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John Arthur Barclay

(Ph. D. Thesis)

September 1969

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SPIN-LATTICE RELAXATION BY NUCLEAR MAGNETIC RESONANCE ON ORIENTED NUCLEI

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SPIN-LATTICE RELAXATION BY NUCLEAR MAGNETIC RESONANCE
ON ORIENTED NUCLEI

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ABSTRACT

Nuclear magnetic resonance was detected at 0.004 - 0.010°K by
perturbation of the gamma-ray anisotropy of $^{60}$Co in Fe, Co, and Ni.
Shirley's work on the response functions describing the perturbation
in the presence of homogeneous broadening has been extended to include
inhomogeneous broadening. The existence of a "hard core" value at
resonance is demonstrated in this case also. Frequency modulation of
the inhomogeneous line was necessary in order to perturb all of the spin
packets in the broadened lines. The optimum conditions for frequency
modulation were found by varying the modulation bandwidth and modulation
frequency. A simple model was proposed to explain the observed degree
of perturbation. In addition, nuclear spin-lattice relaxation times
have been measured in the 0.004 - 0.010°K temperature range. Interpretation
of the data was done by fitting the data with a sum of exponentials.
Precise $T_1$ results are obtained but the accuracy was uncertain due to
the uncertainty of the initial conditions.
I. INTRODUCTION

Nuclear orientation (NO) and nuclear magnetic resonance (NMR) are separate tools which can be used to probe a nucleus and its interaction with the environment. Nuclear moments, nuclear spins, and the magnitude of hyperfine fields at the nuclear site are examples of the knowledge that can be gained by using these tools. Both of these methods have been important sources of the hyperfine field values for impurities in Fe, Co, and Ni. The mechanism leading to the large magnetic fields at the impurity nuclear site is not quantitatively understood. The difficulty arises from the many possible contributions from various hyperfine interaction mechanisms. In order to better sort out some of these contributions, additional data such as nuclear spin-lattice relaxation times are needed.

NMR has measured relaxation times for many cases but it is limited to stable nuclei and macroscopic concentrations. NO has also been applied to this problem but leads to ambiguous results because of warming effects present in this approach. However, NO does have the advantage that it uses radioactive nuclei in microscopic concentrations. The advantages of both methods can be had by combining them leading to nuclear magnetic resonance on oriented nuclei (NMRON). In this combination the anisotropy of the radiation from the oriented nuclei serves as the means of detecting the resonance. However, nuclear spin-lattice relaxation times measured by this method are more complicated because of low temperatures and the measurement by observation of the anisotropy. This thesis attempts to describe and illustrate the NMRON method of measuring spin-lattice relaxation times.
II. THE METHOD; NMR-ON

A. Theoretical

1. Nuclear Orientation

It was realized over thirty years ago\(^1\,^2\) that orientation of an ensemble of nuclei would be a powerful tool to use in the study of nuclear physics. The proposed method of obtaining such an ensemble was the "brute force" method. This method requires a very low temperature and a very large external magnetic field which interacts with the nuclear magnetic moment, lifting its orientation degeneracy. Appreciable orientation occurs when the thermal energy approximates the interaction (Zeeman) energy. However, high magnetic field (\(10^5\) oe) and low temperature (0.01°K) technology had not developed far enough for this direct method to work, so indirect methods were proposed and developed.\(^3\) One of the indirect methods was orientation in ferromagnets which uses their large hyperfine fields in lieu of the large external fields. In 1955 this method was first applied using Co and Fe.\(^4\,^5\) These experiments (Co\(^{60}\) in Co or Fe metal) also illustrated how nuclear orientation could be used as a tool in solid state physics if the nuclear properties were known from a previous experiment, e.g., to determine internal fields in ferromagnets. This was still a limited tool because only a few elements were ferromagnetic but in 1959 it came into its own when Samoilov, et al.\(^6\) found that nuclei of many atoms dissolved in ferromagnets experienced a large induced magnetic field. Since then great advances have been made in understanding several aspects of ferromagnetism using nuclear orientation as a tool.\(^7\)
In order to obtain any experimental information one must explicitly describe the radiation pattern of the oriented nuclei. Such an ensemble (10^8 to 10^{12} nuclei in an ordinary N.O. sample) can be adequately described by a density matrix treatment. A very general description of the initial state of the ensemble can be given in terms of \( \rho(\text{initial}) \) and the entire theory developed from this approach. Fano made use of the development of Racah algebra and introduced the related approach of statistical tensors, \( R_k^q \), which accentuates the geometrical aspects of the theory. The two approaches are related analogously to the two descriptions of an electric charge distribution; namely, by specifying either the charge density \( \rho(r) \) or the complete set of electric multipole moments of the distribution. The relationship between the two can be written as

\[
R_k^q = \sum_{mm'} (-1)^{I-m}(2k+1)^{1/2} \begin{pmatrix} I & I & k \\ m' & -m & q \end{pmatrix} \rho_{mm'},
\]

and inversely by

\[
\rho_{mm'} = \sum_k (-1)^{I-m}(2k+1)^{1/2} \begin{pmatrix} I & I & k \\ m' & -m & q \end{pmatrix} R_k^q.
\]

Using either of these approaches, the angular distribution of gamma

---

* See Appendix I for elaboration on the density matrix.
rays can be expressed by
\[
W(\theta) = 1 + \sum_{k=2}^{EVEN} B_k U_k F_k P_k (\cos \theta).
\]

This is the expression for axial symmetry with the axis being provided by some external \( H_0 \), \( \theta \) being the angle between the counter and the field. In this case the density matrix is diagonal and \( R^q_k \) with \( q \neq 0 \) disappear. The orientation parameter, \( B_k \), can be defined by
\[
B_k = \left( \frac{(2I+1)(2k+1)}{2} \right)^{1/2} \sum_m (-1)^{I-m} \begin{pmatrix} I & I & k \\ m & -m & 0 \end{pmatrix} \rho_{mm}.
\]

From the definition of \( R^q_k \) and \( B_k \) we see they are related by
\[
R^0_k = (2I+1)^{1/2} B_k.
\]

The \( \rho_{mm} \) are just the familiar Boltzmann population factors. \( B_k \) contains the temperature, hyperfine field, and other parameters external to the nucleus.

\( U_k \) is an angular momentum reorientation parameter associated with the unobserved transitions preceding the observed one. For the transition \( I_i \xrightarrow{L} I \), it may be defined as
\[
U_k = \left[ (2I_i+1)(2I+1) \right]^{1/2} (-1)^{I_i+I-L} \begin{pmatrix} I_i & I_i & k \\ I & I & L \end{pmatrix}.
\]
The attenuation described by the $U_k$ is purely geometric in origin and comes from the transformation from one coupling scheme of three angular momenta to a second coupling scheme between three angular momenta. This is essentially a Racah or 6j coefficient. It can be thought of as a depolarization, smearing of angular momentum, or a angular momentum "gate".\textsuperscript{12} For a series of preceding decays, the final $U_k$ will be the product of all the individual $U_k$'s. This attenuation does not account for any additional loss of orientation due to nuclear relaxation in the intermediate state. However, in metals at low temperatures the nuclear relaxation times are on the order of seconds\textsuperscript{13} and therefore most unobserved transitions will retain the total orientation of the parent state except that lost by $U_k$.

The angular correlation coefficient, $F_k$, contains the geometrical part of the angular momentum coupling between the observed gamma ray and its initial and final states. It can be defined for single multipolarity gamma rays as

$$F_k(LLII_l) = (-)^{I+I_i-1} [(2k+1)(2I_i+1)]^{1/2}(2L+1) \begin{pmatrix} L & L & k \\ 1 & -1 & 0 \end{pmatrix} \begin{pmatrix} L & L & k \\ I_i & I_i & I \end{pmatrix}.$$ 

The $F$ coefficients have been tabulated by Ferentz and Rosenzweig.\textsuperscript{14}

This is sufficient background for all cases in this thesis. Additional details on N.O. may be found in Ref. 10 and the references therein.
2. **Nuclear Magnetic Resonance**

In 1946 this technique for studying nuclei and their environment was discovered independently by F. Bloch and E. M. Purcell. They used a static magnetic field to split the nuclear spin energy levels which were subsequently populated according to Boltzmann statistics. A radio frequency oscillating field was applied perpendicular to the d.c. field and the resonance was observed when the ac frequency and the Larmor frequency were equal. The effect was (and is) observed by detecting the precession of the magnetization in the first case and the absorption of power in the second case. Many papers and books have been written describing the theory of NMR in detail.

In 1966 the field of NMR was expanded when Matthias and Holliday used the anisotropy of the radiation pattern from oriented nuclei to detect nuclear magnetic resonance. In this case one observes a quantity transforming as a tensor of rank one or two (sometimes four) and the basic theory of this observation is described below.

Three of the next four sections treat the major points in NMRON. They are the response function of the spins to the radio frequency (r.f.) field, the relaxation of the nuclear spins, and the effects of frequency modulation. Before discussing these points a brief description of NMR in ferromagnets is given.

a. **Ferromagnets.** NMR occurs in the nuclear spin system when it absorbs quanta from an electromagnetic wave with frequency equal to the Larmor frequency. The signal will be proportional to the amplitude of the oscillating field at the nucleus. Given a completely saturated...
(no domain walls) ferromagnetic sample, small compared to the dimensions of the coil producing the oscillating field, we can solve for the amplitude inside the metal by using two of Maxwell's equations for homogeneous, linear, isotropic, and conducting medium.

\[ \nabla \times \vec{E} = -\frac{\mu}{c} \frac{\partial \vec{H}}{\partial t} \]

\[ \nabla \times \vec{H} = \epsilon/c \frac{\partial \vec{E}}{\partial t} + \frac{\hbar \sigma}{c} \vec{E} \]

where \( \sigma \) = conductivity, \( \epsilon \) = dielectric constant, and \( \mu \) = magnetic permeability. Consider a planar sample with \( z \) axis perpendicular to the surface. The electromagnetic wave transmitted along the \( z \) axis has only transverse components which we assume vary as \( \exp(ik \cdot r - i\omega t) \).

Writing out the curl of \( \vec{E} \) and the time derivative of \( \vec{H} \), the first equation gives

\[ i(k \times \vec{E}) = \frac{i\omega}{c} \vec{H} \]

and the second equation gives

\[ i(k \times \vec{H}) = -\frac{i\epsilon \omega}{c} \vec{E} + \frac{\hbar \sigma}{c} \vec{E} \]

Substituting the expression for \( \vec{H} \) (first equation) into the second equation gives

\[ i(k \times \vec{k} \times \vec{E}) \frac{c}{\mu \omega} + \frac{i\varepsilon \omega}{c} \vec{E} - \frac{\hbar \sigma}{c} \vec{E} = 0 \]
Using the vector identity \( \mathbf{a} \times \mathbf{b} \times \mathbf{c} = \mathbf{b}(\mathbf{a} \cdot \mathbf{c}) - \mathbf{c}(\mathbf{a} \cdot \mathbf{b}) \) on the first part gives \( \mathbf{k} \times \mathbf{k} \times \mathbf{E} = \mathbf{k} (\mathbf{k} \cdot \mathbf{E}) - \mathbf{E} (\mathbf{k} \cdot \mathbf{k}) \). Note that \( \mathbf{k} \cdot \mathbf{E} = 0 \) because \( \mathbf{k} \), the propagation vector, and \( \mathbf{E} \) are perpendicular. Therefore

\[
-ik^2 \frac{\mathbf{E}}{c} + \frac{i\epsilon \omega}{c} \mathbf{E} - \frac{4\pi i \omega}{c} \mathbf{E} = 0
\]

which can be rewritten as

\[
\nabla \times \left[ k^2 - \frac{\epsilon \omega^2}{c^2} - \frac{4\pi i \omega}{c^2} \right] \mathbf{E} = 0.
\]

Since \( \mathbf{E}, \nabla \neq 0 \),

\[
k^2 - \frac{\epsilon \omega^2}{c^2} - \frac{4\pi i \omega}{c^2} = 0
\]

or

\[
k^2 = \frac{\omega^2}{c^2} \left[ 1 + \frac{4\pi i \sigma}{\omega e} \right]
\]

which means the propagation vector is complex.

\[
k = \sqrt{\frac{\mu \omega^2 e}{c^2} \left( 1 + \frac{4\pi i \sigma}{\omega e} \right)} \quad \text{since} \quad k = \sqrt{\mu e} \frac{\omega}{c} \quad \text{if} \quad \sigma = 0.
\]

We can write \( k = \alpha + i\beta \) and \( k^2 = \alpha^2 - 2\alpha \beta i - \beta^2 \). Equating parts we find

\[
\alpha^2 - \beta^2 = \frac{\epsilon \omega^2}{c^2} \quad \text{and} \quad 2\alpha \beta = -\frac{4\pi \sigma i \omega}{c^2}.
\]
Eliminating $\alpha$ and using the quadratic formula we obtain

$$\beta^2 = \left( -\frac{\epsilon \mu \omega^2}{c^2} \pm \frac{\epsilon i \omega}{c^2} \sqrt{1 + \frac{16\pi^2 \sigma^2}{\epsilon^2 \omega^2}} \right) / 2 .$$

Taking the positive sign and solving for $\alpha, \beta$, the result is

$$\alpha, \beta = \sqrt{\mu \epsilon \frac{\omega}{c}} \left[ \sqrt{1 + \frac{4\pi \sigma}{\omega \epsilon}} \pm 1 \right]^{1/2} .$$

For a poor conductor $\frac{4\pi \sigma}{\omega \epsilon} \ll 1$. After making a Maclaurin series expansion to first order we obtain

$$k = \alpha + i \beta \approx \sqrt{\mu \epsilon \frac{\omega}{c}} + \frac{i 2\pi}{c} \sqrt{\mu \epsilon} \sigma .$$

For a good conductor $\frac{4\pi \sigma}{\omega \epsilon} \gg 1$ and $k \approx (1+i) \frac{\sqrt{2\mu \epsilon \mu_0}}{c}$. We can write the amplitude as

$$\mathbf{E} = E_0 e^{-\beta \hat{\mathbf{n}} \cdot \hat{\mathbf{r}}} e^{i \alpha \hat{\mathbf{n}} \cdot \hat{\mathbf{r}} - i \omega t}$$

$$\mathbf{H} = H_0 e^{-\beta \hat{\mathbf{n}} \cdot \hat{\mathbf{r}}} e^{i \alpha \hat{\mathbf{n}} \cdot \hat{\mathbf{r}} - i \omega t}$$

where $\hat{\mathbf{n}}$ is a unit vector in the direction of $\hat{\mathbf{k}}$. These are damped transverse waves with $\mathbf{E}_0$ and $\mathbf{H}_0$ related by the first equation;

$$H_0 = \frac{c}{\mu \omega} (\alpha + i \beta) \hat{\mathbf{n}} \times \mathbf{E}.$$ The decay of $1/e$ of the initial value is characterized by the skin depth defined as...
\[ \delta = \frac{1}{\beta} \approx \frac{c}{\sqrt{2\pi \mu_0}} \] for a good conductor in Gaussian units.

