A PULSED N.M.R. STUDY OF THE FERROMAGNETS
Ni, Fe$_2$P and Fe$_3$P

by

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We accept this thesis as conforming
to the required standard

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March, 1972
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Date May 5, 1972
The pulsed N.M.R. technique has been used to study the ferromagnets Ni, Fe$_2$P and Fe$_3$P. The dependence of the N.M.R. free induction decay on the strength of the applied r.f. field and on pulse length has been studied in nickel powder. The results indicate that the applied r.f. field is enhanced and that there is a distribution of enhancement factors. The distribution can be explained in the light of a model in which the domain walls vibrate like pinned membranes. The maximum enhancement factor is estimated to be 4700.

The N.M.R. of $^{31}$P and $^{57}$Fe has been observed in Fe$_2$P. Zero field resonances have been observed at the frequencies 17.5 MHz, 20.5 MHz, 77.5 MHz and 86.6 MHz at 1.5 K. These results allowed the deduction of the hyperfine fields at the various atomic sites. These are $H_n$(FeI)=148 koe., $H_n$(FeII)=123 koe., $H_n$(PI)=50.2 koe. and $H_n$(PII)=45.0 koe.. From the shift of the N.M.R. frequency on application of an external magnetic field the sign of the phosphorous hyperfine fields is shown to be positive. The temperature dependence of the $^{31}$P N.M.R. frequency has also been studied and the data is well fitted by a T$^2$ law. Domain wall enhancement of the applied r.f. field was studied in the light of the pinned membrane model. Studies of the nuclear relaxation times indicate that thermal fluctuations of the domain walls provide the dominant relaxation mechanism.
In Fe₃P a rather complicated N.M.R. spectrum was observed. Resonances occur at 41.7 MHz, 37.2 MHz, 34.5 MHz, 27.5 MHz and 24.8 MHz. These are all attributed to iron sites and correspond to hyperfine fields of 304 koe., 271 koe., 200 koe., and 180 koe. Domain wall enhancements were also studied in the light of the pinned membrane model. Nuclear relaxation times were also determined and the results indicate that thermal fluctuations of the domain walls provide the dominant relaxation mechanism.
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CHAPTER I

INTRODUCTION

The Nuclear Magnetic Resonance (N.M.R.) technique has been established as a powerful tool for the study of hyperfine interactions in a wide variety of materials. In particular, it has proved to be extremely useful in the study of hyperfine fields in ferromagnetically ordered systems (Portis and Lindquist, 1965). Nuclear resonance studies of these systems can elucidate the static and dynamic nuclear hyperfine coupling. The magnitude and direction of the nuclear hyperfine field, its temperature dependence, and the field distributions resulting from impurity substitution are examples of the static magnetic information gained from resonance studies. Measurements of the characteristic relaxation times for spin-spin and spin-lattice coupling, and enhancements of the applied r.f. field due to domain walls provide information concerning the dynamic interactions of the nuclear spin system. The N.M.R. results taken together with measurements of magnetic moments (e.g. neutron scattering experiments) can lead to a fairly complete understanding of the hyperfine field and its sources.

The experimental methods used in N.M.R. work may be divided into steady state and pulse techniques. In the steady state technique the absorption of power by the nuclear spins is detected by the conventional resonance technique of modulating the oscillator frequency and amplifying the modulation envelope.
via lock-in detector to present the first derivative of the resonance line. Since the first derivative decreases with line-width, the use of the steady state technique is usually limited to narrow-line resonance and lineshape studies. The pulse technique is especially useful for the observation of the broad-line resonances often found in ferromagnetic systems as it provides better discrimination against background resonances than do the conventional steady state techniques (Dean et. al., 1967). It also enables direct observation of nuclear relaxation.

The work described in this thesis represents an application of the pulsed N.M.R. technique to a study of the ferromagnets Ni, Fe$_2$P and Fe$_3$P. The experiment on nickel was designed to study domain wall dynamics in the metal. The experiments on Fe$_2$P and Fe$_3$P allowed the measurement of hyperfine fields at various sites, the temperature dependence of the hyperfine field, relaxation times and domain wall characteristics.

A nucleus with total angular momentum $I\hbar$, has associated with it a magnetic dipole moment $\mu=g_\nu\mu_\text{n}I$, where $g_\nu$ is the nuclear $g$ factor and $\mu_\text{n}$ the nuclear magneton. The Zeeman interaction of the magnetic dipole moment, $\mu$, with a magnetic field $H$, is given by

$$\mathcal{H} = -\mu \cdot H$$

(1.1)

The energy eigenvalues $E_m$ corresponding to the eigenstates $|m\rangle$ of this Hamiltonian are given by

$$E_m = g_\nu \mu_\text{n} mH$$

(1.2)

$$m = I, I-1, \ldots, -I$$
where \( m \) denotes the eigenvalue of \( I_z \), and \( z \) is the direction of the applied field \( H \).

In thermal equilibrium the nuclear spin system can be described by the population densities of the energy levels \( E_m \), given by the Boltzmann distribution function

\[
P_m = \frac{e^{-E_m/kT}}{\sum_{m=1}^{\infty} e^{-E_m/kT}}
\]

where \( T \) denotes the lattice temperature, the lattice being the environment in which the nuclear spins are located. The net magnetization of a bulk sample containing \( N \) spins is then given by

\[
M = NT \sum_{m=-J}^{J} P_{m} x (\mu) = N \sum_{m=-J}^{J} P_{m} a_{m} \mu_{m}
\]

\[
= \frac{Ng_{\mu}^{2} \mu^{2}}{3kT} (1+I) H_{0} \quad \frac{g_{\mu} \mu_{0} H_{0}}{kT} \ll 1
\]

The equation of motion of the magnetization, \( M \), in the presence of a field \( H \), neglecting the interaction of the spins with their surroundings, is

\[
\frac{dM}{dt} = \frac{i}{\hbar} [H, M]
\]

where \( H \) is the Zeeman hamiltonian (equation 1.1).

Upon applying the commutation relationships for the components of angular momentum this becomes

\[
\frac{dM}{dt} = \frac{g_{\mu} \mu_{0}}{\hbar} ( M \times H ) = \gamma_{\mu} ( M \times H )
\]
The motion corresponds to an undamped precession of the magnetization about the direction of the applied field with an angular velocity $\gamma H$. $\gamma$ is the nuclear gyromagnetic ratio. If the applied field consists only of a static field $H_0$ in the z direction then it is evident that $M_z$ is time independent while the components $M_x$ and $M_y$ vary sinusoidally with time with a frequency $\omega = \gamma H_0$. $\omega$ is called the Larmor frequency.

In order to solve (1.6) it is convenient to transform to a frame of reference rotating with angular velocity $\omega$ with respect to the laboratory frame. In this rotating frame the equation of motion for $M$ becomes

$$\frac{dM}{dt} = \frac{dM}{dt} + M \times \omega$$

(1.7)

using (1.6) this becomes

$$\frac{dM}{dt} = M \times [H + \omega/\gamma]$$

(1.8)

If $H$ is just the static field $H_0$ along the z direction, and if we choose $\omega = \gamma H_0 \mathbf{k}$, where $\mathbf{k}$ is a unit vector along the z direction, then the magnetization is stationary in the rotating frame. In the laboratory frame it precesses about the field $H_0$ at the Larmor frequency.

Suppose now that the total field $\mathbf{H}$ is the sum of a constant field $H_0$ and a field $H_1$ perpendicular to $H_0$ and rotating about
it with an angular velocity $\omega$. $H_1$ can be written

$$H_1 = H_1 (i \cos \omega t + j \sin \omega t)$$

(1.9)

where $i$ and $j$ denote unit vectors along the x and y axes respectively, of the laboratory frame. Taking $H_1$ to lie along the unit vector $i'$ in the rotating frame, equation (1.7) becomes

$$\frac{\delta M}{\delta t} = \gamma M \times [k(H_0 + \omega/\gamma) + i'H_1]$$

(1.10)

$$= \gamma M \times H_{\text{eff}}$$

where

$$H_{\text{eff}} = k(H_0 + \omega/\gamma) + i'H_1$$

In the rotating frame, therefore, the magnetization precesses about an effective field $H_{\text{eff}}$ with an angular velocity

$$\left\{ (H_0 \gamma + \omega)^2 + (\gamma H_1)^2 \right\}^{1/2}.$$ When $|\gamma H_1|/|\omega|$ the effect of the r.f. field is negligible. The effect of the r.f. field becomes appreciable when $\omega \ll \gamma H_0$. When $\omega = -\gamma H_0$, $M$ precesses about the direction $i'$ with an angular velocity $\omega = \gamma H_1$. This is the phenomenon of nuclear magnetic resonance. If the field $H_1$ is applied for a time $\tau$, then the magnetization would precess through an angle $\omega \tau$, and the solutions of equation (1.6) can be written

$$M_z(\tau) = M_0 \cos(\omega \tau)$$

$$M_\perp(\tau) = M_0 \sin(\omega \tau) \exp(i \omega \tau)$$

(1.11)

$$M_\perp = M_x + i M_y$$
After the r.f. pulse is cut off, the precessing magnetization is given by

\[ M_z(t) = M_0 \cos(\omega t) \]
\[ M_+(t) = M_0 \sin(\omega t) \exp(i \omega t) \tag{1.12} \]

A '90 degree pulse', for which \( \omega t = \frac{\pi}{2} \) or odd multiples thereof, produces the greatest amplitude of precessing magnetization. The amplitude vanishes following an '180 degree pulse', that is, when \( \omega t = \pi \).

In practice, the sample is placed inside a coil which is part of an L-C circuit tuned to the resonance frequency. R.F. voltage is applied to the coil producing a linearly polarized sinusoidal field perpendicular to the static field. This oscillating field can be decomposed into two counter-rotating components, one with frequency \( \omega \), and the other with frequency \(-\omega\). When the resonance condition is satisfied for one component the other is \(2\omega\) off resonance and its effect can be neglected (see e.g. Abragam, 1961). The resonant component turns the magnetization into the \(x,y\) plane. Following the pulse the components of the magnetization in the \(x,y\) plane precess about \(H_0\) with a frequency \(\omega\), and induce a voltage in the pick-up coil. This 'free induction' signal is amplified and detected by the receiver.

It has been assumed until now that the applied field \(H_0\) is uniform. This is not the case in practice as there is
always some inhomogeneity associated with any applied field. The inhomogeneity results in a scatter of Larmor frequencies. This scatter can be described by a shape function \( f(\omega) \). If we now wish to find the precessing magnetization following the application of an r.f. pulse at the central Larmor frequency \( \omega_0 \), then we have to take into account the spread in Larmor frequencies. The precessing magnetization is now given by

\[
M_+(t) = M_0 \int_{-\infty}^{\infty} \sin(\omega t) \exp(i \omega t) f(\omega) d\omega \quad (1.13)
\]

If we assume that \( \omega_i \) is much smaller than the width of the shape function and that the duration of the pulse is the order of \( 1/\omega_i \), then the precessing magnetization will be

\[
M_+(t) = M_0 \sin(\omega_0 t) \exp(i \omega_0 t) \int_{-\infty}^{\infty} f(\omega + \omega_i) \exp(iut) du \quad (1.14)
\]

As \( t \) approaches infinity, because of the destructive interference among the contributions of different parts of the sample to the transverse magnetization, \( M(t) \) goes to zero. If for example, the shape function is a Lorentzian curve

\[
f(\omega_0 + u) = \frac{1}{b^2 + u^2} \]

Then

\[
M(t) = M_0 \sin(\omega_0 t) \exp(-bt) = M_0 \sin(\omega_0 t) \exp(-t/T^*_2) \quad (1.15)
\]

The decay time is then inversely proportional to the linewidth, \( b \).
As the transverse magnetization decays so will the voltage induced in the pick-up coil. It is possible to restore the precessing magnetization to its original value by the application of an '180 degree pulse'. This is the spin-echo technique (Hahn, 1950). In the spin-echo experiment, the 180 degree pulse applied at a time t after a 90 degree pulse, turns the precessing magnetization through 180 degrees about the x axis of the rotating frame. At a further time 2t, the nuclear spins rephase and a signal maximum results. This signal maximum is called a spin-echo. When metallic samples are used, the skin depth effect introduces inhomogeneities in the r.f. field which make it impossible to satisfy the 90,180 degree conditions for all the nuclei. This limits the amplitude of the echo. For metals we take the terms 90 and 180 degree pulses to mean pulses whose widths are such that the free induction decays following the pulses have maximum and minimum amplitudes respectively.

