Determination of long range antiferromagnetic order by powder neutron diffraction

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During the practicum we will try to reproduce the one of the neutron diffraction experiments performed during 1946-1951 for which C.G. Shull was honoured with the Nobel Prize in 1994. We will perform neutron diffraction experiment with MnS using powder diffractometer HRPT/SINQ. From the analysis of the nuclear and magnetic Bragg peak intensities and positions we will verify the crystal and magnetic structures of manganese sulfide MnS and determine the size of the magnetic moment on manganese.

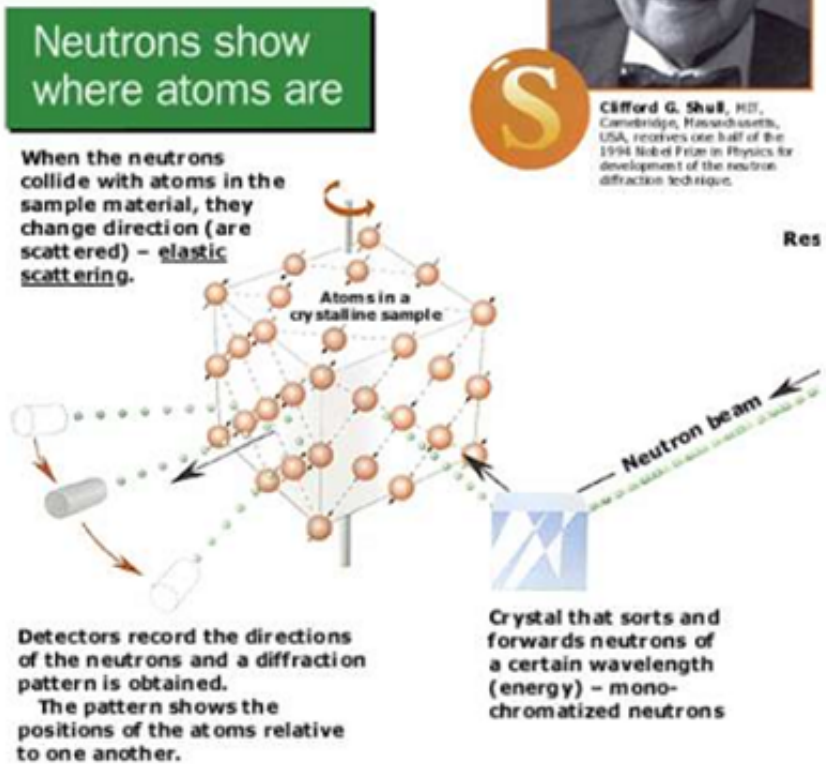
Determination of long range antiferromagnetic order by powder neutron diffraction

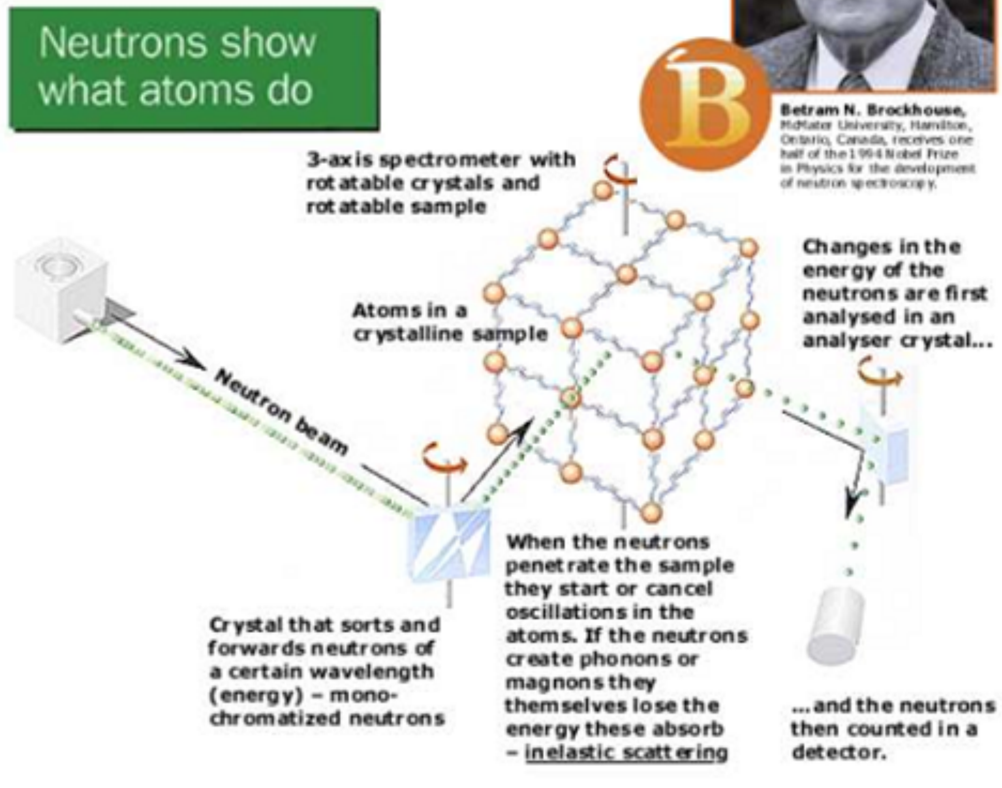
- Historical introduction (4)
- Some experimental details of neutron diffraction experiment at HRPT/SINQ (10)
- Reminder on nuclear and magnetic neutron structure factors (6)
- Practicum problems (6)

1994 Nobel Prize in Physics

Clifford G. Shull
1915 – 2001, USA

Bertram N. Brockhouse
1918 – 2003, Canada





http://www.nobelprize.org/nobel_prizes/physics/laureates/1994/illpres/neutrons.html

Neutron Diffraction by Paramagnetic and Antiferromagnetic Substances

C. G. SHULL, W. A. STRAUSER, AND E. O. WOLLAN
Oak Ridge National Laboratory, Oak Ridge, Tennessee
(Received March 2, 1951)

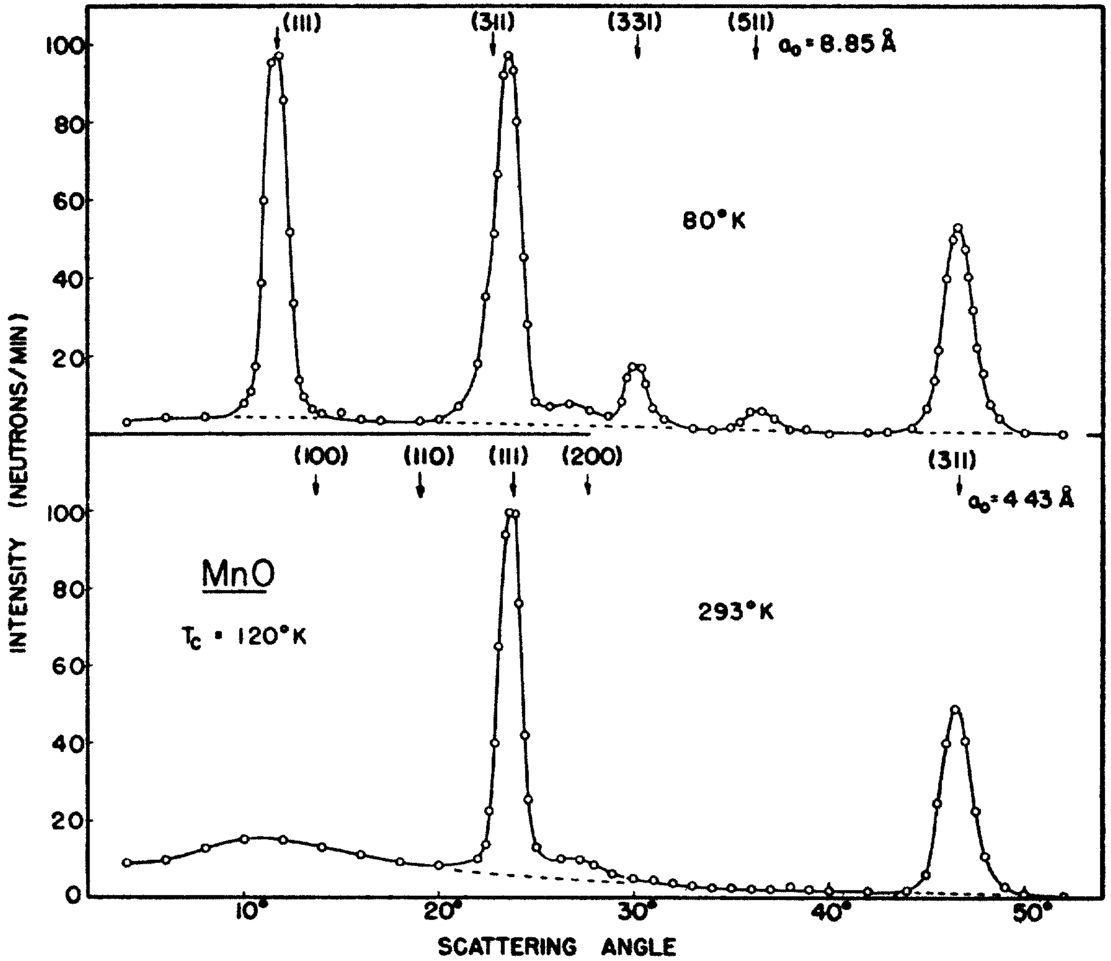
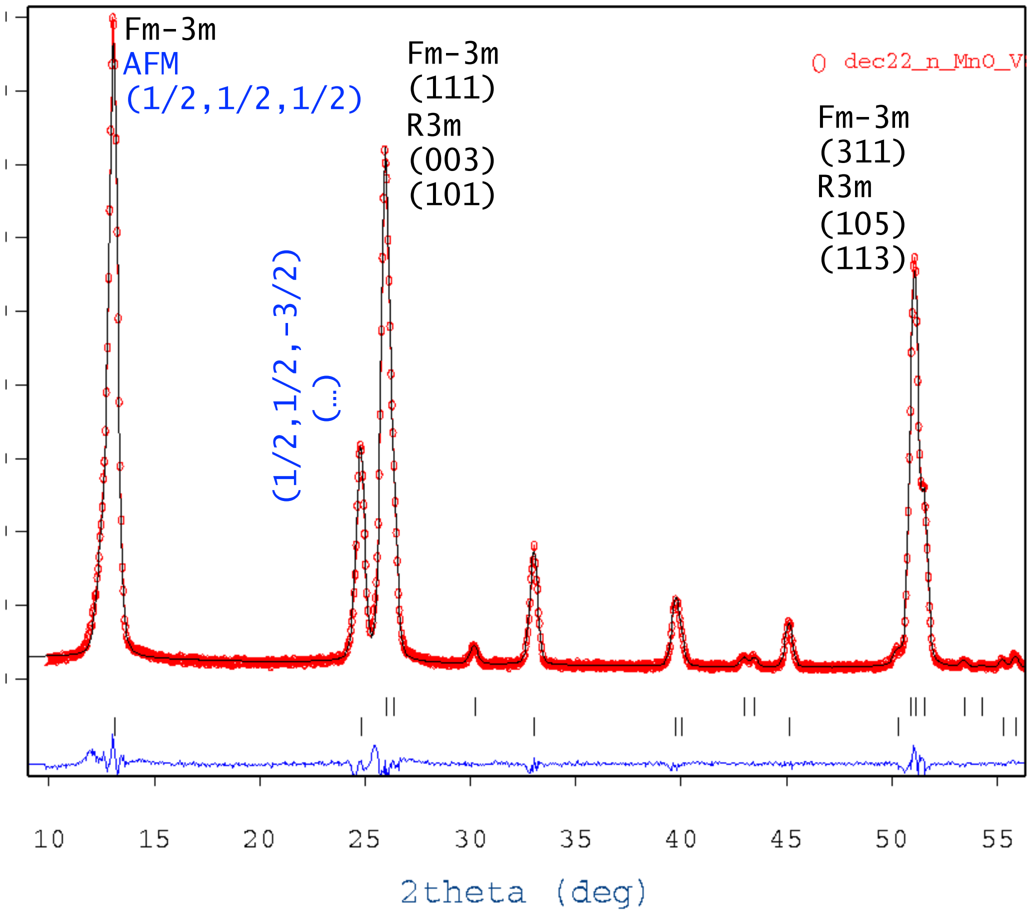


FIG. 4. Neutron diffraction patterns for MnO taken at liquid nitrogen and room temperatures. The patterns have been corrected for the various forms of extraneous, diffuse scattering mentioned in the text. Four extra antiferromagnetic reflections are to be noticed in the low temperature pattern.

HRPT/SINQ nowadays
λ=1.15Å, MnO @ 2K.

