Characterization of semiconductor hetero- and nanostructures by x-ray scattering

Václav Holý,
Department of Physics of Electronic Structures, Charles University, 121 16 Prague, Czech Republic
holy@mff.cuni.cz

in collaboration with

J. Stangl, G. Bauer, *J. Kepler University Linz, Austria*

U. Pietsch, *University of Potsdam, Germany*

T. H. Metzger, T. Schülli, *ESRF Grenoble, France*

Outline:

1. High-resolution x-ray scattering – how it works
2. High-resolution x-ray scattering – what it can do
3. 2D layers and multilayers:
    3.1. thicknesses of layers
    3.2. strains in layers
    3.3. interface roughness
4. What else can be done
5. High-resolution x-ray scattering – what it cannot do

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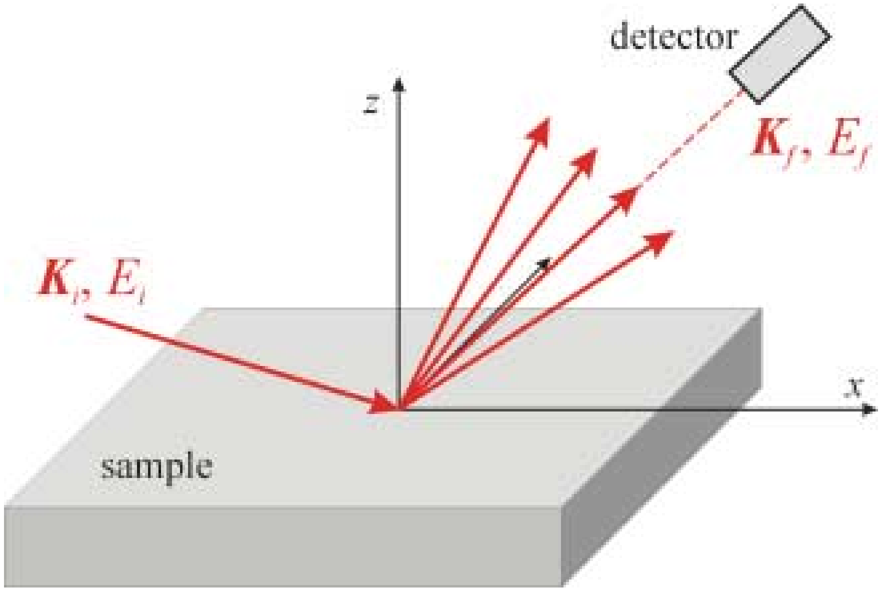
We restrict ourselves to the scattering from electron charges, scattering from magnetic moments of the electrons is neglected here

An idealized arrangement of a high resolution x-ray scattering experiment:



An ideally plane and monochromatic x-ray beam irradiates the sample;
the intensity of a monochromatic plane component of the scattered radiation
is measured.
6 degrees of freedom: 2 angular variables of $\boldsymbol{K}_i$, E_i, 2 angular variables of $\boldsymbol{K}_f$, E_f

Special cases:

- $E_f = E_i$ … **elastic** scattering
- $K_{fz} = -K_{iz}$ … **specular** scattering
- $\boldsymbol{K}_f - \boldsymbol{K}_i = \boldsymbol{h}$ … **coherent** scattering, $\boldsymbol{h} = 0$ …specular reflection, $\boldsymbol{h} \neq 0$ … coherent diffraction

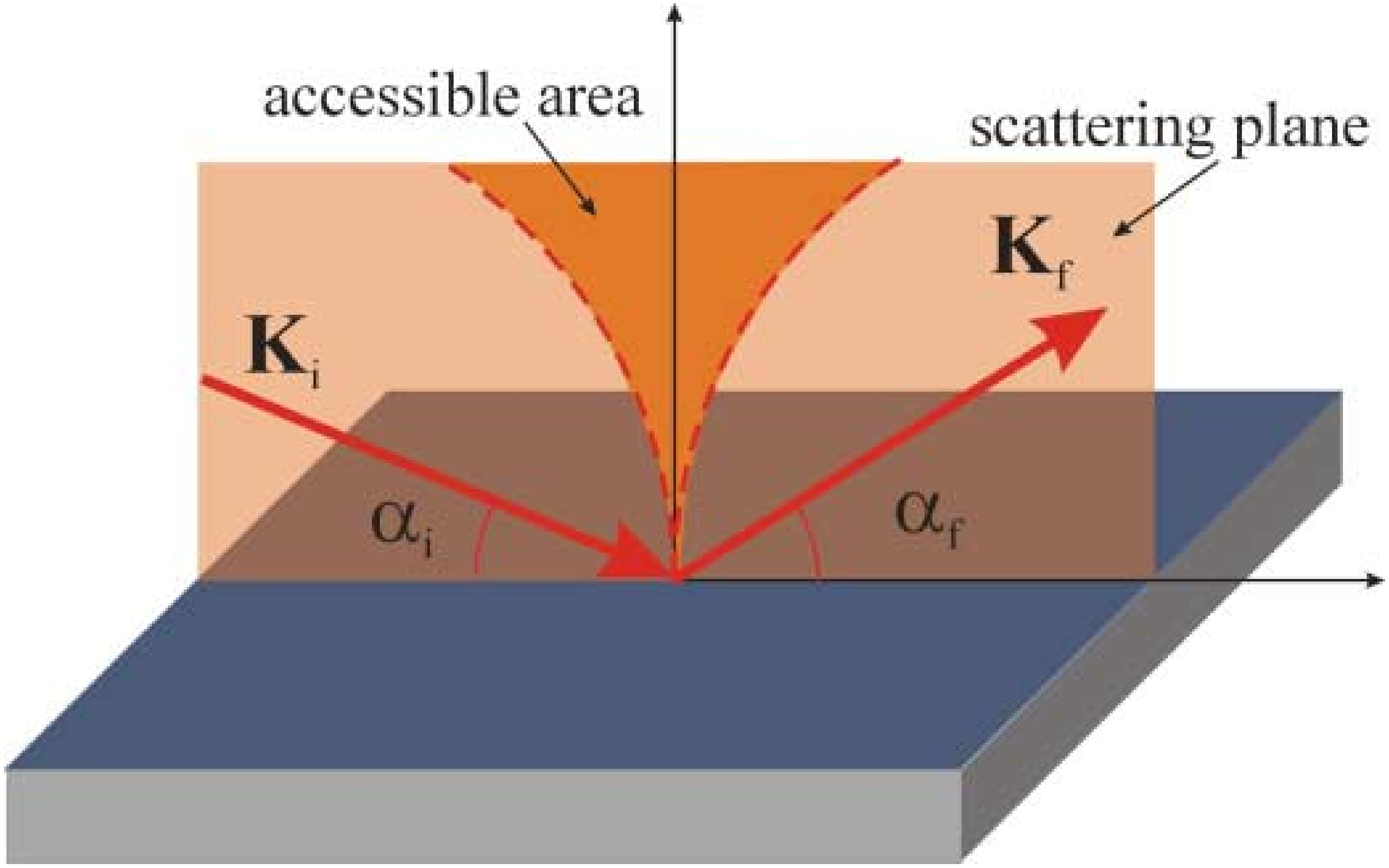
reciprocal lattice vector

- $K_{iy} = K_{fy} = 0$ … coplanar geometry
- $|K_{iz}|, K_{fz} << K_i, K_f$ … grazing-incidence geometry

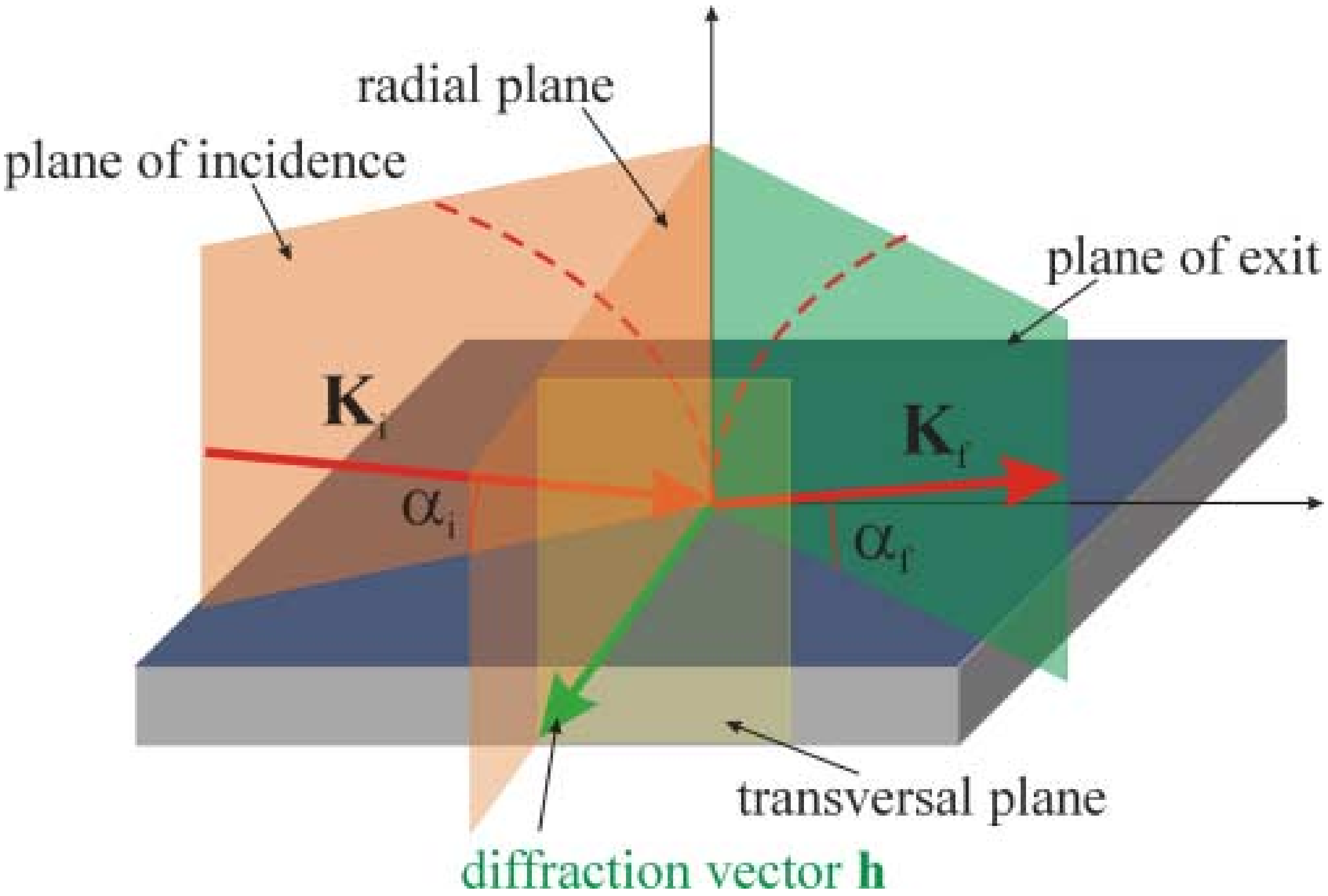
Elastic coplanar geometry $\Rightarrow$ 3 degrees of freedom $\Rightarrow$ The scattered intensity is a function of the constant energy and the scattering vector

$\boxed{\boldsymbol{Q} = \boldsymbol{K}_f - \boldsymbol{K}_i}$ $\Rightarrow$ Reciprocal-space intensity map $\boxed{I = I(E, Q_x, Q_z)}$

coplanar scattering geometry



grazing-incidence scattering geometry



A simple theory of elastic scattering starts from the classical wave equation:

$$(\Delta + K^2)\boldsymbol{E}(\boldsymbol{r}) = \hat{\mathbf{V}}(\boldsymbol{r})\boldsymbol{E}(\boldsymbol{r})$$

The classical scattering potential is $\hat{\mathbf{V}}(\boldsymbol{r}) = \mathrm{graddiv} - K^2\chi(\boldsymbol{r}),\ \chi(\boldsymbol{r}) = \varepsilon_{\mathrm{rel}}(\boldsymbol{r}) - 1$

polarizability

Electron polarizability (other polarization processes can be neglected) is proportional to the density $\rho(\boldsymbol{r})$ of all electrons

$$\chi(\boldsymbol{r}) = -\frac{\lambda^2}{\pi} r_{\mathrm{el}} C \rho(\boldsymbol{r})$$

classical electron radius

linear polarization factor

Exact solution of the wave equation

$$\boldsymbol{E}(\boldsymbol{r}) = \boldsymbol{E}_i(\boldsymbol{r}) + \int \mathrm{d}^3\boldsymbol{r}' G_0(\boldsymbol{r} - \boldsymbol{r}')\hat{\mathbf{T}}(\boldsymbol{r}')\boldsymbol{E}_i(\boldsymbol{r}'),\ \hat{\mathbf{T}} = \hat{\mathbf{V}} + \hat{\mathbf{V}}G_0\hat{\mathbf{V}} + \hat{\mathbf{V}}G_0\hat{\mathbf{V}}G_0\hat{\mathbf{V}} + \ldots$$

scattering operator (T-matrix)

