2.1 INTRODUCTION

The presence of incomplete 3d, 4d, 4f, 5d and (5f, 6d) electronic shells in the ground state of the atoms and ions of iron, palladium, rare earth, platinum and actinide group elements, respectively are responsible for their paramagnetism. The application of paramagnetic resonance and the development of the crystal field theory have led to a good understanding of the magnetic properties of the ions of various transition groups in crystals.

When a free ion with a resultant angular momentum $\vec{J}$ is subjected to a static magnetic field then it has $2J+1$ energy levels and the energies of the various states are given as:

$$E_{M_J} = g\beta BM_J$$  \hspace{1cm} (2.1)

where $M_J = J, J-1, \ldots, -J+1, -J$, $B$ is the static magnetic field, $g$ is the spectroscopic splitting factor and $\beta$ is the Bohr magneton.
In electron paramagnetic resonance (EPR) interest lies in the allowed magnetic dipole transitions between these levels. If the direction of the electromagnetic radiation field of frequency $\nu$ is parallel or perpendicular to the magnetic field $B$, the allowed magnetic dipole transitions are given by the selection rules $\Delta M_j=0$ or $\Delta M_j=\pm 1$, respectively. Hence when the microwave magnetic field is normal to the applied static magnetic field direction, a single absorption line corresponding to the energy difference, $\Delta E=g\beta B$, between the $E_{M_j}$ levels differing in $M_j$ value by $\pm 1$ should be observed. Therefore, the resonance condition becomes:

$$\Delta E = h\nu = g\beta B \quad (2.2)$$

The intensities of these transitions are given by the square of the matrix element connecting $M$th and $(M+1)$th level. The intensities are governed by the following relations

$$P_{M_jM_j+1} = \text{constant} \left[ J(J+1)-M_j(M_j+1) \right]^{\frac{1}{2}} \quad (2.3)$$

Thus it is clear that different $M_j \leftrightarrow M_j+1$ transitions will have different intensities.

2.2 CRYSTAL FIELD EFFECTS

In EPR splitting of energy levels occurs under the effect of two types of fields: internal crystalline field and applied
magnetic field. While studying paramagnetic ions in diamagnetic crystal lattices (hosts), there are two types of interactions observed: interactions between the paramagnetic ions (dipolar) and interactions between the paramagnetic ion and the diamagnetic neighbours (ligand field). Former interaction is reduced effectively to a negligibly small value by doping small amounts of paramagnetic ions in the diamagnetic host. Thus each ion may be considered isolated from other paramagnetic ions and to be independent. The latter interactions of paramagnetic ion with diamagnetic ligands modify the magnetic properties of the paramagnetic ions. The crystal field (CF) theory assumes that the paramagnetic ion experiences a crystalline electric potential produced by neighbouring ions or molecules lying wholly outside the paramagnetic ion. In other words, the ligands influence the magnetic ion through the electric field which they produce at its site and their orbital motions get modified. The crystal field interaction is affected by the electrostatic screening by the outer electronic shells. Depending upon its magnitude relative to other interactions, the crystalline field interaction is generally classified into three categories:

(i) Weak Crystal Field

When the crystal field interaction is weaker than the spin-orbit coupling (this is the case with the rare-earth and
certain actinide compounds). It is due to the fact that the electron's paramagnetic shell, 4f or 5f, lies fairly deep within the ion and is shielded from the crystal field by closed shells of 5s and 5p or 6s and 6p electrons, respectively.

(ii) Intermediate Crystal Field

When the crystal field interaction is greater than spin-orbit interaction but is less than the coulombic interaction between electrons. The best example of these are hydrated salts of the iron group. This situation can be described by regarding the orbital motion as clamped by crystal field and making it unable to respond to an applied magnetic field. This is known as "quenching of orbital angular momentum". In this case, the magnetic properties are all due to spin which is affected only weakly by crystal field through spin-orbit coupling.

(iii) Strong Crystal Field

When the crystal field interaction is of the order of the energy of mutual interaction between electrons. For the ions of 4d and 5d transition groups there is a tendency of covalent bonding due to which the orbitals of paramagnetic ion and neighbouring ligands overlap appreciably. In this case
due to strong covalent bonding the crystal field assumption actually does not hold.

