Rapid reversal of sign of dynamically enhanced polarization in polarized targets

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Results are presented of an experiment aimed at assessing the feasibility of polarization of modern polarized proton targets of the "frozen" type by adiabatic fast passage. The experiments were performed on samples of 1,2-propanediol ($C_3H_8O_2$) with Cr^V paramagnetic impurity. The dependence of the reversible polarization fraction δP on the velocity of the rf passage at different values of the rf field H_1 and at different densities of the paramagnetic impurity. The results are analyzed and compared with the theoretical relations obtained for δP by Goldman *et al.* [Phys. Rev. **168**, 301 (1968)] on the basis of the Provotorov equations. The existence of a short-duration ($t \lesssim 15$ sec) induced radiation of the sample material after turning off the irradiating microwave field was indirectly observed.

INTRODUCTION

Polarized targets (PT), particularly "frozen" proton polarized targets (FPPT), first developed and used at CERN and in Dubna,[1,2] are now indispensable parts of other worldwide accelerators for the study of spin-spin effects in nuclear interactions.

High nuclear polarization is obtained in FPPT by a dynamic method at $T \approx 0.3$ K in a magnetic field $H \approx 2.5$ T within a time 1.5 h, and can be preserved for hundreds of hours when the target material is cooled to the infralow temperature $T \approx 0.02$ K in a magnetic field decreased to $H \approx 0.5$ T.

Notwithstanding the high stability of the FPPT parameters after many hours' accumulation of statistics for target polarization of one sign, the unavoidable instability of the beam and the drift of the recording apparatus can lead to measurement errors. To increase the measurement accuracy it is frequently necessary to reverse the sign of the target polarization (in the ideal case—before dumping the beam to the target). This is practically impossible in the usual dynamic method, since reversal of the polarization (hereafter "polarization reversal") lasts several hours.

In principle there are two radiotechnical means of rapid polarization reversal, well known in NMR spectroscopy, viz., with a high-power 180-degree pulse and by adiabatic fast passage of the NMR line.

The first possibility is not very suitable for FPPT, since the 180-degree pulse requires high power at a duration on the order of several microseconds with high spatial homogeneity of both the pulse itself and of the external magnetic field H_0.

The requirements for the realization of the second possibility are less stringent. The adiabatic-passage (AP) method is already in use for polarization reversal in PT and LMN (lanthanum magnesium nitrate),[3] where close to 100% reversal of positive polarization and 50% of negative were obtained, and in propanediol,[4] where the polarization reversal was insignificant. The reversal mechanism was not systematically investigated in either of the cited papers.

The object of the present study was the mechanism of reversal of dynamically enhanced polarization in AP at infralow temperatures, with an aim at assessing the feasibility of rapid reversal of FPPT polarization by this method.

The object of our investigation is 1,2-propanediol with paramagnetic impurity Cr^V, the most promising material for modern FPPT. High nuclear polarization is reached in this substance by a dynamic method through the "dynamic cooling" mechanism.[5]

1. PRINCIPLES OF THE ADIABATIC PASSAGE METHOD

AP polarization reversal consists essentially of applying to a system of nuclear spins situated in a strong magnetic field H_0 a sufficiently strong rf field of frequency close to the NMR frequency. The rf field is linearly polarized in a plane perpendicular to the field H_0, and passage through the NMR line is effected by varying the rf field frequency ω (or the external field strength at a fixed frequency $\omega_0 = \gamma H_0$). If the conditions of adiabaticity of the passage are satisfied in this case, the polarization is reversed. To minimize the attendant polarization loss, the time τ of passage through the resonance line must be considerably shorter than the time $T_{1\rho}$ of the spin-lattice relaxation in the field H_{eff} in the rotating coordinate frame (RCF).

From the point of view of classical NMR theory,[6] only most general relations can be obtained for the feasibility of maximum polarization reversal in AP:

$$\frac{dH}{dt} \ll \gamma H_1^2, \quad \tau \ll T_{1\rho}, \tag{1}$$

where H is the external magnetic field, H_1 is the rf-field strength, and γ is the gyromagnetic ratio of the given spin species ($\gamma = 4.257 \cdot 10^3$ Hz/Oe for protons).

A more rigorous quantum-statistical NMR theory based on the spin-temperature concept has been quite fully developed in the high-temperature approximation,[7] when the nuclear polarization is low. This theory, generally speaking, describes the behavior of the spin system when acted upon by the rf field H_1 only at a fixed frequency of this field and under the condition $H_1 \ll H'_L$, where H'_L is the local field in the RCF.

