CHAPTER - 1
INTRODUCTION
AND
SURVEY OF LITERATURE
Chapter 1: Introduction

INTRODUCTION

The Lanthanides' (Lns) (Ce-Lu) atomic number 57 to 71 are unique among the elements. These elements resemble each other so markedly in both elemental and combined states that the changes across the series are more in degree than in kind. They also resemble closely the Actinides [Ans] [An-Lw] [89 - 103]. The electronic configuration [1,2] of neutral Ln(III) atom amounts to inner [Xe] core ([Rn] core in case of (Ans) with sub-shell \((n-1)d\), partly filled \((n-2)f\) and \(ns\). The \(n\) in case of Lanthanides represents 6 (for Ans \(n = 7\)). The configuration, however, varies across the series with the beginner, middle and end members having different configurations with regard to the occupancy of d-shell from the rest of the series viz., \((n-1)d^1\), \(ns^2\) for La; \((n-1)d^1,(n-2)f^q\), \(ns^2\) (where \(q = 1,7,14\)) for Ce, Gd and Lu respectively and \((n-2)f^q\), \(ns^2\) (where \(q = 2,3,4,5,6,8,9,10,11,12,13\)) for Pr, Nd, Pm, Sm, Eu, Tb, Dy, Ho, Er, Tm and Yb respectively. The \(f\)-subshell is instantly well outside the [Xe] core and is occupied. However, the development of the deep potential energy well near the nucleus draws the \(f\)-orbitals into the atom, thus permitting their occupancy and hence the existence of a series of fourteen Ln-elements. La(III) with unoccupied \(f\)-orbitals is also included in the series, thereby, making the total number fifteen. The \(f\)-transition elements with their \(f\)-electronic shells are explained on the basis of their probable roles and behaviour [3,4], however, their function as a whole is yet uncertain. All their physical and chemical properties are associated
with the unique behaviour of f-orbitals [5a]. These properties crop up in a wide range of physical phenomena such as atomic structure, magnetic behaviour, super conductivity, crystal field effects etc and the elements of the series exhibit diversity of behaviour not seen in any other series of elements. Thus in view of prevalent ideas it is felt essential to mention general features of f electrons and f-electronic shells so as to understand their role in general in [Ln(III).L] features [5b].

A. The general specific features of f - shells:

The 4f-shells are deep lying shells which lead to the following characteristics:

I. Effective screening of outer lying orbitals by nuclear attractive charge.

II. Effective shielding of outer lying orbitals between the f - shell electrons and the atomic/ionic environment.

III. Gradual increase of nuclear force causing lanthanide contraction.

IV. High relativistic effect having physical as well as chemical significance.

V. Core like or valance like or intermediate behaviour of f-electrons.

VI. High angular momentum values.

VII. f-orbitals are orthogonal on account of their angular nodal plane.

These features give rise to the following characteristics of the f-elements;
i. The crystal field stabilisation energy of (c.f.s.e.) of Ln compounds is low.

ii. Spin orbit interactions have minor effect on the extrastabilisation of (certain) f - configurations.

iii. Relativistic effects are significant and are even comparable to bonding energies.

iv. Ground term values (S and L dependent terms) and their variations become dominant thereby, exhibiting the phenomenon of "REGULARITY" or "PERIODICITY".

v. High angular momentum values make the coupled states challenging.

vi. Electronic configurations at fixed oxidation state may vary for different compounds with different donors.

VII. Delocalisation of f-shells increases as a result of relative contraction of s- and p-shells and consequential expansion of f-shells.

VIII. Relativistic effects and shielding effects are of the same order of magnitude.

IX. It is difficult to assess the involvement of the f-orbital and to decide the extent of covalent/ionic contribution in bonding.

The above mentioned general characteristics and their consequential properties contribute to elaborate the featuristic aspects of f-shells. However, besides these, some aspects like i. span of the
lanthanoid series, ii. lanthanoid contraction, iii. localisation / 
delocalisation, iv. screening and v. relativistic aspects need some ex-
planation.

The screening and shielding effects in lanthanides are im-
portant features used to decide the localisation or delocalisation of f-
orbitals. Delocalisation is more problematic because f-electron system
is known to behave both as core like or as valence shell conduction type
or even sometimes exhibits intermediate character. There are, how-
ever, spectral [6] and thermal [7] evidences supporting direct first and
indirect second order delocalisation of f-electrons.

Relativistic effects [8,9] also influence the value of atomic
number for which the f-orbitals are localised or delocalised. The origin
of relativistic effect is the consequence of the increase in the inertial
mass of electron in the atom and with an eventual contraction [10,11]
of the Bohr radius. Lanthanoid contraction which amounts to ∼18 pm
across the first series, arises out of relativistic effects, calculations
suggest that ∼2 pm of the overall effects arise from relativity in case
of neutral atoms and ions of lanthanoids.

The orthogonality of orbitals [12,13] is a mechanistic as-
pect proposed to explain the transmission of relativistic effect of the
core to valence electrons. The wave functions of the valance orbital
are so diffused that they undergo a considerable contraction so as to
build up sufficient density near the nucleus to render the orthogonal
core. The proportional contraction of the outer ‘s’ orbitals can even be
greater than that of the core, however, the relativist contraction of s- and p- shells increases the effective screening, thereby, pursuing f-orbital to undergo expansion. These 's' perhaps lead to the localisation of f-orbitals as they migrate slightly away from the nucleus [11].

