Today's Polarized Solid Targets in Borghini's Footsteps

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The development, in the early 1960's, of the dynamic nuclear polarization process in solid diamagnetic materials, doped with paramagnetic radicals, led to the use of solid polarized targets in numerous nuclear and particle physics experiments.

In 1965 Michel Borghini moved from Saclay to CERN, where under his leadership of the polarized target group (until 1978) decisive developments have been made. Target material research and the early frozen spin targets were certainly the basis for the successful story of present day polarized solid targets.

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1. Introduction

The prehistory of the Dynamic Nuclear Polarization (DNP) process can be traced back to the late 1940s, specifically to the discovery of the Nuclear Magnetic Resonance (NMR), the simultaneous development of the Electron Paramagnetic Resonance (EPR) and the elucidation of nuclear and electronic spin lattice relaxation processes in solids. These events were, of course, interwoven with the broad and rich development of solid state physics. In 1953 Overhauser made the brilliant prediction, that, for a metal, the radio frequency (RF) saturation of the ESR line of the conduction electrons would enhance the nuclear polarization by a large factor μ_e/μ_n . The next step was taken by Abragam to extend the Overhauser Effect to nonmetals. The first published data for a clear DNP process have been made in 1959. It took another 3 years that large polarizations were achieved by DNP: 70% obtained at 1.5 K and 3.6 T. The first polarized solid target for particle physics experiments has been constructed at Saclay in 1962 (A. Abragam *et al.*), followed by the first polarized solid-target for "high energy" physics experiments at Berkeley (O. Chamberlain *et al.*).

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Since that time, various polarized solid targets have been constructed and have been operated in numerous particle physics experiments worldwide. The quality of such targets is measured in terms of their content of polarizable nuclei compared to all nuclei in the target material and of course depends on the degree of the polarization. The 1970s and early 1980s can be considered as the bloom of the development of these targets, where important technical developments have been employed (i.e. $^3\text{He}/^4\text{He}$ dilution refrigerators and superconducting magnets), to enhance the polarization degree in more appropriate target materials. At that time contacts to chemists were a normal process. Decisive for the progress was the fact that during this time experimental developments have been accompanied by theoreticians and their work, too. The theory which correctly describes the behavior of a dipolar coupled spin system under saturation is the Provotorov theory. Within this framework an expression for the spin temperature can be derived, which depends not only on the degree of saturation but also on the width of the resonance line as well on the time constants of the spin systems. With the exception of the solid state rate equations so far the considerations were restricted to the so called high temperature approximation. Due to the fact that this assumption is far from being valid under usual conditions of a DNP experiment, M. Borghini found a way, which allows the predictions of the spin theory to be tested also in the low temperature regime within special samples. Examples are the partially and fully deuterated alcohols and diols (all of them chemically doped), in which the proton polarization was either compared to the deuteron or to the ^{13}C polarization.

A comprehensive overview about the achievements made in this field up to the late 1980s together with the particular references can be found in Ref. 1. More recent overviews are given in Ref. 2, 3.

2. DNP Parameters

The principles of dynamic nuclear polarization were derived in the 1960s and 1970s^{4,5} and have been reviewed frequently, e.g. in Ref. 3. Here, only a phenomenological description of the DNP process and its relevant parameters will be given, since a comprehensive theoretical treatment of the DNP mechanisms is beyond the scope of this article.

Dynamic nuclear polarization works at low temperatures and high magnetic fields by transferring the high electron polarization of a paramagnetic species, which has to be added to the host material by chemical doping or irradiation, to the nuclei with nonzero spin in the host material. This polarization transfer is achieved in terms of microwave irradiation with frequencies close to the electron spin resonance.

Since polarization is understood as the population difference between corresponding Zeeman levels, and since the thermal equilibrium (TE) polarization is described by the Brillouin function of the Boltzmann factor, high magnetic fields and low temperatures are a precondition in order to achieve high polarization values.

