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Dynamic nuclear polarization in ${}^6\text{LiD}$

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Résumé. — Des polarisations jusqu'à 70 % ont été produites dans un petit échantillon de ${}^6\text{LiD}$ pour les spins nucléaires de lithium et de deutérium. Ces résultats font de ${}^6\text{LiD}$ un matériau pour cibles polarisées d'un grand intérêt potentiel. Quelques autres mesures de RMN et RPE sur cet échantillon sont décrites.

Abstract. — Polarizations up to 70 % have been produced in a small sample of ${}^6\text{LiD}$ for the nuclear spins of lithium and deuterium. These results make ${}^6\text{LiD}$ a polarized target material of great potential interest. A few other NMR and EPR measurements on this sample are reported.

1. Introduction. — Recent experiments on spin effects in strong interaction, high energy physics, have aroused interest in new materials for polarized targets, the important parameters being : higher content of polarizable nucleons, and better resistance to radiation damage. For the case where it is not a disadvantage to have simultaneously polarized neutrons and protons, ${}^6\text{LiD}$ looks very attractive with four polarizable nucleons out of a total of eight [1].

Polarizing ${}^6\text{LiD}$ may find also some applications in solid state physics. The nuclear magnetic moment of ${}^6\text{Li}$ and ${}^2\text{D}$ being nearly equal, ${}^6\text{LiD}$ appears almost as a simple cubic lattice of spins 1, which makes it an interesting case for the study of nuclear dipolar ordering (a difference however between ${}^6\text{LiD}$ and a simple cubic lattice of identical spins is the absence in the truncated dipolar hamiltonian of the *flip-flop* terms $I_i^+ I_j^-$ between ${}^6\text{Li}$ and D).

In the light of the experience of the past five years with ${}^7\text{LiF}$ and ${}^7\text{LiH}$ [2-3], it appeared possible to obtain in ${}^6\text{LiD}$ nuclear polarizations larger than 50 %. The reasons were the following. With ${}^7\text{LiH}$ containing F-centers in a concentration of the order of 10^{-4} , the effect of DNP is to give all the nuclear spins present in the sample (i.e. ${}^7\text{Li}$, H and a small proportion of ${}^6\text{Li}$ and D) the same *spin temperature*. This temperature corresponds currently to a polarization of 95 % for H, 80 % for ${}^7\text{Li}$, but only 35 % for ${}^6\text{Li}$ and D (which have a much smaller magnetic moment). However, better figures are expected in ${}^6\text{LiD}$, because the ESR linewidth of the F-centers, which is due mainly to the interactions of the electrons with the nuclear spins,

is smaller than in ${}^7\text{LiH}$. Roughly speaking, the nuclear spin temperature T_s should be proportional to the ESR linewidth, thus to the nuclear magnetic moment μ_n . Then the polarization (which is a function of μ_n/T_s) should be comparable to that of ${}^7\text{Li}$ in ${}^7\text{LiH}$. Experimental investigation of DNP in ${}^6\text{LiD}$ then also provides a test of the theories of DNP.

2. Preparation of the samples. — Whereas the previously used samples of ${}^7\text{LiF}$ and ${}^7\text{LiH}$ were single crystals cleaved along (100) planes, the pure ${}^6\text{LiD}$ samples, containing in fact a few % of ${}^7\text{Li}$, are cut from a larger ingot of sintered material, and then ground to our standard dimension of $5 \times 5 \times 0.5$ mm.

The paramagnetic impurities necessary for the DNP are F-centers, obtained by irradiation with 2 or 3 MeV electrons, at liquid Argon temperature. As with ${}^7\text{LiH}$, we have used the liquid Argon loop described in reference [4] to control the temperature. The conditions of the irradiation were :

incident current	: 10 $\mu\text{A}/\text{cm}^2$,
incident energy	: 3 MeV,
duration of the irradiation	: 1 h.

With these figures, the total dose received amounts to 2.25×10^{17} el/cm².

As a first step, two samples of sintered LiH were prepared with the same technique, and one was irradiated simultaneously with that of ${}^6\text{LiD}$. Its behaviour for DNP was rapidly tested and found to be very similar to that of the single crystals, and no further studies were made on this sample.

