CHAPTER 1

Introduction

ELECTRON PARAMAGNETIC RESONANCE

Electron paramagnetic resonance (EPR), also known as electron spin resonance (ESR) and electron magnetic resonance (EMR), is the process of resonant absorption of microwave radiation by paramagnetic ions or molecules with an unpaired electron (e.g. free radicals, odd electron molecules, transition ions, lanthanide ions, triplet-state molecules), when placed in a strong static magnetic field. The first EPR experiment was performed in 1944 in Kazan by Zavoisky [1], a physicist, who used samples of CuCl$_2$·2H$_2$O, a radiofrequency (RF) source operating at 133 MHz, and a variable magnetic field in the range of a few millitesla provided by a solenoid. Afterwards, experiments were reported by Cummerow and Halliday [2] and by Bleaney and Penrose [3]. The major developments in the techniques of measurement have come from the Oxford groups of Bleaney and Stevens [4], and Griffith [5] and their co-workers. Abragam and Pryce [6] have developed the theory for the interpretation of above results.

The EPR technique has progressed tremendously and has been successfully applied in diverse disciplines such as biology, physics, geology, chemistry, medical science, material science, anthropology etc. Modern EPR spectrometers are much more complex, having much higher sensitivity and resolution and can be used with different kind of samples (crystalline solids, liquid solutions, powders, etc.) in a broad range of temperatures.

The phenomenon of EPR can be described as the observation of transitions induced by an oscillating source of electromagnetic radiation between the energy levels of a system of electronic magnetic dipoles, described equivalently as a ‘spin’ system. The transitions are observed most commonly between the energy levels of the systems split by an external static magnetic field, the splitting being referred to as Zeeman splitting. Over the years, the frequency range of the electromagnetic
radiation inducing transitions has been extended from the microwave (~9.5 GHz) to high frequency band (95 GHz) [7, 8].

In general, the ‘spin’ may be solely due to

(a) The (real) spin angular momentum of an electron(s), or

(b) Total (paramagnetic) spin angular momentum of a system of unpaired electrons, or

(c) Total angular momentum, which includes both spin and orbital angular momenta.

The physical nature of a given ‘spin’ system gives the origin of the observed spectrum, and thus determines the name applicable to a particular resonance technique, e.g. nuclear magnetic resonance (NMR) for ‘nuclear spin’ systems, whereas EPR (ESR or EMR) for ‘electronic spin’ systems.

A paramagnetic substance possesses no resultant magnetic moment in the absence of an external magnetic field but acquires a magnetic moment in the direction of an applied field. Such a resultant moment of the substance may be partly due to induced dipoles, which appear only through the action of the applied field and result from a change in the motion of the constituent electrons of each atom or ion. In all cases this yields a negative induced moment (i.e. a moment anti-parallel to the applied field), and hence to the diamagnetism, a basic property of all substances. Superimposed on this in certain cases there may be a positive induced moment, resulting in paramagnetism (Van Vleck paramagnetism). Both of these effects are independent of temperature except in temperature regions where excited states become appreciably populated. Paramagnetism occurs whenever a system of charges has a resultant angular momentum. If this momentum is due to electron, one speaks of electron paramagnetism. Such paramagnetism is found

i. In all atoms having an odd number of electrons, e.g. atomic nitrogen or hydrogen,

ii. In ions having partly filled inner electron shells, as 3d (iron group), 4d (palladium group), 5d (platinum group), 4f (lanthanide or rare-earth group), 5f (actinide group),

iii. In molecules having an odd number of electrons such as NO,

iv. In a small number of molecules with an even number of electrons but having a resultant angular momentum as in O₂,
v. In free radicals such as CH₃,

vi. In color centers,

vii. In metals and semiconductors caused by conduction electrons.

The early conventional cw (continuous wave) EMR spectroscopy has evolved from the most common frequency band X (~9.5 GHz) to K (~35 GHz), and today it includes also the lower bands: L (~1.5 GHz), S (~3.0 GHz) and C (~6.0 GHz), as well as the higher bands: V (~50 GHz), W (~95 GHz), far infrared, and broad bands encompassing THz frequencies [9-11].