In the preceding discussion relaxation effects have been ignored. In any real system there are interactions capable of transferring energy from the excited spin systems to the lattice. The rate at which the spin system re-established equilibrium with the lattice is characterized by a spin-lattice relaxation time, $T_1$. The spin-lattice relaxation time is determined essentially by the transverse components of the local fluctuating fields at the Larmor frequency (Slichter, 1963).
Also present are interactions which tend to maintain thermal equilibrium within the spin system. The rate at which these interactions establish equilibrium within the spin system is characterized by a transverse relaxation time \( T_2 \).

In terms of the correlation functions of the local fluctuating fields, \( T_1 \) and \( T_2 \) are given by,

\[
\frac{1}{T_1} = \frac{\gamma^2}{2} \int_{-\infty}^{\infty} <H_+(t)H_-(0)> \exp(-i\omega_t) dt
\]

\[
1/T_2 = \frac{1}{2T_1} + \frac{\gamma^2}{2} \int_{-\infty}^{\infty} <H_Z(t)H_Z(0)> dt
\]

In many cases the approach to equilibrium can be described by the phenomenological equations proposed by Bloch (1946),

\[
\frac{dM_x}{dt} = \gamma M_x H + (M_x i - M_y j)/T_2 + (M_o - M_z) k/T_1
\]

The second and third terms represent relaxation effects. In the absence of the r.f. field the solutions to this equation in the rotating reference frame may be written

\[
M_x(t) = M_x(0) \exp[-t/T_2]
\]

\[
M_y(t) = M_y(0) \exp[-t/T_2]
\]

\[
M_z(t) = M_o + (M_z(0) + M_o) \exp[-t/T_1]
\]

\( T_1 \) and \( T_2 \) can be determined experimentally by observing the time dependence of \( M_x, M_y \) and \( M_z \).
(i) **Ferromagnetism**

In ferromagnetic materials there exists a strong interaction which tends to align the atomic dipoles. As a result a spontaneous magnetization, \( M \), exists: even in the absence of a magnetic field there is a magnetic moment. Above a critical temperature, \( T_c \), called the Curie temperature, the spontaneous magnetization vanishes. The strong interaction which tends to align the atomic dipoles may be considered as equivalent to some internal magnetic field \( H_m \). Thermal agitation of the atoms opposes the orienting effect of the field. Thus the Curie temperature must be the temperature at which the thermal agitation is sufficient to destroy the spontaneous magnetization. This permits an estimate of \( H_m \) to be made.

For atoms with a dipole moment of one Bohr magneton, we have

\[
\mu H_m = kT_c
\]

For \( T_c = 1000 \) K, a value close to that observed for iron, this implies that \( H_m \) is approximately \( 10^7 \) Oe.

Heisenberg (1928), has shown that this field is due to the quantum mechanical exchange interaction. In the simplest case the Hamiltonian describing this strong exchange interaction between the electron spins may be written

\[
\mathcal{H}^{ex} = -J \sum_{i<j} S_i \cdot S_j
\]  

(2.1)
Either a parallel or anti-parallel ordering may result depending on the sign of the exchange integral $J$. In ferromagnetic materials the exchange integral is positive and a parallel ordering is favored.

In ferromagnetic materials such as iron, the ferromagnetism may be attributed to the electrons in the partially filled band corresponding to the d electron states in the free atom. The exchange interaction is such that at low temperatures, instead of electrons occupying the lowest states in balanced pairs, there is an excess of electrons with spins pointing one direction, giving rise to a spontaneous magnetization. The energy due to the exchange interaction decreases as the number of excess parallel spins increases. This decrease in energy is accompanied by an increase in energy due to the electrons moving to states of higher energy in the d band. The equilibrium magnetization depends on the number of electrons, the form of the band, the magnitude of the exchange interaction and the temperature

(ii) **Temperature Dependence of the Magnetization**

(a) Collective Electron Theory

This theory is a band model theory of ferromagnetism. It was first treated in detail by Stoner (1938). The theory is based on the following three assumptions:

1. The 3d band is parabolic in the neighborhood of the Fermi surface, that is, the density of states has the form

$$
\mathcal{C}(E) \, dE \propto E^{\frac{1}{2}} \, dE
$$
2. The exchange interaction between the electrons may be represented by a molecular field.

3. The electrons or holes obey Fermi-Dirac statistics. According to the collective electron theory, the magnetization varies with temperature because of redistribution of electrons among the one-electron states, that is, the transfer of electrons between the up-spin and the down-spin bands. The theory distinguishes between two important cases.

1. All spin-up states lie at least $E$ in energy below the Fermi level. This gives for $T$ much less than $T_c$

$$\frac{M_O - M(T)}{M_O} = A(T) \exp\left[- \frac{E}{kT}\right]$$  \hspace{1cm} \text{(2.2)}

$A(T)$ is a slowly varying function of $T$.

2. Unfilled states occur in both up and down-spin bands at $T=0$ K. For this case we have

$$\frac{M_O - M(T)}{M_O} = ST^2$$  \hspace{1cm} \text{(2.3)}

The coefficient $S$ depends upon the shape of the band.

(b) Spin Wave Theory

Consider a ferromagnetic specimen at absolute zero. The third law of thermodynamics requires that the spin system be completely ordered. Since the system must also be in its ground state, it follows that the spin quantum number of each atom
will have its maximum value. Now assume that the temperature is raised slightly causing one spin to be reversed. The exchange forces will tend to invert the reversed spin. A reversal of the spin would return the system to its ground state. This is unlikely since the temperature has been raised. It turns out that the reversed spin travels from one atom to another, the exchange always occurring between neighboring atoms. This propagation of the reversed spin through a crystal is called a spin wave.

As the temperature is increased the number of spin waves increases and interactions can take place among the spin waves. According to Dyson (1956), who treated the case of a Heisenberg ferromagnet, the error in the calculation of the magnetization when spin wave interactions are neglected is small for $T < 0.5T_c$.

To compute the decrease in the magnetization at a temperature $T$, it is only necessary to know the number of spin waves that have been excited, i.e.,

$$\frac{M_o - M(T)}{M_o} = \frac{g\beta}{M_o} \sum_k \langle \eta_k \rangle$$  \hspace{1cm} (2.4)

where $g\beta$ is the moment associated with a unit of spin excitation, $M_o$ is the magnetization at absolute zero, and $\sum_k \langle \eta_k \rangle$ is the sum over all $k$ values of the thermally excited spin wave numbers. If one now utilizes the fact that spin waves obey Bose statistics, and one knows the energy spectrum of the spin
waves, then according to Dyson one obtains the following result for the temperature dependence of the magnetization

\[ \frac{M_0 - M(T)}{M_0} = CT^{3/2} + DT^{5/2} + \cdots \]  

(2.5)

For a more detailed consideration of spin waves in ferromagnets the reader is referred to the comprehensive review article by Keffer (1966).

Experimental measurements of the temperature dependence of the saturation magnetization in nickel (Pugh and Argyle, 1962) and of neutron diffraction in iron (Lowde and Umakantha, 1960), as well as other experiments, have demonstrated clearly the existence of spin waves of long wavelength in metallic substances. Conclusions have been drawn from this that the model of a Heisenberg ferromagnet and the theory of spin waves is generally applicable.

Studies by Thompson et.al.(1964) have indicated that both spin wave and single particle type excitations can be expected to contribute to the temperature dependence of the saturation magnetization in ferromagnets. Any meaningful analysis of the data will involve a separation into spin wave and single particle contributions. This requires that small changes in the magnetization be known with great accuracy (Wohlfarth, 1970).
(iii) **Hyperfine Fields in Ferromagnets**

It has been found that in many magnetic materials there is, in the absence of an applied magnetic field, a very large effective hyperfine field at the nucleus. The origin of these fields in ferromagnetic metals was first discussed by Marshall(1958). The most authoritative discussion of the subject is by Watson and Freeman(1961,1965). Pris and Lindquist also discuss N.M.R. and hyperfine fields in ferromagnets. The pulsed N.M.R. technique was first demonstrated to be especially useful in the study of the broadline spectra frequently encountered in ferromagnets by Asayama et al.(1963). More recently the application of the pulsed N.M.R. technique to the study of hyperfine field distributions in ferromagnets is discussed by Budnick and Skalski(1967).

Atomic hyperfine fields arise from the interaction of the magnetic moment of the nucleus with the electronic spin and orbital moments. Following Fermi(1930) and Fermi and Segre(1933), the Hamiltonian describing this interaction for a single atom may be written

\[
\mathcal{H} = -g_\text{e} \mu_\text{e} \frac{8\hbar}{3} \delta(r) \mathbf{S} \cdot \mathbf{I} + \frac{(\mathbf{L} - \mathbf{S}) \cdot \mathbf{I}}{r^3} + \frac{3(\mathbf{S} \cdot \mathbf{r})(\mathbf{I} \cdot \mathbf{r})}{r^5} \tag{2.6}
\]

Here \( \mathbf{L}, \mathbf{S}, \) and \( \mathbf{I} \) represent respectively, electron orbital, electron spin and nuclear spin angular momentum operators. \( \mu_\text{e}, \mu_\text{n} \) are the Bohr and nuclear magnetons, and \( g \) and \( g_\text{e} \) are the electronic and nuclear spectroscopic splitting factors. The delta function term is called the Fermi contact term, and is non-zero only for those electrons which have a non-vanishing probability of being found at the nucleus, i.e. the \( s \) electrons.
Equation (2.6) may be rewritten in the form

\[ \chi = -\mu_n \cdot H_n \]  \hspace{1cm} (2.7)

where \( \mu_n \) is the nuclear magnetic moment and \( H_n \) is the total magnetic field at the nucleus arising from the rest of the atom. The contribution to \( H_n \) arising through the Fermi contact term may be written

\[ H_C = \frac{8\pi}{3} g_\mu_n \sum |\Psi(0)|^2 \]  \hspace{1cm} (2.8)

where \( |\Psi(0)|^2 \) is the electron density at the nucleus. The Hamiltonian of the hyperfine interaction for a free atom given in equation 2.6 can also be useful for differentiating the various contributions to the hyperfine field in many electron systems if the 3d electrons are assumed to be localized at the atomic sites.

For a ferromagnetic metal the hyperfine field may be written as

\[ H_n = H_S + H + H_d + H_{loc} \]  \hspace{1cm} (2.9)

where \( H_S \) is the field due to the s electrons, \( H_L \) is the field due to the orbital angular momentum of the 3-d electrons, \( H_d \) is the dipolar field and \( H_{loc} \) is the local field at the nucleus.

The 1-s, 2-s, 3-s and 4-s electrons interact with the nucleus through the Fermi contact term. It is convenient to consider separately the core s electrons and the 4-s electrons.

(a) In the unrestricted Hartree-Fock picture, the core s electrons' wavefunctions are distorted by the exchange potential associated with their interaction with the up-spin 3-d electrons. This interaction is spin-dependent and tends to pull out the up-spin electron wavefunctions. This leaves a net down-spin s electron density at the nucleus.
This gives a negative contribution to the hyperfine field via the Fermi contact term. In iron this contribution has been estimated by Watson and Freeman(1961) to be between -300 and -500 kilogauss.

(b) The exchange interaction of the 3-d electrons with the 4-s electrons is similar to the core 3-d exchange interaction but in this case the up-spin wavefunctions are pulled in. There is then a net up-spin s electron density at the nucleus due to the 4-s electrons which gives a positive contribution. Any admixture of the d band electron wavefunctions and the 4-s band also gives a positive contribution. Anderson and Clogston(1961), however, have suggested that any covalent mixing of the 4-s electron wavefunctions into the unfilled down-spin 3-d band would give a negative contribution which could possibly cancel the admixture contribution to the hyperfine field. The net conduction electron contribution to the hyperfine field is uncertain but is probably about 100 kilogauss.

The orbital contribution, $H_L$, arises from the residual orbital moments associated with the 3-d electrons. For most of the 3-d ferromagnetic metals the angular momentum is almost completely quenched. However, some orbital angular momentum is unquenched by the spin-orbit interaction resulting in a positive contribution to the field at the nucleus given by

$$H = 2\mu_b (2-g) \frac{\langle S \rangle}{r^3}$$  \hspace{1cm} (2.10)

For iron this contribution is about $3\times10^4$ gauss.

In rare earth ferromagnets there is very little quenching
of the orbital angular momentum and this contribution is dominant.

The dipolar field, $H_d$, results from the dipolar interaction of the magnetic moments associated with the nucleus and the electrons. The Hamiltonian describing this interaction is

$$H_D = \frac{\mu_e \cdot \mu_n}{r^3} - \frac{3(\mu_e \cdot \mathbf{r})(\mu_n \cdot \mathbf{r})}{r^5}$$

(2.11)

Here $\mu_n$ and $\mu_e$ are the nuclear and electronic dipole moments respectively. Marshall (1958) has estimated the dipolar contribution in hexagonal cobalt to be +80 kilogauss.

