High deuteron polarization in polymer target materials

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Yamagata, Oct. 2011
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2. The trityl radicals – progress for deuterated target materials

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5. ERP investigation and Polarization results for
   — radiation doped CD$_2$
   — trityl radical doped C$_8$D$_8$

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Polarized Solid Targets

• Used in high energy particle physics experiments for studying the nucleon structure since about 50 years

• Present target materials for high energy spin physics experiments:
  
  - NH$_3$ COMPASS experiment at CERN (160-190GeV)
  - $^6$LiD COMPASS experiment at CERN (160-190GeV)
  - CH$_2$, CD$_2$ GDH experiment in SPRING-8
  - Butanol Experiments at ELAS (Bonn < 3.0GeV) and MAMI (Mainz < 1.5GeV) accelerators

• Physics observable determined by single or double asymmetry measurements $A$

\[
A = \frac{1}{P_T} \cdot \frac{1}{f} \cdot \frac{N \uparrow - N \downarrow}{N \uparrow + N \downarrow}
\]

\[
f = \frac{\text{#polarizable particles}}{\text{#all particles}}
\]

- $P_T$: target polarization
- $N \uparrow, \downarrow$: counting rates for spin $\uparrow, \downarrow$ to magnetic field
- $f = 0.1 \ldots 0.3 \ldots 0.5$

DNP solid targets
The Principle of Dynamic Nuclear Polarization

- **Thermal Equilibrium (TE)**
  \[ P = \frac{\langle I_z \rangle}{I_z^{\text{max}}} = B_I \left( \frac{\mu B}{2kT} \right) \propto \left( \frac{B}{T} \right) \]

- **Dynamic Nuclear Polarization (DNP)**
  - Transfer of polarization from paramagnetic electrons to the nuclei
  - Parameters of DNP: temperature; magnetic field; microwave power; electron relaxation time; the relation of EPR linewidth and nuclear Larmor frequency…

- **Doping with paramagnetic electrons:**
  \~ 10^3 nuclei fed by 1 unpaired electron from:
  - Chemically stable radical \rightarrow Solids
  - Radiation induced defects \rightarrow Solids

In the 1970 already 80-90% in protonated materials
Until 2003 40-50% in deuterated materials

<table>
<thead>
<tr>
<th>B/T</th>
<th>P_p [%]</th>
<th>P_d [%]</th>
<th>P_e [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5T/1K</td>
<td>0.25</td>
<td>0.05</td>
<td>93</td>
</tr>
<tr>
<td>15T/10mK</td>
<td>91</td>
<td>30</td>
<td>100</td>
</tr>
</tbody>
</table>
The Trityl Radicals
— Important Progress for Deuterated Materials

Finland D36’ (AH110355 deutero acid form) used for butanol-d10

Deuteron: up to 79% at 150mK/2.5T

0x063 (AH100136 sodium salt) used for propandiol-d8

Deuteron: up to 81% at 150mK/2.5T

0x063Me (AH 111 501 sodium salt) used for pyruvic acid

$^{13}$C: up to 74% at 900mK/5.0T


Citation: J.H. Ardenkjaer-Larsen, private communication
Important parameter: ESR linewidth and shape

- Zeeman Energy of a free electron

\[ E_Z = -g_e \mu_B \vec{S} \cdot \vec{B} \]

- Contributions to the Electron Zeeman linewidth

\[ \Delta E_{tot} = \mu_B \left( \vec{S} \cdot \hat{g} \cdot \vec{B} \right) + (\vec{S} \cdot A \cdot \vec{I}) + E_D \]

Hom. \( \rightarrow \) Dipol-Dipol interaction \( \rightarrow \) between electrons

Inhom. \( \rightarrow \) Hyperfine interaction \( \rightarrow \) magnetic nuclei \( \rightarrow \) indep. of \( B_0 \)

Inhom. \( \rightarrow \) g-factor anisotropy \( \rightarrow \) crystal field \( \rightarrow \) dep. of \( B_0 \)

- Try to minimize the energy spread \( \Delta E_{tot} \)
  
  - Find a suitable doping method \( \rightarrow \) \( \Delta E_{HFS} \sim \Delta E_D \)
  
