Adiabatic Demagnetization in a Rotating Reference System*

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Redfield has proposed that under some circumstances, a magnetic resonance should be described by saying the spin system has achieved a temperature in a reference system which rotates at the frequency of the applied alternating field. He based his proposal on experiments in which characteristic times of observation were long compared to the spin-lattice relaxation time. A theory of spin-lattice processes was necessary to analyze the results. We describe a set of experiments to verify his hypothesis, using times short compared to the spin-lattice relaxation, which test his hypothesis without need for a theory of spin-lattice relaxation. The experiments are shown to be similar to conventional adiabatic demagnetization, performed, however, in a rotating reference frame. Redfield's ideas are thereby presented in a particularly simple form. The difference between reversible and irreversible losses in magnetization are illustrated, and it is shown, for example, that one can invert the magnetization with respect to the static field by passing through the resonance using alternating fields much less than the linewidth. The studies were made using the Na resonance in NaCl.

I. INTRODUCTION

SEVERAL years ago, Redfield[1] discovered that the behavior of magnetic resonances in strong alternating fields whose frequency was near to resonance was, in many instances, in conflict with generally accepted basic theory. In the absence of the alternating field, one finds customarily in solids that the component of magnetization perpendicular to the static field, H_0, decays to zero in a time (T_2) of about 100 μsec (as for example when one observes the free induction decay following a strong pulse which tilts the direction of the magnetization away from that of H_0). Bloch's[2] phenomenological equations predict a similar decay when the alternating field is present. What Redfield observed was that if the alternating field is present, the magnetization persists for much longer times—times which may be seconds.

In a penetrating analysis, he showed that the slow decay in the presence of the alternating field was closely related to the second law of thermodynamics. He showed, moreover, how one could, in fact, predict much of the observed behavior by introduction of the concept of spin temperature in a properly chosen reference system, one which rotated in the sense of the nuclear precession at a frequency equal to that of the alternating field. It we decompose the alternating field into two rotating components, each of amplitude H_1, we may neglect the component rotating in the opposite sense from the precession. The remaining component appears static in Redfield's rotating reference frame. The system he chose can be called, crudely, that which has the least time-dependent Hamiltonian, for it converts the time-dependent coupling of the spins with H_1 in the laboratory reference system to a static coupling in the rotating frame. In the process, certain other couplings become time dependent, but at a frequency which renders them ineffective. Redfield then argues that the system will achieve the "most probable" distribution among the eigenstates of the rotating reference system, hence will be describable by a temperature. Of vital concern is the rate at which the system achieves thermal equilibrium in the rotating reference system, since the temperature concept will only be valid if the parts of the spin system are more strongly coupled together than to the thermal reservoir provided by the lattice. Recently, Goldburg[3] has extended Redfield's work to NaCl and CaF_2, studying the conditions under which one goes from the usual resonance theory at low H_1 to Redfield's large-H_1 case.

Redfield's and Goldburg's experiments were performed under steady-state conditions, i.e., over time intervals long compared to the spin-lattice relaxation times. Their interpretation therefore requires a theory of the role of spin-lattice relaxation to determine the spin temperature which is effective in the rotating reference system (it is in general quite different from the lattice temperature). By working with times short compared to the spin-lattice relaxation time, one can effectively isolate the spins from the lattice, and demonstrate many of the consequences of Redfield's theory in a particularly simple manner. Such experiments involve a theory which is very similar to that of the standard adiabatic demagnetization. That such a theory applies was, of course, recognized by Redfield, and formed the basis for his measurements of relaxation times in Cu and Al (see Vol. 101 of reference 1); however, a detailed verification has not been published to our knowledge. In this paper we report a set of simple experiments, adiabatic demagnetization in the rotating reference frame,—which demonstrate the validity of Redfield's spin temperature hypothesis. Although we add nothing new to Redfield's basic ideas, we hope that our simple experiments will emphasize the ideas underlying Redfield's

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[1] A. G. Redfield, Phys. Rev. **98**, 1787 (1955); **101**, 67 (1956).
[2] See, for example, G. Pake, *Advances in Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1953), Vol. 2.
[3] W. Goldburg, Phys. Rev. **122**, 831 (1961).

paper; and provide an added verification of his arguments.[4]

II. THEORY

A. Classical Adiabatic Demagnetization

The theory of the classical problem of adiabatic demagnetization is due to a number of workers.[5] We review it briefly as background for the adiabatic demagnetization in the rotating reference system.

The energy of the spins consists of two terms, the Zeeman energy, due to the coupling of the spins to the external field, H_0, and the dipolar energy arising from the coupling of spins to the magnetic fields of their neighbors.[6] They are represented by terms $\mathcal{H}_z$ and $\mathcal{H}_d$ in the Hamiltonian. For example, $\mathcal{H}_z=-\gamma\hbar H_0\sum_k I_{zk}$, where γ is the nuclear gyromagnetic ratio, and I_{zk} the z-component of spin of the kth nucleus.

If the spin system is described by a temperature, θ_s, the relative population of levels is conveniently described by a density matrix $\rho(\theta_s)$ given by the operator

$$\rho(\theta_s)=[\exp(-\mathcal{H}/k\theta_s)/\mathrm{Tr}\exp(-\mathcal{H}/k\theta_s)], \quad (1)$$

where $\mathcal{H}=\mathcal{H}_z+\mathcal{H}_d$, and the symbol "Tr" has its usual meaning of "trace" or "sum over the diagonal elements."

