angle approximation, since increased scattering is predicted when this approximation is improved.

As regards the assumption made throughout this paper that the particle suffers no energy loss in the scattering medium, this too may be improved upon by treating the scattering parameter λ as a function of the distance x.[14] The substitutions

$$\xi \equiv \int_0^x d\tau\{\lambda(\tau)\}^{-1}, \qquad \nu \equiv \int_0^x d\alpha'\{\cos\alpha'\}^{1/2},$$

when made in the elementary scattering formula (2), yield formula (4) with ξ and ν replacing x and s, respectively; thus the formulas in Secs. 2 and 3 may be adapted directly to the new variables. It should be noted, however, that only the zero-order terms in these formulas are valid, since to suppose that the scattering parameter λ is a function of x rather than of actual path length is to employ the small-angle approximation.

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Nuclear-Magnetic-Resonance Single-Shot Passage in Solids

M. Goldman, M. Chapellier, and Vu Hoang Chau

Service de Physique du Solide et de Résonance Magnétique, Centre d'Etudes Nucléaires de Saclay, Gif-sur-Yvette, Essonne, France

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We study both theoretically and experimentally the magnetization loss of a nuclear spin system irradiated with a rf field under a linear field sweep through the resonance. Two limiting cases are considered. The first is that of a slightly saturating passage, in which the loss is simply related to the rf field amplitude, a fact which allows an easy calibration of the latter. The second case is that of a quasiadiabatic passage which reverses the magnetization. Three factors contribute to the magnetization loss: (1) The passage is sudden far in the wings of the line, and it becomes rather abruptly adiabatic at a given distance from resonance. An entropy increase accompanies this transition. (2) The passage through the central part is not quite adiabatic because of the finite sweep rate of the field through the line. (3) The finite spin-lattice relaxation time of the spin-spin term causes a loss of magnetization at the passage on the line. The losses are numerically computed for the fluorine spin system in CaF_2 with $\mathbf{H}_0 \parallel [100]$, and they are found to agree with the experimental values.

I. INTRODUCTION

In this article we study the behavior of a nuclear spin system in a solid, irradiated with a rf field during a single-shot passage, which we define as a linear sweep of the applied dc field through the resonance value. This encompasses the well-known fast, or adiabatic, passage, extensively used in nuclear magnetic resonance: When a suitably large rf field is applied, and when the sweep rate is low enough, this passage results in a reversal of the magnetization orientation with only a small loss in magnitude. The theory of the fast passage in solids is based on the spin-temperature concept.[1–3] It is well verified by experiment,[3] which is a check of the validity of this concept. This theory, however, is developed for the case of a strictly adiabatic passage and would be rigorously valid only if the sweep rate was infinitely low. In practice, the slowness of the sweep is limited by the condition that the entire passage must take place in a time much shorter than the spin-lattice relaxation time T_1, whence its name of fast passage. The passage is then never completely adiabatic, and it is the main concern of this work to analyze the lack of adiabaticity of a quasiadiabatic passage, and the resulting loss in magnetization amplitude. A second limiting case is also studied, the case of a slightly saturating single-shot passage: When the rf field is small and the passage through the line is fast, this passage results in a small decrease of the nuclear magnetization with no change of its orientation. The measurement of this magnetization loss provides a simple, fast, and accurate way of calibrating the rf field amplitude.

The theory of these single-shot passages is developed in the frame of the Provotorov theory of saturation.[4,5] Its validity is then restricted to the following cases:

(1) The temperature is high, that is, the nuclear polarization is so low that it is permissible to develop the density matrix to first order as a function of the

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inverse spin temperature. This excludes the case of dynamically highly polarized nuclear spin systems.

(2) The rf field H_1 is far smaller than the local field experienced by the nuclei due to their coupling with the neighboring spins.

The experimental verification of the theory is performed on the fluorine spin system in CaF_2, with the magnetic field parallel to the [100] direction.

We first recall briefly the Provotorov equations before analyzing in turn the slightly saturating passage and the quasiadiabatic passage.

A. Provotorov Equations

We consider, in a solid, a spin system I in a large magnetic field H_0, irradiated with a rf field of amplitude H_1 rotating with frequency ω. In a frame rotating with frequency ω around the direction of the dc field, the evolution of the density matrix of the system is governed by a time-independent effective Hamiltonian (measured in frequency units),

$$\mathcal{H}=\Delta I_z+\omega_1 I_x+\mathcal{H}_D', \tag{1}$$

where

$$\Delta=-\gamma H_0-\omega,$$

$$\omega_1=-\gamma H_1,$$

and $\mathcal{H}_D'$ is the secular part of the spin-spin interactions.

