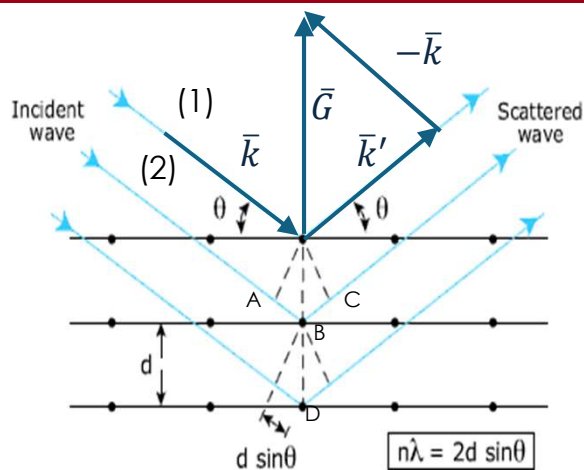


Lab Activity – Part 02

X-ray Diffraction (XRD) on Au NPs

Diffraction: Bragg (1913)

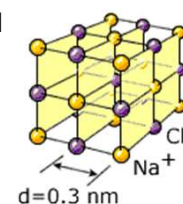


d = interplanar distance

θ = incidence angle

$DB = d$

Es. NaCl



Bragg reflection: atomic planes "reflect" the incident radiation

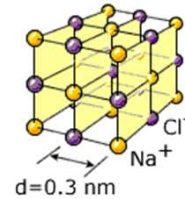
$$2 d \sin \theta = \lambda$$

$$\vec{k}' - \vec{k} = \Delta \vec{k} = \vec{G}$$

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

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

Es. NaCl



Ex.: for $\text{Au}_{(311)}$ $d_{(311)} = \frac{a}{\sqrt{3^2 + 1^2 + 1^2}} = 0.123 \text{ nm}$

$\lambda \sim 0.002 \text{ nm}$ (e, 300kV)

$\lambda \sim 0.1 \text{ nm}$ (X-rays, 12.4 keV)



$\theta \sim 0.46^\circ$

$\theta \sim 23.9^\circ$

Nanoparticle peak broadening Simulation

$$\psi_{out} = \psi_0 \left[e^{ikz} + i f(\theta) \frac{e^{ikr}}{r} \right] = \psi_{in} + i \psi_{sc}$$

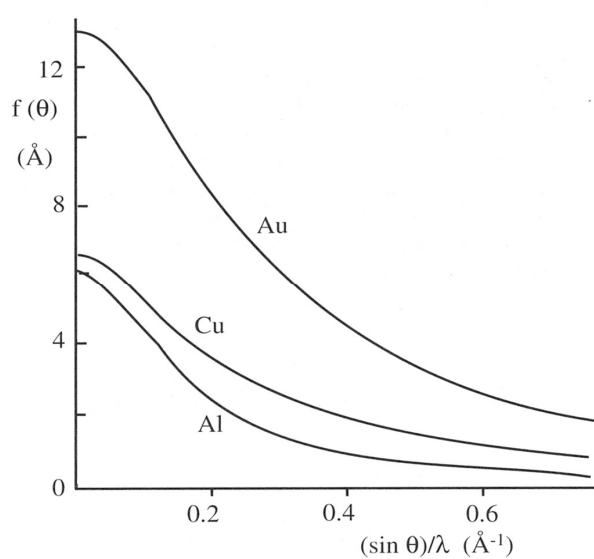
Transmitted planar wave

Scattered spherical wave

Phase Shift of 90°

$f(\theta)$ = scattering amplitude

$$|f(\theta)|^2 = \frac{d\sigma(\theta)}{d\Omega}$$



$$f(\mathbf{Q}) = \int \rho(\mathbf{r}) e^{i\mathbf{Q} \cdot \mathbf{r}} d^3\mathbf{r}$$

$$Q = 2k \sin(\theta)$$

$$k = 2\pi/\lambda$$

$$f^{(e)}(s) = \frac{m_0 e^2}{8\pi^2 \hbar^2} \frac{1}{4\pi\epsilon_0} \frac{[Z - f^{(X)}(s)]}{s^2}$$

electrons X-rays

$$s = \frac{Q}{4\pi} = \frac{\sin \theta}{\lambda}$$

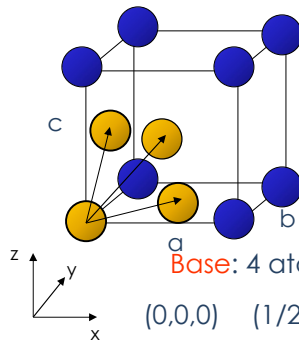


Single atom
(scattering)



