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Neutron spin filtering with dynamically polarized protons using photo-excited triplet states

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Abstract. The use of polarized protons as neutron spin filter is an attractive alternative to the well established neutron polarization techniques. The spin-dependent neutron scattering cross section of protons is usefully large up to the sub-Mev region. Employing optically excited triplet states for the dynamic nuclear polarization (DNP) of the protons, low temperatures and strong magnetic fields are not required and the apparatus can be simplified.

The triplet DNP method can be used to build a reliably working neutron spin filter that is operated in 0.3 T and about 100 K. The high proton polarization of 0.5 obtained is presently still limited by the cooling of the sample. The corresponding analyzing power of $A \sim 0.5$, obtained with the 5 mm thick sample, can be further increased using a longer sample. Interesting possibilities for a triplet spin filter are opened by the use of neutron optics elements that allow to adapt the beam to the filter cross section.

1. Introduction

Dynamic nuclear polarization (DNP) [1], a method traditionally used to create polarized targets with which the role of spin in nuclear and particle interactions is investigated, has also opened new possibilities in neutron science where the strong spin dependence of the neutron scattering on protons is exploited [2, 3, 4]. Proton polarization values close to unity have been achieved in some cases employing the classical scheme of dynamic nuclear polarization (DNP). One polarizes electron spins by cooling them down to low temperature (∼1 K) and applying a strong magnetic field (2.5 - 5 T) and then transfers their high polarization to the nuclear spins by means of a microwave field. These stringent conditions can be relieved with a more recent and very promising DNP method that uses optically excited triplet states as the source of the electron polarization [5]. Here the triplet electron spin is polarized as a result of the selection rules of the intersystem crossing from the excited singlet to the triplet state. Then neither low temperatures nor high fields are required and the apparatus can be simplified, which is very attractive for applications. Recently we have demonstrated that the triplet method can be used to build a reliably working spin filter for neutrons operating at 0.3 T at a temperature of 100 K [6]. This note gives a short introduction to the principles of triplet DNP and reports on recent progress of the "triplet spin filter" project.

[4] academic guest

2. Neutron spin filtering with polarized protons

Shapiro and coworkers demonstrated that dynamically polarized protons offer an attractive possibility to realize a broad band neutron spin filter, as the spin-dependent neutron-proton cross section is usefully large up to the sub-MeV region [7]. However, an actual implementation of a polarized proton spin filter has been so far restricted to a few special cases, e.g., for high precision neutron polarimetry [8, 9] or to polarize neutrons of thermal [11] and epithermal energy where it is the only method currently available [12]. This is probably due to the technical requirements of a classical DNP system, which however can be significantly relaxed when employing the triplet DNP technique to realize a spin filter.

The working principle of a polarized proton spin filter is based on the fact that the singlet cross section for neutron-proton scattering is much higher than the triplet cross section [13]. Hence, neutrons polarized anti-parallel to the protons will thus be much stronger scattered than those polarized parallel. This is the case for coherent and incoherent scattering. It is customary to define a spin-dependent effective cross section

$$\sigma_{\pm} = \sigma_0 \pm \sigma_p P \ , \tag{1}$$

where the + and the − stand for the two eigenstates of the neutron spin with respect to the target's polarization axis. The spin dependent part is the product of the 'polarization cross section' σ_p and the nuclear polarization P. The term σ_0 denotes the neutron spin-independent cross section.

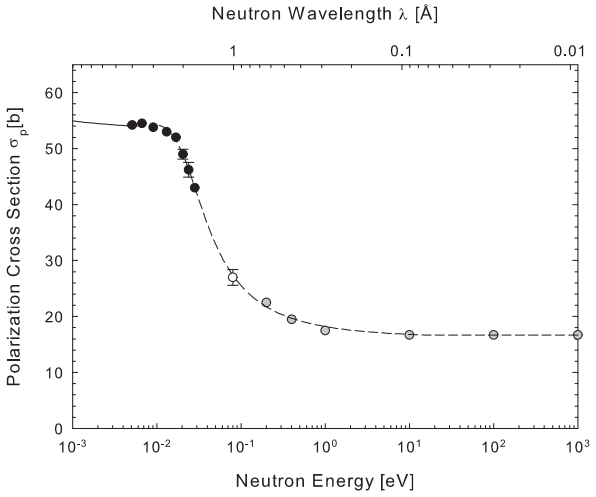

Figure 1. Typical trend of the polarization cross section σ_p as function of the neutron energy (bottom) and wavelength (top), respectively. The data points are a compilation of literature values for different materials: propanediole: black dots [14], ethylene glycol: open dot [11], LMN: gray dots [7]. The dashed line is to guide the eye, and the solid line gives the theoretical value for completely incoherent scattering and absorption.