The first Born approximation of the solution of the wave equation **(kinematical approximation)**

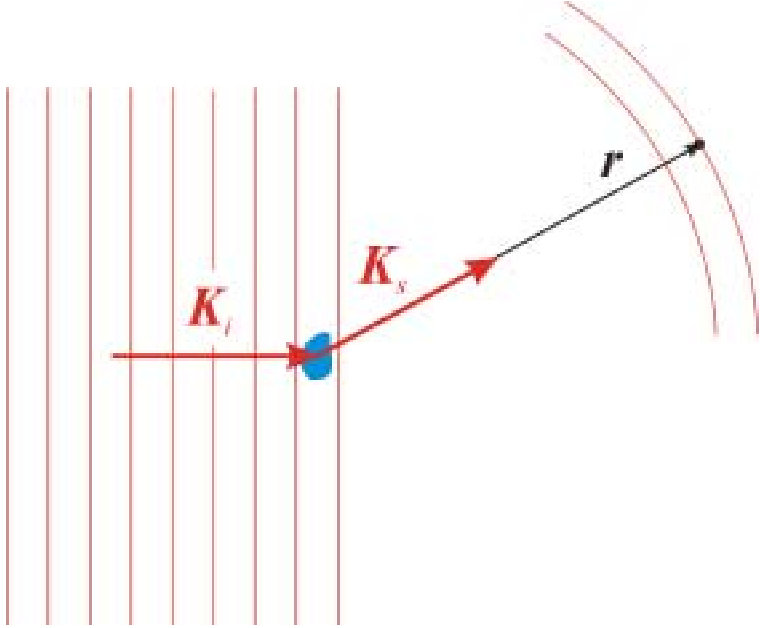
$$\boldsymbol{E}(\boldsymbol{r}) \approx \boldsymbol{E}_i(\boldsymbol{r}) + \int \mathrm{d}^3\boldsymbol{r}' G_0(\boldsymbol{r} - \boldsymbol{r}')\hat{\mathbf{V}}(\boldsymbol{r}')\boldsymbol{E}_i(\boldsymbol{r}'),\ \hat{\mathbf{T}} \approx \hat{\mathbf{V}}$$

Higher approximations ⇒ **dynamical scattering theory** (a Bloch-wave ansatz)

The far-field approximation (the Fraunhofer approximation):

$$E(\boldsymbol{r}) \approx E_i(\boldsymbol{r}) - \frac{1}{4\pi}\frac{\mathrm{e}^{\mathrm{i}Kr}}{r}\langle \boldsymbol{K}_s|\hat{\mathrm{T}}|\boldsymbol{K}_i\rangle,$$

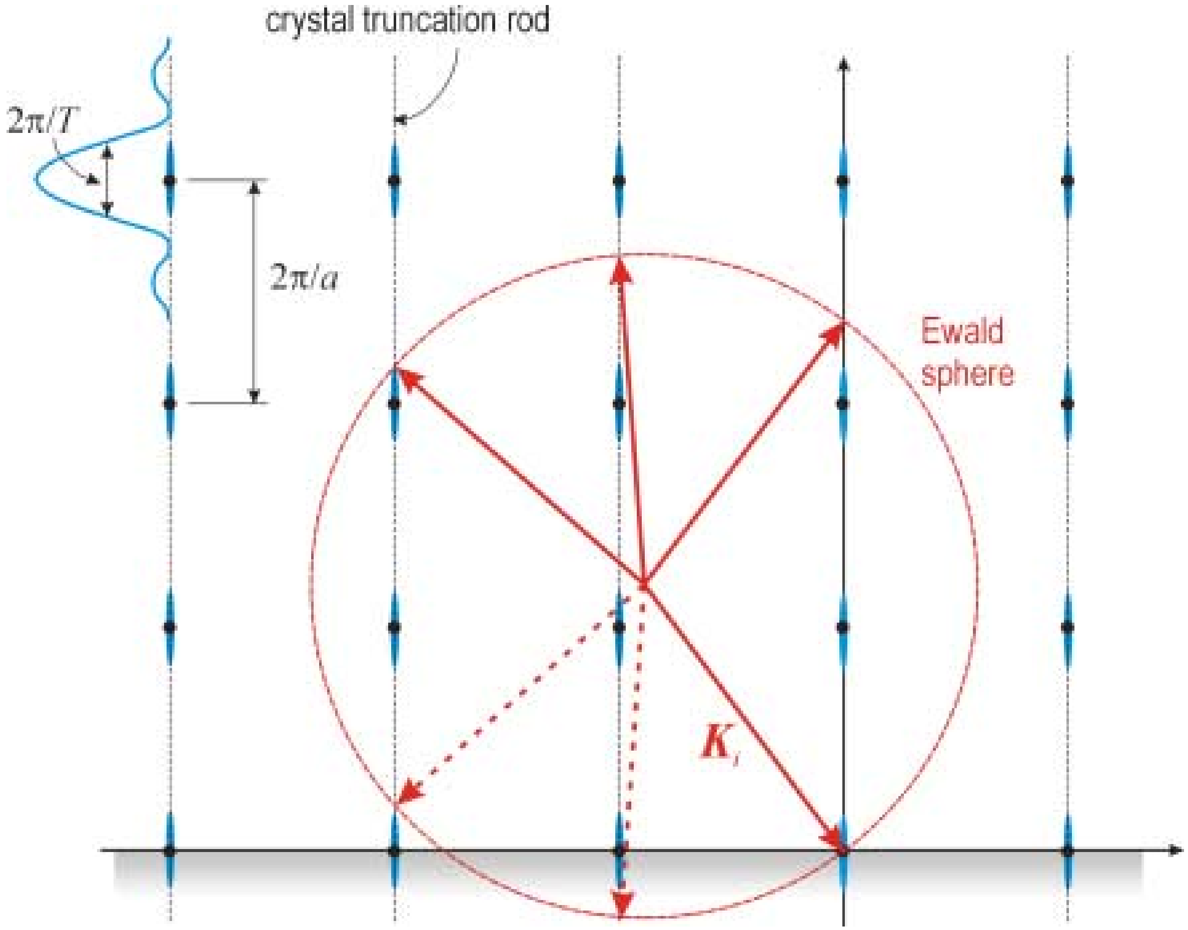
$$\boldsymbol{K}_s = K\boldsymbol{r}/r$$



The approximation of a homogeneous wavefield: the scattered intensity does not depend on $\boldsymbol{r}$. The scattered wavefield is a superposition of plane components, the amplitude of the component with the wave vector $\boldsymbol{K}$ is proportional to $\langle \boldsymbol{K}|\hat{\mathrm{T}}|\boldsymbol{K}_i\rangle$

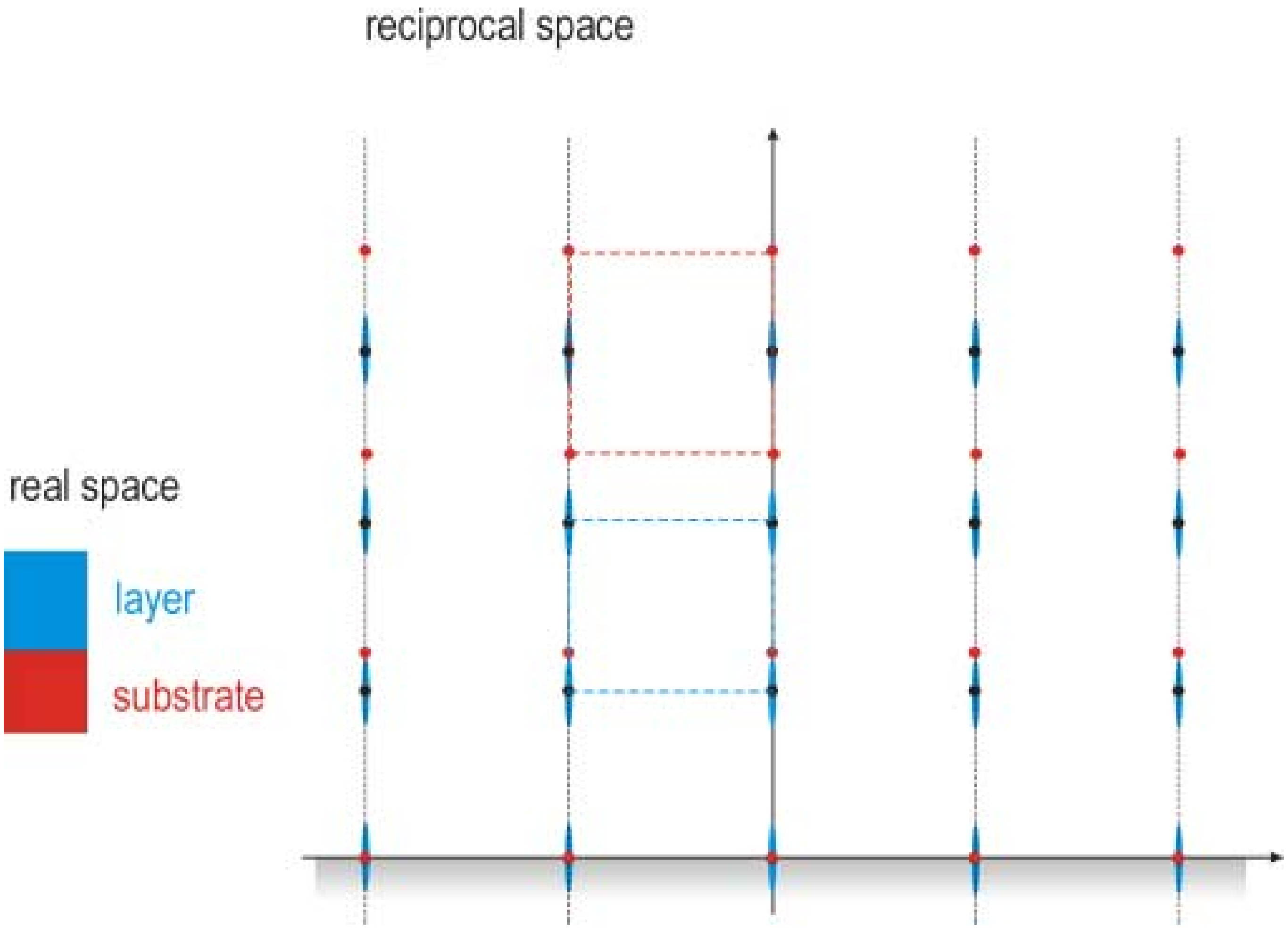
In the kinematical approximation, the amplitude of the scattered wave is proportional to the Fourier transformation of the **total** electron density

Reciprocal-space intensity map of a thin layer:

