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

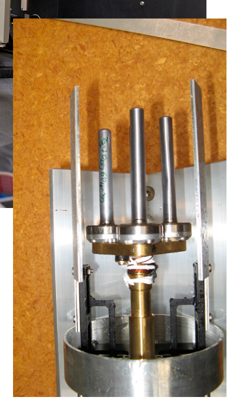
Vladimir Pomjakushin

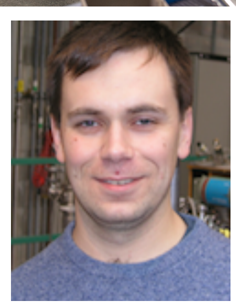
Laboratory for Neutron Scattering and Imaging, LNS, Paul Scherrer Institute

SINQ diffraction instruments overview

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

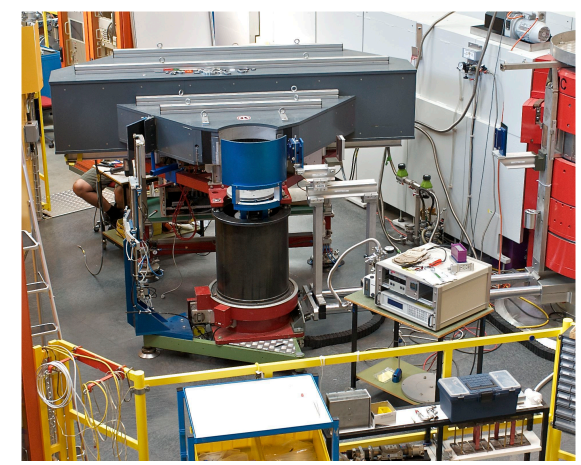
New materials in condensed matter physics, chemistry and materials science with a focus on magnetism
Examples are: energy research, frustrates systems, crystallography, ferroelectrics





λ=0.94 - 2.96 Å

HRPT: V. Pomjakushin, D. Sheptyakov



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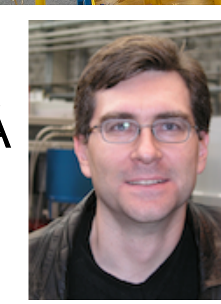


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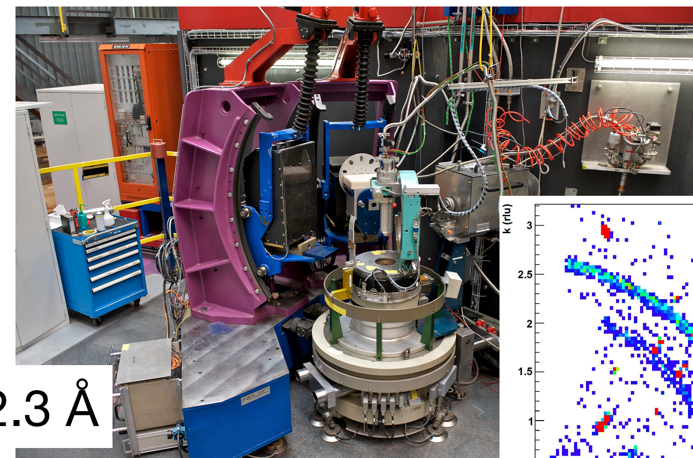
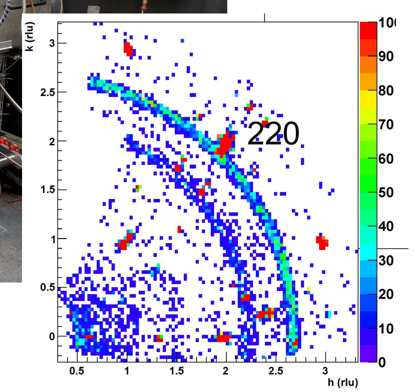
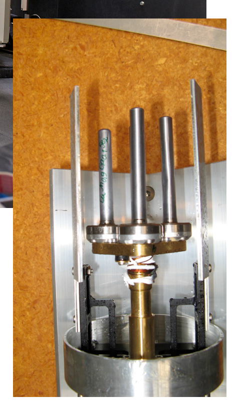
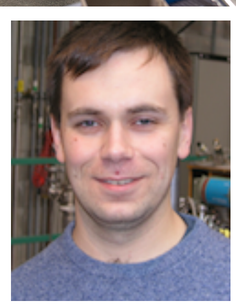



TriCS: O. Zaharko, J. Schefer

λ=1.18, 2.3 Å





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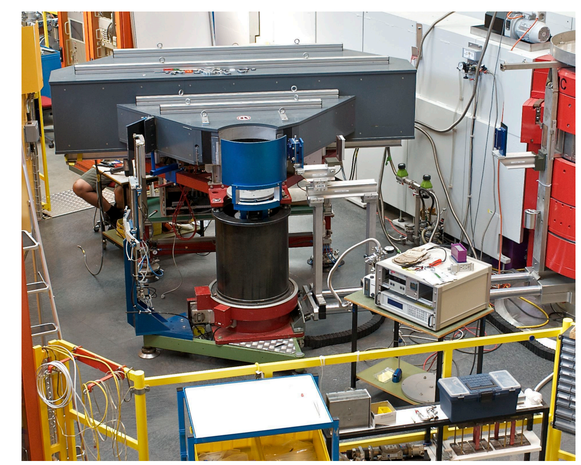

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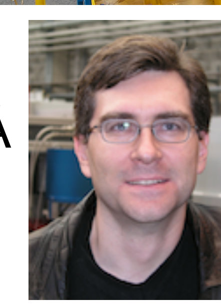


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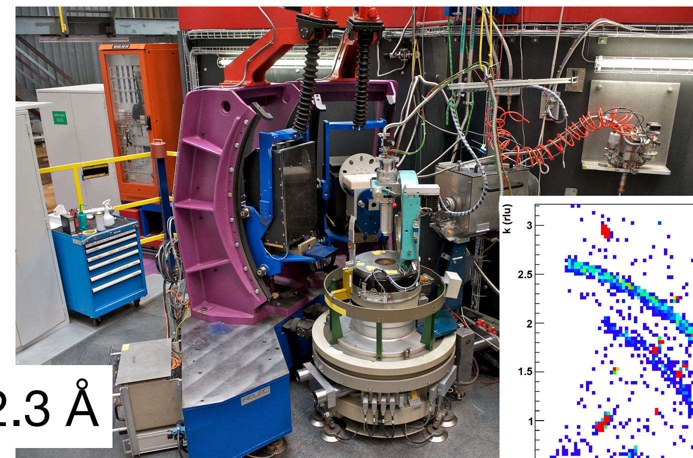
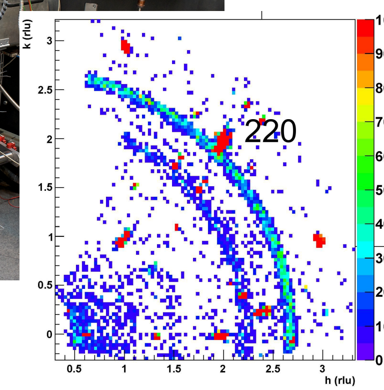
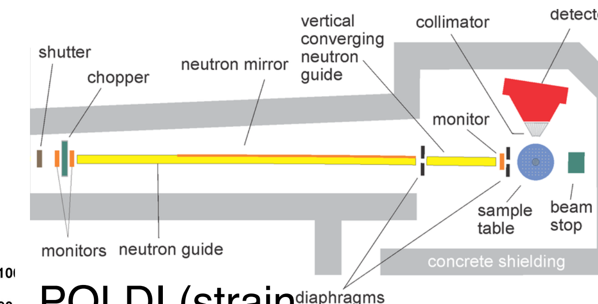
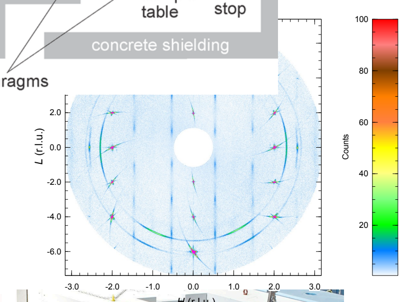
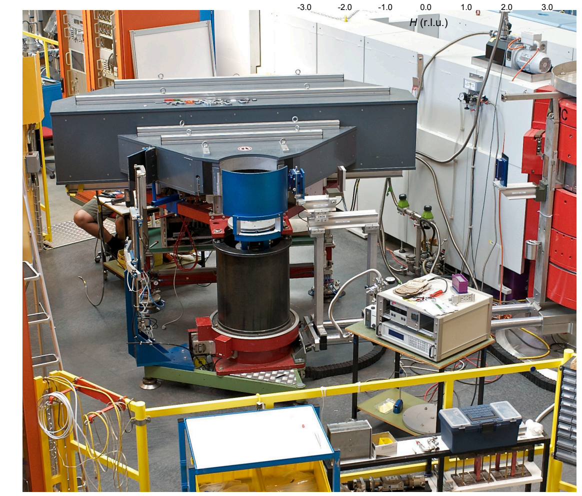


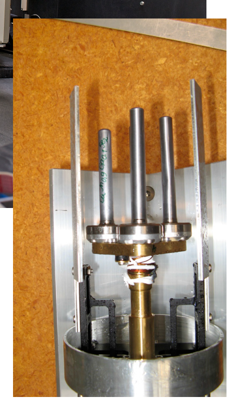


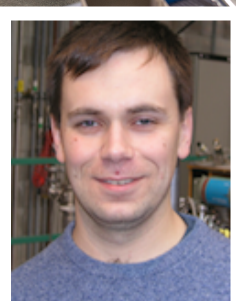


POLDI (strain scanner) TOF Laue option
λ=white beam







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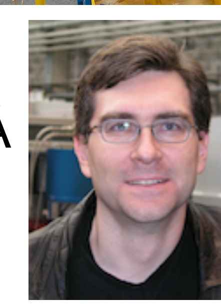


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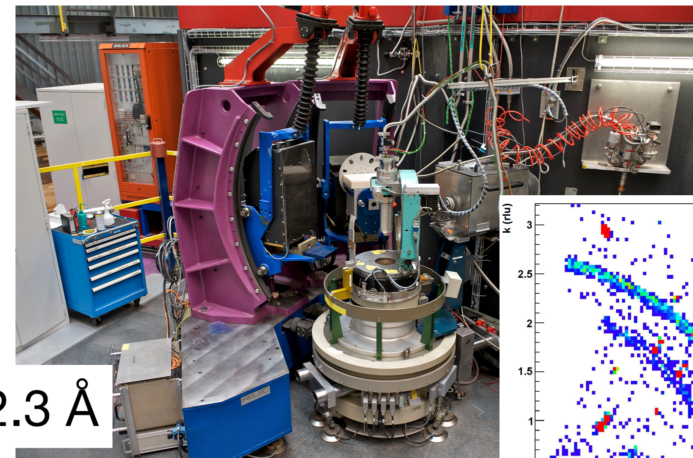

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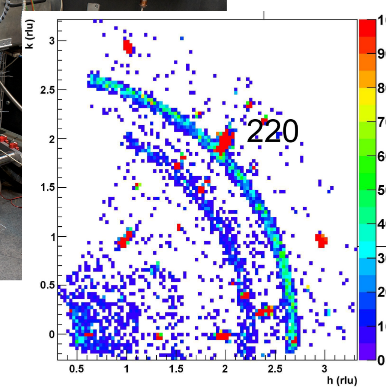

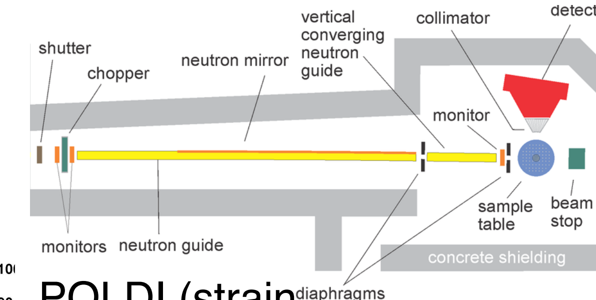

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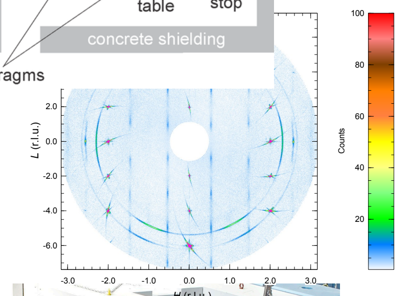

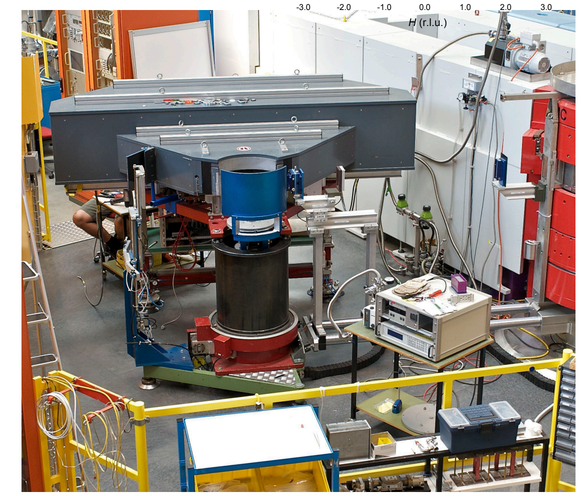

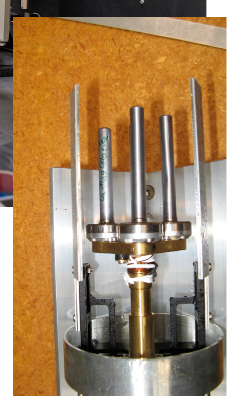


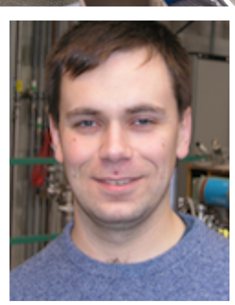

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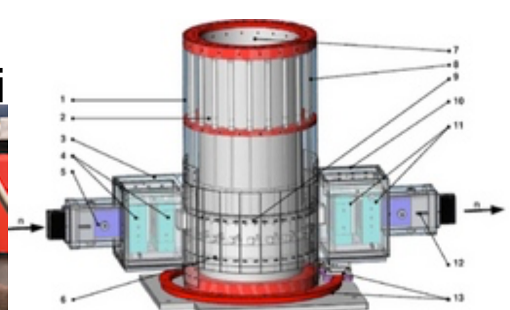
TASP/ MuPAD: B. Roessli



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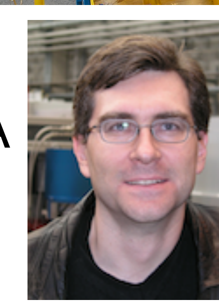


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Scientific case of neutron diffraction (ND) experiments at SINQ

"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

2. Materials science: *def.*== "Discovery and design of new materials."; *a relaxed def.*== "Study of any materials interesting to you if your project got funding"

Materials:
mainly inorganic: oxides, pnictides, selenides, intermetallic, etc…
organic ones or liquids are less common

neutron diffraction experiment (λ=const)

Nuclear structure factor

$$F(\mathbf{q}) = \sum_j b(\mathbf{r}_j) \exp(i\mathbf{q}\mathbf{r}_j)$$

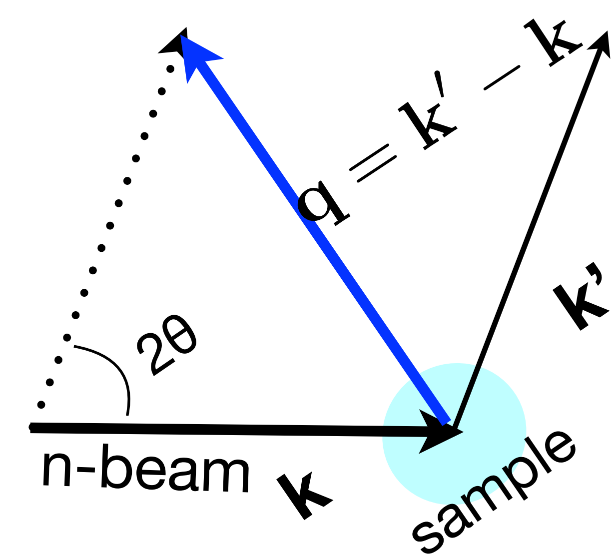
Magnetic structure factor

$$\mathbf{F}(\mathbf{q}) \propto \sum_j \mathbf{S}_{0\perp j} \cdot \exp(i\mathbf{q}\mathbf{r}_j)$$

Intensity in the detector

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

momentum transfer or
scattering vector $\mathbf{q} = \mathbf{k}' - \mathbf{k}$



$$|\mathbf{k}| = |\mathbf{k}'| = \frac{2\pi}{\lambda}$$

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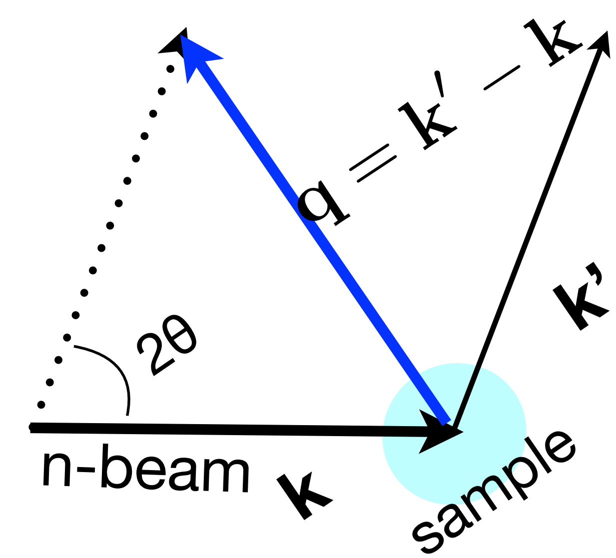

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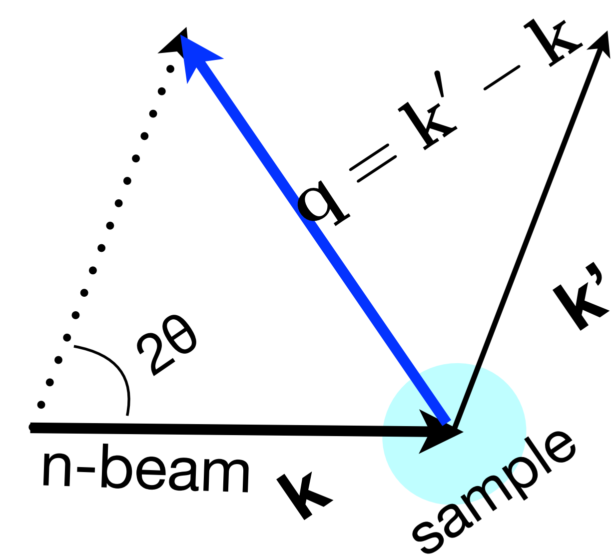


momentum transfer or scattering vector $\mathbf{q} = \mathbf{k}' - \mathbf{k}$

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

$$|\mathbf{k}| = |\mathbf{k}'| = \frac{2\pi}{\lambda}$$

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

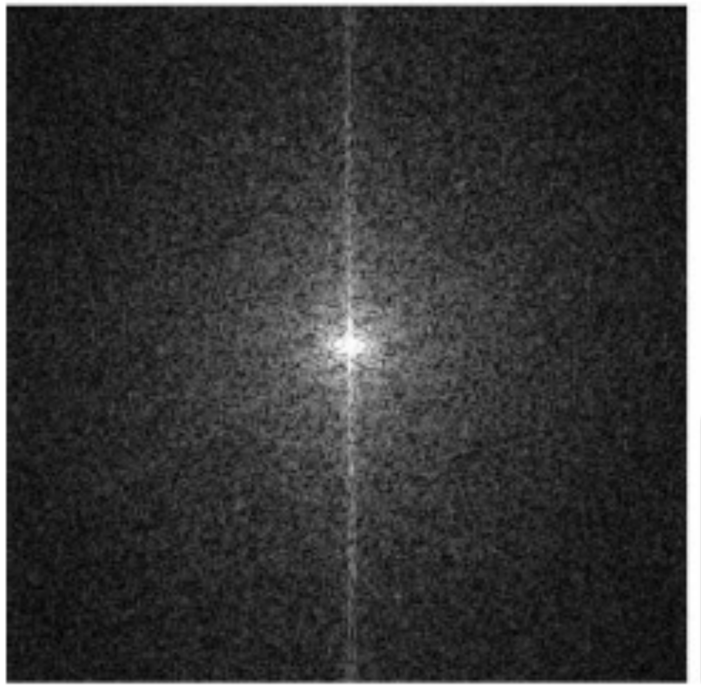
$$(d_{min} = \frac{\lambda}{2})$$

small wavelength is a must to have large q_{max} –> good spatial resolution

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

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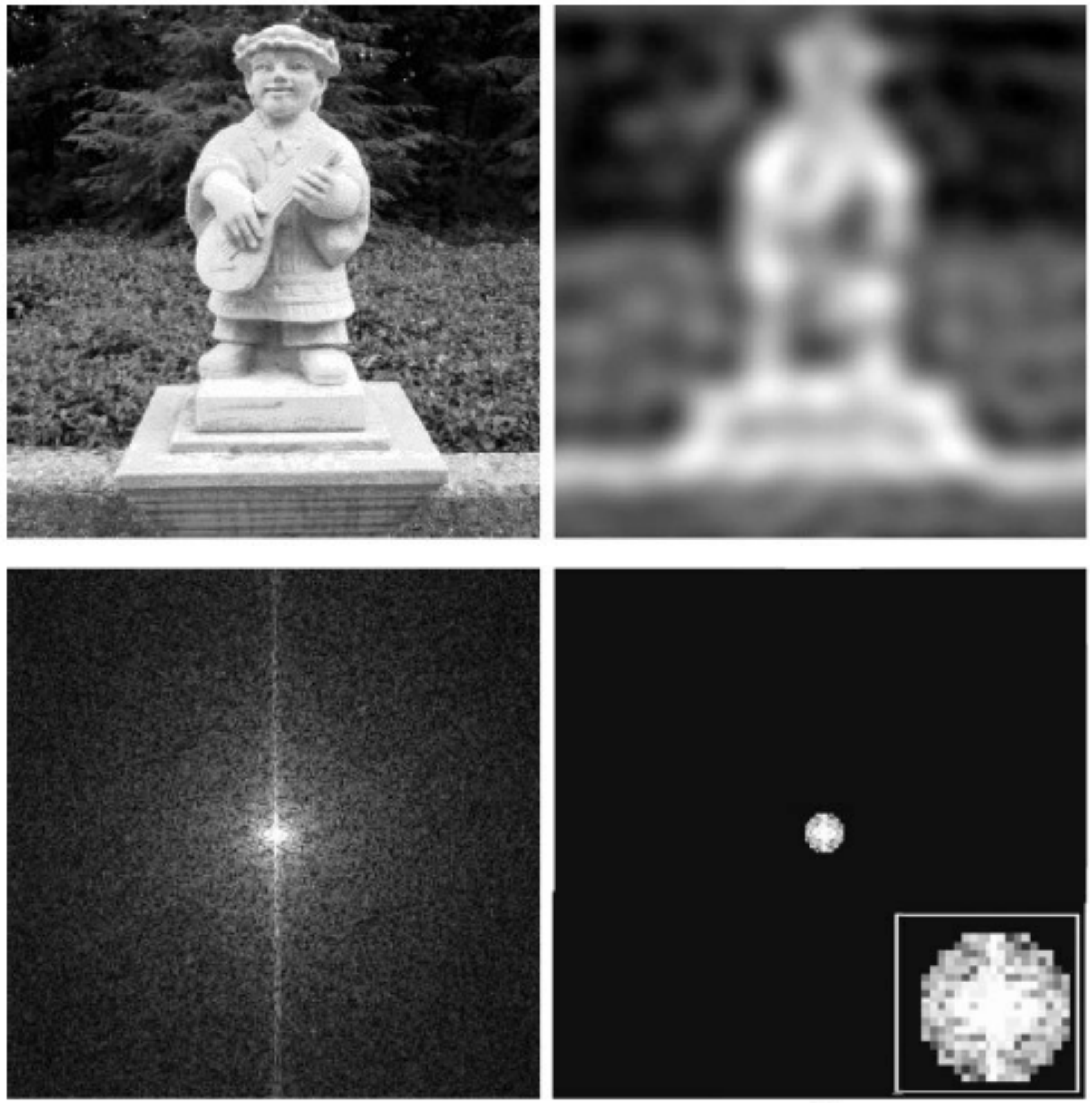

