QUANTUM MECHANICAL COMPUTATION OF ELECTRONIC ENERGY STATES OF TITANIUM ION IN CdS CRYSTAL

BY

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DECLARATION

This thesis is my original work and has not been presented for a degree in any University.

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ABSTRACT

Crystal field parameters and electronic energy states of Ti^{2+} ion in CdS crystal have been computed by taking into account axial (C_{3v}) distortion of tetrahedral symmetry. Crystal fields operators for CdS system, having C_{3v} symmetry have been obtained in point-ion model. Radial wave function of 3d-level has been expressed in terms of double zeta function.

$$R_{3d}(r) = a_1N_1r^2e^{-\xi_{11}r} + a_2N_2r^2e^{-\xi_{12}r}$$

where N_1 and N_2 are expressed in terms of ξ_{11} and ξ_{12} and a_1, a_2, ξ_{11}, ξ_{12} coefficients are determined using parameterization condition. In weak crystal field the total orbital angular momentum (L) and spin angular momentum (S) are good quantum numbers. Thus wavefunctions of the states are represented as $\Psi(LS\ M_LM_S)$, which can be written as product of single electron wavefunctions. Hence the angular part of wave functions for $3d^2$ - configuration has been obtained in the form of Slater determinants in weak field approximation since crystal field splitting is much smaller than the separation of different groups of multiplets. The calculated values of Dq = 338 cm^{-1}, and B = 350 cm^{-1} are close to the experimental values which are 332 cm^{-1} and 360 cm^{-1} respectively. Since C_{3v} distortion is very weak, the calculated energy spectrum does not concide with the experimental one. So crystal field operator for T_d symmetry was obtained in point ion model. By diagonalizing the matrix

of crystal field operator for T_d, the energy spectrum of Ti^{2+} ion in CdS has been computed, which agrees well with experimental values.

INTRODUCTION

The transition metals are those which have partially filled shells of d-electrons. Titanium is one of them and its configuration is $1S^2 2S^2 2P^6 3S^2 3P^6 4S^2 3d^2$. It has two electrons in the outermost d shell. When Ti^{2+} is added as an impurity in CdS crystal, it occupies a substitutional position by replacing Cd^{2+} from its cite. The tetrahedral symmetry of CdS is slightly distorted along the C_3 axis. Ti^{2+} is surrounded by four sulphur ions situated approximately at the four corners of tetrahedral.

Since Ti^{2+} ion has degenerate states in crystals, the interaction of electrons of the central ion with the surrounding ligands leads to Jahn-Teller effect [1], which has been studied by Boyn[2] and Dod[3]. At the same time introduction of Ti^{2+} ion impurity in CdS changes its physical properties and hence application in different fields, quantum optics and crystal spectroscopy. Because of wide application of the crystal, it has been widely used and to make its optimum use a scientist must study it thoroughly both experimentally and theoretically.

The aim of the thesis was to calculate the energy states of Ti^{2+} ion in the CdS crystal by using double zeta function, introducted by Zhao et al [4] for the radial function of 3d outermost electron of Ti^{2+} ion. These are the electrons which take part in optical transition, while the inner electrons which are strongly bound to the nucleus are inert. The results have been compared with the experimental value determined by spectroscopic data. Our results are in good agreement with experimental values.

In chapter one the theory of split of energy terms, which depends upon the angular momentum of atom has been given. The energy of the terms due to the interaction between the electrons of the centre ion are then expressed in terms of racah parameters.

Chapter two deals with the general theory of transition metal ion in a crystal. A review of the literature on the crystal field and ligands theory has been given in this chapter. Secondly the Zhao double zeta wave functions have been eleborated. The parameters a_1, a_2, ξ_{11} and ξ_{12} of double zeta functions have been obtained by using the four parametrization conditions.

In chapter three the crystal field operator for the axially distorted tetrahedral has been derived in point-ion model by using group theory.

The wave functions of ^3F and ^3P terms of Ti^{2+} in crystal have been determined using lowering operator and orthogonality principles respectively.

In Chapter four the energy levels of Ti^{2+} ion in CdS crystal have been computed for both axially distorted and pure tetrahedral symmetries. The crystal field matrix is then diagonalized to obtain the eigen values in each case. The results are then compared with experimental values.

The discussion and conclusion have been given in chapter five.

CHAPTER ONE

THEORY OF FREE TRANSITION METAL ION

1.1 Energy States of Hydrogen-like Atom

The problem of the relative motion of an electron (mass: m and charge: −e) and a Nucleus (mass: M and charge: Ze) reduces, as is well known, to the problem of the motion of particle with an effective mass $\mu = \frac{Mm}{M + m}$ in the Cuolomb potential of $-\frac{Ze^2}{r}$

The Schrodinger equation for such a particle has the form

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r}\right)\psi = E\psi \qquad \ldots(1.1)$$

The wave function ψ, which is the solution of this equation, describes the stationary state with definite value of E.

In the case of a centrally symmetric field the angular momentum is conserved. Because of that, we shall consider stationary states which are characterized by definite values of E, the square of angular momentum and the Z-component of the angular momentum (L). The wave function ψ of these stationary states are eigen functions of the operator L^2 and L_z and must therefore satisfy the equation

$$L^2\psi = l(l + 1)\hbar\psi \qquad \ldots(1.2)$$

$$L_z\psi = m\hbar\psi \qquad \ldots(1.3)$$

where $l(l + 1)\hbar$ and $m\hbar$ are eigen values of the operator L^2 and L_z. The discrete values of l, the orbital quantum number, are 0, 1, 2 .... and that of m, the magnetic quantum number, are 0, ±1, ±2 ....with an additional condition $|m| \leq l$.

The solution of Equation (1.1) is sought in the form

$$\psi = R(r)\; Y_{lm}\,(\theta\Phi) \qquad \ldots(1.4)$$

where $Y_{lm}(\theta\Phi)$ are the spherical function, and the radial part satisfies the equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{l(l + 1)R}{r^2} + \frac{2\mu}{\hbar^2}\left(E + \frac{Ze^2}{r}\right)R = 0 \qquad \ldots(1.5)$$

If $E > 0$, this equation has finite, continuous solutions, for any value of E and l. If $E < 0$, such solution are possible only at certain discrete values of energy

$$E = -\left(1/2\right)\frac{Z^2}{n^2}\frac{\mu e^4}{\hbar^2} \qquad \ldots(1.6)$$

where n, the so called principal quantum number, is an integer, and also $n \geq l + 1$. For a given n, quantum number l can take values 0, 1, 2, ..., n-1. To each value of l, there corresponds (2l +1) states, differing by the values of magnetic quantum number m.

1.2 Central Field Approximation

For atom containing more than one electron, even for the simplest ones, Schrodinger equation cannot be solved directly, either analytically or by numerical methods. A suitable schematic treatment is one in which the concept of the individual state of an electron in an atom is accepted and state of atom as a whole is determined by the set of the states of the electrons, taking into account their interaction. In the limit of this approximation, one succeeds in obtaining general information on the system of energy levels possible for a given atom and on the relative position and grouping of the levels.

To describe electron states in an atom, one proceeds from the assumption that each electron moves in a certain effective centrally symmetric field created by the nucleus and all other electrons. This approximation called the self-consistent field approximation, is taken as the starting point for calculation of the energy levels. This was the theory originally established by Racah,[5] Condon and Shortley[6] and Slater[7].

In this approximation, total Hamiltonian is written as

$$H = \frac{1}{2m} \sum_{i} P_i^2 + \sum_{i} \frac{Ze^2}{r_i} + \sum_{i \neq j} \frac{e^2}{r_{ij}} \qquad \ldots(1.7)$$

where $\sum_{i\neq j} \frac{e^2}{r_{ij}}$ is a two electron operator describing the mutual interaction between i^{th} and j^{th} electrons, separated by a distance r_{ij}. This equation (1.7) is expressed as

$$H = \sum_{i} H_i^o \qquad \ldots(1.8)$$

where H_i^o is a single electron Hamiltonian given by

$$H_i^o = \frac{1}{2m} P_o^2 + U(r) \qquad \ldots(1.9)$$

where U(r) is effective centrally symmetric potential, such that Schrodinger equation becomes

$$-\frac{h^2}{2m}\nabla^2\Psi - \quad U(r)\Psi = E\Psi \qquad \ldots(1.10)$$

The angular momentum is conserved for motion in a arbitrary centrally symmetric filled, therefore each stationary state can be characterized by the assignment of square of angular momentum and its z^{th} component i.e. by the assignment of quantum numbers l and m.

The wavefunctions for the stationary states have the same form as equation (1.4). The radial part of the function R(r) is defined by the equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{l(l+1)}{r^2}R + \frac{2m}{\hbar}(E-U(r))\,R=0 \qquad \ldots(1.11)$$

The equation has bound solution for definite values of E. The set of these values determines the energy spectrum of the particle.

1.3 Total Angular Momentum

The microstates are classified by the angular momentum of states. In a many - electron system the angular momentum of each single electron interact with others via the associated magnetic properties. Just as a bar magnet is forced into a certain direction by an outer magnetic field, each electron is compelled to allign itself in the field of other electrons. The orbital and spin angular momenta of the individual electron are said to be coupled together. There are two ways to calculate the momentum of the system. In the first case the interaction among all individual orbital angular momenta and among all individual spin angular momentum are strong compared with the interaction between spin and orbital angular momentum of each electron. The orbital angular momentum 1 of all electrons then couple to give a total orbital angular momentum $\vec{L}$, the spin angular momentum s also couple to give a total spin angular momentum $\vec{S}$ [8,9]. Quantum mechanics requires $\vec{L}$ and $\vec{S}$ to be quantized. This kind of coupling scheme is chiefly applicable to the ligher elements for Z $\leq$ 30. This scheme is called L-S coupling or Russell - Saunders coupling.

The other limiting way to look at atoms is to assume that $\vec{l}$ and $\vec{s}$ of each electron couple together to give angular momentum $\vec{j}$, and all that j's couple to give the total angular momentum $\vec{J}$. This j-j coupling appears to be a reasonable approximation for excited states of the heavier atoms.

For most elements the actual coupling of angular momentum is somewhere between the two extremes.

Knowing the vectorial character of angular momentum, the coupling may be considered by vector addition. The total orbital angular momentum $\vec{L}$, is then

$$\vec{L} = \sum_i \vec{l}_i \qquad \ldots(1.12)$$

where $\vec{l}_i$ is orbital angular momentum of single electron.

There is a considerable formal analogy between l and the resultant $\vec{L}$. The later is related to a total angular momentum quantum number L by

$$|\vec{L}| = \sqrt{L(L+1)}\ h \qquad \ldots(1.13)$$

L can be zero or a positive integer ($\leq \sum_i l_i$). Only certain orientations in space are allowed for L, which are such that the projection of the vector on a reference axis (e.g. the z-axis) must be $M_L\hbar$, where

$$M_L = L, L-1, L-2, \ldots\ldots -L \qquad \ldots(1.14)$$

Due to the rule of vector addition and the restrictions on m_{l_i} , it turns out that M_L can always be calculated as the algebraic sum of the m_{l_i} of the individual electrons

$$M_L = \sum_i m_{l_i} \qquad \ldots(1.15)$$

This is explained in figure (1.1) below for two d-electrons (l = 2) where m_l can have the values 2, 1, 0, -1, -2.

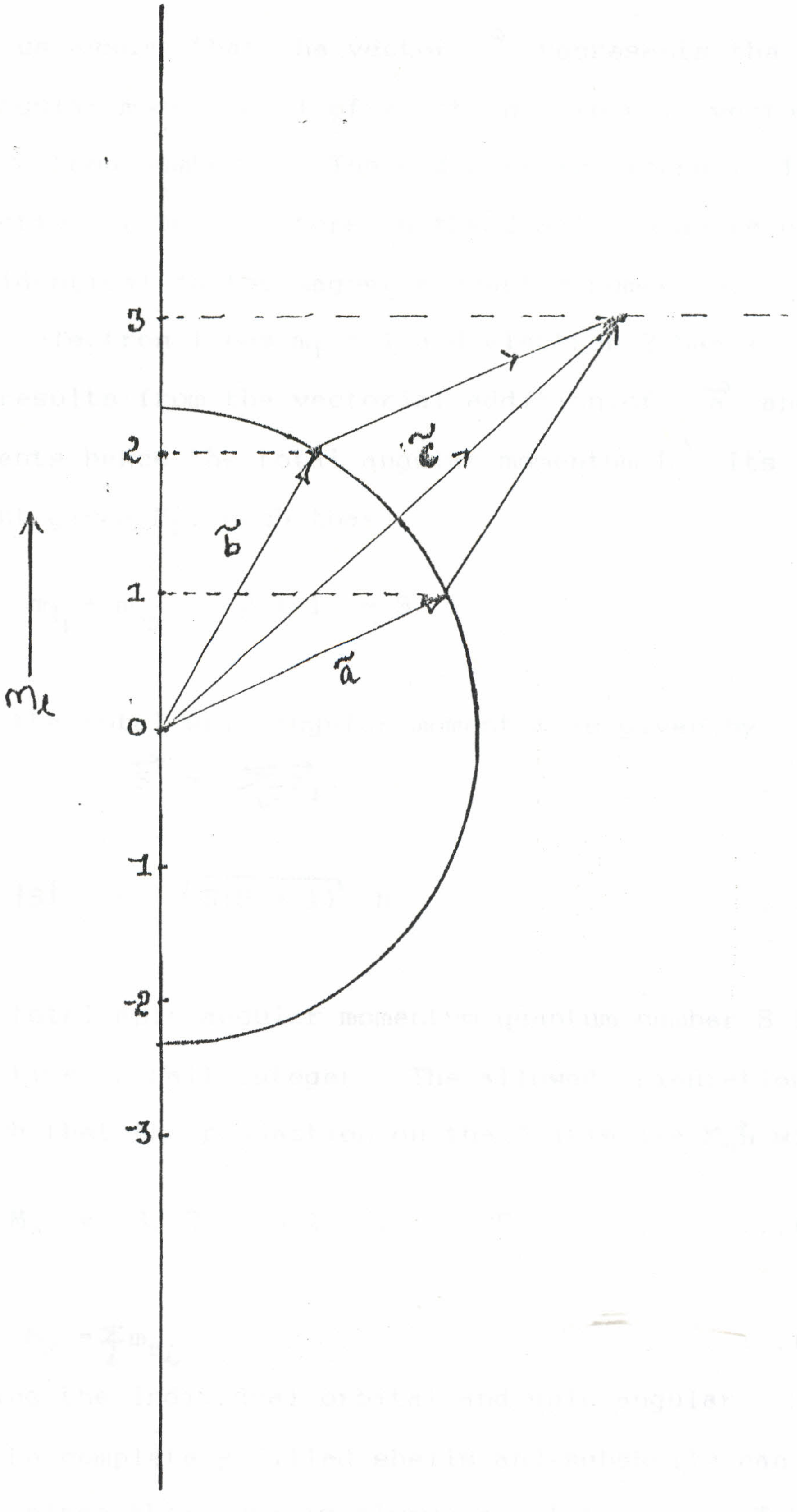

Fig. 1.1 Vectorial addition of orbital angular momenta l of two d-electrons.

Let us assume that the vector $\vec{a}$ represents the orbital angular momentum l of electron number 1, vector $\vec{b}$ that of electron number 2. The ordinate in Figure (1.1) marks the projection of the vectors on the Z-axis in units of $\hbar$, which is identical to the magnetic quantum number m_l. In this case, electron 1 has $m_l = 1$ and electron 2 has $m_l = 2$. Vector $\vec{C}$ results from the vectorial addition of $\vec{a}$ and $\vec{b}$, it represents hence the total angular momentum L. Its z-component gives M_L, such that

$$M_L = m_{l_1} + m_{l_2} = 2 + 1 = 3 \qquad \text{...(1.16)}$$

Similarly the total spin angular momentum is given by

$$\vec{S} = \sum_i \vec{s}_i \qquad \text{...(1.17)}$$

with

$$|S| = \sqrt{S(S + 1)}\ h \qquad \text{...(1.18)}$$

The total spin angular momentum quantum number S is zero, positive or half integer. The allowed orientations of S are such that the projection on the Z-axis are $M_S\hbar$ with

$$M_S = S,\ S-1,\ S-2\ \ldots\ldots,\ -S \qquad \text{...(1.19)}$$

and

$$M_S = \sum_i m_{s_i} \qquad \text{...(1.20)}$$

When summing the individual orbital and spin angular momenta, the completely filled shells and subshells can be neglected, since their sum is always equal to zero. Take as an example the completely filled $3p^6$ subshells of a transition metal ion. There is only one possibility to arrange the six electrons in the three 3p orbitals, two electrons with paired spin in each. The spins evidently compensate to total spin zero. There are two electrons with orbital angular momentum $m_l = 1$, two with $m_l = -1$ and two with $m_l = 0$ and therefore

$$M_L = 2 \times 1 + 2 \times (-1) + 2 \times 0 = 0$$

From equation (1.14) it follows, that the number of allowed projection of L on the z axis is 2L + 1. Since for the $3p^6$ subshell only one projection (M_L=0) is possible, therefore 2L + 1 = 1, and hence L = 0. i.e. the orbital angular momentum of the filled subshell is also zero. Thus the electrons outside the completely filled shells take part in determining the total angular momentum of the state which is done as stated above.

1.4 The Free Ion Terms

The energy levels of many - electron system arise from an electronic configuration with a partially filled outer shell, because of the effects of inter-electronic repulsion. The degenerate energy levels and their wave functions are specified by a set of quantum numbers of single electron states.

A term (energy level) is characterized) by

(i) its total orbital angular momentum number, L, which is zero or positive integer equivalent to sum of l's for all electrons, and

(ii) its total spin angular momentum, S, which is zero, a positive or half-integer equivalent to the sum of quantum number s's for all electrons.

