  
4.2 Irreducible representations of group $C_{3v}$

From equation

$$l_1^2 + l_2^2 + l_3^2 = 6$$  \hspace{1cm} (4.1)

we have $l_1 = 1$, $l_2 = 1$, and $l_3 = 2$, that is, the dimensions of the three irreducible representations are 1, 1, and 2 respectively.

For odd number of electrons, the group $C_{3v}$ becomes a double group $C_{3v}^+$ which has three more classes of operations $RE$, $RC_3$, and $R \sigma$ and hence three more representations called specific presentations are added. The double group has 12 elements which is twice the number of the single group. It is not hard to conclude that the dimensions of the specific representations are 2, 1, and 1 from the equation

$$l_4^2 + l_5^2 + l_6^2 = 6$$  \hspace{1cm} (4.2)

From equation 2.17, we can get

$$\mathcal{D}^{j = \frac{15}{2}} \rightarrow 5 \Gamma_4 + 3 \Gamma_5 + 3 \Gamma_6$$  \hspace{1cm} (4.3)

$$\mathcal{D}^{j = \frac{3}{2}} \rightarrow \Gamma_4 + \Gamma_5 + \Gamma_6$$  \hspace{1cm} (4.4)

At this point, we find that the upper atomic level $^4S_{3/2}$ will split into two energy levels\(^1\). The lower level $^4I_{15/2}$ will split into eight levels, three of whom are of irreducible

\(^1\)We will find that the energy levels of $\Gamma_5$ and $\Gamma_6$ degenerate if we take the approximate tetrahedral potential instead of a $C_{3v}$ potential. More accurate calculations must consider the splitting between $\Gamma_5$ and $\Gamma_6$.\
representation $\Gamma_5$ and $\Gamma_6$ (degenerate) and five others are of $\Gamma_4$. Figure 4.2 gives an illustration of the splitting of the atomic levels of $Er^{3+}$ in $ZnO$ crystal field.

![Energy level diagram](image)

Figure 4.2: An illustration of the energy level splitting of $Er^{3+}$ in $ZnO$.

### 4.3 Selection Rules

In Figure 4.2, selection rules are also considered. From the result of group theory [7, pp. 1877], the direct product of the irreducible representation of the initial energy level and the irreducible representation of the dipole representation $\Gamma_1$ must contain all the final state representations. From the multiplication table of $C_{3v}$ given by reference [14, pp. 55],
we know that

\[ \Gamma_1 \times \Gamma_4 = \Gamma_4 \]  \hspace{1cm} (4.5) 

\[ \Gamma_1 \times \Gamma_5 = \Gamma_5 \]  \hspace{1cm} (4.6) 

\[ \Gamma_1 \times \Gamma_6 = \Gamma_6 \]  \hspace{1cm} (4.7) 

So the dipole transition can only occur between the same irreducible representations. So from Figure 4.2, \( \Gamma_4 \rightarrow \Gamma_4 \) gives five spectrum lines while \( \Gamma_{5,6} \rightarrow \Gamma_{5,6} \) gives three emission lines. Because we will need to fix two parameters in the crystal field Hamiltonian and the actual separation of atomic levels \( ^4S_{3/2} \) and \( ^4I_{15/2} \), we need as many emission lines as possible, so we will try to study the transition \( \Gamma_4 \rightarrow \Gamma_4 \), which hopefully will give us five spectrum lines.

4.4 Basis functions of irreducible representations

Now we have to find the basis states of the irreducible specific representations in terms of the basis states of the system after spin-orbit coupling. That is, we need to know the basis states of \( \Gamma_4, \Gamma_5, \) and \( \Gamma_6 \) by the linear combination of states \( |jm \rangle \), where \( m \in [-j,j] \). Several facts important to these calculations are shown below. (Note: These arguments are only true for point group \( C_{3v} \).)

1. We do not need to know the basis states of the three normal representations because for an odd number electron system like \( Er^{3+} \) (11 4f-electrons), the irreducible representation can only be specific. Although there is well tabulated basis states for the
cubic crystal class[9], we failed to find any ready-to-use basis functions tabulated for hexagonal crystals by previous investigators.

2. The standard method to derive basis functions is to use the simplified “projection operator” introduced in Chapter 2

\[ \mathcal{P}^k = \frac{l_k}{g} \sum_{S \in G} \chi^{*}_k(S) \cdot S \]  \hspace{1cm} (4.8)

The study of the \( C_{3v} \) point group shows that all the operations are about the same symmetric axis, which we can define as the \( z \)-axis. Then the spherical harmonic functions \( |jm\) have the form of

\[ |jm\) \rightarrow \mathcal{F}_n^m(\theta) \times e^{im\phi} \]  \hspace{1cm} (4.9)

3. Any rotational operation around axis \( z \) only changes \( \phi \) and leaves \( \theta \) constant. That is, the rotational operations in point group \( C_{3v} \) will not change any of the spherical harmonic functions except a phase constant. Now assume that rotational operation \( S \) of angle \( \alpha \) about \( z \)-axis will change \( \theta \) into \( \theta' = \theta \) and \( \phi \) into \( \phi' = \phi + \alpha \), then

\[ S^{rot}|jm\rangle = \mathcal{F}^m_n(\theta') \times e^{im\phi'} = \mathcal{F}^m_n(\theta) \times e^{im(\phi + \alpha)} = e^{im\alpha}|jm\rangle \]  \hspace{1cm} (4.10)

4. When we study the three reflection operations in the group, we can find that a reflection operation \( \sigma \) will change \( \theta \) into \( \theta' = \theta \) and \( \phi \) into \( \phi' = \alpha - \phi \). So by the same argument we used for the rotational operations, we can conclude that

\[ S^{ref}|jm\rangle = \mathcal{F}^m_n(\theta') \times e^{im\phi'} = \mathcal{F}^m_n(\theta) \times e^{im(\alpha - \phi)} = e^{im\alpha}|j - m\rangle \]  \hspace{1cm} (4.11)
Now we can start to apply projection operator on the angular momentum basis functions \(|jm\)|. We tabulated some useful information to carry out the calculation in Table 4.2. Tables of reference [14, pp. 55] are always very useful in these kinds of calculations.

<table>
<thead>
<tr>
<th>(S)</th>
<th>(E)</th>
<th>(R E)</th>
<th>(C_3^+)</th>
<th>(C_3^-)</th>
<th>(RC_3^+)</th>
<th>(RC_3^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\chi^4)</td>
<td>2</td>
<td>-2</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>(\chi^5)</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(\chi^6)</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(S</td>
<td>jm\rangle)</td>
<td>(</td>
<td>jm\rangle)</td>
<td>(-</td>
<td>jm\rangle)</td>
<td>(e^{im\frac{\pi}{3}}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(S)</th>
<th>(\sigma^{0^\circ})</th>
<th>(\sigma^{120^\circ})</th>
<th>(\sigma^{240^\circ})</th>
<th>(\mathcal{R} \sigma^{0^\circ})</th>
<th>(\mathcal{R} \sigma^{120^\circ})</th>
<th>(\mathcal{R} \sigma^{240^\circ})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\chi^4)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\chi^5)</td>
<td>i</td>
<td>i</td>
<td>i</td>
<td>-i</td>
<td>-i</td>
<td>-i</td>
</tr>
<tr>
<td>(\chi^6)</td>
<td>-i</td>
<td>-i</td>
<td>-i</td>
<td>i</td>
<td>i</td>
<td>i</td>
</tr>
<tr>
<td>(S</td>
<td>jm\rangle)</td>
<td>(</td>
<td>j - m\rangle)</td>
<td>(e^{im\frac{\pi}{3}}</td>
<td>j - m\rangle)</td>
<td>(e^{-im\frac{\pi}{3}}</td>
</tr>
</tbody>
</table>

Table 4.2: Characters and result vectors of elements of point group \(C_{3v}\).