2.3 HYPERFINE INTERACTION

Hyperfine interactions are mainly magnetic dipole interactions between the electronic magnetic moment and the nuclear magnetic moment of the paramagnetic ion. In the case of S-electrons it is the Fermi contact interaction which is important. The octet in the EPR of vanadyl ion and the quartet in the EPR of divalent copper are the result of hyperfine interactions. The origin of this can be understood simply by assuming that the nuclear moment produces a magnetic field $B_N$ at the magnetic electrons and the modified resonance condition is:

$$
\Delta E = h\gamma = g\beta \left| B + B_N \right|
$$  \hspace{1cm} (2.4)

The hyperfine interaction is highly characteristic one and presents a most convenient means for identification of paramagnetic ions by the observed hyperfine structure in the EPR spectra. The interaction of the magnetic electron with nuclei of the ligands gives rise to super hyperfine structure.

2.4 EFFECTIVE SPIN AND THE SPECTROSCOPIC SPLITTING FACTOR $^g$  

In electron paramagnetic resonance we are concerned with
transition between levels whose splitting is of the order of cm$^{-1}$. Hence our interest mainly lies in groups of levels that are degenerate (or nearly so) in zero magnetic field. To treat this problem quantum mechanically is a matter of great complexity and a convenient method is needed to represent the behaviour of such a group of levels when a magnetic field is applied to the system. A very powerful method has been evolved which uses the concept of an effective spin $S'$, which is a fictitious angular momentum such that the degeneracy of the group of levels involved is set equal to $(2S'+1)$.

The concept of an "effective spin" is useful because it is possible to set up an "effective spin-Hamiltonian" that gives a correct description of the behaviour of the group of levels in very concise terms. The effective spin-Hamiltonian is expected to reflect the local symmetry of the complex and this imposes restrictions on its form. If the observed spectrum does not conform to the spin-Hamiltonian that has been assumed one has to try others until a fit is obtained.

The electronic Zeeman interaction is given by

$$\mathcal{H} = g\beta \cdot \mathbf{S} \cdot \mathbf{S}'$$

(2.5)

This has $(2S'+1)$ states, which, again by analogy, we label by means of a magnetic quantum number $M$ representing the values
of \( S'_z \) (taking \( \vec{B} \) to be along the z-axis). The energies are given by the expression

\[
E_M = g\beta B M
\]  

(2.6)

and the quantum of energy required for an allowed transition of the type \( \Delta M = \pm 1 \) is

\[
h\nu = g\beta B
\]  

(2.7)

giving a resonance condition similar to eqn.(2.2). For a doublet state which we label \( S' = \frac{1}{2} \), the energy levels are shown in Fig. 2.1, two levels, diverging linearly with \( \vec{B} \).

The form of eqn.(2.5) presupposes that the Zeeman interaction depends only on the angle between the effective spin vector \( S' \) and the magnetic field. In practice, the Zeeman interaction depends also on the angle that \( \vec{B} \) makes with certain axes defined by the local symmetry of the magnetic complex. A more general form, which takes into account anisotropy of this kind is

\[
\mathcal{H} = \beta(\vec{B} \cdot \vec{g} \cdot \vec{S}'),
\]  

(2.8)

which is written in expanded form as
Fig. 2.1 Energy level diagram showing Zeeman splitting for free electron spin system.
In the majority of cases (except complexes with rather low symmetry) the quantities \( g_{xy} = g_{yx} \), etc., and the cross terms can then be eliminated by suitable choice for the \( x, y, z \) axes (known as "principal axes") which yield simpler form

\[
\mathcal{H} = \beta \left[ g_{xx} B_x S_x' + g_{yy} B_y S_y' + g_{zz} B_z S_z' + g_{xy} B_x S_y' + g_{yx} B_y S_x' + g_{yz} B_y S_z' + g_{zy} B_z S_y' + g_{zx} B_z S_x' + g_{xz} B_x S_z' \right] \quad (2.9)
\]