3. **Apparatus.** — The apparatus is the same as that built for the study of nuclear magnetic ordering and neutron diffraction [5]. Its essential features are :

1) A dilution refrigerator allowing a minimum temperature of 50 mK, with an axial access for quick insertion of the samples (the latter should not be warmed above 77 K). The only modification, also used for the samples of LiH, is a completely closed mixing chamber with a small teflon tube driving the *dilute* phase down to below the sample (and not the concentrated phase as before). This configuration was found to offer more stable cryogenic conditions, and to cause a smaller absorption of neutrons.

2) A superconducting split-coil magnet operated in the persistent mode and giving a maximum field of 6.5 T with an homogeneity of 5×10^{-6} in a cylinder $\varnothing = h = 6$ mm.

3) A carcinotron to saturate off-center the ESR line and produce the DNP. The resonance frequency of the F-centers is the same in ^6LiD and ^7LiH (182 GHz at 6.5 T). Some experiments were also performed at lower fields using a 136 GHz (4.9 T) and 72 GHz (2.5 T) carcinotron. The NMR absorption signals are recorded with Q -meters during linear sweeps of the magnetic field and accumulated 100 times in a multi-channel analyser to improve the signal to noise ratio. In a field of 6.5 T, the NMR frequencies (supplied by stable quartz driven synthesizers) are :

277 MHz for H
107 MHz for ^7Li
42.5 MHz for D
40.7 MHz for ^6Li .

4. Experimental results. — 4.1 POLARIZATION. —

DNP takes place by cooling of the electronic spin-spin interactions reservoir induced by off-center saturation of the ESR line. The optimum distance ΔH from the center of the line is 30–40 G. As the nuclear polarization increases the ESR line *slips away* and the carcinotron frequency must be readjusted [10]. Because of the smaller ESR linewidth than in LiH, the polarization rate is much more sensitive to small variations of the frequency. The temperature of the sample plays also an important role for DNP. The microwave power was adjusted to get the best results. A carbon resistor, located 20 mm above the sample, indicated a temperature of 200–300 mK, but the dilute phase was probably colder. We have not measured directly the temperature of the sample *during* the DNP.

Figure 1 shows the ^6Li polarization as a function of time for the three carcinotrons used. The D polarization is slightly higher than that of the ^6Li . The initial polarization growth rate seems to be approximately the same for the three curves, but the limiting polarization is an increasing function of the carcinotron frequency : 71 % at 182 GHz, 64 % at 136 GHz and 40 % at 71 GHz. The latter frequency was used to

Fig. 1. — Nuclear polarization of ^6Li as a function of time, with the three different carcinotrons used.

check the possibility of building a polarized target with the more conventional techniques (using a vertical axis, 2.5 T electromagnet). The polarizations obtained for ^6Li and D at 182 GHz are much larger than ever produced before, in ^7LiH or in the deuterated alcohols [6].

4.2 METHOD OF MEASUREMENT. — It is well known that the *area* of the NMR absorption signal is proportional to the polarization. The calibration was achieved by comparison with the signal of the ^7Li isotope, as shown in reference [6]. This method implies :

1) The validity of the hypothesis of equal spin temperature for all nuclear spin species, a fact which is well established by now in those substances. As a check, the mixing time between ^6Li and D was measured at 4.9 T *in the conditions of the DNP* and found to be ~ 1 min., which is much shorter than the polarization times reported here.

2) The exact knowledge of the ^7Li concentration. We have checked the latter by measurements at low polarization (where $P_6/P_7 \sim 0.30$). Our figure agrees within 5 % with that of the supplier.

The method of calibration using the thermal equilibrium signal at 4.2 K was not convenient, because of the bad signal to noise ratio and the long nuclear Zeeman relaxation time.

4.3 NEDOR MEASUREMENTS. — Although our apparatus is not equipped for ESR spectroscopy, we could get informations on the F-centers with the technique of NEDOR. Details on NEDOR have been given in a number of articles [7]. Its essential principle consists in measuring a shift of the NMR line induced by a saturation of the electronic resonance.

