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Nuclear Double Resonance in the Rotating Frame*

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A double nuclear resonance spectroscopy method is introduced which depends upon effects of magnetic dipole-dipole coupling between two different nuclear species. In solids a minimum detectability of the order of 10^{14} to 10^{16} nuclear Bohr magnetons/cc of a rare b nuclear species is predicted, to be measured in terms of the change in a strong signal displayed by an abundant a nuclear species. The a magnetization is first oriented by a strong radio-frequency field in the frame of reference rotating at its Larmor frequency. The b nuclear resonance is obtained simultaneously with a second radio-frequency field; and with the condition that the a and b spins have the same Larmor frequencies in their respective rotating frames, a cross relaxation will occur between the two spin systems. The cross-relaxation interaction, which lasts for the order of a long spin-lattice relaxation time of the a magnetization, is arranged to produce a cumulative demagnetization of the a system when maximum sensitivity is desired. Final observation of the reduced a magnetization indicates the nuclear resonance of the b system. The concepts of uniform spin temperature, when it is valid, and of nonuniform spin temperature where spin diffusion is important, are applied. The density matrix method formulates the double resonance interaction rate in second order. Preliminary tests of the double resonance effect are carried out with a nuclear quadrupole system.

I. INTRODUCTION

THE conventional sensitivity for nuclear magnetic resonance (NMR) detection of nuclear moments, referred to room temperature and optimum absorption, permits the measurement of a minimum[1] of about 10^{18} nuclear Bohr magnetons/cc at resonance frequencies in the range of 20 to 50 Mc/sec. In practice this sensitivity is obtained only in liquids which can be doped with paramagnetic ions to provide the necessary relaxation times for optimum absorption; and the nuclei can also be contained in symmetrical ions in order to minimize nuclear quadrupole broadening. Special electron nuclear double resonance and optical pumping techniques have exceeded the sensitivity quoted above, but are limited to particular materials where a strong electron spin resonance or optical transition is available for excitation. The atomic beam method can be included in this category of sensitive methods, but in general cannot give precision measurements of nuclear g values. A host of nuclear moments remain to be discovered or measured more accurately, particularly of those radioactive isotopes which cannot be put into the proper state to be measured by known methods. It would be useful if a resonance method could be applied to measurements of rare nuclei conveniently available in ordinary diamagnetic crystals. A double nuclear resonance technique[2] is analyzed in this paper, and proposes that a minimum of 10^{14} to 10^{16} nuclear Bohr magnetons/cc can be detected in diamagnetic crystals in the temperature range of 4 to 20°K. As an initial test, measurement of the K^{41} quadrupole interaction in $KClO_3$ shows a sensitivity which greatly exceeds the sensitivity of conventional NMR. The new method appears to have the same practical sensitivity as NMR would have if optimum absorption and signal integration means could be applied to solids at temperatures of 0.01 to 1.0°K, where the spin Boltzmann population would be sufficiently enhanced. In solids the spin-lattice relaxation time T_1 becomes extremely long, and the NMR lines are dipolar or quadrupolar broadened. Solids, in general, cannot be arbitrarily doped with paramagnetic impurities in order to shorten T_1 appreciably, and therefore optimum absorption cannot be obtained in practice. The double nuclear resonance method will capitalize upon the two conditions which forbid optimum signal detection by NMR, namely, a long T_1, and an appreciable dipolar broadening, or a short T_2, which is a measure of the inverse linewidth.

The double resonance method is similar to an earlier transient spin echo experiment.[3] A spin sample is chosen in which the nuclei to be detected, the "b nuclei," have "a nuclei" as abundant neighbors in the same crystal, and the a nuclei yield a large signal. The dipolar field due to b nuclei determines a portion of the local field h_{local} acting upon the a nuclei, and the spin echo formed by the a ensemble depends upon the persistence of this local field. If an rf (radio-frequency) pulse is applied to the b system within the echo memory time T_2 of the a spins, the a echo is attenuated a certain amount because the local field due to the b spins is scrambled. The b resonance is therefore indicated. The sensitivity of this method increases with T_2, but T_2 does not exceed more than a few milliseconds in solids. In the present work we have effectively replaced T_2 by T_1, and we prepare the a system, not to form an echo, but to form a magnetization in the rotating frame which lasts T_1 seconds,

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[1] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

[2] S. R. Hartmann and E. L. Hahn, Bull. Am. Phys. Soc. **5**, 498 (1960); S. R. Hartmann and E. L. Hahn, *Fluctuation, Relaxation and Resonance in Magnetic Systems*, edited by P. Ter Haar (Oliver and Boyd, Ltd., Edinburgh, 1962), p. 247.

[3] M. Emschwiller, E. L. Hahn, and D. Kaplan, Phys. Rev. **118**, 414 (1960).

as long as strong rf fields are applied in a special way. During the time T_1 the b spins can be brought into resonance interaction with the a spins, after which a degradation in the magnetization of the a system is observed.

II. SPIN LOCKING AND DOUBLE RESONANCE

The double resonance (DR) experiment requires a magnetization M_a of the a spins which is aligned along a field H_{1a} in the frame of reference rotating at a frequency ω_a after a rf field $H_a(t)=2H_{1a}\cos\omega_a t$ is applied at exact resonance, so that $\omega_a=\Omega_a=\gamma_a H_0$, where γ is the gyromagnetic ratio, H_0 is the applied polarizing magnetic field, and Ω_a is the nuclear Larmor frequency. Redfield[4] has shown that if $H_{1a}\gg h_{\text{local}}$, then M_a will not decay in a time T_2, but will decay instead in a spin-lattice relaxation time T_{1a}. This orientation condition of M_a will be denoted as "spin locked" along H_{1a}. In our experiments, when spin locking begins, $M_a=M_{0a}$ will be the equilibrium value of magnetization first polarized along the z direction either by the external field H_0, or aligned by the internal electric field gradient of a crystal for $I>\frac{1}{2}$. The conversion of M_{0a} to a spin-locked condition in solids is carried out by a method used by Solomon[5] for nuclear precession studied in liquids. A 90° pulse of $H_a(t)$ lasting for a time $t_w=\pi/2\gamma_a H_{1a}\ll T_2$, T_{1a} is first applied to rotate M_{0a}, initially along the z axis, into the x-y plane. At the time t_w the phase of $H_a(t)$ is shifted by electronic means in a short time $t'\ll 2\pi/\gamma_a H_{1a}$ through an angle $\pi/2$, while keeping the magnitude of H_{1a} essentially constant. Now H_{1a} is parallel to M_{0a}. If M_{0a} is initially in equilibrium with H_0 at the lattice temperature T, it is converted to a lower spin temperature $T_a(0)=TH_{1a}/H_0$ in the rotating frame. In time t, the spins warm up to a temperature

$$T_a(t)=T_a(0)e^{t/T_{1a}}, \tag{1}$$

if $H_0\gg H_{1a}$. When H_{1a} is turned off nonadiabatically after a spin-locking time t, comparable to T_{1a}, then a measurable free precession signal appears with a maximum amplitude given by

$$M_a(t)=M_{a0}e^{-t/T_{1a}}. \tag{2}$$

Figure 1 indicates the sequence of rf fields necessary for spin locking.

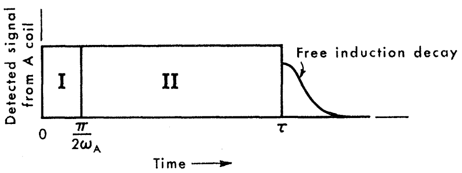

FIG. 1. Formation of the spin-locked free-induction decay.

It is important to note at this point with a rigorous discussion to follow in the next section, that during spin locking the a spins are decoupled to a very high degree from all foreign nuclear dipole fields, namely, the b spins, and their field contribution, h_{ab}, to the internal field h_{local} is removed. A spin-spin interaction among the a spins remains to provide mutual contact for maintenance of a spin temperature T_a in the rotating frame. During spin locking the double resonance detection of the b spins is obtained by reinstating the interaction between the a and b spins. In the simplest case this is brought about by first subjecting the b spins to an rf field $H_b(t)=2H_{1b}\cos\omega_b t$ at the resonance condition

$$\omega_b=\Omega_b=\gamma_b H_0; \tag{3}$$

and the second requirement must be that the rf field amplitudes are adjusted so that

$$\alpha_a\gamma_a H_{1a}=\alpha_b\gamma_b H_{1b}, \tag{4}$$

where $\alpha_a=\alpha_b=1$ for magnetic resonance and $\alpha=[I(I+1)-m(m-1)]^{1/2}$ for an electric quadrupole resonance between the levels $m\leftrightarrow(m-1)$. Unless otherwise noted we will assume that the system is magnetic and $\alpha=1$.

