CHAPTER I

INTRODUCTION TO EPR
Abstract

This chapter gives an introduction to Electron Paramagnetic resonance. The resonance condition is explained. The mechanism of relaxation leading to observable EPR is put forth. Further, the role of electronics in detecting EPR is suitably explained. The chapter ends with giving scope of EPR and explaining EPR as a tool in material research.
1.1 The Magnet

About 2800 years ago a mineral was discovered in the town of MAGNESIA, which had wondrous property. This mineral was called MAGNETITE after the place of its origin. It attracted a piece of iron to itself and a thin strip of this mineral always aligned itself in the same direction, if left to rotate freely. Due to this property it was given the name LEADING STONE or LODESTONE. Such a material was later found to be composed of oxides of iron (Fe$_3$O$_4$) and constitutes a usual magnet. When it is freely suspended, the pole pointing toward North is North Pole and that pointing towards South is South Pole. It is a general observation that like poles repel and unlike poles attract each other. Chinese are believed to be the first to have used a magnetic needle for navigation. However, the first person who carefully studied and recorded the properties of a magnet was William Gilbert of England.

1.2 Electron Paramagnetic Resonance

The seeds of magnetic resonance phenomena were laid in 1936 when Gorter [1] demonstrated that a paramagnetic salt placed in high frequency alternating magnetic field absorbed energy and that this was influenced by the application of a static magnetic field either
parallel or perpendicular to the alternating magnetic field. The development of electronics, during the second world war, placed high frequency oscillators at the disposal of experimentalists. Cummerow and Halliday [2] in U.S.A. and Zavoisky [3] in Russia obtained the first paramagnetic resonance absorption spectra. Since then the phenomenon of paramagnetic resonance has become quite useful in fundamental research.

1.3 The Principle

The principle of the EPR can be explained as follows. Consider an ion which is paramagnetic and thus has a magnetic moment and also a non-zero spin. If this ion is placed in a strong static magnetic field, it may acquire any of the allowed multiple energy levels. In the absence of magnetic field the distinction between such energy levels ceases and the paramagnetic ion is said to be spin-degenerate.

For an assembly of free paramagnetic ions placed in a magnetic field, its different energy levels are suitably occupied and application of an oscillating magnetic field of appropriate frequency will be able to induce transitions between such Zeeman levels and energy is absorbed from the electromagnetic field. Fig. 1.1 shows such a situation for a $S = \frac{1}{2}$ system. The absorption plot between the
absorbed energy and the magnetic field is called the electron paramagnetic resonance or electron spin resonance spectrum (Fig. 1.1). In a practical situation, for better discernability, the first derivative of absorption contour is, however, recorded (Fig. 1.2). The phenomenon itself is called the electron paramagnetic resonance, EPR, or the electron spin resonance, ESR.

For paramagnetic ions embedded in a crystal, however a part of spin-degeneracy is split before hand and when static magnetic field is slowly varied, the absorption shows a series of maxima. Fig. 1.3 depicts such a situation for S=J=5/2 ion.

1.4 Paramagnetic Species

Whenever, a system of charges has a resultant angular momentum, it exhibits paramagnetism. Among the paramagnetic substances mention may be made of the transition group of elements containing 3d, 4f and 5f electrons, monoatomic gases such as atomic hydrogen with its ground state $^2S_{1/2}$, oxygen gas with molecules in the ground states and organic free radicals such as diphenylpicrylhydrazyl (DPPH) having an unpaired electron. Fig 1.4 shows the structure of DPPH which is often used for the calibration of EPR spectra.
If a substance is not paramagnetic, it can be made paramagnetic on exposure to high energy radiation [4] or when subjected to mechanical stresses [5]. This happens due to rupture of normal bonds and creation of new paramagnetic species.