If the Zeeman coupling with the rf field, $\omega_1 I_x$, is small compared with ΔI_z and $\mathcal{H}_D'$, it can be treated as a small perturbation of the main Hamiltonian:

$$\mathcal{H}_0=\Delta I_z+\mathcal{H}_D'. \tag{2}$$

This main Hamiltonian is a sum of two commuting operators which are then separately invariants of the motion. By an extension of the spin-temperature hypothesis, it is assumed that the system reaches, in a time of the order of the spin-spin relaxation time T_2, a state of quasiequilibrium corresponding to a density matrix:

$$\sigma \propto 1-\alpha\Delta I_z-\beta\mathcal{H}_D', \tag{3}$$

with different inverse temperatures α and β for the Zeeman and the spin-spin terms. The effect of the perturbation $\omega_1 I_x$, which commutes with none of these terms, is to cause an evolution of the inverse temperatures α and β toward a common value. A treatment to second order in the perturbation yields the following evolution equations:

$$d\alpha/dt=-W(\alpha-\beta),$$

$$d\beta/dt=W(\Delta^2/D^2)(\alpha-\beta), \tag{4}$$

where D, the local frequency, is defined by

$$D^2=\mathrm{Tr}(\mathcal{H}_D'^2)/\mathrm{Tr}(I_z^2), \tag{5}$$

and the mixing rate W is equal to

$$W(\Delta)=\tfrac{1}{2}\omega_1^2 g(\Delta), \tag{6}$$

where $g(\Delta)$ is the shape of the absorption signal at low rf level, normalized to

$$\int_{-\infty}^{+\infty} g(\Delta)\,d\Delta=2\pi. \tag{7}$$

The conditions for Eqs. (4) to be valid are

$$\omega_1 \ll \Delta,\ D, \tag{8}$$

which means that the term $\omega_1 I_x$ is indeed small compared with ΔI_z and $\mathcal{H}_D'$. Equations (4) are established on a time scale of the order of $T_2 \sim D^{-1}$, and they are meaningful only if

$$W^{-1} \gg T_2. \tag{9}$$

As an order of magnitude, we have $W \sim \omega_1^2 T_2$, and the condition is

$$\omega_1^2 T_2^2 \sim (\omega_1/D)^2 \ll 1.$$

This condition is already met in Eqs. (8).

The Provotorov equations (4) are established for an irradiation at a constant distance Δ from resonance. They have to be modified when Δ is varied, for the following reason: The inverse temperature α is proportional to I_z but it also depends on $\Delta[\alpha \propto (I_z/\Delta)]$, and the first of Eqs. (4) is no longer valid when Δ is not constant. If, instead of Eq. (3) we use a density matrix

$$\sigma \propto 1-\alpha'\omega_0 I_z-\beta\mathcal{H}_D'$$

with $\alpha'=\alpha\Delta/\omega_0$, the system of Eqs. (4) is replaced by

$$d\alpha'/dt=-W[\alpha'-(\Delta/\omega_0)\beta],$$

$$d\beta/dt=W(\Delta/D^2)[\omega_0\alpha'-\Delta\beta]. \tag{10}$$

Both systems are equivalent when Δ is constant. The variation of the inverse temperature α' is the same as that of the magnetization, and Eqs. (10) can be used when the distance Δ is varied, as well as when $\Delta=0$ at the center of the line. Two conditions are necessary for their validity:

(1) Condition (9), which can be rewritten

$$\omega_1 \ll D.$$

(2) The variation of Δ must be very small during time T_2. Consider for instance a linear sweep through the line, i.e., $d\Delta/dt=\dot{\Delta}=Cte$. The linewidth is comparable to D, and the condition means that the time τ necessary for Δ to vary by an amount equal to D must be far longer than T_2:

$$\tau=(D/\dot{\Delta}) \gg T_2 \sim D^{-1}.$$

Introducing the local field $H_L'=(D/\gamma)$, we get

$$dH/dt \ll \gamma H_L'^2. \tag{11}$$

We use, in the rest of this article, a slightly different form of Provotorov equations. We use the quantity $\alpha'\omega_0$, proportional to the magnetization, which we call I_z as a short-hand notation. We then get the following system:

$$dI_z/dt=-W(I_z-\Delta\beta),$$
$$d\beta/dt=W(\Delta/D^2)(I_z-\Delta\beta). \qquad (12)$$

II. SLIGHTLY SATURATING SINGLE-SHOT PASSAGE

We consider a linear passage through the resonance line, starting from a field well above resonance and ending at a field well below resonance, in a time much shorter than the mixing time W^{-1}:

$$\tau=(D/\dot{\Delta})\ll 2\omega_1^{-2}g^{-1}\sim\omega_1^{-2}D.$$

This condition is also

$$dH/dt\gg\gamma H_1^2. \qquad (13)$$

It is supposed to be fulfilled together with condition (11). During such a passage, the quantities I_z and β suffer only a very small change and it is possible to perform an integration of Eqs. (12) taking I_z and β as constants in the right-hand sides. This yields, for the variation of I_z,

$$\delta I_z=-I_z\int_{-\infty}^{+\infty}Wdt+\beta\int_{-\infty}^{+\infty}W\Delta dt.$$

