

CHAPTER I

INTRODUCTION

The study of optical and magnetic properties of matter is intimately connected with our understanding of the electronic structure of matter and in fact provides the incentive for the development of modern quantum mechanical theories for multi-electronic molecular systems. Magnetic, optical and magneto-optical methods play an important role in the exploration of the solid state, notably, semiconductors, ferro- and antiferromagnetic and paramagnetic crystals. Electronic conductivity and ferromagnetism are generally treated as properties characteristic of the crystalline medium as a whole, while paramagnetism, essentially atomic (or molecular) property and persists even in liquid and gaseous states. Optical spectra and paramagnetism, though atomic (or molecular) in origin, show interesting variations with strength and symmetry of the crystal field. The spectroscopic and magnetic measurements of paramagnetic crystals provide important information about molecular as well as crystal fields and their influences on the energies of electronic states in molecules and crystals. The two methods of experimental approach, though very different, provide complementary information in general, with considerable overlap.

The presence of elementary permanent magnetic dipoles in a paramagnetic medium due to partly filled electron shells as found in the elements of transition series, received attention quite early in the development of the modern theory of

magnetism. Back in 1932, Van Vleck¹ produced a quantum-mechanical theory of paramagnetism for non-interacting atoms or ions, such as in the gaseous state. When atoms, similar or dissimilar in nature, combine together, to form molecules or closely associated groups, the electrons are shared or exchanged among the constituent atoms resulting in so much overlap and distortion of the original atomic states that the atomic quantization scheme of the orbital and spin angular momenta no longer holds good. The orbital angular momentum is most affected, and is conserved, if at all, only in certain preferred axial symmetry directions of the molecules, while spin is much less affected and is ordinarily assumed to remain free.

In the solid state the paramagnetic ions lie close to one another in appropriate crystallographic positions and their paramagnetic behaviour may be largely different from that of the "free ion" state because of several interactions that may arise. These interactions may be generally classified into :
1) those between a paramagnetic ion and its diamagnetic neighbours with which it is bound by chemical or quasi-chemical valence force and 2) those between two paramagnetic ions — directly or through other intermediary ions. For example, in iron group of transition elements, the 3d electrons are exposed to the field of the neighbouring ligands and the orbital magnetic moment may be considerably 'quenched', which means that the orbital angular momentum vector is no longer able to

process freely in the external applied magnetic field and hence can contribute only a second order part to the total magnetization of the medium. The electron spin, however, remains more or less unaffected and is so much more free to orient along the direction of the applied magnetic field, that the magnetic behaviour of the medium corresponds to spin-only magnetism to a large extent.

In a classic paper Bethe² showed from group theoretical concepts how the electronic energy levels of a free ion are affected by the electric field of the surrounding neighbours arranged with definite point group symmetry. Van Vleck³ used this result in evolving the theory of crystalline electric field which met with great success in providing a quantitative basis for paramagnetic behaviour of the solids. This theory was extended by Penney and Schlapp^{4,5}, Gorter⁶, Siegert⁷, Polder⁸ and modified in several respects by Abragam and Pryce⁹, Stevens¹⁰, Owen¹¹, Bose et al¹²⁻¹⁴ and others, to find the energy levels of the different ions of the iron group of elements in crystalline environments, so that it is now capable of explaining the majority of the observed facts of recent refined measurements of magnetic susceptibility and anisotropy. The absorption spectra of transition metal ions in solutions were reviewed by Moffitt and Ballhausen¹⁵ and in solids by McClure¹⁶ and Jorgensen¹⁷. Theoretical works directed towards interpretation of spectra of 3d ions were carried out by Finkelstein and Van Vleck¹⁸, Ilse and Hartman^{19,20}, Bleaney

and Stevens²¹, Tanabe and Sugano^{22,23}, Orgel²⁴⁻²⁶, Ballhausen^{27,28} and Jorgensen^{29,30}. For understanding optical spectra of transition ions in complexes one has to consider the number and separation of Stark levels in which the ionic levels are split up. The number of the components of the Stark pattern depends on the symmetry of the complex, while the separations of the split components depend on several parameters, such as the magnitude of the crystal field strength and the various interactions between the excited levels and other ions. From the spectral studies one can evaluate the crystal field strength and the magnitude of these interactions. The intensity of the lines of the pattern depend of course upon the transition probability which again is a complicated function of the field strength and the various interactions.

