which indicates that the parameter associated with $\langle r^6\rangle$ has much less effect on the level splittings than the one with $\langle r^4\rangle$. It is interesting to see if the relation $\mathcal{R}\ll\mathcal{P}$ is borne out by the point-charge picture. Using Eq. (7) of Ref. 5, we write

$$\mathcal{P}/\mathcal{R}=-11.7R^2\alpha_s\langle r^4\rangle/\alpha_s'\langle r^6\rangle\,, \tag{4}$$

where $R$ is the distance between $Yb^{3+}$ and its nearest neighbors, $\alpha_s$ and $\alpha_s'$ are two screening factors as defined by Eqs. (2)–(6) of Ref. 5. An estimate of Eq. (4) can be made if we use the values of $\langle r^4\rangle$ and $\langle r^6\rangle$ calculated by Freeman and Watson[12] and set $\alpha_s=\alpha_s'$. This gives $\mathcal{P}/\mathcal{R}=-74$. The ratio of $\mathcal{P}$ to $\mathcal{R}$ as calculated from the point-charge picture is, therefore, in qualitative agreement with the experimental results.

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[12] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

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# Dynamic Polarization by Thermal Mixing between Two Spin Systems

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A new dynamic nuclear polarization method is described, producing polarizations larger than the maximum polarization arising from a "solid effect." The main effect is a cooling of a spin system $I$ in zero applied or effective field, where its Hamiltonian consists of its dipolar spin-spin interactions only; this cooling is followed by an adiabatic magnetization which produces the polarization. The cooling of the spin system $I$ results from its thermal mixing with a second spin system $S$, having a large quadrupole interaction. Two types of experiments are considered: In zero applied field the thermal mixing is achieved in a frame rotating with respect to spins $S$ and fixed with respect to spins $I$, by irradiating the sample with an rf field of frequency close to the quadrupole frequency of the spins $S$. When a dc field is applied, the mixing takes place in a frame rotating at different frequencies with respect to spins $I$ and $S$, by using two rf fields of frequencies close, respectively, to the resonance frequency of each spin system. The theory is based entirely upon the concept of spin temperature, both in laboratory and rotating frames. Experiments performed on paradichlorobenzene confirm the main features of the theory and provide a further verification of the spin-temperature hypothesis. A maximum proton polarization eight times larger than the polarization arising from a full solid effect has been obtained.

## I. INTRODUCTION

CONTACT between two spin systems in solids has been achieved in the past in various magnetic resonance experiments, where the magnetization of one spin system was influenced by the magnetization of the second one.

Among these are the nuclear calorimetry experiments in lithium fluoride,[1,2] the crossover of two resonance frequencies,[3,4] and the "solid effect," either in the laboratory frame[5] or in the rotating frame.[6] We shall see that all these experiments can be interpreted as thermal mixings, i.e., as the equalization of the temperatures of two systems.

In this description, the dynamic polarization by "solid effect" then appears as the cooling of a spin system. As this spin system experiences a magnetic field, such a cooling results in an enhancement of its polarization.

In the present work, we describe experiments of cooling of a spin system in low or even zero field through thermal mixing with a second spin system.[7] When performed in zero field, this cooling does not produce any polarization. However, the resulting increase of order is conserved if an adiabatic magnetization is performed afterwards, giving rise to a polarization. In contrast with the solid effect, cooling and production of polarization thus take place in two consecutive steps.

These experiments are performed under "low-field" conditions, i.e., when the effective energies of individual spins are comparable with the spin-spin interactions. In contradistinction, "high-field" conditions are realized

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

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

[3] M. Goldman, Compt. Rend. **246**, 1038 (1958).

[4] D. E. Woessner and H. S. Gutowsky, J. Chem. Phys. **29**, 804 (1958).

[5] A. Abragam and W. G. Proctor, Compt. Rend. **246**, 2253 (1958).

[6] N. Bloembergen and P. P. Sorokin, Phys. Rev. **110**, 865 (1958).

[7] M. Goldman and A. Landesman, Compt. Rend. **252**, 263 (1961); and M. Goldman, in *Magnetic and Electric Resonance and Relaxation* (North-Holland Publishing Company, Amsterdam, 1963), p. 688.

when the spin-spin interactions are small compared with the effective energies of individual spins arising from either Zeeman or quadrupole interactions. Low-field conditions can be analyzed only through the use of the concept of spin temperature. The fruitfulness of this concept when used in the laboratory frame has been emphasized by Abragam and Proctor,[1] and in the rotating frame by Redfield.[8]

Before describing our experiments, we discuss the conditions for thermal mixing between two spin systems.

## II. ANALYSIS OF THERMAL MIXING

Thermal mixing between two spin systems occurs when mutual flip processes, induced by spin-spin interactions between these systems, can take place without change of the total energy. The two systems can then be brought to a common temperature in a time much shorter than their spin-lattice relaxation times.

The conditions for such energy conserving mutual flip processes are realized in the crossover between two resonance frequencies. Experiments of this type have been performed on paradichlorobenzene,[3,4] and resulted in a shortening of the proton spin-lattice relaxation time. These same conditions are realized when both spin systems are in low field, as shown by the nuclear calorimetry experiments on lithium fluoride.[1,2] These low-field experiments differ from the high-field crossover experiment previously mentioned insofar that the spin-spin energy and the Zeeman energy of the interacting spins are now comparable. Whereas the crossover experiment, in which the energy spectra of the interacting spin systems were quasidiscrete, could be described if desired without making explicit use of the concept of spin temperature, this cannot be avoided when the two spin systems have continuous spectra.

The "solid effect,"[5] which produces an equalization of the polarizations of two spin systems $I$ and $S$ in a dc magnetic field $H_0$, by use of an rf field of frequency $\omega=\omega_S\pm\omega_I$ can be described in the spin-temperature language.[9] The "solid effect" is then interpreted as a crossover in a frame fixed with respect to spins $I$ and rotating at the frequency $\omega$ with respect to the spins $S$. In this frame, the effective resonance frequency of the spins $S$ is indeed $|\omega_I|$, and their equilibrium polarization corresponds to a spin temperature

$$T_S=\mp T_0(\omega_I/\omega_S),$$

where $T_0$ is the lattice temperature.

The spins $I$, having a longer spin-lattice relaxation time than the spins $S$, reach by thermal mixing this same spin temperature $T_S$. The solid effect then appears as a cooling of the spins $I$, resulting in an enhancement of their polarization. The solid effect in the rotating frame[6] is similarly described as a crossover in a frame rotating at different frequencies with respect to spins $I$ and $S$. In these solid-effect experiments, all the effective Larmor frequencies are large compared with the linewidths, and this is a high-field situation.

TABLE I. Thermal mixing experiments between two spin systems $I$ and $S$.

| Equalization of spin temperature in following frames | | | |
|---|---|---|---|
| For spins $I$ | For spins $S$ | "High-field" situation | "Low-field" situation |
| Fixed | Fixed | (A) Crossover[a] | (B) Nuclear calorimetry in low field[d] |
| Fixed | Rotating | (C) Solid effect in the laboratory frame[b] | Present work Sec. IIIA |
| Rotating | Rotating | (D) Solid effect in the rotating frame[c] | Present work Sec. IIIB |

[a] See Ref. 3.
[b] See Ref. 5.
[c] See Ref. 6.
[d] See Ref. 1.

The mixing method of Hartmann and Hahn[10] also consists in mixing two spin species in high effective fields in a frame rotating at different frequencies with respect to each spin species.

All these mixing experiments can be summarized in tabular form (Table I). Experiments (A), (C), and (D) are all concerned with high-field situations. Experiment (B) is the analog of experiment (A) in a low-field situation. The experiments to be described in this work are similarly the "low-field" analogs of experiments (C) and (D). They realize thermal mixings in a "low-field" situation either in a frame rotating with respect to one spin only as in (C) or in a frame rotating differently with respect to each spin as in (D).

