COMMON NUCLEAR SPIN-SPIN RESERVOIR IN CRYSTALS WITH SEVERAL TYPES OF NUCLEAR SPIN

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NMR experiments have been carried out on the F^{19} and Li^7 spins in LiF and on the Na^{23} and Cl^{35} spins in NaCl at 4.2°K and have proved the existence in each of these crystals of a nuclear spin-spin reservoir common to both types of spin. It is manifested, in particular, in the strong distortion of the shape of one NMR line not being saturated directly, as the other is saturated in the wing. It is shown that the largest value of the spin-spin energy E_{SS} is attained as a result of adiabatic demagnetization in the rotating frame, performed for both types of spin either simultaneously or consecutively in some optimal manner. The enhanced E_{SS} can be again transformed into Zeeman energy of one of the spin types (the spins being polarized positively or negatively) by means of isentropic (adiabatic) passage by the saturating field through their NMR line from the center to the wing. In this way, the Cl^{35} line was amplified by a factor of 2.5. The experimental results are interpreted on the basis of Provotorov's theory and are found to be in good agreement with it.

1. INTRODUCTION

THE concept of a spin-spin (SS) reservoir with temperature T_{SS}, introduced in[1,2] to describe magnetic resonance in solids, has been confirmed experimentally in NMR (cf., e.g.,[3-6]) and also in EPR and in the dynamical polarization of nuclei (cf., e.g.,[7-9]). However, the existence of a common T_{SS} for spins of different types, which follows from theoretical considerations[2,4,5,10], has been indicated, until recently, only by experiments[5] carried out under specific cross-relaxation conditions. Our preliminary experiments on LiF[11] showed that a common SS-reservoir for all the spins in the crystal also exists without cross-relaxation. The purpose of the present work is to continue and develop these experiments on LiF and NaCl crystals. In addition, we set ourselves the problem of attaining the maximum energy E_{SS} of the common SS-reservoir, and of then using this to polarize the "weaker" (with the smaller Curie constant) spins in the crystal by means of isentropic (adiabatic in the thermodynamic sense) passage by a saturating field through their NMR line from the center to the wing. We should expect that the maximum E_{SS} can be obtained on adiabatic demagnetization in the rotating frame (ADRF)[4,12] of both types of spin, i.e., by isentropic passage through their lines (simultaneously or consecutively) from the wing to the center. It was necessary to develop the most effective method of carrying out the ADRF in this case.

The experiments were performed on the F^{19} and Li^7 spins in LiF and on the Na^{23} and Cl^{35} spins in NaCl at 4.2°K. The LiF crystal was convenient for the study of the ADRF and for the observation of the distortion of the shape of the NMR line not being saturated directly as the other was saturated in the wing. The effect of polarization was studied in both crystals, although NaCl was more suitable since the Cl^{35} spins are "weak" and can be significantly polarized.

2. COMMON NUCLEAR SPIN-SPIN TEMPERATURE IN CRYSTALS

The magnetic resonance absorption signal $P(\Delta)$ is a sum of a symmetric Zeeman component $P_Z(\Delta)$ and an antisymmetric spin-spin component $P_{SS}(\Delta)$[1]:

$$P(\Delta) = P_z(\Delta) + P_{ss}(\Delta) = P_0(\Delta)\left(\frac{T_0}{T_z} + \frac{\Delta}{H_0}\frac{T_0}{T_{ss}}\right). \quad (1)$$

Here T_Z and T_0 are the temperatures of the Zeeman (Z) reservoir and the lattice respectively, $\Delta = H - H_0$ is the detuning of the field H relative to its resonance value H_0, and $P_0(\Delta)$ is the equilibrium absorption signal. Therefore, the signal $P(\Delta)$ for spins of each sort can serve as a sort of thermometer for their SS-reservoir. If a common temperature T_{SS} exists for spins of different sorts, a large change in it (e.g., as a result of saturation of spins of one type at $\Delta \neq 0$[1,13]) should lead to a characteristic distortion of the shape of the other, unsaturated, NMR line.

To increase $|T_{SS}^{-1}|$, ADRF was first carried out on one spin type. In Fig. 1 are shown the NMR signals of F and Li taken before and after the ADRF, which was carried out from equilibrium by means of passage through the right ($\Delta > 0$) wing of the F line (a) and through the left wing of the Li line (b, c). In the experiment corresponding to Fig. 1 (c), before the ADRF of the Li spins, the F NMR signal was made to vanish at all Δ by saturating it at the center. It can be seen that after the ADRF of one type of spin, the other NMR line does indeed change; it becomes asymmetric if it was an equilibrium line before the ADRF and even becomes antisymmetric if it had been previously made to vanish; its value at exact resonance is conserved, which confirms the absence of cross-relaxation in these experiments.

