CHAPTER I
INTRODUCTION

Hyperfine Physics, which broadly concerns with the studies of the interactions of the nucleus or its entities (muons, pions etc.) with the extra nuclear electromagnetic fields, has its roots in different branches of physics (e.g. atomic physics, nuclear physics and solid state physics etc.). In general, the atomic nucleus acts as the probe to obtain microscopic information about its outer electronic charge and spin distributions on an atomic size scale via three types of hyperfine interactions, corresponding to nuclear electromagnetic moments:

1. The Coulomb interaction between the finite nuclear charge distribution (electric monopole moment), which can be associated with an effective 'nuclear charge radius', and the surrounding electrons (s-electrons, having finite density at the nucleus) causes the small shifting in the nuclear energy levels and is only measured by the Mössbauer technique. It is known as the isomer shift.

2. The interaction between the current-and spin distributions in the nucleus (magnetic dipole moment) and the effective magnetic field at the nucleus (due to the surrounding spin distribution, orbital motion of electrons and the applied external magnetic field) causes the splitting of nuclear levels.
3. The interaction between the nuclear nonspherical charge distribution (electric quadrupole moment) and the electric field gradient at the nucleus due to the asymmetric electronic charge distribution around the nucleus, also causes the nuclear level splitting and is known as electric quadrupole interaction.

The physical quantity so measured, is essentially the product of two parameters; defining nuclear quantity (nuclear radius, magnetic moment and the electric quadrupole moment) and the electronic quantity (the extranuclear electromagnetic fields and/or their gradients). The knowledge about one parameter can help to study another parameter. This interdependence of the information about the nuclear parameters and the electronic configurational parameters have given a tremendous momentum for the development of the experimental techniques and the theoretical models describing them.

In the nuclear physics, the determination of nuclear electromagnetic moments is of considerable importance in testing the various theories, describing nuclear structure. The single particle properties of a nucleus are mainly tested by the magnetic moments of the nuclear states while the electric quadrupole moments reflect the nuclear shape in equilibrium. The theoretical approaches and the existing data about the electromagnetic moments have been reviewed at various hyperfine interactions conferences [1-4].
The nuclear moments of ground states or of very long-lived isomeric states are known precisely and are measured by the radio frequency resonance spectroscopy. But these methods cannot be applied for the excited nuclear states. For the excited states, Brady and Deutch suggested the possibility of measuring the magnetic moment of the intermediate state, in the decay, by observing the effect of external field on the angular correlation pattern. Aeppli et al. were the first to apply this technique (Perturbed Angular Correlations) successfully to the measurement of the magnetic moment of the 247 keV state in Cd. Since then, the theory and the technique of PAC have reached near perfection and the new nuclear techniques, Mössbauer and In-beam techniques etc., have been developed to determine both the magnetic moments and the electric quadrupole moments.

The precession of the nuclear moment under the influence of extranuclear fields depends on the interaction strength; proportional to the nuclear level life-time and the magnitude of the field at the nucleus. The applicability of the different techniques for the study of nuclear moments depends on the nuclear level life-time . More data is available for nuclear magnetic moments than for quadrupole moments . The reason is obvious; it is not possible to produce appreciable external electric field gradients and the choice is limited to use molecular
and crystalline electric field gradients (except in the Reorientation precession technique) [14]. The same situation is encountered for the magnetic moments of the short-lived states, where one has to use internal magnetic fields inside ferromagnetic materials. Apart from using the calculated hyperfine fields (present possible only in atoms and molecules), another approach has been to calibrate these fields through the ground state moments and measure the excited state moments [15, 16, 17].

For free atoms and simple molecules it is possible to calculate the hyperfine fields acting at the nucleus, but for atoms or ions in solids it is difficult to account for hyperfine fields quantitatively due to the uncertain situation about the localization of outer conduction electrons [18]. Generally in solids, the hyperfine magnetic field acting at the nucleus consists of Fermi contact contribution (nonzero for s-electrons), electronic orbital contribution (unquenched orbital angular momentum) and spin-dipole contribution from surrounding ions. It is difficult to separate out different contributions, but after the measurements by Hanna et al. [19] and Samoilov et al. [20], the systematic studies of the magnetic hyperfine fields in metallic and non-metallic magnetic materials have given much insight into the role of different contributions in the different electronic environments. For example, in transition atoms or ions the major contribution
comes from the Fermi contact interaction (through core-polarization) while in rare earths, orbital contribution is equally important [21]. An asymmetric charge distribution around the nucleus can cause the electric field gradient at the nucleus. Broadly speaking, the electric field gradient at the nucleus arises due to outer ionic charge distributions, conduction electrons and the distortions in the closed shell of the probe atom (and are accounted through Sternheimer i.e. antisheilding factors, \( \gamma \) and \( R \) respectively). There have been different theoretical approaches with limited success [21] to calculate the electric field gradient but there exists a definite correlation between the ionic contributions and the electronic contributions [22].

