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Spin thermodynamics in solids: Pulse techniques in pure nuclear-quadrupole-resonance spectroscopy of $NaClO_3$

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Spin thermodynamics is used to predict relations between various aspects of pulsed spectroscopy in the case of pure nuclear quadrupole resonance (NQR) of spins $\frac{3}{2}$: pulse response for states of quadrupolar or dipolar order, and efficiency of transfer of quadrupolar into dipolar order by a pulse pair. Experimental results are presented on the NQR resonance of ^{35}Cl in $NaClO_3$ single crystals. Although there is a very satisfactory overall agreement between the observations and the predictions based on the usual assumptions underlying spin thermodynamics, experiments suggest that the choice of the quasiinvariant(s) related to the spin-spin interactions in sodium chlorate should be reconsidered.

I. INTRODUCTION

Nuclear-spin thermodynamics[1,2] in solids is usually based on the assumption that spin-spin interactions rapidly bring the spin system into a state of internal quasiequilibrium characterized by a small number of quasiinvariants: The populations of the single-spin energy levels (or combinations of these populations) and the total spin-spin coupling energy. A large number of experimental results have been predicted, understood, and correlated by means of this simple and plausible assumption, mostly in the case of spin Hamiltonians dominated by the interaction of each spin with a large external magnetic field.

However, the basic assumption about the nature of the quasiinvariants (and specifically the invariant associated with spin-spin couplings) has seldom been investigated experimentally in a detailed quantitative way. Such investigations have been carried out, as an example, on single crystals of CaF_2 and LiF in large external magnetic fields, in which it is clear that the relevant invariants are the Zeeman energies of each spin species and the secular part of the total spin-spin—coupling Hamiltonian.[3,4] This straightforward choice of invariants does not always apply to slightly less simple crystal structures or spin Hamiltonians, as shown by the example of the protons in gypsum ($CaSO_4{\cdot}2H_2O$), again in a large external magnetic field, in which the marked difference between the couplings of protons in the same or in different water molecules causes the appearance of three independent quasiinvariants related to spin-spin couplings.[5]

In the present paper, we present a quantitative comparison between some predictions of spin thermodynamics and the results of the corresponding pulse experiments in pure nuclear quadrupole resonance in single crystals of $NaClO_3$. The overall agreement between predictions and observations is very satisfactory, but one group of results suggests that the secular part of the total spin-spin—coupling Hamiltonian might not be the only quasiinvariant related to spin-spin interactions.[6]

II. SPIN-HAMILTONIAN AND DENSITY-MATRIX CALCULATIONS

Sodium chlorate monocrystals have a NaCl arrangement of the ions, distorted to accommodate the ClO_3^- anions in such a way that the overall symmetry remains cubic.[7] The cubic unit cell contains four molecules. The four chlorine atoms, on one hand, and the four sodium atoms, on the other occupy equivalent lattice sites. Since oxygen is essentially nonmagnetic we neglect its presence in the discussion of the properties of the spin system of sodium chlorate. The molecular bonds, joining chlorine atoms and the associated sodium ions, are parallel to the body diagonals of the cell. The electric field gradients (EFG's) at the location of the sodium and chlorine nuclei show axial symmetry, resulting from the (1,1,1) direction (parallel to the molecular bonds) being a threefold-symmetry axis.[8,9] Sodium and the two isotopes ^{35}Cl and ^{37}Cl of chlorine all have spin $\frac{3}{2}$. As a consequence, only one quadrupolar transition frequency is associated with each of the chlorine and sodium isotopes.[10,11]

The nuclear-spin Hamiltonian can be written as a sum of single-spin terms describing the interactions of each nucleus with external magnetic fields and local EFG's and a sum of bilinear two-spin terms describing spin-spin couplings (mainly direct dipolar couplings in the present case). In the absence of external magnetic field, and for the spin-$\frac{3}{2}$ nuclei ^{23}Na, ^{35}Cl, and ^{37}Cl in a perfect $NaClO_3$ crystal, all single-spin terms in the spin Hamiltonian have twofold-degenerate upper- and lower-energy eigenstates with the same energy difference for all nuclei of the same kind. It is convenient at this point to emphasize this simple structure by writing the single-spin Hamiltonian for spin i under the form $\hbar\omega^{(i)}\mathcal{N}^{(i)}$, where $\omega^{(i)}/2\pi$ is the resonance frequency for spin i, and the operator $\mathcal{N}^{(i)}$ is one-half of the sum of the projectors on the two upper-energy eigenstates minus the sum of the projectors on the two lower-energy eigenstates (always for spin i). The eigenvalues of $\mathcal{N}^{(i)}$ are $+\frac{1}{2}$ and $-\frac{1}{2}$.