## III. LOW-FIELD MIXING IN ROTATING FRAMES

### A. Thermal Mixing in a Frame Rotating with Respect to One Spin System and Fixed with Respect to the Other

We consider a crystal with two nuclear species $I$ and $S$: The nuclei $I$ have a spin $\frac{1}{2}$, a gyromagnetic ratio $\gamma_I$, and a long spin-lattice relaxation time $T_1{}^I$. The nuclei $S$ have a spin $\frac{3}{2}$, a pure quadrupole frequency $\Omega_0$, and a gyromagnetic ratio $\gamma_S\ll\gamma_I$. Their spin-lattice relaxation time $T_1{}^S$ is short compared with $T_1{}^I$.

The experiment essentially consists in a cooling of the spins $I$ in zero field, through their thermal coupling with the spins $S$. Polarization of the spins $I$ is produced in a second step, by an adiabatic magnetization.

We begin by outlining briefly the principle of this cooling. Then we analyze in more detail the existence of a spin temperature in the rotating frame and its steady-state value, calculate the polarization arising from the adiabatic magnetization, and compare this polarization method with the solid effect.

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

[9] I. Solomon, in *Magnetic and Electric Resonance and Relaxation* (North-Holland Publishing Company, Amsterdam, 1963), p. 25.

[10] S. R. Hartmann and E. L. Hahn, Phys. Rev. **128**, 2042 (1962).

### *Principle of the Cooling Process*

The crystal being in zero dc magnetic field, we apply a strong rf field $2H_1 \cos\Omega t$, $\Omega$ being close to the quadrupole resonance frequency $\Omega_0$ of the spins $S$. Following Redfield we are led to use an interaction representation in which the effective Hamiltonian is time-independent. This representation defines a frame which is fixed with respect to the spins $I$ and rotating with respect to the spins $S$. In this frame, all splittings are comparable with the spin-spin interactions, thus ensuring the fast establishment of a spin temperature common both to spins $I$ and spins $S$. As in the Zeeman case, the steady-state spin temperature $T_S$ is much lower than the lattice temperature $T_0$. An adiabatic magnetization following this cooling decouples the two spin systems $I$ and $S$, and brings out a polarization of the spins $I$ proportional to $1/T_S$.

### *Existence of a Spin Temperature in the Rotating Frame*

For the sake of simplicity, we make the following assumptions which do not affect the general conclusions: The only spin-spin interactions are the dipolar interactions. Since $\gamma_S \ll \gamma_I$ we neglect the dipolar interactions $\mathcal{H}_{SS}$ between pairs of spins $S$ with respect to the dipolar interactions $\mathcal{H}_{II}$ and $\mathcal{H}_{SI}$.

The field gradient experienced by the spins $S$ is axially symmetric along a direction $OZ$.

The rf field is applied along a direction $OX$ perpendicular to $OZ$.

Neglecting the spin-lattice interactions for the moment, the Hamiltonian for the system is $\hbar\mathcal{H}$:

$$\mathcal{H} = \mathcal{H}_0 - 2\gamma_S H_1 \cos\Omega t \textstyle\sum_i S_x{}^i, \tag{1}$$

$$\mathcal{H}_0 = \tfrac{1}{2}\Omega_0 \textstyle\sum_i \left[S_z{}^{i2} - \tfrac{1}{3}S(S+1)\right] + \mathcal{H}_{SI} + \mathcal{H}_{II}. \tag{2}$$

The density matrix $\sigma$ describing this system obeys the equation

$$i(d\sigma/dt) = [\mathcal{H},\sigma]. \tag{3}$$

We transform this time-dependent Hamiltonian problem into a stationary Hamiltonian problem by use of an interaction representation defined by a unitary operator $U = e^{iAt}$, where

$$A = \tfrac{1}{2}\Omega \textstyle\sum_i \left[S_z{}^{i2} - \tfrac{1}{3}S(S+1)\right]. \tag{4}$$

Any operator $Q$ in the Schrödinger representation is replaced in this representation by an operator $\tilde{Q} = UQU^\dagger$.

Equation (3) is replaced by

$$i(d/dt)\tilde{\sigma} = [(\tilde{\mathcal{H}} - A), \tilde{\sigma}]. \tag{5}$$

The time-dependent part of $\tilde{\mathcal{H}}$ contains terms oscillating at frequencies $\Omega$ and $2\Omega$ which are far from any resonance frequency in the interaction representation, and they are discarded as usual.[8,11] The evolution of $\tilde{\sigma}$ is governed by the effective Hamiltonian:

$$\mathcal{H}^* = \textstyle\sum_i \{\tfrac{1}{2}(\Omega_0 - \Omega)[S_z{}^{i2} - \tfrac{1}{3}S(S+1)] - \gamma_S H_1 \mathcal{S}_x{}^i\} + \mathcal{H}_{SI}' + \mathcal{H}_{II}. \tag{6}$$

$\mathcal{S}_x{}^i$ is obtained by removing from $S_x{}^i$ the matrix elements $\langle \pm 1/2 | S_x{}^i | \mp 1/2 \rangle$ which lead to oscillating terms. $\mathcal{H}_{SI}'$ is the part of $\mathcal{H}_{SI}$ which commutes with $S_z{}^{i2}$.

The use of this interaction representation is the complete analog of the use of a rotating frame in a pure Zeeman case, the rotation operator being here replaced by the operator $U$, which provides no simple geometric picture. Nevertheless, we speak of a rotating frame when using this interaction representation. The effective quadrupole splitting $(\Omega_0 - \Omega)$ being comparable with the dipolar interactions, we are in a situation comparable with the low-field situation in the pure Zeeman case.

In the Hamiltonian $\mathcal{H}^*$, the term $-\gamma_S H_1 \mathcal{S}_x{}^i$ commutes neither with $(S_z{}^i)^2$ nor with $\mathcal{H}_{SI}'$, thus coupling them with a mixing time $\theta_1$ depending on $H_1$.[12] Similarly, these terms are coupled with $\mathcal{H}_{II}$ through $\mathcal{H}_{SI}'$, the mixing time $\theta_2$ being roughly the $I$-$S$ mutual flip time. Following Redfield, we assume the system to be described by a single spin temperature $T_S$ after a time longer than both of these mixing times.

The density matrix at equilibrium is, in the high-temperature approximation,

$$\tilde{\sigma} = ([1] - \beta_S \mathcal{H}^*)/\mathrm{Tr}[1], \tag{7}$$

where $\beta_S = (1/kT_S)$.

### *Steady-State Spin Temperature*

If the spin-lattice interaction were absent, the system would reach a spin temperature in a time of the order of $\theta_1$ or $\theta_2$. We suppose that the spin-lattice interaction is weak enough for its influence on $\tilde{\sigma}$ to be negligible during this time, i.e.,

$$T_1{}^S \gg \theta_1, \theta_2. \tag{8}$$

We then assume that the system is at any time nearly described by a spin temperature, the effect of spin-lattice relaxation resulting only in a slow variation of this temperature.

The condition $T_1{}^S \gg \theta_1$ means that $H_1$ must be well above the saturation level. The condition $T_1{}^S \gg \theta_2$ is an absolute limitation for $T_1{}^S$, since the mutual flip time $\theta_2$ depends only on dipolar interactions.

We outline the principle of calculation of the spin temperature, following the treatment given by Abragam.[11]

Let $\mathcal{H}_1(t)$ be the randomly varying spin Hamiltonian responsible for spin-lattice relaxation. We suppose that its correlation time $\tau_c$ is short, which is inessential for the conclusion.

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[11] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, England, 1961), Chap. XII.

[12] B. N. Provotorov, Zh. Eksperim. i Teor. Fiz. **41**, 1582 (1961) [translation: Soviet Phys.—JETP **14**, 1126 (1962)].

