Applications of Nuclear Magnetic Resonance to Metal Hydrogen Materials

Part I: Basic Principles & General Applications

Robert C. Bowman, Jr. and Son-Jong Hwang

California Institute of Technology
Pasadena, CA

Summer School Lectures
MH2008
23 June 2008
Outline

Part I: Basic Principles & General Applications
- Introduction to Hydrogen Storage Materials
- Nuclear Magnetic Resonance (NMR) Concepts & Terminology
  • The basics of NMR
  • Solid State NMR fundamentals (Low Resolution)
  • Dynamics via nuclear relaxation times – diffusion phenomenon
- References

Part II: High Resolution (HR) Solid State NMR
- Principles & methods of multinuclear spectroscopy (MAS, CP, MQ)
- HR-NMR Studies of MH$_x$ materials – phase compositions, etc.
- Summary & Conclusions
- References
Sorption Methods for Hydrogen Storage
(Mostly reversible reactions, compact, mass issues)

- **ABsorption** (chemisorption) – metal hydride family
- **ADsorption** (physisorption) – zeolites, carbons, etc.

[Images from J. Miller, Chromatography: Concepts and Contrasts (Wiley, NY, 1987)]
Family tree of hydriding alloys and complexes [1,2].
(TM = transition metal)

Extreme range of physical & chemical properties (nearly all solids!)

PART I

General Background of NMR Spectroscopy and its Applications to Solids
What’s NMR?

Nuclear Magnetic Resonance (NMR) spectroscopy is based upon splitting of nuclear spin (I) energy levels in an external magnetic field ($B_0$), where transitions between levels are induced via radiofrequency (rf) radiation at the Larmor frequency $\nu_I$

$$(2\pi) \nu_I = \gamma_I B_0$$

Each non-zero spin I has an unique magnetogyric ratio $\gamma_I$
Types & Properties of NMR Active Nuclei

No NMR for $I = 0$ nuclei (i.e., $^4$He, $^{12}$C, $^{28}$Si, etc.)

NMR active nuclei for M-H Studies

$I = 1/2$: $^1$H, $^3$H*, $^{13}$C, $^{15}$N, $^{29}$Si, etc.

$I = 1$: $^2$H, $^6$Li, $^{14}$N

$I = 3/2$: $^7$Li, $^{11}$B, $^{23}$Na, etc.

$I = 5/2$: $^{25}$Mg, $^{27}$Al, etc.

$I = 7/2$: $^{45}$Sc, $^{51}$V, etc.

Figures from Rob Schurko’s Introductory Solid State NMR Notes (http://mutuslab.cs.uwindsor.ca/schurko/ssnmr/ssnmr_schurko.pdf)
Schematic view of 3 stages in a simple NMR Experiment:
A. Magnetic moment precesses around principal axis of applied Zeeman field $B_o$.
B. Sample irradiated at Larmor frequency with plane-polarized rf radiation generating magnetic field $B_1$, causing net magnetization $M$ to incline. A $\pi/2$ pulse orients $M$ perpendicular to $B_o$.
C. As the spin system coherently precesses in the transverse plane, a voltage is induced in a rf coil to be detected as the FID (Free Induction Decay) signal.

Basic NMR Spin Echo Experiment

Basic pulse sequence \((\pi/2 - \tau - \pi)\) forming a Spin-Echo with effect on the spin packets.

\[
\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2'}
\]

\[
\frac{dM_{x'}}{dt} = -\frac{M_{x'}}{T_2}, \quad M_{x'}(2\tau) = M_{x'}(0)e^{-\tau/T_2}
\]
Schematic Description of FT-NMR Spectrometers

Bruker DSX 500 solids NMR spectrometer ($B_0 = 11.7$ T) in the Caltech Solid State NMR Facility

- A number of solution and solids NMR probes available.
- Capability of variable Temperature Exp. (-100 °C ~ +150 °C).

