NUCLEAR RELAXATION IN FERROMAGNETIC COBALT

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NUCLEAR RELAXATION IN FERROMAGNETIC COBALT

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ABSTRACT

Nuclear magnetic spin-spin relaxation processes of Co$^{59}$ has been studied in magnetically saturated particles of fcc cobalt. The transverse relaxation has been studied experimentally by observing the two rf pulse spin echo envelope decay. This decay is initially oscillatory with the oscillations damping a time of order of the transverse relaxation time, $T_2$, into exponential decay. The oscillatory behavior is dependent on the pulse widths while the relaxation time $T_2$, determined from the exponential decay rate, varies as the square root of the local field, $H_{loc}^{1/2}$. Theory is presented which shows that the observed oscillatory behavior can be explained qualitatively by assuming that the dominant spin-spin interaction is of the Suhl-Nakamura type, $A_{ij} \{I_i^+ I_j^- - I_i^- I_j^+\}$, with the resonant line broadened by microscopic inhomogeneities. The period of the oscillations gives the rms microscopic inhomogeneous linewidth, 100 kHz. Using the correlation function technique, the relaxation function has been derived for this system. This theory is similar to the results of Kubo and Tomita for the exchange narrowing problem and agrees well with the observed nonoscillatory transverse relaxation. From the derived relaxation function and observed transverse relaxation results, a model of the homogeneous line is deduced. The line is assumed lorentzian with a cutoff of order of the second moment of the Suhl-Nakamura interaction. Using this model and the theory of quantum-statistics of irreversible processes, a theory of spectral diffusion is derived. Spectral diffusion
was studied experimentally by monitoring the decay of the three rf pulse stimulated echo. The new theory presented here agrees well with the new experimental results.
INTRODUCTION

The discovery of the Co\textsuperscript{59} resonance in ferromagnetic cobalt by Gossard and Portis\textsuperscript{1} has motivated a considerable amount of work on this system. They immediately recognized that nuclear magnetic resonance in ferromagnetic materials (FNR) provides a valuable probe of the ferromagnetic state, which is not yet satisfactorily understood. Using steady state resonance techniques, Gossard and Portis were able to deduce the essential features of the Co\textsuperscript{59} resonance. Their study of the nuclear spin-spin coupling is of particular interest since the coupling involves spin wave excitation. A more quantitative understanding of the nuclear spin-spin interaction is desirable since this provides a more quantitative understanding of the ferromagnetic state.

A very simple model of the Co\textsuperscript{59} resonance was proposed in Reference 1. The cw linewidth was shown to be due to macroscopic static inhomogeneities. This linewidth is considerably greater than the measured spin-spin coupling which determines the homogeneous linewidth. The dominant spin-spin mechanism was believed to be the Suhl-Nakamura interaction\textsuperscript{2} weakened by microscopic inhomogeneities. The Suhl-Nakamura interaction is an indirect transverse nuclear magnetic coupling through the emission and absorption of virtual spin waves. That is, a nucleus at some site can interact with its local electronic moment through the transverse part of the hyperfine coupling to create a virtual spin wave with a simultaneous nuclear spin flip; this spin wave then travels to a distant site where it is annihilated with a simultaneous nuclear spin flip which conserves nuclear angular momentum. Since this process conserves angular momentum, it conserves energy if the nuclear moments experience an homogeneous static
magnetic field. It is important to note that this interaction is long range, of the order of 30 lattice constants for cobalt in moderate dc magnetic fields. We see then that angular momentum conserving spin flips will not conserve zeeman energy if the inhomogeneity is appreciable in this range. This situation, which is referred to as microscopic inhomogeneous broadening, must be distinguished from the situation where the inhomogeneity is more slowly varying, macroscopic broadening. Momentum conserving spin flips will be impeded among spin pairs where the net zeeman energy change is greater than the spin-spin interaction. This study is concerned with the spin-spin relaxation processes in a system where the spin-spin coupling is of the Suhl-Nakamura type and the microscopic field inhomogeneity is appreciable.

Appreciable macroscopic broadening affects the experimental considerations. A transient resonance technique is more convenient for studying relaxation processes in such systems. For this reason, the work in Reference 1 was extended by Weger, Portis, and Hahn. However, all these studies were made on multidomain particles in zero applied dc magnetic field. The presence of Bloch walls excludes quantitative interpretation of the measured nuclear spin-spin coupling results. This is because of the complexity of Bloch wall processes. The motivation here has been to extend this work under the simple dynamic condition of studying magnetically saturated particles by transient resonance methods. The dynamics of the resonance are elaborated on in Chapter I.

The experimental results of the two rf pulse spin echo studies are presented in Chapter II, where these results are interpreted in the light of new theory which is presented also in that Chapter. Using second order time-dependent perturbation theory, Portis was able to derive an analytic
expression for the dependence of the spin-spin relaxation time on the second moment of a Suhl-Nakamura type interaction, and the distribution function of the microscopic inhomogeneities. And recently Pincus, Jaccarino, Hone, and Ngwe\textsuperscript{5} contributed to the theoretical understanding of this problem using moment techniques. I have extended the above theoretical work using the correlation function technique. This theory, similar to that of Kubo and Tomita\textsuperscript{6} for exchange narrowing, is much more complete and adds new physical insight. The results of this work along with the experimental study has allowed me to describe the spin-spin processes quantitatively.

Portis\textsuperscript{4} pointed out that macroscopic spectral diffusion is possible in a system where the microscopic inhomogeneity is appreciable and the spin-spin coupling is the dominant homogeneous line broadening mechanism. This corresponds to the longitudinal relaxation time $T_1$, being longer than the transverse relaxation time $T_2$. It was pointed out in Reference\textsuperscript{4} that mutual spin flips which do not conserve zeeman energy are possible if the net change in zeeman energy is less than the average spin-spin energy. Thus, sequences of such spin flips may transport zeeman energy across the spectral line. This is clearly a diffusion process. Using the three rf pulse stimulated echo technique, these considerations were confirmed experimentally in Reference\textsuperscript{3}. In Chapter III this experimental work is extended and compared with a new theory of spectral diffusion presented here also. By using the shape of the homogeneous line deduced from the results in Chapter II, I am able to show that theory agrees well with the experimental results. The new theory is quite general and depends only on knowing the shape of the homogeneous line. However since this is derived in Chapter II, the macroscopic and microscopic spin-spin processes are approached in a unified manner. The derivation of the theory was possible
as a result of recent advances in the formulation of the theory of quantum statistics of irreversible processes.\textsuperscript{7,8,9}

In working in magnetically saturated particles one has the experimental disadvantage of having to work at lower signal to noise ratios than in zero magnetic fields.\textsuperscript{1} However, the increased simplicity in the observed results more than offset this disadvantage. Because of this, I have been able to use more powerful theoretical tools to interpret the data. Thus, I have been able to formulate more quantitatively and more completely the model proposed by Gossard and Portis\textsuperscript{1} than has been done previously.
I. DYNAMICS OF THE SINGLE DOMAIN RESONANCE

A. Introduction

The presence of the ordered electronic state is of considerable aid in the excitation and detection of the nuclear magnetic resonance in ferromagnetic metals. This enhancement of the nuclear resonance rf field, and the nuclear induction signal by the electronic magnetization is well documented. However, this same electronic-nuclear interaction often makes it difficult to compare experimental results with theory. For this reason, I will repeat here some of these well known results to help clarify some of the experimental findings discussed in later chapters. The discussion in this section is meant to be complete only to the extent needed for later clarification.

B. Sample

Measurements were made on Co$^{59}$ in Johnson-Matthey 99.999% Co sponge at 77°K. These particles were embedded in Apiezon N-Grease which freezes at 77°K. An rf coil was wound about the frozen cylindrical shaped sample of length 3.5 cm and diameter 1.5 cm. The N-Grease provides high thermal conductivity and thus facilitates temperature stability. This sample was studied in a dc magnetic field perpendicular to the axis of the cylinder and thus perpendicular to the rf field produced in the coil.

The Co sponge is believed to be quite similar to the Johnson-Matthey Ni sponge which has been observed under a microscope and found to be roughly spherical.$^{10}$ Such particles are multidomain in zero applied field.$^{11}$ This can be understood by magnetostatic considerations.$^{11}$ In the same manner it is easy to show that the application of a dc magnetic field results in the growth of domains magnetized in the directions
of the field at the expense of domains oppositely directed. Such growth is often explained in terms of Bloch wall displacement. A Bloch wall is the transition area between domains directed in different directions, see Fig. 1 for an idealized model of a $180^\circ$ Bloch wall. (The width of such walls in cobalt is approximately 30 lattice constants.) In a dc field greater than a particle's demagnetizing field, the particle becomes magnetically saturated, single domain.

C. Field Dependence of Single Domain Resonance Frequency

As stated above, multidomain particles are magnetically saturated in fields larger than the particle's demagnetizing field, $N_p M$. For particles of arbitrary shape, $N_p$ varies from zero to $4\pi$. In Co, $4\pi M = 18$ kOe. Thus for dc fields less than this value not all particles in the sample will be single domain. This is particularly true for the range of dc fields used in this study; $H_0 = 5 - 10$ kOe. However, this is a minor inconvenience since the dc field dependence of the FNR frequency in single domain particles is markedly different from that in multidomain particles. Thus it is possible to separate the signals from single domain particles from that of multidomain particles by using this property. At fields larger than 18 kOe, the dipole-dipole interaction becomes comparable to the Suhl-Nakamura interaction and more seriously complicates the study of the latter interaction.

Compared to the multidomain case, the nuclei in a single domain particle see an additional local field which is the vector sum of four fields: the applied field, the demagnetizing field from the surface of the particle, the cavity field due to the surrounding particles, and the demagnetizing field from the outer surface of the sample. The last two fields will be referred to as bulk demagnetizing fields. Of course the electronic magneti-
zation sees these fields along with an additional field, the anisotropy field, $H_a$. For a spherical particle immersed in a sample with filling factor, \( f \), and $H_o \gg H_a$,

\[ I-1 \quad H_{\text{loc}} = H_o - \frac{4\pi}{3} M + \frac{4\pi}{3} f M - NfM. \]

Since the hyperfine field in cobalt is negative with respect to the magnetization, this will shift the FNR frequency by an amount $\omega_{\text{loc}} = -\gamma H_{\text{loc}}$ with respect to the zero field FNR frequency. $\gamma = 2\pi \times 1.011\text{MHz/kOe}$, is the magnetogyric value for Co$^{59}$. On the other hand the multidomain FNR frequency varies very little with frequency.

In Fig. 2, the measured frequency dependence on field is plotted for the Co$^{59}$ single domain and multidomain signals in the sample I have studied. For small pulse turning angles, it is possible to distinguish two signals. One has large amplitude at low fields; narrow linewidth; strong amplitude dependence on field, and very weak frequency dependence on field. This signal characterizes the multidomain signal.\(^{12}\) The second signal is extremely broad; of considerably smaller amplitude at low fields; the amplitude varies less strongly with field; and the frequency varies much more strongly, approaching at large fields the behavior predicted by Eq. I-1. This signal characterizes the single domain signal.\(^{12}\) The deviation from the linear behavior predicted by I-1 is due to the fact that at fields $H_o \approx H_a$, the bulk demagnetizing fields, and the parallel dc field $H_o$ are not parallel to the particle demagnetizing fields. In I-1 it is assumed these fields are all parallel and this only occurs for $H_o \gg H_a$.\(^{12}\) The data in Fig. 2 is quite similar to that reported in Ref. 12.

Consider the $H_o = 0$ intercept in Fig. 2. The intercept gives a measured value of

\[ \frac{\omega_{\text{loc}}}{\gamma} \biggr|_{H_o = 0} = -5000 \text{ kOe}. \]

For $f \ll 1/3$,\(^{12}\)
\( N \approx 2\pi \), I-1 predicts a value of \( \frac{\omega \text{loc}}{\gamma} (H = 0) = -7000 \text{kOe} \). This agreement is considered good since the resonance is very broad which makes it difficult to locate the exact center at each field and more important since the exact distribution of particle demagnetizing factors is not known. It is this broad distribution of particle demagnetizing factors that cause the broad resonance. Note that because of this uncertainty in demagnetizing factors, \( H_{\text{loc}} \) is the relevant parameter for analysing the data rather than \( H_0 \). It has been demonstrated in this section that the FMR single domain resonance can be separated from the multidomain signal. However it will be shown later that for some processes, such as \( T_{\perp} \) process, where fluctuating fields from near by Bloch walls may affect the results, one has to take this effect in consideration in interpreting the results.

