Principles of X-ray and Neutron Scattering

Lecture 7: Neutrons & Scattering to Determine Structure

14. 02. '24

Lectures by: Prof. Philip Willmott, Prof. Johan Chang and **Dr. Artur Glavic**

Course Outline

Monday	Tuesday	Wednesday	Thursday	Friday
Lecture 1 10-10h45 Philip	**Lecture 4** 10-10h45 Philip	**Lecture 7** 10-10h45 Artur	**Lecture 10** 10-10h45 Artur	**Lecture 13** 10-10h45 Johan
Lecture 2 11-11h45 Philip	**Lecture 5** 11-11h45 Philip	**Lecture 8** 11-11h45 Artur	**Lecture 11** 11-11h45 Artur	**Lecture 14** 11-11h45 Johan
Lunch - Mensa	**Lunch - Mensa**	**Lunch - Mensa**	**Lunch - Mensa**	**Lunch - Mensa**
Lecture 3 13h00-13h45 Philip	**Lecture 6** 13h00-13h45 Philip	**Lecture 9** 13h00-13h45 Artur	**Lecture 12** 13h00-13h45 Artur	**Lecture 15** 13h00-13h45 Johan
		Exercise Class 14h30-16		Exercise Class 14h30-16

X-ray scattering

Neutron Scattering

Resonant x-ray scattering

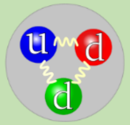
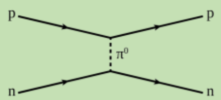
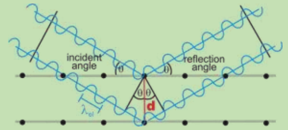
Neutron Lectures:

7: Neutrons & Scattering to Determine Structure
8: Inelastic Neutron Scattering to Investigate Dynamics
9: Magnetic Scattering
10: Neutron Polarization Analysis
11: Studying quantum matter for nanoscale applications
12: Neutron Instrument Development

Lecture 8: Neutrons & Scattering to Determine Structure

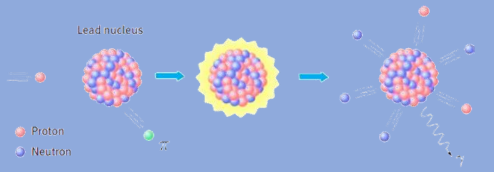
Theoretical Background

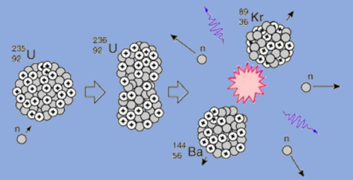
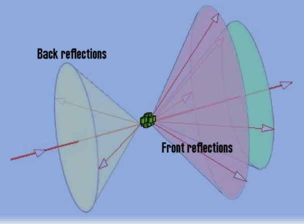
- Motivation and properties of the neutron
- Scattering of periodic and deviating atomic structures

Practical Implementation

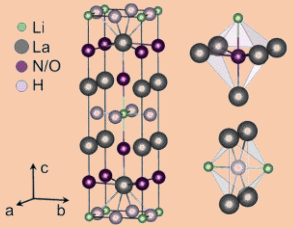
- Neutron sources and basic technologies
- Diffraction techniques



Example Application

- Locate light elements in hydride crystals

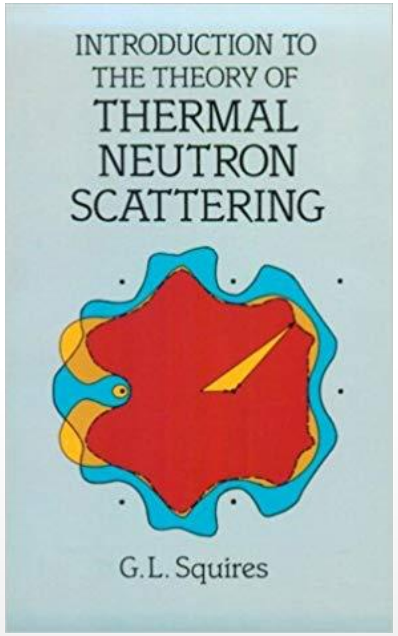


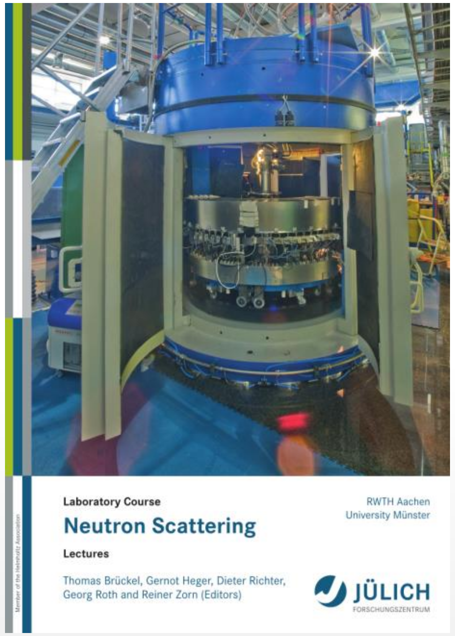
Further Reading

- “Introduction to the Theory of Thermal Neutron Scattering”
  G. L. Squires
  Dover Publication (1978)

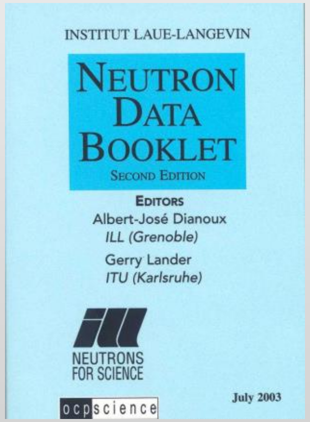
- “Theory of Neutron Scattering from Condensed Matter” Vol.I/II.
  S. W. Lovesey
  Oxford Science Publications (1984).

- “Neutron Scattering”
  T. Brückel, et al. (2012) / Available Open Access:
  https://juser.fz-juelich.de/record/136390/files/Schluesseltech_39.pdf

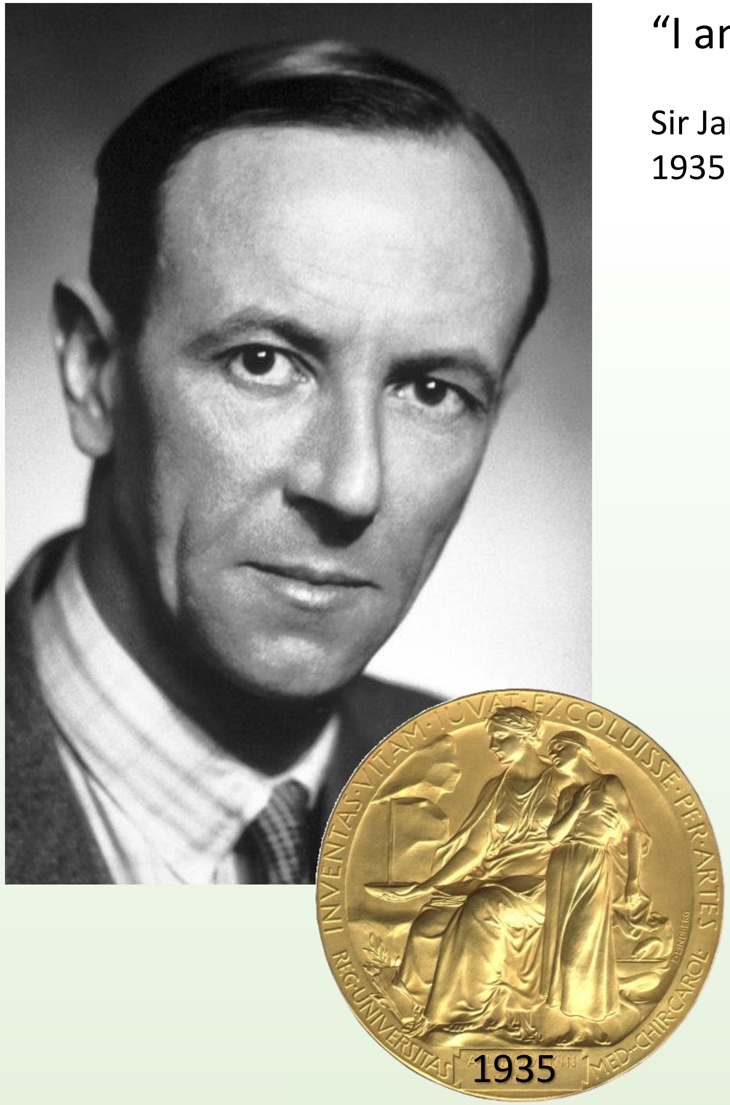




- “Neutron Data Book”
  Albert-José Dianoux and Gerry Lander
  https://www.ill.eu/fileadmin/user_upload/ILL/1_About_ILL/Documentation/NeutronDataBooklet.pdf

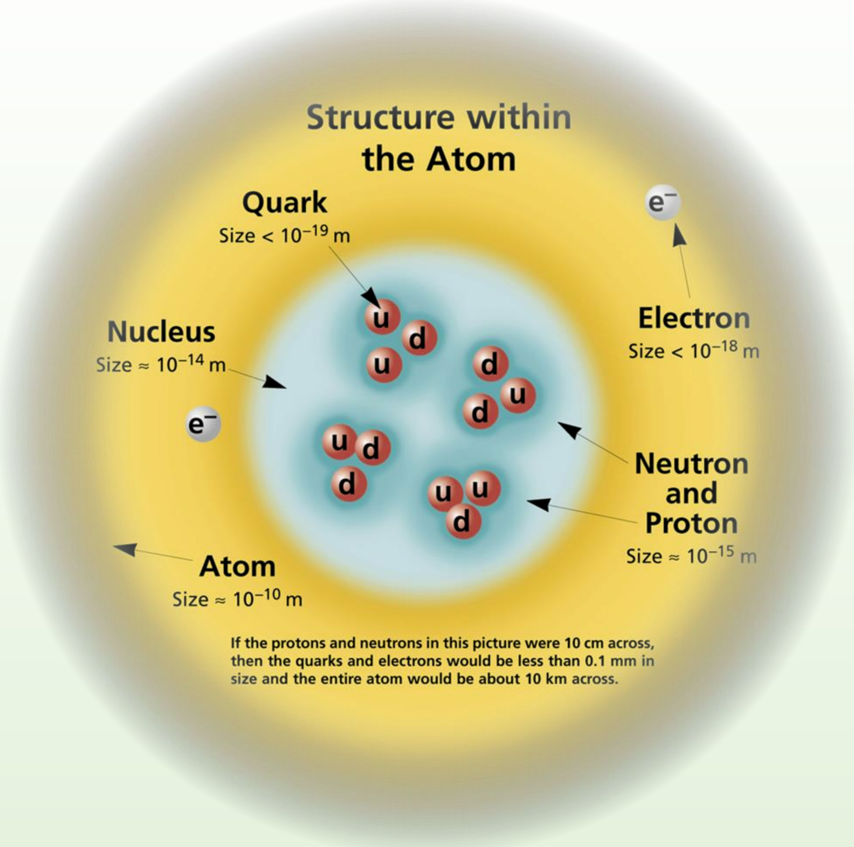


Reminder: Why Neutrons?

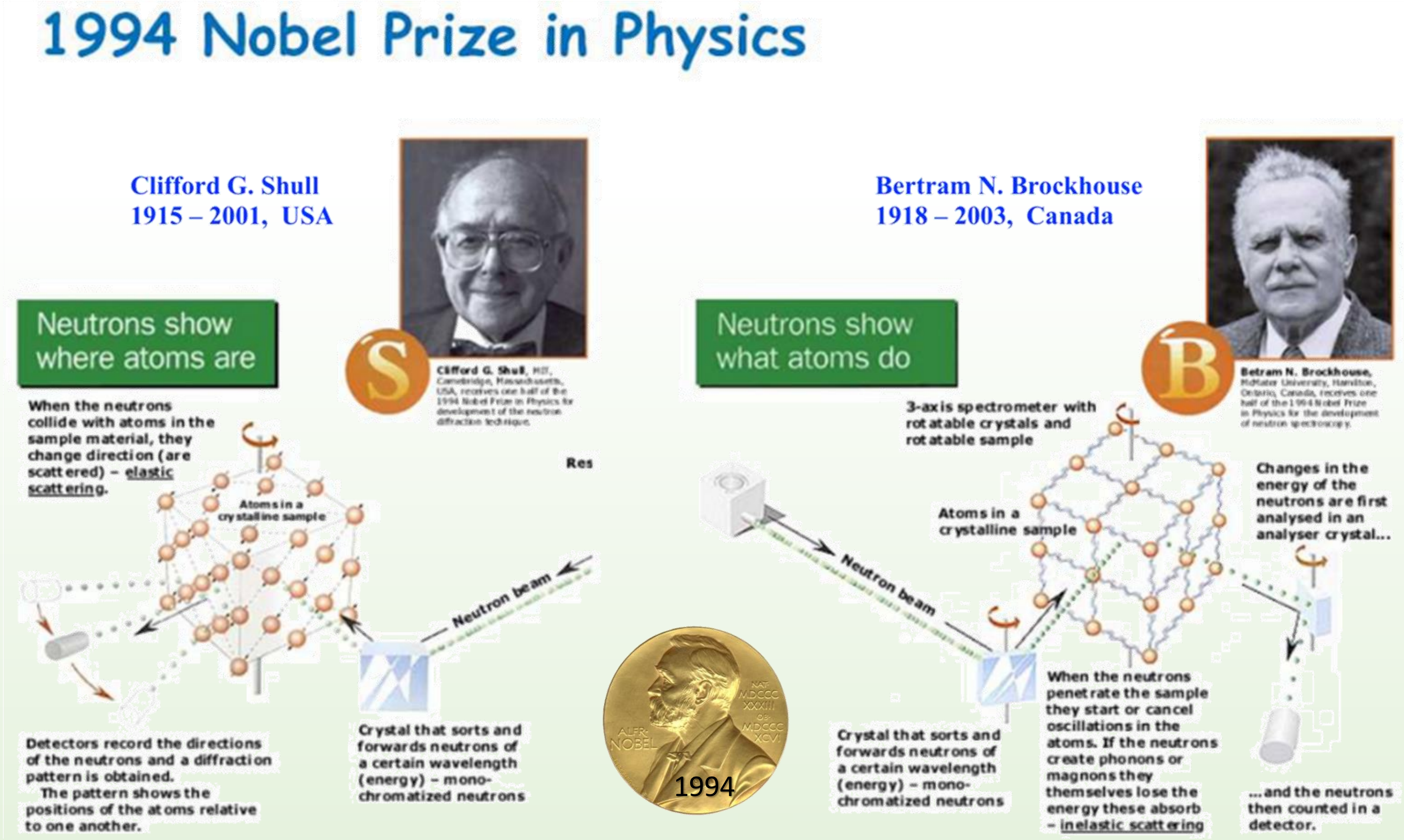


“I am afraid neutrons will not be of any use to any one.”

Sir James Chadwick
1935 Nobel Laureate in Physics



Reminder: Why Neutrons?



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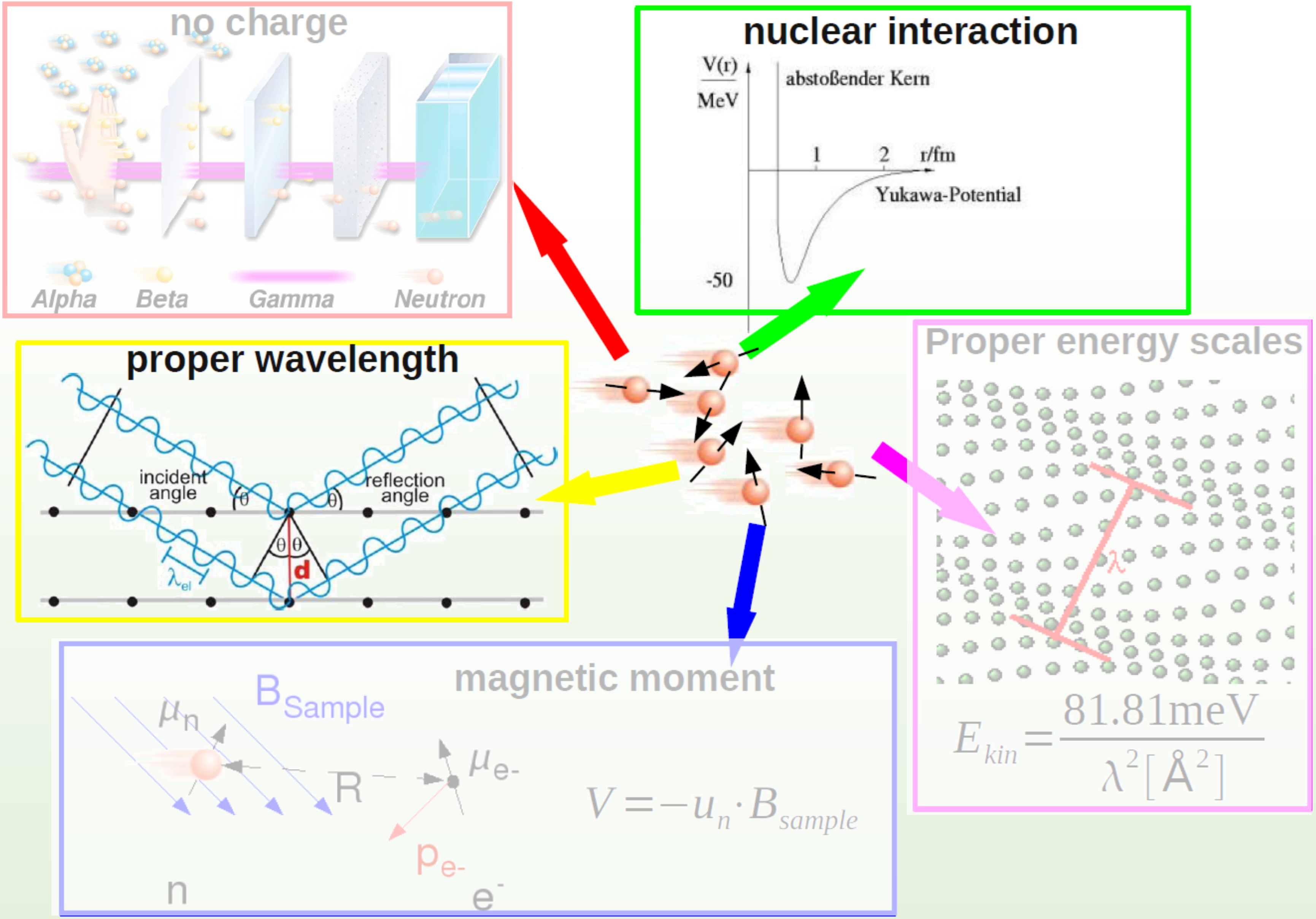
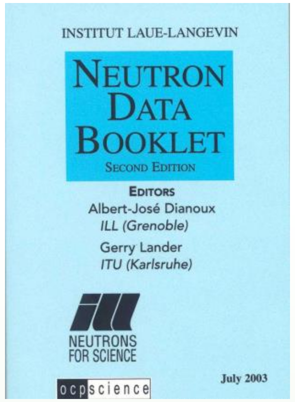
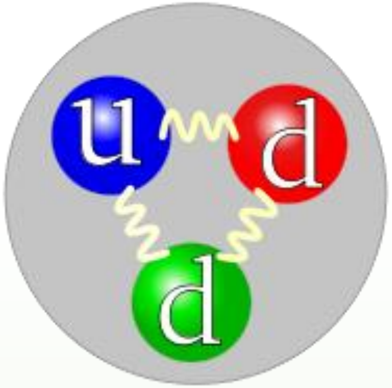


