The use of XRD

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X-Ray Diffraction (XRD):

X-ray diffraction techniques are a family of non-destructive techniques which reveal information about the crystallographic structure, and physical properties of materials. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angles, or wavelength or energy.

X-Ray Diffraction (XRD) is a technique used to characterize the crystallographic structure, crystallite size (grain size), and **preferred orientation** in polycrystalline materials. XRD is commonly used to identify structure of unknown substances (phase analysis).

XRD is one of the most commonly used methods to determine the **residual stress state** in small crystalline volumes.

Hours of lessons:

25th may

26th may

27th may

Why using X-Ray ?

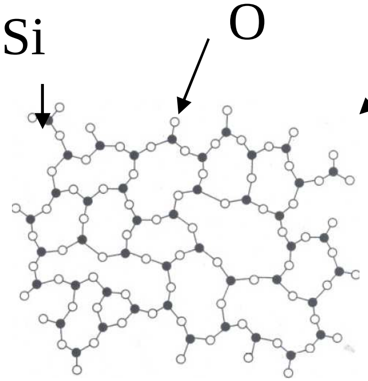
- **Optical :** refractive index, transparency, opacity
- **Mechanical :** strength, scratch
- **Commercial :** design

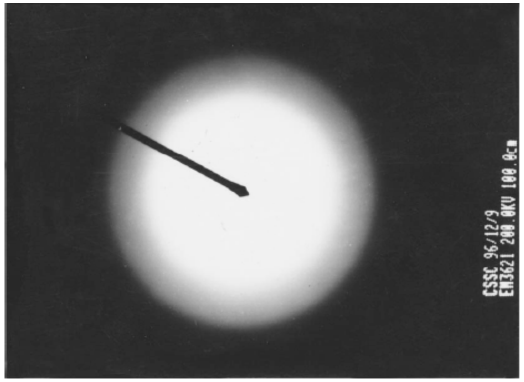
→Coatings or thin films for :

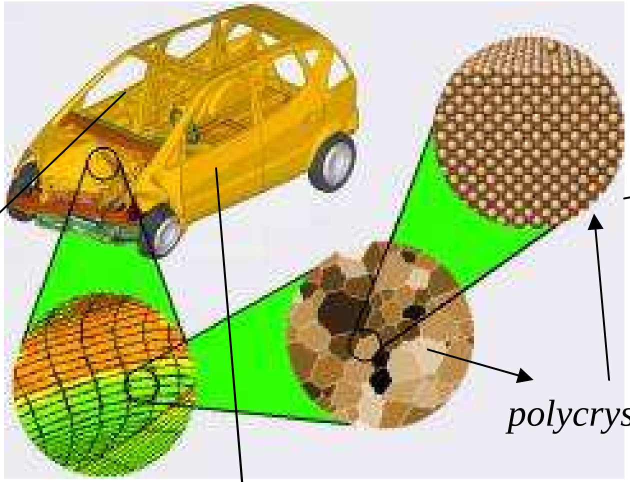
-Wear resistance (or scratch resistant)
-Protection from UV rays
-Hydrophobic (designed to ease cleaning)
-Anti-reflective (eyes more visible, reduces glare, ..)
-Color changes

Why using X-Ray ?

amorphous



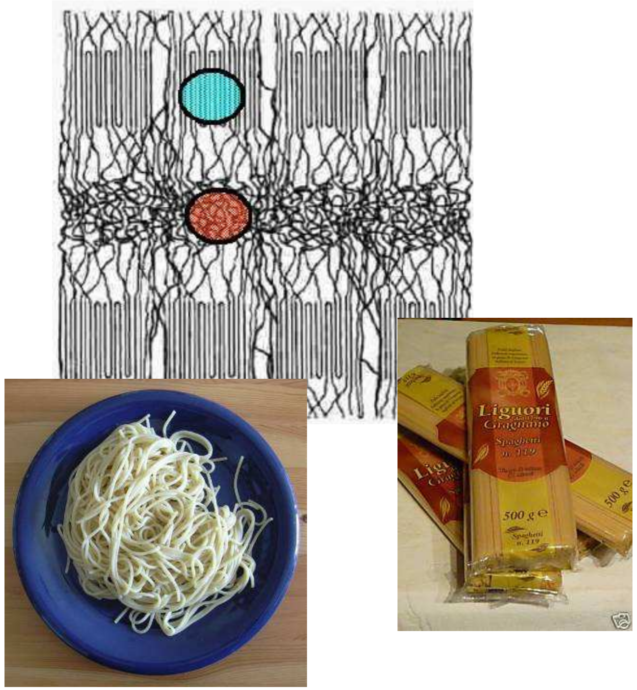


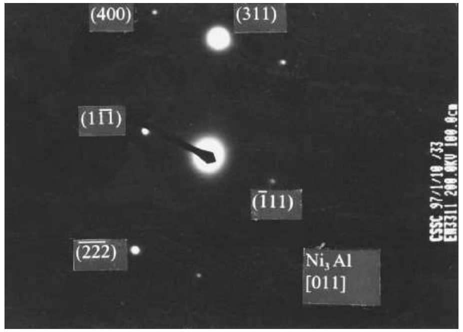


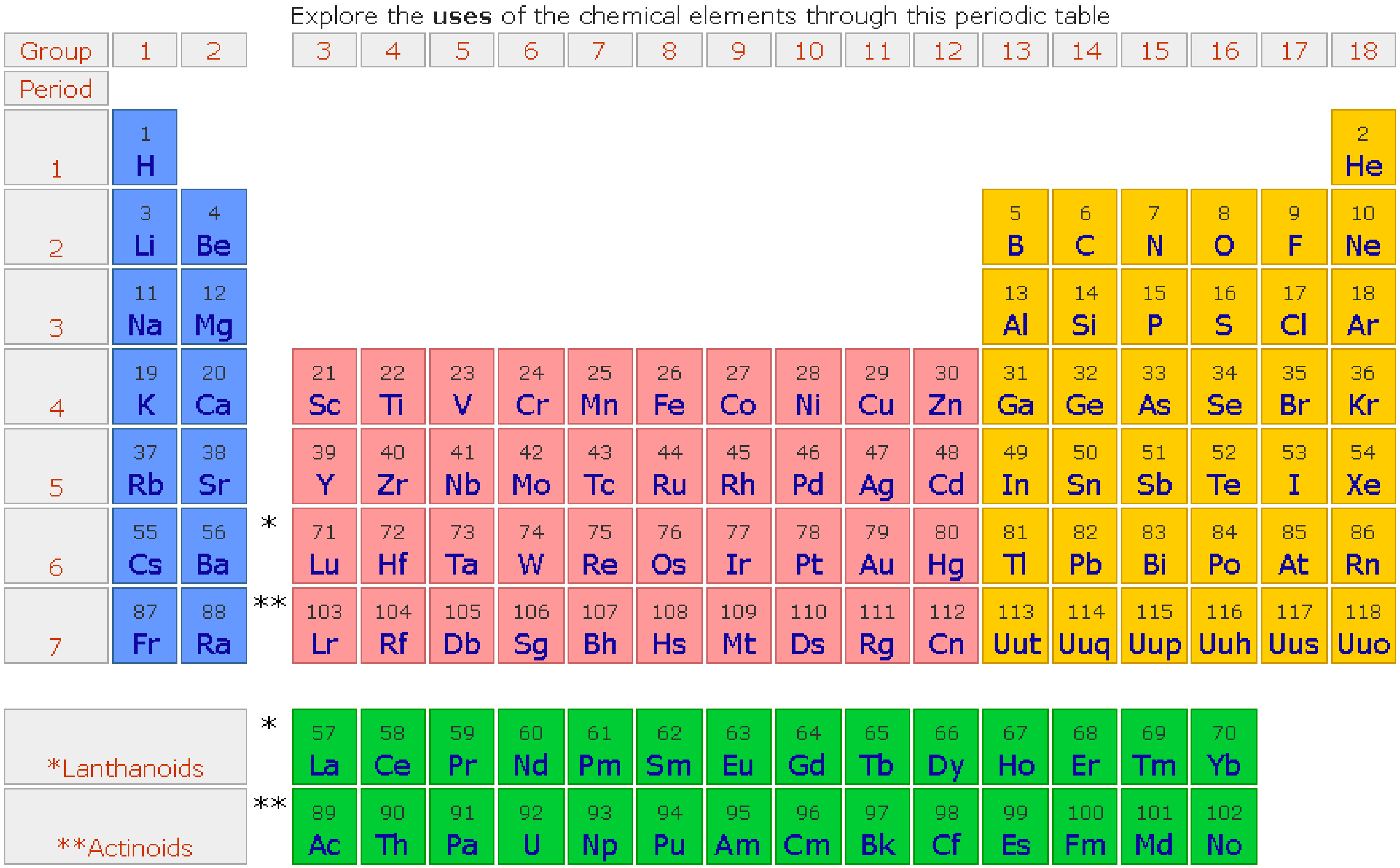
Single crystal

polycrystal

Mixture: amorphous + crystalline







Explore the **uses** of the chemical elements through this periodic table

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanoids			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
**Actinoids			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

http:\\Webelement.com

Properties of copper:

electrical properties:	range
mechanical properties	
elastic properties	E=120 GPa, v=0.345
plastic properties	
A%	range
flow stress	range
max stress	range
hardness	range

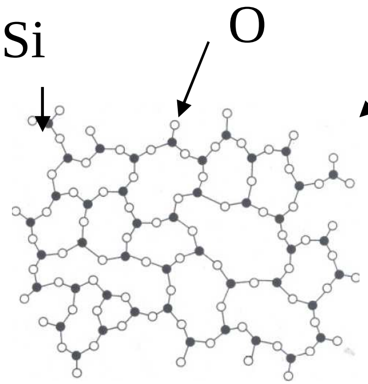
→Example of Annealed copper vs copper

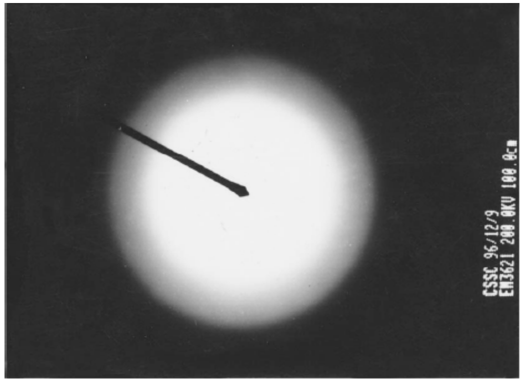
curved tube rigid straight tube

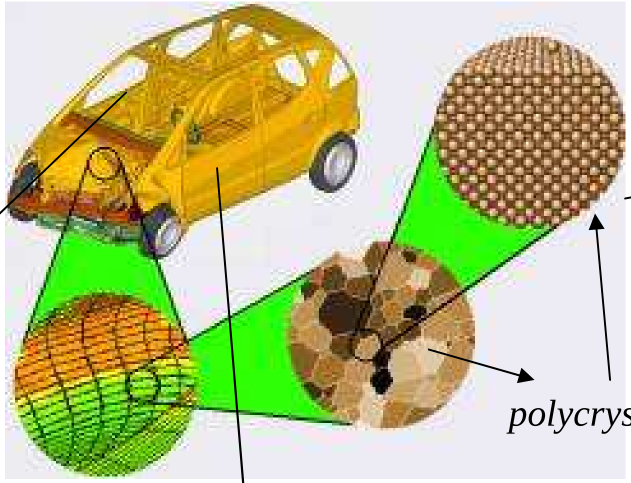
microstructure

Why using X-Ray ?

amorphous



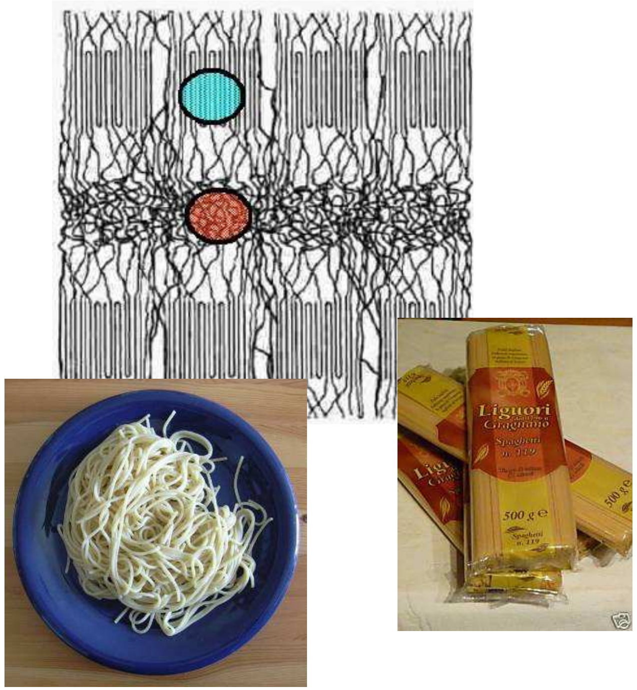


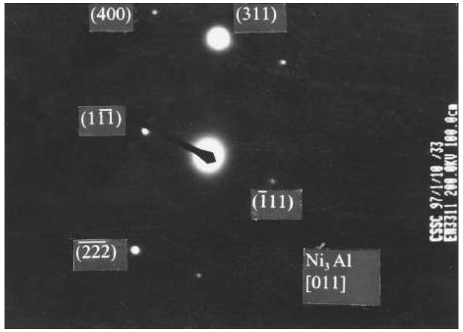


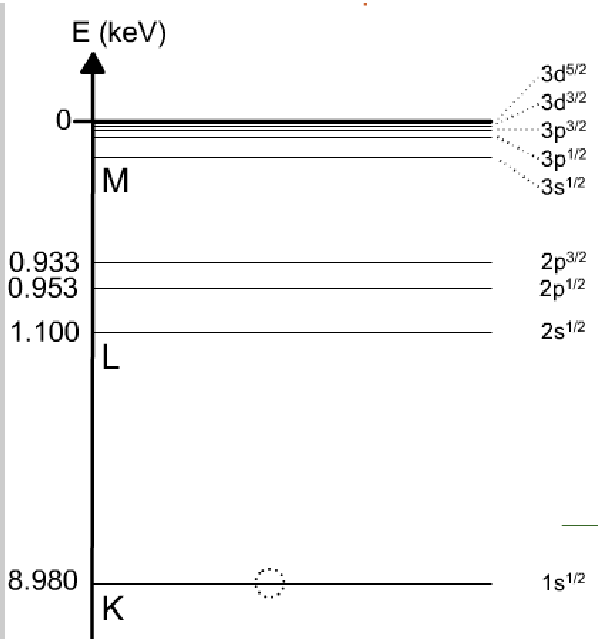
Single crystal

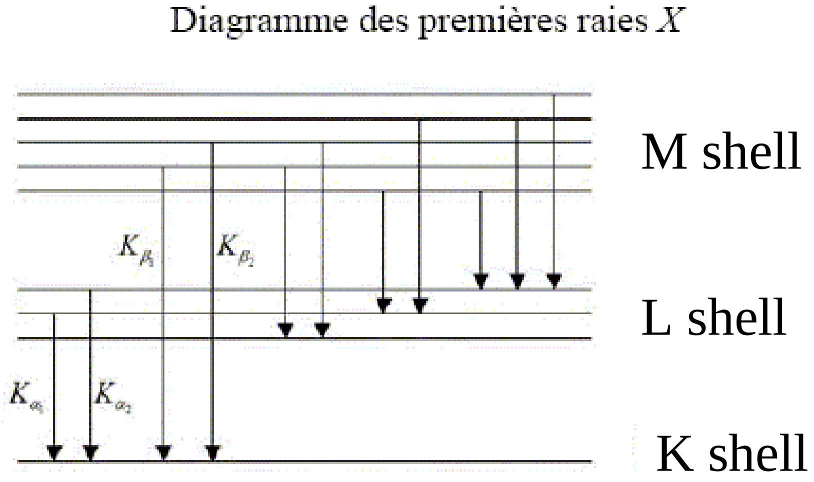
polycrystal

Mixture: amorphous + crystalline

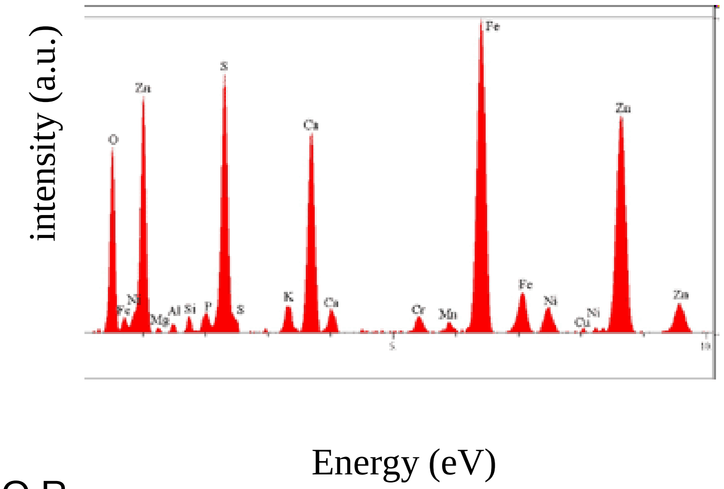


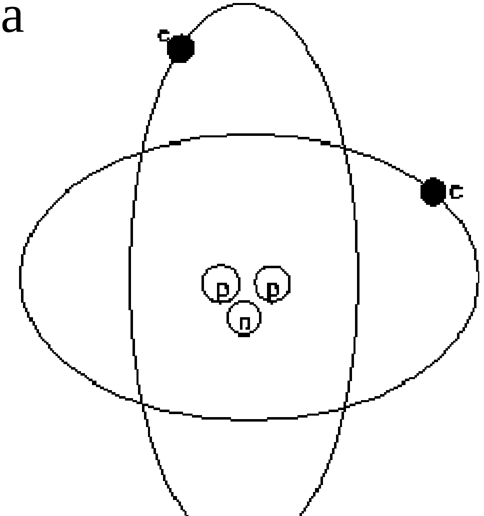






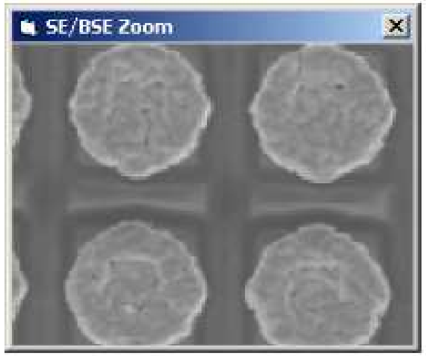
Fluorescence -Atomic spectra

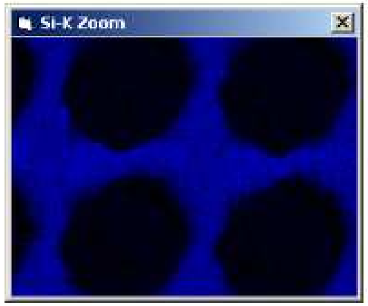


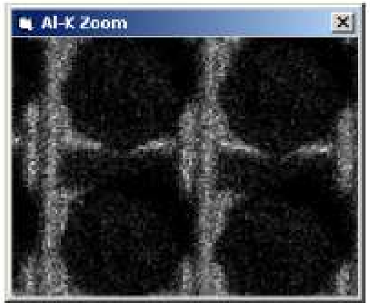


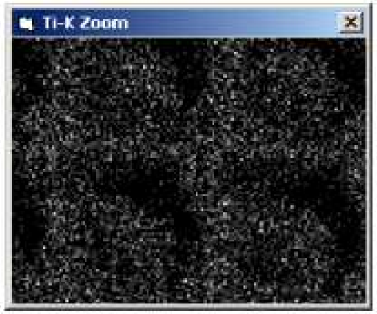
Planetary model of the atom

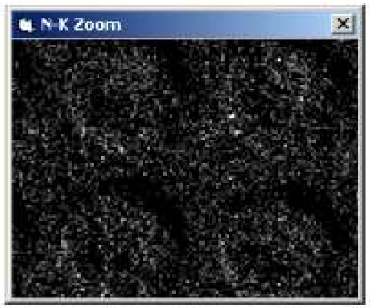
Scanning Electron Microsopy

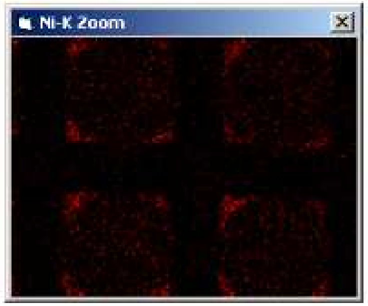


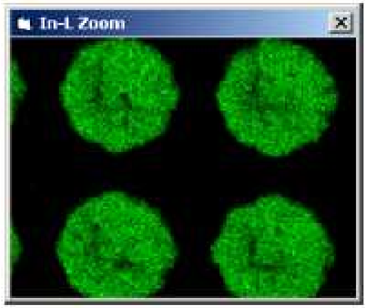


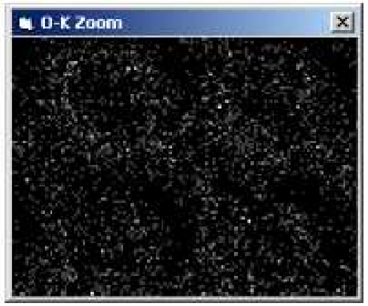


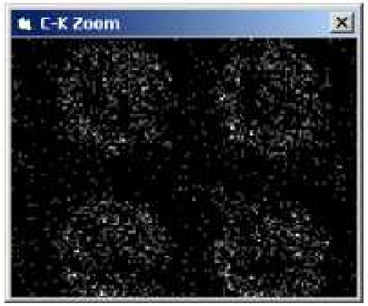








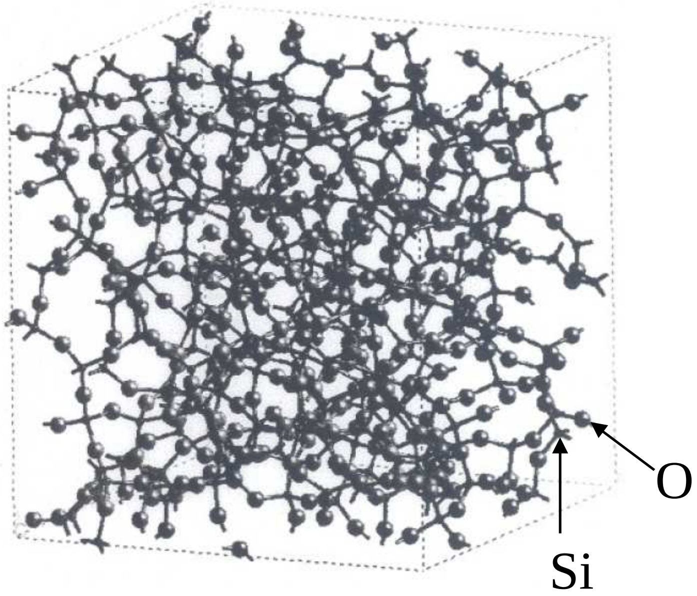




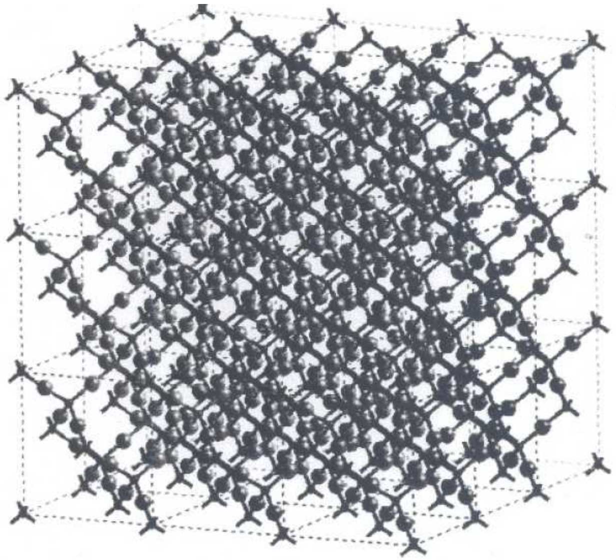
Glass: SiO2

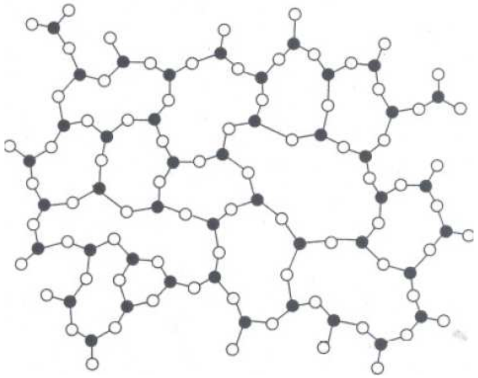
Amorphous silica

Crystalline SiO_2

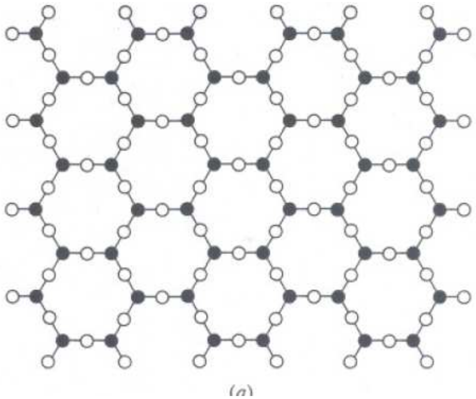


3D





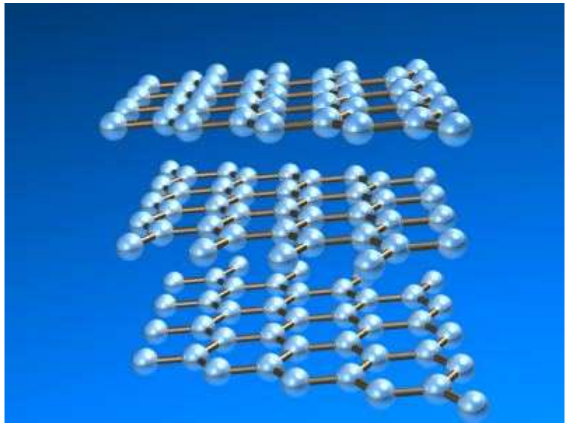
2D



To « see » how atoms are arranged ?

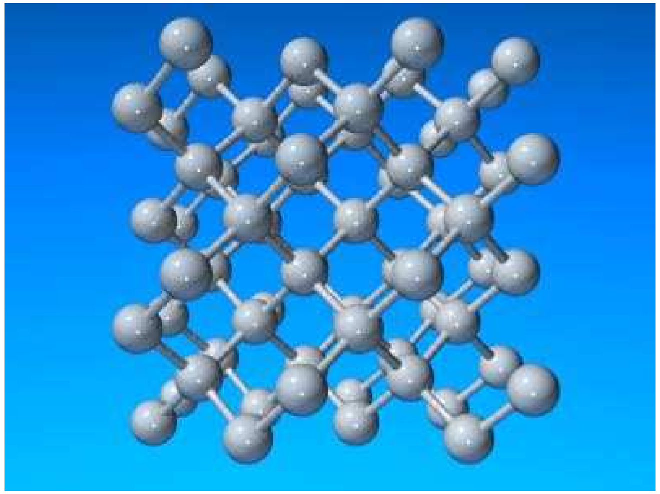
Carbon

graphite



hexagonal

diamond



cubic

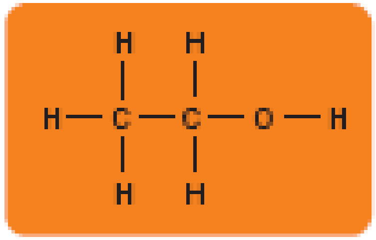
Same element BUT different arrangement, i.e. different crystalline structure

Black
opaque

No color
Transparent

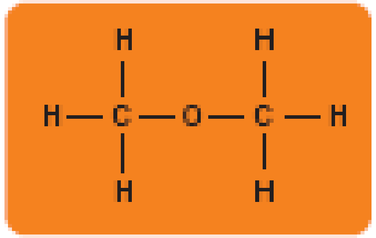
C, H, O

alcohol



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-H$$

Ether-oxide



$$H-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-H$$

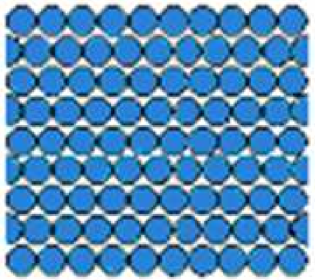
2C, 6 H, 1 O

Alcohol

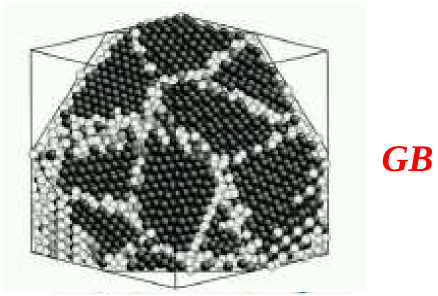
Ether-oxide

Same elements BUT different arrangement, i.e. different bindings

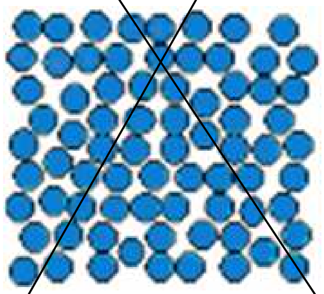
Single Crystal:
Periodic 3D repetition of unit cells to fill the entire volume

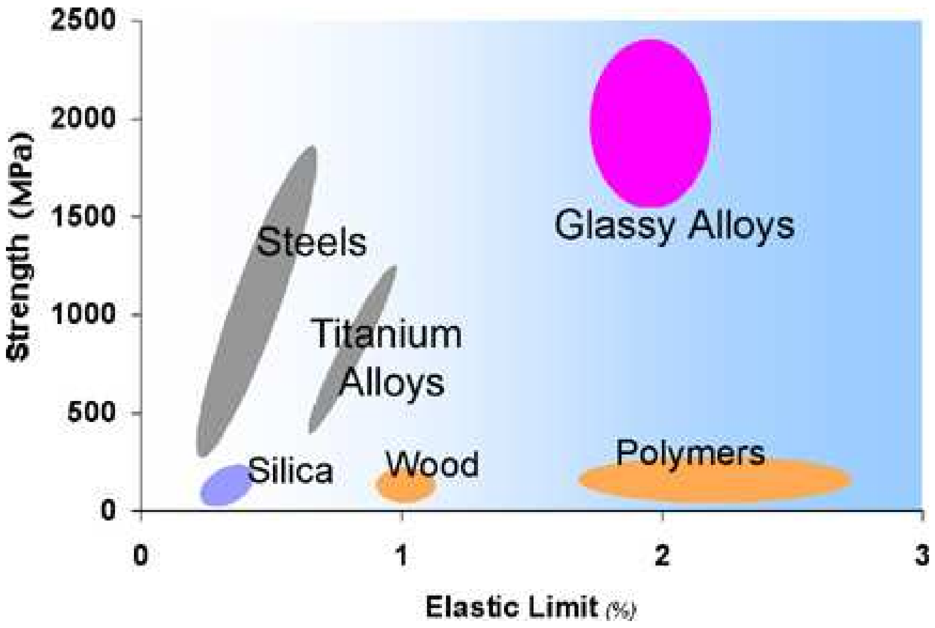


Polycrystal:
Constituted of grain with different orientations



~~*Amorphous:*~~
~~*Random distribution of atoms*~~



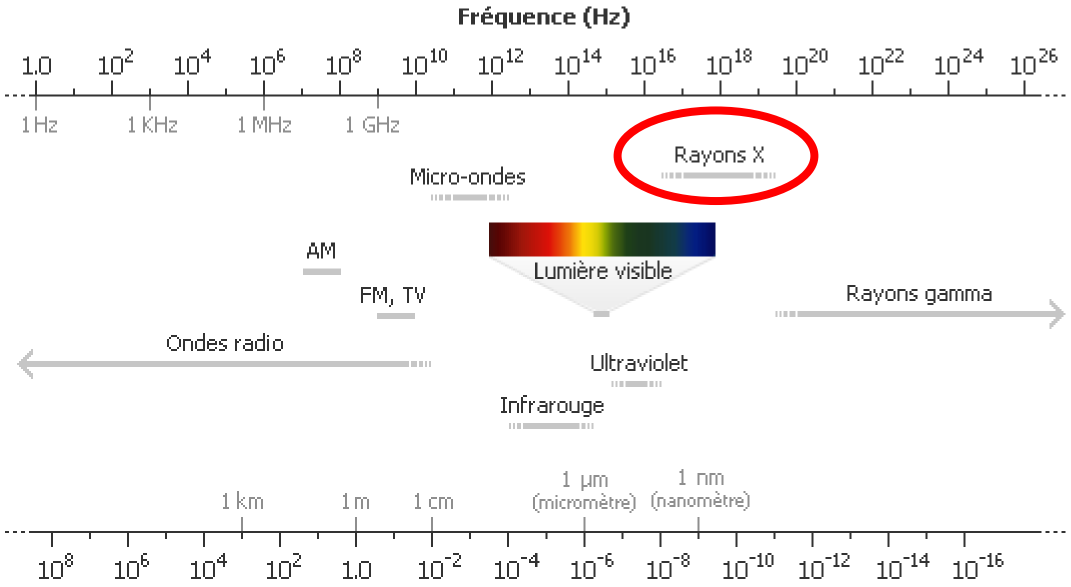


→High yield strength, fracture toughness

→High elastic strain limit (2%)

To study a given specimen:
- we have to « see » it or, in other words, to observe the photon interaction with the matter of the specimen.