The extensive investigations of the hyperfine fields (both static and dynamic) with different external parameters (concentration, temperature and pressure etc.) have not only given important information about their origin and testing different theoretical models (discussed in the chapter II, it has elucidated the sensitivity of these fields for the outer electronic spin and charge distributions. There is a wider use of the hyperfine interactions as a tool for the structural identification and to get microscopic information about different physical phenomena in Physics, Biophysics and Chemistry [23-29] e.g., characterisation of
the properties of magnetic materials, phase transitions in ferroelectric substances, short range order in glasses, imperfections in solids and spin relaxation effects etc. The probe atom of interest is either the part of the host matrix or is substituted by the conventional methods like melting and thermal diffusion, or the forceful methods like ion-implantation. The advantage of the ion-implantation technique is to make the solid solution of the non-soluble impurity in the host matrix, but it involves the radiation damage effects. There is growing activity to study the nature of the lattice defects so produced and in combination with the channeling technique, the hyperfine fields are used to know the electronic structure of the lattice defects around the implanted ion. Recently H. de Waard et al. [33] have reported very informative results about the structure of the trapped He atoms around Sn in Fe, Co and Ni and its effect on the hyperfine field of Sn.

For the hyperfine interaction studies, old techniques are refined and new techniques are developed. In some cases the overlapping of two techniques is made possible (e.g. Mössbauer-effect/radiative detection of NMR), and the complementary information is obtained from them. The different techniques and their advantages and disadvantages are discussed in the book 'Hyperfine Interactions' ed. by Freeman and Franks [34]. The limitations of the Perturbed Angular Correlation technique (used for the present measurements) along with those of the Mössbauer-effect technique, NMR and EPR are given below.
<table>
<thead>
<tr>
<th>PAC</th>
<th>Mössbauer-effect</th>
<th>NMR</th>
<th>EPR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. It involves the radioactive decay among three nuclear levels through γ-γ, β-γ or α-γ emission.</td>
<td>1. Involves radioactive decay between two levels.</td>
<td>1. Involves induced transitions among m-substates of the nuclear ground state through radiofrequency photon absorption.</td>
<td>1. Involves with the induced electronic transitions of an ion or atom through microwave photon absorption.</td>
</tr>
<tr>
<td>2. Perturbation is caused by the interactions of the intermediate excited state moments (I &gt; 1) with the extranuclear fields.</td>
<td>2. Hyperfine interactions occurs through the excited state having energy ≤ 150 keV.</td>
<td>2. Involves ground state (I &gt; 1/2). It cannot be applied to nuclei having ground state angular momentum zero but the PAC and the Mössbauer technique can be used.</td>
<td>2. Similar to the NMR, it can not be used for the hyperfine interaction studies for ions having nucleus with zero momentum ground state. It is limited only for those atoms and ions which have degenerate electronic ground state.</td>
</tr>
</tbody>
</table>
3. The information about the hyperfine interactions is obtained indirectly from the anisotropy attenuation coefficients. The IPAC measures the total sum effect of both the electric and magnetic hyperfine interactions. Through the IPAC technique, interaction frequencies corresponding to the internal magnetic fields and the electric field gradients can be resolved.

3. The characteristics of the hyperfine interactions are displayed directly in the recoil free spectrum.

3. Hyperfine interactions are displayed directly.
4. The concentration of the probe nuclei can be very low and it requires a small quantity of the sample.

5. It is used for both the magnetic hyperfine fields and electric field gradients determination. The sign of the internal magnetic field can be determined.

4. Requires relatively higher concentration and large quantity of the sample. Metallic sample should be in the powder form to reduce the attenuation of the r.f. signal.

