NASA TECHNICAL REPORT

NASA TR R-427

NASA TR R-427

THE SPIN-TEMPERATURE THEORY OF DYNAMIC NUCLEAR POLARIZATION AND NUCLEAR SPIN-LATTICE RELAXATION

by Charles E. Byvik and David S. Wollan

Langley Research Center
Hampton, Va. 23665

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • NOVEMBER 1974

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TR R-427		

4. Title and Subtitle	5. Report Date
THE SPIN-TEMPERATURE THEORY OF DYNAMIC NUCLEAR POLARIZATION AND NUCLEAR SPIN-LATTICE RELAXATION	November 1974
	6. Performing Organization Code

7. Author(s)	8. Performing Organization Report No.
Charles E. Byvik and David S. Wollan	L-9554
	10. Work Unit No. 176-31-21-05
9. Performing Organization Name and Address	11. Contract or Grant No.
NASA Langley Research Center Hampton, Va. 23665	
	13. Type of Report and Period Covered
12. Sponsoring Agency Name and Address	Technical Report
National Aeronautics and Space Administration Washington, D.C. 20546	14. Sponsoring Agency Code

15. Supplementary Notes Part of the information presented herein was included in a thesis entitled "Dynamic Nuclear Polarization in Samarium-Doped Lanthanum Magnesium Nitrate" submitted by Charles E. Byvik in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics, Virginia Polytechnic Institute and State University, Blacksburg, Va., September 1971. David S. Wollan is Assistant Professor of Physics, Virginia Polytechnic Institute and State University, Blacksburg, Va. (Consultant at NASA Langley Research Center).

16. Abstract

A detailed derivation of the equations governing dynamic nuclear polarization (DNP) and nuclear spin-lattice relaxation by use of the spin-temperature theory has been carried to second order in a perturbation expansion of the density matrix. Nuclear spin diffusion in the rapid diffusion limit and the effects of the coupling of the electron dipole-dipole reservoir (EDDR) with the nuclear spins are incorporated. The complete expression for the dynamic nuclear polarization has been derived and then examined in detail for the limit of well-resolved solid-effect transitions. Exactly at the solid-effect transition peaks, the conventional solid-effect DNP results are obtained, but with EDDR effects on the nuclear relaxation and DNP leakage factor included. Explicit EDDR contributions to DNP are discussed, and a new DNP effect is predicted.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Nuclear polarization Nuclear spin-lattice relaxation Spin-temperature theory	Unclassified – Unlimited STAR Category 24

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	61	$3.75

*For sale by the National Technical Information Service, Springfield, Virginia 22151

THE SPIN-TEMPERATURE THEORY OF DYNAMIC NUCLEAR POLARIZATION AND NUCLEAR SPIN-LATTICE RELAXATION[1]

By Charles E. Byvik and David S. Wollan[2]
Langley Research Center

SUMMARY

A detailed derivation of the equations governing dynamic nuclear polarization (DNP) and nuclear spin-lattice relaxation by use of the spin-temperature theory has been carried to second order in a perturbation expansion of the density matrix. Nuclear spin diffusion in the rapid diffusion limit and the effects of the coupling of the electron dipole-dipole reservoir (EDDR) with the nuclear spins are incorporated. The complete expression for the dynamic nuclear polarization has been derived and then examined in detail for the limit of well-resolved solid-effect transitions. Exactly at the solid-effect transition peaks, the conventional solid-effect DNP results are obtained, but with EDDR effects on the nuclear relaxation and DNP leakage factor included. Explicit EDDR contributions to DNP are discussed, and a new DNP effect is predicted.

INTRODUCTION

Soon after the classic work of Bloembergen, Purcell, and Pound (ref. 1), Purcell (quoted by Bloembergen in ref. 2) suggested that the spin temperature of paramagnetic ions in a solid could be raised above the temperature of the lattice by a strong radio-frequency field at the resonance frequency of the electronic spins and, furthermore, that the neighboring nuclear spins would follow the electronic spin temperature. This process of driving the nuclear spin temperature away from the temperature of the lattice by pumping the electron spins suggested the possibility of dynamic nuclear polarization (DNP).

In 1953, Overhauser (refs. 3 and 4) demonstrated theoretically that the spin temperature of nuclei in a metallic solid could be lowered through the contact hyperfine interaction of the nuclei with the conduction electrons when the electron spin resonance transition

---

[1]Part of the information presented herein was included in a thesis entitled "Dynamic Nuclear Polarization in Samarium-Doped Lanthanum Magnesium Nitrate" submitted by Charles E. Byvik in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics, Virginia Polytechnic Institute and State University, Blacksburg, Va., September 1971.

[2]Assistant Professor of Physics, Virginia Polytechnic Institute and State University, Blacksburg, Va. (Consultant at NASA Langley Research Center).

is saturated. The experimental verification of Overhauser's predictions of DNP in metals was reported in 1956 (ref. 5). The idea of dynamic polarization of nuclei was soon extended to nonmetallic materials (refs. 6 to 9). The theory of DNP and nuclear spin-lattice relaxation in ionic crystals with paramagnetic impurities is the subject of the present investigation.

Two theoretical approaches have been used to describe the spin dynamics of such systems: the rate-equation approach (refs. 10 to 14) and the spin-temperature theory (refs. 15 to 23). The rate-equation approach assumes that the paramagnetic electron spins and the nuclear spins are each weakly interacting systems whose states may be completely specified by the populations of the Zeeman levels. The time evolution of the DNP and relaxation processes may then be determined by calculating the rates at which the populations of the Zeeman levels of both the paramagnetic electron and nuclear systems change as a result of interactions with each other (through electron-dipole–nuclear-dipole coupling), with radio-frequency fields, and with the phonon bath of the lattice. In solids, however, it is found that the assumption of weakly interacting spins within a spin system cannot always be made and therefore that conclusions concerning magnetic processes in solids resulting from a rate-equation approach may be erroneous.

The spin-temperature theory includes the effect of the strongly interacting spins as well as the Zeeman interactions and the lattice in a relatively simple way. Within certain limits, to be discussed herein, the Zeeman and spin-spin interactions and the lattice can each be treated as a thermodynamic reservoir. Each reservoir will have associated with it such thermodynamic quantities as temperature and heat capacity. The reservoirs exchange energy with each other through the applied radio-frequency fields, certain dipolar interactions, and spin-lattice interactions. The time evolution of the DNP and relaxation processes are determined by using the density-matrix approach and calculating the rate at which the electron and nuclear magnetizations change as the reservoirs exchange energy.

A detailed derivation of the equations governing DNP and nuclear spin-lattice relaxation by using the spin-temperature theory is made. The results of nuclear spin diffusion theory in the rapid diffusion limit as reported in the literature are incorporated, and various important limits of DNP, including a new effect, are discussed. A detailed derivation is considered necessary since (1) it is not available in the literature, (2) published equations governing DNP and nuclear spin-lattice relaxation are either incomplete or incorrect, and (3) all of the assumptions made in previous works are not clearly stated.

SYMBOLS

a average distance between nuclear spins

b pseudopotential radius, $0.68\left(\frac{C}{D}\right)^{1/4}$

b' pseudopotential radius, $0.68\left(\frac{C'}{D}\right)^{1/4}$

$$C = \frac{3}{10}\left(\hbar\gamma_e\gamma_n\right)^2 \frac{T_e}{1 + \omega_n^2 T_e^2}$$

$$C' = \frac{3}{10}\left(\hbar\gamma_e\gamma_n\right)^2 \frac{T_{2e}}{1 + \omega_n^2 T_{2e}^2}$$

$$C_j(j = 1,2,3,\ldots) = \eta\ \mathrm{Tr}\Big[\underbrace{\Big[\ldots\Big[\rho^R}_{j}, \underbrace{V\left(t^{j-1}\right)\Big],\ldots\Big]}_{j}, V(t)\Big] S_z$$

$$C_j'(j = 1,2,3,\ldots) = \eta\ \mathrm{Tr}\Big[\underbrace{\Big[\ldots\Big[\rho^R}_{j}, \underbrace{V\left(t^{j-1}\right)\Big],\ldots\Big]}_{j}, V(t)\Big] I_z$$

C_n relative-heat-capacity ratio, $\frac{\omega_n^2}{\omega_L^2}$

C_Δ relative-heat-capacity ratio, $\frac{\Delta^2}{\omega_L^2}$

$C_\pm$ relative-heat-capacity ratio, $\frac{\left(\omega_n \pm \Delta\right)^2}{\omega_L^2}$

D diffusion constant, approximately $\frac{1}{10}\frac{a^2}{T_{2n}}$

d diffusion barrier radius, $a\left(\frac{\gamma_e}{\gamma_n}\right)^{1/3}$

d_{kl} distance between the kth electron and the lth nuclear spin

$E(t)$ time-dependent dynamic nuclear polarization enhancement factor, $\frac{\beta(t)}{\beta_L}$

E_{SS} steady state nuclear enhancement factor

f_d leakage factor, $\frac{N_n T_d}{N_e T_n}$

f_e leakage factor, $\frac{N_n T_e}{N_e T_n}$

$f_e^m = f_e\left(\frac{T_n}{T_n^m}\right)$

$g(\omega)$ electron spin-resonance line-shape function

$$g_B(\omega) = \frac{\mathrm{Tr}\sum_{j=1}^{N_e}\int_{-\infty}^{\infty} d\tau\, S_{zj}\,\tilde{S}_{zj}^B(\tau)e^{-i\omega\tau}}{2\pi\,\mathrm{Tr}S_z^2}$$

g_e the electron g-factor, $\frac{\gamma_e\hbar}{\beta_B}$

$\mathcal{H}$ Hamiltonian operator

$\mathcal{H}'$ Hamiltonian operator without spin-lattice interactions

$\mathcal{H}_O$ unperturbed Hamiltonian operator

$\mathcal{H}^R$ Hamiltonian operator in the rotating frame, $R\mathcal{H}'R^{-1}$

$\mathcal{H}_{II}$ nuclear dipole-dipole Hamiltonian operator

$\mathcal{H}_{IL}$ nuclear spin-lattice Hamiltonian operator

$\mathcal{H}_{IS}$ electron-nuclear dipole-dipole Hamiltonian operator

$\mathcal{H}_{IZ}$ nuclear Zeeman Hamiltonian operator

$\mathcal{H}_{rf}$ radio-frequency-interaction Hamiltonian operator

$\mathcal{H}_{SL}$ electron spin-lattice Hamiltonian operator

$\mathcal{H}_{SS}$ electron dipole-dipole Hamiltonian operator

$\mathcal{H}_{SZ}$ electron Zeeman Hamiltonian operator

$\mathcal{H}_{IS}^{O}$ secular electron-nuclear dipole-dipole Hamiltonian operator

$\mathcal{H}_{SS}^{O}$ secular electron dipole-dipole Hamiltonian operator

$\mathcal{H}_{SS}^{m}(m=\pm1,\pm2)$ nonsecular electron dipole-dipole Hamiltonian operator

$$\mathcal{H}_{SS}^{OB} = \gamma_e^2 \sum_{k>l=1}^{N_e} r_{kl}^{-3} B_{kl}$$

H_O externally applied direct current magnetic field

H_1 amplitude of rotating radio-frequency magnetic field

$\hbar$ Planck's constant divided by 2π

I_x, I_y, I_z x-, y-, z-components of the nuclear spin operator, $\sum_j I_{rj}$ $(r=x,y,z)$

$I_j^{\pm} = I_{xj} \pm iI_{yj}$

I_{rj} rth component of the spin operator for the jth nuclei $(r=x,y,z)$

$i = \sqrt{-1}$

k Boltzmann's constant

M_2 second moment of the electron spin resonance line

N_e number of paramagnetic ions per unit volume

N_n number of nuclei per unit volume having spin one-half and gyromagnetic ratio γ_n

P parameter describing the numerator of E_{SS}, eq. (99b)

P' parameter describing the denominator of E_{SS}, eq. (99c)

$P'' = P - P'$

Q parameter defined in the expression for τ_{DNP}, eq. (100b)

$Q' = P' - Q$

R radius of the shell of influence, $\left(\frac{4\pi}{3} N_e\right)^{-1/3}$

$R = \frac{T_d}{T_e}$

$R(t)$ unitary operator, $e^{i\omega S_z t}$

$R_{k\ell}$ distance between the kth and ℓth nuclear spin

$r_{ij}, r_{k\ell}$ distance between the ith and jth or kth and ℓth electron

S_x, S_y, S_z x-, y-, z-components of the electron spin operator, $\sum_j S_{rj}$ $(r = x,y,z)$

$S_j^{\pm} = S_{xj} \pm iS_{yj}$

S_{rj} rth component of the spin operator for the jth electron

S^d saturation parameter, $W^d T_n$

S^O saturation parameter, $W^O T_e$

$S^{\pm}$ saturation parameter, $W^{\pm} T_n$

S_O^- value of saturation parameter at $\Delta = -\omega_n$ in figure 3

$S_m^{\pm} = W^{\pm} T_n^m$

$$\tilde{S}_{zi}^B(\tau) = e^{i\mathcal{H}_{SS}^{OB}\tau} S_{zi} e^{-i\mathcal{H}_{SS}^{OB}\tau}$$

$S^2 = S_x^2 + S_y^2 + S_z^2$

T_d spin-lattice relaxation time of electron dipole-dipole reservoir

T_e spin-lattice relaxation time of electron Zeeman reservoir

T_n spin-lattice relaxation time of nuclear Zeeman reservoir

T_{2e} electron spin-spin relaxation time

$T_{2e}^A = \frac{3}{2} T_{2e}$

$T_{2e}^B = 3\, T_{2e}$

T_{2n} nuclear spin-spin relaxation time

T_d^m measured electron dipole-dipole reservoir spin-lattice relaxation time

T_n^m measured nuclear spin-lattice relaxation time

T_n^L nuclear leakage relaxation time

T_n^z nuclear relaxation time by the paramagnetic impurity

T_{ez} electron Zeeman spin temperature

t time; primes with t indicate integrating parameters

$U(t)$ unitary operator, $e^{-i\mathcal{H}^O t}$

V perturbing Hamiltonian operator

v lattice volume

W^O electron spin resonance transition probability per unit time induced by an interaction with the applied radio-frequency field

W^d nuclear spin transition probability per unit time induced by the fluctuating z-component of the electron spins

$W^{\pm}$ solid effect transition probabilities per unit time induced by the applied radio-frequency field

x,y,z coordinates of spatial axes

α inverse temperature of the electron Zeeman reservoir

β inverse temperature of the nuclear Zeeman reservoir

β_B Bohr magneton

β_L inverse temperature of the lattice reservoir

γ inverse temperature of the electron dipole-dipole reservoir

γ_e electron gyromagnetic ratio, assumed isotropic

γ_n nuclear gyromagnetic ratio

$\Delta = \omega_e - \omega$

ϵ_l ϵ_{kl} in the shell-of-influence of the kth electron where the electron summation index k is suppressed

$$\epsilon_{kl} = -\frac{3}{2}\gamma_e\gamma_n\hbar^2 \sin\theta_{kl}\cos\theta_{kl}\, e^{-i\phi_{kl}}\, d_{kl}^{-3}$$

$$\epsilon_{kl}^{o} = \gamma_e\gamma_n\hbar^2 d_{kl}^{-3}\left(1 - 3\cos^2\theta_{kl}\right)$$

η normalization factor, Tr ρ

θ_{kl} polar angle coordinate associated with the vector $\vec{r}_{kl}$, the z-axis parallel to $\vec{H}_o$

$\nu = \frac{\omega}{2\pi}$

ρ density matrix

ρ^I density matrix in the interaction representation, $U^{-1}\rho^R U$

ρ^R density matrix in the rotating frame, $R(t)\rho(t)R^{-1}(t)$

τ_{DNP} dynamic nuclear polarization pump time

ϕ_{kl} azimuthal angle coordinate associated with the vector $\vec{r}_{kl}$, the z-axis parallel to $\vec{H}_O$

ω angular frequency of applied radio-frequency field

ω_e electron Larmor frequency, $-\gamma_e H_O$

$$\omega_L = \left[\frac{\mathrm{Tr}\left(\mathcal{H}_{SS}^{O}\right)^2}{\hbar^2 \mathrm{Tr}\, S_z^2}\right]^{1/2}$$

ω_n nuclear Larmor frequency, $-\gamma_n H_O$

$\omega_1 = -\gamma_e H_1$

Mathematical conventions:

$[A,B]$ indicates the commutator of the two operators A and B, AB - BA

An arrow $\rightarrow$ over a symbol indicates a vector quantity

Tr indicates the trace or sum of diagonal elements

A tilde $\sim$ over an operator A(t) indicates that $\tilde{A}(t) = e^{i\mathcal{H}_{SS}^{O}t} A e^{-i\mathcal{H}_{SS}^{O}t}$

$\langle A \rangle$ indicates a canonical ensemble average of the operator, A, Tr ρA