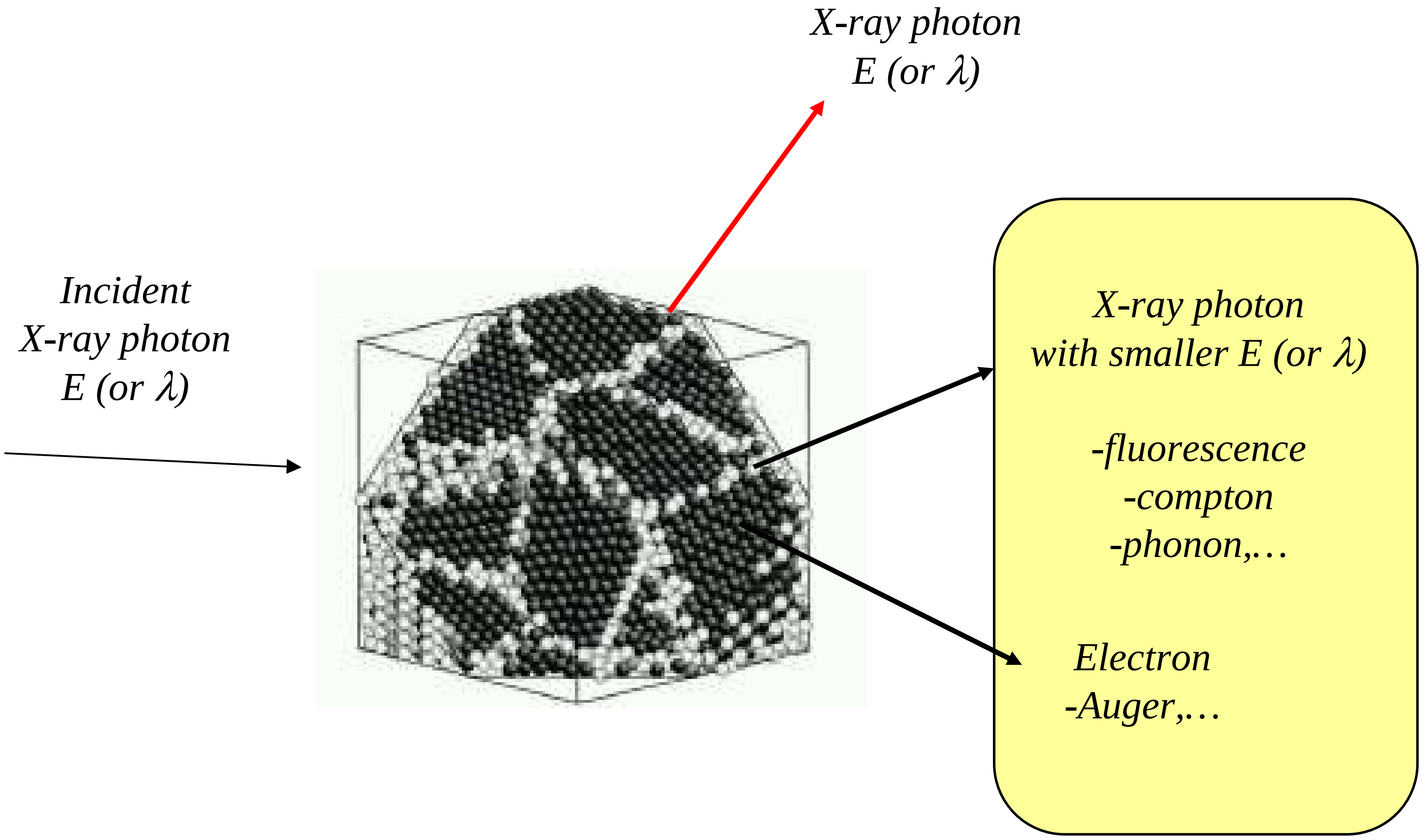
View of the spectrum of electromagnetic waves



Wavelength (m)

To study a given specimen:

- we may observe the x-ray photon interaction with the matter of the specimen.



Incident
X-ray photon
E (or λ)

X-ray photon
E (or λ)

X-ray photon
with smaller E (or λ)

-fluorescence
-compton
-phonon,…

Electron
-Auger,…

X-ray diffraction:
A few applications to microstructural thin film analysis

Objective: The objective of this lecture is to provide the minimum background to understand a few examples of x-ray diffraction analysis

→ X-ray Stress Analysis (XSA)

1) microstructural analysis:
   - → *phase analysis*
   - → texture measurement and analysis
   - → *grain size and microdistortion analysis*

2) analysis of residual stresses – measurement of applied or residual strains:
   - → monocrystalline films
   - → polycrystalline films :
     - → quasi-isotropic thin films (simplest case)
     - → fibre textured thin films (actual case)

- Basic fundamental of x-ray diffraction
- Texture analysis (simple case)
- Grain size - microdistortions
- Elasticity
- X-ray strain measurements- Stress analysis

Bibliography

- Kocks, U. F., C. Tomé, et al., Eds. (1998). *Texture and Anisotropy*, Cambridge University Press, Cambridge, UK.
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- Nye, J. F. (1957). *Physical Properties of Crystals*. Oxford, Clarendon Press.
- Hauk, V. (1997), *Structural and Residual Stress Analysis by Nondestructive Methods*, Elsevier
- Guinier A. (1964), *théorie et technique de la radiocristallographie*, Dunod

What is a thin film or a coating in this lecture ?

→ thin film (a few µm >thickness> 10 nm)

→ substrate (thickness>> thin film)

→Personal Research Areas :

- →Thin film
- →Metallic materials

What is a thin film or a coating in this lecture ?

→ thin film (a few µm >thickness> 10 nm)

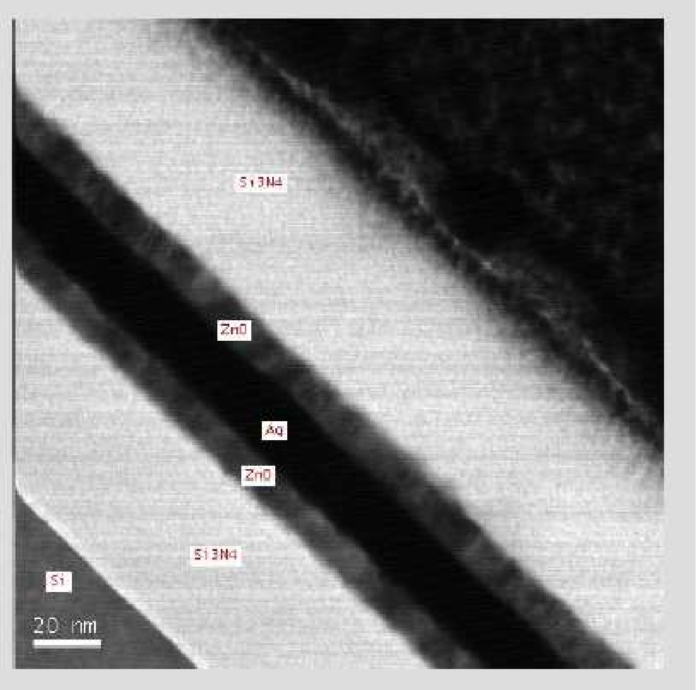
→ substrate (thickness>> thin film)

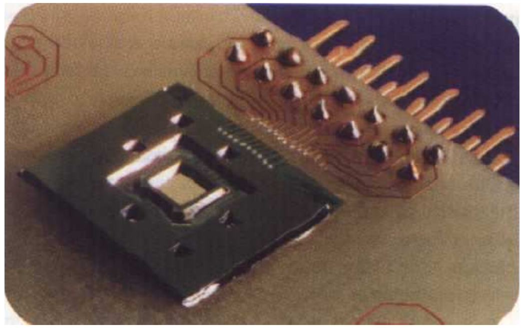
Elaboration:

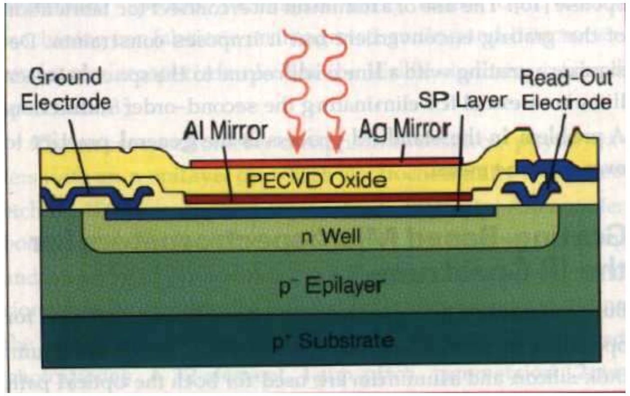
- -physical vapor deposition (thermal, ion beam sputtering,..)
- -chemical vapor deposition
- -electrodeposition
- -oxidation, ….

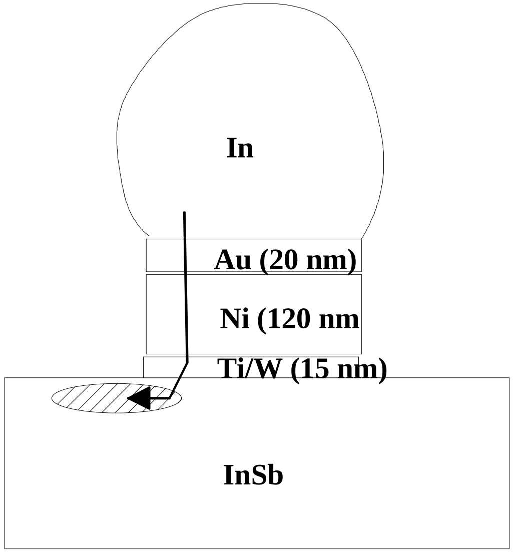
The microstructure of thin films depends on the experimental conditions of elaboration. X-ray diffraction is a powerful non destructive method used to study the microstructure (phase analysis, texture, grain size), the residual stress state, the mechanical properties,…

Thin films have a wide range of applications: electrical, magnetical, optical, corrosion, mechanical properties.



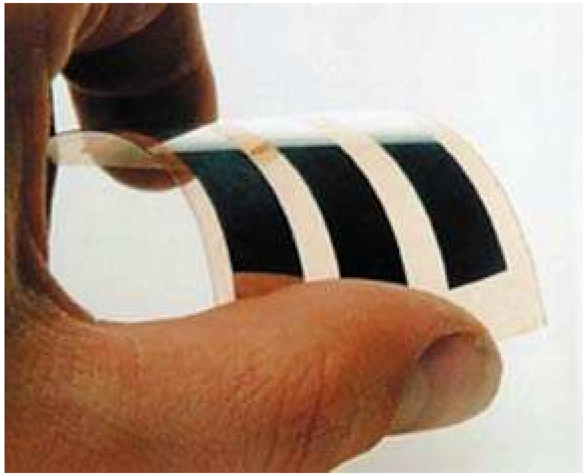






Gold	→ *anti-oxidization*
Nickel	→ *Wetting*
Ti/W	→ *anti-diffusion*

Flexible substrates:

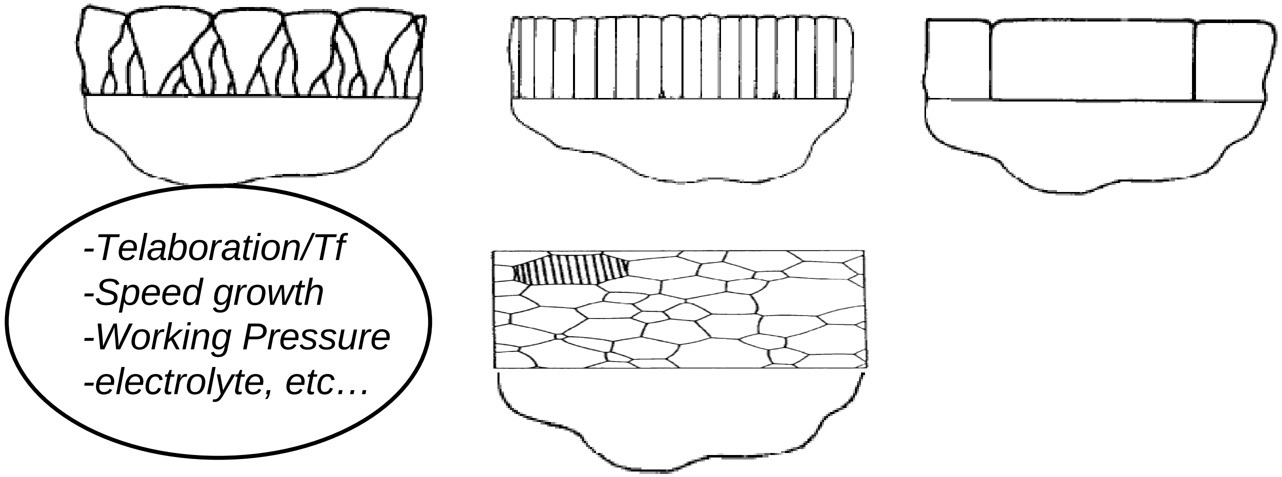


Coatings or thin films for :

-Wear resistance (or scratch resistant)
-Protection from UV rays
-Hydrophobic (designed to ease cleaning)
-Anti-reflective (eyes more visible, reduces glare, ..)
-Color changes

Thin films have a wide range of applications: electrical, magnetical, optical, corrosion, mechanical properties. →Why studying the microstructure ?

- Microstructure contains far more than qualitative descriptions (images) of cross-sections of materials.



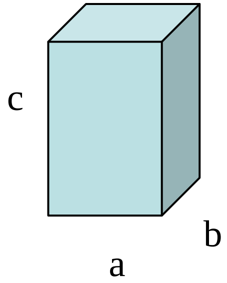
-Telaboration/Tf
-Speed growth
-Working Pressure
-electrolyte, etc…

- Most properties are anisotropic which means that it is critically important for quantitative characterization to include orientation information (texture).
- Lot of properties are size dependent (ex: mechanical properties such as hardness, yield stress,…; optical properties; electronical properties, magnetic properties)
- Many properties can be modeled with simple relationships, although numerical implementations are always necessary.

Optical anisotropy :

Example of cordeirite (rocks)

Orthorhombic (a,b,c)

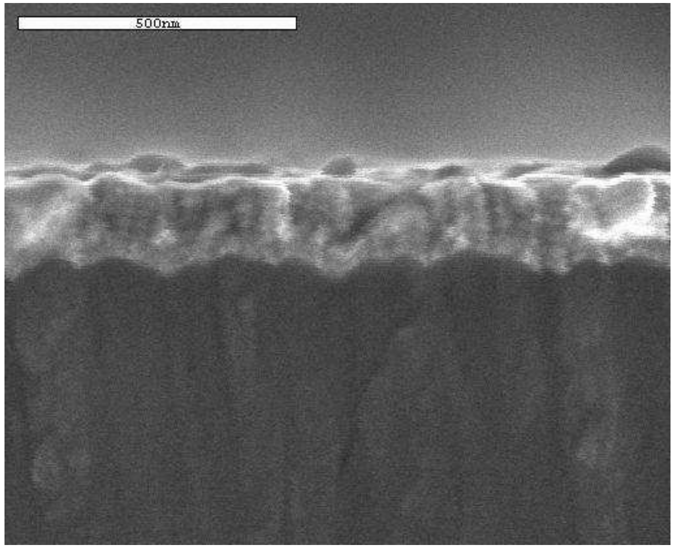


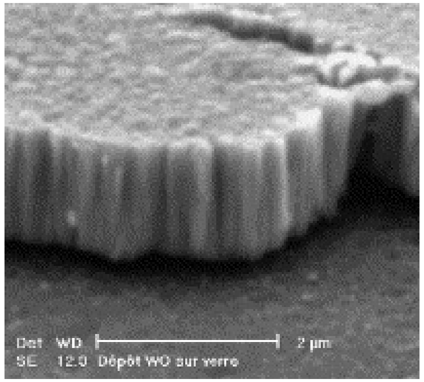
Darkest blue

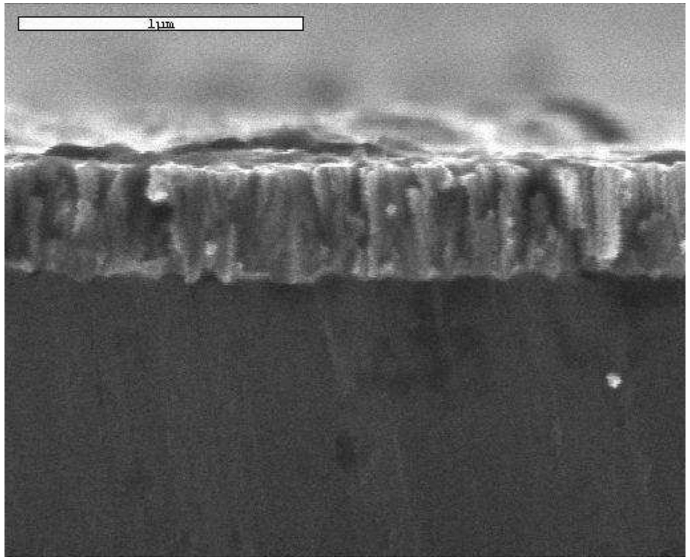
Medium blue

Pale stone - colorless

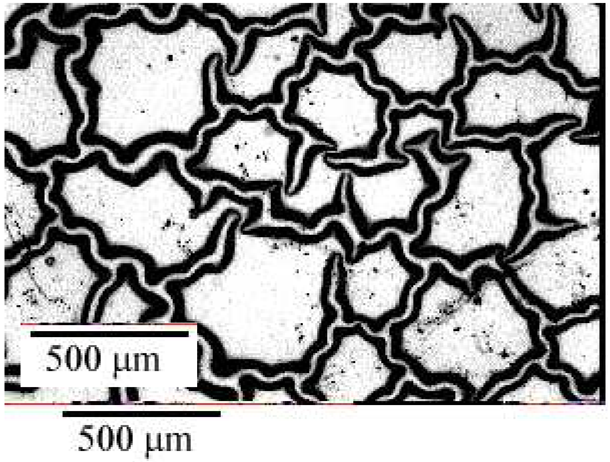
Example of thin film microstructures: Scanning electronic microscopy
Cross sections

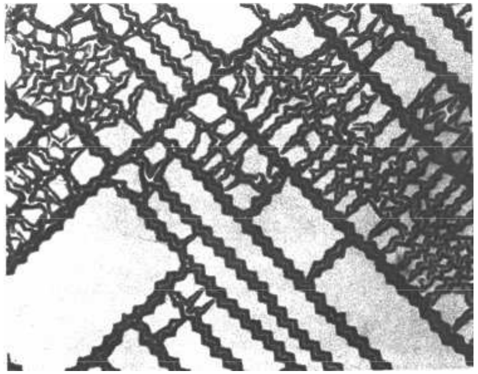


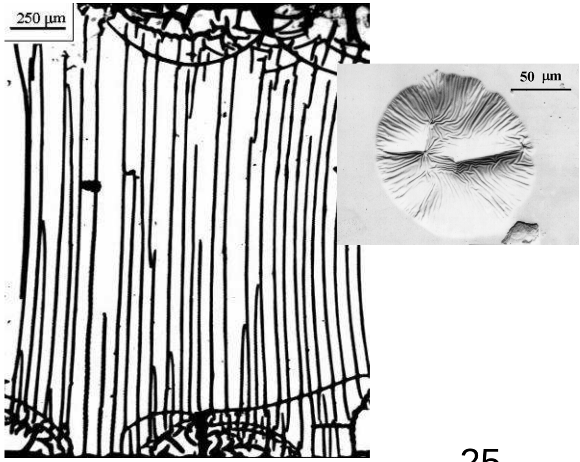




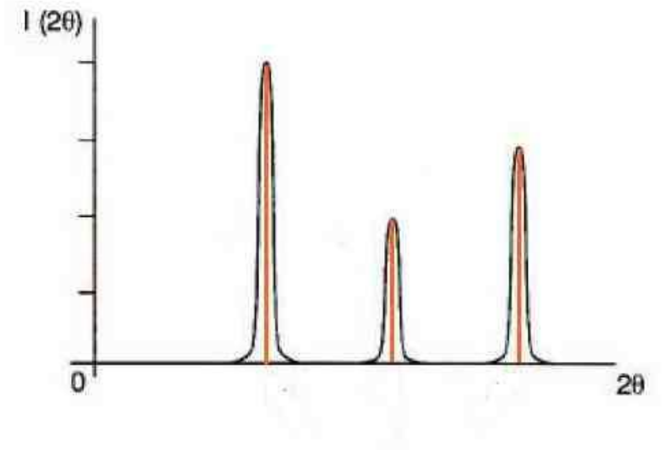
Delaminations→ stress ?







What is the informations in a Bragg peak ?



- **Position**
- **Intensity**
- **Shape → FWHM**

- Phase analysis (peak positions)
- Texture analysis (variation of peak intensity)
- Grain size – microdistortions (peak shape)
- X-ray Strain or Stress analysis (shift of peak position)

XRD can be used to determine

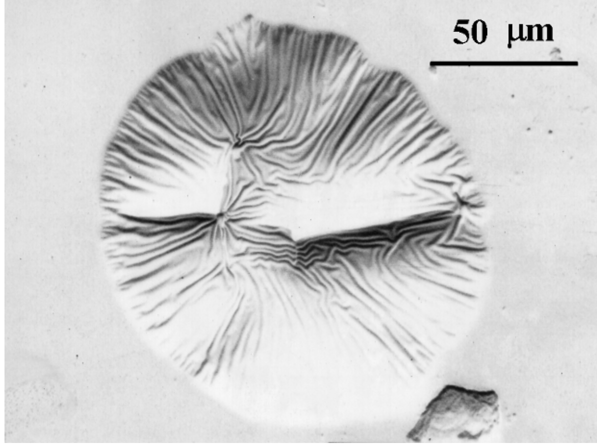
- Phase Composition of a Sample
  - Quantitative Phase Analysis: determine the relative amounts of phases in a mixture by referencing the relative peak intensities
- Unit cell lattice parameters and Bravais lattice symmetry
  - Index peak positions
  - Lattice parameters can vary as a function of, and therefore give you information about, alloying, doping, solid solutions, strains, etc.
- Residual Strain or stress (macrostrain)
- Crystal Structure
  - By Rietveld refinement of the entire diffraction pattern
- Epitaxy (thin film)/Texture (preferred orientation)/Orientation (single crystal)
- Crystallite Size and Microstrain
  - Indicated by peak broadening
  - Other defects (stacking faults, etc.) can be measured by analysis of peak shapes and peak width

→ *in-situ capabilities, too (evaluate all properties above as a function of time, temperature, gas environment, or mechanical tests)*

I

Fundamental of x-ray diffraction

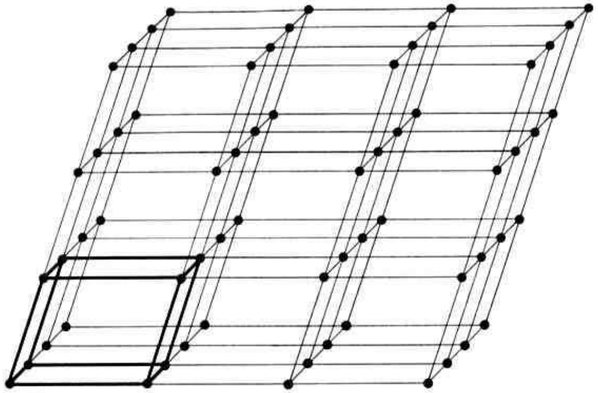
-basics of crystallography
-basics of x-ray diffraction



Crystallography

Outline: Lattice
Points lines, planes
Crystal systems
Primitive and non-primitive cells
Reciprocal Lattice

- Crystal (or single crystal): A solid composed of atoms, molecules arranged in a pattern periodic in three dimensions
- Polycrystals: Solids consisting of many contiguous crystals (or grains or crystallites)
- Lattice: Three dimensional array of points (lattice points), each of which has identical surroundings. Mathematically Lattices can extend to infinity

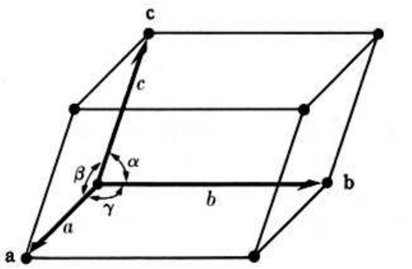


A point lattice.

Crystallography

- Unit cell: Defined by three independent translation vectors a,b and c in a right-handed sense. Different translations of the form $\bar{r} = u\bar{a} + v\bar{b} + w\bar{c}$ will reproduce the whole structure. **Primitive cell** is a unit cell which contains only one atom per cell.

  → FCC example….

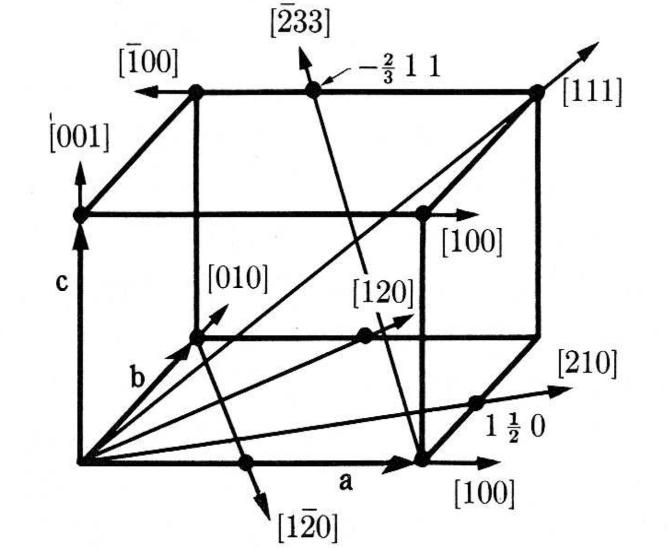


A unit cell

- Directions: The direction of a line can be determined by drawing a line from the origin parallel to the line and assigning a $\bar{r} = u\bar{a} + v\bar{b} + w\bar{c}$
- The line is then represented by the [uvw] bracket. uvw is always converted to the smallest integer number.

- Negative directions are represented by a bar above the number
- Directions of a form: are the directions represented by symmetry

$$[111],[11\bar{1}],[\bar{1}11],[1\bar{1}1] \Rightarrow \langle 111 \rangle$$



Indices of directions

Crystallography

- If the axial lengths are a, b, c, then the planes make the intercepts of a/h, b/k, c/l. The miller indices for the plane is (hkl), and the family of planes are {hkl}.

$$(111),(\bar{1}11),(1\bar{1}1),(11\bar{1}) \Leftrightarrow \{111\}$$

- Planes can be represented by their normal vectors

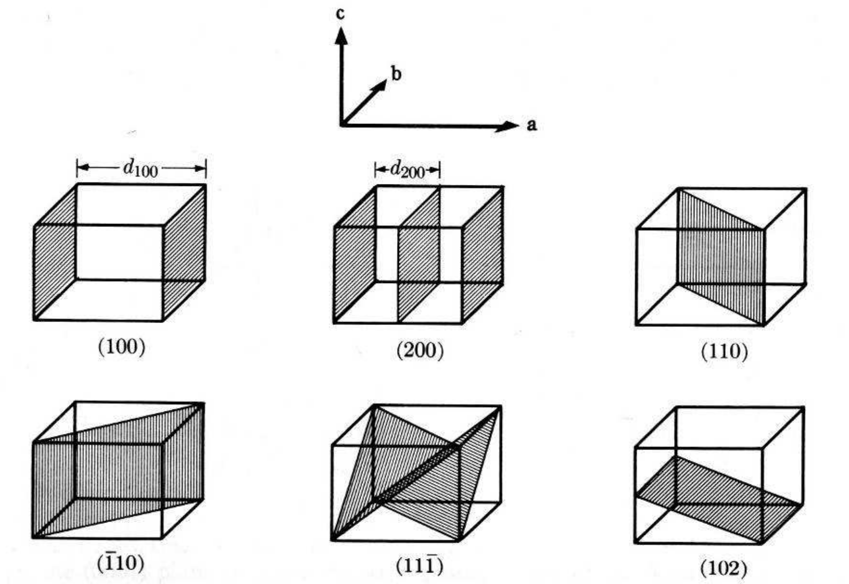
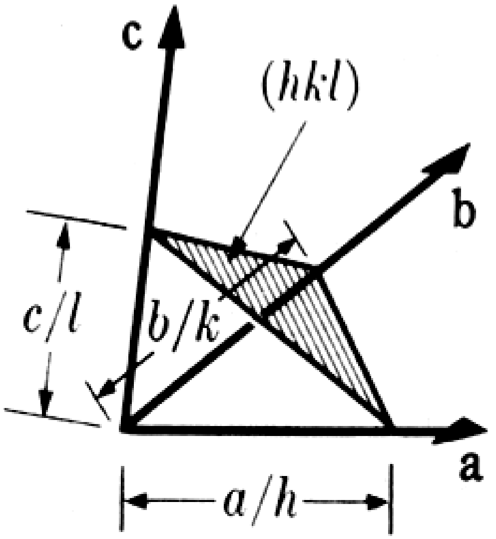


Fig. 2–10 Miller indices of lattice planes. The distance *d* is the plane spacing.



Crystallography

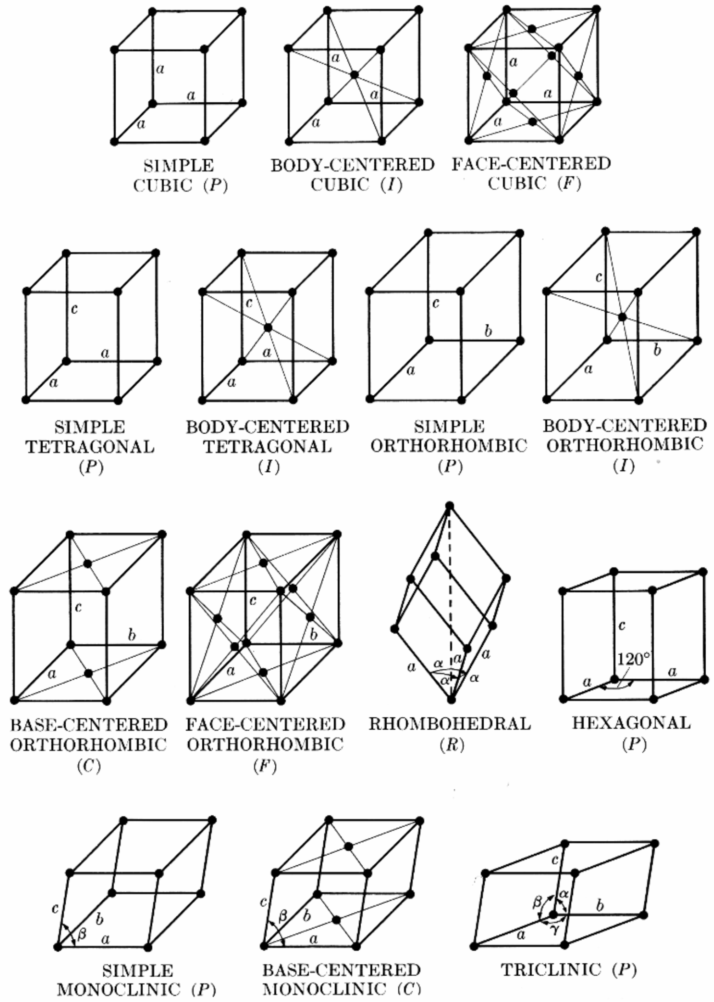
- There are 7 different kinds of unit cells that can include all the possible lattice points **(Crystal Systems)** i.e. cubic, tetragonal, orthorhombic, rhomboedral, hexagonal, monoclinic, triclinic

- There are Fourteen Bravais Lattices. They are categorized in terms of
  - P primitive
  - I Body Centered
  - F Face centered
  - A,B,C Base centered
  - R Rhombohedral

- In the following we will consider the simplest forms of lattice, i.e. the cubic systems, which is a common structure of a lot of metals and semi conductors.

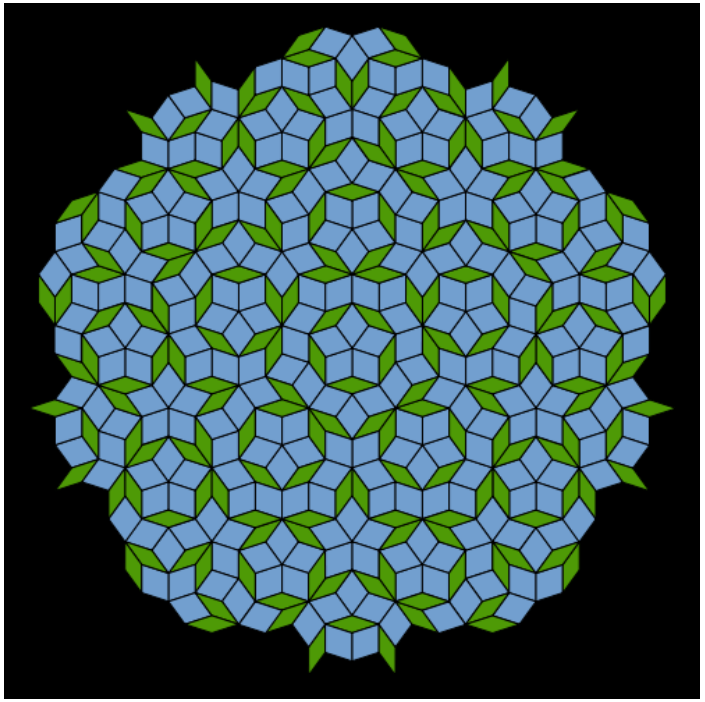
→The interplanar spacing d_{hkl} for {hkl} depends on the crystal system chosen. For cubic system:

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



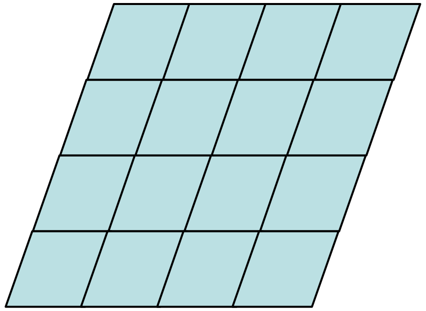
The fourteen Bravais lattices.