If the magnetic field \( \mathbf{B} \) is applied in a direction with cosines \((l, m, n)\) with respect to these principal axes, the energy levels are given by an eqn. of the form (2.6), with a value of \( g \) given by the relation

\[
g^2 = l^2 g_{xx}^2 + m^2 g_{yy}^2 + n^2 g_{zz}^2 \quad (2.11)
\]

In the case when the complex has cubic symmetry, it follows necessarily that \( g_{xx} = g_{yy} = g_{zz} \), so that the Zeeman interaction has the same Hamiltonian as for a free magnetic dipole. In the case of axial symmetry

\[
(g_{xx} = g_{yy} = g_\parallel; \quad g_{zz} = g_\perp)
\]

and the eqn. (2.11) reduces to

\[
g^2 = g_\parallel^2 \cos^2 \theta + g_\perp^2 \sin^2 \theta \quad (2.12)
\]
where $\theta$ is the angle between magnetic field $\mathbf{B}$ and the z-axis.

2.5 THE SPIN-HAMILTONIAN

In EPR, the unpaired electron is not isolated or free, but frequently, interacts with a variety of nuclei and electrons in various degrees so the magnetic field $\mathbf{B}$ in eqn. (2.2) becomes the sum of various components. The state of affairs may be expressed from the quantum mechanical viewpoint in terms of a Hamiltonian. Abragam and Pryce [1] initially and numerous others subsequently described the electronic interactions which contribute to the total energy of the ion by the following Hamiltonian [2-5]

$$H = H_0 + H_{cr} + H_{s-o} + H_{s-s} + H_z + H_{hf} + H_q + H_n + H_e \quad (2.13)$$

where,

- $H_0 =$ Free ion energy ($\sim 10^5 \text{ cm}^{-1}$)
- $H_{cr} =$ Electostatic energy ($\sim 10^4 \text{ cm}^{-1}$)
- $H_{s-o} =$ Spin-orbit interaction energy ($\sim 10^{-2} - 10^{-3} \text{ cm}^{-1}$).
- $H_{s-s} =$ Spin-spin interaction energy ($\sim 1 \text{ cm}^{-1}$)
- $H_z =$ Interaction of electron with the external field or Zeeman energy $= \beta B(L+2S)$ ($\sim 1 \text{ cm}^{-1}$)
- $H_{hf} =$ Dipole-dipole interaction between the electron and nuclear magnetic moments ($\sim 10^{-1} - 10^{-3} \text{ cm}^{-1}$)
- $H_q =$ Quadrupole interaction between electron and nucleus ($\sim 10^{-3} \text{ cm}^{-1}$)
\[ H_n = \text{Nuclear Zeeman energy} = g_N \beta_N B \cdot I (\sim 10^{-4} \text{cm}^{-1}) \]

\[ H_e = \text{Energy of exchange effects between electrons} \]

Practical EPR spectroscopy concerns itself mainly with the \( H_{s-s}, H_z \) and \( H_{h-f} \), i.e. the fine structure, Zeeman splitting and hyperfine interactions as the nuclear Zeeman and quadrupole interactions are usually small. The best way to consider all the energy contributions is to express them in the following form including the nuclear Zeeman and quadrupole terms.

\[
H_s = \beta \vec{B} \cdot \vec{S} + \vec{D} \cdot \vec{S} + \vec{A} \cdot \vec{I} - E_N \vec{B} \cdot \vec{e}_N + \vec{Q} \cdot \vec{I}. \tag{2.14}
\]

where \( \vec{S} \) and \( \vec{I} \) are the electronic spin and nuclear spin operators respectively and are equivalent to \( \vec{J} \) operators from mathematical point of view and \( \vec{g}, \vec{D}, \vec{A}, \vec{Q} \) and \( \vec{e}_N \) are all second rank tensor quantities. The first term represents Zeeman interaction with the applied field \( \vec{B} \), the presence of orbital momentum is taken into account by allowing the splitting factor 'g' to differ from the spin-only value (2.0023). \( \vec{D} \) in the second term represents the quadrupolar coupling to the crystal field. The third term expresses the hyperfine interaction between \( \vec{S} \) and \( \vec{I} \), the fourth expresses nuclear Zeeman interaction and the fifth expresses the quadrupolar coupling between nuclear spin \( \vec{I} \) and the electric field gradient in the
These tensors are diagonalized in a system of orthogonal axes, known as principal axes. In principal axes system eqn. (2.14) can be written as (neglecting the nuclear Zeeman interaction)