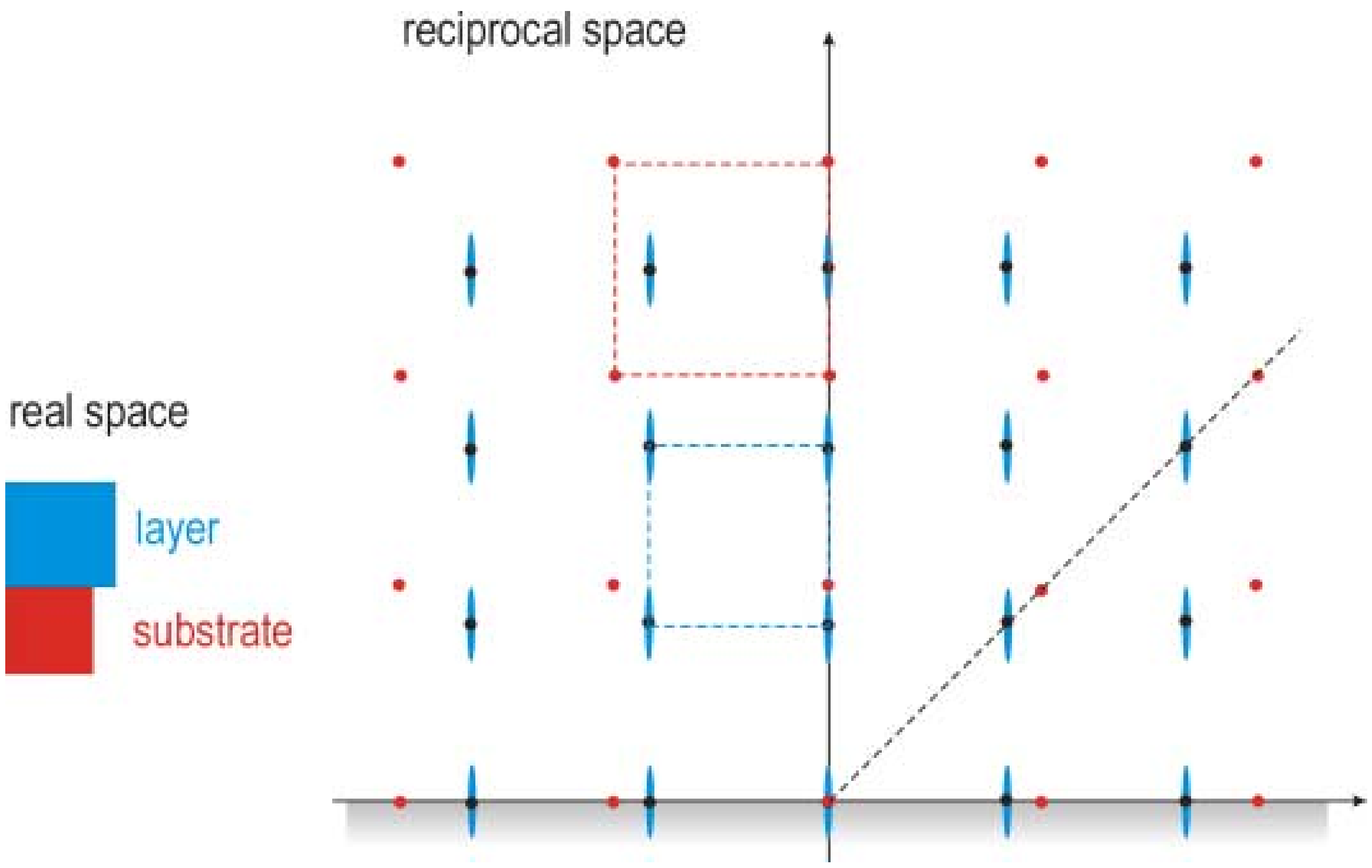


Lateral diffraction condition: $\boxed{K_{h\|} - K_{i\|} = h_{\|}}$

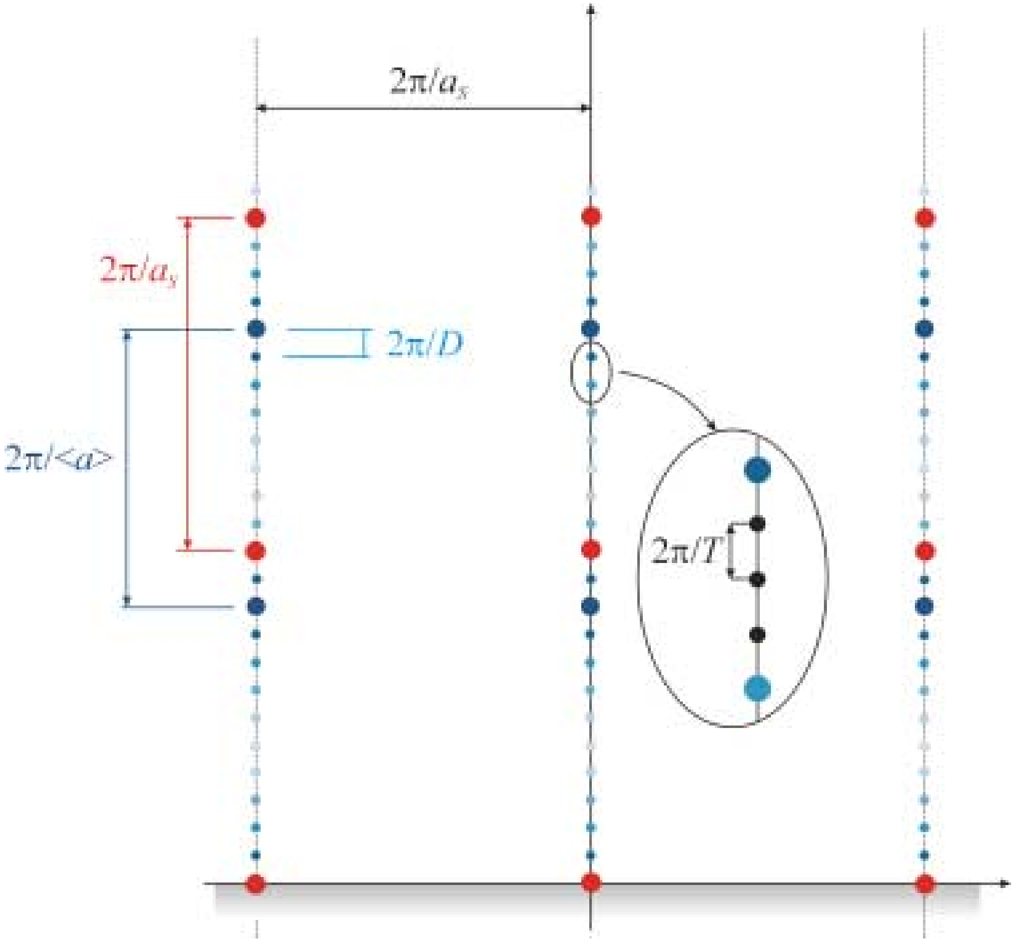
Reciprocal-space intensity map of a **pseudomorph layer** on a semiinfinite substrate

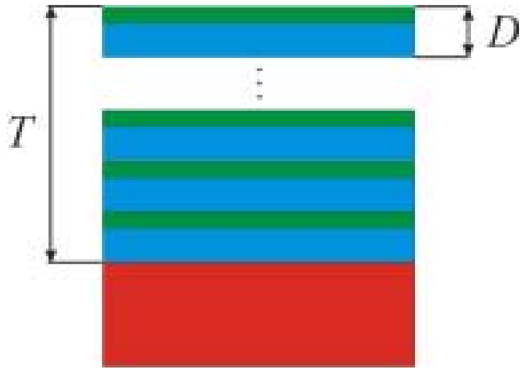


Reciprocal-space intensity map of a **fully relaxed layer** on a semiinfinite substrate



Reciprocal-space intensity map of an ideally pseudomorph periodic superlattice:





mean vertical lattice parameter of the superlattice

$$\langle a\rangle = \frac{n_A a_{Az} + n_B a_{Bz}}{n_A + n_B}$$

$a_{A,Bz}$…vertical lattice parameters of layers A and B,
$n_{A,B}$…numbers of monolayers in layers A and B

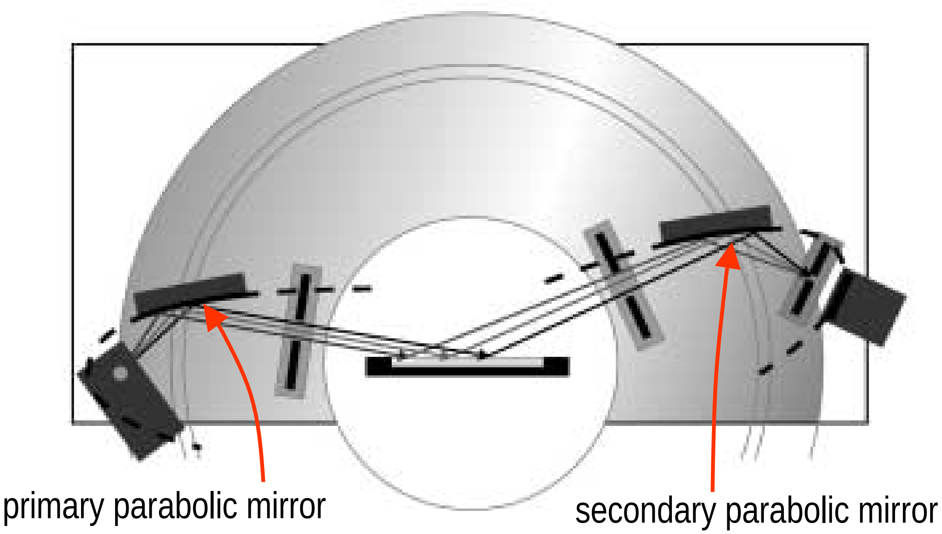
Experimental aspects:

we need

- a parallel and monochromatic primary beam
- an energy- and direction-sensitive detector

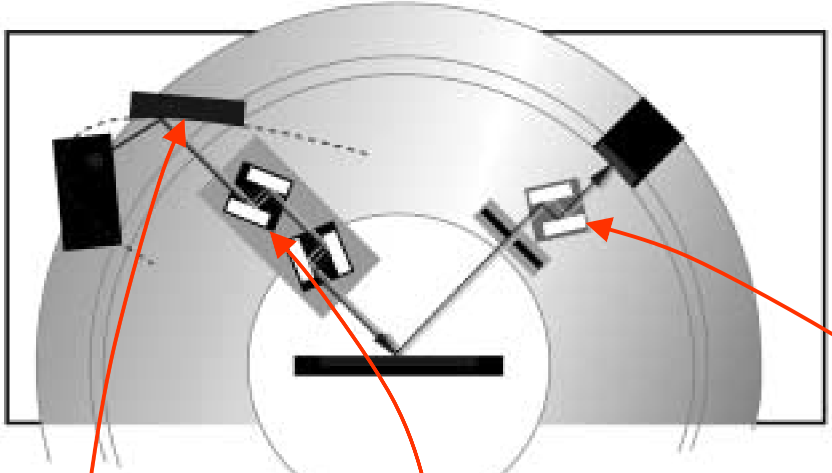
however, the degree of collimation and monochromatization should correspond to the resolution necessary for the particular problem.

A low-resolution set-up:



powder diffraction, reflectometry

A high-resolution set-up:



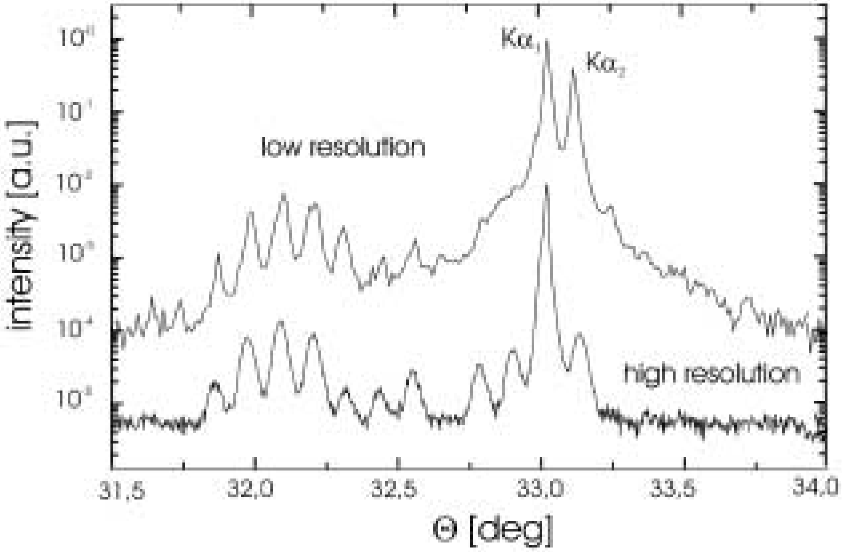
high-resolution coplanar diffraction

2-bounce channel-cut analyser

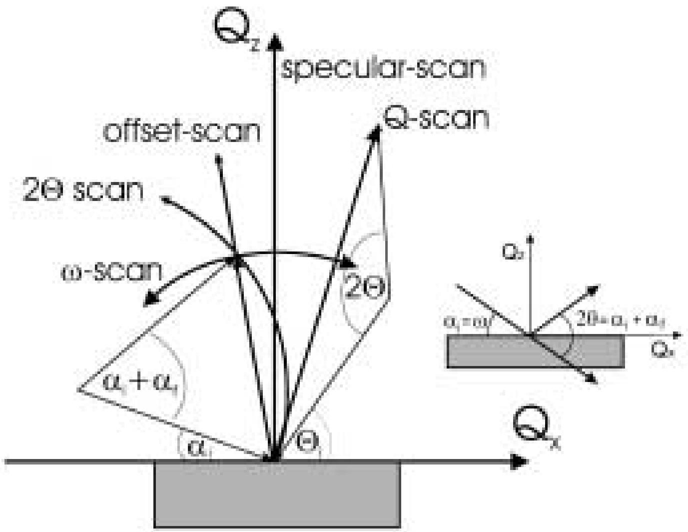
primary parabolic mirror

4-bounce Bartels monochromator

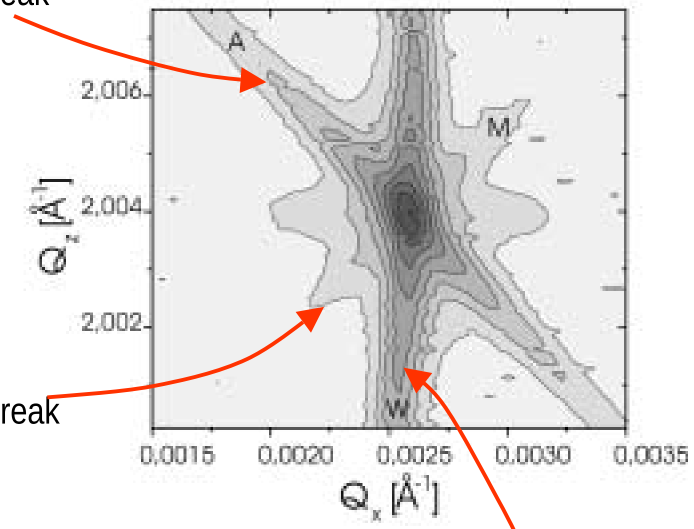
Diffraction curves of a $In_{0.2}Ga_{0.8}As/GaAs$ superlattice measured by low- and high-resolutions set-ups.
Much larger flux in the low-res set-up!!!