2D tilings



Penrose tiling

→ *quasi-crystals*



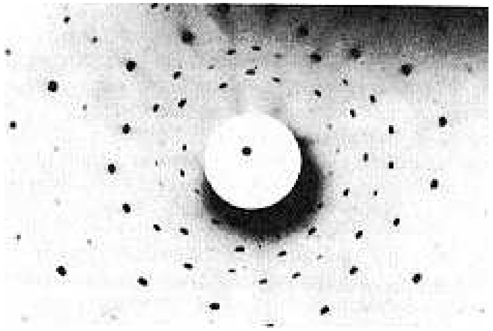
Bravais lattices:

→ *crystals*

Beginnings of X-ray diffraction

- 1895 Discovery of X-ray by German physicist Röntgen → x-rays penetrate materials opaque to visible light→ radiographic analysis

- 1912 Von Laue shows that x-rays are diffracting by crystalline materials.
  A few months later, Bragg derived a simple, elegant set of laws relating diffracting phenomena to crystal structure
  → beginning of radiocrystallography



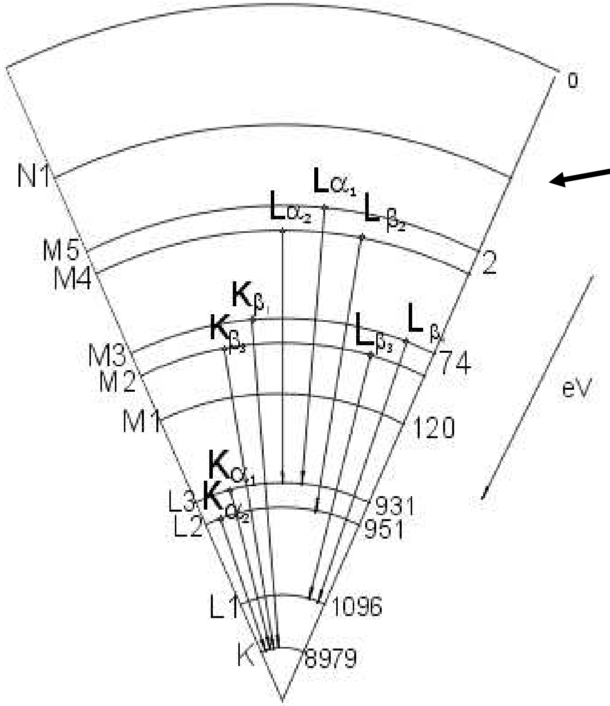
•X-ray production:

X-rays may be produced by 2 fundamentally different methods:

1- the first method utilizes the fact that all electrically charged particles emit radiation during rapid deceleration

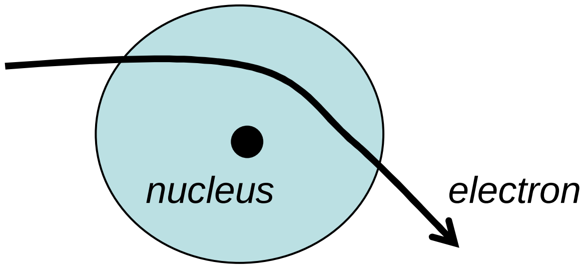
2-the second method involves ionization.

One way to produce X-ray consists to bombard a material (anode) with accelerated electrons. If the incoming electron is energetic enough, it can eject an electron from a K or 1s shell, and excite the atom to a high energy state. The atoms then attains a lower energy state by filling this vacancy by an electron from a higher energy shell (L or M). The difference between the electron energies of the K shell and the higher energy shell is emitted in the form of characteristic x-rays during this process.

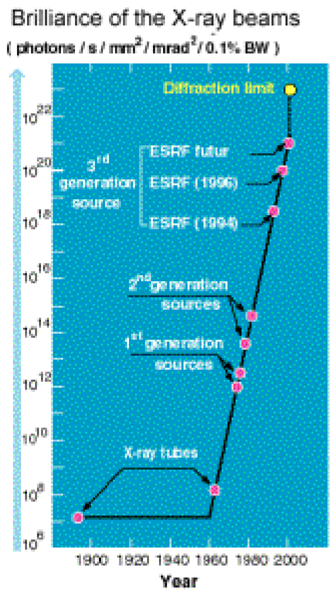


Electronic transition causing emission of characteristic radiation. Electron energy levels of Cu

Bremstrahlung:



→ Decelaration of the incoming electron



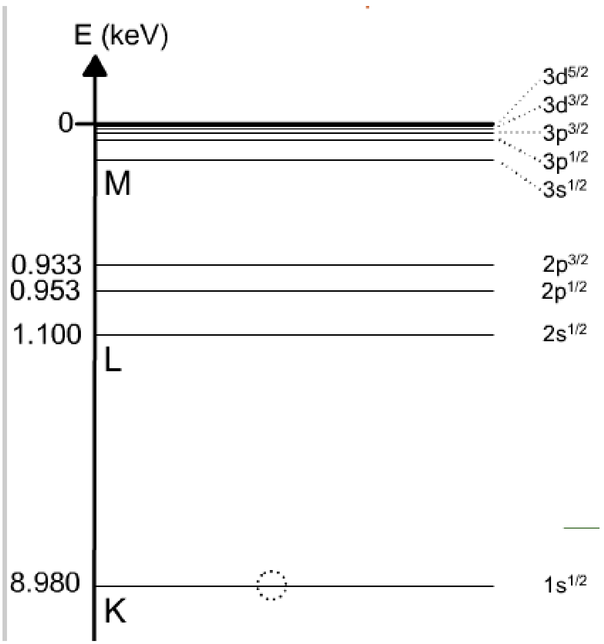
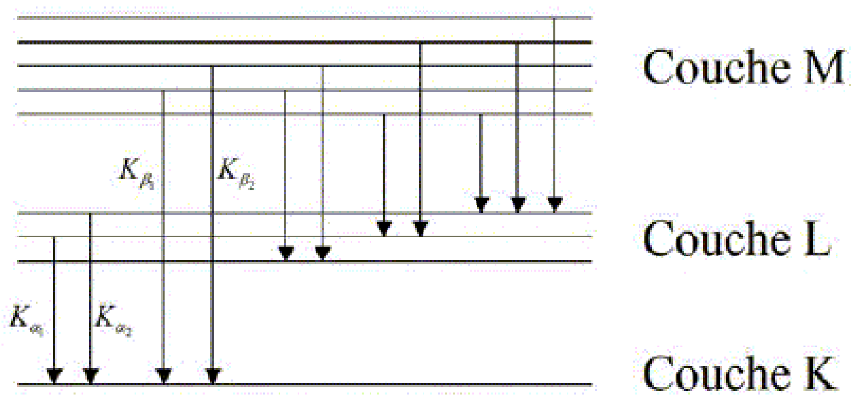
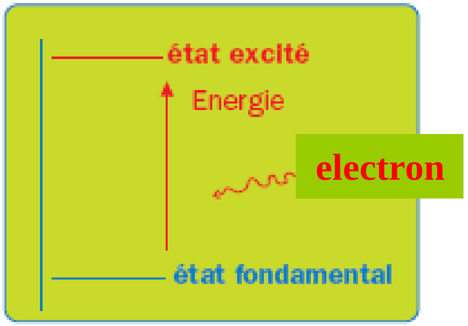


Diagramme des premières raies *X*

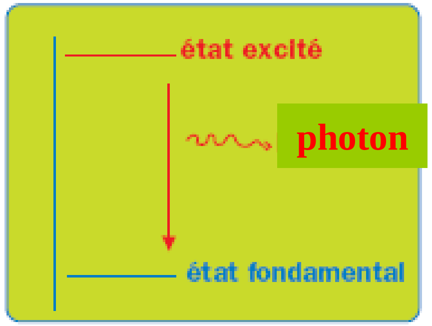


Sealed tube

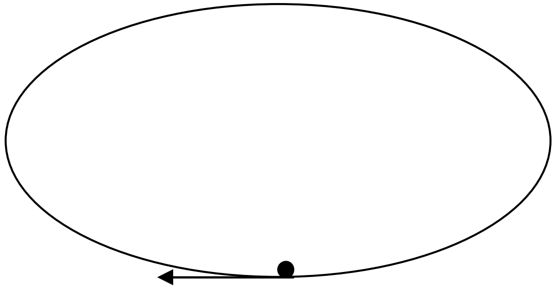
synchrotron source



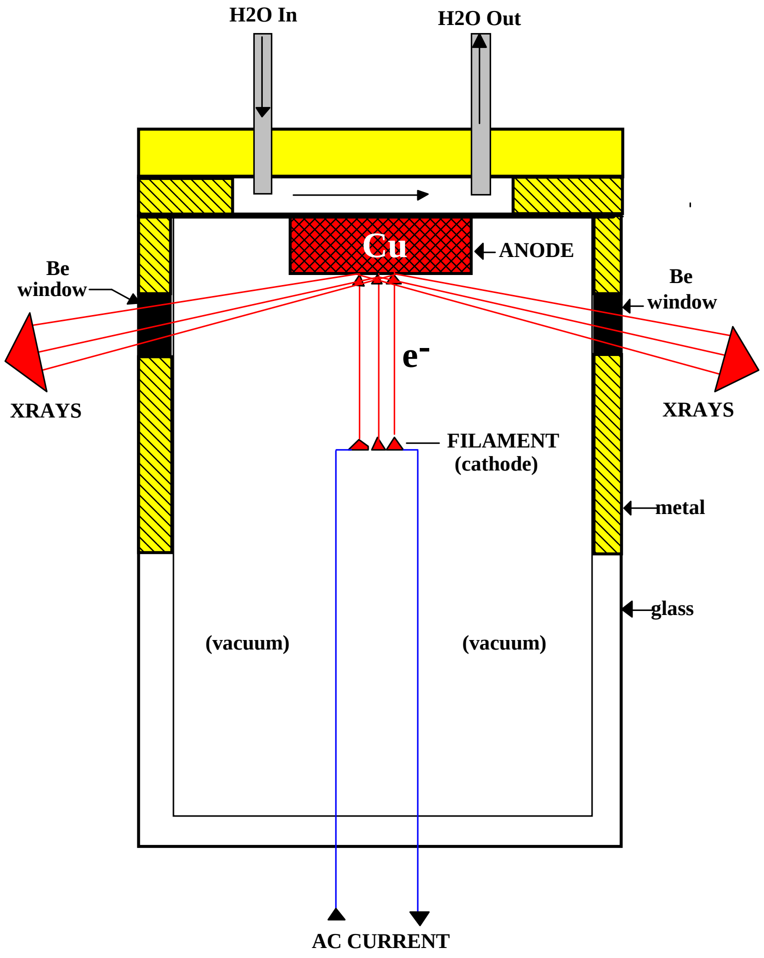
Excitation d'un atome



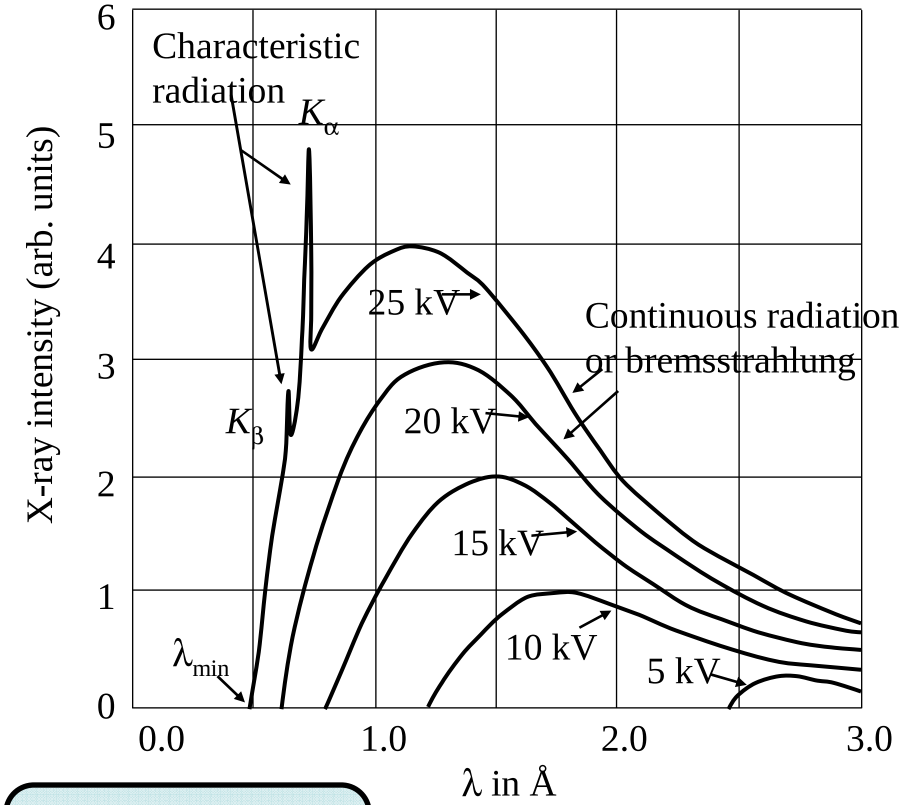
Désexcitation d'un atome



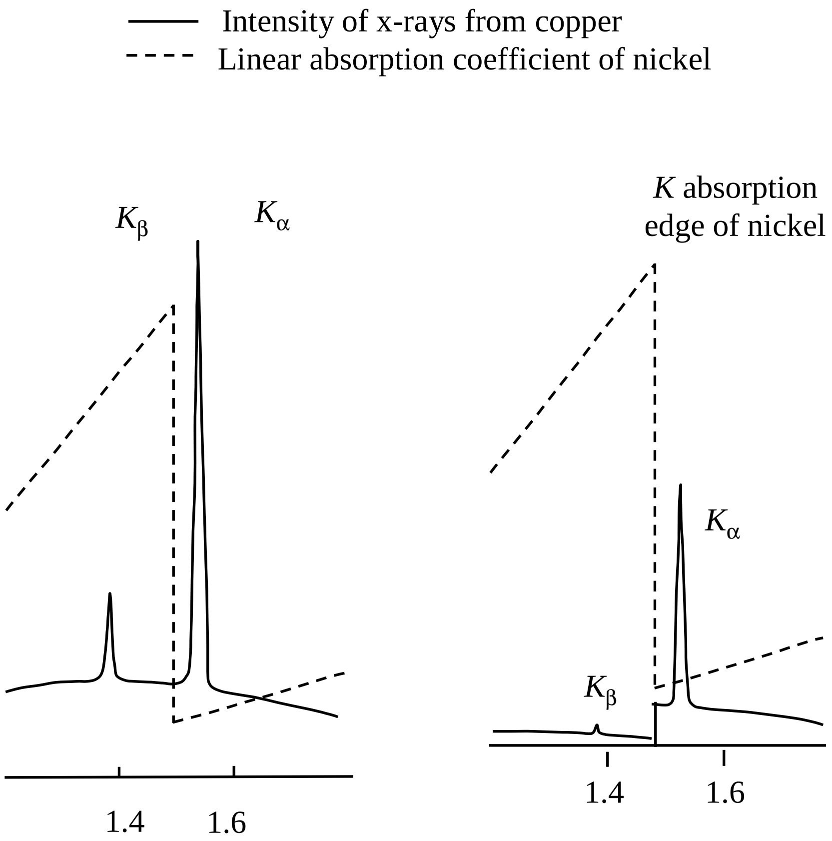
Example of sealed tube or rotating anode.



- Sealed X-ray tubes tend to operate at 0.9 to 2 kW.
- Rotating anode X-ray tubes produce much more flux because they operate at 5 to 18 kW.
- Both sources generate X rays by striking the anode target wth an electron beam from a tungsten filament:
- The target must be water cooled. In a rotating anode the anode spins at a given speed, helping to distribute heat over a larger area and therefore allowing the tube to be run at higher power without melting the target.
- The target and filament must be contained in a vacuum (because of e absorption)



$$\boxed{\lambda_{\min} = \frac{12400}{eV}}$$



λ in Å
(a) No filter

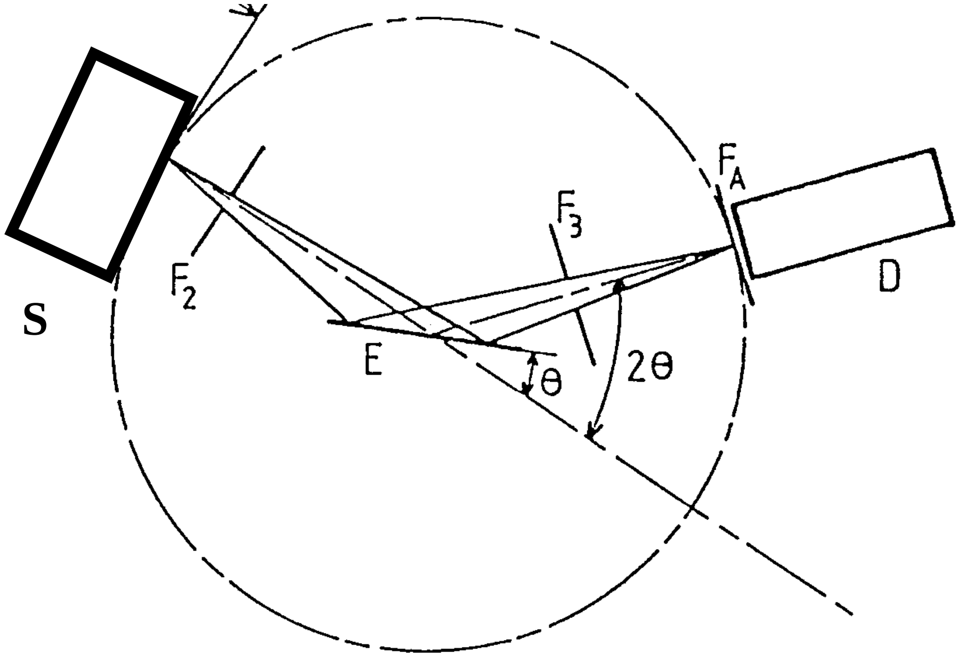
λ in Å
(b) With Ni filter

X-rays: polychromatic background + several peaks with high intensity

The most simple way to reduce the wavelength range, i.e. remove Kβ radiation.

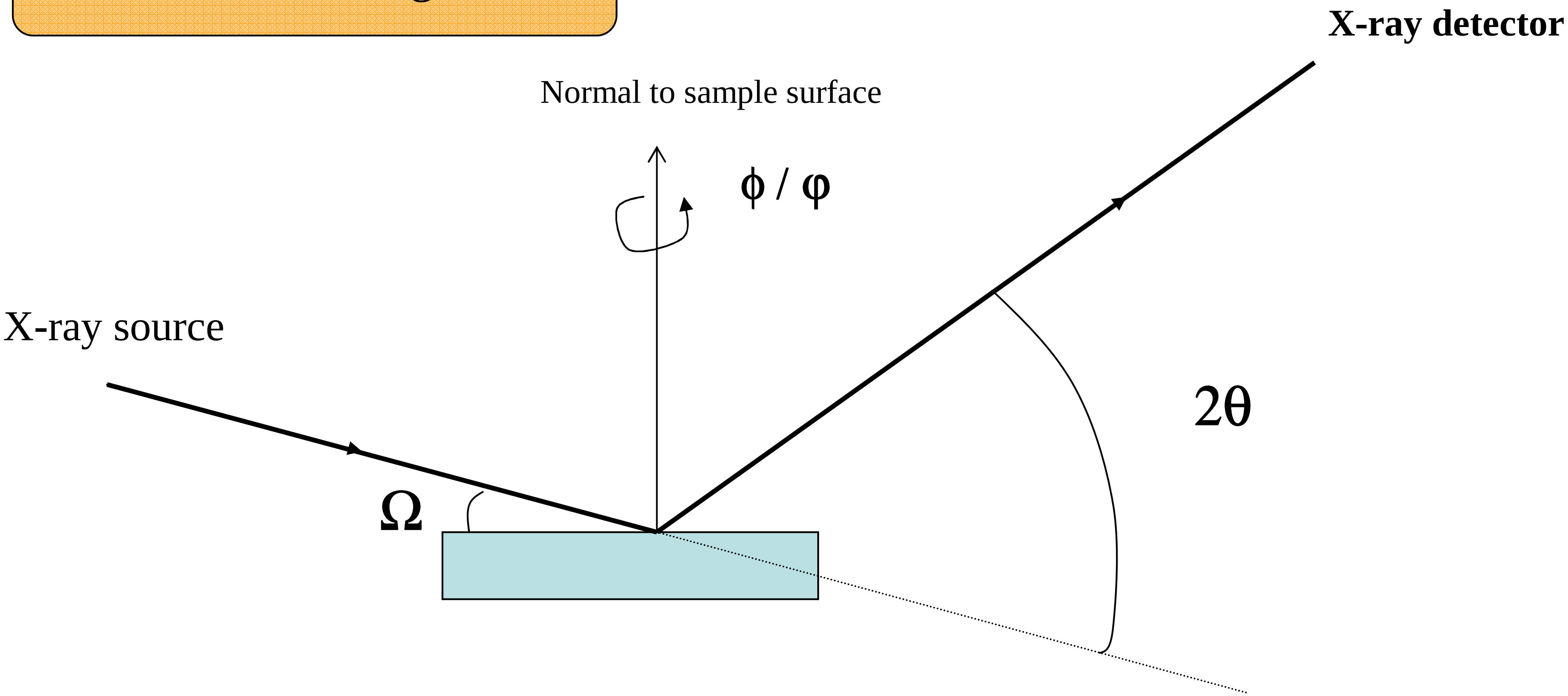
A K line is produced if e is ejected from K shell and the L shell supplies e to it. But L shell has 2 e (with different spins) → 2 lines of different energies in Kα → Kα1 and Kα2. M shell → Kβ

Most of powder diffractometers use the so-called “Bragg-Brentano” geometry.



In the B-B geometry, the incident- and diffracted-beam slits move on a circle that is centered on the sample. Divergent X rays from the source hit the sample at different points on its surface. During the diffraction process the X rays are refocused at the detector slit.
The B-B geometry provides the best combination of intensity, peak shape, and angular resolution for the largest number of samples.

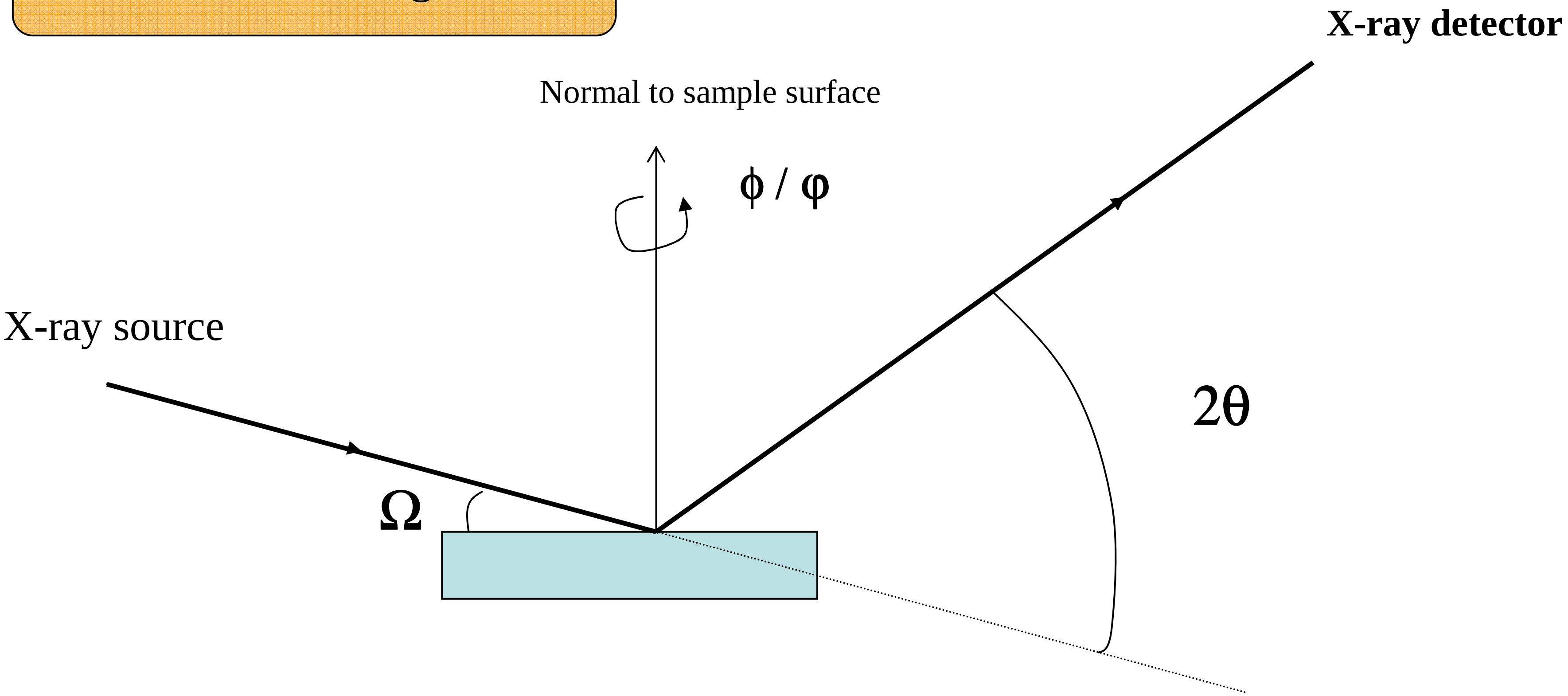
Diffraction angles



Ω → The incident angle is defined as the angle between the X-ray source and the sample

2θ → The diffracted angle is defined as the angle between the incident beam and the detector angle

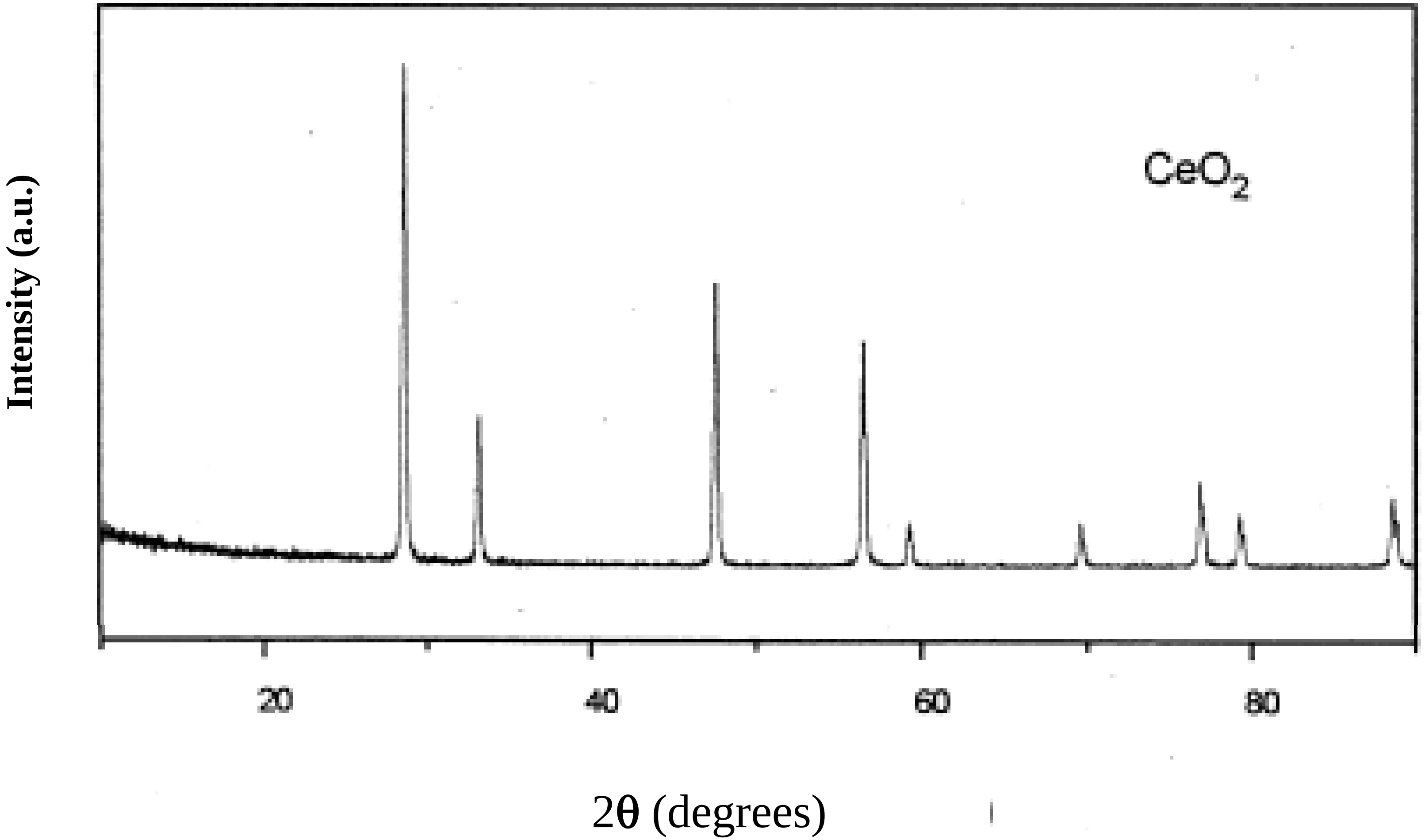
Diffraction angles



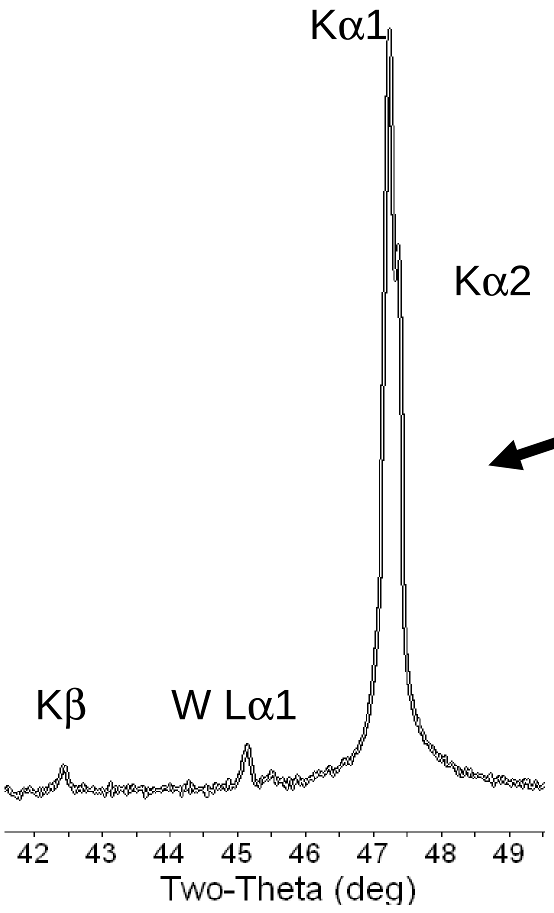
If $\Omega = 2\theta/2 (=\theta)$ → symetric, classical theta/2theta scan

→ the diffracting planes are // to the surface

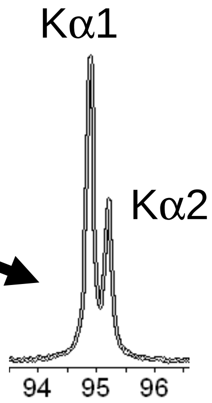
Typical diffractogram: theta/2theta scan



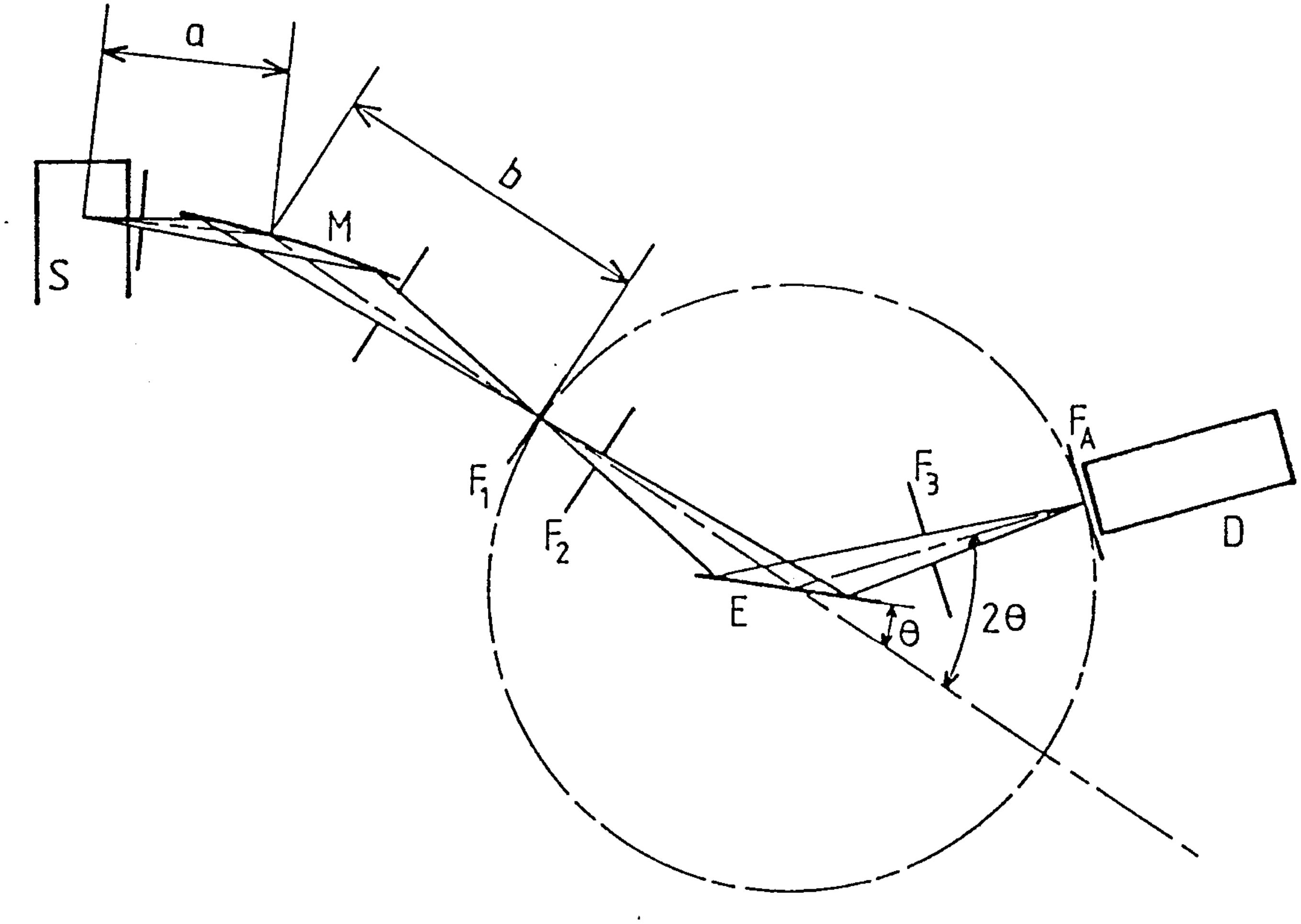
Spectral Contamination in Diffraction Patterns



- The Kα1 & Kα2 doublet will almost always be present
  - Very expensive optics can remove the Kα2 line
  - Kα1 & Kα2 overlap heavily at **low angles** and are more separated at **high angles**