Properties of Neutrons

mass m	$1.674928(1) \cdot 10^{-27}$ kg
charge	0
spin s	-h/2
magnetic moment μ	$-9.6491783(18) \cdot 10^{-27}\ JT^{-1}$
β-decay lifetime τ	885.9 ± 0.9 s
confinement radius	R = 0.7 fm





➔

Wavelength: $$\lambda_n = \sqrt{h^2/2m_nE}$$

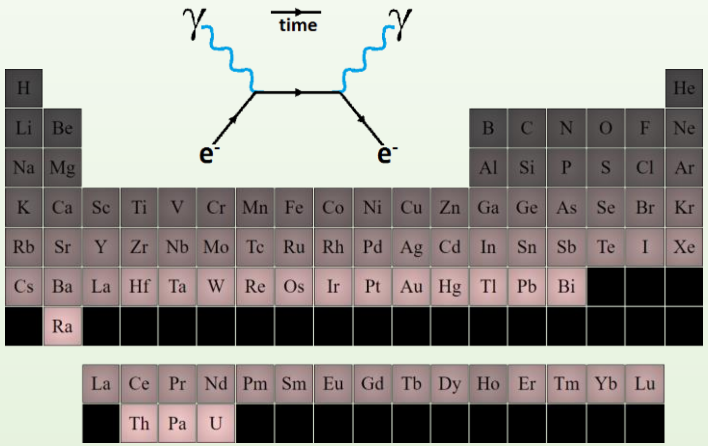
$$\lambda_n(25\,meV) = 1.81\,\mathring{A}$$

Interactions:

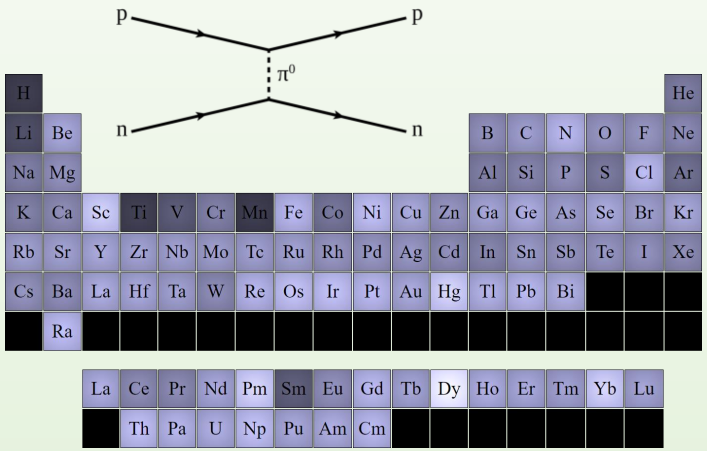
strong-force
&
magnetic

$$\mu_n = -1.913\mu_N$$

x-rays

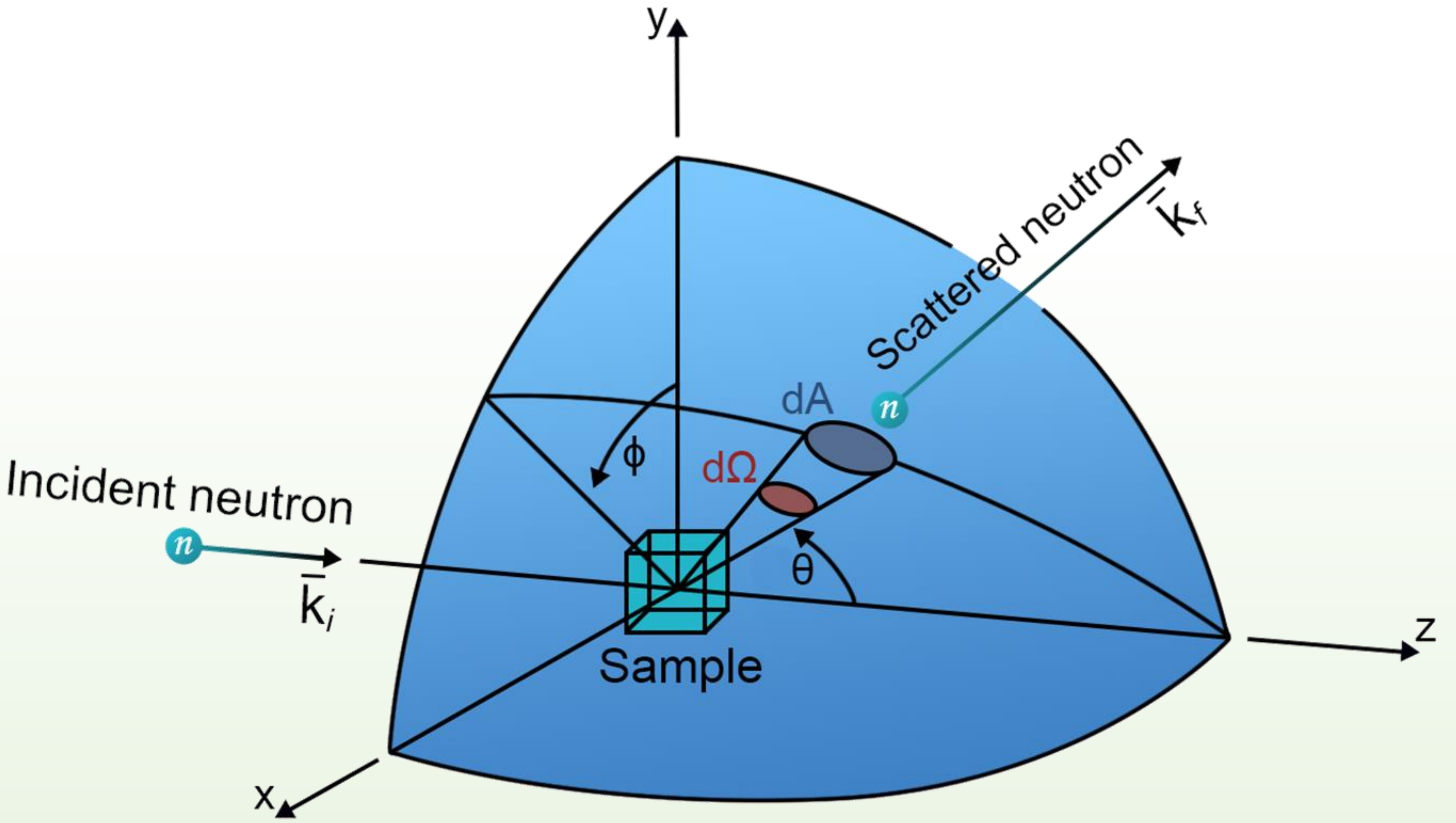


neutrons



https://slddb.esss.dk/slddb/periodic_table

Differential Scattering Cross-Section



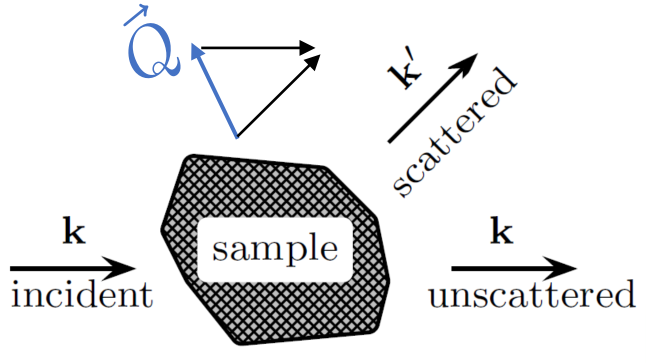
$$\frac{d\sigma}{d\Omega} = \frac{\text{“The number of particles scattered into solid angle } d\Omega \text{ per unit of time”}}{\text{“The number of incident particles per unit of time and area”}}$$

Scattered Neutron Wave

Schrödinger's equation: $\left(-\frac{\hbar^2\Delta}{2m_{red}}+V(\vec{r})\right)\phi(\vec{r})=E\phi(\vec{r})$

Only elastic scattering: $E=\frac{\hbar^2k^2}{2m_{red}}$ $\quad V(\vec{r})=\frac{\hbar^2}{2m_{red}}U(\vec{r})$

➔ Scattering wave equation: $\left(\Delta+k^2\right)\phi(\vec{r})=U(\vec{r})\phi(\vec{r})=\chi$



(same form derived for x-rays from Maxwell's equations)

Ansatz: Introducing a Green's function

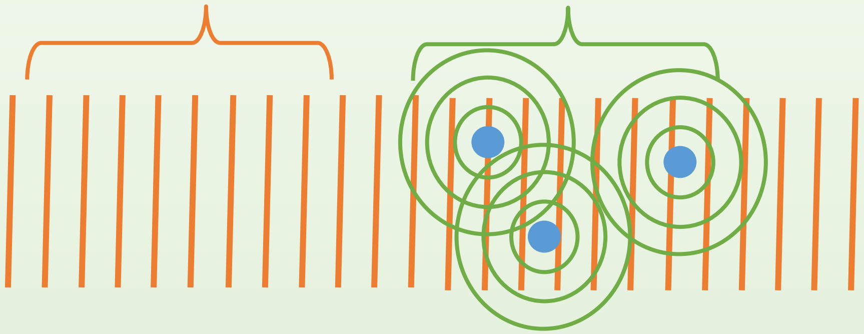
$$(\Delta+k^2)G(\vec{r}-\vec{r}')=\delta(\vec{r}-\vec{r}')$$

$$G(\vec{r}-\vec{r}')=\frac{1}{4\pi}\frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}$$

$$\phi_0(\vec{r})=e^{i\vec{k}\vec{r}}$$

➔ integral wave equation

$$\phi(\vec{r})=\phi_0(\vec{r})+\int G(\vec{r}-\vec{r}')U(\vec{r}')\phi(\vec{r}')\,d^3\vec{r}'$$

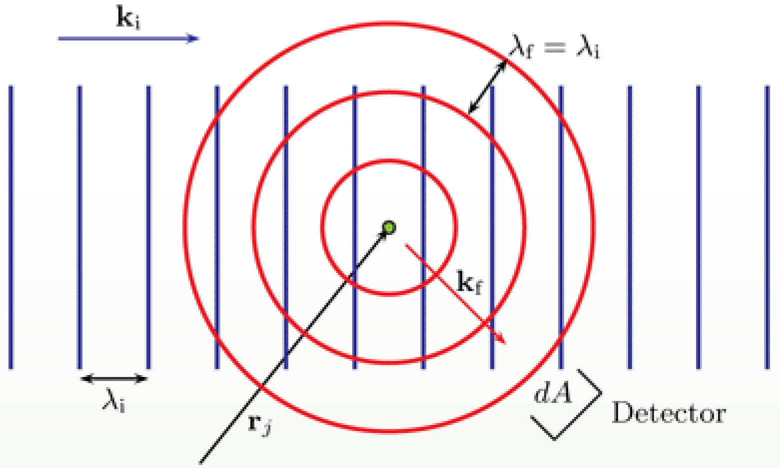


First Born Approximation

Solving integral equation by iterative approach:

$$\phi_{n+1}(\vec{r}) = \phi_0(\vec{r}) + \int G(\vec{r}-\vec{r'})U(\vec{r'})\phi_n(\vec{r'})\ d^3\vec{r'}$$

$$\phi_0\left(\vec{r}\right) = e^{i\vec{k}\vec{r}}$$

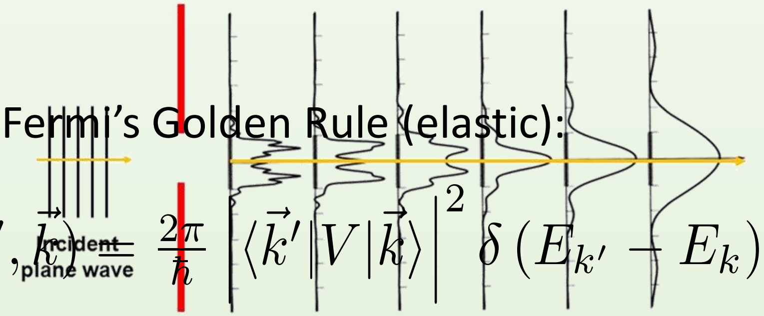


First non-trivial solution: (1st Born approximation)

$$\phi_1(\vec{r}) = e^{i\vec{k}\vec{r}} + \int \frac{1}{4\pi}\frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}U(\vec{r'})e^{i\vec{k}\vec{r}'}\ d^3\vec{r}'$$

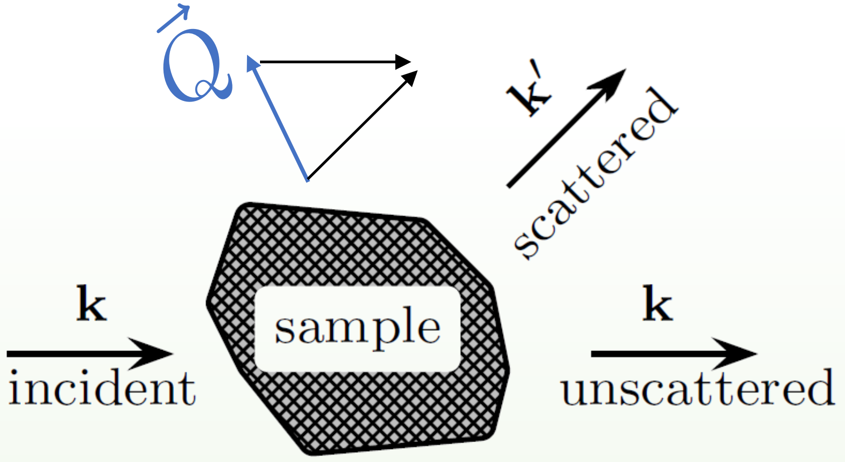
Far field (Fraunhofer) approximation: $|\vec{r}-\vec{r'}| \approx r - \frac{\vec{k_f}}{k}\vec{r'}$

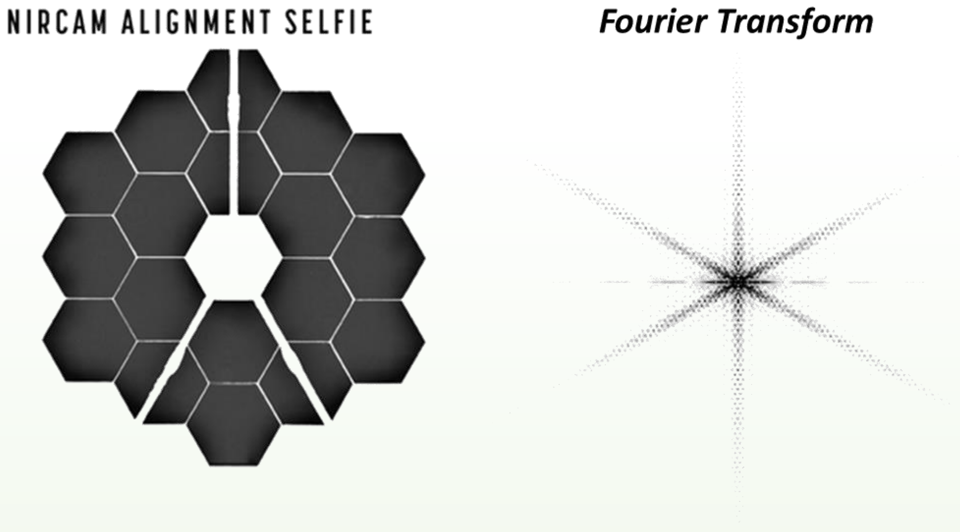
Fermi's Golden Rule (elastic):



➔ $\phi_1(\vec{r}) = e^{i\vec{k}\vec{r}} + \frac{C\ e^{ik|\vec{r}-\vec{r}'|}}{4\pi|\vec{r}-\vec{r}'|}\int e^{-i\vec{k}'\vec{r}'}V(\vec{r'})e^{i\vec{k}\vec{r}'}\ d^3\vec{r}' \Leftrightarrow \Gamma(\vec{k}',\vec{k}) = \frac{2\pi}{\hbar}\left|\langle\vec{k}'|V|\vec{k}\rangle\right|^2\delta\left(E_{k'}-E_k\right)$

First Born Approximation





$$\Phi(\vec{Q}) = \frac{m_n}{2\pi\hbar^2} \int V(\vec{r'}) e^{-i\vec{Q}\vec{r'}} \; d^3\vec{r'}$$

The Scattered wave is the Fourier-transform of scattering potential!

