

electron concentration increases the proportion of the electrons having s character increases and reaches a maximum between V and Cr. Further increase of the electron concentration appears to cause a considerable admixture of s and non- s states, reducing the K_V values. A similar analysis can be applied to the change of proportionality of s and non- s wave functions in the bcc region of the V-Tc system, see Fig. 6.

An alternative view that one may put forth is that ψ^2 remains essentially independent of e/a and that $n_s(E)$, the density of states of the s electrons, changes in accord with K_V . Resistivity measurements in these alloy systems would aid in determining the validity of this argument. The high resistivity in transition metals is generally thought of as due to the scattering of conduction electrons from s to d states where the probability of such processes is proportional to the high density of states in the d band. The view adopted in this investigation is that the conduction electron wave function is composed of an admixture of s and d states with the electrons resonating between them. Thus, the resistivity should reach a maximum where the relative proportion of d states predominates and a minimum where the

relative proportion of s states predominates. Recently, Taylor and Llewellyn Smith¹⁴ have measured the resistivity in alloys of the V-Cr system and find a minimum very nearly in the vicinity where the current analysis postulates a maximum in s character. This strongly supports the view that it is ψ^2 which determines the K_V variation and not $n_s(E)$.

Information on the number of s electrons in pure V can be obtained from the nuclear magnetic relaxation measurements of Butterworth.¹⁵ He finds that the proportion of the electrons at the Fermi surface having s character is very low, roughly 0.17. The present measurements indicate that this value decreases on alloying V with Ti and increases on alloying V with Tc or Cr.

ACKNOWLEDGMENT

The authors wish to thank Dr. M. V. Nevitt for many helpful discussions throughout the preparation of the manuscript.

¹⁴ M. A. Taylor and C. H. Llewellyn Smith, *Physica* **28**, 453 (1962).

¹⁵ J. Butterworth, *Phys. Rev. Letters* **5**, 305 (1960).

Static Spin Temperature Experiments and the Approach to Thermal Equilibrium in the Rotating Reference Frame*

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Nuclear magnetic resonance experiments were performed which further verify Redfield's assumption that, for large rf fields $H_1(\nu)$, a nuclear spin system is properly described by a spin temperature in a reference frame rotating about the Zeeman field with frequency ν . As with similar experiments recently performed by Slichter and Holton, the interpretation of our results does not require any assumption about the spin-lattice relaxation mechanism. The measurements were made on the Na^{23} spins in NaCl and the F^{19} spins in CaF_2 . In both materials the agreement between experiment and theory was very good. From the sodium chloride results it is concluded that quadrupole interactions, caused by strains and imperfections, produce an unobservably small increase in the local field H_l in the crystals used.

Also studied was the rate at which the Na^{23} spin system in NaCl approaches thermal equilibrium in the rotating frame. In these experiments the magnetization M_z was measured as a function of the duration of a saturating pulse of amplitude $2H_1(\nu)$. The measurements were made over a time interval which was much shorter than the spin-lattice relaxation time. Our results provide quantitative verification of a recent calculation by Provotorov, who has shown that when $H_1 \ll H_l$, $M_z(\tau_a)$ approaches its equilibrium value (in the rotating frame) at a rate determined by a master equation. The master equation derived by Provotorov is in disagreement with the predictions of elementary perturbation theory except when the frequency of the rf field is equal to the Larmor frequency (or when τ_a is very short).

I. INTRODUCTION

THE experiments reported here provide additional verification of the hypothesis that spin systems in large rf fields can, at equilibrium, be characterized by a

spin temperature in a frame of reference rotating with the frequency of the perturbing rf field. This important assumption was advanced by Redfield^{1,2} and has, in recent years, been both tested and exploited in many experiments. We also report experiments that measure

* This work was supported by grants from the National Science Foundation and the U. S. Army Research Office (Durham). Preliminary reports of this earlier work appear in *Bull. Am. Phys. Soc.* **6**, 444 (1961); **7**, 295 (1962).

¹ Alfred G. Redfield, *Phys. Rev.* **98**, 1787 (1955).

² A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961).

the rate at which a spin system approaches thermal equilibrium in the rotating frame. The measurements were made over a time interval much shorter than the spin-lattice relaxation time, so such relaxation effects play no role in the establishment of thermal equilibrium. Our results confirm a recent calculation by Provotorov,³ who has attacked the problem using the recently developed methods for solving the master equation.^{4,5} Protorov's results are especially interesting because they are not in accord with the elementary perturbation theory introduced by Bloembergen, Purcell, and Pound⁶ to solve rate problems in nuclear magnetic resonance.

Since Redfield's hypothesis is pivotal to both problems we have studied, it is desirable to state it explicitly at the outset: Consider a nuclear spin system subject to a strong dc field \mathbf{H}_0 and an rf field oriented perpendicular to \mathbf{H}_0 . If the rf field is sufficiently large, the occupation probability P_i of the energy levels of the spin system is given by the Boltzmann distribution,

$$P_i \propto \exp(E_i'/kT'), \quad (1)$$

where E_i' is an energy level of the spin system as viewed by an observer in a frame of reference rotating about the Zeeman field \mathbf{H}_0 with the frequency ν of the rf field. The temperature T' appearing in (1) is then the temperature of the spin system in the rotating frame. When the perturbing rf field is sufficiently weak, the usual assumption is the proper one, namely, that the spin system is characterized by a canonical distribution in the laboratory frame at a temperature which will, of course, be elevated above that of the lattice by the perturbing rf field. In a complete discussion Redfield¹ establishes the reasonableness of the spin temperature assumption⁷ embodied in (1). The subject is further clarified in a recent paper by Slichter and Holton.⁸ We will also have occasion to review Redfield's arguments in Sec. III.