Rhombohedral distortions are explicitly seen

R-3m and k=003/2



raction by Paramagnetic and Antiferromagnetic

λ=1.057Å

C. G. SHULL, W. A. STRAUSER, AND E. O. WOLLAN
Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received March 2, 1951)

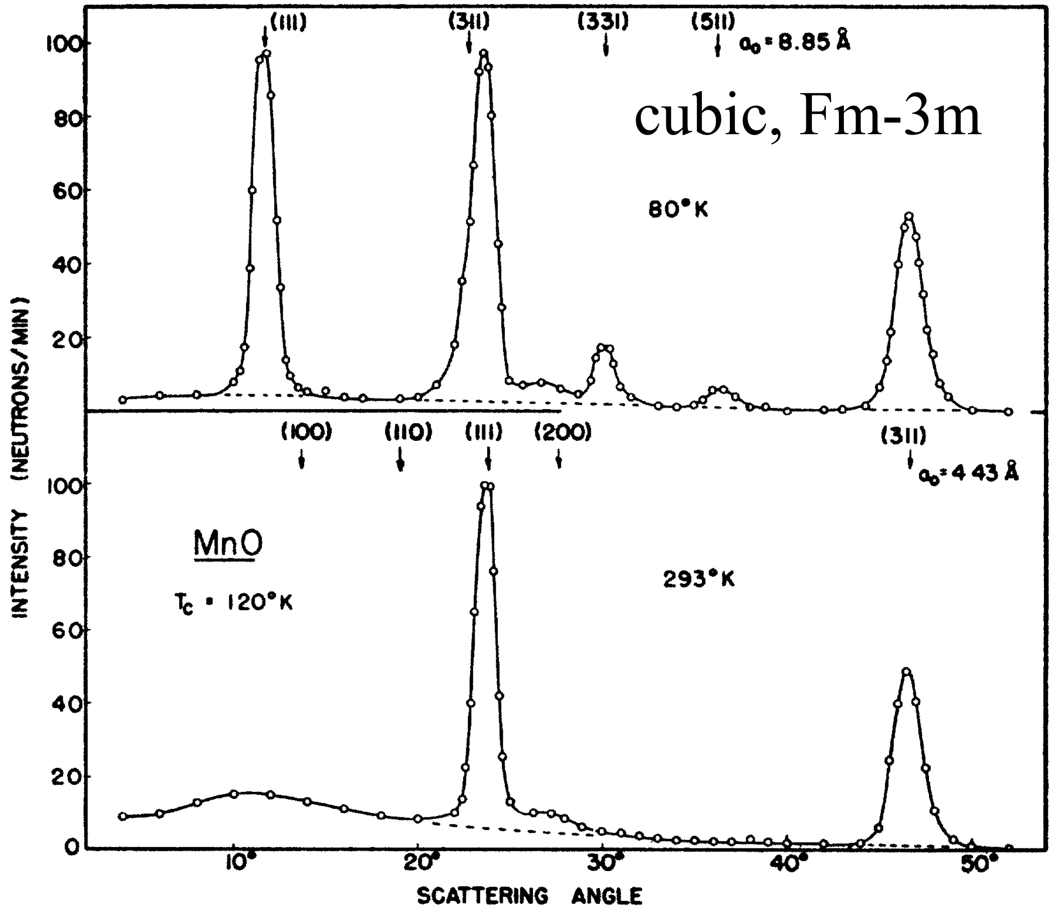
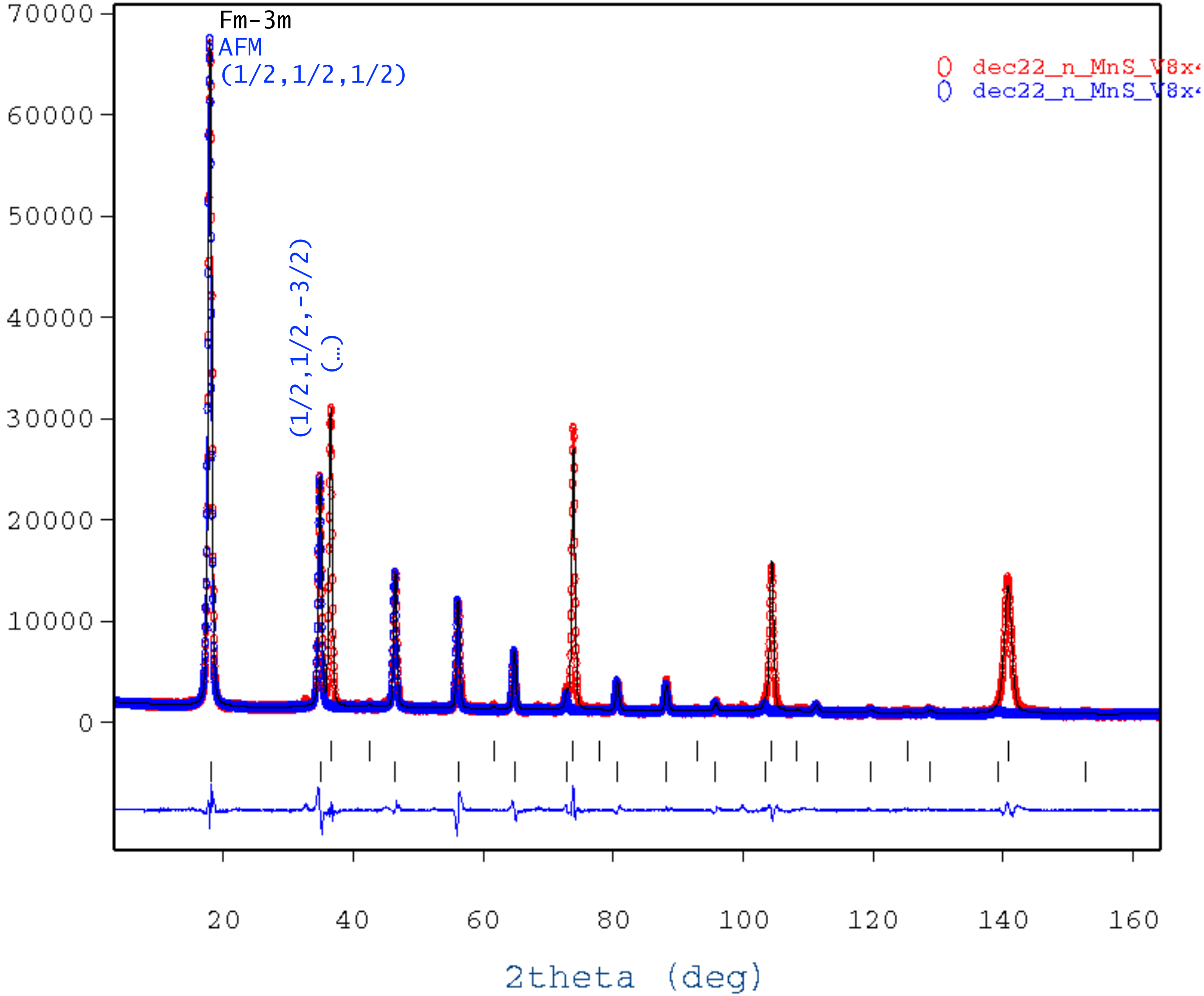


FIG. 4. Neutron diffraction patterns for MnO taken at liqui nitrogen and room temperatures. The patterns have been co rected for the various forms of extraneous, diffuse scatterin mentioned in the text. Four extra antiferromagnetic reflection are to be noticed in the low temperature pattern.

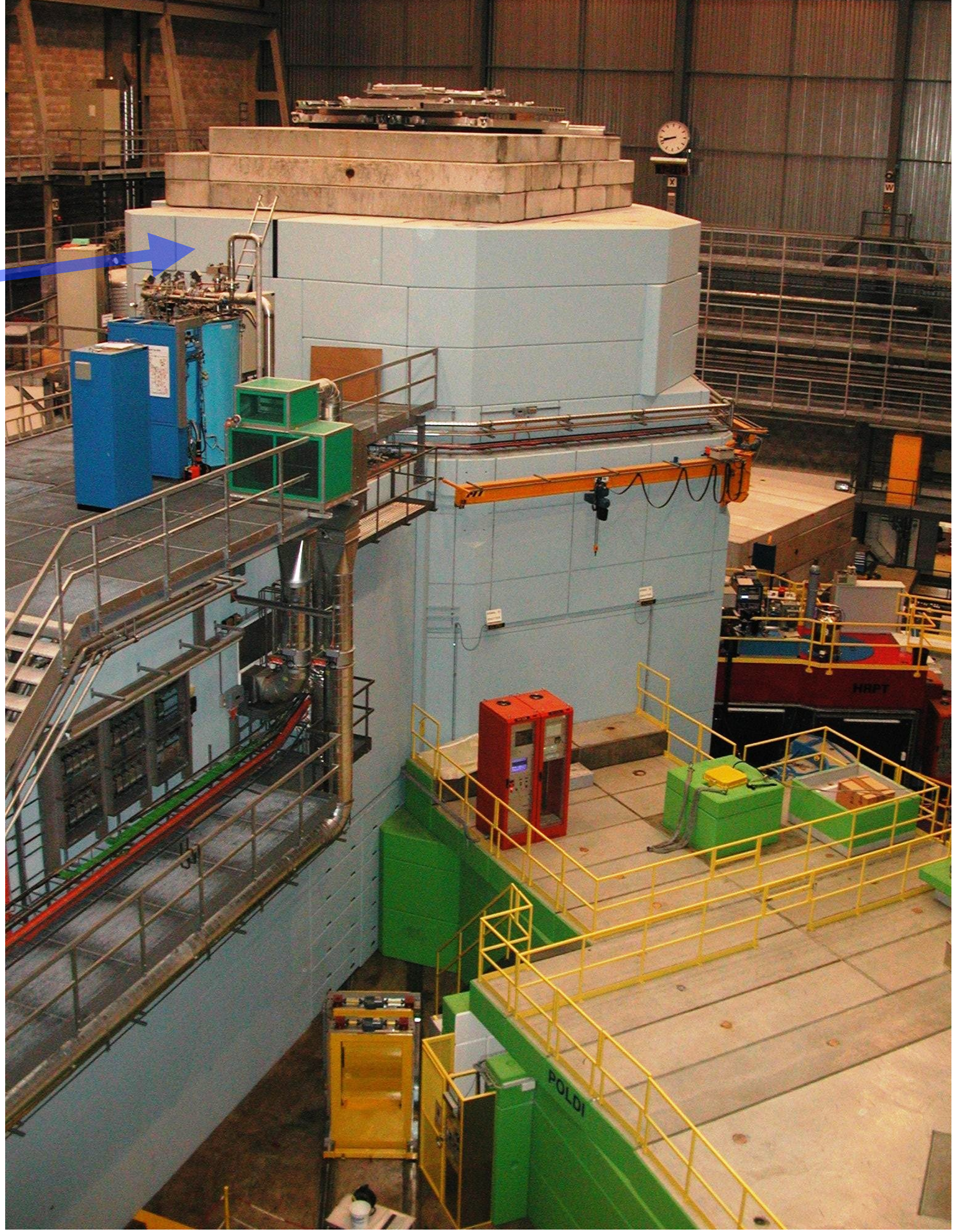
HRPT, 1.9A, MnS @ T=2K, pseudo-cubic Fm-3m



