X-Ray Diffraction as a key to the Structure of Materials
Interpretation of scattering patterns in real and reciprocal space

ESRF | The European Synchrotron

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OUTLINE

1 “Internal” structure of materials – macroscopic characteristics: importance of experimental physics to understand fundamental properties

The dilemma of x-ray optics

2 X-rays in structural analysis: diffraction as a sensing parameter for inter-atomic distances

3 Introduction to diffraction and reciprocal space

4 Limits of reciprocal space

5 Getting the most out of real and reciprocal space

STRUCTURE AND PROPERTIES:
HOW CAN WE KNOW AND WHAT DO WE KNOW?

We know..

Glass is brittle,

(->experiment)

Shape cannot be changed easily

Glass is transparent

electrically insulating
and a poor heat conductor

Metals are much less brittle can be formed/ deformed,

Metals are opaque

Metals conduct well electricity
and heat

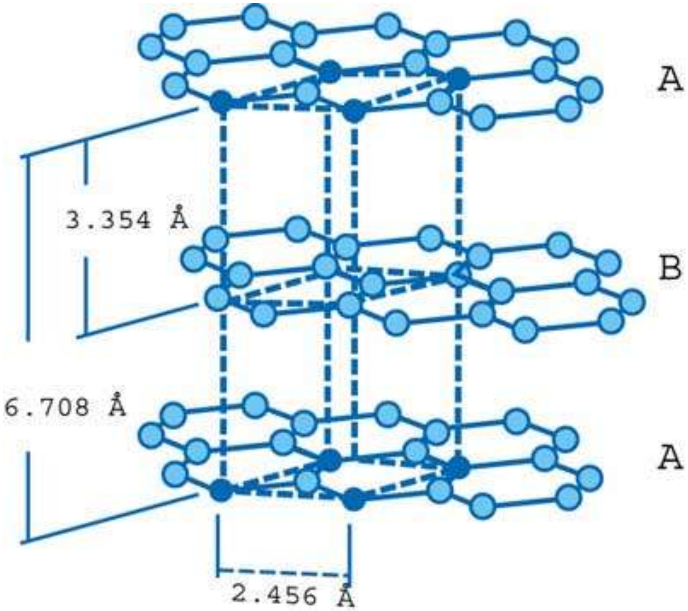
Mechanical properties

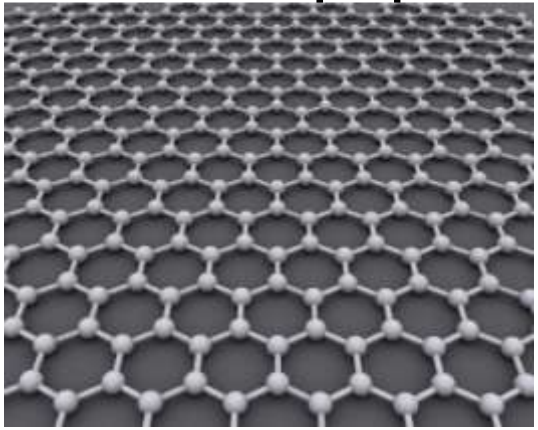
Optical properties

Electrical properties

STRUCUTRE FUNCTION RELATIONSHIP

Novoselov & Geim Nobel Price 2010:
Using scotch tape to lift of one atomic layer of *Graphene,*
With outstanding mechanical and electrical properties





2010: single layers of MoS_2 turn out to have outstanding electronic properties.

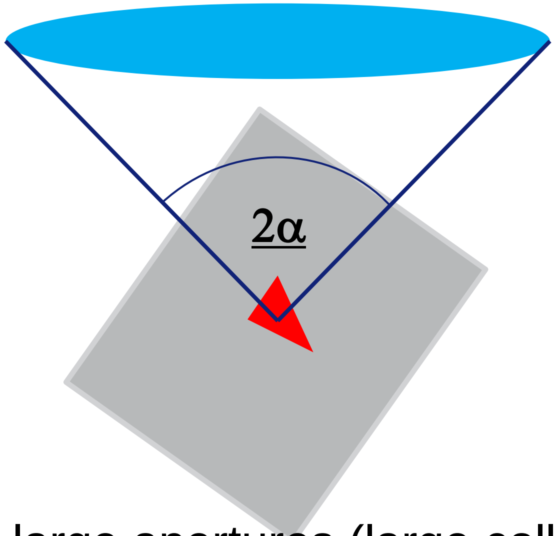
ATOMIC STRUCTURE STUDIED WITH X-RAYS

Atomic distances typically 0.1 nm (1 Å)

X-ray wavelength (typical)
λ=0.01…0.1 nm

Light λ~500nm

Resolution $\mathbf{\Delta x}$ of a light microscope:
$\underline{\mathbf{\Delta x}}$ = $1.22*\lambda/2NA\sim 0.6*\underline{\boldsymbol{\lambda/(n*\sin\alpha)}}$



High resolution means small wavelengths and large apertures (large collection angles)

X-RAY OPTICS: THE DILEMMA OF REFRACTION

interaction of electromagnetic waves (light!) and matter (~electron clouds)

The refractive index is expressed as n=1- $\delta+i\beta=\sqrt{\varepsilon\mu}\approx\sqrt{\varepsilon}=\sqrt{\varepsilon_0(1+\chi)}$

$$n \approx \sqrt{1+\chi}$$

χ=polarizability

The polarizability χ describes the polarization P as a function of a field E: P~χE; in the mechanical equivalent, 1/χ is similar to a spring constant

$$\rho_m\ddot{s}(t)+Bs(t)=\rho_e E(t)$$

Inertia

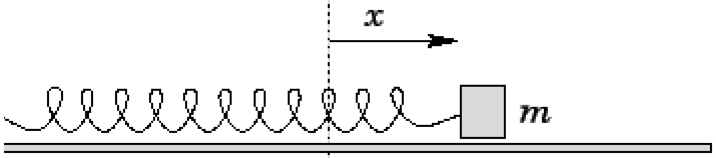
Spring constant

driving force

We replace s(t) by the Polarization P(t)=ρ_es

Damping factor (friction): ϕ (we ignore the origin)

Driven oscillator equivalent to simple mechanical model



$$\ddot{P}(t)+\omega_0^2 P(t)+\phi\dot{P}(t)=\frac{\rho_e^2}{\rho_m}E(t)$$

SOLUTION OF “EQUATION OF MOTION”

$n \approx \sqrt{1+\chi}$

With P~χ

$$\ddot{P}(t) + \omega_0^2 P(t) + \phi \dot{P}(t) = \frac{\rho_e^2}{\rho_m} E(t)$$

What else can we interpret from the mechanical equivalent ?

Amplitude

$$X_0 \cong P \propto \frac{\omega_0^2}{\sqrt{(\omega_0^2 - \omega^2)^2 + \phi^2 \omega^2}}$$

For $\omega \ll \omega_0$: P=const. (does hardly vary with ω)

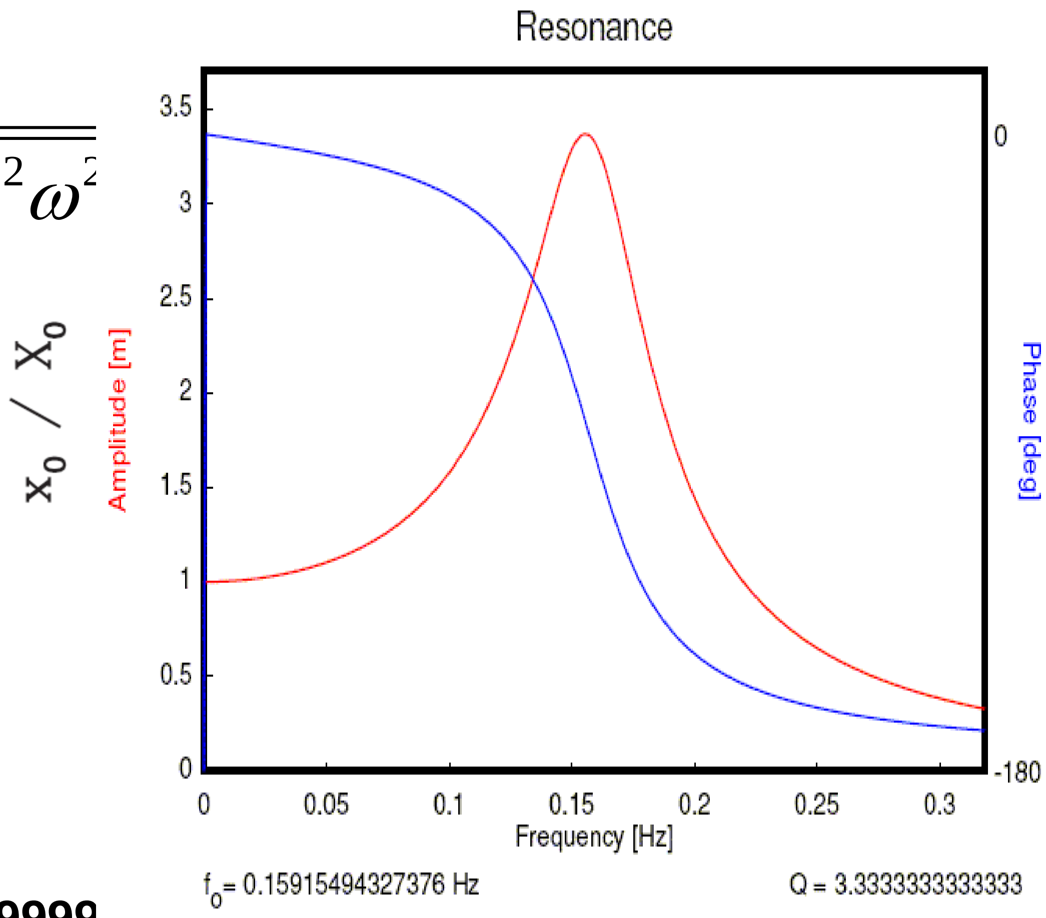
eyeglasses work for all colours,

In this regime, refraction is almost achromatic

For $\omega \gg \omega_0$: P~$1/\omega^2$, thus P-> 0

Refraction in the x-ray regime is very weak and highly chromatic!!,

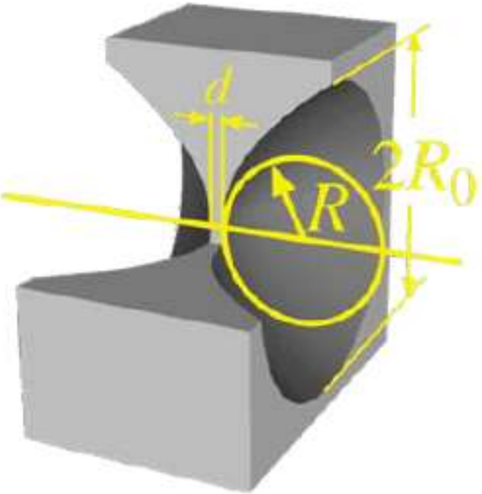
n≈0.99999..