A term is labelled by means of its values of L and S in the following way.

$$^{(2S + 1)}X \qquad \ldots(1.21)$$

where X symbolises the orbital quantum number according to its value

L =	0	1	2	3	4	5	6
X =	S	P	D	F	G	H	I

The quantity (2S + 1) is known as the spin multiplicity of the term i.e. possible values of M_S and is equal to the number of unpaired electrons present plus one. Terms are called

	S	2S + 1
Singlet	0	1
doublet	1/2	2
triplet	1	3
quartet	3/2	4
quintet	2	5
sextet	5/2	6

As discussed in the previous section the total number of M_L, the value of L_Z, is 2L+1, similarly number of M_S, the value of S_Z is 2S+1, for each energy level, thus degeneracy of the term is

$$(2L+1)\ (2S+1) \qquad \ldots(1.22)$$

In d^2 system, there are two electrons in the d-shell. There are always several possibilities to distribute the two available electrons among the five d-orbitals. Each arrangement is called a microstate. The rule of combination tells us that there are a total of 45 microstates.

1.5 Russell-Saunders Term symbols

In this coupling scheme electronic configuration is characterized with the help of two quantum numbers L and S, specifying respectively the total orbital momentum and the total spin momentum.

For a single electron L is of course, equal to l, the orbital momentum of a single electron, but for more than one electron L is given by the addition of all the l_i's. The same holds true for S. Because of the restriction imposed by the Pauli's exclusion principle however not all combination of L and S can be obtained in many electron system.

In the $3d^2$ system both electrons have same principal quantum number n=3 and both have same orbital quantum number l=2. It is thus necessary that the two electrons should differ in either m_l and m_s. We shall write down, the various possibilities, and writing m_s=1/2 as positive superscript and m_s=-1/2 as a negative superscript. We should further arrange them in a scheme of classification according to the value of $M_L = \Sigma m_l$ and $M_S = \Sigma m_s$.

The notation $(2^+ 1^-)$ means that electron one has m_s = 1/2 and m_l = 2 and that the electron two has m_s =-1/2 and m_l = 1. The scheme then should be as shown in Table 1.1.

According to Table 1.1 no state with $M_S = \pm 1$ exists for the highest M_L value of M_L=4. However, a state with M_S=0 does exist. This state must, therefore, belong to $L \geq 4$ and $S \geq 0$. 4 being the highest value of M_L and having no state for M_S >0, the state with M_L=4 and M_S=0 can only belong to L=4, S=0. For L=4, S=0 there are in total nine states with M_L=4, 3, 2, 1, 0, -1, -2, -3, -4, M_S=0.

Table 1.1 MICROSTATES OF d^2-CONFIGURATION

M_S M_L	1	0	-1
4		(2^+2^-)	
3	(2^+1^+)	(2^+1^-) (2^-1^+)	(2^-1^-)
2	(2^+0^+)	(2^+0^-) (2^-0^+) (1^+1^-)	(2^-0^-)
1	$(2^+-1^+)(1^+0^+)$	$(2^+-1^-)(2^--1^+)$ (1^+0^-) (1^-0^+)	(2^--1^-) (1^-0^-)
0	(2^+-2^+) (1^+-1^+)	(2^+-2^-) (2^--2^+) (1^+-1^-) (0^-0^+) (-1^+1^-)	(2^--2^-) (1^--1^-)
-1	$(-2^+1^+)(-1^+0^+)$	(-2^+1^-) (-2^-1^+) $(-1^+0^-)(-1^-0^+)$	$(-2^-1^-)(-1^-0^-)$
-2	(-2^+0^+)	(-2^+0^-) (-2^-0^+) (-1^+-1^-)	(-2^-0^-)
-3	(-2^+-1^+)	(-2^+-1^-) (-2^--1^+)	(-2^--1^-)
-4		(-2^+-2^-)	

The highest M_L and M_S values of the remaining states are $M_L=3$ and $M_S=1$. They belong apparently to L=3, S=1. For L=3, S=1 there are 21 states $M_L=3, 2, 1, 0, -1, -2, -3$, $M_S=1, 0, -1$. The state with $M_L=2$, $M_S=0$ has the highest M_L and M_S values of the remaining states. L=2, S=0 belong to it. The five states with $M_L=2, 1, 0, -1, -2$, $M_S=0$ are likewise states of L=2, S=0.

If the procedure described here is applied further, one also finds the states with L=1, S=1 and L=0, S=0. The totality of microstates belonging to a given L and S values (and to a given configuration) is called a term.

Therefore, using this procedure it could be found that the possible terms in a d^2 system resulting from inter-electronic repulsion are:

L	S	Term	Number of states
4	0	^1G	9
3	1	^3F	21
2	0	^1D	5
1	1	^3P	9
0	0	^1S	1
		Total	45

This total number of states in d^2-configuration is called its statistical weight.

1.6 The Ground State of the d^n Configuration

Energy terms for a configuration has been discussed in previous section. Their position in the energy spectrum is important, especially the ground state. Hund's rules are applied to determine the ground state term easily, as the one, which ensures minimum repulsion between the electrons, having them separated from each other as far as possible.

Hund's rules states that

(i) Out of all the terms of a configuration those with maximum spin multiplicity tend to lie lowest.

(ii) Out of all the terms with maximum multiplicity, that with largest orbital angular momentum lies lowest.

Based on these rules, the following procedure allows one to write down rapidly the ground state of a d^n configuration. Horizontally is listed the m_l values of the orbitals of the relevant incomplete shell in the Table 1.2.

These orbitals are filled with available electrons starting from the left. Single electron is added to each orbital first, if pairing is necessary, start from the right. This step takes care of Hunds rule. The m_l values of unpaired electrons are then added algebraically, that gives total values of L. The number of unpaired electron plus one gives the multiplicity.

TABLE 1.2: THE GROUND TERM OF d^n CONFIGURATION

Configuration , m_l	2	1	0	−1	−2	L	Ground term
d^1	↑					2	^2D
d^2	↑	↑				3	^3F
d^3	↑	↑	↑			3	^4F
d^4	↑	↑	↑	↑		2	^5D
d^5	↑	↑	↑	↑	↑	0	^6S

Hence for a $3d^2$ system the ground term is ^3F. Similarly using the Hund's rules the other energy terms for d^2 configuration in increasing order of energy are obtained, which are ^3P, ^1G, ^1D and ^1S.

1.7 Term Energies in Terms of Interaction Parameters

In order to solve the Schrodinger equation for Hamiltonian H (eq. 1.8) the matrix elements of the following form are to be evaluated.

$$\langle \psi_\alpha|\hat{H}|\psi_\beta\rangle = \langle \psi_\alpha|\hat{H}_0|\psi_\beta\rangle \qquad \ldots(1.23)$$

$$+ \langle \psi_\alpha|\sum_{i\neq j}\frac{e^2}{r_{ij}}|\psi_\beta\rangle$$

where ψ_α and ψ_β are the wavefunctions for first and second electrons respectively.

The first term of the equation (1.23) has the following important properties:

(i) Only diagonal matrix elements ($\alpha = \beta$) are non-zero in a free ion configuration basis.

(ii) all the matrix element of type

$$\langle \Psi_\alpha | \hat{H}_0 | \Psi_\beta \rangle \qquad \ldots(1.24)$$

belonging to the same configuration i.e. for same n and l are equal.

This means that the first term of equation (1.23) in the Hamiltonian will cause a uniform energy shift to all the terms arising from a given configuration i.e the single electron-Hamiltonian is not responsible for any term splitting.

Thus the term splitting originates from the interelectronic repulsion operator, the second term of equation (1.23) i.e.

$$\sum_{i \neq j} \langle \Psi_\alpha | \frac{e^2}{r_{ij}} | \Psi_\beta \rangle \qquad \ldots(1.25)$$

The wavefunction $\Psi's$ are the many-electron component involving products like $\phi_1 \phi_2 \text{-------} \phi_n$, where the $\phi's$ are spin-orbitals for single electron.

The fundamental indistinguishability of electrons demands that term functions be used, which involves all permutations of the n-electrons amongst the n-electron spin-orbitals, as well as it is an antisymmetric wave function. (Pauli's exclusion principle is obeyed).

The usual way of doing this is to write as a Slater-determinant

$$\Psi_\alpha = \frac{1}{\sqrt{N!}} \left| \phi_1^\alpha(1)\,\phi_2^\alpha(2) \cdots\cdots \phi_n^\alpha(n) \right| \qquad \ldots(1.26)$$

The matrix elements (1.25) is therefore written as

$$\sum_{i\neq j} \left\langle \phi_1^\alpha(1)\,\phi_2^\alpha(2) \ldots \phi_n^\alpha(n) \left| \frac{e^2}{r_{ij}} \right| \phi_1^\beta(1)\,\phi_2^\beta(2) \ldots \phi_n^\beta(n) \right\rangle \qquad \ldots(1..27)$$

Now $\sum_{i\neq j} \frac{e^2}{r_{ij}}$ operates on two electrons at a time so that

equation (1.27) breaks down into the following products

$$\langle \phi_1^\alpha(1) | \phi_1^\beta(1) \rangle \langle \phi_2^\alpha(2) | \phi_2^\beta(2) \rangle \ldots\ldots$$
$$\ldots \times \left\langle \phi_a^\alpha(1)\,\phi_b^\alpha(2) \left| \frac{e^2}{r_{12}} \right| \phi_c^\beta(1)\,\phi_d^\beta(2) \right\rangle \qquad \ldots(1.28)$$
$$\ldots \times \langle \phi_n^\alpha(1) | \phi_n^\beta(2) \rangle$$

The matrix elements involves the products in which electrons 1 and 2 are placed in the different orbitals ϕ_i and ϕ_j and so a sum over all electrons is not required because of the orthogonality of single-electron function and the matrix elements are non zero only if Ψ_α and Ψ_β differ by no more than two functions and so we need not sum over all orbital pairs in equation (1.28) either.

If the central integral in equation (1.28) is non-zero, then on interchanging ϕ_a^α and ϕ_b^β, it remians non-zero. Such an example of orbitals corresponds to an odd permutation of the Slater determinant (eq. 1.26) and so a minus sign appears in the general expression for the case where these ϕ's have been interchanged.

Therefore

$$\left\langle \Psi_\alpha \right| \frac{e^2}{r_{ij}} \left| \Psi_\beta \right\rangle = \pm \Big[\left\langle \phi_a^\alpha(1)\, \phi_b^\alpha(2) \right| \frac{e^2}{r_{12}} \left| \phi_c^\beta(1)\, \phi_d^\beta(2) \right\rangle - \left\langle \phi_b^\alpha(1)\, \phi_a^\alpha(2) \right| \frac{e^2}{r_{12}} \left| \phi_c^\beta(1)\, \phi_d^\beta(2) \right\rangle \Big] \quad \ldots(1.29)$$

The $\pm$ signs outside the whole expression reflects the fact that an even or odd permutation may have been necessary to bring the Slater determinants Ψ_α and Ψ_β into the same standard order in which electrons (1) and (2) occupy the non-identical orbitals of the two determinants.

We get a slightly different expression if Ψ_α and Ψ_β differ by only one orbital.

The integrals in eq. (1.29) involve pairs of orbitals. If we regard ϕ_a^α as the 'odd one out' in Ψ_α and ϕ_a^β in Ψ_β .

$$\langle \Psi_\alpha | \frac{e^2}{r_{ij}} | \Psi_\beta \rangle = \pm \sum_t^{n-1} \Big[\langle \phi_a^\alpha(1)\, \phi_t^\alpha(2) | \frac{e^2}{r_{12}} | \phi_a^\beta(1)\, \phi_t^\alpha(2) \rangle \qquad \text{...(1.30)}$$

$$- \langle \phi_t^\alpha(1)\, \phi_a^\alpha(2) | \frac{e^2}{r_{12}} | \phi_a^\beta(1)\, \phi_t^\alpha(2) \rangle$$

the ϕ_a^α may be paired with (n-1) other ϕ^α's in these integrals. The expression for $\langle \Psi_\alpha | \frac{e^2}{r_{ij}} | \Psi_\beta \rangle$ now involves a sum over all these possibilities.

$$\Psi_\alpha = | \phi_1^\alpha \phi_2^\alpha \ldots\ldots\ldots\ldots \phi_n^\alpha |$$

$$\Psi_\beta = | \phi_1^\beta \phi_2^\beta \ldots\ldots\ldots\ldots \phi_n^\beta | \qquad \text{...(1.31)}$$

Finally we have the diagonal case in which Ψ_α and Ψ_β are the same say,

$$\Psi_\alpha = \Psi_\beta = | \phi_1 \phi_2 \ldots\ldots\ldots\ldots \phi_n | \qquad \text{...(1.32)}$$

The same number of permutation is required to send each Ψ_α and Ψ_β into a common order so that there is only a positive (+) sign outside the whole expression. Thus considering any two ϕ's at a time the sum over all possibilities which are distinct is taken, to do so we keep a<b in sum over pairs of orbitals a and b.

$$\langle \psi_\alpha | \frac{e^2}{r_{ij}} | \psi_\beta \rangle = \sum_{a<b}^{n} \Big[\langle \phi_a(1)\, \phi_b(2) | \frac{e^2}{r_{12}} | \phi_a(1)\, \phi_b(2) \rangle$$

$$- \langle \phi_b(1)\, \phi_a(2) | \frac{e^2}{r_{12}} | \phi_a(1)\, \phi_b(2) \rangle \Big] \qquad \ldots(1.33)$$

The first term in equation (1.33) is called the Coulomb integral, J(ab), and the second the exchange integral, K(ab).[8] thus

$$J(ab) = \langle \phi_a \phi_b | \frac{e^2}{r_{ij}} | \phi_a \phi_b \rangle \qquad \ldots(1.34)$$

and

$$K(ab) = \langle \phi_b \phi_a | \frac{e^2}{r_{ij}} | \phi_a \phi_b \rangle \qquad \ldots(1.35)$$

Thus for diagonal matrix elements the following expression is obtained

$$\langle \psi_\alpha | \frac{e^2}{r_{ij}} | \psi_\alpha \rangle = \sum_{a<b}^{n} [J(ab) - K(ab)] \qquad \ldots(1.36)$$

The matrix element equation (1.36) evaluated above is related to interaction parameters, F^k's and for equivalent electron e.g. d-d transition the relationship is[8].

$$\begin{aligned} J\,(ab) &= \sum_{k=0}^{2l} a^k\, F^k \\ K\,(ab) &= \delta\,(S_a S_b) \sum_{k=0}^{2l} b^k\, F^k \end{aligned} \qquad \ldots(1.37)$$

where a^k and b^k are coefficients and $F^k(abcd) = R^k(abcd)$ are interelectronic repulsion parameter and $\delta(s_a S_b)$ is a kroniker delta notation

where

$$R^k(abcd) = \left\langle R_{n_a l_a} R_{n_b l_b} \left| \frac{e^2 r^k_<}{r^{k+1}_>} \right| R_{n_c l_c} R_{n_d l_d} \right\rangle \quad \ldots(1.38)$$

From equation (1.37), it is clear that sums are taken over even values of k only. This means F^o , F^2, F^4, F^6 etc. are required and by using the vector triangle rule, F^o, F^2 and F^4 are needed for d-d transitions.

The term energies are thus expressed in terms of the interelectronic repulsion parameters (F^k's), called Condon-Shortley parameters[6].

Racah [10,11] chose some other parameters, A, B and C, called Racah parameters, to represent linear combination of the Condon-Shortley parameters in such a way so as to make the separation between terms of maximum multiplicity as a function of one parameter only.

$$\begin{aligned} A_o &= F^o - (1/9)F^4 \\ B_o &= (1/49)F^2 - (5/441)F^4 \\ C_o &= (35/441)F^4 \end{aligned} \quad \ldots(1.39)$$

These parameters are simpler ones and accepted as the most standard ones to express the energy terms.

Taking into account interelectronic repulsion the energies of the terms are obtained in terms of interaction parameters and are given in table 1.3.

TABLE (1.3) TERM ENERGIES OF d^2-CONFIGURATION

Term	Condon-Shortley	Racah
^1S	$F^0 + 14/49\ F^2 + 126/441 F^4$	$A_0 + 14B_0 + 7C_0$
^1G	$F^0 + 4/49\ F^2 + 1/144\ F^4$	$A_0 + 4B_0 + 2C_0$
^3P	$F^0 + 7/49\ F^2 - 84/441\ F^0$	$A_0 + 7B_0$
^1D	$F^0 - 3/49\ F^2 + 36/441\ F^4$	$A_0 - 3B_0 + 2C_0$
^3F	$F^0 - 8/49\ F^2 - 9/441\ F^4$	$A_0 - 8B_0$

CHAPTER TWO

THE THEORY OF TRANSITION METAL ION IN A COMPLEX

2.1 Review of Theory

This theory is based on the crystal field approach, namely, that the metal ion in the complexes, is subjected to an electric field originating from the ligands. Thus the Hamiltonian for the electrons of the metal ion consists of two terms

$$H = H_F + V_C \qquad \ldots(2.1)$$

Here H_F is the Hamiltonian for the free ion (equation 1.7) and V_C is the potential due to surrounding ligands. The potential V_C is regarded as the perturbation which determines the electronic motions and the term values of the metal ion of the complex.

The basic idea of the crystal field theory is due to Beaquarel[12], which was further developed into a theory by Bethe[13] in the same year. Bethe investigated by means of symmetry concepts, how the symmetry and strength of a crystalline field affect the electronic levels of the gaseous metal ions. In doing so, he laid down the foundation for all further study in the field. In 1930, Cramers[14] succeeded in proving a very important result that the electronic levels in molecules containing an odd number of electrons must remain at least two fold degenerate, provided that no magnetic field is present.

