

CHAPTER I

GENERAL INTRODUCTION

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The crystalline electric field theory formulated by J.H. van Vleck¹ was established on a firm basis fairly long ago. This could explain in general, the paramagnetic behaviours of crystalline solids containing ions of the iron and transition group elements. Subsequently the crystalline electric field theory was developed to throw light on the electronic energy level pattern of iron and transition metal ions embedded in crystals and to explain the electronic spectrum of the ions. It is well known that the unpaired electrons in the incomplete inner shells of these groups of elements are responsible for the paramagnetism of their compounds. In the rare-earth compounds some of the 4f electrons of the rare-earth atom are often left out unpaired and would result in paramagnetism of the complexes and reflected finally in the crystals constituted by them in the solid state. We shall be mainly interested in the present thesis with the salts of rare-earth complexes.

The rare-earth or 'lanthanide' series forms a distinctive group whose chemical properties are remarkably similar. The valency is usually 3. The interesting feature of the lanthanide group is the partial filling of the inner 4f shell inside a completely filled outer 5s and 5p shell. The closed shells of the electrons form the xenon core i.e. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

$4s^2 4p^6 4d^{10} 5s^2 5p^6$, which is the spectroscopic state of La^{3+} and Ce^{4+} . One more interesting point regarding lanthanides is that most compounds exhibit sharp lines in their optical spectra, particularly at low temperatures. These give us a detailed information for both ground and excited states.

Van Vleck¹ discussed in detail the paramagnetic behaviour of an assembly of non-interacting or free atoms each possessing identical or nonidentical quanta of magnetic moments associated with its resultant orbital and spin angular momenta arising due to statistical mixture of its electronic configuration in thermal equilibrium. The expressions for paramagnetic susceptibility under the three possible conditions, the multiplet intervals larger than, smaller than and comparable to kT , the average thermal energy deciding the distribution of population among the various quantum states of the system, have been derived by Van Vleck¹. He showed that the paramagnetic susceptibility of such a system of free atoms can be described, in general, by a simple Curie-law, except when the multiplet intervals are comparable to kT , in which case the resultant atomic magnetic moment is itself a function of absolute temperature. When a paramagnetic ion goes to form a complex molecule, obviously some of the freedom of the unpaired electrons in the ion is destroyed. Whatever, if any are left free will be able to constitute the paramagnetism of the molecule in the free state, which can be estimated on the basis of the electronic configuration of the

molecule. This will be further modified when the ions or their complexes go into the solid crystalline state in two ways (1) by further association between complexes tending to pair off residual electronic moments, (2) by causing the ions or complexes to take up crystalline anisotropic orientations and thus only the average moments of complexes are found to be along the crystalline directions and as a result the molecular anisotropies are reflected in crystalline anisotropies.

From the early measurements of the susceptibility of the lanthanides at the room temperature it was found that in most of the cases it was generally rather close to that expected from an assembly of free ions and Curie's law was fairly obeyed and the spectral lines found in the rare-earth salts are very sharp. These phenomena can be explained by the fact that 4f electrons are shielded by 5s and 5p subshell from the valence fields of the co-ordinating atoms called ligands. The spin-orbit interaction in case of rare-earth complexes is very high and so L and S are not the good quantum numbers in case of rare-earth complexes but J remains a good quantum number. Now the strong electric fields from ligands and exchange fields from close neighbouring ions are still often effective enough to cause the J-degeneracy to be removed sufficiently. Van Vleck¹ established a number of essential features regarding the behaviours of paramagnetic salts from the quantum mechanical

description. He took into account the correct description of the symmetry properties of the crystal field and also the group theoretical approach given by Bethe². The complete description of the pattern of the eigenstates generated by splitting the ground manifold of the free ion in presence of the ligand atoms depends upon the strength of binding as well as the symmetry of the cluster of ligand atoms. This theory of Bethe² and van Vleck¹ is called the 'crystalline field theory', the ligands are assumed to produce static electric field.

Elliott and Stevens³ tried to explain the magnetic susceptibilities and the e.p.r g-values of rare-earth ethyl sulphates with the help of the crystalline field theory. The optical spectra of the rare-earth complexes was explained with the help of crystal field theory by a number of workers⁴⁻³⁸. The same type of calculations were done by Judd³⁹ also. Their aim was to examine the consistency of the crystalline field theory in explaining mostly the spectral and e.p.r behaviours of rare-earth complexes. It is now well established that elementary crystal field theory though need some modifications, is still fruitful to a first approximation for the interpretation of the optical and magnetic behaviours of rare-earth substances. In the crystal field theory the covalent metal-ligand interaction is ignored. In the rare-earth complexes, though this interaction is small due to shielding effect, sometimes it is

necessary to take into account the metal-ligand covalency effect to interpret the optical and magnetic results. So one has to incorporate the molecular orbital formalism due to Mulliken⁴⁰ in the frame of the crystal field theory. This inclusion of the M.O. method in the crystal field theory resulted in the development of what is known as ligand field theory⁴¹⁻⁴⁷. The full M.O. calculation of rare-earth complexes is extremely complicated. However, in most of the cases ligand field theory which incorporates in it the essential features of M.O. theory by introducing the covalency reduction of some parameters directly or indirectly, is enough for explaining the optical e.p.r and magnetic susceptibility results.

Most of the crystal field calculations of rare-earth complexes are done within the same configuration. The calculations were confined within the ground configuration and thus the mixing of the excited configuration with the ground configuration i.e. the configuration interaction is ignored. The diagonalisation of the combined electrostatic and spin-orbit interaction matrices (for free rare-earth atoms) for a particular configuration yields energy levels which disagree with the experimental value substantially very frequently. This mismatch is due to neglect of configuration interaction.

