Neutron Diffraction

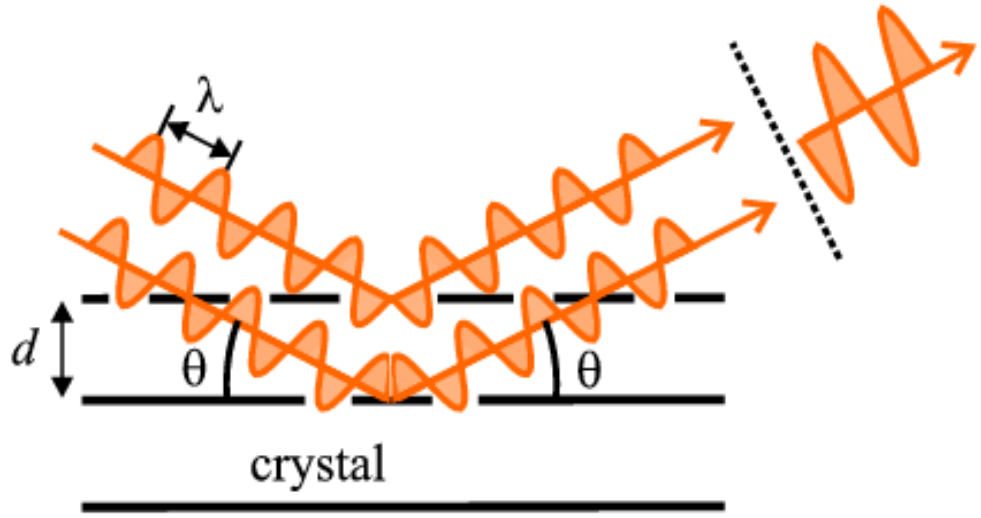
15th Central European Training School on Neutron Techniques

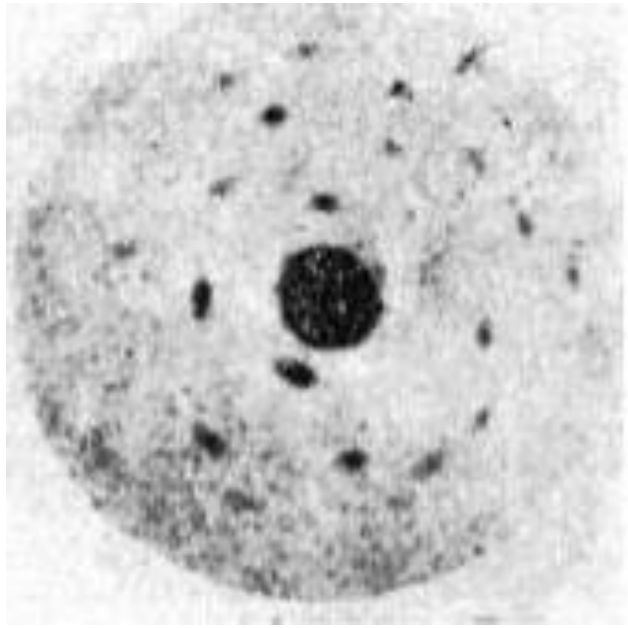
Indu Dhiman

Budapest Neutron Centre, Centre for Energy Research

What is Diffraction

A simplistic view: Laue Diffraction

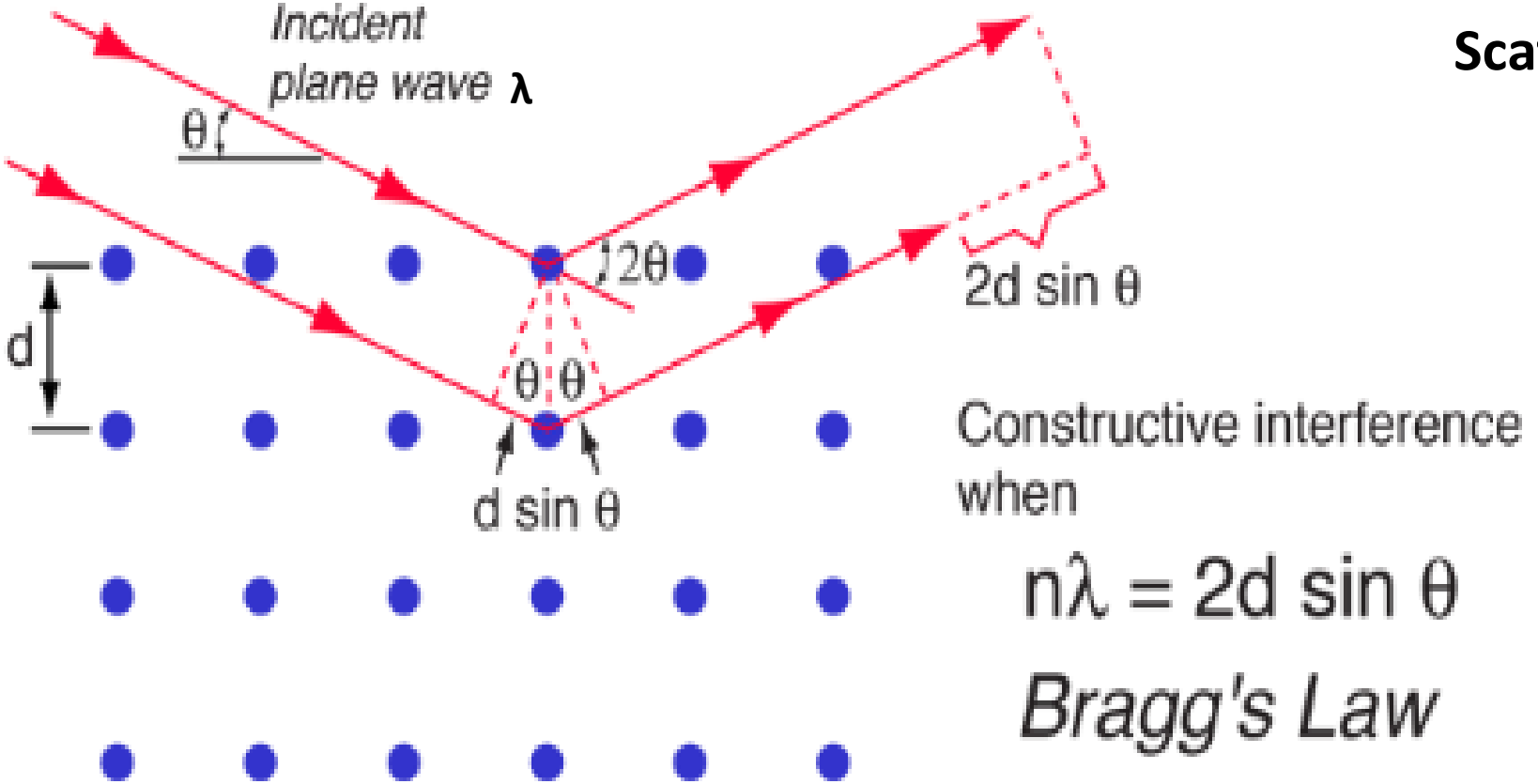




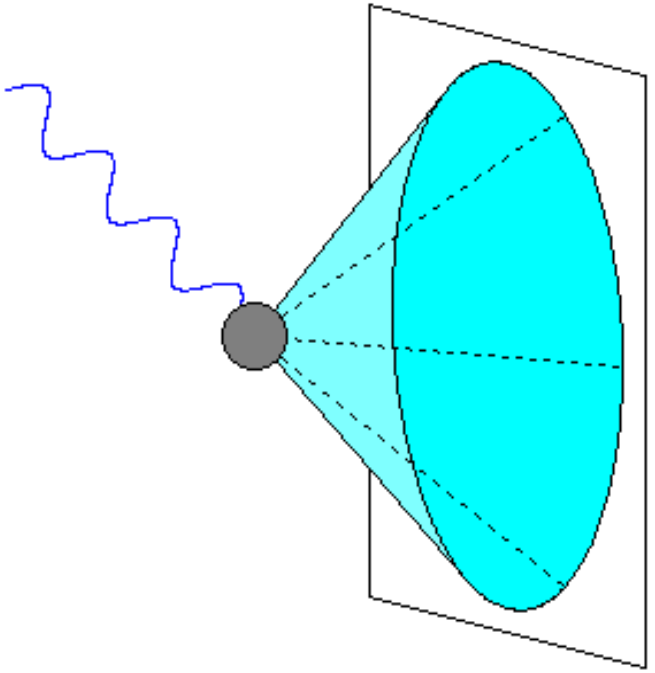
Diffraction

When radiation such as x – rays or neutrons, is shined upon a crystalline materials, the **in – phase** scattering occurs. This leads to the so called **diffraction spots**

Bragg's Law



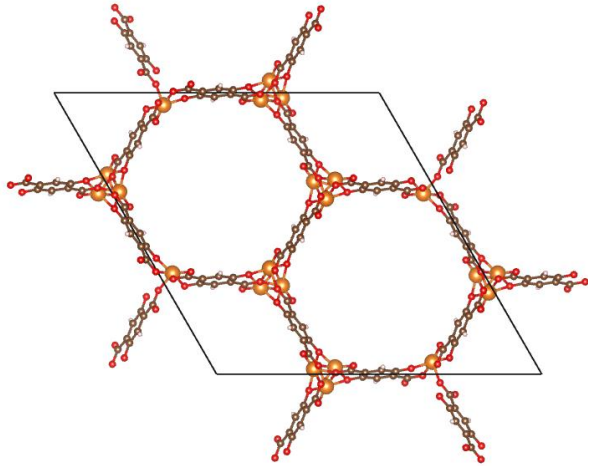
Scattering: Debye –Scherrer cone



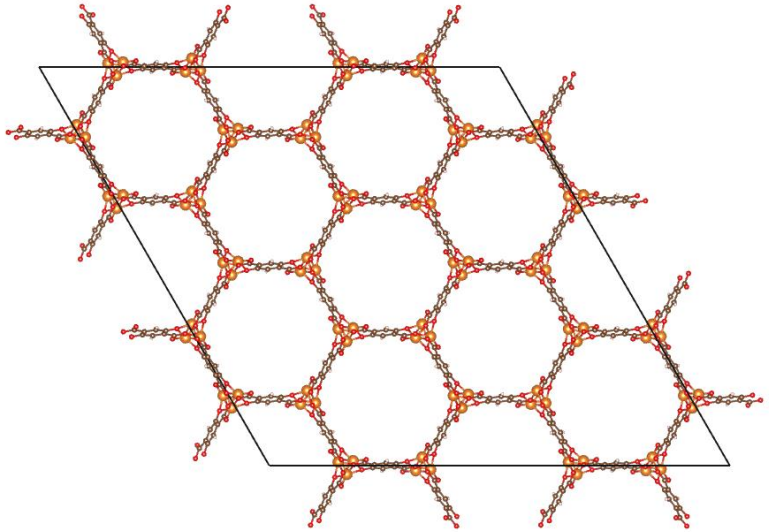
Bragg's law is applicable to both Powder and single crystal diffraction

λ is the incident radiation wavelength, *d* is the inter-planar spacing and θ is the angle between the incident / diffracted beam and the relevant crystal planes; *n* is an integer, known as the order of diffraction

What is Powder



Unit cell

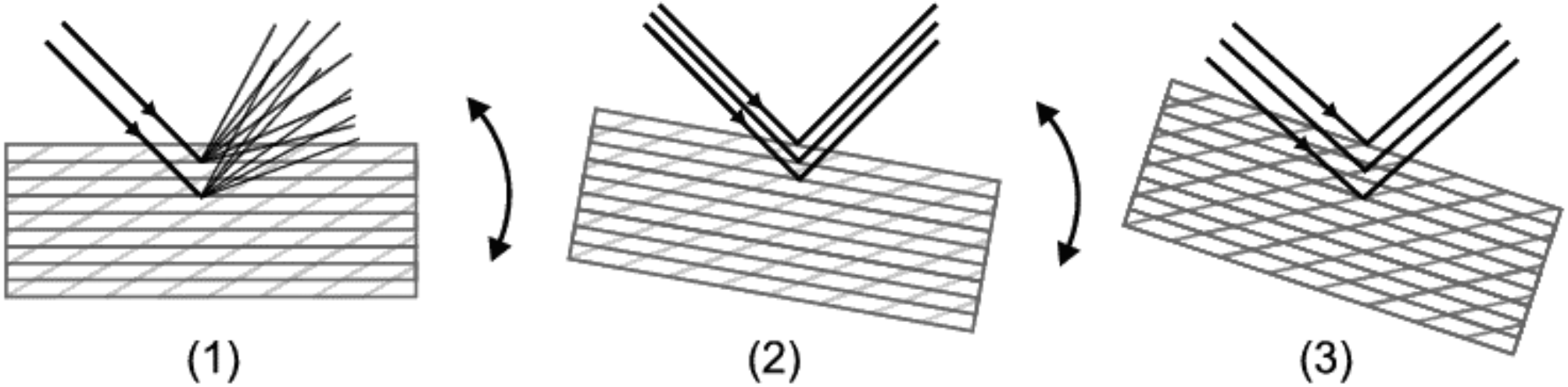


Crystal

In 3D, a crystal is built up by adding identical building blocks, which we call a *unit cell*

In real life, crystals have really larger numbers of unit cells. In our day life we see several such crystalline materials, may typically consist of 1000s of unit cells.