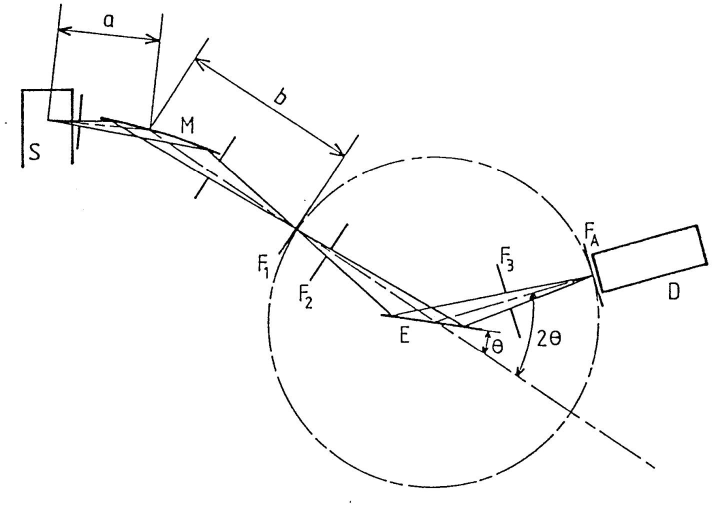
- W lines form as the tube ages: the W filament contaminates the target anode and becomes a new X-ray source
- W and Kβ lines can be removed with optics


a
b
S
M
F_1
F_2
F_3
F_A
D
E
θ
2θ

- Monochromatisation :

simplest case : use a filter → remove kbeta radiation and a part of the background (see former slide)

other cases: use one or several single crystals as monochromator

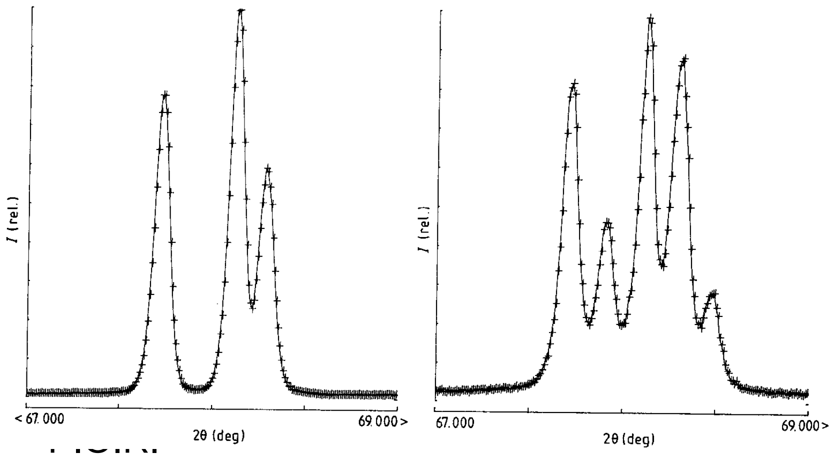


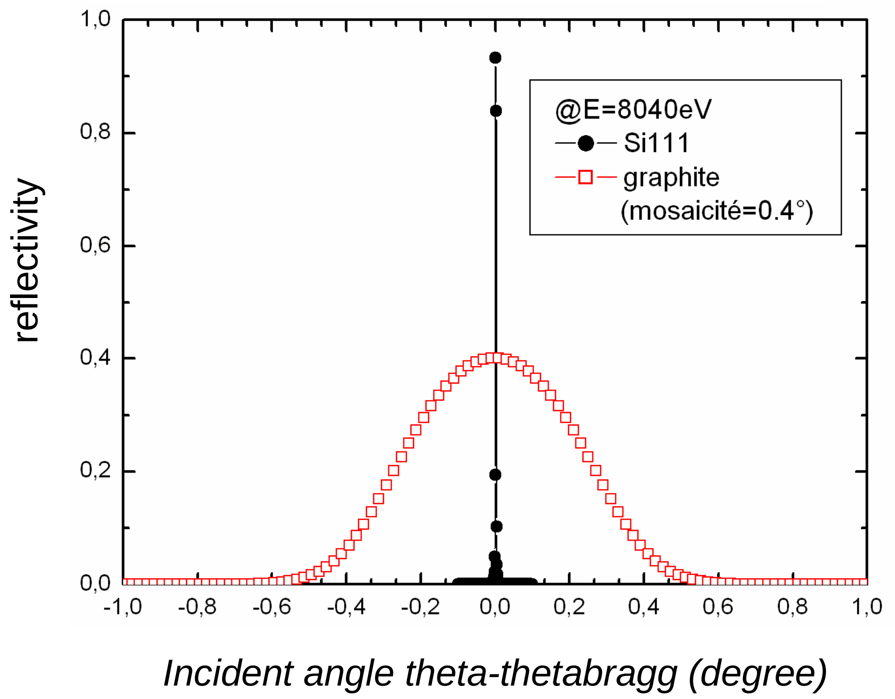
$$\frac{\Delta\lambda}{\lambda}=\frac{\Delta E}{E}=\Delta\theta \cot g\,\theta_B$$

« Good » single Crystal : $\Delta\lambda/\lambda \sim 10^{-4}$

« bad » Single Crystal (exhibiting mosaïcity : $\Delta\lambda/\lambda \sim 10^{-2}$

Flux ∝ integrated reflectivity





Values of Wavelengths for some classical tubes

Copper Anodes	Bearden (1967)	Holzer et al. (1997)		Cobalt Anodes	Bearden (1967)	Holzer et al. (1997)
Cu Kα1	1.54056Å	1.540598 Å		Co Kα1	1.788965Å	1.789010 Å
Cu Kα2	1.54439Å	1.544426 Å		Co Kα2	1.792850Å	1.792900 Å
Cu Kβ	1.39220Å	1.392250 Å		Co Kβ	1.62079Å	1.620830 Å
Molybdenum Anodes				Chromium Anodes		
Mo Kα1	0.709300Å	0.709319 Å		Cr Kα1	2.28970Å	2.289760 Å
Mo Kα2	0.713590Å	0.713609 Å		Cr Kα2	2.293606Å	2.293663 Å
Mo Kβ	0.632288Å	0.632305 Å		Cr Kβ	2.08487Å	2.084920 Å

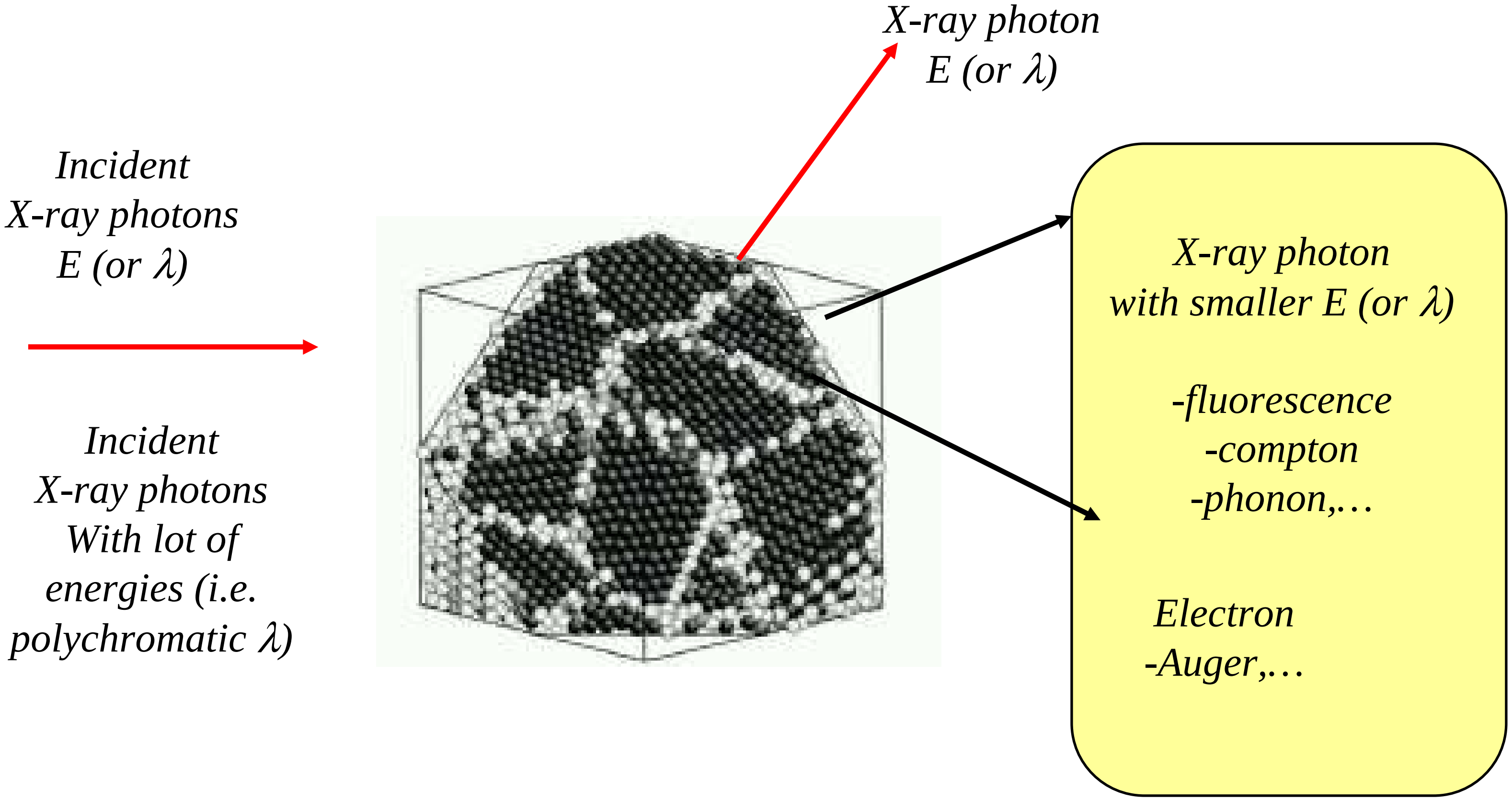
Often quoted values from Cullity (1956) and Bearden, *Rev. Mod. Phys.* **39** (1967) are incorrect.

Lot of XRD textbooks do not have the most recent values Hölzer et al. (1997)

Whatever the wavelength, what happens for the x-ray photon?

X-ray photon interaction with matter:

-difference between scattering, diffraction and refraction



Incident
X-ray photons
E (or λ)

Incident
X-ray photons
With lot of
energies (i.e.
polychromatic λ)

X-ray photon
E (or λ)

X-ray photon
with smaller E (or λ)

-fluorescence
-compton
-phonon,…

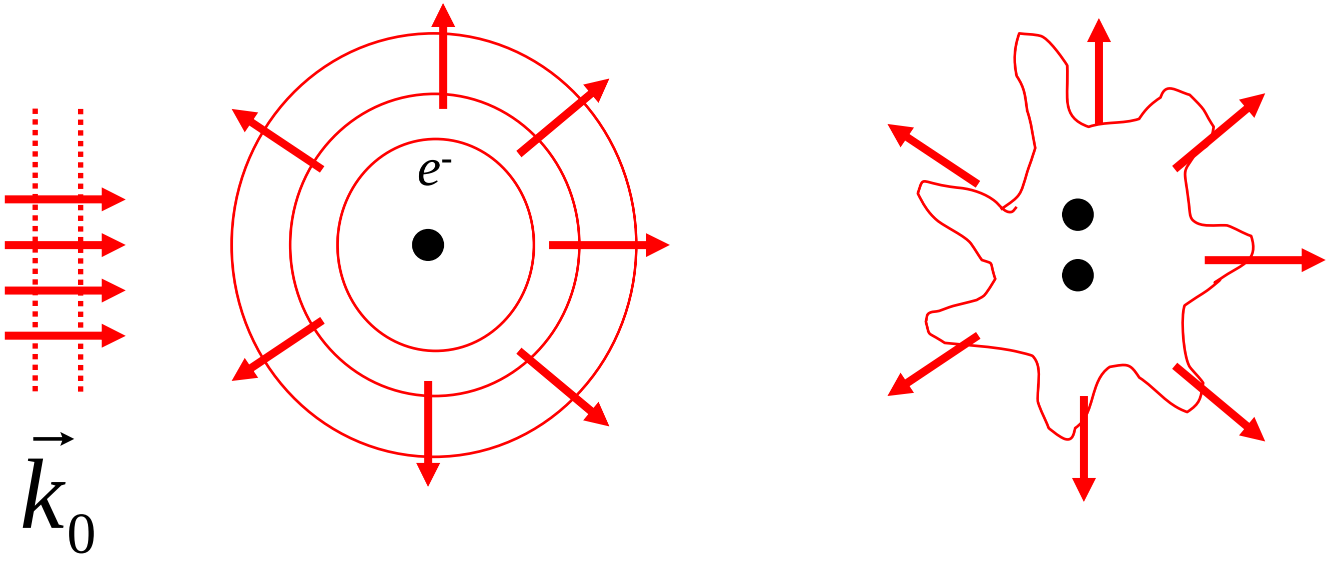
Electron
-Auger,…

x-ray photon interaction with matter

scattering

Incident
X-ray photon
E (or λ)

Incoming plane
wave

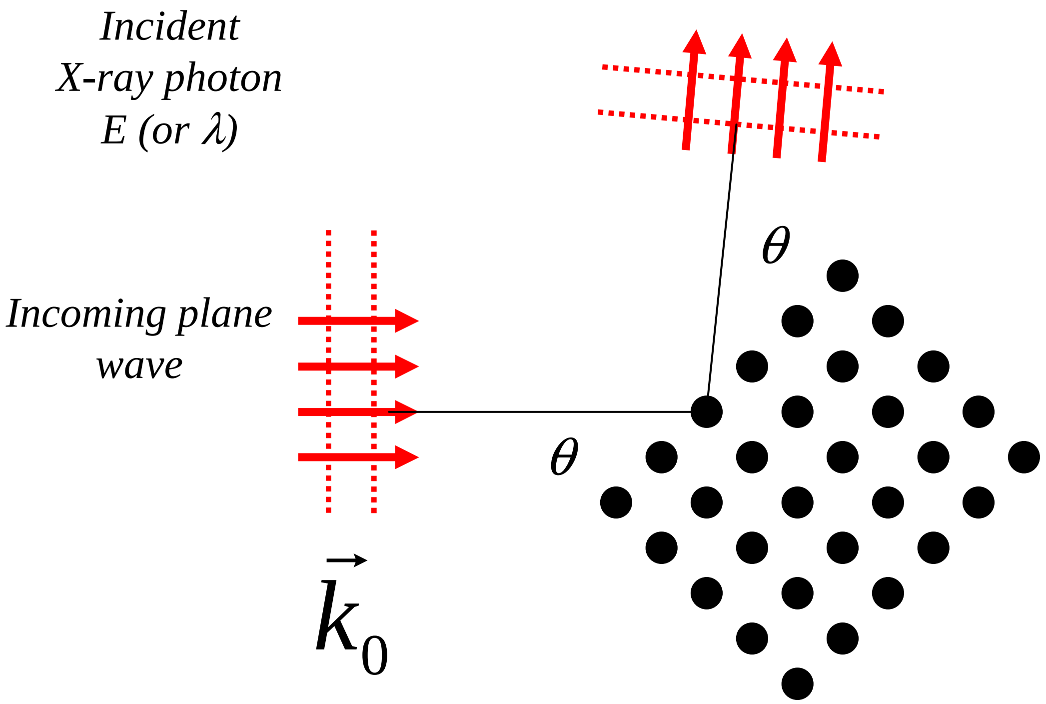


e^- or a few e^- randomly distributed or atom

→The electrons interact with the oscillating electric field of the light wave.
→The electrons in an atom coherently scatter light.

x-ray photon interaction with matter

diffraction

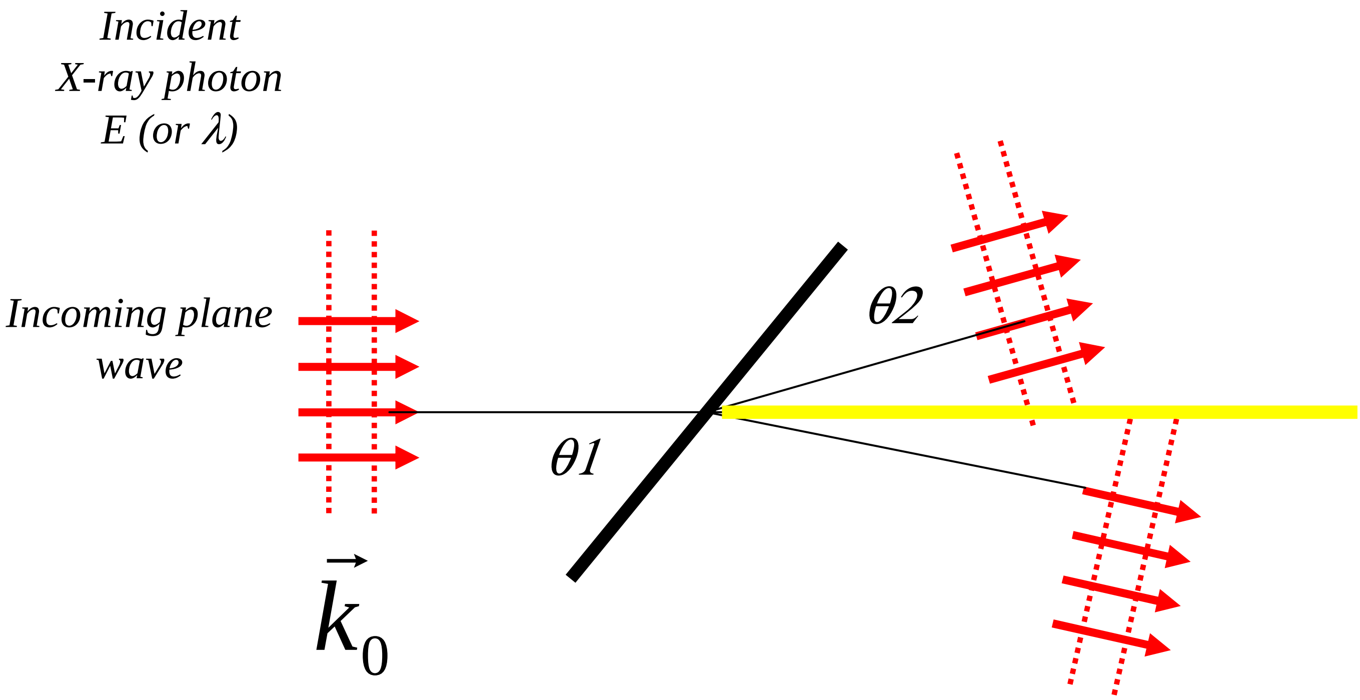


Generally speaking, diffraction occurs when each object in a periodic array scatters radiation coherently, producing concerted constructive interference at specific angles.
Here, the object is the atom or molecule, and the radiation is composed of x-ray photon.

Nice arrays of atoms = cristal

x-ray photon interaction with matter

refraction



→ *Consequence of n<1, existence of a critical angle for which there is a total external reflection*

Conclusion:

The electrons interact with x-rays.

→**diffraction** may occur if the irradiated object is composed of a periodic array of atoms or molecule

→X-rays are also

reflected

scattered incoherently

refracted

absorbed or transmitted

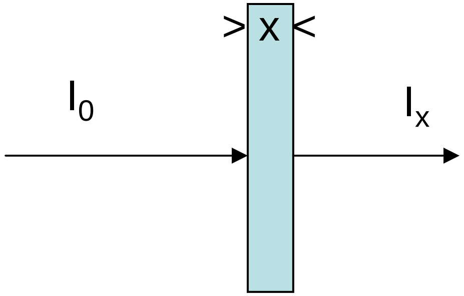
- Absorption of X-rays:

x-rays are attenuated as they pass through matter, so that the transmitted beam is weaker than the incident beam. Various processes contribute to this decrease : coherent scattering, incoherent scattering, fluorescence, …

$$\frac{dI}{I} = -\mu dx$$

Here: ***I is the transmitted beam intensity***
μ linear absorption coefficient (proportional to the density ρ of the material). μ/ρ is the mass absorption coefficient.

For an homogeneous specimen of finite thickness x:



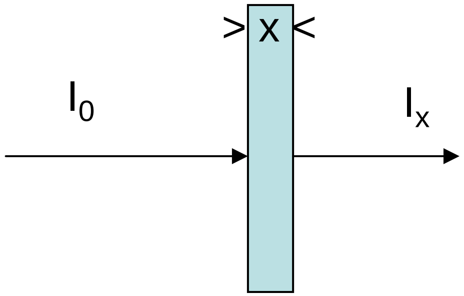
$$I_x = \int_0^x \frac{dI}{I} = I_0.\exp(-\mu x) = I_0.\exp(-\mu / \rho.\rho.x)$$

For a specimen consisting of n substance, the mass absorption coefficient is:

$$\left(\mu/\rho \right) = \sum_{i=1}^{n} w_i \left(\mu/\rho \right)_i$$

With w_i the weight fractions of each substance

- Absorption of X-rays:



For an homogeneous specimen of finite thickness x:

Let us define the penetration depth as : $\frac{I_x}{I_0} = \frac{1}{e}$

Element	Density (g/cm3	Mass absorption coeff. (cm^2.g-1)	Penetration depth (µm)	Penet. Depth (µm) Reflection geometry 90% 2θ=40°	Penet. Depth (µm) Reflection geometry 50% 2θ=40°
Be	1.848	1.5	3607	1420	428
Al	2.7	48.6	76.2	30	9
Si	2.33	60.6	70.8	28	8.4
Fe	7.874	308*	4.1	1.6	0.5
Cu	8.92	52.9	21.2	8.3	2.5
Au	19.3	208	2.5	1	0.3

penetration depth for Cu Kα radiation

The absorption is a function of the wavelength (or the energy):

radiation	Ag Ka	Rh Ka	Mo Ka	Cu Ka	Ni Ka	Fe Ka	Cr Ka
λ (A)	0.5608	0.6147	0.7107	1.5418	1.6591	1.9373	2.2909
Au	63.1	80	115	208	250	365	532

Notes: this is for Kα radiations , i.e. the average of Kα1+Kα2 is defined as: $\lambda_{K\alpha} = \frac{2\lambda_{K\alpha 1} + \lambda_{K\alpha 2}}{3}$

- **Scattering of X-rays:**

When an x-ray beam, containing x-ray photons of wavelength λ, impinges on a specimen, the photons collide with the fundamental particles (electrons and nuclei) making up the specimen, and diffuse or scatter in all directions.

It is possible to have two types of collisions with the electrons:

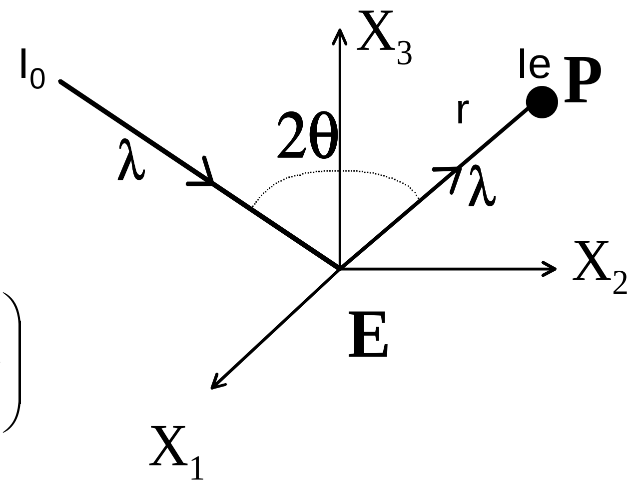
→*elastic* . There is no momentum transfer between electron and photon. Thus the scattered photon has the same energy after the collision as before. This is called the coherent scattering.

→ *non elastic*. There is some momentum transfered from the photon to the electron. Thus the scattered photon will have a longer wavelength than the incident photon. This incoherent scattering is usually called Compton scattering.

In both of the above processes electrons scatter the photons in all directions. However, the intensity of the scattered beam depends on the scattering angle:

- • ***Scattering from electron***:

If an unpolarized beam of intensity I_0 impinges on a single electron, the total coherent scattering at a point P is given by the Thomson equation:



$$I_e = I_0 \cdot \frac{e^4}{r^2 m^2 c^4} \cdot \left(\frac{1 + \cos^2 2\theta}{2} \right) = r_e^2 \cdot \frac{I_0}{r^2} \cdot \left(\frac{1 + \cos^2 2\theta}{2} \right)$$

m:electron mass, e: el. charge, c: light's speed
r: length of vector to P, 2θ :angle between r and incident beam

-The last term is the polarization factor

-the factor 1/m ensures that for scattering from atoms the scattering from the nucleus can be ignored. Indeed, M(proton or neutron) ≈ 1836 x M(electron)

● ● ***<u>Scattering from an atom</u>***:

When the x-ray beam impinges on an atom, with atomic number Z, the total scattered intensity to a point P will be slightly different. There will be Z scattered beam sources at different positions around the atom. Thus Z rays will arrived at the point P away from the atom.

However, the total scattered intensity at P, I_T, will depend on the relative phases of the individual rays. If all the beams are in phase, the total intensity is $Z^2 I_e$. If the beam from individual electrons are out of phase by various amounts, a certain amount of destructive interference will take place.

The term used to describe the total coherent scattering from an atom to a point P is the atomic scattering factor, f, which is defined as:

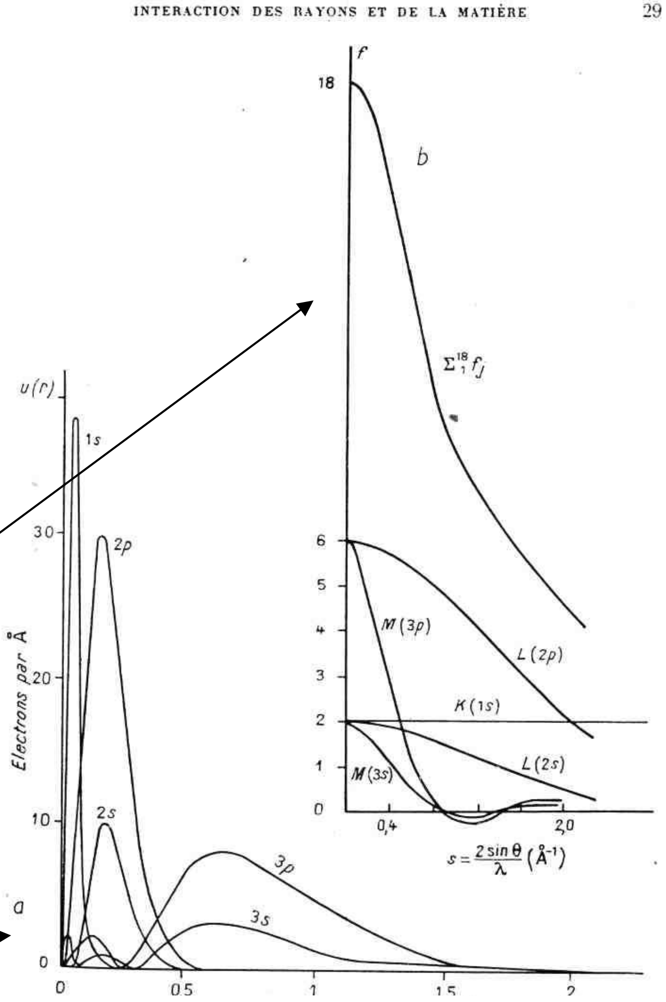
$$f = \frac{\text{amplitude of wave scattered by an atom}}{\text{amplitude of wave scattered by an electron}}$$

$$= f\left(\frac{\sin\theta}{\lambda}\right)$$

Example (atom K, Z=19):

- *electronical density*

b) atomic scattering factor of ion K$^+$



Distance from atomic center (A)

Guinier (1968), radiocristallographie

• • ***Scattering from an atom***:

In an atom, we have to consider the scattering from the cloud of electrons around the nucleus. The nucleus is used as the origin of coordinates.
Then for each electrons we may define a distribution function $\rho_n(\mathbf{r})$ which gives the probability that the electron should be contained in unit volume at the position defined by the vector **r**.

The scattering amplitude for the electron n can be written as:

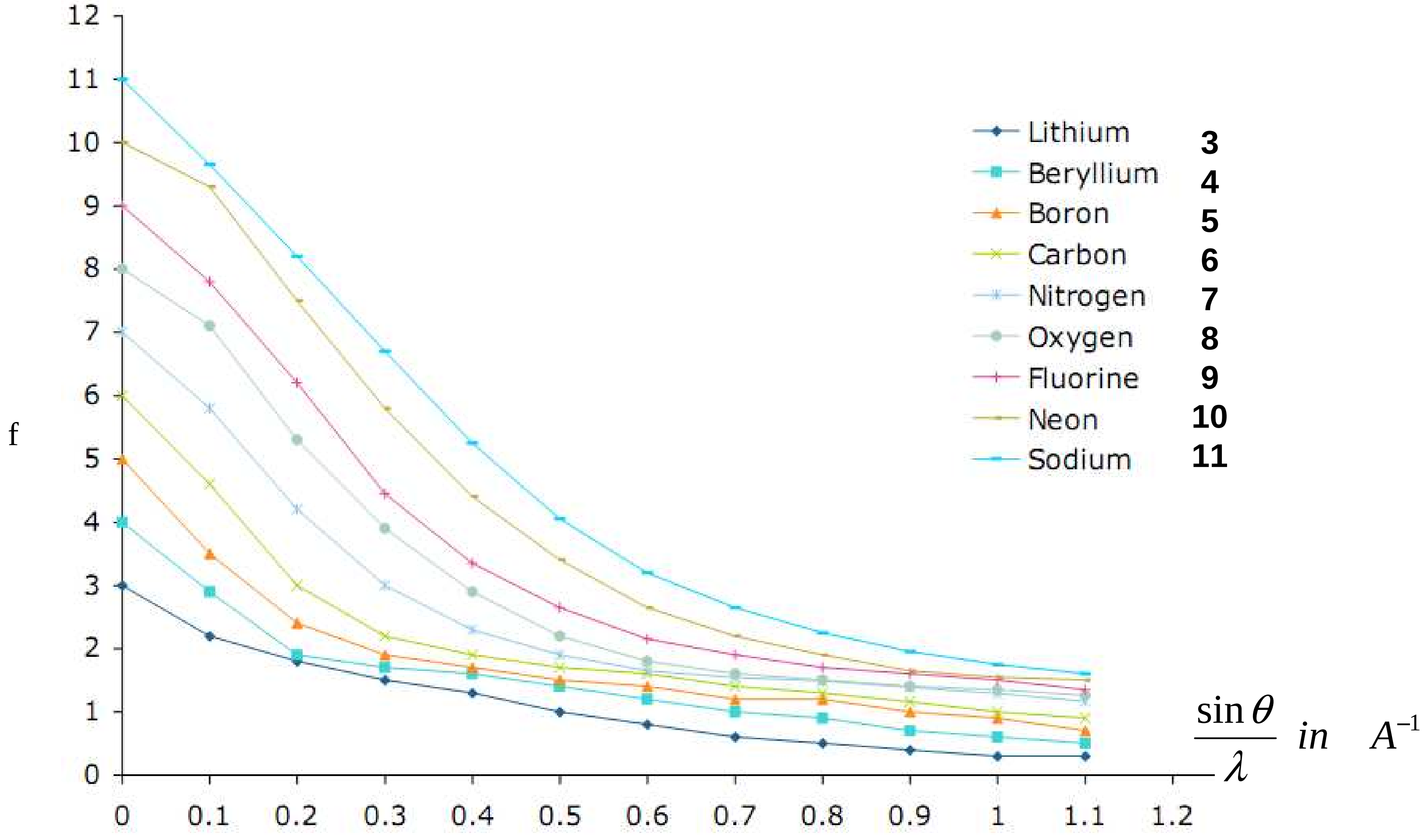
$$f_n(q) = \int \rho_n(r).\exp\left(2i\pi q.r\right)dr$$

Then, for all electrons associated with an atom: $\rho\left(r\right) = \sum_n \rho_n\left(r\right)$

Then, we have the atomic scattering factor: $f\ \ (q) = \int \rho\ \ (r).\exp\left(2i\pi q.r\right)dr$

→The atomic scattering factor can be written as the Fourier transform of the cloud of electron, i.e. the electron density function.

• • ***Scattering from an atom***:



→The atomic scattering factor can be written as the Fourier transform of the cloud of electron:

$$f = \frac{scattering\ \ power\ of\ \ atom}{scattering\ \ power\ of\ \ a\ single\ electron}$$

- • ***<u>Scattering from planes of atoms</u>***:

When the x-ray beam impinges on a crystalline material, all of the atoms will scatter x-rays in all directions. However, the periodic distribution of atoms on planes may cause constructive, or destructive, interference of the coherent component of the scattered radiation from the individual atoms, depending on the spacing between the planes, and the wavelength of the incident radiation.

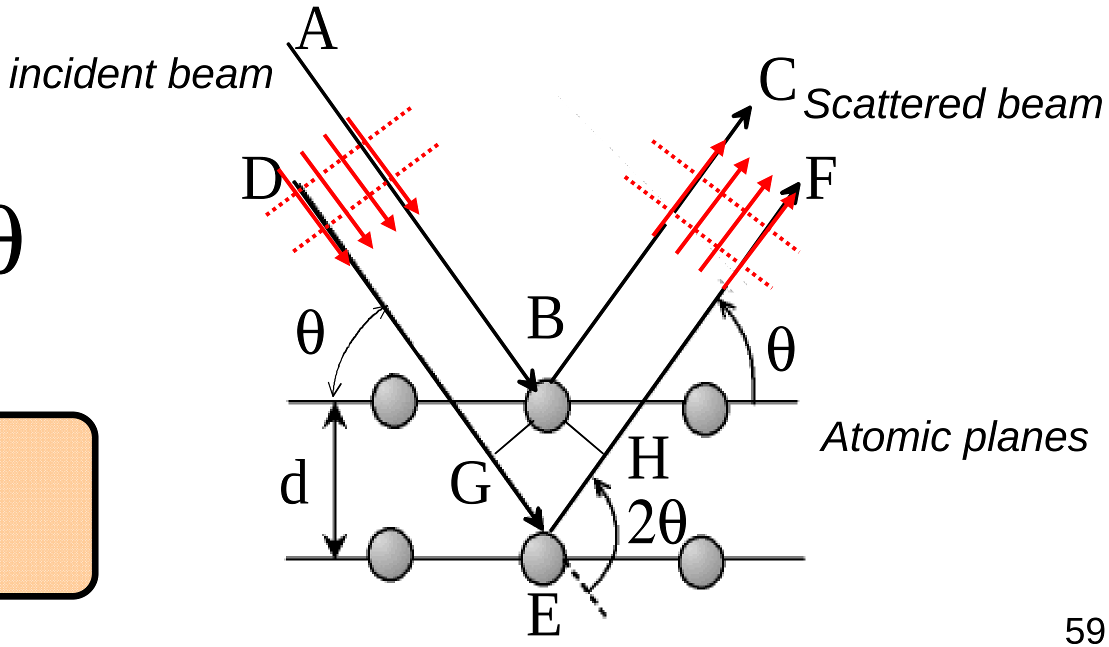
If a parallel x-ray beam impinges on a crystal where the (hkl) planes are parallel to the surface, the 2 waves ABC and DEF will be in phase, and so mutually reinforce each other if the path difference GEH is an integral multiple (n) of the radiation wavelength.