We can now write the complete single-spin part of the spin Hamiltonian under the form

$$\mathcal{H}_0=\hbar\omega^{(23)}\mathcal{N}^{(23)}+\hbar\omega^{(35)}\mathcal{N}^{(35)}+\hbar\omega^{(37)}\mathcal{N}^{(37)} , \tag{1}$$

where $\mathcal{N}^{(23)}$ is the sum of the $\mathcal{N}^{(i)}$ operators for all ^{23}Na nuclei in the crystal, and $\mathcal{N}^{(35)}$ and $\mathcal{N}^{(37)}$ are associated in the same way with all ^{35}Cl and all ^{37}Cl nuclei. The Hermitian operator $\mathcal{N}^{(35)}$, for example, is the quantum observable corresponding to one-half of the difference between the numbers of ^{35}Cl spins in the upper and lower single-spin energy eigenstates. The eigenvalues of $\mathcal{N}^{(35)}$ range from $-\frac{1}{2}N^{(35)}$ to $+\frac{1}{2}N^{(35)}$ in steps of 1, where $N^{(35)}$ is the number of ^{35}Cl spins in the crystal.

The spin-spin—coupling Hamiltonian $\mathcal{H}_D$ is much smaller than the single-spin Hamiltonian $\mathcal{H}_0$ so that, following standard practice, we shall approximate the effects of $\mathcal{H}_D$ by first-order perturbation of the eigenvalues of the spin Hamiltonian, keeping the zeroth-order eigenstates. In this approximation, $\mathcal{H}_D$ is replaced by the part $\mathcal{H}'_D$ which is secular with respect to $\mathcal{H}_0$, and the nonsecular part $\mathcal{H}''_D$ is ignored.

In the absence of rf irradiation, the relevant part of the spin Hamiltonian can, thus, be written as

$$\mathcal{H}=\hbar\omega^{(23)}\mathcal{N}^{(23)}+\hbar\omega^{(35)}\mathcal{N}^{(35)}+\hbar\omega^{(37)}\mathcal{N}^{(37)}+\mathcal{H}'_D , \tag{2}$$

where the four orthogonal and traceless operators $\mathcal{N}^{(23)}$, $\mathcal{N}^{(35)}$, $\mathcal{N}^{(37)}$, and $\mathcal{H}'_D$ all commute with each other. Clearly, the average values of these four operators are independent invariants of the motion. The secular spin-spin—coupling Hamiltonian $\mathcal{H}'_D$ contains "flip-flop" terms which presumably prevent the existence of other thermodynamic invariants, so that we can write the "high-temperature" approximation of the quasiequilibrium density operator for the spin system under the usual form,

$$\rho_{qe}=\frac{1}{\mathrm{Tr}\{\mathbb{1}\}}\left[1+\left[\frac{E_D}{\mathcal{D}}\right]\frac{1}{\mathcal{D}}\mathcal{H}'_D\right.$$
$$\left.+\left[\frac{E^{(35)}}{Z^{(35)}}\right]\frac{\hbar\omega^{(35)}}{Z^{(35)}}\mathcal{N}^{(35)}+\cdots\right] \tag{3}$$

where the ellipsis stands for similar terms for ^{37}Cl and ^{23}Na nuclei, and the nuclear-spin entropy is given by

$$S=S(\text{complete disorder})$$
$$-\frac{k}{2}\left[\frac{E_D}{\mathcal{D}}\right]^2-\frac{k}{2}\left[\frac{E^{(35)}}{Z^{(35)}}\right]^2-\cdots \tag{4}$$

where the ellipsis stands for similar terms for ^{37}Cl and ^{23}Na nuclei. E_D is the average value of $\mathcal{H}'_D$ and $E^{(35)}$ is the average value of $\hbar\omega^{(35)}\mathcal{N}^{(35)}$. $\mathcal{D}^2$ and $(Z^{(35)})^2$ are ratios of traces of spin operators appearing in expression (2) of the spin Hamiltonian.

The pulse experiments described in the present paper were performed with a single-coil spectrometer tuned to the NQR frequency of ^{35}Cl (the nuclei which gave, by far, the largest signals). The Hamiltonian $\mathcal{H}_{\mathrm{rf}}$ describing the coupling of the spins with the linearly polarized rf magnetic field can be written as

$$\mathcal{H}_{\mathrm{rf}}=-AK(t)\cos(\omega_{\mathrm{rf}}t+\varphi) , \tag{5}$$

where $\omega_{\mathrm{rf}}/2\pi$ and φ are the frequency and the phase of the rf field, the real function of time $K(t)$ describes the pulse envelope, and the Hermitian operator A is the projection of the total-spin magnetic moment on the direction χ of the spectrometer coil,