All the features of the signals obtained can be explained if we take into account that for spins (type i) that are demagnetized (by means of ADRF) or previously saturated at the center of the line, the energy $E_Z = 0$)

$(T_Z^{-1} = 0)$, while for spins that have not been subjected to saturation (type j), E_Z remains at its equilibrium value $(T_Z = T_0)$. Then from (1) for the NMR signals of the spins i and j after ADRF, we have, respectively,

$$P_i(\Delta_i) = P_{ss_i}(\Delta_i) = P_{0i}(\Delta_i) \frac{\Delta_i}{H_{0i}} \frac{T_0}{T_{ss}}, \qquad (2)$$

$$P_j(\Delta_j) = P_{0j}(\Delta_j)\left(1 + \frac{\Delta_j}{H_{0j}} \frac{T_0}{T_{ss}}\right). \qquad (3)$$

A calculation of T_{SS} for F and Li independently from their NMR signals and the formulas (2) and (3) at various Δ gave: $(T_0/T_{SS})_F = -820 \pm 60$, $(T_0/T_{SS})_{Li} = -810 \pm 20$ for Fig. 1 (a), $(T_0/T_{SS})_F = 680 \pm 30$, $(T_0/T_{SS})_{Li} = 740 \pm 40$ for Fig. 1 (b), and $(T_0/T_{SS})_F = 650 \pm 50$ (signal $P_0(\Delta)$ for F taken from experiment (b)), $(T_0/T_{SS})_{Li} = 720 \pm 70$ for Fig. 1 (c). Thus, within the limits of accuracy of the measurements, the quantity T_{SS} in each experiment turned out to be the same for the F and Li spins.

A study of the approach of the signals $P(\Delta, t)$ for F and Li to their equilibrium values $P_0(\Delta)$ after ADRF under the influence of the lattice showed that the components $P_{SS}(\Delta, t)$ obtained, using the formulas (2) and (3), from the signals $P(\Delta, t)$ photographed at different moments of time t after ADRF, decay, for all Δ, exponentially with the same time constant $T_1' = 7.5 \pm 0.9$ sec for F and Li. This is the spin-lattice relaxation time of the common SS-reservoir. The recovery of the components $P_Z(\Delta, t)$ for both lines after they had been saturated also proceeded exponentially, but with different time constants: $T_1 = 5.5$ min for F and $T_1 = 14.5$ min for Li. These are the spin-lattice relaxation times of the F and Li Z-reservoirs. Thus, the temperature T_{SS} is the same for F and Li not only immediately after ADRF, but also in the entire process of establishment of equilibrium with the lattice.
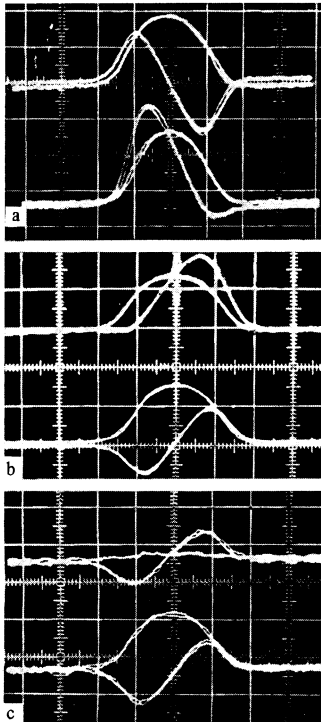

FIG. 1. Oscillograms of the NMR absorption signals of F^{19} and Li^7 in a LiF crystal after ADRF of the equilibrium F^{19}(a) and Li^7 (b, c) spins. The upper signals are from F^{19}, and the lower from Li^7. The antisymmetric and asymmetric signals are the result of ADRF; the symmetric signals are equilibrium signals. In the experiment corresponding to case (c), before the ADRF of the Li^7 spins the F^{19} signal was made zero by saturating it at the center. $H_{1F} = 0.3$ Oe, $H_{1Li} = 0.87$ Oe. One division along the abscissa equals 4.6 Oe in case (a) and 4.2 Oe in cases (b, c).

We remark that similar effects are observed not only after ADRF, but also after saturation in the wing of one of the NMR lines, when there is isolation from the lattice. But they appear more weakly, corresponding to the smaller value of $|T_{SS}^{-1}|$ in this case[1,6,13]. And in all those experiments in which saturation of spins of one of the types, while making T_Z^{-1} zero, did not increase $|T_{SS}^{-1}|$ (isentropic passage through the equilibrium NMR line from the center to the wing or saturation of it with $\Delta = 0$), the NMR signal displayed by these spins vanished at all Δ, while the NMR signal from spins of the other sort remained unchanged. On stationary saturation of the NMR line in the wing, the quantity $|T_{SS}^{-1}|$ increased slowly, this being connected with the relatively fast spin-relaxation of the SS-reservoir $(T_1/T_1' \gg 1)$[1,13].

Similar experiments were also performed with NaCl and gave analogous results; the spin-lattice relaxation times were found to be $T_1' = 94$ sec, $T_{1\,Na} = 19.3$ min and $T_{1\,Cl} = 37$ min.

Thus, in both the LiF and NaCl crystals, the nuclear spin-spin interactions indeed form a common energy reservoir with temperature T_{SS}; we should naturally expect that such a situation is typical for NMR in solids and, evidently, is frequently encountered in EPR (cf., e.g.,[7,8]).

