

and

$$t = (\hbar\alpha_1/m\omega_0)^{1/2}q_x. \quad (\text{A3})$$

It is not difficult to demonstrate that

$$f_{n'n}(-\mathbf{q}) = (-1)^{n'+n}f_{n'n}(\mathbf{q}) \quad (\text{A4})$$

and that

$$f_{nn'}(\mathbf{q}) = \exp(-ist)f_{n'n}^*(-\mathbf{q}).$$

There exist some useful sum rules for the functions $f_{n'n}(\mathbf{q})$ and $X_{n'n}^{(\pm)}(\mathbf{q})$ which are similar to those given in the Appendix of Ref. 3. The reader is referred to this reference for further details.

Variation of Nuclear Spin Polarization Time with Excitation of Electron Resonances*

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In solid dielectric materials where nuclear and electron spins are coupled by dipolar interaction, positive and negative enhancements of the nuclear polarization are produced by inducing simultaneous electron-nuclear transitions (double-flip transitions). The nuclear polarization time τ_N is defined to be the time constant associated with the approach of the nuclear spin system to the enhanced state. We have measured the proton polarization time of several such materials and found that τ_N is less than the thermal relaxation time when double flips are induced and greater, sometimes by two orders of magnitude, when the central electron resonance is excited. The first effect is understandable from the spin polarization rate equations. One expects, qualitatively, that the second effect can be explained by a decoupling of electron and proton spins due to stirring of electron spins by the applied rf field; such an explanation is shown to be incorrect.

I. INTRODUCTION

IN 1953, Overhauser¹ proposed a method whereby the polarization of the nuclear spin states in a metal could be enhanced by saturation of the paramagnetic resonance of the conduction electron spins. It was soon pointed out by others² that spin polarization enhancement is not limited to metals but could be obtained whenever two spin systems are coupled and an rf magnetic field is applied at, or near, the Larmor frequency of one of them. (The term "rf" is understood to include microwave frequencies.) We are here concerned with solid dielectric materials containing paramagnetic centers in which the paramagnetic spins S are coupled to the nuclear spins I by dipolar interaction. It is well known that in such materials the nuclear spin polarization is enhanced when simultaneous electron-nuclear spin flips are induced.³⁻⁵ These double-flip transitions are weakly forbidden and are possible because of mixing of the spin states by the dipolar interaction. When the frequency

of the applied rf magnetic field is $\nu_e - \nu_N$ (ν_e and ν_N are, respectively, the electron and nuclear Larmor frequencies) the polarization is positively enhanced and when the frequency is $\nu_e + \nu_N$ the polarization enhancement is negative. The enhancement is zero when pure electronic transitions only are induced. This type of enhancement is commonly referred to as the "solid-state effect."

When enhancement is caused by exciting a double-flip transition the nuclear spin system approaches the enhanced population distribution exponentially with the characteristic time τ_N , the polarization time. Upon removal of the excitation the spin system decays to thermal equilibrium, the rate being given by the thermal relaxation time T_{1N} .

The electron spins exchange energy with the lattice directly via electron-phonon interaction, while direct contact of the nuclear spins with the lattice is very weak and energy is exchanged via the dipolar interaction with the electron spins. The rate of exchange of energy between the nuclear spins and the lattice depends on the spectral density, at frequency ν_N , of the time varying, electron-induced dipolar field at the nuclear sites. Thus, one would expect nuclear polarization and relaxation times to depend on the rate of stirring of the electron spins by the applied rf field since rapid stirring can alter the spectral density if the rf field is large enough. Qualitatively, we expect the following: (1) When pure electronic transitions are induced, the forced flipping of the electron spins will decouple them from the nuclear spins causing a de-

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¹ A. W. Overhauser, Phys. Rev. **92**, 411 (1953).

² A. Abragam, Phys. Rev. **98**, 1729 (1955); A. Abragam and W. G. Proctor, Compt. Rend. **246**, 2253 (1958); C. D. Jeffries, Phys. Rev. **106**, 164 (1957).

³ A. Abragam and W. G. Proctor, Compt. Rend. **246**, 2253 (1958).

⁴ C. D. Jeffries, Phys. Rev. **106**, 164 (1957).