**D. Enhancement Factor**

In a saturated particle, the electronic magnetization is directed along \( H \), the resultant of the applied field, bulk demagnetizing fields, and the anisotropy field. We assume that \( H \) is essentially parallel to \( H_0 \). If an rf field of amplitude, \( H_X \), is applied perpendicular to \( H \) then the magnetization will be tilted by an angle \( \theta \approx \frac{H_X}{H} \) where \( H_X \ll H \). Since the hyperfine field, \( H_n \) is directed in the negative direction of the magnetization, it is tilted by an angle \( \theta \) also. This produces an additional rf field at the nucleus.

\[
I-2 \quad H_{\text{eff}} = \theta H_n = \eta H_X; \quad \eta = \frac{H_n}{H}.
\]

For Co, \( H_n \equiv 216 \text{kOe}; H_a = 1 \text{kOe}, \) and the bulk demagnetizing fields \( \equiv -1 \text{kOe} \). Since the angle between the anisotropy field and the dc field is random, there will be a distribution of enhancement factors. For \( H_0 = 5 \text{kOe}, 3 \leq H \leq 5 \) and \( 72 \leq \eta \leq 43 \). This is approximately a 50% variance
in enhancement factors for this field. Thus we see that experimental results cannot be interpreted in terms of a unique enhancement factor.

At higher fields the enhancement spread will be smaller, however the detected signal will be smaller because of the smaller enhancement factor. Because of the dual enhancement of the field and the nuclear induction signal, the detected nuclear induction signal varies as $\eta^2$. Thus the signal to noise ratio decreases rather rapidly with increasing fields, $\left(\frac{1}{H}\right)^2$. For the experimental considerations, it was feasible to work at fields in the range of 5 to 10 kOe.
II. TRANSVERSE RELAXATION

A. Introduction

The spin-echo technique is more suited for studying transverse relaxation processes in inhomogeneous broadened lines than cw techniques. This technique separates in a simple way the homogeneous and inhomogeneous contributions to the linewidth. To see this, consider a system where the amplitude of the rf pulse applied at the FNR frequency is unique. The spin system is initially in thermal equilibrium with total magnetization along the z-axis, and we assume the first pulse tips the magnetization through an angle of 90° (90° pulse). The magnetization will now precess in the transverse plane at the FNR frequency (free induction decay). However because of inhomogeneity, different spins will precess at different frequencies and the magnetization will decay. The time dependence of this decay will be given by the fourier transform of the excited inhomogeneous spectrum distribution. The characteristic time of the decay is denoted by $T_2^*$. If the entire line is excited, then $T_2^*$ is essentially the inverse of the linewidth. If the amplitude of the rf field is not sufficiently large to rotate the entire magnetization, then $T_2^* \propto (1/2 \gamma H_{\text{eff}})^{-1}$.

Suppose at $\tau >> T_2^*$, a 180° pulse is applied which differs in phase by $\theta$ from the first pulse. Then a spin whose frequency $\omega_1$ differs from the center resonant frequency $\omega_0$ will have acquired a phase $(\omega_1 - \omega_0)\tau$ with respect to the magnetization at the time, $\tau$, of the second pulse. Immediately after the 180° pulse this spin will have phase $\theta-(\omega_1 - \omega_0)\tau$. In a time $\tau$ later, this spin will have phase $\theta$. This is true of all spins; thus the magnetization will be recovered (see Fig. 3). This transient signal at time $2\tau$ is referred to as a spin echo. We see from the discussion above that the envelope of the spin echo is also determined by the fourier transform
of the inhomogeneous spectrum distribution. However, the total magnetization will not be recovered if there is homogeneous broadening. Cancellation of the phase above occurs only for that part of the phase acquired by the presence of local static fields. Thus a measure of the spin echo amplitude decay gives the Fourier transform of the homogeneous spectrum distribution analogous to the discussion of the free induction decay. This has been pointed out previously by Hahn. In this section we will assume $T_1 = \infty$ since the dominant contribution to the homogeneous line is spin-spin interaction.

It is convenient to relate the information obtained from monitoring the spin echo to the correlation function $\langle I_{\text{tot}}^+(t) I_{\text{tot}}^-(0) \rangle$. $I_{\text{tot}}^+$ and $I_{\text{tot}}^-$ are the nuclear angular momentum operators: $I_{\text{tot}}^+ = I_{\text{tot}}^x + i I_{\text{tot}}^y$; $I_{\text{tot}}^- = I_{\text{tot}}^x - i I_{\text{tot}}^y$; $\mathbf{I}_{\text{tot}} = \sum_i \mathbf{I}_i$ where the summation is over $N$ spins. $I(t)$ is the angular momentum operator in the Heisenberg representation.

$\langle \rangle$ represents an ensemble average over the equilibrium density matrix $\rho \propto \exp(-E/kT)$ where $E$ is the total energy of the system and $T$ is the lattice temperature. At the temperature at which this study was performed, the high temperature approximation is valid for the nuclear spins. Thus $\rho \propto 1$, the identity operator. Then,

$$\langle I_{\text{tot}}^+(t) I_{\text{tot}}^-(0) \rangle = \langle \sum_i I_{\text{tot}}^+(t) \sum_j I_{\text{tot}}^-(0) \rangle = \sum_i \langle I_{\text{tot}}^+(t) I_{\text{tot}}^-(0) \rangle.$$

It is shown in Appendix A that for independent spins

$$\langle I_j^+(t) I_j^-(0) \rangle = \langle I_j^+(0) I_j^-(0) \rangle e^{-i\omega_0 t} = \frac{2}{3} (I)(I+1) e^{-i\omega_0 t}.$$

Let $h(\omega-\omega_0)$ be the inhomogeneous frequency distribution function centered at $\omega_0$ and normalized to one. Then,

$$\langle I_{\text{tot}}^+(t) I_{\text{tot}}^-(0) \rangle = \frac{2}{3} (I)(I+1) \sum_j e^{-i\omega_j t} = \frac{2}{3} (I)(I+1) e^{-i\omega_0 t} \sum_{\omega} h(\omega-\omega_0) e^{-i(\omega-\omega_0)t}.$$
The summation is just the Fourier transform of the inhomogeneous spectrum distribution function. Thus the echo envelope for independent spins is given by

\[ \langle I^+_{\text{tot}}(t-2\tau) I^-_{\text{tot}}(\phi) \rangle \sim e^{i\omega_0(t-2\tau)} \]

For interacting spins, we define the relaxation function \( \phi_j(t) \), \((\phi_j \cdot t) = \phi_j(t); \phi_j(0) = 1\) in the following manner, \( \langle I^+_{j}(t) I^-_{j}(0) \rangle = (I^+_{j}(0) I^-_{j}(0)) e^{-i\omega_0 t} \phi_j(t) \). The relaxation function accounts for the spin-spin interaction. Just as \( \langle I^+_{\text{tot}}(t) I^-_{\text{tot}}(0) \rangle \sim e^{i\omega_0 t} \) is given by the Fourier transform of the inhomogeneous line, \( \langle I^+_{j}(t) I^-_{j}(0) \rangle \sim \phi_j(t) \) is given by the Fourier transform of the homogeneous line. For a Gaussian distribution, \( \phi_j(t) \) is Gaussian, for a Lorentzian distribution \( \phi_j(t) \) is exponential. The relaxation function will only depend on the frequency of the \( j \)'th spin. Thus we may write for interacting spins,

\[ \langle I^+_{\text{tot}}(t) I^-_{\text{tot}}(0) \rangle = \frac{2}{3} N (I(I+1)) e^{-i\omega_0 t} \sum_{\omega} h(\omega-\omega_0) \phi_\omega(t) \]

In the case of extreme inhomogeneous broadening where an appreciable portion of the line is excited, \( \phi_\omega(t) \) varies much slower with time than the trigonometric function and the spin echo envelope shape can still be interpreted in terms of \( \sum_{\omega} h(\omega-\omega_0) e^{-i(\omega-\omega_0)(t-2\tau)} \). The amplitude of the echo as discussed earlier does not depend on the phase factors due to the macroscopic inhomogeneity, but is proportional to \( \sum_{\omega} h(\omega-\omega_0) \phi_\omega(2\tau) \approx \phi_\omega(2\tau) \). Thus we see how to compare the experimental results with theory. The relaxation function can be calculated from \( \langle I^+_{j}(t) I^-_{j}(0) \rangle \) since the time behavior of the operators \( I(t) \) can be calculated from the Hamiltonian of the system. Klauder and Anderson have given an analysis of the relationship between these correlation functions and the spin-echo measurements similar to the one presented here.\(^{15}\)
In this chapter, I have combined both experimental and theoretical considerations to describe the homogeneous broadening processes in a quantitative way. The results of monitoring the spin echo amplitude decay is presented. Then these results are interpreted in terms of new theory derived in this chapter.

B. Experimental Results

The distribution of enhancement factors makes the analysis of the spin echo amplitude dependence on pulse width and amplitude more difficult. I found experimentally that the amplitude of the echo did not depend critically on the second pulse. In all measurements the pulse length of the first pulse was adjusted for maximum signal, and this pulse will be assumed to be a 90° pulse. Here I refer to the second pulse relative to the first pulse.

For applied fields $H_0 = 5 - 10$ kOe, and for maximum power available, $T_2^* \approx 0.75 - 1.5 \mu$sec. Thus the width of the excited spectrum, \[
\frac{\Delta \omega}{2\pi} = \frac{1}{2\pi} \left( \frac{2}{T_2^*} \right) = 400 - 200$ kHz. Therefore, a narrow portion of the single domain resonance was excited for each field value.

The discussion above concerning the spin echo dynamics is only adequate for $\tau \gg T_2^*$. The amplitude of the echo at times $\tau \approx T_2^*$ is the difference between the initial magnetization and the free induction decay at the time of the second pulse. Thus for small $\tau$, the echo amplitude at $2\tau$ is expected to be proportional to $(1 - \frac{\tau}{T_2^*})$. For $T_2^* \ll T_2$, this factor will dominate the echo amplitude time behavior for $\tau \approx T_2^*$. In addition, the receiver recovery time after the rf pulses was the order of 1 $\mu$sec. Thus the echo amplitude time behavior for time $\tau < 2 \mu$sec is not indicative of homogeneous broadening processes.
The result of monitoring the spin echo amplitude for 90° - β pulse sequences is shown in Fig. 4 at fixed frequency for values of β = 90°, 135° and 180°. For β = 180°, the time behavior at moderate short time is essentially gaussian decay transforming into exponential decay at long times. The decrease in the curve at very short time may have several contributions. The receiver saturation and free induction decay may contribute as discussed above. And there may be oscillations that do not depend critically on the pulse width. For β = 180°, there is a much more noticeable oscillatory behavior superimposed on the β = 180° curve at short times. The period of these oscillations in τ is 6.5-7 μsec. This corresponds to a frequency ≈ 140 kHz ± 10%. These oscillations damp out in a time T₂ and have minimum amplitude for the 90° - 180° pulse sequence. T₂ is determined from the slope of the exponential curve which was observed out to 100 μsec. The variation in T₂ with β is within experimental accuracy of 10% and is not significant.

