Approach to Boltzmann Equilibrium of the Nuclear Spins in a Quadrupolar Solid*

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A single crystal of $NaNO_3$ is oriented in an external magnetic field at an angle (θ_1) for which the quadrupole splitting is large. With radio-frequency radiation, a pair of Zeeman levels of the sodium nuclear spin system ($I=\frac{3}{2}$) is saturated. Then the crystal is quickly rotated to an angle where the inequality of the level spacings is a minimum (approximately $\frac{1}{2}$ the line width) and where spin mixing can take place. The crystal is then quickly returned to θ_1 where, by nuclear resonance pulse techniques, the populations of the four sodium levels can be determined. This sequence of operations is completed in a time short compared to the spin-lattice relaxation time. When the $m=\pm\frac{1}{2}$ levels are initially saturated, the spin system rapidly comes to the expected spin temperature $T_S=(10/9)\times$(the lattice temperature). When the outer satellites are saturated, however, the resulting equilibrium populations of the levels are not those of a Boltzmann distribution. Also measured was the rate of approach of the spin system to equilibrium for various larger splittings. For splittings of the order of the line width, an unexpected plateau appears in the spin mixing rate. The usual rate equations do not seem adequate to describe the observed dynamic behavior of this spin system.

I. INTRODUCTION

RECENTLY there has developed a considerable theoretical interest in problems dealing with the rate at which many-body systems approach thermal equilibrium.[1] The experiment to be described here is a measurement, by nuclear magnetic resonance techniques, of the rate at which a relatively simple system—the nuclear spins in a rigid lattice—approaches an equilibrium spin temperature.[2] The spin system being investigated is the sodium spin system ($I=\frac{3}{2}$) in a single crystal of sodium nitrate. This particular solid was chosen because of the relatively large quadrupole coupling between the sodium spins and the electric field gradient in the crystal. As a result of this quadrupole coupling, the four magnetic substates of a sodium nucleus are not equally spaced in a strong magnetic field. The strength of the quadrupole coupling, and hence the inequality of the level spacings, depends on the angle the crystal makes with the external magnetic field. With an rf pulse it is possible to equalize the populations of (saturate) a particular pair of adjacent substates of the system when the crystal is oriented so that the coupling is large. Following this saturation, the crystal is then rotated to an angle where the levels are nearly equally spaced. In a series of measurements at this angle, one can then observe the rate at which the energy added to the system by the saturation distributes itself among the four substates. This phenomenon will be called spin mixing.

Although any problem involving 10^{22} interacting particles is necessarily complicated, the particular system chosen for study has the not insignificant advantage of being characterized by a relatively simple Hamiltonian (the Zeeman and quadrupole energy of the spins plus their dipole-dipole interactions) which does not depend on time. This simplicity is present only if the spins being studied are much more strongly coupled to each other than to the lattice vibrations. This condition was satisfied by performing the experiment at a temperature sufficiently low that the spin lattice relaxation times were long compared to the time interval over which the measurements were made.[3] The principal results of these experiments are briefly described in the following paragraphs.†

It was found that spin mixing is rapid if allowed to take place at an angle where the inequality of the level spacings is not much greater than the width of the nuclear resonance lines. Qualitatively one can say that mixing proceeds relatively rapidly if there is an appreciable overlap of the (three) nuclear resonance absorption lines. At large overlap the system can approach equilibrium by energy-conserving spin flips. In sodium nitrate the dipole-dipole interaction is responsible for the flipping of neighboring pairs of spins. It is also responsible for a major part of the line width, though the lines are partially broadened by inhomogeneities in the field gradient in the solid.

Bloembergen and his co-workers have recently developed a semiquantitative theory of spin mixing, which is based on an overlapping lines point of view.[4] This theory will be briefly outlined in the following section.

Since second-order quadrupole splitting is not negligible in sodium nitrate, there is no orientation of the

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[1] See, for example, *Proceedings of the International Symposium on Transport Processes in Statistical Mechanics* (Interscience Publishers, Inc., New York, 1958).

[2] For an exhustive discussion of the concept of spin temperature see A. Abragam and W. G. Proctor, Phys. Rev. **109**, 1441 (1958). Also R. T. Schumacher, Phys. Rev. **112**, 837 (1958).

[3] Spin-lattice relaxation in a quadrupolar system is described by a sum of exponential terms. Therefore, the process cannot in general be characterized by a single relaxation time.

† *Note added in proof.*—A. Honig and E. Stupp [Bull. Am. Phys. Soc. Ser. II, 3, 9 (1958)] were the first to report a measurement of the dynamics of approach to spin equilibrium of a single discreet level system.

[4] Bloembergen, Shapiro, Pershan, and Artman, Phys. Rev. **114**, 445 (1959).

crystal for which the three resonant frequencies are all equal. At the angle of minimum splitting ($\theta_{\min}$), the three lines are displaced from each other by approximately half a line width.[5] Measurements at $\theta_{\min}$ show that (a) no matter what pair of levels were initially saturated the populations of the four levels (after mixing) reach their equilibrium values in a time equal to or less than 0.06 sec, the smallest mixing time that could be measured; (b) the equilibrium populations of the four levels after mixing depend on which pair of levels has been initially saturated. The populations of the levels following saturation of the central line ($m=\pm\frac{1}{2}$) correspond to a Boltzmann distribution at a temperature 10/9 of the lattice temperature. This result is to be expected assuming energy is conserved within the spin system. The equilibrium populations of the levels following saturation of either of the satellites, however, do *not* correspond to a Boltzmann distribution and hence cannot be characterized by a spin temperature. Rather it is observed that, following the saturation of a satellite, three levels acquire a Boltzmann distribution after mixing, the population of the fourth level remaining approximately at its value before saturation. The three levels that acquire a Boltzmann distribution are the saturated pair and the one adjacent to them. This result is difficult to understand on the basis of the overlapping lines picture.

Data were also taken at several other angles for which the line overlap was appreciable. For example, extensive measurements were made at the angle (to be called "mixing angle") corresponding to the overlap configuration shown in Fig. 3(a). At this mixing angle the level populations were observed to approach quickly to quasi-equilibrium values. The change in the four populations, from their initial values immediately following saturation to their quasi-equilibrium values, takes place in the shortest time that could be measured.[6] These populations remain constant for at least 7 sec. After approximately this length of time the effects of spin-lattice relaxation are no longer negligible compared to the effects of spin mixing. For times longer than about 10 sec little knowledge can be gained about the spin mixing rate alone. These quasi-equilibrium populations do not correspond to a Boltzmann distribution (among either three levels or four) and therefore cannot be characterized by spin temperature. Similar results were also observed at a mixing angle corresponding to greater overlap than shown in Fig. 3(a) but less than at $\theta_{\min}$ [Fig. 3(c)].