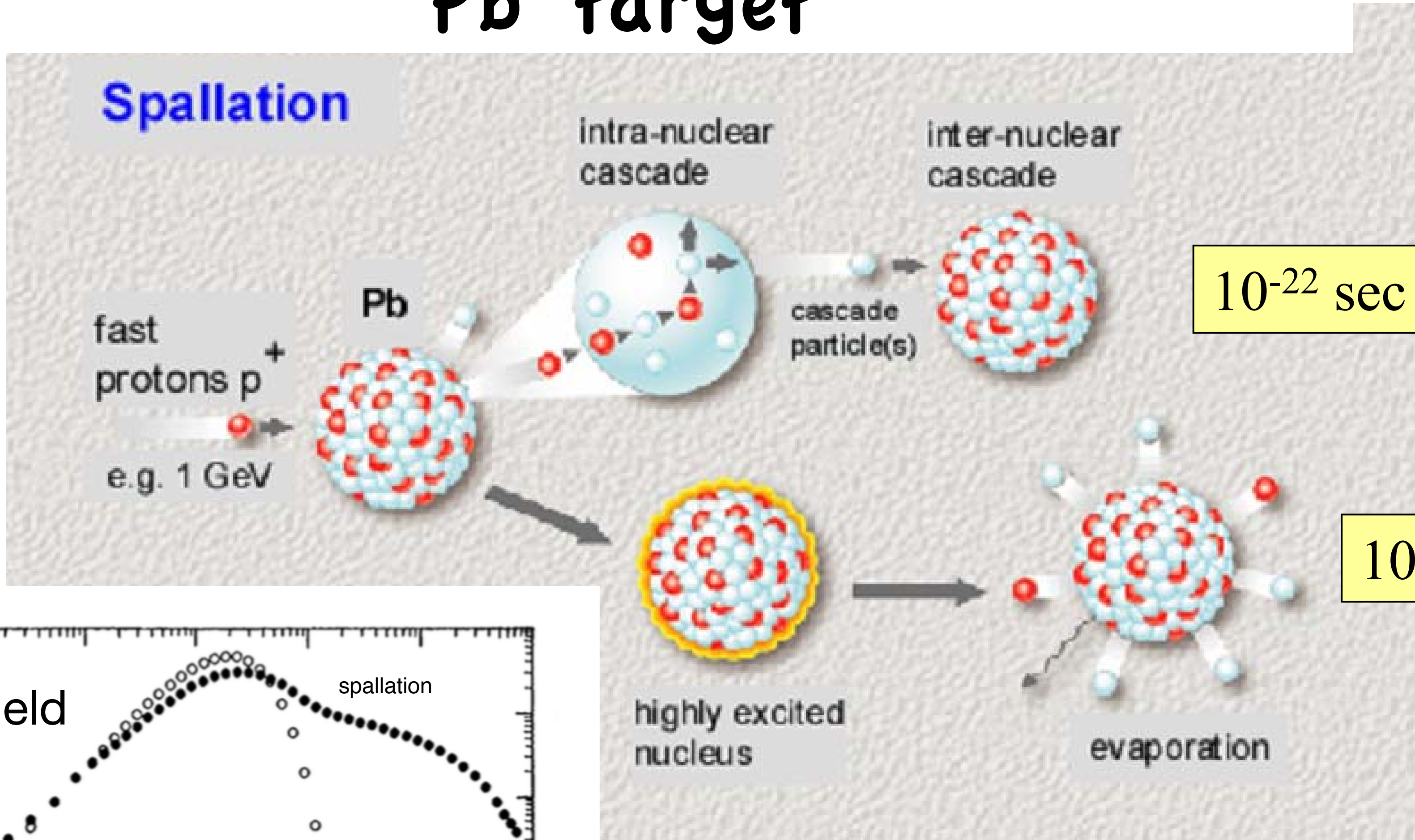
Some experimental details of neutron diffraction experiment at HRPT/SINQ

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/cm²/s**. Beside thermal neutrons, a cold moderator of liquid deuterium (cold source) slows neutrons down and shifts their spectrum to lower energies.

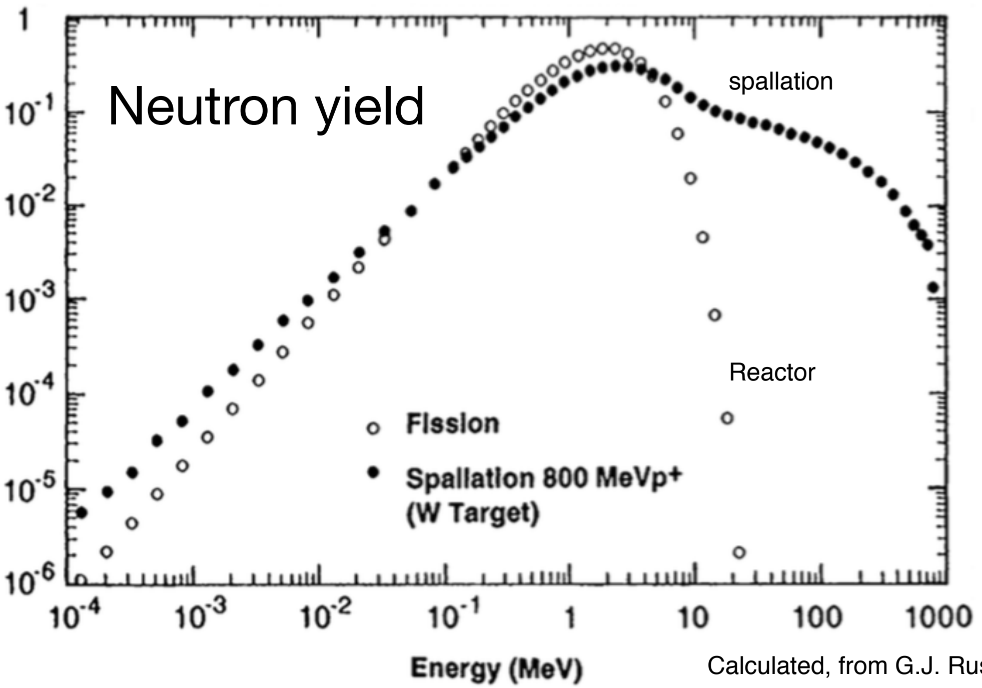


Spallation, SINQ 590MeV protons, Pb target



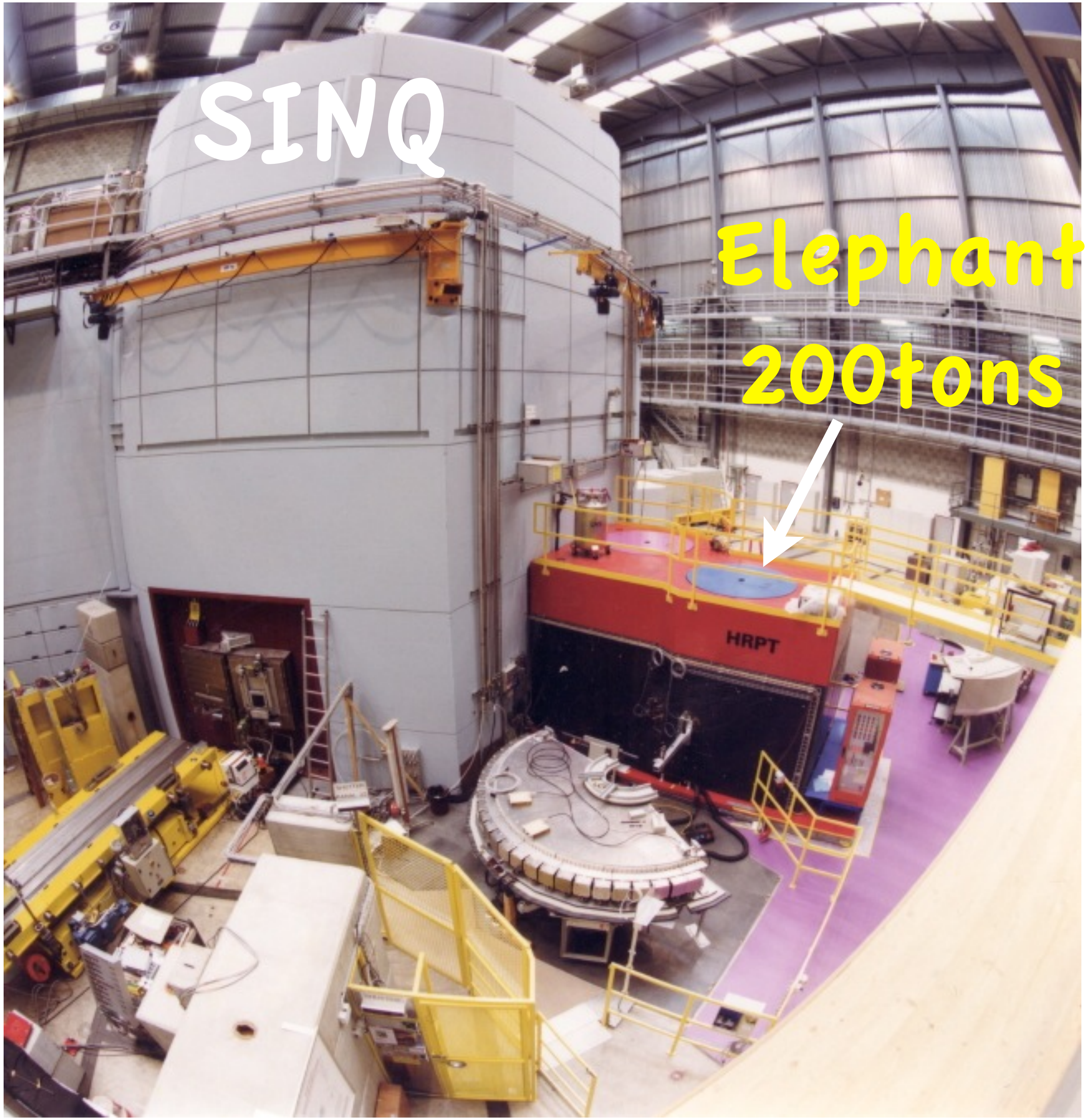
10^{-22} sec

10^{-18} sec



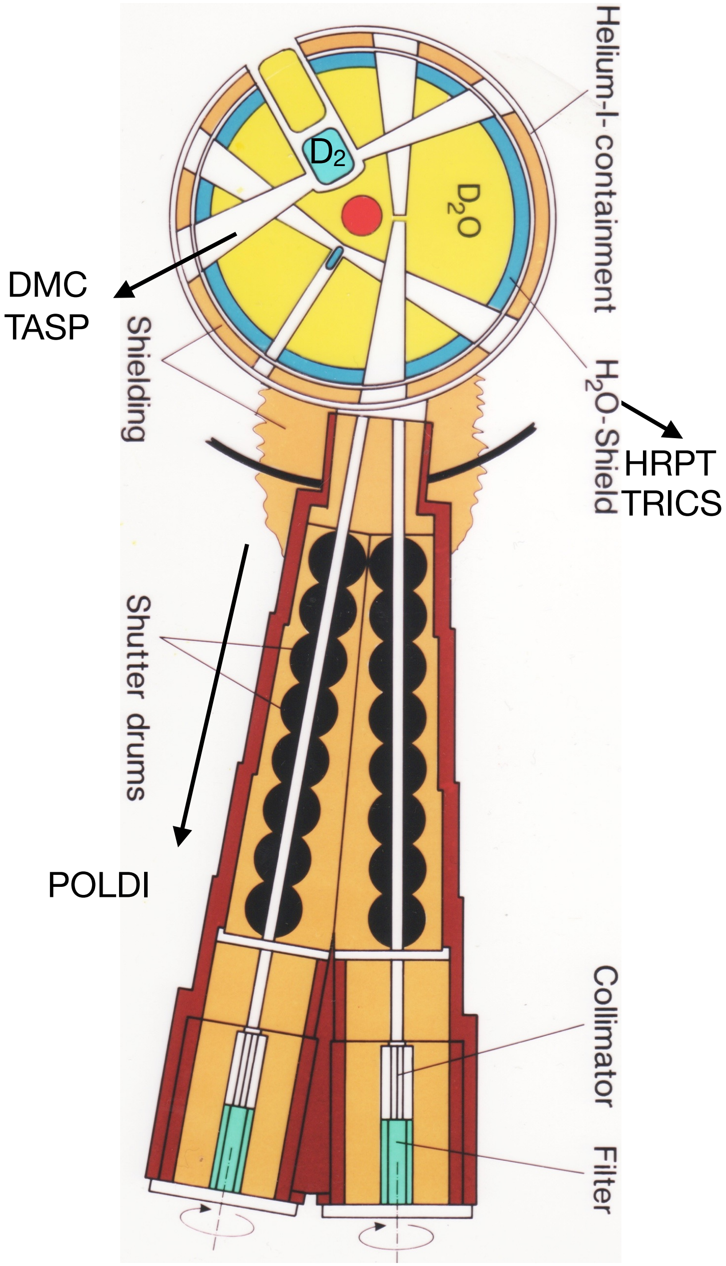
Calculated, from G.J. Russell, Spallation physics–an overview, Proceedings of ICANS-XI

