Nuclear magnetic ordering in fluorene

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Résumé. — Ce travail discute la possibilité d’obtenir de l’ordre magnétique nucléaire dans des cristaux moléculaires de fluorene par polarisation dynamique nucléaire (DNP) suivi par désaimantation adiabatique nucléaire dans le référentiel tournant (ADRF). On trouve que cet ordre est obtenu de la façon la plus facile orientant $\mathbf{B}_0 \parallel$ à l’axe $c$ et choisissant $T < 0$. Alors une polarisation nucléaire de 26% suffit pour obtenir un ordre ferromagnétique. L’importance du fluorene est donnée par la possibilité d’utiliser des triplets photoexcités pour la DNP. Alors, pendant et après la ADRF l’échantillon ne contient pas des centres paramagnétiques et l’étude de l’ordre magnétique nucléaire est plus pure.

Abstract. — The present paper considers the possibility to obtain a magnetic ordering of the proton spins in molecular crystals of fluorene using dynamic nuclear polarization (DNP) followed by adiabatic demagnetization in the rotating frame (ADRF). It is found that such an ordering is most easily reached for $T < 0$ and $\mathbf{B}_0 \parallel c$-axis. Then a polarization of only 26% needs to be reached by DNP in order to obtain a ferromagnetic ordering. The importance of fluorene lies in the possibility to use photoexcited triplet states for DNP. Then, during and after the ADRF the sample is free of paramagnetic centres and a cleaner study of the ordering can be made.

1. Introduction.

Nuclear spins may order magnetically due to nuclear exchange interactions as occurring e.g. in $^3$He [1], or to indirect spin-spin interactions as observed e.g. in TmPO$_4$ [2], or simply to long range dipolar interactions. The first example of this latter dipolar magnetic ordering of nuclear spins was produced by Abragam and coworkers. They created this ordering in two steps. First, the nuclear spins were polarized by Dynamic Nuclear Polarization (DNP). Then an adiabatic demagnetization in the rotating frame (ADRF) was performed on the Nuclear Magnetic Resonance (NMR) transition to cool the spin system down to sub-micro Kelvin temperatures. Such experiments have been performed on simple cubic systems formed by the nuclear spins $I_F = \frac{1}{2}$ of $^{19}$F in CaF$_2$ [3], the nuclear spin $I_{\text{Li}} = \frac{3}{2}$ of $^7$Li and $I_F = I_H = \frac{1}{2}$ of $^{10}$F or protons in LiF and LiH [4, 5] and the hexagonal quasi two-dimensional system of proton
spins in Ca(OH)$_2$ [6, 7]. A second method to produce dipolar magnetic ordering of nuclear spins was introduced by Huiki et al. [8]. Using brute force adiabatic demagnetization they produced an antiferromagnetic ordering of the spins of the Cu nuclei in metallic copper.

The present paper discusses the feasibility of an improvement of the method introduced by Abragam and coworkers. In their first cooling step (conventional DNP) one uses microwave irradiation to transfer the electron spin polarization of permanent paramagnetic centres to the nuclear spins. However, these paramagnetic centres lead to nuclear spin-lattice relaxation and hence to fast heating of the nuclear spin system after the ADRF, so the ordered state is rapidly destroyed. The use of Microwave Induced Optical Nuclear Polarization (MIONP) [9, 10] instead of DNP would solve this problem. Thus far, the best example is protonated fluorene doped with phenanthrene. Using UV-light, the phenanthrene molecules are photo-excited into their lowest triplet state, creating electron spins $S = 1$. Operating at $T = 1.4$ K, in a magnetic field $|B_0| = 2.7$ T, and using a microwave frequency of 75 GHz to transfer the electron spin polarization to the protons, a proton spin polarization of 42% has been achieved [11]. After shutting off the excitation light, the phenanthrene molecules decay to their diamagnetic ground state and the nuclear spin-lattice relaxation becomes very slow. At 1.4 K and 2.7 T dipolar order relaxes with a time constant of $2.3 \times 10^3$ s, which is more than three orders of magnitude longer than in the presence of paramagnetic centres [11].

