Chapter 5

Measurements Using TDPAC/D Techniques

In this chapter the experiments performed to measure the electric field gradients, magnetic hyperfine fields and nuclear moments through TDPAC/D techniques are described. In all, the following different measurements have been presented in this chapter.

TDPAD Measurements at Nuclear Science Centre.

(1) Magnetic hyperfine field at $^{64}\text{Cu}$ in Cobalt at room temperature. This is the test experiment performed at Nuclear Science Centre, New Delhi in order to set-up the PAD methodology at the Nuclear Science Centre.

(2) Electric quadrupole moment of $9/2^+$ isomer in $^{171}\text{Ta}$.

TDPAC Measurements at Chandigarh.

(1) Systematics of electric field gradient at $^{165}\text{Dy}$ in Rare-earth metals

(2) Hyperfine Interaction at $^{147}\text{Pm}$ in Nd and Gd hosts.

(3) Quadrupole interaction of $^{100}\text{Rh}$ in Tb host.

5.1 Magnetic Hyperfine Field at $^{64}\text{Cu}$ in Cobalt.

Different methods have been applied to measure the magnetic hyperfine field at non-magnetic impurities in ferromagnetic hosts, some of them giving less reliable results since only averaged fields are known at the impurity site. The time differential perturbed angular distribution technique following a nuclear reaction has been extensively applied to measure...
the magnetic fields and electric field gradients at impurities in metals. Two different procedures have been applied to measure magnetic hyperfine fields by this method:

(a) the probe nuclei are produced in a ferromagnetic target itself e.g. Fe in Fe [RIE72], Ni in Ni [BLE70], Ge in Ni and Fe [MOR68], Zn in Fe [AGA74] or

(b) the probe nuclei are produced in the first reaction layer (target layer) and taking advantage of the recoil from the nuclear reaction, these nuclei are implanted into a host layer i.e. target is a combination of two layers. Sometimes a multilayer target is used to enhance the production rate. All measurements which are mentioned above indicate that most of the probe nuclei reach substitutional lattice sites after slowing down in the host lattice.

We have applied the second procedure to remeasure the hyperfine field of $^{64}$Cu in cobalt as a test experiment using NaI(Tl) detectors. The magnetic hyperfine field at Cu impurity in a ferromagnetic host is of interest since it is expected to arise only from conduction electron polarization. According to Kolk [KOL81] there are two contributions to conduction electron polarization for diamagnetic impurities in 3d-ferromagnetic hosts e.g. Cu in Co host: a) the s-d exchange contribution and b) the contribution from the itinerant d electrons. In the s-d exchange contribution, the s-like conduction electrons at the impurity site are polarized via their exchange interaction with the host 3d electrons while in second contribution, the d-like conduction electrons at the impurity site have to be orthogonal to the core electrons.

The magnetic hyperfine interaction of the 6', 20.5ns, 1019keV ($g = +0.176(5)$ [RAG89]) isomer of $^{64}$Cu in ferromagnetic host cobalt at room temperature has been measured using the time differential perturbed angular distribution technique. This isomeric state was populated by the heavy-ion reaction $^{51}$V($^{160.4}$pn)$^{64}$Cu using 52 MeV $^{16}$O ion-beam pulsed at 250 ns. The pulse width of the beam burst was 4ns. Measurements have been carried out at the 16UD pelletron accelerator facility at Nuclear Science Centre, New Delhi. A thin vanadium foil of 1.2 mg/cm$^2$ was pressed on cobalt host (±9mg/cm$^2$) by rolling two foils together. The $^{64}$Cu ions were recoil implanted into the cobalt host. The magnetic interaction of these implanted ions in the crystal modifies the angular distribution of the de-exciting $\gamma$-rays and is normally observed in the time evolution of the ratio of intensities
at 0° and 90° to the beam. Since cobalt exists in ferromagnetic phase at room temperature, here in the present case we expect only magnetic modulation of the distribution pattern of de-exciting γ-rays as quadrupole moment of this state (6') is negligibly small. To observe this, the time spectrum of 1019 keV γ-ray was recorded with the two NaI(Tl) detectors positioned at 0° and 90° with respect to the beam direction at a distance of 15 cm from the target with no external magnetic field on the target. The time structure of the emitted radiation pattern was observed by a time-to-amplitude converter (TAC) started by a suitably shaped pulse from the anode of NaI(Tl) detector and stopped by a pulse picked up from the main oscillator of the pulsing system. The on-line data acquisition was in LIST mode with four parameters, comprising of energy and time signals for each NaI(Tl) detector. In an off-line analysis, 2D matrices (E, t) of energy versus time for each NaI(Tl) detector were constructed from the acquired LIST mode data, after proper gain matching for energy and time. For data analysis, the ratio of the time spectra of the two detectors

\[ R(t) = G_{22}(t) = 2 \left( \frac{I(0°, t) - I(90°, t)}{I(0°, t) + 2I(90°, t)} \right) \]  

\[(5.1)\]
was fitted to an appropriate modulation function for randomly oriented magnetic field as

$$R(t) = A_{22} \left[ 0.2 + 0.4 \cos(\omega_B t) + 0.4 \cos(2\omega_B t) \right]. \quad \text{(5.2)}$$

where $I(\theta,t)$ are the background subtracted and normalized time spectra at two angles $0^\circ$ and $90^\circ$. The normalization factor and background counts were determined by fitting the exponential decay curves for the time spectra. In fig. 5.1 the ratio $R(t)$ is shown together with the theoretical fit. The solid line in fig. 5.1 is corresponding to the Larmor precession frequency $\omega_B = 112(5)$ MHz. Using effective anisotropy $A_{22}=0.15$, we could extract $B_{hf}(^{155}\text{CuCo})=142.5(10)$ kG at room temperature which is in good agreement with the earlier measurement $(142.5(10)$ kG) [RAO85].

### 5.2 Electric Quadrupole Moment of $9/2^-$ Isomer in $^{171}\text{Ta}$

#### Introduction

Nuclei can broadly be classified as spherical as well as deformed ones. For the case of deformed nuclei, deformation can be explained as due to the extra particles moving outside the spherical core. It is known fact that the nucleus can exist in deformed states due to two reasons. One is particle excitation at high angular momentum states, other is the rotation of a deformed core, which can carry high angular momentum. Actually nuclei can have both characteristics. In the case of nuclei in the mass region $150 < A < 190$, the value of the quadrupole moment $<Q>$ is found to be 20 to 100 times higher than expected by spherical shell model. The transition probabilities $B(E2)$ values are found to be behaving in a similar fashion. This extraordinarily high value of $<Q>$ as well as $B(E2)$ values compared to what is expected from the spherical shell model case, is attributed to the existence of a deformed core. These nuclei show rotational spectrum near the middle of the closed shell nuclei. The nuclei in the above mentioned mass region exhibit a wide variety of shapes ranging from axially-symmetric to $\gamma$-soft triaxial which even coexist.

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1 Published in Hyperfine Interactions 96 (1995) 223.
These nuclei have attracted a great deal of attention since measurement of nuclear shape parameters can play a decisive role in understanding the structural aspects in this region. Keeping the above viewpoint, the electric quadrupole moment of the $9/2^+$ isomer [BAC85] in $^{171}$Ta has been measured.

**Experimental Details and Results**

The electric quadrupole interaction of the $9/2^+$ (45ns) 184 keV isomer (shown in fig. 5.2) of $^{171}$Ta in polycrystalline terbium at room temperature has been measured using the time differential perturbed angular distribution (TDPAD) technique. This isomeric state was
populated by the heavy-ion reaction $^{159}\text{Tb}(^{16}_{\text{O}},4\text{n})^{171}\text{Ta}$ using 84 MeV [BAC85] pulsed $^{16}\text{O}$ ion-beam having a width of about 4 ns and a repetition time of 250 ns. The optimum beam energy was calculated by using the PACE and CASCADE computer code. Measurements have been carried out at the 16UD pelletron accelerator facility at Nuclear Science Centre, New Delhi. The thick $^{159}\text{Tb}$ foil (9 mg/cm$^2$) serving as target-cum-backing was used so as to implant all the recoiling nuclei within the foil. The quadrupole interaction of these implanted ions in the crystal modifies the angular distribution of the de-exciting $\gamma$-rays and is normally observed in the time evolution of the ratio of intensities at $0^\circ$ and $90^\circ$ to the beam. The $\gamma$-ray energy spectra and corresponding timing spectra were recorded by two NaI(Tl) detectors as described in the previous experiment. The on-line data

![Delayed Energy Spectrum](image_url)

**Fig. 5.3**: Delayed energy spectrum of $^{171}\text{Ta}$ after one half-life.
were collected in LIST mode with four parameters, comprising of energy and time signals for each NaI(Tl) detector. To generate time signal, the fast signal from the NaI(Tl) detector was used as start signal to TAC and the primary rf signal of the buncher as stop signal. The acquired data, after adjusting proper gain for energy and time, were sorted off-line into 2D (500×1500 channels) matrices $E_t$ between energy and time signal of same detector. In order to investigate the delayed gamma rays produced in the reaction, energy spectra gated by different intervals with respect to the beam pulses were created. One such delayed $\gamma$-ray energy spectrum after one half life shown in the fig. 5.3, clearly reveals 131 keV and 184 keV $\gamma$-rays de-exciting the 9/2$^-$ isomeric state. Some of the $\gamma$-rays present in the delayed energy spectrum arise from other radioactivities produced in-beam during the irradiation of the $^{159}$Tb target.

