Time-resolved Polarized Neutron Scattering from Dynamic Polarized Nuclear Spin Targets.

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Abstract. The experiments of time-resolved polarized neutron scattering from dynamically polarized nuclei of the EHBA-Cr(V) complex are reviewed. The analysis of the data is extended to protiated samples, and the existence of polarized proton spin domains in the absence of deuteration is shown. It is concluded that pulsed neutron sources may gain considerable importance in time-resolved neutron scattering.

1. Introduction

It is the huge pseudomagnetic moment of the hydrogen isotope $^1$H which justifies its use in polarized neutron scattering. The concomitant changes of the coherent scattering length, $b$, and of the cross section of incoherent scattering $\sigma_{inc}$ of the hydrogen isotopes $^1$H (=H) and $^2$H (=Deuterium) with nuclear polarization $P$ (-1 $\leq$ $P$ $\leq$ +1) and neutron polarization $p$ ($\pm$1) are given by the following relations [1,2]:

\[
b(H) = (-0.374 + 1.456 \cdot pP(H)) \times 10^{-12} \text{ cm}
\]

\[
\sigma_{inc}(H) = 105 \left( 0.75 - 0.5 \cdot pP(H) - 0.25 \cdot P^2(H) \right) \times 10^{-24} \text{ cm}^2
\]

\[
b(D) = (0.667 + 0.27 \cdot pP(D)) \times 10^{-12} \text{ cm}
\]

\[
\sigma_{inc}(D) = (2 - pP(D) - P^2(D)) \times 10^{-12} \text{ cm}^2
\]

$P$(H) and $P$(D) are the polarization of protons and deuterons, respectively. While almost completely polarized neutron beams are obtained routinely, a high nuclear polarization is achieved less readily.

In terms of its neutron scattering length, deuterium behaves very much like other nuclei, whereas normal hydrogen is ‘exotic’, with a scattering length half the size of deuterium but negative. Moreover, the neutron scattering length varies strongly with the relative orientation of the neutron spin interacting with the proton spin, which led to the following explicit formulation:
“Lorsque la cible diffractante contient des noyaux de spin non nul, les meilleures conditions d’expérimentation sont en principe réalisées lorsque simultanément les neutrons incidents et les noyaux de la cible sont polarisés” [3].

Moreover, it has been argued that for very complex crystals it is beneficial to minimize in some way the amount of data to be refined in order to get the atomic positions of interest [4]. One way is to selectively depolarize nuclei whose Larmor frequencies differ either because of their magnetic moments or because of their proximity to paramagnetic ions in the crystal. In this way, it is concluded that one can control and vary the contribution to the structure factor of individual atoms within the unit cell [4].

The first step in this direction has been taken in the late nineties, when the possibility to use tyrosyl radicals as labels in catalase was studied. The idea was and still is that the formation of polarized proton spin domains near the tyrosyl radicals would enhance their scattering power to such a degree that a radical density map of catalase might be established. In a joint effort of the Institut de Biologie Structurale, Grenoble and of the Paul-Scherrer Institut (PSI), Villigen, it has been shown, that tyrosyl radicals do support DNP. This finding led to an enlarged collaboration which included the Service de Physique de l’Etat Condensé, CEA Saclay, and the Universities of Mainz and Munich. It was agreed that the study of the build up of proton polarization by DNP in organic radicals of different molecular weight would help to analyze the mechanism of DNP with radicals in more complex biological structures. The experiments of time-resolved neutron scattering were done at the Institute Laue-Langevin (ILL), Grenoble, at the Orphée reactor of the Laboratoire Léon Brillouin (LLB), Saclay, and at the PSI, Villigen. In the following we will recall some methods of neutron and nuclear polarization.

2. Neutron polarization

In small-angle scattering, cold neutrons with a wavelength $\lambda > 4 \, \text{Å}$ and band width $\Delta\lambda/\lambda \approx 0.1$ are polarized by a magnetic super mirror, which reflects only one orientation of the spin [5]. A magnetic guide field between the neutron polarizer and the sample preserves their polarization.

