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Nuclear Magnetic Resonance Saturation in NaCl and CaF_2†

WALTER I. GOLDBURG
The Pennsylvania State University, University Park, Pennsylvania

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Experiments were performed to test the hypothesis due to Redfield, that a nuclear spin system in a sufficiently large rf field, $H_1(\nu)$, is properly described by a spin temperature referred to a frame of reference rotating about the Zeeman field with the frequency ν of the rf field. Measurements were made on the Na^{23} spins in NaCl and the F^{19} spins in CaF_2. A combination of steady-state and pulse techniques was used to measure the magnetization M_z as a function of the frequency and amplitude of $H_1(\nu)$. When H_1 is sufficiently large, the data show that Redfield's theory is correct within 10% for NaCl but appreciably in error for CaF_2. The same type of measurement performed at low amplitudes of H_1 show that the theory of Bloembergen, Purcell, and Pound is in agreement with the NaCl measurements but measurably in error for CaF_2. It is suggested that neither theory is correct for CaF_2 because the fluorine spins relax by means of paramagnetic impurities, and, therefore, do not relax independently with characteristic time T_1, as is assumed in both theories. In an intermediate range of saturating field amplitudes, neither theory is expected to apply; this was found to be the case experimentally.

I. INTRODUCTION

IN recent years, a renewed interest in the concept of spin temperature has developed along with fruitful utilization of the spin temperature hypothesis in analyzing experimental results.[1] The measurements reported here are in agreement with the results of others[2,3] in revealing that a spin system in a sufficiently large rf field, $H_1(\nu)$, is properly characterized by a spin temperature referred to a frame of reference rotating with frequency ν about a large fixed external field H_0.

When H_1 is small, i.e., when $\gamma^2 H_1^2 T_1 T_2 \equiv S \ll 1$, the theory of Bloembergen, Purcell, and Pound[4] is expected to be correct. The BPP calculation of the magnetization (M_z), absorption (χ''), and dispersion (χ') is based on the hypothesis that the spin system can be characterized by a temperature referred to the laboratory frame. (The spin temperature will in general differ from the lattice temperature.)

Redfield[2] was the first to recognize the physical importance of describing spin systems by a spin temperature in the rotating frame when the saturating field is large. Several workers, including Redfield,[2] have performed experiments which show that absorption and dispersion behave anomalously above saturation. Recent work by Blume and Redfield[3] has verified that the equations derived by Redfield correctly describe the dispersion in lithium metal above saturation.

The measurements described here were made on the fluorine and sodium spin systems in single crystals of calcium fluoride and sodium chloride. We have measured the magnetization M_z as a function of the frequency and magnitude of the saturating rf field, unlike previous experiments, where χ' and χ'' were determined. The results obtained reveal quite clearly the lower limit on the amplitude of H_1 for which the spin systems are in a canonical system in the rotating frame and the upper limit on H_1 for which the spins are in a canonical distribution in the laboratory frame.

For NaCl, there is very good agreement between experiments and the predictions of BPP and of Redfield in the appropriate limits where these theories are applicable. In CaF_2, however, the agreement with these theories is not as good. This disagreement can be attributed to effects associated with the spin-diffusion-type relaxation mechanism, which is operative in this material.

II. THEORETICAL CONSIDERATIONS

In the experiments described below, the quantity that is measured is M_z, the component of the magnetization along the direction of the external field H_0. The magnetization is usually given by the following equation, originally derived by BPP[4]:

$$M_z/M_0 = [1+\tfrac{1}{2}\gamma^2 H_1^2 T_1 g(\nu)]^{-1}, \qquad (1)$$

where M_0 is the equilibrium magnetization, $g(\nu)$ is the normalized absorption line shape centered at the Larmor frequency $\nu_0 = \gamma H_0/2\pi$, and T_1 is the spin-lattice relaxation time.

Equation (1) is expected to hold for the steady state provided: (a) the spin-lattice interaction relaxes the nuclear spins independently with relaxation time T_1;

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[1] See, for example, L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959) and R. T. Schumacher, Phys. Rev. **112**, 837 (1958). An excellent discussion of the concept of spin temperature is given by A. Abragam and W. G. Proctor, Phys. Rev. **109**, 1441 (1958).