The first application of the new theory to chemistry was made by Van Vleck[15]. By realizing that the quenching of the "orbital angular momentum would be a consequence of the crystalline field model, he succeeded in explaining why the paramagnetism of the complexes of first transition series correspond to a "spin-only" value.

The field model was able to predict the cases in which there would be small deviations from the empirical rule. These predictions were completely justified by the calculations done by Schlapp and Penney et al[16] and by Jordahl et al[17]. They showed that both the anisotropy and variation of magnetic susceptibility with temperature could be easily predicted and calculated. Their very important papers directly confirmed the basic idea in the crystal field approach, namely, that the crystal field reduces the degeneracy of the electronic levels of the gaseous metal atom. Later Gorter[18] showed that the crystal field of a regular tetrahedron will produce the same levels as those produced by a regular octahedron but with the level order inverted. In the years before World War II the efforts were mostly concentrated on explaining and calculating the magnetic behaviour of complex ions. Later Van Vleck[19] treated the problem of absorption bands of inorganic complexes. He pointed out that it is necessary to couple the electronic wave functions with the odd vibrations of a molecule in order to get band intensities different from zero, if one assumes that the absorption bands are due to transitions between various split $3d^n$ or $4f^n$ configurations. Jahn and Teller[1] had shown in 1937 that no non-linear molecule could be stable in a degenerate state. If therefore a certain configuration is predicted to give rise to an electronic degeneracy, such a configuration must immediately, distort via nuclear displacements in the molecule in such a way that the degeneracy if removed. In the same period Van Vleck's[20] investigated into the Jahn-Teller theorem as applied to octahedral molecules. He calculated the Jahn-Teller distortions for octahedral molecules of the form XY_6 and showed that the configurational instability affected the magnetic moment of the molecules.

The development of the spectrophotometer and of the paramagnetic resonance technique after the war brought new life into theoretical and experimental development of the crystal field theory. This led to a steadily increasing flood of papers dealing with the subjects. Blearney and Stevens[21] have reviewed the detailed theory and the experimental techniques associated with paramagnetic resonance, with particular emphasis on the application of the method to salts containing transition group ions. In these complexes the paramagnetism arises from electrons in an unfilled d or f shell.

Bowers and Owen [22] reviewed a report which is a complementary to that of Bleaney and Stevens. The complementary purpose of the report is to collect together the available paramagnetic resonance data on these salts, and to present in fairly simple way such part of the theory as, is necessary for understanding the results. In general these data give valuable information on some properties of transition group ion in crystal e.g. susceptibility, specific heat, hyperfine structure, lowest electronic energy levels and width of absorption lines etc.

The manifestations of the Jahn-Teller effect in the optical spectra of impurity have received growing interest in recent years. In particular such phenomena have been discussed for transition metal ion in group II-IV compounds by many investigators [3,23-25]. An interesting problem, on which information can be obtained from experimental spectra, is the magnitude of the coupling to the modes of various symmetry and the types of impurity centres. For centres with tetrahedral symmetry including substitutional impurities in zinc blend and Wutzite type II-VI compounds, this problem have received less attention than in the case of octahedral centres. The properties of cadmium sulphide have already been extensively investigated by spectroscopic method, both for emission and absorption spectra[26,28]. These measurements were as a rule directed to the intrinsic absorption edge and its fine structure. Numerous data are also available on emission properties at different temperatures. Those studies did not extend far beyond the wavelength limit of visible light. Collins[29] was the first to give information on fundamental modes of vibration of the lattice by studying the optical absorption.

Rosenfield et al[2] made study of electron-phonon interaction of Ti^{2+} ion with the ligands in CdS and CdSe by analysing the temperature dependence of absorption bands of these systems. The Absorption bands were discussed on the basis of cluster model involving coupling of the impurity ion and ligands in harmonic approximation.

The earlier works investigated the quantitative relationship between spectra and crystalline parameters on the basis of Slater orbital[7], Richardson's double-zeta[30-33] and Watson's self consistent field (SCF)[34].

J.C. Slater[35] proposed a kind of radial function in which he gave, a set of emperical rule for taking into account the influence of shielding effect. The Slater orbitals are the rough approximations and are totally inadequate for accurate calculation of electron distribution. Thus to find a way of solving the schrodinger equation numerically, Hartree[36] introduced the method of self consistent fields, which was modified by Fock[37] and Slater[38] to include the effect of electron exchange.

The orbitals by this method are called Hartree Fock self consistent field.

In general the Slater orbital's are not capable of yielding good spin-orbit fine structures. On the other hand Watson's SCF d-orbitals are not in good agreement with the experimental crystal field splittings but yields a good spin-orbit coefficient.

Therefore Zhao et al[39-41] introduced double-zeta parametrilization functions, which must satisfy some parametrilization conditions in order to be consistent with the d-orbital theory of Slater and Watson. These double zeta orbitals give a good agreement between the experimental spectra and the crystal field parameters.

2.2 The Theory of d-electron States in Crystal

For the d^n configurations, the d electrons experience the coulomb action of the nucleus and also the electrostatic actions of various inner shell electrons. In the central field approximation, the effective potential consists of the spherical shell potential, the coulomb potential and the potential arising from the uniform electric charge distribution and can be expressed by[41].

$$V_i(r\ ) = C_o + C_i r_i^{-1} + C_2 r_i + C_3 r_i^2 \qquad \ldots(2.2)$$

where C's are the coefficients.

The exponential function of the double - zeta type satisfies the physical requirement expressed by equation (2.2). This will be proven as follows; In a central field, the wavefunction of a single d-electron is approximately given by

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + 3r^{-2} - V(r) - E\right] rR_{3d}(r) = 0 \qquad \ldots(2.3)$$

in atomic unit. The double zeta exponential function [39-41] is

$$R_{3d}(r) = a_1N_1r^2\exp(-\xi_1 r) + a_2N_2r^2\exp(-\xi_2 r) \qquad \ldots(2.4)$$

where

$$N_j = \left[\frac{(2\xi_j)^7}{6!}\right]^{1/2} \quad \text{and } j = 1,2 \qquad \ldots(2.5)$$

and

$$a_1^2 + a_2^2 - 2a_1a_2\left[\frac{2\sqrt{\xi_1\xi_2}}{\xi_1 + \xi_{12}}\right]^{1/2} = 1 \qquad \ldots(2.6)$$

substituting equation (2.4) into (2.3), one obtains

$$-\frac{1}{2}\frac{d^2}{dr^2}\left(a_1N_1\, r^3e^{-\xi_1 r} + a_2N_2r^3e^{-\xi_2 r}\right)$$

$$+\, 3\left(a_1N_1e^{-\xi_1 r} + a_2N_2re^{-\xi_2 r}\right)$$

$$-(V(r) + E)\left(a_1N_1r^3e^{-\xi_1 r} + a_2N_2r^3e^{-\xi_2 r}\right) = 0 \qquad \ldots(2.7)$$

Hence the effective central potential can be expressed as

$$V(r) = -\frac{3}{r}\,\frac{a_1N_1\xi_1 e^{-\xi_1 r} + a_2N_2\xi_2 e^{-\xi_2 r}}{a_1N_1 e^{-\xi_1 r} + a_2N_2 e^{-\xi_2 r}},$$

$$-\frac{1}{2}\,\frac{a_1N_1\xi_1^2 e^{-\xi_1 r} + a_2N_2\xi_2^2 e^{-\xi_2 r}}{a_1N_1 e^{-\xi_1 r} + a_2N_2 e^{-\xi_2 r}} - E \qquad \ldots(2.8)$$

Expanding equation (2.8) into series, collecting the like terms together and simplifying, one obtains

$$V(r) = \frac{-3a_1N_1a_2N_2(\xi_1-\xi_2)^2}{(a_1N_1 + a_2N_2)^2} - \frac{1}{2}\,\frac{a_1N_1\xi_1^2 + a_2N_2\xi_2^2}{a_1N_1 + a_2N_2} - E$$

$$+\frac{3}{r}\left[\frac{a_1N_1\xi_1 + a_2N_2\xi_2}{a_1N_1 + a_2N_2}\right]$$

$$-\frac{a_1N_1a_2N_2(\xi_1-\xi_2)^2}{(a_1N_1 + a_2N_2)^3}\left\{a_1N_1(\xi_1-2\xi_2) + a_2N_2(\xi_2-2\xi_1)\right\} r$$

$$+\left\{\frac{1}{4}\,\frac{a_1N_1a_2N_2\left[\xi_1-\xi_2\right]^3}{(a_1N_1 + a_2N_2)^3}\left[a_1N_1 - a_1N_2\right]\left[\xi_1 + \xi_2\right]\right.$$

$$\left.-\frac{1}{2}\,\frac{a_1N_1a_2N_2\left[\xi_1-\xi_2\right]^4}{\left[a_1N_1 + a_2N_2\right]^4}\left[a_1^2N_1^2 + a_2^2N_2^2 - 4a_1N_1a_2N_2\right]\right\} r^2$$

$$+ - - - - - - - - - - - - - - - - - \qquad \ldots(2.9)$$

The expression of equation (2.9) have the form of equation (2.2) which is consistent with the physical model. Therefore it is seen that the adoption of the exponential function of the double zeta type as the radial d-orbital is reasonable.

2.3 Spin-Orbital Coupling Coefficient

The electrostatic interaction in an atom or ion is responsible, for the break up of a given orbital configuration into a number of levels or terms, each characterized by the given L and S (L-S coupling). Each of orbit lists some of this degeneracy, giving rise to a multiplet or set of fine structure components in each term.

The Hamiltonian operator (H_{SO}) of spin-orbital interaction of an n-electron system is given by [41-43].

$$H_{SO} = \sum_{i=1}^{n} H_i \qquad \ldots(2.10)$$

with
$$H_i = \xi_d(r)\, \vec{l}_i\, \vec{s}_i \qquad \ldots(2.11)$$

and
$$\xi_d(r_i) = \frac{e}{2m^2c^2r}\, \frac{d}{dr}\, V(r_i) \qquad \ldots(2.12)$$

where c is the speed of light and H_i is the Hamiltonian operator for spin orbital interaction of single electron and $V(r_i)$ is the effective potential due to the atomic nucleus and all the other electrons of the system acting on the

i^{th} electron, which is given by equation (2.9).

For a d-orbital, the spin-orbit coefficients ξ_d is

$$\xi_d = \hbar^2 \langle R_d(r) \,|\, \xi_d(r) \,|\, R_d(r) \rangle$$

$$\xi_d = \frac{e\hbar^2}{2m^2c^2} \langle R_d(r) \left| \frac{1}{r} \frac{d}{dr} V_{(r)} \right| R_d(r) \rangle \qquad \ldots(2.13)$$

Using equations (2.4) and (2.9) in equation 2.13, an expression is obtained for ξ_d, which is

$$\xi_d = \frac{e\hbar^2}{2m^2c^2} -3\left(\frac{a_1N_1\xi_1 + a_2N_2\xi_2}{a_1N_1 + a_2N_2}\right)$$

$$\left[\frac{a_1^2N_1^2 3!}{(2\xi_1)^4} + \frac{a_2^2N_2^2 3!}{(2\xi_2)^4}\right.$$

$$\left. + \frac{2a_1N_1a_2N_2\ 3!}{(\xi_1 + \xi_2)^4}\right]$$

$$- \frac{a_1N_1a_2N_2(\xi_1 - \xi_2)^2}{(a_1N_1 + a_2N_2)^3}$$

$$[a_1N_1(\xi_1 - 2\xi_2) + a_2N_2(\xi_2 - 2\xi_1)]$$

$$\left[\frac{a_1^2N_1^2 5!}{(2\xi_1)^6} + \frac{a_2^2N_2^2 5!}{(2\xi_2)^6} + \frac{2a_1N_1a_1N_2 5!}{(\xi_1 + \xi_2)^6}\right]$$

$$+ \quad 2\left[\frac{1}{4} \frac{a_1N_1a_2N_2(\xi_1 - \xi_2)^3}{(a_1N_1 + a_2N_2)^3} \quad (a_1N_1-a_2N_2)(\xi_1+\xi_2) \right.$$

$$\left. - \frac{1}{2}\left(\frac{a_1N_1a_2N_2(\xi_1-\xi_2)^4}{(a_1N_1 + a_2N_2)^4}\right)\right]$$

$$\left[\frac{a_1^2N_1^2\, 6!}{(2\xi_1)^7} + \frac{a_2^2N_2^2}{(2\xi_2)^7} + \frac{2a_1N_1a_2N_2 6!}{(\xi_1 + \xi_2)^7}\right] \qquad \ldots(2.14)$$

Substituting the values of e, h, m and c the above equation is simplified and expanded in units of cm^{-1} as

$$\xi_d = 5.844167\left[-\left(\frac{9}{8}\frac{a_1^2N_1^2}{\xi_1^3} + \frac{a_2^2N_2^2}{\xi_2^3} + \frac{16a_1N_1a_2N_2}{(\xi_1 + \xi_2)^3}\right)\right.$$

$$\left. + \; 12a_1N_1a_2N_2 \frac{(\xi_1 - \xi_2)^2}{(\xi_1 + \xi_2)^5}\right] \qquad \ldots(2.15)$$

Thus ξ_d is expressed in terms of a_1, a_2, ξ_1 and ξ_2

2.4 Racah Electrostatic Parameters

The Hamiltonian operator of electron-electron repulsion interaction can be written as

$$H_e = \frac{1}{2}\sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \qquad i, j = 1, 2, 3 \ldots\ldots n$$

$$\ldots(2.16)$$

The contribution of the electron-electron interaction to levels of the d^n system can be described in terms of Racah parameters, as discussed in chapter one.

In equation (1.39) F^k's are expressed as

$$F^k = e^2 \int_0^\infty \int_0^\infty r_1^2 r_2^2 \frac{r^k_<}{r^{k+1}} R_{3d}^2(r_1) R_{3d}^2(r_2) dr_1 dr_2 \qquad \ldots(2.17)$$

where $R_{3d}(r_1)$, $R_{3d}(r_2)$ are the double zeta orbitals for r_1^{th} and r_2^{th} electrons.

Thus the Racah parameters can be computed once F^k's are known. Using the known formula[41,42].

$$J^k(\alpha\beta) = \int_0^\infty \int_0^\infty r_1^6 r_2^6 \frac{r^k_<}{r^{k+1}_>} e^{-\alpha r_1} e^{-\alpha r_2} \quad dr_1 dr_2 =$$

$$e^2 \left\{ \frac{(6+k)!}{\beta^{7+k}} \left[\frac{(5-k)!}{\alpha^{6-k}} - \sum_{m=0}^{6+k} \frac{\beta^m}{m!} \frac{(5-K+m)!}{(\beta+\alpha)^{6-k+m}} \right] + \right.$$

$$\left. \frac{(6+k)!}{\alpha^{7+k}} \left[\frac{(5-k)!}{\beta^{6-k}} - \sum_{m=0}^{6+k} \frac{\alpha^m}{m!} \frac{(5-k+m)!}{(\beta+\alpha)^{6-k+m}} \right] \right\} \qquad \ldots(2.18)$$

a general expression for F^k's can be obtained

$$
\begin{aligned}
F^k = e^2 \Bigg\{ & 2a_1^4 \, N_1^4 \, \frac{(6+k)!}{(2\xi_1)^{7+k}} \left[\frac{(5-k)!}{(2\xi_1)^{6-k}} - \sum_{m=1}^{6+k} \frac{(2\xi_1)^m}{m\,!} \, \frac{(5-k+m)!}{(4\xi_1)^{6-k+m}} \right] \\
& + 2a_2^4 N_2^4 \, \frac{(6+k)!}{(2\xi_2)^{7+k}} \left[\frac{(5-k)!}{(2\xi_2)^{6-k}} - \sum_{m=0}^{6+k} \frac{(2\xi_2)^m}{m\,!} \, \frac{(5-k+m)!}{(4\xi_2)^{6-k+m}} \right] \\
& + 8a_1^2 N_1^2 a_2^2 N_2^2 \, \frac{(6+k)!}{(\xi_1+\xi_2)^{7+k}} \left[\frac{(5-k)!}{(\xi_1+\xi_2)^{6-k}} - \sum_{m=0}^{6+k} \frac{(\xi_1+\xi_2)^m}{m\,!} \, \frac{(5-k+m)!}{(2\xi_1+\xi_2)^{6-k+m}} \right] \\
& + 2a_1^2 N_1^2 a_2^2 N_2^2 \Bigg(\frac{(6+k)!}{(2\xi_2)^{7+k}} \left[\frac{(5-k)!}{(2\xi_1)^{6+k}} - \sum_{m=0}^{6+k} \frac{(2\xi_1)^m}{m\,!} \, \frac{(5-k+m)!}{(2\xi_1+2\xi_2)^{6-k+m}} \right] \\
& + \frac{(6+k)!}{(2\xi_1)^{7+k}} \left[\frac{(5-k)!}{(2\xi_2)^{6-k}} - \sum_{m=0}^{6+k} \frac{(2\xi_1)^m}{m\,!} \, \frac{(5-k+m)!}{(2\xi_1+2\xi_2)^{6-k+m}} \right] \Bigg) \Bigg\}
\end{aligned}
$$

$$+ \; 4a_1N_1a_2^3N_2^3 \left\{ \frac{(6+k)!}{(2\xi_2)^{7+k}} \left[\frac{(5-k)!}{(\xi_1+\xi_2)^{6-k}} - \right.\right.$$

$$\left. \sum_{m=0}^{6+k} \frac{(5-k+m)\,!}{(\xi_1+3\xi_2)^{(6-k+m)}} \frac{(2\xi_2)^m}{m\,!} \right]$$

$$\left. + \; \frac{(6+k)!}{(\xi_1+\xi_2)^{7-k}} \left[\frac{(5-k)!}{(2\xi_2)^{6-k}} - \sum_{M=0}^{6+K} \frac{(\xi_1+\xi_2)^m}{m\,!} \frac{(5-k+m)!}{(2\xi_1+\xi_2)^{6-k+m}} \right] \right\}$$

$$+ \; 4a_1^3N_1^3a_2N_2 \left\{ \frac{(6+k)!}{(\xi_1+\xi_2)^{7+k}} \left[\frac{(5-k)!}{(2\xi_1)^{6-k}} - \right.\right.$$

$$\left. \sum_{m=0}^{6+k} \frac{(\xi_1+\xi_2)^m}{m\,!} \frac{(5-k+m)!}{(3\xi_1+\xi_2)^{6-k+m}} \right] + \frac{(6+k)!}{(2\xi_1)^{7+k}} \left[\frac{(5-k)!}{(\xi_1+\xi_2)^{6-k}} \right.$$

$$\left.\left. - \sum_{m=0}^{6+k} \frac{(2\xi_1)^m}{m\,!} \frac{(5-k+m)!}{(3\xi_1+\xi_2)^{6-k+m}} \right] \right\} \qquad \textbf{(2.19)}$$

Hence using equation (2.19) the expression in F^0, F^2, and F^4 can be computed in terms of a_1, a_2, ξ_1 and ξ_2 for the corresponding values of k=0,2 and 4.