The trivial but laborous algebra is omitted here and the result basis functions are:

When \(J = \frac{3}{2}, J_\frac{3}{2} \rightarrow \Gamma_4 + \Gamma_5 + \Gamma_6\)

\[ \Phi_1^4 = |\frac{3}{2}, -\frac{1}{2}\rangle, \Phi_2^4 = |\frac{3}{2}, \frac{1}{2}\rangle \]

\[ \Phi_5^5 = \frac{1}{\sqrt{2}}(|\frac{3}{2}, -\frac{3}{2}\rangle - i|\frac{3}{2}, \frac{3}{2}\rangle) \]
\( \Phi^6 = \frac{1}{\sqrt{2}}(-|\frac{3}{2}, \frac{3}{2}\rangle - i|\frac{3}{2}, -\frac{3}{2}\rangle) \)

\begin{equation}
(4.12)
\end{equation}

When \( J = \frac{15}{2}, J_{\frac{15}{2}} \rightarrow 5\Gamma_4 + 3\Gamma_5 + 3\Gamma_6 \)

\( \Phi^4_{1,1} = |\frac{15}{2}, -\frac{7}{2}\rangle, \Phi^4_{1,2} = |\frac{15}{2}, \frac{1}{2}\rangle \)

\( \Phi^4_{2,1} = |\frac{15}{2}, \frac{3}{2}\rangle, \Phi^4_{2,2} = |\frac{15}{2}, -\frac{3}{2}\rangle \)

\( \Phi^4_{3,1} = |\frac{15}{2}, -\frac{5}{2}\rangle, \Phi^4_{3,2} = |\frac{15}{2}, \frac{3}{2}\rangle \)

\( \Phi^4_{4,1} = |\frac{15}{2}, \frac{11}{2}\rangle, \Phi^4_{4,2} = |\frac{15}{2}, -\frac{11}{2}\rangle \)

\( \Phi^4_{5,1} = \frac{1}{\sqrt{2}}(|\frac{15}{2}, -\frac{13}{2}\rangle, \Phi^4_{5,2} = |\frac{15}{2}, \frac{13}{2}\rangle \)

\( \Phi^5_1 = |\frac{1}{\sqrt{2}}(|\frac{15}{2}, \frac{3}{2}\rangle - i|\frac{15}{2}, \frac{3}{2}\rangle) \)

\( \Phi^5_2 = \frac{1}{\sqrt{2}}(|\frac{15}{2}, \frac{9}{2}\rangle - i|\frac{15}{2}, \frac{9}{2}\rangle) \)

\( \Phi^5_3 = \frac{1}{\sqrt{2}}(|\frac{15}{2}, -\frac{15}{2}\rangle - i|\frac{15}{2}, \frac{15}{2}\rangle) \)

\( \Phi^5_6 = \frac{1}{\sqrt{2}}(|\frac{15}{2}, \frac{3}{2}\rangle - i|\frac{15}{2}, \frac{3}{2}\rangle) \)

\( \Phi^5_6 = \frac{1}{\sqrt{2}}(|\frac{15}{2}, \frac{9}{2}\rangle - i|\frac{15}{2}, \frac{9}{2}\rangle) \)

\( \Phi^5_5 = \frac{1}{\sqrt{2}}(|\frac{15}{2}, \frac{15}{2}\rangle - i|\frac{15}{2}, -\frac{15}{2}\rangle) \)

\begin{equation}
(4.13)
\end{equation}

### 4.5 Calculation of the Hamiltonian

If the \( Er^{3+} \) takes the substitional position of the \( Zn^{2+} \) in the ZnO crystal, which is wurtzite, all the symmetric operations with regard to the \( Er^{3+} \) ion from a \( C_{3v} \) point group. The following figure is an illustration of the wurtzite structure (Figure 4.3).

We will just consider the four \( O^{2-} \) ions that are closest to the cation, which is illustrated in Figure 4.4.

From Figure 4.4, we can easily derive the central coordinates:
Figure 4.3: The 3-D wurtzite crystal structure.
Figure 4.4: An illustration of the four closest $O^2-$'s to the $Er^{3+}$.

\[ R_1 = \left( \frac{\sqrt{6}a}{4}, 0, 0 \right) \]  
\[ R_2 = \left( \frac{\sqrt{6}a}{4}, \theta, 0 \right) \]  
\[ R_3 = \left( \frac{\sqrt{6}a}{4}, \theta, \frac{\pi}{3} \right) \]  
\[ R_4 = \left( \frac{\sqrt{6}a}{4}, \theta, \frac{2\pi}{3} \right) \]

where

\[ a = 3.2495\text{Å}, \cos \theta = -\frac{1}{3}, \sin \theta = \frac{2\sqrt{2}}{3} \]  

Using the method introduced in section 2.2, we can expend the electrostatic potential of these four point charges into tesseral functions $C_n^m$ and $S_n^m$. We have

\[ V(r, \theta, \phi) = \sum_{n=0}^{\infty} r^n \sum_{m=0}^{n} \left( c_n^m C_n^m + s_n^m S_n^m \right) \]
where

\[
c^n_m = \frac{4\pi}{2n+1} \sum_i \frac{q_i}{R_i^{n+1}} C^n_m(\theta_i, \phi_i) \tag{4.20}
\]

\[
s^n_m = \frac{4\pi}{2n+1} \sum_i \frac{q_i}{R_i^{n+1}} S^n_m(\theta_i, \phi_i) \tag{4.21}
\]

It can be proved [21, pp. 10] by symmetry properties that the non-vanishing terms in the expansion are \( c^0_1, c^0_2, c^0_3, c^0_4, c^0_5, c^3_3, c^3_4, c^3_5, c^3_6, \) and \( c^6_5 \). We will expect many of them to be equal to zero, because we are only considering the electrostatic potential of the closest ions and it really has tetrahedral symmetry, which is higher than the symmetry of the \( C_{3v} \) point group. Now we calculate each of them one by one using the tesseral functions tabulated by Prather [21, pp.4-5]. We also show the tesseral functions we will use in the following table for the convenience of the reader.

If we define

\[
K_n = -\frac{8\pi e}{(2n+1)} \left(\frac{\sqrt{6}a}{4}\right)^{-(n+1)}, \tag{4.22}
\]
some useful tesseral functions