Recap: Fourier Transform

$$f(\vec{x}) = \frac{1}{2\pi}\int \mathscr{F}(\vec{Q})e^{i\,\vec{Q}\cdot\vec{x}}d^3\vec{q}$$

forward transform

backward transform

$$\mathscr{F}(\vec{Q}) = \int f(\vec{x})e^{-i\,\vec{Q}\cdot\vec{x}}d^3\vec{x}$$

$$f\left(a\vec{x}\right) \Rightarrow \frac{1}{|a|}\mathscr{F}\left(\frac{\vec{Q}}{|a|}\right)$$

inverse scaling

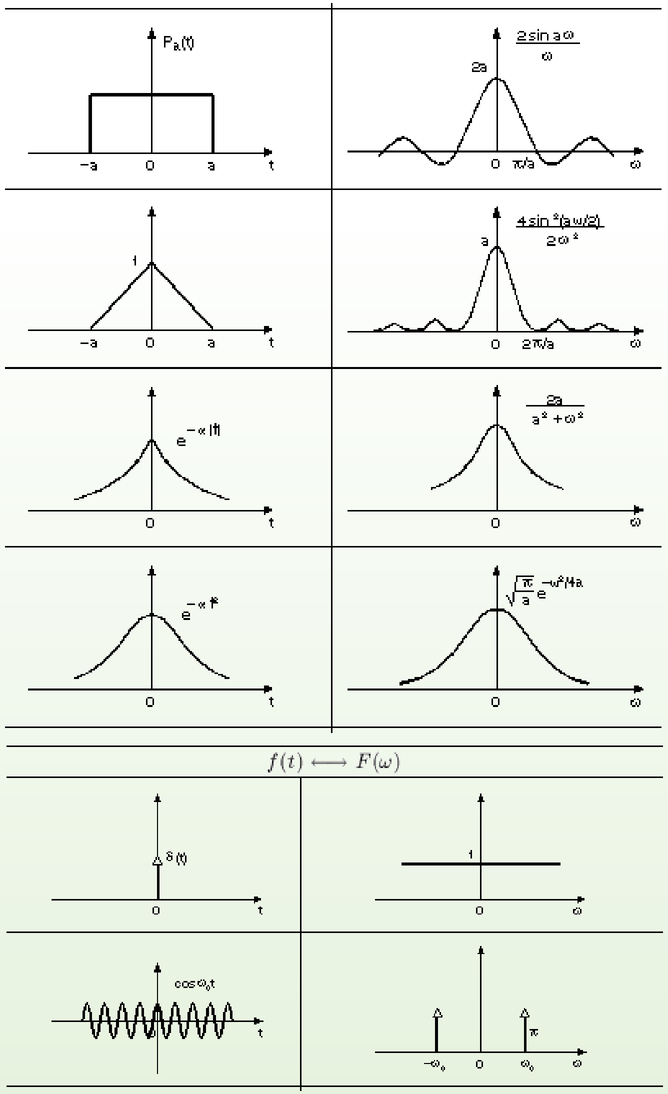
$$f^*\left(\vec{x}\right) \Rightarrow \mathscr{F}^*\left(-\vec{Q}\right)$$

inverse complex

➔ FT of real function symmetric around 0

$$f\left(\vec{x}-\vec{x}_0\right) \Rightarrow \mathscr{F}\left(\vec{Q}\right)e^{-i\,\vec{Q}\cdot\vec{x}_0}$$

translation ➔ phase factor



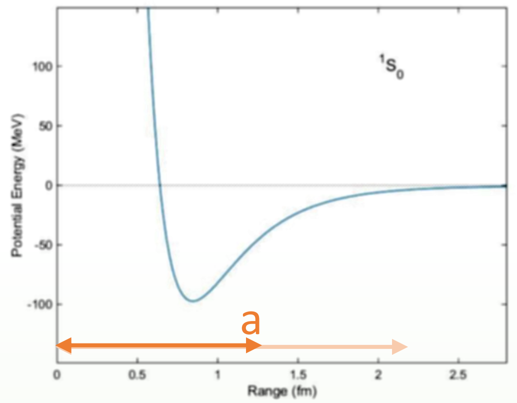
Convolution theorem:

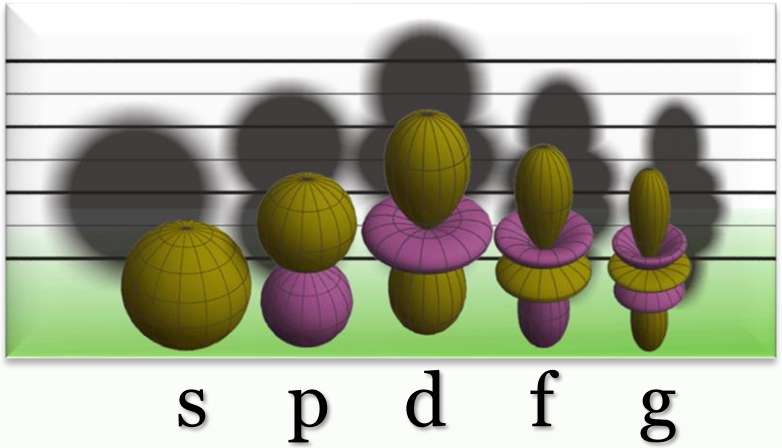
$$f\left(\vec{x}\right)\cdot g\left(\vec{x}\right) \Rightarrow \int \mathscr{F}\left(\vec{\xi}\right)\mathscr{G}\left(\vec{Q}-\vec{\xi}\right)d\vec{\xi} = \mathscr{F}\left(\vec{Q}\right)*\mathscr{G}\left(\vec{Q}\right)$$

Scattering from Single Nucleus

$$\color{orange}{a}\color{black}{k} = \frac{10^{-15}\,\mathrm{m}}{10^{-10}\,\mathrm{m}} << 1$$

➔ s-wave: $\sigma_{tot} = \int d\Omega \frac{d\sigma}{d\Omega} = 4\pi b$





Potential very short range ➔ introducing Fermin pseudo-potential:

$$V_{Nuk}(\vec{r}) = a\delta^3(\vec{r} - \vec{r_j})$$

$$\Rightarrow \frac{d\sigma}{d\Omega} = \left(\frac{m_n}{2\pi\hbar^2}a\right)^2$$

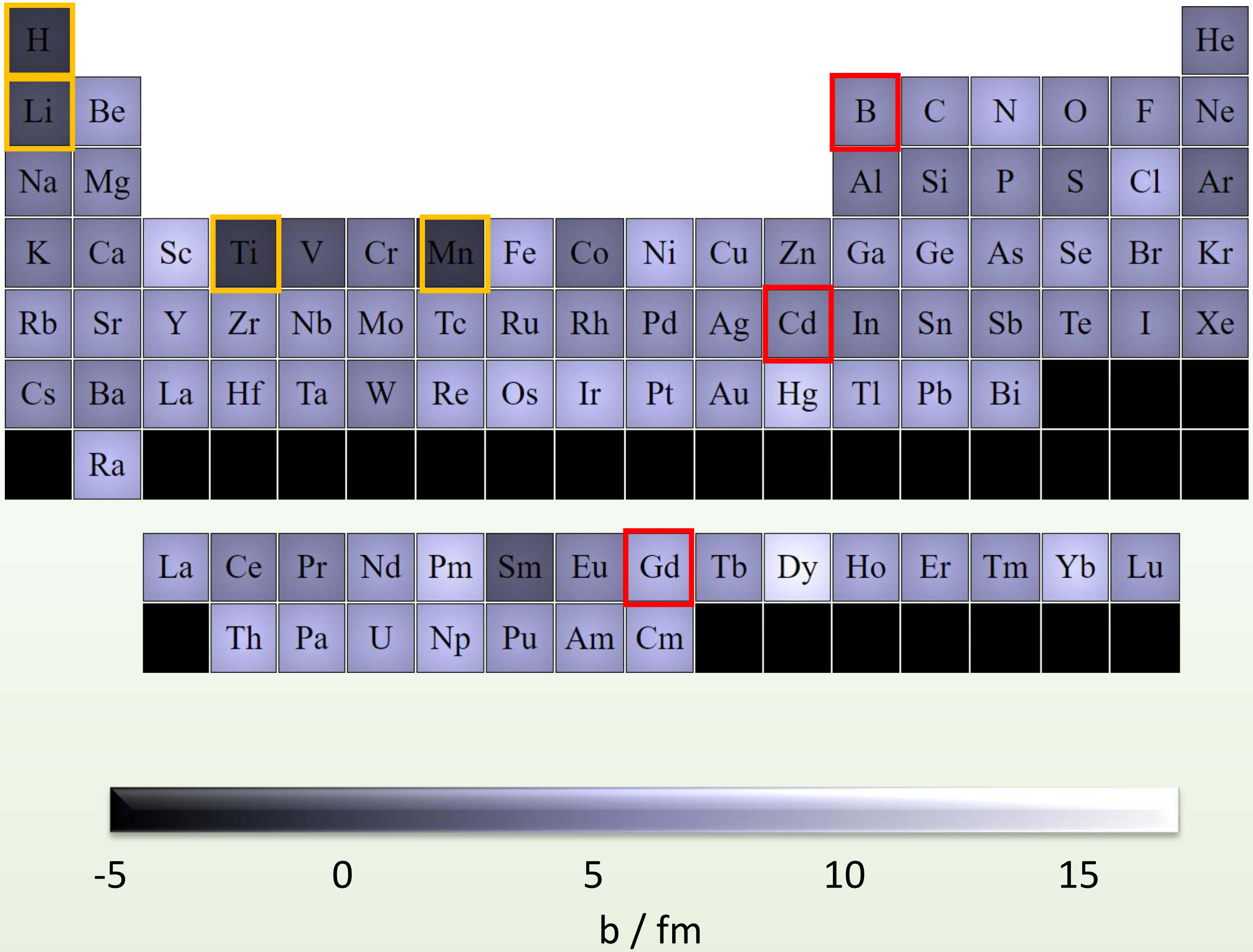
$$\Phi(\vec{Q}) = \frac{m_n}{2\pi\hbar^2}\int V(\vec{r'})e^{-i\vec{Q}\vec{r'}}\; d^3\vec{r'}$$

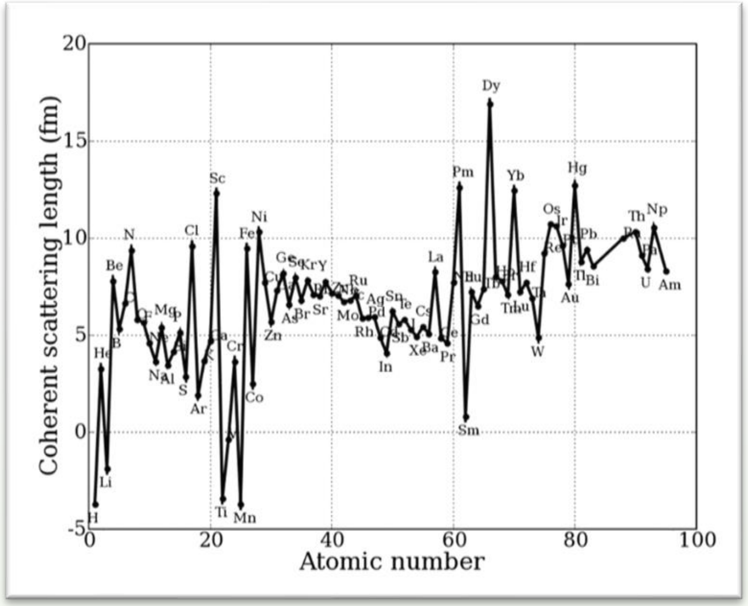
$$\frac{d\sigma}{d\Omega} = \left|\Phi\left(\vec{Q}\right)\right|^2$$

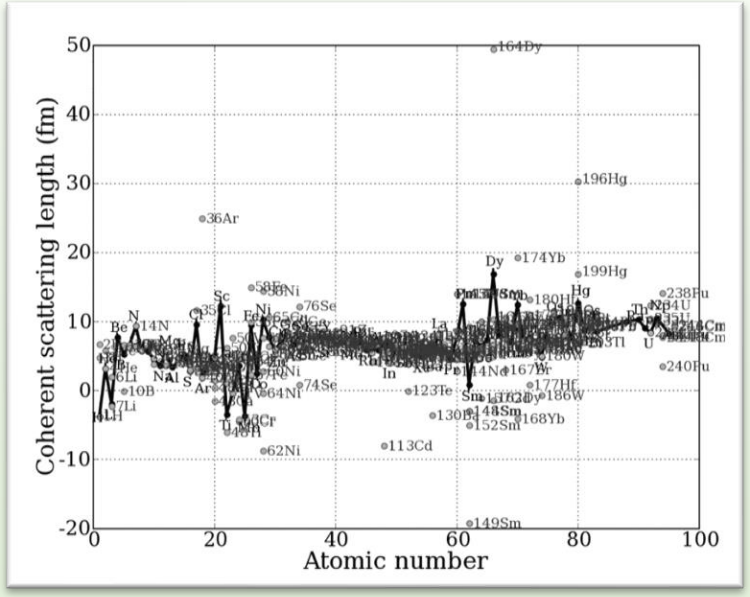
$$V_{Nuk}(\vec{r}) = \frac{2\pi\hbar^2}{m_n} b\delta^3(\vec{r} - \vec{r_j})$$

The complex scattering length *b* is sufficient to describe the neutron – nucleus interaction!

Neutron Scattering Length of Elements

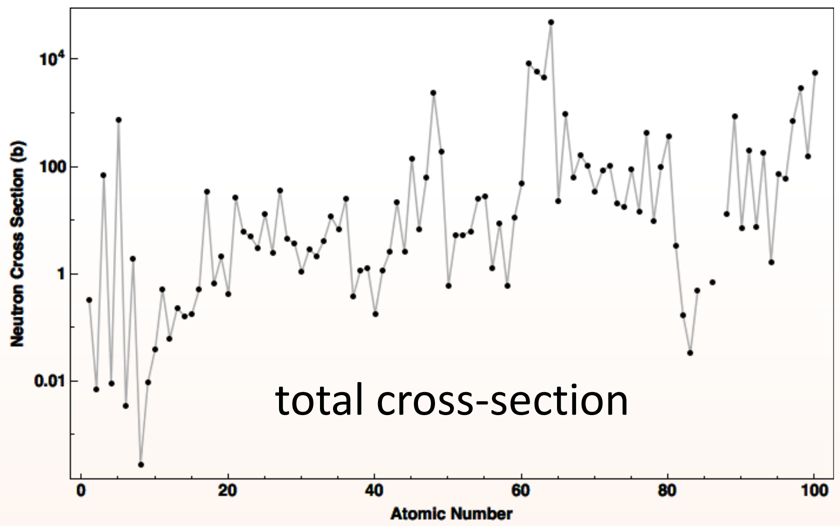




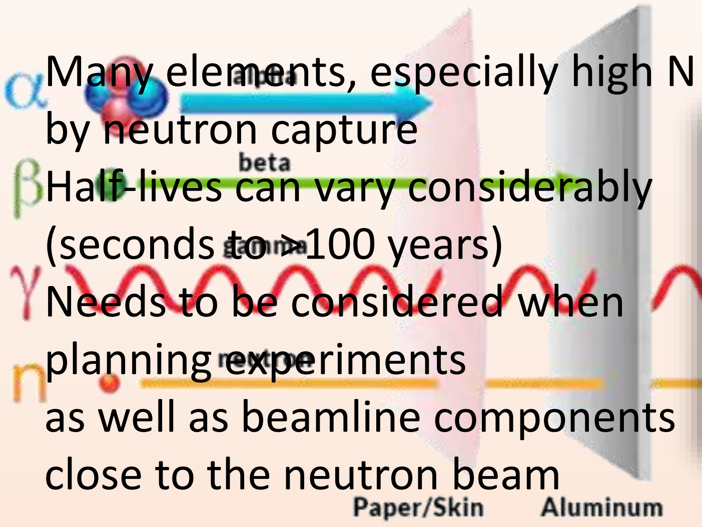


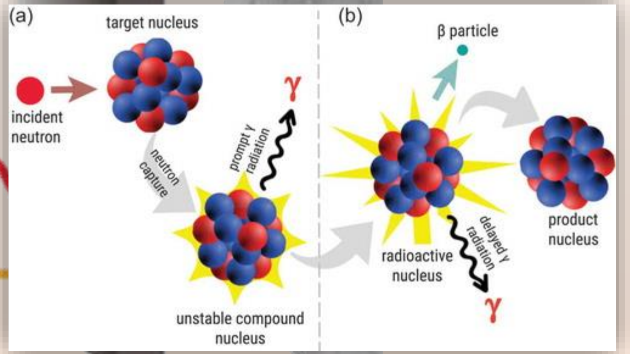
Intermezzo – Attenuation and Shielding

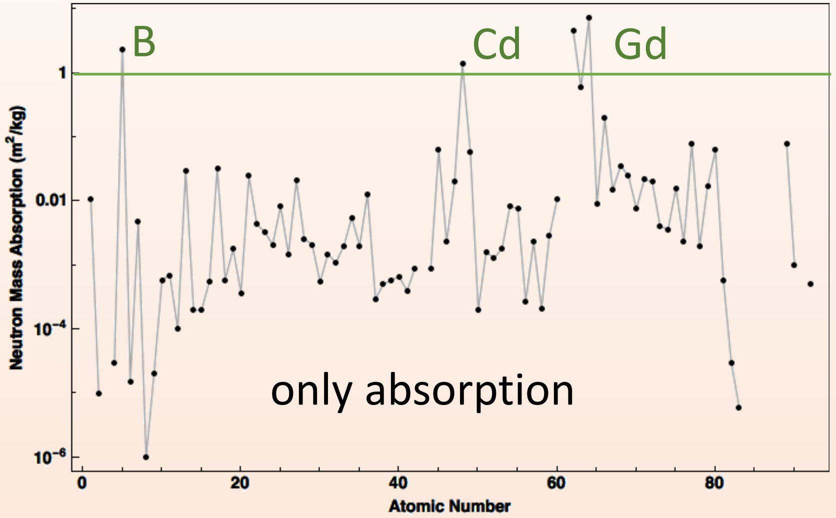
- The total cross-section for neutrons is dominated by scattering besides for a few elements (B, Cd, Gd)
- For most neutron capture reactions, a secondary charged particle and/or γ-photo is emitted
- To shield from thermal neutron radiation it is therefore most efficient to capture the neutron in a first layer and then reduce γ with heavy materials
- An alternative is a larger amount of concrete due to its lower price, in this case the hydrogen is the main absorber



- Many elements, especially high N isotopes can get activated by neutron capture
- Half-lives can vary considerably (seconds to >100 years)
- Needs to be considered when planning experiments as well as beamline components close to the neutron beam