3. MAXIMUM INCREASE OF $|T_{SS}^{-1}|$ IN THE PRESENCE OF TWO TYPES OF SPIN

In the experiments described, a large increase of $|T_{SS}^{-1}|$ was attained by means of ADRF of spins of one type. A further increase of $|T_{SS}^{-1}|$ is also possible, if spins of the second type are also subjected to ADRF. These two ADRF's can be carried out simultaneously or consecutively. We shall examine the saturation of spins of types α and β by two HF fields on the basis of Provotorov's equations[1], written in the laboratory frame. For isolation from the lattice they have the form

$$\frac{d}{at}\left(\frac{1}{T_{z_i}}\right) = -W_i(\Delta_i)\left(\frac{1}{T_{z_i}} + \frac{\Delta_i}{H_{0i}} \frac{1}{T_{ss}}\right), \qquad i = \alpha, \beta, \quad (4)$$

$$\frac{d}{dt}\left(\frac{1}{T_{ss}}\right) = -\frac{C_\alpha}{C_\alpha + C_\beta} \frac{\Delta_\alpha H_{0\alpha}}{H_L^2} W_\alpha(\Delta_\alpha)\left(\frac{1}{T_{z_\alpha}} + \frac{\Delta_\alpha}{H_{0\alpha}} \frac{1}{T_{ss}}\right)$$
$$- \frac{C_\beta}{C_\alpha + C_\beta} \frac{\Delta_\beta H_{0\beta}}{H_L^2} W_\beta(\Delta_\beta)\left(\frac{1}{T_{z_\beta}} + \frac{\Delta_\beta}{H_{0\beta}} \frac{1}{T_{ss}}\right).$$

Here $W_i(\Delta_i) = \frac{1}{2}\gamma_i^2 H_{1i}^2 g_i(\Delta_i)$ is the transition probability for spins of type i under the influence of an HF field with amplitude H_{1i} and detuning Δ_i; $g_i(\Delta_i)$ is the normalized absorption line-shape function of the i-spins; $C_i = N_i \hbar^2 \gamma_i^2 I_i (I_i + 1)/3k$ is the Curie constant for the i-particles, where N_i, I_i and γ_i are respectively their number, spin magnitude and gyromagnetic ratio; $H_L^2 = Tr(\hat{\mathscr{H}}_{SS}^0)^2/Tr(\hat{M}_\alpha + \hat{M}_\beta)^2$ is the square of the magnitude of the local field, where $\hat{\mathscr{H}}_{SS}^0$ is the secular part of the spin-spin interactions, and M_α and M_β are the total magnetizations of the spins of types α and β[5]; it is assumed that $H_1 \ll H_L$[1].

For given Δ_α and Δ_β, it follows, irrespective of the magnitudes of $W_\alpha(\Delta_\alpha)$ and $W_\beta(\Delta_\beta)$, from (4) that

$$\frac{C_\alpha}{C_\alpha + C_\beta} \frac{\Delta_\alpha H_{0\alpha}}{H_L^2} \frac{d}{dt}\left(\frac{1}{T_{z_\alpha}}\right) + \frac{C_\beta}{C_\alpha + C_\beta} \frac{\Delta_\beta H_{0\beta}}{H_L^2} \frac{d}{dt}\left(\frac{1}{T_{z_\beta}}\right) - \frac{d}{dt}\left(\frac{1}{T_{ss}}\right) = 0, \qquad (5)$$

or

$$-\frac{\Delta_\alpha}{H_{0\alpha}}E_{z_\alpha} - \frac{\Delta_\beta}{H_{0\beta}}E_{z_\beta} + E_{ss} = E_{z_\alpha}^{RF} + E_{z_\beta}^{RF} + E_{ss} = \text{const}, \quad (6)$$

where

$$E_{z_\alpha} = -\frac{C_\alpha H_{0\alpha}^2}{T_{z_\alpha}} = -\frac{H_{0\alpha}}{\Delta_\alpha}E_{z_\alpha}^{RF}, \quad E_{z_\beta} = -\frac{C_\beta H_{0\beta}^2}{T_{z_\beta}} = -\frac{H_{0\beta}}{\Delta_\beta}E_{z_\beta}^{RF},$$

$$E_{ss} = -\frac{(C_\alpha + C_\beta)H_L^2}{T_{ss}} = E_{ss}^{RF};$$

E_{Z_α} and E_{Z_β} are the energies of the Z_α and Z_β reservoirs in the laboratory frame, and $E_{Z_\alpha}^{RF}$ and $E_{Z_\beta}^{RF}$ are the energies of these same reservoirs in coordinate frames rotating with the frequencies of the fields $H_{1\alpha}$ and $H_{1\beta}$[14-16].

The relation (6) implies thermal mixing of the energies $E_{Z_\alpha}^{RF}$, $E_{Z_\beta}^{RF}$ and E_{SS}; for simultaneous strong saturation of the α- and β spins, when

$$\frac{1}{T_{z_\alpha}} = -\frac{\Delta_\alpha}{H_{0\alpha}}\frac{1}{T_{ss}}, \quad (7a)$$

$$\frac{1}{T_{z_\beta}} = -\frac{\Delta_\beta}{H_{0\beta}}\frac{1}{T_{ss}}, \quad (7b)$$

in both rotating frames, a common temperature T_{SS} is established:

$$\frac{1}{T_{ss}} = -\left[\frac{C_\alpha \Delta_\alpha H_{0\alpha}}{T_{z_\alpha}^i} + \frac{C_\beta \Delta_\beta H_{0\beta}}{T_{z_\beta}^i} - \frac{(C_\alpha + C_\beta)H_L^2}{T_{ss}^i}\right] \quad (8)$$
$$\times \left[C_\alpha \Delta_\alpha^2 + C_\beta \Delta_\beta^2 + (C_\alpha + C_\beta)H_L^2\right]^{-1},$$

where $T_{Z_\alpha}^i$, $T_{Z_\beta}^i$ and T_{SS}^i are the initial values of the temperatures T_{Z_α}, T_{Z_β} and T_{SS}.