BASIC ASSUMPTIONS AND MODEL

Consider a paramagnetic system consisting of $N_e v$ paramagnetic ions (hereinafter to be called "electrons") each of gyromagnetic ratio γ_e, and $N_n v$ nuclei having gyromagnetic ratio γ_n, uniformly distributed in a dielectric, diamagnetic lattice of volume v (assumed to be a unit volume here). The Hamiltonian operator for this paramagnetic system, when placed in a homogeneous magnetic field which has a steady component $\vec{H}_O$ and a high-frequency component $\vec{H}_1(t)$, is given by

$$\mathcal{H} = \mathcal{H}_{SZ} + \mathcal{H}_{IZ} + \mathcal{H}_{SS} + \mathcal{H}_{II} + \mathcal{H}_{IS} + \mathcal{H}_{SL} + \mathcal{H}_{IL} + \mathcal{H}_{rf} \tag{1}$$

where the terms are the electron Zeeman, the nuclear Zeeman, the electron dipole-dipole, the nuclear dipole-dipole, the electron-nuclear dipole-dipole, the electron spin-lattice, the nuclear spin-lattice, and the radio-frequency interaction Hamiltonians. Explicitly, they are:

$$\mathcal{H}_{SZ} = -\gamma_e \hbar \sum_{j=1}^{N_e} \vec{S}_j \cdot \vec{H}_O \tag{2}$$

$$\mathcal{H}_{IZ} = -\gamma_n \hbar \sum_{l=1}^{N_n} \vec{I}_l \cdot \vec{H}_O \tag{3}$$

$$\mathcal{H}_{SS} = \gamma_e^2 \hbar^2 \sum_{i>j=1}^{N_e} r_{ij}^{-3} \left[\vec{S}_i \cdot \vec{S}_j - 3 r_{ij}^{-2} \left(\vec{S}_i \cdot \vec{r}_{ij} \right) \left(\vec{S}_j \cdot \vec{r}_{ij} \right) \right] \tag{4}$$

$$\mathcal{H}_{II} = \gamma_n^2 \hbar^2 \sum_{k>l=1}^{N_n} R_{kl}^{-3} \left[\vec{I}_k \cdot \vec{I}_l - 3 R_{kl}^{-2} \left(\vec{I}_k \cdot \vec{R}_{kl} \right) \left(\vec{I}_l \cdot \vec{R}_{kl} \right) \right] \tag{5}$$

$$\mathcal{H}_{IS} = \gamma_e \gamma_n \hbar^2 \sum_{k=1}^{N_e} \sum_{l=1}^{N_n} d_{kl}^{-3} \left[\vec{S}_k \cdot \vec{I}_l - 3 d_{kl}^{-2} \left(\vec{S}_k \cdot \vec{d}_{kl} \right) \left(\vec{I}_l \cdot \vec{d}_{kl} \right) \right] \tag{6}$$

$$\mathcal{H}_{rf} = -\gamma_e \hbar \sum_{k=1}^{N_e} \vec{H}_1(t) \cdot \vec{S}_k - \gamma_n \hbar \sum_{l=1}^{N_n} \vec{H}_1(t) \cdot \vec{I}_l \tag{7}$$

where $\vec{S}_j\left(\vec{I}_l\right)$ is the spin operator of the jth electron (lth nucleus); $\gamma_n(\gamma_e)$ is the nuclear (electron) gyromagnetic ratio; $\hbar$ is Planck's constant divided by 2π; $\vec{r}_{ij}$ is the vector distance between the ith and jth electron; $\vec{R}_{kl}$ is the vector distance between the kth and lth nuclear spin; $\vec{d}_{kl}$ is the vector distance between the kth electron and the lth nuclear spin; and $\vec{H}_1(t)$ is the high-frequency magnetic field interacting with the electrons and nuclei. The $\mathcal{H}_{SL}$ and $\mathcal{H}_{IL}$ terms are discussed in references 10 and 24. The calculations to follow will be for electrons having effective spin $\frac{1}{2}$ and nuclei having a spin $\frac{1}{2}$. A complete discussion of the concept of effective spin and effective spin Hamiltonians can be found in reference 25.

The following assumptions are now introduced:

(1) The magnetic field H_O is much larger than the magnetic field experienced by each dipole as a result of the effects of the neighboring dipoles. The latter field is called the local magnetic field.

(2) The magnitude of the electron gyromagnetic ratio γ_e is much larger than that of the nuclear gyromagnetic ratio γ_n, and the inequality $N_n >> N_e$ holds.

(3) The effective electronic gyromagnetic ratio γ_e is isotropic.

(4) The electron and nuclear spin-lattice relaxation times, T_e and T_n, respectively, are very long compared with the electron and nuclear spin-spin relaxation times, T_{2e} and T_{2n}, respectively, and there exist times t such that

$$T_{2e}, T_{2n} << t << T_e, T_n, T_d, (W^O)^{-1}, \left(\frac{N_n}{N_e} W^d\right)^{-1}, \left(\frac{N_n}{N_e} W^{\pm}\right)^{-1} \tag{8}$$

where T_d is the spin-lattice relaxation time of the electron dipole-dipole reservoir, W^O is the electron spin resonance transition probability per unit time induced by the interaction with the applied radio-frequency field, W^d is the nuclear spin transition probability per unit time induced by the fluctuating z-component of the electron spins, and $W^{\pm}$ are the solid effect transition probabilities per unit time induced by the applied radio-frequency field. These terms are discussed in subsequent sections.

(5) The effects of the lattice may be ignored for times t satisfying the inequality (8), and the rate of energy exchange between the various spin systems and the high-frequency magnetic field $\vec{H}_1(t)$ calculated. The effect of the lattice is then reintroduced.

(6) The electron and nuclear resonance lines are homogeneously broadened (refs. 16, 26 to 28).

(7) There is no phonon bottleneck (refs. 10, 13, 16, 19, 29, 30 and 31), i.e., the lattice heat capacity is assumed to be infinite.

(8) Additional assumptions will be introduced where appropriate.

Consider the large constant magnetic field $\vec{H}_O$ to be applied along the z-axis in the laboratory reference frame. Then

$$\mathcal{H}_{SZ} = -\gamma_e \hbar H_O \sum_{j=1}^{N_e} S_{zj} \tag{9}$$

and

$$\mathcal{H}_{IZ} = -\gamma_n \hbar H_O \sum_{l=1}^{N_n} I_{zl} \tag{10}$$

Define

$$\omega_e = -\gamma_e H_O \tag{11}$$

$$\omega_n = -\gamma_n H_O \tag{12}$$

$$S_z = \sum_{j=1}^{N_e} S_{zj} \tag{13}$$

$$I_z = \sum_{l=1}^{N_n} I_{zl} \tag{14}$$

where ω_e and ω_n are the electron and nuclear Larmor frequencies, and S_z and I_z are the z-components of the total electron and nuclear spins, respectively. Since $|\gamma_e| >> |\gamma_n|$, then $|\omega_e| >> |\omega_n|$; thus, if oscillating field $\vec{H}_1(t)$ has a frequency ω of the order of ω_e, then the direct interaction of the nuclear spins with this field is negligible.

This oscillating field is applied in a plane perpendicular to $\vec{H}_0$, so that equation (7) becomes

$$\mathcal{H}_{rf} = -\gamma_e \hbar H_1 \left(S_x \cos \omega t + S_y \sin \omega t \right)$$

where S_x and S_y are defined in a fashion similar to S_z in equation (13). Defining $\omega_1 = -\gamma_e H_1$ and noting the identity

$$e^{-i\omega S_z t} S_x e^{+i\omega S_z t} = S_x \cos \omega t + S_y \sin \omega t$$

yields

$$\mathcal{H}_{rf} = \hbar \omega_1 e^{-i\omega S_z t} S_x e^{+i\omega S_z t} \tag{15}$$

Using equations (9) to (15) with equation (1) gives

$$\mathcal{H}' = \omega_e S_z + \omega_n I_z + \mathcal{H}_{SS} + \mathcal{H}_{IS} + \mathcal{H}_{II} + \omega_1 e^{-i\omega S_z t} S_x e^{i\omega S_z t} \tag{16}$$

where the prime is used to indicate that the spin-lattice interactions have been omitted in accordance with assumption (5). Note that the Hamiltonian has been written in frequency units, that is, $\hbar = 1$.

The time evolution of the system described by the Hamiltonian can be determined from the equation of motion of the density matrix ρ for the system. The density matrix obeys the relation (ref. 32)

$$\frac{d\rho}{dt} = i\left[\rho, \mathcal{H}'\right] \tag{17}$$

again noting that $\hbar = 1$.

The density matrix may be transformed by the unitary operator $R(t)$ to become

$$\rho^R(t) = R(t)\rho(t)R^{-1}(t) \tag{18}$$

where $\rho^R(t)$ is the density matrix in the rotating frame and

$$R(t) = e^{i\omega S_z t} \tag{19}$$

This transformation corresponds to a transformation to a frame of reference rotating about the laboratory z-axis with frequency ω. Discussions of transformations to rotating frames can be found in references 20, 28, 33, and 34.

The equation of motion for the density matrix then becomes

$$\frac{d\rho^R}{dt} = i\left[\rho^R(t), \mathcal{H}^R(t)\right] \tag{20}$$

where

$$\mathcal{H}^R(t) = \Delta S_z + \omega_n I_z + \omega_1 S_x + R(t)\left(\mathcal{H}_{SS} + \mathcal{H}_{IS} + \mathcal{H}_{II}\right)R^{-1}(t)$$

and

$$\Delta = \omega_e - \omega \tag{21}$$

The operator $\mathcal{H}_{II}$ is not altered by the unitary transformation since

$$\left[R(t), \mathcal{H}_{II}\right] = 0 \tag{22}$$

The operators $\mathcal{H}_{SS}$ and $\mathcal{H}_{IS}$ are of the form

$$R(t)\mathcal{H}_{SS}R^{-1}(t) = \mathcal{H}_{SS}^{O} + \sum_{m} \mathcal{H}_{SS}^{m} \tag{23}$$

$$R(t)\mathcal{H}_{IS}R^{-1}(t) = \mathcal{H}_{IS}^{O} + \sum_{m} \mathcal{H}_{IS}^{m} \tag{24}$$

where the sums are over the values $m = \pm 1, \pm 2$. The operators $\mathcal{H}_{SS}^{O}$ and $\mathcal{H}_{IS}^{O}$ are the secular parts of the dipolar Hamiltonians, that is, those parts which commute with R(t):

$$\left[\mathcal{H}_{IS}^{O}, R(t)\right] = \left[\mathcal{H}_{SS}^{O}, R(t)\right] = 0 \tag{25}$$

and $\mathcal{H}_{SS}^{m}$ and $\mathcal{H}_{IS}^{m}$ are the nonsecular parts of the dipolar interactions. The nonsecular terms in equations (23) and (24) oscillate at frequencies $\pm\omega$, $\pm 2\omega$ in the rotating

reference frame and may be ignored. A complete discussion of the effects of these terms can be found in references 20, 28, and 33. Explicitly, the secular dipolar interactions can be found by carrying out the operation indicated by equation (25) with the result that, in the notation of appendix A,

$$\mathcal{H}_{SS}^{O} = \gamma_e^2 \sum_{k>l=1}^{N_e} r_{kl}^{-3} \left(A_{kl} + B_{kl}\right) \tag{26}$$

and

$$\mathcal{H}_{IS}^{O} = \sum_{k=1}^{N_e} \sum_{l=1}^{N_n} \left(\epsilon_{kl}^{o} S_{zk} I_{zl} + \epsilon_{kl} S_{zk} I_l^{+} + \epsilon_{kl}^{*} S_{zk} I_l^{-}\right) \tag{27}$$

where

$$\epsilon_{kl}^{o} = \gamma_e \gamma_n d_{kl}^{-3} \left(1 - 3 \cos^2 \theta_{kl}\right) \tag{28}$$

$$\epsilon_{kl} = -\frac{3}{2} \gamma_e \gamma_n \sin \theta_{kl} \cos \theta_{kl} e^{-i\phi_{kl}} d_{kl}^{-3} \tag{29}$$

and the star indicates complex conjugate. The Hamiltonian in the rotating frame is reduced to

$$\mathcal{H}^{R} = \Delta S_z + \omega_n I_z + \omega_1 S_x + \mathcal{H}_{SS}^{O} + \mathcal{H}_{IS}^{O} + \mathcal{H}_{II} \tag{30}$$

Now, define

$$\mathcal{H}_{O} = \Delta S_z + \omega_n I_z + \mathcal{H}_{SS}^{O} \tag{31}$$

and

$$V = \omega_1 S_x + \mathcal{H}_{IS}^{O} + \mathcal{H}_{II} \tag{32}$$

so that

$$\mathcal{H}^R = \mathcal{H}_0 + V \tag{33}$$

It is assumed that $\langle \mathcal{H}_0 \rangle >> \langle V \rangle$ so that V may be treated as a perturbation. Transforming to an interaction representation by the unitary transformation

$$\rho^I(t) = U^{-1}(t)\, \rho^R(t)\, U(t) \tag{34}$$

where

$$U(t) = e^{-i\mathcal{H}_0 t} \tag{35}$$

results in

$$\frac{d\rho^I}{dt} = i\left[\rho^I, V^I(t)\right] \tag{36}$$

where

$$V^I(t) = U^{-1}(t) V\, U(t) \tag{37}$$

Equation (36) may be integrated and then iterated to obtain the form

$$\rho^I(t) = \rho^I(0) + \sum_{n=1}^{\infty} (i)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \times \left[\left[\left[\cdots \left[\rho^I(0), V^I(t_n)\right], V^I(t_{n-1})\right], \cdots\right], V^I(t_1)\right] \tag{38}$$

and this result may be differentiated to obtain

$$\frac{d\rho^I}{dt} = i\left[\rho^I(0), V^I(t)\right] + \sum_{n=1}^{\infty} (i)^{n+1} \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \times \left[\left[\left[\cdots \left[\rho^I(0), V^I(t_n)\right], V^I(t_{n-1})\right], \cdots\right], V^I(t)\right] \tag{39}$$

Note that $\rho^I(0) = \rho^R$.

The basis of the spin-temperature theory is to assume at this point that the density matrix in the rotating frame will have the canonical form for times t satisfying equation (8). This means that, for the assumptions made thus far, a temperature can be assigned to each of the constants of the motion, and these temperatures will represent the canonical distribution achieved by each of the commuting terms in $\mathcal{H}_O$ for the times t of equation (8). Thus

$$\rho^R(t) = \frac{\exp\left[-\alpha(t)\Delta S_z - \beta(t)\omega_n I_z - \gamma(t)\mathcal{H}_{SS}^O\right]}{\mathrm{Tr}\left\{\exp\left[-\alpha(t)\Delta S_z - \beta(t)\omega_n I_z - \gamma(t)\mathcal{H}_{SS}^O\right]\right\}} \tag{40}$$

The inverse temperature α is defined as

$$\alpha = \frac{1}{kT_{ez}}$$

where k is the Boltzmann constant and T_{ez} is the electron Zeeman spin temperature. The inverse temperatures β and γ are similarly defined.

The physical model utilized by the spin-temperature theory of DNP and nuclear spin-lattice relaxation is that the electron Zeeman, nuclear Zeeman, and secular electron dipole-dipole systems in the rotating frame, corresponding to the terms ΔS_z, $\omega_n I_z$, and $\mathcal{H}_{SS}^O$ in equation (40), will realize a canonical distribution in a time of the order of the electron and nuclear spin-spin relaxation times. Therefore, these systems can be treated as thermodynamic reservoirs having thermodynamic parameters such as temperature and heat capacity. These reservoirs exchange energy with each other through the perturbing terms of V. This mixing is realized if the operators represented by the reservoirs do not commute with perturbing terms. For times t indicated in equation (8), the rate of exchange of energy between the various spin reservoirs is calculated by using the density matrix approach. This will result in a time evolution of the temperatures of the spin reservoirs. The effect of the lattice reservoir on the evolution of the spin temperature is then included. A pictorial representation of the reservoirs considered and the various energy exchange processes is given in figure 1. The heat capacity of the lattice reservoir is assumed to be infinite in comparison with the heat capacities of the spin reservoirs. When this situation is not realized, a phonon bottleneck may occur. The effect of the phonon bottleneck phenomenon on the DNP and nuclear relaxation processes is treated elsewhere (refs. 10, 13, 16, 19, 29, 30, and 31).