Redfield's experimental work provided a qualitative verification of his fundamental assumption, and more recent experiments⁹ by the present author afforded a more quantitative verification of his ideas. These experiments did not, however, provide an unambiguous verification of Eq. (1), for their interpretation required an additional assumption as to the mechanism by which the spins are coupled to the lattice vibrations.

Assuming, as did Redfield, that each nucleus relaxes its energy to the lattice independently of all the others with a characteristic time T_1 , one finds excellent agree-

ment between theory and experiment in NaCl, a quadrupolar solid, and only fair agreement in CaF₂. The disagreement in the calcium fluoride experiments can be attributed to the fact that the fluorine spins in that material do not relax their energy to the lattice independently.¹⁰

Recognizing the value of an unambiguous test of Eq. (1), Slichter and Holton⁸ performed resonance experiments of the transient type on the Na²³ nuclei in a single crystal of NaCl. These experiments were performed in a time interval which was short compared to the spin-lattice relaxation time; the interpretation of their results therefore requires no assumption whatsoever concerning the spin-lattice relaxation mechanism. Slichter and Holton's experiments provided additional support for Redfield's hypothesis, but quantitative agreement with theory was not obtained. These authors suggested that there might be an additional interaction term in the spin Hamiltonian arising from the coupling of the sodium quadrupole moments with the electric field gradients produced by strains and impurities within the crystal. The discrepancy could also be explained if their calibration of the amplitude of the rf field H_1 was in error by approximately 50%.

The experiments described in Secs. II and IV were undertaken to check Slichter and Holton's results using a somewhat different experimental technique. Toward that end we have performed experiments using the same NaCl sample they used and also made measurements on fluorine spins in a single crystal of CaF₂. The latter experiments are a valuable compliment to the NaCl measurements, for in CaF₂ there can be no quadrupole effects to complicate the theoretical calculation (the fluorine nucleus has spin $\frac{1}{2}$ and hence no quadrupole moment). In both NaCl and CaF₂ our results are in excellent agreement with Redfield's theory. In NaCl we find no evidence for the quadrupole interaction suggested as a possibility by Slichter and Holton.

In order to interpret the results of our spin temperature experiments it was important to have some idea how large the perturbing field $H_1(\nu)$ must be in order for Redfield's hypothesis to be valid. It was also necessary to have an estimate of how rapidly the spins established thermal equilibrium in the rotating frame among themselves. In answer to the first question, it is found that Eq. (1) will not hold unless

$$\gamma^2 H_1^2 T_1 g(\Delta\nu) \equiv S \gg 1, \quad (2)$$

where $\Delta\nu \equiv \nu - \nu_0$, γ is the gyromagnetic ratio of the resonant nuclei, and T_1 is their spin-lattice relaxation time. The function $g(\Delta\nu)$ is the normalized absorption line shape centered at the Larmor frequency $\nu_0 = \gamma H_0 / 2\pi$. It is also required that H_0 and H_1 be large enough so that time dependent terms in the dipole interaction (transformed to the rotating frame) produce

¹⁰ This conclusion has been confirmed in a recent study by I. Solomon and J. Ezzratty, Phys. Rev. **127**, 78 (1962).

³ B. N. Provotorov, J. Exptl. Theoret. Phys. (U.S.S.R.) **41**, 1582 (1961).

⁴ L. Van Hove, Physica **21**, 517 (1955).

⁵ Robert W. Zwanzig, in *Lectures in Theoretical Physics*, edited by Wesley E. Brittin, B. W. Downs, and Joanne Downs (Interscience Publishers, Inc., New York, 1961), Vol. 3, p. 106.

⁶ N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

⁷ A rigorous argument for the correctness of this assumption is given in reference 3.

⁸ C. P. Slichter and W. C. Holton, Phys. Rev. **122**, 1701 (1961).

⁹ Walter I. Goldberg, Phys. Rev. **122**, 831 (1961).

negligibly small physical effects. This condition, as well as the inequality (2), was satisfied in our experiments.

Measurements of the rate of approach to equilibrium are described in Sec. V. It is observed that when $H_1 \ll H_0$, $S \gg 1$, the sodium spin system in NaCl approaches thermal equilibrium at an exponential rate. The measured time constant characterizing this rate is in quite good agreement with the time constant calculated from Provotorov's theory. Provotorov assumes that, when H_1 is small, the spin system can be characterized by two temperatures, one corresponding to a Boltzmann distribution in the population of the Zeeman states of the spin system and the other corresponding to a Boltzmann distribution in the population of the states of the dipolar part of the Hamiltonian.

II. EXPERIMENTAL TECHNIQUE

As in the earlier work,⁹ the signal observed in these experiments was the peak value of the nuclear free induction decay signal following a $\pi/2$ pulse. This signal is proportional to the z component of the magnetization, M_z . The pulse apparatus was of the coherent type with the transmitter operated at a crystal-controlled frequency of 10.000 Mc/sec.