In the solid state we are concerned mostly with ions rather than atoms. Many such ions have closed electron shells, which have no resultant angular momentum and hence no permanent electron magnetic dipole moment. Partially filled shells, with permanent dipole moments due to the orbital motion of the electrons, or to their intrinsic spin or both, occur in the ‘transition groups’. Other paramagnetic ions may occur as defects or may be created by irradiation. We shall mainly be concerned with localized states of transition group ions in non-conducting crystals. Furthermore, we are primarily concerned with ‘paramagnetic’ substances in which each permanent dipole is substantially unaffected by the presence of the other permanent dipoles. The theory then treats each dipole separately, and the interaction with neighboring permanent magnetic dipoles enters only in a subsidiary manner.

Nevertheless, in the solid state a paramagnetic ion is by no means ‘free’. It is surrounded by a number of diamagnetic ions, the nearest at distances of order 0.2 to 0.3 nm [12], the complex forming part of an extended lattice. These charged ‘ligand’ ions have a strong interaction with the paramagnetic ion, producing a strong electrostatic field (the ‘ligand’ field), the interaction between the paramagnetic electrons and this ligand field varies roughly from 10² -10⁴ cm⁻¹.

In EPR, we are concerned with transitions between levels split at most by a few cm⁻¹. Hence we are immediately interested only in a group of levels that are degenerate (or nearly so) in zero magnetic field, and a convenient method is needed to represent the behavior of such a group of levels when a static magnetic field is applied to the system. A suitable method has been evolved which uses the concept of an
‘effective spin’ $\vec{S}$, which is a fictitious angular momentum such that the degeneracy of the group of levels involved is set equal to $(2\vec{S} + 1)$. However, electron paramagnetic resonance, gives the most direct and accurate description of the ground state and of the effect of the crystalline environment on the energy levels of the paramagnetic ion. The results permit the calculation of the magnetic susceptibility and the specific heat at low temperatures. The precision with which the resonance spectra can be measured enables to determine the significant ‘crystal field’ parameters.

Its range of application is extremely broad. In ionic crystals it makes it possible to determine the structure of the energy levels of magnetic centers, elucidate the fine structure of the crystalline lattice, and define the parameters that characterize the kinetics of magnetization. The study of crystal lattice defects by means of EPR is of extreme interest. In liquid salt solutions, EPR affords the possibility of investigating solvate shell structure. Interesting data concerning the properties of conduction electrons in metals and semiconductors have been obtained through it.

In nuclear physics, paramagnetic resonance has proved valuable as a method for determining nuclear moments, and it is one of the most effective means of polarizing nuclei. The method of paramagnetic resonance has been quite fruitful in chemistry. It has enabled the first detection of free radicals in $10^{-10}$ to $10^{-13}$ mole quantities.

Recently, the importance of metal ions to the vital functions of living organisms has become increasingly apparent. The metabolism and transport of metal ions and their complexes is being studied and new models for complicated natural structures and processes are being devised and tested. We hope the understanding of the chemistry of metal-amino acid (or polyamino acid) complexes will eventually help in our understanding of more complex problems concerning the role of metals in biological systems [13].

EPR spectroscopy is quite applicable for observing the effect of ligand on the metal ion. However, there is a limitation that only paramagnetic metal ions (those with unpaired electron) may be observed. Most recently, electron paramagnetic resonance has found important applications in radio engineering in the construction of a new kind of low-noise amplifier. In these amplifiers one usually utilizes variable fields
at two different frequencies lying in the microwave region. Radiation at one frequency is used to supply energy to the paramagnetic substance, and the other frequency is used for amplification. These examples explain the intense current interest in this method that is shown not only by physicists but also by chemists, biologists, radio engineers and others. From the present perspective, the fundamental theories underlying EPR have been represented in the form of a flow chart by Rudowicz and Mishra [14].

