CHAPTER IV

HYPERFINE FIELD MEASUREMENTS

A. ORIGIN OF THE HYPERFINE FIELDS, HYPERFINE FIELD MODELS AND SYSTEMATICS OF HYPERFINE FIELDS

Hyperfine field determinations are often used as a tool in the study of the magnetism and magnetic materials. Hyperfine fields at impurities in ferromagnets can be studied with respect to (a) variation with atomic number A (or Z) for different impurities in the same host\(^57\), (b) variation with temperature \(^57\), and (c) changes with the impurity content \(^58\). The first case will give information on spin polarization, transfer and overlap effects. From (b) one can find out a possible local moment behaviour, whereas case (c) is used to study neighbour effects for higher concentrations. Most of the experiments reported in the literature have been carried out in iron and nickel hosts. The interpretations of the measurements is then relatively simple, since impurity atoms usually occupy regular cubic sites. The general trends in the variation of the magnetic hyperfine fields with impurity A (or Z) are reasonably understood. The hyperfine fields are discussed in terms of a semiempirical model by Shirley et al.\(^57\). In the Daniel-Friedel theory\(^59\), we consider the scattering of the electrons around the impurity which
results in a net spin polarization at the nucleus. This model was further extended by Campbell\footnote{60}.

When we measure the hyperfine fields on dilute impurities we essentially sample the magnetization on the impurity nuclei alone. These measurements need not strictly confirm to the bulk magnetization measurements like susceptibility etc. In fact, experimental measurements on the temperature variations of the hyperfine fields have clearly showed these effects\footnote{61,62}.

The hyperfine field measurements as a function of temperature on many dilute impurity atoms showed that the magnetization at the impurity does not follow the host magnetization curve. As suggested by Jaccarino et al.\footnote{62} in those cases there is a possibility for a localized moment around the impurity atom. Similar experimental studies are made by Rosenblum et al.\footnote{57} and Pramila et al.\footnote{63} also confirm the above conclusions. However, the hyperfine fields as a function of temperature are found to follow the bulk magnetization properties of the host\footnote{64,65}.

Till 1967, the most precise values have, in general, been obtained by spin-echo magnetic resonance exploited extensively by Kontani and Itoh\footnote{66}, though it should be emphasized that these measurements are probably on solutes in domain walls while other methods sample the entire bulk material. This difference may account for the discrepancies
in $H_{\text{hf}}$ reported from different techniques. The time-differential perturbed angular correlation (TDPAC) technique is a powerful tool for precision hyperfine field measurements in ferromagnetic lattices. The TDPAC technique has two important advantages over other methods such as nuclear magnetic resonance; the measurements can be performed (i) at low impurity concentrations, and (ii) over a wide temperature range.

(i) **Origin of hyperfine fields on impurities in ferromagnets**

Before we start discussion on our measurements on $^{44}$Sc and $^{187}$Re, we give a discussion of the observed solute hyperfine fields in iron, cobalt and nickel lattices. Taken individually the solute fields are of little importance but their variation with host magnetization and particularly with solute atomic number can lead to an understanding of their origins. The origin of hyperfine interactions in ferromagnets is still not well understood. However, further theoretical work on the manybody problem may better our understanding of these interactions. Here we shall try to define the 'hyperfine field' and shall elaborate the mechanisms that can give rise to these fields in ferromagnets. These mechanisms can then be related to the electronic configurations of solute and the solvent atoms.

In a ferromagnet the effective field experienced by a nucleus may be defined as,
\[
\hat{H}_{\text{eff}} = \hat{H}_{\text{hf}} + \hat{H}_L \quad (\text{in a domain wall})
\]
or
\[
\hat{H}_{\text{eff}} = \hat{H}_{\text{hf}} + \hat{H}_L + \hat{H}_0 - \hat{D}M \quad (\text{in a domain})
\]

Here \( \hat{H}_{\text{hf}} \) and \( \hat{H}_0 \) represent the hyperfine field and the applied field, \( \hat{D}M \) is the demagnetizing field and \( \hat{H}_L \) is the Lorentz field \((4\pi/3 \hat{M})\) plus the field arising from dipoles in Lorentz cavity. \( \hat{H}_{\text{hf}} \) and \( \hat{H}_L \) are found, in general parallel (or antiparallel) even in domain walls. In order to understand that how the hyperfine fields in ferromagnetic metals arise from hfs; Shirley et al.\(^{57}\) defined a Hamiltonian which is applicable to both a ferromagnetic host metal and solute,

\[
\begin{align*}
\hat{H} & = V_{\text{cf}} + 2 \beta \cdot \hat{H}_{\text{ex}} \cdot \hat{S} + \chi \hat{L} \cdot \hat{S} - \gamma_I \hat{H}_c \cdot \hat{I} \\
& + 2 \beta \gamma_I \cdot r^{-3} \left[ \hat{L} \cdot \hat{I} + \left( \chi \hat{L}(\hat{L}+1) - \kappa \right) \hat{S} \cdot \hat{I} \right] \\
& - \frac{3}{2} \gamma^2 \left[ (\hat{I} \cdot \hat{S})(\hat{L} \cdot \hat{I}) + (\hat{L} \cdot \hat{I})(\hat{I} \cdot \hat{S}) \right]
\end{align*}
\]