Although Eqs. (3) and (4) give two resonance conditions which must be satisfied at the same time for double resonance, it is usually necessary to adjust only one variable. In a magnetic system the relation

$$\omega_b H_{1b}=\gamma_a H_0 H_{1a} \tag{5}$$

follows by eliminating γ_b from Eqs. (3) and (4). Since the quantity on the left is proportional to the voltage induced in a single loop and can be measured and calibrated, it is only necessary to search for γ_b by varying ω_b, keeping $\omega_b H_{1b}$ and H_{1a} constant. In a double resonance experiment involving an electric quadrupole system one must know γ_b or else be required to search by varying the two independent variables ω_b and H_{1b}. If γ_b is not known, one would first choose a suitable nuclear environment so that the electric field gradient is zero and determine γ_b. Then one would proceed to a second crystal in which only the electric quadrupole interaction is to be determined, and thereby only ω_b is required to be varied.

Equation (4) signifies that the Zeeman splittings for both spin groups are equal in their respective rotating frames, and an interaction or cross relaxation between the a and b spins will occur. While the condition (3) is satisfied by continuous wave (cw) application of $H_{1b}(t)$, the condition (4) is only satisfied during the time t when the a spins are locked. Before spin locking is started, the b spin temperature is $T_b=\infty$ owing to the saturation caused by the intense field H_{1b}. During time t the hot b spins and the cold a spins are brought into contact, and spin exchange takes place as the two systems approach a common spin temperature. The b spins have then gained the population difference lost by the a spins.

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[4] A. G. Redfield, Phys. Rev. **98**, 1787 (1955).

[5] I. Solomon, Compt. rend. **248**, 92 (1959).

This description[6] is useful when the spin-lattice relaxation rates are small compared to the rate of spin population exchange.

The coupling between a and b spins can be compared to the rotary saturation effect[4] where an rf coil with its axis along the z or H_0 direction induces transitions in the a system if the coil is directly excited at a frequency $\gamma_a H_{1a}$. In the present case the coil is replaced by b nuclei and they produce oscillations of the dipole field h_{ab} along the z direction at the condition given by Eq. (4). These dipole fields can be decomposed into oppositely rotating components in the y-z plane, and one of these components will follow the precession of M_a about H_{1a} along the x axis. The interaction results in a depolarization of M_a along H_{1a} accompanied by a corresponding increase of b spin magnetization, M_b, along H_{1b} because mutual spin flips will conserve energy. After a locking time t the double resonance is detected by a signal change which is proportional to

$$\Delta M_a = M_{0a}(1-R)e^{-t/T_{1a}}, \tag{6}$$

where $R=1$ for no double resonance detection and $R<1$ for the presence of double resonance detection.

For analysis in this paper the a and b spins are polarized in a large field H_0, and all have spin $I=\frac{1}{2}$, giving a total of four principal Zeeman levels. In a qualitative sense the results obtained will apply also to pure quadrupole resonance where both groups have $I=\frac{3}{2}$. Let n_a and n_b represent the spin population differences between the Zeeman levels in the rotating frame for each of the spin groups. The corresponding magnetizations are therefore

$$M_a = \tfrac{1}{2} n_a \gamma_a \hbar; \quad M_b = \tfrac{1}{2} n_b \gamma_b \hbar; \tag{7}$$

which are polarized, respectively, along H_{1a} and H_{1b}.

A. Spin Temperature Assumption in the Rotating Frame

The assumption of uniform spin temperatures T_a and T_b in the rotating frame for each ensemble is embodied in expressions for the rate of cross coupling of spin populations, or equations, of detailed balance

$$\partial n_a/\partial t = -\partial n_b/\partial t = W_0(n_b N_a - n_a N_b), \tag{8}$$

where N_a and N_b are the number per cc of a and b spins, respectively, and W_0 represents the average rate of interaction per a-b spin pair. The effect of spin lattice relaxation is omitted for the condition $T_{1a}, T_{1b} \gg 1/N_a W_0$, $1/N_b W_0$. These equations conserve energy in the rotating frame as required by Eq. (4). The solution of Eq. (8) gives

$$n_a(t) = n_{a0}(1-\xi\zeta) + n_{b0}\eta\zeta, \tag{9a}$$

$$n_b(t) = n_{b0}(1-\eta\zeta) + n_{a0}\xi\zeta, \tag{9b}$$

where n_{a0} and n_{b0} are the initial populations at $t=0$, $\xi = N_b/(N_a+N_b)$, $\eta = N_a/(N_a+N_b)$, and $\zeta = 1 - \exp[-(N_a+N_b)W_0 t]$. The effect of very long spin lattice relaxation times can be included by replacing n_{a0} by $n_{a0}\exp[-\frac{1}{2}t(\eta/T_{1a}+\xi/T_{1b})]$ and n_{b0} by $n_{b0}\exp[-\frac{1}{2}t(\eta/T_{1a}+\xi/T_{1b})]$. The short time $t_w + t'$ required to lock the a nuclei can be neglected, and with the saturation condition that $n_{b0}=0$ at $t=0$, then in a time $t \gg \tau_{DR}$ where $\tau_{DR} = [W_0(N_A+N_B)]^{-1}$, Eqs. (9) give $n_a(t) = n_{a0}(1-\xi)$; $n_b(t) = n_{a0}\xi$. Therefore, the total population difference $n_a(t)+n_b(t) = n_{a0}$ is conserved, but a loss of magnetization $-\Delta M_a$ occurs along H_{1a} and a corresponding gain ΔM_b occurs along H_{1b}. With this result the quantity R in Eq. (6) is given by $R=\xi$. For a sensitive detection of rate b spins, when $\xi \ll 1$, assuming that Eqs. (9) are still valid, the fractional signal change due to the a magnetization will be negligibly small, proportional to $\Delta M_0/M_{0a} = \xi$. The question of the validity of Eqs. (9) for ξ too small will arise, because in this case a uniform spin temperature T_a will not apply, particularly, to the a spins. This case is deferred to the next discussion of spin diffusion among the a spins.

If the buildup in the magnetization $\Delta M_c \approx \frac{1}{2}\gamma_b \hbar n_{a0}\xi$ is destroyed or reversed in sign after approximately every τ_{DR} seconds, then over a much longer spin locking time $t \gg \tau_{\mathrm{DR}}$, the average value of $\bar{n}_b \approx 0$ can be assumed. This will result if the phase of the rf field $H_b(t)$ is switched nonadiabatically by 180° in a periodic manner every τ_{DR} seconds, so that $M_b \rightarrow -M_b$, and conversion of the b spins to a "hot" negative temperature occurs periodically. The solution for $n_a(t)$ can then be written as

$$n_a(t) = n_{a0}\exp(-N_b W_0 t). \tag{10}$$

After a locking time $t = T_{1a}$ seconds, for $N_b W_0 T_{1a} \ll 1$, the fractional signal change of the free induction a signal is

$$\Delta M_a/M_{a0} = (1/e)(T_{1a}/\tau_{ab}), \tag{11a}$$

with

$$\tau_{ab} = (N_b W_0)^{-1} = (1/f)(8/\pi)^{1/2}(T_{ab}{}^2/T_{aa}), \tag{11b}$$

$$f = N_b/N_a, \tag{11c}$$

and where later analysis (Sec. IV B) shows that

$$N_a W_0 = (T_{aa}/T_{ab}{}^2)(\pi/8)^{1/2}. \tag{12}$$

The factor $1/e$ is introduced to take the spin lattice interaction into account. $T_{ab}{}^{-2}$ is the contribution to the a spin second moment $\langle\Delta\omega^2\rangle_{ab}$ due to b spins[7] and $T_{aa}{}^{-2}$, obtained later in Sec. IV B, is approximated by the second moment due to the a spins. Both quantities are calculated as if $N_a = N_b$.

The solutions given by Eqs. (9) can be adapted to predict the average behavior of n_a and n_b when sudden phase shifts are applied to H_{1b} every τ_s seconds, and M_b is suddenly transformed to sM_b, where s can have the range of values $1 \geq s \geq -1$. The periodic phase shift

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[6] A. Abragam and W. G. Proctor, Phys. Rev. **109**, 1441 (1958).

[7] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

of H_{1b} will produce Fourier harmonics which appear at the frequency ω_a, but these produce a negligible effect upon the a spin signal in our experiments. As ω_b passes through the resonance of the b spins the periodic phase shifts will not modify the width of the double resonance appreciably providing $1/\tau_s$ is less than the linewidth of the double resonance as discussed later in Sec. IV B. Also, we make the assumption that $n_b=0$ throughout the resonance line, although there would be a slight modification of the linewidth owing to the fact that s or n_b is not constant as ω_b varies through the resonance condition.