The frequency dependence of the echo decay is shown in Fig. 5 for a 90° - 90° pulse sequence. The oscillatory behavior is less apparent at lower frequencies where the enhancement factor is smaller and thus the signal is smaller. Also the relaxation time, T₂, monotonically increases with the decreasing frequency. The increase in T₂ indicates that the indirect nuclear spin-spin coupling is weakened by the increase of the local field. In Fig. 6, T² is plotted versus frequency. I have reported this result previously. The data is fit well by a straight line that extrapolates to 221.5 MHz for T² = 0. This is 4.6 MHz above the zero field resonance. In the following sections, these results are predicted from the initial model suggested for this system by Gossard and Portis. That is, the homogeneous line is determined by the Suhl-Nakamura interaction weakened by microscopic inhomogeneities.
C. Microscopic Theory

1. The Hamiltonian of the System

The Hamiltonian of the N particle system consists of two terms: the Zeeman energy $H_z$ and the spin-spin interaction term $H_{SN}$.

$$ H = H_z + H_{SN} = -\hbar \sum_{l} \omega_l I_l^z + \sum_{l \neq m} A_{lm} I_l^+ I_m^- $$

$$ A_{lm} = \frac{\hbar^2 \omega^2_0}{2SN} \sum_{k \sim l} \frac{-i \mathbf{k} \cdot \mathbf{r}_{lm}}{E_k} $$

$S$ is the effective electronic spin; $k$ is the spin-wave wave-number; $E_k$ is the unperturbed (by nuclear effects) spin wave energy for the spin wave of wave-number $k$; $\omega_0$ is the FNR frequency; $\mathbf{r}_{lm}$ is the vector between the $l$'th and m'th sites. The spins of interest are within the microscopic range of the interaction. Thus it is assumed $A_{lm}$ which varies with the frequency, does not vary appreciably in the range of interest. This will be a good approximation for the width of the spectrum excited experimentally, and since spins of different frequency interact weakly. It is assumed that the microscopic inhomogeneity may be represented by a distribution function $g(\omega - \omega_0)$ centered at the resonant frequency of the observed spins and of rms standard deviation $\sigma$. $E_k$ is derived in Ref. 17 and may be written

$$ E_k = \hbar \left[ \gamma_e (H_{loc} + H_a) + \alpha_E \mathbf{a}^2 k^2 \right]^{1/2} \left[ \gamma_e (H_{loc} + H_a) + \alpha_E \mathbf{a}^2 k^2 + \omega_M \sin^2 \theta_k \right]^{1/2} $$

here $\gamma_e$ is the electronic magnetogyratic value.

With $\cos \theta_k = \frac{\mathbf{k} \cdot \mathbf{r}_{lm}}{||\mathbf{k}||}$; $\alpha_E$ is the electronic exchange frequency; $\mathbf{a}^3$ = volume of a primitive unit cell, and $\omega_M = \frac{4\pi \gamma_e M}{\hbar}$. $A_{lm}$ is often
given for $\theta_k = 0$. Then, $E_k = \hbar \gamma_e \left[ (H_{\text{loc}} + H_a) + \omega_E \hat{a}^2 k^2 \right]$. For 

$$\gamma_e \left( \frac{H_{\text{loc}} + H_a}{\omega_E} \right) \approx 10^{-3} \ll 1,$$

we get the familiar result:

$$A_{lm} = \frac{\hbar \omega_0}{8\pi \omega_E} \left( \frac{\hat{a}}{r_{lm}} \right) \left( \frac{\omega_E}{\gamma_e (H_{\text{loc}} + H_a)} \right)^{1/2} r_{lm}.$$

$$\left( \frac{\omega_E}{\gamma_e (H_{\text{loc}} + H_a)} \right)^{1/2} \hat{a} \text{ is the range of the interaction. Since}$$

$$\left( \frac{\omega_E}{\gamma_e (H_{\text{loc}} + H_a)} \right)^{1/2} \hat{a} \approx 30 \hat{a},$$

we see that the interaction is long range.

The range of the interaction is determined by the ratio of the spin wave energy gap, $\hbar \gamma_e (H_{\text{loc}} + H_a)$ to the exchange energy, $\hbar \omega_E$. However, the plot in Fig. 7 of the spin wave energy band shows that for $\frac{\omega_M}{\gamma_e} \gg (H_a + H_{\text{loc}})$, the band width, $[E_0(\theta_k = \frac{\pi}{2}) - E_0(\theta_k = 0)]$ is larger than the band $E_0(\theta_k = 0)$. For this case, the $\theta_k = 0$ approximation will not give an accurate value for the range of the interaction. This approximation can be improved very simply by noting that $E_k$ may be rewritten

$$E_k = \hbar \left\{ \left( H_{\text{loc}} + H_a \right) \gamma_e + \frac{\omega_M}{2} \sin^2 \theta_k + \omega_E \hat{a}^2 k^2 \right\}$$

$$\left\{ 1 - \left[ \frac{1/2 \omega_M \sin^2 \theta_k}{\gamma_e (H_{\text{loc}} + H_a) + \omega_M \sin^2 \theta_k + \omega_E \hat{a}^2 k^2} \right]^2 \right\}^{1/2}$$

II-3

$$E_k = \hbar \left\{ \left( H_{\text{loc}} + H_a \right) \gamma_e + \frac{\omega_M}{2} \sin^2 \theta_k + \omega_E \hat{a}^2 k^2 \right\}$$
\[
\frac{1}{E_{nk}} \text{ is now averaged over } \theta. \text{ It is shown in Appendix B that this is approximately equivalent to taking the average } \langle \sin^2 \theta_k \rangle \text{ in II-3. Thus, we use }
\]
\[
E_{nk} = \hbar [\gamma_e H_{\text{loc}} + \gamma_e H_a + \frac{\alpha_M}{3} + \alpha_E \mathbf{a}^2 k^2]
\]
and get finally
\[
\text{II-4} \quad A_{lm} = -\left(\frac{\hbar}{\mathbf{a}} A_{0}^2 \right) \frac{\mathbf{a}}{r_{lm}} \left(-\frac{\gamma_e (H_{\text{loc}} + H_a) + \frac{\alpha_M}{3}}{\alpha_E}\right)^{1/2} \frac{r_{lm}}{\mathbf{a}}
\]
Using II-4 and the values in Table I the calculated second moment,
\[
\omega_{\text{SN}}^2 = \frac{4}{3} \frac{(I)(I+1)}{\hbar^2} \sum_{m+l} A_{lm}^2,
\]
is
\[
\omega_{\text{SN}}^2 = \left[\frac{(I)(I+1)}{24\pi S^2}\right] a_0^2 \left(\frac{a_0}{a}\right)^2 \left(\frac{a}{\gamma_e (H_{\text{loc}} + H_a) + \frac{\alpha_M}{3}}\right)^{1/2}
\]
\[
(\omega_{\text{SN}})^{-1} \approx 7 \mu\text{sec.}
\]
In this study, \(H_{\text{loc}} + H_a \approx 2-5\) kOe, \(\frac{\alpha_M}{3\gamma_e} = 6\) kOe. If we substitute the average value of \(\sin^2 \theta, \langle \sin^2 \theta \rangle = 2/3,\) in Eq. II-3, we estimate an error of 35-15% in neglecting the multiplicative factor. This estimate is only meant to serve as a rough measure of the confidence that can be placed in the approximation. It will be shown that this approximation is certainly better than the \(\theta_k = 0.\) approximation. The approximation that the Suhl-Nakamura interaction is spherical symmetric will be particularly accurate for \(H_{\text{loc}} + H_a >> \frac{\hbar T}{3} M.\)
2. The Oscillatory Behavior of the Spin Echo Amplitude

The oscillatory behavior of the spin echo amplitude cannot be explained by any relaxation phenomenon. This can be understood by remembering that the measured relaxation function is an average relaxation function, \( \Sigma h(\omega - \omega_0) \phi_{\omega}(2\tau) = \phi_{\omega_0}(2\tau) \), and any oscillatory effect from this sum will be damped in a time \( T_2^* \). Thus, the oscillatory effect has to be explained in terms of the dynamics of the spin echo. That is, the echo amplitude must be calculated as a function of pulse width.

Modulation of the spin echo amplitude has been reported previously, although no effect that has the dependence on pulse width, illustrated in Fig. 4, has been reported. Previously, this effect has had two origins. For \( I > 1/2 \), quadrupolar effects in an inhomogeneous broadened line will modulate the echo decay if the entire line is excited. This occurs because the echo amplitude decay is related to the Fourier transform of the homogeneous spectrum. Therefore, the period of the oscillations will be related to the quadrupole splittings. For large \( I \) there will be several splittings, and different pulse sequences will mix these modes differently leading to very complicated echo modulation dependence on \( \beta \). These effects have been observed in hcp structures where the local electric field gradient has a unique non-zero value. Quadrupolar effects are not thought to be the origin of the modulation observed here. For one reason the fcc structure has zero field gradient at the nuclear position for the perfect crystal, and it is doubtful that imperfections would lead to a well defined modulation frequency. For a second reason, in the quadrupole case, the 90°-180° pulse sequence, gives directly the Fourier transform of the homogeneous line and there is no reason to expect the decrease in amplitude observed in Fig. 4 for this sequence. The second
origin is the pair coherence that exists between the spins in a microscopic inhomogeneous broadened system where the spin-spin coupling is strong. As pointed out by Hahn and Maxwell for spin coupling in molecules both microscopic inhomogeneity and spin-spin coupling is necessary. These authors discussed the coupling, \( \hbar J_{12} \cdot S_1 \cdot S_2 \), and showed that the echo will have two modulation frequencies, \( J \) and the pair frequency difference due to microscopic inhomogeneity. In a similar manner, the origin of the oscillatory behavior observed here is pair coherence due to the Suhl-Nakamura interaction. This coupling is different however since the Suhl-Nakamura interaction is transverse, \( A_{ij} \{ I_i^+ I_j^- + I_i^- I_j^+ \} \). It is clear that pair coherence will be destroyed when one spin of a pair interacts with other spins. Since the Suhl-Nakamura interaction is long range, many spins are in communication. Therefore the oscillations are expected to be damped in a time of order \( T_2 \) as observed.

To see how the coupling effects the spin echo amplitude, it is necessary to consider the equation of motion of the Heisenberg operators \( I(t) \). The time behavior is given by the well known results, \( \frac{\partial I}{\partial t} = -\frac{i}{\hbar} [I, \mathcal{H}] \), where \( \mathcal{H} \) is the hamiltonian of the system. For simplicity the two-particle nearest neighbor interaction is considered.

\[
\mathcal{H}_{12} = -\hbar \omega_1 I_1^z - \hbar \omega_2 I_2^z + A_{12} \{ I_1^+ I_2^- + I_1^- I_2^+ \}.
\]

The equation of motion of \( I_1^+ \) is written

\[
\frac{\partial I_1^+}{\partial t} = -i\omega_1 I_1^+ - 2i \frac{A_{12}}{\hbar} I_1^z I_2^+.
\]
Equation II-4 gives for nearest neighbors,
\[
|A_{12}|^2 = \frac{\omega_0^2}{8\pi\omega_E} = (450 \mu\text{sec})^{-1}, \quad \text{and} \quad \frac{2|A_{12}|^1}{\hbar} = (65 \mu\text{sec})^{-1}.
\]

For times, \( t \ll \left\lfloor \frac{2A_{12}}{\hbar} \left( \frac{4A_{12}}{\sqrt{2}\hbar} \right) \right\rfloor \approx 2 \text{ millisecond} \), which apply for the oscillations observed here, the second term can be neglected. Then we have the following solutions,
\[
\begin{align*}
I_1^+(t) &= I_1^+(0) e^{i\omega_1 t} \\
I_2^+(t) &= I_2^+(0) e^{i\omega_2 t} \\
I_1^-(t) &= I_1^-(0) e^{i\omega_1 t} \\
I_2^-(t) &= I_2^-(0) e^{i\omega_2 t}
\end{align*}
\]

it is convenient to consider \( I_1^+(0) \) to have the value \(-iI\) and similarly for \( I_2^+(0) \). Assuming these spins are initially along the positive z axis, this is the initial value for these operators following the first 90° pulse. Consider now, the equations of motion for the z-component of angular momentum.

\[
\frac{dI_z}{dt} = -\frac{iA_{12}}{\hbar} \left\{ I_1^+ I_2^- - I_1^- I_2^+ \right\}.
\]

Using the solutions for the transverse component, the equations of motion for \( I_1^z \) becomes
\[
\frac{dI_1^z}{dt} = \frac{2A_{12}I_2^2}{\hbar(\omega_2-\omega_1)} \left\{ \begin{array}{c}
\frac{-i(\omega_1-\omega_2)t}{2i} - \frac{i(\omega_1-\omega_2)t}{2i} \\
\end{array} \right\} = \frac{2A_{12}I_2^2}{\hbar} \sin(\omega_2-\omega_1)t;
\]

\[
I_1^z(\tau) = \frac{2A_{12}I_2^2}{\hbar(\omega_2-\omega_1)} \left\{ 1-\cos(\omega_2-\omega_1)\tau \right\} = -I_2^z(\tau).
\]

This oscillatory behavior of the z component of angular momentum is the origin of the observed modulation. If a 90° pulse is applied at \( \tau \),
then this component of magnetization will be rotated into the transverse plane. It was shown in Eq. II-4 that the transverse angular momentum can be considered to simply rotate in the plane at the static frequency which each spin experiences. Immediately after the pulse, the two spins give equal and opposite contributions to the net magnetization in the transverse plane. However the spins rotate at different frequencies, and this will add a modulating contribution to the echo (see Fig. 8). This signal gives the observed dependence on pulse width; for example it gives zero contribution to the echo for $\beta = 180^\circ$. Note that for either $A_{12} = 0$, or $\omega_1 - \omega_2 = 0$, or if one spin is not resonated, $I(0) = 0$, the modulation does not occur. This is analogous to the result of Hahn and Maxwell.20

The final results are now derived. Hahn has shown earlier that the non-oscillatory spin echo amplitude is proportioned to $\sin^2 \beta/2$; here, only the oscillatory term is considered.