In using and explaining this Hamiltonian we think of a particular solute atom characterized by the quantum numbers \( L, S, \) and \( I \) acted upon by all the other impurity atoms in the lattice characterized by the crystal field interaction \( V_{\text{cf}} \), the exchange field \( \hat{H}_{\text{ex}} \), and the conduction electron polarization \( \hat{H}_c \). The \( \chi \hat{L} \cdot \hat{S} \) term is the electronic spin-orbit interaction and the terms in curly brackets represent the magnetic hfs interaction\(^{67}\).
in operator equivalent notation\textsuperscript{68}. The $\mathbf{L} \cdot \mathbf{I}$ term represents the interaction of the electronic orbital angular momentum with the nuclear spin, the $\mathbf{hS} \cdot \mathbf{I}$ term, the polarization and the three terms in $\mathbf{\omega}$, the interaction of the electronic spin with the nuclear spin. Here $\beta$ is the Bohr magneton, and $\langle r^{-3} \rangle$ is evaluated for open electronic shell (if any) of the solute\textsuperscript{72}. The first three terms are the largest and must be evaluated first to give the zero order wave functions. Except for rare earth solutes, the $\mathbf{hS} \cdot \mathbf{I}$ is smaller than the other two parts. The fourth term describes conduction-electron polarization, $\vec{H}_c$. It is approximately proportional to the lattice magnetization.

For the situation in which the spin–orbit coupling is smaller than both the crystal field and the exchange field, we can assume that the electronic orbital angular momentum is quenched by the crystal field. For cubic lattices the Hamiltonian can be written as a sum of two parts,

$$\mathcal{H} \mid = \mathcal{H}_1 + \mathcal{H}_2$$

where $\mathcal{H}_1 = H_{\text{cf}}$, which determines the zero order wave function and

$$\mathcal{H}_2 = 2 \beta \mathbf{H}_{\text{ex}} \cdot \mathbf{S} - \gamma_I \mathbf{h}_c \cdot \mathbf{I} - 2 \beta \gamma_I \langle r^{-3} \rangle \mathbf{hS} \cdot \mathbf{I}$$

$$= 2 \beta \mathbf{H}_{\text{ex}} \cdot \mathbf{S} - \gamma_I \mathbf{h}_c \cdot [\mathbf{h}_c + 2 \beta \langle r^{-3} \rangle \mathbf{hS}]$$

$$= 2 \beta \mathbf{H}_{\text{ex}} \cdot \mathbf{S} - \gamma_I \mathbf{h}_c \cdot \mathbf{H}_{\text{hf}}$$
In the above equation the second term is in the form of magnetic field interacting with magnetic dipole. The exchange term is the largest among the other terms involved in $\mathbf{B}_2$. If it is considered that this is evaluated first to give $\langle S_z \rangle$, the expression for $\mathbf{H}_{\text{hf}}$ can be written as scalar

$$\mathbf{H}_{\text{hf}} = H_c + 2 \langle S_z \rangle H_d$$

where $H_d = \beta k \langle r^{-3} \rangle$, the core polarization hyperfine field arising from a single unpaired d-electrons. According to Shirley and Westenbarger$^{69}$ $H_c = p \cdot H_{\text{ns}}$ where $H_{\text{ns}}$ is the free atomic hyperfine field arising from atom in ns state. This substitution is permissible because it is expected that conduction band s-wave states resemble the atomic functions near the nucleus. Thus the final expression for the hyperfine field is$^{57}$,

$$\mathbf{H}_{\text{hf}} = p \cdot H_{\text{ns}} + 2 \langle S_z \rangle H_d$$

The first term on the right hand side is the conduction electron polarization (CEP) contribution and the second is the core polarization (CP) contribution, which arises only in cases where there are unpaired magnetic electrons (i.e., open p,d shells). This equation should be valid for all impurities in ferromagnets except for those with incomplete f-subshells, because we assumed
to study the relative importance of the mechanisms that produce hyperfine fields at solutes in ferromagnets, it is useful to survey the fields reported in iron, cobalt, and nickel lattices. The earlier observation $^{79}$ that solute fields vary smoothly with atomic number has been very nicely confirmed for all the three host lattices. An up-to-date such compilation $^{71}$ is displayed for all the three lattices Fe, Co and Ni in Figs. 30, 31 and 32 respectively. In the case of iron, cobalt, and nickel the electrons involved in this exchange interaction are the unpaired d-electrons. A reasonably good approximation can be made that these d-electrons are localized on individual atoms and the spontaneous magnetization can be considered to arise from the summation of all the atomic moments. It is the same d-electrons which are also responsible for the large magnetic hyperfine fields at the nuclei of atoms in ferromagnets. In cubic ferromagnets these fields arise principally from the Fermi contact interaction of s-electrons which have been polarized by the d-electrons. The mechanism by which this polarization results is not quantitatively understood as yet, but the theoretical treatment given by Freeman and Watson $^{72}$ is encouraging. The exchange interaction arises from purely electrostatic forces as a result of the Pauli exclusion principle and is
That the sign of the PIAD has not been determined. The atomic number Z (or A) of the solute atom, open circles, indicates Fig. 11. Magnetic hyperfine fields at solute nuclei in cobalt matrix plotted.
written most generally as,
\[ \hat{J} \hat{e} = -2 \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j \]
where \( J_{ij} \) is the strength of the interaction and \( \vec{S}_i \) and \( \vec{S}_j \) are electron spin operators. The summation is carried out for all atoms \( i \) with all other atoms \( j \neq i \). The exchange interaction is not generally isotropic.