[Bruker 4 mm triple resonance CP-MAS probe.]
Overview of Nuclear Spin Interactions in Solids

**Notation:** I = NMR resonant spin and S = Non-resonant spin(s)

In the solid-state, there are seven ways for a nuclear spin to communicate with its surroundings:

1. **Zeeman interaction of nuclear spins**
2. **Direct dipolar spin interaction**
3. **Indirect spin-spin coupling (J-coupling), nuclear-electron spin coupling (paramagnetic), coupling of nuclear spins with molecular electric field gradients (quadrupolar interaction)**
4. **Direct spin-lattice interactions**
5. **Indirect spin-lattice interaction via electrons**
6. **Chemical shielding and polarization of nuclear spins by electrons**
7. **Coupling of nuclear spins to sound fields**

Nuclear spin interactions are distinguished on the basis of whether they are external or internal:

\[ \mathcal{H} = \mathcal{H}_{\text{ext}} + \mathcal{H}_{\text{int}} \]

Interactions with external fields \( B_0 \) and \( B_1 \)

The “size” of these external interactions is larger than \( \mathcal{H}_{\text{int}} \):

\[ ||\mathcal{H}|| = \left[ \text{Tr}\{\mathcal{H}^2}\right]^{1/2} \]

The Hamiltonian describing internal spin interactions:

\[ \mathcal{H}_{\text{int}} = \mathcal{H}_{J} + \mathcal{H}_{SS} + \mathcal{H}_{LS} + \mathcal{H}_{Q} + \mathcal{H}_{CS} + \mathcal{H}_{L} \]

- **1:** Zeeman interaction of nuclear spins
- **2:** Direct dipolar spin interaction
- **3:** Indirect spin-spin coupling (J-coupling), nuclear-electron spin coupling (paramagnetic), coupling of nuclear spins with molecular electric field gradients (quadrupolar interaction)
- **4:** Direct spin-lattice interactions
- **3-5:** Indirect spin-lattice interaction via electrons
- **3-6:** Chemical shielding and polarization of nuclear spins by electrons
- **4-7:** Coupling of nuclear spins to sound fields

\( B_0 = \) Zeeman external magnetic field

\( B_1 = \) rf magnetic field (NMR pulses)

Figure & next few charts adapted from: [http://mutuslab.cs.uwindsor.ca/schurko/ssnmr/ssnmr_schurko.pdf](http://mutuslab.cs.uwindsor.ca/schurko/ssnmr/ssnmr_schurko.pdf)
Nuclear Spins Couple to External Magnetic Fields
via Interaction Tensors:

All NMR interactions are anisotropic - their three dimensional nature can be described by second-rank Cartesian tensors, which are $3 \times 3$ matrices.

Using Cartesian tensors, the spin part of the Hamiltonian (which is the same as in solution NMR) is separated from the spatial anisotropic dependence, which is described by the second-rank Cartesian tensor.

Chemical shielding

$$\mathcal{H}_{CS} = \gamma I \cdot \vec{\sigma} \cdot B_0$$

Dipolar interaction

$$\mathcal{H}_{DD} = \sum_{i,j} D_{ij} \gamma I_i \cdot r_{ij} \cdot \left( I_i \cdot I_j - \frac{3(I_i \cdot r_{ij})(I_j \cdot r_{ij})}{r_{ij}^2} \right)$$

Indirect spin-spin ($J$) coupling

Spin-rotation coupling

Quadmpolar coupling

$$\mathcal{H}_Q = \frac{eQ}{2I(I-1)\hbar} \sum_i I_i \cdot \nabla_i$$

$$\nabla = \{V_x, V_y, V_z\}; \ \alpha, \beta = x, y, z$$

Dipolar Interactions

The dipolar interaction results from interaction of one nuclear spin with a magnetic field generated by another nuclear spin, and vice versa. This is a direct through space interaction which is dependent upon the $\gamma$ of each nucleus, as well as $r_{jk}^{-3}$:

$$D_{ij} = \frac{\hbar}{\gamma} \sum_{\alpha} e_{\alpha} e_{\beta}$$

$$\gamma = \frac{\mu_0 \gamma_i / \mu_0 \gamma_j}{4\pi \langle r_{jk}^3 \rangle}$$

Nuclear Pair  Internuclear Distance  $R_{DD}$ (Hz)

$^1\text{H}, ^1\text{H}$  10 Å  120 kHz

$^1\text{H}, ^{13}\text{C}$  1 Å  30 kHz

$^1\text{H}, ^{13}\text{C}$  2 Å  3.8 kHz
Chemical Shielding in NMR of Solids

Chemical shielding is an anisotropic interaction characterized by a shielding tensor \( \sigma \), which can also be diagonalized to yield a tensor with three principal components.

