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Spin-Lattice Relaxation of $^{19}$F in Ca F$_2$

at

Low Temperatures

by

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ABSTRACT

A study of nuclear relaxation due to paramagnetic impurities has been made, using the system of $^{79}$ nuclei in Ca F$_2$. $T_1$ was measured at helium, hydrogen, and nitrogen temperatures.

The field dependence of $T_1$ at helium temperatures consists of three parts: at fields less than a few hundred gauss, the dependence of $T_1$ on the field is parabolic; between a few hundred gauss and about 2.5 Kg, the dependence is linear; and at higher fields, it is linear, but has a steeper slope. Moreover, there is a strong orientation dependence in the helium range for a single crystal, and a size effect appears at higher fields. At temperatures above $14^\circ$K, $T_1$ has only a weak orientation dependence. The experimental data indicate that $T_1$ is minimum between $14^\circ$K and $63^\circ$K. An analysis of the experimental results with existing theories permits a determination of the field and temperature dependence of the relaxation time $\varphi$ of the spin of the paramagnetic impurity. The analysis gives $\varphi \sim H^{-2}T^{-1}$ for nitrogen and hydrogen temperatures. In the helium range, $\varphi \sim H^{-2}T^{-1}$ for $H_0 \leq 2.5$ Kg and $\varphi \sim H^{-1}T^{-2}$ for $H_0 \geq 2.5$ Kg. $\varphi$ is calculated to be $\sim 10^6$ sec. at $14^\circ$K and the impurity concentration is calculated to be approximately one part in $10^6$, assuming the impurity is iron.
I. INTRODUCTION

Since the first successful experiments in nuclear magnetic resonance (henceforth called nmr) were performed in 1946,¹² nmr has developed into a valuable tool in the study of the structure of matter. The experimentalist can gain information about interactions among the constituent atoms or molecules in solids by using the atomic nucleus as a probe.

Interactions involving nuclear spins can be divided conveniently into three broad categories. The first category takes in interactions of a spin with magnetic fields set up by other magnetic dipoles (both nuclear and electronic) in the solid. This magnetic dipole-dipole interaction gives rise to a mechanism which permits the redistribution of Zeeman energy in the spin system. This process is referred to as spin diffusion. A detailed analysis of the dipole-dipole interaction is considered in the theoretical section.

Another type of interaction is present only when the nuclei have an electronic quadrupole moment. In this case, the interaction is between the quadrupole moment and the crystalline electric field gradients at the nuclear sites. Reviews of quadrupolar effects have been given by Das and Hahn³ and Cohen and Reif⁴. The electric quadrupole interaction is only present when the nuclei have a spin \( I \geq 1 \). In this work, the nuclei under consideration have \( I = 1/2 \), therefore quadrupole interactions are absent.

The third category is the interaction of spins with
phonons or lattice vibrations of the solid. The modulation of the nuclear dipole-dipole interactions by the lattice vibrations was treated by Waller and later by Heitler and Teller, and has been shown to be ineffective in relaxing a nuclear spin system. However, in considering an electronic spin, it is the lattice vibrations which play the important role in relaxation.

Before going further, it would be well to define a few of the parameters used in a discussion of resonance phenomena. The principal quantities of interest in nmr are $T_1$, $T_2$, and $M_0$. The spin-spin relaxation time $T_2$ is the time constant associated with the decay of the component of the total nuclear magnetization perpendicular to the large externally applied field, $H_0$. This effect arises from local variations in $H$, which causes dephasing of the individually precessing magnetic moments. The spin-lattice or longitudinal relaxation time $T_1$ is the time constant associated with the exponential growth or decay (usually assumed to take place at the same rate) of the component of total magnetization in the direction of $H_0$. All degrees of freedom in the solid other than the spin degrees of freedom are collectively known as the lattice. $T_1$ may be regarded as a measure of the spin-lattice coupling and is in fact the time constant characteristic of the processes by which the spin system comes into equilibrium with the lattice. $M_0$ is the equilibrium value of the magnetization and is in the direction of $H_0$. More detailed definitions of these
parameters have been given in excellent reviews dealing with nuclear resonance.

In 1949, Bloembergen investigated spin-lattice relaxation of a system of nuclear spins both theoretically and experimentally in several dielectric materials. His results indicated that the observed $T_1$'s for the materials investigated were far shorter than those predicted by any previous theory. In addition to this discrepancy, the temperature dependence of $T_1$ was wrong. Bloembergen showed that the presence of small amounts of paramagnetic impurities could greatly shorten the spin-lattice relaxation time of the nuclei. He proposed that the unpaired electronic spins of the paramagnetic impurities were tightly coupled to the lattice. By means of a dipole-dipole interaction between the impurity spin and nuclear spins adjacent to it, these nuclear spins also could be coupled to the lattice. In addition, he showed that nuclear Zeeman energy could diffuse through the nuclear spin system to the vicinity of a paramagnetic impurity and be transferred to the lattice via the impurity spin. Bloembergen measured the temperature dependence of $T_1$ and showed that $T_1$ was a function of the impurity concentration.

Since 1949, some work has been reported in the literature with regard to a further experimental verification of Bloembergen's original proposals. However, most of this verification has been of a qualitative nature. Several authors have considered theoretically the nuclear relaxation process due to paramagnetic impurities in the lattice.
These theories have shown that a measurement of $T_1$, can give information concerning the number of impurities present and the strength of the coupling of the paramagnetic impurity to the lattice vibrations.

Although Bloembergen's original explanation for the relaxation process was generally accepted, it seemed advisable to make a thorough investigation of the validity of the model. With this in mind, a systematic study of $T_1$ for $F^{19}$ in CaF$_2$ was undertaken to test both the qualitative and quantitative agreement of the theory with experimental results.

In comparing experimental and theoretical results, it is necessary to know how the coupling of the impurity spins to the lattice depends on the parameters which were varied during the course of the experiment. The strength of the coupling of the impurity spin to the lattice is indicated by the size of the impurity spin-lattice relaxation time $\rho$ and it is this quantity which enters explicitly into all theoretically derived expressions for $T_1$. Therefore, to make a consistent comparison of theory and experiment for $T_1$ as a function of $H_0$, $T$ and sample size, it is necessary to know $\rho$ as a function of $H_0$, $T$ and sample size.

The theoretical problem concerning electron-paramagnetic spin-lattice relaxation has been treated by various authors and a review of the subject has been given by Van Vleck. Van Vleck's calculations have been successful in predicting the temperature dependence of $\rho$ at higher temperatures,
but at low temperatures his theory has met with some difficulties. Most other theories proposed for \( \varphi \) are applicable only when the concentration of paramagnetic spins is high enough so that there is an appreciable interaction between electron paramagnetic spins. In the samples used in this experiment the impurity concentration was very low, therefore, it is doubtful that a theory based on high concentrations of paramagnetic spins would be applicable. Recently Mattuck and Strandberg have proposed a theory for \( \varphi \) in which they consider the relaxation of low concentration paramagnetic spins at low temperatures. The field and temperature dependence which we conclude for \( \varphi \) at low temperatures is in agreement with the predictions of their theory. This theory for \( \varphi \) is discussed further in the theoretical section.

Very little progress has been made experimentally in understanding the spin-lattice relaxation process at low temperatures for low concentration impurities. Therefore, it would be of considerable interest to obtain information concerning the dependence of \( \varphi \) on field, temperature and particle size. We have conducted such an investigation to determine the behavior of \( \varphi \), in addition to verifying the theoretical predictions of the nuclear spin-lattice relaxation time.
II. THEORY OF NUCLEAR RELAXATION

A. Hamiltonian

We want to consider a system of $N_F$ fluorine nuclear spins ($I = 1/2$) in the presence of $N_p$ paramagnetic impurities where we will assume $N_p \ll N_F$. The Hamiltonian for the complete system may be written as

$$H = H_{\text{imp. spins}} + H_{\text{nuclear spins}} + H_{\text{interaction and lattice}}$$

The first term includes the energy of the lattice vibrations, orbital energy of the impurity in the crystalline field, magnetic energy of the impurity in the field $H_0$, interaction energy between lattice vibrations and orbits, spin-orbit coupling and spin-spin interaction between impurities. The second term contains the nuclear Zeeman energy and the nuclear dipole-dipole interaction energy. The third term represents the magnetic interaction between the impurities and the nuclear spins.

It is convenient to divide the Hamiltonian into two parts: one containing all terms involving nuclear spin interactions (last two terms) and the other in which interactions involving nuclear spins are absent. The terms dealing with nuclear spin interactions will be considered first. The last two terms of equation II-1 can be written:

$$H_2 + H_3 = -\sum_{i=1}^{N_F} \vec{\mu}_i \cdot \vec{H}_0 + \sum_{i=1}^{N_F} \sum_{j=1}^{N_F} \sum_{j=1}^{N_F} \left[ \frac{\vec{\mu}_i \cdot \vec{\mu}_j}{\lambda_{ij}^2} - \frac{3(\vec{\mu}_i \cdot \vec{\mu}_j)(\vec{\mu}_j \cdot \vec{\lambda})}{\lambda_{ij}^3} \right]$$

$$+ \sum_{i=1}^{N_F} \sum_{j=1}^{N_F} \sum_{j=1}^{N_F} \left[ \frac{\vec{\mu}_i \cdot \vec{\mu}_j}{\lambda_{ij}^2} - \frac{3(\vec{\mu}_i \cdot \vec{\lambda})(\vec{\lambda} \cdot \vec{\lambda})}{\lambda_{ij}^3} \right]$$
where \( N_F \) = number of fluorine spins
\( N_P \) = number of impurity spins
\( \mu = g \hbar \mathbf{I} \) = magnetic moment of fluorine nucleus
\( \mu_P = g_P \hbar \mathbf{S} \) = magnetic moment of impurity spin

and the Larmor frequencies are
\( \gamma = \frac{\mu}{I \hbar} H_0 \) for fluorine spins
\( \gamma_P = \frac{\mu_P}{S \hbar} H_0 \) for impurity spins.

The prime on the last sum means that nuclear spins very close to the impurities are omitted from the sum. The interaction of the nuclei very close to impurities is of the Fermi contact type and can be omitted as these nuclei have their resonant frequencies shifted far out on the wings of the absorption curve. The last two terms in equation II-2 are considered as perturbations on the Zeeman energy term. The zero order wave functions are those characteristic of the Zeeman energy.

B. Line Shape

The last two terms of II-2 give rise to a broadening of the Zeeman levels, and thereby cause a broadening of the resonance line shape. For very dilute impurity concentrations, less than 1% of the nuclei are directly affected by the impurities, and therefore, the last term can be neglected in determining the line shape. This leaves only the second term. This interaction \( \langle \mathbf{S} \cdot \mathbf{V} \rangle \) may be written in the form appropriate for the \( m_i, m_j \) representation by expanding the dot products in terms of the components of \( \mathbf{I} \) and the direction cosines of \( \mathbf{r}_{ij} \) in a coordinate system where
\( H_0 \) is parallel to the \( z \)-axis. We can then make a transformation to spherical polar coordinates, where \( \Theta_{ij} \) is the polar angle between \( \hat{z}_{ij} \) and \( H_0 \), and \( \Phi_{ij} \) is the azimuthal angle. Using the exponential forms for sine \( \phi_{ij} \) and cosine \( \phi_{ij} \), we have

\[
V_{ij} = \hat{z}_{ij} + \hat{z}_{ij}^3 (A + B + C + D + E + F)
\]

\[
A = I_{i;j} I_{j;i} (1 - 3 \cos^2 \Theta_{ij})
\]
\[\Delta M = M_f - M_i = 0, \quad M = \frac{1}{2} m_i
\]
\[\Delta m_i = \Delta m_j = 0
\]

\[
B = -\frac{i}{4} \left[ I_i^+ I_j^- + I_i^- I_j^+ \right] (1 - 3 \cos^2 \Theta_{ij})
\]
\[\Delta m_i = -\Delta m_j = \pm 1, \quad \Delta M = 0
\]

\[
C = -\frac{3}{2} \left[ I_i^+ I_{j;i} + I_j^+ I_{i;i} \right] \sin \Theta_{ij} \cos \Theta_{ij} e^{-i\Phi_{ij}}
\]
\[\Delta m_i = 0, \quad \Delta M = 1
\]
\[\Delta m_i = 1, \quad \Delta M = 0
\]

\[
D = -\frac{3}{2} \left[ I_i^- I_{j;i} + I_j^- I_{i;i} \right] \sin \Theta_{ij} \cos \Theta_{ij} e^{i\Phi_{ij}}
\]
\[\Delta m_i = 0, \quad \Delta M = -1
\]
\[\Delta m_i = -1, \quad \Delta M = 0
\]

\[
E = -\frac{3}{4} I_i^+ I_j^+ \sin^2 \Theta_{ij} e^{-2i\Phi_{ij}}
\]
\[\Delta m_i = \Delta m_j = 1, \quad \Delta M = 2
\]

\[
F = -\frac{3}{4} I_i^- I_j^- \sin^2 \Theta_{ij} e^{2i\Phi_{ij}}
\]
\[\Delta m_i = \Delta m_j = -1, \quad \Delta M = -2
\]
where
\[ I^- = I_x - i I_y \]
\[ I^+ = I_x + i I_y. \]

The A and B terms involve no energy change, because with these \( \Delta M = 0 \). Hence, they are secular in nature and are effective even when the spin system has no contact with an external lattice to which it can transfer energy.