The time sequence of experimental operations is shown in Fig. 1. The spin system was allowed to come to thermal equilibrium in the external field H_0 . Then the saturating rf pulse of amplitude $2H_1$ was initiated and remained on for a time τ_a which was much less than the shortest spin-lattice relaxation time in the sample. The saturating pulse was then abruptly turned off. After another time interval τ_b , the $\pi/2$ pulse was initiated and the subsequent free induction decay signal was observed on an oscilloscope. Again, the time interval τ_b was kept short compared to T_1 though it was long compared to the spin-spin relaxation time T_2 . In NaCl and CaF₂ the sodium and fluorine spin-lattice relaxation times were 15 and 13 sec, respectively. The spin-spin relaxation times were approximately 0.2 msec and 20 μ sec, respectively.

For the experiments described in the Sec. III, τ_a was chosen to be 100 msec. This interval was more than long enough to permit establishment of thermal equilibrium in the rotating frame for the values of H_1 which were used (see Sec. V). The time interval τ_b was chosen, quite arbitrarily, as 90 msec. It is to be expected and indeed it was observed that the peak amplitude of the free induction signal was independent of τ_b provided τ_b was much less than T_1 . When measuring the approach to equilibrium, τ_a was the independent variable. The independent variable for all the other experiments was $\Delta\nu$, the difference between the Larmor frequency of the nuclei and the frequency of the rf field.

The saturating field¹¹ $H_1(\nu)$ originated in a crystal-controlled oscillator. A set of seven crystals was used

¹¹ We henceforth refer to the rf field by the amplitude of its effective rotating component. This amplitude is one-half the measured field amplitude.

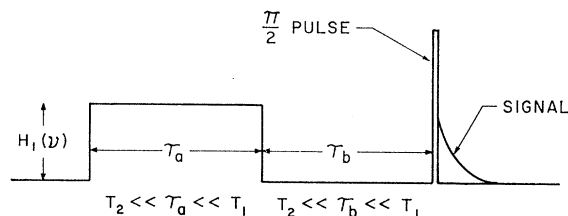


FIG. 1. Schematic diagram showing pulse sequence used in this experiment.

to cover the desired frequency range. The frequency of each crystal could be continuously varied over a few kc/sec by "pulling" it with a series variable condenser. The rise time of the rf pulse was kept short enough so that its variation produced no observable variation in M_z . It was never longer than 1 msec and never shorter than 20 μ sec. The decay time of the pulse was roughly 0.1 msec.

The amplitude of the pulse was measured by a test coil inserted in the transmitter coil (with receiver coil removed) as described in reference 9. This rf field was inductively coupled into the transmitter coil of the pulse apparatus. The field was uniform over the sample volume to better than 4%.

The frequency difference $\Delta\nu$ was accurately measured by counting the number of beats in a preset time interval which lay within the larger time interval τ_a . The Larmor frequency of the nuclei, $\gamma H_0/2\pi$, was set as closely as possible to the 10.000 Mc/sec pulse transmitter frequency by adjusting H_0 so that there were no "beats" in the free induction decay of a signal in a liquid sample containing sodium or fluorine ions. With this technique it was possible to set the Larmor frequency within ~ 24 cps of the transmitter frequency. The drift in the Larmor frequency of the sodium line was usually no more than 100 cps in a several hour run. The sodium and fluorine lines are sufficiently broad so that this drift was tolerable, though the experiment could have been improved if the magnet current had been stabilized on a nuclear resonance signal.

In all experiments the field H_0 was parallel to the [100] axis. The measurements described in Sec. IV were made at room temperature; some of the measurements of section V were performed at 77°K. The low-temperature measurements were made by placing the crossed coil assembly in a styrofoam box containing liquid nitrogen.

The sodium chloride and calcium fluoride crystals were synthetic and were manufactured by the Harshaw Chemical Company.

III. REDFIELD'S THEORY

A spin system can be characterized by a temperature if it can be described by a density matrix of especially simple form

$$\rho \propto \exp(-\mathcal{H}/kT), \quad (3)$$

where \mathcal{H} is the Hamiltonian of the system and T its temperature. The density matrix (3) is only an approximation to the proper one, which must satisfy the differential equation

$$i\hbar(\partial\rho/\partial t)=[\mathcal{H},\rho]. \quad (4)$$

If \mathcal{H} is explicitly dependent on time, as it is for a spin system in an rf field, (3) and (4) will almost certainly be inconsistent and one cannot then describe the spin system by a temperature. Of course, if the time-dependent term in \mathcal{H} is very small, (3) may still be a good approximation. Redfield recognized that even when the time-dependent term is large, the solution to (4) may still be approximated by a density matrix of canonical form provided ρ is expressed in a suitable moving frame of reference. This is because a large time-dependent perturbation in one reference frame may be small (or at least ineffective) in another frame moving with respect to the first. In this second frame the laws of statistical mechanics can hold, in which case ρ can then have the form of Eq. (3).¹²