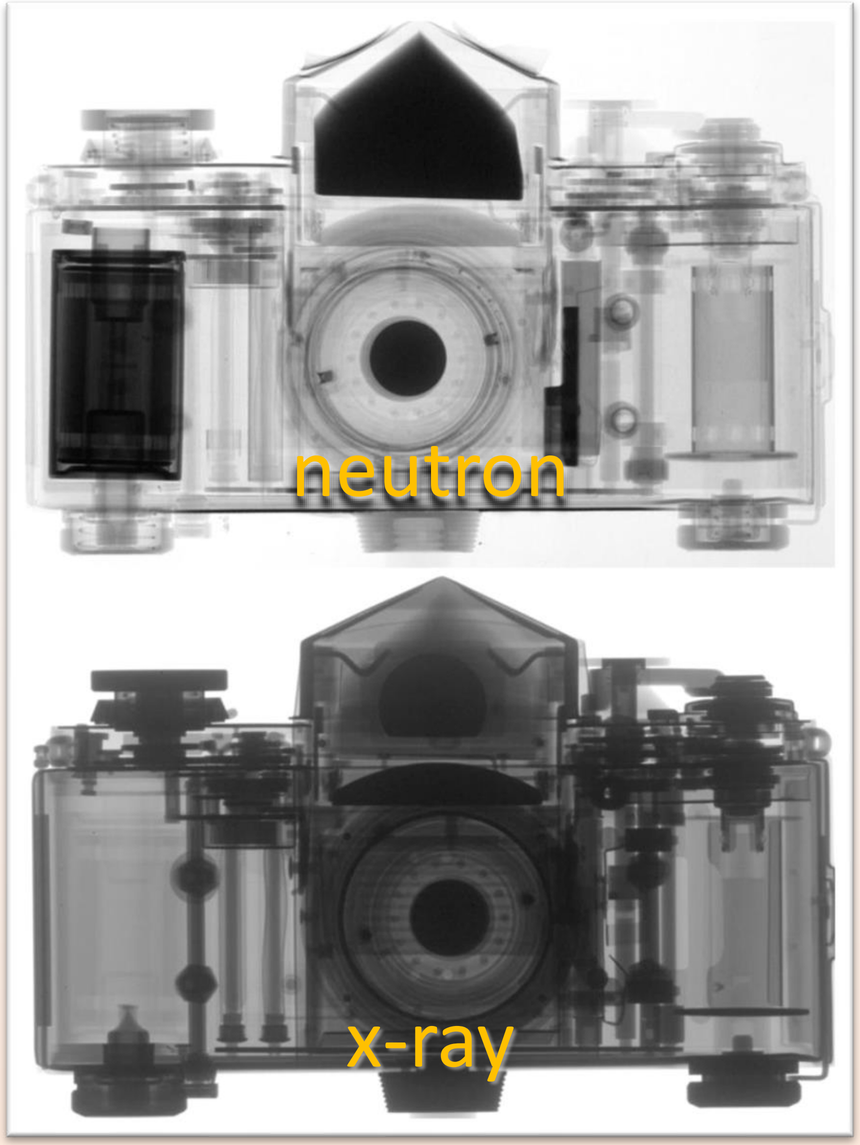


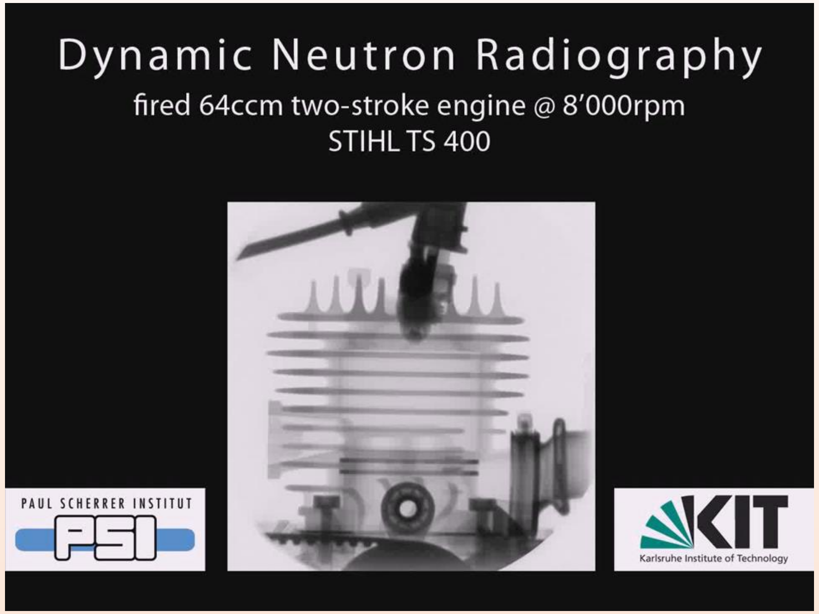




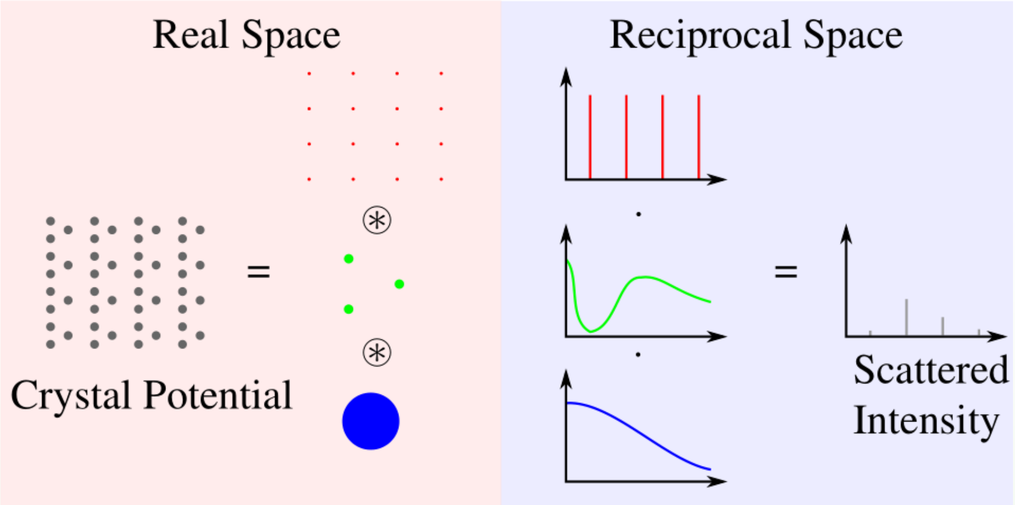
https://www-nds.iaea.org/relnsd/vcharthtml/VChartHTML.html

Intermezzo – Neutron Imaging





Scattering from Periodic Crystals



Real-space lattice: $\vec{R} = n_1\ \vec{a}_1 + n_2\ \vec{a}_2 + n_3 \vec{a}_3$

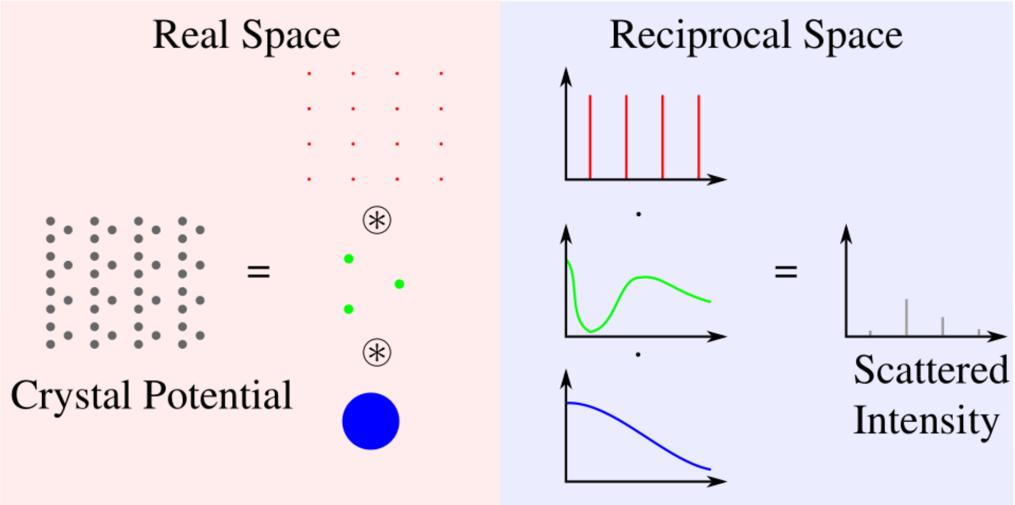
Reciprocal lattice: $\vec{G} = h\ \vec{b}_1 + k\ \vec{b}_2 + l\ \vec{b}_3$

Laue scattering condition: $\vec{G} = \vec{Q}$

$$S(\vec{Q}) \sim \overbrace{\sum_j \underbrace{f_j(\vec{Q})}_{\text{Atomic Form Factor}} e^{i\vec{Q}\vec{r}_j}}^{\text{Unit Cell Structure Factor } (S_{hkl})} \cdot \overbrace{\sum_{h,k,l} \delta(\vec{Q} - (h\vec{b_1} + k\vec{b_2} + l\vec{b_3}))}^{\text{Reciprocal Lattice}}$$

Convolution theorem: $f\left(\vec{x}\right) \cdot g\left(\vec{x}\right) \Rightarrow \mathscr{F}\left(\vec{Q}\right) * \mathscr{G}\left(\vec{Q}\right)$

Scattering from Periodic Crystals



Real-space lattice: $\vec{R} = n_1\ \vec{a}_1 + n_2\ \vec{a}_2 + n_3 \vec{a}_3$

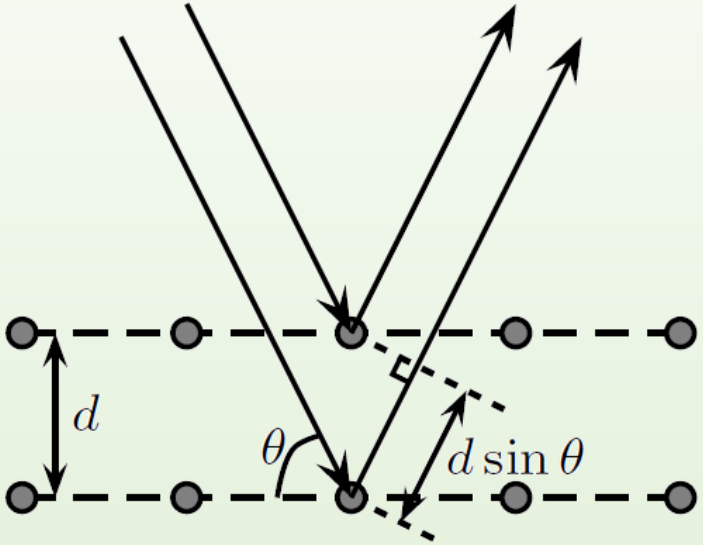
Reciprocal lattice: $\vec{G} = h\ \vec{b}_1 + k\ \vec{b}_2 + l\ \vec{b}_3$

Laue scattering condition: $\vec{G} = \vec{Q}$

Equivalent Bragg equation: $n\lambda = 2d \sin\theta$

Measured neutron intensity:

$$I_{hkl} = |S_{hkl}|^2 = \left| \sum_j b_j e^{i\vec{Q}\vec{r}_j} \right|^2$$

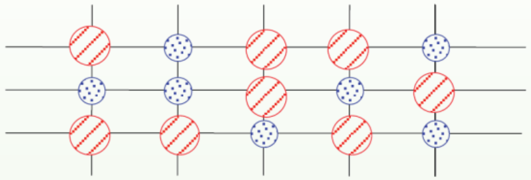


Deviations from Regular Structure

If a lattice that contains random variations of the potential, one needs to consider the average contributions:

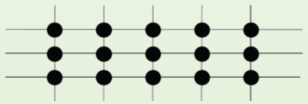
$$\frac{d\sigma}{d\Omega}\left(\vec{Q}\right) \propto \left|S(\vec{Q})\right|^2 = \left\langle \sum_j b_j e^{i\vec{Q}\vec{r}_j} \cdot \sum_{j'} b_j^* e^{-i\vec{Q}\vec{r}_{j'}} \right\rangle$$

Variation of Scattering Length (e.g. isotopes)

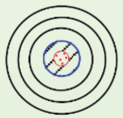


$$\langle b_j b_{j'}^* \rangle = \begin{cases} \langle b \rangle^2 & j = j' \\ \langle b \rangle^2 + \langle (b - \langle b \rangle)^2 \rangle & j \neq j' \end{cases}$$

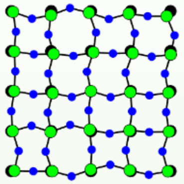
$$\frac{d\sigma}{d\Omega}\left(\vec{Q}\right) \propto \underbrace{\langle b \rangle^2 \left| \sum_j b_j e^{i\vec{Q}\vec{r}_j} \right|^2}_{\text{"coherent"}} + \underbrace{N \left\langle (b - \langle b \rangle)^2 \right\rangle}_{\text{"incoherent"}}$$

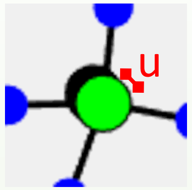


$N\times$



Variation of Position (e.g. thermal motion)



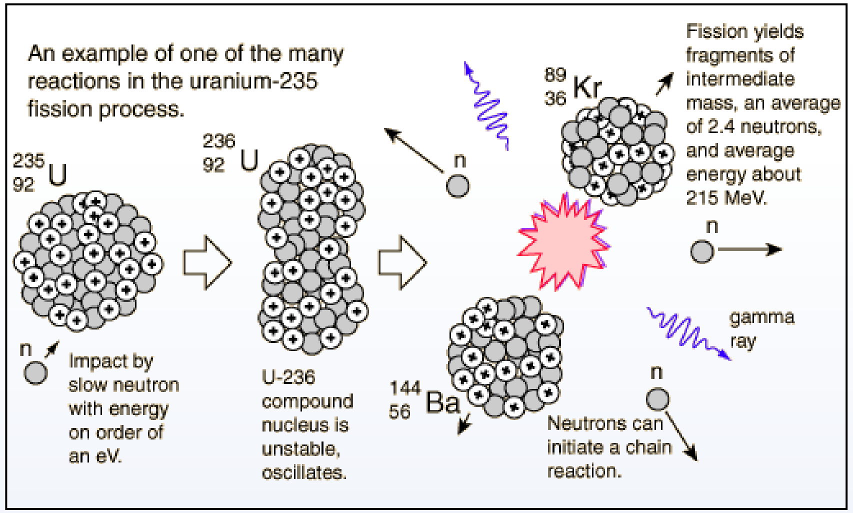


$$\left|S(\vec{Q})\right|^2 = \left\langle \sum_{j,j'} |b_j|^2 e^{i\vec{Q}\left(\vec{r}_j - \vec{r}_{j'}\right)} \right\rangle$$

$$|S_{hkl}|^2 = \left| \sum_j b_j e^{i\vec{Q}\langle \vec{r}_j \rangle} \right|^2 \underbrace{e^{-Q^2 \langle u^2 \rangle / 3}}_{\text{Debye-Waller}}$$

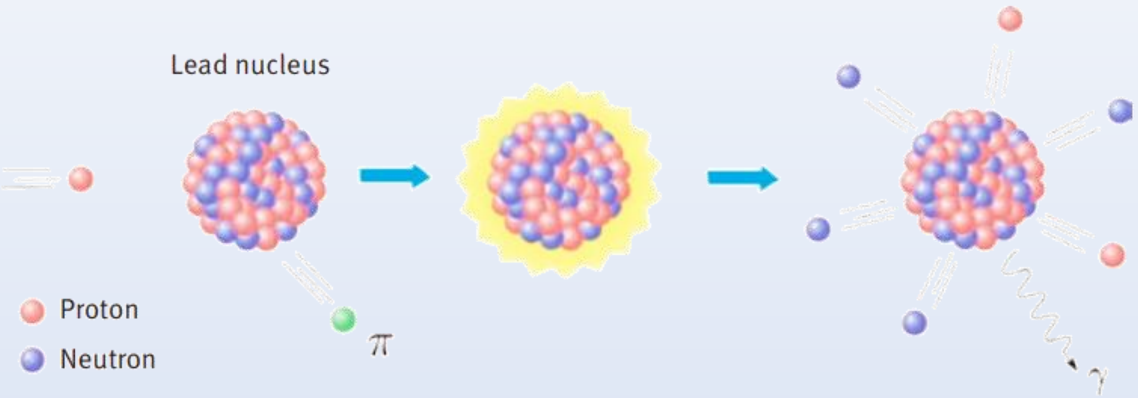
Neutron Sources

U-fission: ILL, FRM2, HZB, LLB, IBR-2 (reactor based)

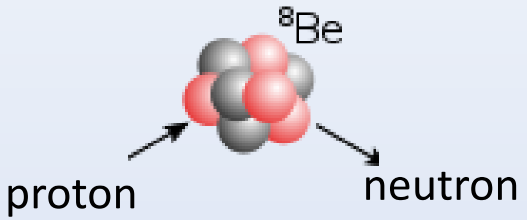


$$^{235}_{92}U_{143} + n \rightarrow \left[^{236}_{92}U_{144}\right]^* \rightarrow X + Y + 2.44n$$

Spallation: SINQ, ISIS, SNS, JPARC (accelerator based)