$$A=\sum_{\text{all spins}}\gamma_i I_i\cdot\hat{\chi} , \tag{6}$$

where γ_i is the magnetogyric ratio of spin i. The observable A is also the property of the spin system which will eventually be measured by recording the emf induced in the coil. When attention is focused on ^{35}Cl nuclei, it is convenient to decompose A into a sum of terms which have simple commutation relations with $\mathcal{N}^{(35)}$,

$$A=\sum_{m=-1,0,+1}A_{(m)}^{(35)},$$

with

$$[\mathcal{N}^{(35)},A_{(m)}^{(35)}]=mA_{(m)}^{(35)} . \tag{7}$$

Further discussions of spin dynamics will be simplified by the use of an "interaction representation" in which a transformed operator

$$\widetilde{B}(t)=\exp(it\mathcal{H}_0/\hbar)B(t)\exp(-it\mathcal{H}_0/\hbar)$$

is associated with each operator $B(t)$ defined at time t. This interaction representation has the same advantages as the "rotating frame" used in conventional NMR, but it does not have the same simple geometrical interpretation.

Using this interaction representation and neglecting irrelevant terms which oscillate at high frequencies, we can write the equation of motion of the spin system (including rf irradiation at the resonance frequency of ^{35}Cl: $\omega_{\mathrm{rf}}=\omega^{(35)}$) under the following form:

$$i\hbar\frac{\partial}{\partial t}\widetilde{\rho}(t)=\{[\mathcal{H}'_D+\tfrac{1}{2}K(t)A_{+}^{(35)}(\varphi)],\widetilde{\rho}(t)\} ,$$

where (8)

$$A_{+}^{(35)}(\varphi)=A_{(+1)}^{(35)}e^{-i\varphi}+A_{(-1)}^{(35)}e^{i\varphi} .$$

Whenever no rf pulses occur in the time interval from t_0 to t_1, a simple formal solution of Eq. (8) for $\widetilde{\rho}(t)$ is

$$\widetilde{\rho}(t_1)=Q(t_1-t_0)\widetilde{\rho}(t_0)Q^{\dagger}(t_1-t_0) , \tag{9}$$

where the unitary operator Q is given by

$$Q(t_1-t_0)=\exp[-i(t_1-t_0)\mathcal{H}'_D/\hbar] . \tag{10}$$

In our experiments the peak rf magnetic field during the pulses was much larger than the local fields so that $\mathcal{H}'_D$ can be neglected during the pulse. In this approximation, we can describe the effects of an rf pulse as

$$\tilde{\rho}_{\text{just after}} = R\tilde{\rho}_{\text{just before}} R^{\dagger} , \tag{11}$$

where the unitary operator R is given by

$$R = \exp[-(i/2) S A_{+}^{(35)}(\varphi)] , \tag{12}$$

where S is the integral of $K(t)/\hbar$ over the pulse. R is a product of unitary operators $R^{i}(\theta^{(i)}\varphi)$ operating on each individual ^{35}Cl spin i. The "rotation angle" $\theta^{(i)}$ is given by

$$\theta^{(i)} = \frac{\sqrt{3}}{2} \gamma^{(35)} \hbar S \, | \sin\alpha^{(i)} | , \tag{13}$$

where $\alpha^{(i)}$ is the angle between the rf magnetic field and the EFG symmetry axis at the location of spin i. The dimensionless quantity $\theta^{(i)}$ has the usual cyclic property of a rotation angle:

$$R^{(i)}(\theta^{(i)} + 2\pi, \varphi) = R^{(i)}(\theta^{(i)}, \varphi) .$$

In a perfect $NaClO_3$ single crystal, there are four possible directions for the EFG symmetry axis so that any ^{35}Cl spin will belong to one of four subsets, and an rf pulse will, in general, have different effects on spins belonging to different subsets. Fortunately, when the rf field is oriented in a [100] direction, $| \sin\alpha^{(i)} |$ has the same value $\sqrt{2/3}$ at all spin locations, making all spins equivalent in their interactions with the rf magnetic field and in their contribution to observable A. All experimental results reported in the present paper have been obtained under these simplifying conditions.

We shall now examine the influence of various simple sequences of short rf pulses on the nuclear-spin system of $NaClO_3$, using the techniques outlined in Refs. 2–4. All pulses will be applied at the exact ^{35}Cl resonance frequency. The results of the calculations will be given only in the particular case of an rf field linearly polarized in a [100] direction. Each pulse can then be completely characterized by its rf phase ϕ, the common value θ of the rotation angle of all spins ^{35}Cl, and the time at which it occurs.