The local magnetic field at the nucleus is given by

$$H_{loc} = H_0 - D M + \frac{4\pi}{3} M$$

(2.12)

where $H_0$ is the external field, $-D M$ is the demagnetizing field and $(4\pi/3)M$ is the usual Lorentz field. Although small, this contribution is important for determining the sign of the hyperfine field. This can be determined by observing the shift in resonance frequency when an external field is applied.

Since in a ferromagnetic material the electronic spins are ordered it is seen from equation (2.6) that the effective hyperfine field has a well defined direction, that is, it is proportional to the average value of the electronic spin. This ordering of the spins then, permits one to perform the N.M.R. experiment without the use of externally applied fields as is necessary in conventional N.M.R.

The magnetization, $M$, is directly proportional to the
average value of the electronic spins. It follows then that the hyperfine field is proportional to the magnetization, if the mechanisms responsible for $H_n$ are not temperature dependent. Thus the measurement of $H_n$ as a function of the temperature can give a direct measurement of the variation of the magnetization with temperature.

Hyperfine fields have also been observed at the nuclei of nonmagnetic ions in dilute solution in ferromagnetic metals and at the nuclei of nonmagnetic ions in ferromagnetic compounds such as Fe$_2$B, Fe$_3$Al and Fe$_3$Si. Campbell (1969) has analyzed the experimental data for hyperfine fields on a wide range of impurities in ferromagnetic metals using a model based on that of Daniel and Friedel (1963). In this model the d moment, $\mu_h$, of the host metal is assumed to act as an effective field on a free electron-like conduction band, giving a uniform conduction electron polarization proportional to $\mu_h$ except at the impurity site. There, local square well potentials $V_\uparrow$ and $V_\downarrow$ act on the spin $\uparrow$ and spin $\downarrow$ conduction electrons respectively. These local potentials produce phase shifts in the conduction electron wavefunctions. The phase shifts, which are spin dependent, and the resulting conduction electron polarization depends on the strength of the impurity potential. For s-p impurities in iron the model predicts a conduction electron polarization at the nonmagnetic impurity site which depends on the impurity charge, $Z_i$, to be screened. On the basis of this model Campbell predicts that for impurities with $Z_i$ less than about 2, the conduction electron polarization
results in a negative hyperfine field. For impurities with $Z_i$ greater than 2 a positive hyperfine field is predicted. This behaviour has been observed for the s-p series Ag to Xe as impurities in Fe (Campbell, 1969, fig 5).

Studies by Budnick and Skalski (1967) of the Al and Si hyperfine fields in Fe$_3$Al and Fe$_3$Si suggest that these transferred hyperfine fields are due primarily to the Fermi contact interaction of the s electrons at the nonmagnetic ion site, which have been polarized by the local moments of the magnetic ions. The problem of transferred hyperfine fields in magnetic compounds has been treated in some detail by Watson and Freeman (1967). Although they deal with non-metallic systems they suggest that the results of their investigations may be applicable to metallic systems. They find that unpairing of the closed s shells in the nonmagnetic ion site; e.g. F$^-$ in MnF$_2$, occurs when the 3-d wavefunctions of the magnetic ion and the s wavefunctions of the nonmagnetic ion are orthogonalized. Any covalent admixture of the 3-d wavefunctions with the nonmagnetic ion's wavefunctions conveys a spin density onto the nonmagnetic ion site which is parallel to that of the local moment. The spin density thus conveyed can lead to some unpairing of the closed shell s electrons via the exchange interaction. Any unpairing of the closed shell s electrons will result in a hyperfine field at the nucleus of the nonmagnetic ion. However, the resultant fields due to these effects are difficult to estimate.
(iv) **R.F. Enhancement in Ferromagnets**

In ferromagnetic N.M.R. the nuclear resonance is driven indirectly via the nuclear-electronic hyperfine coupling. This indirect coupling produces an enhanced r.f. field, $H_{n1}$, at the nuclear site which is much larger than the applied r.f. field, $H_1$. One can show that the enhancement factor, $H_{n1}/H_1$, is directly proportional to the angle through which $\langle S \rangle$ is turned by the applied r.f. field. Since the hyperfine field is directly proportional to $\langle S \rangle$, the enhancement is strongly influenced by the detailed properties of the exchange coupled electron spin system. In part (i) of this chapter it was pointed out that the ordering of the spins gives rise to a spontaneous magnetization. In a bulk sample it is found that there are domains of uniform magnetization which arrange themselves so as to minimize the total free energy of the bulk sample. Between domains of opposite magnetization there exist domain walls through which the orientation of the electronic magnetic moments changes progressively through 180 degrees. In multi-domain particles there are two sources of enhancement, coherent domain rotation and domain wall movement.

We first consider the enhancement due to coherent domain rotation. The rotation due to an applied r.f. field, $H_1$, is limited by an increase in the anisotropy energy. This energy acts in such a way that the magnetization tends to be directed along certain definite crystallographic directions, which accordingly are called directions of easy magnetization. This effect
may be thought of as arising from an anisotropy field, $H_a$, which lies in the direction of easy magnetization.

Consider a single domain which has an electronic magnetization, $M$, aligned along the anisotropy field. Application of a weak transverse field, $H_\perp$, produces an angular displacement of the hyperfine field given by

$$\Theta = \tan^{-1}\left(\frac{H_\perp}{H_a}\right) \approx \frac{H_\perp}{H_a} \quad H_\perp \ll H_a$$

(2.13)

The resulting transverse hyperfine field, $H_{nl}$, and the total transverse driving field, $H_{tl}$, are given by

$$H_{nl} = H_n \sin \Theta \approx H_n \frac{H_\perp}{H_a}$$

(2.14)

and

$$H_{tl} = H_\perp + H_{nl} = H_\perp (1 + \eta)$$

(2.15)

Typically for a spherical sample of nickel

$$H_a \approx 135 \text{ Oe.}$$

$$H_n \approx 75 \text{ koe.}$$

$$\eta \approx 600$$

The enhancement of the applied r.f. field due to domain wall motion will now be considered. Following Kittel and Galt (1956), the equation of motion for a domain wall subject to an r.f. field, $H_\perp$, is for small displacements, $x$, (i.e. displacements small compared to the wall thickness), written as follows

$$\alpha x + \beta \frac{dx}{dt} + m_w \frac{d^2x}{dt^2} = 2M_s H_\perp$$

(2.16)
where $\alpha$ is a constant describing the stiffness of the wall, $\beta$ is a damping constant and $m_w$ is an effective mass of the domain wall. $M_s$ is the saturation magnetization.

For a periodic driving field of frequency $\omega_m$, the maximum displacement is given by

$$x_0 = \frac{2M_s H_l}{\delta m_w \left[ (\Delta^2 - \omega_m^2)^2 + \left( \frac{\beta}{m_w} \right)^2 \omega_m^2 \right]^{1/2}}$$

(2.17)

where $\Delta = (\frac{\omega_m}{m_w})^{1/2}$ is the natural frequency of the domain wall. As a result of the displacement $x$, the electronic spins will rotate through an angle $\Psi$, and hence the resulting transverse hyperfine field at the nuclear site will, for small $\Psi$, be given by

$$H_{n,\perp} \approx \Psi H_{\perp} \approx x \left( \frac{d\Psi}{dx} \right) H_{\perp}$$

(2.18)

for a 180 degree wall

$$\frac{d\Psi}{dx} = \frac{1}{\delta} \text{sech} \left( \frac{x}{\delta} \right)$$

From equations (2.17) and (2.18) the enhancement factor is found to be

$$\eta = \frac{H_{n,\perp}}{H_{\perp}} = \frac{M_s H_{n,\perp} \text{sech} \left( \frac{x}{\delta} \right)}{\delta m_w \left[ (\Delta^2 - \omega_m^2)^2 + \left( \frac{\beta}{m_w} \right)^2 \omega_m^2 \right]^{1/2}}$$

(2.19)

Unfortunately this expression does not lend itself to a simple estimate of the enhancement factor as the required parameters are not always readily available.

For the purpose of obtaining a simple estimate of the domain enhancement factor it is useful to consider the case of a spherical particle of diameter, $d$, split by a single domain
wall in which the magnetization turns through 180 degrees in a distance \( \delta \) as indicated in the following diagram.

![Diagram showing domain wall](image)

When no external field is applied, the size of the two oppositely magnetized domains are equal, and the average magnetization of the particle is zero. When an external field \( H_1 \) is applied parallel to the bulk magnetization \( M_s \), the wall shifts until the sum of the interaction and demagnetizing energies is a minimum (see e.g. Morrish, 1965). The interaction energy is given by \(-H_1 \Delta M\), and the demagnetizing energy is approximately given by \( \frac{1}{4} N (\Delta M)^2 \), where \( N \) is the demagnetizing factor. For a sphere \( N = 4\pi / 3 \). The minimum of the sum \(-H_1 \Delta M + \frac{1}{4} N (\Delta M)^2\) occurs for \( M = H_1 / N = (3/4\pi) H_1 \). Since,

\[
M = \frac{V_2 - V_1}{\text{total volume}} \times M_s = 3M \frac{x}{sd}
\]

therefore

\[
\frac{x}{d} = \frac{H_1}{4\pi M_s}
\]

As the domain wall shifts by a distance \( x \), the magnetization rotates by an angle

\[
\psi = \frac{\pi x}{\delta}
\]

and therefore the component of the internal field which is perpendicular to the equilibrium magnetization is
\[ H_{nl} = H_n \psi = \frac{H_n dH_1}{4M_s \delta} = \eta H_1 \]

Thus the enhancement factor is
\[ \eta = \frac{H_{nl}}{H_1} = \frac{H_n d}{4M_s \delta} \]  

(2.20)

This domain wall enhancement is in general one or two orders of magnitude larger than the domain enhancement. In iron this domain wall enhancement is about 2000. In pulsed N.M.R. experiments the enhancement has two effects. First, the magnitude of the required driving field is reduced by the factor \( \eta \). Secondly, after removal of the excitation the precessing nuclear magnetization induces through the hyperfine interaction a coherent precession of the electronic magnetization. This has the effect of enhancing the signal by a factor \( \eta \).

(v) **Nuclear Magnetic Relaxation in Ferromagnets**

Studies of the longitudinal spin-lattice relaxation, e.g. Weger (1962), have an exponential decay for long times, while the short time decay is very rapid and non-exponential. The relaxation time increases with power level to some limiting value. This value is generally assumed to be characteristic of nuclei in domains. It was observed by Weger that in Fe, Ni and Co, the limiting values of \( T_1 \) were inversely proportional to temperature. This suggests that the relaxation was due to conduction electron mechanisms (Korringa, 1950). Moriya (1964) has suggested that for the domain nuclei the relaxation rate is determined primarily by the 3-d electrons owing to the
interaction of their orbital currents with the nuclear spin dipoles. This mechanism gives rise to a $T_1 T_2$ constant relationship.

The short time and low power rapid relaxation must be attributed to domain wall mechanisms, since at low power levels one detects the effect of those nuclei situated mainly in domain walls. It has been suggested by Weger (1962) that the dominant relaxation mechanism is that due to the thermal fluctuations of the domain walls. To estimate the order of magnitude of this relaxation consider a small spherical particle of diameter $d$, consisting of two equal and opposite domains with a 180 degree domain wall between them. Imagine also that the only low lying wall excitation is a uniform displacement. If the wall shifts by a distance $x$, a net magnetization $M=3M_s x/d$ is created. The demagnetizing energy resulting from this magnetization is

$$E = \frac{N}{2} M^2 \left( \frac{\pi d^3}{6} \right)$$  (2.21)\

where $N$ is a demagnetizing factor of order $4\pi/3$. Applying the equipartition theorem an average energy $\frac{1}{2}kT$ is ascribed for each degree of freedom, thus $E = \frac{1}{2}kT$ since here only one degree of freedom is considered. The mean squared displacement is thus given by

$$\langle x^2 \rangle = \frac{kT}{2\pi^2 M_s^2 d}$$  (2.22)\

The component of the internal field perpendicular to the static
field is \( H_{n1} = H_n \mathcal{M} \delta /\delta \), where \( \delta \) is the domain wall thickness.

Thus

\[
H_{n1}^2 = \frac{H_n^2 kT}{2 M_S^2 d \delta^2}
\]

(2.23)

Assuming a Lorentzian correlation spectrum

\[
P(\omega) = \frac{2 \gamma_c}{\pi(1 + \omega^2 \gamma_c^2)}
\]

where \( \gamma_c \) is the correlation time, the relaxation rate caused by these fluctuations is, according to Bloembergen et al. (1948) given by

\[
\frac{1}{T_1} = \frac{(\mathcal{M} H_n)^2}{\pi} \left( \frac{d}{\delta} \right)^2 \frac{kT}{M_S} \frac{\gamma_c}{1 + \omega^2 \gamma_c^2}
\]

(2.24)

Weger found that this mechanism gave results in reasonable accord with the observed values of \( T_1 \) for Fe, Ni and Co. The relaxation time at room temperature is typically a few hundred microseconds.