⁵ Edmond Erb, Jean-Loup Motchane, and Jean Uebersfeld, Compt. Rend. **246**, 2121 and 3050 (1958).

crease in the rate at which energy is exchanged between the nuclear spin system and the lattice, if the decoupling is large enough. (2) When double-flip transitions are induced there is an increase in the indirect participation of the nuclear spins in the electron relaxation process increasing the rate of energy exchange between nuclear spins and the lattice.

In the work reported in this paper⁶ we have measured proton polarization times as a function of the magnitude of the exciting rf field and the value of the external dc magnetic field, the rf frequency being constant. Leifson and Jeffries⁷ have also reported experimental observation of a decrease in the nuclear polarization time when one of the double-flip transitions is excited.

In Sec. IV we solve the spin polarization rate equations, the solutions being in agreement with the experimental results for double-flip excitation. Attempts to calculate the affect of stimulating pure electronic transitions are not in agreement with the experimental results as will be shown also in Sec. IV.

II. EXPERIMENTAL PROCEDURE

The nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) data were obtained using the Rutgers University 21-in. electromagnet and homemade spectrometers. 200-cps field modulation was used and the derivative of the resonance signals were recorded, or for the measurements of polarization time the absorption signal was observed directly on an oscilloscope. The experiments were performed in an external magnetic field of 3500 G, at a proton resonance frequency of 14.79 Mc/sec and an electron resonance frequency of 9750 Mc/sec.

In the EPR spectrometer a Varian X-13 klystron delivers energy to a tunable, cylindrical, reflection cavity oscillating in the TE₀₁₁ mode. In order to utilize the full output power of 200 mW the circuits for monitoring the input and reflected power, and for stabilizing the microwave frequency are coupled to the waveguide via directional couplers.

A Pound, Knight, Watkins spectrometer⁸ with the oscillator tank coil placed in the center of the microwave cavity was used to detect the proton resonance. The transient behavior of the nuclear spin system was measured by observing the audio output of the spectrometer on a triggered oscilloscope, relaxation times being measured by observing the decay of the resonance signal from the enhanced state to thermal equilibrium upon switching off the microwave power, while polarization times were measured by observing the growth to the enhanced state upon switching on

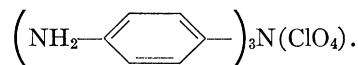
the power. All polarization and relaxation times were measured at the center of the nuclear resonance absorption signal and in all cases the rates measured were well represented by a single exponential. The external magnetic field was varied so that various points of the electron or double-flip absorptions were excited, the microwave frequency remaining constant.

Five different materials were investigated: (1) asphalt, (2) 5% Ce in (Ce,Ln)₂Mg₃(NO₃)₁₂·24H₂O (abbreviated CMN), (3) and (4) 1% and 10%, by weight, of diphenyl picryl hydrazil dissolved in polystyrene (abbreviated 1% DPPH and 10% DPPH), and (5) tris (*p*-aminophenyl) aminium perchlorate⁹ (abbreviated AMI). Table I lists the general details of the proton and paramagnetic resonances and the enhancement obtained for these materials. The enhancement is defined as $(A - A_0)/A_0$ where A and A_0 are, respectively, the enhanced and unenhanced magnitude of the proton resonance signal.

A flat hexagonal crystal of CMN was grown from aqueous solution. All measurements were made with the broad face of the crystal parallel to the external magnetic field with the field perpendicular to one of the edges of the hexagon. For this alignment we observed a proton resonance spectrum of two partially resolved lines; the linewidth listed in Table I was measured over the whole spectrum. Extensive measurements of proton resonance enhancement in this material have been reported by Leifson and Jeffries,⁷ their results being in good agreement with those reported here.

DPPH was dissolved in polystyrene by dissolving both substances in a solvent and allowing the mixture to dry. Precautions were taken to insure that the DPPH dissolved completely but there is no assurance that microscopic clusters of the free radical are not present in the plastic.

AMI is an organic free radical with the following chemical structure¹⁰:



At room temperature, the proton polarization enhancement is of the Overhauser type, while at 1.7°K pure solid-state effect enhancement is observed. A similar changeover from Overhauser to solid-state effect enhancement has been reported previously.¹¹

III. RESULTS

Figure 1 shows the measured dependence of the proton polarization time on the value of the external magnetic field for all of the materials investigated.