Lastly, poor shielding of f-orbitals and the associated lanthanoid contraction is ascribed to a high angular character of the orbitals. Their radial character has a greater significance [14] than the orbital characteristics. It may be noted that the 4f-orbitals make only a minor contribution to the electron density - and thus the electron density in 5s- and 5p- orbitals determine the atomic radius. Since the first maximum of the 4f-orbitals lies just outside the fourth and the third radial maxima of 5s- and 5p-orbitals respectively the latter orbitals penetrate deep into the 4f-orbitals quite effectively and experience only a weak shielding. As a result their overall extent is reduced which infact determines the atomic/ionic radii.

The above discussion reveals interesting features of f (4f-) shells. It is difficult to make any direct line of correlation between the features and the experimental exhibition of the properties of metal ion as a whole, but all these features, to a greater or lesser extent, share a causative role in their experimental exhibition. To find their qualitative and quantitative relative roles in the experimental exhibition of properties is one of the major aims of the present thesis. Besides these few characteristics such as hypersensitivity and the quantum member profiles of lanthanoids have also been attempted to seek possible probable
dependency statement.

1. ELECTRONIC SPECTRA OF LANTHANOIDS

The early spectroscopists chose initially the study of simple spectra such as hydrogen rather than going straight to f-elements. The complexity of the spectra of lanthanoids was recognised in the study of the neutral and singly ionised atoms in the gaseous states. The study of triply ionised lanthanoids proved easier though such studies were not seriously undertaken till early sixties.

The complexity of the f-element spectra may be directly attributed to the existence of f-orbitals, a single electron with spin, in an f-orbital has 14 states available to it. Moreover seven electrons in it at a half filled shell level there are about 3432 states in magnetic field and considering the effect of other electrons the system reaches almost an astronomical situation. Condon And Shortley [15] were the first to give any theoretical model in their *The theory of Atomic Spectra*. Racah in 1949 introduced the full machinery of Lie groups realising that the 14 states of the f-electrons would span like a vector representation of an unitary group in 14 dimensions and the orbitals states can be represented in the absence of external fields, with rotational symmetry and physical three spaces. Racah laid the foundation of the subsequent analysis of the spectroscopic properties of the f-elements. The significance of Racah's work was appreciated early by C.K. Jorgensen[16] and by Judd and Runncican [17]. However, the earlier application of the Racah's techniques were not to isolate f-element atoms but rather to find f-element atoms trapped in crystalline environments. The solid state
and even the solution spectra exhibited same sharp spectral line characteristics of the partly forbidden f-f transitions. The spherical symmetry of the free ion was broken by the lower symmetry of crystalline environments in accord with the early idea of Bethe [18] and Oechowskil[19]. This made it possible to theoretically calculate free ion energy levels by calculating the coulomb and spin orbit interaction matrix for the \( p^0 \) electron configurations and digonalise the matrices for appropriate value of spectral parameters. Thus it became possible to understand the broad spectral features of lanthanoids and there after the magnetic properties of f-elements.

The 4f - 4f transitions are sharp because the 4f electrons are very effectively shielded by the filled 5s and 5p shells, which have a higher energy than the 4f shells. The absorption and luminescence spectra in the region of f-f transition was demonstrated by Freed et al. [20-23]. It is difficult to observe the f-f transition in gaseous Ln\(^{3+}\) spectra [24] as they are partly forbidden. The energy level of 4f\(^n\) configuration may be determined from the parity allowed 4f\(^{n-1}\),5d \( \leftarrow \) f\(^n\) transitions observed in the near and vacuum ultraviolet regions. So far they have been identified only for Ce\(^{3+}\) ion (4f\(^1\)) [25], Pr\(^{3+}\) (4f\(^2\)) [26,27], and, partially for Er\(^{3+}\) (4f\(^{1}\)) [28].

As regards the intensity of the transition in lanthanoids they are in general weak. Three mechanisms have been considered [29] for the interpretation of the observed transitions,

I. **Magnetic dipole mechanism**

II. **Induced electric dipole mechanism** and

III. **The electric quadrupole mechanism**
Magnetic dipole mechanism - is caused by interaction of the spectroscopic active ion with the magnetic field component of the light through a magnetic pole, Induced electric dipole mechanism - arising as a consequence of the interaction of ion with the electric field vector through an electric dipole and the electric quadrupole mechanism - arising from the displacement of charge having (quadrupole) four point charges with overall zero charge and zero dipole moment.

The procedure for theoretical calculation of the energy levels and the analysis of Ln$^{3+}$ spectra have been developed [30-33]. To define the energy levels scheme of the 4f$^1$ configuration, two sets of Hartee - Fock radial 4f - functions have been calculated by Rajnak [30] for Pr$^{3+}$ and Tm$^{3+}$ and the others by Freeman and Watson [34] for Ce$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, Gd$^{3+}$, Dy$^{3+}$, Er$^{3+}$ and Yb$^{3+}$. The theory was improved by involving second order electrostatic interaction, i.e., configuration interaction in defining the energy level schemes. Most systematic calculations based on “the expanded parameterisation model” have been carried out by Carnall [35] et al. for lanthanoid aqua ions. It has also been shown [36-38] that the theoretical analysis of the spectra for Ln$^{3+}$ free ions can be further improved by taking into account the higher magnetic interactions such as a spin-spin coupling ($E_{ss}$) and spin - of - one - electron with the orbit - of - the - other - one - coupling.

Numerous attempts to improve calculation procedure by taking into account the additional electrostatic effect such as the 5s$^2$p$^6$ shell polarisation [39], configuration interaction [40-43] and the charge penetration [44-45] gave no satisfactory results. Jorgensen [46] has shown the possibility of interpreting the lanthanoid crystal field with the framework of another distinct approach of “angular over-
lap model” which is one of the simplest approaches of the MO-LCAO method. On the basis of the AO-model [47] using only one empirical parameter, taking into account only the s-overlap, the crystal fields have been successfully interpreted for a series of lanthanoid ions in ethylsulphates [46], for Er\(^{3+}\) in ortho-vanadate and orthophosphate [48] and hydroxides [49].