-Since GE=EH= d. sinθ, constructive interference will occur when:

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

Bragg's law (1912)

$$\boxed{\lambda = 2d_{hkl}.\sin\theta}$$



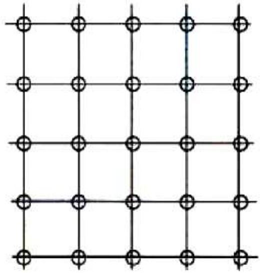
● ● ***<u>Scattering from planes of atoms (other approach)</u>***:

When the x-ray beam impinges on an actual three dimensional crystalline material, there are a very large number of atomic planes. Thus the large number of mutually reinforcing beams causes appreciable diffracted intensity at the correct angles (Bragg angles).

Along directions that do not satisfy Bragg's law, the scattered waves are out of phase, resulting in destructive interference and no diffracted intensity.

The other, more satisfactory, way to think about diffraction from lattices is the method due to von Laue, which does emphasise scattering from atoms and their constituent electrons and nuclei. The scattering angle is 2θ. The planes of the crystal are characterised by the Fourier coefficients of the electron density ρ(r) *(for X-ray scattering) or of the interaction potential V(r) (for electron scattering)*. *In either case we can write the scattering agent in terms of a Fourier series based on the reciprocal lattice.*

i.e. the other approach we have done for atoms can be employed for the crystal, it consist to consider that the electron density of a crystal may be written:



$$\rho(r) = \sum_i \rho_i(r).\delta(r - r_i)$$

where $\rho_i(\mathbf{r})$ is the electron density associated with the atom centered at the vector $\mathbf{r}\text{-}\mathbf{r}_i$.

We have seen that scattering amplitudes of atoms may be expressed in terms of the Fourier transform of a electron distribution in real space. $\rho_i(\mathbf{r})$ is the electron density associated with the atom centered at the vector $\mathbf{r}-\mathbf{r}_i$.
It is the same for the crystal. Let us define an unit cell (a,b,c) containing only one atom with an electron distribution of $\rho_0(\mathbf{r})$ *(for a sake of simplification → we will see later the changes induced by several atoms : structure factor):*

$$\rho(r) = \rho_0(r).\sum_l \sum_m \sum_n \delta\big(r - (la + mb + nc)\big).s(r)$$

s(r) is a shape function

→The scattering from planes of atoms is written as FT(density of electron)

To perform this calculatus, we need to define « the reciprocal lattice » or « the reciprocal space ».

The reciprocal lattice is difficult to comprehend from a physical standpoint. It is an imaginary construct used for the convenience of crystallography.
The reciprocal lattice is just as 'real' to the crystallographer or 'solid stater' as the real lattice, as it is the natural space in which to discuss waves in lattices, and to enumerate the available states .

Reciprocal space

The reciprocal space is defined by vectors a*,b*, c* such that (with V unit cell volume):

$$\vec{a}^* = \frac{\vec{b} \wedge \vec{c}}{\vec{a}.(\vec{b} \wedge \vec{c})} = \frac{\vec{b} \wedge \vec{c}}{V}$$

$$\vec{b}^* = \frac{\vec{c} \wedge \vec{a}}{V}, \quad \vec{c}^* = \frac{\vec{a} \wedge \vec{b}}{V}$$

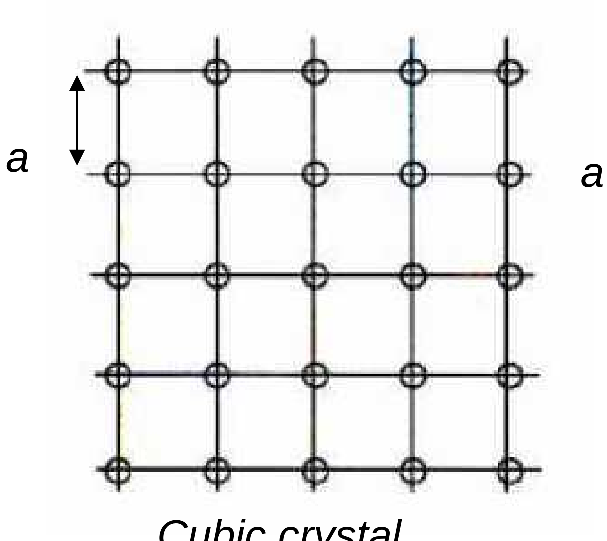
$$\xrightarrow{\textit{So that}} \begin{cases} a^*.b=a^*.c=b^*.c=b^*.a=\ldots.=0 \\ a.a^*=b.b^*=c.c^*=1 \end{cases}$$

Then , the Fourier transform of a crystal gives:

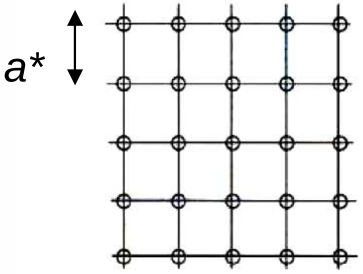
$$F(u) = FT[\rho(r)] = F_0(u).\sum_{l}\sum_{m}\sum_{n} \delta\big(u - (ha^* + kb^* + lc^*)\big).S(u)$$

Thus, we have scattering intensities only at the reciprocal lattice points. The distribution of the scattered intensities is described by S(u).

• *NOTES ON RECIPROCAL SPACE*

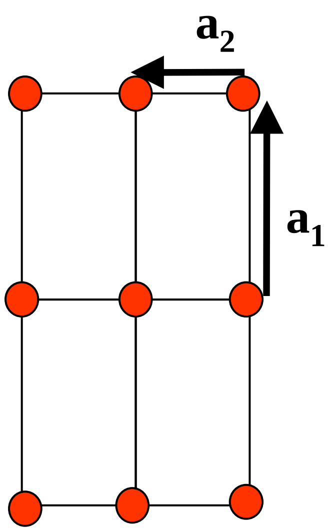


Cubic crystal

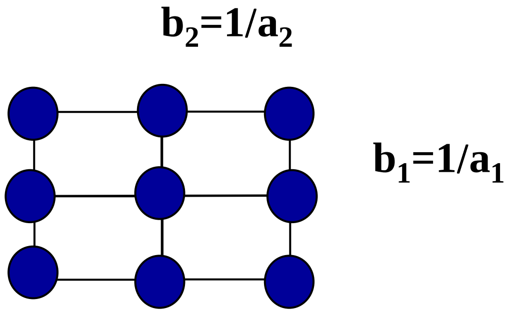


Reciprocal space

- The reciprocal space of the reciprocal space is the real space
- The reciprocal space of a FCC crystal is a bcc structure.
- The reciprocal space of a BCC crystal is a fcc structure.
- 2 definitions:
  - → $a.a^*=1$
  - $a.a^*=2\pi$



Real

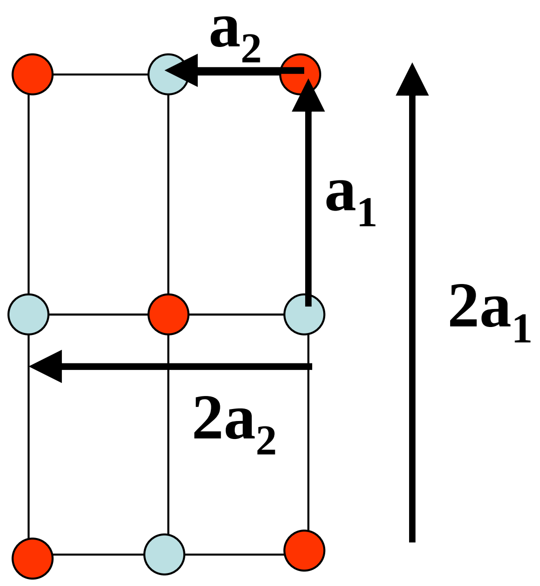


Reciprocal

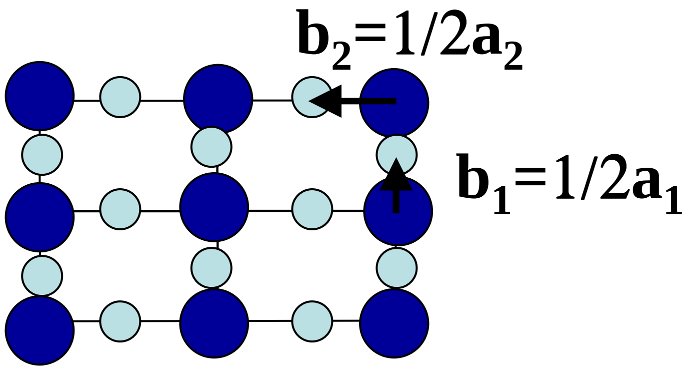
- The reciprocal space of a cubic crystal structure is cubic
- The reciprocal space of tetragonal crystal structure is tetragonal.

• *NOTES ON RECIPROCAL SPACE*

- Doubling the periodicity in real space produces twice as many diffraction spots in reciprocal space.
- This effect can be produced chemically with an ordered binary alloy.
- A doubling of the periodicity in real space will produce half-order spots in reciprocal space.



Real



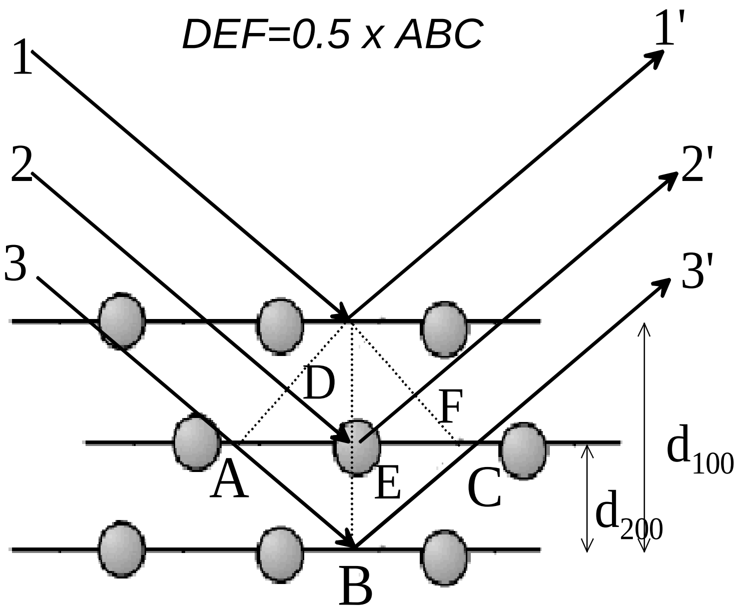
Reciprocal

●The structure factor of a unit cell:

For the actual derivation of bragg’s law, the three-dimensional symmetry of the unit cell has to be taken into account. Indeed, if Bragg’s law is not satisfied no diffraction can occur, but in certain cases there is no diffracted intensity at angles predicted by Bragg’s law. This effect is due to the particular positions of the atoms in the unit cell.

Illustration:
-Consider a BC crystal.
-if the phase difference between the rays 1 and 3 is λ
→diffraction should occur

-But phase difference between 1 and 2 is 1/2xλ. Thus, ray 2 will interfere destructively with ray 1
→ No diffracted intensity



●The structure factor of a unit cell:

The total intensity diffracted by a given unit cell can be determined from the summation of the waves from the individual atoms. If the scattering amplitude from the jth atom, with fractionnal dimensionless coordinates uj, vj,wj, is fj, the relative intensity scattered by the unit cell for a given reflection hkl is proportional to

$$F_{hkl} = \sum_{j=1}^{N} f_j.\exp\left(2\pi i\left(h.u_j + k.v_j + l.w_j\right)\right)$$

N *is the number of atoms present in the unit cell.*

Bravais lattice	Structure factor	Reflections for	NO Reflections
Simple Cubic	F=f	All	None
BCC	F=f(1+exp(iπ(h+k+l))	(h+k+l) even	(h+k+l) odd
FCC	F=f[1+exp(iπ(h+k)+exp(iπ(h+l)+exp(iπ(l+k)]	h,k,l unmixed	h,k,l mixed

Examples of structure factors for selected lattices

The total scattered intensity is proportional to the square of the absolute value of Fhkl:

$$I \propto \left|F_{hkl}\right|^2 \propto \left|\sum_{j=1}^{N} f_j.\exp\left(2\pi i\left(h.u_j + k.v_j + l.w_j\right)\right)\right|^2$$

Experimental utilization of Bragg's law

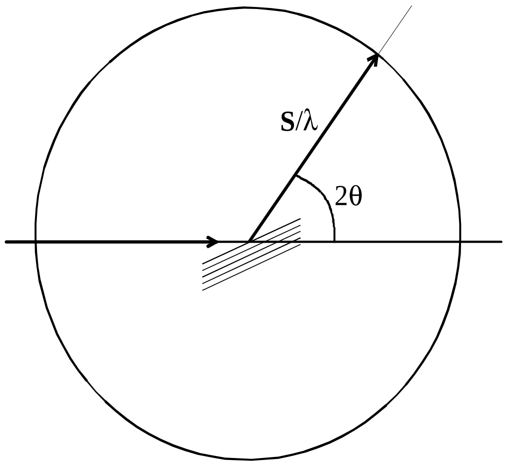
-<u>**Monochromatic**</u>
-*Polychromatic*

●*The diffraction condition can be written as :* $\mathbf{S}=\mathbf{S}_0+\lambda.\mathbf{r}^*$ *where* $\mathbf{r}_{hkl}^*=n(ha^*+kb^*+lc^*)$
With n integer et hkl indices of the smallest hkl (first reciprocal node)
●*the incident beam has the propagation direction : vector* $\mathbf{S}_0$
●*the diffracted beam has the propagation direction : vector* $\mathbf{S}$ *(situated in the plane defined by* $\mathbf{S}_0$ *and the normal to the diffracting planes (vector* $\mathbf{r}_{hkl}^*$*)*

● ● *the diffracted beam is such that: the angle θ between plane and incident beam is the same the between diffracted beam and planes.*
● ● *this angle theta satisfied the Bragg's law*

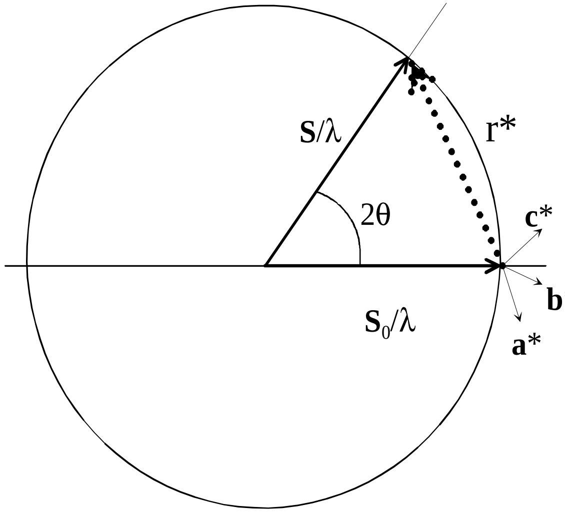
● ● **Bragg**

$$\lambda = 2d_{hkl}.\sin\theta$$



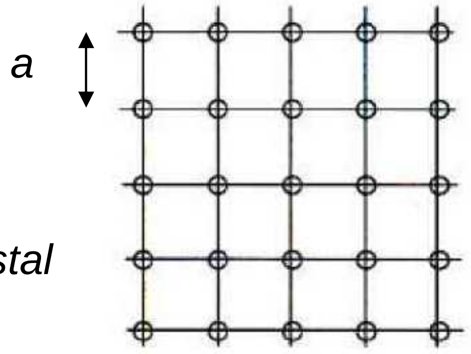
● **Laue**

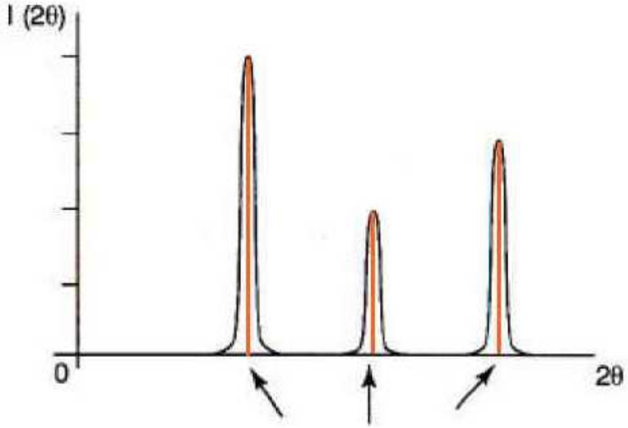
$$\vec{s} = \vec{s}_0 + \lambda.\vec{r}^*_{hkl} \quad \textit{with} \quad \vec{r}^*_{hkl} = h.\vec{a}^* + k.\vec{b}^* + l.\vec{c}^*$$



Example of diffractogram of a polycrystalline specimen :

cubic crystal

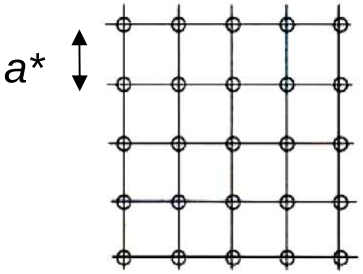




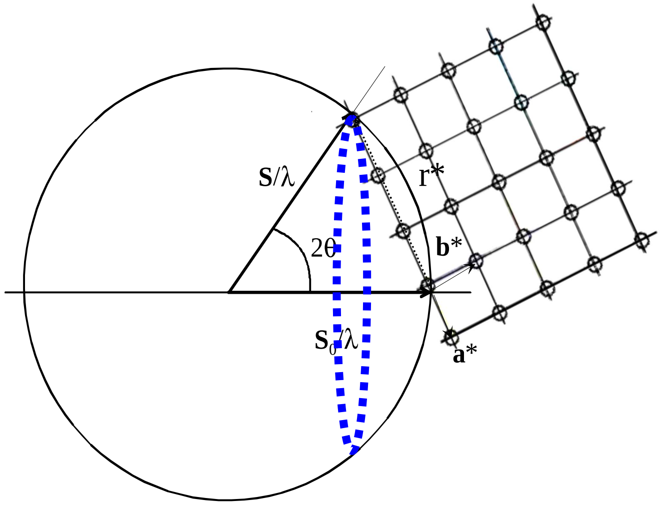
Bragg’s peak

- The Ewald construction is a way to visualize the Laue condition that the change is wavevector is a vector of the reciprocal lattice – **K= k’ – k**, (or r*=S/λ-S_0/λ) where k= 1/λ is the magnitude of the incident wavevector.

Ewald



Reciprocal space



Scattered intensity :if theta is a Bragg’s angle or if r is a reciprocal space vector.*

Intensity scattered by a small crystal:

-incident beam I_0
-the effect of absorption are negligible as the crystal is small.
-the crystal has the dimensions A, B, C where $A=N_a.a$, $B=N_b.b$, $C=N_c.c$
-there is only one atom per unit cell (a,b,c) of atomic scattering factor f

The scattering wave is the sum of the Na.Nb.Nc waves of amplitude $f.I_e$. *If we use the complex notation (as we have done for the scattering factor), the amplitude wave scattered by an atom can be written as :*

$$f.I_e \exp(i\varphi) = f.I_e.\exp(-2i\pi(hu+kv+lw))$$

Thus the intensity for the whole crystal is :

$$I = f^2.I_e^2 \left| \sum_0^{N_a-1} \sum_0^{N_b-1} \sum_0^{N_c-1} \exp(-2i\pi(hu+kv+lw) \right|^2$$

Using the fact that:

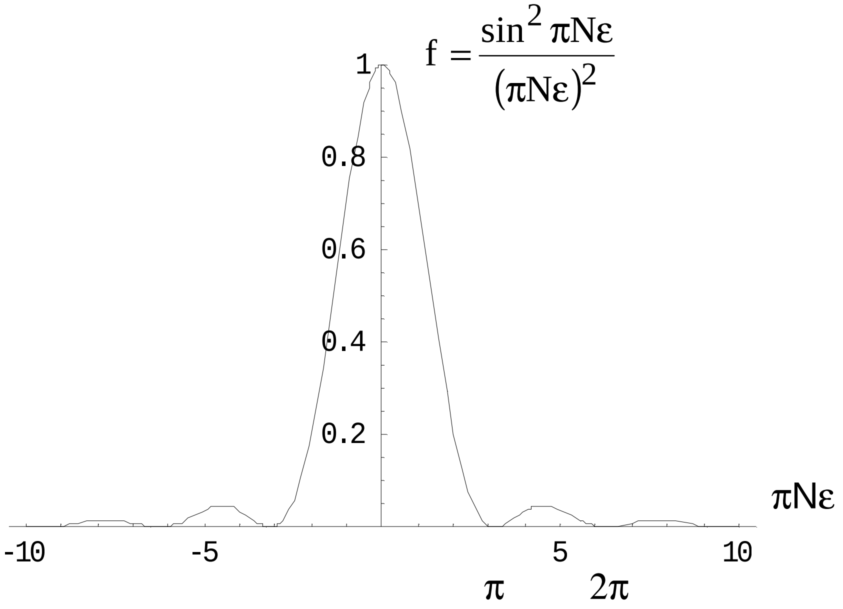
$$\sum_{0}^{N-1} \exp(-2\pi i h) = \frac{\exp(-2\pi i N h) - 1}{\exp(-2\pi i h) - 1} = \frac{\sin \pi N h}{\sin \pi h} \exp(-i\pi(N-1)h)$$

$$I = f^2 . I_e^2 \frac{\sin^2 \pi N_a h}{\sin^2 \pi h} . \frac{\sin^2 \pi N_b k}{\sin^2 \pi k} . \frac{\sin^2 \pi N_c l}{\sin^2 \pi l}$$

If h,k,l are integers $I = f^2 I_e^2 . N_a^2 . N_b^2 . N_c^2$ exact condition of reflection. But if N_i are large numbers, the range where I≠0 is very small.

If we substitute:

$$h \rightarrow h + \varepsilon_a$$
$$k \rightarrow k + \varepsilon_b$$
$$l \rightarrow l + \varepsilon_c$$

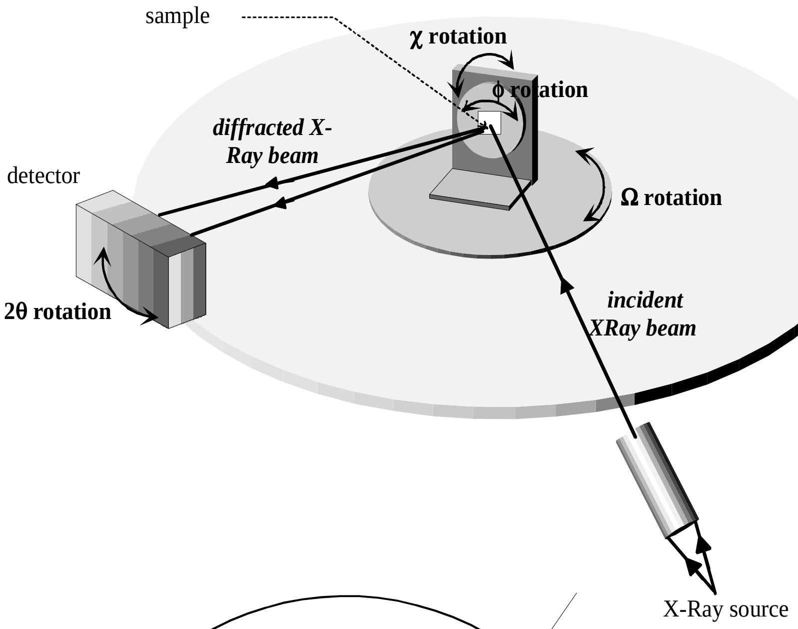


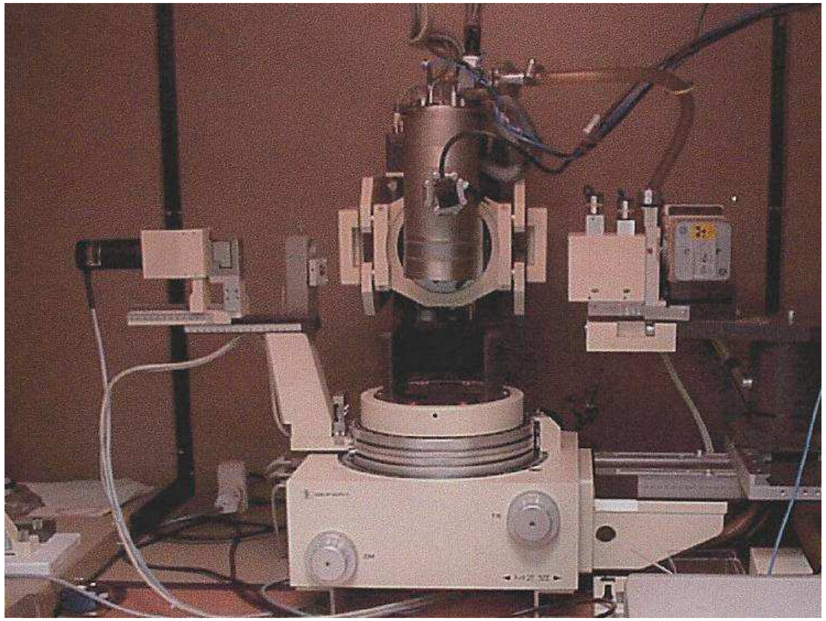
$$f = \frac{\sin^2 \pi N \varepsilon}{(\pi N \varepsilon)^2}$$

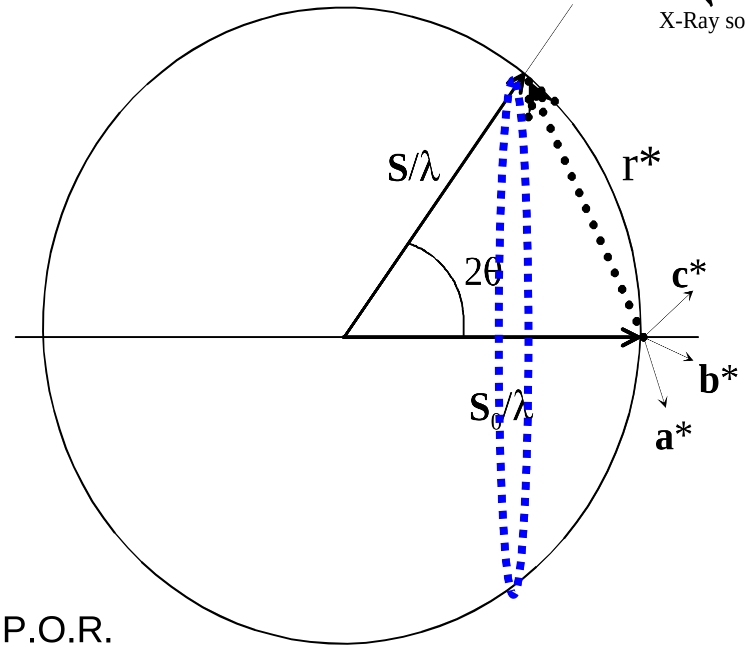
We obtain a domain in the reciprocal space where I≠0. The intensity is non negligible if ε<1/N.

→ Thus if the size of the crystallite decreases, the domain where I≠0 is increasing. In other word, the FWHM increases…

Diffractometer geometry

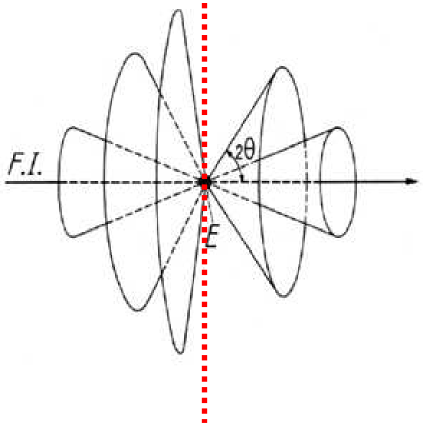






Reflection geometry *Transmission geometry*

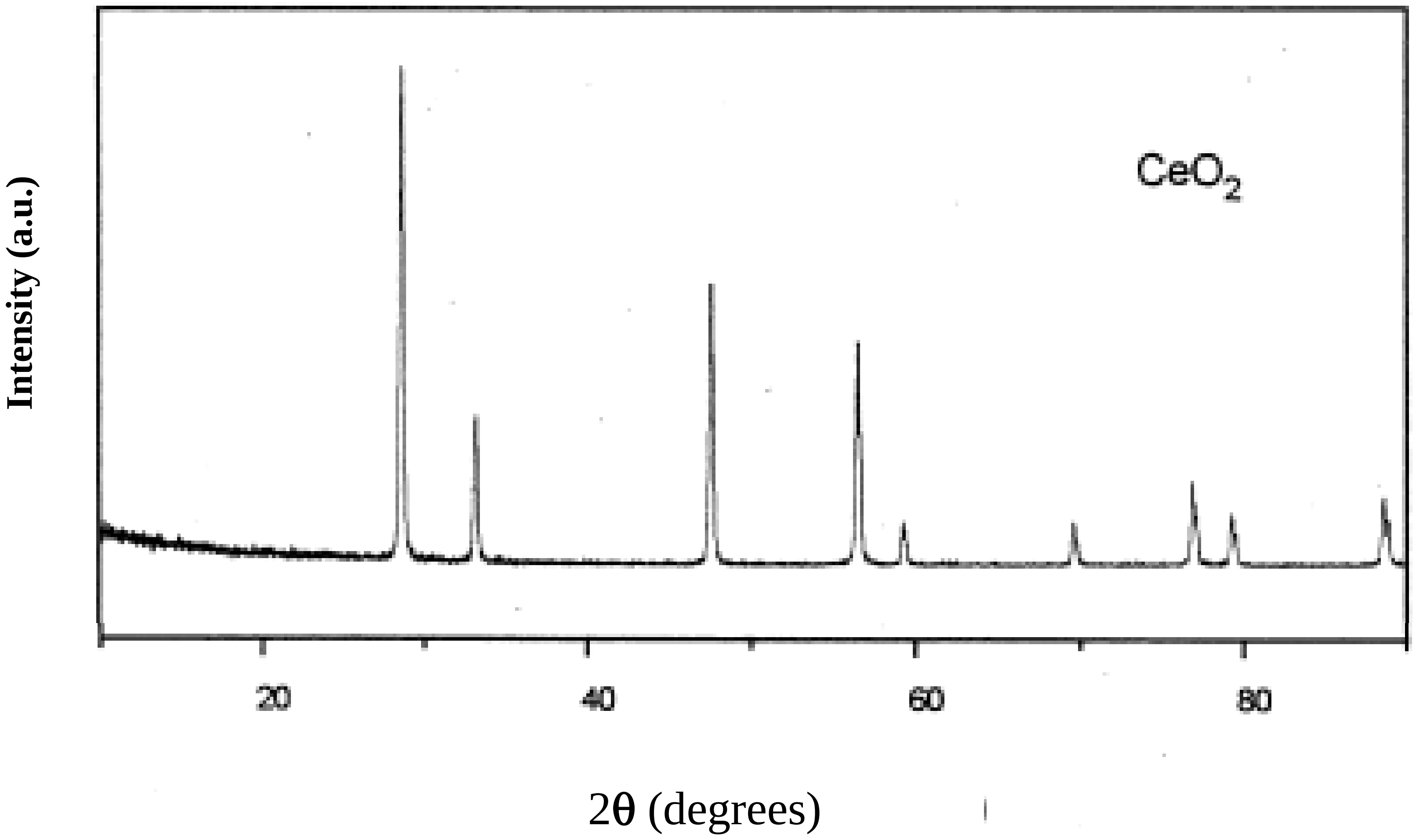
Incoming XR

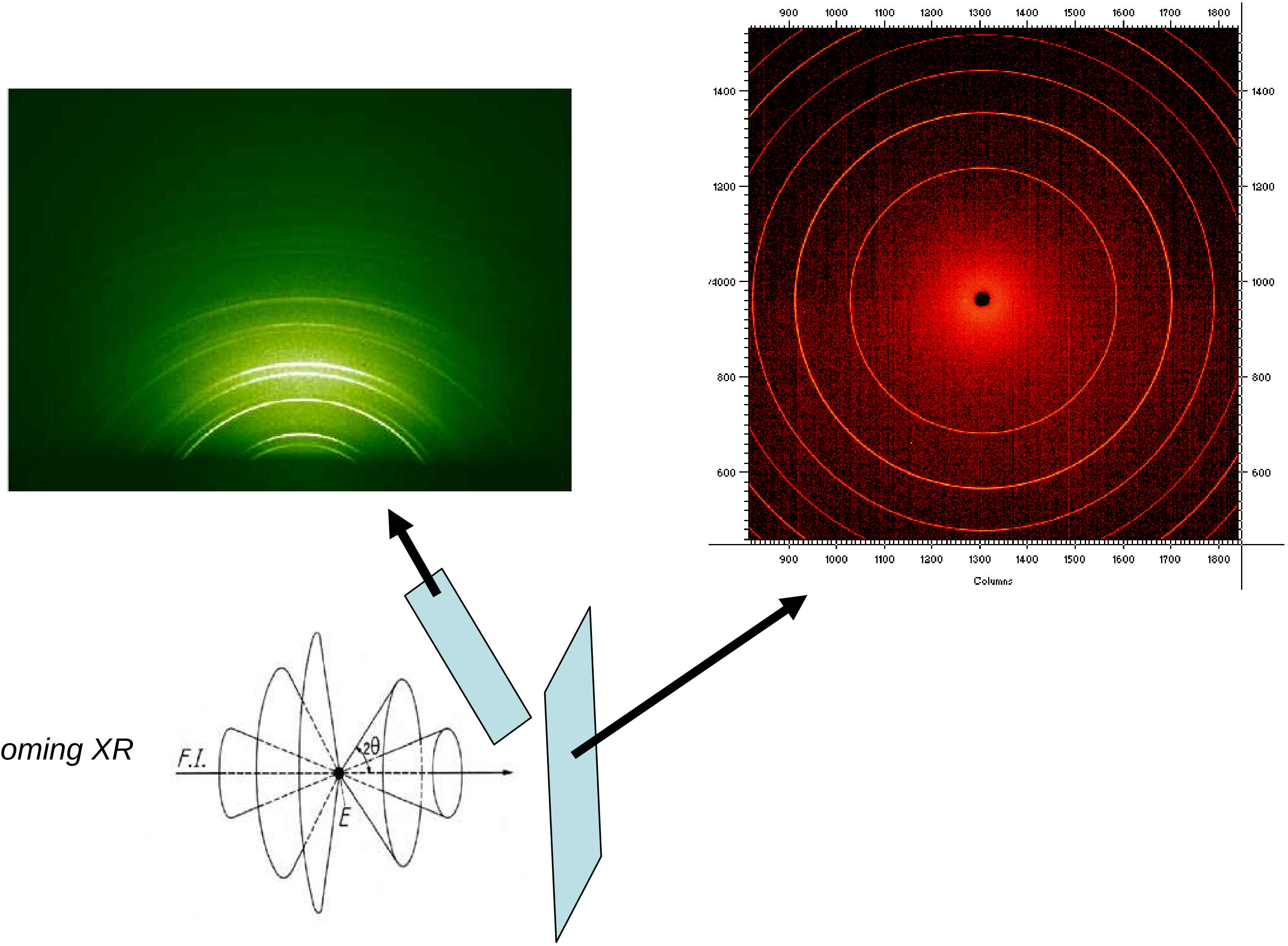


Each cone is characteristic of a given dhkl

P.O.R.