\[ \mathcal{H}_s = \beta(g_x B_x S_x + g_y B_y S_y + g_z B_z S_z) + D[S_z^2 - \frac{1}{2} S(S+1)] + E(S_x^2 - S_y^2) + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z + Q'[I_z^2 - \frac{1}{2} (I+1)] + Q''(I_x^2 - I_y^2) \] (2.15)

where

\[ D = D_z - \frac{1}{2} [D_x+D_y], \quad E = \frac{1}{2} [D_x-D_y] \]
\[ Q' = Q_z - \frac{1}{2} [Q_x+Q_y], \quad Q'' = \frac{1}{2} [Q_x-Q_y] \]

and \( g_x, g_y, g_z \) and \( A_x, A_y, A_z \) are the components of \( \bar{g} \) and \( \bar{A} \) tensors respectively along principal axes.

2.6 FINE STRUCTURE PARAMETERS

In eqn. (2.15) the parameters "D" and "E" are generally known as fine structure constants and are the measure of the internal splitting in the group of energy states, described by spin-Hamiltonian. "D" and "E" represent the axial and rhombic parts of the crystal field respectively. For Mn\(^{2+}\), fourth order cubic field parameter, "a" also contributes to the zero-field splitting and is important for interpretation of EPR spectra.
2.7 HYPERFINE CONSTANT

Because of interactions with nuclear spin and electronic spin, hyperfine interaction comes into play, which gives the separation between hyperfine levels. In the spin-Hamiltonian it is represented by the term $\mathcal{H}_{\text{A}}$.

Another term which often contributes to the hyperfine structure is the quadrupole interaction $\mathcal{H}_{\text{Q}}$. $Q'$ and $Q''$ express the quadrupole interaction and are the axial and rhombic parts respectively. The magnitudes of these are very small and are determined from hyperfine forbidden transitions.

2.8 COVALENCY EFFECTS AND SUPERHYPERFINE STRUCTURE

A detailed examination reveals that the experimental observations do not agree completely with the theoretical predictions based on the static crystalline field approximation. In particular it is found that the spin-orbit coupling and the hyperfine interaction in crystal differ from those obtained for a free ion. This is due to the fact that the point charge or point dipole approximation of ligand ions is not strictly valid, and the overlap of the wave functions of the ligand ions with that of the metal ion must be taken into account. Stevens [6] considered this problem for the first time for
the 4d and 5d groups which are bonded in a strongly covalent manner. It was also considered by Owen [7,8] for some ions of the 3d group. The effects of the covalency on the paramagnetic resonance spectrum can be listed as:

(a) The covalent bond reduces the orbital contributions to the g-factor. The evidence for reduction of the orbital contribution has been obtained from the spectra of (i) Ti$^{3+}$ in alum [9], (ii) Fe$^{2+}$ in MgO [10,11] and ZnF$_2$ [12] and (iii) Co$^{2+}$ in MgO [13,14] and ZnF$_2$ [12].

(b) The hyperfine interaction parameter 'A' is reduced. The experimental evidence comes from the work of Title [15] who studied the paramagnetic resonance of Mn$^{2+}$ in a variety of host lattices and proved that the hyperfine constant, "A", decreases linearly with the increase of covalency.

(c) There may be additional hyperfine structure due to the interaction between the magnetic electrons and the surrounding nuclei called superhyperfine structure. The effect was first found by Owen and Stevens in ammonium chloroiridate [16], and subsequently for a number of transition metal ions in ZnF$_2$ by Tinkham [12] and by several other workers [17-20] in various host lattices.