After passing through the spin filter with a proton density N and a thickness d, the two spin components of the neutron beam are attenuated by a factor $\exp(-\sigma_{\pm} N d)$. Thus, an initially unpolarized neutron beam will have a polarization after the filter of

$$A = \tanh(\sigma_p P N d) \tag{2}$$

which is called the filter analyzing power. The thicker the filter, the higher the filter analyzing power for given $(\sigma_p N)$, and the lower the transmission T of the neutron beam

$$T = \exp(-\sigma_0 N d)\cosh(\sigma_p P N d) \ . \tag{3}$$

Note that for a given analyzing power A, the total transmission T increases with the filter polarization P.

The polarization cross section σ_p for a specific material is normally determined experimentally as structural effects observed for slow neutrons can only be treated well theoretically if the sample structure is sufficiently well known. Fig. 1 gives the general trend for the value of σ_p as a function of the neutron energy. It is qualitatively correct for most hydrogenous materials. For long wavelengths above about 5 Å, the cross section is determined by incoherent scattering and absorption on bound nuclei. With decreasing wavelength the neutrons start to resolve the chemical structure of the sample, giving rise to coherent scattering, most prominent between 2 and 5 Å. For even shorter wavelengths inelastic scattering starts to have an effect and the cross section approaches for energies larger than inter-atomic bonds ($E > 1$ eV) the one given by the scattering of isolated free protons [15].

3. Polarizing protons via photo-excited triplet states

A proven system for triplet DNP is a naphthalene molecular host crystal doped with a small concentration of pentacene guest molecules (Fig. 2). The latter can be optically excited into a triplet state where the triplet electron spin is strongly aligned. Using a short optical pulse the

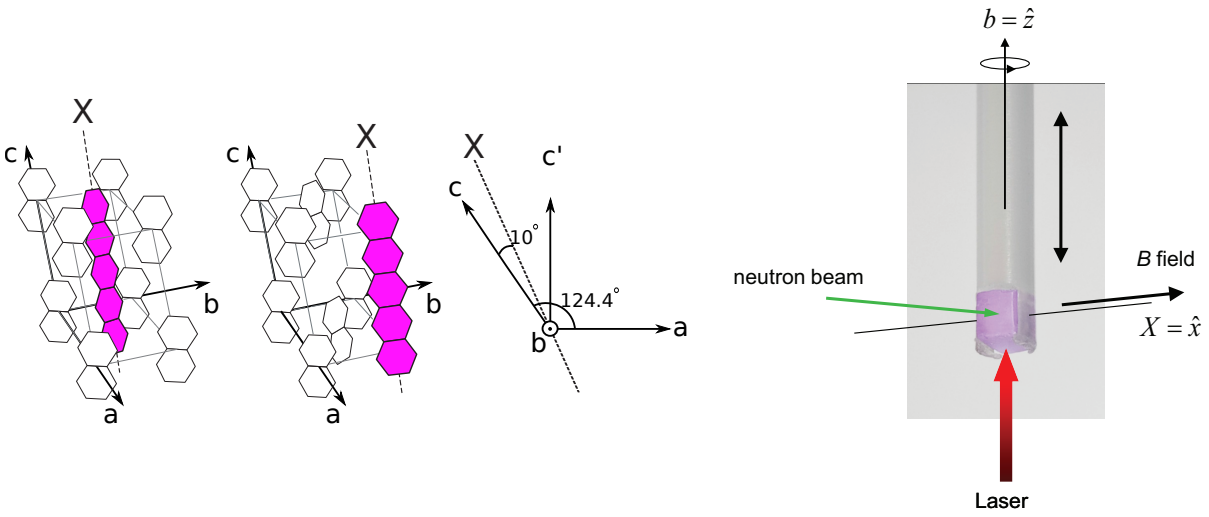

Figure 2. Left: The crystal structure of pure naphthalene is monoclinic with a unit cell with axes $a \sim 8.1$ Å, $b \sim 5.9$ Å, $c \sim 8.6$ Å and $\beta = 124.4°$ [16]. The a-b plane is the cleavage plane. Two naphthalene molecules can be replaced at two sites by one pentacene molecule whose X-axis lies in the a-c plane at an angle of 10° to the c-axis. Right: The crystal is cut such that its bottom/top corresponds to the crystal a-c plane and is mounted on a holder made of polychlorotrifluorethylene (PCTFE). By rotation around the vertical b-axis the orientation $B \parallel X$ can be set.