B. Case of Spin Diffusion

When performing a double resonance experiment with rare b nuclei, the success of the experiment depends upon spin diffusion among a spins. The b nuclei interact mainly with the nearest a neighbors, and consequently it is necessary that the spin diffusion among a spins communicate the high spin temperature of the rare b nuclei to the cold and abundant a nuclei. When $T_{aa} \ll T_{ab}$, the a spins interact among themselves much more strongly than with the neighboring b nuclei. In this case spin diffusion among a spins does not appreciably slow down the rate at which the a spins are warmed up by the double resonance contact with the hot b spins. It is only when $T_{aa} \geq T_{ab}$ that the bottleneck due to spin diffusion affects the double resonance response, and Eqs. (9) cannot be applied to the description of the experimental results. In the event that $T_{aa} \gg T_{ab}$ it is necessary to apply the diffusion equation for the a spin magnetization density p, given by

$$\partial p/\partial t = D\nabla_p{}^2 - Cp \textstyle\sum_n |\mathbf{r}-\mathbf{r}_n|^{-6}, \tag{13}$$

where D is the nuclear spin diffusivity, and C is a constant defined by the relation

$$P = C|\mathbf{r}-\mathbf{r}_n|^{-6}. \tag{14}$$

P represents the space-averaged transition probability of an a nucleus at $\mathbf{r}$ due to a b nucleus at $\mathbf{r}_n$. In this treatment the pertinent spin magnetization density is that which is along the direction of the rotating magnetic field vector of the applied a rf field, and n_b is assumed to be zero. In the diffusion limiting case, an expression[8,9] for T_1 has been obtained for a set of nuclei which are relaxed by rare paramagnetic impurities, and this expression applies to our problem for the relaxation of a spins. When the relaxation is diffusion limited, we define $T_1 = T_d$, and it is found that

$$1/T_d = 8.5 N_b C^{1/4} D^{3/4}, \tag{15}$$

where[10]

$$D \cong a^2/50T_{aa}, \tag{16}$$

and a is the distance between a nuclei.

When the relaxation of the nuclei is not diffusion limited, T_1 is given by

$$1/T_1 = (4\pi/3)(N_b C/b^3), \tag{17}$$

where b is approximated by the distance between the a and b nearest-neighbor nuclei. To evaluate C, it is noted that when relaxation is not limited by diffusion the previous result, Eq. (11b), should agree with the expression for T_1 given by Eq. (17). By eliminating T_1, one obtains

$$C = \frac{3}{8(2\pi)^{1/2}} \frac{fb^3}{N_b} \frac{T_{aa}}{T_{ab}{}^2}. \tag{18}$$

Substitution of D and C into Eq. (15) yields

$$1/T_d \approx (0.28) f/(T_{aa}T_{ab})^{1/2}, \tag{19}$$

where we have made use of the relation $N_b ba^2 \approx f$. On comparing Eqs. (18) and (11b) we note that for $T_{aa} \approx T_{ab}$ we obtain

$$T_d \approx \tau_{ab}, \tag{20}$$

from which we conclude that for $T_{ab} > T_{aa}$, Eq. (8) is valid, whereas for $T_{ab} < T_{aa}$, Eq. (13) is to be used. The exponential decay law with the rate given by Eq. (19) is not valid[8,9] for times shorter than $T_{aa}{}^2/T_{ab}$.

C. Sensitivity of Double Resonance Detection

For $t/T_d \ll 1$, the fractional signal change of the free induction signal after a locking time t is given by

$$\Delta V/V_0 = \Delta M_a/M_{a0} \approx (t/T_d)e^{-t/T_{1a}}. \tag{21}$$

If $S = V/\Delta V_n$ is the signal-to-noise ratio of the signal at $t = T_{1a}$ without double resonance, the minimum value of f which can be detected is obtained by letting $\Delta V = \Delta V_n$ and is given by

$$f_{\min} = (T_{aa}T_{ab})^{1/2}/(0.3)ST_{1a}. \tag{22}$$

A value of $f_{\min} = 10^{-7}$ is obtained if typical values of $(T_{ab}T_{aa})^{1/2} \approx 10^{-4}$ sec, $S = 300$, and $T_{1a} = 30$ sec are assumed. For $N_a = 10^{22}$ sec, a minimum concentration of $N_b = 10^{15}$/cc could be detected. This rough calculation suggests only the order of magnitude of the sensitivity which could be far greater or less than the figure quoted depending upon the chosen parameters.

The double resonance method can be applied for the detection of b nuclei which are abundant, but instead may have extremely small magnetic moments μ_b'. The sensitivity given by Eq. (11a) will apply in this case, and let $N_a = N_b$. If T_{ab} corresponds to a value of μ_b, then

$$(T_{ab}')^{-2} = (\mu'_b/\mu_b)^2 T_{ab}{}^{-2} \tag{23}$$

expresses the relationship where μ_b' determines the time T_{ab}', and other parameters remain the same. The procedure which obtained $f_{\min}$ of Eq. (22) gives in this case

$$(\mu_b'/\mu_b)_{\min} \approx T_{ab}/(T_{1a}T_{aa}S)^{1/2} \approx 10^{-4}, \tag{24}$$

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[8] G. R. Khutsishvili, Proc. Acad. Sci. Georgian S. S. R. 4, 3 (1956); P. G. de Gennes, J. Phys. Chem. Solids **6**, 345 (1958).

[9] W. E. Blumberg, Phys. Rev. **119**, 79 (1960).

[10] N. Bloembergen, Physica **25**, 386 (1949).

if the same parameter values are chosen with $T_{ab} > T_{aa}$. However, it would be prohibitive in practice to detect 10^{-4} nm, but practical to detect ~0.1 nm, because H_{1b}, required by the condition of Eq. (4), cannot be made arbitrarily large in the experiment. A special case of double resonance involving adiabatic demangetization in the rotating frame, to be referred to later, removes the restriction of Eq. (4), and the measurement of extremely small μ_b' is then worth consideration.

III. THE DOUBLE RESONANCE PROCESS

The density matrix method[4,11] is now applied to the formulation of the rate at which the a and b systems interact in several cases. Other foreign nuclear ingredients will be omitted from our consideration because they will have no effect upon the double resonance interaction between the a and b spins as long as the applied rf fields are sufficiently intense. The spin system is described by the Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{rf}}, \tag{25}$$

where

$$\mathcal{H}_0 = -\hbar\Omega_a I_z{}^a - \hbar\Omega_b I_z{}^b; \tag{26}$$

$$\begin{aligned}\mathcal{H}_{\text{int}} = -\hbar \sum_i \sum_{i>j} [A_{ij}{}^a \mathbf{I}_i{}^a \cdot \mathbf{I}_j{}^a + B_{ij}{}^a I_{zi}{}^a I_{zj}{}^a] \\ -\hbar \sum_k \sum_{k>l} [A_{kl}{}^b \mathbf{I}_k{}^b \cdot \mathbf{I}_l{}^b + B_{kl}{}^b I_{zk}{}^b I_{zl}{}^b] \\ -\hbar \sum_i \sum_k [C_{ik} I_{zi}{}^a I_{zk}{}^b + J_{ik} \mathbf{I}_i{}^a \cdot \mathbf{I}_k{}^b];\end{aligned} \tag{27}$$

$$\mathcal{H}_{\text{rf}} = -2\hbar\omega_{1a} I_x{}^a \cos\omega_a t - 2\hbar\omega_{1b} I_x{}^b \cos\omega_b t; \tag{28}$$

and the indice pairs i, j and k, l are summed over the a and b spins, respectively. Also

$$\begin{aligned} I_q{}^a = \textstyle\sum_i I_{qi}{}^a; \quad I_q{}^b = \textstyle\sum_k I_{qk}{}^b; \\ C_{ik} = (3\gamma_a\gamma_b\hbar/2r_{ik}{}^3)(3\cos^2\theta_{ik} - 1); \\ A_{ij}{}^a = \tfrac{1}{3}B_{ij}{}^a + J_{ij}{}^a, \\ B_{ij}{}^a = (3\gamma_a{}^2\hbar/2r_{ij}{}^3)(3\cos^2\theta_{ij} - 1);\end{aligned} \tag{29}$$

and $A_{k1}{}^b$, $B_{k1}{}^b$ are similarly defined for the b spins. The J_{ik} term expresses the indirect dipole-dipole exchange interaction caused by the hyperfine coupling of electrons communicated between nuclear spin pairs.[12] The remaining terms in $\mathcal{H}_{\text{int}}$ represent only the secular or truncated[7] part of the tensor magnetic dipole-dipole interaction, where r is the radial distance between spin pairs and θ is the angle between $\mathbf{r}$ and $\mathbf{H}_0$. The terms $\mathcal{H}_0$ and $\mathcal{H}_{\text{rf}}$ represent, respectively, the nuclear Zeeman interaction and the interaction with applied rf fields.

First it will be convenient to apply certain unitary transformations to the density matrix ρ, and to justify the existence of an invariant magnetization of the a spins in the rotating frame as Redfield did.[4] The decay of the magnetization owing to very long spin lattice times T_{1a} will be neglected.

