Chapter II
CHAPTER II

EXPERIMENTAL TECHNIQUES

The instrumentation of EPR, the experimental technique and the crystal structure of the host lattices are discussed briefly in this chapter. The evaluation of the principal values of $g$ and $A$ tensors from the recorded EPR spectra are evaluated through the EPR-NMR computer program. The recorded powder spectrum of the sample is verified through the computer aided Simfonia program. The EPR spectrum is generally recorded for the transition metal ions doped in crystal lattices. But the EPR spectra are not usually recorded in pure paramagnetic samples except when co-operative phenomena are to be investigated. The samples used for EPR study are of any nature of matter.

If the sample happens to be a solid, two methods are available. The first method is to dope the paramagnetic impurity, mostly of transition ions, into the diamagnetic host lattice. A well resolved EPR spectrum is generally obtained in these cases where the concentration of the paramagnetic impurity happens to be of low concentration. The obtained EPR spectrum is found to be free from dipolar and exchange effects and the treatment of the system as independent centers is quite justified. Such doping is quite common with transition metal complexes. If the dopant concentration happens to be low, then the statistical distribution of the dopant centers is sufficiently low enough to achieve the desired isolation. Experiments show that the environment of the host lattice is invariably imposed on the dopant, thus making it possible to study the dopant complex under circumstances that do not exist in its pure form. Second method is to develop the paramagnetic centers in a diamagnetic lattice. This can be generally acquired by the
radiation damage by making use of UV, X-ray or γ-rays. This technique may be employed in a pure host lattice or a doped host lattice. The experimental technique followed for the present work is done generally by employing the first method and not the second method. So in the present thesis, only the first method has been elaborated.

**Instrumentation**

The instrumentation techniques and its measurements have been extensively discussed in the literature survey [1-4]. The schematic diagram of the instrumentation of EPR is shown in Fig. II.1. The main principal components of the instrument comprises of Source, Resonator, Magnetic field and Detector.

**Source:** The microwave source is usually the klystron. It is a vacuum tube that is characteristic for its low noise property. The valve of this klystron consists of a heater filament, a cathode, a reflector filament and a resonant cavity in which the electrical oscillations are maintained. The field is generated by oscillations within its own tunable cavity.

**Resonator:** This is a resonant cavity that allows the microwave through the hole called iris. The frequency of the source is tuned to the appropriate resonate frequency of the cavity. The corresponding wavelength of the resonant are related to the cavity dimensions.

**Magnetic field:** The static magnetic field for the EPR must be stable. An electromagnet of field strength of about 10000 gauss is connected with the sweep generator and the subsidiary coils to provide variable field strength. The sample is placed in the magnetic
Fig. II.1: Block diagram of a typical X-band EPR spectrometer.
field of a cavity resonator. The sample placed inside the cavity is such that the static magnetic field is perpendicular to the microwave magnetic field.

**Detector**: All modern EPR spectrometers use the semiconducting crystal diode rectifiers as the basis for the detecting system. The essential requirements for the detector is that the signal leaving the crystal with the frequency and amplitude corresponds to the modulation frequency applied the sample. The subsequent amplification of the signal with or without phase selection leads the ultimate display of the spectrum either by an oscilloscope or pen recorder.

Ingram [1] and Poole [2] have given detailed description of the basic principles involved in EPR instrumentation. In order to observe a well resolved EPR spectrum, one has to operate the spectrometer under optimum conditions of microwave power, modulation amplitude, spectrometer gain, filter time constant, scan range and scan time. From the resonance condition $hv = g\beta B$, it follows that the EPR spectra are measured by using fixed frequency and variable field or fixed field and variable frequency; it is always convenient to follow the former procedure. From the resonance condition $hv = g\beta B$, it follows that the EPR spectra are measured by either fixing frequency and varying the field or fixing the field and varying the frequency. But it is always convenient to follow the former procedure. The EPR spectrometers are classified depending on the irradiation frequency as follows.
The crystal samples are mounted at one end of the perspex rod with the help of quick-fix and the rod is fitted into the EPR cavity. A large protractor, which is calibrated in degrees is attached at another end of the perspex rod, enabled the accurate rotations of the crystal about the axis preferred. The error in mounting the crystal is about ±2° and that in orientation is about ±1°. The work carried out in this thesis is done on a JEOL JES-TE100 ESR spectrometer operating at X-band frequencies, having a 100 kHz field modulation to obtain a first derivative EPR spectrum. DPPH, with a g value of 2.0036, has been used for g-factor calculations.
Crystal growth

