Diffraction overview

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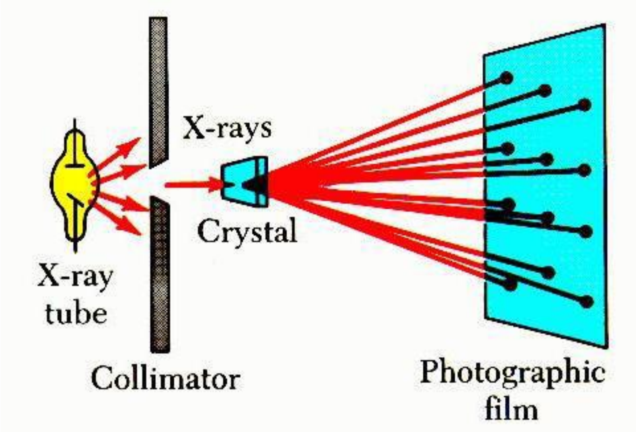
Diffraction overview

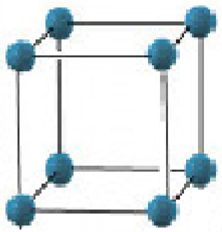
- Diffraction history
- Crystalography
- Single-crystal diffraction
- Powder diffraction
- Magnetic diffraction
- Instruments

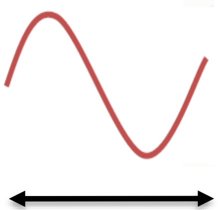
Diffraction history

Max von Laue
(1879-1960)

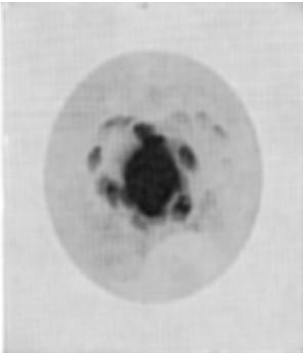
Nobel prize in 1914 “for his discovery of the diffraction of X-Ray by crystals”





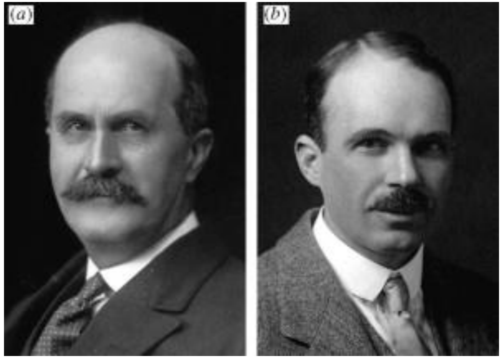


λ~1Å



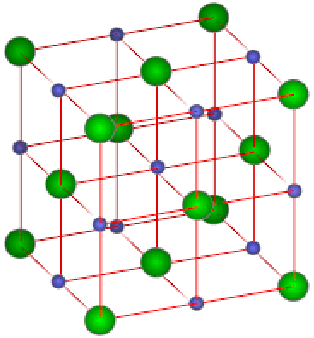
First diffractogram with X-Rays

Bragg family

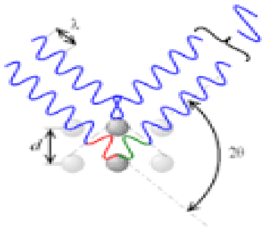


a) William (1862-1942)
b) Lawrence (1890-1971)

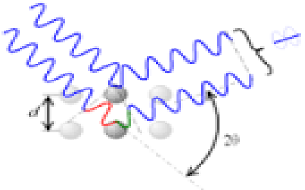
Nobel prize in 1915 “for their services in the analysis of crystal structure by means of X-rays”



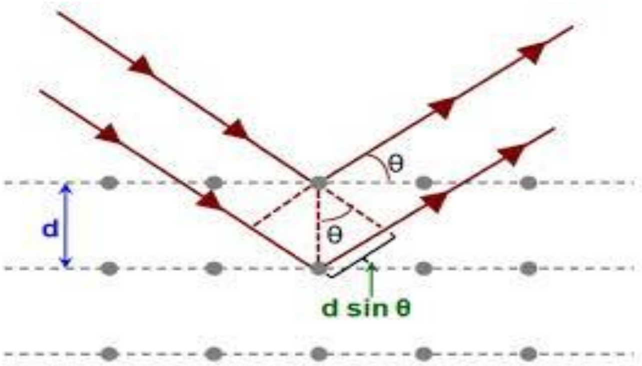
NaCl Fcc



Constructive interference



Destructive interference



Bragg law

$$2d_{hkl} \sin \theta_{hkl} = n\lambda$$

James Chadwick (1897-1974)

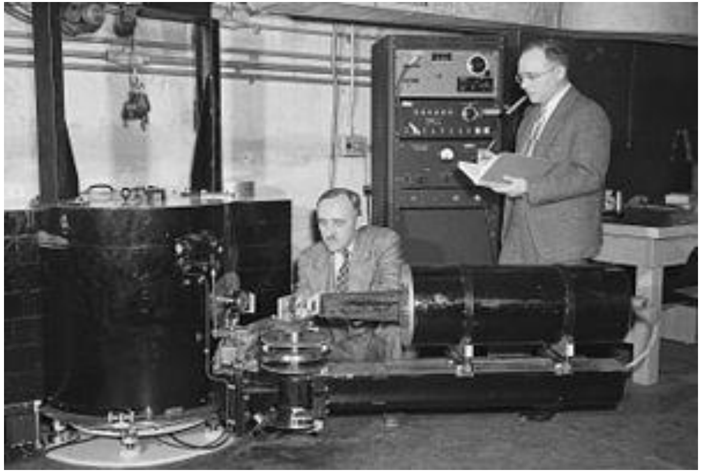
Discover the **neutron** in 1932

In 1936 it proves that **neutron** can be used to make **diffraction** due to wave-particle duality

Problem: weak source

Solution: nuclear reactors in 1942

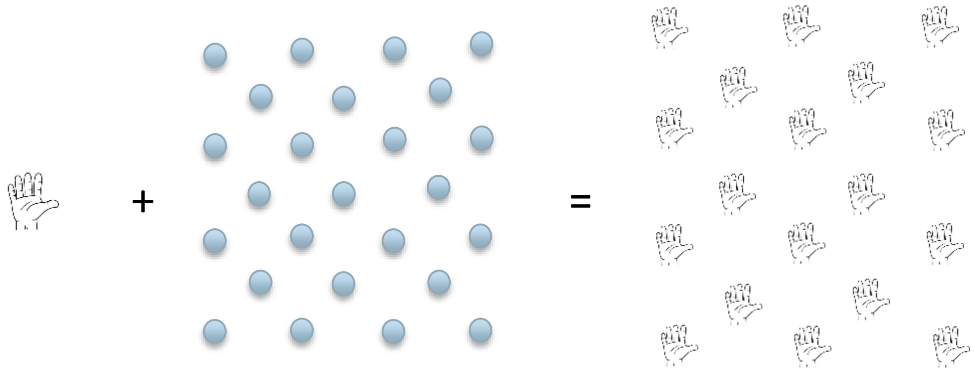
Fist neutron diffraction experiment was carried out by Cliffor Shull and Ernest Wollan in 1946



Clifford Shull (right) and Ernest Wollan working with a double-crystal neutron spectrometer in 1949. Nobel prize in 1994 “for the development of the neutron scattering technique”

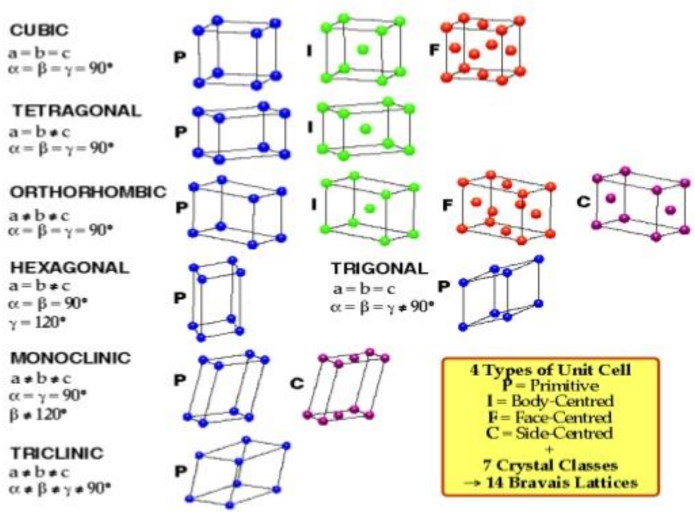
Crystallography

What is a crystal?