\[
\sigma_{\text{molecule}} = \begin{bmatrix}
\sigma_{11} & \sigma_{12} & \sigma_{13} \\
\sigma_{12} & \sigma_{22} & \sigma_{23} \\
\sigma_{13} & \sigma_{23} & \sigma_{33}
\end{bmatrix}
\]

\[
\sigma^{\text{PAS}} = \begin{bmatrix}
\sigma_{11} & 0 & 0 \\
0 & \sigma_{22} & 0 \\
0 & 0 & \sigma_{33}
\end{bmatrix}
\]

The principal components are assigned such that \( \sigma_{11} \leq \sigma_{22} \leq \sigma_{33} \) (i.e., \( \sigma_{11} \) is the least shielded component and \( \sigma_{33} \) is the most shielded component).

\( \sigma_{\text{iso}} \) is the isotropic chemical shielding (measured in solution as a result of averaging by isotropic tumbling). The trace of the chemical shielding tensor is non-zero!

\( \Omega \) is the span, which measures in ppm the breadth of the CSA powder pattern.

\( \kappa \) is the skew, which measures the asymmetry of the powder pattern.

It can be shown that chemical shielding anisotropy gives rise to frequency shifts with the following orientation dependence:

\[
\nu_{CS} - \nu_0 = \sigma_{11} \sin^2 \theta \cos^2 \phi + \sigma_{22} \sin^2 \theta \sin^2 \phi + \sigma_{33} \cos^2 \theta
\]

In order to calculate powder patterns (for any anisotropic NMR interaction), one must calculate frequencies for a large number of orientations of the interaction tensor with respect to the magnetic field - many polar angles over a sphere: \( \theta, \phi \).

Methods for reducing dipolar broadening and CSA effects to yield high resolution spectra from solids where peaks are narrowed to only \( \sigma_{\text{iso}} \) will be given in Part II.
Solid State NMR of Quadrupolar Nuclei

The EFGs at the quadrupolar nucleus can be described by a symmetric traceless tensor, which can also be diagonalized:

\[
\mathbf{V} = \begin{bmatrix}
V_{xx} & V_{xy} & V_{xz} \\
V_{yx} & V_{yy} & V_{yz} \\
V_{zx} & V_{zy} & V_{zz}
\end{bmatrix}
\]

\[
\mathbf{V}^{\text{PAS}} = \begin{bmatrix}
V_{11} & 0 & 0 \\
0 & V_{22} & 0 \\
0 & 0 & V_{33}
\end{bmatrix}
\]

The principal components of the EFG tensor are defined such that \(|V_{11}| \leq |V_{22}| \leq |V_{33}|\). Since the EFG tensor is traceless, isotropic tumbling in solution averages it to zero (unlike J and o).

The magnitude of the quadrupolar interaction is given by the nuclear quadrupole coupling constant:

\[
C_Q = eQ\cdot V_{33}/\hbar \text{ (in kHz or MHz)}
\]

The asymmetry of the quadrupolar interaction is given by the asymmetry parameter, \(\eta = (V_{31} - V_{22})/V_{33}\), where \(0 \leq \eta \leq 1\). If \(\eta = 0\), the EFG tensor is axially symmetric.

**I = 5/2 Spectra for \(C_Q(A) > C_Q(B)\)**

Static spectra of quadrupolar nuclei are shown below for the case of spin 5/2:

\[\text{A} \quad \begin{cases} 1/2 \rightarrow -1/2 \\ -1/2 \rightarrow 1/2 \\ 1/2 \rightarrow 3/2 \\ -3/2 \rightarrow -1/2 \\ 3/2 \rightarrow 5/2 \\ -5/2 \rightarrow -3/2 \\ 2\nu_Q \\ -2\nu_Q \\ \nu_Q \end{cases} \]

\[\text{B} \quad \begin{cases} \theta = 41.8^\circ \\ \nu_0 \cdot (169)A \\ \theta = 90^\circ \\ \theta = 0^\circ \end{cases} \]

The quadrupolar interaction, unlike all of the other anisotropic NMR interactions, can be written as a sum of first and second order interactions:

\[
\mathcal{H}_Q = \mathcal{H}_Q^{(1)} + \mathcal{H}_Q^{(2)}
\]

Below, the effects of the first- and second-order interactions on the energy levels of a spin-5/2 nucleus are shown:

\[
\begin{array}{c}
\text{m}_z \\
-5/2 \\
-3/2 \\
-1/2 \\
+1/2 \\
+3/2 \\
+5/2
\end{array}
\]

\[\mathcal{H}_Q^{(1)} \quad \mathcal{H}_Q^{(2)} \]

The first-order interaction is proportional to \(C_Q\), and the second-order interaction is proportional to \(C_Q^2/\nu_Q\), and is much smaller (shifts in energy levels above are exaggerated). Notice that the first-order interaction does not affect the central transition.