$$b(r) \sim \int_0^{q_{max}} e^{-iqr} f(q)dq$$

Fourier image

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

Fourier image without high q

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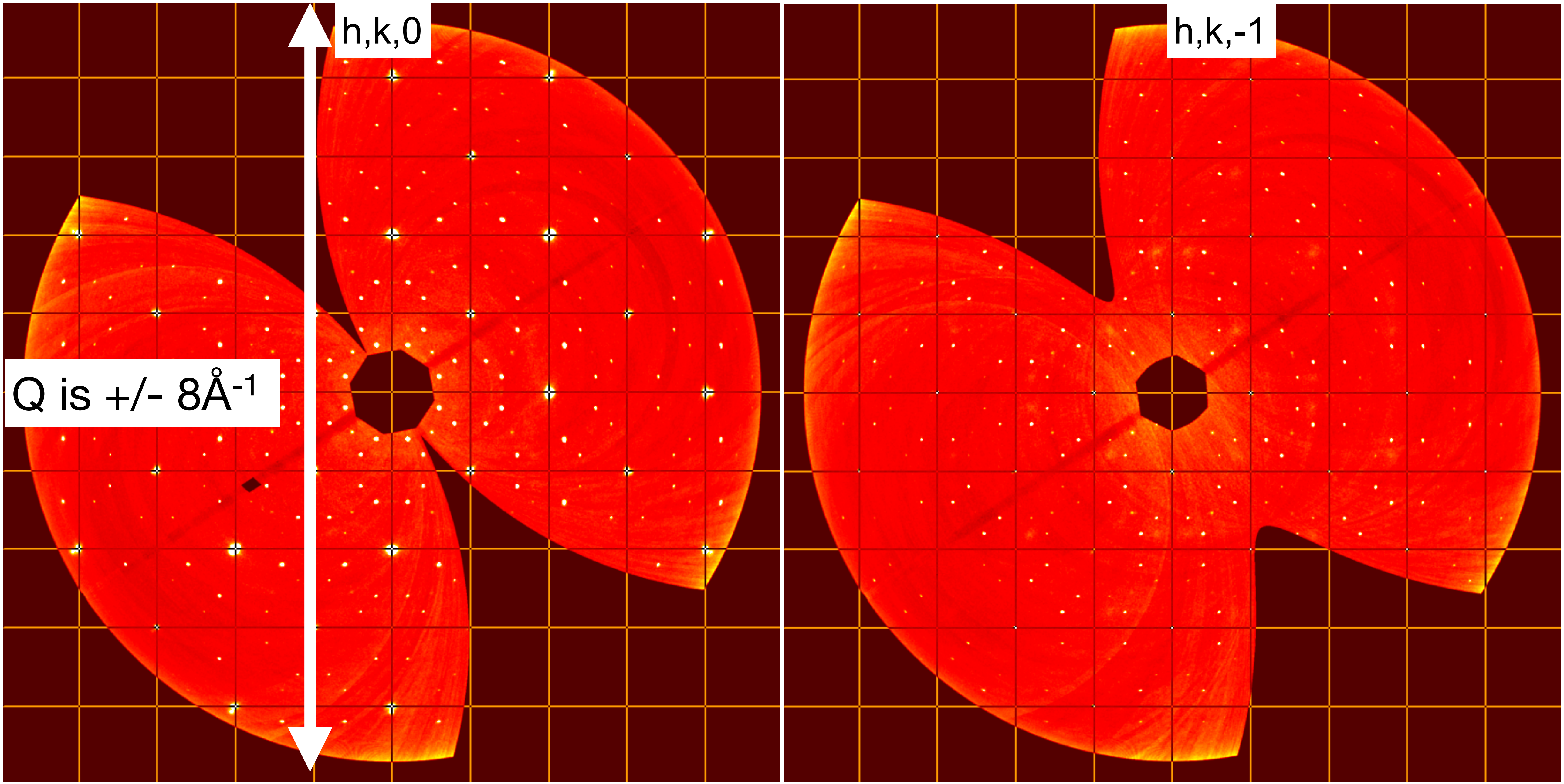
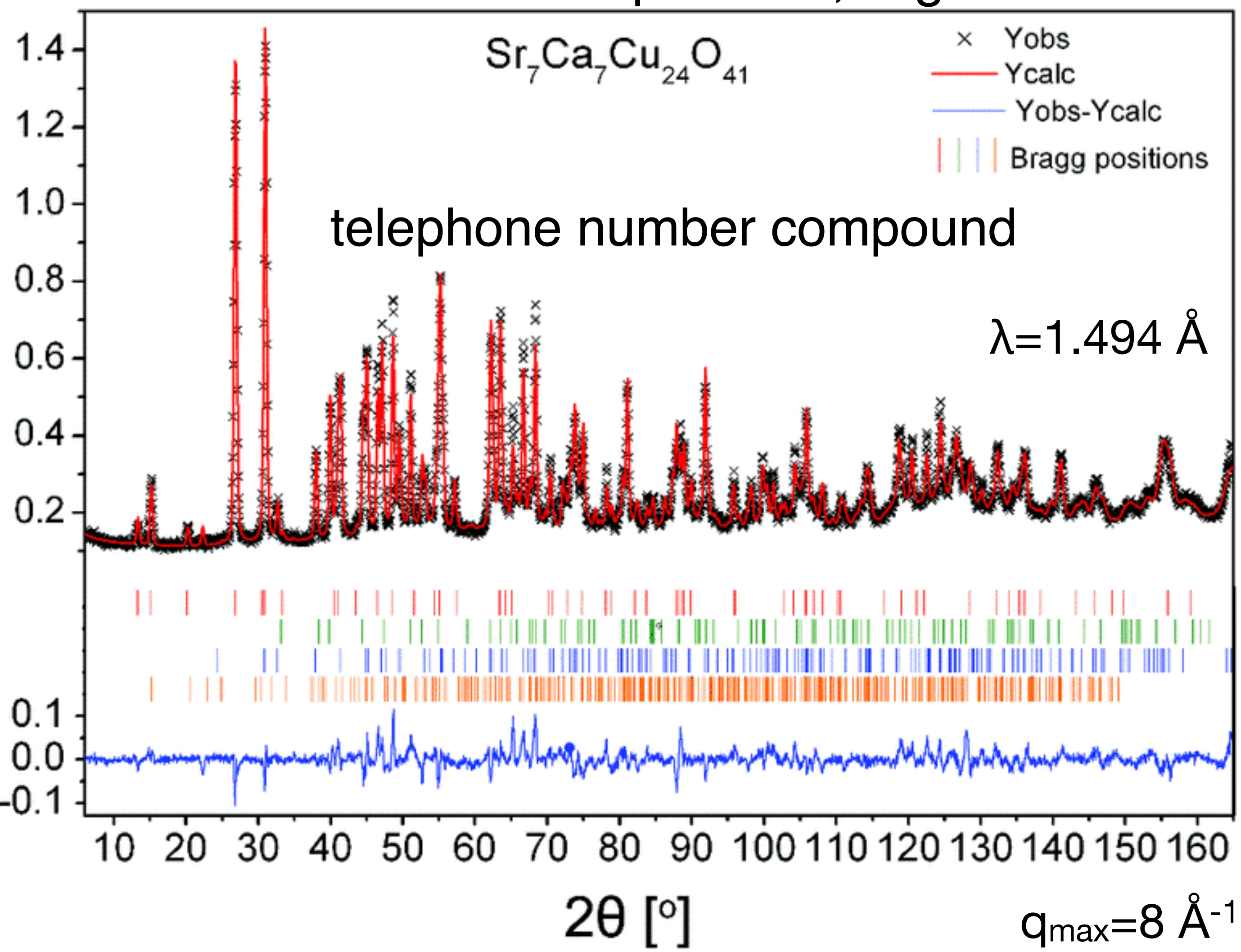
$\delta q/q$ resolution limitations

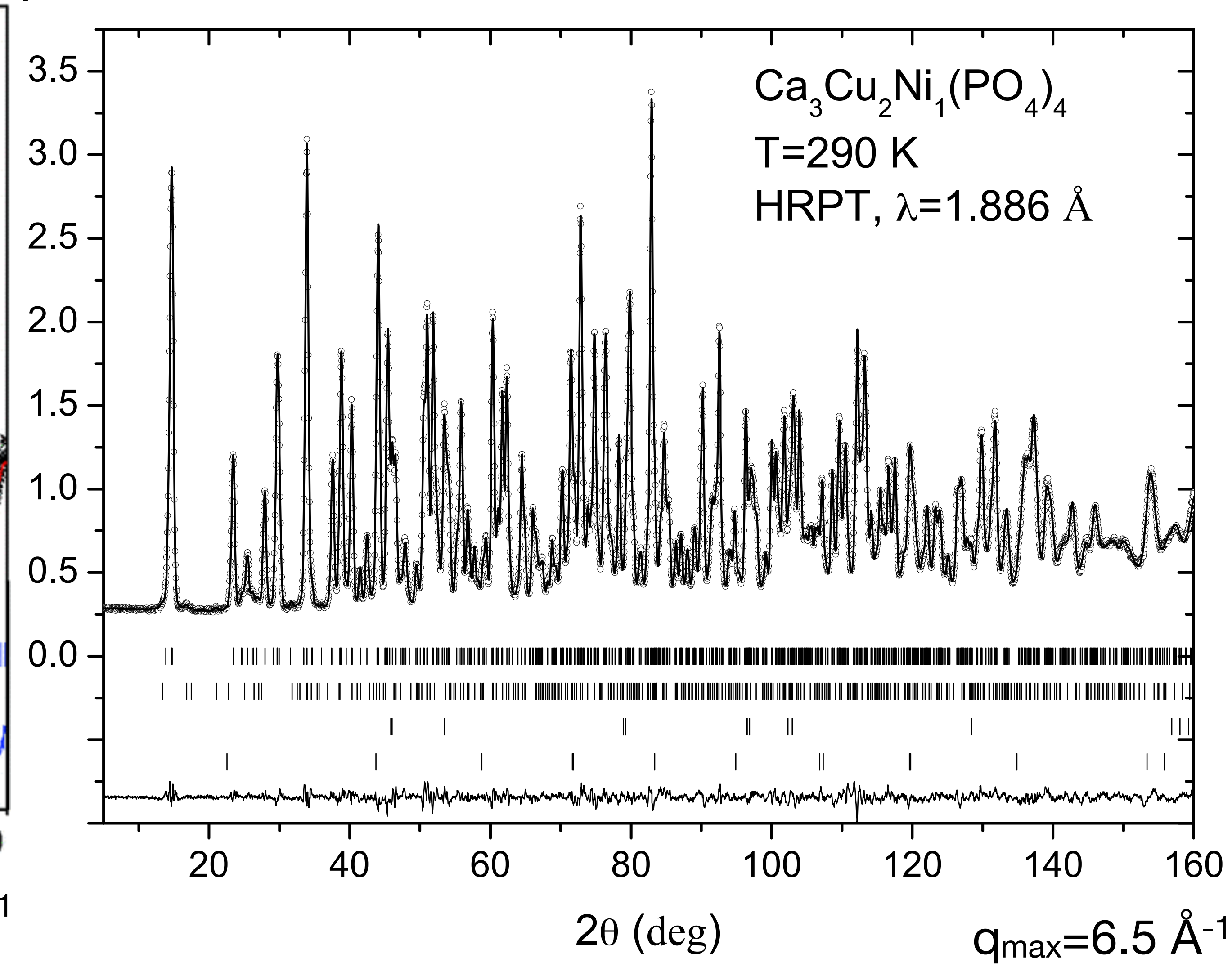
the mesh is for the parent I4/mmm cell a=4Å
T=300K, (hk0) plane of $Cs_yFe_{2-x}Se_2$



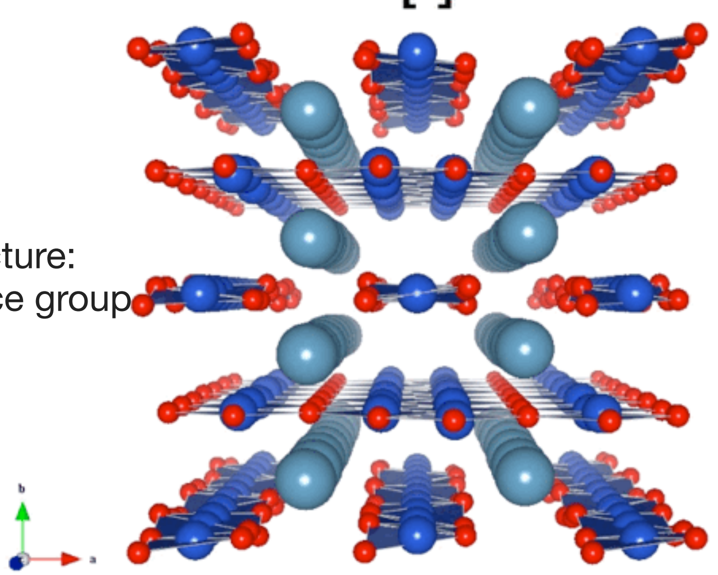
Q-range/resolution in powder diffraction. Peak overlap.

Diffraction patterns, High resolution powder diffractometer HRPT @ SINQ

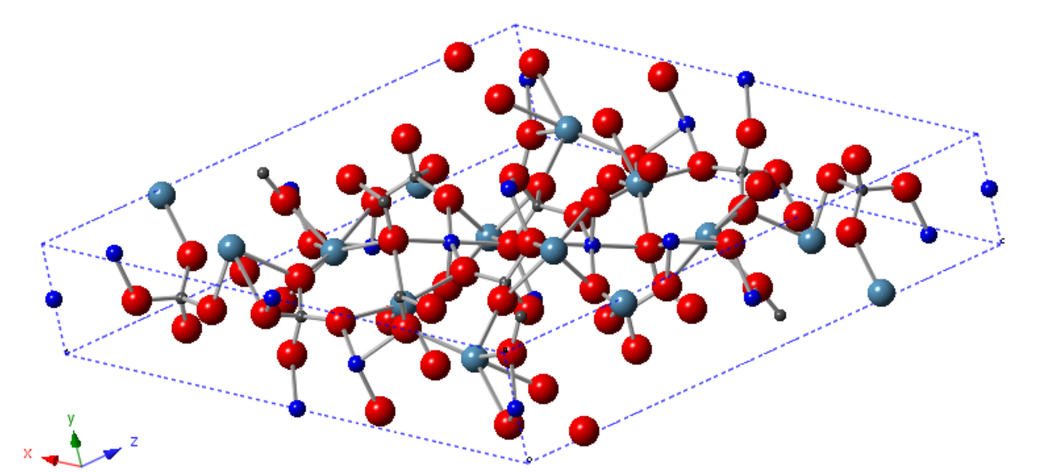




Modulated structure:
3D+1 superspace group
Xmmm(00γ)ss0



Pomjakushin diffr
SINQ, 2015, Her



Limitations on maximal unit cell volume (number of atoms) in powder neutron diffraction

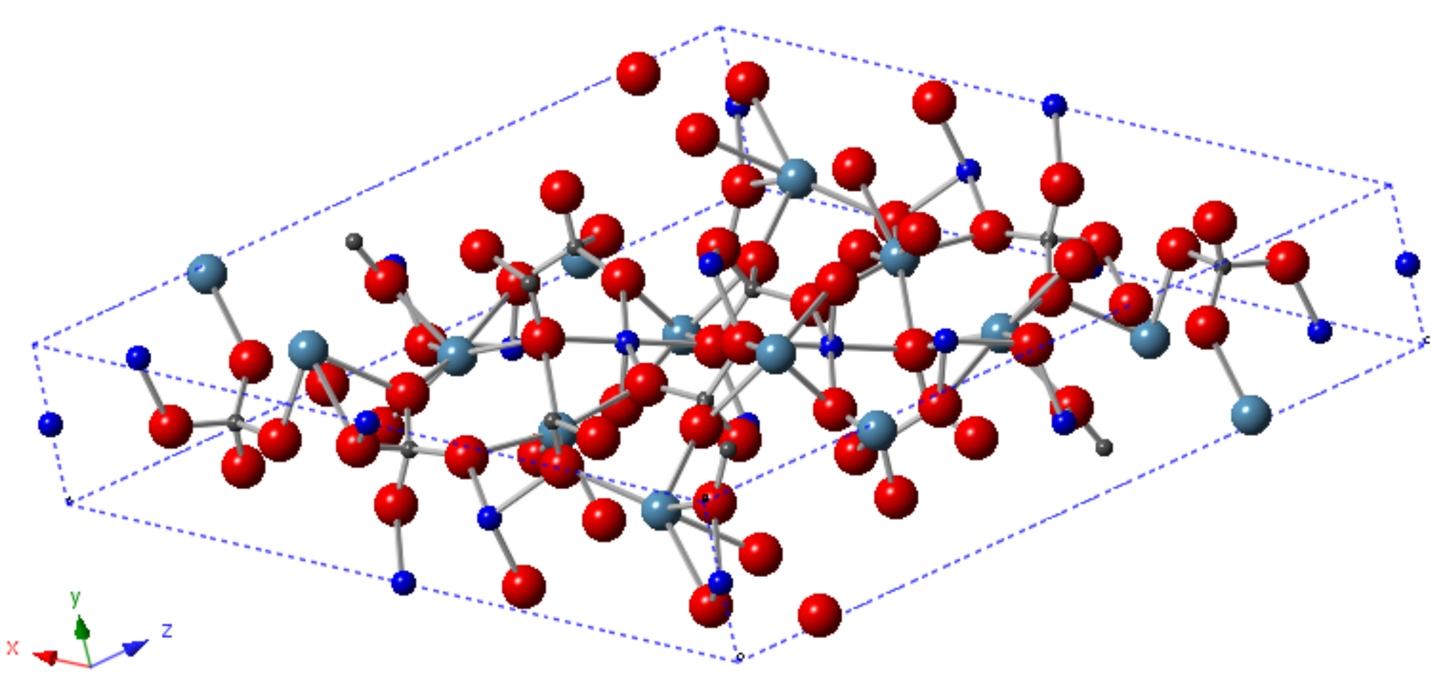
Volumes up to 1000-2000Å, about 100-200 atoms, concentration 0.08-0.1 at/A^3

bond lengths accuracy ~0.001Å

$Ca_3Cu_xNi_{2-x}(PO_4)_4$

18x5x18Å, V=1300Å^3

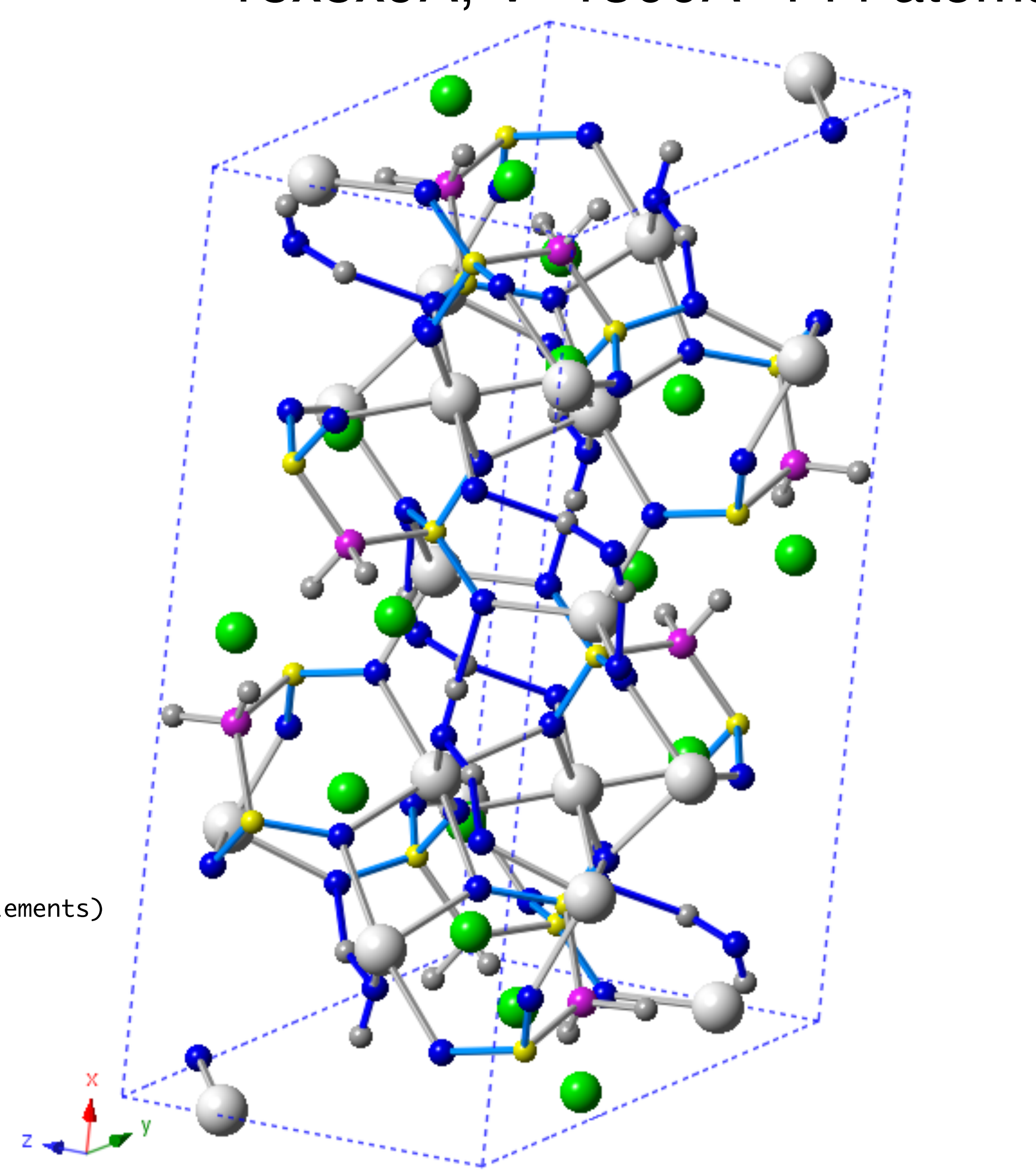
C2/c sp.gr.



(114 atoms, 14 sites, 4 elements)

$LixFe[CH_2(PO_3)_2]$

18x8x9Å, V=1300Å^3 144 atoms



(148 atoms, 19 sites, 6 elements)

Structures: solved/refined from HRPT NPD data

Magnetic structure - limitations

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1. High q-range is not needed (usually)
   - Atomic positions are known
   - Magnetic form-factor f(q) ~ exp(-q²)

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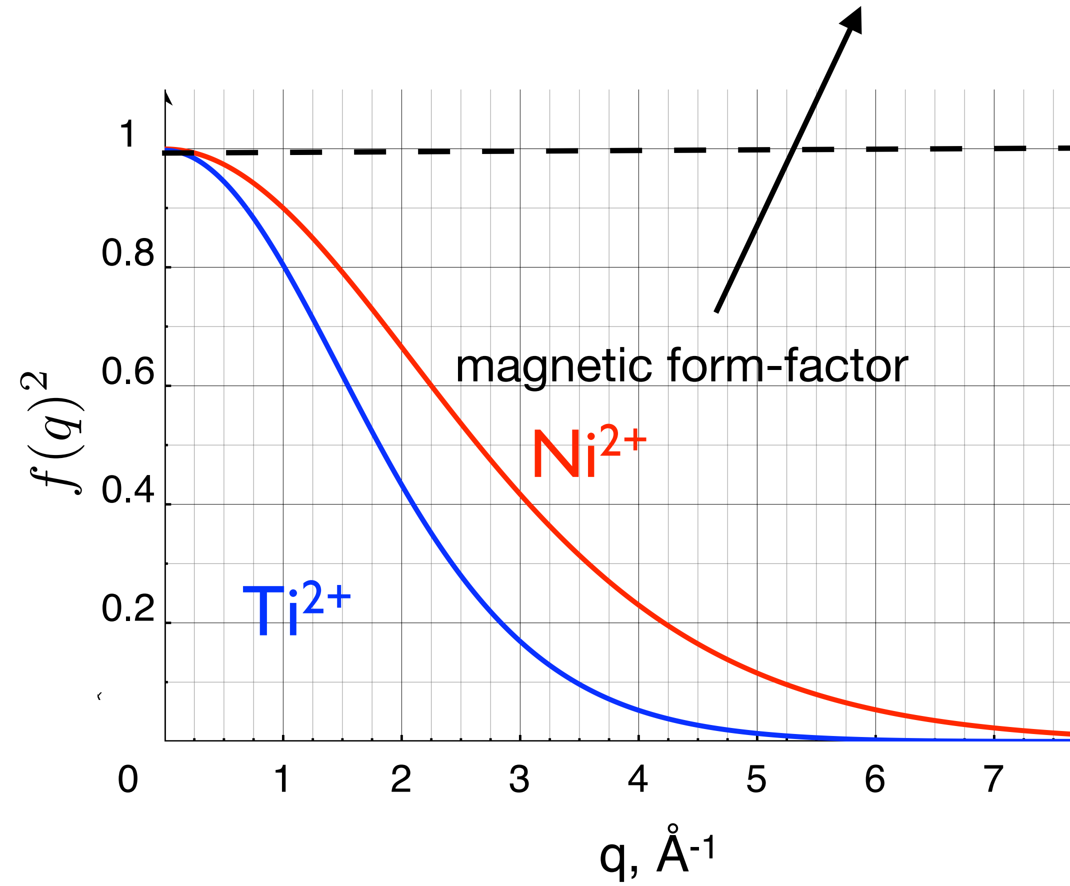

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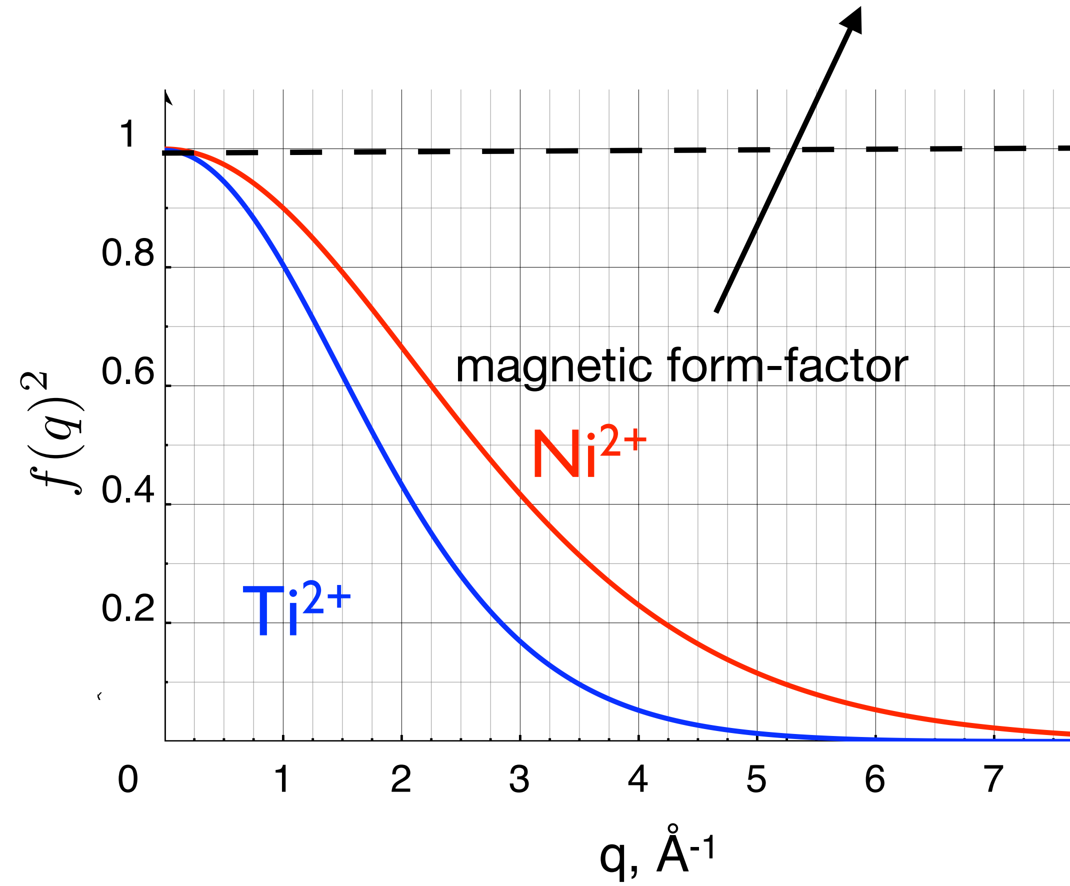

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    - Intensity & peak/BG should be large for small moments (~0.1 μ_B)