Group of atoms
(diffraction)

Unit Cell
f.c.c. (es. Au)
 $a = b = c = 0.4078 \text{ nm}$
 $\alpha = \beta = \gamma = 90^\circ$



Vector of the Bravais lattice (cubic)

$$\vec{R} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$$

Base: 4 atoms with coordinates $r_j, j=1,4$

(0,0,0) (1/2,1/2,0) (1/2,0,1/2) (0,1/2,1/2)

f.c.c. = simple cubic + base

	base (spherical symm.)	base (no-symm.)
Point groups	7 crystalline systems	32 point groups
Space groups	14 Bravais lattices	230 space groups



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26

26

$$\psi_{sc}^{at} = \psi_0 \left[f(\theta) \frac{e^{ikr}}{r} \right] \quad \text{Atom}$$

$$\psi_{sc}^{cell} = \psi_0 \left[F(\theta) \frac{e^{ikr}}{r} \right] \quad \text{Unit cell}$$

$$F(\theta) = \sum_j f_j(\theta) e^{i\vec{G} \cdot \vec{r}_j} \quad \text{Structure factor}$$

$$e^{i\vec{G} \cdot \vec{R}} = 1$$

$$\vec{G} = h\vec{a}' + k\vec{b}' + l\vec{c}' \quad \text{Reciprocal lattice vector (h,k,l) Miller indices}$$

$$\vec{R} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c} \quad \text{Bravais lattice vector}$$

$$\vec{a} \cdot \vec{a}' = \vec{b} \cdot \vec{b}' = \vec{c} \cdot \vec{c}' = 2\pi$$



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27

27

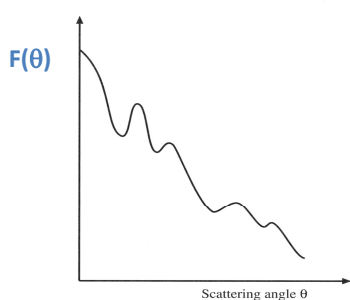
E.g.: for monoatomic f.c.c. structure:

$$F(\theta) = F(\vec{G}) = \sum_j f_j(\vec{G}) e^{i\vec{G} \cdot \vec{r}_j} = f(\vec{G}) \sum_j e^{i\vec{G} \cdot \vec{r}_j} =$$

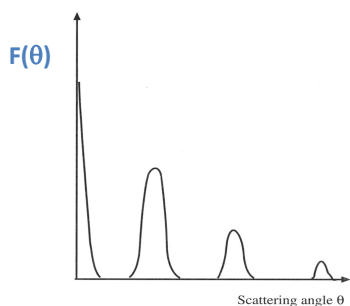
$$= f(\vec{G}) [1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}] = \begin{cases} 4f(\vec{G}) & \text{h,k,l all even or odd} \\ 0 & \text{h,k,l mixed even and odd} \end{cases}$$

$$I_{hkl} \propto |F_{hkl}|^2 = \left| \sum_j f_j(\vec{G}) \exp(i \vec{G} \cdot \vec{r}_j) \right|^2$$

Comparison between the scattering factor for
amorphous and crystalline structures

