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NMR in solids: Thermodynamic effects of a pair of rf pulses on a system with two spin species

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NMR pulse experiments performed simultaneously on ^{7}Li and ^{19}F in a LiF crystal, provide a quantitative verification of various theoretical predictions about relations between the Zeeman and dipolar components of the free-induction-decay signals, and the efficiency of transfer of Zeeman order into dipolar order by a phase-shifted pulse pair. An internal relaxation time of about 400 μsec is observed on the dipolar subsystem when the field is along the [111] direction. An interpretation is proposed for this "slow" approach to internal equilibrium.

I. INTRODUCTION

In a previous paper[1] we described the theory of the efficiency of the transfer of Zeeman order into dipolar order by a pair of phase-shifted rf pulses,[2] and we presented experimental results which provide a quantitative verification of some of the theoretical prediction in the case of a single spin species (^{19}F in CaF$_2$). These experimental results are compatible with the assumption that, after one or two pulses, the state of the spin system can be described as a state of internal quasiequilibrium (completely specified by the values of the two quasi-invariants Zeeman energy and dipolar energy) as soon as the free precession signal has died out.

In the present paper, we present a quantitative verification of some of these theoretical predictions in the more complicated case of two spin species (LiF).

We have also observed a new "long" internal relaxation time after transferring Zeeman order into dipolar order when the large external field $\vec{H}_0$ is parallel to the [111] axis of the LiF crystal. In this crystal orientation, all first-neighbor Li-F pairs are at the "magic angle" with respect to $\vec{H}_0$, so that the Li-F interactions are definitely weaker than the Li-Li or F-F interactions. If we make the very rough short-time approximation of neglecting the Li-F interactions completely, the dipolar subsystem breaks down into two independent subsystems, one associated with the Li-Li interaction and one with the F-F interaction. In this approximation, a transfer of Zeeman order into dipolar order by irradiation of Li, for instance, will create Li-Li order, but no F-F order, a situation in which only the Li (and not the F) absorption spectrum or pulse response will display dipolar order. Of course, one anticipates that the weaker Li-F interactions will rather rapidly bring the dipolar subsystem into the usual state of internal equilibrium in which Li and F both display dipolar signals. We have observed these short- and long-time behaviors and our experimental results are in good quantitative agreement with the predictions of the proposed model, as far as the magnitude of the signals are concerned.

II. DENSITY-MATRIX CALCULATIONS

A. Generalities

We shall consider the same type of spin system as in Ref. 1 and use the same notation: the spin Hamiltonian $\mathcal{H}$ is the sum of a large Zeeman term $\mathcal{H}_0^a$ for each spin species a and a much smaller spin-spin coupling term $\mathcal{H}_D$ and does not involve atomic motion or any other mechanism for spin-lattice relaxation. As usual, $\mathcal{H}_D$ will be decomposed into a "secular part" $\mathcal{H}'$ which commutes with $\sum_a \mathcal{H}_0^a$ and a "nonsecular part" $\mathcal{H}''$ which does not, and the effects of $\mathcal{H}''$ will be neglected.

For convenience, the spin Hamiltonian will be decomposed in such a way that the operators $\mathcal{H}'$, $\mathcal{H}''$, and the various $\mathcal{H}_0^a$ are traceless and orthogonal to each other.

We shall assume that the independent thermodynamic quasi-invariants of the motion are the Zeeman energies E^a associated with each spin species a and the spin-spin coupling energy E_D so that the quasiequilibrium density matrix ρ_{qe} will be given by the usual expression (in the high-temperature approximation)

$$\rho_{qe} = \mathcal{P}\left(1 - \frac{\mathcal{H}'}{kT_D} - \sum_a \frac{\mathcal{H}_0^a}{kT^a}\right), \tag{1}$$

where the various temperatures T_D and T^a are the inverses of the partial derivatives of the spin entropy with respect to the corresponding quasi-invariant component of the spin energy.

Following standard practice, we shall use a frame of coordinates with a Z axis pointing in the direction of the external magnetic field $\vec{\mathrm{H}}_0$, and simplify a number of calculations by means of the representation defined by

$$\hat{A} = \exp\left(+\frac{it}{\hbar}\sum_a \mathcal{H}_0^a\right) A \exp\left(-\frac{it}{\hbar}\sum_a \mathcal{H}_0^a\right), \tag{2}$$

which, as far as the spin variables of spins b is concerned, is equivalent to the use of a new frame of reference rotating around the Z direction at the Larmor frequency of the b spins.