Ferromagnets have a large magnetization which leads to a second attenuating effect, that of demagnetizing fields. The effect of the boundary condition \((\vec{B}_1)_{\text{in}} = (\vec{B}_1)_{\text{out}}\) can be described by magnetic poles on the surface which give rise to the field which cancels the magnetization contribution to \(\vec{B}\). These demagnetizing fields will be shape-dependent and are usually taken into account by using a product of a demagnetizing factor and the magnetization in the corresponding direction. Osborn\(^ {22}\) has tabulated these for many cases.

Fortunately, after these two attenuation effects, there is an enhancement factor of the r.f. field at the nucleus. The hyperfine field at the nucleus is proportional to the electronic magnetization as in a molecular field approximation (Weiss field). The r.f. field acts on the electronic magnetization to cause a transverse component of \(\vec{M}\) which in turn causes a transverse field at the nucleus. The existence of ferromagnetic resonance (FMR)\(^ {23}\) proves that the electronic magnetization follows the r.f. field even up to 35 GHz. A simple approach to the enhancement factor is as follows

\[ (\vec{H}_x)_{\text{eff}} = \vec{H}_x + \lambda \vec{M}_x \]

where \(\lambda = H_n / M_0\), the molecular field parameter. We want to solve for \(M_x\) but this has been done in the theory of FMR. Modifying one of the
early treatments by Kittel \(^2\) slightly, one obtains \(M_x = \chi_x H_x\) with 
\[\chi_x = \chi_0 / (1 - \omega/\omega_0)^2\]
where

\[\omega_0 = \gamma [H_0 + H_A^x + (N^x - N^z)M_z]^{1/2} \left[ H_0 + H_A^y + (N^y - N^z)M_z \right]^{1/2}\]

\[\chi_0 = M_z / [H_0 + H_A^z + (N^x - N^z)M_z]\]

which includes both demagnetizing and anisotropy field effects but no exchange or damping terms. This also applies only to directions close to the axis of a crystal. The nuclear resonance frequencies are usually far below the FMR frequencies so \(\omega/\omega_0 \ll 1\) and \(\chi_x = \chi_0\) which implies \(M_x = \chi_0 H_x\). If \(H_A^z = 0\) and \(N^x = N^z\), then

\[(H_x)_{\text{eff}} = (H_1)_{\text{eff}} = H_1 + H_{hf} M_0 H_0 = H_1 + H_{hf} H_0 = \eta H_1\]

where \(\eta = 1 + H_{hf}/H_0\), the normal saturation enhancement factor. In most dilute, ferromagnetic alloy, single crystals \(H_A^z \neq 0\) but \(N^z\) can be made equal to \(N^x\) so

\[\eta = \left( 1 + \frac{H_{hf}}{H_0 + H_A^z} \right)^{-1}\]

This particular approach applies when \(H_0\) is along or close to an axis of the crystal because the concept of the anisotropy field is only defined for small deviations. If this is not the case, then the approach taken involves the solution of the general free energy equation for the susceptibility tensor as calculated by Artman. \(^25\) In terms of the
susceptibility, the enhancement factor is just $\eta = \chi_e' \frac{H_n}{M}$ as shown above and by Gossard, et al. The latter give the general expression for the power absorbed when doing NMR in ferromagnets under the restriction of being far from the FMR frequency. It is

$$P = \frac{1}{2} \omega \chi_e^{xx} \left\{ 1 + 2\chi_n' \left( \frac{H_n}{M} \right) \left[ 1 + \chi_e' \left( \frac{H_n}{M} \right) \right] \right\} H_x^2$$

$$+ \frac{1}{2} \omega \chi_n^{xx} \left\{ 1 + \chi_e' \left( \frac{H_n}{M} \right) \left[ 2 + \chi_e' \left( 1 - \frac{\chi_e''}{\chi_e'^2} \right) \left( \frac{H_n}{M} \right) \right] \right\} H_x^2$$

where $\chi_e^{xx} = \chi_e' - i\chi_e''$, $\chi_n^{xx} = \chi_n' - i\chi_n''$, $H_x$ equals the field in the $x$ direction. This also illustrates the frequency dependence of the power absorbed.

b. Response. The traditional way of treating an oscillating magnetic field is to decompose it into left and right circularly rotating components and transform into the rotating frame. One of the components will become stationary and the other will be rotating at $\pm 2\omega$ with respect to the first and can be neglected. Figure 1 illustrates the orientation of $H_0$, $H_1$, the sample and the detector.

The effect of the r.f. field on the nuclear spins is found by calculating the response function for the observable. When the precession of the magnetization is detected the response function is the r.f. susceptibility, i.e., $\vec{M} = \chi \vec{H}$. In the case of NMRON the response function can be defined as

$$B_k(\omega, t) = G_k(\omega, t)B_k(0)$$
MACROSCOPIC FRAME (LABORATORY)

DETECTOR

\[ H_0 \]

\[ 2H_1 \text{ (OSCILLATING AT } \omega \text{)} \]

MICROSCOPIC FRAME (ROTATING AT } \omega \text{)}

\[ H_0 \text{ eff} \]

\[ H_1 \]

\[ K_1 \]
where now the effect of the r.f. field is contained in the perturbation factor $G_k(\omega,t)$. This is analogous to the definition of the perturbation factor used in perturbed angular correlation. In NMRON the lifetimes of the oriented nuclei are very long compared to the time required for a transition to occur ($t = 1/\omega_1$). Therefore we need $G_k(\omega,\infty)$ which can be calculated by two general methods.

The first method involves calculating the time-integral value of the angular correlation perturbation factors for a dc plus ac field. A method related to this is that developed by D. A. Shirley which consists of using the explicit transition probabilities (Majorana factors) in the calculation of $G_k(\omega,\infty)$. It is restricted to axial symmetry which is the usual case in NMRON. The second general method consists of using rotation matrices to calculate the instantaneous angle between $\vec{K}_1$ and the counter. $\vec{K}_1$ is the axis of symmetry of the observables of the system which is the direction of the spin rotating about $\vec{H}_{\text{eff}}$ in the rotating frame (shown in Fig. 1). Figures 2 and 3 illustrate the behavior of the $G_k(\omega,\infty)$'s for the axially-symmetric, random-phase case. The dashed lines were calculated for the completely homogeneous case by the Majorana approach. The width of the lines is proportional to $H_1/H_0$. $G_1(\omega,\infty)$ is Lorentzian as expected because $B_1$ is directly proportional to $\vec{M}$ and the absorption response function for the magnetization, $\chi''$, is well known as Lorentzian. Also notice that the higher rank tensors do not have Lorentzian behavior, but exhibit hard core values at resonance in conjunction with their multipole structure; i.e., the number of minima is equal to the rank of the tensor. This structure in $G_k(k > 1)$ is
Fig. 2.
Fig. 3.
caused by the coherence between the r.f. field and the $P_k(\cos \theta)$ distribution that describes the radiation of the oriented nuclei. Consider the motion of $P_k(\cos \theta)$ with respect to the rotating frame. Far off resonance $P_k(\cos \theta)$ is axially symmetric about $H_{\text{eff}}$ which is very close to $H_0$, but on resonance $P_k(\cos \theta)$ is rotating about $H_1$ which is perpendicular to $H_0$. The observed effect in the rotating frame is given by the integral of $P_k(\cos \theta)$ over the appropriate angles. However, at $\theta = 0$, the lab frame and rotating frame coincide and the hard core value is identical in both frames. Reference 28 has a more detailed description of the properties of $G_k(\omega, \infty)$. This multipole structure has been experimentally observed by D. Quitmann et al. in a nuclear reaction-NMR experiment on the 5.8 microsecond state of As$^{73,31}$.

So far we have only response functions for completely homogeneous samples and the question arises whether or not this multipole structure is still present for a inhomogeneously broadened line. The homogeneous broadening of the line may come from several sources such as

1) lifetime of the nuclear state
2) spin-lattice relaxation
3) interaction with radiation field
4) dipolar and Suhl-Nakamura broadening between like spins in a homogeneous sample and perhaps others which are neglected for now. For dilute alloys, dipolar broadening is not important because the samples have approximately 1 impurity in $10^5$ host atoms. The first mechanism is not important because for NO samples the lifetime is long (days) which gives a very narrow line. The spin-lattice relaxation times are on the
order of seconds and therefore the linewidth will be governed by the strength of $H_1$ in all but the very weak $H_1$ cases. If one assumes a Lorentzian line shape, $(G_1)$, the linewidth is governed by $H_1$ for $H_1 \geq 10^{-5}$ oe if $T_1 = 20$ seconds and $\gamma_N = 3.59 \times 10^3 (g \sec)^{-1}$. $H_1$ broadening is exactly the linewidth that appears in the Majorana factor approach. Appreciable transitions occur only when $\omega - \omega_0$ is of the order of $\omega_1$ and therefore the linewidth will be of order $\omega_1$ for the cases of interest.

In all real samples there will be an inhomogeneous broadening due to:

1) strains, dislocations, vacancies, etc.
2) dipole-dipole coupling between unlike spins or like spins with different $\omega_0$
3) inhomogeneity in external $H_0$; also caused by surface roughness which leads to demagnetizing field variations
4) any anisotropic effects influencing the hyperfine fields and probably others which we again neglect. Effects two and four are presumably small in ferromagnetic alloy samples or are at least overwhelmed by the others. The other effects are usually random which leads to a Gaussian distribution of hyperfine fields and therefore $\omega_0$'s.

The inhomogeneous time-integral response function will then be given by

$$G_k(\omega - \omega_0, \infty) = \frac{\int_0^\infty G_k(\omega - \omega', \infty) h(\omega' - \omega_0) d\omega'}{\int_0^\infty h(\omega' - \omega_0) d\omega'} = 1$$
with

\[ h(w' - w_0) = \frac{1}{\pi^{1/2} \Delta \omega_G} \left[ \exp - \left( \frac{w' - w_0}{\Delta \omega_G} \right)^2 \right] \]

where \( \Delta \omega_G \) is the Gaussian width of the inhomogeneously broadened line. This integral can be done numerically. The solid curves in Figs. 2 and 3 show the results of this calculation for the same conditions as the homogeneous line for a series of homogeneity ratios. We define the homogeneity ratio as \( a = \omega_1 / \Delta \omega_G \). \( G_1(\bar{\omega}, \infty) \) shows expected results as does \( G_2(\bar{\omega}, \infty) \) but there are some interesting features in the latter. If \( a = 0 \), then this is the totally inhomogeneous line and \( G_2(\bar{\omega}, \infty) \) approaches unity over an infinite frequency range. As \( a \) becomes closer to but still less than 1, \( G_2(\bar{\omega}, \infty) \) decreases about \( \omega_0 \) to a minimum value of 0.25 at \( \omega_0 \) but has no multipole structure. When \( a \geq 1 \), then \( G_2(\bar{\omega}, \infty) \) gradually shows the multipole structure again and has a value less than 0.25 at \( \omega_0 \). As \( a \rightarrow 1 \) or as \( h \) goes to a delta function, \( G_2(\bar{\omega}, \infty) \) goes to \( G_2(\omega, \infty) \) with the hard core value growing in again. The usual NMRON experiment has \( \frac{H_1}{H_0} \approx 10^{-7} \) to \( 10^{-4} \); \( a \approx 10^{-3} \) and therefore \( G_k(\overline{w}, \infty) \) will be close to 1 and spread over a wide frequency range. This is the quantitative explanation for experimentally observing no effect with a single r.f. frequency. In order to see any effect there must be an integration over a large frequency range. One method for this integration is frequency modulation. This leads one to the conclusion that the size of the effect in NMRON is determined by the effectiveness of the frequency modulation and the magnitude of \( a \). Figure 4 shows a plot of \( G_2(\bar{\omega}, \infty) \)
\( \omega = \omega_0 \cdot H_t / H_0 = 10^{-1} \)
vs. a at $\omega_0$. This illustrates the existence of a hard core value even for inhomogeneously broadened lines. In concluding this section we note that Portis\textsuperscript{33} and Castner\textsuperscript{32} have developed similar discussions for electron paramagnetic resonance.

c. **Relaxation.** Consider a system of nuclear spins in contact with a lattice in such a way that energy can be transferred but they are essentially independent systems. This is true for metals at very low temperatures because even though the electronic relaxation or correlation times are very fast (about $10^{-10}$ seconds) the nuclear-lattice or nuclear conduction electron relaxation times are of the order of seconds.