Assuming quasiequilibrium [Eq. (3)] before a single pulse of rotation angle θ and phase ϕ, applied at $t=0$, the quasiinvariants immediately after the pulse can be expressed easily in terms of the quasiinvariants immediately before the pulse,

$$\begin{aligned} \langle E^{(23)} \rangle_{\text{after}} &= \langle E^{(23)} \rangle_{\text{before}} , \\ \langle E^{(37)} \rangle_{\text{after}} &= \langle E^{(37)} \rangle_{\text{before}} , \\ \langle E^{(35)} \rangle_{\text{after}} &= \langle E^{(35)} \rangle_{\text{before}} \cos\theta , \\ \langle E_D \rangle_{\text{after}} &= \langle E_D \rangle_{\text{before}} [1 - (1-\cos\theta) P_1 \\ &\qquad - (1-\cos 2\theta) Q_1] , \end{aligned} \tag{14}$$

where P_1 and Q_1 are ratios of traces of spin operators which can be evaluated easily. The pulse response of the spin system can be written as

$$\begin{aligned} \langle A(\theta,\phi,t) \rangle = \mathrm{Tr}[A Q(t) R(\theta,\phi) \rho_{qe} R^{\dagger}(\theta,\phi) Q^{\dagger}(t)] = {} & \left[\frac{E^{(35)}}{Z^{(35)}} \right] [M'^{(35)}(\theta,t) \cos(\omega^{(35)} t + \phi) + M''^{(35)}(\theta,t) \sin(\omega^{(35)} t + \phi)] \\ & + \left[\frac{E_D}{\mathscr{D}} \right] [M'_D(\theta,t) \cos(\omega^{(35)} t + \phi) + M''_D(\theta,t) \sin(\omega^{(35)} t + \phi)] , \end{aligned} \tag{15}$$

where the θ and t dependences of the quantities M can be written as

$$\begin{aligned} M'^{(35)}(\theta,t) &= \sin\theta \, m'^{(35)}(t) , \\ M''^{(35)}(\theta,t) &= \sin\theta \, m''^{(35)}(t) , \\ M'_D(\theta,t) &= \sin\theta \, h'_D(t) + \tfrac{1}{2} \sin 2\theta \, n'_D(t) , \\ M''_D(\theta,t) &= \sin\theta \, h''_D(t) + \tfrac{1}{2} \sin 2\theta \, n''_D(t) , \end{aligned} \tag{16}$$

where $m'^{(35)}(t), \ldots, n''_D(t)$ are traces of the general type

$$\mathrm{Tr}[A_\alpha Q(t) S_\alpha Q^{\dagger}(t)] ,$$

where A_α denotes $A_{+}^{(35)}(\pi/2)$ for single-primed terms and $A_{+}^{(35)}(0)$ for double-primed terms, and where the spin operator S_α, arising from the effect of the pulse on ρ_{qe}, involves single resonant spins for m, coupling between pairs of resonant spins for n and coupling between resonant and nonresonant spins for h. All double-primed quantities are even functions of t, whereas all single-primed quantities are odd functions of t. The six functions $m'^{(35)}(t), \ldots, n''_D(t)$ and their low-order time derivatives can be evaluated easily immediately after the pulse (i.e., at $t=0$). For instance, $m''^{(35)}(0)$ is different from zero, and the five other functions are zero at $t=0$, also the second time derivative of $m''^{(35)}(t)$, at $t=0$, is very simply related to the trace of the square of the commutator $[A_{+}^{(35)}(0), \mathscr{H}'_D]$, as expected for such a "second moment." This whole behavior is quite analogous to that of the single-pulse response of a spin system with a purely Zeeman unperturbed Hamiltonian. The only qualitative difference is that dipolar couplings in Zeeman systems lead to symmetric Zeeman absorption lines and, consequently, quantities analogous to $m'^{(35)}(t)$, $h''_D(t)$, and $n''_D(t)$, which are identically zero at all times. In the present quadrupolar case, these quantities are in general different from zero, with the consequence that the "quadrupolar" (i.e., proportional to $E^{(35)}$) and "dipolar" contributions to the pulse response do not have the nicely constant and mutually orthogonal rf phases which are usual in the Zeeman case.

Pursuing the analogy with the Zeeman case, we can transform "quadrupolar order" ($E^{(35)}/Z^{(35)}$) into "dipolar order" $(E_D/\mathscr{D})$ and *vice versa* by applying a sequence of two rf pulses separated by a time interval of the order of the duration of the pulse response. Starting again with a spin system in quasiequilibrium characterized by amounts of order $(E^{(35)}/Z^{(35)})_0$, $(E_D/\mathscr{D})_0$, ..., we apply a first pulse of angle θ_1 and phase ϕ at time 0, followed by a second pulse of angle θ_2 and phase 0 at time τ. The quasi-invariants of the motion immediately after the second pulse can be evaluated formally as, for instance,