A short intense pulse of transverse rf magnetic field at the Larmor frequency ω^b of the b spins has an appreciable effect on the b spins only, which can be described in the rotating frame of coordinates by the rotation operator

$$R(\theta, \varphi) = \exp[-i\theta(\mathcal{L}_x^b \cos\varphi + \mathcal{L}_y^b \sin\varphi)], \tag{3}$$

where θ is the angle through which the b-spins magnetization is rotated, φ is the rf phase of the pulse and $\hbar\mathcal{L}^b$ is the total angular momentum of all b spins.

B. Symmetry properties of the free-precession signals

As a starting point in this discussion, let us consider the representation $\{|\{m^{a,n}\}\rangle\}$ for the states of the spin system which is the tensorial product of the "standard representations" for each individual spin $I^{a,n}$. This is the representation in which traces are usually evaluated, in which each individual $I_z^{a,n}$ is diagonal, each $I_x^{a,n}$ has real matrix elements and each $I_y^{a,n}$ has pure imaginary matrix elements. In this representation, $\mathcal{H}'$ and each $\mathcal{H}_0^a$ have *real* matrix elements. As a consequence of this reality, there exists a representation $\{|\{m^a\},n\rangle\}$ the basic kets of which are linear combinations of those of $\{|\{m^{a,n}\}\rangle\}$ with *real* coefficients, and which simultaneously diagonalizes $\mathcal{H}'$ and each $\mathcal{H}_0^a$:

$$\begin{aligned}\mathcal{H}'|\{m^a\},n\rangle &= E'(\{m^a\},n)|\{m^a\},n\rangle\,,\\ \mathcal{H}_0^b|\{m^a\},n\rangle &= m^b\hbar\omega^b|\{m^a\},n\rangle\,.\end{aligned} \tag{4}$$

The quantum numbers m^a are integers (or half-integers) and n denotes all the additional quantum numbers which are required to completely specify each state.

Let us now assume that the spin system is initially in the state of quasiequilibrium described by Eq. (1), and that at time $t=0$ it is subjected to an rf pulse at the b-spins frequency such that $\varphi = \frac{1}{2}\pi$ in Eq. (3) ("$\vec{\mathrm{H}}_1$ in the y direction in the rotating frame"). At later times, the components $\underline{\mathrm{M}}_x^b(t)$ and $\underline{\mathrm{M}}_y^b(t)$ of the b-spins magnetization in the rotating frame of coordinates will be given by

$$\underline{\mathrm{M}}_\alpha^b(t) = \gamma^b\hbar\,\mathrm{Tr}[\mathcal{L}_\alpha^b Q(t) R(\theta, \tfrac{1}{2}\pi)\rho_{qe} R^\dagger(\theta, \tfrac{1}{2}\pi) Q^\dagger(t)]\,, \tag{5}$$

where γ^b is the gyromagnetic ratio of spins b and the subscript α denotes x or y. As a preparation for the evaluation of the trace in Eq. (5) in the $\{|\{m^a\},n\rangle\}$ representation, we note that ρ_{qe} and $R(\theta, \frac{1}{2}\pi)$ both have real matrix elements in this representation, so that the matrix elements of $R(\theta, \frac{1}{2}\pi)\rho_{qe}R^\dagger(\theta, \frac{1}{2}\pi)$ are also real. Furthermore, $\mathcal{H}'$ is a diagonal operator so that $Q(t)$ is also a diagonal operator with matrix elements given by

$$\langle\{m^a\},n|\,Q(t)\,|\{m^a\},n\rangle = \exp[-iE'(\{m^a\},n)t/\hbar]\,, \tag{6}$$

and, of course, the matrix elements of $\mathcal{L}_x^a$ are still real and those of $\mathcal{L}_y^a$ pure imaginary.