Since a ground state is hardly ever a pure state, knowledge of the positions of the excited levels is necessary to understand the paramagnetic resonance spectrum and magnetic susceptibility. The positions of the excited states can be determined directly only by the optical spectral measurements. But unfortunately there have been few measurements of the optical spectra for the crystal of which the magnetic behaviours have also been studied. In the study of 3d-transition ions in

octahedral diamagnetic lattice reported in this thesis the author has measured, where possible, all the three properties i.e. optical absorption spectra, magnetic susceptibility and anisotropy, and paramagnetic resonance spectra of the same crystal and has tried to correlate all these properties on the basis of the theory of ligand fields.

Scope of the Thesis

The study of the physical properties of paramagnetic ions embedded in diamagnetic host lattice (i.e. of doped crystal) has been of great ~~scientific~~ interest due to rapidly expanding technological applications, especially in the field of phosphors, lasers and electronics. Doped crystals offer several advantages as regards spectral and magnetic studies. Incorporation of the paramagnetic ions into diamagnetic lattice in low dilution reduces magnetic dipole-dipole type of interaction to the minimum and thereby helps to investigate the pure ligand-ion interaction properties. The e.s.r. measurements of such crystals give comparatively sharp signals owing to very much reduced exchange and magnetic dipole broadening. The magnetic susceptibility and anisotropy measurements of single crystals are also practically free from the above complications. The optical absorption bands are narrowed down, particularly at low temperatures, and the fine structures, as revealed from low temperature polarized spectrum of single crystals, give

information about the low-symmetry fields present around the metal ion and of the Coulomb and spin-orbit interaction parameters. Moreover, the low dilution of colouring species allows one to investigate the intense charge-transfer bands in addition to normal d-d bands. Doped crystals of a given species permit a systematic study of the ligand fields by varying dopant transition metal ion giving an idea of the bond structure of the ligand complexes as depending on the charge configuration of the metal ion. Doped crystals often permit study of structural geometries that are not possible in pure crystals. Similarly, the doped medium can be varied to find the effect of systematic variation of the host lattice on the dopant ion.

Though there exists a fairly good amount of study of oxide and sulphide systems doped with transition metal ions [Optical spectra of transition metal ions in Al_2O_3 by McClure³¹, optical absorption spectra of Co^{2+} in MgO and ZnO by Pappalardo, Wood and Linares³², optical absorption and e.s.r. studies of Cr^{3+} , V^{2+} , Co^{2+} , Ni^{2+} in MgO by Low³³⁻³⁶, magnetic susceptibility of Ni^{2+} in ZnO and CdS by Brumage³⁷, polarized absorption spectra of Cu^{2+} , Ni^{2+} , Co^{2+} in ZnO at low temp by Weakliem and McClure³⁸], systematic and comprehensive works on the effect of chloride octahedron on divalent transition metal ions are rather limited. We have thus chosen CsCdCl_3 as host crystal and dissolved in it various divalent metal ions of first transition series. Gruen and McBeth³⁹ made some preliminary investigations on the optical spectra of some of the above

crystals. But the study was limited to unpolarized light, narrow wave length region, low dispersion and to room temperature. We felt that in order to have a clear idea of ligand fields in crystals a more systematic and multipronged attack on different media doped with various transition elements should be made. As a first step we have made studies of polarized optical spectra, e.s.r. spectra and magnetic susceptibility and anisotropy of the above chloride system doped with a number of 3d ions, over wide range of temperature. The Stark patterns of the energy levels of ions that emerge from these separate studies are found to be consistent with each other, and the different properties could be explained on the basis of a unified theoretical basis in parametral terms. Several interesting features of the present studies on CsCdCl_3 containing Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} , to be described in due course, encourage our immediate contemplation of similar studies of other doped crystals.

In the next section we shall present a broad outline of the theory and the requisite mathematical formalism to explain our observations.