REFRACTIVE X-RAY OPTICS

Lens surfaces must be paraboloids of rotation

single lens



parameters for Be lenses:

$R = 50$ to $1500\mu m$

$2R_0 = 0.45$ to $2.5mm$

d below $30\mu m$

To achieve reasonable refraction, many of such lenses need to be put in series.
The useful aperture is generally absorption limited And of the order of 100 μm for 100 mm focal distance.
-> NA~10^{-3} (around 1 in the visible)

Resolution $\Delta x = 1.22*\lambda/2NA \sim 0.6*\lambda/(n*\sin\alpha)$

parabolic profile: no spherical aberration

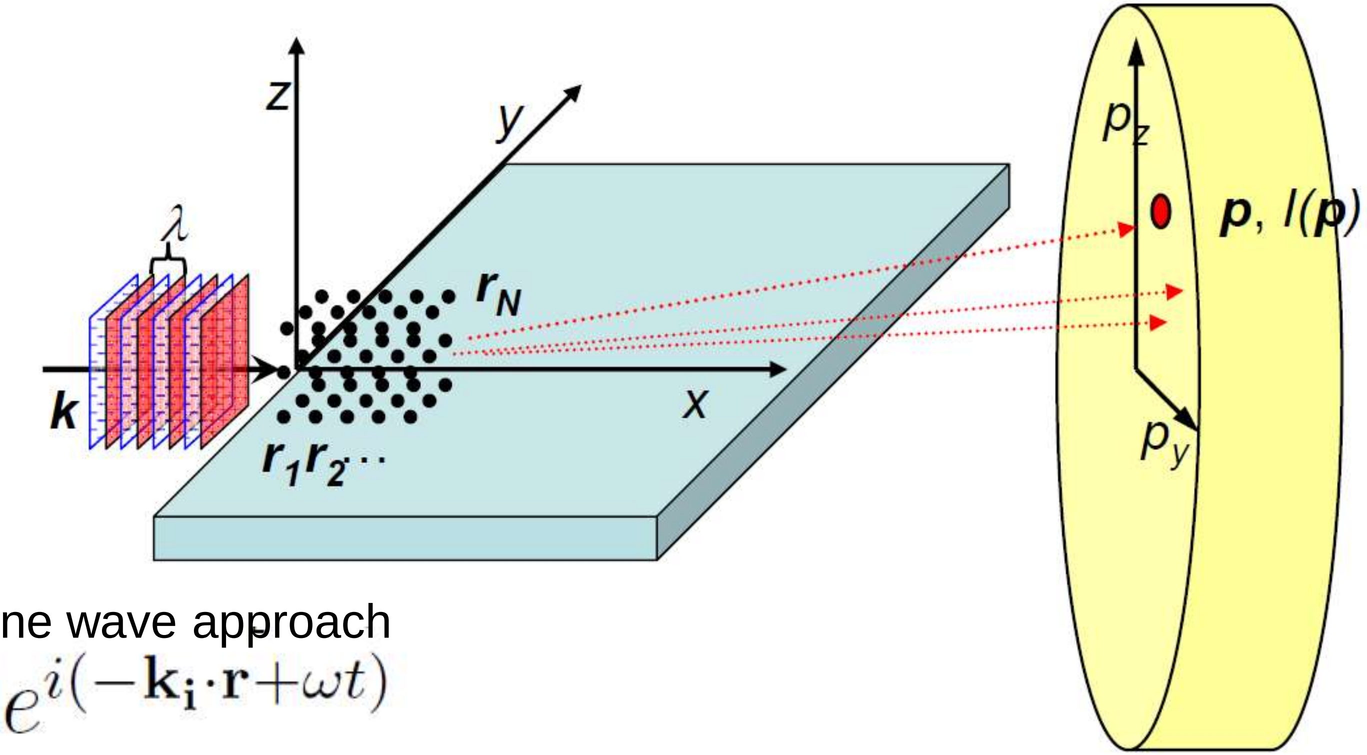
focusing in full plane

=> excellent imaging optics

From visible to x-rays, we win a factor of 10 000 in λ and loose a factor of 1000 in NA

Slide: A. Snigirev

DIFFRACTION AND RECIPROCAL SPACE



Plane wave approach

$$\hat{A} e^{i(-\mathbf{k_i}\cdot\mathbf{r}+\omega t)}$$

At the observation point we record

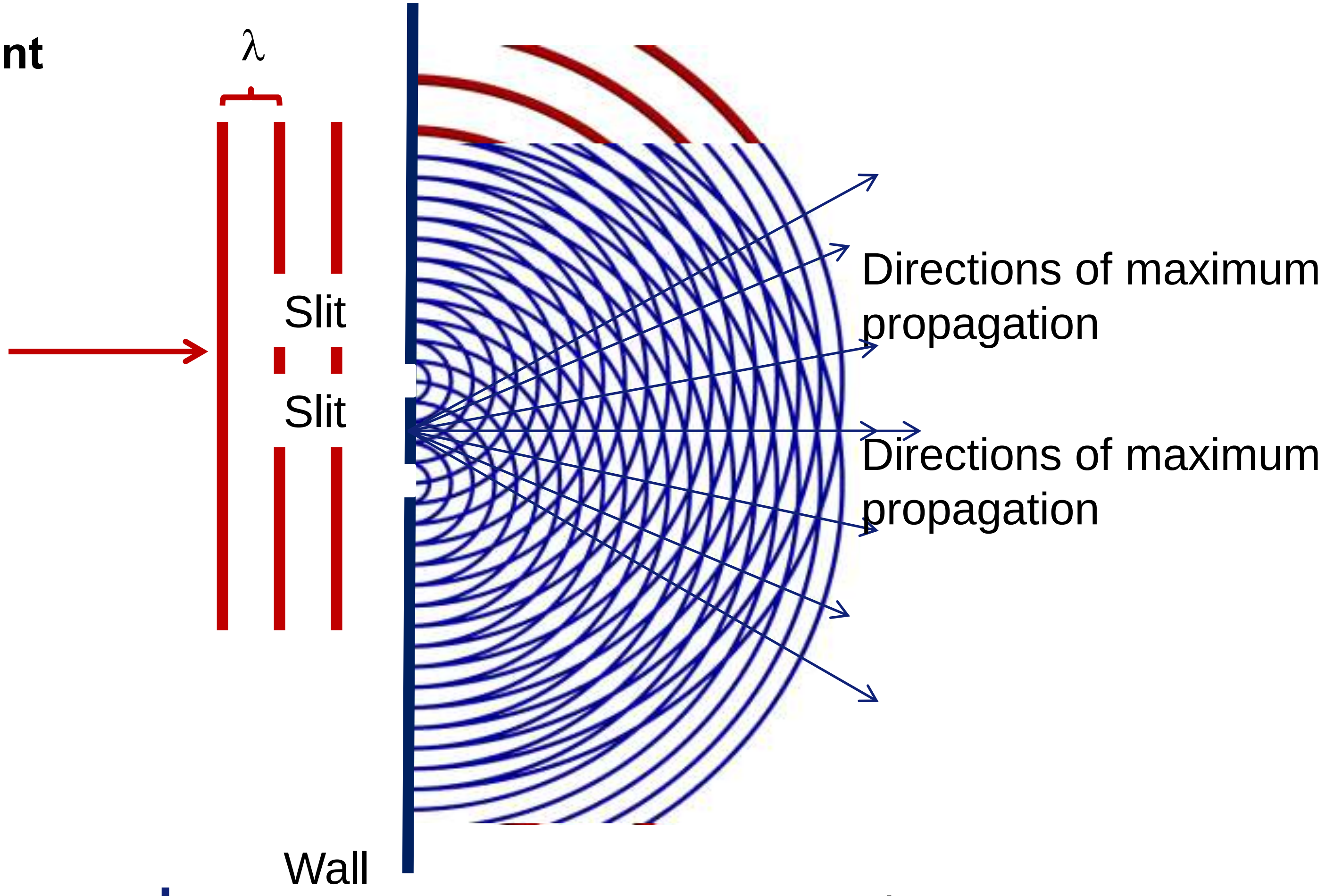
$$I = <| \sum_{j=1}^{N} \hat{A}_j e^{i\boxed{(\mathbf{k_f}-\mathbf{k_i})}\cdot\mathbf{r_j}} e^{i\omega t} |^2>_t = |\boxed{\int \rho(\mathbf{r})\, e^{i\boxed{\mathbf{Q}}\cdot\mathbf{r}} \cdot d\mathbf{r}}|^2$$

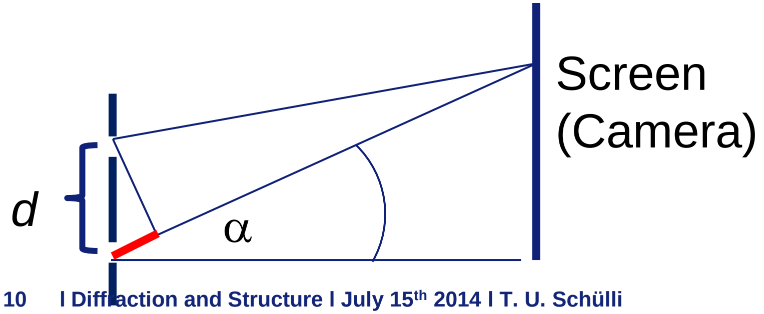
Fourier Transform
r->Q

We admit that only the time averaged Intensity can be measured and that the point scatterers can be described as $\rho(\mathbf{r}) = \sum_{j=1}^{N} \hat{A}_j \delta(\mathbf{r_j})$

