PHYSICAL REVIEW B VOLUME 16, NUMBER 11 1 DECEMBER 1977

Nuclear magnetic resonance in LiF: A single nuclear-dipolar-spin temperature in crystals with more than one spin species*

Harold T. Stokes and David C. Ailion
Department of Physics, University of Utah, Salt Lake City, Utah 84112
(Received 26 July 1977)

In a crystal containing more than one species of nuclear spin in a large dc magnetic field, the secular dipolar interactions between all spins, unlike as well as like, form a single reservoir described by a single spin temperature. We demonstrated this concept with experiments on LiF. In particular, we showed that T_{1D} of ^{7}Li and ^{19}F are equal. We also measured T_1 and $T_{1\rho}$ of ^{19}F using ^{7}Li detection. Finally we applied this concept to the Provotorov theory of saturation, which we extended to the case of a two-spin system, and demonstrated experimentally the validity of the treatment.

I. INTRODUCTION

It has long been known that in small magnetic fields, nuclei of different spin species cross relax very rapidly. Pound[1] demonstrated this fact in LiF by showing that the spin-lattice relaxation times of ^{7}Li and ^{19}F were identical in zero field, although very much different in high magnetic field. This phenomenon was later explained[2,3] to be due to the fact that in zero field the spin-spin dipolar interaction between unlike spins as well as between like spins may be described by a single spin temperature; that is, the dipolar system maintains internal thermal equilibrium.

In large magnetic fields the concept of "secular" dipolar interactions is introduced. Redfield[4] and others[5,6] asserted that such interactions could also be described by a spin temperature. Many experiments have been successfully interpreted using this concept.[6]

In solids with two or more different nuclear species, this concept has a natural extension: namely, the spin-spin "secular" dipolar interaction between unlike spins as well as between like spins may be described by a single spin temperature. As a consequence, one cannot speak of a dipolar spin temperature of one spin species separate from the dipolar spin temperature of any other spin species in the same crystal.

In this paper, we present pulse NMR data in LiF which directly demonstrate the validity of the concept of a single dipolar temperature in multispin systems. A variety of experiments have been performed by others[7-13] whose interpretation depends upon this concept.

II. THEORY

Here we demonstrate theoretically that the secular dipolar interaction for a two spin system is a quasi-invariant of motion. Accordingly, it may be characterized by a spin temperature which may be different from the spin temperatures of either Zeeman interaction.

Consider a system of two different spin species (I spins and S spins) in a large dc magnetic field $\vec{H}_0$. We may write the Hamiltonian in units of frequency:

$$\mathcal{H} = \mathcal{H}_{ZI} + \mathcal{H}_{ZS} + \mathcal{H}_D \; . \tag{1}$$

The first two terms in the above expression are the Zeeman interactions with $\vec{H}_0$, which is chosen to be along the z axis:

$$\mathcal{H}_{ZI} = -\omega_{0I} \sum_k I_{zk} \tag{2}$$

and

$$\mathcal{H}_{ZS} = -\omega_{0S} \sum_k S_{zk} \; , \tag{3}$$

where ω_{0I} and ω_{0S} are the resonant frequencies $\gamma_I H_0$ and $\gamma_S H_0$ of the I and S spins, respectively. The term $\mathcal{H}_D$ is the spin-spin dipolar interaction which is written

$$\mathcal{H}_D = \frac{1}{2} \sum_{j,k} \sum_{p=-2}^{2} F_{jk}^{(p)} A_{jk}^{(p)}(I,I) + \frac{1}{2} \sum_{j,k} \sum_{p=-2}^{2} F_{jk}^{(p)} A_{jk}^{(p)}(S,S) + \sum_{j,k} \sum_{p=-2}^{2} F_{jk}^{(p)} A_{jk}^{(p)}(I,S) \; , \tag{4}$$

where

$$F_{jk}^{(0)} = r_{jk}^{-3}(1 - 3\cos^2\theta_{jk}) \; , \tag{5}$$

$$F_{jk}^{(\pm 1)} = r_{jk}^{-3} \sin\theta_{jk} \cos\theta_{jk} \exp(\mp i\phi_{jk}) \; , \tag{6}$$

$$F_{jk}^{(\pm 2)} = r_{jk}^{-3} \sin^2\theta_{jk} \exp(\mp 2i\phi_{jk}) \; , \tag{7}$$

$$A_{jk}^{(0)}(I,S) = \gamma_I \gamma_S \hbar (I_{zj}S_{zk} - \tfrac{1}{4} I_{+j}S_{-k} - \tfrac{1}{4} I_{-j}S_{+k}) \; , \tag{8}$$

$$A_{jk}^{(\pm 1)}(I,S) = -\tfrac{3}{2} \gamma_I \gamma_S \hbar \, (I_{zj}S_{\pm k} + I_{\pm j}S_{zk}) \; , \tag{9}$$

and

$$A_{jk}^{(\pm 2)}(I,S) = -\tfrac{3}{4}\gamma_I\gamma_S\hbar I_{\pm j}S_{\pm k} \ . \tag{10}$$

We have similar expressions for $A_{jk}^{(p)}(I,I)$ and $A_{jk}^{(p)}(S,S)$.