Typical diffractogram: theta/2theta scan




900
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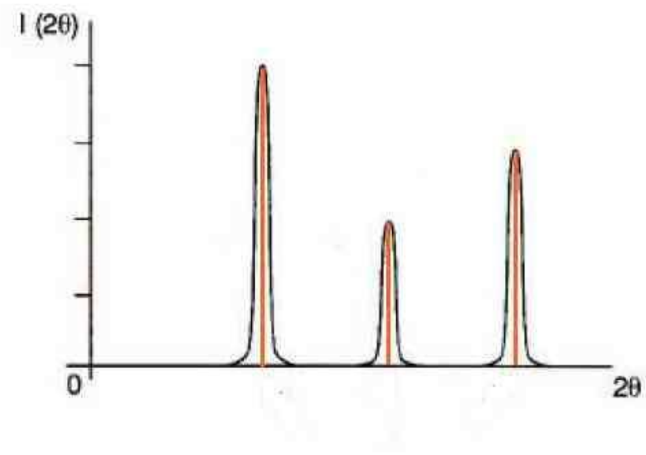
Incoming XR

- Intensity of diffracted lines for polycrystals:



From an experimental scan, we can observed that the diffracted intensity is not equal for each peak.
Why ?

The relative diffracted intensities of Bragg peaks for a given diffraction pattern are dependent on six parameters:

+ structure factor (previously discussed)
+ polarization factor
+ Lorentz factor
+ multiplicity
+ absorption factor
+ temperature factor.

●Polarization factor and Lorentz factor:

a) The polarization factor is a trigonometric factor that is a function of 2theta, it described the variation of scattered intensity with scattering angle (x-ray beam is an electromagnetic wave). This correction has already be seen in thomson equation.

Obviously, the use of a monochromator is changing the polarization correction.

b) The Lorentz factor is a collection of trigonometric terms that describes the dependence of the diffracted intensity (maximum or integrated) on the diffraction angle. There are different factors that contribute to the Lorentz factor (the dependence of diffracted intensity from any one crystallite, the diffracted intensity per unit length of the diffraction cone, the number of grains which are oriented such that they can diffract at a given angle 2theta.

⊗The Lorentz factor and the polarization factor are usually combined together to form the LP factor:

$$L.P. = \frac{1+\cos^2 2\theta}{\sin^2\theta.\cos\theta}$$

This relation is valid only for an unpolarized incident beam

$$\mathrm{L.P.} = \frac{1+\cos^2 2\alpha.\cos^2 2\theta}{1+\cos^2 2\theta}$$

This relation is valid only for a polarized incident beam, i.e. using a monochromator (α is the incident angle on the monochromator)

- Multiplicity factor:

this term describes the number of equivalent planes that can diffract at a given Bragg angles. For example, for a cubic crystal all eight members of the {111} family have the same d spacing and any grains in which one of these planes satisfy the Bragg conditions diffract at the same angle.

Ex: cubic crystal,
m=6 for {100}, m=12 for {110},

- Temperature factor:

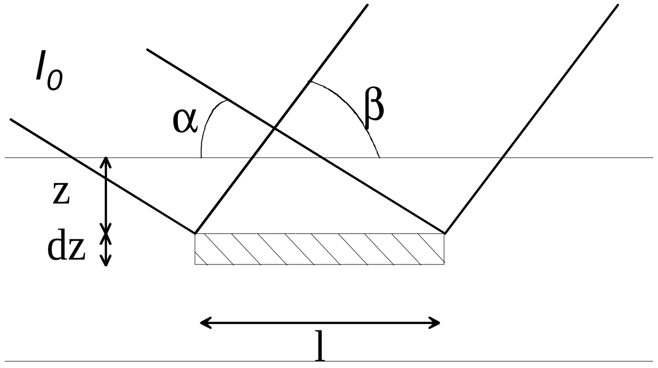
Atoms vibrate around their mean positions, with an average displacement that is proportional to the temperature. This displacement is approximately 5-10% of the atomic spacing at room temperature and increases with increasing temperature.

The values of atomic scattering factor f do not include a vibration term and must be corrected for the temperature effect: $f(T)=f.\exp(-B\sin^2\theta/\lambda^2)$ where B is a constant related to the atomic displacement and are tabulated.

This affects constructive interference and the total diffracted intensity decreases. These decreases are especially noticeable at high 2theta angles.

- Absorption factor:

Relatived diffracted intensities may also be affected by absorption, which is directly related to the path length the incident and diffracted beams traverse in the specimen for a given geometry.



The total energy reaching a layer of length l and thickness dz, located at depth z, is proportional to aI0 . exp(-µ. distance) where a is the fraction of incident energy by unit volume.

If a is the volume fraction of crystallites that can diffract at this angles:

$$dI_{diff.} = \frac{I_0.a.b.l}{\sin\alpha}.\exp(-\mu.z\left(\frac{1}{\sin\alpha}+\frac{1}{\sin\beta}\right)).dz$$

In some experiment, an additional rotation can be added, inclinaison ψ, and the substitutions have to be performed in the above equation:

$$\alpha = \theta + \psi \quad \text{and} \quad \beta = \theta - \psi$$

The total diffracted intensity is obtained by integrating for a thin film of thickness z:

$$I_{diff.} = \int_{z=0}^{z} dI_{diff}$$

The diffracted intensity recorded at a distance r from the specimen is (for small crystallites and isotropic texture (random distribution of crystallite)):

$$dI = I_0 . r_e^2 . \frac{1+\cos^2 2\theta}{2} . \frac{1}{16\pi r \sin^2\theta \cos\theta} . \lambda^3 . F_{hkl}^2 . n . \frac{1}{V^2} . DW . dV$$

*dI intensity by unit length of diffraction line recorded at the distance r from the specimen

*r_e^2=7;9x10^{-26} cm²

*Polarisation factor and lorentz factor (for Debye Scherrer geometry)

*Fhkl structure factor

*n multiplicity factor

*DW: Debye-Waller correction (or temperature factor)

*V: volume of the unit cell

***dV: volume of the powder specimen. If the absorption was negligible in the whole irradiated volume V, dV can be replaced by V to obtain the total diffracted intensity**

Difference between elect. diffraction and XRD:

$$\lambda = 2d_{hkl}.\sin\theta$$

XR ~5 – 10 keV ~ 1.5 Å → 2θ from 10° to "180°"

el. ~ 100-200 keV ~ 0.07 Å → 2θ from 0° to 10°

Radius of Ewald sphere : $R_{ES}=1/\lambda$ ⇒ $R_{ES}(XRay) << R_{ES}(elect)$

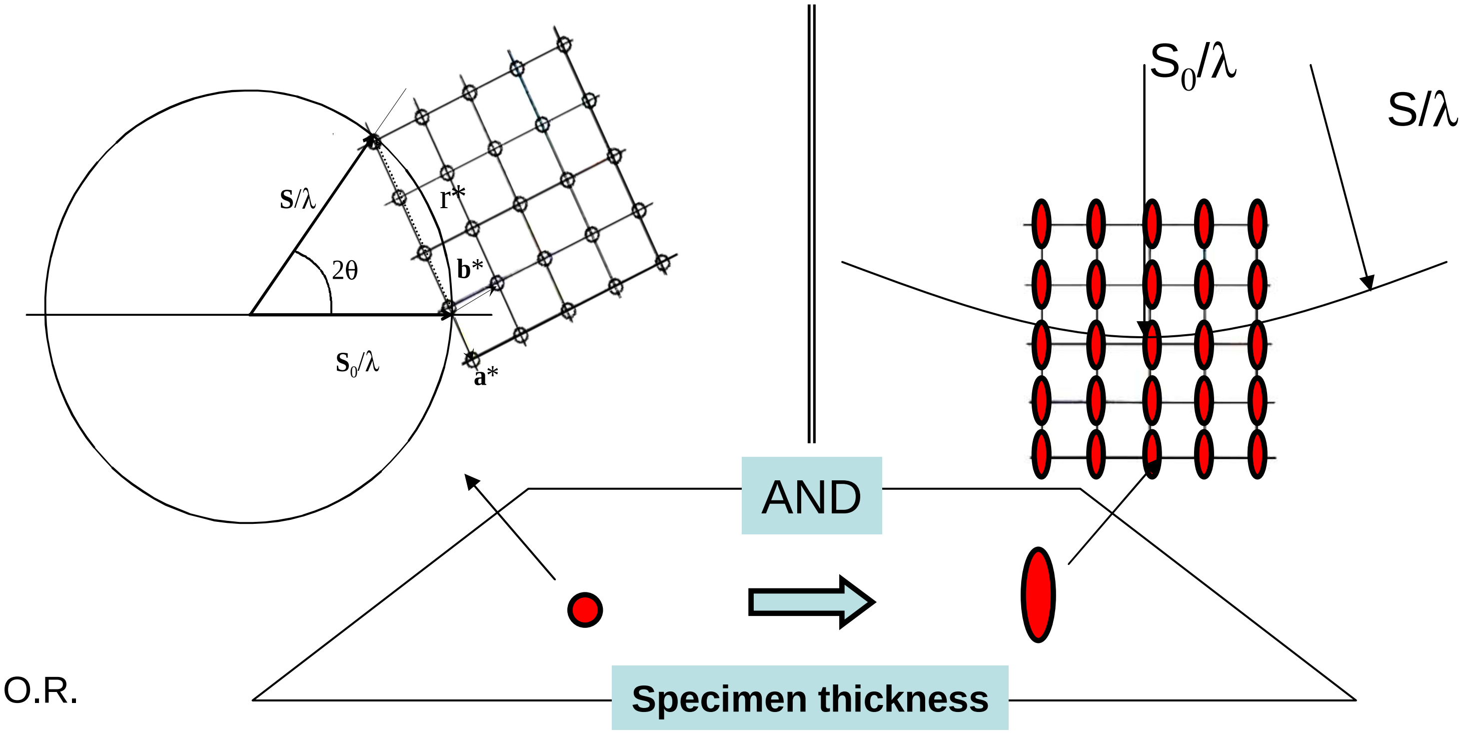
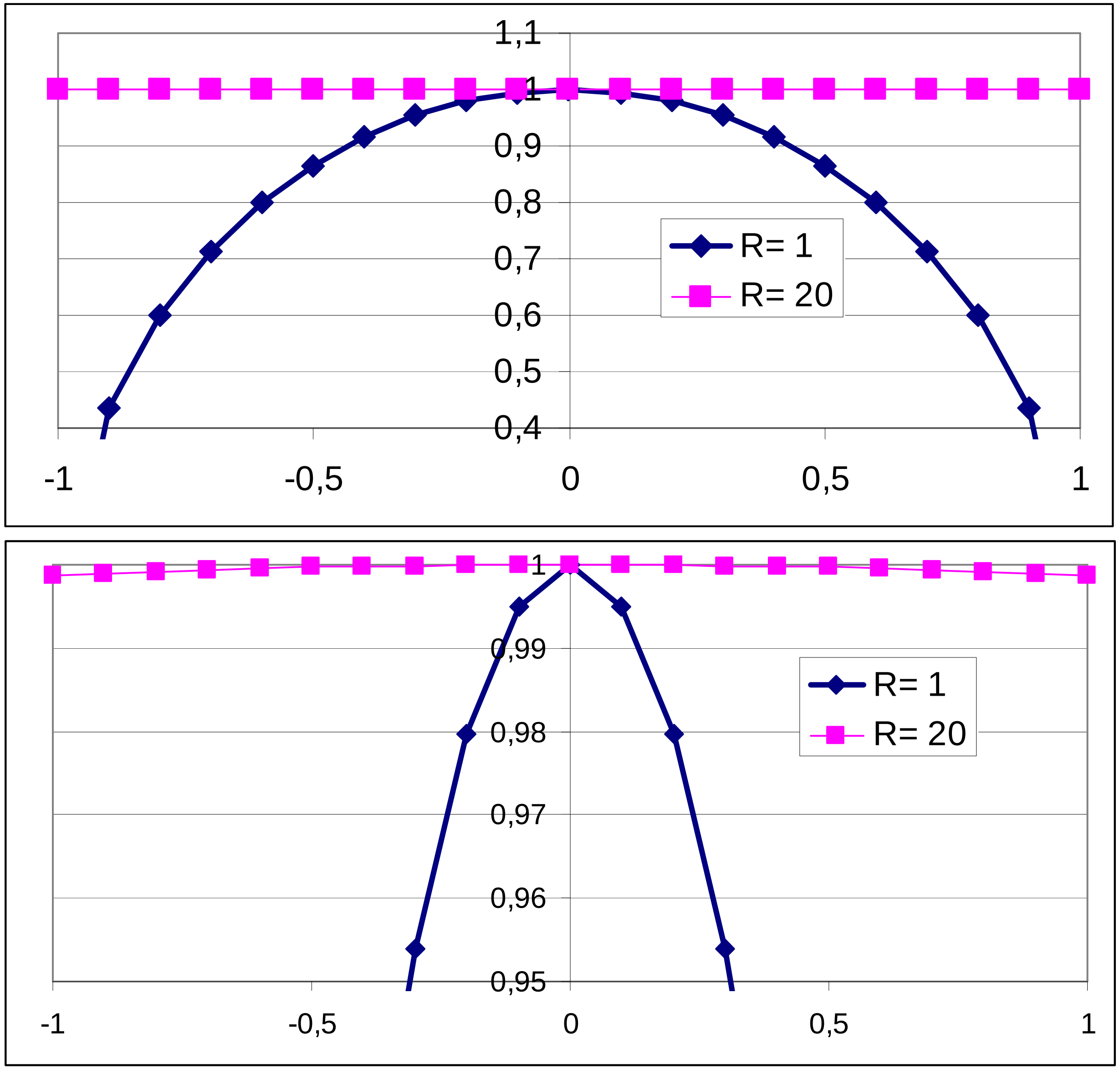
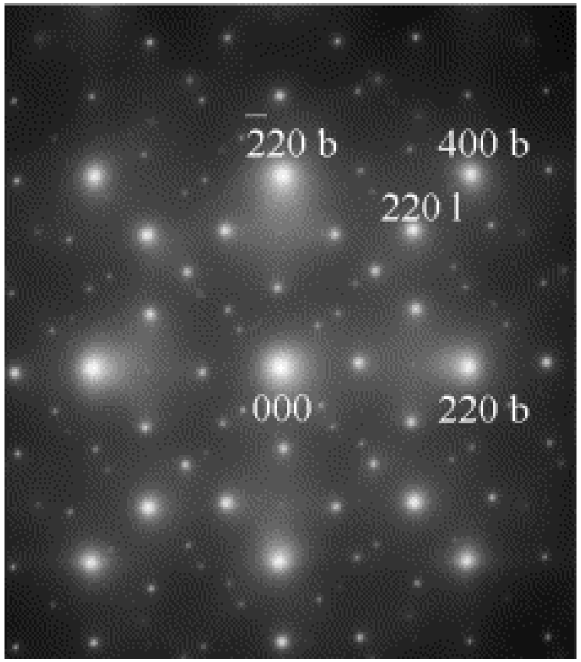


Illustration: Let us plot a circle for a radius (XRay)=1 and for a radius of 20 (Electron)

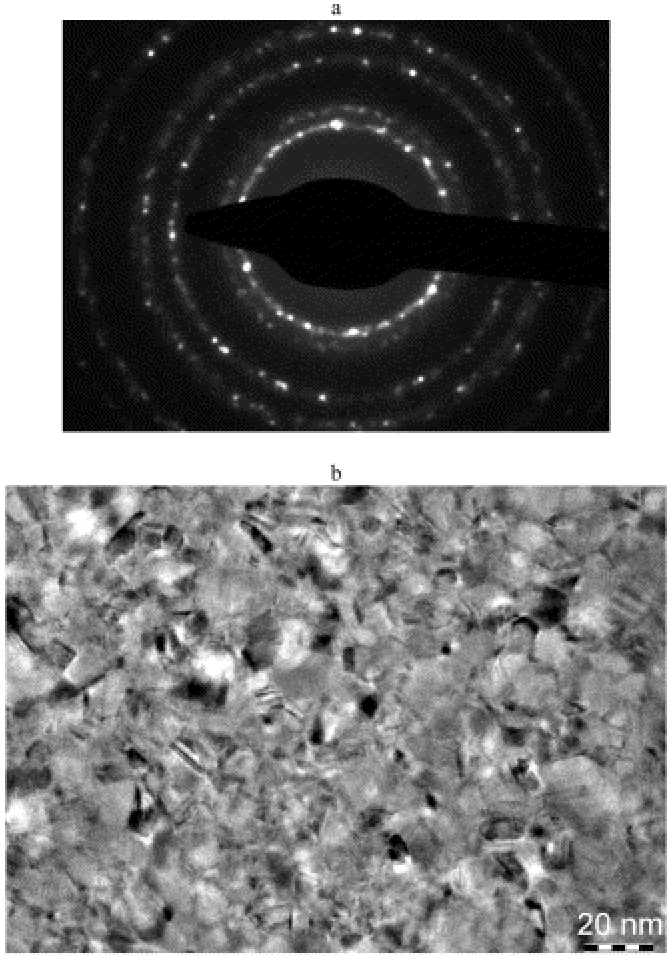


Difference between elect. diffraction and XRD:



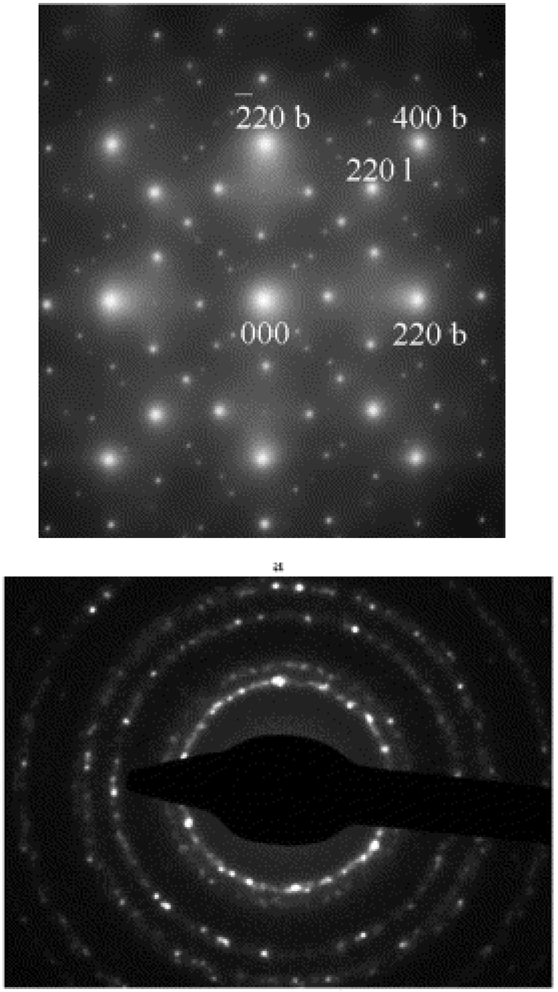
TEM plane-view diffraction patterns of the compliant structure **(single crystal GaAs)** . Index ‘b’ is for the substrate and ‘l’ for the layer

ED pattern of **polycrystalline gold**. (face-centered cubic lattice, a=0.408 nm)

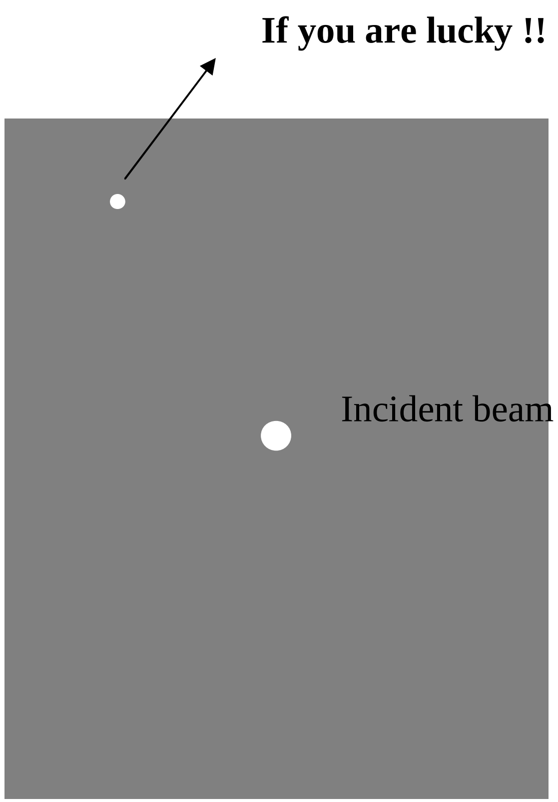


TEM plan view diffraction pattern (a) and image (b) of the 8.9 nm thick Au film. In (a) the {111}, {200}, {220}, {311} rings are observed at increasing diffraction angles, none of the ring have higher intensities regions arranged in symmetric pattern (three-fold or four-fold) showing no discernible texture.

Difference between elect. diffraction and XRD:



TEM
(100 keV)



XRD
(~8 keV)

Experimental applications of XRD:

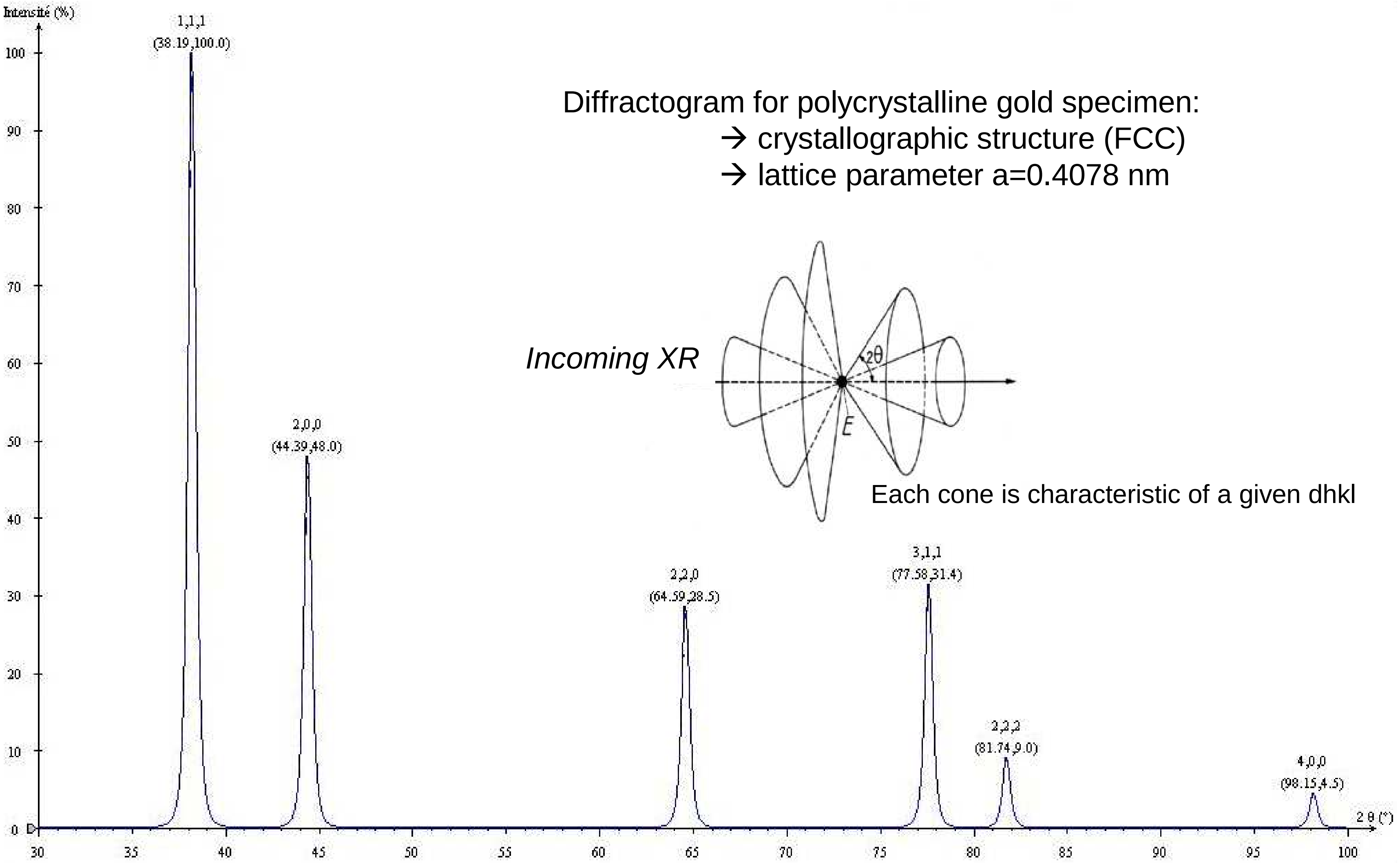
Phase identification: relies mainly on the positions of the peaks on the diffractogram and to some extent on the relative intensities of the peaks.

From the shapes of the peaks, additional and often valuable informations can be extracted. The shape, particularly the width, of the peak is a measure of a distribution of d-spacing. For example, this distribution results from ponctual defects (as vacancy, interstitials, impurities) or defects such as dislocations.
Crystallite size can also cause peak broadening:

- The well known Scherrer equation may be used in some specific cases. Once instrument effects have been excluded, the crystallite size is easily calculated as a function of peak width, peak position and wavelength.
- More sophisticated methods takes not only the peak width into account but also the shape of the peak. (ex: Williamson-Hall, Warren-Averback). Those methods are capable of yielding both the crystallite size distribution and lattice microstrain. The Warren Averback method is based on a Fourier deconvolution of the measured peaks and the instrument broadening to obtain the true diffraction profile.

N.B.: The width of the peak is characterized by the full width at half maximum (FWHM). It is the simplest way to interpret measure of peak width. However, there is a second characterisation of peak width which is integral breadth. Integral breadth is simply the area under the peak divided by the peak height (after background removal). In other word, it is the width of a rectangle as high as the peak. The use of FWHM, compared to integral breadth, can for example overestimate the crystallite size.

Phase identification:



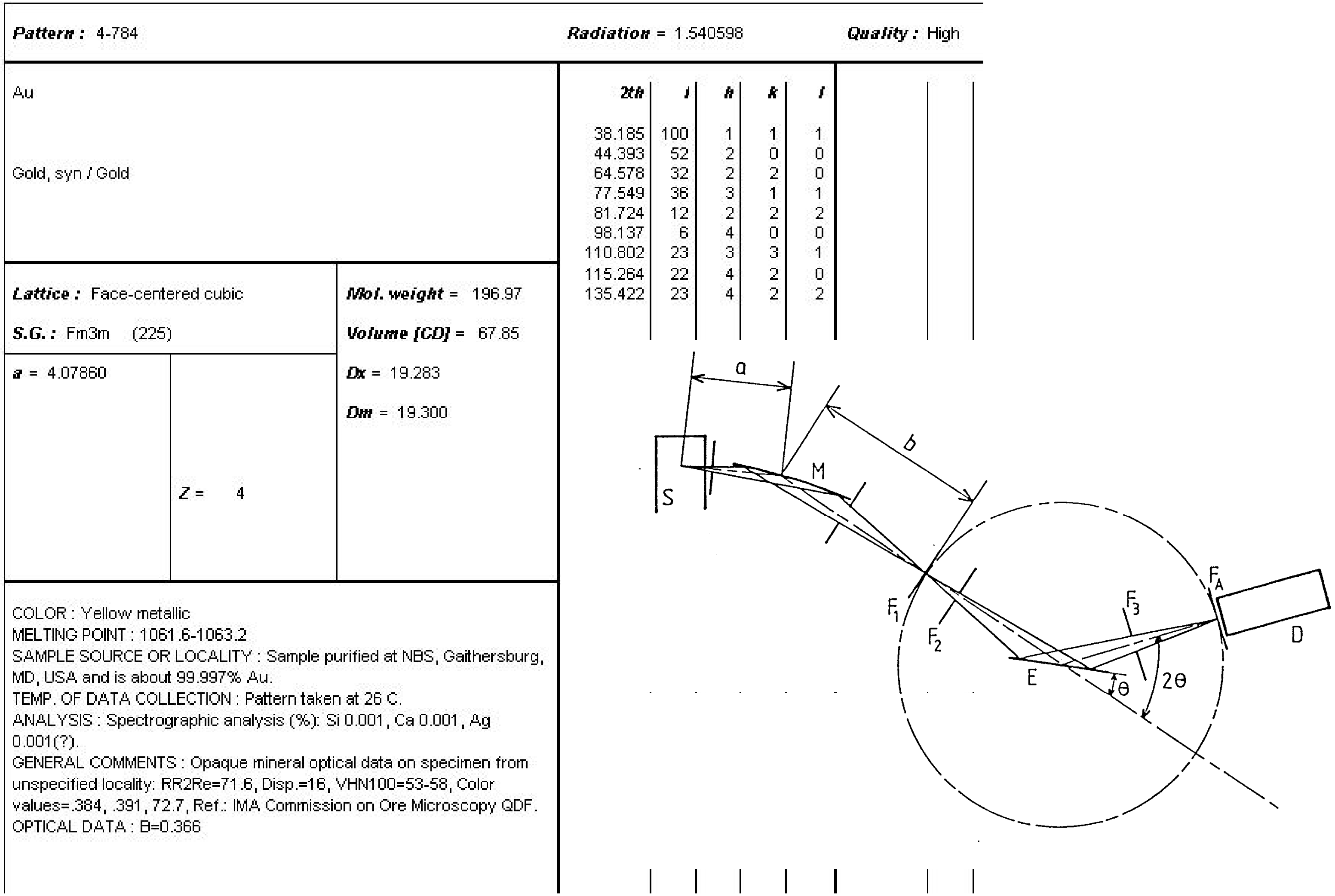
Diffractogram for polycrystalline gold specimen:
→ crystallographic structure (FCC)
→ lattice parameter a=0.4078 nm

Incoming XR

Each cone is characteristic of a given dhkl

What about the relative intensity ?

Typical database informations:



Pattern : 4-784

Radiation = 1.540598

Quality : High

Au

Gold, syn / Gold

2th	**i**	**h**	**k**	**l**
38.185	100	1	1	1
44.393	52	2	0	0
64.578	32	2	2	0
77.549	36	3	1	1
81.724	12	2	2	2
98.137	6	4	0	0
110.802	23	3	3	1
115.264	22	4	2	0
135.422	23	4	2	2

Lattice : Face-centered cubic

S.G. : Fm3m (225)

a = 4.07860

Z = 4

Mol. weight = 196.97

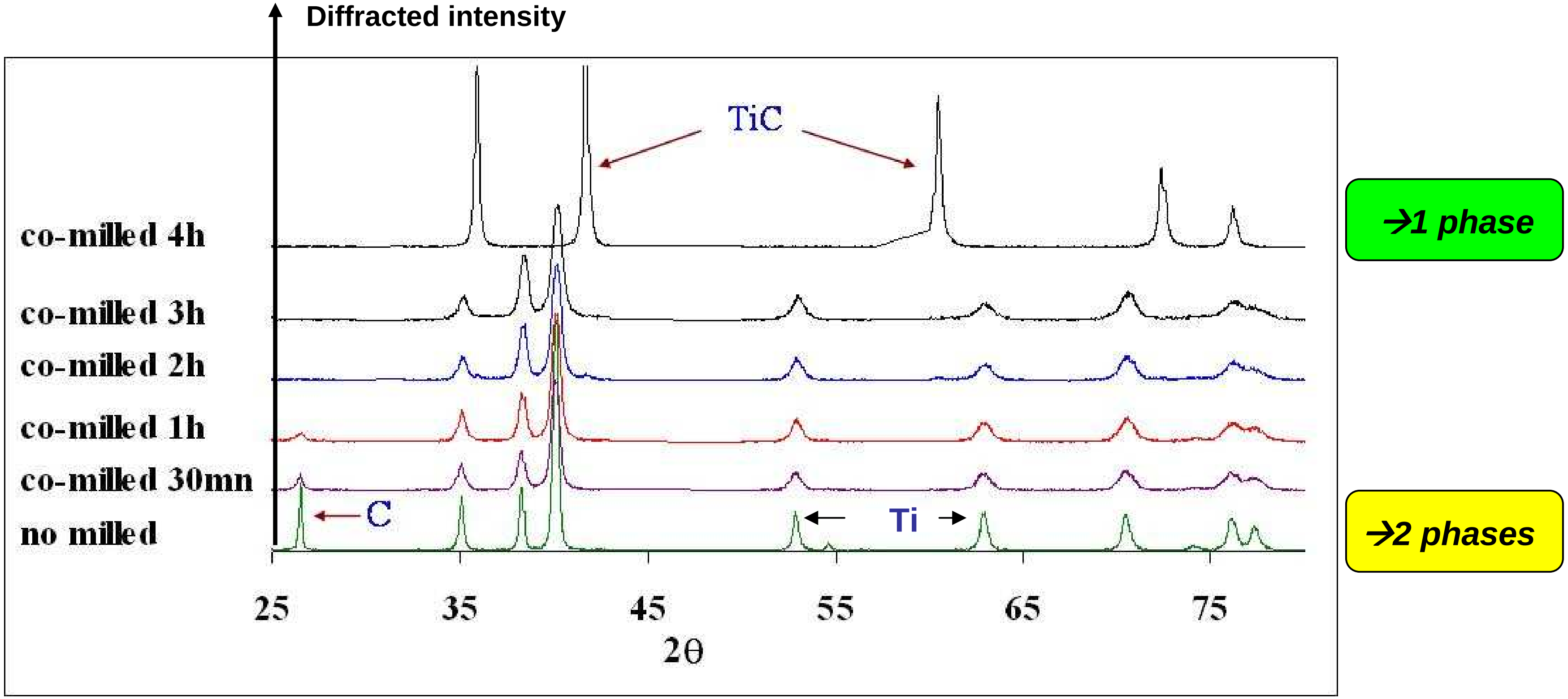
Volume [CD] = 67.85

Dx = 19.283

Dm = 19.300

COLOR : Yellow metallic
MELTING POINT : 1061.6-1063.2
SAMPLE SOURCE OR LOCALITY : Sample purified at NBS, Gaithersburg, MD, USA and is about 99.997% Au.
TEMP. OF DATA COLLECTION : Pattern taken at 26 C.
ANALYSIS : Spectrographic analysis (%): Si 0.001, Ca 0.001, Ag 0.001(?).
GENERAL COMMENTS : Opaque mineral optical data on specimen from unspecified locality: RR2Re=71.6, Disp.=16, VHN100=53-58, Color values=.384, .391, 72.7, Ref.: IMA Commission on Ore Microscopy QDF.
OPTICAL DATA : B=0.366

Phase identification: example of diffractogram



→Phase identification from the peak position and peak intensities

What about additional microstructural information ?