The C, D, E and F terms, however, involve selection rules, \( \Delta M = \pm 1 \) and \( \Delta M = \pm 2 \), and are non-secular in nature. In the absence of a radio-frequency field, they can only be effective when the spin system is in contact with the external lattice in some way, so that the spin system can exchange energy with the lattice with a resultant change in \( M \). It has been shown that the direct coupling of the nuclei to the lattice is negligible. Therefore, terms C, D, E, and F need not be considered.

It is interesting to note the different physical mechanisms implied by the A and B term in producing the broadening of the resonance line. A precessing nucleus \( j \) produces at another nucleus \( i \) a precessing field (precessing around \( H_0 \)), which has a static \( z \)-component and a rotating component perpendicular to \( z \). The static component, taken care of by the A term, causes a broadening effect by virtue of its contribution to the externally applied field \( H_0 \). The rotating component can produce reciprocal transitions or mutual spin flips, with the
j^{th} nucleus undergoing a transition $\Delta m_j = \pm 1$ and the $l^{th}$ nucleus $\Delta m_l = \mp 1$. This additional process limits the life times of the spin states and consequently, a broadening effect appears. As will be seen later, this mutual spin exchange provides a mechanism by which Zeeman energy can be redistributed in the spin system and is responsible for spin-diffusion.

The problem of calculating the line shape $g(\nu)$ for a system of spins has been carried out only for the special case of a cubic lattice of spin 1/2 nuclei. However, Van Vleck has derived an expression for the general case for the second and fourth moments of the normalized line shape function $g(\nu)$, where the $n^{th}$ moment of $S_n$ is defined as

$$\Delta \nu^n = S_n = \int_{-\infty}^{\infty} (\nu - \nu_0)^n q(\nu - \nu_0) d(\nu - \nu_0).$$

Van Vleck's calculations give

$$<w^2> = \frac{3}{4} \chi^2 h^2 J(J+1) \leq (1 - 3 \cos^2 \Theta_{ij}) \frac{1}{n^{2-6}}$$

for the second moment, and we define $T_{2}''$ as

$$T_{2}'' = \frac{1}{<w^2>^{1/2}}.$$ 

This expression for calculating the line width has been investigated thoroughly by several authors and is very accurate.

C. Impurity Dependent Spin-Lattice Relaxation

1. Direct Interaction between Impurity and Nuclear Spin
The model we want to consider is a simple cubic lattice of nuclear spins with a low concentration \(10^6 \text{ cm}^{-3}\) or less of paramagnetic impurities uniformly distributed throughout the lattice. We can divide the crystal into volumes such that each volume will contain one impurity spin \(N = \frac{N_\text{crystal}}{N_p}\) at the center. Each volume will then be representative of the entire crystal. The impurity is very tightly coupled to the lattice and lattice vibrations will cause the spin to make transitions between the various Zeeman levels. This coupling is measured by the size of the impurity spin-lattice relaxation time \(\varphi\). The inverse of \(\varphi\) is a measure of the number of times transitions occur per second, and is of the order of \(10^6/\text{sec}\). This rapid flipping of the impurity spin induces transitions in the surrounding nuclear spins because of the fluctuating dipole field. It will be necessary to find the Fourier spectrum of these fluctuating fields.

The interaction discussed above is represented by the last term of II-2.

\[
H_{i-s} = \sum_{i,j} \frac{N_p N_\pi}{N_\pi} \gamma_\pi \hbar^2 \mathbf{S}_i \cdot \left[ \frac{3}{\Lambda^2} - \frac{3(\mathbf{S}_i \cdot \mathbf{L} \cdot \mathbf{p})\mathbf{L} \cdot \mathbf{p}}{\Lambda^4} \right].
\]  

\(N_p = \frac{N_\pi}{N_\pi}\) number of nuclear spins associated with each impurity spin.

This term may be written in the form of II-3.

\[
\nu_{i,j} = \gamma_\pi \hbar^2 \mathbf{L} \cdot \mathbf{p} (A' + B' + C' + D' + E').
\]  

\(A' = \mathbf{I}_{ii} S_{ji} (1 - 3 \cos^2 \theta \mathbf{L} \cdot \mathbf{p})\) \(\Delta m_i = \Delta S = 0\).
\[ B' = -\frac{1}{4} \left[ I_i^- S^+ + I_i^+ S^- \right] (1 - 3 \cos^2 \Theta_i \rho). \]
\[ \Delta m_i = -\Delta S = \pm 1. \]

\[ C' = -\frac{3}{2} \left[ I_i^+ S_\rho + S^+ I_i^\rho \right] \sin \Theta_i \rho \cos \Theta_i \rho e^{i \Phi_i \rho}. \]
\[ \Delta m_i = 0, \Delta S = +1. \]
\[ \Delta m_i = +1, \Delta S = 0. \]

\[ D' = -\frac{3}{2} \left[ I_i^- S_\rho + S^- I_i^\rho \right] \sin \Theta_i \rho \cos \Theta_i \rho e^{i \Phi_i \rho}. \]
\[ \Delta m_i = 0, \Delta S = -1. \]
\[ \Delta m_i = -1, \Delta S = 0. \]

\[ E' = -\frac{3}{4} I_i^+ S^+ \sin^2 \Theta_i \rho e^{2i \Phi_i \rho}. \]
\[ \Delta m_i = \Delta S = 1. \]

\[ F' = -\frac{3}{4} I_i^- S^- \sin^2 \Theta_i \rho e^{2i \Phi_i \rho}. \]
\[ \Delta m_i = \Delta S = -1. \]

We expect the frequency spectra for \( S^+ \) and \( S^- \) to be peaked at a frequency \( \gamma_p \) associated with the energy difference between the states these operators connect. On the other hand, \( S_\rho \) being diagonal, will have a spectrum peaked at zero frequency. Since the impurity-spin states have a finite lifetime, their spectra will have a certain width, \( \Delta \gamma_p \). This width is approximately \( \gamma_p^{-1} \), since the spin-spin interactions between impurities and the broadening effect of the nuclei on the impurity spin states can be neglected. At fields of several kilogauss, the Larmor frequencies of the fluorine spins and impurity spins are \( 10^7 \) cps and \( 10^{10} \) cps respectively. With \( \gamma_p \sim 10^6 \) sec, the width of the spectrum for the impurity is \( 10^6 \) cps. The
width of the nuclear spin spectrum is \( \sim 10^4 \) cps. The
contribution of the spectrum for \( S^+ \) and \( S^- \) at the nuclear
resonant frequency is negligible compared to the contribution
of \( S_x \) provided \( \gamma > 10^{-10} \) sec or \( \Delta \gamma F < 10^{10} \) cps.
This means only terms \( C' \) or \( D' \) of II-6 will contribute to the
transition probability, \( W \), that a nuclear spin \( i \) will make
a transition in the field of the impurity spin.

Using first-order perturbation theory on term \( C \) to
calculate the probability that a single nucleus \( i \) will
undergo a transition, we have

\[ W = \frac{q}{4} (\gamma \gamma_F h)^2 |< \frac{1}{2} | I^+ | - \frac{1}{2} >|^2 \sin^2 \Theta_F \cos^2 \Theta_F \ | J_x (\gamma_F) |. \]  II-7

where \( J_x (\gamma_F) \) is the intensity of the Fourier spectrum
of the expectation value of \( S_x \) evaluated at the nuclear
Larmor frequency \( \gamma_F \). Now since \(|< \frac{1}{2} | I^+ | - \frac{1}{2} >|^2 \sim 1 \), we have
for \( W \)

\[ W = \frac{q}{4} (\gamma \gamma_F h)^2 \sin^2 \Theta_F \cos^2 \Theta_F \ | J_x (\gamma_F) |. \]  II-8

In this calculation, we have assumed that any variation in
\( \Theta \) and \( \gamma_F \) due to lattice vibrations is negligible in comparison to the fluctuations produced by the flipping
impurity spin.

By using the techniques of generalized harmonic analysis
and assuming an exponential correlation function with a
correlation time \( T_c = \frac{\lambda}{2\pi} \), we have

\[ J_x (\gamma_F) = \frac{1}{2\pi} S(S+1) \frac{\lambda}{1+\lambda^2}\gamma_F^2 . \]  II-9

(See Appendix A)
The transition probability becomes

$$W = \frac{9}{16\pi} (\gamma \nu \pi)^2 \sin^2 \Theta \cos^2 \Theta \rho \frac{\rho}{1 + \frac{\rho^2}{\nu^2}}.$$  

II-10

The spin-lattice relaxation time $T'_1$ for nucleus 1 is

$$T'_1 = \frac{1}{2W},$$  

so we have

$$T'_1 = \frac{3\pi}{\rho} \left[ (\gamma \nu \pi)^2 \sin^2 \Theta \cos^2 \Theta \rho \right]^{-1} \frac{\rho}{\nu} \frac{1 + \frac{\rho^2}{\nu^2}}{\rho}.$$  

II-11

The relaxation of nuclei very close to paramagnetic impurities is not observed, as their Larmor frequency is shifted far into the wings of the absorption curve, due to the presence of the large magnetic moment of the impurity spin. Therefore, in considering direct nuclear relaxation, it is necessary to consider only nuclei whose resonant frequency is not greatly affected by the impurity spin. We consider only nuclei farther than a critical radius $\lambda_c$ from the impurity spin. The radius is defined as that distance from the impurity such that the dipole field of the impurity is equal to the local field $H_L$, arising from the nuclear dipoles.

$$H_{imp} = \frac{\mu_{eff}}{\lambda_c^3} = H_L = \langle H^2 \rangle^{1/2}$$  

II-12

where

$$\langle H^2 \rangle^{1/2} = \frac{1}{6} \langle \omega^2 \rangle^{1/2}.$$  

$\mu_{eff}$ is the effective magnetic moment of the impurity spin. When the impurity spin flips rapidly compared to the nuclear spins, ( $\varphi < 2 \pi T_2$ ), then the nuclei feel only an effective moment which is given by the thermal average:

$$\mu_{eff} = \frac{\mu_p^2 H}{kT}.$$  

II-13a
When the impurity flips slowly compared to the nuclear spins \((\varphi > 2\pi T_2)\), then the nuclei feel the effect of a static dipole and \(\mu_{\text{eff}}\) is given by:
\[
\mu_{\text{eff}} = \mu_p. \tag{II-13b}
\]

To determine the \(T_1\) due to direct relaxation for the entire nuclear spin system, we average \(W\) over the volume associated with each impurity,\n\[
\frac{1}{T_1} = \frac{\int \int \int 2W n^2 \, d\alpha \, d\Omega}{\int \int \int n^2 \, d\alpha \, d\Omega}, \tag{II-14}
\]
where \(2R\) is the average distance between impurities given by
\[
R = \left(\frac{4}{3}\pi N\right)^{-\frac{1}{3}}.
\]
Substituting II-10 into II-14 and integrating, we obtain
\[
\frac{1}{T_1} = \frac{4 (\delta \delta_p + \delta) S (S+1) N}{15 h^3} \left[\frac{\varphi}{1+\varphi^2} \right], \tag{II-15}
\]
where it has been assumed that \(n_c \ll R\).