In the dynamic case, i.e. under irradiation with microwaves inducing combined electronic and nuclear spin flips, several additional parameters determine the efficiency of the polarization transfer from the paramagnetic electrons to the nuclei, and hence the achievable nuclear polarization. These are quantities like microwave power fed to the sample, cooling power of the polarization refrigerator, the relation of the EPR linewidth to the nuclear Larmor frequency, and nuclear as well as electronic relaxation times, which are dependent on the properties and the concentration of the used radical. Some of these parameters show either a magnetic field dependency (e.g. the EPR linewidth), a temperature dependency or both (e.g. relaxation times). Hence for a given sample there might be an optimum in the DNP conditions, instead of a continuous increase of polarization with increasing magnetic field and decreasing temperature.

In this article special focus is put on recent alcohol target material research (especially for deuterated materials) and recent developments on the use of the so called frozen spin target technology

3. Solid Target Materials Doped with Trityl Radicals

In 1965 one priority of polarized target research at CERN like in many other laboratories was the development of 'better' polarized target materials using chemical dopants for DNP. I recommend for reading to anybody interested in this type of research the article of M. Borghini 'Choice of substances for polarized proton targets'.⁶ The breakthrough happened in 1968 with the development of a butanol + 5 % H₂O + porphyrexide mixture.⁷

Since then the paramagnetic radicals of all of the solid target materials used in particle physics experiments feature EPR lines with linewidths at least as large as the corresponding nuclear Larmor frequencies. Thus for a correct description of the DNP process the spin temperature theory is the only valid model.⁵ Whereas proton polarization values of more than 90 % could be obtained already in the early 1970s,⁸ deuteron polarization values have been considerably lower, typically 30-50 %. This changed with the use of trityl radicals for deuterated compounds. After very promising studies of Ox063 (AH 100136 sodium salt) in propanediol-d₈ and 'Finland 036' (AH 110 355 deuterio acid form) in butanol-d₁₀ with deuteron polarizations of 80 % at 2.5 T in a dilution refrigerator,⁹ a trityl doped butanol d₁₀ target was successfully used in the GDH experiment at MAMI.¹⁰ To ensure sufficient solubility of the radical, different types of trityl are used depending on the polarity of the host material. While Ox063 is readily solved in highly polar substances like diols, it is not soluble in the longer chained alcohols as it is the case for 'Finland 036'. Both radicals feature EPR linewidths of about four times smaller than the conventionally used radicals (like Porphyrexide and TEMPO as members of the nitroxyl family) and one order of magnitude smaller than EHBA-Cr(V) at 2.5 T as reported in Ref. 11. In this reference the implication of the EPR linewidth on the maximum nuclear polarization of deuterated solid target materials is discussed in detail.

Fig. 1. Molecular structure of three trityl radicals. Left: 'Finland D36' (AH 110355 deuterio acid form) used for butanol-d₁₀ Center: Ox063 (AH 100 136 sodium salt) used for propanediol-ds Right: Ox063Me (AH 111 501 sodium salt) used for pyruvic acid.

Due to their rather small gyromagnetic ratio ¹³C nuclei are — similar to deuterons - comparably difficult to polarize highly with conventional radicals. Because of their small EPR linewidth, even at higher fields, trityl radicals work very well as DNP agents also for ¹³C nuclei. For the use with pyruvic acid, which is quite polar, a third type of trityl Ox063Me is used, where the 12 hydroxyl groups are substituted with methoxy groups (see Fig. 1) to prevent reactions of the pyruvic acid with the radical. The EPR linewidth of Ox063Me is slightly larger than that of the Ox063 radical (0.28 mT compared to 0.22 mT at 335 mT).

4. Frozen Spin Targets for Particle Physics Experiments

An important question in any experiment is the optimization of the reaction counting rate

$$N = \mathcal{L} \frac{d\sigma}{d\Omega} \Delta\Omega \quad (1)$$

where $d\sigma/d\Omega$ is the cross section of interest and $\Delta\Omega$ the detector solid angle. The luminosity

$$\mathcal{L} = I \cdot n_t \quad (2)$$

is defined as the product of beam current I (number of beam particles per second) and the areal target thickness n_t (number of target particles per cm²). Thus, luminosity is one of the main quality factors in determining how fast an experiment can be done.

