SYNOPSIS

The present thesis is devoted to the theoretical studies on magnetic, thermal, e.p.r and optical absorption results of some rare-earth complexes. Attempts have also been made here to present a model calculation on the optical activity of a rare-earth double nitrate crystal. The thesis consists of four chapters and we give below a brief description of the contents of the different chapters.

Chapter I opens with a general introduction of the crystal field (CF) and its modifications to what is called ligand field theory followed by a qualitative discussion on the effect of configuration interaction (C.I.) in the rare-earth group. This chapter also discusses the origin of paramagnetic behaviours of rare-earth complexes. The phenomenon of optical activity of some types of rare-earth complexes is also discussed at the end of this chapter.

Chapter II discusses the mathematical preliminaries specifically necessary for our work in the subsequent chapters. In order to make the thesis self sufficient we have started with a discussion of the Hamiltonian of an ion embedded within a crystal lattice. Then we have mentioned the different coupling schemes that are used generally in the calculation of atomic energy levels. The scheme of perturbation calculation

depending on the relative magnitudes of the various interactions present in the case of rare-earth complexes as well as the forms of the crystal field under various symmetries of the ion are also discussed systematically. The tensor operator technique has been discussed fully along with the concept of coefficient of fractional parentage (c.f.p). The tensor operator technique in the calculation of CF problems in the case of rare-earth ions has also been discussed. The method of calculation of magnetic susceptibility, g-value of a paramagnetic ion has been indicated. The introduction of the covalency reduction factor of the orbital angular momentum operator has also been discussed. The concept of charge and polarizability contribution to the CF parameter and the method of calculation of electric-dipole transition moment from both static and dynamic contribution have been dealt with in this chapter. The method of calculation of the magnetic dipole transition moment for $f \rightarrow f$ transition is also discussed. Finally, we give in this chapter the theoretical method of calculation of the rotational strength of an optically active RE ion.

The chapter III describes a consistent interpretation of the principal magnetic susceptibilities, g-values, optical absorption spectra and the magnetic heat capacity (where available) for various rare-earth ions namely Nd^{3+}, Pr^{3+}, Tm^{3+} in ethyl sulphate lattice and Pr^{3+} in double nitrate

lattice with the aid of a unified theory that simultaneously explains the results of all the different types of experiments mentioned above. Each system was treated rigorously with due consideration of intermediate coupling (IC) scheme and different J-mixing under the crystal field. The effect of C.I. in the CF level pattern were also taken into account in the case of praseodymium ethyl sulphate where the inclusion of this effect is found to be indispensable. A rigorous treatment gives a very reliable information regarding the crystal field (CF) parameters, interelectronic repulsion parameters (ES) and the spin-orbit (SO) coupling coefficient of the rare-earth ion. Investigation by direct diagonalisation of the complete energy matrix (consisting of SO, ES and CF interactions in general) is presented in case of Pr^{3+} and Tm^{3+} ion. It gives the full J-mixing. The theoretical interpretation on the optical, magnetic and e.p.r behaviours (and also specific heat behaviour where available) has been done for the concentrated crystal of Pr^{3+}, Nd^{3+} and Tm^{3+} ions in ethyl sulphate lattice and the Pr^{3+}-ion in double nitrate lattice. Systematic analysis for each sample is given separately in the different sections under this chapter. The results show that in the case of Nd^{3+} in ethyl sulphate we have an excellent agreement between the theory and experiment when a small covalency reduction is introduced in the orbital angular momentum during the calculation of magnetic susceptibility and the g-values.

The results obtained for Pr^{3+}, Tm^{3+} show that the theory simultaneously describes both the aspects of magnetic and optical behaviours within certain limitations. Further scope for future refinement of the theory has been mentioned. Moreover, the need of more experimental work with the presently available refined techniques has been pointed out.

The chapter IV describes a model calculation on the optical activity of anhydrous $K_3Pr_2(NO_3)_9$ single crystal. A brief account of the experimental details of both optical absorption and circular dichroism spectra has been described. The rotational strength was theoretically obtained by evaluating the imaginary part of the product of electric dipole transition moment and the magnetic dipole transition moment and then it was checked with the experimental value for both magnitude and relative sign for different transitions obtained. The calculation of electric dipole transition moment uses the odd order harmonics of the crystal field and the odd order harmonics were calculated with the point charge model including polarizability contribution. The CF energy level calculations were done first by the parameters obtained from point charge model and polarizability contribution and then the values of even order CF parameters thus obtained were adjusted to give the best fit to the experimental CF levels and also the rotational strengths. The contributions of both the electric

and magnetic dipole transition moments were calculated after due consideration of the J-mixing in the CF states. It is to be noted that for electric dipole transition moment both the static and dynamic contribution were taken into consideration. We also have mentioned the few discrepancies that arise in this model calculation.

The investigations presented in the chapters III and IV contain the original work of the candidate, most of which have been published in different journals (see the list of publications). No part of this thesis has been submitted for any degree elsewhere.