In other words, the theory covers neither the case of infralow temperatures, nor nuclear polarization enhanced by hundreds of times, nor the case of adiabatic passage.

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AP was analyzed in Ref. 8 on the basis of the Provotorov kinematic equations for spin temperatures, and the possible polarization loss in AP was calculated. This analysis, however, is not quite complete, since no account is taken of the presence in the target material of another spin species, viz., the electron spins needed for the dynamic polarization. The number of electron spins is usually relatively small (one electron per 10^3 protons), but experience has shown that they influence substantially the behavior of the system of proton spins in AP.

There is thus at present no good AP theory applicable to our case. We could guide ourselves in our experiments only by most general considerations.

2. EXPERIMENTAL SETUP

A block diagram of the setup is shown in Fig. 1. Its basic element is a vertical cryostat in which a superconducting solenoid is placed in a solution of ^{3}He in ^{4}He. The investigated sample, consisting of small spheres of ≈ 1 mm diam, is placed in a fluoroplastic (Teflon) stub of the dissolution chamber; the stub extends into the homogeneous zone of the solenoid's magnetic field. The sample dimensions are 6 mm diam and $l = 6$ mm. Outside the fluoroplastic stub, in the sample region, are located two rf coils of the dipole type. One is designed to operate in a 2.7 T magnetic field, the other in a field lowered to 0.6 T.

The protons in the sample are dynamically polarized by irradiating the latter with a microwave field in the traveling-wave regime. The microwave power from a backward-wave-tube oscillator enters the sample through a circular waveguide terminated with a horn radiator. A conical absorbing load is placed behind the sample.

The low-temperature microwave cell operates thus in the traveling-wave regime, so that in the case of small samples the microwave amplitude is highly homogeneous at each point of the sample. The emitter and the absorbing load have a temperature ≈ 1 K, i.e., they are separated from the ^{3}He–^{4}He dissolution chamber.

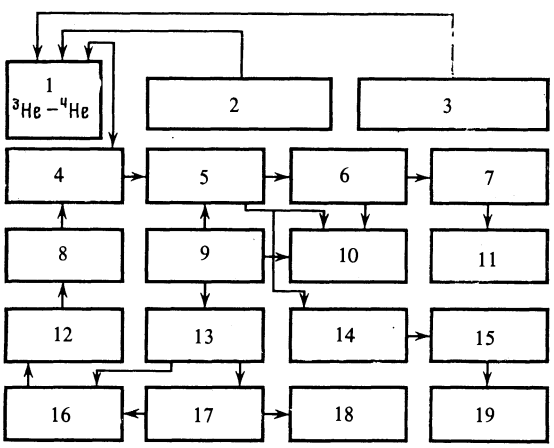

FIG. 1. Block diagram of setup. 1) ^{3}He–^{4}He crysostat 2) Microwave oscillator 3) Solenoid power supply 4) Coaxial switch 5) Q-meter 6) Storage 7) Integrator 8) rf amplifier II 9) Control block 10) oscilloscope 11) Digital voltmeter 12) rf amplifier I 13) rf-oscillator sweep block 14) Selective amplifier 15) Synchronous detector 16) Electronic gate 17) rf oscillator 18) Frequency meter 19) Automatic plotter

The proton polarization was measured with a traditional Q-meter with a series automatically tunable circuit. The NMR output signals of the Q meter can be fed through a calibrated attenuator and an amplifier to an oscilloscope and to an analog integrator, or else through a selective amplifier to a synchronous detector and an automatic plotter.

The field H_1 was produced by an independent RF unit consisting of a master oscillator (type G4-107), an electronic gate, an rf transistor amplifier with output power $\lesssim 40$ W, and a supplementary power amplifier rated up to 120 W. A special electronic unit synchronized with the Q-meter operation generated a sawtooth voltage to sweep the frequency of the master oscillator, and a rectangular pulse that opened the gate only during the passage time. The same sawtooth voltage could be fed to the superconducting solenoid power supply, thereby effecting the magnetic passage. The rf coils used in the reversal regime were the same as for the Q meter. The limits of the frequency sweep and the passage time were monitored with an electronic computing frequency meter (type ChZ-34).

3. MEASUREMENTS AND RESULTS

The experiments on reversal of dynamically enhanced and frozen polarization were carried at a temperature ≈ 0.05 K in a 2.7-T magnetic field. Some experiments were performed in a magnetic field decreased to 0.6 T. The working medium was propanediol ($C_3H_8O_2$) with Cr^V ions produced via a chemical reaction with $K_2Cr_2O_7$ or by dissolving the stable radical $K[OCr(O_2CCOMeEt)_2]H_2O$ (Ref. 9).

