EXPERIMENTAL INVESTIGATION OF MANIFESTATIONS OF THE NUCLEAR SPIN-SPIN RESERVOIR IN NMR

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Submitted March 3, 1970

Zh. Eksp. Teor. Fiz. 59, 404–413 (August, 1970)

A number of new NMR experiments were performed on the nuclear spins of F^{19} in CaF_2 at 4.2°K: (a) an investigation of the dependence of the time of establishment of saturation on the detuning, (b) indication of the line shape after not-strictly-resonant saturation of the line, and also after two successive saturations at different points on the line under conditions of isolation from the lattice, and (c) observation of the character of the restoration of the equilibrium line and measurement of the times T_1 and T_1' of the spin-lattice relaxation of the Zeeman and spin-spin reservoirs. All the experimental results strongly contradict the theory of Bloembergen, Purcell, and Pound[11] and are in good agreement with Provotorov's theory[2] based on the concept of the temperature T_{SS} of the spin interaction reservoir in paramagnetic crystals.

INTRODUCTION

A new description of magnetic resonance in solids, based on separating the secular part of the energy of the spin-spin interaction into an independent reservoir with temperature T_{SS}, which varies relatively easily and differs in the general case from the temperature T_Z of the Zeeman energy of the spins in an external field H, has gained some popularity in recent years. The T_{SS} concept was a development of an idea of Redfield[1] concerning a single spin temperature in a coordinate system rotating together with the strongly-saturating alternating field. For magnetic resonance at any degree of saturation, the theory was developed by Provotorov[2] and only requires that the amplitude H_1 of the alternating field be much smaller than the amplitude of the local field H_L produced by the remaining spins and determining the widths of the resonance line. This theory was confirmed by a number of experimental data in NMR (see, for example[1,3-7]) and recently also in EPR[8,9] Nevertheless, the experiments in this field are far from completed, and many undoubtedly interesting physical facts that follow from the new theory have not yet been observed. Thus, in NMR there has been no verification as yet of the predicted[2,10] form of the absorption line produced by the weak field after saturation not exactly at resonance: owing to the srtong increase of $|T_{SS}^{-1}|$, the signal does not tend to zero within the limits of the entire line, as would follow from the previously assumed theory[11] 1), and acquires a sharply asymmetrical shape (see Fig. 2); there have been practically no investigations of the transient processes, namely the establishment of saturation and stationarity, the establishment of the equilibrium line shape, etc.

In the present article, which is part of a series of experimental papers of the manifestations of the spin-spin temperature[8,9], we report the results of new NMR experiments undertaken by us to verify Provotorov's theory and its consequences, particularly the indication of the line shape after saturation of the line at a definite frequency. We chose for the experiment a CaF_2 crystal with one species of spins of F^{19}, the NMR line of which is homogeneously broadened and has been investigated many times[12]. Inasmuch as the time T' of the spin-lattice relaxation of the spin-spin reservoir turned out to be much shorter than the Zeeman spin-lattice time T_1 (our measurements yielded $T_1/T_1' \approx 24$), the stationary increase of $|T_{SS}^{-1}|$ is certainly negligible[2,10], and experiments in the stationary regime offer no promise. However, the absolute value of T_1' is so large (experiment has shown that $T_1' = 20$ sec), that it became possible to investigate the effects of interest to us under conditions of isolation from the lattice. A similar procedure was already used to determine the EPR line shape[8] and also in our preliminary experiments[13] with a crystal of poor quality ($T_1' = 3.7$ sec, $T_1 = 5$ min), in which the spin-lattice relaxation was partly manifest. Using a better and purer crystal, we have performed a number of additional experiments, namely, an investigation of the establishment of saturation, and also a study of the line shape after two successive saturations in different points on the line.

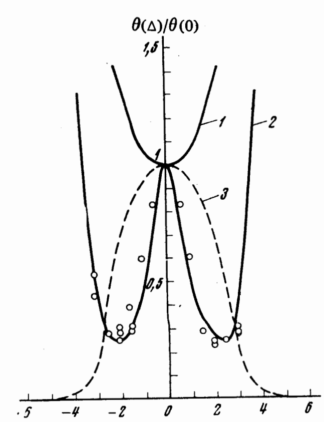

FIG. 1. Dependence of the time θ of establishment of saturation on the detuning Δ of the saturating pulse: 1, 2—theoretical values of $\theta(\Delta)/\theta(0)$ in accordance with formulas (1) and (2); O—experimental values; 3—experimental equilibrium line $g(\Delta)/g(0)$ at $g(0) = 52$ μsec; $\theta(0) = 0.82 \pm 0.02$ msec, $H_1 = 0.27$ Oe.