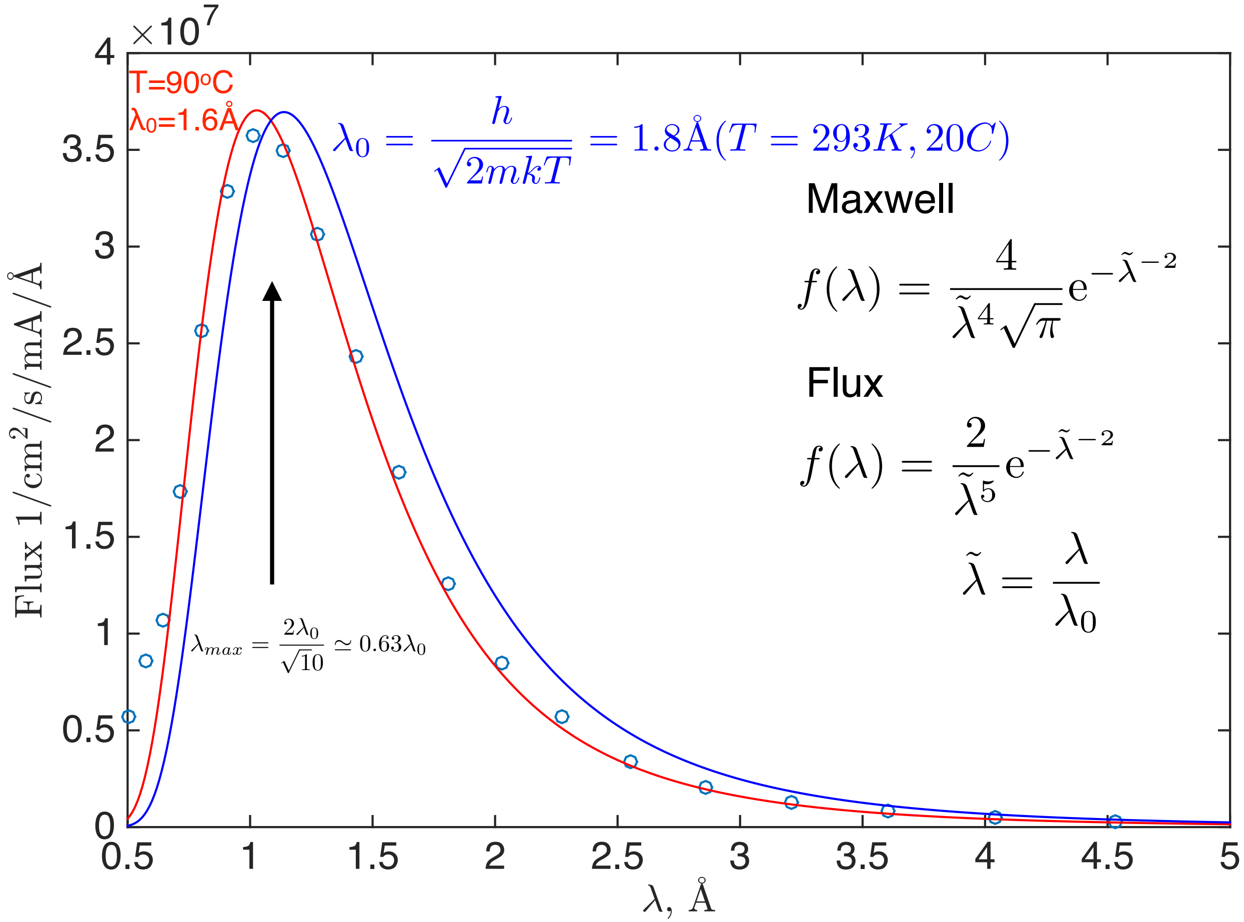
SINQ hall



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)

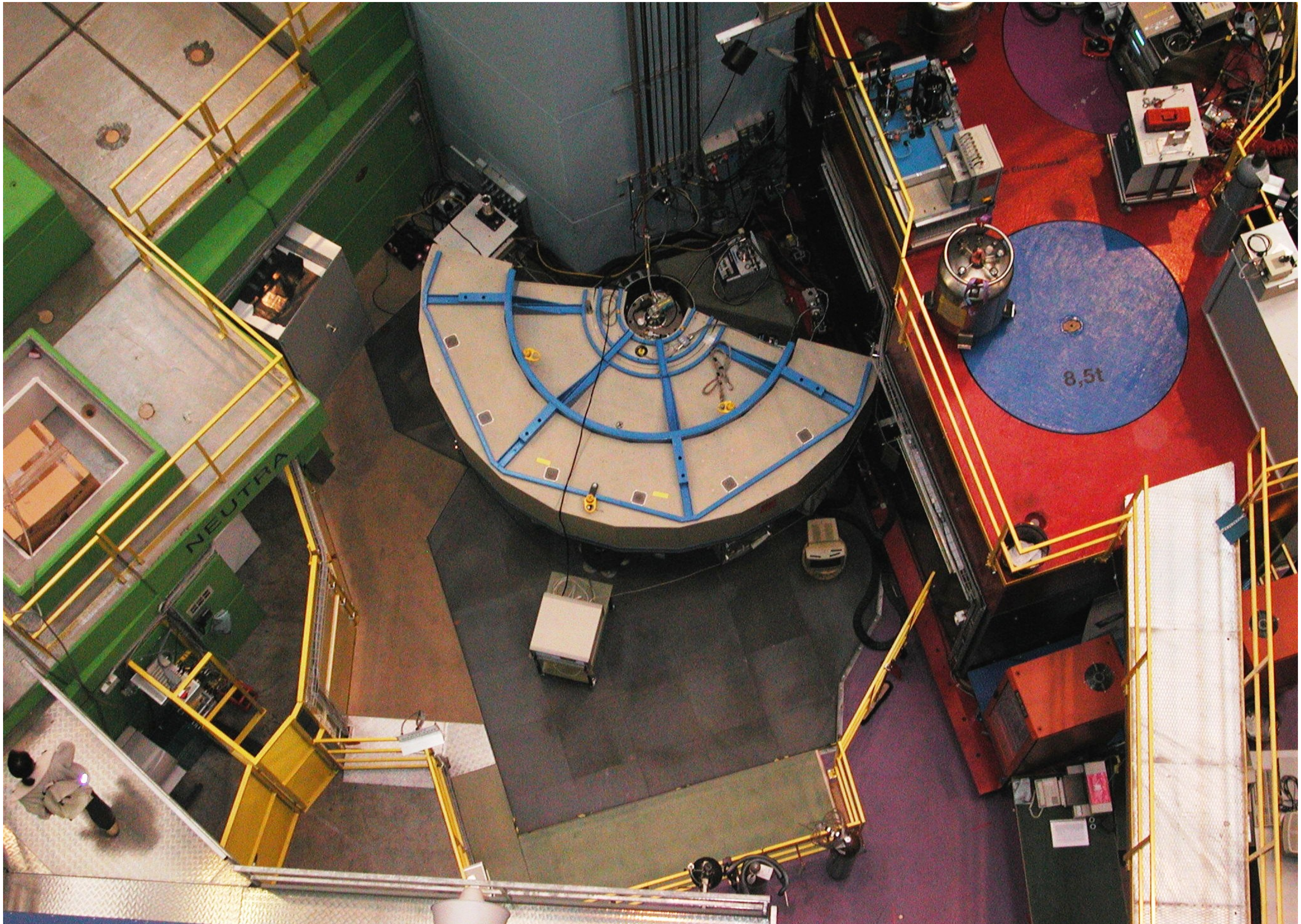




Total: $5 \cdot 10^7$ 1/cm^2/s/mA

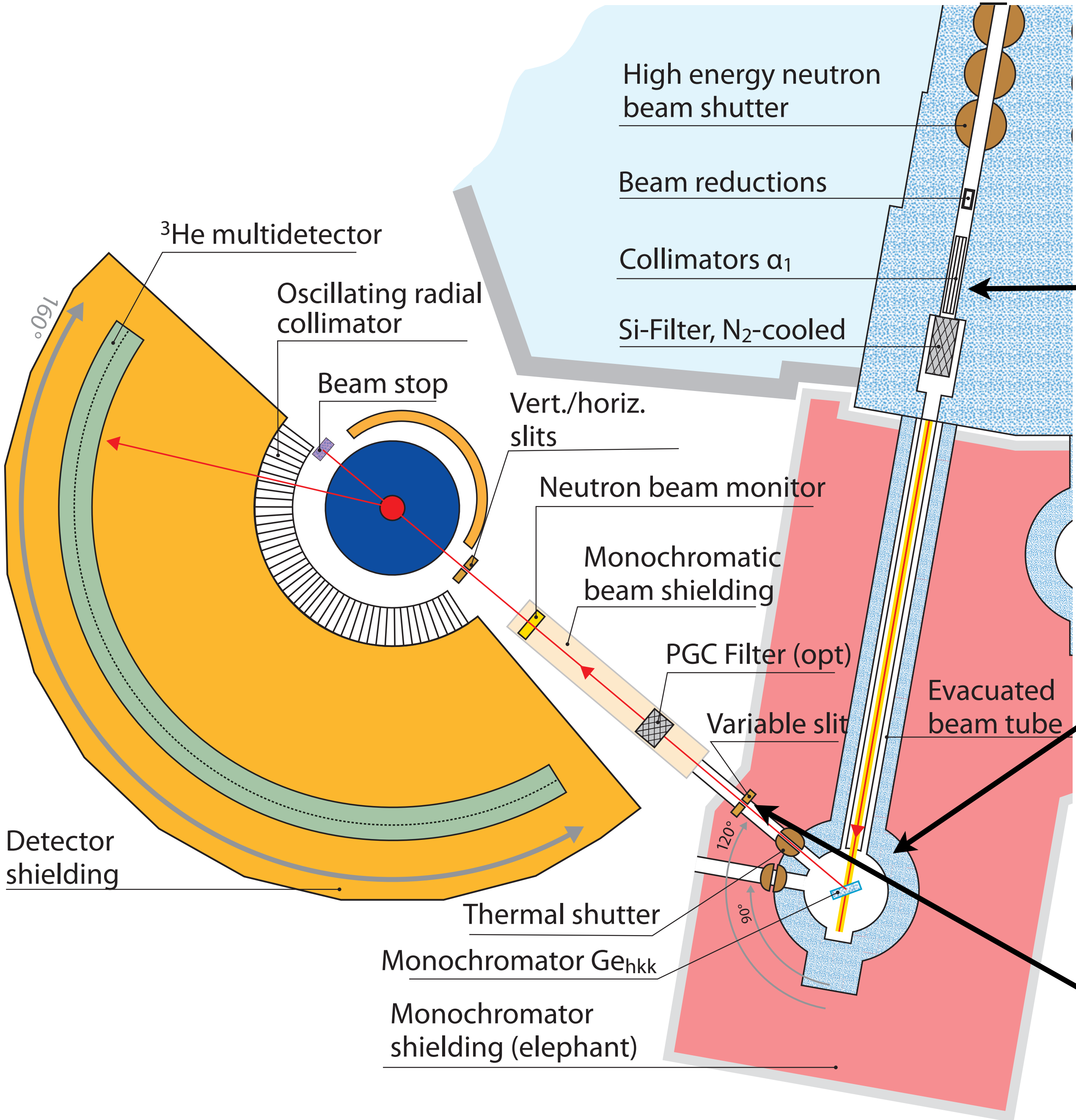
at SINQ current 2mA: 10^8

HRPT areal



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

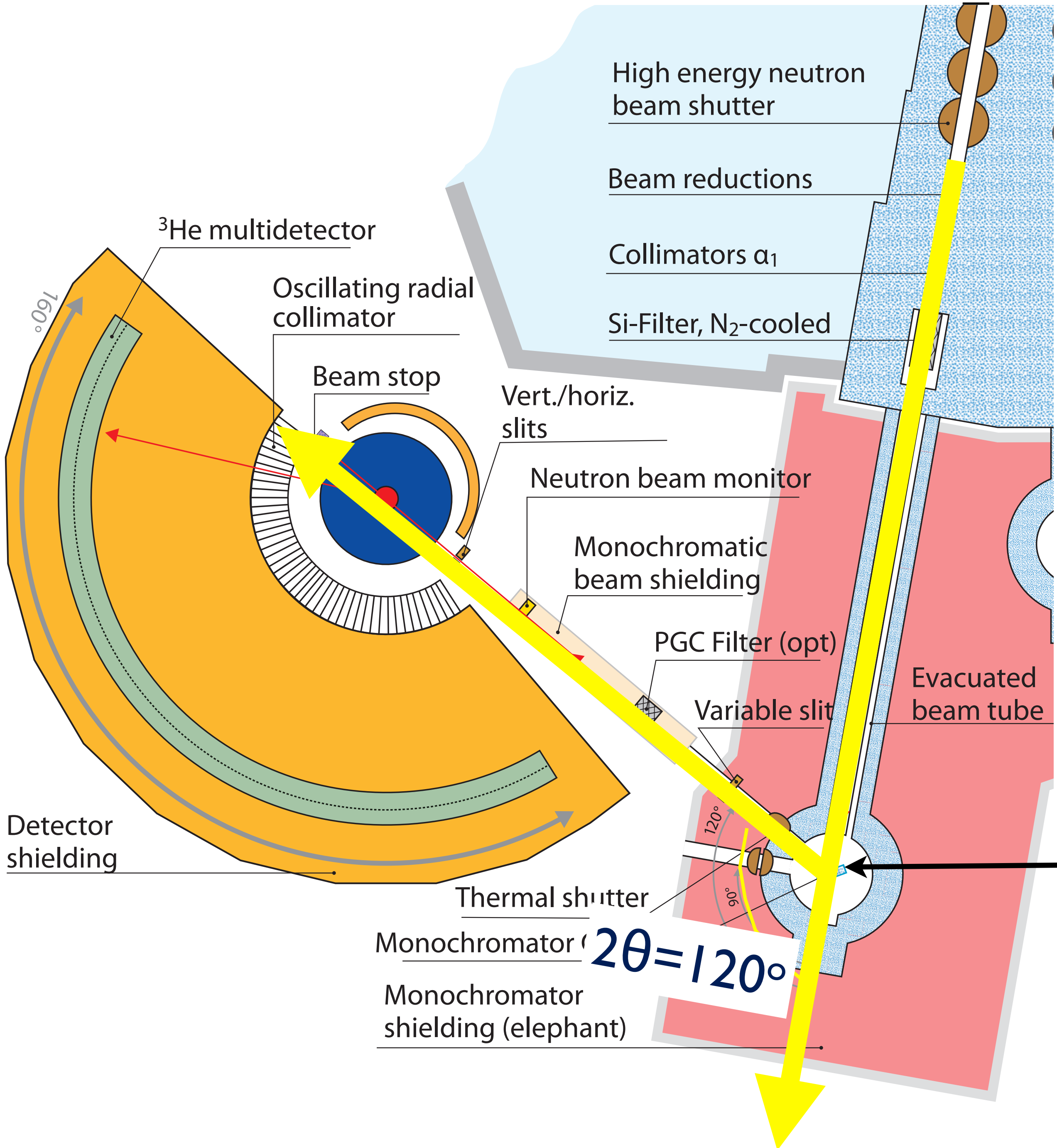
mosaic spread of the monochromator 15'