Redfield was concerned with the experimental situation usually encountered in nuclear magnetic resonance experiments, where the spin system is placed in a magnetic field

$$\mathbf{H}=\hat{k}H_0+\mathcal{H}2H_1\cos\omega t.$$

The Zeeman field \mathbf{H}_0 is usually of the order of kilogauss, and the perturbing rf field has a frequency of many megacycles and an amplitude which is much smaller than H_0 . Consider the Hamiltonian describing such a system of N nuclear spins of magnetic moment $\mathbf{u}=\gamma\hbar\mathbf{I}$ immersed in the field \mathbf{H}

$$\mathcal{H}C=-\gamma\hbar H_0\sum_k I_{Z^k}-2\gamma\hbar H_1\cos\omega t\sum_k I_{X^k}+\mathcal{H}C_d+\mathcal{H}C_Q.$$

The dipole-dipole interactions between spin pairs are designated by $\mathcal{H}C_d$. The term $\mathcal{H}C_Q$ denotes the interaction between the nuclear quadrupole moments and the electric field gradient at the nuclear sites.

Consider now the transformation of $\mathcal{H}C$ to a frame of reference rotating about the direction of \mathbf{H}_0 with the rf frequency ω . Using primes to designate quantities in the rotating frame,

$$\mathcal{H}C'=\mathcal{H}C_S'+\mathcal{H}C_d'(t),$$

where

$$H_S'=-\gamma\hbar(H_0-\omega/\gamma)\sum_k I_{Z^k}-\gamma\hbar H_1\sum_k I_{X^k}+\mathcal{H}C_d'+\mathcal{H}C_Q'. \quad (5)$$

It is often convenient to rewrite

$$\mathcal{H}C_S'=-\gamma\hbar\mathbf{H}_{\text{er}}\cdot\sum_k \mathbf{I}_k+\mathcal{H}C_d'+\mathcal{H}C_Q', \quad (6)$$

with

$$\mathbf{H}_{\text{er}}=H_1\hat{v}+(H_0-\omega/\gamma)\hat{k}. \quad (7)$$

With this transformation, some of the terms in $\mathcal{H}C'$ acquire a time dependence. These terms, which we

denote by $\mathcal{H}C_d'(t)$, contain factors of the form $\exp(\pm i\omega t)$ and $\exp(\pm 2i\omega t)$. All the remaining terms in $\mathcal{H}C'$ are time independent (static) and are denoted by $\mathcal{H}C_S'$. In most nuclear resonance experiments, $\mathcal{H}C_S'$ is of the order of tens of kilocycles or less, while the rf frequency $\omega/2\pi$ is of the order of Mc/sec. Therefore, the time-dependent terms in $\mathcal{H}C_d'(t)$ will be extremely ineffective in inducing transitions among the eigenstates of H_S' , and the density matrix should be stationary with its form given by Eq. (3).

As yet the effect of the spin-lattice interaction has not been considered. Only when this interaction is small compared to that due to the rf field will Redfield's hypothesis be valid. This requirement, which is implied by Redfield's calculations, and which has been demonstrated by previous experiments,⁹ is satisfied when the inequality (2) holds and, therefore, when

$$\gamma^2 H_1^2 T_1 T_2 \gg 1, \quad (8)$$

where

$$T_2 \equiv \frac{1}{2}g(0).$$

In the experiments to be discussed in the next section, the above inequality was well satisfied.¹³ Also H_1 and H_0 were large enough so that the nonsecular terms in the transformed Hamiltonian were of totally negligible effect.

Our experiments differ from the nonadiabatic pulsing experiments of Slichter and Holton in that we have measured M_z whereas Slichter and Holton measured M_x . Since their calculation requires only a slight modification in order to apply to our experimental conditions, it will not be necessary to repeat their work. It is desirable, however, to restate the assumptions on which their calculations are based: (1) The saturating rf pulse (of duration τ_a) must be turned on suddenly so that the nonadiabatic condition is satisfied. (2) The spin system must establish itself in a state of thermal equilibrium *in the rotating frame* in a time less than τ_a . (3) Each measurement of M_z must be completed in a time $\tau_a + \tau_b \ll T_1$. When these conditions are satisfied and Redfield's hypothesis is valid, one finds

$$M_z/M_0 = \frac{\Delta\nu^2}{\Delta\nu^2 + (\gamma H_1/2\pi)^2 + (\gamma H_l/2\pi)^2}, \quad (9a)$$

where M_0 is the thermal equilibrium value of the magnetization. The local field H_l can be calculated in terms of the second moment of the absorption lines of the various nuclear species present in the crystal. In order of magnitude, H_l is the field that one nucleus produces at its nearest neighbor. The precise definition of H_l can be

¹³ To establish the inequality (8) we anticipate results given in Sec. V. According to Eqs. (10) or (11), the magnetization M_z approaches its equilibrium value in the rotating frame with time constant $\tau_R = (\gamma^2 H_1^2 T_2)^{-1}$. This result holds only when $\Delta\nu = 0$ and when T_1 is infinite. The presence of spin-lattice interactions will not prevent the spin system from establishing thermal equilibrium in the rotating frame as long as this interaction represents a small perturbation compared to the effect of H_1 , i.e., as long as $T_1 \gg \tau_R$. This inequality is identical to (8).

¹² If ρ is expressed in a representation in which \mathcal{H} is diagonal, Eq. (3) has the same form and meaning as Eq. (1).