The dipolar interaction can be divided into two parts, $\mathcal{H}_D^{(0)}$ and $\mathcal{H}_D^{(n)}$, the secular and nonsecular dipolar interactions, respectively,

$$\mathcal{H}_D = \ {}_D^{(0)} + \mathcal{H}_D^{(n)} \ . \tag{11}$$

The secular dipolar interaction is defined to be that part which commutes with $\mathcal{H}_{ZI} + \mathcal{H}_{ZS}$ and is given by

$$\mathcal{H}_D^{(0)} = \frac{1}{2}\sum_{j,k} F_{jk}^{(0)}A_{jk}^{(0)}(I,I) + \frac{1}{2}\sum_{j,k} F_{jk}^{(0)}A_{jk}^{(0)}(S,S) + \gamma_I\gamma_S\hbar\sum_{j,k} F_{jk}^{(0)}I_{zj}S_{zk} \ . \tag{12}$$

This interaction commutes with both $\mathcal{H}_{Zi}$ and $\mathcal{H}_{ZS}$. Thus transitions due to its fluctuations conserve Zeeman energy along $\vec{H}_0$. For large $\vec{H}_0$ the secular dipolar interactions form a reservoir parametrized by a spin temperature. As will be shown below, $\mathcal{H}_{ZI}$, $\mathcal{H}_{ZS}$, and $\mathcal{H}_D^{(0)}$ are separately constants of motion and the density operator is given, for a system in thermal equilibrium, by

$$\sigma = 1 - \beta_I\mathcal{H}_{ZI} - \beta_S\mathcal{H}_{ZS} - \beta_D\mathcal{H}_D^{(0)} \ . \tag{13}$$

To show this, we must properly divide the total Hamiltonian into three main parts which commute with each other plus a perturbation which is smaller than any of the three main parts. It is clear that $\mathcal{H}_{ZI}$, $\mathcal{H}_{ZS}$, and $\mathcal{H}_D^{(0)}$ commute with each other. However, the remaining part $\mathcal{H}_D^{(n)}$ of the total Hamiltonian is not smaller than the other three parts. In fact, it turns out in general that

$$Tr(\mathcal{H}_D^{(n)})^2 > Tr(\mathcal{H}_D^{(0)})^2 \ . \tag{14}$$

To put the Hamiltonian into the right form, we use a procedure which closely parallels that used by Goldman (pp. 138–141 in Ref. 6) for the case of a single spin species. We introduce a transformation via a unitary operator U such that

$$U^\dagger(\mathcal{H}_{ZI} + \mathcal{H}_{ZS} + \mathcal{H}_D^{(n)})U = \mathcal{H}_{ZI} + \mathcal{H}_{ZS} + O(\mathcal{H}_D^2/\mathcal{H}_Z) \ . \tag{15}$$

Let

$$U\mathcal{H}_{ZI}U^\dagger \equiv \mathcal{H}_{ZI}^* \tag{16}$$

and

$$U\mathcal{H}_{ZS}U^\dagger \equiv \mathcal{H}_{ZS}^* \ . \tag{17}$$

It is convenient to write U in the following form:

$$U = \exp(-iR) \ . \tag{18}$$

For large $\vec{H}_0$, $R \ll 1$ and, thus, expanding Eqs. (16) and (17) in powers of R yields

$$\mathcal{H}_{ZI}^* + \mathcal{H}_{ZS}^* = \mathcal{H}_{ZI} + \mathcal{H}_{ZS} - i[R, \mathcal{H}_{ZI} + \mathcal{H}_{ZS}] + O(\mathcal{H}_D^2/\mathcal{H}_Z) \ . \tag{19}$$

From Eq. (15) we also obtain

$$\mathcal{H}_{ZI}^* + \mathcal{H}_{ZS}^* = \mathcal{H}_{ZI} + \mathcal{H}_{ZS} + \mathcal{H}_D^{(n)} + O(\mathcal{H}_D^2/\mathcal{H}_Z) \tag{20}$$

Thus, neglecting terms of order $\mathcal{H}_D^2/\mathcal{H}_Z$, we obtain

$$-i[R, \mathcal{H}_{ZI} + \mathcal{H}_{ZS}] = \mathcal{H}_D^{(n)} \ . \tag{21}$$