2.5 Analytical Approximation of SCF d-orbit

To dbtain the double zeta parameterization function for Ti^{2+} the coefficients a_1, a_2, ξ_1 and ξ_2 are to be determined using the following mathematical condition[4].

(i) The overlap condition between R_d and R_d^W is given by

$$\langle R_d \mid R_d^W \rangle = 1 \qquad \ldots(2.20)$$

where R_d is the double zeta function given by equation (2.4) and R_d^W is the Watson's SCF d-orbit. Using the expression for Watson's function[36,45]

$$R_d^W(r) = 1.628901r^2e^{1.7316r} + 14.714366r^2e^{-3.4276r} + 28.997185r^2e^{-6.4619r} + 13.010719r^2e^{-11.9171}, \qquad \ldots(2.21)$$

equation (2.20) becomes

$$1172.8087\left[\frac{a_1N_1}{(\xi_1+1.7316)^7} + \frac{a_2N_2}{(\xi_2+1.7316)^7}\right]$$

$$+\ 10594.344\left[\frac{a_1N_1}{(\xi_1+3.4276)^7} + \frac{a_2N_2}{(\xi_2+3.4276)^7}\right]$$

$$+ \quad 20877.973 \left[\frac{a_1 N_1}{(\xi_1 + 6.4619)^7} + \frac{a_2 N_2}{(\xi_2 + 6.4619)^7} \right]$$

$$+ \quad 9367.344 \left[\frac{a_1 N_1}{(\xi_1 + 11.9171)^7} + \frac{a_2 N_2}{(\xi_2 + 11.9171)^7} \right] = 1 \qquad \ldots(2.22)$$

substituting the values of N_1 and N_2 in terms of ξ_1 and ξ_2 from equation (2.5), equation (2.22) becomes

$$494.49954 \frac{a_1 \xi_1^{7/2}}{(\xi_1 + 1.7316)^7} + \frac{a_2 \xi_2^{7/2}}{(\xi_2 + 1.7316)^7}$$

$$+ \; 4966.9674 \frac{a_1 \xi_1^{7/2}}{(\xi_1 + 3.4276)^7} + \frac{a_2 \xi_2^{7/2}}{(\xi_2 + 3.4276)^7}$$

$$+ \; 8802.9254 \frac{a_1 \xi_1^{7/2}}{(\xi_1 + 6.4619)^7} + \frac{a_2 \xi_2^{7/2}}{(\xi_2 + 6.4619)^7}$$

$$+ \; 3949.7764 \frac{a_1 \xi_1^{7/2}}{(\xi_1 + 11.9171)^7} + \frac{a_2 \xi_2^{7/2}}{(\xi_2 + 11.9171)^7}$$

$$= \quad 1 \qquad \ldots(2.23)$$

(ii) a spin-obit coefficient condition given by

$$-\xi_d^o = \langle R_d \left| (e\hbar^2/2m^2c^2)\ (1/r)\ \frac{dV}{dr} \right| R_d \rangle$$

$$= \langle R_d^W \left| (e\hbar^2/2m^2c^2)(1/r)\ \frac{dV}{dr} \right| R_d^W \rangle$$

...(2.24)

Here experimental value of spin-orbit coefficient ξ_d=120 cm^{-1} has been taken as parameter of the theory, so using double zeta-d-orbital in equation (2.24) one obtains

$$a_1^2\xi_1^4 + a_2^2\xi_2^4 + \frac{16a_1a_2(\xi_1\xi_2)^{7/2}}{(\xi_1 + \xi_2)^3} +$$

$$\frac{32}{3}\, a_1a_2(\xi_1\xi_2)^{7/2}\ \frac{(\xi_1 - \xi_2)^2}{(\xi_1 + \xi_2)^5} = 102.66647$$

...(2.25)

(iii) The third parameterization condition is given by

$$\langle R_d \left| r^4 \right| R_d \rangle = \langle R_d^W \left| r^4 \right| R_d^W \rangle$$

Using equation (2.4) and 2.21) one obtains

$$a_1^2/\xi_1^4 + a_2^2/\xi_2^4 + \frac{4096\ a_1a_2(\xi_1\xi_2)^{7/2}}{(\xi_1 + \xi_2)^{11}} = 0.0453761$$

...(2.26)

With the help of numerical method[46,47] a system of non-linear equations (2.6), (2.23), (2.25) and (2.26) in a_1, a_2, ξ_1, ξ_2 are solved on IBM computer and hence values obtained are

$a_1 = 0.58$
$a_2 = 0.56$
$\xi_1 = 3.8900$
$\xi_2 = 1.6656$

Thus exact double zeta radial 3d-function for Ti^{2+} is expressed as

$$R_{3d}(r) = 0.58 \left[\frac{7.78^7}{6!}\right]^{1/2} r^2 \exp(-3.8900r) + 0.56\left[\frac{3.3312^7}{6!}\right]^{1/2} r^2 \exp(-1.6656r) \quad \ldots(2.28)$$

This radial function will be used for computation of energy states of Ti^{2+} in CdS crystal.

CHAPTER THREE

CRYSTAL FIELD OPERATOR AND d^2 WAVE FUNCTION

3.1 Expansion of Functions

The crystal-field model considers isolated molecules or complex-ions in which the central electrons are subjected to an electric field originating from the surrounding ligands. The electric field of the ligand ions produces V_c, which acts as a perturbation on the electrons of the central ion, such that energy operator of the system is

$$\hat{H} = \hat{H}_o + \hat{V}_c \qquad \ldots(3.1)$$

H_o is the unpertubed Hamiltonian. Energy calculations of crystal-field splittings require evaluation of matrix elements of the form

$$\int \psi_i^* V_c \psi_j \, d\tau = \langle \psi_i | \hat{V}_c | \psi_j \rangle \qquad \ldots(3.2)$$

in which ψ's represent wave functions of central ion. To solve the integral (3.2), V_c is expressed in explicit form using the expansion theorem.

Any functions of a set of variables may be expressed as a linear combination of a complete set of eigenfunctions, of the same variables of any operator.

For example

$$f(x_1x_2 \ldots . x_n) = a_1\Phi_1(x_1x_2 \ldots \ldots . x_n) +$$
$$a_2\Phi_2(x_1x_2 \ldots . x_n) + \text{-------} + a_n\Phi_n(X_1,X_2\text{-----}x_n) \qquad \ldots(3.3)$$

where f is a function of the variables $(x_1,x_2 \ldots . x_n)$ expanded in terms of the Φ's, with expansion coefficients a_i, where the Φ's forms a complete set of eigenfunctions of some operator $\hat{\Omega}$, such that

$$\hat{\Omega}\Phi_i = \lambda_i\Phi_i \qquad \ldots(3.4)$$

Any other way of looking at the expansion theorem is by noting the close mathematical functions and vectors. We may write a vector A as a linear combination of the base vectors

$$\vec{A} = b_1\vec{x}_1 + b_2\vec{x}_2 + b_3\vec{x}_3 = \sum_{k=1}^{3} b_k\vec{x}_k \qquad \ldots(3.5)$$

where the base vectors are independent and orthogonal. The coefficients b_k determines the value of each base vector in A. They are the projection of A on the base vectors and given by the dot product

$$b_k = \vec{x}_k . \vec{A} \qquad \ldots(3.6)$$

and so equation 3.5 may be written as

$$A = \sum_{k=1}^{3} \vec{x}_k \, (\vec{x}_k . \vec{A}) \qquad \text{...(3.7)}$$

Both of these have a formal analogy in the expansion of functions. So f(x) is expanded as

$$f(x) = a_1\Phi_1(x) + a_2\Phi_2(x) + \ldots + a_n\Phi_n(x) \qquad \text{...(3.8)}$$

We have expressed the functions of f(x) in terms of basic functions $\Phi(x)$. We could equally well expand them in terms of any other basis e.g.

$$f(x) = b_1\Psi_1(x) + b_2\Psi_2(x) + \ldots + b_n\Psi_n(x) \qquad \text{...(3.9)}$$

The bases must be complete. In the case of vectors in three-dimensional space we require three basis vectors. There may be more, even an infinite number as in the many-dimensional Hilbert space.

The analogy between vectors and functions extends also to coefficients a_k and b_j. Thus premultiplying equation (3.8) by Φ_n^* and integrating one obtains,

$$\int \Phi_n^*(x) f(x) dx = a_1 \int \Phi_n^*(x)\Phi_1(x) dx + a_2 \int \Phi_n^*(x)\Phi_2(x) dx + \ldots + a_n \int \Phi_n^*(x)\Phi_n(x) dx \qquad \text{...(3.10)}$$

So that, the orthogonality of the basis functions Φ_1's gives

$$a_n = \int \Phi_n^*(x).f(x)dx = \langle \Phi_n | f \rangle \qquad \ldots(3.11)$$

The integral $\langle \Phi_n | f \rangle$ corresponds to the dot products of the vectors x_k and A in equation (3.6), and substituting equation (3.11) in equation (3.8), f(x) can be expressed as

$$f(x) = \sum_{k=1}^{n} |\Phi_k\rangle\langle\Phi_k|f\rangle \qquad \ldots(3.12)$$

This relationship will be utilized to determine the crystal field potential V_c.

3.2 The Crystal-Field Potential

The potential V_c is set up by an arrangement of ligands around a central metal. To solve the integral of the form of (3.2), V_c operates on electronic wavefunctions of the metal ion, which are referred to a single origin of the central metal ion.

It is therefore convenient to express V_c in the form referred to the same origin. The usual way of doing this is to expand the potential V_c as series of spherical harmonics centred on the metal ion[44]. Normally a ligand is regarded as a point charge or collection of point charges. The electronic potential set up by these ligands is inversely proportional to the distance of the charges from the central ion. The potential or rather the sum of the potentials from all the ligands is expressed in a coordinate frame whose origin lies elsewhere on the metal ion. This can be done with the help of the expansion theorem. Since the potential occurs in three dimension space, the three coordinates for the basis functions are required in the expansion. It is particularly convenient to deal with spherical polar coordinates such that V_c is expressed as [48,49].

$$V_c = \sum_{k=o}^{\infty} \sum_{q=-k}^{+k} C_k^q R_k(r)\, Y_k^q\,(\Theta\Phi) \qquad \ldots(3.13)$$

where C_k^q's are expansion coefficients of V_c with respect to the basis functions $R_k(r)Y_k^q\,(\Theta\Phi)$. Note that the basis functions involves all three coordinates r, Θ, Φ even though they have been separated as spherical harmonics $Y_k^q\,(\Theta\Phi)$ and radial functions $R_k(r)$. To be quite clear equation (3.13) is expanded as

$$V_c = C_o^o R_o Y_o^o + C_1^1 R_1 Y_1^1 + C^{-1}_{1} R_1 Y^{-1}_{1} + C_2^2 R_2 Y_2^2 + \ldots. \qquad \ldots(3.14)$$

this includes harmonics from Y_o^o to Y_∞^∞ but symmetry and group theory impose an early termination of these harmonics.

The power of group theory is only realised in the present problem when the operator is viewed in context in which it is to be used. Matrix elements are the observable quantities, not the operators. The matrix element of intergral (3.2) may be factorized into radial and angular parts. Let $R(\Psi)$ and $A(\Psi)$ stand for the radial and angular parts of Ψ respectively and $R(V_c)$ and $A(V_c)$ for radial and angular part of V_c. Then a typical matrix element is factorized as

$$\langle \Psi_i | V_c | \Psi_j \rangle = \langle R(\Psi_i) | R(V_c) | R(\Psi_j) \rangle \times \langle A(\Psi_i) | A(V_c) | A(\Psi_j) \rangle \qquad \ldots(3.15)$$

Substituting equation (3.15) into equation (3.14), one obtains an expression for matrix element as

$$\begin{aligned} \langle \psi_i | V_c | \psi_j \rangle = {} & C_0^0 \langle R(\psi_i) | R_0 | R(\psi_j) \rangle \langle A(\psi_i) | Y_0^0 | A(\psi_i) \rangle \\ & + C_1^1 \langle R(\psi_i) | R_1 | R(\psi_j) \rangle \langle A(\psi_i) | Y_1^1 | A(\psi_j) \rangle + \cdots \\ \cdots\cdots & + C_k^q \langle R(\psi_i) | R_k | R(\psi_j) \rangle \langle A(\psi_i) | Y_k^q | A(\psi_j) \rangle + \cdots\cdots \qquad \ldots(3.16) \end{aligned}$$

For a particular problem, if any of these angular integrals vanishes by virtue of symmetry then there is no point in knowing the associated radial integral and more so, no point in knowing the associated expansion coefficient C_k^q. Thus by looking at the group theoretical behaviour of the angular parts of the matrix-elements of V_c the number of terms are restricted and hence V_c shall have only limited terms in its expansion.

3.3 Series Termination

A most useful series terminator is derived from the specification of the wave function Ψ. If Ψ_i, Ψ_j are metal d-orbitals, the angular part of matrix elements of equation (3.16) vanish for Y_k^q with K>4, which can be seen as follows: The wave function expressed as

$$R(\Psi)Y_l^m = R_\psi(r)\,\Theta_l^m\,\Phi_m(\varphi) \qquad \ldots(3.17)$$

where r, θ, Φ are spherical coordinates of the electron.

For the d-orbitals the angular part of the wavefunction has the spherical harmonics Y_2^m. Thus matrix elements in equation (3.16), therefore, involve angular integral of the form

$$\langle Y_{l'}^{m'}\,|Y_k^q|\,Y_l^m\rangle \qquad \ldots(3.18)$$

The letters k and q have been used to label l and m quantum numbers of the harmonics appearing in the potential. The Y_l^m's in equation (3.18) refer to the orbitals of the electrons. The matrix elements of equation (3.18) vanishes unless a vector triangle can be constructed from the three indices l', k, and l.

For d-orbitals, $l' = l = 2$, thus the matrix element

$$\int Y_{l'}^{m'}\,Y_k^q\,Y_l^m\,\sin\theta\,d\theta\,d\Phi = o \qquad \ldots(3.19)$$

for $K>2l$. Thus it will be non-zero for K=0, 2, and 4.

In spherical symmetry the representations have dimensions of the order of 1,3,5 ....$(2l + 1)$ corresponding, for example, to s, p, d orbital sets as bases. Such representations are written as D_o, D_1, D_2 .....D_n corresponding to l = 0, 1, 2--------n.

Suppose a spherical atom or ion has electrons which respectively belong to the representations D_k and D_l (say a d-electron). Then what representations of the spherical group do these electrons, as a pair, span? That is, the product of wave functions of the type $\Psi_i(1).\Psi_j(2)$ etc. or $Y^l_m(1).Y^l_m(2)$ is to be considered.

Taking the direct product of the individual electron representations the coefficients a_i are determined by reducing it.

$$D_k \wedge D_l = \sum_i a_i D_i \qquad \ldots(3.20)$$

A well known result that the character of the direct product representation equals the product of the individual representation's character[48,49] i.e.

$$X(D_l \wedge D_k) = X(D_i)X(D_k) \qquad \ldots(3.21)$$

Considering electronic wavefunctions transforming in the spherical group in the representation D_l, which is expressed as

$$D_l = \begin{bmatrix} e^{ila} & & & \\ & e^{i(l-1)a} & & \\ & & \ddots & \\ & & & e^{-ila} \end{bmatrix} \qquad \ldots(3.22)$$

the character of D_l is obtained as the sum of diagonal elements.

$$X(D_l) = (e^{ila} + e^{i(l-1)a} + \ldots\ldots\ldots\ldots + e^{-ila}) \qquad \ldots(3.23)$$

On substituting in equation (3.21), one finds

$$\begin{aligned} X\,(D_k \wedge D_l) &= (e^{ika} + e^{i(k-1)a} + \ldots + e^{-ika}) \times \\ &\quad (e^{ila} + e^{i(l-1)a} + \ldots + e^{-ila}) \\ &= (e^{i(k+l)a} + e^{i(k+l-1)a} + \ldots\ldots e^{-i(k+l)a}) + \\ &\quad (e^{i(k+l-1)a} + e^{i(k+l-2)a} + \ldots\ldots e^{-i(k+l-1)a}) + \text{-----} \\ &\quad + (e^{i(k-l)a} + e^{i(k-l-1)a} + \ldots + e^{-i(k-l)a}) \end{aligned} \qquad \ldots(3.24)$$

$$X(D_k \wedge D_l) = X(D_{k+l}) + X(D_{k+l-1}) + \text{---} + X(D_{k-l}) \qquad \ldots(3.25)$$

Thus

$$D_k \wedge D_l = D_{k+l} + D_{k+l-1} + --- + D_{k-l} \qquad \ldots(3.26)$$

Hence equation (3.26) shows that the product wavefunctions span representation with suffices ranging from sum to the differences of original representations.

