Preface

Electron Paramagnetic Resonance (EPR) spectroscopy—also sometimes termed as Electron Spin Resonance (ESR) spectroscopy—has manifold potential uses in chemistry, physics, biochemistry, mineralogy, medicine etc. Under appropriate conditions, EPR spectroscopy has the ability to characterize the local chemical environment of paramagnetic transition-metal and rare-earth ions present in the lattice in the interlayer region or adsorbed to the surface of clays. EPR spectroscopy can be used to get information about the magnetic interactions, minor structural substitutions and lattice interactions. In cases where two or more paramagnetic species co-exist, the spectral EPR lines arising from each can be simultaneously observed and their dipolar interactions can be studied. Often definitive identification of the individual species is realized solely from the analysis of an EPR spectrum. Furthermore, EPR spectroscopy is capable of providing molecular structural details of small amount of paramagnetic ions doped in diamagnetic lattices, inaccessible by any other analytical tool.

The doping of a paramagnetic impurity in a diamagnetic lattice reveals the information about the distortion caused by the dopant. When a paramagnetic impurity is doped in a paramagnetic lattice, additional information about their dipolar interaction between the two paramagnetic ions (host and dopant) is obtained from the spin-lattice relaxation times. Hence in this thesis, single crystal EPR studies of (a) VO(II) ion doped in paramagnetic and diamagnetic lattices, and (b) Mn(II), Cu(II) and Ni(II) ions in different
Paramagnetic host lattices are reported in this thesis. The main aim of the present thesis is to incorporate a paramagnetic ion in diamagnetic and paramagnetic lattices and study the location at which that ion enters and the type of distortion it undergoes. In addition, low temperature EPR studies reveal the lattice (paramagnetic host) interaction with the doped paramagnetic ions, which will facilitate in the estimation of the spin-lattice relaxation time. It is noticed that when VO(II) ion is doped, it enters the lattice substitutionally most readily except in the case of hexaimidazole cobalt sulphate (HCoS). We have been successful in obtaining the results of both substitutional and interstitial site in case of magnesium ammonium phosphate hexahydrate; a substitutional site in the case of cadmium potassium phosphate hexahydrate and cadmium sodium phosphate hexahydrate, and two interstitial sites in HCoS. Mn(II) doped in cobalt sodium sulphate hexahydrate has been found to have entered the interstitial site. Two sites for Cu(II) ion is noticed in cobalt ammonium phosphate and both are found to have entered the lattice substituting the cobalt ion. Ni(II) doped in hexaimidazole cobalt nitrate has also exclusively entered the lattice substitutionally.

An outline of the theory and general principles of EPR spectroscopy is given in chapter 1, since EPR is the principal 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 Kramer's theorem has been mentioned in this chapter, as they are important in EPR spectroscopy.
Chapter 2 deals with the details of the instrumentation of EPR spectrometer. The procedures like Schonland and EPR-NMR programs used to calculate the g and A matrices have been discussed. The procedure for calculating the spin-lattice relaxation times from the line width measurements has also been mentioned. Finally, EPR simulation programs, i.e., EPR-NMR and SimFonia (supplied by Bruker), used to simulate the angular frequency plots and powder spectra are also discussed.

Part A (Chapters 3, 4, and 5) contains the discussion of the behaviour of the paramagnetic ion, vanadyl, i.e., VO(II), in different diamagnetic host lattices. Chapter 3 deals with the single crystal EPR studies of VO(II) doped magnesium ammonium phosphate hexahydrate (MgNH₄PO₄·6H₂O, abbreviated as MAPH). MAPH is analogous to the biomineral struvite and it crystallises in the orthorhombic space group Pmn2₁. The crystal rotations are done about the three mutually orthogonal axes. The results indicate that the paramagnetic impurity has entered substitutional and interstitial sites in the lattice. The maximum hyperfine coupling value for one site and the minimum hyperfine constant for the other site occur at the same angle and vice versa. The spin Hamiltonian parameters obtained from single crystal data for these two sites are Site 1: \( g_\parallel = 1.941, \ g_\perp = 1.994, \ A_\parallel = 19.23 \text{ mT, } A_\perp = 7.14 \text{ mT,} \) Site 2: \( g_\parallel = 1.946, \ g_\perp = 1.997, \ A_\parallel = 19.07 \text{ mT, } A_\perp = 7.29 \text{ mT.} \) From these observations, it is concluded that the two-vanadyl impurities are located approximately at right angles to each other. EPR powder spectrum of the sample showed a set of eight parallel and perpendicular features indicating the
presence of only one magnetically distinct site and the spin Hamiltonian parameters calculated from this spectrum have matched with single crystal data. The powder spectrum is simulated using SimFonia program and the fit is perfect. The angular variation plots are simulated, where the agreement is good. The admixture coefficients have also been calculated.