The aim of this article is to investigate how much nuclear polarization is required to create magnetic dipolar ordered states in fluorene. Thus we can evaluate whether MIONP is developed far enough to start studies of dipolar magnetic ordering of nuclei. As is well known, after cooling the nuclear spins with DNP and a subsequent ADRF, these spins still experience a strong externally applied magnetic field $B_0$, so they order due to the truncated dipolar interaction

\[ \mathcal{H} = \frac{1}{2} \sum_{i,j} A_{i,j} (3I_i^z I_j^z - I^z \cdot I^z). \]  

(1)

In this Hamiltonian

\[ A_{i,j} = \frac{\mu_0 \gamma_i^2 \hbar}{4\pi} \frac{1 - 3 \cos^2 \theta_{i,j}}{r_{i,j}^3} \]  

for $i \neq j$  

(2)

\[ A_{i,i} = 0, \]  

(3)

where $r_{i,j}$ is the vector connecting spins $I^i$ and $I^j$, $\theta_{i,j}$ is the angle between $r_{i,j}$ and $B_0$ and $r_{i,j} = |r_{i,j}|$. Finally, $\gamma_i$ is the gyromagnetic ratio of the nuclear spins.

By choosing the sign of the frequency change during the ADRF one has the possibility to create at will negative or positive spin temperatures. In the former case the energy tends to a maximum, while in the latter case it tends to a minimum. The case of the truncated dipolar interaction allow for two types of orderings, longitudinal orderings where the nuclear spins are directed parallel or anti-parallel to the externally applied magnetic field and transverse orderings where they are oriented in the plane perpendicular to $B_0$. In the effective field approximation, each longitudinal magnetic structure with an energy $+E_D$ has a counterpart in a transverse magnetic structure with an energy $-\frac{1}{2}E_D$ [12]. Therefore, to predict which magnetic structure actually occurs, one only needs to determine which longitudinal structures correspond to maximum and minimum energy. Subsequently, one can deduce directly whether transverse structures with higher or lower energies exist.

The crystalline structure of fluorene is very complicated. As shown in figure 1, the orthorhombic unit cell contains 4 molecules and 40 proton spins [13]. Therefore we did not venture to calculate the space Fourier transform of the coupling constants $A_{i,j}$ [14]. Instead, to
determine the structure of the ordered phases, we use a Monte Carlo simulation of the nuclear spin system. This method has proven to give reliable results for truncated dipolar interactions between nuclear spins in a simple cubic arrangement [15] and the full dipolar interaction between nuclear spins in a face centered cubic lattice [16]. For negative spin temperatures, we always find a longitudinal ferromagnetic ordering, while for positive temperature the ordering is always transverse ferromagnetic or helicoidal. Next, using the molecular field approximation [12, 14], we calculate the critical polarization, which must be minimally produced by MIONP in order to reach an ordered state after the ADRF. For negative spin temperature and $B_0 \parallel c$-axis, we find that only 26% nuclear spin polarization is needed for this purpose. In experiments the observed critical polarization is usually about 1.3 times higher [12], which is still below 42%. So a ferromagnetic ordering of the proton spins is within reach.

Fig. 1. — The crystallographic unit cell of fluorene, with the definitions of the crystal axes.

2. Monte Carlo simulations.

In the proposed experiment, nuclear dipolar magnetic ordering in fluorene is created by first polarizing the nuclei by MIONP. After MIONP the strong external magnetic field $B_0$ is oriented along one of the crystalline $a$, $b$ or $c$-axes (see Fig. 1) and an ADRF is performed by applying a strong rf-field with a frequency $\omega$ and sweeping this frequency towards the nuclear Larmor frequency $\omega_L = \gamma_L |B_0|$. Finally, the amplitude of the rf-field is reduced to zero. Note that the strong magnetic field is still present.

To describe the nuclear spin system we use a frame of reference rotating with the nuclear Larmor frequency about the direction of the external magnetic field. Then the nuclear spin system is described by the truncated dipolar interaction (1) between the nuclear spins. For the prediction of the properties of the ordered states we calculate the dipolar energy, using the molecular field approximation. As discussed in the introduction we only need to calculate the energy $E_D$ of so-called longitudinally ordered states, where the spins $I^i$ are oriented either parallel or anti-parallel to $B_0$. The energy of transversely ordered states can be deduced from
these values. Then this energy is given by

$$E_D = \frac{1}{4} \sum_{i,j} A_{ij} p_i p_j,$$

(4)

where \( p_i = <I_i^i > / I \) is the polarization of the \( i \)th spin. In order to determine the structure of the dipolar ordering, i.e., to determine for each spin whether \( p_i \) is positive or negative, we first consider the case that the dipolar temperature is very close to zero [21], so \( p_i \approx \pm 1 \). Then,

$$E_D = \frac{1}{4} \sum_{i,j} A_{ij} f_{ij},$$

(5)

where \( f_{ij} \) is the structure parameter: \( f_{ij} = +1 \) if the spins \( I^i \) and \( I^j \) are parallel, \( f_{ij} = -1 \) in the opposite case. We note that the dipolar interaction is long range so the sum (5) is generally dependent on the shape of the sample.