The density matrix ρ is defined so that the expectation value of any operator Q is given by

$$\langle Q \rangle = \text{Tr}(\rho Q), \tag{30}$$

and ρ satisfies the equation

$$d\rho/dt = -(i/\hbar)[\mathcal{H}, \rho], \tag{31}$$

which has the formal solution

$$\rho = \exp[-(i/\hbar)\mathcal{H}t]\rho_0 \exp[(i/\hbar)\mathcal{H}t], \tag{32}$$

if $\mathcal{H}$ is time independent. Before any rf pulses are applied, the spin system is in thermal equilibrium with the lattice at a temperature T and is described by

$$\rho_0 = \exp(-\mathcal{H}_0/kT)/\text{Tr}\exp(-\mathcal{H}_0/kT), \tag{33}$$

if $\mathcal{H}_0$ is large compared to $\mathcal{H}_{\text{int}}$. As described in Sec. II, the net effect of the 90° pulse and the 90° phase shift of the field H_{1a} is to bring the magnetization M_{0a} into alignment with H_{1a} along the x axis in the rotating frame. This is equivalent to a 90° rotation about the y axis, and the resulting density matrix is

$$\rho_0{}^* = R^{-1}\rho_0 R = \frac{1}{\alpha}\exp\left(\frac{+\hbar\Omega_a I_x{}^a + \hbar\Omega_b I_z{}^b}{kT}\right), \tag{34}$$

where $\alpha = \text{Tr}\exp(-\mathcal{H}_0/kT)$, and $R = \exp(-i\pi I_y{}^a/2)$. We apply a series of transformations, beginning with

$$\rho^* = R_0{}^{-1}\rho R_0, \tag{35}$$

$$\mathcal{H}^* = R_0{}^{-1}\mathcal{H}R_0 + \hbar\omega_a I_z{}^a + \hbar\omega_b I_z{}^b, \tag{36}$$

where

$$R_0 = \exp[-i(\omega_a I_z{}^a + \omega_b I_z{}^b)t]. \tag{37}$$

In this manner further transformations $\rho^* \rightarrow \rho_r$ and $\mathcal{H}^* \rightarrow \mathcal{H}_r$ are carried out with the transformation operator R_1, where

$$\begin{aligned} R_1 = \exp(-i\beta I_x{}^b t)\exp(-i\theta I_y{}^b)\exp(-i\omega_{1a} I_x{}^a t), \\ R_1{}^{-1} = \exp(i\omega_{1a} I_x{}^a t)\exp(i\theta I_y{}^b)\exp(i\beta I_x{}^b t), \\ \theta = \tan^{-1}(\Delta\omega_b/\omega_{1b}), \quad \beta = [\Delta\omega_b{}^2 + \omega_{1b}{}^2]^{1/2},\end{aligned}$$

and

$$\Delta\omega_b = \omega_b - \Omega_b. \tag{38}$$

The new quantities ρ_r and $\mathcal{H}_r$ satisfy an equation of the same form as Eq. (31). Their expressions written below do not include high-frequency nonsecular terms involving oscillations at frequencies ω_{1a} and ω_{1b} as these terms are assumed to average to zero. The summation signs over various indices are omitted, and A_a, B_a, A_b, B_b, C_{ab}, J_{ab} replace $A_{ij}{}^a$, $B_{ij}{}^b$, $A_{kl}{}^b$, $B_{kl}{}^b$, C_{ik}, J_{lk}, respectively. With

$$\mathcal{H}_r = \mathcal{H}_{r0} + \mathcal{H}_{r1}, \tag{39}$$

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[11] F. Bloch, Phys. Rev. **102**, 104 (1956).

[12] H. S. Gutowsky, D. W. McCall, and C. P. Slichter, J. Chem. Phys. **21**, 279 (1953); E. L. Hahn and D. E. Maxwell, Phys. Rev. **88**, 1070 (1952).

therefore,

$$\mathcal{H}_{r0}=-\hbar(A_a+B_a/2)\mathbf{I}_i^a\cdot\mathbf{I}_j^a+\hbar(B_a/2)I_{xi}^aI_{xj}^a -\hbar(A_b+\tfrac{1}{2}B_b\cos^2\theta)\mathbf{I}_k^b\cdot\mathbf{I}_l^b +\hbar\tfrac{1}{2}B_b(1-3\sin^2\theta)I_{xk}^bI_{xl}^b; \quad (40)$$

$$\mathcal{H}_{r1}=-\tfrac{1}{2}\hbar(C_{ab}+J_{ab})\cos\theta[(I_{zi}^aI_{zk}^b+I_{yi}^aI_{yk}^b)\times\cos(\omega_{1a}-\beta)t +(I_{zi}^aI_{yk}^b-I_{yi}^aI_{zk}^b)\sin(\omega_{1a}-\beta)t]; \quad (41)$$

and

$$\rho_{r0}\approx\hbar\Omega_aI_x^a/\alpha kT. \quad (42)$$

The initial density matrix ρ_{r0} for the a spins is obtained from expansion of Eq. (34) according to the high-temperature approximation; and the initial density matrix of the b spins is zero at $t=0$ because of the saturation caused by H_{1b} before spin locking occurs. Significant properties to be noted are

$$[\mathcal{H}_{r0},\rho_{r0}]=0; \quad (43a)$$

$$[\mathcal{H}_{r1},\rho_{r0}]\neq 0. \quad (43b)$$

When $\omega_{1b}\neq\beta$, the term $\mathcal{H}_{r1}$ is nonsecular and it is effectively averaged to zero. Under this condition the state of the spin system in the rotating frame remains constant because of Eq. (43a). When the magnitudes of the rf fields applied to the a and b spins are adjusted so that $\omega_{1a}\cong\beta$ then the term $\mathcal{H}_{r1}$ can no longer be neglected and because of Eq. (43b) a double resonance effect takes place. Density matrixes ρ_{ra} and ρ_{rb} exist for the a and b systems, respectively, so that

$$\rho_r(t)=\rho_{ra}+\rho_{rb}, \quad (44)$$

where ρ_{rb} is generated for $t>0$. It follows from

$$[I_x^a+I_x^b, \mathcal{H}_r]=0 \quad (45)$$

that the sum of population differences $n_a+n_b=n_{a0}$ is a constant when the double resonance conditions are satisfied.

IV. SOLUTIONS FOR THE *a–b* SPIN-SPIN INTERACTIONS

A. *J* Coupling in Liquids

The exact interaction of a-b coupled nuclei can be calculated for isolated pairs in liquids where only the J interaction is present. From Eq. (41) we write

$$\mathcal{H}_{r1}=-\tfrac{1}{2}\hbar J_{ab}(I_{zi}^aI_{zk}^b+I_{yi}^aI_{yk}^b) \quad (46)$$

to obtain M_a by calculating

$$M_a=\gamma\hbar\,\mathrm{Tr}(\rho_rI_x^a) \quad (47)$$

at the exact resonant condition $\omega_{1a}=\beta=\omega_{1b}$. The quantity ρ_{r0} is obtained from Eq. (42). For $I_a=I_b=\frac{1}{2}$, and using a basis in which combinations of the individual spin states are diagonal[12] along H_0, it is easily shown from Eq. (31) for this particular problem that

$$\langle m|\rho_r(t)|m\pm1\rangle=\tfrac{1}{2}\exp(\pm iJ_{ab}t). \quad (48)$$

The magnetic state quantum numbers are restricted to $-1\leqq m$, $m\pm1\leqq1$, and all the elements $\langle m|\rho_r|m\rangle$ are identically zero. It follows from Eq. (47) that

$$M_a(t)=M_{a0}\cos^2(J_{ab}t/4), \quad (49)$$

and similarly, it is found that

$$M_b(t)=M_{a0}\sin^2(J_{ab}t/4). \quad (50)$$

The a and b spin populations are exchanged in a coherent sinusoidal fashion and the total population is conserved.

These results have been confirmed by measurements of the proton magnetization coupled with phosphorous nuclei in hypophosphorous acid, $HPO(OH)_2$. The result $J_{ab}/2\pi=708$ cps agrees with previous measurements[12] and in particular with a related double resonance pulsed echo measurement.[3]

B. Dipole-Dipole Interaction in Solids (Spin Temperature Assumption)

The more general case in which an exact solution is not possible must now be considered where $\mathcal{H}_{r1}$ can be treated as a perturbation so that ρ_r may be expanded in the form[13]

$$\rho_r=\rho_{r0}-\frac{i}{\hbar}\int_0^t d\lambda[\mathcal{H}_{r1}^*(\lambda),\rho_{r0}] -\frac{1}{\hbar^2}\int_0^t d\lambda\int_0^\lambda d\lambda'[\mathcal{H}_{r1}^*(\lambda),[\mathcal{H}_{r1}^*(\lambda'),\rho_{r0}]]+\cdots \quad (51)$$

where

$$\mathcal{H}_{r1}^*(\lambda)=\left[\exp\left(-\frac{i}{\hbar}\mathcal{H}_{r0}\lambda\right)\right]\mathcal{H}_{r1}(\lambda)\left[\exp\left(\frac{i}{\hbar}\mathcal{H}_{r0}\lambda\right)\right]. \quad (52)$$

The density matrix ρ_r will refer only to the a spins, and the b spin density matrix is assumed to be zero at all times because of saturation, discussed in Sec. II.