The equation of motion for the density matrix in the interaction representation is

$$\frac{d}{dt}\tilde{\sigma}=-i[\mathcal{H}^*,\tilde{\sigma}]-\tau_c\langle[\tilde{\mathcal{H}}_1(t),[\tilde{\mathcal{H}}_1(t),(\tilde{\sigma}-\sigma_0)]]\rangle_{\text{av}}, \qquad (9)$$

where $\langle\ \rangle_{\text{av}}$ means an ensemble average. The density matrix $\sigma_0$ is

$$\sigma_0\propto[1]-\beta_0\mathcal{H}_0,$$

with $\beta_0=1/kT_0$, $T_0$ being the lattice temperature.

The assumption that a spin temperature exists at any moment, i.e., that

$$\tilde{\sigma}\propto[1]-\beta_S\mathcal{H}^*,$$

leads to the following equation for the evolution of $\beta_S$:

$$(d\beta_S/dt)\operatorname{Tr}\mathcal{H}^{*2}=-\beta_S\tau_c\operatorname{Tr}\langle[\mathcal{H}^*,\tilde{\mathcal{H}}_1][\tilde{\mathcal{H}}_1,\mathcal{H}^*]\rangle_{\text{av}} +\beta_0\tau_c\operatorname{Tr}\langle[\mathcal{H}^*,\tilde{\mathcal{H}}_1][\tilde{\mathcal{H}}_1,\mathcal{H}_0]\rangle_{\text{av}}. \qquad (10)$$

The straightforward calculation of these traces, using a definite spin-lattice Hamiltonian $\mathcal{H}_1(t)$, yields the rate of variation of $\beta_S$ and its equilibrium value.

As shown by Solomon and Ezratty,[13] a physical picture of this evolution can be obtained by analyzing Eq. (9). We separate the effective Hamiltonian $\mathcal{H}^*$ in a sum of four operators, the cross products of which are traceless,

$$\mathcal{H}^*=Q+Z+\mathcal{H}_{IS}'+\mathcal{H}_{II}. \qquad (11)$$

$Q$ is the effective quadrupole interaction

$$Q=\tfrac{1}{2}(\Omega_0-\Omega)\textstyle\sum_i[S_z^{i2}-\tfrac{1}{3}S(S+1)]. \qquad (12)$$

$Z$ is the effective Zeeman interaction

$$Z=-\gamma_S H_1\textstyle\sum_i S_x^i. \qquad (13)$$

$\mathcal{H}_{IS}'$ and $\mathcal{H}_{II}$ have been defined earlier. As $T_1^I$ is assumed to be infinite, the Hamiltonian $\mathcal{H}_1(t)$ depends on spin operators of nuclei $S$ only. The heat capacities of these four parts are, respectively, $\operatorname{Tr}Q^2$, $\operatorname{Tr}Z^2$, $\operatorname{Tr}\mathcal{H}_{IS}'^2$, and $\operatorname{Tr}\mathcal{H}_{II}^2$.

Under very general assumptions, it can be shown that relaxation acts independently on the parts $Q$, $Z$, $\mathcal{H}_{IS}'$, with relaxation times $T_1^S$, $T_Z$, and $T_D$ which are of the same order of magnitude. The part $Q$ relaxes toward the value

$$Q_0=-\beta_0\frac{\Omega_0}{\Omega_0-\Omega}\operatorname{Tr}Q^2, \qquad (14)$$

which is the equilibrium value corresponding to the low temperature $T_0(\Omega_0-\Omega)/\Omega_0$, whereas the parts $Z$ and $\mathcal{H}_{IS}'$ relax toward values corresponding to lattice temperature $T_0$.

Since we assume the entire system to be described by a single spin temperature $T_S=1/\beta_S$, the steady-state value of this temperature is a weighed average,

$$\beta_S=\left[\beta_0\left(\frac{\Omega_0}{\Omega_0-\Omega}\right)\frac{\operatorname{Tr}Q^2}{T_1^S}+\beta_0\frac{\operatorname{Tr}Z^2}{T_Z}+\beta_0\frac{\operatorname{Tr}\mathcal{H}_{IS}'^2}{T_D}\right] \Big/\left(\frac{\operatorname{Tr}Q^2}{T_1^S}+\frac{\operatorname{Tr}Z^2}{T_Z}+\frac{\operatorname{Tr}\mathcal{H}_{IS}'^2}{T_D}\right). \qquad (15)$$

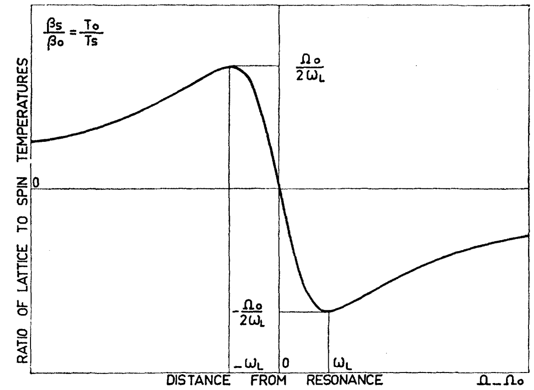

FIG. 1. Theoretical variation of the equilibrium ratio of lattice to spin temperatures with the frequency $\Omega$ of the rf field producing the mixing.

Since the term $\beta_0[\Omega_0/(\Omega_0-\Omega)](\operatorname{Tr}Q^2)/T_1^S$ is the dominant term in the numerator because of the large factor $\Omega_0/(\Omega_0-\Omega)$, this expression can be written

$$\frac{\beta_S}{\beta_0}=\frac{\Omega_0(\Omega_0-\Omega)}{(\Omega_0-\Omega)^2+\lambda^2\gamma_S^2H_1^2+\omega_L^2}, \qquad (16)$$

with

$$\lambda^2=\frac{4T_1^S}{T_Z}\frac{\sum_i \operatorname{Tr}S_x^{i2}}{\sum_i\operatorname{Tr}[S_z^{i2}-\frac{1}{3}S(S+1)]^2}, \qquad (17)$$

$$\omega_L^2=\frac{4T_1^S}{T_D}\frac{\operatorname{Tr}\mathcal{H}_{IS}'^2}{\sum_i\operatorname{Tr}[S_z^{i2}-\frac{1}{3}S(S+1)]^2}. \qquad (18)$$

The relaxation of $Z$ and $\mathcal{H}_{IS}'$ toward the lattice temperature thus appears as the factor limiting the maximum value $\beta_S$ can reach. The basic point is that the large term $\mathcal{H}_{II}$, because of its infinitely long relaxation time $T_1^I$, does not contribute to this limitation.

The orders of magnitude of $\lambda^2$ and $\omega_L^2$ are

$$\lambda^2\sim1,$$
$$\omega_L^2\sim\hbar^2\gamma_S^2\gamma_I^2r_{IS}^{-6},$$

as shown in the Appendix by explicit calculations performed with a definite model for the spin-lattice interaction.

Equation (16), which describes the variation of the equilibrium value of $\beta_S$ with the irradiation frequency $\Omega$, is of the usual type encountered in pure Zeeman case experiments. This variation is represented in Fig. 1. $|\beta_S|$ reaches its maximum value when

$$(\Omega_0-\Omega)^2=\lambda^2\gamma_S^2H_1^2+\omega_L^2.$$

If

$$\omega_L^2\gg\lambda^2\gamma_S^2H_1^2,$$

then

$$|\beta_S|_{\max}=\beta_0(\Omega_0/2\omega_L). \qquad (19)$$

Taking into account the direct relaxation of spins $I$ leads to terms in $\mathcal{H}_1$ depending on spin operators of nuclei $I$. Following the picture, we can say that the part

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

$\mathcal{H}_{II}$ relaxes toward the lattice temperature with a partial relaxation time $T_1{}^I$. This results in an increase of the local frequency $\omega_L$, and thus in a decrease of $|\beta_S|_{\max}$. The condition for the increase of $\omega_L$ to be small is roughly

$$T_1{}^I/T_1{}^S \gg \mathrm{Tr}\mathcal{H}_{II}{}^2/\mathrm{Tr}\mathcal{H}_{IS}'^2. \tag{20}$$

It is assumed to be fulfilled.