TABLE I. Parameters relevant to this work. The local fields H_l were calculated using Eq. (15) of reference 8. The relaxation times T_1 and T_2 and the absorption line shape function $g(\Delta\nu)$ were measured. All parameters refer to the crystal orientation, for which $H_0 \parallel [100]$.

Parameter	Crystal	Nuclear species	Value of the parameter
H_l	NaCl ^(a)	Na ²³	0.61 gauss
H_l	CaF ₂	F ¹⁹	2.08 gauss
T_1 (24°C)	NaCl	Na ²³	15 sec
T_1 (77°K)	NaCl	Na ²³	380 sec
$T_2 = \frac{1}{2}g(0)$	NaCl	Na ²³	0.19 msec
g (600 cps)	NaCl	Na ²³	0.87 $g(0)$

^a In the low- H_l measurements of Sec. IV Slichter and Holton's sodium chloride crystal was used. All other sodium chloride measurements were made using another Harshaw crystal. The parameters in this table refer to that crystal.

found in references 2 and 8. For a spin system consisting of two magnetic ingredients (containing N_I resonant spins and N_S nonresonant spins), one finds

$$H_l^2 = \frac{1}{3} \langle \Delta H^2 \rangle_{II} + \langle \Delta H^2 \rangle_{IS} + \frac{1}{3} \left(\frac{\gamma_S}{\gamma_I} \right)^2 \frac{N_S S(S+1)}{N_I I(I+1)} \langle \Delta H^2 \rangle_{SS}, \quad (9b)$$

where $\langle \Delta H^2 \rangle_{II}$ is the contribution of the resonant spins to their own second moment, $\langle \Delta H^2 \rangle_{SS}$ is the contribution of the S spins to their own second moment, and $\langle \Delta H^2 \rangle_{IS}$ is the contribution of the S spins to the second moment of the I spins. In Table I can be found the numerical values of H_l in NaCl and CaF₂ as well as other parameters relevant to the experimental results described in the next two sections.¹⁴

IV. STATIC EXPERIMENTS AND COMPARISON WITH THEORY

Figure 2 shows the results of measurements on the Na²³ spin system in NaCl. The normalized magnetiza-

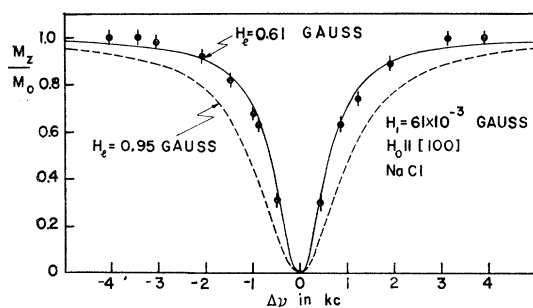


FIG. 2. Relative magnetization vs $\Delta\nu$ for the sodium spin system in NaCl. The solid and dashed lines are the theoretical curves [Eq. (9)] with $H_l = 0.61$ and 0.95 G, respectively.

¹⁴ The expression for H_l corresponding to Eq. (9b) is incorrectly given in references 1, 2, and 8. The errors in these references occur in the coefficient of $\langle \Delta H^2 \rangle_{SS}$. Fortunately, this term is very small in sodium chloride, and the conclusions drawn in these papers and in reference 9 require no alteration as a result of this correction. I wish to thank Professor C. P. Slichter for verifying that Eq. (9b) is correct.

tion M_z/M_0 is plotted as a function of $\Delta\nu$ (in kc/sec). The sample was the same as that used in the experiments of Slichter and Holton. The field H_1 was 61×10^{-3} G, which, from Table I is seen to be approximately one-tenth of the local field.

The solid line in Fig. 2 is a plot of the theory, Eq. (9), using the calculated value of $H_l = 0.61$ G. Our measurements, which are in excellent agreement with the theory, indicate that the local field arises almost entirely from dipolar interactions. The results are not in agreement with those of Slichter and Holton. These authors treat H_l as a parameter in the theory and obtain a best fit to their data with a value of $H_l = 0.95 \pm 0.1$ G. To display the discrepancy between their results and ours, we have inserted this value of H_l in Eq. (9) and plotted the resulting curve in Eq. (2) (dashed line). If our results are correct, there is no need to invoke the presence of quadrupole interactions in this particular sample. In the experiments reported here, as well as those of Slichter and Holton, $\Delta\nu$ is the only independent variable on which the amplitude of the measured nuclear induction signal depends, provided $H_1 \ll H_l$. Fortunately, $\Delta\nu$ is easily measured with great accuracy. On the other hand, when $H_1 \gtrsim H_l$, the rf field must be carefully measured and care must be taken to assure that H_1 is uniform over the sample volume. In measuring a signal proportional to M_z , as we have, there is no reason *not* to use a small value of H_1 [but not so small that the inequality (8) is violated]. With the technique of Slichter and Holton, however, the observed nuclear signal becomes small when $H_1 \ll H_l$ so the signal-to-noise ratio is affected adversely. The most precise measurements of Slichter and Holton were, for this reason, made with H_1 comparable to H_l . Our results suggest that their H_1 calibration was in error.