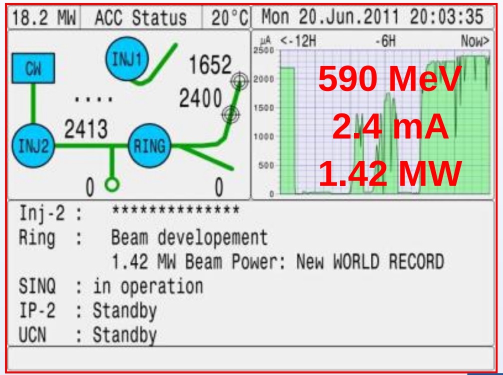


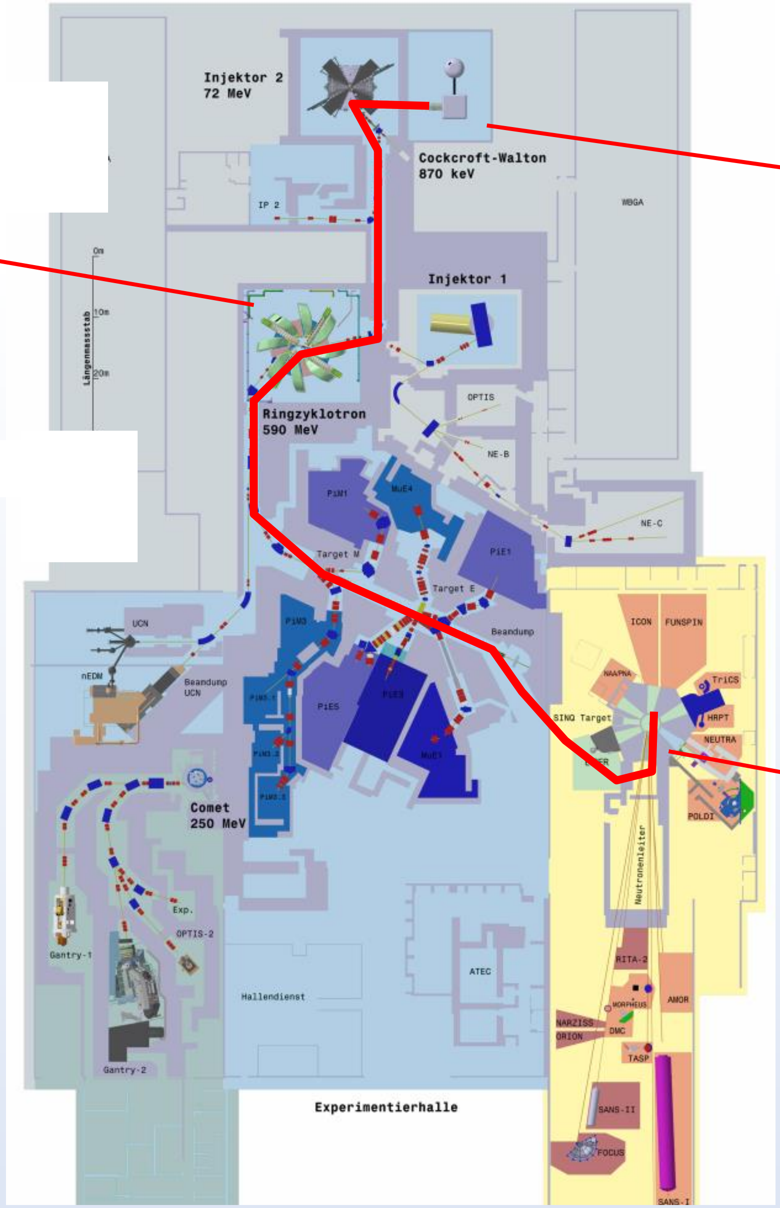
Other Reaction: HBS,…

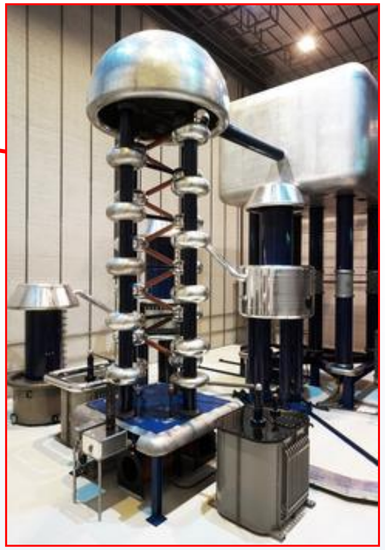


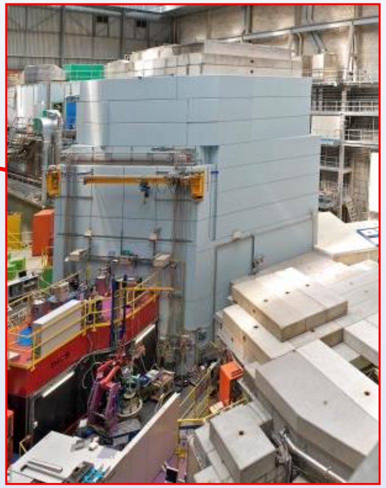
SINQ at PSI – Continuous Spallation Source

HIPA – Proton Accelerator

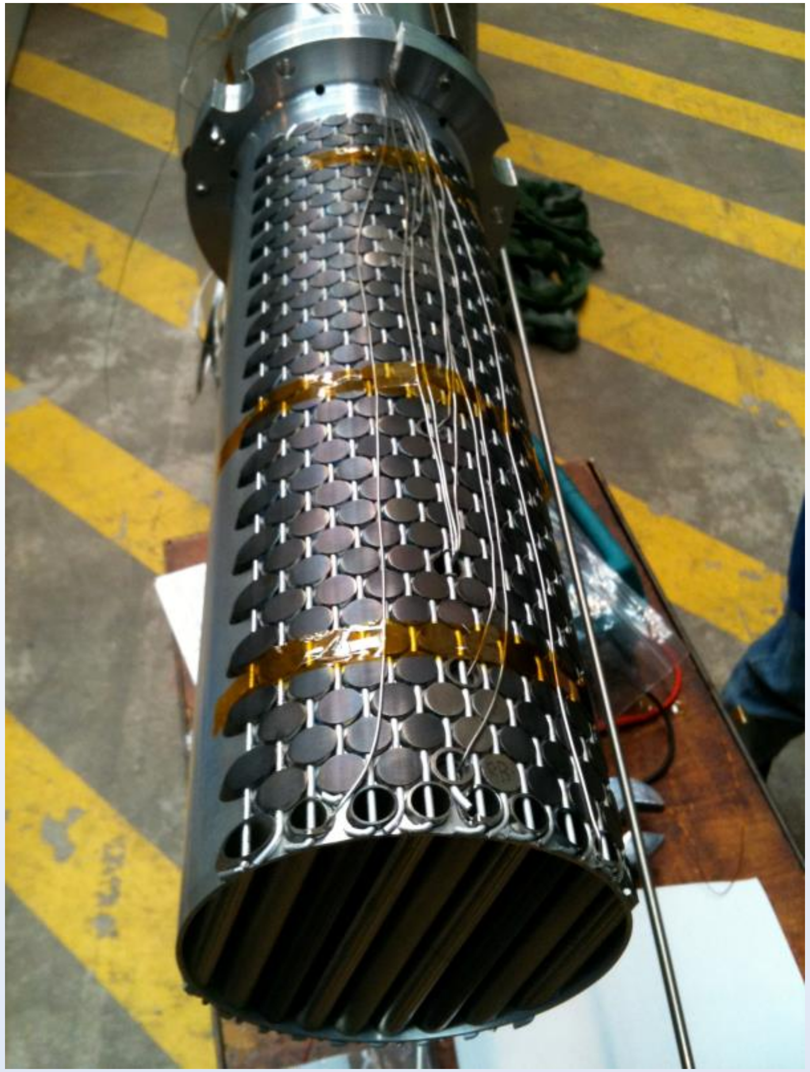






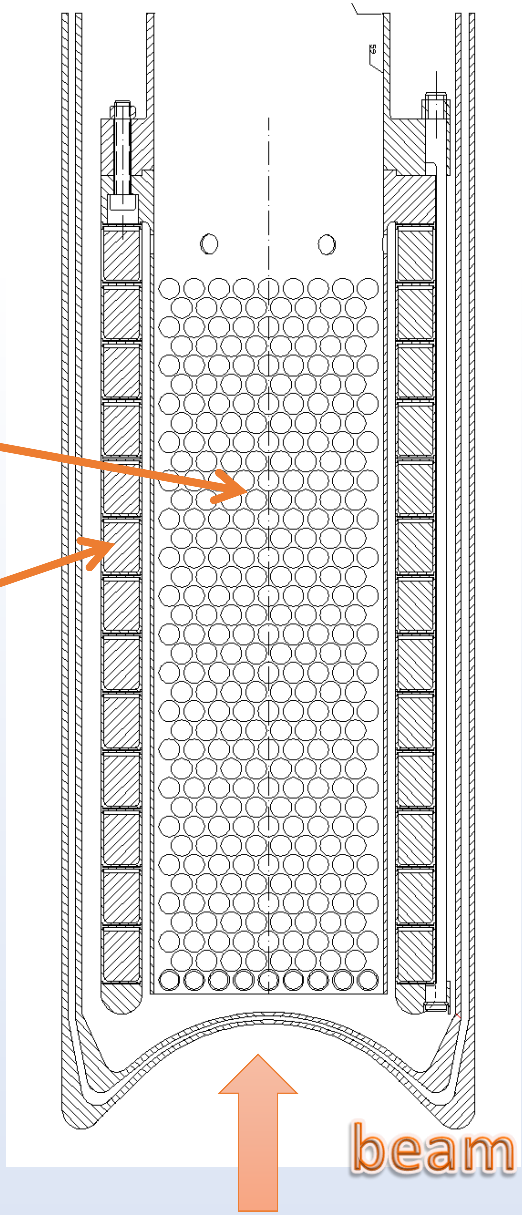


SINQ at PSI – Continuous Spallation Source



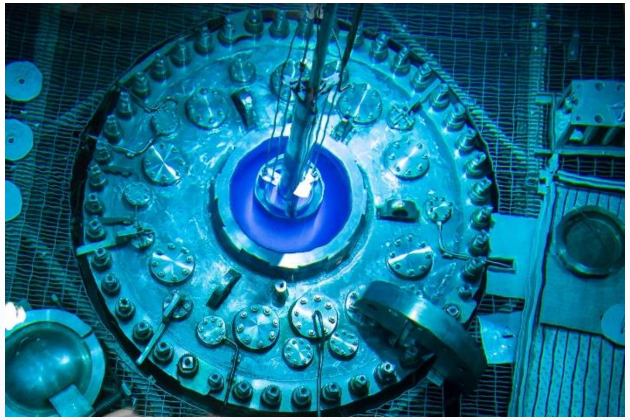
Zircalloy tubes, filled with lead, D_2O cooling

lead blankets (reflector for thermal neutrons)



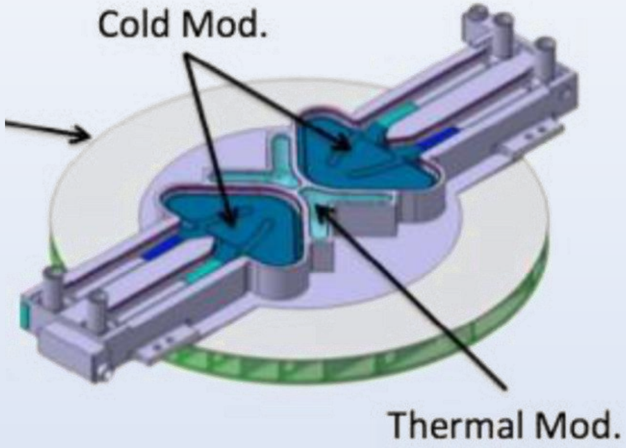
Energy Moderation

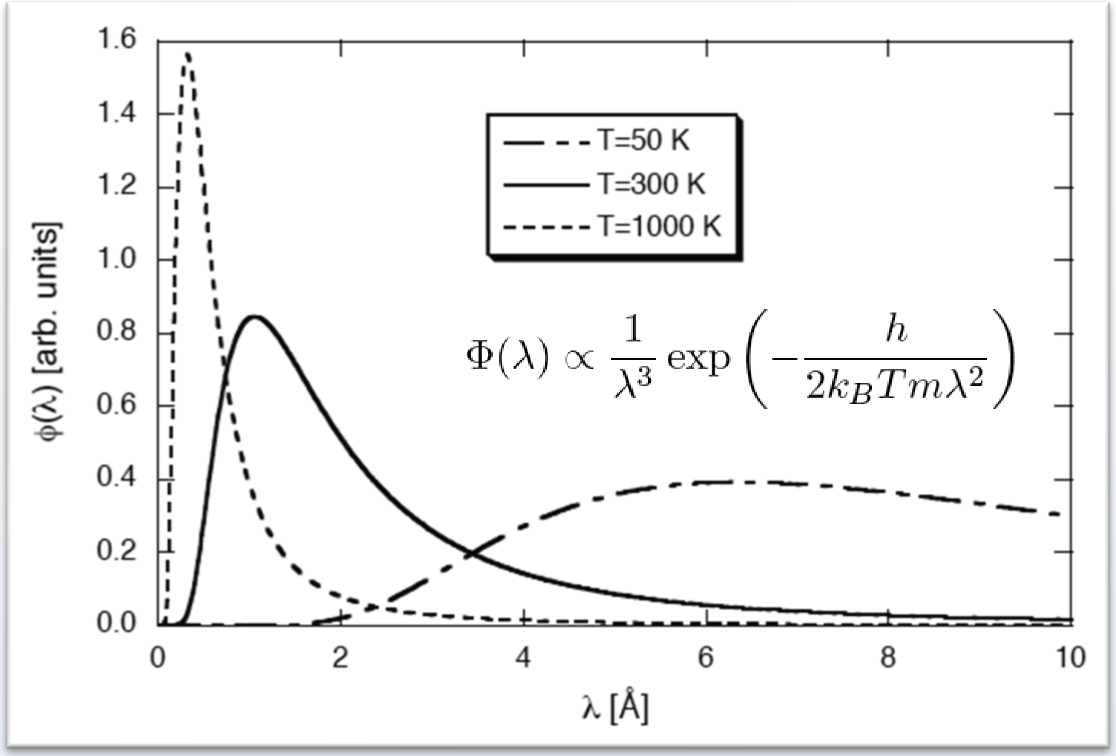
Moderation of neutrons to usable energies:



traditional moderator HFIR reactor (ORNL)

modern thermal/cold moderator (ESS)





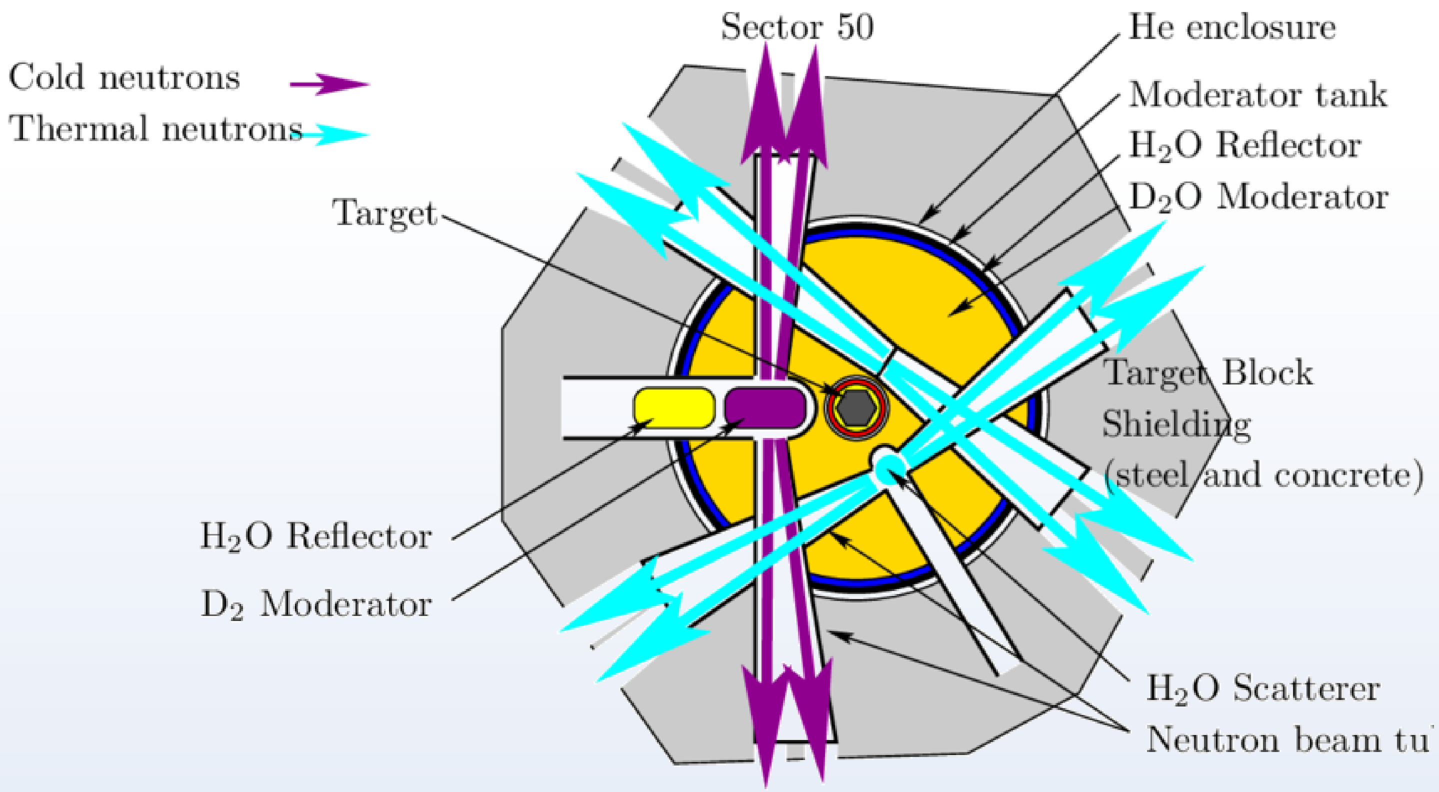
$$E = 81.81 \cdot \frac{1}{\lambda^2} = 2.072 \cdot k^2 = 5.227 \cdot v^2 = 0.08617 \cdot T$$

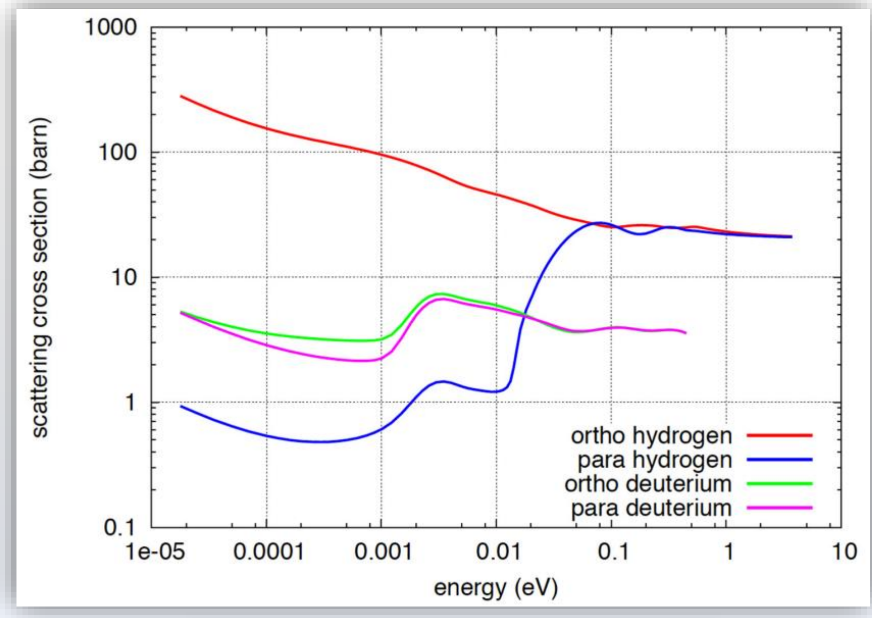
$$1\,\mathrm{meV} = 0.242\,\mathrm{THz} = 8.07\,\mathrm{cm}^{-1} = 11.6\,\mathrm{K} = 17.3\,\mathrm{T}$$