The average value, $\langle G\rangle$, of any operator G is then given by

$$\langle G\rangle=\mathrm{Tr}[G\rho(\theta_s)]=\{\mathrm{Tr}[G\exp(-\mathcal{H}/k\theta_s)]/\mathrm{Tr}\exp(-\mathcal{H}/k\theta_s)\}. \quad (2)$$

For example, the average energy, $\langle E\rangle$, is given by

$$\langle E\rangle=\{[\mathrm{Tr}\mathcal{H}\exp(-\mathcal{H}/k\theta_s)]/\mathrm{Tr}\exp(-\mathcal{H}/k\theta_s)\}. \quad (3)$$

Using the facts (which can be verified explicitly) that

$$\begin{gathered}\mathrm{Tr}\mathcal{H}_z=0,\\ \mathrm{Tr}\mathcal{H}_d=0,\\ \mathrm{Tr}(\mathcal{H}_z\mathcal{H}_d)=\mathrm{Tr}(\mathcal{H}_d\mathcal{H}_z)=0,\end{gathered} \quad (4)$$

and that $\exp(-\mathcal{H}/k\theta_s)\cong 1-(\mathcal{H}/k\theta_s)$ (since the nuclear energies are all small compared to $k\theta_s$).

We get that

$$\langle E\rangle\equiv(1/k\theta_s)[\mathrm{Tr}(\mathcal{H}_z{}^2+\mathcal{H}_d{}^2)/\mathrm{Tr}\exp(-\mathcal{H}/k\theta_s)], \quad (5)$$

which can be written as

$$=[-C(H_0{}^2+H_l{}^2)/\theta_s], \quad (6)$$

where C is the nuclear Curie constant $N\gamma^2\hbar^2I(I+1)/3k$, N being the number of nuclei, γ their gyromagnetic ratio, and I their spin. Equations (5) and (6) define the quantity $H_l{}^2$, which is a magnetic field of the order of the local field at one nucleus due to its neighbors. In any case, one can compute $H_l{}^2$ by evaluating $\mathrm{Tr}\mathcal{H}_d{}^2$, a straightforward procedure. We give the result of an analogous problem later for the rotating reference system.

The average magnetization is given by the average of its components, M_x, M_y, and M_z, where

$$\mathbf{M}=\gamma\hbar\sum_k\mathbf{I}_k. \quad (7)$$

Using Eq. (2) and taking the static field H_0 along the z direction, we find, for example

$$\langle M_z\rangle=\{\mathrm{Tr}[M_z\exp(-\mathcal{H}/k\theta_s)]/\mathrm{Tr}\exp(-\mathcal{H}/k\theta_s)\}=(1/k\theta_s)[\mathrm{Tr}H_0M_z{}^2/\mathrm{Tr}\exp(-\mathcal{H}/k\theta_s)]=(CH_0/\theta_s), \quad (8)$$

and

$$\langle M_x\rangle=\langle M_y\rangle=0.$$

Equation (8) is Curie's law. We note several important points:

(1) The magnetization is parallel to H_0;

(2) Curie's law holds irrespective of the relative size of H_0 and H_l.

Adiabatic demagnetization involves changes in the external field. One then uses the first and second laws of thermodynamics to write[5]

$$\theta dS=dE+MdH=C_Hd\theta+\theta(\partial M/\partial\theta)_Hd H, \quad (9)$$

where

$$C_H=[C(H_0{}^2+H_l{}^2)/\theta_s{}^2].$$

Setting $dS=0$, one can solve for the variation in spin temperature from its value $\theta_s(H_i)$ for the initial field H_i to its value at the final field H_f. The result is

$$\theta_s(H_f)=\theta_s(H_i)\{[H_l{}^2+H_f{}^2]^{\frac{1}{2}}/[H_l{}^2+H_i{}^2]^{\frac{1}{2}}\}. \quad (10)$$

If we demagnetize from a field large compared to H_l, with an initial magnetization M_i, we then get a final magnetization (using Curie's law) of

$$M_f=M_iH_f/[H_l{}^2+H_f{}^2]^{\frac{1}{2}}. \quad (11)$$

The results of Eqs. (10) and (11) are shown in Fig. 1. We see that in demagnetizing, the spin temperature is proportional to H_0 for $H_0>H_l$, but when H_0 is less than the local field, the spin temperature is independent of H_0. The physical origin of this result may be seen by considering the degree of alignment of nuclei along the resultant of the external field and the field of the neighbors. This alignment depends on the Boltzmann factor, hence on $\mu H_T/k\theta_s$, where H_T is some sort of effective sum of the external and local fields ($H_T{}^2=H_0{}^2+H_l{}^2$) and μ the nuclear moment. If we decrease H_0 slowly, the degree of alignment of spins along H_T

[4] In addition to references 1 and 3, other interesting references on the subject include: N. Bloembergen and P. P. Sorokin, Phys. Rev. **110**, 865 (1958); D. F. Holcomb, *ibid.* **112**, 1599 (1958); I. Solomon, Comptes rend. **248**, 92 (1958).

[5] A good summary of important equations, together with basic references to the work of J. H. Van Vleck, H. B. G. Casimir, and F. K. du Pré, C. J. Gorter, and others, is found in the book, *Paramagnetic Relaxation* by C. J. Gorter (Elsevier Publishers, New York). Further references for applications to nuclear resonance are: N. F. Ramsey and R. V. Pound, Phys. Rev. **81**, 278 (1951); A. Abragam and W. G. Proctor, *ibid.* **106**, 160 (1957); and **109**, 1441 (1958); A. Anderson and A. G. Redfield, *ibid.* **116**, 583 (1959).