Figure 3 shows additional measurements in NaCl, this time with $H_1 = 1.5$ G, which is much larger than H_l . The solid line is a plot of Eq. (9), again with $H_l = 0.61$ G. Aside from the "dip" on the positive $\Delta\nu$ side of the graph, agreement between theory and experiment is quite good. This dip could be produced by a spurious side band resulting from a small amount of amplitude

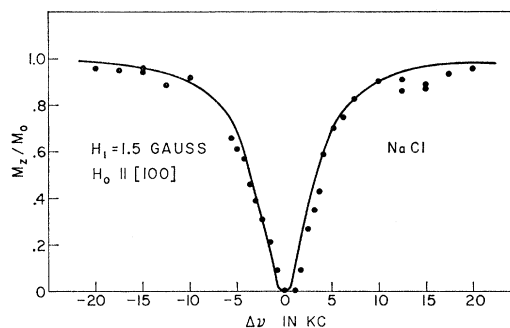


FIG. 3. Relative magnetization vs $\Delta\nu$ for the sodium spin system in NaCl. The solid line is the theoretical curve [Eq. (9)] corresponding to $H_l = 0.61$ G and $H_1 = 1.5$ G.

modulation of the saturating rf pulse at the frequency $\Delta\nu = 15$ kc/sec, where the dip occurs. A careful search was made for this very small modulation, but none was detected.

It seemed desirable to check Redfield's hypothesis, as well as our experimental technique, by making measurements on a spin system in which quadrupole effects cannot possibly be present. A logical choice was the fluorine spin system in calcium fluoride. Since there are no other magnetically active ingredients in calcium fluoride, it is easy to calculate H_l in this cubic crystal (see Table I). The experimental results for calcium fluoride, together with the theoretical curves, are shown in Figs. 4 and 5. The measurements of Fig. 4 correspond $H_1 = 4.3 \times 10^{-3}$ G and 5.3×10^{-3} G; those in Fig. 5 correspond to $H_1 = 3.2$ G. The good agreement between experiment and theory (solid lines) apparent in both of these graphs not only provides additional verification of Redfield's hypothesis but also gives us further confidence that there were no systematic errors in these experiments.

V. THE APPROACH TO THERMAL EQUILIBRIUM IN THE ROTATING FRAME

We have stated that in the above described experiments, the duration τ_a of the saturating pulse was sufficient to permit establishment of thermal equilibrium of the spin system in the rotating frame. To be sure that this condition was met, we measured, in sodium chloride, the rate at which the sodium spin system approaches equilibrium. The rf fields used in this study were large enough to assure that $\gamma^2 H_1^2 T_1 T_2 \gg 1$. It was found that the spin system approached equilibrium exponentially if H_1 was much less than H_l .

Figure 6 shows measurements of M_z/M_0 vs τ_a in the time interval $50 \text{ msec} < \tau_a < 350 \text{ msec}$. The crystal was oriented with $H_0 \parallel [100]$. The saturating field $H_1 = 26 \pm 1$ mG and $\Delta\nu = 0$. In order to assure that spin-lattice relaxation played no role in the establishment of equilibrium, some of the measurements (solid circles) were made at 77°K . At this temperature $T_1 = 380$ sec. The measurements designated by open circles were made at room temperature.

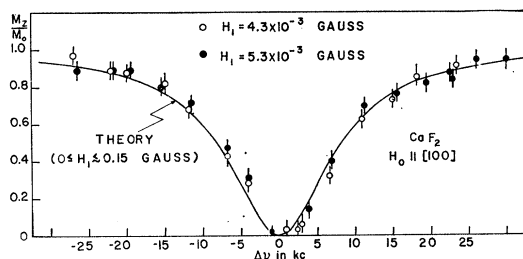


FIG. 4. Relative magnetization vs $\Delta\nu$ for the fluorine spin system in calcium fluoride. The measurements were made at two very low values of H_1 . The solid line is the corresponding theoretical curve [Eq. (9)].

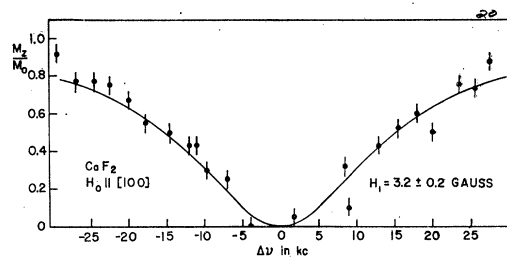


FIG. 5. Relative magnetization vs $\Delta\nu$ for the fluorine spin system in calcium fluoride. The solid line represents the theory [Eq. (9)].

The vertical scale in Fig. 6 is logarithmic, the straight line representing a good fit to the data corresponds to a relaxation time of 110 ± 10 msec. This relaxation time will be designated as τ .