(ii) **Hyperfine field models**: The large magnetic hyperfine fields observed experimentally at the nuclei of impurities dissolved in metallic iron, nickel and cobalt can be explained by the following three existing models.

1. **Conduction electron polarization (CEP)**
2. **Core polarization (CP)**
3. **Overlap polarization (OP)**

1. **Conduction electron polarization**: The contribution of the conduction electron polarization to the hyperfine field \( H_{\text{CEP}} \) at the site of the nucleus is largely due to the contact interaction of those conduction electrons that have S-character with respect to the impurity atom. This model was proposed by Daniel and Friedel. In this model the d moments \( \mu_h \) of the host atoms are assumed to act as an effective field on conduction electrons, giving rise to a difference in energy of the conduction electrons with spin up and spin down. Since the electrons with spin up and spin down should fill the conduction band,
therefore, a difference in their density is resulted. The
sign of the difference depends on the character of the
coupling between the 3d electrons and the conduction
electrons, which may be parallel or antiparallel.

The impurity nucleus is considered as a rectangular
potential well, having a depth $Z_i - Z_h$ between the impurity
atom and host atom (where $Z_i$ is the valence of the impurity
atom and $Z_h$ is the valence of the host atom). The radius
of this potential well is defined as 'a' and is set by
certain assumed number of S-electrons per atom in the
conduction band. Due to their difference in energy in
conduction band both types of electrons will see a dif­
ferent potential at the impurity site. This means there
will be two wave functions, $\psi_S^\uparrow$ and $\psi_S^\downarrow$. This implies a
difference in density of both types of S-electrons at the
site of the nucleus, $|\psi_S(0)^\downarrow|^2$ and $|\psi_S(0)^\uparrow|^2$. The resulting
net conduction electron polarization will be $|\psi_S(0)^\uparrow|^2 -
|\psi_S(0)^\downarrow|^2$. It may be positive or negative, depending
on which effect is stronger.

Daniel and Friedel assumed the conduction band to
contain one S-electron per host atom and calculated this
polarization at the impurity site $P_i$ as a function of the
valence (see Fig. 33, curve a). They predicted the reversal
in sign of the hyperfine field at $Z_i \sim + 3$ and concluded that
the experimental results show that the host conduction electron
FIG. 33  CALCULATED POLARIZATION $P_i$ OF THE $3$-ELECTRONS AT THE IMPURITY SITE AS A FUNCTION OF THE VALENCE $Z_i$ OF THE IMPURITY ATOM. CURVE 'a' REPRESENTS THE ESTIMATE OF DANIEL AND FRIEDEL; CURVE 'b' REPRESENTS THE ESTIMATE OF CAMPBELL. FOR IRON $P_h = 1$. 
polarization is positive.

This model is later on modified by Campbell when Daniel and Friedel model could not explain certain experimental results of $H_{hf}$ (say for example CuFe). In the modified version of Daniel and Friedel model, Campbell assumed that the conduction band is taken as a composite band with 4 electrons (in S-p shell) for each direction of spin; one of these 4 electrons is S, and there is the same density of states curve for all electrons. The non S-electrons can be thought of as being d-like near the bottom of the band and p-like elsewhere. For the details we refer reference 60). On the basis of Campbell's model the behaviour of the polarization at the impurity site, $P_i$, as function of the valence is given in Fig. 33 curve b. Finally he gave the following expression which will give the contribution of the $H_{hf}$ due to conduction electron polarization,

