Diffraction at Swiss spallation neutron source SINQ: applications to magnetic structure solutions

Vladimir Pomjakushin
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SINQ diffraction instruments overview

Instruments HRPT&DMC (Powder), TriCS (Single crystal), POLDI (strain)
and TASP/MuPAD (polarised, 3D spherical neutron polarimetry)

New materials in condensed matter physics, chemistry and materials science with a focus on magnetism.
Examples are: energy research, frustrates systems, crystallography, ferroelectrics.

HRPT: V. Pomjakushin, D. Sheptyakov

DMC: L. Keller, M. Frontzek

\[ \lambda = 0.94 - 2.96 \, \text{Å} \]

\[ \lambda = 2.35 - 5.4 \, \text{Å} \]
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$\lambda = 1.18, 2.3 \text{ Å}$

POLDI (strain scanner) TOF Laue option

$\lambda = \text{white beam}$

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Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institute, Villigen, Switzerland
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Pomjakushin diffraction
SINQ, 2015, Hercules
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Scientific case of neutron diffraction (ND) experiments at SINQ

“hard matter” topics:

Atom and spin ordering. Indirectly charge and orbital ordering. Finding crystal and magnetic symmetry adapted structures in “any” material...

1. Strongly correlated electrons
   (quantum/low D, frustrated) magnetism, superconductivity (SC), multiferroics...
   SANS: very long period mag. str., like skyrmions or flux lattice in SC


Materials:
   mainly inorganic: oxides, pnictides, selenides, intermetallic, etc...
   organic ones or liquids are less common
Neutron diffraction experiment ($\lambda = \text{const}$)

Nuclear structure factor

$$F(q) = \sum_j b(r_j) \exp(iqr_j)$$

Magnetic structure factor

$$F(q) \propto \sum_j S_{0\perp j} \cdot \exp(iqr_j)$$

Intensity in the detector

$$\frac{d\sigma}{d\Omega} \propto F(q)F^*(q) \cdot \delta(H - q)$$

Momentum transfer or scattering vector

$$q = k' - k$$

$$|k| = |k'| = \frac{2\pi}{\lambda}$$
neutron diffraction experiment ($\lambda$=const)

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**Sample**

$$|k| = |k'| = \frac{2\pi}{\lambda}$$
# Neutron Diffraction Experiment ($\lambda = \text{const}$)

<table>
<thead>
<tr>
<th>Nuclear structure factor</th>
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<tbody>
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</tr>
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<td>atom position and spin</td>
<td></td>
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</table>

Intensity in the detector

$$\frac{d\sigma}{d\Omega} \propto F(q)F^*(q) \cdot \delta(H - q)$$

momentum transfer or scattering vector $q = k' - k$

$$q = \frac{4\pi \sin(\theta)}{\lambda}, \theta = 0.. \leq 90\deg.$$  

$$q_{\text{max}} = \frac{4\pi}{\lambda}$$  

small wavelength is a must to have large $q_{\text{max}} \rightarrow$ good spatial resolution

$$d_{\text{min}} = \frac{\lambda}{2}$$

$$|k| = |k'| = \frac{2\pi}{\lambda}$$
Q-range limitation — image quality (min δr)

Object

\[ b(r) \sim \int_0^{\infty} e^{-iqr} f(q) dq \]

Fourier image

\[ f(q) \sim \int e^{iqr} b(r) dr \]

Structure factor

\[ F(q) = \sum_j b(r_j) \exp(iqr_j) \]
Q-range limitation — image quality (min δr)

\[ b(r) \sim \int_0^{q_{\text{max}}} e^{-iqr} f(q) dq \]

Object

\[ \infty \]

\[ b(r) \sim \int_0 e^{-iqr} f(q) dq \]

Fourier image

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Structure factor

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\( \delta q/q \) resolution limitations

the mesh is for the parent I4/mmm cell \( a=4\text{Å} \)

\( T=300\text{K} \), (hk0) plane of Cs\(_{y}\)Fe\(_{2-x}\)Se\(_2\)

\( Q \) is +/- 8Å\(^{-1}\)
Q-range/resolution in powder diffraction. Peak overlap.