Consider the reference frame that rotates at $\omega_0$, the frequency of the rf pulses. Both pulses are assumed to give a static field, $\frac{1}{2} H_{\text{eff}}$, along the x-axis during the time the rf field is nonzero. In this frame the echo signal will appear along the positive y-axis at $2\tau$. For $\omega_1 > \omega_2$, $A_{12} < 0$, $\beta \leq \pi$, the component of the magnetization along this axis at $2\tau$ is

$$\sin \beta I^2_1(\tau) [\cos(\omega_2 - \omega_0) \tau - \cos(\omega_1 - \omega_0) \tau] = -2 \sin \beta I^2_1(\tau) \sin(\omega_2 - \omega_1) \frac{\tau}{2} \times \sin(\omega_1 + \omega_2 - 2\omega_0) \frac{\tau}{2}.$$ 

We see here that for $\omega_1 + \omega_2 = 2\omega_0$, no contribution to the echo occurs.

Rewriting $1 - \cos(\omega_2 - \omega_1) \tau = 2 \sin^2(\omega_2 - \omega_1) \frac{\tau}{2}$, the echo amplitude $E(2\tau)$ may be written
Note that this oscillatory behavior is not affected by the interchange of the spins. Since only the magnitude of \( \omega_1 - \omega_2 \) is important, the rms of the frequency terms is taken in order to give physical interpretation to the observed modulation period. \[
\langle [\omega_1-\omega_0] - [\omega_2-\omega_0] \rangle^2 = \langle (\omega_1-\omega_0)^2 \rangle + \langle (\omega_2-\omega_0)^2 \rangle = 2\sigma^2 \quad \text{since} \quad \langle \omega_1-\omega_0 \rangle = \langle \omega_2-\omega_0 \rangle = 0.
\]

Similarly \( \langle [\omega_1-\omega_0] + [\omega_2-\omega_0] \rangle^2 = 2\sigma^2 \). The final result is written,

\[
\text{II-6} \quad E(2\tau) \propto 2I \left[ \sin^2 \frac{\beta}{2} - \sin \beta \left\{ \frac{2A_{12} I}{\hbar \omega_0} \sin \frac{\sqrt{2} \sigma \tau}{2} \right\} \right].
\]

Thus the period of the oscillations in \( \tau \) is equal \( \left( \frac{\sqrt{2} \pi \sigma}{2\pi} \right)^{-1} \).

Therefore we get \( \frac{\sigma}{2\pi} \approx 100 \text{ kHz} \pm 10\% \) as the measured microscopic inhomogeneity linewidth. The relative amplitude of the oscillations to the echo is

\[
2 \left( \frac{2A_{12} I}{\hbar} \right) \left( \frac{1}{\sqrt{2 \sigma}} \right) \approx \frac{1}{30} \quad \text{or} \quad -30 \text{ DB}
\]

These results are consistent with the observations shown in Fig. 4 and 5. This calculation was simplified considerably by the assumption that the observation time was short compared to the nearest neighbor spin-spin relaxation time. This was justified because of the long range of the interaction and thus, the rapid rate at which the pair coherence is destroyed.

3. Spin-Spin Relaxation Theory

The correlation function \( \langle I_1^+(t) I_1^-(0) \rangle \) is calculated in this section. From the hamiltonian of the system, the equation of motion of the angular momentum operators are calculated:
The equation of motion for $I_z^I$ is formally solved to give

$$I_z^I(t) = I_z^I(0) - \frac{i}{\hbar} \sum_{m+\ell} A_{\ell m} \int_{0}^{t} \left\{ I^+_\ell(t') I^-_m(t') - I^-_\ell(t') I^+_m(t') \right\} dt'$$

Now it is possible to rewrite for the transverse component

$$\frac{\partial I_z^{\perp}(t)}{\partial t} = i \omega \, I_z^{\perp}(t) - \frac{2i}{\hbar} \sum_{m+\ell} A_{\ell m} \bar{I}_m^I(0) \bar{I}_m^I(t)$$

$$- \frac{2}{\hbar^2} \sum_{j+\ell} \sum_{m+\ell} A_{\ell m} A_{\ell j} \int_{0}^{t} \left\{ I^+_\ell(t') I^-_m(t') - I^-_\ell(t') I^+_m(t') \right\} dt' I_j^{\perp}(t).$$

Normally, the order of the $m = j$ terms would have to be handled with care but this will not be necessary here. With this results the equation of motion of $(I^+I(0))$ can be calculated. Since the ensemble average, $(\cdot)$, is a finite sum of traces, it is permissible to interchange the operation of differentiation and integration with the ensemble average. For example $\frac{\partial}{\partial t} \langle I^+(t) I^-(0) \rangle = \langle \frac{\partial}{\partial t} I^+(t) I^-(0) \rangle$. Therefore, using the equation for $\frac{\partial}{\partial t} I_z^{\perp}(t)$, $\frac{\partial}{\partial t} \langle I^+(t) I^-(0) \rangle$ may be written,

$$\frac{\partial}{\partial t} \langle I^+_\ell(t) I^-_\ell(0) \rangle = -i \omega \langle I^+_\ell(t) I^-_\ell(0) \rangle - \frac{2i}{\hbar} \sum_{m+\ell} \sum_{m+\ell} A_{\ell m} A_{\ell j} \int_{0}^{t} \left\{ \langle I^+_\ell(t') I^-_m(t') \rangle \langle I^+_j(t) I^-_\ell(0) \rangle \right\} dt' I_j^{\perp}(t).$$
As stated previously, the high temperature approximation is valid for the work being considered here. That is, nuclear spin wave effects, that would cause spacial correlation between spins located at different sites, have no affect on results reported here. The density matrix \( \rho \) is taken to be proportional to the identity operator \( 1 \). Thus \( \langle I \rangle \alpha \text{trace} (I I) = \text{trace} I \). We see that since the trace of the components of the angular momentum operators is zero, odd multiples of these operators will be zero. Also product terms such as \( \langle I_\ell I_m \rangle \), where \( \ell \neq m \) is proportional to \( \text{trace} I_\ell \text{trace} I_m \). And finally terms \( \langle I^+ I^+ \rangle \) and \( \langle I^- I^- \rangle \) are equal to zero since the hamiltonian will not support double spin flip processes. In the integral in Eq. II-8 only the \( m = j \) terms contribute. We may rewrite Eq. II-8

\[
\frac{3}{\Delta t} \langle I^\ell(t) I^-\ell(0) \rangle = -i \omega I^\ell \langle I^\ell(t) I^-\ell(0) \rangle - \frac{2}{\hbar^2} \sum_{m \neq \ell} A_{\ell m}^2 \int_0^t \langle I^\ell(t') I^-\ell(0) \rangle \langle I^-m(t') I^m(t') \rangle dt'.
\]

We can now use the earlier definition of the relaxation function

\[
\left( \langle I^\ell(t) I^-\ell(0) \rangle = \langle I^\ell(0) I^-\ell(0) \rangle e^{-i \omega I^\ell t} \phi(t) = \frac{2}{\beta} (I)(I+1) e^{-i \omega I^\ell t} \phi(t) \right)
\]

to derive an equation of motion for \( \phi(t) \). This function as defined is complex having a frequency pulling phase factor. However it is shown in Appendix C that this term is negligible for \( \frac{\alpha_{SN}^2}{\alpha_0^2} \sim 10^{-5} \ll 1 \). The equation of motion for \( \phi(t) \) is
Let us consider Eq. II-9 in the limit of small time. From the uncertainty principle, at sufficiently small times energy conservation is not a critical consideration. Thus we can set \( \omega_\perp = \omega_j \), homogeneous field. In the same limit we take \( \phi(t') \approx \phi(0) = 1; \phi(t'-t) \approx \phi(-t) = \phi(t) \).

Equation II-9 becomes

\[
II-10 \quad \frac{\partial \phi_l}{\partial t} = -\frac{\hbar}{3} (I)(I+1) \sum_{j,l} \frac{A^2_{l,j}}{\hbar^2} \int_0^t \phi_j(t') \phi_l(t'-t) \cos (\omega_j - \omega_\perp)(t-t') \, dt'
\]

where \( \phi(t) = \phi(-t); \phi(0) = 1 \).

The relaxation is initially gaussian. This result is consistent with the theoretical results of Klauder and Anderson where they predict "lorentzian diffusion" in a concentrated homogeneous system,\(^\text{15}\) and the results of Pincus, Jaccarino, Hone and Ngwe whereby moment analysis they predict a gaussian line for the Suhl-Nakamura interaction.\(^\text{5}\) Of course this is consistent with our experimental results in Figs. 4 and 5.

To consider the long time behavior, frequency must be averaged over position in Eq. II-9. Each spin interacts with some \((30)^3\) other spins so this average using the microscopic distribution function, \( g(\omega-\omega_0) \), should be a good approximation. This procedure was first suggested by Portis.\(^\text{4}\) The assumption here is that there is no correlation between a spin's position and its frequency, random microscopic inhomogeneity. If we take this average, and substitute \( \tau = t-t' \), the sum over position can be made and Eq. II-9 becomes:

\[
II-9 \quad \frac{\partial \phi_l}{\partial t} = -\frac{\hbar}{3} (I)(I+1) \sum_{j,l} \frac{A^2_{l,j}}{\hbar^2} \int_0^t \phi_j(t') \phi_l(t'-t) \cos (\omega_j - \omega_\perp)(t-t') \, dt'
\]
Remember $\phi_j$ only depends on the frequency $\omega_j$ not on the $j$th position. As $t$ approaches $\infty$, the trigonometric term oscillates rapidly for $\omega_j \neq \omega_i$ giving zero contribution to the integral. The spin system becomes essentially diluted in this limit, since spins interact only with other spins of the same frequency. In the limit of extreme inhomogeneous broadening (extreme dilution) it is reasonable to expect the decay to be exponential, particularly in the light of our experimental results in Fig. 4 and 5.

In this limit $\phi(t=\tau) = \phi(t)$. Thus Eq. II-11 becomes

\[
\frac{\partial \phi_i}{\partial t} = -\omega_{SN}^2 \int_{-\infty}^{\infty} \int_0^t \phi_i(t-\tau) \phi_j(\tau) g(\omega_j-\omega_0) \cos(\omega_j-\omega_0) \tau \mathrm{d}\tau \mathrm{d}\omega_j .
\]

At long times we have exponential decay. In Appendix D, it is shown that the ansatz solutions I have derived for short and long times are consistent with the interaction solution of Eqs. II-9 and II-11 to second order in the limits discussed above.

