Introduction to X ray diffraction

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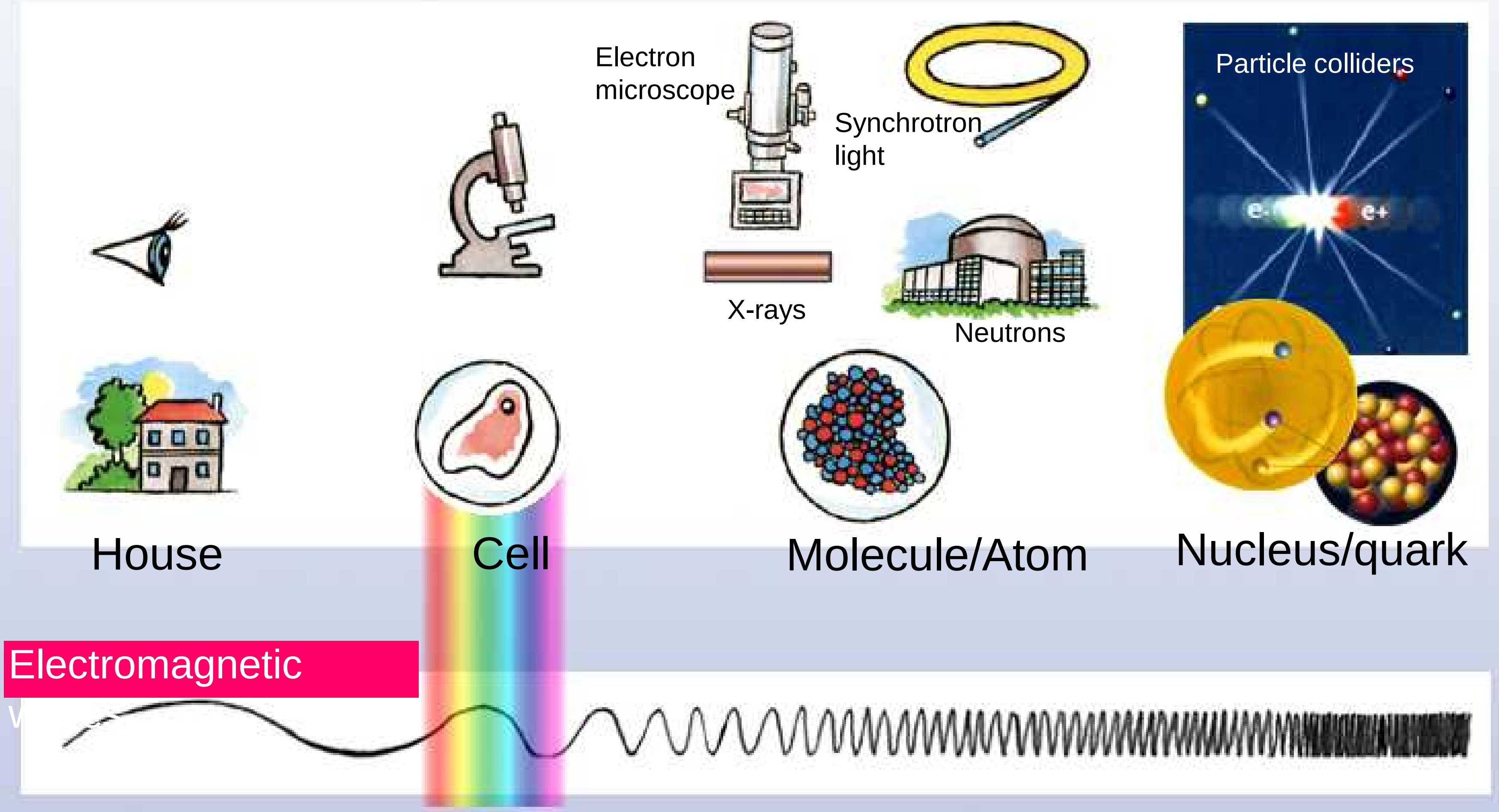
Outline

- Introduction
- History
- How Diffraction Works
  - Demonstration
  - Analyzing Diffraction Patterns
- Neutron diffraction?
- Summary and Conclusions

Introduction

To see the invisible

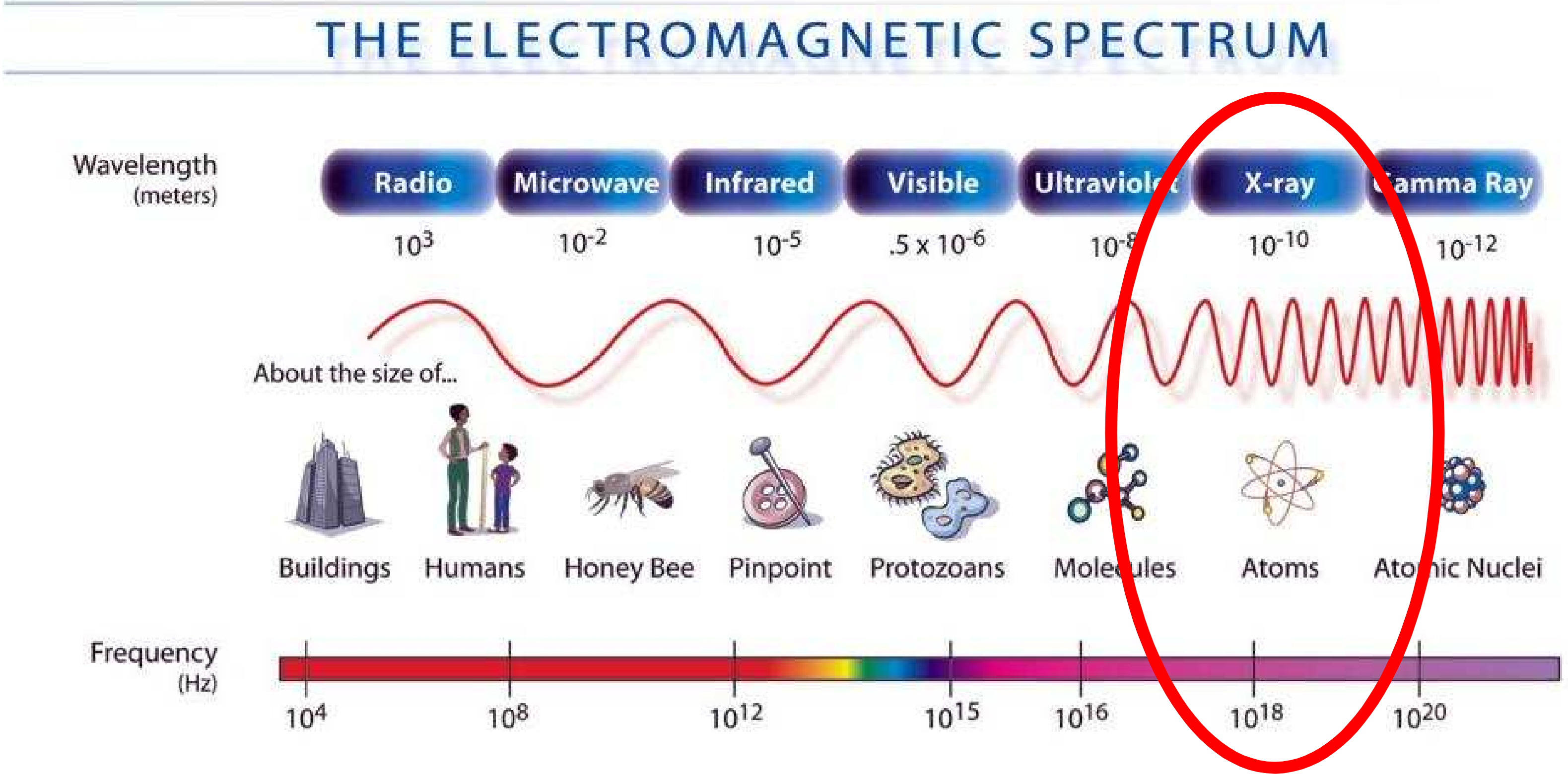


House | Cell | Molecule/Atom | Nucleus/quark

Electromagnetic

Radio waves | IR | Visible light | UV | Soft X-rays | Hard X-rays | Gamma rays

Introduction to X-ray diffraction



- X-rays are used to probe the atomic scale
- Why are x-rays used? $\lambda \sim$ Å
- How do the x-rays probe the crystal structure?

X-rays interact with the electrons surrounding the molecule and "reflect". The way they are reflected will be prescribed by the orientation of the electronic distribution (Electron Density)

Introduction to X-ray diffraction

Motivation:

- X-ray diffraction is a non-destructive analytical technique for identification and quantitative determination of the various crystalline forms, known as ‘phases’.
- Identification is achieved by comparing the X-ray diffraction pattern
- Bridge the gaps between physics, chemistry, biology…..

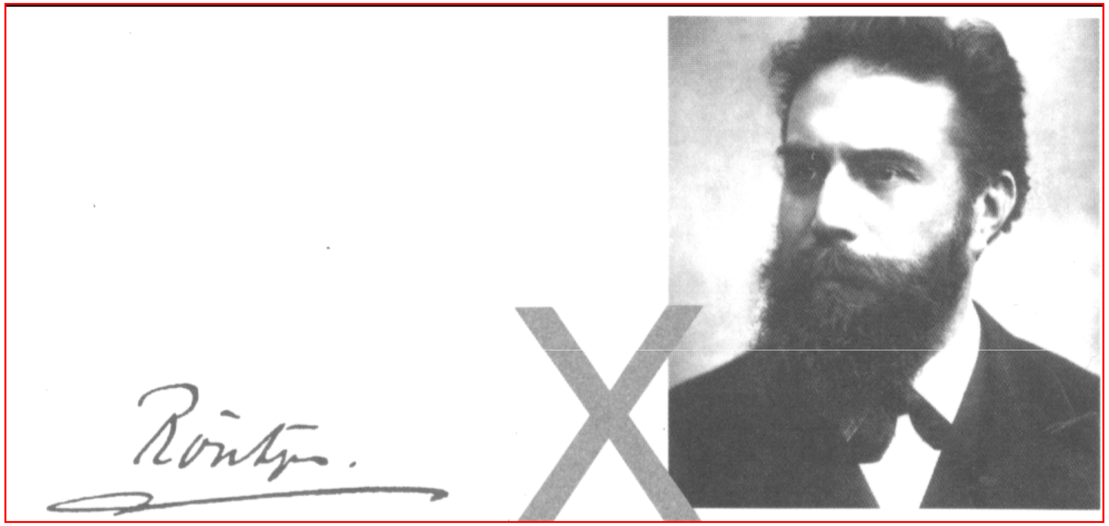
X-ray diffraction is important for:

- Solid-state physics
- Biology - Biophysics
- Medical physics
- Chemistry and Biochemistry
- Geophysics
- ……..

X-ray Diffractometer

History of X-ray diffraction

1895 X-rays discovered by Wilhelm Conrad Röntgen



Wilhelm Conrad Röntgen discovered 1895 the X-rays. 1901 he was honoured by the Noble prize for physics. In 1995 the German Post edited a stamp, dedicated to W.C. Röntgen.

The first X-ray

History of X-ray Diffraction

1895	X-rays discovered by Roentgen
1914	First diffraction pattern of a crystal made by Knipping and von Laue
1915	Theory to determine crystal structure from diffraction pattern developed by Bragg.
1953	DNA structure solved by Watson and Crick
Now	Diffraction improved by computer technology; methods used to determine atomic structures and in medical applications

The first X-ray

History of X-ray Diffraction

Laue's Experiment in 1914

Single Crystal X-ray Diffraction

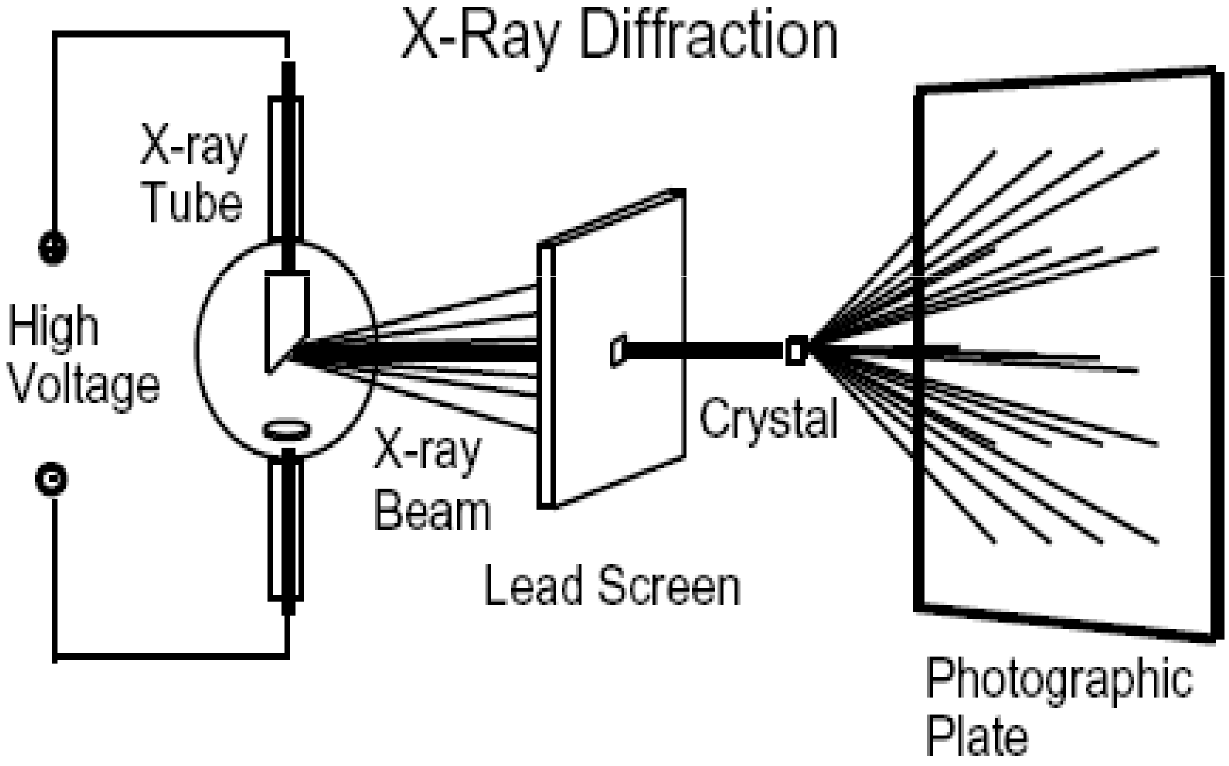


Figure 2. A schematic of X-ray diffraction.

http://mrsec.wisc.edu/edetc/modules/xray/X-raystm.pdf

History of X-ray Diffraction

Laue's Experiment in 1914

Single Crystal X-ray Diffraction

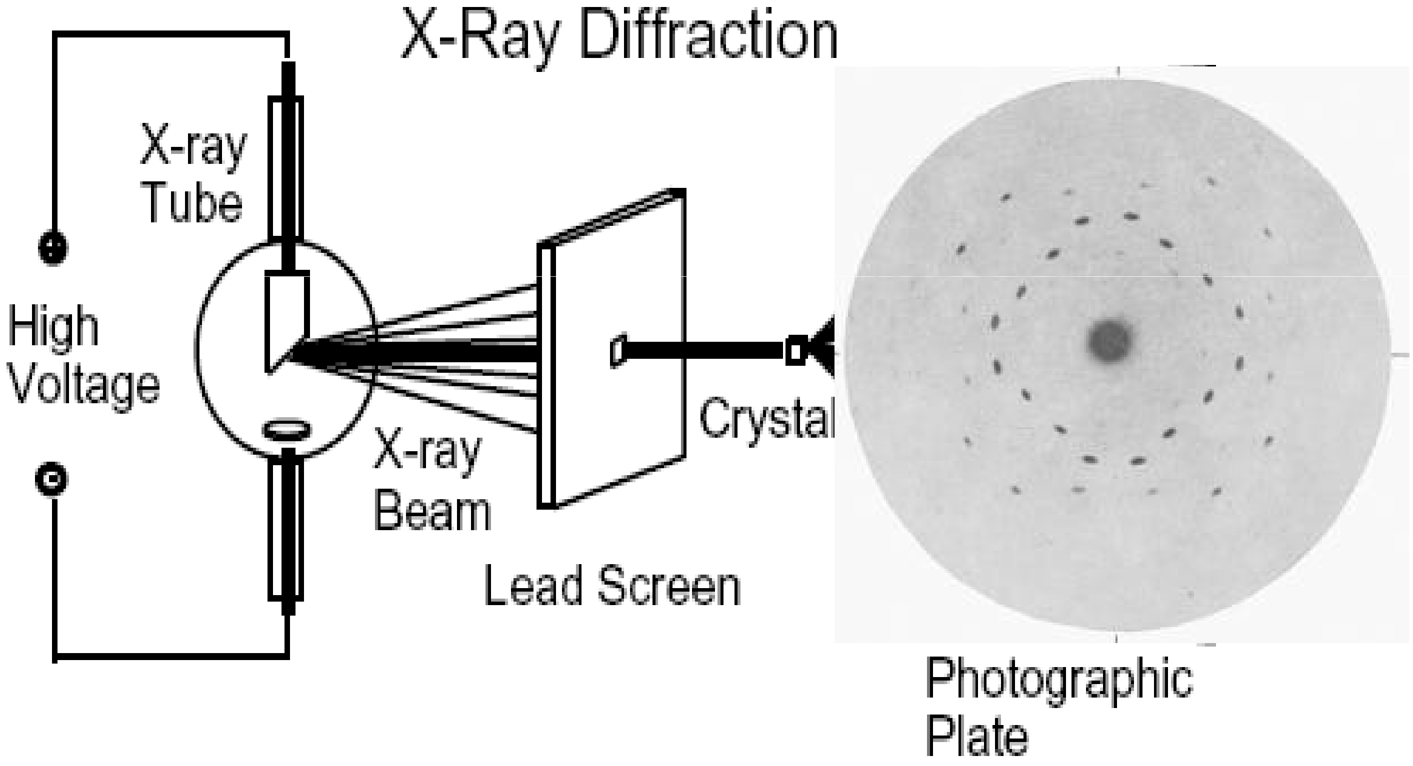
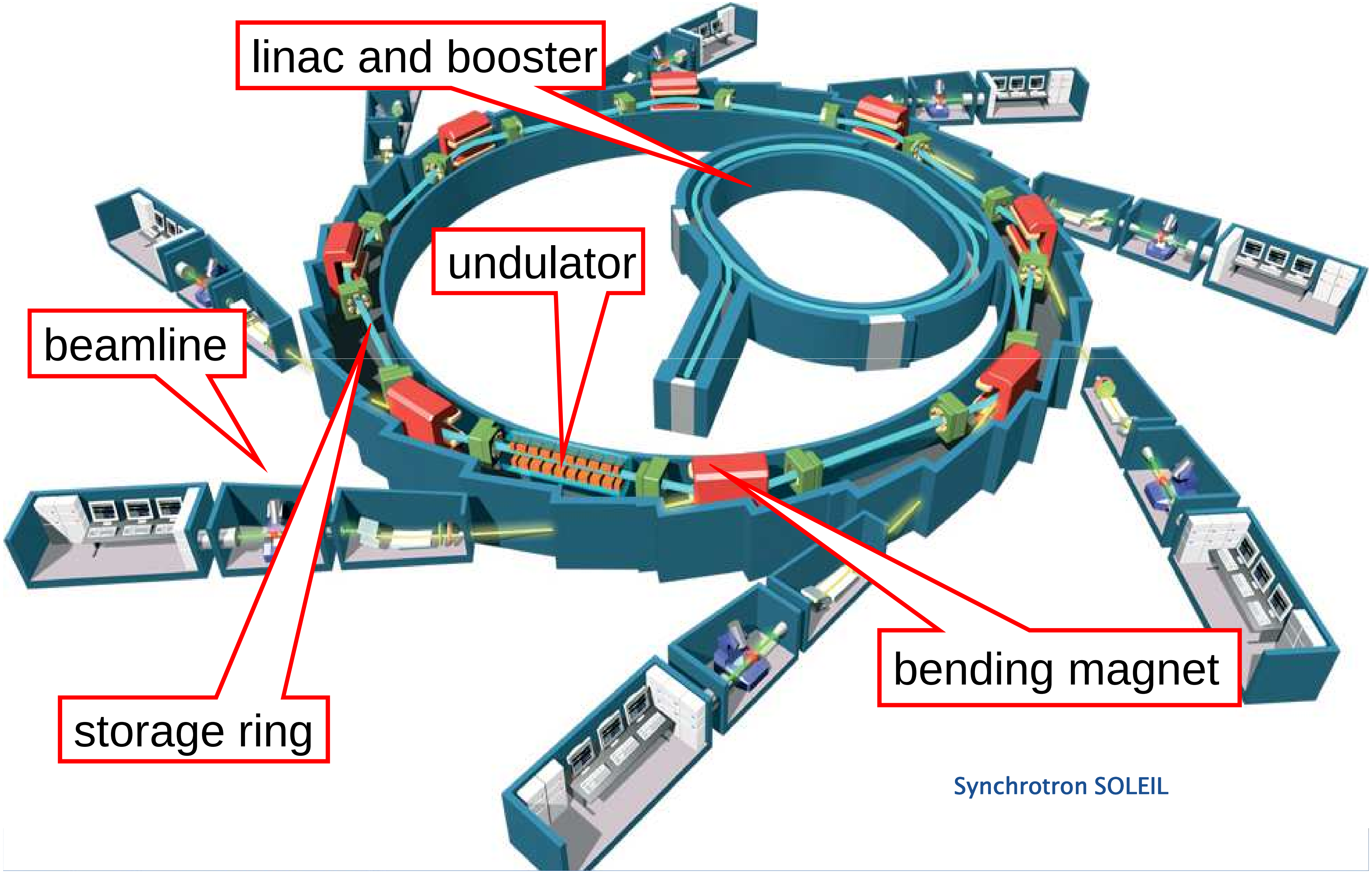


Figure 2. A schematic of X-ray diffraction.