Winter (1961) has considered this model in detail for the case of a uniaxial anisotropy and found that for a 180 degree wall the relaxation rate at a temperature \( T \) is given by

\[
\frac{1}{T_1} = \text{sech}^2 \left( \frac{\mathcal{X}}{\delta} \right) \frac{\omega_c kT}{16 J S} \left( \frac{K^1}{J} \right) \tan^{-1} \left( \frac{\omega_c \Gamma}{\Delta^2 - \omega_c^2} \right)
\]

(2.25)

where \( J \) and \( K \) are the exchange and crystalline anisotropy constants respectively. \( \Gamma \) is a damping constant associated with domain wall motion.

Spin-spin relaxation time studies in the iron group metals have shown that there is an unusually strong coupling between
the nuclear spins (see e.g. Weger et al., 1961). It has been pointed out by Suhl (1958) and Nakamura (1958) that such a strong coupling arises because the nuclei through their hyperfine interaction will virtually excite electronic spin waves. These spin waves may be re-absorbed by other nuclei resulting in a static coupling between the nuclear spins. Stearns (1969) has estimated that in iron this effect gives a contribution of 2.5 sec$^{-1}$ to the rate of transverse relaxation, 1/T$_2$. The spin-lattice interaction also contributes to T$_2$ (see equation (1.17)) and can produce non-exponential relaxation with qualitatively the same character as T$_1$. 
CHAPTER III

Apparatus and Experimental Procedure

Apparatus

Essentially the spectrometer was a broadband unit capable of delivering r.f. pulses over the frequency range 10-200 MHz. The receiving system was characterized by good recovery characteristics and high sensitivity, features which are necessary for the observation of the weak signals that arise from the broad lines encountered in ferromagnetic materials. It could be used in either a swept or fixed frequency mode. The swept frequency mode was used in the search for zero field resonances. Measurements of relaxation times and enhancement factors were performed at fixed frequencies. A block diagram of the spectrometer is shown in figure 3-1.

(i) Pulsed Oscillators

Two pulsed oscillators were employed; one was used primarily for applications requiring a relatively high power level, about 300 volts peak to peak into 100 ohms, and the other was a low power pulsed oscillator which could be operated with about 10 volts across its tank circuit. Frequency could be swept in both oscillators by means of an external motor drive. The high power pulsed oscillator was an Arenberg model PG-650-c with the modifications for extra fast, .2 microseconds, rise and fall times. The oscillator consists of a 6907 tube which is cross-connected to form a push-pull Colpitts oscil-
Fig. 3-1 Block Diagram of Pulsed Spectrometer
lator. The plate current in the tube is normally cut-off and in order to cause oscillations a large positive pulse is applied to the screen and grid of the tube. This pulse is supplied by a pulse amplification and shaping network that is driven by an external 10 volt gate. A frequency range of 2 MHz to 130 MHz is obtained through the use of a set of interchangeable tank coils. The r.f. output is taken from the secondary windings of these coils. A more detailed description of this oscillator can be found elsewhere, Koster(1968).

As the applied r.f. field is enhanced, a relatively low r.f. field is required when searching for zero field resonances. The Arenberg oscillator did not function well at low power levels. For this reason the low power pulsed oscillator was constructed. A schematic diagram of this oscillator is shown in figure 3-2. The oscillator consists of a 6939 tube which is cross-connected to form a push-pull Colpitts oscillator. Although the anode voltage is continuously supplied, the plate current is normally cut off because the screen and grid voltages are negatively biased. In order to cause oscillations a large positive pulse of about 150 volts is applied to the screen and grid leak resistors. This pulse was produced by the pulse forming circuit shown in figure 3-3. This circuit requires about 10 volts input for full output. The frequency of the pulsed oscillator could be changed over the range 15 - 220 MHz with the use of interchangeable tank coils.
Fig. 3-2 Low Power Pulsed Oscillator
Fig. 3-3 Pulse Forming Circuit
(ii) **Dewar System**

The cryostat consisted of an exposed tip helium dewar and a suitable nitrogen dewar constructed by J. Lees, glass blower. The tip of the helium dewar was left unsilvered to allow penetration of the r.f. field. In the experiments the dewar tip holding the sample was placed inside the sample coil. Cooling of the exposed tip was achieved by allowing liquid nitrogen to drip over it.

(iii) **Sample Coil**

The search for zero field N.M.R. lines was made with the sample situated directly in the tank coil of the oscillator. The signal was taken out through the secondary of the tank coil. For fixed frequency work an external coil system was employed.

In the ideal receiving system all the noise originates as thermal noise in the sample coil. If this is the case then the signal-to-noise ratio depends on the coil parameters as follows

\[ \frac{S}{N} \propto KV^{\frac{1}{2}}Q^{\frac{1}{2}} \]

where \( K \) is the filling factor, \( V \) is the volume of the coil and \( Q \) is the quality factor of the coil.

For fast recovery of the receiver following the r.f. pulse it is necessary that the resulting transient in sample coil circuit be damped out quickly (i.e. in a time much less than the recovery time of the amplifiers in the receiving circuit). This condition requires the sample coil circuit to have a low \( Q \) during and just after the application of the pulse. Thus
for good signal to noise ratios and fast recovery of the receiver it is necessary to have a low Q circuit during and a high Q circuit after the pulse. The low Q-high Q requirements for the sample coil circuit are met by the circuit shown in figure 3-4. This circuit is passively switched between a high Q and a low Q configuration. When the r.f. pulse is applied the diodes conduct heavily and the diode gate behaves like a short circuit. The tuned circuit is then effectively shunted by the 50 ohm resistor. This effects a low Q circuit and provides proper matching to the pulsed oscillator. When the transient following the pulse has decayed to less than about 0.5 volts, the diodes are no longer in the conducting state and the gate behaves like an open circuit. This effects a relatively high Q circuit which is used to observe the nuclear signal. The nuclear signal was tapped from the tuned circuit through a 12 pf capacitor. This value was arrived at by a trial and error method which was used to maximize the signal to noise ratio.

The entire coil assembly was mounted inside a mini-box for shielding, a hole being provided through which the tip of the helium dewar penetrated.

(iv) The Receiving System

The receiving system varied according to the particular application. For work at fixed frequencies the system consisted of a narrow-banded preamplifier followed by a wideband amplifier and detector. For studies at frequencies less than 40 MHz an Arenberg model W-600D wideband amplifier was used.
Fig. 3-4 Sample Coil Circuit
A custom built amplifier was used for frequencies in the range 40 MHz to 110 MHz.

The preamplifier served to supply enough gain to override the noise of the following wideband amplifier and to narrow the bandwidth of the receiver, thus improving the attainable signal to noise ratio. The circuit shown in figure 3-5, consists of two pentode connected 7788 tubes in a cascaded amplifier configuration followed by a 6CW4 cathode follower output stage. The bandpass characteristics of each stage could be changed individually to obtain the desired overall bandpass characteristics. The maximum bandwidth employed with the preamplifier was about 6 MHz. The preamplifier has a gain of about 30 db, and has low-noise and fast recovery characteristics. It proved to be useful over the frequency range 10 MHz to 100 MHz.

The custom built amplifier is a low noise figure (6 db), fast recovery unit which was constructed commercially to our specifications. It has a frequency response which is flat to within 1.0 db from 40 MHz to 110 MHz and a gain which is variable between 60 db and 80 db. The recovery time is defined as the time elapsed before the amplifier noise is visible after the amplifier has been subjected to an overload. With the amplifier in the r.f. output mode the recovery time was about 2 microseconds, while in the detected output mode it was about 4 microseconds. In practice the influence of the recovery characteristics of the amplifier can be minimized by observing the echo, which can be made to appear well after
Fig. 3-5 Preamplifier
the receiver has recovered from the overload. The circuit diagrams of the wideband amplifier are shown in figures 3-6 and 3-7.

The fixed frequency receiving systems just described allowed a 2 microvolt peak-to-peak input signal to be detected with a one-to-one signal to noise ratio.

In the frequency swept mode of operation wide-band receiving systems were employed. In the range 10 MHz to 40 MHz the receiver consisted on the previously described preamplifier followed by the Arenberg wideband amplifier. The preamplifier was set to have a bandpass of about 6 MHz and its center frequency altered as the spectrometer was swept through the 10 MHz to 40 MHz range. For sweeping over the range 40 MHz to 110 MHz the afore mentioned custom built wide-band amplifier was employed as a preamplifier, and this was followed by a Hewlett-Packard model 461A wideband amplifier, the output of which was detected. These receivers allowed a 4 microvolt peak-to-peak input signal to be detected with a one to one signal to noise ratio.

For all the above cases the detected output was fed into a Princeton Applied Research Corp. model 160 boxcar integrator in order to improve the signal to noise ratio. The output of the boxcar integrator was monitored with a strip-chart recorder.

(v) **Timing Apparatus**

A suitable combination of Tektronix pulse and waveform
Fig. 3-6  Cascode Input stage and first Gain Controlled stage
Fig. 3-7  Second gain Controlled, Output and Detector Stages
generators was used to supply the sequence of pulses used to
gate the pulsed oscillators and the boxcar integrator. For
the $T_1$ measurements a $180^\circ-90^\circ-180^\circ$ pulse sequence was used,
otherwise a $90^\circ-180^\circ$ pulse sequence was used. In both cases
the overall repetition rate was controlled by a free running
Tektronix type 162 waveform generator. For the $T_1$ measurements
this generator supplied a sawtooth voltage which triggered
two type 163 pulse generators. One supplied the $180^\circ$ pulse
and the other supplied a delayed pulse which triggered a pair
of 163 pulse generators used to supply the pulses for the
$90^\circ-180^\circ$ sequence. In practice the time between the first
and second pulses was swept linearly with time and the time
between the second and third kept fixed. The time between
the first and second pulses was recorded by a Hewlett-Packard
model 5245C electronic counter. For the non-$T_1$ measurements
the free running waveform generator supplied a gate which was
used to trigger another 162 waveform generator which in turn
triggered the two type 163 pulse generators used to provide
the $90^\circ-180^\circ$ sequence. More details about this system can
be found elsewhere (Koster, 1968).

Experimental Technique

(i) Search for Zero Field N.M.R. Lines

The search for zero field N.M.R. lines was made using
the variable frequency pulsed N.M.R. spectrometer which has
been described in the first part of this chapter. The specimen,
situated in the transmitter coil, was cooled in a bath of liquid helium and the spectrometer swept through its entire range. On observing a spin echo, the resonance frequency could be determined by beating the N.M.R. signal with the signal from an r.f. signal generator the operating frequency of which could by accurately monitored. In cases where it was not feasible to beat directly with the N.M.R. signal it was assumed that the signal frequency was the same as the operating frequency of the pulsed spectrometer. Dean and Urwin (1970) have shown that this is a reasonable assumption under the following conditions, if the maximum value of $H_1$ is $\omega/\gamma$ then the shape function characterizing the resonance line, $S(\omega + \omega')$, should not change significantly in the interval $-\omega < \omega' < \omega$.

For measurements at higher temperatures the sample was immersed in baths of liquid nitrogen, liquid methane, or cooled by a stream of cold nitrogen gas. In the latter case the sample temperature was monitored with a calibrated thermistor thermometer.

(ii) Measurement of the Enhancement Factor

Measurement of the enhancement factor $\eta$ was accomplished by observing the amplitude of the free induction decay or spin echo as a function of the applied r.f. field. In a simplified picture the condition for a $\pi/2$ pulse is as
(iii) Measurement of Relaxation Times

(a) Longitudinal Relaxation Time

The longitudinal spin-lattice relaxation time, $T_L$, was determined by changing the z component of the nuclear magnetization, $M_z$, from its equilibrium value, $M_{z0}$, to say, $M_{z1}$, by applying an r.f. pulse at the resonant frequency and measuring $M_z$ at a later time $t$. This was accomplished by monitoring the
amplitude of the echo following a two pulse sequence that was applied at a time \( t \) after the initial saturating pulse as indicated in the following diagram.

The components of the magnetization in the \( x,y \) plane following the two pulse sequence induce a voltage in the pick up coil which is proportional to the precessing magnetization in the \( x,y \) plane. The amplitude of the echo is therefore directly proportional to the value of \( M_z \) just before the two pulse sequence is applied.