$$H_{CEF} = A(Z) P_h (0.6 + 0.4 \frac{\mu_i}{\mu_h})$$

$A(Z)$ are the free atomic hyperfine fields. If we know the host and impurity moments, we can calculate the contribution from $H_{CEF}$. For iron $\mu_h = 2.22 \mu_B$ and for nickel $\mu_h = 0.606 \mu_B$ where $\mu_B$ is Bohr magneton. Shirley and Westenbarger and later Shirley, Rossenblum and Matthias also assumed this proportionality of $H_{CEF}$ with $A(\mu)$ and deduced from the experimental values the empirical relation,
2. **Core polarization**: This model is due to Freeman and Watson\(^{72}\) and they have extensively treated it by means of Hartree-Fock calculations. Core polarization is chiefly caused by the exchange interaction of an unfilled d shell with the filled S shells giving rise to a net spin density at the nucleus. The resulting hyperfine field \(H_{\text{CP}}\) being a superposition of the contributions from all S shells. The regular variation of \(H_{\text{hf}}\) with solute atomic number in the 3d, 4d and 5d transition series is very interesting. In Fe, Co and Ni hosts, the fields are negative across the three series, but they increase suddenly at the solutes Mn, Ru and Os, and remain large for several elements before returning to the CEP 'base line' (see Figs. 30, 31 and 32). Freeman and Watson\(^{72}\) have calculated hyperfine fields per unpaired spin for 3d group, 4d group and 5d group,
\[
H_{3d} = -125 \text{ Koe}, \quad H_{4d} = -375 \text{ Koe} \quad \text{and} \quad H_{5d} = -1200 \text{ Koe}
\]
respectively. They have also shown that within 4d elements, the magnitude of the \(H_{\text{hf}}\) unpaired d-spin does not vary considerably for different elements. This was later on confirmed by experiments. For diamagnetic atoms the contribution of Core polarization is relatively small.

3. **Overlap polarization**: It is a new model proposed by Stearns\(^{73}\). The hyperfine field contribution arising from

\[H_{\text{CEP}} = 0.027 \mu_h A(Z).\]
Overlap polarization is due to S electron wave functions in outer shells of the impurity atom overlapping with the wave functions of the polarized d electrons of the host. The magnitude of this contribution depends strongly on the size of the impurity atom. Overlap polarization is likely to be of considerable importance for impurities with high valency, where the outer shell is not completely ionized and there is a remaining density of bound outer shell S-electrons at the impurity site. Stearns\textsuperscript{73} has given this possible explanation for the measured hyperfine field of solute atoms in Fe.

(iii) The systematics of the hyperfine fields: The systematics of the hyperfine fields in ferromagnetic hosts have been studied in detail by Shirley et al.\textsuperscript{57,74}. Since they published their studies on systematics, many more data have become available. Our aim is to review the systematics in the light of more comprehensive data available now. Taking the values of the hyperfine fields from the recently compiled table\textsuperscript{71}, we have plotted the impurity hyperfine fields in the host matrices of Fe, Co, and Ni respectively in Figs. 30, 31 and 32. The following systematic trends are clearly seen,

1) The magnitude of the hyperfine field is proportional to the magnetic moment of the host matrix.
2) The hyperfine field $H_{hf}$ is negative in 3d, 4d and 5d impurities in all the three hosts Fe, Co, Ni. Exceptions are in 4d impurities for $^{39}$Y, $^{40}$Zr in Fe and $^{40}$Zr in Co.

3) The field increases gradually with the increase in the d-electrons and reaches a maximum value when the d-shell is approximately half-full. For 3d impurities, for example, the field is maximum for Fe in Fe, Fe in Co, and Mn in Ni.

In iron host, the field increases gradually for Ru, Rh and Pd; the maximum value is obtained for Pd in Fe. However, the reverse trend is clearly seen for the same impurity metals in the other host matrices Co and Ni.

4) In the case of 5d impurities, the maximum value of $H_{hf}$ is obtained at Ir for all the three hosts.

5) For 5p impurities, the field starts with a negative value when 5p electrons are one or two and gradually reaches a maximum positive value for $^{53}$I and falls off to zero and then to a small negative value as the shell gets full.

6) In 4f impurities, as we increase gradually the number of 4f electrons, the field changes from a negative value to a large positive value somewhere between Eu and Cd and then to a large negative value. The curve is very steep with a large slope.
B. **THE HYPERFINE FIELD AT $^{187}$Re NUCLEI IN NICKEL LATTICE AT ROOM TEMPERATURE**

1. **Source Preparation**: For the present measurement pure tungsten metal (99.99\%) in powder form is sealed in vacuum in quartz tube and got irradiated with thermal neutrons in the CIRUS reactor at Trombay (India). Traces of radioactive tungsten metal powder are melted with pure nickel powder (99.9\%) in an argon atmosphere using an induction furnace. The resulting shining ball of the alloy is hammered into a flat disc (thickness less than 0.5 mm); annealed at 850°C for 15 hrs and is gradually cooled to room temperature.

2. **Experimental Set-up**: The electronic set up is the same as described in the magnetic moment measurement except that a NaI(Tl) scintillator is replaced by a 5.1 cm x 5.1 cm lead loaded plastic scintillator (covered by an aluminium cover of sufficient thickness to absorb β-rays) in stop channel for the detection of 72-keV γ-rays. It is done to improve the time resolution of the electronics. The time resolution of this arrangement for the start and stop channel energy settings respectively at 480- and 72-keV is found to be 1.3 nsec (FWHM) with a slope of 0.24 nsec. An external polarizing field of 2 KOe is applied perpendicular to the plane of the detectors and the data are accumulated in a Packard 400 channel analyzer.
3. Experimental Results and Analysis of the Data: The observed counts in the time spectrum $W(H,t)$ in the presence of an external magnetic field $H$ perpendicular to the plane of the detectors may be written for the case under study as,

$$W(H,t) = A + B e^{-t/\tau} \left[ C \sin \left( 4\omega_L t + \phi \right) \right]$$  \hspace{1cm} (4-1)