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

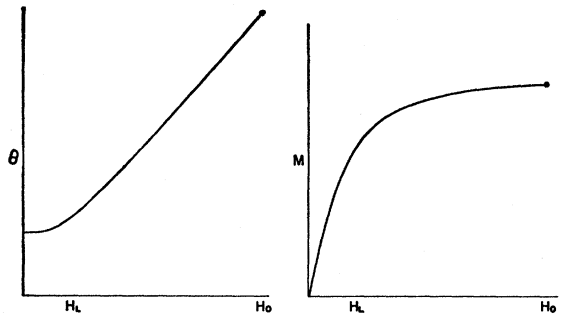

FIG. 1. Spin temperature, θ_s, and magnetization, M, as a function of applied field, H_0, for an adiabatic demagnetization [Eqs. (10) and (11) of the text].

will remain constant so that H_T/θ_s will not vary. Consequently, θ_s will be independent of H_0 when H_0 becomes less than H_l.

From Curie's law, we find that M is independent of H_0 as long as $\theta_s \propto H_0$, which is the case when H_0 is greater than H_l. However, if H_0 is less than H_l, we find M is proportional to H_0. Physically, we always maintain the same degree of alignment of nuclei along the total field, but when H_0 is less than H_l, the total field at different nuclei is rather randomly oriented in space and the *bulk* magnetization is less than it is for H_0 greater than H_l, for which the total fields at all nuclei are parallel.

The important point for us to realize is that a nuclear system which has been adiabatically demagnetized to zero field still has the same degree of order as it had at high fields. The "loss in magnetization" is entirely reversible—one can recover the original magnetization simply by turning H_0 back on again sufficiently slowly for the nuclei to follow it.

B. Adiabatic Demagnetization in the Rotating Reference System

Redfield's theory for the case in which one has an alternating field is very similar to that outlined in the preceding section. He transforms away the time dependence of the alternating field by a coordinate change to the reference system rotating at the frequency of H_1. In so doing, he finds a new Hamiltonian.

$$\begin{aligned}\mathcal{H}=\gamma_I\hbar(\mathbf{H}_0-\hat{k}\frac{\omega}{\gamma_I}+H_1\hat{\imath})\cdot\sum_p \mathbf{I}_p+\sum_{p>q}(A_{pq}\mathbf{I}_p\cdot\mathbf{I}_q \\ +B_{pq}I_{zp}I_{zq})+\sum_{p,q}C_{pq}I_{zp}S_{zq}+\sum_{r>p}(A_{rp}\mathbf{S}_r\cdot\mathbf{S}_p \\ +B_{rp}S_{zr}S_{zp})+\gamma_s\hbar(\mathbf{H}_0-\frac{\hat{k}\omega}{\gamma_s}+H_1\hat{\imath})\cdot\sum_r\mathbf{S}_r \\ +\text{time dependent terms.}\end{aligned} \quad (12)$$

We have assumed two species of nuclei to be present, and we are using the symbol I to denote the nucleus whose resonance we are observing, S to denote the other.

The terms A_{pq}, B_{pq}, and C_{pq} are defined as

$$\begin{aligned}A_{pq}&=A_{pq}'+(\gamma_I^2\hbar^2/r_{pq}^3)(\tfrac{3}{2}\cos^2\theta_{pq}-\tfrac{1}{2}),\\ B_{pq}&=3(\gamma_I^2\hbar^2/r_{pq}^3)(\tfrac{3}{2}\cos^2\theta_{pq}-\tfrac{1}{2}),\\ C_{pq}&=A_{pq}'-(\gamma_I\gamma_s\hbar^2/r_{pq}^3)(3\cos^2\theta_{pq}-1),\end{aligned} \quad (13)$$

where A_{pq}' is the pseudo-exchange coupling between nuclei p and q a distance r_{pq} apart, whose line of centers makes an angle θ_{pq} with the direction of H_0 (the z direction). ω is the angular frequency of H_1.

The time-dependent terms have a frequency ω or 2ω, and come from those terms of the dipolar coupling which, in the laboratory reference system, would have nonvanishing matrix elements between states of different m, where m is the quantum number describing the z component of the total nuclear spin. They correspond to fields of the order of H_l, rotating at either ω or 2ω.

Equation (12) has, so to speak, traded a time-dependent H_1 in the laboratory system for a time-dependent dipolar coupling in the rotating system. However, as Redfield points out, H_1 in the laboratory system is in resonance, whereas the dipolar terms in the rotating system are far from resonance. (In the rotating system, the resonance occurs for zero magnetic field and zero frequency, whereas the time-dependent dipolar terms are at ω or 2ω.)

As a result of the nonresonant character of the dipolar coupling, it is ineffective. If we overlooked the nonresonant character, we might erroneously suppose that we should use the rotating system only when $H_1>H_l$, whereas in fact the rotating system must be "more static" than the laboratory system as long as H_1 is greater than H_l^2/H_0, since the dipolar terms can at most be nearly secular in the rotating system in second order. It would be interesting to see whether there are any observable changes for H_1 in this range of $H_1\sim H_l^2/H_0$, although it is probable that the only effect of the nonsecular terms is a slight change in the spin specific heat. The term $\gamma_s\hbar H_1\hat{\imath}\cdot\sum_r\mathbf{S}_r$ is likewise off-resonance, and can be neglected. The term $\gamma_s\hbar(\mathbf{H}_0-\hat{k}\omega/\gamma_s)\cdot\sum_r\mathbf{S}_r$ commutes with the rest of the Hamiltonian and may therefore be removed from the Hamiltonian since it will have no influence of the changes in magnetization of the system "I" during our experiments.

We now make Redfield's hypothesis that in the rotating reference system the spin system is described by a temperature, θ_s. The density matrix is as before $\rho(\theta_s)=\exp(-\mathcal{H}/k\theta_s)/\mathrm{Tr}[\exp(-\mathcal{H}/k\theta_s)]$ except that for $\mathcal{H}$ we use Eq. (12), omitting the time-dependent terms and the term $\gamma_s\hbar(\mathbf{H}_0-\hat{k}\omega/\gamma_s+H_1\hat{\imath})\cdot\sum_r\mathbf{S}_r$.