Another important ingredient is the neutron spin flipper. Various kinds exist: an adiabatic spin flipper relies on the method of adiabatic fast passage (AFP). It requires a radio frequency (rf) coil to be placed into a magnetic field gradient such the neutron will be resonant while it crosses the flipper [6]. Another way of reversing the direction of neutron polarization is provided by a flat coil spin flipper, which is due to F. Mezei [7]. The polarization of the beam measured at the sample is better than 0.96.

3. Nuclear polarization

As the magnetic moment of a nuclear spin is very small, the natural polarization even under the conditions of a strong magnetic field and low temperatures remains negligibly small. In a field of 2.5 T, a proton polarization of 0.25% is reached at a temperature of 1K. In order to obtain higher nuclear polarization, the method of dynamic nuclear polarization is used. As we are interested in the nuclear polarization of organic hydrogenous material, the method of Abragam is used [8]. In this case, the nuclear spins are polarized in the presence of paramagnetic centres that have been added in small amount. The temperature is kept between 0.1 and 1 K, and a magnetic field of 2.5 or 3.5 T is used.

The macroscopic aspects of DNP are well understood in the frame of spin temperature theory [9]. The thermodynamic model assigns heat reservoirs to various degrees of freedom of the electronic and the nuclear spin system that are coupled via mutual and external interactions. The mechanism of DNP then is described as a two step process: the cooling of the non-Zeeman reservoir by a non-saturating microwave field and the subsequent transfer of entropy to the nuclear spin system via thermal mixing. Irradiation of the system at a frequency below the electron paramagnetic resonance,
\( \omega < \omega_c \), with \( \omega_c - \omega \approx \omega_l \) (nuclear Zeeman transition) leads to positive nuclear polarization. Irradiation at a frequency \( \omega > \omega_c \) leads negative nuclear polarization. The magnitude of the mixing is strongly influenced by the microscopic structure of the material and in particular the nuclear spins close to the unpaired electrons \([10]\).

In a simple microscopic picture of DNP, the nuclear polarization develops near the paramagnetic centers through the electron nuclear dipolar interaction decreasing with the third power of the distance between electron and nuclear moments. More distant bulk protons are polarized by dipolar interactions between nuclei (spin diffusion). The same mechanism in the reverse order is responsible for nuclear relaxation in most insulating solids.

In spite of considerable theoretical and experimental work, the mechanism of DNP is not fully understood. The problem is complicated by the fact that the local field created by the paramagnetic moment shifts the Larmor frequencies of close nuclei with respect to that of bulk nuclei, thus suppressing spin diffusion. Furthermore, interaction between the paramagnetic centers (the electron non-Zeeman reservoir in the thermodynamic model) plays an important role in the establishment of a common spin temperature between close and bulk nuclei and also between isotopes in a sample.

4. Experimental

A facility for DNP meeting the requirements of neutron diffraction has the following features:

1. The sample is cooled by liquid helium (\(^4\)He).

2. For temperatures below 1 K, the \(^4\)He bath of the sample cell is coupled to the mixing chamber of the dilution refrigerator, the \(^3\)He/\(^4\)He mixture of which reaches temperatures slightly below 0.1 K.

3. The liquid helium consumption is moderate: between 1 and 2 liter/h.

4. The magnet is designed so as to allow a large solid angle for the scattered neutrons.

5. The sample exchange time is short: less than 0.5 h for 1 K cells, less than half a day for 0.1 K cells.

6. The sample volume is slightly less than 1 ml. A typical size of the platelets is 15 x 15 x 3 mm\(^3\).

The NMR signal is detected by a continuous wave (cw) spectrometer. It consists of a radio frequency (rf) source, a NMR coil, a detection system called Q-meter, and a digitization unit. The system is sensitive to a change of the impedance of the sample due to polarization. For proton NMR with magnetic fields of 2.5 T and 3.5 T the system is operating at 106 MHz and 150 MHz respectively. Through a coaxial switch inserted in the (3/2)\(_1\) cable connecting the NMR coil with the Q-meter a separate dedicated rf system can be connected to the coil. It is used to manipulate selectively the nuclear spin systems of the samples, e.g. to perform AFP polarization reversals \([11]\) or to destroy the nuclear polarization.