In principle, the method consists of observing the power absorbed from a microwave radiation by an assembly of unpaired electrons in a d. c. magnetic field when the H-vector of the electromagnetic radiation is perpendicular to the d. c. magnetic field. It has now become one of the most important tools for the study of magnetic behavior of paramagnetic substances.

If a d. c. magnetic field is applied to a system of free electrons (L=0, S=1/2). The electrons align themselves either with their spins and moments parallel or antiparallel to the applied magnetic field (Fig. 1.1).

![Diagram](image)

**Fig. 1.1 Energy levels for s = 1/2, Zeeman effect in an applied field B, with allowed transition at \( h\nu = g\mu_B B \) (basic electron resonance condition).**
If a free ion with a resultant angular momentum $j$ is placed in a magnetic field $B$, the energy levels are given by

$$ W = g \mu_B B M $$

(1.1)

In this case, $g$ is the Landé’s $g$ factor given by

$$ g = 1 + \sum_{l=0}^{j} \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} $$

(1.2)

and,

$$ \mu_B = e \hbar / 4\pi mc $$

is the Bohr magneton

where $e$, $m$ are the charge and mass of the electron, $c$ is the velocity of light, $h$ is the Planck’s constant, $l$, $s$ are the orbital and spin angular momentum, $M$ is the component of angular momentum $j$ along the field acting on the ion. If an alternating field of frequency $\nu$ is applied at right angles to $B$, magnetic dipole transitions are produced according to the selection rule $\Delta M = \pm 1$. The magnetic field required for a given frequency quantum is

$$ h\nu = g \mu_B B $$

(1.3)

The simplest case is that of a single electron whose orbital moment $L$ is zero. The $g$ factor is then 2 or more accurately 2.00229.

**Eq. (1.3)** can be written more conveniently as

$$ g = \frac{21.478}{\lambda B} $$

(1.4)

where, $B$ is measured in Kilogauss and $\lambda$ is the wavelength measured in centimeters. Actually, from **Eq. (1.3)** one could infer that paramagnetic resonance is observable, even at low frequencies. This, indeed, has been done by a number of workers [15].

Energy will be absorbed if the spin of the electron is flipped from a direction parallel to the magnetic field to that of the anti-parallel direction. When the converse occurs, one speaks of induced emission. Both transitions have the same a priori probability. In a system at thermal equilibrium, the lower state has a greater
population. Therefore, in such a case, there is a greater absorption than emission of energy.

The distribution of electrons between the two states is governed by the Maxwell-Boltzmann expression

\[
\frac{N_1}{N_2} = e^{-\Delta E/kt}
\]  

(1.5)

where, \( N_1 \) and \( N_2 \) are the number of free electrons in the upper and lower state, respectively and \( \Delta E \) is the energy separation between the two levels. For a single spin system the excess of population of the ground state over the upper state is very small. In fact for a temperature of about 300 K and magnetic field 3000 gauss, the excess population in the ground state is only about 0.07%, yet the whole phenomenon of EPR depends upon this difference. If this resonance absorption of radiation is to continue, there must be some other mechanism, which allows electrons in the upper energy state to lose energy and drop back to the lower state. This mechanism must allow energy transfer of \( h\nu \) by interaction with some system other than the incident radiation. If this were not so, the large number of electrons absorbing energy in the ground state would tend to equalize \( N_1 \) and \( N_2 \) and further absorption would stop. Such important processes are called relaxation processes.

The hyperfine splitting of an electron spin resonance line is observed when there is an interaction between the unpaired electron and the nucleus having non-zero spin within the molecule. It is of great importance in determining the actual electronic states of the paramagnetic ions and gives valuable information about the intra- and intermolecular interactions. The general Hamiltonian of the system involving hyperfine interaction is represented by,

\[
\mathcal{H} = \mu_B \overrightarrow{B} \cdot \overrightarrow{S} + \overrightarrow{S} \cdot \overrightarrow{A} \overrightarrow{I} 
\]  

(1.6)

where ion is assumed to be free. But it is not always the case and the unpaired electron is bound to the molecule by a number of forces. Therefore for a macroscopic body having paramagnetic as well as diamagnetic components, the above Hamiltonian will be modified as discussed in chapter two of the thesis.