Reciprocal-space mapping –
scans in reciprocal space



Resolution function in reciprocal space
of a high-resolution setup



analyzer streak

monochromator streak

wavelength streak

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Small-angle x-ray scattering is sensitive to the 0-th Fourier component χ_0 of the polarizability $\Rightarrow$ to the electron density averaged over the unit cell

sample morphology – thicknesses of the layers, interface roughness, shape of nanostructures

Since the refraction index is $n \approx 1$, the x-ray reflectometry measures the true layer thickness T and not the optical thickness nT as is the case of optical reflectometry

Accessible range of thicknesses – from approx. 0.5 nm up to about 1000 nm.
Accessible range of root-mean-square (rms) roughnesses – from 0.2 nm up to approx. 2 nm

high-resolution x-ray diffraction is sensitive to the $\boldsymbol{h}$-th Fourier component χ_h of the polarizability
⇒ to the deformation in the structure

degree of plastic relaxation in a heterostructure, chemical composition…

x-ray diffraction can also be used for determining the layer thicknesses, especially if the contrast in χ_0 is low.

Measurable range of the deformation ε depends on the diffraction used

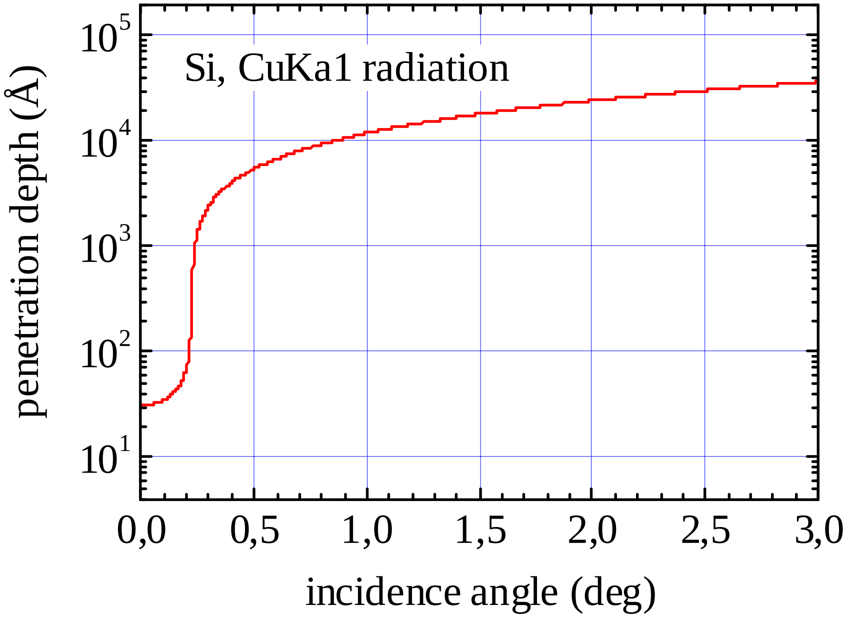
$$h\varepsilon > \Delta q_{\mathrm{min}}$$

where Δq_{min} is the experimental resolution in reciprocal space $(\approx 10^{-3}\ \mathrm{nm}^{-1})$

the minimum measurable deformation is of the order of 10^{-4}

Grazing-incidence diffraction is sensitive mainly to the lateral periodicity of the lattice ⇒ it is good for measuring lateral relaxation in thin layers and nanostructures.

Advantage: the penetration depth of the primary beam can be tuned by changing the incidence angle



Disadvantage: the primary beam must be collimated in two orthogonal directions ⇒ it can be performed only using a synchrotron source.

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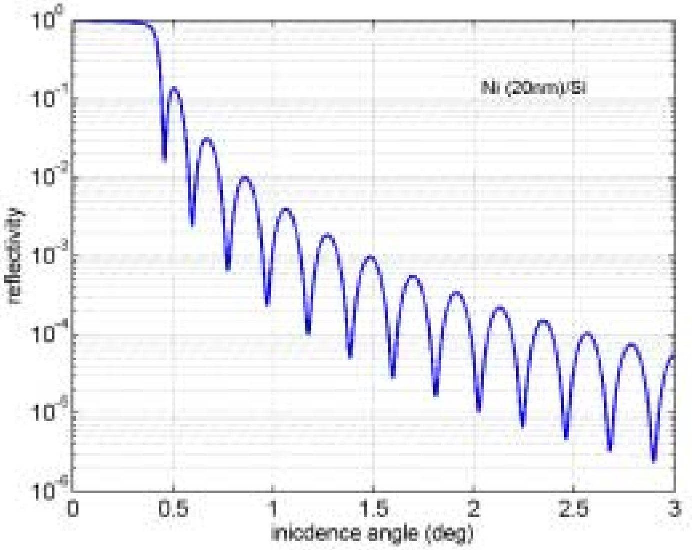
Determining the thickness of a layer **from x-ray reflection**

Thin layer on a semiinfinite substrate – intensity distribution around $\boldsymbol{h} = 0$ (x-ray reflection) interference of the waves **specularly reflected from the interfaces** $\Rightarrow$ thickness oscillations on the reflection curve



distance of the interference maxima

$$\Delta\alpha_i = \frac{\lambda}{2T}\cos\alpha_i \approx \frac{\lambda}{2T}$$

The maximum thickness is limited by the divergence of the primary beam

$T \leq 800\,\mathrm{nm}$ for the divergence of 20 arc sec

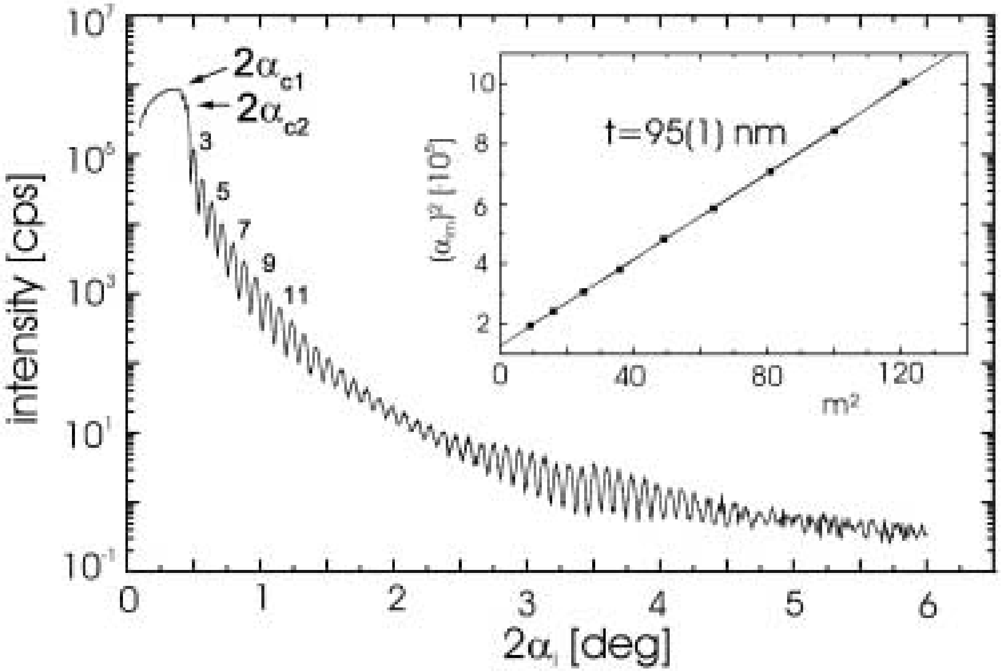
The minimum thickness depends on the accessible dynamical range, i.e. on the maximum measurable incidence angle $T_{\min} \approx 0.5\,\mathrm{nm}$

The position of the interference maxima approximately obeys the modified Bragg law

$$2T\sqrt{\sin^2\alpha_i - 2\delta} = m\lambda$$

where $\delta = 1 - n$, n is the refraction index of the layer. For small angles of incidence

$$\alpha_i^2 = m^2\left(\frac{\lambda}{2T}\right)^2 + 2\delta$$

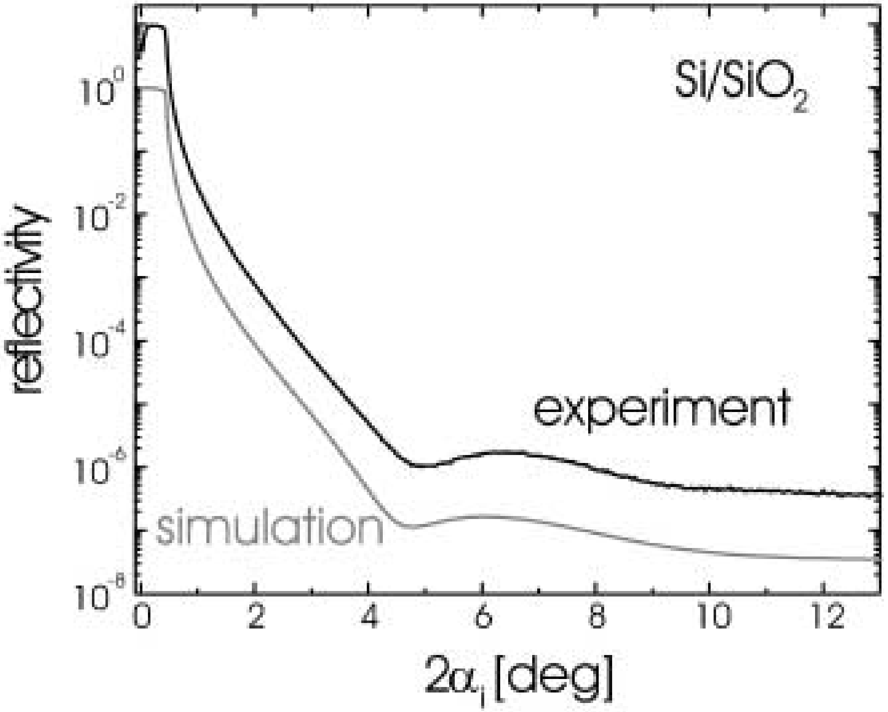


Example: a BN layer on Si

α_{c1} and α_{c2} are the critical angles of the layers and the substrate, respectively