For an exponential relaxation the echo amplitude is proportional to

\[
M_z(t) = M_{z0} - (M_{z0} - M_{z1})e^{-t/T_1}
\]  

For the case of non-exponential relaxation often encountered in ferromagnets an instantaneous relaxation rate, \( 1/T_1 \), can be defined according to the following definition

\[
\frac{1}{T_1} = \frac{\partial M_z(t)}{\partial t} / (M_z(t) - M_z(\infty))
\]
(b) Transverse Relaxation Time

The transverse relaxation time, $T_2$, was determined by monitoring the amplitude of the spin echo as a function of the spacing between the $90^\circ$ and $180^\circ$ pulses. If the spacing between these pulses is $t$ then the echo amplitude varies, for exponential relaxation, according to

$$M(t) = M(0)e^{-2t/T_2}$$

(3.6)

For a non-exponential decay one can define an instantaneous relaxation rate by the equation

$$\frac{1}{T_2} = -\frac{\partial M(t)}{\partial t}/(2M(t))$$

(3.7)
CHAPTER IV

NICKEL

It has been pointed out by Stearns (1967) and by Stearns and Overhauser (1968), that a study of the variation with r.f. field strength and pulse length of the free induction decay (FID) signal can yield information about the structure and motion of domain walls. Stearns studied the FID signal in iron; we have performed similar experiments in nickel. The specimen studied was an unannealed powder sample of nickel metal of purity 99.995%. The powder used in the experiments was passed through a 40 micron sieve. This powder was immersed in paraffin wax to suppress magnetostrictively excited acoustic resonances (Rubenstein and Stauss, 1968).

(a) Experimental Results

The experimental data was obtained by setting the spectrometer to the resonant frequency, adjusting the pulse length to a given value, $\tau$, and then monitoring the FID amplitude as a function of the r.f. field strength using a boxcar integrator. The experiments were performed at room temperature since, as Streever and Bennett (1961) have shown, the N.M.R. line broadens considerably at lower temperatures.

In figure 4-1 the variation of the FID amplitude with r.f. field strength is shown.
Fig. 4-1  FID Amplitude versus R.F. Field Strength
The variation of the FID amplitude with transmitter frequency for a fixed field strength and pulse length was also studied. A typical measurement is shown in figure 4-2.

(b) **Discussion**

For an r.f. field $H_1$ parallel to the plane of the domain wall and a constant enhancement factor $\eta$, the FID amplitude is given by

$$S = C\eta \sin(\gamma \eta H_1^+)$$  \hspace{1cm} (4.1)

where $\gamma$ is the nuclear gyromagnetic ratio and $C$ is a calibration constant for the detection apparatus.

In a sample of many particles the orientation of $H_1$ with the plane of the domain wall (defined by an angle $\phi$) is random, so that one must average over all orientations. For a domain wall which makes an angle $\phi$ with $H_1$, the effective component of $H_1$ is $H_1 \cos(\phi)$. The motion of the domain wall through a distance $\delta x$ at a position $x$, defined in domain wall width units from the central plane of the wall, corresponds to a rotation of electronic spins through an angle $x \alpha / dx$. The variation $\alpha / dx$ is proportional to $(\cosh(x))^{-1}$. Thus the enhancement factor as a function of $x$ and angle $\phi$ is given by

$$(x,\phi) = \eta_0 [\cosh(x)]^{-1} \cos(\phi)$$  \hspace{1cm} (4.2)

If we now take into account the distribution in angles and the variation of $\eta$ with $x$, the expression for the FID amplitude becomes

$$S = C \int_0^\infty \int_0^{\pi} 4\pi \eta \sin(\gamma \eta H_1^+) \sin(\phi) d\phi dx$$  \hspace{1cm} (4.3)
Fig. 4-2 Frequency Dependence of the FID Amplitude

\[ \nu_0 = 26.13 \text{ MHz} \]

\[ H_1 = 0.4 \text{ GAUSS} \]

\[ \tau = 3 \mu \text{S} \]
where $\eta$ is as defined in equation (4.2).

This expression is plotted in figure 4-3. It is evident that this does not describe the observed behaviour. It is clear then that representing the walls as rigidly oscillating with proper account taken of the $H_1$ angular variation and the enhancement factor distribution due to the spatial arrangement of the spins in the domain wall does not agree well at all with the observed FID behaviour.

Following Stearns it is now assumed that the domain walls vibrate like circular membranes of radius $a$, which are bound on their circumferences. The displacement of the wall at a point $r$ distant from the center is proportional to $[1 - (r/a)^2]$. The maximum displacement of a given wall, at the center, is denoted by $h$, and the probability of a nucleus being in a wall with this maximum displacement is $P(h)$. The greatest value of $h$ is $h_m$. If these parameters are averaged over the expression for the FID amplitude becomes

$$S = C \int_0^{h_m} \int_0^\infty \int_0^{2\pi} 4\pi^2 \eta \sin(\gamma H_1 \gamma) P(h) \sin(\phi) d\phi dx dh$$

(4.4)

where

$$\eta = \frac{h_m}{h} [1 - (r/a)^2] \cos(\phi) [\cosh(x)]^{-1}$$

This expression has been integrated by computer for various values of $\eta_0$. It is found that excellent fit with experiment for $\gamma = 1.0$ microsecond is obtained by taking $P(h)$ as constant and $\eta_0 = 4700 \pm 400$. Figure 4-1 shows the theoretical and experimental values for the FID amplitude. It is noted that for
Fig. 4-3 $H_1$ Dependence of the FID Amplitude: Rigid Plane Model
high values of $H_1$, the experimental points lie consistently above a theoretical curve fitted to experimental points for low $H_1$. This is almost certainly due to the contribution to the signal from nuclei in the domains. This contribution can be significant in nickel at high values of $H_1$, since the domain enhancement factor is about 300 at room temperature according to the measurements of Aubrun and Le Dang Khoi (1966).

Stearns estimated $\eta = 6700$ for iron. It is noted that there is reasonable agreement between the pulsed N.M.R. experiments and the rotary saturation experiments of Cowan and Anderson (1965). The pulsed N.M.R. measurements give $\frac{n_0(n_i)}{n_0(f_0)} \approx 0.7$, while the absorption maxima in the rotary saturation experiments correspond to $\frac{n_0(n_i)}{n_0(f_0)} \approx 0.8$. Of course, the latter experiments determine some average value of $\eta$, since the signal depends both on $\eta$ and the number of nuclei excited.

**Domain Wall Diameter**

The measured enhancement factor can be used to obtain an estimate of the maximum domain wall diameter. For a domain wall moving like a circular membrane pinned at its circumference the average enhancement factor is $\approx \eta/3$. By equation (2.20) we have

$$\frac{n_0}{3} = \frac{H_n d}{4M_s \delta}$$ (4.5)

For nickel $M_s$ is 485 oe., $H_n$ is about $75 \times 10^3$ oe., $\eta$ is 4700 and $\delta$ is about 260 Å (Lilley, 1950). The domain wall diameter if found from the above equation to be $\approx 1$ micron. This result
and the measured enhancement factor can be used to obtain an estimate of the relaxation time $T_1$ for domain wall nuclei.

**Estimate of $T_1$**

In chapter II section v the relaxation due to thermal fluctuations of the domain walls was considered. Here a similar procedure will be followed to obtain an expression for the relaxation time in terms of the enhancement factor. Consider a small sphere of diameter, $d$, consisting of two equal oppositely directed domains and a domain wall at the center. As a result of a thermal excitation of the domain wall a net magnetization, $M$, will be created. The demagnetizing energy resulting from this magnetization is $NM^2/2$. Here $V$ is the volume of the particle and $N$ is the demagnetizing factor. For a sphere $N$ is $4\pi/3$. By the theorem of equipartition of energy the average energy associated with this degree of freedom is $\frac{1}{2}kT$. Hence we have

$$\frac{kT}{2} = \frac{NM^2 4\pi d^3}{2 \cdot \frac{3}{8}}$$  \hspace{1cm} (4.6)

The magnetization $M$ can also be produced by an external field, $H = NM$, applied parallel to the domain wall. From equation (4.7) this field is given by

$$H = \left(\frac{8kT}{d^3}\right)^{\frac{1}{2}}$$  \hspace{1cm} (4.7)

The nuclei will see an enhanced field $H_x = \eta H$. If we assume that the fluctuations are associated with a Lorentzian
correlation spectrum

\[ P(\omega) = \frac{2\gamma c}{\eta(1 + \omega^2 \tau^2)} \]  

(4.8)

where \( \tau \) is the correlation time. The relaxation rate caused by the fluctuations is given by

\[ \frac{1}{T_1} = 4(\gamma H_x)^2 P(\omega) \]  

(4.9)

For nickel \( \gamma = 2300, \omega_o = 1.64 \times 10^8 \text{ sec}^{-1}, d = -1 \text{ micron}, \eta = 4700 \) and \( \gamma_\zeta = 4.3 \times 10^{-9} \text{ sec} \) (Bhagat and Chicklis, 1969). Substituting these values in equation yields \( T_1 = 70 \) microseconds at room temperature. This compares well with the value of 40 microseconds deduced by Reeves et al. (1970) from fast passage measurements on powdered nickel. In view of these results the measured enhancement factor can be said to be reasonable.

The variation of the FID amplitude with transmitter frequency given in figure 4-2 shows considerable asymmetry, i.e. \( S(-\delta \omega) = S(\delta \omega) \). Similar behaviour has been reported by Stearns (1967) for iron. The reason for this asymmetry is not understood. It is tempting to say that it is caused by a frequency dependent enhancement factor. Recalling equation (2.19), the enhancement factor is given by

\[ \eta = \frac{M_s H n \text{sech}(\frac{X}{\delta})}{\delta m_w [(\Delta - \omega_o)^2 + (\beta/m_w)^2 \omega_o^2]} \]  

(4.10)

It is seen that a frequency dependence can be expected if \( \omega_o \) is close to the domain wall resonance frequency \( \Delta \). However
this frequency is estimated by Winter (1961) to be of the order of 500 MHz for nickel. Since the nuclear resonance frequency in nickel is about 30 MHz one would not expect the asymmetry to arise from domain wall resonance effects.
CHAPTER V

Fe₂P

(a) Introduction

The physical properties of Fe₂P have been the subject of many investigations in recent years. There is considerable disagreement in the reported Curie points and magnetic moments obtained from bulk magnetization measurements. The Curie temperature of Fe₂P was reported to be 353 K by Le Chatelier and Wolodgine (1909), 306 K by Chiba (1960) and 266 K by Meyer and Cadeville (1961). Belavance et al. (1970) report a Curie point of 255 K. The value of the magnetic moment observed per iron atom varied from 0.85μₜₜ as reported by Chiba to 1.32μₜₜ as reported by Meyer and Cadeville. The latter corresponds to a saturation magnetization per unit volume of 708 Oe./cm³. Meyer and Cadeville have shown that non-stoichiometric Fe₂₋ₓP exhibits extreme magnetic hardness, this makes it difficult to determine the magnetic moment and may account for the discrepancies in the reported values of the magnetic moments per iron atom. In view of this the value of the magnetic moment per iron atom given by Meyer and Cadeville is accepted by most people as being the most reliable (e.g. Wappling et al., 1971) and will be used in this thesis.

The crystal structure of Fe₂P has been determined by Rundquist and Jellinek (1956). It is a hexagonal (C22) type, with space group P6/m, and a=5.865 Å and c=3.546 Å (Pearson,
1967). The unit cell arrangement is shown in figure 5-1. There are two crystallographically distinct iron sites, Fe(I) and Fe(II), and two distinct phosphorous sites, P(I) and P(II). Fe(I) is surrounded by an approximate tetrahedron of phosphorous atoms, whereas Fe(II) is near the base of a square pyramid of phosphorous atoms. The different sites and their nearest neighbour configurations are illustrated in figure 5-2.

Fe₂P has been the subject of Mossbauer experiments. The results of these experiments also exhibit disagreement. Mossbauer studies were performed by Duncan and Bailey (1967) and more recently by Sato et al. (1969) and Wuppling et al. (1971). Duncan and Bailey measured hyperfine fields of 110 koe. and 140 koe. at 90 K for the two iron sites whereas Sato et al. reported hyperfine fields of 117 koe. and 175 koe.. Wappling et al. report hyperfine fields of 109 koe. and 169 koe..

The motivation for the N.M.R. results is the measurement of the hyperfine fields in Fe and P atoms. Also we hope to clarify the magnetic structure. Two samples were employed for the N.M.R. experiments. One was obtained commercially and was chemically analyzed as Fe₂.₀₈P, the other was prepared as described below and analyzed as Fe₁.₉₆P.

Powders of 99.99% pure iron (325 mesh) and 99.9% pure red phosphorous (100 mesh) were weighed out in the desired proportions, mixed well in a mortar and enclosed in an evacuated silica glass tube. Since the boiling point of red phosphorous is 416 °C, rapid heating of the mixture above this
Fig. 5-1 Diagram of Fe₂P Crystal Structure
Fig. 5-2 Nearest Neighbour Configurations in Fe$_2$P
point could induce an explosion of the reaction tube due to the heat of the reaction and the vapor pressure of the phosphorous. Therefore, the mixture was fired in an electric furnace initially at 400 °C for 24 hours and then heated up to 1000 °C at the rate of 20 degrees per hour. The mixture was then heated for another 24 hours at 1000 °C. The resultant product could easily be reduced to a powder with a mortar and pestle. The powder was then annealed at 500 °C for 48 hours to remove strains induced by the cold working. The crystal structure of the samples were verified by X-ray powder analysis.