⁶ A portion of this work has been reported earlier: G. E. Schacher and H. C. Torrey, Bull. Am. Phys. Soc. 7, 85 (1962).

⁷ O. S. Leifson and C. D. Jeffries, Phys. Rev. 122, 1781 (1961).

⁸ R. V. Pound and W. D. Knight, Rev. Sci. Instr. 21, 219 (1950).

⁹ The author wishes to thank Dr. Robert I. Walter, Department of Chemistry, Haverford University for supplying this material.

¹⁰ R. I. Walter, R. S. Codrington, Amedo F. D'Adamo, Jr., and H. C. Torrey, J. Chem. Phys. 25, 319 (1956).

¹¹ R. H. Webb, Phys. Rev. Letters 11, 611 (1961).

TABLE I. General data for the samples used. The resonance linewidths are measured between absorption derivative extrema. The enhancement width is measured between points of maximum positive and maximum negative enhancement.

Sample	Temperature (°K)	EPR line-width (gauss)	NMR line-width (gauss)	Enhancement width (gauss)	Maximum enhancement ^a
Asphalt	~300	3.40	3.30	11.9	7.29
	1.7	1.58	9.26	13.8	13.3
10% DPPH	~300	2.50	2.90	19.6	0.39
	1.7	16.5	8.80	35.0	5.85
1% DPPH	~300	13.0	3.30	15.9	4.30
	77	21.0	8.0	18.4	14.0
	1.7	20 (5 lines 10 G apart)	9.25	38.3	21.6
AMI	~300	0.84	9.5	Overhauser effect	0.65
	1.7	3.82	7.85	23.1	3.20
CMN	1.7	13.5	10.2	73.3	41.5

^a For 200-mW input power to the microwave cavity.