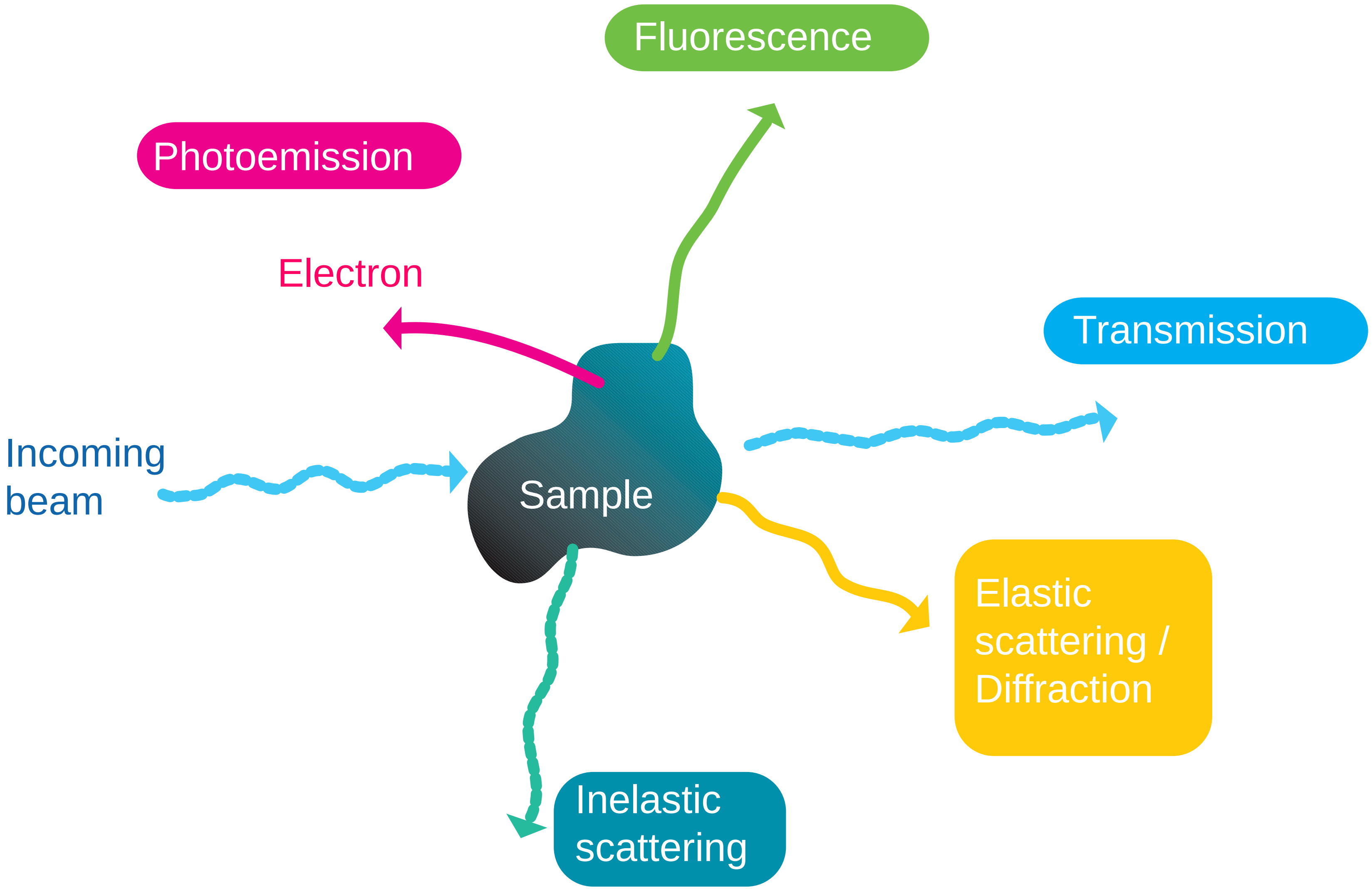
http://mrsec.wisc.edu/edetc/modules/xray/X-raystm.pdf

X-Ray generation: Synchrotron radiation



Synchrotron SOLEIL

Interaction between X-ray and Matter



What is X-ray diffraction?

XRD able to determine :

- **Which phases are present?**
- **At what concentration levels?**
- **What are the amorphous content of the sample?**

How does XRD Works???

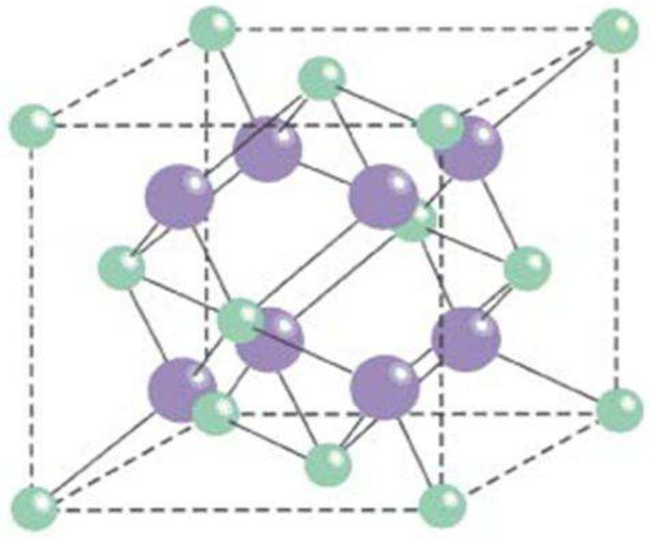
- Every crystalline substance produce its own XRD pattern, which because it is dependent on the internal structure, is characteristic of that substance.

•The XRD pattern is often spoken as the “***FINGERPRINT***” of a mineral or a crystalline substance, because it differs from pattern of every other mineral or crystalline substances.

(Some formulas and definitions)

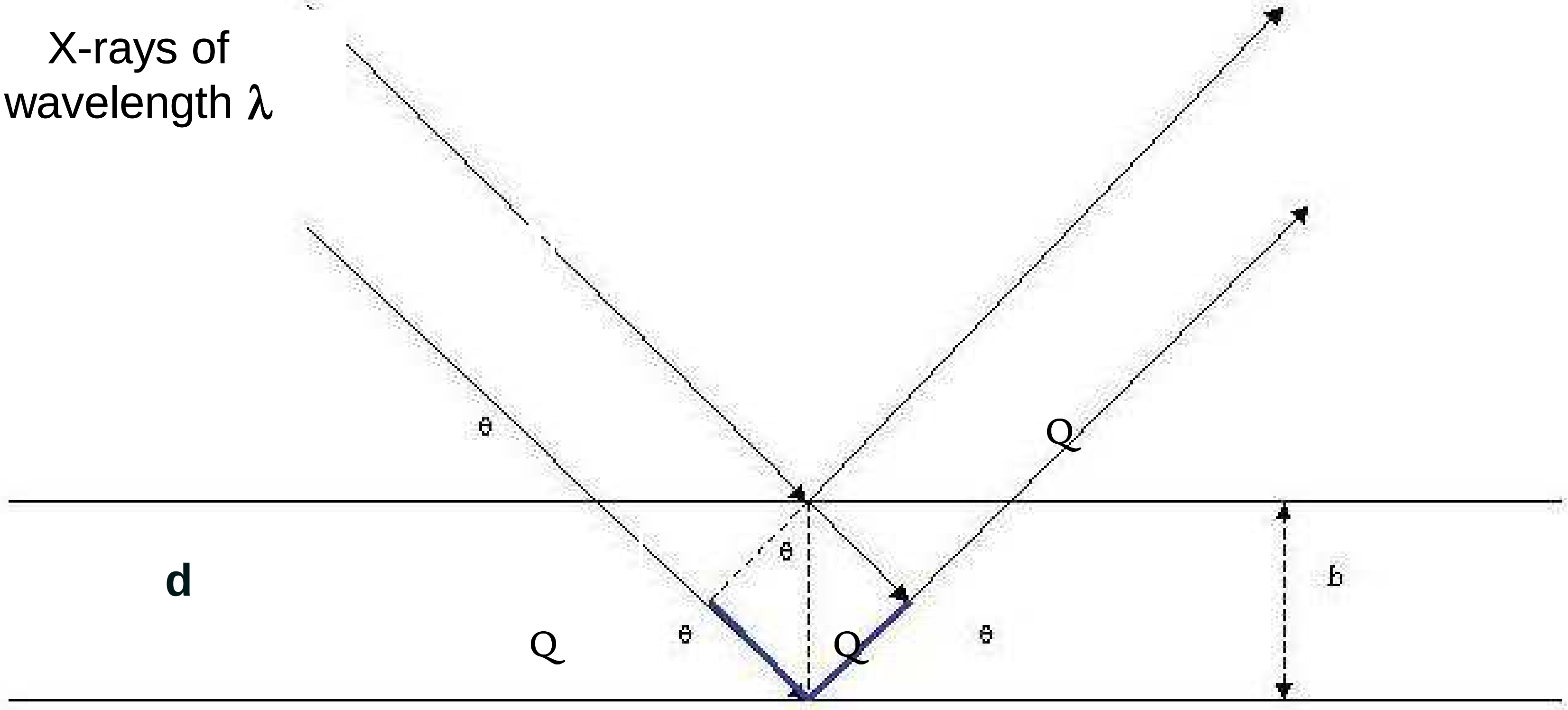
Crystal lattice

- A crystal lattice is a regular three-dimension distribution (cubic, tetragonal, etc.) of atoms in space. These are arrange so that they form a series of parallel planes separated from one another by a distance d, which varies according to the nature of the material. For any crystal planes exist in a number of different orientations- each with its own specific d-spacing



CaF_2 crystal, a face-centred cubic structure

How Diffraction Works: Bragg's Law

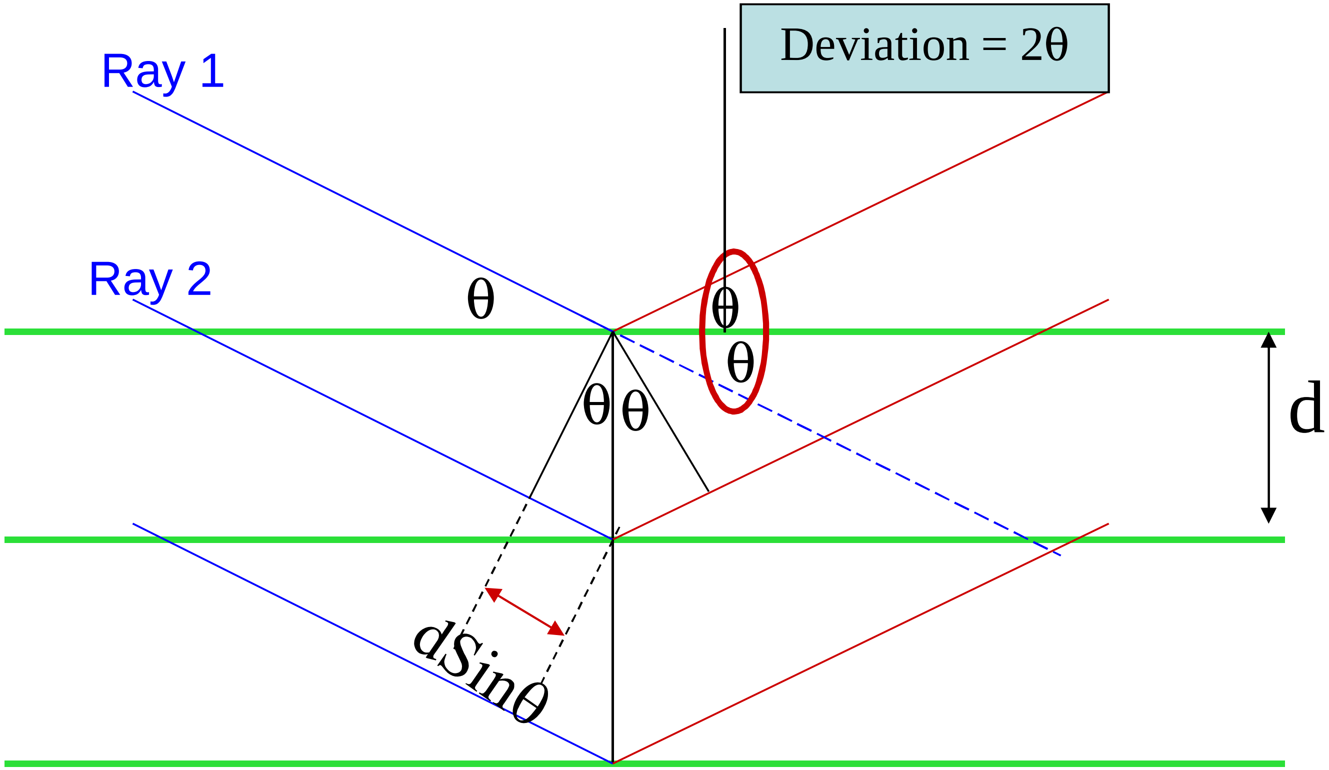


X-rays of
wavelength λ

d

- Similar principle to multiple slit experiments
- Constructive and destructive interference patterns depend on lattice spacing (d) and wavelength of radiation (λ)
- By varying wavelength and observing diffraction patterns, information about lattice spacing is obtained

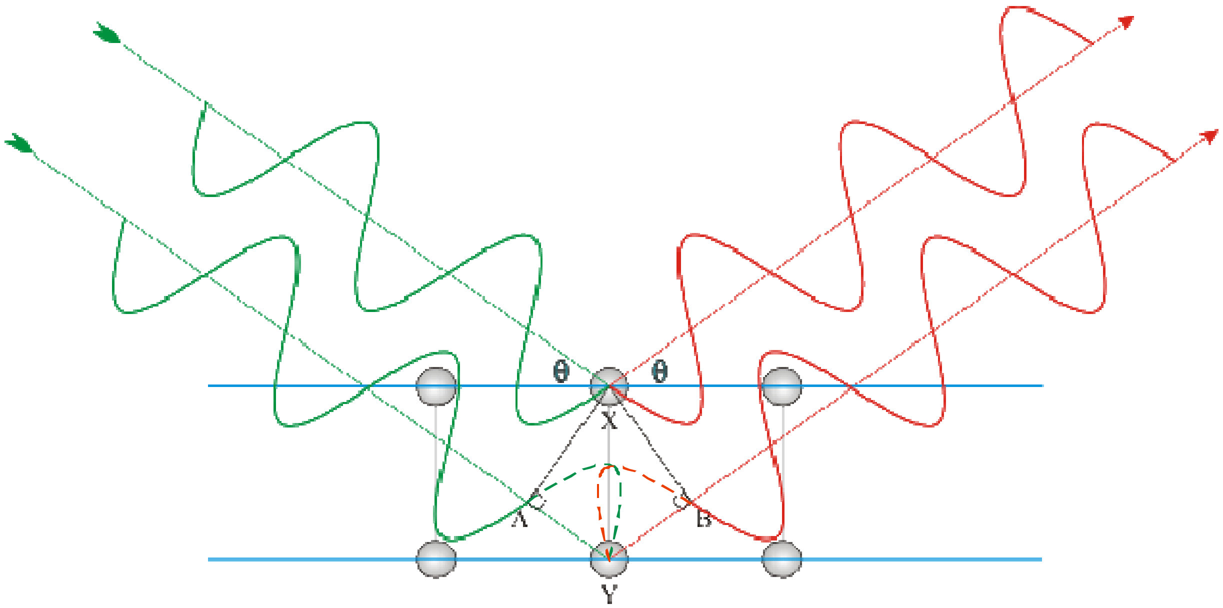
How Diffraction Works: Bragg's Law



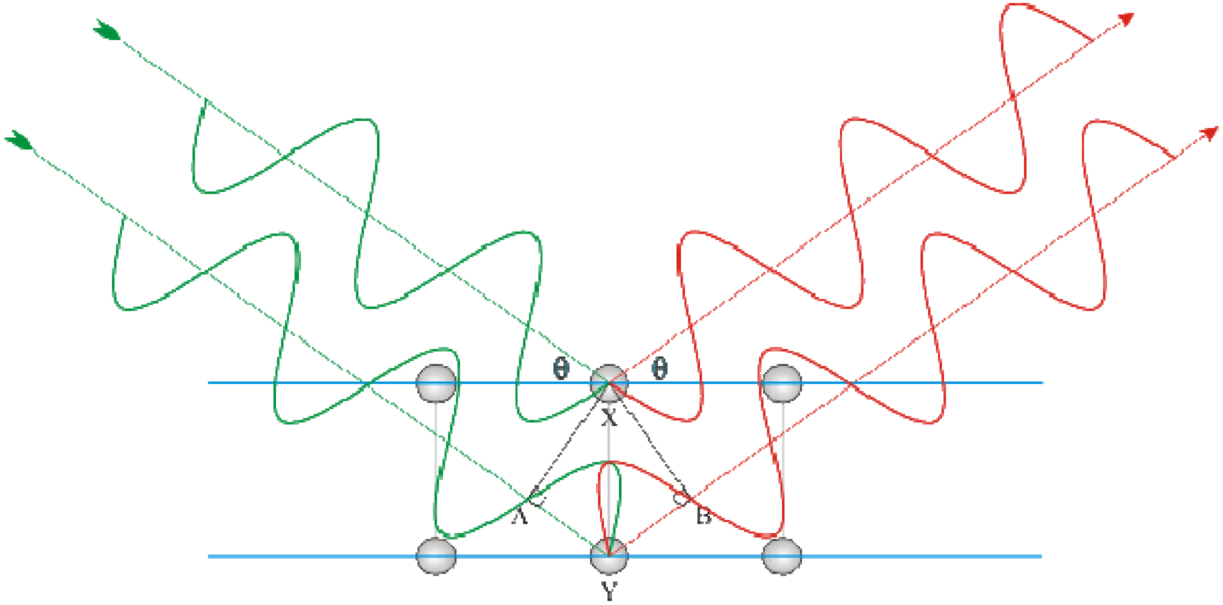
$d\sin\theta + d\sin\theta = n\lambda$

- The path difference between ray 1 and ray 2 = $2d\sin\theta$
- For constructive interference **$n\lambda = 2d\sin\theta$**