These rather suprising results seem to imply that, at least at small mixing angles, spin mixing cannot be described by the rate Eqs. (8).

Spin mixing data were also taken at larger splitting angles where no plateau in the spin mixing rate appears. Even when the splitting was as large as nine times the line width, the rate of change of the level populations due to spin mixing was not small compared to the rate change produced by spin-lattice relaxation.

II. HAMILTONIAN AND BLOEMBERGEN'S THEORY

In these experiments the sample, a single crystal of $NaNO_3$, was placed in a strong external field $\mathbf{H}_0$ which was approximately 9000 gauss. Neglecting for a moment the relatively small dipole-dipole interaction between the spins in the sample, each nucleus interacts not only with the external magnetic field but also with an axially symmetric field gradient.

The Hamiltonian characterizing this interaction is[7]

$$\mathcal{H}_0=-\gamma\hbar\sum_k I_z^k H_0+A\sum_k[3(I_z^k)^2-(\mathbf{I}^k)^2]+\mathcal{H}_q'. \quad (1)$$

The last two terms represent the quadrupole interaction. The constant A is proportional to the field gradient at the nuclear sites and the quadrupole moment of the sodium nuclei. Equation (1) holds in a coordinate system whose z axis is along the direction of the external field $\mathbf{H}_0$. The summation index k runs over the N sodium nuclei, each of which has a z component of spin I_z^k and total spin $\mathbf{I}^k$. The gyromagnetic ratio of the spins is γ. The coefficient A, previously measured for sodium nitrate,[7] is small compared to the Zeeman energy, $-\gamma H_0\hbar$. The energy levels of an *individual spin* to first order (i.e., neglecting the term $\mathcal{H}_q'$) are

$$E_m^{(1)}=-(2\pi)^{-1}\gamma m H_0 +83.5\ \text{kc/sec}(m^2-5/4)(\tfrac{3}{2}\cos^2\theta-\tfrac{1}{2}), \quad (2)$$
$$m=-\tfrac{3}{2},\cdots,\tfrac{3}{2},$$

where θ is the angle between $\mathbf{H}_0$ and the axis of symmetry of the field gradient in the crystal. The energy of the unperturbed system is, of course, the sum of the energies E_m of the individual spins.

Figure 1 shows schematically (and not to scale) the energy of an individual nuclear spin given by Eq. (2). It is convenient to denote the three energy differences $E_{\frac{3}{2}}-E_{\frac{1}{2}}$, $E_{\frac{1}{2}}-E_{-\frac{1}{2}}$, $E_{-\frac{1}{2}}-E_{-\frac{3}{2}}$ as $h\nu_{-1}$, $h\nu_0$, and $h\nu_1$, respectively. By virtue of Eq. (2) it is seen that in first order $\nu_1-\nu_0=\nu_0-\nu_{-1}$.

The last term in Eq. (1) (written out in full in references 7) does not commute with I_z^k. It results in higher-order splitting of the resonance lines as well as a small amount of mixing ($<2\%$) of the otherwise pure magnetic sub-states of an individual spin. In a later discussion it will be necessary to consider the second-

[5] The term "line width" will henceforth denote the measured full width of the resonance line at half maximum.

[6] The saturating rf field generally produces phase coherence among the nuclear spins. Until this phase coherence has disappeared it is not meaningful to describe the state of the system by four level populations. For the sodium spins in $NaNO_3$, this phase coherence is expected to disappear in $\sim$250 μsec, the spin-spin relaxation time for the system. This time is, of course, much shorter than the smallest mixing time which could be measured in these experiments.

[7] See, for example, M. H. Cohen and F. Reif, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 321. Also R. V. Pound, Phys. Rev. 79, 685 (1950).

order contribution to the quadrupole splitting. Taking this term into account, the frequency differences $\nu_1-\nu_0$ and $\nu_0-\nu_{-1}$ become[7]

$$\begin{aligned}\nu_1-\nu_0=&[167\text{ kc/sec}][\tfrac{3}{2}\cos^2\theta-\tfrac{1}{2}]\\&+[4.18\text{ kc/sec}][\sin^2 2\theta]\\&+[0.523\text{ kc/sec}][1-\cos^2\theta][9\cos^2\theta-1],\\\nu_0-\nu_1=&[167\text{ kc/sec}][\tfrac{3}{2}\cos^2\theta-\tfrac{1}{2}]\\&-[4.18\text{ kc/sec}][\sin^2 2\theta]\\&+[0.523\text{ kc/sec}][1-\cos^2\theta][9\cos^2\theta-1].\end{aligned}\tag{3}$$

Figure 2 is a plot of $\nu_1-\nu_0$ and $\nu_0-\nu_{-1}$ as a function of θ in an angular interval in which the splitting is small. Referring to Eq. (3), it is seen that in the interval $53°\leqslant\theta\leqslant 56°$ the change in ν_0 with changing θ is much less than the line width. In ensuing discussions it will be convenient to characterize the level spacings by a single function $\delta f(\theta)\equiv\frac{1}{2}[(\nu_1-\nu_0)+(\nu_0-\nu_{-1})]$. This function will be referred to as the average splitting at the angle θ.

The dipole-dipole interaction, $\mathcal{H}_d$, between the nuclear spins will now be considered. It is convenient to write[8]

$$\mathcal{H}_d=\sum_{j<k}H_{jk}=A+B+C+D+E+F,$$

where

$$\begin{aligned}A\equiv\sum_{j<k}A_{jk}&=+\gamma^2\hbar^2\sum_{j<k}\frac{1}{r_{jk}^3}[I_z^k I_z^j(1-3\cos^2\theta_{jk})],\\B\equiv\sum_{j<k}B_{jk}&=-\tfrac{1}{4}\gamma^2\hbar^2\\&\quad\times\sum_{j<k}[I_+^j I_-^k+I_-^j I_+^k](1-3\cos^2\theta_{jk}),\\C\equiv\sum_{j<k}C_{jk}&=-\tfrac{3}{2}\gamma^2\hbar^2\\&\quad\times\sum_{j<k}[I_+^j I_z^k+I_z^j I_+^k]\sin\theta_{jk}\cos\theta_{jk}e^{-i\varphi_{jk}},\\D\equiv\sum_{j<k}D_{jk}&=-\tfrac{3}{2}\gamma^2\hbar^2\\&\quad\times\sum_{j<k}[I_-^j I_z^k+I_z^j I_-^k]\sin\theta_{jk}\cos\theta_{jk}e^{i\varphi_{jk}},\\E\equiv\sum_{j<k}E_{jk}&=-\tfrac{3}{4}\gamma^2\hbar^2\sum_{j<k}I_+^j I_+^k\sin^2\theta_{jk}e^{-2i\varphi_{jk}},\\F\equiv\sum_{j<k}F_{jk}&=-\tfrac{3}{4}\gamma^2\hbar^2\sum_{j<k}I_-^j I_-^k\sin^2\theta_{jk}e^{2i\varphi_{jk}},\end{aligned}\tag{4}$$

where $\mathbf{r}_{jk}$ is the vector running from the jth to the kth nucleus and θ_{jk}, φ_{jk} are the polar angles that this vector makes with the direction of $\mathbf{H}_0$. The raising and lowering operators, I_+^k and I_-^k, are defined as $I_x^k+iI_y^k$ and $I_x^k-iI_y^k$, respectively.