The measurement procedure was the following. First, 30–40% proton polarization (+ or −) was "pumped" at $T \approx 0.1$–0.2 K. After turning off the microwave pump for a certain time needed to lower the sample temperature to $T \leqslant 0.05$ K, the integral intensity of the NMR signal was measured and its derivative plotted. The latter described well the evolution of the signal waveform. After the rf passage the NMR signal was again recorded. The passage effect was estimated from the ratio of the final and initial intensities of the NMR signal, with account taken of the sign of the polarization.

In all the experiments the linear sweep was 400 kHz for the frequency and 94 Oe for the field. The samples with optimum Cr^V ion density had an NMR line half width at half maximum $\Delta_1 = 10$ Oe. The spin-lattice relaxation time T_1 in a field $H_0 = 2.7$ T at $T \approx 0.05$ K was longer than 1000 h.

We investigated under these conditions the reversible fraction of the polarization

$$\delta P = P(-\Delta_0)/P(\Delta_0), \tag{2}$$

[$P(\Delta_0)$ and $P(-\Delta_0)$ are the intensities of the NMR signals before and after the passage, $\Delta = |H - H_0|(2\Delta_0 = 94$ Oe)]. The varied arguments were: 1) the rate of passage dH/dt for certain fixed values of H_1; 2) the paramagnetic-impurity density at three densities $0.1C_0$, C_0, and $3C_0$, where $C_0 \approx 10^{19}$ ions/cm^3 corresponds to the optimal density from the viewpoint of obtaining maximum target polarization; 3) the instant of time after turning off the microwave field that saturates the ESR line; 4) the sample temperature at which the polarization was reversed.

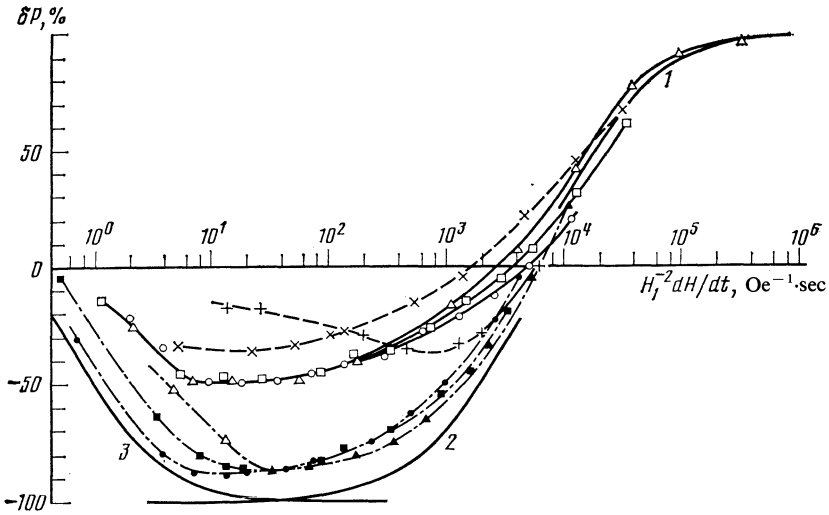

FIG. 2. Dependence of δP on the parameter $H_1^{-2}dH/dt$ at different values of the paramagnetic-impurity density and in different values of the field H_1: 0.1 C_0 (▲—$H_1 \approx 0.7$ Oe, ●—$H_1 \approx 1.3$ Oe, ■—$H_1 \approx 2.0$ Oe); C_0 (△—$H_1 \approx 1.4$ Oe, □—$H_1 \approx 2.7$ Oe, ○—$H_1 \approx 4.7$ Oe): $3C_0$ (×—$H_1 \approx 1.4$ Oe, +—$H_1 \approx 6.0$ Oe).

It was observed in the course of the investigations that the reversible polarization fraction δP does depend neither on the initial value (up to 80%) and on the sign, nor on the direction of the passage of the NMR line.

The experimental results on the dependences on 1) and 2), averaged over many experiments, are shown as functions of the parameter $H_1^{-2}dH/dt$ in Fig. 2. It can be seen from the figure that more than 90% reversal of the nuclear polarization in propanediol with Cr^V paramagnetic impurity could not be obtained. Similar results were obtained in a magnetic field lowered to 0.6 T.

