Preface

The present thesis mainly deals with the results of the investigations carried out using Electron Paramagnetic Resonance (EPR) technique, UV and IR on some first row transition metal ions having electronic configurations d\(^1\), d\(^5\) or d\(^9\) doped in selected lattices. EPR spectroscopy is a method to investigate the behavior of samples containing unpaired electrons (free radicals or complexes, whose outer electronic shell is incomplete) in an applied magnetic field. EPR has been successfully applied in diverse disciplines such as biology, physics, geology, chemistry, medical science, material science, anthropology, to name but a few. Solids, liquids and gases are all accessible to EPR. By utilizing a variety of specialized techniques such as spin-trapping, spin-labeling, ESEEM and ENDOR in conjunction with EPR, researchers have obtained information about many topics of scientific interest. For example, chemical kinetics, electron exchange, electrochemical processes, crystalline structure, fundamental quantum theory, catalysis and polymerization reactions have all been studied with great success.

EPR is a spectroscopic technique that detects chemical species that have unpaired electrons. A large number of materials contain paramagnetic entities, which may occur either as electrons trapped in radiation damaged sites, free radicals, various transition metal ions, bi-radicals, triplet states, impurities in semiconductors etc. EPR is a result of the unpaired electron’s spin magnetic moment being very sensitive to local magnetic fields within the sample. These fields often arise from the nuclear magnetic moments of various nuclei that may be present
within the bulk medium. Examples of such nuclei are interstitial atoms (or ions) within a crystal or glass matrix, nuclei (such as nitrogen) within the molecular structure that also contains the unpaired electron, and so on. Thus EPR provides a unique means of studying the internal structures in great detail.

One of the fundamental roles of any spectroscopic technique is identification of the chemical species being studied. As such, EPR spectroscopy is capable of providing molecular structural details, not easily obtained by any other analytical tool. First-row transition metal ions are the most extensively studied paramagnetic ions using EPR spectroscopy in a variety of ligand environments. Hence in this thesis, single crystal EPR studies of VO(II), Mn(II), Fe(III) and Cu(II) ions doped in different host lattices are reported. The study of these ions by EPR spectroscopy gives information about crystal symmetry, defects, orientation effect, site determination, distortion etc. In addition, the other aim of the present thesis is to study the location at which the dopant ion enters and the type of distortion it undergoes. The thesis is presented in eight chapters. A brief description of each chapter is given below.

An outline of the theory and general principles of EPR spectroscopy is given in Chapter 1, since EPR is the principle experimental technique employed in this thesis. The spin Hamiltonian formalism has been introduced and the various tensors and its properties have been mentioned. A brief reference to Jahn-Teller and Kramers’ theorem is given in this chapter.
Chapter 2 deals with EPR instrumentation, methods used for crystal growth, crystal structures of host lattices studied, evaluation of the principal values of g and hyperfine tensors from EPR spectra, evaluation of the direction cosines of the host lattices and finally a brief discussion about the computer programs (EPR-NMR, designed to calculate the spin Hamiltonian parameters and to simulate the isofrequency plots and Bruker’s SimFonia program for powder spectra simulation) used.

Chapter 3 deals with single crystal EPR studies on Cu(II) doped \textit{Diaquamalonatozinc(II)} (abbreviated as DAMZ), carried out at room temperature. The crystal data indicates the presence of four molecules per unit cell. The unit cell is monoclinic with \(a = 1.258\), \(b = 0.741\), \(c = 0.723\) \(\text{nm}\); \(\beta = 119.0^\circ\). Each Zinc atom is surrounded by a distorted octahedron of two water molecules at a distance 0.206 \(\text{nm}\) and 0.215 \(\text{nm}\) and four oxygen atoms of the two malonato groups at 0.213 \(\text{nm}\) and 0.202 \(\text{nm}\). Angular variation of copper hyperfine lines in the three orthogonal planes shows the presence of a single site in an interstitial position.