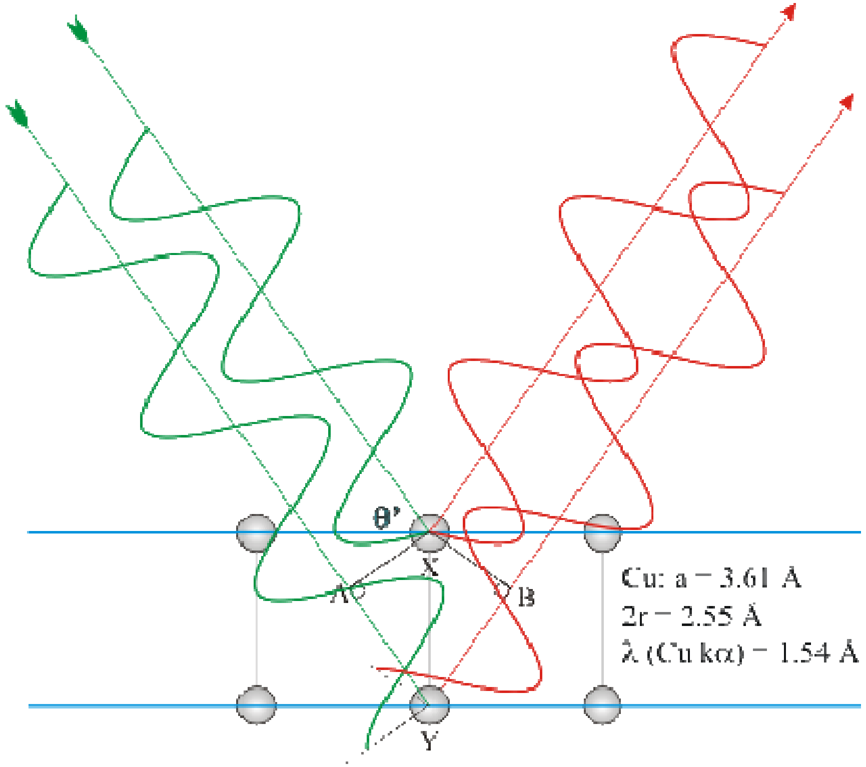
How Diffraction Works: Bragg's Law



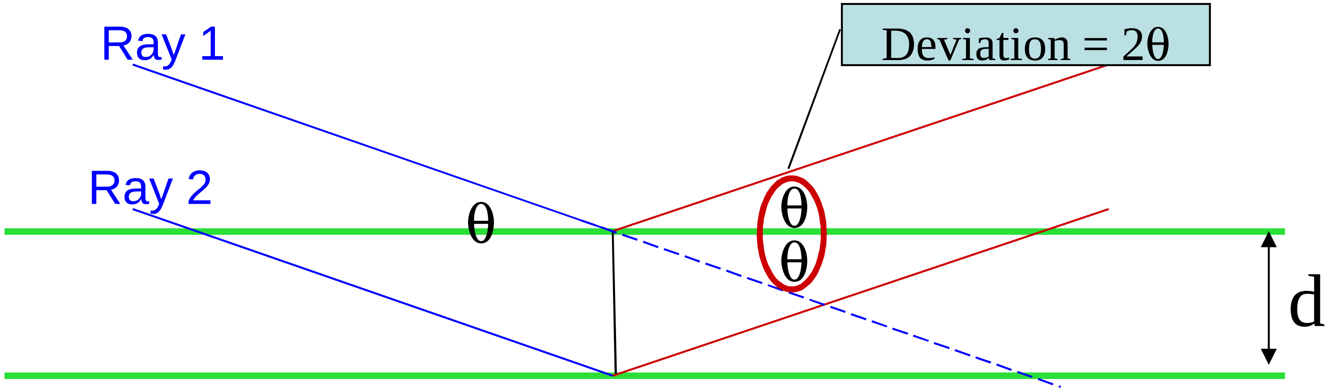
How Diffraction Works: Bragg’s Law

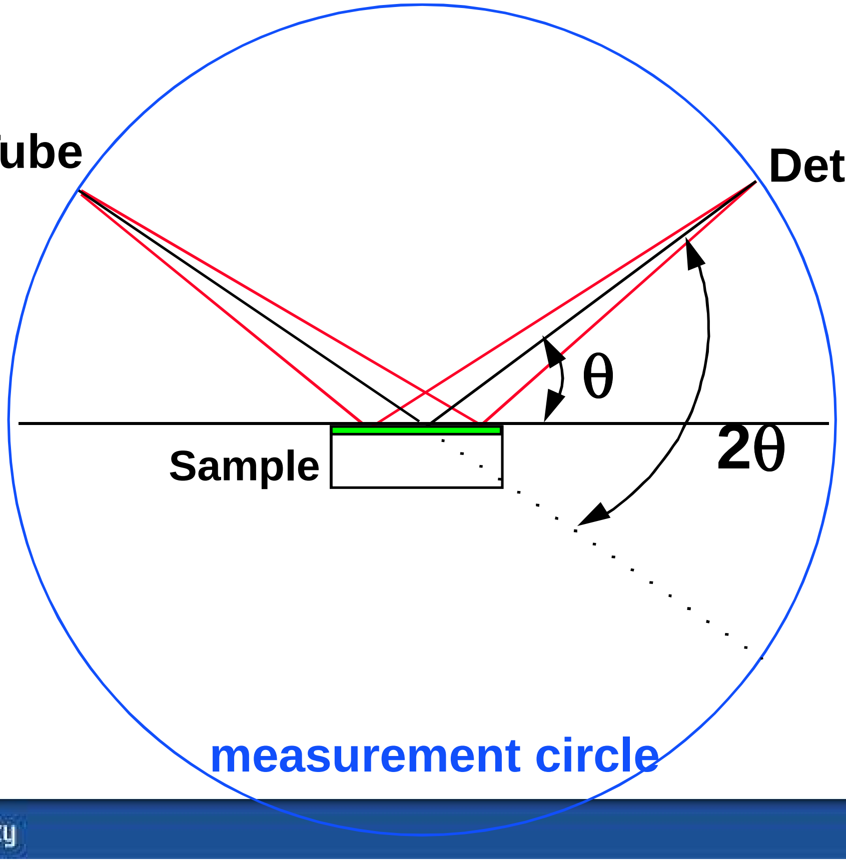


How Diffraction Works: Bragg’s Law



How Diffraction Works: Bragg’s Law



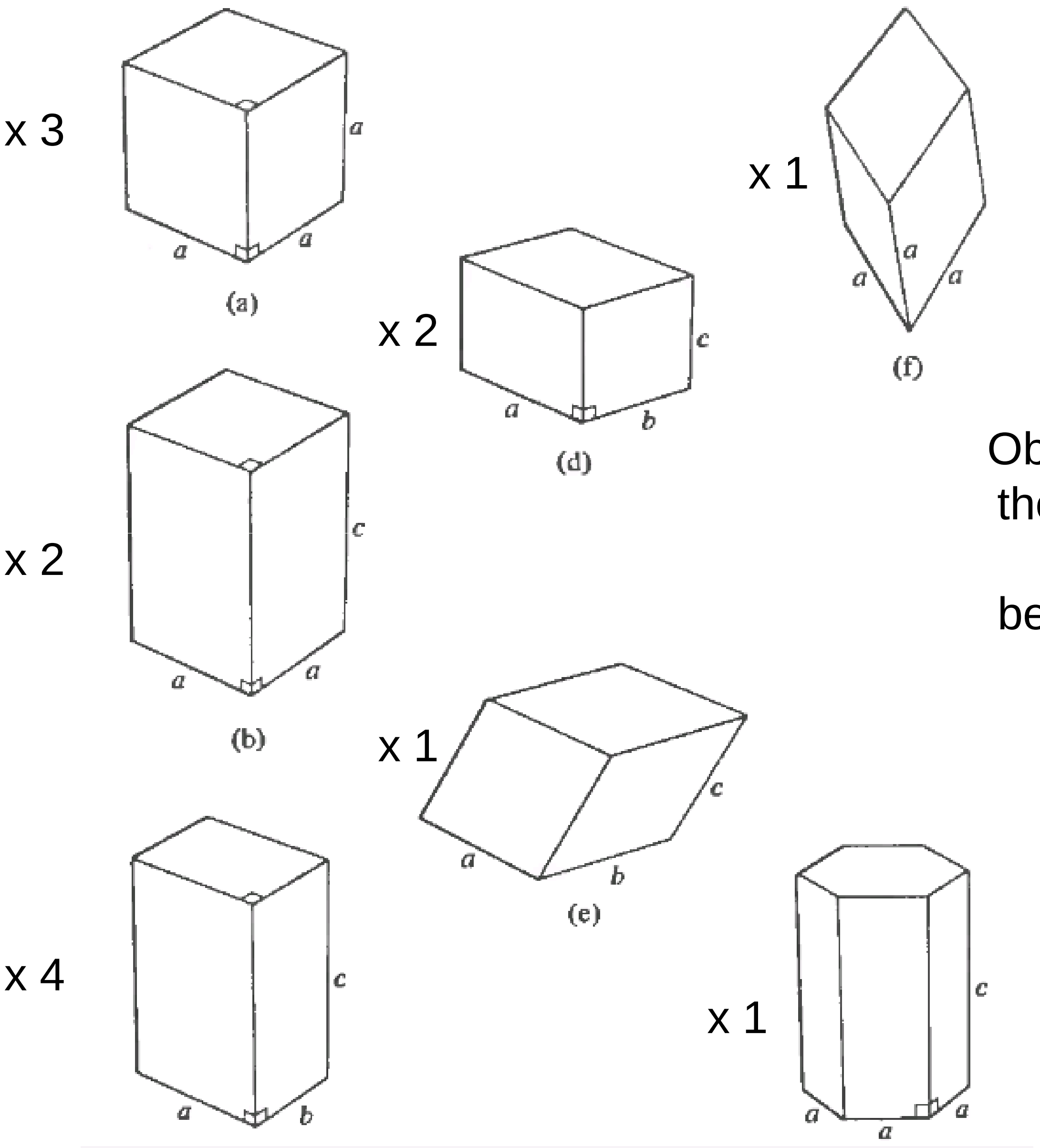


How Diffraction Works: Bragg’s Law

- Bragg’s equation is a negative law
  - If Bragg’s eq. is NOT satisfied → NO reflection can occur
  - If Bragg’s eq. is satisfied → reflection *MAY* occur
- Diffraction = Reinforced Coherent Scattering

Diffraction
Occurs throughout the bulk
Takes place only at Bragg angles
Small fraction of intensity is diffracted

Bravais Lattice

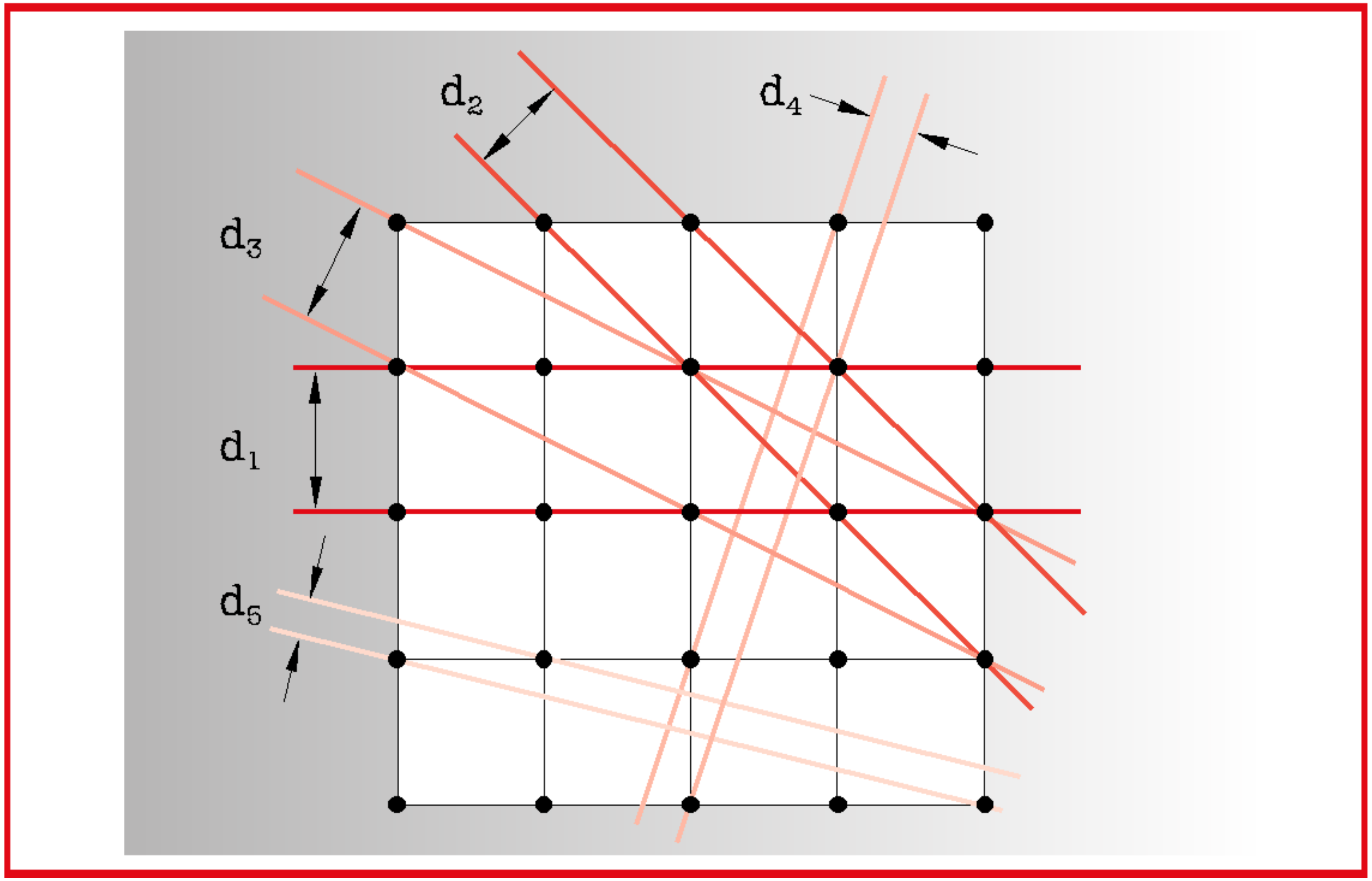


Objects whose symmetries are the point-group symmetries of Bravais lattices belonging to the seven crystal systems

Bravais Lattice

Crystal systems	Axes system
cubic	$a = b = c , \alpha = \beta = \gamma = 90°$
Tetragonal	$a = b \neq c , \alpha = \beta = \gamma = 90°$
Hexagonal	$a = b \neq c , \alpha = \beta = 90°, \gamma = 120°$
Rhomboedric	$a = b = c , \alpha = \beta = \gamma \neq 90°$
Orthorhombic	$a \neq b \neq c , \alpha = \beta = \gamma = 90°$
Monoclinic	$a \neq b \neq c , \alpha = \gamma = 90° , \beta \neq 90°$
Triclinic	$a \neq b \neq c , \alpha \neq \gamma \neq \beta°$

Reflection Planes (Miller indices)



$d_1 \rightarrow$ (0 1 0) $d_2 \rightarrow$ (1 -1 0) $d_3 \rightarrow$ (2 -1 0) ….

Allow to “name” different plane where the Bragg law is satisfied → diffraction peaks

Relationship between d-value and the Lattice Constants

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

Bragg´s law

- The wavelength is known
- Theta is the half value of the peak position
- d will be calculated

$$1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2$$

Equation for the determination of the d-value of a tetragonal elementary cell

- h,k and l are the Miller indices of the peaks
- a and c are lattice parameter of the elementary cell
- if a and c are known it is possible to calculate the peak position
- if the peak position is known it is possible to calculate the lattice parameter

How does it work?

Laue’s Experiment in 1914
Single Crystal X-ray Diffraction

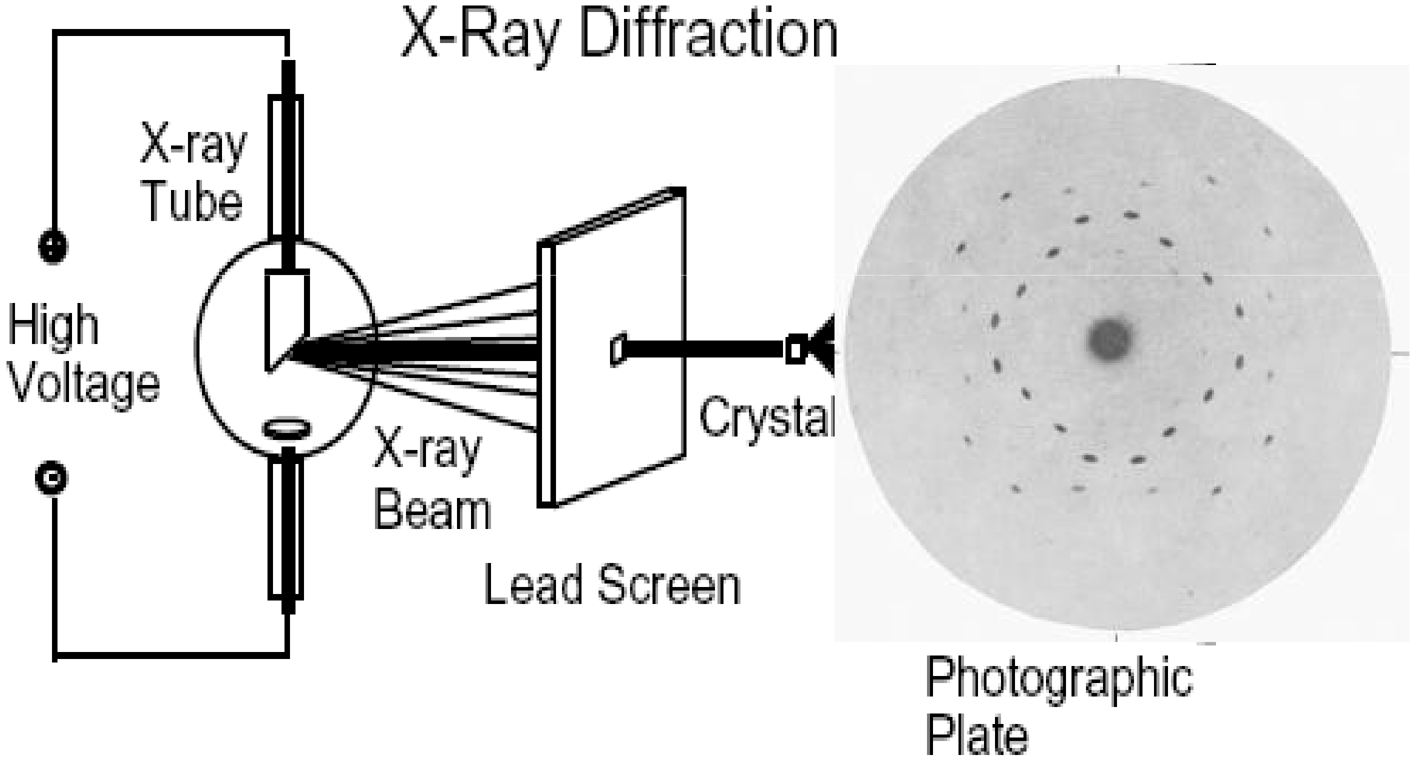


Figure 2. A schematic of X-ray diffraction.

http://mrsec.wisc.edu/edetc/modules/xray/X-raystm.pdf

How does it work?

Powder **X-ray Diffraction**

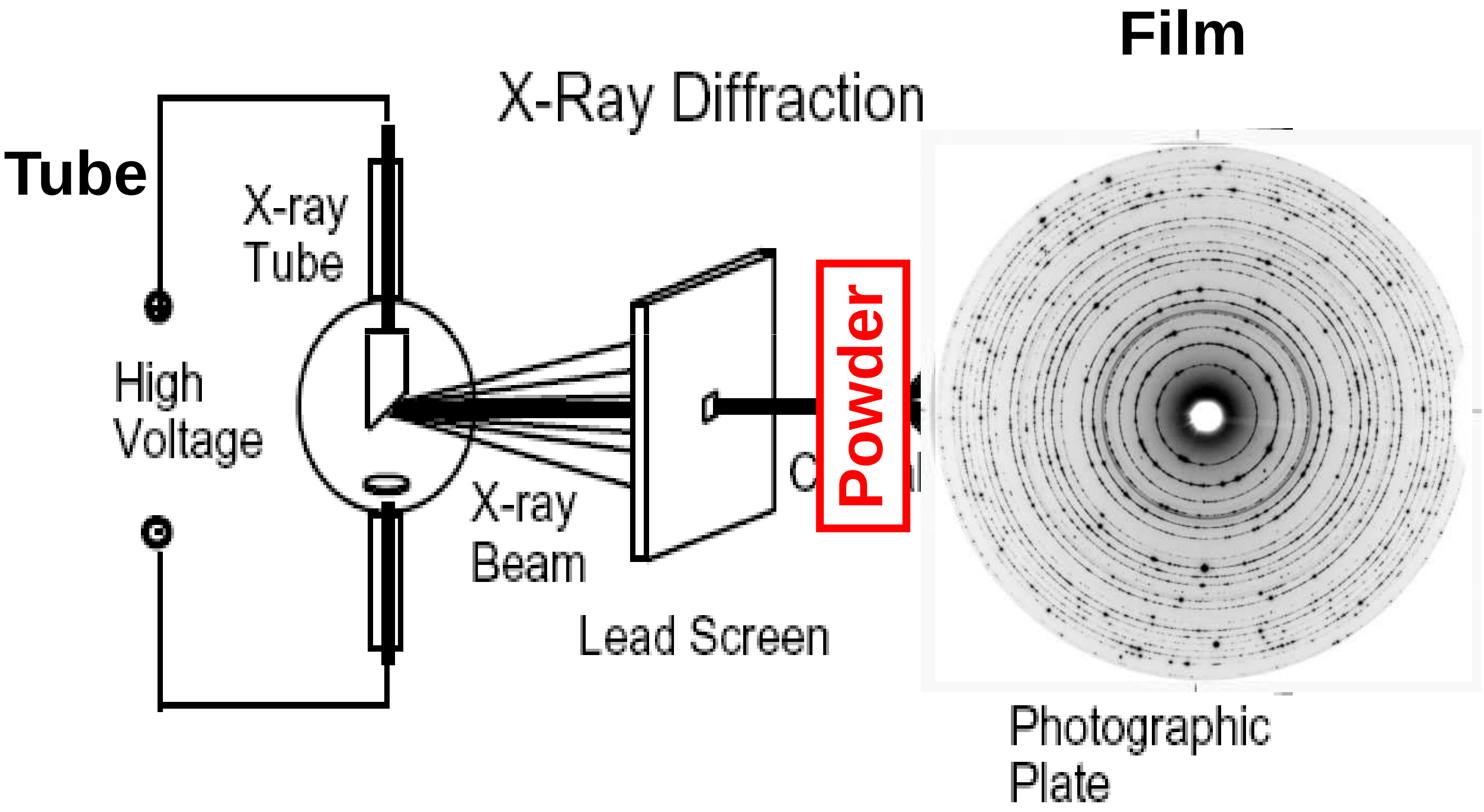
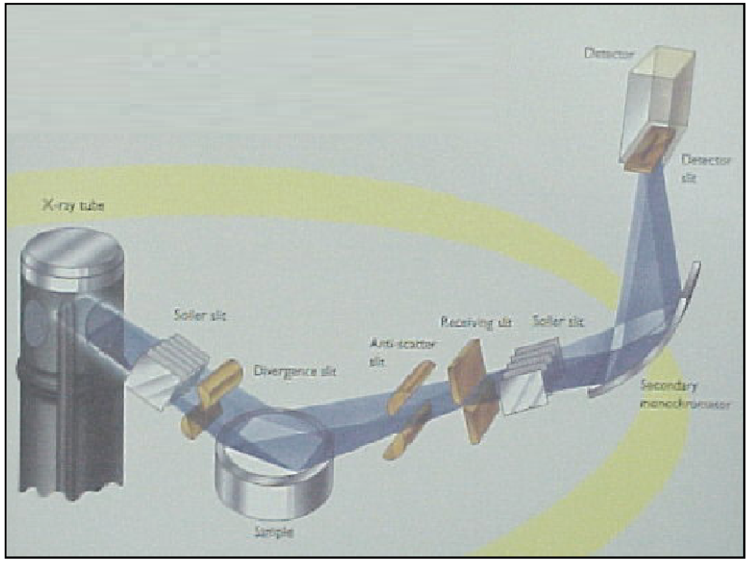


Figure 2. A schematic of X-ray diffraction.

Basic component of XRD machine

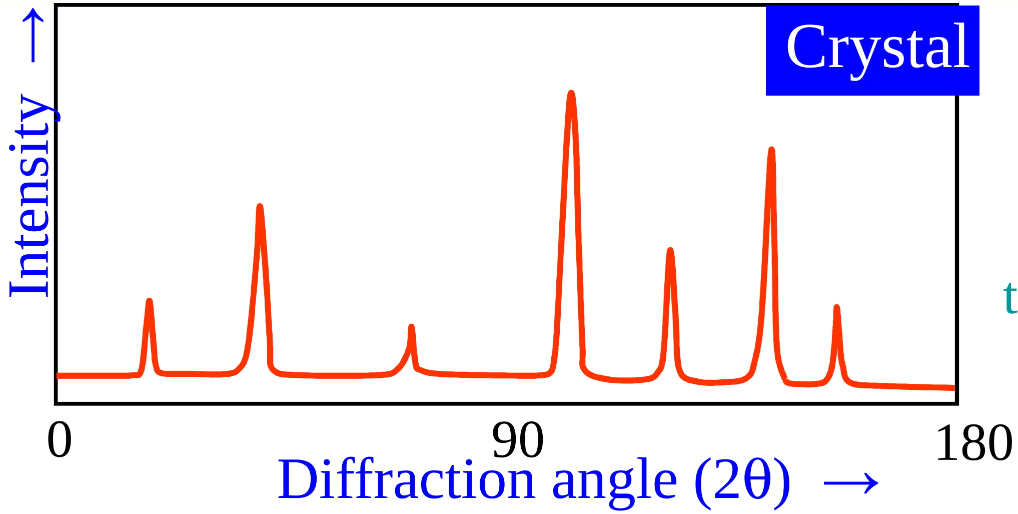
Therefore any XRD machine will consist of three basic component.

- **Monochromatic X-ray source (λ)**
- **Sample**
- **Data collector**



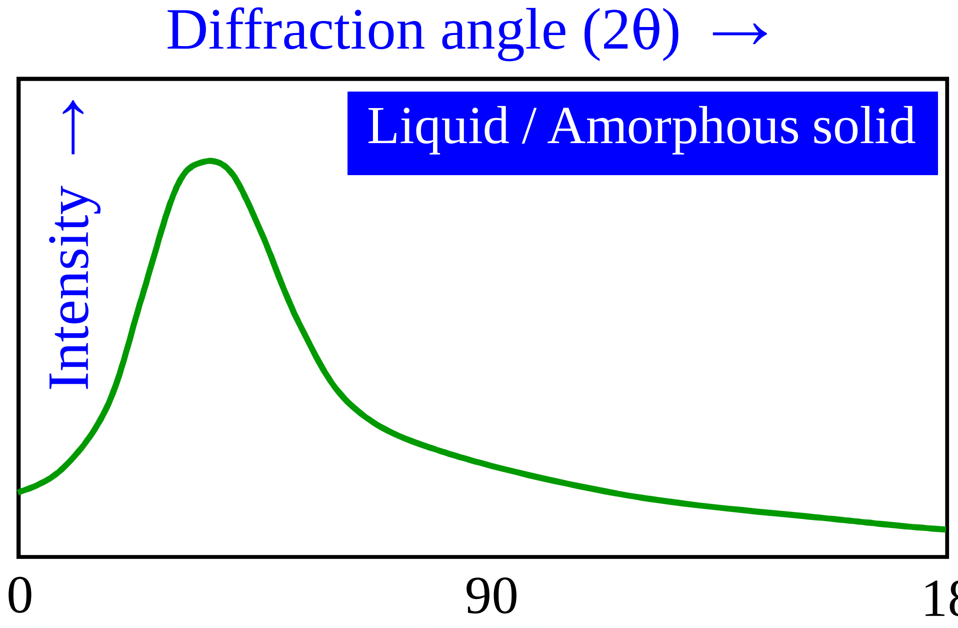
By varying the angle θ, the Bragg's Law conditions are satisfied by different d-spacing in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffraction peaks produces a pattern which is characterised of the sample

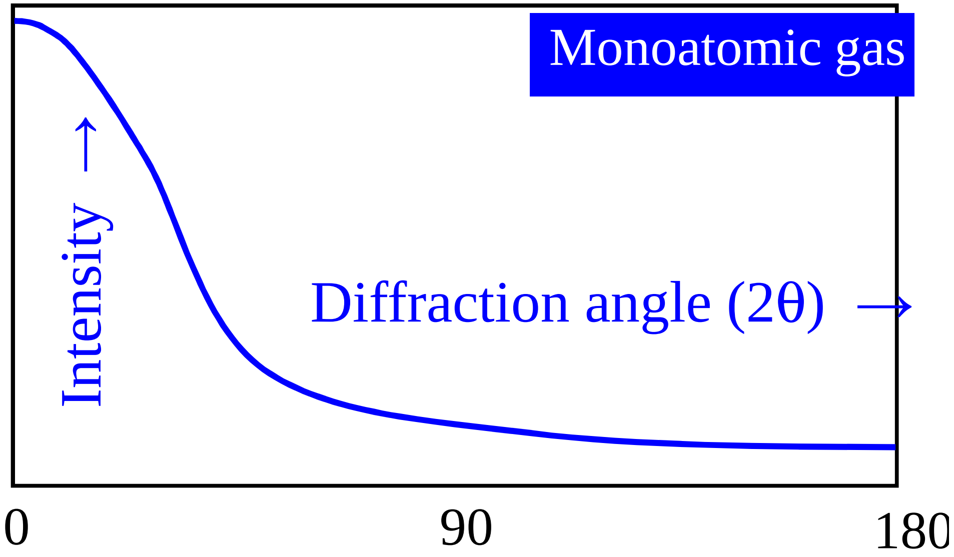
Basic component of XRD machine



Sample

Schematic of difference between
the diffraction patterns of various phases



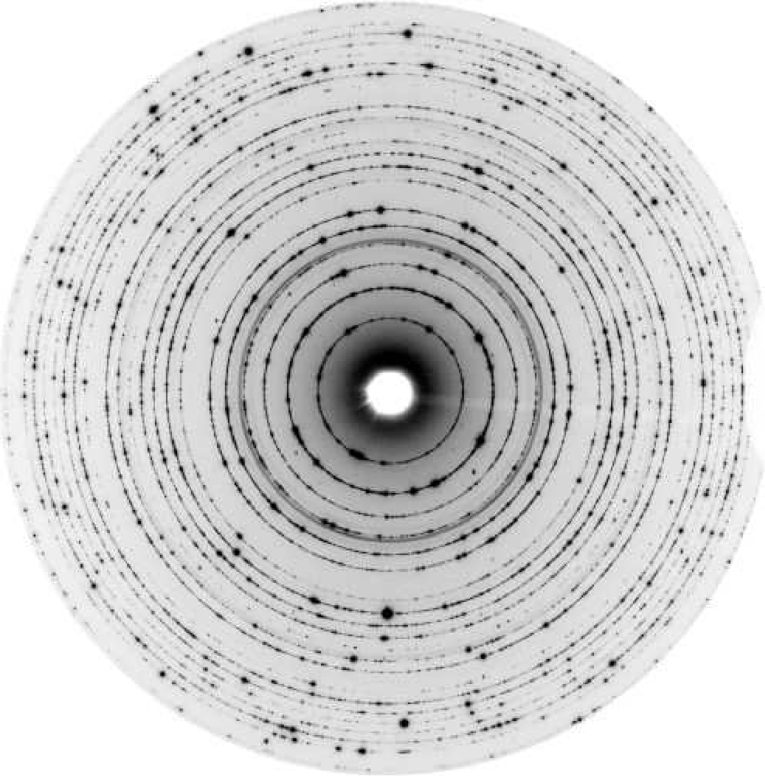


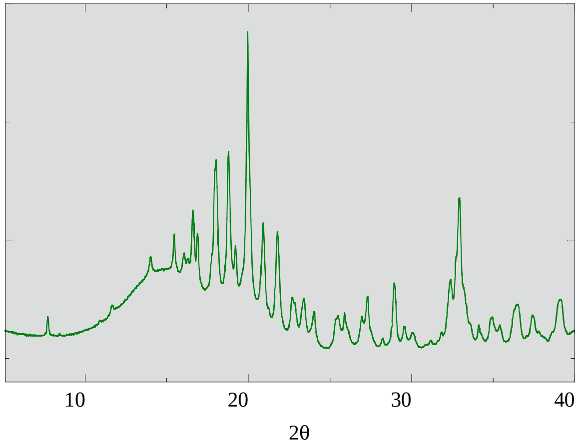
Basic component of XRD machine

Therefore any XRD machine will consist of three basic component.