The $\gamma$-ray angular distribution, perturbed by the electric quadrupole interaction, results in the time dependent modulation of the $\gamma$-ray intensities. From the measured intensities, a ratio function $A_{22}G_{22}(t)$ was formed

$$A_{22}G_{22}(t) = \frac{I(0^\circ, t) - I(90^\circ, t)}{I(0^\circ, t) + 2I(90^\circ, t)}$$

and is shown in the fig. 5.4. Here $I(\theta, t)$ is the time spectrum at angle $\theta$ to the beam direction after background subtraction and normalization. The normalization factors and background were determined by fitting the exponential decay curves for the time spectra (with fixed half life) in the range 40 ns to 200 ns. The usual theoretical perturbation expression [STE75] of $A_{22}G_{22}(t)$ for polycrystalline sample and spin $I = 9/2$ [STE75]

$$A_{22}G_{22}(t) = A_{22}[\sum \cos(n\omega_{01}t)e^{-\frac{1}{2}(n\lambda\omega_{\gamma}t)^2} + (1-f)\sum \cos(n\omega_{02}t)e^{-\frac{1}{2}(n\lambda\omega_{\gamma}t)^2}]$$

has been used. The slope of the fitted curve is non-linear due to the presence of slow frequency component. The amplitude of the modulation spectra is determined by the effective anisotropy contribution of both 184 keV and 131 keV gamma ray transitions. The uncorrected effective anisotropy is close to the measured anisotropy of 131 keV gamma ray.
The experimental $A_{22G}(t)$ function were least squares fitted to two fractions:

- The fraction $f$ corresponds to the self implanted nuclei at regular sites experiencing a unique axially-symmetric quadrupole interaction and
- The rest of the fraction $(1-f)$ is assumed to be at irregular sites experiencing very low quadrupole interaction and is not sensitive to any distribution.

The solid line, shown in Fig. 5.4, corresponds to the interaction frequencies $\omega_{01} = 116(3) \text{ MHz}$, $\omega_{02} = 7(4) \text{ MHz}$ corresponding to fraction $f$ and $(1-f)$ respectively. The fraction ($f$) and the distribution ($\delta$) at the regular sites are observed to be 60% and 0.015 respectively. The poor fit in the region between main peaks may possibly be due to small non-zero value of the asymmetry parameter of the electric field gradient. For half integer spin, the quadrupole interaction frequency $\omega_0$ is given by

$$
\omega_0 = 6 \frac{eQ V_{zz}^{\text{eff}}}{4 I (2 I - 1) \hbar} 
$$

Fig. 5.4: Spin rotation pattern of recoil implanted $^{173}\text{Ta}$ in Terbium host at room temperature.
where $Q$ is the spectroscopic quadrupole moment and $V_{zz}^{\text{eff}}$ is the electric field gradient. Using the measured value of electric field gradient (EFG) of $^{181}$Ta in Tb at room temperature [FOR81] as $V_{zz}^{\text{eff}} = 593(35) \times 10^{17}$ V/cm$^2$ and the value of $\omega_o$ quoted above for substitutional site, we evaluate $|Q|$ as $|Q| = 3.09(19)$ b.

The investigated $I=9/2$ isomer has been identified to be the bandhead state of the band based on the $\pi[514]9/2'$ orbital [BAC85]. The intrinsic quadrupole moment ($Q_0$) for this band can be deduced, using the Bohr-Mottelson relation [EDE83], and is 5.61b. The $B(M1)/B(E2)$ ratios were evaluated from the existing gamma ray spectroscopic data [BAC85] in the following expression

$$\frac{B(M1)}{B(E2)} = 0.693 \left[ \frac{E_y (I I - 2)}{E_y (I I - 1)} \right]^{5} \frac{1}{\lambda (1 + \delta^2)} \quad \text{...}(5.6)$$

Using theoretical expressions given by Donau [DON87] and Hamamoto [HAM87] for $B(M1)/B(E2)$ ratios and quadrupole moment $Q_0$, respectively

$$\frac{B(M1)}{B(E2)} = \frac{12 K^2}{5 Q_0^2 \cos^2 (30^0 + \gamma)} \left( \frac{1 - \frac{1}{1 + \frac{K^2}{(1 - 0.5)^2}}} \right)^{3/2}, \quad \text{...}(5.7)$$

$$Q_0 = \frac{4 Z R^2 \beta_2 \cos \gamma}{5}, \quad \text{...}(5.8)$$

we calculate $\beta_2 = 0.22(1), \gamma = 0^\circ \pm 10^\circ$, the deformation parameters for $\pi[514]9/2'$ band. In eq. (5.7), the g-factor $g_\pi = 1.30$ [SCH92] and the aligned angular momentum $i_p = 3h$ [BAC85] for the valence proton in the $\pi[514]9/2'$ orbital have been used.

The sign of the quadrupole moment could not be measured in the present experiment which restricted in ascertaining the nature of the quadrupole deformation. However the positive sign of mixing ratios of M1 transitions [BAC85] band favour the prolate deformation. Such a deformation may possibly be attributed to the dilution of shape-driving effects of the $\pi[514]9/2'$ extruder orbital by the deformed core.
5.3 Systematics of Electric Field Gradient at Dy in Rare-Earth Metals

Introduction

The hyperfine interaction studies of rare-earth and non rare-earth nuclei in rare-earth (RE) metals and alloys have given much insight into the origin of hyperfine fields and crystalline electric field effects, local magnetic moment formation, their coupling mechanisms and dynamic behaviour of 4f spins etc. The available systematic data of hyperfine fields at RE nuclei in heavy RE metals and alloys, mostly by Mössbauer and NMR measurements [BAR79] at low temperatures in the ferromagnetic phase, have shown that the hyperfine fields are dominated by intra-ionic contributions (due to unfilled 4f-shell) over inter-ionic contributions (due to conduction electron polarization and charge distribution) in solids. It is observed that at low temperatures,

- The 4f-shell contribution to electric and magnetic hyperfine interactions is nearly equal to that of free ion value.
- The extra-ionic hyperfine magnetic field contribution comes from the conduction electron polarization due to probe spin and the average spin value of the alloy.
- The extra-ionic electric field gradient is proportional to the lattice contribution.

The electric field gradient studies at RE nuclei in RE metals are important to understand its origin and other related electrostatic interactions, e.g. crystalline electric fields (CEF), magnetocrystalline anisotropy etc. The EFG at RE nuclei is analyzed as the sum of the external contributions (due to ionic and conduction electron distributions) and the local contributions (due to aspherical 4f-shell) [BAR79]. The available EFG and CEF parameters are usually analyzed under the phenomenological point charge approximation inspite of doubts about its validity in case of metals (due to the presence of conduction electrons). In the point charge approximation the EFG at the nucleus due to geometrical arrangement

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2 Submitted for publication in Phys. Lett. A.
of the ions \((V_{1}^{\text{loc}})\) is related to the EFG at 4f-shell \((A_{0}^{0})\) through the relation [BAR79],
\[
A_{0}^{0} = -\frac{1}{4} \frac{(1 - \sigma_{2})}{(1 - \gamma_{e})} V_{zz}^{\text{loc}}
\]

There is much uncertainty involved in the values of the screening parameters \(\sigma_{2}\) due to the 5d\(^5\)p\(^6\) closed shells and, the antishielding parameter \(\gamma_{e}\) due to core electrons of RE ions. It is a complex problem to determine conduction electron contributions to the EFG and the CEF parameters in metals and requires full potential calculations of 4f-shell charge distributions and the conduction electron charge distributions self consistently. Recently, first-principles self consistent band structure calculations of EFG/CEF parameters in some of the RE metals, RE transition metal intermetallics and in simple cubic metals Ag and Au have shown that the aspherical charge density [COE90, KUR93, STE94] of 5d\(^6\)p \(6\) valence shells of the RE atoms is the major source influencing the EFG and the CEF parameters as compared to that due to neighbouring atoms (conceived in point charge models). These calculations are limited to either S-type of RE ions (treating 4f states as band states) or strongly localized 4f-shell (4f-shell as open core states) approximations and does not give complete picture about electrostatic interactions between the aspherical 4f-shell charge distributions and the conduction electrons throughout the RE series. The photoemission spectroscopy [KAN94], the magnetization measurements in pure RE metals [BEL87] and their transition metal alloys and the RE crystal structure investigations [DUT77] have shown strong hybridization effects between the 4f-shell and valence shell electrons in the beginning of RE series (LRE metals) and it becomes negligible at the end of the RE series (HRE metals). The total number of valence electrons may be same across RE series but various intra-atomic and inter-atomic hybridization effects interpreted in terms of the variations in the various valence band occupation numbers. The EFG measurements are very sensitive to local electronic structure and can give direct information about the exact valence electron structure across RE series as compared to CEF parameters. The systematic measurements of EFG at RE nuclei in RE metals can throw light on various intra-atomic and inter-atomic interactions influencing charge distributions and test the significance of valence electron contributions as pointed out by first-principles band structure
calculations. The available systematics of EFG at non-RE nuclei have surprisingly shown the influence of the 4f-shell occupancy of the host atoms [FOR85] which are considered to be screened by conduction electrons. The variation of EFG at non-RE nuclei across RE metal series is explained in terms of impurity-host atoms volume mismatch [MIS82] and charge transfer [FOR79] models but the real mechanism is still not clear.