Now in the matrix element of the type (3.18)

$$M = \langle Y_{l'}^{m'} | Y_k^q | Y_l^m \rangle, \qquad \ldots(3.27)$$

if any two are coupled together (because the spherical harmonics commute) and the span of the product is deduced, then $Y_k^q|Y_l^m\rangle$ gives rise to harmonics Y_L^M in which L takes all values from $|k+l|$ to $|k-l|$ because of the orthogonality of spherical harmonics.

Therefore

$$M = C_1\langle Y_{l'}^{m'}|Y_{k+l}\rangle + C_2\langle Y_{l'}^{m'}|Y_{k+l-1}\rangle + --- + C_n\langle Y_{l'}^{m'}|Y_{(k-l)}\rangle \qquad \ldots(3.28)$$

The individual matrix elements in equation (3.28) may vanish because of the orthogonality in the quantum numbers. It is demanded that l', k and l in equation (3.27) form at least a vector triangle. In this way, for crystal field matrix elements between d-orbitals, the terms in the potential V_C of order k greater that 4 are in-operative. The second generally useful series terminator for equation (3.18) is derived from the parity of the three functions in $\langle \Psi_i | Y_k^q | \Psi_j \rangle$.

The general rule is that the triple product of the functions under the integral sign in these matrix element must be of even parity. Since inversion operator inverts only the electrons, the above parity rule remains pertinent even for molecules which lack centre of symmetry.

For example, if Ψ_i and Ψ_j are both d-orbitals, Y_k^q must have k even, for the matrix elements not to vanish and this is true regardless of the symmetry of the molecule. So far, by noting the spherical basis of the functions used and their parity, the series in equation (3.16) is greatly shortened.

For matrix elements of d-electrons, the effective potential is reduced to terms involving Y_2^0, Y_2^q and Y_4^q and further limitations are imposed by the requirements of ligands arrangement round the metal ions that is by the site symmetry.

3.4 Axial Distortion

Returning to the crystal-field potential in C_{3v} symmetry the transformation properties of the harmonic set Y_2^m are considered, using the well know formula for character of a spherical representation under a rotation

$$X(\ ) = \frac{\sin (l + 1/2)\alpha}{\sin (1/2)\alpha}, \qquad \dots(3.29)$$

the following characters are found under operation of C_{3V}.

	E	$2C_3$	$2\sigma_d$
X(l=2)	5	−1	1

and thus from the character table of C_{3V}, the irreducible components of Y_2^m in C_{3V} are $3A_1 + E$. Here it can be seen that totally symmetrical representation are involved and so Y_2^m's appear in the potential V_c.

From the set Y_4^m the character table is as follows

	E	$2C_3$	$3\sigma_d$
X(l=4)	9	0	1

which gives the irreducive components of Y_4^m's in V_c as $2A_1 + A_2 + 3E$. Thus two linear combination of the Y_4^m's transforming as A_1 and one as A_2 occurs in the potential.

By specific investigation of the transformation properties of the individual spherical harmonics in C_{3V} symmetry, it can be determined that which representation is involved. A case is considered in which the system is quantized along the three fold C_3 axis, that is the C_3 corresponds to the Z-axis to which the spherical harmonics is referred.

In this case, rotations about axis parallel to Z only affects the Φ function, transforming $e^{im\Phi}$ into $e^{im(\Phi+\alpha)}$ Hence

$$C_3 \quad e^{4i\Phi} = e^{4i(\Phi+2\pi/3)}$$

$$C_3 \quad e^{3i\Phi} = e^{3i(\Phi+2\pi/3)}$$

Now it is required that $V_{C_{3v}}$ is to be transformed as A_1 and A_2, which are totally symmetrical representation and so $C_3 \hat{V}_c = \hat{V}_c$ which will only be true if

$$V_c = dY_2^0 + bY_4^0 + c(Y_4^3 + Y_4^{-3}) \qquad \ldots(3.30)$$

In case of a tetrahedron transforming under C_3 axis the ratio c/b is fixed. This happens because there is only one A_1 combinations of the Y_4^m which exists and so it is defined completely. But in the present case of the C_{3v} symmetry there are two A_1 representations and hence the ratio of c/b cannot be fixed. Thus no relationship between d and b or d and c are defined by symmetry as there are no symmetry operations which can transform one order of harmonic into an other e.g Y_4^m into Y_2^m. Thus C_{3v} symmetry defines potential involving three unknowns as distinct coefficients or parameters. These coefficients are determined easily in point charge model of the crystal field[48,49]. Actually this only involves relating d, b, and c of equation (3.30) and it is with this aim in view that the determination of $V_{C_{3v}}$ in the point charge model are made in next section.

3.5 The Point-Charge Model

The structure of Cadmium Sulphide can be viewed as a cubic-packing of Cd^{2+} cations with S^{2-} anions occupying all the tetrahedral holes, isostructural with the Cadmium Fluorite[50,51]. Based on X-ray structure data[52] the lattice constant of tetrahedrally coordinated sulphide is given as 5.78 Å and, the distance of the nearest neighbour, R = 2.52Å. The figure 3.1 shows CdS structure with tetragonal and triagonal system of coordinates. If figure 3.1 is viewed from Z-direction, it looks like figure 3.2 below, where X,Y,Z forms a trigonal coordinate system.

The spherical polar coordinates of the point charges in trigonal systems of coordinates are shown in table 3.1 where θ' is the angle of ligand with Z-axis and Φ' the angle of projection of ligand on XY plane from X-axis, r is the distance of the neighbour which is 2.52Å for CdS. Here sperical polar coordinates of electron of metal ion are expressed as (r, θ, Φ) while that of ligands as (r', θ', Φ').

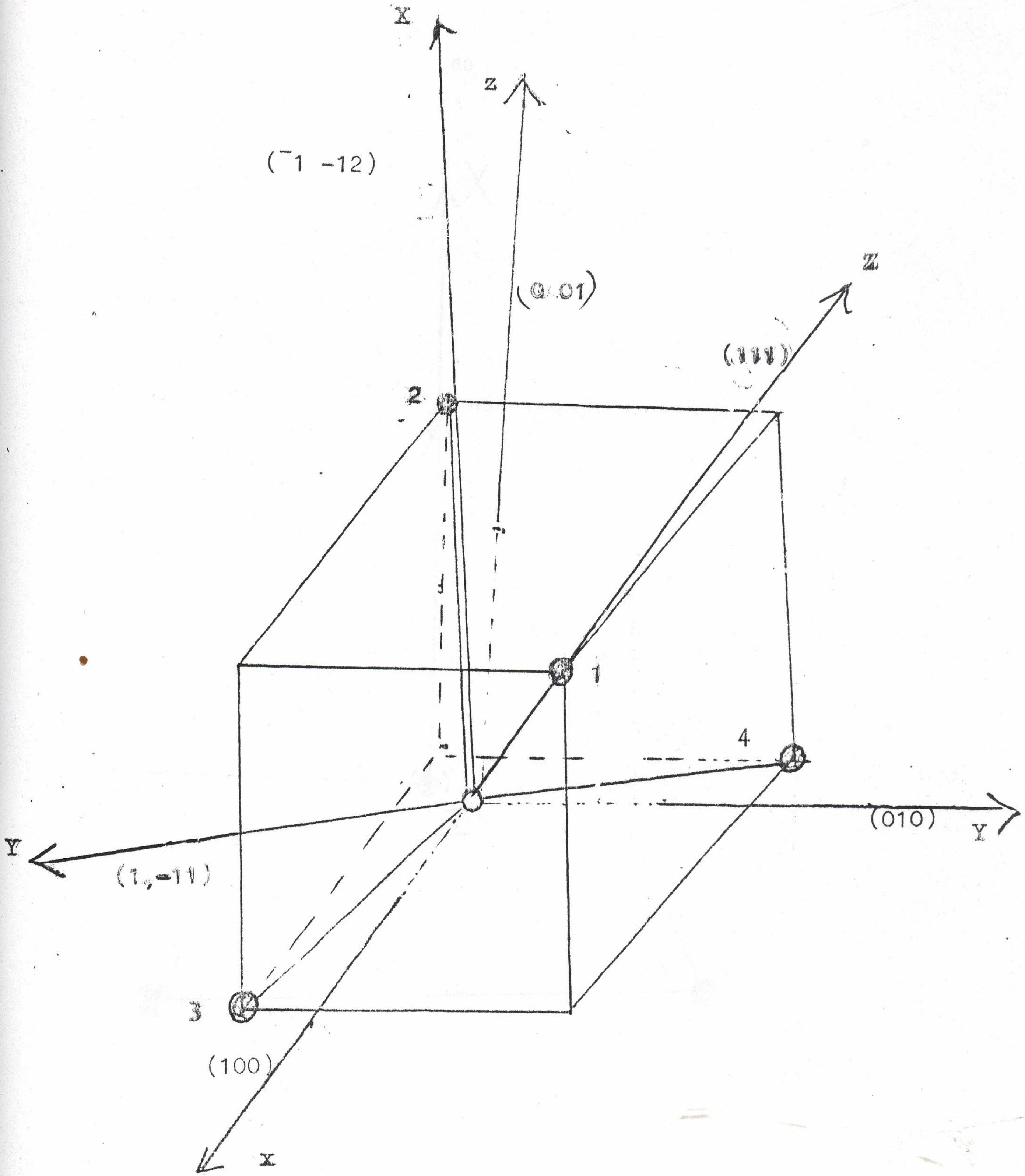

Figure 3.1 Tetrahedral Cubic Structure for CdS O-Cd; ●-S, with tetragonal coordinate system (x,y,z) and trigonal coordinate system (X,Y,Z).

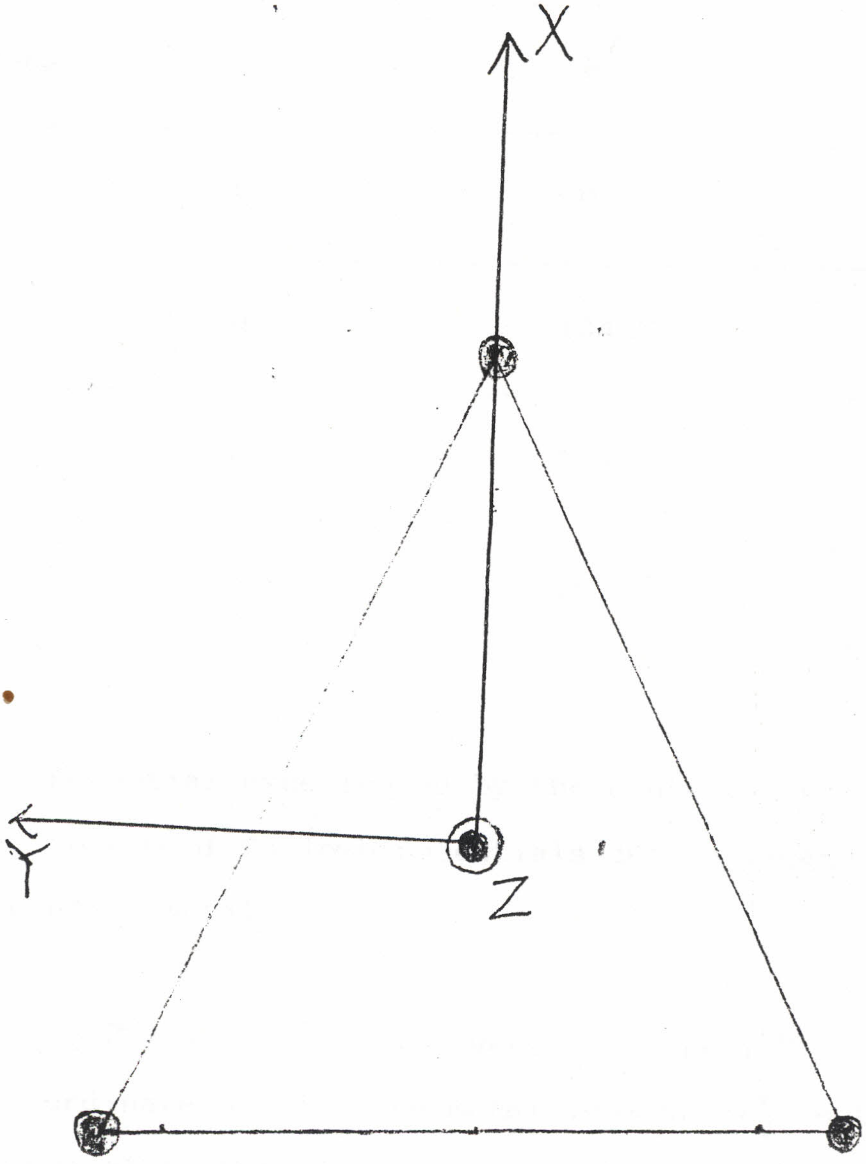

Figure 3.2 Trigonal (X,Y,Z) coordinates system for T_d-symmetry.

Table 3.1: Spherical polar coordinates for ligands with T_d symmetry

Ligand	r'	θ'	Φ'
1	R	0	0
2	R	104.9	0
3	R	104.9	120
4	R	255.1	240

Potential experienced by the central ion electrons is equal to sum of Coulomb potentials due to ligand ions surrounding metal ion.

If $\vec{r}_i$ is the position vector of the i^{th} ligand from the coordinate origin (the metal ion) and $\vec{r}_j$ is that of electron of central ion, the crystal potential may be written as

$$V_c = \frac{1}{4\pi\varepsilon_0} \sum_{i=1}^{4} \sum_{j=1}^{2} \frac{Ze}{|r'_i - r_j|} \qquad \ldots(3.31)$$

where Z is the charge of ligand and e is charge of electron.

The expansion theorem for $\dfrac{1}{|\vec{r'_i} - \vec{r_j}|}$ allows equation (3.31) to be expressed as a linear combination of functions of the form

$$R_k(r)\; Y_k^q\,(\Theta\phi)$$

where $Y_k^q\,(\Theta\phi)$ are the spherical harmonics

Thus one obtain [48].

$$\sum_{i'=1}^{4} \frac{ze}{|\vec{r'_i} - \vec{rj}|} = \sum_{k=0}^{\infty}\sum_{q=-k}^{k} \frac{r^k}{r'^{(k+1)}}\left[\sum_{i=1}^{4} ze\sqrt{(2\pi)}\left(\frac{2}{2k+1}\right)\right.$$

$$\left.\Upsilon_k^{q*}(\Theta'_i\phi'_i)(\sqrt{2\pi})\left(\sqrt{\frac{2}{2k+1}}\right).\Upsilon_k^q\quad(\Theta_j\phi_j)\right] \qquad ....(3.32)$$

Equation (3.32) and (3.13) are nearly equal to make them look more alike, regrouping is done as follows

$$\sum_{i=1}^{4} \frac{ze}{|\vec{r}'_i - \vec{r}_j|} = \sum_{k=0}^{\infty}\sum_{q=-k}^{k}\left[\frac{4\pi}{2k+1}\sum_{i=1}^{4} ze\;\Upsilon_k^{q*}(\Theta'_i\phi'_i)\right.$$

$$\left.\frac{r^k}{r'^{(k+1)}}\Upsilon_k^q\;(\Theta_j\phi_j)\right]$$

$$= \sum_{k=0}^{\infty}\sum_{q=-k}^{k} R(r)\; C_k^q\; \Upsilon_k^q\;(\Theta_i\phi_j)$$

$$....(3.33)$$

where
$$C_K^q = \frac{4\pi}{2K+1} Ze \sum_{i=1}^{4} Y_K^{q*}(\theta_i' \phi_i') .$$

$$R_K(r) = \frac{r^K}{r'^{(K+1)}} \qquad \ldots(3.34)$$

However the expansion of equation (3.32) has specified the unknown in equation (3.13) as per equation (3.33), which are calculated explicitly by substituting the explicit values of $(r_i' \theta_i' \Phi_i')$ for the four ligands as in figure 3.1 in equation (3.34). With the help of group theory, equation (3.32) for C_{3v} symmetry is expressed as

$$V_{C_{3v}} = \sum_{i=1}^{4} \frac{Ze}{|\vec{r}_i' - \vec{r}_j'|} = C_2^0 R_2(r) Y_2^0 + C_4^0 R_4(r) Y_4^0 \qquad \ldots(3.35)$$
$$+ C_4^3 R_4(r) Y_4^3 + C_4^{-3} R_4(r) Y_4^{-3} ,$$

where Y_0^0 has been ignored because it just gives the shift of all the energy levels and

$$Y_K^q = \Theta_{kq}(\theta)\Phi_q(\varphi)$$

are spherical harmonics for central electron. In general normalized functions $\Theta_{kq}(\theta)$ and $\Phi_q(\Phi)$ are expressed as

$$\Phi_q = \frac{1}{\sqrt{2\pi}} e^{iq\Phi} \quad (q = 0, \pm 1, \pm 2 \ldots) \qquad \ldots(3.36)$$

$$\Theta_{kq} = (-1)^q \left[\frac{2k+1}{2} \quad \frac{(k-q)!}{(k+q)!}\right] P_k^q \,(\cos\theta) \quad (q \geq 0)$$

and

$$\Theta_{kq} = \left[\frac{2k+1}{2}\right] \quad \frac{(k-|q|)!}{(k+|q|)!} \; P_k^q \,(\cos\theta) \quad (q \leq 0)$$

$$\ldots\ldots(3.37)$$

where P_k^q (cos θ) is legendre polynomial.