[2] Alfred G. Redfield, Phys. Rev. **98**, 1787 (1955). This paper contains a complete physical and mathematical discussion of the concept of spin temperature in the rotating frame.

[3] D. F. Holcomb, Phys. Rev. **112**, 1599 (1958); N. Bloembergen and P. P. Sorokin, *ibid.* **110**, 865 (1958); R. Blume and A. Redfield, Bull. Am. Phys. Soc. **5**, 176 (1960). Additional theoretical discussion is given by K. Tomita, Progr. Theoret. Phys. (Kyoto) **19**, 541 (1958).

[4] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948) (henceforth referred to as BPP).

TABLE I. Parameters appearing in Eqs. (1) and (2). The second moments were calculated by the method of Van Vleck.[a] The relaxation times T_1 and T_2 were measured.

Parameter	Units	Crystal	Values of the parameter for several crystal orientations $H_0\|[100]$	$H_0\|[110]$	$H_0\|[111]$
$\langle(\Delta\nu)^2\rangle_{\text{Na}}$	sec^{-2}	NaCl	4.19×10^5	6.08×10^5	6.72×10^5
$\langle(\Delta\nu)^2\rangle_{\text{Cl}}$	sec^{-2}	NaCl	6.6×10^3	9.7×10^3	10.7×10^3
$\langle(\Delta\nu)^2\rangle_{\text{Cl-Na}}$	sec^{-2}	NaCl	2.71×10^5	0.75×10^5	0.097×10^5
$\langle(\Delta\nu)^2\rangle_{\text{F}}$	sec^{-2}	CaF_2	20.7×10^7	8.03×10^7	3.75×10^7
$T_2(\text{Na})$[b]	μsec	NaCl	190 ± 10	190 ± 10	
$T_1(\text{Na})$[c]	sec	NaCl	14.5 ± 0.3	14.5 ± 0.3	
$T_1(\text{Cl})$	sec	NaCl	4.5[d]		
$T_1(\text{F})$	sec	CaF_2	12.9 ± 0.3	12.9 ± 0.3	11.5 ± 0.3

[a] See reference 8.

[b] This quantity is defined as $\frac{1}{2}g(\nu_0)$. It was determined, for sodium chloride, by a measurement of the absorption line shape using a Varian spectrometer.

[c] In neither the sodium chloride nor the calcium fluoride crystals did the spin-lattice relaxation time show a dependence on crystal orientation. Mieher has shown theoretically that T_1 should not be orientation dependent in quadrupolar solids such as NaCl [R. L. Mieher, Phys. Rev. Letters **4**, 57 (1960)]. All quoted spin-lattice relaxation times were measured at room temperature.

[d] Indirect measurement by R. T. Schumacher.[1] The crystal orientation was not noted. See, however, the footnote directly above. This value of T_1 is in good agreement with that of Wikner *et al.*,[13] who found $T_1(\text{Cl}^{35})$ in NaCl to be 5.2 sec at 298°K.

(b) the resonance line is homogeneously broadened[2,5]; and (c) the rf field H_1 is a relatively weak perturbation on the spin system, i.e., $\gamma^2H_1^2T_1T_2\ll1$, where T_2 is the transverse relaxation time. When this third condition is satisfied, the spin system can be characterized by a spin temperature, the reciprocal of which is proportional to M_z and to the difference in population between adjacent magnetic sublevels ($2I+1$ in number).

When H_1 is large, in particular when $S\equiv\gamma^2H_1^2T_1T_2\gg1$, Eq. (1) can be grossly incorrect. In this domain of large S the spin system, according to Redfield's spin-temperature hypothesis, can still be characterized by a temperature but not as measured in the laboratory frame of reference. Rather, the spin system will be in a cononical distribution in a frame of reference which rotates with the rf frequency ν about the direction of H_0. In this case, the magnetization vector, $\langle\langle\mathbf{M}_r\rangle\rangle$,[6] can be shown[2] to be along the direction of the effective field $\mathbf{H}_{er}$, which is given by

$$\mathbf{H}_{er}=H_1\hat{\imath}'+(H_0-\omega/\gamma)\hat{k}',$$

where the primed coordinate system rotates with angular frequency $\omega=2\pi\nu$ about the $\hat{k}'$ axis. The direction of the unit vector $\hat{k}'$ is that of the external field H_0.