The microwave system consists of a source, a wave guide, and a multimode cavity. The high frequency of 70 GHz source is a carcinotron operated at B = 2.5 T. The frequency is easily modulated: a frequency jump of 300 MHz takes only a few microseconds \([12]\).
experiments with time resolved polarized neutron scattering were done with a different microwave system: Two IMPATT diodes of 100 mW output power, tuned to frequencies corresponding to positive and negative DNP, respectively (97.0 GHz and 97.5 GHz, with B=3.5 T), can be connected alternatively to the sample cavity (Fig. 1) by an electro-mechanical wave guide switch. This is the microwave system from PSI (Fig. 1).

In many cases DNP has been performed in the presence of a chromium-(V) complex, C_{12}H_{22}CrO_7Na.H_2O (EHBA-Cr(V)) (Fig 2), dissolved in a mixture of glycerol and water. The synthesis of EHBA-Cr(V) is done in one step [13]. EHBA-Cr(V) is very soluble in water. It is stable in acid pH. Glassy slabs of 3 mm thickness are obtained by injecting the solution into a copper mould cooled to by liquid nitrogen. This is done in a dry nitrogen atmosphere of a glove box.

**Dynamic nuclear spin contrast**

By dynamic nuclear spin contrast we mean a time-dependent nuclear spin contrast, which is observed in time-resolved polarized neutron scattering. The nuclear polarization obtained by DNP is far from the polarization at thermal equilibrium. It will decay more or less readily depending on the temperature of the sample. At a temperature of 1 K and in magnetic field of 3.5 T, the relaxation time is about 10 to 20 minutes. The build up of a local proton polarization near paramagnetic centres or its decay is expected to occur in a much shorter time. An abrupt and selective change of the polarization leads to a strong polarization gradient near paramagnetic centres. The observation of the subsequent relaxation process by neutron scattering tells us how the perturbed polarization distribution finds its way to equilibrium.

Among the various ways of creating a strong spatial non-equilibrium polarization, the method of AFP seems to be the obvious choice. An rf scan restricted to the central peak of the proton NMR signal, will lead to a reversal of proton spins not too close to paramagnetic centers, i.e. of the bulk protons. The polarization of the protons close to the paramagnetic centre, i.e. of the ‘close’ protons, will hardly be affected. An rf scan across the wings of the proton NMR signal will reverse the
polarization of the ‘close’ protons. This method requires a reasonable high initial nuclear polarization that is achieved after prolonged microwave irradiation.

The other way is to address to the paramagnetic centers directly. Again the method of AFP can be considered. The more promising way is a periodic change in the direction of DNP. This is most easily done by changing the microwave frequency. Typically, the direction of dynamic polarization was changed each 10 seconds. During a half-cycle 100 pictures were taken. The cycle was repeated several thousand times [14]. Most of the data shown below have been obtained in that way.

4.1. EHBA-Cr(V) in deuterated solvents.

We recall some of the results on this compound which have been published some years ago [14][15]. Then we will extend the analysis to that part of experimental data which remained unexploited for reasons which will be outlined below.

Time-resolved neutron scattering from a solution of EHBA-Cr(V) in a mixture of deuterated glycerol and D$_2$O shows most clearly the build up of proton polarization (Fig. 3). Within 10 seconds the polarization of the protons of the EHBA-Cr(V) molecules changes from -0.35 to +0.22, i.e. by 57%, whereas the polarization of the few protons of the solvent (< 0.02) as monitored by NMR varies by 12 %, only. This difference in the evolution of the polarization between the close and the bulk protons reflects the mechanism of DNP: a strong initial gradient develops due to the fast polarization of the protons close to the paramagnetic centre that then spreads out to the bulk with a slower rate [14].