α_3

slit system for monochromatic beam and sample diameter

HRPT layout

High Resolution Powder Diffractometer for Thermal Neutrons

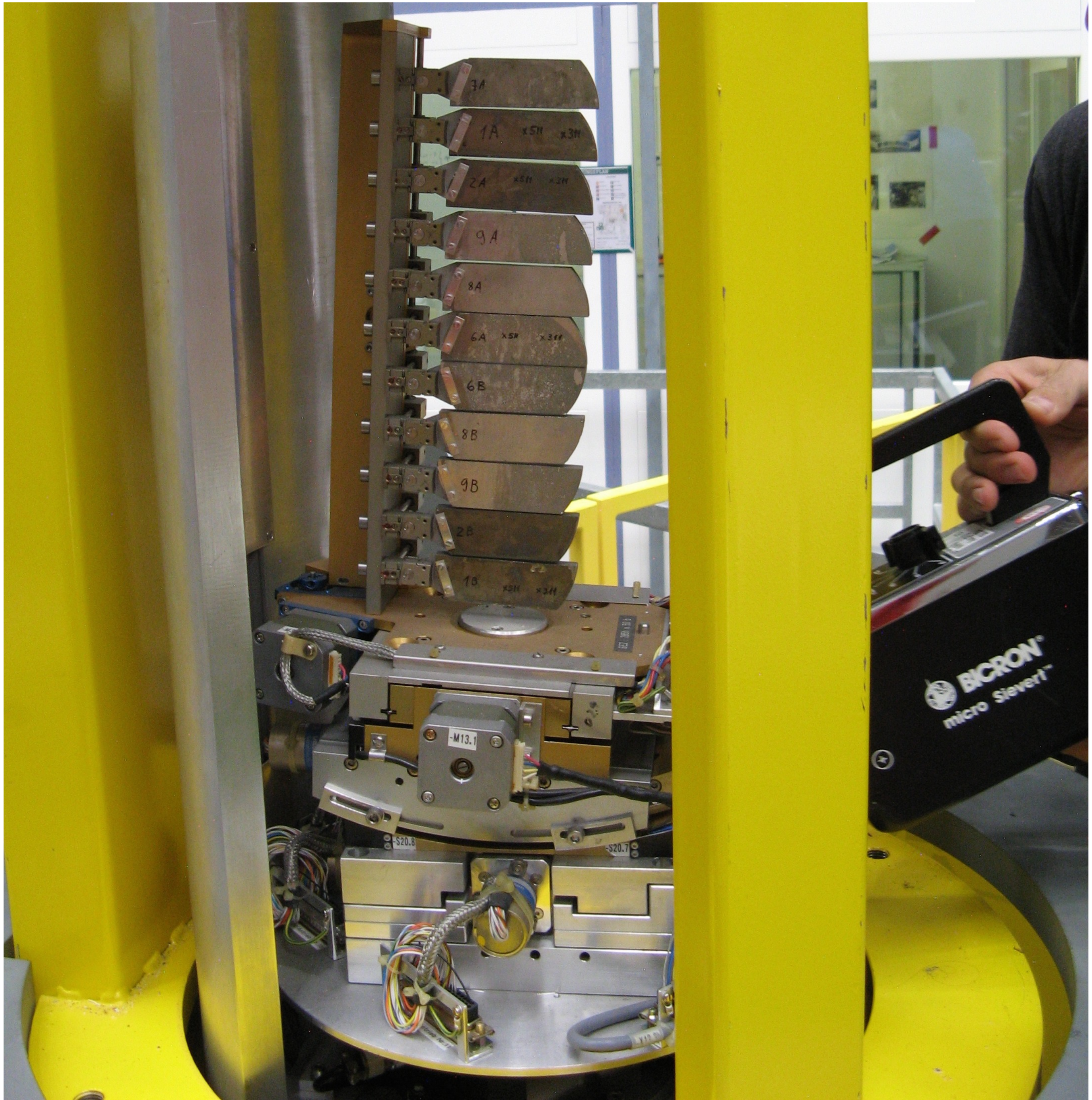


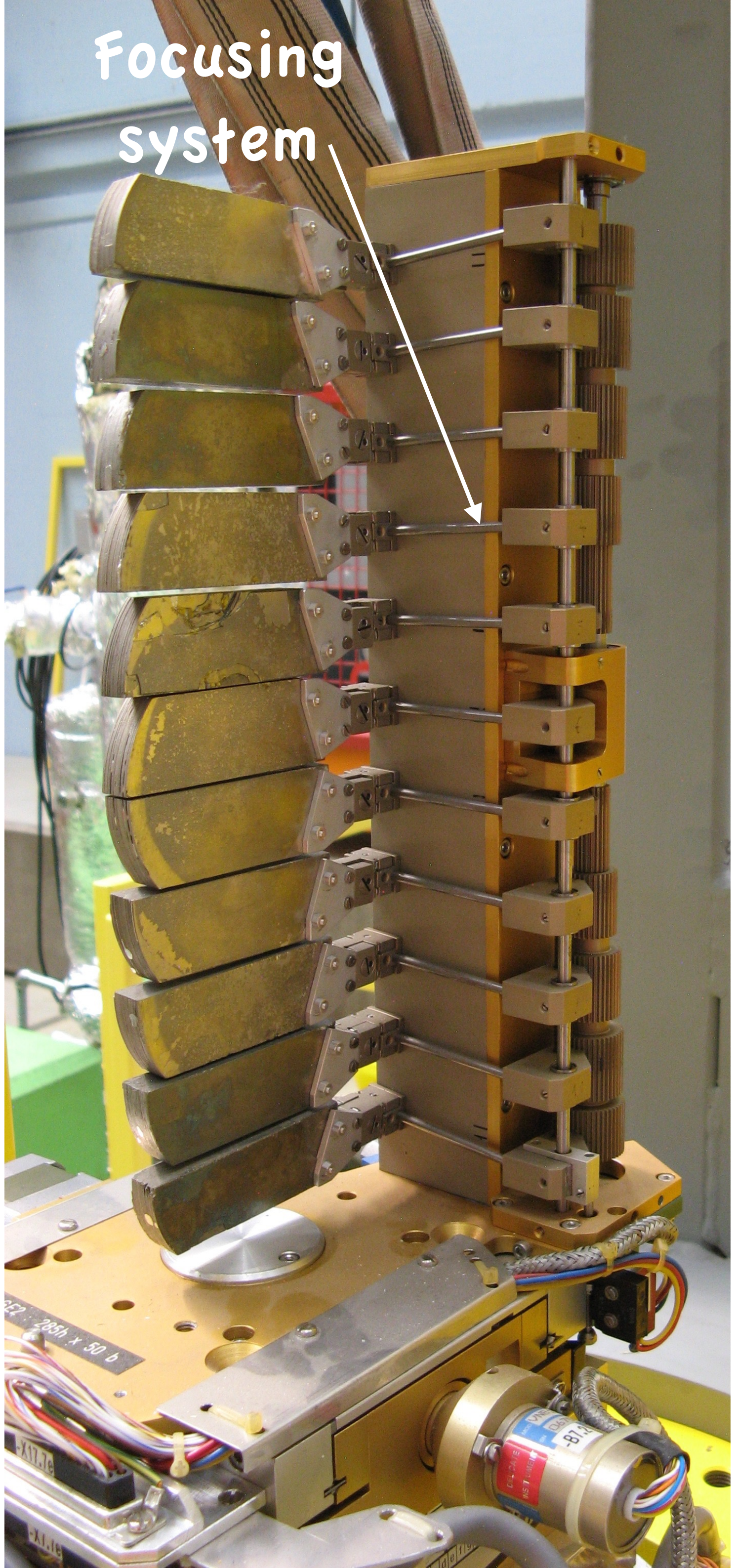
neutron monochromator
fixed 120 take off angle

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

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

Ge single crystal monochromator, 7 motors



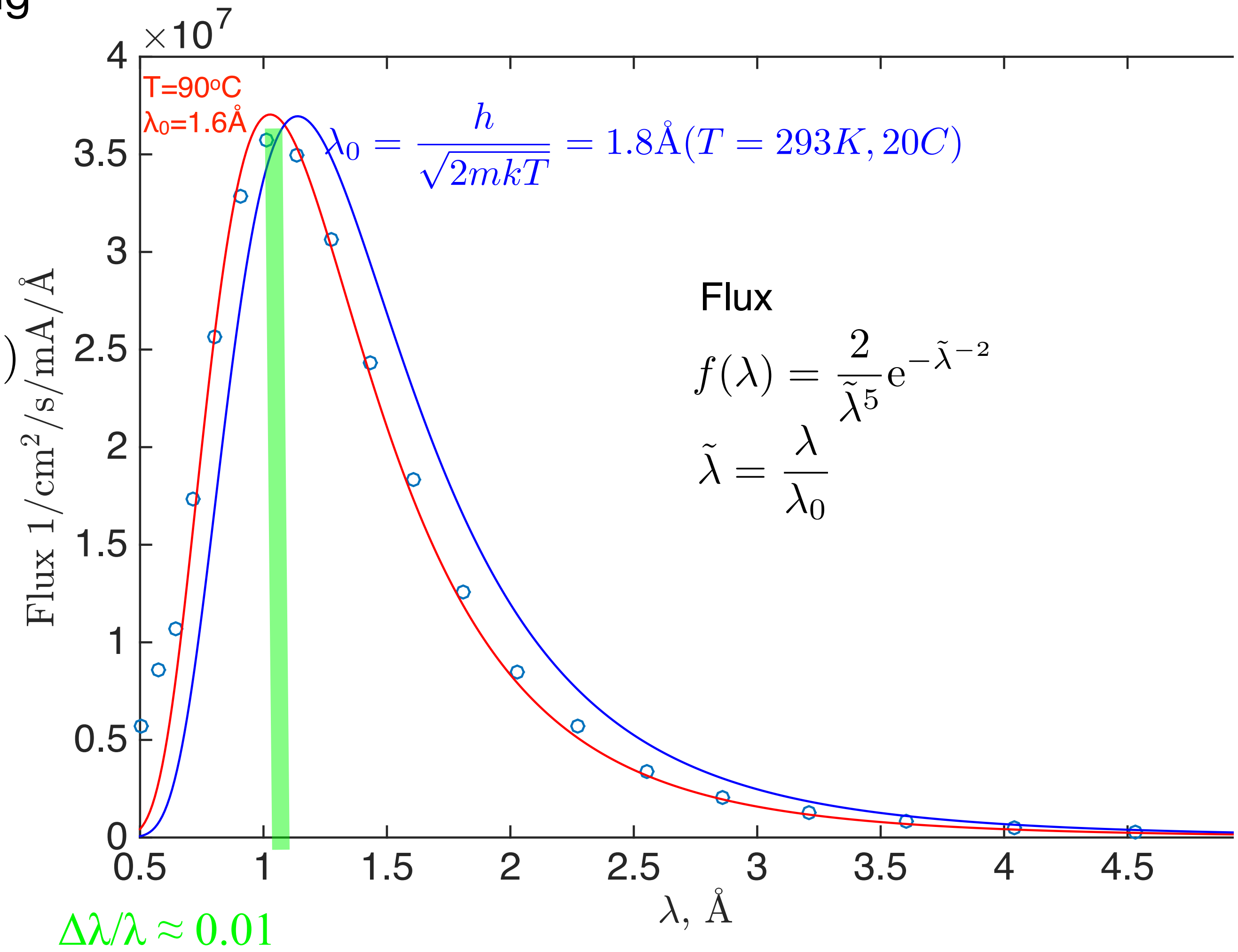


Monochromator cuts narrow wavelength range from the "white" flux. HRPT λ=0.94 - 2.96 Å