(b) Experimental Results

(i) Zero Field Spectra

The zero field resonances were sought employing the spectrometer described in chapter 3. Both samples were used and the same N.M.R. spectrum was obtained. Four resonances were observed and these are assigned to the four crystallographically distinct sites in Fe$_2$P. Representative traces are shown in figures 5-3 and 5-4.

The resonances occur at 20.5 MHz, 17.5 MHz, 77.7 MHz and 86.6 MHz at 1.5 K. The resonant frequencies were determined by beating the nuclear signal with a reference signal from a V.H.F. signal generator. The accuracy of this determination was limited by the finite width of the echo to ± 0.2 MHz. The lines at 17.5 MHz and 20.5 MHz are relatively weak and have a full width at half height of about 2 MHz and 1 MHz respectively. The high frequency lines are much stronger.
Fig. 5-3. Zero Field Frequency Dependence of the Spin-Echo Amplitude in Fe$_2$P at 1.5 K
Fig. 5-4  Zero Field Frequency Dependence of the Spin-Echo Amplitude in Fe$_2$P at 1.5 K
The relative integrated intensities of the 77.7 MHz and the 86.6 MHz lines are about 2 to 1.

(ii) Temperature and Field Dependence of the Resonant Frequency

The strongest resonance, the 77.7 MHz line, which (as will be discussed in part c of this chapter) is a $^{31}\text{P}$ resonance, was studied as a function of external field and as a function of temperature. Figure 5-5 shows the change in the resonance frequency as a function of the applied field.

The temperature dependence of the lower and stronger $^{31}\text{P}$ resonance frequency is summarized in the following table.

**TABLE I : Variation of $^{31}\text{P}$ N.M.R. frequency with temperature**

<table>
<thead>
<tr>
<th>T(K)</th>
<th>(MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>77.7 $\pm$ .2</td>
</tr>
<tr>
<td>77.7</td>
<td>72.5 &quot;</td>
</tr>
<tr>
<td>112 $\pm$ 2</td>
<td>67.5 &quot;</td>
</tr>
<tr>
<td>122 $\pm$ 2</td>
<td>64.8 &quot;</td>
</tr>
<tr>
<td>136 $\pm$ 2</td>
<td>62.7 &quot;</td>
</tr>
<tr>
<td>147 $\pm$ 2</td>
<td>60.0 &quot;</td>
</tr>
</tbody>
</table>
Fig. 5-5 Change in $^{31}$P Resonance Frequency with Applied Field at 1.5 K
(iii) **Enhancement Factors**

As was demonstrated in chapter 4, a study of the signal intensity as a function of the applied r.f. field strength can yield information about the distribution of enhancement factors within a domain wall. The FID decay time was too short to enable a study of its behaviour, and instead, the amplitude of the spin echo was determined as a function of the r.f. field strength. Results of the measurements for the P(II) and P(I) sites are given in figures 5-6 and 5-7 respectively.

(iv) **Nuclear Spin Relaxation in Fe$_2$P**

Longitudinal spin-lattice relaxation times, $T_1$, and transverse relaxation times, $T_2$, were determined for the P(I), P(II) and Fe(I) nuclei. For the P(II) nuclei the relaxation times were determined at 1.5 K, 4.2 K and 77 K. P(I) nuclear relaxation times were determined at 1.5 K and 4.2 K. Fe(I) relaxation times were determined only at 1.5 K due to poor signal to noise. Typical longitudinal relaxation curves for the P(I), P(II) and Fe(I) sites at 1.5 K and various power levels are given in figures 5-8, 5-9 and 5-10 respectively. These curves indicate that the relaxation is non-exponential and power dependent. An instantaneous relaxation rate can be defined as follows

$$\frac{1}{T_1} = \frac{\partial M_z(t)}{\partial t} \frac{1}{[M_z(t) - M_z(\infty)]}$$

(5.1)

where $M(t)$ is the amplitude of the echo at time $t$. The experimental results indicate that the initial relaxation rate at
Fig. 5-6 Spin-Echo Amplitude vs R.F. Field Strength: P(II) 1.5 K
Fig. 5-7. Spin-Echo Amplitude vs R.F. Field Strength: P(I) 1.5 K
Fig. 5-8. Longitudinal Relaxation of $^{31}\text{P}(I)$ in Fe$_2$P at 1.5 K
Fig. 5-9 Longitudinal Relaxation of $^{31}\text{P}(\text{II})$ in Fe$_2$P at 1.5 K
Fig. 5-10  Longitudinal Relaxation of $^{57}$Fe(I) in Fe$_2$P at 1.5 K
low power levels is most rapid, and that the relaxation rate decreases with time and power level.

Representative transverse relaxation curves for the P(I), P(II) and Fe(I) sites are presented in figures 5-11, 5-12 and 5-13 respectively. The transverse relaxation curves for the P(II) nuclei at 77 K (figure 5-12b) exhibit a distribution in times, $T_2$, and a power level dependence similar to that of the longitudinal relaxation curves. At 4.2 K (figure 5-12a) and at 1.5 K, the distribution and the power dependence of the $T_2$s are not very great. The P(I) relaxation curves exhibit some power dependence. The Fe(I) $T_2$ is much less than $T_1$, and the relaxation in exponential.

The results of the relaxation time measurements are summarized in the following table

<table>
<thead>
<tr>
<th>atom</th>
<th>T(K)</th>
<th>$T_1$(msec.)</th>
<th>$T_2$(msec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(I)</td>
<td>1.5</td>
<td>0.10 - 0.35</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>0.05 - 0.35</td>
<td>0.12</td>
</tr>
<tr>
<td>P(II)</td>
<td>1.5</td>
<td>0.60 - 8.50</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>0.40 - 6.40</td>
<td>0.20 - 0.35</td>
</tr>
<tr>
<td></td>
<td>77.7</td>
<td>0.04 - 0.40</td>
<td>0.06 - 0.36</td>
</tr>
<tr>
<td>Fe(I)</td>
<td>1.5</td>
<td>1.0 - 10</td>
<td>0.18</td>
</tr>
</tbody>
</table>
Fig. 5-11 Transverse Relaxation of $^{31}\text{P(I)}$ in $\text{Fe}_2\text{P}$ at 1.5 K
Fig. 5-12 Transverse Relaxation of $^{31}\text{P}$(II) in Fe$_2$P at 1.5 K and 77 K
Fig. 5-13 - Transverse Relaxation of $^{57}$Fe(I) in Fe$_2$P at 1.5 K
The relaxation times listed in table II have an uncertainty of about 10%. This arises because there was some uncertainty in the experimental data and hence in the relaxation times which were deduced from the slopes of the relaxation curves.

(c) Discussion of Experimental Results

(i) Zero Field Spectra

Four resonances are observed. Since there are four distinct sites one line will be assigned to each site. It was noted in chapter 2 section iii that the hyperfine field is proportional to the electronic magnetic moment. In Fe$_2$P the average magnetic moment per iron atom is 1.32$\mu_B$ while in pure Fe it is about 2.2$\mu_B$. Thus we expect the hyperfine field at the iron nuclei to be depressed relative to the pure iron value. The resonance frequency in pure iron is about 45 MHz, therefore the two low frequency lines in the Fe$_2$P spectrum are undoubtably Fe$^{57}$ resonances. These correspond to hyperfine fields of 123 + 2 koe. and 148 + 2 koe.. These results are in fairly good agreement with those of Bailey and Duncan (1967).

The two high frequency lines are assigned to the phosphorous sites. Since the unit cell contains one P(I) site and two P(II) sites, consideration of the relative intensities of the two lines leads us to assign the 77.7 MHz line to the P(II) site. The deduced hyperfine fields for the two sites
are \(45.0 \pm 0.1\) koe. and \(50.2 \pm 0.1\) koe. These results are summarized in the following table.

TABLE III: N.M.R. data for \(\text{Fe}_2\text{P}\) at helium temperatures

<table>
<thead>
<tr>
<th>(\nu_0) (MHz)</th>
<th>(\Delta\nu) (MHz)</th>
<th>Nucleus</th>
<th>Site</th>
<th>(H_n) (Koe.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.0 (\pm 0.2)</td>
<td>2</td>
<td>(^{57}\text{Fe})</td>
<td>Fe(II)</td>
<td>123 (\pm 2)</td>
</tr>
<tr>
<td>20.5 (\pm 0.2)</td>
<td>1</td>
<td>(^{57}\text{Fe})</td>
<td>Fe(I)</td>
<td>148 (\pm 2)</td>
</tr>
<tr>
<td>77.5 (\pm 0.2)</td>
<td>0.6</td>
<td>(^{31}\text{P})</td>
<td>P(II)</td>
<td>45.0 (\pm 0.1)</td>
</tr>
<tr>
<td>86.6 (\pm 0.2)</td>
<td>1.2</td>
<td>(^{31}\text{P})</td>
<td>P(I)</td>
<td>50.2 (\pm 0.1)</td>
</tr>
</tbody>
</table>

The magnetic structure of \(\text{Fe}_2\text{P}\) can be interpreted by assuming that the hyperfine fields observed at the different sites are directly proportional to the magnetic moment at those sites. The observed saturation moment of \(1.32\mu_s\) per iron atom can then be apportioned between the two iron sites to give \(1.21\mu_s\) and \(1.44\mu_s\) for the moments associated with the Fe(II) and Fe(I) sites respectively. From the bulk magnetic measurements of Meyer and Cadeville (1962) it is known that the direction of the magnetization and hence the direction of the atomic moments is parallel to the hexagonal axis.

The validity of the preceding method of apportioning the magnetic moments is illustrated by the work of Shirane
et al. (1962) with Fe₄N. The magnetic moments obtained by apportioning the average magnetic moment were found to be in excellent agreement with the moments obtained by neutron diffraction. The study of a number of Laves phase compounds of the formula MFe₂ by Wallace (1964) also shows a good correlation between the magnetic moment and the hyperfine field. An average value of $H_n/\mu = 140$ koe./µₙ was found. This is in agreement with basic theoretical considerations which predict that the hyperfine field is proportional to the magnetic moment.

The observed iron hyperfine fields can be interpreted by assuming that the bonding in Fe₂P involves donation of phosphorous valence electrons to the iron d bands thus reducing the average moment from that observed in pure iron. While this is contrary to the direction expected from electronegativity considerations, it does provide a reasonable explanation of the reduced moments observed in the iron phosphides.

Fischer and Meyer (1967) have shown that for the iron series phosphides Fe₃P, Fe₂P and FeP, the average magnetic moment per iron atom varies according to the relation

$$M = M_0 - \frac{cq}{1 - c}$$

(5.2)

where c is the concentration of P, and q is the number of electrons donated by each phosphorous ion. They find that for the iron phosphides q=2.6 for $M_0 = 2.7$ (which is the value observed for iron in strongly diluted alloys). From these
values the expected moments can now be estimated.

The phosphorous atoms each have nine iron nearest neighbours, hence each phosphorous atom will donate 2.6/9 electrons to each of its iron nearest neighbours. Thus for Fe(I) which has four phosphorous nearest neighbours the moment will be given by

\[ \mu_{\text{Fe(I)}} = 2.7 - 4 \times 2.6/9 = 1.55 \mu_\beta \]  

(5.3)

For Fe(II) which has five phosphorous nearest neighbours one expects

\[ \mu_{\text{Fe(II)}} = 2.7 - 5 \times 2.6/9 = 1.26 \mu_\beta \]  

(5.4)

The ratio of these moments is 1.23 which compares well with 1.20, the ratio of the moments as deduced from the hyperfine fields.

If it is assumed that the phosphorous hyperfine fields are proportional to the sum of the magnetic moments on the nearest neighbour Fe sites, then one finds from the model that

\[ H_n[P(I)] \propto \sum_{nn} \mu_{\text{Fe}}^{nn} = 13.08 \]  

(5.5)

\[ H_n[P(II)] \propto \sum_{nn} \mu_{\text{Fe}}^{nn} = 12.21 \]  

(5.6)
The ratio predicted is 1.07 while the observed value is 1.11. This good agreement may only be fortuitous as the assumption that the hyperfine fields are proportional to the sum of the iron moments is a rather restrictive one. It is most likely valid if there is only one dominant mechanism responsible for the transferred hyperfine field. In Fe$_2$P both conduction electron polarization and covalency effects may be important (c.f. chapter 2 section iii). However the result is consistent with the assumed model.