1.5 The Resonance Condition

In the semi-classical picture, the resonance can be visualized by considering a paramagnetic ion with magnetic dipole moment to be a spinning charge. When placed in a static magnetic field $H$, it will precess with a certain angular frequency, called the Larmor frequency, given by

$$\Omega_0 = g_L \frac{e}{2m} H$$

where '$g_L$' is Lande’s g-factor which equals 1 for pure orbital motion and is of value 2 for a free electron spin.

Now, if an additional oscillating magnetic field $H'$ is also applied to the system, the resonance absorption of energy by the paramagnetic centre / dipole may be realized as follows:

As shown in Fig. 1.5, the oscillating magnetic field $H'$ is set perpendicular to $H$. This $H'$ is equivalent to two circularly polarized magnetic fields, one rotating in the sense of the precessing magnet and the other in the opposite direction. If the angular frequency of $H'$
is equal to $\Omega_0$, one of its circularly polarized components may be thought to follow the precessing dipole constantly in phase. This may be supposed to exert a torque on $\mu$, tilt it and finally invert it, after absorption of energy quantum $\hbar \nu_0$.

Obviously, the resonance condition is:

$$2\pi \nu_0 = \Omega_0 = \frac{g_L e}{2m} H$$

or,

$$\nu_0 = \frac{g_L e}{4\pi m} H$$

or,

$$\hbar \nu_0 = g_L \frac{e h}{4\pi m} H$$

$$= g_L \beta H$$

where $\beta$ is the Bohr magneton, being equal to magnetic moment of electron in the first Bohr orbit.

In the quantum mechanical picture, however, one considers an ion placed in a magnetic field $H$ to obey the Russel-Saunders or LS-coupling. In this situation the total orbital magnetic moment represented by $L$ (total value being $\sqrt{L(L+1)} \ h / 2 \pi$, with component $L \ h/2\pi$) and the total spin moment $S$ (total value being $\sqrt{S(S+1)} \ h / 2 \pi$, with component $S \ h/2\pi$) combine to give a resultant $J$. Quantum
mechanically there will be 2J+1 equally spaced energy levels of the ion with energy values,

\[ E_M = g\beta HM, \]

\( M \) taking integral or half-integral values between \(-J\) and \(+J\).

The above expression \( E_M \), represents the energy of dipole with classical expression as \(-\mu H\).

The application of a periodic magnetic field \( H' \cos 2\pi \nu_0 t \) perpendicular to the direction of static magnetic field \( H \), results in magnetic dipole transitions between the adjacent levels, such that \( \Delta M = \pm 1 \). When the resonance condition is satisfied, the expression \([E_M - E_M'] \) equivalent to \( g\beta H \) for \( \Delta M = \pm 1 \), equals \( \nu_0 \).

The resonance condition thus again acquires the familiar shape as:

\[ \nu_0 = g\beta H \]

**1.6 The Spectroscopic splitting factor**

For the case of a paramagnetic ion inside a crystal, the environment of \( \mu \) affects the \( g \) – value which is in general called the ‘spectroscopic splitting factor’ [6] and determines the magnitude of the splitting of energy levels in a magnetic field. This is an important quantity which is obtained even in those cases where the resonance spectrum consists of even a single line.
For a free ion the value of $g$ is very nearly 2. Fidone and Stevens [7] pointed out that the effects of covalent bonding can give positive contributions to $g$-value. However, if the ion is subjected to a crystalline field [7,8], the departure from the free-ion value of 2.002322 in either direction gives an idea of the effective covalent bonding. In crystals the value of $g$ may further vary with the direction of the applied field. The anisotropy in $g$-value is related to the spin-orbit coupling which mixes the ground state of the free ion with the excited states.