It should be emphasized that, unlike the known experiments[17-20] in which a common spin temperature was also established in two rotating frames when two strong HF fields were imposed, in our case, thanks to the condition $H_1 \ll H_L$, it would be possible not to introduce the rotating frame. In essence, the whole description in our case is carried out by means of temperatures in the laboratory frame, and the energy balance (6) does not include the HF fields, which only maintain the thermal mixing. The experiments of[17-20] differ from ours (see below) both in procedure and in interpretation[17,18] 1).

A. Simultaneous Isentropic Passage Through the α and β Lines

If the conditions (7) are fulfilled for each value of the continuously changing field, than from (5) we obtain the equation

$$d\left(\frac{1}{T_{ss}}\right)\bigg/\left(\frac{1}{T_{ss}}\right) = -\frac{C_\alpha(H - H_{0\alpha}) + C_\beta(H - H_{0\beta})}{C_\alpha(H - H_{0\alpha})^2 + C_\beta(H - H_{0\beta})^2 + (C_\alpha + C_\beta)H_L^2}dH,$$

from which follows the constancy of the entropy S:

$$2S = -[C_\alpha \Delta_\alpha^2 + C_\beta \Delta_\beta^2 + (C_\alpha + C_\beta)H_L^2]T_{ss}^{-2} = \text{const}. \quad (9)$$

It can be seen that on going from the wings of both lines to the center, the quantity $|T_{SS}^{-1}|$ increases and attains a maximum at $\Delta_\alpha = \Delta_\beta = 0$, which for changing H is possi-

ble only when the passage is synchronous ($H_{0\alpha} = H_{0\beta} = H_0$, $\Delta_\alpha = \Delta_\beta = \Delta$); in this case, $(\Delta^2 + H_L^2)T_{SS}^{-2} = \text{const}$, and passage through the equilibrium α and β lines from the initial detuning $\Delta = \Delta^i$ to $\Delta = 0$ (synchronous ADRF) gives, using (8),

$$\left(\frac{1}{T_{ss}}\right)_{\text{sync}} = -\frac{1}{T_0}\frac{H_0}{H_L}\left(\frac{k^i}{1 + k^i}\right)^{1/2}\frac{\Delta^i}{|\Delta^i|} \approx -\frac{1}{T_0}\frac{H_0}{H_L}\frac{\Delta^i}{|\Delta^i|}, \quad (10)$$

where $k^i \equiv (\Delta^i/H_L)^2$; the final form (10) requires that $k^i \gg 1$, and corresponds to a value of $|\Delta_i|$ sufficiently large to ensure the transformation of the ordering of the α and β spins in the external field $H_0 + \Delta^i$ into ordering of the spins in the local fields.

Analogously, on passage through the α line only, the condition

$$\left(\Delta_\alpha^2 + \frac{C_\alpha + C_\beta}{C_\alpha}H_L^2\right)T_{ss}^{-2} = \text{const}, \quad (11)$$

is fulfilled, and as a result of the ADRF of the equilibrium α spins, T_{SS}^{-1} takes the value

$$\left(\frac{1}{T_{ss}}\right)_\alpha = -\frac{1}{T_0}\frac{H_{0\alpha}}{H_L}\left(\frac{C_\alpha}{C_\alpha + C_\beta}\frac{k_\alpha^i}{1 + k_\alpha^i}\right)^{1/2}\frac{\Delta_\alpha^i}{|\Delta_\alpha^i|}; \quad (12)$$
$$k_\alpha^i \equiv \frac{C_\alpha}{C_\alpha + C_\beta}\left(\frac{\Delta_\alpha^i}{H_L}\right)^2$$

Here Δ_α^i is the initial magnitude of the detuning Δ_α. Obviously, $|1/T_{SS}|_\alpha < |1/T_{SS}|_{\text{sync}}$.

B. Consecutive ADRF's of Spins of Both Types

After ADRF of the α spins and before the passage through the β line begins, T_{SS} is determined by (12), while $T_{Z_\beta} = T_0$. As a result of the subsequent ADRF of the β spins with these initial conditions, from (8) and (11) we have for T_{SS}^{-1}

$$\left(\frac{1}{T_{ss}}\right)_{\alpha\beta} = \left(\frac{1}{T_{ss}}\right)_\beta + \frac{1}{(1 + k_\beta^i)^{1/2}}\left(\frac{1}{T_{ss}}\right)_\alpha. \quad (13)$$

Thus, consecutive ADRF's give a no greater amplitude of $|T_{SS}^{-1}|$ than does synchronous ADRF when $k^i \gg 1$. But if the ADRF of the β spins is begun from a certain detuning $\Delta_\beta^i = -H_{0\beta}/T_0(T_{SS}^{-1})_\alpha$, then the quantity $|T_{SS}^{-1}|$ will grow continuously throughout the consecutive ADRF's, without any jump at the moment when the second ADRF begins, i.e., isentropically, and attains a maximum

$$\left|\left(\frac{1}{T_{ss}}\right)_{\alpha\beta}\right|_{max} = \left[\left(\frac{1}{T_{ss}}\right)_\alpha^2 + \frac{1}{T_0^2}\frac{H_{0\beta}^2}{H_L^2}\frac{C_\beta}{C_\alpha + C_\beta}\right]^{1/2} \approx \frac{1}{T_0}\frac{H_\beta}{H_L}, \quad (14)$$

equal to the result of the synchronous ADRF (the final form (14) corresponds to $k_\alpha^i \gg 1$, $H_{0\alpha} \approx H_{0\beta}$).