### *Polarization Arising from the Adiabatic Magnetization. Comparison with the "Solid Effect"*

The result of an irradiation at a frequency close to the spin $S$ quadrupole resonance frequency has been a cooling of the system to a temperature $T_S \ll T_0$. The introduction of a magnetic field $H$ decouples the spins $I$ from the spins $S$. The spins $I$ are still described by a spin temperature

$$\beta_S \propto [\omega_D{}^2 + \gamma_I{}^2 H^2]^{-1/2}, \tag{21}$$

where $\omega_D$ is the local frequency corresponding to the heat capacity of the system at zero field. This second local frequency $\omega_D$ is thus completely different from $\omega_L$, which depends on the spin-lattice relaxation mechanism.

As long as $(\Omega_0 - \Omega)$ is of the order of $\omega_L$, the dominant contribution to the heat capacity is given by the term $\mathcal{H}_{II}$. We then have

$$\omega_D{}^2 \approx \frac{\mathrm{Tr}\mathcal{H}_{II}{}^2}{\sum \mathrm{Tr} I_z{}^2} \tag{22}$$

and

$$\left(\frac{\omega_D}{\omega_L}\right)^2 \sim \frac{\mathrm{Tr}\mathcal{H}_{II}{}^2}{\mathrm{Tr}\mathcal{H}_{IS}'^2} \times \frac{\sum \mathrm{Tr}[S_z{}^2 - \frac{1}{3}S(S+1)]^2}{\sum \mathrm{Tr} I_z{}^2}.$$

If the distances $I$-$I$ and $I$-$S$ between pairs of like spins and unlike spins are of the same order, we have further

$$\omega_D/\omega_L \sim \gamma_I/\gamma_S.$$

In a field $H_0 \gg \omega_D/\gamma_I$, the spin temperature of the spins $I$ is, from formula (21)

$$(\beta_S)_{H_0} = (\beta_S)_0 \omega_D/\gamma_I H_0. \tag{23}$$

The corresponding polarization is

$$P = \tfrac{1}{2}(\beta_S)_{H_0} \hbar \gamma_I H_0 = \tfrac{1}{2}(\beta_S)_0 \hbar \omega_D. \tag{24}$$

The only effect of the external magnetic field is to make the fields seen by individual spins almost parallel, thus bringing out a bulk polarization.[14] The polarization of spins $I$ in field $H_0$ is proportional to the spin temperature $(\beta_S)_0$ realized in zero field; its measurement then allows a determination of $(\beta_S)_0$.

The maximum polarization, corresponding to

$$(\beta_S)_0 = |\beta_S|_{\max} = \beta_0(\Omega_0/2\omega_L)$$

is

$$|P_{\max}| = \tfrac{1}{2}|\beta_S|_{\max} \hbar \omega_D = \tfrac{1}{2}\beta_0 \hbar \Omega_0 (\omega_D/2\omega_L). \tag{25}$$

Since

$$(\omega_D/\omega_L) \sim (\gamma_I/\gamma_S),$$

then

$$|P_{\max}| \sim \tfrac{1}{2}\beta_0 \hbar \Omega_0 (\gamma_I/2\gamma_S).$$

Since the magnetic field decouples the spins $I$ from the spins $S$, this polarization then decays to the equilibrium value at the lattice temperature $T_0$ with the relaxation time $T_1{}^I$.

By comparison, a "solid effect" performed in a field $H_0$ where the resonance frequency $\Omega_0'$ of the spins $S$ is nearly equal to $\Omega_0$ yields, for the spins $I$, a maximum polarization

$$P = \tfrac{1}{2}\beta_0 \hbar \Omega_0' \approx \tfrac{1}{2}\beta_0 \hbar \Omega_0.$$

The Zeeman splitting $\gamma_I H_0$ of the spins $I$ being large compared with the local fields, thermal mixing will occur with the spins $S$ only if the effective splitting of the latter is equal to $\gamma_I H_0$

$$|\Omega_0' - \Omega| = \gamma_I H_0. \tag{26}$$

This condition limits the temperature the spins $S$ are allowed to reach, to the value

$$\beta_S = \beta_0 \Omega_0'/(\Omega_0' - \Omega) = \beta_0(\Omega_0'/\gamma_I H_0).$$

In the present experiment, the quasicontinuous character of the spectra in low fields allows a mixing to occur without condition (26) being fulfilled. Thus, we can choose the value $\Omega = \Omega_0 \pm \omega_L$, for which the spin temperature is minimum. The maximum polarization is here larger than that for a solid effect, the enhancement factor being

$$G = \tfrac{1}{2}(\omega_D/\omega_L) \sim \tfrac{1}{2}(\gamma_I/\gamma_S) > 1$$

since

$$\gamma_I \gg \gamma_S.$$

The new feature of this polarization process, with respect to known polarization methods is that the resulting ratio of populations between the levels of the spins $I$ is larger, by a factor $\frac{1}{2}(\omega_D/\omega_L)$, than the ratio of populations between the levels of the spins $S$ which are used to polarize the spins $I$.

### *Summary of Experimental Conditions*

Cooling is achieved and gives rise to a polarization of the spins $I$ larger than the solid effect if the following conditions are fulfilled: (1) $\gamma_S \ll \gamma_I$: The spins $S$ must be a nuclear species. (2) The spins $S$ must have a zero-field splitting, which can only result from a quadrupole interaction. (3) The spin-lattice relaxation time $T_1{}^S$ of the spins $S$ must be longer than the mutual flip time $\theta_2$ between a spin $I$ and a spin $S$. This condition can always be satisfied by lowering the lattice temperature, which increases $T_1{}^S$. (4) The spin-lattice relaxation time $T_1{}^I$ of spins $I$ must be very much longer than the relaxation time $T_1{}^S$ of spins $S$.

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[14] C. P. Slichter and W. C. Holton, Phys. Rev. **122**, 1701 (1961).

More precisely [Eq. (20)], one has

$$\frac{T_1{}^I}{T_1{}^S} \gg \frac{\mathrm{Tr}\mathcal{H}_{II}{}^2}{\mathrm{Tr}\mathcal{H}_{IS}{}'^2} = \frac{N_I \sum_k \mathrm{Tr}\mathcal{H}_{I^jI^k}{}^2}{N_S \sum_k \mathrm{Tr}\mathcal{H}_{S^iI^k}{}'^2},$$

where $N_I$ and $N_S$ are the numbers of spins $I$ and spins $S$ in the sample.

The relaxation of the spins $S$ occurs through their quadrupole interaction with the lattice vibrations, whereas the relaxation of the spins $I$ is due to the paramagnetic impurities of the sample. $T_1{}^S$ is then expected to increase faster than $T_1{}^I$ when the lattice temperature is lowered, thus decreasing the ratio $(T_1{}^I/T_1{}^S)$. For a given sample, conditions (3) and (4) are then simultaneously fulfilled only in a limited range of lattice temperatures.

### *Extensions of the Theory*

We examine briefly how the theory has to be modified in several experimental conditions slightly different from that already analyzed. These modified cases are (i) Mixing performed when the saturation by the rf field is incomplete. (ii) Mixing performed in a low-external magnetic field. (iii) Mixing performed with an inhomogeneously broadened quadrupole line.