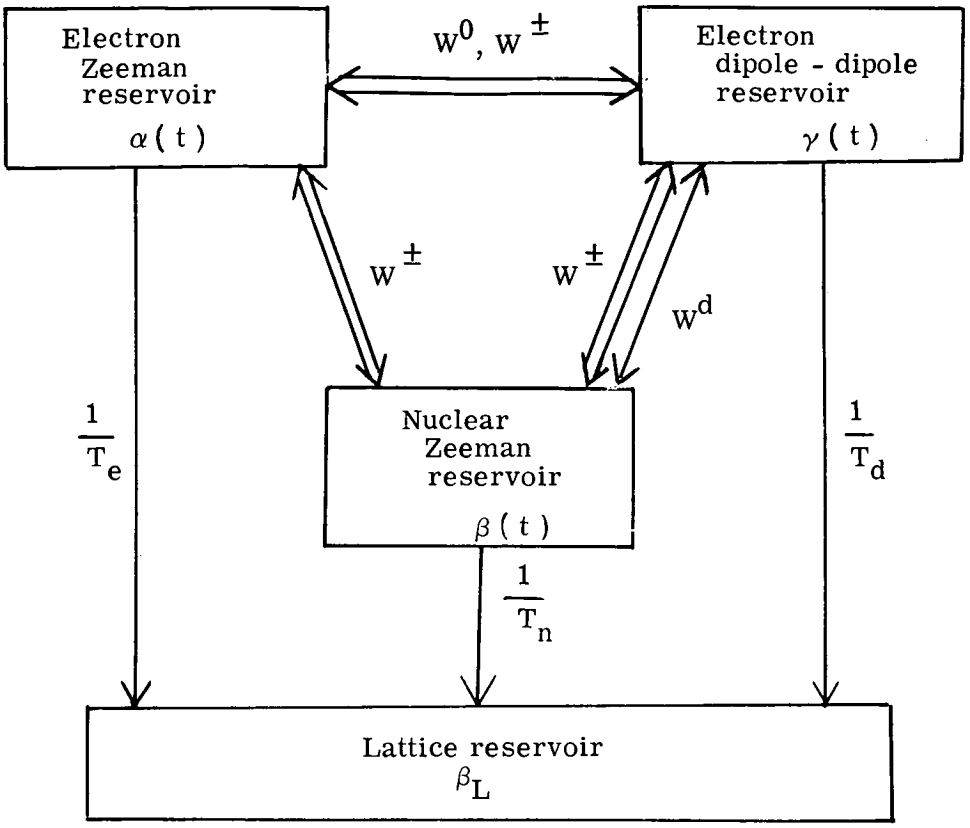


Figure 1.- Schematic representation of the thermodynamic reservoirs and interactions governing dynamic nuclear polarization and nuclear spin-lattice relaxation.

The electron-nuclear dipole-dipole reservoir and the nuclear dipole-dipole reservoir, as well as the off-diagonal part of the density matrix, have been ignored in equation (40). The electron-nuclear dipole-dipole reservoir (that is, the $S_{zk}I_{zl}$ term in equation (27)) contributes to the inhomogeneous broadening of the electron spin-resonance line and is assumed to be negligible (ref. 26). This term also gives rise to a barrier to spin diffusion, and this barrier is treated phenomenologically when spin diffusion is taken into account. The off-diagonal $S_{zk}I_l^{\pm}$ terms in $\mathcal{H}_{IS}^{O}$ are retained in V as a perturbation. The nuclear dipole-dipole interaction may be ignored since its energy (typically $\sim 5 \times 10^{-29}$ J) is very small in comparison with those of the electron Zeeman, nuclear Zeeman, and electron dipole-dipole interactions in the rotating frame (typically $\sim 5 \times 10^{-27}$ J). This term is important only when spin diffusion is taken into account. The perturbation $V(t)$ reduces to

$$V^I(t) = \omega_1 S_x(t) + \mathcal{H}_{IS}^{O}(t) = \omega_1 S_x(t) + \sum_{k=1}^{N_e} \sum_{l=1}^{N_n} \left(\epsilon_{kl} S_{zk} I_l^+ + \epsilon_{kl}^* S_{zk} I_l^- \right)$$

The size of the contribution made by the off-diagonal part of the density matrix is discussed by Goldman (ref. 20), and for the time scale considered here, the off-diagonal part may be ignored. The validity of the assumption of a canonical form has been shown (ref. 35) to be correct within the conditions assumed here. Experimental evidence has been published (refs. 20, 33, 36 to 40) verifying the assumption of a canonical form for the density matrix for nuclear and electron spin systems. With these approximations,

$$\rho^{I}(t) = \rho^{R}(t)$$

The representation used for the electron system is one in which $\mathcal{H}_{SS}^{O}$, S^2, and S_z are diagonal. Since the nuclear dipole-dipole interaction has been neglected, the nuclei are considered independent particles, and the representation used is one in which all the single particle operators I_l^2 and I_{zl} are diagonal.

The high temperature approximation is assumed to hold for this calculation, that is,

$$\left|\langle\alpha(t)\Delta S_z\rangle\right|, \left|\langle\beta(t)\omega_n I_z\rangle\right|, \left|\langle\gamma(t)\mathcal{H}_{SS}^{O}\rangle\right| << 1$$

Then,

$$\rho^{R}(t) = \eta^{-1}\left\{1 - \alpha(t)\Delta S_z - \beta(t)\omega_n I_z - \gamma(t)\mathcal{H}_{SS}^{O}\right\} \tag{41}$$

where η is the normalizing factor.

Note that the electron and nuclear magnetizations along the z-axis are proportional to the ensemble averages of the operators S_z and I_z, respectively. Using the density matrix, these values are found as

$$\langle S_z\rangle = \mathrm{Tr}\ \rho^{R}(t)S_z$$

and

$$\langle I_z\rangle = \mathrm{Tr}\ \rho^{R}(t)I_z$$

where $\langle\ \rangle$ indicates the canonical ensemble average value and Tr indicates a sum over the diagonal elements in a space that includes both the electron and nuclear eigenstates. It follows that the time rate of change of these expectation values are (in the high temperature limit)

$$\frac{d\langle S_z\rangle}{dt} = \mathrm{Tr}\,\frac{d\rho^R(t)}{dt}\,S_z = -\Delta\eta^{-1}\,\mathrm{Tr}\,S_z^2\,\frac{d\alpha}{dt} \tag{42}$$

and

$$\frac{d\langle I_z\rangle}{dt} = \mathrm{Tr}\,\frac{d\rho^R(t)}{dt}\,I_z = -\omega_n\eta^{-1}\,\mathrm{Tr}\,I_z^2\,\frac{d\beta}{dt} \tag{43}$$

Equations (42) and (43) indicate that the changes in the magnetization are proportional to the changes of the corresponding inverse temperatures of the reservoirs. The calculation of the time evolution of the inverse spin temperatures are derived in the next section.

TIME EVOLUTION OF INVERSE SPIN TEMPERATURES

Derivation of Equation of Motion for Electron Zeeman Inverse Spin Temperature $\alpha(t)$

The time evolution of the electron Zeeman inverse temperature $\alpha(t)$ is determined by combining equations (39) and (42); that is,

$$\begin{aligned}
-\left(\Delta\,\mathrm{Tr}\,S_z^2\right)\frac{d\alpha}{dt} = {} & i\,\eta\,\mathrm{Tr}\left[\rho^R, V(t)\right]S_z + (i)^2\,\eta\,\mathrm{Tr}\int_0^t dt'\left[\left[\rho^R, V(t')\right], V(t)\right]S_z \\
& + (i)^3\,\eta\,\mathrm{Tr}\int_0^t dt'\int_0^{t'} dt''\left[\left[\left[\rho^R, V(t'')\right], V(t')\right], V(t)\right]S_z \\
& + (i)^4\,\eta\,\mathrm{Tr}\int_0^t dt'\int_0^t dt''\int_0^{t''} dt''' \\
& \times\left[\left[\left[\left[\rho^R, V(t''')\right], V(t'')\right], V(t')\right], V(t)\right]S_z + \ldots
\end{aligned} \tag{44}$$

where the superscript I, indicating the interaction representation, has been dropped and $\rho^R = \rho^R(0)$. (Henceforth, a time-dependent operator will be explicitly stated.) On the assumption that the trace and the time integrals commute, the following terms must be evaluated:

$$
\left.
\begin{aligned}
C_1 &\equiv \eta \, \mathrm{Tr} \left[\rho^R, V(t)\right] S_z \\
C_2 &\equiv \eta \, \mathrm{Tr} \left[\left[\rho^R, V(t')\right], V(t)\right] S_z \\
C_3 &\equiv \eta \, \mathrm{Tr} \left[\left[\left[\rho^R, V(t'')\right], V(t')\right], V(t)\right] S_z \\
C_4 &\equiv \eta \, \mathrm{Tr} \left[\left[\left[\left[\rho^R, V(t''')\right], V(t'')\right], V(t')\right], V(t)\right] S_z \\
&\;\;\vdots
\end{aligned}
\right\} \tag{45}
$$

Using the identity

$$
\mathrm{Tr}\left[A, B\right] C = \mathrm{Tr}\, A\left[B, C\right] \tag{46}
$$

yields

$$
C_1 = \eta \, \mathrm{Tr}\left[S_z, \rho^R\right] V(t) = 0 \tag{47}
$$

since

$$
\left[S_z, \rho^R\right] = 0
$$

Using the same identity allows C_2 to be rewritten as

$$
C_2 = \eta \, \mathrm{Tr} \left\{\left[\rho^R, V(t')\right]\right\} \left\{\left[V(t), S_z\right]\right\} \tag{48}
$$

The density matrix $\rho^R(t)$ can be written in the following way

$$
\rho^R = \eta^{-1} \left\{1 - (\alpha - \gamma)\, \Delta S_z - (\beta - \gamma)\, \omega_n I_z - \gamma \mathcal{H}_O\right\} \tag{49}
$$

Inasmuch as

$$
V(t) = \omega_1 S_x(t) + \mathcal{H}_{IS}^{O}(t)
$$

where $S_{x,y}(t)$ and $\mathcal{H}_{IS}^{O}(t)$ are in the interaction representation, C_2 becomes

$$C_2 = -\omega_1^2 \Delta(\alpha - \gamma)\ \mathrm{Tr}\ S_y(t')\ S_y(t)$$

$$+ i\ \omega_1 \omega_n\ (\beta - \gamma)\ \mathrm{Tr}\ S_y(t) \left[I_z, \mathcal{H}_{IS}^{O}(t')\right]$$

$$+ i\ \gamma \omega_1 \mathrm{Tr}\ S_y(t) \left[\mathcal{H}_O, V(t')\right] \tag{50}$$

The second term is zero as can easily be seen by using equation (46) and noting that

$$\left[S_y(t), I_z\right] = 0$$

Using the fact that

$$i\ \mathrm{Tr}\ S_y(t) \left[\mathcal{H}_O, V(t)\right] = \frac{d}{dt'}\ \mathrm{Tr}\ S_y(t - t')\ V$$

and integrating C_2 as noted in equation (44) yields

$$\int_0^t dt' C_2 = -\omega_1^2 \Delta(\alpha - \gamma) \int_0^t dt'\ \mathrm{Tr}\ S_y S_y(t - t')$$

$$+ \gamma \omega_1 \int_0^t dt' \frac{d}{dt'}\ \mathrm{Tr}\ S_y(t - t')\ V \tag{51}$$

The second term in equation (51) is also zero. This result is shown by letting $\tau = t - t'$; then

$$\int_0^t dt' \frac{d}{dt'}\ \mathrm{Tr} \left\{S_y(t - t')V\right\} = -\int_0^t d\tau \left\{\frac{d}{d\tau}\ \mathrm{Tr}\left[\omega_1 S_x S_y(\tau) + S_y(\tau) \mathcal{H}_{IS}^{O}\right]\right\} \tag{52}$$

But

$$\mathrm{Tr}\ S_y(\tau) \mathcal{H}_{IS}^{O} = \mathrm{Tr}\ S_y(\tau) \left[\sum_{k=1}^{N_e} \sum_{l=1}^{N_n} \left(\epsilon_{kl} S_{zk} I_l^{+} + \epsilon_{kl}^{*} S_{zk} I_l^{-}\right)\right] = 0 \tag{53}$$

since $I_l^{\pm}$ has no diagonal elements. The $S_{zk}I_{zl}$ terms in $\mathcal{H}_{IS}^{O}$ have been previously dropped but the result shown in equation (53) would not be changed if they had been included. Note the identity

$$S_y(\tau) = -\tilde{S}_x(\tau) \sin \Delta\tau + \tilde{S}_y(\tau) \cos \Delta\tau \tag{54}$$

where

$$\tilde{S}_{x,y}(\tau) = e^{i\mathcal{H}_{SS}^{O}\tau} S_{x,y} e^{-i\mathcal{H}_{SS}^{O}\tau} \tag{55}$$

The remaining term in equation (52) then becomes

$$-\omega_1 \int_0^t d\tau \frac{d}{d\tau} \left[\text{Tr } S_x S_y(\tau)\right] = -\omega_1 \int_0^t d\tau \frac{d}{d\tau} \left[\text{Tr } S_x \tilde{S}_y(\tau) \cos \Delta\tau - \text{Tr } S_x \tilde{S}_x(\tau) \sin \Delta\tau\right]$$

But

$$\text{Tr } S_x \tilde{S}_y(\tau) = 0$$

since a rotation of π about the y-axis sends S_x into $-S_x$ and leaves $\tilde{S}_y(\tau)$ unchanged. Since the trace is invariant the result follows. Then

$$-\omega_1 \int_0^t d\tau \frac{d}{d\tau} \left[\text{Tr } S_x S_y(\tau)\right] = \omega_1 \int_0^t d\tau \frac{d}{d\tau} \text{Tr } S_x \tilde{S}_x(\tau) \sin \Delta\tau$$

The term $\text{Tr } S_x \tilde{S}_x(\tau)$ is proportional to the correlation function of the transverse magnetization, with a correlation time $\approx T_{2e}$. Since t is assumed to be very much larger than T_{2e}, the upper limit of the integration may be taken to infinity; thus,

$$-\omega_1 \int_0^{\infty} d\tau \frac{d}{d\tau} \left[\text{Tr } S_x S_y(\tau)\right] = \omega_1 \left[\text{Tr } S_x \tilde{S}_x(\tau) \sin \Delta\tau\right]\Big|_{\tau=0}^{\tau=\infty} = 0$$

since the correlation function is zero at $\tau = \infty$. Equation (51) is reduced to

$$\int_0^t dt' \, C_2 = -\omega_1^2 \Delta(\alpha - \gamma) \int_0^{\infty} dt' \, \text{Tr } S_y S_y(t - t')$$

If the same arguments that were previously used are applied,

$$\int_0^t dt' \, C_2 = -\omega_1^2 \Delta(\alpha - \gamma) \int_0^\infty d\tau \, \mathrm{Tr} \, S_y \tilde{S}_y(\tau) \cos \Delta\tau \tag{56}$$

Equation (56) will be further discussed after C_3 and C_4 are deduced. The parameter C_3 may be calculated by using some of the relations developed in finding C_2. Expanding C_3 and performing the obvious commutation relations results in

$$\begin{aligned} C_3 = & -\omega_1^2 \Delta(\alpha - \gamma) \, \mathrm{Tr} \, S_y(t'') \left[\mathcal{H}_{IS}^O(t'), S_y(t) \right] \\ & + i\omega_n \omega_1^2 (\beta - \gamma) \, \mathrm{Tr} \left[I_z, \mathcal{H}_{IS}^O(t'') \right] \left[S_x(t'), S_y(t) \right] \\ & + i\omega_1 \omega_n (\beta - \gamma) \, \mathrm{Tr} \left[I_z, \mathcal{H}_{IS}^O(t'') \right] \left[\mathcal{H}_{IS}^O(t'), S_y(t) \right] \\ & + i\gamma\omega_1 \, \mathrm{Tr} \left[\mathcal{H}_O, V(t'') \right] \left[V(t'), S_y(t) \right] + 0\left(\omega_1^3\right) \end{aligned} \tag{57}$$

The first term in equation (57) can be written as

$$\mathrm{Tr} \, S_y(t'') \left[\mathcal{H}_{IS}^O(t'), S_y(t) \right] = \mathrm{Tr} \left[S_y(t), S_y(t'') \right] \mathcal{H}_{IS}^O(t')$$

This term is zero for the same reason that equation (53) was zero. The second term in equation (57) can be written as

$$\mathrm{Tr} \left[I_z, \mathcal{H}_{IS}^O(t'') \right] \left[S_x(t'), S_y(t) \right] = \mathrm{Tr} \left[\left[S_x(t'), S_y(t) \right], I_z \right] \mathcal{H}_{IS}^O(t'') = 0$$

since

$$\left[\left[S_x(t'), S_y(t) \right], I_z \right] = 0$$

The third term in equation (57) is easily seen to be zero by applying the unitary operator $e^{i\pi S_z}$ to the argument of the trace. Since S_z commutes with I_z and $\mathcal{H}_{IS}^O(t)$, the rotation sends $S_y(t)$ into $-S_y(t)$ with the result that

$$\mathrm{Tr}\left[I_z, \mathcal{H}_{IS}^{O}(t'')\right]\left[\mathcal{H}_{IS}^{O}(t'), S_y(t)\right] = -\mathrm{Tr}\left[I_z, \mathcal{H}_{IS}^{O}(t'')\right]\left[\mathcal{H}_{IS}^{O}(t'), S_y(t)\right] = 0 \tag{58}$$

The fourth term in equation (57) when integrated over t'' becomes

$$\begin{aligned} i\gamma\omega_1 \int dt'' \ \mathrm{Tr}\left[\mathcal{H}_O, V(t'')\right]\left[V(t'), S_y(t)\right] &= \gamma\omega_1 \ \mathrm{Tr}\left(V(t') - V(0)\right)\left[V(t'), S_y(t)\right] \\ &= \gamma\omega_1 \ \mathrm{Tr}\left[V(t'), V(t')\right] S_y(t) \\ &\quad -\gamma\omega_1 \ \mathrm{Tr}\ V(t')\left[S_y(t), V\right] \end{aligned} \tag{59}$$

The first term in this equation is obviously zero, and the second term can be expanded to give

$$\begin{aligned} \omega_1 \ \mathrm{Tr}\ V(t')\left[S_y(t), V\right] &= \omega_1^2 \ \mathrm{Tr}\left\{\left[S_y(t), S_x\right]\mathcal{H}_{IS}^{O}(t') + \left[S_x(t'), S_y(t)\right]\mathcal{H}_{IS}^{O}\right\} \\ &\quad + \omega_1 \ \mathrm{Tr}\ S_y(t)\left[\mathcal{H}_{IS}^{O}, \mathcal{H}_{IS}^{O}(t')\right] + 0\left(\omega_1^3\right) \end{aligned}$$

The first term on the right-hand side is zero for the same reason that equation (53) was zero, and the second term is zero when the previous argument leading to equation (58) is used. Therefore, to order of ω_1^3, $C_3 = 0$.