As is well known, A and B are responsible for the line breadth of the nuclear resonance. The term B probably plays the major part in bringing the sodium nuclei into internal spin equilibrium since it induces energy-conserving transitions between pairs of spins.

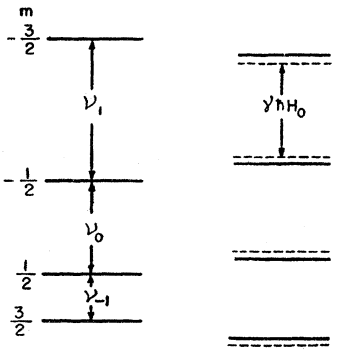

FIG. 1. Quadrupole splitting of the energy levels of a nucleus of spin $I=\frac{3}{2}$ in a strong magnetic field. The diagram on the left shows the crystal oriented at an angle θ_1, where the splitting is large. The diagram on the right shows the crystal at the small-splitting orientation θ_2, where internal spin mixing can take place. The dashed lines represent the energy levels when the quadrupole interaction is zero.

There is an additional term in the Hamiltonian of the sodium spin system representing the interaction between these spins and the lattice vibrations. This term is responsible for spin-lattice relaxation. The spin lattice relaxation time, T_1, depends of course on the temperature of the crystal; for $NaNO_3$ this time is of the order of a minute at 77°K,[9] the temperature at which all of the experiments were performed. It was necessary to go to this low temperature in order that the rate of spin-lattice relaxation would be slow compared to the internal spin relaxation (spin mixing) rate.

Bloembergen and his co-workers[4] have developed a theory of spin mixing which has been successfully applied to the interpretation of many experiments including the classic experiments on LiF done by Abragam and Proctor.[2] In this theory one calculates, using perturbation theory, the rate at which a pair of spins undergo a mutual spin flip which tends to bring the spin system (or interacting systems) into equilibrium. It is assumed that the dominant mechanism which brings the spins to their equilibrium configuration is the dipole-dipole interaction. The theory is only applicable to experiments completed in a time short compared to T_1.

In the strong-field case, where the jth nucleus can be characterized by its individual quantum number m_j, the mutual spin flip transition probability w_{jk} can be written

$$w_{jk}(m_j m_k;m_j' m_k')=\hbar^{-2}|(m_j' m_k'|H_{jk}|m_j m_k)|^2 g_{\alpha\beta}(0),\tag{5}$$

corresponding to the transition $m_j\rightarrow m_j'$, $m_k\rightarrow m_k'$. In the transition, spin j is assumed to increase its energy by $h\nu_\alpha$, while spin k loses energy $h\nu_\beta$. This expression is

[8] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

[9] In sodium nitrate the shortest spin lattice relaxation time at 77°K was found to be 70 sec. It is this time which will be designated as T_1.

expected to have validity only when the time characterizing the above transition is long compared to the spin-spin relaxation time T_2. The density-of-states function $g_{\alpha\beta}(0)$ is calculated in principle by the moments method of Van Vleck. The terms in H_{jk} used in calculating $g_{\alpha\beta}(0)$ and the matrix element of Eq. (5) must be chosen in a way appropriate to the problem in question, as emphasized in reference 4. For experiments of the type reported here, it would seem necessary to consider only the term B_{jk} in the matrix element.[10] In calculating $g_{\alpha\beta}(0)$ the Hamiltonian can be truncated to include only the terms $A+B$.

Since it is impossibly difficult to construct a full line shape by the moments method, it is useful in making semiquantitative calculations to replace Eq. (5) by

$$w_{jk}(m_j m_k; m_j' m_k') = \hbar^2 |(m_j' m_k'|B_{jk}|m_j m_k)|^2 \times \int\int g_\alpha(\nu') g_\beta(\nu'') \delta(\nu'-\nu'') d\nu' d\nu'', \quad (6)$$

where now $g_\alpha(\nu')$ and $g_\beta(\nu'')$ are the observed magnetic resonance line shapes.

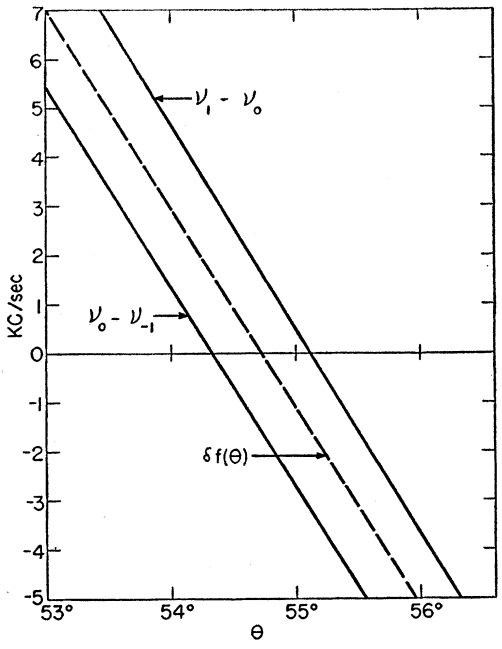

FIG. 2. The frequency differences $\nu_1-\nu_0$ and $\nu_0-\nu_{-1}$ for Na^{23} in $NaNO_3$ as a function of θ, the angle between the external magnetic field and the crystal axis. The dashed line is the average splitting defined as $\delta f(\theta)\equiv\frac{1}{2}[(\nu_1-\nu_0)+(\nu_0-\nu_{-1})]$. In the angular interval shown in this graph, ν_0 can be regarded as independent of θ.

[10] It is certainly possible that there are transitions which involve the simultaneous flip of more than two neighboring spins. However, since the pairwise spin-flip terms B_{jk} provide a mechanism for this system to approach equilibrium, it seems unnecessary to invoke less probable multiple spin-flip processes.