1.7 Relaxation Processes

When a system consisting of a large number of magnetic dipoles is acted upon by an exciting e.m. field, at the resonance frequency, the ‘a priority’ probability of absorption of radiation quantum is exactly equal to that of stimulated emission (Einstein radiation laws). Thus for a two level arrangement, the rates of upward ($1 \rightarrow 2$) and downward ($2 \rightarrow 1$) transitions are proportional to the number of ions $N_1$ and $N_2$ in the states 1 & 2 respectively. The net rate of absorption or emission is thus determined by the difference between the upward and downward transitions.
Under thermal equilibrium conditions, the populations are, however, determined by the Boltzmann distribution function:

\[ N_i \propto \exp \left( -\frac{E_i}{kT} \right) \]

where \( T \) is temperature of the system in Kelvin & \( k \) is the Boltzmann constant. Therefore, the ratio of populations in the lower & upper states equals:

\[ \frac{N_1}{N_2} = \exp \left( -\frac{E_2 - E_1}{kT} \right) \]

At resonance,

\[ E_2 - E_1 = \hbar \nu_0 \]

Therefore,

\[ \frac{N_1}{N_2} \text{ becomes } \exp \left( \frac{\hbar \nu_0}{kT} \right) \]

Thus, under thermal equilibrium, \( N_1 > N_2 \), resulting in an excess of upward transitions and a net absorption of energy from the exciting e.m. field. However, such a state of affairs will obviously lead to an increase in \( N_2 \). This will continue, until \( N_2 = N_1 \) and the net absorption of energy will finally become zero. The magnetic
system can then absorb no more power and is said to be saturated. However, the system can be made to remain in the net absorbing state by lowering the system temperature to liquid nitrogen or liquid helium temperatures.

1.7.1 Spin – Lattice Relaxation

The saturation of absorption as above is, however, controlled by relaxation processes, which make the population $N_1$ to increase at the expense of $N_2$. One such relaxation process is spin-lattice relaxation. In the process the lattice plays an important role. It acts like a huge reservoir and spin system exchanges energy with it, leading to heating of the lattice. The rate of this process is characterized by spin-lattice relaxation process and is intimately connected to the width of the paramagnetic resonance line.

1.7.2 Exchange Interaction

When relaxation of excited paramagnetic centre occurs through the exchange of energy with other spins in lattice, exchange interaction comes into play. In such a situation the paramagnetic centre under consideration looses energy and other spins in the host are excited.
The effect of such an interaction changes the shape of paramagnetic absorption line from the usual Gaussian to Lorentzian shape and is often met, when the concentration of paramagnetic centres in the material under study is quite high or else the host also contains paramagnetic centres.

1.8 Role of Electronics in detecting EPR

The microwave electronics plays a big role in proper detection of the EPR signal. As the transition probability \( W_{ij} \) is proportional to the square of the exciting e.m. field amplitude \( H' \), the sample is placed in a cavity resonator which serves to enhance \( H' \). When paramagnetic resonance absorption occurs, the total cavity losses increase leading to the decrease in the effective Q-factor of the cavity. The consequent changes occurring in the coupled wave guide system may be observed by a suitable detector and the detected signal is fed to receiver and associated display system [9]. The block diagram of an X-band EPR spectrometer is shown in Fig. 1.6, the microwave frequency used being at X-band.

1.8.1 EPR and magnetic susceptibility

The power absorbed by a paramagnetic specimen in a resonant cavity is proportional to the magnetic susceptibility. In the dynamic
phenomenon it is usual to consider the susceptibility as a complex quantity \( \chi' - i \chi'' \). Here \( \chi' \) is the dynamic susceptibility and represents the magnetization which changes in phase with the field, while \( \chi'' \) determines the absorption of energy from the periodic magnetic field. The general relation between these two quantities is given by the usual Kramers-Kronig equations.

### 1.8.2 The Resonant Cavity

The resonant cavity arrangement should provide a region of high exciting e.m. field & low electric field. This is needed to enhance the resonant absorption of microwave power, while reducing the non-resonant dielectric loss. A suitable arrangement for this purpose is provided by the H\(_{011}\) cylindrical cavity [10] shown in Fig. 1.7. In this arrangement \( H' \) is vertical along the cylindrical axis and always perpendicular to the steady magnetic field, even when it is rotated in a horizontal plane.