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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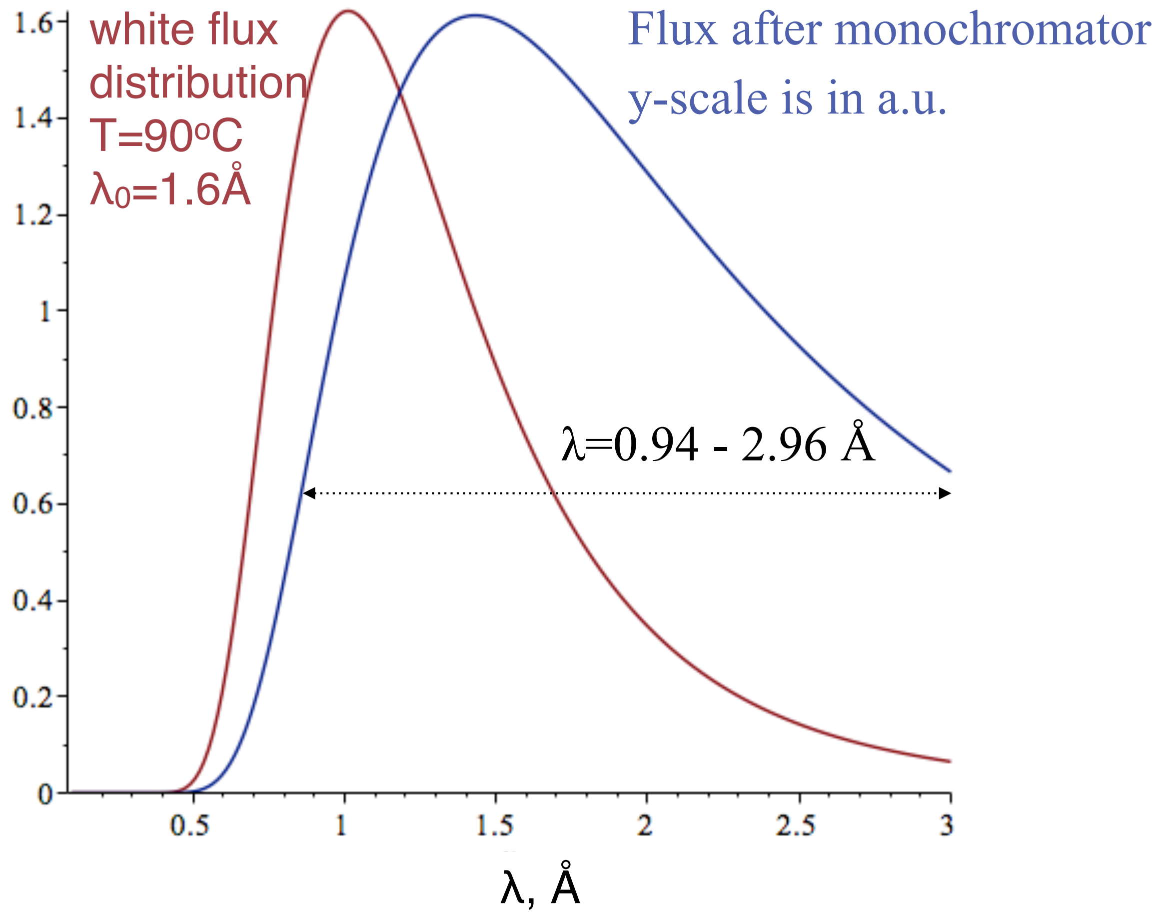
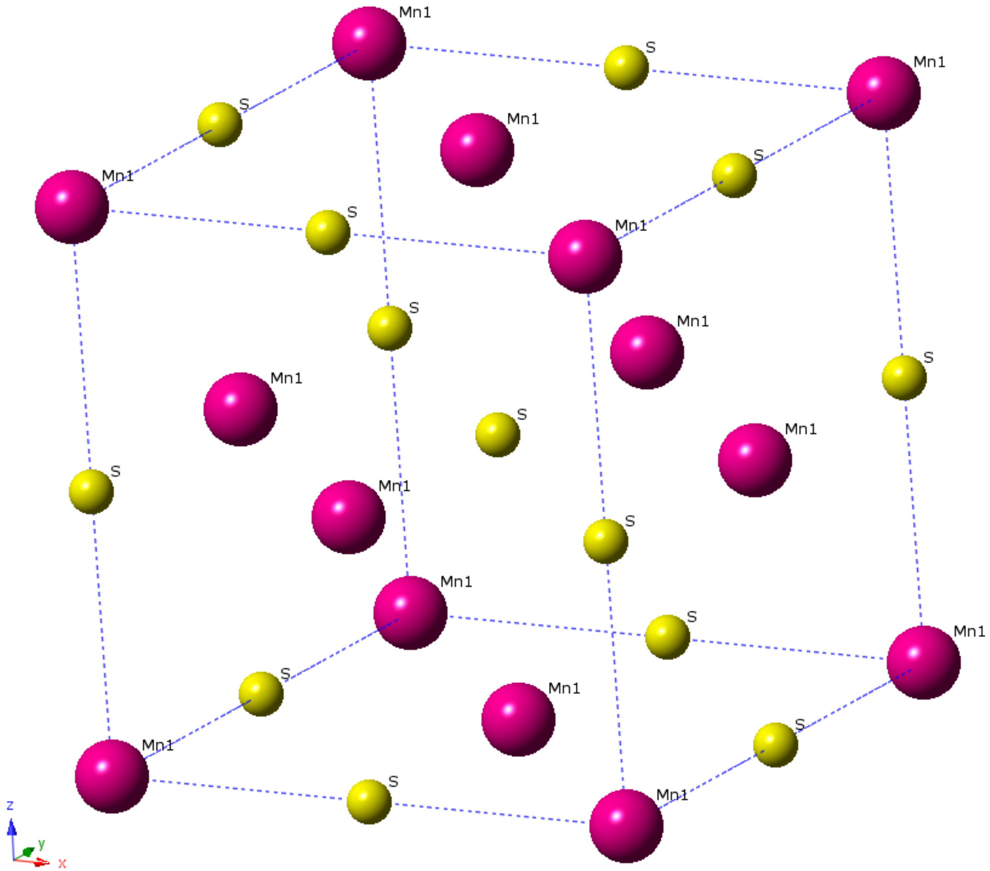
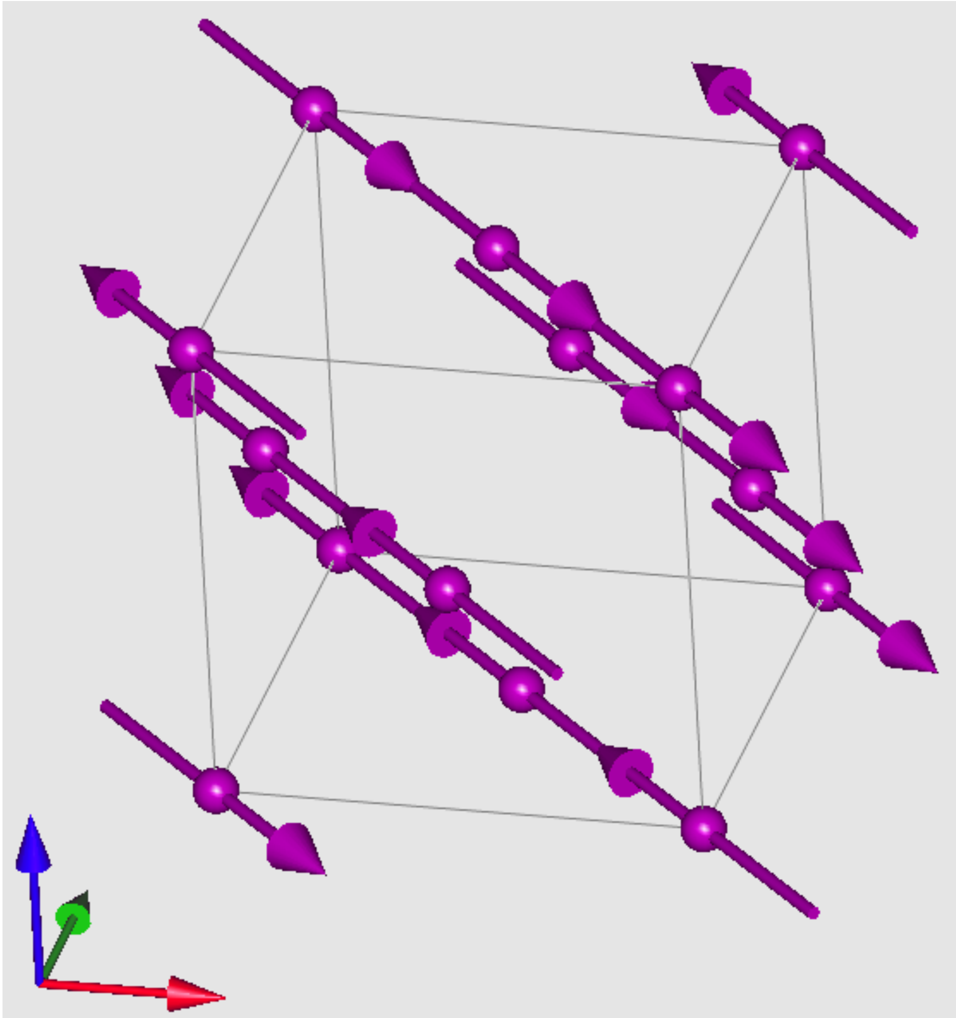


Reminder on nuclear and magnetic neutron structure factors

Approximate crystal and magnetic structures of MnS below Néel temperature





neutron diffraction experiment (λ=const)

Nuclear structure factor

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

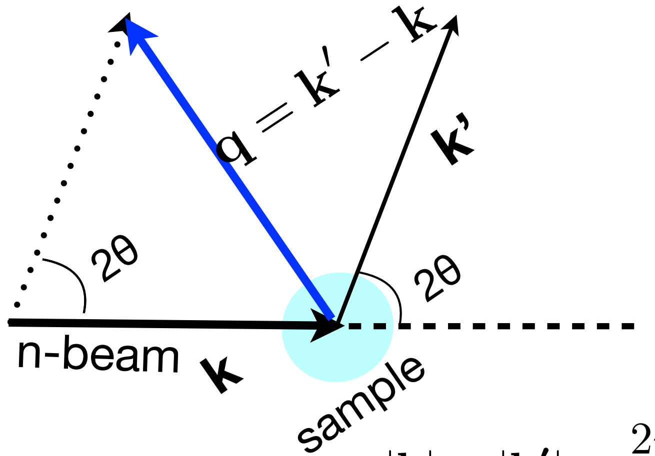
Magnetic structure factor

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

atom position and spin

Intensity in the detector

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



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

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

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

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

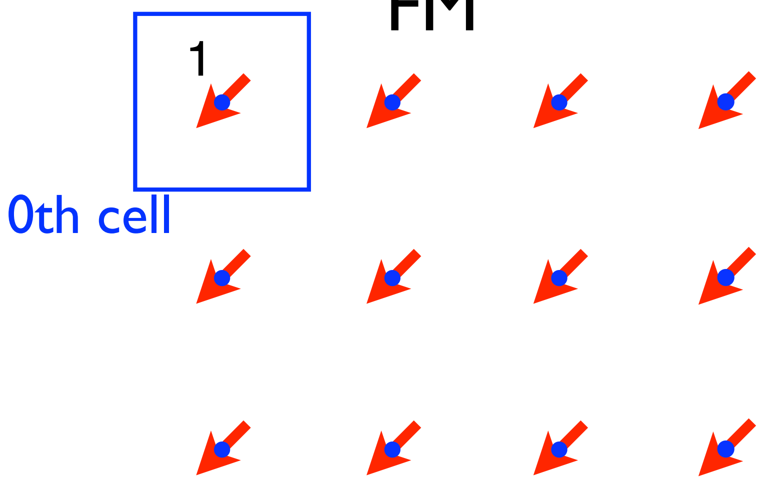
large q_{max} –> good spatial resolution

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

Magnetic structure

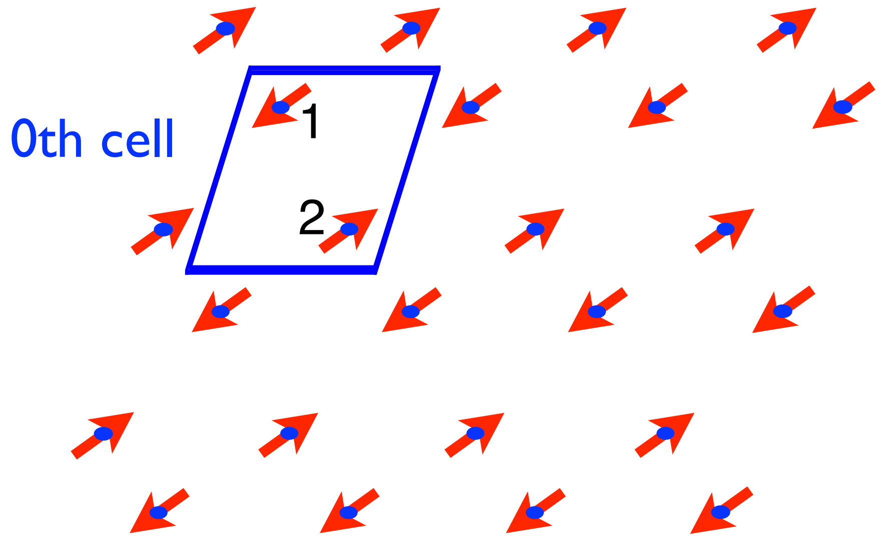
Examples

k=[0,0]
FM



$$\mathbf{S}_{01} = \mathbf{S}_x + \mathbf{S}_y$$

k=[0,0]
AFM



$$\mathbf{S}_{01} = \mathbf{S}_x + \mathbf{S}_y$$

$$\mathbf{S}_{02} = -\mathbf{S}_{01}$$

Examples of magnetic structures. Propagation vector formalism k≠0.