Single crystal EPR analysis gives valuable information than that obtained from powders and liquids. So, a brief discussion of the crystal growth is given in this chapter. The slow evaporation method technique is employed for the crystal growth. Growing crystals by allowing a saturated solution of a material to lose solvent by evaporation is one of the simplest methods [5, 6]. Many interesting crystals are grown simply by evaporation of solvent or temperature change. The evaporation of solvents makes the solution supersaturated so that, it attains the equilibrium saturated state by eliminating the seed crystals to solution. But, if the solution becomes too much supersaturated, crystals then would appear spontaneously throughout the solution. The factors that control the crystal growth technique are (i) character of the solution (ii) effect of additives and (iii) operating variable such as the degree of supersaturation and the temperature range.

The choice of solvent is an important factor that determines the growth of a crystal from solution. Growth of a large crystal is almost impossible unless a solvent is found in which the solute is appreciably soluble. For the present work, water is used as the solvent for all crystal growth. No additives are added to the solution except the paramagnetic impurity. The rate of growth depends on the temperature at which the solution is maintained. At higher temperatures, the growth rate will be high. However, fine crystals are obtained by slow evaporation at room temperature. All the crystals are grown at room temperature.
Interpretation of EPR spectra

As one can measure EPR spectra for solution, powder and single crystal samples, the procedure to obtain spin Hamiltonian parameters from these spectra must be known. In order to calculate g and A values, the following expression is used.

\[ g = \left( \frac{g_{\text{DPPH}} B_{\text{DPPH}}}{B} \right) \]

where,

- \( B \) is the magnetic field position at the EPR peak
- \( B_{\text{DPPH}} \) is the field position corresponding to DPPH
- \( g_{\text{DPPH}} \) is the g-value of DPPH (\( g = 2.0036 \))

One can as well calculate the g-value directly using the spectrometer frequency at which resonance occurs. The expression is as follows.

\[ g = \left( \frac{\nu}{\beta B} \right) \]

where, \( \nu \) is the resonance frequency.

The hyperfine (hf) coupling constant 'A' is given by the field separation between the hyperfine components. If the spacing is unequal, an average of them is taken to be the value for A. For \( n \) number of hyperfine lines, the average hyperfine value is,

\[ A = \left( \frac{B_n - B_1}{n-1} \right) \]

where,

- \( B_n \) is the field position for the \( n^{\text{th}} \) hyperfine line
- \( B_1 \) is the first hyperfine line field position.

Spectra are measured both in single crystal and poly-crystalline forms.
Powders and glasses

In powders and glasses, the observed spectrum is a result of superposition of all possible orientations of single crystals giving rise to statistically weighted average. The theory of powder line shapes in EPR has been given in detail by Kneubuhl [7], Sands [8] and Ibers and Swalen [9]. A brief pictorial summary of the evaluation of principal magnetic tensors such as g and A, for a few representative examples is given in Fig. II.2. In favorable cases, the principal values are calculated from powder data. However powder line shapes become complicated when more than one type of species is present and/or when hyperfine lines overlap, and especially so when the tensors do not coincide. The first two complications are overcome to some extent by measuring the spectra at two different frequencies, say X and Q bands, then sorting out the field-dependent and field-independent terms in the Hamiltonian. Sometimes, power saturation techniques [1,2] and temperature variation will also help in this respect.

However, the orientation of the magnetic tensors relative to crystallographic axes and hence with respect to molecular framework cannot be obtained from powder data. In such a case, measurements are to be done on single crystals. Nevertheless, powder data are obtained easily with a single measurement and often serves as a useful check for the interpretation of single crystal data. There is almost a parallel analogy between powder and single crystal data in EPR and X-ray crystallography.