C
hexagonal
a=0,24704 nm
c=0,67244 nm
radiation 0,1540598 nm

graphite -2H
P63/mmc

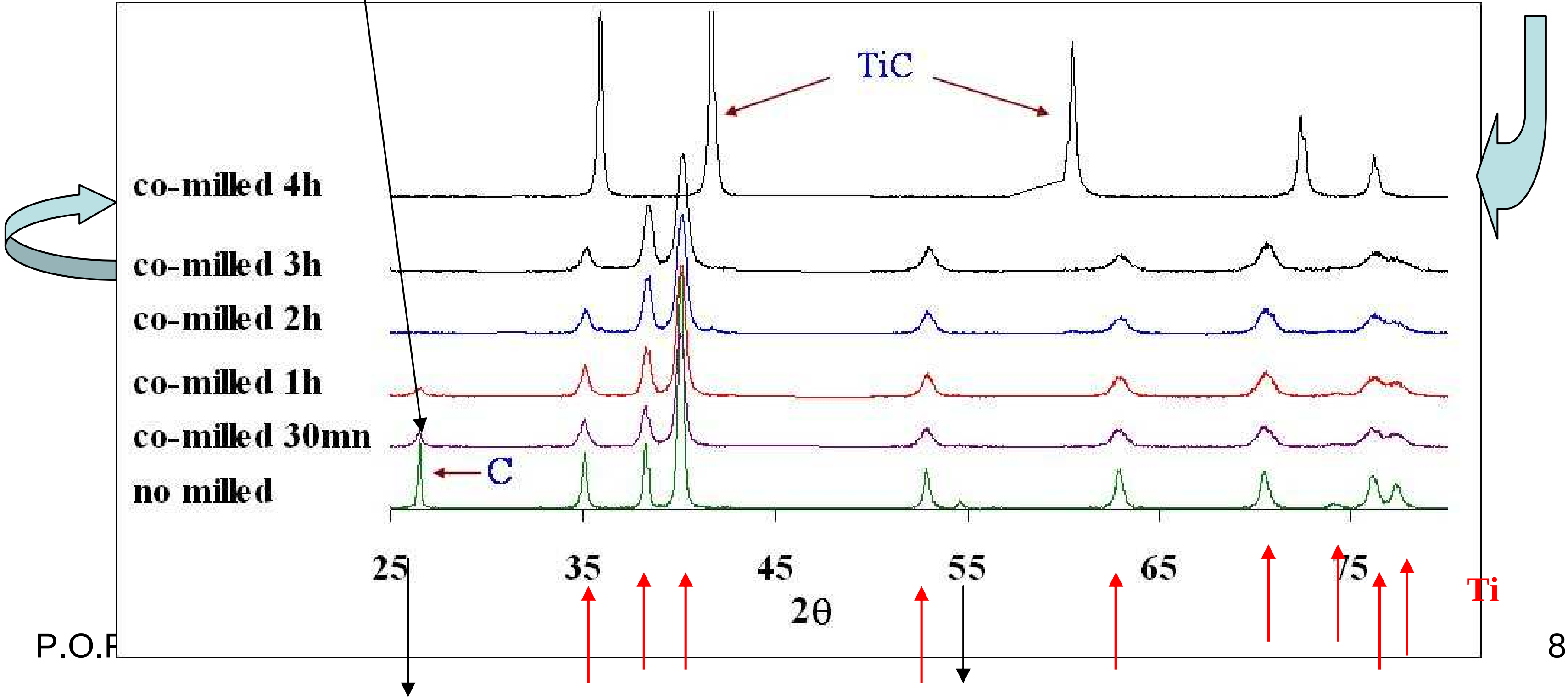
2th	rel. Int.	h	k	l
26,38	100	0	0	2
42,22	2	1	0	0
44,39	6	1	0	1
50,45	1	1	0	2
54,54	4	0	0	4
59,69	1	1	0	3
77,245	3	1	1	0
83,186	3	1	1	2
86,826	1	0	0	6
93,597	1	2	0	1

Ti
hexagonal P63/mmc
a=0,29505
c=0,46826

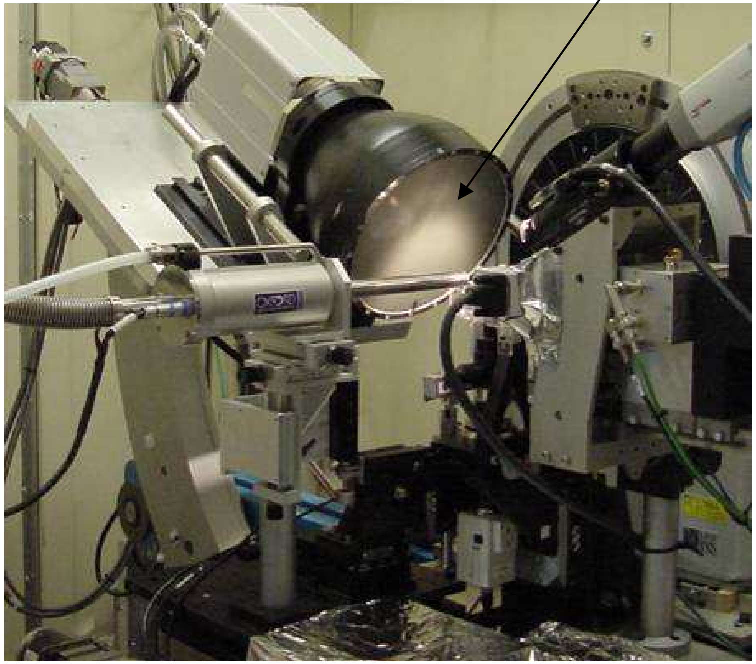
dhkl	2th	rel. Int.	h	k	l
2,555	35,09	25	1	0	0
2,341	38,42	30	0	0	2
2,243	40,17	100	1	0	1
1,7262	53,01	13	1	0	2
1,4753	62,95	11	1	1	0
1,332	70,66	11	1	0	3
1,2776	74,16	1	2	0	0
1,2481	76,22	9	1	1	2
1,2324	77,37	6	2	0	1
1,1707	82,29	1	0	0	4

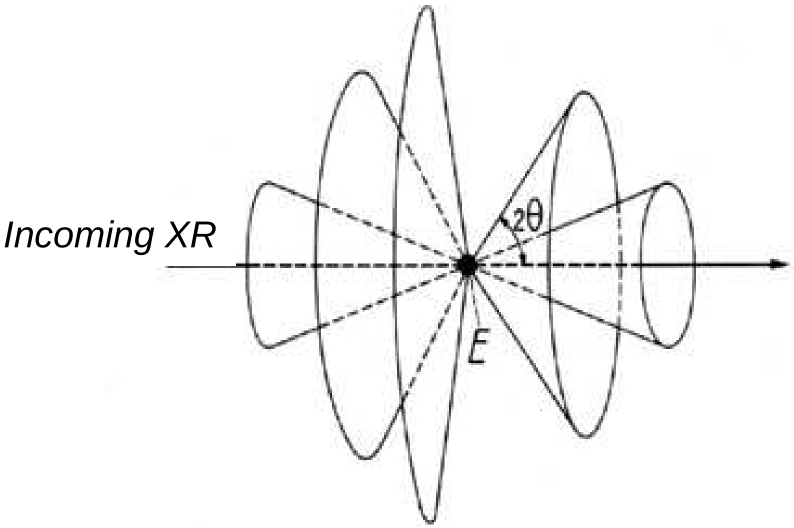
TiC
FCC Fm3m
a=0,43274

2th	rel. Int.	h	k	l
35,907	80	1	1	1
41,71	100	2	0	0
60,45	60	2	2	0
72,371	30	3	1	1
76,141	17	2	2	2
90,8	10	4	0	0
101,785	13	3	3	1
105,502	25	4	2	0
121,377	25	4	2	2
135,355	16	5	1	1

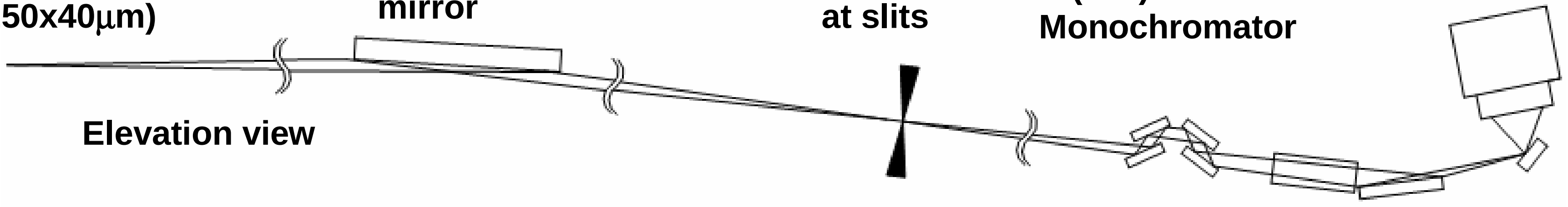


Different kinds of diffractogram: 2D detectors (example of ALS Berkeley USA beamline 11.3.1 and 7.3.3; Nobumichi Tamura, Sirine Fakra)





Each cone is characteristic of a given dhkl



Bend Magnet Source (250x40μm)

1:1 Toroidal mirror

1:1 image at slits

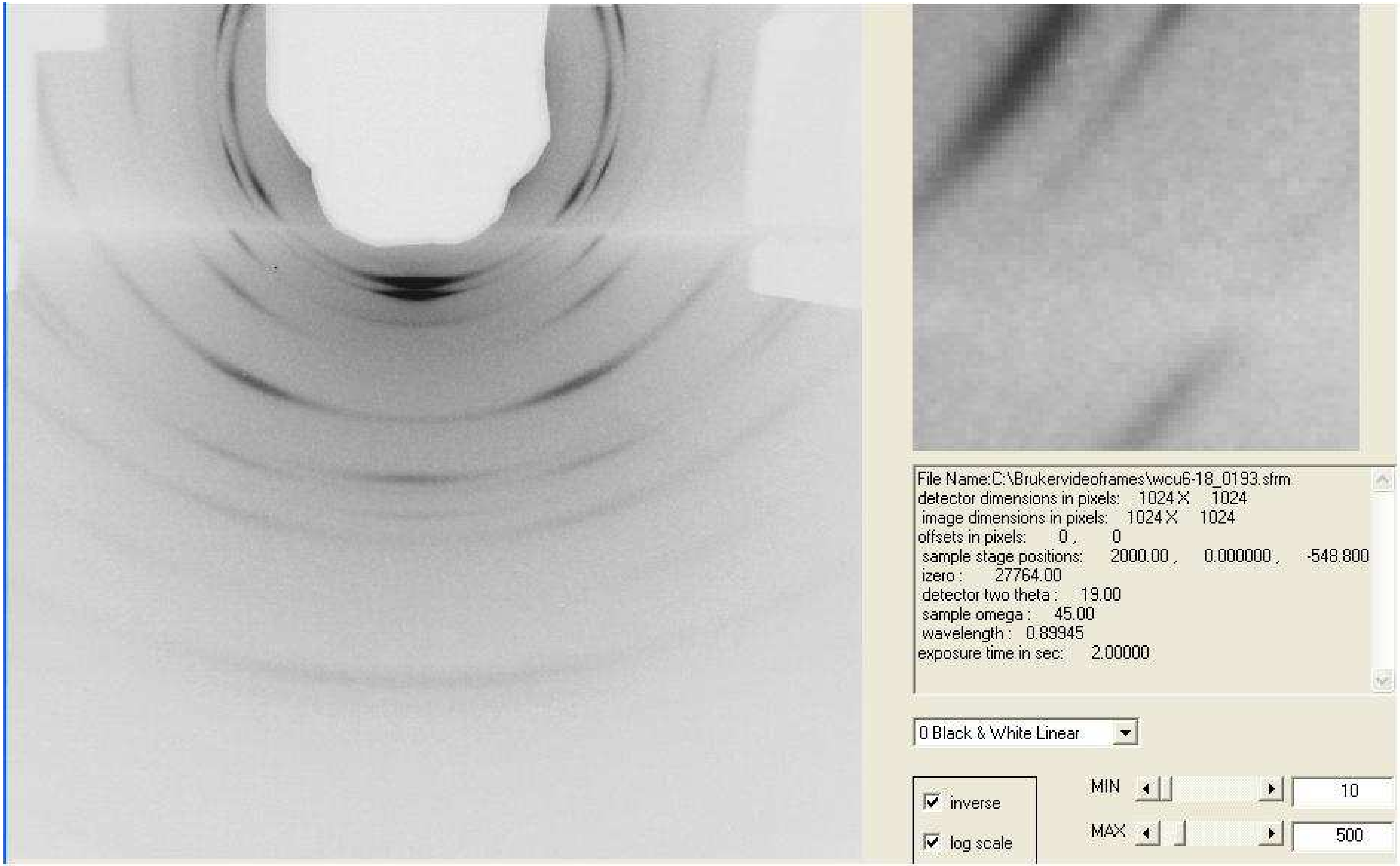
4 Crystal Si(111) Monochromator

CCD camera

Elevation view

Sample on scanning XY stage

Different kinds of diffractogram: 2D detectors



```
File Name:C:\Brukervideoframes\wcu6-18_0193.sfrm
detector dimensions in pixels:    1024 X    1024
 image dimensions in pixels:    1024 X    1024
offsets in pixels:      0 ,      0
 sample stage positions:      2000.00 ,     0.000000 ,     -548.800
 izero :      27764.00
 detector two theta :    19.00
 sample omega :    45.00
 wavelength :  0.89945
exposure time in sec:     2.00000
```

0 Black & White Linear

☑ inverse

☑ log scale

MIN 10

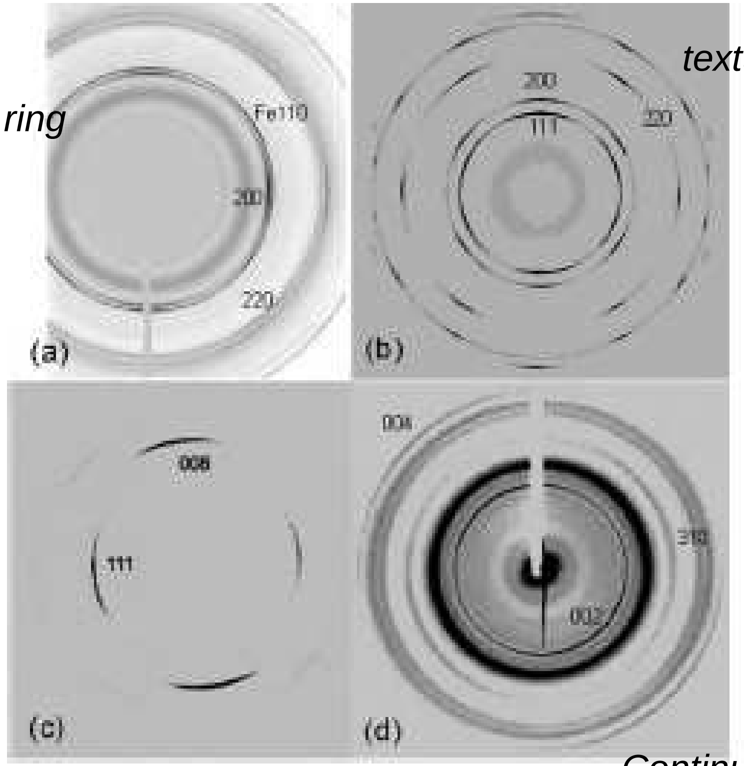
MAX 500

Multilayer W/Cu period 24 nm (6 nm of W and 18 nm of Cu) total thickness 240 nm

Different kinds of diffractogram: 2D detectors Goudeau *et al*.

Transmission mode

reflection mode



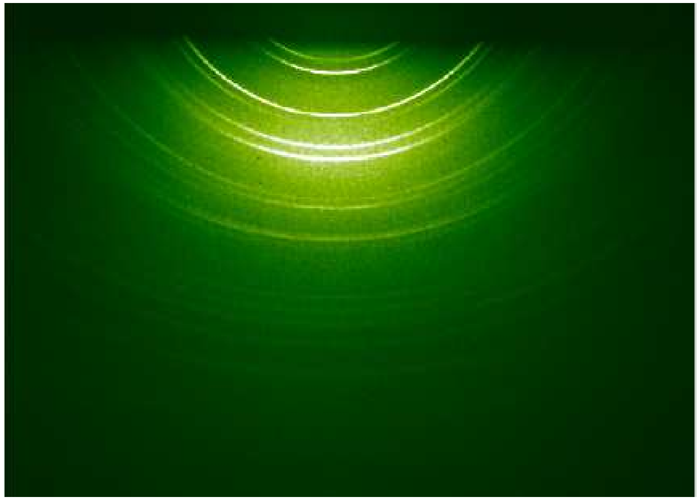
texture

Continuous ring

Strong texture

Continuous ring

Figure 1
Diffraction images illustrating preferred orientation. (*a*) Periclase (MgO) powder compressed in a diamond anvil cell at 25 GPa, recorded with an image plate at APS (GSECARS); compression axis is horizontal (Merkel *et al.*, 2002). (*b*) Gold wire, measured with a CCD detector at ESRF-ID11. (*c*) Fiber-reinforced γ-polypropylene, measured with a CCD detector at ESRF-ID11. (*d*) Fetal bone consisting of oriented hydroxyapatite, measured at ESRF- ID13 with a 2048 CCD detector.



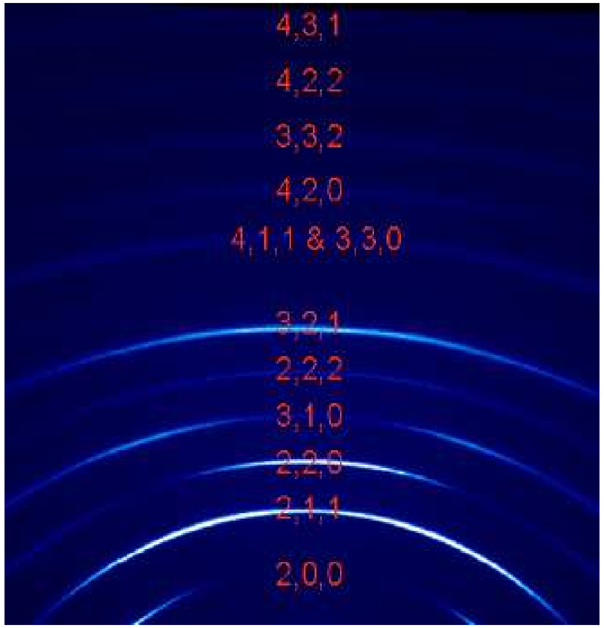
2D diffraction pattern of a SnO_2 thin film deposited on glass recorded in reflection mode. (Beamline 11.3.1 ALS Berkeley).

Different kinds of diffractogram: 2D detectors

Diffraction pattern of w polycrystalline film
/ discontinuous diffraction rings

Diffraction pattern of a W film

Almost continuous ring

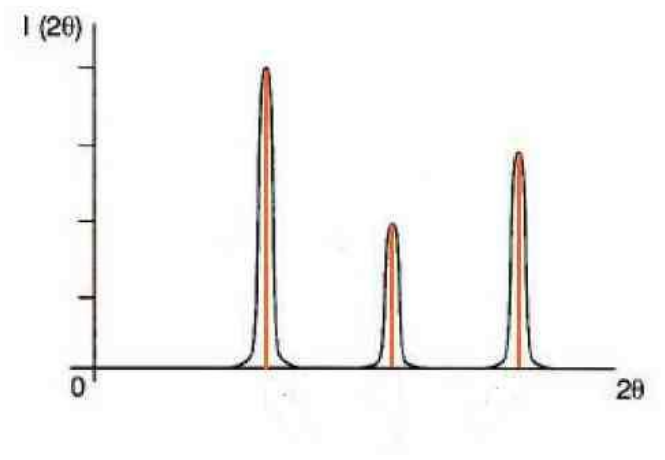


textured

Recorded in reflection mode at 16 keV (0.775 Å), at a 100 μm spatial resolution.

ALS beam line 7.3.3 ***N. Tamura, S. Fakra, & M.A Brown, ALS and Caltech***

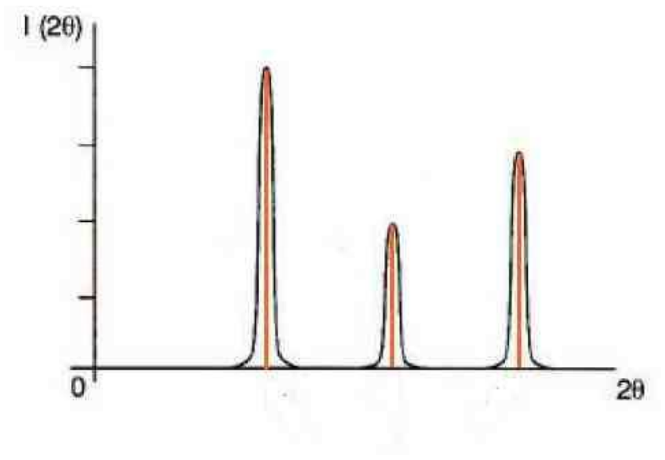
Summary of x-ray diffraction:



- **Position**
- **Intensity**
- **Shape → FWHM**

XRD is based on the assumption that XR radiation (with λ on the order of A) can elastically scatter of the electronic structure of a crystal. The periodicity of the crystal will induce this scattering of the XR plane-wave to constructively interfere at certain scattering directions while destructively interfering at other scattering directions. The diffracted X-Rays are detected at a distance much larger than the periodicity of the lattice, so that the diffraction can be approximated by the Fraunhofer diffraction conditions. It has been shown that the diffraction conditions are related to the Fourier transform of the electronic structure.

What is the informations in a Bragg peak ?



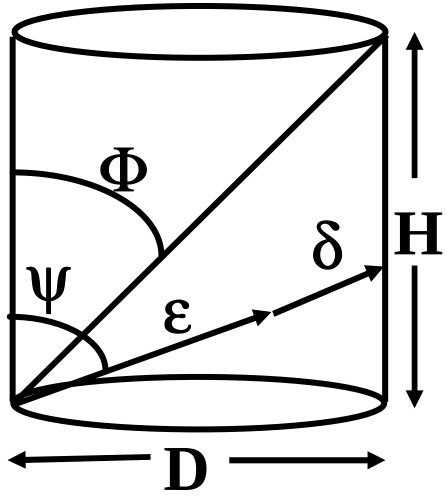
- **Position**
- **Intensity**
- **Shape → FWHM**

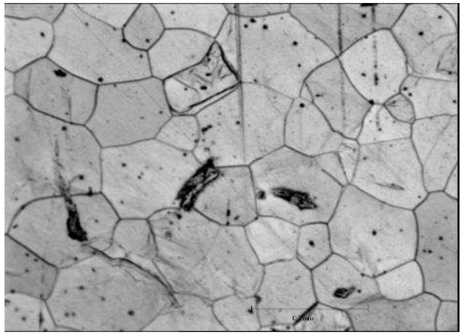
- Phase analysis (peak positions)
- Texture analysis (variation of peak intensity)
- <u>Grain size – microdistortions</u> (peak shape)
- X-ray Strain or Stress analysis (shift of peak position)

What is the crystallite size ? (DCD≠grain size)

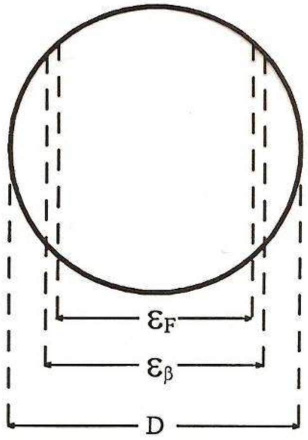
(Langford & Louër, J. Appl. Cryst. 15, 20,1982)

Cylinder





Sphere



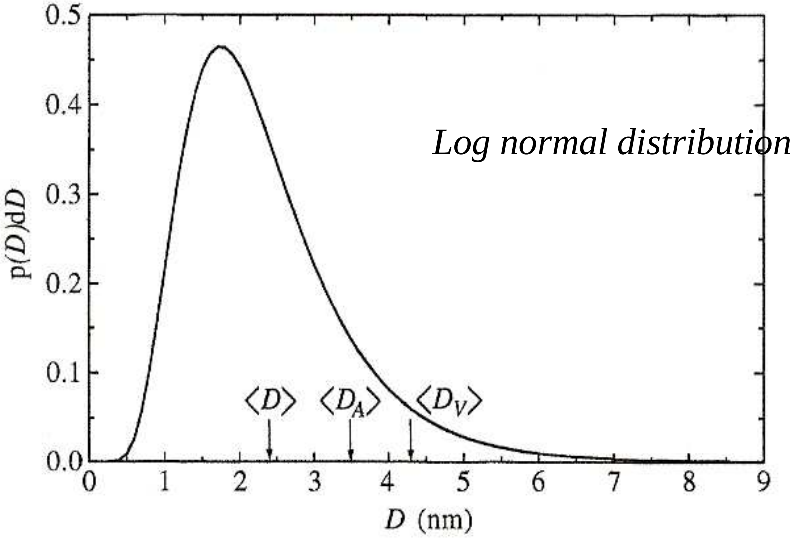
$D = 3\varepsilon_F/2$; $D = 4\varepsilon_\beta/3$

$\varepsilon_\beta/\varepsilon_F = 1.125$

Fourier analysis

Weighted Diameters

surface $\langle D_A \rangle$
volume $\langle D_V \rangle$



(Krill, Birringer, *Phil. Mag*. 77, 621, 1998; Langford, Louër, Scardi, *J. Appl. Cryst*. 33, 964, 2000)

XRD peak broadening is a function of the convolution of instrumental and microstructural broadening (such as grain size, microstrain, strain gradients, dislocations,…)

1-Scherrer crystallite size:

$$D_S = \frac{K\lambda}{B.\cos\theta_B}$$

K~0.9, θ = Bragg angle
B: FWHM of the peak after correcting from instrumental effects (broadening caused by the diffractometer).

$$\searrow B^2 = B^2_{meas.} - B^2_{inst.}$$

In this equation, the broadening is due to the finite size of the crystallite. Indeed, for very small crystals the intensity of x-rays at close to, but not exactly, the Bragg condition is not zero.

2-Separation of crystallite size and microstrain:

Some methods consist simply to write that the broadening is the sum of both size and microstrain:

$$B = B_{size} + B_{microstrain}$$

$$B_{microstrain} = \eta.2.\tan\theta$$

$$B = \frac{K\lambda}{D.\cos\theta} + \eta.2.\tan\theta$$

η *microstrain*

$$\frac{B\cos\theta}{\lambda} = \frac{1}{D.} + \eta\frac{1}{d}$$

$$\beta = \frac{1}{D} + \eta.d^*$$

3-Warren-Averback crystallite size and microstrain:

The warren averback method is based on a Fourier analysis of the diffraction peak. The measured peak profile h(s) is actually the convolution of a function for the pure peak profile f(s) and a function for the instrumental broadening g(s):

$$h(s)= g(s) * f(s)$$

This can also be represented by the product of the Fourier transforms for instrumental broadening:

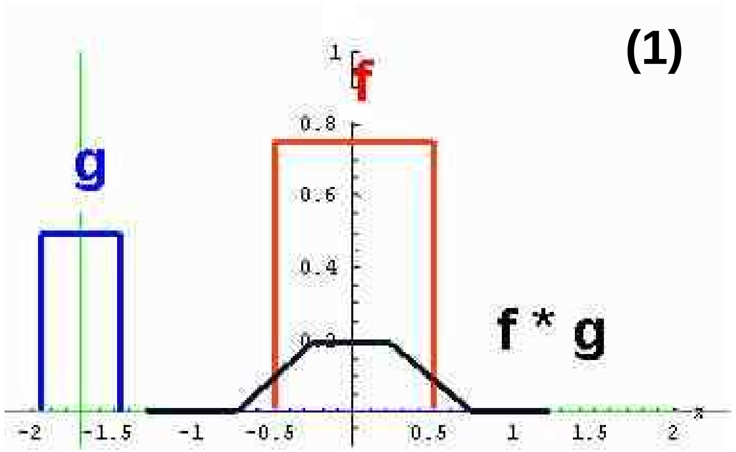
$$FT(h)= FT(g) . FT(f)$$

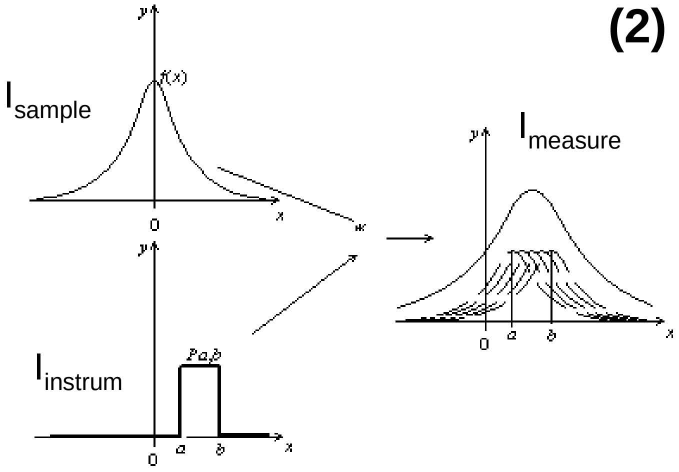
$$FT(f) = \sum_{L=-\infty}^{+\infty} A(L).\cos\left(2\pi\left(s-s_0\right)L\right) + B(L).\sin\left(2\pi\left(s-s_0\right)L\right)$$

Where A(L) and B(L) are the cosine and sine coefficients and L is the length of a column of unit cells perpendicular to the diffracting planes. A plot of A(L) versus L is used to determine the area weighted crystallite size La and lattice microstrain. If two peaks of the same plane family are used in this analysis, the contribution of microstrain to peak broadening can be separated from the crystallite size.

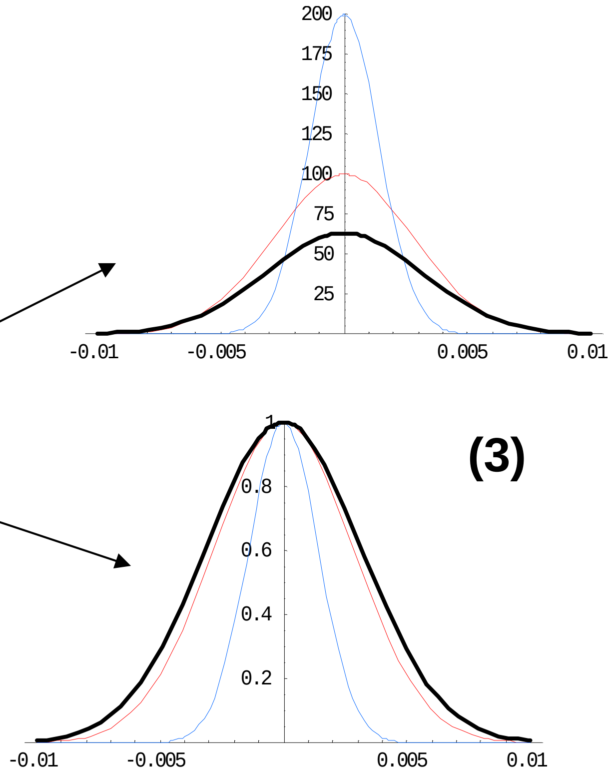
Examples of convolution :

On this picture, convolution of a lorentzian function (which can be assumed to represent the real sample intensity distribution) and a rectangle function results (which can be assumed to represent the instrumental intensity distribution).