At this point, the immediate build up of a proton polarization domain near paramagnetic centers may be attributed to two circumstances: (i) The most evident one is the gradient of isotopic composition. The scarcity of protons in the strongly deuterated solvent impedes nuclear spin diffusion from the high proton density region of the radical molecule to the deuterated solvent almost completely deprived of its protons. (ii) There may be an influence of the local magnetic field of the paramagnetic centre which changes the Larmor frequency of the close protons rendering them less apt for nuclear spin state exchange. This spin diffusion barrier might also contribute to a confinement of nuclear polarization near paramagnetic centers. A crude estimate yields 8 Å for the radius of an isotropic diffusion barrier. This is the distance at which the difference in the z-component of the field created by the paramagnetic centre at neighboring nuclei is comparable with the bulk NMR line width. The field gradient is of the order of $3\mu_0 r^2$, which gives 250 GÅ$^{-1}$ at 5 Å, roughly outside the EHBA-Cr(V) molecule [14].

In order to show the efficiency of a spin diffusion barrier in creating a polarization gradient near paramagnetic centers the time resolved neutron scattering experiments on proton spin polarized samples should done with protiated samples, i.e. in the absence of deuteration. In fact the French-Swiss-German collaborative team (see Acknowledgements) started experiments on EHBA-Cr(V) in glycerol/H$_2$O at the very beginning, i.e. in 2000. The hope to see a neat contrast from a local proton polarization was drowned by the apparent impossibility to extract any structural information from time-resolved neutron scattering intensity data dominated by incoherent scattering. We will come back to this point further below.
Fig. 3. Close proton polarization deduced from the time-resolved neutron scattering data (○) and bulk proton polarization measured by NMR (□). The deuteration of the solvent is 0.98 [14].

Fig. 4. Close proton polarization deduced from the coherent neutron scattering intensity of EHBA-Cr(V) and bulk proton polarization from NMR (□). The deuteration of the solvent is 0.8.

Fig. 5. The variation of the short time constant $\tau_1$ of the build up of proton polarization with the deuteration of the solvent. The squares result from the periodic variation of the direction of DNP. The triangles present NMR data from the relaxation of the proton polarization in the absence of microwaves. Open symbols indicate less accurate values. The lines are fixed to black symbols.
The more prudent approach was to decrease the deuteration gradually, and to try to extrapolate to the state of a completely protiated sample [15]. The results of the experiments using alternating direction of DNP will be recalled briefly. The analysis of the data of time-resolved neutron scattering starts with the determination of the variation of the proton polarization with time and its analysis in terms of exponentials. From the data of EHBA-Cr(V) in a deuterated solvent shown in Fig. 3, a short and a long relaxation time, $\tau_1 = 1.1$ s and $\tau_2 = 5.5$ s, are obtained. With decreasing deuteration of the solvent, the intensity of incoherent scattering from the protons increases, while the intensity of coherent scattering due to the contrast of the solute decreases. The analysis of the data from sample of lower deuteration shown in Fig. 4 is more difficult, also because $\tau_1$ becomes shorter and $\tau_2$ becomes much longer [15]. The variation of the characteristic time constant $\tau_1$ with the deuteration of the solvent is shown in Fig. 5. From the double logarithmic plot we expect a characteristic time $\tau_1$ of about 0.3 s in the absence of deuteration.

4.2. EHBA-Cr(V) solution in the absence of deuteration.

The study of the proton polarization build up in solutions of EHBA-Cr(V) in the absence of deuteration is most conveniently observed by proton NMR in the absence of microwave irradiation. In practice, a high proton polarisation is achieved after prolonged microwave irradiation. Immediately thereafter, the polarization of the bulk protons is reversed by AFP. Fig. 6 shows the variation of the proton polarization after positive DNP and reversal of the bulk protons to negative polarization by AFP. The short relaxation time of 1 s may be attributed to the exchange of polarisation between positively polarized close protons near the unpaired electron of an EHBA-Cr(V) molecule and the more distant negatively polarized bulk protons. This short relaxation time of $\tau_1 = 1$ s measured in the absence of microwave irradiation is about three times longer than the expected relaxation time from cyclic change of the direction of DNP, i.e. in the presence of microwave irradiation (Fig. 5).