The spectra obtained with the magnetic field up ($\uparrow$) and the magnetic field down ($\downarrow$) have modulations of opposite phase when the detectors are kept at $135^\circ$ to each other. The function $R(t)$ is plotted in Fig. 34. The Larmor frequency of the oscillations is extracted from the data using the Fourier transform technique, described by Matthias and Shirley (see Fig. 35). In this case also the double Larmor frequency is obtained from the absolute transform $F(\omega)$ and it is $184.0 \pm 1.0$ MHz. The measured Larmor frequency is related to effective magnetic field through relation,

$$\omega_L = - \frac{g \mu_N H_{eff}}{\hbar}$$  \hspace{1cm} (4-2)

The effective field $H_{eff}$ is, thus, calculated from the experimentally measured $g$-factor. The effective magnetic field,

$$\vec{H}_{eff} = \vec{H}_{ext} + \vec{H}_{int}$$  \hspace{1cm} (4-3)

where $\vec{H}_{ext}$ is the external polarizing field. The $\vec{H}_{int}$ is calculated using the sign of the $\vec{H}_{eff}$ and the known direction of $\vec{H}_{ext}$. The hyperfine field
FIG. 34 $R(t)$ vs. TIME $t$ FOR THE TDDAC SPECTRA OF $^{187}$ReNi IN AN EXTERNAL POLARIZING MAGNETIC FIELD OF 2 kOe.
FIG. 35 THE FOURIER TRANSFORMS OF $R(t)$ FOR $^{187}$ReNi IN AN EXTERNAL POLARIZING MAGNETIC FIELD OF 2 KOe.
where the second and the third terms on the right hand side in relation (4-4) are respectively the correction terms due to the Lorentz field and the demagnetization field.

In the present experiment $H_{ext} = 2.0 \text{ Koe}$; $4\pi M_s D = 2.0 \text{ Koe}$ (for the source shape used) according to the table given by Bozorth. The saturation magnetization $4\pi M_s$ for nickel is 6.08 Koe. The final value of the hyperfine field at $^{187}\text{Re}$ nuclei in nickel matrix at $300^\circ\text{K}$ (room temp.) is

$$H_{hf} (300^\circ\text{K}) = -107 \pm 3 \text{ Koe}.$$ 

C. THE HYPERFINE FIELD AT $^{44}\text{Sc}$ NUCLEI IN IRON MATRIX AT ROOM TEMPERATURE

1. Source Preparation: The liquid source, obtained from NSEC (USA), is evaporated on a thin iron foil (99.99% pure) which is later melted in Argon atmosphere inside an induction furnace and slowly cooled down to room temperature. The resulting shining ball is rolled into a thin foil thickness less than 0.5 mm and is annealed at 850°C for about 24 hrs. and then slowly cooled down to room temperature.

2. Experimental Set-up: The electronic set-up is exactly same as it was used in the magnetic moment measurement of the 68-keV state in $^{44}\text{Sc}$ discussed in Chapter III. Here a different geometry of the detectors and magnet is used since
rough estimates showed that the attenuation of the 
amplitude is considerable because of the finite time 
resolution of the detectors. The time resolution (FWHM) 
of the system for energy gating around 70 keV is 15 nsec. 
The external polarising field is 3 KOe. Nuclear data 512 
Channel analyzer is used to accumulate the data.

3. **Experimental Results and Analysis of the Data**: The 
time dependent angular correlation perturbed by the 
external magnetic field in Z-direction may be written as
\[ W(\mathbf{k}_1, \mathbf{k}_2, t, H) = \sum_{\mathbf{k}} \mathbf{A}_k \cdot (1) \mathbf{A}_k \cdot (2) \frac{1}{2k+1} \exp \left( -iN^n \mathbf{H} t \right) \]
\[ \times Y^N_{\mathbf{k}} (\theta_1, \phi_1) Y^N_{\mathbf{k}} (\theta_2, \phi_2) \]  
(4-5)

This may be simplified to the following form for \( k \leq 2 \)
\[ W(t, H) = 1 + A_{22} P_2 (\cos \theta_1) P_2 (\cos \theta_2) + 3A_{22} \sin \theta_1 \]
\[ \times \sin \theta_2 \cdot \cos \theta_1 \cdot \cos \theta_2 \cos 2(\omega_L t + \phi_1 - \phi_2) \]
\[ + \frac{3}{4} A_{22} \sin^2 \theta_1 \times \sin^2 \theta_2 \cos 2(\omega_L t + \phi_1 - \phi_2) \]
(4-6)