DIFFRACTION AND RECIPROCAL SPACE

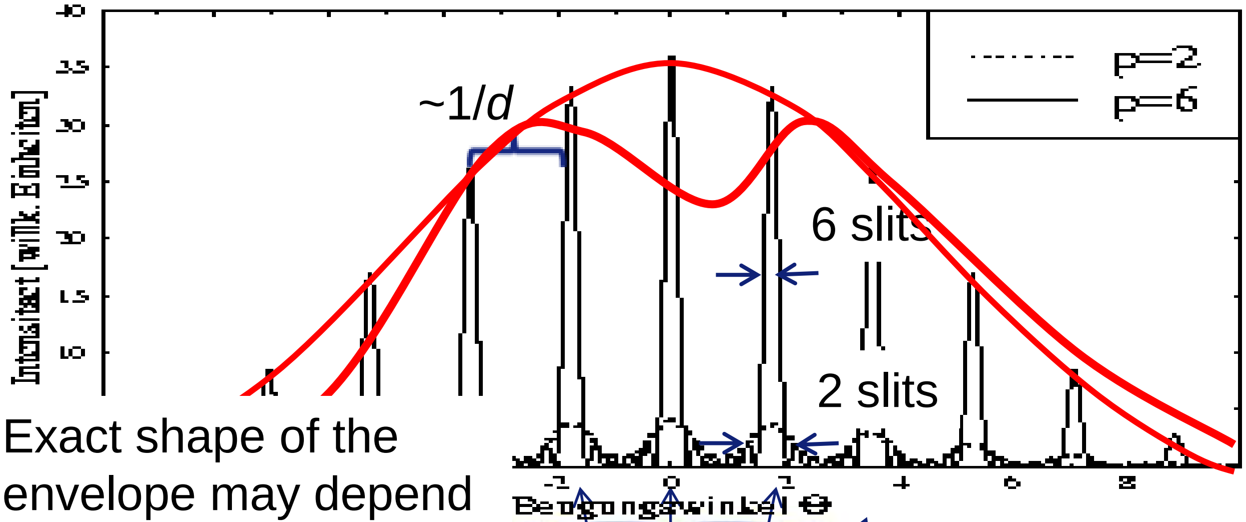
Young's experiment





— $=\text{Path difference} \overset{!}{=} n*\lambda=d*\sin\alpha$

DIFFRACTION FROM A PERIODIC GRATING

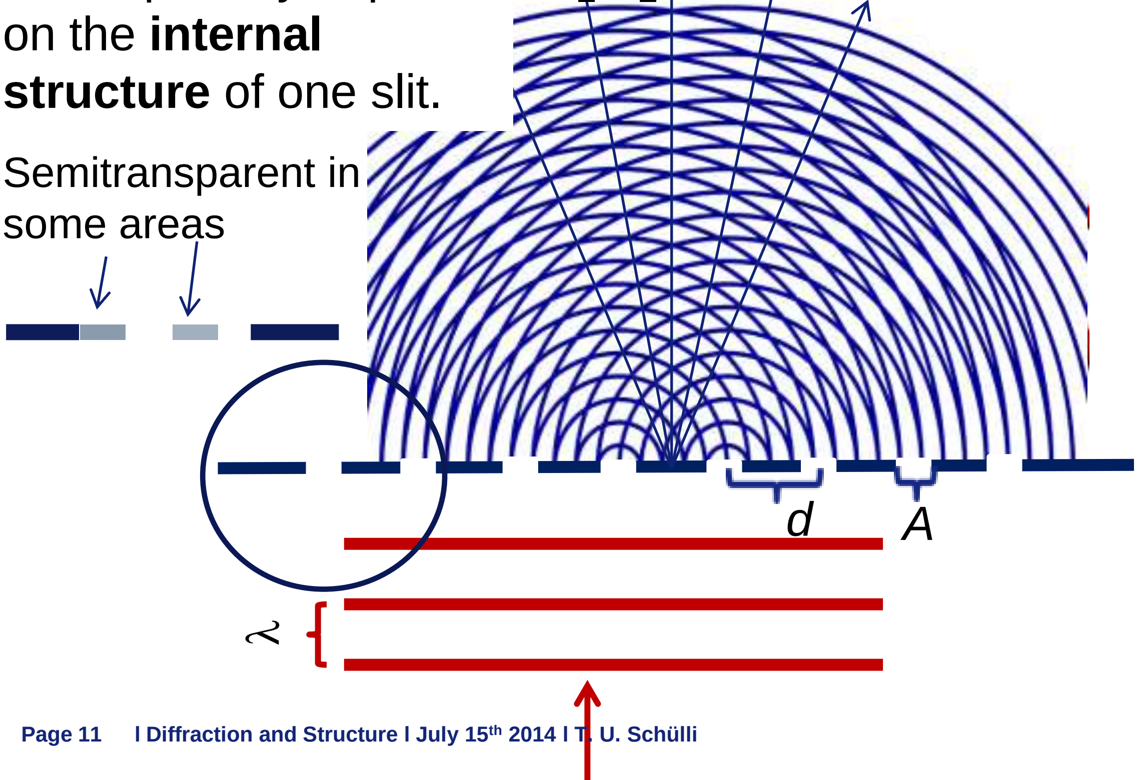


Angular distance of the peaks<->determines distances of the slits (grating parameter)

The width of the peaks (FWHM) depends on the number *p* of illuminated slits
FWHM~*1/p*

Exact shape of the envelope may depend on the **internal structure** of one slit.

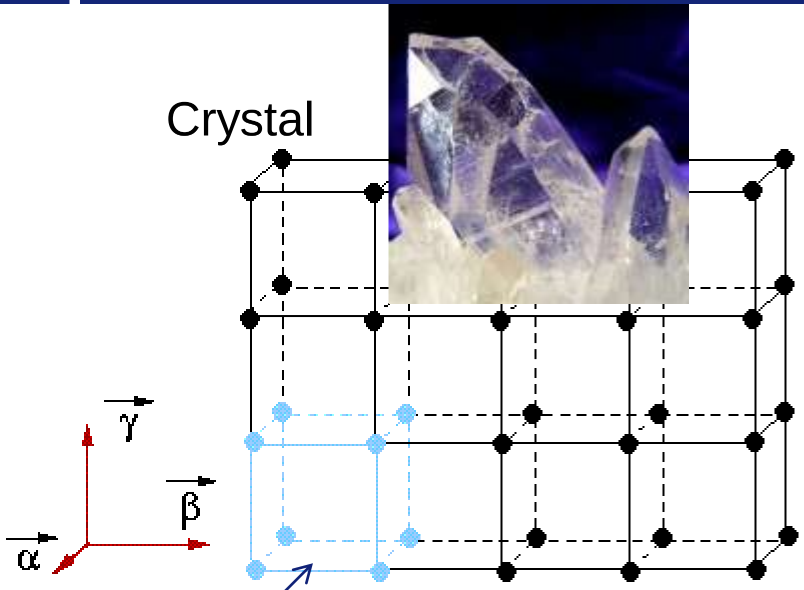
Semitransparent in some areas



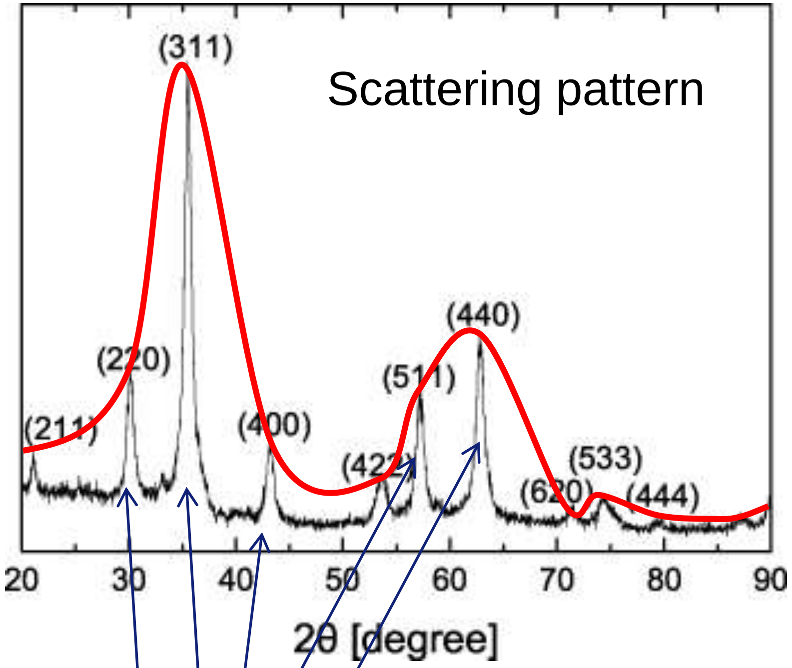
The **envelope** of the peaks determines the **width *A*** of one slit.
FWHM~*1/A*

STRUCTURE RESOLUTION IN RECIPROCAL SPACE

Crystal

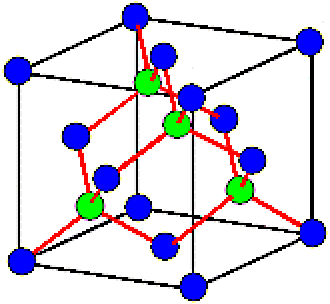


“Unit cell” (smallest repetitive building block)