Let us now evaluate $\underline{\mathrm{M}}_x^b(t)$ using Eq. (5) in the $\{|\{m^a\},n\rangle\}$ representation:

$$\underline{\mathrm{M}}_x^b(t) = \gamma^b\hbar\sum_{v,w}\langle v|\,\mathcal{L}_x^b\,|w\rangle\langle w\,|R(\theta, \tfrac{1}{2}\pi)\rho_{qe}R^\dagger(\theta, \tfrac{1}{2}\pi)|\,v\rangle \times\exp\left(-i[E'(w)-E'(v)]\frac{t}{\hbar}\right), \tag{7}$$

where $|v\rangle$ and $|w\rangle$ denote basic kets of the representation. $\underline{\mathrm{M}}_x^b(t)$ is a real quantity, and the coefficients of the exponentials in the double summation are also real, so that only the real part of the exponentials effectively contribute to the sum and, as a consequence, $\underline{\mathrm{M}}_x^b(t)$ is an even function of t. A similar discussion, using the fact that the matrix elements of $\mathcal{L}_y^b$ are pure imaginary, leads to the conclusion that $\underline{\mathrm{M}}_y^b(t)$ is an odd function of t.

In the present case, we can further use the traditional argument that $\mathcal{H}'$ and thus also $Q(t)$ are invariant for 180° rotations around the x or y axis to show that $\underline{\mathrm{M}}_x^b(t)$ only arises from the $\mathcal{H}_0^b$ term in ρ_{qe} and $\underline{\mathrm{M}}_y^b(t)$ only from the $\mathcal{H}'$ term in ρ_{qe}.

C. Predictions to be compared with experiment

We can now write the components of the free-precession signal in the usual form

$$\underline{\mathrm{M}}_x^b(t) = \gamma^b\hbar(E^b/\mathfrak{Z}^b)\sin\theta\, g(t)\,, \tag{8}$$

$$\underline{\mathrm{M}}_y^b(t) = \gamma^b\hbar(E_D/\mathfrak{D})F(t, \theta)\,, \tag{9}$$

where

$$F(t, \theta) = \tfrac{1}{2}(\sin 2\theta) f(t) + (\sin\theta) h(t)\,,$$

where $F(t, \theta)$, $f(t)$, and $h(t)$ are odd functions of t, whereas $g(t)$ is even, E^b and E_D are the amounts of b-spins Zeeman energy and spin-spin coupling energy present before the pulse, and $\mathfrak{Z}^b$ and $\mathfrak{D}$ are amounts of b-spins Zeeman energy and spin-spin coupling energy which would give equal contributions to spin entropy. The function $f(t)$ arises from initial couplings among b spins whereas $h(t)$ arises from initial couplings between b spins and other spins.

By considering the limit of small values of θ,

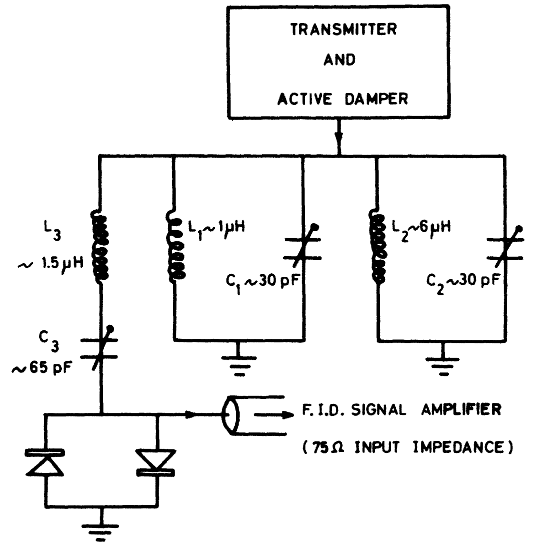

FIG. 1. Double-tuned sample circuit (sample in L_2).

one can show easily that the functions $f(t), g(t), h(t)$ are related by

$$\frac{dg(t)}{dt}=[f(t)+h(t)]\left|\frac{\{\mathrm{Tr}[(\mathcal{H}')^2]\}^{1/2}}{\hbar\{\mathrm{Tr}[(\mathfrak{L}_z^b)^2]\}^{1/2}}\right|\frac{-\gamma^b}{|\gamma^b|}\,. \tag{10}$$

When the spin system is in complete equilibrium with the lattice, the amount of spin-spin order $(E_D/\mathfrak{D})$ is much too small to give rise to observable effects. Various methods have been proposed and used for generating observable amounts of spin-spin order at the expense of the observable amounts of Zeeman order $(E^a/\mathfrak{Z}^a)_0$ which are easily available in equilibrium with the lattice. A convenient figure of merit for comparing these methods is the ratio $K^b_{Z\to D}$ of the amount of spin-spin order $(E_D/\mathfrak{D})$ effectively created to the amount $(E^b/\mathfrak{Z}^b)_0$ which would be created by a reversible transformation of the initially available b-spins Zeeman order into dipolar order.