Configuration interaction plays a very important and frequently unrecognized role in the electronic properties of rare-earths, which sometimes, has a profound effect on their hyperfine

structure, spectral intensities and their behaviour in crystal fields. The configuration interaction in free rare-earth atom may be divided into two classes :

(1) strong configuration interactions where the perturbing configurations are energetically close to the perturbed configuration and there is appreciable coupling of the configurations by way of the Coulomb field.

(2) weak configuration interactions where the perturbing configurations are well separated from perturbed configuration and the coupling of the configurations in the Coulomb field is weak.

Where the configuration interaction is strong it becomes necessary to diagonalise energy matrices which include all the electrostatic interactions within and between the configurations. The eigenvectors resulting from the diagonalisation then allow us to express the states in terms of linear combinations of the states of the connected configurations. The effect of configuration interaction can be accommodated by introducing effective operators that act only within the configuration under study. The additional parameters that enter in the lowest order of perturbation theory are associated with two body operators (α , β , γ are the three related parameters) introduced by Rajnak and Wybourne⁴⁹ or with three electron operators (T^1 , T^2 , T^3 , T^4 , T^5 , T^6) introduced by Judd⁵⁰. Another contribution of the configuration interaction in the free

atom coming from spin-spin and spin-other-orbit which is called by Judd et al.⁵¹ as 'Intra-atomic magnetic interactions for f electrons' (the related parameters are M^0 , M^2 , M^4 , M^6 and P^0 , P^2 , P^4 , P^6). To improve the free ion calculation⁵¹ of the rare-earth crystals this C.I. part should be taken into consideration. Recently Carnall et al¹¹ did this type of calculation⁵² for the rare-earth complexes to improve the theoretical crystal field levels and hence to have a good fit with the experimental levels. In the case of rare-earth ion embedded in a crystal lattice, the configuration interaction is brought about in the second order by both the crystal field interaction and inter-electronic repulsion. The odd harmonics of the crystal field interaction are known to have a profound effect on the intensity of transition between crystal field levels.⁵²⁻⁵³

The theoretical approach for interpreting the spectral, magnetic, e.p.r and specific heat consists in finding a unique set of relevant parameters which enter into the theory and consistent with the results of all the aforesaid experiments. These parameters in the case of rare-earth complexes are the Slater-Condon parameters⁵⁴ for the electrostatic part (F_2 , F_4 , F_6), spin-orbit (SO) coupling constant (ζ) and crystal field (CF) parameters and sometimes some additional parameters such as two and three body parameters, intra-atomic magnetic interaction

parameters mentioned earlier and covalency reduction factors⁵⁵ for the orbital angular momentum may be necessary. It may be noted that covalency affects almost all the parameters. However, in a theory where the parameters are deduced from experiments by adjusting them to give a good fit between the theory and experiment, the covalency effect on the parameters is automatically included in them.

The information obtained from optical spectra, electron paramagnetic resonance, magnetic specific heat of the rare-earth ions in crystalline solid can be supplemented with magnetic susceptibility and anisotropy results. When the results of the optical spectra are not available in detail, it is difficult to get a unique set of parameters from the optical experiments alone. Even when the fine structure details are available, the validity of the parameters deduced from such optical experiments can only be confirmed if they are consistent with other experimental results. So by studying the susceptibility, anisotropy and g_{\perp} values we have an opportunity to check the validity of the crystal field parameters suggested by optical data.

Optical activity⁵⁶⁻⁶¹ is the ability to rotate the plane of polarization of circularly polarized light. An optically active medium may owe its rotatory power to one or both of two causes: molecular dissymmetry and macroscopic anisotropy, the latter of these two may be due to the spatial arrangement of molecules (e.g.

crystal lattice) or to the presence of fields (e.g. the Faraday effect).

The circular dichroism (CD) is the differential absorption of left circularly polarized light and right circularly polarized light. After eventual transmission from the system the incident circularly polarized light gets elliptically polarized due to the differential absorption. Circular dichroism (CD) and optical activity are like twins with their origins in the dyssmetric environment, the former being related to the difference in imaginary parts of the refractive indices of right and left circularly polarized light and the latter to the real parts. An important application of CD measurements lies in the identification of magnetic dipole transitions, since the magnitude of these effects depends on the product of electric dipole transition moment and the magnetic dipole transition moment. It has been found that the weak $f \rightarrow f$ transition (oscillator strength $f \leq 10^{-6}$) has some magnetic dipole character and in some special cases, magnetic dipole transitions have actually been detected.⁶²⁻⁶⁴

We have chosen trivalent RE compound ($K_3Pr_2(NO_3)_9$) for our optical activity calculation. The $f^N \rightarrow f^N$ transitions in trivalent RE complexes are frequently forced electric dipole allowed⁶⁵⁻⁶⁶, sometimes magnetic dipole allowed.⁶²⁻⁶³ We discuss a model calculation regarding the electric dipole moment and the magnetic dipole moment of the aforesaid compound. Rotational

strength⁶⁷ is then calculated by considering the imaginary contributions of their product. Static and dynamic contribution to the electric dipole moment were calculated after Richardson and Faulkner⁶⁸. The contribution of the magnetic dipole moment for term to term was calculated after Sen and Chowdhury.⁶⁹ The rotational strength can also be obtained from experiment.⁷⁰ The relative changes in sign of the rotational strengths of CF transitions were compared with the experimental CD spectrum.