At temperatures above 1°K it is well known that the spin lattice relaxation time for simple metals is inversely proportional to $T$, i.e., $T_1T = \text{constant.}^{34}$ We are interested in the temperature dependence at the relaxation time below 1°K. It has been experimentally observed that $T_1$ becomes constant at very low temperatures.\textsuperscript{35} There are at present at least two theories which quantitatively describe such temperature behavior of $T_1$.

The first of these by Brewer, Shirley, and Templeton,\textsuperscript{35} is easier to understand so it will be described first. The basic assumptions of their treatment are

1) an isotropic Hamiltonian,

2) lattice in thermal equilibrium

3) lattice is not disturbed by the spin transitions\textsuperscript{36}
They show the upward and downward transition probabilities of this type of spin system to be given by

$$w_{\pm} = C\langle f|l_{\pm}|i\rangle^2\langle m\mp 1|l_{\mp}|m\rangle^2\int_0^\infty f(\epsilon_i)[1-f(\epsilon_i+\gamma Hh)]d\epsilon_i$$

where $C$ is a temperature-independent constant which contains, along with other constants, density of states information. There are two temperature dependent effects which are contained in the integral of the Fermi functions, $f$. The first effect is the principle of detailed balance. It applies because the nuclear spins are in contact with the lattice. This means that as a spin makes a transition from $|m\rangle$ to $|m'\rangle$, the lattice goes from $|i\rangle$ to $|f\rangle$ conserving energy as required. If the lattice is in equilibrium with itself and is not disturbed by the spin transition then it follows that

$$w_{m+l \rightarrow m} = w_{m \rightarrow m+l} e^{\gamma Hh/kT}$$

The upward transition probability is inhibited as the temperature decreases to a value such that the thermal energy is comparable to the Zeeman energy. The solution to the integral can be written as

$$\left(\frac{\gamma Hh}{e^{\gamma Hh/kT}}\right)\frac{\gamma Hh}{e^{\gamma Hh/kT} - 1}$$

This implicitly contains the principle of detailed balance expressed above.
The second effect comes from the change in temperature dependence of $W_+$ and $W_-$ which is caused by Fermi statistics of the conduction electrons. Since energy must be conserved, the only electron transitions that are allowed are from states with energy $\epsilon_i$ to states with energy $\epsilon_i \pm \gamma \hbar$. For conduction electrons the number of such states is given by the Fermi function. See Fig. 5. Thermal excitation only affects the conduction electrons within $\sim kT$ of the Fermi energy and thus it is reasonable to expect that the number of allowable states at higher temperature would be proportional to $kT$. Explicit evaluation of the expression for $W_\pm$ reduces to this linear temperature dependence at high temperatures. When $\gamma \hbar \geq kT$ the full form of the integral must be used and leads to the differences in temperature dependence.

Figure 6 shows the temperature dependences of the evaluated integral.

In order to understand the relaxation behavior we will neglect the second effect for the moment and develop rate equations for the nuclear spin system. The master equation for the population of the nuclear spin levels can be written as

$$\frac{dN_m}{dt} = \sum_{m'} N_{m'} W_{m' \rightarrow m} - N_m W_{m \rightarrow m'} .$$

If we define the fractional departure from equilibrium as

$$n_m = \frac{N_m - \tilde{N}_m}{\sum N_m} .$$
SPINS

<table>
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<tr>
<th>W</th>
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LATTICE

<table>
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<th>ε+γHₚ</th>
<th>ε-γHₚ</th>
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FERMI FUNCTION $T = 0^\circ K$

$g(\epsilon)$

$\epsilon + \gamma H_p$ (ALLOWED)

$\epsilon - \gamma H_p$

TRANSITIONS 1 ARE ALLOWED
TRANSITIONS 2 ARE HINDERED

Fig. 5.
\[ \alpha = \gamma \beta \]

\[ \beta = kT \]

Fig. 6.
then this equation can be rewritten as

\[ \frac{dn_m}{dt} = \sum_{m'} n_{m'} W_{m' \rightarrow m} - n_m W_{m \rightarrow m'} \]

For magnetic dipole transitions only \( \Delta m = \pm 1 \) transitions are allowed.

Using this fact and the principle of detailed balance which is the label for the first effect we obtain

\[ \frac{dn_m}{dt} = n_{m+1} [I(I+1)-m(m+1)] W n_{m-1} [I(I+1)-m(m-1)] W Q - n_m [I(I+1)-m(m+1)] W Q - n_{m-1} [I(I+1)-m(m-1)] W \]

which can be condensed into the form

\[ \frac{dn_m}{dt} = + W \sum_{m'} A_{mm'} n_{m'}(t) \]

where \( A \) is a matrix having nonzero elements

\[ [I(I+1)-m(m+1)] \delta_{m,m'} , m' = m+1 \]

\[ Q[I(I+1)-m(m-1)] \delta_{m,m'} , m' = m-1 \]

\[ -[[I(I+1)-m(m+1)] Q + [I(I+1)-m(m-1)]] \delta_{m,m'} , m' = m \]

where \( Q = e^{-\gamma \hbar / kT} \). This rate equation can describe either growth or decay simply by a sign change. The presence of \( Q \) depends on whether the system is isolated, e.g., absorption of r.f. quanta, (then microscopic reversal makes \( Q = 1 \)) or in contact with a lattice where \( Q \) is as
stated above. The general solution has the form

\[ n_m(t) = \sum_{m'} \beta_{mm'} \exp(-\lambda_{m'} t) \]

where \( \lambda_{m}/W \) are the eigenvalues of \( A \) and the \( \beta_{mm'} \) are the components of the corresponding eigenvectors determined by the initial state of the nuclear spin system. We can define a vector \( \tilde{\eta} \) by the relationship

\[ \beta_{mm'} = C_{mm'} \tilde{\eta}_m \]

where \( C \) is a matrix of the eigenvectors with an arbitrary normalization (usually to 1). By inverting and using the above solution at time zero we obtain

\[ \tilde{\eta}_m = \sum_{m''} (c^{-1})_{m'm} \eta_{m''}(0) \]

Therefore,

\[ \beta_{mm'} = C_{mm'} \sum_{m''} (c^{-1})_{m'm} \eta_{m''}(0) \]

and

\[ n_m(t) = \sum_{m'} C_{mm'} e^{-\lambda_{m'} t} \sum_{m''} (c^{-1})_{m'm} \eta_{m''}(0) \]

We immediately see from this solution that the population time evolution depends on the initial state of the system and in general is not a single exponential but a sum of exponentials. In order to illustrate this behavior better we work through the \( I = 1 \) case. For the high
temperature case, \( Q = 1 \), the equation for decay gives

\[
A = \begin{bmatrix}
2 & -2 & 0 \\
-2 & 4 & -2 \\
0 & -2 & 2
\end{bmatrix} \cdot W
\]

which has eigenvalues \( \lambda/W = 0, 2, 6 \). After solving for the eigenvectors the \( C \) matrix is given by

\[
C = \begin{bmatrix}
1 & -1 & 1 \\
1 & 0 & -2 \\
1 & 1 & 1
\end{bmatrix}
\]

which inverts to give

\[
C^{-1} = \begin{bmatrix}
0.333 & 0.333 & 0.333 \\
-0.5 & 0 & 0.5 \\
0.167 & -0.333 & 0.167
\end{bmatrix}
\]

Now the time dependence of \( n_m \) can be solved for with various initial conditions. For example, take an equilibrium distribution at \( T = 0.01^\circ K \) (assuming no other temperature behavior for the moment) and equal population \( (T = \infty) \) after excitation, then

\[
\bar{n}_m(0) = \begin{bmatrix}
0.1707 \\
0.0368 \\
-0.2078
\end{bmatrix}
\]

Note that the constraint of \( \frac{d}{dt} \left( \sum m n_m \right) = 0 \) is built into the initial
conditions. Solving for the $\beta_{mm'}$ and the populations we obtain

$$n_1(t) = 0.189 e^{-2Wt} - 0.018 e^{-6Wt}$$

$$n_0(t) = 0.037 e^{-6Wt}$$

$$n_{-1}(t) = -0.189 e^{-2Wt} - 0.018 e^{-6Wt}$$

$B_k(t)$ is actually observed and it can be calculated from the equilibrium population and $n_m(t)$. Figure 7 illustrates the relaxation of $B_k$. The amplitudes of the various terms in the relaxation equations have positive or negative signs depending on the initial conditions which means oscillations can occur in the decay of the populations. $B_k$ is less sensitive because it sums over all the populations but still shows weak oscillations. For the aligned initial conditions at $1^\circ K$ only the amplitudes for $\exp(-6Wt)$ are nonzero. Since $W = 1/2 T_1$ at $1^\circ K$ this reduces to $\exp(-3t/T_1)$. This is a property of the initial conditions and has been experimentally observed by MacLaughlin and Butterworth in the measurement of $T_1 T$ for In metal by nuclear quadrupole resonance.

This effect of the initial condition is emphasized because it can be confused with another property of relaxation times which is characteristic of the rank of the tensor being observed. At high temperatures $T_1(\text{eff}) = T_1(k(k+1))$ which reduces to $T_1(\text{eff}) = T_1$ only for first rank tensors such as $\hat{M}$ or $B_1$. See Appendix II for a proof.

In order to show the sum of both effects the total equation must be used leading to curves for $W_+, W_-$ as shown in Fig. 8 reproduced from Brewer, Shirley and Templeton's paper.
Fig. 7.

$B_1(EQ) = -0.464$

$B_2(EQ) = 0.78$
Figure 8.
The usual definition of $T_1 = 1/2 W$ is a high temperature limit which also changes as the temperature is lowered. Using the spin temperature approximation D. A. Shirley and M. Odehnal have derived expressions for the general case. Odehnal's expression can be written in our notation as

$$\frac{1}{T_1} = \sum_{m,m'} W_{mm'} (E_m - E_{m'}) [1 - \exp\{(\beta_L - \beta_I)(E_m - E_{m'})\}] \exp(-\beta_I E_{m'})$$

where $\beta_L, \beta_I = \frac{1}{kT_L}, \frac{1}{kT_I}$ and $W_{mm'}$ corresponds to $W_{\pm}$. However, in general the spin temperature approximation is not a valid description of the initial state of the relaxation and therefore this expression doesn't apply. In this particular formulation $T_1$ will not have a unique definition.

Gabriel has also developed a theory to explain tensor relaxation at any temperature. Although it is more difficult to understand because of the Liouville formalism, it is a very general and elegant approach to spin-lattice relaxation. His basic assumption is that there is a weak coupling between the lattice and spins and that the lattice correlation time is very rapid compared with the spin-lattice relaxation time. In order to gain a primitive insight into the theory one can write down the time dependence of the density matrix operator, $\rho(t)$, as

$$\frac{d\rho}{dt} = \frac{-i}{\hbar} [H\rho - \rho H]$$
One can solve this by the usual Heisenberg method obtaining

\[ \rho(t) = e^{\frac{it\mathcal{H}}{\hbar}} \rho(0) e^{\frac{-it\mathcal{H}}{\hbar}} \]

but it can also be solved by means of Liouville operators. A Liouville operator is defined as follows: Given an arbitrary operator \( A \), another operator \( C \) can be constructed by the rule \( C = (\mathcal{H}A - A\mathcal{H}) \) or \( C = LA \) where \( L \) is called the Liouville operator. We see that \( L \) is the commutator with \( \mathcal{H} \). These operators can be represented by tetradics algebra very similar to ordinary matrix algebra. In the Liouville formalism the density matrix operator equation becomes

\[ \frac{d\rho}{dt} = -\frac{i}{\hbar} L\rho \]

with the solution

\[ \rho(t) = e^{\frac{-itL}{\hbar}} \rho(0) e^{\frac{itL}{\hbar}} \]

The Liouville formulation has two advantages, one being the compactness of the perturbation expansions, e.g., in some treatments of relaxation a perturbation expansion is made of \( \exp(-it\mathcal{H}/\hbar) \). (See for example Wangness and Bloch.) In the Liouville case it is on only one side of \( \rho(0) \). The second advantage is that it can easily be solved and handled by Laplace transforms. Gabriel combines this technique with a multipole relaxation theory and works in a space spanned by general tensor operators, \( U^k_N \). He separates the effect of the lattice on the spins into a relaxation operator which is a sum of spectral density functions. For
dipole transitions, $T \equiv$ is defined as

$$T \equiv = 2\gamma^2 N J_{11}(\omega_L)$$

$$J_{11}(\omega_L) = -\frac{1}{2} \int_{-\infty}^{\infty} \text{d}t \text{e}^{i\omega t} \left\langle \frac{1}{2} [h^+(t), h^-(0)]_R \right\rangle_R$$

and

$$h = H_{\text{eff}} - \langle H_{\text{eff}} \rangle_R; R = \text{bath parameters.}$$

The spectral density functions are the Fourier transforms of the second order correlation functions of the fluctuating magnetic fields. These spectral density functions have Fermi statistics implicitly in them as shown by Bernard and Callen in their treatment of the fluctuation dissipation theorem in irreversible thermodynamics. The theory gives the relaxation of $B_{k'}$ as

$$\Delta B_{k'}(t) = B_{k'}(t) - B_{k'}(\text{eq}) = \sum_{k'} G_{k'k'}^{00}(t) \Delta B_{k'}(t = 0),$$

where $G_{k'k'}^{00}$ is the axial symmetric relaxation operator. This can be written as

$$\Delta B_{k'}(t) = \sum_{k'} (U_{k'}^k | U_{k'}^0) e^{-\Lambda_{k'} t} \sum_{k''} (U_{0}^{k''} | U_{0}^{k''}) \Delta B_{k''}(t = 0),$$

where $(U_{k'}^k | U_{k'}^0)$ is a matrix with $\Lambda_k$ as its eigenvalues. This is
mathematically totally analogous to the previous treatment with a different matrix. The relaxation is a sum of exponentials with decay constants dependent only on temperature and amplitudes dependent on both temperature and initial conditions. The theory is too elaborate and complex to present in detail but the reader can refer to Gabriel's paper and the references therein for further details.