Electronic concentration. — The concentration of the F-centers was found to be :

$$N_e \sim 1.3 \times 10^{19} \text{ cm}^{-3}.$$

Electronic relaxation time. — The recovery of the NMR shift is not fully exponential, indicating probably a distribution of relaxation times in the sample. The typical figures are :

$$T_{1e} \sim 1 \text{ s at } 182 \text{ GHz and } 136 \text{ GHz}$$

$$T_{1e} \sim 2.8 \text{ s at } 71 \text{ GHz}.$$

These results, obtained under the conditions of the DNP, can explain that the initial polarization rate $(dP/dt)_i$ is approximately the same at 182 GHz and 71 GHz : we expect $(dP/dt)_i$ to be proportional to the electronic relaxation rate $1/T_{1e}$ times the ratio of the heat capacity of the electronic spin-spin reservoir to that of the nuclear Zeeman reservoir :

$$(dP/dt)_i \propto \frac{1}{T_{1e}} \frac{N_e}{H},$$

and the variation of H is almost compensated by the variation of $T_{1e}(H)$ as observed in this sample.

ESR linewidth. — In order to measure the ESR lineshape, the microwave frequency was kept constant, with a power small enough to induce a saturation of 20 % only at the center of the ESR line, and the NMR shift was measured as a function of magnetic field. Since the ESR lineshape is due mainly to interactions of the electrons with the neighbouring nuclei, it depends on the nuclear polarization. The latter was always sufficiently small during these experiments, to avoid this effect. Figure 2 shows the NEDOR spectrum obtained at 136 GHz. The linewidth at half height is equal to 38 G. By comparison, a conventional ESR spectrum was made on the same sample at a frequency

Fig. 2. — NEDOR signal in ${}^6\text{LiD}$ in arbitrary units, as a function of the magnetic field (shift field) for a ${}^6\text{Li}$ polarization of 25 %.

of 10 GHz and the linewidth was 15 G. Broadening by Δg splitting seems ruled out by the fact that the NEDOR linewidths were almost the same at 71, 136 and 182 GHz. The discrepancy may lie in the techniques themselves (ESR and NEDOR spectra are the same only if there is a unique relaxation time T_{1e}). A pure ${}^7\text{LiH}$ sample (n° 48) was tested with the same technique and its ESR linewidth was found to be 41 G at 10 GHz, whereas its NEDOR linewidth was of the order of 90 G at 71, 136 and 182 GHz. The width ratio ${}^7\text{LiH}/{}^6\text{LiD}$ is then 2.7 by ESR and 2.35 by NEDOR. The inverse spin temperatures reached by DNP at 182 GHz are respectively 825 K^{-1} ($P_6 = 70\%$) with ${}^6\text{LiD}$ and 360 K^{-1} ($P_6 \sim 35\%$) for ${}^7\text{LiH}$; their ratio 2.3 compares very well to the width ratio, which confirms the influence of the linewidth on DNP.

4.4 ZEEMAN RELAXATION. — The nuclear Zeeman relaxation time (relaxation time of the polarization) was measured in a field of 2.5 T for temperatures between 1.9 K and 0.43 K (when it is not too long to measure). The results are shown on figure 3. The experimental points fit reasonably well a curve of the type $T_{1n} = A \exp(\mu_e H/kT)$. We conclude that in the experimental conditions mentioned above ($H = 2.5 \text{ T}$ and $0.43 \text{ K} < T < 1.9 \text{ K}$) the nuclear Zeeman relaxation is due to the F-centers, or to centers in the sample with g -values near to 2.

Fig. 3. — Zeeman relaxation time in a field of 2.55 T as a function of inverse temperature (semi-log scales).

4.5 DIPOLAR RELAXATION. — The dipolar relaxation time has been measured only at 2.5 T and 45 mK. We started from low nuclear polarization ($P_6 \sim 10\%$)

in order to avoid non-linear effects. An adiabatic demagnetization (ADRF) was performed using the techniques described in reference [12], the NMR absorption signal was monitored at constant field as a function of time with a lock-in detector. Since the Zeeman relaxation time is almost infinite at 2.5 T and 45 mK, the variations of the signal are due only to dipolar relaxation.