  - Try radiation doping if only low \( \mu \) nuclei present
**Bochum measurement**

<table>
<thead>
<tr>
<th>Material</th>
<th>Radical</th>
<th>$\Delta g/\tilde{g} \ [10^{-3}]$</th>
<th>FWHM [mT]</th>
<th>$P_{D,max} \ [%]$ at 2.5T</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-Butanol</td>
<td>EDBA</td>
<td>$5.98 \pm 0.03$</td>
<td>$12.30 \pm 0.20$</td>
<td>26</td>
</tr>
<tr>
<td>D-Butanol</td>
<td>TEMPO</td>
<td>$3.61 \pm 0.13$</td>
<td>$5.25 \pm 0.15$</td>
<td>34</td>
</tr>
<tr>
<td>D-Butanol</td>
<td>Porphyrin</td>
<td>$4.01 \pm 0.15$</td>
<td>$5.20 \pm 0.23$</td>
<td>32</td>
</tr>
<tr>
<td>$^{14}$ND$_3$</td>
<td>$^{14}$ND$_2$</td>
<td>$\approx 2 \ldots 3$</td>
<td>$4.80 \pm 0.20$</td>
<td>44</td>
</tr>
<tr>
<td>$^{15}$ND$_3$</td>
<td>$^{15}$ND$_2$</td>
<td>$\approx 2 \ldots 3$</td>
<td>$3.95 \pm 0.15$</td>
<td>-</td>
</tr>
<tr>
<td>D-Butanol</td>
<td>Hydroxyalkyl</td>
<td>$1.25 \pm 0.04$</td>
<td>$3.10 \pm 0.20$</td>
<td>55</td>
</tr>
<tr>
<td>$^6$LiD</td>
<td>F-center</td>
<td>$0.0$</td>
<td>$1.80 \pm 0.01$</td>
<td>57</td>
</tr>
<tr>
<td>D-Butanol</td>
<td>Finland D36</td>
<td>$0.50 \pm 0.01$</td>
<td>$1.28 \pm 0.03$</td>
<td>79</td>
</tr>
<tr>
<td>D-Propanediol</td>
<td>Finland H36</td>
<td>$0.47 \pm 0.01$</td>
<td>$0.97 \pm 0.04$</td>
<td>-</td>
</tr>
<tr>
<td>D-Propanediol</td>
<td>OX063</td>
<td>$0.28 \pm 0.01$</td>
<td>$0.86 \pm 0.03$</td>
<td>81</td>
</tr>
</tbody>
</table>


**Result:** The smaller the EPR linewidth, the higher the deuteron polarization value
Deuteron with rather small gyromagnetic ratio
Thermal Mixing is DNP mechanism for deuteron enhancement

The Spin Temperature Theory

Three spin exchange process:
EZZ-EDS-NZZS

\[
P_{I,\text{max}} = B_I \left( I \beta_L \omega_e \frac{\omega_I}{2D} \frac{1}{\sqrt{\eta(1+f)}} \right)
\]

\[
\beta_L = \frac{\hbar}{kT_L}
\]

\[
h\delta = g_e \mu_B D
\]

\[
\eta = t_z / t_D \quad f: \text{a leakage factor}
\]

The smaller EPR linewidth, the higher polarization
Introduction to D-polymer materials

Poly(Ethylene-D4) \( \text{CD}_2 \)

Styrene-D8, polymerized \( \text{C}_8\text{D}_8 \)

dilution factor

\[
f = \frac{8 \text{ from } D}{24 \text{ from } C + 8 \text{ from } D} = 0.25
\]

\[
f = \frac{16 \text{ from } D}{96 \text{ from } C + 16 \text{ from } D} = 0.14
\]
Motivation to use D-polymer materials

• Spin physics
  ➢ Thin targets for scattering experiments at low energies
  ➢ Polarized scintillator targets

• Merits of CD₂, C₈D₈
  1. High purity of D 0.98, 0.99
  2. D with spin 1 and C with spin 0
  3. Easy formable to any thickness at room temperature

• Up to now the maximum polarizations of D-polymer
  1. D-polyethylene CD₂ : Paramagnetic Center---Irradiation
     35% at 6.5T/1K
  2. D-Polystyrene C₈D₈ : Paramagnetic Center---D-TEMPO
     40% at 2.5 T/100mK
Doping methods for DNP