It should be emphasized that Gabriel's approach does not assume a spin temperature and that $T_1$ is defined over the entire temperature range. We conclude that if the initial conditions are known $T_1$ can be measured consistently over the entire temperature range.

d. **Frequency modulation.** We found in a previous section that it is necessary to frequency modulate in order to see any signal at all in NMRon because of the very small homogeneity ratio. We must describe frequency modulation in such a way that the effective integral over the inhomogeneous line can be performed. A sinusoidal modulation given by

$$e = E_0 \sin(\omega t + \sin \omega_{\text{mod}} t + \phi)$$

is usually written as an infinite series of sums and differences of the carrier and modulating frequencies with the amplitudes given by Bessel functions of proper index and argument. This description will be impractical if the phase memory time of the system is shorter than $(\text{modulation frequency})^{-1}$.

Another way to look at frequency modulation is to picture the rotating frame to be rotating at an instantaneous frequency given by
the carrier frequency. Sinusoidal modulation becomes a non-linear change in the rotating frame's frequency while triangular modulation becomes a linear change over the $\Delta \omega$ caused by the amplitude of the modulation signal. The mathematics of this approach are much more obscure but it can be applied at any modulation frequency.

The experimentally observed $\gamma$-ray intensity along the symmetry axis, $\theta = 0$, can be written as

$$W(0) = \sum_{k} A_k B_k P_k(0) = \sum_{k} A_k G_k B_k$$

where $A_k = U_k F_k Q_k$ and $P_k(0) = 1$ for all $k$. $U_k$ and $F_k$ were defined earlier and $Q_k$ is a solid angle correction. $B_k$ is the orientation parameter and $G_k$ is the perturbation coefficient described in the section on response. The signal describing the effect of modulation can be written in terms of $\gamma$-ray intensities as

$$S = \frac{C_{\text{mod}} - C}{C - W}$$

where by definition,

$$C_{\text{mod}} \equiv W(\theta = 0, \text{nuclei oriented, r.f. on, modulation})$$

$$C \equiv W(\theta = 0, \text{nuclei oriented, r.f. on, no modulation})$$

$$W \equiv W(\theta = 0, \text{nuclei not oriented})$$

For $I = 1$, noting that $B_k = 0$ for $k > 2I$, we have
\[ \begin{align*}
C_{\text{mod}} &= 1 + B_2 A_2 \overline{G}_2(\omega) \\
C &= 1 + B_2 A_2 \overline{G}_2(\bar{\omega}) \\
W &= 1
\end{align*} \]

Therefore
\[ S = \frac{\overline{G}_2(\bar{\omega}) - G_2(\bar{\omega})}{G_2(\bar{\omega})} \]

and can be recognized as the normalized ratio the response function with and without modulation. \( G_2(\bar{\omega}) \) was defined in the section on response as the response function including inhomogeneous broadening. \( \overline{G}_2(\bar{\omega}) \) can be written as
\[
\overline{G}_2(\bar{\omega}) = \int_{\omega_0 - \frac{\Delta \omega}{2}}^{\omega_0 + \frac{\Delta \omega}{2}} G_2(\bar{\omega},t')d\omega_{\text{mod}}dt
\]

where \( \oint \) is a time integral over one modulation cycle.

Figure 9 will help elucidate the discussion. Part I of Fig. 9 shows the inhomogeneous line made up of small homogeneous spin packets which have a response function as indicated. Part II illustrates the frequency change during modulation and the timing involved. \( \oint \) in the expression for \( \overline{G}_2(\bar{\omega}) \) is the integral over all combinations of \( T' \) in Fig. 9. The second time variable that must be taken into account is the total time the modulation is left on which is represented by \( dt \) in the expression for \( \overline{G}_2(\bar{\omega}) \). Instead of the time-integral value
Fig. 9.
of $G_2(\omega)$ shown in part I, time-differential values of $G_2(\omega)$ must be used with this time equal to $T'$ or $\frac{2\pi}{\omega_{\text{mod}}} - T'$. This is further complicated because the frequency dependence of the time-differential $G_2(\omega,T')$ changes as $T'$ changes. In addition to this, we must devise a method which maintains the right amount of memory between the times $\omega(\text{modulated} = \omega_0(\text{of small packet})$. This coupling between frequency change and time change along with memory makes direct calculation of $G_2(\omega)$ difficult. We can propose a simple model to estimate the effect of $T_1$ on the magnitude of the frequency modulation signal. It is easier to go back to the homogeneous line and calculate the response function for frequency modulation and later add the effect of inhomogeneous broadening. We start with a single passage through a spin packet responding as if it were located at $\omega_0$. Consider a spin in this spin packet along the $z'$ axis at $t = 0$. If we pass through the resonant frequency the spin will be rotated by some amount depending on $H_1$ and the time that $\omega$ is within $\omega_1$ of $\omega_0$. After going off resonance the spin will precess again, only now it has a reduced $z'$ component, and a $x'$ and $y'$ component as well. There will be a tendency for the $z'$ component to relax back to its $t = 0$ position with time constant $T_1$. If the r.f. frequency hits right at $\omega_0$ the next time, then there is again a precession with the $z'$ components having the tendency to be moved further down but with the $x'$ and $y'$ components going any direction in space depending on their position in the rotating frame with respect to $H_1$ i.e., the phase relation. Therefore there is actually a certain probability that the spin will move back. The memory will be the length of time the decrease in the $z'$ component achieved in
the former passages through $\omega_0$ is maintained. The limit on this memory will be the spin lattice relaxation time.  

If we consider populations of spin levels we can take an initial distribution and calculate $B_2$, then turn on the r.f. at $\omega_0$ for a time equal to the time it takes to pass through the homogeneous line to obtain a new population distribution. Now we can allow spin-lattice relaxation until the next pass through. The relaxation gets stronger as the deviation from the initial distribution gets larger so a steady state will eventually be reached. This model assumes $T_1$ is much greater than the time to pass through the homogeneous line. This is very reasonable because for the ratio of $H_1/H_0 = 10^{-3}$ to $10^{-4}$ the homogeneous line is very narrow and therefore $\Delta t$(passage) is very short even at the lowest modulation frequencies. In order to illustrate this model the following calculation was performed. A square spin packet of width $\sqrt{2} \omega_1 \approx 0.5$ kHz was located at $\omega_0$, the center of the inhomogeneous (Gaussian) line of width $\Delta \omega_G = 628$ kHz. The modulation frequency was 25 Hz. The time the r.f. was on the spin packet was $t' = \frac{\sqrt{2} \omega_1 \pi}{(\Delta \omega_G) \omega_{\text{mod}}}$ and the time off the spin packet was $t'' = \frac{\pi}{\omega_{\text{mod}}} - t'$. The populations change according to the Majorana factors during the time $t'$ and relax with time constant $T_1$ during the time $t''$. The initial population was for $I = 1$, $g = 0.75$, $T = 0.002^\circ K$, $H = 219.0$ Koe. The r.f. and relaxation were turned on sequentially using the population from the preceding process until a steady state was reached.  

Curves illustrating the result of this calculation for a specific case are shown in Fig. 10. There is indeed a saturation lower than
Fig. 10.

\[ \frac{\Delta B_2}{B_2} \]

- \( I = 1 \times 10^3 \)
- \( \gamma N = 3.59 \times 10^3 \)
- \( H_0 = 1 \text{ G} \)
- \( H = 1 \text{ G} \)
- \( \Delta \omega_0 = 25 \text{ Hz} \)
- \( \omega_0 = 125 \text{ MHz} \)
would be achieved on a single passage with an equivalent sum of $H_\perp$ or $t$. The saturation value depends on $T_1$, $H_\perp$, and the modulation frequency. The relaxation behavior assumed here is the free decay theory. The applicability of this depends on the ensemble density matrix having only diagonal elements.

For a large inhomogeneously broadened ensemble it has been shown by Abragam that the off-diagonal elements of the density matrix decay with a time $T_2^*$ characteristic of the width of the inhomogeneous line (microseconds) rather than the homogeneous line (seconds). This simply means the $x, y$ coherence of the total sample will be lost extremely rapidly, even if it were possible to move it coherently in the first instant.

This model leads to another method of measuring $T_1$. In the section on relaxation and countless other times in this thesis it was pointed out that the initial conditions are extremely important in obtaining a true $T_1$ by the free decay model. This is difficult (practically impossible) because in order to know the amplitude of $H_\perp$ at the nucleus, one must integrate $H_\perp$ attenuated by the skin depth over the depth of the sample and accurately know the enhancement factor. This is also complicated by the microscopic fluctuations in the surface which cause inhomogeneities in $H_\perp$, e.g., via demagnetizing factors. Frequency modulation also makes it difficult to calculate exactly what $H_\perp$ is at the nuclear site. However, all of these effects should be independent of the amplitude of $H_\perp$ and only weakly dependent on temperature in the range of interest. Therefore we can write
\[ H_1^{\text{effective}} = \xi H_1^{\text{applied}} \]

and

\[ S = F(T_1 T; \xi H_1^{\text{applied}}) \]

where \( S \) is the modulation signal observed for a given crystal orientation, constant \( H_0 \), and constant modulation frequency. \( F \) is a function representing the model proposed above extended to all time combinations including frequency dependence and \( \xi \) is a constant containing all of the unknown \( H_1 \) effects. By measuring \( S \) at two different values of \( H_1^{\text{applied}} \) at the same temperature one can solve for \( T_1 \) and \( \xi \) eliminating the necessity of knowing the initial conditions. The temperature dependence can then be obtained by measuring \( S \) as a function of temperature at constant \( H_1^{\text{applied}} \). The sensitivity of the method is limited and the accuracy depends on a measurement of \( H_1 \) but within these limitations the value obtained will be correct. If both methods are combined there is the possibility of obtaining both accurate and precise \( T_1 \) values.

e. Frequency dependence. The inherent frequency dependence of the effect is of interest because experimentally it has been difficult to observe resonances very much above 210 MHz. The detection of NMR observes the direct absorption of power. In the Section on ferromagnets we found that the power absorbed from the r.f. field is proportional to \( \omega \) and to \( H_1^2 \). The frequency dependence of \( H_1 \) arises from the skin effect and the enhancement factor. As also seen in a
previous section the frequency dependence of the enhancement factor comes from the ratio \((\omega/\omega_0)\) where \(\omega_0\) is the electron Larmor frequency. This ratio is much less than 1 except in rare cases when the ferromagnetic resonance frequency approaches the nuclear frequency because of anisotropy. Therefore the skin effect is the only factor of concern. The classical skin depth is proportional to \(\omega^{-1/2}\) if we are not in the anomalous region. This would give \((\omega)(\frac{1}{\omega}) = 1\) or no frequency dependence if we are not in the anomalous region and the response curve is \(H_1\) limited. If the linewidth of the homogeneous response function was limited by \(T_1(H_1 \leq 10^{-5} \text{oe in dilute alloys})\), then the frequency dependence would be given by \((\omega)(\frac{1}{\omega}) = \omega^{-1}\) since \(T_1\) is proportional to \(\gamma_N^2 H_1\). In the previous section we found that the effect was \(T_1\) limited for frequency modulated inhomogeneous lines. Therefore, inhomogeneous lines will lead to a inverse frequency dependence of the effect.