Diffraction patterns, High resolution powder diffractometer HRPT @ SINQ

Sr$_7$Ca$_7$Cu$_{24}$O$_{41}$

television number compound

$\lambda=1.494$ Å

$\theta$-range/q-resolution in powder diffraction. Peak overlap.

Modulated structure:
3D+1 superspace group
$Xmmm(00\gamma)ss0$

Pomjakushin diffraction: 
SINQ, 2015, Her
Limitations on maximal unit cell volume (number of atoms) in powder neutron diffraction

Volumes up to 1000-2000Å, about 100-200 atoms, concentration 0.08-0.1 at/A³

bond lengths accuracy ~0.001Å

\[ \text{Ca}_3\text{Cu}_x\text{Ni}_{2-x}(\text{PO}_4)_4 \]
18x5x18Å, \( V=1300\text{Å}^3 \)

\[ \text{LixFe}[	ext{CH}_2(\text{PO}_3)_2] \]
18x8x9Å, \( V=1300\text{Å}^3 \) 144 atoms

Structures: solved/refined from HRPT NPD data

Pomjakushin diffraction
SINQ, 2015, Hercules
Magnetic structure - limitations
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1. High q-range is not needed (usually)
   • Atomic positions are known
   • Magnetic form-factor $f(q) \sim \exp(-q^2)$

\[ F(q) \propto \sum_j S_{0,j} \cdot \exp(iq r_j) \]
\[ I \sim |F(q)|^2 f^2(q) \sim S^2 f^2(q) \]
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3. Magnetic cell is often large -> low-q domain with good $\Delta q/q$
   • Large neutron wavelengths are needed
   • Intensity & peak/BG should be large for small moments (~0.1 $\mu_B$)

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\begin{align*}
\text{from 2theta min } &-4 \\
\text{degrees, d max 30A, } &\text{for A1.3A} \\
\text{Pomjakushin diffraction} &\text{SINQ, 2015, Hercules} \\
\lambda=\text{const resolution, powder diffraction} &
\end{align*}
Magnetic structure - limitations

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\[
F(q) \propto \sum_j S_{0\parallel j} \cdot \exp(i q r_j)
\]

\[
I \sim |F(q)|^2 f^2(q) \sim S^2 f^2(q)
\]
Antiferromagnetic three sub-lattice ordering in Tb$_{14}$Au$_{51}$

Conventional magnetic unit cell $a=38$ Å, $c=9$ Å
(Volume $=11'137$ Å$^3$) contains 126 spins of Tb$^{3+}$.

$k$-vector=$[1/3, 1/3, 0]$

Example: Magnetic structure solved from DMC & HRPT NPD data
# Diffraction instruments at swiss spallation source SINQ

- **HRPT** - High Resolution Powder Diffractometer for Thermal Neutrons, $\lambda=0.94 - 2.96$ Å, High Q-range $\leq 11\text{Å}^{-1}$

- **DMC** – High Intensity Powder Diffractometer for Cold Neutrons, $\lambda=2.35 - 5.4$ Å, High flux and good resolution at low and moderate $Q \leq 4\text{Å}^{-1}$

- **TriCS** - Single crystal diffractometer, $\lambda=1.18, 2.3$ Å, Thermal Neutrons

- **TASP** (triple axes) with MuPAD for polarised ND, Cold Neutrons
The spallation neutron source SINQ is a continuous source - the first and the only of its kind in the world - with a flux of about $10^{14}$ n/cm$^2$/s. Beside thermal neutrons, a cold moderator of liquid deuterium (cold source) slows neutrons down and shifts their spectrum to lower energies.
Spallation, SINQ 590MeV protons, Pb target