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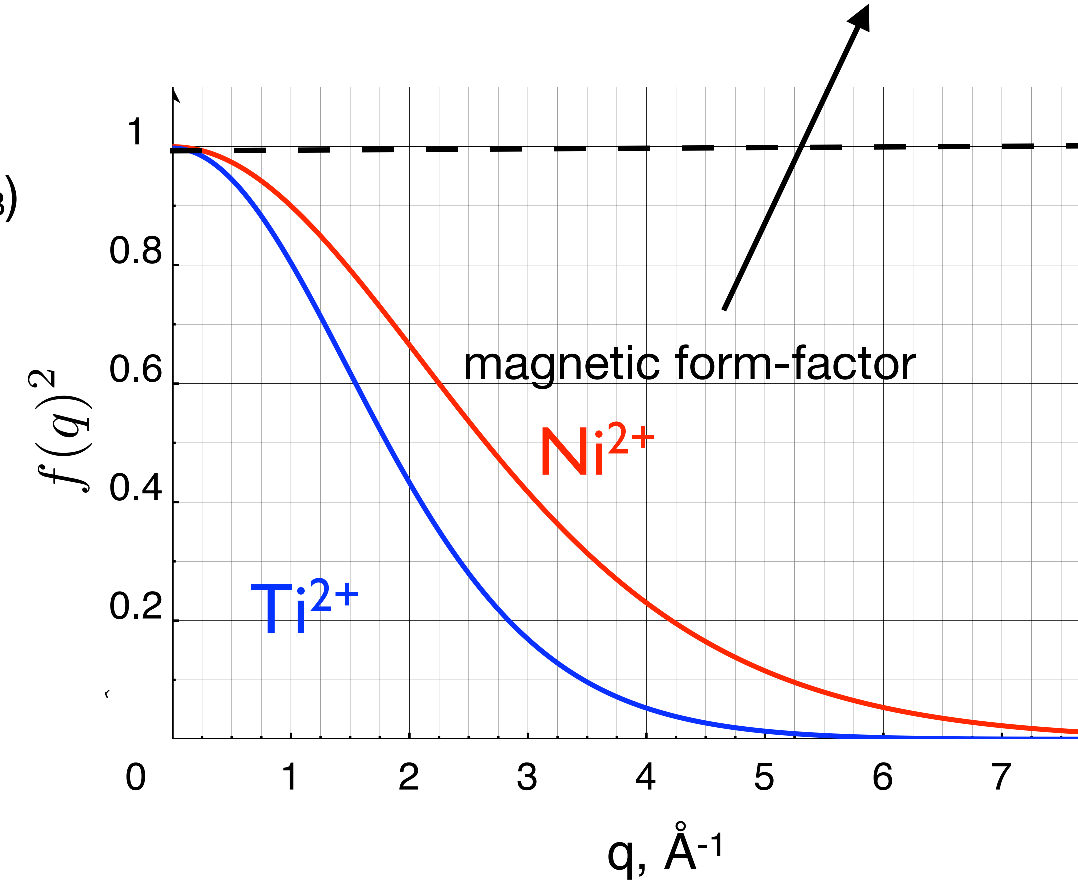

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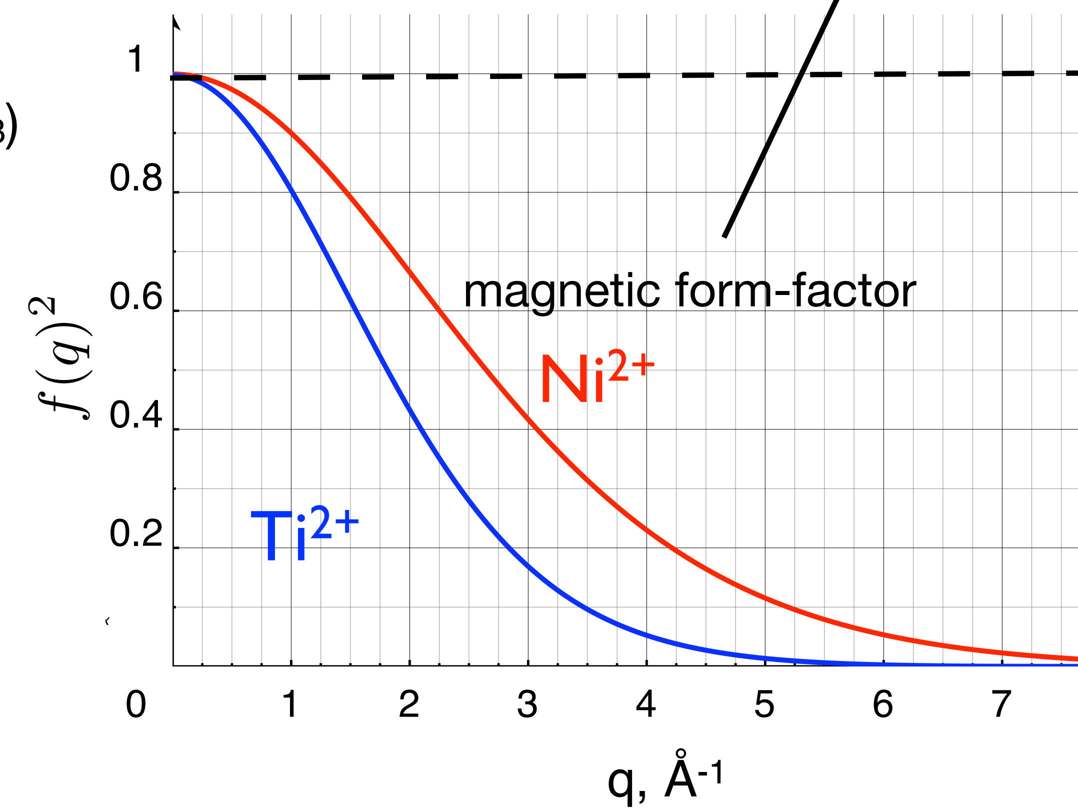

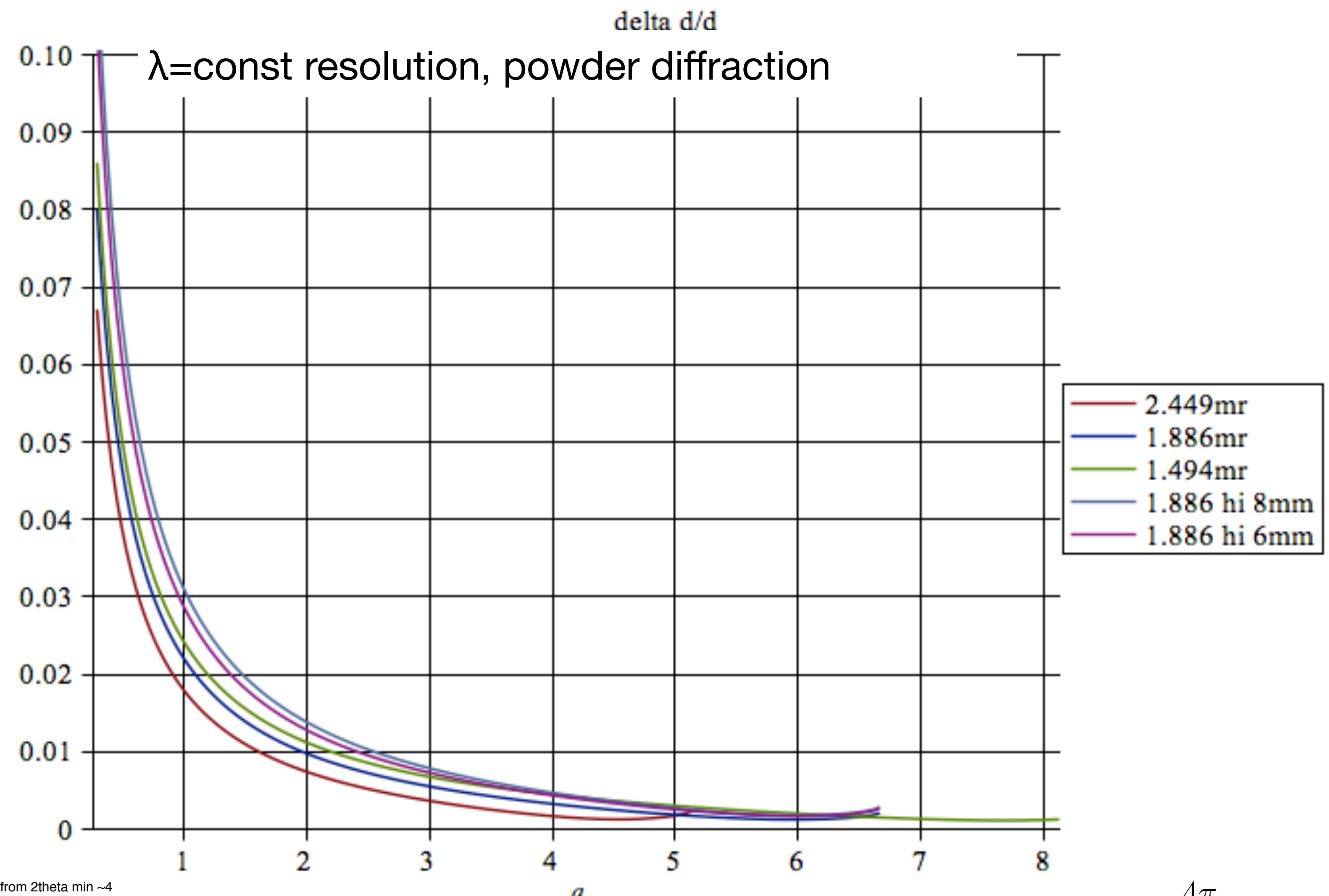

from 2theta min ~4 degrees, d max 30A, for λ=1.9A

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

4.2 Å 2.449Å λ=1.494Å

Pomjakushin diffraction SINQ, 2015, Hercules

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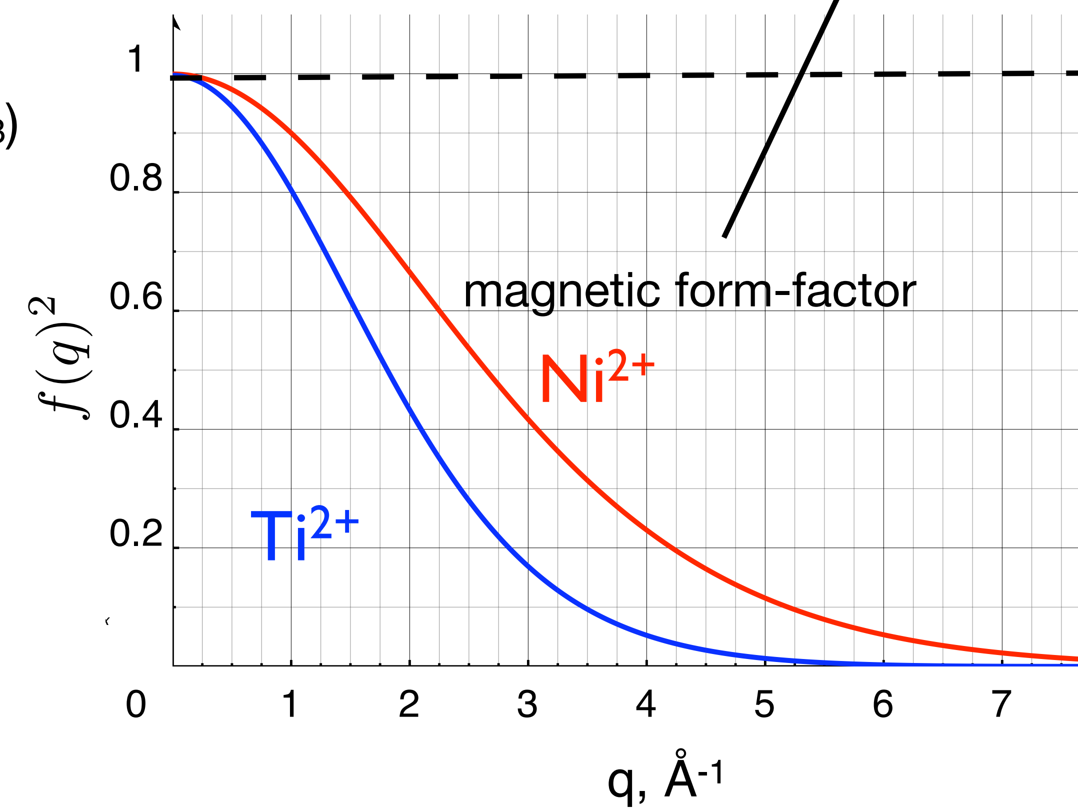

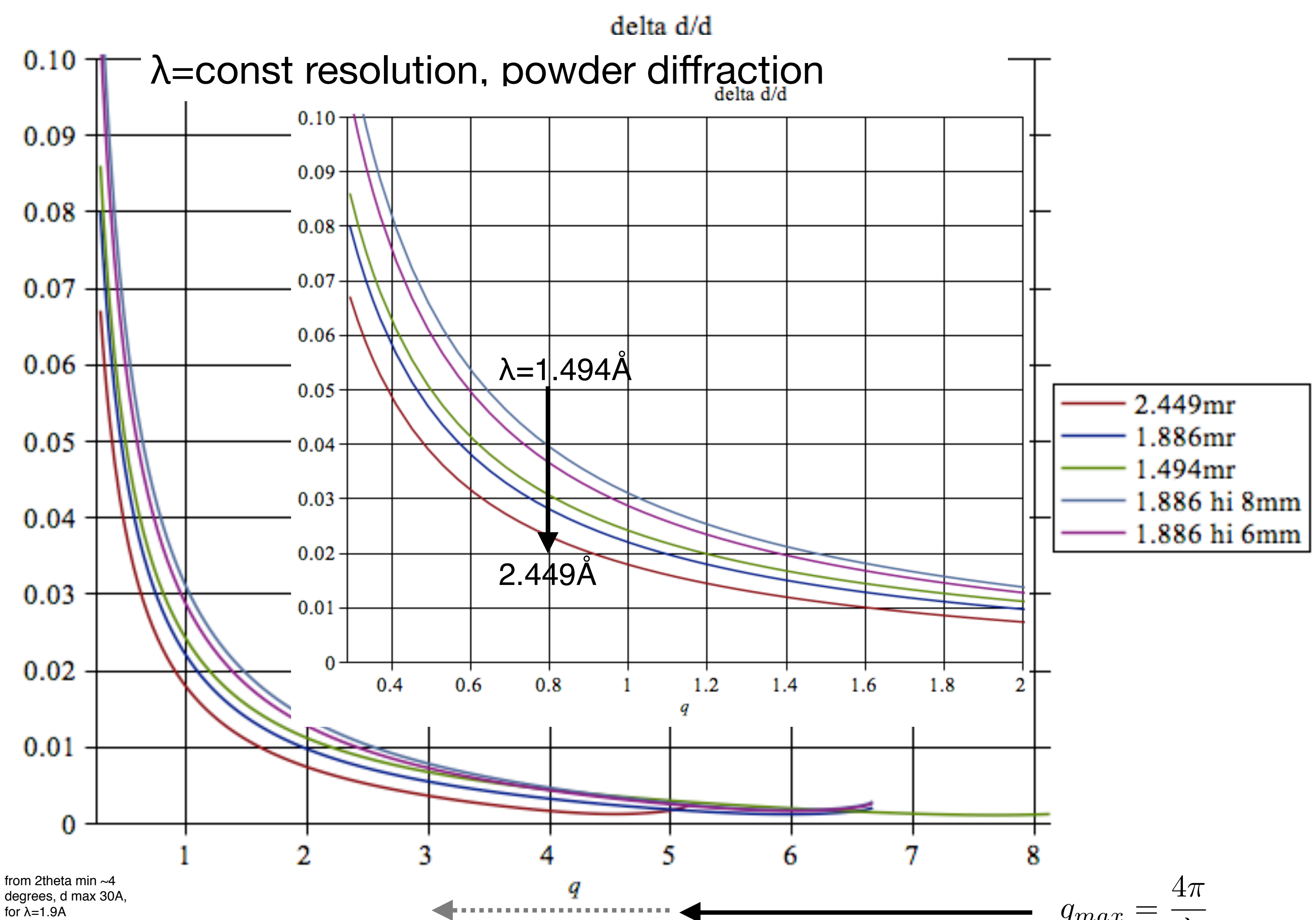

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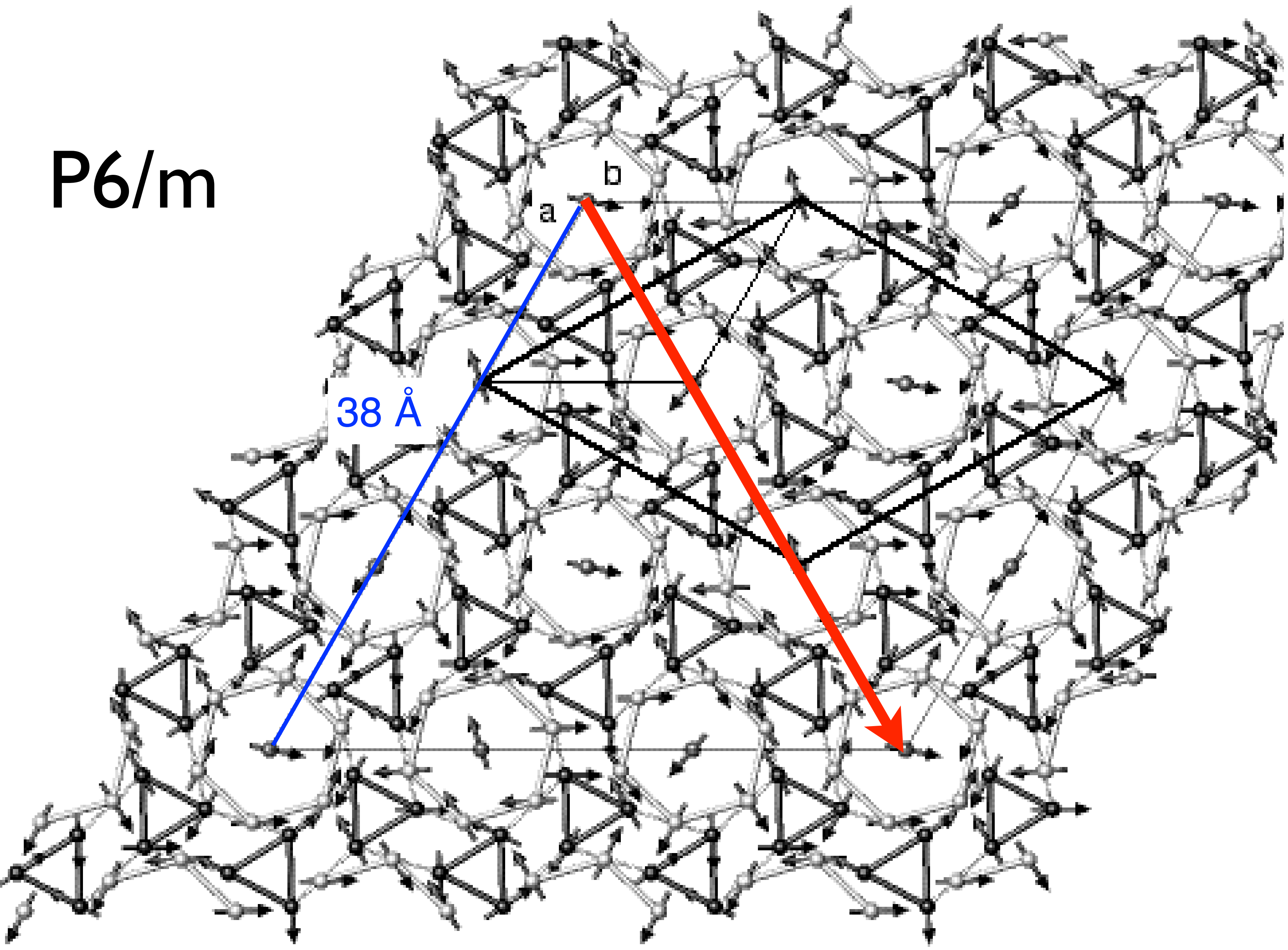
Pomjakushin diffraction SINQ, 2015, Hercules

Example: Magnetic structure solved from DMC & HRPT NPD data

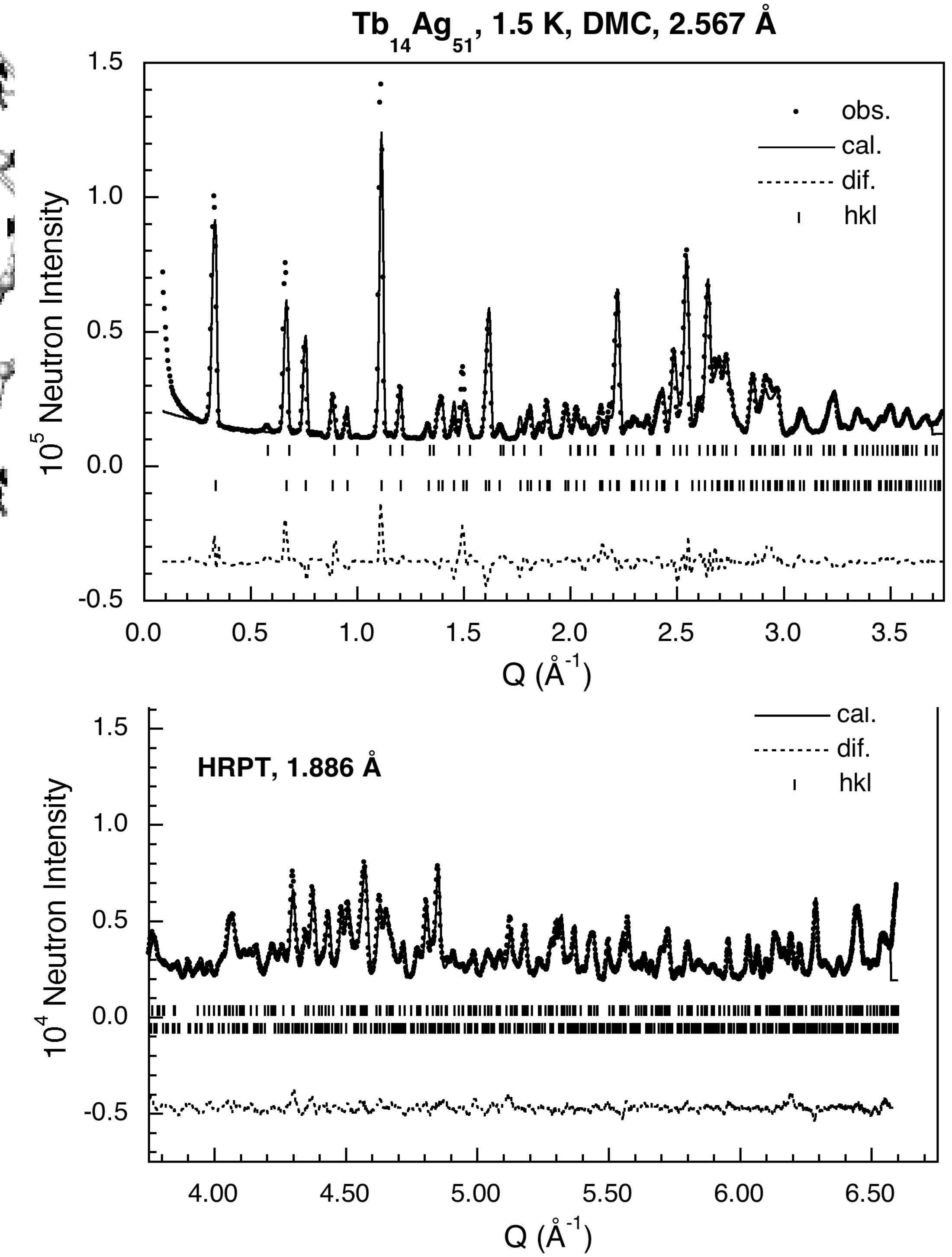
Antiferromagnetic three sub-lattice ordering in $Tb_{14}Au_{51}$