Chapter 4 contains single crystal EPR studies of VO(II) doped cadmium potassium phosphate hexahydrate (CdKPO4·6H2O, abbreviated as CPPH). This lattice also belongs to the struvite variety and crystallizes in the orthorhombic space group Pmn21. The angular variation spectra in the three orthogonal planes indicate that the paramagnetic impurity has entered the lattice only substitutionally in place of Cd(II). Spin Hamiltonian parameters have been obtained from single crystal data and powder spectrum. Powder spectrum shows a set of eight parallel and perpendicular features indicating the presence of only one site. The admixture coefficients have been calculated from the data, which agree well with the literature values. The spin-Hamiltonian parameters obtained from the single crystal data are g∥ = 1.943, g⊥ = 1.989, A∥ = 18.45 mT, A⊥ = 8.71 mT. The powder spectrum, simulated using SimFonia program matches with the experimental one.

Chapter 5 deals with VO(II) ion in yet another lattice, i.e., cadmium sodium phosphate hexahydrate (CdNaPO4·6H2O abbreviated as CSPH). The EPR analysis shows the presence of two magnetically different sites and both have entered the lattice substitutionally. The powder spectra indicates the presence of two chemically inequivalent sites out of which one with low
intensity is not followed in the crystal rotations. The spin-Hamiltonian parameters obtained from the single crystal analysis have matched with the values of site-1 of powder spectra, the values being: \( g_\parallel = 1.922, \quad g_\perp = 1.980, \quad A_\parallel = 19.72 \text{ mT}; \quad A_\perp = 8.63 \text{ mT} \). The spin-Hamiltonian parameters evaluated from powder EPR spectrum are: Site I: \( g_\parallel = 1.922; \quad g_\perp = 1.995, \quad A_\parallel = 19.86 \text{ mT}; \quad A_\perp = 8.24 \text{ mT} \); Site II: \( g_\parallel = 1.933; \quad g_\perp = 1.996, \quad A_\parallel = 20.72 \text{ mT}; \quad A_\perp = 7.77 \text{ mT} \). The admixture coefficients have matched fairly well with reported values. The powder spectrum of the two chemically inequivalent sites and the angular variation plots are also simulated.

Part B (chapters 6, 7, 8 and 9) deals with the paramagnetic ions doped in paramagnetic host lattices. Chapter 6 contains the electron paramagnetic resonance studies on single crystals of hexamidazole cobalt(II) sulphate tetrahydrate \([\text{Co(C}_3\text{H}_4\text{N}_2\text{)}_6\text{SO}_4\cdot 4\text{H}_2\text{O}], \text{abbreviated as HCoS}\), doped with VO(II). The studies are carried out in the temperature range of 77-300 K at X-band frequencies. Single crystal EPR spectra at room temperature indicate the presence of four sites with intensity ratios of 45:36:6:1. Angular variation studies in all the three planes confirm that both the intense vanadyl sites have entered the lattice interstitially. The spin Hamiltonian parameters are: Site I: \( g_{xx} = 1.995, \quad g_{yy} = 1.985, \quad g_{zz} = 1.941, \quad A_{xx} = 7.48 \text{ mT}, \quad A_{yy} = 7.74 \text{ mT}, \quad A_{zz} = 18.90 \text{ mT} \); Site II: \( g_{xx} = 1.986, \quad g_{yy} = 1.979, \quad g_{zz} = 1.942, \quad A_{xx} = 6.30 \text{ mT}, \quad A_{yy} = 7.72 \text{ mT}, \quad A_{zz} = 18.60 \text{ mT} \). However, powder spectrum indicates only one site. The spin-lattice relaxation parameters, calculated at various temperatures from line width measurements, vary from \( 1.52 \times 10^{-12} \text{ s} \) at 300 K to \( 4.04 \times 10^{-12} \text{ s} \) at
133 K. The admixture coefficients have also been calculated and the powder spectrum and the angular variation plots are simulated.