The quality of a polarization experiment is, however, not only given by the reaction counting rate, but is very much dependent on other factors like background from other sources and the polarization degree of the target material. In designing an experiment, one has to consider seriously these factors in addition to the luminosity. A 'Figure of merit' for polarized solid targets $FOM_{solid\ target}$, can then be defined

$$FOM_{solid\ target} = n_t \cdot P_t^2 \cdot f^2 \quad (3)$$

i.e. the larger $n_t \cdot P_t^2 \cdot f^2$ the shorter the running time required to achieve a chosen accuracy in the measured asymmetry observed observable. Here P_t is the measured

target polarization degree and f is the dilution factor (ratio of polarizable nucleons to all nucleons in the target material). As can be seen from eq. (1) another factor is $\Delta\Omega$, which in the optimal case can be 4π .

Depending on the beam intensities there are two modes of operation for a polarized solid state target system. (Polarized) electron beams have to be operated at intensities of less than 100 nA in order to handle cooling requirements and radiation damage of the target materials. In this case polarized targets with ^4He evaporative cooling are used, which have to work in a continuous mode, i.e. with permanent microwave irradiation to maintain the DNP process at 1 K.¹² At this temperature the nucleus (nucleon) polarization relaxation time T_1 is relatively short. This continuous mode operation puts strong constraints on the design of the polarizing magnets. Due to the field homogeneity requirements over the entire target volume, the large dimensions of the magnet coils limit the angles for the outgoing particles. This mode of operation has been used for the SLAC experiments in the 1990s and is presently used for experiments at TJNAF (see Fig. 2 (l)). Other electromagnetic probes such as tagged photon beams are intensity limited by their production techniques to about 10^8 particles/s. To obtain a reasonable counting rate, a wide opening angle with the ability to simultaneously measure a large kinematic range is needed. This can be achieved with the concept of the frozen spin target.

The operation of the frozen spin target is based on the experimental fact that the nucleon polarization relaxation time T_1 is a very strong function of the temperature and magnetic field. T_1 characterizes the polarization decay after switching off the DNP mechanism (microwaves). Typical values for T_1 are minutes at a temperature of 1 K and days below 100 mK. The principle of the frozen spin target operation is to polarize the target material at a high field (e.g. 2.5 T) and in the temperature range 0.15–0.3 K. Once the target material is optimally polarized, the microwaves

Fig. 2. (l) 5 T polarizing superconducting magnet with a vertically operated ^4He evaporation refrigerator. (r) The CERN dilution $^3\text{He}/^4\text{He}$ dilution refrigerator with a superconducting 2.5 T magnet and a 0.5 T dipole magnet.

are switched off and the polarization is frozen at temperatures around 50 mK (frozen spin mode). Due to the very long T_1 at these temperatures, it is possible to reduce the field to a value of around 0.5 T where the polarization decay is acceptable (holding field).

A very specific target design has been developed for the CERN polarized target experiments SMC and COMPASS.¹³ A huge $^3\text{He}/^4\text{He}$ dilution refrigerator ($T \sim 50$ mK) is connected to a 2.5 T superconducting solenoid which is surrounded by a dipole magnet (see Fig. 2 (r)). With a beam intensity of $\sim 10^7 \mu^+/s$, which was more than four orders of magnitude less than at the SLAC experiments, the luminosity was increased by having a target two orders of magnitude longer than at SLAC or TJNAF. In the CERN experiments it was not possible to flip the beam polarization (unless one changed to μ^- !) and with a polarization build-up time of hours, it was not very easy to change the target polarization frequently. So a strategy of rotating the solenoid field to the opposite direction was adopted. With 190 GeV muons and a longitudinal field, the effect on the scattered particles was minimal. A dipole magnet was turned on at a strategic time so that the total magnetic field never went below 0.5 T while the solenoid was crossing zero and the target was in the frozen spin mode. Thus the CERN polarized target can be operated in the continuous mode at 2.5 T as well as in a frozen spin mode $T \leq 50$ mK for horizontal or transverse polarization direction. Other systems using the frozen spin mode with external holding magnets have been operated by SACLAY¹⁴ and PSI¹⁵ groups.