<table>
<thead>
<tr>
<th></th>
<th>In spherical coordinates</th>
<th>In Cartesian coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C^0_1$</td>
<td>$\frac{1}{\sqrt{2\pi}} \frac{\sqrt{6}}{2} \cos \theta$</td>
<td>$\frac{\sqrt{6}}{2} \frac{1}{\sqrt{2\pi}} \frac{z}{r}$</td>
</tr>
<tr>
<td>$C^2_2$</td>
<td>$\frac{1}{\sqrt{2\pi}} \frac{\sqrt{15}}{4} (3 \cos^2 \theta - 1)$</td>
<td>$\frac{\sqrt{15}}{4} \frac{1}{\sqrt{2\pi}} \frac{2z^2 - x^2 - y^2}{r^2}$</td>
</tr>
<tr>
<td>$C^4_3$</td>
<td>$\frac{1}{\sqrt{2\pi}} \frac{\sqrt{14}}{4} (5 \cos^3 \theta - 3 \cos \theta)$</td>
<td>$\frac{\sqrt{14}}{4} \frac{1}{\sqrt{2\pi}} \frac{2z^3 - 3z^2 x - 3z^2 y}{r^3}$</td>
</tr>
<tr>
<td>$C^6_3$</td>
<td>$\frac{1}{\sqrt{2\pi}} \frac{\sqrt{70}}{8} \sin^3 \theta \cos 3\phi$</td>
<td>$\frac{\sqrt{70}}{8} \frac{1}{\sqrt{2\pi}} \frac{z^3 - 3z^2 x}{r^3}$</td>
</tr>
<tr>
<td>$C^8_4$</td>
<td>$\frac{1}{\sqrt{2\pi}} \frac{3\sqrt{2}}{16} (35 \cos^4 \theta - 70 \cos^3 \theta + 15 \cos \theta) \cos 3\phi$</td>
<td>$\frac{3\sqrt{2}}{16} \frac{1}{\sqrt{2\pi}} \frac{8z^4 + 3z^2 x^2 + 3z^2 y^2 - 24z^2 x^2 - 24z^2 y^2 + 6z^2 y^2}{r^4}$</td>
</tr>
<tr>
<td>$C^6_4$</td>
<td>$\frac{1}{\sqrt{2\pi}} \frac{3\sqrt{70}}{8} \cos \theta \sin^3 \theta \cos 3\phi$</td>
<td>$\frac{3\sqrt{70}}{8} \frac{1}{\sqrt{2\pi}} \frac{(z^2 - 3z^2 y^2) x}{r^4}$</td>
</tr>
<tr>
<td>$C^8_5$</td>
<td>$\frac{1}{\sqrt{2\pi}} \frac{5\sqrt{770}}{16} (103 \cos^5 \theta - 105 \cos^4 \theta + 21 \cos^3 \theta - 15 \cos \theta) \cos 3\phi$</td>
<td>$\frac{5\sqrt{770}}{16} \frac{1}{\sqrt{2\pi}} \frac{(8z^5 - 40z^3 x^2 + 15z^2 y^2)^2}{r^5}$</td>
</tr>
<tr>
<td>$C^6_5$</td>
<td>$\frac{1}{\sqrt{2\pi}} \frac{\sqrt{770}}{32} (9 \cos^2 \theta - 1) \sin^3 \theta \cos 3\phi$</td>
<td>$\frac{\sqrt{770}}{32} \frac{1}{\sqrt{2\pi}} \frac{(8z^2 - x^2 - y^2)^2 (3z^2 y - y^3)}{r^5}$</td>
</tr>
<tr>
<td>$C^8_6$</td>
<td>$\frac{1}{\sqrt{2\pi}} \frac{\sqrt{770}}{32} (231 \cos^3 \theta - 315 \cos^2 \theta - 5) \cos 3\phi$</td>
<td>$\frac{\sqrt{770}}{32} \frac{1}{\sqrt{2\pi}} \frac{16z^6 - 120(z^2 + y^2)^2 + 90(z^2 + y^2)^2 z^2 - 5(z^2 + y^2)^3}{r^6}$</td>
</tr>
<tr>
<td>$C^6_6$</td>
<td>$\frac{1}{\sqrt{2\pi}} \frac{\sqrt{770}}{32} (11 \cos^3 \theta - 3 \cos \theta) \sin^3 \theta \cos 3\phi$</td>
<td>$\frac{\sqrt{770}}{32} \frac{1}{\sqrt{2\pi}} \frac{(8z^3 - 3z^2 x - 3z^2 y^2) (z^2 - 3z^2 y^2) x}{r^6}$</td>
</tr>
<tr>
<td>$C^8_6$</td>
<td>$\frac{1}{\sqrt{2\pi}} \frac{\sqrt{6506}}{64} \sin^6 \theta \cos 3\phi$</td>
<td>$\frac{\sqrt{6506}}{64} \frac{1}{\sqrt{2\pi}} \frac{(z^6 - 15z^4 x^2 + 15z^2 y^2)^2 - y^6}{r^6}$</td>
</tr>
</tbody>
</table>

Table 4.3: Table of some tesseral functions.
we have

\[ c_1^0 = K_1 \sum_{i=1}^{4} \frac{1}{\sqrt{2\pi}} \frac{\sqrt{6}}{2} \cos \theta_i = 0 \]

\[ c_2^0 = K_2 \sum_{i=1}^{4} \frac{1}{\sqrt{2\pi}} \frac{\sqrt{10}}{4} (3 \cos^2 \theta_i - 1) = 0 \]

\[ c_3^0 = K_3 \sum_{i=1}^{4} \frac{1}{\sqrt{2\pi}} \frac{\sqrt{14}}{4} (5 \cos^3 \theta_i - 3 \cos \theta_i) = \frac{10}{9} \sqrt{\frac{7}{\pi}} K_3 \]

\[ c_3^1 = K_3 \sum_{i=1}^{4} \frac{\cos 3\phi_i}{\pi} \frac{\sqrt{70}}{8} \sin^3 \theta_i = \frac{4}{9} \sqrt{\frac{35}{\pi}} K_3 \]

\[ c_4^0 = K_4 \sum_{i=1}^{4} \frac{1}{\sqrt{2\pi}} \frac{3\sqrt{2}}{8} (35 \cos^4 \theta_i - 30 \cos^2 \theta_i + 3) = \frac{14}{9} \sqrt{\frac{1}{\pi}} K_4 \]

\[ c_4^3 = K_4 \sum_{i=1}^{4} \frac{\cos 3\phi_i}{\pi} \frac{3\sqrt{70}}{8} \cos \theta_i \sin^3 \theta_i = -\frac{4}{9} \sqrt{\frac{35}{\pi}} K_4 \]

\[ c_5^0 = K_5 \sum_{i=1}^{4} \frac{1}{\sqrt{2\pi}} \frac{\sqrt{22}}{8} (63 \cos^5 \theta_i - 70 \cos^3 \theta_i + 15 \cos \theta_i) = 0 \]

\[ c_5^3 = K_5 \sum_{i=1}^{4} \frac{\cos 3\phi_i}{\pi} \frac{\sqrt{770}}{32} (9 \cos^2 \theta_i - 1) \sin^3 \theta_i = 0 \]

\[ c_6^0 = K_6 \sum_{i=1}^{4} \frac{1}{\sqrt{2\pi}} \frac{\sqrt{26}}{8} (231 \cos^6 \theta_i - 315 \cos^4 \theta_i + 105 \cos^2 \theta_i - 5) = \frac{64}{81} \sqrt{\frac{13}{\pi}} K_6 \]

\[ c_6^3 = K_6 \sum_{i=1}^{4} \frac{\cos 3\phi_i}{\pi} \frac{\sqrt{2730}}{32} (11 \cos^3 \theta_i - 3 \cos \theta_i) \sin^3 \theta_i = \frac{16}{243} \sqrt{\frac{1365}{\pi}} K_6 \]

\[ c_6^6 = K_6 \sum_{i=1}^{4} \frac{\cos 6\phi_i}{\pi} \frac{\sqrt{6060}}{64} \sin^6 \theta_i = \frac{8}{243} \sqrt{\frac{6060}{\pi}} K_6 \]

(4.23)

So the electrostatic potential due to the four closest \(O^{2-}\) ions can be written as

\[ V = \frac{10}{9} \sqrt{\frac{7}{\pi}} K_3 r^3 (C_3^0 + \frac{2\sqrt{5}}{5} C_3^3) + \frac{14}{9} \sqrt{\frac{1}{\pi}} K_4 r^4 (C_4^0 - \frac{2\sqrt{35}}{7} C_4^3) \]

\[ + \frac{64}{81} \sqrt{\frac{13}{\pi}} K_6 r^6 (C_6^0 + \frac{\sqrt{105}}{12} C_6^3 + \frac{\sqrt{462}}{24} C_6^6) \]

(4.24)

Omitting those electrons in the full shells, the hamiltonian of the 11-electron system will be

\[ \mathcal{H}_C = \sum_{i=1}^{11} (-e)V(r_i) \]

(4.25)

---

\[ ^2 \text{This result disagrees with reference [21, pp.14]. The reference gives } C_3^0 : C_3^3 = \sqrt{5} : 2 \text{ (agree), } C_4^0 : C_4^3 = -\sqrt{35} : 5 \text{ (off by a factor of 2), and } C_6^0 : C_6^3 : C_6^6 = 4\sqrt{2310} : 77\sqrt{5} : 35\sqrt{22} \text{ (the ratio of } C_6^0 \text{ and } C_6^3 \text{ is switched).} \]
where the sum is over the 11 4-f electrons. By Stevens's "operator equivalent" method introduced in section 2.2, we can transform the hamiltonian into the equivalent expression of angular momentum operators.