Obviously, it makes sense to subject both types of spin to the ADRF process only in the case $C_\alpha \approx C_\beta$, when $|T_{SS}^{-1}|$ after synchronous ADRF is a factor $\sqrt{2}$ greater than after ADRF of one type of spin; but if C_α and C_β differ greatly, ADRF of the "stronger" spins gives practically the same T_{SS} as does synchronous ADRF.

4. INCREASE OF POLARIZATION OF THE "WEAK" SPINS

The large energy E_{SS} obtained by ADRF can be again transformed into energy E_Z of one of the types of spin by means of isentropic passage through their NMR line

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1)We note that in [17-20], at least one of the HF fields $H_1 \gtrsim H_L$.

from the center to the wing. In this way, it is possible to increase the energy E_Z and polarization of the weak spins by means of the strong spins.

Indeed, if initially the SS-reservoir has temperature T_{SS}, then from (7a) and (11) we obtain for the polarization coefficient p_α of the α spins

$$p_\alpha \equiv \frac{P_\alpha(0)}{P_{0\alpha}(0)} = \frac{T_0}{T_{Z_\alpha}} = -\frac{T_0}{T_{SS}} \frac{H_L}{H_{0\alpha}} \left(\frac{C_\alpha + C_\beta}{C_\alpha} \frac{k_\alpha^f}{1 + k_\alpha^f} \right)^{1/2} \frac{\Delta_\alpha^f}{|\Delta_\alpha^f|}, \quad (15)$$

where $P_{0\alpha}(0)$ and $P_\alpha(0)$ are respectively the values of the equilibrium and amplified NMR signals of the α spins when $\Delta_\alpha = 0$.

$$k_\alpha^i \equiv \frac{C_\alpha}{C_\alpha + C_\beta} \left(\frac{\Delta_\alpha^f}{H_L} \right)^2,$$

and Δ_α^f is the final value of Δ_α. It can be seen that the largest value of $|p_\alpha|$ is attained when $k_\alpha^f \gg 1$ (this corresponds to the maximum transfer of energy E_{SS} to the reservoir Z_α) and, according to (10), (14) and (15), is equal to

$$|p_\alpha|_{max} \approx \left(\frac{C_\alpha + C_\beta}{C_\alpha} \right)^{1/2} \ll \frac{|\Delta_\alpha^f|}{H_L}. \quad (16)$$

This quantity can be large, if $C_\beta \gg C_\alpha$. But when $C_\beta \gg C_\alpha$, the condition $k_\alpha^f \gg 1$ may not be realizable, since it is difficult to attain saturation in such a remote wing. Then $|p_\alpha|$ is less than its maximum, and if $k_\alpha^f \ll 1$, then

$$|p_\alpha| \approx \frac{|\Delta_\alpha^f|}{H_L} \ll \left(\frac{C_\alpha + C_\beta}{C_\alpha} \right)^{1/2}. \quad (17)$$

In the latter case, only an insignificant part of the energy E_{SS} is transferred to the reservoir Z_α. We note that practically the same result as (17) is also obtained with complete isentropic passage through the line of the weak α-spins ($k_\alpha^i = k_\alpha^f \ll 1$), performed after ADRF of the strong spins (we must resort to this when it is difficult to locate the center of the line). But if the α line was equilibrium before the complete passage, then for $|\Delta_\alpha^i| = |\Delta_\alpha^f|$, it follows from (12) and (15) that

$$p_z = -k_\alpha^i / (1 + k_\alpha^i), \quad (18)$$

i.e., $|p_\alpha| \ll 1$, if $k_\alpha^i \ll 1$.

We note that the idea of polarizing weak spins by means of strong ones was put forward earlier[4], albeit by another method, requiring that $H_1 \gg H_L$.

5. EXPERIMENTAL TECHNIQUE

The F^{19} and Li^7 spins in LiF were detected by two Q-meters with crossed coils in a field $H_{0F} = H_{0Li} = 3500$ Oe; analogously, the Na^{23} and Cl^{35} spins in NaCl were detected in a field of 5140 Oe. The time constant of the low-frequency filter ($\tau_f = 1.5$ msec) was the same for all the Q-meters and was chosen from considerations of the permissible distortion of the NMR signal (this did not exceed 3%[21]). The field H was modulated harmonically with frequency $\nu_r = 2$ Hz and with amplitudes 17.9 ± 0.6 Oe in the experiments with LiF and 8.2 ± 0.4 Oe in the experiments with NaCl; lower values of ν_r were also used.

The two NMR lines in the crystal were simultaneously detected by non-saturating fields and observed continuously on the screen of a double oscillograph with a sweep synchronous with the modulation of the field H. For the saturation, in each experiment two pulses were formed—each at the detection frequency of the corresponding line; they were suppressed (separately or simultaneously) in the time of passage of the field H through those parts of the lines that were subjected to saturation. The pulses started simultaneously, and the duration τ of each of them and their delay relative to the beginning of the sweep could be regulated from 4×10^{-5} to 1 sec; consequently, saturation was possible both at constant detuning and during the passage (in particular, during a half sweep or a whole sweep). For a definite Δ, the time lag ($\tau_{lag} = \tau_f^{[21]}$) of the line on the screen relative to the passage through it by the field H was taken into account. The maximum duration of the experiment, which was determined by the recovery time of the apparatus after saturation (up to 1.5 sec) and by the photographing time (about 0.5 sec), was much shorter than the time T_1 in both crystals.