Axe and Burns [50] using a semi-empirical MO-method have calculated the ground level splitting from Tm\(^{3+}\) (f\(^3\)) in the cubic field of CaF\(_2\) where the splitting of Tm\(^{3+}\) was found to be \(\sim 50\%\). Newman [51] summarised the modern data on the origin of lanthanoid crystal fields, and showed that the overlap and covalency (charge transfer) make dominant contributions to crystal files parameters. The energy levels of lanthanoid “free-ions” in crystals and solutions determined by the absorption spectra differ somewhat from those of gaseous Ln\(^{3+}\) ions and depend on the environment [52-54]. This approach was called the Red Shift or nephelauxetic effect [55] and was discussed in detail by Jørgensen [56-57]. The phenomenon of the nephelauxetic effect, however, cannot be interpreted in the framework of electrostatic model as it takes into account exclusively the first-order effects of the crystal field [58]. To define the nephelauxetic effect Jørgensen proposed [59] an equation taking into account the ground level stabilisation in the complex compared to the aqua-ions.

Carnall [60] used the energy levels of lanthanide ions in LaF\(_3\) as standards in comparison to the aqua-ions where the dependence of the nephelauxetic effect upon the nature of coordinated ligands was expressed by nephelauxetic series of the ligands. For lighter
lanthanoids the ligands got arranged in order: \( F < H_2O < Tart < Aca < Bacc < Edta < Dipy < Phen < Cl < Br < I < O^2- \) which in general coincides with the ligand nephelauxetic series for ions of d-transition elements. The highest nephelauxetic effect was found to be in sulfides [61], tri-cyclopentadienes [62] and oxides [59,63]. The dependence of nephelauxetic effect on coordination numbers was also noticed in early investigations of Jorgensen [53] and Rayan and Jorgensen [64]. Laughlin and Conway [65] reported the absorption spectra for \( Pr^{3+} \) isostructural crystals where the data prove identical structures for the complexes with coordination number of 9 (in \( D_{3h} \)) symmetry and a linear correlation between the wave number for \( ^3P_{0,1,2} \leftrightarrow ^3H_4 \) transition assignment and Pr-ligand distance.

Yatsimirskii and Devidenko pointed out [66-68] almost linear correlation between \( R(Ln-O) \) and the wave numbers of some f-f transitions in the absorption spectra of some Pr(III) and Nd(III) complexes having numbers and symmetry (\( R(Ln-O) = Ln-O \) bond distance).

In 1962 Judd [69] and Ofelt [70] independently developed an electrostatic model to calculate the intensities of the forced electric-dipole transitions in the \( Ln^{3+} \) ion spectra assuming that the f-f transitions arising out of the mixing of \( 4f^{r-1} 5d \) and \( 4f^{r-1} ns \) states with \( 4f^r \) states via odd terms of crystal field. The oscillator strength of the \( \Psi J \rightarrow \Psi J' \) transitions at energy of transition was expressed by the product of set of reduced matrix elements connecting initial \( < f^P \Psi J | U | f^P \Psi J' > \) and final states of the transitions for unit tensor operators of the rank \( L \) (where \( L = 2, 4, 6 \)). The matrix element values have been observed to be independent [71] of the environment. Carnall [32-34] calculated a set of reduced matrix for aquo ions of all the lanthanoids (\( Ln^{3+} \)). The reduced
matrix in general termed as Judd-Oelft parameters ($T_\lambda$) for $\lambda=2, 4, 6$ has been observed to be functions of refractive index of the medium, the radial wave functions of the initial and final states and the environmental perturbation mechanism parameters. The attempts to calculate the $T_\lambda$ parameters on the basis of electrostatic point charge model failed [72] and finally the $T_\lambda$ parameters were considered as empirical parameters and calculated from the experimental intensities. The data obtained on various systems and their analysis and interpretations have been reported in two critical reviews [73,74] and an article [75].

Since the 4f shells are effectively shielded by the closed 5s- and 5p- shells, the ligand environment has only a weak influence on the electronic cloud of the lanthanoid ion. Though weak, these perturbations are responsible for spectral fine structures. The peak positions of the spectral lines reveal the electronic structure of the 4f$^n$ configuration. The crystal field splitting gives information about symmetry of the rare earth site and shape of the coordination polyhedron. The intensities of spectral transitions also reflect the interaction between the lanthanoid ion and the environment. These aspects have been discussed in detail by Gorller-Walrand and Binnemans [76] in the Handbook of Physics and Chemistry of Rare Earths. Special attention to the theory, derivation of expressions, units and dimensions and expression for the dipole strength of rare earth ions in solution, to offer clear presentation of the ideas behind the fundamental intensity formulas have been dealt in detail by Gorller-Walrand and Binnemans [77].

2. SURVEY OF LITERATURE

The discovery of lanthanoids got carried over two centuries (1737 the discovery of Gd to 1937 discovery of Pm). After their discovery
the growing interest in rare earths and their application has brought about the compilation of various standard texts [78-90], reviews [91-106] and recently a handbook [107-129] of Rare Earth and Inorganic Chemistry. Amongst various fields of interests, studies on the electronic spectral aspects of lanthanoids have gathered greater interest. A brief survey of the relevant literature on lanthanoid spectral studies and their fundamental properties have been incorporated in the best possible chronological order in the following paragraphs.

Amongst the preliminary works on the structure of f-configurations, the calculations of the energy levels by Racah [25] and Wybourne [28, 130] seek special mention. Similarly Taylor series expansion [131] of the intermediate coupling energy levels for Ln\(^{3+}\) calculated without rediagonalizing the matrix need special mention.