Upon taking the time derivative of ρ_r and letting $\tau=t-\lambda$ we obtain

$$\frac{d\rho_r}{dt}=-\frac{i}{\hbar}[\mathcal{H}_{r1}^*(t),\rho_{r0}] -\frac{1}{\hbar^2}\int_0^t[\mathcal{H}_{r1}^*(t),[\mathcal{H}_{r1}^*(t-\tau),\rho_{r0}]]d\tau. \quad (53)$$

We now make the assumption that ρ_{r0} may be replaced by ρ_r, the upper limit in the integral may be replaced by ∞, and the a spins are always described by a spin temperature. The density matrix will then be of the form of Eq. (42) which we rewrite as

$$\rho_r=\omega_{1a}I_x^a/\alpha kT_a, \quad (54)$$

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[13] A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, New York), Chap. VIII.

where T_a is a slowly varying function of the time. At $t=0$ the spin temperature T_a is equal to $(\omega_{1a}/\Omega_a)T$, the low temperature being a consequence of the large magnetization now polarized along the relatively small rf field. On calculating the rate of change of the magnetization in the rotating frame from

$$\dot{M}_a = \mathrm{Tr} M_{xa}\dot{\rho}_r = \frac{\gamma\hbar^2\omega_{1a}\,\mathrm{Tr}(I_x^a)^2}{\alpha k}\left(\frac{1}{T_a}\right) \tag{55}$$

using Eq. (47), we find that

$$\frac{dM_a(t)}{dt} = -\frac{\gamma_a\omega_{1a}}{\alpha k T_a} \times \int_0^\infty \mathrm{Tr}\{I_x^a[\mathcal{H}_{r1}^*(t),[\mathcal{H}_{r1}^*(t-\tau),I_x^a]]\}d\tau. \tag{56}$$

Now write

$$\mathcal{H}_{r1}^*(t) = \mathcal{H}_1^*(t)\cos(\omega_{1a}-\beta)t + \mathcal{H}_2^*(t)\sin(\omega_{1a}-\beta)t, \tag{57}$$

and define

$$\mathcal{H}_p^*(t) = \mathcal{H}_1^*(t) + \mathcal{H}_2^*(t), \tag{58}$$

where

$$\begin{aligned} \mathcal{H}_1^*(t) &= \exp\left(-\frac{i}{\hbar}\mathcal{H}_{r0}t\right)\mathcal{H}_1\exp\left(\frac{i}{\hbar}\mathcal{H}_{r0}t\right); \\ \mathcal{H}_2^*(t) &= \exp\left(-\frac{i}{\hbar}\mathcal{H}_{r0}t\right)\mathcal{H}_2\exp\left(\frac{i}{\hbar}\mathcal{H}_{r0}t\right); \end{aligned} \tag{59}$$

and

$$\begin{aligned} \mathcal{H}_1 &= -\hbar C_{ab}\,(I_{zi}^a I_{zk}^b + I_{yi}^a I_{yk}^b)\cos\theta, \\ \mathcal{H}_2 &= -\hbar C_{ab}\,(I_{zi}^a I_{yk}^b - I_{yi}^a I_{zk}^b)\cos\theta. \end{aligned} \tag{60}$$

The exchange interaction J is omitted. Then it follows that

$$\frac{dM_a(t)}{dt} = -\frac{\gamma_a\omega_{1a}}{\alpha k T_{1a}}\int_0^\infty \mathrm{Tr}\{I_x^a[\mathcal{H}_p(0),[\mathcal{H}_p^*(-\tau),I_x^a]]\} \times\cos(\omega_{1a}-\beta)\tau d\tau, \tag{61}$$

and the trace of terms involving coefficients of $\sin(\omega_{1a}-\beta)\tau$ are identically zero. Consequently, we write

$$\frac{dM_a(t)}{dt} = -\frac{1}{T_a}\int_0^\infty g(\tau)\cos(\omega_{1a}-\beta)\tau d\tau, \tag{62}$$

where

$$g(\tau) = (\gamma_a\omega_a/\alpha k)\,\mathrm{Tr}\{I_x^a[\mathcal{H}_p(0),\,[\mathcal{H}_p^*(-\tau),\,I_x^a]]\}. \tag{63}$$

In the above treatment it is to be understood that the b system is continually reheated by the applied field H_{1b} so that $T_b \approx \infty$. Therefore, if n_b were not zero, then Eq. (62) would contain the factor $(1/T_b - 1/T_a)$ in place of $1/T_a$. It should be noted that Eq. (8) is not valid when the double resonance conditions are not precisely met, and that in general, in the absence of irreversible absorption caused by externally applied rf fields, it is the total spin energy, and not the net population difference which remains constant. In order to calculate the line shape of the double resonance it is necessary to use Eq. (62). An explicit expansion of $g(\tau)$ into its first two terms gives

$$\begin{aligned} g(\tau) &= (\gamma_a\omega_a/\alpha)\,\mathrm{Tr}\{\mathcal{H}_p(0)\mathcal{H}_p^*(\tau)\} \\ &= (\gamma_a\omega_a/\alpha)[\mathrm{Tr}\{\mathcal{H}_p^2(0)\} \\ &\qquad -\tfrac{1}{2}\,\mathrm{Tr}\{\mathcal{H}_p(0),\mathcal{H}_{r0}\}^2\tau^2 + \cdots]. \end{aligned} \tag{64}$$

The complete expression for $g(\tau)$ can be approximated by writing

$$g(\tau) = g(0)\exp(-\tau^2/2T_p^2), \tag{65}$$

where

$$g(0) = (\gamma\omega_a/\hbar\alpha)\,\mathrm{Tr}\{\mathcal{H}_p(0)\}^2, \tag{66}$$

and

$$T_p^2 = \mathrm{Tr}\{\mathcal{H}_p(0)\}^2/\mathrm{Tr}\{\mathcal{H}_p(0)\mathcal{H}_{r0}(0)\}^2. \tag{67}$$

We find from Eq. (62) that

$$dM_a(t)/dt = -M_a(t) f W_{ab}, \tag{68}$$

where

$$W_{ab} = \left(\frac{\pi}{8}\right)^{1/2}\frac{T_\rho}{T_{ab}^2}\left(\frac{\omega_{1b}}{\beta}\right)^2\exp\left(-\frac{(\omega_{1a}-\beta)^2 T_\rho^2}{2}\right), \tag{69}$$

with

$$1/T_{ab}^2 = \langle\Delta\omega_{ab}^2\rangle = \tfrac{1}{3}I_b(I_b+1)\textstyle\sum_{i,k} C_{ik}^2. \tag{70}$$

The above sum is taken over all a and b sites for the case in which both the a and b nuclei are 100% abundant. The factor f in Eq. (68) takes into account any deviations from this condition. Equation (68) predicts a simple exponential behavior for the spin-locked magnetization which is valid for locking times long compared with T_ρ. However for locking times short compared with T_ρ one would expect a Gaussian-like decay. The expression for $M_a(t)$ in this region is approximated by letting the temperature T_a be constant, and by not setting the upper limit in the integral of Eq. (53) equal to infinity. After performing the integration, one obtains

$$\frac{dM_a(t)}{dt} \cong M_{0a}\frac{f}{2T_{ab}^2}\left(\frac{\omega_{1b}}{\beta}\right)^2\frac{\sin(\omega_{1a}-\beta)t}{(\omega_{1a}-\beta)}, \tag{71}$$

which gives

$$\frac{dM_a}{dt} = -M_{0a}\frac{f}{2T_{ab}^2}\left(\frac{\omega_{1b}}{\beta}\right)^2 t \tag{72}$$

for $(\omega_{1a}-\beta)t \ll 1$, where

$$M_{0a} = N_a\gamma_a\hbar^2\Omega_a I_a(I_a+1)/3kT. \tag{73}$$

When the double resonance interaction is coherent, one expects an oscillatory exchange of magnetization as in Eqs. (71), (49), and (50). In solids the coupling is made incoherent by the effect of T_ρ in Eq. (69), but one may observe the initial Gaussian character predicted by Eq. (72) before the decay becomes a simple exponential. In the remaining part of this paper we will assume that the spin-locking times are long compared with T_ρ so

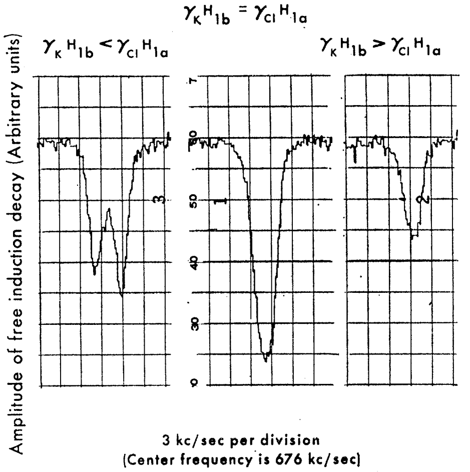

FIG. 2. The amplitude of the spin-locked Cl^{35} free-induction decay as a function of the frequency of the double-resonance rf field applied to the K^{39} nuclei, for three values of the K^{39} rf field intensity H_{1b} in $KClO_3$ at 77°K. The Cl^{35} rf field H_{1a} is fixed throughout.

that the spin-temperature approach is valid and the decay of $M_a(t)$ is described by simple exponential function. At the optimum double resonance when $\omega_{1a}=\beta$, $W_{ab}=N_aW_0$ is given by Eq. (12), where $T_p \approx T_{aa}$ is identified as the spin flip time among the a spins, which serves effectively as a short correlation time, and causes the disappearance of coherence in a-b spin coupling for times $t>T_{aa}$.