The measurements of EFG at RE nuclei in pure RE metals exclude the possibility of volume mismatch or charge transfer between the probe atoms and the host atoms as they have similar chemical characteristics and very small decrease of atomic volume across the RE series. The earlier investigations of the electric quadrupole interaction of RE nuclei in pure RE metals and alloys [SHI78, MAC74] were carried out through NMR technique. In an approximate analysis, these authors have found a linear relationship between the ionic contribution and the conduction electron contribution to the EFG in addition to the 4f-shell contribution (with non-S state RE ions) at RE nuclei. The 4f-shell contribution was calculated under the free ion approximation for the completely polarized state \( \langle J_z \rangle = J \). The small difference between the experimentally observed value of EFG and the 4f-shell contribution under free ion approximation was attributed to the conduction electron and ionic contributions. At low temperatures in the presence of exchange interaction, it is difficult to have unambiguous interpretation about various contributions to EFG due to various factors e.g. complex magnetic structure, distortion in the lattice structure and the extrapolated values of lattice constants etc. In these measurements the variation of EFG in various intra RE alloys can be equally accounted for by the small variation of \( \theta \), the angle between electronic angular momentum \( J \) and crystal axis \( c \). From these measurements it seems that the ionic EFG enhancement (ratio of conduction and lattice contributions) to conduction electrons depends on the 4f-shell occupancy of probe ions.

The temperature dependence studies of the EFG at RE nuclei have been carried out to ascertain the relative magnitude of various contributions to the EFG in RE metals. For the S-state of RE ions the temperature dependence is either constant or weak [HAU80, BOH80]. But in case of non-S RE ions the results depend on the technique used for such type of investigations. e.g. \(^{166}\)ErEr [REE67]. \(^{154}\)ErEr [RAF83]. The Mössbauer measurements in the ferromagnetic phase of Dy [SWE73] and Er [REE67] and in the
paramagnetic phase at low temperature in Tm [UHR67] are explained in terms of free ion approximation. The Mössbauer measurements in the paramagnetic phase are limited by the fast electronic relaxation effects and has small recoil free fraction and it has not been possible to have more measurements to observe host associated effects. The time differential perturbed angular correlation/ distribution (TDPAC/D) techniques concern with the measurements in time domain and in some favorable cases depending on the nuclear relaxation time, it is possible to carry out measurements in the paramagnetic phases at high temperature e.g. $^{147}$GdGd [HAU80], $^{154}$ErEr [RAF83]. Further such type of studies in other metals can throw light on the conduction electron effects.

At present there is no systematic measurement of EFG available at RE nuclei across RE series. The present measurements are a part of the investigations of host associated effects on the EFG at RE nuclei in RE metals using the TDPAC technique. The TDPAC technique is limited by the number of suitable radioactive nuclei. Now many more excited states of radioactive RE nuclei can be used in pure RE metals using BaF$_2$ scintillators (for the improvement of time resolution) for TDPAC measurements, e.g. 2$^+$ states in RE nuclei, even in the presence of much faster nuclear relaxation rate as it has been shown in the present measurements. Previous measurements of time dependent hyperfine interactions were carried out for rare-earths in ferromagnetic and diamagnetic metals using the IPAC and DPAC technique. It was observed that the aspherical 4f-shell rare-earths followed the calculations of Blume [BLU68] for a magnetic time dependent interaction but the spherical 4f-shell rare-earths ($^{154}$Gd & $^{174}$Yb) followed the Abragam and Pound [ABR53] theory. It is pointed out that a small admixture of quadrupole interaction could give agreement with Abragam and Pound theory for aspherical 4f-shell rare-earths. It was expected that further studies with better time resolution can confirm the observation of quadrupole effects superimposed upon a time dependent magnetic interactions. In view of the fact that the observed nuclear relaxation time for $^{160}$Dy in Dy metal [WAG71] is comparable to the nuclear lifetime of 2$^+$ state, we have attempted to use $^{160}$Dy probe for the EFG measurements in Pr, Nd, Gd, Tb, Dy, Ho and Er metals at room temperature where all these RE metals exist in paramagnetic phase.
Experimental Details and Results

The $^{160}$Tb activity decaying to $^{160}$Dy through $\beta^-$ decay was obtained by neutron irradiation of 99.9 % pure Tb metal for five days at Cirrus reactor, Trombay. Dy is a doubly even nucleus in the deformed region and its level scheme is shown in the fig. 5.5. Some of the important features of this probe are tabulated as

<table>
<thead>
<tr>
<th>Parent nuclei</th>
<th>$^{160}$Tb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Probe nuclei</td>
<td>$^{160}$Dy (stable)</td>
</tr>
<tr>
<td>Half life of parent nuclei</td>
<td>72.1d</td>
</tr>
<tr>
<td>Half life of intermediate state $2^+$</td>
<td>1.94±0.04 ns [RAG89]</td>
</tr>
<tr>
<td>$\gamma$-$\gamma$ Cascade</td>
<td>$\gamma_1 = 87$ keV, $E2+13% M1$ $\gamma_2 = 1172$ keV, $E1+15% M2$</td>
</tr>
<tr>
<td>Quadrupole moment of $2^+$ state</td>
<td>2.07(45) b [RAG89] (corrected for Sternheimer factor $R_s=0.15$ [TAN83])</td>
</tr>
<tr>
<td>g-factor of $2^+$ state</td>
<td>0.696(32) nm [RAG89]</td>
</tr>
<tr>
<td>Anisotropies</td>
<td>$A_{22}=0.183(17)$, $A_{44}=0.03(3)$ [SIN84]</td>
</tr>
<tr>
<td>Sternheimer Antishielding factor</td>
<td>$\gamma_K = -80.0$ [PEL72]</td>
</tr>
</tbody>
</table>

$^{160}$DyR (R = Pr, Nd, Gd and Tb) samples were prepared by melting under high vacuum ($10^{-5}$ mm of Hg), a very tiny speck of $^{160}$Tb activity with high purity host metal in a quartz capsule (which was flushed with pure argon gas several times before producing high vacuum) with the help of oxy-acetylene flame. In case of $^{160}$DyR (R=Dy, Ho and Er), after high vacuum, a small pressure ($10^{-1}$ mm Hg) of Ar gas was allowed during melting to suppress the evaporation of metal. Before using the part of the sample for DPAC measurements, its surface was cleaned with dilute HCl without any further heat treatment. DyPr and DyNd samples were kept under high vacuum during measurements. The reliability of the melting and the proposed site identification was checked up by carrying out the DPAC measurements for both (a) unmelted neutron irradiated Tb metal and (b) the melted Tb metal activity with natural Tb metal. We observed the same results for both the samples.

Two coincidence spectra were recorded simultaneously in three detector geometry at
180° and 90°, detecting 87 keV γ-ray in 15mm × 44mm BaF₂ crystal and 1172 keV γ-ray in 25mm × 44mm BaF₂ crystals coupled to XP2020Q PM-tubes. The background subtracted and normalized spectra were used to derive the perturbation function.

$$G_{22}(t) = \frac{2}{A_{22}} \left[ \frac{C(180^\circ, t) - C(90^\circ, t)}{C(180^\circ, t) + 2C(90^\circ, t)} \right]$$  \text{(5.10)}

The $G_{22}(t)$ factors were least squares fitted to the two site expression

$$G_{22}(t) = \sum_i f_i^2 \ G_{22}^i(t) \ e^{ - \lambda_i^2 t} , \ \sum f_i^2 = 1$$  \text{(5.11)}

where exponential damping factor $e^{-\lambda_i^2 t}$ was included for the paramagnetic relaxation of Dy³⁺ ions at site $i$. The damping constant, $\lambda_i^2$, carries the damping effect on the $G_{22}(t)$ spectra due to the nuclear magnetic relaxation at different sites. At room temperature, the perturbation function $G_{22}^i(t)$ for pure electric quadrupole interaction in case of $I=2$ [BEL76] is

$$G_{22}^i(t) = \sum_{n=0}^{1,3,4} S_{2n} \cos(\omega_n(\eta) t) \ \exp \left[ -\frac{1}{2} (\delta \omega_n(\eta) t)^2 \right]$$  \text{(5.12)}
where \( \omega_s = \omega_0 = n.3eQV_{zz}^{\text{eff}} /4I(I-1) \tau_1 \) for \( \eta = 0 \) and is periodic. The major fraction of probe atoms, corresponding to site 1, experiences a unique axially symmetric electric field gradient with higher magnitude. This fraction was minimum in case of Er(73%) and maximum in case of Dy(94%). The quadrupole interaction frequency corresponding to smaller fraction (site 2) had magnitude of approximately 50% of that at the first site and the value of \( \eta \) was between 0.2(Nd) and 1(Er, Tb, Dy). In the presence of nuclear relaxation at the first site, the LSQ fitting was not sensitive to the field distribution. The effect of time resolution (650ps), corresponding to 87 keV and 1172 keV energy windows, was considered in LSQ fitting through convolution of the theoretical function. The extracted values from the LSQ fitting are tabulated in table 1 and PAC spectra are shown in fig. 5.6(a, b).