1)The classical paper of Bloembergen, Purcell, and Pound will be designated, as is customary, by BPP.

1. APPARATUS AND EXPERIMENTAL PROCEDURE

The experiments were performed with a natural single crystal CaF_2 prepared in the form of a cylinder of 8 mm diameter and 8 mm length, and at 4.2°K and H ∥ [111] (accurate to 5°). To detect the NMR absorption signal we used a bridge circuit of the Q-meter type, which was fed from a quartz oscillator of 14 MHz frequency with stabilized generation amplitude. The field H was modulated harmonically at a frequency of 2 Hz and an amplitude 9.9 ± 0.4 Oe. The NMR line was determined by means of a weak (non-saturating) HF field: the signal was observed continuously on the screen of an oscilloscope whose sweep was synchronized with the modulation of the field H. At the instant of passage through the line-contour point to be saturated, a relatively short saturating pulse at the indication frequency was applied (from the same generator, using a modulating stage). By delaying the pulse relative to the start of the sweep it was possible to ensure saturation of any section of the line, i.e., any detuning Δ of the saturation relative to the resonant value H_0 of the field H. The duration τ of the pulses could be regulated from 0.2 to 150 msec[2)]. The time constant of the low-frequency filter (1.5 msec) was chosen from considerations of the permissible distortion of the signal (it did not exceed 3%[14]); the filter-produced delay of the NMR line on the oscilloscope screen, relative to the passage of the field, was taken into account in the determination of the detuning Δ of the pulse. The maximum duration of one experiment, including the time of recovery of the receiver after the saturating pulse (up to 1.5 sec) and the time needed for photography (above 0.5 sec) were much shorter than the times T_1 and T_1'.

The formulas of the theory contain, as an essential parameter, the local field H_L, and also the factor $g(\Delta)$ of the form of the NMR absorption line. The line H_L was determined from the known relation $M_2 = 3H_L^2$ [12], and the second moment M_2 was obtained from the experimental equilibrium line by graphic integration. The factor $g(\Delta)$ was determined in similar fashion, and it turned out that $H_L = 0.92 \pm 0.05$ Oe and $g(0) = 52 \pm 3$ μsec, in agreement with other investigations[12]. The inhomogeneity of the external magnetic field H over the volume of the sample, determined from the width of the NMR signal of the protons of water in the same volume, reached 0.5 Oe. This is not much less than H_L, but, as will be shown below, it did not prevent realization of all the effects predicted by the theory, although it lowered their magnitude somewhat.

2. ESTABLISHMENT OF SATURATION

For a spin system isolated from the lattice, it follows from the BPP theory[11] that saturation is established exponentially with an exponent $[\theta(\Delta)]^{-1}$ in the form

$$[\theta(\Delta)]^{-1} = p(\Delta) = {}^1\!/_2\gamma^2 H_1^2 g(\Delta), \tag{1}$$

where $p(\Delta)$ is the probability of transition under the influence of the field at the frequency $\gamma H = (H_0 + \Delta)$, and ν is the gyromagnetic ratio. Provotorov's theory[2] also indicates that under these conditions saturation is established exponentially, but with a more complicated dependence of θ on Δ:

$$[\theta(\Delta)]^{-1} = p(\Delta)\,(1 + \Delta^2 / H_L^2). \tag{2}$$

To verify formula (2), and also as a preparation for other experiments, we undertook an experiment on the determination of $\theta(\Delta)$. We note that in the only experiment of this kind known to us, performed on Na^{23} in NaCl[5], the agreement with (2) was only partial, something attributed by the author to quadrupole effects.