Lets continue ……



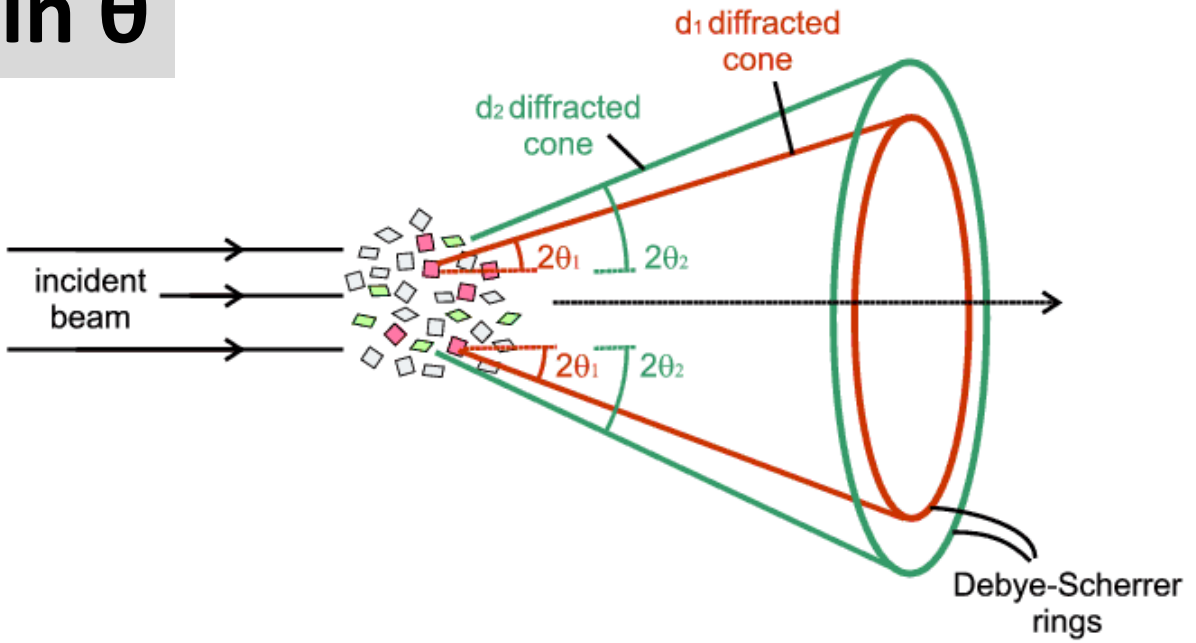
$$n\lambda = 2d\sin\theta$$

Lets consider 3 scenarios

Case 1: Incorrect crystal orientation with respect to Bragg's law

Case 2: If we rotate the crystal: A set of planes satisfy Bragg's law; diffraction occurs

Case 3: Crystal is rotated again: another set of planes satisfy Bragg's law; diffraction occurs



Single Crystal Vs Powder Diffraction Experiments

Single crystal Diffraction Experiments

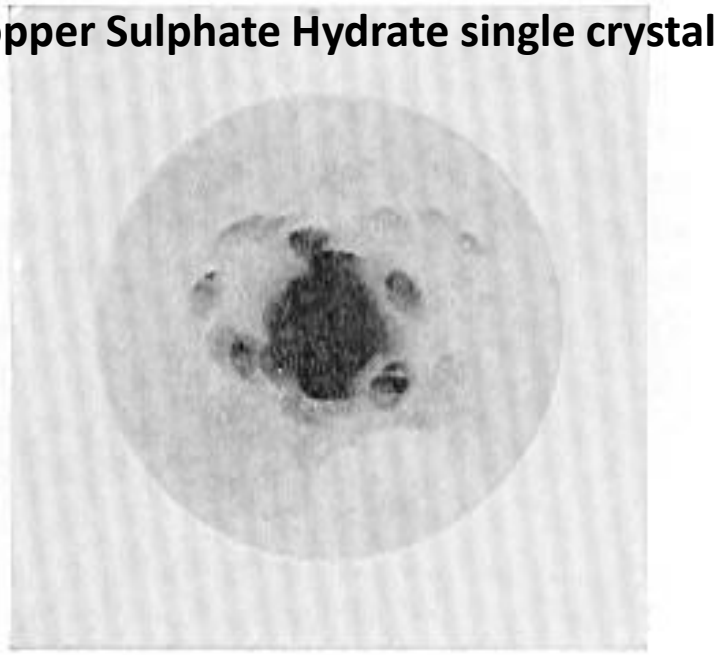
- Difficult to grow single crystals
- Data collection easy, in both access/setup, usually requires sample rotation
- Simpler to determine unit cell for a good quality single crystal
- Data reduction and structure determination (often easy)
- Structure Optimization, refinement method

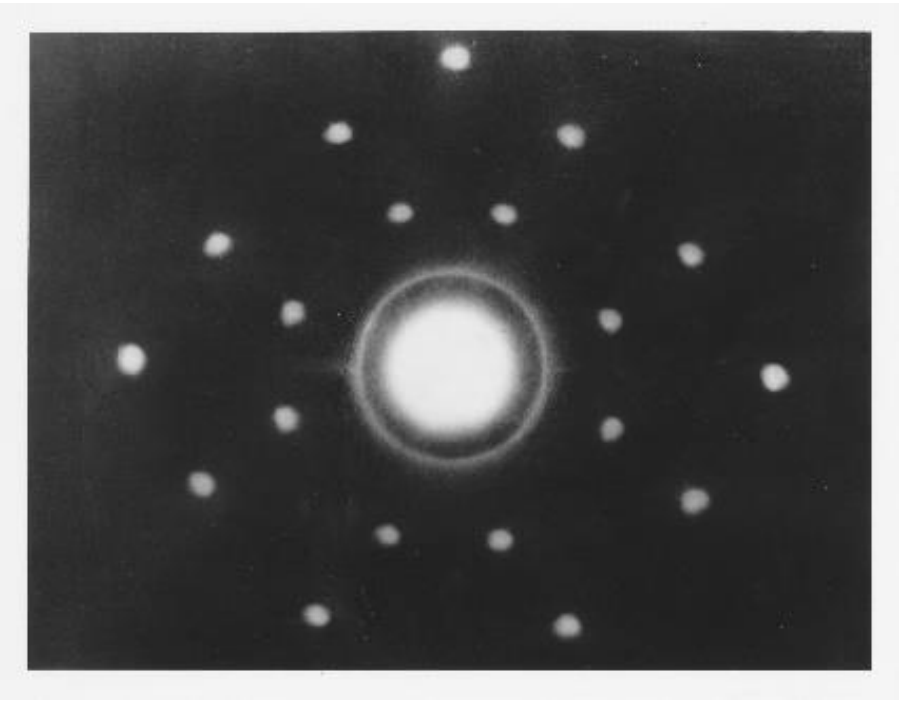
Powder experiments

- Powder sample preparation is rather easy
- Data collection is usually easy, but also easy to make mistakes !!
- Unit cell determination can be tricky
- Solving structure can be difficult – requires expert knowledge
- Structure optimization – Rietveld refinement with considerable care
- Solving magnetic structure – can be really difficult

History of Powder Diffraction

- **Diffraction of X-rays: von Laue, 1912 (Nobel Prize 1914)**
- **Diffraction laws: Bragg & Bragg, 1912-1913 (Nobel Prize 1915)**
- **Powder diffraction: Developed independently by**
  - **Debye and Scherrer in Germany, 1916**
  - **Hull in the United States, 1917**

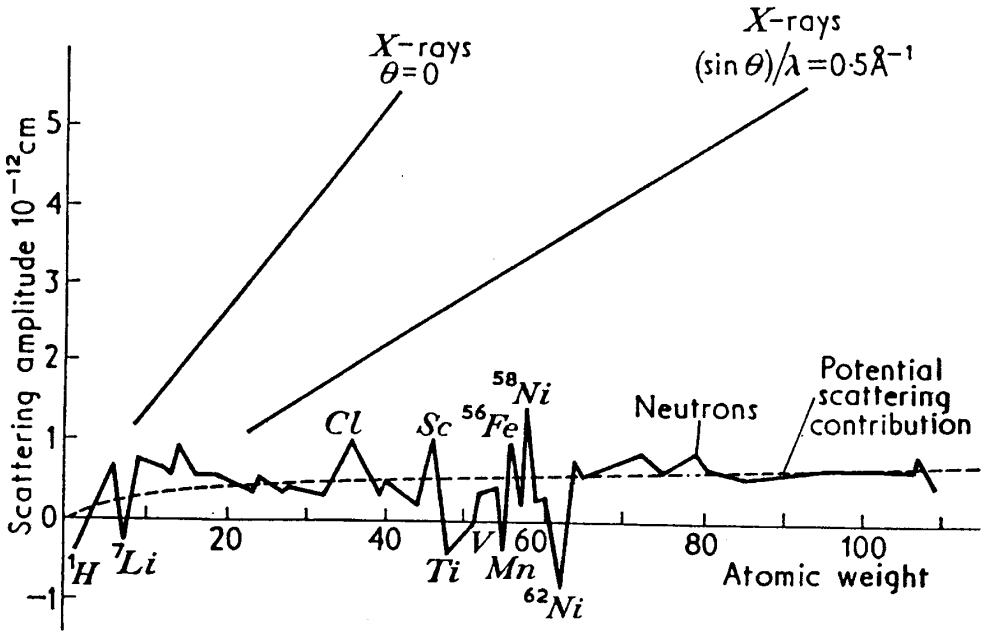

Copper Sulphate Hydrate single crystal



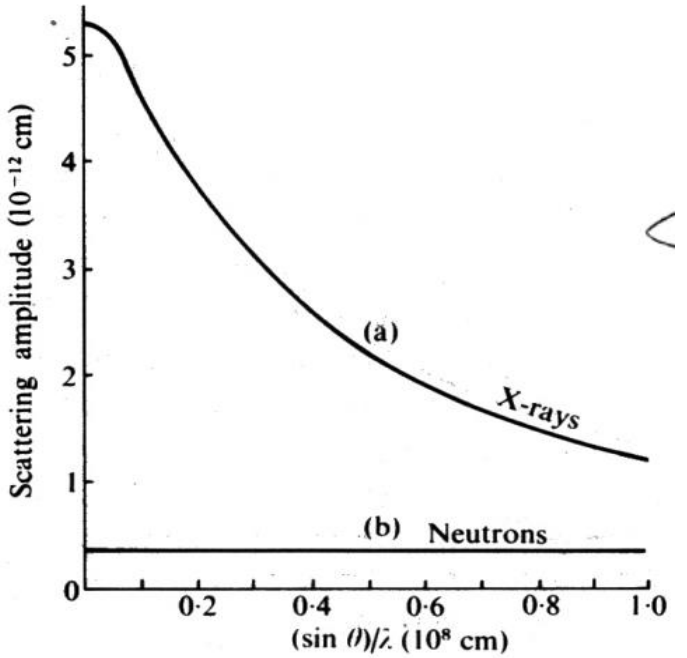
- **The first neutron diffraction experiments were carried out in 1945-46 by Ernest O. Wollan and Clifford Shull (Nobel Prize 1994) using the Graphite Reactor at Oak Ridge.**
- **The first neutron Laue diffraction pattern of NaCl measured by Wollan, Shull, and Milton Marney in 1948 at the Graphite Reactor.**

Neutrons Vs X-rays

X-ray Vs Neutron Scattering Power



X-ray Vs Neutron Scattering Amplitude for Potassium



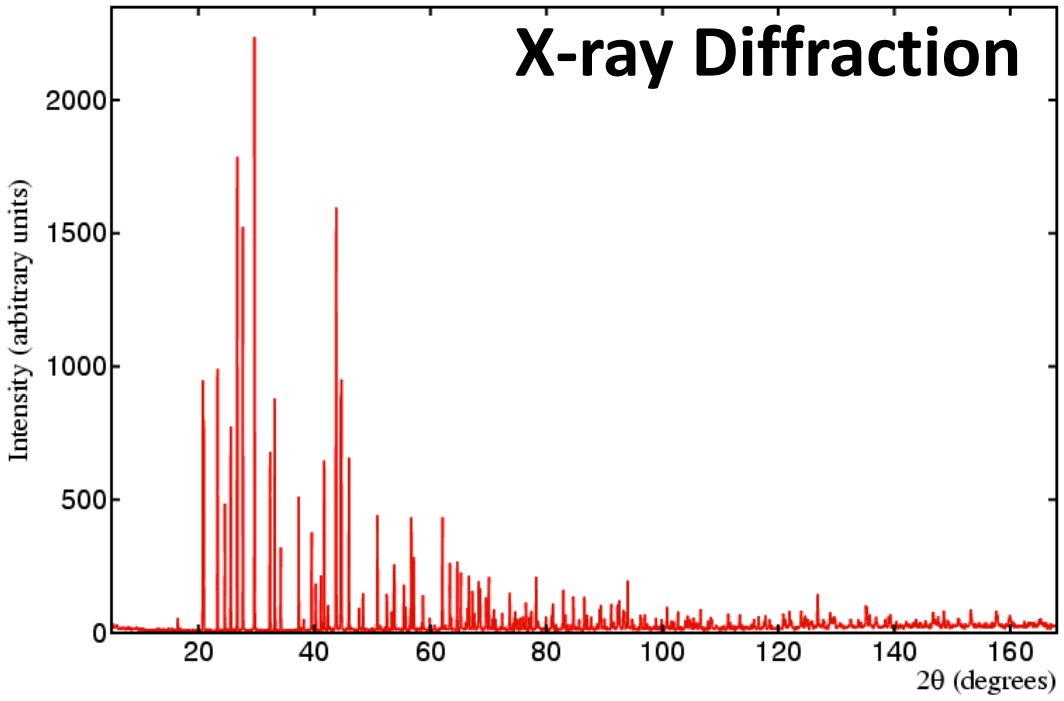
Atomic scattering factor (form factor) f_j for X-rays