Scattering pattern

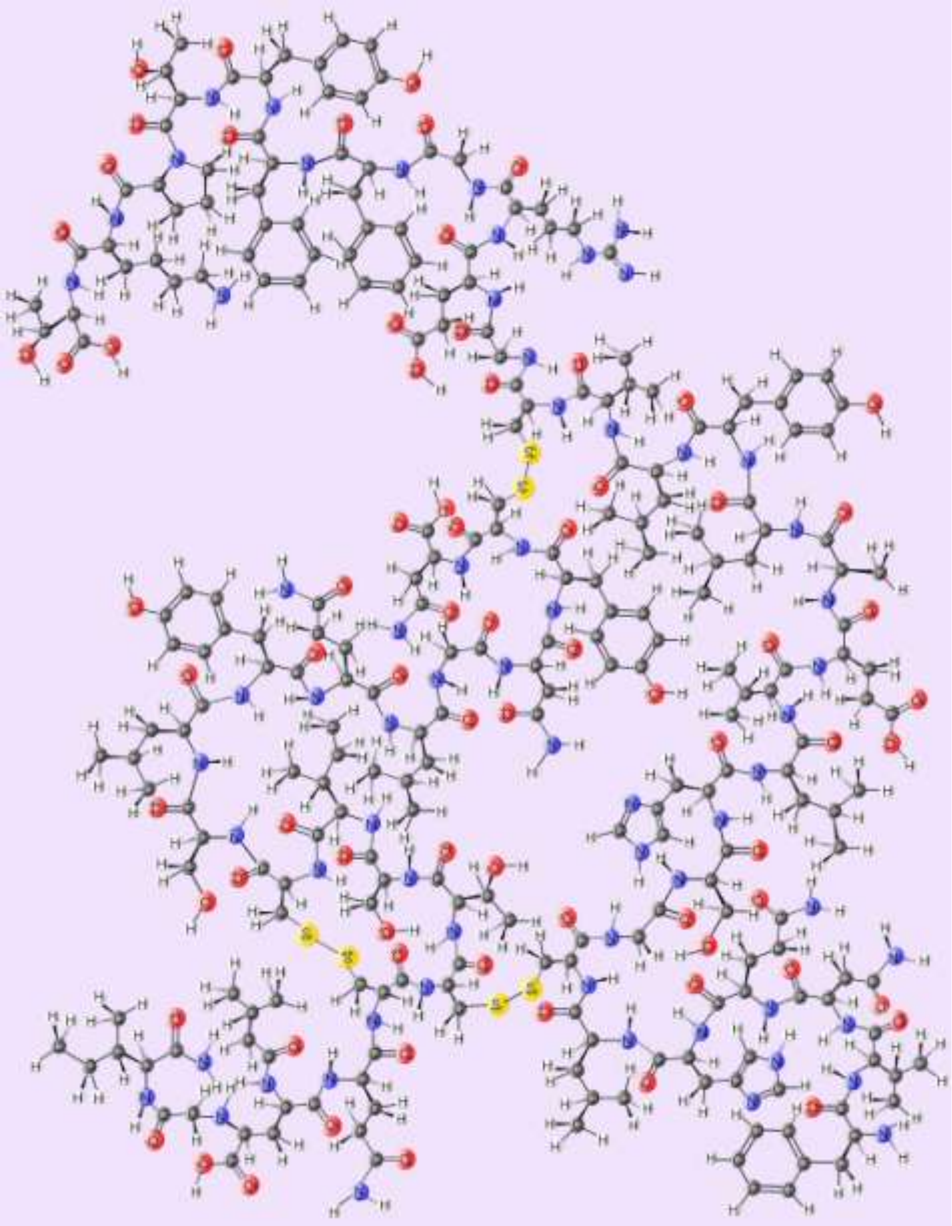
“Bragg-peaks” corresponding to different net planes)



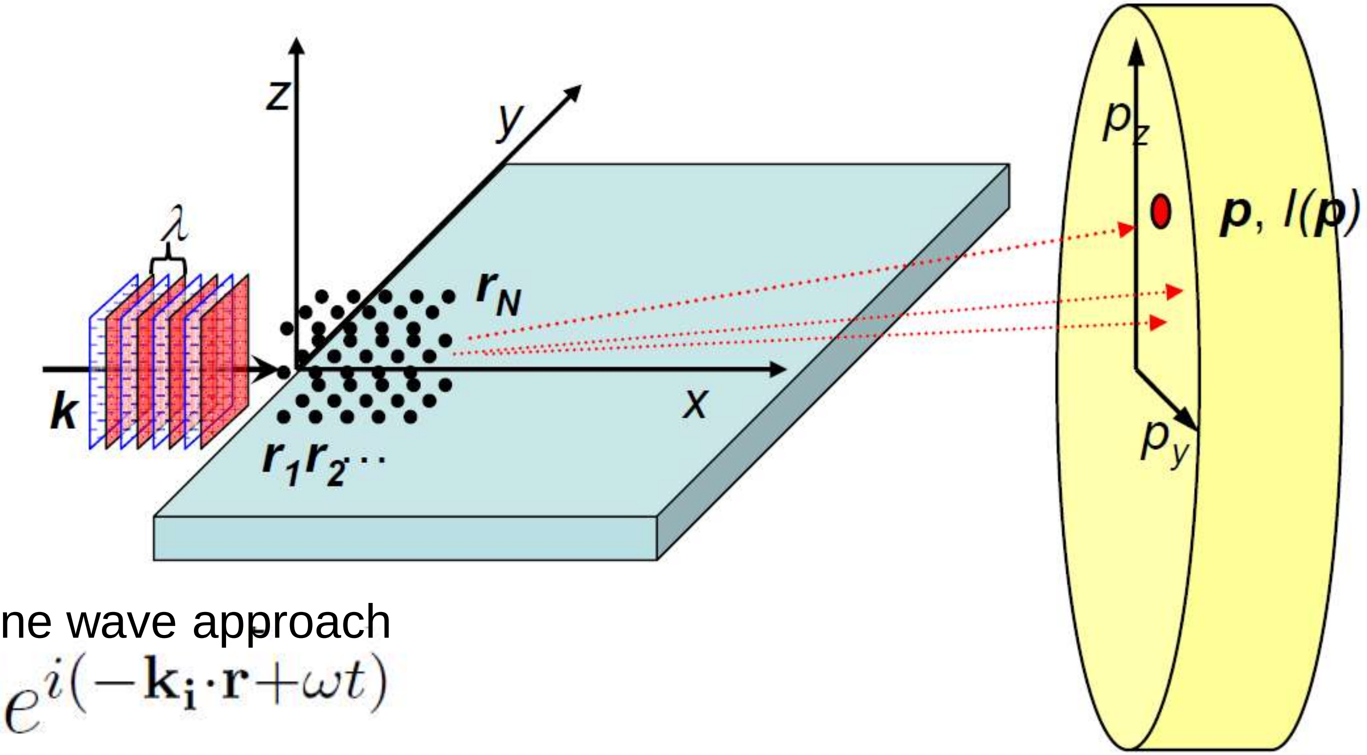
Envelope->

Information about the atomic arrangement inside the unit cell.

COMPLEX MOLECULE: INSULIN



DIFFRACTION AND RECIPROCAL SPACE



Plane wave approach

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At the observation point we record

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Fourier Transform

r->Q

We admit that only the time averaged Intensity can be measured and that the point scatterers can be described as $\rho(\mathbf{r}) = \sum_{j=1}^{N} \hat{A}_j \delta(\mathbf{r_j})$

FOURIER TRANSFORM: USEFUL RELATIONS

Fourier Transform
r->Q

$$I = <\left| \sum_{j=1}^{N} \hat{A}_j e^{i\boxed{(\mathbf{k_f}-\mathbf{k_i})}\cdot\mathbf{r_j}} e^{i\omega t} \right|^2>_t = \left| \boxed{\int \rho(\mathbf{r})\, e^{i\boxed{\mathbf{Q}}\cdot\mathbf{r}} \cdot d\mathbf{r}} \right|^2$$

1. **Linearity**: The FT of $\rho(\vec{r}) = f(\vec{r}) + g(\vec{r})$ is

$$FT\left[f(\vec{r}) + g(\vec{r})\right] = FT\left[f(\vec{r})\right] + FT\left[g(\vec{r})\right]$$

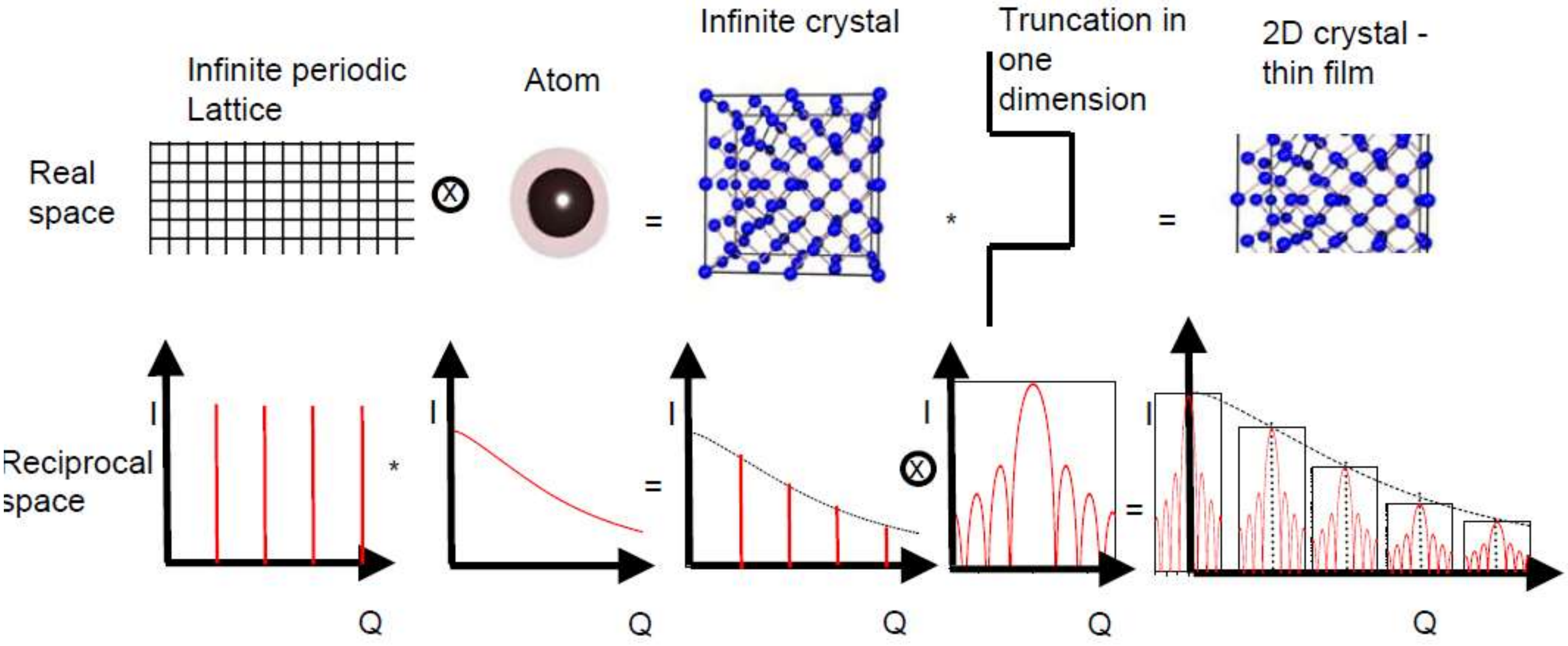
2. Convolution:

$$\rho(\vec{r}) = \int f\left(\vec{\xi}\right) g\left(\vec{r} - \vec{\xi}\right) d\vec{\xi}$$

$$FT\left[f(\vec{r}) * g(\vec{r})\right] = FT\left[f(\vec{r})\right] \bullet FT\left[g(\vec{r})\right]$$