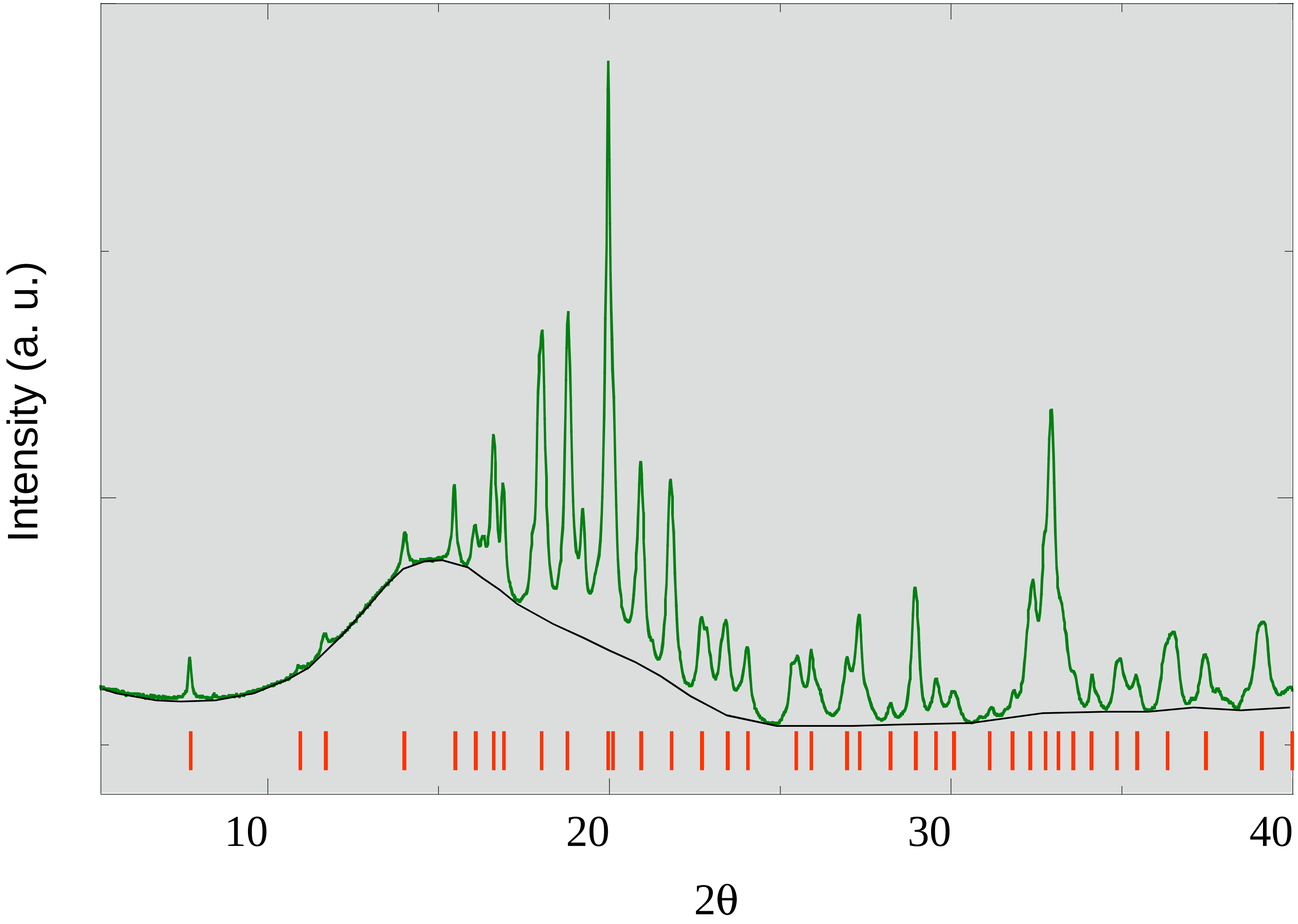
- **Monochromatic X-ray source (λ)**
- **Sample**
- **Data collector:** 1D 2D

such as film, strip chart or magnetic medium/storage, CCD camera, image plate

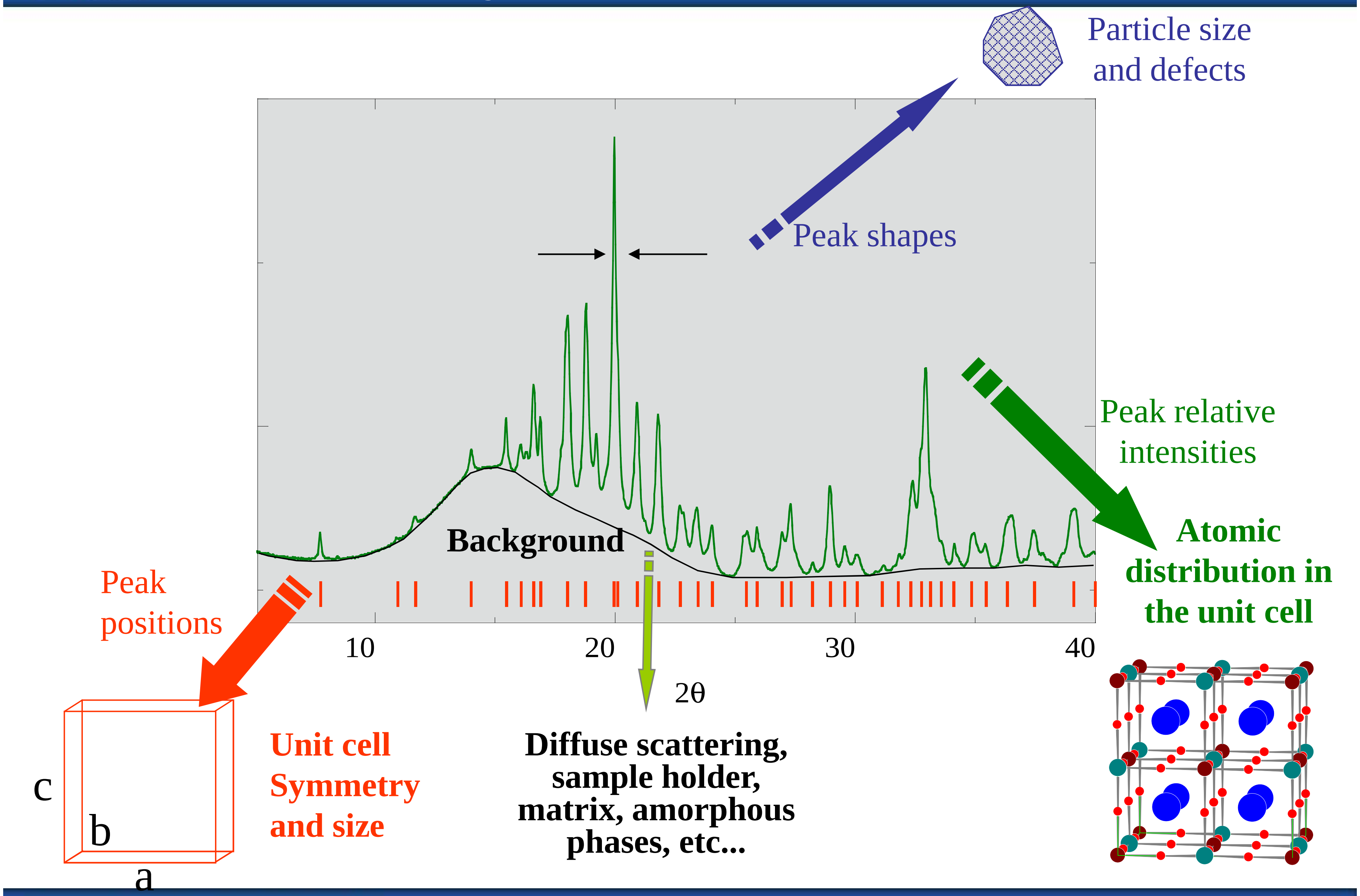




X-ray Powder Diffraction



X-ray Powder Diffraction



Particle size
and defects

Peak shapes

Peak relative
intensities

**Atomic
distribution in
the unit cell**

Background

Peak
positions

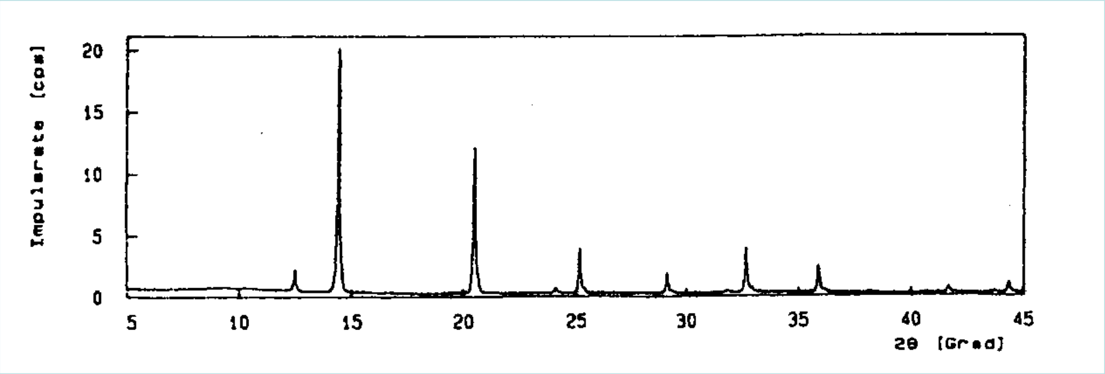
**Unit cell
Symmetry
and size**

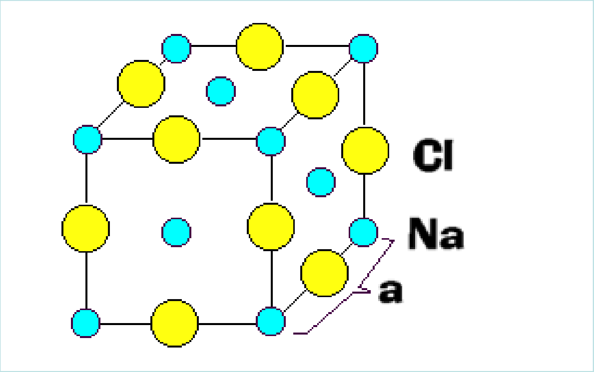
**Diffuse scattering,
sample holder,
matrix, amorphous
phases, etc...**

Which Information does a powder pattern offer?

peak position	dimension of the elementary cell
peak intensity	content of the elementary cell
peak broadening	strain/crystallite size
scaling factor	quantitative phase amount
diffuse background	false order
modulated background	close order

Powder Pattern and Structure





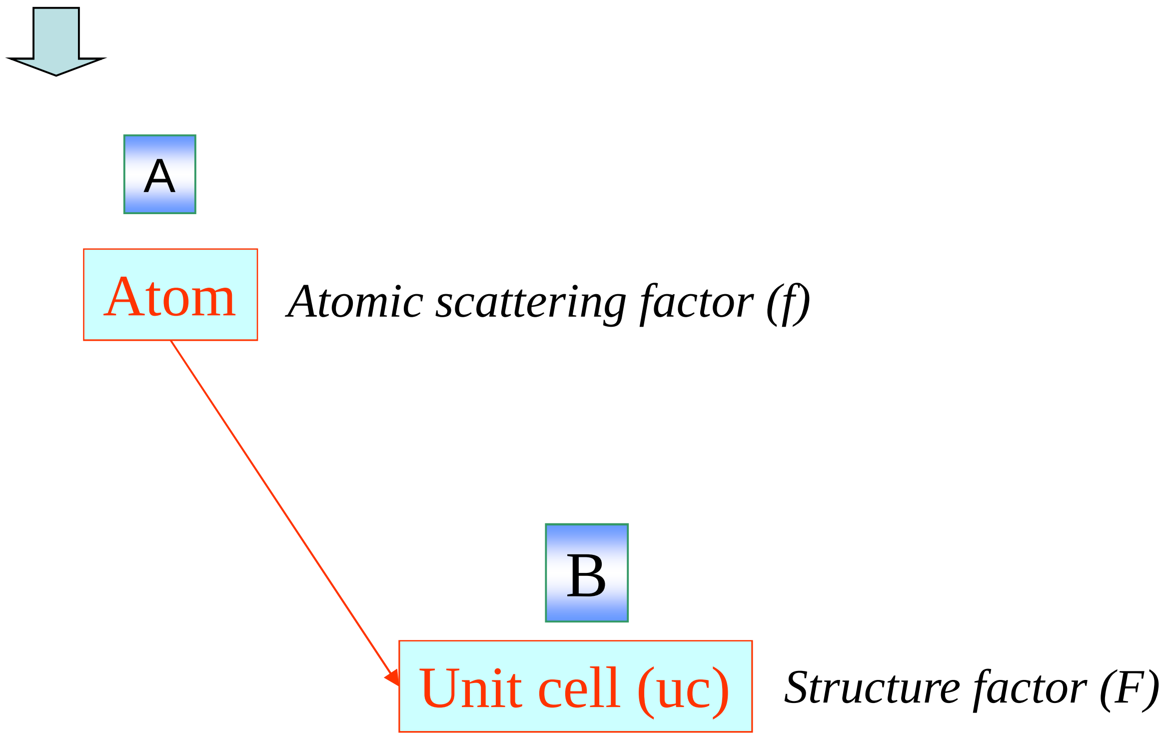
1. The d-spacings of lattice planes depend on the size of the elementary cell and determine the position of the peaks.
2. The intensity of each peak is caused by the crystallographic structure, the position of the atoms within the elementary cell and their thermal vibration.
3. The line width and shape of the peaks may be derived from conditions of measuring and properties - like particle size - of the sample material.

Powder Pattern and Structure

2. The intensity of each peak

Intensity of the Scattered electrons

Scattering by a crystal



A

Atom

Atomic scattering factor (f)

B

Unit cell (uc)

Structure factor (F)

Powder Pattern and Structure

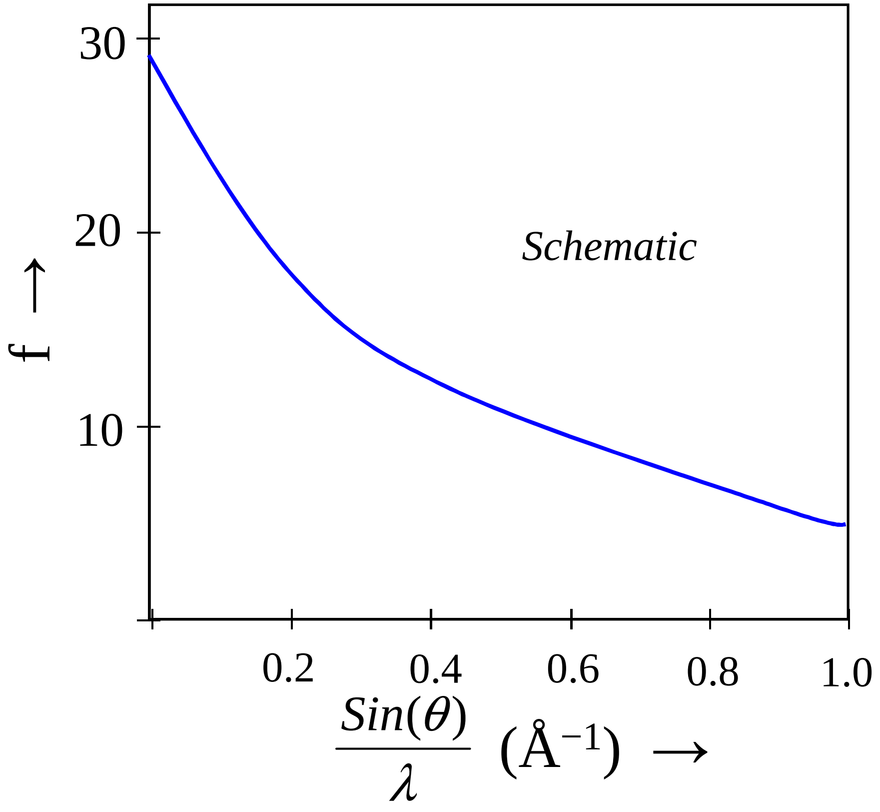
2.1 Scattering by an Atom

Scattering by an atom ∝ [Atomic number, (path difference suffered by scattering from each e^-, λ)]

Scattering by an atom ∝ [Z, (θ, λ)] → $\frac{Sin(\theta)}{\lambda}$

- *Angle of scattering leads to path differences*
- *In the forward direction all scattered waves are in phase*

$$f = \text{Atomic Scattering Factor} = \frac{\text{Amplitude of wave scattered by an atom}}{\text{Amplitude of wave scattered by an electron}}$$



Powder Pattern and Structure

2.1 Scattering by an Atom

	Coherent scattering	Incoherent (Compton) scattering
Z ↑	↑	↓
Sin(θ) / λ ↓	↑	↓

Powder Pattern and Structure

2.2 Scattering by the Unit cell (uc)

- *If atom B is different from atom A → the amplitudes must be weighed by the respective atomic scattering factors (f)*
- *The resultant amplitude of all the waves scattered by all the atoms in the UC gives the scattering factor for the unit cell*
- *The unit cell scattering factor is called the* ***Structure Factor*** *(**F**)*

Scattering by an unit cell = f(position of the atoms, atomic scattering factors)

$$\text{F} = \text{Structure Factor} = \frac{\text{Amplitude of wave scattered by all atoms in uc}}{\text{Amplitude of wave scattered by an electron}}$$

$$I \propto F^2$$

$$F_n^{hkl} = \sum_{j=1}^{n} f_j \; e^{i\varphi_j} = \sum_{j=1}^{n} f_j \; e^{i[2\pi(h\,x'_j + k\,y'_j + l\,z'_j)]}$$

For n atoms in the UC

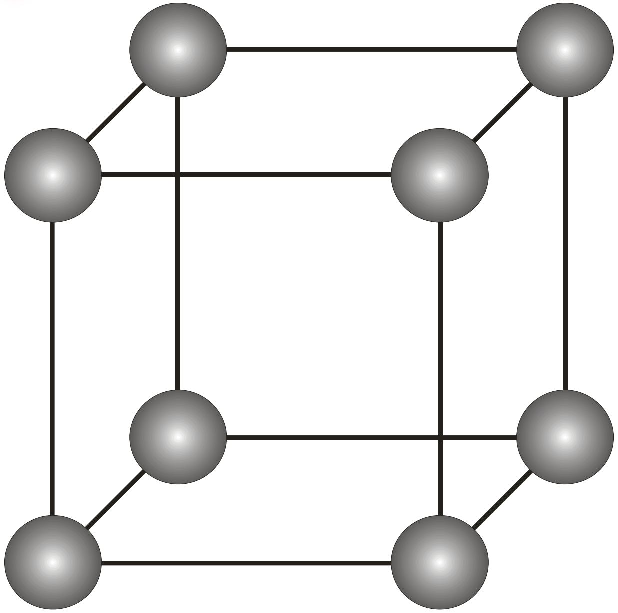
Powder Pattern and Structure

2.2 Scattering by the Unit cell (uc)

Structure factor calculations

Simple Cubic

A Atom at (0,0,0) and equivalent positions



$$e^{ni\pi} = (-1)^n$$

$$e^{(odd\ n)\, i\pi} = -1$$

$$e^{(even\ n)\, i\pi} = +1$$

$$e^{ni\pi} = e^{-ni\pi}$$

$$\frac{e^{i\theta} + e^{-i\theta}}{2} = Cos(\theta)$$

$$F = f_j \quad e^{i\varphi_j} = f_j \quad e^{i[2\pi(\,h\ x'_j + k\ y'_j + l\ z'_j\,)]}$$

$$F = f \quad e^{i[2\pi(\,h\cdot 0 + k\cdot 0 + l\cdot 0)]} = f\, e^0 = f$$

$$F^2 = f^2$$

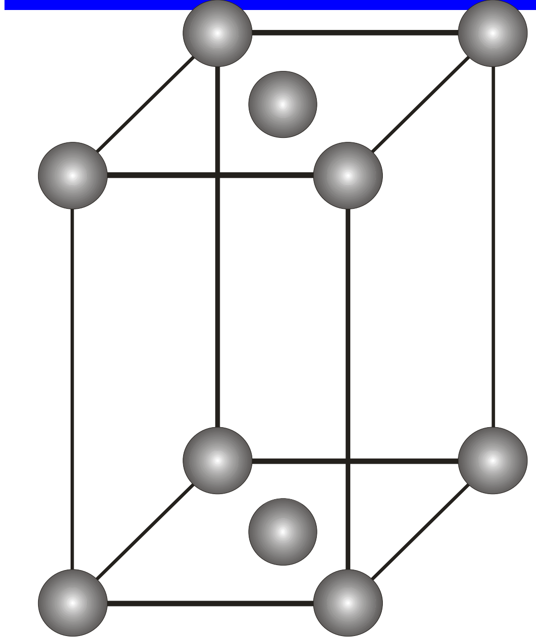
$\Rightarrow$ *F is independent of the scattering plane (h k l)*