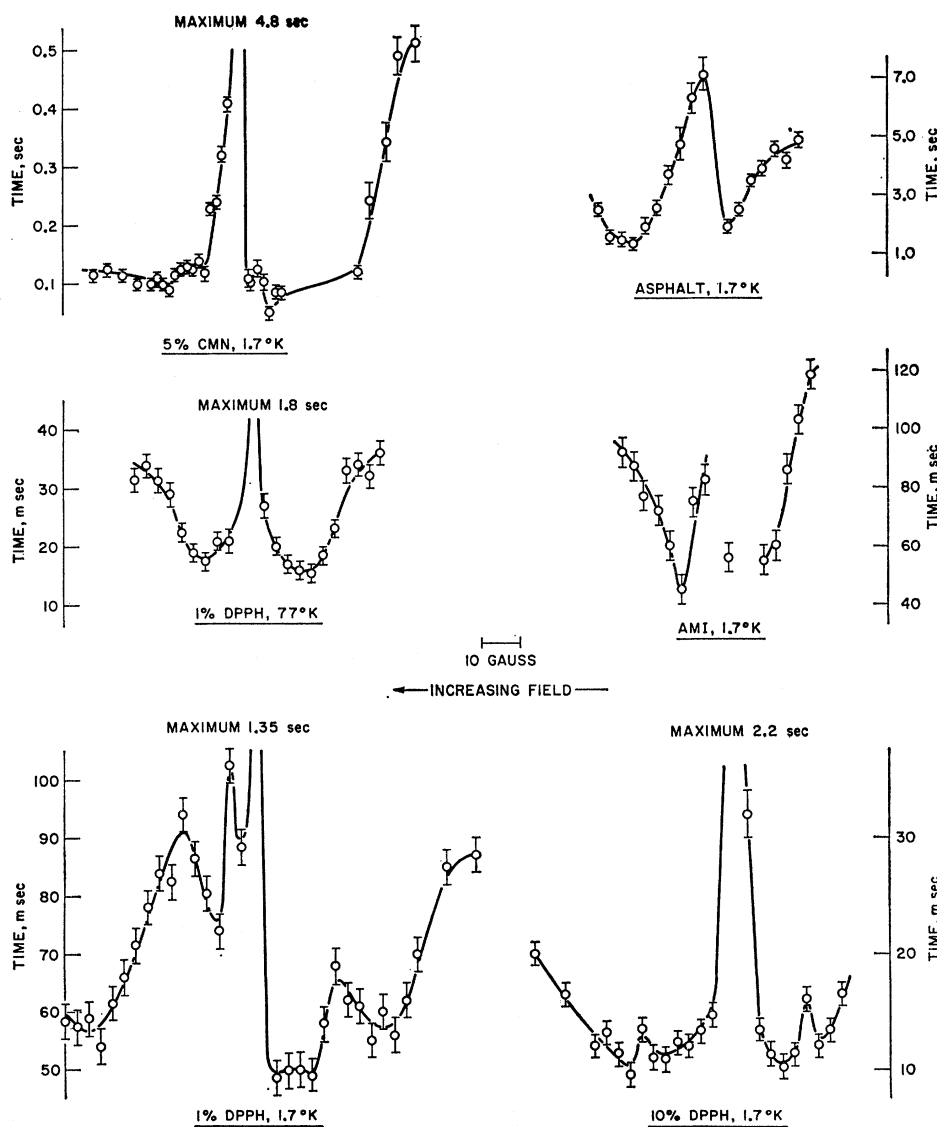


FIG. 1. Proton polarization time versus external magnetic field for 200-mW input power to the microwave cavity. The horizontal scale for CMN is one-half that indicated.

TABLE II. Measured proton spin relaxation and polarization times.

Sample	Relaxation time (sec)	Polarization time	
		Electronic transitions excited (sec)	Double-flip transitions excited (sec)
Asphalt 1.7°K	4.0	6.75	1.15
10% DPPH 1.7°K	0.026	2.25	0.010
1% DDPH 77°K	0.036	1.85	0.014
1.7°K	0.087	1.35	0.045
CMN 1.7°K	1.28	4.80	0.145
AMI 1.7°K	0.116	a	0.045

* Not possible to measure.

The center of each curve, where the polarization time increases sharply, is at the center of the electron resonance. In all materials investigated the polarization time follows, qualitatively, the expected behavior, i.e., decreasing with excitation of double-flip transitions and increasing with excitation of pure electronic transitions with τ_N approaching T_{1N} as the far wings of the double-flip absorption lines are approached (as the double-flip transition probability approaches zero).

Upon examination of Fig. 1 and Table I we see that the minima in the polarization time correspond approximately to the maxima in enhancement, an expected result since both extrema should occur when the effective double-flip transition probabilities are maximum. The maximum effective probabilities do not occur at the fields $H_e \pm (\gamma_N/\gamma_e)H_N$ (a separation of 5 G to either side of the electron resonance), as one might expect, due to overlap of the wings of the electron resonance line with the double-flip absorption lines which leads to competing effects. An analytical expression for the dependence of the nuclear polarization on the rf and lattice-induced transition probabilities^{7,12}

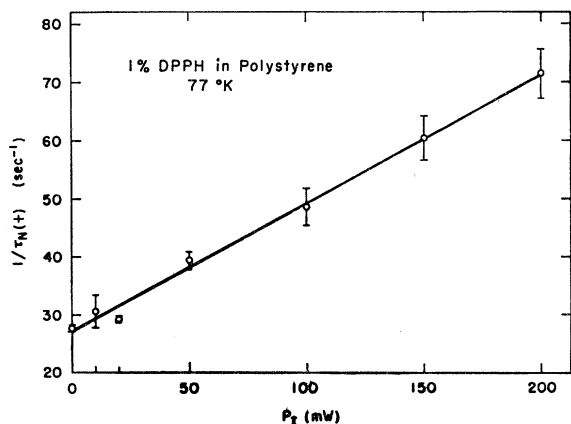


FIG. 2. Reciprocal proton polarization time versus input power to the microwave cavity.

¹² R. H. Webb, thesis, Rutgers University, 1959 (unpublished).

shows that the effects produced by rf excitation of double-flip transitions are reduced if the rf-induced transition probability for pure electronic transitions is nonzero. The transition probability for pure electronic transitions is much larger than that for the forbidden double-flip transitions quite far into the wings of the electron resonance absorption, resulting in the extrema of polarization time and enhancement being much further than 5 G from the center of the electron resonance.