5. It is used when the magnetic interaction energy is more than the electric interaction energy. But for the cases when electric interaction energy

4. Requires relatively higher concentration and large quantity of the sample. The studies with poly-crystalline materials are usually not possible.

5. It is applicable only to the paramagnetic compounds. Similar to the NMR it has been applied for both the magnetic and electric hyperfine interactions. Single
For electric field gradient, one cannot get its sign directly. One has to employ single crystal and one of the X-ray should be polarized. The $\beta$-$\gamma$ correlation can also give sign with single crystal measurements.

6. For a minimum measurable level splitting, $\Delta E = \hbar \gamma E$ equal to the line width in the Mössbauer-effect, is comparable to or more than the magnetic interaction energy, a complementary method NQR, is employed. The sign of electric field gradient cannot be determined. For the complete determination of the electric field gradient tensor, the single crystal is required.

6. Involves the very long lived states and has the higher accuracy of measurements.

6. For Mössbauer levels of shorter mean lifetime, a line broadening is observed instead of a splitting

NMR measurements involve the nuclei of relatively very long lifetime, therefore the line-
the measured equivalent precession angle (for the same source) in the angular correlation method would be \( 36 = 2 \) radians. In PAC, the angle of rotation through \( 5^\circ \) can be measured. It makes the PAC technique more sensitive for hyperfine fields compared to other methods.

7. It has been used for the measurements of the electromagnetic moments of the excited nuclear states, but with less accuracy than the other methods.

and the accuracy of a hyperfine field determination becomes about equal to or less than that of typical PAC determination.

width is infinitely narrow. Hence, the precision of NMR measurements is much higher. For NMR experiments involving excited states, situation is similar to the Mössbauer method.

7. Electromagnetic moments of the ground states are measured.
8. No temperature limitations on the PAC experiments. It can be used over a wide range of temperatures.

9. The radioactive decay of the parent nucleus gives rise to the after-effects (e.g., recovery of the electronic shells of the daughter atom). But in metals the recovery time is very short compared to that of nuclear level lifetime (involved in the PAC measurements) and for $\gamma-\gamma$ correlation work it does not affect the surrounding of the probe atom [8].

There is a temperature limit, above which the recoil-free fraction becomes so low that the resonance cannot be observed. Sometimes it is required to carry out experiments at low temperatures to avoid broadening of the resonance line.

It is the only technique to measure the isomer shift. There are no after-effects.

It is the only technique to measure the isomer shift. There are no after-effects. Sometimes it is required to carry out experiments at low temperatures to avoid broadening of the resonance line.

Experiments can be performed only at low temperatures to avoid broadening of the line.

There is a upper temperature limit, above which the recoil-free fraction becomes so low that the resonance cannot be observed. Sometimes it is required to carry out experiments at low temperatures to avoid broadening of the resonance line.
Apart from these techniques, there are two other important techniques, i.e. the Nuclear specific heats and the Nuclear Orientation, which are limited to very low temperatures (< 1 K). The former method is based on the measurement of the dominant contribution of the nuclear specific heat of the system, giving the average properties of the metal in its natural isotopic compositions. The technique is applicable only to those isotopes, having electromagnetic moments in their ground states. Another method, i.e., nuclear orientation, can be used with very low concentration (even less than that required for PAC) of the probe nuclei in the excited state. Its sensitivity and the accuracy to resolve the magnetic and the electric hyperfine interactions has been increased in combination with NMR i.e. NMR/ ON (NMR detected by the destruction of the nuclear orientation anisotropy). Both methods are used to get the sign of the electric field gradients.

The Mössbauer technique and the NMR technique are well developed methods and due to their higher accuracy have become important tools for the analytical work in the various branches of science. The nuclear techniques, the PAC (Perturbed Angular Correlation) and the PAD (Perturbed Angular Distribution) have gained much importance for the studies of solid state effects due to their higher sensitivity and applicability over a wider temperature
range, reviewed by Haas and Hovey [24], Recknagel [28], Haas [35], and Forster [29]. These techniques are based on the measurement of the perturbations (caused by the hyperfine interactions) on the anisotropic intensity distribution of the γ-ray emitted by an ensemble of the nuclei having the excited state spins in a particular direction, determined by the observation of the first γ-ray in the fixed direction (PAC), or by the incoming beam (PAD). Depending on the time-resolution (2t) with respect to level lifetime (\( \tau_N \)), integrated effect of the perturbation (for \( 2t > \tau_N \)) or the perturbation with respect to time (Differential) \( 2t < \tau_N \) can be measured. The magnetic and the electric interaction frequency can be resolved and measured with good accuracy by the time differential perturbed angular correlation/distribution (TAPAC/TAPAD). The theory is reviewed by Frauenfelder and Steffen [8] and Steffen and Alder [9] and the experimental techniques are reviewed by Recknagel [10].

