SYNOPSIS

The thesis, which deals with the study of optical and magnetic behaviours of some of the 3d-transition metal ions, doped in Caesium Cadmium Chloride lattice, is divided into two parts. Whereas the various theoretical aspects related mainly with our problem have been discussed in Part I of the thesis, Part II deals with our own works in the field.

First part of the thesis which consists of four chapters, opens with a short discussion about the necessity of a dual approach to the problem of crystalline interactions on paramagnetic ions embedded in a host diamagnetic lattice, in the perspective of optical and magnetic studies which provide information complementary to each other and thus determine uniquely the energy states and wavefunctions of the paramagnetic ions in the crystals. The behaviours of paramagnetic ions in crystalline compounds have been discussed briefly, giving detailed references to the theoretical and experimental works of different authors in this field. The aim and scope of our work has been delineated at the end of this section.

Chapter II, which is rather long, has been divided into eleven articles and is justified by a fairly complete review presentation of the general theoretical basis of the work undertaken. The first article deals with the general Hamiltonian of a paramagnetic ion in a crystalline electric

field. In considering the Hamiltonian we have omitted the terms which are not much related with our works i.e. nuclear-nuclear interaction etc. The atomic states of the free ions have been discussed in article 2. The nature of the Stark splittings of terms of an ion, when placed in a lattice, has been illustrated from group theoretical reasoning in article 3 of this chapter. Article 4 of this chapter deals with the different forms of the crystal field potential. The different cases that arise when the magnitude of the crystal field potential V_c is compared with the spin-orbit interaction and electron repulsion terms have been discussed. As the interest of the thesis lies only with slightly distorted octahedral complexes, we have shown, to begin with, the spherical harmonic expression for the crystal field potential V_c for O_h symmetry. The calculation of the matrix elements of the crystal field potential using Wigner's formula has been discussed in brief in article 5 and also the simpler method of using Steven's Equivalent Operator. Article 6 of the chapter deals with the calculation for splitting of the ground term of $3d^n$ (only S, D, F terms) configurations in O_h symmetry. The nature of the splitting of the excited G, H and I terms has also been discussed here. As our actual problem departs from pure O_h symmetry, we discussed in article 7, the various forms of low symmetry fields, showing particularly the splittings of terms under C_{3v} symmetry, an axial field connected with our actual problem. Spin-orbit coupling, the action of which is very important in explaining optical and magnetic behaviours,

has become the subject matter of discussion of article 8 of the chapter. Since the old crystal field theory, with point charges or dipoles at fixed positions, has been found inadequate to explain various observed phenomenon, we have discussed the molecular orbital theory in article 9. In article 10 we have discussed the essential features of the ligand field theory which makes the best use of both the crystal field theory and the molecular orbital theory and tries to explain in great details the various optical and magnetic properties of paramagnetic crystals, particularly the considerable reductions in orbital moments, spin orbit interactions and Coulomb interactions. The last article of the chapter deals with the rather puzzling Jahn-Teller distortion - 'an effect which arises only where it is required.'

Chapter III deals with the optical and magnetic properties. In article 1 under the heading of optical properties we have discussed various kinds of absorption bands that can arise out of the transitions from ground state to excited state configurations. As all the transitions are not allowed, one must know the proper selection rules for transition to occur and this is included in article 2. Article 3 on the same heading deals with the transition probabilities under various symmetries, with a table relating to C_{3v} - a symmetry of our interest. Under the heading of the magnetic properties, we have discussed the elegant spin Hamiltonian formalism of Abragam and Pryce[9]. We discussed the form of spin Hamiltonian

for both orbitally degenerate and non-degenerate ground levels and deduced expressions for magnetic susceptibility after Van Vleck[1].

In the last chapter of the first part of the thesis we have reviewed the optical and magnetic properties of some 3d - transition metal ions in chlorine ligand surroundings, keeping in mind doped compounds, in tabular form for octahedral or near octahedral and tetrahedral symmetries.

Part II of the thesis which contains mainly our works opens with the discussion of the crystal structure of the host lattice $CsCdCl_3$[134] in which several 3d ions are doped in turn. Section 2 of this chapter deals with the preparation of doped single crystal samples by Bridgeman technique and the estimation of the transition metal ions in same samples by micro and spectral analysis. While in section 3 we have described the magnetic susceptibility and anisotropy balances for magnetic measurements, along with necessary diamagnetic corrections and the processing of the magnetic data, the optical measurements have been dealt with in section 4. Various optical instruments and cryostatic arrangements suitable for them have been discussed in section 4.

Chapter II contains optical and magnetic findings on Co^{2+} doped in $CsCdCl_3$. Absorption spectra at room temperature, 77°K and 20°K, and magnetic susceptibility and anisotropy in the range 300°K to 90°K are discussed, The theory and the corresponding theory in Co^{2+} under O_h symmetry has been

developed. We have solved Tanabe and Sugano matrices[22] with various electronic parameters and compared out optical findings with calculated values. We have also calculated the small splittings of warious terms taking into consideration the trigonal field and spin-orbit interaction, and compared them with the fine structures obtained from our polarized spectrum at 20°K. The trigonal field parameter and the spin orbit coupling constant necessary to fit our magnetic data come out very close to those obtained from our optical studies.

Chapter III deals with our optical and magnetic measurement on Fe^{2+} doped in $CsCdCl_3$. We have studied charge-transfer bands in addition to the usual d-d bands. We have calculated the trigonal field strength and the Jahn-Teller splitting of the upper excited T_2 level which plays an important role in the present case. Proceeding to paramagnetic fittings of our magnetic anisotropy and susceptibility from 300°K to 90°K, we find that the trigonal field strength agrees very well with that found from optical measurement.

In Chapter IV we have given an account of our optical and magnetic measurement of $CsCdCl_3$ crystal doped with Ni^{2+}. We have compared our absorption spectrum at 77°K with spin-orbit energy levels calculated from Liehr-Ballhausen Model[52]. Magnetic susceptibility and anisotropy have been measured from 300°K to 80°K. Proceeding to parametric fittings of the data it was seen that the zero field splitting and g-values are in good agreement with $CsMgCl_3 : Ni^{2+}$ [151]. Spin-orbit coupling constant found from magnetic fittings agrees well with the optical value.

In Chapter V we have given the optical and e.s.r. findings of Cu^{2+} in $CsCdCl_3$. Like Fe^{2+} here also we have observed charge-transfer band in addition to the usual d-d band. Both the d-d band and the C-T band split at 77°K. The e.s.r. spectrum at room temperature reveals isotropy in g-value which in turn corroborates our optical finding i.e. the presence of a [redacted] Jahn-Teller distortion. All the compounds described above have significant reduction in the orbital moments and spin-orbit interaction and Racah parameters showing considerable overlap of 3d and ligand charge clouds and justifies the molecular orbital model.

Chapter VI deals with our optical, magnetic and e.s.r. measurements of $CsCdCl_3 : Mn^{2+}$. We have compared our observed levels at room temperature and at 77°K with those obtained by solving Tanabe and Sugano[22] matrices. Our magnetic susceptibility measurement between 300°K and 80°K shows only a slight deviation from the Curie law at low temperatures, and the high frequency term and the Curie-Weiss constant is found to be very small. Isotropic g-value from e.s.r. findings is very near to the spin only value and is in good agreement with that calculated from magnetic data.