\[ \sum_i r^n C_n^m \quad \text{Stevens's operator equivalent} \]

\[ \sum_i r^3 C_3^0 = \frac{\sqrt{14}}{4} \frac{1}{\sqrt{2\pi}} \delta_j \langle r^3 \rangle (5J_z^3 - 3J_z J^2) \]

\[ = \frac{\sqrt{14}}{4} \frac{1}{\sqrt{2\pi}} \delta_j \langle r^3 \rangle O_3^0 \]

\[ \sum_i r^3 C_3^3 = \frac{\sqrt{70}}{16} \frac{1}{\sqrt{\pi}} \delta_j \langle r^3 \rangle (J_z^2 + J^3) \]

\[ = \frac{\sqrt{70}}{16} \frac{1}{\sqrt{\pi}} \delta_j \langle r^3 \rangle O_3^3 \]

\[ \sum_i r^4 C_4^0 = \frac{3\sqrt{2}}{16} \frac{1}{\sqrt{2\pi}} \beta_j \langle r^4 \rangle (35J_z^4 - 30J^2 J_z^2 + 25J_z^2 - 6J^2 + 3J^4) \]

\[ = \frac{3\sqrt{2}}{16} \frac{1}{\sqrt{2\pi}} \beta_j \langle r^4 \rangle O_4^0 \]

\[ \sum_i r^4 C_4^3 = \frac{3\sqrt{70}}{8} \frac{1}{\sqrt{\pi}} \beta_j \langle r^4 \rangle (J_z (J_z^3 + J^3) + (J_z^3 + J^3) J_z)/4 \]

\[ = \frac{3\sqrt{70}}{8} \frac{1}{\sqrt{\pi}} \beta_j \langle r^4 \rangle O_4^3 \]

\[ \sum_i r^6 C_6^0 = \frac{\sqrt{26}}{32} \frac{1}{\sqrt{2\pi}} \gamma_j \langle r^6 \rangle (231J_z^6 - 315J^2 J_z^4 + 735J_z^4 + 105J^4 J_z^2 - 525J^2 J_z^2 + 294J_z^2 - 5J^6 + 40J^4 - 60J^2) \]

\[ = \frac{\sqrt{26}}{32} \frac{1}{\sqrt{2\pi}} \gamma_j \langle r^4 \rangle O_6^0 \]

\[ \sum_i r^6 C_6^3 = \frac{\sqrt{2730}}{64} \frac{1}{\sqrt{\pi}} \gamma_j \langle r^6 \rangle ((11J_z^3 - 3J^2 J_z - 59J_z) (J_z^3 + J^3) + (J_z^3 + J^3) (11J_z^3 - 3J^2 J_z - 59J_z))/4 \]

\[ = \frac{\sqrt{2730}}{64} \frac{1}{\sqrt{\pi}} \gamma_j \langle r^4 \rangle O_6^3 \]

\[ \sum_i r^6 C_6^6 = \frac{\sqrt{6006}}{64} \frac{1}{\sqrt{\pi}} \gamma_j \langle r^6 \rangle (J_z^6 + J^6)/2 \]

\[ = \frac{\sqrt{6006}}{64} \frac{1}{\sqrt{\pi}} \gamma_j \langle r^4 \rangle O_6^6 \]

where \( \langle r^n \rangle \) is the expectation value of the n-th power of the radius of a 4-f electron, and \( \delta_j, \beta_j, \) and \( \gamma_j \) are the angular integral in the calculation of the "operator equivalent".

The radial factor \( r^n \) is given by A. J. Freeman and R. E. Watson [10, pp. 2070] for several rare-earth elements. They used Hartree-Fock method in their calculations.

And the angular integrals \( \alpha_j, \beta_j, \) and \( \gamma_j' \)s of the ground state of \( Er^{3+}(4f^{11} \ 4I_{15/2}) \) is given by R. J. Elliott and K. W. H. Stevens [6, pp. 252]
<table>
<thead>
<tr>
<th></th>
<th>(&lt;r^2&gt;/a_0^2)</th>
<th>(&lt;r^4&gt;/a_0^4)</th>
<th>(&lt;r^6&gt;/a_0^6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>1.200</td>
<td>3.455</td>
<td>21.226</td>
</tr>
<tr>
<td>Pr&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>1.086</td>
<td>2.822</td>
<td>15.726</td>
</tr>
<tr>
<td>Nd&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>1.001</td>
<td>2.401</td>
<td>12.396</td>
</tr>
<tr>
<td>Sm&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>0.883</td>
<td>1.897</td>
<td>8.775</td>
</tr>
<tr>
<td>Eu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.938</td>
<td>2.273</td>
<td>11.670</td>
</tr>
<tr>
<td>Gd&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>0.785</td>
<td>1.515</td>
<td>8.281</td>
</tr>
<tr>
<td>Dy&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>0.726</td>
<td>1.322</td>
<td>5.102</td>
</tr>
<tr>
<td>Er&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>0.666</td>
<td>1.126</td>
<td>3.978</td>
</tr>
<tr>
<td>Yb&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>0.613</td>
<td>0.960</td>
<td>3.104</td>
</tr>
</tbody>
</table>

Table 4.4: The radial integrals \(<r^n>\) in the “operator equivalent” calculations.
Angular integrals given by Elliott and Stevens

<table>
<thead>
<tr>
<th>Equivalent Operator</th>
<th>Angular Integral</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O^m_2$</td>
<td>$\alpha_j$</td>
<td>$\frac{2^2}{3^2 \cdot 5^2 \cdot 7}$</td>
</tr>
<tr>
<td>$O^m_4$</td>
<td>$\beta_j$</td>
<td>$\frac{2}{3^2 \cdot 5 \cdot 7 \cdot 11 \cdot 13}$</td>
</tr>
<tr>
<td>$O^m_6$</td>
<td>$\gamma_j$</td>
<td>$\frac{2^3}{3^3 \cdot 7 \cdot 11^2 \cdot 13^2}$</td>
</tr>
<tr>
<td>$O^m_8$</td>
<td>$\delta_j$</td>
<td>$0^3$</td>
</tr>
</tbody>
</table>

Table 4.5: The angular integrals for "operator equivalent" given by Elliott and Stevens.

The Hamiltonian can then be expressed by standard operator notations $O^m_n$ \(^4\)

\[
\mathcal{H}_{CF} = A_4(O^0_4 - 20\sqrt{2}O^3_2) + A_6(O^0_6 + \frac{35\sqrt{2}}{4}O^5_6 + \frac{77}{8}O^9_6)
\]

\[
= A_4H_4 + A_6H_6
\]

where

\[
A_4 = \frac{14}{9} \sqrt{\frac{1}{\pi}} K_4 \cdot \frac{3}{16} \sqrt{\frac{1}{\pi}} \beta_j(r^4) = \frac{7}{27} (\sqrt{\frac{6a}{4}})^{-5} \beta_j(r^4)
\]

\[
= 1.724 \times 10^{-8}(a.u.) = 3.36 \times 10^{-3}(cm^{-1})
\]

\[
A_6 = \frac{64}{81} \sqrt{\frac{15}{\pi}} K_6 \cdot \frac{\sqrt{26}}{32} \frac{1}{\sqrt{2\pi}} \gamma_j(r^6) = \frac{16}{81} (\sqrt{\frac{6a}{4}})^{-7} \gamma_j(r^6)
\]

\[
= 1.53 \times 10^{-10}(a.u.) = 3.357 \times 10^{-5}(cm^{-1})
\]

\(^4\)The $O^m_8$ terms vanishes because $\delta_j = 0$. The Hamiltonian here is really a Hamiltonian for tetrahedral potential because we only used the four closest ions in the calculation. The $O^2_2$ term that should appear in a $C_{3v}$ Hamiltonian can be considered a second order perturbation because the local environment of the $Er^{3+}$ resembles a tetrahedral symmetry. It is given [6, pp. 247] that the nonzero terms in $C_{3v}$ potential expansion are $O^0_2$, $O^2_2$, $O^4_2$, $O^6_2$, $O^8_2$, and $O^6_8$. 

---
The unit system we used in the calculations is the **natural atomic units (a.u.)**, described in reference [24, Appendix] and defining \( e = \hbar = \mu = 1 \).

Because it is very hard to calculate the \( \langle r^n \rangle \)'s exactly and consider the screening of the crystal field by the full outer shells, we do not expect the \( A_4 \) and \( A_6 \) we just calculated to be even close to the experimental value. But it will be interesting to compare the experimental value to the value derived simply from Hartree-Fock approximation. In general, we would expect the calculated value to be larger than the experimental value because the former does not consider the screening effect of outer shells at all. So we will try to fit these constants to some of the observed data and compare the calculated and experimental factors. Now we are ready to estimate the matrix elements \( \langle jm | \mathcal{H}_{CF} | jm' \rangle \).

As a first step we will tabulate the matrix elements of \( \mathcal{H}_4 \) in Table 4.6 and \( \mathcal{H}_6 \) in Table 4.7.