Powder Pattern and Structure

B

Atom at (0,0,0) & (½, ½, 0) and equivalent positions

C- centred Orthorhombic



$$F = f_j \; e^{i\varphi_j} = f_j \; e^{i[2\pi(h\,x'_j + k\,y'_j + l\,z'_j)]}$$

$$F = f \; e^{i[2\pi(h\cdot 0 + k\cdot 0 + l\cdot 0)]} + f \; e^{i[2\pi(h\cdot\frac{1}{2} + k\cdot\frac{1}{2} + l\cdot 0)]}$$

$$= f\,e^{0} + f\,e^{i[\cancel{2}\pi(\frac{h+k}{\cancel{2}})]} = f[1 + e^{i\pi(h+k)}]$$

Real

$$F = f[1 + e^{i\pi(h+k)}]$$

(h + k) even

Both even or both odd

$$F = 2f \rightarrow F^2 = 4f^2$$

e.g. (001), (110), (112); (021), (022), (023)

Mixture of odd and even

(h + k) odd

$$F = 0 \rightarrow F^2 = 0$$

e.g. (100), (101), (102); (031), (032), (033)

$\Rightarrow$ *F is independent of the ‘l’ index*

Powder Pattern and Structure

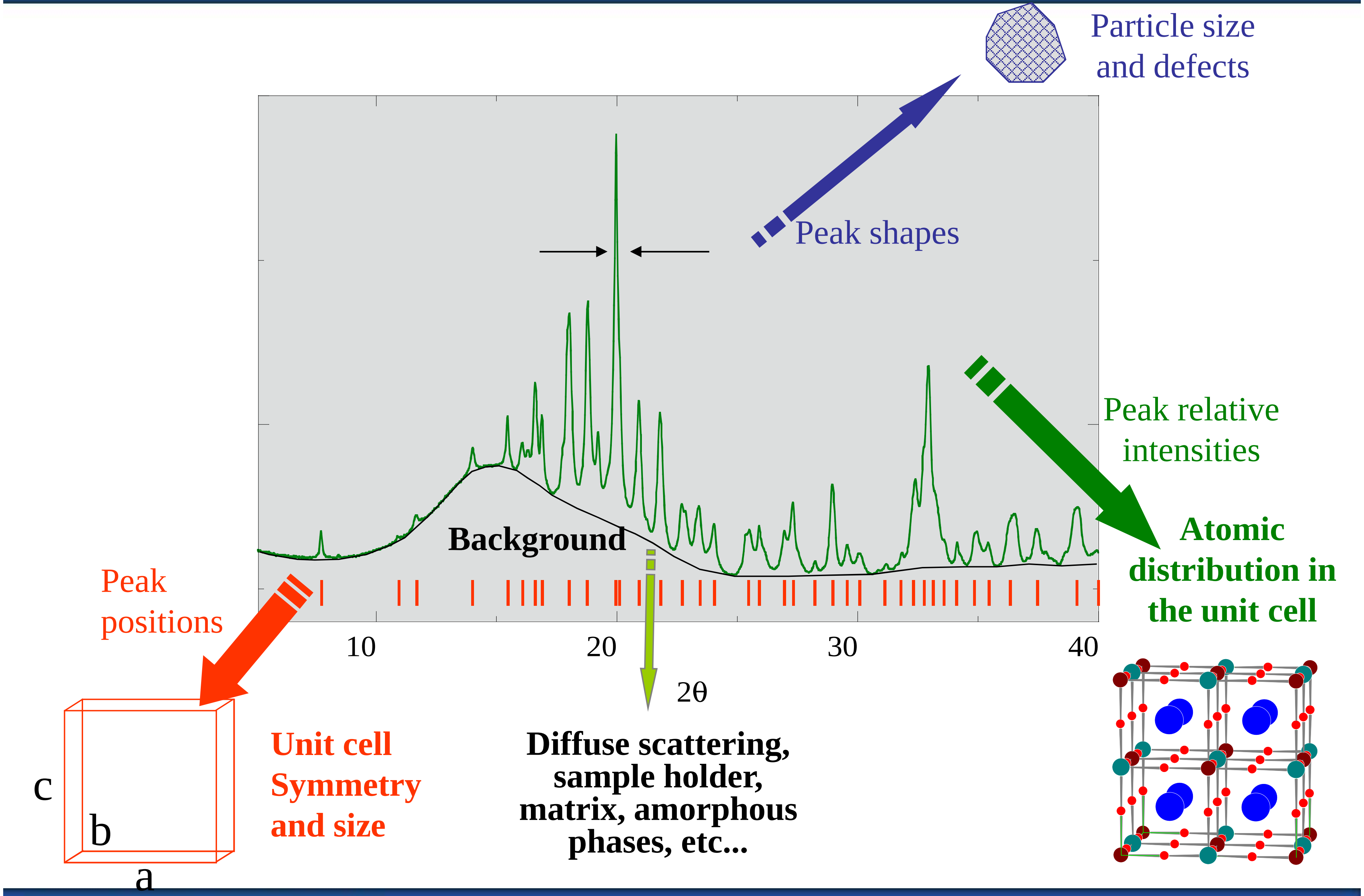
$\Rightarrow$ *Presence of additional atoms/ions/molecules in the UC can alter the intensities of some of the reflections*

Selection / Extinction Rules

Bravais Lattice	**Reflections which *may be* present**	**Reflections necessarily absent**
Simple	all	None
Body centred	(h + k + l) even	(h + k + l) odd
Face centred	h, k and l unmixed	h, k and l mixed
End centred	h and k unmixed *C centred*	h and k mixed *C centred*

Bravais Lattice	**Allowed Reflections**
SC	All
BCC	(h + k + l) even
FCC	h, k and l unmixed
DC	h, k and l are all odd *Or* all are even *& (h + k + l) divisible by 4*

X-ray Powder Diffraction



Particle size and defects

Peak shapes

Background

Peak relative intensities

Atomic distribution in the unit cell

Peak positions

Unit cell Symmetry and size

Diffuse scattering, sample holder, matrix, amorphous phases, etc...

Powder Pattern and Structure

Crystallite size and Strain

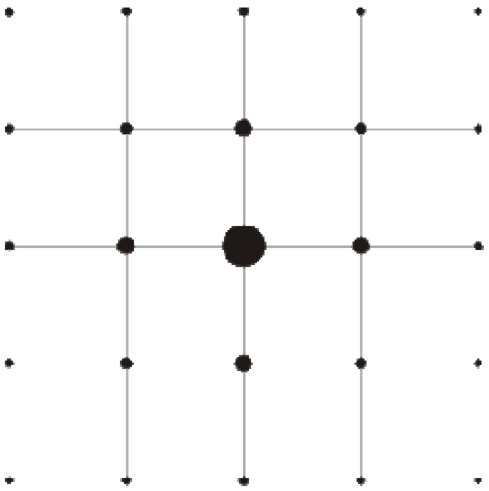
- Bragg’s equation assumes:
  - Crystal is perfect and infinite
  - Incident beam is perfectly parallel and monochromatic
- Actual experimental conditions are different from these leading various kinds of deviations from Bragg’s condition
  - Peaks are not ‘δ’ curves → Peaks are broadened
- There are also deviations from the assumptions involved in the generating powder patterns
  - Crystals may not be randomly oriented *(textured sample)* → Peak intensities are altered

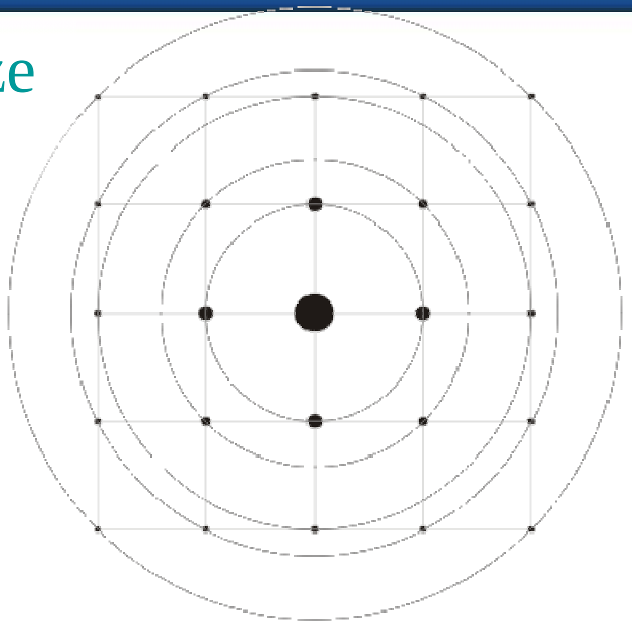
- In a powder sample if the crystallite size < 0.5 μm
  - there are insufficient number of planes to build up a sharp diffraction pattern

⇒ *peaks are broadened*

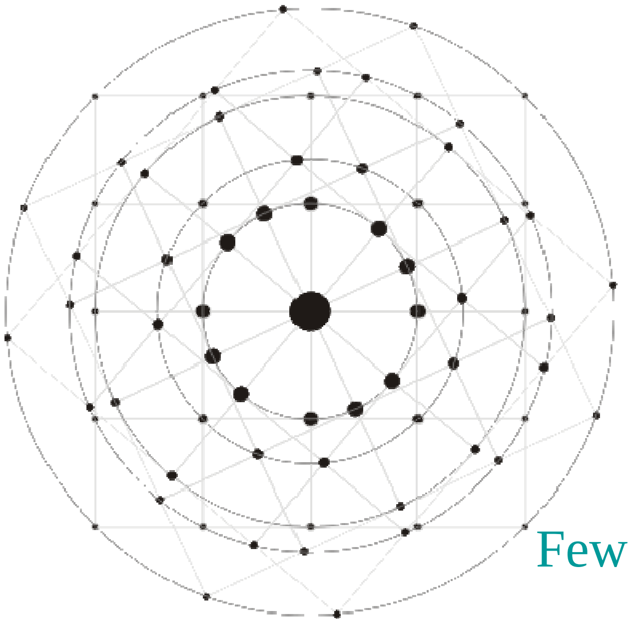
Powder Pattern and Structure

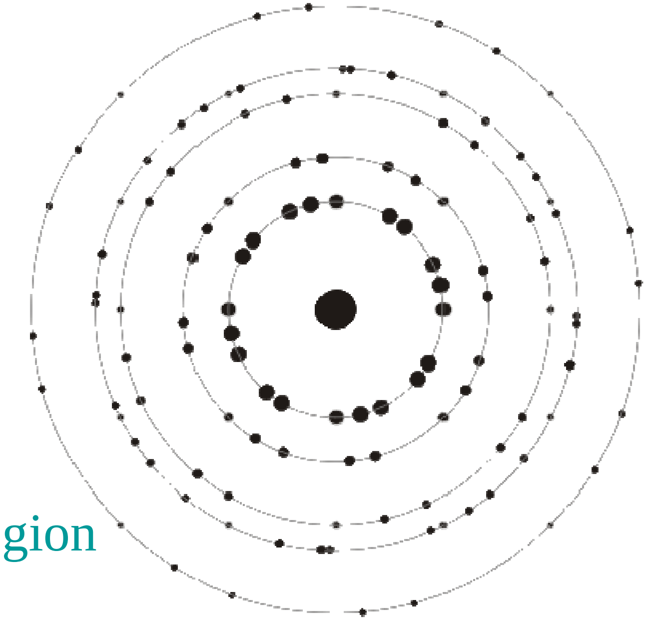
Effect of crystallite size on XRD patterns





Single crystal

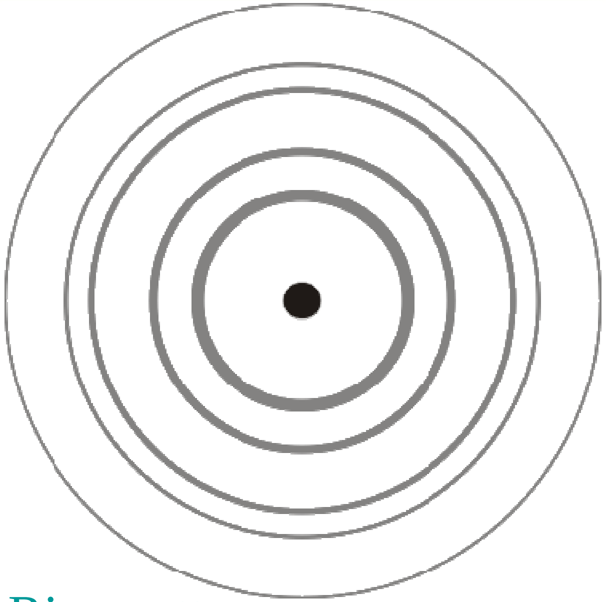




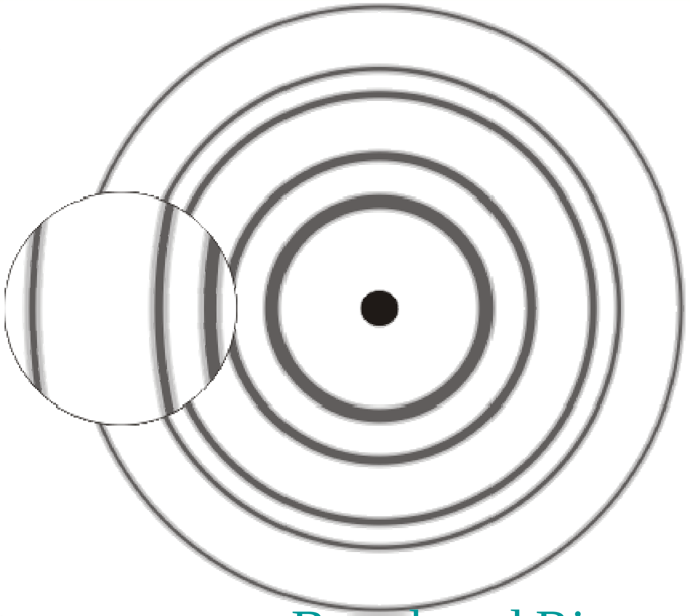
Few crystals in the selected region
“Spotty” pattern

Powder Pattern and Structure

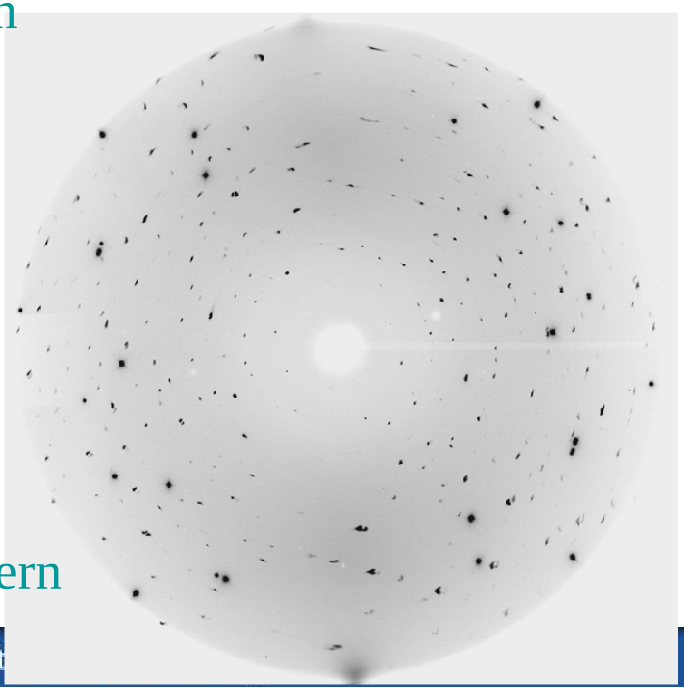
Effect of crystallite siz on XRD patterns



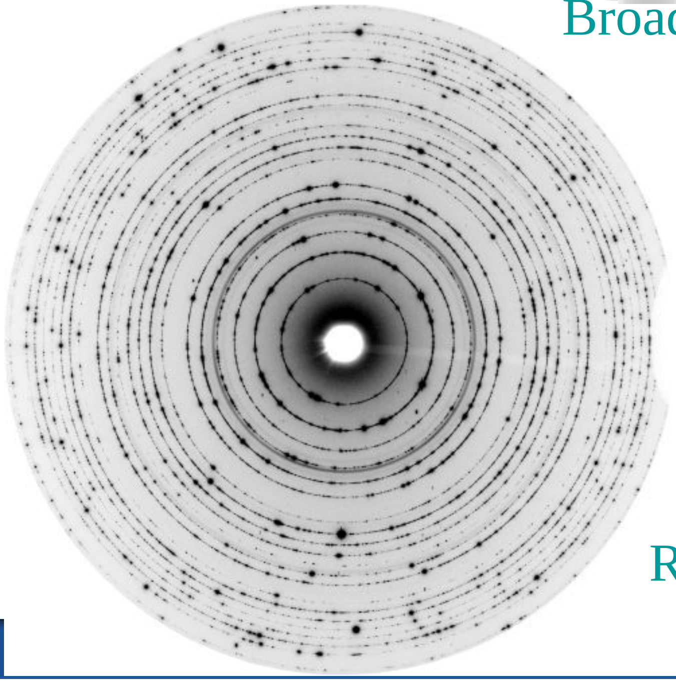
Ring pattern



Broadened Rings



Spotty pattern



Ring pattern

Powder Pattern and Structure

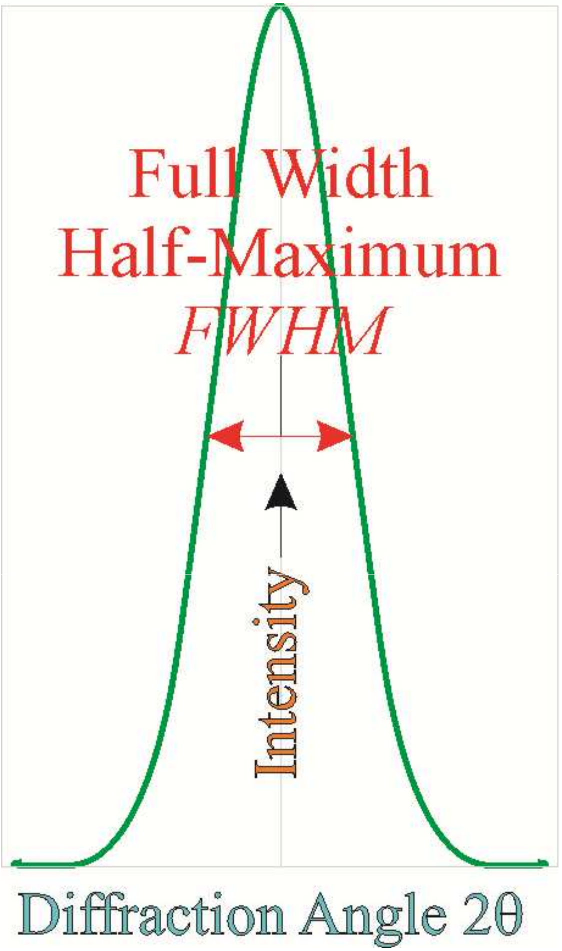
XRD Line Broadening

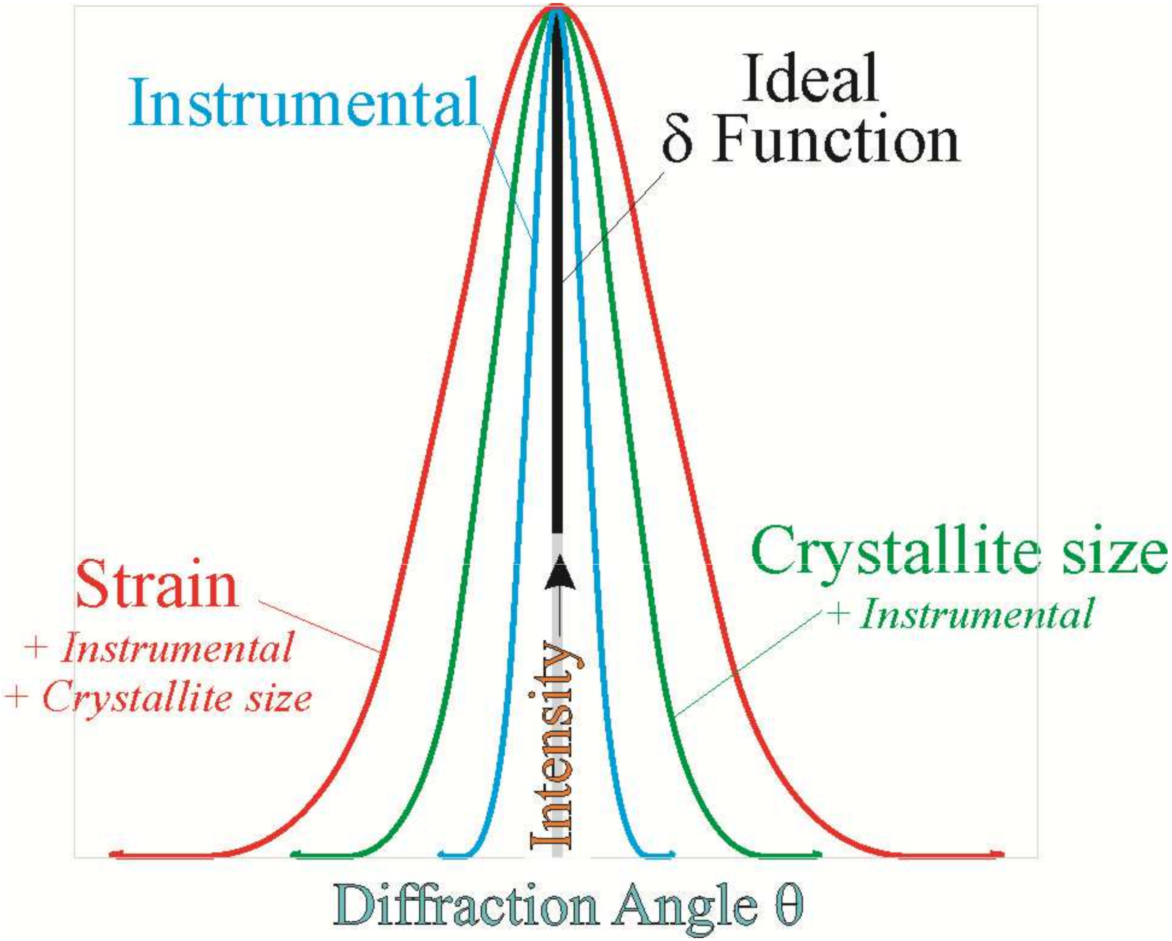
- **Instrumental** B_i
  - Unresolved α_1 , α_2 peaks
  - Non-monochromaticity of the source (finite width of α peak)
  - Imperfect focusing
- **Crystallite size** B_c
  - In the vicinity of θ_B the −ve of Bragg’s equation not being satisfied
- **Strain** B_s
  - ‘Residual Strain’ arising from dislocations, coherent precipitates etc. leading to broadening
- **Stacking fault**
- **Other defects**