This theory contains the essential features of the observed relaxation process; it predicts gaussian decay at short times and lorentizian decay at long times. The relaxation times at long times is given by

\[
\frac{1}{T_2(\omega_0)} = \pi \omega_{SN}^2 g(0) = \sqrt{\frac{\pi}{2}} \frac{\omega_{SN}^2}{\eta}
\]
for $g(0)$ assumed gaussian as was previously done in Section 2. Using the observed value for $T_2 = 28.3$ µsec, for $\omega_0/2\pi = 215.9$ MHz, and the value of $\frac{\sigma}{2\pi} = 100$ kHz deduced in the last section, this expression gives a value of $(\omega_{SN})^{-1} = 7.5$ µsec. This is well within all estimated experimental uncertainty to the value of 7 µsec calculated from the values in Table I. We see also that this expression predicts the linear dependence of $T_2$ on dc field giving $T_2 \propto \omega_{SN}^{-4} \propto H_{loc} + H_a + \frac{4\pi}{3} M$. The value of $H_{loc}/\gamma$ for which $T_2 = 0$ gives the value of the quantity $H_a + \frac{4\pi}{3} M$. The predicted value of 5-7 kOe corresponding respectively to $H_a$ aligned antiparallel and parallel to the magnetization is reasonably close to the measured value of 4.6 kOe. Again this agreement is well within all estimated experimental and theoretical uncertainty. Note that the $\theta_0 = 0$ approximation would predict an intercept of $H_a = 1$ kOe which is far in error of the observed results.

The nature of the homogeneous line is of interest. As discussed previously, the homogeneous spectrum is the fourier transform of the relaxation function. Thus the spectrum is lorentzian near the center of the line, with the linewidth given by $T_2^{-1}$, and gaussian in the wings. The gaussian behavior occurs for spins at a distance of order of the second moment of the Suhl-Nakamura interaction from the center of the line. This model is similar to the Anderson Model for exchange narrowing. Similarly, the theory is analogous to the theory of Kubo and Tomita for exchange narrowing. For simplicity we will consider the line to be lorentzian with a cutoff at $\frac{\omega_{SN}}{2}$ (see Fig. 9). This value is determined from the data in Figs. 4 and 5. It is at time $(\omega_{SN})^{-1} = 15$ µsec that the exponential decay becomes a fair approximation. We refer to spins in the homogeneous line as forming a "Spin Packet."
concept since different spin packets are in different inhomogeneous static fields and thus can only interact weakly. Therefore the spin packets are essentially independent. Since spins interact only with spins in the same packet, all spectral diffusion must occur within a packet. Thus the relaxation function contains the microscopic physics for the macroscopic diffusion process. This is shown formally in the next chapter where a theory of spectral diffusion is derived.

I have shown that the theory and experimental results presented in this chapter agree quantitatively. The original model proposed in Ref. 1 has been studied more quantitatively here, both theoretically and experimentally, than previously.
III. SPECTRAL DIFFUSION

A. Introduction

Spectral diffusion may be studied by monitoring the three pulse stimulated echo (see Fig. 3). For convenience of discussion, consider a three 90° pulse sequence. After the second pulse, there will be a periodic variation in the z-component of angular momentum due to the spread in Larmor frequencies. Thus modulation is best described by the density operators \( I^z(\omega) = \sum_{i \in \omega} I^z_i \), where the sum is over all spins that have frequency \( \omega \). After two coherent 90° pulses, these spins contribute 
\[-(I^z(\omega))_L \cos(\omega - \omega_0)\tau\] 
to the modulation along the z-axis. This periodic variation is only destroyed by longitudinal processes. That is, processes that do not conserve zeeman energy. It has been mentioned earlier that spectral diffusion is a longitudinal process. It differs from other longitudinal processes in that the characteristic relaxation rate will depend on the separation, \( \tau \), between the first and second pulse. The reason for this is that the spectral diffusion process is driven by the imbalance in thermal equilibrium within the spin packet, while other processes are driven by the imbalance in thermal equilibrium between the spin systems and the lattice. For the spectral diffusion process, \( 1/\tau \) is a measure of how far in frequency energy must be transmitted in order to bring the spin packet into internal thermal equilibrium. Consider the limit \( \tau \ll T_2 \). Many spin flips will be necessary to traverse the distance \( 1/\tau \) in frequency since each mutual spin flip can only traverse a distance \( 1/T_2 \) in frequency. This is a one dimensional random walk problem. The number of jumps necessary to reach \( 1/\tau \) is \( \left( \frac{1}{\tau} / \frac{1}{T_2} \right)^2 \) and the time of each jump is \( \frac{1}{T_2} \). Thus the rate at which the modulation is destroyed is
Therefore, if at a time $T$ after the first pulse, a third $90^\circ$ pulse is applied, an echo will appear a time $\tau$ later, analogous to the $90^\circ$-$180^\circ$ sequence, and this echo will decay in $T$ approximately at the rate $\frac{\tau^2}{T^2}$. This method has been used previously and the considerations above have been shown to be qualitatively correct.\

Using the results of the last chapter the random walk model as described above may be refined. In this limit, the spectral diffusion constant $D$ is the ratio of the (mean free path)$^2$ to the average jump time. Therefore $D$ may be written:

$$D = \frac{\langle (\omega_i - \omega_j)^2 \rangle}{T_2} = \frac{2\langle (\omega_1 - \omega_0)^2 \rangle}{T_2^2}$$

For the simplified model of the homogeneous line, lorentzian with a cutoff at $(\omega_1 - \omega_0) = \frac{\omega_{SN}}{2}$, $D = \frac{2}{T_2^2} \left[ \frac{1}{\pi} \left( \frac{T_2^2 \omega_{SN}^{-2}}{T_2^2} \right) \right]$. It is shown later that this result is essentially correct for the random walk limit. Since this is the model used in the general formulation of the spectral diffusion problem, it is instructive to discuss its expected limitations at this point. In particular, what is the effect of the cutoff? The diffusion constant is linearly dependent on this cutoff value. With the wings of the line actually gaussian, it is reasonable to expect a distribution constant of diffusion constants rather than a unique diffusion constant. This affects the experimental situation in that the rate of decay, $\frac{1}{T_S} = D\tau^2$, of the stimulated echo will not be unique. Thus the decay law will be non-exponential rather than exponential as would be expected otherwise. The spins with the largest diffusion constant will dominate the decay at short times and the spins with the smallest will
dominate at long times. Clearly, the spins in the wings of the spin-packet would be assigned the large diffusion constants. The experimental results presented in a later section supports this hypothesis. Also, some of the observations of Weger$^{13}$ support this hypothesis. In studying spectral diffusion in multidomain cobalt, he found that the long time diffusion rate was surprisingly large in the limit of very small $\tau$. At very small $\tau$ all diffusion rates are small and it becomes increasingly difficult in this limit to know when one is measuring the smallest rate. In this study where the observed experimental results are more simple than the multidomain results, I observed no anomalous behavior at short $\tau$ of the long time diffusion rate. Since the choice of cutoff was made by determining when the experimental measured transverse decay becomes approximately exponential, this model should accurately describe the long time diffusion processes. Thus, I will compare the results of the experimental study of the long time diffusion processes to the calculated predictions of the simplified spin packet model.

The theory derived in this chapter predicts the general dependence of the diffusion relaxation rate on $\tau$ and reduces to the random walk results in the limit $\tau \ll T_2$. The presentation of the general diffusion problem in a particular physical manner by Kubo$^7$ and in a very elegant manner by Zubarev$^8$ has been of considerable help in formulating the spectral diffusion problem. The physical considerations presented for the remainder of the introduction are motivated by the discussion of Kubo.$^7$

Diffusion processes are governed by the behavior of the currents of the macroscopic variables (that characterize the macroscopic state of the system) after the system has been disturbed from its equilibrium state. For spectral diffusion, the ensemble average of the zeeman energy
density function, \( \langle H(\omega) \rangle = \langle -\hbar \omega \sum_{l \omega} I^Z \rangle \) are the variables of interest. Here the ensemble average is taken over the nonequilibrium density matrix. The current is defined by the continuity equation \( \frac{\partial \langle J(\omega) \rangle}{\partial \omega} = -\frac{\partial \langle H(\omega) \rangle}{\partial t} \).

In a time of order \( T_2 \) after the system is disturbed the spin temperature approximation is valid. That is, local equilibrium is established in the subsystems of the spin packet. These subsystems are characterized by their frequencies (homogeneous frequencies). After a time of order \( T_2 \) the macroscopic variables proceed at a slower rate and the various subsystems can be considered in quasi-equilibrium. This means that the spin temperature in each subsystem is well defined, but it has a slow varying time dependence. A description of this type of process is prescribed by quasi-thermodynamical theory.

In quasi-thermodynamical theory, the behavior of the currents are governed by the law of increase in entropy. The macroscopic state is described by the variable \( \langle H(\omega) \rangle - \langle H(\omega) \rangle_L \), where \( \langle H(\omega) \rangle_L \) designates the ensemble average taken over the equilibrium distribution. Then, in equilibrium, all these variables equal zero. If the system is not far from equilibrium, it is assumed that the macroscopic state and all physical parameters that describe the state will depend linearly on the terms \( \langle H(\omega) \rangle - \langle H(\omega) \rangle_L \). In particular, the currents \( \langle J(\omega) \rangle - \langle J(\omega) \rangle_L \) and the derivatives of the entropy \( \frac{\partial S}{\partial \langle H(\omega) \rangle} \) can be represented by a linear expansion in these variables, since in equilibrium both these quantities are zero. Therefore it is a simple matter of algebra to express the mutual linear dependence of the quantities \( \langle J(\omega) \rangle - \langle J(\omega) \rangle_L \) and \( \frac{\partial S}{\partial \langle H(\omega) \rangle} \). This relationship is written in the following form:

\[
\langle J(\omega) \rangle - \langle J(\omega) \rangle_L = \frac{1}{k_{\text{B}} L} \sum_{\omega, \omega'} L(\omega, \omega') \frac{\partial S}{\partial \langle H(\omega) \rangle}.
\]
The $L(\omega, \omega')$ terms are called kinetic coefficients, and the symmetry between $L(\omega, \omega')$ and $L(\omega', \omega)$ is referred to as the Onsager relation. For the case considered here, $(J(\omega))_L$ is zero in the high temperature limit and this term will be dropped.

Thermodynamics gives the quantity $\frac{\partial S}{\partial (H(\omega))}$. Consider a closed system consisting of two subsystems with energy $E_1$ and $E_2$ and entropy $S_1$ and $S_2$. The total energy $E = E_1 + E_2$ is a constant. Thus

$$\frac{\partial S}{\partial E_1} = \frac{\partial (S_1 + S_2)}{\partial E_1} = \frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_2} \frac{\partial E_2}{\partial E_1} = \frac{\partial S_2}{\partial E_1} - \frac{\partial S_2}{\partial E_2} = \frac{1}{T_1} - \frac{1}{T_2}$$

Generalizing this discussion, $\frac{\partial S}{\partial (H(\omega))}$ becomes $\frac{K_B}{\delta \omega} \Delta \omega$ with the assumption of quasi-equilibrium. Here $K_B(\omega)$ is the reciprocal temperature of the spins of frequency $\omega$. The current may now be written

$$\langle J(\omega) \rangle = \frac{1}{\beta L} \sum_{\omega'} L(\omega, \omega') \frac{\partial \beta(\omega')}{\partial \omega'} \Delta \omega'$$

and in the continuous limit

$$\langle J(\omega) \rangle = \frac{1}{\beta L} \int_{-\infty}^{\infty} L(\omega, \omega') \frac{\partial \beta(\omega')}{\partial \omega'} \, d\omega'$$

Remembering the definition of the current, $\frac{\partial (H(\omega))}{\partial t} = -\frac{\partial \langle J(\omega) \rangle}{\partial \omega}$, the general diffusion equation is written:

$$III-1 \quad \frac{\partial (H(\omega))}{\partial t} = -\frac{\partial}{\partial \omega} \int_{-\infty}^{\infty} L(\omega, \omega') \left( \frac{1}{\beta L} \right) \frac{\partial \beta(\omega')}{\partial \omega'} \, d\omega'$$

This derivation has only depended on the concept of local equilibrium, spin temperature considerations, and the validity of quasi-thermodynamic theory. Therefore this result is quite general for the case considered here, $T_2 \ll T_1$. 