In Chapter 3, we introduced the algorithm to calculate the level splitting based on the perturbation theory. Let us consider only the splitting of the \( ^4I_{15/2} \) atomic level. For the five energy levels associate to the irreducible representation \( \Gamma_4 \), we need to solve the equation

\[
\begin{vmatrix}
H_{11} - E & H_{12} & H_{13} & H_{14} & H_{15} \\
H_{21} & H_{22} - E & H_{23} & H_{24} & H_{25} \\
H_{31} & H_{32} & H_{33} - E & H_{34} & H_{35} \\
H_{41} & H_{42} & H_{43} & H_{44} - E & H_{45} \\
H_{51} & H_{52} & H_{53} & H_{54} & H_{55} - E
\end{vmatrix} = 0, \quad (4.29)
\]

where \( H_{ij} \) are the integrals \( \langle \Phi_{i,1}^4 | \mathcal{H}_{CF} | \Phi_{j,1}^4 \rangle \). By applying the basis vectors derived in section 4.2 and hamiltonian derived in section 4.5, we have
\[
\mathcal{H}_4(m, m') = \langle jm | \mathcal{H}_4 | jm' \rangle \quad (J = 15/2)
\]

| \(|m - m'| = 0\) | \(|m - m'| = 3\) |
|-----------------|-----------------|
| \(\mathcal{H}_4(-\frac{15}{2}, -\frac{15}{2}) = 16380\) | \(\mathcal{H}_4(-\frac{15}{2}, -\frac{9}{2}) = 360\sqrt{910}\) |
| \(\mathcal{H}_4(-\frac{13}{2}, -\frac{13}{2}) = -5460\) | \(\mathcal{H}_4(-\frac{13}{2}, -\frac{7}{2}) = 1200\sqrt{182}\) |
| \(\mathcal{H}_4(-\frac{11}{2}, -\frac{11}{2}) = -13260\) | \(\mathcal{H}_4(-\frac{11}{2}, -\frac{5}{2}) = 480\sqrt{1430}\) |
| \(\mathcal{H}_4(-\frac{9}{2}, -\frac{9}{2}) = -12060\) | \(\mathcal{H}_4(-\frac{9}{2}, -\frac{3}{2}) = 3600\sqrt{22}\) |
| \(\mathcal{H}_4(-\frac{7}{2}, -\frac{7}{2}) = -6060\) | \(\mathcal{H}_4(-\frac{7}{2}, -\frac{1}{2}) = 600\sqrt{462}\) |
| \(\mathcal{H}_4(-\frac{5}{2}, -\frac{5}{2}) = 1380\) | \(\mathcal{H}_4(-\frac{5}{2}, \frac{1}{2}) = 480\sqrt{210}\) |
| \(\mathcal{H}_4(-\frac{3}{2}, -\frac{3}{2}) = 7740\) | \(\mathcal{H}_4(-\frac{3}{2}, \frac{3}{2}) = 0\) |
| \(\mathcal{H}_4(-\frac{1}{2}, -\frac{1}{2}) = 11340\) | - |
| \(\mathcal{H}_4(-m, -m) = \mathcal{H}_4(m, m)\) | \(\mathcal{H}_4(-m, -m') = -\mathcal{H}_4(m, m')\) |

Table 4.6: non-vanishing matrix elements of \(\mathcal{H}_4\).
\[ \mathcal{H}_6(m, m') = (jm|\mathcal{H}_6|jm') (J = 15/2) \]

| \(|m - m'| = 0\) | \(|m - m'| = 3\) | \(|m - m'| = 6\) |
|---|---|---|
| \(\mathcal{H}_6(-\frac{15}{2}, -\frac{15}{2}) = 900900\) | \(\mathcal{H}_6(-\frac{15}{2}, -\frac{9}{2}) = -34650\sqrt{910}\) | \(\mathcal{H}_6(-\frac{15}{2}, -\frac{3}{2}) = 3465\sqrt{5005}\) |
| \(\mathcal{H}_6(-\frac{13}{2}, -\frac{13}{2}) = -162160\) | \(\mathcal{H}_6(-\frac{13}{2}, -\frac{7}{2}) = -51975\sqrt{182}\) | \(\mathcal{H}_6(-\frac{13}{2}, -\frac{1}{2}) = 24255\sqrt{429}\) |
| \(\mathcal{H}_6(-\frac{11}{2}, -\frac{11}{2}) = -540540\) | \(\mathcal{H}_6(-\frac{11}{2}, -\frac{5}{2}) = 0\) | \(\mathcal{H}_6(-\frac{11}{2}, -\frac{1}{2}) = 13860\sqrt{3003}\) |
| \(\mathcal{H}_6(-\frac{9}{2}, -\frac{9}{2}) = 817740\) | \(\mathcal{H}_6(-\frac{9}{2}, -\frac{3}{2}) = 121275\sqrt{22}\) | \(\mathcal{H}_6(-\frac{9}{2}, -\frac{1}{2}) = 291060\) |
| \(\mathcal{H}_6(-\frac{7}{2}, -\frac{7}{2}) = 1205820\) | \(\mathcal{H}_6(-\frac{7}{2}, -\frac{1}{2}) = 34650\sqrt{462}\) | \(\mathcal{H}_6(-\frac{7}{2}, -\frac{3}{2}) = 145530\sqrt{55}\) |
| \(\mathcal{H}_6(-\frac{5}{2}, -\frac{5}{2}) = 623700\) | \(\mathcal{H}_6(-\frac{5}{2}, \frac{1}{2}) = 34650\sqrt{210}\) | - |
| \(\mathcal{H}_6(-\frac{3}{2}, -\frac{3}{2}) = -346500\) | \(\mathcal{H}_6(-\frac{3}{2}, \frac{3}{2}) = 0\) | - |
| \(\mathcal{H}_6(-\frac{1}{2}, -\frac{1}{2}) = -1039500\) | - | - |

\(\mathcal{H}_6(-m, -m) = \mathcal{H}_6(m, m)\) \(\mathcal{H}_6(-m, -m') = -\mathcal{H}_6(m, m')\) \(\mathcal{H}_6(-m, -m') = \mathcal{H}_6(m, m')\)