Intensities of the solution spectra of a number of heteropoly complexes of Pr\(^{3+}\) and Ho\(^{3+}\) for the intensities of these elements in complex mediums have been discussed in detail by Peacock [132] in the light of the Judd Ofelt theory. Hypersensitivity has also been considered in connection with the complexes studied. The fundamental work related to the reduction of Slater parameters for lanthanoid ions substituted into crystals has been shown [133] to be a dielectric effect of the host crystals and their contribution to the crystal field parameters. In a comparison of the nephelauxetic effect and the spectrochemical series an existence of a strong empirical correlation between nephelauxetic effect and the ligand polarizability has been discussed [134] as a result of factors other than admixture of ligand and open shell wave function of 4f electrons.

"The oscillator strengths of quasi-quadrupolar tran-
sitions with intensities sensitive to the ligand environment arise principally from the coulombic correlation between transient induced electric dipoles in the ligand and the f-electron quadrupole moments of the metal ions". These observations have been made by Meson et al. [135] on the basis of the ligand polarisation contributions to the intensity of hypersensitive trivalent lanthanoid transitions. The restriction of hypersensitivity to the quadrupolar f-electronic transitions has also been discussed. The oscillator strengths for some lanthanoid nitrates in tributylphosphates have been reported [136] and interpreted in terms of relative effects of symmetry and covalency of the T₄ parameters of the Judd-Ofelt theory. Simultaneously the shift in the Slater integrals and the spin-orbit parameters have been predicted [137] to be the interactions between the host dependent shifts in 4fn → 4fn-1 configurations.

The optical absorption spectra of tri-positive Thulium [Tm(III)] in Thulium, Ammonium, Magnesium, Potassium and Sodium nitrate solutions[138-139] and various other environments [140-145] have been reported where the second derivative of the spectra was recorded. The splitting observed at certain levels have been explained to be arising from the super-position of vibrionic transitions on electronic spectra. The radiative life times has been calculated theoretically for the fluorescent levels of the ion in all mediums. Similar studies of Er³⁺ ion in NH₄(CH₃COO), Mg(CH₃COO)₂, K(CH₃COO) and Na(CH₃COO)·3H₂O mediums [146-147] and for their second derivatives have been recorded where the splitting has been tentatively explained as a cause of cubic crystalline field. The radiative transition probabilities for fluorescent levels of ¹I₁₃/₂, ¹I₁₁/₂, ¹I₉/₂, ⁴F₉/₂, ⁴S₅/₂, ⁴F₇/₂, ⁴F₅/₂, ⁴H₉/₂ and ⁴G₁₁/₂, in complexes
have been theoretically [148-150] estimated. The lifetime of \( ^7G_{11/2} \) has been reported to be the lowest in all the complex mediums.

High resolution fluorescence spectra of the aquo Sm(III), Eu(III), Gd(III), Tb(III) and Dy(III) ions have been revised by Sinha [151-153] in order to establish the energy levels of the ground state multiplets. The energy levels of the aquo Eu(III) ions have been established using both fluorescence and excitation spectra. The effect of coordination of simple inorganic and organic ligands has been discussed in the light of changes in fluorescence intensities and lifetimes of the aquo ions and rare earth ions in organic environments.

A method of analysis of \( 4f^{n-1}5d \) final state splittings and a qualitative interpretation in terms of radial distribution of \( 4f \) and \( 5d \) wave functions in magneto-optical spectra of rare earths using differentiation between strongly localised and delocalised \( 4f \)-states as observed in intermediate valent materials have been reported by Schoenens and Reim [154-157].

Caro revealed [158-160] from known crystal field parameters for Nd(III) (~112 crystallographic sites) and Gd(III) (~34 crystallographic sites) that there is no correlation between the crystal field strength and the chemical bonding parameters. Theoretical interpretations have existed where the nephelauxetic effect has been conferred to be dependent on chemical nature of the material, whereas the exact relationship of the nephelauxetic effect with structure has been argued to be a theoretical challenge. Simultaneously, the optical absorption spectrum of Nd(III) oxysulfides has been fitted [161-162] with Hamiltonian involving 14 free ion parameters and six \( C_{3v} \) crystal field parameters to derive the magnetic susceptibilities and compared with values derived from wave
vectors and lowest Kremer doublets through applying Van Vleck formula. The values of spin-orbit coupling constants versus Slater parameters have also been given for the Nd(III) nephelauxetic series.

In landmark works of Mishra et al. [163-169] great changes in the theoretical interpretations of the absorption of lanthanide compounds and ions both in crystalline as well as in solutions have been witnessed. The different approaches of origin of f-f transitions and the concept of hypersensitivity have been presented and interpreted in more modest and simple ways. The critical nature of the solution spectra of lanthanoids due to solvolysis, ionisation, association, dissociation, isomerisation interactions and the magnitude of substantial information on structural features on the coordination polyhedra have been made more clear. Through the analysis of at least ~200 spectra each of Pr(III) and Nd(III) Mishra et al. have clearly indicated that hypersensitivity - a typical phenomenon observed in terms of exceptional excitation of some electronic transitions in the ligand environments, cannot be restricted to hypersensitive transitions only but the nature of the ligand, the coordinating ability of the cation and the ligand, chelating power of the ligand, normalised bite, conformation of ligand and the nature of the complex specie may induce hypersensitivity to non-hypersensitive transitions. They proposed the induced hypersensitive bands as pseudo-hypersensitive or ligand mediated pseudo-hypersensitivity [170-175]. Mishra et al. also argued that larger interaction between metal 4f - orbitals and ligand orbitals may induce enhanced oscillator strength values for the hypersensitive transitions.