2.9 KRAMERS' THEOREM

The Kramers' theorem distinguishes the behaviour in the
crystalline field of ions containing an even or odd number of electrons. It is concerned with the effect of crystal field on the degeneracy of the ground state of a doped paramagnetic ion. Kramers' theorem [21] states that in a crystalline field of any symmetry, a system having an odd number of electrons will always possess at least a two-fold degeneracy. There are at least two states with the same energy in the crystal field for odd electron system and these are split by the application of a magnetic field. These states are referred to as Kramers' doublet and assures the observation of EPR in the so called Kramers' ion (odd number of electrons).

2.10 JAHN-TELLER EFFECT

According to this effect [22,23], a symmetrical non-linear molecule having a degenerate electronic energy level can not have stable configuration and will therefore distort to a configuration of lower symmetry and thus the degeneracy of the electronic state is lifted, or in other words the disposition of the nuclei adjusts in such a way that the symmetry of a complex gets lower.

Van Vleck [24] estimated that for iron group, a splitting of few hundred cm\(^{-1}\) and for rare earth group about 10\(^{-2}\)cm\(^{-1}\) may be caused by Jahn-Teller effect. In the case of paramagnetic ions embedded in diamagnetic hosts, the symmetry of the ligand
field is also reduced due to Jahn-Teller effect. This effect is prominently noticeable in the case of Cu$^{2+}$ in trigonal field [25-27] and Fe$^{2+}$ in octahedral field [10,11].

The theory of Jahn-Teller effect has been explained in very simple terms by Low [28]. The proof of the theorem is based on group theoretical methods which is not easily understandable. However, the physical reason is quite simple. A perturbation is assumed to act which is able to remove the degeneracy and split the levels. The centre of gravity of the levels will remain the same as before the application of perturbation. This means that one of these levels must have lower energy than that before splitting. Since a molecule will tend to the minimum energy state, there will be an influence on the surroundings of such a nature as to distort the molecule and remove the degeneracy. Presumably the same arguments are true for ions in crystals.

Since the original work of Jahn and Teller and the pioneer work of Van Vleck, a large number of articles, some of them of a highly sophisticated nature, have been published on the theory of Jahn-Teller effect [28,29].

2.11 ZERO-FIELD SPLITTING

When a metal ion is placed in a crystalline field, the degeneracy of the d-orbitals will be removed by the electrostatic
interactions. The spin degeneracy will remain until a magnetic field is applied. When the species contains more than one unpaired electron, the spin degeneracy can also be resolved by crystal field. Thus the spin levels may be split even in the absence of a magnetic field; this phenomenon is called zero-field splitting.

The theoretical explanation of zero-field splitting in S-state ions was given by Van Vleck and Penny [30], Sharma et al. [31], Narayana [32], Chatterjee et al. [33] and Watanabe [34]. Zero-field splitting is generally observed in Ni$^{2+}$ and Mn$^{2+}$ [35,36]. Recently Starch and Bramley [37], and Bertrand et al. [38] have observed the zero-field splitting in EPR studies of VO$^{2+}$ ion in Tutton salts and in iron (II) parphyrin respectively.

2.12 FORBIDDEN TRANSITIONS

In the paramagnetic resonance spectra of ions which have a more than doubly degenerate ground state, split by the crystalline electric field by amounts of the order $10^{-2}$ to $10^{-1}$ cm$^{-1}$, and which also have a hyperfine structure, a number of extra hyperfine lines have often been observed which appear to correspond to transitions in which the nuclear magnetic quantum number $m$ changes by $\pm 1$. These were first reported by Bleaney and Ingram [39] in manganese ammonium sulphate and
manganese fluosilicate; they appeared when the external magnetic field was inclined at an angle between parallel and perpendicular to the crystal axis, and were inexplicably large in intensity. They arise from second-order effects due to cross terms in the spin-Hamiltonian between the 'fine structure' splitting and the hyperfine structure splitting, as shown by Bleaney and Rubins [40].

2.13 LINE WIDTH AND RELAXATION

In microwave spectroscopy generally, resolution of the spectrum is limited, not by instrumental effects, but the width of the lines themselves. In paramagnetic resonance transitions the electrons are transferred to the higher levels from the lower one and they return to lower levels by relaxation processes so that the absorption of the microwave radiation is continued. There are two types of relaxation processes, the spin-lattice relaxation and spin-spin relaxation. The process in which the energy flows from the spin system to the lattice is called spin-lattice relaxation process and that in which the spins exchange energy among themselves is called spin-spin relaxation process.