$$\alpha_c = \sqrt{2\delta}$$

Another example: a Si surface with a native oxide layer



T_{SiO2} = (1.0 ± 0.1) nm

σ = (0.35 ± 0.05) nm

r.m.s. roughness
of the Si/SiO_2 interface

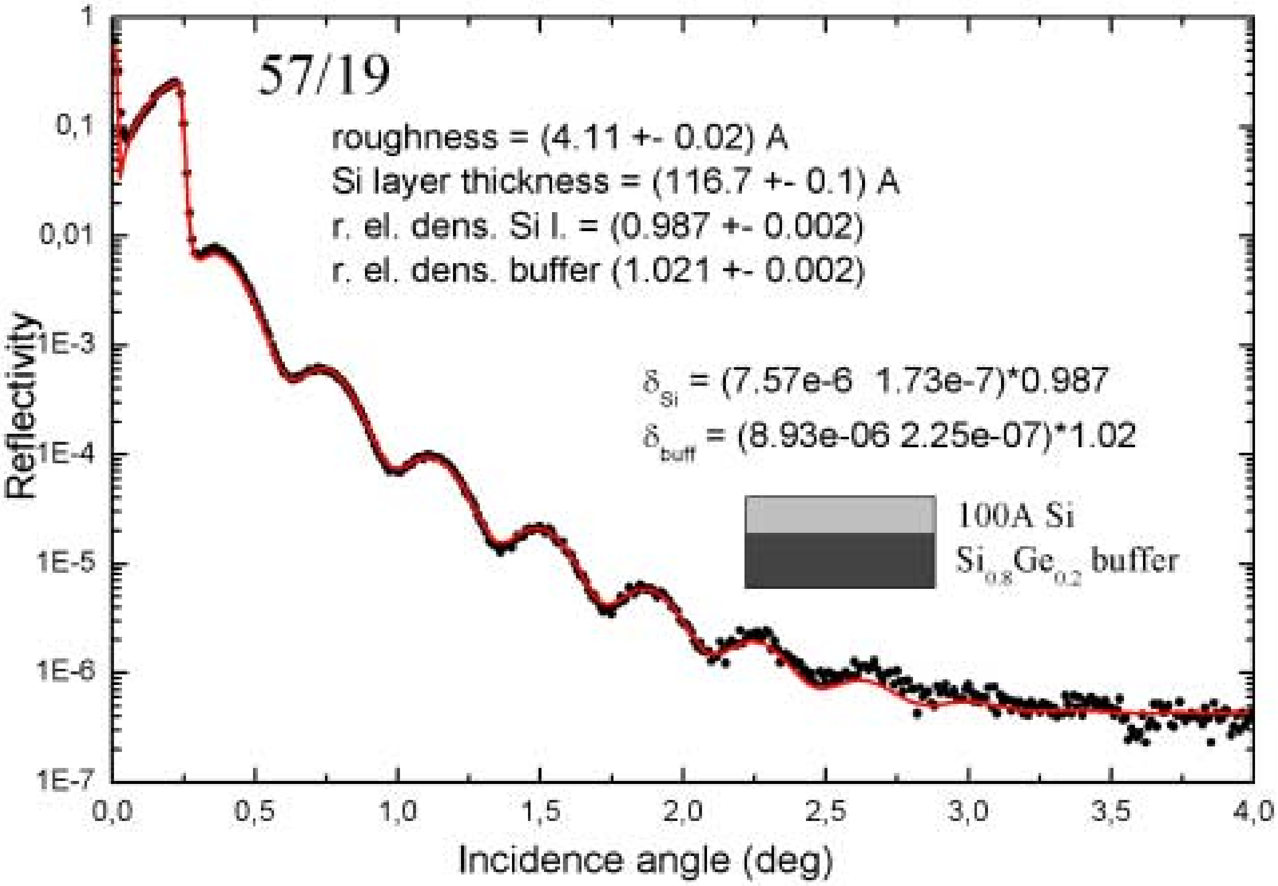
In this case, a simulation of the whole reflection curve is necessary!

Simulation codes are based on the Parrat formalism

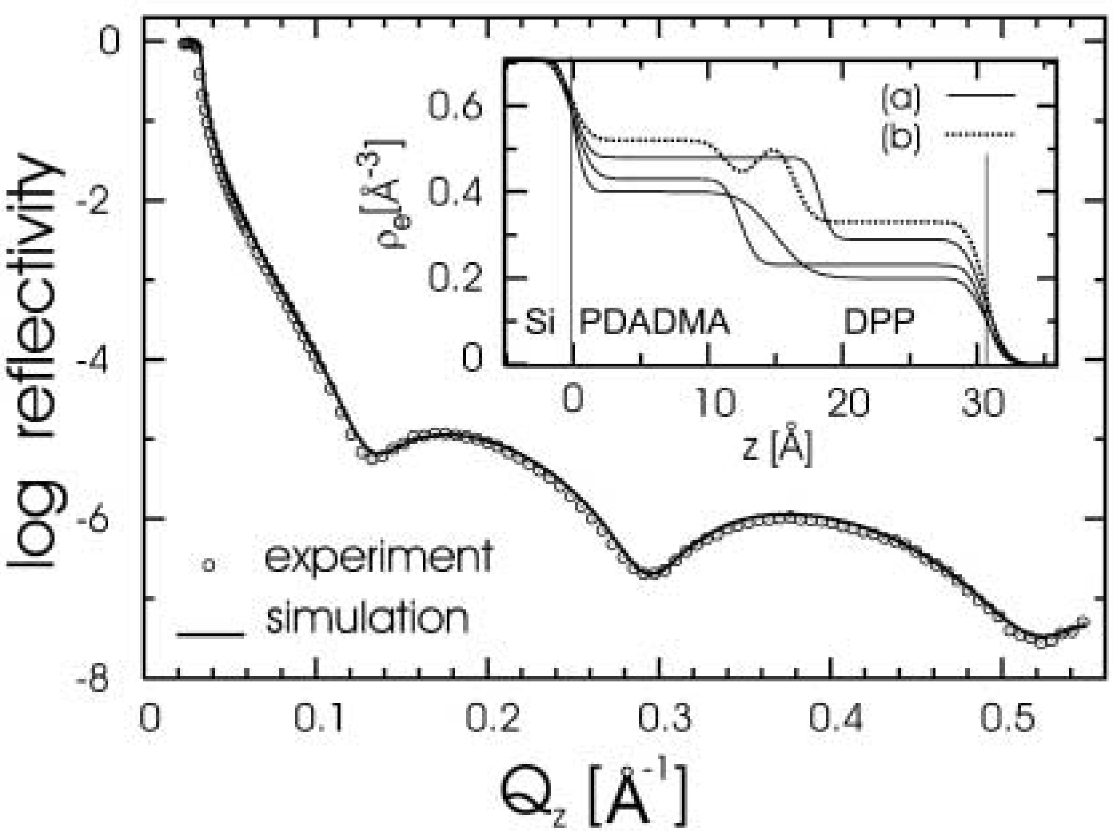
L. G. Parrat, Phys. Rev. **95**, 359 (1954)

Interface roughness is included according to L. Nevot, P. Croce, Rev. Phys. Appl. **15**, 761 (1980).

Another nice example:

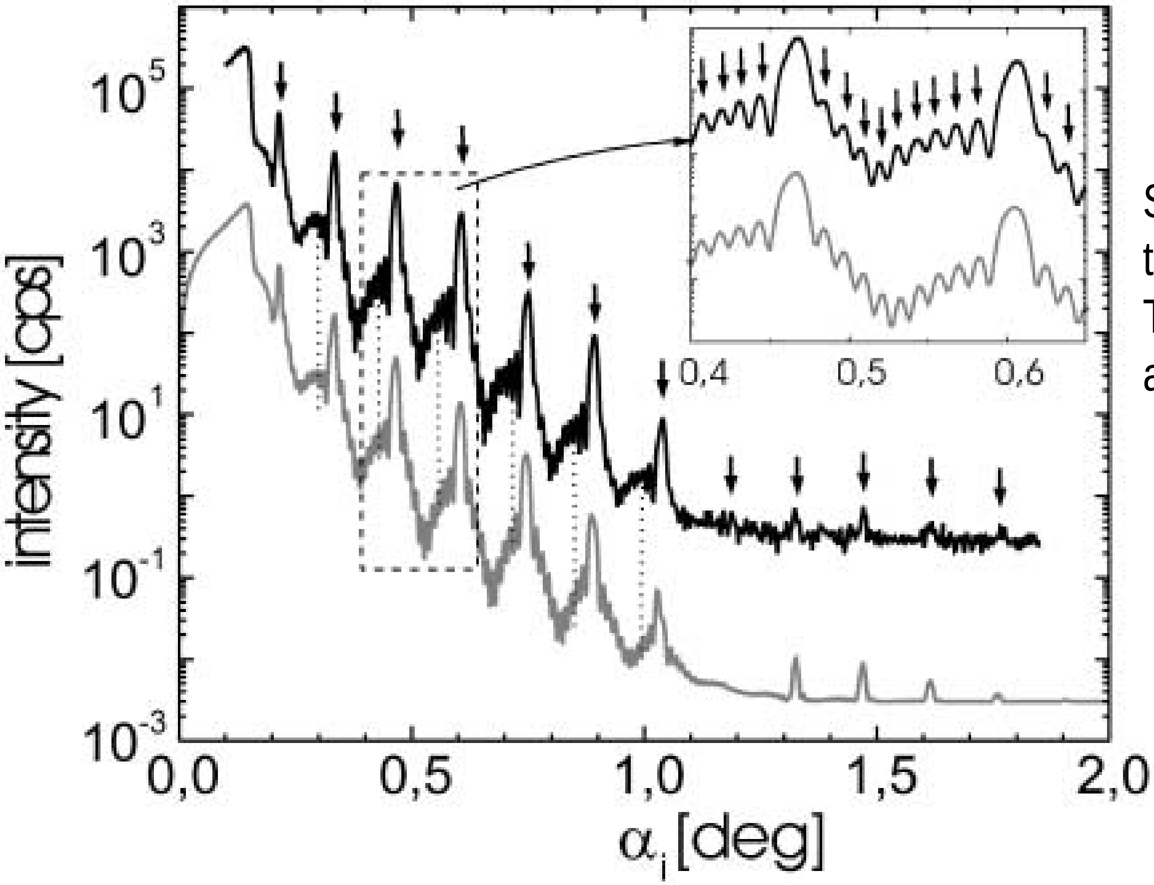


Sometimes, the solution of the problem is not unique:

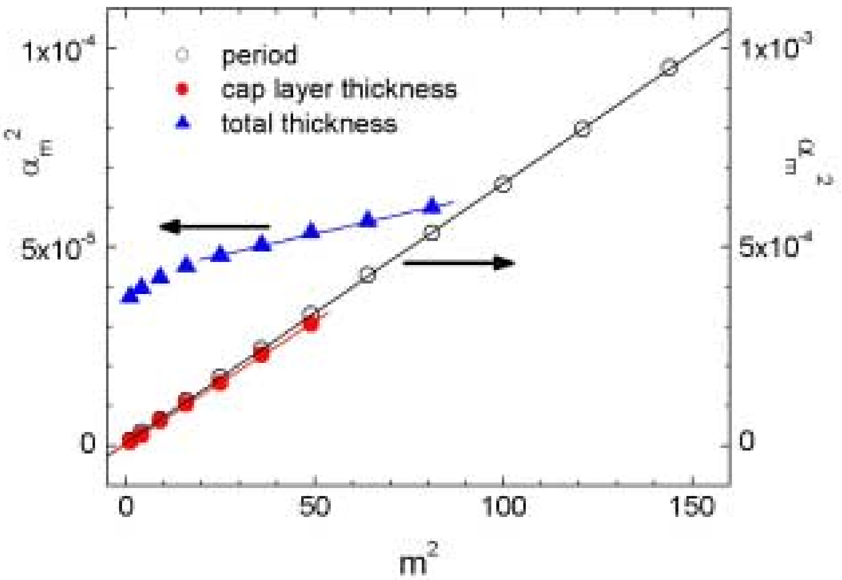


Lipid monolayers attached to polyelectrolyte molecules on Si. several different models (in the inset) yield the same fit. Additional structure information is necessary!!

X-ray reflection from a periodic superlattice:



SiGe/Si multilayer with a 21 nm thick Si cap layer.
Thickness (Kiessig) fringes are denoted by arrows



$$D = (20.5 \pm 0.3)\ \mathrm{nm},\ T = (232 \pm 5)\ \mathrm{nm},$$
$$T_{\mathrm{cap}} = (21 \pm 2)\ \mathrm{nm}$$

These values are used as starting estimates for a whole-curve fitting

From the fit, we obtained:

$$T_{\mathrm{oxide}} = (3 \pm 1)\ \mathrm{nm},\ T_{\mathrm{cap}} = (21.0 \pm 0.5)\ \mathrm{nm},\ D = (20.6 \pm 0.2)\ \mathrm{nm},$$
$$T_{\mathrm{Si}} / T_{\mathrm{SiGe}} = 7.0 \pm 0.2,\ x_{\mathrm{Ge}} = 0.35 \pm 0.15,\ \sigma = (0.7 \pm 0.1)\ \mathrm{nm}$$

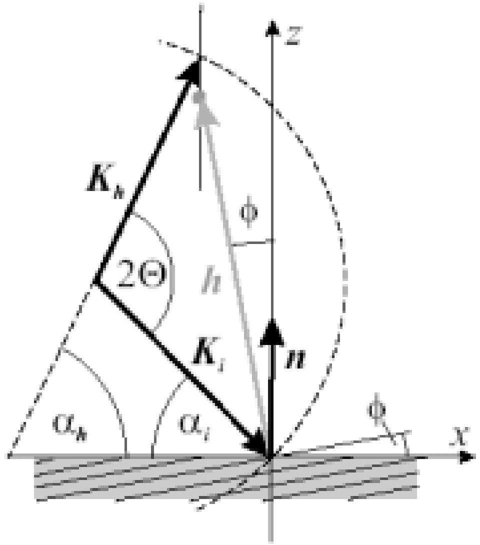
Determination of layer thickness from x-ray diffraction – interference of waves **diffracted from the layer and from the substrate**