The parameter C_4 can be evaluated by using arguments identical with those used in evaluating C_1, C_2, and C_3, along with the condition that the terms of the order of ω_1^3 and ϵ^3 and higher are neglected. The result is

$$\begin{aligned} C_4 = &-\Delta\omega_1^2(\alpha - \gamma)\ \mathrm{Tr}\left[S_y(t'''), \mathcal{H}_{IS}^{O}(t'')\right]\left[\mathcal{H}_{IS}^{O}(t'), S_y(t)\right] \\ &+ i\omega_n\omega_1^2(\beta - \gamma)\left\{\mathrm{Tr}\left[\left[I_z, \mathcal{H}_{IS}^{O}(t''')\right], S_x(t'')\right]\left[\mathcal{H}_{IS}^{O}(t'), S_y(t)\right]\right. \\ &\left. + \mathrm{Tr}\left[\left[I_z, \mathcal{H}_{IS}^{O}(t''')\right], \mathcal{H}_{IS}^{O}(t'')\right]\left[S_x(t'), S_y(t)\right]\right\} \end{aligned} \tag{60}$$

It is now assumed that each nuclear spin interacts with only one electron. For dilute systems, this approximation is an excellent one. Thus, the sample is broken up into N_e equivalent "shells-of-influence," each containing one electron and N_n/N_e nuclei. In

this approximation,

$$\mathcal{H}_{IS}^{O} = S_z \sum_{j=1}^{N_n/N_e} \epsilon_j I_j^+ + S_z \sum_{j=1}^{N_n/N_e} \epsilon_j^* I_j^- \tag{61}$$

where the summation is over one shell of influence, and ϵ_j corresponds to the jth proton referenced to an electron at the center of the shell. Integrating C_4 as indicated in equation (44) yields

$$\int C_4 dt = -\Delta\omega_1^2(\alpha - \gamma)\,\mathrm{Tr} \sum_{j=1}^{N_n/N_e} \left|\epsilon_j\right|^2 I_j^+ I_j^- \int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt'''$$

$$\times S_x(t''')\, S_x(t) \left[e^{i\omega_n(t''-t')} + e^{-i\omega_n(t''-t')}\right]$$

$$+ i\omega_n\omega_1^2(\beta - \gamma)\,\mathrm{Tr} \sum_{j=1}^{N_n/N_e} \left|\epsilon_j\right|^2 I_j^+ I_j^- \int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt'''$$

$$\times S_y(t'')\, S_x(t) \left[e^{i\omega_n(t'''-t')} - e^{-i\omega_n(t'''-t')}\right] \tag{62}$$

Equation (62) can be integrated as carried out in appendix B. If it is assumed that $\left|\epsilon_j\right|^2$ may be replaced by an average over the shell-of-influence of the electron, that is, an ϵ^2 such that

$$\epsilon^2 = \frac{N_e}{N_n} \sum_{j=1}^{N_n/N_e} \left|\epsilon_j\right|^2 \tag{63}$$

then,

$$\int C_4 dt = -\Delta(\alpha - \gamma) \frac{N_n}{N_e} \frac{2\epsilon^2}{\omega_n^2} W^O(\Delta) \left(\mathrm{Tr}\, S_z^2\right)$$

$$+ \Delta(\alpha - \gamma) \frac{N_n}{N_e} \left[W^-\left(\omega_n - \Delta\right) + W^+\left(\omega_n + \Delta\right)\right] \mathrm{Tr}\, S_z^2$$

$$- \omega_n(\beta - \gamma) \frac{N_n}{N_e} \left[W^-\left(\omega_n - \Delta\right) - W^+\left(\omega_n + \Delta\right)\right] \mathrm{Tr}\, S_z^2 \tag{64}$$

where

$$W^O(\Delta) = \pi\omega_1^2\, g(\Delta) \tag{65}$$

$$W^{\pm}\left(\omega_n \pm \Delta\right) = \pi\left(\epsilon^2/\omega_n^2\right)\omega_1^2\, g\left(\omega_n \pm \Delta\right) \tag{66}$$

The electron spin resonance absorption line shape function $g(\omega)$ is defined as

$$g(\omega) = \frac{\mathrm{Tr} \int_0^\infty d\tau\, \tilde{S}_x(\tau)\, S_x \cos \omega\tau}{\pi\, \mathrm{Tr}\, S_z^2} \tag{67}$$

and normalized so that

$$\int_{-\infty}^{\infty} d\omega\, g(\omega) = 1 \tag{68}$$

Since S_x commutes with neither the A nor the B terms in $\mathcal{H}_{SS}^O$ (see eq. (26) and appendix A), $\tilde{S}_x(\tau)$ and thus $g(\omega)$ depend on both the A and B terms, as discussed in reference 28. The relation (see appendix C)

$$\frac{\mathrm{Tr}\, I_j^+ I_j^- \int_0^\infty d\tau\, \tilde{S}_x(\tau)\, S_x \cos \omega\tau}{\mathrm{Tr}\, S_z^2} = \frac{1}{2} \frac{\mathrm{Tr} \int_0^\infty d\tau\, \tilde{S}_x(\tau)\, S_x \cos \omega\tau}{\mathrm{Tr}\, S_z^2}$$

was used to obtain equation (64) from equation (62). The W^O and $W^{\pm}$ are the transition probabilities per unit time associated with the allowed electron spin-resonance transition and with the solid-effect transitions, respectively. Terms higher than C_4 are of order $\frac{\epsilon^3}{\omega_n^3}$, $\frac{\omega_1^3}{\omega_n^3}$, $\frac{\epsilon^3}{\Delta^3}$, $\frac{\omega_1^3}{\Delta^3}$, and higher, and are therefore neglected.

Combining equation (44) with equations (56) and (64) to (68) leads to

$$\frac{d\alpha}{dt} = -\left(1 - \frac{N_n}{N_e}\frac{2\epsilon^2}{\omega_n^2}\right) W^O(\Delta)(\alpha - \gamma)$$

$$+ \frac{N_n}{N_e}\frac{1}{\Delta} W^-(\omega_n - \Delta)\left[\omega_n\beta - \Delta\alpha - (\omega_n - \Delta)\gamma\right]$$

$$- \frac{N_n}{N_e}\frac{1}{\Delta} W^+(\omega_n + \Delta)\left[\omega_n\beta + \Delta\alpha - (\omega_n + \Delta)\gamma\right] \qquad (69)$$

where $\frac{N_n}{N_e}\frac{2\epsilon^2}{\omega_n^2}$ is a correction factor to the allowed transition probability per unit time due to the C_4 term in the perturbation expansion. It is essentially the wavefunction renormalization factor given by Jeffries (ref. 13) and Borghini (ref. 31). Because this factor is often negligible in comparison with unity, it is omitted hereinafter. The terms α, β, and γ in equation (69) are rigorously $\alpha(0)$, $\beta(0)$, and $\gamma(0)$. For times t satisfying equation (8), they are approximately equal to $\alpha(t)$, $\beta(t)$, and $\gamma(t)$, respectively, and this approximation is used in subsequent calculations herein.

Derivation of Equation of Motion for Nuclear Zeeman Inverse Spin Temperature $\beta(t)$

The derivation of the equation of motion for $\beta(t)$ is similar to the derivation of the equation of motion for $\alpha(t)$. Start with equations (39) and (43):

$$-\omega_n\left(\mathrm{Tr}\, I_z^2\right)\frac{d\beta}{dt} = i\eta\, \mathrm{Tr}\left[\rho^R, V(t)\right] I_z + (i)^2\eta\, \mathrm{Tr}\int_0^t dt' \left[\left[\rho^R, V(t')\right], V(t)\right] I_z$$

$$+ (i)^3\eta\, \mathrm{Tr}\int_0^t dt' \int_0^{t'} dt'' \left[\left[\left[\rho^R, V(t'')\right], V(t')\right], V(t)\right] I_z$$

$$+ (i)^4\eta\, \mathrm{Tr}\int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt'''$$

$$\times \left[\left[\left[\left[\rho^R, V(t''')\right], V(t'')\right], V(t')\right], V(t)\right] I_z + \ldots \qquad (70)$$

Traces analogous to the values of C of equation (45) may be defined; thus,

$$\left.\begin{aligned} C_1' &= \eta\, \mathrm{Tr}\left[\rho^R, V(t)\right] I_z \\ C_2' &= \eta\, \mathrm{Tr}\left[\left[\rho^R, V(t')\right], V(t)\right] I_z \\ C_3' &= \eta\, \mathrm{Tr}\left[\left[\left[\rho^R, V(t'')\right], V(t')\right], V(t)\right] I_z \\ C_4' &= \eta\, \mathrm{Tr}\left[\left[\left[\left[\rho^R, V(t''')\right], V(t'')\right], V(t')\right], V(t)\right] I_z \\ &\vdots \end{aligned}\right\} \qquad (71)$$

Both C_1' and C_3' are easily shown to be zero. Evaluating C_2' yields

$$C_2' = \eta\, \mathrm{Tr}\left[\rho^R, V(t')\right]\left[V(t), I_z\right]$$

$$= -(\beta - \gamma)\,\omega_n\, \mathrm{Tr}\left[I_z, \mathcal{H}_{IS}^O(t')\right]\left[\mathcal{H}_{IS}^O(t), I_z\right]$$

where the other terms are zero.

Using equation (27), carrying out the commutation relations, and integrating C_2' as indicated in equation (70), gives

$$\int_0^t dt'\, C_2' = -\omega_n(\beta - \gamma)\, \mathrm{Tr} \sum_{i,k=1}^{N_e} \sum_{j=1}^{N_n} \epsilon_{ij}\epsilon_{kj}^*\, I_j^+ I_j^- \int_{-t}^{t} d\tau\, S_{zi}\tilde{S}_{zk}(\tau)\, e^{-i\omega_n\tau}$$

The product $S_{zi}\tilde{S}_{zk}(\tau)$ is related to the correlation function for the z-component of the individual electron spins, which involves a correlation time of the order of T_{2e}. The limits on the integral may then be taken as infinity. This expression reduces to

$$\int dt'\, C_2' = -\omega_n(\beta - \gamma) \left(\mathrm{Tr}\, I_z^2\right) W^d \tag{72}$$

where

$$W^d = \frac{1}{2}\frac{N_e}{N_n} \frac{\mathrm{Tr} \sum_{j=1}^{N_n} \sum_{i>k=1}^{N_e} \epsilon_{ij}\epsilon_{kj}^* \int_{-\infty}^{\infty} d\tau\, S_{zi}\tilde{S}_{zk}(\tau)\, e^{-i\omega_n\tau}}{\mathrm{Tr}\, S_z^2} \tag{73}$$

In the shell-of-influence model, only $i = k$ terms contribute significantly to equation (73), and

$$W^d = \frac{\epsilon^2}{2} \frac{\mathrm{Tr} \sum_{i=1}^{N_e} \int_{-\infty}^{\infty} d\tau\, S_{zi}\tilde{S}_{zi}(\tau)\, e^{-i\omega_n\tau}}{\mathrm{Tr}\, S_z^2} \tag{74a}$$

where ϵ^2 is defined in equation (63). A tempting approximation is

$$\mathrm{Tr} \sum_{i=1}^{N_e} \int_{-\infty}^{\infty} d\tau\, S_{zi}\tilde{S}_{zi}(\tau)\, e^{-i\omega_n\tau} \cong \mathrm{Tr} \int_{-\infty}^{\infty} d\tau\, S_x\tilde{S}_x(\tau)\, e^{-i\omega_n\tau}$$

in which case W^d becomes (by using equation (67))

$$W^d \cong \pi\epsilon^2 g(\omega_n) \tag{74b}$$

The significance of this term for DNP and nuclear relaxation is discussed below.

The validity of the approximation made in the previous paragraph may be checked by recalling that $g(\omega)$ depends on both the A and B terms in $\mathcal{H}_{SS}^{O}$. (See equations (26) and (67) and appendix A.) Abragam (ref. 28) shows that the second moment M_2 of a resonance line is $(3/2)^2$ larger when both the A and B terms are used, as compared with the case where only the A terms are involved in the M_2 calculation. If the line width $\Delta\omega$ is taken to be $(M_2)^{1/2}$, the A(B) terms are found to contribute the proportions $\frac{2}{3}\left(\frac{1}{3}\right)$ to $\Delta\omega$. Now $\left(T_{2e}\right)^{-1}$ is proportional to $\Delta\omega$. Let T_{2e}^{A} and T_{2e}^{B} be the contributions to T_{2e} from the A and B terms in $\mathcal{H}_{SS}^{O}$. Then

$$\Delta\omega \propto \frac{1}{T_{2e}} = \frac{1}{T_{2e}^{A}} + \frac{1}{T_{2e}^{B}}$$

Abragam's result shows that

$$\frac{1}{T_{2e}^{A}} = \frac{2}{3}\frac{1}{T_{2e}}$$

$$\frac{1}{T_{2e}^{B}} = \frac{1}{3}\frac{1}{T_{2e}}$$

In equations (73) and (74a), the S_{zi} operators commute with the A terms in $\mathcal{H}_{SS}^{O}$ but not with the B terms. Hence, W^d can be written as

$$W^d = \pi\epsilon^2 g_B(\omega_n)$$

where

$$g_B(\omega_n) = \frac{\mathrm{Tr}\sum_{i=1}^{N_e}\int_{-\infty}^{\infty} d\tau\, S_{zi}\tilde{S}_{zi}^{B}(\tau)\, e^{-i\omega_n\tau}}{2\pi\ \mathrm{Tr}\ S_z^2}$$

$$\tilde{S}^{B}_{zi}(\tau) = e^{i\mathcal{H}^{OB}_{SS}\tau} S_{zi} e^{-i\mathcal{H}^{OB}_{SS}\tau}$$

$$\mathcal{H}^{OB}_{SS} = \gamma_e^2 \sum_{k>l=1}^{N_e} r_{kl}^{-3} B_{kl}$$

and B_{kl} is given in appendix A. Thus, $g_B(\omega_n)$ is related to the correlation time T^B_{2e}. For Lorentzians, (ref. 28)

$$g(\omega) = \frac{(T_{2e}/\pi)}{1 + (T_{2e}\omega)^2}$$

$$g_B(\omega) = \frac{(T^B_{2e}/\pi)}{1 + (T^B_{2e}\omega)^2}$$

Since $T^B_{2e} \cong 3T_{2e}$, $g(\omega)$ and $g_B(\omega)$ are noted to be the same to within a factor ≈ 3, and thus equation (74b) is correct to within a factor ≈ 3.