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

P6/m



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

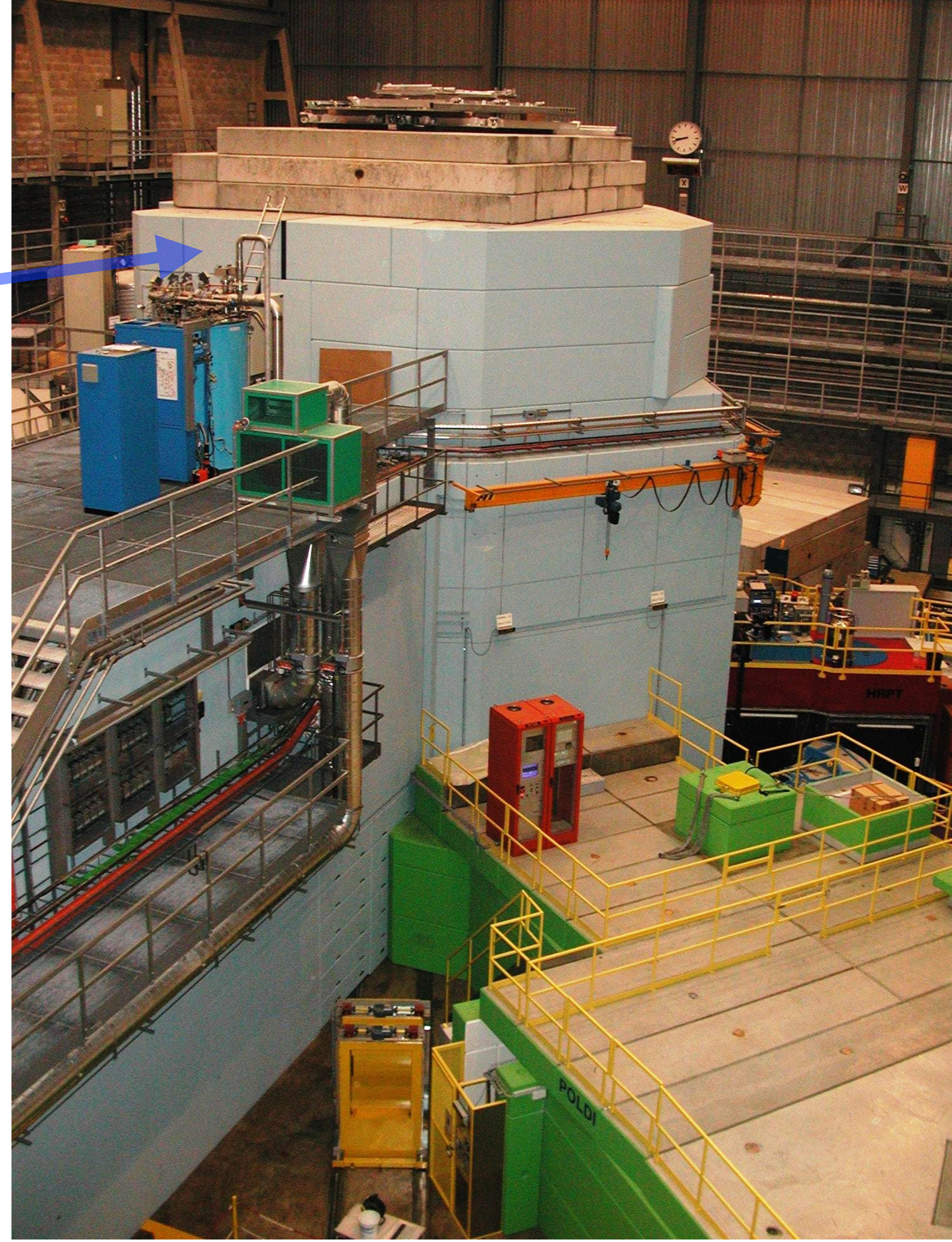


Pomjakushin diffraction
SINQ, 2015, Hercules

Diffraction instruments at swiss spallation source SINQ

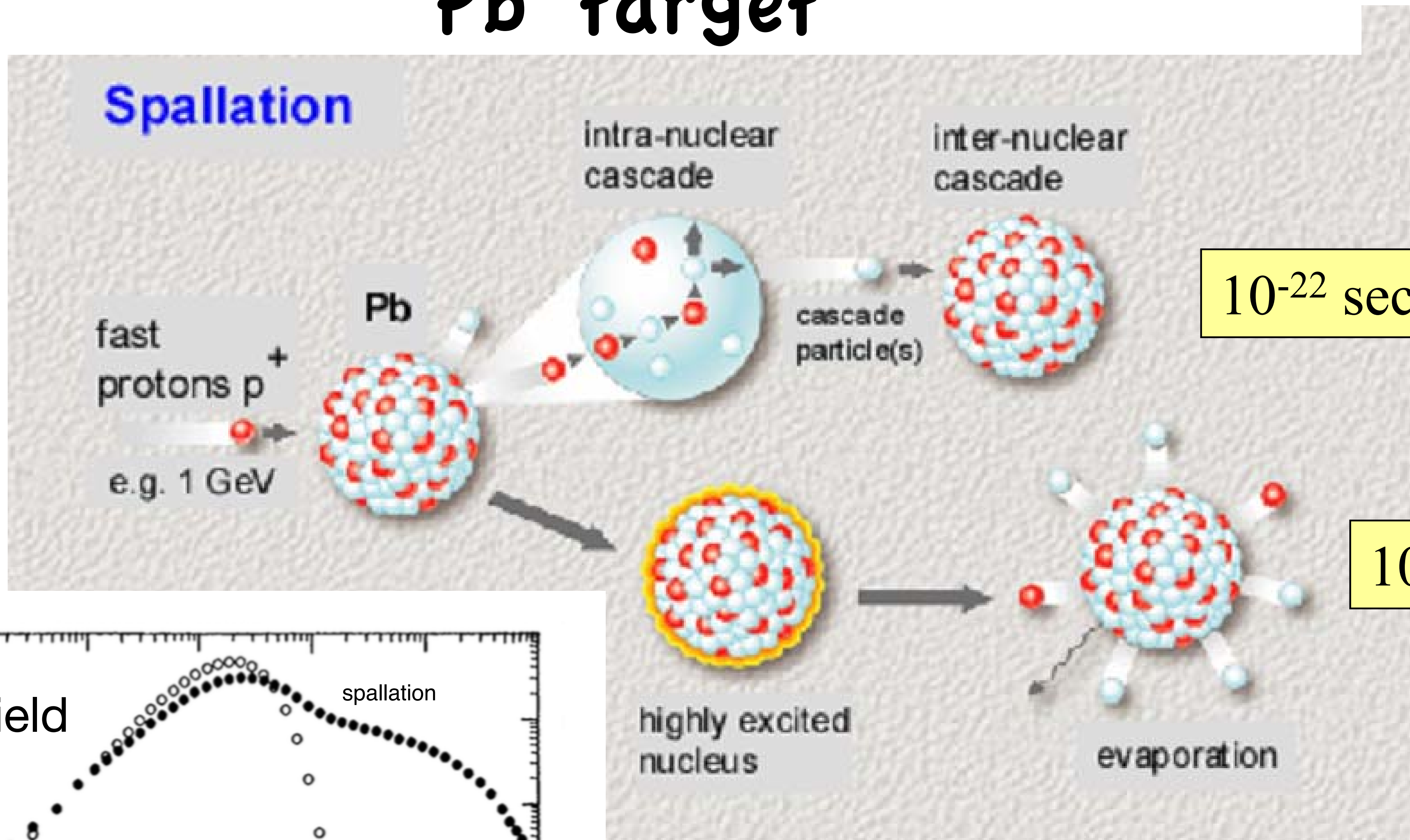
- HRPT - High Resolution Powder Diffractometer for Thermal Neutrons, λ=0.94 - 2.96 Å, High Q-range ≤11$Å^{-1}$
- DMC – High Intensity Powder Diffractometer for Cold Neutrons, λ=2.35 - 5.4 Å, High flux and good resolution at low and moderate Q ≤4$Å^{-1}$
- TriCS - Single crystal diffractometer, λ=1.18, 2.3 Å, Thermal Neutrons
- TASP (triple axes) with MuPAD for polarised ND, Cold Neutrons

SINQ hall



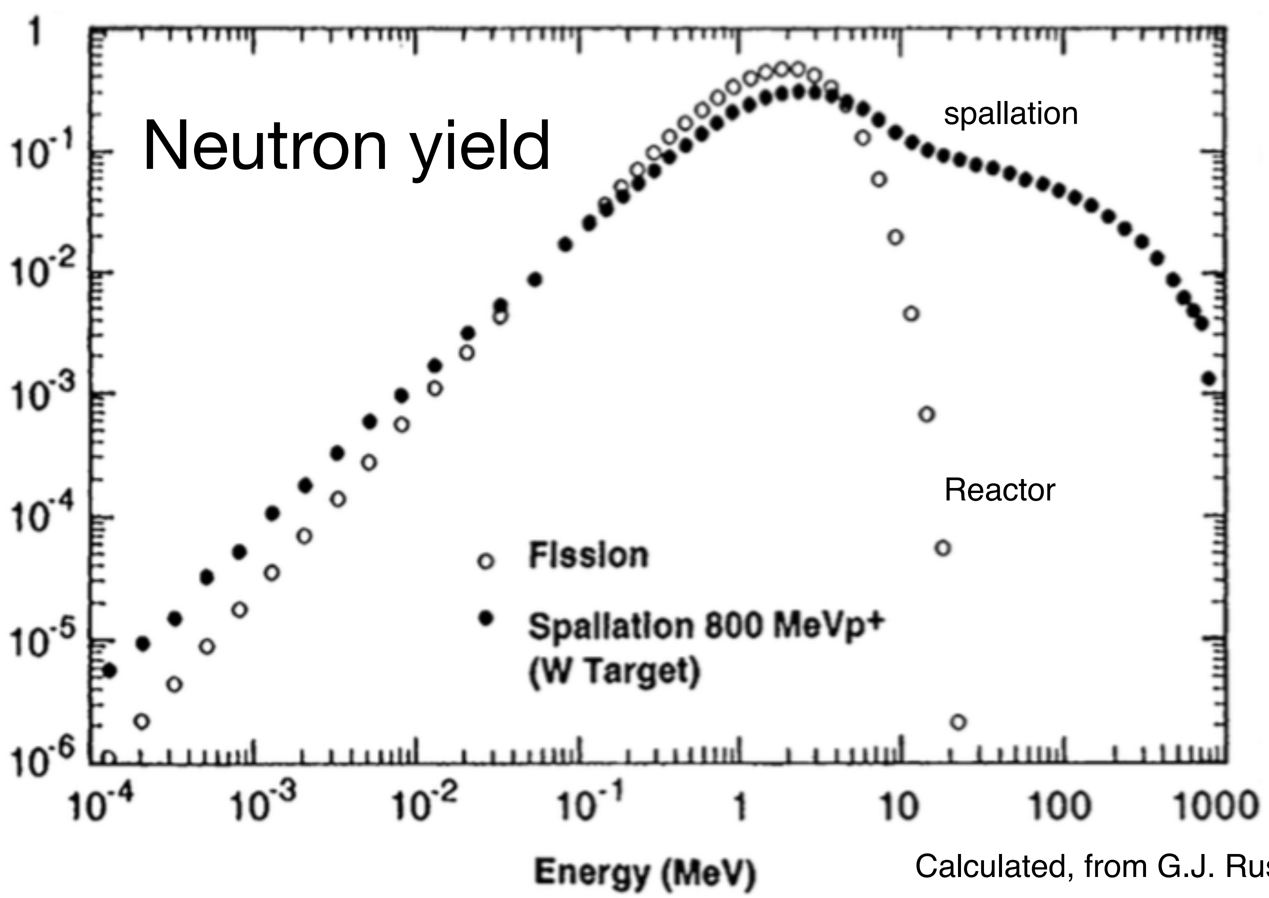
The *spallation neutron source* SINQ is a *continuous* source - the first and *the only of its kind in the world* - with a **flux of about 10^{14} n/cm^2/s**. Beside thermal neutrons, a cold moderator of liquid deuterium (cold source) slows neutrons down and shifts their spectrum to lower energies.

Spallation, SINQ 590MeV protons, Pb target



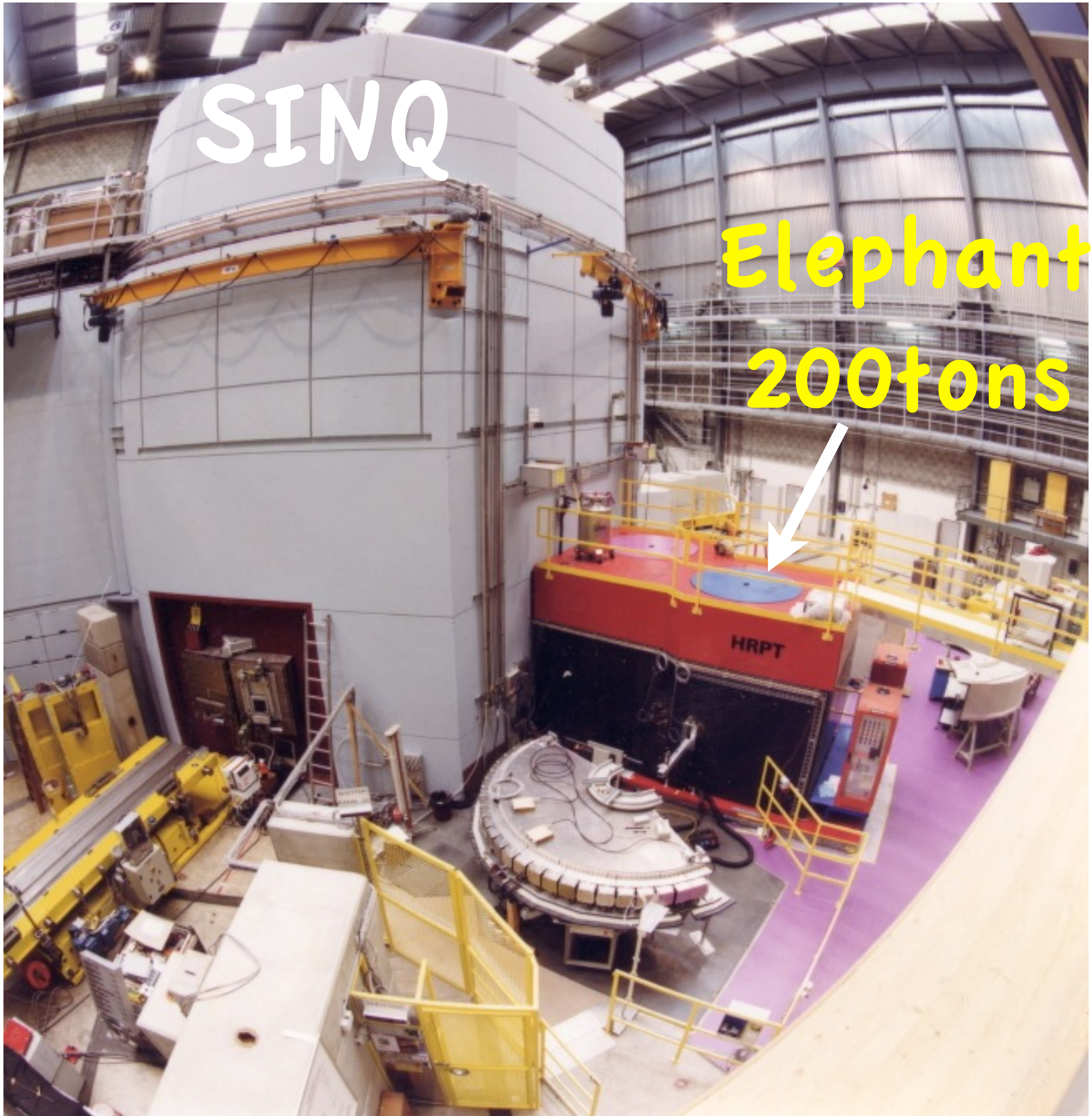
10^{-22} sec

10^{-18} sec



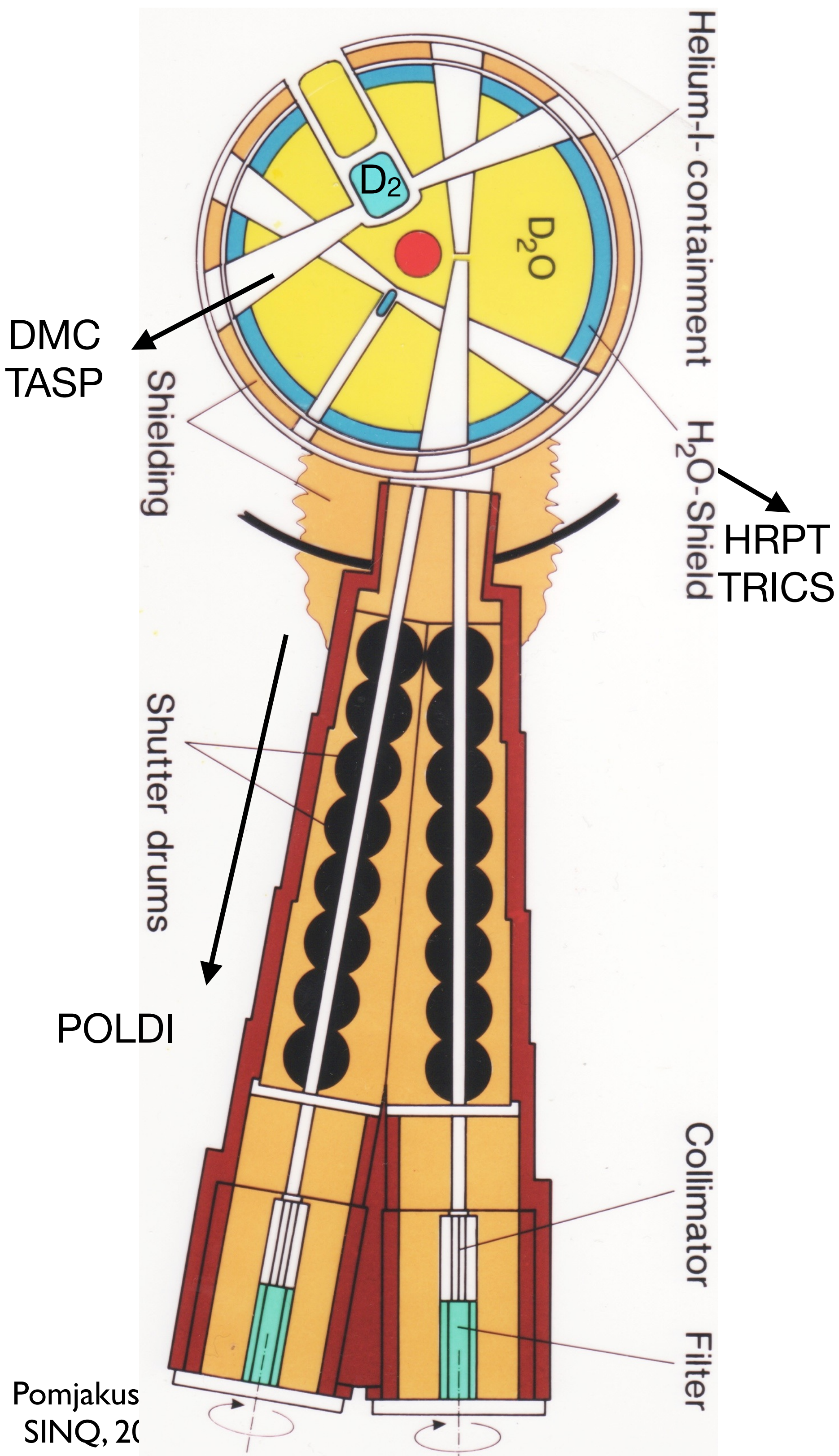
Calculated, from G.J. Russell, Spallation physics–an overview, Proceedings of ICANS-XI

SINQ hall

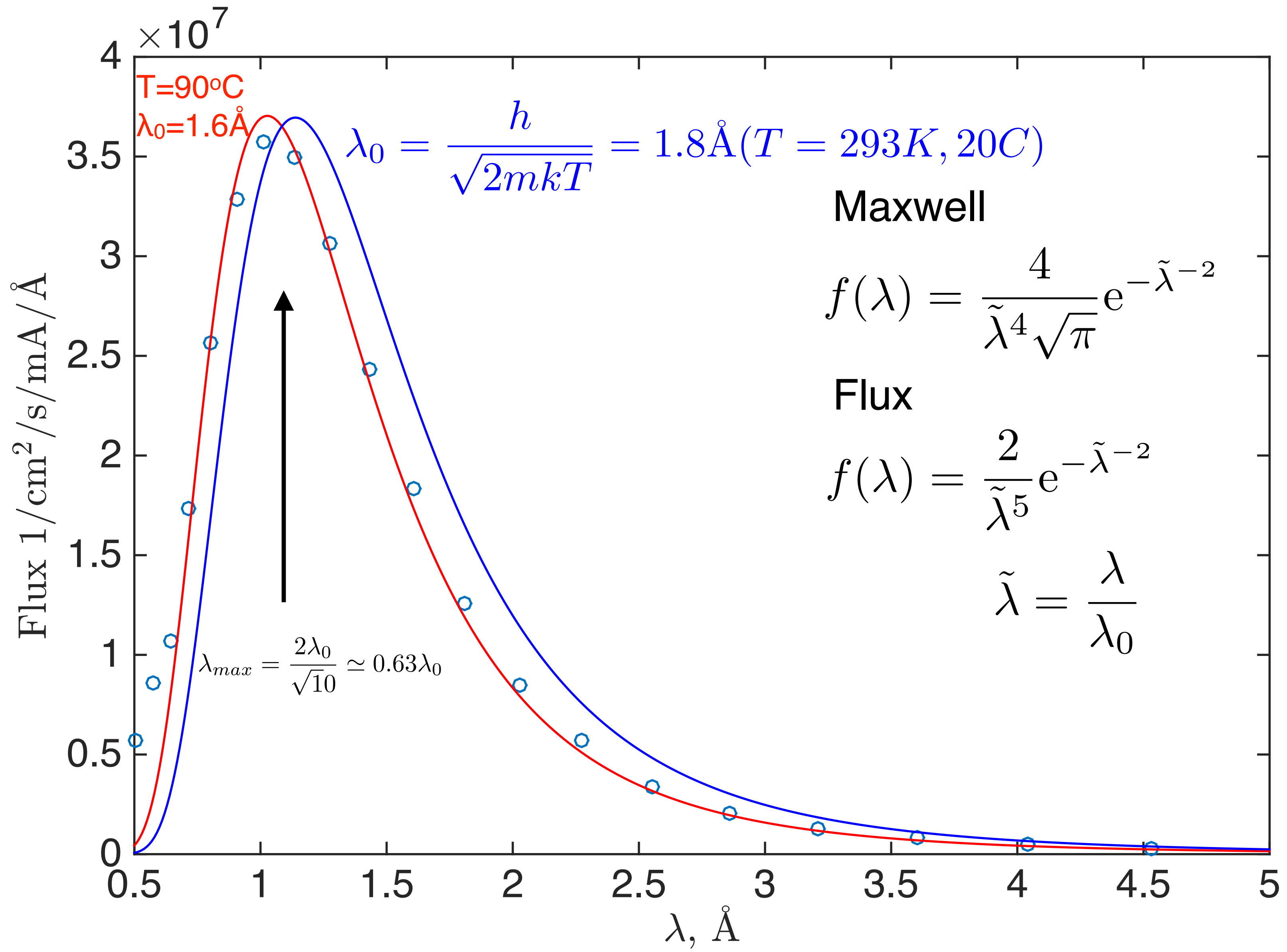


Elephant is:
Shielding of the direct neutron beam also from fast neutrons for diffraction instruments

Neutron (thermal) flux from the D_2O moderator, Maxwellian at 90°C (HRPT,TRICS)

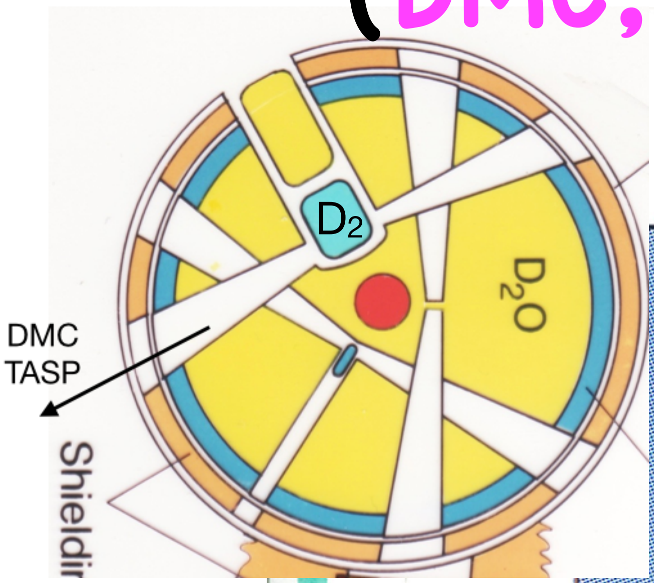


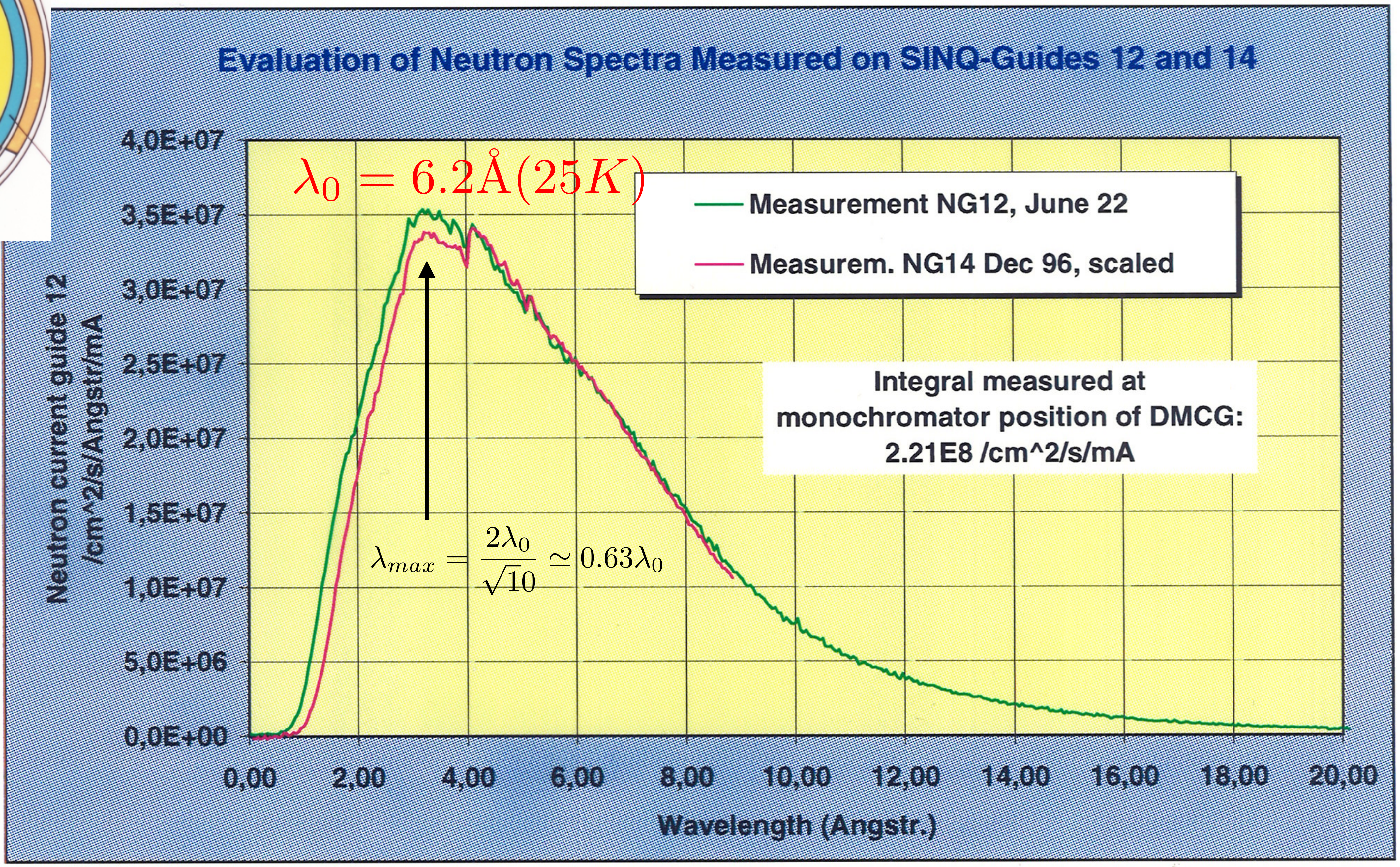
Pomjakus
SINQ, 20



Total: $5 \cdot 10^7$ $1/\text{cm}^2/\text{s}/\text{mA}$
at SINQ current 2mA: 10^8

Neutron flux from cold moderator ($\color{magenta}{DMC,TASP}$), liquid D_2, T=25K or -248C