$$\left[\frac{E_D}{\mathscr{D}}\right]_2 = \mathrm{Tr}\left[\frac{\mathscr{H}'}{\mathscr{D}}R(\theta_2,0)Q(\tau)R(\theta_1,\phi) \times \rho_{qe}R^\dagger(\theta_1,\phi)Q^\dagger(\tau)R^\dagger(\theta_2,0)\right] , \quad (17)$$

and they can be related to the invariants before the first pulse,

$$\begin{aligned} \left[\frac{E_D}{\mathscr{D}}\right]_2 &= k_{D\leftarrow 35}\left[\frac{E^{(35)}}{Z^{(35)}}\right]_0 + K_{D\leftarrow D}\left[\frac{E_D}{\mathscr{D}}\right]_0 , \\ \left[\frac{E^{(35)}}{Z^{(35)}}\right]_2 &= K_{35\leftarrow 35}\left[\frac{E^{(35)}}{Z^{(35)}}\right]_0 + K_{35\leftarrow D}\left[\frac{E_D}{\mathscr{D}}\right]_0 , \qquad (18) \\ \left[\frac{E^{(37)}}{Z^{(37)}}\right]_2 &= \left[\frac{E^{(37)}}{Z^{(37)}}\right]_0 , \quad \left[\frac{E^{(23)}}{Z^{(23)}}\right]_2 = \left[\frac{E^{(23)}}{Z^{(23)}}\right]_0 . \end{aligned}$$

The efficiencies of transfer of order K defined here are normalized in such a way that, as an example, $K_{D\leftarrow 35}=1$ would describe a *reversible* transfer from quadrupolar into dipolar order (i.e., at constant spin entropy).

Let us now focus our attention on the efficiency $K_{D\leftarrow 35}$ of transfer from quadrupolar order (available in complete thermal equilibrium with the lattice) into dipolar order (virtually absent in complete thermal equilibrium). The traces which appear in the evaluations of $A(\theta,\phi,t)$ and $K_{D\leftarrow 35}$ are very closely related, and $K_{D\leftarrow 35}$ can be expressed as

$$K_{D\leftarrow 35}(\theta_1,\phi,\theta_2,\tau) = \sin\theta_1 \frac{1}{m''^{(35)}(0)}[M_D''(\theta_2,\tau)\cos\phi + M_D'(\theta_2,\tau)\sin\phi] . \quad (19)$$

$K_{D\leftarrow 35}$ depends upon the rotation angle θ_1 of the first pulse by the same simple factor $\sin\theta_1$ as, for instance, the quadrupolar part of the response to a θ_1 pulse.

The θ_2, ϕ, and τ dependencies of $K_{D\leftarrow 35}$ can be visualized as follows: Start with a spin system in quasiequilibrium in which $(E_D/\mathscr{D})$ is the only quasiinvariant different from zero, and apply an rf pulse at time 0, with phase 0, causing a rotation angle θ_2. Now, wait for a time τ after the pulse and focus attention on the component of the pulse response $\langle A(\theta_2,0,\tau)\rangle$ with a fast time dependence in $\sin(\omega^{(35)}t+\phi)$, i.e., phase-shifted by $(\pi/2-\phi)$ with respect to the pulse rf field. The θ_2, ϕ, and τ dependencies of this quantity are exactly the same as those of $K_{D\leftarrow 35}$, except for an overall scale factor. As a consequence of this, maximization of $K_{D\leftarrow 35}$ and optimization of the observation of the dipolar component of the pulse response are essentially the same thing. If the quadrupolar absorption line were symmetric, as in the Zeeman case, $M_D''(\theta_2,\tau)$ would be identically zero and the ϕ dependence of $K_{D\leftarrow 35}$ would be through a factor $\sin\phi$ independent of any other parameter. In practice, in the quadrupolar case, the lines are not far from symmetric and the optimum value of ϕ is very close to $\pi/2$.

Further exact relations between various aspects of the pulse response of the spin system can be obtained by considering the limit of very small pulses

$$\begin{aligned} \frac{d}{dt}m'^{(35)}(t) &= \gamma^{(35)}H_L^{(35)}[h_D''(t)+n_D''(t)] , \\ \frac{d}{dt}m''^{(35)}(t) &= -\gamma^{(35)}H_L^{(35)}[h_D'(t)+n_D'(t)] , \qquad (20) \end{aligned}$$

where

$$(H_L^{(35)}\gamma^{(35)})^2 = \mathrm{Tr}[(\mathscr{H}'_D)^2]/\mathrm{Tr}[(\mathscr{N}^{(35)})^2] .$$

Clearly, in the limit of small pulses, these equations make it possible to predict the *exact* relation between the quadrupolar and dipolar responses corresponding to equal amounts of quadrupolar order $(E^{(35)}/Z^{(35)})$ and dipolar order $(E_D/\mathscr{D})$, and to end up with an exact prediction about quantities such as $K_{D\leftarrow 35}$, for instance, starting only from the observed quadrupolar pulse response. A quantitative comparison between $K_{D\leftarrow 35}$ predicted in this way and $K_{D\leftarrow 35}$ derived from the observed dipolar pulse response can provide a very sensitive overall test of the set of assumptions on which the calculations are based.