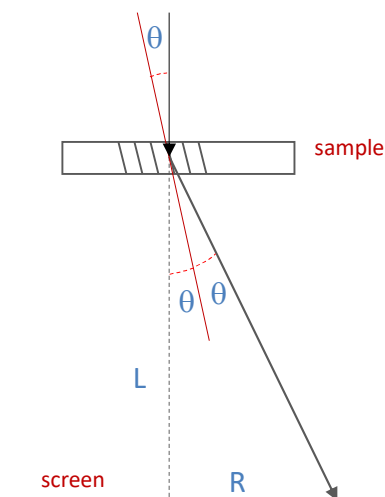


Diffuse and modulated
intensity



Intensity peaked at
particular angles

XRD



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

R = distance from transmitted beam

L = camera length

L is geometrically defined for X-rays

L is an electro-optical length for electrons in TEM

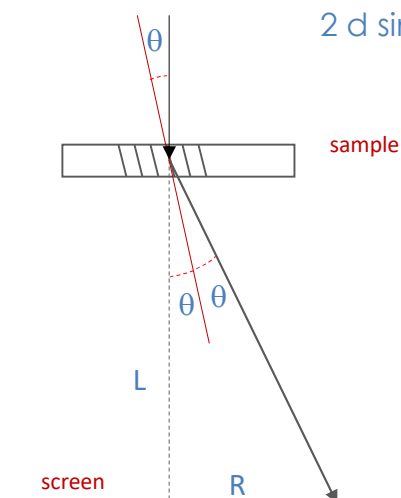


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30

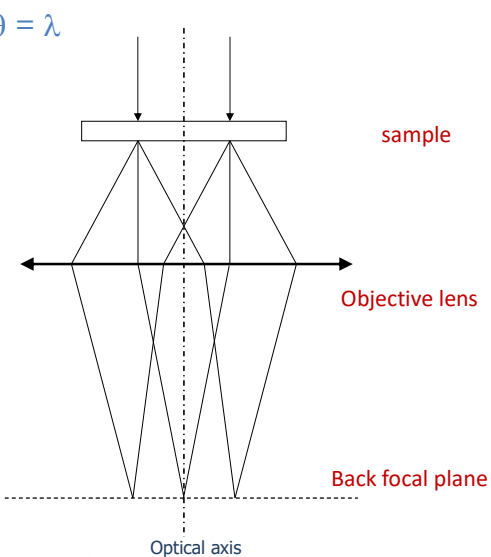
30

XRD



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

ED



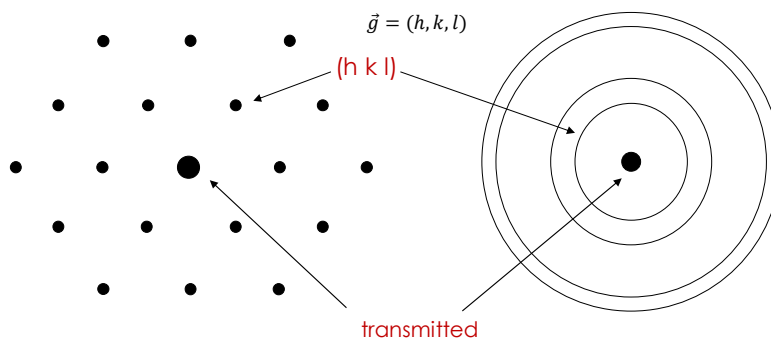
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31

31

SAED from a single
crystal SPOTs

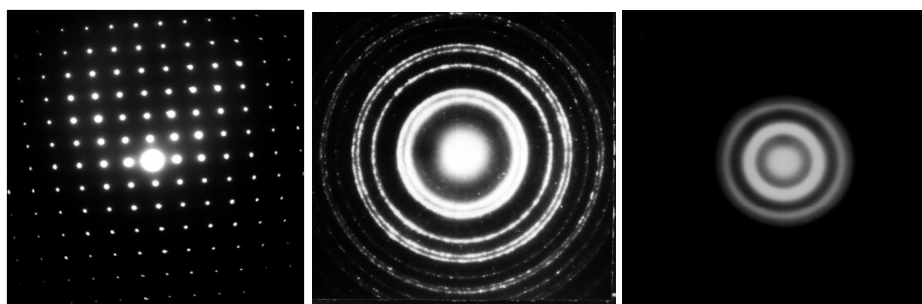
SAED from a
poly-crystalline sample
Debye-Scherrer rings