The distance of the thickness fringes

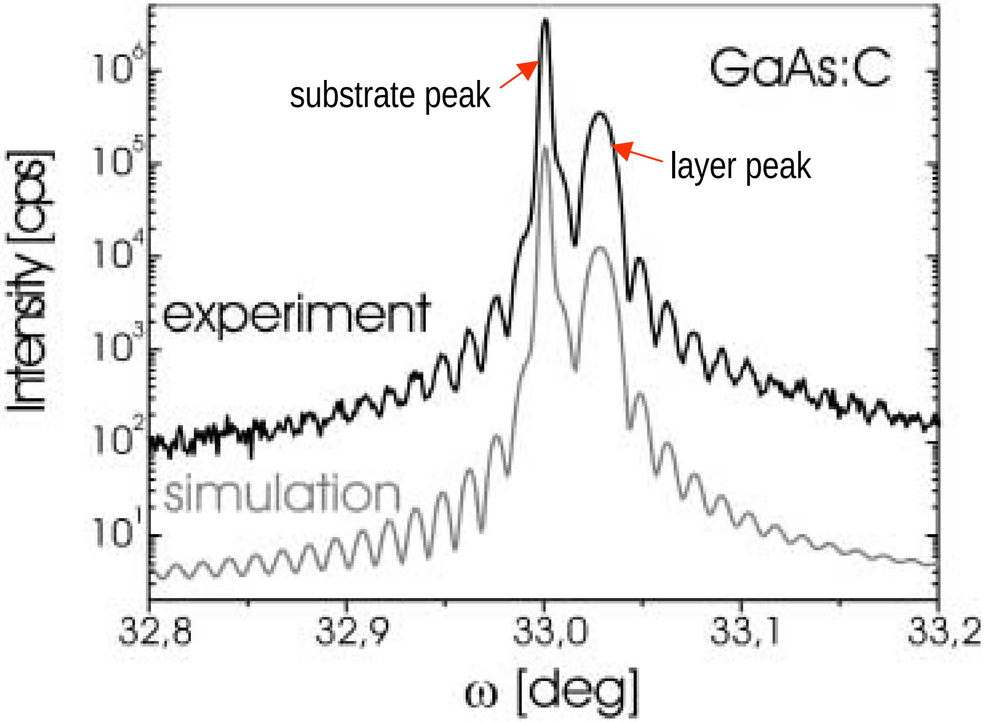
$$\Delta\alpha_i = \frac{\lambda\gamma_{\boldsymbol{h}}}{T\sin(2\Theta_B)}$$

Θ_B is the Bragg angle, $\gamma_{\boldsymbol{h}}$ is the direction cosine of the diffracted wave with respect to the surface normal. For a symmetric diffraction (the diffracting planes are parallel to the surface)

$$\Delta\alpha_i = \frac{\lambda}{2T\cos\Theta_B}$$



sketch of the diffraction geometry. $\phi = 0$ corresponds to the symmetric diffraction a simple example: a symmetric 004 diffraction curve of a GaAs:C layer on GaAs(001)



From the thickness fringes:

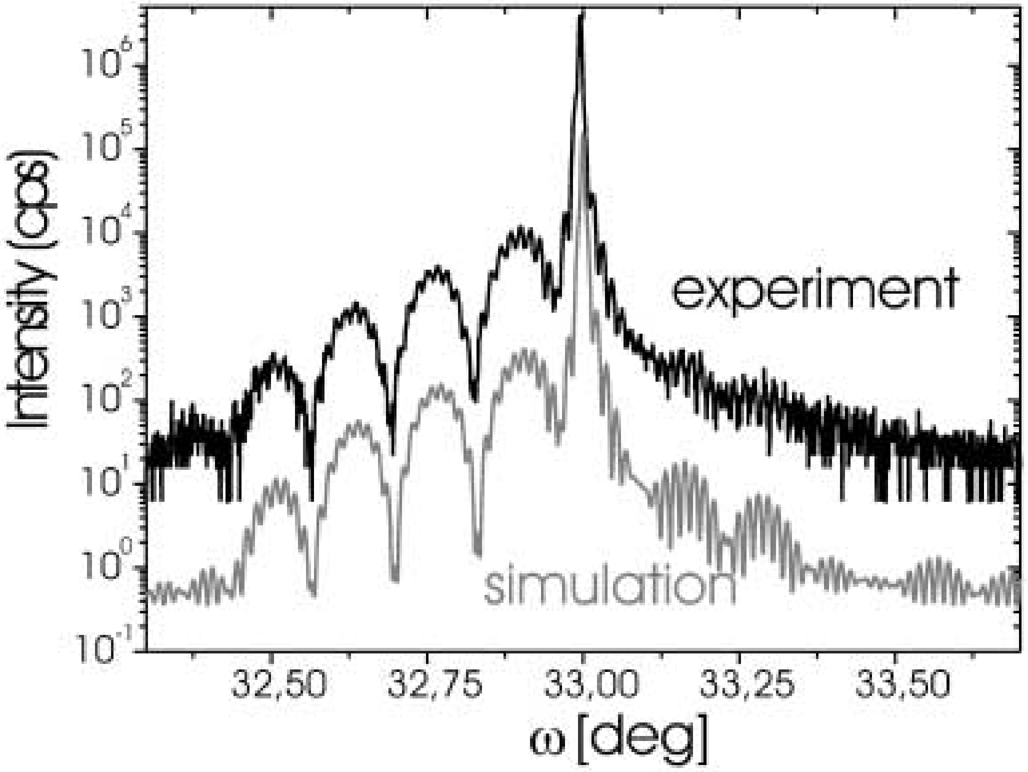
$$T = (392 \pm 32)\ \mathrm{nm}$$

From the distance of both peaks:

$$\frac{\Delta a}{a} \approx -390\ \mathrm{ppm} \Rightarrow x_{\mathrm{C}} \approx 5\times10^{19}\ \mathrm{cm}^{-3}$$

For the simulation, a dynamical diffraction theory must be used, the formulas can be found in
W.J. Bartels, J. Hornstra, D.J.W. Lobeek: Acta Cryst. A **42**, 539 (1986)

Another example: 004 symmetric diffraction on a GaAs/$In_{0.06}Ga_{0.94}As$/GaAs/ $In_{0.06}Ga_{0.94}As$ /(001)GaAs heterostructure



rapid oscillations ⇒

$$T_1 = (300 \pm 3)\ \mathrm{nm}$$

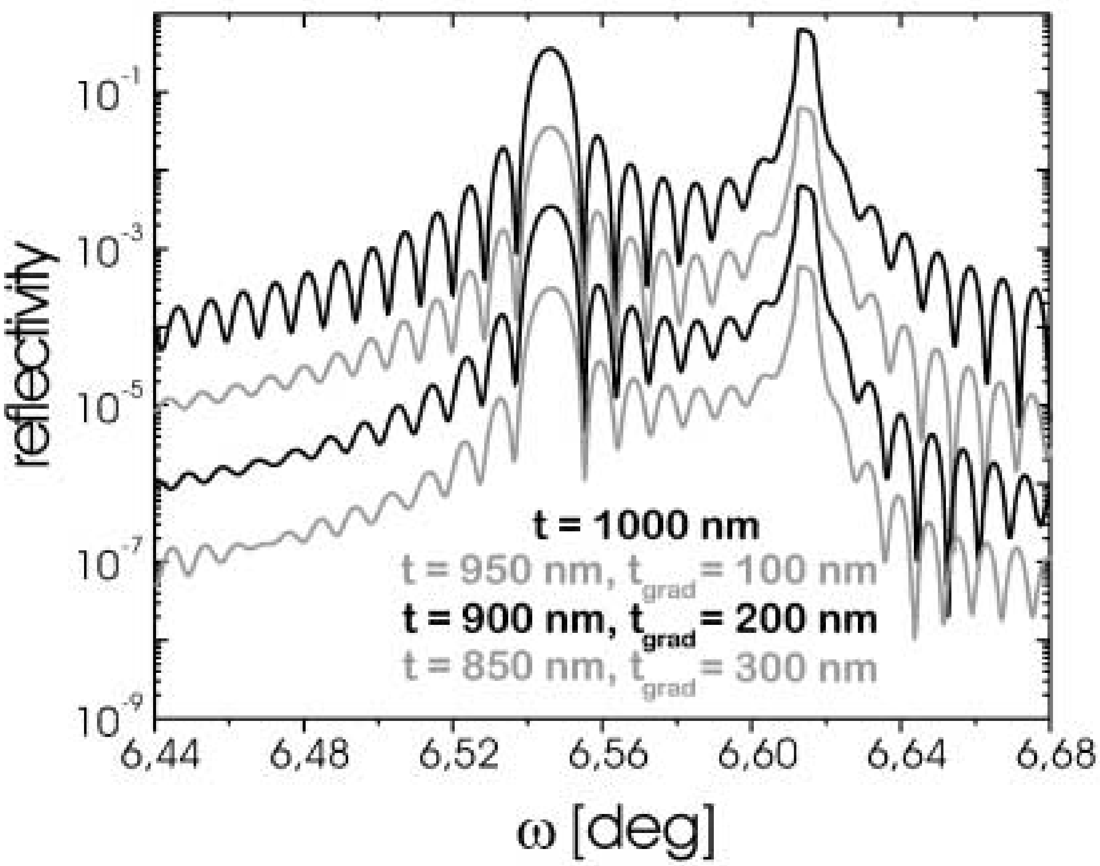
total thickess of the stack

slow oscillations ⇒

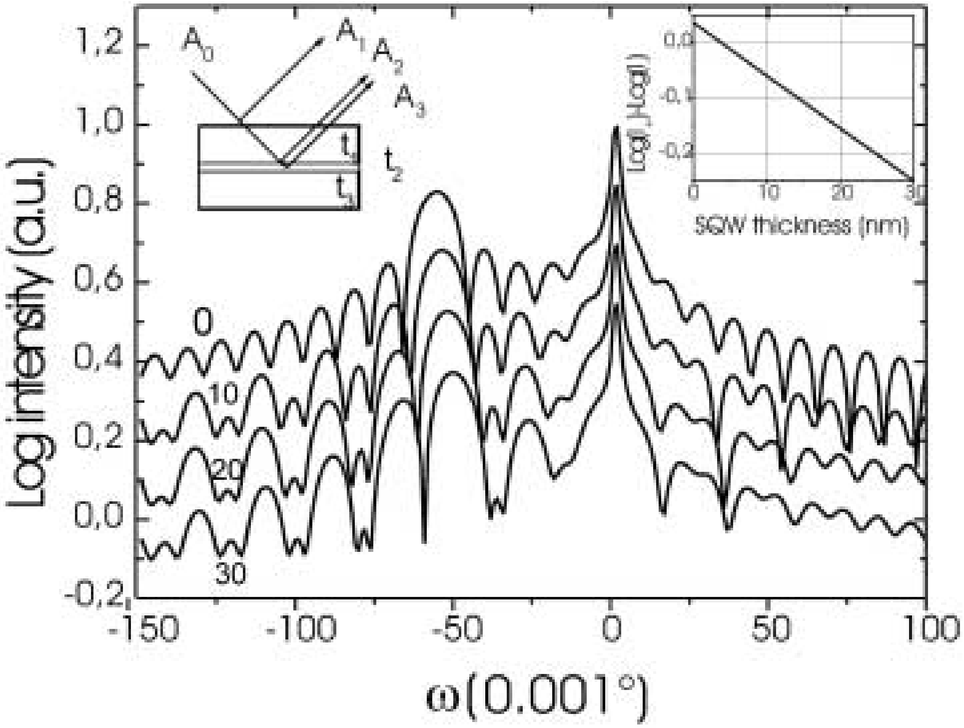
$$T_2 = (33 \pm 5)\ \mathrm{nm}$$

thickness of the upper GaAs layer

Influence of an interface grading on a diffraction curve, asymmetric 224 diffraction curves calculated for a $Ga_{0.6}Al_{0.4}As$/GaAs heterostructure, linearly graded interface