We use a Monte Carlo simulation [17, 15] to determine the spin configuration i.e., the factors \( f_{ij} \), yielding the highest and lowest value of \( E_D \). Our model consists of a small rectangular crystal with six crystallographic unit cells [13], containing in total 240 proton spins. The Monte Carlo calculation is started with random values for \( p_i \). Then the dipolar energy \( E_D \) is calculated using equation (5). We restrict the sum to spins where \( r_{ij} \leq 8 \) Å. Thus, on the average 48 to 96 neighbouring spins are taken into each sum, depending on the distance between the spins and the surface of the crystal. Then we allow one spin to flip and calculate the dipolar energy again. This new dipolar energy, \( E'_D \), is compared with the previous one, \( E_D \). We accept the spin flip if

$$e^{-\frac{E_D - E'_D}{k_B T_D}} > \mathcal{R}$$

(6)

where \( \mathcal{R} \) is a pseudorandom rational number between 0 and 1 determined in the way described in [18], \( k_B \) is Boltzmann’s constant and \( T_D \) is chosen to be \( \pm 1 \) nK which is far below the expected transition temperature. If the spin flip is not accepted, the spin is set back in its original orientation. We continue this procedure by sequentially flipping all 240 proton spins. After passing about 20 times through these 240 spins, a stable spin configuration is reached where the dipolar energy is maximal for \( T_D = -1 \) nK and minimal for \( T_D = +1 \) nK.

In order to characterize the thus obtained spin configuration, we perform a space Fourier transform yielding

$$p(k) = \sum_{i=1}^{240} p_i e^{i k \cdot r_i},$$

(7)

and investigate whether \( p(k) \) has a profound maximum. If such a maximum is found for a value of \( k \) such that \( \lambda = 2\pi |k|^{-1} \) is of the order of the distance between the nuclear spins, the order is antiferromagnetic. If however \( \lambda = 2\pi |k|^{-1} \) is comparable to the dimensions of the model, the nuclei order in a ferromagnetic domain structure.

We performed these Monte Carlo simulations for the external magnetic field \( \mathbf{B}_0 \parallel \) to the \( a, b \) an \( c \)-axis. As an example figure 2 shows the development of the total magnetization and the total energy of the spin system during the Monte Carlo procedure for the case that magnetic field is oriented along the crystal \( b \)-axis. Figure 3 shows the \( b \)-component of the space Fourier transform (7) of the obtained structure as a function of \( k_b \). A profound peak is observed for \( k_b = 0.42 \) Å\(^{-1} \).

Table I summarizes the results for the dipolar energy for each direction of \( \mathbf{B}_0 \) and for both signs of \( T_D \). The first column gives the sign of \( T_D \). The next column gives the direction
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Fig. 2. — Example of a Monte Carlo simulation of $E_D$ and magnetization of the model. Orientation of the magnetic field is along the $b$-axis, $T_D = -1$ nK.

Fig. 3. — Space Fourier transform of the obtained ordered phase with the magnetic field along the $b$-axis, $T_D = -1$ nK.

The following 3 columns show the dimensions $e_a$, $e_b$ and $e_c$ of the model used for the Monte Carlo simulation in the $a$, $b$ and $c$-direction ($a = 8.365$ Å, $b = 5.654$ Å, $c = 18.745$ Å, see Fig. 1). The sixth column presents the dipolar energy of the longitudinal orderings simulated in our Monte Carlo calculations. Note that this value still depends on the shape of the crystal. Therefore the results are given in arbitrary units. Using the argument presented in the introduction we have calculated the maximum and minimum dipolar energies of the transverse orderings. These are shown in the last column of Table I. As for $T_D < 0$, the energy should be maximal, the ordering is always longitudinal, while for $T_D > 0$, where the energy should be minimal, the ordering is always transverse. Furthermore, for a given direction of the magnetic field the structure of the longitudinal ordering at negative temperature is the same...
Table I. — Monte Carlo results for $E_D$. The units are arbitrary. Note that the results depend on sample shape.