From this equation, we can solve for R and obtain

$$R = \tfrac{1}{2}i\sum_{j,k}\sum_{p\neq 0}\frac{1}{p\,\omega_{0I}}F_{jk}^{(p)}A_{jk}^{(p)}(I,I) + \tfrac{1}{2}i\sum_{j,k}\sum_{p\neq 0}\frac{1}{p\,\omega_{0S}}F_{jk}^{(p)}A_{jk}^{(p)}(S,S)$$
$$+\gamma_I\gamma_S\hbar\sum_{j,k}\left[-\tfrac{1}{4}iF_{jk}^{(0)}\left(\frac{I_{+j}S_{-k}}{\omega_{0I}-\omega_{0S}}\right) - \tfrac{3}{2}iF_{jk}^{(1)}\left(\frac{1}{\omega_{0S}}I_{zj}S_{+k} + \frac{1}{\omega_{0I}}I_{+j}S_{zk}\right) - \tfrac{3}{4}iF_{jk}^{(2)}\left(\frac{I_{+j}S_{+k}}{\omega_{0I}+\omega_{0S}}\right) + \text{c.c.}\right] \ . \tag{22}$$

Using this expression, we find that

$$\mathcal{H}_{ZI}^* = \mathcal{H}_{ZI} + \frac{1}{2}\sum_{j,k}\sum_{p\neq 0}F_{jk}^{(p)}A_{jk}^{(p)}(I,I) + \gamma_I\gamma_S\hbar\sum_{j,k}\left[-\frac{1}{4}\frac{\omega_{0I}}{\omega_{0I}-\omega_{0S}}F_{jk}^{(0)}I_{+j}S_{-k}\right.$$
$$\left. - \tfrac{3}{2}F_{jk}^{(1)}I_{+j}S_{zk} - \frac{3}{4}\frac{\omega_{0I}}{\omega_{0I}+\omega_{0S}}F_{jk}^{(2)} + \text{c.c.}\right] + O\left(\frac{\mathcal{H}_D^2}{\mathcal{H}_Z}\right) \tag{23}$$

and

$$\mathcal{H}_{ZS}^{*} = \mathcal{H}_{ZS} + \frac{1}{2} \sum_{j,k} \sum_{p \neq 0} F_{jk}^{(p)} A_{jk}^{(p)}(S,S) + \gamma_I \gamma_S \hbar \sum_{j,k} \left[-\frac{1}{4} \frac{\omega_{0S}}{\omega_{0S} - \omega_{0I}} F_{jk}^{(0)} I_{+j} S_{-k} - \tfrac{3}{2} F_{jk}^{(1)} I_{zj} S_{+k} - \frac{3}{4} \frac{\omega_{0S}}{\omega_{0S} + \omega_{0I}} F_{jk}^{(2)} I_{+j} S_{+k} + \text{c.c} \right] + O\left(\frac{\mathcal{H}_D^2}{\mathcal{H}_Z} \right) . \quad (24)$$

We can also see that

$$\mathcal{H}_D^{(0)*} = \mathcal{H}_D^{(0)} + O(\mathcal{H}_D^2/\mathcal{H}_Z) . \quad (25)$$

Combining Eqs. (20) and (25), we finally have the total Hamiltonian in the following form:

$$\mathcal{H} = \mathcal{H}_{ZI}^{*} + \mathcal{H}_{ZS}^{*} + \mathcal{H}_D^{(0)*} + \mathcal{H}' , \quad (26)$$

where $\mathcal{H}'$ is of order $\mathcal{H}_D^2/\mathcal{H}_Z$. Even though this Hamiltonian is identical to the original Hamiltonian given by Eq. (1), the term $\mathcal{H}_D^{(n)}$ no longer appears explicitly. Our transformation has effectively distributed its value among other terms. Since U is a unitary operator, $\mathcal{H}_{ZI}^{*}$, $\mathcal{H}_{ZS}^{*}$, and $\mathcal{H}_D^{(0)*}$ commute with each other. (For example,

$$\begin{aligned}[\mathcal{H}_{ZI}^{*}, \mathcal{H}_{ZS}^{*}] &= [U\mathcal{H}_{ZI}U^{\dagger}, U\mathcal{H}_{ZS}U^{\dagger}] \\ &= U[\mathcal{H}_{ZI}, \mathcal{H}_{ZS}]U^{\dagger} = 0.\end{aligned}$$

We thus have written the Hamiltonian in terms of three constants of motion $\mathcal{H}_{ZI}^{*}$, $\mathcal{H}_{ZS}^{*}$, and $\mathcal{H}_D^{(0)*}$, plus a perturbation $\mathcal{H}'$ which in this case is smaller than any of the other three terms. The density operator is

$$\sigma = 1 - \beta_I \mathcal{H}_{ZI}^{*} - \beta_S \mathcal{H}_{ZS}^{*} - \beta_D \mathcal{H}_D^{(0)*} . \quad (27)$$

For large $\vec{H}_0$, the terms $\mathcal{H}_{ZI}^{*}$, $\mathcal{H}_{ZS}^{*}$, $\mathcal{H}_D^{(0)*}$ approximately equal $\mathcal{H}_{ZI}$, $\mathcal{H}_{ZS}$, $\mathcal{H}_D^{(0)}$, respectively. Thus Eq. (27) can be written to a good approximation as Eq. (13). The effect of the perturbation $\mathcal{H}'$ is to cause cross relaxation between $\mathcal{H}_{ZI}$, $\mathcal{H}_{ZS}$, and $\mathcal{H}_D^{(0)}$ to a common spin temperature but can be neglected for large $\vec{H}_0$.