Calling the first term of Eq. (12) $\mathcal{H}_z$ and the remaining $\mathcal{H}_d$, we find, following Redfield, a set of equations identical to Eqs. (6)–(11), with H_0 replaced by

$$[(H_0-\omega/\gamma_I)^2+H_1^2]^{\frac{1}{2}}, \quad (14)$$

and

$$H_l^2=\tfrac{1}{3}\langle\Delta H^2\rangle_{II}+\langle\Delta H^2\rangle_{IS}+\tfrac{1}{3}(\gamma_S/\gamma_I)^4(f_I/f_S)\langle\Delta H^2\rangle_{SS} \quad (15)$$

(we have here set $A_{pq}'=0$). In units of magnetic field, $\langle\Delta H^2\rangle_{II}$ is the contribution of spins I to their own second moment,[6] $\langle\Delta H^2\rangle_{IS}$ is the contribution of spins S to the second moment of spins I, and $\langle\Delta H^2\rangle_{SS}$ is the contribution of spins S to their own second moment. f_I and f_S are the fraction of spins which are of type I and S, respectively.

III. EXPERIMENTAL PROCEDURE AND APPARATUS

The experiments were performed on the Na^{23} resonance in a single crystal of Harshaw NaCl. The static field was oriented along a [100] direction. In addition to the pulse experiments described below, steady-state resonances were run of both the Na^{23} and Cl^{35} nuclei using a Pound-Knight-Watkins spectrometer, built by W. W. Simmons of our laboratory.

The basic procedure of our experiments is to sit off-resonance with H_1 turned off for a time long enough to achieve thermal equilibrium between the spins and the lattice. H_1 is then turned on, and the static field brought closer to the resonance. Denoting the final amount we are off-resonance by h, we measure the magnetization as a function of h and of H_1. The change in H_0 is sufficiently slow for thermodynamic reversibility to be possible, but fast enough to prevent spin-lattice relaxation to be significant. In order to have thermodynamic reversibility, the nucleus must precess many cycles in the time it takes the effective field to change significantly. Since H_1 is the minimum value of the effective field, and since the precession period for H_1 is $2\pi/\gamma H_1$, thermodynamic reversibility is satisfied when $(\gamma H_1^2/2\pi)\gg dH_0/dt$. (In our experiments, at the *lowest* H_1 used, $(\gamma H_1^2/2\pi)=92$ gauss/sec. dH_0/dt measured from oscilloscope pictures of the emf produced in a pickup coil was not constant in time, but its maximum value, which occurred off resonance, was 50 gauss/sec, and its value near resonance was at most 25 gauss/sec. The necessary inequality was therefore fairly well satisfied at the lowest H_1, and quite well satisfied for larger values.)

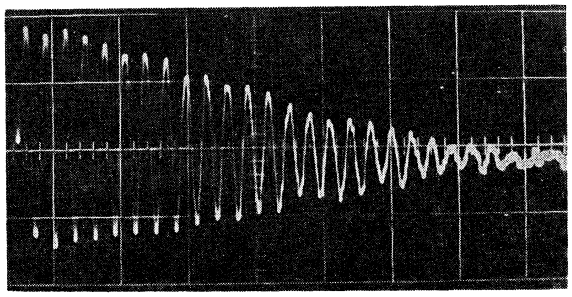

FIG. 2. Resonance signal due to free precession of nuclei following turn-off of H_1. The beats occur between the nuclear signal and an rf voltage injected into the early stages of the receiver. (Time scale: 50 μsec/scale division).

The apparatus used has been described elsewhere.[7] It consisted of a crystal-controlled 7 mc/sec oscillator, a gated power amplifier, a bridge, and a receiver. Observation of the magnetization while H_1 is on is not possible, particularly with the H_1's of around 1 gauss which are needed for our experiments, because the amplifier is blocked by the signal passed by the bridge. Accordingly, we determined the magnetization by turning off H_1 and measuring the initial size of the free induction decay after the amplifier recovered (a time of about 20 μsec). Although dH_0/dt was not strictly zero when H_1 was turned off, the turn-off served to define the value of h appropriate to the data. In order to have linear operation of the detector, a small rf signal was fed into the input stages of the amplifier at a frequency of a few kilocycles from the nuclear precession frequency. The detector output shows the beat between the nuclear signal and the injected rf voltage (see Fig. 2).

The variation in H_0 was produced by discharging a condenser through a pair of coils mounted on the magnet gap. The initial high current through the coils kicked the field about 40 gauss, following which it drifted back to its initial value in about 2 sec. The rate of return was determined partly by the condenser discharge time constant, and partly by the time for fields to penetrate the magnet iron.

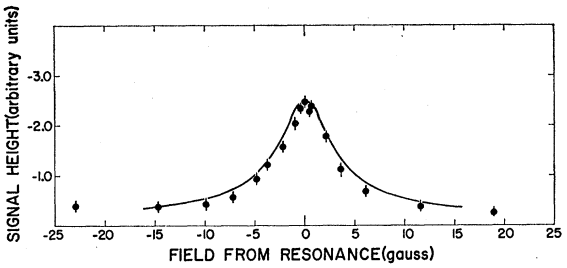

FIG. 3. Signal height vs h for H_1 large compared to H_l. ($H_1=1.9$ gauss, $H_l=0.9$ gauss).

A gating signal was taken from the switch, which connected the condenser to the gap coils, was delayed one-half second (the time for the field to reach its maximum excursion), and used to trigger a gate which turned on H_1 for 2 sec. The turn-off of H_1 triggered the sweep of a Tektronix 545A oscilloscope, on whose screen the free induction decay was displayed and photographed.