molecule is excited from the singlet ground state S_0 to the lowest excited singlet state S_1 (Fig. 3). From there the system either decays back to ground state under the emission of fluorescence, or decays via intersystem crossing (ISC) to the lowest triplet state T_1. While the life time of the

lowest excited singlet state S_1 is only about 20 ns, the life time of the lowest triplet state T_1 is of the order 50 μs, allowing its use for DNP. The triplet spin levels are split by fine coupling and can be further split with an externally applied magnetic field, typically oriented along the X-axis of the pentacene molecule (see Fig. 2). With $B \parallel X$ two ESR lines are observed at $\sim 0.3\,\mathrm{T}$ — separated by about 1.5 GHz — corresponding to the transitions -1 to 0 and 0 to 1. In triplet DNP only one of the two ESR transitions is used and the two energy levels involved may be regarded as a highly polarized effective spin-$\frac{1}{2}$ system. For $B \parallel X$ the selection rules for the ISC process strongly favor the occupation of the triplet level T_0 resulting in a high "effective" electron spin polarization of ~ 0.9 [17]. Furthermore the electron spin lattice relaxation time is longer than the life time of the triplet state. Hence, the triplet electron spin polarization is not only independent of temperature and strength of the applied field, but also almost completely maintained during the life time of the triplet state.

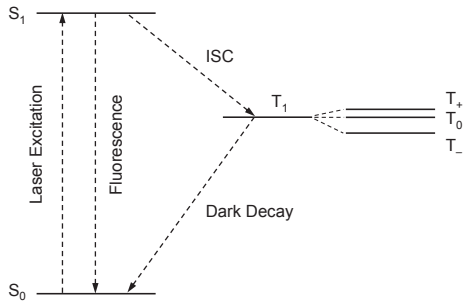

Figure 3. Simplified energy level scheme of the pentacene molecule, showing the photo physical processes during illumination with laser light. The triplet spin levels are split by fine coupling and can be further split with an externally applied magnetic field, typically oriented along the X-axis of the pentacene molecule. They are denoted as T_+, T_0 and T_-.

The Integrated Solid Effect (ISE) scheme is proven to be the most efficient method to transfer the triplet electron polarization to the nuclear spins [5]. In this method the externally applied magnetic field is adiabatically swept over the inhomogeneously broadened ESR line (typically in 15 μs) under microwave irradiation, which allows all electron spin packets to constructively participate in the polarization transfer. For more details we refer to [18, 19]. As in classical DNP, the nuclear spin polarization thus created is localized around the triplet guest molecules but spreads out further over the host molecules via spin diffusion. By repeating the cycle many times the proton spin polarization is accumulated and approaches the maximum value given by the electron polarization. Since the proton spin lattice relaxation time in naphthalene is already very long at liquid nitrogen temperature, $\sim 24\,\mathrm{h}$ in a field of 0.3 T, compared to a typical polarization build-up time of ~ 1 - 2 h, triplet DNP experiments need moderate cryogenic means only. High proton polarizations of $P > 0.30$ had been reached in fields of only 0.3 T at temperatures of 77 and 100 K [20, 21].

4. Spin filter apparatus

A detailed description of the apparatus is given in [22] and we only shortly overview its main components in the following. The large high quality spin filter crystals are grown with a self-seeding vertical Bridgman technique [23] from zone-refined protonated naphthalene and pentacene-h_{14} or pentacene-d_{14} purified by sublimation. The pentacene concentration is determined with optical transmission spectroscopy and is typically between 2 and 4×10^{-5} mol pentacene per mol naphthalene. From the single crystal samples of approximately $5 \times 5 \times 5\,\mathrm{mm}^3$ are cut such that its bottom/top corresponds to the crystal a-c plane and are mounted on a

PCTFE holder (see Fig. 2). The sample is introduced in a helium flow cryostat, cooled to typically 100 K and the pentacene molecules are excited into the triplet state with a Yb:YAG disk laser (Jenlas disk IR50) feeding an LBO crystal to generate the second harmonic at 515 nm, which proved to work excellent for DNP with pentacene-d_{14} [24]. The light is transported via a multi mode fiber to an optical stage at the bottom of the cryostat which collimates the unpolarized light to a beam of 7 mm waist shining along the b-axis of the sample crystal. In typical experiments we use pulses of 400 ns length with a repetition rate of 400 Hz up to 4 kHz and an energy of approximately 1 mJ per pulse at the entrance window of the cryostat. A static magnetic field of about 0.3 T is applied using a small electro magnet and DNP is performed with an X-band pulsed ESR system operating at 9.3 GHz that generates the ISE passages synchronized to the laser. The latter also enables us to observe the ESR signal of the triplet states and orient the static magnetic field along the X-axis of the pentacene molecules. The proton polarization is measured both by NMR, where the enhanced signal is compared to the signal measured in thermal equilibrium, and neutron transmission.