A prescription must be given for finding the kinetic coefficients \( L(\omega, \omega') \). The theory of quantum statistics of irreversible processes provides this prescription. It gives

\[
L(\omega, \omega') = \lim_{s \to +0} \frac{1}{\beta_L} \int_{-\infty}^{\infty} d\lambda \int_{-\infty}^{0} ds \left[ \frac{d}{dt} \langle J(\omega), J(\omega', t + i\lambda) \rangle_L \right]
\]

Note that the ensemble average is taken over the equilibrium density matrix. The correlation function will be shown to be related to the results of the microscopic theory in Chapter II and we will be able to use those results directly. It is convenient to rewrite Eq. III-1, in the Curie law limit, in terms of \( \langle I^Z(\omega) \rangle \) since this is the quantity that is measured experimentally.

\[
\text{III-2} \quad \frac{1}{\hbar \omega} \frac{\partial}{\partial t} \langle I^Z(\omega) \rangle = \int_{-\infty}^{\infty} L(\omega, \omega') \frac{\partial}{\partial \omega'} \left( \frac{\langle I^Z(\omega') \rangle}{\langle I^Z(\omega) \rangle_L} \right) d\omega'
\]

A spectral diffusion equation for \( \langle I^Z(\omega) \rangle \) was first given in Ref. 4. In summary, the hamiltonian of the system is used to define the zeeman current operator; then this operator is used to calculate the kinetic coefficients; and finally this quantity is substituted into Eq. III-2 to derive the diffusion equation. The method is tedious algebraically but straightforward.
B. Experimental Results

The experimental procedure is to monitor the stimulated echo amplitude as a function of the time separation between the first and third pulse, $T$, for a fixed time separation between the first and second pulse, $\tau$. In Fig. 10 the log of the signal is plotted versus $T$ for $\tau = 2$, $9$, and $13.8$ μsec. Consistent with our earlier discussion, the decay is initially non-exponential with the relaxation rate faster at short times than at long times. The decay law is exponential at long times. The short time decay rate is roughly twice the long time decay rate. Note also that the rate of decay is $\tau$ dependent at both long and short times. This confirms our earlier discussion concerning the possibility of a distribution of diffusion constants. All effort was made to measure the slowest relaxation rate. The noise level of the experimental setup was the limiting factor. That is, where there was doubt, the signal was monitored until the noise level was comparable to the signal. This means that the rate determined for large $\tau$ has greater uncertainty than that at short $\tau$. However, the overall accuracy is estimated to be within 20%.

The rate of decay determined from the slope of the exponential portion of the curves in Fig. 10 is plotted versus $\tau^2$ in Fig. 11 for various values of $\tau$. Initially the decay rate is directly proportional to $\tau^2$ as expected in the random walk limit. From the slope of the curve, $D$ is determined to be $3.77 \times 10^{-5}$ (μsec)$^{-3} = 0.85/T_2^3$. This is of the order expected from the introductory remarks. For larger $\tau$ the rate of the decay varies less than $\tau^2$.

The value of the decay rate obtained by extrapolating the curve in Fig. 11 to $\tau = 0$ gives a measure of the other longitudinal relaxation processes. A value of $T_1 = 950$ μsec is determined. This value is quite
smaller than the value 3200 μsec reported in Ref. 25 and 26 for the intrinsic Co\textsuperscript{59} single domain longitudinal relaxation time. The ratio of the measured $T_1$ to the intrinsic value is .3. This is very close to the ratio of .33 ± .03 value reported in Ref. 25 for the ratio of the long time Bloch wall longitudinal relaxation time to the intrinsic value. This indicates that the $T_1$ determined by the stimulated echo in ferromagnetic metals at moderate d.c. fields ($H_0 < 4\pi M$) is due to Bloch wall processes. Evidence has been reported in Ref. 10 that also supports this conclusion. In a similar study to this one, the relaxation time determined by the stimulated echo technique was smaller than that determined by observing the magnetization recovery after a series of saturating pulses. Also the relaxation time was shown to be field independent for fields $H_0 < 4\pi M$ when determined by the stimulated echo, in contradiction to the results obtained by the other method. This may be explained by remembering that when one studies nuclear magnetic resonance in metals, the spins observed are in the rf skin depth, about 1 micron for cobalt. If there are nearby Bloch walls, unsaturated particles, fluctuating fields can relax these spins in a manner similar to the way that spins are relaxed in the wings of Bloch walls. In the saturation technique a larger portion of the sample will be saturated.\textsuperscript{3} Then, during the recovery of the magnetization this energy may diffuse back to the surface to delay the recovery of the spins that are observed, since the observed spins are at a lower temperature. This is a diffusion in space problem. As stated previously the range of the interaction is of the order of 30 lattice spacings, .01 micron. In the time $T_1$, spin energy can diffuse a distance of $\sqrt{T_1/T_2} .01 \approx .1$ micron. The number of spins in this distance is approximately $\frac{1}{10}$ the number of spins in the skin depth. It is thus
conceivable that because of spacial diffusion, the stimulated echo technique gives the shorter $T_1$.

Returning to Fig. 12, we see that the diffusion relaxation is essentially independent of field in the range of applied d.c. fields. The tendency for the diffusion rate to be larger at larger fields is probably due to the fact that the signal is smaller because of the smaller enhancement factor. This makes the noise limitation more of a factor and increases the uncertainty in obtaining the smallest relaxation rate. To understand the lack of dependence of the diffusion constant on field, consider the diffusion constant derived in the introduction,

$$D = \frac{2}{\pi} \left( \frac{T_2 \omega_{SN} - \pi}{\frac{T_2^3}{T_2}} \right).$$

It is shown in the next section that this result is essentially correct. For $v_0 = 215.9$ mHz, $T_2 \omega_{SN} \approx 3.78$. Thus the numerator is quite small. For the range of fields considered, as the field increases, the numerator will increase and this effect will be essentially nullified by the increase of the denominator. Using this equation and the values of $T_2$ determined from Fig. 5, a decrease in the diffusion constant of 6% is estimated in going from 215.9 to 213.9 mHz. This is less than experimental uncertainty.

The experimental results for spectral diffusion are in agreement with our qualitative considerations. This is particularly true for the random walk limit. In the next section, we will consider the theory quantitatively and it will be shown that these results can be predicted from the cutoff lorentzian model.
C. Macroscopic Theory

In the introduction, it was shown that the starting point of the macroscopic theory is the diffusion equation

\[ \frac{\partial}{\partial t} \langle I_z(\omega) \rangle = \frac{1}{\hbar \omega} \frac{\partial}{\partial \omega} \int_{-\infty}^{\infty} L(\omega, \omega') \frac{\partial}{\partial \omega'} \left( \frac{\langle I_z(\omega') \rangle}{L} \right) \, d\omega', \]

\[ L(\omega, \omega') = \beta_L \int_{-\infty}^{0} t^{st} \langle J(\omega, 0) J(\omega', t) \rangle_L \, dt. \]

For convenience \( s \) is set equal to zero at this point rather then after the integration over time since this does not affect the results here. The hamiltonian for the system which has been discussed earlier will now be used to derive the zeeman energy current operators. The hamiltonian is written

\[ H = \sum_{l} H_{l}^z + \sum_{l,j} A_{l,j} I_{l}^+ I_{j}^- , \quad H_{l}^z = -\hbar \omega_{l} I_{l}^z. \]

Consider the equation of motion of \( H_{l}^z \).

\[ \frac{\partial H_{l}^z}{\partial t} = -\frac{i}{\hbar} \left[ H_{l}^z, H \right] = i\omega_{l} \sum_{j+l} A_{l,j} \left\{ I_{l}^+ I_{j}^- - I_{l}^- I_{j}^+ \right\}. \]

From the continuity condition the current operator may be written

\[ \frac{\partial J}{\partial \omega} = -\frac{\partial H_{l}^z(\omega)}{\partial t} = -\sum_{l, \omega} H_{l}^z = -i\omega \sum_{l, \omega} \sum_{j+l} A_{l,j} \left\{ I_{l}^+ I_{j}^- - I_{l}^- I_{j}^+ \right\}. \]

If we take \( J(- \infty) = 0 \), we have
Having the current operator, the procedure is now to calculate the kinetic coefficients which is written

\[
J(\omega) = -i \int_{-\infty}^{\infty} \sum_{l \epsilon \omega} \sum_{j \epsilon l} A_{ij} \left\{ I^+_k I^-_j - I^-_k I^+_j \right\} d\omega.
\]

The handling of the correlation function is exactly the same as in II-8. Namely, the high temperature limit is assumed. \(L(\omega, \omega')\) can now be written

\[
L(\omega, \omega') = -\beta L \int_{-\infty}^{0} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \sum_{i \epsilon \omega''} \sum_{j \epsilon i} \sum_{k \epsilon \omega'''} \sum_{l \epsilon k} A_{ij} A_{kl} \left\{ (I^+_i I^-_j - I^-_i I^+_j)(0)(I^+_k I^-_l - I^-_i I^+_j)(t)\right\}_L \times d\omega'' d\omega'' d\omega'
\]

The correlation functions here were the subject of discussion in Chapter II. It is clear now why the simplified model of the spin packet was introduced. These correlation functions are too complex functionally to handle in closed form. Thus I will take for example,

\[
(I^+_i(t) I^-_i(0))_L = \ell \int_{-t/T_2}^{t/T_2} (I^+_i(0) I^-_i(t))_L
\]
and remember that the integration over frequency is restricted to the spectrum width of the spin packet model. For simplicity of notation I will not write the limits in until the calculation is completed. Note that in Eq. III-5, the summation over $k$ and $\ell$ can be made. The term

$$\delta_{i k} \delta_{j k} - \delta_{i k} \delta_{j \ell}$$

leads to the frequency criteria

$$\delta(\omega'' - \omega_j) - \delta(\omega'' - \omega_j) .$$

Remembering that $A_{ij} = A_{ji}$, and using the following definition

$$\frac{1}{T^2(\omega')} + \frac{1}{T^2(\omega_j)} = \frac{1}{T^2(\omega_j, \omega_j)} ,$$

Eq. III-5 can be written

$$L(\omega, \omega') = -2 \beta_L (I^+(0) I^-(0)) L \left\{ \int_{-\infty}^{0} \int_{-\infty}^{\omega} \int_{-\infty}^{\omega'} \omega'' \omega''' \sum_{i} \sum_{j+1} (A_{ij})^2 \right\} \frac{t/T^2(\omega'', \omega_j)}{\cos(\omega'' - \omega_j)} t \times [\delta(\omega'' - \omega_j) - \delta(\omega'' - \omega_j)] \right\} d\omega'' d\omega' dt$$

Note that for $\omega_j = \omega_j L(\omega, \omega') = 0$. This shows that only terms are presented that lead to spectral diffusion. The integral over $\omega'''$ can be made and gives

$$\int_{-\infty}^{\omega'} \omega'' \left\{ \delta(\omega'' - \omega_j) - \delta(\omega'' - \omega_j) \right\} d\omega''' = \omega_j K(\omega', \omega_j) - \omega'' K(\omega', \omega'')$$

where $K(x, y) = \begin{cases} 1 & x \geq y \\ 0 & x < y \end{cases}$. Since the total energy of the system, zeeman plus spin-spin, must be conserved, $|\omega'' - \omega_j| \approx \frac{1}{T^2}$ and since $\omega \approx \frac{4x10^4 h}{T^2} \gg \frac{1}{T^2}$, we set $\omega'' = \omega_2$ and obtain

$$\int_{-\infty}^{\omega'} \omega'' \left\{ \delta(\omega'' - \omega_j) - \delta(\omega'' - \omega_j) \right\} d\omega''' \approx \omega'' \left\{ K(\omega', \omega_j) - K(\omega', \omega'') \right\} .$$
The integral over $t$ can be made also.