The convolution of two gaussians is another gaussian:



(3)

FWHM:

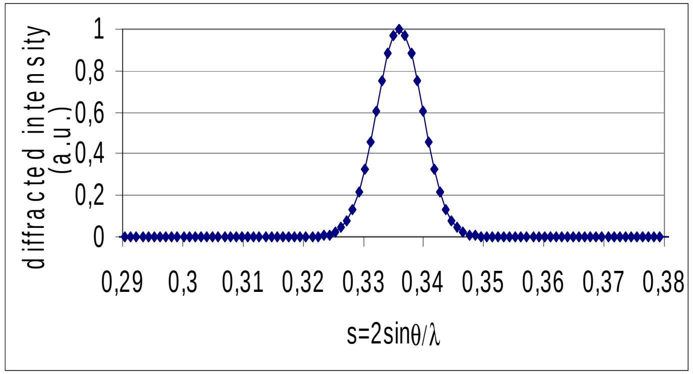
→In black the measured intensity distribution → 0.00745
→In blue the instrumental → 0.00333
→In red the sample → 0.00666

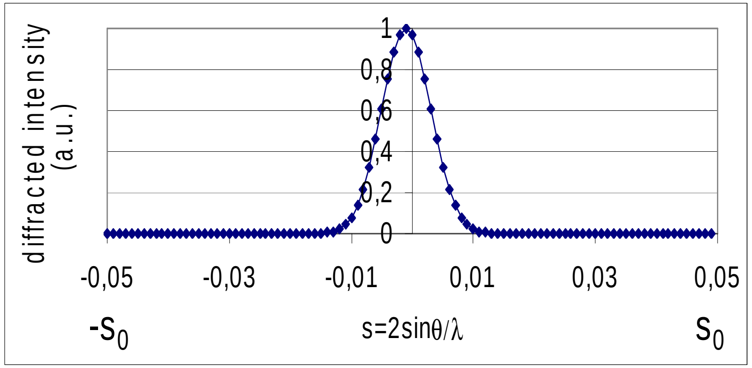
Fourier analysis:

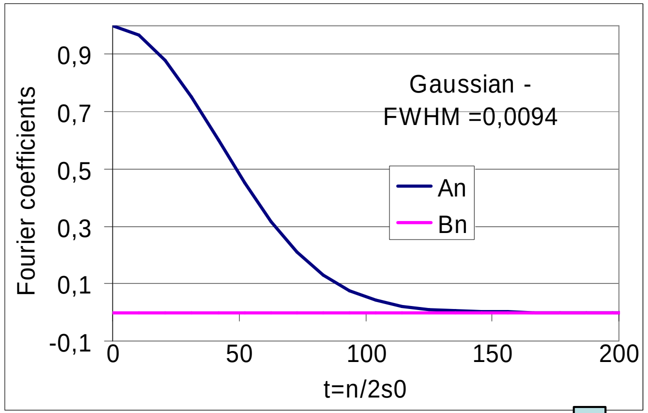
A periodic function (with period a) can be decomposed into an infinite Fourier series of sine and cosine terms:

$$f(x) = A_0 + 2\sum_{n=1}^{+\infty} A_n.\cos\left(\frac{2\pi nx}{a}\right) + B_n.\sin\left(\frac{2\pi nx}{a}\right)$$

In the case of x-ray analysis, the diffraction peaks is considered periodic : $2s_0$







- -Calculation of An and Bn
- -instrumental corrections
- -plots of A_n and B_n vs $t=n/2s_0$

Information on crystallite size and microstrain, the separation of these parts can be made if several orders of a peak are studying.

- *Grain size evolution:*

annealing effect → diffusion → grain growth (ex: O. Proux et al.)

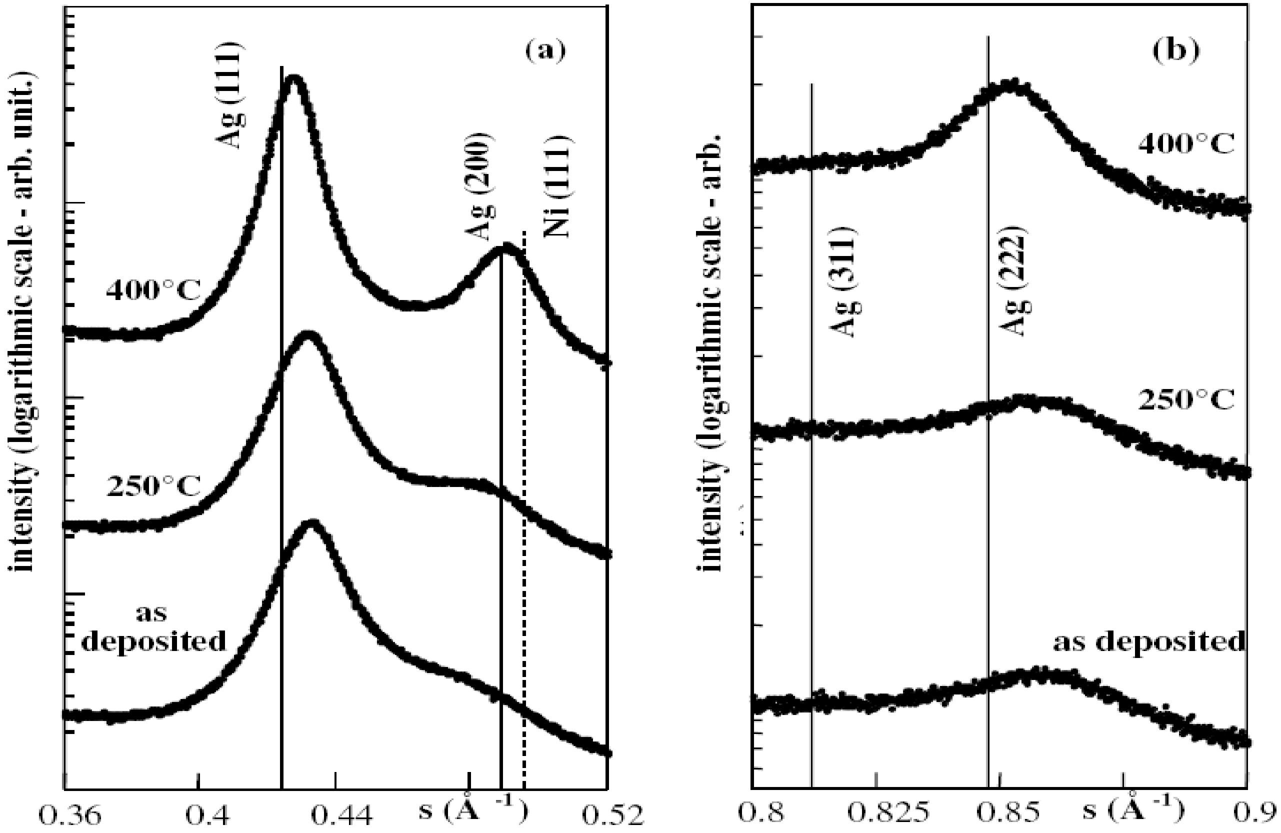
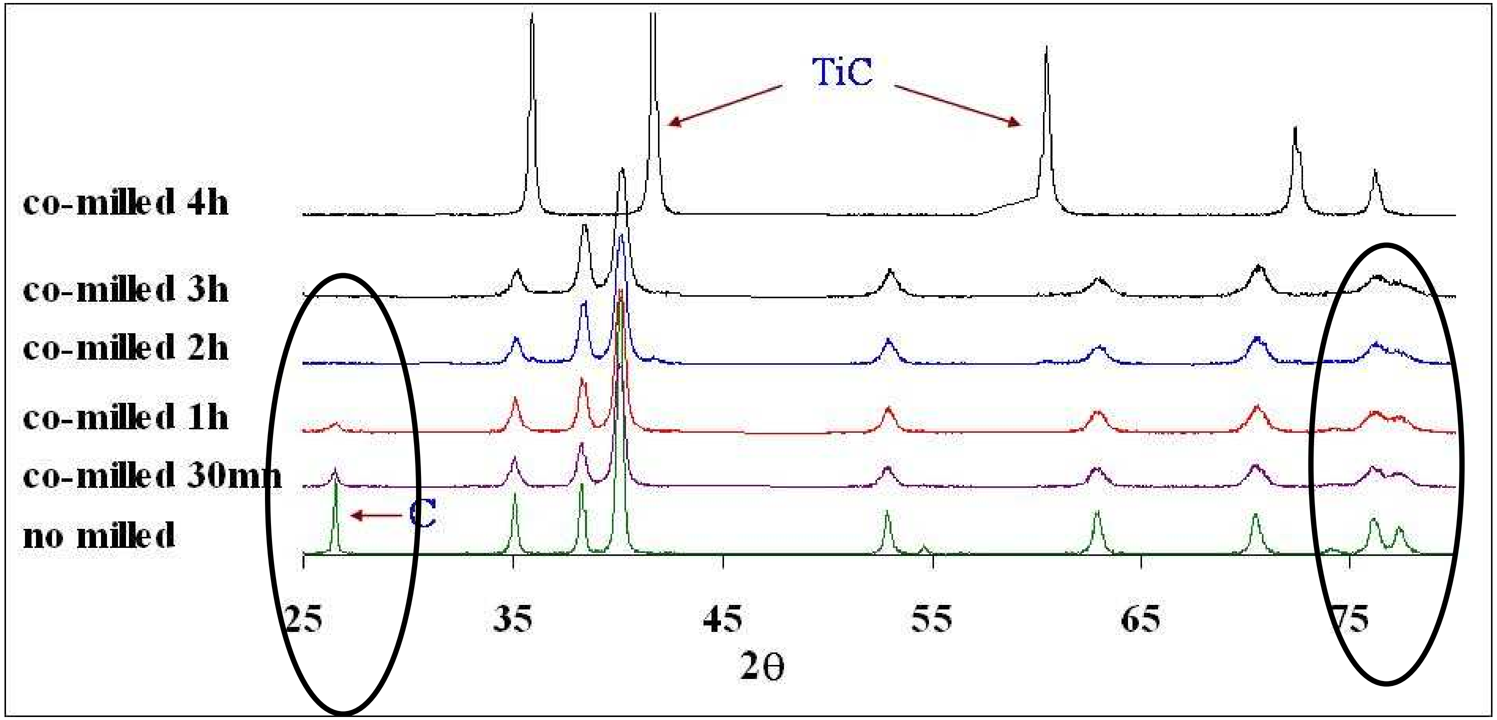


Figure 2. XRD patterns of the as-deposited and 250, 400 °C annealed $Ni_{0.35}Ag_{0.65}$ alloys limited to the reciprocal-lattice areas near and between the theoretical reflections Ag(111) and Ni(111) (a) and the theoretical reflections Ag(311) and Ag(222) (b).

Example of measurement of grain size and phase evolution: (Dubois et al. LMP Poitiers)



ball milling → high density of dislocation and decrease of the diffracting coherent domain (DCD) or crystallite.

1-Phase evolution: elaboration of TiC by ball milling.

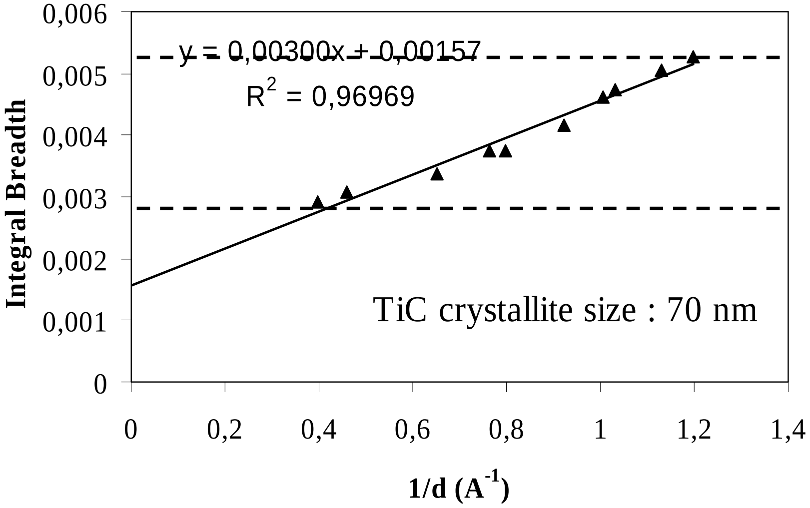
From two powders, pure Ti and pure C, TiC is elaborated by ball milling

2-before the phase transformation, the evolution of the Bragg peak shape can be observed.
As for example, intensity decreasing and disappearence of the first Bragg peak of C.
Decreasing of the intensity and broadening of Bragg peaks of Ti.

What about the TiC elaborated ?

TiC				intensity	Area
hkl	**2theta**	**FWHM**	**IB**	**Ka1**	**Ka1**
111	35,87	0,2588	0,3411237	423,6	144,5
200	41,6727	0,2587	0,36231217	652,2	236,3
220	60,4283	0,3919	0,41710324	324,5	135,35
311	72,3553	0,4422	0,47086801	168,2	79,2
222	76,1324	0,4502	0,47866205	86,7	41,5
400	90,8177	0,3614	0,56766257	51,21	29,07
331	101,8104	0,6449	0,68514851	50,5	34,6
420	105,55	0,4632	0,72781065	118,3	86,1
422	121,4724	0,6086	0,95583596	95,1	90,9
511	135,4454	0,8179	1,28478964	61,8	79,4

Step 2:
Then diffractogram on LaB6 to perform the instrumental correction
Step 3:
Williamson-Hall plots , i.e. Int. B. vs 1/d (or d*)



Scherrer’s equation
does not lead to the same values:
the crystallite size increases with diffraction angle from :

hkl	size (nm)
111	51
200	48
220	48
311	46
222	47
400	47
331	48
420	48
422	56
511	69

●*Grain size evolution (WH plots):*

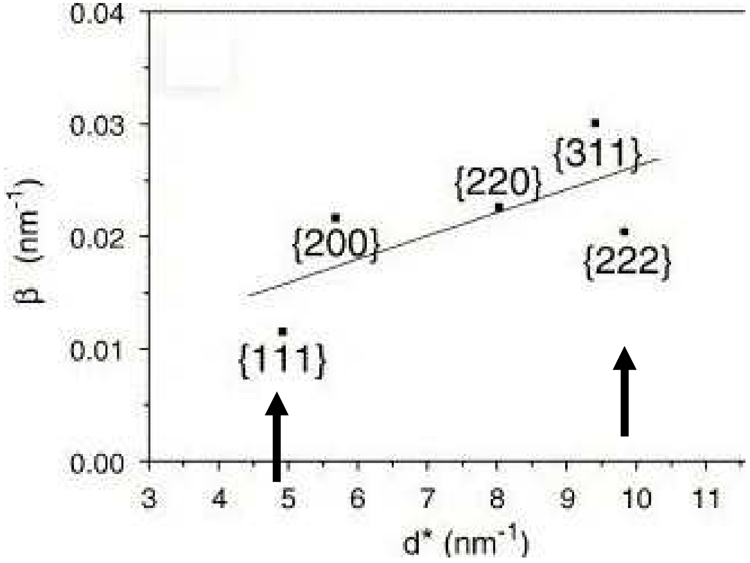
$$\beta = \frac{1}{D} + \eta . d^*$$

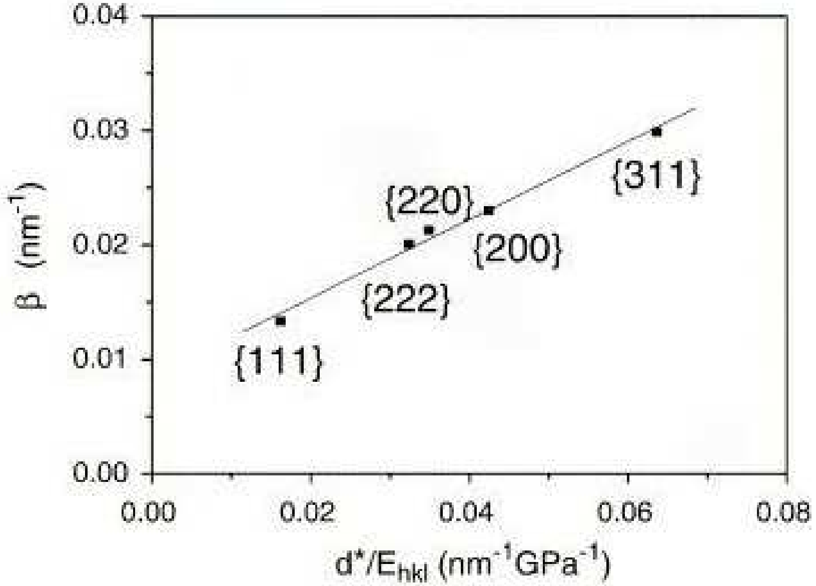
the peak broadening is strongly anisotropic with respect to the crystallographic directions <hkl> (Ni specimen)

→Contribution of anisotropic elasticity for deformed metals.

→To check this assumption, we substitute *d** with *d** / *E*hkl, where *E*hkl is the elastic modulus at the crystallographic direction <hkl> . *(slide 110 case of Ni)*

N.B.: it must be noted that other microstructural factors may also have an effect on the anisotropic peak broadening.



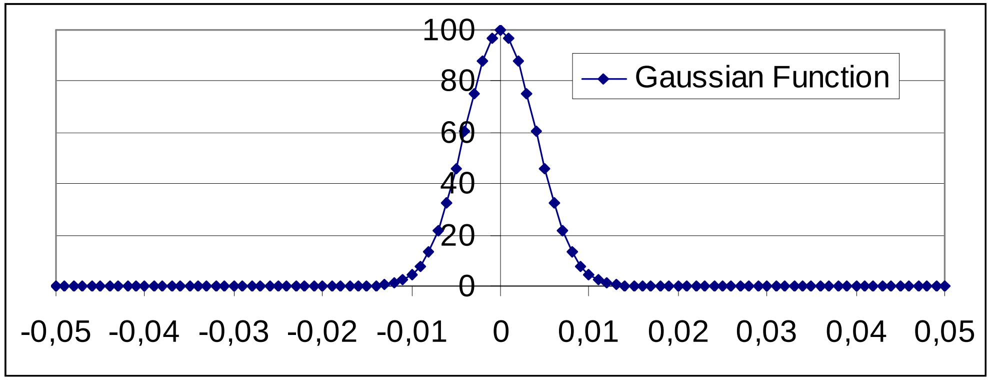


- *Grain size:*

In Fourier analysis, the measurement should be performed over a wide range in 2theta. It is recommended to record at least four to five times the breadth of a peak on either side, and to compare the background of a standard and the pattern to be analyzed; the background in both should be the same. These precautions will minimize oscillations in the coefficients. The peaks to be analyzed should be at least 20% broader than the standard peaks.

Example of the effect on the range of measurement on the Fourier coefficients:

Consider a Gaussian function: $$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-0.5\left(\frac{x-\bar{x}}{\sigma}\right)^2\right)$$

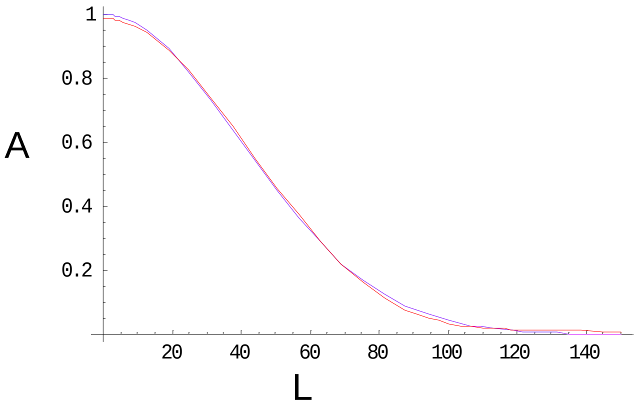


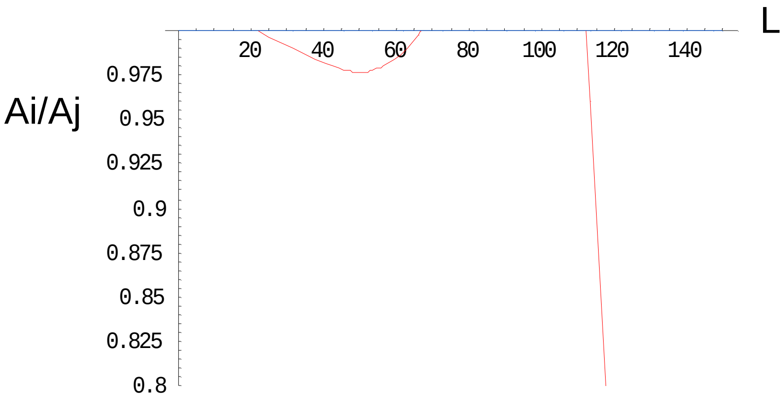
$$\mathrm{FWHM} = 2\sigma\sqrt{2\ln 2} = 0.00942$$

$\underline{x}$ = the centroid of the peak =0

- *Grain size:*

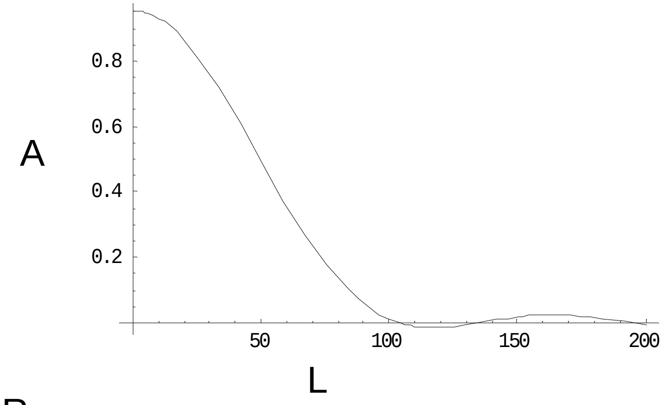
For the gaussian function, we saw the effect of the range investigation on the value of the Fourier coefficients.





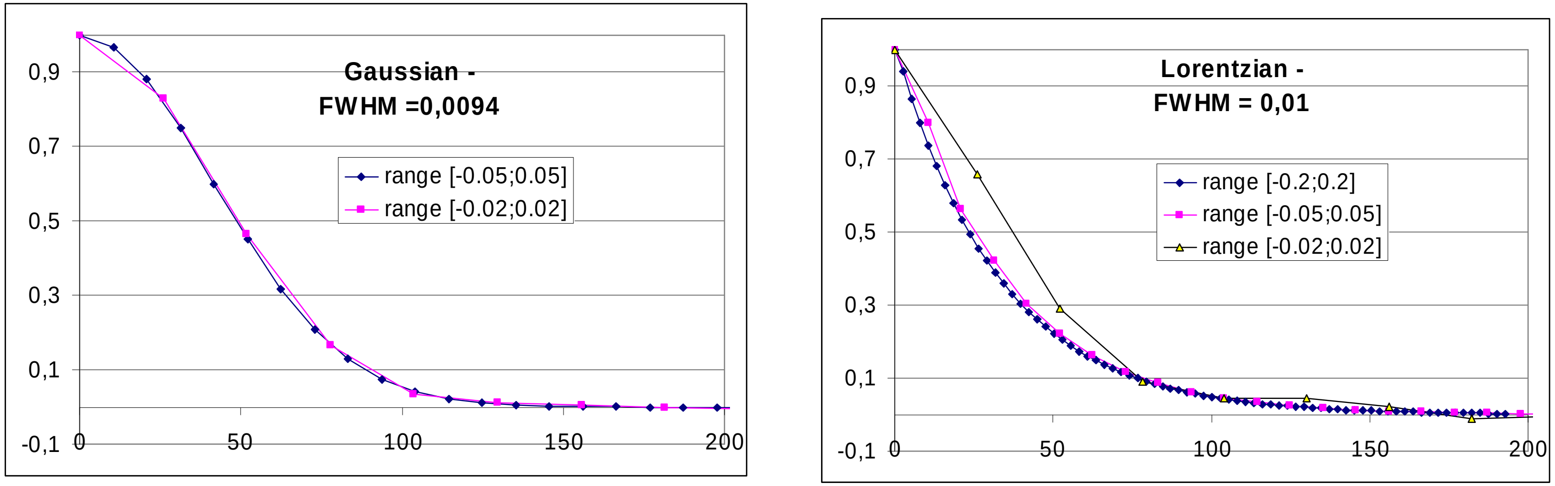
Fourier coefficient for 2 cases:
→case 1: over a range = 2 x FWHM
→case 2: over a range =10 x FWHM

Ratio of Fourier coefficient for 2 cases:
-Fourier cas 2/fourier case 1
-Fourier cas 2/real fourier coefficient



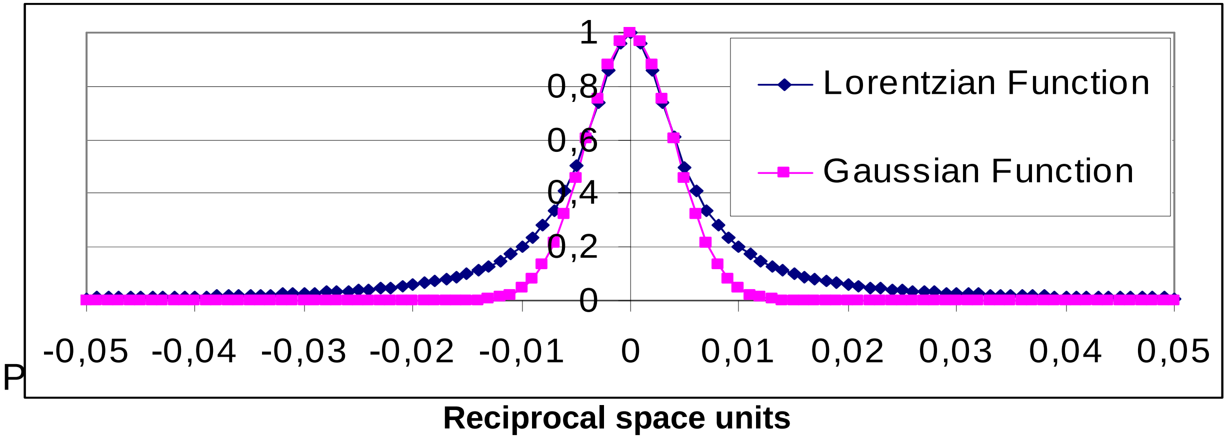
Oscillation of the Fourier coefficient, if the range decreases (ex. here for range [-0.008, 0.008])

●*Grain size:*



Fourier coefficient An vs t=n/2s_0 for two analytical functions : Gauss and Lorentz

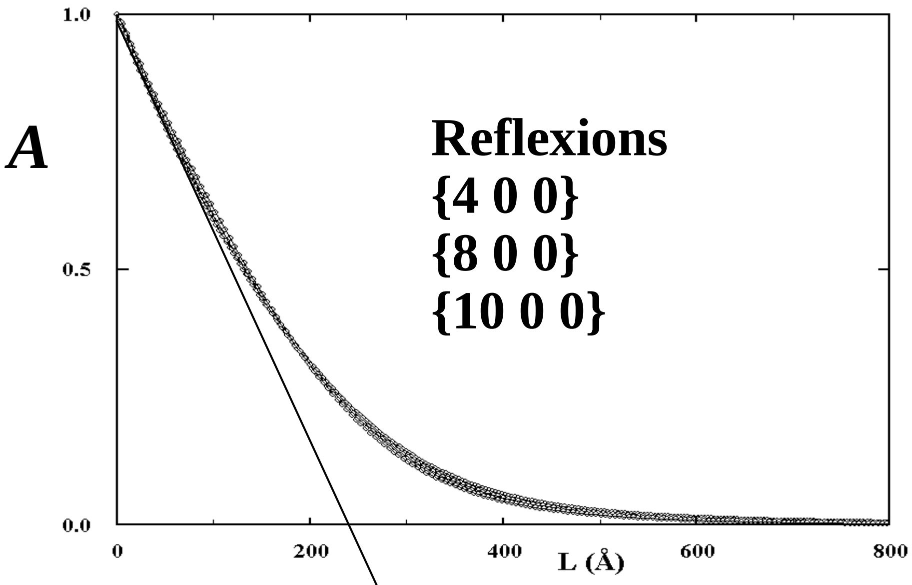
The effect of the scan range depends of the shape of the Bragg peak. Particularly of the shape of the bottom of the Bragg peak.



$$s - s_{center} = \frac{2\sin\theta}{\lambda} - \frac{2\sin\theta_{Bragg}}{\lambda}$$

- **Example of Fourier analysis**

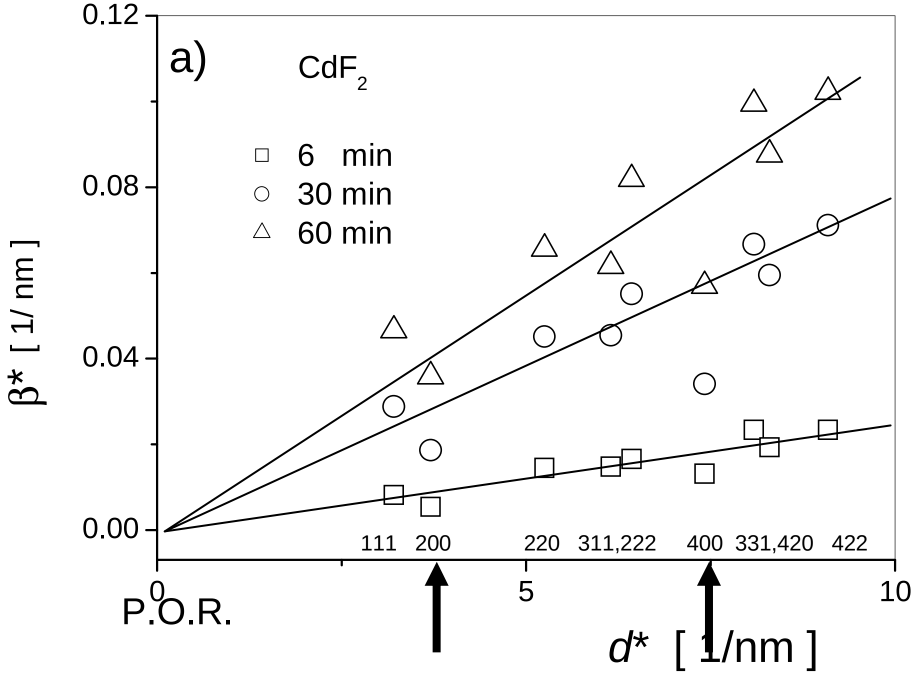
Size :ε_F = 224 Å

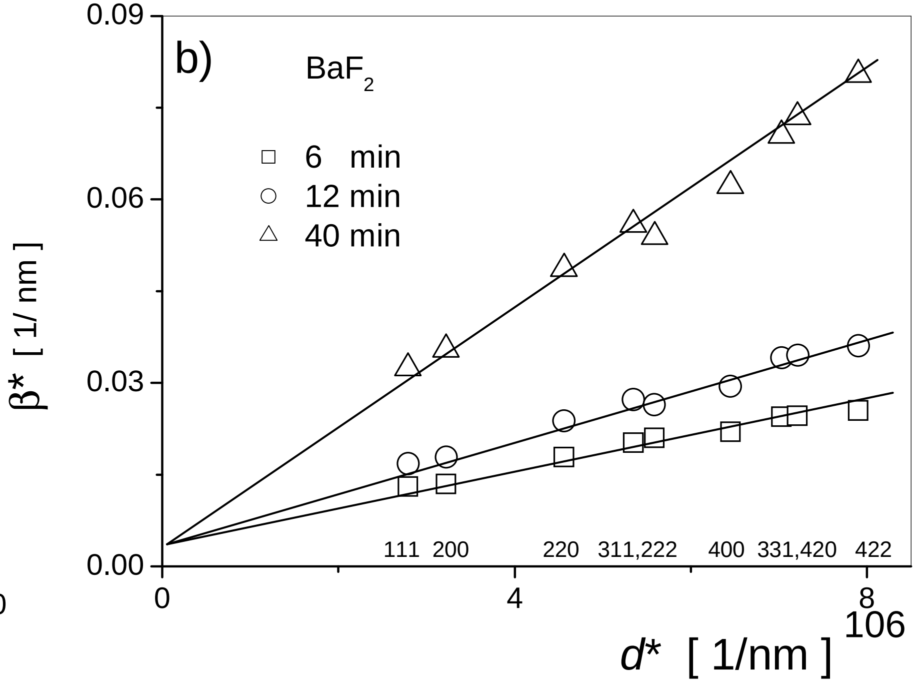


Williamson-Hall plots
(microdistortion effect):

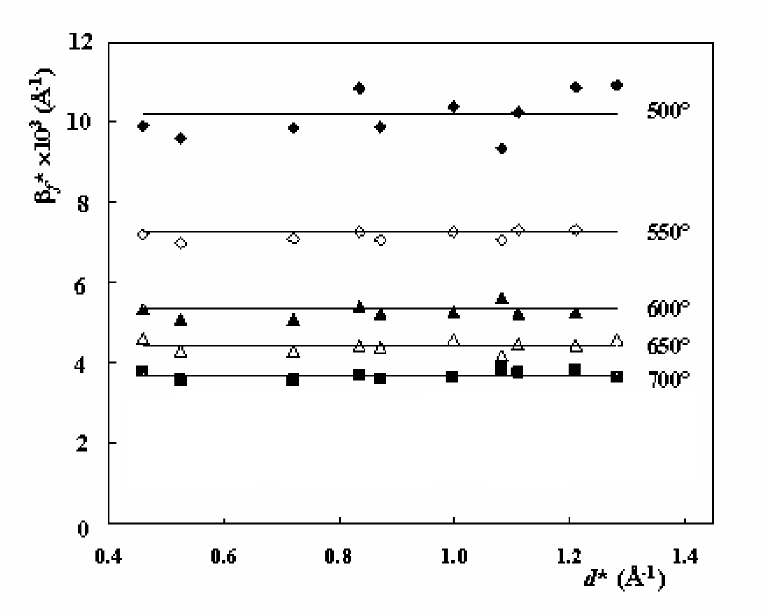
CdF_2 Zener anisotropy A_z = 0.56

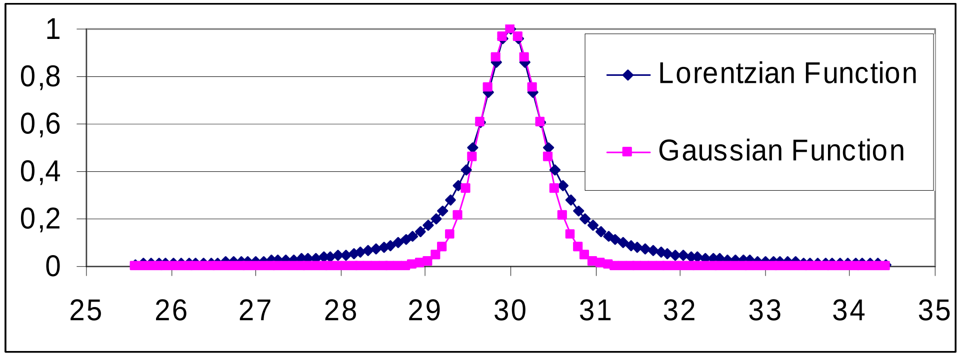
BaF_2 Zener anisotropy A_z = 1.03





Williamson-Hall plots (size effect):





2theta(°)

- *Pseudo-voigt: PV= a.G + (1-a).L*

- Pearson VII

$$PVII(x) = a\left(1 + \frac{(x-\bar{x})^2}{b^2}\right)^{-m}$$

m=1 Cauchy
m=2 lorentz
m=∞ Gauss

- Gauss $$G(x) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(-0.5\left(\frac{x-\bar{x}}{\sigma}\right)^2\right)$$

FWHM~2.3548σ

- Lorentz $$L(x) = \frac{\sigma}{2\pi}\frac{1}{(0.5\sigma)^2 + (x-\bar{x})^2}$$

FWHM~σ