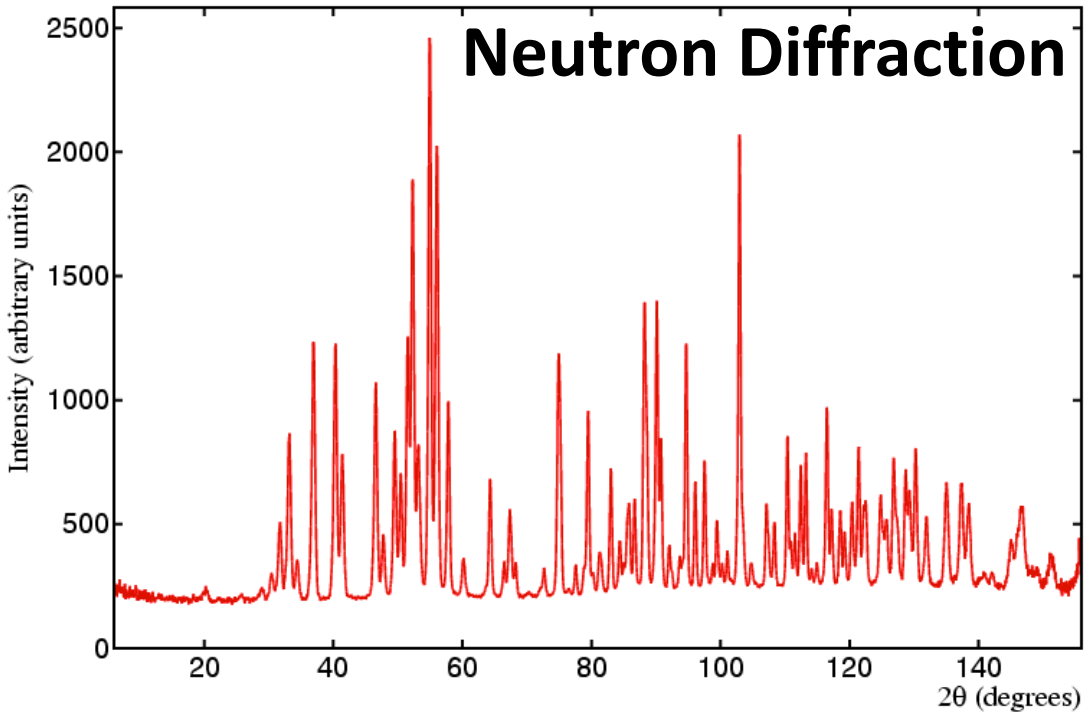
- Depends on number of electrons in atom and Q ($\propto \sin\theta/\lambda$)

Scattering length b_j for neutrons

- Depends on isotope, independent of Q; detect light elements, distinguish isotopes
- Neutron moment interaction with unpaired spins of magnetic atoms: magnetic structure and spin excitation
- For some isotopes, b_j can be negative

Let us look at Neutrons Vs X-rays diffraction pattern





- Data sets collected at different wavelengths, peaks due to identical d spacings appear at different angles
- Relative intensities of adjacent peaks are different in two data sets.
- In X-ray data, the intensity of the reflections decays with increasing 2θ, as against neutron data set
- Peaks are a broader in the neutron data
- Neutron data set has higher background than the equivalent X-ray data set, thus giving a worse peak to background ratio.

Neutron Interaction with Nuclei

Elastic scattering

Inelastic scattering

Elastic scat **or** **netic**

on:

Neutron capture/Absorption: neutron may be captured or absorbed by a nucleus…..

Coherent scattering – in phase. **Incoherent scattering – random phases between scattering from different nuclei**

Diffraction Theory

Fundamental structure factor equation

$$F(hkl) = \sum_{j=1}^{N} f_j \exp(2\pi i(hx_j + ky_j + lz_j)).\exp[-8\pi^2\langle u^2\rangle(\sin^2(\theta)/\lambda^2]$$

Structure factor is determined by summing over all atoms in the crystal /unit cell: f_j represents the scattering power of an atom, <*u*> is the average displacement of an atom from its ideal site

For neutrons f_j in the above equation is replaced by b_j

Intensity of diffraction peaks is proportional to square of structure factor

$$I \propto F(hkl)^2$$

From the Structure Factor to Measured Intensities

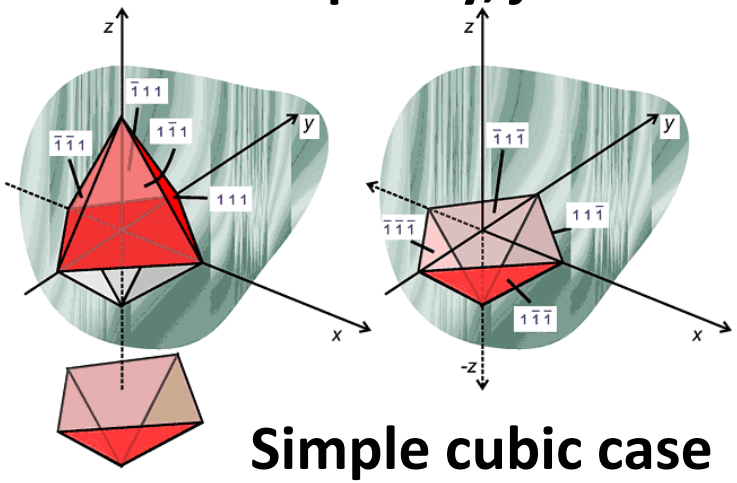
In reality measured intensity will have additional experimental effects and have to be taken into account:

(1) Multiplicity, j (2) Polarisation factor, P (3) Lorentz factor, L (4) Absorption factor, A (5) temperature

$$I = jPLA\,F(hkl)^2$$

Lets try to calculate this during hands on training !!!!!

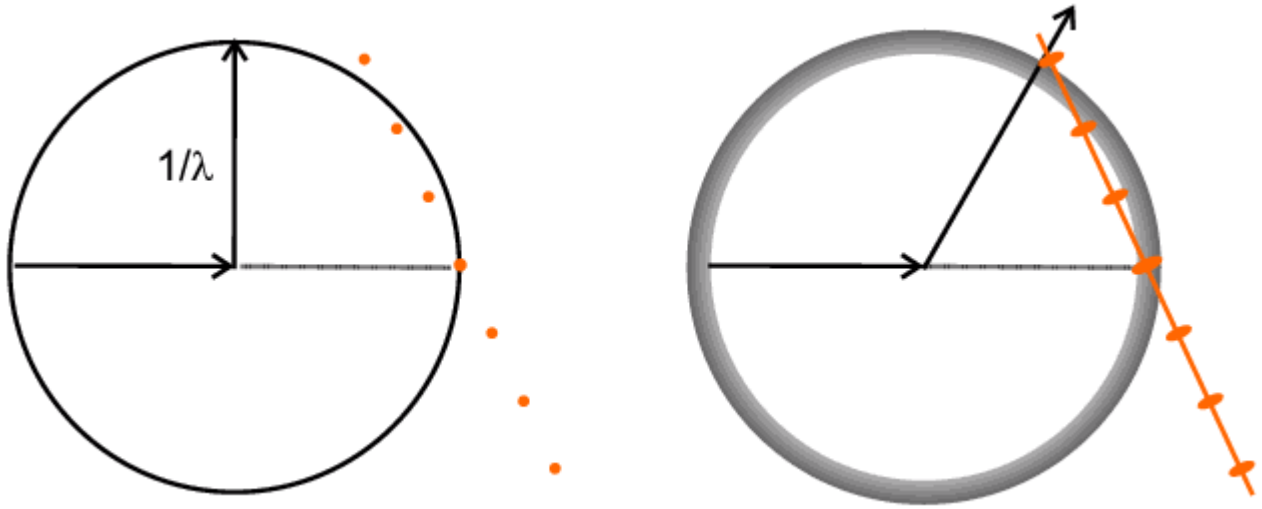
Multiplicity, *j*



Simple cubic case

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

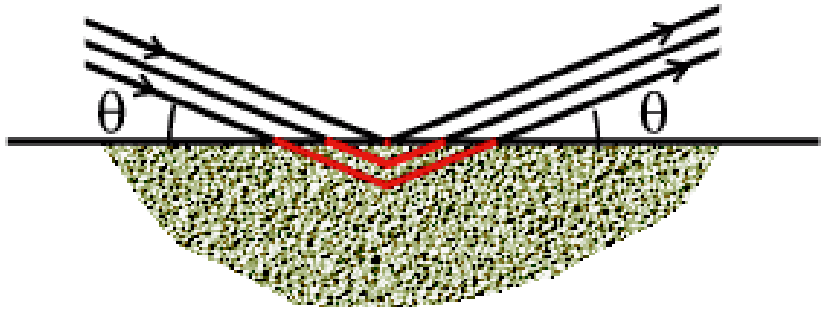
Lorentz factor, *L*



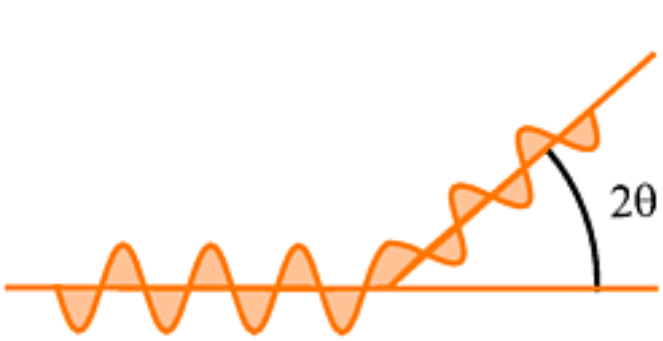
$$L = c \,/\, (\sin\theta \sin 2\theta)$$

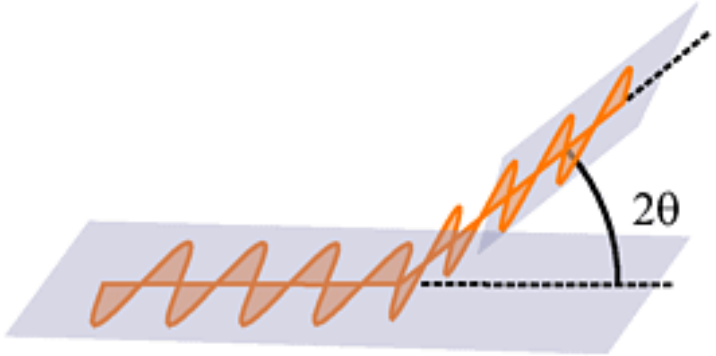
Absorption factor, *A*

$$I = I_0 e^{-\mu t}$$



Polarization factor, *P*

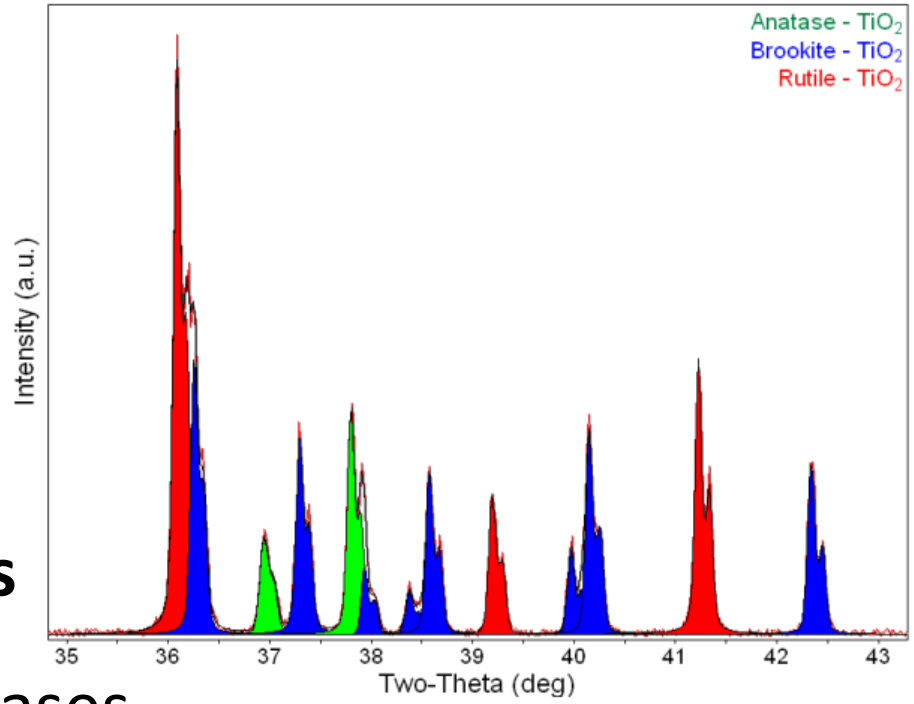




Structural Information Hidden in the Diffraction Plot

Qualitative phase identification

- Start with database search to identify phases
- Known starting composition, likely impurities etc.
- Assumption: Material is in the database