The error in the value of \( V_{zz}^{\text{eff}} \) may be more due to uncertainty in the value of quadrupole moment. On comparing our results for Dy metal with NMR results, we interpret that the quadrupole interaction frequency at first site corresponds to the substitutional site. It is also supported by the value of \( \eta=0 \) expected for substitutional site at hcp lattice. We have extracted the nuclear relaxation times from the exponential damping factor in eq. (5.11) and are listed in table 1 for different RE metals. In case of magnetic interaction, the nuclear relaxation time \( (\lambda_2) \) is related to the 4f-spins electronic relaxation time \( \tau_e \) by the following relation [ABR53],

\[
\lambda_2 = 2 \omega_2^2(0) (J + 1) J^{-2} \tau_e
\]

\[\ldots(5.13)\]

where

\[
\omega_2(0) = \frac{g \mu_B B_{hf}(0)}{r}
\]

\[\ldots(5.14)\]

using the extrapolated value of hyperfine magnetic field \( (B(0)) \) [SAN75] in Dy, the electronic relaxation time \( \tau_e \) at room temperature is \( \approx 2.3 \times 10^{-12} \) s. This value is in the range of 4f spin relaxation times in RE metals. This shows that in such a fast electronic relaxation rate, the hyperfine structure in Mössbauer measurements will collapse and with poor resolution it is difficult to observe the quadrupole splitting in the paramagnetic phase.
Fig. 5.6a: TDPAC spectrum of $^{160}$Dy in Pr, Nd and Gd hosts at room temperature.
Fig. 5.6b: TDPAC spectrum of $^{150}$Dy in Tb, Dy and Er hosts at room temperature.
Discussion

The observed EFG at $^{160}$Dy in Dy metal is much higher than that observed for any other impurity at room temperature [VIA87] but it is comparable to the EFG at $^{163}$Dy in Dy at 4.2 K ($4.31 \times 10^{18}$ V/cm$^2$) [SHI78]. This is surprising in the light of previous measurements [SWE73] where the EFG at Dy was found to decrease approximately proportional to the internal magnetic field and the variation in the EFG was compared with the change in single ion anisotropy with temperature in the ferromagnetic phase. It appears that in the presence of fast electronic relaxation and poor resolution, Mössbauer measurements have not been able to give true picture about quadrupole interactions. In the paramagnetic phase the average internal magnetic field may be zero but it is not necessary for the EFG in non-cubic metals. We observe appreciable 4f-shell contribution at temperature much higher than that of the paramagnetic transition temperature which is clear from the following discussion.

The total EFG at RE nuclei in non-cubic metals arises mainly from the non-cubic arrangement of ions, unfilled 4f-shell (except for Gd$^{3+}$, Eu$^{2+}$ and Yb$^{2+}$) and the conduction electrons. It is difficult to separate out different contributions and in metals a self-consistent approach is required to calculate the total EFG at the nucleus. In the absence of any other measurement of the EFG at Dy in Dy at room temperature to compare our findings, we do so with main contributions to the EFG. Although it is not fully justified, but in order to compare with various theoretical approaches and to understand the origin of EFG in metals, the EFG at RE nuclei is analysed in the following phenomenological form,

$$V_{zz}^{eff} = (1 - \gamma_e) V_{zz}^{latt} + V_{zz}^{ce} + (1 - R_q^2) V_{zz}^{4f}$$  \hspace{1cm} \text{(S.15)}$$

where all the symbols have their usual meaning [KAU79]. The closed shell effects for the extra-ionic EFG and the EFG due to 4f shell are taken through Stemheimer antishielding factors, $\gamma_e$ and $R_q$, respectively. Usually, the lattice contribution $V_{zz}^{latt}$ and the unfilled 4f-shell contribution $V_{zz}^{4f}$ (through second order crystal electric field parameter $A_2^0$) are calculated under point charge approximation and considering the various shielding factors [BAR64]. It is difficult to calculate the conduction electron contribution $V_{zz}^{ce}$ but its probable
relative contribution has been extracted experimentally from the concentration dependence studies of EFG at a particular probe in inter heavy rare-earth alloys [SHI78, MAC74]. In the ferromagnetic saturated state of HRE alloys, the extracted 4f-shell contribution was observed nearly equal to that of the free-ion value ($\gamma(J_z=J)$) and the conduction electron contribution $V^c_{zz}$ was fitted proportional to the lattice contribution [SHI78],

$$V^c_{zz} = (1 - \gamma_c + \delta) V^l_{zz} + (1 - R_c) V^{lf}_{zz}$$  \hspace{1cm} (5.16)

where $\delta$ defines the relative contribution from the conduction electrons. The extracted value of $(1-\gamma_c+\delta)$ for Dy probe is about 273 [SHI78]. In this analysis, the extrapolated values of lattice constants were used and the results are uncertain due to unknown values of $\Theta$ between J and the crystal axis c. Mackenzie et al. [MAC74] corrected their NMR results for the pseudoquadrupole effect and observed the enhancement of the ionic contribution [$V^m_{zz}(1-\gamma_c)$] due to the conduction electrons by a factor of about 7.5. We do not expect any abrupt change in the magnitude of the enhancement factor $\alpha \left[ = \frac{V^e_{zz}}{V^m_{zz}(1-\gamma_c)} \right]$ for the transition from the ferromagnetic state into the paramagnetic state except the change in the 4f shell contribution. However, a weak temperature dependence is observed for the enhancement factor for non-RE impurities [FEC73, FOR79] and S-type of RE impurities in RE metals $^{147}$GdGd [HAU80] and $^{145}$EuEu [BOH80]. In the paramagnetic phase at room temperature the lattice constants of RE metals are precisely known. The calculated values of $V^m_{zz}$ for various RE hosts at room temperature, assuming the charge of the host metal ions to be $z=+3$ and using the lattice constants [TAY72] in the formula given by Das and Pomerantz [DAS61], are tabulated in table 1. At room temperature, assuming enhancement factor 7.5, the total EFG due to conduction electrons and the ionic contributions in Dy comes out to be $6.78\times10^{17}$ V/cm$^2$ for $\gamma_c=-76.0$, which is much smaller than the experimentally observed value of $V^e_{zz}$ ($4.33(95)\times10^{18}$ V/cm$^2$) and is comparable to the error in the value of $V^e_{zz}$. The above approximate analysis shows the major contribution due to 4f-shell at room temperature.

In the magnetic ordered state the major contribution to the EFG at RE nuclei is from the unfilled 4f-shell and it was observed to be strongly temperature dependent [SWE73]. At 4.2K there is a small difference between the extracted value of 4f-shell
contribution [SHI78] and the theoretically predicted value [BLE72]. This difference is explained in terms of redistribution of d-type conduction electrons at the Fermi level. At higher temperatures, in the point charge approximation and single electron approach, the charge asphericity of the 4f-shell can be calculated through the second order CEF parameter by taking thermal average of \(3J^2-J(J+1)\) [BAR64]. The 4f-shell contribution to the EFG at room temperature is calculated in the higher temperature approximation [BAR64] by assuming value of \(R_0=0.15\), \(\sigma_2=0.2\) and is found negligible (about 30th part of the EFG due to 4f-shell in the state \(J=J_0\)). It is also known from the susceptibility measurements [TOU77] that the overall CEF splitting of Dy in metals is about 200K so that one expects negligible 4f-shell contribution at room temperature. It can not account for the observed difference of EFG in Dy at room temperature. As expected, this phenomenological approach using bare CEF parameters, based on point charge approximation, can not give true picture about the interaction of the aspherical 4f charge distribution with the conduction electrons and the finite ionic charge distributions in metals. Contrary to the indirect information about CEF from the susceptibility measurements (which give only macroscopic information) we have observed strong host associated effects. The NMR results are also confined to inter-RE alloys only between GD, Tb and Dy, where we have also observed the variation of the EFG at Dy proportional to the lattice contribution. But after Dy to Er and before Gd to Pr the observed EFG does not vary proportional to the lattice contribution. Also the trend is opposite to that observed at low temperatures.