As cyclic phenolic oligomers, calixarenes [176] constitute
macrocyclic, multidentate ligands which are readily obtained in ring sizes
varying greatly in respect of ionic radii, can be chemically modified at
the phenolic oxygen and the aromatic and methylene linkages. In con-
trast to related cyclo-oligomers such as the cyclo-veratrtylenes, and re-
sorcinol derived calixaranes appear much more readily able to adopt con-
formations in which all donor atoms are directed towards a common
point. This potential [177-181] coordination ability of calixaranes makes
them exceptionaly interesting groups of molecule for investigation as
lanthanoid ion binding agent.

J.-B. Terziatowska and coworkers [182-83] reported low
temperature spectroscopy of LASER excited luminescence spectra of Eu³⁺
perchlorate in non-aqueous solutions with a view to determine the site
symmetry of the Eu³⁺ species in solution where the fine structures have
been used to determine the site symmetry. Analysis of the f-f transi-
tions probability have revealed a steric effect on structures in n-propanol
and iso-propanol.

On the basis of formation constants of ~308 complexes (with
poly amino carboxylates ligands ) a covalent and electrostatic contribu-
tion to the [M(III).L] bonds involving lanthanoids have been attempted by
Carugo [184-186]. He used equations log K₁ = C₁B₁ + E₁E₁ where param-
eters C and E indicate the tendency of each ions A and B to undergo
covalent and ionic bonding. The features of the [Ln(III).L] bondings have
been interpreted in terms of LUMO energy of the Ln³⁺ ions.A break in the
examining parameter has been reported between the first (La-Gd) and
second (Gd-Lu) halves of the Ln(III) series.

Shukla et al. [187-188] attempted potentiometric complex equi-
libria of Ln³⁺ with fluorinated β-ketoesters in aqueous dioxane mediums (50% v/v) at controlled temperatures. The validity of the chosen equilib-
rium model was confirmed by error analysis, scattered plots and slopes and intercepts of Abrhams-Kave probability plots. Standard thermody-
namic parameters have also been reported.

The emission spectrum of anhr Eu³⁺ ion doped in LnCl₃ has been studied 77K with high resolution. The data have been used [189] to rectify the previously reported UCl₃ type of crystal to a D₃h site symmetric ion. The X-ray diffraction data, however, support the Eu³⁺ ion into a site symmetry of Csₐ. Similarly, synthesis, IR characterisation, elemental analysis and luminescence lifetime and quenching studies [190] of Eu(III) with 5 - 5 methyl-2, 4 - hexanedione and 1, 10 phenanthroline, 2, 2'-dipyridyl or 5-nitro, 1,10 phenanthroline have been carried out. The coordination of Eu(III) has been confirmed via nitrogen atom of 5-
5 methyl-2,4-hexanedione.

Well resolved absorption and luminescence spectra for Ln(III) dipeptide- glycylglycine single crystals at room and Helium tem-
peratures were reported and compared with available X-ray data for Ca(II) compounds. The absorption probabilities of f-f transitions were analysed and the temperature effect on intensities have been examined. The studies conclude in support of the relevant texts [191] that the lanthanoid coordination in glycylglycine (or dipeptides) remain the same as in glycine[192-194]. The coordination of the Ln³⁺ ion with particular amino acids residues of peptides have also been found to be the same as that of single amino acids. The validity of these types of bonding was also tested in case of glycyl-L-tyrosine [195].

FT-IR and fluorometric investigations between [Ln.DMSO]
[Ln= La, Pr, Sm, Tb, Dy, and Lu] perchlorates in anhydrous acetonitrile have been reported by Bunzli et al, [196-198] where none of the systems reported showed any interaction with either perchlorate ions or acetonitrile molecules. The average coordination number of the Ln(III) ions was observed to be equal to the number of DMSO molecules, ranging from six to ten which has been discussed in light of the expansion of the first coordination sphere in accommodating incoming ligand molecules.

Planar aromatic tridentate nitrogen ligands: 2,6-bis(1-methyl benzimidazole-2-yl)pyridine (mbzimpy) [199] or macrocyclic octophenols :p-tert-butyl calix [8] arene [200] have been investigated as luminescent labels and have been proposed [201-203] to be potential luminescent building blocks as light converting devices of the molecules. Besides these potential molecules, Bunzli [204] reviewed the Solution and Anion interaction of rare earths in both inorganic anions and simple, monodentate neutral molecules in anhydrous organic solutions.

Crystal studies and fluorescence spectra of Nd(III) and Eu(III) with NTA and α-picolinic acid or hexa-aza macro cyclic complexes were examined for coloring properties in water, pyridine, DMSO, benzene, alcohol or acetonitrile [205-207]. Annapurna and Budhudu [208] also reported indium tri-fluoride based optical glasses of the type :48 InF$_3$-24BaF$_2$-7AlF$_3$-20RF (where RF is LiF, NaF and KF). It was shown from the fluorescence characteristics of these glasses that, the LiF network acted as a better optical modifier. Four additional fluorescent levels for Eu$^{3+}$ at 580nm, 592nm, 598nm and 653nm were also reported.