Quantitative phase fraction analysis

- Applied to a mixture of two or more crystalline phases
- Comparison between intensities of selected peaks for all phases, better accuracy with multiple peaks
- Accurate analysis requires standardization, mix known quantities of two phases in several different ratios

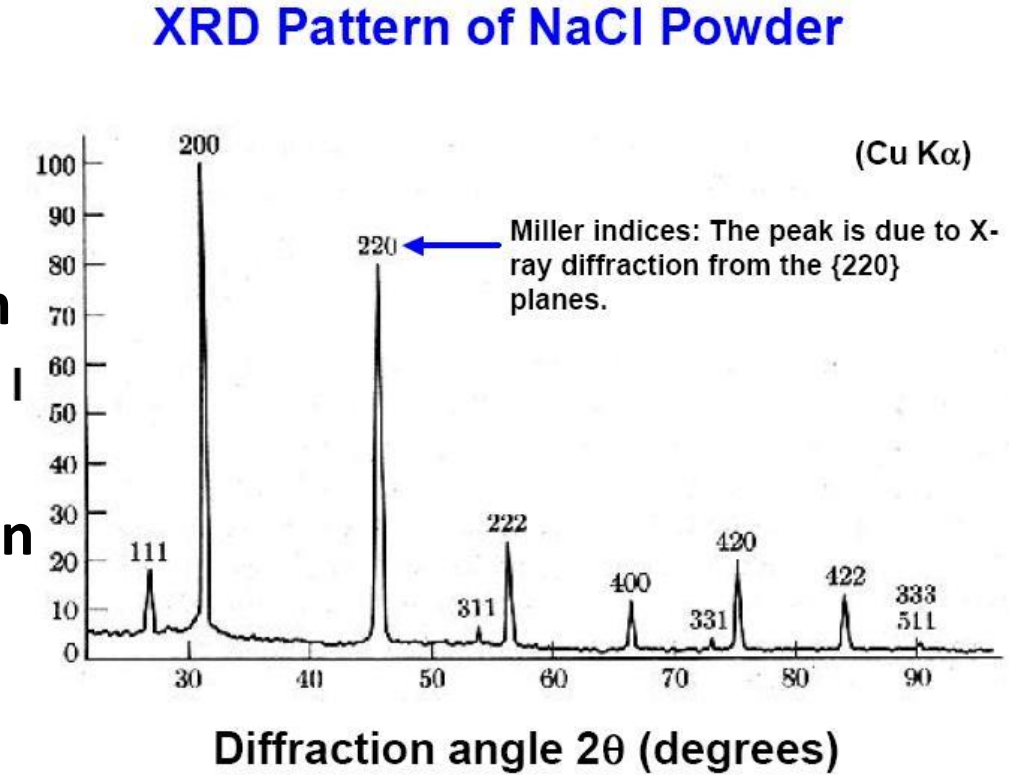
Structural Information Hidden in the Diffraction Plot

Diffraction pattern contains three crucial parameters

Peak positions, Peak intensities, and Peak shapes

Peak positions can resolve

- **Unit cell dimensions, d-spacing is related to unit cell constants**
- **Refinement of a known starting cell or a determination of an unknown structure by indexing**
- **Possible space groups, systematic absence of diffraction peaks is also an information !!!!!!!!!!**
- **<u>Qualitative</u> phase analysis, what's in the sample**



Structural Information Hidden in the Diffraction Plot

Diffraction pattern contains three crucial parameters

Peak positions, Peak intensities, and Peak shapes

Peak Intensities can resolve

- **Position and type of atoms**
- **Site occupancy of atoms** $F(hkl) = \sum_{j=1}^{N} f_j \exp(2\pi i(hx_j + ky_j + lz_j))$ $.\exp[-8\pi^2\langle u^2\rangle(\sin^2(\theta)/\lambda^2]$
- **Atomic displacement parameters, also referred to as a "temperature or Debye-Waller factor"**
- **Accurate intensities are necessary for, quantitative phase analysis, Rietveld refinement, complete structure solution of powder diffraction data**

Structural Information Hidden in the Diffraction Plot

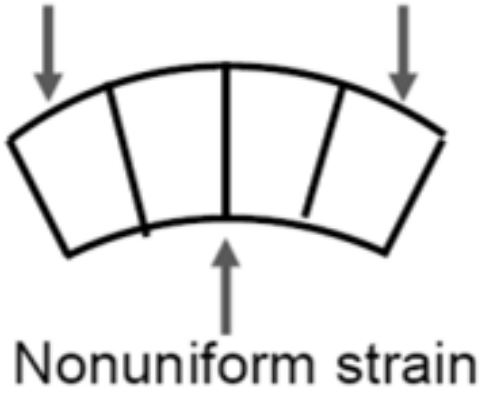
Diffraction pattern contains three crucial parameters

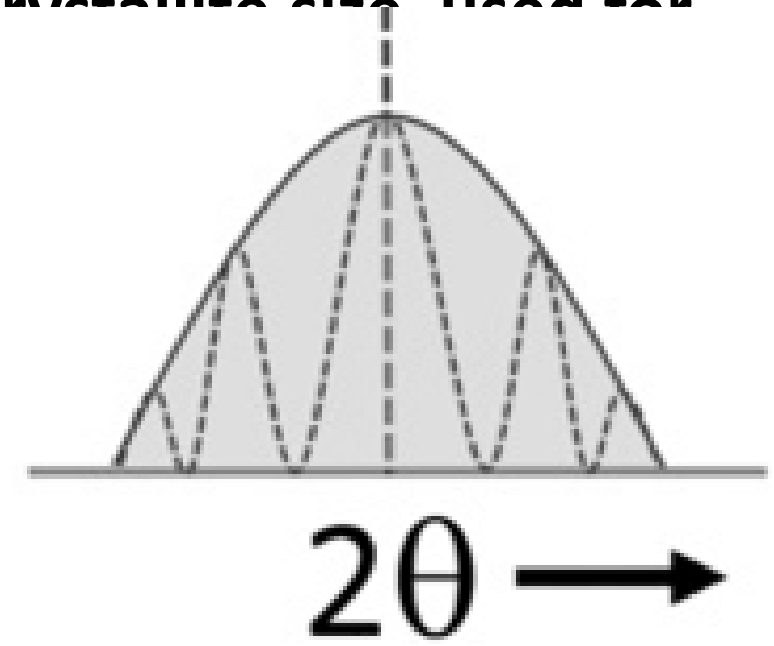
Peak positions, Peak intensities, and Peak shape

Peak shape can resolve

- **Width of Bragg peaks is inversely related to c**
- **M**
- **Fo**

Microstrain
nonuniform strain
(both tensile and
compressive stresses)
(lattice distortion).
Dislocations, vacancies,
defects, thermal effects.

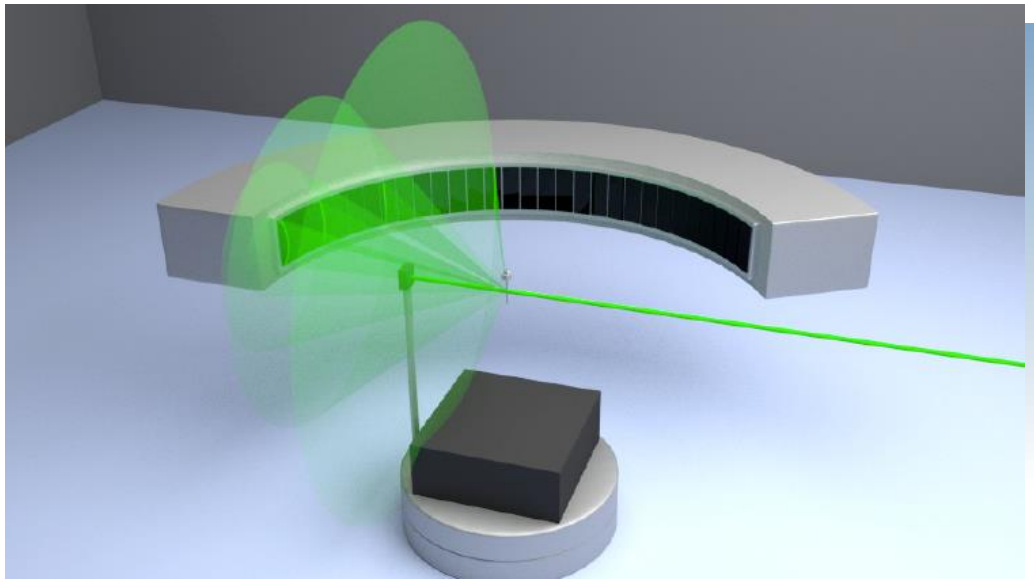




ch as

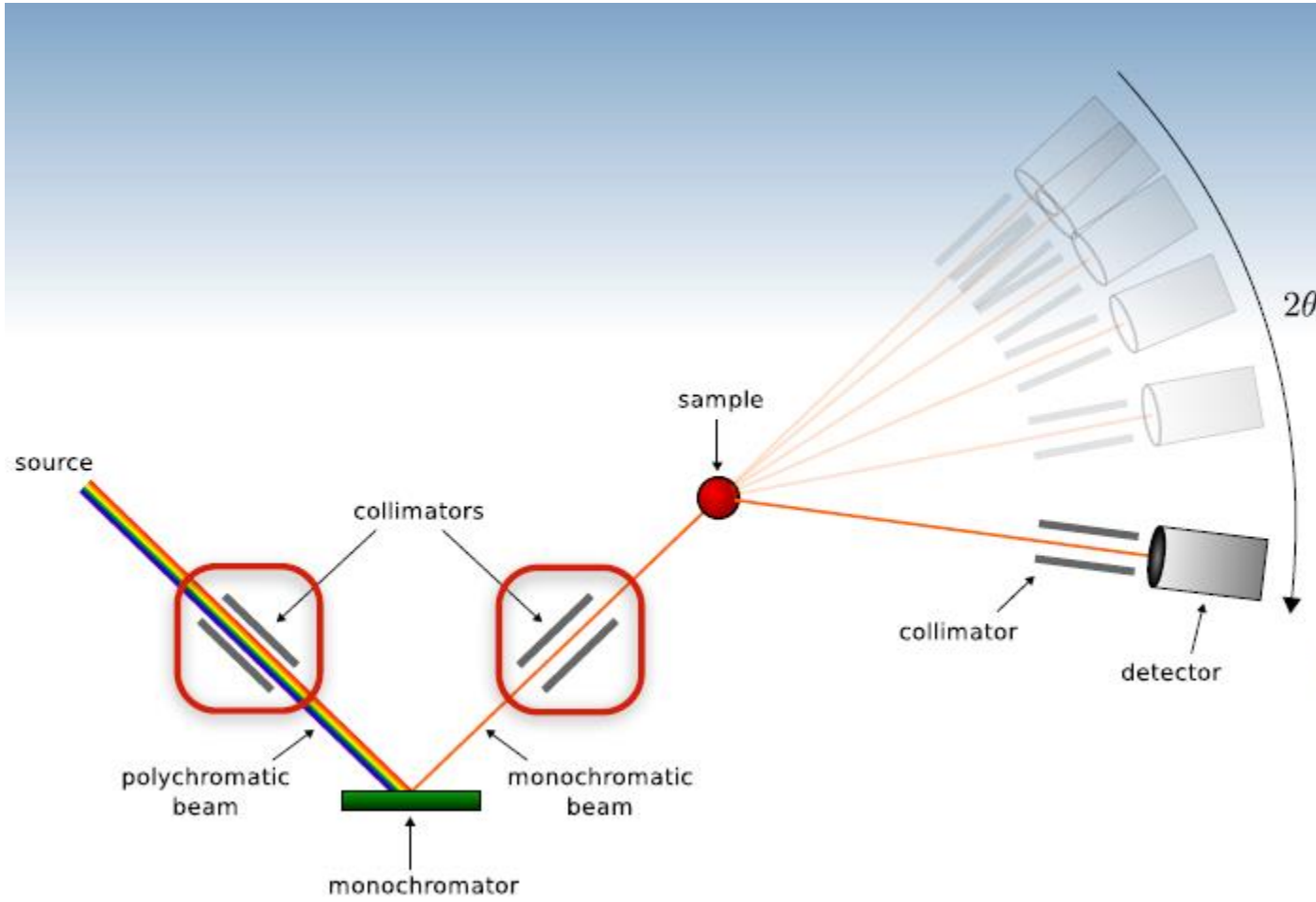
broadening must be used to determine the instrumental contribution