From this calculation, it is obvious that nuclei far away from the impurity are not relaxed directly by the impurity. Therefore, we must consider a mechanism by which Zeeman energy is transferred to a region of the crystal where the impurity is effective in producing relaxation.

2. Spin Diffusion

The mechanism by which Zeeman energy can be transferred to the vicinity of an impurity is called spin diffusion. Spin diffusion is possible because of the spin-spin interactions term (term B in II-3) which has already been dis-
cussed. We define a quantity \( P_{\uparrow} (\vec{r}, t) \) which is the probability of finding a nuclear spin at position \( \vec{r} \) in the crystal aligned parallel to \( H_0 \) at time \( t \). Similarly, \( P_{\downarrow} (\vec{r}, t) \) can be defined for the spin anti-parallel to \( H_0 \), and also the difference

\[
P(\vec{r}, t) = P_{\uparrow} (\vec{r}, t) - P_{\downarrow} (\vec{r}, t),
\]

where

\[
M_\uparrow (t) = \sum_{\text{sites}} g \mu_0 p(\vec{r}, t).
\]

\( M_\uparrow (t) \) is the component of magnetization of the sample along the direction of \( H_0 \). Consider a crystal with no spin-lattice relaxation processes and assume a distribution \( p(\vec{r}, 0) \) at \( t = 0 \), the spin-flipping process will smooth out \( p(\vec{r}, t) \) in time and result in a final value of \( p \) independent of \( \vec{r} \). This approach of \( p(\vec{r}, 0) \) toward \( p(t=\infty) \) can be described by a diffusion equation by assuming a continuum of \( p \):

\[
\frac{\partial p}{\partial t} = D \nabla^2 p, \tag{II-16}
\]

where \( D \) is the diffusion constant.

In order to calculate \( D \), we must consider term \( B \) in

\[
V_{ij} = -\frac{1}{4} \gamma^2 \hbar^2 \Lambda_{ij}^{-3}(1-3\cos^2 \theta_{ij})(I_i^- I_j^+ + I_i^+ I_j^-), \tag{II-17}
\]

\[\Delta m_i = \Delta m_j = \pm 1, \quad \Delta M = 0.\]

We want to find the probability per unit time, \( u \), that a mutual spin flip will occur. Bloembergen has made this calculation based on the following model: consider the interaction of nuclei \( i \) and \( j \) with all other nuclei
in the lattice, except with each other, and then introduce
VI. above, as a small perturbation between them. Generally,
nuclei \( i \) and \( j \) will precess at different Larmor frequencies
because of the difference in local fields. The spread in fre-
quency about the Larmor frequency \( \nu_F \) from the dipole-dipole
interaction will be \( \Delta \nu_F = \frac{1}{2 \mu} T_2 \). The probability that nucleus
\( i \) has a Larmor frequency \( \nu_F \) is \( g(\nu_i) \).

Using first-order perturbation theory with \( \Gamma_i = \Gamma_j = \frac{1}{2} \),
we have

\[
\mathcal{U}_{\Delta m_i = \Delta m_j = 1} = \frac{1}{16} v^4 \hbar^2 \langle n_j \rangle \left( 1 - 3 \sin^2 \theta_{ij} \right)^2 \frac{\Delta}{\epsilon},
\]

where

\[
\Lambda = \frac{\epsilon}{4} \int_0^\infty d\nu_i \int_0^\infty d\nu_j \frac{g(\nu_i)g(\nu_j)}{(2\pi)^2 (\nu_i - \nu_j)^2} \left[ \frac{4 \sin^2 \left( \pi (\nu_i - \nu_j) t \right)}{(2\pi)^2 (\nu_i - \nu_j)^2} \right].
\]

The bracket factor is one representation of the delta func-
tion, therefore

\[
\Lambda = \frac{\epsilon}{4} \int_0^\infty q^i(\nu) d\nu.
\]

To make the definition of \( T_2 \) from a line shape calculation
consistent with the identification of \( T_2 \) as the decay time
of the transverse component of the macroscopic magnetization,
we define

\[
T_2 = \frac{1}{2} \left[ g(\nu) \right]_{\max}.
\]

We assume we can write \( g(\nu) = 2 T_2 f(\nu T_2) \) where
\( f(\nu T_2) \) is a homogeneous function of \( \nu T_2 \) and we have

\[
\Lambda = \tau T_2 \int_0^\infty |f(x)|^2 d\lambda = \tau T_2 \lambda,
\]

II-19
where \( \lambda \) depends only on the shape of the distribution function and is of the order of one. Therefore

\[
U_{\Delta m_i = \Delta m_j = 1} = \frac{1}{16} \xi^4 \hbar^2 \nu_{ij}^{-6} \left( 1 - 3 \cos^2 \theta_{ij} \right)^2 \nu_{ij}^{-6} T_2 \lambda.
\]

Using II-4 for \( T_2 \) and setting \( I = 1/2 \), we have

\[
U_{\Delta m_i = \Delta m_j = 1} = \frac{8^2 \hbar \lambda}{12} \frac{\left( 1 - 3 \cos^2 \theta_{ij} \right)^2 \nu_{ij}^{-6}}{\left[ \sum_j (1 - 3 \cos^2 \theta_{ij})^2 \nu_{ij}^{-6} \right]^{1/2}}. \tag{II-20}
\]

The inverse of \( U_{\Delta m_i = \Delta m_j = 1} \) is the average time required for one mutual flip to occur at a separation \( \nu_{ij} \). In calculating \( D \) we must consider all neighbors because, even though \( U \) falls off rapidly with increasing \( \nu_{ij} \), the distance over which Zeeman energy is transferred is greater as \( \nu_{ij} \) increases. Using the usual definition for \( D \), we have by summing over all lattice sites:

\[
D = \sum_{i,j} U_{\Delta m_i = \Delta m_j = 1} \nu_{ij}^{-2}. \tag{II-21}
\]

Substituting II-20 into II-21, we have

\[
D = \frac{\xi^2 \hbar \lambda}{12} \frac{\sum_j (1 - 3 \cos^2 \theta_{ij})^2 \nu_{ij}^{-6}}{\left[ \sum_j (1 - 3 \cos^2 \theta_{ij})^2 \nu_{ij}^{-6} \right]^{1/2}}. \tag{II-22}
\]

Andrew, Swanson and Williams have carried out the sum in the numerator of II-22 for 383 neighbors and integrated the remainder. The lattice sum in the denominator has been carried out to 122 neighbors and the remainder integrated.

For Ca \( F_2 \), II-22 gives:

\[
D_{[100]} = 5.43 \times 10^{-12} \lambda \text{ cm}^2 \text{ sec}^{-1} \quad \text{for } [100] \parallel H_0,
\]

\[
D_{[110]} = 5.34 \times 10^{-12} \lambda \text{ cm}^2 \text{ sec}^{-1} \quad \text{for } [110] \parallel H_0,
\]

\[
D_{[111]} = 6.21 \times 10^{-12} \lambda \text{ cm}^2 \text{ sec}^{-1} \quad \text{for } [111] \parallel H_0. \tag{II-23}
\]
3. The Diffusion Equation

If we consider the $z$-component (along $H_0$) of the magnetization per unit volume, then $M$ can change in time due to diffusion and direct relaxation. Combining these two effects, we have

$$\left(\frac{\partial M}{\partial t}\right)_{\text{Total}} = \left(\frac{\partial M}{\partial t}\right)_{\text{Diffusion}} + \left(\frac{\partial M}{\partial t}\right)_{\text{Relaxation}}.$$  

II-24

The diffusion term is given by

$$\left(\frac{\partial M}{\partial t}\right)_{\text{Diff.}} = D \nabla^2 M,$$  

II-25

while the relaxation term is given by

$$\left(\frac{\partial M}{\partial t}\right)_{\text{Rel.}} = -\frac{1}{T_1} (M - M_0),$$  

II-26

where $M_0$ is the equilibrium value of $M$ and $T_1$ is given by II-11. For the complete diffusion equation, we have

$$\frac{\partial M}{\partial t} = D \nabla^2 M - \frac{1}{T_1} (M - M_0).$$  

II-27

13,14,15,16

Several authors have solved this equation under special conditions. We will consider in particular the solution by Forschach (see Appendix B) in which he used the following conditions:

a) Steady state: $\frac{\partial M}{\partial t} = 0$ or $\nabla^2 M - \frac{1}{T_1} D (M - M_0) = 0$,

b) For $n \rightarrow \infty$, $M \rightarrow M_1$ ($M_1$ constant boundary value of $M$)

c) The total flow of $M$ in from $\infty$ by diffusion equals total amount of $M$ relaxed outside the critical radius $r_c$ (here it is assumed $r_c$ is given by II-12):

$$\lim_{n \rightarrow \infty} (D |\nabla M|) 4\pi r_c^2 = \int_{r_c}^{\infty} \left(\frac{\partial M}{\partial t}\right)_{\text{Rel.}} \, dV.$$
Rorschach found that $M$ followed an exponential growth after complete saturation,

$$\frac{2M}{\partial t} = -\frac{1}{T_1} (M - M_c), \quad \text{II-28}$$

where $T_1$ is given by

$$T_1 = \frac{1}{8\pi N D^{3/4} C^{3/4}} \frac{\Gamma(\nu)}{\Gamma(3/4)} \frac{I - \xi_0(\delta)}{I_0(\delta)}, \quad \text{II-29}$$

and

$$C = \frac{1}{5\pi} (\gamma \gamma_p h)^2 J(\nu+1) \frac{Q}{1 + \nu^2} \nu^2 \quad \text{II-29a}$$

$\gamma_p$ - magnetogyric ratio of the impurity

$\gamma$ - magnetogyric ratio of the nuclei

$S$ - spin of impurity

$D$ - diffusion coefficient (II-22)

$\tau$ - impurity relaxation time

$\nu$ - nuclear Larmor frequency

$N$ - number of paramagnetic impurities per unit volume

$$\delta = \left( \frac{C}{D} \right)^{1/2} \frac{1}{2} \frac{1}{R_c}^2 \quad \text{II-29a}$$

$$I_m(\delta) = i^{-m} J_m(\nu \delta) \quad \text{II-29a}$$

$R_c$ - critical radius defined in II-12.

Equation II-29 has two asymptotic limits which $T_1$ approaches depending on whether $\delta > 1$ or $\delta < 1$.

For $\delta < 1$, $I_m(\delta) \rightarrow \frac{1}{\Gamma(m+1)} \left( \frac{2}{2} \right)^m$ and

$$T_1 \rightarrow \frac{3 \Lambda_c^3}{4\pi NC}, \quad \text{II-30}$$

while for $\delta > 1$, $I_m(\delta) \approx I_m(\delta)$ and

$$T_1 \rightarrow \frac{3}{8\pi N D^{3/4} C^{3/4}} \quad \text{II-31}$$
There are two processes which govern the observed value of $T_1$: a) the rate at which Zeeman energy can be transferred, via diffusion, to those nuclei which are in good thermal contact with the impurity spin, and b) the rate at which nuclei near an impurity can exchange energy with the lattice via the impurity.

When process b) is much faster than a), the relaxation process is said to be diffusion-limited and $T_1$ is given by equation II-31. When process a) is much faster than process b), we say we are in the rapid-diffusion region where $T_1$ is given by equation II-30. The latter is also called the direct-interaction region.

It is interesting to note that the $T_1$ of II-30 is identical to that of II-15, in which the diffusion term was omitted. This means that the calculation leading to II-15 only has significance when we assume there is a mechanism which transfers Zeeman energy to the vicinity of an impurity very rapidly, where the nuclei can be relaxed directly.