Single crystals

Many authors, for example, Schonland [10], Weil and Anderson [11], Pryce [12], Geusic and Brown [13], Lund and Vanngard [14] and Waller and Rogers [15] have
Fig. II.2: The powder spectra line shapes for systems with electron spin $S = \frac{1}{2}$ interacting with nuclear spin $I = \frac{1}{2}$. 
discussed in detail the procedure for the evaluation of the principal values of magnetic
tensors from single crystal measurements. The method consists of measuring the
variation of $g(\theta)^2$ for rotations about three mutually perpendicular axes in the crystal,
which may coincide with the crystallographic axes or are related to the crystallographic
axes by a simple transformation. From the maxima and minima obtained in the three
orthogonal planes, the matrix elements of the $g^2$ tensor are derived easily [10]. A Jacobi
diagonalization of this matrix gives rise to the Eigen values corresponding to the
principal values of the $g$ tensor and the transformation matrix, which diagonalises the
experimental $g^2$ matrix, provides the direction cosines of these tensors with respect to the
three orthogonal rotations. However, one can encounter complications, when more than
one magnetically distinct site per unit cell are present, because no a priori predictability of
the relations between sites and spectra in the three planes. This leads to several possible
permutations leading to many $g^2$ tensors. For example, if a system has $n$ sites, then one
can end up with $2n^3$ tensors, including for not performing a proper rotation, i.e.,
clockwise or anticlockwise. A careful examination, however, invariably leads to the
identification of the proper combinations and the corresponding direction cosines. In the
case of hyperfine tensor, when $g$ is not highly anisotropic, the same procedure as above is
adopted. When this is not the case, Schonland has suggested that it is necessary to follow
the variation of $g^2A(\theta)$ in the three principal planes. The reason for this is given below:

The Hamiltonian for a paramagnetic system, including only the electronic
Zeeman and Hyperfine terms are expressed as

$$H = \beta (g_{11}B_1S_1 + g_{22}B_2S_2 + g_{33}B_3S_3) + (A_{11}S_1I_1 + A_{22}S_2I_2 + A_{33}S_3I_3)$$
Let \((n_1, n_2, n_3)\) be the direction cosines of the magnetic field \(B\) with respect to the axes of the \(g\) and hyperfine tensors. Here, it is assumed that \(g\) and hyperfine tensors are coincident. If \(M\) and \(m\) are the electron and nuclear spin quantum numbers, then the energy levels are given by

\[
\varepsilon_{M,m} = g\beta BM + \beta KMm
\]

Here \(g\) and \(K\) are given by the equations

\[
g = (g_{11} n_1^2 + g_{22} n_2^2 + g_{33} n_3^2)^{1/2}
\]

and

\[
K = \frac{1}{g^2} \left( g_{11} n_1^2 + g_{22} n_2^2 + g_{33} n_3^2 \right)^{1/2}
\]

The magnetic field \(B_m\) where the transition |\(M,m\rangle \leftrightarrow |M+1,m\rangle\) occurs is given by

\[
h\nu = g\beta B_m + \beta K m
\]

i.e.,

\[
B_m = h\nu g^2(K/g)m
\]

If \(A\) is hyperfine splitting and the lines are centered on \(h\nu g\beta\), then

\[
A = K/g
\]

In order to evaluate the matrix elements of the hyperfine tensor, one has to consider the angular variation of \((gK)^2\) since \((gK)\) has a linear angular dependence on \(g\).

Therefore,

\[
(gk)^2 = g^4 A^2
\]

From this equation, the matrix elements of the hyperfine tensor matrix are evaluated using the same procedure used to get \(g\) tensor matrix.

Schonland has indicated the probable errors in the method described above to get the principal values of \(g\) and hyperfine tensors. But, the errors are very small compared
with the experimental errors involved, such as mounting the crystal along the specified axis.

**Crystal-structure of the host-lattices**

A brief introduction is given for the various host lattices used in this thesis. Single crystals of Cadmium Ammonium Phosphate Hexahydrate are grown by slow evaporation of an equimolar aqueous solution of cadmium sulphate and ammonium dihydrogen phosphate. CAPH is analogous to the naturally occurring biomineral, struvite which belongs to orthorhombic system with unit cell dimensions \( a = 0.6873(2), b = 0.6160(2) \) and \( c = 1.1087(3) \) nm. The space group is \( \text{Pmn2}_1 \) and there are two molecules per unit cell i.e., \( Z = 2 \). The structure consists of \( \text{PO}_4^{3-} \) tetrahedra and the metal ion is surrounded by six water molecules in a distorted octahedral configuration, which are all held together by hydrogen bonding, with metal - oxygen distances ranging from 0.2046-0.2108 nm [16].