The behaviour of the relaxation is strongly non-exponential (Fig. 4) with an initial time constant of 5 min. and a final value of about 16 min. These figures are much shorter than the theoretical value which can be calculated with formula (3.27) of reference [10] : we conclude that for $H = 2.55$ T and $T = 45$ mK, the dipolar relaxation is not longer governed by the mechanism considered in [10], namely the thermal coupling between the dipolar reservoirs of the nuclear and the electronic spins. It is already known that in LiH, the dipolar relaxation time begins to vary much more slowly than $\exp(\mu_e H/kT)$ for $H/T > 5$ T/K [11].

Fig. 4. — Dipolar signal of ${}^6\text{Li}$ nuclei as a function of time after an ADRF starting from a polarization of 10 %.

4.6 FAST PASSAGES. — In the experiments of high energy physics using polarized targets it is often desirable to reverse rapidly the polarization of the target, in order to get rid of systematic errors and drifts occurring with a typical period of one day. In general the polarization is reversed every two hours. With the very long polarization times reported here, the reversal by straight DNP would last too long, and other techniques must be found. One of them could consist in a double target with two opposite polarizations, each part being brought alternatively into the beam. Another possibility is the NMR *fast passage* which consists in applying a radiofrequency field H_1 and sweeping the static field through the NMR line at a rate $\dot{H}$ such that :

$$\kappa = \pi \gamma_n H_1^2 / \dot{H} \gg 1$$

where γ_n is the nuclear gyromagnetic ratio. Ideally, the

entropy of the spin system is conserved during such a passage, resulting in a reversal of the magnetization with no change of its amplitude. Near the *center* of the passage, the magnetization is reduced and the order of the system is temporarily established among the dipolar interactions [12]. In practice, several types of irreversibility concur to reduce the yield of the passage :

1) When the system is in a *dipolar* state, the losses are due to the dipolar relaxation which is much faster than the Zeeman one. An analysis made in [12] establishes that the losses due to dipolar relaxation are :

$$\text{Log} \left| \frac{M_z^{\text{initial}}}{M_z^{\text{final}}} \right| \sim \pi H_L' / T_D | \dot{H} |$$

where H_L' is the local field of the nuclear spin system [12] and T_D the dipolar relaxation time.

2) Because of the finiteness of κ , the system slightly departs from equilibrium at all times, and the entropy increases.

We have performed the experiment at 2.55 T, reversing simultaneously ${}^6\text{Li}$ and ${}^2\text{D}$ nuclei. The value of H_1 was of the order of 200 mG, which is already a high value compared to those used in the study of nuclear dipolar ordering. There were in fact two radio-frequency fields simultaneously, one for each nuclear species, and we have tried three different values of $\dot{H}$: 0.5, 0.25 and 0.125 G/s. The results are shown in table I. We have calculated the theoretical losses due to dipolar relaxation using values of $H_L' = 2$ G (deduced from the experimental linewidth) and $T_D = 5$ min. = 300 s. The losses due to the finiteness of κ are then *deduced* from the above values.

Table I.

$\dot{H}$	0.5	0.25	0.125
Relax losses (calc.)	5 %	10 %	20 %
Total losses (exp.)	26 %	24 %	30 %
Losses due to finiteness of κ (deduced)	21 %	14 %	10 %

As a summary the optimum reversal using a field of 200 mG is achieved with the value of $\dot{H}$ of 0.25 G/s, and the corresponding loss is 24 %

$$(M_z^{\text{final}} = -0.76 M_z^{\text{initial}}).$$

These losses are quite large, and in disagreement with theoretical calculations. The discrepancy is not well understood at the present time. It is not possible to reverse the polarization every two hours with the figures reported here.

5. Conclusion. — We have demonstrated experimentally the possibility of obtaining high nuclear polarizations in small samples of ${}^6\text{LiD}$. It is clear that

the extrapolation to the large samples used in polarized targets for high energy physics would imply a considerable amount of additional work. Also, the long polarization times may be inconvenient for some applications. An important problem that remains to solve for building a large target concerns the reproducibility of the creation of paramagnetic centers by irradiation of the samples. This is believed to depend upon a better control of the temperature of the sample during irradiation. A cooling system using a closed loop of circulating helium gas is at present under study for that purpose.

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