Rukmimi and Jayashankar [209] reported the optical properties of Tm$^{3+}$ ions in Zinc borosulphate and comparative energy levels of
Tm\textsuperscript{3+} ions in various glasses. Radiative transition rates for fluorescence levels of these glasses have been determined by Judd Ofelt theory. From the magnitudes of the radiative parameters various potential LASER transition properties have been compared and discussed with similar results. Similar compositional dependence [210-216] of the optical properties of, Pr\textsuperscript{3+}, Nd\textsuperscript{3+}, Ho\textsuperscript{3+} and Tm\textsuperscript{3+} ions have also been investigated in the lithium borate glasses of the type Li\textsubscript{2}CO\textsubscript{3} + H\textsubscript{2}BO\textsubscript{3} and MCO\textsubscript{3} + Li\textsubscript{2}CO\textsubscript{3} + H\textsubscript{3}BO\textsubscript{3}, (M = Mg, Ca, Sr and Ba).

Absorption spectra and hypersensitivity of the mixed ligand complexes of lanthanoids viz., Pr(III), Nd(III), Ho(III), Er(III), in non-aqueous solutions have been reported by Iftikhar et al., [217-219] for the adducts of 1,10-phenanthroline, 2,2'-dipyridyl, thiocynates. The chemical shifts recorded have been observed to be dipolar in origin. Shifts have been found to be larger for bipyridyl adduct than the corresponding phenanthroline adducts. The oscillator strength values for the hypersensitive and non-hypersensitive transitions have been determined and rationalised with respect to solvent type, solvent structures and coordination properties of the ligands.

Optical absorption spectra and the Judd Ofelt theory of Nd(III) ion in lead acetate glasses, have been calculated [220]. The radiative life times (\(T_r\)) branching ratios (\(\beta_k\)) and integrated absorption cross-section (\(\sigma\)) have also been reported for certain excited levels. Similarly optical properties of Pr(III) in fluoro borates have been characterised by determining their stimulated absorption cross-sections [221].

Cd- borosulphate glasses of the type CdSO\textsubscript{4} + B\textsubscript{2}O\textsubscript{3} and R\textsubscript{2}SO\textsubscript{4} + CdSO\textsubscript{4} + B\textsubscript{2}O\textsubscript{3} (R\textsubscript{2}SO\textsubscript{4} = Li\textsubscript{2}SO\textsubscript{4}, H\textsubscript{2}O, Na\textsubscript{2}SO\textsubscript{4}, K\textsubscript{2}SO\textsubscript{4} and Gd\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}, 8H\textsubscript{2}O) and the comparative energy level analysis of Nd(III) ions
in various glasses have been reported by C.K.Jayashankar [222-223]. The systematic theoretical energy level analysis with uniform $H_p$ results have been found to be in good correlation with calculated and observed energies. Radiative properties for fluorescence levels of Nd$^{3+}$ ions in Borosulphate glasses have also been reported.

Magnetic circular dichroism and optical absorption and spectra of Nd(III) doped fluorozirconate (ZBLAN) glasses have been reported by Beinnemans et al.[224-226]. Analysis of the absorption spectrum in the framework of the Judd Ofelt theory has been carried out where the use of J-O parameters have been made to compare the status of Nd in different environments. The spectral features of the magnetic circular dichroism (MCD) have been described qualitatively. The MCD signals have shown a strong temperature dependence. The $C_0/D$ ratio (where $C_0$=Faraday parameter and $D$=dipole strength] of Nd(III) in different environments has also been reported. Rai and coworkers [227] reported a detailed study of the physical, absorption and fluorescence studies on Er$^{3+}$ doped fluoroborate glasses at 300K and 77K. Judd-Ofelt parameters, transition probabilities, radiative branching ratios and stimulated emission cross section for the different transitions have been evaluated. It was concluded that the presence of Al in fluoroborate glasses shows better results.

Lanthanoid aqueous ion molecular dynamics have been studied [228] as body potential function actions on account of polarization due to water molecules in first hydration shell. Landmark publications [229-236] of Merbach's research on the lanthanoid aqueous complex water exchange rate constants from computer simulated reports,
have been utilised to ascertain the changes in the coordination sphere in the middle of the lanthanoid series. The observations on the change in the rate constants within the series have been interpreted in terms of relative stabilities of ennea- and octa-coordinated aquo ions.

Near-IR tunable solid state lasers in solid materials have been reported recently for their potential applications [237]. In continuation, the optical properties of rare earth elements Tm$^{3+}$, Ho$^{3+}$ and Yb$^{3+}$ were systematically investigated in various rare earth in near infrared laser glasses by Peng [238] et. al. Tm$^{3+}$ doped aluminozirco fluoride glass showed higher quantum efficiency, longer lifetime for $^3H_4 \rightarrow ^3H_6$ transition and stronger fluorescence intensity as compared with YSGG crystals and other Tm$^{3+}$ doped glasses. Similar results were reported for Ho$^{3+}$ doped aluminozircofluoride for the $^5I_7 \rightarrow ^5I_6$ transition. The fluorescence mechanisms and energy transfer in Yb$^{3+}$-Tm$^{3+}$ system, Yb$^{3+}$-Ho$^{3+}$ system and Yb$^{3+}$-Tm$^{3+}$-Ho$^{3+}$ systems were also studied.

To guide the design of the light converting molecular devices, a new theoretical methodology was developed [239] using the complexes of tris(3-amino pyrazine-2-carboxylate)(1,10-phenanthroline) of Eu(III). The ligand has been observed to possess a richer quasi-resonant energy level structure. These ligand and metal energy levels were used in dipole-2-pole models for energy transfer rate calculations where the high quantum yield for these complexes have been observed to be due to calculated high yield energy transfer from these several ligand states to the quasi-resonant Eu(III) energy levels.