Methods for extracting information from NMR of quadrupolar nuclei will be covered in Part II.
Examples of General NMR Studies for some representative Metal Hydrides
NMR for Crystal Structure & H-Site Locations

NMR spectra can be used to determine the location(s) of protons within the host crystal structure as well as detect different phases (i.e., H₂ gas in the solid or metal particles in the hydride).

• Second Moments are extracted from the time domain signal G(t) where the rigid-lattice dipolar interactions are used.

\[ M_n = (-i)^n \frac{d^n G(t)}{dt^n G(0)} \bigg|_{t=0} \]

\[ M_{2D} = (3/5)C_{II} \Sigma_n (1/r_{mn})^6 + (4/15)C_{IS} \Sigma_n' (1/r_{mn'})^6 \]

• NMR is not as powerful to solve crystal structures as neutron diffraction for deuterides but sometimes an advantage when samples are nanocrystalline or “amorphous” as dipolar terms rapidly decay with spin separations (~1/r⁶).

• Most examples involve protons with one or two locations in rather simple structures.

Sometimes there can be complications!
Variable Temperature Proton Spectra for YH$_3$

This splitting is anomalous! Not predicted for protons in the known P63cm structure for YH$_3$ – should be just a single peak from dipolar interactions in rigid lattice.

Dipolar M$_{2d}$ for YH$_3$ in rigid lattice limit (T < 310 K)

---

FIG. 1. Proton resonance spectra in YH$_3$ at a resonance frequency of 37.1 MHz at temperatures of (a) 300, (b) 355, and (c) 424 K. The peak-to-peak splitting of the outer peaks at 300 K is 65.0 kHz. The spectra were obtained by Fourier transformation of the free-induction decay following a single 90° rf pulse. Typically, a total of 100 shots were added to obtain the final spectrum.

“Magic-Echo” method will give proton spectra without distortions due to very large dipolar interactions seen in many MHx coming from instrumental recovery limitations.

**FIG. 1.** Magic-echo pulse sequence reverses the dipolar dephasing to create an echo at time \( \tau \). The use of a 180° phase inversion in the middle of the time-reversal pulse compensates for RF field \( B_1 \) nonuniformity. The alternating (blinking) 180° pulse allows adding signal averaging to eliminate non-NMR signals such as acoustic probe ringing. The time \( \tau \) (equals \( \tau_1 = \tau_2 \)) was 12.5 \( \mu \text{s} \). The delay \( T \) was chosen to be 1 ms, short compared to \( T_1 \) but much longer than \( T_2 \).

**FIG. 2.** Rigid-lattice free induction decay (upper curve) and magic echo (lower curve) of YH\(_{2}\)O\(_{6}\). Data were acquired at 186±4 K and 53.14 MHz. The dotted portion of the FID is a Gaussian curve replacing the values recorded during the spectrometer’s dead time. The echo has been left-shifted 12.4 \( \mu \text{s} \) so its peak lines up with the zero in time. The curves are vertically offset from each other for viewing.

\[
\begin{align*}
M_2 \text{ (E)} &= 17.5 \text{ Oe}^2 \\
M_2 \text{ (D)} &= 18.3 \text{ Oe}^2
\end{align*}
\]

**FIG. 3.** Accurate rigid-lattice spectrum (a) of YH\(_{2}\)O\(_{6}\) obtained by left-shifting the magic echo (see Fig. 2) by 12.4 \( \mu \text{s} \) to bring its peak to zero time, then Fourier transforming. The other two plots are distorted spectra resulting from left-shifting the magic echo by an additional 5.0 \( \mu \text{s} \) (b) and 11.6 \( \mu \text{s} \) (c) before Fourier transformation. The 68 kHz doublet splitting of the spectrum (c) is the same value quoted in the original paper. The vertical scales are arbitrary units. The spectra have been scaled to give equal peak heights.