<table>
<thead>
<tr>
<th>$T_D$</th>
<th>$B_0$</th>
<th>model size</th>
<th>$E_D$</th>
<th>$E_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>to</td>
<td>$e_a$</td>
</tr>
<tr>
<td>$&lt; 0$</td>
<td>$a$</td>
<td>$3a$</td>
<td>$2b$</td>
<td>$c$</td>
</tr>
<tr>
<td>$&lt; 0$</td>
<td>$b$</td>
<td>$2a$</td>
<td>$3b$</td>
<td>$c$</td>
</tr>
<tr>
<td>$&lt; 0$</td>
<td>$c$</td>
<td>$2a$</td>
<td>$b$</td>
<td>$3c$</td>
</tr>
<tr>
<td>$&gt; 0$</td>
<td>$a$</td>
<td>$3a$</td>
<td>$2b$</td>
<td>$c$</td>
</tr>
<tr>
<td>$&gt; 0$</td>
<td>$b$</td>
<td>$2a$</td>
<td>$3b$</td>
<td>$c$</td>
</tr>
<tr>
<td>$&gt; 0$</td>
<td>$c$</td>
<td>$2a$</td>
<td>$b$</td>
<td>$3c$</td>
</tr>
</tbody>
</table>

as the structure of the transverse ordering at positive temperature.

We now consider these ordered structures in more detail. Table II presents the values of $k_a$, $k_b$ and $k_c$ where $p(k)$ has a profound maximum for the longitudinal orderings expected at $T_D < 0$. Note that the same values of $k_a$, $k_b$ and $k_c$ are expected for the transverse orderings expected at $T_D > 0$. The last column shows the wavelength $\lambda = 2\pi|k|^{-1}$ of the ordered structure. From table II, it is evident that $k$ is always found to be parallel to $B_0$. Furthermore, all values $\lambda = 2\pi|k|^{-1}$ are much larger than the typical distance between nuclear spins and of the order of the size of the model used for the Monte Carlo simulation. The values of $\lambda$ are also incommensurate with the size of the unit cell excluding some kind of long wavelength “antiferromagnetic” ordering. Therefore we conclude that at negative spin temperatures ferromagnetic longitudinal orderings are obtained. Again using the argument of the introduction, this means that at positive temperature ferromagnetic transverse orderings are predicted. We note however that in this latter case, the ordering might also be helicoidal [12].

Table II. — Monte Carlo results for the structure of the longitudinal orderings at $T_D < 0$.

| $T_D$ | $B_0$ | model size | $k_a$ | $k_a$ | $k_a$ | $\lambda = 2\pi|k|^{-1}$ |
|-------|-------|------------|-------|-------|-------|-----------------|
|       | || to | $e_a$ | $e_b$ | $e_c$ | (Å)$^{-1}$ | (Å)$^{-1}$ | (Å)$^{-1}$ |
| $< 0$ | $a$   | $3a$ | $2b$ | $c$  | 0.46  | 0.00  | 0.00  | 13.6    |
| $< 0$ | $b$   | $2a$ | $3b$ | $c$  | 0.00  | 0.42  | 0.00  | 14.8    |
| $< 0$ | $c$   | $2a$ | $b$  | $3c$ | 0.00  | 0.00  | 0.33  | 18.8    |

3. Properties of the ferromagnetic phases.

We now proceed to calculate the dipolar energy per spin, the critical temperature and the critical polarization needed to reach the three ferromagnetic phases found above. One could use the Monte Carlo method for this purpose [19]. However, to save numerical time we used the well proven molecular field method introduced by Goldman [14]. We first consider the orderings at negative temperature. From the Monte Carlo simulations, we conclude that the nuclear spin
system orders as a so-called ferro-sandwich for all three orientations of the magnetic field. This ordering is characterized by a domain structure, where the domains have the shape of large flat pancakes, with their surface perpendicular to the externally applied magnetic field.

We first calculate the dipolar energy of the nuclear spin system at \( T_D = 0 \). Goldman [14] calculated the dipolar energy of the \( i \)-th spin in the case of a ferro-sandwich. The result is given by

\[
E_D^i = \frac{\mu_0 \gamma_i^2 \hbar}{4\pi} \left( \frac{1}{2} \sum_{j \neq i} \frac{1 - 3 \cos^2 \theta_{ij}}{r_{ij}^3} - \frac{N_f}{V} \frac{8\pi}{3} \right).
\]

Here the contribution of all spins \( I^j \) within a sphere with radius \( R \) is calculated by discrete summation, while the contribution of spins \( I^j \) that are further away is approximated by an integral.