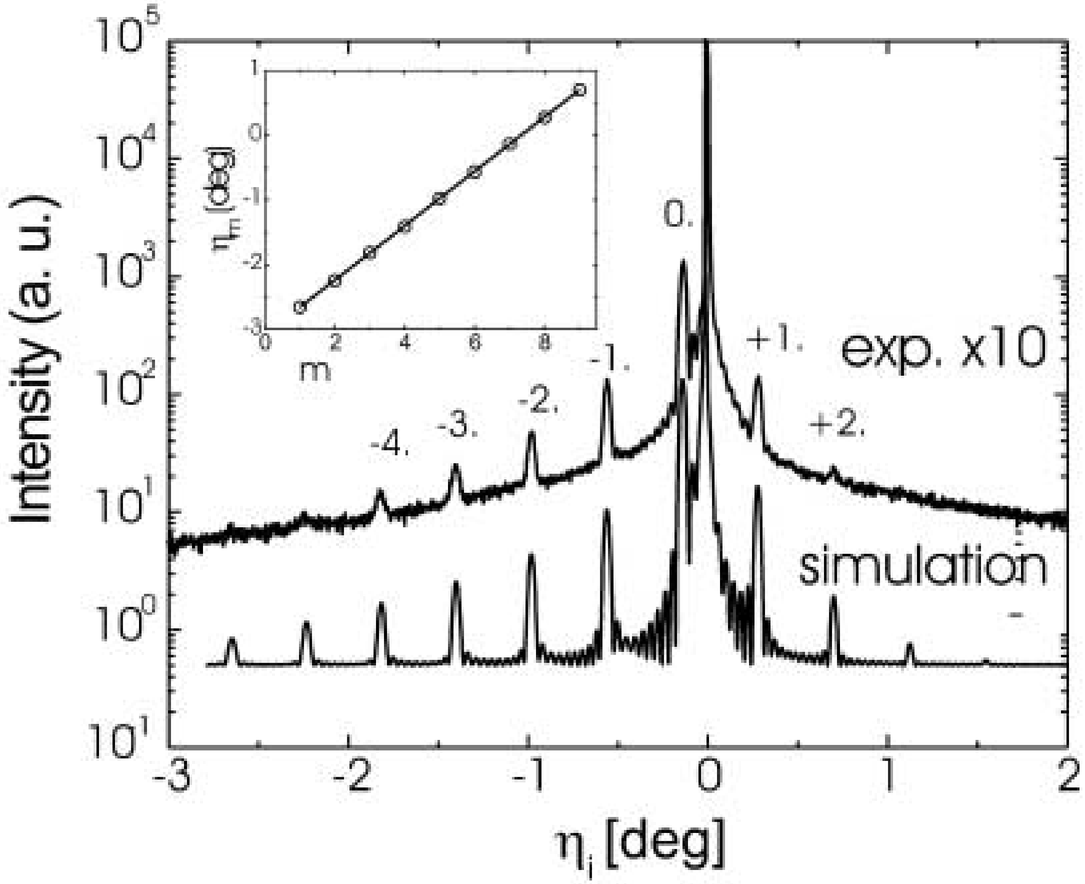
X-ray diffraction from a system with a thin buried layer – the diffraction curve depends on the phase shift of the waves diffracted from the crystal above and below the layer:



Calculated 004 diffraction curves for a $Ga_{0.6}Al_{0.4}As/GaAs/\ Ga_{0.6}Al_{0.4}As$ heterostructure on GaAs(001).
The thickness of GaAs quantum well varies from 0 to 30 nm.

X-ray diffraction from a periodic superlattice – a sequence of satellite maxima with the distance

$$\Delta\alpha_i = \frac{\lambda\gamma_{\boldsymbol{h}}}{D\sin(2\Theta_B)}$$



A SiGe/Si superlattice, asymmetric 224 diffraction. From the inset:

$$D = (20.6 \pm 0.7)\ \mathrm{nm}$$

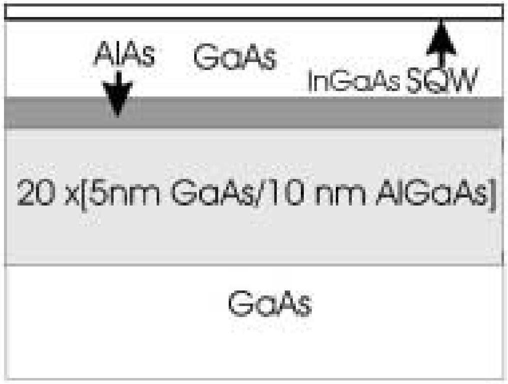
From the fitting of the whole curve:

$$D = (20.5 \pm 0.1)\ \mathrm{nm},$$

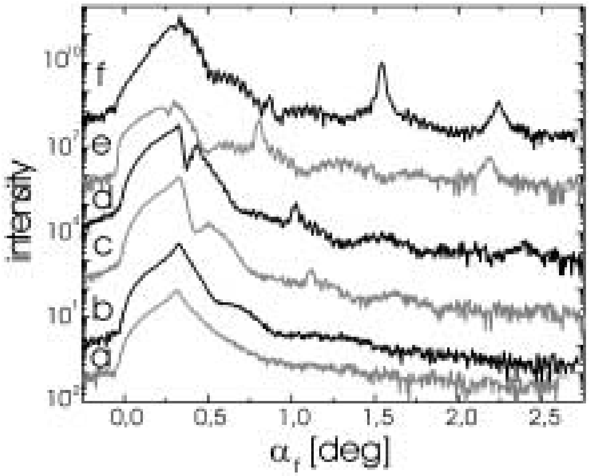
$$T_{\mathrm{Si}} / T_{\mathrm{SiGe}} = 7 \pm 0.5,$$

$$x_{\mathrm{Ge}} = 0.36 \pm 0.02$$

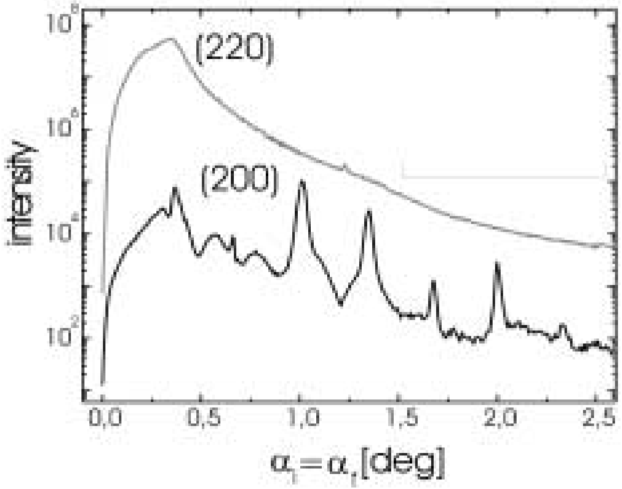
Grazing-incidence diffraction on the heterostructure:



weak diffraction
200



various incidence angles from $\alpha_i = 0.2^{\circ}$(a) to $1.0°$ (f)



nearly no contrast in the strong 220 diffraction, the weak 200 diffraction is much more sensitive to the chemical contrast

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How to determine the strain status of the layer by means a **double-axis diffractometer** (open detector window), i. e., by measuring $I(\alpha_i)$, regardless of α_f?

Two independent diffraction curves are necessary

Horizontal and vertical **lattice misfits** of the layer $\delta_{\parallel} = \frac{a_{L\parallel} - a_S}{a_S}, \quad \delta_{\perp} = \frac{a_{L\perp} - a_S}{a_S}$

don't mix it with the **lattice mismatch** $f = \frac{a_L^{\infty} - a_S}{a_S}$

connection with the relaxation degree r: $\delta_{\parallel} = rf \qquad r = \frac{a_{L\parallel} - a_S}{a_L - a_S}$

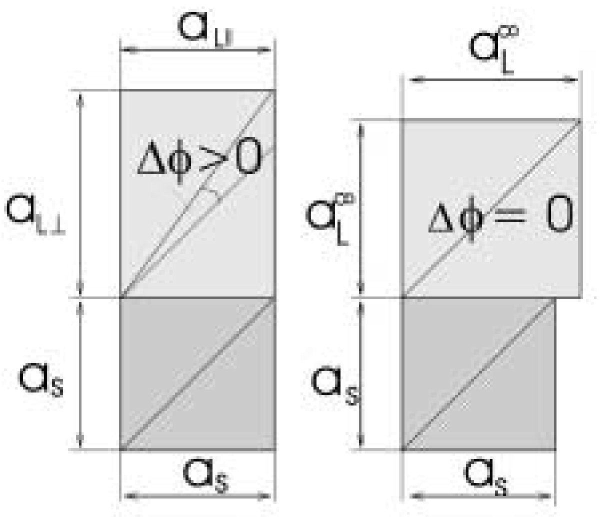
The angular separation of the layer and substrate peaks

$$\Delta\alpha_i = \Delta\Theta_0 + \Delta\Theta_B + \Delta\varphi$$

difference in refraction

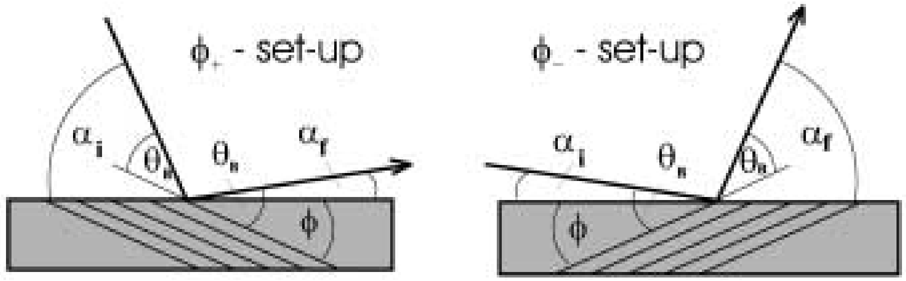
difference in the Bragg angles

difference in the orientation of the net planes



here we assume a **tetragonal distortion** of the layer

If $\Delta\Theta_0$ can be neglected, both components of misfit can be determined from the angular separations $\Delta\alpha_{i\pm}$ of the peaks measured in two opposite geometries:



$$\Delta\alpha_{i\pm} = \Delta\Theta_B \pm \Delta\varphi$$

The misfit components are

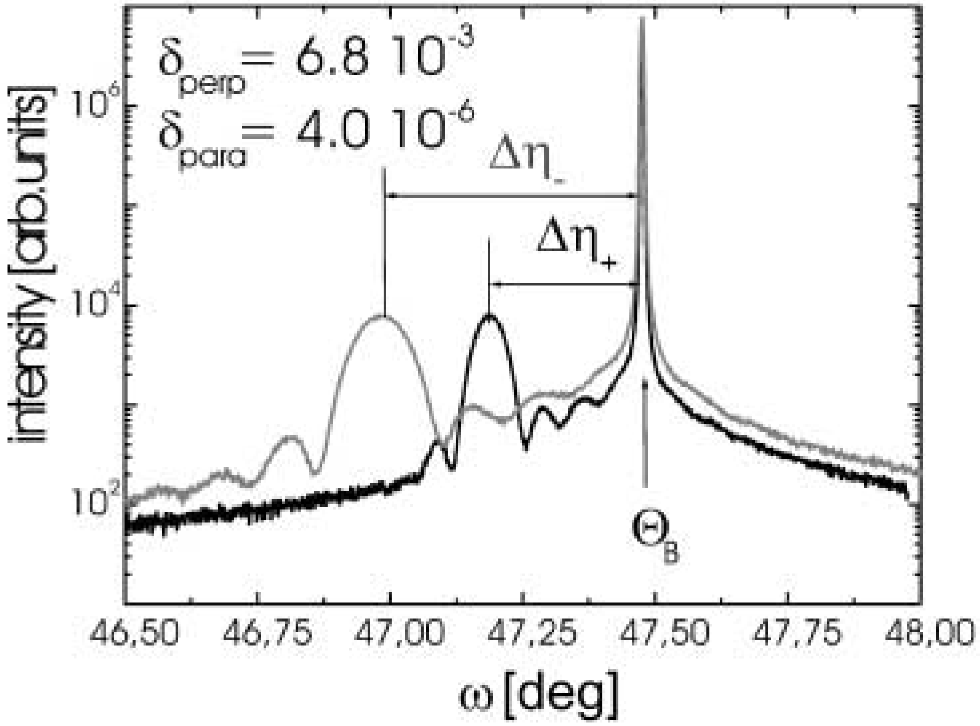
$$\delta_\perp = \Delta\varphi \tan\varphi - \Delta\Theta_B \cot\Theta_B,\ \delta_\parallel = -\Delta\varphi \cot\varphi - \Delta\Theta_B \cot\Theta_B$$

If the layer is pseudomorph ($r = 0$)

$$(\Delta\alpha_{i+} - \Delta\alpha_{i-})\tan\varphi = (\Delta\alpha_{i+} + \Delta\alpha_{i-})\cot\Theta_B$$

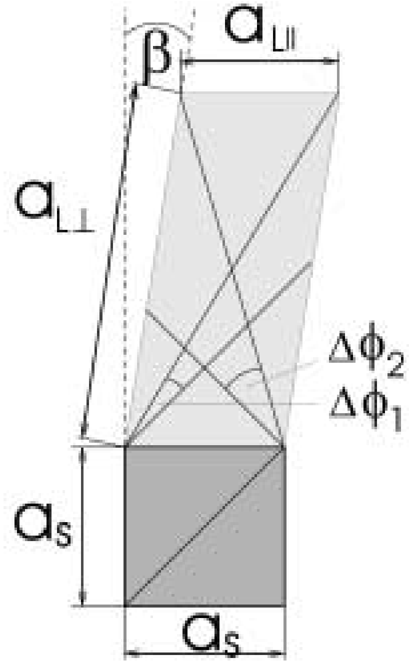
must hold.