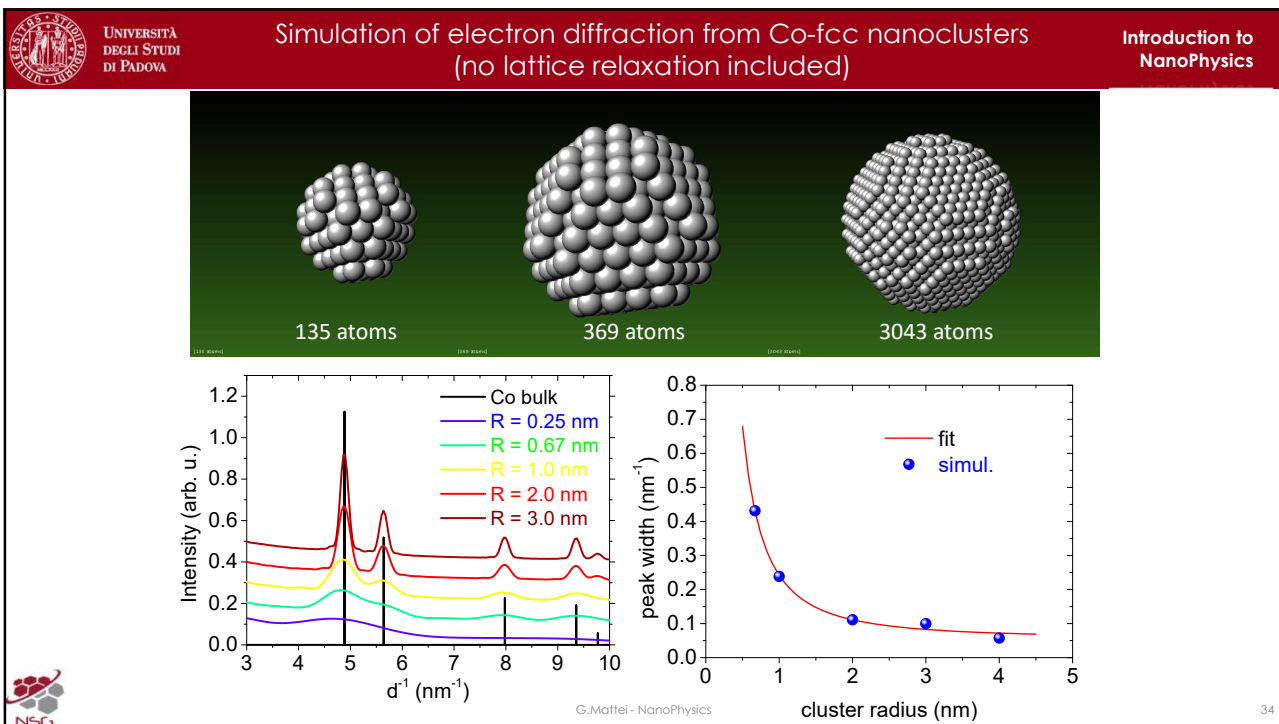


Crystalline
sample

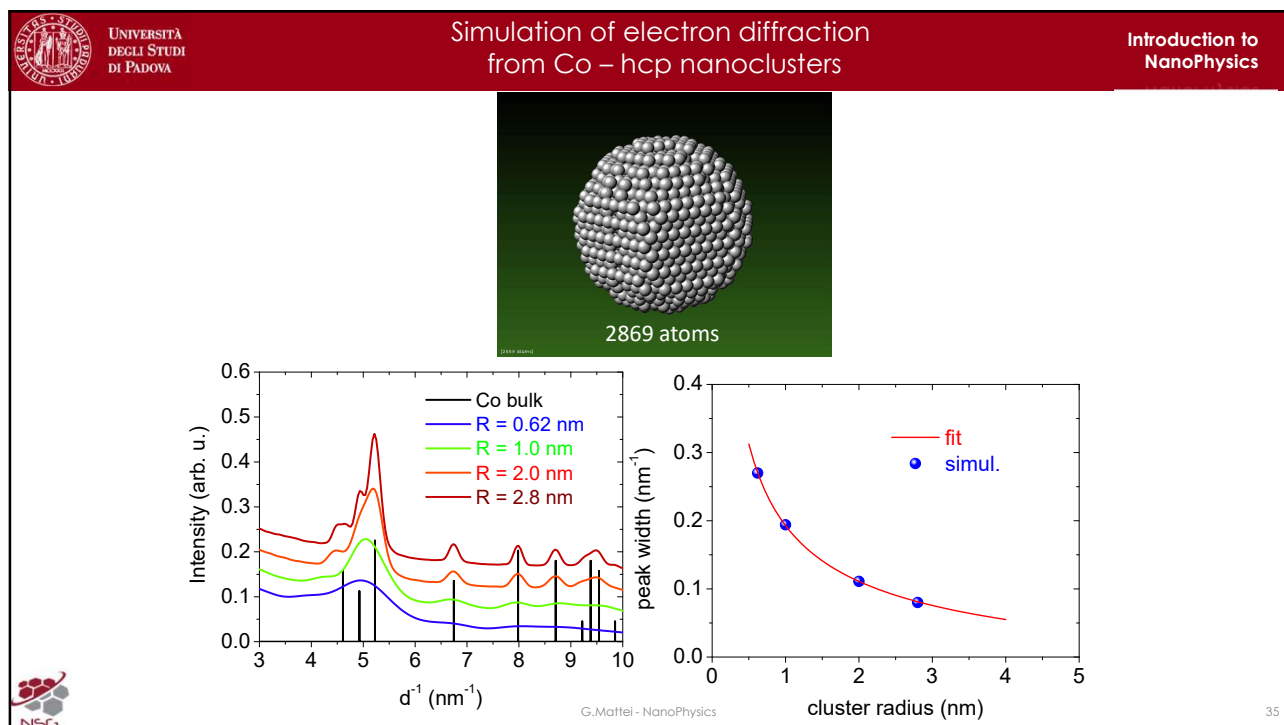
Poly-crystalline
sample

Amorphous
sample





34



35



16/05/2025
10:30 a.m.