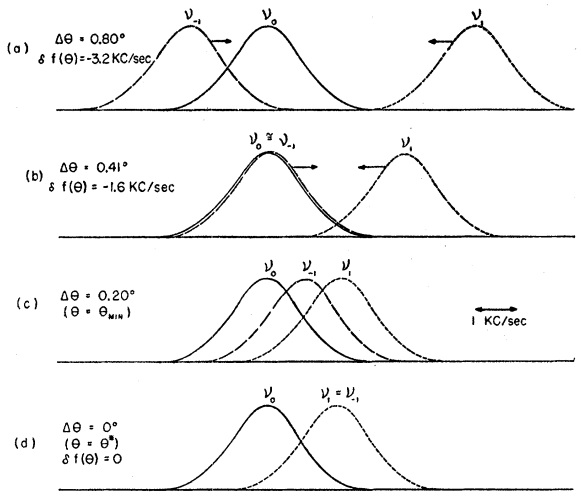

FIG. 3. Various overlap configurations of interest in these experiments. The line shapes are assumed to be Gaussian with a full width at half maximum equal to the measured value, $\Delta\nu=1.8$ kc/sec. The angular difference $\Delta\theta$ is defined in Eq. (7).

Shown in Fig. 3 are several overlapping configurations that can exist for sodium nitrate. Two of these configurations (*a* and *c*) correspond to mixing angles that were used in these experiments. All three lines in $NaNO_3$ were observed to have a width $\Delta\nu=1.8$ kc/sec.[5] The lines in Fig. 3 have a Gaussian shape with the above width. Each of the line configurations is designated by the parameter $\delta f(\theta)$ (previously defined) and also by the angular difference

$$\Delta\theta\equiv\theta-\theta^*, \quad \theta^*\equiv\cos^{-1}(\tfrac{1}{3})^{\frac{1}{2}}, \quad (7)$$

where θ^* is the angle at which the quadrupole splitting vanishes in first order.

It is seen from Fig. 3 that as one rotates the crystal so that $\Delta\theta$ decreases from large positive values toward zero, the level order changes. An angle of special interest is $\Delta\theta=0.20°$. At this angle, henceforth to be designated as $\theta_{\min}$, the maximum amount of overlap exists. It should be noted that at this splitting the central line is of lower frequency than either of the satellites. Since the experimental line widths were used in Fig. 3, some of the overlap is the result of inhomogeneous broadening. The cause of this broadening is spatial inhomogeneity of the field gradient produced by strains and imperfections in the crystal.

Bloembergen assumes that the approach of a spin system to equilibrium can be described by the usual rate equations. These equations implicitly contain the assumption that there are no correlations between the states of neighboring spins. Experimental evidence will later be presented which indicates that correlations might be present and that the rate equations are not adequate to describe the dynamic behavior of the sodium spin system.

The four rate equations appropriate to this problem are

$$\begin{aligned}
\dot{N}_{\pm\frac{3}{2}} &= W_{\pm1}(N_{\pm\frac{1}{2}}{}^2 - N_{\pm\frac{3}{2}}N_{\mp\frac{1}{2}}) \\
&\quad + W_3(N_{\frac{1}{2}}N_{-\frac{1}{2}} - N_{\frac{3}{2}}N_{-\frac{3}{2}}) \\
&\quad - [W_{\pm1}(N_{\pm\frac{1}{2}}{}^2 - N_{\pm\frac{3}{2}}N_{\mp\frac{1}{2}})_{ad} \\
&\quad\quad + W_3(N_{\frac{1}{2}}N_{-\frac{1}{2}} - N_{\frac{3}{2}}N_{-\frac{3}{2}})_{ad}], \\
\dot{N}_{\pm\frac{1}{2}} &= 2W_{\pm1}(N_{\pm\frac{3}{2}}N_{\mp\frac{1}{2}} - N_{\pm\frac{1}{2}}{}^2) \\
&\quad + W_{\mp1}(N_{\mp\frac{1}{2}}{}^2 - N_{\pm\frac{1}{2}}N_{\mp\frac{3}{2}}) \\
&\quad + W_3(N_{\frac{3}{2}}N_{-\frac{3}{2}} - N_{\frac{1}{2}}N_{-\frac{1}{2}}) \\
&\quad - [2W_{\pm1}(N_{\pm\frac{3}{2}}N_{\mp\frac{1}{2}} - N_{\pm\frac{1}{2}}{}^2)_{ad} \\
&\quad + W_{\mp1}(N_{\mp\frac{1}{2}}{}^2 - N_{\pm\frac{1}{2}}N_{\mp\frac{3}{2}})_{ad} \\
&\quad\quad + W_3(N_{\frac{3}{2}}N_{-\frac{3}{2}} - N_{\frac{1}{2}}N_{-\frac{1}{2}})_{ad}],
\end{aligned} \tag{8}$$

where

$$W_{\pm1} = N^{-1}\sum_i w_{ij}(\pm\tfrac{1}{2}\pm\tfrac{1}{2};\ \mp\tfrac{1}{2}\pm\tfrac{3}{2}),$$

$$W_3 = N^{-1}\sum_i w_{ij}(\tfrac{1}{2}-\tfrac{1}{2};\ \tfrac{3}{2}-\tfrac{3}{2}).$$

The number of spins in the system is

$$N = \sum_{m=-\frac{3}{2}}^{\frac{3}{2}} N_m.$$

The "adiabatic" terms (in brackets) describe the level populations at $t=\infty$. If the 4-level populations approach a Boltzmann distribution, these terms are zero. The experiments described in the following section will be discussed in terms of Eqs. (8) and their solutions.

In the high-temperature approximation, which is applicable here, $N_m=\frac{1}{4}N[1+\delta_m(t)]$, where $\delta_m(t)\lesssim 1$. With this approximation, Eqs. (8) are readily solved. The time dependence of each N_m is in general given by a sum of three exponential terms of the form $A_\alpha \exp(-t/\tau_\alpha)$ plus a constant term. The τ_α will be called internal relaxation times.

III. EXPERIMENTS AT $\theta_{\min}$

In these particular experiments a pair of levels of the sodium spin system is initially saturated (in a time short compared to T_1) with the crystal oriented at an angle (to be called θ_1) for which the quadrupole splitting is large. All measurements were made at $\theta_1\sim 10°$, $\delta f(\theta_1)\sim 160$ kc/sec.[11] The crystal is then rapidly rotated to the mixing angle, which will be designated θ_2. The measurements described in this section were made at $\theta_2=\theta_{\min}$, the angle at which the overlap is maximum. [See Fig. 3(c).] The aim was to determine the equilibrium populations of the four sub-states (the rate of approach to equilibrium was too rapid to be measured at this angle).