Redfield's spin-temperature hypothesis[7] is equivalent to the statement that, at all times, the spin system is completely characterized by the density matrix

$$\rho\sim\exp(-\mathcal{H}_{er}/kT_r),$$

where T_r is the temperature of the spin system in the rotating frame. The Hamiltonian $\mathcal{H}_{er}$ is the spin Hamiltonian transformed to the rotating frame. This Hamiltonian includes the dipole-dipole interactions and also the interactions of the spins with H_0 and with $H_1(\nu)$.

It is worth noting that Redfield's hypothesis cannot be correct for small H_1. For example, this hypothesis implies that, at resonance, $\mathbf{H}_{er}$ and hence $\langle\langle\mathbf{M}_r\rangle\rangle$, will be perpendicular to the z axis, giving $M_z=\langle\langle\mathbf{M}_r\rangle\rangle\cdot\hat{k}'=0$. Of course, one finds a relatively large value of M_z at resonance if $S\lesssim1$.

To derive an expression for M_z in terms of $H_1(\nu)$, it is also necessary to make an assumption about the spin-lattice relaxation mechanism. Redfield assumed, for simplicity, that each nuclear spin relaxes independently of the others with a relaxation time T_1. He then obtained the following result for the (normalized) magnetization as a function of H_1 and $\Delta\nu\equiv(2\pi)^{-1}(\nu-\gamma H_0)$:

$$\frac{M_z}{M_0}=\frac{(\Delta\nu)^2}{[\gamma^2H_1^2(\nu)/4\pi^2]+(\Delta\nu)^2+\frac{2}{3}\langle(\Delta\nu)^2\rangle}, \tag{2a}$$

$$\frac{M_z}{M_0}=\frac{(\Delta\nu)^2}{[\gamma^2H_1^2(\nu)/4\pi^2]+(\Delta\nu)^2+\frac{2}{3}\langle(\Delta\nu)^2\rangle_u+\frac{2}{3}\langle(\Delta\nu)^2\rangle_pT_1/T_1'+\langle(\Delta\nu)^2\rangle_{p-u}[1+T_1/T_1']}, \tag{2b}$$

Equations (2a) and (2b) apply to solids in which there are, respectively, one and two magnetic ingredients present. The unprimed symbols in both equations denote parameters of the spin system on which measurements are made; the primed symbols in Eq. (2b) characterize the second ingredient—in these experiments the Cl nuclei in NaCl. The second moments appearing in Eqs. (2) are calculated by the method of Van Vleck.[8] The second moments $\langle(\Delta\nu)^2\rangle$, $\langle(\Delta\nu)^2\rangle_p$, and $\langle(\Delta\nu)^2\rangle_{p-u}$ appearing in Eq. (2b) are, for sodium chloride, the contribution of the sodium nuclei to the second moment of the sodium-absorption line, the contribution of the chlorine nuclei to the second moment of the chlorine-absorption line, and the contribution of the chlorine nuclei to the second moment of the sodium line, respectively. These moments depend on the orientation of the crystals with respect to the direction of $\mathbf{H}_0$.

In the subsequent sections of this paper, measurements will be compared with Eqs. (1) and (2). Table I lists all the parameters, either calculated or measured, which are required in order to apply these equations.

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[5] A. M. Portis, Phys. Rev. **91**, 1071 (1953).

[6] The double brackets indicate that the expectation value of the magnetic moment operator has been averaged over the canonical ensemble.

[7] Redfield's hypothesis, while reasonable, would be extremely difficult to justify in any particular problem. Similar difficulties would be encountered in trying to establish that any physical system consisting of many interacting particles can be characterized by a canonical distribution and therefore by a temperature.