Table II lists the measured values of proton relaxation and polarization times for 200-mW incident power to the microwave cavity. The values listed for double-flip excitation were obtained with the field set to give maximum positive enhancement.

In all of the materials investigated exciting pure electronic transitions reduces the rate of approach of the proton spin system to the enhanced state. The increase in the polarization time is quite large (as much as two orders of magnitude for DPPH in polystyrene) indicating that the proton spin system ex-

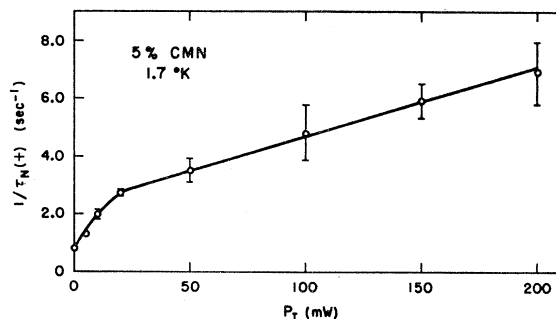


FIG. 3. Reciprocal proton polarization time versus input power to the microwave cavity.

changes energy with the lattice predominantly via dipolar interaction with electron spins, as expected. These data are very difficult to obtain due to the small enhancement near the center of the electron resonance. We attempted to measure the dependence of the increase of polarization time on the input microwave power but because of experimental difficulties no accurate results could be obtained. There is some indication the dependence is linear.

Measurements of the dependence of the polarization time on microwave power P_I for exciting double-flip transitions are shown in Figs. 2 and 3 for two of the samples. Theoretically, one expects τ_N^{-1} to depend linearly on the microwave power (see Sec. IV) and this dependence was found for all materials except asphalt and CMN. In the latter two materials τ_N^{-1} rises very quickly then becomes linear in P_I for higher powers (Fig. 3). This anomalous behavior at low powers is not understood.

The structure seen on the graphs in Fig. 1 is due to the fine structure (or hyperfine structure) of the elec-

tron resonance line, e.g., 1% DPPH has an EPR spectrum of five partially resolved lines at 1.7°K and five peaks are seen on the plot of polarization time versus field.

IV. DISCUSSION

We shall calculate the transient behavior of the nuclear spin system when double-flip transitions are excited by finding solutions to the spin polarization rate equations. The behavior when pure electronic transitions are excited cannot be evaluated in the same way since under these conditions there is no net change in nuclear spin populations. Although the qualitative interpretation of the experimental result when stimulating pure electronic transitions seems reasonable, the theoretical interpretation remains obscure. We will solve for the character of the electron induced local field at nuclear sites caused by rf and lattice-induced electron spin flips, the transient behavior of the electron spin system upon turning on an rf pulse at the electron resonant frequency being treated by the method of transient nutations.¹³

A. Exciting Double-Flip Transitions

Let N be the total number of nuclear spins, n the total number of electron spins, N_+ and N_- the number of spins aligned parallel and antiparallel to the external magnetic field, etc. Figure 4 is the diagram of the Zeeman energy levels of an electron-nucleus pair placed in an external magnetic field. The coupling of

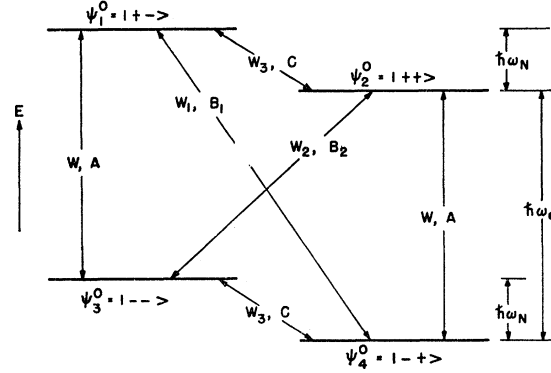


Fig. 4. Zeeman energy levels and transition probabilities for an electron-nucleus pair.