The absorption by a paramagnetic sample and corresponding loss in \( Q \) of the resonant cavity is related to \( \chi'' \) as

\[
\frac{\Delta Q}{Q_0} = 4\pi\chi'' \eta
\]
where \( \eta \) is the cavity filling factor. For a uniform magnetic distribution in the cavity \( \eta \) is simply the ratio of sample volume to cavity volume. But it may be increased by placing the sample at regions of higher \( H' \).

Both the real and imaginary parts of \( \chi \) are plotted together as function of \( H \) in Fig. 1.8. As explained earlier, the absorption by a paramagnetic centre is controlled \( \chi'' \) only. The real part \( \chi' \), however, changes the resonant frequency of the cavity & it is apparent that at the centre of the resonance line, the detuning effect is zero, but it rises to higher values (of opposite signs) on either side.

1.9 Scope of EPR

EPR would be of academic interest only if the magnetic states of electron in question were independent of its surroundings. But it so happens that the interactions between the electron and its surroundings perturb the magnetic state of the system, giving rise to additional transitions. Thus EPR can be used with advantage and serves as a powerful tool in various applications in solid state physics.

Again in some paramagnetic complexes, for example those of doped vanadyl ions, the state of the unpaired electron is determined
by the covalent interaction of the ion with the surrounding ligands or molecules. In such a situation, the molecular orbitals of the whole entity, the vanadyl ion and its surroundings, are to be considered to determine the state of unpaired electron & thus corresponding EPR spectrum gives information about the covalent bonding as well.

Low and Offenbacher [11] reviewed the success of paramagnetic resonance as an important structural tool in perovskites, spinels and garnets, as it often determines the site preference of a particular magnetic ion, the point symmetry, distortion of cubic symmetry and the number of inequivalent magnetic sites.

A survey of the physical and solid state applications of EPR was given long back by Ingram [12]. Bennet and Blackmore [13] even used electron spin resonance spectroscopy to determine the absolute concentrations of hydrogen atoms in a gas-flow system at room temperature at total pressures between one and ten Torr.

**1.10 EPR as a tool in Material Research**

The present application of EPR studies may be enumerated as in the following:

(a). It gives a direct and accurate description of the crystalline environment on the low lying energy levels of a paramagnetic
ion. Careful measurements of EPR spectra enable us to measure the zero-field splitting [14], which in turn decides the role of a paramagnetic system towards designing a solid state maser and for producing very low temperatures by the technique of adiabatic demagnetization.

(b). As the EPR spectra are extremely sensitive to the strength and symmetry of the crystalline field [15] the ion experiences, the EPR technique helps to determine the various crystal field parameters, nature of vacancy (vacancies) associated with the ion, position of paramagnetic ions in the lattice, etc.

(c). It gives information about the spins and quadrupole moments of the nuclei [16] in the paramagnetic complex.

(d). EPR also helps to determine the physical changes taking place in a material on application of pressure [17].

(e). One can study the phase transformation in solids [18] with the help of EPR. In some situations, X-ray studies seem to lag behind the EPR studies in the assessment of phase changes in a material.

(f). EPR studies also give information about the bonding of the doped ion with the surrounding ligands in the lattice [19].
1.11 Proposed work

In this work, it is planned to undertake EPR studies in vanadyl ion, when doped in rubidium chloride host. The effect of temperature on corresponding EPR spectra is also sought to further understand the line-width characteristics.

It has also been proposed to undertake EPR studies for VO\textsuperscript{2+} ions doped in 1:1 mixed system of Zn(NH\textsubscript{4})\textsubscript{2}(SO\textsubscript{4})\textsubscript{2}.6H\textsubscript{2}O and Mg(NH\textsubscript{4})\textsubscript{2}(SO\textsubscript{4})\textsubscript{2}.6H\textsubscript{2}O and to obtain relevant parameters.

It is further planned to undertake optical absorption studies in this system. The results of two studies will then be correlated to estimate various molecular orbital and other parameters involving doped vanadyl ions and surrounding host lattice.
1.12 References