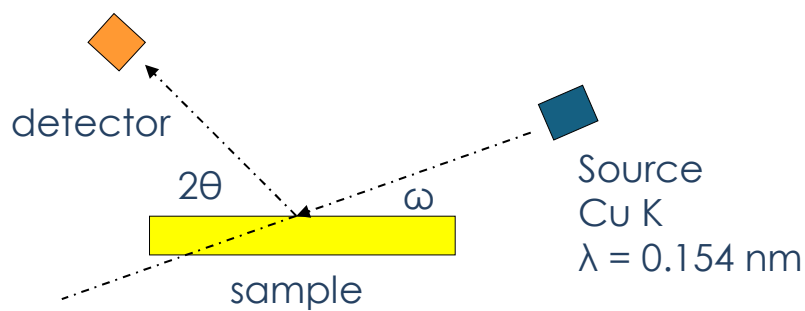
Schedule

G1: 10:30 am

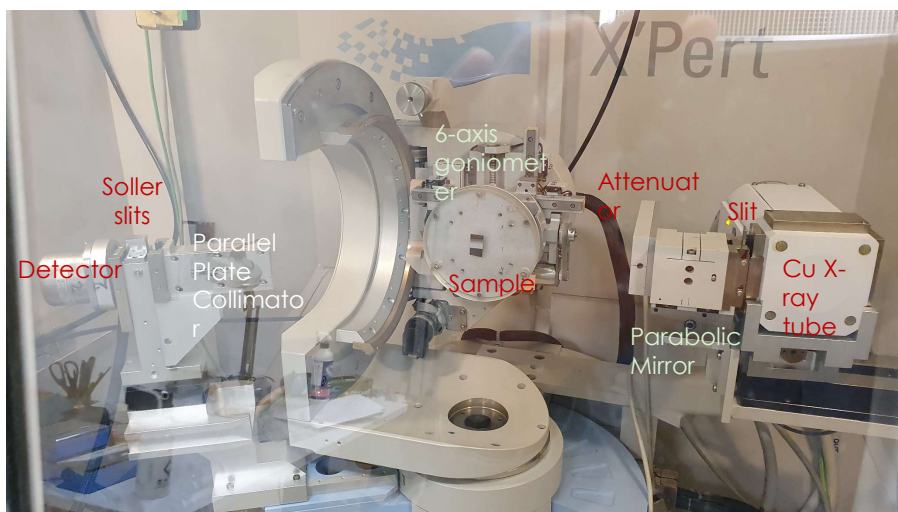
G2: 11:20 am

G3: 12:10 pm

G4: 13:00 pm



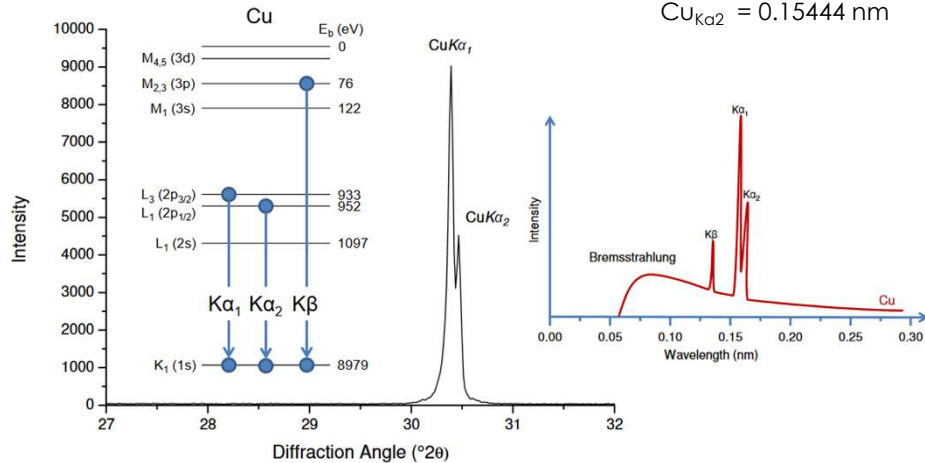
- Diffraction (at grazing incidence)
- Reflectivity
- High-resolution Diffraction



β_{inst} calibration from LaB_6 standard

$\text{Cu}_{K\alpha 1} = 0.15406 \text{ nm}$

$\text{Cu}_{K\alpha 2} = 0.15444 \text{ nm}$



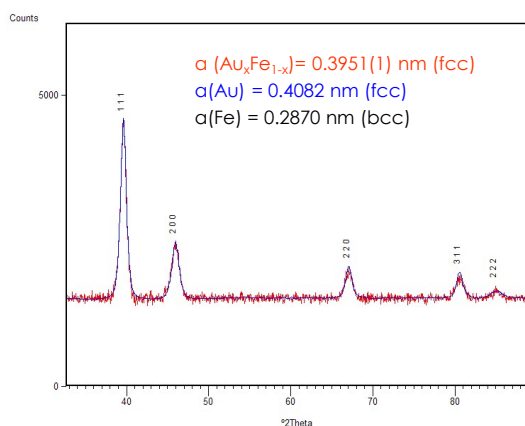
LaB_6 pattern, Cu radiation, Graphite monochromator, secondary beam (PANalytical CubiX³)

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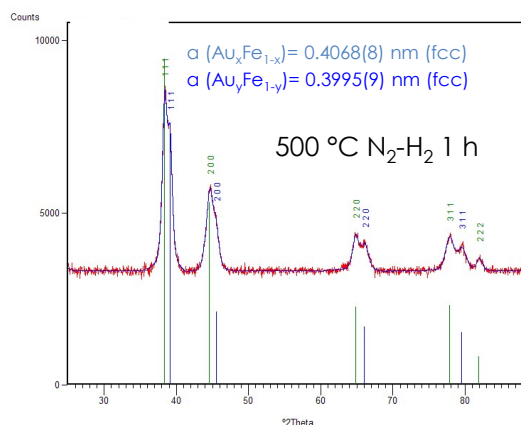
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40

Intermetallic nano-alloys $\text{Au}_x\text{Fe}_{100-x}$



Alloy AuFe fcc
Peak broadening $D = 5 \text{ nm}$



Decomposition

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43

43



Nanoparticle size from GIXRD peak broadening



44



Size Broadening

Scherrer (1918) observed that **small crystallite size** could give rise to **line broadening**. He derived a well-known equation for relating the crystallite size D_V to the broadening β , which is called the "Scherrer Formula".

$$D_V = K \frac{\lambda}{\beta \cos \theta}$$

D_V = Volume-weighted crystallite size (Diameter)

K = Scherrer constant, value that falls in the range 0.7-1.4 (shape dependent).

λ = The wavelength of the radiation (e.g., $\text{Cu}_{K\alpha 1} = 0.15406 \text{ nm}$)

β = The integral breadth (area/height) of a reflection (in radians 2θ) located at 2θ (or the FWHM).