$$
\int_{-\infty}^{0} t^{2} T_{2}^{2}(\omega'', \omega_{j}) \cos (\omega'' - \omega_{j}) t \, dt = \frac{T_{2}(\omega'', \omega_{j})}{1 + (\omega'' - \omega_{j})^{2} T_{2}^{2}(\omega'', \omega_{j})}
$$

Combining these results, III-5 becomes

$$
L(\omega, \omega') = -2 \beta_{L} \langle I^{+}(0) I^{-}(0) \rangle_{L} \int_{-\infty}^{\omega} (\omega'')^{2} \sum_{i \omega''} \sum_{j+1} A_{ij}^{2} \{K(\omega', \omega_{j}) - K(\omega', \omega'')\}
\left[ \frac{T_{2}(\omega'', \omega_{j})}{1 + (\omega'' - \omega_{j})^{2} T_{2}^{2}(\omega'', \omega_{j})} \right] d\omega''
$$

It is worth noting that the integral over $\omega'$ in the diffusion equation is quite simple. It will be simply

$$
\int_{-\infty}^{\omega} \{K(\omega', \omega_{j}) - (\omega', \omega'')\} \frac{\partial}{\partial \omega'} \left( \frac{\langle I^{2}(\omega') \rangle}{\langle I^{2}(\omega') \rangle_{L}} \right) = \frac{1}{\beta_{L}} \int_{-\infty}^{\omega} \{K(\omega', \omega_{j}) - K(\omega', \omega'')\}
\left[ \frac{\beta(\omega') - \beta(\omega_{j})}{\beta_{L}} \right]
$$

Also the derivative with respect to $\omega$ is simple. Using these results and substituting into II-2, we get for the diffusion equation:

$$
\frac{\partial}{\partial t} \langle I^{2}(\omega) \rangle = -\frac{2}{\beta_{L}} \langle I^{+}(0) I^{-}(0) \rangle_{L}^{2} \omega^{2} \sum_{i \omega''} \sum_{j+1} A_{ij}^{2} \left[ \frac{T_{2}(\omega, \omega_{j})}{1 + (\omega - \omega_{j})^{2} T_{2}^{2}(\omega, \omega_{j})} \right]
\left\{ \beta(\omega) - \beta(\omega_{j}) \right\}
$$
Although the calculation so far has been tedious algebraically, no series approximation has been made other than the assumption of pure exponential decay which seemed absolutely necessary. The assumption based on energy conservations should not effect our results. At this point, it is again assumed that the microscopic inhomogeneity is spatially random and average over position using the distribution function $g(\omega_j - \omega)$. Also we assume that the $\sum_{i=e\omega} A^2_{ij}$ can be written $Ng(\omega) A^2_{ij}$. Writing

$$\frac{1}{T_2(\omega)} = \frac{N\pi}{\lambda^2} \sum_{j} A^2_{ij} n_x(\omega),$$

summing over $j$ in the diffusion equation:

$$\frac{\partial}{\partial t} \langle I^z(\omega) \rangle = \frac{-2\pi\omega}{3} \frac{(I)(I+1)}{T_2(\omega)} \frac{N}{\pi} \int g(\omega_j) \frac{T_2(\omega,\omega_j)}{1 + (\omega - \omega_j)^2 T_2(\omega,\omega_j)} d\omega_j.$$

Remembering our spin packet model, the integral must be restricted to $\omega_0 - \frac{\omega_{SN}}{2}$ and $\omega_0 + \frac{\omega_{SN}}{2}$. Also the lorentzian distribution is more sharply peaked than the gaussian so $g(\omega_j)$ can be set equal to $\tilde{g}(\omega)$; $T_2(\omega,\omega_j)$ can be set equal to $T_2(\omega,\omega) = \frac{T_2(\omega)}{2}$. Writing $\langle I^z(\omega) \rangle = \frac{1}{2} Ng(\omega)(I)(I+1) \tilde{g}(\omega)$ in the Curie law limit; and assuming periodic modulation, the final result is written

$$\frac{\partial}{\partial t} \langle I^z(\omega) \rangle = -\frac{1}{\pi} \int \left[ \frac{\omega_{SN}}{2} \right] \left\{ \frac{1 - \cos(\omega - \omega_j) \tau}{1 - (\omega - \omega_j)^2 (\frac{T_2(\omega)}{2})^2} \right\} \langle I^z(\omega) \rangle$$

$$\frac{\partial}{\partial t} \langle I^z(\omega) \rangle = \frac{1}{T_2} \langle I^z(\omega) \rangle.$$
The result \( \cos (\omega J \omega_0) \tau = \cos(\omega J \omega) \tau \cos(\omega_0 \omega) \tau - \sin(\omega_0 \omega) \tau \sin(\omega_0 \omega) \tau \), is used where the sine term gives a negligible contribution since it is an odd function.

Note that the diffusion equation predicts exponential decay. Also in the limit of \( \tau \ll \frac{1}{T_2} \), \( 1 - \cos(\omega - \omega_0) \tau \to \frac{(\omega - \omega_0)^2}{2} \tau ^2 \), and

\[
\text{III-7} \quad \frac{3}{\delta t} \langle I^2(\omega_0) \rangle = -\tau ^2 + \frac{2}{\pi} \left[ \frac{\omega SN T_2 - 4 \tan^{-1}(T_2 \omega SN/4)}{T_2^3} \right] \langle I^2(\omega_0) \rangle
\]

This is the random walk limit. The diffusion constant

\[
D = \frac{2}{\pi} \left[ \frac{\omega SN T_2 - 4 \tan^{-1}(T_2 \omega SN/4)}{T_2^3} \right] \approx \frac{5}{T_2^3}
\]

slightly underestimates the measured diffusion constant, \( \frac{85}{T_2^3} \). I have plotted the result of the numerical integration of III-6 in Fig. 11. The results were adjusted to fit at \( \tau = 0 \). It is seen that the agreement for all \( \tau \) is quite good. For comparison, the dashed line gives the predicted spectra diffusion relaxation rate for a gaussian relaxation function,

\[
\phi(t) = \frac{t}{1 + 2 / T_2 ^2}
\]

For this relaxation function,

\[
\frac{1}{T_S \text{ (gaussian)}} = \frac{2}{T_2} [1 - t^2 / T_2 ^2]
\]

is to be compared with III-6 which gives \( \frac{1}{T_S} = \frac{2}{T_2} [1 - t^{-2\tau / T_2}] \) in the limit \( \tau \omega \frac{SN}{2} \to \infty \). Both functions lead to a maximum relaxation rate of \( \frac{2}{T_2^2} \), however the gaussian relaxation function leads to saturation much more rapid than the observed results. Considering the uncertainty in choosing the cutoff, and the obvious oversimplification of the actual experimental situation, this agreement between theory and experiment is quite remarkable.
Here I have shown that the simple model of the homogeneous line, a lorentzian distribution of width, $T_2^{-1} = \sqrt{\pi/2} \frac{\omega_{SN}}{\sigma}$ and cutoff $\frac{\omega_{SN}}{2}$, gives a simple physical picture of the spectral diffusion problem.
IV. APPARATUS

The main considerations in designing and building the transient study apparatus was detection sensitivity and minimizing the adverse effect the large rf pulses have on the detection system. The latter consideration is necessary since the rf pulses are of the order of 100 volts and the induction signals are of the order of microvolts. Thus receiver saturation following the rf pulses is a common problem in this type of study. The system had a measured sensitivity greater than 3 microvolts, and under most conditions, data could be taken as close as 1 μsec after a rf pulse. The IF amplifier was most vulnerable to saturation, and since it was preceded by an attenuator, saturation was more of a problem at small signals and less attenuation. A block diagram of the apparatus is given in Fig. 13.

The oscillator was borrowed from Prof. Hahn's experimental group and the design was that of the Arenberg PG 650 random phase pulsed oscillator. I designed and constructed the wide band converter, see Fig. 14. The converter consisted of a two stage grounded grid preamplifier and a pentode mixer and cathode-follower stage. The grounded grid designed pre-amplifier stage had the advantage of being stable and easily adjusted. The low impedance input, approximately 50 ohms, was convenient for matching to the series tuned sample network by 50 ohm coaxial cable. The low Q of the two stages, approximately 10 - 15, prevented excessive ringing due to the large rf pulses. The mixer stage had a Q of approximately 10 for the same reason. To minimize saturation of the IF amplifier, diode gates were placed after the mixer oscillator and after the converter. These gates were closed during the pulse excitation. However the effectiveness of these gates is limited at 200 MHz because of the capacitance of the diodes, mpa 1001. A boxcar integrator was used to improve the signal
to noise ratio. The box car integrator, and pulse generator system was
built by the Physics Department Electronic Shop. A pulse amplifier for
the system was built by Dr. J. N. Aubrun and myself patterned after the
type designed by Arenberg for the Arenberg PG 650 oscillator. The pulse
delay units were analogue devices. For pulses delayed a long time such
as occur in $T_1$ measurements, pulse jitter was excessive. To correct this,
the pulse delayed for a long time was first applied to a coincidence
circuit along with a signal from a pulse generator tuned to 25 kHz. The
pulse generator was synchronized by the reference signal from an electronic
frequency counter HP524-c. The width of the pulse from the pulse delay
unit was made large enough so that jitter did not destroy the coincidence
with the signal from the pulse generator. Then the signal from the coin­
cidence circuit was used to trigger a pulse delayed short time. Thus,
measurements were made in steps of 40 µsec and this system essentially
eliminates pulse jitter noise. This system was designed and constructed
by Dr. J. N. Aubrun. This method was also used for $T_2$ measurements to
facilitate time measurements. Here measurements were made in steps of
2 µsec, this corresponds to steps of 4 µsec in 2$\tau$.

The sample matching circuit illustrated in Fig. 15 was used to direct
the rf pulse to the sample and the nuclear induction signal to the receiver.
For large pulse signals, the diodes at the receiver input produce a low
input impedance which is transformed by the quarter wave line into a large
impedance at the sample. Therefore the rf pulse is directed toward the
sample while the diodes at the transmitter output has little effect since
they are essentially shorts at this rf level. However for the small in­
duction signal the impedance of the diodes at the transmitter output is
large; this causes a large impedance in the direction of the transmitter
while the impedance in the direction of the receiver is now small. In
actually the coaxial cable lengths were adjusted for maximum signal and
the stub used as a fine tune impedance match network. The sample coil
winding was also adjusted for maximum signal.