Magnetic mode S_0 is specified in zeroth block of the cell == parent cell without centering translations

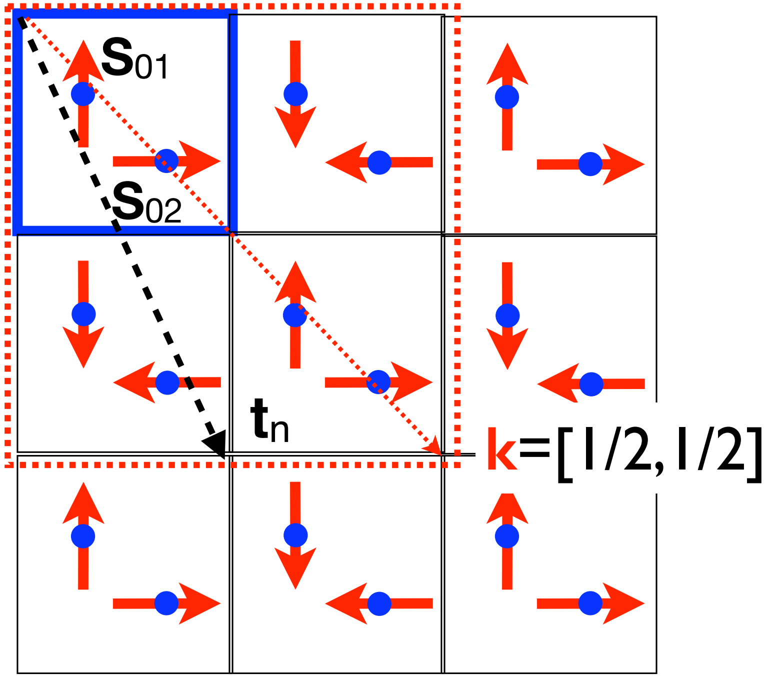
Magnetic moment below a phase transition

$$\mathbf{S}(\mathbf{t}_n) = Re\left(C\mathbf{S}_0 e^{2\pi i \mathbf{t}_n \mathbf{k}}\right) \quad \sim \cos(2\pi \mathbf{t}_n \mathbf{k} + \varphi)$$

amplitude or mixing coefficients (C)

magnetic mode ($\mathbf{S}_0$)

0th cell with many atoms in general



E.g., atom1 $\mathbf{S}_{01} = \mathbf{e}_y$

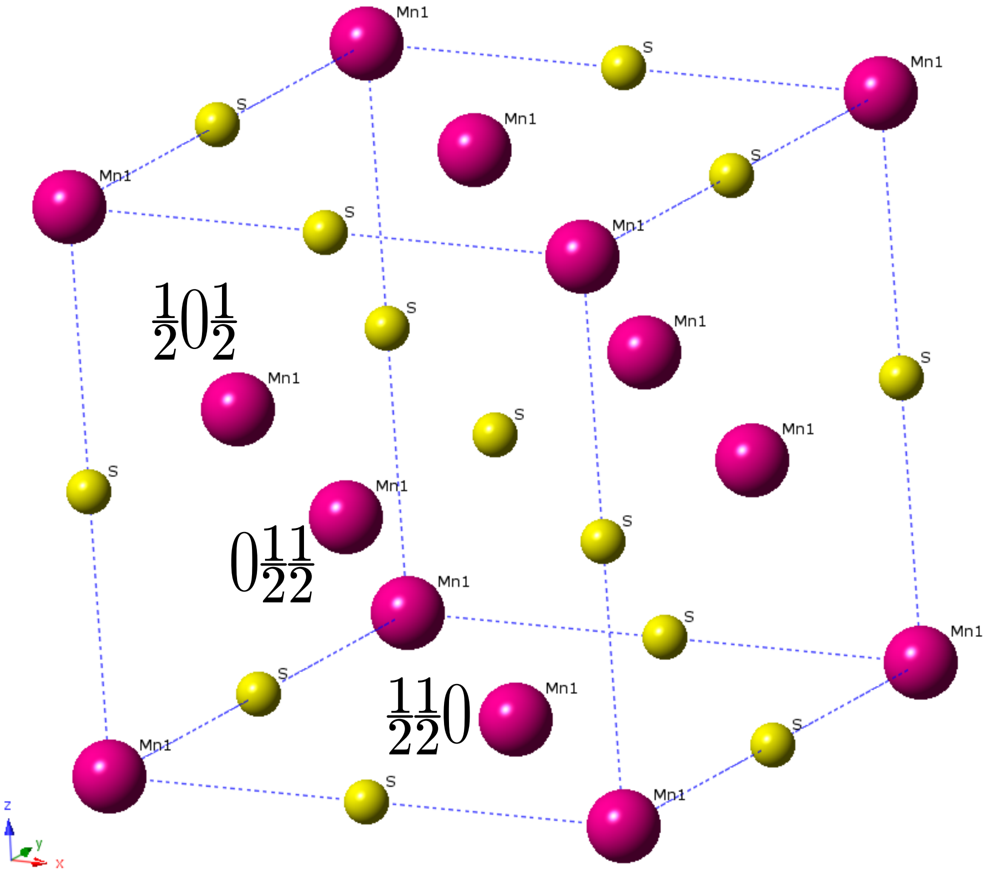
atom2 $\mathbf{S}_{02} = \mathbf{e}_x$

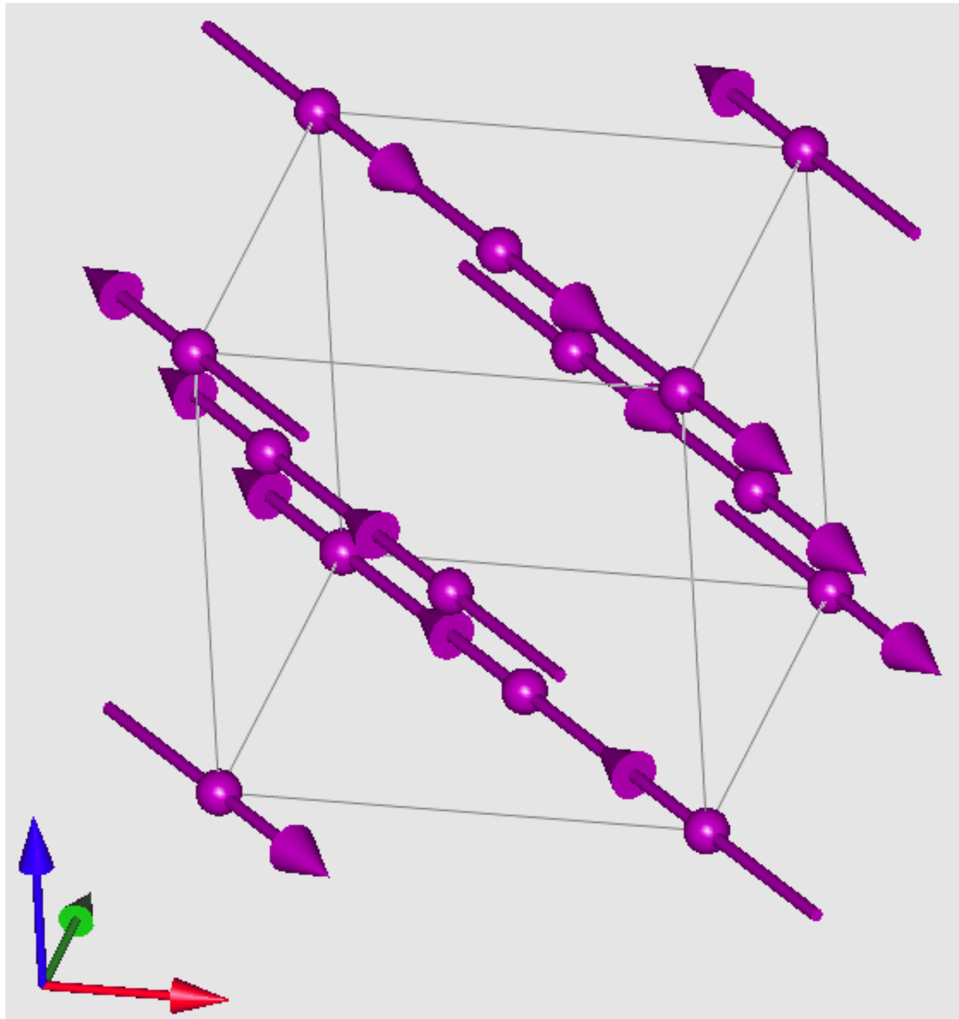
$$\mathbf{S}_1(\mathbf{t}_n) = C\mathbf{e}_y \cos(\pi(t_{nx} + t_{ny}))$$
$$\mathbf{S}_2(\mathbf{t}_n) = C\mathbf{e}_x \cos(\pi(t_{nx} + t_{ny}))$$

$$t_n = \mathrm{n}\cdot 1 \text{ or } \mathrm{n}\cdot\tfrac{1}{2}$$

Approximate crystal and magnetic structures of MnS below Néel temperature

single propagation vector
k=[1/2,1/2,1/2]





cubic, Fm-3m: Mn-atom in (000),
three other Mn-atoms are generated
by F-centering translations

Scattering from magnetic structure with propagation vector k

In ND experiment we measure correlators of Fourier transform of magnetic lattice

$$\frac{d\sigma}{d\Omega} \propto (\mathbf{F}(\mathbf{q}) \cdot \mathbf{F}^*(\mathbf{q}) + i\mathbf{P} \cdot [\mathbf{F}(\mathbf{q}) \times \mathbf{F}^*(\mathbf{q})]) \cdot \delta(\mathbf{H} \pm \mathbf{k} - \mathbf{q})$$

structure factor

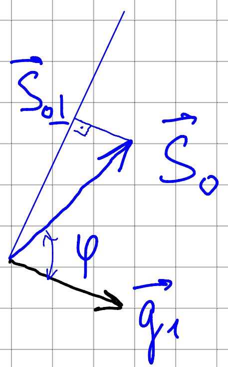
polarized neutron (chiral) term.

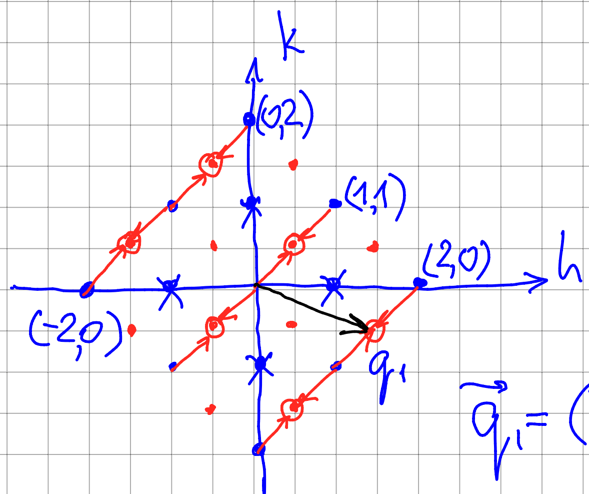
Bragg peak at $\mathbf{q} = \mathbf{H} \mp \mathbf{k}$

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

$$\vec{S}_\perp = \frac{\vec{q} \times \vec{S} \times \vec{q}}{|\vec{q}|^2}$$

$$|\vec{S}_\perp| = |\vec{S}_0| |\sin\varphi|$$





$\vec{H} = (h,k)$

$\vec{k} = (\frac{1}{2}, \frac{1}{2})$

new peaks at $\vec{H} \pm \vec{k}$

$\vec{q}_1 = (2,0) - \vec{k} = (\frac{3}{2}, -\frac{1}{2})$

. . . .