The integrations can be taken from $-\infty$ to $+\infty$, since the passage starts and ends at field values where W is negligibly small. Since W is an even function of Δ, the last integral vanishes, and we get

$$\delta I_z=-I_z\int_{-\infty}^{+\infty}Wdt$$
$$=-I_z\dot{\Delta}^{-1}\int_{-\infty}^{+\infty}Wd\Delta$$
$$=-I_z\frac{\omega_1^2}{2\dot{\Delta}}\int_{-\infty}^{+\infty}gd\Delta.$$

Using the normalization equation (7), we obtain

$$\delta I_z=-I_z(\pi\omega_1^2/\dot{\Delta})$$
$$=-I_z\pi\gamma H_1^2/(dH/dt). \qquad (14)$$

The variation of I_z does not depend on the value of the inverse temperature β, nor on the exact shape of the absorption curve. The result (14) could have been obtained with the standard formula for the transition probability under the effect of a harmonic perturbation. The only advantage of using Provotorov's equations is to make sure that no trouble arises from the existence of the spin-spin heat reservoir.

The magnetization loss after a single passage must be very small for the theory to apply, and it is then very difficult to measure it with any precision. The magnetization loss is appreciable only after many passages. If the resonance line is swept n times per second and if the rf field is applied during a time t, the magnetization decreases from its initial value I_0 to the value

$$I_z=I_0\exp[-n\pi\gamma H_1^2t/(dH/dt)]. \qquad (15)$$

The measurement of the time constant of this decay, together with the knowledge of n and (dH/dt) yields an unambiguous value for the rf field amplitude H_1, since there are no adjustable parameters. It is of course necessary that this time constant be far shorter than the spin-lattice relaxation time T_1. If this is not the case, we can choose the sweep frequency so that many passages occur during the time T_1 ($nT_1\gg 1$), and we get the following equation:

$$dI_z/dt=-\frac{n\pi\gamma H_1^2}{(dH/dt)}I_z-(T_1)^{-1}(I_z-I_{\mathrm{eq}}),$$

which, by a study of the decay rate and of the equilibrium magnetization as a function of n and (dH/dt), can yield the values of H_1 and T_1.

The experimental study of Eq. (15) was performed on the F^{19} spin system in CaF_2, with the magnetic field parallel to the [100] direction. The magnetic field was about 27 kG, and the fluorine resonance frequency about 107 Mc/sec. The temperature was 1°K. The sample was a sphere of 1-mm diameter and the saturating coil was a single turn of wire, of diameter between 4 and 5 mm, so as to produce a reasonably homogeneous rf field over the volume of the sample. The nuclear polarization was first increased to an absolute value of about 10% by the solid effect,[6] so as to increase the signal-to-noise ratio. The paramagnetic impurities used for the solid effect were U^{3+} ions in tetragonal sites[7] at the concentration of 1 U^{3+} per 10^4 F^-. The nuclear spin-lattice relaxation time T_1 was in these conditions approximately equal to 60 min.

The linear sweep was performed by a triangular modulation of the field with a peak-to-peak amplitude far larger than the resonance linewidth. Let H_p be this amplitude; we then have $dH/dt=nH_p$, and the saturation rate becomes equal to

$$W_{\mathrm{sat}}=\pi\gamma H_1^2/H_p. \qquad (16)$$

It is independent of the modulation frequency. The experimental sequence was the following: After the initial polarization of the nuclei, two absorption signals were recorded with a very low H_1 level on a

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[7] B. Bleaney, P. M. Llewellyn, and D. A. Jones, Proc. Roy. Soc. (London) **B69**, 858 (1956).

chart paper after lock-in detection, the field modulation and the rf field to be measured were applied during a given time, after which two absorption signals were again recorded. The use of two signals before and after saturation made it possible to correct for the extra decrease in magnetization due to the effect of spin-lattice relaxation.

We have verified that the magnetization did actually decrease exponentially as a function of the time of irradiation. We have also checked the following points:

(1) independence of the saturation rate as a function of the modulation frequency, between 50 cps and 250 cps;

(2) dependence on the modulation amplitude,

$$W \propto H_p^{-1},$$

with H_p ranging from 40 to 70 G;

(3) dependence on the rf field amplitude,

$$W \propto H_1^2,$$

when the voltage across the tank circuit was varied by a factor of 3. Care was taken that the magnetization loss during a single passage never exceeded 5%. All measurements were consistent to within a few percent.

No comparison could be made with other methods of calibration of the rf field which were all quite unpractical in the present experimental situation. The theoretical derivation of Eq. (15) seems however to be safe enough that no fundamental error should be suspected.