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

III. EXPERIMENTAL TECHNIQUE

The signal observed in these experiments was the peak value of the nuclear free-induction decay following a $\pi/2$ pulse. This signal is proportional to M_z. The pulse apparatus was of the coherent type[9] with the transmitter operated at a crystal-controlled frequency of 10.000 Mc/sec. It was capable of turning sodium spins through 90 deg in 5 μsec. Under optimum conditions, the receiver fully recovered in 5 μsec after the end of the pulse.[10]

The saturating rf field $H_1(\nu)$ was furnished by a conventional cw transmitter, whose output was inductively coupled into the transmitter coil of the pulse apparatus. This transmitter was driven by a variable-frequency oscillator—a BC 221. The independent variable in most of the experiments was $\Delta\nu$, the difference between the frequency of the cw oscillator and that of the pulse transmitter. The Larmor frequency of the spins was set as closely as possible to the pulse transmitter frequency by adjustment of the external field H_0. When the Larmor frequency was set equal to the 10.000-Mc/sec transmitter frequency, the curve of M_z versus $\Delta\nu$ was observed to be symmetrical about $\Delta\nu=0$.[11]

To set the frequency difference $\Delta\nu$ at a desired value, a small portion of the output of the 10.000-Mc/sec crystal oscillator was coupled into a commercial receiver which simultaneously picked up the signal from the cw transmitter. The difference between these two frequencies appeared at the output of the receiver and was measured, with the aid of a calibrated audio oscillator, by observing the appropriate Lissajous figure on an oscilloscope. For $\Delta\nu \gtrsim 10$ kc/sec, this method was unsatisfactory, and it became necessary to utilize the calibration of the BC 221 to measure $\Delta\nu$. With one or the other of these calibration methods, it was possible to determine $\Delta\nu$ within better than 1% in every case. The sequence of events in measuring M_z at a given $\Delta\nu$ was as follows: The cw transmitter was turned on and allowed to remain on for a time much greater than T_1 (and T_1') in order that the steady state might be established. The cw transmitter (i.e., H_1) was then switched off, and, after a preset but variable time interval, the $\pi/2$ pulse was initiated. The subsequent free-induction decay was visually observed on an oscilloscope. The time interval between turnoff of $H_1(\Delta\nu)$ and the initiation of the 90° pulse was much greater than T_2 but much less than T_1. A sequence of measurements at a given $\Delta\nu$ and a given H_1 showed no effect of the changing of this time interval provided it remained within the above stated limits.

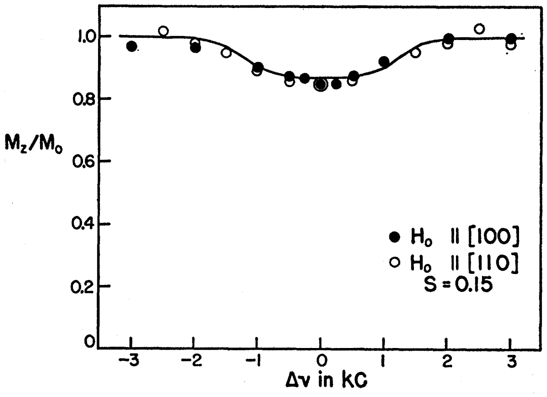

FIG. 1. Relative magnetization vs $\Delta\nu$ for the sodium spin system in NaCl. The solid line represents Eq. (1).

The amplitude of H_1 was determined by a test coil inserted in the transmitter coil (with receiver coil removed). This test coil was calibrated from a knowledge of the geometry of the coil and its natural resonant frequency and by measurement of the peak voltage induced in the test coil by a $\pi/2$ pulse (of known duration) in the transmitter coil. Using these two calibration methods, it was believed possible to determine $H_1(\nu)$ within $\pm 3\%$.

All measurements were made at room temperature. The sodium chloride and calcium fluoride crystals were synthetic and were obtained from the Harshaw Chemical Company.

IV. EXPERIMENTAL RESULTS

A. NaCl

Figure 1 shows the magnetization versus $\Delta\nu$ (in kc/sec) for two orientations of the NaCl crystal. The measurements were made at a value of $H_1=1.03$ mgauss for which $S=0.15$. The solid and open circles represent data taken with the [100] and [110] directions of the crystal, respectively, parallel to $\mathbf{H}_0$. The solid curve in Fig. 1 is a plot of Eq. (1) in which $g(\nu)$ is the *measured* shape of the sodium absorption line.[12] The line shapes in these two directions are almost exactly the same, and the same T_1 was measured for both orientations of the crystals (see Table I). Therefore, the theoretical curves for the two orientations are coincident.

