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DYNAMIC NUCLEAR POLARIZATION IN IRRADIATED AMMONIA BELOW 0.5 K

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SUMMARY

We have reached +90.5% and -93.6% dynamic proton polarizations in solid NH_3 using paramagnetic radicals created by proton irradiation of 40 Mrad total dose. The dynamic polarization experiments were performed at 25 kG field in a dilution refrigerator. These results may indicate a breakthrough in the development of better polarized target materials for high-energy physics experiments.

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Ammonia (NH_3) has been studied rather vigorously in the past for its suitability as a polarized target material, because it possesses several desirable properties: i) it contains 17.8% of hydrogen, compared with two common target materials, propanediol (10.6%) and butanol (13.6%); ii) it solidifies at -77.7°C and can therefore be easily made into solid beads by dropping it into liquid nitrogen (LN_2); iii) ammonia has a relatively high solid density, 0.836 g/cm^3 (at LN_2 temperature), resulting in an over-all hydrogen density even slightly higher than that in solid methane (CH_4). All previous work was concentrated on chemical doping with paramagnetic radicals such as ethanediol-Cr(V) [1], propanediol-Cr(V) [2,3], or HMBA-Cr(V) [4].

The best results were obtained by Scheffler [1] in ammonia doped with ethanediol-Cr(V), who explained the relatively slow growth of polarization with a model based on the formation of clusters of the complex, surrounded by a relatively pure ammonia matrix. The 70% polarization [1] was not confirmed by later work [2,3], and ammonia was not introduced as a polarized target material. The reason for the weak polarization of the solvent ammonia lies probably in the fact that a phase separation takes place upon crystallization when solidifying the solution. In the work of ref. 4, a chemical destruction of the paramagnetic dopant probably takes place.

In this work solid ammonia beads of 2 mm diameter were exposed to the extracted 580 MeV proton beam of the CERN Synchro-cyclotron. The material was held in LN_2 during irradiation, and then during one week in between the irradiation and the dynamic polarization experiments. The loading to the dilution refrigerator [5] was done in such a way that at no time were the beads at a temperature higher than that of liquid nitrogen. The accumulated flux was 0.95×10^{15} protons/ cm^2 , corresponding to a deposit of 40 Mrad in the material.

The beads had an opaque white colour before irradiation, suggesting a microcrystalline structure. The colour after irradiation was pale violet. Figure 1 shows the EPR absorption in the sample at 0.15 K temperature and 70.35 GHz frequency with a field sweep. The spectrum was obtained with a carbon resistor

bolometer loosely coupled with the multimode cavity; the absorption scale is roughly logarithmic, and cannot be used for accurate quantitative measurements. The spectrum shows that the EPR line has a rather small width of about 50 G or 140 MHz, but no conclusion can be drawn as to whether this width arises from hyperfine interactions or g-factor anisotropy. The centre of the line corresponds to $g = 2.0090$, just above the value for free electrons, 2.0023. No doublet of atomic hydrogen could be observed. Among the possible radicals giving rise to this line are $\dot{\text{N}}\text{H}_4$, $\dot{\text{N}}\text{H}_2$, and $\dot{\text{N}}$; ions and trapped electrons are probably completely excluded, because the sample was exposed to light during irradiation, and held at LN_2 temperature during an extended period.

Figure 2 shows the line shapes of proton magnetic resonance in thermal equilibrium at 0.9 K, and at 90% and -93% polarizations. At high polarization the resonance line becomes somewhat more narrow and asymmetric. The asymmetry is reversed at reverse polarization. The shape of the asymmetric line has a resemblance to that arising from an axially symmetric g-tensor in EPR, and is most likely due to dipolar interactions among the proton spins themselves.

Figure 3 shows the growth of the polarization as a function of time for the two signs of polarization. The total microwave power in the cavity per unit mass of the 3 g sample was about 2 mW/g in the beginning, and at the end about 0.5 mW/g for both curves. It is likely that a major part of the losses occurred in the cavity walls, because of the large volume ratio cavity/sample, and because of the small amount of electron spins in the sample (see below). The optimum microwave frequencies were 70.215 GHz at positive and 70.480 GHz at negative polarization in a magnetic field corresponding to 106.45 MHz centre frequency of the protons in the sample. The ultimate polarization values reached in this first sample were 90.5% and -93.6%. We noted that the optimum microwave frequency (which gives the maximum polarization speed) shifted upwards as the polarization grew on the positive side. This kind of shift could be explained by a change in the hyperfine broadening of the EPR due to growing nuclear polarization.

The calibration of the Q-meter NMR signal was obtained by measuring the signal area arising from the sample in thermal equilibrium with helium at 900 ± 3 mK,

after waiting for 10 and 16 relaxation times. The calibration error is estimated to be 0.5%, coming from signal area uncertainty (0.3%) and temperature measurement uncertainty (0.4%). The temperature was measured with an encapsulated Speer carbon resistor calibrated previously against the vapour pressure of ^3He . The calibration was checked after the run against the vapour pressure of both ^3He and ^4He in a 25 kG field and was found to reproduce exactly. The linearity of the signal measurement did not need to be corrected because real-part detection was employed; neither was correction needed for saturation, because very small excitation was used.