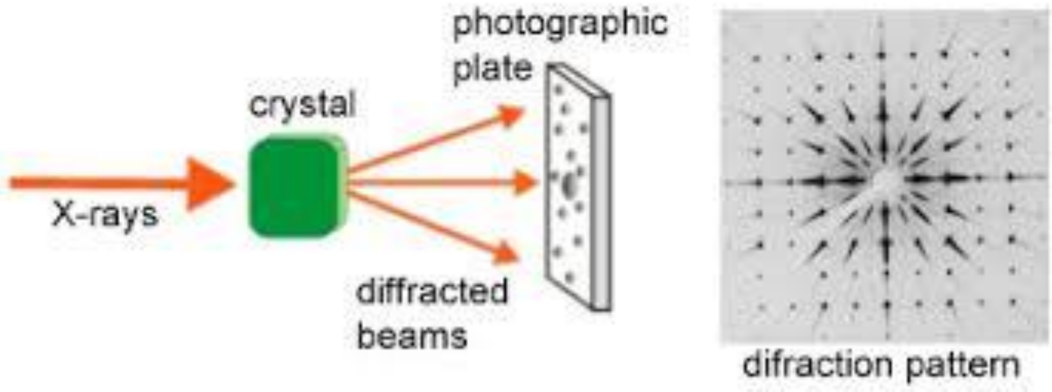
Motif Lattice Crystal

Crystal lattice structures



Reciprocal space

The diffraction pattern obtained in the experiments is in **reciprocal space**



Reciprocal lattice is a network of points in the **Fourier space** defined for the vector:

$$\vec{\tau} = h\vec{a}^{*} + k\vec{b}^{*} + l\vec{c}^{*}$$

$$\vec{a}^{*}.\vec{a} = 1$$
$$\vec{b}^{*}.\vec{b} = 1$$
$$\vec{c}^{*}.\vec{c} = 1$$

Structure factor

For X-rays

$$F_{hkl} = \sum_j f_j e^{2\pi i(hx_j+ky_j+lz_j)} e^{-B_j(sin^2\theta)/\lambda^2}$$

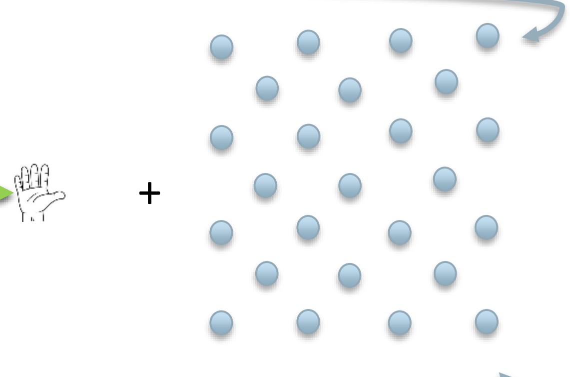
For neutron

$$F_{hkl} = \sum_j b_j e^{2\pi i(hx_j+ky_j+lz_j)} e^{-B_j(sin^2\theta)/\lambda^2}$$

F_{hkl}: structure factor
f_j: X-rays form factor
b_j: neutron from factor
hkl: Miller indices
x_j, y_j, z_j: coordinates of atom j
B_j: thermal parameter
λ: wavelenght

Structure factor

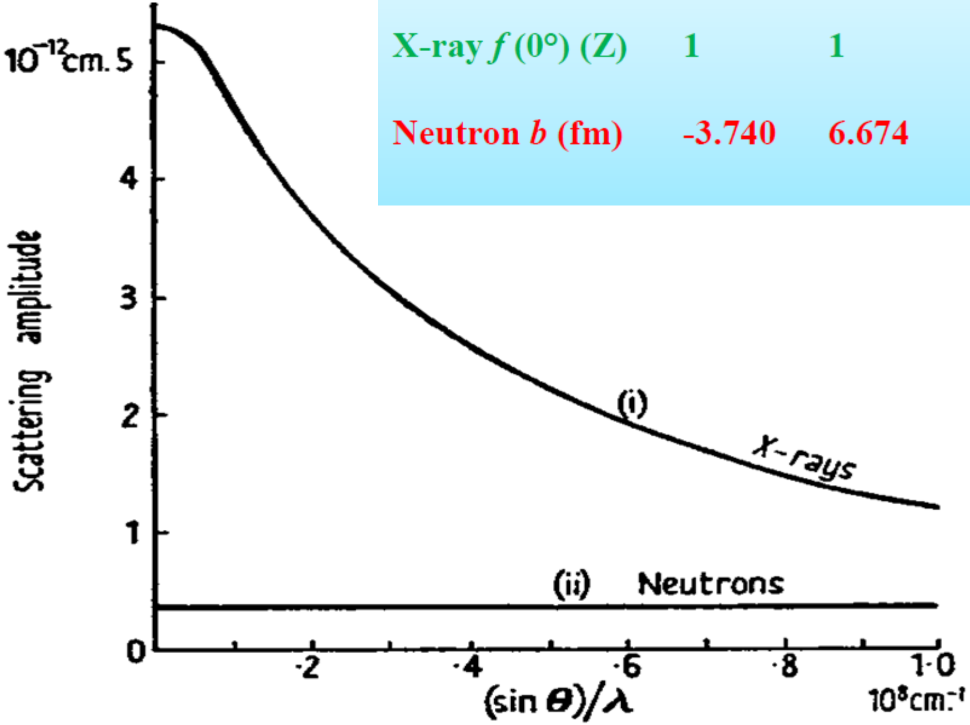
$$F_{hkl} = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)} e^{-B_j(\sin^2\theta)/\lambda^2}$$



$$F_{hkl} = \sum_j b_j e^{2\pi i(hx_j + ky_j + lz_j)} e^{-B_j(\sin^2\theta)/\lambda^2}$$

Structure factor

Element	H	D	U	Fe	Co	O	V	Ti
X-ray *f* (0°) (Z)	1	1	92	26	27	8	23	22
Neutron *b* (fm)	-3.740	6.674	8.420	9.450	2.780	5.805	-0.3824	-3.438