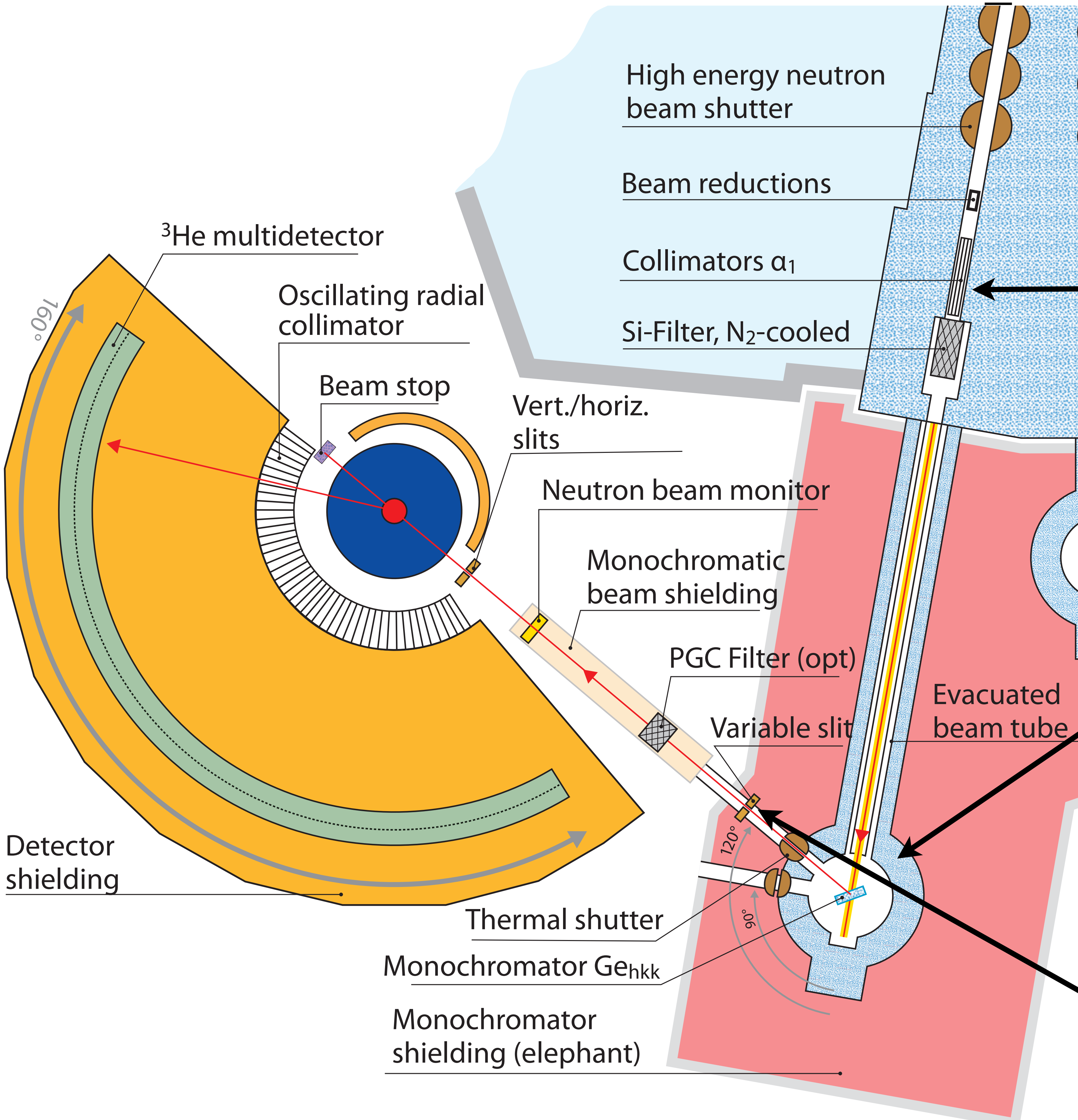




BQ36 / 23.07.1997 SINQ-NL12_tof.xls Diagramm4

HRPT layout

High Resolution Powder Diffractometer
for Thermal Neutrons



horizontal angular divergence control

α_1

primary beam collimator(s):
6', 12', 24', 30'

α_2

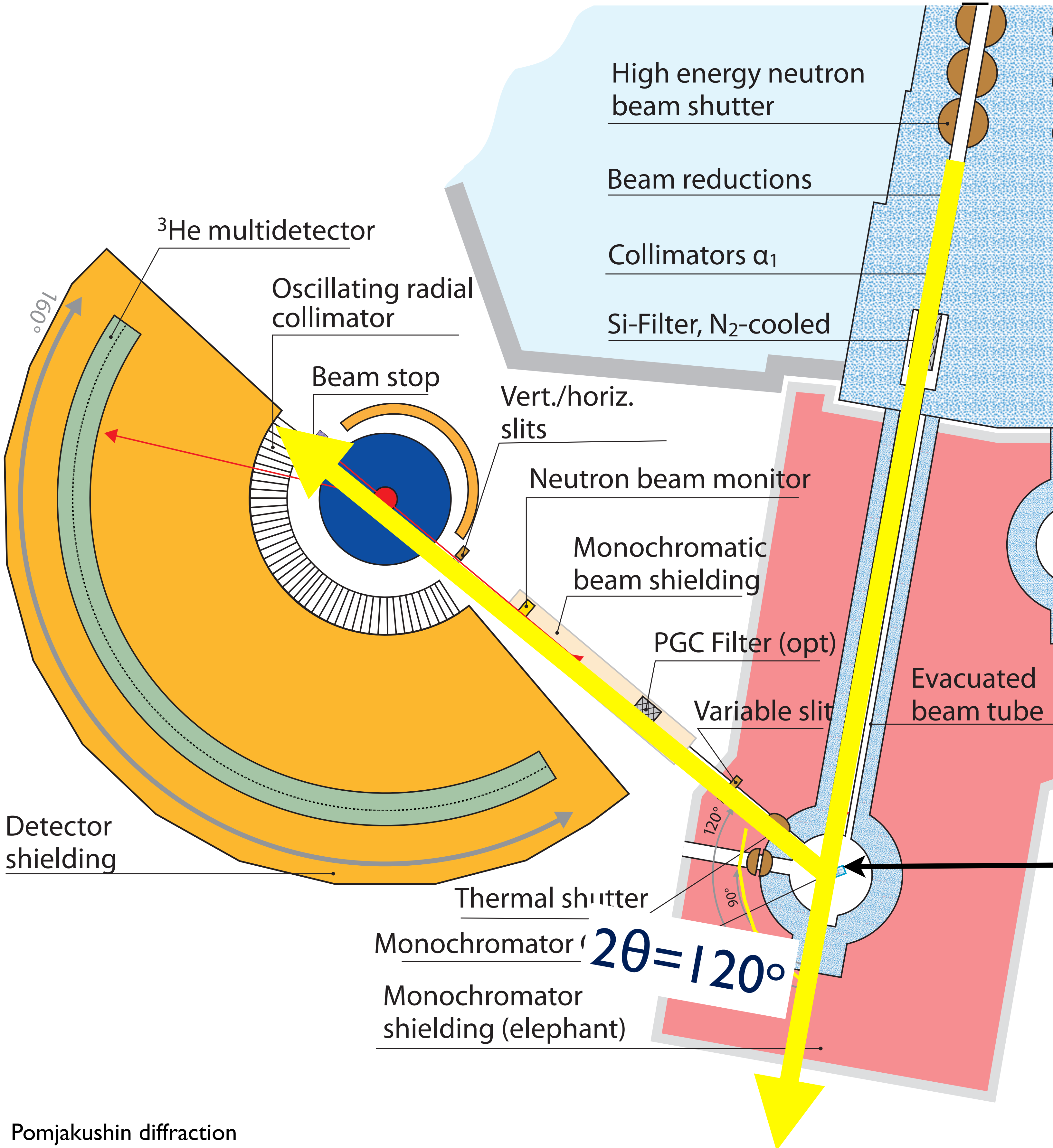
mosaic spread of the monochromator 15'

α_3

slit system for monochromatic beam and sample diameter

HRPT layout

High Resolution Powder Diffractometer for Thermal Neutrons

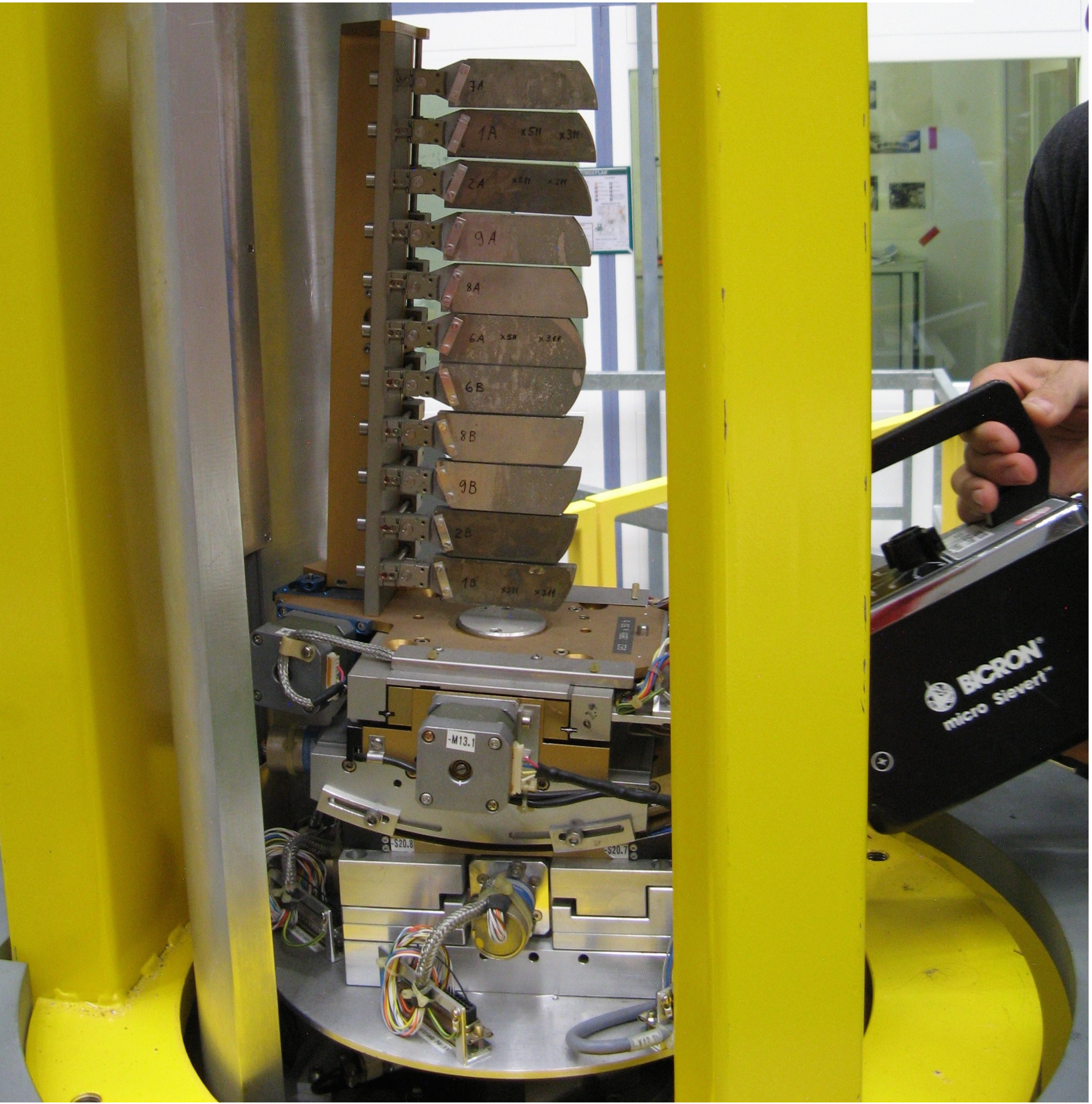


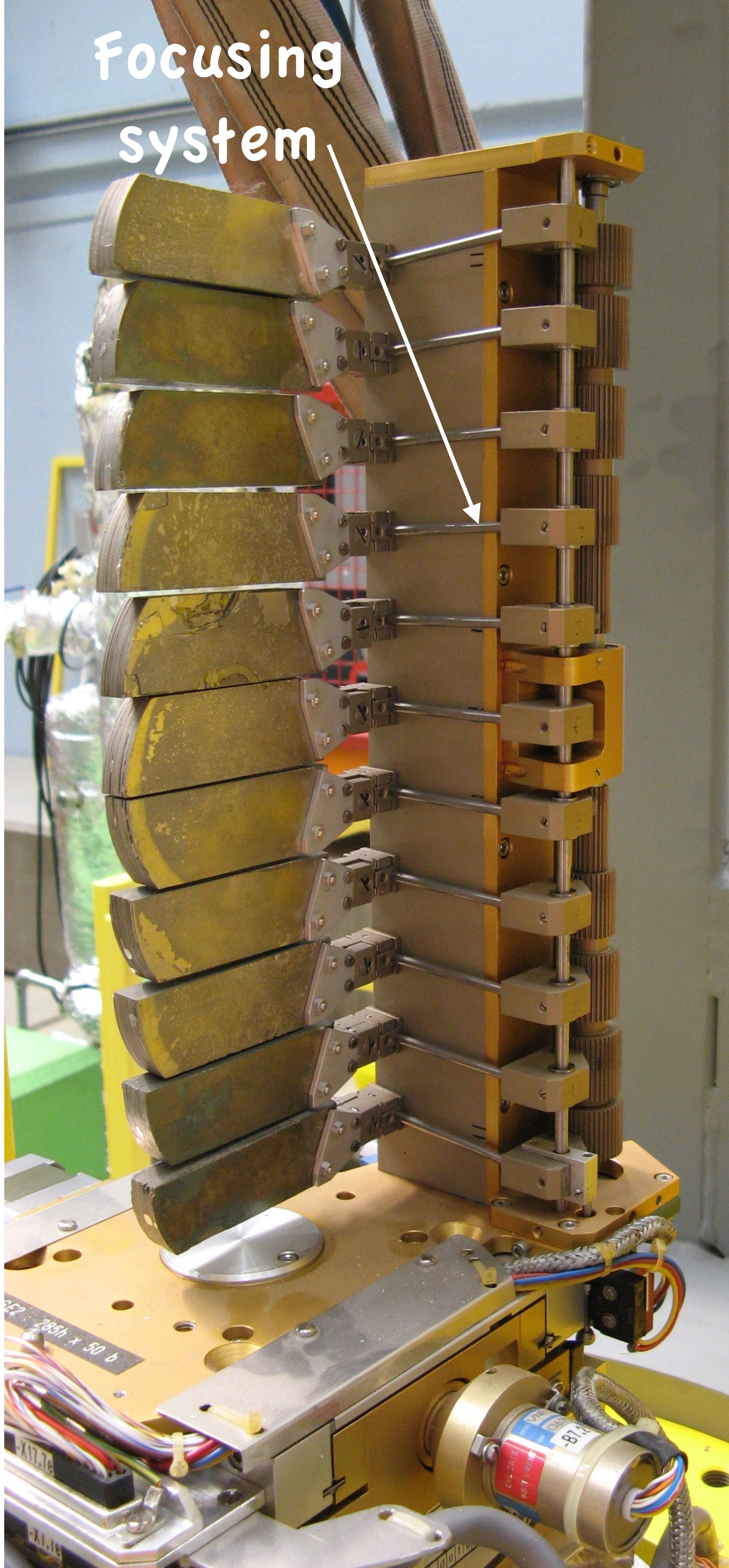
neutron monochromator fixed 120 take off angle

$$\lambda = 2\,d\sin(\theta)$$

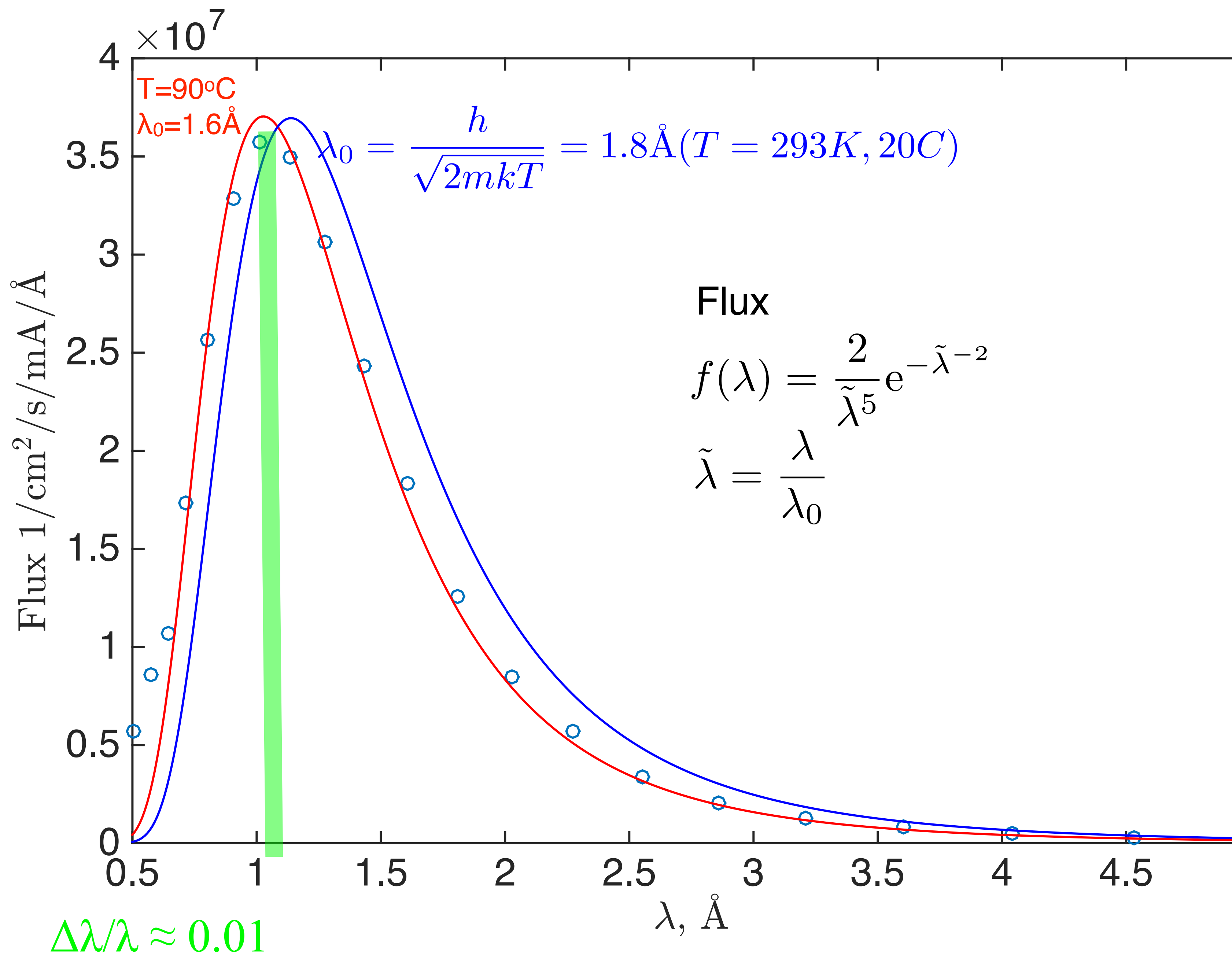
$$\lambda = 2\,d\sin(60^\circ)$$

Ge single crystal monochromator, 7 motors





Monochromator cuts narrow wavelength range from the “white” flux. HRPT λ=0.94 - 2.96 Å



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

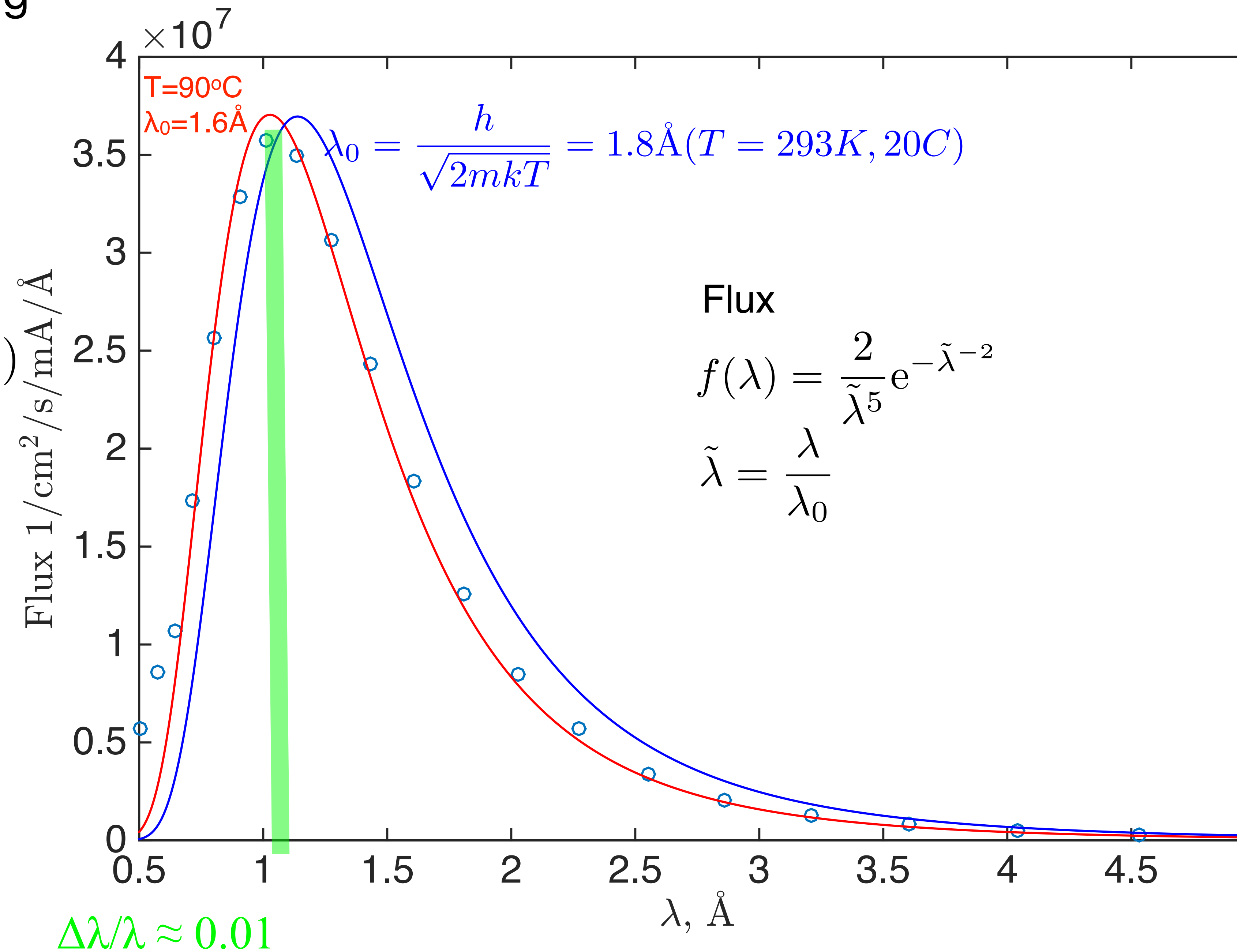
at SINQ current 2mA: 10^8

Monochromator cuts narrow wavelength range from the "white" flux. HRPT λ=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



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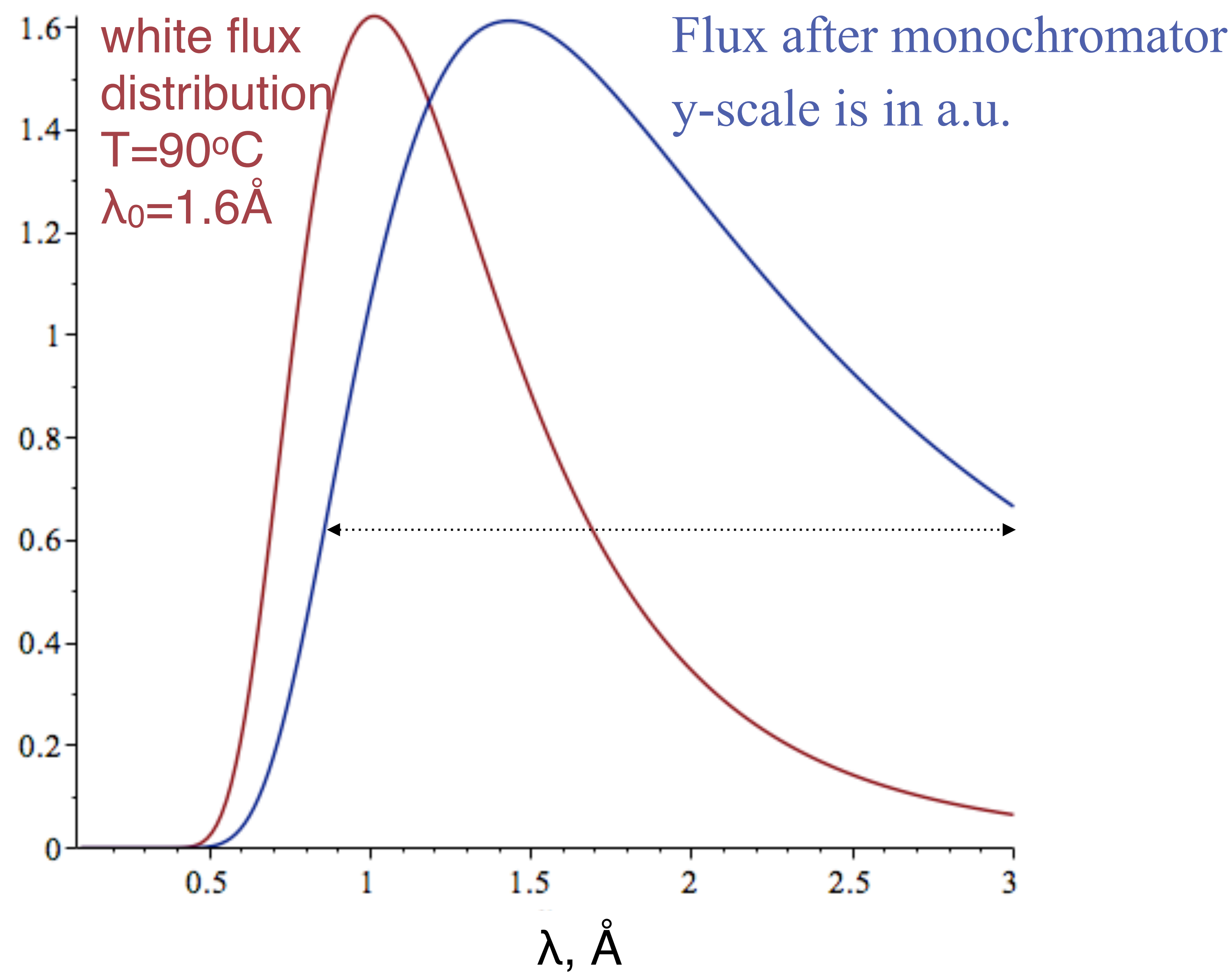
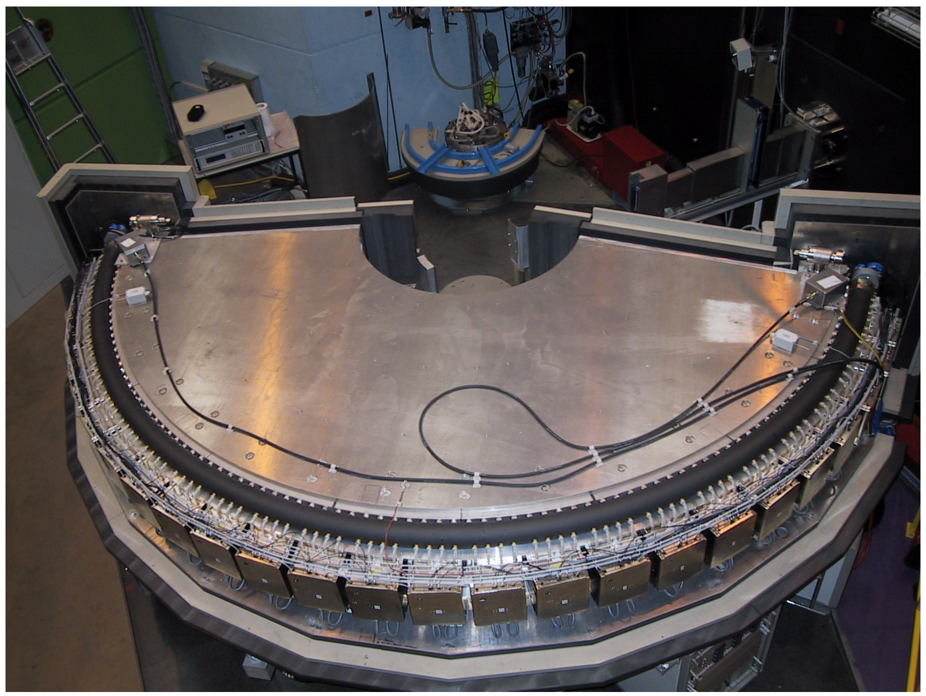