Let us now briefly discuss the "local field" $H_L^{(35)}$ defined above. $\mathrm{Tr}[(\mathscr{H}'_D)^2]$ and thus also $(H_L^{(35)})^2$ can be decomposed into a sum of terms according to the various types of spin-spin couplings involved in NaClO$_3$. Assuming direct dipolar couplings between nuclei on an undistorted rigid lattice, the dominant contribution (7.050 G^2) comes from ^{23}Na-^{23}Na interactions, ^{23}Na-^{35}Cl interactions contribute 3.285 G^2, ^{23}Na-^{37}Cl interactions contribute 0.742 G^2, and all other interactions provide almost negligible contributions, the sum being $(H_L^{(35)})^2=11.19$ G^2.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

A. Experimental techniques

The NaClO$_3$ monocrystals used in the experiments were grown by slowly evaporating an aqueous solution at room temperature. Crystals of about 1 cm^3 were grown in 3–4 weeks. Care was taken to avoid spurious line distortions from magnetic fields and temperature gradients ($d\omega^{(35)}/dT$ is about -8π kHz/deg in NaClO$_3$ at room temperature). The sample was enclosed in a μ-metal box in which stray fields were less than 5 mG. This box and the rf coil around the sample were thermally connected to a thermostat regulated to better than 0.01 °C at about 40 °C. The average rf power input to the coil was kept constant during each complete sequence of experiments to ensure that changes in pulse sequences did not cause minute temperature excursions in the crystal.

We used a single-coil coherent rf pulse spectrometer providing $\theta=\pi/2$ pulses on ^{35}Cl which lasted 35 μsec (at

$\omega^{(35)} \sim 2\pi 30$ MHz). The transmitter (with active damping), the sample tank circuit and the amplifier were connected together with the cable and diode arrangement described by Lowe and Tarr.[12] A piece of thin insulated copper foil was wrapped closely around the crystal as a slightly overlapping open cylinder in order to improve the rf magnetic field homogeneity. The phase of each rf pulse with respect to the master oscillator was adjustable in increments of $\pi/2$. The ^{35}Cl nuclear-quadrupole-resonance (NQR) signals were amplified, processed by two (approximately) orthogonal phase-sensitive detectors, digitized, accumulated, and transferred to a minicomputer.

The components of the NQR signal in phase and out of phase with the rf pulse were computed using the techniques described in Ref. 13, which perform complete software corrections for the overall phase shift of the spectrometer and for the (small) instrumental misalignments such as nonorthogonality of the phase-sensitive detectors, difference in their sensitivities, and offset between the exact NQR frequency and the frequency of the reference oscillator. These corrections are exact if they are derived from observation of pulse responses of a spin system with a symmetric absorption line. All experiments were started with the ^{35}Cl spin system in the same initial state of pure quadrupolar order

$$\left[\left(\frac{E^{(35)}}{Z^{(35)}}\right)=\left(\frac{E^{(35)}_{\text{th eq}}}{Z^{(35)}}\right),\ \left(\frac{E_D}{\mathscr{D}}\right)\simeq 0\right]$$

(where th eq denotes thermal equilibrium) by just waiting for a time of at least 0.7 sec, much longer than the quadrupolar or dipolar spin-lattice relaxation times measured on ^{35}Cl.

B. Pure NQR signals

The pure NQR signals of ^{35}Cl were observed as the response to a single rf pulse of a crystal which was previously in a state of pure quadrupolar order. If the pure NQR absorption line of ^{35}Cl was *exactly* symmetric, the software processing of the pure NQR pulse response would have resulted in an *exactly* zero $m'^{(35)}(t)$ in-phase component and *exact* corrections for overall phase shift, frequency offset, etc. Figure 1 shows that $m'^{(35)}(t)$ is different from zero as anticipated. Using a NMR signal, we have checked that our instrumentation and data processing leads to an essentially zero $m'(t)$ in the case of a (presumably) symmetric absorption line. The in-phase component of the pure NQR pulse response was somewhat variable from crystal to crystal, and very much smaller than the out-of-phase component in all cases. We have not investigated this small signal any further, except to conclude that its existence did not appreciably disturb our software evaluation of the spectrometer overall phase shift and frequency offset from the observed pure NQR pulse response.