III. QUASIADIABATIC FAST PASSAGE

The adiabatic fast passage consists of a sweep of the magnetic field through the resonance value in a time much longer than the mixing time W between the Zeeman and the spin-spin terms. This condition is exactly opposite to the condition for a slightly saturating passage, and can be written

$$dH/dt \ll \gamma H_1^2. \tag{17}$$

During such a slow passage, the system is at any time nearly at equilibrium, which, after Eqs. (4), corresponds to equal inverse temperatures ($\alpha=\beta$) and its entropy is approximately constant.

The entropy is equal to

$$S=-k\,\mathrm{Tr}(\sigma \ln\sigma). \tag{18}$$

Using the density matrix,

$$\sigma=\exp(-\beta\mathcal{H}_0)/\mathrm{Tr}\{\exp(-\beta\mathcal{H}_0)\},$$

we get, to the lowest order in β,

$$S=-\tfrac{1}{2}k\beta^2(\Delta^2+D^2)+Cte. \tag{19}$$

The evolution of the inverse spin temperature during an adiabatic passage is then given by

$$\beta=A(\Delta^2+D^2)^{-1/2}, \tag{20}$$

where A is a constant.

If we start, for instance, the passage at $\Delta=\Delta_0$, with $\Delta_0>0$, $\Delta_0 \gg D$, the initial magnetization is $I_0=\Delta_0\beta(\Delta_0)=\Delta_0 A\Delta_0^{-1}=A$. At the end of the passage, at $\Delta=\Delta_1$, with $\Delta_1<0$, $|\Delta_1|\gg D$ the magnetization is $I_z=\Delta_1 A|\Delta_1|^{-1}=-I_0$. The magnetization is reversed with no change of its magnitude.

Turning now to the realistic case when the time of passage through the line is finite, we consider three factors of increase of the entropy:

(1) At a large distance from the center of the line, the absorption function g, and therefore the mixing rate W, are very small. However small the sweep rate, the passage cannot be adiabatic when Δ is large; it can only be sudden, that is take place without change of the density matrix. It is only at a given distance from resonance that, W being large enough, equilibrium can be reached in a short time and the passage can become adiabatic. The transition between the sudden part and the adiabatic part of the passage gives rise to an increase of the entropy.

(2) In the adiabatic part of the passage, the system is nearly at equilibrium, but not rigorously. The entropy is not rigorously constant, but it increases slightly by an amount which can be calculated.

(3) Another cause of saturation, that is of increase of the entropy, is the spin-lattice relaxation, which we disregarded so far. We consider only the case when the spin-lattice relaxation rate T_D^{-1} of the spin-spin interactions is finite whereas the Zeeman spin-lattice relaxation rate T_{1z}^{-1} is negligible. This is the case for nuclear spin systems at low temperature relaxed by paramagnetic impurities whose relaxation time T_{1e} is long.

The saturation of the line due to relaxation then occurs only during the passage through the line. It is larger the slower the passage, whereas the saturation due to the nonadiabaticity of the passage decreases as the sweep rate is decreased. There is thus an optimum sweep rate for which the entropy increase, and therefore the magnetization loss, are minimum.

We now analyze in turn these three factors in conditions where the passage is however reasonably adiabatic and any of the three losses is small.

A. Sudden-Adiabatic Transition

The function g, and the mixing rate W, decrease very sharply as a function of Δ on the edges of the resonance line, approximately as a Gaussian function. As a consequence, the transition between the situation when the mixing between the Zeeman and spin-spin terms is fast and the passage is adiabatic, and the situation when the mixing is negligible and the passage is sudden takes place in a very small field interval around a distance Δ_0 from resonance. The evolution of the system due to this transition is then to a good approximation the same as if the system was suddenly brought to the distance Δ_0, and time allowed for equilibrium to be reached at this distance before proceeding toward the center of the line. The same approximation was already used to account for the establishment of a spin temperature in low fields.[8,9] Starting with a system whose magnetization is I_0 and whose spin-spin inverse temperature β is zero, the equilibrium at the distance Δ_0 corresponds to the magnetization:

$$I_z=I_0[\Delta_0^2/(\Delta_0^2+D^2)]. \tag{21}$$

If, as we suppose, the distance Δ_0, where equilibrium is reached, is far larger than D, the magnetization loss due to the transition is small. It is then possible to analyze more fully the occurrence of the transition in the following way: We integrate the equation (12) of evolution of β, taking I_z to be a constant. We write $\beta=uv$, and $du/dt=-W(\Delta^2/D^2)u$. With the initial condition that $\beta(0)=0$, we get the following result:

$$\beta(t)=I_z\int_0^t W(\Delta/D^2)\exp\left\{-\int_{t'}^t W(\Delta^2/D^2)dt''\right\}dt'.$$