It was expected—though not observed in all cases—that at this splitting the equilibrium populations of the states N_m would have a Boltzmann distribution. If the spin system does come to Boltzmann equilibrium, the magnetic sub-state populations will be given by

$$N_m' = \tfrac{1}{4}N(1+m\Delta'), \tag{9}$$

where $\Delta'=\gamma\hbar H_0/kT_S$. It is easily shown that for $I=\frac{3}{2}$ the energy of saturation should raise the temperature of the spin system from the lattice temperature, T_L, before saturation to the spin temperature, $T_S=(10/9)T_L$, after mixing has taken place, no matter which of the three adjacent pairs of levels is saturated. The calculation only assumes that energy is conserved within the spin system. The energy conservation condition is expected to be fulfilled if each experiment is completed in a time short compared to T_1.

TABLE I. Normalized signals at $\theta_{\min}$.

$\bar{S}_{-1-1}$	$\bar{S}_{-10}$	$\bar{S}_{-11}$
0.63±0.05	0.78±0.05	1.22±0.05
$\bar{S}_{0-1}$	$\bar{S}_{00}$	$\bar{S}_{01}$
0.97±0.05	0.87±0.03	0.90±0.05
$\bar{S}_{1-1}$	$\bar{S}_{10}$	$\bar{S}_{11}$
1.13±0.05	0.90±0.05	0.74±0.10

In practice the state of the spin system after mixing is determined by returning the crystal to θ_1 and then measuring the population differences with nuclear magnetic resonance pulse techniques. The initial saturation and subsequent rotations ($\theta_1\rightarrow\theta_{\min}\rightarrow\theta_1$) could be completed in a time less than 0.5 sec. As long as the individual experiments were completed in a time short compared to T_1, the measured signal amplitudes were independent of the time that the crystal remained at $\theta_{\min}$. The shortest attainable mixing time was ~ 0.06 sec.

The mixing angle (θ_2) was established to be $\theta_{\min}$ by a "zero beat" method. Beats will appear on the free induction decay envelope at those angles for which the quadrupole splitting is comparable to the line width. These beats appear since the pulse is short enough to contain large-intensity Fourier components over the frequency interval which includes all three resonance lines. The method of determining $\theta_{\min}$ was to set the angle between magnetic field and crystalline field axis so that no visible beats appeared on the free induction decay. This angular setting could be reproduced to within $\pm 0.15°$.

The quantity of interest in these experiments is the ratio of the nuclear signal, S_{ij}, after mixing to the presaturation nuclear signal. The first subscript of S_{ij} denotes the saturating frequency (ν_1,ν_0,ν_{-1}), and the second subscript designates the frequency of the measured free induction decay signal. The symbol $\bar{S}_{ij}$ will be used to denote the normalized signal S_{ij}/S_j^0, where S_j^0 represents the magnitude of the presaturation signal of frequency ν_j. The magnitude of S_j^0 corresponds to the lattice temperature, T_L. For $I=\frac{3}{2}$ there are nine independent experiments that can be performed at any given splitting. They correspond to the saturation of three adjacent pairs of levels and, after mixing, the

[11] For $\delta f(\theta_1)\gtrsim 80$ kc/sec the experimental results were independent of the choice of θ_1.

TABLE II. Population numbers at $\theta_{\min}$. Experimental values calculated from data in Table I.

	$P_{-1,\frac{3}{2}}$	$P_{-1,\frac{1}{2}}$	$P_{-1,-\frac{1}{2}}$	$P_{-1,-\frac{3}{2}}$	
1	1.50	0.05	−0.50	−1.50	Lattice temperature equilibrium
2	1.35	0.45	−0.45	−1.35	4-level Boltzmann equilibrium
3	1.25	0.50	−0.25	−1.50	3-level Boltzmann equilibrium
4	1.17±0.05	0.54±0.03	−0.24±0.03	−1.46±0.05	Experimental
	$P_{0,\frac{3}{2}}$	$P_{0,\frac{1}{2}}$	$P_{0,-\frac{1}{2}}$	$P_{0,-\frac{3}{2}}$	
5	1.50	0.50	−0.50	−1.50	Lattice temperature equilibrium
6	1.35	0.45	−0.45	−1.35	4-level Boltzmann equilibrium
7	1.25	0.50	−0.25	−1.50	3-level Boltzmann equilibrium
8	1.39±0.04	0.42±0.02	−0.45±0.02	−1.35±0.04	Experimental
	$P_{1,\frac{3}{2}}$	$P_{1,\frac{1}{2}}$	$P_{1,-\frac{1}{2}}$	$P_{1,-\frac{3}{2}}$	
9	1.50	0.50	−0.50	−1.50	Lattice temperature equilibrium
10	1.35	0.45	−0.45	−1.35	4-level Boltzmann equilibrium
11	1.50	0.25	−0.50	−1.25	3-level Boltzmann equilibrium
12	1.48±0.05	0.35±0.05	−0.55±0.05	−1.29±0.08	Experimental

measurement of population differences between any three adjacent pairs of levels. If Boltzmann equilibrium is established among all four levels,

$$\bar{S}_{ij}=9/10, \quad i, j=-1, 0, 1. \tag{10}$$

Table I shows the nine measured signals $\bar{S}_{ij}$. It is seen from these data that when the saturating frequency is ν_0, the system comes to Boltzmann equilibrium at a temperature $T_S=(10/9)T_L$. When either of the satellites is saturated, however, the subsequent equilibrium populations do *not* correspond to a Boltzmann distribution.

The data in Table I are based on measurements made on various days. At the beginning of each day's measurements the magnet angle corresponding to $\theta_{\min}$ was redetermined by the method described above. Measurements made on different days were in agreement within an error which could be attributed to the available signal-to-noise ratio. It would appear then that the unexpected results of this section are not extremely sensitive to the angle at which mixing takes place.

A check can be made of the internal consistency of the entries in Table I. When the energy of the spin system *before* mixing but *after* saturation is equated to the energy of the system *after* mixing, the following restriction is placed on the $\bar{S}_{ij}$:

$$3(\bar{S}_{i-1}+\bar{S}_{i1})+4\bar{S}_{i0}=9 \quad \text{for all } i. \tag{11}$$

This relation is obeyed, within the quoted experimental errors, for all of the data in Table I.