Chapter 7 contains the single crystal EPR studies of Mn(II) doped cobalt sodium sulphate hexahydrate. Cobalt sodium sulphate hexahydrate [CoNa$_2$(SO$_4$)$_2$.6H$_2$O, abbreviated as CoSSH] is analogous to Tutton’s salt. CoSSH belongs to monoclinic with space group P(2$_1$/a). Two different types of Mn(II) ions, with intensity ratios of 10:3 are identified. The low intensity set of resonance lines exhibit a larger $D$ value and has entered interstitially, while the high intense, with a $D$ value close to zero, has entered substitutionally into the lattice. The crystal rotations done along the three axes at room temperature for the low intensity lines have given the spin-Hamiltonian parameters: $g_{xx} = 1.9636; g_{yy} = 1.9636; g_{zz} = 1.9763; A_{xx} = 8.58$ mT; $A_{yy} = 8.61$ mT; $A_{zz} = 10.13$ mT; $D_{xx} = 20.44$ mT; $D_{yy} = 0.94$ mT; $D_{zz} = -21.38$ mT. The isofrequency plots have been simulated. However, the powder spectrum contains only the central sextet, corresponding to both the ions. The variable temperature studies on powder and single crystal (at a particular orientation) samples indicate a change in the line-width, from which spin-lattice relaxation times have been calculated.

Chapter 8 contains the single crystal EPR studies of Cu(II) doped cobalt ammonium phosphate hexahydrate (CoNH$_4$PO$_4$.6H$_2$O, abbreviated as CoAPH). CoAPH is analogous to struvite and it crystallises in the orthorhombic space group Pmn21. Single crystal rotations have been done in all the three planes at 153 K, since the spectra are well resolved at this
temperature only. The angular variation studies indicate only one site in substitutional position with spin Hamiltonian parameters as $g$: 2.404, 2.155, 2.063 and $A$: 11.58, 3.49, 2.07 mT. The reduction in principal $A$ value has been explained by considering considerable admixture of $d_{x^2-y^2}$ ground state with $d_{y^2}$ excited state. The admixture coefficients of ground state wave function are: $a = 0.2500; b = 0.9663; c = 0.0520; d = 0.0210; e = -0.0210,$ where $a$ and $b$ corresponds to admixture coefficients for $dz^2$ and $d_{x^2-y^2}$ respectively. Parameters $\kappa = 0.514; P = 113 \times 10^4$ cm$^{-1}; \alpha^2 = 0.7897; \alpha = 0.8887$ and $\alpha' = 0.5262$ have also been calculated, indicating considerable covalency. The powder spectrum at room temperature is unresolved, whereas it is better resolved at 77 K, with spin-Hamiltonian parameters matching well with the single crystal values of 153 K. Powder spectrum at 77 K has been simulated, which agrees with the experimental one. The spin-lattice relation times are measured from the line width of the resonance lines recorded at different temperature.

Chapter 9 deals with the room temperature EPR studies of Ni(II) doped in a paramagnetic host, hexaimidazole cobalt(II)nitrate [Co(C$_3$H$_4$N$_2$)$_6$(NO$_3$)$_2$, abbreviated as HCoN]. Even though $S = 1$, only a single resonance is observed at room temperature itself in all the three orthogonal planes. Since only one peak is seen throughout the rotations, it is not possible to obtain the D value experimentally. So, the D value has been calculated theoretically using the standard computer programs and compared with the powder data. The angular variation studies confirm that the Ni(II)
ion has entered the lattice substituting Co(II) ion, with spin-Hamiltonian parameters as: \( g_{11} = 2.407; g_{22} = 2.307; g_{33} = 1.956 \) and \( D_{11} = 682.2 \text{ mT}; D_{22} = -331.5 \text{ mT}; D_{33} = -350.7 \text{ mT} \). Cooling the sample to 77 K does not broaden the spectrum, confirming the absence of dipolar-dipolar interaction between the guest and host ions. This indicates that resonances from Co(II) ions can be seen only below 77 K.

Important observations of the thesis, along with the future scope of the work are discussed in chapter 10. The paramagnetic ion VO(II) is doped in both the paramagnetic and diamagnetic lattices and their behaviour in each lattice has been studied. The location of the VO(II) ion differs in each lattice. The Mn(II) ion has entered the lattice interstitially that is not a common observation. The Cu(II) ion behaved in a normal way and has entered the lattice substitutionally. The low hyperfine value has been explained considering the admixture of ground state with the excited state. The study of Ni(II) ion has become interesting, because we obtain the spectra of Ni(II) at room temperature itself. This is a rare case, as usually Ni(II) ions are EPR active only at low temperatures. The dipolar interactions between the two paramagnetic ions (in the case of paramagnetic lattice) are studied from the spin-lattice relaxation times. Further work will confirm the location of substitution by incorporating +3 ions such as Fe(III) and Cr(III). Also measurements at Q-band frequencies and temperatures below 77 K may throw further insight into the explanation of low hyperfine values.