We are very far in the wings at the time 0 and we reach the value $\Delta=\Delta_0$ at the time t. Since the largest contribution to the integral comes from times t' close to t, we have

$$\beta(t)\simeq(I_z/\Delta_0)\int_0^t W(\Delta^2/D^2)\times\exp\left\{-\int_{t'}^t W(\Delta^2/D^2)dt''\right\}dt'$$

or else, with $t-t'=\tau$,

$$\beta=(I_z/\Delta_0)\int_0^t W(\Delta^2/D^2)\exp\left\{-\int_0^\tau W(\Delta^2/D^2)d\tau'\right\}d\tau. \tag{22}$$

The sweep rate being equal to $\dot{\Delta}$, we have

$$\tau=(\Delta-\Delta_0)/\dot{\Delta}=\delta/\dot{\Delta}.$$

The function W is approximately a steep decreasing Gaussian function at the distance Δ_0. In the vicinity of Δ_0, the function $\ln[W(\Delta^2/D^2)]$ is roughly parabolic and can be locally approximated by a straight line. This corresponds to writing

$$W\Delta^2/D^2\simeq A\exp(-\lambda\delta). \tag{23}$$

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[9] B. Sapoval and D. Lepine, J. Chem. Phys. Solids **27**, 115 (1966).

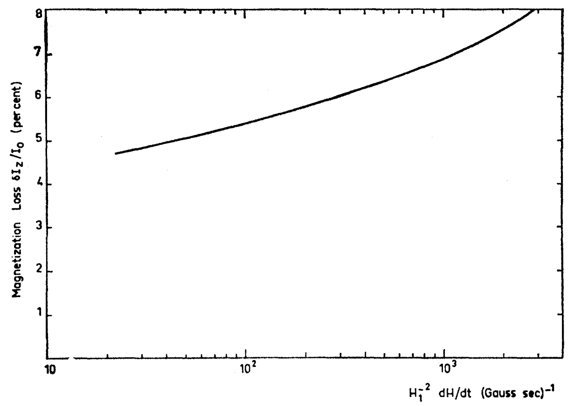

FIG. 1. Theoretical magnetization loss due to the sudden-adiabatic transition in CaF_2 with $\mathbf{H}_0 \parallel [100]$, as a function of $H_1^{-2}dH/dt$.

Equation (22) then becomes

$$\beta=(I_z/\Delta_0)\dot{\Delta}^{-1}\int_0^{\dot{\Delta}t}A\exp(-\lambda\delta)\times\exp\left\{-\dot{\Delta}^{-1}\int_0^\delta A\exp(-\lambda\delta')d\delta'\right\}d\delta. \tag{24}$$

We get, after integration, the following result:

$$\beta=(I_z/\Delta_0)[1-\exp\{-(A/\lambda)\dot{\Delta}[1-\exp(-\lambda\dot{\Delta}t)]\}]. \tag{25}$$

The factor $\exp(-\lambda\dot{\Delta}t)$ is the ratio of the rate $W\Delta^2/D^2$ at the beginning of the mixing to the same rate at the end of the mixing. It is far smaller than unity and can be neglected. The final result is

$$\beta=(I_z/\Delta_0)[1-\exp(-A/\lambda\dot{\Delta})]. \tag{26}$$

In this approximation, β varies from 0 to I_z/Δ_0. The transition can be considered as completed when $\beta\sim0.9I_z/\Delta_0$, which corresponds to $A/(\lambda\dot{\Delta})=2$, or else, using Eq. (23),

$$\omega_1^2/4\dot{\Delta}=-[(\Delta_0^2/D^2)g(\Delta)]^{-2}\times(d/d\Delta)\{(\Delta^2/D^2)g(\Delta)\}_{\Delta=\Delta_0}. \tag{27}$$

Using an experimental shape of the function $g(\Delta)$, one can calculate the distance Δ_0 of the transition and the loss of magnetization [Eq. (21)] as a function of H_1^{-2} dH/dt. On Fig. 1 are reported the calculated magnetization losses in the sudden-adiabatic transition as a function of $H_1^{-2}dH/dt$ for the case of CaF_2 with $\mathbf{H}_0 \parallel [100]$. The absorption shape $g(\Delta)$ was taken from Bruce.[10]

The transition begins when $\beta\simeq0.1I_z/\Delta_0$, which, from Eq. (26), corresponds to $A/(\lambda\dot{\Delta})\simeq0.1$. The beginning of the transition then takes place at a distance Δ_1 such that $g(\Delta_1)\simeq g(\Delta_0)/20$. In the case of CaF_2 with

[10] C. R. Bruce, Phys. Rev. **107**, 43 (1957).

$\mathbf{H}_0 \parallel [100]$, the field interval where the transition takes place varies from 1 to 1.5 G when the field of transition (Δ_0/γ) is varied from 10 to 8 G. This field interval is not entirely negligible and there is some arbitrariness in the choice of the value Δ_0 to be made to calculate the loss. The error involved in the final magnetization is not very large and does not amount to more than 1%, which is amply sufficient for all practical purposes. It should be noted that the loss varies very little as a function of $H_1^{-2}dH/dt$, going from 5 to 8% when $H_1^{-2}dH/dt$ is varied by a factor of the order of 100.