The saturating field H_1 for $H_1 \ll H_L$ was determined from the relation $[\theta(0)]^{-1} = \frac{1}{2}\gamma^2 H_1^2 g(0)$[1,13] using measured values of the time constant $\theta(0)$ for establishment of the saturation[6] and of the form factor $g(0)$ of the line at $\Delta = 0$. Because of the weak intensity of the Cl line, the calibration of the Q-meter detecting it was performed using the Na line in a field of 1900 Oe, and $\theta(0)$ for Cl was then calculated.

In the table are given the values obtained for $\theta(0)$, $g(0)$ and H_1. Other magnitudes of H_1 were determined by measuring the HF intensity at the coil with the sample. For the crystal orientations used, the parameters H_L were found from the formula

$$(H_L^\alpha)^2 = \frac{Sp(\hat{\mathcal{H}}_{ss}^0)^2}{Sp(\hat{M}_\alpha)^2} = \frac{C_\alpha + C_\beta}{C_\alpha} H_L^2$$

and from the values of H_L^{Li} and H_L^{Na} calculated in[20] and[3,12] respectively. For $\nu_r = 2$ Hz, the condition for isentropic passage[22]

$$f(\Delta) \equiv \frac{1}{H_L} \frac{dH}{dt} \theta(\Delta) \ll 1$$

for Cl is not fulfilled (cf. the table). For a further check that the passage was isentropic at these H_1, a complete passage of the equilibrium NMR lines was effected. For $\nu_r = 2$ Hz, we obtained for the ratio T_0/T_Z of the Zeeman temperatures of the F and Li spins before and after passage through their NMR lines: $T_0/T_{Z_F} = -0.87 \pm 0.05$, $T_0/T_{Z_{Li}} = -0.87 \pm 0.03$. Since these $|T_0/T_Z|$ did not increase by more than 3% on decreasing ν_r by a factor of 2.5, the passage through the F and Li NMR lines with $\nu_r = 2$ Hz was practically isentropic. Therefore, from formula (20) and these T_0/T_Z one can find the parameters k_F^i and k_{Li}^i, and then also the maximum detunings $|\Delta_F^i|$ and $|\Delta_{Li}^i|$ from which the passage becomes isentropic. In this way, we obtained $k_F^i = k_F^f = 6.7 \pm 2.9$, $|\Delta_F^i| = |\Delta_F^f| = 6.6 \pm 1.5$ Oe, $|k_{Li}^i| = |k_{Li}^f| = 6.7 \pm 1.8$, and $|\Delta_{Li}^i| = |\Delta_{Li}^f| = 7.5 \pm 1.0$ Oe.

Analogous experiments with NaCl showed that with $\nu_r = 0.75-2$ Hz, only the passage through the Na line can be considered isentropic. The apparatus did not permit us to work at lower ν_r, and, therefore, below we have also used $H_{1Cl} \sim H_L$.

Experimental values of the form factor and time constant
for establishment of saturation at detuning $\Delta = 0$ for
the NMR lines of F^{19} and Li^7 in LiF and Na^{23} and Cl^{35}
in NaCl

Crystal	H_L, Oe	NMR line	$g(0) \times 10^6$, sec	$\theta(0) \times 10^3$, sec	H_1, Oe	$f(0)$
LiF, [111]‖H	$\Big\{$ 1.91	F^{19}	22 ± 2	0.4 ± 0.05	0.61 ± 0.05	0.04
		Li^7	52 ± 2	0.47 ± 0.06	0.87 ± 0.06	0.06
NaCl, [100]‖H	$\Big\{$ 0.54	Na^{23}	310 ± 20	1.35 ± 0.2	0.31 ± 0.02	0.26
		Cl^{35}	530 ± 40	6.1	0.3 ± 0.03	1.2

6. RESULTS AND DISCUSSION

Experiments on ADRF of two types of spin have been
performed on LiF and have been confined to synchronous
ADRF. Passage from $\Delta = -17$ Oe to $\Delta = 0$ at the values
of H_1 given in the table and with $\nu_r = 2$ Hz gave T_0/T_{SS}
$= 1000 \pm 120$. But from formula (10) it follows for the
Δ_F^i and Δ_{Li}^i found that $(T_0/T_{SS})_{sync} = 1700 \pm 60$ (allow-
ance for the small difference between these detunings
does not take the result outside these error bars). For
ADRF of F only or of Li only, we find from (12):
$(T_0/T_{SS})_F = 1280 \pm 40$, and $(T_0/T_{SS})_{Li} = 1140 \pm 30$. The
divergence of the experimental results (cf. also Sec. 2)
and the theory could be due to the comparatively large
inhomogeneity of the field H over the sample (about
0.5 Oe), the effect of spin-lattice relaxation of the
SS-reservoir, the fact that the inequality $H_1 \ll H_L$ was
not strictly fulfilled in the experiments, and also the use
in the calculations of a too low value of H_L, taken for
the strict orientation [111] ‖ H_0 (the accuracy of setting
it up was about $10°$). We note that each of these causes
could only increase the divergence.