The phase-shifted pulse pair technique for performing this transfer of order, in which a (θ_1, φ_1) pulse is applied to the b-spins at $t=0$, followed by a (θ_2, φ_2) pulse also on the b spins at $t=\tau$, has a theoretical efficiency of transfer of order $K^b_{Z\to D}$ (see Ref. 1):

$$K^b_{Z\to D}=-\sin\theta_1\sin(\varphi_2-\varphi_1)F(\tau,\theta_2)/g(0)\,, \tag{11}$$

where Z is Zeeman and D is dipolar.

III. EXPERIMENTAL TECHNIQUE AND RESULTS

A. Pulse spectrometer and sample

The experiments described in the present paper have been performed on a single crystal of LiF. This compound has been chosen because of its simple crystal structure and of the possibility of observing both the ^{19}F and the ^{7}Li free-precession signals.

The spectrometer is very similar to the one described in Ref. 1, except for the fact that the present spectrometer enables us to generate rf pulses at the ^{19}F and ^{7}Li resonant frequencies (28.7 and 12.8 MHz) in rapid succession and to observe the two components of the free-precession signals at either frequency. A single coil, double tuned, sample circuit provided a reasonable compromise as far as filling factor, homogeneity of the rf field, and easy manipulation of the crystal are concerned. The sample volume was approximately 0.8 cm^3.

Figure 1 shows the circuit surrounding the sample coil L_2. The L_2C_2 circuit was first isolated and separately tuned to the lower of the two NMR frequencies (12.8 MHz), and the L_1C_1 circuit was similarly tuned to the higher NMR frequency (28.7 MHz). The whole circuit was then connected together and returned to both NMR frequencies by adjusting C_3 and L_3. We used an active damping circuit for the large rf signals, whereas small rf signals were effectively damped (without unnecessary addition of noise) by the input impedance of the fid signal amplifier.

The experiments have been performed at room temperature on a single crystal of LiF supplied by Harshaw. This crystal was strongly irradiated by γ rays in order to decrease spin-lattice relaxation times to convenient values, with results similar to those of Lang and Moran,[3] as shown in Table I.

B. Experimental investigation of relations (10) and (11)

These experiments have been performed using pulses only at the ^{7}Li NMR frequency (of about 12.8 MHz) always starting with the spin system in equilibrium with the lattice.

In a first set of experiments, dipolar order was prepared using the values $\theta_1=\frac{1}{2}\pi$, $\varphi_2-\varphi_1=\frac{1}{2}\pi$ and $\theta_2=\theta_{\max}$ which maximize the efficiency of the transfer from Zeeman order to dipolar order. After this, the spin system was left to relax for a time t_1, long enough for all transient effects of the pulses to have died out but much shorter than the

TABLE I. Spin-lattice relaxation times of the γ-irradiated single crystal of LiF used in the present experiments.

	H_0 along [111] (sec)	H_0 along [110] (sec)
T_{1Z} for ^{7}Li	7.7	10.1
T_{1Z} for ^{19}F	3.2	3.3
T_{1D}	0.070	0.105