Thus the explicity form of these spherical harmonics for the ligand ions are [49].

$$\Upsilon_2^0(\theta'_i\phi'_i) = \frac{1}{\sqrt{2\pi}} \; \frac{\sqrt{5}}{\sqrt{2}} \; (3\cos^2\theta'_i - 1)$$

$$\Upsilon_4^0(\theta'_i\phi'_i) = \frac{1}{\sqrt{2\pi}} \; \frac{3}{8\sqrt{2}} \; (35\cos^4\theta'_i - 30\cos^2\theta'_i + 3)$$

$$\Upsilon_4^{\pm 3}(\theta'_i\phi'_i) = \mp \frac{1}{\sqrt{2\pi}} \; \frac{3\sqrt{35}}{4\sqrt{2}} \sin^3\theta'_i \, \cos\theta'_i \, e^{\pm 3i\phi'} \qquad \ldots\ldots(3.38)$$

by using equation (3.34) one obtains

$$C_2^0 \, R_4(r) = ze \left(\frac{\pi}{5}\right)^{\frac{1}{2}} \sum_{i=1}^{4} \left[3\cos^2\theta'_i - 1\right] \frac{r^2}{R^3}$$

$$C_4^0 \, R_4(r) = ze \, \frac{r^4}{R^5} \, \frac{\pi^{\frac{1}{2}}}{12} \sum_{i=1}^{4} \left[35\cos^4\theta'_i - 30\cos^2\theta'_i + 3\right]$$

$$C_4^{\pm 3} R_4(r) = ze \frac{r^4}{R^5} \, \frac{(35\pi)^{\frac{1}{2}}}{6} \sum_{i=1}^{4} \sin^3\theta'_i \, \cos\theta'_i \, e^{\pm 3i\phi'} \qquad \ldots\ldots(3.39)$$

Therefore

$$V_{c3v} = ze\frac{r^2}{R^3}\left(\frac{\pi}{5}\right)^{\frac{1}{2}} (3\cos^2\Theta'_i - 1)\Upsilon_2^0$$

$$+ze\frac{r^4}{R^5}\frac{\pi^{\frac{1}{2}}}{12}\sum_{i=1}^{4}\left[35\cos^4\Theta'_i - 30\cos^2\Theta'_i + 3\right]\Upsilon_4^0$$

$$+ ze\frac{r^4}{R^5}\frac{(35\pi)^{\frac{1}{2}}}{6}\sum_{i=1}^{4}\sin^3\Theta'_i \cos\Theta'_i e^{\pm 3i\phi'}\left[\Upsilon_4^{-3} - \Upsilon_4^{3}\right]$$

...(3.40)

Using the values of Θ'_i and ϕ'_i from table (3.1), one obtains

$$Vc_{3v} = -ze\frac{r^2}{R^3}\left(\frac{\pi}{5}\right)^{\frac{1}{2}} (0.4049445)Y_2^0$$

$$+ \quad ze\frac{r^4}{R^5}\frac{(\pi)^{\frac{1}{2}}}{12} (11.508452)Y_4^0$$

$$+ \quad ze\frac{r^4}{R^5}\frac{(35)^{\frac{1}{2}}}{6} (0.2320577)\left[Y_4^3 - Y_4^{-3}\right]$$

.....(3.41)

This expression for Vc allows to do numerical calculations of the energy levels of Ti^{2+} ions in CdS having C_{3v} symetry distortion.

3.6 Electronic State of Ti^{2+} Ion in T_d Crystal Field

Ti^{2+} free ion has two electrons in its unfilled d-orbitals, having ground state as ^3F and first excited triplet states ^3P. In CdS crystal Ti^{2+} ion replaces central Cd ion in the lattice. This leads to a week axial distortion along C_3 axis of T_d symmetry. This configuration belongs to point group C_{3v}.

The wavefunctions for these terms are constructed in weak crystal field approximation, since for first transition series, this holds good[53]. For the ^3F term, there are seven orbital functions. The seven orbital functions are constructed from information found in Table 1.1. The M_L values for a ^3F term run from +3 to -3 and from the Table of d^2 configuration, the corresponding products are found. For two electron system of Ti^{2+} ion, in the weak field scheme, the corresponding wave functions are given in Table 3.2, where d_2, d_1, d_o, d_{-1}, d_2 specify the hydrogen like d-wave functions as designed by the m_l quantum number used as a subscript. Their explicit form are

$$
\begin{aligned}
d_2 &= R_2Y_{22}(\Theta\Phi) \\
d_1 &= R_2Y_{21}(\Theta\Phi) \\
d_o &= R_2Y_{20}(\Theta\Phi) \qquad \ldots(3.42) \\
d_{-1} &= R_2Y_{2-1}(\Theta\Phi) \\
d_{-2} &= R_2Y_{2-2}(\Theta\Phi)
\end{aligned}
$$

TABLE 3.2 POSSIBLE d-ORBITAL FOR DIFFERENT VALUES OF M_L FOR ^3F TERM

M_L	d-orbitals
3	(d_2d_1)
2	(d_2d_o)
1	$(d_2d_{-1}),(d_1d_o)$
0	$(d_2d_{-2}),(d_1d_{-1})$
-1	$(d_1d_{-2}),(d_od_{-1})$
-2	(d_od_{-2})
-3	$(d_{-1}d_{-2})$

...(3.43)

Representing two-electron wave functions as $(L\ M_L)$, it is readily seen that four of the functions are

$$\begin{aligned}\Psi(33) &= (d_2d_{-1})\\ \Psi(32) &= (d_2d_o) \qquad \ldots(3.44)\\ \Psi(3-2) &= (d_od_{-2})\\ \Psi(3-3) &= (d_{-1}d_{-2})\end{aligned}$$

These are the only products of one-electron wavefunctions which give the appropriate M_L value. Since the one-electron d-functions are normalized, so the resultant products are also normalized.

However a problem exists with respect to the $\Psi(3,1)$, $\Psi(3,0)$ and $\Psi(3-1)$ functions. Since there are two products of one electron functions which have the requisite M_L values, there is no good reason for choosing one of these functions over the other. Therefore a linear combination of both functions is taken.

To do this the raising or lowering operators can be used. But for this calculations, the lowering operator L_, which is defined as

$$L_-\Psi(L,M_L) = \sqrt{(L-M_L+1)\ (L+M_L)}\ \Psi(L,M_L-1)$$

has been used.

Starting with $\Psi(32) = d_2d_o$, operating the equation by L_, one obtains

Left hand side

$$L_-\Psi(32) = \sqrt{(3-2+1)(3+2)}\ \Psi(31) \qquad \ldots(3.45)$$

and

Right hand side

$$L_-\ (d_2d_o) = \sqrt{(2-2+1)\ (2+2)}\ (d_1d_o) + \sqrt{(2-0+1)(2+0)}\ (d_2d_{-1}) \qquad \ldots(3.46)$$

equating equations (3.45) and (3.46) one gets

$$\Psi(31) = \sqrt{2/5}\ d_1d_o + \sqrt{3/5}\ d_2d_{-1}$$

Repeating the same procedure for the others, one obtains the seven orbital function for ^3F as follows

$$
\begin{aligned}
\Psi(33) &= d_2d_1 \\
\Psi(32) &= d_2d_o \\
\Psi(31) &= 2/5\ d_1d_o + 3/5\ d_2d_{-1} \qquad \ldots(3.47) \\
\Psi(30) &= 4/5\ d_1d_{-1} + 3/5\ d_2d_{-2} \\
\Psi(3-1) &= 2/5\ d_od_{-1} + 3/5\ d_1d_{-2} \\
\Psi(3-2) &= d_od_{-2} \\
\Psi(3-3) &= d_{-2}d_{-1}
\end{aligned}
$$

For the ^3p term there are three orbital functions. Since the three orbital functions $\Psi(11)$, $\Psi(10)$. $\Psi(1-1)$ have same M_L as with the orbital functions $\Psi(31)$, $\Psi(30)$, $\Psi(3-1)$ for ^3F term, therefore they are obtained from the same products of hydrogen like d wave functions. But since ^3p and ^3F are different terms then the orbital functions can't be same but they are othogonal thus using orthogonality relationship

$$\alpha\alpha' + \beta\beta' = 0$$

where α and α' are coefficient for ^3F orbital functions and β and β' are coefficients for the ^3p orbital functions.

Finally the following orbital functions for ^3p term are obtained

$$
\begin{aligned}
(11) &= \sqrt{2/5}\, d_2d_{-1} - \sqrt{3/5}\ d_1d_o \\
(10) &= \sqrt{4/5}\, d_2d_{-2} - \sqrt{1/5}\, d_1d_{-1} \qquad \ldots(3.48) \\
(1-1) &= \sqrt{2/5}\, d_{-2}d_1 - \sqrt{3/5}\, d_{-1}d_o
\end{aligned}
$$

The equations (3.47) and (3.48) represent the two electrons wavefunctions of Ti^{2+} ions, which will be used for energy calculations.

CHAPTER FOUR

COMPUTATION OF ENERGY STATES OF Ti^{2+} ION IN CdS

4.1 Term Energies

The energy levels of a configuration (terms) are given as a function of the three racah parameters A, B, C which are related to F^k'S through the equation (1.39). Using equations (2.19) and (2.27) one obtains the following values of F^k'S

$$F^o = 144944 \text{ cm}^{-1}$$
$$F^2 = 53270 \text{ cm}^{-1} \qquad \ldots(4.1)$$
$$F^4 = 34146 \text{ cm}^{-1}$$

Here conversion factor 1 a.u = 2.19474×10^5 cm^{-1} has been used. Using equation (1.39), one obtains

$$A_o = 141150 \text{ cm}^{-1}$$
$$B_o = 700 \text{ cm}^{-1} \qquad \ldots(4.2)$$

and

$$C_o = 2710 \text{ cm}^{-1}$$

where A_o , B_o and C_o are electrostatic parameters in the free state. Thus the energy terms of ^3F and ^3P have the values (from Table 1.3)

$$^3F = 135550 \text{ cm}^{-1}$$
$$^3P = 146050 \text{ cm}^{-1} \qquad \ldots(4.3)$$

The two particle operator parameters B and C describing electron-electron repulsion would be reduced in crystal[44] as

$$B = N^4 B_o$$
$$C = N^4 C_o \qquad \ldots(4.4)$$

where N^4 denotes the average covalency reduction factor and B and C denote Racah electrostatic parameters in the crystal. The reason behind the reduction is the possibility of the polarization of the ligand. The role of polarisable ligands in the spectroscopy of transition metal clusters has been extensively investigated[44].

For the $Ti^{2+}-S^{2-}$ clusters[24], the value obtained is $N^4 = 0.5$.

Hence

$$B = 350\ cm^{-1}$$
$$C = 1355\ cm^{-1} \qquad \ldots(4.5)$$

For the same reason the single particle operator parameter describing crystal field would be reduced in crystal as

$$\langle d|V|d\rangle = N^2 \langle d|V|d\rangle_o, \qquad \ldots(4.6)$$

equivalently, $\langle r^n\rangle$ will be reduced as

$$\langle r^n\rangle = N^2 \langle d|r^n|d\rangle_o$$
$$= N^2 \langle r^n\rangle_o \qquad \ldots(4.7)$$

where $\langle r^n \rangle$ and $\langle r^n \rangle_o$ denote expectation values in the crystal field and free state respectively.

Therefore crystal field parameter Dq, in tetrahedral crystal field, is obtained using.

$$Dq = \frac{-2Ze}{27R^5} \langle r^4 \rangle \qquad \ldots(4.8)$$

with

$$\langle r^4 \rangle = N^2 \langle r^4 \rangle_o$$

and

$$\langle r^4 \rangle_o = \int r^6 |R_{3d}(r)|^2 dr \qquad \ldots(4.9)$$

where $R_{3d}(r)$ is given by equation (2.28). The value obtained is

$$Dq = 338 \text{ cm}^{-1} \qquad \ldots(4.10)$$

4.2 Integrals Involving Three Spherical Harmonics

It is well known that the integral

$$\int_0^{2\pi} Y_{l_1}^{m_{l_1}} Y_{l_2}^{m_{l_2}} Y_{l_3}^{m_{l_3}} d\phi = \int_0^{2\pi} Y_{l'}^{m'} d\phi = 0 \qquad \ldots(4.11)$$

only if $m' = m_{l_1} + m_{l_2} + m_{l_3} = 0$

Applying this type of integral for our case of $V_{C_{3V}}$ crystal operator, which is given by

$$V_c = d\, Y_2^0 + bY_4^0 + c(Y_4^3 + Y_4^{-3}) \qquad \ldots (4.12)$$

(i) Consider the matrix elements of Y_2^0, Y_4^0 of the type

$$\int_0^{2\pi} Y_{l_1}^{*m_{l_1}} Y_{l_2}^{0} Y_{l_3}^{m_{l_3}} \, d\phi ,$$

which is non-zero, when

$$m_{l_1}^* + m_{l_3} = 0$$
$$-m_{l_1} + m_{l_3} = 0$$
$$m_{l_1} = m_{l_3}$$

This shows that the matrix element arising from these terms of potential, i.e. from Y_2^0 and Y_4^0 are diagonal.

(ii) The integral involving Y_4^3 are zero unless

$$m_{l_1}^* + 3 + m_{l_3} = 0$$
$$-m_{l_1} + m_{l_3} = 0$$
$$m_{l_1} = m_{l_3} + 3$$

These are <2,-1> and <1,-2>

(iii) Also integrals involving Y_4^{-3} are zero unless

$$m_{l_1}^* - 3 + m_{l_3} = 0$$
$$-m_{l_1} + m_{l_3} = 3$$
$$m_{l_1} = m_{l_3} - 3$$

These are <-1 2> and <-2 1>. Thus total number of matrix elements of $V_{C_{3v}}$ for d-configuration are reduced.

4.3 Matrix Elements of Single Electron Operator

According to degenerate perturbation theory the secular equation

$$\left| H_{ij} - E\delta_{ij} \right| = 0 \qquad \ldots(4.13)$$

is to be solved in order to obtain the energy levels. Here H is the Hamiltonian, E is the eigen value and δ_{ij} is Kroniker δ symbol, having values $\delta_{ii} = 1$ and $\delta_{ij} = 0$. Thus the integrals of the form

$$\int \psi_i^* \hat{V} \psi_j \, d\tau = \langle \psi_i | \hat{V} | \psi_j \rangle \qquad \ldots(4.14)$$

are to be evaluated.

In the weak-field approximation, the basis set of wave functions are expressed as

$$N\ R(r)\ \Theta(\theta)\Phi(\Phi)$$

where N is normalization constant.

Thus the integrals of the type

$$\langle R(r)\,\Theta(\theta)\,\Phi(\varphi) | \hat{V}_{(r\theta\varphi)} | R(r)\,\Theta(\theta)\,\Phi(\varphi) \rangle \qquad \ldots(4.15)$$

are to be evaluated.

Evaluation of one of the matrix elements is illustrated as follows

$$<d_2|V_c|d_2>$$

where

$$d2=R_{3d}(r)Y_2^2 \qquad \ldots.(4.16)$$

$$=R_{3d}(r)\Theta_2^2\Phi_2$$

since $\Phi_2=\frac{1}{\sqrt{2\pi}}\,e^{2i\varphi}$

Then

$$d_2=\frac{1}{\sqrt{2\pi}}\,R_{3d}(r)\Theta_2^2 e^{2i\varphi} \qquad \ldots.(4.18)$$

Taking the expression of Vc_{3v} equation (3.41), one obtains

$$<d_2|V_{c_{3v}}|d_2>=<R_{3d}(r)\,\frac{1}{\sqrt{2\pi}}\,\Theta_2^2 e^{2i\varphi}\Big| - 0.4049445x$$

$$ze\frac{r^2}{r^3}\left(\frac{\pi}{5}\right)^{\frac{1}{2}}Y_2^0 + 11.508452\ ze\frac{r^4}{R^5}\,\frac{(\pi)^{\frac{1}{2}}}{12}\,Y_4^0\Big|$$

$$R_{3d}(r)\frac{1}{\sqrt{2\pi}}\,\Theta_2^2\,e^{-2i\varphi}> \qquad \ldots.(4.19)$$

while the contribution due to Y_4^3 and Y_4^{-3} will be zero

$$\langle d_2|\hat{V}_{C_{3v}}|d_2\rangle = \frac{ze}{R^3}\,(-0.4049445)\left(\frac{\pi}{5}\right)^{\frac{1}{2}}\langle R_{3d}(r)|r^2|R_{3d}(r)\rangle$$

$$x\langle\Theta_2^2|\Theta_2^0|\Theta_2^2\rangle\,\frac{1}{2\pi}\langle e^{2i\varphi}|e^{0i\varphi}|e^{-2i\varphi}\rangle\frac{1}{\sqrt{2\pi}}$$

$$+\ 11.508452\ \frac{ze}{R^5}\ \frac{\pi^{\frac{1}{2}}}{12}\ \langle R_{3d}(r)|r^4|R_{3d}(r)\rangle x$$

$$\langle\Theta_2^2|\Theta_4^0|\Theta_2^2\rangle\ \frac{1}{2\pi\sqrt{2\pi}}\ \langle e^{2i\varphi}|e^{0i\varphi}|e^{-2i\varphi}\rangle \qquad \ldots(4.20)$$

but

$$\langle e^{2i\varphi}|e^{0i\varphi}|e^{-2i\varphi}\rangle = \int_0^{2\pi} e^{2i\varphi}\ e^{0i\varphi}\ e^{-2i\varphi}\ d\varphi$$

$$= \int_0^{2\pi} e^{2i\varphi}\ d\varphi$$

$$= 2\pi$$

and

$$\langle R_{3d}(r)|r^2|R_{3d}(r)\rangle = \int_0^{\infty} |R_{3d}(r)|^2 r^4\ dr$$

$$= \int_0^{\infty}(a_1^2N_1^2r^8e^{-2\xi_1 r}$$

$$+\ a_2^2N_2^2r^8e-\xi_2 r\ +\ 2a_1N_1a_2N_2r^8\ e^{-(\xi_1+\xi_2)r}\ )dr$$

$$\ldots(4.21)$$

By integrating, one gets

$$\langle R_{3d}(r) | r^2 | R_{3d}(r) \rangle$$

$$= 40320 \left[\frac{a_1^2 N_1^2}{(2\xi_1)^9} + \frac{a_2^2 N_2^2}{(2\xi_2)^9} + \frac{2a_1 N_1 a_2 N_2}{(\xi_1+\xi_2)^9} \right] \qquad \ldots(4.22)$$