It is convenient to represent the populations of the four substates after mixing by

$$N_m=\tfrac{1}{4}N(1+P_{im}\Delta).$$

This equation defines the P_{im}. The subscript i designates the saturating frequency, ν_i. Using the requirement that

$$\sum_m P_{im}=0, \quad i=-1, 0, 1,$$

the four "population numbers" P_{im} can be calculated from the $\bar{S}_{ij}$, giving for all i

$$\begin{aligned}
P_{i,-\frac{3}{2}}&=\tfrac{1}{4}N\Delta[-\bar{S}_{i-1}-2\bar{S}_{i0}-3\bar{S}_{i1}],\\
P_{i,-\frac{1}{2}}&=\tfrac{1}{4}N\Delta[-\bar{S}_{i-1}-2\bar{S}_{i0}+\bar{S}_{i1}],\\
P_{i,\frac{1}{2}}&=\tfrac{1}{4}N\Delta[-\bar{S}_{i-1}+2\bar{S}_{i0}+\bar{S}_{i1}],\\
P_{i,\frac{3}{2}}&=\tfrac{1}{4}N\Delta[3\bar{S}_{i-1}+2\bar{S}_{i0}+\bar{S}_{i1}].
\end{aligned} \tag{12}$$

Shown in Table II, rows 4, 8, and 12, are the population numbers P_{im} calculated from Eq. (12) and the data in Table I. In rows 1, 5, and 9 are the population numbers $P_{im}=m$ corresponding to Boltzmann equilibrium at the lattice temperature. The population numbers in rows 2, 6, and 10 correspond to the establishment of Boltzmann equilibrium among all four levels at the spin temperature $T_S=(10/9)T_L$ [$P_{im}=(9/10)m\Delta$].

Consistent with the conclusions drawn from the "raw data" shown in Table I, it is seen that only for $i=0$ can level populations be characterized by a spin temperature. However, the equilibrium populations of the levels following saturation of a satellite are consistent with the assumption that *three* levels, the saturated pair and the one level adjacent to them, come to a Boltzmann distribution; the population of the fourth level remains unchanged in the mixing process.

Consider, for example, the case $i=1$, where mixing follows saturation of the $m=-\frac{3}{2}$, $-\frac{1}{2}$ levels. Assume that this mixing brings about a Boltzmann distribution of the populations of the $m=-\frac{3}{2}$, $-\frac{1}{2}$, $+\frac{1}{2}$ levels, leaving the population number of the $m=\frac{3}{2}$ level at $P_{1,\frac{3}{2}}=\frac{3}{2}$. This assumption yields the values of P_{1m} shown in row 11. There is good agreement between these results and the experimental values shown in row 12. The entries in row 3 are calculated assuming that a Boltzmann distribution is established among the $m=\frac{3}{2}$, $\frac{1}{2}$, $-\frac{1}{2}$, levels following saturation of the $\frac{3}{2}$ and $\frac{1}{2}$ states. The observed populations (row 4) are again seen to be in good agreement with the calculated 3-level equilibrium hypothesis.

The experimental results in Table II are difficult to understand on the basis of the overlapping lines theory. Three-level Boltzmann equilibrium might be expected

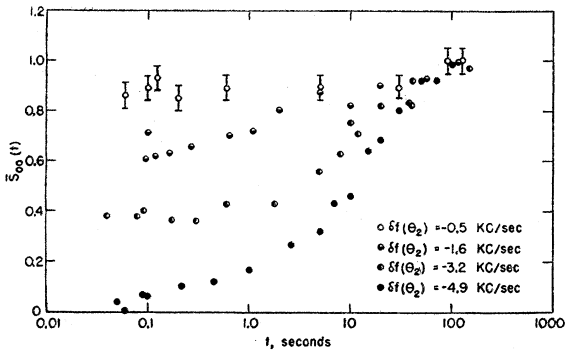

FIG. 4. Relative nuclear signal amplitudes as a function of time for various mixing angles. In these measurements ν_0 is the saturating frequency as well as the frequency of the observed resonance. The errors shown on the open circles are applicable to all the points in the figure.

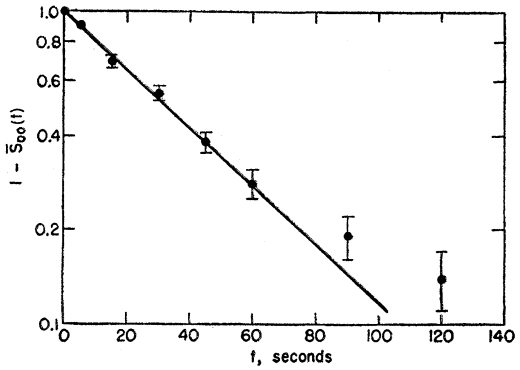

FIG. 5. Relative signal amplitude for the splitting, $\delta f(\theta_2)=17$ kc/sec. The straight line represents the equation $\bar{S}_{00}(t)=1-\exp[-t/47\ \text{sec}]$. This line is a best fit to the data for $t\lesssim 45$ sec. The spin-lattice relaxation time at this angle is at least 70 sec.

to be encountered in a configuration in which two lines centered at almost the same frequency overlap only slightly with a third line. Reference to Fig. 3(c), however, shows that this situation does not exist at $\theta_{\min}$. Rather, the line ν_0 overlaps sufficiently with ν_1 (and hence ν_{-1}) to bring about 4-level (Boltzmann) equilibrium when ν_0 is saturated. Yet only 3-level equilibrium results when its "neighbor" ν_{-1} is saturated. Perhaps even more surprising is the observation that the population of the $m=\frac{3}{2}$ level is not changed by the mixing which follows saturation at ν_1. The population of the $\frac{3}{2}$ level would be expected to be altered in this case since the lines centered at ν_1 and ν_{-1} overlap greatly.

It can be argued that since $\theta_{\min}$ can only be determined to within $\pm 0.15°$, the conclusions drawn in the above discussion have limited validity as they are based on the assumed level order of Fig. 3(c). On the other hand, there seems to be no line configuration in the interval $\theta_{\min}-0.15°\leqslant\theta_2\leqslant\theta_{\min}+0.15°$ at which the above data lend themselves to a simple interpretation on the basis of Bloembergen's overlapping lines theory. Furthermore, the experimental results are not very sensitive to the setting of θ_2 as remarked above.

It is certainly possible that if T_1 were sufficiently increased (by lowering the temperature of the sample), one would observe, for all saturating frequencies, the eventual approach of all four populations to their Boltzmann equilibrium values. In terms of the rate equations the experimental results might possibly be accounted for by the presence of a long internal relaxation time (as well as a short one) in the solution for the N_m. It is reasonable to suppose that for the experiments at $\theta_{\min}$, $W_1\sim W_{-1}\sim W_3$. Equations (8) were solved assuming $W_1=W_{-1}$ with no restriction on W_3.[12] Also, it was assumed that the equilibrium level populations were those of (9). It was found that there was no choice of W_1 and W_3 which could account for the observed P_{im}, even if the errors in the P_{im} were taken to be many times those quoted in Table II. In light of the insensitivity of the measurements to the exact setting of θ_2 (and hence to the exact values of $W_{\pm 1}$ and W_3), it seems safe to say that the rate Eqs. (8) are inadequate to describe the dynamic behavior of the sodium spin system.