B. Entropy Increase in the Quasiadiabatic Part of the Passage

When the inverse spin temperatures α and β are not equal, i.e., when the density matrix is of the form

$$\sigma = \exp(-\alpha\Delta I_z - \beta\mathcal{H}_D')/\mathrm{Tr}\exp(-\alpha\Delta I_z - \beta\mathcal{H}_D'),$$

the entropy of the system is, after Eq. (18) and to lowest order in α and β, equal to

$$S = -\tfrac{1}{2}k(\alpha^2\Delta^2 + \beta^2 D^2) + Cte$$
$$= -\tfrac{1}{2}k(I_z^2 + \beta^2 D^2) + Cte.$$

The evolution of the quantity

$$s = \tfrac{1}{2}[I_z^2 + \beta^2 D^2],$$

is given, after Eqs. (12), by

$$ds/dt = I_z(dI_z/dt) + D^2\beta(d\beta/dt),$$
$$ds/dt = -W(I_z - \Delta\beta)^2. \qquad (28)$$

Let us study the variation of the quantity x $(x = I_z - \Delta\beta)$, when the passage is quasiadiabatic. We have

$$dx/dt = (dI_z/dt) - \Delta(d\beta/dt) - \dot{\Delta}\beta$$
$$= -Ux - \dot{\Delta}\beta, \qquad (29)$$

where, from Eqs. (12),

$$U = W(1 + \Delta^2/D^2).$$

We solve Eq. (29) by taking

$$x = uv \quad \text{and} \quad du/dt = -Uu.$$

The result is

$$x(t) = x(0)\exp\left\{-\int_0^t U(t')dt'\right\} - \dot{\Delta}\int_0^t \beta(t') \times \exp\left\{-\int_{t'}^t U(t'')dt''\right\} dt'. \qquad (30)$$

That the passage is adiabatic means that U is so great that β and U vary very little during the time interval U^{-1}. We choose, in Eq. (30), a value $t \gg U^{-1}$. Then

(1) The term

$$\exp\left\{-\int_0^t U(t')dt'\right\}$$

is negligibly small.

(2) The term

$$\exp\left\{-\int_{t'}^t U(t'')dt''\right\}$$

is non-negligible only for such values of t' that we have $t - t' \lesssim U^{-1}$.

As a consequence, we can replace, in Eq. (30), $\beta(t')$ by $\beta(t)$ and $U(t'')$ by $U(t)$ and we get

$$x = -\dot{\Delta}\beta\int_0^t \exp\{-U(t-t')\}dt',$$
$$x = -\dot{\Delta}\beta/U$$
$$= -\dot{\Delta}\beta/[W(1+\Delta^2/D^2)]. \qquad (31)$$

That this result indeed corresponds to a quasiadiabatic passage is verified by inserting this value of x in the Provotorov equations:

$$d\beta/dt = W(\Delta/D^2)x$$
$$= -\beta\dot{\Delta}\Delta/(\Delta^2 + D^2),$$

whence $\beta = A(\Delta^2 + D^2)^{-1/2}$,

$$dI_z/dt = -Wx$$
$$= \dot{\Delta}\beta(1 + \Delta^2/D^2)^{-1}$$
$$= A\dot{\Delta}D^2(\Delta^2 + D^2)^{-3/2},$$

whence $I_z = A\Delta(\Delta^2 + D^2)^{-1/2}$. We have, as we should, $I_z = \Delta\beta$ to first order, but we also know their first-order difference x.

Reporting the value of x in Eq. (28) yields

$$ds/dt = -Wx^2$$
$$= -\dot{\Delta}^2\beta^2/[W(1+\Delta^2/D^2)^2]. \qquad (32)$$

Since $I_z \simeq \Delta\beta$, the quantity s is, to first order,

$$s \simeq \tfrac{1}{2}\beta^2(\Delta^2 + D^2),$$

and we get

$$d[\beta(\Delta^2+D^2)^{1/2}]/dt = -[\beta(\Delta^2+D^2)^{1/2}]\dot{\Delta}^2/[D^2W(1+\Delta^2/D^2)^3],$$

or

$$d\ln[\beta(\Delta^2+D^2)^{1/2}]/d\Delta = -\dot{\Delta}/[D^2W(1+\Delta^2/D^2)^3]. \qquad (33)$$