The initial value of H_0 was monitored by measuring the frequency of a proton magnetic resonance. Since dH_0/dt was not strictly zero when H_1 was turned off, h is not that given simply by the value of field measured from the proton resonance. Rather, it differs by an amount which is the same for all measurements. The correction was determined by plotting the resonances

[7] J. J. Spokas and C. P. Slichter, Phys. Rev. **113**, 1462 (1959).

as a function of the *initial* field values, (i.e., fields measured by the proton resonance), and finding that value of initial field which corresponded to the peak of the resonance. We feel this procedure is justified since the resonances were symmetric about their center for a given H_1, and the position of their centers was independent of H_1.

The relative size of H_1 in various runs was determined by photographing the bridge output voltage during the pulse. Since this signal depends on the degree of bridge balance, it is necessary to take the data without changing the balance. The degree of balance was sufficiently low to be highly stable, as monitored by checking the unbalance voltage for the same power supply voltages. No doubt much of the stability is due to the facts that the oscillator frequency is crystal controlled and that the bridge design gives balance conditions which are nearly frequency independent. Reproducibility of output for the same voltages leads us to believe the relative values of H_1 are known to about $\pm 10\%$.

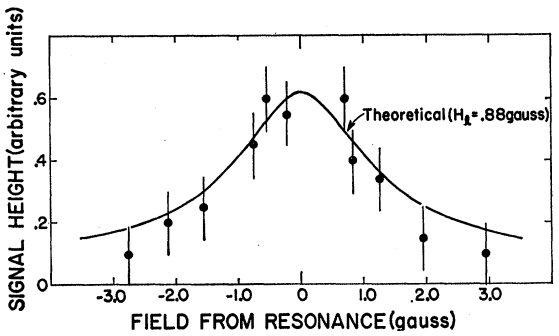

FIG. 4. Signal height vs h for H_1 small compared to H_l. ($H_1=0.19$ gauss, $H_l=0.9$ gauss).

The absolute values of H_1 were determined by measuring (a) the width of the resonance for large H_1 and (b) rotary saturation. In addition, a rough check was made by measuring the bridge-unbalance voltage and pulse duration for a $\pi/2$ pulse.

The apparatus built by Spokas[7] was intended for short pulses. The amplifier recovery from the 2-sec bursts of H_1 was much slower than it was after a 50 μsec, $\pi/2$ pulse. We succeeded in getting fast recovery by putting a pair of diodes in parallel opposing across the plate loads of the first two amplifier stages (since no dc flowed through the plate loads, the diodes had no dc bias).

IV. EXPERIMENTAL RESULTS

A. Adiabatic Demagnetization

The experiments on adiabatic demagnetization as described in the preceding section all involve starting well off resonance, and coming to a field $H_0-(\omega/\gamma)\equiv h$ away from the resonance. The effective field (H_e) in the rotating coordinate system is then

$$H_e=[H_1^2+h^2]^{\frac{1}{2}}. \tag{16}$$

Since the magnetization off resonance is M_0, the thermal equilibrium magnetization, we find that

$$M=M_0\{H_e/[H_e^2+H_l^2]^{\frac{1}{2}}\}. \tag{17}$$

Our experimental method measures M_x

$$M_x=M(H_1/H_e)=M_0\{H_1/[H_1^2+h^2+H_l^2]^{\frac{1}{2}}\}$$
$$=\{M_0H_1/[H_l^2+H_1^2]^{\frac{1}{2}}[1+h^2/(H_1^2+H_l^2)]^{\frac{1}{2}}\}. \tag{18}$$

From Eq. (18), we see that if we plot signal vs h for a fixed H_1, we should obtain a universal curve, the width of which is proportional to $[H_1^2+H_l^2]^{\frac{1}{2}}$ and the peak height of which is $M_0H_1/[H_1^2+H_l^2]^{\frac{1}{2}}$. Figure 3 shows experimental points for an H_1 much larger than H_l ($H_1=1.9$ gauss) together with a theoretical curve whose peak-height and width have been chosen to approximate the data. Figure 4 shows experimental points for an H_1 which is smaller than H_l ($H_1=0.19$ gauss) together with a theoretical curve calculated assuming $H_l=0.88$ gauss. We see that an equation of the general form of Eq. (18) describes the data. It is interesting to note that the magnetic field was pulsed to lower magnetic fields and the experiments done while the field was increasing to its original value. Thus, points to the *right* of the center of the resonance line involve a cycle of the effective field in which it has gone down to a minimum of H_1, and then come back up to $[H_1^2+h^2]^{\frac{1}{2}}$. The symmetry of the experimental curves about their center illustrates that the magnetization loss at the center is *reversible*. This symmetry was found for all values of H_1.

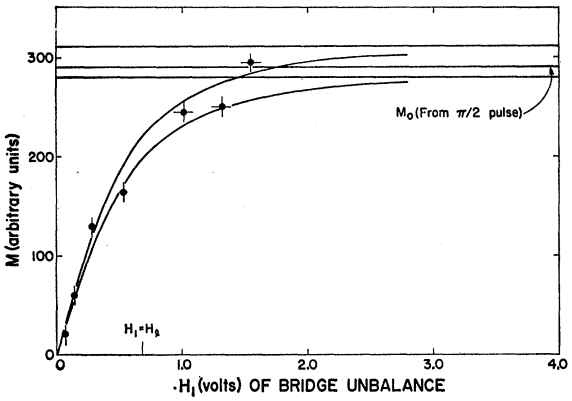

FIG. 5. Signal height vs H_1 for $h=0$. (H_1 expressed in volts bridge unbalance.) 1.4 gauss for 1 v unbalance. The two theoretical curves [Eq. (18)] assume different values for M_0.