The excellent agreement between experiment and the BPP theory, as seen in Fig. 1, is not unexpected, since S is small compared to unity.

On comparing the predictions of Eq. (2b) [canonical distribution in *rotating* frame] with the data in Fig. 1, one finds the agreement to be extremely poor. For example, as we have already noted, Eqs. (2) give $M_z=0$ at $\Delta\nu=0$.

Figure 2 shows measurements at two crystal orienta-

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[9] John J. Spokas and Charles P. Slichter, Phys. Rev. **113**, 1462 (1959).

[10] The circuit closely followed a design by W. G. Clark (unpublished).

[11] A small missetting of the external field H_0 causes the measured points to be centered at a frequency differing slightly from ν_0. The effect of such a missetting can be seen in Fig. 3(a).

[12] The width of the sodium absorption line is greater by approximately a factor of 1.4 than the width arising from dipole-dipole interactions alone. This results from interactions between the sodium nuclear quadrupole moments and strain-produced field gradients in the crystal. If the local strains are not too large, the resonance line is still expected to be homogeneously broadened.

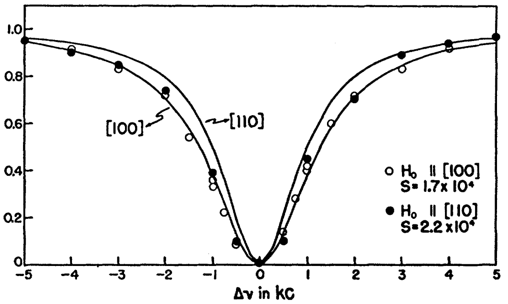

FIG. 2. Relative magnetization vs $\Delta\nu$ for the sodium spin system in NaCl. The solid lines were calculated using Redfields' theory, Eq. (2b).

tions for which S is very large ($S\simeq 10^4$). In this domain, one expects Redfield's hypothesis and Eq. (2b) to be valid. Indeed, the curves (solid lines) calculated using this equation (and the appropriate parameters in Table I) are in very good agreement with the measurements. It should be remarked that T_1', the relaxation time of the chlorine nuclei in NaCl, was not directly measured for the sample used, but rather was inferred by Schumacher from low-field cross relaxation measurements performed on the sodium nuclei in NaCl.[1] The second moments, $\langle(\Delta\nu)^2\rangle_{\mathrm{Na}}$, $\langle(\Delta\nu^2)\rangle_{\mathrm{Cl}}$, and $\langle(\Delta\nu^2)\rangle_{\mathrm{Cl-Na}}$ were, of necessity, calculated[8] and therefore do not take into account the observed quadrupolar broadening.

Referring again to Fig. 2, the BPP theory predicts values of M_z that are too small by many orders of magnitude. For example, Eq. (1) predicts a value of M_z/M_0 at $\Delta\nu=\pm 1$ kc/sec which is smaller than the observed values by a factor of approximately 5×10^3.

The validity of Redfield's hypothesis for large S is further supported by many additional measurements at $S\geq 10$, which showed that $M_z(\nu)/M_0$ is independent of the amplitude of $H_1(\nu)$. Inspection of Eqs. (2) shows that this is to be expected when $|\Delta\nu|\gg\gamma H_1/2\pi$.

When S is neither very large nor very small compared to unity, Eqs. (1) and (2) are not expected to be valid; i.e., the spin system is not in a canonical distribution in either the rotating or stationary frames. Figure 3 shows measurements in this transition region.