In principle every defect contributes to some broadening

$$\boxed{B(FWHM) = B_i + B_c + B_s + B_{SF} + \ldots}$$

Powder Pattern and Structure





$$\boxed{B(FWHM) = B_i + B_c + B_s + B_{SF} + \ldots}$$

Crystallite size

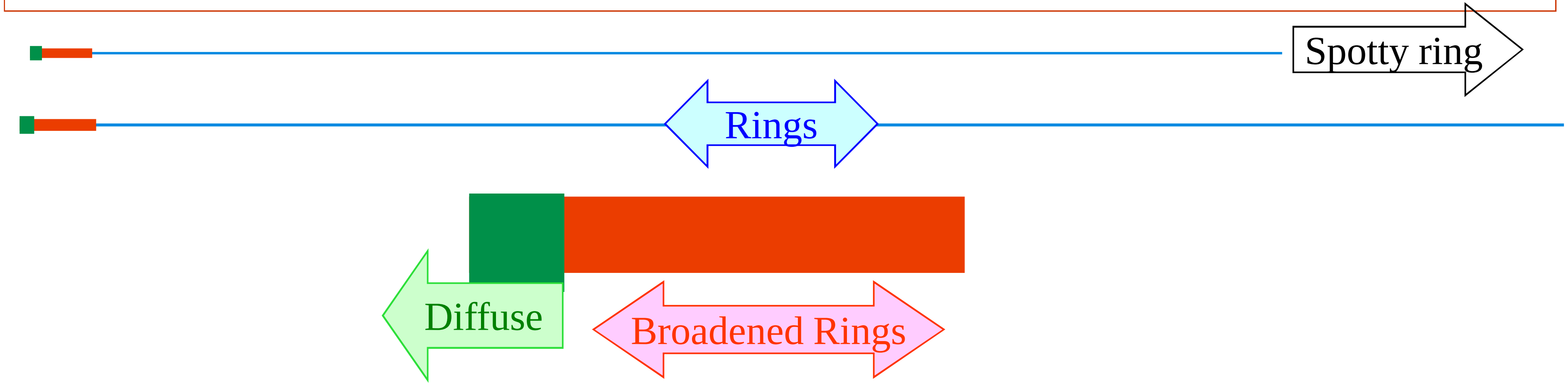
Powder Pattern and Structure

- Size $> 10\ \mu\text{m}$ ➢ Spotty ring

  (no. of grains in the irradiated portion insufficient to produce a ring)

- Size $\in (10, 0.5)\ \mu$ ➢ Smooth continuous ring pattern
- Size $\in (0.5, 0.1)\ \mu$ ➢ Rings are broadened
- Size $< 0.1\ \mu$ ➢ No ring pattern

  (irradiated volume too small to produce a diffraction ring pattern & diffraction occurs only at low angles)



Powder Pattern and Structure

Subtracting Instrumental Broadening

- Instrumental broadening has to be subtracted to get the broadening effects due to the sample

1

- Mix specimen with known coarse-grained (~ 10μm), well annealed *(strain free)* → does not give any broadening due to strain or crystallite size *(the only broadening is instrumental).* A brittle material which can be ground into powder form without leading to much stored strain is good.
- If the pattern of the test sample (standard) is recorded separately then the experimental conditions should be identical *(it is preferable that one or more peaks of the standard lies close to the specimen's peaks)*

2

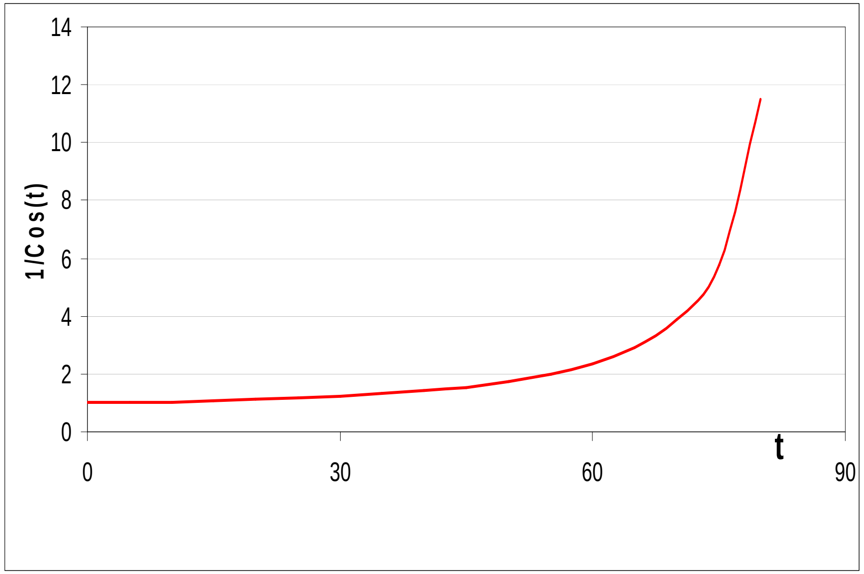
- Use the same material as the standard as the specimen to be X-rayed but with large grain size and well annealed

Powder Pattern and Structure

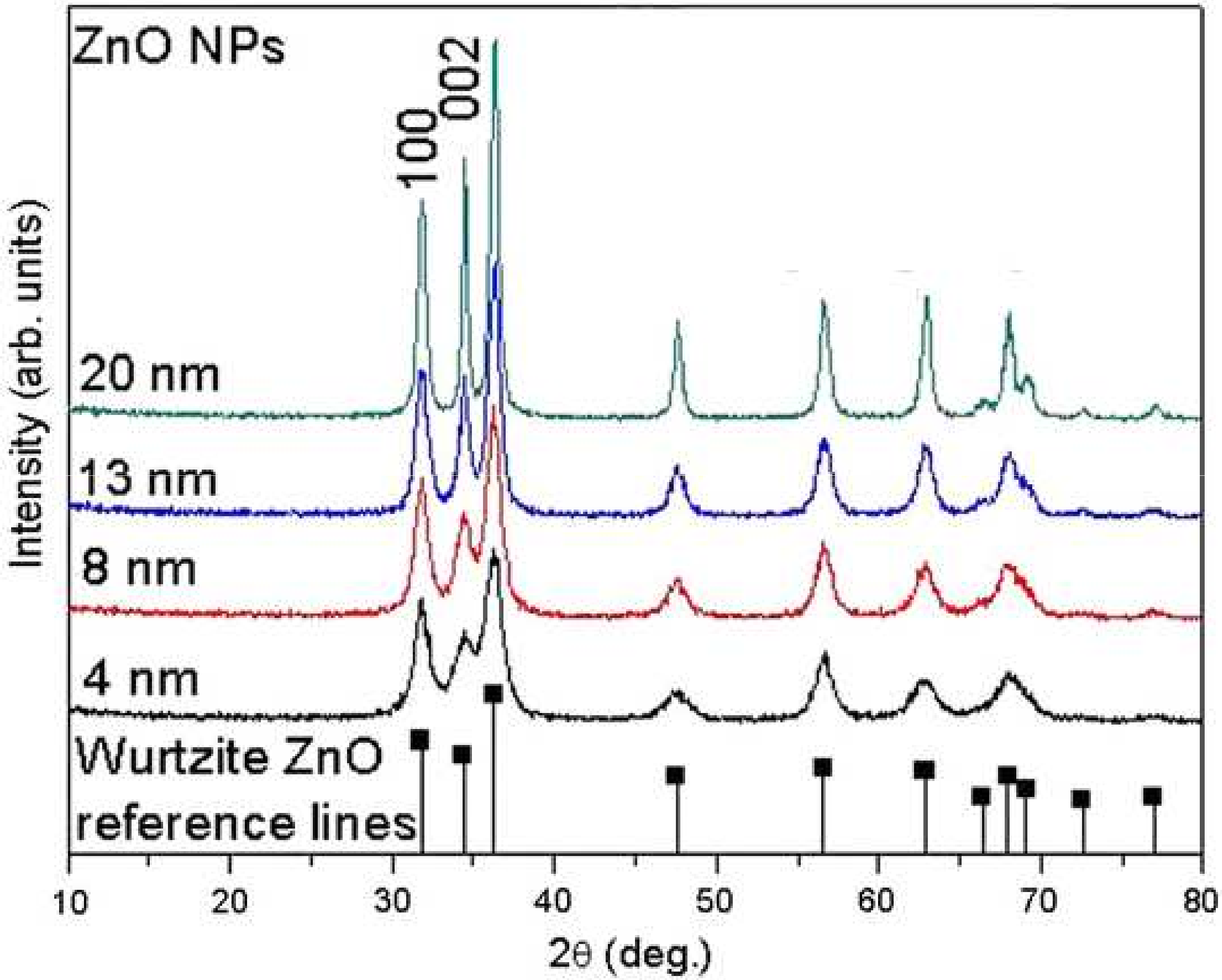
Scherrer's formula *For Gaussian line profiles and cubic crystals*

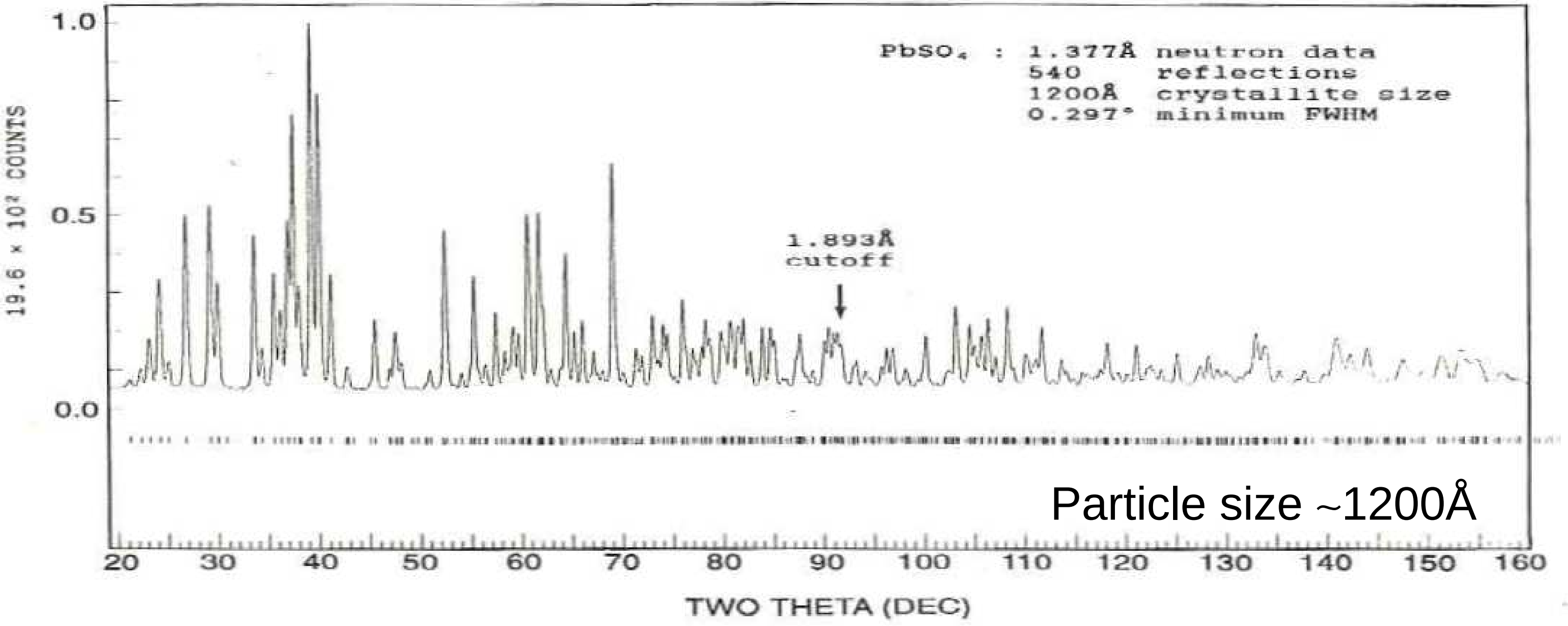
$$B_c = \frac{k\,\lambda}{L\,Cos(\theta_B)}$$

- λ → Wavelength
- L → Average crystallite size
- k → 0.94 [k ∈ (0.89, 1.39)]
  ~ 1 *(the accuracy of the method is only 10%)*

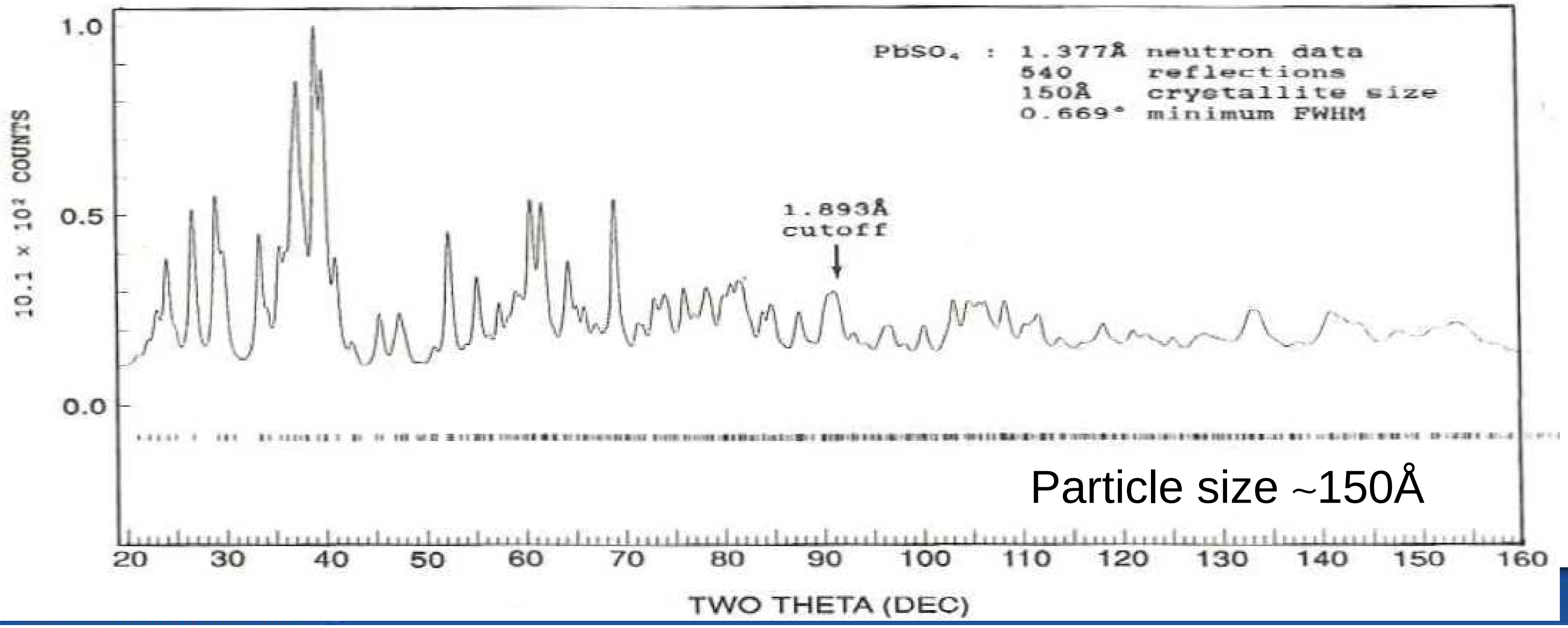


Powder Pattern and Structure





Particle size ~1200Å



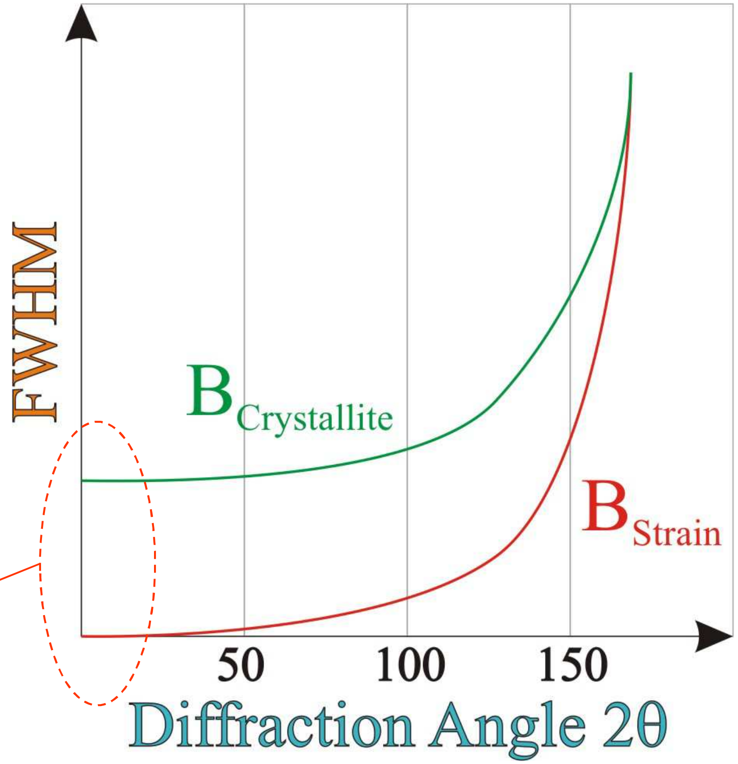
Particle size ~150Å

Powder Pattern and Structure

Strain broadening

$$B_s = \eta \quad Tan(\theta_B)$$

- η → Strain in the material



Smaller angle peaks should be used to separate B_s and B_c

Powder Pattern and Structure

Separating crystallite size broadening and strain broadening

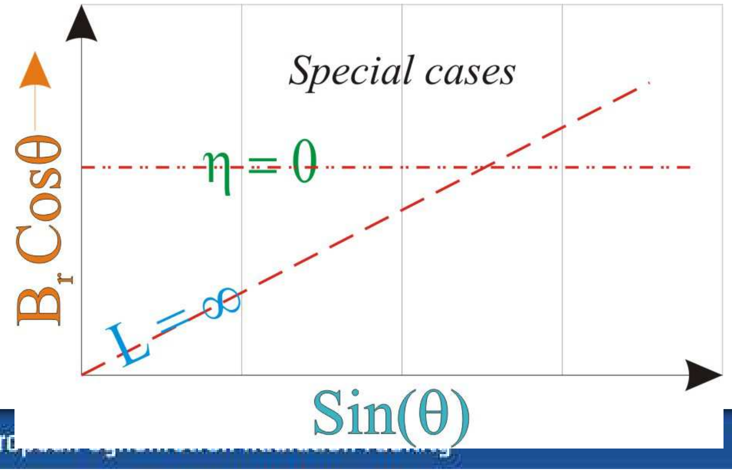
$$B_r = B_c + B_s$$

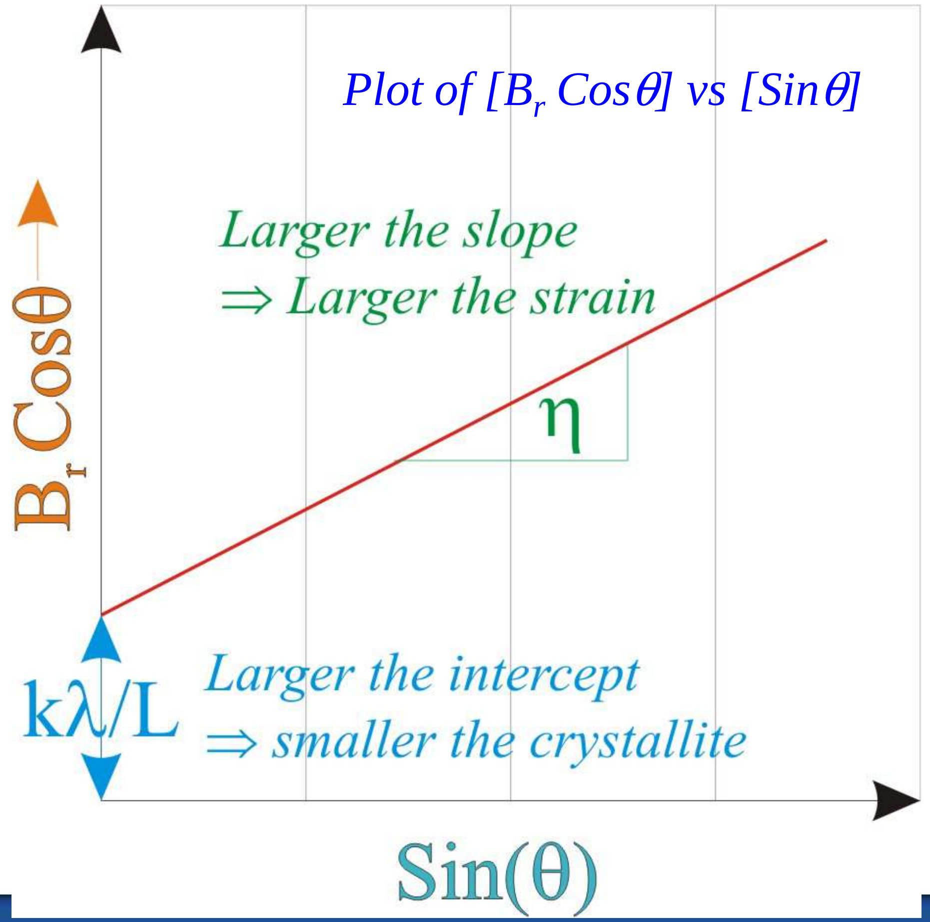
$$B_c = \frac{k\,\lambda}{L\,Cos(\theta)}$$

$$B_s = \eta\,Tan(\theta)$$

$$B_r = \frac{k\,\lambda}{L\,Cos(\theta)} + \eta\,Tan(\theta)$$

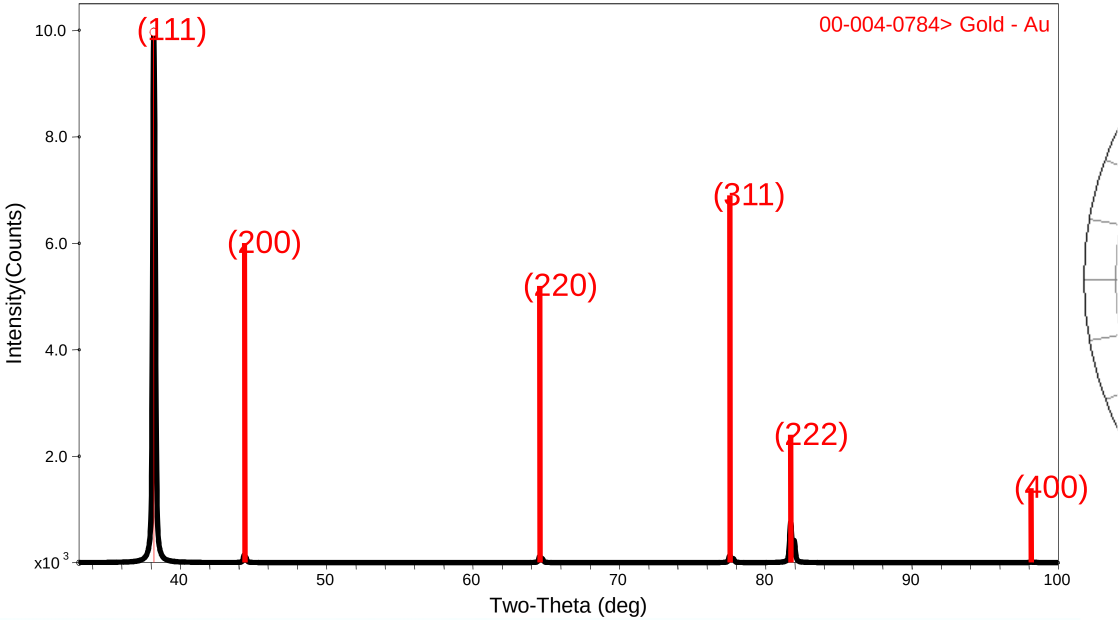
$$B_r\,Cos(\theta) = \frac{k\,\lambda}{L} + \eta\,Sin(\theta)$$