5. Performance of the spin filter

The neutron spin filter apparatus has been operated and characterized at the BOA beam line of the continuous spallation neutron source SINQ at the Paul Scherrer Institute in Switzerland [25]. In a first experiment the wavelength dependent polarization cross section $\sigma_p(\lambda)$ for naphthalene has been determined over the spectrum of the white cold beam to high precision with a moderate proton polarization only [6]. The knowledge of the polarization cross section then provides a method complementary to NMR, to characterize the samples DNP performance, i.e. the filter polarization is readily determined with a high absolute precision (better than 3 %) via a simple flipping ratio measurement. Moreover, the neutron beam can be used to measure the proton spin polarization as a function of position in the naphthalene sample, which was found to be homogeneous, even at low laser power.

The filter performance could be considerably improved employing a more efficient disk laser system in combination with pentacene-d_{14} doped naphthalene crystals. A proton spin polarization of $P > 0.40$ is now achieved in two hours and can furthermore be increased to $P > 0.50$ by reducing the heat input by lowering the repetition rate of the pulsed DNP scheme [24]. This corresponds to an analyzing power of $A \sim 0.5$ for the 5 mm thick filter.

First experience was gained with focusing elements that adapt the large beam diameter to the small filter sample. A focus de-focus scheme was set up where a parabolic mirror focuses the incoming beam of 25×25 mm horizontally and vertically on the sample and a second mirror of identical focal length restores the original beam properties [26].

6. Outlook and Conclusions

With a filter polarization of $P \sim 0.5$ already considerable analyzing powers can be achieved as is illustrated in Fig. 4 for different sample thicknesses. Taking into account the figure of merit $Q = A^2 \times T$, a thickness of 7.5 mm is ideal for cold neutrons and filter polarizations up to 0.8. For shorter wavelengths the lower cross sections suggest an optimum filter thickness of about 10 mm.

We expect that the maximum filter polarization can be further increased by a better cooling of the sample and by optimizing the DNP process. An improved cryogenic system under construction addresses the former aspect. Furthermore a detailed study of the ISE scheme used for the dynamic polarization of the protons has just been completed [18, 19] and should provide the necessary information to further optimize the parameters of the DNP process. In a next step the scaling of the filter size will be addressed which requires a redesign of the microwave cavity structure. Here a cross section of around 1 cm^2 will be envisaged.

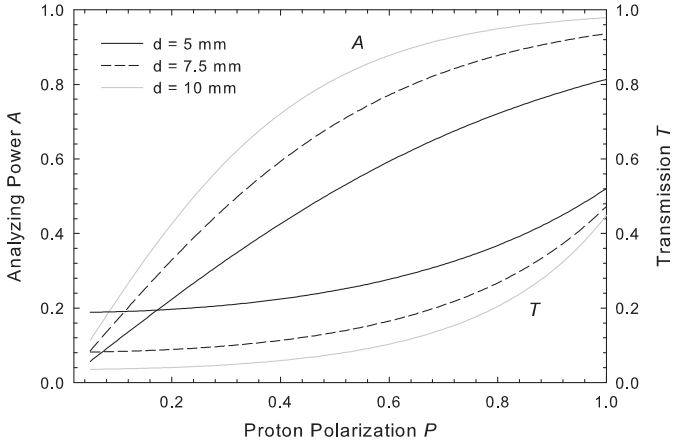

Figure 4. Analyzing power (left axis) and transmission (right axis) for different thicknesses of the naphthalene filter for the cold white neutron beam at BOA, which is peaked at $\lambda \sim 3$ Å.

A key point of the project will be the study of the filters' integration with neutron optical devices. Different neutron optics concepts for standard scattering schemes will be evaluated by Monte Carlo simulations and the most promising cases experimentally investigated. Here the use of the spin filter as primary beam polarizer for a very broad range of neutron energies will be the first scheme to study.

7. Acknowledgements

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