As can be seen from Eq. (13), the secular dipolar interactions when in equilibrium form a reservoir parametrized by a spin temperature β_D. It should be noted especially that $\mathcal{H}_D^{(0)}$ includes *all* secular interactions, those between unlike spins as well as those between like spins. They all form a *common* reservoir with a *common* spin temperature.

Consider some of the consequences of this treatment. First of all, it is obvious that one cannot speak of "dipolar order" of the I spins separate from "dipolar order" of the S spins. The rate T_{1D}^{-1} of relaxation of dipolar order is thus the same for both I and S spins and is given by the time evolution of β_D towards the lattice temperature. Also the dipolar reservoir of *both* spins can be "cooled" by adiabatic demagnetization in the rotating frame (ADRF) of *either* the I spins or S spins. In short, if anything is done to the dipolar order of the I spins, it is also done to the dipolar order of

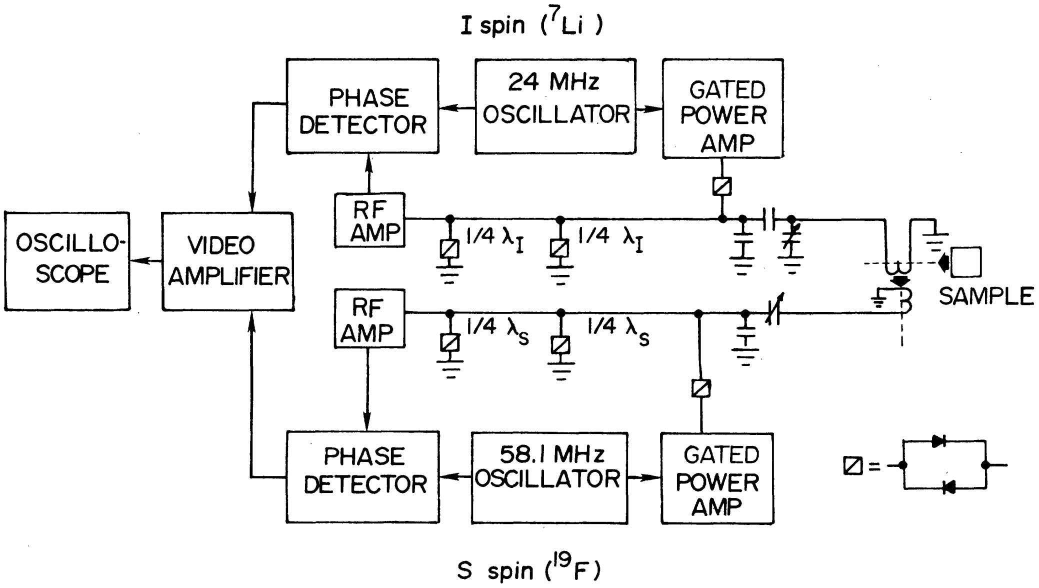

FIG. 1. Pulse double-resonance spectrometer described in text. The sample was placed inside a small coil tuned at 24 MHz. This coil was then placed inside a larger coil tuned at 58.1 MHz in a crossed-coil configuration. This entire assembly of sample, coils, and capacitors was then placed between the pole faces of a magnet such that $\vec{H}_0$ was perpendicular to the axes of both coils.

the S spins and vice versa. These concepts are demonstrated by a few simple experiments described in Sec. V.

III. EXPERIMENTAL APPARATUS

The experiments described in this paper were performed using a pulse double-resonance spectrometer (see Fig. 1). The probe uses a cross-coil configuration with each coil matched to 50 Ω. The rf amplifiers used for detection are protected during the rf pulses by quarter-wavelength cables at the appropriate frequencies and crossed diodes connected to ground, as shown in Fig. 1. A video amplifier (Tektronix AM 502) is used to observe the NMR signal from one of the phase detectors, depending on which spin we wish to observe. TTL logic (not shown in Fig. 1) is used to operate the gates for the various pulse sequences desired.

IV. SAMPLE

The sample used in all of the experiments, unless otherwise specified, is a single crystal of LiF grown by the Crystal Growth Laboratory of the University of Utah Physics Dept. It was cleaved into a cube of dimensions approximately 5 mm per side. The sample was then irradiated in a Van de Graaff accelerator by 1.5 MeV electrons having an intensity of about 5 $\mu A/cm^2$ for 1.5 h on each of the two opposite sides. The sample attained a dark red color, probably due to M centers.[14] Nevertheless, the primary effect of the irradiation on the NMR relaxation was the creation of F centers[15] which substantially increased the relaxation rates[16] in the crystal. (F-centers do not affect the color in LiF.[14]) The sample was oriented in the probe with $\vec{H}_0$ making angles approximately 30°, 60°, and 90° with the three [100] crystal axes.