We saturated the NMR line by means of pulses whose duration τ was varied in the range 0.2–1 msec, at a constant amplitude H_1, and the signal at the saturation frequency was attenuated by not more than a factor of 5. Within a time τ, as can be readily calculated, the field H changed during the course of modulation by not more than 0.1 Oe. It is also necessary to estimate the role of the broadening of the spectrum of the pulse as a result of its short duration. Calculating in analogy with[15] the simultaneous action on T_Z and T_{SS} of two saturating fields with slightly different detunings $\Delta + \delta/2$ and $\Delta - \delta/2$, we find, in the case of isolation from the lattice, the condition for neglecting the difference δ between these two detunings, in the form $\delta^2 \ll 4(\Delta^2 + H_L^2)$. We note that the indicated condition is satisfied for pulses not shorter than 0.2 msec, i.e., the central part of the spectrum of the pulse can be regarded as sufficiently narrow, whereas its components on the far ends have no time to cause appreciable saturation. It can thus be assumed that in each experiment the saturation was carried out at a single definite detuning Δ.

The experiment has shown that at all Δ the saturation is established exponentially, and that with increasing $|\Delta|$ the time θ first decreases, reaches a minimum, and then increases sharply. Figure 1 shows the experimental values of $\theta(\Delta)/\theta(0)$ within the range $|\Delta| \lesssim 3$ Oe, where the signal was sufficient for measurement, and the theoretical curves 1 and 2. We see that the experimental $\theta(\Delta)/\theta(0)$ agree well with (2) and, as in[5], they contradict strongly formula (1) of the BPP theory.

We note that the measured $\theta(0)$ was used to determine the amplitude H_1, which turned out to equal 0.27 ± 0.01 Oe; thus, the condition $H_1 \ll H_L$, needed for the theory of[2] to be valid, is satisfied.

3. SHAPE OF NMR LINE AFTER SATURATION ON THE WING

All the succeeding experiments were performed using longer saturating pulses, with τ equal to 2 or 4 msec, which certainly made it possible to neglect the width of their spectrum (see Sec. 2). Figure 2 shows the results of indication, by means of a weak field, of the NMR absorption line after saturation with detuning $\Delta_1 < 0$ (a) and $\Delta_1 > 0$ (b). In both cases, the time θ of establishment of saturation was not larger than 0.7 msec (see Fig. 1), so that the line was sufficiently strongly saturated. We see that not-strictly-resonant saturation leads to strong line asymmetry: induced radiation, reaching 50% of the maximum of the equilibrium signal, is observed on the wing beyond the point

2)In order for the temperature description to be valid, it is necessary, of course, that τ, as well as all the times observed in the experiment, be much longer than the time of formation of the temperatures, namely the T_2 of the spin-spin relaxation (in our case $T_2 \approx 0.03$ msec, see below).

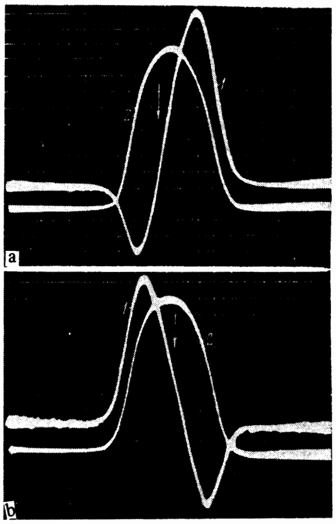

FIG. 2. Oscillograms of NMR absorption signals $P(\Delta_2)$ after saturation by a pulse with initial and final detunings $\Delta_1(0)$ and $\Delta_1(\tau)$ (line 1): a—$\Delta_1(0) = -1.4$ Oe, $\Delta_1(\tau) = 0.9$ Oe; b—$\Delta_1(0) = 1.1$ Oe, $\Delta_1(\tau) = 0.6$ Oe; $\tau = 4$ msec, $H_1 = 0.27$ Oe; 2—equilibrium line. The arrows indicate $\Delta_1(\tau)$. One horizontal division equals 1 Oe. The base line of curve 1 is shifted for apparatus reasons.