Substituting the values of a_1, N_1, a_2, N_2 from (2.27) the value obtained is

$$\langle R_{3d}^{(r)} | \; r^2 \; | \; R_{3d}^{(r)} \rangle = 2.533221 \text{ a.u}$$

$$= 555976 \text{ cm}^{-1}$$

Similarly

$$\langle R_{3d}(r) | r^4 | R_{3d}(r) \rangle = \int_0^\infty |R_{3d}(r)|^2 r^6 \, dr$$

$$= 3628800 \left[\frac{a_1^2 N_1^2}{(2\xi_1)^{11}} + \frac{a_2^2 N_2^2}{(2\xi_2)^{11}} + \frac{2a_1 N_1 a_2 N_2}{(\xi_1+\xi_2)^{11}} \right]$$

$$= 15.162524 \text{ a.u}$$

$$= 3327780 \text{ cm}^{-1} \qquad \ldots(4.23)$$

and

$$\langle \theta_2^2 | \theta_2^0 | \theta_2^2 \rangle = \frac{15\sqrt{10}}{64} \int_0^\pi (3\cos^2\theta \sin^5\theta - \sin^5\theta) \, d\theta \qquad \ldots(4.24)$$

Using the formulas

$$\int_0^{\pi/2} \sin^{n-1}\theta \cos^{m-1}\theta \, d\theta = \frac{1}{2} B\left(\frac{n}{2}, \frac{m}{2}\right) \qquad \ldots(4.25)$$

and

$$B\left(\frac{n}{2},\frac{m}{2}\right)=\frac{\Gamma\left(\frac{n}{2}\right)\left(\frac{m}{2}\right)}{\Gamma\left(\frac{n+m}{2}\right)} \qquad \ldots(4.26)$$

where $\Gamma j = (j-1)!$ ...(4.27)

and

$$\Gamma(j+1/2) = 1 \ \ldots\ldots\ldots\ (2j-1) \qquad \ldots(4.28)$$

Integral (4.24) can be evaluated and thus substituted in equation (4.20) to obtain

$$\langle d_2 | V_{C_{3v}} | d_2 \rangle = 1876 \ \mathrm{cm}^{-1}$$

Similarly

$$\begin{aligned}
\langle d_1 | V_{C_{3v}} | d_1 \rangle &= -2632 \ \mathrm{cm}^{-1} \\
\langle d_o | V_{C_{3v}} | d_o \rangle &= 1260 \ \mathrm{cm}^{-1} \qquad \ldots(4.29) \\
\langle d_{-1} | V_{C_{3v}} | d_2 \rangle &= -622 \ \mathrm{cm}^{-1} \\
\langle d_1 | V_{C_{3v}} | d_{-2} \rangle &= 622 \ \mathrm{cm}^{-1}
\end{aligned}$$

The effective nuclear charge, Z for the sulphide ion, used in the calculation has been determined by using the Slater rule[53].

4.4 Crystal Field Calculations for two Electrons

The crystal field calculation in the weak field scheme for two (or more) d-electrons proceed essentially in the same manner as that described for one d-electron. The seven orbital wave function for the ^3F ground state of the free ion are used in the perturbation calculation with the triagonal crystal field potential.

The crystal field potential energy operator for two electron system is written as

$$V_{C_{3v}} = \overset{1}{V}_{C_{3v}} + \overset{2}{V}_{C_{3v}} \qquad \ldots(4.30)$$

where the superscripts designate the electrons 1 and 2. Recalling that the summation ($\sum_j$) in equation (3.31) was over the number of two electrons.

The seven orbital wave functions for d^2-configuration have already been constructed in equation (3.47).

The seven orbital wave functions for ^3F state need to be modified to meet the requirements of the Pauli's exclussion principle, which stipulates that there must be a change in the sign of the wave functions if the coordinates of any two electrons are interchanged.

The general expression for N electron wave function, which obey the Pauli's principle, is given by Slater determinant[8].

$$|\psi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |n_1 l_1 m_1\rangle^1 & \cdots\cdots & |n_1 l_2 m_1\rangle^2 \\ \vdots & \ddots & \vdots \\ |n_N l_N m_N\rangle^1 & \cdots\cdots & |n_N l_N m_N\rangle^n \end{vmatrix} \quad \ldots(4.31)$$

where the superscript j on the ket $|n_1 l_1 m_1\rangle^j$ designates the electrons, whose coordinates are to appear in the orbital designated by the indicated quantum number $(n_1 l_1 m_1)$.

One of the ^3F functions $\psi(33)$ can now be expressed for two electron, d^2-orbital as

$$\psi(33) = d_1 d_2$$

$$\psi(33) = \frac{1}{\sqrt{2}} \begin{vmatrix} d_1^1 d_1^2 \\ d_2^1 d_2^2 \end{vmatrix}$$

Therefore

$$\langle\psi(33)|V^1_{C_{3v}} + V^2_{C_{3v}}|\psi(33)\rangle = \left\langle \frac{1}{\sqrt{2}} \begin{vmatrix} d_1^1 d_1^2 \\ d_2^1 d_2^2 \end{vmatrix} (V^1_{C_{3v}} + V^2_{C_{3v}}) \right.$$

$$\left. \begin{vmatrix} d_1^1 d_1^2 \\ d_2^1 d_2^2 \end{vmatrix} \frac{1}{\sqrt{2}} \right\rangle$$

$$= \frac{1}{2} \langle (d_1^1\, d_2^2 - d_2^1\, d_1^2)|V^1_{C_{3v}} + V^2_{C_{3v}}|(d_1^1\, d_1^2 - d_2^1\, d_1^2)\rangle \quad \ldots.(4.32)$$

$$= \frac{1}{2}\Big\{<d_2^2\, d_1^1|V^1_{c_{3v}}|d_2^2 d_1^1>+<d_2^2 d_1^1|V^2_{c_{3v}}|d_2^2 d_1^1>$$

$$-<d_2^2 d_1^1|V^1_{c_{3v}}|d_1^2 d_2^1>-<d_2^2 d_1^1|V^2_{c_{3v}}|d_1^2 d_2^1>$$

$$-<d_2^1 d_1^2|V^1_{c_{3v}}|d_2^2 d_1^1>-<d_2^1 d_1^2|V^2_{c_{3v}}|d_2^2 d_1^1>$$

$$+<d_2^1 d_1^2|V^1_{c_{3v}}|d_2^1 d_1^2>+<d_2^2 d_1^1|V^2_{c_{3v}}|d_2^2 d_1^1> \qquad \ldots.(4.33)$$

The crystal field potentials operates only on one electron, for example

$$<d_2^1 d_1^2|V^1_{c_{3v}}|d_2^1 d_1^2>=<d_2^1|V^1_{c_{3v}}|d_2^1><d_1^2 d_1^2>$$

$$=<d_2^1|V^1_{c_{3v}}|d_2^1> \qquad \ldots\ldots(4.34)$$

Since $<d_1^2:d_1^2>=1$ by normalization.

Using the same procedure the non-zero matric elements for two-electron system are

$$<\psi(33)|V^1_{c_{3v}}+V^2_{c_{3v}}|\psi(31)>=1002\ \text{cm}^{-1}$$

$$<\psi(32)|V^1_{c_{3v}}+V^2_{c_{3v}}|\psi(32)>=3136^{-1}\text{cm}$$

$$<\psi(31)|V^1_{c_{3v}}+V^2_{c_{3v}}|\psi(31)>=1002\ \text{cm}^{-1}$$

$$<\psi(30)|V^{1}_{C_{3v}} + V^{2}_{C_{3v}}|\psi(30)>=-3461\mathrm{cm}^{-1}$$

$$<\psi(33)|V^{1}_{C_{3v}} + V^{2}_{C_{3v}}|\psi(3,0)>=835\ \mathrm{cm}^{-1}$$

$$<\psi(32)|V^{1}_{C_{3v}} + V^{2}_{C_{3v}}|\psi(3-1)>=393\ \mathrm{cm}^{-1}$$

$$<\psi(31)|V^{1}_{C_{3v}} + V^{2}_{C_{3v}}|\psi(3-2)>=-393\ \mathrm{cm}^{-1}$$

Equations (4.27) and (4.28) were used for calculating these values

Hence to obtain the eigen values the determinant of the matrix bacomes

$$\begin{array}{c|ccccccc|}
M_L & 3 & 2 & 1 & 0 & -1 & -2 & -3 \\
\hline
3 & -756-E & & & 835 & & & \\
2 & & 3136-E & & & 393 & & \\
1 & & & 1002-E & & & -393 & \\
0 & 835 & & & -3461-E & & & 835 \\
-1 & & 393 & & & -1002-E & & \\
-2 & & & -393 & & & 3136-E & \\
-3 & & & & 835 & & & -756-E \\
\end{array}$$

Since square matrices have the same eigen value as a triagonal matrices then its necessary to triagonalize the matrix, so that it is easier to find the determinant[46].

The triangular matrix looks like

$$\begin{array}{c|ccccccc|}
M_L & 3 & 0 & 3 & -2 & +1 & -2 & +1 \\
\hline
3 & -756-E & 835 & 0 & & & & \\
0 & 835 & -3461-E & 835 & & & & \\
-3 & 0 & 835 & -756-E & & & & \\
-2 & & & & -3136-E & -393 & & \\
+1 & & & & -393 & 102-E & & \\
-2 & & & & & & 3136-E & 393 \\
+1 & & & & & & 393 & 1002-E \\
\hline
\end{array}$$

Finding the determinant of the triangular matrix, the values obtained are

$E_1 = -512 \text{ cm}^{-1}$

$E_2 = -756 \text{ cm}^{-1}$

$E_3 = -3904 \text{ cm}^{-1}$

$E_4 = 932 \text{ cm}^{-1}$

$E_5 = 3206 \text{ cm}^{-1}$

$E_6 = E_7 = 0$

Thus the ^3F term is split into five states in axial crystal field $\hat{V}_{C_{3v}}$.

The crystal field calculation for the ^3P term yield only the diagonal elements. Calculation of one of the matrix elements are as follows

$$\langle \psi(11) | V^1_{C_{3v}} + V^2_{C_{3v}} | \psi(11) \rangle$$

$$= \Big\langle \Big\{ \frac{1}{\sqrt{2}} \sqrt{\frac{2}{5}} \left(d^1_2 d^2_{-1} - d^1_{-1} d^2_2 \right)$$

$$- \frac{1}{\sqrt{2}} \sqrt{3/5} \left(d^1_1 d^2_0 - d^2_1 d^1_0 \right) \Big\} \Big| V^1_{C_{3v}} + V^2_{C_{3v}} \Big| \Big\{ \frac{1}{\sqrt{2}} \sqrt{\frac{2}{5}} \left(d^1_2 d^2_{-1} - d^1_{-1} d^2_2 \right)$$

$$- \frac{1}{\sqrt{2}} \sqrt{\frac{3}{5}} \left(d^1_1 d^2_0 - d^2_1 d^1_0 \right) \Big\} \Big\rangle$$

Out of all the matrix elements the following diagonal matrix elements are non-zero.

$$\frac{3}{10} \Big\{ \langle d^1_2 | V^1_{C_{3v}} | d^1_2 \rangle + \langle d^2_0 | V^2_{C_{3v}} | d^2_0 \rangle$$

$$+ \langle d^2_1 | V^2_{C_{3v}} | d^2_1 \rangle + \langle d^1_0 | V^2_{C_{3v}} | d^1_0 \rangle \Big\}$$

$$= -1126 \text{ cm}^{-1}$$

Similarly

$$\langle \psi(1\,-1) | V^1_{C_{3v}} + V^2_{C_{3v}} | \psi(1\,-1) \rangle = -1126 \text{ cm}^{-1}$$

$$\langle \psi(10) | V^1_{C_{3v}} + V^2_{C_{3v}} | \psi(10) \rangle = 1949 \text{ cm}^{-1}$$

Equation (4.29) were used to calculate this values.

The matrix obtained should be

$$\begin{array}{c|ccc}
M_L & 1 & 0 & -1 \\
\hline
1 & -1126-E & 0 & 0 \\
0 & 0 & 1949-E & 0 \\
-1 & 0 & 0 & -1126-E
\end{array}$$

Solving the matrix by equating determinant to zero, the eigen values obtained are

$$E_8 = -1126 \text{ cm}^{-1}$$

$$E_9 = 1949 \text{ cm}^{-1}$$

$$E_{10} = -1126 \text{ cm}^{-1}$$

Finally the splitting of the $3d^2$ configuration of Ti^{2+} in the axially distorted crystal field (neglecting-spin-orbit-interaction) has been shown in figure 4.1.

The calculated spectrum of Ti^{2+} ion in axially distorted crystal field ($V_{C_{3V}}$) is a fine spectrum which does not agree with the observed spectrum. Since the distortion along C_{3v} axis is small this splitting is not observed experimentally.

Thus in the next section the tetrahedral symmetry for Ti^{2+} in CdS has been taken into account.

4.5 Energy Spectrum in Tetrahedral Symmetry

Since in the case of the present complex the electronic states are essentially localized on the Ti ion and the four S ligands are arranged nearly in the form of a regular tetrahedral in CdS, the deviation from the real Wurtzite structure is very small[24]. It will be a good approximation to consider crystal field operator $\hat{V}_c$ in T_d symmetry, and to neglect the trigonal (C_{3v}) component. This approximation is also supported by the optical spectra of the transition metal

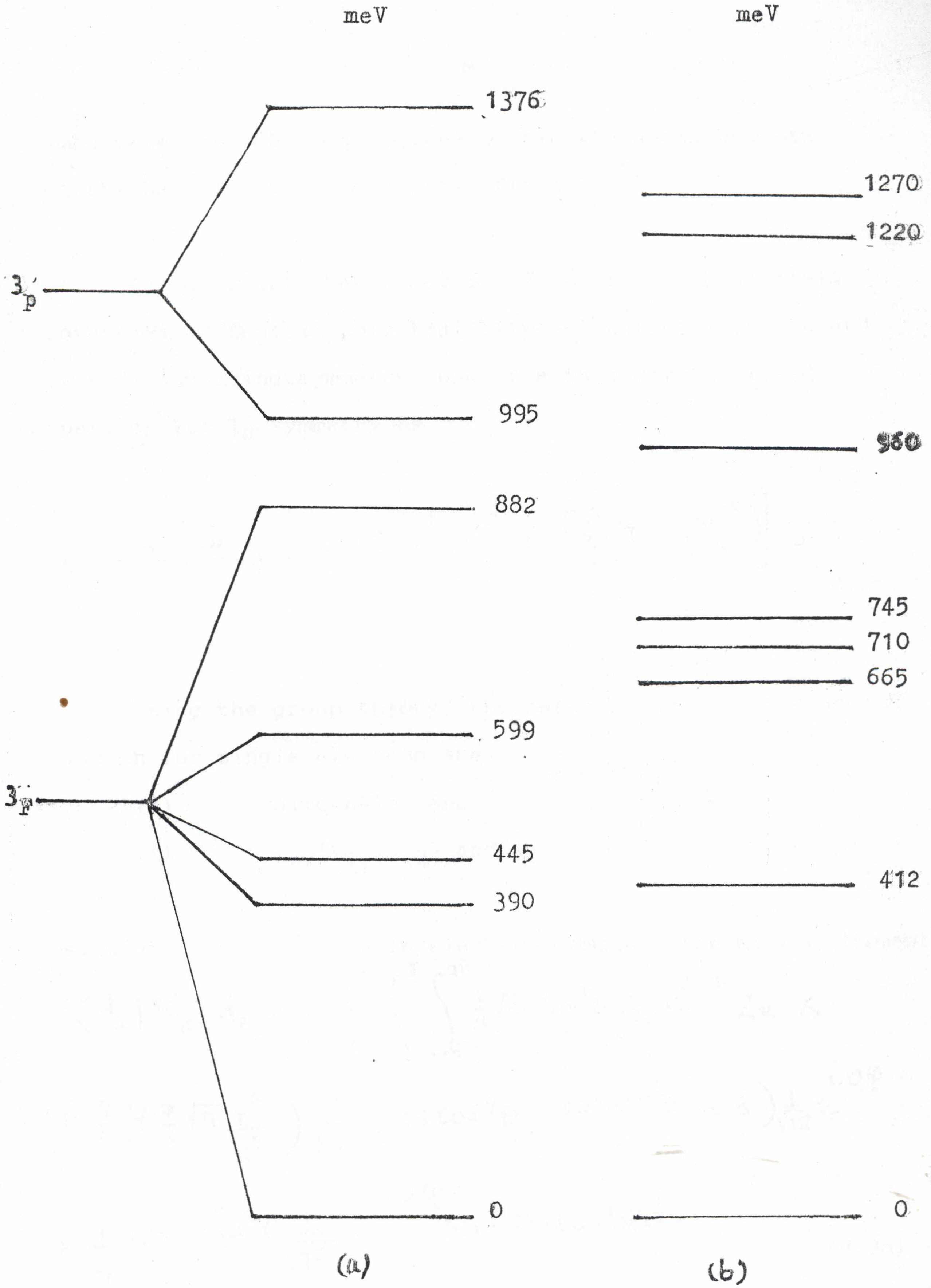

Fig. 4.1 Energy spectrum of Ti^{2+} ion in CdS (a) in C_{3V} symmetry (b) experiment.

impurities in CdS investigated so far which can be understood on the basis of a cubic crystal field[55].