The C'_4 is found by using the same arguments used to obtain equation (60); thus

$$C'_4 = -i\omega_1^2 \Delta(\alpha - \gamma)\, \mathrm{Tr} \left\{ \left[\left[S_y(t'''), S_x(t'') \right], \mathcal{H}^O_{IS}(t') \right] \left[\mathcal{H}^O_{IS}(t), I_z \right] \right.$$
$$\left. + \left[\left[S_y(t'''), \mathcal{H}^O_{IS}(t'') \right], S_x(t') \right] \left[\mathcal{H}^O_{IS}(t), I_z \right] \right\}$$
$$- \omega_n \omega_1^2 (\beta - \gamma)\, \mathrm{Tr} \left[\left[\left[I_z, \mathcal{H}^O_{IS}(t''') \right], S_x(t'') \right], S_x(t') \right] \left[\mathcal{H}^O_{IS}(t), I_z \right]$$

Making the same assumptions which led to equation (61) and integrating C'_4 as indicated by equation (70) yields

$$\int dt\, C_4' = i\Delta(\alpha - \gamma)\omega_1^2\, Tr \sum_{j=1}^{N_n/N_e} \left|\epsilon_j\right|^2 I_j^+ I_j^- \int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt'''$$

$$\times S_x(t''')S_y(t')\left(e^{i\omega_n(t''-t)} - e^{-i\omega_n(t''-t)}\right)$$

$$- \omega_n(\beta - \gamma)\omega_1^2\, Tr \sum_{j=1}^{N_n/N_e} \left|\epsilon_j\right|^2 I_j^+ I_j^- \int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt'''$$

$$\times S_y(t'')S_y(t')\left(e^{i\omega_n(t'''-t)} + e^{-i\omega_n(t'''-t)}\right) \tag{75}$$

When the integration indicated in appendix B is made and equations (63), (66), and (67) are used, equation (75) becomes

$$\int dt\, C_4' = -\Delta\left(Tr\, I_z^2\right)(W^- - W^+)(\alpha - \gamma) + \omega_n\left(Tr\, I_z^2\right)(W^- + W^+)(\beta - \gamma) \tag{76}$$

Combining equations (72) and (76) with equation (70) yields

$$\frac{d\beta}{dt} = -W^d(\beta - \gamma) - \frac{1}{\omega_n} W^-\left(\omega_n - \Delta\right)\left\{\omega_n\beta - \Delta\alpha - \left(\omega_n - \Delta\right)\gamma\right\}$$

$$- \frac{1}{\omega_n} W^+\left(\omega_n + \Delta\right)\left\{\omega_n\beta + \Delta\alpha - \left(\omega_n + \Delta\right)\gamma\right\} \tag{77}$$

Derivation of the Equation of Motion for the Electron Dipole-Dipole Inverse Temperature $\gamma(t)$

The derivation of the equation of motion for the electron dipole-dipole inverse temperature $\gamma(t)$ can be accomplished by using the fact that energy is conserved in the rotating reference frame for times t satisfying equation (8), provided that

$$\left\langle \mathcal{H}_0 \right\rangle \gg \left\langle V \right\rangle$$

where $\mathcal{H}_0$ and V are defined in equations (31) and (32), respectively. Then

$$\frac{d\langle \mathcal{H}_O \rangle}{dt} = 0 = \mathrm{Tr}\left(\Delta S_z + \omega_n I_z + \mathcal{H}_{SS}^O\right)\frac{\partial \rho^R}{\partial t}$$

so that

$$+\Delta^2\left(\mathrm{Tr}\, S_z^2\right)\frac{d\alpha}{dt} + \omega_n^2\left(\mathrm{Tr}\, I_z^2\right)\frac{d\beta}{dt} + \mathrm{Tr}\left(\mathcal{H}_{SS}^O\right)^2\frac{d\gamma}{dt} = 0 \tag{78}$$

Substituting equations (69) and (77) into (78) and using $\frac{\mathrm{Tr}\, I_z^2}{\mathrm{Tr}\, S_z^2} = \frac{N_n}{N_e}$ yields

$$\frac{d\gamma}{dt} = +\frac{N_n}{N_e}\frac{\omega_n^2}{\omega_L^2}W^d(\beta - \gamma) + \frac{\Delta^2}{\omega_L^2}W^O(\Delta)(\alpha - \gamma)$$

$$+\frac{N_n}{N_e}\frac{(\omega_n - \Delta)}{\omega_L^2}W^-(\omega_n - \Delta)\left\{\omega_n\beta - \Delta\alpha - (\omega_n - \Delta)\gamma\right\}$$

$$+\frac{N_n}{N_e}\frac{(\omega_n + \Delta)}{\omega_L^2}W^+(\omega_n + \Delta)\left\{\omega_n\beta + \Delta\alpha - (\omega_n + \Delta)\gamma\right\} \tag{79}$$

where

$$\omega_L^2 = \frac{\mathrm{Tr}\left(\mathcal{H}_{SS}^O\right)^2}{\hbar^2\, \mathrm{Tr}\, S_z^2}$$

The term ω_L^2 is related to the line width of the electron spin resonance line. It is found to be (refs. 19 and 28)

$$\omega_L^2 = \frac{1}{3}M_2$$

where M_2 is the second moment of the electron spin resonance line.

Effects of the Lattice Reservoir

The effect of the lattice vibrations (phonons) is introduced by assuming that each spin-lattice relaxation process takes place exponentially with a characteristic spin-lattice relaxation time, and that these processes may be added to the equations of evolution for α, β, and γ (refs. 10, 19, 20, 28, and 41). Thus, equations (69), (77), and (79) become

$$\frac{d\alpha}{dt} = - W^{O}(\Delta)(\alpha - \gamma) + \frac{N_n}{N_e}\frac{1}{\Delta} W^{-}(\omega_n - \Delta)\left\{\omega_n\beta - \Delta\alpha - (\omega_n - \Delta)\gamma\right\}$$

$$- \frac{N_n}{N_e}\frac{1}{\Delta} W^{+}(\omega_n + \Delta)\left\{\omega_n\beta + \Delta\alpha - (\omega_n + \Delta)\gamma\right\} - \frac{1}{T_e}\left(\alpha - \frac{\omega_e}{\Delta}\beta_L\right) \tag{80a}$$

$$\frac{d\beta}{dt} = -W^{d}(\beta - \gamma) - \frac{1}{\omega_n} W^{-}(\omega_n - \Delta)\left\{\omega_n\beta - \Delta\alpha - (\omega_n - \Delta)\gamma\right\}$$

$$- \frac{1}{\omega_n} W^{+}(\omega_n + \Delta)\left\{\omega_n\beta + \Delta\alpha - (\omega_n + \Delta)\gamma\right\} - \frac{1}{T_n}(\beta - \beta_L) \tag{80b}$$

$$\frac{d\gamma}{dt} = \frac{\Delta^2}{\omega_L^2} W^{O}(\Delta)(\alpha - \gamma) + \frac{N_n}{N_e}\frac{\omega_n^2}{\omega_L^2} W^{d}(\beta - \gamma)$$

$$+ \frac{N_n}{N_e}\frac{(\omega_n - \Delta)}{\omega_L^2} W^{-}(\omega_n - \Delta)\left\{\omega_n\beta - \Delta\alpha - (\omega_n - \Delta)\gamma\right\}$$

$$+ \frac{N_n}{N_e}\frac{(\omega_n + \Delta)}{\omega_L^2} W^{+}(\omega_n + \Delta)\left\{\omega_n\beta + \Delta\alpha - (\omega_n + \Delta)\gamma\right\} - \frac{1}{T_d}(\gamma - \beta_L) \tag{80c}$$

where T_e, T_n, and T_d are the spin-lattice relaxation times of the electron Zeeman (EZR), nuclear Zeeman (NZR), and electron dipole-dipole reservoirs (EDDR), respectively, and β_L is the inverse temperature of the lattice. Note that the electron-Zeeman inverse temperature does not approach the inverse lattice temperature, but the "colder" temperature $\frac{\omega_e}{\Delta}\beta_L$. This effect is a result of the transformation to the rotating frame which affects the electron Zeeman interaction, but does not affect the nuclear Zeeman and the secular electron dipole-dipole interactions.

Nuclear Spin Diffusion

The nuclear dipole-dipole interaction $\mathcal{H}_{II}$ was ignored in the derivation of equations (80). This interaction becomes significant if $N_e << N_n$, for there may be large regions in the solid where the electron-nuclear dipole-dipole interaction is very small compared with the nuclear dipole-dipole interaction. The nuclear magnetization in these regions will be spatially transported by energy conserving transitions resulting from the terms $I_j^{\pm} I_k^{\mp}$ of $\mathcal{H}_{II}$. This process is called nuclear spin diffusion. Only a brief discussion of spin diffusion in the rapid diffusion limit will be given here. More elaborate discussions of spin diffusion are given elsewhere (refs. 2, 20, 28, 42 to 50).

For dilute samples each electron can be considered to interact directly only with the nuclei within its shell-of-influence having an outer radius R defined by

$$R = \left(\frac{4\pi}{3} N_e\right)^{-1/3} \tag{81}$$

where N_e is the number of paramagnetic ions per unit volume. An important parameter is the pseudopotential radius b, which is the distance from the electron at which a nucleus has approximately the same probability of being relaxed to the lattice by the electron as of being flipped by the $\mathcal{H}_{II}$ terms due to neighboring nuclei, and is given by (ref. 44)

$$b = 0.68\left(\frac{C}{D}\right)^{1/4} \tag{82a}$$

The term C is

$$C = \frac{3}{10}\left(\gamma_e \gamma_n \hbar\right)^2 \frac{T_e}{1 + \omega_n^2 T_e^2} \tag{82b}$$

and D is the diffusion constant given approximately by (ref. 45)

$$D = \frac{1}{10} \frac{a^2}{T_{2n}} \tag{83}$$

Here a is the average distance between nuclei and T_{2n} is the nuclear spin-spin relaxation time. This idea is now extended to the W^d processes, and a second pseudopotential radius b' is defined by

$$b' = 0.68\left(\frac{C'}{D}\right)^{1/4} \tag{84a}$$

where

$$C' = \frac{3}{10}\left(\gamma_e \gamma_n \hbar\right)^2 \frac{T_{2e}}{1 + \omega_n^2 T_{2e}^2} \tag{84b}$$

A Lorentzian form is thus assumed for equation (74b). Another important parameter in spin-diffusion theory is the diffusion barrier radius d, which is defined as the distance from the paramagnetic ion at which the magnetic field at the site of the nuclear spin due to the ion is equal to the nuclear line width (ref. 20), and given very approximately as

$$d = a\left(\frac{\gamma_e}{\gamma_n}\right)^{1/3} \tag{85}$$

Nuclear spin diffusion is assumed negligible for $r \leqq d$, so that d is the inner radius of the shell-of-influence. Finally, the diffusion length $(DT_n)^{1/2}$, which is the distance spin energy diffuses in a time $t = T_n$, is used.

The regime of "rapid diffusion" is defined when the following relation holds (refs. 44 and 47):

$$a, b, b' \ll d \ll R \ll (DT_n)^{1/2} \tag{86}$$

The physical picture is that within the region $d \leqq r \leqq R$, the relaxation and radio-frequency transitions tend to drive the nuclear Zeeman inverse temperature to a steady-state value, and at the same time the spin diffusion mechanism attempts to keep the total nuclear magnetization spatially homogeneous.

In the rapid diffusion limit and the shell-of-influence approximation, ϵ^2, defined in equation (63), is an angular and radial average of $|\epsilon_j|^2$ over the shell-of-influence ($d \leqq r \leqq R$) which ignores the crystal structure. One finds (refs. 10 to 13, 19, 29, 47, 48, and 51)

$$\epsilon^2 = \frac{3}{10}\frac{\left(\gamma_e \gamma_n \hbar\right)^2}{d^3 R^3} \tag{87}$$

so that T_n is given by

$$\frac{1}{T_n} = \frac{1}{T_n^z} + \frac{1}{T_n^L} \tag{88a}$$

where the first term $\left(1/T_n^z\right)$ is due to nuclear relaxation by the desired paramagnetic impurity and can be expressed as

$$\frac{1}{T_n^z} = \frac{\epsilon^2 T_e}{1 + \left(\omega_n T_e\right)^2} \tag{88b}$$

The second term $\left(1/T_n^L\right)$ in equation (88a) is nuclear leakage relaxation by other impurities and by other modes of spin-lattice interaction. The expressions given by equations (87) and (88) are the appropriate expressions to be used in equations (66), (74), and all three equations (80), where β is to be understood as an average value over the shell-of-influence.

Nuclear Spin-Lattice Relaxation

The measured nuclear spin-lattice relaxation rate $\left(T_n^m\right)^{-1}$ has yet to be determined. In the absence of any radio frequency fields, equation (80b) reduces to

$$\frac{d\beta}{dt} = -W^d(\beta - \gamma) - \left(\frac{1}{T_n}\right)(\beta - \beta_L) \tag{89a}$$

where

$$W^d = \frac{\epsilon^2 T_{2e}}{1 + \left(\omega_n T_{2e}\right)^2} \tag{89b}$$

Physically, equation (89a) states that energy in the nuclear Zeeman reservoir can be transferred to the electron dipole-dipole reservoir through the W^d interaction as well as to the lattice reservoir at the rate $1/T_n$ through processes described by equations (88). Therefore, the time evolution of γ must also be taken into account. From equation (80c) for no applied radio frequency fields

$$\frac{d\gamma}{dt} = -\left(\frac{N_n}{N_e}\frac{\omega_n^2}{\omega_L^2}\right)W^d(\gamma - \beta) - \frac{1}{T_d}\left(\gamma - \beta_L\right) \tag{90}$$

The general solution for β exhibits two time constants. There are several limiting cases for which the longer time constant can be easily evaluated; this time constant will be the measured nuclear spin-lattice relaxation time T_n^m. One limit is $W^d << (1/T_n)$, in which case

$$T_n^m = T_n \tag{91}$$

A second limit is the situation in which $(1/T_d) >> (1/T_n)$ and $\left(N_n\omega_n^2/N_e\omega_L^2\right) >> 1$. In this case γ comes to quasiequilibrium $\left(\text{i.e., } \frac{d\gamma}{dt} \approx 0\right)$ in times t such that

$$T_d, \left(\frac{N_e\omega_L^2}{N_n\omega_n^2}\right)\left(W^d\right)^{-1} << t << \left(W^d\right)^{-1}, T_n \tag{92}$$

Thus, equation (90) may be solved for γ, which is then substituted into equation (89a). The latter can be rewritten as

$$\frac{d\beta}{dt} = -\frac{1}{T_n^m}\left(\beta - \beta_L\right) \tag{93}$$

where

$$\frac{1}{T_n^m} = \frac{1}{T_n} + \frac{W^d}{1 + \frac{N_n\omega_n^2}{N_e\omega_L^2} W^d T_d} \tag{94}$$

If $\left(N_n\omega_n^2/N_e\omega_L^2\right) W^d T_d << 1$, equation (94) becomes

$$\frac{1}{T_n^m} = \frac{1}{T_n} + W^d \tag{95}$$

On the other hand, if $\left(N_n\omega_n^2/N_e\omega_L^2\right) W^d T_d >> 1$, the result is

$$\frac{1}{T_n^m} = \frac{1}{T_n} + \frac{N_e\omega_L^2}{N_n\omega_n^2}\frac{1}{T_d} \tag{96}$$

Combining equations (88a) and (94) yields

$$\frac{1}{T_n^m} = \frac{1}{T_n^z} + \frac{1}{T_n^L} + \frac{W^d}{1 + \frac{N_n\omega_n^2}{N_e\omega_L^2} W^d T_d} \tag{97}$$

The last term on the right side of equations (94) to (97) is a result of the coupling of the nuclear spins with the electron dipole-dipole reservoir. (See refs. 52 and 53.)

It should be noted that T_d is often taken to be $\frac{1}{2} T_e$ (refs. 16 to 20). Experimental results given in reference 54 have shown that, for the system studied, the measured EDDR spin-lattice relaxation time T_d^m was of the order of T_n^m and about two orders of magnitude longer than T_e. Often it is found that $T_d^m = T_d$; however, for the limit $\left(N_n\omega_n^2/N_e\omega_L^2\right)W^d >> (1/T_d)$, equations (89a) and (90) show that γ comes into quasi-equilibrium with β with the shorter time constant approximately equal to $\left(\left(N_n\omega_n^2/N_e\omega_L^2\right)W^d\right)^{-1}$, and that β and γ relax together to the lattice with the longer time constant $T_d^m \approx T_n^m$, where T_n^m is given in equation (96). Thus, the electron dipole-dipole reservoir must be included in order to account properly for the nuclear spin-lattice relaxation rate.

THEORETICAL DYNAMIC NUCLEAR POLARIZATION RESULTS

As was assumed previously, the electron Zeeman and electron dipole-dipole reservoirs are assumed to come to quasiequilibrium $\left[(d\alpha/dt) \approx 0 \approx (d\gamma/dt)\right]$ in times $t << T_n^m$, so that equations (80a) and (80c) may be solved for α and γ, and substituted into equation (80b), with all terms retained. This solution is valid provided that $(1/T_e)$, $(1/T_d) >> (1/T_n)$, $W^O >> W^{\pm}$, and $N_n/N_e >> 1$. After a tedious calculation, the dynamic nuclear polarization enhancement $E \equiv (\beta/\beta_L)$ can be written as

$$\frac{dE(t)}{dt} = \frac{-1}{\tau_{DNP}} \left[E(t) - E_{SS}\right] \tag{98}$$

where τ_{DNP} is called the DNP pump time and the sample average, steady-state enhancement E_{SS} is

$$E_{SS} = \frac{P}{P'} \tag{99a}$$

where

$$P = 1 + S^d(1 + f_d C_n) + S^O(1 + C_\Delta R)$$

$$+ S^+\left[-\frac{\omega_e}{\omega_n} + \frac{\omega_n + \Delta}{\omega_n} + f_e + f_d C_+\right]$$

$$+ S^-\left[\frac{\omega_e}{\omega_n} + \frac{\omega_n - \Delta}{\omega_n} + f_e + f_d C_-\right]$$

$$+ \left[S^O(S^d + S^+ + S^-) + f_e(S^+ + S^-)S^d\right]\left[\frac{\omega_e}{\omega_n}\frac{\omega_n \Delta}{\omega_L^2} R + 1 + f_d C_n\right] \qquad (99b)$$

and

$$P' = 1 + S^d(1 + f_d C_n) + S^O(1 + C_\Delta R)$$

$$+ S^+(1 + f_e + f_d C_+)$$

$$+ S^-(1 + f_e + f_d C_-)$$

$$+ \left[S^O(S^d + S^+ + S^-) + f_e(S^+ + S^-)S^d\right]\left[C_\Delta R + 1 + f_d C_n\right] \qquad (99c)$$

Use is made of the saturation parameters $S^d \equiv W^d T_n$, $S^O \equiv W^O T_e$, $S^\pm \equiv W^\pm T_n$; the relative heat-capacity ratios $C_n \equiv \omega_n^2/\omega_L^2$, $C_\Delta \equiv \Delta^2/\omega_L^2$, $C_\pm \equiv (\omega_n \pm \Delta)^2/\omega_L^2$; the DNP leakage factors $f_e = N_n T_e / N_e T_n$, $f_d = f_e R$; and the electron relaxation ratio $R \equiv T_d / T_e$. Negligible $S^\pm S^\mp$ terms are omitted in equations (99b) and (99c) and in equations (100b), (101b), and (102b) that follow. The DNP pump time τ_{DNP} is

$$\frac{1}{\tau_{DNP}} = \frac{1}{T_n}\frac{P'}{Q} \qquad (100a)$$

where

$$Q = 1 + S^{d}\left(f_{d}C_{n}\right) + S^{O}\left(1 + C_{\Delta}R\right)$$

$$+ S^{+}(f_{e} + f_{d}C_{+}) + S^{-}(f_{e} + f_{d}C_{-})$$

$$+ \left[S^{O}(S^{d} + S^{+} + S^{-}) + f_{e}(S^{+} + S^{-})S^{d}\right] f_{d}C_{n} \qquad (100b)$$

and P' is given by equation (99c).