![Fig. 6. Time-resolved proton NMR from EHBA-Cr(V) in glycerol-water (1/1) after positive DNP and subsequent polarization reversal of the bulk protons by AFP. The time of fast relaxation is 1 s. Microwaves OFF.](image)

![Fig. 7. Time-resolved neutron scattering from EHBA-Cr(V) during one cycle of positive and negative DNP. The solid line represents the approximation by (2), with the restriction that the periodic function is continuous. Microwaves ON.](image)
Let us turn to time-resolved neutron scattering using alternating direction of DNP. From Fig. 5 a fast characteristic time $\tau_1 = 0.3$ s is expected. The variation of the neutron scattering intensity shown in Fig. 7 seems to confirm the estimated value.

The variation of the intensity of time-resolved neutron scattering is analyzed for intervals of the modulus of momentum transfer $Q$ of different total $\Delta Q \geq 0.04$ Å$^{-1}$. As we expect a linear variation with time of the intensity of neutron scattering with a short non-linear variation after each change of the direction of polarization, the following approximation was used

$$I(Q,t) = a(Q) + b(Q)t + c(Q)e^{t/\tau_1}$$

The decrease of the intensity at the onset of positive DNP shown in Fig. 7 seems to be slightly slower at the start of the cycle, which leads to a negative coefficient $c(Q)$. At the onset of negative polarization a similar non-linear change of the scattering intensity with time is observed.

![Fig. 8. The Q-dependence of the change c of the neutron scattering intensity characterized by $\tau_1$. The solid and open squares present c(Q) at the start of positive (lower part) and negative (upper part) DNP, respectively. Results obtained with $\Delta Q \geq 0.09$ Å$^{-1}$ are shown. Lines are calculated from the EHBA-Cr(V) model surrounded by a spherical distribution of selectively polarized protons of two different widths close to that of the protons of the EHBA-Cr(V) molecule (see text).](image1)

![Fig.9. The variation of the scattering length of the EHBA-Cr(V) molecule (full line) and of the solvent molecules displaced the EHBA-Cr(V) molecule (dashed line) as function of proton polarization. The horizontal arrows present the nearly constant scattering density of the solvent at the onset of positive DNP (right) and negative DNP (left). The vertical bars present the contrast.](image2)
The coefficient $c(Q)$ of the exponential term in (2) varies with $Q$ as shown in Fig. 8. $c(Q)$ is negative at the start of positive DNP, and its modulus decreases with $Q$. Changing to negative DNP at the start of the second half cycle, $c(Q)$ tends to be slightly positive.

We assign the exponential term in (2) to the polarization of the protons close to the unpaired electron of the EHBA-molecule. As the solvent is not deuterated and neglecting the angular dependence of the electron spin proton spin interaction [16], the domain of preferentially polarized close protons is assumed to be spherical. In other words, the domain will comprise close hydrogen atoms mostly of the EHBA-Cr(V) molecule and those hydrogen atoms of the solvent molecules which are close to the unpaired electron of the EHBA-Cr(V) molecule.

The change of the neutron small-angle scattering intensity from spherical domains of selectively polarized protons is most conveniently described by a development of the scattering amplitude, $A(Q)$, as a series of spherical harmonics, $Y_{l,m}(\Omega)$.

$$A(Q) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} A_{l,m}(Q) Y_{l,m}(\Omega)$$

where $\Omega = (Q, \Omega)$. $\Omega$ is a unit vector in the momentum space. With the amplitude $V(Q)$ of the selectively polarized close nuclei and $U(Q)$ as the amplitude of the residual structure including the slowly polarizing bulk nuclei, the intensity of neutron scattering will vary with the nuclear polarization $P$ and the neutron polarization $p$ as follows.

$$I(Q, P) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \left| U_{l,m}(Q) \right|^2 + 2 PP_{\alpha,0}(Q) V_{0,0}(Q) + P^2 V_{0,0}^2(Q)$$

The spherical structure of the polarization domain implies that the polarization dependent scattering intensity functions will be dominated by the monopole term ($l=0$). In a first approximation, a change of the intensity of neutron scattering due to the build up of the polarization domain is given by $U_{0,0}(Q)V_{0,0}(Q)$, i.e. this cross term is proportional to $c(Q)$ in (2).