Kinetics of Ln(III) complexes with the isomeric pendant arm macromolecular ligands - 1,4,7,10 - tetrakis (2-hydroxyethyl) -1,4,7,10 - tetraaza cyclododecane in acetonitrile or methanol reported by Bunzl
[240] indicated the presence of two enantiomers and the interconversion of which proceeded through both a ring inversion and a rearrangement of the pendant arm. The behaviour of these complexes were compared with similar 12-membered tetraaza macrocycle complexes bearing pendant arms. Luminescence properties of such complexes and some substituted bis-(benz imidazolyl) pyridines have been reported[241] where the quantum efficiency of the ligand-centered luminescence has been observed to decrease with substitution.

In recent publication, Beinneman and C.-G. Walrand have reported their studies on the spectroscopic properties of Eu(III) doped fluorozirconate glasses [242-245] where the validity of Judd Ofelt intensity parameters to express the sensitivity to reflect small compositional changes in lanthanoid doped glasses has been confirmed [246].

3. HYPERSENSITIVITY

Though the intensities of the induced electric dipole transitions in lanthanoids are in general not affected by the environment, yet a few transitions have been observed to be very sensitive to the environment and have been observed to be usually more intense for complexed lanthanoid ion than for lanthanoid ions in aqueous solutions [247-8]. Jorgensen and Judd called these transitions hypersensitive transitions [249] and noted these transitions to obey the selection rule $|\Delta S| = 0, |\Delta L| \leq 2, |\Delta J| \leq 2$. Since these selection rules are the same as the rules for quadrupolar transistions, the hypersensitive transitions have also been called pseudo-quadrupolar transitions. Since then much attention has been given to the explanation of the phenomenon of hypersensitivity as the phenomenon has been reviewed by Peacock [73], Henrie [74], Judd [250], Mishra [163] and Sommer [251]. Mishra and
Sommer [172,252-253] used the term *ligand mediated pseudo-hypersensitivity* for this phenomenon, because the coordination number, coordinating power, the denticity, the bite angle and the size of chelate rings of the different ligands have been argued to affect the sensitivity of these non-hypersensitive transitions to a different degree. Karrakar studied the hypersensitive transition of Nd, Ho and Er in detail [254]. He concluded that the hypersensitive transitions show dependences that are characteristic of coordination and the symmetry of the lanthanoid ion. The increase in the intensity of hypersensitive transitions for Nd, Er and Ho with respect to electrolyte or temperature has been examined by these authors.

The first case of hypersensitive transition in case of Pr was reported by Choppin and Peacock [255-256]. Some authors also tried to correlate the intensity of hypersensitive transitions with site symmetry of rare earth ions. Poluektov [257] showed that the intensity of hypersensitive bands increase with increase in the number of coordinating ligands. Changes in the coordination number have also been suggested by Katzin et. al. [258] as a possible cause for intensity and fine-structure differences. Surana et. al. [259] found that the intensity of hypersensitive transitions in Nd complexes follows the order of the ligands: oxygen donor > nitrogen - oxygen donor > nitrogen - nitrogen donor > sulfur donor > aquo ion.

*Pseudo-hypersensitivity* in the complexes of Nd³⁺- with fluorinated nucleic bases and nucleosides have been reported by Mishra and Mehta [260]. Henrie et al. [74] worked a direct relationship between the hypersensitivity and the nephelauxetic effect. Hypersensitive transi-
tions can be useful for the study of structure, conformation and binding modes of bio-molecules and of reaction mechanism of biochemical reactions involving calcium ions. A practical application of the spectral intensity of hypersensitive transitions in lanthanide ions is the determination of stability constants. Bukietynska et al. [261,262] evaluated the stability constant of lanthanide complexes from the changes of the oscillator strength for hypersensitive transitions as a function of the ligand concentration.

4. RECENT ADVANCES

On the basis of varied properties lanthanoids, these metal ions have acquired applications in various forms in industries and industrial developments, technological advancements and commercial projects. The areas may be listed as semi- and super-conductors (263), supermagnetic materials (264), fuel cells and solid state batteries[265], artificial diamonds [266], ceramics and their coloration [267], steel and glass industries[268], oxygen sensors [269], agriculture [270], medical imagery [271], florescence and glasses [272], phosphorescence and electroluminescence [273], thermoelectric power materials [274], lasers [275], optical switches [276], magnetic/optical refrigeration[277], catalysis[278] and humidity sensors [279]. The thermoelectric power materials include Ni-Co oxides [as p-side] and Nd-Cu oxides [as n-side] where the new device has been reported to generate 200 mV with temperature difference of 200°C. Sintered NFB (Nd-Fe-B) permanent magnets have been devised [264] where the residual magnetic flux density was measured to be 15.14 KG ~95% of the theoretical flux density. These devices have been said to be applicable in small electric motors for computer disc drives, magnetic resonance imaging equipments and also for hybrid -
electric automobiles. Similarly lanthanum Gallium Oxides has been developed for used as solid electrolyte for fuel cells which features at an operating temperatures of ~1000°C and can produce 0.4 W/m². A flexible Ni-alloy tape coated with YBa₂Cu₃O₇ (YBCO) on flexible tape has been used as superconductor to carry electrical power. A super powerful YAG laser which is able to produce 4KW power output and which is able to weld Aluminium sheet has been devised. Artificial diamonds produced from Zirconium oxide and Yttrium Oxides have been reported as American diamonds. Cerium oxide is one of the most widely used glass polishing agents particularly for optical and ophthalmic glasses. A compound YSZ (Y₂O₃ZrO₂) has been used as powerful compound for ceramic coating for efficient engines.