the spins with the external field is much larger than the dipolar interaction so that the zero-order wave functions shown may be used to characterize the energy states, e.g., in the state function $|+->$ the first sign indicates that the electron spin is aligned parallel to the external field while the second indicates that the nuclear spin is aligned antiparallel. We consider only $I=S=\frac{1}{2}$. The W 's are the lattice-induced transition probabilities while A , B_1 , B_2 , and C are the rf-induced transition probabilities. Referring to Fig. 4 and defining all transition probabilities to be values averaged over the whole sample we write the rate equations for spin population as follows^{7,11}:

$$\begin{aligned} dN_+/dt = & [(W_3 + W_x)e^{+\beta\delta} + W_1e^{+\beta(\Delta+\delta)} + B_1 + C]N_-n_+/n + [(W_3 + W_x)e^{+\beta\delta} + W_2e^{-\beta(\Delta-\delta)} + B_2 + C]N_-n_-/n \\ & - [(W_3 + W_x)e^{-\beta\delta} + W_2e^{+\beta(\Delta-\delta)} + B_2 + C]N_+n_+/n - [(W_3 + W_x)e^{-\beta\delta} + W_1e^{-\beta(\Delta+\delta)} + B_1 + C]N_+n_-/n, \end{aligned} \quad (1)$$

$$\begin{aligned} dn_+/dt = & [We^{-\beta\Delta} + W_2e^{-\beta(\Delta-\delta)} + B_2 + A]n_-N_-/N + [We^{-\beta\Delta} + W_1e^{-\beta(\Delta+\delta)} + B_1 + A]n_-N_+/N \\ & - [We^{+\beta\Delta} + W_1e^{+\beta(\Delta+\delta)} + B_1 + A]n_+N_-/N - [We^{+\beta\Delta} + W_2e^{+\beta(\Delta-\delta)} + B_2 + A]n_+N_+/N, \end{aligned} \quad (2)$$

where $\Delta = \frac{1}{2}\hbar\omega_e$, $\delta = \frac{1}{2}\hbar\omega_N$, $\beta = 1/kT$, N_+/N is the probability that a nuclear spin will be aligned with the field, etc. W_x is the natural, nuclear transition probability due to all causes other than relaxation via dipolar interaction with the electron spins. Equations (1) and (2) are the same as Eqs. (10) and (11) of Ref. 7 in all respects save one: In Eq. (10) of Ref. 7, all transition probabilities that are due to electron-nuclear dipolar coupling are multiplied by the factor n/N to take into account the number of electron spins being much less than the number of nuclear spins. The transition probabilities used in the rate equations given in this paper are defined to be values averaged over the whole sample (which are the parameters measured experimentally). With this definition, the factor n/N should not appear. Spin diffusion effects are not included since they will not change the qualitative features of the calculation.

¹³ H. C. Torrey, Phys. Rev. **76**, 1059 (1949).

The nuclear and electron spin polarizations are defined as $P = (N_+ - N_-)/N$ and $p = (n_- - n_+)/n$. Solving Eqs. (1) and (2) for the polarizations the rate equations become:

$$\begin{aligned} dP/dt = & -2(W_x + W_1 + W_3)(P - P_0) - 2CP \\ & - B_1(P - p) - B_2(P + p), \end{aligned} \quad (3)$$

$$\begin{aligned} dp/dt = & -2(W + W_1)(p - p_0) - 2Ap \\ & - B_1(p - P) - B_2(p + P), \end{aligned} \quad (4)$$

where $p_0 = -\frac{1}{2}\beta\Delta$, $P_0 = \frac{1}{2}\beta\delta$, and we have assumed that $W_1 = W_2$. When we set $A = B_1 = B_2 = C = 0$, we obtain the thermal equilibrium relaxation rates:

$$1/T_{1N}^0 = 2(W_x + W_1 + W_3), \quad (5)$$

$$1/T_{1e}^0 = 2(W + W_1). \quad (6)$$

Using the Laplace transform method, and assuming that $A, C \approx 0$, Eqs. (3) and (4) are easily solved to find the time-dependent solutions for the polarizations,

and the characteristic relaxation rates for the coupled spin system. Both the electron and nuclear spin systems will display two relaxation rates; however, from the solutions for the polarizations we see that one rate may be associated with the nuclear spin system and the other with the electron spin system. Making this identification we find

$$1/\tau_N = (1/T_{1N}^0) + (B_1 + B_2). \quad (7)$$

Equation (7) shows that exciting either of the double-flip transitions will reduce the polarization time and that $1/\tau_N$ should depend linearly on the induced transition probability B_1 or B_2 . Since B_1 and B_2 are proportional to the input power to the microwave cavity, a plot of $1/\tau_N$ versus P_I should yield a straight line. These results are in agreement with the data presented in Sec. III.