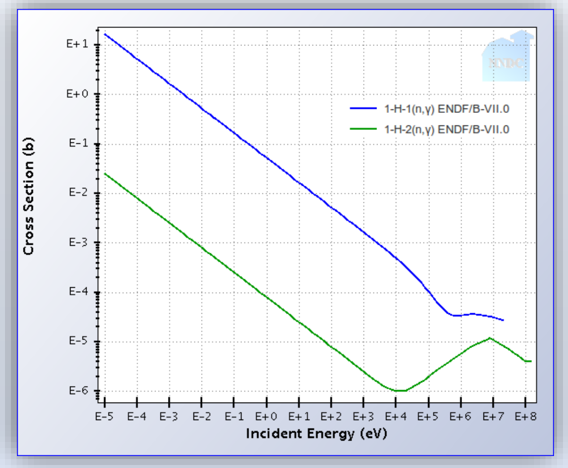
- W. Wagner, ASQ, Paul Scherrer Institute

SINQ Cold Source (D_2) Bulk

Continuous source, time structure irrelevant





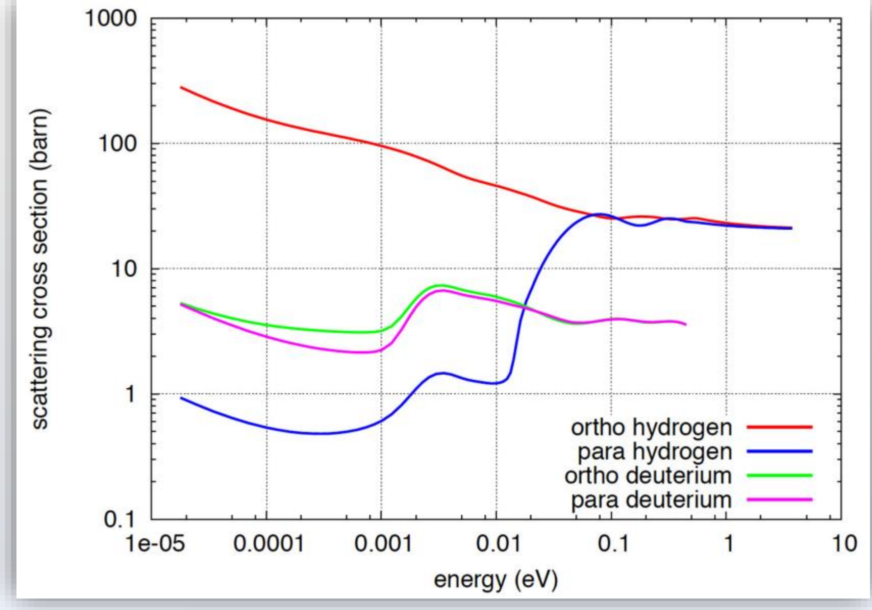


Moderator for cold neutrons:

- Light atoms (H/D)
- Low temperature (liquid H_2/D_2)
- Minimize absorption

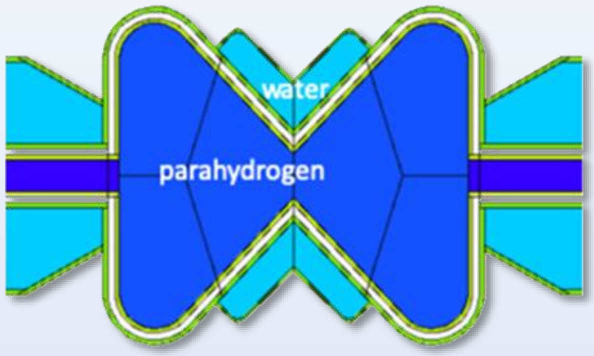
ESS Cold Source (para-H_2) “Butterfly”

Pulsed source, time structure determines wavelength resolution

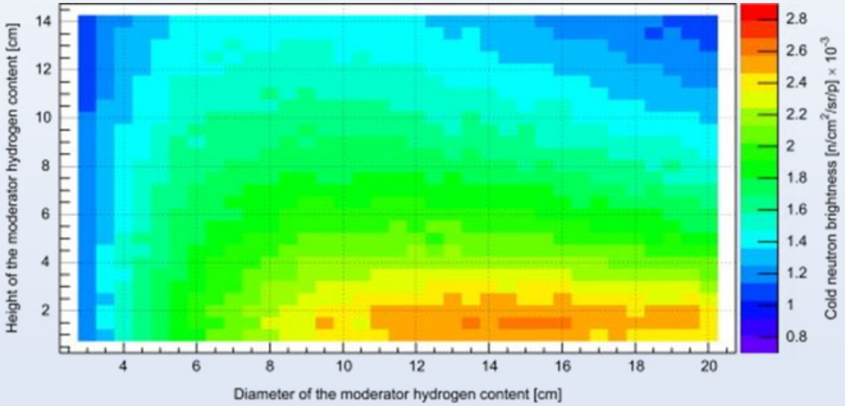


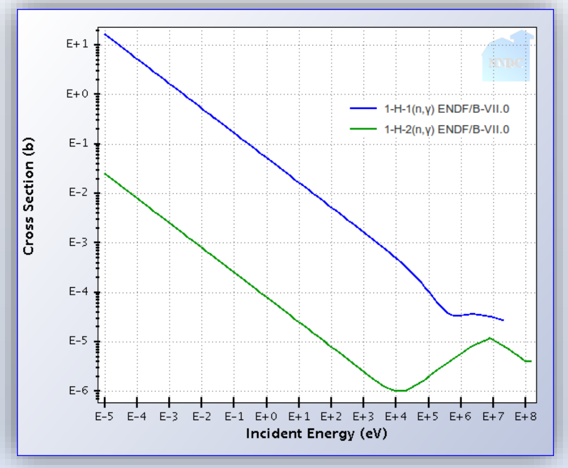
Moderator for cold neutrons:

- Light atoms (H/D)
- Low temperature (liquid H_2/D_2)
- Keep time structure
- Minimize absorption



➔ low height para-H_2

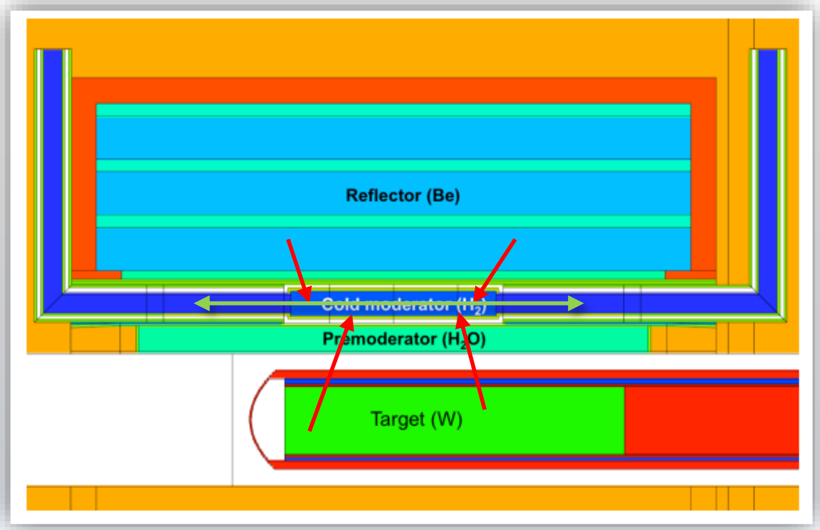


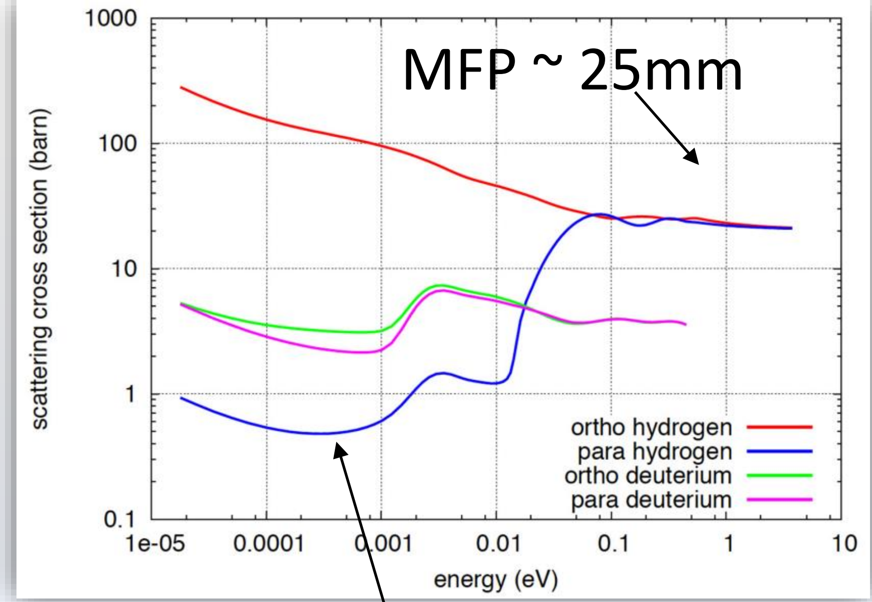


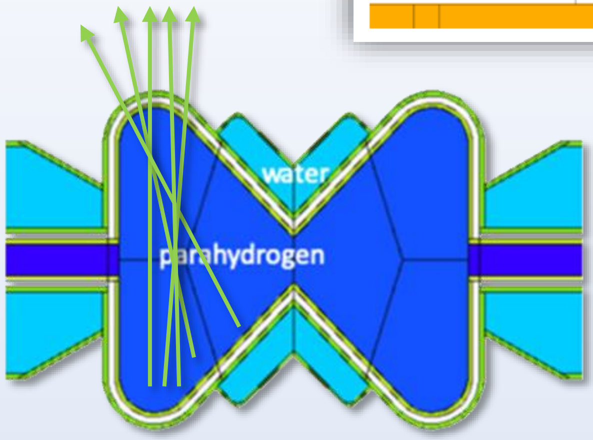
DOI: 10.1016/j.nima.2020.163402

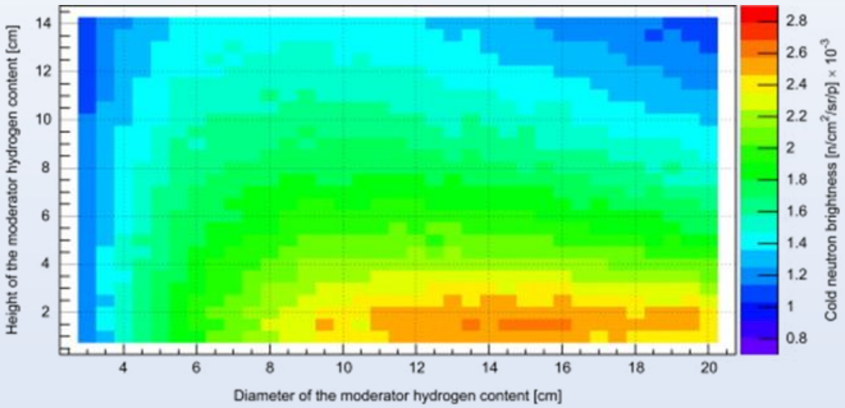
ESS Cold Source (para-H_2) “Butterfly”

Pulsed source, time structure determines wavelength resolution









MFP > 500mm

➔ **gain factor ≈ 3**

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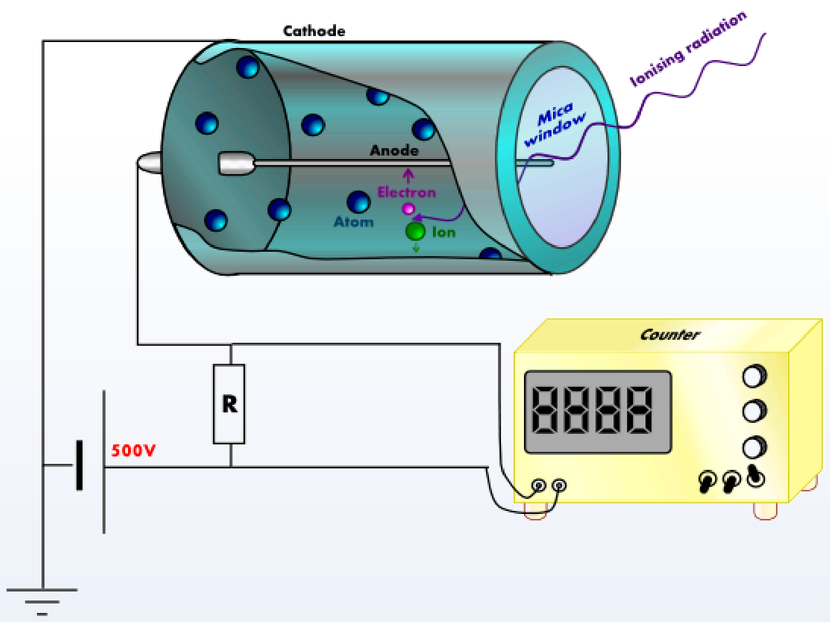
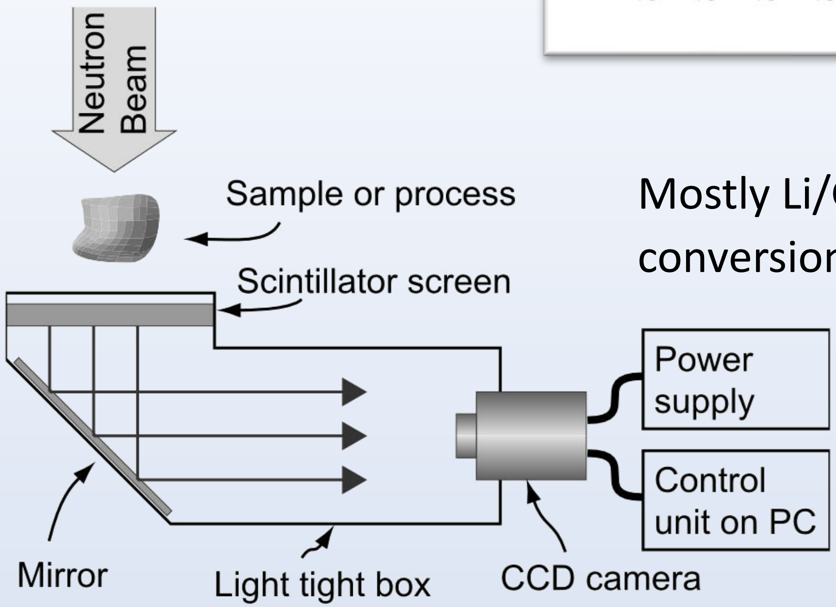
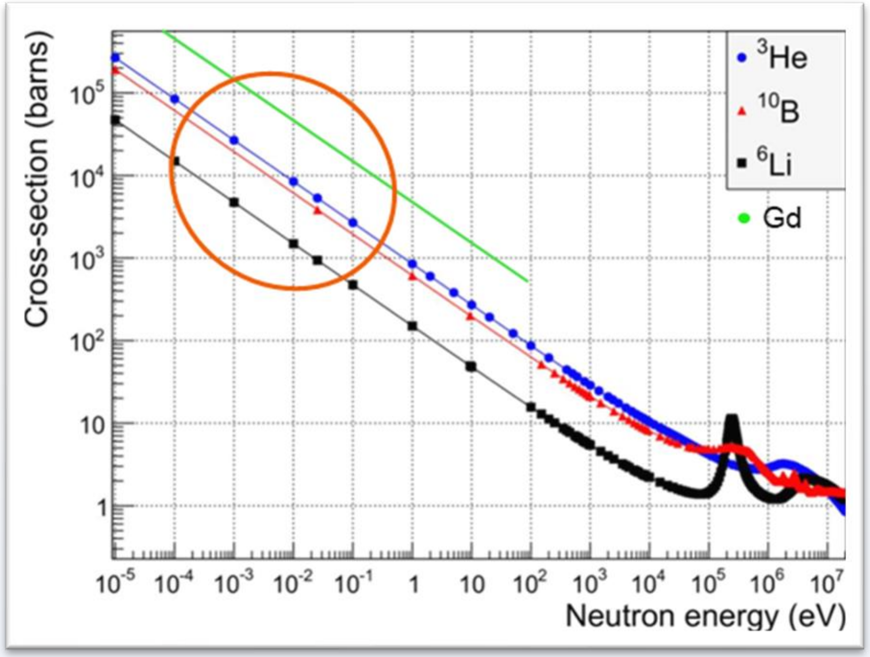
Neutron Detection