2.14 SPIN LATTICE RELAXATION

The three commonly discussed mechanisms for transferring energy from the spin system to the lattice are described as
direct, Raman and Orbach processes. In the direct process for the two-level system, relaxation occurs through transfer of energy from a single spin to a single vibrational mode of the crystalline lattice which has essentially the same frequency \[41\]. When relaxation is by the direct process, \( T_1 \propto 1/B^2 T \) \[42\] (where \( T_1 \) is the spin lattice relaxation time) and is independent of the spin concentration. Therefore, the temperature and magnetic field can serve as variables either for the study or for the control of \( T_1 \). Actually, the "direct" process is important only at low temperatures.

At high temperatures, the indirect or Raman process predominates. Here a phonon is inelastically scattered in the process of flipping a spin. Energy is conserved and this process is strongly temperature dependent with \( T_1 \propto 1/T^7 \) for \( T<\Theta \), and \( T_1 \propto 1/T^2 \) for \( T>\Theta \), where \( \Theta \) is the Debye temperature \[43\]. Experimental results are in fair agreement with theory at high temperatures but not at low temperature where the direct process is important.

In the Orbach process, there are two transitions one after the other which occur via an intermediate state. When electron is transferred from a level \( i \) to level \( j \) in the ground manifold of states by absorbing energy equal to \( h\nu \), then by stimulated transition, it goes to a level \( p \) which is higher
in energy than \( j \) by an amount \( \delta \). Spontaneous transition takes place from level \( p \) to \( i \) which releases a phonon of energy \( (\delta + \hbar \nu) \). The relaxation rate is given by

\[
\frac{1}{T_1} \propto e^{-\delta/kT}
\]

(2.16)

where \( k \) is the Boltzmann constant. This relaxation process is active in the case of rare-earth impurities in crystal lattice.

2.15 SPIN-SPIN RELAXATION

The theory of spin-spin relaxation has been developed by Van Vleck [44] and Pryce and Stevens [45]. In this process two main types of interactions between the ions have been recognized, the dipole-dipole and the exchange interactions. The dipoles are close enough so that they experience various local fields resulting from the dipolar fields of their neighbours. In the case of exchange interactions, the energy transfer takes place by means of mutual spin flips between neighbouring spins. As the spins are in thermal equilibrium among themselves and if the equilibrium is disturbed, it is re-established exponentially with time constant \( T_2 \) which is called spin-spin relaxation time.
2.16 EXCHANGE INTERACTION

The usual treatment of the exchange interaction was given by Dirac [46], showing that the coulomb interactions between electrons can be replaced (when all spin-orbit couplings are neglected) by an interaction between their spins of the form \( \frac{1}{4} J(1+4 \vec{S}_1 \cdot \vec{S}_2) \). The constant term is usually neglected as of no interest and the value of \( J \) depends on the overlap of the orbital wave functions. The custom is to assume that the interaction is \( J \vec{S}_1 \cdot \vec{S}_2 \) where \( \vec{S}_1 \) and \( \vec{S}_2 \) refer to the actual spins of the ions, which are not necessarily \( \frac{1}{2} \). This interaction is normally considered to be isotropic. For deeper understanding, it may however be noted that the value of \( J \) will depend not only on the separation but also on the orientations of the spins, because, in the crystal field, the charge densities are not spherically symmetric, and this leads to, what is called "anisotropic exchange". However, for the most part in the paramagnetic resonance the exchange has usually been assumed to be purely isotropic [47].