*(i) Mixing performed when saturation is incomplete.* If the rf field $H_1$ is small, the mixing time $\theta_1$ between the effective quadrupole term and the dipolar term is not infinitely short compared with the spin-lattice relaxation time $T_1{}^S$. On the other hand, the heat capacity of the term $Z$ in Eq. (11) is now small with respect to the heat capacities of the other terms. Extending to the quadrupole case the analysis made by Provotorov[12] in the Zeeman case, we assume the density matrix to be of the form

$$\tilde{\sigma} \propto [1] - \alpha Q - \beta(\mathcal{H}_{IS}{}' + \mathcal{H}_{II}).$$

A perturbation treatment of Eq. (9) yields coupled equations for the evolution of $\alpha$ and $\beta$. In the steady state one finds the following value for the inverse spin temperature of the dipolar part

$$\frac{\beta}{\beta_0} = \frac{\Omega_0(\Omega_0-\Omega)}{(\Omega_0-\Omega)^2+\omega_L{}^2(1+\theta_1/T_1{}^S)}, \tag{27}$$

where $1/\theta_1 = 3\gamma_S{}^2H_1{}^2g(\Omega_0-\Omega)$, $g(\Omega_0-\Omega)$ being the normalized line shape of the quadrupole resonance absorption line. As expected, for any value of $\Omega_0-\Omega$, this equilibrium inverse spin temperature is smaller than in the strong saturation case previously developed $(\theta_0/T_1{}^S \ll 1)$. We also show that the maximum of $\beta$ occurs for a value of $|\Omega_0-\Omega|$ smaller than $\omega_L$.

The dipolar broadening of the quadrupole line of the spins $S$ is due to the truncated $I$-$S$ dipolar interaction $\mathcal{H}_{IS}{}'$. Its second moment, $M_2 = -\mathrm{Tr}[\mathcal{S}_x, \mathcal{H}_{IS}{}']^2/\mathrm{Tr}\mathcal{S}_x{}^2$, is close to $\omega_L{}^2$. However, since $\gamma_I \gg \gamma_S$, the fourth moment $M_4$ of the line is much larger than $(M_2)^2$. The quadrupole line is then quasi-Lorentzian, with a half-width $\sigma$ smaller than the rms half-width $(M_2)^{1/2}$. The value of $\sigma$ is given by[15]

$$\frac{\sigma}{(M_2)^{1/2}} \approx \left[\frac{(M_2)^2}{M_4}\right]^{1/2} \sim \frac{\gamma_S}{\gamma_I}.$$

The normalized line shape is then

$$g(\Omega_0-\Omega) = \frac{\sigma}{\pi}\frac{1}{(\Omega_0-\Omega)^2+\sigma^2}$$

and

$$\frac{1}{\theta_1} = \frac{3}{\pi}\gamma_S{}^2H_1{}^2\frac{\sigma}{(\Omega_0-\Omega)^2+\sigma^2}.$$

When this value of $1/\theta_1$ is inserted in Eq. (27), it is readily seen that the maximum of $\beta$ occurs for a value of $|\Omega_0-\Omega|$ which decreases from $\omega_L$, when $\theta_1/T_1{}^S \ll 1$, to $\sigma$ when $H_1$ is so small that $\theta_1/T_1{}^S \gg 1$.

*(ii) Mixing performed in a low external magnetic field.* In a magnetic field $H$, the quadrupole levels of the spins $S$ are split by the Zeeman interaction, giving rise to four resonance lines. If the field is low, the frequency separation between these lines is not very much larger than the dipolar width of each line. All lines then contribute to the cooling when an rf field is applied. Following the lines of Provotorov's theory the contribution to the cooling is more important from the lines the resonance frequency of which is closer to the rf field frequency. Cooling will occur in a broader frequency range than in zero field, covering all resonance frequencies of spins $S$. On the other hand, the heat capacity of the spins $I$ system is now larger than in zero field, being proportional to $(\gamma_I{}^2H^2+\omega_D{}^2)$.

The polarization of the spins $I$, after an adiabatic magnetization performed up to a high field $H_0$ is now

$$P = \tfrac{1}{2}(\beta_S)_H\hbar[\gamma_I{}^2H^2+\omega_D{}^2]^{1/2}.$$

This polarization may be larger than that achieved by mixing in zero field, depending upon the value of $(\beta_S)_H$ resulting from the mixing in field $H$. The field $H$ at which the mixing is performed cannot be raised indefinitely; the mixing gives rise to a cooling of the dipolar interactions of the spins $I$, which must get mixed with their Zeeman interaction in order to produce a polarization of the spins $I$. The mixing rate between dipolar and Zeeman interactions decreases very quickly when the field $H$ is raised, being approximately a Gaussian function of the field. A maximum polarization is expected to occur for a value of $H$ of the order, or a few times larger, than $(\omega_D/\gamma_I)$.

*(iii) Mixing performed with an inhomogeneously broadened quadrupole line.* When imperfections are present in the crystal, the quadrupole line of the spins $S$ is inhomogeneously broadened. Its width may be far

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[15] See Ref. 11, p. 124.

larger than the dipolar linewidth. Since the mixing rate between quadrupolar and dipolar terms decreases very quickly when the effective quadrupole splitting is increased, only those spin packets, the resonance frequency of which is close to the frequency of the rf field, get mixed to the dipolar part and contribute to its cooling. They give rise to a differential effect. These "efficient" packets correspond to a small fraction of the total number of spins $S$. The heat capacity of the part $Q$ of these packets is then small compared to the heat capacity of the dipolar part, which corresponds to all spins $S$. The combination of differential effect and small heat capacity leads to a drastic decrease of the polarization of the spins $I$ produced by the mixing, as soon as the inhomogeneous linewidth is several times larger than the dipolar linewidth.

### B. Thermal Mixing in a Frame Rotating at Frequencies Different for Each Spin System

We have seen in the preceding experiment how it was possible to realize a thermal mixing between a spin system $I$ in a zero field situation and a spin system $S$ in a high-field situation by bringing the latter into a low effective field. This was done by applying an rf field at a frequency $\Omega$ close to the resonance frequency of the spins $S$ and using a frame rotating at the frequency $\Omega$ with respect to the spins $S$.

If the crystal is in a dc magnetic field $H_0$ high enough for the Zeeman interactions $\omega_I=-\gamma_I H_0$ and $\omega_S=-\gamma_S H_0$ to be large compared with the dipolar interactions, both spin systems are in high-field situations. In order to realize a low-field thermal mixing between the spins $I$ and the spins $S$, it is then necessary to bring both spin systems to low-effective-field situations. This is performed for the spins $I$ by applying an rf field of frequency $\omega$ close to the resonance frequency $\omega_I$ of the spins $I$, and by using a frame rotating at the frequency $\omega$ with respect to the spins $I$.

The spins $S$ being subjected to quadrupole as well as Zeeman interactions, their levels are unequally spaced. We apply a second rf field of frequency $\Omega$ close to one resonance frequency $\Omega_S$ and we use a frame rotating at the frequency $\Omega$ with respect to the spins $S$. The effective Hamiltonian in this rotating frame corresponds to a small splitting only between the levels $|a\rangle$ and $|b\rangle$ separated by $\Omega_S$; the other levels remain separated from these by frequency intervals much larger than the dipolar interactions.

We are then led to ascribe a spin temperature only to the "low-field" part of the effective Hamiltonian. This low-field part consists of (1) the effective Zeeman interaction of the spins $I$ in their rotating frame; (2) the part of the dipolar interactions which is secular with respect to both rotations; (3) the effective quadrupole and Zeeman interactions of the spins $S$, restricted to the matrix elements within the subspace of states $|a\rangle$ and $|b\rangle$.