- Mechanism of Dynamic Nuclear Polarization
  **Paramagnetic centers are needed**
- Chemical (Tempo, Trityl radical) doping

**Tempo** (stable free radical)

- Irradiation with electron beam

**Melting point** 36°C
**Boiling point** 67°C

**Trityl radicals Finland D36**

**Paramagnetic center for DNP**
Radiation-doping of CD$_2$ foil

- Find an optimal radiation dose
  - 7MeV electron beam (Osaka Uni.)
  - Beam spot ø60mm × 20mm
  - Irradiation dose ~10$^{14}$ - ~10$^{17}$e$^{-}$/cm$^2$
  - Irradiation at liquid Nitrogen 77K
  - CD$_2$ foil thickness 40 μm
  - Density 0.93 g/cm$^3$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$[e^{-}/cm^2]$</th>
<th>Spin density $[e^{-}/g]$</th>
<th>Irradiation temp. [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>3.0 × 10$^{14}$</td>
<td>1.8 × 10$^{18}$</td>
<td>77</td>
</tr>
<tr>
<td>b</td>
<td>7.0 × 10$^{14}$</td>
<td>2.7 × 10$^{18}$</td>
<td>77</td>
</tr>
<tr>
<td>c</td>
<td>4.0 × 10$^{15}$</td>
<td>1.9 × 10$^{19}$</td>
<td>77</td>
</tr>
<tr>
<td>d</td>
<td>6.0 × 10$^{15}$</td>
<td>2.3 × 10$^{19}$</td>
<td>90</td>
</tr>
<tr>
<td>e</td>
<td>8.0 × 10$^{15}$</td>
<td>3.2 × 10$^{19}$</td>
<td>77</td>
</tr>
<tr>
<td>f</td>
<td>1.0 × 10$^{16}$</td>
<td>3.6 × 10$^{19}$</td>
<td>77</td>
</tr>
<tr>
<td>g</td>
<td>1.2 × 10$^{16}$</td>
<td>4.0 × 10$^{19}$</td>
<td>90</td>
</tr>
<tr>
<td>h</td>
<td>5.0 × 10$^{16}$</td>
<td>2.3 × 10$^{20}$</td>
<td>77</td>
</tr>
<tr>
<td>i</td>
<td>1.0 × 10$^{17}$</td>
<td>1.4 × 10$^{21}$</td>
<td>77</td>
</tr>
</tbody>
</table>
The Bochum EPR Apparatus
The Bochum DNP Apparatus

Magnet+cryostat
EPR spectra of irradiated CH$_2$ and CD$_2$ at 77K

- According to HFS, 6-line pattern corresponds to 5 adjacent H, $m = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.
EPR spectra of Radiation-doped CD$_2$

According to HFS, 11-line pattern corresponds to 5 adjacent D,

\[ m = 5, 4, 3 \ldots - 5 \]

\[ D_\alpha = 0.485 \text{ mT} (1D); \]
\[ D_\beta = 0.480 \text{ mT} (4D) \]
\[ D(\text{FWHM}) = 3.0 \pm 0.2 \text{ mT} \]
Polarization of radiation-doped CD$_2$

NMR Signal of Deuteron

-31%

MW power:
70 GHz IMPATT diode, 150 mW

<table>
<thead>
<tr>
<th>Dose [e^-/cm$^2$]</th>
<th>DNP Temp.[mK]</th>
<th>$f_{mw}$[GHz]</th>
<th>d-Pol[%]</th>
<th>$T_{build-up}$[min.]</th>
<th>$f^+ - f^-$[MHz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0 \times 10^{15}</td>
<td>150</td>
<td>69.860</td>
<td>+21.0</td>
<td>110</td>
<td>215</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70.075</td>
<td>-31.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Temperature = 150mK     Magnetic field=2.5T

\[ P = \frac{r^2 - 1}{r^2 + r + 1}, \quad r = \frac{I_R}{I_L} \]
Preparation of trityl radical in D-Polystyrene

- **g-factor anisotropy:** \( \frac{\Delta g}{g} \leq 3.0 \times 10^{-4} \)