where \( \theta_1, \theta_2, \phi_1 \) and \( \phi_2 \) are the polar and azimuthal angles 
of the two \( \gamma \)-rays respectively. In normal geometry, \( \theta_1 = \theta_2 = \frac{\pi}{2} \) but in the present hyperfine field (\( H_{hf} \))
measurements \( \theta_1 = \frac{\pi}{4} \) and \( \theta_2 = \frac{3\pi}{4} \) (or \( \frac{\pi}{4} \)) and the expression
for \( W(H, t) \) is,
\[ W(H, t) = 1 + 1/16 A_{22} \pm 3/4 A_{22} \cos \omega_L t + 3/16 A_{22} \cos 2\omega_L t \]
(4-7)
where \( w(\mathbf{H}, t) \) is phase shifted by \( 180^\circ \) for the two values of \( \Theta_2 \). In the geometry suggested by Raghavan and Raghavan the magnetic field is in the plane of the detectors at \( 45^\circ \) to the first detector, while the second detector is placed successively at \( 180^\circ \) and \( 90^\circ \) to the first. The normalized sum and difference in the coincidence counting rates at these two angles give the ratio,

\[
R(t) = 2 \left[ \frac{N(180^\circ) - N(90^\circ)}{N(180^\circ) + N(90^\circ)} \right]^{3/2}
\]

\[
= \frac{3/2 A_{22} \cos \lambda_L t}{1 + 1/16 A_{22} + 3/16 A_{22} \cos 2 \lambda_L t}
\]

The modulation frequency in this geometry is simply Larmor frequency \( \omega_L \) compared to \( 2\omega_L \) in the conventional geometry. The function \( R(t) \) vs time is plotted in Fig. 36. Using the Fourier transform technique the Larmor frequency \( \omega_L \) obtained from the absolute transform \( F(\tau) \) (see Fig. 37) is \( = 34.0 \pm 0.3 \text{ MHz} \). With the help of experimentally known g-factor the value of \( H_{\text{eff}} \) is calculated. The \( H_{\text{int}} \) is calculated using the sign of the \( H_{\text{eff}} \) and the known direction of \( H_{\text{ext}} \). The sign of the internal field is measured by us for the first time. It is obtained from the known anisotropy of the unperturbed angular correlation and the phase of the sign wave (when the modulated time spectrum is carefully extrapolated to zero time). Using the relation (4-4) the value of \( H_{\text{hf}} \) is obtained.
FIG. 36 \( R(t) \) vs TIME \( t \) FOR THE TDPA C SPECTRA OF \(^{44}\text{ScFe}\) IN AN EXTERNAL POLARIZING MAGNETIC FIELD OF 7 KOE.
FIG. 37 THE FOURIER TRANSFORMS OF R(t) FOR $^{44}\text{ScFe}$ IN AN EXTERNAL POLARIZING MAGNETIC FIELD OF 3 KOe.
OPEN CIRCLES INDICATE THAT THE SIGN OF THE FIELD HAS NOT BEEN DIRECTLY MEASURED.

PROTERTS OF THE ATOMIC NUMBER Z (OR N) OF THE SOLUTE ATOM.

PICT: MAGNETIC HYPERFINE FIDBOS AT SCALPE NOEL R IN IRON MATRIX.
after appropriate corrections for the Lorentz field and the demagnetization field. In the present experiment on $^{44}$Sc Fe $H_{\text{ext}} = 3.00$ Koe, $4\pi M_s D = 4.18$ (the value of $D$ is obtained from the table of Bozoroth$^{74}$). The saturation magnetization $\frac{4\pi}{3} M_s$ for iron is 6.97 Koe. The final value of the hyperfine field at $^{44}$Sc nuclei in iron lattice at 300° K is $H_{hf} (300^0K) = -94\pm3$ Koe.

D. RESULTS AND DISCUSSION

Our measured values of $H_{hf}$ at room temperature are tabulated in Table 7 along with the other available experimental values in literature. Table 7 also gives a view of $H_{hf}$ in ReNi and ScFe systems using various techniques. Our value is in excellent agreement with Raghavan's$^{75}$ who has quoted a value $= -105 \pm 3$ Koe. However, they used a different geometry$^{76}$ of detectors and magnet because the time resolution of their spectrometer was comparable with the expected time period of the oscillations.

Kontani and Itoh$^{77}$ using spin-echo technique obtained $H_{\text{int}} = -100 \pm 2$ Koe at 4.20 K for the internal field on Re in Ni matrix. If we presume that the impurity magnetization follows the Broullioun function obeyed by the host matrix, the value of the hyperfine field at room temperature is expected to be $\sim 50\%$ less. Our value is $\sim 10\%$ larger than the value reported by Kontani. It may be probably because our impurity concentration is low thus reducing the impurity-
impurity interactions which would result in a larger field. The other possible explanation is that the impurity does not follow the host magnetization curve with the possibility of a localized moment at the impurity.

Kogan et al. \textsuperscript{73)} from their nuclear orientation experiments have determined the hyperfine field $H_{\text{hf}}$ on Sc in $\text{Fe}$. Measured to an order of magnitude, they reported a value of 100 K0e. The nuclear magnetic resonance studies of Koi \textsuperscript{79)} gave them a value of 58 K0e. The values reported by them vary by a factor of 2. Moreover, the NMR studies often contain impurity-impurity interactions because of the poor sensitivity of the technique. Therefore, we have measured the hyperfine field using TDPAC technique and it is $-94 \pm 3$ K0e. In this technique, the concentration of the impurity atoms is so small that the impurity-impurity interactions are completely negligible. None has measured the sign of the hyperfine field so far. The determination of the sign of the hyperfine field on Sc in $\text{Fe}$ is important for the studies of the systematics. The $-$ve sign determined by us agree with the prediction from the systematics of the hyperfine fields.