Alternative forms for E_{SS} and τ_{DNP} are easily derived from these equations. E_{SS} can be rewritten as

$$E_{SS} = 1 + \frac{P''}{P'} \qquad (101a)$$

where

$$P'' = (S^{-} - S^{+})\frac{\omega}{\omega_{n}}$$

$$+ \left[S^{O}(S^{d} + S^{+} + S^{-}) + f_{e}(S^{+} + S^{-})S^{d}\right] \frac{\omega}{\omega_{n}} \frac{\omega_{n}\Delta}{\omega_{L}^{2}} R \qquad (101b)$$

and P' is given by equation (99c). When $\omega_{e} >> \omega_{n}$, ω_{L}, as is usually the case, ω in equation (101b) can be replaced to excellent approximation by ω_{e}. Note that $E_{SS} = 1$ when $S^{O} = 0 = S^{+} = S^{-}$, as expected. The $\left[S^{-} - S^{+}\right]$ term in equation (101b) is DNP by the traditional solid effect (SE), discussed in references 10 to 14, 19, 20, 29, 31, and 44, and in the special Case 1 that follows. The remaining terms in equation (101b) are DNP through EDDR processes, and are discussed in a subsequent section. The DNP pump time τ_{DNP} can be rewritten as

$$\frac{1}{\tau_{DNP}} = \frac{1}{T_{n}}\left[1 + \frac{Q'}{Q}\right] \qquad (102a)$$

where

$$Q' = \left[S^{d} + S^{+} + S^{-}\right]$$

$$+ \left[S^{O}(S^{d} + S^{+} + S^{-}) + f_{e}(S^{+} + S^{-})S^{d}\right]\left[C_{\Delta}R + 1\right] \qquad (102b)$$

and Q is given by equation (100b). It is easy to see that τ_{DNP} reduces to the T_n^m expression in equation (94) when $S^o = 0 = S^+ = S^-$.

Equations (98) to (102) give complete expressions for DNP and are not to be found in the previous literature. It should be noted that the nuclear spin-lattice relaxation time T_n used in S^d, $S^{\pm}$, f_e, and f_d, is not necessarily the measured nuclear relaxation time T_n^m. The times T_n and T_n^m are the same in the rapid diffusion limit only when the effect of the electron dipole-dipole reservoir is negligible, that is, $W^d \approx 0$.

The wave function renormalization factor $\left(2N_n\epsilon^2/N_e\omega_n^2\right)$ has been dropped from the W^o term in equation (69). This factor would also appear in other terms if the calculation were to be carried to higher order. This factor is now estimated for the materials yttrium ethylsulphate (YES) and lanthanum magnesium nitrate (LMN), which are often doped with paramagnetic impurities and used in DNP experiments. (See refs. 10 to 14, 16 to 19, 29, 30, 31, and 51 for details and the values used below.) Using equations (12), (81), and (87), and the relation $g_e\beta_B = \gamma_e\hbar$, where g_e is the electron g-factor and β_B is the Bohr magneton, one shows that

$$\frac{2N_n\epsilon^2}{N_e\omega_n^2} = \frac{4\pi}{5}\frac{N_n}{d^3}\left[\frac{g_e\beta_B}{H_o}\right]^2 \tag{103}$$

or

$$\frac{2N_n\epsilon^2}{N_e\omega_n^2} = \frac{2K}{d^3}\left[\frac{g_e}{H_o}\right]^2 \tag{104}$$

where $K = 6.06 \times 10^{-18}$ and 8.56×10^{-18} CGS units for YES and LMN, respectively. The smallest possible value is assumed for d, namely the distance from the electron to the nearest nucleus [$d = 0.31$ nm (for YES), 0.436 nm (for LMN), for protons]. It is then easy to calculate $\left(2N_n\epsilon^2/N_e\omega_n^2\right)$ for any case of interest, and, in particular, to find that

$$\frac{2N_n\epsilon^2}{N_e\omega_n^2} < 0.18 \tag{105}$$

for YES and LMN <u>if</u> $g_e \leqq 2$ <u>and</u> $H_o > 2.39 \times 10^5$ A/m (3000 Oe). Finally, note that $2N_n\epsilon^2/N_e\omega_n^2 = 2f_e$ in the limit $\left(\omega_n T_e\right)^2 >> 1$ and $\left(T_n^Z/T_n^L\right) << 1$. (See equations (87) and (88).)

Now the results just given are discussed for the limit of well-resolved solid-effect transitions ($\omega_n >> \omega_L$), in which no more than one of the three transition probabilities W^O, $W^{\pm}$ may be nonzero for a given value of Δ. Three cases are considered: (1) $(\omega_n \pm \Delta) = 0$, (2) $\Delta \approx 0$, and (3) $(\omega_n \pm \Delta) \approx 0$. Other limits, such as the important case of unresolved $(\omega_n \lessapprox \omega_L)$ solid-effect transitions, have been discussed extensively in the literature (refs. 16 to 23) and are mentioned only briefly herein.

Case 1: $\omega_n \pm \Delta = 0$

For Case 1, look first at the DNP exactly at the peak of the solid-effect transitions $W^{\pm}$; that is, $\omega_n \pm \Delta = 0$. Then, $W^{\mp} = 0 = W^O$. It is useful to write equation (94) in the form

$$\frac{1}{T_n^m} = \frac{1}{T_n}\left[\frac{1 + S^d(1 + f_d C_n)}{1 + S^d f_d C_n}\right] \tag{106}$$

For this case, equation (99) becomes

$$E_{SS} = \frac{1 + S^d\left[1 + f_d C_n\right] + S^{\pm}\left[\left(\mp \frac{\omega_e}{\omega_n}\right) + f_e\right] + f_e S^{\pm} S^d\left[\left(\frac{\omega_e}{\omega_n}\right)\left(\frac{\mp \omega_n^2}{\omega_L^2}\right) R + 1 + f_d C_n\right]}{1 + S^d\left[1 + f_d C_n\right] + S^{\pm}\left[1 + f_e\right] + f_e S^{\pm} S^d\left[C_n R + 1 + f_d C_n\right]}$$

This equation can be rewritten by dividing the numerator and denominator by $\left[1 + S^d(1 + f_d C_n)\right]$ and by rearranging terms using equation (106), the definitions $S_m^{\pm} \equiv W^{\pm} T_n^m = S^{\pm}\left(T_n^m / T_n\right)$ and $f_e^m \equiv f_e\left(T_n / T_n^m\right)$, and the relation $f_e S^{\pm} = f_e^m S_m^{\pm}$. Then,

$$E_{SS} = \frac{1 + S_m^{\pm}\left[\mp \frac{\omega_e}{\omega_n} + f_e^m\right]}{1 + S_m^{\pm}\left[1 + f_e^m\right]} \tag{107}$$

For the usual limit $(\omega_e / \omega_n) >> 1$, this equation can be expressed as

$$E_{SS} = 1 + \frac{S_m^{\pm}\left[\mp \frac{\omega_e}{\omega_n}\right]}{1 + S_m^{\pm}\left[1 + f_e^m\right]} \tag{108}$$

Similarly,

$$\frac{1}{\tau_{DNP}} = \frac{1}{T_n^m}\left[\frac{1 + S_m^{\pm}\left(1 + f_e^m\right)}{1 + S_m^{\pm} f_e^m}\right] \tag{109}$$

or

$$\frac{1}{\tau_{DNP}} = \frac{1}{T_n^m}\left[1 + \frac{S_m^{\pm}}{1 + S_m^{\pm} f_e^m}\right] \tag{110}$$

These equations for the pure solid effect agree with references 10 to 13, 19, 29, and 31, but include the important EDDR contributions to T_n^m and thus f_e^m that these references did not include.

In the limit of saturating microwave power $\left(S_m^{\pm} >> 1\right)$, the DNP enhancement E_{SS} becomes

$$E_{SS} = 1 + \left[\frac{\left(\mp \frac{\omega_e}{\omega_n}\right)}{1 + f_e^m}\right] \tag{111}$$

and the ideal solid-effect enhancement E_i is attained in the limit of negligible DNP leakage $\left(f_e^m << 1\right)$:

$$E_{SS} = E_i = \left(\mp \frac{\omega_e}{\omega_n}\right) \tag{112}$$

In equation (112), the $1 \ll \left(\omega_e/\omega_n\right)$ is dropped. Equation (112) is true only in the high-temperature limit, since, in general (see references 11, 13, and 19),

$$E_i = \mp \frac{\tanh\left(\hbar\omega_e/2kT\right)}{\tanh\left(\hbar\omega_n/2kT\right)} \tag{113}$$

The DNP leakage factor f_e^m reduces E_{SS} from E_i, as in equation (111). Finally, note that τ_{DNP} approaches $T_n^m\left[f_e^m/\left(1 + f_e^m\right)\right]$ at $S_m^{\pm}$, $S_m^{\pm} f_e^m >> 1$, and reduces to T_n^m at $S_m^{\pm} = 0$.

This limit ($\omega_n \pm \Delta = 0$) of DNP by the solid effect has been discussed theoretically (refs. 10 to 14, 19, 20, and 31) and has been observed experimentally (refs. 10 to 12, 29, and 51), and is the case for which the results of the rate-equation approach (refs. 10 to 14)

coincide with the results of the spin-temperature theory (refs. 15 to 23), except that the latter provides an additional nuclear relaxation mechanism through the electron dipole-dipole reservoir.

Case 2: $\Delta \approx 0$

For Case 2, we look at DNP near the main ESR line ($\Delta \approx 0$), and still assume that $\omega_n >> \omega_L$. Thus, $W^O \neq 0$ but $W^+ = 0 = W^-$. If it is assumed that $(\omega_e/\omega_n) >> 1$, equations (99c) and (101) become

$$E_{SS} = 1 + \frac{S^O S^d \left[\left(\frac{\omega_e}{\omega_n}\right)\left(\frac{\omega_n \Delta}{\omega_L^2}\right) R\right]}{1 + S^d\left(1 + f_d C_n\right) + S^O\left(1 + C_\Delta R\right) + S^O S^d\left(C_\Delta R + 1 + f_d C_n\right)} \tag{114}$$

If S^d is negligible, E_{SS} approaches unity. On the other hand, when $S^d >> 1$, the result at strong ESR saturation ($S^O >> 1$) is found to be

$$E_{SS} = \left(\frac{\omega_e}{\omega_n}\right) \frac{\omega_n \Delta}{\Delta^2 + \left(T_e/T_d\right) \omega_L^2 + f_e \omega_n^2} \tag{115}$$

which has peak values E_{SS}^{peak} of

$$E_{SS}^{peak} = \left(\pm \frac{\omega_e}{\omega_n}\right) \frac{\omega_n}{2\left[\left(T_e/T_d\right) \omega_L^2 + f_e \omega_n^2\right]^{1/2}} \tag{116a}$$

at

$$\Delta = \pm \left[\left(T_e/T_d\right) \omega_L^2 + f_e \omega_n^2\right]^{1/2} \tag{116b}$$

If $\left(T_e/T_d\right) \omega_L^2 >> f_e \omega_n^2$, which may not be easy to satisfy when $\omega_n >> \omega_L$, and if $\left(T_e/T_d\right) = 2$, then

$$E_{SS}^{peak} = \pm E_i \frac{\omega_n}{2\sqrt{2}\omega_L} >> E_i \tag{117}$$

This effect has been discussed previously (refs. 16 to 20) for unresolved ($\omega_n \ll \omega_L$) and partially resolved ($\omega_n \approx \omega_L$) solid-effect transitions, but it appears to be relevant for the well-resolved case ($\omega_n \gg \omega_L$) when $S^d \gg 1$. The basic idea is that the S^O transitions cool EDDR, and that the nuclei (NZR) are then cooled by the S^d transitions connecting these two reservoirs.

A set of parametric curves obtained by using equation (114) with $R = (T_d/T_e) = 1$, with a Gaussian line shape function for the electron spin resonance (ESR) transition W^O and with the parameters in table I, is shown in figure 2. The effect of a nonzero value

TABLE I.- PARAMETRIC VALUES USED IN CALCULATING CURVES IN FIGURES 2 AND 3

[The values given are typical of values found for samarium doped into lanthanum magnesium nitrate at X-band.]

Parameter	Value
ω_e	$2\pi \cdot 9100$ MHz
ω_n	$2\pi \cdot 37$ MHz
ω_L^2	$(2\pi)^2 \cdot 18.8$ MHz^2

for S^d on the enhancement E_{SS} can easily be seen in figure 2. It has not previously been observed experimentally or predicted theoretically for the limit of well-resolved solid-effect transitions. It should be pointed out that strong coupling between the nuclear Zeeman reservoir and the electron dipole-dipole reservoir, indicated by the size of the term S^d, can be very effective in polarizing the nuclei. For example, the curve indicated by $\left(S^d, S_O^O, f_d\right) = (10, 1, 0)$ has a peak enhancement larger than the ideal enhancement, which in this case is 246, and for values of $\left(S^d, S_O^O, f_d\right) = (10, 10, 0)$, the peak steady-state enhancement is over 800 (more than 3 times E_i). The effect of leakage ($f_d = f_e R$) is to decrease the steady-state enhancement E_{SS}, but even for large leakage factors, polarization should still be observable.

Case 3: $\omega_n \pm \Delta \approx 0$

Case 3 is near the solid-effect transitions $\left(\omega_n \pm \Delta \approx 0\right)$ with $S^{\pm} \neq 0$, but $S^O = 0 = S^{\mp}$, $\omega_n \gg \omega_L$. Exactly at the $S^{\pm}$ peaks, Case 1 ($(\omega_n \pm \Delta) = 0$), EDDR contributes indirectly to the DNP only through nuclear relaxation processes, that is, through T_n^m and f_e^m. However, slightly off the $S^{\pm}$ peaks ($\omega_n \pm \Delta \approx 0$), EDDR may contribute explicitly to the DNP. Using equations (99c) and (101), yields for this case (taking $\omega = \omega_e$)

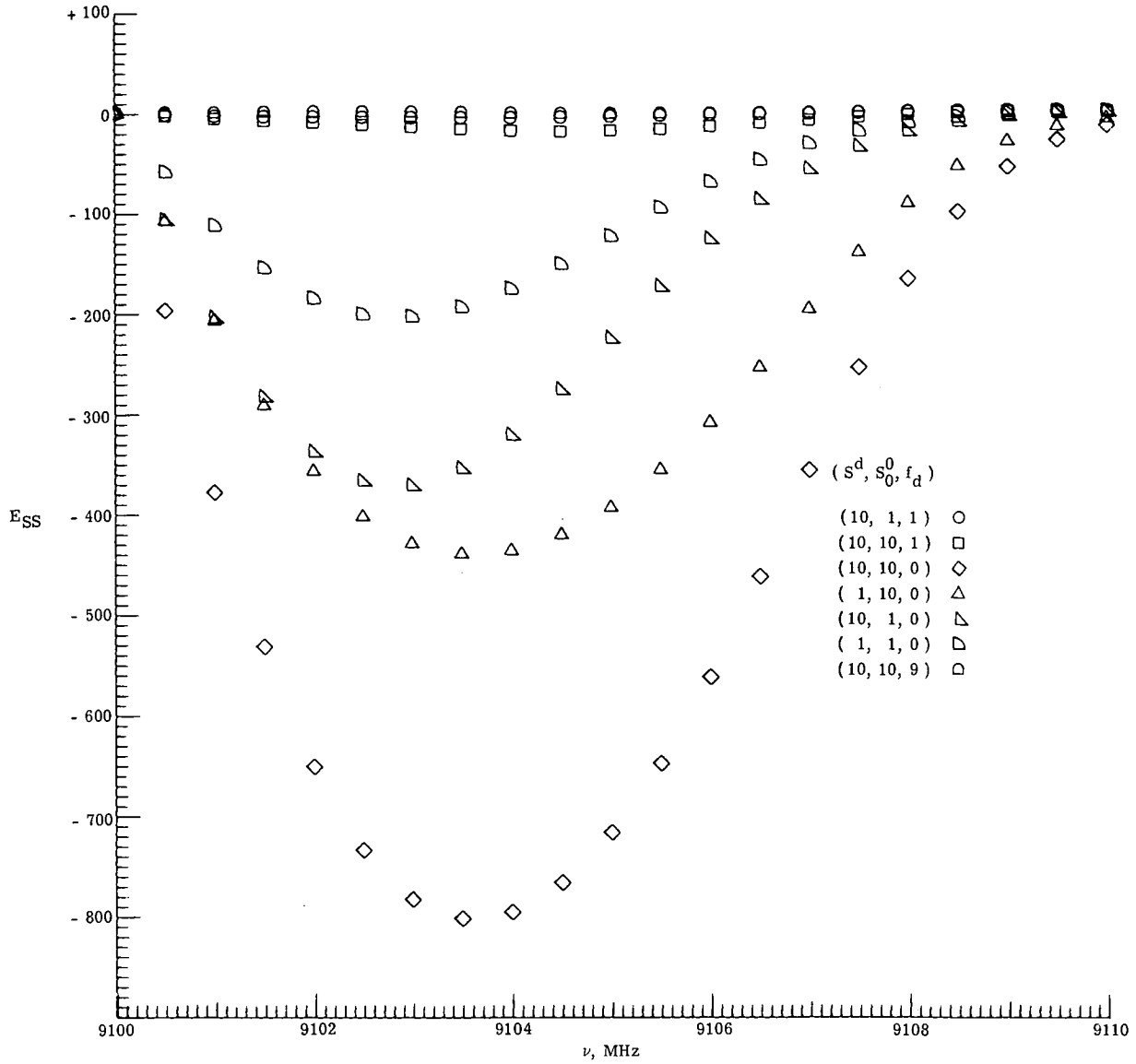


Figure 2.- Parametric curves of the steady-state enhancement E_{SS} from equation (114), as a function of the applied microwave frequency $\nu = (\omega/2\pi)$, near the main ESR transition W^O. The solid-effect transition W^-, centered at 9137 MHz, is well separated from W^O. The E_{SS} curves are labelled by $\left(S^d, S_O^O, f_d\right)$. $R = \left(T_d/T_e\right) = 1$. W^O is assumed to be a Gaussian: $S^O(\nu) = S_O^O \exp\left[-(\nu-9100)^2/12.5\right]$, where S_O^O is a constant.