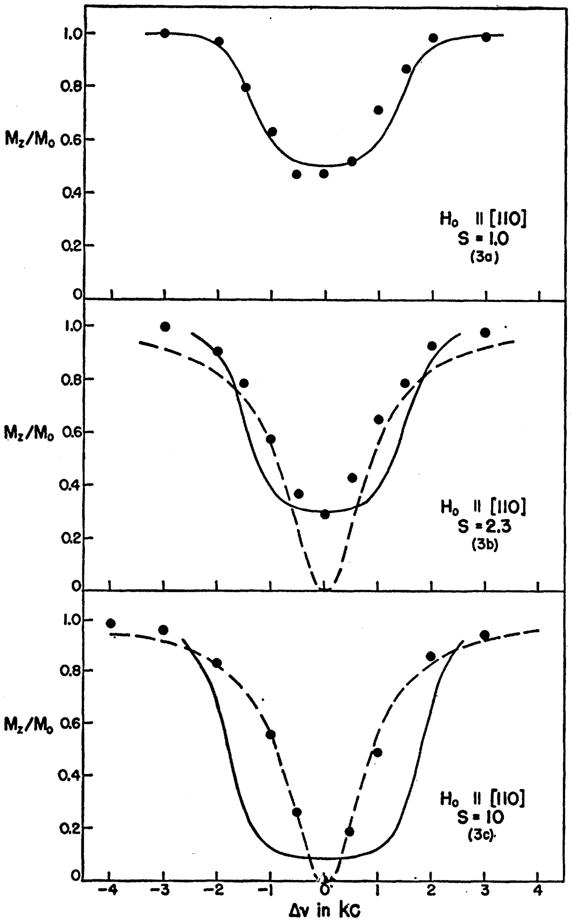

FIG. 3. Relative magnetization vs $\Delta\nu$ for the sodium spin system in NaCl. The dashed and solid lines were calculated using the theories of Redfield and of BPP, respectively.

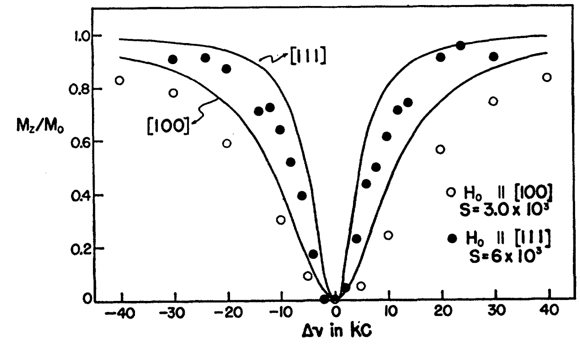

FIG. 4. Relative magnetization vs $\Delta\nu$ for the fluorine spin system in CaF$_2$. The solid lines were calculated using Eq. (2a).

Figure 3(a) shows measurements for which $H_0\|[110]$, $S=1.0$. The solid line, which is a plot of Eq. (1), is seen to be in slight disagreement with the data; the resonance line appears slightly narrower[11] than the BPP theory predicts. This characteristic narrowing at the onset of saturation has been referred to as "saturation narrowing." This narrowing becomes very apparent in Figs. 3(b) and 3(c). In these figures, S is equal to 2.3 and 10, respectively. Also shown in these figures are theoretical curves representing Eq. (1) (solid lines) and Eq. (2b) (dashed lines). It is observed that while neither theory is correct at $S=2.3$, there is good agreement between experiment and Redfield's theory at $S=10$.

To summarize, the sodium chloride measurements well below and well above saturation support the spin temperature hypotheses of BPP and of Redfield. They also reveal that the spin-lattice relaxation assumption used by these authors is a good one. The latter result is not surprising, for it is now well established[13] that the

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

sodium spins in NaCl are relaxed by a direct coupling between the sodium nuclear quadrupole moments and the fluctuating field gradients produced by the lattice vibrations. Since the mutual interaction between the spins plays no role in the process, the spins should relax independently.

B. CaF_2

Measurements on calcium fluoride are not so well suited for testing Redfield's hypothesis as are the sodium chloride measurements. In CaF_2, the spin lattice relaxation rate is in part governed by the rate of diffusion of spin energy to the paramagnetic impurities in the sample.[14–16] Then Eq. (2) is not expected to be exactly correct even when Redfield's spin-temperature hypothesis should be valid, since the spins do not relax independently. Nevertheless, qualitative agreement with Eqs. (2) might be expected and was indeed observed.