The overall importance of the method is as follows:
(1) The data obtained from resonance measurements under certain conditions are found very useful when considering the bulk properties of the system such as susceptibility and specific heat;

(2) Resonance spectra are obtained by electronic transition; a reliable interpretation about the nuclear spin of paramagnetic ion can also be obtained. Approximate value of nuclear dipole and nuclear quadrupole moments may be found;

(3) The resonance spectrum is extremely sensitive to the surroundings of the paramagnetic ion in the system. Thus it also provides information about the symmetry of the surroundings, the nature and the strength of bonding between the ion and its immediate diamagnetic neighbor;

(4) The width of the resonance line depends upon a number of factors such as

   (a) Spin lattice interaction

   (b) Spin-spin interaction and

   (c) Exchange interaction.

Thus the study of widths of resonance spectra will provide some information on these factors, which is not available from any other technique.

(5) Magnetic interaction between the nuclear spin and the unpaired electron spin gives hyperfine structure in the resonance spectrum. There also exists an electrostatic interaction between the gradient of electric field at the nucleus and the electric charge, which gives rise to electric quadropole moment of the nucleus. This quadrupole interaction changes the energy of hyperfine levels. Therefore the study of hyperfine structure provides information about nuclear spin, nuclear moment and electric quadropole moment.

(6) It is one of the unique methods in which magnetic as well as non-magnetic properties of the system are combined together to study the various properties and nature of the compound containing the magnetic ion; and thus there are various parameters of ESR spectrum e.g. line shape, linewidth, g-factor, intensity of the signal and hyperfine splitting constant etc. from which a number of information about the paramagnetic molecule can be obtained. Apart from these points the
information drawn from the EPR spectrum also depends upon the nature and form of the specimen used. If concentrated specimen is used for EPR study, usually single broad line spectrum is obtained [16-20]. For polycrystalline samples, linewidth and g-factor are averaged out over all possible orientations of the crystallites present in the system. Diluted solutions of the complexes are used in order to study the hyperfine structure [21-29]. Most important and useful information is obtained when magnetically diluted single crystals are used for Results of directional anisotropies in g-value and linewidth, which are observed only from single crystal study, give interesting information about the configuration of the ions present in the complexes EPR study [30-36].

Results of directional anisotropies in g-value and linewidth, which are observed only from single crystal study, give interesting information about the configuration of the ions present in the complexes. Bleaney, Griffiths, Abragam, Pryce, Stevens and others have developed most of the theory on crystalline fields and EPR [4-6, 37-38].

In the iron group, Mn$^{2+}$ is of interest because the shell of 3d-electrons responsible for the paramagnetism is just half-filled by the five electrons; there is no orbital contribution to the magnetic moment because the average component of orbital angular momentum $L$ in any direction is zero. The ground state is $^6S_{5/2}$. When paramagnetic ions are introduced in host lattices, local distortions will take place due to mismatch of paramagnetic ion size to that of the host ions. The crystalline electric field can affect the electron spins only through high-order interactions [39-41] so that the spins are almost completely free to orient themselves in an external magnetic field.

It has generally been assumed that as the crystalline electric field has predominantly cubic symmetry, the six-fold levels will split into one four-fold and one two-fold level, as indicated by the group-theory calculations [42]. This splitting is due to rather high-order interactions, corresponding to a Hamiltonian, which may be written as proportional to $\left(S_x^4 + S_y^4 + S_z^4\right)$. A departure from cubic symmetry causes a further splitting of the four-fold level, but this was expected to be smaller than that due to the cubic field, as is the case in other paramagnetic ions of the 3d transition group.

The free ion Mn$^{2+}$ has the configuration 3d$^5$($^6$S). Its ground state term is $^6A_{1g}(S)$. The first four excited states are $^4G$, $^4P$, $^4D$, and $^4F$. 