5. AIM AND SCOPE OF THE PRESENT STUDIES

A perusal of the above stated studies on lanthanoid fundamental properties, and their electronic spectral investigations, fluorescence excitation studies and varied application studies, reveal that besides the detailed studies performed in various fields on lanthanoids, there are still some fallacies associated with the role and behaviour of the 4f-shells in different environments. Such areas may be listed as: 1. The delocalisation of the 4f - shells with respect to specific environment, 2. The nephelauxetic phenomenon and a possible nephelauxetic series for lanthanoids with respect to different ligands, 3. Possible probable covalency and the magnitude of covalency in [Ln.L] bonds, 4. The itinerancy of 4f-shells with respect to different ligand environments, 5. Probable possible coordination numbers assigned to these elements within
the series, 6. Their varied hydration behaviour, 7. The exact possible role of the fundamental quantum numbers: S (spin), L (Orbital angular) or J (total quantum number) and 8. The phenomenon of hypersensitivity and a possible generalised statement on its mechanism.

Keeping in view these intricacies and in continuation with the work being carried out in our laboratories [280-303], the present work on the electronic spectral investigation on lanthanoids in different ligand environments has been chosen. Lanthanoids being Class A and hard acids, which vary more in their size than in structures or properties, make them aptly suited for such studies. Thus the present investigation which deals with the Sarcocine, Pyrazinamide, Lycine and Histidine involve amino acids and an antituberculosis drug. The ligands chosen for the present investigations are basically organic in nature where emphasis has been placed on the effect of their donor atom types and the ligand softness values on the electronic spectral parameters. The rare earths chosen for the study represent both pre- and post-Gd series elements viz., Pr(III), Nd(III), Sm(III), Eu(III), Dy(III), Er(III) and Tm(III). The elements have been chosen in a manner that these not only resemble each other in their electronic configurations, but also show similar spin and orbital angular momentum quantum numbers besides being different in their sizes and their total quantum numbers. In spectral properties, it is generally assumed that the f-f transitions originate from their transitions from one J state to J+1 state. Thus the examination of these specific electronic configurations in similar
ligand environments for the investigations on their electronic spectral parameters and radiative properties, and their analysis with respect to the ligand characteristics and Ln ion behaviour, may be able to project a better comparative picture of the [Ln.L] bonding phenomenon. A comparative account of the ligand softness values and the matching constants have also been attempted to explain and interpret the mode of Ln(III)-L bonding patterns. Through a comparison of these spectral features specifically for the hypersensitive transitions we may derive a semi qualitative statement on the probable dependence of hypersensitivity on the ligand and/or metal ion characteristics. Attempts have been made to discuss these aspects under the given titled work of the thesis.
REFERENCES

21. S.Freed and S.I. Weisssmann, F.E. Forttress and H.F. Jacobson, 
   and Ref: there in.
31. B.G. Wybourne, *Spectroscopic Properties of Rare Earths*, Interscience, 
32. G.H. Dieke, in H.M. Crosswhite and H. Crosswhite (Eds.), *Spectra and 
   Energy levels of Rare Earth ions in Crystals*, Wiley Eastern, New York, 
   1968.
   1970, 52, 4054.
Chapter 1: Introduction

73. R.D.Peacock, Struct. & Bonding, 1975, 22, 84.


105. D.K. Koppikar, P.V. Sivapulliah, L Ramakrishnan, S. Sounderrajan,


117. J.Reuben Ch. 39, p. 515, in *Hand Book on Physics and Chemistry of Re*
Chapter 1: Introduction

Solution studies on Rare ....Amino acids


118. Xiaoxia Gao, Ch. 55, p. 164, in Hand Book on Physics and Chemistry of 

119. J.-C.G. Bunzli, Ch. 60, p. 321, in Hand Book on Physics and Chemistry of 

120. B. Johansson, N. Martenson, Ch. 69, p. 363 in Hand Book on Physics and 

121. F. Szabadvary, Ch. 73, p. 33 in Hand Book on Physics and Chemistry of 

122. B. R. Judd, Ch. 74, p. 81 in Hand Book on Physics and Chemistry of Rhee, 

123. C. K. Jorgensen, Ch. 75, p. 197 in Hand Book on Physics and Chemistry of 

124. K. L. Nash, J. C. Sullivan, Ch. 102, p. 347, in Hand Book on Physics and 

125. E. N. Rizkalla and G. R. Choppin, Ch. 103, p. 393, in Hand Book on Phys 
ics and Chemistry of Rhee, (Ed.) L. Eyring, North Holland Publishing Co., 

126. L. M. Villarino, Ch. 104, p. 443 in Hand Book on Physics and Chemistry of 

127. Magnetic Properties of Nonmetallic Lanthamide Compounds, Ch. 150, 
in Hand Book on Physics and Chemistry of Rhee, (Ed.) L. Eyring, North 

128. Coherent Emission in Rare Earth Materials, Ch. 151, in Hand Book on 
Physics and Chemistry of Rhee, (Ed.) L. Eyring, North Holland Publishing 
Co., 1996.

129. Electronic Structure Calculations for Molecules Containing Lanthanoid 
Atoms, Ch. 152, in Hand Book on Physics and Chemistry of Rhee, (Eds.) 

36(9), 2295.


Chapter 1: Introduction

Solution studies on Rare .....Amino acids

148. R.Reisfield, Structure and Bonding, 1975, 22, 123.
158. P.Caro, J.Derouet, L.Beaury, J.P.Chaminade, J.Aride and M.Pouchard,
Chapter 1: Introduction

Solution studies on Rare ..... Amino acids


36


188. J. P. Shukla and R. S. Sharma, Montaschiete fur Chemie, 1994, 125, 247.


Chapter 1: Introduction

Chapter 1: Introduction

Solution studies on Rare ....Amino acids

46, 84.


39
Chapter 1: Introduction


268. J.Rare Earths, 1992, 10(1), 61.


270. Rare Metals, 1997, 16(3), 238.


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Solution studies on Rare ....Amino acids

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