$^{3}He/^{10}B$ **proportional counter**



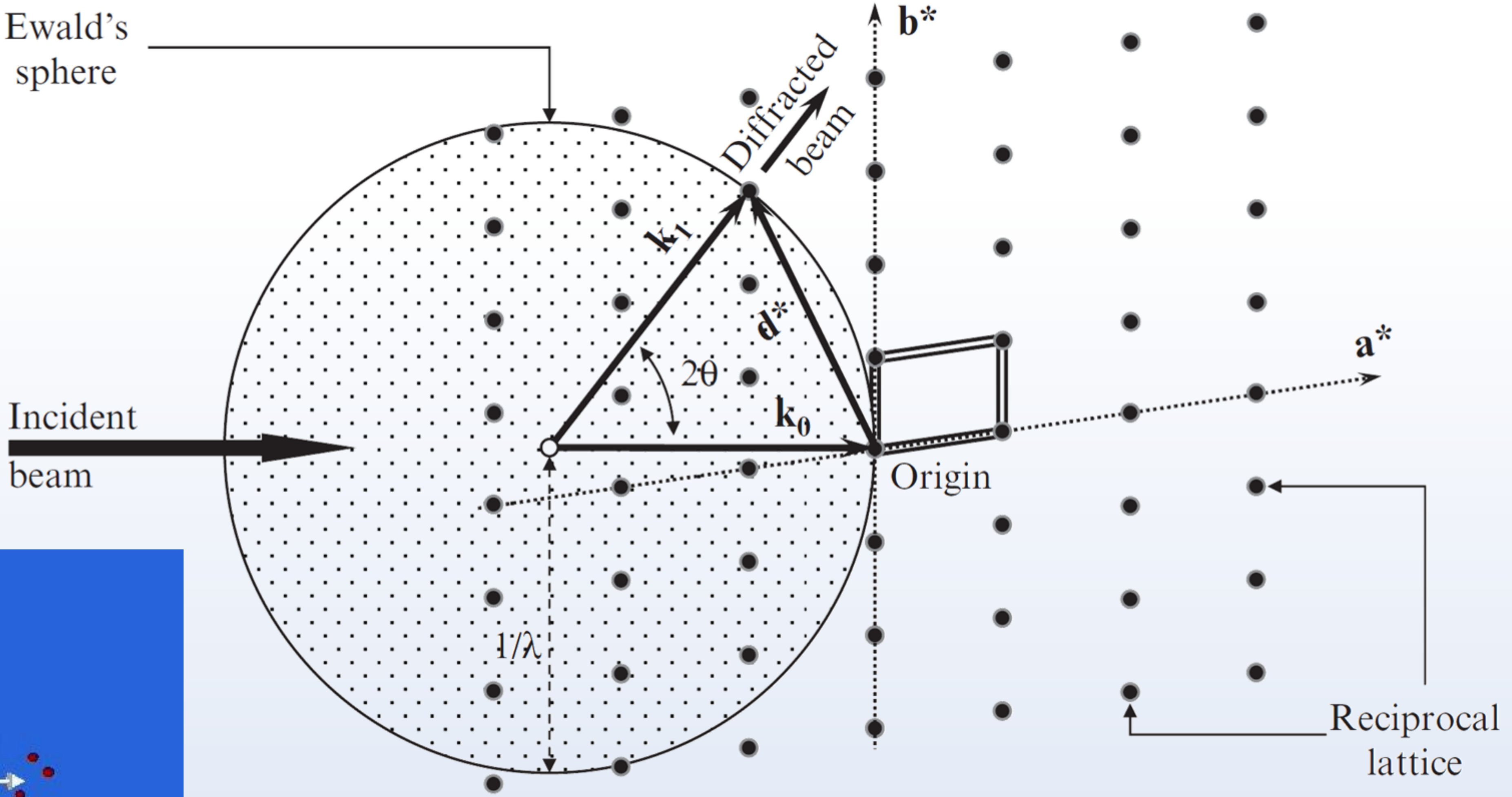
scintillator based

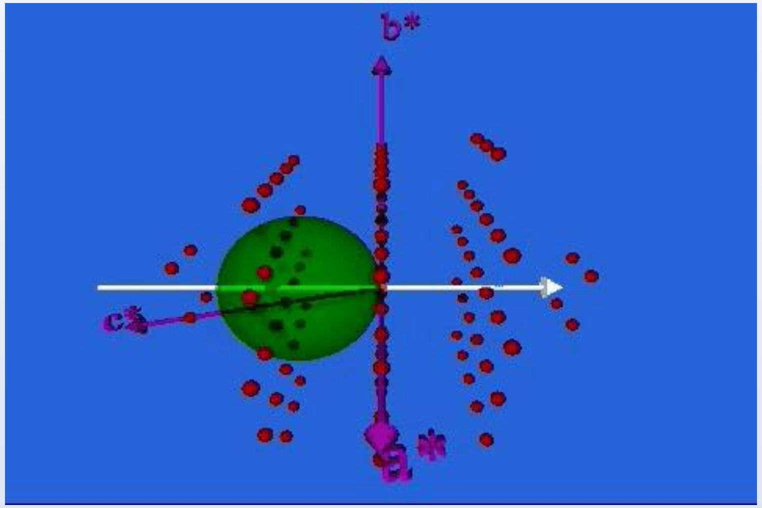




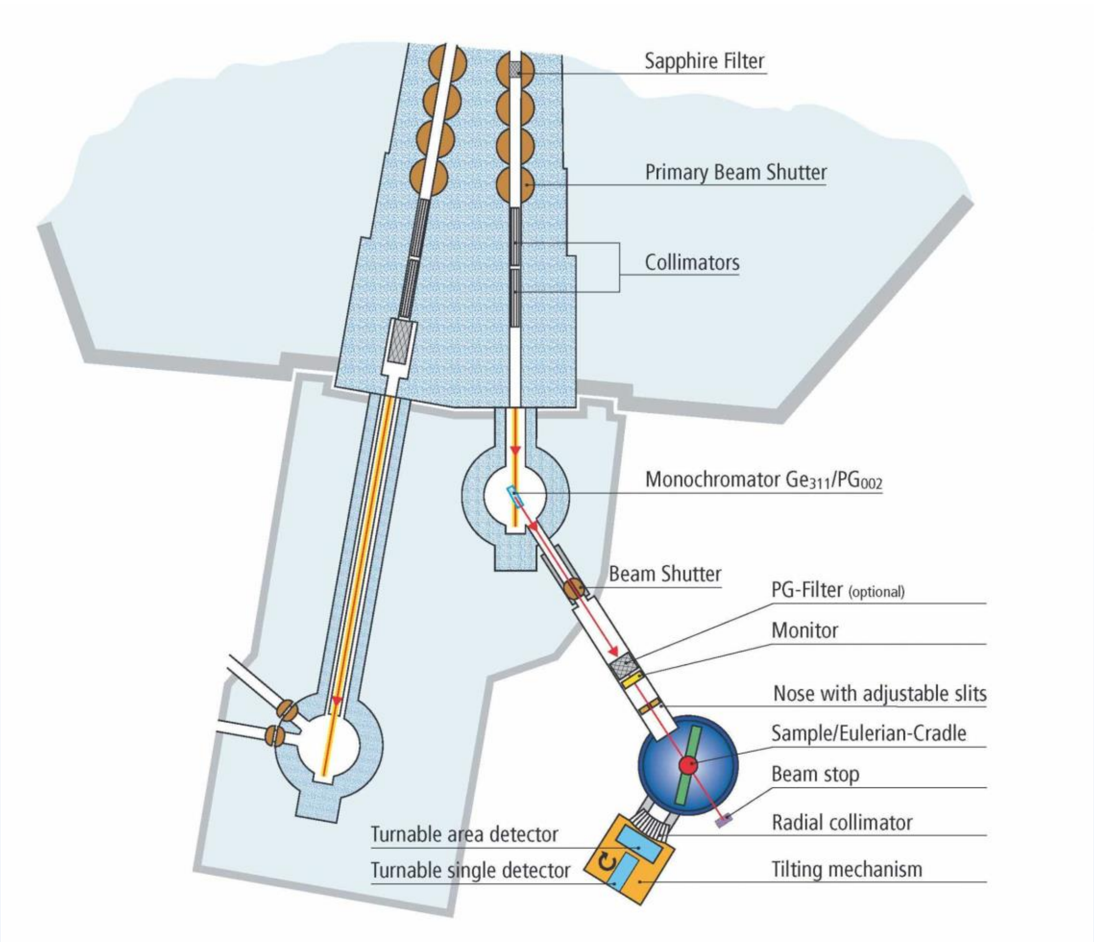
Mostly Li/Gd/B based absorption,
conversion of n➔γ factor 300-20'000

Diffraction Techniques: Single Crystal Diffraction

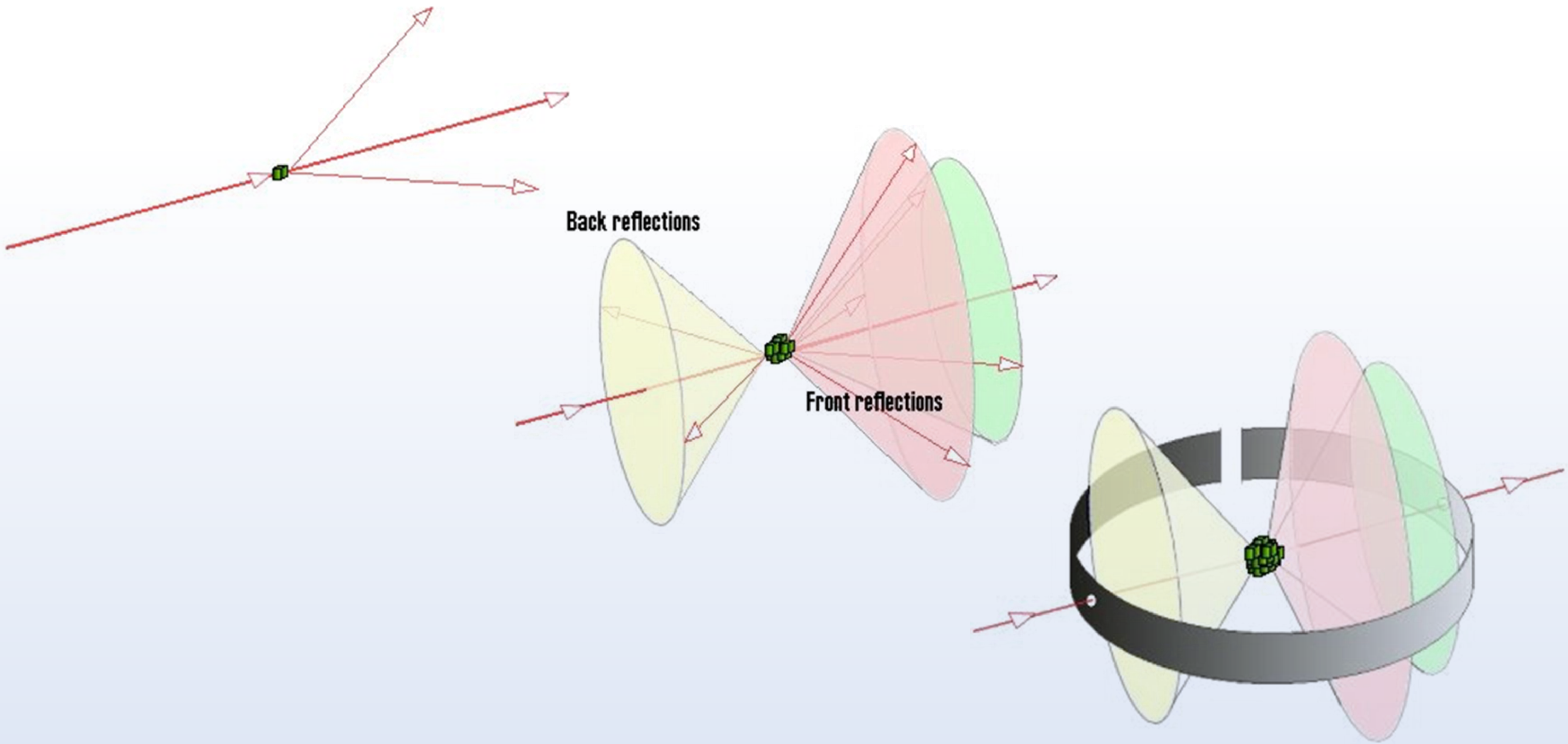




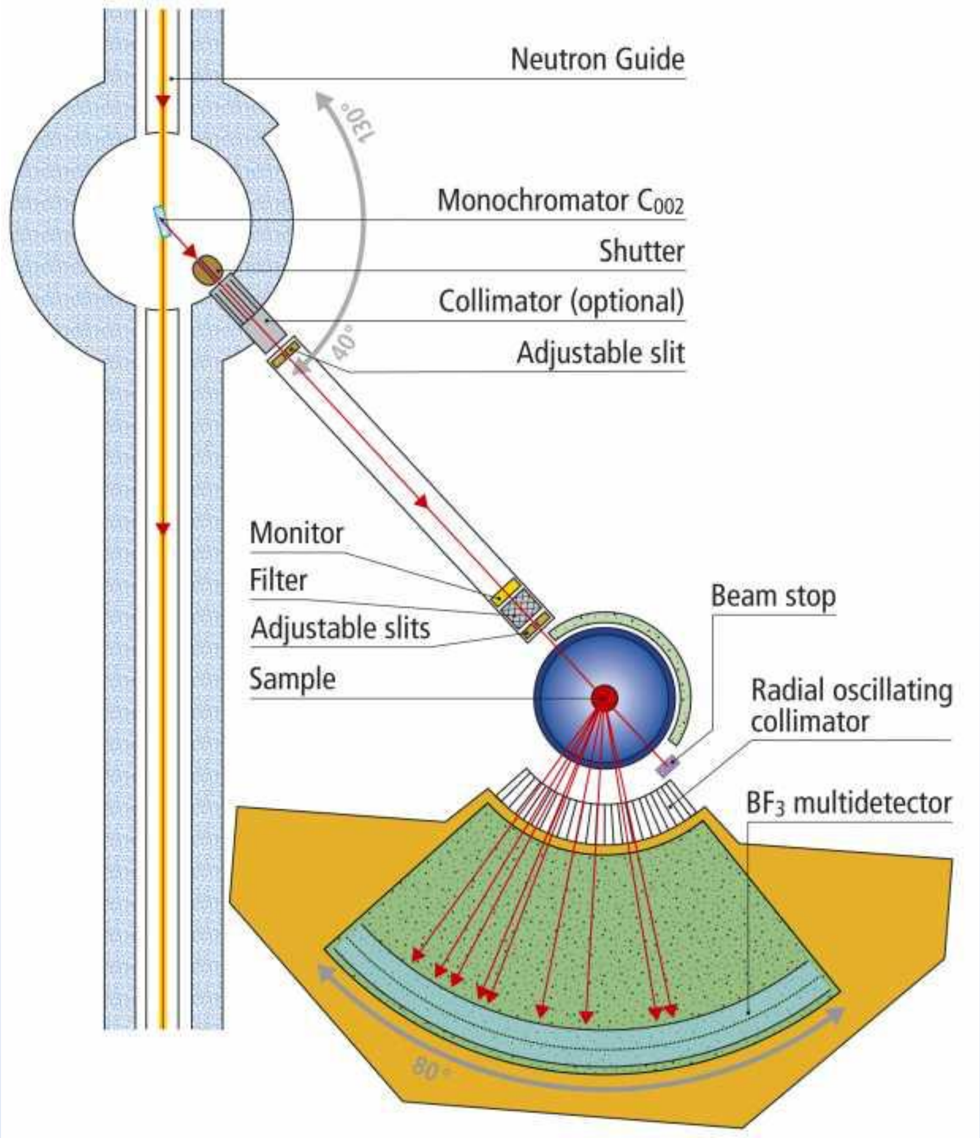
Single Crystal Diffraction: ZEBRA at SINQ