Writing II-30 and II-31 explicitly in terms of the field $H_0$, the temperature $T$, the impurity relaxation time $\tau$, and the local field, we have:

Rapid-Diffusion Case:

$$T_1 = \frac{15}{4} \frac{\mu^2 H}{kT <H^2> N} \left( \frac{1}{(5/4^2)S(S+1)} \right) \frac{1 + \frac{e^2 V^2}{\rho}}{\rho} \quad \text{II-32}$$
Diffusion-Limited Case:

\[ T_1 = \frac{3}{8\pi \mathbf{N} \mathbf{D}^{2/3}} \left( \frac{5\pi}{(2D\rho)^2 S(S+1)} \right)^{1/4} \left[ \frac{1 + \frac{2\gamma F^2}{\gamma F}}{\gamma F} \right]^{1/4} \]

In both equations, II-32 and II-33, \( T_1 \) is minimum when \( \gamma F = 1 \). \( T_1 \) increases when \( \gamma \) gets either larger or smaller than \( \sqrt[3]{\gamma F} \). When \( \gamma \) becomes much larger than \( \sqrt[3]{\gamma F} \), the rate at which the impurity spin can transfer energy to the lattice becomes small, thus increasing \( T_1 \). When \( \gamma \) becomes much smaller than \( \sqrt[3]{\gamma F} \), the impurity spin is flipping too fast to couple effectively to adjacent nuclear spins and again \( T_1 \) is increased.

4. Orientation Dependence of \( T_1 \)

If we assume that \( \gamma \) is orientation-independent, then an orientation-dependent \( T_1 \) can arise only from \( <H^2>^{1/2} \) and \( D \). From II-23, the ratio of \( D_{Liu} \) to \( D_{100} \) is 1.14 while the ratio of \( <H^2>^{1/2}_{Liu} \) to \( <H^2>^{1/2}_{100} \) calculated from Van Vleck's formula (II-4) is 2.3. It is clear then that the principal orientation dependence of \( T_1 \) arises from \( <H^2>^{1/2} \). This indicates that the \( T_1 \) for the direct interaction case will have a relatively strong orientation effect while the \( T_1 \) for the diffusion-limited case will be only weakly orientation-dependent.

5. Field and Temperature Dependence of \( T_1 \)

Picking out only those terms which are field or temperature dependent, the \( T_1 \)'s for the two cases become:
Direct Interaction Case:

\[ T_1 \propto \frac{H}{T} \frac{1 + (v^2 \tau^2)^{3/2}}{T} \]  \hspace{1cm} \text{II-34}

where \( v_F = \frac{v}{2\pi} \) \( H_0 \) and \( \tau \ll 2\pi T_2 \)

Diffusion-Limited Case:

\[ T_1 \propto \left[ \frac{1 + (v^2 \tau^2)^{3/2}}{T} \right]^{1/4} \]  \hspace{1cm} \text{II-35}

In general, \( \varphi \) depends on the external magnetic field and the temperature. Therefore, to consider the explicit field and temperature dependence of \( T_1 \), we must know the field and temperature dependence of \( \varphi \).

D. Theory of Impurity Spin-Lattice Relaxation

Spin-lattice relaxation of paramagnetic ions in crystals has been worked on for nearly thirty years with only limited success. There are two main categories, depending on whether the theory is based on detailed microscopic interactions or on a macroscopic thermodynamic approach. The latter is only applicable when the concentrations of paramagnetic ions is sufficiently large so that there is an appreciable interaction between the spins. This is necessary so that one can define a temperature for the spin system. The spin temperature is defined by the distribution of spins over the Zeeman levels of the system according to the Boltzmann distribution. If the spins did not interact with each other, the spins would not necessarily have a Boltzmann distribution, and the
concept of a spin temperature would be meaningless. In the thermodynamic approach, we speak of a heat capacity for the spin system and the lattice separately. If one raises the temperature of the spin system above that of the lattice, then in time the spin system will come into equilibrium with the lattice by means of the spin-lattice interaction. Since the thermodynamic approach is not applicable to very dilute impurity concentrations, no further discussion will be given here. An excellent text on the subject has been written by Gorter.26

Two important papers have been published in which the spin-lattice relaxation time $\rho$ has been calculated from a detailed microscopic model. Both theories are based on the same model, but the calculations differ in the perturbation procedure that is employed. The theories apply only to iron group ions that have non-zero orbital angular momentum in the ground state. Relaxation arises as follows: the fluctuating crystalline electric field arising from the lattice vibrations of neighboring ions causes fluctuations in the orbital angular momentum. Through the spin-orbit coupling, the spin angular momentum is caused to fluctuate in time. The spin-orbit coupling provides the key to the transfer of energy from the spin to the lattice or phonon field.

Waller5 pointed out sometime ago that the exchange of energy between the magnetic ions and the lattice can take
place in two essentially different ways. In the first way, a phonon is absorbed or emitted by the ions, the frequency of the phonon being given by the Einstein condition. This process is called a direct or one-phonon process. The second way is a two-phonon, or Raman process. In this process, a phonon is scattered inelastically and the energy lost or gained by the phonon is equal to the change in Zeeman energy of the magnetic ion. The Raman process is a second-order process while the direct process is a first-order process. This would indicate that the Raman process would have less probability of occurring. However, the Raman process can make use of almost all the phonons in the phonon field, whereas the direct process uses only phonons in a narrow band centered at the Larmor frequency. Usually the assumption is made that the phonon distribution $G(\nu) \sim \nu^2$ (Debye Theory) where the cut-off frequency $\sim 10^{13}$ cps. For fields of the order of several kilogauss, the resonant frequency for paramagnetic ions is $\sim 10^{10}$ cps. Therefore it is clear that the second-order process can be more effective in relaxation than the first-order process. Van Vleck's calculations suggest that the two-phonon process is important at high temperatures because at higher temperatures more phonons are available in the high-frequency end of the Debye spectrum. However, as the temperature is lowered, the phonons tend to occupy the lower energy levels and the two-phonon process becomes
ineffective. For Raman processes, the theoretical temperature dependence for \( \bar{\rho} \) at \( T > \Theta_D \) (\( \Theta_D = \frac{\hbar \nu_{\text{eff}}}{k} \)) is independent of the magnetic field and varies as \( T^{-2} \). At low temperatures (\( T < \Theta_D \)), because of the paucity of phonons at the high end of the frequency spectrum,

\[ \bar{\rho} \sim T^{-7}. \]

Because of the extreme temperature dependence of \( \bar{\rho} \) for the Raman process at low temperatures, it is expected that the one-phonon process would take over at low temperatures.

Mattuck and Strandberg recently have carried out an order-of-magnitude calculation of \( \bar{\rho} \) for iron group impurities with non-zero orbital angular momentum in the ground state for the Raman process and the direct-process at low temperatures. Their calculation of \( \bar{\rho} \) for the Raman process agrees with previous calculations. For the direct-process, they find that

\[ \bar{\rho} \sim \frac{1}{H^2 T} \quad \text{(Spin-Lattice bottleneck).} \]

Several authors have suggested that the bottleneck in the transfer of energy at low temperatures may not be between the paramagnetic ions and the lattice, but between the lattice and the bath. Gorter has considered this case theoretically using a thermodynamic argument and shows that

\[ \bar{\rho} \sim \frac{1}{H T^2} \quad \text{(Lattice-Bath bottleneck).} \]
If the lattice-bath bottleneck were to apply, the ratio of the surface area to the volume of the crystal should affect the relaxation time.

E. Summary of Field and Temperature Dependence of $T_1$ and $\xi$

The following two tables summarize the theoretical field and temperature dependence of $T_1$ when the field and temperature dependence of $\varphi$ is substituted into equations II-34 and II-35. Also included is the field and temperature dependence of $\xi$. 
TABLE 1
Theoretical Field and Temperature Dependence of $T_1$
Rapid Diffusion Case ($\delta << 0.8$); Orientation Dependent

<table>
<thead>
<tr>
<th>$\varphi$ $^*$</th>
<th>$\delta$ $\sim$</th>
<th>$T_1$ $\sim$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varphi &lt; 2\pi T_2$</td>
<td>$\varphi &gt; 1$</td>
<td>$T^{-1} H^{-2}$</td>
</tr>
<tr>
<td>$\varphi &lt; 1$</td>
<td>$T^{-1} H^{-2}$</td>
<td>$T^{-2} H^{-1}$</td>
</tr>
<tr>
<td>$\varphi &gt;&gt; 2\pi T_2$</td>
<td>$\varphi &gt; 1$</td>
<td>$T^{-1} H^{-2}$</td>
</tr>
<tr>
<td>$\varphi &lt; 1$</td>
<td>$T^{-1} H^{-2}$</td>
<td>$T^{-2} H^{-1}$</td>
</tr>
</tbody>
</table>

It is not possible for $\varphi$ to be larger than $2\pi T_2$ and $\varphi$ $^*$ to be smaller than one for $H_0$ greater than 50 gauss.

$^*$ $\varphi \sim T^{-1} H^{-2}$
Direct Process, S-L Bottleneck

$\varphi \sim T^{-2} H^{-1}$
Direct Process, L-B Bottleneck

$\varphi \sim T^{-7} H^0$
Raman Process, $T << \Theta_0$

$\varphi \sim T^{-2} H^0$
Raman Process, $T \approx \Theta_0$
TABLE 2

Theoretical Field and Temperature Dependence of $T_1$
Diffusion Limited Case ($\delta > 0.8$); Orientation Independent

<table>
<thead>
<tr>
<th>$\rho &lt; 2\pi T_2$</th>
<th>$\rho &lt; 1$</th>
<th>$\rho &gt; 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho &lt; 2\pi T_2$</td>
<td>$T^{-1} H^{-1}$</td>
<td>$T^{-1} H^{-1}$</td>
</tr>
<tr>
<td>$\rho &gt; 2\pi T_2$</td>
<td>$T^{-1} H^{-1}$</td>
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<tbody>
<tr>
<td>$T^{-1} H^{-1}$</td>
<td>$T^{-1} H^{-1}$</td>
</tr>
<tr>
<td>$T^{-2} H^{-1}$</td>
<td>$T^{-2} H^{-1}$</td>
</tr>
<tr>
<td>$T^{-7} H^{0}$</td>
<td>$T^{-7} H^{0}$</td>
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<tr>
<td>$T^{-2} H^{0}$</td>
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</tr>
<tr>
<td>$T^{-7} H^{0}$</td>
<td>$T^{-7} H^{0}$</td>
</tr>
<tr>
<td>$T^{-2} H^{0}$</td>
<td>$T^{-2} H^{0}$</td>
</tr>
</tbody>
</table>

It is not possible for $\rho$ to be larger than 2 and to be smaller than one for $H$ greater than 50 gauss.

* $\rho \sim T^{-1} H^{-2}$
* $\rho \sim T^{-2} H^{-1}$
* $\rho \sim T^{-7} H^{0}$
* $\rho \sim T^{-2} H^{0}$

Direct Process, S-L Bottleneck
Direct Process, L-B Bottleneck
Raman Process, $T << \Theta_0$
Raman Process, $T \gtrsim \Theta_0$
III. EXPERIMENTAL APPARATUS

A. Nuclear Magnetic Resonance Spectrometer

Figure 1 is a block diagram of the components of the spectrometer. The magnetic field was supplied by a six-inch water-cooled electromagnet constructed by Varian Associates. The power supply for the magnet was also constructed by Varian Associates. The oscillator, r.f. amplifier, and detector were part of a commercial unit obtained from Nuclear Magnetics Corporation, and based on a design of Watkins.28

The radio frequency coil wound around the sample in the magnetic field, \( H_0 \), supplied an oscillating field, \( H_1 e^{i\omega t} \), satisfying the conditions \( H_1 \ll H_0 \) and \( H_1 \perp H_0 \). If this coil is made part of a tank circuit in a marginal oscillator, then any small change in its impedance, due to the absorption of r.f. energy by the nuclear spin system, results in a modulation of the r.f. voltage across the coil. If this voltage is amplified and detected, it can be displayed on an oscilloscope. (References concerning the techniques of observation of nmr can be found in the literature.)

In all temperature ranges in this experiment, the absorption amplitude was observed on an oscilloscope. To provide the modulation field, several hundred turns of copper wire were wound around the pole faces of the magnet. The audio voltage was provided by an audio oscillator and amplified by a Dynakit Power Amplifier.
B. Cryogenics

To obtain the various low temperatures used in the experiment, the sample was held in a lucite holder at the end of a rigid coaxial line inside the dewar assembly. The outer dewar contained liquid nitrogen or air and the inner space contained liquid nitrogen, hydrogen, or helium, depending on the temperature range of interest. When lower temperatures than the normal boiling point were required, they were obtained by pumping on the bath with a mechanical pump. By measuring the vapor pressure above the bath with a manometer, it was possible to determine the temperature of the bath. Since these techniques are conventional in low temperature research, no further details will be given. An adequate description of the construction of the transmission line is given elsewhere, and therefore will not be discussed here.