V. EXPERIMENTAL RESULTS

A. Dipolar relaxation

One of the consequences of a single dipolar spin temperature is that T_{1D} is identical for different spin species in the same crystal. To illustrate this, we measured T_1 and T_{1D} for ^{7}Li and ^{19}F in three different samples of LiF: an ultrapure powder sample, a reagent-grade powder sample, and the irradiated sample described in Sec. IV. As can be seen in Table I, T_{1D} of ^{7}Li and ^{19}F are equal within experimental accuracy in each of the three samples, even though T_1 is clearly different.

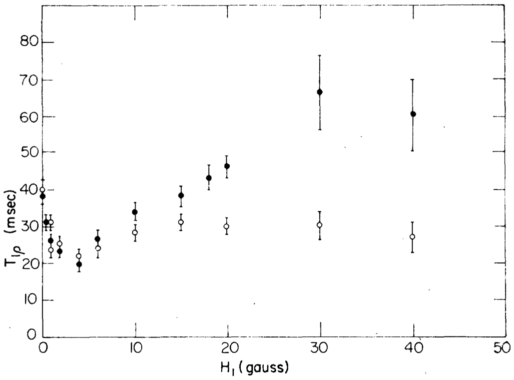

FIG. 2. $T_{1\rho I}$ and $T_{1\rho S}$ as a function of H_{1I} and H_{1S}, respectively, in LiF (●: ^{7}Li, I; ○: ^{19}F, S).

We also measured $T_{1\rho}$ as a function of H_1 for both ^{7}Li and ^{19}F in the irradiated sample of LiF. As can be seen in Fig. 2, $T_{1\rho I} \sim T_{1\rho S}$ for small H_1, although considerably different for large H_1. This again is a result of a single dipolar reservoir for both spins in small H_1. Note also that, for some values of H_1, $T_{1\rho}$ is less than T_{1D}. Similar unusual behavior was also observed in Mn^{+2}-doped CaF$_2$ by Humphries and Day.[17] Also, within experimental scatter, $T_{1\rho}$ vs H_1 levels off at large H_1.

B. Dipolar cross relaxation

Here we demonstrate explicitly two features of the single dipolar reservoir. The first feature is that the dipolar reservoir can be "cooled" by ADRF of *either* the I or S spins. Second, the spin temperature of the dipolar reservoir can be monitored by pulsing likewise *either* the I or S spins and then observing the dipolar

TABLE I. T_1 and T_{1D} for ^{7}Li and ^{19}F in three samples of LiF. All data were taken at 24 MHz except for the ^{19}F data in the irradiated sample which were taken at 58 MHz.

	T_1		T_{1D}	
Sample	^{7}Li	^{19}F	^{7}Li	^{19}F
Ultrapure powder	26 ± 2 min	6.5 ± 0.5 min	2.0 ± 0.3 min	2.0 ± 0.2 min
Reagent powder	2.3 ± 0.2 sec	0.55 ± 0.05 sec	0.40 ± 0.05 sec	0.40 ± 0.05 sec
Irradiated single crystal	2.0 ± 0.1 sec	0.72 ± 0.05 sec	38 ± 4 msec	40 ± 3 msec

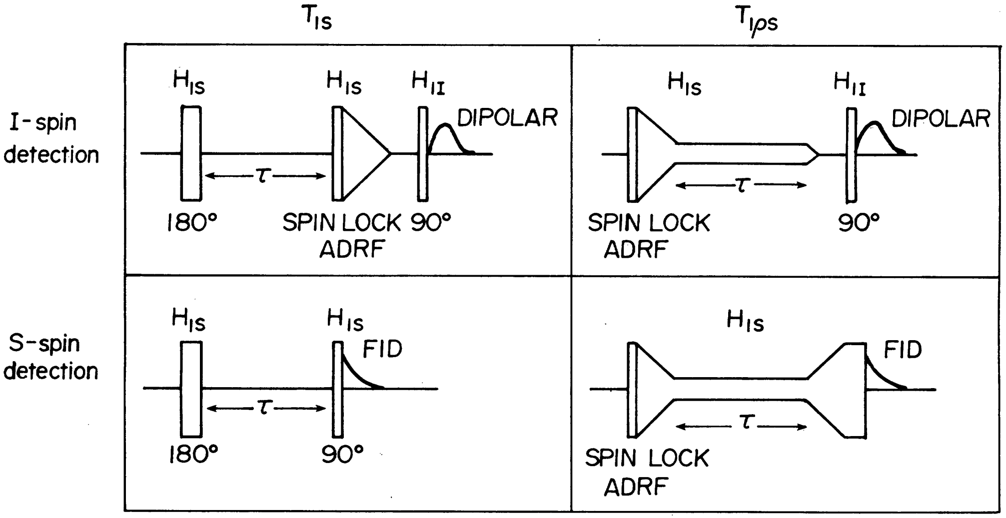

FIG. 3. Pulse sequences for measuring T_{1S} and $T_{1\rho S}$ using I-spin detection and the usual S-spin detection, as described in the text.

signal. In particular, we measured both T_1 and $T_{1\rho}$ of ^{19}F (S spins) by using a double-resonance sequence in which we monitored only the ^{7}Li magnetization (I spins) as shown in Fig. 3. Separately, we measured T_1 and $T_{1\rho}$ of ^{19}F by conventional single-resonance techniques and verified that the results were the same.