To obtain the total dipolar energy per spin, we need to calculate the sum of the dipolar energies of the individual spins

\[
E_D = \frac{1}{2n} \sum_i E_D^i.
\]

Note that a factor \( \frac{1}{2} \) is introduced because the interaction between two given spins is encountered twice in the sums in equations (8) and (9). In fluorene there are 40 different proton sites in the crystallographic unit cell. However, due to the symmetry of the crystal \( (P_{nam}) \), there are only \( n = 12 \) magnetically inequivalent proton sites so the summation in equation (9) needs to be taken over these 12 sites only.

The calculation of \( E_D \) is performed numerically. To study the convergence of the sum in equation (8), we increase the radius \( R \) stepwise to 200 Å where the sphere contains about \( 1.2 \times 10^6 \) spins. Clean curves with increasing \( R \) are obtained. From these curves the limit for \( R \to \infty \) is obtained. The results are presented in the first three rows of table III. We estimate the relative accuracy of these limits to be \( 2 \times 10^{-4} \).

Table III. — Properties for the ferromagnetic ordering of the proton spins of fluorene at \( T_D < 0 \) for different orientations of the magnetic field, the dipolar energies are given per spin.

<table>
<thead>
<tr>
<th>( T_D )</th>
<th>( B_0 )</th>
<th>( \overline{E_D} )</th>
<th>( T_c )</th>
<th>( P_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(( \mu )K)</td>
<td>(( \mu )K)</td>
<td></td>
</tr>
<tr>
<td>&lt; 0</td>
<td>a</td>
<td>+0.940</td>
<td>-0.469</td>
<td>0.40</td>
</tr>
<tr>
<td>&lt; 0</td>
<td>b</td>
<td>+0.543</td>
<td>-0.271</td>
<td>0.85</td>
</tr>
<tr>
<td>&lt; 0</td>
<td>c</td>
<td>+1.081</td>
<td>-0.539</td>
<td>0.26</td>
</tr>
<tr>
<td>&gt; 0</td>
<td>a</td>
<td>-0.470</td>
<td>+0.235</td>
<td>0.80</td>
</tr>
<tr>
<td>&gt; 0</td>
<td>b</td>
<td>-0.271</td>
<td>+0.136</td>
<td>1.70</td>
</tr>
<tr>
<td>&gt; 0</td>
<td>c</td>
<td>-0.540</td>
<td>+0.269</td>
<td>0.52</td>
</tr>
</tbody>
</table>
The critical spin temperature \( T_c \) where the phase transition from the paramagnetic to the ferromagnetic phase occurs is calculated from \( E_D \) using [20]

\[
T_c = \frac{h}{2k_B}E_D. \tag{10}
\]

The values of \( T_c \) are also given in the first three rows in table III. We note however that in our case these results can only be approximate because the Weiss field is different at different proton sites, so the so-called strong constraint [21] is not fulfilled. Again using the argument presented in the introduction, also the values of \( E_D \) and \( T_c \) for the transverse orderings at positive spin temperature can be found. These are shown in the last three rows of table III.

Finally we determine the critical polarization \( P_c \), which must be reached by MIONP in order to obtain the ferromagnetic orderings by a subsequent ADRF. According to Goldman [14]

\[
P_c \approx \frac{1}{8} \sqrt{3} \frac{\mu_0}{4\pi k_B T_c} \sum_{i=1}^{n} \left( \frac{1 - 3 \cos^2 \theta_{ij}}{r_{ij}^3} \right)^2. \tag{11}\]

The dipole sum converges rapidly and is calculated numerically with the same accuracy as \( E_D \). For both positive and negative temperature and for each of the three directions of \( \mathbf{B}_0 \) the resulting critical polarizations are also given in table III. Note that the result for \( T_D > 0 \) and \( \mathbf{B}_0 \parallel b \)-axes is larger than 1. Evidently, our method fails for this case.

4. Conclusion.

Using Monte Carlo methods we find that the magnetic dipolar ordered phase of the proton spins of fluorene is expected to be longitudinally ferromagnetic for negative nuclear spin temperature and transverse ferromagnetic or helicoidal for positive temperature. Using the molecular field method of Goldman [14] we calculated the critical polarizations for each of these orderings. It is found that the case that \( T_D < 0 \) and \( \mathbf{B} \parallel c \)-axis is the most favourable for creating a dipolar magnetic ordering in fluorene. Then, according to the molecular field approximation a proton spin polarization of only 26% is needed. It is noted that in actual experiments the critical polarization is typically a factor 1.3 higher [14]. Still, as at present 42% can be reached with MIONP, such an ordering is well within reach.

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