We have also checked that the time dependence of $m''^{(35)}(t)$ for times ranging from 80 to 400 μsec is very close to a Gaussian with the second moment $\langle(\Delta\omega^2)\rangle = 8.28$ kHz^2 evaluated for the perfect NaClO$_3$ rigid lattice. Finally, experiments on spin-lattice relaxation have shown an exponential recovery of the quadrupolar signal, with a spin-lattice relaxation time T_{1Q} of 39 msec at 40 °C.

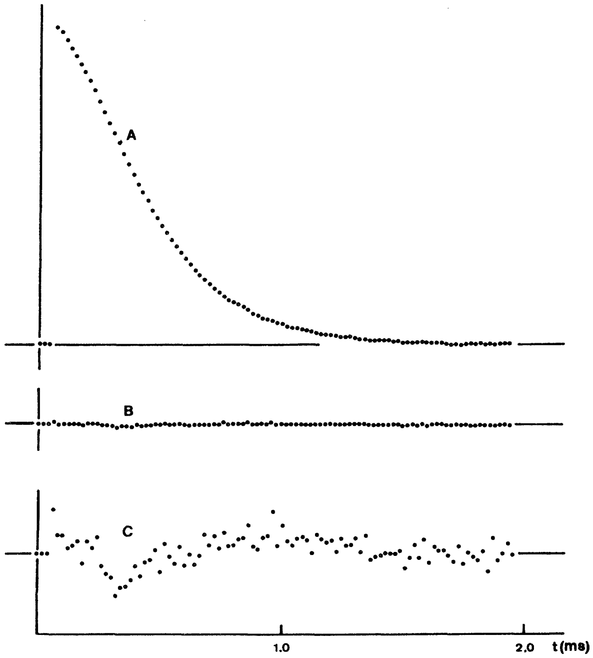

FIG. 1. Pure NQR signal of ^{35}Cl spins in a sodium chlorate monocrystal: Spin response to a single rf pulse (at the quadrupolar resonance frequency $\omega^{(35)}/2\pi$ of the ^{35}Cl spins) applied to the spin system in a state of pure quadrupolar order. Trace *A* represents the out-of-phase component $m''^{(35)}(t)$. Both traces *B* and *C* represent the (slightly misaligned) in-phase component $m'^{(35)}(t)$, the former with the vertical scale sensitivity used for display of trace *A*, and the latter with a vertical scale sensitivity having been enhanced with a factor 32.

C. Dipolar signals and $K_{D\leftarrow 35}$

In sodium chlorate, the local field at a ^{35}Cl nucleus arises mainly from the dipolar interactions with the neighboring ^{23}Na nuclei. As a consequence of this, we anticipate that the θ dependence of the dipolar pulse response and the θ_2 dependence of the efficiency of transfer $K_{D\leftarrow 35}$ will be dominated by the $\sin\theta$ and $\sin\theta_2$ contributions. The pure NQR pulse response in NaClO$_3$ is almost exactly out of phase with the pulse. This indicates that the dipolar pulse response will be mainly in phase with the pulse (M_D'' very small) and that the ϕ dependence of $K_{D\leftarrow 35}$ will be dominated by the $\sin\phi$ contribution. We have checked that these expectations are indeed valid and, for simplicity, most experiments have been performed with $\pi/2$ pulses and $\pm\pi/2$ phase shifts ϕ.

The results of all experiments on dipolar signals were corrected for overall phase shifts and frequency misalignments using values of the correction parameters derived from observations of pure NQR pulse responses taken at regular intervals. Further isolation of the dipolar pulse response from contamination by the small in-phase component of the quadrupolar pulse response was achieved by alternating the phase shift between the two pulses used to prepare dipolar order in successive experiments (thus changing the sign of E_D and not that of $E^{(35)}$) and subtracting the corresponding responses to an observation pulse of constant phase.

Figure 2 shows the result of an experimental verification of Eq. (19) for $\theta_1=\theta_2=\pi/2$ and $\phi=\pi/2$. Each experiment started with the spins in complete thermal equilibrium with the lattice (pure quadrupolar order). An observable amount of dipolar energy was then created by a sequence of two $\pi/2$ pulses, phase-shifted by $\pi/2$, and separated by a time interval t_1. Immediately after this pulse sequence, the spin system is clearly not in a state of internal quasiequilibrium (for instance, a pulse response is present). After waiting for a time interval t_3 longer than a few lifetimes of the pulse response, the properties of the spin system do not change any more, except for a very slow evolution due to spin-lattice relaxation. We shall assume that under these conditions, the spin system can be described again by a quasiequilibrium density operator of the type (3), with the same values of the quasiinvariants as immediately after the pulse pair (except for the small effects of spin-lattice relaxation). A $\pi/2$ observation pulse is then applied and the dipolar pulse response can be measured as a function of the time t_2 after the observation pulse. In a first set of experiments, the separation t_1 between the preparation pulses was varied and the observation time t_2 was kept at the maximum of the dipolar pulse response ($t_2\simeq300$ μsec). In a second set of experiments, the separation time t_1 was kept at the maximum of the efficiency of transfer $K_{D\leftarrow35}$ ($t_1\simeq300$ μsec) and t_2 was varied. The very good agreement between the results of the two experiments strongly supports the whole scheme of spin thermodynamics and, in particular, the assumption that the spin system has reached internal quasiequilibrium during the time interval t_3 between preparation and observation of dipolar energy.