In complete analogy with the situation dealt with in Sec. IIIA, the effect of spin-lattice relaxation is a slow variation of this temperature toward a steady-state value depending on $\Omega$, according to an equation of the same type as Eq. (16)

$$\frac{\beta_S}{\beta_0}=\frac{\Omega_S(\Omega_S-\Omega)}{(\Omega_S-\Omega)^2+\lambda'^2\gamma_S^2H_1^2+\omega_L'^2}\,. \tag{28}$$

$\lambda'^2$ and $\omega_L'^2$ are expected to be of the same order of magnitude as $\lambda^2$ and $\omega_L^2$.

If $h$ is the effective field seen by the spins $I$ in their rotating frame, the heat capacity of the system is approximately $[\omega_D'^2+\gamma_I^2h^2]^{1/2}$. The polarization of the spins $I$, following a rapid passage up to a high effective field $H$, is

$$P=\tfrac{1}{2}\beta_S\hbar[\omega_D'^2+\gamma_I^2h^2]^{1/2}. \tag{29}$$

Its maximum value,

$$|P|_{\max}=\tfrac{1}{2}\beta_0\hbar\Omega_S[\omega_D'^2+\gamma_I^2h^2]^{1/2}/2\omega_L'\,, \tag{30}$$

corresponds to an enhancement factor with respect to the polarization arising from a solid effect

$$G=\frac{[\omega_D'^2+\gamma_I^2h^2]^{1/2}}{2\omega_L'}\sim\frac{\gamma_I}{2\gamma_S}\,\frac{[\omega_D'^2+\gamma_I^2h^2]^{1/2}}{\omega_D'}\,.$$

Equation (29) is valid if $h$ is not too large compared with $(\omega_D'/\gamma_I)$. In this range the polarization increases with $h$. If $h$ becomes too large, the Zeeman interaction of the spins $I$ gets decoupled from their dipolar interactions and relaxes toward the lattice temperature. A maximum of polarization is expected to occur for a value of $h$ a few times larger than $\omega_D'/\gamma_I$. The variation of $|P|_{\max}$ with $h$ can be calculated by using Provotorov's theory for the mixing rate between Zeeman and dipolar interactions.[12]

## IV. EXPERIMENTAL PROCEDURE

Experiments of thermal mixing between chlorine nuclei and protons have been performed on paradichlorobenzene, at liquid-nitrogen temperature. Single crystals have been mostly used, but powder samples were also used in mixing experiments performed in low-external fields. The single crystals were obtained from slow crystallization of the melt in a temperature-gradient oven. The spin-lattice relaxation time of the protons, $T_1^I$, was about 5 h in 60 G at 77°K. The spin-lattice relaxation time of the chlorine nuclei, $T_1^S$, is about 0.56 sec at the same temperature.[16] The chlorine isotope used for the mixing was $\mathrm{Cl}^{35}$, the pure quadrupole resonance frequency of which is 34.779 Mc/sec at 77°K. The samples were cylinders having 2-cm length and 1-cm diam. The magnetic field was provided by a pair of Helmholtz coils. The proton signals were observed by fast passage in a crossed-coils spectrometer

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[16] A. Hirai, J. Phys. Soc. Japan, **15**, 201 (1960).

at a frequency of 400 kc/sec, which corresponds to a resonance field of 94 G. The rotating field was typically 0.2 G.

The accuracy of signal amplitude measurements was about 10%. Calibration was provided by observing the fast passage signal of a crystal polarized overnight in a field of 1800 G at room temperature; the accuracy of this calibration was about 20%. A hf coil parallel to the transmitting rf coil of the head allowed irradiation of the sample at the chlorine quadrupole frequency with rotating fields up to a few tenths of a gauss. The head was situated in a stainless steel box filled with a mixture of liquid nitrogen and oxygen, which was immersed in a pure liquid-nitrogen bath, in a Dewar vessel. This arrangement prevented boiling liquid being around the sample and the rf coils and thus reduced the noise.

## V. EXPERIMENTAL RESULTS

### A. Thermal Mixing in Low Fields

### (*i*) *Spin Temperature "Line Shape"*

We investigated the variation of the spin temperature with the irradiation frequency in a series of experiments.

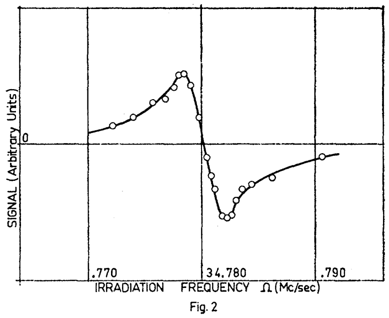

FIG. 2. Proton fast passage signal amplitudes in paradichlorobenzene after 20-sec mixings in zero field at various rf field frequencies. rf field amplitude $=H_1^0 \sim 0.1$ G.

The experimental sequence was the following: The crystal in zero magnetic field was irradiated by the rf field during a given time (10 to 60 sec); a magnetic field was then applied adiabatically, reaching about 70 G in a fraction of a second; the proton signal was then observed by fast passage at 400 kc/sec.

After saturation of the proton signal, the crystal was brought back to zero field and another sequence was started with a slightly different frequency of the rf field. The rf amplitude $H_1$ and the mixing time were kept constant within each set of sequences. Figure 2 shows the observed proton fast-passage signal amplitudes in a set of 20-sec mixings in zero field for various frequencies of the rf field. The rotating field amplitude was of the order of 0.1 G. We call it $H_1^0$ for later reference. Figure 3 shows the observed proton signals in a set of 10-sec mixings in zero field with an rf amplitude $4H_1^0$. These proton signals are proportional to the inverse spin temperature achieved in zero field at the end of the cooling process. The spin temperature "line shape" displayed on both figures is in correct agreement with the theoretical shape (Fig. 1). The linewidth is smaller in Fig. 2 than in Fig. 3 in qualitative agreement with the narrowing effect of a decrease of the rf field amplitude. The center of the line of Fig. 3 is slightly shifted toward lower frequencies with respect to the line of Fig. 2. This is attributed to a heating of the sample and the surrounding ($N_2+O_2$) bath by the rf field, which decreases the chlorine quadrupole resonance frequency. This frequency shift has been observed to increase steadily, when the rf amplitude is increased.

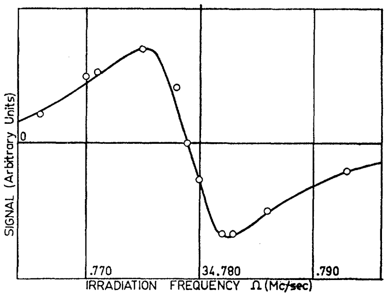

FIG. 3. Proton fast-passage signal amplitudes in paradichlorobenzene, after 10-sec mixings in zero field at various rf field frequencies. rf field amplitude $=4H_1^0$.

Figure 4 shows the observed proton signals in a set of 10-sec mixings performed in a dc magnetic field of 10 G. The orientation of the crystal in the field was arbitrary. The linewidth is larger, and its wings fall off more abruptly than in a zero field mixing, in accordance with the qualitative theoretical discussion. This experiment clearly establishes the difference between this mixing effect and the solid effect. Indeed, the solid effect has also been observed on paradichlorobenzene at low-magnetic fields.[17] In a field of 10 G, solid effect occurs at rf frequencies 42 kc/sec away from the chlorine quadrupole frequency, and is completely distinct from the present polarization effect. Figure 5 shows the entire variation of the proton polarization with the frequency of the rf field.

We have been able to observe proton polarizations produced by such mixings in dc fields up to 17 G. At 17 G, the line begins to display a structure, due to the separation of the chlorine resonance lines.

### (*ii*) *Steady-State Proton Polarizations*

After having determined the spin-temperature line shape in various experimental conditions, we have

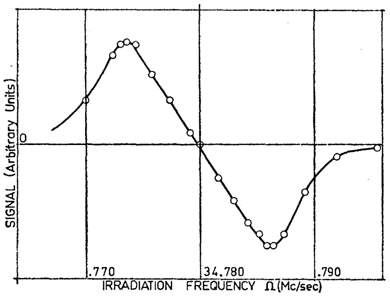

FIG. 4. Proton fast-passage signal amplitudes in paradichlorobenzene, after 10-sec mixings in a field of 10 G, at various rf field frequencies. rf field amplitude $=2H_1^0$.