T_{1S} was measured by applying a 180° pulse to the S spins, waiting a time τ, and then transferring the resulting Zeeman order into dipolar order by ADRF. We then observe the dipolar signal following a 90° pulse on the I spins. (Note that in a spin system where coupling between unlike spins dominates, as in LiF, the maximum dipolar signal occurs following a 90° pulse.[7,12] This contrasts to the case where coupling between like spins dominates, as in single-spin systems,[18] in which the maximum signal follows a 45° pulse.) By varying τ, one can easily obtain T_{1S}. The value of T_{1S} obtained in this manner was compared to that obtained by the usual 180°-τ-90° pulse sequence (see Fig. 3) and within experimental error was found to be in agreement (see Table II).

$T_{1\rho S}$ was measured by spin locking the S spins, then adiabatically decreasing H_{1S} to some finite value, waiting a time τ, and finally adiabatically decreasing H_{1S} to zero, thus transferring any remaining Zeeman order into dipolar order. As before, we observe the dipolar signal of the I spins following a 90° pulse. By varying τ, we obtain $T_{1\rho S}$. Again, we compared this value to that obtained by the usual ADRF method (see Fig. 3) in which order is monitored as Zeeman order via a free-induction decay (FID) and found them to agree (see Table II).

C. Provotorov saturation

Consider a single spin system (S spins) irradiated by an rf field $\vec{H}_{1S}$ of frequency ω_S near the S-spin resonant frequency ω_{0S}. For $\vec{H}_{1S}$ large enough to cause saturation and yet smaller than the local field, we can treat the irradiation as a perturbation which causes thermal mixing between Zeeman and dipolar reservoirs. Here it is appropriate to use a rotating reference frame[4] of frequency ω_S. This simply alters the Zeeman interaction [see Eq. (1)] to be

TABLE II. T_1 and $T_{1\rho}$ of ^{19}F in LiF (I, ^{7}Li; S, ^{19}F) by the double-resonance and single-resonance methods shown in Fig. 3. $T_{1\rho}$ was measured at $H_{1S} = 10$ G.

	Double-resonance method (I-spin detection)	Single-resonance method (S-spin detection)
T_{1S}	650 ± 50 msec	720 ± 50 msec
$T_{1\rho S}$	25 ± 4 msec	29 ± 2 msec

$$\mathcal{H}_{ZS} = -(\omega_{0S}-\omega_S)\sum_k S_{zk} \quad . \tag{28}$$

The S-spin interaction with $\vec{H}_{1S}$ is not included as part of the Zeeman reservoir since it comprises the perturbation.

We define a thermal mixing rate T_m^{-1} by

$$\frac{d}{dt}(\beta_S-\beta_D) = -T_m^{-1}(\beta_S-\beta_D) \quad . \tag{29}$$

From the Provotorov theory[19] of saturation as developed by Goldman,[6,20] we obtain an expression for T_m^{-1} [Eq. (4.20) in Ref. 6]:

$$T_m^{-1} = \pi\gamma_S H_{1S}^2 \left[1+\frac{(\omega_{0S}-\omega_S)^2}{\gamma_S^2 H_{LS}^2}\right] g_S(\omega_{0S}-\omega_S) \quad , \tag{30}$$

where $g_S(\omega)$ is the normalized absorption line shape of the S spins. One might expect this expression to be valid only if the system is off resonance by an amount which is large compared to H_{1S}. However, Goldman shows that this result is valid even for H_{1S} on resonance.

Now consider the case of a two-spin system (I and S). As in the single-spin case, irradiation of the S-spins causes thermal mixing between the S-spin Zeeman reservoir and the dipolar reservoir. The I-spin Zeeman reservoir remains isolated (i.e., β_I is time independent). In this two-spin case, though, the dipolar reservoir includes *all* secular dipolar interactions (I-I, S-S, and I-S). Thus, the Provotorov theory of saturation may be extended to the two-spin case simply by substituting in Eq. (30) the total local field H_{LS} defined by

$$\gamma_S^2 H_{LS}^2 = Tr(\mathcal{H}_D^{(0)})^2 / Tr\left(\sum_i S_{zi}\right)^2 \quad , \tag{31}$$

where $\mathcal{H}_D^{(0)}$ is the total secular dipolar interaction given by Eq. (12). Thus the only effect of the I spins is to increase the heat capacity of the dipolar reservoir.