At room temperature the anomalous skin depth frequency for a pure ferromagnet is in the many GHz region. By lowering the temperature the electron mean free path will increase and the frequency will decrease. The resistivity ratio is a measure of this effect. For pure polycrystalline samples the resistivity ratio is only of order 2 - 10 and therefore will only reduce the frequency by a factor of 1.4 to 3.3. Pure single crystals have a much higher resistivity ratio and the reduction will be much larger. Experimentally, Rodbell \(^{45}\) and Bhagat and Hirst \(^{46}\) have observed the onset of the anomalous skin depth slightly below 770°K in FMR experiments on Fe and Ni whiskers at 9 GHz. In the latter
case they had a resistivity ratio $\frac{\rho(300)}{\rho(4)}$ of only 30 which is probably the magnitude for the pure single crystals that have been used in NMRO. We know thermal conductivities decrease approximately linearly in temperature down to 0.01°K but the residual resistance sets in at about 4 - 10°K. Therefore the resistivity ratio should still be about 30 at 0.01°K. Estimating $\frac{\rho(300)}{\rho(77)} = 5$, the anomalous frequency would become $\frac{\omega_{NMR}}{\omega_{FMR}} = \sqrt{\frac{5}{30}}$ or $\omega_{NMR} = 3.5$ GHz. This is far above the region of interest in NMRO.
B. Experimental

1. Requirements

A typical, successful NMRON experiment must fulfill a series of conditions. First, the nuclei must be oriented at some equilibrium temperature long enough to do NMR on the sample. The conditions for N.O. are as follows:

(1) A suitable nucleus must be chosen, i.e., it must have a reasonable half life (usually at least a day), a reasonable decay scheme ($I \geq 1$ for $B_2$) and magnetic moment large enough to produce anisotropy with the available $H$ and $T$.

(2) The atom picked must have suitable metallurgical properties. This normally means that it form a good solid solution in the host metal however implantation techniques are reducing this restriction. The additional conditions for NMR are as follows:

(3) The sample must be thin due to the skin depth limitation on $H_1$ penetration.

(4) The sample must be of reasonably high purity (0.01 - 0.5% impurities) in order to avoid destroying the resonance due to large field inhomogeneity.

(5) The nuclear condition becomes more restrictive because the $g$ factor must be suitable in order to avoid high r.f. frequencies which lead to problems as can be seen from the previous section on the frequency dependence of NMR in inhomogeneous ferromagnets.
2. **Apparatus**

Low temperature techniques have developed substantially in the past few years so the apparatus will be described in more detail than usual. Explanation of Fig. 11 will provide the best format.

The 4°K helium dewar is made of 1/4 inch thick aluminum outer wall and 0.035 inch stainless steel inner wall. It has a liquid nitrogen tank (not shown) between the two walls. There is a common vacuum with "superinsulation" (aluminized mylar) wrapped between the 4°K and 77°K walls and again between the 77°K - 298°K walls. Once it is leak tight the dewar can be pumped to $1 \times 10^{-5}$ mm. at room temperature which provides good insulation at 4°K. It has a helium volume of 21 liters and if the magnet leads and other heat leaks are minimized the dewar will keep the magnets superconducting (18°K) for about 36 hours. The 1°K dewar is formed by adding a 0.035 inch brass jacket to the lower two-thirds of the 0.025 inch thick stainless steel tube and adding a pumping tube for evacuating the walls. In a typical run about 280 mm. of helium gas is added to the 1°K dewar walls at 298°K and pumped out at 4°K. It takes about 1 hour to pump back down to $1 \times 10^{-5}$ mm. pressure between the walls.

The volume of the 1°K helium pot is 3.75 liters and if filled with everything in equilibrium at 4°K it has a 1°K helium pot life of 12 hours if it is pumped down at a reasonable rate (20 - 45 minutes).

The magnets are all made from 0.015/0.030 inch T48B Supercon wire i.e., 0.015 inch diameter niobiumtitanium covered to 0.030 inch diameter with copper. The copper is surface-oxidized and then wound onto forms which are made from Cu for the polarizing magnet, brass for
Fig. 11.
the compensating magnet, and mu metal for the cooling magnet. The mu metal is required because there is a residual field in the cooling magnet. The net field is zero but only when averaged over the total volume. There are local flux peaks up to approximately a hundred gauss (as large as ± 255 g in one measured case). The mu metal reduces the residual field over the cryostat area to less than 10 g everywhere. The dipolar field in CMN, cerium magnesium nitrate, is 60 oe. and so 10 g is no problem.

The cryostat pumping tube is 1-1/2 inch o.d. stainless steel with a 0.020 inch wall. The cryostat is brass with 0.035 walls. All joints are made with hard solder which is not superconducting or the eutectic BiCd (40% wt. Cd, 60% wt. Bi) solder which has a critical field and temperature of about 30 oe. and 0.5 K.50

The r.f. coil is located between the inside wall of the polarizing magnet and the outer wall of the 1K dewar. It is made of three turns of 0.040 inch diameter copper wire in a 0.75 inch circle on each side of the dewar. The r.f. coil is attached to a coaxial stainless steel thinwall tubing (3/8", 1/4", 1/8", 1/16" O.D. with 0.01 to 0.006" wall) transmission line. It was made with a final impedance of about 60 ohms which closely matches the oscillators used in the experiments. Attempts were made to tune the coil to a Q of 10 - 20 but the close proximity of the Cu form of the polarizing magnet increases the reluctance of the magnet circuit, i.e., the flux cannot travel as freely as it would if the form were further away, and therefore the effective inductance is decreased. This effect can be taken into account with
appropriate length line but the eddy currents losses in the Cu also
must be supplied by the coil thus increasing the effective resistance
of the coil. There is also a smaller coil inside one of the big coils
which is calibrated with a third coil of standard dimensions placed in
the sample position preceding the experiments. Typical voltages on the
sensing coil are millivolts. The 1⁰K dewar and cryostat tips are all
glass to allow r.f. penetration. Since Housekeeper seals (Cu-pyrex)
will eventually crack due to copper's work hardening on repeated heat
cycling, kovar (Co, 31%, Fe, 56%, Ni, 29%)—pyrex seals were used. They
are far enough from the sample so the magnetic properties are of ne-
gligible influence.

The heart of the apparatus is shown in Fig. 12. The CMN
(cerium magnesium nitrate; Ce₂Mg₃(NO₃)₁₂·24H₂O) pill is made by grinding
up single crystals to a fine powder, at least a NBS#50 gauge sieve, and
mixing with glycerol to form a slurry. This is thermally guarded by
a C.A. (chrome alum; CrK(SO₄)₂·12H₂O) pill above and below with a copper
shield connecting the two. The supports are pitch-bonded graphite⁵²
and the base plates for the parts of the assembly are fiberglass. The
walls of the bottom CA pill are 0.010" mylar. Joints are made with
small brass screws and sealed with epoxy.⁵³ The thermal link to the
sample is made with Cu wires or Cu fins whichever will maximize the
contact area with the CMN. In the case shown there are 18 fins made
from 0.005" Cu that is 99.999% pure. They have a total contact area
with the CMN of 1600 cm². The sample is attached with BiCd solder. There
are two points of interest which D. Shirley has emphasized and,
if mentioned, they may save some blood, sweat, and tears for some
Fig. 12.
future graduate student. The first is that there should be a tortuous path for the heat flow into the CMN pill, i.e., one should force the heat to go through the CA. guard pill. The outer 0.010" mylar is the only direct path in the above apparatus and should be a negligible leak because of its low thermal conductivity and the CA in contact with it. The second point is one of shielding the entire CMN system with CA or copper anchored in CA. This point is extremely important in any system using exchange gas. The following approximate calculation illustrates why.

In pumping down the inner bath from 4°K to 1°K with exchange gas present, there is a pressure drop of about $1 \times 10^{-2}$ mm to $5 \times 10^{-5}$ mm. This is a change of about $2.5 \times 10^{-3}$ mm after the expected factor of 4 is taken into account. Using $\Delta n = \frac{\Delta PV}{RT}$ to estimate the amount adsorbed we get

$$\Delta n = \frac{(2.5 \times 10^{-3})(2.4)}{(760)(0.082)(2.5)} = 3.92 \times 10^{-5} \text{ moles.}$$

$V_{total \text{ system}} = 2.4$ liters and 2.5°K were used because the system has temperatures ranging from 1°K to 298°K but the adsorption takes place between 4°K and 1°K. We assume most of this was adsorbed in the cryostat since the stainless steel pumping tube is clean and polished and is only a small part of the apparatus at 1°K. The total surface area in the cryostat is $1560 \text{ cm}^2$. The walls that remain at 1°K upon demagnetization make up 600 cm$^2$ of this area. The amount of He$^4$ gas absorbed per unit area for this cryostat is

$$\frac{3.92 \times 10^{-5} \text{ mole}}{1.56 \times 10^3} = 2.5 \times 10^{-8} \text{ moles/cm}^2.$$
In Fig. 12 the design shown has about $42 \text{ cm}^2$ of unshielded CMN system in the heat link. If we assume 50% will come off (estimated from the accommodation coefficient) and a 10%/hour cryopumping efficiency which probably is an underestimate since the pressure drops very rapidly upon demagnetization, the heat leak is

$$Q = \frac{(2.5 \times 10^{-8})(42)(70)(4.18 \times 10^7)}{(2)(3.6 \times 10^3)(10)} = 0.043 \text{ erg/sec} = 2.6 \text{ erg/min.}$$

The heat of absorption is 70 cal/mole. In a well shielded assembly we obtain a final temperature of about 5 millidegrees K and we assume a heat leak of about 1 erg/min. From the H/T that we have CMN powder should cool to about 2.5 m°K. Calculating a total thermal impedance we obtain

$$R = \frac{\Delta T}{Q} = \frac{0.0025}{0.016} = 0.155 \frac{\text{°K sec}}{\text{erg}}.$$  

Assuming the same thermal impedance the unshielded case reaches 13 m°K and yields

$$Q = \frac{\Delta T}{R} = \frac{0.105}{0.155} = 0.068 \text{ erg/sec} = 4.1 \text{ erg/min.}$$

The difference is 3.1 erg/min and this is the order of magnitude of the cryopumping heat leak. After adding a shield to cover the entire CMN part of the cryostat, the CMN heat link reached 3.8 m°K and stayed below 10 m°K for up to nine hours.

The final part of the apparatus is the external pumping system. There are three parts; one for the cryostat, one for both dewars, and one for the 1°K bath. The cryostat is pumped by a 160 liter/sec Consolidated Vacuum oil diffusion pump using Dow Corning 704 diffusion pump oil which is backed by a 150 liter/min Precision Scientific Model 150 mechanical pump. The dewars are pumped with a Welch Duo Seal.
1402 KGB(5cfm) mechanical pump. The helium bath was pumped down to 10K (60 - 120 μ) by a KMBV 1250 Kinny vacuum pump and the pressure monitored with a U. S. Gauge Co. 15-30" pressure vacuum gauge and a McLeod gauge. The pressure in the dewar walls and cryostat is monitored with a Philips gauge and NRC thermocouple gauges.

3. Sources

One of the most difficult stages of a NMRON experiment is source preparation. For N.O. the samples usually are polycrystalline and the order of 0.001" thick for gamma sources since the major considerations are good thermal contact, good thermal homogeneity, and in some cases, minimal radiation absorption. NMR adds two additional conditions, namely, skin depth and resonance linewidth. This requires thin samples (of the order of the skin depth) and also polished, high purity single crystals. The source preparation techniques evolved over a period of a year for these experiments and will now be described.

The first technique used Fe or Ni foils of about 20,000 Å thick with diffusion of the activity into them. Using the solution of Fick's second law of diffusion, \( \frac{3c}{\delta t} = D \frac{3c}{\delta x^2} \), for the proper boundary conditions and calculating the mean square displacement one obtains \( \Delta x^2 = 2Dt \). D is usually tabulated as \( D = D_0 e^{-Q/RT} \) and if D is known the diffusion distance can be calculated. For example, in order to diffuse Co 10,000 Å into Ni, approximately 2 hours at 900°C is the treatment required. Diffusion is not a reliable method of preparing sources in some cases because grain boundary and dislocation diffusion can result in the activity going to a poor lattice site. This is usually detected
by less anisotropy than expected or discrepancies in the $0^\circ$ and $90^\circ$
anisotropies. In order to avoid this the samples were melted and then
rolled to the desired thickness with a small hand operated roller.\textsuperscript{66}
Mo or Ta was used as a holder but anything slightly harder than the
material to be rolled works. The secret for good Fe and Ni foils is
several annealing stages as they are rolled and a good final anneal.

If one wants to use single crystals there are three available
alternatives; bulk single crystals, vapor deposited single crystal films
and electrodeposited single crystal films. Single crystals of 99.999\%
purity can be purchased from Materials Research Corporation.\textsuperscript{67} They can
be oriented using the back-reflection Laue method. Source-size crystals
(usually the order of millimeters) can be cut from the stock rod with a
spark cutter.\textsuperscript{68} They are then prepared by mechanically polishing with a
series of papers down to 0000 grade and finally diamond polishing to 1
micron particle diameter. Just before adding the activity they are
electropolished with various baths\textsuperscript{69} to a final finish which is usually
observed under a microscope with 400X magnification. The final surfaces
have scratches of 0.1 to 1.0 micron depending on how carefully everything
is done. The activity is again diffused into the crystal. The biggest
problem with these sources is calculating the demagnetizing factors.
This difficulty can be avoided by using films and applying $H_0$ and $H_1$ in
the plane of the film. Vapor deposition of Fe, Ni, or Co onto a single
crystal of freshly cleaved, heated NaCl will result in a single crystal
film of the ferromagnet.\textsuperscript{70} The secret here is to heat the highly dis-
located NaCl up to about 600°C for a few minutes in high vacuum, then
cool it to about $300^\circ$C and vapor deposit the sample by opening a shutter. Although the literature is full of recipes and contradicting observations about the parameters of this system we found the key to be the dislocation density of the NaCl. G. A. Somorjai has found the rate of evaporation of NaCl to be controlled by the dislocation density and Hyder and Wilkov have shown conclusively that it is also the main parameter in single crystal formation. In a purchased single crystal of NaCl the average density is $10^5$/cm$^2$ and $10^7$/cm$^2$ are required for good single crystal films. Our results with Fe agree with this. This technique has the drawback that it is very difficult to remove the film from the NaCl and put it undamaged onto Cu.