The use of PAC technique is limited by the number of isotopes available through radioactive decay, and is discussed by Erik et al. [36], along with other experimental limitations. The available metals and alloys as a host matrix for a particular nuclear probe are again limited, if the conventional alloying methods (diffusion and melting) are used. The use of a mass separator to implant insoluble
probe in different host matrices by De Waard and Brentjens [37] have extended the use of PAC also. But there is another novel method of solving the solubility problem, i.e., recoil implantation. The recoil energy imparted during nuclear reaction to the product nuclei is enough to implant them into the desired matrix. The PAD technique is not only more sensitive (due to higher anisotropy of the resulting de-exciting γ-ray emission) but it has overcome the many limitations of the PAC technique, i.e., solubility of the impurity, increase of the available excited states and the coincidence condition no longer limits the time range (in HAD) [28]. The major disadvantage with the use of the PAD technique is the radiation damage associated with the implantation. There have been consistent and ever-growing efforts to understand the nature of the radiation damage through the hyperfine interactions [33, 38].

The main advantage with the PAC technique is that the initial nuclear spin orientation is independent of the external parameters of the probe, e.g., temperature and pressure etc. The interatomic distance is a basic parameter in all theoretical models and its change under external pressure can be measured directly. The volume dependence of hyperfine fields puts the critical test of different theoretical models [39, 40], as the pressure not only changes the lattice parameters but it brings the controlled
continuous variation in the parameters like, exchange interactions, electron-phonon coupling, or density of states. Varying these solid state parameters by adjusting the chemical composition of a system, can effect relatively large changes in the properties, but has the distinct disadvantage that these changes are less well defined than in analogous pressure studies.

The temperature dependence of the internal magnetic field with respect to the host bulk magnetisation have been used for the study of the impurity host coupling and the electronic structure around impurity in the ferromagnetic metals. Anomalous temperature dependence have been observed for both dilute transition impurities [41] and the diamagnetic impurities [42]. Generally the local moment formation [43, 44] or local demagnetisation effects [45, 46] are attributed for the deviations in the temperature dependence. These effects have no direct volume or structure dependence therefore, give very limited information on band structure effects. The study of the pressure dependence of the internal magnetic field can give more direct information on the polarization and hybridization of the conduction band [39].

Most of the temperature dependence studies of the electric field gradients are concerned with the non-cubic host metals [47]. A $T^{3/2}$ temperature dependence has been
observed for most of the metals (generally sp-metals) \[^{48}\] \(>\)
while in transition metals a linear dependence is observed \[^{49}\] . Different models have been proposed taking lattice vibrations into account, reviewed by Kaufmann and Vianden \[^{21}\] . It is observed that effects associated with the impurity core and the valence difference play an important role as far as temperature variations are concerned. The measurement of pressure dependencies at different temperature can provide a critical test for these models \[^{50}\] .

This thesis is based on the following work:

1. The hyperfine magnetic fields at Pd\(^{106}\) in \(X_2\)MnSn (\(X = \text{Pd, Ni, Co}\)) alloys at X-site and their temperature dependence in \(Pd_2\)MnSn alloy.
2. Pressure dependence of the hyperfine magnetic field at Cd\(^{111}\) in the Cu\(_2\)MnIn alloy.
3. The temperature dependence of the hyperfine magnetic field at Pd\(^{106}\) in the Pd\(_{0.95}\)Fe\(^{0.05}\) alloy.
4. The hyperfine fields at Hf in Ni and Co.
5. The pressure and temperature dependence of the electric field gradient at Cd\(^{111}\) in Ho metal.
6. The electric field gradient at Ta in Pd metal due to Oxygen trapping and its temperature dependence.
References