Using conservation of energy,

$$Tr(\mathcal{H}_{ZS})^2\frac{d\beta_S}{dt} + Tr(\mathcal{H}_D^{(0)})^2\frac{d\beta_D}{dt} = 0 \quad , \tag{32}$$

we can solve Eq. (29) and obtain

$$\beta_D(\tau) = \beta_D(\infty) + [\beta_D(0)-\beta_D(\infty)] \times \exp(-\tau/T_m) \quad , \tag{33}$$

where

$$\beta_D(\infty) = \frac{(\omega_{0S}-\omega_S)^2\beta_S(0) + \gamma_S^2 H_{LS}^2 \beta_D(0)}{(\omega_{0S}-\omega_S)^2 + \gamma_S^2 H_{LS}^2} \quad . \tag{34}$$

T_m^{-1} can be evaluated from Eq. (30) using a Gaussian line shape[3,21]

$$g_S(\omega) = (2\pi\langle\Delta\omega^2\rangle_S)^{-1/2}\exp(-\omega^2/2\langle\Delta\omega^2\rangle_S) \quad , \tag{35}$$

where $\langle\Delta\omega^2\rangle_S$ is the Van Vleck second moment[22] given by

$$\langle\Delta\omega^2\rangle_S = Tr\left[\sum_k S_{zk}, H_D^{(0)}\right]^2 \Big/ Tr\left[\sum_k S_{zk}\right]^2 \quad . \tag{36}$$

To demonstrate the validity of this theory for the case of two spin species, we apply the pulse sequences shown in Fig. 4. In each case, the dipolar reservoir is prepared at a different initial temperature $\beta_D(0)$. In case (a), the I spins are spin locked followed by ADRF. This gives us $\beta_D(0)=\beta_0$. In case (b), we do the same except that the I spins are spin locked in a direction opposite to $\vec{H}_{1I}$ instead of along $\vec{H}_{1I}$. This gives us $\beta_D(0)=-\beta_0$. In case (c), we do nothing to prepare the system which gives us $\beta_D(0)=\beta_L$, the lattice temperature, which is much smaller than β_0 and can be considered to be zero for our purposes.

In all of the above cases, an $\vec{H}_{1S}$ pulse of frequency ω_S and length τ is applied after the initial preparation. Then we observe the dipolar signal of the I spins following a 90° pulse as in experiments described in previous sections. The observed signal should be proportional to $\beta_D(\tau)$ given by Eq. (33).

A particularly nice feature of this experiment in a two-spin system is that a transfer of I-spin Zeeman order to dipolar order does not affect the S-spin Zeeman order. Thus we can prepare the dipolar reservoir to have a number of different initial temperatures, keeping the temperature of the Zeeman reservoir the same. It would be very difficult to achieve these initial conditions for a single spin system.

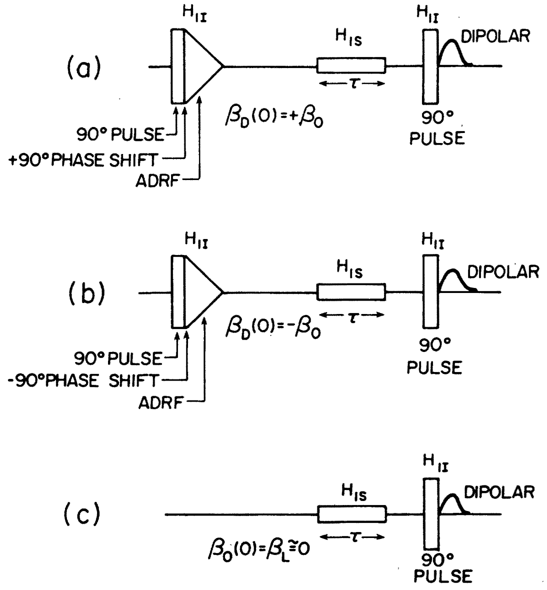

FIG. 4. Pulse sequences used for obtaining the data shown in Fig. 5 as described in the text.

In the case of LiF (I, ^{7}Li; S, ^{19}F), we have $H_{LS}^2 = 16.0\ \mathrm{G}^2$ and $\gamma_S^{-2}\langle\Delta\omega^2\rangle_S = 19.8\mathrm{G}^2$. In doing the experiment, we used $H_{1S} = 0.5$ G and $\tau = 1$ msec. The results are shown in Fig. 5 along with theoretical curves obtained from Eq. (33). Two adjustable parameters were used: a scaling factor and β_0. (Note that the same values for the scaling factor and for β_0 were used in all three curves.) Also $\beta_S(0)$ is given by

$$\beta_S(0) = \frac{\omega_{0S}}{\omega_{0S} - \omega_S}\beta_L = \frac{H_0}{h}\beta_L \quad . \tag{37}$$

We see that when h is negative, for example, $\beta_S(0)$ is also. This is reasonable since the S spins (aligned along $\vec{\mathrm{H}}_0$) would then also be aligned antiparallel to the off-resonant field $\vec{\mathrm{h}}$. This asymmetrical dependence of $\beta_S(0)$ on the sign of $(\omega_{0S} - \omega_S)$ results in a similar asymmetric frequency dependence of $\beta_D(\tau)$ [through $\beta_D(\infty)$] which is clearly observed in Fig. 5.