The above approximate analysis shows that the major contribution at room temperature is due to 4f-shell and from the comparison of the NMR and the present measurements one can expect weak temperature dependence for the EFG at Dy in Dy as observed by the TDPAC/D techniques for other RE probes in RE metals [VIA87]. In RE metals free ion approximation does not give complete picture about the conduction electron effects on the state of 4f-shell electrons as it is confirmed by the EFG measurements in other RE metals. In variance to the information available about host associated effects (e.g. c/a ratio etc.) on CEF parameters from the susceptibility measurements in RE metals and their dilute alloys [TOU77], giving only macroscopic information, we have observed the effect of the charge distributions on the nearest neighbours. In fig. 5.7 the EFG variation
at Dy is shown alongwith that at Ta and Cd impurities in RE metals. It is surprising to observe the similar variation of EFG at the three impurities in HRE metals while in LRE metals it is entirely different. All the impurities have completely different electronic structures. For both the impurities Cd (having closed shell structure and no localization effect) and Dy (having strong localized 4f-shell effects also), the observed EFG tends to have smaller value in the beginning and at the end of the RE series. In between, the EFG values are higher and change systematically. The EFG at Dy is higher in Nd and goes down sharply in Pr. All these features indicate the effect of the filling of 4f-shell on the conduction electron distributions. The total EFG at Dy in RE metals does not vary in proportion to the lattice contribution except in the middle of RE series (fig. 5.7), inspite of the same crystal structure (if the crystal field splitting is taken to be proportional to the lattice contribution in the absence of exchange interactions) and the same valence electron configuration (5d6sp) across RE series. This behaviour can neither be explained on the basis of earlier semi-empirical theoretical approaches, visualizing host associated effects through lattice contributions enhanced by the conduction electrons treated under APW [DAS70] or OPW [DEV73] approximations by several workers, nor in terms of recent on-site valence
electron charge density approaches [COE90, KUR93].

The deviation from any proportionality between the lattice contribution and the total EFG for a given RE ion can be seen by plotting electronic enhancement factor $\alpha$ for each RE metal. As per systematic of EFG in other metals [VIA87], its value lies between 1 and 4 for the probe ions experiencing EFG due to non-spherical distribution of conduction electrons only and having hardly any localized electronic contributions. The variation of $\alpha$

![Diagram](attachment:image.png)

Fig. 5.8: Enhancement factor $\alpha$ for different impurities as a function of RE atomic number.

for the three impurities across the rare-earth series is shown in the fig 5.8. Again for Ta, Cd and Dy impurities in HRE, the variation of parameter $\alpha$ is similar except that the change is slower for Ta probe and faster for Dy probe. In our case the value of $\alpha$ for Dy at room temperature for the considered RE metals lies between 10 to 72. The higher and the wide variation in the value of $\alpha$ for Dy indicates strong host associated effects through inter-atomic electronic interactions. In LRE hosts the value of $\alpha$ seems to have same trend for Cd and Dy (with greater amplification of lattice contribution in LRE) but it is opposite to that for Ta impurity. The variation of EFG at non-RE nuclei in HRE metals is explained in terms of charge transfer [FOR79] and impurity-host atoms volume mismatch [MIS82]
models but both the approaches fail in light rare earths. For Dy impurity one can neglect these two mechanisms as host and impurity both belong to the same RE series. The trend of increasing value of $\alpha$ in any RE metal for different impurities, i.e. Cd, Ta and Dy, shows increasing modification of the EFG due to surrounding ions, by the localized electrons of probe atoms. Comparatively, the higher and the wide variation in the value of $\alpha$ for Dy indicates the modification of the valence electron charge distributions of Dy across RE series. From fig. 5.7, it is clear that the EFG at Dy is influenced by the 4f-shell charge asphericity of host atoms in the ground state, i.e. $J(2J-1)$, which is maximum at Nd and Ho (fig. 5.9). The EFG due to near neighbour 4f-shell asphericity is more enhanced in the case of LRE as compared to that in HRE. It shows that the contribution from the aspherical charge distribution from the neighbouring Wigner-Seitz shell cannot be neglected. It is interesting to note that the variation of $\alpha$ is proportional to the temperature range of bcc phase in RE metals and it is known in alkaline earth metals that the bcc structure is favoured by sp-d hybridization near the Fermi level [FRE72]. It may be an exaggerated extrapolation of crystal structure associated effects but it may be taken as a relative measure of various interactions taking place to give a particular phase structure and their variation across RE series. At present the real mechanism of the influence of near neighbour 4f-shell charge asphericity is not clear but we may look into various intra-atomic 4f-5d6sp and inter-atomic 5d6sp-5d6sp overlap/hybridization effects in modifying the valence charge distributions to explain the observed variation of the EFG and hence the related CEF parameters in RE metals. The relationship between the exact valence electron structure and the radial extension of 4f wavefunction has been considered to explain RE metal crystal structures [DUT77] and photo-emission spectra [KAN94] by various workers.

The band structure calculations in RE metals [FRE72] have shown the presence of 5d band and their hybridization with 6sp bands near the Fermi level. Following this, Onofrio and Iraldi [ONO77] considered the redistribution of conduction electrons with predominant d-character at Fermi level by including asphericity in the Coulomb interaction between 4f-shell electrons and valence electrons (5d'6s^2) and predicted correct sign of the EFG in HRE. For Gd, Coehroon et al. [COE90] have shown recently that the EFG at the nucleus is mainly determined by the asphericity of the 6p shell while at the 4f-shell it is
both the 5d and 6p valence shells. In these calculations they have neglected the effect of charge distributions at neighbouring atoms. It may not be true in case of non-S-state RE ions as neighbouring ions. The EFG/CEF due to distant neighbours may not be effective but the nearest neighbour influences on-site valence electron charge density distributions strongly. Kunplach [KUR.93] extended these calculations to non-S-type HRE metals in the ferromagnetic phase but the calculated values are higher than the observed ones. These calculations lack self-consistent full potential calculations between 4f-shell charge distributions and the valence shell charge distributions as is shown by Steinbeck et al. [STE94] in the much simpler system for the CEF parameters for Dy and Er in Ag and Au. This picture is further strengthened by various magnetic, optical and crystal structure investigations where the variation in 5d band occupancy is considered as a result of the variation of the radial extension of 4f-wave functions across RE series. While in LRE there is a 4f-wave function overlap with valence electron wave functions and strong CEF effects to modify magnetic properties, in HRE the 4f-wave function is more localized and their radial extension reduces much faster as compared to the ionic size giving weak CEF effects.
Duthie and Pettifor [DUT77] explained crystal structure in rare-earths in terms of d-band occupancy. They observed theoretically the variation of d-band occupancy from 2.5 to 1.5 for La to Lu RE metals. It may be one of the factor for increasing the value of $\alpha$ in LRE. Similar effects are observed in transitional metals. The above observation confirms the strong CEF effects in LRE and in Pr it give non-magnetic singlet state. It points towards the mechanism of CEF effects at 4f-shell via modification of valence electron distribution and where the radial extension of 4f-wavefunction plays a crucial role. In any theoretical approach it is required to consider 4f-shell associated effects all over the RE series. The variation of the radial extension of the 4f-wave functions appears in different forms in magnetic interactions and in stabilization of various crystal structures at different pressures. It is well known that the radial extension of 4f-wavefunction [COU62] goes down very fast as compared to the atomic size across RE series. Gschneidner and Valletta [GSC68] have shown qualitatively the occurrence of various crystal structures in

### Table 1: LSQ fitted parameters, lattice EFG and electronic enhancement factor for $^{160}$Dy.

<table>
<thead>
<tr>
<th>Host</th>
<th>$\lambda^2_1$ (ns)</th>
<th>$\omega_{41}$ (MHz)</th>
<th>$\omega_{42}$ (MHz)</th>
<th>$f_1$ %</th>
<th>$V_{44}^{\text{AIM}} \times 10^{15}$ V/cm$^2$</th>
<th>$V_{44}^{\text{eff}} \times 10^{18}$ V/cm$^2$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr</td>
<td>4.6±9</td>
<td>1240±23</td>
<td>741±23</td>
<td>79±4</td>
<td>0.894</td>
<td>3.16±0.68</td>
<td>43.6</td>
</tr>
<tr>
<td>Nd</td>
<td>3.3±5</td>
<td>1892±30</td>
<td>1103±29</td>
<td>85±4</td>
<td>0.828</td>
<td>4.81±1.00</td>
<td>71.8</td>
</tr>
<tr>
<td>Gd</td>
<td>2.7±4</td>
<td>1292±20</td>
<td>748±31</td>
<td>83±3</td>
<td>1.706</td>
<td>3.29±0.76</td>
<td>23.8</td>
</tr>
<tr>
<td>Tb</td>
<td>2.1±5</td>
<td>1629±48</td>
<td>736±50</td>
<td>93±3</td>
<td>2.188</td>
<td>4.15±0.91</td>
<td>23.4</td>
</tr>
<tr>
<td>Dy</td>
<td>2.0±4</td>
<td>1701±52</td>
<td>672±66</td>
<td>94±4</td>
<td>2.475</td>
<td>4.33±0.95</td>
<td>21.6</td>
</tr>
<tr>
<td>Ho</td>
<td>2.0±4</td>
<td>1237±51</td>
<td>682±36</td>
<td>89±5</td>
<td>2.564</td>
<td>3.15±0.69</td>
<td>15.1</td>
</tr>
<tr>
<td>Er</td>
<td>2.8±6</td>
<td>767±37</td>
<td>888±23</td>
<td>73±4</td>
<td>2.640</td>
<td>1.95±0.50</td>
<td>9.0</td>
</tr>
</tbody>
</table>
terms of 4f-bonding by considering the ratio of metallic radius to the 4f radius of the elements. In the beginning of RE-series there is direct 4f-wavefunction overlapping but in HRE, 4f-shell is strongly localized. The high value of $\alpha$ for Dy in LRE may be taken as a measure of strong hybridization between valence shells and also the hybridization of 4f-shell with valence shells of host atoms. In HRE its only valence shells hybridization in the beginning but Ho onwards, the hybridization of valence shells also goes down to decrease the value of $\alpha$ further.