FT “ converts” a convolution in a product and vice versa

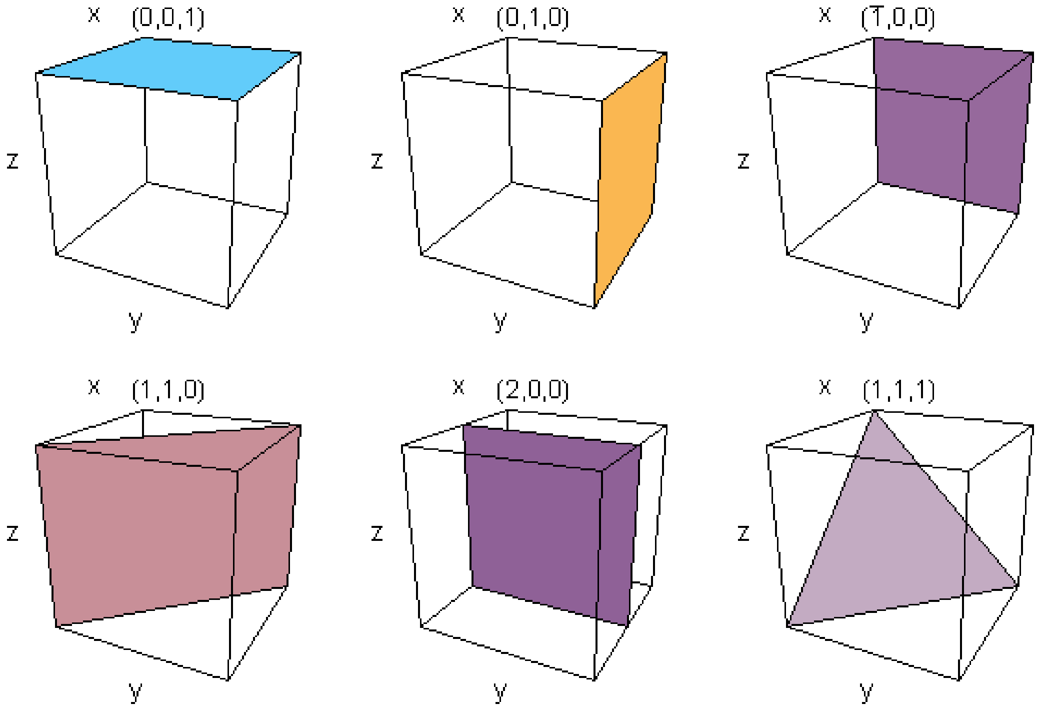
WE CAN BUILT A SMALL CRYSTAL



Big Crystals-sharp peaks, small crystals broad peaks. Peak intensities depend on the structure factor.

SUMMARY ON DIFFRACTION AND RECIPROCAL SPACE

Miller indices “naming of Bragg peaks”: “*(hkl)-peak”* means that the considered netplanes intercept the unit cell axes at positions a/h, b/k, c/l or x/h, y/k, z/l.

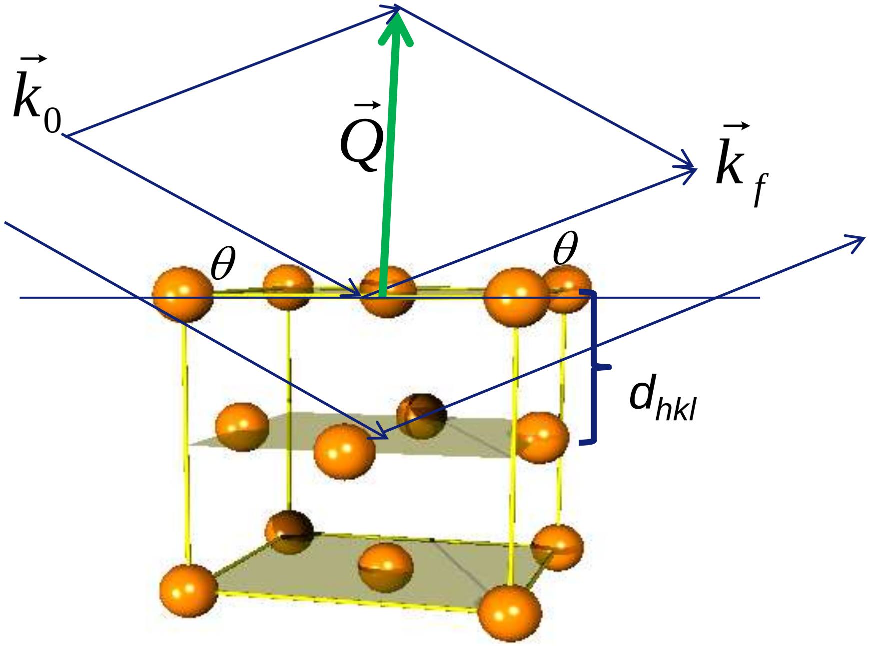


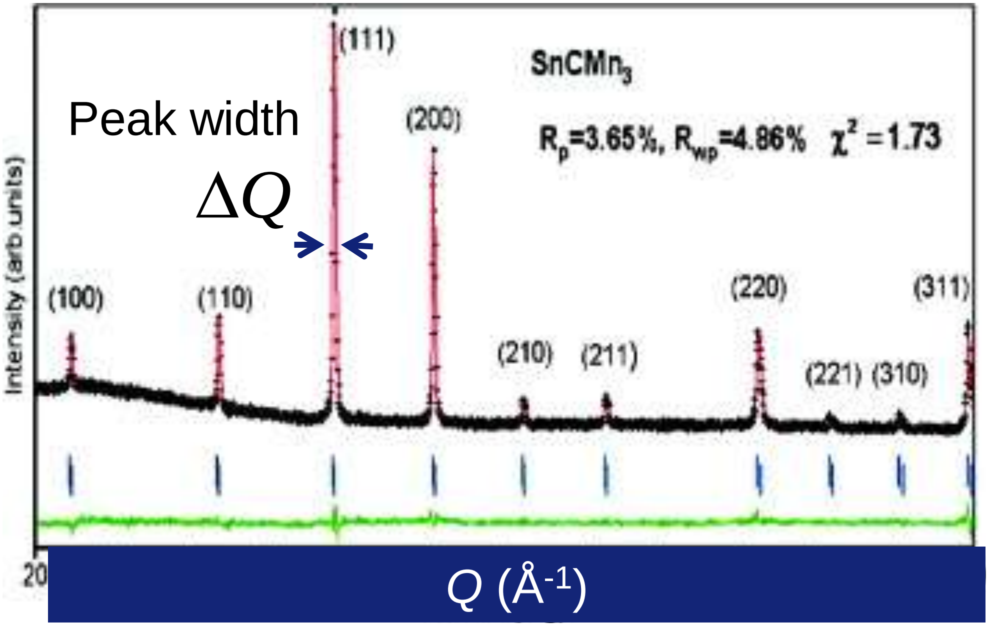
Higher indices ->closer net-plane spacings -> higher Q-values.

USEFUL RELATIONS IN (RECIPROCAL) Q-SPACE:

Braggs law: $\sin\theta = \lambda / 2d$

$$Q = \frac{4\pi \sin\theta}{\lambda} \qquad \text{with} \qquad k = \frac{2\pi}{\lambda}$$




Peak width ΔQ

Useful relations:

1)Lattice spacing: $$d_{hkl} = \frac{2\pi}{Q_{hkl}}$$

2)Particle size: $$D = \frac{2\pi}{\Delta Q}$$

SIZE BROADENING AND STRAIN BROADENING

Strain may lead to lattice parameter changes or gradients within one crystal.

Assuming a *d*-spacing change *Δd*:

$$Q = \frac{4\pi \sin\theta}{\lambda} = \frac{2\pi}{d} \qquad \frac{\Delta Q}{\Delta d} = -\frac{2\pi}{d^2}$$

Strain broadening

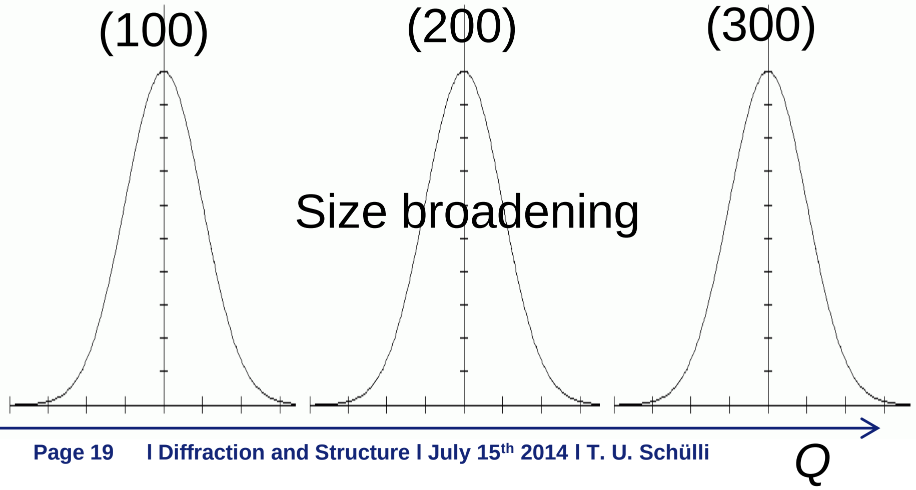
$$\Delta Q(\Delta d) = -\frac{\Delta d}{d}\frac{2\pi}{d} = -\frac{\Delta d}{d}Q$$