The last technique used was electrodeposition onto Cu single crystal substrates. As far as the literature shows, this technique has not been successful with Fe but has worked with Ni and Co. D. Callahan has worked out all the details for Ni on Cu and I have done this for Co and Cu. The Cu substrates are prepared by mechanical and electropolishing. The plating is done from a sulfate bath (pH 3.5 for Co) at 50-300 μamps/cm$^2$. The films were checked with a Perkin-Elmer X-Ray diffractometer. Excellent results are obtained if the Cu substrate is prepared carefully and the plating process is controlled continually. The major advantage of this method is that the film is already on Cu which is necessary for mounting into the cryostat. There is a question about the strain between the Cu and Co or Ni but this is discussed below. One last note should be made about adding activity in the various methods. The last two methods use coprecipitation of the activity as
the film is formed and so good alloys are expected. The diffusion method usually requires the activity plated onto the host and melting requires plating or direct addition of the activity. With Fe and Ni another convenient and specific approach is to produce the activity in situ by a \((n,\gamma)\) reaction. This works in many cases because of the small neutron cross sections and the relative abundances of the competing Fe and Ni isotopes.

4. Detection System

The basic counting system consisted of a NaI or Ge (Li) gamma ray counter with appropriate preamplifier which was connected to a linear amplifier with a single channel analyzer. The output of the SCA was fed into a pulse height analyzer.

The basic r.f. system consisted of a Hewlett Packard Model 608-F or Marconi Instruments Model TF1066B/6 oscillator with a Hewlett Packard 5245L frequency counter. The Marconi had internal sine wave frequency modulation up to 400 kHz at 1 or 5 kHz modulation frequency. The HP 608-F had an external frequency modulation input which was -3 to -40 volts of any shape. An EXACT Model 250 function generator with a d.c. bias was used to frequency modulate the 608-F. The effective coil impedance was large so the r.f. had to be amplified in

* The oxidation potentials have to be similar otherwise one of the species will plate out first; e.g., Cu and Ni won't work in 1% Cu in Ni.
order to obtain sufficient $H_1$. This was accomplished by using a wide band amplifier. The voltages on the input coil and pickup coil were measured using a Tektronix type 661 oscilloscope.

For time-differential measurements a time base oscillator (TIBO) was used having a time range of $10^{-5}$ to $10^3$ seconds. For $T_1$ measurements the r.f. was on all the time and the modulation was turned on for a certain length of time during the sweep. The small effect in some cases and/or fast relaxation times required many sweeps. Figure 13 shows the electronic schematic for this general case.
III. THE EXPERIMENTS

The following experiments were performed during the same period of time that the theory was developed. They illustrate the principles involved in NMRON as described in the theoretical sections and lead to a good understanding of the system and its application to measurement of nuclear spin lattice relaxation times.

A. Co in Ni

Co$^{60}$ is almost an ideal NMRON case. Figure 14 shows the decay scheme plus other pertinent data. It was used in all but one of the following experiments.

The first experiment was done on Co$^{60}$ in polycrystalline Ni. The Co$^{60}$ was purchased from New England Nuclear and was found to contain several ppm Al. Therefore all of the Co$^{60}$ was purified by running it through a Dowex 1 × 8 100 - 200 mesh anion exchange column. The Co sticks at 10M HCl while all impurities of importance except Fe go through. By reducing the concentration of HCl to 4M, Co can be removed while retaining all the Fe. A solution containing several microcuries of activity was evaporated to dryness on 99.99% pure Ni foil. This sample was then put in a quartz tube inside the induction furnace coil and heated to 700°C with an H$_2$ pressure of 1 torr for three hours. After this the pressure was lowered to $1 \times 10^{-6}$ mm and the activity was left to diffuse for 10 hours. The sample was finally melted in 200 microns H$_2$ and rolled to 0.001" thickness before annealing for 1 hour at 950 - 1025°C in 100 - 200 microns H$_2$. The second rolling took it to 69,000 Å before annealing, then to 16,000 Å, and a final anneal of
$5.26 \times 10^3$ (G-SEC)$^{-1}$

$U_2F_2(1173) = U_2F_2(1332) = -0.420$

$U_4F_4(1173) = U_4F_4(1332) = -0.243$

$\gamma_N = 3.592 \times 10^3$ (G-SEC)$^{-1}$

$H_{\text{HYPERFINE}} (0^\circ K)$

CoNi f.c.c. = -120.9 kOe
CoCo f.c.c. = -219.8
CoCo h.c.p. = -228.4$

CoFe b.c.c. = -290.1$

* REF 81
** REF 84
12 hours at 900°C. A 0.5 cm² circular sample was cut and counted to yield 60,000 counts/minute in both Co⁶⁰ peaks at 10 cm with a 3" × 3" NaI detector. This foil was soldered onto Cu with BiCd solder and "Rotomet" flux. Care was taken to keep flux off the top surface and to keep it as smooth as possible. It was washed in alcohol and put into the cryostat within two hours. The sample was cooled to $1/T = 150 - 185\,\text{K}^{-1}$ as indicated by the γ ray anisotropy. With $H_0 = 1\,\text{Koe}$, the resonance was searched for in the range of 64 - 73 MHz with the results shown in Fig. 15. The large power change which is inherent in any frequency dependent impedance obscured the resonance. The major conclusion was that the line was very broad.

In order to overcome the broad line the obvious experiment was Co⁶⁰ in a bulk Ni single crystal. A Materials Research 99.999% pure single crystal was oriented, cut and mechanically polished into the shape of a flying saucer with the long axis in the (111) plane. It was electropolished using Tegart's $H_2SO_4$ solution at 50 volts and 0.55 amps for 6 minutes. The surface was bright and shiny to the eye but showed shallow pits of about $10^5\,\text{Å}$ in diameter under a microscope. The final dimensions were 1cm diameter by 1.9 mm thick at the center.

A solution of CoCl₂ (pH 7) with activity was evaporated onto a small spot at the center of the crystal. The activity was reduced at 725°C for 9 hours with H₂ flowing over it continuously. Two quartz tubes, one inside the other, were used in a horizontal tube furnace with the sample in the inner most one. A thermocouple was located at the sample position in the outer one in order to obtain a reasonably
$H_i$ CONSTANT = 2.4 mOe
$H_o$ = 10.27 Oe
$\Delta \nu_{FM} = 2.67$ MHz
$\nu_{FM} = 1$ KHz

INPUT VOLTAGE CONSTANT

FREQUENCY (MHz)

W (COLD)
accurate temperature measurement. After reduction at 725°C, the temperature was raised to 985 - 1000°C for 25 minutes and then cooled rapidly to about 800°C with slow reduction to room temperature for annealing. Under these conditions the mean diffusion distance is about 10,000 Å. The surface was electropolished again for 7 seconds at 50 v and 0.6 amps to remove any undiffused surface activity. The final source had about 100,000 counts/minute in 2 x 3 x 3" NaI counters at 16.5 cm. The demagnetizing field was calculated to be 807 oe. using Osborn's tables. Figure 16 shows the magnetization curve illustrating the difficulty in getting an accurate value of DM. The resonance shown in Fig. 17 was found by stepping the frequency in 0.2 MHz steps with 390 kHz modulation bandwidth, \( \Delta v_m \). This is the total deviation in \( v \), i.e., \( v = v_0 \pm 195 \text{ kHz} \). \( T_1 \) measurements were performed by the free decay method but the resonance was so small that it was extremely difficult to measure anything but temperature-integral values. The r.f. coil was re-built in the interim period to eliminate a power resonance. The power level for these measurements was increased to a optimum point where the warm-up rate was obvious but not sufficient to completely dominate the \( T_1 \) curve. The value found by a single exponential fit to the data was \( T_1T = 0.078 \pm 0.01 \text{ sec} \) measured in the region of \( 1/T = 130 - 165 \).

The third experiment with Co\(^{60}\) in Ni used a sample that was prepared by electrodeposition of a single crystal of Ni onto a Cu single crystal. The Cu (110) surface (0.5 cm\(^2\) area) was prepared by very carefully mechanically polishing down to 1 micron diamond particles and then a final electropolish for about 12 minutes at 1.6 volts and 8
Fig. 16.
$^{60}\text{Co}$ in Ni (111)
$H_{0} || [100] = 1247 \text{ Oe}$
$H_i = 2 \text{ mOe}$
$\Delta \nu_{FM} = 390 \text{ KHz}$
$\nu_{FM} = 1 \text{ KHz}$
$W(WARM) = 106,000$

Fig. 17.
milliamps. The Cu was removed from the polishing bath with the potential on the circuit, quickly washed with H₂O to prevent a film formation, then immediately transferred without drying to the plating solution after potential had been applied in that circuit. This causes a current surge up to about 300 microamps initially but after a few seconds the current drops to 50 - 100 microamps. The Ni(Co) was plated for 2 hours at 50 microamps. If 100% efficiency is assumed Faraday's law gives a 6250 Å foil. A x-ray diffractometer measurement gave strong peaks at 2θ = 76.5° and 74.2° which is very close to the angles expected for d(220) Ni and d(220) Cu. The 2θ region for (100) and (111) was also searched with absolutely no signal even at 1000 times more gain on the analyzer. The only thing to note was that both peaks were doublets with about 0.2° separation in the tops of both peaks. This probably means the Cu s.c. was twinned. The Laue pattern was used to find the crystalline directions of the Cu and according to the literature (see Ref. 74) the epitaxial crystal of Ni should have the same directions as the Cu for the (110) plane. The final sample was very shiny and smoother than the surface of the bulk Ni single crystal. In order to search for any possible anisotropy in the magnetic field at the nucleus of Co, H₀ was aligned parallel to the [111] and then the [100] direction of Ni. The magnetization curves measured by γ-ray anisotropy are shown in Fig. 18. The first puzzling thing is that the [100] is the direction of the easiest magnetization which is opposite to bulk Ni single crystals. There are three possible explanations for this. The Ni plated out in the (110) plane but perhaps with a different direction orientation than the
Fig. 18.
Cu or there is some sort of shape anisotropy term. The latter isn't too plausible because shape anisotropy would be isotropic in the plane. The third possibility would be anisotropic effects of the stress induced upon cooling. Cu and Ni contract different amounts upon cooling\(^5\) which leads to a stress in the Ni foil because the volume of Cu is so much larger.

The magnetoelastic energy is given by \(-\lambda_s \sigma\) where \(\lambda_s\) is the spontaneous magnetostrictive strain in a domain and \(\sigma\) is the stress. The equilibrium position of \(\vec{M}\) will be at a minimum in the sum of the magnetoelastic energy and crystalline anisotropy energy. For a cubic crystal like Ni,

\[
W = K_1 (l^2 m^2 + m^2 n^2 + n^2 l^2) - \frac{3}{2} \lambda_{100} \sigma (l^2 l^2 + m^2 m^2 + n^2 n^2 - 1/3) - 3 \lambda_{111} \sigma (m_1 l_1 + n_1 n_1 + m_1 n_1 l_1)\
\]

where \(l_1, m_1, n_1\) are the direction cosines of \(\sigma\) and \(l, m, n\) are the direction cosines of \(\vec{M}\) with respect to a cube axis.\(^7\) For Ni; \(K_1, \lambda_{100},\) and \(\lambda_{111}\) are negative.\(^5\) Therefore, if the stress is large enough the [100] direction could become the easy direction in Ni foils on Cu. The third reason is probably the explanation but the first reason can't be ruled out. The question could be answered by taking an electron diffraction picture but facilities for active crystals were not available.

The second unexpected thing was that upon reducing the external field to zero after going up to 2.5 Koe leads to no hysteresis. The magnetic character of these foils is apparently not understood but it is not extremely important except for the calculation of the exact enhancement factor and this is academic for any real source. The external field was measured by recording the voltage across a precision shunt in the magnet circuit. The resonant frequency was measured as a function of external
field with results shown in Fig. 19. The slight shift at low fields was first thought to be due to crystalline anisotropy fields but this can only affect the nuclear resonance frequency if the sample is a single domain as explained by Gossard et al. The shift appears at the same place as the departure from saturation magnetization and is expected because the walls being formed move to decrease the effect of \( H_0 \). The slope of the curve gives the magnitude of the \( g \) factor of Co\(^{60} \) and the sign of the internal field. Constraining the slope to the known value of the \( g \) factor for Co\(^{60} \), the zero intercept, \( \nu_0 = 69.08 \pm 0.05 \) MHz, gives the hyperfine field of Co in Ni = 120.9 ± 1 Koe. This is excellent agreement with the value quoted by Shirley, Rosenblum, and Matthias.