Even though the detailed mechanisms responsible for the observed large hyperfine fields on the impurity nuclei in ferromagnetic hosts are not well understood, the studies of the systematics of the observed fields show a definite
trend as a function of the impurity atomic number. If we expect a smooth variation of the hyperfine field values around the Sc and Re impurities in Fe and Ni respectively, the expected values from the systematics\(^71\) (see Figs. 30-32) are,

\[
\begin{align*}
H_{\text{hf}} \text{ Sc (3d impurity) } \text{Fe} &= -90 \text{ Koe} \\
H_{\text{hf}} \text{ Re (5d impurity) } \text{Ni} &= -120 \text{ Koe}.
\end{align*}
\]

which are consistent with our experimental values.

It is often found that the hyperfine fields on dilute diamagnetic impurity atoms are proportional to the host magnetic moment. Benski et al.\(^83\) reported \(H_{\text{hf}} \text{ ScNi} = 25.9 \pm 0.3 \text{ Koe}\). Our measured value \(H_{\text{hf}} \text{ ScFe}\) is \(-94 \pm 3\). These values are proportional to the respective host magnetic moments \((\mu_{\text{Ni}} = 0.606 \mu_\text{B}, \mu_{\text{Fe}} = 2.22 \mu_\text{B})\).

In the case Rhenium, Kontani et al.\(^77\) reported \(H_{\text{hf}} \text{ ReNi} = -100; H_{\text{hf}} \text{ ReCo} = 442; H_{\text{hf}} \text{ ReFe} = -760 \text{ Koe}\). Our measurement for \(H_{\text{hf}} \text{ ReNi}\) is in agreement with that of Kontani et al. However, the observed fields are not proportional to the host magnetic moments \((\mu_{\text{Ni}} = 0.606 \mu_B, \mu_{\text{Co}} = 1.72 \mu_B, \mu_{\text{Fe}} = 2.22 \mu_B)\). This may be due to the formation of localized moments as pointed out in the earlier part of the discussion.

A formal Hamiltonian of the impurity atom is quite complicated and may be written\(^57\),
\[ H = V_{cf} + 2\beta H_{ex} \cdot S + \alpha \cdot L \cdot S - \gamma I \cdot H_c \cdot I + 2\beta I \cdot \langle r^{-3} \rangle \cdot L \cdot I + \]

\[ \frac{\hbar}{2} L(L+1) - \kappa |S \cdot I| - \frac{2}{3} \kappa \left[ (L \cdot S)(L \cdot I) + (L \cdot I)(L \cdot S) \right] \]

the symbols are explained in reference 57. The present measurements on the impurity hyperfine fields were carried out in cubic matrices and the impurity concentration is negligibly small and, therefore, the electronic spin dipole contribution is zero. For the impurities of our interest i.e., Sc and Re in the ferromagnetic hosts of Fe and Ni respectively, the orbital contribution to the impurity hyperfine fields is also small. The main contribution to the impurity hyperfine fields in ferromagnets come from

a) Conduction electron polarization (CEP)
b) Core polarization (CP)
c) Overlap polarization (OP).

The conduction electron polarization arises largely from the polarization at the nucleus from the conduction electrons having an S-character. From the fact that the conduction band S-electron states are similar to atomic states near the solute nucleus, it was shown by Shirley, Rosenblum and Matthias\(^{57}\) that,

\[ H_{CEP} = p H_{ns} \]

where \( H_{ns} \) is the free atomic hyperfine field and \( p \) is the
polarization at the solute. From the experimental data it was derived \(57, 78\) 

\[
H_{hf} = 0.027 \mu_{Fe} H_{ns} \text{ for dilute impurities in } Fe \\
= 0.030 \mu_{Co} H_{ns} \text{ for dilute impurities in } Co \\
= 0.024 \mu_{Ni} H_{ns} \text{ for dilute impurities in } Ni 
\]

so that the predicted values are

\[
H_{hf\, ScFe} = -47 \text{ KOe} \\
H_{hf\, ReNi} = -155 \text{ KOe} 
\]

The free atomic hyperfine fields were obtained from Campbell \(60\).

However, for the transition element impurities,

\[
H_{hf} = pH_{ns} + 2 \langle S_z \rangle H_d
\]

where \(H_d\) is the Core polarization hyperfine field arising from one unpaired d-electron. The calculations of Freeman and Watson \(72, 80\) showed that

- for 3d elements \(H_{hf} \sim -125 \text{ KOe per unpaired spin}\)
- for 4d elements \(H_{hf} \sim -375 \text{ KOe per unpaired spin}\)
- for 5d elements \(H_{hf} \sim -1200 \text{ KOe per unpaired spin}\)

They have also shown that within the 4d elements, the magnitude of the \(H_{hf}\) does not vary considerably for different elements. This result was later confirmed by the experimental results. For diamagnetic atoms, the contribution from the core polarization is small. Since the
core polarization of the d-electrons is always negative, the sign of the field on Sc in Re can be explained using this model. However, since the magnitude of the d-electron spin moment on the solute is \(0.3 \mu_B\). The observed field of \(-107\) KOe for Re in Ni cannot be explained using this model.