Table 4.7: non-vanishing matrix elements of \(\mathcal{H}_6\).
\[ H_{11} = \langle \Phi_{1,1}^4 | \mathcal{H}_{CF} | \Phi_{1,1}^4 \rangle = \mathcal{H}(\frac{-1}{2}, -\frac{1}{2}) = 11340A_4 - 1039500A_6 \]
\[ H_{12} = \langle \Phi_{1,1}^4 | \mathcal{H}_{CF} | \Phi_{2,1}^4 \rangle = \mathcal{H}(\frac{-1}{2}, \frac{5}{2}) = 480\sqrt{210}A_4 - 34650\sqrt{210}A_6 \]
\[ H_{13} = \langle \Phi_{1,1}^4 | \mathcal{H}_{CF} | \Phi_{3,1}^4 \rangle = \mathcal{H}(\frac{-1}{2}, \frac{11}{2}) = 13860\sqrt{3003}A_6 \]
\[ H_{14} = \langle \Phi_{1,1}^4 | \mathcal{H}_{CF} | \Phi_{4,1}^4 \rangle = \mathcal{H}(\frac{-1}{2}, -\frac{7}{2}) = 600\sqrt{462}A_4 + 34650\sqrt{462}A_6 \]
\[ H_{15} = \langle \Phi_{1,1}^4 | \mathcal{H}_{CF} | \Phi_{5,1}^4 \rangle = \mathcal{H}(\frac{-1}{2}, -\frac{13}{2}) = 24255\sqrt{429}A_6 \]
\[ H_{22} = \langle \Phi_{2,1}^4 | \mathcal{H}_{CF} | \Phi_{2,1}^4 \rangle = \mathcal{H}(\frac{5}{2}, \frac{5}{2}) = 1380A_4 + 623700A_6 \]
\[ H_{23} = \langle \Phi_{2,1}^4 | \mathcal{H}_{CF} | \Phi_{3,1}^4 \rangle = \mathcal{H}(\frac{5}{2}, \frac{11}{2}) = -480\sqrt{1430}A_4 \]
\[ H_{24} = \langle \Phi_{2,1}^4 | \mathcal{H}_{CF} | \Phi_{4,1}^4 \rangle = \mathcal{H}(\frac{5}{2}, -\frac{7}{2}) = 145530\sqrt{55}A_6 \]
\[ H_{25} = \langle \Phi_{2,1}^4 | \mathcal{H}_{CF} | \Phi_{5,1}^4 \rangle = \mathcal{H}(\frac{5}{2}, -\frac{13}{2}) = 0 \]
\[ H_{33} = \langle \Phi_{3,1}^4 | \mathcal{H}_{CF} | \Phi_{3,1}^4 \rangle = \mathcal{H}(\frac{11}{2}, \frac{11}{2}) = -13260A_4 - 540540A_6 \]
\[ H_{34} = \langle \Phi_{3,1}^4 | \mathcal{H}_{CF} | \Phi_{4,1}^4 \rangle = \mathcal{H}(\frac{11}{2}, -\frac{7}{2}) = 0 \]
\[ H_{35} = \langle \Phi_{3,1}^4 | \mathcal{H}_{CF} | \Phi_{5,1}^4 \rangle = \mathcal{H}(\frac{11}{2}, -\frac{13}{2}) = 0 \]
\[ H_{44} = \langle \Phi_{4,1}^4 | \mathcal{H}_{CF} | \Phi_{4,1}^4 \rangle = \mathcal{H}(\frac{-7}{2}, -\frac{7}{2}) = -6060A_4 + 1205820A_6 \]
\[ H_{45} = \langle \Phi_{4,1}^4 | \mathcal{H}_{CF} | \Phi_{5,1}^4 \rangle = \mathcal{H}(\frac{-7}{2}, -\frac{13}{2}) = 1200\sqrt{182}A_4 - 51975\sqrt{182}A_6 \]
\[ H_{55} = \langle \Phi_{5,1}^4 | \mathcal{H}_{CF} | \Phi_{5,1}^4 \rangle = \mathcal{H}(\frac{-13}{2}, -\frac{13}{2}) = -5460A_4 - 1621620A_6, \]
where \( \mathcal{H}(m, m') = A_4 \mathcal{H}(m, m') + A_6 \mathcal{H}_6(m, m'). \)

For the levels due to the representations \( \Gamma_5 \) and \( \Gamma_6 \), it can be shown that they can be derived by exactly the same matrix, that is, energy levels of \( \Gamma_5 \) and \( \Gamma_6 \) will be 2-fold degenerate. So it is only necessary to solve the eigenvalue problem for \( \Gamma_5 \), and the solution of \( \Gamma_6 \) will be the same. Again we have a equation
\[
\det \begin{bmatrix}
H_{11} - E & H_{12} & H_{13} \\
H_{12} & H_{22} - E & H_{23} \\
H_{13} & H_{23} & H_{33} - E
\end{bmatrix} = 0, \quad (4.31)
\]

And in the same way we have

\[H_{11} = \langle \Phi_1^5 | H_{CF} | \Phi_1^5 \rangle = \frac{1}{2} (\mathcal{H}(-\frac{3}{2}, -\frac{3}{2}) + \mathcal{H}(\frac{3}{2}, \frac{3}{2}) + i\mathcal{H}(\frac{3}{2}, -\frac{3}{2}) - i\mathcal{H}(-\frac{3}{2}, \frac{3}{2})) = 7740A_4 - 346500A_6\]

\[H_{12} = \langle \Phi_1^5 | H_{CF} | \Phi_2^5 \rangle = \frac{1}{2} (\mathcal{H}(-\frac{3}{2}, -\frac{9}{2}) + \mathcal{H}(\frac{3}{2}, \frac{9}{2}) + i\mathcal{H}(\frac{9}{2}, -\frac{9}{2}) - i\mathcal{H}(-\frac{9}{2}, \frac{9}{2})) = 0\]

\[H_{13} = \langle \Phi_1^5 | H_{CF} | \Phi_3^5 \rangle = \frac{1}{2} (\mathcal{H}(-\frac{3}{2}, -\frac{15}{2}) + \mathcal{H}(\frac{3}{2}, \frac{15}{2}) + i\mathcal{H}(\frac{15}{2}, -\frac{3}{2}) - i\mathcal{H}(-\frac{15}{2}, \frac{3}{2})) = 3465\sqrt{5005}A_6\]

\[H_{22} = \langle \Phi_2^5 | H_{CF} | \Phi_2^5 \rangle = \frac{1}{2} (\mathcal{H}(-\frac{9}{2}, -\frac{9}{2}) + \mathcal{H}(\frac{9}{2}, \frac{9}{2}) + i\mathcal{H}(\frac{9}{2}, -\frac{9}{2}) - i\mathcal{H}(-\frac{9}{2}, \frac{9}{2})) = -13260A_4 + 817740A_6\]

\[H_{23} = \langle \Phi_2^5 | H_{CF} | \Phi_3^5 \rangle = \frac{1}{2} (\mathcal{H}(-\frac{9}{2}, -\frac{15}{2}) + \mathcal{H}(\frac{9}{2}, \frac{15}{2}) + i\mathcal{H}(\frac{15}{2}, -\frac{9}{2}) - i\mathcal{H}(-\frac{15}{2}, \frac{9}{2})) = 0\]

\[H_{33} = \langle \Phi_3^5 | H_{CF} | \Phi_3^5 \rangle = \frac{1}{2} (\mathcal{H}(-\frac{15}{2}, -\frac{15}{2}) + \mathcal{H}(\frac{15}{2}, \frac{15}{2}) + i\mathcal{H}(\frac{15}{2}, -\frac{15}{2}) - i\mathcal{H}(-\frac{15}{2}, \frac{15}{2})) = 16380A_4 + 900900A_6\]  

(4.32)

4.6 Fitting with experimental data

We will use the standard fitting procedure suggested by Lea et al. [9]. To make the scale of the matrix elements of \(\mathcal{H}_4\) and \(\mathcal{H}_6\) comparable, we use the regulation factor \(F_4\) and \(F_6\) and write equation 4.5 as

\[\mathcal{H}_{CF} = A_4 F_4^4 \frac{\mathcal{H}_4}{F_4} + A_6 F_6^6 \frac{\mathcal{H}_6}{F_6}\]  

(4.33)
where for the state $J = 15/2$, $F_4 = 60$, and $F_6 = 13860$ [6, Table IX]. If we let

$$A_4F_4 = Wx$$

(4.34)

$$A_6F_6 = W(1 - |x|)$$

(4.35)

where $-1 < x < 1$. Then we can reform the crystal field hamiltonian into

$$\mathcal{H}_{CF} = W[x(\frac{\mathcal{H}_4}{F_4}) + (1 - |x|)(\frac{\mathcal{H}_6}{F_6})]$$

(4.36)

Thus $W$ is the scale factor that has no relation with the relative spacing of the energy levels and $x$ is the factor we want to fit with respect to the observed spectra.

We have written a program in MATLAB to do semi-automatic fitting. First we sweep the variable $x$ from -1 to 1 with step 0.001 and derived the eigenvalues of Hamiltonian $\mathcal{H}_{CF}/W$ and plotted a graph as shown in Figure 4.5.

On the other hand, we observed a photoluminescence spectrum of a ZnO : Er$^{3+}$ sample as shown in Figure 4.6. The excitation wavelength was the 488nm line of an Argon ion laser at the power of 300mW. The temperature was 10K and the slit on the monochromator was 50$\mu$m $\times$ 5mm. From the graph we can see that around the wavelength 558nm, there are four well resolved lines. Presumably, we consider these four lines are caused by the crystal field splitting of the $^4I_{15/2}$ level in the $\Gamma_4$ irreducible representation. The four peaks are located at 555.720nm, 556.652nm, 557.565nm, and 558.255nm respectively.