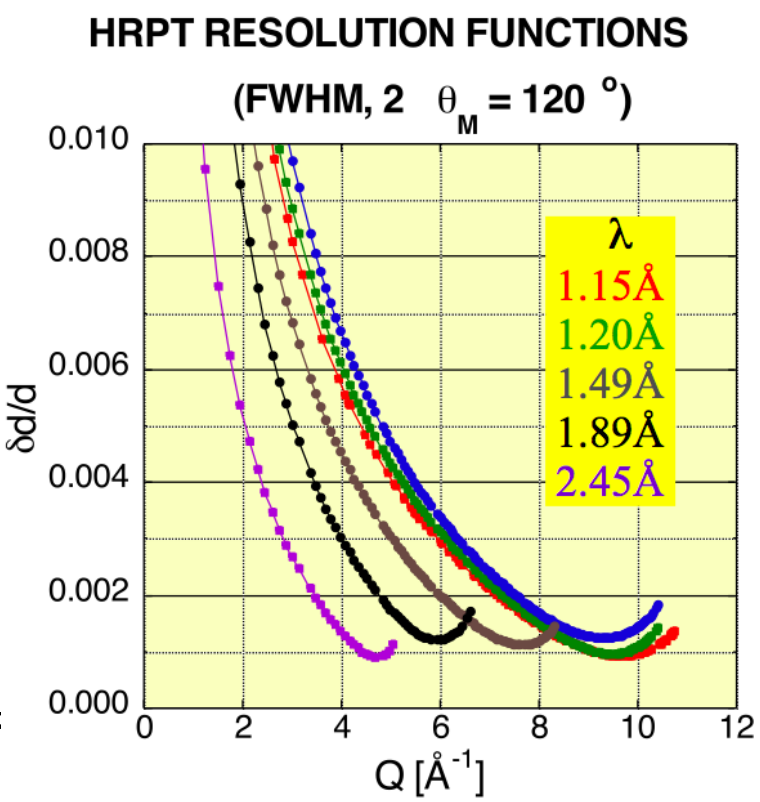
Powder ND at SINQ/PSI

HRPT - High Resolution Powder Diffractometer for Thermal Neutrons.

linear detector with 1600 channelss, 0.1°

Responsible: Vladimir Pomjakushin, Denis Sheptyakov



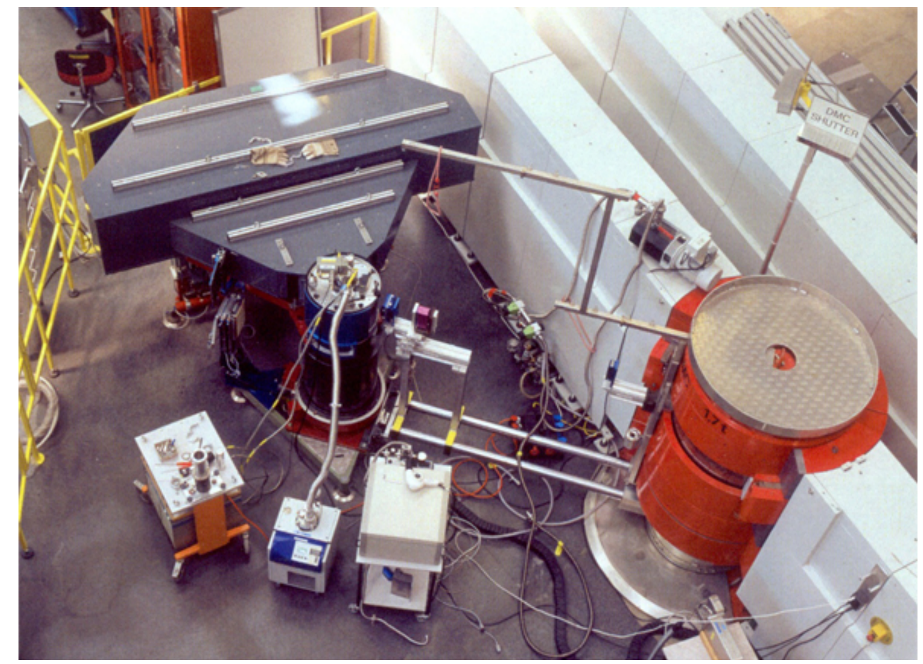


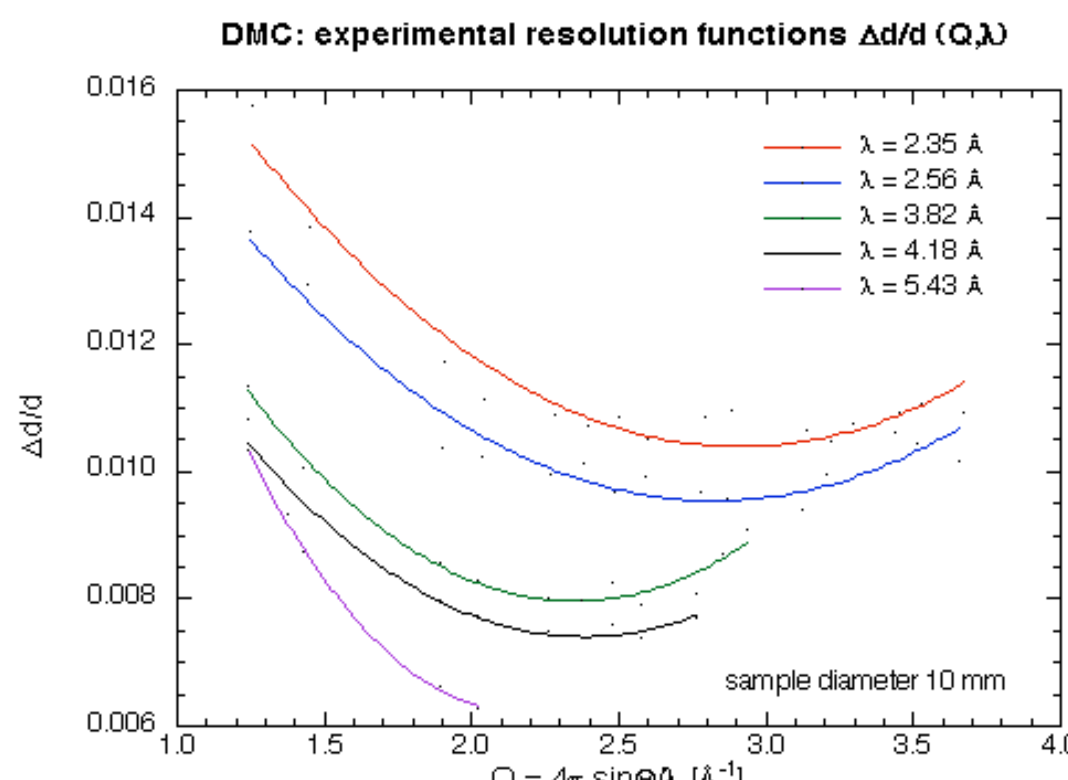
Pomjak
SINQ,

DMC - cold neutron powder diffractometer

linear detector with 400 channels, 0.2°

Responsible: Lukas Keller, Matthias Frontzek



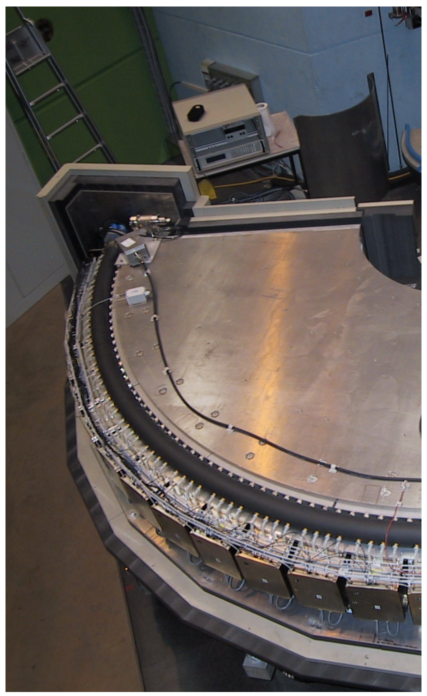


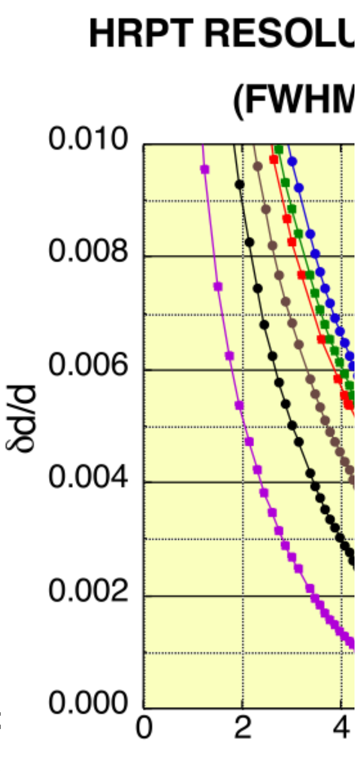
Powder ND at SINQ/PSI

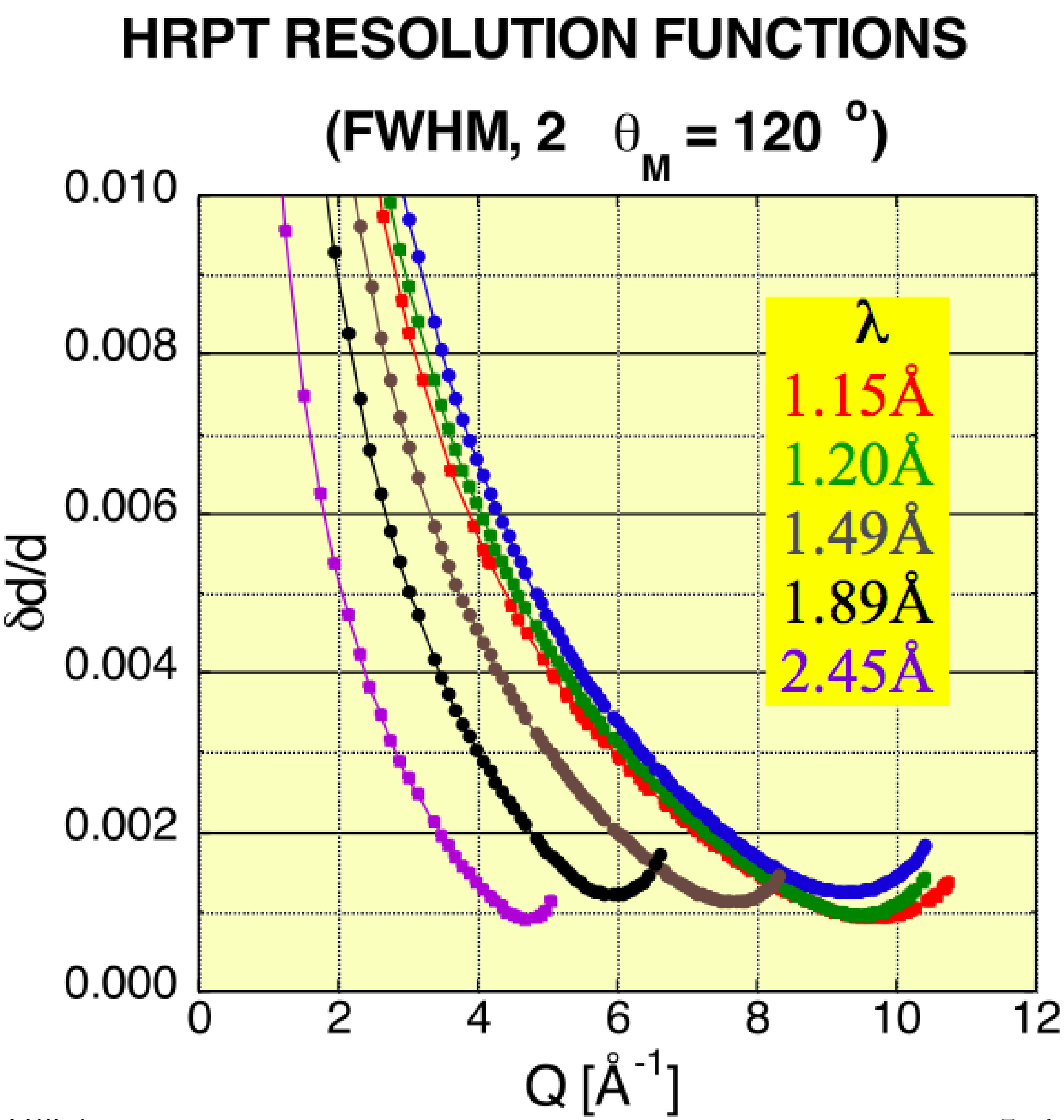
HRPT - High Resolution Powder Diffractometer for Thermal Neutrons

linear detector wi

Responsible: Vladimir P



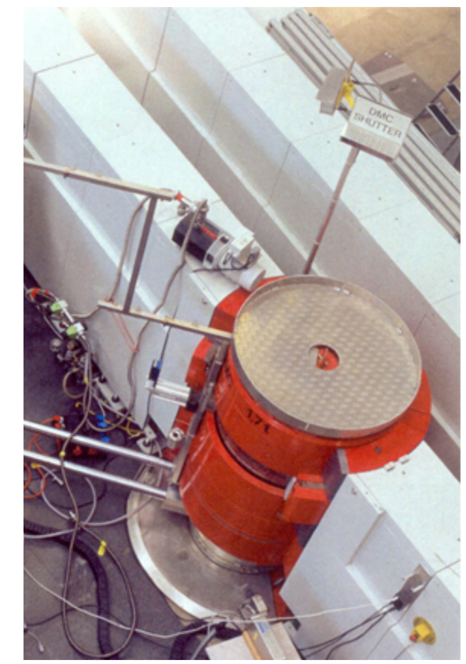


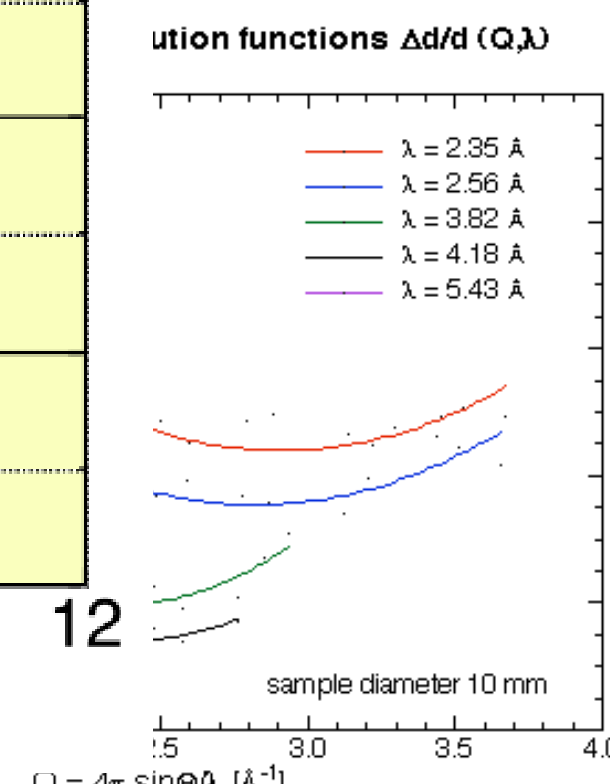


DMC - cold neutron powder diffractometer

hannels, 0.2°

ias Frontzek

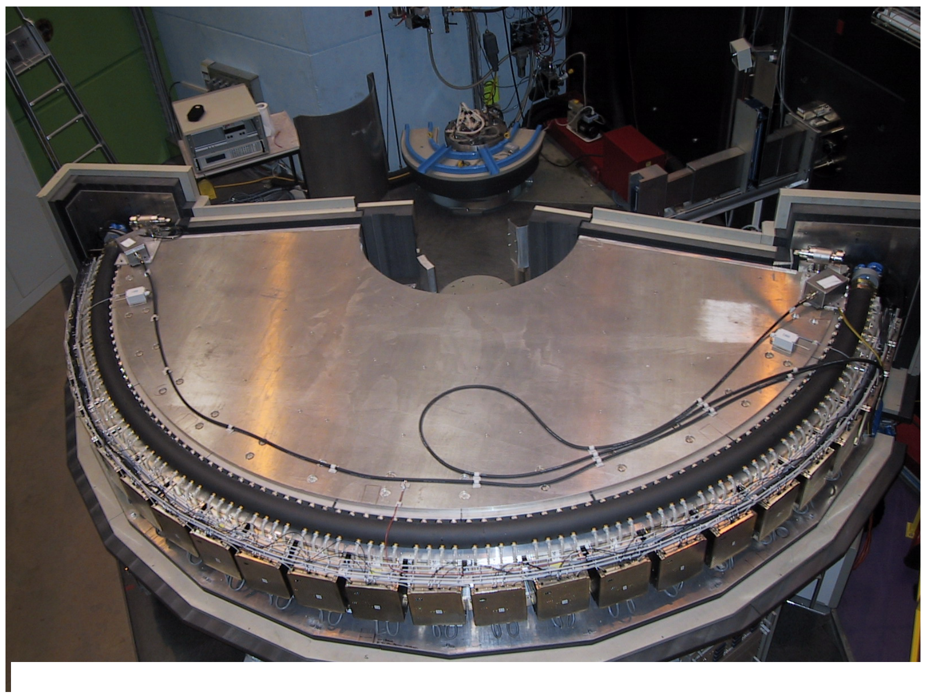


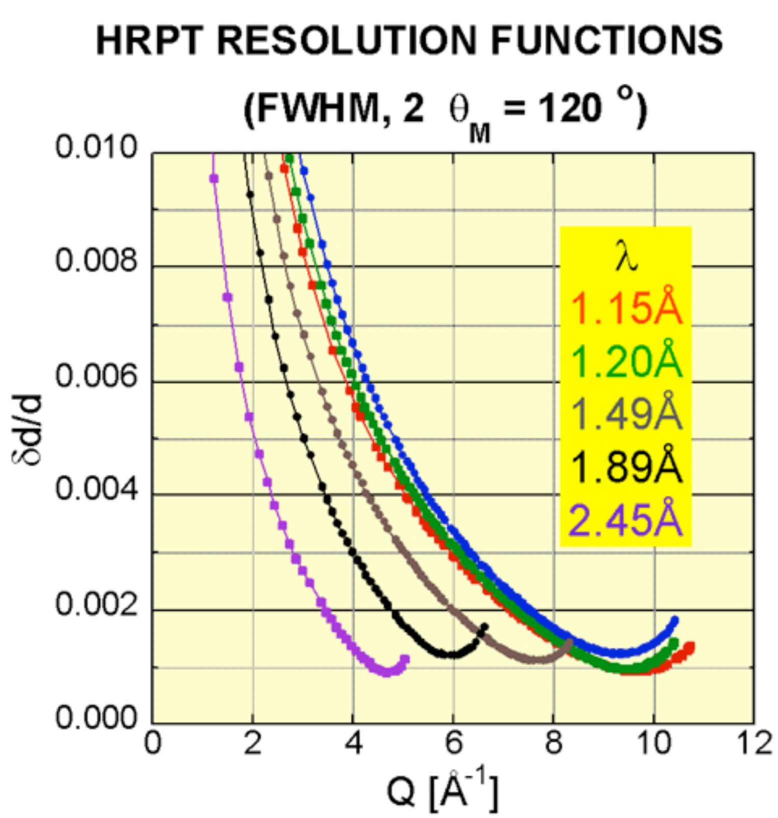


Pomjak
SINQ,

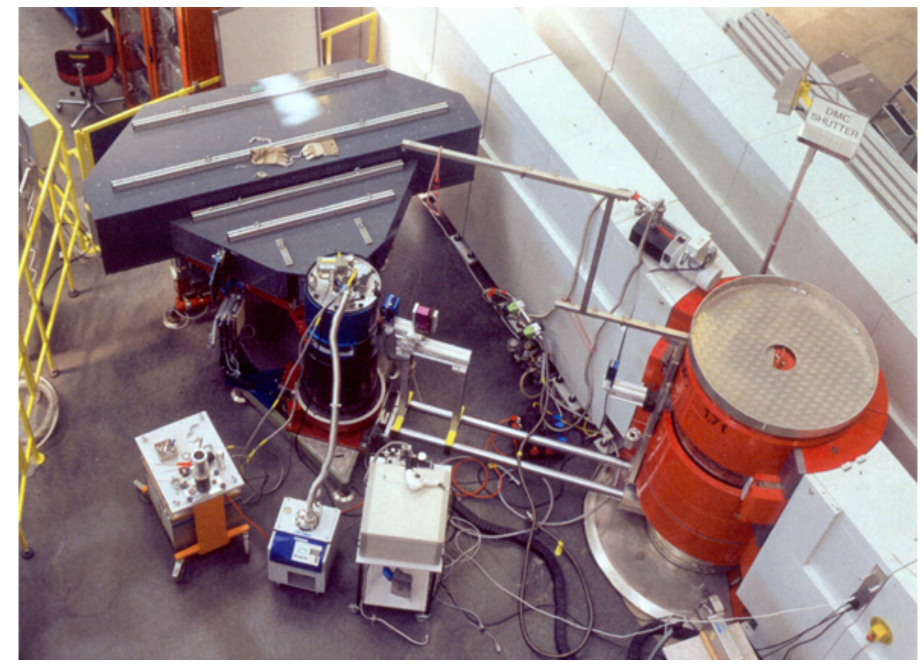
Powder ND at SINQ/PSI

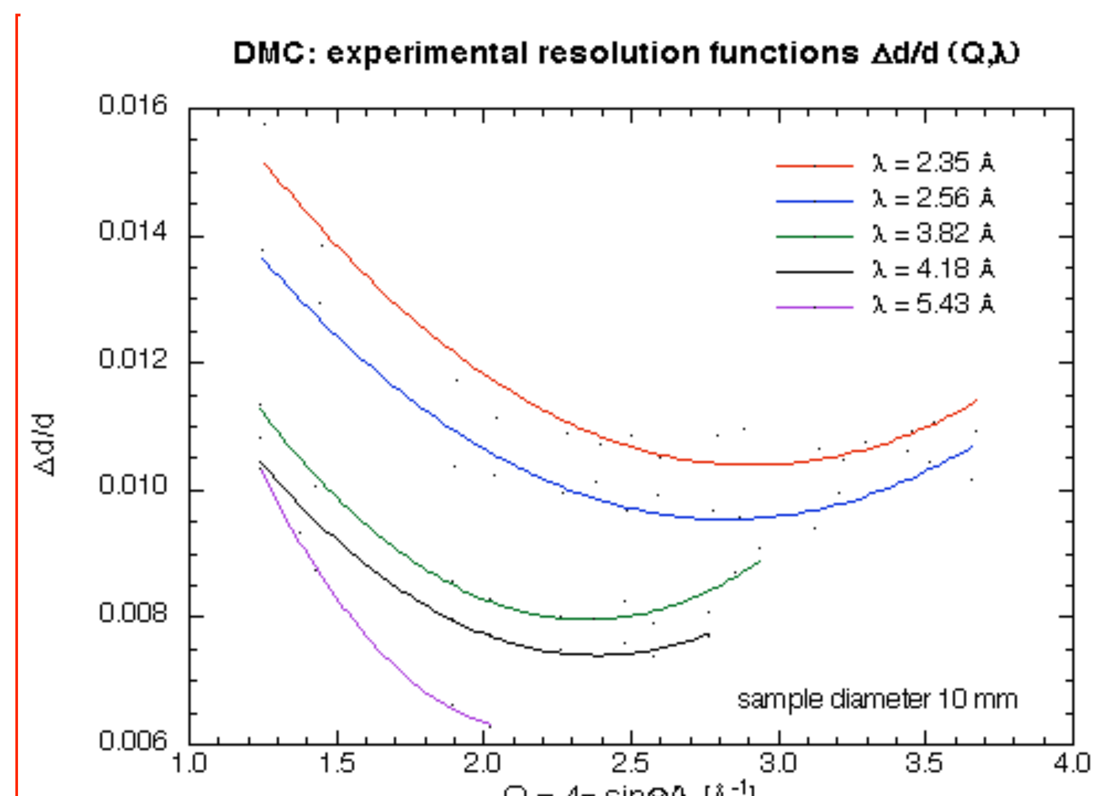
HRPT - High Resolution Powder Diffractometer for Thermal Neutrons at SINQ