- **Introduce Finland D36 Radicals in C\(_8\)D\(_8\)**

![Diagram](image)

- **D-polystyrene**
  - \( \text{C}_8\text{D}_8 \)
- **Trityl radical**
  - 'Finland D36'
- **Solvent**
  - THF
- **Mix + evaporate**
  - At Room Temperature
- **C\(_8\)D\(_8\) + Trityl radical**

Homogenous and transparent foil (70\(\mu\)m)
Polarization of Finland D36-doped C₈D₈

**Graph 1:**
- **X-axis:** Spin concentration [10¹⁹ spins/g]
- **Y-axis:** Deuteron Polarization [%]
- **Legend:**
  - □ 5.0T
  - ○ 2.5T

**Graph 2:**
- **X-axis:** Time [min]
- **Y-axis:** Deuteron Polarization [%]

**Table:**
<table>
<thead>
<tr>
<th>Spin conc. (spins/g)</th>
<th>Mag. Field (T)</th>
<th>T_{\text{build-up}} (min)</th>
<th>T_{d,d} (min)</th>
<th>Microwave Freq. (GHz)</th>
<th>d-pol. (%)</th>
<th>f^+ - f^- (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.87 × 10¹⁹</td>
<td>2.5</td>
<td>76</td>
<td>80 (T=1.01K)</td>
<td>69.877</td>
<td>+10.2</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>69.933</td>
<td>-12.5</td>
<td></td>
</tr>
<tr>
<td>1.16 × 10¹⁹</td>
<td>5.0</td>
<td>47</td>
<td>139 (T=0.99K)</td>
<td>139.736</td>
<td>+29.5</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>139.828</td>
<td>-31.0</td>
<td></td>
</tr>
</tbody>
</table>
Polarization of Finland D36-doped C₈D₈

\[ P_T = -61.5\% \]

<table>
<thead>
<tr>
<th>Sample</th>
<th>MW (GHz)</th>
<th>d-pola. (%)</th>
<th>T_{1,d} (min)</th>
<th>T_{build-up} (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-PS(98%-d)</td>
<td>139.723</td>
<td>+56.1</td>
<td>863</td>
<td>100</td>
</tr>
<tr>
<td>+Finland D36</td>
<td>139.825</td>
<td>-61.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( T_{d,NMR} )</td>
<td>32.6MHz</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Temperature = 400mK   Magnetic field= 5.0 T
1. Irradiated D-polyethylene with a relative high dilution factor can be polarized to more than 30% at 2.5T/150mK. The produced paramagnetic centers have hyperfine interaction with the 5 neighboring deuterons.

2. Chemically doped D-polystyrene with a trityl radical can be polarized to more than 30% at 5.0T/1K and 60% at 5.0T/400mK within several hours. But the dilution factor is much lower than that of D-polyethylene.

3. An approach for D-polyethylene with trityl radical doping is needed.
Thanks for your attention!
Deuteron Polymer Polarization

<table>
<thead>
<tr>
<th>Material</th>
<th>Doping</th>
<th>Magnetic field (T)</th>
<th>Temperature</th>
<th>$T_{ld}$</th>
<th>FWHM-bolometric</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2.5</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polarization (%)</td>
<td></td>
<td>20</td>
<td>-30</td>
<td>150mK</td>
<td></td>
</tr>
</tbody>
</table>

- **CD$_2$**: Irradiation $(8.0 \times 10^{16} \text{e}^-/\text{cm}^2)$
- **CD$_2$**: Tempo $(3.0 \times 10^{19} \text{spins/cm}^3)$
- **C$_8$D$_8$**: Tempo $(2.3 \times 10^{19} \text{spins/g})$
- **C$_8$D$_8$**: Trityl $(1.16 \times 10^{19} \text{spins/g})$
- **C$_8$D$_8$**: Trityl $(1.16 \times 10^{19} \text{spins/g})$

- **CD$_2$**: Tempo $(3.0 \times 10^{19} \text{spins/cm}^3)$
- **C$_8$D$_8$**: Trityl $(1.16 \times 10^{19} \text{spins/g})$
- **C$_8$D$_8$**: Trityl $(1.16 \times 10^{19} \text{spins/g})$
ACKNOWLEDGEMENTS