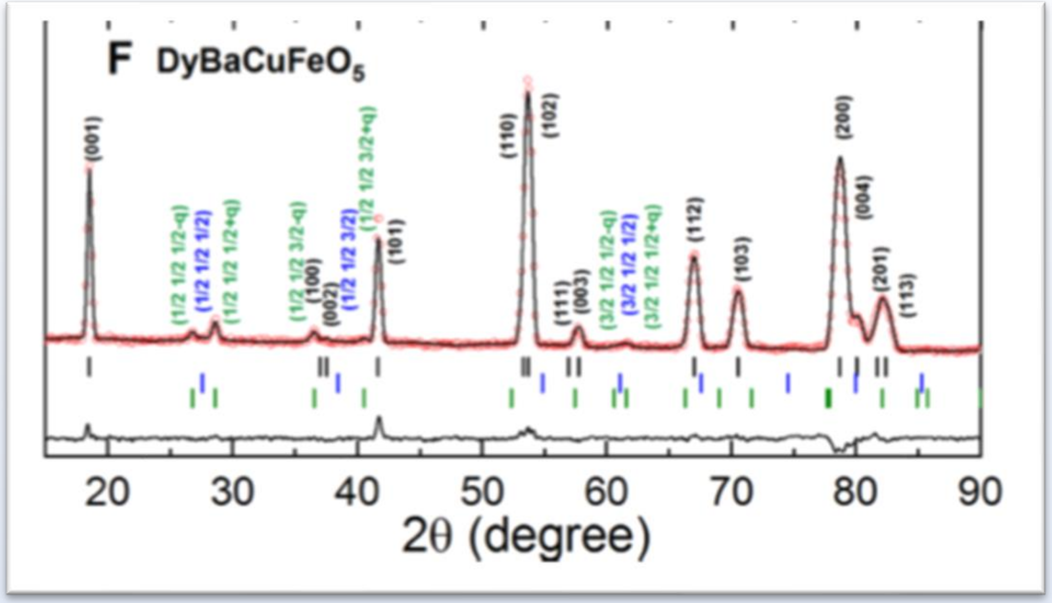


Diffraction Techniques: Powder Diffraction



Powder Diffraction: DMC instrument at SINQ

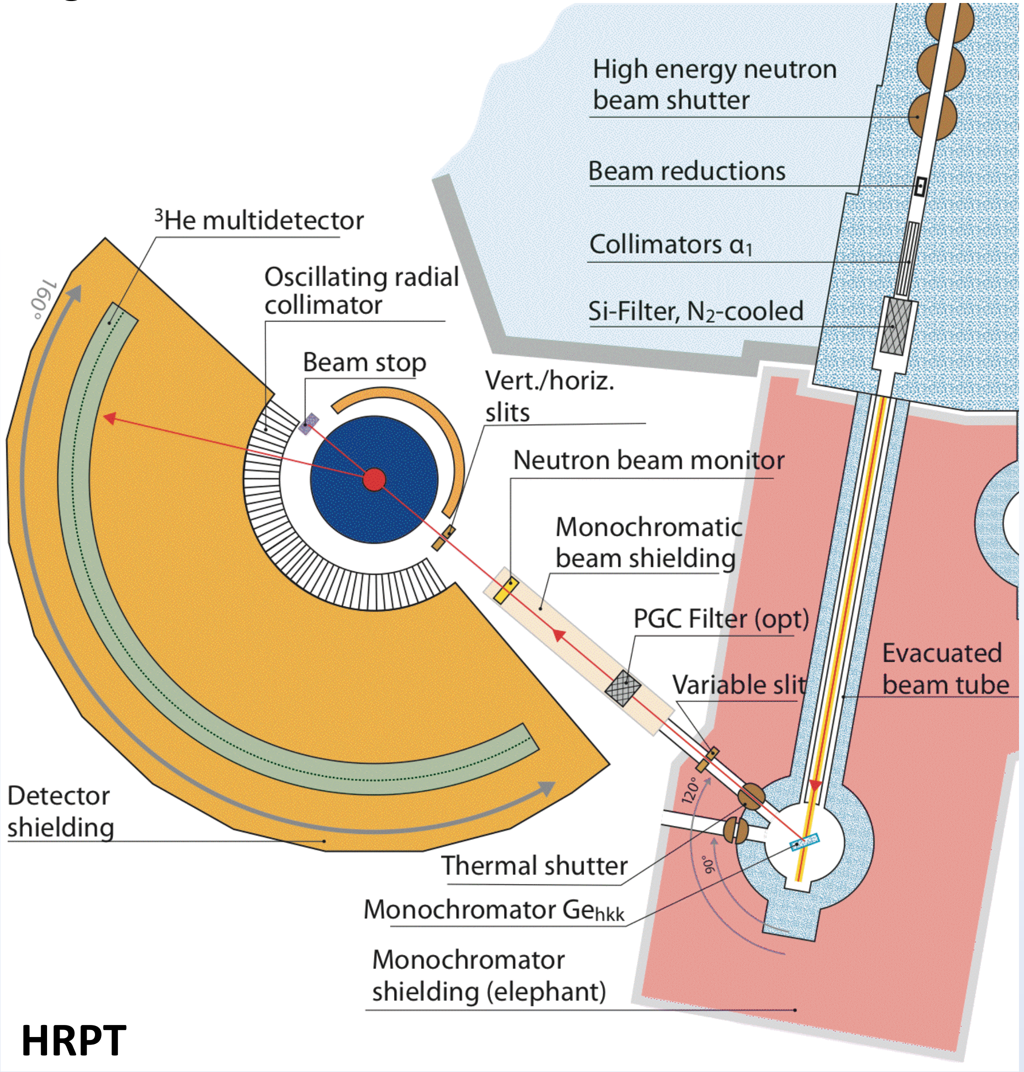


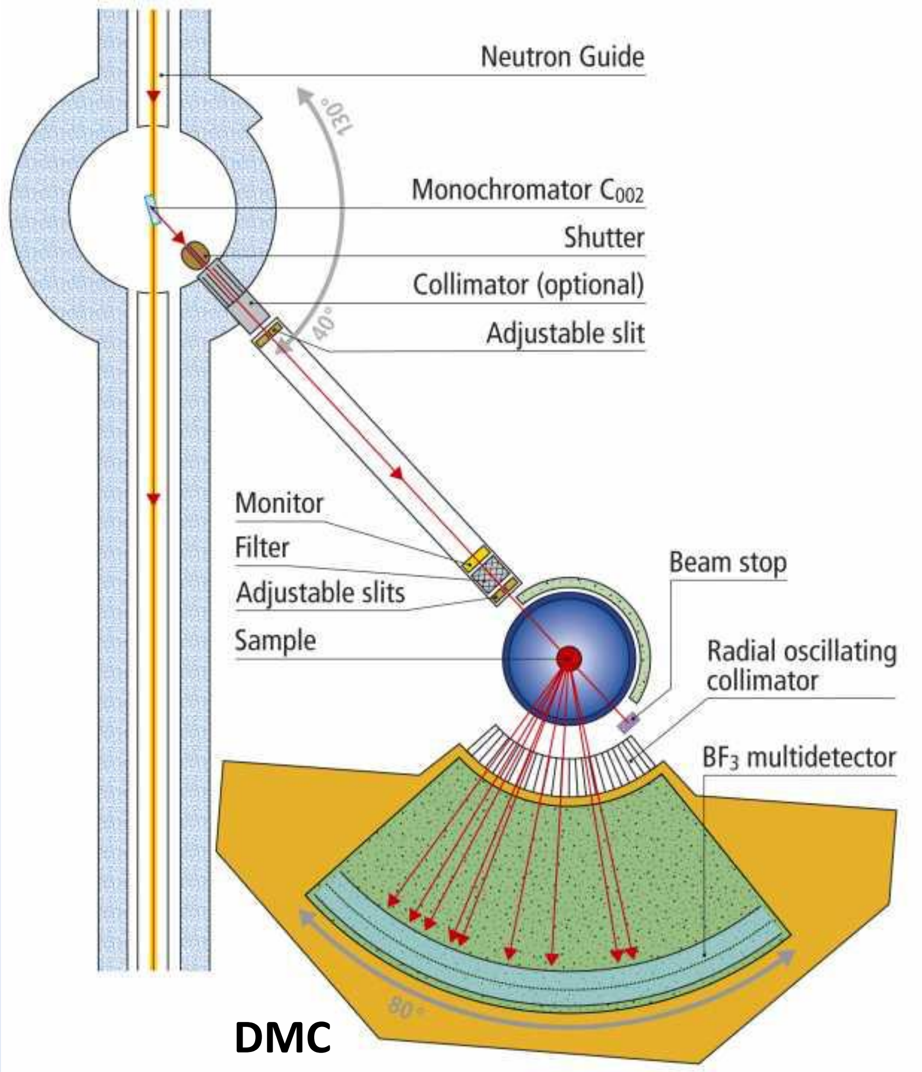


Tian Shang *et al.,* Science Advances , **4,** 6386 (2018)

Powder Diffraction: HRPT instrument at SINQ

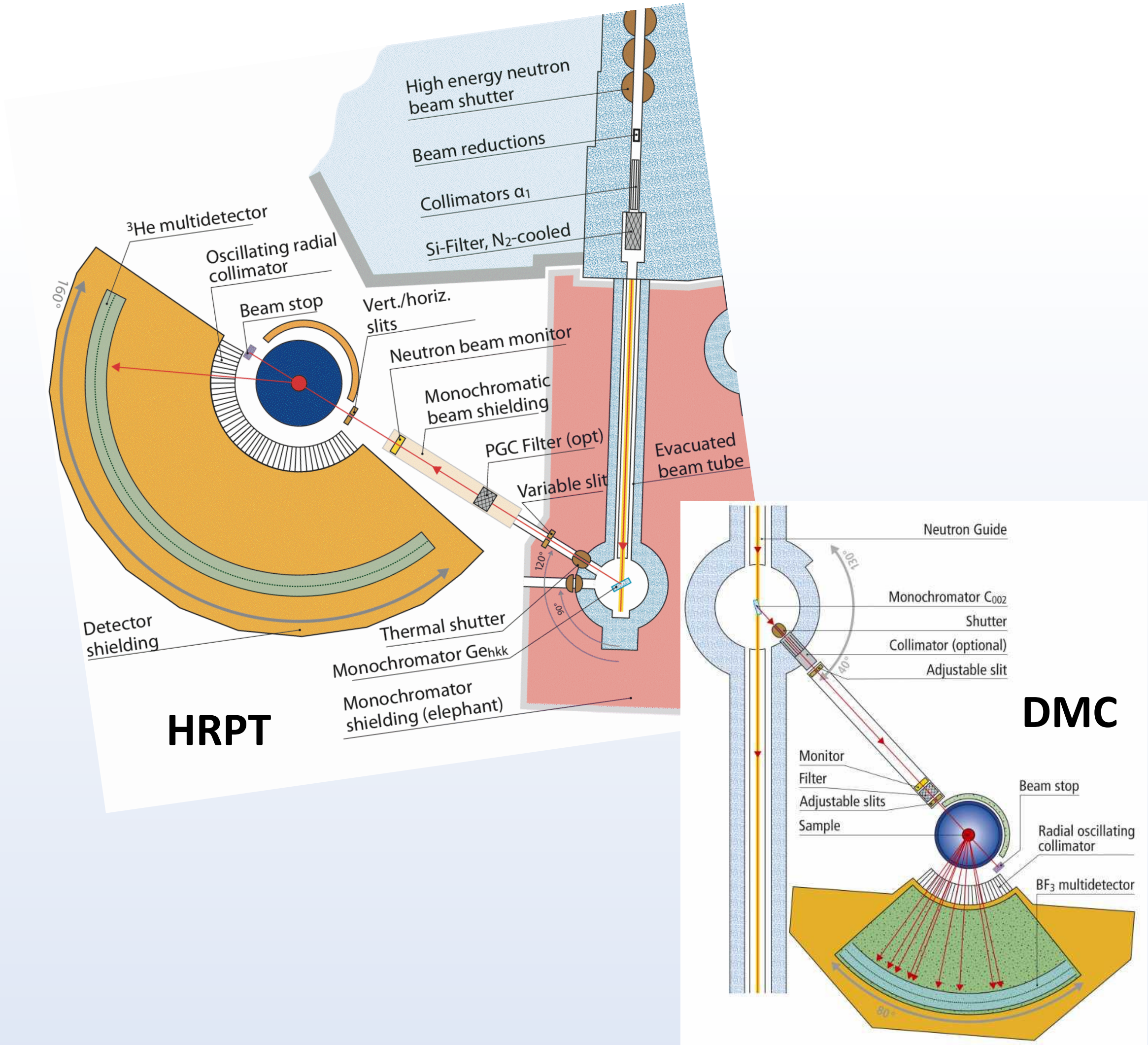
High Resolution Powder Diffractometer for Thermal Neutrons



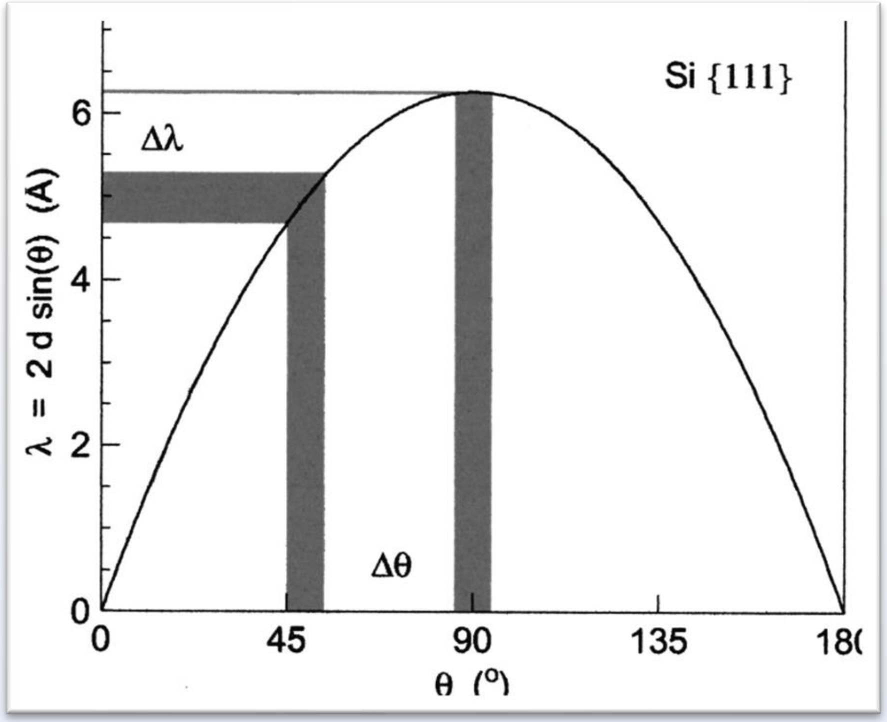


What makes HRPT higher resolution than DMC???

Powder Diffraction: HRPT instrument at SINQ



Wavelength Resolution of a Crystal Monochromator



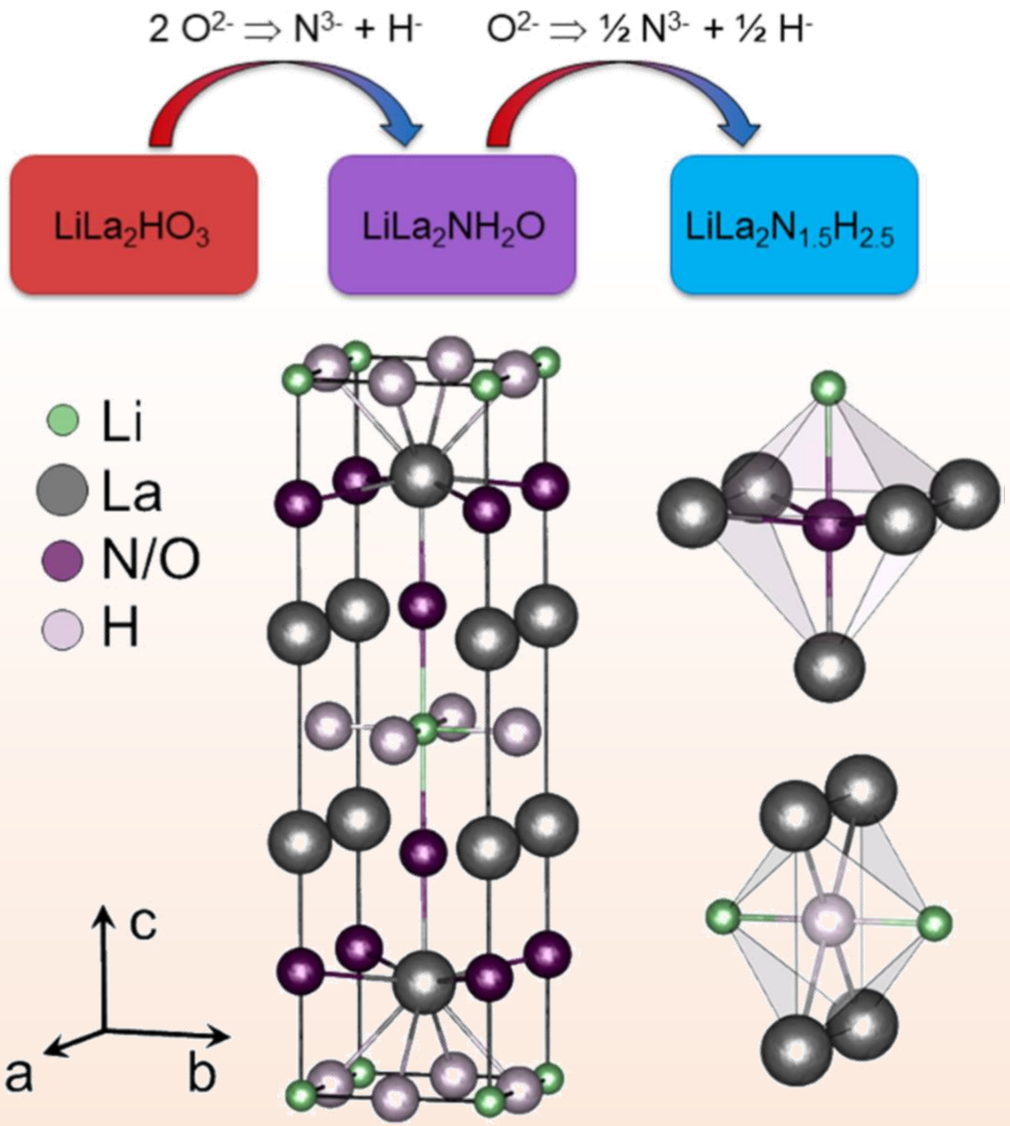
$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta d}{d} + \cot\theta \, d\theta$$

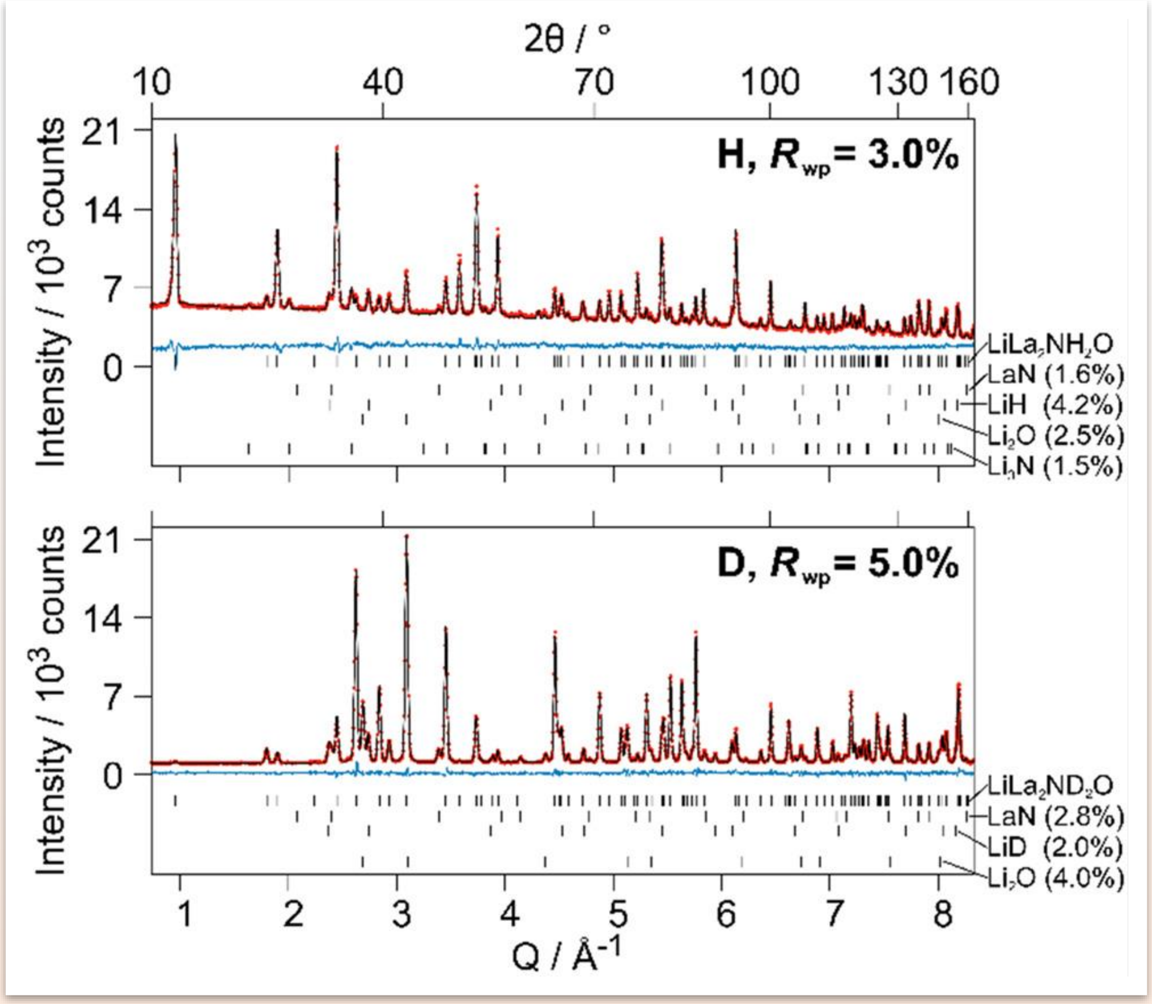
Depends on Crystal Quality

Depends on Scattering Angle!!!!

Depends on Beam Divergence

Locate light elements in hydride crystals





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