Figure 5 shows the magnetization at the center of the resonance ($h=0$) as a function of H_1. The ordinate is in units of bridge unbalance voltage. Two theoretical curves are shown: one for $M_0=2.8$ divisions, the other for $M_0=3.1$ divisions. From the decay following a $\pi/2$ pulse, we measure $M_0=2.9\pm0.1$ divisions. A large

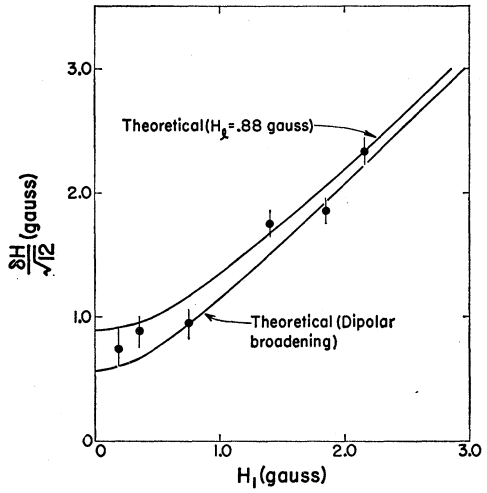

FIG. 6. Linewidth between points whose signal is half of the maximum signal vs H_1.

amount of data at large H_1 leads us to believe 3.0 divisions is the best value.

The theoretical curves in Fig. 5 have been fitted to $H_l=0.68$ v. Since our calibration of bridge unbalance gives 1.4 ± 0.15 gauss/v, we find $H_l=0.95\pm0.1$ gauss. We note in any event that the data fit the general form expected. It would be desirable to have larger H_1's to establish the large H_1 asymptotic behavior; however, we were limited by the power available from the oscillator for 2-sec pulses.

Figure 6 shows the linewidth vs H_1, where the values of H_1 have been calculated from the bridge unbalance voltage. The quantity δH is defined as the full width of the resonance between points where it is half of its peak height. From Eq. (18), we find $\delta H=[12(H_l^2+H_1^2)]^{\frac{1}{2}}$. In the limit of large H_1, $\delta H=(12)^{\frac{1}{2}}H_1$. Accordingly, we have plotted $\delta H(12)^{-\frac{1}{2}}$ vs H_1. Two theoretical curves are given. The upper one is based on the assumption that $H_l=0.88$ gauss, a value chosen to approximate the data at low H_1 where $\delta H(12)^{-\frac{1}{2}}=H_l$. Note that this measure of H_l does *not* depend on our knowledge of H_1, but solely on our measurements of h. Since h was found using a proton resonance, we consider it to be exceedingly reliable. On the other hand, since signals for low H_1 are small, the signal-to-noise ratio is at its worst, and reliable measurement of width corresponding difficult.

Equation (15) enables us to calculate H_l from first principles. Using it, we find $H_l=0.57$ gauss. This is significantly below the values of 0.88 ± 0.1 gauss obtained from the low H_1 linewidth, or 0.95 ± 0.1 gauss obtained from Fig. 5. We believe the discrepancy between these values and the theoretical value are outside of experimental error. Three possible sources of error might arise: (1) errors in calibrating H_1, (2) inhomogeneities in H_1 over the sample, and (3) inhomogeneities in H_0 due to the magnet. Neither items (1) or (2) would affect the low H_1 linewidth. However, as pointed out above, the signal-to-noise ratio is at its worst for low H_1's, and we may be unrealistic in quoting the linewidth. To some extent, our calibration of H_1 by observing either rotary saturation or the large H_1 linebreadth should compensate for inhomogeneities. The magnet homogeneity was checked by observing the Na^{23} resonance in a solution of NaCl in water using a Pound-Knight spectrometer. Assuming a uniform field gradient deduced from these measurements, the corrections to the resonance curves are only about 1%.

One possible explanation for the large H_l is the presence of a quadrupolar coupling. There are several ways of seeing that a quadrupole effect might increase H_l. For example, H_l represents a coupling to the nuclear spin. The more such couplings, the larger H_l. Or, one may view H_l as simply a measure of the spin specific heat. A quadrupole interaction would increase the spin specific heat.[8] Of course, the quadrupolar coupling would vanish in a perfect NaCl crystal, since each Na site has cubic symmetry, but might be nonzero if there were strains or impurities. The presence of quadrupole couplings can be checked by measuring the second moment of the resonance lines. Such measurements were made on both the Na^{23} and Cl^{35} nuclei. The second moments of both Na^{23} and Cl^{35} provide checks on Eq. (15). For Na^{23}, the free induction decays enable one to measure the Na^{23} second moment, since the coefficient of the t^2 term in the decay is proportional to the second moment. The theoretical root-second moment is 0.73 gauss, whereas the Bloch decays gave values such as 0.71 gauss or 0.77 gauss. A steady-state absorption derivative was also run. Assuming a Gaussian shape, the peak-to-peak distance on the derivative gave 0.76 gauss for the second moment. For Cl^{35}, an absorption derivative gave a second moment for the Cl^{35} of 1.07 kc/sec (assuming a Gaussian shape), whereas the theoretical value is 1.10 kc/sec.

We conclude that the width of the steady-state resonance curves is given well by the dipolar coupling. If there are quadrupolar couplings, they must affect only a small number of nuclei and be correspondingly large. We note that if 1% of the Na nuclei had a quadrupole energy which was ten times the magnetic energy of a Na^{23} nucleus in its local field, the discrepancy would be resolved. As a corollary, measurements such as we describe provide a sensitive measure of quadrupole couplings, provided the "quadrupole nuclei" are able to maintain a spin temperature equilibrium with the rest of the nuclei. Anderson and Redfield, and Hebel[8] have shown similar effects in Al using standard adiabatic demagnetization. Our experiment has the advantage of being done with larger M_0's.