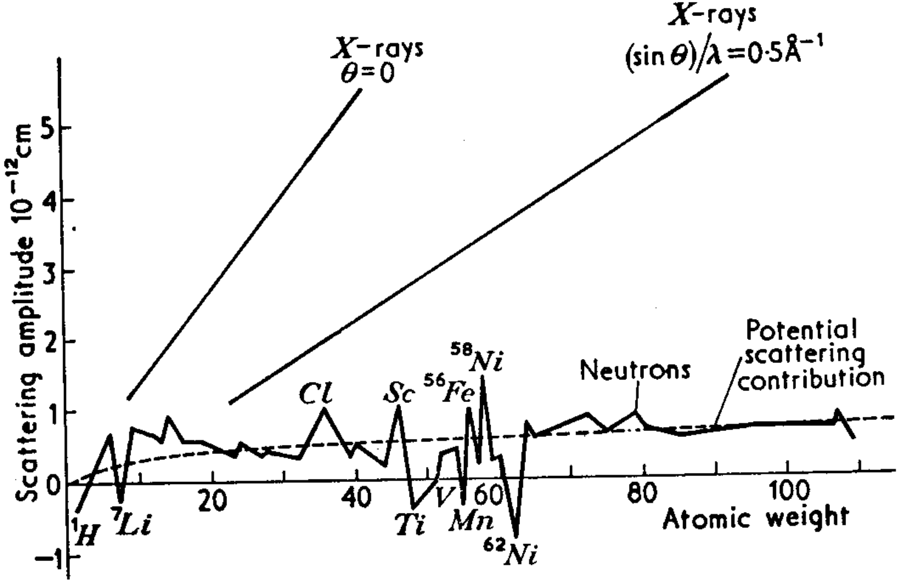


For same atom:

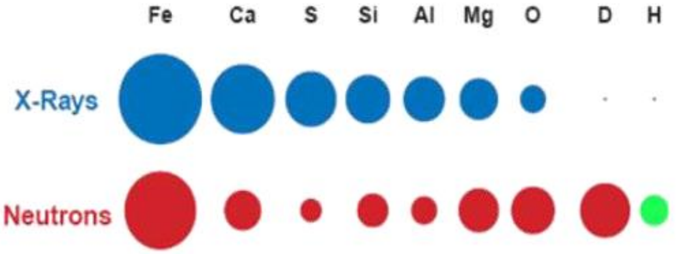
- X-Rays: scattering amplitude ↓ when (sinθ)/λ ↑
- Neutron: scattering amplitude is constant

Structure factor

In X-ray the magnitude of **f is proportional to Z**
In neutrons nuclear factor determine b



Relative scattering factors



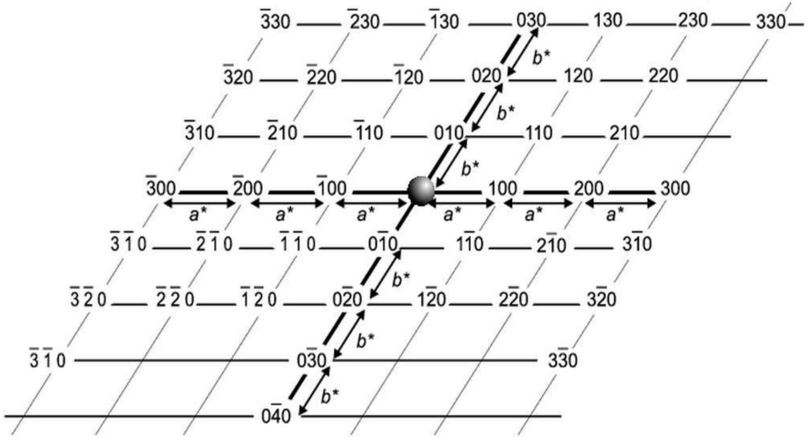
Single-crystal diffraction

Crystal lattice continuum in the whole sample
All oriented in the same direction

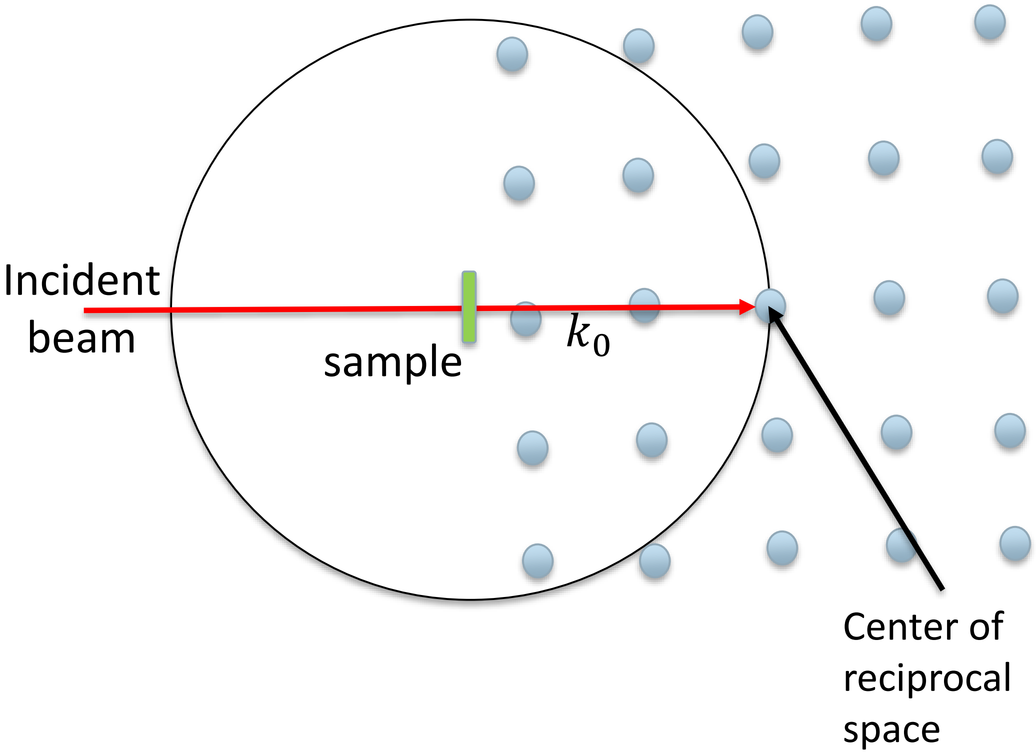
Real space

Diffraction

Reciprocal space



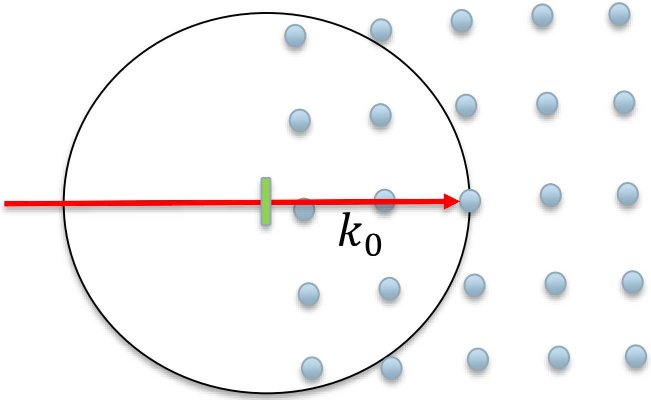
Ewald sphere



Ewald sphere characteristics:

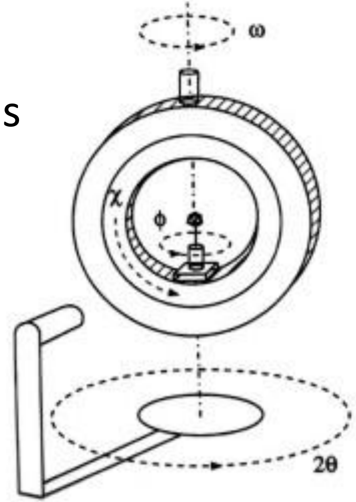
- Lives in reciprocal space
- Radious 1/λ
- Centered in the crystal
- Diffraction direction