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A lot of work, both theoretical and experimental, has been done about the ground state. The absorption spectra of these complex ions are characterized by the presence of several bands in the near infrared, visible and ultra violet region. Some of them show several sharp absorption lines besides broad bands. All the observed absorptions are considered due to forbidden transitions. This fact supports the interpretation that they are the transitions between the levels arising from the $d^5$-configuration, since all the levels then have the same parity so that the transitions between them are forbidden.

Thus EPR and optical absorption are two supplementary powerful tools to investigate the site symmetry and associated distortions. EPR of Mn$^{2+}$ has been studied extensively in the investigation of structural and dynamic aspects of crystalline state, since the zero field splittings in these ions are sensitive to even small distortions [43].

EPR of transition ions have been studied extensively for structural and dynamic behavior in crystals [44-50]. Keeping these points into consideration, the work of this thesis presents a research in the field of electron paramagnetic resonance along with optical absorption of Mn$^{2+}$ ions doped in different systems in order to predict associated distortion in the lattice and nature of surrounding crystal field, to find separation of various orbital levels as well as to discuss bonding of central metal ion with its ligands.

L+ glutamic acid is one of the 20-22 proteinogenic amino acids. It is a non-essential amino acid. The carboxylate anions and salts of L+ glutamic acid are known as glutamates. In neuroscience, glutamate is an important neurotransmitter that plays a key role in long-term potentiation and is important for learning and memory.

Tri potassium citrate (TPC) is potassium salt of citric acid and this is used as a food additive to regulate acidity. Medicinally, it may be used to control kidney stones derived from either uric acid or cystine. It is also used in soft drink as buffering agent. Thus these citrates are very useful for biological and medical purposes [51-52].

Many amino acids readily form complexes with metallic halides and they exhibit interesting physical properties [53-58]. Sarcosinium oxalate monohydrate (SOM) contains sarcosine (N-methylglycine), an α amino acid, and belongs to a group of biologically important compounds [59].
Potassium chloride (KCl) is used in medicine, in making fertilizers, in food processing and in judicial execution through lethal injection. It is also used as a beta radiation source for calibration of radiation monitoring equipment. Tin chloride (SnCl) is widely used as mild reducing agent in acid solution. The dihydrate is commercially used in electrolytic tin-plating baths, as sensitizer in silvering mirrors, in the plating of plastics and as a perfume stabilizer in toilet soaps. Monohydrated dipotassium stannic chloride, K₂SnCl₄·H₂O (DPSC) may have some different properties.

Keeping in view, the above mentioned applications, Mn²⁺ doped L+ glutamic acid, TPC, SOM and DPSC have been chosen for the study. The work of the thesis is divided into eight chapters.

Chapter one gives brief introduction of EPR technique and its importance. It also contains nature of work presented in the thesis. Chapter two of the thesis reports a brief review of EPR theories. Chapter three describes the experimental techniques and methods of analysis of EPR and optical spectra. Description of the experimental arrangements and instrumentation are also given in this chapter.

Chapter four gives interpretation of EPR and optical spectra of Mn²⁺ doped L+ glutamic acid together with theoretical study of zero field splitting (ZFS) parameter using microscopic spin Hamiltonian (MSH) theory and crystal field parameters from superposition model (SPM). Chapter five contains the results and interpretation of EPR and optical spectra of Mn²⁺ doped TPC. Chapters six and seven contain the results and interpretation of EPR and optical spectra of Mn²⁺ doped SOM and DPSC single crystals along with theoretical study of ZFS parameters, respectively. Chapter eight presents theoretical study of zero-field splitting parameters of Mn²⁺ doped zinc lactate trihydrate, cadmium ammonium phosphate hexahydrate and potassium trihydrogen selenite single crystals. The procedures adopted for the preparation of single crystals are given in their respective chapters. Single crystal spectra are used for drawing out information about the local field symmetry of the Mn²⁺ ions. The optical absorption has been used to obtain ordering of different orbital levels and to discuss whether the Mn²⁺ ions have entered the lattice substitutionally or interstitially. The EPR results together with the optical data give the molecular orbital (MO) coefficients. These MO coefficients are further used to discuss the nature of bonding of metal ion with different ligands in the crystal.