As we have remarked above, the symmetry of the signal about the center of the resonance illustrates that

[8] See, for example, the paper by Anderson and Redfield, reference 5, or L. C. Hebel, Bull. Am. Phys. Soc. **5**, 176 (1960).

the loss in magnetization at the center of the resonance when $H_1 < H_l$ is reversible, as assumed in the spin temperature hypothesis. If one were to pass through the resonance with a value of $H_1 < H_l$, the magnetization should follow the effective field direction, but decrease in magnitude to a minimum value at the center of the resonance, and grow back to M_0 when one is through the resonance an amount much greater than H_l. (In other words, the "loss" in magnetization at the center of the resonance is *reversible.*) In the process, since the effective field is inverted in space, the magnetization will likewise be inverted. It should therefore be possible to invert M_0 with respect to the external field by passage through the resonance with $H_1 < H_l$ provided the passage is slow enough for the magnetization to follow the effective field and for a spin temperature to be established, yet fast enough to make spin-lattice relaxation negligible.

This technique has been used by Redfield to measure spin-lattice relaxation in Cu and Al. (See Vol. 101 of reference 1). To illustrate it, we performed the following experiment. Two passes were made through the resonance, the first pass of low $H_1 (H_1 \cong H_l/4$, corresponding to 0.14 v in Fig. 5) to invert the magnetization, the second pass of large H_1 ($H_1 = 2.5 H_l$ corresponding to 1.5 v on Fig. 5) to inspect. As before, the static field was pulsed to lower fields, and H_1 turned on while the field returned to its original value. The static field was set about $2\frac{1}{2}$ gauss *above* the resonance. The first pass (at low H_1), therefore carried through the resonance, but the second pass (large H_1) did not since the large H_1 was comparable to h, permitting us to observe a signal. The signal strength following the second pulse was measured as a function of the time, T, between pulses. It is shown in Fig. 7. (In this procedure, the change from low to high H_1 was accomplished by manually changing the screen voltage of the 3*E*29 rf power output tube, a fact which made it impossible to start the second pass any sooner than about 1 sec after the end of the first). We note from Fig. 7 that the signal strength decreases with T initially, then increases. This behavior is just what we would expect if the first pass inverted M_0, and if spin-lattice relaxation took place before the second pass. The z component of magnetization then would obey the equation

$$(dM_z/dt) = (M_z - M_0)/T_1, \tag{19}$$

where T_1 is the spin-lattice relaxation time. Inserting the initial condition $M_z(0_+) = -M_0$ gives

$$M_z = M_0 - 2M_0 e^{-T/T_1}. \tag{20}$$

Therefore, a plot of $M_0 - M_z$ would give an exponential with a slope of $1/T_1$ and an intercept $2M_0$. Deducing M_z from Fig. 7, and taking the value of M_0 as the long-time asymptote (2.0 divisions), we have deduced $M_0 - M_z$ and plotted it on semilog paper in Fig. 8. Note that the slope agrees well with that predicted from Wikner, Blumberg, and Hahn's[9] measurement of T_1, and that the intercept of 3.7 is close to the predicted value of 4.0 divisions. (Actually, we have plotted signal heights, which are proportional to M_x—but M_x is related to M by a simple projection, the same for each measurement, so that in effect, M_x, M, and M_z are constant multiples of one another.) Although the signal height extrapolated to $T=0$ gives $|M_z|$ only 85% of M_0, we should remember that at the center of the line during the pass at this H_1, M has diminished to 20% of M_0. Therefore, it is clear that the decrease in magnetization on passage with low H_1 is essentially reversible.

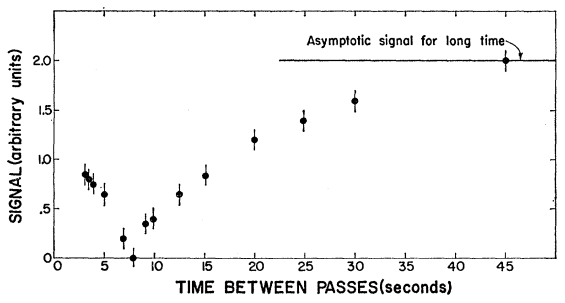

FIG. 7. Signal after second of two passes through resonance (the first of small H_1, the second of large H_1) as a function of the time between passes.

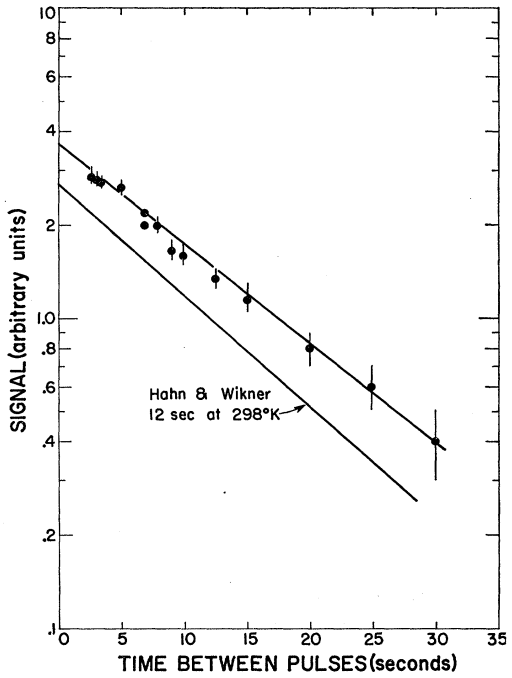

FIG. 8. Semilog plot of data of Fig. 7 replotted as described in the text.

B. Nonadiabatic Pulsing

In the experiments described so far, the effective magnetic field is always changed slowly since even

[9] E. G. Wikner, W. E. Blumberg, and E. L. Hahn, Phys. Rev. **118**, 631 (1960).