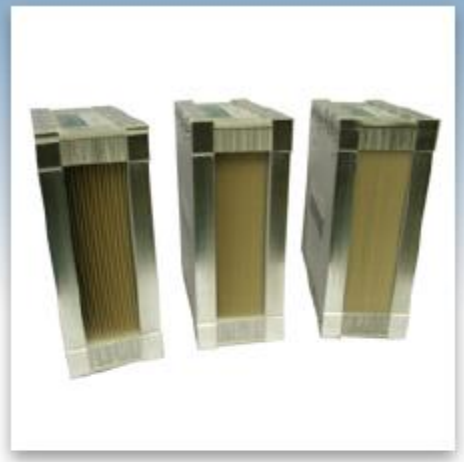
Typical Diffraction Instrument



Lets look at each component individually

Collimator



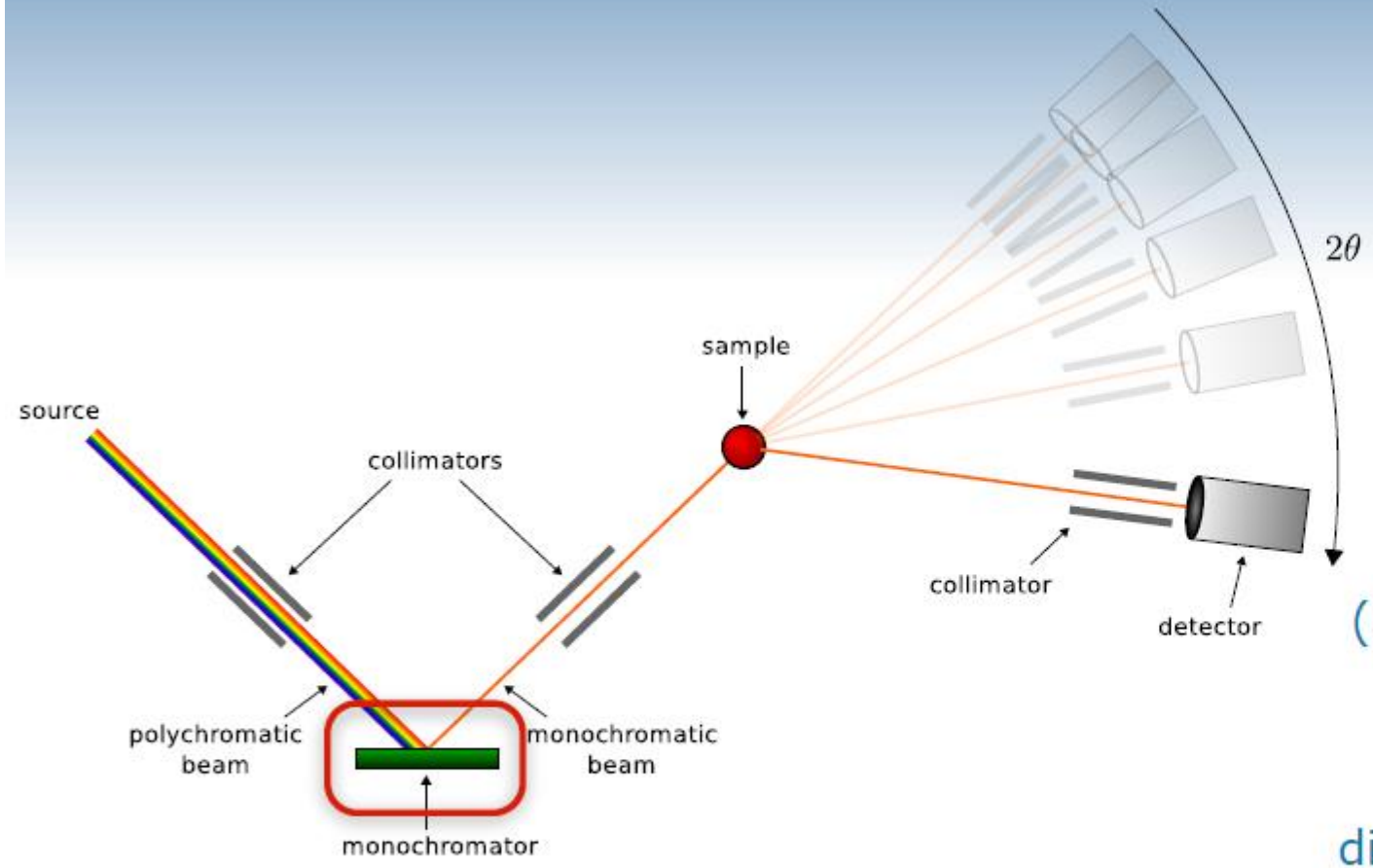


collimator

defines the beam shape and divergence
Soller collimators, slits

Lets look at each component individually

Monochromator



monochromator

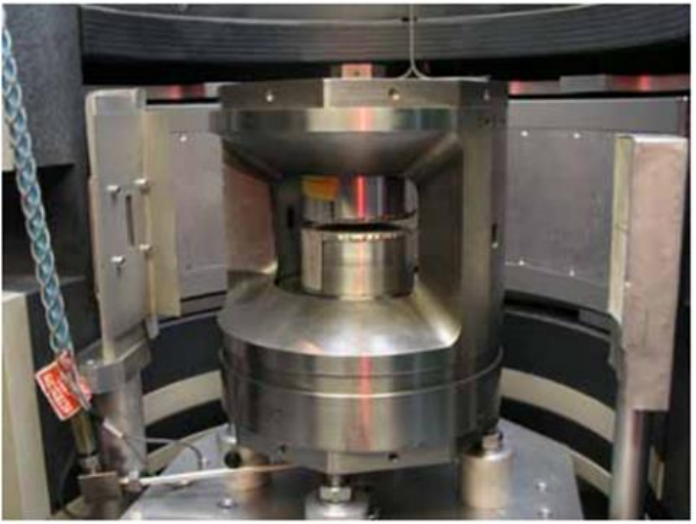
(assembly of) high quality single crystals
choice of wavelength
choice of resolution (take-off angle)
typically Cu, Ge, HOPG, Si
diffracts also higher harmonics $\lambda/2$, $\lambda/3$, ...

$$n\lambda = 2d\sin\theta$$

Remember its only for constant wavelength based set-up

Lets look at each component individually

Sample Environment

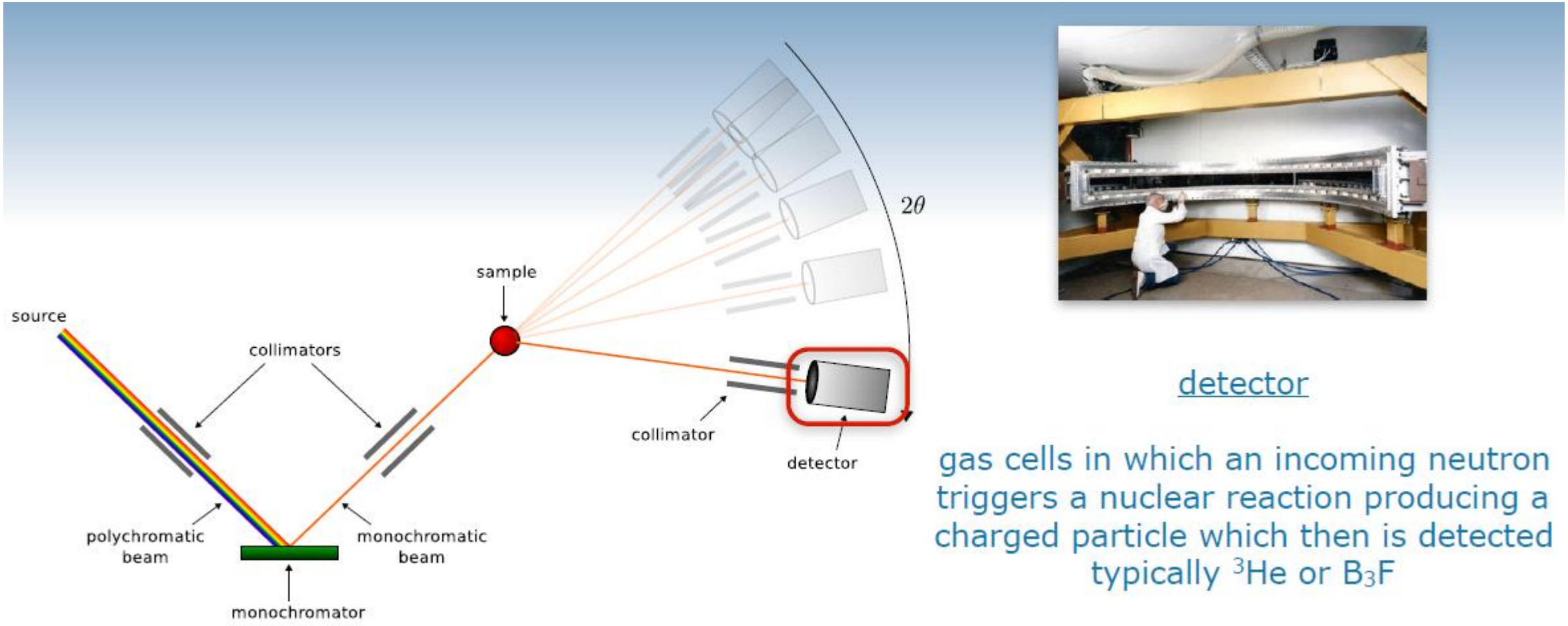


sample environment

cryostat, cryomagnet,
furnace, pressure cell, CryoPAD

Lets look at each component individually

Detectors

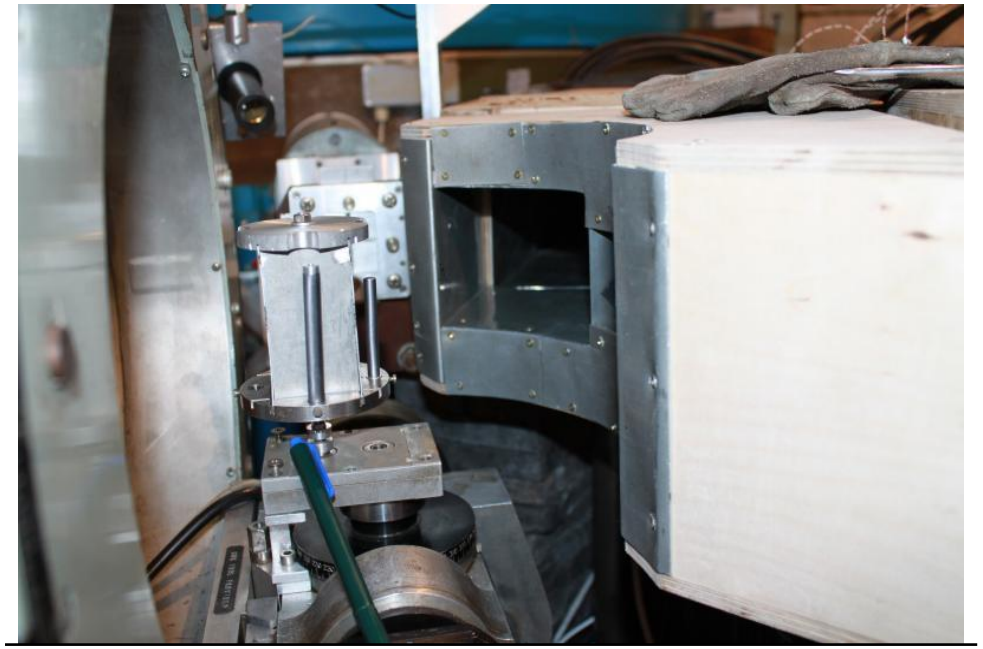


detector

gas cells in which an incoming neutron triggers a nuclear reaction producing a charged particle which then is detected typically ^3He or B_3F

Budapest Neutron Centre: Material Test Diffractometer (MTEST)

Vanadium sample containers



Name	Monochro.	λ [Å]	Q [Å^{-1}]	Intensity
Disordered crystal	Cu(111)	1.45	0.35-8.2	100
Medium res. crystal	Cu(220)	1.35	0.4-8.8	40
Liquid/amorphous	Cu(111)	1.11	0.45-10.7	85
Medium-Q liq./am.	Cu(220)	0.89	0.55-13.3	10
Low-Q liq./am.	Ge(111)	2.27	0.25-5.2	6.5

Powder Diffraction Data Analysis: Beyond Database Search

Structure refinement

Most essential aspect of structure refinement is to remember that its not the same as the structure solution

Refinement as the name implies is the refinement of the calculated structural model which has the closest match to the experimentally measured data

→

Very critical to have the starting model as close as possible to the measurement

INPUT
Model Structure
+
Diffraction Data

→

BLACK BOX

→

OUTPUT
Refined Crystal Structure

Powder Diffraction Data Analysis: Beyond Database Search

Least Square Fitting

Lets consider two parameters

1. *Y*(obs) set of observables/measured values from the diffraction experiment

2. *Y*(calc) set of values obtained from the structural model used

For our case of powder diffraction, Y is the intensity of the individual profile points measured with 2θ scan y_i,

Quantity minimized in refinement is $\Sigma_i\{Y_i(\mathrm{obs}) - Y_i(\mathrm{calc})\}^2$

Therefore, the expression "least-squares" minimization

Powder Diffraction Data Analysis: Beyond Database Search

Hugo Rietveld around 1966-1969 introduced a whole diffraction data fitting approach measured with neutron

- Fitting method is known as “Rietveld Refinement method”
- Also used for X-ray data
- With increasing computational power structural refinement became more feasible
- Now it’s a “Routine” and essential part of crystallography
- Rietveld method is now regularly be used to refine structures, determine lattice parameters, microstructural sample characteristics, phase fractions in mixtures, solving magnetic structures etc.

Powder Diffraction Data Analysis: Beyond Database Search

$$\Delta = \Sigma_i w_i \{y_i(obs) - y_i(calc)\}^2$$

w_i is the attributed weight to each observation

***"The method of using the total integrated intensities of the separate groups of overlapping peaks in the least-squares refinement of structures, leads to the loss of all the information contained in the often detailed profile of these composite peaks. By the use of these profile intensities instead of the integrated quantities in the refinement procedure, however, this difficulty is overcome and it allows the extraction of the maximum amount of information contained in the powder diagram."* H. M. Rietveld.**

H. M. Rietveld: *A profile refinement method for nuclear and magnetic structures.* J. of Appl. Cryst., 1969, **2**, 65-71.