The disadvantage of the external holding coil arrangement is the large size and strong fringe field of the superconducting magnets. Therefore such frozen spin targets cannot be operated in combination with detection systems, where modern detector components are placed close to the target refrigerator. To overcome this problem, the scheme of an internal superconducting 'holding coil' has been discussed in 1980 by Niinikoski¹⁶ but not technically realized. In 1992 a new type of a small superconducting holding magnet has been built by the Bonn polarized target group.¹⁷ The superconducting wire has been wound as a solenoid on the inner cooling shield of the vertical $^3\text{He}/^4\text{He}$ -dilution refrigerator around the target area. For the first time this technique was used in an experiment to measure the target asymmetry in a real photon photoproduction experiment at the Bonn accelerator ELSA in 1994.

This concept of a small superconducting holding magnet has been further developed in Bonn (see Fig. 3) leading to an internal holding magnet with a total thickness of ~ 1 mm, placed inside a horizontal $^3\text{He}/^4\text{He}$ dilution refrigerator.¹⁷ Thus the fringe field and its influence on nearby detector components is minimized and that makes it possible to operate polarized solid targets in a 4π -detector (e.g. DAPHNE in Mainz).¹⁸

In the meantime this scheme is adopted by TJNAF and Mainz for the operation of their frozen spin targets in the CLAS detector and CRYSTAL BALL detector, respectively.

Fig. 3. The Bonn superconducting holding magnet (0.6 T) with a total thickness of ~ 1 mm, placed inside a horizontal $^3\text{He}/^4\text{He}$ dilution refrigerator.

Meanwhile the Bonn, Mainz and TJNAF polarized target groups are able to replace the internal solenoidal holding coil by a saddle coil geometry which gives access to y- and x-polarization directions in the frozen spin mode.

5. Perspectives

The frozen spin target operation is a powerful tool for (double) polarization experiments at low intensity beams. Nevertheless the price for the good particle detection acceptance is a loss in beam time, which is needed to repolarize the target material. Furthermore a dedicated railway system to move the detector and external polarizing magnet for the polarization procedure is needed. In best cases a beam time efficiency of 80 % is attainable. The second restriction from the 'figure of merit' point of view is the decay of the polarization during the data taking. The overall target polarization of an experiment using a frozen spin target is given by the nucleon relaxation time and limited to approximately $0.8 P_{max}$. The goal for the future is to combine the advantages of the frozen spin technique with those of the 'continuous mode' operating target to a so called '4 π continuous mode' polarized target. This new polarized target scheme leads to an improvement in the 'figure of merit' by a factor of 2 compared to the existing frozen spin target operation. The important points of such a target system are:

- large angular acceptance close to 4π
- high average polarization during the data taking (continuous DNP at high polarizing field and low temperature)
- high luminosities up to $10^{33} \text{cm}^{-2} \text{s}^{-1}$
- no moving system for the polarization process required
- good beam time efficiency (fast repolarization in case of radiation damage)

In practice, starting from the existing 'internal superconducting holding coil' a new coil capable of providing an increased field (polarizing field) has to be implemented into the $^3\text{He}/^4\text{He}$ refrigerator as an internal polarizing magnet. It has to fulfill the requirements of the high homogeneity of the external polarization magnet

and the low mass distribution of the internal holding coil to ensure a good detection probability for the outgoing particles. The most crucial point which has to be considered in the development of the internal polarizing magnet is the homogeneity of the small coil. Because of the minimized dimensions of the solenoid the magnetic volume is only a factor of about 20 larger than the target volume, which needs the good homogeneity of $\Delta B/B \leq 10^{-4}$. The investigation of this problem has led to a new approach for the design of this magnet, which relies on the geometrical shape of the winding.¹⁹

Presently internal thin superconducting magnets with a field strength of ~ 2.0 T and a field homogeneity $\Delta B/B$ of 10^{-3} have been manufactured in Mainz and Bonn²⁰ and first tests in a $^3\text{He}/^4\text{He}$ dilution refrigerator will follow soon.