We can explain our results qualitatively based on the theoretical calculations in Gd. Harmon and Freeman [HAR74] have shown in their APW band calculations the high density of 5d electrons near the Fermi surface and the magnetic ordering in RE metals is explained in terms of f-d hybridization. In their calculation of d-band polarization by f-electrons, the effect of charge distribution is not considered. The extension of theoretical calculation by Coehoorn et al. to other RE metals can confirm the change in the charge asphericity of 5d6p valence shells through overlapping with 4f-wavefunction.

Present measurements in pure RE metals have shown that the valence electron charge distribution of RE probe atom is influenced through intra-atomic (4f-5d6p) aspherical Coulombic interactions and the on-site 4f-state has electrostatic interaction with neighbouring atom 4f state via valence electron charge distributions. In any theoretical approach for the valence electron charge distributions in RE metals it is required to consider the variation in the overlap/hybridization of 4f-5d6p orbitals and the 5d-6sp orbitals across RE series. It can explain the variation of the quadrupole moment of Dy$^{3+}$ ion across RE series which is proportional to the charge asphericity of valence shells of host atoms. Further systematic EFG studies are required at other RE probe atoms in RE metals to clarify the relationship between the exact 4f radial extension and the sub-band structure.
5.4 Hyperfine Interactions of Pm in Nd and Gd Hosts

Introduction

The magnetic ordering and electronic structure of heavy rare-earth metals are well understood as compared to that of light rare-earth metals and much of the efforts have been concentrated on light rare-earth metals. The LRE metals have more complex crystal structures and the crystal field splitting of the magnetic energy levels of the more extended 4f-electron distribution are comparable with the exchange energies. There is a systematic change (reduction) in the ratio of 4f radial extension to the atomic radius across the rare-earth series and it influences the relative strength of the exchange interaction to the crystal field interaction of the 4f electrons in RE metals. In LRE this relative strength not only determines the type of magnetic ordering but it is also a sensitive parameter to decide the occurrence of magnetic order. There is considerable hybridization of f-electrons with the conduction electrons and it is a formidable task to predict theoretically the magnetic behaviour in metals. The present measurements will help to through light on the various contributions to the crystalline electric fields and the internal magnetic hyperfine fields at Pm nuclei in Nd and Gd metals.

Neodymium crystallizes in dhcp structure where the stacking sequence of the layers is ABACABAC... At 19.9K the atoms of the B & C layers, which have a hexagonal environment, order antiferromagnetically while the A layers with cubic (exactly trigonal symmetry) nearest neighbour arrangement remain disordered until 7.5K. The difference in the ordering temperature at the two non-equivalent sites is attributed to the different CEF splitting of Nd ions at two sites. The magnetic and neutron diffraction studies of pure Nd metal [MOO64] have shown the magnetic moments to be 1.8±0.2 $\mu_B$ and 2.3±0.2 $\mu_B$ at cubic and hcp sites respectively. The magnetic moments at both the non-equivalent sites lie in the basal plane perpendicular to the c-axis. The maximum theoretical value of the Nd moment, $g\mu_B J = 3.27 \mu_B$, is reached only in the presence of 23 kG field [JOH70] and

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it is attributed to the crossing of CEF levels in the presence of magnetic field.

Another host metal gadolinium has hcp crystal structure and exists in ferromagnetic phase below Curie temperature $T_C=294\,K$. It is an S-state ion (no orbital momentum contribution to the saturation magnetic moment) with saturation magnetic moment $7.55\,\mu_B$. The excess moment of about $0.55\,\mu_B$ with respect to theoretical magnetic moment ($J=7.0\,\mu_B$) is observed due to conduction electron polarization. It is almost isotropic ferromagnet with small anisotropy effects. The direction of magnetic moment depends strongly on the temperature. The moment direction is parallel to the c-axis from $T_C$ to $232\,K$, moves away from c-axis to a maximum deviation $65^0$ near $180\,K$, and then back to within $32^0$ of the c-axis at low temperatures [COR62].

In the present measurements we have tried to investigate the behaviour of Pm ions in Nd and Gd through the DPAC measurements of $5/2^+$ state of $^{147}\text{Pm}$ nucleus. Previous DPAC measurements were carried out to determine the magnetic moment of $5/2^+$ state. It is more sensitive to magnetic interactions because the quadrupole moment of this state is small. The crystalline electric field is weaker in Gd metal as compared to that in Nd but the exchange interaction is stronger.

Experimental Details and Results

The mother activity $^{147}\text{Nd}$ ($T_{1/2}=11\,\text{d}$) was obtained by neutron irradiation of natural Nd metal. The sample $^{147}\text{PmNd}$ was prepared by melting natural Nd metal with $^{147}\text{Nd}$ activity in high vacuum after flushing by pure argon. The $^{147}\text{PmGd}$ sample was also prepared in a similar way. The TDPAC measurements were carried out with the same three detector setup as described in previous section 5.3. In the present measurements we have used the 91 keV, $I=5/2^+$, $T_{1/2}=2.46\pm0.6\,\text{ns}$ [RAG89] level of $^{147}\text{Pm}$. A $\gamma$-ray cascade of energy (91-319) keV passing through this level was used to perform the DPAC measurements. The background subtracted and normalized spectra were used to deduce the ratio function, $G_{22}(t)$ as
$G_{22}(t) = \frac{2}{A_{22}} \cdot \frac{C(180^\circ, t) - C(90^\circ, t)}{C(180^\circ, t) + 2C(90^\circ, t)} \quad ...(5.17)$

where $A_{22} (=0.107\pm0.008 \text{ [BHA74]})$ is the angular correlation coefficient and is greater than $A_{44} (=0.005\pm0.015 \text{ [BHA74]})$ for the present cascade. This ratio function was LSQ fitted with the theoretical perturbation function for spin $5/2^+$ and for randomly oriented combined electric and magnetic field as

$G_{22}(t) = 0.2 + 0.4 \cos \omega_b t \cdot [10 \cos^2 \omega_q t + 4 \cos \omega_q t]/14 + 0.4 \cos^2 \omega_q t \cdot [5 \cos^3 \omega_q t + 9 \cos \omega_q t]/14 \quad ...(5.18)$

with $\omega_q = 6\omega_q$

and

$\omega_q = \frac{eQV_{zz}}{4I(I-1)} \cdot \frac{3 \cos^2 \beta - 1}{2} \quad ...(5.19)$

where $\beta$ is the angle between local magnetic field and electric field gradient. A possible Gaussian distribution was included in the LSQ fitting for magnetic interaction in the above expression. This expression is valid in the present case as the electric quadrupole interaction
frequency is much smaller than the magnetic interaction frequency. The LSQ fitting of the $G_{22}(t)$ spectra around $t=0$ is not well reproduced and it may be due to prompt contribution. In the finally reported results we have not considered the first few channels. We have used $Q=0.6\pm0.3b$ [RAG89] and $g_N=1.29\pm0.15$ [RAG89] for extracting the electric field gradient and the hyperfine magnetic field values respectively.

The TDPAC spectrum of $^{147}$PmNd (fig. 5.10a) in the magnetically ordered phase at 10K shows attenuation of the anisotropy with time which may be due to the distribution in the magnetic hyperfine field values in Nd and a similar effects has been observed in Gd also. The TDPAC spectrum of PmNd at 10K was analyzed by fitting the theoretical perturbation function for combined magnetic and electric hyperfine interaction of nuclear spin $5/2^+$ for two sites. Besides the magnetic hyperfine and quadruple interactions, the
analysis of the spectra also yields the angle $\beta$ between magnetic hyperfine field and the EFG component. The solid line in $G_{22}(t)$ spectrum (fig. 5.10) corresponds to the theoretical perturbation function. The large error in the extracted value of EFG is due to the uncertainty in the measurement of quadrupole moment of $5/2^+$ state in Pm.

Some of the relevant LSQ fitted parameters are listed in table 2. Relatively slow electric quadrupole frequency was not sensitive to the distribution parameter and was not incorporated in LSQ fitting. One can expect value of $\beta$ between $0^\circ$ and $90^\circ$ as the Stevens parameter for Nd and Pm has opposite sign. In the present measurements we have considered $\beta$ equal to $90^\circ$ which improved the value of $\chi^2$. $\omega_0$ was observed to be unaffected by $\omega_0$ and $\beta$. In the short time window of $G_{22}(t)$ spectra it is difficult to distinguish these effects.