C. Specimen

The CaF$_2$ sample used in the experiment was obtained from the Harshaw Chemical Company, and had an impurity concentration of the order of one part in $10^6$ or less. The single crystal sample and the powdered sample were obtained from the same original crystal. The single crystal was fashioned into a cylinder about $1/2$ inch in length by $1/2$ inch in diameter. The cylindrical axis was along the 110 axis of the crystal in order to make orientation measurements with the [100] or [111] direction of the crystal parallel to the external field. The average particle size of the pow-
dered specimen was between 0.1mm. and 0.01mm. The powdered sample was loosely held in the sample chamber to insure good thermal contact between the sample and the bath.
IV. PROCEDURE

If we consider a system of nuclear spins with $I = 1/2$ in the presence of a large steady magnetic field and a radio frequency field $H_f e^{i \omega_0 t}$, then the differential equation governing the time variation of the excess number $n$ of nuclei per $cm^3$ in the lower state is given by:

$$\frac{dn}{dt} = \frac{n_0 - n}{T_1} - 2n P$$  \hspace{1cm} IV-1$$

$n_0$ is the equilibrium population difference of the two levels, $T_1$ is the nuclear spin-lattice relaxation time and $P$ is the probability per unit time of a transition by a nucleus between the two levels under the influence of the radiation field $H_f$. Bloembergen, Purcell, and Pound found by standard radiation theory, that for $I = 1/2$, $P$ is given by the following:

$$P = \frac{1}{4} \gamma^2 H_f^2 g(\gamma)$$  \hspace{1cm} IV-2$$

where $\gamma$ is the magnetoogyric ratio, $H_f$ is the amplitude of the radio frequency field perpendicular to $H_0$ and $g(\gamma)$ is the normalized absorption shape function.

It can be seen from IV-1 in the absence of spin-lattice relaxation or $T_1$ large that the solution for $n$ when $n = n_0$ at $t = 0$ is

$$n = n_0 e^{-2Pt}$$  \hspace{1cm} IV-3$$

Now if $P$ is large ($H_f$ large), $n$ approaches zero. This is called complete saturation and refers to the equalization of the populations in the two levels.

* See Andrew for a derivation of this equation.
On the other hand, if \( P = 0 \) equation IV-1 has the solution
\[
\eta = n_0 (1 - e^{-t/T_1}),
\]
where \( n = 0 \) at \( t = 0 \). This is called the simple growth process.

Another case of interest is the solution of IV-1 with \( H_1 = 0 \) where initially \( n = n_i \) and \( n_i > n_0 \). This solution is
\[
(\eta - n_0) = (n_i - n_0) e^{-t/T_1}
\]
and describes a decay of \( n \) from an initial equilibrium value to a final equilibrium value of \( n \) with a characteristic time \( T_1 \). In these equations, \( n \) can be replaced by the component of the magnetization along the direction of \( H_0 \) (see Equation IV.1) as \( M_z \) is given by \( M_z = n \mu \) where \( \mu \) is the nuclear moment (see Andrews).

The power absorbed from the radiation field by the nuclear spin system is proportional to \( \frac{dn}{dt} \). Considering a time interval short compared to \( T_1 \), then equation IV-1 shows that the power absorbed is simply proportional to \( n \) and therefore the absorption amplitude of the nuclear resonance signal is proportional to the magnetization during this short time interval.

The above discussion serves as a basis by which to describe the techniques used to measure \( T_1 \). The method used to measure \( T_1 \) for large magnetic fields was the simple growth process (IV-4). The resonance was completely
saturated \((n=0)\) at the measuring field \(H_0\) by making \(H_1\) large and the modulation field small compared to the line width. \(H_0\) was changed to the field in which the relaxation was to take place. After a known time interval, \(t\), the field was returned to the measuring field \(H_0\) where the absorption amplitude was recorded with \(H_1\) small and the modulation field large. By repeating this process for different values of \(t\), it was possible to plot the growth curve \((IV-4)\) and determine \(T_1\). When measuring \(T_1\) at small fields, it was inconvenient to use the simple growth process because of unfavorable signal-to-noise ratios. In this case, the decay technique was used. The magnetization was allowed to grow from zero to a large value in a large field for a given amount of time, then the field was lowered to the low field value for a time \(t\). After the magnetization decayed for a time \(t\), the field was raised to the measuring field and the absorption amplitude was recorded. Repeating this process for different values of \(t\) permitted a determination of \(T_1\) \((IV-5)\).

The time required to change the field was always short compared to \(T_1\) and long compared to \(T_2\). This insured the fact that the populations of the energy levels remained constant while \(H_0\) was being changed. This process is referred to as an adiabatic process in the Ehrenfest sense and has been discussed by Proctor and Abragam.\(^\text{32}\)

The absorption line width for \(F^{19}\) in \(\text{CaF}_2\) depends strongly on the crystal orientation with respect to \(H_0\).
It was this property that was used in aligning the crystal for measuring the orientation dependence of $T_1$. Because of the strong orientation dependence of $T_2$, it is felt that little error ($\sim 2^\circ$) resulted from this alignment procedure. The orientation dependence of $T_2$ has been determined by several authors and served as a check for the alignment procedure.
V. RESULTS

A. Nitrogen Temperature Range

The experimental values of $T_1$ in the liquid nitrogen temperature range are shown in Table 3. At 78°K, $T_1$ was measured as a function of $H_o$ for two orientations of the single crystal. These results are shown in Figure 2. The solid curves drawn through the experimental points are parabolas and indicate $T_1$ is roughly proportional to $H_o^{1/2}$. The results at this temperature indicate that $T_1$ is approximately orientation independent. Measurements of $T_1$ for a given $H_o$ at temperatures of 63°K and 78°K suggest that $T_1$ has a weak temperature dependence. In this temperature range, it was not possible to determine the weak dependence of $T_1$ on temperature because of the poor signal-to-noise ratios encountered.
### TABLE 3

\( T_1 \) of \( \text{F}^+ \) in \( \text{Ca F}_2 \) as a Function of Field, Temperature, and Orientation

<table>
<thead>
<tr>
<th>( T ) (°K)</th>
<th>( H_0 ) (Kg)</th>
<th>Axis Parallel to ( H_0 )</th>
<th>( T_1 ) (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>0.032</td>
<td>(100)</td>
<td>4</td>
</tr>
<tr>
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<tr>
<td>63</td>
<td>4.83</td>
<td>(111)</td>
<td>38</td>
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</tbody>
</table>
$T_1$ OF $^{19}$F IN $\text{CaF}_2$

$T = 78^\circ \text{K}$

$\times -$ (111) // $H_0$

$\circ -$ (100) // $H_0$

FIGURE 2
B. Hydrogen Temperature Range

The experimental values of $T_1$ in the hydrogen temperature range are shown in Table 4. $T_1$ was measured as a function of $H_0$ for several different temperatures and two orientations of the single crystal. Figure 3 shows a typical plot of $\ln T_1$ vs. $\ln H$ for several different temperatures with $[1\overline{1}1]//H_0$. The results for the field dependence of $T_1$ as a function of temperature suggest that there is a temperature between $14^\circ\text{K}$ and $20^\circ\text{K}$ where the field dependence is a minimum. Figure 4 is a graph of $\ln T_1$ vs. $\ln T$ for $H_0 = 1.95 \text{ Kg}$ with $[100]//H_0$. At $H_0 = 1.95 \text{ Kg}$, the slope of $\ln T_1$ vs. $\ln T$ changes rapidly at $T = 14^\circ\text{K}$, but remains unchanged from its value slightly above $14^\circ\text{K}$ up to $20^\circ\text{K}$. Figure 5 is a graph of $\ln T_1$ vs. $\ln T$ for $H_0 = 3 \text{ Kg}$ and $[100]//H_0$. Although the break at $14^\circ\text{K}$ for $H_0 = 3 \text{ Kg}$ appears to be the same as for $H_0 = 1.95 \text{ Kg}$, the data suggests that the slope becomes positive for higher temperatures ($\sim 20^\circ\text{K}$) when $H_0 = 3 \text{ Kg}$. This change in sign of the slope means that $T_1$ has a minimum between $14^\circ\text{K}$ and $20^\circ\text{K}$ for $H_0 = 3 \text{ Kg}$. Therefore the results indicate that the minimum of $T_1$ as a function of temperature shifts to lower temperatures as $H_0$ is increased.
TABLE 4

$T_1$ of $F^{19}$ in Ca $F_2$ as a Function of Field, Temperature, and Orientation

<table>
<thead>
<tr>
<th>$T$ (°K)</th>
<th>$H_0$ (Kg)</th>
<th>Axis Parallel to $H_0$</th>
<th>$T_1$ (sec)</th>
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<tbody>
<tr>
<td>20.4</td>
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<td>(111)</td>
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<td>40.0</td>
</tr>
<tr>
<td>8.6</td>
<td>3.00</td>
<td>(100)</td>
<td>25.0</td>
</tr>
</tbody>
</table>


$T_i$ OF $F^{10}$ IN $CaF_2$

$H_0 = 1.95$ KG

$(100) // H_0$

FIGURE 4
$T_1$ OF $^{19}$F IN CaF$_2$

$H_0 = 3$ KG

(100) // $H_0$

**Figure 5**
C. Helium Temperature Range

In this temperature range, $T_1$ was measured as a function of $H_0$, orientation and particle size at three temperatures. Figure 6 gives $T_1$ as a function of $H_0$ at $4.20^\circ K$ for the single crystal with the [100] // $H_0$, with the [111] // $H_0$, and for a powder sample. $T_1$ appears to be a simple linear function of $H_0$ for fields below 3.5 Kg. However, when $H_0$ is raised above a certain critical field, the slope of the curve increases. The critical field is a function of orientation and sample size. Figure 7 gives a similar plot of $T_1$ as in Figure 6 for $T=2.19^\circ K$. Measurements were also made of $T_1$ as a function of $H_0$ at low fields ($H_0<250$ gauss) at $T=1.4^\circ K$, $2.19^\circ K$ and $4.2^\circ K$, and the results are given in Figure 8. The solid curves are curves drawn through the data points. Figures 4 and 5 show how well the data taken in the helium range extrapolates to the hydrogen range data. For not too large fields ($H_0<3$ Kg), $T_1$ has an inverse square dependence on temperatures below $14^\circ K$.

At temperatures below $14^\circ K$, there is a relatively strong orientation dependence of $T_1$ and there is little or no size effect. At not too large fields ($H_0<3$ Kg), $T_1$ for the powder sample is close to the average obtained for the two extreme orientations of the single crystal. At high fields, the powder data deviates from the average of the two orientations and indicates that there is a size effect.
$T_1$ OF $^{19}$F IN CAF$_2$ AT LOW FIELDS

- (111) // $H_o$
- (100) // $H_o$
- Powder

$H_o$ (GAUSS)

FIGURE 8
VI. DISCUSSION OF RESULTS

Table 5 contains an analysis of the experimental results and serves as a guide in the discussion.

A. Helium Temperature Range

In this temperature range, the only way the theory can be made to agree with the experimental results is by taking $\varphi > 1$. This requires $\varphi > 10^{-7}$ seconds.