The observed small field in magnitude compared to the predicted value from the systematics of the core polarization model on ReNi may be due to a finite positive field arising from the overlap polarization\(^{73}\) of the host 3d electrons and the impurity valence electrons. This effect is expected to be larger in heavier solutes like Re.

In the model due to Campbell\(^{60}\) the contribution from conduction electron polarization could be calculated using the formula

\[
H_{\text{CEP}} = A(Z) P_h (0.6 + 0.4 \mu_i/\mu_h)
\]

\(A(Z)\) are the free atomic hyperfine fields and are tabulated by Campbell; the host polarization \(P_h = -0.12\) S-electrons.\(^{66}\) If we know the host and impurity moments viz., \(\mu_i\) and \(\mu_h\), we can calculate the contribution from \(H_{\text{CEP}}\).

Balabanov and Delyagin\(^{82}\) have obtained a very good fit of the experimental hyperfine fields to an empirical equation

\[
H/\mu = Z^3 \left[ -2.48 + 0.113 (\nu - 9)^2 \right]
\]
where \( \gamma \) is the number of electrons outside the closed shell, \( Z_0 \) is the number of closed shell electrons and is equal to 18, 36, 68 for IV, V and VI group elements. The values predicted by this model for hyperfine fields of our interest are \( H_{hf} \text{ScFe} \approx +152 \text{ KOe} \) and \( H_{hf} \text{ReNi} \approx -304 \text{ KOe} \). In the case of Sc in Fe the predicted value is \(+152 \text{ KOe} \) compared to the experimental value of \(-94 \text{ KOe} \). For Re in Ni the prediction of the sign of the hyperfine field is correct but the magnitude is three times the experimental value. This model is quite empirical with the result that no plausible explanation for the observed large deviations may be offered.

It looks that none of the existing models can correctly explain the observed fields in ScFe and ReNi. The observed field on ScFe both in magnitude and sign may be qualitatively explained by the conduction electron polarization and the core polarization model suggested by Shirley et al. The field on Re in Ni may be understood if we assume that the conduction electron polarization and the overlap polarization are vectorially added to give the final experimental value.\(^{84}\)

The observed width (FWHM) for \(^{44}\text{ScFe}\) is \(29 \times 10^{-9} \text{ eV} \) compared to the natural width of \(4.4 \times 10^{-9} \text{ eV} \) is considerably large. This discrepancy is attributed to some finite probability where the Sc atom is not substitutional with iron.
matrix. Since the spin of the intermediate state 68-keV in $^{44}$Sc is 1, the quadrupole interactions are zero.

Similarly, the observed width (FWHM) for $^{187}$Re$_{Ni}$ $\sim 80 \times 10^{-9}$ eV compared to the natural width of $1.25 \times 10^{-9}$ eV is also considerably large. This may be, (i) Re atom is not substitutional to the nickel matrix and (ii) since the spin of the intermediate state 206-keV in $^{187}$Re is 5/2, hence there may be quadrupole interactions.
### TABLE 7
Comparison of the present hyperfine field measurements with available published values

<table>
<thead>
<tr>
<th>Element</th>
<th>At. No.</th>
<th>Host</th>
<th>Temp. (°K)</th>
<th>Hyperfine field</th>
<th>Technique</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re</td>
<td>187</td>
<td>Ni</td>
<td>293</td>
<td>-105 ± 3</td>
<td>DPAC</td>
<td>75</td>
</tr>
<tr>
<td>Re</td>
<td>-</td>
<td>Ni</td>
<td>L.He</td>
<td>-105 ± 2</td>
<td>SE</td>
<td>77</td>
</tr>
<tr>
<td>Re</td>
<td>187</td>
<td>Ni</td>
<td>300</td>
<td>-107 ± 3</td>
<td>DPAC</td>
<td>Present measurement</td>
</tr>
<tr>
<td>Sc</td>
<td>46</td>
<td>Fe</td>
<td>-</td>
<td>100 ± 30</td>
<td>NPL</td>
<td>78</td>
</tr>
<tr>
<td>Sc</td>
<td>45</td>
<td>Fe</td>
<td>-</td>
<td>58</td>
<td>NMR</td>
<td>79</td>
</tr>
<tr>
<td>Sc</td>
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<td>Fe</td>
<td>Low</td>
<td>100</td>
<td>NPL</td>
<td>81</td>
</tr>
<tr>
<td>Sc</td>
<td>44</td>
<td>Fe</td>
<td>300</td>
<td>-94 ± 3</td>
<td>DPAC</td>
<td>Present measurement</td>
</tr>
</tbody>
</table>