After a spin-locking time t the amplitude of the free precession signal M_a can be plotted as a function of $\Delta\omega_b$, where ω_b is changed slightly to a new setting for each repeated spin-locking sequence. For the condition that $fW_{ab}t \ll 1$, the line shape function is proportional to

$$\mathcal{S}=(\omega_{1b}/\beta)^2 \exp[\tfrac{1}{2}(\omega_{1a}-\beta)^2 T_{aa}^2]. \qquad (74)$$

Figure 2 shows the signal shapes obtained for cases $\omega_{1a}>\omega_{1b}$, $\omega_{1a}=\omega_{1b}$, and $\omega_{1a}<\omega_{1b}$ where ω_{1a} and ω_{1b} do not differ by much more than $1/T_{aa}$. When $\omega_{1a}>\omega_{1b}$ two resonances occur at approximately

$$\Omega_b=\omega_b \pm [\omega_{ab}^2-\omega_{1a}^2]^{1/2}, \qquad (75)$$

assuming that ω_{1a}, $\omega_{1b} \gg 1/T_{aa}$. If $\omega_{1a}=\omega_{1b} \gg 1/T_{aa}$, and $\Delta\omega_b$ is varied, the half-width of the resonance is given by

$$(\Delta\omega_b)_{1/2}=2(8\ln 2)^{1/4}(\omega_{1a}/T_{aa})^{1/2}. \qquad (76)$$

Figure 3 shows how the linewidth $(\Delta\omega_b)_{1/2}$ for $H_{1b}=10$ G is $\sqrt{2}$ greater than the width for $H_{1b}=5$ G, in agreement with Eq. (76). If $\omega_b=\Omega_b$, and ω_{1b} is varied through the double resonance, then

$$(\Delta\omega_b)_{1/2}=(2/T_{aa})(2\ln 2)^{1/2}. \qquad (77)$$

Equation (76) expresses the criterion for the precision which is possible in measuring values of $\omega_b=\Omega_b$. With $\omega_{1a}T_{aa}\approx 10$, and assuming that the center of the resonance can be reliably ascertained to within 1/10 of the observed linewidth, the accuracy is given roughly by

$$\Delta\nu_b/\nu_b \approx 1/(\omega_b T_{aa}). \qquad (78)$$

For $T_{aa}\approx 10^{-4}$ sec and $\omega_b \approx 2\pi\times 10^7$ sec^{-1} or greater, $\Delta\nu_b/\nu_b \approx 10^{-4}$. It is not impossible to carry out the double resonance when $\omega_{1a}T_{aa} \leqq 1$, referred to later, in which case the calculation is more complicated. It is expected on this basis that the precision given above could be improved.

C. Cross Coupling Between Rotating and Laboratory Frames

Double resonance detection of b spins is not only possible by means of population exchange between two rotating frames, analyzed so far, but it can also occur between the a system in its rotating frame and the b system initially at equilibrium in the laboratory frame. Among several possibilities,[14] let $\mathcal{H}_{\mathrm{int}}$ of Eq. (27) include the particular neglected truncated term

$$\mathcal{H}'=\hbar \sum_i \sum_k [E_{ik}I_{zi}^a I_{xk}^b + E_{ik}^* I_{zi}^a I_{yk}^b], \qquad (79)$$

where

$$E_{ik}=\tfrac{3}{2}(\sin\theta_{ik}\cos\theta_{ik})e^{-i\Phi}\gamma_a\gamma_b/r_{ik}^3, \qquad (80)$$

and Φ defines the azimuthal direction of r_{ik}. The perturbation $\mathcal{H}'$ will play the role of $\mathcal{H}_{r1}$ in Eq. (39) if $\mathcal{H}'$ is transformed to $\mathcal{H}_r'$ by the same set of transformations used in Sec. III. The importance of $\mathcal{H}_r'$ is shown in experiments[14,15] where ω_a is determined by a strong quadrupole interaction and Ω_b is determined by a small Zeeman splitting of the b spin levels. When the conditions

$$H_{1b}=0 \quad \text{and} \quad \omega_b=\Omega_b=\gamma_b H_0=\gamma_a H_{1a} \qquad (81)$$

apply, then

$$\mathcal{H}'=\mathcal{H}_r'. \qquad (82)$$

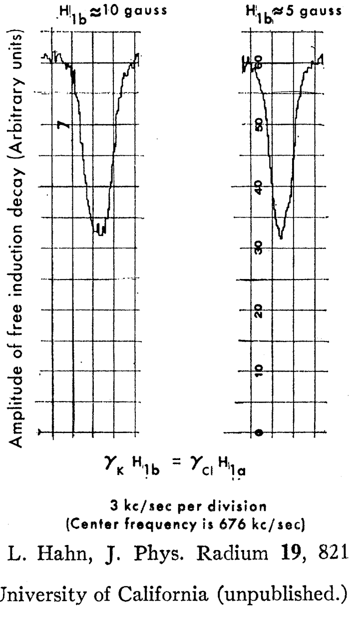

FIG. 3. The amplitude of the spin-locked Cl^{35} free-induction decay as a function of the frequency of the double-resonance rf field applied to the K^{39} nuclei, for two values of the K and Cl rf field intensities in $KClO_3$ at 77°K.

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[14] D. E. Kaplan and E. L. Hahn, J. Phys. Radium 19, 821 (1958).

[15] D. E. Kaplan, thesis, University of California (unpublished.)

The rate of a spin degradation is then similar to the previous case caused by the perturbation $\mathcal{H}_{r1}$, and is given by results similar to those expressed in Sec. III if C_{ik}^2 in Eq. (70) is replaced by $E_{ik}E_{ik}^*$.

D. Double Resonance Following Adiabatic Demagnetization in the Rotating Frame (ADRF)

Anderson and Hartmann[16] discuss various properties of the a system after it has been locked along H_{1a}, and adiabatically demagnetized by reducing H_{1a} to zero. Internal order and energy will reside in the a system. For $N_a \gg N_b$, and with $H_{1a} \rightarrow 0$, $\omega_a = \Omega_a$, we write Eq. (39) as

$$\mathcal{H}_r = \mathcal{H}_a + \mathcal{H}_b + \mathcal{H}_{ab},$$

where

$$\mathcal{H}_a = -\hbar \sum_{ij} (A_{ij}{}^a \mathbf{I}_i{}^a \cdot \mathbf{I}_j{}^a + B_{ij}{}^a I_{zi}{}^a I_{zj}{}^a), \qquad (83)$$

$$\mathcal{H}_{ab} = -\hbar \sum_{ik} (C_{ik} + J_{ik}) I_{zr}{}^a I_{zk}{}^b, \qquad (84)$$

and it is assumed that $\mathcal{H}_a \gg \mathcal{H}_b$. A spin temperature T_s is defined for the system after ADRF, and the density matrix is written as

$$\rho_r = \exp[-(\mathcal{H}_a + \mathcal{H}_{ab})/kT_s]/\mathrm{Tr}1 \qquad (85)$$

with $\mathcal{H}_b$ neglected. The energy

$$\langle \mathcal{H}_a \rangle = \mathrm{Tr}(\rho_r \mathcal{H}_a) \qquad (86)$$

resides only in the a system, but can be transferred to some extent into an energy sink represented by the a-b nearest-neighbor interaction of energy

$$\langle \mathcal{H}_{ab} \rangle = \mathrm{Tr}(\rho_r \mathcal{H}_{ab}). \qquad (87)$$

The perturbation $\mathcal{H}_{ab}$ will reduce the energy $\langle \mathcal{H}_a \rangle$ by a given amount after $\langle \mathcal{H}_{ab} \rangle$ is reduced in energy to essentially zero magnitude by bursts of saturating rf field H_{1b} at the laboratory resonance condition $\omega_b = \Omega_b$. After H_{1b} is applied for a short time t', it is turned off for a time interval $\Delta t > t'$ and $\langle \mathcal{H}_a \rangle$ then couples energy into $\langle \mathcal{H}_{ab} \rangle$, causing an increase in T_s. The coupling between a and b spins during the short time t' is negligible and any condition similar to Eq. (4) is not required. The elimination of this condition is an added experimental convenience because rf heating is reduced with $H_{1a} = 0$. If n saturating pulses are applied then the effective a-b interaction time is $n\Delta t = t$. The cumulative reduction in $\langle \mathcal{H}_a \rangle$ energy will be reflected in a reduction of M_a which is recovered and observed after H_{1a} is adiabatically turned on, and then abruptly turned off. The times for demagnetization and remagnetization are neglected compared to the time t given above.