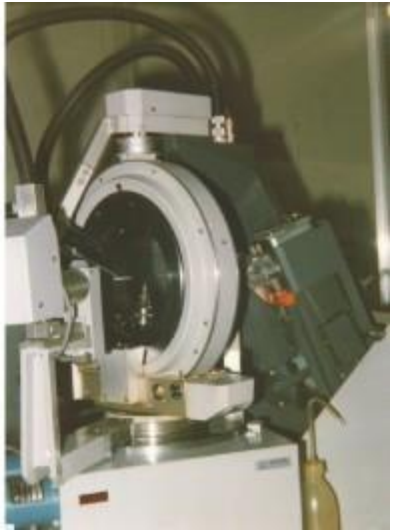
Ewald sphere

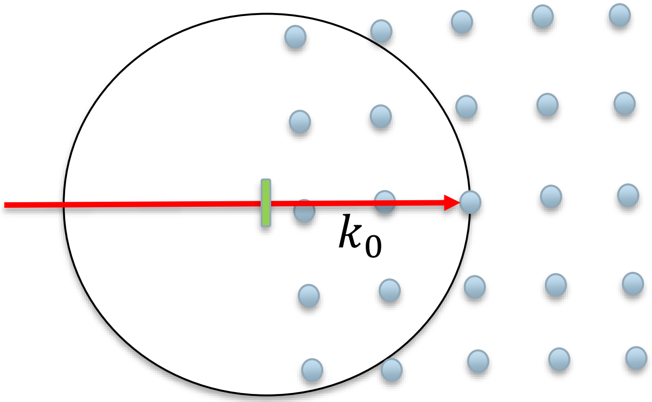


NO REFLEXION!!
There is not any point in the sphere's border

Move the real space is move the reciprocal space

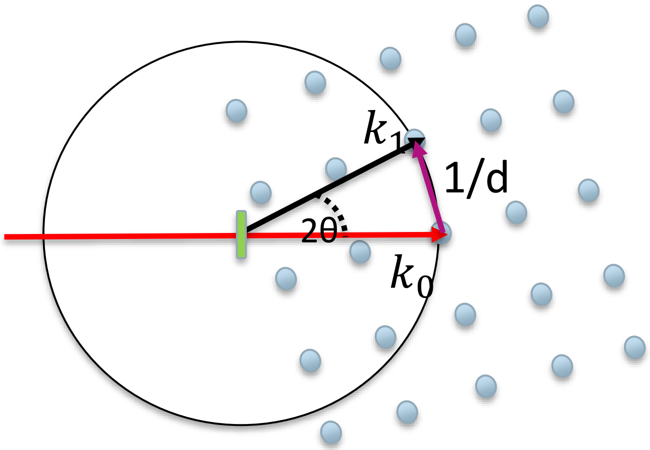






NO REFLEXION!!

There is not any point in the sphere's border

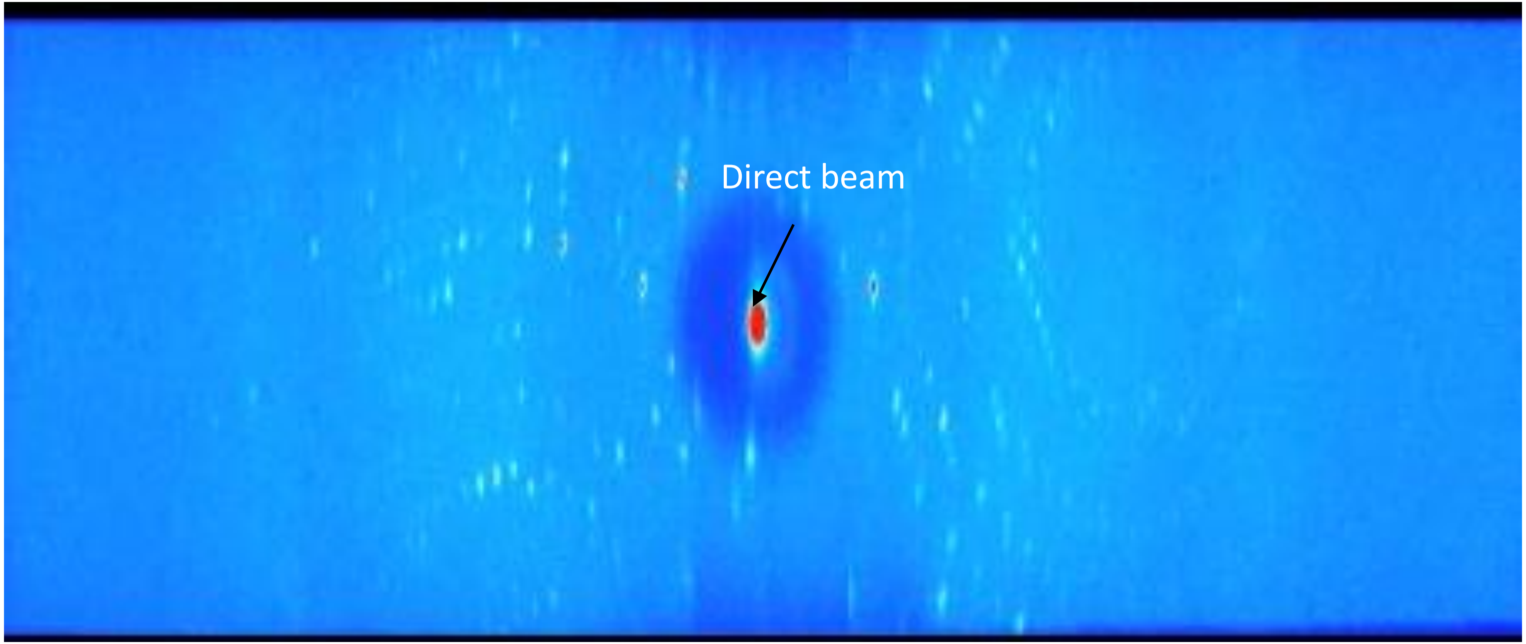


REFLEXION!!

One point of the reciprocal space is sphere's border

$$\frac{1}{d} = d^* = ha^* = kb^* = lc^*$$

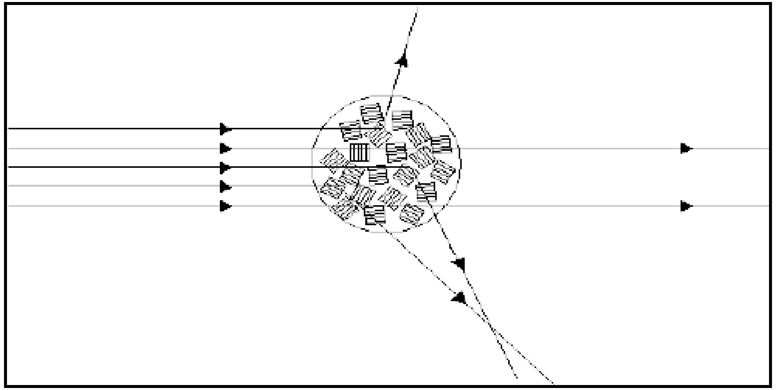
D19 monochromatic single-cristal diffractometer



Powder diffraction

What is powder?

Polycrystalline sample formed by a big number of single-crystals **randomly oriented**



1 cm^3 of powder =>
10^9 $(10\ \mu m)$ - 10^{12} $(1\ \mu m)$
little crystals

Always there are thousand of crystals that respect the diffraction conditions!!

Why powder samples?

Large number of preparative methods available

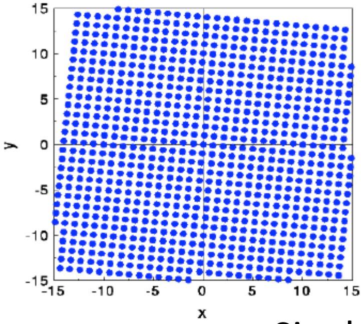
Can be prepared in large quantities (g, kg, etc.)