At 30K (fig. 5.10b) we expect $G_{22}(t)$ spectra corresponding to static electric quadrupole interaction because of slow paramagnetic relaxation but it could not be accounted for either by static or dynamic hyperfine interactions. The solid line corresponds to the combined magnetic and electric hyperfine interaction at one site and the pure electric

![Figure 5.11a: Spin rotation spectrum of $^{141}$Pm in Gd host at 10K.](image)
quadrupole interaction at another site. This shows the existence of short range order above Curie temperature \((T_C=19.9K)\). At 130K we have tried to fit only paramagnetic relaxation which does not reproduce the experimental \(G_{22}(t)\) spectra.

![TDPAC spectra of \(^{147}\text{Pm}\) in Gd host at 130K and room temperature.](image)

**Fig. 5.11b**: TDPAC spectra of \(^{147}\text{Pm}\) in Gd host at 130K and room temperature.

The TDPAC spectra for \(^{147}\text{PmGd}\) at different temperatures are shown in fig. 5.11a,b. Below room temperature, the magnetic effects start to appear in the TDPAC spectrum e.g. at 10K and 130K. The solids lines in the \(G_{22}(t)\) spectra are a result of combined magnetic and electric quadrupole interactions as well as an additional function (which may be due to pure electric or pure magnetic interaction only or combined interaction) to account for a possible second site. Table 2 summarizes the LSQ fitted parameters.
Table 2: LSQ fitted parameters ($\beta=90^\circ$ fixed) for $^{147}$PmNd and $^{149}$PmGd.

<table>
<thead>
<tr>
<th>Host</th>
<th>Temp</th>
<th>Sites (Fraction $f_1$ (%) )</th>
<th>Magnetic &amp; Electric Int. frequency (MHz)</th>
<th>Distribution $\delta$ (%)</th>
<th>Magnetic and Electric hyperfine field values (kG or $\times10^{18}$ V/cm$^2$).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd</td>
<td>10K</td>
<td>I ($f_1=53\pm6$)</td>
<td>$\omega_{b1}=2228(48)$</td>
<td>2.0</td>
<td>$B_{\text{eff}}=361(42)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>$\omega_{a1}=475(40)$</td>
<td>-</td>
<td>$V_{zz}^{\text{eff}}=3.47(1.74)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\omega_{b2}=2133(52)$</td>
<td>2.0</td>
<td>$B_{\text{eff}}=343(40)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\omega_{a2}=149(28)$</td>
<td>-</td>
<td>$V_{zz}^{\text{eff}}=1.08(0.57)$</td>
</tr>
<tr>
<td>Nd</td>
<td>30K</td>
<td>I ($f_1=45$)</td>
<td>$\omega_{b1}=696(56)$</td>
<td>2.0</td>
<td>$B_{\text{eff}}=111(15)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>$\omega_{a1}=128(40)$</td>
<td>-</td>
<td>$V_{zz}^{\text{eff}}=0.93(0.54)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\omega_{b2}=0.0$</td>
<td>5.0</td>
<td>$B_{\text{eff}}=0.0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\omega_{a2}=268(24)$</td>
<td>-</td>
<td>$V_{zz}^{\text{eff}}=1.95(0.99)$</td>
</tr>
<tr>
<td>Gd</td>
<td>10K</td>
<td>I ($f_1=62\pm4$)</td>
<td>$\omega_{b1}=1577(31)$</td>
<td>4.0</td>
<td>$B_{\text{eff}}=255(30)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>$\omega_{a1}=156(13)$</td>
<td>-</td>
<td>$V_{zz}^{\text{eff}}=1.14(0.57)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\omega_{b2}=770(38)$</td>
<td>3.0</td>
<td>$B_{\text{eff}}=124(15)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\omega_{a2}=753(27)$</td>
<td>-</td>
<td>$V_{zz}^{\text{eff}}=5.51(2.76)$</td>
</tr>
<tr>
<td>Gd</td>
<td>130K</td>
<td>I ($f_1=62\pm7$)</td>
<td>$\omega_{b1}=1530(35)$</td>
<td>2.0</td>
<td>$B_{\text{eff}}=247(29)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>$\omega_{a1}=174(16)$</td>
<td>-</td>
<td>$V_{zz}^{\text{eff}}=1.27(0.64)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\omega_{b2}=712(47)$</td>
<td>2.0</td>
<td>$B_{\text{eff}}=115(15)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\omega_{a2}=696(33)$</td>
<td>-</td>
<td>$V_{zz}^{\text{eff}}=5.10(2.56)$</td>
</tr>
<tr>
<td>Gd</td>
<td>294K</td>
<td>I ($f_1=62\pm5$)</td>
<td>$\omega_{b1}=1330(30)$</td>
<td>2.0</td>
<td>$B_{\text{eff}}=215(15)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>$\omega_{a1}=202(13)$</td>
<td>-</td>
<td>$V_{zz}^{\text{eff}}=1.47(0.74)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\omega_{b2}=0.0$</td>
<td>-</td>
<td>$B_{\text{eff}}=0.0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\omega_{a2}=277(17)$</td>
<td>-</td>
<td>$V_{zz}^{\text{eff}}=2.03(1.02)$</td>
</tr>
</tbody>
</table>
Discussion

Pm exists only in the radioactive form and is observed to have dhcp structure [TAY72] similar to that of Nd. There is no experimental information about the hyperfine fields at Pm nuclei in metals except the ESR measurements in insulators [BAR79]. The expected free-ion values (in the state J_z=4) of total hyperfine magnetic field and the electric field gradient for Pm^{3+} ions are; B_u =4.20 MG and V_{eff}^{ef} =1.30×10^{18} V/cm^2 [FOR85]. In case of metals, particularly in LRE metals where radius of the 4f-shell is comparatively larger, one can expect the modification of free-ion hyperfine field values due to conduction electrons. The observed maximum hyperfine magnetic field at Pm in Nd at 10K is much smaller (about one tenth of the free ion value). The corresponding value of the total electric field gradient is comparable to that of free-ion value and is uncertain due to large error in quadrupole moment value. We can interpret our results based on very limited hyperfine interaction measurements in LRE as follows.

The magnetic hyperfine field at Pm nucleus in Nd can be estimated provided one knows the CEF splitting of the ground state multiplet of Pm^{3+} ion in Nd and the exchange interaction between Pm and Nd ions. Touborg et al. [TOU78] have extracted crystal field parameters for LRE except for Pm from the susceptibility measurements of dilute LRE alloys with Y and Lu. In LRE the CEF interaction energy is comparable with the exchange energies. This fact is investigated for the occurrence of magnetic ordering in Pr metal [LEB75]. The crystalline electric fields in LRE limit the magnitude of the ordered moments in zero field.

The reduction of hyperfine magnetic field at Pm nucleus at 10K may be considered mainly due to two reasons: (i) reduction in the host spontaneous magnetization with temperature (T/T_c=0.5) and (ii) the ionic magnetic moment of Pm is smaller due to CEF effects. Pm being the non-Kramer ion, this effect can be visualized similar to that for Pr ion in the absence of any theoretical or experimental information about electronic structure of Pm metal.

Assuming crystalline electric field at Pm in Nd similar to that at Nd (although there are evidences of ion-dependence of CEF in a particular host) and following crystal field
parameters deduced by Rainford [RAI72] for Pr, the crystal field slitting of non-Kramer Pm$^{3+}$ (J=4) ion in Nd may be taken to favour singlet crystal field ground state $|4,0\rangle$ at both the cubic and hcp sites. The first excited state is expected to be a doublet state at hcp site and the triplet state at the cubic site. In case when there is no exchange interaction, one may have non-magnetic state of ground manifold at very low temperatures. When exchange interaction is comparable to the CEF interactions, there can be admixture of higher eigen states of crystalline field and $\langle J_\alpha \rangle$ is considerably less than J. The extent to which this mixing occurs depends on the relative strength of the CEF and the exchange interactions. The induced moment effects are observed for light rareearths (both for Kramer Pr$^{3+}$ and non-Kramer Sm$^{3+}$ ions with different mechanisms). Assuming the measured magnetic hyperfine field only due to local magnetic moment, the induced ionic magnetic moment at Pm must correspond to about 10% that of free ion magnetic moment in the state $J_z=4$.

Generally the CEP contribution in RE metals is of the order of 20T but in the present case we expect it to be small. In RE metals the conduction electron contributions to the hyperfine magnetic field at RE nuclei are analyzed in terms of following contributions:

(i) Direct contribution from 4f-electrons of the parent RE ion plus the contribution due to core polarization of inner shells by these electrons.

(ii) From the conduction electron polarization induced by the 4f-spin of the parent ion (self polarization field).

(iii) From the conduction electron polarization induced by neighbouring ion spins.

(iv) Lorentz field contribution (which is small in LRE due to larger atomic volume).

Since in Nd metal ionic magnetic moments in alternate layers are coupled antiferromagnetically, the effect of the conduction electron polarization due to neighbouring ions would be small. Any remaining small contribution will be of opposite sign to that of conduction electron polarization due to the localized magnetic moment of the parent ion. The net effect of all these contributions will be a small contribution to the hyperfine magnetic field at temperature 10K ($T/T_c\approx0.5$) and the observed magnetic hyperfine field may be due to localized magnetic moment.