It is interesting to note that all of the measurements described in this section are consistent with the following assumptions: (a) the mixing which follows saturation at ν_1 involves only the transitions of the type W_{-1} in Eq. (8) ($m_j=\frac{1}{2}\rightarrow-\frac{1}{2}$; $m_k=-\frac{3}{2}\rightarrow-\frac{1}{2}$); (b) the mixing which follows saturation at ν_{-1} involves only transitions of the type W_1 ($m_j=\frac{1}{2}\rightarrow-\frac{1}{2}$, $m_k=\frac{1}{2}\rightarrow\frac{3}{2}$); (c) to account for the data at saturating frequency ν_0 both of these types of transitions are required, but it is not necessary to invoke spin flips of the type W_3 ($m_j=\frac{1}{2}\rightarrow\frac{3}{2}$, $m_k=-\frac{1}{2}\rightarrow-\frac{3}{2}$). It is not at all obvious why all three kinds of transitions are not present in each of the above three cases.

IV. TIME DEPENDENCE OF THE APPROACH TO EQUILIBRIUM

The measurements described in this section were made at splittings sufficiently large to allow measurement of the change in the N_m as a function of time. The procedure followed in these experiments was identical to that described in the previous section.

Figure 4 shows $\bar{S}_{00}(t)$ for the splittings $\delta f(\theta_2)=-0.5$ kc/sec, -1.6 kc/sec, -3.2 kc/sec, and -4.9 kc/sec. At the smallest of these splittings (open circles) the spin system is observed to reach equilibrium in the shortest measurable time. At $\delta f(\theta_2)=-4.9$ kc/sec (solid circles), $S_{00}(t)$ rises smoothly from $\sim$zero at $t=0.06$ sec to unity for $t\gg T_1\simeq 70$ sec. In the interval $0.06\ \text{sec}\lesssim t\lesssim 7$ sec the signal amplitudes are due almost entirely to spin mixing. At $t=10$ sec spin lattice relaxation alone would give $S_{ij}=0.1$, which is roughly the experimental error in these measurements.

At $\delta f(\theta_2)=-1.6$ kc/sec, and even more noticeably at $\delta f(\theta_2)=-3.2$ kc/sec (half-filled circles), an un-

[12] Only two internal relaxation times appear in the solution for the N_m in this case.

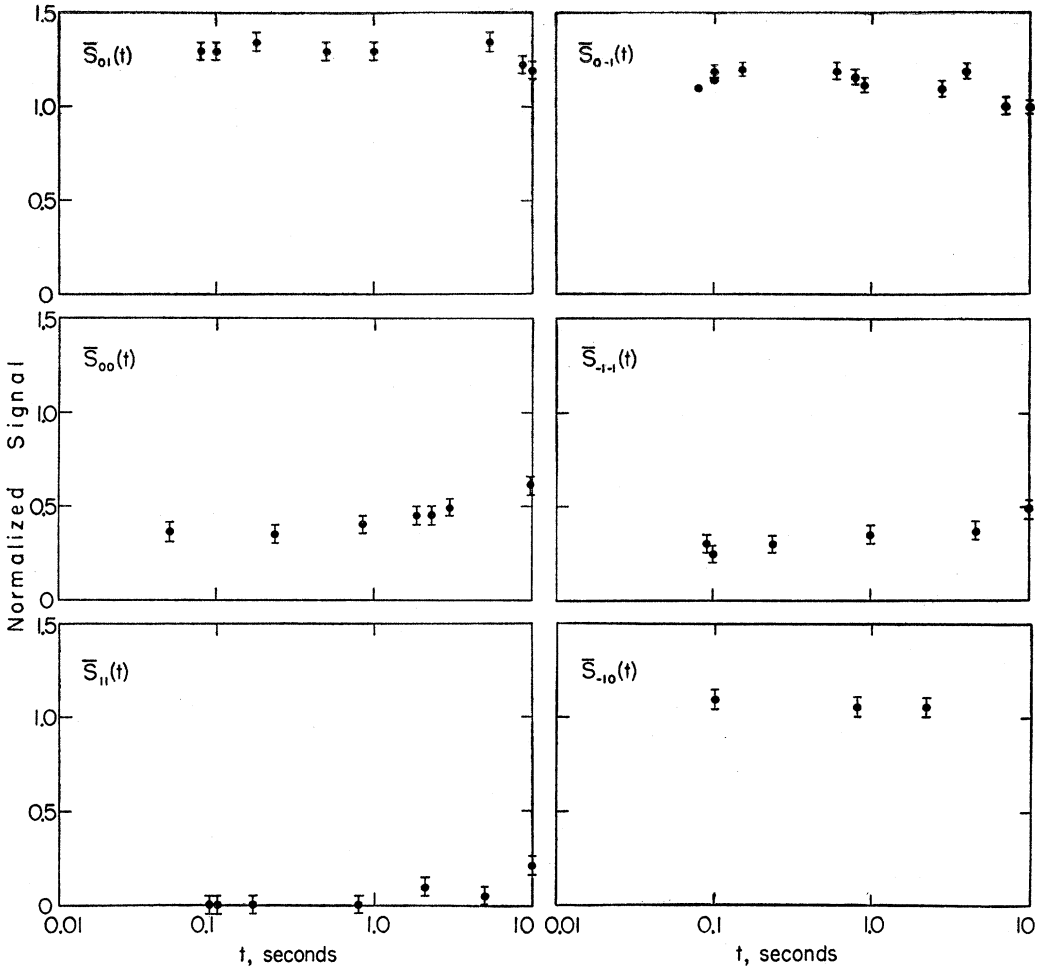

FIG. 6. Mixing rate measurements at the splitting $\delta f(\theta_2) = -3.2$ kc/sec. The first subscript on $\bar{S}_{ij}(t)$ denotes the saturating frequency; the second index denotes the frequency of the nuclear resonance signal.

expected plateau appears in the spin mixing rate. The existence at these splittings of what appears to be a quasi-equilibrium of the spin system is one of the most striking results of this investigation.

