PREFACE

Electron Paramagnetic Resonance (EPR) study of transition metal ions doped in diamagnetic host can yield accurate and detailed information about the interactions of the unpaired electron with the surroundings. One can learn a great deal about the structure, nature of chemical bonds within a molecule and fine, hyperfine and super hyperfine interactions of the paramagnetic complexes diluted with the diamagnetic host.

The technique of EPR has been used to investigate, over the last five decades, a variety of problems ranging from medical science and organic chemistry to inorganic chemistry, physical chemistry and solid state physics etc.

Very few researchers have done simultaneous EPR and optical absorption studies for the same host. Since the EPR results can be better interpreted if the positions of excited levels are also studied, as the ground state is hardly, ever, a pure state. It is accordingly better to study a system with both the absorption phenomena.
The first purpose of this thesis is to open a new gate to the EPR and optical absorption studies of the VO$^{2+}$ doped compounds of M'SO$_4$ series where M' stands for Rb, NH$_4$, Cs and K etc. which have not been explored in detail by both absorption phenomenon.

Secondly, the hexahydrated double sulphates (Tutton salts) with the general formula $M_2M''\,(SO_4)_2\cdot\,6H_2O$ where $M_2$ is (K, Rb, Cs and NH$_4$ etc) and $M''$ is (Mg, Zn and Cd etc) form an interesting isomorphous series of salts for EPR and optical absorption studies. Few authors have studied both EPR and optical absorption on the same host, we have carried out EPR and optical absorption studies of VO$^{2+}$ doped in Cd(NH$_4$)$_2\,(SO_4)_2\cdot\,6\,H_2O$ written as CdASH and the results are presented here.

Our third effort is to explore an iso of carnallite series M'MgCl$_3\cdot\,6H_2O$ where M' is NH$_4$, Rb etc by doping VO$^{2+}$. It is found in marine deposits formed by evaporation of sea water. It is an important source of potassium and magnesium. New habits of growth of crystals can be explored by replacing M' or Mg in the
carnallite system. We will replace K by Rb and investigate the ions site.

The first chapter describes, in brief, a general introduction to the subject of EPR in solids, particularly in single crystals. The term Electron Paramagnetic Resonance (EPR) is defined and the basic principle of EPR is explained. The detection of resonance is discussed. Zero field splitting, g-factor and how various transitions take place under a static magnetic field and oscillating electromagnetic radiation is illustrated with figures.

The second chapter describes the theory of EPR with its theory. The Hamiltonian of a free paramagnetic ion & paramagnetic ions in a crystal field & the theory of crystal field splitting is discussed. How the spin Hamiltonian is arrived at and the spin Hamiltonian parameters are obtained is explained briefly. The selection rules, spin lattice relaxation processes viz the Direct process, Raman process and Orbach process are well discussed the spin-spin relaxation process is also explained.
The third chapter gives the theory of VO\(^{2+}\) ion in general. The molecular orbital scheme for VO(H\(_2\)O)\(^{2+}\), along with the transformation scheme for metal and ligand orbitals is described. The theory of optical absorption in octahedral and tetragonal symmetry is explained. The spin Hamiltonian for Vo\(^{2+}\) ion is given, and finally the EPR and optical data are correlated and discussed.

The fourth chapter describes the equipment used for EPR and the technique of optical absorption studies.

The fifth chapter describes the results of EPR and optical absorption of VO\(^{2+}\) doped in cesium sulphate, a compound of cesium, which is an element of eight series of periodic table of elements & is not explored in this area of research field. Through a correlation of optical and EPR data the molecular parameters for the bonding of vanadyl complex have been obtained and discussed. The site symmetry of vanadyl ion in cesium sulphate has been established.

The sixth chapter describes the EPR and optical absorption study of vanadyl ion doped in cadmium
ammonium sulphate hexahydrate. This system is interesting because the hexahydrated double sulphates (Tutton salts) with the general formula $M'M''(SO_4)_{2.6}H_2O$ where $M'$ is K, Rb etc and $M''$ is Mg, Zn etc. form an interesting iso series of Tutton slats for EPR and optical absorption which are explored simultaneously by very few authors. Since impurities also play an important role in the crystal growth and its growth habits, so we have replaced Mg by Cd and have reported the results of its EPR and optical absorption studies which affords an opportunity to compare the distortion and covalency in its isomorphous hosts.

In the seventh chapter the electron paramagnetic resonance (EPR) and optical absorption data of VO$^{2+}$ doped carnallite series is explored. It is $M'MgCl_3.6H_2O$ where $M'$ is K, Rb etc. It is obtained by the evaporation of marine deposits, which is an important source of potassium and magnesium. We can explore some new habits of crystal growth in these systems by taking different combinations and investigate ion's site. We have investigated Rb MgCl$_3.6H_2O$ by doping it with VO$^{2+}$. A phase transition i.e. a structural change, observed in this system is studied at LNT (liquid nitrogen temperature)