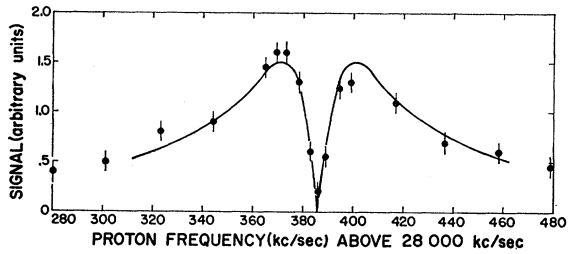

FIG. 9. Signal vs h for constant H_0 and a large H_1. The theoretical curve is given by Eq. (22).

when H_1 is turned on, one is so far off resonance that $H_e \cong h$. We now describe some experiments in which H_0 is *not* varied, but in which H_1 is pulsed on for a few msec, a time long compared to the decay time of free induction signals (about 0.2 msec). Since H_1 is turned on in a few microseconds, we may think of these experiments as being non-adiabatic switching of the effective field. They would be described by the sudden approximation of quantum mechanics, i.e., immediately after turning on H_1, the system wave function is identical to its value prior to switching, but the Hamiltonian has changed discontinuously.

These experiments are interesting because of their contrast with the adiabatic switching. Figure 9 shows the signal vs h for a large H_1. Unfortunately, bridge unbalance data cannot be used to give the H_1, but the power supply voltages are consistent with a value of 3.3 gauss deduced from Fig. 9 as described below. The striking point about Fig. 9 is the sharp null at the center. (Note: The ordinate is the proton resonance frequency in the magnet—4.257 kc/sec equals 1 gauss.)

A simple physical picture serves to explain the data. Prior to turning on H_1, the magnetization is M_0 and points along the z direction. After H_1 is turned on, the nuclear magnetization precesses around the effective field. Since the local fields may aid or oppose H_e, there is a spread in precession frequencies. However, since $H_e \gg H_l$, to a good approximation, the precession is about a field whose *direction* is that of H_e. Consequently, components of magnetization perpendicular to H_e get out of step in a time of the order of T_2, eventually cancelling each other. Components parallel to H_e are preserved. As a result, after about 0.2 msec (the free induction decay time) we expect to find M parallel to H_e, and in length simply the projection of M_0 on H_e. Hence

$$M = M_0(h/H_e). \tag{21}$$

The signal is proportional to M_x,

$$M_x = M(H_1/H_e) = M_0 h H_1/(H_1^2+h^2). \tag{22}$$

Such a curve has been plotted in Fig. 9, the height and width being adjusted to fit the data. The width of the curve corresponds to $H_1 = 3.3$ gauss.

The peak height should be $M_0/2$. This gives $M_0 = 3$ divisions, which is the value obtained from the adiabatic experiments, the amplifier gains all being the same.

The theory above applies to $H_e \gg H_l$. If $H_e \sim H_l$, there would be corrections due to the exchange of energy between the spin-spin couplings and the energy in the effective field.

The magnetic energy immediately after switching is

$$-(CH_l^2/\theta_L) - M_0 h = -M_0[(H_l^2/H_0)+h], \tag{23}$$

since the degree of alignment of spins in the local fields of their neighbors is that of the lattice temperature. After a spin temperature has been reached, the magnetic energy is

$$-MH_e - (CH_l^2/\theta_s) = -MH_e - (MH_l^2/H_e). \tag{24}$$

Equating Eqs. (23) and (24), we find

$$M = (M_0 h/H_e)(H_e^2/H_e^2+H_l^2)(1+H_l^2/H_0 h), \tag{25}$$

in agreement with the simple projection theory when $H_e^2 \gg H_l^2$. Equation (25) has a simple physical interpretation. It is the product of three terms. The first is the projection of M_0 on the effective field. The second factor represents the change in M_0 due to the exchange of the Zeeman energy with spin-spin energy. When $H_e \gg H_l$, this exchange does not occur, and the factor is unity. The third term involves a correction $H_l^2/H_0 h$ which arises because of the spin-spin energy present before turning on H_1. It is in general negligible. It prevents M from being strictly zero when one is at the center of the resonance. To a good approximation, the last factor can be called unity.

It would be interesting to verify Eq. (25) as a function of H_1. Note that the loss in magnetization here ($M < M_0$) is irreversible, in contrast to the "loss" from the slow changes in H_0. The irreversibility results from the sudden change in H_e on the application of H_1. From an experimental viewpoint, we wish to emphasize that turning on H_1 quickly is very easy, since it is at such a high frequency. It is quite easy to satisfy the sudden approximation in the rotating reference frame.

V. CONCLUSIONS

The experiments described demonstrate the principles proposed by Redfield in a very simple way. The basic point of *reversibility* in the demagnetization is clearly demonstrated. There is a close similarity between the adiabatic demagnetization experiments in the rotating reference frame and the conventional ones such as those of Anderson, Redfield, and Hebel. There are indications that the spin specific heat in our samples is larger than that calculated only from dipolar coupling. Using the rotating frame, studies of quadrupole couplings of point defects may be possible.

ACKNOWLEDGMENTS

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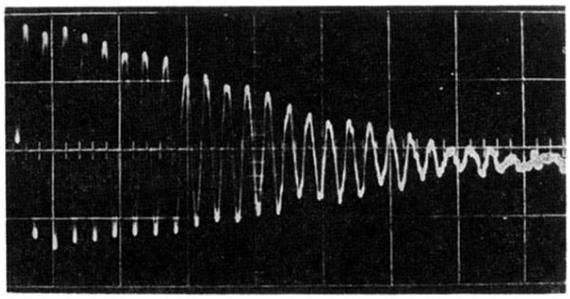

FIG. 2. Resonance signal due to free precession of nuclei following turn-off of H_1. The beats occur between the nuclear signal and an rf voltage injected into the early stages of the receiver. (Time scale: 50 μsec/scale division).