Neutron yield

Calculated, from G.J. Russell, Spallation physics—an overview, Proceedings of ICANS-XI
Elephant is: Shielding of the direct neutron beam also from fast neutrons for diffraction instruments.
Neutron (thermal) flux from the D$_2$O moderator, Maxwellian at 90$^{\circ}$C (HRPT, TRICS)

\[ \lambda_0 = \frac{h}{\sqrt{2mkT}} = 1.8\text{Å}(T = 293\text{K}, 20\text{C}) \]

Maxwell

\[ f(\lambda) = \frac{4}{\lambda^4\sqrt{\pi}} e^{-\tilde{\lambda}^{-2}} \]

Flux

\[ f(\lambda) = \frac{2}{\tilde{\lambda}^5} e^{-\tilde{\lambda}^{-2}} \]

\[ \tilde{\lambda} = \frac{\lambda}{\lambda_0} \]

\[ \lambda_{\text{max}} = \frac{2\lambda_0}{\sqrt{10}} \approx 0.63\lambda_0 \]

Total: $5 \cdot 10^7 \text{1/cm}^2/\text{s/mA}$

at SINQ current 2mA: $10^8$
Neutron flux from cold moderator (DMC, TASP), liquid D₂, T=25K or -248°C

\[ \lambda_0 = 6.2 \text{Å (25K)} \]

\[ \lambda_{\text{max}} = \frac{2\lambda_0}{\sqrt{10}} \approx 0.63\lambda_0 \]

Integral measured at monochromator position of DMCG:
\[ 2.21 \text{E8/cm}^2/\text{s/mA} \]
HRPT layout

High Resolution Powder Diffractometer for Thermal Neutrons

horizontal angular divergence control
\[ \alpha_1 \]
primary beam collimator(s):
6', 12', 24', 30'

\[ \alpha_2 \]
mosaic spread of the monochromator 15'

\[ \alpha_3 \]
slit system for monochromatic beam and sample diameter

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Pomjakushin diffraction
SINQ, 2015, Hercules
HRPT layout

High Resolution Powder Diffractometer for Thermal Neutrons

neutron monochromator
fixed 120 take off angle

\[ \lambda = 2d \sin (\theta) \]
\[ \lambda = 2d \sin (60^\circ) \]
Ge single crystal monochromator, 7 motors

Focusing system
Monochromator cuts narrow wavelength range from the “white” flux. HRPT $\lambda = 0.94 - 2.96 \, \text{Å}$

$$\Delta \lambda / \lambda \approx 0.01$$

\[ \lambda_0 = \frac{h}{\sqrt{2mkT}} = 1.8 \, \text{Å} \quad (T = 293K, 20C) \]

Flux
$$f(\lambda) = \frac{2}{\tilde{\lambda}^5} e^{-\tilde{\lambda}^{-2}}$$
$$\tilde{\lambda} = \frac{\lambda}{\lambda_0}$$

Total: $5 \cdot 10^7 \, \text{1/cm}^2/\text{s/mA}$
At SINQ current 2mA: $10^8$
Monochromator cuts narrow wavelength range from the “white” flux. HRPT $\lambda = 0.94 - 2.96$ Å

Intensity of Bragg scattering from big single crystal: Lorentz factor, extinction, geometry, ...

$I \sim f(\lambda) \Delta \lambda C(\lambda, \theta) \sim f(\lambda) \lambda^{2.5} C'(\theta)$

for fixed monochromator take-off 2θ for HRPT

$\lambda_0 = \frac{h}{\sqrt{2mkT}} = 1.8$ Å ($T = 293K, 20C$)

 Flux $f(\lambda) = \frac{2}{\tilde{\lambda}^5} e^{-\tilde{\lambda}^{-2}}$

$\tilde{\lambda} = \frac{\lambda}{\lambda_0}$

$\Delta \lambda / \lambda \approx 0.01$

Total: $5 \cdot 10^7$ 1/cm²/s/mA at SINQ current 2mA: $10^8$
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for fixed monochromator take-off 2\(\theta\) for HRPT