We have carried out these measurements in Gd and Co also to see the effect of
exchange interactions. To our surprise the hyperfine magnetic field value at Pm in Gd has reduced slightly as compared to that in Nd. The field value almost remain same with temperature upto the transition temperature of Gd. At low temperature the hyperfine magnetic field values at Nd in Nd and in Gd are also observed to have the same values with reduced magnetic moment of Nd. In the magnetization studies of Pr-Nd system the exchange interaction parameters between Pr-Pr, Pr-Nd and Nd-Nd are observed proportional to the de-Gennes factor, which indicates the importance of RKKY type interaction among ionic magnetic moments in LRE. The constancy or small variation in the value of hyperfine field at LRE ion in LRE metals and Gd shows the role of other factors in addition to conduction electron polarization (f-s and f-d) e.g. f-d hybridization.

![Fig. 5.12: TDPAC spectrum of $^{141}$Pm in cobalt host at room temperature.](image)

These measurements are extended to Pm in cobalt (fig. 5.12) at room temperature. The effective exchange interaction is of 3d-4f type. The transfer hyperfine field in case of LRE should be positive. The hyperfine magnetic field corresponding to major fraction is slightly higher as compared to that in Nd and Gd hosts. As the solubility of REs in Co is small, it is difficult to identify the site. At first site the deduced magnetic field value is $B_m = 396 \pm 46$ kG and the EFG is equal to $V_{zz}^{\text{eff}} = 2.75 \pm 1.40 \times 10^{18}$ V/cm$^2$. At the second
site the hyperfine field values have wide distributions and may be due to local compound formation with varying composition. The first site field values may correspond to the substitutional site or unique interstitial site occupied by Pm atoms. In any case the possibility of Pm atoms surrounded by Co atoms increases and it indicates the 4f-3d hybridization effect as observed in LRE and transition metal alloys. Further investigations are planned in Co and Nd alloys.

5.5 Quadrupole Interaction of $^{100}$Rh in Tb Host.

Introduction

The electric field gradient at different impurity probes in metals have been widely studied during the past few years [VIA87]. Exceptionally large enhancement factor $\alpha$ have been observed for the impurities belonging to second half of the transition series, such as Ru, Os, Ir and Au, in rare-earth metals and have been mainly attributed to large contribution from impurity d electrons. The unfilled d-shell of the transition metal seem to have more effect on the field gradient than the f-shell of rare-earth metals. The high value of $\alpha$ shows that the electronic contributions are significant. According to Miedema et al. [MIE82] it is the interstitial impurity site which is responsible for exceptionally large enhancement factor. It has also been assumed that the solid solubility of these impurities in RE hosts (because of atomic radii difference) is rather small so there is possiblity of these impurities to form intermetallic compounds even at low concentration [FOR83]. After going through the results of different impurity-host combinations it is observed that the electronic contribution [BHU87] to the EFG is determined mainly by the band structure of the host lattice and the outer electrons of the probe atom play a very little role in influencing the electronic EFG.

In RE hosts, the major contribution to the electric field gradient is from the incomplete and hence non-spherical d or f valence electrons shell. Even though the c/a ratio

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is similar for all the RE hosts, the EFG and its temperature dependence varies widely. These variations can be correlated to the properties of the f electrons, which are different across the RE series. An unfilled f electron shell has a non spherical charge distribution which produces an EFG component at the nucleus. The available systematics of EFG at non-RE nuclei in RE host have shown the influence of the 4f-shell occupancy of the host atoms [FOR85] which are considered to be screened by conduction electrons. Considerable enhancement is observed for transitional metal impurities in RE hosts [PER76, VIA87]. The exceptionally high value of EFG in RhGd ($V_{zz}^{\text{eff}} = 1.31(34) \times 10^{18}$ V/cm$^2$) raised our interest to measure the EFG in other HRE metal hosts. The Present measurement is a part of the systematic investigation of the EFG at 4d impurity in different heavy rare-earth metals and is only confined to terbium host.

**Experimental Details and Results**

The parent radioactivity $^{100}$Pd(3.6d) was produced at Variable Energy Cyclotron, Calcutta through IUC DAE facility by using 50 MeV α beam on enriched Ru through the nuclear reaction $^{99}$Ru(α,xn)$^{100}$Pd. A part of the $^{100}$Pd activity was melted with large quantity of terbium host to make it dilute solid solution. The quadrupole interaction frequency was measured using a probe level at 75 keV with half life $T_{1/2} = 215$ ns and I=2. A gamma ray cascade of energy 84 keV - 75 keV through this level was used for the TDPAC studies. A conventional three detector TDPAC setup was used. From the time spectra at angles 90° and 180°, a spin rotation spectra $A_{22}G_{22}(t)$ was formed as

$$A_{22}G_{22}(t) = 2 \left[ \frac{C(180°, t) - C(90°, t)}{C(180°, t) + 2C(90°, t)} \right] \quad \cdots (5.20)$$

and is shown in fig. 5.13. The best fit to the spectrum was obtained with a two fraction model: A fraction f of nuclear probes occupies regular substitutional sites (I) where they experience a unique EFG, while the rest (1-f) on non-regular sites (II) due to imperfections, nearby impurities etc. This leads to the expression
\[ A_{22} G_{22}(t) = A_{22} \left( f \cdot G_{22}^I(t) + (1-f) G_{22}^H(t) \right) \]  \hspace{1cm} (5.21)

A usual theoretical expression of \( A_{22} G_{22}(t) \) for polycrystalline sample and spin 1/2 was used:

\[ A_{22} G_{22}(t) = A_{22} \sum_{n=0}^{1,3,4} S_{2n} \cos(n\omega_0 t) \ e^{-\frac{1}{2} \left( \frac{n\omega_0 t}{\eta} \right)^2} \]  \hspace{1cm} (5.22)

Here the fundamental frequency is defined by \( \omega_0 = 3eQV_{eff}/4I(2I-1) \) where \( Q \) is the nuclear quadrupole moment and \( V_{eff} \) is the principal component of the EFG. The exponential factor takes care of a small Gaussian distribution in the EFG. The amplitude \( S_{2n} \) for the different frequency components were fixed in the least squares fit procedure. The solid line in the fig. 5.13 is corresponding to \( \omega_{01} = 22.2(3) \) MHz with \( \eta = 0 \) (regular site), \( f = 55\% \) and \( \omega_{02} = 13.2(8) \) MHz with \( \eta = 0.38(11) \).

Using \( Q = 0.076(20)b [VIA79] \) for the quadrupole moment of the 2+ state (75 keV) in \(^{100}\text{Rh}\) we obtain a EFG for Rh in Tb \( V_{eff} = 1.54(40) \times 10^{18} V/cm^2 \) corresponding to the regular site. The measured EFG is comparable to \(^{100}\text{RhGd}\) system and the enhancement

![Fig. 5.13: Spin rotation spectrum of \(^{100}\text{Rh}\) in terbium host at room temperature.](image-url)
factor $\alpha$ for $^{100}$RhTb is also more than 40 like $^{100}$RhGd system. Clearly the very large EFG of $^{100}$RhGd and $^{100}$RhTb is due to an exceptionally high electronic contribution in these metals. The strong contribution to the EFG is expected from the localized 4d electrons at the impurity as in the RuRE systems [FOR83]. According to Watson et al. [WAT65] and Pieuch & Janot [PIE76], contribution to the EFG from electrons localized in the Wigner-Seitz cell of the nucleus under consideration should be proportional to the density of states at the Fermi energy $\eta(E_F)$. The value of $\eta(E_F)$ for heavy rare-earths Gd to Lu varies negligibly small and as a result the total EFG at these impurities in RE hosts changes very small. The EFG $V_{zz}^{\text{eff}}$ and enhancement factor $\alpha$ for other 4d and 5d impurities in Tb lattice are tabulated in table 3.

**Table 3:** Effective EFG, ionic field gradient and electronic enhancement factor for different impurities in terbium host at room temperature.

<table>
<thead>
<tr>
<th>Probe</th>
<th>$V_{zz}^{\text{eff}} \times [10^{15} \text{ V/cm}^2]$</th>
<th>$(1-\gamma_e)V_{zz}^{\text{int}} \times [10^{15} \text{ V/cm}^2]$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{99}$Ru</td>
<td>540</td>
<td>46.99</td>
<td>11.49 [VIA87]</td>
</tr>
<tr>
<td>$^{100}$Rh</td>
<td>1540</td>
<td>33.62</td>
<td>45.80 [Present work]</td>
</tr>
<tr>
<td>$^{181}$Ta</td>
<td>593</td>
<td>107.00</td>
<td>5.54 [VIA87]</td>
</tr>
<tr>
<td>$^{193}$Ir</td>
<td>1539</td>
<td>79.68</td>
<td>19.20 [VIA87]</td>
</tr>
<tr>
<td>$^{197}$Au</td>
<td>2130</td>
<td>100.00</td>
<td>21.30 [VIA87]</td>
</tr>
</tbody>
</table>

In Gd metal it is observed that the electronic EFG increases with the increase of 5d electrons at the impurity across the 5d series. It will not be surprising to observe the similar behaviour across the 4d series in the light of well defined systematics of hyperfine magnetic field at transitional impurities in Gd and Tb.