Shape	K (β from FWHM)	K (β from Int. Breadth)
sphere	0.89	1.07



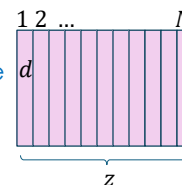
45

Heuristic derivation of the Debye-Scherrer equation

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

$$N d = z$$

Crystallite size



$$N 2 d \sin \theta = 2 z \sin \theta = N \lambda$$

Differentiate both side (with constant $N \lambda$)

$$2 \Delta z \sin \theta + 2 z \cos \theta \Delta \theta = 0$$

$\Delta \theta$ can be either positive or negative

$$z = \frac{\Delta z \sin \theta}{\cos \theta \Delta \theta} = \frac{d \sin \theta}{\cos \theta \Delta \theta} = \frac{\lambda}{2 \cos \theta \Delta \theta} = \frac{\lambda}{\beta \cos \theta}$$

$$\beta \equiv 2 \Delta \theta$$

Integral Breadth or FWHM

A more accurate derivation gives:

$$z = D_V = K \frac{\lambda}{\beta \cos \theta} \quad \text{with } K = 1.07$$

$$\beta_{\text{obs}} = \sqrt{\beta_{\text{inst}}^2 + \beta_{\text{size}}^2}$$

$$\text{or } \beta_{\text{obs}} = \beta_{\text{inst}} + \beta_{\text{size}}$$



Stokes and Wilson (1944) observed that **strained** or **imperfect** crystals produced **line broadening** of a different kind with respect to the broadening arising from small crystallite size.

$$\varepsilon_{\text{str}} = \frac{\beta}{4 \tan \theta}$$

ε_{str} = average strain

β = the integral breadth of a reflection (in radians 2θ) located at 2θ .

Note that "size" and "strain" broadening show a different θ dependence. This provides a way to separate the two effects.



Simplified Integral Breadth Methods

Williamson and Hall (1953) proposed a method for deconvolving **size and strain broadening** by looking at the peak width as a function of 2θ , described by the Williamson-Hall relationship:

$$(\beta_{obs} - \beta_{inst}) \cos \theta = K \frac{\lambda}{D_v} + 4\epsilon_{str} \sin \theta$$

To make a Williamson-Hall plot:

- Plot $(\beta_{obs} - \beta_{inst}) \cos \theta$ on the **y-axis** (θ in radians)
- Plot **$4 \sin \theta$** on the **x-axis**

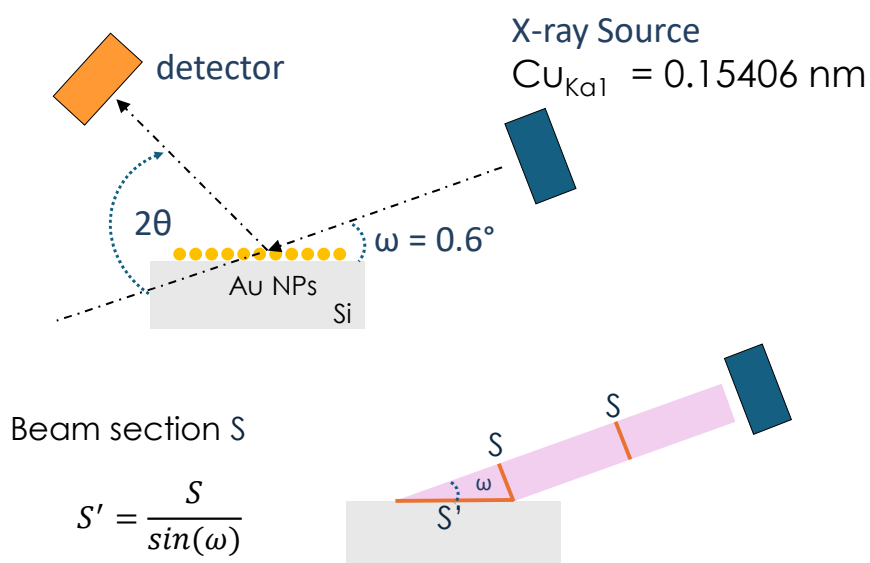
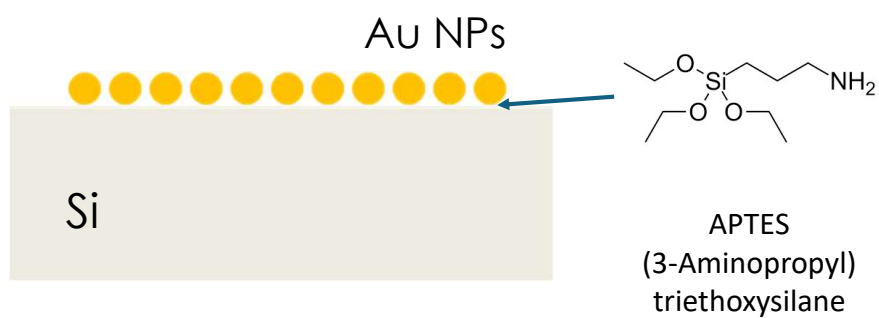
From the linear fit to the data it is possible to extract:

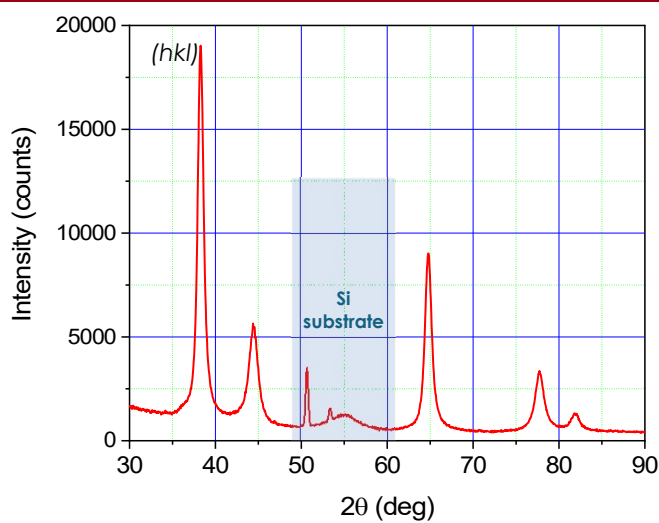
- the **crystallite size** from the y-intercept of the fit
- the **strain** from the slope of the fit

Lab Activity

HomeWork n.2

Analysis of the XRD Peak Broadening





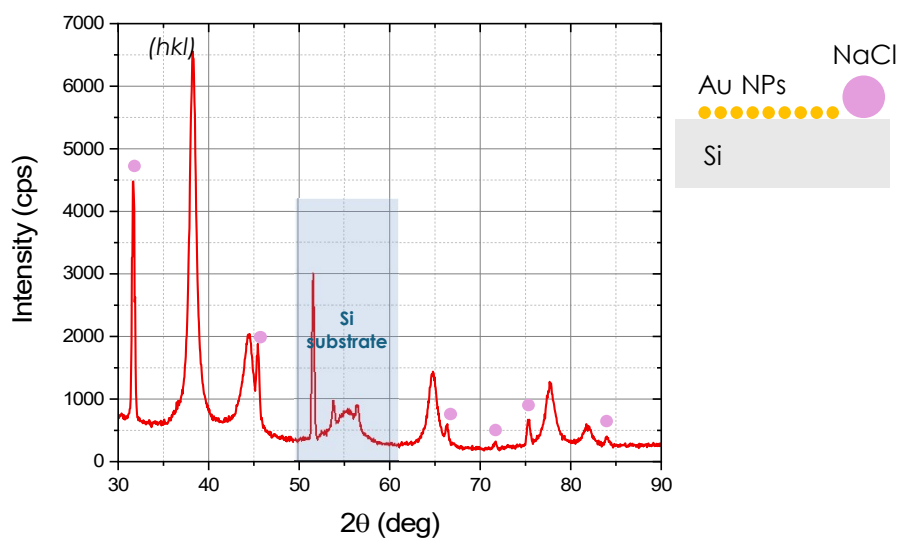
Peak shape: Pseudo-Voigt $PV(x) = \eta L(x) + (1 - \eta)G(x)$



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52

52



Peak shape: Pseudo-Voigt $PV(x) = \eta L(x) + (1 - \eta)G(x)$



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53



HW2: Aim

Analyze the Grazing Incidence X-Ray Diffraction (**GI-XRD**) → size

HW2: Tools

Use any software you are familiar with

HW2: Activity

1. Fit each peak to find center, height and FWHM (subtract a linear background and assume Pseudo-Voigt peak shape) (*disregard peaks from about 50° to 60°, related to the Si substrate*)
2. Assign the Miller indexes ($h\ k\ l$) to each peak in the spectrum assuming f.c.c structure for Au (assume $Cu_{K\alpha1} = 0.15406\text{ nm}$)
3. Calculate the Au lattice parameter and compare it with the bulk experimental one ($a_{Au} = 0.408\text{ nm}$).
4. Calculate the crystallite size for each peak with Scherrer eq. and comment on the dispersion of the values (assume $K = 0.89$ and $\beta_{inst} = 0.27^\circ$)

Hint: convert all angles in radians