Practicum problems

MAGNETIC ORDER IN MnS

5. Practical course at SINQ

5.1 Manganese sulfide MnS

- rock salt crystal structure
- ionic crystal: Mn^{2+}, S^{2-}
- lattice constant a = 5.199 Å at T = 4.2 K
- space group $Fm\overline{3}m$
- electronic configuration of Mn^{2+}: $3d^5$
- Néel temperature T_N = 161 K
- long-range antiferromagnetic order: antiferromagnetic stacking along (111) of ferromagnetic planes
- therefore doubling of the magnetic unit cell with respect to the crystallographic unit cell

Task 1: positions of nuclear Bragg peaks, indexing of the peaks

5.2 Neutron diffraction of MnS at room temperature

For all measurements at HRPT we will use $\lambda = 1.886 Å$

$\lambda = 2d_{hkl} \sin\theta_{hkl}$ Bragg law (1)

λ: neutron wavelength, d_{hkl}: d-spacing of scattering plane hkl
θ_{hkl}: (half) scattering angle of reflection hkl in diffraction pattern

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2)$$

a: cubic lattice constant, h, k, l indices of scattering plane

$$\vec{\tau}_{hkl} = \frac{2\pi}{a}(h, k, l) \qquad \vec{\tau}_{hkl} \equiv \vec{H} \quad (3)$$

corresponding vector in reciprocal space ; a node of reciprocal lattice

(1)

Tasks:

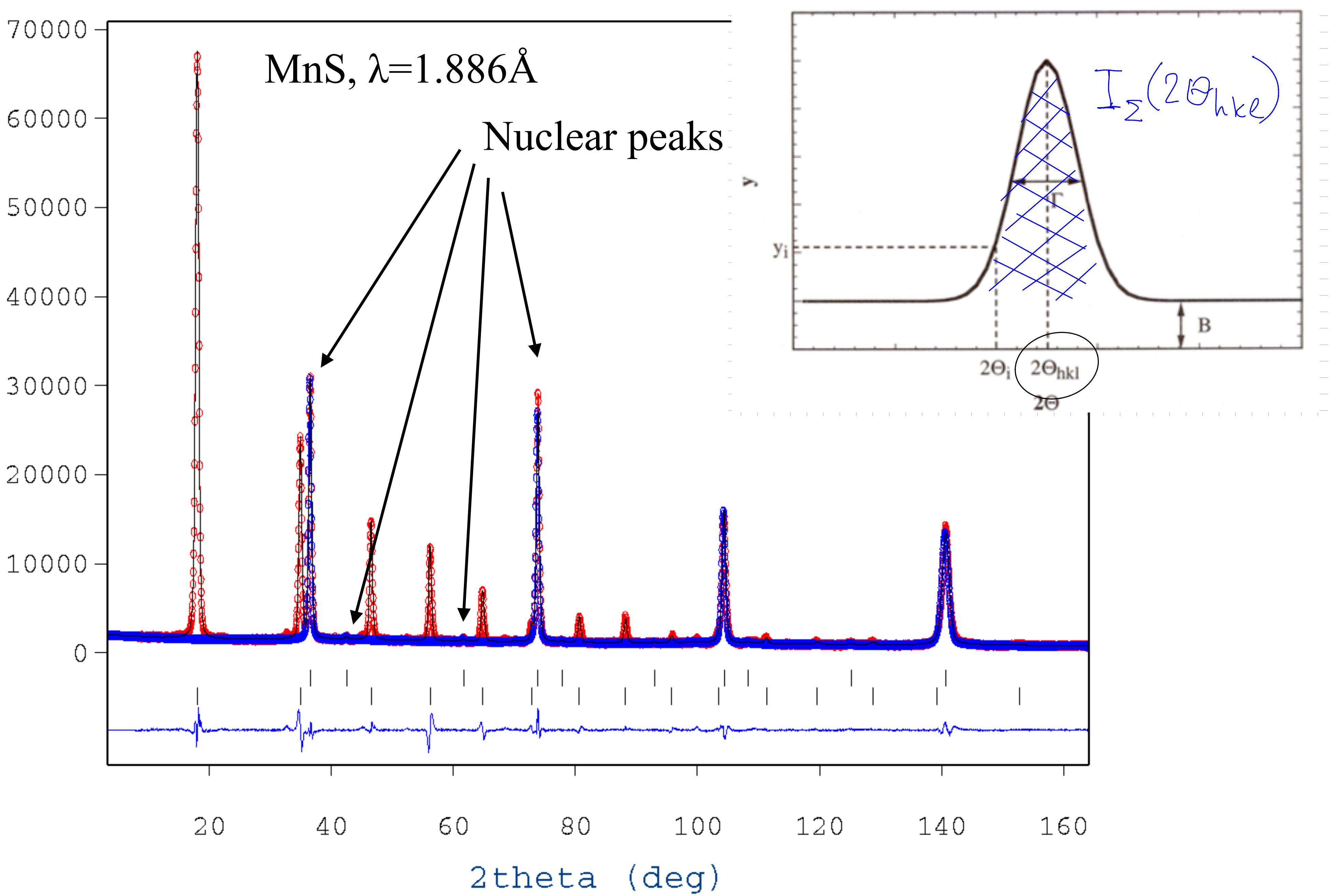
- measure a diffraction pattern of MnS at T = 300 K in the paramagnetic state [$I(2\theta)$; $> T_N \simeq 150 K$]
- determine peak positions Θ, d-spacings and indices (h, k, l) for ~~all~~ first 4 observed peaks

Coherent elastic cross section for nuclear neutron diffraction:

$$\frac{d\sigma}{d\Omega} \sim \sum_{\vec{\tau}_{hkl}} |F_{\vec{\tau}_{hkl}}|^2 \delta(\vec{Q} - \vec{\tau}_{hkl}) \quad (4) \rightarrow \vec{Q} = \vec{\tau}_{hkl} \qquad |\vec{Q}| = \frac{4\pi \sin\theta}{\lambda}$$

$\vec{Q}$: scattering vector, $\vec{\tau}_{hkl}$: reciprocal lattice vector defining scattering planes
$\delta(\vec{Q} - \vec{\tau}_{hkl})$ → **peak position given by crystal lattice (unit cell)**

All the calculations/fits of experimental integrated intensities and peak positions will be done with ‘fit’ program under HRPT linux-computer



Task 2a: Calculation of structure factors and Bragg peak intensities and comparison with experiment

Coherent elastic cross section for nuclear neutron diffraction:

$$\frac{d\sigma}{d\Omega} \sim \sum_{\vec{\tau}_{hkl}} |F_{\vec{\tau}_{hkl}}|^2 \delta(\vec{Q} - \vec{\tau}_{hkl})$$ (4) → $\vec{Q} = \vec{\tau}_{hkl}$ $|\vec{Q}| = \frac{4\pi \sin\theta}{\lambda}$

$\vec{Q}$: scattering vector, $\vec{\tau}_{hkl}$: reciprocal lattice vector defining scattering planes

$\delta(\vec{Q} - \vec{\tau}_{hkl})$ → **peak position given by crystal lattice (unit cell)**

$F_{\vec{\tau}_{hkl}}$: structure factor of unit cell

$$F_{\vec{\tau}_{hkl}} = \sum_{\vec{d}_i} \left(b_{\vec{d}_i} e^{i\vec{\tau}_{hkl}\cdot\vec{d}_i} \cdot e^{-B_i (Q/4\pi)^2} \right)$$, we assume $B=0$, but actually $B \simeq 0.8\,Å^2$ @ RT (5)

$\vec{d}_i$: atomic coordinate of i-th atom in real space, sum runs over all atoms in unit cell

$b_{\vec{d}_i}$: scattering length of atom at position $\vec{d}_i$

Intensity ~ $|F_{\vec{\tau}_{hkl}}|^2$ → **peak intensity is mainly given by arrangement of atoms in unit cell**

The sum runs over all atoms in unit cell.

For MnS: b_{Mn} = -3.73 fm, b_S = 2.85 fm   femto or fermi: 1 fm = 10^{-13} cm = 10^{-15} m

$\vec{d}$-vectors:	Mn:	$\vec{d}_1$= a(0, 0, 0)	$\vec{d}_2$= a(0, ½, ½)
		$\vec{d}_3$= a(½, 0, ½)	$\vec{d}_4$= a(½, ½, 0)
	S:	$\vec{d}_5$= a(½, ½, ½)	$\vec{d}_6$= a(½, 0, 0)
		$\vec{d}_7$= a(0, ½, 0)	$\vec{d}_8$= a(0, 0, ½)

F-centering. (8)

Task 2b: Calculation of structure factors and Bragg peak intensities and comparison with experiment

$I_{\Sigma}(2\theta)$ is measured in the experiment $|\vec{Q}| = \frac{4\pi \sin\theta}{\lambda}$

For cylindrical geometry of the powder sample container the integrated intensity of the scattered neutrons of the Bragg peak at $|\vec{Q}|$ is given by

$$I(Q) = C \cdot A(\theta) \cdot L(\theta) \cdot \frac{d\sigma}{d\Omega} = C \cdot A(\theta) \cdot L(\theta) \cdot |F(Q)|^2 \cdot mult$$

assume: $A(\theta) \simeq 1$ (6)

C: scale factor, $A(\theta)$: absorption factor, $L(\theta)$: Lorentz factor, *mult*: multiplicity

$$L(\theta) = \frac{1}{\sin\theta \sin 2\theta} \quad (7)$$

The Lorentz factor $L(\theta)$ is a geometrical correction depending on the scattering geometry.

(2)

Tasks:

- calculate $|F_{\vec{\tau}_{hkl}}|^2$ for (h,k,l) = (1,1,1), calculate the multiplicity → (111), (-111), ...
- calculate $|F_{\vec{\tau}_{hkl}}|^2$ for (h,k,l) = (2,0,0), calculate the multiplicity
- compare ratio of $I(|\vec{\tau}_{111}|) / I(|\vec{\tau}_{200}|)$ with the measured intensity ratio

Task 3: Indexing of the magnetic Bragg peaks. Calculation of magnetic structure factors and determination of the value and direction of the Mn-spins.

5.3 Neutron diffraction of MnS in the magnetically ordered state

3

Tasks:

- measure a neutron diffraction pattern of MnS at T = 50 K (or lower T) in the magnetically ordered state
- compare this date with the paramagnetic pattern at room temperature
- index the magnetic peaks, i.e. find (h, k, l) for ~~each~~ first 3 magnetic peak
- based on the indices, what is the magnetic unit cell compared to the crystallographic one
- Using eq. (6) for (111)-peak and eq. (10) for $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ magnetic peak determine $\vec{\mu}$. Consider $\vec{\mu} \parallel (111)$ in calculations
- Which direction of $\vec{\mu}$ can be excluded?

Task 3: Indexing of the magnetic Bragg peaks. Calculation of magnetic structure factors and determination of the value and direction of the Mn-spins.

Coherent elastic cross section for antiferromagnetic order

$$\frac{d\sigma}{d\Omega} \sim \sum_{\vec{\tau}_{M,hkl}} |F_{M,hkl}|^2 \delta(\vec{Q} - \vec{\tau}_{M,hkl})$$

$F_{M,hkl}$: antiferromagnetic structure factor

Formula (10) is actually formula (6) with $|\vec{F}_{M\perp}|$ instead of $|F|^2$ with the same scale factor C!

The intensity of the magnetic Bragg peak at $|\vec{Q}_M|$ is

$$I(Q_M) = C \cdot A(\theta) \cdot L(\theta) \cdot |F_{M\perp}|^2 \cdot mult \quad (10)$$

$A(\theta) = 1$

multiplicity is 2 for $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ peak. Can you explain why?

where

$$\vec{F}_{M\perp} = \frac{1}{2} r_0 \sum_{j=1}^{4} e^{i\vec{Q}_M \vec{d}_j} \vec{\mu}_{j\perp} \quad (11) \quad \text{and} \quad \vec{\mu}_\perp = \left(\vec{\mu} - \frac{\vec{Q}_M(\vec{\mu}\cdot\vec{Q}_M)}{Q_M{}^2}\right) \quad (12)$$

where $\vec{\mu}$ is the magnetic moment in units μ_B and r_0 = -0.54·10^{-12} cm, $\vec{Q}_M \equiv \vec{\tau}_{M,hkl}$

The sum runs over Mn-atoms.

$\vec{\mu}_1 \uparrow\downarrow \vec{\mu}_{2,3,4}$ Can you explain why?