The presence or absence of an orientation-dependence for $T_1$ can be used to determine whether the relaxation process is rapid diffusion or diffusion-limited. From figures 6 and 7, it is apparent that $T_1$ has an orientation dependence. This means $T_1$ is determined by the rapid diffusion process. Setting $\varphi > 1$ and using II-34 for the rapid diffusion case, we have theoretically

$$T_1 \propto \frac{H^3}{T} \varphi.$$  \hspace{1cm} VI-1

For $H_0$ less than 3 Kg and for temperatures in the helium range, we have from figures 4, 5, 6 and 7:

$$T_1 \propto \frac{H}{T^2}. \hspace{1cm} VI-2$$

By comparing VI-1 and VI-2, we conclude that

$$\varphi \propto \frac{1}{H^2 T}. \hspace{1cm} VI-3$$

This means that for low temperatures, the relaxation process for the impurity spin is governed by the one-phonon process. The fact that the results for the powdered sample
### TABLE 5
Summary of Analysis of Results

#### Single Crystal

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Field</th>
<th>$T_1$</th>
<th>$\rho$</th>
<th>$S$</th>
<th>$\rho_Y$</th>
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</thead>
<tbody>
<tr>
<td>$1.4^\circ \leq T \leq 4.2^\circ$ K</td>
<td>$250g \leq H_o \leq 3Kg$</td>
<td>$HT^{-2}$</td>
<td>$H T^{-2}$</td>
<td>$&lt; 0.8$</td>
<td>$&gt; 1$</td>
</tr>
<tr>
<td>$1.4^\circ \leq T \leq 4.2^\circ$ K</td>
<td>$3Kg \leq H_o \leq 7Kg$</td>
<td>$HT^{-3}$</td>
<td>$H T^{-2}$</td>
<td>$&lt; 0.8$</td>
<td>$&gt; 1$</td>
</tr>
<tr>
<td>$9^\circ \leq T \leq 14^\circ$ K</td>
<td>$1Kg \leq H_o \leq 6Kg$</td>
<td>$HT^{-2}$</td>
<td>$H T^{-2}$</td>
<td>$&lt; 0.8$</td>
<td>$&gt; 1$</td>
</tr>
<tr>
<td>$14^\circ \leq T \leq 20^\circ$ K</td>
<td>$1Kg \leq H_o \leq 6Kg$</td>
<td>$H T^{-4}$</td>
<td>$H T^{-2}$</td>
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<td>$&gt; 1$</td>
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<tr>
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<td>$1Kg \leq H_o \leq 6Kg$</td>
<td>$H T^{-4}$</td>
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<td>$&gt; 0.8$</td>
<td>$&lt; 1$</td>
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</tbody>
</table>

#### Powdered Sample

<table>
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<tr>
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<th>Field</th>
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<th>$\rho$</th>
<th>$S$</th>
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<td>$H T^{-1}$</td>
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<td>$6Kg \leq H_o \leq 7Kg$</td>
<td>$HT^{-3}$</td>
<td>$H T^{-2}$</td>
<td>$&lt; 0.8$</td>
<td>$&gt; 1$</td>
</tr>
<tr>
<td>$9^\circ \leq T \leq 14^\circ$ K</td>
<td>$1Kg \leq H_o \leq 6Kg$</td>
<td>$HT^{-2}$</td>
<td>$H T^{-2}$</td>
<td>$&lt; 0.8$</td>
<td>$&gt; 1$</td>
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<tr>
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<td>$H T^{-4}$</td>
<td>$H T^{-1}$</td>
<td>$&lt; 0.8$</td>
<td>$&gt; 1$</td>
</tr>
</tbody>
</table>
in this region lie between the $T_1$'s for the extreme orientations $[\text{III}]$ axis parallel to $H_0$ and the $[\text{100}]$ axis parallel to $H_0$ indicates that there is no size effect. Hence the spin-lattice bottleneck prevails.

The results at low fields ($50 < H_0 < 250$ gauss) appear to be an extension of the results at high fields. An analysis at these low fields is not possible within the framework of the theory. At very low fields, the Zeeman energy gets to be of the order of the dipolar interactions and the perturbation procedure is not valid. Another perturbation approach which regards the Zeeman energy as a perturbation of the dipolar interaction energy has been developed, but it has not been applied to impurity relaxation.

At higher fields (above 3 to 4 Kg) the previous analysis breaks down. A possible explanation for the high field behavior of $T_1$ could be that it is due to the increasing importance of a lattice-bath bottleneck. (See page 26). The spin-lattice and lattice-bath stages of the relaxation process act in series, and the slowest process will determine the characteristics of the overall relaxation process. From equations II-35 and II-36, we see that as $H_0$ is increased at constant temperature, $\tau_{5-L}$ gets shorter faster than $\tau_{L-B}$. At higher fields, the overall relaxation of the impurity should be characterized by the lattice-bath bottleneck. In this
case, \( T_1 \) would be of the form

\[
T_1 \propto \frac{H^2}{T^2}.
\]

If the above analysis is correct, we would expect to see a size effect at high fields. The lattice-bath bottleneck should dominate the relaxation process at a lower value of \( H_0 \) for the single crystal as compared with the powder, because of the increased surface area of the powder. With the magnet available for these experiments, it was not possible to go to higher fields.

B. Hydrogen Temperature Range

The results between 9\(^0\)K and 14\(^0\)K can be explained by the same arguments used for the intermediate-field values at helium temperatures. In this range, \( \phi_{S-L} \) is always larger than \( \phi_{L-B} \) by virtue of its temperature dependence, and \( \phi_{L-B} \) can always be neglected. The spin-lattice bottleneck is responsible for the characteristic relaxation process at temperatures higher than the helium range.

As the temperature is raised above 14\(^0\)K, the rapid-diffusion case gives way to the diffusion-limited case. To see this, consider the temperature dependence of \( \delta \).

For \( \tau_0 > 1 \) and \( \phi_{S-L} \propto \frac{1}{T} \), we have for the temperature and field dependence of \( \delta \):

\[
\delta \propto T^{-7/6} H^{-2/3}.
\]

The above expression for \( \delta \) also applies to the helium
region where we concluded \( S < 0.8 \) (Rapid-Diffusion Case). As the temperature is raised \( S \) gets larger and passes through the value for which

\[(T, ) \text{ Rapid-Diffusion } = (T, ) \text{ Diffusion-Limited}\]

This value of \( S \) is just given by:

\[
\frac{3 \lambda^2}{4\pi NC} = \frac{3}{8\pi NC^{1/4}} D^{3/4} \quad \text{VI-7}
\]

or

\[
S = \left[ \frac{C}{D} \right]^{1/2} \frac{1}{2 \lambda^2} = 0.8. \quad \text{VI-8}
\]

The ratio of \( \left[ I - \chi_4(\delta)/I \chi_4(\delta) \right] \) in equation II-29 changes rapidly near \( S = 0.8 \) which means that the transition should be sharp, in agreement with the experimental results as shown in figures 4 and 5.

For \( S > 0.8 \), \( T \) is given by

\[
T = \frac{3}{8\pi NC^{1/4}} D^{3/4}. \quad \text{VI-9}
\]

If the one-phonon impurity-spin relaxation process applies, then \( \frac{C}{D} \sim \frac{1}{T} \) and we have for \( C \nu > 1 \):

\[
T \propto \frac{H^0}{T^{1/4}}. \quad \text{VI-10}
\]

Equation VI-10 shows that the temperature dependence of \( T \) changes sharply across the transition from the rapid-diffusion case to the diffusion-limited case. This is in agreement with the results shown in figures 4 and 5. Also,
the change in the field dependence of \( T_1 \) agrees with the experimental results (see figure 3).

Further support for the suggestion that the diffusion-limited case applies above \( 14^0 \)K is the absence of a strong orientation dependence of \( T_1 \).

In all previous discussion, we have assumed that \( \phi^\nu \geq 1 \) (VI-10). However, as \( T \) is increased, \( \phi^\nu \) gets smaller and the assumption becomes poorer. In the case of diffusion-limited relaxation with \( \phi^\nu < 1 \), we have:

\[
T_1 \propto \frac{1}{\phi^{1/4}}. \tag{VI-11}
\]

The temperature dependence of \( T_1 \) in the diffusion-limited region also becomes inverted. Figure 5 shows some indication that the slope changes from negative to positive in the range from \( 14^0 \)K to \( 20^0 \)K. The minimum in the ln \( T_1 \) vs. ln \( T \) curve in figure 5 should occur when \( \phi^\nu = 1 \). In figure 4, this minimum is outside of the accessible temperature range, because at lower fields, \( T \) must be higher to make \( \phi^\nu = 1 \).

C. Nitrogen Temperature Range

The small orientation dependence of \( T_1 \) indicates that \( T_1 \) is governed by the diffusion-limited process in this temperature range. \( T_1 \) at nitrogen temperatures is longer than in the liquid hydrogen temperature range. Therefore, \( T_1 \) cannot have an inverse dependence on temperature between \( 20^0 \)K and \( 63^0 \)K. The only way \( T_1 \) can have a
direct dependence on temperature is for $\phi^\nu$ to be smaller than one. In this case, $T_1$ is given by equation VI-11.

In order to explain the $H_0^{1/2}$ dependence of $T_1$ at $78^\circ K$ as shown in figure 2, we must conclude $\phi \propto \frac{1}{\sqrt{T}}$. This means that the one-phonon process is still dominant at nitrogen temperatures.

D. Quantitative Discussion of Results

To make a quantitative analysis of the impurity relaxation mechanism and the validity of the theory of the nuclear relaxation process, several things must be known. They are as follows: the number of paramagnetic impurities, the type of impurities and the impurity relaxation time at a field and temperature covered in the experiment. There should be only one principal impurity, or the significance of $\phi$ is obscure. The impurities should not be clustered but should be uniformly distributed throughout the sample.

Unfortunately, we did not know the type of impurity, although analyses of other crystals of Ca $F_2$ by Harshaw show that the only detectable paramagnetic impurity is Fe. These same analyses indicate that the probable concentration of Fe is one part in $10^6$ or less. Color centers could also act a paramagnetic impurities, but Ca $F_2$ does not seem to support most color centers except those which arise from vacancies caused by substitutional impurities. As there are no published results on $\phi$ for Fe in Ca $F_2$. 
at any field or temperature, we have to assume our value calculated, using the theory for $T_1$ is correct. We have to assume that clustering of impurities does not take place, because there is no published information in this regard.

We can calculate $\varphi$ at one temperature and field by determining the field and temperature for which $\delta = \delta_T = 0.8$. This can be done because $\delta$ is independent of the impurity concentration. After determining $\varphi$, we can determine $N$ from equation II-30 or II-31 by using the measured $T_1$ at the above values of field and temperature. Since $N$ and $\varphi$ are the only unknowns in the theory, a quantitative analysis can be made.

Figure 4 indicates that $\delta = \delta_T = 0.8$ at $T = 14^\circ K$ and $H_0 = 1.95$ Kg when the crystal has the [100] axis parallel to $H_0$. Assuming the impurity is Fe$^{++}$ with $S = 2$ and $\mu_p = 6.23 \times 10^{-20}$ cgs units, we obtain for $\lambda_c$ using II-12,

$$\lambda_c = 11 \times 10^{-8} \text{ cm.}$$

Using this value for $\lambda_c$, $\varphi$ can be calculated from II-29a.

$$\varphi = 1.8 \times 10^{-6} \text{ sec.}$$

Substituting the above values for $\lambda_c$ and $\varphi$ at $T = 14^\circ K$ and $H_0 = 1.95$ Kg into II-30, and setting $T_1 = 11.5$ seconds, we have

$$N = 1.4 \times 10^{16} \text{ imp./cc.}.$$
This is close to one part in $10^6$.

Knowing $N$, $\varphi$ can now be calculated for all fields and temperature ranges, using the qualitative analysis as a guide.
VII. CONCLUSION

From an analysis of $T_1$ based on Bloembergen's theory and Rorschach's solution to the resulting diffusion equation, it has been found that the impurity relaxation process in the helium and hydrogen temperature range is a one-phonon process. For intermediate fields ($350 \text{g} < H_0 < 3.5 \text{ Kg}$) the bottleneck in transfer of Zeeman energy from the impurity spin to the bath is between the impurity spin and the lattice. At higher fields, there is a size effect at helium temperatures which can be explained if one assumes a lattice-bath bottleneck exists at higher fields.

A calculation of $\varphi$ and $N$ from data taken at $14^\circ\text{K}$ and $H_0 = 1.95 \text{ Kg}$ gives $\varphi = 1.8 \times 10^{-6} \text{ sec.}$ and $N = 1.4 \times 10^{16} \text{ imp/cc or about } 1/10^5$.

To explain the longer $T_1$'s at nitrogen temperatures than at hydrogen temperatures requires $\varphi \propto 1/H_T$. The field dependence of $T_1$ at $78^\circ\text{K}$ can only be explained by taking $\varphi \propto 1/H_T$. This means that the one-phonon process dominates over the Raman process at least up to temperatures of $78^\circ\text{K}$.

Considering the crudeness of the model and the assumptions which had to be made in the analysis, the theory agrees very well with the experimental results.