Single crystal of Cadmium Sodium Sulphate Hexahydrate (CSSH) is grown by slow evaporation of a saturated solution containing equimolar amounts of Cadmium sulphate and sodium sulphate. These Tutton’s salts have monoclinic crystal structure with space group \( \text{P2}_1/\text{m} \). The lattice parameters of CSSH (\( M'' \) is Cd, \( M' \) is Na and X is S) obtained from the already reported Tutton’s salts Magnesium Potassium Phosphate Hexahydrate are given as, \( a = 0.613, b = 1.223, c = 0.909 \) nm, \( \beta = 104.78^0 \) and \( Z = 2 \). The Cadmium ion in CSSH is surrounded by six water molecules in the form of a distorted octahedron. In all Tutton’s salts, the shortest Mg-O bond is unique, whereas the longest bond depends on the nature of \( M' \) and \( M'' \) [17]. The single crystals of Zinc
Sodium Sulphate Hexahydrate (ZSSH) also belongs to the group of Tutton's salts of which it is grown by slow evaporation of aqueous equimolar solution of zinc sulphate and sodium sulphate.

Single crystal of Zinc Maleic Tetrahydrate (ZMTH) is grown by the usual procedure. The stiochiometric solution of zinc sulphate was precipitated with ammonium hydroxide and by warming the excess ammonia present was eliminated. The resultant solution was treated with warm maleic acid. The ZMTH crystals belongs to a group of compounds having a general formula of \( H_2M(C_4H_2O_4)_{2.4}H_2O \), where 'M' denotes the zinc ion. It belongs to the triclinic system. As reported by Saroja et al., the unit cell parameters are \( a = 0.536, b = 0.729, c = 0.973 \text{ nm, } \alpha = 116.48, \beta = 63.18, \gamma = 103.36^\circ \). There is only one molecule present per unit cell. The unit cell parameters reported by Antsyshkina et al. [18] are, \( a = 0.730, b = 0.982, c = 0.528 \text{ nm, } \alpha = 110.2, \beta = 77.1, \gamma = 117^\circ \). As the X-ray data reported by the two groups are close, data given by the Saroja et al. [19] are used for calculation purposes.

Detailed X-ray data of these crystal lattices are given in their respective chapters.

**Direction cosines of the Substitutional sites**

The single crystal X-ray analysis data provides the positional parameters \( p, q, r \) and the unit cell dimensions \( a, b, c \) and \( \alpha, \beta, \gamma \). For crystal system with non-orthogonal crystal axes, the positional parameters \( p, q, r \) of the various atoms can be changed over to an orthogonal framework and the Cartesian co-ordinates \( x, y, z \) could be calculated using the relation
\[
\begin{pmatrix}
  x \\
  y \\
  z
\end{pmatrix} =
\begin{pmatrix}
  a & b \cos \gamma & c \cos \beta \\
  0 & b \sin \gamma (c/sin\gamma) (\cos \alpha - \cos \beta \cos \gamma) \\
  0 & 0 & d
\end{pmatrix}
\begin{pmatrix}
  p \\
  q \\
  r
\end{pmatrix}
\]

where,
\[d = [c^2 - c^2 \cos^2 \beta - (c^2/sin^2\gamma)(\cos \alpha - \cos \beta \cos \gamma)^2]^{1/2}\]

By setting the metal atom as the origin, the coordinates of the various atoms in the crystal surrounding the metal are calculated. The normalized Cartesian co-ordinates of these atoms give the direction cosines of the metal-ligand bond of the co-ordination polyhedron. The direction cosines of these metal-ligand bonds can be compared with the direction cosines of the g and A- tensors, obtained by the procedure described in the previous section. Sometimes, it is found that the magnetic tensor directions coincide with some of the bond directions, which may not be so in low symmetry cases.

**SimFonia powder simulation**

The simulation of the powder spectrum is generally carried out to verify experimentally calculated values with that of the already predicted theoretical values. The simulation of the powder spectrum is done using the computer programme SimFonia supplied by Bruker Company. The algorithm used in the SimFonia programme for powder simulation is based on perturbation theory, which is an approximation. Previously, perturbation theory has been used in the interpretation of EPR spectra because of the speed of calculation and the intuitiveness of the results. It is an
approximate technique for finding the energy eigen values and eigen vectors of the spin Hamiltonian. The assumption is made that there is a dominant interaction, which is much larger than the other interaction. As the dominant interaction becomes larger when compared to the other interactions, the approximation becomes better. The five interactions that are considered in the SimFonia simulation programme for the powder sample are:

1. Electronic Zeeman interaction: It is the interaction of the magnetic moment of the electron with externally applied magnetic field i.e., the magnetic field from the spectrometer magnet.