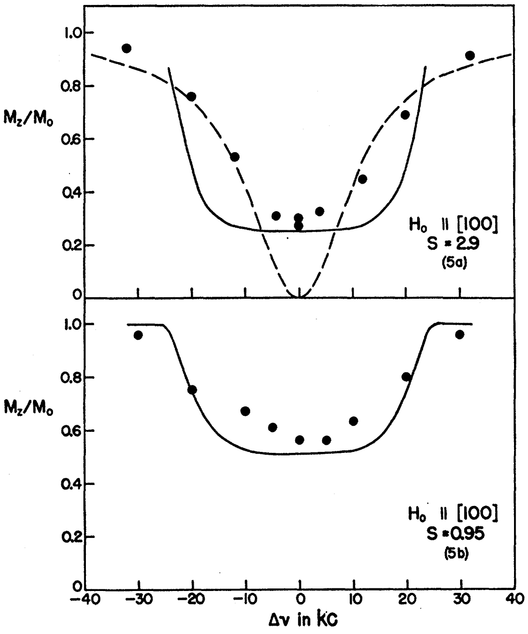

FIG. 5. Relative magnetization vs $\Delta\nu$ for the fluorine spin system in CaF_2. The solid and dashed lines represent Eqs. (1) and (2a), respectively.

Figure 4 shows measurements at large S for two orientations of the CaF_2 crystal. The open circles ($S=3\times10^3$) and closed circles ($S=6\times10^3$) denote measurements for which $H_0\|[100]$ and $H_0\|[111]$, respectively. It was found that, as long as $S\gtrsim10$, the magnetization at a particular value of $|\Delta\nu|$ is independent of the amplitude of H_1 when $|\Delta\nu|\gg\gamma H_1/2\pi$. This result is in accord with Eqs. (2). The theoretical curves in Fig. 4 were calculated from Eq. (2a). The calculated second moments for the two crystal orientations appear in Table I. The second moment in calcium fluoride shows a strong dependence on the orientation of the crystal with respect to the external field. The measurements in Fig. 4 show a correspondingly large orientation dependence, but the measured magnetization for both crystal orientations is appreciably smaller, at a given $\Delta\nu$, than the corresponding calculated values.

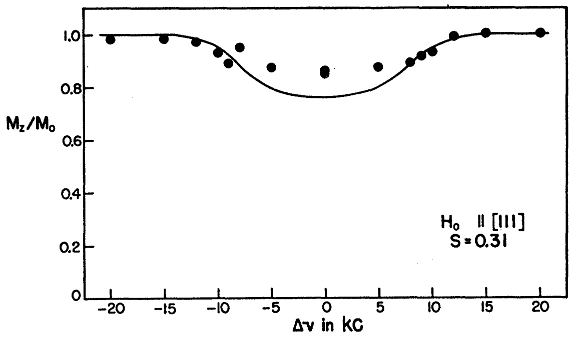

FIG. 6. Relative magnetization vs $\Delta\nu$ for the fluorine spin system in CaF_2. The solid line represents Eq. (1).

Figure 5 shows measurements at $H_1=5.1$ mgauss ($S=2.9$) and $H_1=2.8$ mgauss ($S=0.95$). The crystal was oriented so that $H_0\|[100]$. The solid and dashed lines in this figure represent the predictions of Eqs. (1) and (2a), respectively. Again, since S is neither very large nor very small compared to unity, the lack of agreement between experiment and both theories is not unexpected.

It is of interest to check Eq. (1) well below saturation, where the theory of BPP might be expected to be correct. Figure 6 shows such measurements with $S=0.31$, $H_0\|[111]$. The solid line is the theoretical curve. The disagreement between experiment and the BPP theory is greater than the experimental error in the interval $|\Delta\nu|<5$ kc.