Upon integration of this equation, from $\Delta_0 \gg D$, the distance at which the passage begins to be adiabatic, to $-\Delta_0$, the distance at which the passage ceases to be adiabatic and I_z ceases to vary, we find

$$\begin{aligned}\ln[\Delta_0\beta(-\Delta_0)/\Delta_0\beta(\Delta_0)] &= \ln[-I_z(-\Delta_0)/I_z(\Delta_0)] \\ &= \ln[|I_z(-\Delta_0)|/|I_z(\Delta_0)|] \\ &= -\dot{\Delta}\int_{\Delta_0}^{-\Delta_0}[D^2W(1+\Delta^2/D^2)^3]^{-1}d\Delta,\end{aligned}$$

$$\ln[|I_z(-\Delta_0)|/|I_z(\Delta_0)|] = -(2\dot{\Delta}/\omega_1^2D^2)\int_{\Delta_0}^{-\Delta_0}[(1+\Delta^2/D^2)^3g(\Delta)]^{-1}d\Delta. \quad (34)$$

This is again a function of $\omega_1^{-2}\dot{\Delta}\propto H_1^{-2}dH/dt$ which depends on the exact shape of the absorption curve $g(\Delta)$. The function under the integral diverges for large values of Δ, because of the decrease of $g(\Delta)$. This happens, however, for values of Δ far larger than Δ_0. In fact, for $\Delta\sim\Delta_0$ this function is even far smaller than for $\Delta=0$, so that the integral has a value independent, to within a percent, of the exact value of Δ_0 in the range where Δ_0 can vary.

This integral was graphically integrated for the case of CaF_2 with $\mathbf{H}_0 \parallel [100]$. The result is

$$\ln[|I_z(-\Delta_0)|/|I_z(\Delta_0)|] = -8.1\times10^{-5}\,H_1^{-2}dH/dt. \quad (35)$$

Numerical example. Let us choose $H_1=0.315$ G, that is $H_1^2=0.1$ G^2, and $dH/dt=125$ G/sec. The F^{19} gyromagnetic ratio is

$$\gamma\simeq2.5\times10^4 \text{ rad sec}^{-1}\text{ G}^{-1}.$$

We then have

$$\gamma H_1^2=20dH/dt,$$

so that condition (17) is amply satisfied. The magnetization loss due to the sudden-adiabatic transition is, after Fig. 1, equal to 7%, and the loss due to the quasiadiabatic part of the passage is, after Eq. (35), equal to 9%. The total decrease of magnetization amplitude due to the lack of adiaticity of this passage then amounts to 16%, which is quite a significant loss.

C. Magnetization Loss Due to Spin-Lattice Relaxation

Let T_D be the spin-lattice relaxation time of the spin-spin interactions and let the Zeeman spin-lattice relaxation time be infinite. The spin-lattice relaxation time T_1 in the rotating frame is then given by[11]

$$T_1^{-1}=T_D^{-1}D^2/(\Delta^2+D^2). \quad (36)$$

[11] I. Solomon and J. Ezratty, Phys. Rev. **127**, 78 (1962).

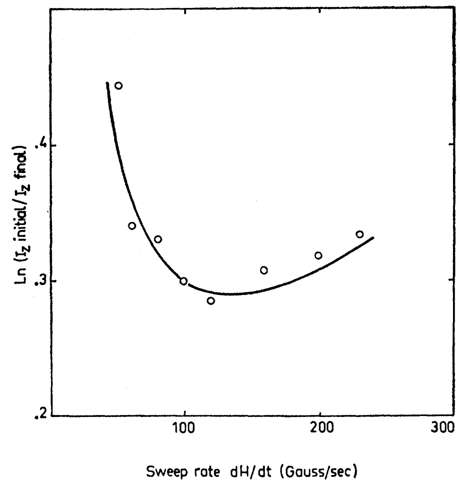

FIG. 2. Ratio of initial to final magnetizations for a fast passage in CaF_2 with $\mathbf{H}_0 \parallel [100]$ as a function of dH/dt. The rf field is $H_1=0.32$ G. The full curve is the theoretical expression (39) using the best-fit value $T_D=0.36$ sec.

The variation of β due to relaxation is

$$d\beta/dt=-\beta T_D^{-1}D^2/(\Delta^2+D^2),$$

that is,

$$d\beta/d\Delta=-\beta\dot{\Delta}^{-1}T_D^{-1}D^2/(\Delta^2+D^2). \quad (37)$$

Integrating this equation from Δ_0 to $-\Delta_0$ yields

$$\ln[|I_z(-\Delta_0)|/|I_z(\Delta_0)|]_{\text{rel}} = -(2D/T_D\dot{\Delta})\tan^{-1}(\Delta_0/D). \quad (38)$$

The quantity $\tan^{-1}(\Delta_0/D)$ varies very little within the limits of variation of Δ_0. Its value is slightly less than $\frac{1}{2}\pi$. Summing all contributions to the magnetization loss, the ratio of the magnetization amplitudes before and after the fast passage is given by

$$\ln[|I_z|_i/|I_z|_f]=\xi(H_1^{-2}dH/dt) + \eta H_1^{-2}dH/dt+\zeta T_D^{-1}(dH/dt)^{-1}, \quad (39)$$

where the three terms correspond, respectively, to the sudden-adiabatic transition, to the quasiadiabatic part of the passage, and to the effect of spin-lattice relaxation.