As can be seen in Fig. 5, the agreement between experimental data and theory is good, thereby demonstrating the validity of our extension of the Provotorov theory to a two-spin system and also the fact that the entire dipolar system must be described by a single temperature for a two-spin system.

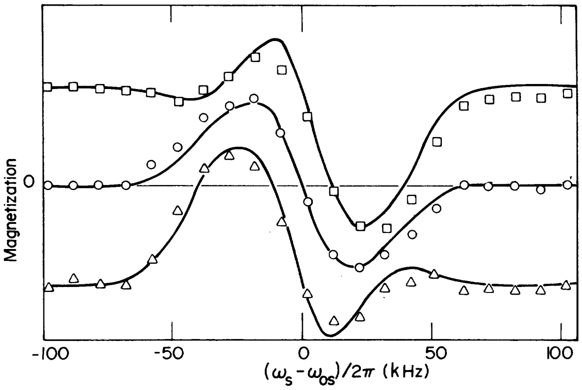

FIG. 5. Experimental data using the pulse sequences shown in Fig. 4. The solid lines are calculated from the Provotorov theory of saturation using two adjustable parameters: a scaling factor and β_0. [□, $\beta_D(0) = \beta_0$; ○, $\beta_D(0) = 0$; △, $\beta_D(0) = -\beta_0$.]

VI. CONCLUSIONS

We have shown that for multispin systems in a large field $\vec{\mathrm{H}}_0$, a single dipolar reservoir exists which contains all secular dipolar interactions, those between unlike spins as well as those between like spins. Thus one cannot speak of different dipolar temperatures for different spins in a multispin system. We have demonstrated this concept with a variety of experiments on LiF, finding good agreement between data and theory in each case.

ACKNOWLEDGMENTS

We gratefully acknowledge Professor F. Rosenberger for providing us with the LiF samples and Dr. J. Corey for his generous technical assistance with the Van de Graaff accelerator.

---

*Research supported by the NSF under Grant Nos. GH 31671 and DMR76-18966.

[1] R. V. Pound, Phys. Rev. 81, 156 (1951).

[2] A. Abragam and W. G. Proctor, Phys. Rev. 109, 1441 (1958).

[3] P. S. Pershan, Phys. Rev. 117, 109 (1960).

[4] A. G. Redfield, Phys. Rev. 98, 1787 (1955).

[5] B. N. Provotorov, Fiz. Tverd. Tela 4, 2940 (1962) [Sov. Phys.-Solid State 4, 2155 (1963)].

[6] M. Goldman, *Spin Temperature and Nuclear Magnetic Resonance in Solids* (Oxford U. P., London, 1970).

[7] A. G. Anderson and S. R. Hartmann, Phys. Rev. 128, 2023 (1962).

[8] M. E. Zhabotinskii, A. E. Mefed, and M. I. Rodak, Zh. Eksp. Teor. Fiz. Pis'ma Red. 11, 482 (1970) [JETP Lett. 11, 328 (1970)]; Zh Eksp. Teor. Fiz. 61, 1917 (1971) [Sov. Phys.-JETP 34, 1020 (1972)].

[9] W. de Boer, M. Borghini, K. Morimoto, T. O. Niinikosko, and F. Udo, Phys. Lett. A 46, 143 (1973).

[10] W. de Boer, Phys. Rev. B 12, 828 (1975).

[11] V. D. Shchepkin, D. I. Vainshtein, R. A. Dautov, and V. M. Vinokurov, Zh. Eksp. Teor. Fiz. 70, 178 (1976) [Sov. Phys.-JETP 43, 93 (1976)].

[12] P. Broekaert and J. Jeener, Phys. Rev. B 15, 4168 (1977).

[13] H. T. Stokes and D. C. Ailion, Phys. Rev. Lett. 38, 1159 (1977).

[14] D. Pan, University of Utah (private communication).

[15] S. F. J. Cox, V. Bouffard, and M. Goldman, J. Phys. C 6, L100 (1973).

[16] R. V. Pound, J. Phys. Chem. 57, 743 (1953).

[17] L. J. Humphries and S. M. Day, Phys. Rev. B 12, 2601 (1975).

[18] J. Jeener and P. Broekhaert, Phys. Rev. 157, 232 (1967).

[19] B. N. Provotorov, Zh. Eksp. Teor. Fiz. 70, 1582 (1961) [Sov. Phys.-JETP 14, 1126 (1962)].

[20] M. Goldman, J. Phys. (Paris) 25, 843 (1964).

[21] B. T. Gravely and J. D. Memory, Phys. Rev. B. 3, 3426 (1971).

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