Depends on *Q* itself

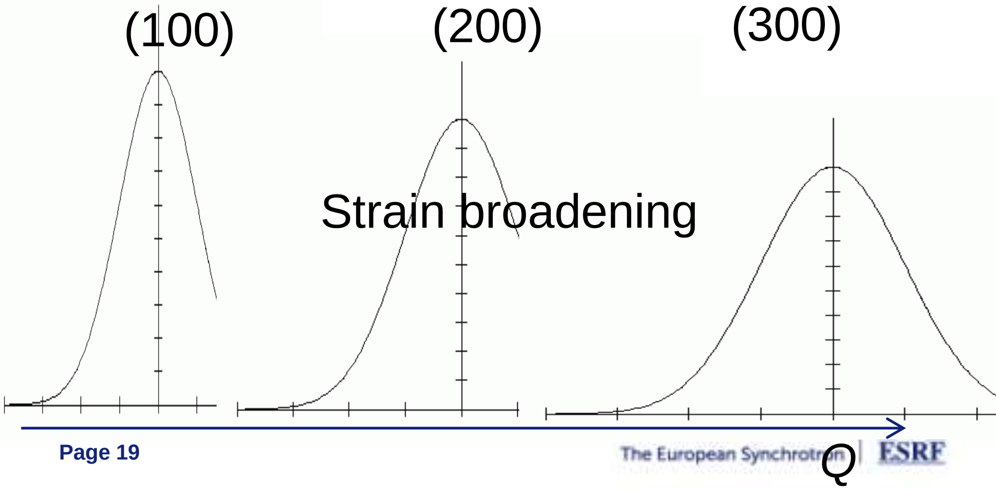
Particle size (D) broadening:

$$\Delta Q(D) = \frac{2\pi}{D}$$

No *Q* - dependence



Size broadening



Strain broadening

DETERMINATION OF LATTICE PARAMETERS

$$Q = \frac{4\pi \sin\theta}{\lambda} = \frac{2\pi}{d}$$

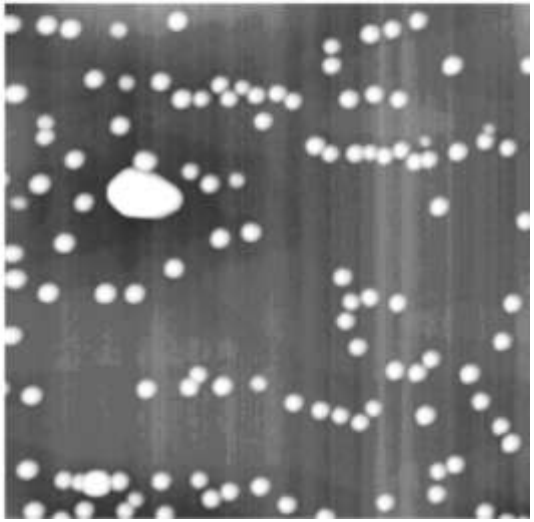
Resolution only limited by well-definition of the wavelength λ and beam divergence.

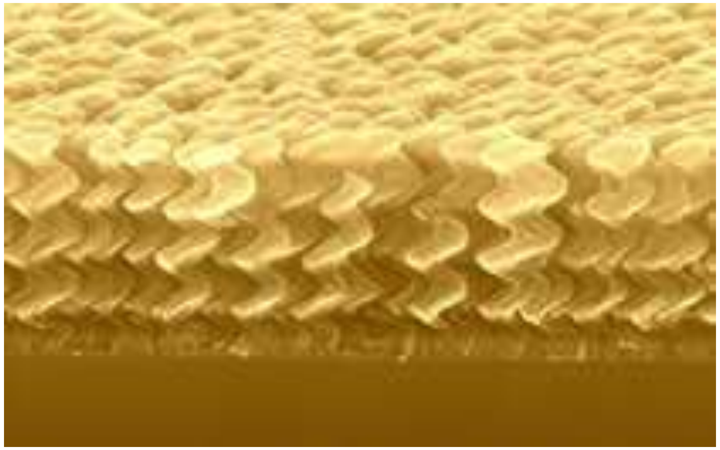
Typical absolute resolution of 10^{-4}-10^{-5} possible without too much effort

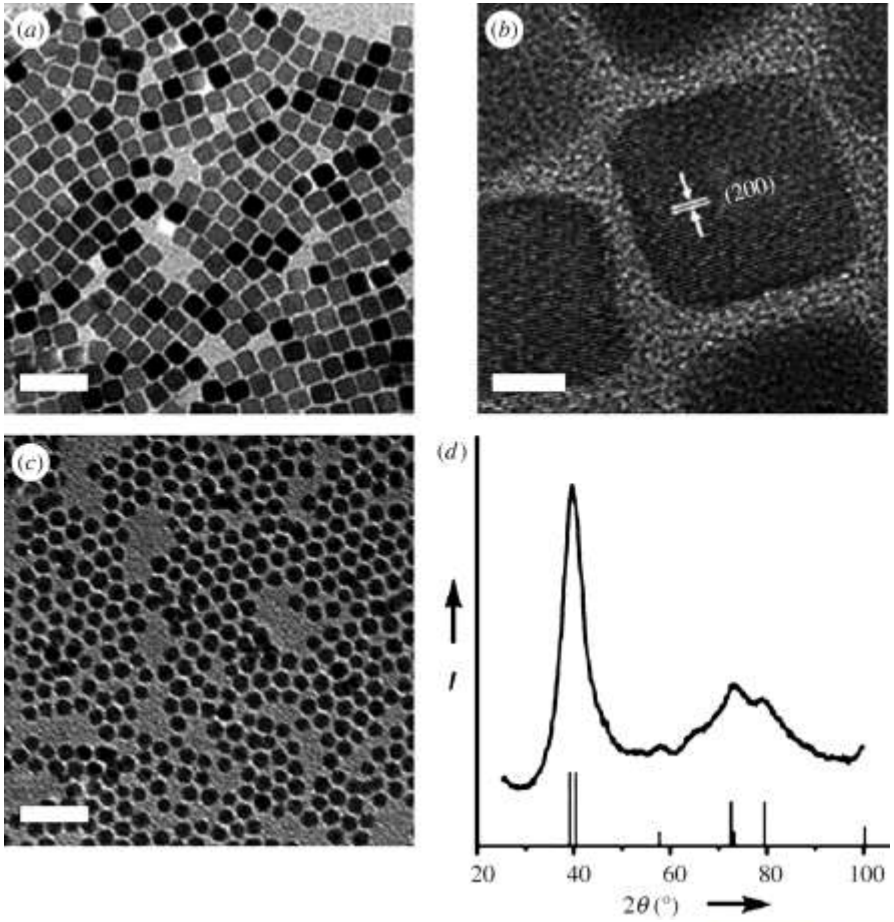
Simple structure resolution may not require that. But in order to separate different phases or in order to measure small perturbations in perfect crystals (strain) this is important

LIMITS OF RECIPROCAL SPACE

Most of diffraction experiments use “big and homogeneous” samples, like Homogeneous ensembles of nanostructures, chemical solutions or 2D “infinite” structures as surfaces, thin films, …

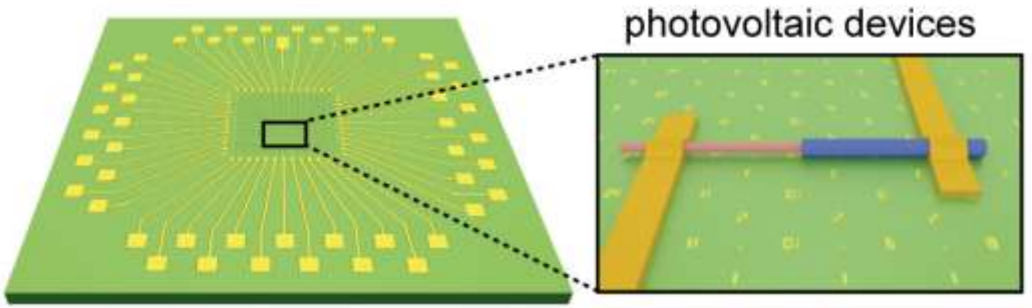


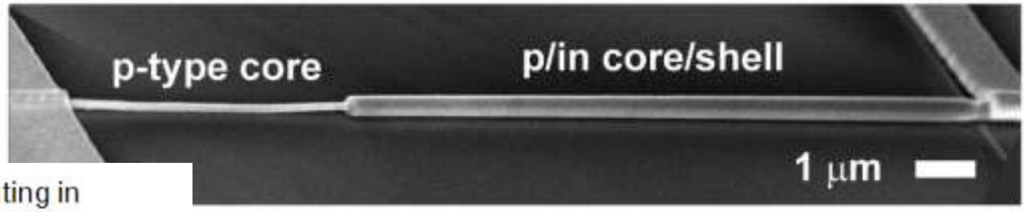


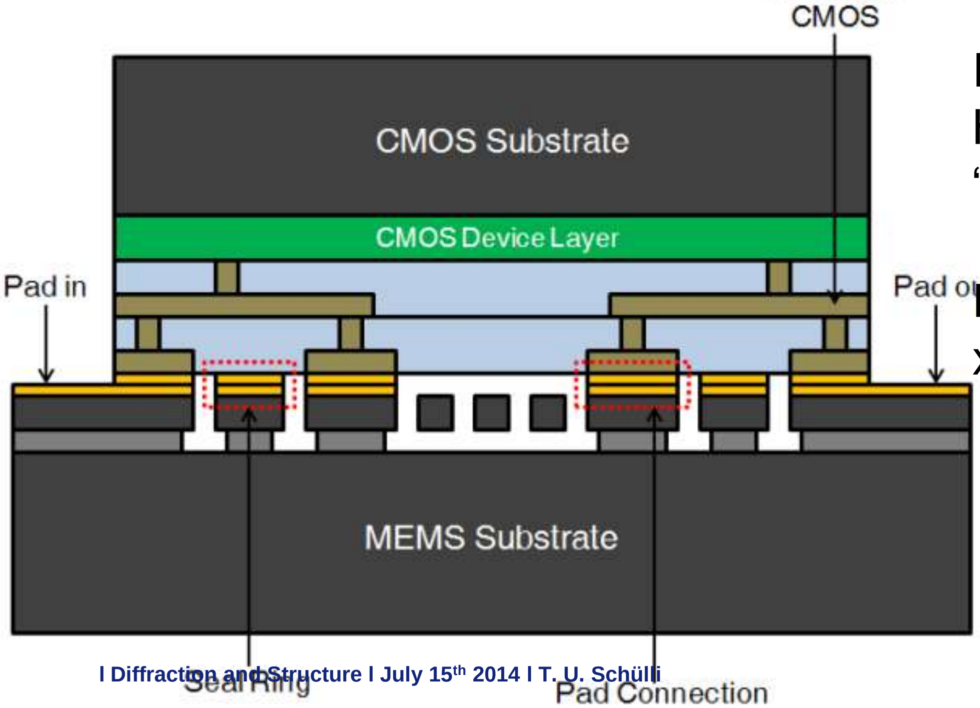


HETEROGENEOUS STRUCTURES (DEVICES)

Presence of multiple materials on different lengths scales:
new strategy required.