As we have stated before, we would expect a 5-fold splitting in this situation from the result of group theory. However, if we study the eigenvalues we have calculated(Figure 4.5), we can find that when $0.3 < x < 1$, the two lowest eigenvalues are very close to each
Figure 4.5: Eigenvalues of the Hamiltonian $H_{CF}/W$ with sweeping $x$. 
Figure 4.6: The photoluminescence spectrum of ZnO : Er$^{3+}$. 
other. If we compare it with the spectrum (Figure 4.6), we find that the peak at the small wavelength, high energy end is much wider than the other three of them. Then we make an assumption that the 555.72nm peak is caused by the two lowest levels of splitting and the peak position is at the average of the two eigenvalues. Also we assume that the variable $x$ is in the region $0.3 < x < 1$.

According to the observed spectrum, the four peaks correspond to energy levels of $17912.96 \text{ cm}^{-1}(558.255\text{nm})$, $17935.12 \text{ cm}^{-1}(557.565\text{nm})$, $17964.54 \text{ cm}^{-1}(556.652\text{nm})$, and $17994.67 \text{ cm}^{-1}(555.72\text{nm})$ respectively. Because the initial state $^4S_{3/2}$ will split in the $C_{3v}$ potential into two levels, we assume that the emission is from the lower state. The ratio of the energy splitting of the ground state is, from low to high, $1.024 : 1 : 0.7532$. The procedures of the fitting is shown in Figure 4.7. The source code of the fitting program is provided in the Appendix.

### 4.7 Results

From the fitting procedure, we got the parameters in the Hamiltonian that fits the spectrum best. We got the fitting parameters $x=0.5093$ and $W=0.1885 \text{ cm}^{-1}$ with a mean square root of fitting error equals to 0.0887.

From the formula

$$A_4 F_4 = Wx$$

(4.37)

and

$$A_6 F_6 = W(1 - |x|)$$

(4.38)

where $F_4 = 60$ and $F_6 = 13860$,
Let \( M_4 = H_4/F_4W \), and \( M_6 = H_6/F_6W \)

Sweep \( x \) from -1 to 1, get the eigenvalue of matrix \( xM_4 + (1-|x|)M_6 \)

Plot the eigenvalues with changing \( x \)

Average the two lowest levels

Find a \( x \) that the ratio of the separations between the levels is the closest to \( 0.7532:1:1.0241 \)

Output \( x \) and \( W \) derived from the fitting

Fit the vacuum level separation with respect to the observed data

Figure 4.7: The flow chart illustrating the algorithm of the fitting procedure.
<table>
<thead>
<tr>
<th></th>
<th>Hatree-Fock</th>
<th>data fitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_4$ ($cm^{-1}$)</td>
<td>$3.36 \times 10^{-3}$</td>
<td>$1.58 \times 10^{-3}$</td>
</tr>
<tr>
<td>$A_6$ ($cm^{-1}$)</td>
<td>$3.357 \times 10^{-5}$</td>
<td>$6.76 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Table 4.8: Comparison of the experimental and Hatree-Fock coefficients.

We get $A_4 = 1.58 \times 10^{-3}$ $cm^{-1}$ and $A_6 = 6.76 \times 10^{-6}$ $cm^{-1}$. So the Hamiltonian describing the crystal field is

$$H_{CF} = 4.45 \times 10^{-2} \, cm^{-1} \left( O_4^0 - 20\sqrt{2} O_4^3 \right) + 1.90 \times 10^{-4} \, cm^{-1} \left( O_6^0 + \frac{25\sqrt{2}}{4} O_6^3 + \frac{77}{8} O_6^6 \right)$$

(4.39)

The coefficients $A_4$ and $A_6$ derived by experimental data fitting can be compared in Table 4.8. We found that the result is just what we have expected. The calculated values are larger because the calculation failed to consider the screening effect.

The observed levels and the fitted levels are illustrated in Figure 4.8. We can see that they fit very well.

The fitting procedure also found that the energy difference of the vacuum level $^4S_{3/2}$ and $^4I_{15/2}$ is 17955 $cm^{-1}$. 
Figure 4.8: An illustration of the observed peaks and calculated peaks.
Chapter 5

Related Experiments

The photoluminescence and kinetics measurements of this chapter were done in collaboration with B. Patel and W. Jadwisienzak of the optoelectronics group.

5.1 Sample Preparation

The ZnO : Er sample we discussed is prepared by the method of co-sintering with Li doping. The reason to co-dope Li with Er is because there is some evidence to show that the element can improve the luminescence of RE-doped semiconductors. As the first stage of our research on the Er-doped ZnO, we chose the easiest way to prepare a sample – co-sintering.

We measured and mixed the powders of 0.9295g ZnO, 0.0305g Er(NO₃)₃, and 0.0244g Li₂CO₃. The powders were mixed for 1 hour. The mole ratio of the elements Zn : Er : Li was 93.62% : 0.6% : 5.78%. Then the mixture was moistened by a little ethanol and compressed into tablets of about 10mm × 10mm × 2mm by a pressure of 5000 psi. Then the tablets were annealed for 5 hours at 1000°C in air.

5.2 Equipment Setup

The equipment setup of the experiments is shown in Figure 5.1. We used a Laser Ionics argon ion laser as the photonic excitation source. The laser beam was focused on a 0.1
area on the surface of the sample tablet. The photoluminescence is so strong that it can be observed by naked eye. Then the luminescence was collected and focused by another lens. Before the light beam goes into the monochromator, a filter was used to block the overwhelmingly strong laser lines. Then the computer controlled monochromator will select to pass a very narrow band of wavelength (< 0.1 Å). Then the light of the selected wavelength was amplified and transferred into electronic pulses by a photon multiplier. The photon counter gives the number of pulses that are amplified again by a pre-amp. The last step of a measurement cycle is to send the total number of photon counts, which is proportional to the luminescence at this wavelength, to the computer. The computer stores the number of photon counts and instructs the monochromator to select another wavelength and start another measuring cycle.

5.3 Measurements

We have observed a strong emission line group at 550nm under various optical excitation wavelengths at up to the room temperature. Other than the high resolution measurement of the 550nm line group (Figure 4.6), some general study on the visible PL spectrum of the sample was also done. They are shown in Figure 5.2, Figure 5.3, Figure 5.4, Figure 5.5, Figure 5.6.

Another measurement we have done was the photoluminescence kinetics measurements. The equipment setup is similar to the normal photoluminescence measurements but an acousto-optics modulator is used to generate excitation pulse and a Multi-Channel Scaner (MCS) is used to record the photoluminescence response to the excitation pulse in the time domain. The setup is illustrated in Figure 5.7 and the result is shown in
Figure 5.1: The equipment setup of the photoluminescence measurements.
Figure 5.2: The photoluminescence of ZnO: Er, Li excited by the 457.9nm line of an argon ion laser with changing temperature. The peaks at about 540nm can be assigned to transition $^4H_{11/2} \rightarrow ^4I_{15/2}$, the strong peaks at 555nm can be assigned to transition $^4S_{3/2} \rightarrow ^4I_{15/2}$, the wide band at 770nm was assigned to transition $^4I_{9/2} \rightarrow ^4I_{15/2}$, and the peaks at 862nm was assigned to be $^4S_{3/2} \rightarrow ^4I_{13/2}$. 
Figure 5.3: The photoluminescence of ZnO: Er, Li excited by the 476.5nm line of an argon ion laser with changing temperature. The peaks at 556nm can be assigned to transition $^4S_{3/2} \rightarrow ^4I_{15/2}$, the wide band at 750nm was assigned to transition $^4I_{9/2} \rightarrow ^4I_{15/2}$, and the peaks at 862nm was assigned to be $^4S_{3/2} \rightarrow ^4I_{13/2}$. 
Figure 5.4: The photoluminescence of ZnO : Er, Li excited by the 488.0nm line of an argon ion laser with changing temperature. The peaks at about 540nm can be assigned to transition $^4H_{11/2} \rightarrow ^4I_{15/2}$, the strong peaks at 555nm can be assigned to transition $^4S_{3/2} \rightarrow ^4I_{15/2}$, the wide band at 750nm was assigned to transition $^4I_{9/2} \rightarrow ^4I_{15/2}$, and the peaks at 862nm was assigned to be $^4S_{3/2} \rightarrow ^4I_{13/2}$. 
Figure 5.5: The photoluminescence of ZnO:Er, Li excited by the 496.5nm line of an argon ion laser with changing temperature. The peaks at about 540nm can be assigned to transition $^4H_{11/2} \rightarrow ^4I_{15/2}$, the strong peaks at 555nm can be assigned to transition $^4S_{3/2} \rightarrow ^4I_{15/2}$, the peaks at wavelength 667nm was assigned to $^4F_{9/2} \rightarrow ^4I_{15/2}$, the wide band at 740nm was assigned to transition $^4I_{9/2} \rightarrow ^4I_{15/2}$, and the peaks at 860nm was assigned to be $^4S_{3/2} \rightarrow ^4I_{13/2}$. 
Figure 5.6: The photoluminescence of ZnO : Er, Li excited by the 514.5nm line of an argon ion laser with changing temperature. The peaks at about 540nm can be assigned to transition $^4H_{11/2} \rightarrow ^4I_{15/2}$, the strong peaks at 555nm can be assigned to transition $^4S_{3/2} \rightarrow ^4I_{15/2}$, the peaks at wavelength 667nm was assigned to $^4F_{9/2} \rightarrow ^4I_{15/2}$, the wide band at 750nm was assigned to transition $^4I_{9/2} \rightarrow ^4I_{15/2}$, and the peaks at 862nm was assigned to be $^4S_{3/2} \rightarrow ^4I_{13/2}$. 
Table 5.1: Double Exponential Curve Fitting for the Rise and Decay time of the PL kinetic response of the 550nm($^4S_{3/2} \rightarrow ^4 I_{15/2}$) line group of ZnO : Er, Li at 10K.