At $Q = 0$, $c(Q)$ is proportional to the product of the contrast of the polarized proton spin domain and the contrast of the EHBA-Cr(V) molecule. The effective scattering length (= contrast * volume) of the solute as a function of the proton polarization is obtained from Fig. 9 as the difference between the scattering length of the EHBA-Cr(V) molecule and the scattering length of the solvent molecules displaced by the latter. The proton spin contrast vanishes at $P=0.2$.

For a further analysis we make the simplifying assumption that the variation of the polarization of the close protons during one cycle of DNP hardly exceeds that of the bulk protons ($\Delta P = 0.10$). The polarization of both the close protons and those of the bulk then varies between -0.05 and +0.05. What is going to happen during one cycle? At the start of positive DNP ($t=0$ in Fig. 7, left side of Fig. 9) the close protons may have a polarization of $P = -0.05$, the same as that of the solvent (left side of Fig. 9). DNP will lead to a fast polarization of close protons in a fraction of a second. During this time the polarization of the bulk protons will have hardly changed (horizontal arrow in Fig. 9). The contrast (vertical bars in Fig. 9) increases rapidly for a very short time. The concomitant increase of coherent scattering will compensate for a short time the decrease if the intensity due to incoherent scattering (Fig. 7). At the end of the first half cycle, i.e. after 5 seconds of DNP, the polarization of the bulk protons will have come close to that of the close protons. The next half cycle starts from a positive polarization of both close protons and bulk protons. For a short time negative DNP will decrease the
polarization and the scattering density of the close protons more rapidly than those of the bulk. During this short period the contrast of the solute will decrease compensating to some extent the increase of the intensity due to incoherent scattering (right side of Fig. 7 and of Fig. 9).

The cycle of dynamic proton spin contrast variation allows an estimate of the change of the scattering curves of EHBA-Cr(V) at very short times after the start of each half cycle. Assuming an isotropic distribution of polarized close protons with a range similar to that of the protons of EHBA the change of the scattering intensity due to the preferential polarization of the close protons has been calculated for the contrast at P= -0.05 and P= +0.05. The widths of the radial distribution of the close protons were those of the EHBA-Cr(V) molecule multiplied by 0.8 (full line in Fig. 8) and 1.2 (dashed line in Fig. 8). The corresponding scattering intensity profiles \( U_{0,0}(Q)V_{0,0}(Q) \) agree with the experimental data (Fig. 8). From the present stage of the data analysis it may be assumed that the size of the spherical magnetic diffusion barrier is close to the size of the EHBA-Cr(V) molecule. A more rigorous treatment of the data using a thermodynamic model for the dynamics of nuclear polarization [15] of the data is in progress.

Conclusions

The analysis of time resolved neutron scattering from EHBA-Cr(V) in a protiated solvent shows the existence of a proton spin polarization gradient near the paramagnetic centres. This observation can be taken as a clear manifestation of a magnetic spin diffusion barrier near paramagnetic centres.

The low contrast is a real technical challenge for time-resolved neutron scattering experiments from dynamic polarized nuclei in hydrogenous material. Similar experiments with polyethylene illustrate this [17]. Apart from the rather complex set up for dynamic polarization a very powerful source of thermal neutrons is needed. The reactor of the Institute Laue-Langevin is most appropriate for this purpose. At this point the use of a pulsed neutron source might offer some additional advantages. One them is the fact that fast neutron of a pulse are the first to arrive at the sample. These neutrons with a short wavelength are well suited for probing the short range order, e.g. the onset of dynamic nuclear polarization near paramagnetic centers. The slower neutrons arriving slightly later are more apt to see the expansion of the polarized proton spin domain. Other aspects concern the way how a stroboscopic experiment is conducted. The cyclic repetition of DNP in different directions, eventually coupled with AFP, offer new possibilities of a pulsed neutron source. The pulse width and the pulse repetition rate of IBR2 [18] matches well the characteristic times of nuclear polarization build up in dynamic polarized targets.

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