The philosophy in taking the measurements was to maintain a constant
nuclear induction signal at the IF detector input. Thus as the signal
increased, attenuation was increased. This way, the measurements were
independent of the detector response. Since the smallest increment of
attenuation was 1 dB it was necessary to extrapolate for signal changes
less than this amount. The converter was linear within 10% over a
range of 30 dB. Therefore the relaxation measurements represent
accurately the relaxation processes.
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Appendix A

\( \langle I^+(t) I^-(0) \rangle \) is calculated for independent spins in the high temperature limit. The hamiltonian of the system is \( H = -\hbar \omega I^Z \). The density matrix is \( \rho = \frac{1}{2I+1} \). For this case

\[
I^+(t) = i\frac{\hbar}{\omega} H t I^+(0) = i\frac{\hbar}{\omega} \dot{I}^Z wt \ I^+(0) I^Z wt .
\]

The rotation relations for \( I^X \) and \( I^Y \) can be written:

\[
\begin{align*}
I^X & = I^X \cos \phi + I^Y \sin \phi \\
I^Y & = I^X \sin \phi + I^Y \cos \phi
\end{align*}
\]

Thus,

\[
\langle I^+(t) I^-(0) \rangle = i\frac{\hbar}{\omega} \dot{I}^Z wt \ I^+(0) I^-(0) = i\frac{\hbar}{\omega} \dot{I}^Z wt (I^X + I^Y + I^Z) = \frac{2}{3} \langle I \rangle
\]

\[
(I + 1) i\frac{\hbar}{\omega} \dot{I}^Z wt
\]

Appendix B

Here

\[
\left\langle \frac{1}{\gamma_e (H_{loc} + H_A) + \omega E \frac{\hbar^2}{2} + \frac{\alpha_m}{2} \sin^2 \theta} \right\rangle
\]

\[
= \frac{1}{2} \int_0^\pi \frac{\sin \theta \ d\theta}{\gamma_e (H_{loc} + H_A) + \omega E \frac{\hbar^2}{2} + \frac{\alpha_m}{2} \sin^2 \theta}
\]

is calculated. Let

\[
b = \frac{\omega m}{2} ; a = \gamma_e (H_{loc} + H_A) + \omega E \frac{\hbar^2}{2} + \frac{\alpha_m}{2} ;
\]

then \( b < a \). In terms of \( a \) and \( b \) the average may be expressed
\[
\left\langle 1 \right\rangle = \frac{1}{2} \int_{0}^{\pi} \frac{\sin \theta \, d\theta}{a-b \cos^2 \theta} = \frac{1}{2a} \int_{0}^{\pi} \frac{\sin \theta \, d\theta}{1 - \frac{b}{a} \cos^2 \theta} = \frac{1}{2a} \int_{0}^{\pi} \sum_{n=0}^{\infty} \left( \frac{b}{a} \right)^n (\cos \theta)^{2n} \sin \theta \, d\theta
\]
\[
= \frac{1}{2a} \sum_{n=0}^{\infty} \frac{b}{a} \left( \cos \theta \right)^{2n+1} \bigg|_{0}^{\pi} = \frac{1}{a} \sum_{n=0}^{\infty} \frac{1}{2n+1} \left( \frac{b}{a} \right)^n \approx \frac{1}{a} \left( 1 + \frac{b}{3a} \right)
\]

Thus,
\[
\frac{1}{\gamma_e (H_{\text{loc}} + H_a) + \omega_E a^2 k^2 + \frac{\omega_m}{2} \sin^2 \theta_k} \approx \frac{1}{\gamma_e (H_{\text{loc}} + H_a) + \omega_E a^2 k^2 + \frac{\omega_m}{2}}
\]

Appendix C

If \( \langle I_j^+(+I_j^-(-) \rangle = e^{-imj} \varnothing_j(t) \langle I_j^+(0) I_j^-(0) \rangle \) is substituted into II-8, II-9 becomes

C-1 \[ \frac{\partial \varnothing_j}{\partial t} = - \frac{4}{3} \frac{(I(I+1))}{\hbar^2} \sum_{I \neq j} \sum_{l \neq j} \int_{0}^{t} \varnothing_j(t') \varnothing_j^*(t'-t) I \frac{\omega_l - \omega_j}{\omega_l - \omega_j} (t'-t) \, dt' \]

Let \( \varnothing_j(t) = \phi(t) e^{i\varnothing_j(t)} \). Then C-1 becomes

\[ \frac{\partial \phi_j(t)}{\partial t} + i \phi_j(t) \frac{\partial \varnothing_j}{\partial t} = - \frac{4}{3} \frac{(I(I+1))}{\hbar^2} \sum_{I \neq j} \sum_{l \neq j} \int_{0}^{t} dt' \phi_j(t') \phi_l(t'-t) \left[ (\omega_l - \omega_j)(t'-t) + \varnothing_j(t') - \varnothing_j(t) - \varnothing_l(t'-t) \right] \]

Equating the imaginary parts and real parts:
In order to estimate $\theta_j$, the iteration method is used. $\theta$ is set equal to zero and $\phi$ equal to one in the integrand. Averaging frequency over position as was done in the text and substituting $\tau = (t-t')$, the first order iteration gives

$$
\frac{\partial \theta_j(t)}{\partial t} = -\frac{4}{3} \frac{(I)(I+1)}{n^2} \sum_{l+j} \int_0^t \phi_j(t') \phi_i(t'-t) \int_0^t \cos [(\omega_i-\omega_j)(t'-t) + \theta_j(t') - \theta_j(t) - \theta_i(t'-t)]
$$

$$
\frac{\partial \theta_j(t)}{\partial t} = -\frac{4}{3} \frac{(I)(I+1)}{n^2} \sum_{l+j} \int_0^t \phi_j(t') \phi_i(t'-t) \int_0^t \sin [(\omega_i-\omega_j)(t'-t) + \theta_j(t') - \theta_j(t) - \theta_i(t'-t)]
$$

The identity

$$
\sin(\omega_j-\omega_i) \tau = \sin(\omega_i-\omega_j) \tau \cos(\omega_j-\omega_i) \tau \sin(\omega_j-\omega_i) \tau \cos(\omega_i-\omega_j) \tau
$$

is used to evaluate the integrand.

The second term is odd and will not contribute to the integral over $\omega_j$. Let $\tilde{g}(\tau) = \frac{1}{2\pi \tau} \int_0^\infty g(\omega_j-\omega_0) \cos(\omega_j-\omega_0) \tau \cos(\omega_i-\omega_i) \tau$.

Then $\frac{\partial \theta_j}{\partial t}$ may be written,

$$
\frac{\partial \theta_j}{\partial t} = 2\pi \frac{\omega_j}{SN} \int_0^t \sin(\omega_i-\omega_j) \tau \tilde{g}(\tau).
$$
Note: \( \tilde{g}(0) = \frac{1}{2\pi} \) and \( \int_{-\infty}^{\infty} \tilde{g}(\tau) \, d\tau = g(0) \).

We approximate
\[
g(\tau) = \begin{cases} 
\frac{1}{2\pi} : & -\pi \leq \tau \leq \pi g(0) \\
0 : & \text{otherwise}
\end{cases}
\]

Thus, for \( t \gg \pi g(0) \)
\[
\frac{\partial \Phi_{l}(t)}{\partial t} = \omega_{SN}^2 \int_{0}^{\pi g(0)} \sin(\omega_{0} - \omega_{l}) \tau \, d\tau = \frac{\omega_{SN}^2 (1 - \cos \pi g(0) (\omega_{0} - \omega_{l}))}{\omega_{0} - \omega_{l}} \ll \omega_{0}
\]
\[
= \frac{\pi \omega_{SN}^2}{2} g^2(0) (\omega_{0} - \omega_{l}) \ll \omega_{0}
\]

Appendix D

Here we calculate II-9 and II-11 by iteration. In II-9, for \( \omega_{i} = \omega_{j} \)

D-1 \[
\frac{\partial \phi_{i}(t)}{\partial t} = -\omega_{SN}^2 \int_{0}^{t} \phi_{i}(t') \phi_{i}(t'-t) \, dt', \text{ for the first iteration set}
\]
\( \phi(t') = \phi(t'-t) = 1 \). Then D-1 is
\[
\phi_{i}(t) = 1 - \frac{\omega_{SN}^2}{2} t^2 \approx \frac{\omega_{SN}^2 t^2}{2}
\]

In II-11 in the limit \( t \to \infty \), in first order iteration
\[
\frac{\partial \phi_{i}}{\partial t} = -\frac{\omega_{SN}^2}{2} \lim_{t \to \infty} \int_{-\infty}^{t} \int_{-\infty}^{t} g(\omega_{j} - \omega_{0}) \cos(\omega_{j} - \omega_{1}) \tau \, d\tau \, d\omega_{j}
\]
\[
= -\frac{\omega_{SN}^2}{2} \int_{-\infty}^{\infty} 2\pi \delta(\omega_{j} - \omega_{1}) g(\omega_{j} - \omega_{0}) \, d\omega_{j} = -\frac{\omega_{SN}^2 \pi g(\omega)}{2}
\]
In second order,

\[
\phi_i(t) = 1 - \omega_{SN}^2 \nu g(\omega_i) \tau \quad \phi_i(t-\tau) = 1 - \omega_{SN}^2 \nu g(\omega) (t-\tau).
\]

\[
\frac{\partial \phi_i}{\partial t} = \omega_{SN}^2 \nu g(\omega_i) + \omega_{SN}^2 \nu g(\omega) t \left[ + \frac{\omega_{SN}^2}{2} \lim_{t \to \infty} \int_{-t}^{t} g(\omega_j - \omega_0) \cos(\omega_j - \omega_0) \tau \, d\tau \, d\omega_j \right]
\]

\[
= -\pi \omega_{SN}^2 g(\omega) + \left[ \omega_{SN}^2 \nu g(\omega) \right]^2 \frac{t}{2}.
\]

\[
\phi_i(t) = 1 - \pi \omega_{SN}^2 g(\omega) t + \left[ \pi \omega_{SN}^2 g(\omega) \right]^2 \frac{t^2}{2}.
\]

\[
\sim -\pi \omega_{SN}^2 g(\omega) t.
\]
REFERENCES


13. Experimental support for this statement has been recently reported by J. Barak and N. Kaplan in private correspondence.

22. In private correspondence with Professor Hahn, M. B. Stearns reports
   that the theory in Ref. 20, in the limit of extreme microscopic inhomogeneous
   broadening, predicts no echo amplitude modulation for a 90°-180°
   pulse sequence applied to a system of spin 1/2 particles coupled by the
   Suhl-Nakamura interaction.
   (1962) pg. 91.
29. C. P. Bean, J. D. Livingston, and D. S. Rodbell, J. Phys. Radium 20,
   298 (1959).
Table I

<table>
<thead>
<tr>
<th>I</th>
<th>( \omega_E )</th>
<th>S</th>
<th>( \omega_0 )</th>
<th>( H_a )</th>
<th>( \omega_E )</th>
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<tr>
<td>7/2</td>
<td>3.9 ( 10^{13} ) sec(^{-1} )</td>
<td>0.85</td>
<td>1.36 ( 10^{9} ) sec(^{-1} )</td>
<td>1 kOe</td>
<td>10(^3)</td>
</tr>
</tbody>
</table>

I, \( \omega_E \), and S are taken from Reference 28.

\( H_a \) is taken from Reference 29.

\[
\gamma_f (H_{loc} + H_a + \frac{4\pi}{3} M)
\]
FIG. 1. Spherical ferromagnetic particle with a 180° Bloch wall. The arrows indicate the variation in the component of the magnetization parallel to the easy axis.
FIG. 2. Resonance frequency of Co$^{59}$ as a function of applied field in cobalt sponge.
Fig. 3  

(a) Spin echo pulse sequence.

(b) Stimulated echo pulse sequence.

\[ v_0 = 215 \text{ MHz} \]

\[ \frac{1}{2} \gamma H_{\text{eff}} t_{w_1} = \frac{\pi}{2} \]

\[ \frac{1}{2} \gamma H_{\text{eff}} t_{w_2} = \beta \]

\[ \tau \gg T_2^* \]
FIG. 4. Log of the spin echo amplitude versus time and turning angles.

- $\nu_0 = 215.9$ MHz
- $T_2 = 28.3$ microsec
FIG. 5. Log of the echo amplitude versus time and frequency for a 90°-90° pulse sequence.
FIG. 6. The square of the transverse relaxation time versus frequency.
Fig. 7 Spin wave band in cobalt for $H_{\text{LOC}} = 5$ kOe.
Fig. 8 Pair coherence model in a frame which rotates at frequency $\omega_0$. 

\[ t = \tau \]

\[ \omega_1 > \omega_2 \]

\[ A_{12} < 0 \]

\[ I_1^z(\tau) \propto \sin^2(\omega_1 - \omega_2) \frac{\tau}{2} \]

\[ I_2^z(\tau) \]

\[ t = \tau + \frac{\pi}{2} \text{ pulse} \]

\[ XBL699 - 3756 \]
Fig. 9  Spin packet model.
Fig. 10 Log of the stimulated echo amplitude versus T and τ.
FIG. 11. Longitudinal relaxation rate versus $\tau^2$ at 215.9 MHz.
Fig. 12 Longitudinal relaxation rate versus $\tau^2$ and frequency.
FIG. 13. Block diagram of the apparatus.
Fig. 14 Schematic of the wide band converter.
Fig. 15 Sample matching network.
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