2.17 EPR OF LIQUIDS

The paramagnetic complexes in liquid solutions can be considered as microcrystals tumbling in a random way as they are jostled by the molecular motions of the solvent [48].
However, the immediate environment of the paramagnetic ion in these microcrystals can be as high as cubic with strong possibility of an axial component. In a coordinate system (x,y,z) fixed in the molecule the axial spin-Hamiltonian can be written as [42,48]

\[ \mathcal{H} = g \left[ g_{II} B_z S_z + g_A (B_x S_x + B_y S_y) \right] + d S_z^2 + A_{II} I_z S_z + A_1 (I_x S_x + I_y S_y) \]  

(2.17)

and the \( g \) and \( A \) values are given by

\[
\begin{align*}
g &= \frac{1}{3} \sum \epsilon_{11} = \frac{1}{3} \left( g_{II} + 2g_A \right) \quad (2.18a) \\
A &= \frac{1}{3} \sum A_{11} = \frac{1}{3} \left( A_{II} + 2A_1 \right) \quad (2.18b)
\end{align*}
\]

McConnell [48] has shown that the anisotropies in \( g \) and \( A \) values, which are averaged out to zero due to rapid tumbling of the molecule, contribute to the line-widths of the isotropic spectrum and the line-widths are predicted to obey a formula of the type

\[
\Delta y \approx \frac{1}{2} \approx \tau_c \left( \Delta g \beta B + A m_I^2 \right)^2 / \hbar^2
\]

where \( \Delta g = g_{II} - g_A \) and \( \tau_c \) is the correlation time, describing the random motion of the molecule. Rogers and Pake [49] first studied these line-width effects in their study of EPR of VO\(^{2+}\) complexes in solutions.
2.18 EPR SPECTROMETER USED

EPR spectra were recorded on a Varian E-line century series spectrometer model E-109. The spectrometer operates at X-band frequency (~ 9.4 GHz). All the EPR spectra have been recorded with 100 kHz field modulation. The maximum power available with this spectrometer is 200 mW. The recording of EPR spectra both in absorption or dispersion modes is possible and the first as well as second derivative of absorption signal can be recorded. The recorded spectra presented in this thesis are the conventional first derivative of absorption signal.

A Varian rectangular cavity E-231 which operates in TE_{102} mode with unloaded Q > 7000 has been used throughout the experiments. The modulation amplitude usually has been kept small around $\frac{1}{2} G$ (gauss) peak to peak (p-p) amplitude. For the normal EPR recording a power level of ~2 mW has been found adequate to give good signal height at normal gain levels of $1x10^3$. The field stability of these spectrometers after stabilization is of the order of 10 ppm with temperature coefficient of 2 ppm/C° between 3 KG and 15 KG. The signal to noise ratio with E-231 cavity at 100 kHz field modulation is approximately equal to 180.
For EPR studies with single crystals it is required to know the crystal field \((X,Y,Z)\) axis. For this purpose a two axes goniometer was used which provides a possibility of rotation of the magnetic field in any desired plane of the crystal. The \(X,Y,Z\) were determined employing the following method. The crystal was rotated first independently about a horizontal and a vertical axis and a particular orientation was searched where the spread of the fine structure was maximum. Thus knowing one direction of maximal spread in fine structure, the other two directions of extremum in fine structure spread were searched in a plane normal to the first direction of maximal spread. The directions are referred to \(Z, Y\) and \(X\) according to the spread of spectrum.

Once the axes are known the crystal can be cut to facilitate the angular rotation of the crystal about a desired direction. The Varian model E-229 goniometer permits an accurate rotation of samples in steps of 0.1°.

2.19 VARIABLE TEMPERATURE ACCESSORY

The Varian model E-257/WL-257 variable temperature accessory automatically controls the sample temperature within the range of 573 K to 88 K. It provides a means to maintain the desired temperature with an accuracy better than 1 K. For
attaining the temperature of 77 K a quartz Dewar compatible with E-231 cavity, provided with a cold finger, was used. In this arrangement liquid nitrogen cools a copper paddle whose tip is in thermal contact with the sample inside the cavity. The actual temperature at the sample was measured with the help of a potentiometer using a copper constantan thermocouple at the sample. The overall accuracy of the measured temperature is 1 K. The temperature stability at the sample was found to be within ±1 K, after stabilization. The general experimental techniques have been narrated here. Variations or specification of experimental details, if any, will be given at appropriate places.
REFERENCES