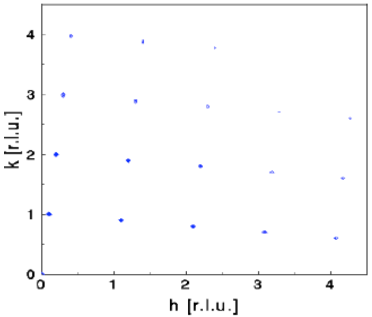
Fast synthesis

Real world materials are often in polycrystalline

Real space

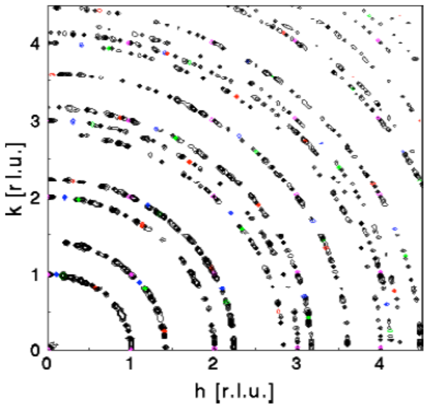
Reciprocal space

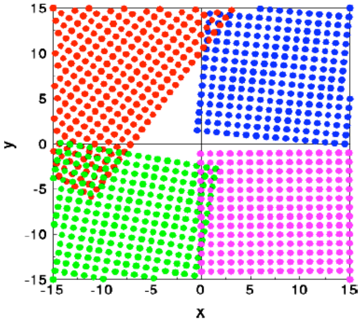


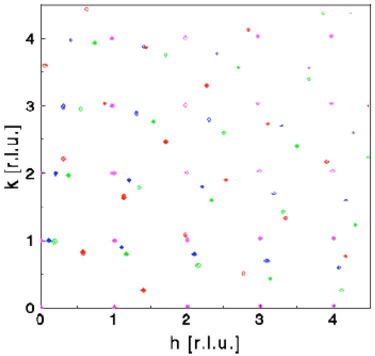


Single crystal

Forty single crystal

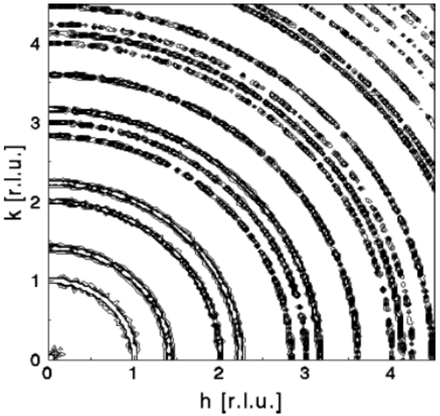




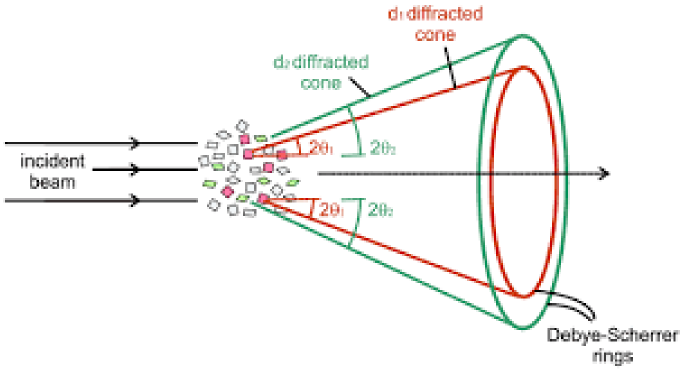


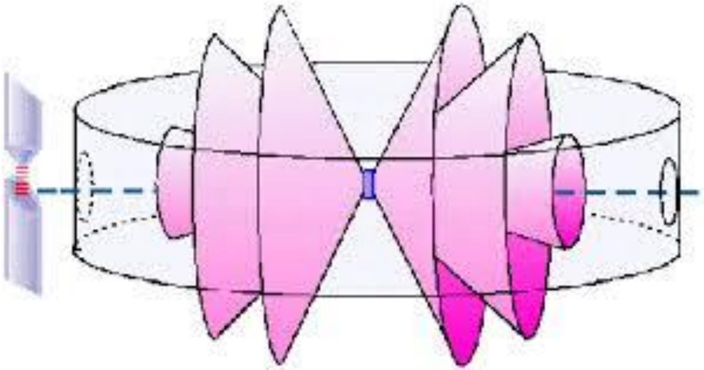
Four single crystal

Two thousand single crystal



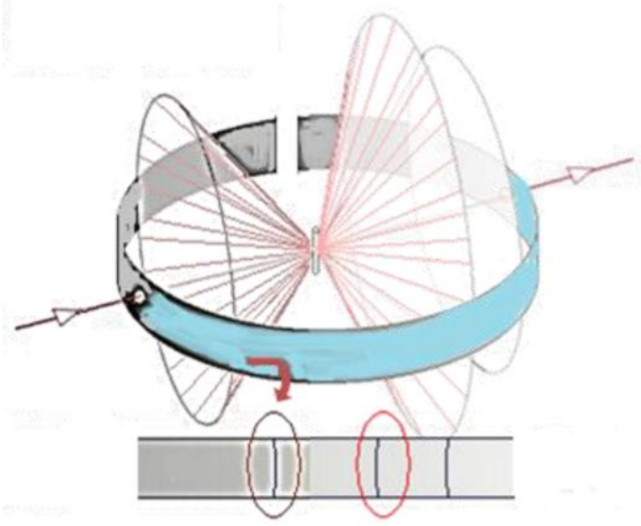
Debye-Scherrer configuration





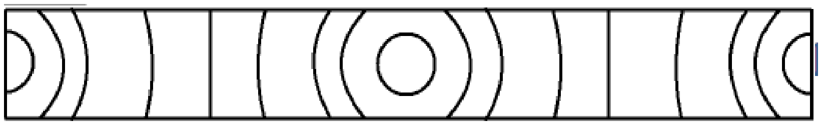
Big number of small crystal have **same orientation** => **same diffraction conditions** => reflection with **same angle**

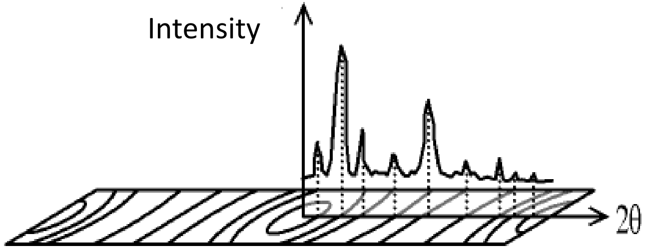
Debye-Scherrer configuration



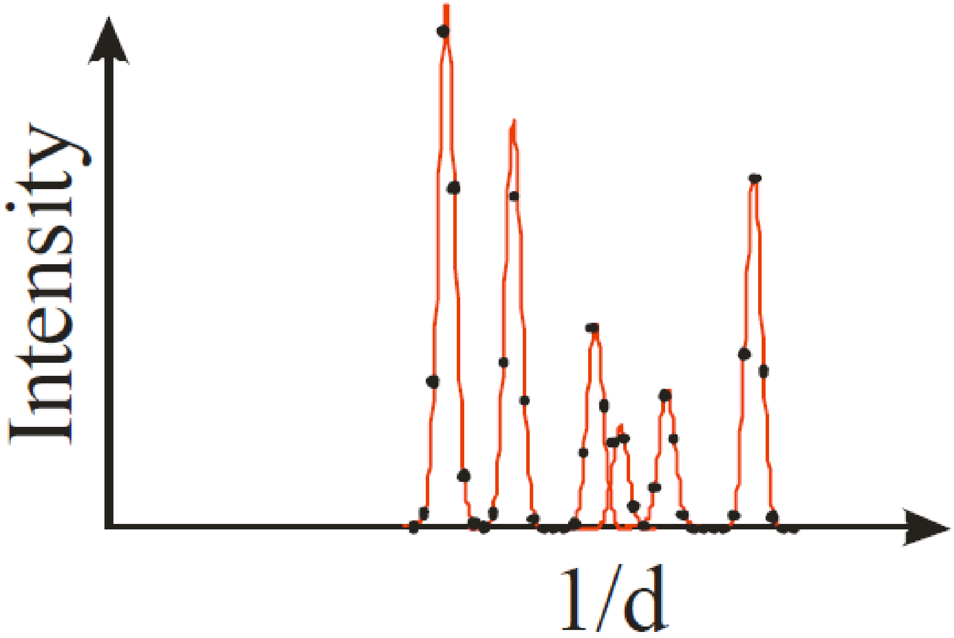
The diffracted cones intersect a banana-detector