(ii) Temperature and Field Dependence of the P(II) Resonance Frequency

The variation with temperature of the frequency of the lower and more intense $^{31}$P resonance frequency was studied and the results shown in table II. The data were analyzed by computer using a least square fit technique. It was found that the data fit very well a relation

$$\nu(T) = \nu(0) [1 - AT^2]$$  \hspace{1cm} (5.7)

The analysis shows a value of $A=(1.05 \pm .03) \times 10^{-5} \text{K}^{-2}$. Here the quoted is the standard deviation of the mean. The fit is illustrated in figure 5-14a where $[\nu(0) - \nu(T)]/\nu(0)$ is plotted against $T^2$.

However, it is also possible to describe the temperature dependence by a relationship

$$\nu(T) = \nu(0) [1 - aT^{3/2} - bT^{5/2}]$$  \hspace{1cm} (5.8)
Fig. 5-14 Temperature Dependence of the $^{31}$P(II) N.M.R. Frequency

a) Fractional change in frequency vs $T^2$

b) Fractional change in frequency $\times T^{-3/2}$ vs $T$
The fit in this case is much poorer, the values of the constants being: \( a = (6.6 \pm 1.1) \times 10^{-5} K^{-3/2} \), \( b = (4.1 \pm 0.8) \times 10^{-7} K^{-5/2} \).

Obviously fits of varying degrees of accuracy could be made with any admixture of equations (5.7) and (5.8). Thus, although our present results favor a \( T^2 \) dependence, implying single-particle excitations, it is difficult to ascertain the contribution of spin-wave excitations. This problem has been discussed in chapter 2 section ii of this thesis.

In previous work (Weisman et al., 1969) on Fe\(_2\)B it has been assumed that the frequency of the non-magnetic site (B) is proportional to the magnetization. This assumption is confirmed by our present results on the temperature variation of the \( ^{31}\!P \) N.M.R. frequency which favor a \( T^2 \) dependence, which we note, is also the temperature dependence of the bulk magnetization according to the data of Meyer and Cadeville.

The field dependence of the change in the resonance frequency shown in figure 5-5 indicates that the applied field is initially shielded to some extent. The initial shielding effect can arise from the random distribution of the nuclear hyperfine field directions with respect to the applied field. For domain nuclei the applied field is initially compensated for by the demagnetizing fields that arise as the domain walls are swept out. This may also have a shielding effect on the domain wall nuclei. In magnetically hard materials domain
wall motion and domain rotations are expected to occur almost simultaneously. As the applied field is increased the nuclear hyperfine fields tend to line up along the applied field. The result is that at high fields, in our case above 6 koe., the frequency changes almost linearly with applied field. The slope of the curve in the high field region is expected to be \( \gamma/2n \), where \( \gamma \) is the nuclear gyromagnetic ratio. This is observed to be the case as indicated by the dashed line in figure 5-5.

The frequency shift with applied field is positive, hence, the hyperfine field is positive. This is not surprising since \( p^3 \) elements dissolved in iron are expected to exhibit positive hyperfine fields (c.f. chapter 2 section iii).

(iii) Enhancement Factors

The spin-echo versus r.f. field strength curves presented in figures 5-6 and 5-7 are qualitatively similar to the nickel FID results (figure 4-1). This motivates an analysis based on the model presented in chapter 4. To apply this model the term \( \sin(H_1 t) \) in equation (4.4) must be replaced by an expression which gives the amplitude of the spin echo as a function of the pulse lengths \( t_1, t_2 \) employed in the two pulse sequence. According to Bloom (1955)

\[
E(t_1, t_2) = \sin(\omega_1 t_1)\sin^2\left(\frac{\gamma \omega_1 t_2}{2}\right)
\]

\( \omega_1 = \gamma n_{11} \)
With this modification equation (4.4 becomes

\[ S = C \int_{0}^{h_0} \int_{0}^{t_2} \int_{0}^{t_1} \eta E(t_1, t_2) P(h) \sin(\varphi) d\varphi dx dr dh \]

(5.10)

This expression has been evaluated by computer. The dashed curve in figure 5-6 was obtained for \( t_1 = 1.3 \) sec. and \( t_2 = 2.0 \) sec. using \( \eta_0 = 1500 \) and \( P(h) \) constant. A compromise was made to obtain the best fit at high and low power level. Fits with \( P(h) = \) constant were also tried but gave worse agreement. It is evident that the model does describe the general behaviour but does not give a good account of the observations. Nevertheless we can use the results to obtain estimates of the maximum enhancement factors. These are found to be 1500 ± 200 and 4500 ± 500 for the P(II) and P(I) sites respectively.

Similar measurements on the Fe(I) site gave 3000 ± 400 for the maximum enhancement factor.

It should be noted that the discrepancies at higher power levels cannot be attributed to domain nuclei contributing to the signal. The domain enhancement factor is given approximately by \( H_n / H_a \). For \( Fe_2 P \) \( H_a \) is about 23000oe. and hence, the domain enhancement factor is about 2. This precludes any significant contribution by the domain nuclei to the observed signal.

The magnitude of the observed enhancement factors can be understood in terms of the following calculation. It was shown in chapter 2 that for a spherical particle with a single domain wall, the enhancement factor due to domain wall
motion is given approximately by

\[ \eta = \frac{H_n d}{4M_s \delta} \]  

(5.11)

For Fe₂P, \( M_s \) is about 700 oe., \( \delta \) is of the order of 200 A°. Then for \( d \) in the range 20,000 A° to 40,000 A°, one finds for \( H_n = 50 \) koe. that the enhancement factor will be of the order of 2000. This is in reasonable accord with the experimental result for the P(II) nuclei. It is not understood why the enhancement factor associated with the P(I) site is about three times that of the P(II) nuclei. However, spin lattice relaxation times (to be discussed) are also consistent with \( \eta(P(I)) \approx 3 \eta(P(II)) \).

(iv) Nuclear Spin Relaxation

(a) Longitudinal Spin-lattice Relaxation

The results of the \( T_1 \) measurements were summarized in table II. Since the domain nuclei do not contribute significantly to the nuclear signal (see section iii), the observed distribution in relaxation times must be characteristic of the domain walls. From equation (2.25) the shortest relaxation time is taken to be characteristic of nuclei situated at the center of the domain walls.

The present results can be accounted for by assuming that thermal fluctuations of the domain walls provide the dominant relaxation mechanism.

Recalling equation (2.25), the spin-lattice relaxation
rate is given by

\[
\frac{1}{T_1} = \frac{kT}{16nJS} \left(\frac{K}{J}\right)^{1/2} \tan^{-1} \left( \frac{-\omega_0 \gamma}{\Delta^2 - \omega_0^2} \right) \text{sech}^2 \left( \frac{x}{\delta} \right)
\] (5.12)

K is related to the anisotropy field, \(H_a\), by \(KS^2 = g\mu_b SH_a\), where \(g\) is the Bohr magneton, and \(g\) is the spectroscopic splitting factor. Fischer (1966) has determined \(g\) to be 2.4 for Fe in \(Fe_2B\). Since there is no data available for \(Fe_2P\) this value will be used. According to Meyer and Cadeville (1962) \(S = 1.32\) and \(H_a = 23,000\) oe. \(K\) is then found to be \(4.18 \times 10^{-16}\) ergs.

\(\Gamma\) is a damping constant associated with domain wall motion. This has not been measured for \(Fe_2P\). Gossard (1960) measured \(\Gamma\) for Co and found it to be \(\sim 10^{10}\) sec\(^{-1}\). It will be assumed to be of the same order for \(Fe_2P\) at 4.2 K. From data presented in table III of Kittel and Galt (1956) this seems to be a reasonable assumption.

In order to estimate \(J\), a molecular field approach is used. Hence

\[
kT_c = S\mu_b H_m
\]

where

\[H_m = \frac{zSJ}{\mu_b}\]

\(z\) is the number of nearest neighbours. For iron in \(Fe_2P\) \(z\) is 8, \(T_c\) is about 300 K, and \(S\) is 1.32. \(J\) is then estimated to be \(3 \times 10^{-15}\) ergs.

The wall resonance frequency, \(\Delta\), is not known for \(Fe_2P\) but can be estimated in the following way; recalling equation (2.19) the enhancement factor is given by
\begin{equation}
\eta = \frac{2H n s \text{sech}(\frac{2}{\delta})}{m_w \delta \left[ \left( \Delta^2 - \omega_o^2 \right)^2 + \left( \beta/m_w \right)^2 \omega_o^2 \right]^{1/2}} \tag{5.13}
\end{equation}

From this equation the value of \eta can be deduced using the measured value of \( m \), the relationship \( m_w \delta = (2\pi \gamma^2)^{-1} \) (Kittel and Galt, 1956), where \( \gamma \) is the electron gyromagnetic ratio, and the assumption that \( (\beta/m_w)\omega_o \) is small compared to \( \Delta^2 - \omega_o^2 \). For a typical ferromagnet \( \beta/m_w = 10^{11} \text{sec}^{-1} \). \( \gamma \) has been determined by Fischer (1966) for Fe in Fe₂B to be 2.4. Since there is no data available for Fe₂P this value will be used. \( M_s \) is about 700 oe., \( \delta \) is of the order of 200 A°. Using the measured value of \( \eta_o \) for Fe(I) in equation (5.13), with \( x=0 \), yields \( \lambda^2 = 2.3 \times 10^{22} \text{sec}^{-1} \).

Using equation (5.12) one obtains for the relaxation times associated with the Fe(I) site and the P(II) site at 1.5 K \n
\( T_1 = 3 \) msec. and \( .2 \) msec. respectively. The observed values are 1 msec. and \( .6 \) msec. respectively. Thus it appears that thermal fluctuations can account for the magnitude of the relaxation times associated with the domain wall nuclei. Since \( \Gamma \) is in general temperature dependent (Kittel and Galt, table III), it decreases with temperature, the relaxation rate is not expected to be proportional to temperature. This is in accordance with the experimental results.

If we now compare equations (5.12) and (5.13) we see that \( T_1 \) is inversely proportional to the square of the enhancement factor. Since the enhancement factor for P(I) nuclei is about
three times that of the P(II) nuclei, one expects that the shortest relaxation time for the P(I) nuclei would be about one-ninth that for the P(II) nuclei. This is in good agreement with the experimental results.

From equation (5.12) we can write \( \frac{1}{T_1} = \frac{1}{T_{10}} \text{sech}^2 \left( \frac{x}{\delta} \right) \), that is to say, there will be a distribution of \( T_1 \)'s within the domain walls. The shortest time being for \( x=0 \), i.e. at the center of the wall. Thus the observed distribution in relaxation times can be accounted for.

(b) Transverse Relaxation Times

In order to comment on these results it is useful to recall equation (1.17)

\[
\frac{1}{T_2} = \frac{1}{2T_1} + \frac{\gamma}{2} \int_{-\infty}^{\infty} \leftlangle H_z(t)H_z(0) \rightrangle dt \tag{5.14}
\]

From this equation we see that in the absence of low frequency field fluctuations the transverse relaxation rate is given by \( 1/2T_1 \). This is observed for the P(I) nuclei. The P(II) results indicate that at 77 K the transverse relaxation has a large contribution from the \( T_1 \) processes. This is reflected by the power dependence and the distribution in \( T_2 \)'s. The relatively rapid and exponential relaxation for the Fe(I) nuclei indicates that the \( T_1 \) contribution is a minor one.
CHAPTER VI

\textbf{Fe}_3\textbf{P}

(a) \textit{Introduction}

The magnetic properties of \textit{Fe}_3\textit{P} have been the subject of previous investigations. Its Curie point was first determined by Le Chatelier and Lolodgine (1909) to be in the range 706 K to 717 K. More recently Meyer and Cadeville (1962) have studied the bulk magnetic properties of \textit{Fe}_3\textit{P}. They reported a Curie point of 714 K and a saturation magnetization at room temperature of 1025 oe. They deduced a value of 1.84\(\mu_b\) for the average magnetic moment per iron atom. Later measurements by Fruchart et al. (1964) yielded a Curie temperature of 686 K and an average magnetic moment of 1.91\(\mu_b\) per iron atom.

Rundquist (1962) has determined the crystal structure of \textit{Fe}_3\textit{P}. Its crystal structure is a tetragonal (DOe) type (Pearson, 1967), with space group \textit{I4}, \(a=9.107\ \text{Å}\) and \(c=4.46\ \text{Å}\). It has 32 atoms per unit cell. There are three crystallographically distinct iron sites, \textit{Fe(I)}, \textit{Fe(II)}, and \textit{Fe(III)}, and one phosphorous site. \textit{Fe(I)} has two phosphorous nearest neighbours, \textit{Fe(II)} has four and \textit{Fe(III)} has three. The crystal structure is illustrated in figure 6-1.