The spin-Hamiltonian parameters calculated from the spectra are: \(g_{11} = 2.077\), \(g_{22} = 2.087\), \(g_{33} = 2.442\); \(A_{11} = 1.83\), \(A_{22} = 2.88\); \(A_{33} = 14.74\) \(\text{mT}\). The slightly lower \(A_{33}\) value noticed for copper nucleus is explained by involving a small admixture of excited state with ground state. Optical and infra-red data have been collaborated with EPR data to obtain various admixture and molecular orbital coefficients.

Single crystal EPR study of Cu(II) doped \textit{Diaquamalanato(1,10 phenanthroline)zinc(II)} (abbreviated as DAMPZ) carried out at room
temperature, forms the basis for Chapter 4. Crystals of DAMPZ belong to monoclinic of space group C2/c, with unit cell parameters a = 1.034, b = 0.967 and c = 1.548 nm, $\beta = 105.72^0$ and $Z = 4$. Two magnetically nonequivalent Cu(II) complexes have been observed. The spin Hamiltonian parameters (g and A tensors) have been evaluated from single crystal rotations, which indicate a $d_{x^2-y^2}$ ground state for the copper ion. The spin-Hamiltonian parameters are found to be orthorhombic and the values are

Site I: $g_{11} = 2.057$, $g_{22} = 2.092$, $g_{33} = 2.336$, $A_{11} = 2.59$ mT, $A_{22} = 4.04$ mT, $A_{33} = 14.61$ mT

Site II: $g_{11} = 2.023$, $g_{22} = 2.192$, $g_{33} = 2.322$, $A_{11} = 5.39$ mT, $A_{22} = 5.76$ mT, $A_{33} = 12.35$ mT,

Angular variation studies for both the sites suggest that the Cu(II) ions are interstitially incorporated in the host lattice. The covalency parameter ($\alpha^2$), dipolar contact term (P) and Fermi contact term ($\kappa$) are calculated. By correlating EPR and optical data, molecular bonding coefficients and Fermi contact interaction term have been evaluated.

Chapter 5 contains the results of investigation of EPR studies of vanadyl impurity in single crystals of Zinc sodium sulphate hexahydrate (abbreviated as ZSSH) carried out at room temperature to understand the nature of substitution and symmetry of the dopant. ZSSH belongs to the family of Tutton’s salt. The unit cell dimension values are $a = 0.613$ nm, $b = 0.1223$ nm, $c = 0.909$ nm, $\beta = 104.78^0$ and $Z = 2$. The central metal ion is coordinated by six oxygen atoms of
water molecules. Room temperature single crystal EPR spectrum consists of a
number of resonances, indicating various incorporations. Spin Hamiltonian
parameters obtained from single crystal rotations carried out in the three
orthogonal planes are:

Site I: $g_{11} = 1.979$, $g_{22} = 1.976$, $g_{33} = 1.927$, $A_{11} = 8.71\text{mT}$, $A_{22} = 7.93\text{mT}$,
$A_{33} = 18.89\text{ mT}$;

Site II: $g_{11} = 1.979$, $g_{22} = 1.966$, $g_{33} = 1.929$, $A_{11} = 8.22\text{ mT}$, $A_{22} = 7.05\text{ mT}$,
$A_{33} = 18.77\text{ mT}$

An interesting observation is that the vanadyl impurities occupied interstitial
position for both the sites and are at right angles to each other. Various admixture
coefficients have been calculated, by collaborating EPR and optical data.

Chapter 6 describes EPR and optical studies carried out on VO(II) doped in
cis-diaquabis(1,10-phenanthroline-N,N')zinc(II) (1,10-phenanthroline-N,N')bis
(thiosulfato-S)zincate(II)monohydrate (abbreviated as DPZSZM). DPZSZM
belongs to triclinic crystal class, having space group $P\bar{1}$ with unit cell parameters
$a = 1.0545$, $b= 1.2924$, $c= 1.4856$ $\text{nm}$, $\alpha = 90.60^\circ$, $\beta = 100.06^\circ$ and $\gamma = 99.47^\circ$ and $Z=2$.
Single crystal rotations indicate that the paramagnetic impurity has entered
substitutional and interstitial sites in the lattice. The spin-Hamiltonian parameters
(A are in units of $\text{mT}$) for the two sites are:

Site I: $g_{11} = 1.981$, $g_{22} = 1.978$, $g_{33} = 1.929$, $A_{11} = 7.18$, $A_{22} = 8.55$, $A_{33} = 19.01$

Site II: $g_{11} = 1.987$, $g_{22} = 1.981$, $g_{33} = 1.931$, $A_{11} = 7.15$, $A_{22} = 8.02$, $A_{33} = 18.98$
The FT-IR spectrum exhibits bands attributed to stretching and bending vibrations of V=O, M-OSO$_3$ and C–O groups. By correlating EPR and optical data, molecular bonding coefficients and Fermi contact interaction term have been evaluated.

Chapter 7 describes single crystal EPR study of Mn(II) doped Bis(ammonium) tris(hexaqua-magnesium) tetrakis(hydrogenphosphite) (abbreviated as BAMP), carried out at room temperature. BAMP belongs to monoclinic system and the space group is C2/m. There are two molecules per unit cell and the lattice parameters are: a = 3.436, b = 0.704, c = 0.617 nm and $\beta$ = 91.349°. The coordination around the two independent Mg(1) and Mg(2) atoms is quite similar. Each Mg atom is strongly coordinated by six water molecules, forming a slightly distorted octahedron. The spin Hamiltonian parameters obtained for the single site is:

$$g_{xx} = 2.049, g_{yy} = 2.005, g_{zz} = 1.993; A_{xx} = -8.06, A_{yy} = -9.17, A_{zz} = -8.36 \text{ mT;}$$

$$D_{xx} = -31.55, D_{yy} = -7.13, D_{zz} = 38.68 \text{ mT;}$$

The direction cosines of g and A matrices do not match with any of the direction cosines of metal-oxygen bond in the host lattice. It confirms the impurity entered into the lattice as interstitially. The optical spectrum confirms the distorted octahedral symmetry of Mn(II) doped BAMP.

Chapter 8 elucidates the results of single crystal EPR studies of Iron(III) doped Dipotassium diaquabis(malonato-κ²O₂O')zincate(II) dihydrate (abbreviated as PMZD) at room temperature. PMZD, K$_2$[Zn(C$_3$H$_2$O$_4$)$_2$(H$_2$O)$_2$].2H$_2$O is isomorphous with K$_2$[Ni(C$_3$H$_2$O$_4$)$_2$(H$_2$O)$_2$]$_2$.2H$_2$O and belongs to monoclinic crystal
class with the space group C\textsubscript{2h}, having unit cell parameter \(a = 0.9397\), \(b = 1.0876,\)
\(c = 0.7628\) nm, \(\beta = 115.03^\circ\) and \(Z = 2\). The zinc atom, which is coordinated by the
two malonate dianions and two water molecules, has an elongated octahedral
environment. Since a trivalent ion has been incorporated in a divalent host lattice,
a number of vacancies have been expected and in fact, four have been analyzed
successfully. These four vacancies are directed along a particular crystallographic
axis suggesting that the impurity has entered the lattice and substituted for the
Zn(II) ion in the host lattice. Powder spectrum indicates a number of sites, which
have comparable \(g_{\text{eff}}\) values, obtained from single crystal analysis.

Chapter 9 gives summary of the research work and future scope of the
present work. In fact, the present study enriched the field of EPR in several ways.
In the case of Cu(II) impurities, the paramagnetic impurity entered an interstitial
site for the DAMZ and DAMPZ lattices, with a low hyperfine value, which is a
very rare observation. However the location of another paramagnetic impurity,
i.e., VO(II), in DPZPST lattice is both interstitial and substitutional. However,
Mn(II) is found to enter the lattice in an interstitial lattice position. A trivalent
ion such as Fe(III) entered the lattice substitutionally, considering the location of
the vacancies. Study of these systems, especially Fe(III) at Q-band frequencies
with low temperature measurements below 77K may also help to understand this
differential and preferential behaviour of the paramagnetic impurities.