Arcs produced in banana-detector are our diffraction pattern





The importance of the peak shape



Rietveld method consist in use all **intensity profile data** of each reflection instead of integrated intensities

Rietveld method makes possible to obtain all the information that is buried in the superposed peaks:

* Space group
* Atom position
* Occupancy

The importance of the peak shape

Two contribution to broadening:

a) Instrumental

b) Sample

$$I(2\theta) = \int_{-\infty}^{\infty} I_{instrument}(\psi)\, I_{sample}(2\theta - \psi) d\psi$$

Gaussian

$$B_{total}^2 = B_{instrument}^2 + B_{sample}^2$$

Lorentzian

$$B_{total} = B_{instrument} + B_{sample}$$

Ψ is dummy variable, cover the full range of possibilities

Particle size

$$\tau = \frac{K\lambda}{\beta cos\theta}$$ → Scherrer equation

τ is the mean size of the ordered domains, which may be smaller or equal to the grain size

K is a dimensionless shape factor, with a value close to unity

λ is the wavelength

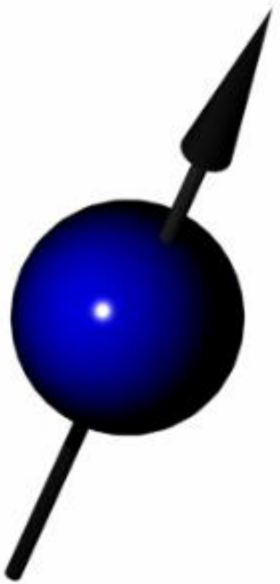
β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians

θ is the Bragg angle

Magnetic diffraction

Fundamental neutron properties

- **Non-charged** particle $m_N = 1{,}67 \cdot 10^{-27} kg$
- Total orbital momentum (nuclear spin) I=1/2
- Neutron moment is around 960 times smaller than the electron moment



	proton	neutron
Nuclear magnetons: $\mu_N = \frac{e\hbar}{2m_p}$	$\mu_p = 2{,}793\mu_N$	$\mu_n = 1{,}913\mu_N$

For neutrons: $\mu_n = -\gamma\mu_N\sigma$ with $\gamma_n = 1{,}913$

Magnetic diffraction

Magnetic form factor

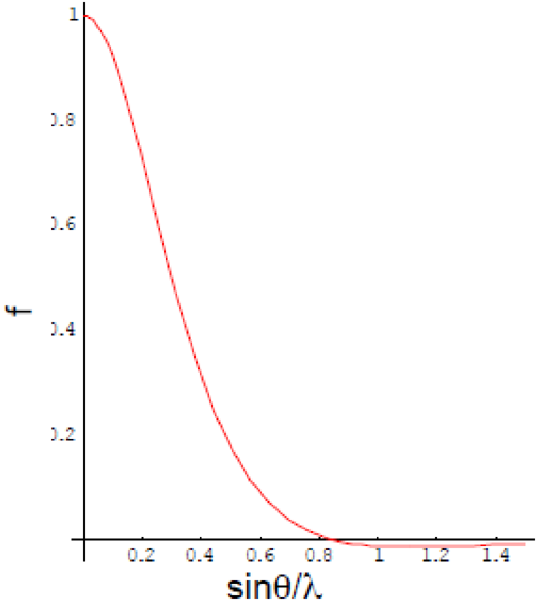
Like for nuclear scattering the Born approximation holds and the scattered amplitude is the Fourier transformation of the potential function (atomic magnetization density), the **magnetic form factor**

$$f(\boldsymbol{k}) = \int \rho(\boldsymbol{r}) \exp(i\boldsymbol{k}\boldsymbol{r})\, d\boldsymbol{r}$$

$$f(\boldsymbol{k}) = \frac{g_S}{g} j_0(\boldsymbol{k}) + \frac{g_L}{g} [j_0(\boldsymbol{k}) + j_2(\boldsymbol{k})]$$

g, g_S, g_L: g-factors

j_n: spherical Bessel functions



Magnetic information is in small Q peaks

Magnetic diffraction

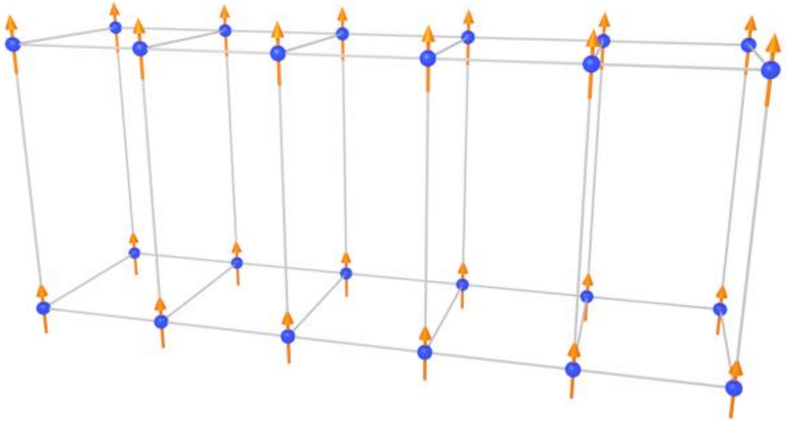
Magnetic form factor

$$f(\boldsymbol{k}) = \int \rho(\boldsymbol{r}) \exp(i\boldsymbol{kr})\, d\boldsymbol{r}$$

Magnetic information

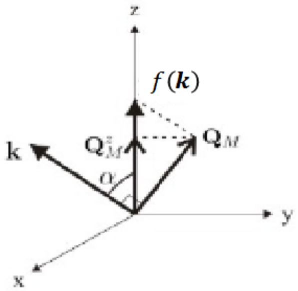
- Magnetic moment
- Orientation

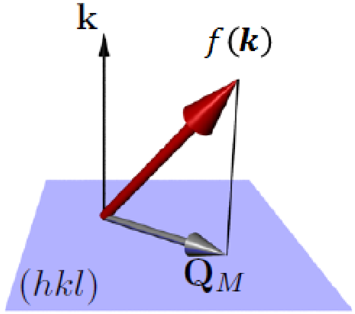
Information about the lattice



Only the component of f(**k**) which is **perpendicular** to **k** contributes to magnetic scattering

$$Q_M = \hat{k}\text{x}\left(f(\boldsymbol{k})\text{x}\hat{k}\right)$$





Magnetic diffraction

Propagation vector

Magnetic structure can have different periodicity and symmetry that nuclear structure