2. Zero-field splitting: It occurs in electronic systems in which the spin is greater than 1/2.

3. Nuclear hyperfine interaction: It is an interaction between the magnetic moment of the electron with the magnetic moment of the nucleus.

4. Nuclear Quadrupole interaction: It is the interaction between the Quadrupole moment of the nucleus with the local electric field gradients in the complex (for system having nuclear spin greater than 1/2).

5. Nuclear Zeeman interaction: It is the interaction of the magnetic moment of the nucleus with the externally applied magnetic field.

The assumption made in the simulations is that the electronic Zeeman interaction is the largest, followed by the zero-field splitting, hyperfine interaction, nuclear quadrupole interaction and the nuclear hyperfine term is the smallest. Perturbation theory works best when the ratio between the successive interactions is atleast ten. If the limits are exceeded, perturbation theory still gives a good picture of EPR spectrum; however, it
may not be suitable for the quantitative analysis. If an EPR spectrum is to be simulated with larger hyperfine interactions, then second order perturbation theory is selected to increase the accuracy of the simulation. The zero-field splitting is always treated to second order because they do not produce a non-zero first order term.

Only allowed EPR transitions are simulated, but under some circumstances forbidden transitions can also appear. These corresponds to simultaneous flip of the nucleus and flop of the electron and the forbidden EPR lines occur between the allowed transitions or an $\Delta M_s = \pm 2$ electronic transitions. These forbidden lines are not simulated because perturbation theory is not the optimal method for calculating their positions and intensity. The SimFonia powder simulation programme simulates EPR spectra for spin 1/2 to spin 7/2 electronic systems. For spins greater than 1/2, D and E zero-field splitting terms are implemented. There are essentially no restrictions on the spin of the nuclei. All the naturally occurring spins have been programmed. The principal axes of the electronic Zeeman interaction and the zero-field splitting are assumed to be coincident.

SimFonia can simulate both types of line shapes i.e. Lorentzian and Gaussian, as well as combination of the two. This technique is most efficient for many line-complicated spectra. Detailed theory of the powder spectra simulation can be obtained from the references [20, 21]

**Computer Program EPR-NMR [22]**

The program sets up spin-Hamiltonian (SH) matrices and determines their eigenvalues (energies) using "exact" diagonalization. It is a versatile program, having
many operating modes tailored to a variety of applications. These modes can be grouped into four categories, in increasing order of complexity as follows:

1. Energy-level calculation.
2. Spectrum simulation.
3. Comparison with observed data.
4. Parameter optimization.

For each category, most of the operations of the lower categories remain available, so that a good way to learn how to use the program effectively is to start at the lowest category and work one's way up.

Category I: In this category, the user provides the program with SH parameters, and directions and magnitudes of applied magnetic fields.

Category II: In category II, the user also specifies an experiment, chosen from field-swept or frequency-swept electron paramagnetic resonance (EPR) or nuclear magnetic resonance (NMR), electron nucleus double resonance (ENDOR), or electron spin echo envelope modulation (ESEEM). Also, the user must identify the transitions of interest. The "spectra" simulated consist of sets of transition frequencies or magnetic field magnitudes, and possibly relative transition probabilities. The program can also convolute these data with a line-shape function (Lorentzian or Gaussian) to produce a plot.

Category III: For this category, the user also supplies appropriate observed single-crystal data, with transition labels assigned, and the program determines the degree of consistency with data calculated from the given SH parameters. This can include an error analysis on a user-selected subset of SH parameters and/or magnetic-field directions.
**Category IV:** In the category IV, the user-selected subset of parameters may be optimized, so as to give better agreement between observed and calculated transition frequencies. This uses a non-linear least squares routine, which systematically varies the parameters so as to minimize weighted differences between observed and calculated transition frequencies (or fields). In this category, user-supplied SH parameters need only be estimates or outright guesses. This programme has been used in the calculation of SH parameters for all the systems studied in this thesis.
References