Figure 7 presents additional data indicating that Eq. (1) is incorrect even for small S. This figure displays

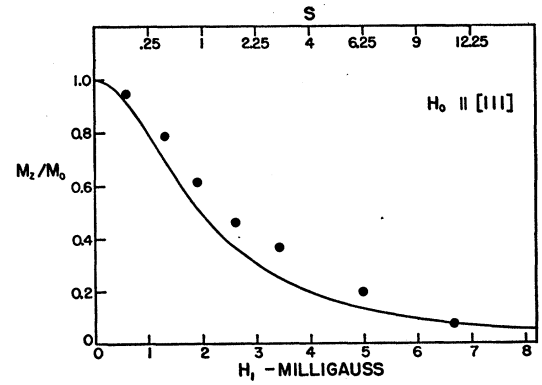

FIG. 7. Relative magnetization vs H_1 for the fluorine spin system in CaF_2. The measurements were made at $\Delta\nu=0$. The solid line represents the theory of BPP, Eq. (1). At the top of the graph are shown values of S corresponding to the values of the field H_1 appearing directly below.

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

[15] P-G de Gennes, J. Phys. Chem. Solids **7**, 345 (1958).

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

M_z/M_0 as a function of H_1 (in milligauss) at $\Delta\nu=0$. The crystal is oriented so that $H_0\|[111]$. At the top of the graph are shown values of S with corresponding values of the field H_1 appearing directly below. Attention is called to the fact that the usual spin-temperature hypothesis, and therefore Eq. (1), should be most nearly correct when the frequency of the saturating field is very near resonance, i.e., when $|\Delta\nu|\lesssim\gamma H_1/2\pi$.[17] In NaCl, it was found that Eq. (1) was in agreement with measurements at $\Delta\nu=0$ for S as large as 3. From Fig. 7, however, it is seen that Eq. (1) (solid line) is in measurable disagreement with the data even when S is as small as $\frac{1}{3}$. These measurements at small values of H_1 provide added evidence that the fluorine spins in CaF_2 do not relax independently and therefore cannot be characterized by a single relaxation time T_1.

If spin-lattice relaxation cannot be characterized by a single time constant, one would expect a transient-type experiment to show nonexponential recovery of the magnetization following sudden saturation. Experiments of this type were performed to measure T_1; they did not reveal any deviation from exponential recovery. The measurements of $M_z(t)$ following saturation at $t=0$ were accurate within $\pm3\%$. The measurements were made in the time interval $0.1T_1\lesssim t\lesssim 3T_1$.

The question might be raised whether T_1, as measured in a transient-type experiment, should have the same numerical value as that obtained from a steady-state saturation experiment. De Gennes[15] has found that it should, provided the magnetization in the transient experiment recovers exponentially.

To summarize, those measurements, well below saturation, which employed the steady-state technique, did reveal the failure of the relaxation assumption of BPP and of Redfield; the transient measurement technique did not demonstrate this failure.

V. SUMMARY

The primary aim of the experiments herein reported was to verify that for $S\equiv\gamma^2H_1T_1T_2\gg1$, a nuclear spin system is properly characterized by a canonical distribution in a frame of reference rotating about H_0 with the frequency of the saturating rf field $H_1(\nu)$. To test this hypothesis in a steady-state experiment it is also necessary to make an assumption about the spin-lattice relaxation mechanism in the crystal. In deriving Eq. (2), Redfield assumed that the nuclear spins relax independently with a characteristic time T_1. His theory is in very good agreement with measurements at $S\gg1$ in sodium chloride but only in fair agreement in calcium fluoride. It appears that his spin-temperature hypothesis is valid in both crystals when $S\gg1$ but that the relaxation assumption is a good one only in NaCl. These results are in accord with what is known about the spin-lattice relaxation mechanisms in both types of solids.

The secondary aim of this work was to check the validity of Eq. (2) when $S\ll1$. To derive Eq. (2), one assumes that the spin system is in a canonical distribution in the laboratory frame of reference and that the nuclear spins relax independently with relaxation time T_1. In the domain of small S, there was again better agreement between experiment and theory for sodium chloride than for calcium fluoride. This is additional evidence that the simple relaxation assumption employed by Redfield and by BPP is a good one when the relaxation is quadrupolar as in NaCl but is inadequate when the relaxation is produced by paramagnetic impurities as in CaF_2.

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[17] Near resonance the effective field is small and consequently so is the energy of the spin system as viewed in the rotating reference frame. It is just when this energy is small (much less than $\hbar T_1^{-1}$) that the BPP theory should be valid.