Dr. Stefan Goertz
Bonn University

Dr. Florian Piegsa
PSI Group
The Solid State Effect

Dipolar Coupling

Positive

Negative

\[ B = 2.5 \, T \]
EPR spectra of Finland D36-doped \( \text{C}_8\text{D}_8 \)

**X-band**

\[ \nu = 9.4\text{GHz} \]

**Bolometric**

\[ \nu = 70\text{GHz} \]

- Introduce Finland D36 Radicals in \( \text{C}_8\text{D}_8 \)

1. dissolve \( \text{C}_8\text{D}_8 \) polymer in toluene
2. dissolve Finland D36 in isobutanol
3. mix and evaporate solvents
Polarized target system

- Cooling system ~ 100mK
- Magnet system 2.50T
  C-yoke normal conduction magnet 611 made by JEOL
  Homogeneity: $2 \times 10^{-4}$ (ø70mm × 25mm)
- Microwave system 70GHz
  Oscillator: 68.5GHz-71.5GHz  150mW
  (IMPATT-47134H-1115 made by HUGHES)
- NMR measurement system
  Larmor frequency of D: 16.35MHz
  Digital Synthesizer: 1MHz-250MHz
  Accuracy: 0.1MHz
  (PTS250 made by PTS inc.)
ESR linewidth and shape

- Zeeman Energy of a free electron

\[ E_Z = -g_e \mu_B \vec{S} \cdot \vec{B} \]

- Contributions to the Electron Zeeman linewidth

\[ \Delta E_{tot} = \mu_B (\vec{S} \cdot \hat{g} \cdot \vec{B}) + (\vec{S} \cdot \vec{A} \cdot \vec{I}) + E_D \]

Hom. \rightarrow Dipol-Dipol interaction \rightarrow between electrons

Inhom. \rightarrow Hyperfine interaction \rightarrow magnetic nuclei \rightarrow indep. of \( B_0 \)

Inhom. \rightarrow g-factor anisotropy \rightarrow crystal field \rightarrow dep. of \( B_0 \)

- Try to minimize the energy spread \( \Delta E_{tot} \)
  - Find a suitable doping method \( \Delta E_{HFS} \sim \Delta E_D \)
  - Try radiation doping if only low \( \mu \) nuclei present
DNP Mechanism CW&B ≤ 5T

▶ Depend on the relationship of $\delta$, $\Delta$ and $\omega_{0I}$

- Solid Effect (SE) $\delta, \Delta < \omega_{0I}$ $\delta$ a homogeneous EPR linewidth
- Cross effect (CE) $\delta < \omega_{0I}, \Delta > \omega_{0I}$ $\Delta$ an inhomogeneous EPR linewidth
- Thermal mixing (TM) $\delta \approx \omega_{0I}$ $\omega_{0I}$ the nuclear Larmor frequency

▶ Contributions to the Electron Zeeman linewidth

$$\Delta E_{\text{tot}} = \mu_B \left( \vec{S} \cdot \vec{g} \cdot \vec{B} \right) + \left( \vec{S} \cdot \vec{A} \cdot \vec{I} \right) + E_D$$

Hom. Dipol-Dipol interaction between electrons

Inhom. Hyperfine interaction magnetic nuclei indep. of $B_0$

Inhom. g-factor anisotropy crystal field dep. of $B_0$
# Polarized Deuteron Targets

## Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Doping method</th>
<th>Polarization</th>
<th>Field</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^6\text{LiD}$ D-butanol</td>
<td>Irradiation</td>
<td>&gt; 50%</td>
<td>2.5T</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55%</td>
<td>2.5T</td>
</tr>
<tr>
<td></td>
<td></td>
<td>71%</td>
<td>5.0T</td>
</tr>
<tr>
<td>D-butanol D-propanediol</td>
<td>chem. dop.</td>
<td>79%</td>
<td>2.5T</td>
</tr>
<tr>
<td></td>
<td>with trityl</td>
<td>81%</td>
<td>2.5T</td>
</tr>
</tbody>
</table>
Trityl radical as dopant for D-Butanol

- Boiling point: >200°C
- Very stable radical

Introduce Trityl radical

Weak g-factor anisotropy in D-Butanol