Since meaningful values of \( T_1 \) can be measured only if the initial conditions are known, a series of experiments were undertaken to determine the optimum conditions. This series also was done to answer the question, "why don't we destroy all the anisotropy at resonance?" \( H_1 \) was optimized by adjusting the power until the warm-up rate was significant. The magnitude of \( H_1 \) possible depends on the apparatus and is an experimental limitation. The characteristics of this apparatus limit \( H_1 \) outside the sample to about 10 moersted at the Co\(^{60} \) in Ni frequency.

Upon applying the field the lattice temperature of the Ni would rise to some steady-state value depending on the magnitude of \( H_1 \). The limiting thermal impedance is the boundary between the CMN and the Cu fins. The temperature reached also depends on this boundary, e.g., if \( Q \) is large during demagnetization due to eddy currents, then a temperature gradient
is established which limits the final temperature. After maximizing $H_1$ and reducing $H_0$ so the sample was just completely magnetized, the frequency modulation was changed. Figure 20 shows the effect of increasing the frequency bandwidth, $\Delta v_{fm}$. If one takes the value at half the maximum as the linewidth of the resonance this gives about 200 kHz as the linewidth. This is the narrowest line observed to date in NMRON experiments. This curve will eventually come back down as the bandwidth is increased because the effective $H_1$ on the peak will decrease. The effect vs. modulation frequency is shown in Fig. 21. The dashed curve had an average temperature of $1/T = 240$ and $H_1$ (applied at the sample site) = 1 moe. The solid curve had an average temperature of $1/T = 95$ and $H_1$ (applied) = 5.6 moe. These curves illustrate the theory of frequency modulation very well. Both curves fall off at the low frequency end because the time between r.f. excitation is long compared to the relaxation time and thus one obtains the inhomogeneously broadened response signal at each frequency which is very small. G.V.H. Wilson has worked out a spin temperature response function for frequency modulation and shows the effect of modulation broadening. The low frequency end of the above curve qualitatively agrees with his treatment. The solid curve falls off much sooner than the dashed curve because the relaxation time is much faster at the higher temperature. The middle region of the curves shows the limit predicted and explained in the theory. The exact height is difficult to calculate because of the reasons stated in the section on frequency modulation. One can understand this by realizing that $H_1$ should affect the increase in signal non-linearly and $T_1$ is
Fig. 20.

- $H_o = 1.002$ kOe
- $V_{FM} = 1$ Hz
- $1/T = 140$ °K$^{-1}$
- $H_i$(applied p-p) = 2 mOe
Fig. 21.
changing in a non-linear way with temperature. These effects tend to
cancel each other. The third part of the curve was unexpected but a
little thought leads to the following explanation. The higher the
frequency of modulation, the further apart the sidebands spread and
when they are further apart than the linewidth of the intrinsic homo-
gendously broadened lines there is a decrease in the signal. The solid
curve decreases at a higher frequency than the dashed one and this shows
that the intrinsic line is power broadened.

In order to test the idea of frequency line overlap with the
homogeneous line, the modulation frequency was raised to a value where
the signal was almost zero and then a second modulation frequency added.
The effect is plotted against bandwidth of the second frequency in Fig. 22.
If the picture is correct the signal should return as the bandwidth of
the second modulation increases because it spreads each discrete side-
band into a broader band. The fact that the higher power curve increases
faster again supports the power broadening of the intrinsic line. The
maximum is restored at about 5 kHz which is the separation of the dis-
crete sidebands due to the first modulation.

\( T_1 \) measurements were made at that time even though we didn't
understand why the anisotropy wasn't completely destroyed. The data were
fitted with a single exponential but showed a lot of scatter due to poor
statistics and the small signal. See Table I for a summary of Co\(^{60}\) in
Ni \( T_1 \) data. The signal was small because \( H_1 \) had to be about one
moersteds if the total temperature range was to be measured at the same
initial conditions.
Fig. 22.

\[ \frac{C_{mod} - C}{C - W} \text{ vs } \Delta \nu_{FM} (\text{KHz}) \]

- \( H_1(\text{applied p-p}) = 2.8 \text{ mOe} \)
- \( I/T = 175 \)
- \( H_1(\text{app}) = 1 \text{ mOe} \)
- \( I/T = 250 \)

- \( \Delta \nu_{FM1} = 650 \text{ KHz} \)
- \( \nu_{FM1} = 5000 \text{ Hz} \)
- \( \nu_{FM2} = 20 \text{ Hz} \)
Table I. $^{60}\text{Co}$ in Ni $T_1$ measurements

A) $^{60}\text{Co}$ in BULK SINGLE CRYSTAL NI  
30 April, 1968

Fitting function: $F(T) = P(1)e^{-P(2)T} + P(3)T + P(4)$

Summation of Runs 18-1,2; 19-1,2; 20; 21; 23

$P(1) = 2868 \pm 204$

$P(2) = 0.083 \pm 0.014$

$P(3) = 2.49 \pm 0.054$

$P(4) = 225,773 \pm 458$

Average (temperature)$^{-1} = 1/T = 155 \pm 15(°K)^{-1}$

$T'_1 = 1/P(2) = 12 \pm 1$ seconds

$T_1T = 0.078 \pm 0.01$ sec K.

B) $^{60}\text{Co}$ in NI SINGLE CRYSTAL FOIL  
12 May, 1969

<table>
<thead>
<tr>
<th>Number of Runs</th>
<th>Average (temperature)$^{-1}$</th>
<th>$T'_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7,8,9,22,23</td>
<td>255 ± 6</td>
<td>18.6 ± 0.9 seconds</td>
</tr>
<tr>
<td>1,2,10,24</td>
<td>226 ± 5</td>
<td>13.9 ± 1.1</td>
</tr>
<tr>
<td>11,15,16,17,25</td>
<td>195 ± 6</td>
<td>15.2 ± 1.0</td>
</tr>
<tr>
<td>3,12,18,26</td>
<td>165 ± 3</td>
<td>15.5 ± 1.5</td>
</tr>
<tr>
<td>4,13,19,27</td>
<td>140 ± 6</td>
<td>12.7 ± 1.4</td>
</tr>
<tr>
<td>14,20,28</td>
<td>121 ± 1</td>
<td>19.1 ± 3.8</td>
</tr>
<tr>
<td>5,21,29</td>
<td>101 ± 4</td>
<td>12.9 ± 3.0</td>
</tr>
</tbody>
</table>
Another series of experiments illustrating the use of NMRON was done on Co\textsuperscript{60} and Co\textsuperscript{57} in Co. NMR spin lattice relaxation times for Co\textsuperscript{59} in completely saturated Co at high temperatures were available for comparison.\textsuperscript{79} In this way the NMRON measurement could be compared to the value obtained by NMR. Co is also interesting because it exists in two lattice symmetries, fcc and hcp. There is a possibility of observing the dipolar contribution to the hyperfine field if one can accurately measure the shift in the NMR frequency parallel and perpendicular to the c axis of hcp Co. This was attempted by Perlow, et al.\textsuperscript{80} using the Mössbauer effect on Fe\textsuperscript{57} in a Co single crystal. They concluded that the dipolar field contribution was less than ± 0.4 KG at room temperature. It is known that the difference in the hyperfine fields in cubic and hexagonal Co increases as the temperature is lowered\textsuperscript{81} which may be due to the increase of the dipolar contribution. And, of course, NMRON on the trio, Fe, Co, and Ni, wasn't complete without the third member.

The first experiment was on Co\textsuperscript{57} in Co hcp. The source was prepared by cutting a Co single crystal with the c axis in the plane of the crystal. It was mechanically polished and electropolished to a final dimension of 0.12mm thick and 3.12 mm diameter. Orientation was checked with Laue patterns and the c axis located in the plane by the same method. The activity was plated onto the surface in the following way. A small glass pipette-shaped solution holder was made so it confined the activity to a spot two thirds of the total diameter. Using 5 drops of Perlow's\textsuperscript{82} solution with Co\textsuperscript{57} added and a Pt anode 1/16" wide and
0.005" thick, the plating was carried out at 3 volts and 1 ma for seconds. The voltage must be low enough to avoid producing $H_2$ because a small bubble on the surface forces the plating solution away. In order to test the epitaxiality of the plated Co$^{57}$ a Mössbauer experiment was performed with the c axis at 15 degrees to the transmission direction. An Fe$^{57}$ enriched sodium ferricyanide absorber was used. With the c axis pointing toward the absorber the relative intensities of the Fe$^{57}$ lines will be 3:2:1:1:2:3 if the sample is unpolarized (random), 3:4:1:1:4:3 if polarized perpendicular to the c axis and 6:6:2:2:6:6 if polarized parallel to the c axis but with the axis $15^\circ$ to the transmission direction. The observed pattern was almost equal to the last case and proved that the plated Co had its c axis along the c axis of the bulk. The only unexplained observation was that the intensity of absorption was about half that of Perlow, et al. For nuclear orientation the 137 kev gamma ray was observed using a Ge(Li) detector. At $H_0 = 0$, the anisotropy along the c axis indicated a temperature of $1/70^\circ$K. The zero field resonance was searched for with no luck. The external field, aligned along the c axis, was then increased to 2.4. koe ($DM = 550$oe) and the resonance again searched for by sweeping through the 224 - 230 MHz range. The power level was maintained as high as possible for the apparatus. Co$^{57}$ has the same g factor as Co$^{59}$ and therefore a resonance was expected at about 227 MHz. Assuming that the decreased intensity of the Mössbauer absorption might be due to some cubic Co, the lower frequency range was also swept with similar negative results. See Fig. 23 for experimental curves. The conclusion from this
CO$^{57}$ in CO hcp
$H_0 = 2.4$ kOe
$DM = 0.55$ kOe

$W(\text{WARM}) = 88,000$
$123$ kev $\gamma$-RAY
$\Delta \nu_{FM} = 200$ KHz
$H_i(\text{applied p-p}) = 7$ mOe

$W(\text{WARM}) = 18,000$
$137$ kev $\gamma$-RAY
$\Delta \nu_{FM} = 200$ KHz
$H_i(\text{applied p-p}) = 6$ mOe
experiment was that $T_1$ was too fast and the inhomogeneous broadening too large for the permissible $H_1$. The next step was to use Co$^{60}$ in Co because $T_1$ is proportional to $\gamma_n^2$ and thus would be almost a factor of three longer. Since Co$^{60}$ would take years to diffuse into hcp Co and due to the ambiguity of the Mössbauer intensity for Co$^{57}$, electrodeposition on Cu was tried. The first source was checked on the diffractometer and found to contain hcp and cubic single crystal Co in a ratio of 1:7. When the sample was cooled we found at optimum conditions there were 5 small humps in the frequency spectrum from 119 to 134 MHz shown in Fig. 24. The data shown is the sum of four sweeps. The sloped, humped background was due to warm up and a slight power resonance. From this it was concluded that the previous experiment had failed because of the mixture of phases in addition to the other reasons. Several more samples were prepared but we never succeeded in obtaining either a pure cubic or hexagonal single crystal. Finally, one of the samples was heated to 500°C for 30 seconds and quenched in $H_2O$. This removed the hcp phase completely as indicated by diffractometry. The magnetization curve of this foil measured by $\gamma$ ray anisotropy was identical to that measured by Sucksmith and Thompson.\textsuperscript{83} The frequency sweep up and down shown in Fig. 25 gave a single average resonance at 125.10 MHz with $H_0 = 600 \text{ oe}$. This yields a hyperfine field of Co in cubic Co of $219.8 \pm 1.5 \text{ koe}$. This is good agreement with the NMR value for single domain particles by Gossard et al.\textsuperscript{76} The best linewidth at half maximum was 1.26 MHz compared to 1.85 MHz for the single domain particles. However, Gossard et al.
$\Delta \nu_{FM} = 300$ KHz
DM = 0 Oe
$H_0 = 820$ Oe
$H_1$(applied p-p) = 6.8 mOe

SUM of 4 SWEEPS
W(WARM) = 130,400
$W_{\text{COLD}}$ vs $\nu$ (MHz)

- $\nu_{FM} = 1$ KHz
- $\Delta \nu_{FM} = 250$ KHz
- $H_0 = 600$ Oe
- $H_1(\text{applied p-p}) = 6$ mOe
- $W(\text{WARM}) = 159,000$
also found a linewidth of 0.4 MHz for polycrystalline, multidomain, powder samples. This indicates that the inhomogeneous broadening is much larger in the foil. This is probably due to the strain frozen into the sample by the quench. All samples in NMRO will have a lower limit on their linewidth because of strain-induced inhomogeneities. Even in the best sample there will be the strain of the differential contraction of the Cu and the sample of the solder and the sample.