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[17] A. Landesman, J. Phys. Chem. Solids 18, 210 (1961).

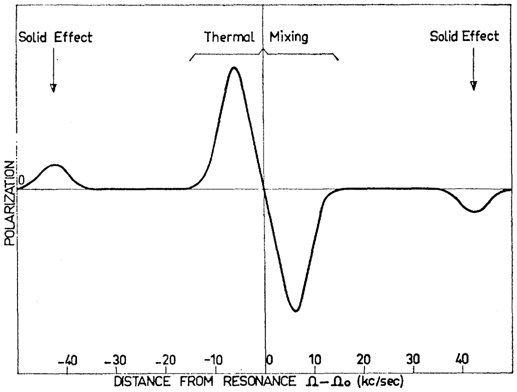

FIG. 5. Proton polarization in paradichlorobenzene resulting from rf irradiation at various frequencies, in a dc field of 10 G. A full solid effect yields a polarization 5 times smaller than the thermal mixing, in this field (see Table II).

measured the equilibrium proton polarizations arising from mixings performed at the maximum of each line during times longer than the polarization times. These polarization times ranged from about 20 sec at zero field and rf amplitude $4H_1^0$ to about 2 min at 10 G and rf amplitude $4H_1^0$. We express these polarizations in two ways: first as the enhancement factor $G$ with respect to the polarization which would result from a full solid effect,

$$P=(\tfrac{1}{2}\hbar\Omega_0/kT_0)G;$$

secondly as an equivalent field $H_0$, that is, the field in which the protons would have the same polarization at thermal equilibrium at the lattice temperature,

$$P=\tfrac{1}{2}\hbar\gamma_I H_0/kT_0.$$

A full solid effect corresponds to an equivalent field of 8150 G.

Figure 6 shows the variation of the equilibrium proton polarization with the amplitude of the rf field $H_1$ for mixings performed in zero field. This rf field is expressed in units of $H_1^0$, which is roughly equal to 0.1 G. The polarization first increases with $H_1$, showing that saturation is incomplete, in accordance with the fact that the line broadens in the same range of values of $H_1$. The decrease of polarization at higher values of $H_1$ cannot be accounted for by the heat capacity of the term $Z$ in Eq. (15) which is too small by an order of magnitude. This decrease is attributed to an inhomogeneous heating of the crystal by the rf field, which broadens the quadrupole line.

The maximum polarization, occurring at $H_1=3H_1^0$, corresponds to an enhancement factor $G\approx 3$, i.e., an equivalent field $H_0 \approx 25\,000$ G. We are led to think that this polarization corresponds to the full theoretical effect $G=\tfrac{1}{2}(\omega_D/\omega_L)$. Indeed the ratio $(\omega_D/\omega_L)$ can be determined independently by using the value of the proton spin-lattice relaxation time in zero field. Measurements performed on a variety of samples always yielded the same result

$$T_1^I=50\pm 5 \text{ sec}.$$

This relaxation time is then ascribed only to the coupling of the protons with the chlorine nuclei. It is related to the quadrupole relaxation time $T_D$ of the part $\mathcal{H}_{IS}'$ by the formula

$$T_1^I=T_D\frac{\mathrm{Tr}(\mathcal{H}_{II}^2+\mathcal{H}_{IS}'^2)}{\mathrm{Tr}\mathcal{H}_{IS}'^2}\approx T_D\frac{\mathrm{Tr}\mathcal{H}_{II}^2}{\mathrm{Tr}\mathcal{H}_{IS}'^2}.$$

We express the traces as functions of quantities already introduced in the theory of mixing [Eqs. (18) and (22)]

$$\mathrm{Tr}\mathcal{H}_{II}^2=N_I\omega_D^2\times\tfrac{1}{4}\mathcal{N},$$

$$\frac{1}{T_D}\mathrm{Tr}\mathcal{H}_{IS}'^2=\tfrac{1}{4}N_S\omega_L^2(T_1^S)^{-1}\times\mathcal{N},$$

where $N_I$ is the number of protons in the sample and $N_S$ the number of $\mathrm{Cl}^{35}$ nuclei. $\mathcal{N}$ is the number of levels of the whole system.

We then have

$$T_1^I=T_1^S(N_I\omega_D^2)/(N_S\omega_L^2),$$

which yields

$$\omega_D/\omega_L=(T_1^I/T_1^S)^{1/2}(N_S/N_I)^{1/2}.$$

In paradichlorobenzene, there are twice as many protons as chlorine nuclei, three quarters of which are $\mathrm{Cl}^{35}$. Thus, $N_I/N_S=8/3$.

Using the experimental values $T_1^I=50$ sec, and $T_1^S=0.56$ sec,[16] we get finally

$$\omega_D/\omega_L=(270/8)^{1/2}=5.8,$$

which corresponds to a theoretical enhancement factor $G\text{th}=\tfrac{1}{2}(\omega_D/\omega_L)=2.9$, to be compared with the experimental value $G\approx 3$. Such a close agreement is probably accidental, but shows that the theory is essentially correct.

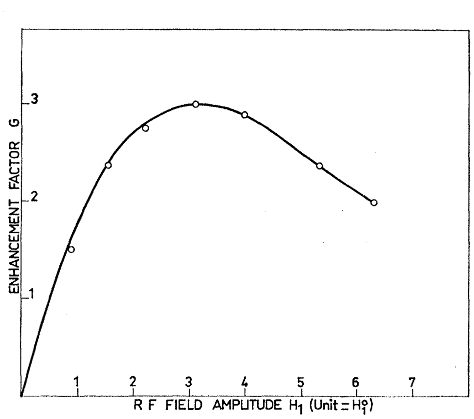

FIG. 6. Steady-state proton polarization resulting from mixing in zero field, with various rf field amplitudes. The unit $H_1^0$ is approximately 0.1 G.

TABLE II. Maximum proton polarizations produced by mixing at various low dc magnetic fields. The mixing takes place in a frame rotating with respect to the chlorine nuclei and fixed with respect to the protons.

| Mixing performed in magnetic field $H$ (G) | Enhancement factor with respect to solid effect $G$ | Equivalent field for observed polarization $H_0$ (kG) |
|---|---|---|
| 0 | 3 | 25 |
| 5 | 8 | 65 |
| 10 | 6 | 50 |

We have also measured the equilibrium polarization following mixings performed in low-magnetic fields, without attempting any quantitative justification. Table II displays the experimental results of mixings performed in fields of 5 and 10 G, together with the result of mixing in zero field. The enhancement factor $G=8$ obtained in the field of 5 G is the largest we were able to observe.

## B. Thermal Mixings in High Fields

### (*i*) *Spin-Temperature Line Shape*

Mixing experiments have been performed in dc magnetic fields close to 94 G.

The experimental sequence was the following: The crystal, experiencing an rf field of typically 0.2 G at the frequency of 400 kc/sec, was irradiated during a fixed time by a second rf field, of frequency close to 34.8 Mc/sec; the dc magnetic field was then varied adiabatically to values far from resonance, the high-frequency rf field turned off and the proton signal observed by fast passage at 400 kc/sec. Figure 7 shows the observed amplitudes of proton signals in a set of 2-min mixings performed at various frequencies of the second rf field on a crystal of unknown orientation. It displays the expected polarization effect corresponding to two of the chlorine resonance lines.