The relation between one and another is expressed by the **propagation vector**

The propagation vector is given by **satellite peaks**

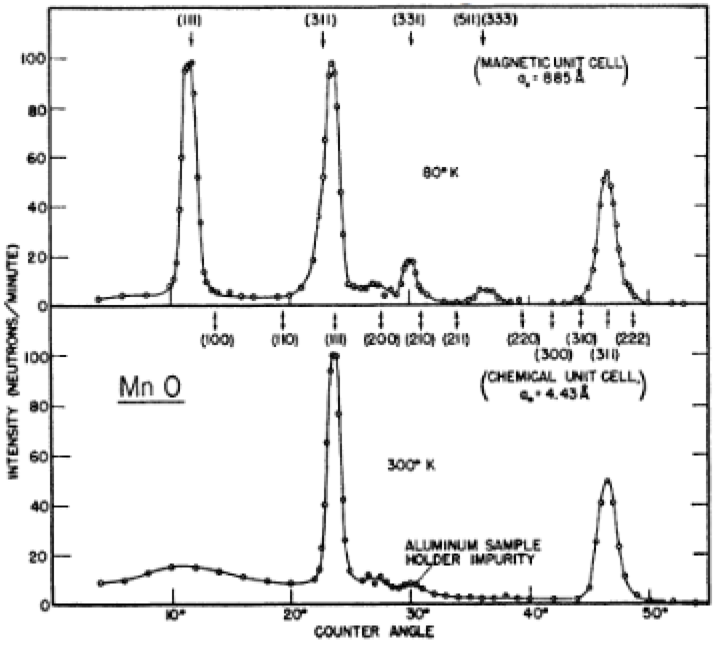
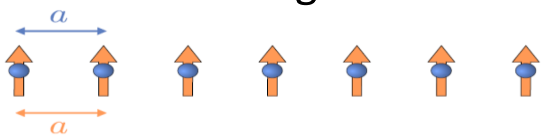


FIG. 1. Neutron diffraction patterns for MnO at room temperature and at 80°K.

Magnetic diffraction

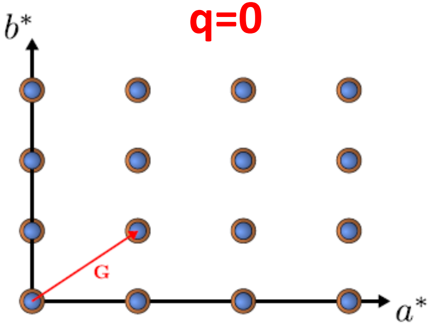
Some magnetic structures

ferromagnetic

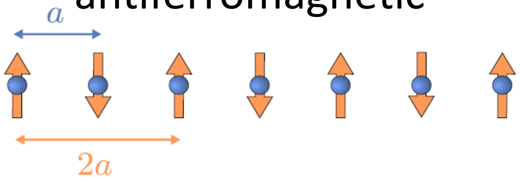


magnetic periodicity=nuclear periodicity

q=0

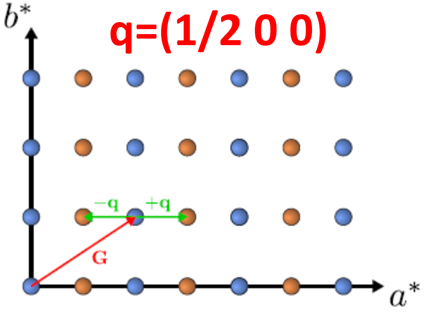


antiferromagnetic

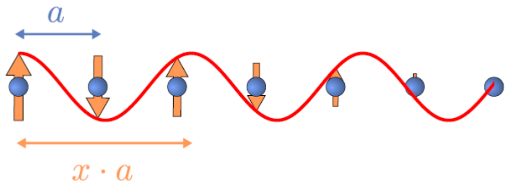


magnetic periodicity=2x nuclear periodicity

q=(1/2 0 0)

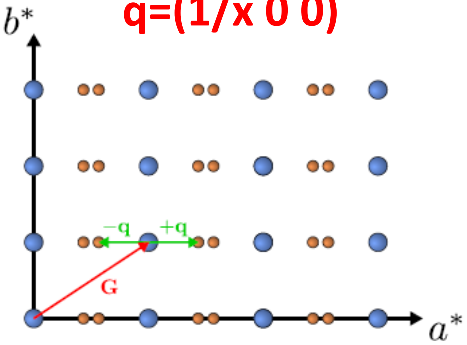


Inconmensurate antiferromagnetic



magnetic periodicity=x times nuclear periodicity

q=(1/x 0 0)



Instruments

Single-crystal

Nuclear structures:

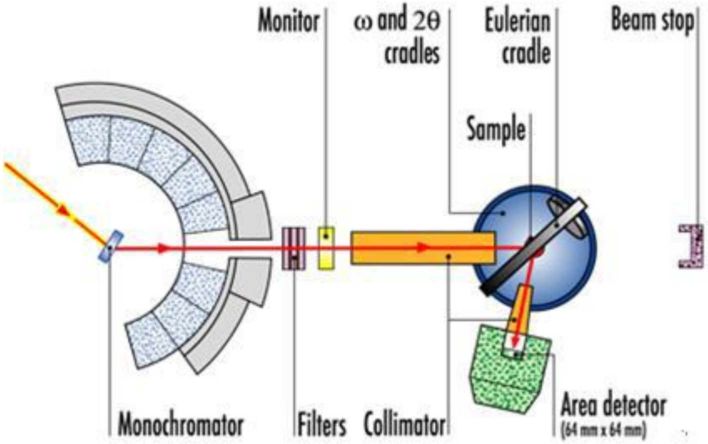
- D9
- D19
- Laue diffractometers

Magnetic structures:

- D3
- D23
- D10

Instruments

D9: hot neutron 4-cicle diffractometer



Technical characteristics:

- 4-circle configuration
- Normal beam

Sample environment:

- Presure cells
- Dilution 50mk
- Cryofurnace (1.8-520K)
- Displex and furnace (2/12K-1200K)

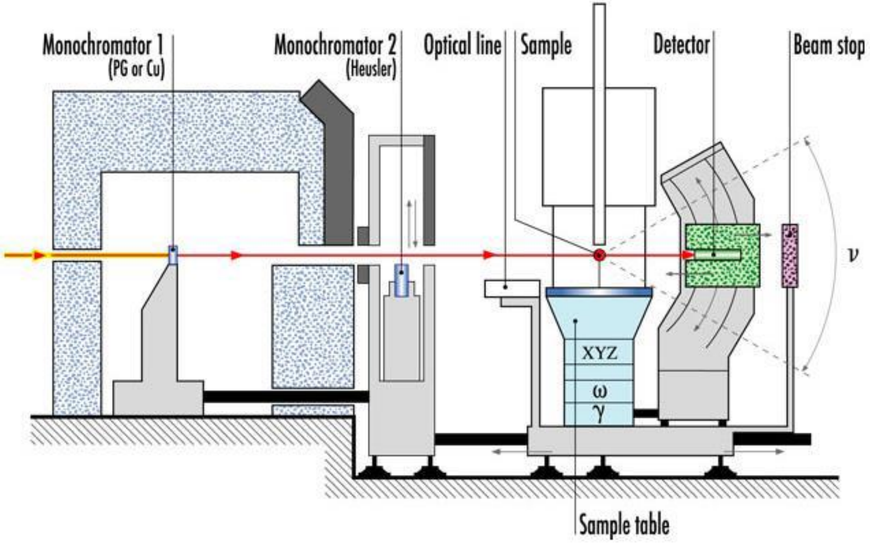
Detector:

- Pixel size 2x2mm^2 / $0{,}25^{\circ}$ x $0{,}25^{\circ}$

Inorganic compounds or small molecules

Instruments

D23: lifting-counter two-axis diffractometer



- Thermal neutron
- Either polarized or unpolarised neutron

Sample environment:
- Cryostat (1,5-300K)
- High field cryomagnet (~15T)
- Pressure cells (~30kbar)