Powder Diffraction Data Analysis: Beyond Database Search

Additional parameters to be known before starting to data refinement and extract structural parameters

Instrumental zero error, 2θ zero

Peak width /asymmetry parameters, U,V,W

Peak shape parameters

Preferred orientation parameter

Background

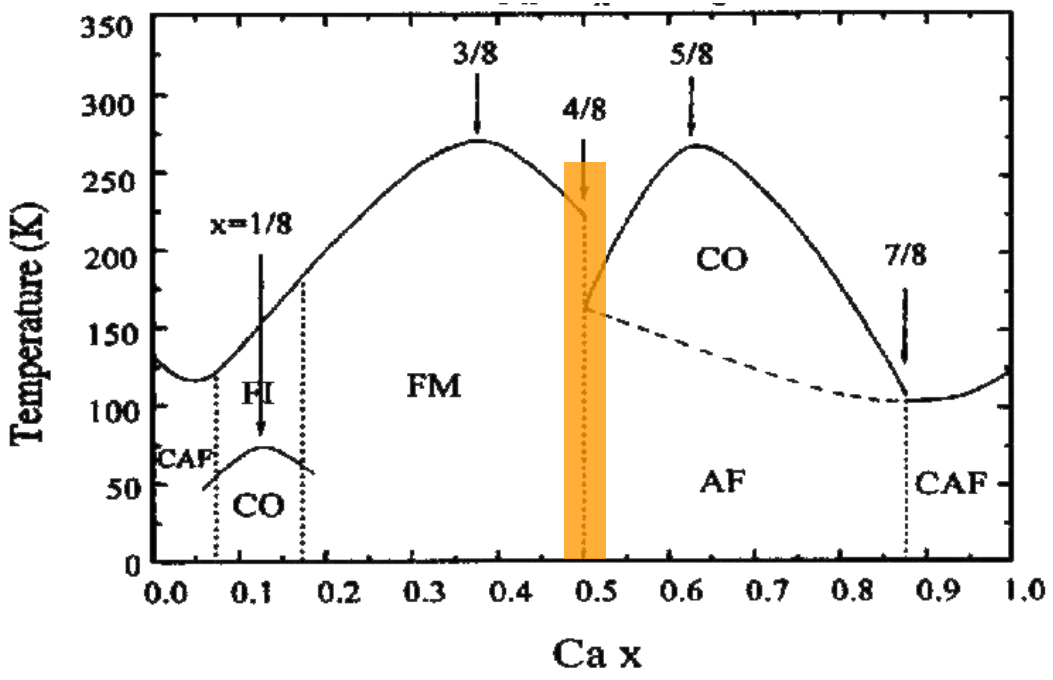
Powder Diffraction Data Analysis: Beyond Database Search

Rietveld Application

- Crystallographic structure determination
  - Lattice constants, Site occupancies, atomic positions etc.
- Quantitative analysis of crystalline phases
- Temperature factor
- Engineering properties
  - Residual stress
  - Preferred orientation

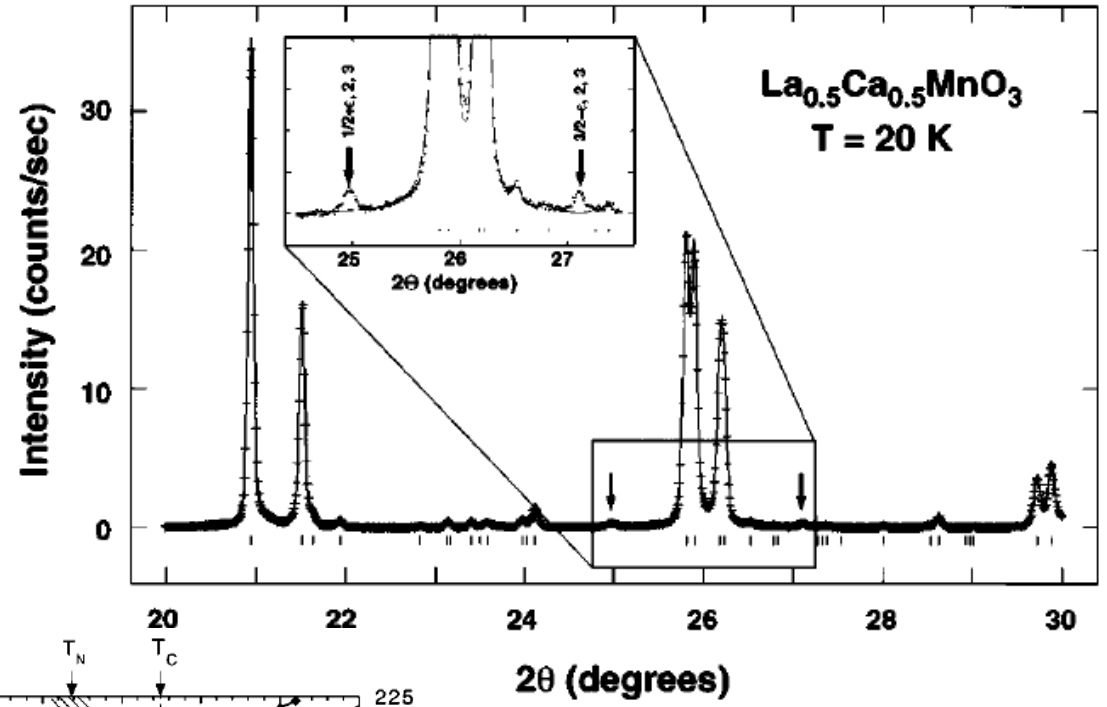
Few Scientific Case Studies

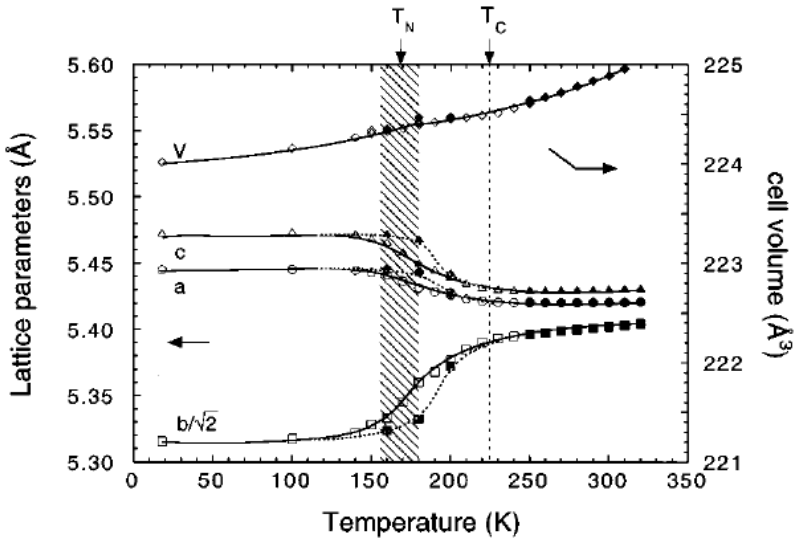
$La_{1-x}Ca_xMnO_3$ Phase Diagram



S.-W. Cheong et al., Colossal magnetoresistance Oxides, Gordon & Breach, New York (1997)

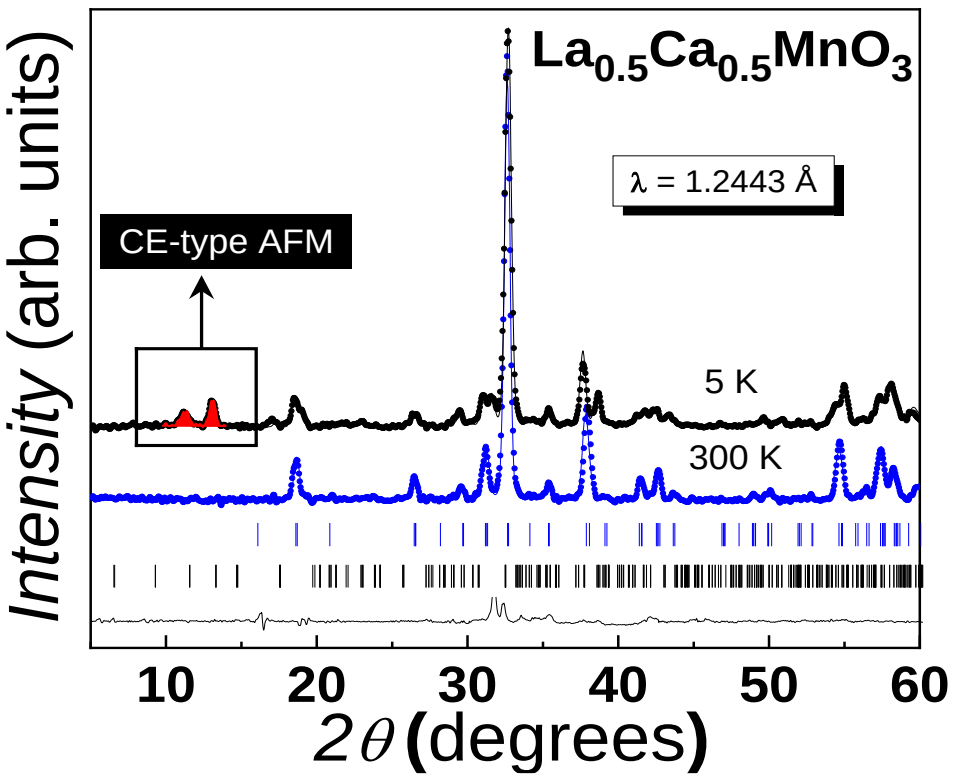
$La_{0.5}Ca_{0.5}MnO_3$ X-ray Diffraction



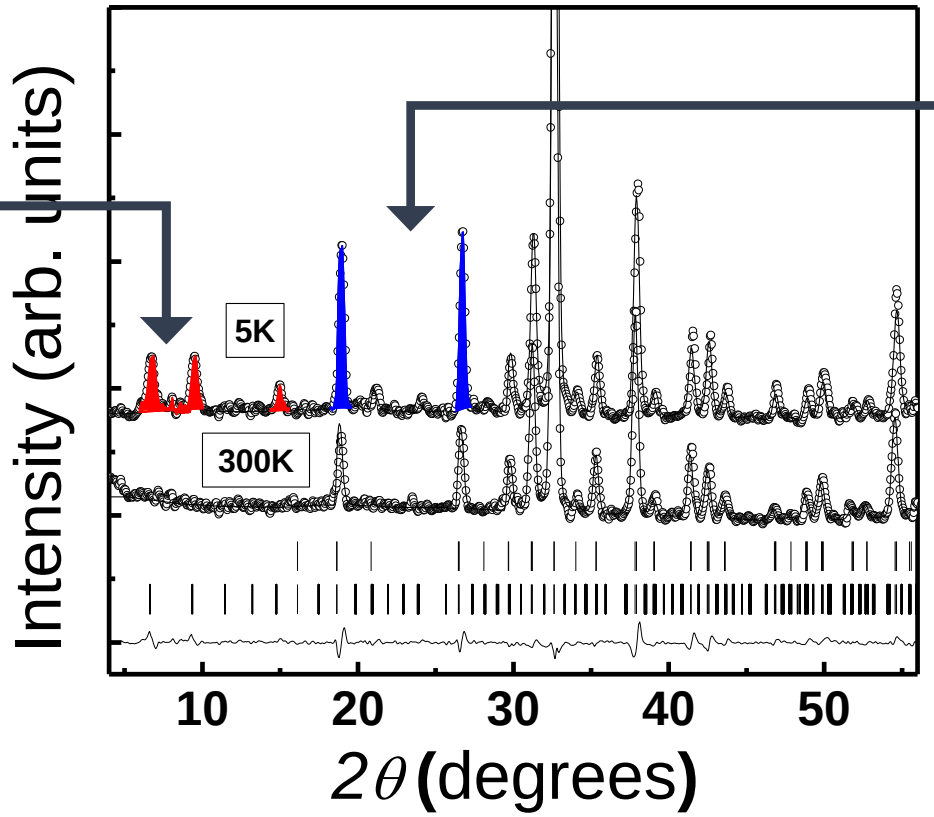


PG Radaelli, DE Cox, M Marezio, SW Cheong, Phys. Rev. B 55 (5), 3015

Neutron Diffraction data for $La_{0.5}Ca_{0.5}MnO_3$



AFM peaks



FM peaks

Point to Ponder: Difference between FM and AFM diffraction peaks !!!