DMC - cold neutron powder diffractometer

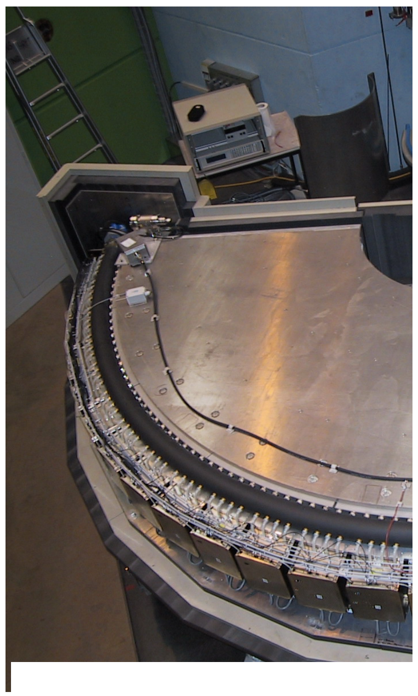


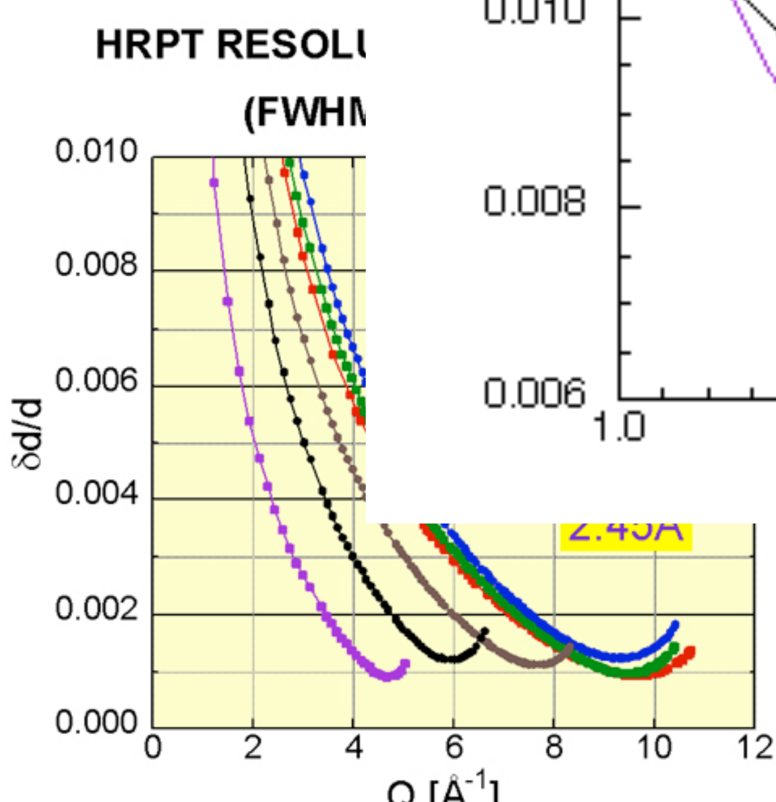


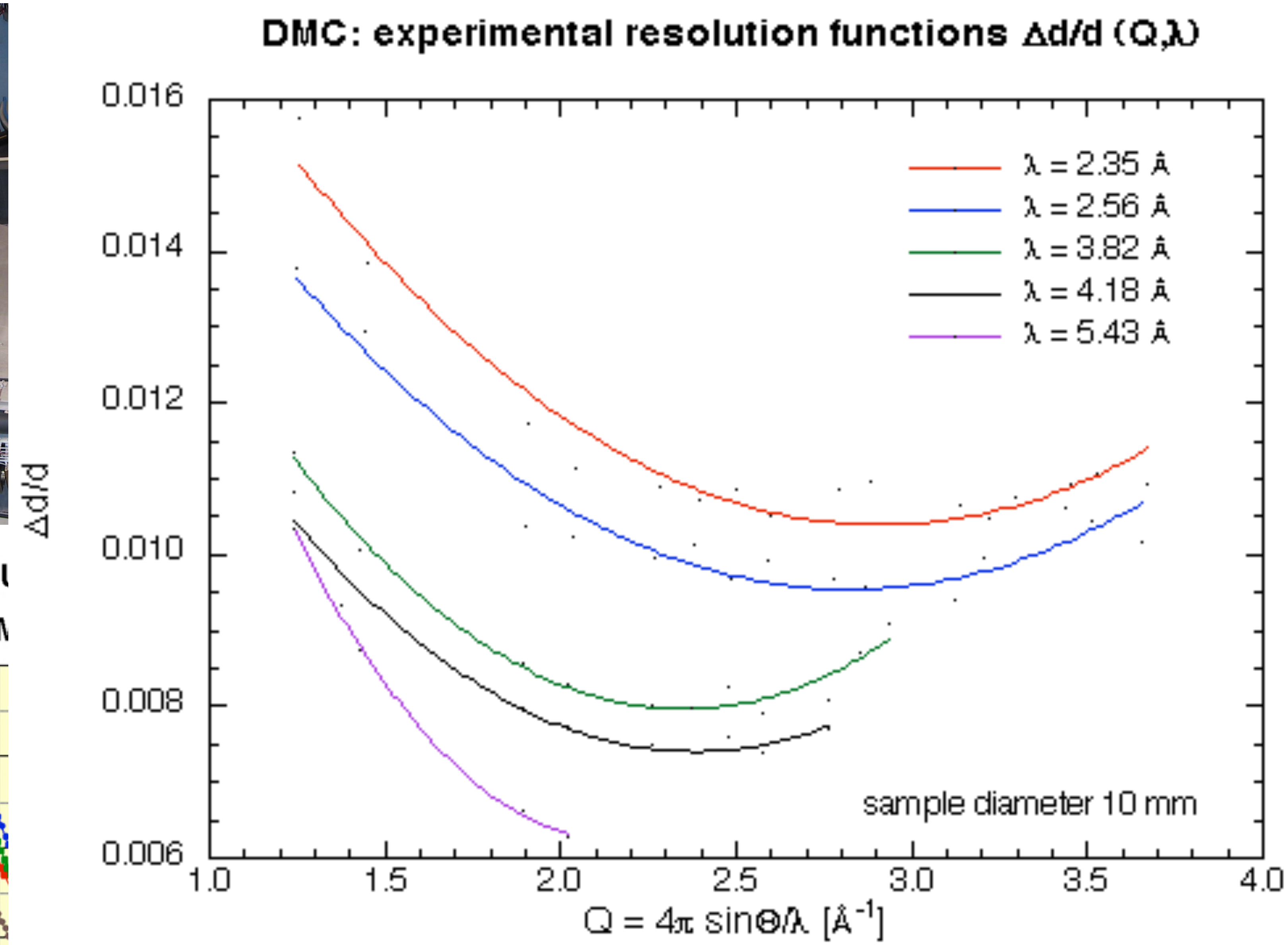
Powder ND at SINQ/PSI

HRPT - High Resolution Powder Diffractometer for Thermal Neutrons at SINQ

DMC - cold neutron powder diffractometer



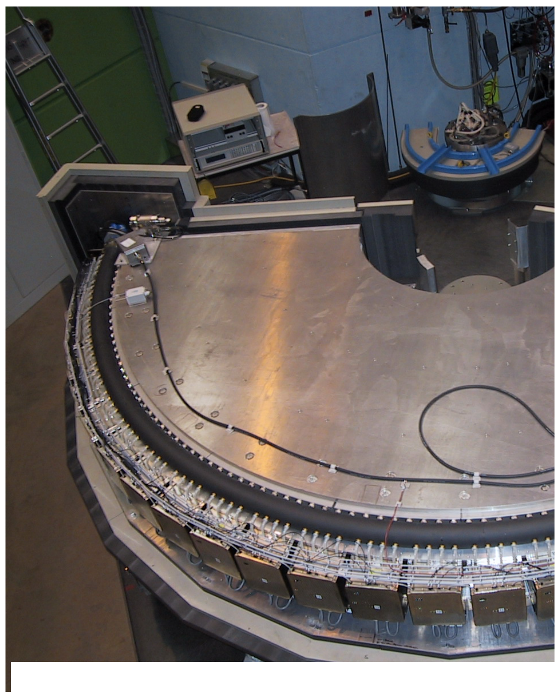


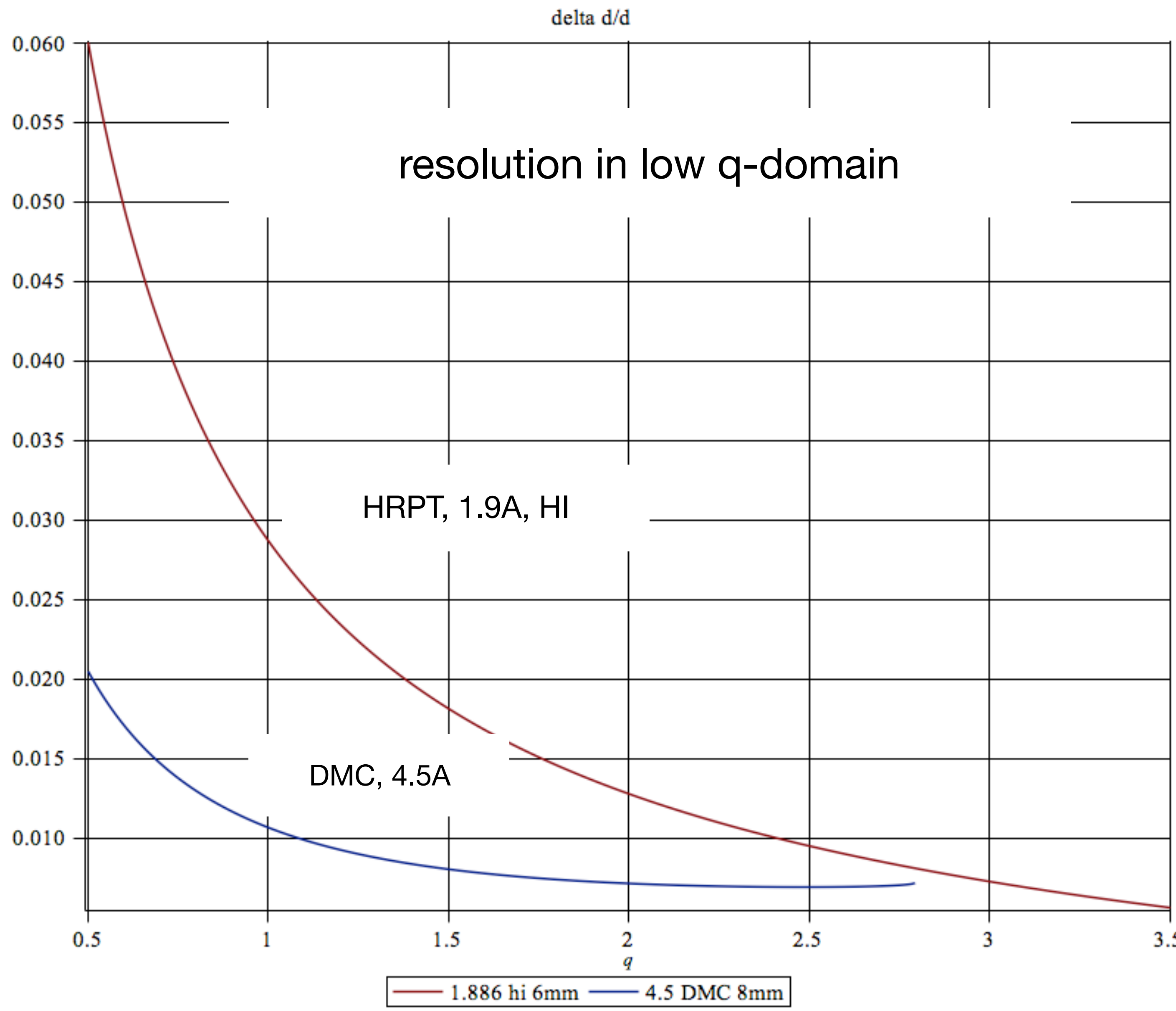


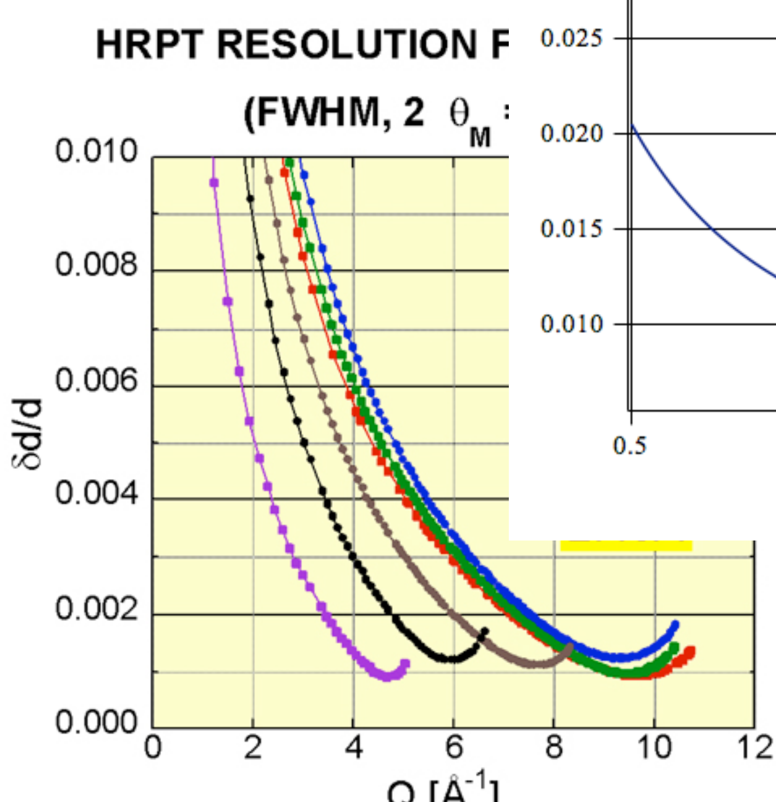
Powder ND at SINQ/PSI

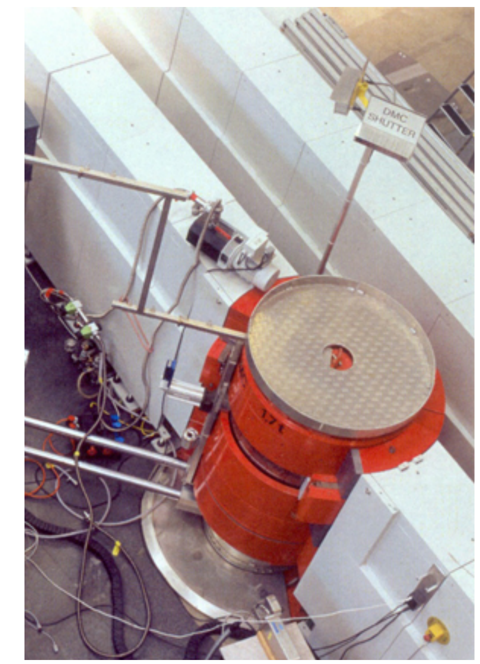
HRPT - High Resolution Powder Diffractometer for Thermal Neutrons at SINQ

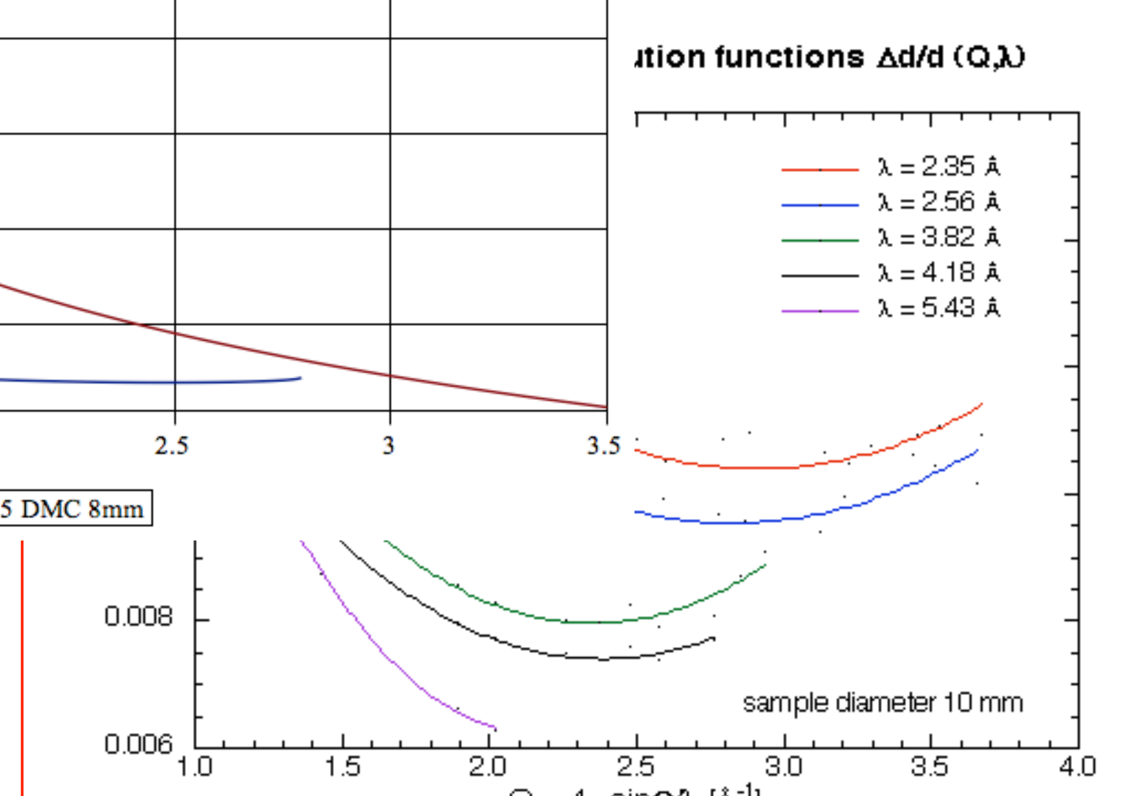
DMC - cold neutron powder diffractometer











Por
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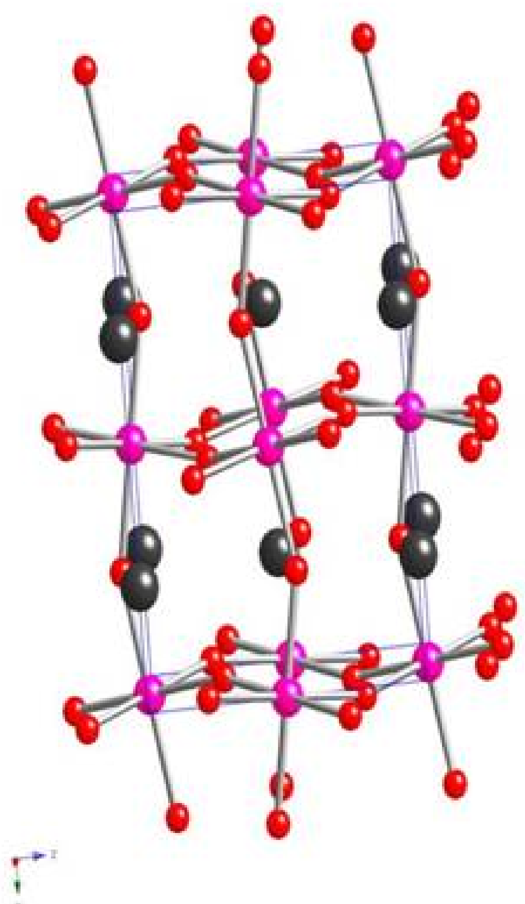
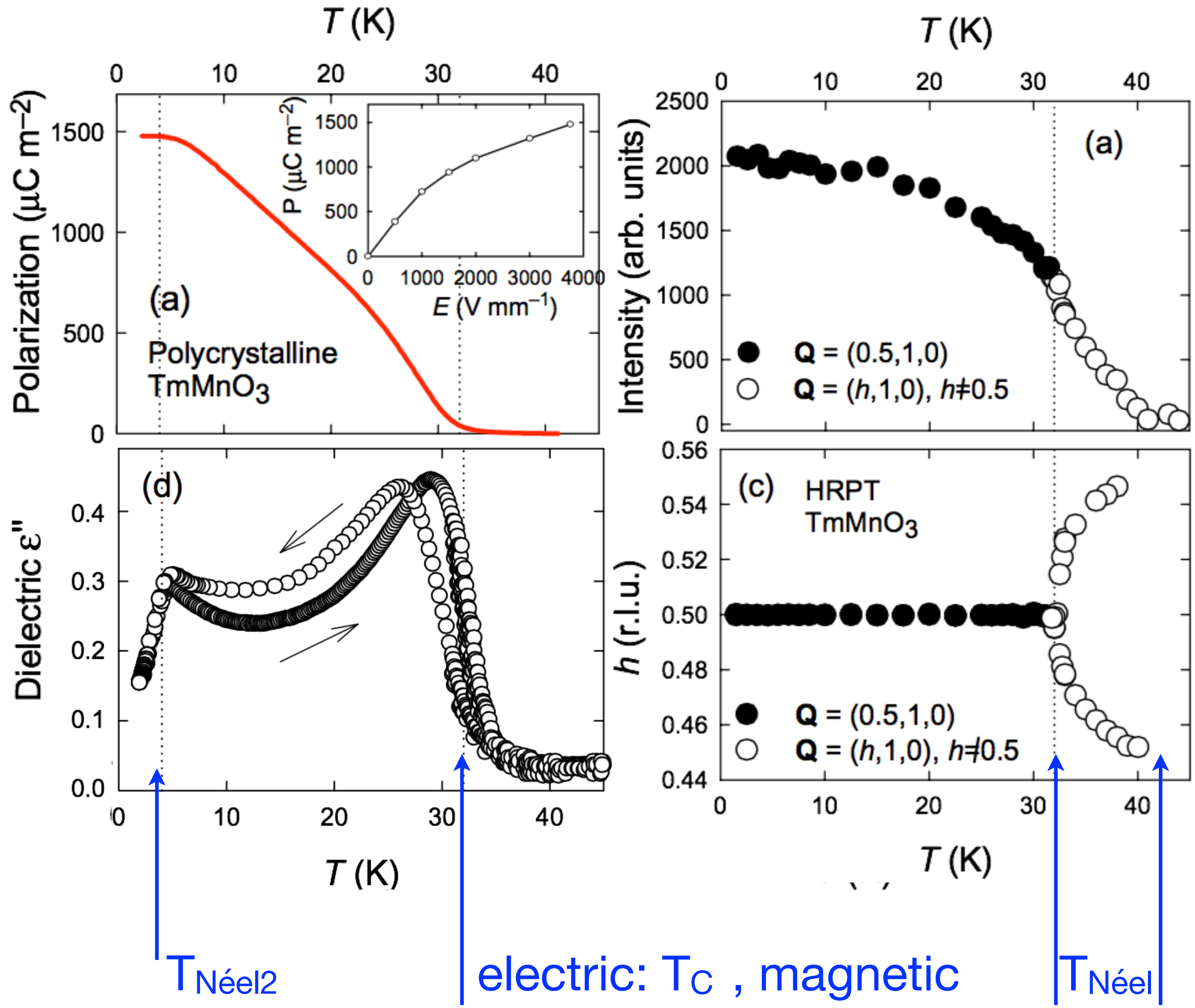
Example of HRPT & DMC complementarity

Spin-lattice coupling and antiferromagnetic order in orthorhombic multiferroic* $TmMnO_3$