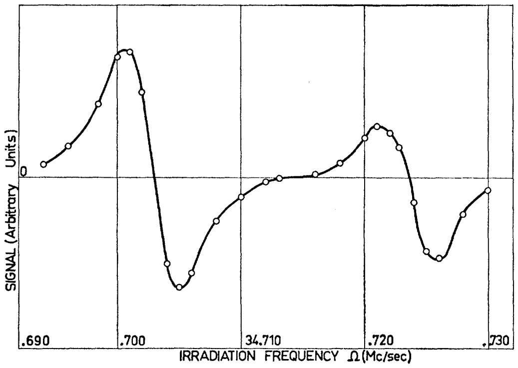

FIG. 7. Proton fast-passage signal amplitudes after 2-min mixings in 94 G at various frequencies Ω of high-frequency rf field. Low-irradiation frequency = 400 kc/sec.

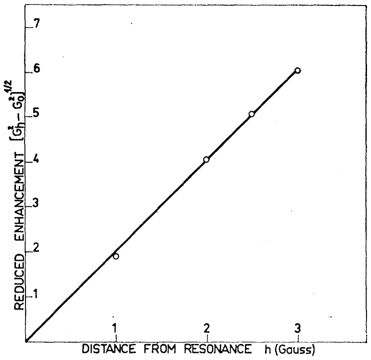

FIG. 8. Reduced enhancement factor $[G_h^2-G_0^2]^{1/2}$ resulting from mixings performed at different field distances $h$ from 94 G, the resonance field of protons at 400 kc/sec.

### (*ii*) *Steady-State Proton Polarizations*

We have measured the steady-state proton polarizations arising from mixings performed at the maximum of a given line in magnetic fields at various distances from the proton resonance fields at 400 kc/sec. Table III reports the observed polarization for mixings performed at distances $h$ from resonance varying from 0 to 3 G. According to Eq. (30), these polarizations must have the proportionality

$$(P)_h \propto [\omega_D'^2+\gamma_I^2 h^2]^{1/2}.$$

TABLE III. Maximum proton polarizations produced by mixing in high field, at various distances $h$ from proton resonance field. The mixing takes place in a frame rotating at different frequencies with respect to the chlorine nuclei and the protons.

| Distance from proton resonance field $h$ (G) | Enhancement factor with respect to solid effect $G$ | Equivalent field for observed polarization $H_0$ (kG) |
|---|---|---|
| 0 | 1.1 | 9 |
| 1 | 2.2 | 18 |
| 2 | 4.2 | 34 |
| 2.5 | 5 | 42 |
| 3 | 6 | 50 |

Then the experimental quantities $[(P)_h^2-(P)_0^2]^{1/2}$ must be proportional to $h$. Figure 8 is a plot of $[(G)_h^2-(G)_0^2]^{1/2}$ as a function of $h$, the distance between the mixing field and the proton resonance field using the experimental enhancement factors $G$ of Table III. It agrees with the theoretical proportionality.

## VI. CONCLUSION

A new dynamic polarization method has been described, which results from a thermal mixing between two spin systems in frames rotating differently with respect to each spin system. Extensive use of the spin-temperature concept has been made in the theoretical derivation of this method; it has been shown, in particular, that this concept can be used in rotating-like reference frames when quadrupole interactions are present, as illustrated in different experiments by Redfield.[18]

Although other contact experiments have been shown to be describable as thermal mixings, most of them can be and actually are described without any reference to spin temperature. On the contrary, the present method can hardly be understood without using it. This polarization method then appears as an illustration of the validity and usefulness of the spin-temperature concept. The experimental results display a qualitative verification of the main features of the theory.

Interest in this method, as a polarization method, may arise from the fact that it produces polarizations larger than polarizations produced by a solid effect. Thus, proton polarizations of a few percent are expected from mixings performed at 1.5°K with iodine-containing crystals, requiring only low dc magnetic fields and irradiation frequencies of a few hundred Mc/sec. Such relatively low irradiation frequencies allow the polarization of large crystals. Still higher polarizations might be expected when using, as the $S$ spin species $\mathrm{Au}^{197}$ or $\mathrm{U}^{235}$, which have gyromagnetic ratios 50 to 60 times smaller than the proton gyromagnetic ratio, and large quadrupole moments. However, it is to be feared that even slight imperfections in the crystal give rise, because of the large quadrupole moments, to inhomogeneous broadenings of the lines exceeding the dipolar line widths, and thus reduce the expected polarizations.

## ACKNOWLEDGMENTS

We wish to thank Professor A. G. Redfield and Dr. I. Solomon for many helpful discussions on this work and on spin temperature problems. We wish to gratefully acknowledge the guidance of Professor A. Abragam, his constant interest in this work and the many discussions which made its completion possible.

## APPENDIX

The equilibrium value of the inverse spin temperature $\beta_S$ is given, from formula (10), by

$$\frac{\beta_S}{\beta_0}=\frac{\mathrm{Tr}\langle[\mathcal{H}^*,\tilde{\mathcal{H}}_1][\tilde{\mathcal{H}}_1,\mathcal{H}_0]\rangle_{\mathrm{av}}}{\mathrm{Tr}\langle[\mathcal{H}^*,\tilde{\mathcal{H}}_1][\tilde{\mathcal{H}}_1,\mathcal{H}^*]\rangle_{\mathrm{av}}}. \tag{A1}$$

We adopt the relaxation model proposed by Bayer.[19] We neglect the spectral densities $J_I$ corresponding to transitions $|\Delta m|=1$. The relaxation Hamiltonian $\mathcal{H}_1(t)$ can be written as[20]

$$\mathcal{H}_1(t)=\sum_i \mathcal{H}_1{}^i(t)=\sum_i \alpha_i(t) \times\{6S_z{}^{i2}+(S_+{}^{i2}+S_-{}^{i2})\}, \tag{A2}$$

where $\alpha_i(t)$ are randomly varying parameters, of equal rms $\langle\alpha^2\rangle_{\mathrm{av}}$.

Using this expression for $\mathcal{H}_1$, we calculate the following traces:

$$\sum_i \mathrm{Tr}\langle[S_z{}^{i2},\tilde{\mathcal{H}}_1{}^i][\tilde{\mathcal{H}}_1{}^i,S_z{}^{i2}]\rangle_{\mathrm{av}}=\mathfrak{N}\times 48\langle\alpha\rangle^2{}_{\mathrm{av}},$$

$$\sum_i \mathrm{Tr}\langle[\mathcal{S}_x{}^i,\tilde{\mathcal{H}}_1{}^i][\tilde{\mathcal{H}}_1{}^i,\mathcal{S}_x{}^i]\rangle_{\mathrm{av}}=\mathfrak{N}\times 90\langle\alpha^2\rangle_{\mathrm{av}},$$

$$\sum_i \mathrm{Tr}\langle[\sum_j\mathcal{H}_{S^iI^j}{}',\tilde{\mathcal{H}}_1{}^i][\tilde{\mathcal{H}}_1{}^i,\sum_j\mathcal{H}_{S^iI^j}{}']\rangle_{\mathrm{av}} =\mathfrak{N}\times 27\langle\alpha^2\rangle_{\mathrm{av}}\hbar^2\gamma_I{}^2\gamma_S{}^2\sum_j\frac{1+\cos^2\theta_j}{r_j{}^6},$$

where $\mathfrak{N}$ is the number of levels of the complete system, $r_j$ is the distance between the spins $S_i$ and $I_j$ and $\theta_j$ is the angle between the vector $\mathbf{r}_j$ and the field gradient principal axis at the site of the spin $S_i$.

This yields as a final result

$$\lambda^2=15/2,$$

$$\omega_L{}^2=9/4\,\hbar^2\gamma_I{}^2\gamma_S{}^2\sum_j\frac{1+\cos^2\theta_j}{r_j{}^6}.$$

These values are of the order of magnitude expected from qualitative arguments.

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[18] A. G. Redfield, Phys. Rev. **130**, 589 (1963).

[19] H. Bayer, Z. Physik, **130**, 227 (1951).

[20] See Ref. 11, p. 468.