Polarization of the Li spins was carried out at the
same H_1 and ν_r. In Fig. 2 (a) are shown the NMR signals
of the F and Li spins when they are in equilibrium with
the lattice and after synchronous ADRF effected in the
left wings ($\Delta < 0$) of the F and Li lines, with a subse-
quent passage through the Li line from $\Delta = 0$ to $\Delta = 17$
Oe. As a result, the Li line was inverted and amplified
approximately 1.4 times. A calculation using formula
(15) with $T_0/T_{SS} = 1700$ and $k_{Li}^f = 6.7$ gave $|p_{Cl}| = 1.30$
± 0.03. The better agreement of these experiments with

the theory can be explained by the decrease of the effect
of relaxation of the SS-reservoir to the lattice, since in
this case this was manifested only in the passage proc-
ess; in addition, for complete passage the inhomogeneity
of the field H and the magnitudes of H_1 and H_L must
have played a lesser role. It can be seen from the anti-
symmetric F-signal after ADRF that at the end of the
experiment the ratio T_0/T_{SS} is still large. A calcula-
tion has shown that T_0/T_{SS} is the same for F and Li and
is approximately equal to 250, which is in agreement
with the theory, e.g., with[12].

The Cl^{35} spins in NaCl were also subjected to polar-
ization. For these, according to (16), $|p_{Cl}| = 3.3$. In
Fig. 2 (b) are shown the Na and Cl NMR signals, obtained
with synchronous passage ($\nu_r = 2$ Hz) by the fields H_{1Na}
$= 0.31$ Oe and $H_{1Cl} = 0.9$ Oe through the Na and Cl lines
from $\Delta = -8$ Oe to $\Delta = 0$, with a subsequent passage by
the same field H_{1Cl} through the Cl line from $\Delta = 0$ to
$\Delta = 8$ Oe. It can be seen that the Cl line was inverted
and amplified 2.3 times. However, the residual value of
T_{SS}^{-1} is still very great $(T_0/T_{SS} \approx 2000)$. This means that
only a small part of the energy E_{SS} was transformed
into $E_{Z_{Cl}}$, and this, clearly, was associated with the
insufficient saturation of the Cl line in the far wing.
Increasing H_{1Cl} with the previous H_{1Na}, as seen from
Fig. 3 (a), only decreased $|p_{Cl}|$, and this agrees qualita-
tively with the theory[12,14,15] for $H_1 \gtrsim H_L$. But the fall
in $|p_{Cl}|$ with decrease of H_{1Cl} with $H_{1Cl} < H_L$ is brought
about by non-isentropic passage (cf. Sec. 5), and, there-
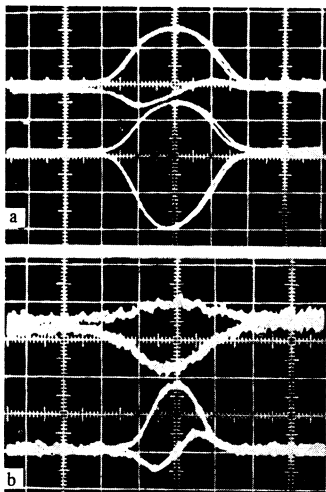fore, on decrease of ν_r, the magnitude of $|p_{Cl}|$ increased

FIG. 2. Oscillograms of the
NMR absorption signals of F^{19}
and Li^7 in LiF (a) and Na^{23} and
Cl^{35} in NaCl (b) after synchro-
nous ADRF of the equilibrium
spins of both types in each crys-
tal and a subsequent isentropic
passage through the Li^7 and Cl^{35}
NMR lines from the center to the
wing. The upper signals are from
F^{19} and Cl^{35} respectively, and the
lower from Li^7 and Na^{23}. The
symmetric positive signals are the
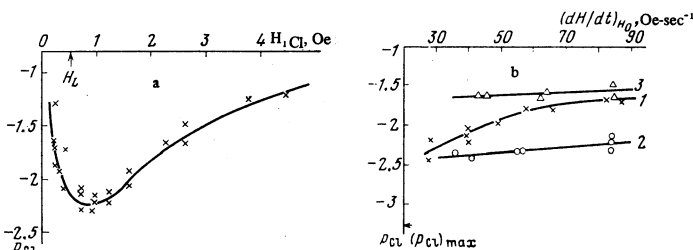equilibrium signals.

FIG. 3. Experimental values of the polarization coefficients p_{Cl} of
Cl^{35} in NaCl, obtained as the result of synchronous passage by saturating
fields H_{1Na} and H_{1Cl} through the Na^{23} and Cl^{35} equilibrium NMR lines
from a deturning $\Delta = -8$ Oe to the center and subsequent passage by the
same field H_{1Cl} through the Cl^{35} NMR line from $\Delta = 0$ to $\Delta = 8$ Oe. In
case (a), $(dH/dt)_{H_0} = 84$ Oe $\times$ sec^{-1} and $\nu_r = 2$ Hz; in case (b) (curve 1),
$H_{1Cl} = 0.2$, (2) 0.96, (3) 2.64 Oe; in all the experiments $H_{1Na} = 0.31$ Oe.

sharply (cf. curve 1 in Fig. 3 (b)). But even when dH/dt = 30 Oe · sec^{-1}, the passage through the Cl line is still non-isentropic (an estimate gives $f(0) \approx 1$), and this, evidently, is the reason why $|p_{Cl}|$ is smaller than the theoretical value. For large H_{1Cl}, the magnitude of $|p_{Cl}|$ increased slightly with decrease of ν_r (curves 2 and 3), which may be explained by the improvement in the isentropicity of the passage through the Na line. Thus, experiments with NaCl ought to be carried out with ν_r $\ll 0.75$ Hz and with better homogeneity of the field H, in order to attain the maximum value of $|p_{Cl}|$.