D. Experimental Results

The same crystal was used as for the calibration of the rf field, in the same experimental conditions. The dc field orientation was within 2° of the [100] direction, as derived from the electronic resonance field of the U^{3+} ions, whose g factor is anisotropic. The magnetization loss was determined by measuring the

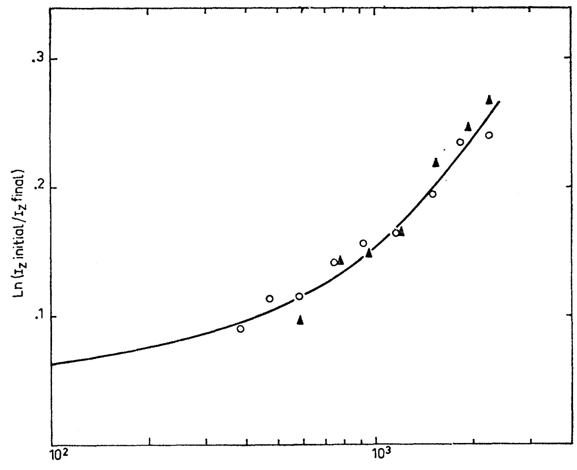

FIG. 3. Ratio of initial to final magnetizations for a fast passage in CaF_2 with $\mathbf{H}_0 \parallel [100]$, corrected for the effect of spin-lattice relaxation, as a function of $H_1^{-2}dH/dt$. The open circles correspond to $dH/dt=100$ G/sec and H_1 variable; the black triangles correspond to $H_1=0.32$G and dH/dt variable. The full curve corresponds to the computed theoretical loss.

decrease of the nuclear lock-in signal after several fast passages. Two series of experiments were performed. In the first series, the same rf field amplitude $H_1=0.32$ G was used and the sweep rate dH/dt was varied from one experiment to the other. On Fig. 2 are reported the experimental results for $\ln(I_i/I_f)$ as a function of dH/dt.

The solid curve is the computed theoretical expression (39). The only adjusted parameter was the relaxation time T_D, taken, for a best fit, equal to 0.36 sec, whereas a direct measurement of this relaxation time yielded a value of the order of 0.3 sec. At the optimum sweep rate of 120 G/sec, the magnetization after a fast passage is decreased to 75% of its initial value. This is a high loss quite unexpected on the simple grounds of condition (17). In a second series of experiments, the sweep rate was kept constantly equal to 100 G/sec, and the rf field amplitude was varied from one experiment to the other, in the range between 0.21 to 0.51 G. On Fig. 3 are reported, as a function of $H_1^{-2}dH/dt$, the experimental values of $\ln(I_i/I_f)$ corrected for the effect of spin-lattice relaxation. The open circles correspond to the experiments with variable H_1 and constant dH/dt, and the black triangles correspond to the experiments with constant H_1 and variable dH/dt. The solid curve is the theoretical loss due to the lack of adiabaticity of the passage. It corresponds to the terms $\xi+\eta H_1^{-2}dH/dt$ of Eq. (39). It was not possible to use rf field amplitudes smaller than 0.2 G, because the losses then became excessive and the theory, developed for the case of nearly adiabatic fast passages, ceased to be valid. Neither was it possible to use rf field amplitudes much larger than 0.5 G, since they would then be no longer small compared with the local field, equal to 2.08 G. and the Provotorov equations would cease to be valid,

Using large rf field amplitudes evidently decreases the loss, which can be of interest for practical purposes. Such situations cannot be treated with the present theory.

IV. CONCLUSION

We have developed an analysis of the magnetization loss in a nuclear spin system under the effect of a single-shot passage in two limiting cases: that of a passage whose only effect is a slight saturation of the system, and that of a nearly adiabatic passage, which results in a reversal of the magnetization at a small cost in its amplitude.

The first type of passage presents little theoretical problem and provides a simple practical method for calibrating the rf field amplitude in a nuclear-magnetic-resonance coil, where the sample itself to be studied is used as a testing probe.

The second type, the fast passage, is a fundamental tool in magnetic resonance, very commonly used to reverse the magnetization or to measure its amplitude by observing the dispersion signal on the run, whose main advantage lies in the possibility of restoring in principle the system to its unperturbed initial state by reversing back the magnetization with a second fast passage. As is apparent from the present work the magnetization loss is definitely higher than might be expected at first sight and very often it is far from negligible. The theory offers a quantitative way of determining this loss in practical applications. The calculation of the losses is based on the use of Provotorov equations. It is an illustration of their usefulness for practical purposes, and the experimental verification provides a quantitative confirmation of their validity.

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