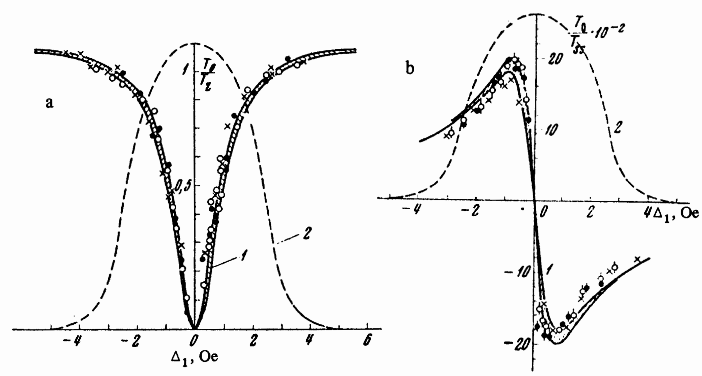

FIG. 3. Dependence of the Zeeman and spin-spin temperatures on the detuning of the saturating pulse: a—$T_0/T_Z(\Delta_1)$; b—$10^{-2}T_0/T_{SS}(\Delta_1)$. The experimental values of T_0/T_Z and T_0/T_{SS} were taken for $\Delta_1(\tau)$ and denoted as follows: O—$\tau = 4$ msec, $H_1 = 0.27$ Oe; O—$\tau = 4$ msec, $H_1 = 0.2$ Oe; X—$\tau = 2$ msec, $H_1 = 0.27$ Oe; 1—theoretical curve in accordance with formula (4), 2—equilibrium line. The thicker sections of the curve 1 reflect the uncertainty of T_Z^{-1} and T_{SS}^{-1} due to the inaccuracy with which H_L is determined; the vertical bars denote the spread of the values of T_{SS}^{-1} obtained from the oscillogram $P(\Delta_2)$ at different Δ_2.

of saturation, while on the other wing, starting with a definite value of the detuning, the absorption exceeds the equilibrium value and may even exceed the maximum equilibrium signal; the absorption maximum is strongly shifted in a direction opposite to the detuning of the saturation. Such a line shape, which deviates strongly from the BPP theory[11], was predicted earlier[2,10] and follows from the general formula that takes into account the possibility of a strong increase of $|T_{SS}^{-1}|$:

$$P(\Delta_2) = P_z(\Delta_2) + P_{ss}(\Delta_2) = P_0(\Delta_2)T_0(T_z^{-1} + \Delta_2 H_0^{-1} T_{ss}^{-1}), \quad (3)$$

where T_Z and T_{SS} pertain to the instant of indication, $P_0(\Delta_2)$ is the equilibrium line form. If the state with temperatures T_Z and T_{SS} is obtained as a result of saturation with a detuning Δ_1, under conditions of isolation from the lattice and under equilibrium initial conditions, then we can write

$$\frac{T_0}{T_z} = -\frac{\Delta_1}{H_0}\frac{T_0}{T_{ss}} = \frac{\Delta_1^2 - \Delta_1 H_0^{-1} H_L^2}{\Delta_1^2 + H_L^2} \approx \frac{\Delta_1^2}{\Delta_1^2 + H_L^2}. \quad (4)$$

Substituting (4) in (3) we obtain, assuming $\Delta_1 H_0 \gg H_L^2$, the line shape corresponding to Fig. 2:

$$P(\Delta_2) \approx P_0(\Delta_2)\frac{\Delta_1(\Delta_1 - \Delta_2)}{\Delta_1^2 + H_L^2}. \quad (5)$$

In NMR, the only observed singularity of the $P(\Delta_2)$ curve was a shift of its maximum[6]. Recently a line shape qualitatively in agreement with Fig. 2 was obtained in EPR[8], but at a much lower asymmetry, due to the smaller increase of $|T_{SS}^{-1}|$.

For a quantitative estimate of the results, let us compare T_Z and T_{SS} obtained from the experimental curves of the type of Fig. 2, with the theoretical values calculated from the given H_0, H_L and Δ_1; for T_S this was already done in[5] (without indication of the $P(\Delta_2)$ line) and by us in[13]. Figure 3 shows the curves for T_Z^{-1} and T_{SS}^{-1}, calculated in accordance with formula (4). The experimental values were obtained from photographs similar to Fig. 2, with the aid of formula (3): T_Z^{-1} was determined from the ratio $P(0)/P_0(0)$, and T_{SS}^{-1} from $P(\Delta_2)/P_0(\Delta_2)$ at different Δ_2; the obtained values of T_{SS}^{-1} turned out to be slightly different, and this spread is designated by the vertical bars on the experimental points; the same figure shows the experimental values for slightly altered τ and H_1.