In the point charge model, expressing crystal field potential as Coulomb potential between central electron and ligands and using symmetry, one obtains a crystal field operator for T_d symmetry as

$$V_{T_d} = Ze\left(-\frac{4}{9}\right)\left(\frac{7}{3}\sqrt{\pi}\,\frac{r^4}{R^5}\right)\left[Y_4^0 + \sqrt{\frac{5}{14}}\left(Y_4^4 + Y_4^{-4}\right)\right] \qquad \ldots(4.35)$$

Using the group theory, the matrix elements that do not vanish for single electron are

(i) diagonals and

(ii) $\langle d_2 | V_{T_d} | d_{-2} \rangle$ and $\langle d_{-2} | V_{T_d} | d_2 \rangle$

Using equations for single electron complex, the matric element

$$\langle d_2 | V_{T_d} | d_2 \rangle = \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \frac{1}{4}\sqrt{15}\,\sin^2\theta \cdot \frac{1}{\sqrt{2\pi}}\,e^{2i\varphi}\, Ze \times$$

$$\left(-\frac{4}{9}\right)\left(\frac{7}{3}\sqrt{\pi}\,\frac{r^4}{R^5}\right)\frac{3}{8\sqrt{2}}\left(35\cos^4\theta - 30\cos^2\theta + 3\right)\frac{1}{\sqrt{2\pi}}\,e^{i0\varphi}$$

$$\times \frac{1}{4}\sqrt{15}\,\sin^2\theta\,\frac{1}{\sqrt{2\pi}}\,e^{-i2\varphi}\,\sin\theta\, d\theta\, d\varphi\, dr \qquad \ldots(4.36)$$

Which has computational values as

$$\langle d_2 | V_{T_d} | d_2 \rangle = -338\ \mathrm{cm}^{-1}$$

Similarly

$$\langle d_1|V_{Td}|d_1\rangle = \langle d_{-1}|V_{Td}|d_{-1}\rangle = 1352\,cm^{-1}$$

$$\langle d_{-2}|V_{Td}|d_2\rangle = -1690\,cm^{-1}$$

$$\langle d_0|V_{Td}|d_2\rangle = -2025\,cm^{-1} \qquad \ldots(4.37)$$

As done in section 4.4, the matrix element for two-electrons system are obtained as

$$\langle \psi(33)|V_{Td}^1 + V_{Td}^2|\psi(33)\rangle = \langle \psi(3-3)|V_{Td}^1 + V_{Td}^2|\psi(3-3)\rangle = 1014\,cm^{-1}$$

$$\langle \psi(32)|V_{Td}^1 + V_{Td}^2|\psi(32)\rangle = \langle \psi(3-2)|V_{Td}^1 + V_{Td}^2|\psi(3-2)\rangle = -2366\,cm^{-1}$$

$$\langle \psi(32)|V_{Td}^1 + V_{Td}^2|\psi(3-2)\rangle = -1690$$

$$\langle \psi(31)|V_{Td}^1 + V_{Td}^2|\psi(31)\rangle = \langle \psi(3-1)|V_{Td}^1 + V_{Td}^2|\psi(3-1)\rangle = 338\,cm^{-1}$$

$$\langle \psi(30)|V_{Td}^1 + V_{Td}^2|\psi(30)\rangle = 2028\,cm^{-1}$$

$$\langle \psi(33)|V_{Td}^1 + V_{Td}^2|\psi(3-1)\rangle = \langle \psi(3-3)|V_{Td}^1 + V_{Td}^2|\psi(31)\rangle = 1309\,cm^{-1}$$

The matrix element of single electrons complex (equation 4.37) has been used to calculate the above values.

Thus the matrix obtained for ^3F state will be

$$\begin{array}{c|ccccccc|}
M_L & 3 & 2 & 1 & 0 & -1 & -2 & -3 \\
\hline
3 & 1014-E & & & & 1309 & & \\
2 & & -2366-E & & & & -1690 & \\
1 & & & 338-E & & & & 1309 \\
0 & & & & 2028-E & & & \\
-1 & 1309 & & & & 338-E & & \\
-2 & & -1690 & & & & -2366-E & \\
-3 & & & 1309 & & & & 1014-E
\end{array}$$

Converting the above matrix into triangular matrix form as done in section 4.4, one obtains

$$\begin{array}{c|ccccccc|}
M_L & 3 & -1 & 2 & -2 & 0 & -3 & 1 \\
\hline
3 & 1014-E & 1309 & & & & & \\
-1 & 1309 & 338-E & & & & & \\
2 & & & -1690-E & -2366 & & & \\
-2 & & & -2366 & -1690-E & & & \\
0 & & & & & 2028-E & & \\
-3 & & & & & & 1014-E & 1309 \\
1 & & & & & & 1309 & 338-E \\
\hline
\end{array}$$

Solving the above triangular matrix, the following values were obtained

$$E_1 = 2028 \ \text{cm}^{-1}$$

$$E_2 = -676 \ \text{cm}^{-1}$$

$$E_3 = -4056 \ \text{cm}^{-1}$$

Repeating the same procedure for ^3P state, it is found that

$$\langle \psi(31) \mid V_{T_d} \mid \psi(31) \rangle = \langle \psi(3-1) \mid V_{T_d} \mid \psi(3-1) \rangle$$

$$= \langle \psi(30) \mid V_{T_d} \mid \psi(30) \rangle = 0$$

Thus ^3p term does not split in the T_d symmetry.

Therefore the spectrum obtained is as in figure 4.2.

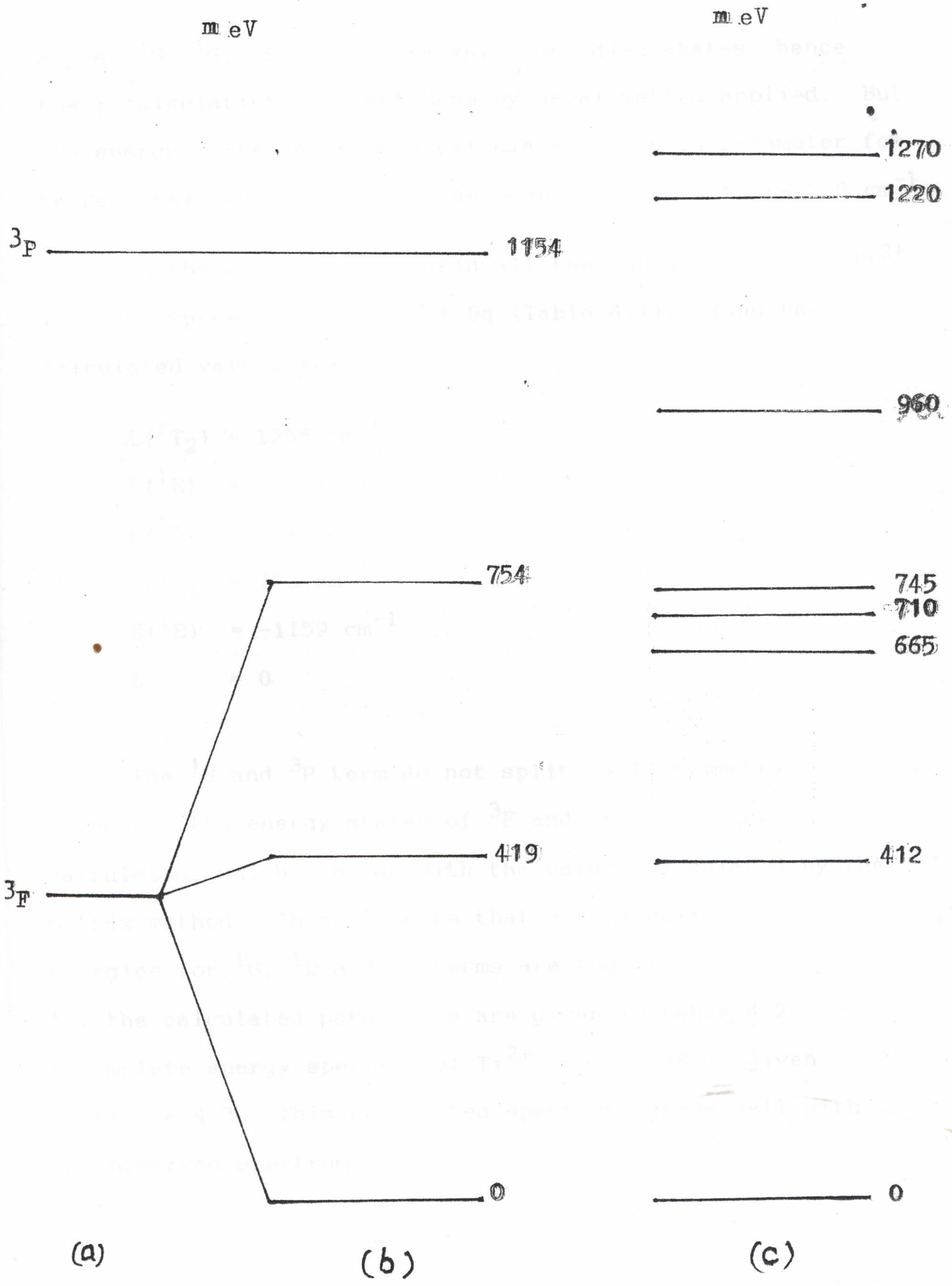

Fig. 4.2 Energy spectrum of Ti^{2+} in CdS (a) Free ion (b) in T_d symmetry (c) experimental value[24]

Since ^1S, ^1G, ^1D states are spin forbidden states, hence their calculation were not done by usual method applied. But the energy states, have been calculated using Dq parameter for tetrahedral symmetry, which has been calculated to be 338 cm^{-1}.

In the weak crystal field all the energy states of Ti^{2+} ion are expressed in terms of Dq (Table 4.1). Thus the calculated values are

^1G $E(^1T_2) = 1255\ cm^{-1}$

$E(^1E) = -193\ cm^{-1}$

$E(^1T_1) = -676\ cm^{-1}$

^1D $E(^1T_2) = 773\ cm^{-1}$

$E(^1E) = -1159\ cm^{-1}$

^1S $E = 0$

The ^1S and ^3P term do not split in T_d symmetry. Using Dq, the energy states of ^3F and ^3P were also calculated, which concide with the values calculated by the matrix method. This supports that our calculation of energies for ^1G, ^1D and ^1S terms are logical.

All the calculated parameters are given in table 4.2.

A complete energy spectrum of Ti^{2+} ion in CdS is given in figure 4.3. This calculated spectrum agrees well with the observed spectrum.

TABLE 4.1 TERM ENERGIES OF TETRAHEDRALLY BOUND d^2 SYMMETRY IN WEAK FIELD[53]

Terms of the Free ion	Term energy	Splitting of Terms in T_d symmetry	Tetrahedral split
^3F	A-8B	$^3T_1$	6Dq
		$^3T_2$	-2Dq
		$^3A_2$	-12Dq
^3P	A + 7B	$^3T_1$	0
^1S	A + 14B + 17C	$^1A_1$	0
^1D	A - 3B + 2C	$^1T_2$	16/7Dq
		^1E	-24/7Dq
^1G	A + 4B + 2C	$^1T_2$	26/7Dq
		^1E	-4/7Dq
		$^1T_1$	-2Dq
		$^1T_2$	-4Dq

TABLE 4.2 PARAMETERS FOR Ti^{2+} ION IN CdS CRYSTAL

Parameters	Observed (cm^{-1})	Calculated (cm^{-1})
F_o	–	144944
F_4	32206	34146
F_2	54206	53270
A_o	–	141150
B_o	720	700
C_o	2629	2710
ξ_d	120	120
Dq	332	338
A	–	70575
B	360	350
C	–	1355

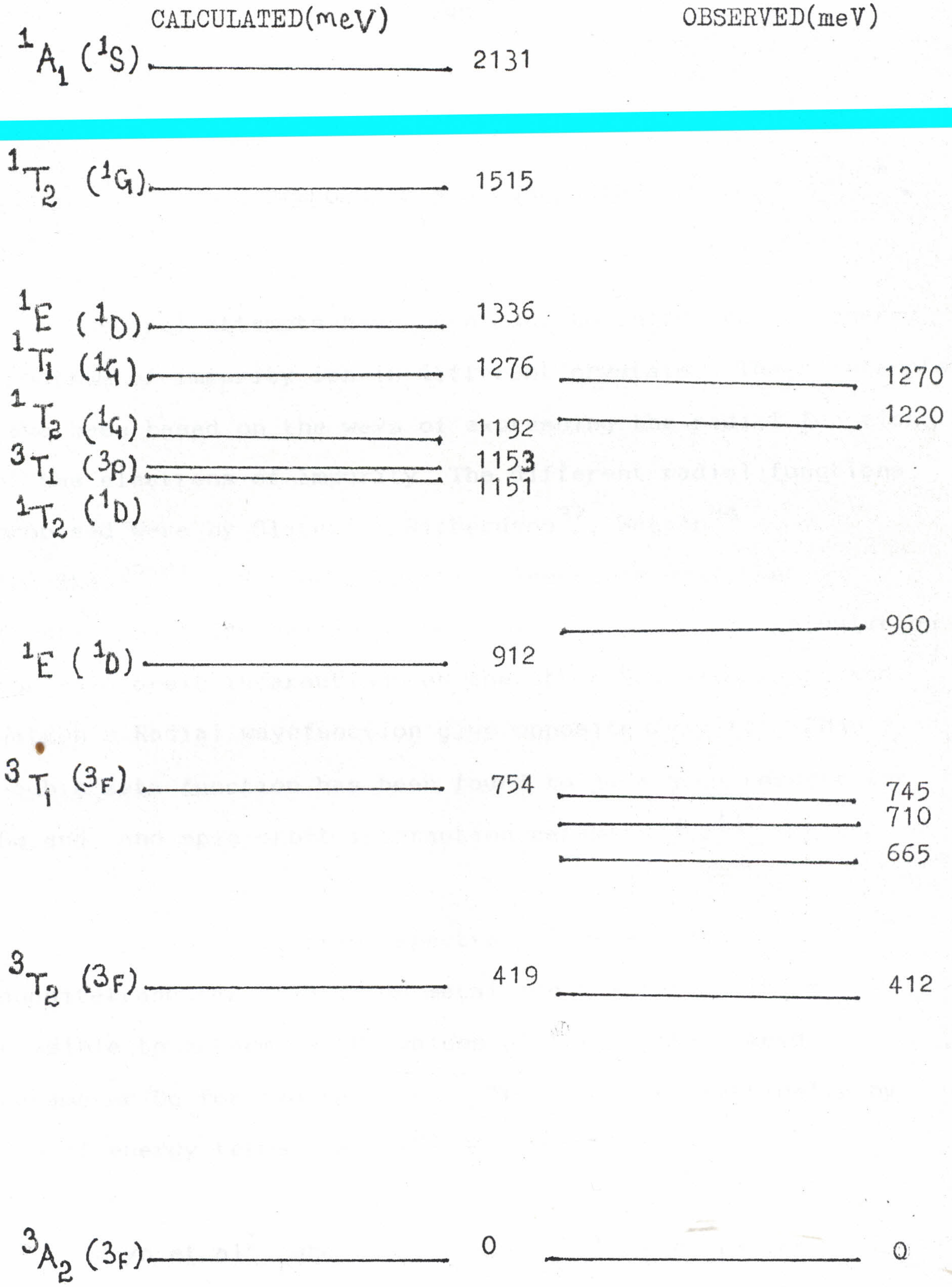

Fig. 4.3 Calculated and observed energy level of Ti^{2+} ($3d^2$) ions in the tetrahedral crystal field in CdS.

CHAPTER FIVE

DISCUSSION AND CONCLUSION

Several attempts have been made to calculate the energy spectrum of impurity ion in different crystals. These attempts have been based on the ways of expressing the radial function of the electrons of impurity. The different radial functions proposed were by Slater[7], Richardson[32], Watson[34] and Zhao[39-41]. Slater's function describes well the crystal splitting parameter Dq, while it gives bad calculation for spin orbit interaction, on the other had Richardson and Watson's Radial wavefunction give opposite results. Zhao's double zeta function has been found to give good results for Dq and and spin orbit interaction parameter ε_{1d}[44].

From the absorption spectra of tetrahedral or quasitetrahedral transition metal ion complexes, it is possible to determine the values of the crystal field parameter Dq for central ions. This is done graphically by use of energy terms diagram[8].

Boyn et al[2], who studied absorption spectra for CdS:Ti^{2+} system, used a number of parameter of theory to compare their observed spectrum with the calculated one.

In this study all calculation have been performed for the system using Zhao double zeta function.

The calculated values of crystal field parameter Dq, Racah parameters A, B and C, and interaction parameter F^0, F^2, F^4, have been given in Table 4.2 along with the experimental value. The agreement between the two values is fairly good.

Energy spectrum of Ti^{2+} ion in axially distorted tetrahedral CdS was obtained by diagonalizing the matrix $\hat{V}_{C_{3v}}$ for ^3P and ^3F states. The obtained energy states were more than the observed one. This indicates that axial distortion is so small, that it is not observed. By neglecting the distortion, matrix for V_T was obtained and diagonalized. The agreement between the observed and calculated energy states is good as shown in Fig. 4.3.

The small deviation of the theoretical values from the experimental results can be attributed to the approximation applied in the calculation, which are:

(1) The crystal field operator has been obtained in point-charge model.

(2) The interaction of the optical electrons (electrons of the impurity centre) was considered with first nearest neighbours only.

In conclusion it is found that

1. Zhao double zeta function describes the 3d-radial function for transitional metal ion well,
2. The weak crystal field approximation, which has been used to calculate the wave functions of $3d^2$-configuration is a good one,
3. Point-charge model is a good approximation to express the crystal field operator for Wurtzite type crystals

This is validated by a good agreement between calculated and observed values of energy spectrum of Ti^{2+} ion in CdS crystal.

Suggestions for further research

(1) It is possible to include interactions of other neighbours with the optical electrons.

(2) The electron-phonon interaction can be included in crystal operator.

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