As mentioned above, luminosities of up to $10^{33} \text{cm}^{-2} \text{s}^{-1}$ at high polarization can be achieved with this '4 π continuous mode' polarized target i.e. beam intensities higher than $10^{10} \text{particles/s}$ upon some extended target area ($\sim \text{cm}^2$) can be accepted. However, at such levels of beam intensities the radiation resistance of the polarization due to material damage has to be considered. Then inorganic materials like ammonia (NH_3 and ND_3) or ^6LiD and ^7LiH are the target materials of choice.^{21–23}

6. DNP Polarized Target Materials for Medical Applications

Magnetic Resonance Imaging (MRI) is a very successful imaging modality in terms of temporal and spatial resolution of morphological details. The sensitivity of NMR, imaging or spectroscopy, is strongly limited by the low polarization that can be reached at room temperature and any achievable field strength. In an attempt to improve this, DNP-hyperpolarization was invented. Several imaging applications will benefit from the strong signal available from the ^{13}C agent, e.g. angiography and perfusion studies. Other applications have so far been impossible by MRI, e.g. studying the metabolic fate of a hyperpolarized agent during the first minute after injection. The ability to study metabolism of endogenous molecules could have great implications in e.g. oncology and cardiology. Conventional MRI contrast parameters have not been correlated with processes at the cellular level. The idea behind hyperpolarized ^{13}C — labeled contrast agents was to directly image by MRI an agent (e.g. endogenous molecule) that would have specificity to certain diseases.

An apparatus and method for producing strongly polarized molecules in solution has been developed.²⁴ The nuclear spins of a solid sample doped with a paramagnetic agent (Trityl or Tempo radicals) can be strongly polarized at low temperature (~ 1.2 K) and moderate magnetic field (3.35 T) by exposing the sample to microwave irradiation (94 GHz) close to the electron paramagnetic resonance. The solid sample is rapidly dissolved and an image or spectrum is acquired within a time of the order of the nuclear relaxation time T_1 (within minutes). By this method it has been possible to produce solutions of ^{13}C — labeled molecules with polarization of up to ~ 40 %.²⁵ A ^{13}C -polarization of ~ 80 % has been measured in trityl doped pyruvic

acid by increasing the magnetic field up to 5.0 T.²⁶ This very high ^{13}C polarization is certainly a result of the small EPR — linewidth of the trityl radical even at high field.¹¹ As it is shown elsewhere²⁷ the DNP mechanism in trityl doped partially deuterated pyruvic acid is Borghini's spin — temperature model.

Progress in this field is reported in a series of DNP symposia, the latest held in Copenhagen (2013).

7. Conclusion

The subsequent developments of all aspects of a polarized solid state target system have opened up new experimental possibilities and allowed a choice of approaches to a particular physics problem. There are a variety of polarizable solid target materials available with dilution factors varying between 0.13 and 0.5. The highest polarization resistance against radiation damage is shown in materials which are prepared for DNP by irradiation. Polarizing them in ^4He evaporation refrigerators with their high cooling power at 1 K beam intensities upon the targets up to $\sim 6 \cdot 10^{11}$ particles/s can be tolerated. Thus luminosities of higher than $10^{35} \text{cm}^{-2} \cdot \text{s}^{-1}$ can be achieved.

Polarized target experiments performed with low intensity beams such as polarized muons or (polarized) tagged photons have to rely on solid target materials. At intensities up to 10^8 particles/s the frozen spin mode operation of the target system is favorable in order to allow a particle detection over a large (4π) angular acceptance.

Maximum polarization values for protons $> 90\%$ and for deuterons up to 80 % are achieved. Polarization measurements are done by the NMR technique to a relative accuracy of $< \pm 3\%$ for protons and $< \pm 5\%$ for deuterons. Future developments as discussed will certainly improve the experimental situation for experiments with polarized solid targets in the next decade.

Latest developments open up the possibility to use DNP-hyperpolarized substances in the field of medicine and others. Thus DNP experiences a second spring-time and a new huge research community will profit from it enormously.

Finally I conclude with a remark of the Nobel laureate O. Chamberlain, who listed in 1985 the people that he felt to be "the heroes — the people who have given spin physics a special push". M. Borghini is the only one that he cites twice: with A. Abragam and colleagues for the first polarized target and the first experiment to use such a target; and with T. Niinikoski, for their introduction of the frozen spin target and showing the advantages of powerful (dilution) refrigerators.

For me his name on its own is manifested in DNP theory by the developments of the so called 'Borghini spin temperature model'.

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