$$E_{SS} = 1 + \frac{S^{\pm}\left(\mp \frac{\omega_e}{\omega_n}\right)\left(1 \mp f_e S^d \frac{\omega_n^{\Delta}}{\omega_L^2} R\right)}{1 + S^d(1 + f_d C_n) + S^{\pm}\left[1 + f_e + f_d C_{\pm} + f_e S^d (C_{\Delta} R + 1 + f_d C_n)\right]} \tag{118}$$

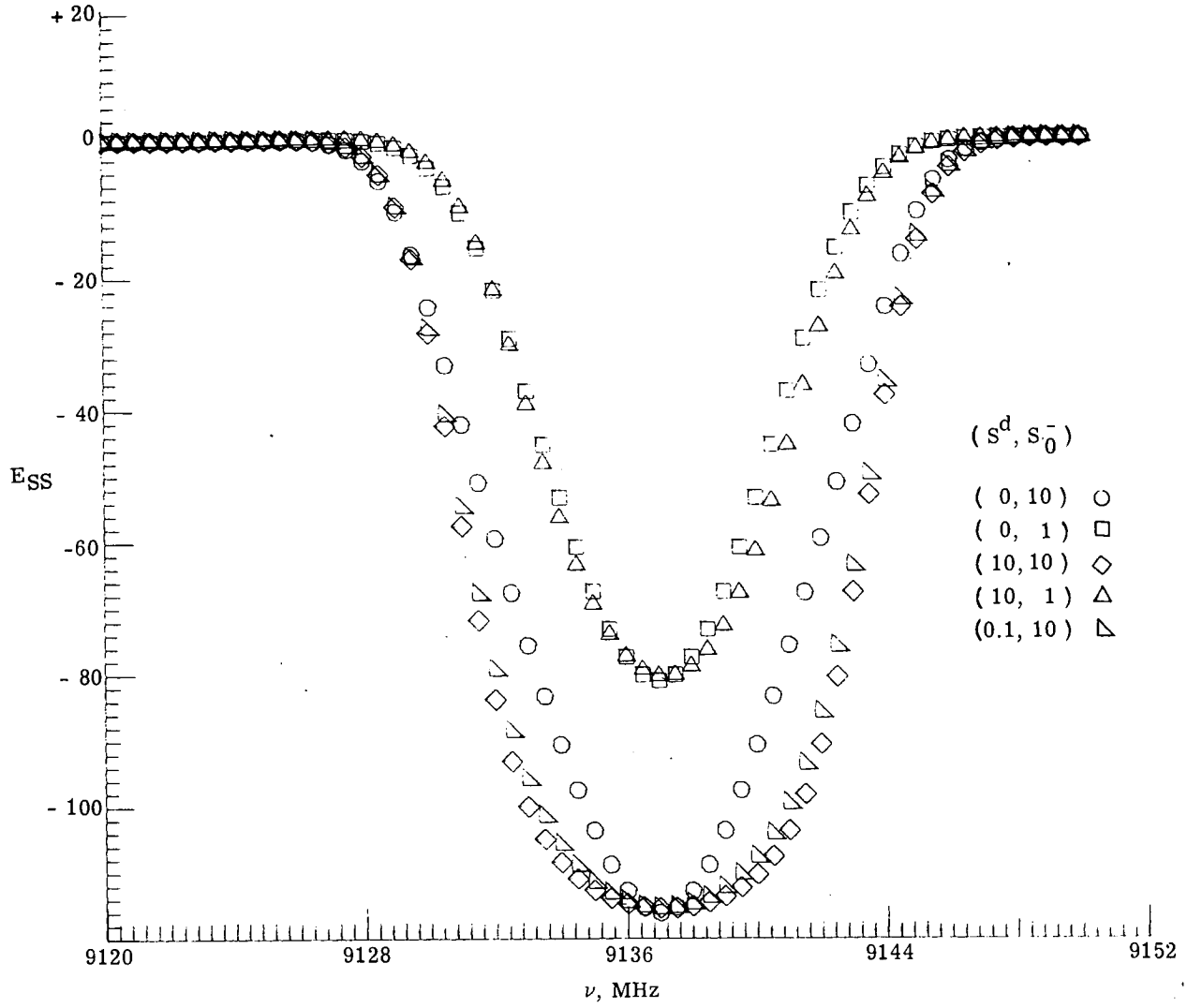
If $f_e S^d << 1$, EDDR and DNP effects are negligible, as equation (118) reduces to equation (108) for all Δ values near $(\mp \omega_n)$. However, if $f_e S^d \gtrapprox 1$, equation (118) predicts asymmetries in E_{SS} as a function of Δ, as well as slightly higher E_{SS} values than those in equation (108). In this case EDDR is cooled by the solid-effect transitions $S^{\pm}$, and this cooling is conveyed to the nuclei by the S^d transitions. This proposed new DNP effect involving the terms $(f_e S^{\pm})S^d$ is a higher order analog of the Case 2 $(S^O)S^d$ mechanism discussed previously for the limit $\omega_n >> \omega_L$. In the general case of unresolved satellite transitions $\left(\omega_n \lessapprox \omega_L\right)$, both mechanisms operate simultaneously, as is easily seen from the $\left[S^O(S^d + S^+ + S^-) + f_e(S^+ + S^-)S^d\right]$ terms in equations (99) and (101); however, the well-known $S^O(S^d + S^+ + S^-)$ mechanism would then ordinarily predominate. The two mechanisms are in principle separable for well-resolved satellites, which should be useful for experimental tests of them.

It is interesting to note that equation (118) reduces to equation (115) with $\Delta \approx \mp \omega_n$ when $f_e S^d >> 1$ and $S^{\pm} >> \left[1 + S^d(1 + f_d C_n)\right]$, and that this equals the solid effect enhancement $E_{SS} = \frac{(\mp \omega_e/\omega_n)}{1 + f_e^m}$ from equation (111) exactly at $\Delta = \mp \omega_n$.

Figure 3 presents parametric curves of the steady-state enhancement E_{SS} given in equation (118) for various nonzero values of S^d and two values of $f_e = f_d$ (for the ratio $R = 1$). The electron spin resonance line shape is assumed Gaussian, and relevant parameters are given in table I. The curves for $S^d = O$ are also shown in figures 3(a) and 3(b) for comparison purposes. It can be seen from both figures that even small values of S^d will distort and broaden the enhancement curve when $S_O^- = 10$. The distortion at lower levels of saturation is not as evident but there is a noticeable broadening effect especially when $f_d = 10$. Comparing figures 3(a) and 3(b), it is evident that the effect of the leakage term is to broaden the enhancement curve for fixed S_O^-.

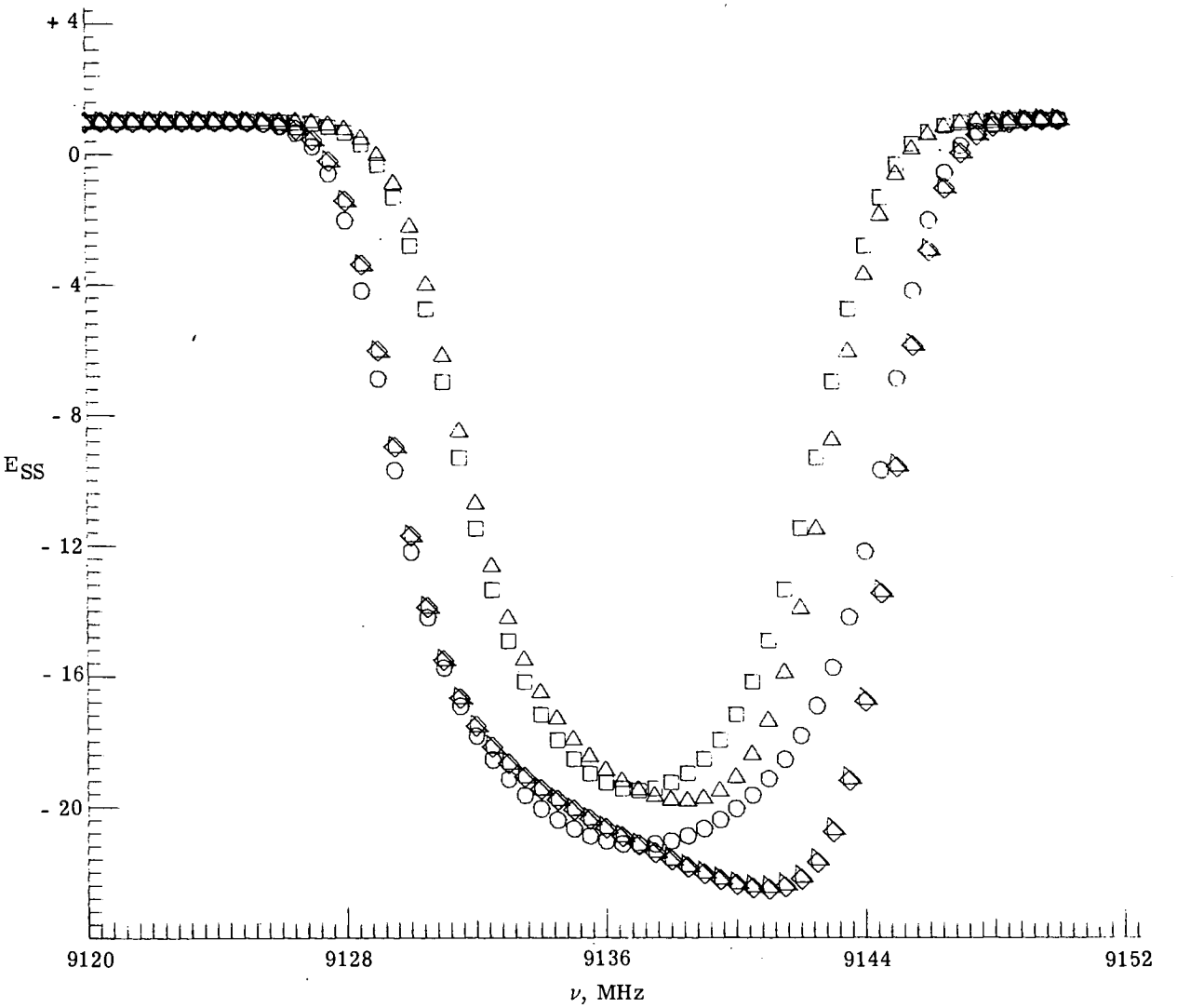
CONCLUSIONS

A detailed derivation of the equations governing dynamic nuclear polarization (DNP) and nuclear spin-lattice relaxation using the spin temperature theory has been carried to second order in a perturbation expansion of the density matrix. This theory is valid for ionic crystals weakly doped with paramagnetic impurities assuming (1) a completely homogeneously broadened electron spin resonance line, (2) an isotropic electron



(a) $f_e = f_d = 1.$

Figure 3.- Parametric curves of E_{SS} from equation (118), as a function of $\nu = (\omega/2\pi)$, near the solid-effect transition W^-. The main ESR line W^O, centered at 9100 MHz, is well separated from W^-. The E_{SS} curves are labelled by $\left(S^d, S_O^-\right)$. $R = \left(T_d/T_e\right) = 1$. W^- is assumed to be a Gaussian: $S^-(\nu) = S_O^- \exp\left[-(\nu - 9137)^2/12.5\right]$ where S_O^- is a constant.



(b) $f_e = f_d = 10.$

Figure 3.- Concluded.

g-factor, (3) rapid nuclear spin diffusion, (4) the high temperature limit, and (5) no phonon bottleneck. Complete expressions for the DNP steady state enhancement E_{SS}, the DNP pump time, and the measured nuclear spin-lattice relaxation time, which include effects of the electron dipole-dipole reservoir (EDDR) on the nuclei, have been derived.

Several cases for the limit of well-resolved solid effect transitions have been examined. The conventional results for DNP by the solid effect exactly at the solid effect transition peaks have been obtained, but with EDDR effects on the nuclear relaxation and DNP leakage factor included. It is suggested that direct EDDR contributions to DNP excited by saturation of the main ESR line, previously studied for unresolved and

partially-resolved solid effect transitions, may be extended to the well resolved case, leading to E_{SS} values greater than the conventional solid effect. A new DNP effect is proposed: saturation of the solid effect transitions may cool EDDR in favorable cases and lead to asymmetries in the shape of the DNP enhancement curve as well as to slightly higher peak polarizations than those at the solid-effect transition peaks. Parametric curves of these EDDR effects on DNP are given for typical parameter values.

Langley Research Center,
National Aeronautics and Space Administration,
Hampton, Va., May 21, 1974.

APPENDIX A

DIPOLE-DIPOLE HAMILTONIAN OPERATORS

It is customary to write the magnetic dipole-dipole interaction Hamiltonian for a single spin species as follows:

$$\mathcal{H}_{SS} = \gamma_e^2 \hbar^2 \sum_{k>l=1}^{N_e} r_{kl}^{-3} \left\{ A_{kl} + B_{kl} + C_{kl} + D_{kl} + E_{kl} + F_{kl} \right\} \tag{A1}$$

where

$$A_{kl} = S_{zk} S_{zl} \left(1 - 3 \cos^2 \theta_{kl} \right) \tag{A2}$$

$$B_{kl} = -\frac{1}{4} \left(1 - 3 \cos^2 \theta_{kl} \right) \left(S_k^+ S_l^- + S_k^- S_l^+ \right) \tag{A3}$$

$$C_{kl} = -\frac{3}{2} \sin \theta_{kl} \cos \theta_{kl} e^{-i\varphi_{kl}} \left(S_{zk} S_l^+ + S_{zl} S_k^+ \right) \tag{A4}$$

$$D_{kl} = -\frac{3}{2} \sin \theta_{kl} \cos \theta_{kl} e^{i\varphi_{kl}} \left(S_{zk} S_l^- + S_{zl} S_k^- \right) \tag{A5}$$

$$E_{kl} = -\frac{3}{4} \sin^2 \theta_{kl} e^{-2i\varphi_{kl}} S_k^+ S_l^+ \tag{A6}$$

$$F_{kl} = -\frac{3}{4} \sin^2 \theta_{kl} e^{+2i\varphi_{kl}} S_k^- S_l^- \tag{A7}$$

where θ_{kl} and φ_{kl} are the polar coordinates of the vector $\vec{r}_{kl}$, the z-axis is parallel to $\vec{H}_O$, and

$$S_k^{\pm} = S_{kx} \pm i S_{ky} \tag{A8}$$

The Hamiltonians $\mathcal{H}_{IS}$ and $\mathcal{H}_{II}$ can be similarly written.

APPENDIX B

EVALUATION OF TRIPLE TIME INTEGRALS

The triple integrals in equations (62) and (75) are carried out by integration by parts. The first term on the right-hand side of equation (62) is integrated to illustrate the method. The remaining integrals in equations (62) and (75) are treated in the same manner and lead to equations (64) and (76), respectively.