Many Factors Influence MH$_x$ Absorption/Desorption Kinetics

• Heat transfer (bed design)
• H$_2$ gas permeability in powder
• Surface Reactivity/Activation
  – Native oxide layers (barrier)
  – Selective oxidation (AB$_2$, AB$_5$)
  – Poisoning (CO, SO$_2$, etc.)
  – Surface area/decrepitation
  – Permeable layers (Pd, fluorides)
• Diffusion processes
  – Grain boundaries/microfractures
  – Bulk diffusion ($D_{\text{bulk}}$) in metal/hydride phases

**Horizontal Dash Line Indicates:**

$D_{\text{Bulk}} = 1.67 \times 10^{-8}$ cm$^2$/s

$= d^2/6t = (10 \ \mu\text{m})^2/6(10 \ \text{s})$

Condition when $D$ rarely limits reaction rates in activated MH$_x$


**Note:** While researchers can change/improve many kinetic parameters, but usually do **NOT** improve the intrinsic diffusion constants except by raising operating temperature!
When $D(T) > 10^{-12}$ m$^2$/s, it can be directly measured without using any models.

The Stejskal-Tanner pulsed gradient spin-echo sequence for direct measurement of $D$.

\[ \ln \left( \frac{A(2\tau)}{A_0(2\tau)} \right) = -\gamma^2 D^2 G^2 \left( \Delta - \delta/3 \right) \]

FIG. 1. Alternating pulsed field gradient (APFG) sequence. The echo amplitude at $t = 10\tau$ is a function of the diffusion coefficient. The deviation of the gradient pulses from a rectangular shape is somewhat exaggerated. The background gradients ($G_0$) are not shown.

FIG. 2. Diffusion coefficients $D$ of hydrogen in LaNi$_{5.0}$H$_{6.0}$ and LaNi$_{4.8}$Sn$_{0.2}$H$_{5.3}$ measured by APFG-NMR. The solid lines represent fits of Arrhenius terms to the diffusivities. The fit parameters are given in Table I. For comparison, a fit to the diffusivities measured by Karlicek and Lowe (Ref. 14) on LaNi$_{5}$H$_{6.5}$ is included as a dashed line.

NMR Relaxation Times & Diffusion
(Very General - Focus on Hydrogen)

Pulsed NMR Sequences:
- $T_1$ Spin-Lattice: from 180°-τ-90° and (90°-τ)n-τ-90°
- $T_2$ Spin-Spin: from free induction decays ($T_2^*$), 2-pulse echoes ($T_2'$), and Carr-Purcell-Meiboom-Gill (CPMG) echo trains ($T_2m$).
- $T_{1p}$ Rotating-Frame: from CW (not chopped) spin-locking.
- $T_{1D}$ Dipolar: ($T_1$ of dipolar-ordered state, essentially $T_1$ in zero field)

• Correlation time, $\tau_c$:
  \[
  1/T_2 = K \cdot M_2 \cdot \tau_c
  \]

• Mean residence time, $\tau$ = $1/\omega_H$:
  \[
  \tau_c = \tau / 2
  \]

• Activation energy (Arrhenius), $E_A$:
  \[
  1/\tau = (1/\tau_o) \exp(-E_A/kT)
  \]
  $\tau_o^{-1}$ = attempt frequency

$T_1$, $T_2$ depend on $\tau_c$ and $M_2$
($M_2$ = mean-squared dipolar interaction)

Diffusion Coefficient:
\[
D(T) = f<l^2>/(6 \tau)
\]
Temperature Dependence of NMR Relaxation Rates for an Arrhenius Diffusion Process

Idealized BPP Model

\[
\frac{1}{T_1} = \frac{1}{T_{1d}} + \frac{1}{T_{1e}} + \frac{1}{T_{1p}}
\]

\[
(\frac{1}{T_{1d}})^{-1} = \frac{3}{2} c_H \left[ J^{(1)}(\omega_0) + J^{(2)}(2\omega_0) \right]
\]

\[
(\frac{1}{T_{1p}})^{-1} = \frac{3}{8} c_H \left[ J^{(0)}(2\omega_1) + 10 J^{(1)}(\omega_0) + J^{(2)}(2\omega_0) \right]
\]

\[
(\frac{1}{T_2})^{-1} = \frac{3}{8} c_H \left[ J^{(0)}(0) + 10 J^{(1)}(\omega_0) + J^{(2)}(2\omega_0) \right]
\]

\[
J^{(p)}(\omega) = \int_{-\infty}^{\infty} G(q)(t) \exp(-i\omega t) \, dt.
\]

\[
J^{(p)}(\omega) = \frac{2 \tau_c}{1 + \omega^2 \tau_c^2} \cdot \frac{G(q)(0)}{G(q)(0)}
\]