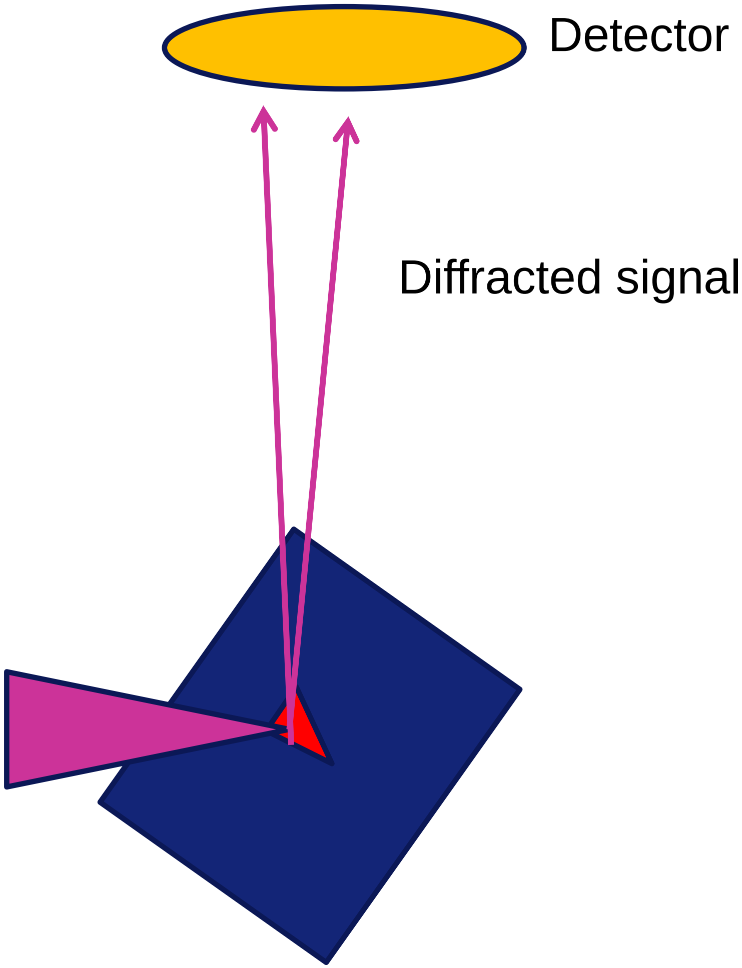
In many intersting systems, heterogeneity happens to be on the “mesoscale” (not atomic scale).

Beams of 100 nm can be produced by x-ray optics

DIFFRACTION IMAGING: SCANNING PROBE

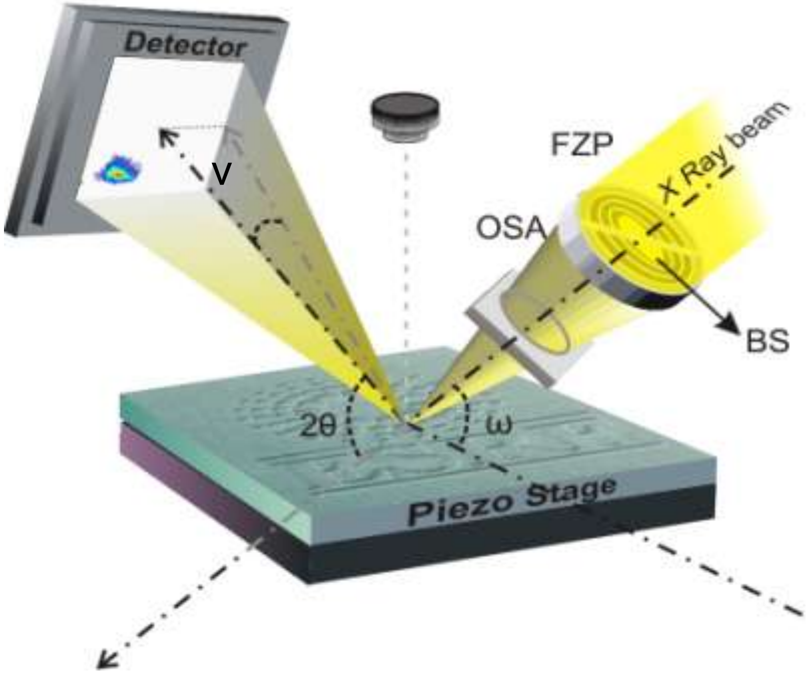
Use of focused beam/ scanning technique.

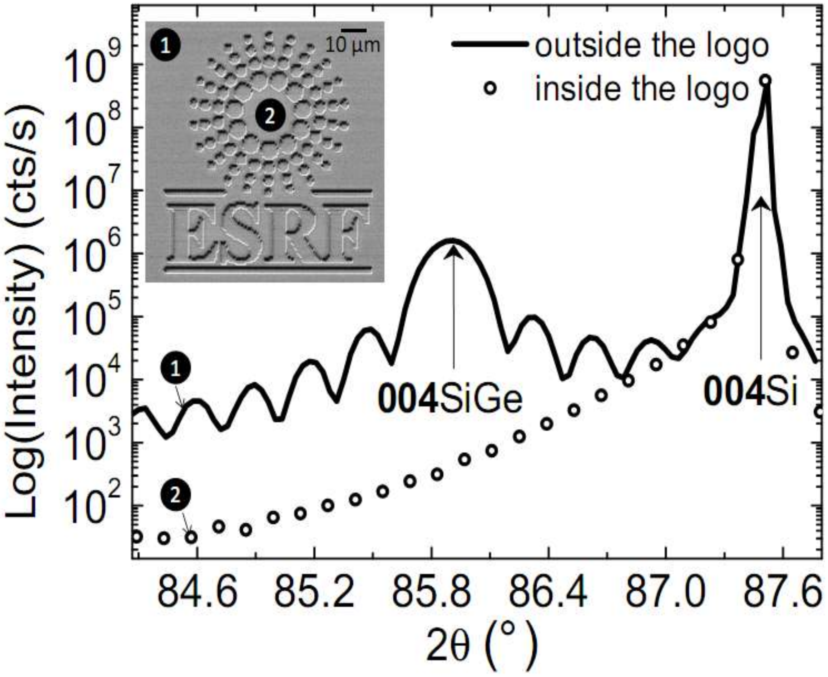
Resolution limited by beam spot; limits imposed by source size, working distance and optics
Sub 100 nm are possible



STRUCTURED THIN FILM: TYPICAL FOR A DEVICE

○ $Si_{0.8}Ge_{0.2}$ layer grown on a Si (001) substrate patterned by focused ion beam (FIB) to draw the ESRF logo.





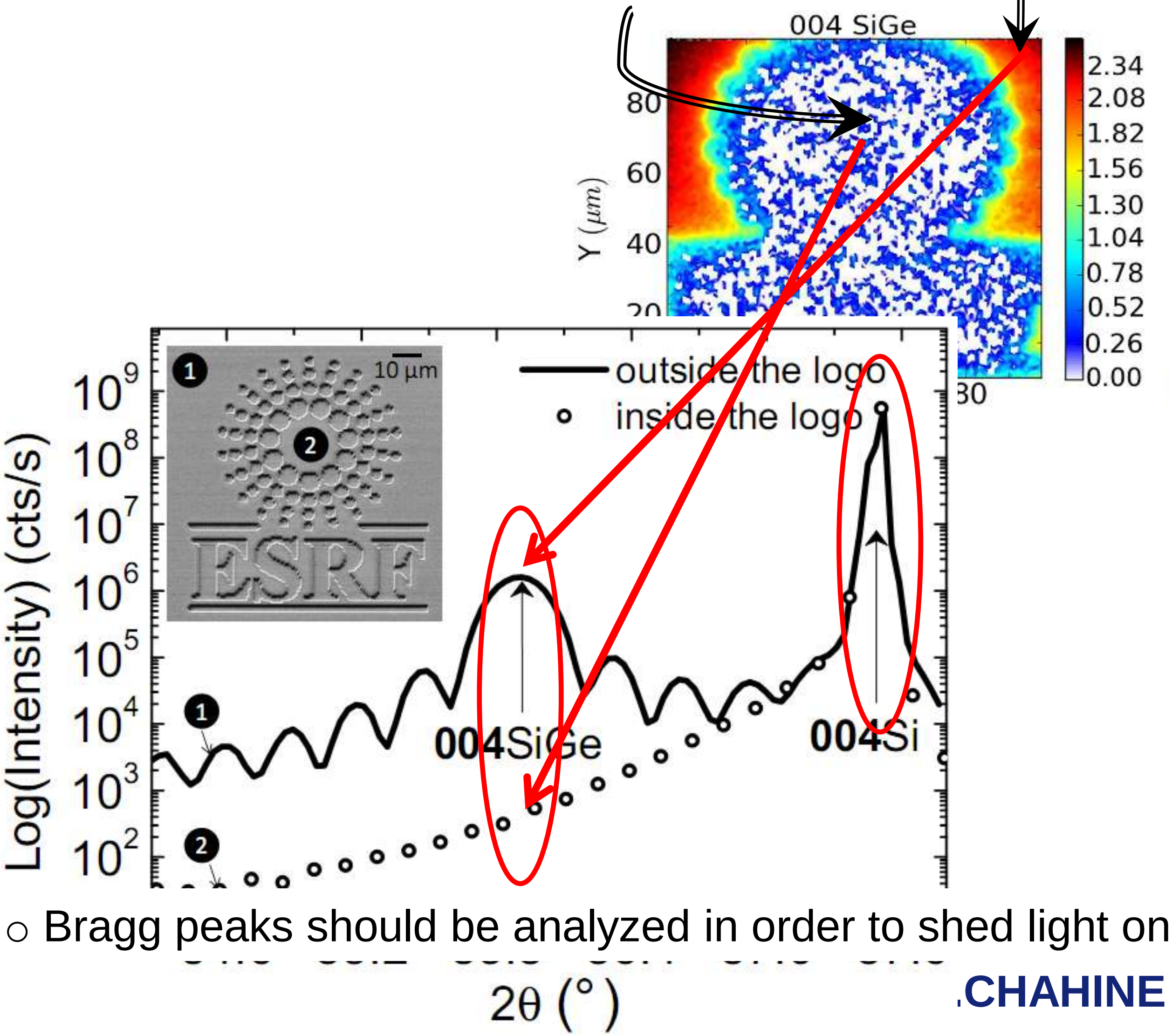
❶
- ➢ Broad peak is observed around 2θ = 86°.
- ➢ Thickness fringes from the SiGe thin film (40nm) can be observed.

❷
- ➢ SiGe layer inside the logo has been damaged during the FIB process.