Flux after monochromator y-scale is in a.u.

white flux distribution

\( \lambda_0 = 1.6 \text{Å} \)

\( T = 90^\circ \text{C} \)
HRPT - High Resolution Powder Diffractometer for Thermal Neutrons. linear detector with 1600 channels, 0.1°

Responsible: Vladimir Pomjakushin, Denis Sheptyakov

DMC - cold neutron powder diffractometer linear detector with 400 channels, 0.2°

Responsible: Lukas Keller, Matthias Frontzek

![HRPT RESOLUTION FUNCTIONS](image1)

![DMC: experimental resolution functions Δd/d (Q,λ)](image2)
Powder ND at SINQ/PSI

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HRPT RESOLUTION FUNCTIONS

\( (\text{FWHM}, 2 \theta_M = 120 ^\circ) \)

\( \lambda \\
1.15 \text{Å} \\
1.20 \text{Å} \\
1.49 \text{Å} \\
1.89 \text{Å} \\
2.45 \text{Å} \)

\( Q [\text{Å}^{-1}] \)

Sample diameter 10 mm

\( Q = 4\pi \sin \theta / \lambda [\text{Å}^{-1}] \)
Powder ND at SINQ/PSI

HRPT - **High Resolution Powder Diffractometer for Thermal Neutrons at SINQ**

DMC - **cold neutron powder diffractometer**

**HRPT RESOLUTION FUNCTIONS**
(FWHM, $2 \theta_M = 120 ^\circ$)

**DMC: experimental resolution functions $\Delta d/d(Q, \lambda)$**

Sample diameter 10 mm
Powder ND at SINQ/PSI

HRPT - High Resolution Powder Diffractometer for Thermal Neutrons at SINQ

DMC - cold neutron powder diffractometer

DMC: experimental resolution functions $\Delta d/d(Q,\lambda)$

Sample diameter 10 mm
Powder ND at SINQ/PSI

HRPT - **High Resolution Powder Diffractometer for Thermal Neutrons at SINQ**

DMC - **cold neutron powder diffractometer**

Resolution in low q-domain

**HRPT RESOLUTION FUNCTION**

$\delta d/d$ vs $q [\text{Å}^{-1}]$

\[ \text{FWHM, } 2 \theta _{\text{M}} \]

DMC, 4.5Å

HRPT, 1.9Å, HI

Sample diameter 10mm

$Q = 4\pi \sin \theta / \lambda [\text{Å}^{-1}]$
Spin-lattice coupling and antiferromagnetic order in orthorhombic multiferroic $^* \text{TmMnO}_3$

$^*$ materials that have coupled electric, magnetic and structural order parameters
cf. resolution/q-range

HRPT 1.9Å

magnetic contribution

DMC range at 4.5Å
Complementarity 1.9Å HRPT and 4.5Å DMC

excellent resolution and high Q-range

excellent resolution at low Q and high neutron intensity
Complementarity 1.9Å HRPT and 4.5Å DMC

excellent resolution and high Q-range

excellent resolution at low Q and high neutron intensity
Magnetic structure TmMnO$_3$

(a) IC Structure for $T_C < T < T_N$

Para-electric phase
(3D+1) superspace magnetic group
$Pmcn1'(00g)000s$

(b) C Structure ($E_+$) for $T < T_C$

Ferro-electric phase
polar magnetic group $Pbmn2_1$

Pomjakushin diffraction
SINQ, 2015, Hercules
Example of accuracy on metric: orthorhombic multiferroic TmMnO$_3$ material that have coupled electric, magnetic and structural order.
ECM-2016: August 28 – Sept. 1
European Conference on Crystallography

http://ecm30.ecanews.org/
Thank you