Using Eq. (7) and the available data we can, in principle, measure the rf-induced, double-flip transition probabilities, B_1 and B_2 , and determine the shape and width of the double-flip absorption lines. Such results would be of great interest since these transitions are very difficult to observe directly. However, the aforementioned overlap with the central electron resonance line makes such a procedure impossible for the materials used in these investigations.

B. Exciting Pure Electronic Transitions

In solids where nuclear and electron spins are coupled by dipolar interaction the nuclear relaxation process induced by the operator

$$\frac{3}{2} \sin\theta \cos\theta e^{-i\varphi} S_z I_+ \quad (8)$$

is much more important than all other processes. Here θ and φ are the polar coordinates that give the relative orientation of the vector between S and I and the external magnetic field. The nuclear relaxation time due to this process is given by¹⁴

$$\frac{1}{T_{1N}} = \frac{9 \gamma_e^2 \gamma_N^2 \hbar^2 \sin^2\theta \cos^2\theta}{2 r^6} \int_{-\infty}^{\infty} S_z(0) S_z(t) e^{-i\omega_N t} dt, \quad (9)$$

where r is the distance between S and I .

¹⁴A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961).

We assume that S_z obeys the Bloch equation in the presence of the rf field and calculate its time dependence when the rf pulse is turned on. We find¹³

$$S_z(t) = S_z(0) e^{-t/T_{1e}}, \quad (10)$$

for $\gamma_e H_{1e} T_{1e} \ll 1$ and

$$S_z(t) = S_z(0) e^{-\frac{1}{2}[(1/T_{1e}) + (1/T_{2e})]t} \cos \gamma_e H_{1e} t, \quad (11)$$

for $\gamma_e H_{1e} T_{1e} \gg 1$. For conditions of exact electron resonance substituting Eq. (10) in Eq. (9) and integrating we find

$$\frac{1}{T_{1N}} = \frac{9 \gamma_e^2 \gamma_N^2 \hbar^2}{4 r^6} \frac{\sin^2\theta \cos^2\theta}{1 + \omega_N^2 \tau_0^2}, \quad (12)$$

where $\tau_0 = T_{1e}$. For large H_{1e} , Eq. (11) is substituted into Eq. (9) and integrated to give the same result with $\tau_0/(1 + \omega_N^2 \tau_0^2)$ replaced by

$$\frac{\tau/2}{1 + (\omega_N + \gamma_e H_{1e})^2 \tau^2} + \frac{\tau/2}{1 + (\omega_N - \gamma_e H_{1e})^2 \tau^2}, \quad (13)$$

where $\tau^{-1} = (T_{1e}^{-1} + T_{2e}^{-1})/2$. For $T_{2e} \ll T_{1e}$, which is the case for the materials investigated, T_{1N} will be greatly changed if H_{1e} is large enough so that $\gamma_e H_{1e} T_{1e} \gg 1$. However, T_{1N} as given by Eq. (13) will not be greater than that given by Eq. (12) unless one of the following two conditions hold: (1) $\omega_N T_{1e} \lesssim 1$; (2) $(\omega_N T_{1e})^{-1} > T_{2e}$ for $\omega_N T_{1e} \gg 1$. (Use has been made of the fact that $\omega_N > \gamma_e H_{1e}$ for these experiments.) In 7 5% CMN $T_{1e} \sim 10^{-2}$ sec, $T_{2e} \sim 10^{-8}$ sec, $\omega_N \sim 10^7$ cps and it is immediately seen that neither condition 1 nor 2 are appropriate.

It must be concluded that the above calculation is inadequate in treating the effect of exciting pure electronic transitions on the nuclear spin system. At the present time the theoretical interpretation of this effect remains unsolved.

ACKNOWLEDGMENTS

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