We see that the experimental values of T_Z^{-1} fit well the theoretical curve 1 obtained from formula (1) at all values of Δ, as was the case in[5] and[13]. There is a somewhat poorer fit between curve 1 and the values of T_{SS}^{-1}, namely, at large $|\Delta|$ the values of $|T_{SS}^{-1}|$ turn out to be somewhat smaller than expected for a homogeneously broadened line. We note that allowance for the variation of the field during the course of modulation within the time τ of the pulse, based as in[13] on formulas of isentropic origin (see Sec. 4 below), did not improve the agreement. This, as well as the spread of $T_{SS}(\Delta_2)$ at different values of Δ_2, can be explained, in our opinion, as being due to the influence of the only factor unaccounted for by us, namely the inhomogeneity of the external magnetic field (see Sec. 2), as a result of which the observed NMR line is a superposition of independent homogeneous lines. Such an uncertainty, as follows from simple reasoning, can decrease the measured value of $|T_{SS}^{-1}|$ and weaken all the effects connected with the increase of $|T_{SS}^{-1}|$ (see also Sec. 4). It is important to emphasize that the general character of the behavior of T_{SS}^{-1} turned out to agree fully with the theory[2] and, as in the case of T_Z, to contradict the BPP theory even qualitatively[11].

4. NMR LINE SHAPE AFTER TWO SUCCESSIVE SATURATIONS WITH DIFFERENT DETUNINGS

The long times T_1 and T_1' in our sample have made it possible to apply to the spin system, under the same conditions of isolation from the lattice, a sequence of two different saturating pulses during continuous indication of the line shape. In the first experiment, one pulse ($\tau_1 = 4.4$ msec) saturated the line on the wing, and in the other ($\tau_2 = 1.6$ msec) was turned on 2.5 sec after the first and saturated the line at the center (Fig. 4). Since the second pulse acting on T_{SS} caused T_0/T_Z to vanish, indication after the second pulse should, in accord with (3), reveal an antisymmetrical line of the form

$$P(\Delta_2)=P_{ss}(\Delta_2)=P_0(\Delta_2)\frac{\Delta_2}{H_0}\frac{T_0}{T_{ss}}, \quad (6)$$

where T_{SS} is the result of the first pulse (a similar procedure was already used in EPR[8,9]). Figure 4 confirms this. It is possible to verify, for example, that in accordance with (3) the photographed indication signal after the first pulse (curve 1) is, with good accuracy, the sum of the photographed signal after the second pulse (curve 2) and the symmetrical Zeeman part $P_Z(\Delta_2)$ of the signal after the first pulse (constructed from the value of P(0) at the center and from the equilibrium line 3). A slight excess of the positive part of curve 2 over a negative one could result from inhomogeneity of the magnetic field, as a result of which the second pulse is not exactly resonant for all the homogeneous component lines.

In the second experiment, the line was saturated by a long pulse (τ = 88 msec), starting on the far wing and terminating at the center. Let us verify that in this case the isentropic condition is satisfied, i.e., the passage was so rapid that it overtook the relaxation to the lattice (this was certainly satisfied in our case) and at the same time was so slow that at each instant the temperatures T_Z and T_{SS} had time to be formed and saturation could set in3); for the coordinate system rotating with the saturating field, this means establishment of a single spin temperature at each instant of time[1]. Indeed, at $H_1 \ll H_L$, when the time T_2 is much shorter than the time θ of establishment of saturation, the isentropic condition can be written in the form[11]

$$\theta\frac{dH}{dt}\ll H_L. \quad (7)$$

Taking from our experiment $(dH/dt)_{max}$ = 125 Oe/sec, θ_{max} = 1.5 msec, and H_L = 0.92 Oe, we verify that (7) is well satisfied.

The passage from the far wing to the center of the line, as follows from the general relation for an isentropic process[12],

$$\sqrt{[\Delta(t)]^2+H_L^2}=\mathrm{const}\cdot T_{ss}(t), \quad (8)$$

terminates in vanishing of the Zeeman energy (T_0/T_Z = 0) and in a limiting increase of the value $T_0/|T_{SS}|$, and is called adiabatic demagnetization in a rotating coordinate frame (ADRF)[3,4,12]. Indeed, from (8) we have

$$\frac{T_0}{T_{ss}}=-\frac{H_0}{H_L}\frac{\Delta_1}{\sqrt{\Delta_1^2+H_L^2}}\approx-\frac{H_0}{H_L}\frac{\Delta_1}{|\Delta_1|} \quad (9)$$

where Δ_1 is the initial detuning at ADRF, and the final form (9) requires $|\Delta_1| \gg H_L$. We recall that the increase of $|T_{SS}^{-1}|$ is in this case exactly double the maximum value of $|T_{SS}^{-1}|$ in the case of saturation on the wing.