\(T_{1d} = \text{Dipolar (i.e., protons)}\)
\(T_{1e} = \text{Conduction electrons (metals)}\)
\(T_{1p} = \text{Paramagnetic species}\)
Examples: LaNi$_{5}$H$_{6.0}$ & LaNi$_{4.8}$Sn$_{0.2}$H$_{5.8}$

Diffusion in LaNi$_{5}$H$_{x}$ involves superposition of localized hops within subset of protons in the mid-plane region of the Ni(3) layer as well as long range motion that cause deviation from the Arrhenius relation for the proton relaxation times.

In LaNi$_5$H$_x$ magnetic precipitates (presumably Ni) distort field uniformity and keep $T_2^*$ of FID very short (~10 µs). The $T_2$ data is from two-pulse spin echoes. The $T_1$ data are from 53.14 MHz (upper) and 21.25 MHz (lower).

Guide to Interpreting NMR Results

\( \omega_H \equiv \text{rate of H hopping motion} \)

- Motional averaging of local dipolar fields is evident as increase of \( T_2 \) with temperature.
  - At onset,
    \[ \omega_H \sim 10^5 \, \text{s}^{-1} \] (approx. the low-T linewidth).

- At \( T_{1\rho} \) minimum,
  \[ \omega_H \sim 5 \times 10^5 \, \text{s}^{-1} \] (about \( 1.6 \gamma B_1 \)).

- At \( T_1 \) minimum at 21 MHz,
  \[ \omega_H \sim 2 \times 10^8 \, \text{s}^{-1} \] (about \( 1.6 \gamma B_0 \)).

- \( T_{1D} \) is approx the mean time between hops,
  \[ T_{1D} \sim 1/\omega_H \], a strong-collision result.
Dipolar order = spins oriented along local dipolar field.

Dipolar field varies from site-to-site, almost 100%.

If spin jumps to neighbor site, it is no longer oriented along the local dipolar field.

Signal decays $\sim \exp(-\tau/T_{1D})$ and $T_{1D} \approx 1/\omega_H$.

Measured $T_{1D}$ detects motions when $D(T)$ is in range $\sim 10^{-15} - 10^{-11}$ cm$^2$/s, which is much slower (i.e., 3-6 orders of magnitude) than other relaxation times.

Conradi, et al. [J. Alloys Compounds 446–447 (2007) 499–503] have measured H hopping rate $\omega_H$ using various proton relaxation times for Mg$_{65}$Sc$_{35}$Pd$_{2.4}$H$_{22.0}$ and compared to MgH$_2$, ScH$_2$, and LaNi$_5$H$_x$.

• Hydrogen diffusion in MgH$_2$ could only be detected using $T_{1D}$ times
Comparing $\omega_H$ give increasing mobility in the sequence: MgH$_2$, ScH$_2$, MgScH$_x$, and LaNi$_5$H$_{6.8}$

Fits are $\omega_H = 10^{13} \, \text{s}^{-1} \, \exp(-E_a/kT)$

Data points are from $T_1$ and $T_{1\rho}$ minima, onset of increase of $T_2$, and $T_{1D}$ ($\omega_H = 1/T_{1D}$).
Solid State NMR is a powerful & versatile method to assess numerous properties of hydrogen storage materials

Multi-nuclear spectroscopy (hydrogen isotopes & host species)

- Monitor phase compositions and transformation from spectra and relaxation times.
- Local structure & site occupancy from dipolar interactions of “rigid lattice” spectra

Diffusion behavior over large dynamic range

- Direct measurement ($D > 10^{-12} \text{ m}^2/\text{s}$) via Pulsed Field Gradients
- Several types of relaxation times are available to cover wide range of rates; however, quantitative analyses are difficult for complex materials with multiple diffusion processes and/or complicated structures.