Figure 5.8.

From the observed kinetics (PL response to a square pulse), we fitted the response curve with a double exponential model. The fast and slow rise and decay time are listed in Table 5.1.

The double exponential model assumes that the rising edge is in the form of

$$f(t) = A(1 - e^{-t/\tau_1}) + B(1 - e^{-t/\tau_2})$$

(5.1)

where $\tau_1$ and $\tau_2$ are time constants that will be derived from curve fitting. The smaller one of $\tau_1$ and $\tau_2$ is called the time constant of the fast process, while the larger one is defined as the time constant of the slow process.

In same manner, the falling curve can be fitted to function

$$f(t) = Ce^{-t/\tau_3} + De^{-t/\tau_4}$$

(5.2)
Figure 5.7: The equipment setup of the photoluminescence kinetics response measurements.
Figure 5.8: The photoluminescence kinetics of ZnO : Er, Li excited by the 488.0nm and the 514.5nm lines of an argon ion laser at 10K.
Chapter 6

Discussions and Conclusions

- The crystal field fitting was successfully performed and the result is smaller than the Hatree-Fock parameters, which is reasonable because the Hatree-Fock approximation does not consider the screening effect of the outer shells of the $Er^{3+}$ ion. So the Phenomenological Hamiltonian was derived and the eigenvalues fit very well with the observed energy levels (refer to Figure 4.7).

- On the other hand, why we picked the four lines in Figure 4.6 is somewhat a problem of instinct. We observed many different emission lines around 550nm in various measurements, but these four lines always stay together and keep a fixed relative relation as a group. So we ASSUMED these four lines are due to the $C_{3v}$ splitting of the ground state and excluded other lines as the result of low symmetry splittings. The result was pretty good but still the assumption was not proved. For future studies, we can make improvement in two points. The first one is to make $Er^{3+}$ implanted into single crystal $ZnO$ instead of the microcrystal sample we have used. In this case we would expect the peaks due to lower symmetry $Er^{3+}$ ions, defects, and surface effects would be greatly diminished so that we will have much clearer spectrums and better resolved peaks. The second expected improvement is to measure the emission of $Er^{3+}$ between the first excited state and the ground state,
namely the 1.54nm emission. This emission is supposed to have a much more clear spectrum. However, the equipment of our laboratory is not sufficient to conduct measurement in the infrared region. Hopefully, our new YAG laser arriving in fall will make the measurement possible.

- Although the in-depth analysis of the PL and kinetics measurements from a experimentalist’s point of view is out of the range of this thesis, the job should be done as soon as possible.

- As one of the first investigations on RE-doped ZnO, the research of this project has suffered from the lack of reference on the topic, especially the up-to-date references (the field was most active in the 60's). Hopefully, the thesis will help the optoelectronics group to open the topic and collect references.
Bibliography


Appendix A

The source code of the fitting algorithm in MATLAB

```matlab
%Name: fit.m
%Func: 1. plot the eigenvalues of the Hamiltonian H(CF) with x as changing variable.
% 2. fit the value of x and W to the experimental value
% 3. fit the level separation of atomic levels.
%By: Kanyu Cao (May, 1997)

M4=[189 8*sqrt(210) 0 10*sqrt(462) 0
   8*sqrt(210) 23 -8*sqrt(1430) 0 0
   0 -8*sqrt(1430) -221 0 0
   10*sqrt(462) 0 0 -101 20*sqrt(182)
   0 0 0 20*sqrt(182) -91]

M6=[-75 -2.5*sqrt(210) sqrt(3003)
   -2.5*sqrt(210) 45 0
   sqrt(3003) 0 -39
   2.5*sqrt(462) 10.5*sqrt(55) 0
   1.75*sqrt(429) 0 0
   87 -3.75*sqrt(182)
   -3.75*sqrt(182) -117]

i=1;
for x=-1:.001:1
    H=x.*M4+(1-abs(x)).*M6;
    D=eig(H);
    for j=1:5
        Eigen(i,j)=D(j);
    end
    i=i+1;
end

x=-1:0.001:1;
plot(x,Eigen,'.');
xlabel('x');
ylabel('(Eigenvalue of H_CF)/W');
title('Eigenvalues of Hamiltonian with x as a variable from -1 to 1');
print -deps eigen.eps
```
The theoretical estimation of \( x \) is around 0.56, so we will fit the spectrum in the region 0.4-0.8 (Eigen() index 1400 to 1801. Also from graph we noticed that the two lowest levels are very close to each other so we regard it as an unresolved peak and assume the peak is at the average.

\[
\begin{align*}
\text{minpos} &= 0; \\
\text{minw} &= 0; \\
\text{min} &= 100000; \\
\text{for } i &= 1400:1801 \\
& \quad a = \text{sort} (\text{Eigen}(i,1:5)); \\
& \quad \text{dis1} = a(5) - a(4); \\
& \quad \text{dis2} = a(4) - a(3); \\
& \quad \text{dis3} = a(3) - (a(2) + a(1))/2; \\
& \quad \text{dis1} = \text{dis1}/\text{dis2}; \\
& \quad \text{dis3} = \text{dis3}/\text{dis2}; \\
& \quad \text{err} = (\text{dis1} - 0.7532)(\text{dis1} - 0.7532) + (\text{dis3} - 1.0241)(\text{dis3} - 1.0241); \\
& \quad \text{if err} < \text{min} \\
& \quad \quad \text{min} = \text{err}; \\
& \quad \quad \text{minpos} = i; \\
& \quad \quad \text{minw} = 29.42/\text{dis2}; \\
& \quad \end{align*}
\]

end

display('The best fit happens at x=');
\( \text{fitx} = (\text{minpos} - 1000)/1000; \)
display(\text{fitx});
display('w=');
display(\text{minw});
display('Mean square root=');
display(\text{sqrt}(\text{min}/2));
\( \text{min} = 10000000000000000000000000; \)
\( \text{calcO} = \text{minw}.*\text{sort} (\text{Eigen}(\text{minpos},1:5)); \)
\( \text{calcO}(1) = (\text{calcO}(1) + \text{calcO}(2))/2; \)
for \( i = 2:4 \)
\( \quad \text{calcO}(i) = \text{calcO}(i+1); \)
end

Experimental values derived from the peak positions.
\text{expr} = [17994.67 17964.54 17935.12 17912.96];

fit the vacuum level separation.
\text{for } i &= 17500:0.01:18020 \\
& \quad \text{calc} = i - \text{calcO}(1:4);
errmat=(calc-expr).*(calc-expr);
errsum=sum(errmat);
if(errsum<min)
    min=errsum;
    fitgap=i;
end

display('The fitted vacumm level sparation is:');
fitgap

display('The fitted emissions:');
display(fitgap-minw.*sort(Eigen(minpos,1:5)));
display('Mean square root');
display(sqrt(min./4));