At 2.5 sec after the termination of the ADRF, we turned on the saturating pulse with a detuning Δ on the same wing as the ADRF. Calculation of the result of saturation with detuning Δ under initial conditions ensuring the ADRF (see[10] and formula (9)) yield

$$\frac{T_0}{T_z}=-\frac{\Delta}{H_0}\frac{T_0}{T_{ss}}=\frac{\Delta\,\Delta_1 H_L}{(\Delta^2+H_L^2)\sqrt{\Delta_1^2+H_L^2}}\approx\frac{\Delta H_L}{\Delta^2+H_L^2}\frac{\Delta_1}{|\Delta_1|}, \quad (10)$$

$$P(\Delta_2)=P_0(\Delta_2)\frac{\Delta_1 H_L(\Delta-\Delta_2)}{(\Delta^2+H_L^2)\sqrt{\Delta_1^2+H_L^2}}\approx P_0(\Delta_2)\frac{H_L(\Delta-\Delta_2)}{\Delta^2+H_L^2}\frac{\Delta_1}{|\Delta_1|}. \quad (11)$$

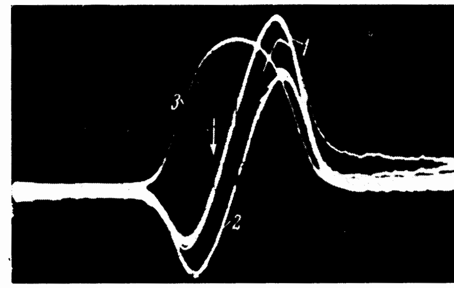

FIG. 4. Oscillograms of NMR absorption signals $P(\Delta_2)$ after saturation by two successive pulses: 1—result of saturation by the first pulse with detunings $\Delta_1(0)$ = −1.5 Oe, $\Delta_1(\tau)$ = −0.9 Oe (marked by the arrow); 2—result of additional saturation by a second pulse at the center of the line: $\Delta_1(0)$ = −0.2 Oe, $\Delta_1(\tau)$ = 0; 3—equilibrium line; H_1 = 0.27 Oe.

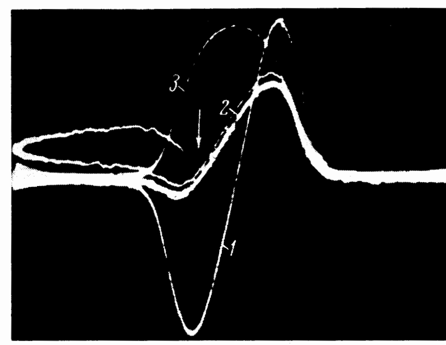

FIG. 5. Oscillograms of the NMR absorption signals $P(\Delta_2)$ after passage of the saturation field from the following to the center of the line (ADRF) and additional saturation on the same wing. 1—Result of ADRF: $\Delta_1(0)$ = −7.9 Oe, $\Delta_1(\tau)$ = 0, τ = 88 msec; 2—result of additional saturation by a second pulse: $\Delta(0)$ = −0.9 Oe, $\Delta(\tau)$ = −1.4 Oe (marked by the arrow), τ = 4 msec; 3—equilibrium line; H_1 = 0.27 Oe.

Figure 5 shows the results of both pulses: 1—antisymmetric line after ADRF and 2—line after additional saturation on the same wing. Since in the experiment we had $|\Delta(\tau)| > H_L$, the value of $|T_{SS}^{-1}|$ and the asymmetry of the line 2 turned out to be smaller than in saturation with the same detuning Δ, but under equilibrium initial conditions (see Fig. 2 and formulas (4), (5), (10), and (11)).

Besides the two described experiments, we also executed a complete passage from one far wing to the other, using inversion of T_S and of the AMR line[3,12]. The decrease of the rate of passage by a factor of 4 produced practically no change in the final results (within 5%); this is additional proof that the process is isentropic. The result of passage, estimated from the ratio of the inverted signal to the equilibrium signal, was in good agreement with the theoretical prediction[16] —better than in all the preceding experiments described in Secs. 3 and 4. This confirms that the experiments with the partial passage of the line were influenced by the inhomogeneity of the magnetic field, which

3)By tradition, such a process is frequently called in the literature adiabatic [3,4,16], the adiabaticity being taken in the thermodynamic sense (but not in the sense of quantum mechanics after Ehrenfest!). We shall use the term "isentropic," which is more exact and is unambiguous [12].

certainly should become less manifest in an experiment with complete passage.