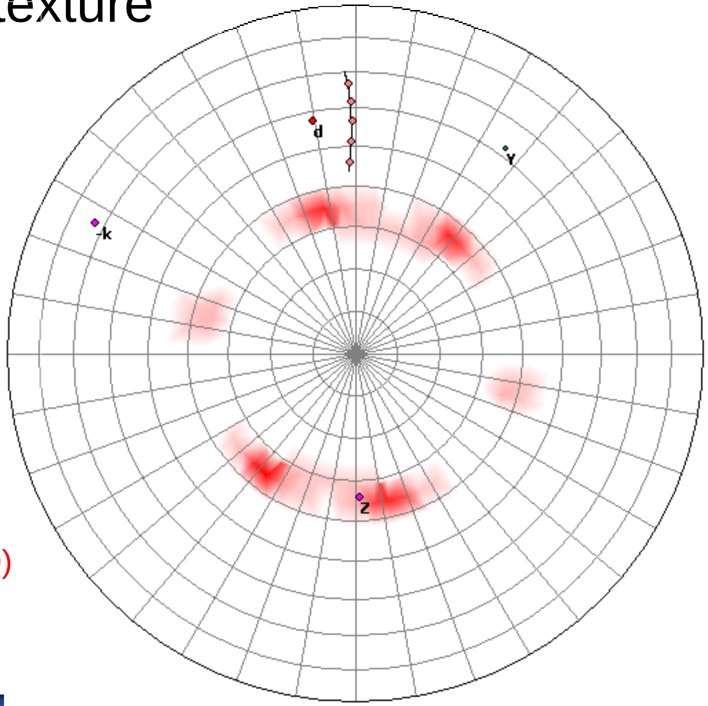


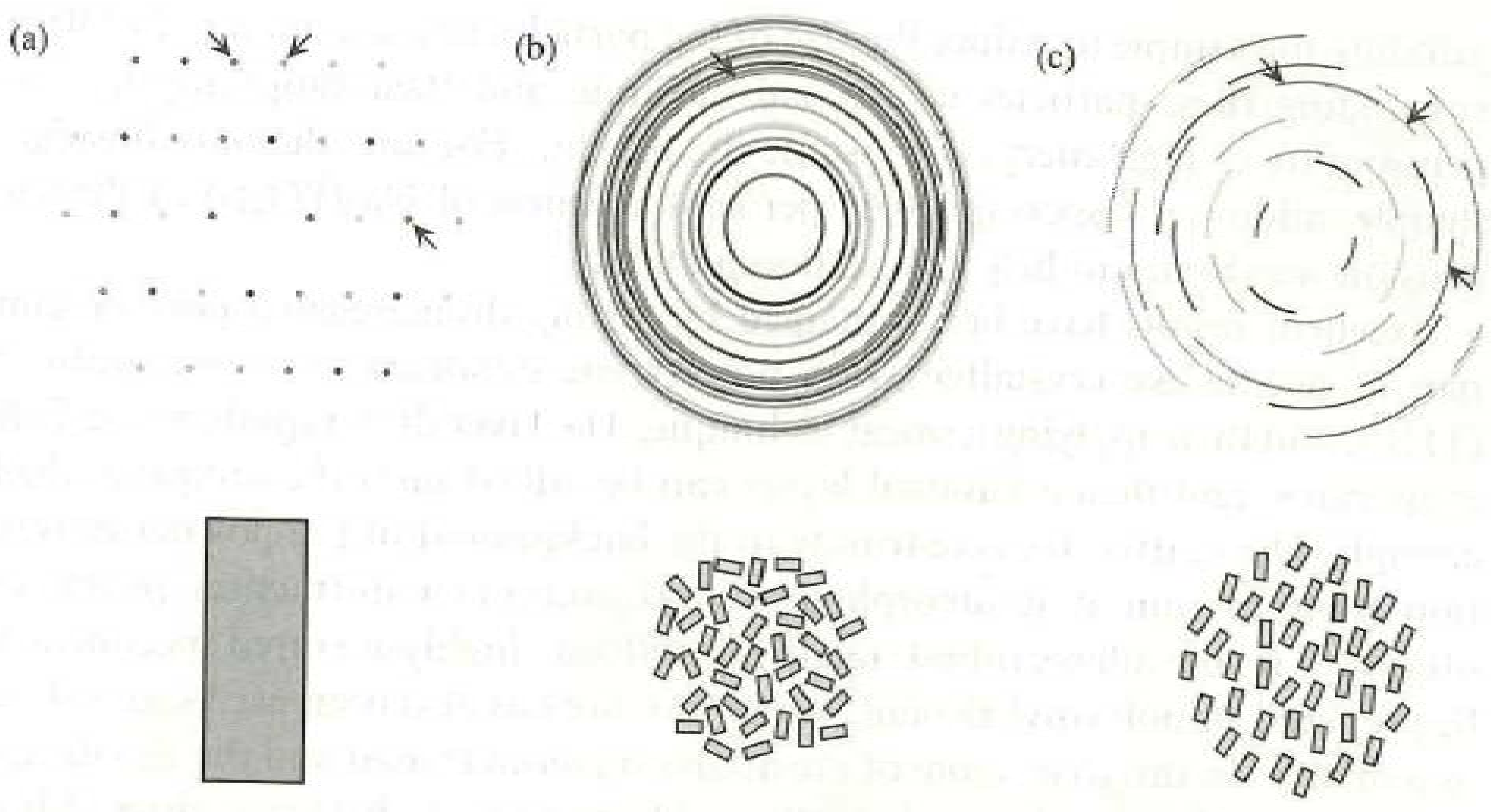


Preferred Orientation (texture)

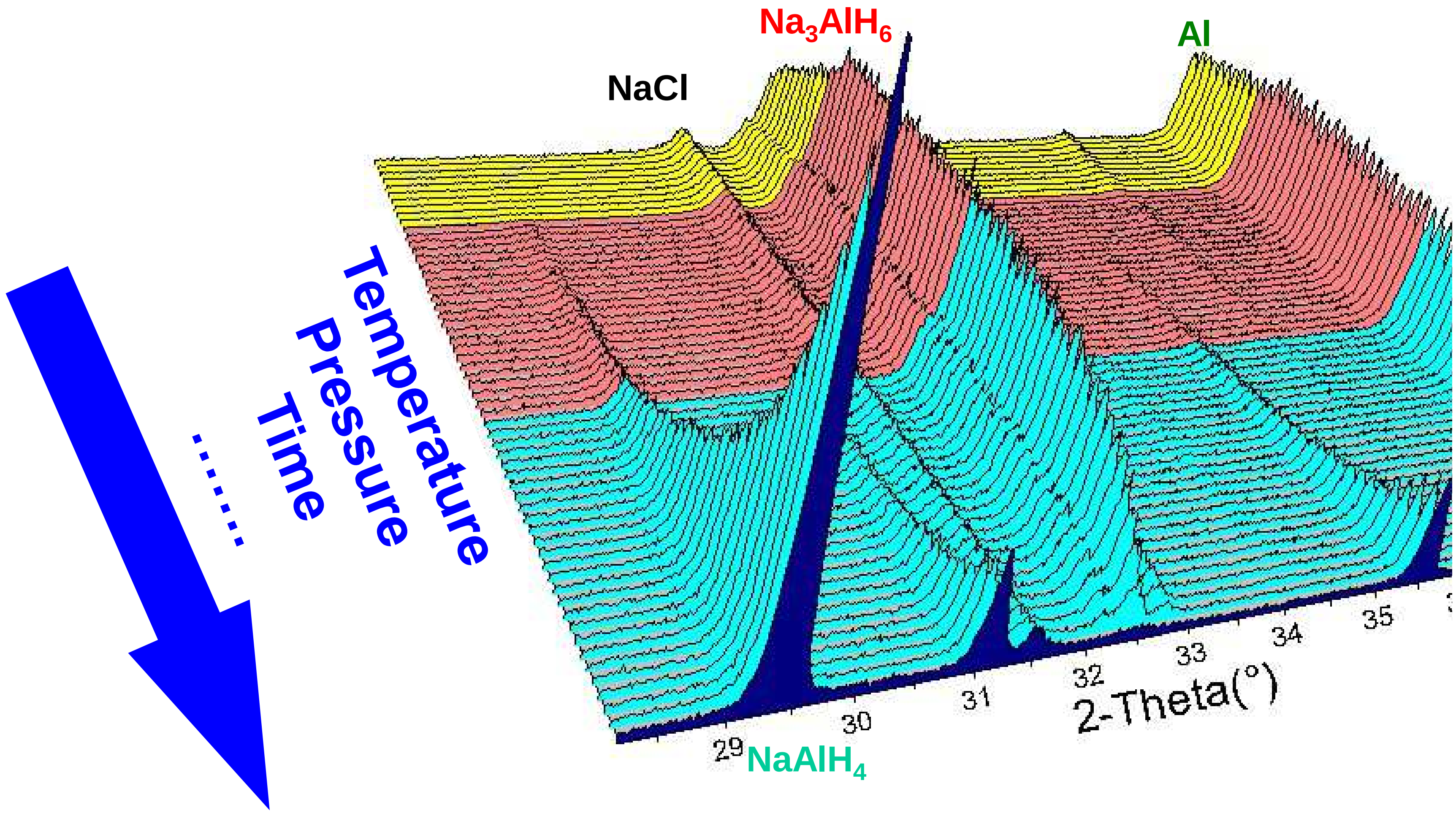
- Preferred orientation of crystallites can create a systematic variation in diffraction peak intensities
  - can qualitatively analyze using a 1D diffraction pattern
  - a pole figure maps the intensity of a single peak as a function of tilt and rotation of the sample
    - this can be used to quantify the texture





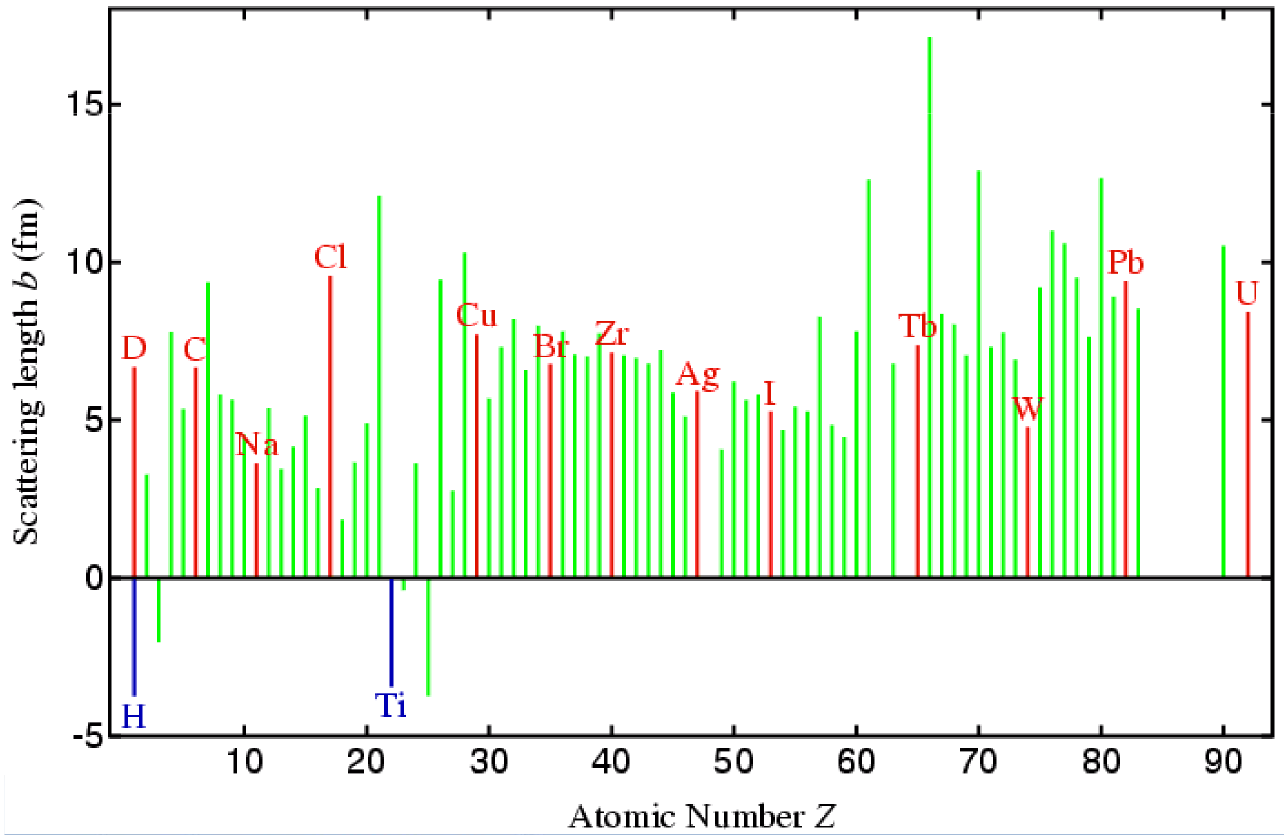

(a)
(b)
(c)

In-situ XRD can yield quantitative analysis to study reaction pathways, rate constants, activation energy, and phase stability



Not always X rays is the best tool, neutron are also very useful

- Resolution of X rays instruments is generally better
- Cheaper to produce X rays than neutrons
- Neutron cross section varies much less than with Z than X-rays, it is pseudo-random *(Atomic scattering factor f)*



Extremely usefull to “see” light elements and determine thermal parameters

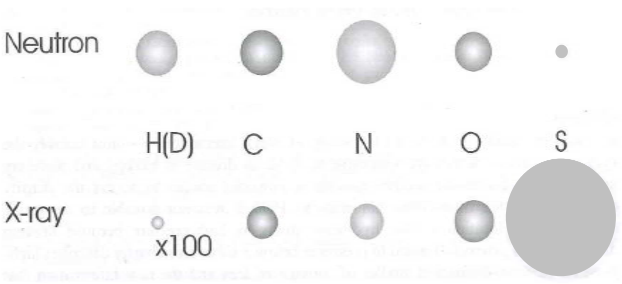


Figure 1: Neutron and x-ray cross-sections for elements found in ices [2]

Not always X rays is the best tool, neutron are also very useful

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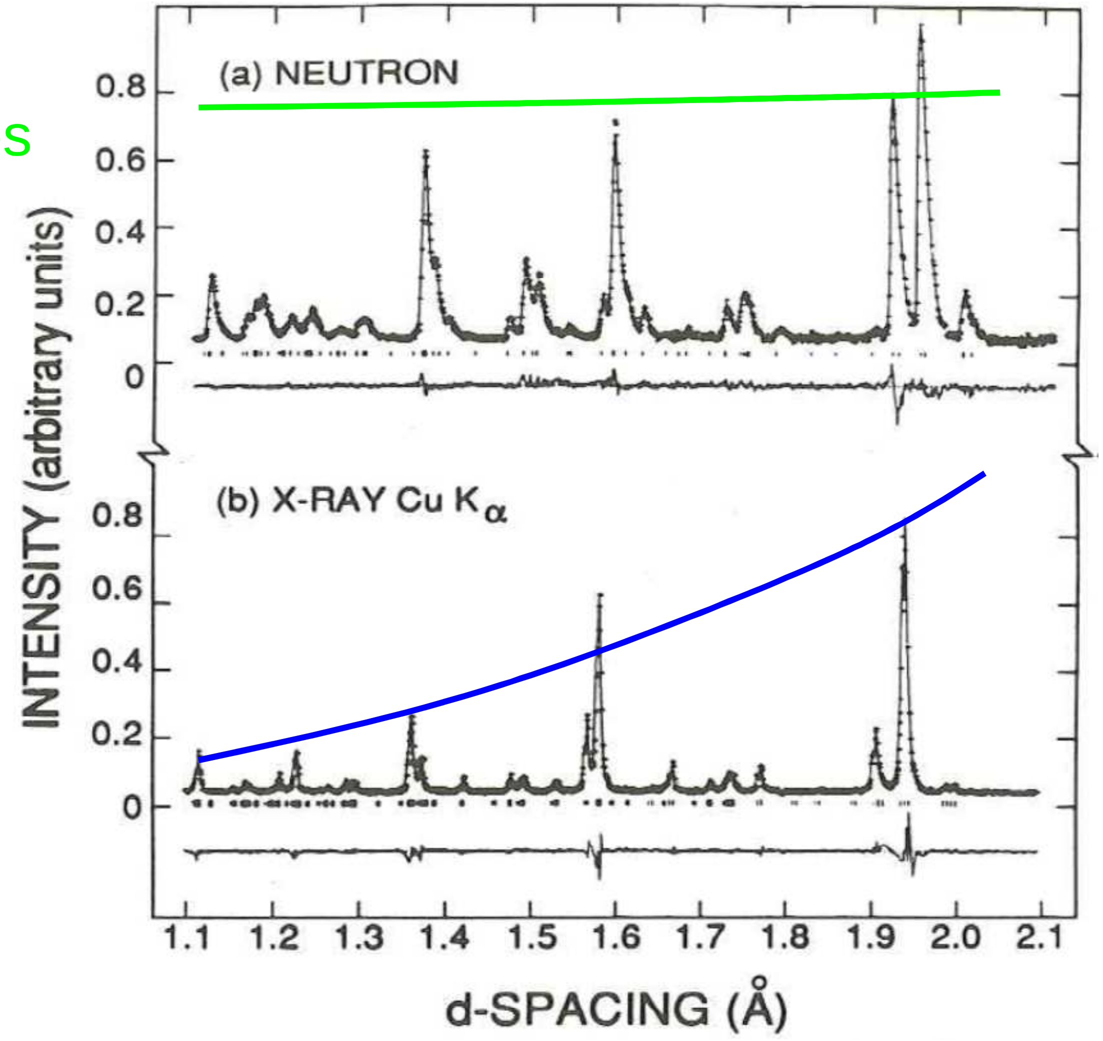
- Neutron scatters from the nucleus

(X ray from e^- cloud surrounds nucleus)

so scattering is aprox constant with increasing 2θ.



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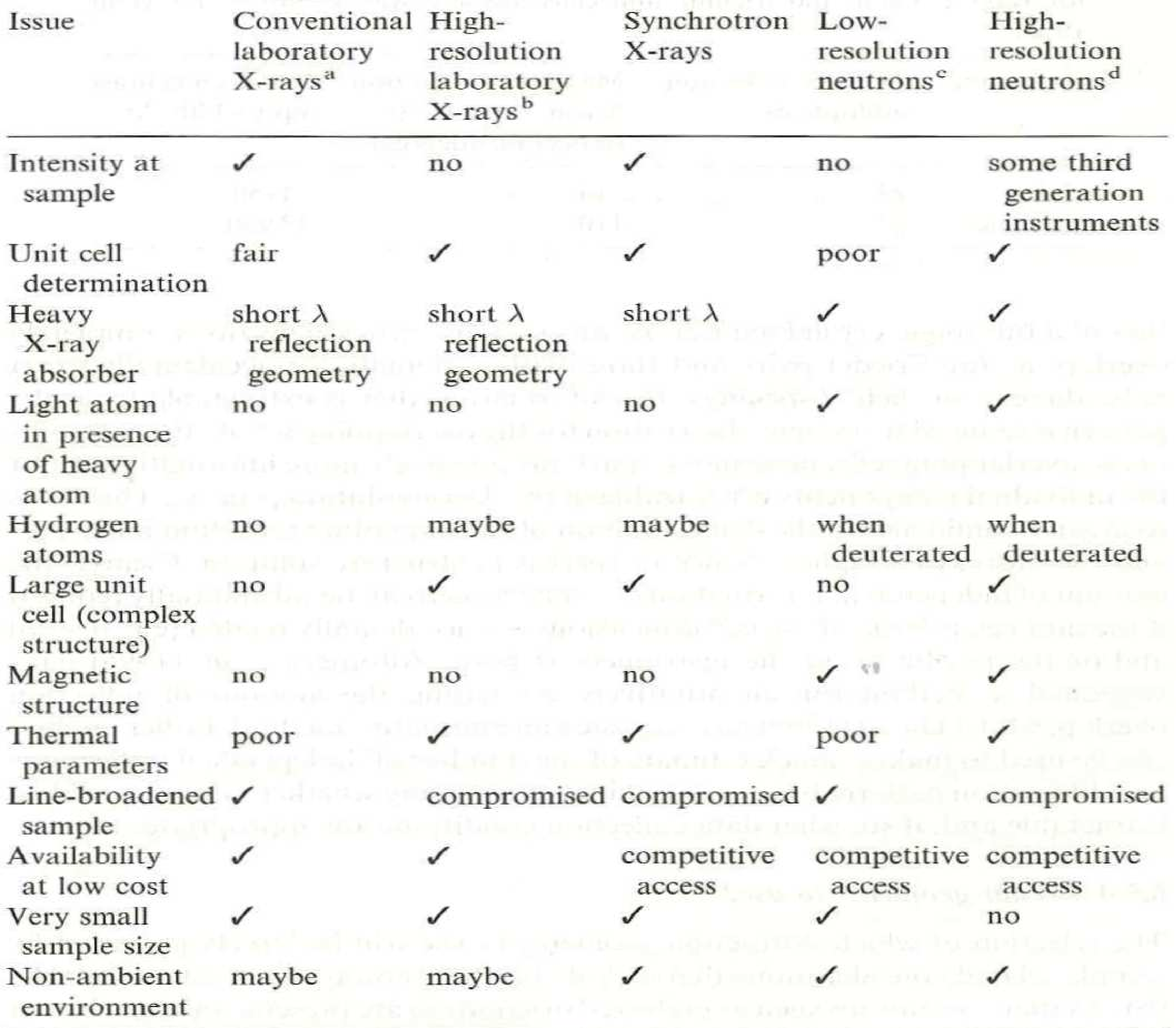
- The neutron is a particle with a spin of one-half. It is the interaction of this spin with the spin state of the nucleus of an atom that determines the scattering property of a neutron with that atom. So we can use this property to analyze magnetic structure.