D. Absolute magnitude of the dipolar signals

Using Eq. (19) for $K_{D\leftarrow35}$ and the experimental results shown on Fig. 2, we can evaluate the efficiency of transfer $K_{D\leftarrow35}$, which turns out to be 0.27 in the most favorable case $\theta_1=\theta_2=\pi/2$, $\phi=\pi/2$, and $\tau\simeq300$ μsec. Having prepared a known (and relatively large) amount of dipolar order in this way, we can predict the exact magnitude of the corresponding dipolar pulse response to a small pulse (normalized to the quadrupolar pulse response) by using Eq. (20). We have also performed the corresponding experiment. Prediction and experiment are in perfect agreement as far as the shape of the dipolar pulse response is concerned, but the observed signals are significantly larger than the predictions of Eq. (20) by a factor which ranges from 1.5 in our best crystal to almost 2.0 in less perfect crystals.

In an attempt to understand this discrepancy, we examined a conjecture in which only part of the dipolar spin-spin coupling would contribute to the quasi-invariant which gives rise to the in-phase component of the ^{35}Cl pulse response. In this conjecture, Eq. (19) remains valid, so that the conjecture is compatible with the experimental results shown in Fig. 2. On the other hand, the conjecture leads to relations similar to Eq. (20) with $\mathcal{H}'_D$ replaced by the part of the couplings which contribute to the conjectured invariant. This would of course decrease $H_L^{(35)}$ and increase the predicted dipolar signals. In such a conjecture, the rest of the spin-spin couplings would presumably contribute to an additional quasi-invariant. An experimental indication that such an additional quasi-invariant indeed exists is given by our investigation of the (presumably spin-lattice) relaxation of the dipolar signals prepared and observed at $\omega^{(35)}$: The relaxation is nonexponential and many results can be described as a combination of a "short" relaxation time of 19—29 msec and a long relaxation of 180—350 msec, depending upon the crystal. These results will be described and discussed in a forthcoming paper.

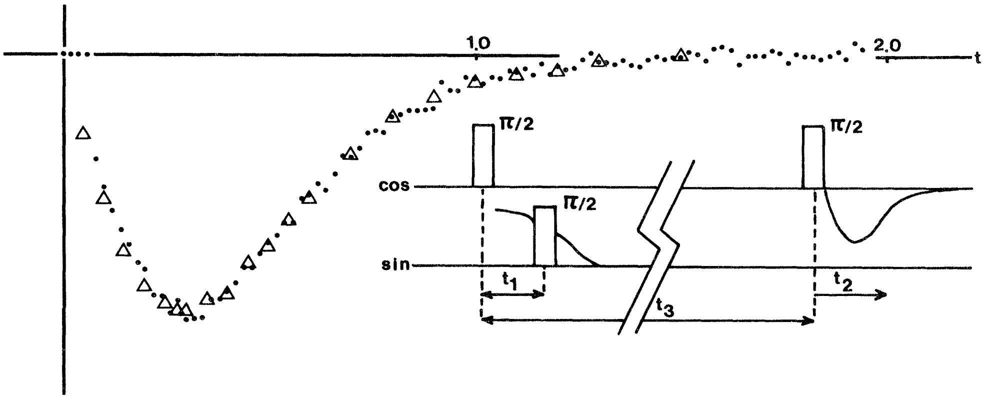

FIG. 2. Starting from complete thermal equilibrium, dipolar order is prepared by a pair of phase-orthogonal rf pulses (on ^{35}Cl) separated by a delay t_1. The spin system presumably relaxes to internal quasiequilibrium for a long time $t_3\sim5$ msec, and a third pulse is used to observe the in-phase dipolar response of the ^{35}Cl spins (shown on the vertical scale). Triangles correspond to a fixed value of t_2 (set at the maximum of the dipolar response) and variable $t_1=t$ (shown on the horizontal scale) causing a variable efficiency of transfer of quadrupolar into dipolar order. Dots correspond to a fixed value of t_1 (equal to the fixed value of t_2 used for the other set of experiments and providing maximum order transfer), and variable $t_2=t$ shown on the horizontal scale.

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