5. RESTORATION OF EQUILIBRIUM NMR LINE AFTER SATURATION ON THE WING

According to the theory[2], the Zeeman and the spin-spin reservoirs relax to the lattice independently of each other, in exponential fashion with times T_1 and T_1', respectively, and usually $T_1 \geq 2T_1'$[1,4,12]. On the other hand, if $T_1 \gg T_1'$, then it is possible to separate two exponential stages in the process of reestablishment of the equilibrium line after the not-strictly-resonant saturation of the line: a) decay, within a time T_1', of the antisymmetrical component $P_{SS}(\Delta_2, t)$, as a result of which the total indication signal $P(\Delta_2, t)$ assumes the symmetrical form $P_Z(\Delta_2, t)$, and b) a slower growth of $P_Z(\Delta_2, t)$ to the equilibrium line, within a time T_1, as called for by the BPP theory[11]. This indeed occurred in our experiment.

Figure 6 shows five $P(\Delta_2, t)$ lines plotted at definite time intervals t after determination of saturation on the wing, and indicates a gradual decrease of their asymmetry. During the photography time (approximately 30 sec), the symmetrical part $P_Z(\Delta_2, t)$ of the signal did not increase noticeably, and therefore all the $P(\Delta_2, t)$ curves intersect at one point at $\Delta_2 = 0$; near this point, the peak of the curve appeared 50–60 sec after the end of the saturation. An analysis of the $P(\Delta_2, t)$ curves show that the decay of $P_{SS}(\Delta_2, t)$ is exponential for all Δ_2, with a time $T_1' = 20 \pm 1$ sec. Further growth of the symmetrical line $P_Z(\Delta_2, t)$ to the equilibrium value $P_0(\Delta_2)$ followed the same law with a time $T_1 = 8 \pm 0.7$ min. The equilibrium is reestablished in similar fashion also after any other perturbation of the system (ADRF or a combination of pulses). On the other hand, if $T_1 \gtrsim T_1'$, then both temperatures T_Z and T_{SS} relax simultaneously, but nonetheless, the separation of each of the exponentials entails no difficulty. Such a procedure, which was already used earlier in NMR after ADRF[4] and in EPR[8] makes it possible to measure sufficiently accurately, by simple means, not too small values of T_1'—in addition to the known pulse methods[17].

The large value of the measured ratio T_1/T_1' is not unexpected, since F^{19} in CaF_2 relaxes to the lattice via paramagnetic impurities, and for this relaxation mechanism both theory and experiment[18-20] predict large values of T_1/T_1', in a wide range.

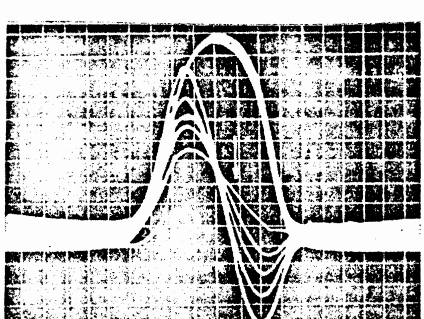

FIG. 6. Restoration of equilibrium after saturation on the wing. The five experimental NMR lines $P(\Delta_2)$ with decreasing degree of asymmetry pertain to five successive instants (0, 5, 10, 15, and 30 sec) after saturation with the tuning Δ_1 (at the point marked by the arrow). Symmetrical line—equilibrium.

CONCLUSION

The results of all three experiments on the NMR of F^{19} in CaF_2, namely (a) measurements of the time of establishment of saturation as a function of the detuning, (b) indication of the line shape after one or two saturating pulses under conditions of isolation from the lattice, and (c) observation of the character of the restoration of the equilibrium line, turned out to be in sharp qualitative contradiction to the BPP theory[11] and in good agreement with the theory of Provotorov[2]. By the same token our investigation, together with the other experimental investigations of this series[8,9], on EPR and DNP confirm the great applicability and fruitfulness of the concept of the spin-spin temperature in paramagnetic crystals.

The authors thank M. E. Zhabotinskiĭ and E. N. Bazarov for constant attention to the work and V. A. Atsarkin for numerous stimulating discussions, and also V. I. Grigor'ev and V. P. Gubin for help in developing and constructing the apparatus.

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Translated by J. G. Adashko
47