Figure 3a shows the dependence of $|\delta p|$ on the time elapsed from turning off the microwave field. The power fed to the sample ranged from 10^{-5} to 10^{-3} W. In frequency passage with the microwave pump turned off, the initial polarization is completely destroyed. This occurred independently of the magnitude and sign of the initial polarization and of the sign of the applied pump. The initial polarization was destroyed also for AP immediately after turning off the microwave power. The reversal ability was gradually restored after ≈ 15 sec. To our knowledge, ours is the first observation of this phenomenon.

These investigations and those of the temperature dependence of $|\delta P|$ were made for samples with paramagnetic-ion density C_0. The results of investigations of the dependence on 4) are shown in Fig. 3b, from which it follows qualitatively that lowering the sample temperature contributes to an increase of the reversible fraction of the polarization.

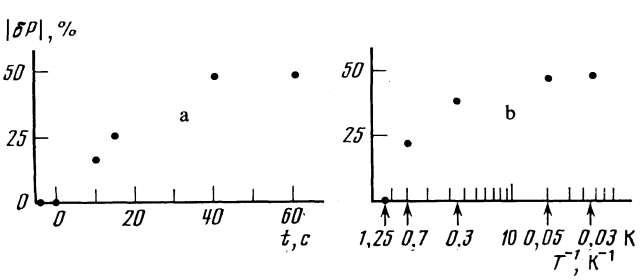

FIG. 3. Dependence of $|\delta P|$ on the time elapsed from the turning off the microwave field at the instant $t = 0$ (a) and on the sample temperature (b).

4. DISCUSSION OF RESULTS

As already noted, we did not succeed in obtaining 100% polarization reversal in propanediol with Cr^V ions by the method of linear rf passage at infralow temperatures (i.e., in FPPT). Even though particular attention was paid in the experiment to the region in which maximum polarization reversal occurs ($5 < H_1^{-2}dH/dt < 5 \cdot 10^4$), the results were obtained in a wide range, from weakly saturating to adiabatic passage (see Fig. 2).

Let us compare the results with the theoretical relations obtained for δP in Ref. 8 (discussed in detail in Ref. 10) on the basis of the Provotorov equations.[7]

For the estimates that follow we shall assume that the investigated samples are powdered and have an electron spin density C_0. The absorption line shape of the enhanced NMR signal of the samples is close to Gaussian and has a half width at half maximum $\Delta_1 = 10$ Oe. In our case the spin-spin interactions are purely dipole-dipole, so that the following relations are valid:

$$H_L^2 = {}^5/_3 M_2, \quad H_L'^2 = {}^1/_3 M_2, \quad M_2 = \Delta_1/2 \ln 2, \tag{3}$$

where H_L is the local field in the lab and M_2 is the second moment of the sample-material absorption line in a strong field.[10] From relations (3) we get

$$H_L = 1.1\Delta_1 = 11 \text{ Oe}, \quad H_L' = 0.49\Delta_1 = 4.9 \text{ Oe}.$$

Weakly saturating passage

This passage should be, on the one hand, much slower than the spin-spin relaxation in the field H_L', and on the other hand much faster than the thermal mixing of the Zeeman and spin-spin subsystems:

$$W(\Delta) = \pi\gamma^2 H_1^2 g(\Delta), \tag{4}$$

where $g(\Delta)$ is the normalized absorption-signal form function for a weak rf field. In our case these conditions take the form

$$\gamma' \ll H_1^{-2} dH/dt \ll \gamma (H_L'/H_1)^2. \tag{5}$$

The polarization does not reverse in this case, and its decrease is described by the expression

$$\delta P = \exp[-\pi\gamma H_1^2 (dH/dt)^{-1}], \tag{6}$$

if the spin-lattice relaxation is neglected.

The experimental data in this region agree well with this relation, which is represented by curve 1 of Fig. 2.

Quasi-adiabatic passage

The distinguishing feature of adiabatic passage is that the magnetic field goes through the resonant value very slowly, so that the system is all the time in a state of internal equilibrium characterized by a single value of the spin temperature. In such a passage the entropy is conserved, and the polarization reverses without loss. The condition of slow passage means that the passage must be much slower that the mixing rate W, the converse of the first condition of (5). The passage, however, cannot be too slow, for then the polarization loss increases and becomes substantial. The passage must therefore be adiabatically fast, i.e., the conditions (1) must be satisfied.