Define $J(\omega_n)$ as

$$J(\omega_n) = \int_0^t dt' \int_0^{t'} dt'' \, e^{i\omega_n(t''-t')} \int_0^{t''} dt''' \, S_x(t''') \, S_x(t) \tag{B1}$$

and integrate this expression by parts

$$J(\omega_n) = \frac{1}{i\omega_n} \int_0^t dt' \left\{ e^{i\omega_n(t''-t')} \int_0^{t''} dt''' \, S_x(t''') \, S_x(t) \Bigg|_{\substack{t''=t' \\ t''=0}} \right.$$

$$\left. - \int_0^{t'} dt'' \, e^{i\omega_n(t''-t')} \, S_x(t'') \, S_x(t) \right\} \tag{B2}$$

which reduces to

$$J(\omega_n) = \frac{1}{i\omega_n} \int_0^t dt' \int_0^{t'} dt'' \, S_x(t'') \, S_x(t)$$

$$- \frac{1}{i\omega_n} \int_0^t dt' \int_0^{t'} dt'' \, e^{i\omega_n(t''-t')} \, S_x(t'') \, S_x(t) \tag{B3}$$

Integrate the second term on the right in the same manner,

$$J(\omega_n) = \frac{1}{i\omega_n} \int_0^t dt' \int_0^{t'} dt'' \, S_x(t'') \, S_x(t) - \frac{1}{\omega_n^2} \int_0^t dt' \, e^{i\omega_n(t'-t)} \, S_x(t') \, S_x(t)$$

$$+ \frac{1}{\omega_n^2} \int_0^t dt' \, S_x(t') \, S_x(t) \tag{B4}$$

The first term on the right of equation (62) is

$$F = -\Delta\omega_1^2(\alpha - \gamma)\,\mathrm{Tr}\sum_{j=1}^{N_n/N_e} \left|\epsilon_j\right|^2 I_j^+ I_j^- \left\{J(\omega_n) + J(-\omega_n)\right\}$$

$$= -\frac{2\Delta\omega_1^2}{\omega_n^2}(\alpha - \gamma)\,\mathrm{Tr}\sum_{j=1}^{N_n/N_e} \left|\epsilon_j\right|^2 I_j^+ I_j^- \int_0^t dt'\,\tilde{S}_x(t'-t)S_x \cos\Delta(t'-t)$$

$$+\frac{\Delta\omega_1^2}{\omega_n^2}(\alpha - \gamma)\,\mathrm{Tr}\sum_{j=1}^{N_n/N_e} \left|\epsilon_j\right|^2 I_j^+ I_j^-$$

$$\times \int_0^t dt'\,\tilde{S}_x(t'-t)\,S_x\left[\cos\,(\omega_n + \Delta)(t'-t) + \cos\,(\omega_n - \Delta)(t'-t)\right] \qquad \text{(B5)}$$

If equations (63) and (65) through (68) are used, equation (B5) reduces immediately to equation (64).

APPENDIX C

TRACE CALCULATIONS

This appendix illustrates some of the trace calculations used in the shell-of-influence approximation. The numerical values cited are for nuclei and paramagnetic ions (called electrons herein) of spin-$\frac{1}{2}$, that is, for $I_j = \frac{1}{2}$ and $S = \frac{1}{2}$, respectively. Since there are two spin spaces involved, the trace must be taken over the product space. For example,

$$\mathrm{Tr}\ 1 = \mathrm{Tr}_S \cdot \mathrm{Tr}_I\, 1 = \mathrm{Tr}_S\, 1 \cdot \mathrm{Tr}_I\, 1 \tag{C1}$$

where $\mathrm{Tr}_S(\mathrm{Tr}_I)$ signify the traces in the subspace of the electron S (or nuclei I), and where

$$\mathrm{Tr}_S 1 = 2 \cdot S + 1 \tag{C2}$$

and

$$\mathrm{Tr}_I 1 = (2 \cdot I + 1)^{N_n/N_e} \tag{C3}$$

Here the number of nuclei in the subspace of I is N_n/N_e, that is, the number in each shell-of-influence. There is one electron in each shell-of-influence. Other trace identities used are

$$\mathrm{Tr}_S S_z^2 = (1/3)\, S(S + 1)(2S + 1) \tag{C4}$$

$$\mathrm{Tr}_I I_z^2 = (1/3)\left(N_n/N_e\right) I(I + 1)(2I + 1)^{N_n/N_e} \tag{C5}$$

and

$$\mathrm{Tr}_I I_{zj}^2 = (1/3)\, I(I + 1)(2I + 1)^{N_n/N_e} \tag{C6}$$

These identities are used to evaluate equations involving traces over the product space of the S- and the I-spins, for example, in evaluating the quantity $\mathrm{Tr}\ I_j^+ I_j^-\ F(S)/\mathrm{Tr}\ S_z^2$, where $F(S)$ is some function of the S-spins only. This evaluation is carried out as follows:

$$\frac{\mathrm{Tr}\ I_j^+ I_j^-\ F(S)}{\mathrm{Tr}\ S_z^2} = \frac{\mathrm{Tr}_I I_j^+ I_j^-}{\mathrm{Tr}_I 1} \frac{\mathrm{Tr}_S F(S)}{\mathrm{Tr}_S S_z^2}$$

$$= \frac{1}{2} \frac{\mathrm{Tr}_S F(S)}{\mathrm{Tr}_S S_z^2}$$

$$= \frac{1}{2} \frac{\mathrm{Tr}_S F(S)}{\mathrm{Tr}_S S_z^2} \frac{\mathrm{Tr}_I 1}{\mathrm{Tr}_I 1}$$

$$= \frac{1}{2} \frac{\mathrm{Tr}\ F(S)}{\mathrm{Tr}\ S_z^2} \qquad \text{(C7)}$$

REFERENCES

1. Bloembergen, N.; Purcell, E. M.; and Pound, R. V.: Relaxation Effects in Nuclear Magnetic Resonance Absorption. Phys. Rev., vol. 73, no. 7, Apr. 1, 1948, pp. 679-712.

2. Bloembergen, N.: On the Interaction of Nuclear Spins in a Crystalline Lattice. Physica, vol. XV, no. 3-4, May 1949, pp. 386-426.

3. Overhauser, Albert W.: Paramagnetic Relaxation in Metals. Phys. Rev., vol. 89, no. 4, Feb. 15, 1953, pp. 689-700.

4. Overhauser, Albert W.: Polarization of Nuclei in Metals. Phys. Rev., vol. 92, no. 2, Oct. 15, 1953, pp. 411-415.

5. Carver, Thomas R.; and Slichter, Charles P.: Experimental Verification of the Overhauser Nuclear Polarization Effect. Phys. Rev., vol. 102, no. 4, May 15, 1956, pp. 975-980.

6. Abragam, A.: Overhauser Effect in Nonmetals. Phys. Rev., vol. 98, no. 6, June 15, 1955, pp. 1729-1735.

7. Bloch, Felix: Recent Developments in Nuclear Induction. Phys. Rev., second ser., vol. 93, no. 4, Feb. 15, 1954, p. 944.

8. Overhauser, A. W.: Polarization of Nuclei in Metals by Magnetic Resonance. Phys. Rev., second ser., vol. 94, no. 3, May 1, 1954, p. 768.

9. Korringa, J.: Orientation of Nuclei by Saturation of Paramagnetic Resonance. Phys. Rev., vol. 94, no. 5, 1954, p. 1388.

10. Jeffries, Carson D.: Dynamic Nuclear Orientation. Interscience Publ., 1963.

11. Schmugge, T. J.; and Jeffries, C. D.: High Dynamic Polarization of Protons. Phys. Rev., vol. 138, no. 6A, June 14, 1965, pp. A1785-A1801.

12. Leifson, O. S.; and Jeffries, C. D.: Dynamic Polarization of Nuclei by Electron-Nuclear Dipolar Coupling in Crystals. Phys. Rev., vol. 122, no. 6, June 15, 1961, pp. 1781-1795.

13. Jeffries, C. D.: Notes on Dynamic Proton Polarization. Tech. Rep. No. UCB-34P20-T-1 (Contract At-(11-1)-34), Univ. of California, Berkeley, Sept. 23, 1966.

14. Jeffries, C. D.: Dynamic Orientation of Nuclei by Forbidden Transitions in Paramagnetic Resonance. Phys. Rev., vol. 117, no. 4, Feb. 15, 1960, pp. 1056-1069.

15. Kozhushner, M. A.; and Provotorov, B. N.: On the Theory of Dynamic Nuclear Polarization in Crystals. Soviet Phys. – Solid State, vol. 6, no. 5, Nov. 1964, pp. 1152-1154.

16. Swanenburg, T. J. B.; van den Heuvel, G. M.; and Poulis, N. J.: The Influence of a Phonon Bottleneck on the Dynamic Polarization of Protons in $(La,Ce)_2Mg_3(NO_3)_{12}.24H_2O$. Physica, vol. 33, no. 3, 1967, pp. 707-733.

17. Swanenburg, T. J. B.; van den Heuvel, G. M.; and Poulis, N. J.: The Influence of the Leakage Factor on the Dynamic Polarization of Protons in $(La,Nd)_2Mg_3(NO_3)_{12}.24H_2O$. Physica, vol. 35, no. 3, 1967, pp. 369-385.

18. Swanenburg, T. J. B.; Booy, R.; and Poulis, N. J.: The Influence of Paramagnetic Impurities on the Dynamic Polarization of Protons in $(La,Nd)_2Mg_3(NO_3)_{12}.24H_2O$. Physica, vol. 37, no. 1, 1967, pp. 65-81.

19. Abragam, A.; and Borghini, M.: Dynamic Polarization of Nuclear Targets. Progress in Low-Temperature Physics, Vol. IV, C. J. Gorter, ed., Interscience Publ., 1964, pp. 384-449.

20. Goldman, Maurice: Spin Temperature and Nuclear Magnetic Resonance in Solids. Clarendon Press (Oxford), 1970.

21. Goldman, M.: Thermal Mixing Between Spin Systems in Solids. Phys. Rev., vol. 138, no. 6A, June 14, 1965, pp. A1668-A1674.

22. Boucher, Jean-Paul; and Nechtschein, Maxime: Modèle du Réseau de Réservoirs Appliqué aux Effets de Polarisation Dynamique dans les Solides. J. Phys., tome 31, no. 8-9, Aug.-Sept. 1970, pp. 783-796.

23. Goldman, M.; and Landesman, A.: Dynamic Polarization by Thermal Mixing Between Two Spin Systems. Phys. Rev., vol. 132, no. 2, Oct. 15, 1963, pp. 610-620.

24. Poole, Charles P., Jr.; and Farach, Horacio A.: Relaxation in Magnetic Resonance. Academic Press, Inc., 1971.

25. Low, William: Paramagnetic Resonance in Solids. Academic Press, Inc., 1960.

26. Portis, A. M.: Electronic Structure of F Centers: Saturation of the Electron Spin Resonance. Phys. Rev., vol. 91, no. 5, Sept. 1, 1953, pp. 1071-1078.

27. Abragam, A.; and Bleaney, B.: Electron Paramagnetic Resonance of Transition Ions. Clarendon Press (Oxford), 1970.

28. Abragam, A.: The Principles of Nuclear Magnetism. Clarendon Press (Oxford), 1961.

29. Wollan, David Strand: Dynamic Proton Polarization in Some Rare Earth Ethyl Sulphates. Ph. D. Thesis, Univ. of Illinois, 1966.

30. Borghini, M.: Dynamic Polarization by "Effet Solide" With Phonon Bottle-Neck. Phys. Lett., vol. 20, no. 3, Feb. 15, 1966, pp. 228-229.

31. Borghini, M.: Dynamic Polarization of Nuclei by Electron-Nucleus Dipolar Coupling ("Effet Solide"). Phys. Rev. Lett., vol. 16, no. 8, Feb. 21, 1966, pp. 318-322.

32. Messiah, Albert (G. M. Temmer, transl.): Quantum Mechanics. Vol. I. Interscience Publ., Inc., 1964.
Messiah, Albert (J. Potter, transl.): Quantum Mechanics. Vol. II. Interscience Publ., 1965.

33. Redfield, Alfred G.: Nuclear Magnetic Resonance Saturation and Rotary Saturation in Solids. Phys. Rev., vol. 98, no. 6, June 15, 1955, pp. 1787-1809.

34. Rabi, I. I.; Ramsey, N. F.; and Schwinger, J.: Use of Rotating Coordinates in Magnetic Resonance Problems. Rev. Mod. Phys., vol. 26, no. 2, Apr. 1954, pp. 167-171.

35. Shimizu, Toshihiro: Theory of Saturational Narrowing. J. Phys. Soc. Japan, vol. 28, no. 4, Apr. 1970, pp. 811-817.

36. Gill, J. C.; and Vinall, N. P.: The Saturation of Dipolar-Broadened Electron Resonance Lines in the Presence of a Phonon Bottleneck. J. Phys. C (Solid State Phys.), ser. 2, vol. 2, no. 8, Aug. 1969, pp. 1512-1527.

37. Clough, S.: Magnetic Resonance Saturation and Thermodynamics: Comments on a Paper by J. C. Gill and N. P. Vinall. J. Phys. C (Solid St. Phys.), ser. 2, vol. 2, no. 8, Aug. 1969, pp. 1528-1529.

38. Gill, J. C.: Magnetic Resonance Saturation and Thermodynamics: A Reply to Comments by S. Clough on a Paper by J. C. Gill and N. P. Vinall. J. Phys. C (Solid St. Phys.), ser. 2, vol. 2, no. 8, Aug., 1969, pp. 1529-1531.

39. Atsarkin, V. A.; and Morshnev, S. K.: Confirmation of the Existence of Spin-Spin Interaction Temperature in EPR. JETP Lett., vol. 6, no. 4, Aug. 15, 1967, pp. 88-90.

40. Atsarkin, V. A.: Verification of the Spin-Spin Temperature Concept in Experiments on Saturation of Electron Paramagnetic Resonance. Soviet Phys. – JETP, vol. 31, no. 6, Dec. 1970, pp. 1012-1018.

41. Provotorov, B. N.: Magnetic Resonance Saturation in Crystals. Soviet Phys. – JETP, vol. 14, no. 5, May 1962, pp. 1126-1131.

42. Khutsishvili, G. R.: Spin Diffusion and Magnetic Relaxation of Nuclei. Soviet Phys. – JETP, vol. 15, no. 5, Nov. 1962, pp. 909-913.

43. Khutsishvili, G. R.: Spin Diffusion, Magnetic Relaxation, and Dynamic Polarization of Nuclei. Soviet Phys. – JETP, vol. 16, no. 6, June 1963, pp. 1540-1543.

44. Khutsishvili, G. R.: Spin Diffusion. Soviet Phys. – Usp., vol 8, no. 5, Mar.-Apr. 1966 pp. 743-769.

45. Khutsishvili, G. R.: Spin Diffusion and Nuclear Magnetic Relaxation in a Crystal Containing a Magnetic Impurity. Soviet Phys. – Usp., vol. 11, no. 6, May-June 1969, pp. 802-815.

46. Khutsishvili, G. R.: Diffusion and Relaxation of Nuclear Spins in Crystals Containing Paramagnetic Impurities. Progress in Low Temperature Physics, Vol. VI, C. J. Gorter, ed., American Elsevier Pub. Co., Inc., 1970, pp. 375-404.

47. Blumberg, W. E.: Nuclear Spin-Lattice Relaxation Caused by Paramagnetic Impurities. Phys. Rev., vol. 119, no. 1, July 1, 1960, pp. 79-84.

48. De Gennes, P-G: Sur la Relaxation Nucleaire dans les Cristaux Ioniques. J. Phys. of Chem. Solids, vol. 7, 1958, pp. 345-350.

49. Horvitz, E. Philip: Nuclear Spin Diffusion Induced by Paramagnetic Impurities in Nonconducting Solids. Phys. Rev. B, vol. 3, no. 9, May 1, 1971, pp. 2868-2872.

50. Lowe, I. J.; and Tse, D.: Nuclear Spin-Lattice Relaxation Via Paramagnetic Centers. Phys. Rev., vol. 166, no. 2, Feb. 10, 1968, pp. 279-291.

51. Byvik, Charles E.: Dynamic Nuclear Polarization in Samarium Doped Lanthanum Magnesium Nitrate. Ph. D. Thesis, Virginia Polytechnic Inst. & State Univ., Sept. 1971.

52. Van den Heuvel, G. M.; Heyning, C. T. C.; Swanenburg, T. J. B.; and Poulis, N. J.: Experimental Evidence of the Influence of Electron Dipole Dipole Interaction on Nuclear Spin Lattice Relaxation. Phys. Lett. A, vol. 27A, no. 1, May 20, 1968, pp. 38-39.

53. Van den Heuvel, G. M.; Swanenburg, T. J. B.; and Poulis, N. J.: Proton Spin-Lattice Relaxation in LaMN With Nd. Physica, vol. 56, no. 2, Nov. 30, 1971, pp. 365-387.

54. Wenckeback, W. Th.; van den Heuvel, G. M.; Hoogstraate, H.; Swanenburg, T. J. B.; and Poulis, N. J.: Experimental Proof of the Strong Coupling Between the Electron Spin-Spin Reservoir and a Nuclear Spin System in Dilute Paramagnetic Crystals. Phys. Rev. Lett., vol. 22, no. 12, Mar. 24, 1969, pp. 581-583.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE $300

SPECIAL FOURTH-CLASS RATE
BOOK

POSTAGE AND FEES PAID
NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION
451

U.S.MAIL

POSTMASTER: If Undeliverable (Section 158 Postal Manual) Do Not Return

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons. Also includes conference proceedings with either limited or unlimited distribution.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include final reports of major projects, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION OFFICE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546