QUALITATIVE ANALYSIS

○ **004** SiGe layer (a):
- Remains crystalline
- Is damaged during the FIB process

○ At the diffuse **004** Si Bragg reflections, the ESRF logo appears (b), (c), (d).



○ Bragg peaks should be analyzed in order to shed light on these defects nature...

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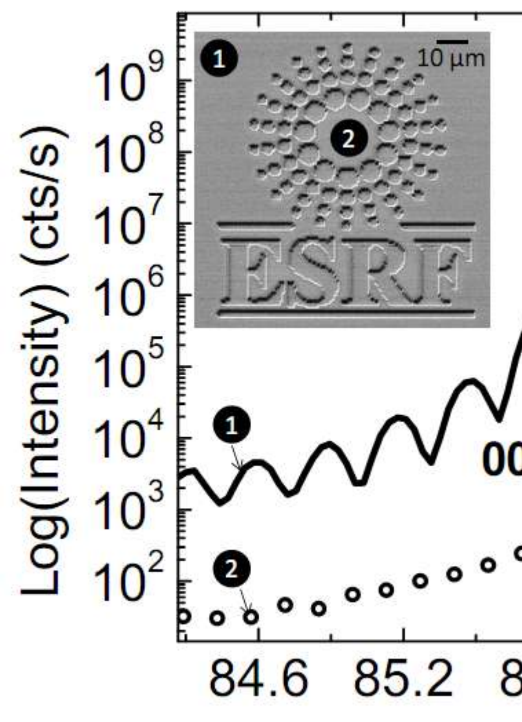
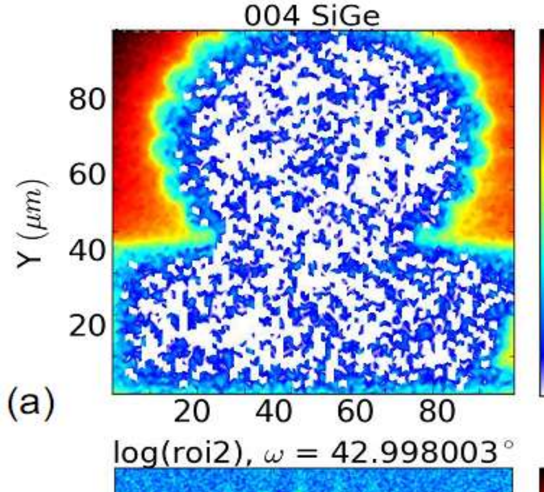
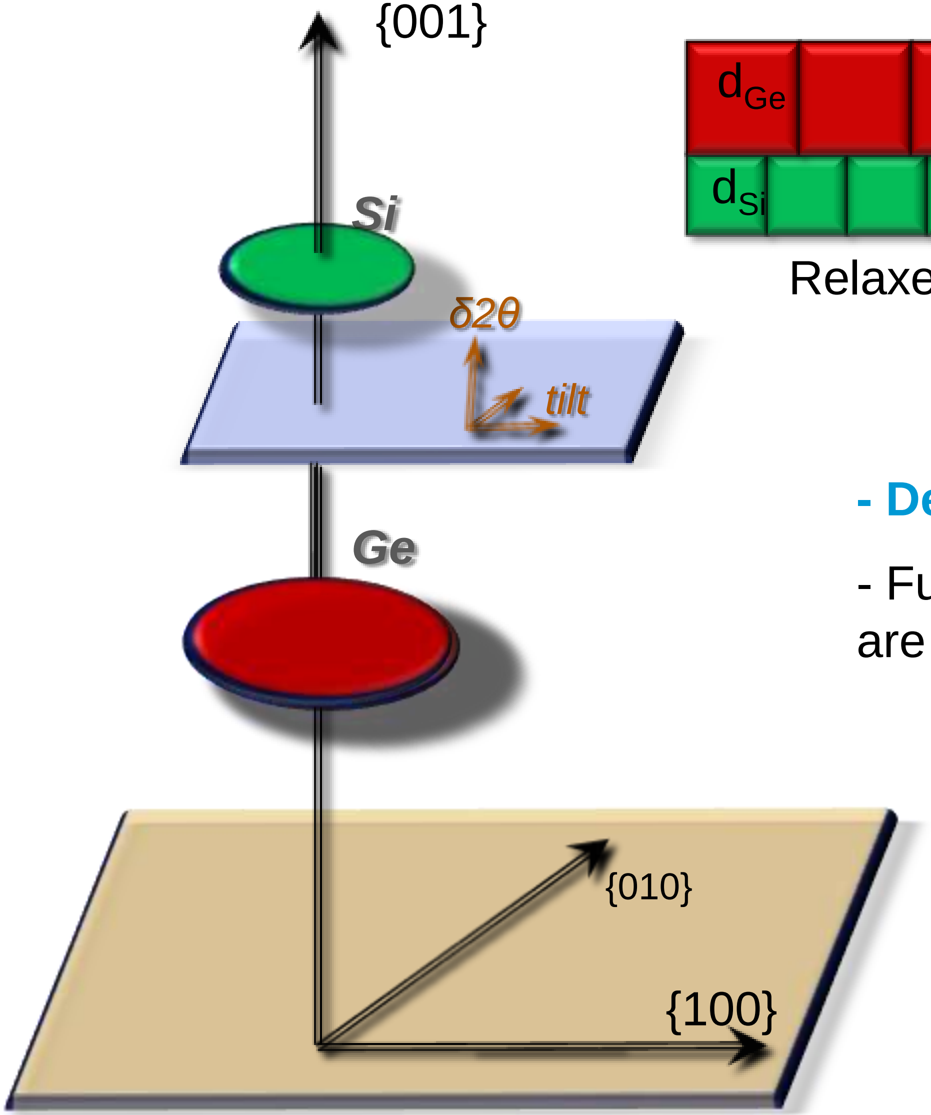
FIB seen by a traditional scanning probe microscopist

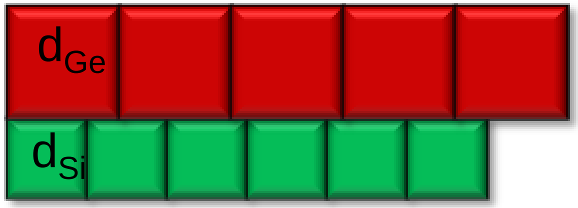


…and seen by x-rays …

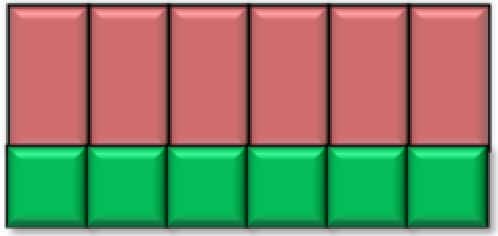


STRAIN AND ORIENTATION





Relaxed Film

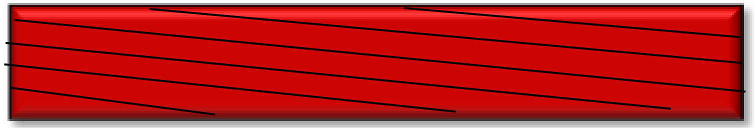


Strained Film

- Determine the degree of strain:

- Fully strained: the lattice parameters of the film are strained to fit to the substrate

- Tilts appears as perpendicular shifts



○ The Bragg peak position in reciprocal space is essential for retrieving all information related to strain and/or tilts in the structure.

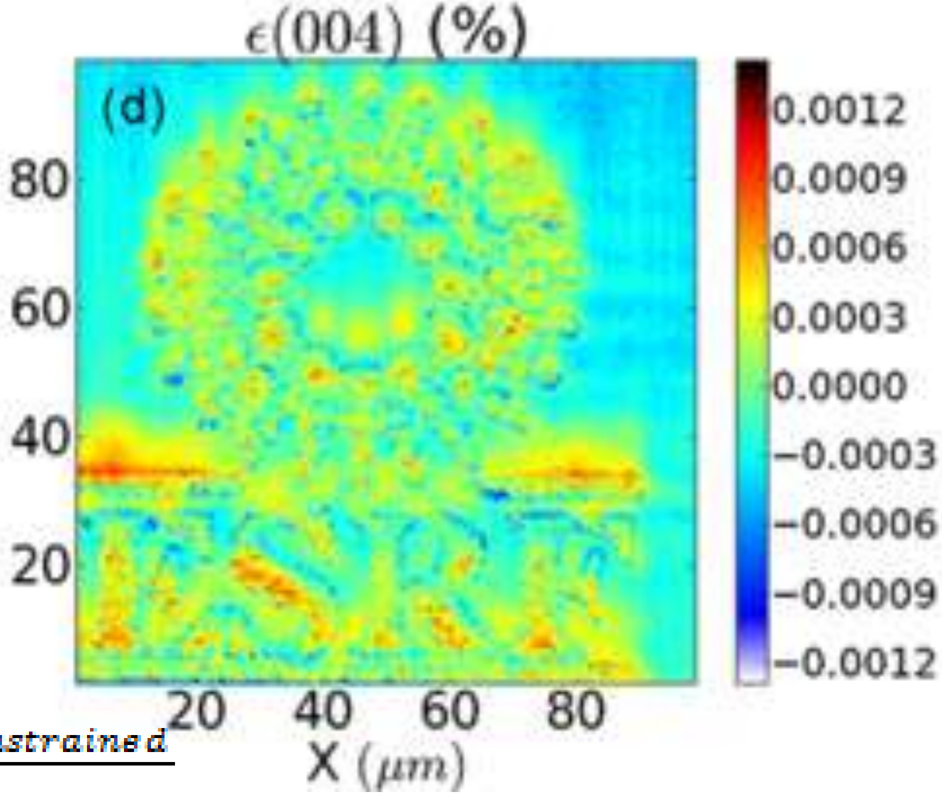
STRAIN MICROSCOPY

- numerical Gaussian peak fitting to locate the Q_x, Q_y and Q_z position of the Bragg peak in the corresponding reciprocal dimension.

- This generates maps of strain and orientation profiles rather than intensity

$$d_{hkl} = \frac{2*\pi}{\overrightarrow{\|Q\|}} = \frac{2*\pi}{\sqrt{Q_x^2+Q_y^2+Q_z^2}}$$

Few 10^{-6} lattice parameter variation are enough to trace a landscape !!



$$\varepsilon_{hkl} = \frac{d_{hkl,experiment} - d_{hkl,unstrained}}{d_{hkl,unstrained}}$$

- The Si layer underneath the SiGe structured logo is slightly strained (<0.0015%)

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