A better test of the theory could be made using a sample with a known concentration of an impurity for
which the relaxation time has been determined. If this were done, it would then be possible to study various paramagnetic ions indirectly by studying nuclear relaxation. This would be very valuable, since other techniques (epr and hypersound) which are used to look at the impurity relaxation directly, have serious experimental difficulties. For example, it is virtually impossible to study the field dependence of $\varphi$ solely with microwave techniques. In addition, there is often the problem of poor signal-to-noise ratios when studying very low concentration of impurities.

In conclusion, although the work reported in this thesis was of an exploratory nature with regard to studying impurity relaxation, it certainly justifies continued research using crystals with controlled impurity dopings.
APPENDIX A

Generalized Harmonic Analysis

We consider time dependent perturbation theory where the perturbation varies in time. We will use the method of variation of constants (See for example, Schiff, p 195).

The Hamiltonian under consideration is

\[ H = H_0 + H'(t), \]  

where \( H'(t) \) varies randomly in time,

\[ H_0 \psi_n = E_n \psi_n \]  

and

\[ \psi_n = \psi_n e^{-\frac{i}{\hbar} E_n t}. \]

Since \( H' \) depends on time, we must use the time-dependent Schrödinger equation

\[ \frac{i}{\hbar} \frac{\partial \psi}{\partial t} = H \psi. \]

We expand \( \psi \) in terms of the unperturbed functions \( \psi_n \), where the expansion coefficients depend on time:

\[ \psi = \sum_n a_n(t) \psi_n e^{-\frac{i}{\hbar} E_n t}. \]

It can be shown that

\[ a_k(t) = \frac{1}{\hbar} \sum_n H'_{kn} a_n(t) e^{i \omega_{kn} t}, \]

where

\[ \omega_{kn} = \frac{E_r - E_n}{\hbar} \]

and

\[ H'_{kn} = \int \psi_k^* H' \psi_n \, dV. \]
Assuming we can expand \( a_n(t) \) in a power series in \( \lambda \) where

\[ H = H_0 + \lambda H'(t), \]

we have:

\[ a_n(t) = a_n^{(0)}(t) + \lambda a_n^{(1)}(t) + \cdots. \tag{A-7} \]

Substituting A-7 into A-6 and equating coefficients of \( \lambda \):

\[ \frac{d a^{(0)}_k}{dt} = 0 \quad ; \quad \frac{d a^{(1)}_k}{dt} = \frac{1}{\hbar} \leq H'_{km}(t) a^{(1)}_k(t) e^{i \omega_{km} t}. \]

In particular, if \( a^{(0)}_k = \delta_{km} \), we obtain for the first-order term:

\[ \frac{d a^{(1)}_k}{dt} = \frac{1}{\hbar} \leq H'_{km}(t) e^{i \omega_{km} t}. \tag{A-8} \]

The solution of A-8 is:

\[ a^{(1)}_k(t) = \frac{1}{i \hbar} \int_{-\infty}^{t} H'_{km}(t') e^{i \omega_{km} t'} dt', \tag{A-9} \]

where it is assumed \( a^{(0)}_k = 0 \) at \( t = -\infty \) before perturbation is applied.

Up to here, the treatment has been the same as in the usual time dependent perturbation theory.

We assume the ergodic hypothesis, that is, the time average of an element is the same as the time average of the ensemble.

From A-9, we have for \( |a^{(1)}_k|^2 \):

\[ |a^{(1)}_k|^2 = \frac{1}{\hbar^2} \int_{-\infty}^{t} \int_{-\infty}^{t} H'_{km}(t') H_{km}(t'') e^{-i \omega_{km} (t'-t'')} dt' dt''. \tag{A-10} \]
Now we let \( t'' = t' + \tau \), so that
\[
|\alpha^{(i)}_{kl'}|^2 = \frac{i}{\hbar^2} \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dt H_{km}(t') H_{km}(t'+\tau) e^{i\omega_{km} \tau}.
\]

\( H_{km} \) is a randomly-fluctuating function. We assume its average value is zero. Hence, any contribution to \( dt \) integration in A-11 can occur only in a narrow region near \( \tau = 0 \). This region is of the order of the correlation time \( \tau_c \), which is very small compared to \( t \). Over the remainder of the region, the integrand of A-11 averages to zero. Hence, we let the upper limit of \( dt \) integration become infinite with only a negligible error near \( t' = \tau \).

We define the transition probability per unit time from the state \( m \) to \( k \) as:
\[
W_{km} = \lim_{t \to \infty} \frac{1}{t} |\alpha^{(i)}_{kl}(t)|^2 = \langle |\alpha^{(i)}_{kl}(t)|^2 \rangle_{\text{ave}}.
\]

Therefore,
\[
W_{km} = \frac{1}{\hbar^2} \lim_{t \to \infty} \int_{-\infty}^{t} dt' \int_{-\infty}^{\infty} dt H_{km}(t') H_{km}(t'+\tau) e^{i\omega_{km} \tau}.
\]

Reversing the order of integration and taking the limit inside, we have
\[
W_{km} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt e^{i\omega_{km} \tau} \left[ \lim_{t \to \infty} \frac{1}{t} \int_{-\infty}^{t} H_{km}(t') H_{km}(t'+\tau) dt' \right] \langle H_{km}(t) H_{km}(t+\tau) \rangle_{\text{ave}}.
\]

The factor in brackets is written \( \langle H_{km}(t) H_{km}(t+\tau) \rangle_{\text{ave}} \).
whereupon A-14 becomes

\[ W_{km} = \frac{1}{\hbar} \int_{-\infty}^{\infty} d\tau \, e^{i\omega_{km}\tau} \langle H'_{km}(t) H'_{km}(t+\tau) \rangle_{\text{av}}. \]  

A-15

In many cases, \( H' \) will factor into a time dependent part \( g(t) \) and a time-independent part \( f \):

\[ H' = f \cdot g(t). \]  

A-16

Then A-15 is of the form

\[ W_{km} = \frac{1}{\hbar} \mid f_{km} \mid^2 \int_{-\infty}^{\infty} d\tau \, e^{i\omega_{km}\tau} \langle g_{km}(t) g_{km}(t+\tau) \rangle_{\text{av}}. \]  

A-17

We now show that the Fourier transform of

\[ \langle g_{km}(t) g_{km}(t+\tau) \rangle_{\text{av}} \]  

is the power spectrum of \( g(t) \).

Let \( y(t) \) be a real random function defined over an interval \( T \) and zero outside. Let \( y(t) \) be stationary or

\[ y(t) = \lim_{T \to \infty} \int_{-T}^{T} y(t') dt' = 0. \]

The Fourier transform of \( y(t) \) is:

\[ y(\nu) = \int_{-\infty}^{\infty} d\nu \ A(\nu) e^{i2\pi \nu t}. \]

Since \( y(t) \) is real, then \( A(\nu) = A^*(-\nu) \).

By the Parseval Theorem:

\[ \int_{-\infty}^{\infty} y^2(t) dt = \int_{-\infty}^{\infty} |A(\nu)|^2 d\nu \]

and we can define

\[ \langle y(t)^2 \rangle_{\text{av}} = \lim_{T \to \infty} \frac{1}{T} \int_{-T}^{T} y^2(t) dt = \int_{-\infty}^{\infty} G(\nu), \]
where:

\[
G(\nu) = \lim_{T \to \infty} \frac{1}{T} |A(\nu)|^2. \tag{A-18}
\]

\(G(\nu)\) is called the spectral density. Consider

\[
\langle y(t) y(t+\tau) \rangle_{\omega e} = \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} y(t) y(t+\tau) dt
\]

Using the Fourier expansion

\[
\langle y(t) y(t+\tau) \rangle_{\omega e} = \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} A(\nu) e^{2\pi i \nu t} \times
\]

\[
\int_{-\infty}^{\infty} d\nu' A^*(\nu') e^{2\pi i \nu' t} e^{-2\pi i \nu' \tau}
\]

or

\[
\langle y(t) y(t+\tau) \rangle_{\omega e} = \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{\infty} d\tau e^{2\pi i \nu (\nu-\nu') t} \times
\]

\[
\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\nu d\nu' A(\nu) A^*(\nu') e^{-2\pi i \nu \tau}
\]

The first integral in A-20 is equal to \(\delta(\nu-\nu')\), therefore A-20 becomes

\[
\langle y(t) y(t+\tau) \rangle_{\omega e} = \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{\infty} d\nu |A(\nu)|^2 e^{-2\pi i \nu \tau}
\]

\[
= \int_{-\infty}^{\infty} d\nu G(\nu) e^{2\pi i \nu \tau}. \tag{A-21}
\]

We define the correlation function \(K(\tau)\) to be

\[
K(\tau) = \frac{\langle y(t) y(t+\tau) \rangle_{\omega e}}{\langle y(t)^2 \rangle_{\omega e}}. \tag{A-22}
\]
Hence the correlation function is the Fourier transform of the normalized spectrum \( \mathcal{J}(\nu) \), where

\[
\mathcal{J}(\nu) = \frac{G(\nu)}{\int_{-\infty}^{\infty} G(\nu)}.
\]

From A-21, A-22, and A-23, we have

\[
\mathcal{J}(\nu) = \int_{-\infty}^{\infty} K(\tau) e^{-2\pi i \nu \tau} d\tau.
\]

\( g(t) \) in A-16 satisfies the requirements set down for \( \gamma(t) \), therefore A-17 can be written as:

\[
W_{km} = \frac{1}{h^2} \left| f_{km} \right|^2 \mathcal{J}(\nu_{km}),
\]

where

\[
\mathcal{J}(\nu_{km}) = \int_{-\infty}^{\infty} <g_{km}(t)g_{km}(t+\tau)\omega e^{-2\pi i \nu_{km} \tau} d\tau.
\]

A-25 gives the transition probability per unit time of a system in the presence of a radiation field, the spectral density of which is given by \( \mathcal{J}(\nu_{km}) \). Here the transition considered is between states \( m \) and \( k \).

We want to calculate \( W_{km} \) for a nuclear spin in the field of a rapidly flipping impurity spin. The perturbation \( H' \) is term \( C' \) of II-6. If we take \( \Psi_{m,M} \), as the zero order wave function, then we can write

\[
\Psi_{m,M} = \phi_m \phi_M; \quad \phi_m - \text{nuclear wave function}
\]

\[
\phi_M - \text{imp. wave function}
\]

\[
\Phi_{m,M} = \Phi_m \Phi_M; \quad \Phi_m - \text{imp. wave function}
\]
The perturbation $H'$ can be written as

$$H' = f \cdot g(t),$$

where

$$f = -\frac{\delta \sigma_p \hbar^2}{\hbar c_p} \frac{3}{2} \sin \Theta_p \cos \Theta_p \exp \left( -i \phi_p \right) I^+_i$$

and

$$g(t) = S_x(t).$$

We want to consider the matrix element of $H'$:

$$\langle \psi_{m', M'} | H' | \psi_{m, M} \rangle = \langle \phi_{m'} | f | \phi_m \rangle \langle \phi_{m'} | g(t) | \phi_m \rangle \times S(-m, m+1) S(M, M').$$

The matrix element $\langle \phi_{m'} | f | \phi_m \rangle$ is independent of time and can be readily evaluated, so that:

$$|\langle m+1 | f | m \rangle|^2 = \left( \frac{\delta \sigma_p \hbar^2}{\hbar c_p} \right)^2 \frac{9}{4} \sin^2 \Theta_p \cos^2 \Theta_p |\langle m+1 | I^+_i | m \rangle|^2.$$ (A-31)

To determine $W_{m \rightarrow m + 1}^{m'}$, we use equation A-14. Using A-30 and A-31, $W$ is given by

$$W_{m \rightarrow m + 1}^{m'} = \left( \frac{\delta \sigma_p \hbar^2}{\hbar c_p} \right)^2 \frac{9}{4} \sin^2 \Theta_p \cos^2 \Theta_p |\langle m+1 | I^+_i | m \rangle|^2 x \left[ \lim_{t \to \infty} \frac{1}{t} \int_{-\infty}^{t} dt' \langle M(\frac{1}{2}) | M | M(\frac{1}{2}) \rangle \right].$$ (A-32)