The proton spin lattice relaxation time was measured at 25 kG between 0.4 K and 1 K. The measured values, shown in fig. 4, follow rather closely a curve which is based on the assumption that the nuclear spin relaxation rate depends on the number of electron spin flip-flops (simultaneous flips of two opposite spins). At low temperature and high field the electron spin-lattice relaxation does not depend on temperature; the flip-flop rate therefore depends only on the population of the upper energy level, given by the Boltzmann factor $\exp(-h\nu/kT)$. This temperature dependence of the nuclear spin-lattice relaxation rate is valid in many materials containing paramagnetic impurities, for example in our standard target material propanediol-Cr(V) [6].

The rather slow dynamic nuclear polarization and spin-lattice relaxation, together with the relatively small EPR absorption as seen with the bolometer, suggest that the electron spin density N_e in the material is rather small. A semiquantitative estimate for N_e can be obtained by using the relation for the proton spin-lattice relaxation time $\tau_{1p} \sim \tau_{1e} N_e^{-1}$ at constant field and temperature and comparing this with a known substance such as propanediol. With the values given in ref. 6 we obtain

$$N_e = 6.4 \times 10^{18} \frac{\text{spin}}{\text{cm}^3} \times \frac{\tau_{1e}(\text{NH}_3)}{\tau_{1e}(\text{PD})}.$$

Another estimate for N_e is found by noting that the maximum polarization speed $\dot{P}_0^{\text{max}}$ (or cooling speed of nuclear spins) at full off-resonance saturation of the

EPR is proportional to the ratio of the densities of electrons and protons in the material multiplied by the electron spin lattice relaxation rate: $\dot{P}_0^{\max} \propto (N_e/N_p)\tau_{1e}^{-1}$. Again, comparison of the well-known material, propanediol, with the data of ref. 6 gives

$$N_e = 3.6 \times 10^{18} \frac{\text{spin}}{\text{cm}^3} \times \frac{\tau_{1e}(\text{NH}_3)}{\tau_{1e}(\text{PD})}.$$

With the assumption that the ratio of the two electron spin-lattice relaxation times would be near to unity, the order of magnitude of the electron spin density in our ammonia sample would then be 5×10^{18} spins/cm³. This electron spin density corresponds to one radical molecule per 6000 NH₃ molecules. It is therefore clear that 10-100 times larger doses could be absorbed in ammonia, before significant chemical destruction will occur in the solid, or before unwanted radical reactions (such as $\dot{H} + \dot{H} \rightarrow H_2$) take place during irradiation or annealing. It would seem to us that a ten times higher radical concentration would give ammonia polarization properties comparable to those of propanediol.

Doping by radicals generated by ionizing radiation can be made to result in an homogeneous distribution of paramagnetic molecules, a clear advantage in dynamic polarization. The most important potential advantage of this method, however, would be an inherent resistance of the target to radiation, because no interference would arise between the wanted and unwanted paramagnetic impurities (or at least the original impurities could be restored by annealing), and because no final chemical destruction of the paramagnetic dopant would take place before the chemical composition of the whole target will start to change significantly. In NH₃ this might correspond to an accumulated flux of more than 10^{17} minimum ionizing particles/cm². At present the propanediol, ethanediol, or butanol targets must be changed after irradiation with less than 10^{15} particles/cm² [7]; ammonia might thus bring about an improvement of more than one order of magnitude in the radiation resistance of polarized targets.

We conclude that this is the first time that substantial polarization has been obtained in an irradiated hydrogen-rich substance, which is easy to handle

and which can be assembled to a sizeable target. With some increase in the radical concentration, NH_3 will have a figure of merit much higher than the present target materials.

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Figure captions

- Fig. 1 : EPR absorption in irradiated solid NH_3 at 0.15 K temperature and 70.35 GHz frequency. The hysteresis is due to the slow response of the carbon resistor bolometer. The absorption scale is roughly logarithmic.
- Fig. 2 : NMR absorption lines for protons in solid NH_3 at 25.02 kG with polarizations: a) 90%, b) 0.3%, and c) -93%. The curve (d) is the first derivative of curve (a). The frequency sweep in the first three curves is 400 kHz and the centre frequency 106.45 MHz.
- Fig. 3 : Growth of polarization in irradiated solid NH_3 for both signs of polarization. At negative polarization the microwave frequency was held constant at about 70.48 GHz and power was gradually decreased as the polarization increased. At positive polarization the best frequency appeared to be 70.17 GHz in the beginning, but it had to be readjusted during the growth of the polarization, the optimum being about 70.215 GHz at the end. The power was also decreased towards the end at positive polarization. The dip in the negative curve is due to an interrupt of the microwave supply.
- Fig. 4 : Temperature dependence of the proton spin-lattice relaxation time in irradiated solid NH_3 at 25 kG field. The curve fitted to the points is explained in the text.

Fig. 1

d)

NH_3
 $P = 89\%$
 $f_0 = 106.45 \text{ MHz}$

Fig. 2

Fig. 3

Fig. 4