Mossbauer investigations of \textit{Fe}_3\textit{P} by Bailey and Duncan (1966) and Wappling et al. (1971) have indicated that the magnetic structure of \textit{Fe}_3\textit{P} is not as simple as its crystal structure. Bailey and Duncan deduced hyperfine fields of
Fig. 6-1 The structure of Fe₃P projected onto the basal plane
295 koe., 265 koe. and 185 koe. for the three iron sites at 90 K. Wappling et al. found that at least four magnetically non-equivalent types of iron atoms could be distinguished from the Mossbauer spectrum. The corresponding hyperfine fields, at 300 K, are 278.7 koe., 251.7 koe., 228.4 koe., and 175.6 koe. The quoted accuracy is ± 0.1 koe. A motivation for the N.M.R. result is the determination of the hyperfine fields associated with the various sites as these results could help to clarify the magnetic structure of Fe₃P.

For the present studies two samples were employed, a commercial one and a 'home-made' one. The 'home-made' sample was prepared in the same manner as the Fe₂P sample (chapter 5 section a). The crystal structures of the samples were verified by X-ray powder analysis. The samples were also subjected to chemical analysis. The commercial sample analysed as Fe₃.16P, the other as Fe₃.06P.

(b) **Experimental Results**

(i) **Zero Field Resonances**

The zero field resonances were sought employing the spectrometer described in chapter 3, which was swept over the range 10-200 MHz. Both samples were used and the same N.M.R. spectrum was obtained. Three sets of doublets were observed; one was only partially resolved the other two were almost completely resolved. Representative traces of the observed spectra at 1.5 K are given in figures 6-2, 6-3 and 6-4. The resonances occur at 41.7 MHz, 37.2 MHz, 34.5 MHz, 27.5 MHz and 24.8 MHz.
Fig. 6-2 Zero Field Spin-echo Spectrum of Fe$_3$P of Fe$_3$P at 1.5 K
Fig. 6-3 Zero Field Spin-echo Spectrum of Fe₃P at 1.5 K
Fig. 6-4 Zero Field Spin-echo Spectrum of Fe$_3$P at 1.5 K.
The resonant frequencies were determined by beating the nuclear signal with the reference signal from a v.h.f. signal generator, the output frequency of which was monitored by a frequency counter. The accuracy of this determination was limited by the finite width of the echo to ± 0.2 MHz. Poor signal to noise ratios precluded measurements at temperatures greater than 1.5 K.

(ii) Enhancement Factors

As was demonstrated in chapter 4, a study of the signal intensity as a function of the applied r.f. field strength can yield information about the distribution of enhancement factors within a domain wall. Due to the rapid decay time it was not possible to study the behaviour of the FID, instead, the amplitude of the spin echo was determined as a function of the r.f. field strength. In figure 6-5 is shown a plot of the spin echo amplitude for the 41.7 MHz. line as a function of the applied r.f. field strength at 1.5 K. The two pulse sequence for stimulating the echo used pulse lengths of 1 and 2 microseconds for the 90 and 180 degree pulses respectively.

(iii) Nuclear Relaxation Times

Longitudinal spin-lattice relaxation times, \( T_1 \), and transverse relaxation times, \( T_2 \), were measured at 1.5 K for the 41.7 MHz line. Typical longitudinal and transverse relaxation curves are given in figures 6-6 and 6-7 respectively. As was
Fig. 6-5 $H_1$ dependence of the $^{57}$Fe(I) spin-echo amplitude in Fe$_3$P at 1.5 K
Fig. 6-6 Longitudinal Relaxation of $^{57}\text{Fe}(I)$ in Fe$_3$P at 1.5 K
Fig. 6-7 Transverse Relaxation of $^{57}\text{Fe}(I)$ in $\text{Fe}_3\text{P}$ at 1.5 K
the case for Fe$_2$P a distribution in relaxation times and a power dependence of the relaxation times is observed. The observed $T_1$'s range from 2.4 ± 0.2 msec. to 14 ± 1 msec.

The transverse relaxation curves are exponential and yield $T_2$'s of 4.8 ± 0.4 and 15 ± 1.5 msec. at power levels of 0 db and -10 db respectively.

(c) Discussion of the Experimental Results

(i) Zero Field Resonances

Since the average magnetic moment per iron atom in Fe$_3$P, 1.84$\mu_B$, is larger than that in Fe$_2$P, 1.32$\mu_B$, it is reasonable to expect that the hyperfine field at the P nucleus and hence its resonance frequency in Fe$_3$P will be greater than the resonance frequency in Fe$_2$P, i.e. greater than 77 MHz. For this reason it is likely that all the observed resonance are due to the iron nuclei. The observed resonance frequencies correspond to hyperfine fields of 304 ± 2 koe., 271 ± 2 koe., 251 ± 2 koe., 200 ± 1 koe., and 180 ± 1 koe.. Since these fall in the range of the Mossbauer results present N.M.R. results are not inconsistent with the Mossbauer results. It is clear however that the Mossbauer results are not useful. Our N.M.R. results suggest that the Mossbauer data should be reinterpreted assuming that there are 5 magnetically non-equivalent iron sites.

The assignment of the observed hyperfine fields to particular crystallographic sites is complicated by the fact that there are only three crystallographically distinct iron sites. Since there are three sets of doublets it is reasonable to
assign each set to one iron site. The average hyperfine fields for the doublets are 304 koe., 261 koe. and 190 koe.. If we assume that the iron hyperfine fields are proportional to the magnetic moment associated with the particular iron site we can deduce the following magnetic moments: $2.21\mu_B$, $1.91\mu_B$, and $1.38\mu_B$. The average moment is less than that observed in pure iron. This suggests that there is electron donation from the phosphorous valence band to the iron 3-d bands.

A simple electron donation model was presented in chapter 5 section a-ii, this will be followed here. Each P is assumed to donate 2.6 electrons which are shared among its nine iron nearest neighbours. Then for Fe(I) which has two P nearest neighbours the model predicts

$$\mu_{\text{Fe(I)}} = 2.7 - \frac{2 \times 2.6}{9} = 2.12\mu_B \quad (6.1)$$

For Fe(II) which has four P nearest neighbours we get

$$\mu_{\text{Fe(II)}} = 2.7 - \frac{4 \times 2.6}{9} = 1.54\mu_B \quad (6.2)$$

For Fe(III) which has three P nearest neighbours we get

$$\mu_{\text{Fe(III)}} = 2.7 - \frac{3 \times 2.6}{9} = 1.83\mu_B \quad (6.3)$$

On the basis of these results we can assign the 41.7 MHz line to the Fe(I) site, the 36 MHz doublet to the Fe(III) site and the 26 MHz doublet to the Fe(II) site. The physical reason for the presence of the doublets is not yet understood. There
are at present neutron scattering experiments underway (Wilkinson, 1971) which may help to clarify the situation. Preliminary results show that Fe$_3$P is not simple magnetically. Although the statistics are poor it does not seem that just three magnetic states fit the data.

A simple estimate of the expected P hyperfine field, and hence the resonance frequency, can be made if we assume that the P hyperfine field is proportional to the sum of the nearest neighbour iron moments. This sum for Fe$_3$P is 15.72, for Fe$_2$P it is 11.88. Taking the constant of proportionality to be the same for both Fe$_2$P and Fe$_3$P the expected resonance frequency should be about 115 MHz. However, no resonance was observed above 41.7 MHz. It is possible that the P resonance was so broad as to make it undetectable on the apparatus used. Otherwise the resonance is out of the frequency range swept by the spectrometer.

(ii) Enhancement Factors

The curve of the spin echo amplitude versus r.f. field strength given in figure 6-5 bears a qualitative resemblance to the nickel FID curve, figure 4-1. The dashed line in figure 6-5 was obtained employing the drumhead model with a maximum enhancement factor of 14000. It is evident that the model does describe the general behaviour but does not give a good account of the observations. Using equation (3.2) an average enhancement factor can be deduced from the position
of the maximum by

$$\tilde{\eta} = \frac{H_n}{\nu t_1 H_1} \quad (6.4)$$

This gives $\tilde{\eta} = 4400$. According to equation (2.20) the enhancement factor due to domain wall motion is given by

$$\eta = \frac{H_n d}{4 M_s \delta} \quad (6.5)$$

For Fe$_3$P $M_s$ is about $10^3$ oe. and $\delta$ is the order of 300 $\text{A}^\circ$. Then for $d$ in the range 20,000 $\text{A}^\circ$ to 40,000 $\text{A}^\circ$ one finds for $H_n = 300$ koe. that the enhancement factor will be of the order of 7000 which is in reasonable accord with the observed value. Thus the magnitude of the observed enhancement factor can be accounted for.

The enhancement factor for domain nuclei in Fe$_3$P is about 50 so that domain nuclei are not expected to make a significant contribution to the observed signal.

(iii) **Nuclear Spin Relaxation Times**

Since the domain nuclei do not contribute significantly to the nuclear signal the observed distribution in relaxation times must be characteristic of the domain walls. The present results can be accounted for by assuming that thermal fluctuations of the domain walls provide the dominant relaxation mechanism.

Recalling equation (2.25), the spin-lattice relaxation
rate is given by

\[ \frac{1}{T_1} = \frac{\omega_s k T}{16 \pi J S} \left( \frac{K}{J} \right)^{1/2} \tan^{-1} \left( \frac{-\omega_s \Gamma}{\Delta^2 - \omega_s^2} \right) \]  \hspace{1cm} (6.6)

For Fe$_3$P $K$ is $\sim 8 \times 10^{-17}$ ergs, $S=1.86$ and $J=3 \times 10^{-15}$ ergs. $\Gamma$ has not been determined for Fe$_3$P so it is taken to be about $10^{10}$ sec$^{-1}$ as for Fe$_2$P. The wall resonance frequency is estimated as for the Fe$_2$P case (chapter 5-c section iv). The resonance frequency is estimated to be $\sim 4.5 \times 10^{10}$ sec$^{-1}$.

Using equation (6.6) one obtains $T_1=\sim 4$ milliseconds. The shortest observed $T_1$ is 2.4 milliseconds. It is seen then that thermal fluctuations of the domain walls can account for the observed relaxation times.

The shortest transverse relaxation time is, within experimental error, twice the shortest longitudinal relaxation time. This suggests that the dominant contribution to the transverse relaxation rate is from the spin-lattice processes. This contribution is reflected in the power dependence of the transverse relaxation.
CHAPTER VII

CONCLUSIONS

The pulsed N.M.R. technique has proved to be useful in the study of the dynamic and static properties of the hyperfine interactions in Ni, Fe$_2$P and Fe$_3$P. The present results indicate that the motion of domain walls in nickel may be likened to that of a circular membrane pinned at its circumference. This 'drumhead' model accounts for the general behaviour of the experimental results but does not give good agreement with the results in Fe$_2$P and Fe$_3$P. This suggests that the motion of domain walls in these systems is more complicated than that of a vibrating membrane.

The relaxation of the domain wall nuclei in Fe$_2$P and Fe$_3$P can be attributed to thermal fluctuations of the domain walls. This assumption accounts for both the distribution and magnitude of the observed longitudinal relaxation times.

We have determined the hyperfine fields associated with the various $^{57}$Fe sites in Fe$_2$P and Fe$_3$P. These results suggest that the bonding in these systems involves donation of phosphorous valence electrons to the iron d bands with a resultant depression of the iron moments from the pure iron value. The magnetic structure of Fe$_2$P was readily determined. The situation in Fe$_3$P is not so clear. There appear to be six magnetically non-equivalent iron sites while there are only
three crystallographically distinct iron sites. The reason for this is not yet understood. Neutron diffraction experiments may help to clarify the magnetic structure of Fe₃P.

The present measurements show the usefulness of the N.M.R. results as compared to the Mossbauer measurements. Previous Mossbauer measurements of Fe₂P and Fe₃P have exhibited disagreement in the magnitude of the hyperfine fields. In the case of Fe₃P the Mossbauer measurements also exhibit disagreement in the number of magnetically distinct iron sites. These disagreements can be attributed to the complicated unfolding procedure required to extract hyperfine fields from the Mossbauer spectrum. To each hyperfine field there correspond six lines so that when several hyperfine fields are being considered the unfolding procedure can become very complicated and the result is by no means unambiguous. The N.M.R. experiment though in principle less sensitive than the Mossbauer experiment has the advantage of yielding an unambiguous result as it yields.

It is not clear which mechanisms are responsible for the transferred hyperfine fields at the phosphorous nuclei in Fe₂P and Fe₃P. The positive sign of this field in Fe₂P is consistent with experimental observations and theoretical considerations that p³ elements dissolved in iron should have positive hyperfine fields. The theoretical considerations assume that conduction electron polarization is the dominant mechanism. It is unfortunate that the ³¹P resonance in Fe₃P was not observed as it could have helped to clarify the mechanisms responsible for the transferred hyperfine fields.
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