\( T_1 \) measurements were made by the free decay method. The initial conditions aren't known exactly but they are kept identical over the entire temperature range. A typical curve used for \( T_1 \) measurement is shown in Fig. 26. The effect is large enough to make reasonably precise measurements. The change in anisotropy is used in \( T_1 \) measurements. This can be related to the relaxation of \( \Delta B_k \) as follows:

\[
\Delta B_2(t) = \beta_1 e^{-\lambda_1 t} + \beta_2 e^{-\lambda_2 t} + \beta_3 e^{-\lambda_3 t} + \beta_4 e^{-\lambda_4 t}
\]

\[
\Delta B_4(t) = \beta_1 e^{-\lambda_1 t} + \beta_2 e^{-\lambda_2 t} + \beta_3 e^{-\lambda_3 t} + \beta_4 e^{-\lambda_4 t}
\]

\[
\Delta W(t) = A_2(\Delta B_2) + A_4(\Delta B_4).
\]

The eigenvalues of the relaxation matrix are proportional to each other so this additional constraint can be added. There is a baseline and warm up background curve in the data so the final function which is fitted to the data can be written as

\[
P(t) = (\Sigma 1)e^{-\Lambda t} + (\Sigma 2)e^{-(K1)At} + (\Sigma 3)e^{-(K2)At} + (\Sigma 4)e^{-(K3)At} + P(1) + P(2)t
\]
RUN 14  

$^{60}$Co in CO fcc

$W(WARM) = 26,010$

$H_1$ (applied p-p) = 4 mOe

$H_0 = 1$ kOe

$\Delta \nu_{FM} = 1.2$ MHz

$\nu_{FM} = 500$ Hz

$1/T = 170$ °K$^{-1}$

Fig. 26.
where \((\Sigma_1) = \Lambda_2 \beta_{21} + \Lambda_4 \beta_{41}, \) etc. and \((K_1) = \lambda_2 / \lambda_1, \) etc.

Tables II and III have the values used for Co\(^{60}\) in Co. The data fitted by a single exponential and the sum of exponentials are shown in Fig. 27. The initial conditions were taken from the average, steady state temperature during r.f. excitation. The deviation from the Korringa law at low temperatures as first observed in NMRON by Brewer, Shirley, and Templeton for Co\(^{60}\) in Fe\(^{35}\) is obvious.
\[ \text{Co}^{60} \text{ in cubic Co} \]
\[ H_0 = 1 \text{ kOe} \]

\[ T, T = 0.75 \text{ sec} \degree K \]
\[ (\text{Co}^{59} \text{ in Co NMR}) \]

- Data fit by single exp.
- Data fit by sum of exp.

![Graph showing data fit](XBL692-1948)

**Fig. 27.**
Table II. $T_1$ Measurement For Co$^{60}$ in Cubic Co

<table>
<thead>
<tr>
<th>Run</th>
<th>Temp($^\circ$K)</th>
<th>Tspin($^\circ$K)</th>
<th>Single Exponential $T_1$ (seconds)</th>
<th>Sum of Exponentials $T_1$ (seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0099</td>
<td>0.01265</td>
<td>26.0 ± 1.8</td>
<td>62.0 ± 3.7</td>
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<tr>
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<td>23.0 ± 1.1</td>
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<tr>
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</tr>
<tr>
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</tr>
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<td>0.0122</td>
<td>0.0156</td>
<td>22.2 ± 1.5</td>
<td>43.0 ± 3.4</td>
</tr>
<tr>
<td>6</td>
<td>0.0123</td>
<td>0.0161</td>
<td>18.0 ± 1.3</td>
<td>32.7 ± 2.4</td>
</tr>
<tr>
<td>7</td>
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<td>0.0171</td>
<td>22.0 ± 1.9</td>
<td>33.6 ± 2.9</td>
</tr>
<tr>
<td>8</td>
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<td>0.0178</td>
<td>20.5 ± 1.7</td>
<td>36.8 ± 3.1</td>
</tr>
<tr>
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<td>25.8 ± 2.3</td>
</tr>
<tr>
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<td>21.3 ± 2.6</td>
<td>33.2 ± 4.2</td>
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<tr>
<td>11</td>
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<td>19.0 ± 2.4</td>
<td>31.0 ± 4.2</td>
</tr>
<tr>
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<td>19.5 ± 2.9</td>
<td>32.9 ± 5.4</td>
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<tr>
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<td>0.00825</td>
<td>22.9 ± 0.8</td>
<td>87.5 ± 4.3</td>
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<tr>
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<tr>
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<td>31.3 ± 3.7</td>
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<td>0.0197</td>
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continued
Table II. continued

<table>
<thead>
<tr>
<th>Run</th>
<th>Temp(°K)</th>
<th>Tspin(°K)</th>
<th>Single Exponential $T_1$</th>
<th>Sum of Exponentials $T_1$(seconds)</th>
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<td>16.5 ± 1.1</td>
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<td>39</td>
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Table III. Exponential Fit Constants

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<th>$K_1$</th>
<th>$K_2$</th>
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<th>$\Sigma_1$</th>
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<td>0.289</td>
<td>0.0095</td>
<td>0.0003</td>
<td>0.0</td>
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<tr>
<td>13</td>
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<td>2.413</td>
<td>4.633</td>
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<td>0.0095</td>
<td>0.0003</td>
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C. Co in Fe

The final experiment was performed with Co$^{60}$ in a Fe single crystal in order to corroborate the Co$^{60}$ in Ni frequency modulation experiments. The sample was a single crystal of Fe with Co$^{60}$ diffused into the polished surface. The final shape was a elongated spheroid of dimensions $8 \times 2 \times 0.138$ mm with the [112] of the (110) plane in the long axis and the [110] direction perpendicular to the [112] direction. $H_0$ was applied parallel to the [112] direction. It was truly beautiful to watch the 75% anisotropy appear as the sample was magnetized after cooling to 3.8 m°K. The resonance shown in Fig. 28 was easily found at 165.4 MHz($H_0 = 1kOe$) and had a FWHM of about 600 kHz in the presence of 340 kHz modulation. The effect vs modulation frequency was determined at various sets of conditions as shown in Fig. 21. All curves had $\Delta\nu_{fm} = 1280$ kHz. The top curve (dashed) had an average reciprocal temperature of 100 and $H_1$ (applied at the sample site) = 0.5 moe, the solid curve had $1/T = 125$ and $H_1$ (applied) = 0.25 moe and the dotted curve had an average $1/T = 200$ and $H_1$ (applied) = 0.12 moe. The results are as expected from the model on frequency modulation and are consistent with the Co$^{60}$ in Ni experiment.
IV. CONCLUSION

It can be safely concluded that the method on NMRON is now reasonably well understood. The saturation behavior of the resonance has been qualitatively explained. The frequency modulation integral of the inhomogeneously broadened line is limited by $H_1$, $T_1 T$, and the modulation frequency. The method will become a very powerful tool if the inhomogeneous broadening can be reduced to the level of the homogeneous broadening or an apparatus can be built which will allow larger $H_1$'s. The long spin lattice relaxation times at low temperatures require very small power levels in order to detect the nearly homogeneous case but as soon as the sample is inhomogeneously broadened the intrinsic limit ($T_1$) for frequency modulation will make many cases impossible to observe.

$T_1$ measurements can be made by the free decay method and lead to precise, but only relative answers because of the uncertainty in the initial conditions. A second method, the modulation method, for $T_1$ measurement is proposed which eliminates knowing the explicit initial condition. A combination of both methods should lead to accurate and precise results. At the present time $T_1$ measurements from modulation method are not available because of the difficulty in calculating $G_2(\omega)$. 
ACKNOWLEDGMENTS

It has been said that a thesis is 85% hard work and 15% ability. In both of these areas I have benefitted from many people who I now gladly acknowledge.

Professor David A. Shirley deserves special thanks because of the skillful manner in which he was able to maintain the delicate balance between independence and direction necessary for the maturing, educational process of which this thesis is the end product. Dr. Eckart Matthias also deserves my thanks for the direction which he provided during my third year as a graduate student.

It is almost impossible to properly thank my friends and fellow graduate students for the many helpful discussions on research and other worldly topics but those deserving special mention are: James J. Huntzicker, Stephen S. Rosenblum, Warren C. Easley, Dan B. J. Salomon, William D. Brewer, Arthur Soinski, and Roger A. Pollak. Of the several postdoctoral fellows who have visited our research group I would like to thank Drs. H. Gabriel, D. Quitmann, and E. Klein for their part in clarifying my concepts of NMRON.

Of the many people who offered technical help I would like to especially thank Mr. Dimitri, "Ed" Voronin and Mrs. Winifred Heppler.

Finally, I want to thank my family for their faith in me which served as a great source of strength. My wife, Kathleen, has shared the burden of writing this thesis and knows my gratitude for her help and encouragement.

I also wish to acknowledge the financial support of the United States Atomic Energy Commission during the last three and a half years of my graduate career.
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28. D. A. Shirley, University of California Lawrence Radiation Laboratory Report UCRL-18315.


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36. Abragam discusses the last two assumptions in Ref. 19, page 267.


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48. Supercon Division of Norton Corporation, 9 Erie Drive, Natick, Massachusetts.


51. Tubesales, 500 Sansome Street, San Francisco, California.

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53. Several different kinds have been used: (1) EPON 828 Resin + VERSAMIDE 125 Hardener; (2) Adeprene L-100 Resin + Moca Hardener; (3) Hardmen Inc., Epoweld.


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63. Chromium Corporation of America, Waterbury, Connecticut for Ni; Hamilton Watch Company, Precision Metals Division, Lancaster, Pennsylvania for Fe.


66. B. D. Abram designed the roller.
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Appendix I

The density matrix is essentially a matrix whose elements are ensemble averages of probabilities. In order to clarify this, assume we have an ensemble of \( N \) nuclei all with spin \( I \). If we use the \(|\text{Im}\rangle\) representation and assume pure states, then knowledge of all the pure states implies that the \( n^{th} \) nucleus has a state vector \( \psi_n = |\text{Im}\rangle \). In large ensembles two things happen which makes this picture wrong. One, it is impossible to have knowledge of all the state vectors; only a statistical average is possible, and two, the states are not pure but have only a probability of being in a certain state. The state vector of the \( n^{th} \) nucleus can now be written

\[
\psi_n = \sum_m C_{mn} |\text{Im}\rangle.
\]

What is observable in an experiment is the ensemble average of the expectation value of some operator. In the \( n^{th} \) state the expectation value of operator \( Q \) has the average value

\[
\langle Q \rangle_n = \langle \psi_n |Q|\psi_n \rangle = \sum_{m,m'} C_{m'n} C_{mn} \langle \text{Im}'|Q|\text{Im}\rangle.
\]

In the ensemble this operator has the average value

\[
\langle Q \rangle = \frac{1}{N} \sum_n \langle Q \rangle_n = \frac{1}{N} \sum_n \sum_{m,m'} C_{m'n}^* C_{mn} Q_{m'm}.
\]
A density matrix element is defined by

$$\rho_{mm'} = \frac{1}{N} \sum_n c_{m'n}^* c_{mn}$$

which, according to matrix mechanics, can be written as

$$\langle Q \rangle = \sum_{m,m'} \rho_{mm'} Q_{m'm} = \sum_m (\rho Q)_{mm} = \text{TR}(\rho Q).$$

Thus, the density matrix is the matrix representation of the density matrix operator which when multiplied by the matrix equivalent of an observable operator and the trace of the product matrix taken, gives the mean value of the operator for the entire ensemble. 85,86
Appendix II

This proof relating $T_1$ (effective) for the higher rank tensors to $T_1$ for the rank 1 tensor (NMR) was developed by D. A. Shirley. A more general proof is given in H. Gabriel's paper.

\[
\rho_1^0(t) = \bar{M}_1 \cdot \Delta \bar{\rho} \cdot \bar{I}
\]

where

\[
\Delta \bar{\rho} = \bar{\rho}(t) - \bar{\rho}(0)
\]

Now

\[
\rho_1^0 = \bar{M}_1 \cdot (\Delta \bar{\rho}) \cdot \bar{I}
\]

with

\[
\Delta \bar{\rho} = \bar{T} \cdot \Delta \bar{\rho}.
\]

Thus

\[
\rho_1^0 = \bar{M}_1 \cdot \bar{T} \cdot \Delta \bar{\rho} \cdot \bar{I}
\]

\[
\bar{M}_1 = \bar{M}
\]

\[
\bar{M}_2 = 3M^2 - I(I+1)
\]
\[
\begin{pmatrix}
-2I & -2I & 0 \\
-2I & 6I-2 & 2-4I \\
2-4I & 10I-8 & \\
0 & 6-6I & \\
\end{pmatrix}
\]

\[\bar{T} = -W\]

\[\bar{T} = - W \]

\[T_1 = \bar{T} \cdot \Delta \bar{\rho} \cdot \bar{1}\]

one can show that

\[\bar{M}_1 \cdot \bar{T} = -2W \bar{M}_1\]

\[\bar{M}_2 \cdot \bar{T} = -6W \bar{M}_2\]

therefore

\[\dot{\bar{\rho}}_1^0 = -2W\bar{M}_1\Delta \bar{\rho} \cdot \bar{1} \quad \text{or} \quad \dot{\bar{\rho}}_2^0 = -6W\bar{M}_2\Delta \bar{\rho} \cdot \bar{1}\]

or

\[\dot{\bar{\rho}}_1^0 = -2W\bar{\rho}_1^0 \quad \text{and} \quad \dot{\bar{\rho}}_2^0 = -6W\bar{\rho}_2^0\]

\[\bar{\rho}_1(t) = \bar{\rho}_1(0)e^{-t/T_1} \quad \text{with} \quad T_1 = \frac{1}{2W}\]

and

\[\bar{\rho}_2(t) = \bar{\rho}_2(0)e^{-3t/T_1}\]
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