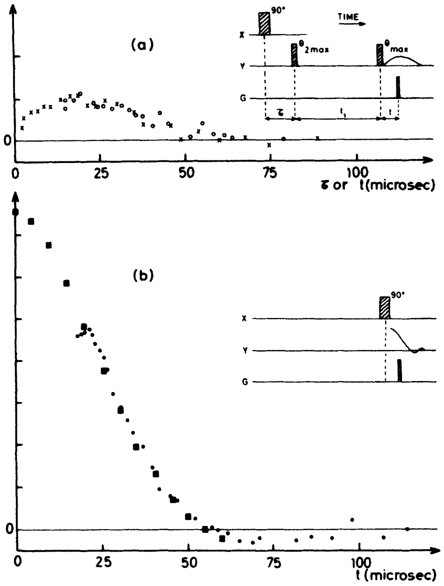

FIG. 2. Behavior of ^{7}Li signals in LiF in a field of about 7 kG oriented along a [110] direction. (a) Comparison of the t dependence of the dipolar component of the free-induction-decay signal (circles) with the τ dependence of the efficiency of transfer of Zeeman order into dipolar order (crosses). The circles were obtained with τ at the maximum of the curve and the crosses with t at the maximum of the curve, always with the same short gate. (b) Comparison of the t dependence of the observed Zeeman component of the equilibrium free-induction-decay signal (circles) with the t dependence of the corresponding signal derived from the observed dipolar signal by graphical integration using Eqs. (10) and (11) and the value of $\mathrm{Tr}[(\mathcal{H}')^2]$ evaluated from the known geometry of the crystal (squares). The vertical scales are the same, with no adjustable parameter.

spin-lattice relaxation time of dipolar energy, a "read pulse" of angle $\theta \approx \theta_{\max}$ was then applied and the resulting dipolar free precession signal $\underline{M}_y^7(t)$ was observed by averaging during a short "gate interval" at time t after the pulse. The observed signal is expected to be proportional to the product of the efficiency $K_{Z \to D}$ of the preparation of dipolar energy (which depends upon τ) with the "shape" of the dipolar signal (which depends upon t). Figure 2 clearly shows that, as indicated by Eq. (11), the τ dependence of the efficiency of transfer of order $K_{Z \to D}$ exactly duplicates the t dependence of the dipolar free precession signal. This enables one to obtain direct experimental information about the function $F(t, \theta)$ for short values of t without the usual limitations due to the recovery time of the pulse spectrometer.

In a second set of experiments, we made a quantitative verification of Eqs. (10) and (11). This implied obtaining experimental information about

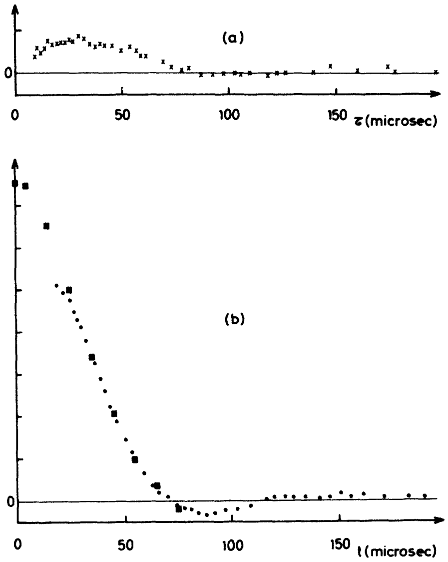

FIG. 3. Behavior of ^{7}Li signals in LiF in a field of about 7 kG oriented in a [111] direction. Crosses, circles, and squares have the same meaning as in Fig. 2.

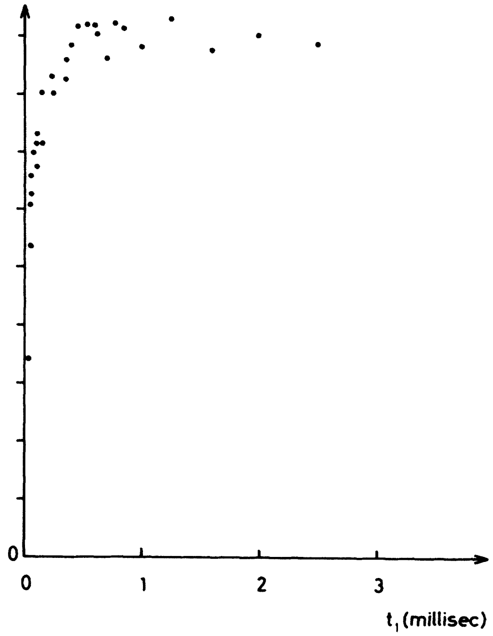

FIG. 4. Behavior of the amplitude of the dipolar component of the ^{7}Li free-induction-decay signal as a function of the delay t_1 from a preparation of dipolar order by a phase-shifted pulse pair applied on ^{19}F, in a LiF crystal in a field of about 7 kG oriented in the [110] direction.