*Random fluctuations in $\sigma_p, \Theta_p$ and $\phi_p$ can be neglected in first approximation.
\[
\frac{(\tau \gamma p t)^2}{\lambda_p^2} \sin^2 \theta_p \cos^2 \theta_p |\langle m+1|\hat{I}^+|m \rangle|^2 \times \\
\int_0^\infty d\tau e^{-i\omega_m \tau} \langle S_e'(t) S_e'(t+\tau) \rangle_{\text{ave}},
\]

where
\[
S_e'(t) = \langle M | S_e(t) | M \rangle.
\]

From equation A-26, we have
\[
J_e(\gamma^2, m, \nu) = \int_0^\infty d\tau e^{-i\omega_m \tau} \langle S_e'(t) S_e'(t+\tau) \rangle_{\text{ave}}.
\]

We must now determine the correlation function. The simplest assumption one can make is that the "force" which is causing \( S_e'(t) \) to vary is completely uncorrelated. The "motion" of \( S_e'(t) \) can be determined from the Langevin equation:
\[
\frac{d}{dt} S_e'(t) + \frac{1}{\tau_c} S_e'(t) = F(t),
\]
where the force, \( F(t) \), is completely uncorrelated:
\[
\langle F(t) F(t+\tau) \rangle \sim \delta(\tau).
\]

It can then be shown that \( S_e'(t) \) will have an exponential correlation function with a correlation time \( \tau_c \),
\[
\langle S_e'(t) S_e'(t+\tau) \rangle_{\text{ave}} = \langle (S_e(t))^2 \rangle_{\text{ave}} e^{-\tau/\tau_c},
\]
so that:
\[
J_e(\gamma^2, m, \nu) = 2 \int_0^\infty d\tau e^{-i\omega_m \tau} \langle (S_e'(t))^2 \rangle_{\text{ave}} e^{-\tau/\tau_c}
\]
\[
= \langle (S_e'(t))^2 \rangle_{\text{ave}} \frac{2 \tau_c}{1 + \frac{\tau_c^2}{\omega_m^2, m, \nu}},
\]

A-32 (cont)
Now \( \langle (S^z(t))^2 \rangle_{\text{ave}} = \frac{1}{3} S(S+1) \), so that A-34 becomes

\[
J_z(\nu_m, m+1) = \frac{2}{3} S(S+1) \frac{T_c}{1 + T_c^2 \omega_m^2, m+1}.
\]

A-35

The correlation time \( T_c \) is the impurity relaxation time \( \rho \) divided by \( 2\pi \) and \( \omega_m, m+1 = 2\pi \nu_F \), where \( \nu_F \) is the nuclear Larmor frequency. Finally, A-35 becomes

\[
J_z(\nu_F) = \frac{1}{3\pi} S(S+1) \frac{\rho}{1 + \rho^2 \nu_F^2},
\]

A-36

or, since \( |\langle m+1 | I^+ | m \rangle|^2 = 1 \),

\[
\omega_m, m+1 = \frac{(\gamma \gamma_F \rho)^{1/2}}{\hbar \gamma F} \frac{3}{4\pi} \sin^2 \theta_{\rho} \cos^2 \theta_{\rho} S(S+1) \frac{\rho}{1 + \rho^2 \nu_F^2}.
\]

A-37
APPENDIX B

Solution of the Diffusion Equation

The equation to be solved is II-26.
\[ \frac{\partial M}{\partial t} = D \nabla^2 M - \frac{C'}{\Lambda^2} (M - M_0), \quad \text{II-26} \]

where \( M \) is the magnetization per unit volume along the direction of \( H_0 \), \( D \) is the diffusion coefficient, \( M_0 \) is the equilibrium value of \( M \) and
\[ \frac{C'}{\Lambda^2} = \frac{1}{T'_1}, \]

where \( T'_1 \) is given by II-11.

We will neglect any orientation dependence of \( D \) and use the average over angle of \( C' \) and call it \( C \).
\[ C = \frac{1}{4\pi} \int C' d\Omega = \frac{1}{5\pi} \left( \frac{\gamma H_0}{1 + \gamma H_0^2} \right)^2 \frac{1}{(S+1)} \frac{1}{1 + \frac{S}{\gamma H_0^2}}. \]

II-26 then becomes
\[ \frac{\partial M}{\partial t} = \frac{1}{\Lambda^2} \frac{\partial}{\partial \Omega} \left( \frac{\partial^2 M}{\partial \Omega^2} \right) - \frac{C}{\Lambda^2} (M - M_0). \quad \text{B-1} \]

The boundary conditions used by Rorschach are as follows:

a) Steady state \( \frac{\partial M}{\partial t} = 0 \Rightarrow \nabla^2 M - \frac{\beta}{\Lambda^2} (M - M_0) \),
where \( \beta = \frac{C}{D} \).

b) For \( \Lambda \to \infty \), \( M \to M_1 \), (a constant).

c) The total flow of magnetization in from \( \infty \) by diffusion equals the total amount of magnetization relaxed outside the critical radius, \( \Lambda_c \):
\[ \lim_{\Lambda \to \infty} (D | \nabla M|). 4\pi \Lambda^2 = - \int_{\Lambda_c}^{\infty} \frac{1}{T'_1} (M - M_0) dV. \]

The steady state solution of B-1 is
\[ M = M_0 + \Lambda^{-1/2} \left\{ A J_{x_4} (i \frac{\beta}{2 \Lambda^2}) + B J_{-x_4} \left( i \frac{\beta}{2 \Lambda^2} \right) \right\}. \]
For condition b), we use the expansion of \( J_{3/4}(x) \) for \( x \to 0 \)

\[
J_{3/4}(x) \xrightarrow{x \to 0} \frac{1}{\Gamma(m+1)} \left( \frac{x}{2} \right)^m,
\]

therefore

\[
M_1 - M_0 = B \frac{2^{3/4}}{\Gamma(3/4)} i^{-3/4} B^{3/4} \tag{7.8}
\]
or

\[
B = (M_1 - M_0) \Gamma(3/4) i^{-3/4} B^{3/4} 2^{-3/2}.
\]

For condition c) we must evaluate integrals of the form

\[
\int_{\mathcal{L}_c} n^{-3/2} J_{3/4}(\frac{i \sqrt{B}}{2 \Lambda_c}) \, 4\pi n^2 \, dn
\]
or

\[
K_+ = 4\pi \int_{\mathcal{L}_c} n^{3/2} J_{3/4}(\frac{i \sqrt{B}}{2 \Lambda_c}) \, dn,
\]

\[
K_- = 4\pi \int_{\mathcal{L}_c} n^{3/2} J_{-3/4}(\frac{i \sqrt{B}}{2 \Lambda_c}) \, dn.
\]

Letting \( u = \frac{i \sqrt{B}}{2 \Lambda_c} \) we have

\[
n = \left( \frac{i \sqrt{B}}{2} \right)^{1/2} u^{-1/2}
\]

and

\[
dn = \left( \frac{i \sqrt{B}}{2} \right)^{1/2} (-\frac{i}{2} u^{-3/2}) \, du.
\]

\( K_+ \) and \( K_- \) become

\[
K_+ = -4\pi \int_0^\infty \bigg[ 2^{3/4} B^{3/4} i^{-3/4} u^{3/4} J_{3/4}(u) \bigg] \, du,
\]

\[
K_- = -4\pi \int_0^\infty \bigg[ 2^{3/4} B^{3/4} i^{-3/4} u^{3/4} J_{-3/4}(u) \bigg] \, du,
\]

where

\[
\delta = \frac{\sqrt{3}}{2 \Lambda_c}.
\]

\( K_+ \) and \( K_- \) can be evaluated from the following

\[
\int x^{3/4} J_{3/4}(x) \, dx = -x^{3/4} J_{3/4}(x)
\]

and

\[
\int x^{3/4} J_{-3/4}(x) \, dx = x^{3/4} J_{-3/4}(x)
\]
$K_+$ and $K_-$ become, using the above

$$K_+ = -4\pi 2^{3/4} \beta^{1/4} \left[ S^{3/4} J_{-3/4}(i\delta) - \frac{1}{\Gamma(1/4)} Z^{3/4} \right],$$

$$K_- = -4\pi 2^{3/4} \beta^{1/4} \left[ -i S^{3/4} J_{3/4}(i\delta) \right].$$

Since we have assumed spherical symmetry

$$|\nabla M| = \frac{dM}{d\alpha}.$$

Using

$$2 \frac{d}{dx} J_m(x) = J_{m-1}(x) - J_{m+1}(x),$$

we get

$$|\nabla M| = \frac{d}{d\alpha} \left\{ \frac{n^{1/2}}{2} \left[ A J_{1/4}(ix) + B J_{-1/4}(ix) \right] \right\}$$

$$= A \left\{ -\frac{1}{2} n^{-3/2} J_{1/4}(ix) - i \frac{\beta}{2} n^{-3/2} \left[ J_{-1/4}(ix) - J_{3/4}(ix) \right] \right\}$$

$$+ B \left\{ -\frac{1}{2} n^{-3/2} J_{-1/4}(ix) - i \frac{\beta}{2} n^{-3/2} \left[ J_{1/4}(ix) - J_{3/4}(ix) \right] \right\},$$

where

$$x = \frac{\beta}{2^n}.$$

Considering the limit, we have

$$\lim_{n \to \infty} n^2 |\nabla M| = -A 2^{1/2} i^{1/4} \frac{\beta^{1/4}}{\Gamma(1/4)},$$

therefore condition b) is:

$$2^{3/4} \beta^{1/4} \left\{ A \left( S^{3/4} J_{-3/4}(i\delta) - 2^{3/4} \frac{1}{\Gamma(1/4)} \right) \right\}$$

$$- B S^{3/4} J_{3/4}(i\delta) \right\} = -A 2^{3/4} i^{1/4} \frac{\beta^{1/4}}{\Gamma(1/4)}$$

or

$$A = B \frac{J_{3/4}(i\delta)}{J_{-3/4}(i\delta)}.$$

To determine $T_1$, we calculate the amount of magnetization disappearing:

Let

$$\frac{\Delta m}{dt} = \text{total amount of magnetization disappearing per unit time for each impurity},$$

$$\frac{\Delta m}{dt} = \lim_{n \to \infty} 4\pi D |\nabla M| n^2.$$
The right hand term is the amount of $M$ flowing in through the surface of the sphere far from the impurity.

We have

$$\frac{2m}{\partial t} = -4 \pi DA \frac{\sqrt{2}}{2^{\nu_4}} \beta^{\nu_4} \frac{\Gamma(\nu_4)}{\Gamma(\nu_4)}$$

$$= 4 \pi D 2 \sqrt{2} i^{-\nu_4} \frac{\beta^{\nu_4}}{\Gamma(\nu_4)} \frac{\Gamma(\nu_4)}{\Gamma(\nu_4)} \frac{J_{\nu_4}(i\delta)}{J_{-\nu_4}(i\delta)} \frac{\Gamma(\nu_4)}{\Gamma(\nu_4)} \frac{i^{\nu_4} \beta^{\nu_4}}{2^{\nu_4}} (M_1 - M_0).$$

If $N$ is the number of impurities per unit volume, then the loss of $M$ per unit time is

$$\frac{2M}{\partial t} = N \frac{2m}{\partial t} = -4 \pi N D \frac{\Gamma(\nu_4)}{\Gamma(\nu_4)} \frac{J_{\nu_4}(i\delta)}{J_{-\nu_4}(i\delta)} 2 i^{\nu_4} \beta^{\nu_4} (M_1 - M_0)$$

$$= \frac{1}{T_1} (M_1 - M_0).$$

If the impurity separation is very large compared to the critical radius $\eta_c$ or $\beta^{\nu_4}$, then $M$ is nearly constant over most of the sample and therefore, $M_1 \approx M$.

Finally we have then

$$\frac{2M}{\partial t} = -\frac{1}{T_1} (M - M_0)$$

with

$$T_1 = \frac{1}{4 \pi D N} \beta^{\nu_4} \frac{\Gamma(\nu_4)}{\Gamma(\nu_4)} \frac{J_{\nu_4}(i\delta)}{J_{-\nu_4}(i\delta)}$$

where

$$I_m(x) = \frac{1}{\pi} J_m(ix)$$

$$\frac{\Gamma(\nu_4)}{\Gamma(3\nu_4)} \approx 3.$$
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