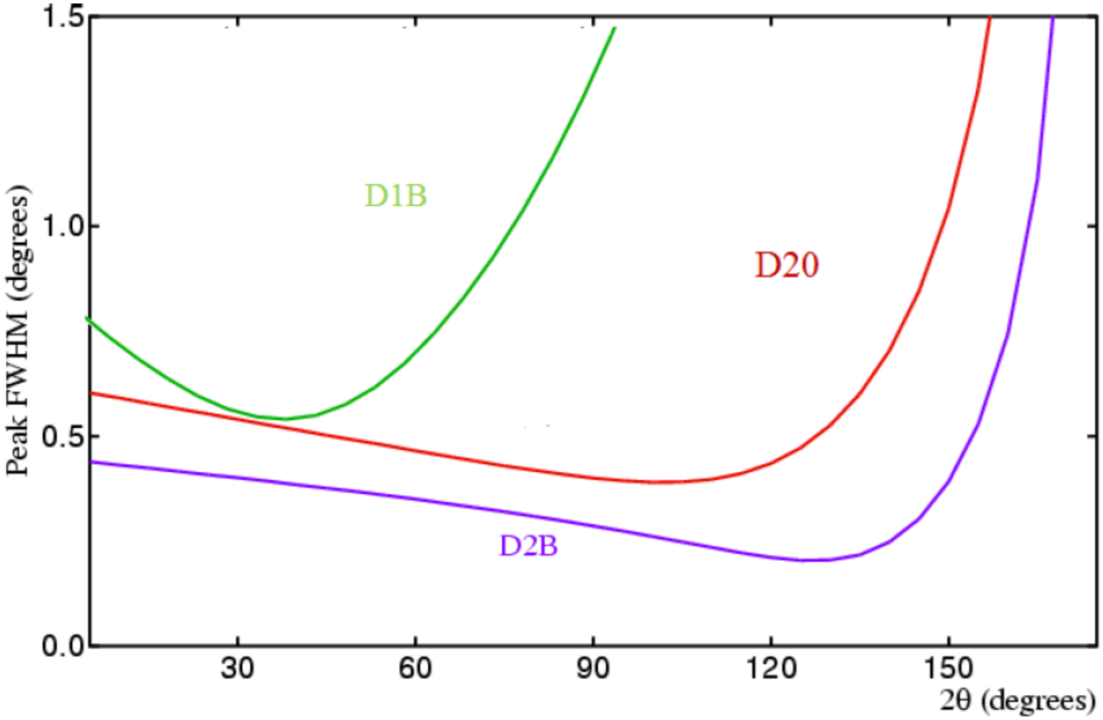
Angular ranges:
- -181<w<181 °
- -124< γ<128,5 °
- -28<α<29 °

Instruments

Powder diffractometers

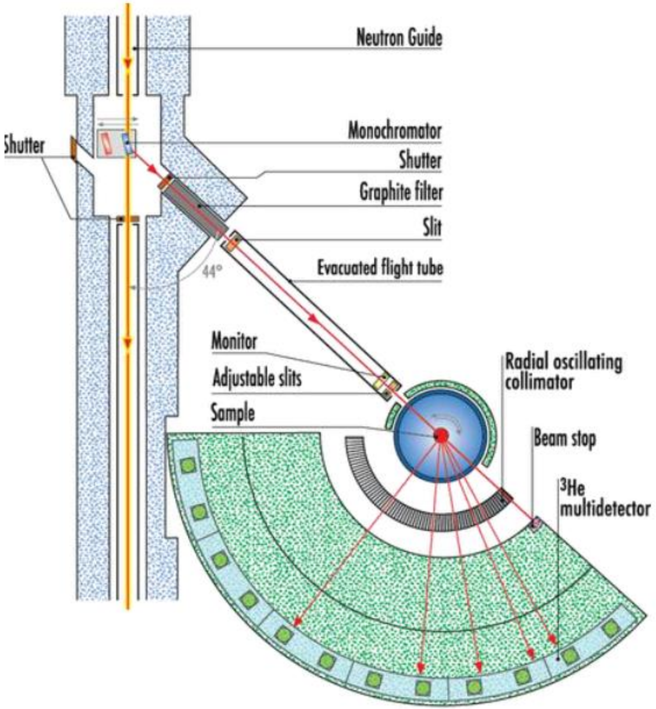
Depending of the range of better resolution, the diffractometer is useful for magnetic or for nuclear structure. The resolution depends strongly of the **take-off-angle** (diffraction angle of monochromator)

D1B magnetic structure
D2B and **D20** (high-res. config) nuclear structure



Instruments

D1B: Two-axis diffractometer



Take-off-angle: 44.22 °

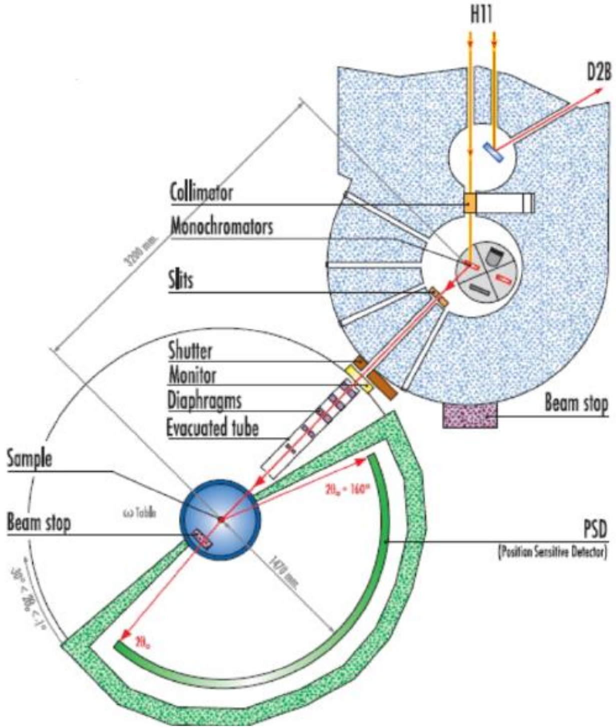
λ= 1.28Å, 2.52Å

Angular range sample: 0.8 ° <2θ<128 °

^{3}He multidetector 1280 cells

Instruments

D20: high-intensity two-axis diffractometer with variable resolution



5 Take-off-angle (low)= 26 °, 28 °, 30 °, 42 °

Take-off-angle (high)= 65 °, 90 °, 120 °

λ=0.82-0.94Å, 1.30Å and 2.41Å

^{3}He microstrip gas-detector (PSD) 1536 cells

Neutron or X-rays?

	X-Rays	Neutron
Indentify phase	YES	YES
Space group	YES	YES
Structure refinement	YES	YES
Light elements	NO	YES
Neighbouring elements	NO	YES
Structure solution	YES	YES
Magnetic structures	NO	YES

NEUTRONS FOR SOCIETY

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Magnetic cross section

For elastic neutron magnetic scattering, is necessary evaluate the cross section

$$\frac{d\sigma}{d\Omega} = \left(\frac{m}{2\pi\hbar}\right)^2 \sum p_i \left| \langle \mathbf{k}_f, \chi_f | V_m | \mathbf{k}_i, \chi_i \rangle \right|^2$$

- χ_i initial spin-state of the neutron
- χ_f final spin-state of the neutron
- $\mathbf{k}_i$ incident wave-vector
- $\mathbf{k}_f$ scattered wave-vector
- **Q** momentum transfer
- V_m magnetic interaction potential
- p_i : probability to find the initial spin-state i