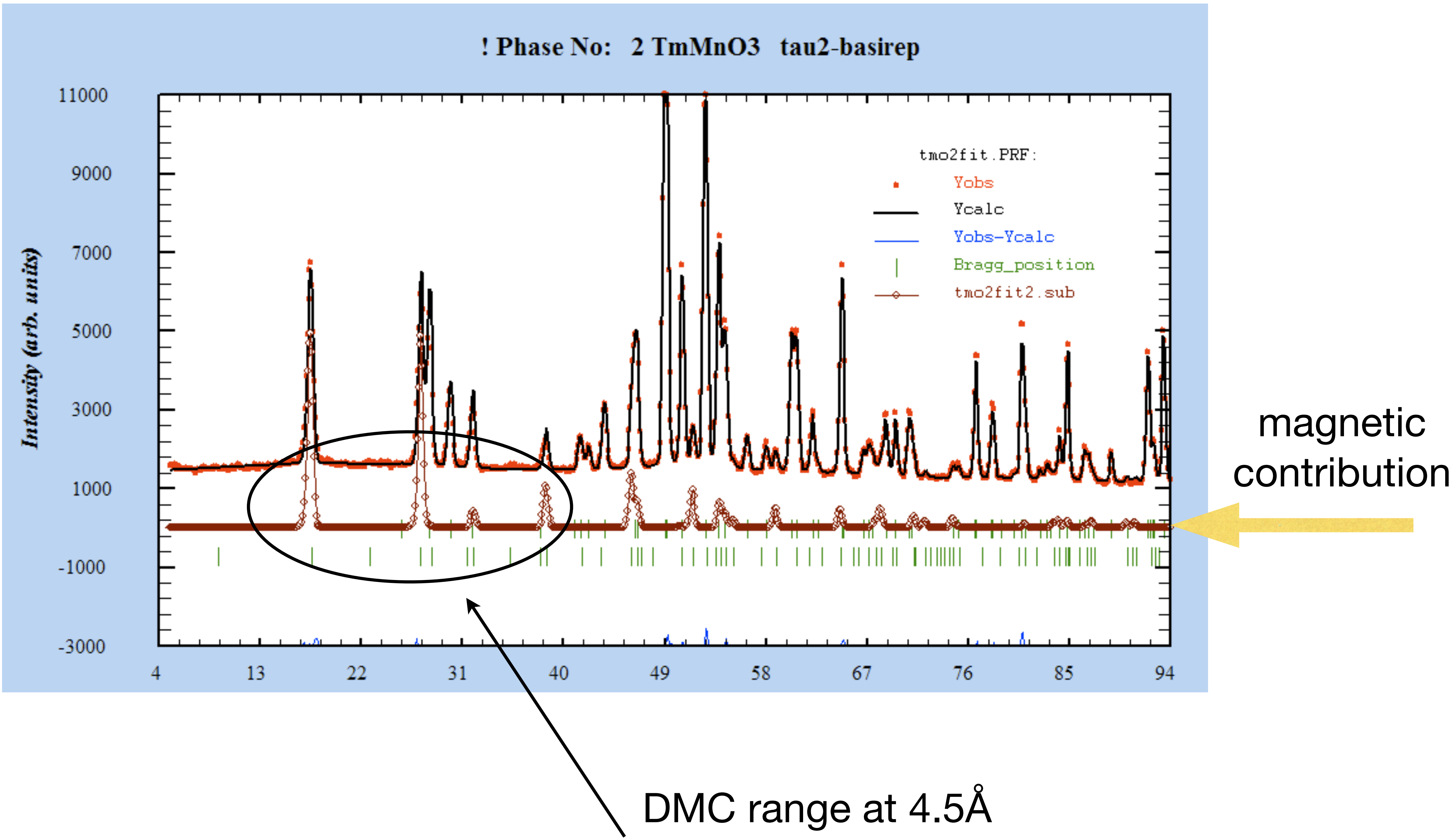




* materials that have coupled electric, magnetic and structural order parameters

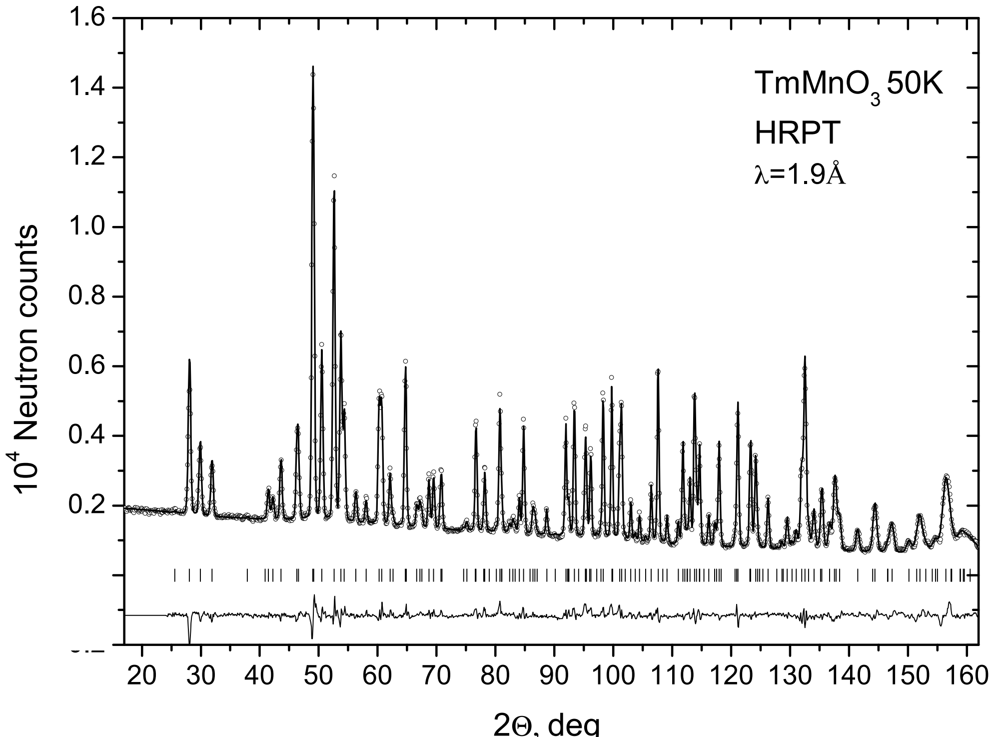
cf. resolution/q-range

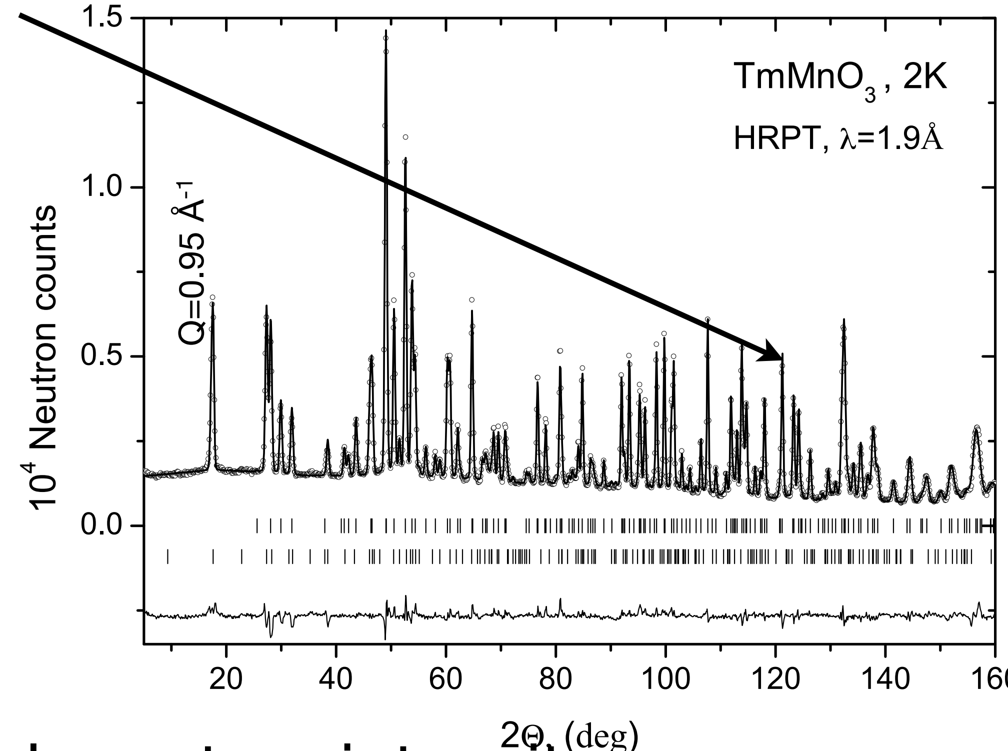
HRPT 1.9Å



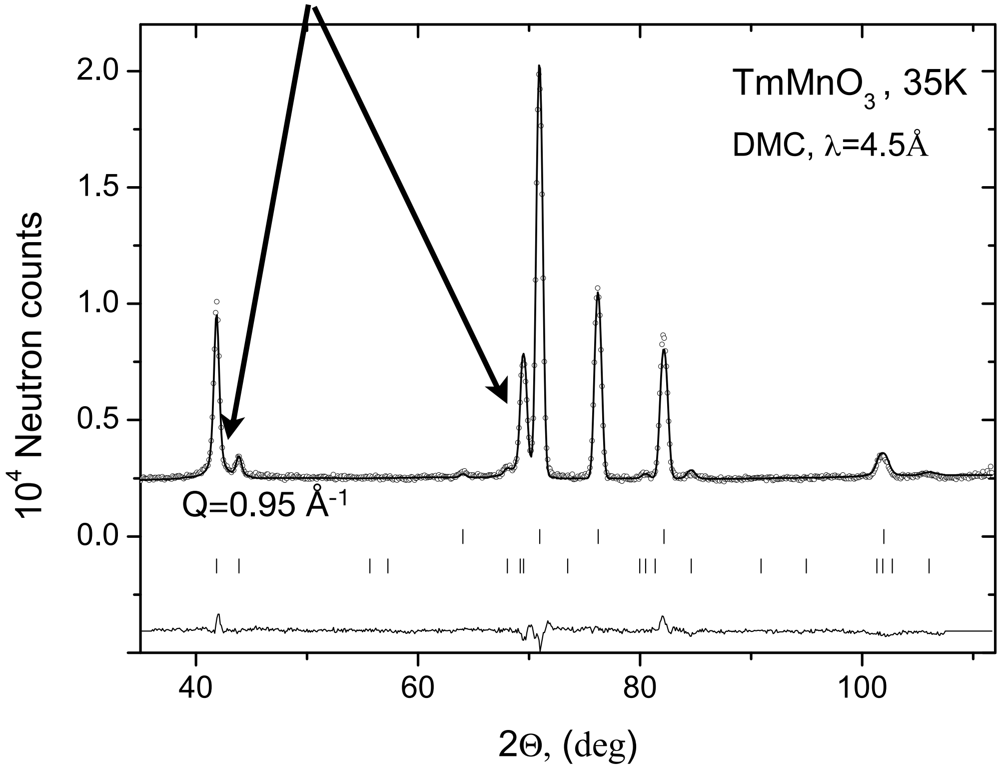
Complementarity 1.9Å HRPT and 4.5Å DMC

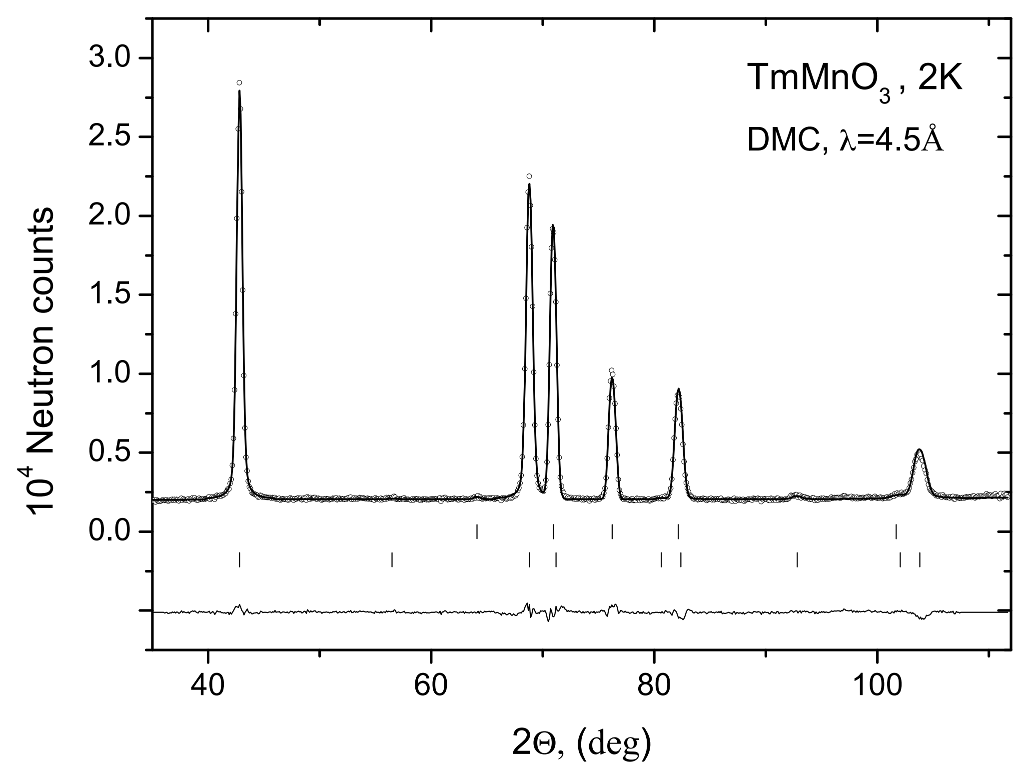
excellent resolution and high Q-range





excellent resolution at low Q and high neutron intensity





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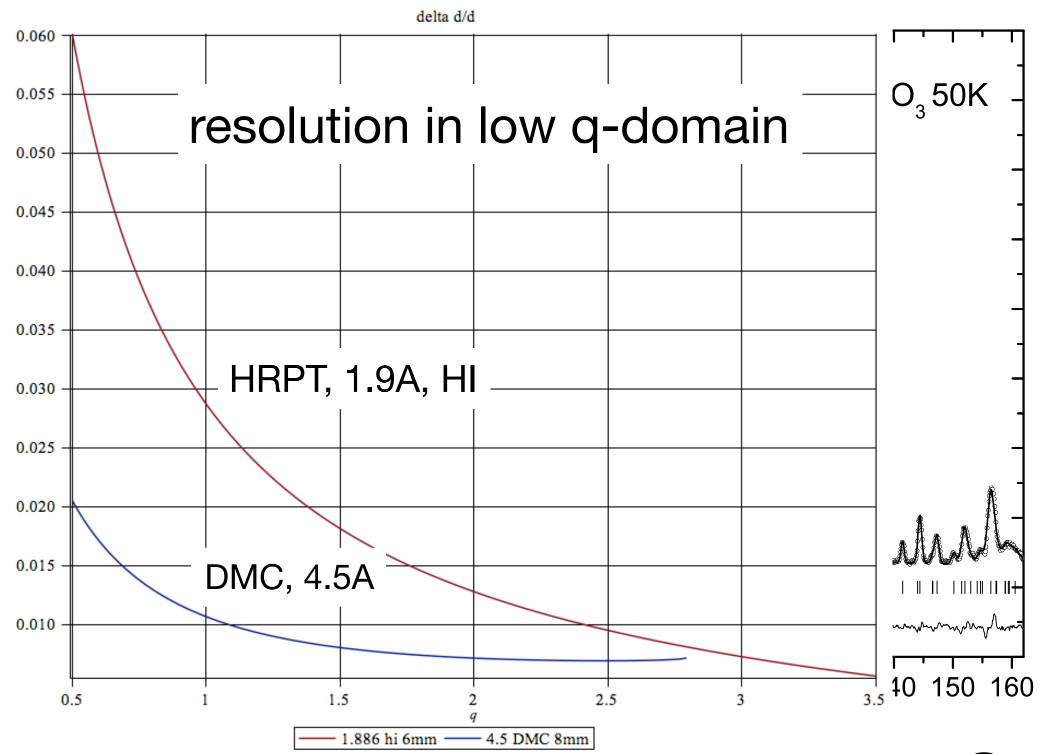
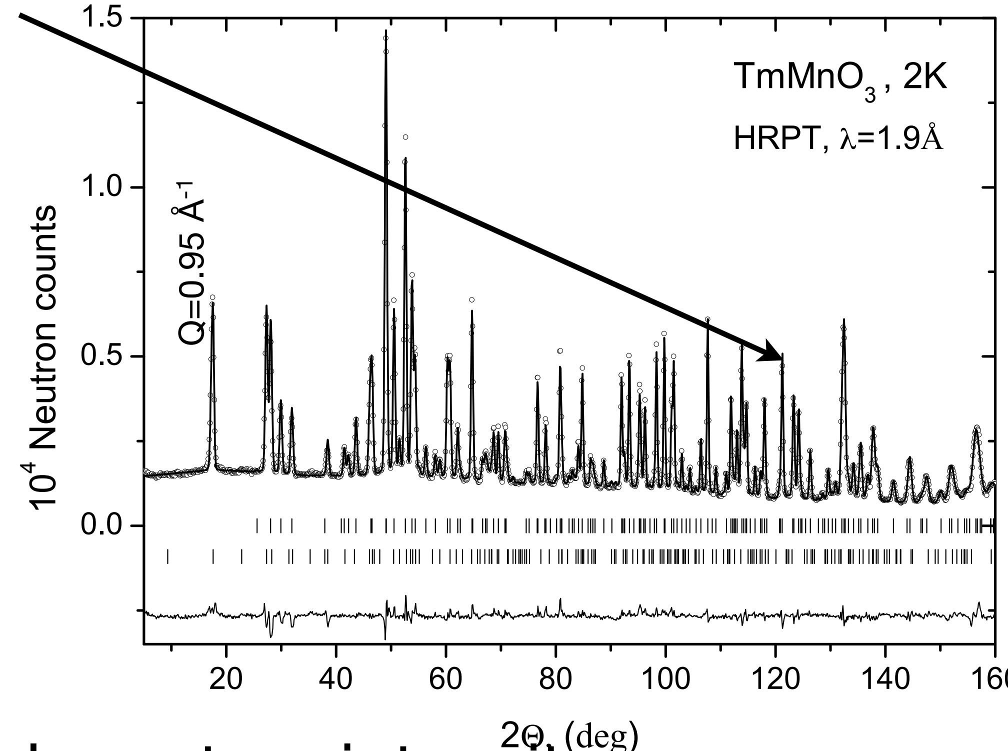
excellent resolution and high Q-range





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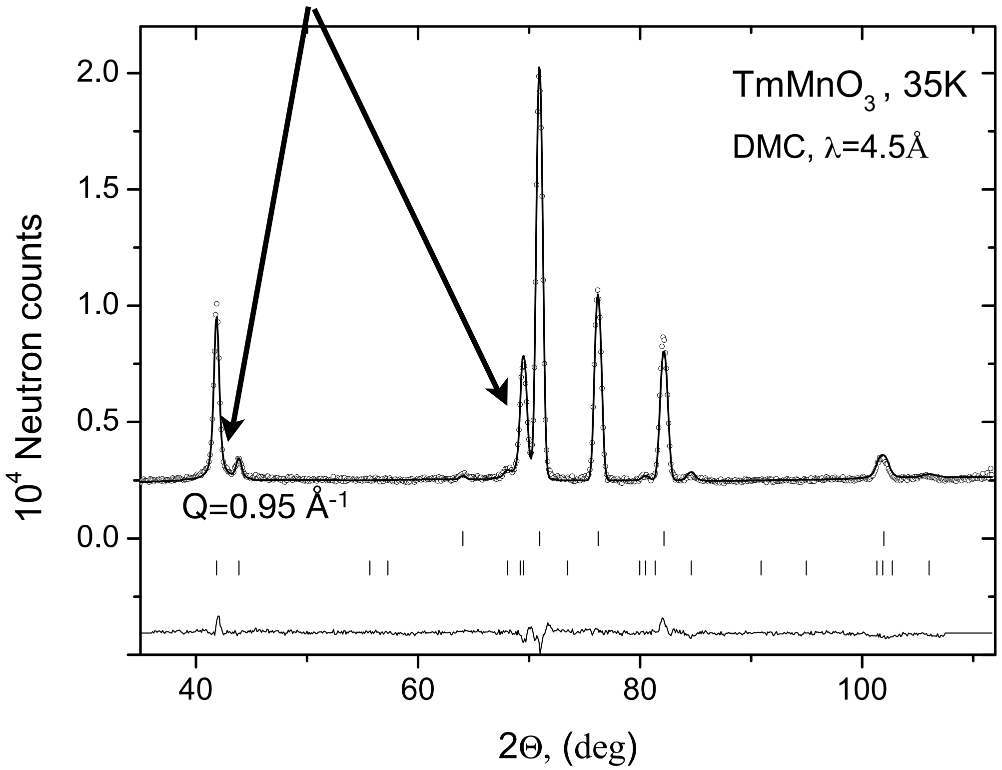

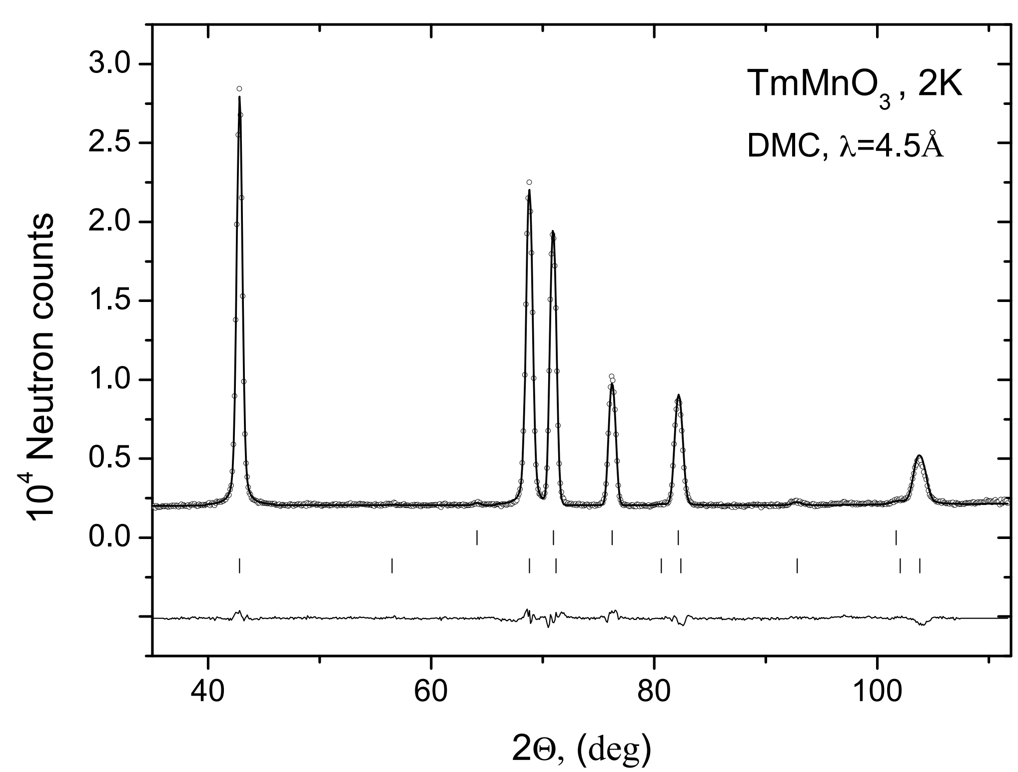

Pon
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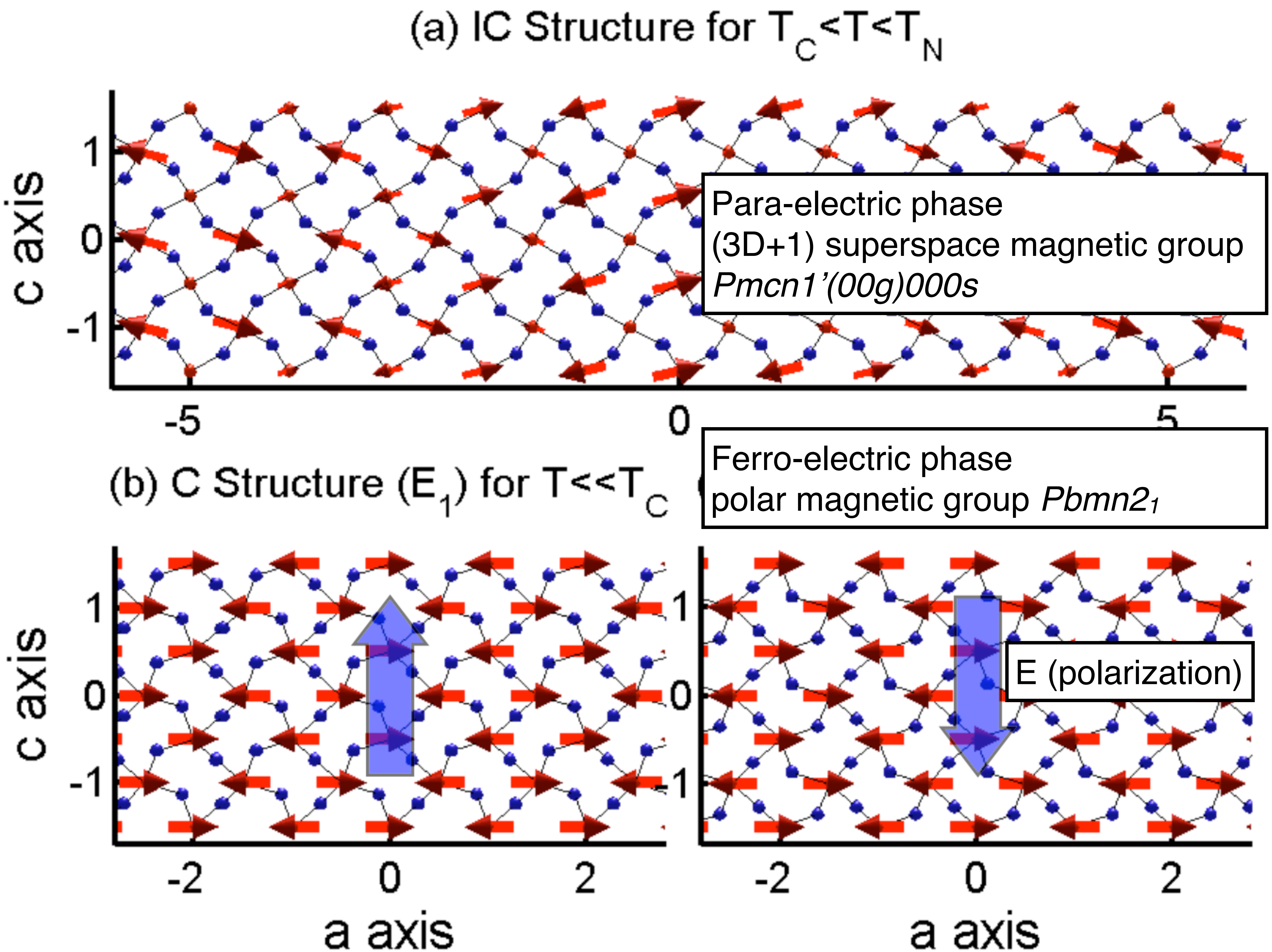
Magnetic structure $TmMnO_3$

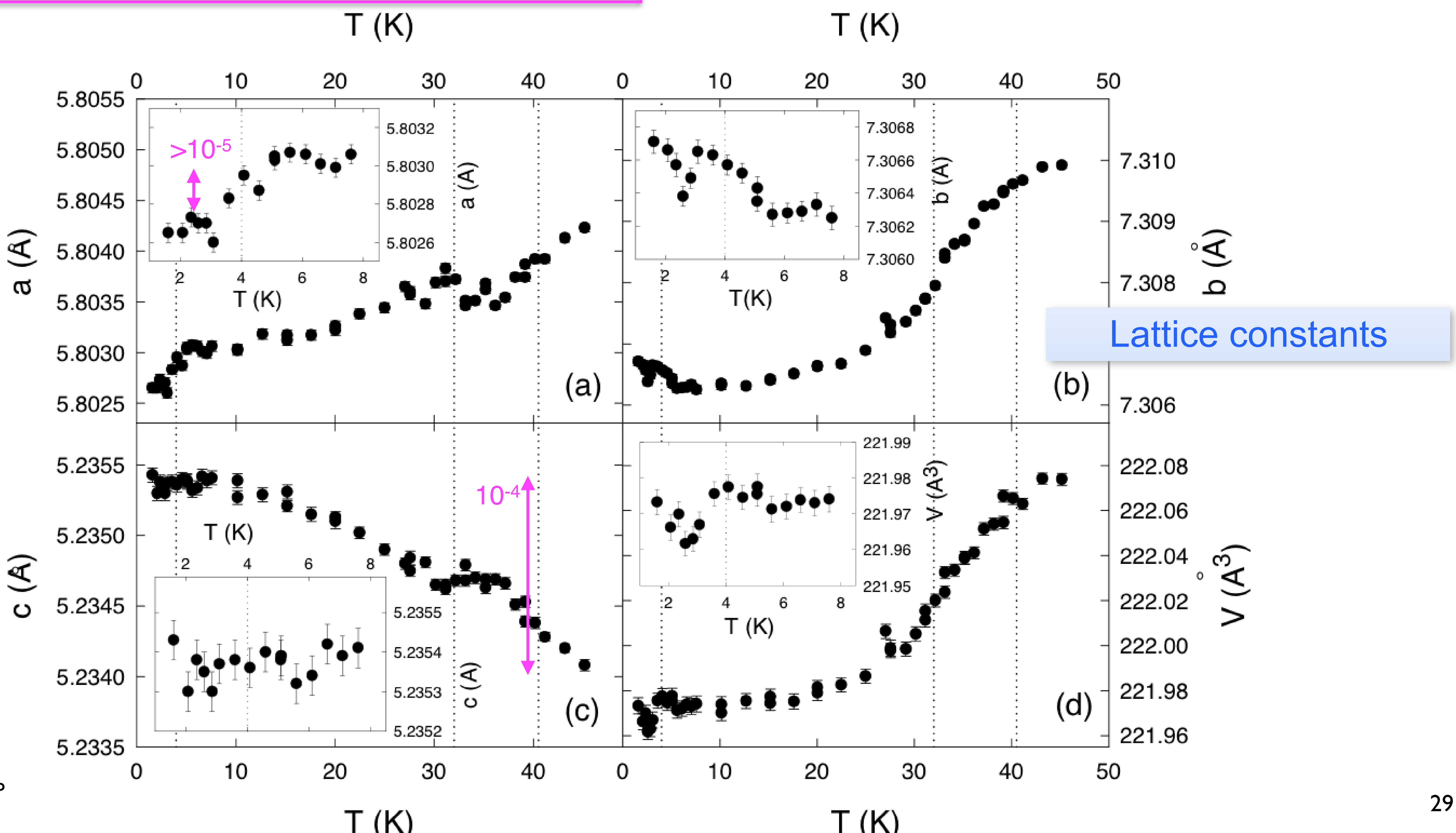


E = 0

Example of accuracy on metric: orthorhombic multiferroic $TmMnO_3$

material that have coupled electric, magnetic and structural order

~0.0001Å=10 fm (proton radius 2fm)



ECM-2016: August 28 – Sept. 1
European Conference on Crystallography

http://ecm30.ecanews.org/

Thank you