The perturbation method is applied again, as in Sec. IV B but we now assume that the density matrix to be perturbed by the b system can be written as

$$\rho_r = \exp(-\mathcal{H}_a/kT_s)/\mathrm{Tr}1, \qquad (88)$$

and the rf pulses applied to the b system are supposed to increase the entropy of the a-b interaction system. Therefore, $d\langle \mathcal{H}_a \rangle/dt = \mathrm{Tr}(\mathcal{H}_a \dot{\rho}_r)$ is computed and the result, similar to Eq. (62), is

$$(d/dt)(1/T_s) = -K_{ab}/T_s, \qquad (89)$$

where

$$K_{ab} = \frac{1}{\hbar^2 \,\mathrm{Tr}(\mathcal{H}_a{}^2)} \int_0^\infty c(\tau) d\tau \qquad (90)$$

compares to $\tau_{ab}{}^{-1}$ in Eq. (11b). The correlation function is given by

$$c(\tau) = \mathrm{Tr}[\mathcal{H}_a, \mathcal{H}_{ab}][\mathcal{H}_a, \mathcal{H}_{ab}{}^*(\tau)], \qquad (91)$$

where

$$\mathcal{H}_{ab}{}^*(\tau) = \exp(-i\mathcal{H}_a \tau/\hbar) \mathcal{H}_{ab} \exp(+i\mathcal{H}_a \tau/\hbar). \qquad (92)$$

Expansion of $c(\tau)$ yields

$$c(\tau) = \mathrm{Tr}[\mathcal{H}_{ab}, \mathcal{H}_a]^2 + (-\tau^2/2) \times \mathrm{Tr}[[\mathcal{H}_{ab}, \mathcal{H}_a], \mathcal{H}_a]^2 + \cdots, \qquad (93)$$

and the Gaussian approximation of $c(\tau)$ gives

$$c(\tau) = \mathrm{Tr}[\mathcal{H}_{ab}, \mathcal{H}_a]^2 e^{-\tau^2/2T_q{}^2}, \qquad (94)$$

where

$$T_q{}^2 = \mathrm{Tr}[\mathcal{H}_{ab}, \mathcal{H}_a]^2 / \mathrm{Tr}[[\mathcal{H}_{ab}, \mathcal{H}_a], \mathcal{H}_a]^2. \qquad (95)$$

From Eq. (90) therefore,

$$K_{ab} = -(\pi/2)^{1/2} (T_q/\hbar^2) (\mathrm{Tr}[\mathcal{H}_{ab}, \mathcal{H}_a]^2 / \mathrm{Tr}[\mathcal{H}_a{}^2]). \qquad (96)$$

According to the above assumption of spin temperature,

$$M_a(t) = M_{0a} e^{-K_{ab} t}. \qquad (97)$$

It does not appear that the two methods for double resonance detection, in the extremes when H_{1a} is large, and when $H_{1a} = 0$, should differ widely in sensitivity. Measurements of K_{ab}, compared to $\tau_{ab}{}^{-1}$ given in Eq. (11b), have not yet been carried out, although a double resonance experiment after ADRF has been performed by Anderson and Hartmann[17] which shows that the effect does take place. Redfield has successfully applied a double resonance technique of a somewhat similar nature for the investigation of quadrupole interactions in metals at zero dc magnetic field.[18]

V. EXPERIMENTAL RESULTS

Experimental data are incomplete, at this writing, for confirmation of all the features of the theory which is the main presentation of this paper. For reasons of experimental development in our laboratory, it was first convenient to test some of the gross predictions with a nuclear quadrupole system. Although the NMR

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[16] A. G. Anderson and S. R. Hartmann, preceding paper [Phys. Rev. **128**, 2023 (1962)].

[17] C. P. Slichter and W. C. Holton, Phys. Rev. **122**, 1701 (1961).

[18] A. G. Redfield (private communication).

theory cannot be applied rigorously to the few results which are presented here, they do give a semiqualitative confirmation of the NMR theory. The anomalies characteristic of a quadrupole system will be discussed in a later report.

Figure 4 shows various plots of M_a vs t, the spin locking time, of 75% abundant Cl^{35} in a single crystal of $KClO_3$ at 77°K. The Cl^{35} nuclei, representing the a system, have a pure quadrupole resonance frequency $\omega_a/2\pi = 28.95$ Mc/sec, and relax according to Eq. (2) with $T_{1a} \sim 0.69$ sec as shown by the top plot. The second plot from the top shows how the K^{39} isotope (93% abundant b nuclei), when excited at the quadrupole resonance frequency $\omega_b/2\pi = 676.23$ kc/sec (with the rf amplitude adjusted so that $\omega_{1a} = \omega_{1b}$), depolarizes the Cl^{35} signal and saturates [according to Eqs. (6), (9a)] at $\tau_{DR} \approx [(N_a + N_b)W_0]^{-1}$. The condition of Eq. (9a) applies, $\xi = 0.55$, and H_{1b} is not shifted in phase periodically. The bottom plot shows the Cl^{35} decay when phase shifts of H_{1b} with a period of $\tau_s = 10$ msec are applied, and Eq. (10) describes the decay. Figure 5 indicates the large sensitivity for detection of K^{41} (6.9% abundant) at 20°K, where $T_{1a} \approx 60$ sec, $\omega_a/2\pi = 29.04$ Mc/sec, and $\omega_b/2\pi = 853.5$ kc/sec. With no phase shift on H_{1b} the Cl^{35} plot, not shown, is degraded about 7% for large t. With H_{1b} phase shifts of period $\tau_s = 10$ msec beyond a locking time of ~ 7 sec the Cl^{35} signal is reduced by more than 50%. The lowest curves in Figs. 4 and 5 are expected to be straight lines corresponding to simple exponential behavior. As indicated in Figs. 4 and 5 there is a small but definite curvature to the double resonance curves which indicates that the double resonance conditions are not completely satisfied throughout the crystal.

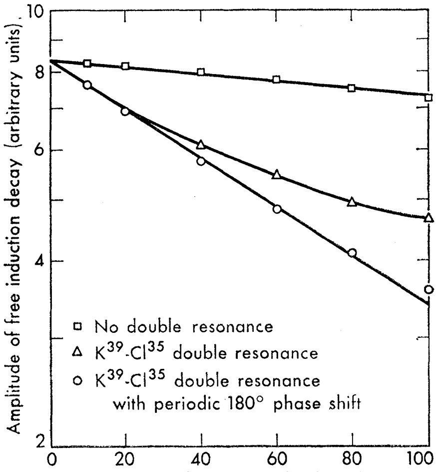

FIG. 4. K^{39}–Cl^{35} double resonance in $KClO_3$ at 77°K.

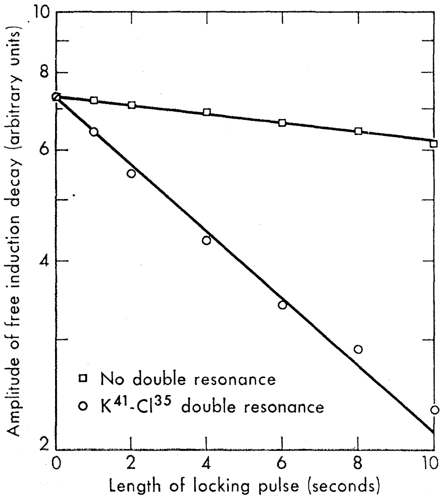

FIG. 5. K^{41}–Cl^{35} double resonance in $KClO_3$ at 20°K.

Equations (2), (7), and (9a) can be combined to give

$$\exp - \{W_{ab}(N_a + N_b)t/N_a\} = 1 + (A_{DR} - A)/A\xi, \quad (98)$$

where A_{DR} is the measured signal proportional to $n_a(t)$ in Eq. (9a) (with $n_{b0} = 0$), and A is the measured signal proportional to $n_a(t)$ of Eq. (2) when double resonance is absent. Equation (10) is used for $n_b(t) \approx 0$, and is rewritten as

$$A' = A_0 \exp[-(1/T_{1a} + N_b W_0)t] \quad (99)$$

to include the effect of T_{1a}. Separate plots of Eqs. (98) and (99) from the data represented in Fig. 4, give values of $W_0 N_a = (W_{ab})_{K^{39}} = 7.2$ sec^{-1} and 6.7 sec^{-1}, respectively, showing roughly an internal consistency in the data, although it was again found that a plot of Eq. (98) showed a departure from simple exponential behavior. From the K^{41} double resonance data of Fig. 5, Eq. (99) yields $(W_{ab})_{K^{41}} \approx 1.21$ sec^{-1} after correcting for the effect of T_{1a}. On the assumption that

$$\frac{(W_{ab})_{K^{41}}}{(W_{ab})_{K^{39}}} = \left[\frac{(T_{ab})_{K^{39}}}{(T_{ab})_{K^{41}}}\right]^2, \quad (100)$$

a value of $(W_{ab})_{K^{41}} \approx 2.1$ sec^{-1} would be predicted from the experimentally determined value of $(W_{ab})_{K^{39}}$. The discrepancy between this predicted value and the measured value of 1.2 sec^{-1} is not surprising, in view of the assumptions and possible errors involved. For K^{40} nuclei one obtains

$$\left[\frac{(T_{ab})_{K^{40}}}{(T_{ab})_{K^{41}}}\right]^2 \cong \left(\frac{\gamma_{41}}{\gamma_{40}}\right)^2 \cong 0.05,$$

where we have considered the species as 100% abundant. Using the experimentally determined value of $(W_{ab})_{K^{41}}$ together with Eqs. (99) and (100) it is found that for a double resonance time of 30 sec one can expect a 6% change in the Cl^{35} signal when the 0.012% abundant K^{40} nuclei are excited. Since this is an electric quadrupole system with $I = 4$ a factor of 4/9 is included to take into account the incomplete excitation of the spin system due to the uneven spacing of the energy levels. With the present signal to noise ratio of $S=100:1$ at $t=30$ sec the K^{40} resonance is expected to yield a signal to noise ratio of 6:1.