To explain the above results it is tempting to use the rate equations first introduced by Bloembergen, Purcell, and Pound.⁶ From them one deduces that, at exact resonance,

$$dM_z/dt = -\tau^{-1}(0)M_z,$$

which has the solution

$$M_z/M_0 = e^{-t/\tau(0)}. \quad (10a)$$

From elementary perturbation theory

$$\tau^{-1}(\Delta\nu) = (\gamma^2 H_1^2 / 2) g(\Delta\nu). \quad (10b)$$

The above three equations can be shown to be rigorously correct for time intervals, t , sufficiently short that $M_0 - M_z/M_0 \ll 1$.¹⁵ For longer times, with which our

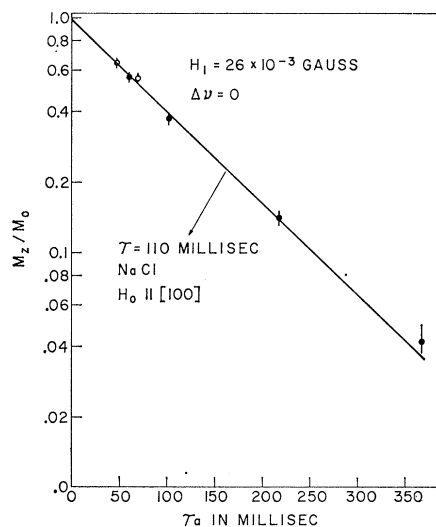


FIG. 6. Relative magnetization vs the duration of the saturating pulse with $\Delta\nu = 0$ the measured relaxation time, which corresponds to the straight line, is 110 msec. The closed and open circles designate measurements made at 77°K and room temperature, respectively.

¹⁵ I am grateful to Dr. A. G. Redfield for bringing this fact to my attention.

experiments are concerned, the above equations can be derived by elementary perturbation theory only. In such a derivation the absorption line shape function $g(\nu)$ is regarded as the density-of-state available to a single spin, which undergoes transitions induced by the oscillating rf field.

Elementary perturbation theory was used by Bloembergen, Purcell, and Pound to derive Eq. (10) for spin $\frac{1}{2}$ nuclei. For nuclei of spin greater than $\frac{1}{2}$, Eq. (10) can be obtained only when the magnetic sublevels of an individual spin are populated according to a Boltzmann distribution; i.e., when the spin system can be characterized by a temperature. (Even then this equation is only correct in the high-temperature limit $kT \gg \gamma \hbar H_0$.) Using a less restrictive spin temperature assumption Eq. (10) can also be derived from more rigorous arguments for the special situation $\Delta\nu = 0$ only, as we will see.

In order to compare the measured value of $\tau(0)$ with Eq. (10b), it is necessary to know $T_2 = g(0)/2$. Using a Varian spectrometer to measure the absorption line shape, it was found that $T_2 = 190 \pm 10 \mu\text{sec}$ for the sample used. Inserting this spin-spin relaxation time into Eq. (10b) yields $\tau(0) = 160 \text{ msec}$, which is approximately 50% larger than the measured value of 110 msec. It should be noted that the sodium absorption line in our sample was considerably broadened by quadrupole interactions. The measured second moment was about 60% larger than the calculated Van Vleck second moment. It is interesting to note that the ratio of the measured value of τ to the calculated value is almost equal to the ratio of the measured to the calculated moments. This suggests that the sodium line is appreciably inhomogeneously broadened, yet other experiments indicate that this is not the case.¹⁶

Recently Provotorov³ has derived the master equation using the method of Zwanzig. Zwanzig's formalism⁵ is physically equivalent to Van Hove's classic derivation of the master equation⁴ but has a much more compact form. To carry through the calculation, Provotorov assumes that the perturbing rf field H_1 is much less than H_0 . He then calculates, for $t \ll (\gamma H_1)^{-1}$, the magnetization M_z using the relation

$$M_z = \text{Tr}[\rho_1 \hat{M}_z] / \text{Tr} \rho_1$$

where \hat{M}_z is the magnetization operator. In order to define ρ_1 it is first necessary to consider the differential equation

$$i\hbar(\partial \rho' / \partial t) = [H_s', \rho'],$$

where, as before, the primes indicate that the transformation has been made to the rotating reference frame. Imagine ρ' to be expressed in a representation such that ρ' is diagonal when $H_1 = 0$ [we henceforth assume that the quadrupolar term H_Q' of Eq. (5) is absent]. Then ρ_1 is defined as a matrix consisting only

¹⁶ See reference 9, Sec. II and also the discussion of the low- H_1 sodium chloride measurements in Sec. IV of that reference.

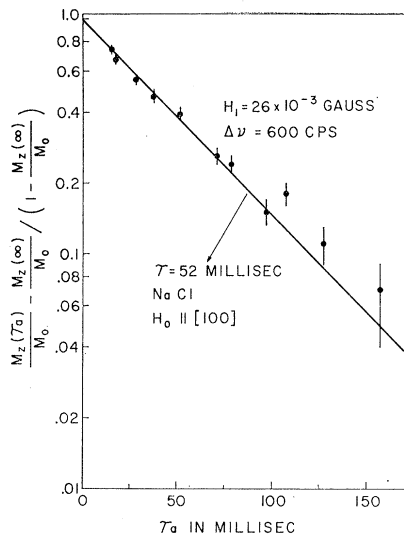


FIG. 7. Relative magnetization vs the duration of the saturating pulse with $\Delta\nu = 600 \text{ cps}$. The measured relaxation time, which corresponds to the straight line, is 52 msec.

of the diagonal elements ρ' , all other elements being zero.