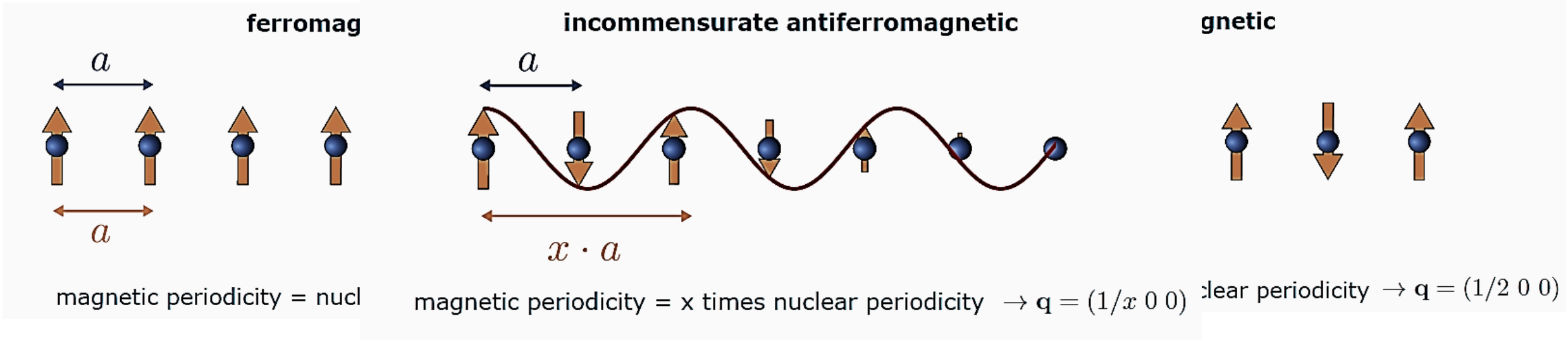
Time to learn about Magnetic Structure and Neutrons Relation

Magnetic Structure Factor

$$\mathrm{F}_M(\mathrm{k}) = \sum_j \mu_j f_j(\mathrm{k}) \exp(i\mathrm{k}\mathrm{r}_j) \exp\left(-B_j \frac{\sin^2\theta}{\lambda^2}\right)$$

It is not necessary that the magnetic and crystal / nuclear structures to have the same periodicity and symmetry

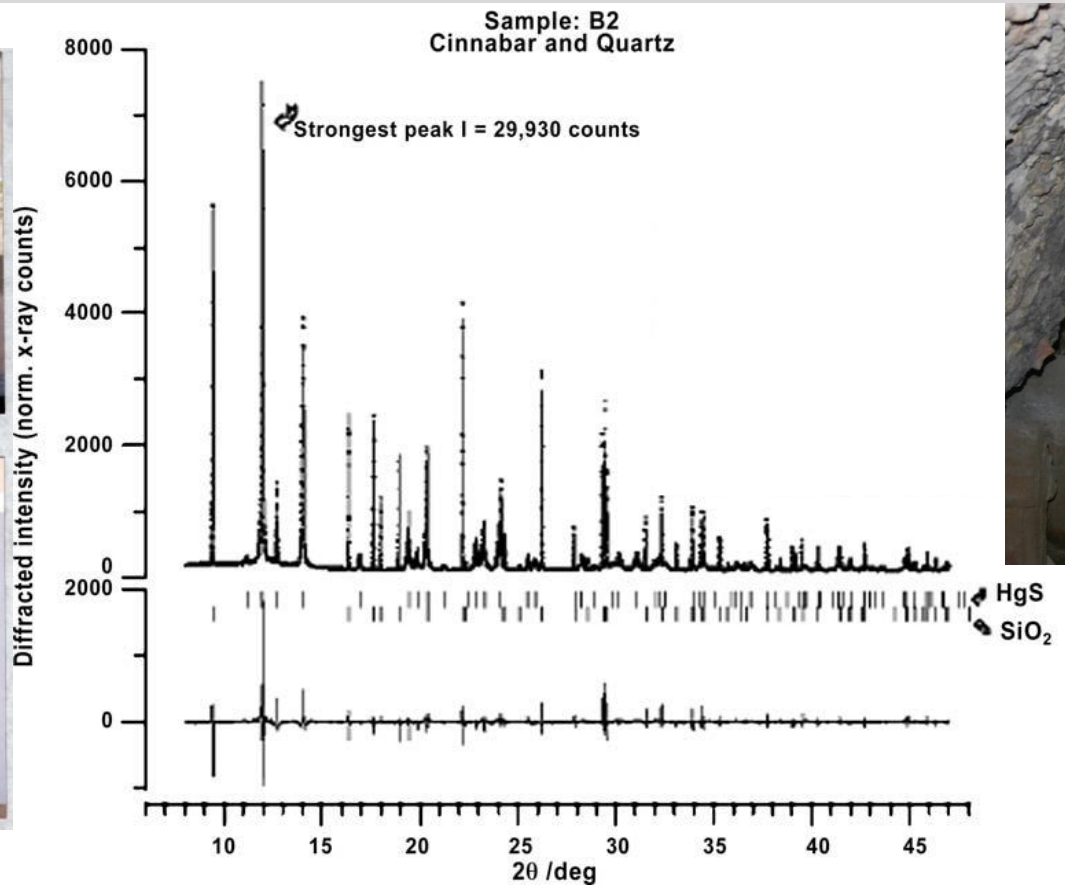
Let us see the few cases here, relation between them is expressed is in terms of propagation or wave vector 'a'

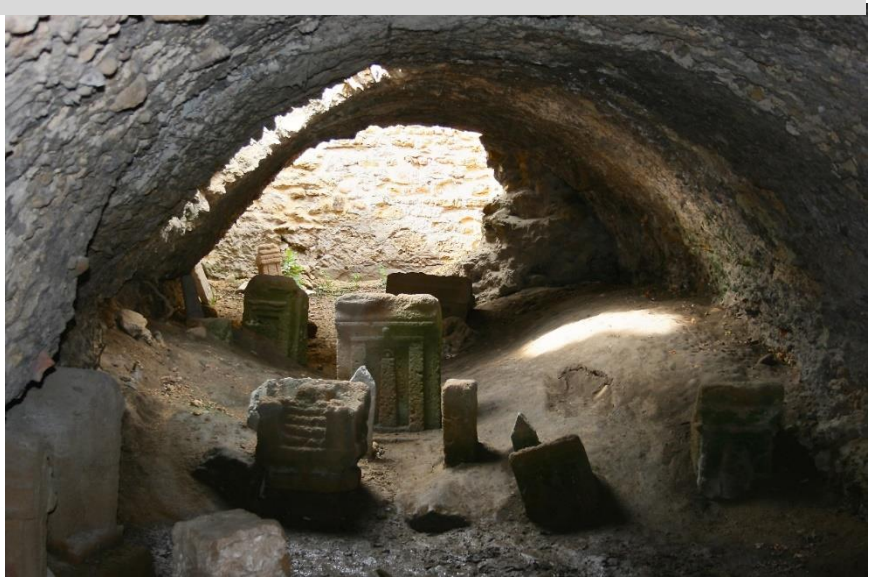


Diffraction in Archeology

Excavation of Carthaginian tombs in Tunisia, residue of cosmetic products in were found in small vessels. Smaller quantities of these pigment material also discovered in receptacles, like sea-shells, possibly also used as make-up components.

Comparative study was performed between make-up used by living beings vs the ones used to vivify and embellish the dead as a ritual (Punic - Roman periods). Some unguents containing cinnabar or ochre used as 'mourning reds', applied on the face - forehead of the dead.



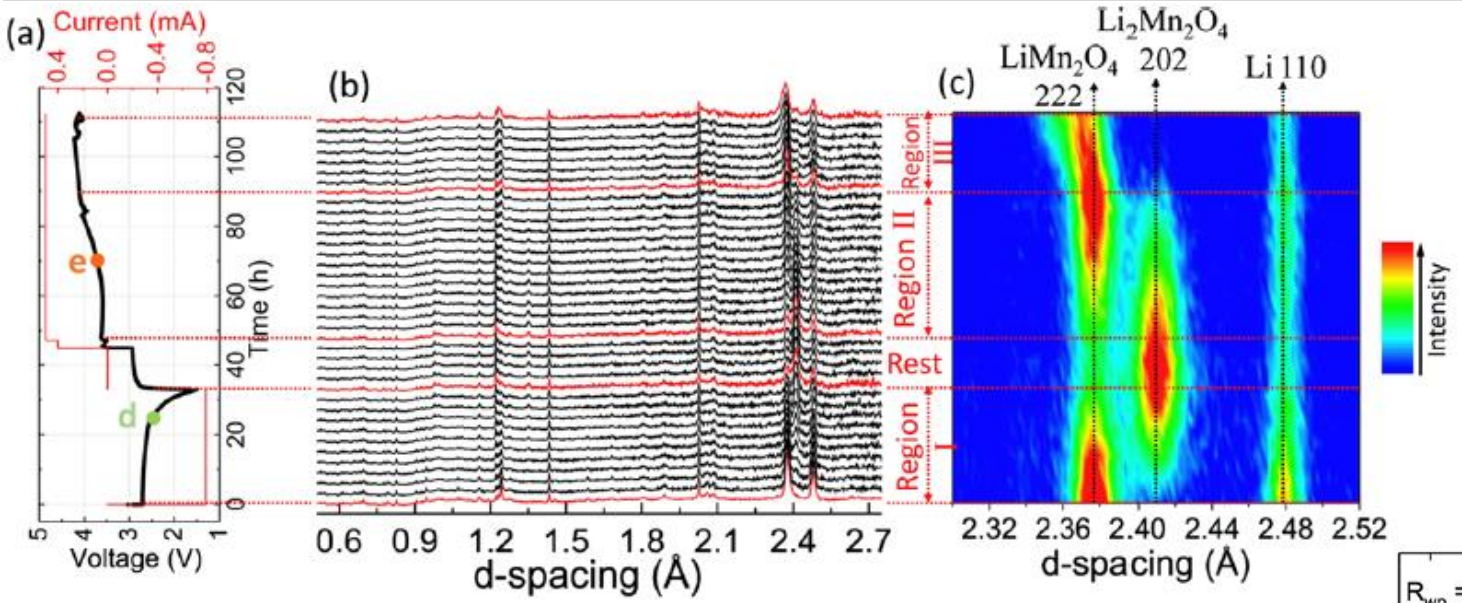


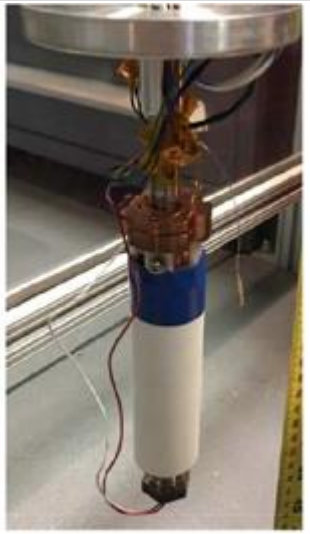
A. Huq et al. Appl. Phys. A 83, 253 (2006)

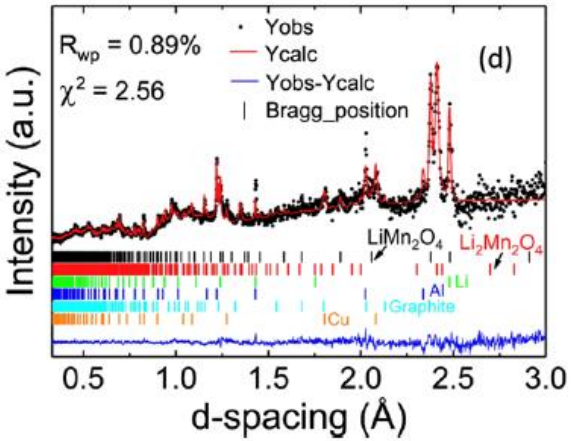
Diffraction in Li ion Batteries

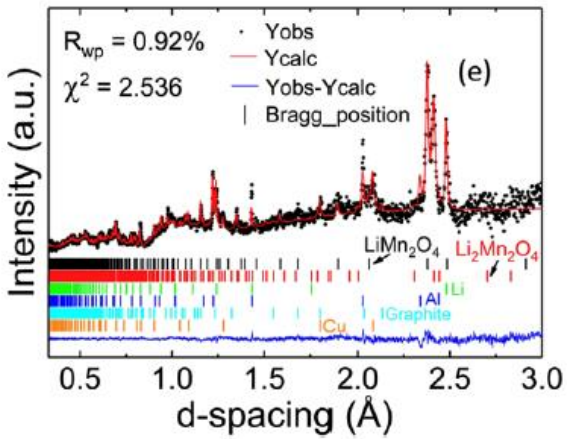
In operando neutron diffraction study of $Li_{1+\delta}Mn_2O_4$ ($0 \leq \delta \leq 1$) to study the new reaction mechanisms occurring within both cubic and tetragonal spinel phases

Powder neutron diffraction is an ideal tool to study light elements like Lithium and Oxygen in cathode materials, key to understand their structural evolution in Li ion batteries









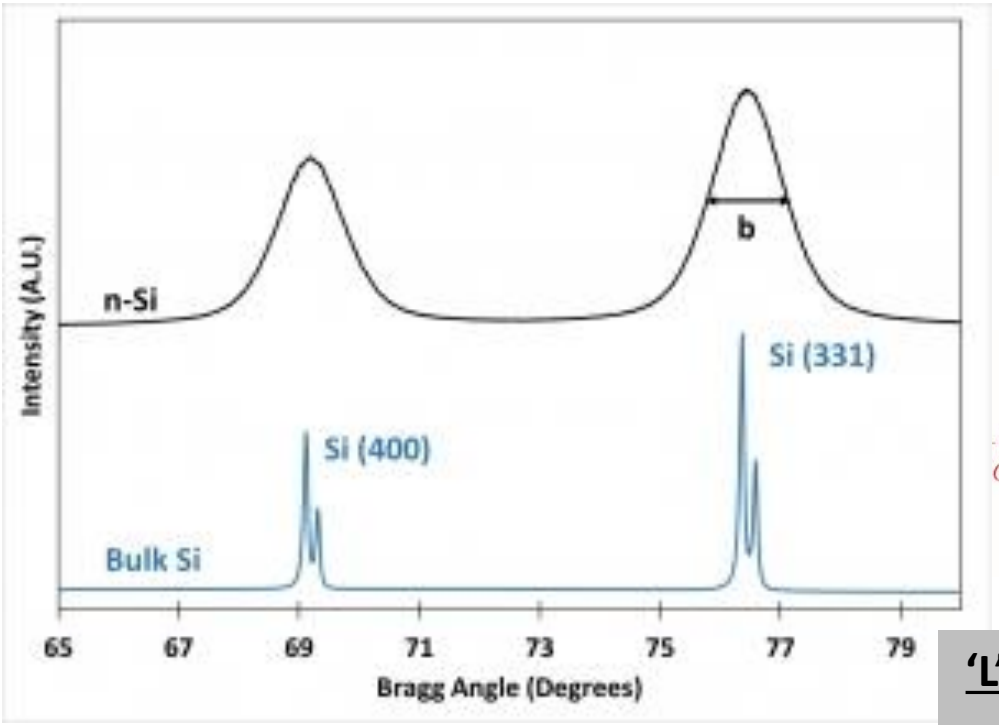
B. Song et al., Chem. Mater. 2019, 31, 124−134