A. Stability Conditions

The amplitude stability of the spin-locked signal depends directly upon the average deviation of ω_a from resonance and the phase stability of H_{1a}. These represent different effects although they appear to be the same. A radical phase shift of H_{1a} caused by an impulse deviation of ω_a will cause spin transitions, or an effective depolarization of M_a about the new direction of H_{1a}. However, if the frequency deviation $\Delta\omega_a(t)$ is slowly changing so that $d[\Delta\omega_a(t)]/dt \ll \omega_{1a}^2$, the phase effect is not important although the frequency deviation can be important. The latter effect can be seen from a solution of the Bloch equations as modified by Redfield.[4] If M_{0a} is assumed first to be perfectly aligned along H_{1a} when spin locking begins, then thereafter

$$M_a(t)=M_{0a}\frac{[e^{-t/T_{1a}}\omega_{1a}{}^2+(1-e^{-t/T_{1a}})\Delta\omega_a\omega_{1a}]}{\omega_{1a}{}^2+\Delta\omega_a{}^2}. \qquad (101)$$

The dispersion mode involving $\Delta\omega_a/\omega_{1a}$ causes the most serious effect, giving a fractional signal deviation of

$$\Delta M_a/M_{0a} \approx \Delta\omega_a/\omega_{1a} \qquad (102)$$

for $\Delta\omega_a/\omega_{1a} \ll 1$. This deviation will compete with noise when $\Delta\omega_a/\omega_a \approx 1/eS$. With $S=100$ and $H_{1a}=5$ G for the Cl^{35} resonance in $\mathrm{KClO_3}$, the frequency must be stable to $\Delta\omega_a/\omega_0 \approx 10^{-6}$. The stability requirement on ω_b is not critical and ω_b need only be appreciably less than the double resonance linewidth given by Eq. (76).

The experiment reveals instability mainly because of phase shift fluctuations due to power amplifier instabilities, and by possible sudden changes in the impedance of the tuned sample coil. The coil is contained in a cryostat at low temperatures, and it may easily suffer disturbances because of the high power input of the H_{1a} field. For this reason it is attractive to carry out double resonance while $H_{1a}=0$, as discussed in Sec. IV. Rapid and steady fluctuations of H_{1a} can cause a reproducible reduction of M_a when the correlation time τ_c of the fluctuations is very short compared to the locking time t. However, serious disturbances arise from fluctuations with $\tau_c \sim t$, so that M_a, as measured from one spin-locking interval to the next, varies unpredictably. The signal-to-noise parameter S should include effects of such fluctuations, and our experiments have indicated rather high values of $S=200$ for $t=30$ sec.

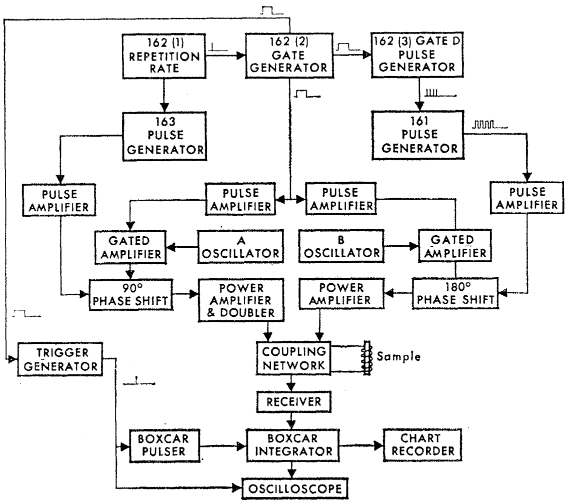

FIG. 6. Block diagram of spin-locked double-resonance apparatus.

B. Apparatus

In Fig. 6 a block diagram is given to illustrate the function of the separate units which comprise the double resonance apparatus. The overall repetition rate of spin locking is controlled by a Tektronix type 162 waveform generator, and a second type 162 generator produces a dc gating pulse, when triggered, which actuates the *a* and *b* power amplifiers. The 90° phase shift between the initial 90° rf pulse and the locking rf pulse is obtained by applying a dc pulse to a phase-shifting circuit while the initial 90° rf pulse is applied. When the dc pulse is removed, the phase of the rf changes by 90°. A third Tektronix type 162 waveform generator is operated in the gated mode to produce a series of pulses at a selected repetition rate. These pulses trigger a Tektronix type 161 pulse generator which then produces a series of dc pulses which actuate a phase-shifting circuit causing the phase of the rf pulse in the *b* amplifier to alternate by 180° at a regular rate.

A Hewlett Packard type 650 A test oscillator is used as the *b* system oscillator while a Gertch type FM-5 frequency divider driven by a Gertch type FM-6 frequency meter serves as the *a* system oscillator. In order to keep the rf radiation leakage at the *a* resonance frequency small, it is necessary to employ a frequency doubler stage before the final power amplifier and to gate the preamplifier which operates at half the *a* resonance frequency. Since the output of the FM-6 is rich in harmonics, and since rf leakage at the *a* resonance frequency interferes with the observed nuclear signal, it is necessary to operate the FM-6 at 1/14 of the *a* resonance frequency so that rf leakage is not serious.

The receiver recovery time after the application of the intense locking pulse is less than 50 μsec. The output of the receiver is detected and then sampled by a "box-car" integrator,[19] and its output drives a Brown 10-mV recorder. It is also possible to monitor the detected receiver signal with an oscilloscope. When the locking pulse is turned off, a trigger generator generates a pulse which triggers the oscilloscope and a pulse

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[19] D. Holcomb and R. E. Norberg, Phys. Rev. **98**, 1074 (1955).

generator of delayed output pulses which gates the "box-car" integrator.

The coil which encloses the sample is turned bimodally to ω_a and ω_b, and has three functions: It acts as the a signal receiver coil, and a transmitter coil, and the b transmitter coil. In order to observe an electric quadrupole resonance free-induction decay signal, it is necessary to have the receiver coil colinear with the transmitter coil. For this reason it is simpler to use one coil as both the receiver and transmitter coils for the a spins. Moreover, when one coil is made to serve as both the a and b transmitter, it is easier to satisfy the double resonance condition $\omega_{1a}=\omega_{1b}$ over individual volume elements of the sample.

IV. CONCLUDING REMARKS

The spin-locking method in solids has been applied for the purpose of double resonance spectroscopy, but it has other uses for investigations which are much less difficult. The method is a useful aid in studies of adiabatic demagnetization in the rotating frame,[16] and enables the measurement of modified T_{1a} values in H_{1a} fields comparable to h_{local}. These measurements compare to previous measurements[20,21] in the laboratory frame, and reveal additional properties of the local field.

With b nuclei present, T_{1a} in the rotating frame would conceivably be less than T_{1a} in the laboratory frame if the relaxation is determined by spin diffusion toward paramagnetic impurities. This should result because the "detuning effect" of b local fields, acting to reduce the a spin-spin coupling, is removed in the spin locked state. The nature of spin diffusion under various controlled values of the local field can, therefore, be studied. The double resonance process itself enables the determination of separate spin-spin interaction parameters between a chosen a-b pair of systems.

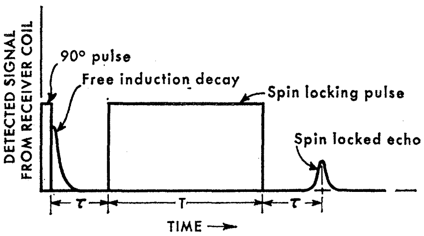

FIG. 7. Formation of the spin-locked echo.

The attenuation of the stimulated echo lifetime due to spin diffusion among the a spins alone can be studied in the rotating frame. Figure 7 illustrates how the dephased components of magnetization, which develop in a time τ after a 90° pulse, are locked in the rotating frame for a time T. During T the magnetization has "x-axis memory" along H_{1a}, giving rise to an echo at time τ after the locking pulse is removed. This echo behaves similarly in its amplitude dependence to a stimulated echo formed after a three pulse 90°–90°–90° sequence,[22] where τ is the interval between the first two pulses, T is the interval between the second and third pulses, and the stimulated echo occurs at $T+2\tau$ with respect to the first pulse. The nuclei in this case display "z-axis memory" in the laboratory frame during time T.

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[21] A. G. Anderson and A. Redfield, Phys. Rev. **116**, 583 (1959).

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