Issue	Conventional laboratory X-rays[a]	High-resolution laboratory X-rays[b]	Synchrotron X-rays	Low-resolution neutrons[c]	High-resolution neutrons[d]
Intensity at sample	✓	no	✓	no	some third generation instruments
Unit cell determination	fair	✓	✓	poor	✓
Heavy X-ray absorber	short λ reflection geometry	short λ reflection geometry	short λ	✓	✓
Light atom in presence of heavy atom	no	no	no	✓	✓
Hydrogen atoms	no	maybe	maybe	when deuterated	when deuterated
Large unit cell (complex structure)	no	✓	✓	no	✓
Magnetic structure	no	no	no	✓	✓
Thermal parameters	poor	✓	✓	poor	✓
Line-broadened sample	✓	compromised	compromised	✓	compromised
Availability at low cost	✓	✓	competitive access	competitive access	competitive access
Very small sample size	✓	✓	✓	✓	no
Non-ambient environment	maybe	maybe	✓	✓	✓

Thank you
for your attention

References

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B.D. Cullity & S.R. Stock, Prentice Hall, Upper Saddle River (2001)

X-Ray Diffraction: A Practical Approach
C. Suryanarayana & M. Grant Norton, Plenum Press, New York (1998)

Structure determination from powder diffraction data
W.David, K.Shanklnad, L.B.McCusker, Ch.Caerlocher, Oxford Univ. Press. (2002)

For comments, suggestions, support request etc…

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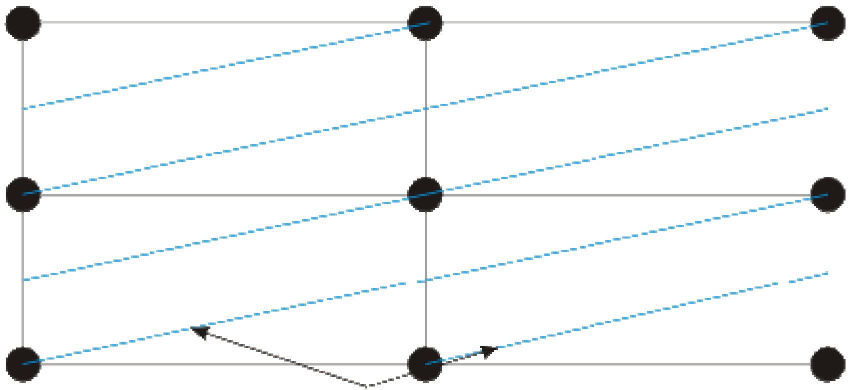
address: European Synchrotron Radiation Facility (ESRF)
6 Rue Jules Horowitz, 38043, Grenoble, France

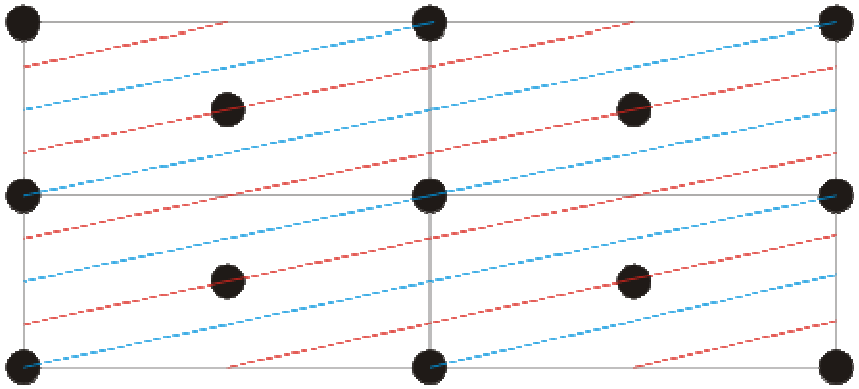
Powder Pattern and Structure

Simple Orthorhombic lattice [001] projection



These (210) planes form a translationally equivalent set: pass through all lattice points

C-Centred Orthorhombic lattice [001] projection

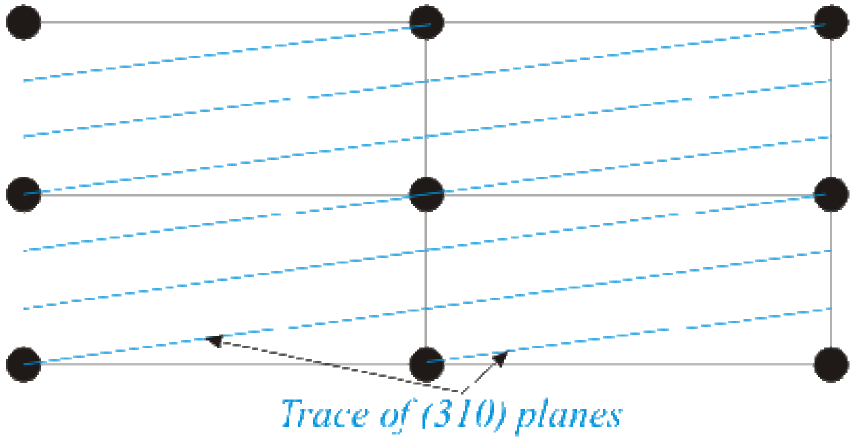


To form a translationally equivalent set of planes (passing through all lattice points) the red set of planes have to be drawn

- If the blue planes are scattering in phase then on C- centering the red planes will scatter out of phase (with the blue planes- as they bisect them) and hence the (210) reflection will become extinct
- This analysis is consistent with the extinction rules: (h + k) odd is absent

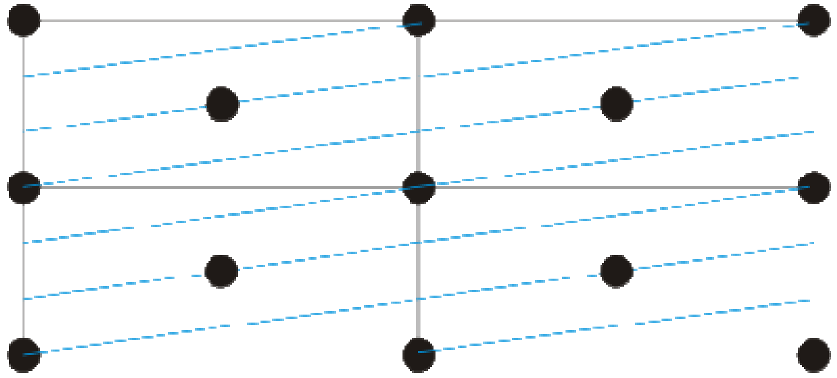
Powder Pattern and Structure

Simple Orthorhombic lattice [001] projection



These (310) planes form a translationally equivalent set: pass through all lattice points

C-Centred Orthorhombic lattice [001] projection



No new planes are to be added to form a translationally equivalent set of planes on C-centering

- In case of the (310) planes no new translationally equivalent planes are added on lattice centering ⇒ this reflection cannot go missing.
- This analysis is consistent with the extinction rules: (h + k) even is present

Powder Pattern and Structure

Body centred Orthorhombic

C

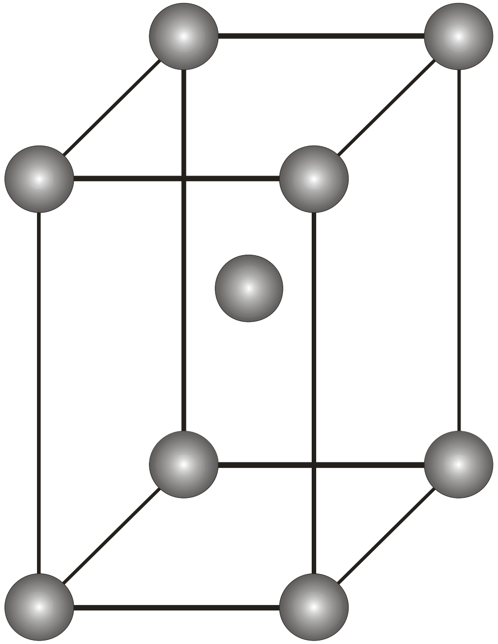
Atom at (0,0,0) & (½, ½, ½) and equivalent positions

$$F = f_j \quad e^{i\varphi_j} = f_j \quad e^{i[2\pi(h\, x'_j + k\, y'_j + l\, z'_j)]}$$

$$F = f \quad e^{i[2\pi(h\cdot 0 + k\cdot 0 + l\cdot 0)]} + f \quad e^{i[2\pi(h\cdot\frac{1}{2} + k\cdot\frac{1}{2} + l\cdot\frac{1}{2})]}$$

$$= f\, e^0 + f\, e^{i[\cancel{2}\pi(\frac{h+k+l}{\cancel{2}})]} = f[1 + e^{i\pi(h+k+l)}]$$

Real



$$F = f[1 + e^{i\pi(h+k+l)}] \xrightarrow{(\mathrm{h}+\mathrm{k}+\mathrm{l})\ \text{even}} F = 2f \longrightarrow F^2 = 4f^2$$

e.g. (110), (200), (211); (220), (022), (310)

$$F = f[1 + e^{i\pi(h+k+l)}] \xrightarrow{(\mathrm{h}+\mathrm{k}+\mathrm{l})\ \text{odd}} F = 0 \longrightarrow F^2 = 0$$

e.g. (100), (001), (111); (210), (032), (133)

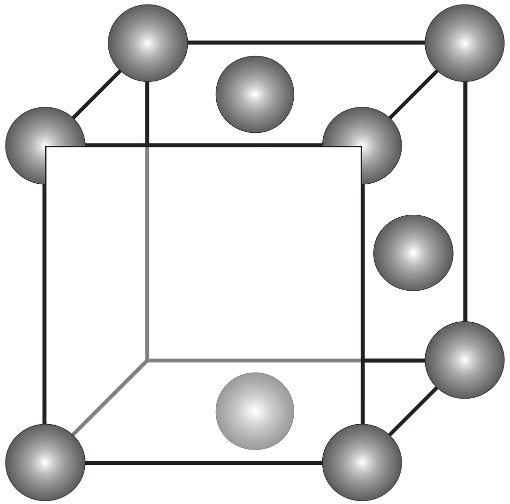
Powder Pattern and Structure

D

Atom at (0,0,0) & (½, ½, 0) and equivalent positions

Face Centred Cubic

(½, ½, 0), (½, 0, ½), (0, ½, ½)



$$F = f_j \quad e^{i\varphi_j} = f_j \quad e^{i[2\pi(h\,x'_j + k\,y'_j + l\,z'_j)]}$$

$$F = f\left[e^{i[2\pi(0)]} + e^{i[2\pi(\frac{h+k}{2})]} + e^{i[2\pi(\frac{k+l}{2})]} + e^{i[2\pi(\frac{l+h}{2})]}\right]$$

$$= f[1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}]$$

Real

$$F = f[1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}]$$

(h, k, l) unmixed → $F = 4f$ → $F^2 = 16f^2$

e.g. (111), (200), (220), (333), (420)

(h, k, l) mixed → $F = 0$ → $F^2 = 0$ *e.g. (100), (211); (210), (032), (033)*

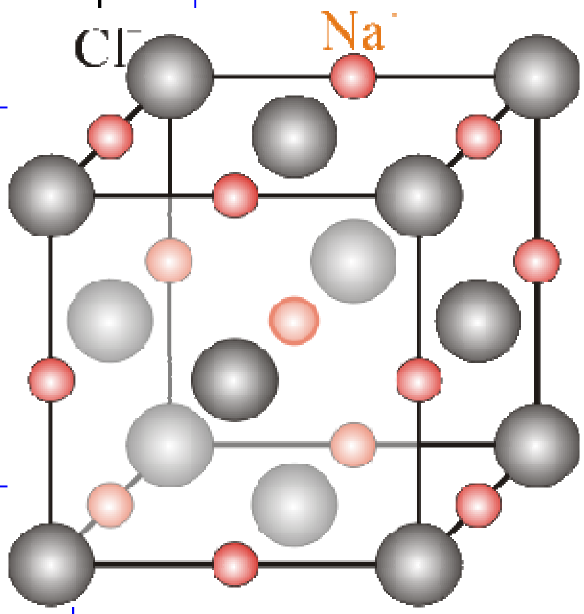
Two odd and one even (e.g. 112); two even and one odd (e.g. 122)

Na^+ at (0,0,0) + Face Centering Translations → *(½, ½, 0), (½, 0, ½), (0, ½, ½)*
Cl^- at (½, 0, 0) + FCT → *(0, ½, 0), (0, 0, ½), (½, ½, ½)*

NaCl:
Face Centred Cubic

$$F = f_{Na^+}\left[e^{i[2\pi(0)]} + e^{i[2\pi(\frac{h+k}{2})]} + e^{i[2\pi(\frac{k+l}{2})]} + e^{i[2\pi(\frac{l+h}{2})]}\right] +$$
$$f_{Cl^-}\left[e^{i[2\pi(\frac{h}{2})]} + e^{i[2\pi(\frac{k}{2})]} + e^{i[2\pi(\frac{l}{2})]} + e^{i[2\pi(\frac{h+k+l}{2})]}\right]$$

$$F = f_{Na^+}[1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}] +$$
$$f_{Cl^-}[e^{i\pi(h)} + e^{i\pi(k)} + e^{i\pi(l)} + e^{i\pi(h+k+l)}]$$



$$F = f_{Na^+}[1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}] +$$
$$f_{Cl^-}\ e^{i\pi(h+k+l)}[e^{i\pi(-k-l)} + e^{i\pi(-l-h)} + e^{i\pi(-h-k)} + 1]$$

$$F = [f_{Na^+} + f_{Cl^-}\ e^{i\pi(h+k+l)}][1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}]$$

Powder Pattern and Structure

$$F = [\, f_{Na^+} + f_{Cl^-}\, e^{i\pi(h+k+l)}][1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}]$$

$$F = [Term-1][Term-2]$$

Zero for mixed indices

Mixed indices

Mixed indices	CASE	h	k	l
	A	o	o	e
	B	o	e	e

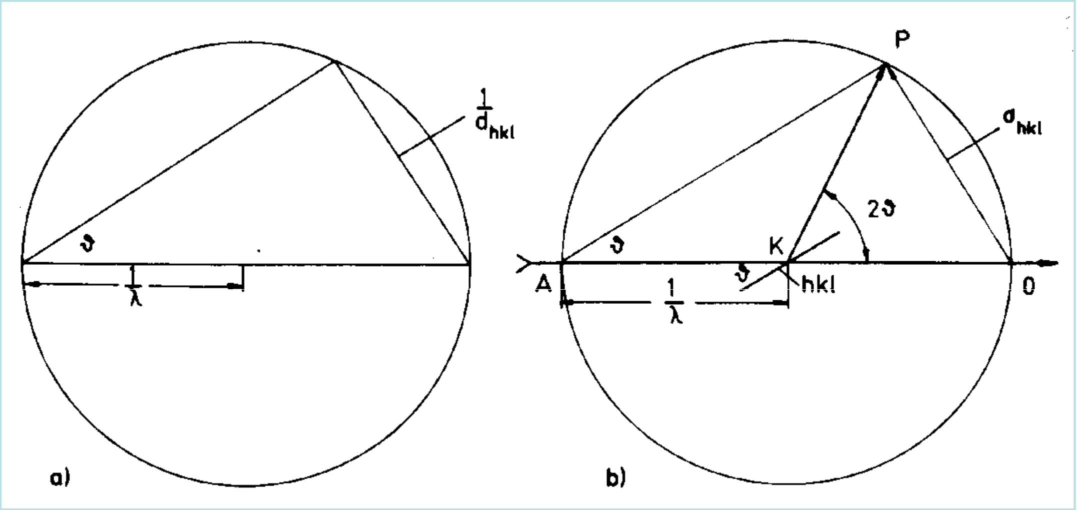
$$\text{CASE A}: Term-2 = [1 + e^{i\pi(e)} + e^{i\pi(o)} + e^{i\pi(o)}] = [1+1-1-1] = 0$$

$$\text{CASE B}: Term-2 = [1 + e^{i\pi(o)} + e^{i\pi(e)} + e^{i\pi(o)}] = [1-1+1-1] = 0$$

(h, k, l) mixed → $F = 0$ → $F^2 = 0$ *e.g. (100), (211); (210), (032), (033)*

Anode	(kV)	Wavelength λ (Å)	Filter
Mo	20,0	Kα1 : 0,70926 Kα2 : 0,71354 Kβ1 : 0,63225	Zr 0,08mm
Cu	9,0	Kα1 : 1,5405 Kα2 : 1,54434 Kβ1 : 1,39217	Ni 0,015mm
Co	7,7	Kα1 : 1,78890 Kα2 : 1,79279 Kβ1 : 1,62073	Fe 0,012mm
Fe	7,1	Kα1 : 1,93597 Kα2 : 1,93991 Kβ1 : 1,75654	Mn 0,011mm

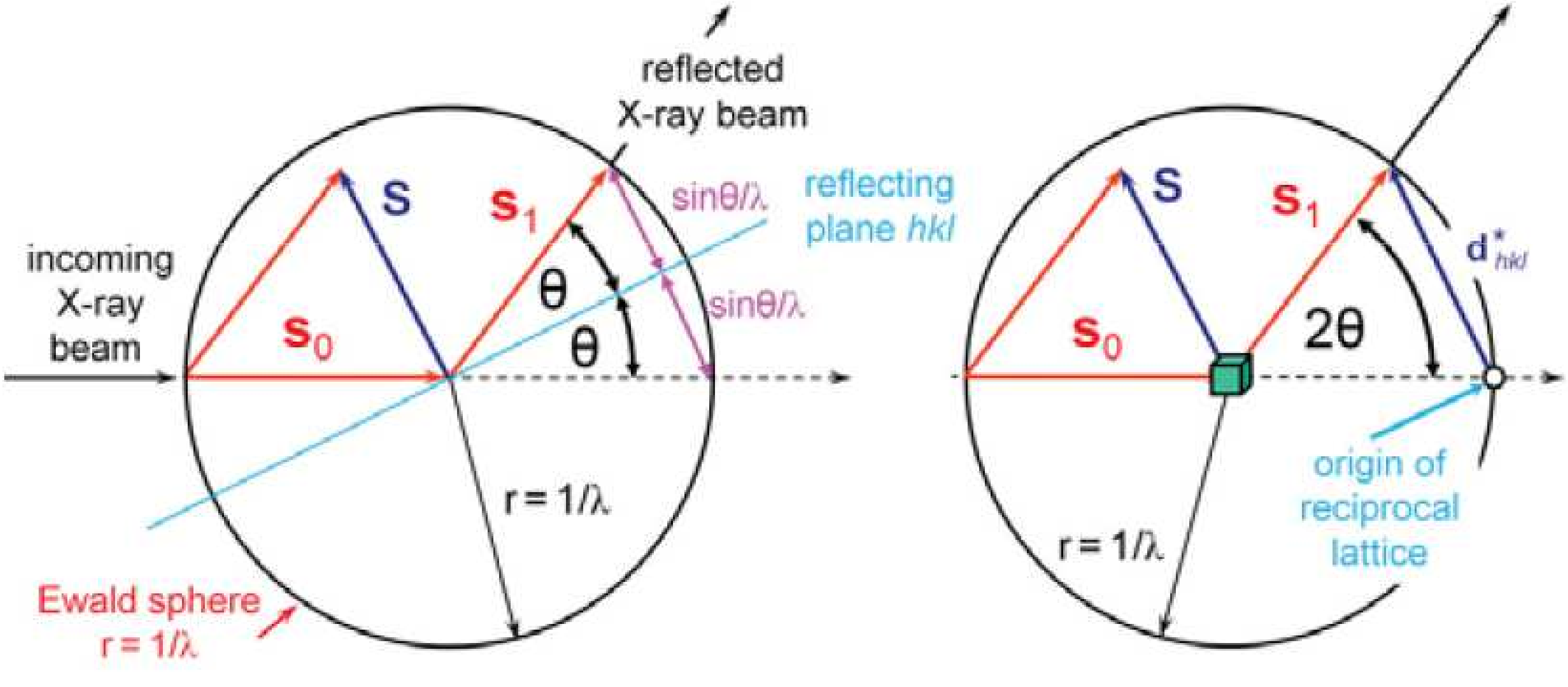
History (5): P. P. Ewald

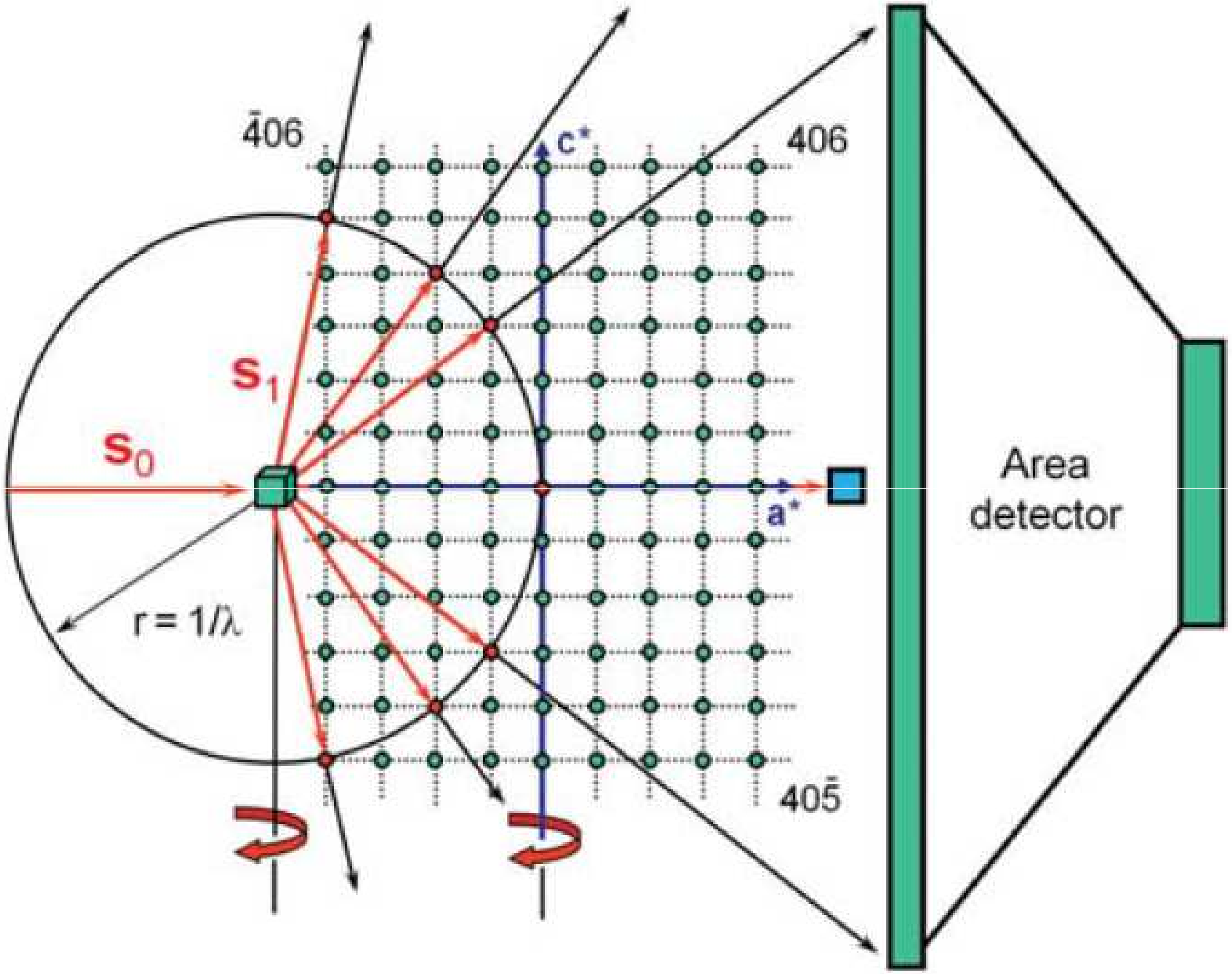


P. P. Ewald 1916 published a simple and more elegant theory of X-ray diffraction by introducing the reciprocal lattice concept. Compare Bragg's law (left), modified Bragg's law (middle) and Ewald's law (right).

$$d = \frac{n \cdot \lambda}{2 \cdot \sin\theta} \qquad \sin\theta = \frac{1/d}{2/\lambda} \qquad \sin\theta = \frac{\sigma}{2 \cdot 1/\lambda}$$

The Ewald sphere




$\bar{4}06$
406
c*
s_1
s_0
a*
r = 1/λ
$40\bar{5}$
Area detector