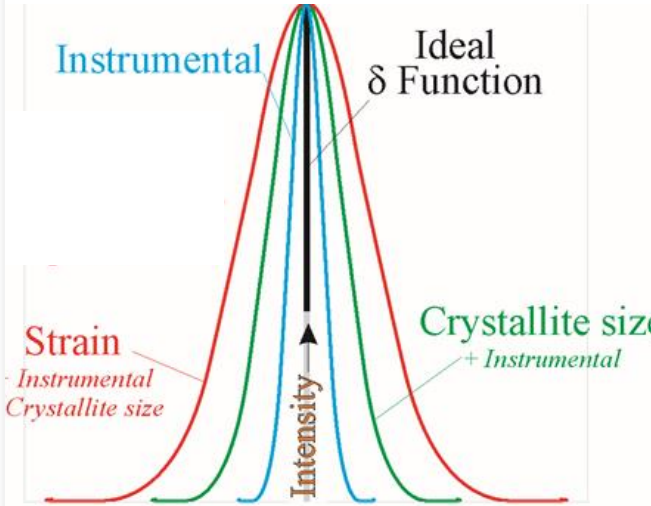
Diffraction for particle size estimation in Nano Materials

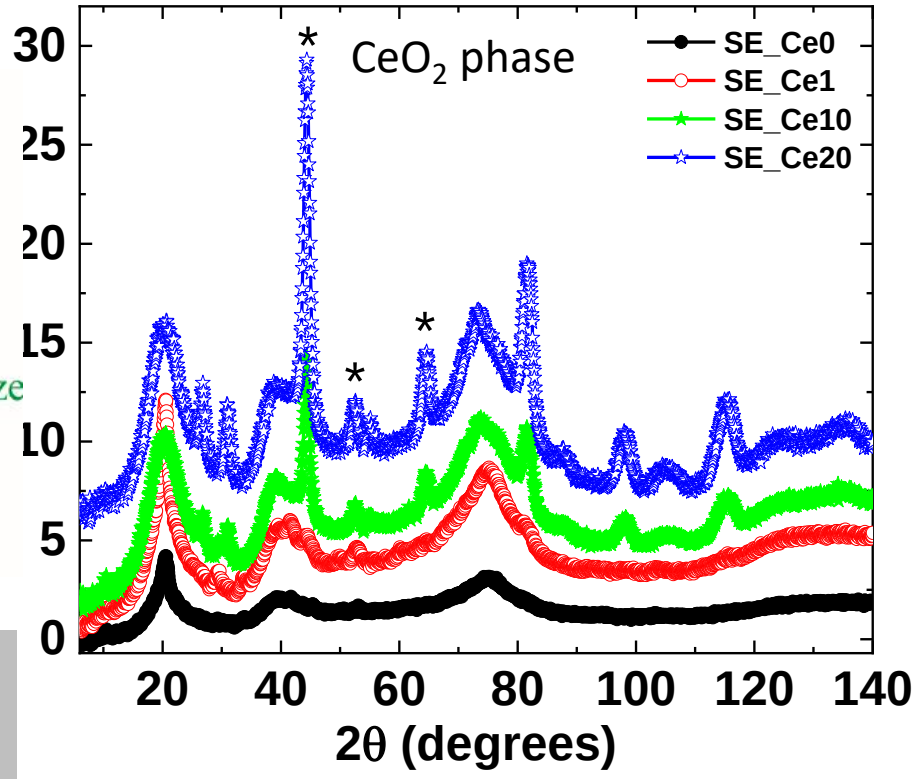
Average nano-crystallite size can be estimated using Scherrer formula,

$$L = k\lambda / \beta \cos\theta$$, (J. Appl. Cryst. (1978). 11, 102-113)

where D is particle diameter size, k is a geometrical constant, λ is neutron wavelength, β is the full width at half maximum (FWHM) and θ is the diffraction angle







Word of caution: other factors also contribute to peak broadening !!!!!

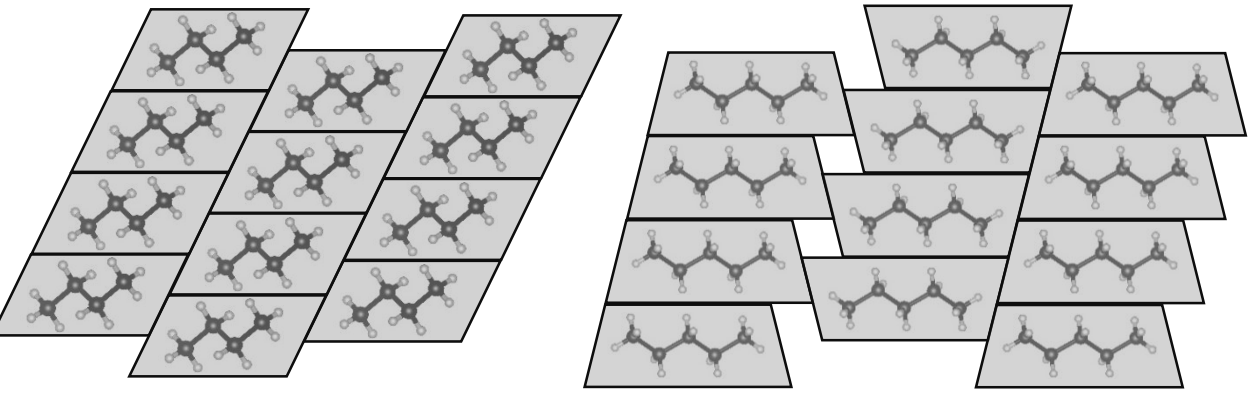
'L' the crystallite size values (nm)			
Ce 1%	19.15	9.17	9.72
Ce 10%	6.86	7.15	7.02
Ce 20%	6.42	6.21	6.14

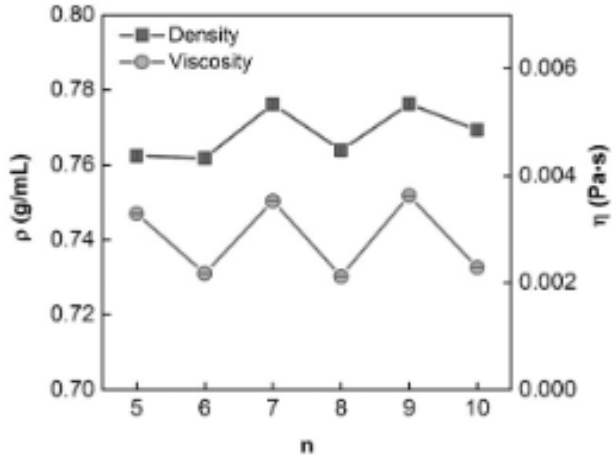
Diffraction for Local structure studies in Liquids

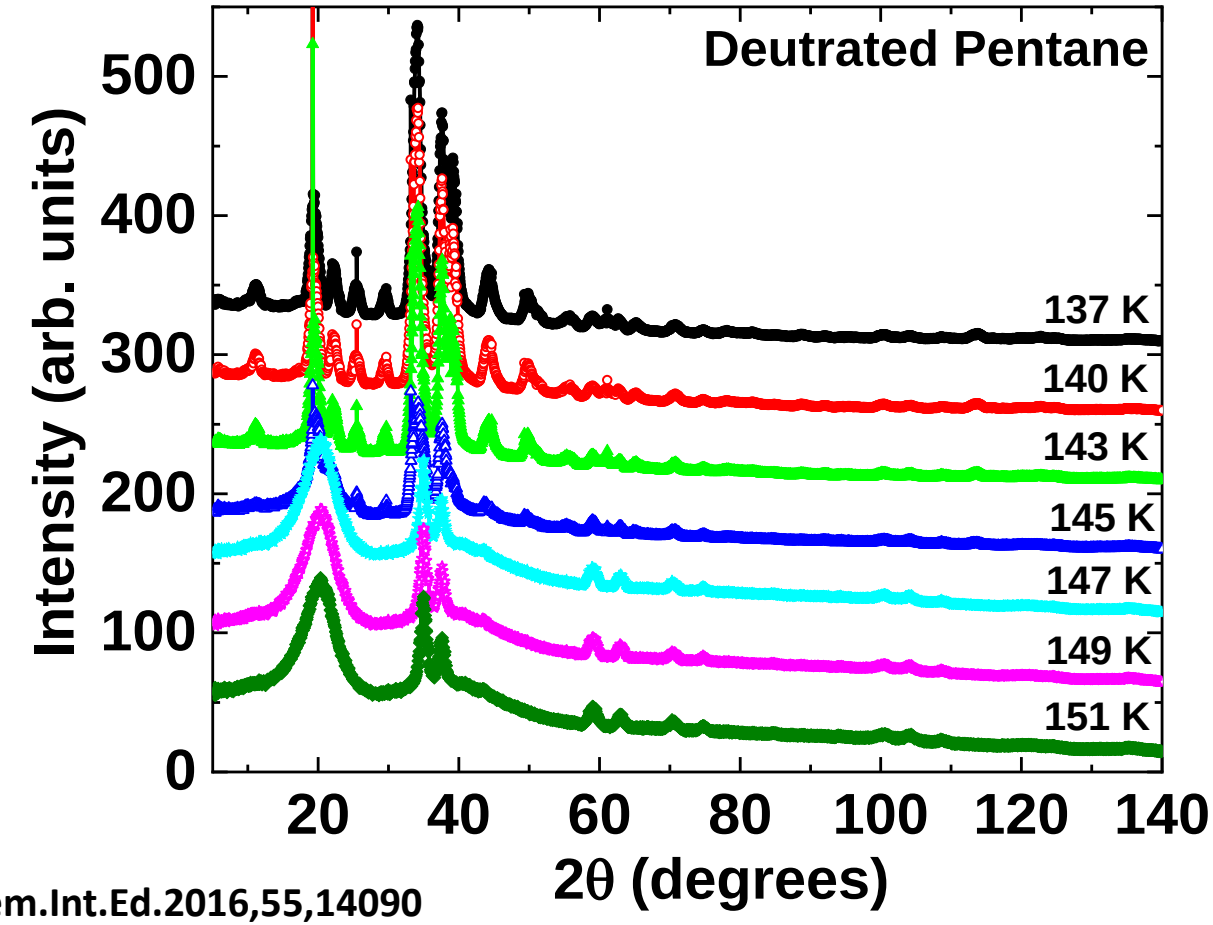
Physical properties of homologous systems is correlated with the difference in packing density of odd - even numbered chains homologous systems.
Although, this behavior is also present above the MP. For complete understanding of structural properties diffraction studies are important.

Butane: Even number

Pentane: Odd number







Ke Yang et al., Angew.Chem.Int.Ed.2016,55,14090

Why choose Neutron

- **Neutrons (uncharged) do not interact with electrons in the crystal; higher penetration**
- **Have intrinsic magnetic moment, useful for magnetic studies**
- **Can detect light elements, isotopes**
- **Down side is that neutron sources and therefore neutrons are expensive and not as widely available as X –rays. So choose carefully !!!!!!!!!!!**

Resources (databases)

CCDC (Cambridge Crystallographic database): Organic structures https://www.ccdc.cam.ac.uk/

ICDD (International Center for Diffraction Data): Minerals, Organics and Inorganics http://www.icdd.com/

ICSD (Inorganic crystal structure database):
https://www.fiz-karlsruhe.de/de/leistungen/kristallographie/icsd.html

NIST & MPDS
https://www.ncnr.nist.gov/resources/n-lengths/

http://pd.chem.ucl.ac.uk/pdnn/pdindex.htm#powintro, http://img.chem.ucl.ac.uk/

Powder Diffraction: Neutron Diffraction by G. E. Bacon, Diffraction of slow neutrons by V.F. Turchin , Elements of X-Ray Diffraction by B. D. Cullity, Neutron Scattering from Magnetic Materials by Tapan Chatterji, Theory and Practice: Edited by R.E. Dinnebier and S.J.L. Billinge

Fundamentals of Powder Diffraction and Structural Characterization of Materials (2nd edition): V. K. Pecharsky and P. Y. Zavalij

The Rietveld Method: Edited by R.A. Young
Softwares: Rietveld Analysis: GSAS (GSAS-II), Fullprof, Topas, Structure Solution: GSAS-II, Topas, Fullprof, DASH