Figure 5 shows relaxation measurements for $\delta f(\theta_2) = 17 \pm 2$ kc/sec. At this splitting spin mixing proceeds so slowly that signals measured at times much less than T_1 are too small to be determined accurately. To obtain a relaxation rate curve one then must make measurements over a time interval comparable to T_1. Therefore, the relaxation rate observed at this splitting is certainly due to both spin-lattice relaxation as well as spin mixing. In the time interval $t \lesssim 45$ sec, the measurements are described by the equation $\bar{S}_{00}(t) = 1 - \exp[-(t/47 \text{ sec})]$. For longer times, $\bar{S}_{00}(t)$ rises more slowly, indicating that for $t \gtrsim 80$ sec, spin lattice relaxation dominates.

Shown in Fig. 6 are various $\bar{S}_{ij}(t)$ at $\delta f(\theta_2) = -3.2$ kc/sec, the splitting at which the plateau in the mixing rate is most pronounced. Several qualitative features of the data are to be noted: (a) The plateau that appears in $\bar{S}_{00}(t)$ also appears for all the other $\bar{S}_{ij}(t)$, (b) The signal $\bar{S}_{11}(t)$ is very small. This is to be expected since the overlap of ν_1 with the other two lines is quite small. Therefore, energy fed into the system at ν_1 cannot rapidly distribute itself throughout the entire spin system, (c) Since the overlap of ν_1 with the other two lines is small, it might be expected that saturation of either of the closely spaced lines ν_0 or ν_{-1} would be followed by the establishment of 3-level Boltzmann equilibrium between the $m = \frac{3}{2}$, $\frac{1}{2}$, and $-\frac{1}{2}$ states. The normalized signals expected in this case are $\bar{S}_{0-1} = \bar{S}_{00} = \bar{S}_{-10} = \bar{S}_{-1-1} = 0.75$; $\bar{S}_{01} = 1.25$. Comparison of these numbers with the data in Fig. 6 shows that 3-level equilibrium is not established.

The measurements $\bar{S}_{0-1}(t)$ and $\bar{S}_{-1-1}(t)$ are also difficult to understand. Since the lines ν_0 and ν_{-1} overlap greatly with each other but only slightly with ν_1 [as indicated by the measurements $\bar{S}_{11}(t)$], it might be expected that the relative populations of the $\frac{3}{2}$ and $\frac{1}{2}$ states after mixing would depend only weakly on which of the lines ν_0 or ν_{-1} were initially saturated.

Expressed in another way, one would expect $\bar{S}_{0-1} \sim \bar{S}_{-1-1}$. The data, however, show $\bar{S}_{0-1} \simeq 1.2$, $\bar{S}_{-1-1} \simeq 0.3$.[13] It has not been possible to provide a simple interpretation of these results.

V. APPARATUS

The pulse apparatus used in these experiments was operated at a frequency of 10 Mc/sec and is described elsewhere.[14] The cryostat was exceedingly simple, consisting of a Styrofoam box with $\frac{3}{8}$-in. walls. The crystals used were cylindrical in shape with a diameter of $\frac{1}{2}$ in. and a length of $\frac{5}{8}$ in. It was deemed necessary to establish to a high degree of certainty that the crystals used in these experiments were indeed single crystals. This was done by x-ray diffraction. It was found that the experimental results could be reproduced using various crystals.

The source of the rf saturating field was the signal from a *BC* 221, which was amplified with conventional circuitry and finally coupled inductively into the transmitter coil of the pulse apparatus. The field produced with this arrangement was sufficiently large to produce saturation of the sodium spins (at 77°K) in a small fraction of a second.

The desired mixing angle, θ_2, was established by rotating the magnet rather than the crystal. This involved first finding $\theta_{\min}$ (using the zero beat method described in the foregoing) and then rotating the magnet to the desired angle through the small angular difference $\theta_{\min} - \theta_2$. The magnet angle could be set with a precision of $\pm 0.005°$. The rotations involved in making the measurements at a given splitting were accomplished by rotating the crystal. While the time of transit between the orientations θ_1 and θ_2 was not small compared to the smallest measured mixing times, the fraction of that transit time during which mixing could take place was negligible.‡

VI. SUMMARY

It is found that for small mixing angles ($0 \lesssim \theta \lesssim 0.80°$) the level populations of the sodium spin system after mixing show an unexpected dependence on which pair of levels is initially saturated. It is also found for these small mixing angles that the spin system is in a quasi-equilibrium state after mixing. Both of these results are difficult to understand on the basis of Bloembergen's theory.

The experimental results seem to imply that there are correlations between the orientations of neighboring nuclear spins which have the effect of reducing the probability of certain types of transitions in spite of the fact that they are allowed by pairwise interaction terms in the dipole-dipole Hamiltonian. If correlations of this type do play an important role in determining the behavior of the spin system, then one would not expect Eq. (8) to be applicable.

It should be noted that the spin mixing phenomenon is quite different from that of spin-lattice relaxation where, at sufficiently high temperatures, the rate equations have been very successful in describing the dynamic behavior of spin systems. In spin-lattice relaxation one observes the interaction of a system of relatively small specific heat with a "reservoir," the lattice vibrations, whose temperature does not change in the relaxation process. In the spin mixing, however, no reservoir is present to absorb the energy of saturation. The spins must rearrange themselves to produce a more probable energy distribution. The experiments described here present some evidence that correlations between neighboring spins might make the thermal equilibrium distribution inaccessible.[15]

VII. ACKNOWLEDGMENTS

I wish to express my particular thanks to Professor R. T. Schumacher for his interest and help at every stage of this work, to Professor M. Baranger, Professor W. Kohn, and Professor F. Keffer for many stimulating discussions, and to Professor L. Van Hove for valuable comments. I am indebted to Professor C. P. Slichter for pointing out the necessity of considering second-order quadrupole splitting. Thanks are also due the Harshaw Chemical Company who kindly furnished the sodium nitrate crystals used in these experiments.

[13] The measurements at saturating frequency ν_0 in Fig. 6 satisfy the internal consistency requirement expressed by Eq. (11).

[14] R. T. Schumacher, reference 2. The circuitry closely resembles a design by Dr. John Spokas [John J. Spokas and Charles P. Slichter, Phys. Rev. **113**, 1462 (1959)].

‡ *Note added in proof.*—The experimental results were not sensitive to the rate of rotation of the crystal as long as the rotations were completed in a time short compared to T_1.

[15] The exponential time dependence of the relaxation at the relatively large splitting $\delta f(\theta_2) = 17$ kc/sec might be produced by a higher-order process in which the spins exchange their energy through an intermediate interaction with the lattice phonons. If this happens, one might expect Eq. (8) to hold, and the observed exponential rise in $\bar{S}_{00}(t)$ would not be unexpected.