7. CONCLUSIONS

From experiments on the F^{19} and Li^7 spins in LiF and on the Na ^{23} and Cl^{35} spins in NaCl it follows that in each of these crystals there exists a SS-reservoir with temperature T_{SS} common to both types of nuclear spin. The maximum $|T_{SS}^{-1}|$ is attained as a result of ADRF of both types of spin, the most effective being synchronous ADRF and consecutive ADRF's performed isentropically (without a jump in T_{SS}). Transfer of the energy E_{SS} into energy E_Z of the weaker spins by means of isentropic passage through their line from the center to the wing leads to polarization of these spins. The maximum of the latter quantity is greater when the spins being polarized are weaker, but then it is necessary to saturate too far into the wing, and, therefore, the maximum may turn out to be unattainable in practice.

The method of polarization proposed can be used, for example, to increase the intensity of weak NMR lines, for rapid polarization of weak and relatively slowly relaxing spins, and so on.

^{1} B. N. Provotorov, Zh. Eksp. Teor. Fiz. 41, 1582 (1961) [Sov. Phys.-JETP 14, 1126 (1962)]; Fiz. Tverd. Tela 4, 2940 (1962) [Sov. Phys.-Solid State 4, 2155 (1963)]; Phys. Rev. 128, 75 (1962).

^{2} B. N. Provotorov, Zh. Eksp. Teor. Fiz. 42, 882 (1962) [Sov. Phys.-JETP 15, 611 (1962)].

^{3} W. I. Goldburg, Phys. Rev. 128, 1554 (1962); S. Clough, Phys. Lett. 24A, 49 (1967).

^{4} A. G. Anderson and S. R. Hartmann, Phys. Rev. 128, 2023 (1962).

^{5} J. Jeener, H. Eisendrath and R. van Steenwinkel, Phys. Rev. 133, A478 (1964).

^{6} A. E. Meféd and M. I. Rodak, Zh. Eksp. Teor. Fiz. 59, 404 (1970) [Sov. Phys.-JETP 32, 220 (1971)].

^{7} V. A. Atsarkin and S. K. Morshnev, ZhETF Pis. Red. 6, 578 (1967) [JETP Lett. 6, 88 (1967)]; V. A. Atsarkin, Zh. Eksp. Teor. Fiz. 58, 1884 (1970); 59, 769 (1970) [Sov. Phys.-JETP 31, 1012 (1970); 32, 421 (1971)]; J. C. Gill and N. P. Vinall, J. Phys. C 2, 1512 (1969).

^{8} V. A. Atsarkin, A. E. Meféd and M. I. Rodak, ZhETF Pis. Red. 6, 942 (1967) [JETP Lett. 6, 359 (1967)]; Phys. Lett. 27A, 57 (1968); Zh. Eksp. Teor. Fiz. 55, 1671 (1968) [Sov. Phys.-JETP 28, 877 (1969)].

^{9} W. Th. Wenkebach, G. M. van den Heuvel, H. Hoogstraate, T. J. B. Swanenburg and N. J. Poulis, Phys. Rev. Lett. 22, 581 (1969).

^{10} L. L. Buishvili, M. D. Zviadadze and G. R. Khutsishvili, Zh. Eksp. Teor. Fiz. 56, 290 (1969) [Sov. Phys.-JETP 29, 159 (1969)].

^{11} M. E. Zhabotinskiĭ, A. E. Meféd and M. I. Rodak, ZhETF Pis. Red. 11, 482 (1970) [JETP Lett. 11, 328 (1970)].

^{12} C. P. Slichter and W. C. Holton, Phys. Rev. 122, 1701 (1961).

^{13} M. I. Rodak, Fiz. Tverd. Tela 6, 521 (1964) [Sov. Phys.-Solid State 6, 409 (1964)].

^{14} A. Abragam, Chapters 5 and 12 of The Principles of Nuclear Magnetism, Oxford University Press (1961) (Russ. Transl., IIL, M., 1963).

^{15} A. G. Redfield, Phys. Rev. 98, 1787 (1955).

^{16} M. Goldman, J. de Phys. 25, 843 (1964).

^{17} S. R. Hartmann and E. L. Hahn, Phys. Rev. 128, 2042 (1962).

^{18} F. M. Lurie and C. P. Slichter, Phys. Rev. 133, A1108 (1964).

^{19} Y. Tsutsumi, M. Kunitomo and T. Hashi, J. Phys. Soc. Japan 20, 2095 (1965).

^{20} D. V. Lang and P. R. Moran, Phys. Rev. B1, 53 (1970).

^{21} G. J. Butterworth, J. Sci. Instrum. (J. Phys. E) 1 (Ser. 2), 1165 (1968).

^{22} M. Goldman, M. Chapellier and Vu Hoang Chau, Phys. Rev. 168, 301 (1968).

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