Provotorov further assumes that the Zeeman and dipolar term in \mathcal{H}_S' will, in general, be characterized by different temperatures; i.e., that

$$\rho_1(t) \propto \exp[\alpha(t) \sum I_z^k + \beta(t) \mathcal{H}_d'].$$

He is then able to derive a differential equation for dM_z/dt which has the solution

$$\left(\frac{M_z(t) - M_z(\infty)}{M_0 - M_z(\infty)} \right) \left(1 - \frac{M_z(\infty)}{M_0} \right)^{-1} = e^{-t/\tau(\Delta\nu)}, \quad (11a)$$

$$\tau(\Delta\nu) = \left(\frac{1}{1 + [\Delta\nu / (\gamma H_1 / 2\pi)]^2} \right) \left(\frac{\gamma^2 H_1^2}{2} g(\Delta\nu) \right)^{-1}, \quad (11b)$$

where $M_z(\infty)$ is the equilibrium value of the magnetization appearing in Eq. (9) and designated in that equation as M_z . At exact resonance Eq. (11) is equivalent to Eq. (10).

Provotorov considers a spin system consisting of only one magnetically active nuclear species, but his results are equally valid for a crystal such as NaCl in which both the sodium and chlorine spins contribute to $g(\Delta\nu)$ and H_1 . Quadrupole interactions are not included in his calculation. To check this more exact theory for the case $\nu \neq \nu_0$, measurements were made in NaCl with $\Delta\nu = 600 \pm 40 \text{ cps}$, and $H_0 \parallel [100]$ as before. The rather large uncertainty in $\Delta\nu$ arose from a drift in the Zeeman field H_0 . The measurements were made at room temperature with $H_1 = 26 \pm 2 \text{ mG}$. Our results, which are displayed in Fig. 7, reveal that M_z approaches its equilibrium value exponentially with a characteristic time $\tau(600 \text{ cps}) = 52 \pm 4 \text{ msec}$.

To compare our results with Provotorov's, we have calculated $\tau(0)/\tau(600 \text{ cps})$ and find, using Eq. (11) and the same value of H_1 at both frequencies, that

$$\frac{\tau(0)}{\tau(\Delta\nu)} = \frac{g(\Delta\nu)}{g(0)} \left[1 + \frac{(\Delta\nu)^2}{(\gamma H_1/2\pi)^2} \right] = 1.6 \pm 0.1. \quad (12)$$

The quoted error arises from the uncertainty in $\Delta\nu$. The numerical value of this ratio was calculated using $H_1 = 0.61 \text{ G}$, $\Delta\nu = 600 \text{ cps}$, and $g(600 \text{ cps}) = 0.87g(0) \pm 2\%$, for the crystal used. We compare the above result with the measured ratio of relaxation times:

$$(\tau(0)/\tau(600 \text{ cps}))_{\text{measured}} = 2.1 \pm 0.2.$$

It is seen that the observed and calculated relaxation time ratios are in fair but not perfect agreement. Note that Eq. (10) predicts a value of $\tau(0)/\tau(600 \text{ cps})$ which is less than unity, whereas our results and Eq. (12) show this ratio to be much greater than one.

It has been noted that Provotorov's calculation is expected to be correct only when $H_1 \ll H_l$. One would expect, in fact, that when H_1 is very large, i.e., $H_1 \gg H_l$, the magnetization will not approach $M_z(\infty)$ in a monotonic fashion. Rather one expects M_z to oscillate about $M_z(\infty)$, the oscillations decaying in amplitude as τ_a increases. These oscillations, which we have observed experimentally in both NaCl and CaF₂, correspond to the classical precession of the magnetization vector about the field \mathbf{H}_{er} . In the domain $H_1 \gg H_l$ the spin system cannot be characterized a temperature except at initial time $\tau_a = 0$. It should be possible to calculate M_z as a function of τ_a by calculating the time evolution of the density matrix without assuming the existence of a spin temperature (except at $\tau_a = 0$).^{17,18} An investigation of this problem of the approach to thermal equilibrium in the presence of strong fields is now in progress.

¹⁷ I. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957).

¹⁸ I am grateful to Dr. Provotorov for pointing out to me the relevance of the work of Lowe and Norberg to this problem.

VI. SUMMARY

The measurements described in Sec. IV provide additional support for Redfield's spin-temperature hypothesis. The interpretation of these experiments does not require any knowledge of the spin-lattice mechanism. Excellent agreement between theory and experiment was observed in both CaF₂ and NaCl where the resonant spins (F¹⁹ and Na²³) relax their energy to the lattice by quite different mechanisms. In NaCl the imperfection-induced quadrupole interactions produced no observable increase in the local field H_l , though the crystal did show a considerably broadened absorption line.

The purpose of experiments described in Sec. V was to measure the rate at which the sodium spins in NaCl approach thermal equilibrium in the rotating frame. These measurements, for which $H_1 \ll H_l$, are in partial agreement with theoretical results obtained by Provotorov. Provotorov has shown that when the perturbing rf field is small, the spin system is expected to approach equilibrium in the rotating frame at an exponential rate. In deriving this result he assumes that the spin system can be characterized by two temperatures, one describing the population of states of the Zeeman energy and the other describing the population of states of the dipolar energy. The frame of reference in which these portions of the Hamiltonian are described by a temperature is the rotating one. It is possible that quadrupolar effects in NaCl give rise to the disagreement between our measurements and Provotorov's results.

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