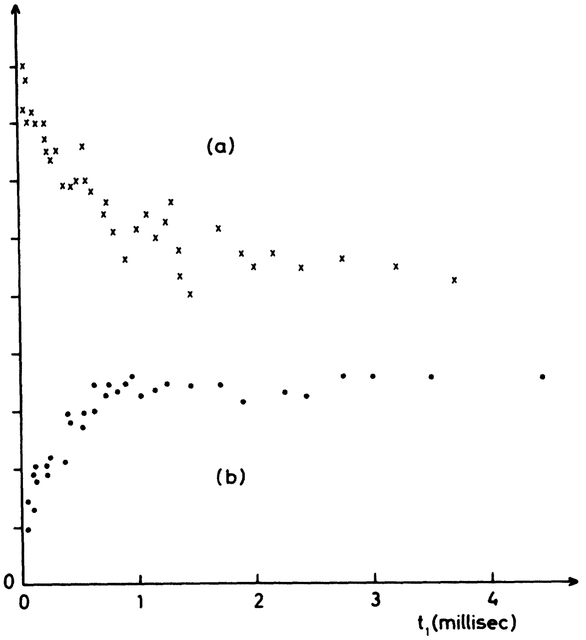

FIG. 5. Behavior of the amplitude of the dipolar component of the ^{7}Li free-induction-decay signal [(b) circles] or the ^{19}F free-induction-decay signal [(a) crosses] as a function of the delay t_1 from a preparation of dipolar order by a phase-shifted pulse pair applied on ^{19}F, in a LiF crystal in a field of about 7 kG oriented in the [111] direction. The amount of "^{19}F-^{19}F energy" corresponding to one unit of the (a) vertical scale is meant to be the same as the amount of "^{7}Li-^{7}Li" energy corresponding to one unit of the (b) vertical scale. For this purpose, the scales have been adjusted in such a way that the ratio of the two observed signals in complete internal equilibrium ($t_1 \geq 2$ msec) has its theoretical value of 1.55 calculated from the known spin-spin Hamiltonian, in the rough approximation which leads to Eq. (12).

$F(t, \theta)$ in the limit of small values of θ. For this purpose, we prepared dipolar order using the optimum values $\theta_1 = \frac{1}{2}\pi$, $\varphi_2 - \varphi_1 = \frac{1}{2}\pi$ and $\tau = \tau_{\max}$ and a range of values of θ_2, and we measured the amount of dipolar order by means of an optimum read pulse ($\theta = \theta_{2\,\max}$) followed by averaging during a wide "gate interval." We did not observe any influence of θ upon the t dependence of $F(t, \theta)$. A last problem was the presence in Eq. (11) of the initial values $g(0)$ of the Zeeman free-precession signal, which we could not measure directly because of the rather long recovery time of our spectrometer. This difficulty was solved by assuming some value of $g(0)$, using Eqs. (9)–(11) with the known values of $\mathrm{Tr}[(\mathcal{H}')^2]$ and $\mathrm{Tr}[(\mathcal{L}_z^7)^2]$ to evaluate $dg(t)/dt$ for all values of t, and integrating this quantity to obtain a final value of $g(0)$. Only one value of $g(0)$ led to a self-consistant solution in which the assumed and final values coincided. Figures 2 and 3 show that the function $g(t)$ directly observed as the Zeeman free-precession signal is in very good agreement with the function $g(t)$ evaluated by a time integral of the dipolar response, as explained above. At the optimum value of all pulse parameters, the efficiency $K_{Z\to D}$ for the transfer of ^{7}Li Zeeman order into dipolar order in LiF is 32% when the external field is in the [111] direction, and 37% when it is in the [110] direction.

C. Approach towards quasiequilibrium after the pulse pair

Immediately after the second pulse of the pulse-pair transfer of order, the spin-spin energy of the system (the average value of $\mathcal{H}'$) has the "large" value which we are interested in, but the state of the spin system is far from quasiequilibrium. It seems plausible to assume that, for most purposes, the spin system can be considered to relax from this initial state of nonequilibrium to a state of quasiequilibrium [Eq. (1)] with characteristic times not much longer than the duration of the observable free-precession signals. This is indeed what has been observed[1] in CaF$_2$.

We have investigated this problem in LiF by preparing a state of appreciable dipolar order by the phase-shifted pulse-pair technique applied either to ^{7}Li or to ^{19}F, and by observing the response to a "read pulse" applied to the same or to the other spins a variable time t_1 after the second pulse of the preparation sequence.