Let us estimate the polarization loss due to the quasi-adiabaticity of the passage and to spin-lattice relaxation.

a. During the time of quasi-adiabatic passage the system is not exactly at equilibrium, only close to it. The reversible fraction of the polarization is then given by

$$\delta P = -\exp\left\{-\frac{dH/dt}{\pi\gamma H_1^2 H_L'^2}\int_{-\Delta_0}\left[\left(1+\frac{\Delta^2}{H_L'^2}\right)^3 g(\Delta)\right]^{-1} d\Delta\right\}; \tag{7}$$

for a Gaussian line shape we have $g(\Delta) = g(0)\exp(-\Delta^2/6H_L'^2)$ and the integrand decreases very rapidly with increasing Δ within the limits of the NMR line. To calculate the integral we shall assume that $g(\Delta) = \text{const} = g(0) = 1/2\Delta_1$, and we extend the integration limits to $-\infty$ and $+\infty$. The integral can then be easily evaluated and we get

$$\delta P = -\exp\left(-\frac{3\Delta_1}{4\gamma H_L'} H_1^{-2}\frac{dH}{dt}\right).$$

This dependence is represented by curve 2 of Fig. 2, and its qualitative agreement with experiment improves with decreasing electron spins in the samples.

b. The rate of the Zeeman spin-lattice relaxation is negligibly small and it is necessary to take into account the rate $T_{1\rho}^{-1}$ of the spin-lattice relaxation of the spin-spin subsystem, which comes into play only on passage of the line. The reversible fraction of the polarization is then

$$\delta P = -\exp\{-2H_L' T_{1\rho}^{-1}(dH/dt)^{-1}\operatorname{arctg}(\Delta_0/H_L')\}. \tag{8}$$

Curve 3 of Fig. 2 shows this dependence at $H_1 = 0.7$ Oe, $T_{1\rho} = 45$ sec, $H_L' = 4.9$ Oe, and $\arctan(\Delta_0/H_L') = \pi/2$. Similar relations are obtained up to $H_1 = 13$ Oe at $T_{1\rho} = 5$ sec and $H_1 = 2$ Oe at $T_{1\rho} = 1$ sec.

If the frequency of H_1 or of the magnetic field H_1 varies, linear AP is apparently not the best method. The point is that for total reversal of the nuclear polarization the passage must really be adiabatic. In such a passage of the NMR line, the high ordering (polarization) in the Zeeman subsystem of the proton spins is initially transferred to its dipole-dipole subsystem and then returns to the Zeeman subsystem, but now with its sign reversed. To this end it is necessary that at each instant of passage both subsystems be at equilibrium with each other. Since the coupling of the subsystems is via the field H_1 with a mixing rate $W(\Delta)$, it is difficult to achieve equilibrium on the line wing, where W is small, and the passage in this part is not adiabatic. As the resonance is approached, W increases very rapidly and an abrupt transition to adiabatic passage takes place. The transition from the "fast" to the adiabatic passage causes loss of polarization. If this loss is assumed to be 5–6%, at the values of H_1 and $T_{1\rho}$ given above the theoretical relation (8) agrees well in the region $H_1^{-2}dH/dt < 30$ with the experimental data for samples with concentration $0.1C_0$ of the paramagnetic impurity.

The plot shown in Fig. 3 of $|\delta P|$ vs the time elapsed from the instant when the microwave field that saturates the EPR lines is turned off can be attributed to the presence of damped radiation in the sample during the time of restoration of the EPR line shape. This radiation is due to the presence of an induced section of the EPR absorption line.[11,12] The physical action of this radiation on the electron-nuclear system manifests itself in the dependence observed by us.

5. CONCLUSIONS

1. Our experiments were performed at values of H_1 from 0.7 to 6.0 Oe and at $H_L' = 4.9$ Oe, i.e., $H_1 \sim H_L'$. Even though the basic condition for the validity of the Provotorov-theory equations ($H_1 \ll H_L'$) was not satisfied, the results (for samples with low paramagnetic-ion density) are in satisfactory agreement with the theoretical relations obtained on the basis of these equations.

2. From the investigations performed, principally from investigation of the dependence of the reversal on the density of the Cr^V ions and from the experiments with the microwave pump turned on, it can be concluded that the principal role in the reversal efficiency is played by the presence of the paramagnetic impurity, viz., the reversible fraction of the polarization decreases with increasing density. The AP method can therefore not used in practice to reverse rapidly the polarization of FPPT, owing to the large attendant loss of the initial polarization ($\sim 50\%$).

3. The existence of a short-duration ($t \lesssim 15$ sec) induced radiation of the sample material after the termination of its irradiation by the microwave field was observed indirectly.

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