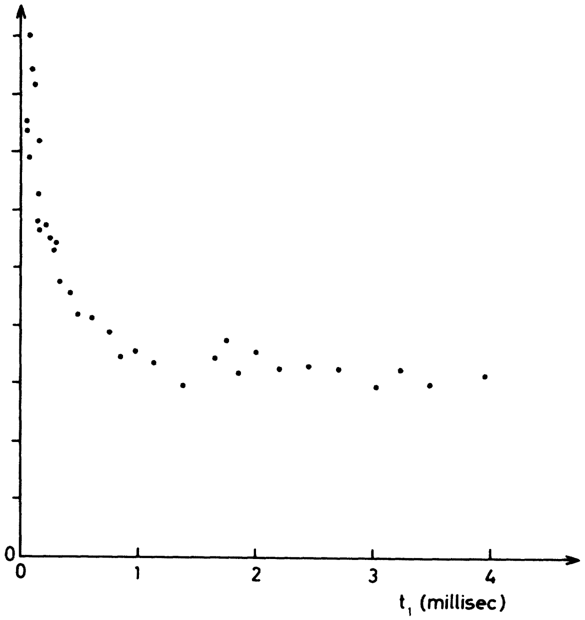

FIG. 6. Same as Fig. 5 except that preparation and observation of dipolar order both occur on ^{7}Li.

When the external field is in the [110] direction, the spin system behaves in the usual way: the response to the "read pulse" is independent of t_1 whenever t_1 exceeds a few hundred microseconds, as shown in Fig. 4 for instance (in that case, the approach to the long $-t_1$ value is roughly exponential, with a characteristic time of the order of 80 μsec).

When the external field is in a [111] direction, a much slower evolution towards quasiequilibrium is observed, with a characteristic time of the order of 400 μsec. The various features of this slow evolution, which are shown in Figs. 5 and 6, can be understood in the following way.

When the external field is in the [111] direction, all pairs of first neighbor Li-F are at the "magic angle," so that these dipolar couplings are ineffective and the largest terms in the spin-spin Hamiltonian are the couplings between like spins (essentially ^{19}F-^{19}F and ^{7}Li-^{7}Li).

In a very rough first approximation, let us neglect all couplings between unlike spins: thus ^{7}Li and ^{19}F spins completely ignore each other so that the ^{7}Li-^{7}Li coupling energy and ^{19}F-^{19}F coupling energy are now independent invariants of the motion.

A phase-shifted pulse pair applied to ^{7}Li, for instance would then create ^{7}Li-^{7}Li spin-spin order, and this would cause the ^{7}Li pulse response to show a "dipolar" signal, but have absolutely no effect on the ^{19}F pulse response. Of course, in reality, ^{19}F and ^{7}Li spins are coupled by the third-neighbor dipolar interaction which does not disappear when the field is in the [111] direction. As a consequence of this, we anticipate that the rough first approximation described above will be useful in the limit of very short t_1, and that the temperatures of the ^{7}Li-^{7}Li and ^{19}F-^{19}F subsystems will thereafter progressively come to a common value (at constant total spin-spin energy). In this simple model we have

$$\begin{aligned}\langle \mathcal{H}' \rangle &= \langle \mathcal{H}'_{\text{Li-Li}} \rangle + \langle \mathcal{H}'_{\text{F-F}} \rangle \\ &= -\beta_{\text{Li-Li}} \operatorname{Tr}[(\mathcal{H}'_{\text{Li-Li}})^2] - \beta_{\text{F-F}} \operatorname{Tr}[(\mathcal{H}'_{\text{F-F}})^2],\end{aligned} \tag{12}$$

and the observable Li dipolar signal is proportional to $\beta_{\text{Li-Li}}$. The experimental results shown in Fig. 5 clearly indicate that the slow decrease in ^{19}F-^{19}F coupling energy is accompanied by an equal increase in ^{7}Li-^{7}Li coupling energy, thus keeping total spin-spin energy a constant.

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[2] These results have been generalized to the case of other unperturbed Hamiltonians, such as pure quadrupolar resonance, in J. Jeener, Adv. Magn. Reson. 3, 205 (1968).

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