A 66 nm thick SiGe layer on Si(001), asymmetric diffractions 115 with opposite asymmetries:



since $\delta_{||}$ is very small, the layer can be assumed pseudomorph

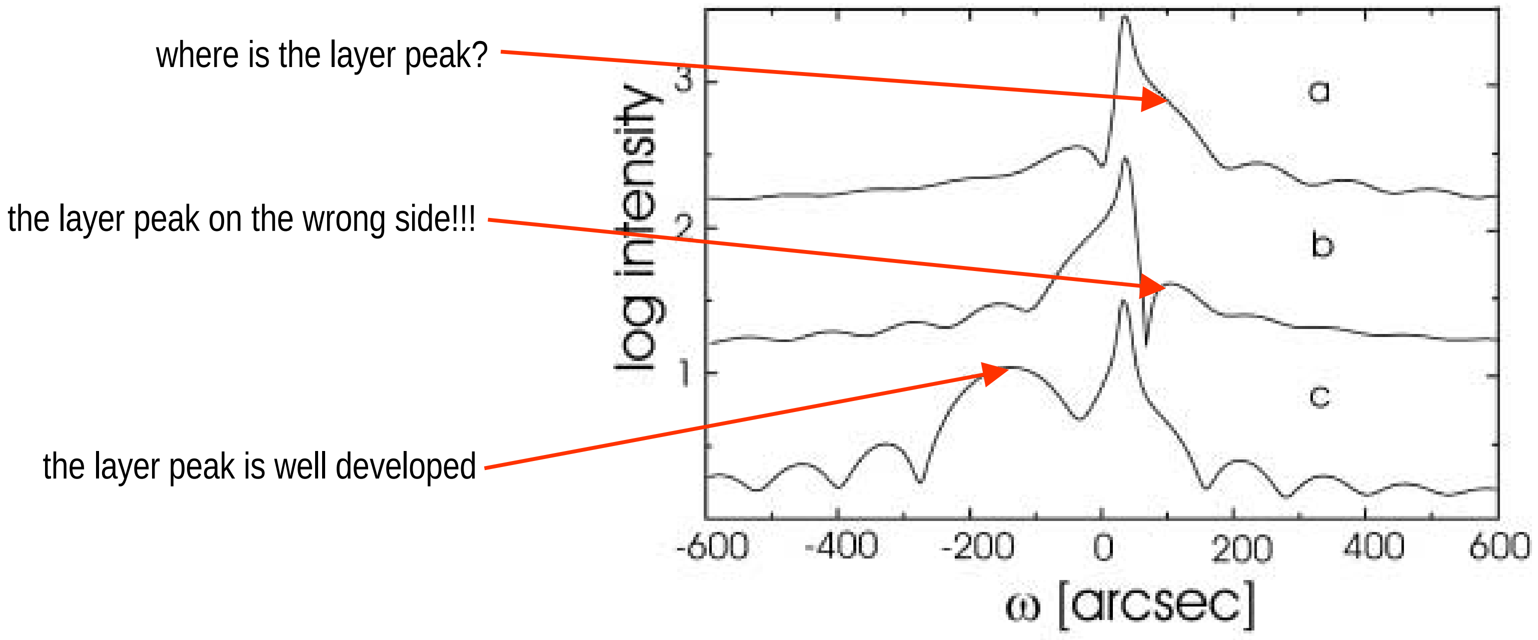
If the distortion of the layer is general (i.e., non-tetragonal), the situation is more complicated:



several crystallographic equivalent diffractions with various azimuthal directions must be measured

Another problem: if the mismatch is too small, the measured angular separation of the layer and substrate peaks might be misleading:

Diffraction curves of a GaInAsP (250nm) layer on InP simulated in asymmetric 224 diffraction for various values of vertical misfit: (a) 0, (b) 2.5×10^{-4}, (c) 10^{-3}.

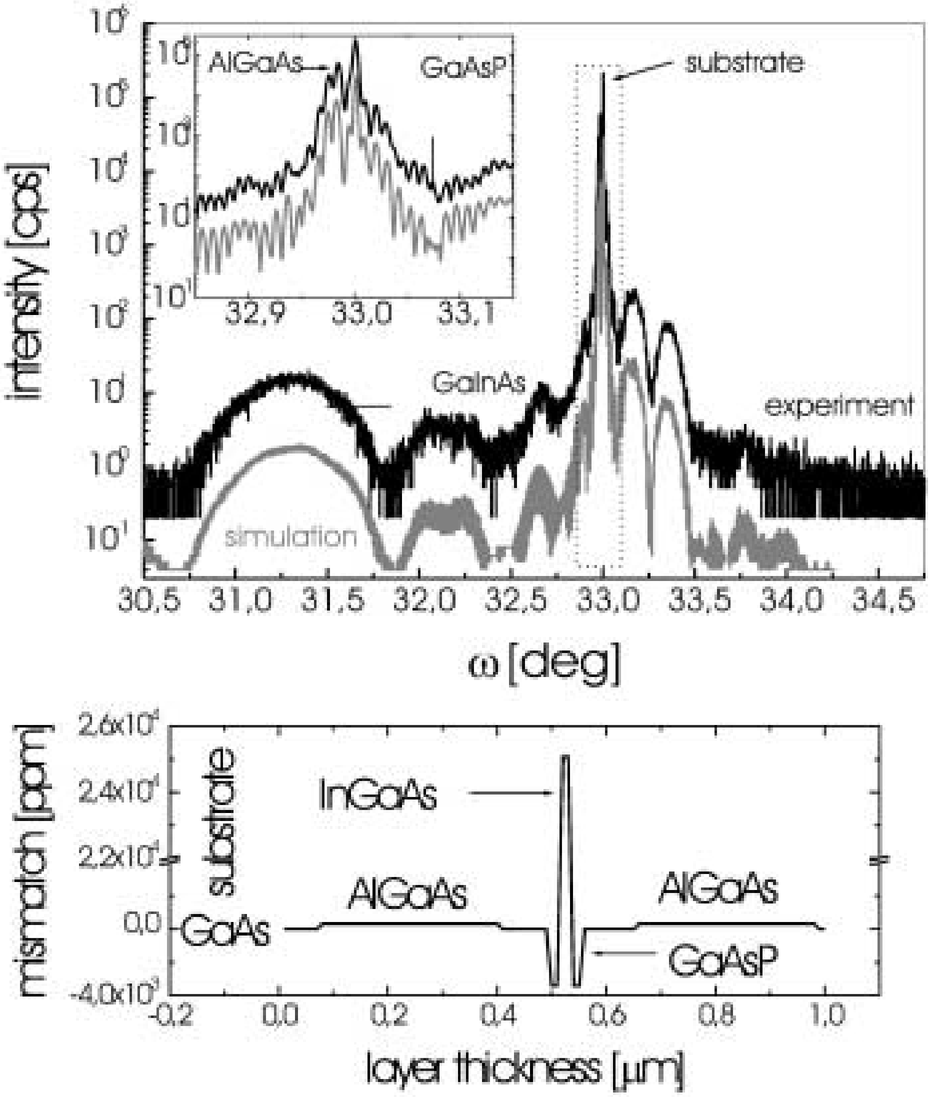


where is the layer peak?

the layer peak on the wrong side!!!

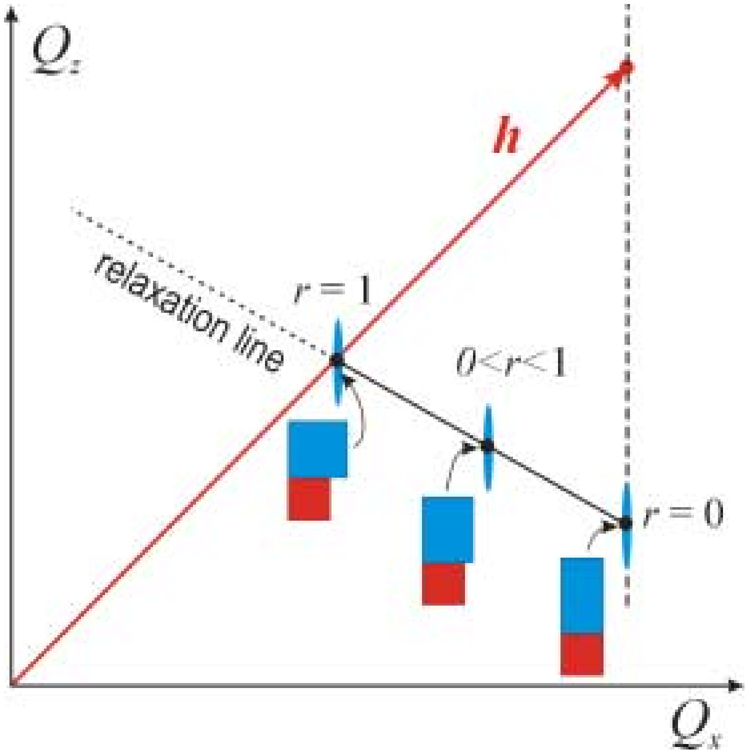
the layer peak is well developed

The state-of-the-art measurement,
a 004 diffraction from a laser structure



Determination of the strain status of a layer by means of a **reciprocal-space mapping:**

How to determine the degree of relaxation?



degree of relaxation $r = \frac{a_{L\parallel} - a_S}{a_L - a_S}$

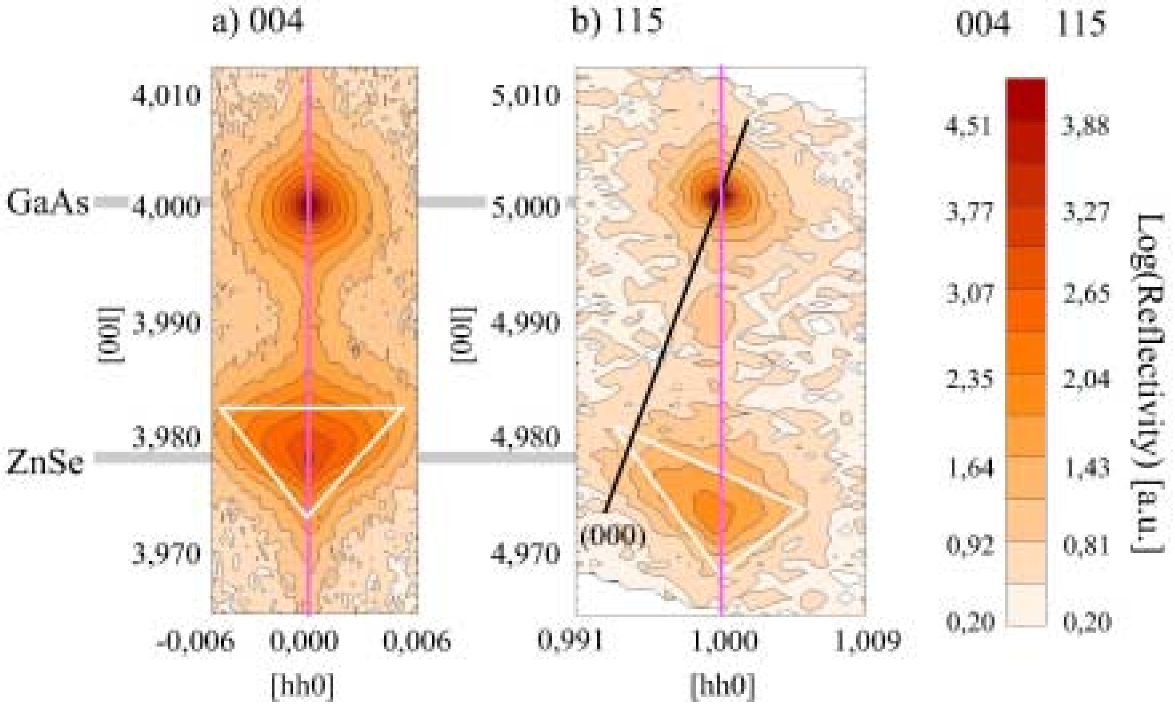
lattice mismatch $f = \frac{a_L^\infty - a_S}{a_S}$

position of the layer peak with respect to the substrate

$$\Delta Q_x = -f\, r\, h_x, \quad \Delta Q_z = -f\, h_z \frac{1 + \nu - 2r\nu}{1 - \nu}$$

ν is the Poisson ratio

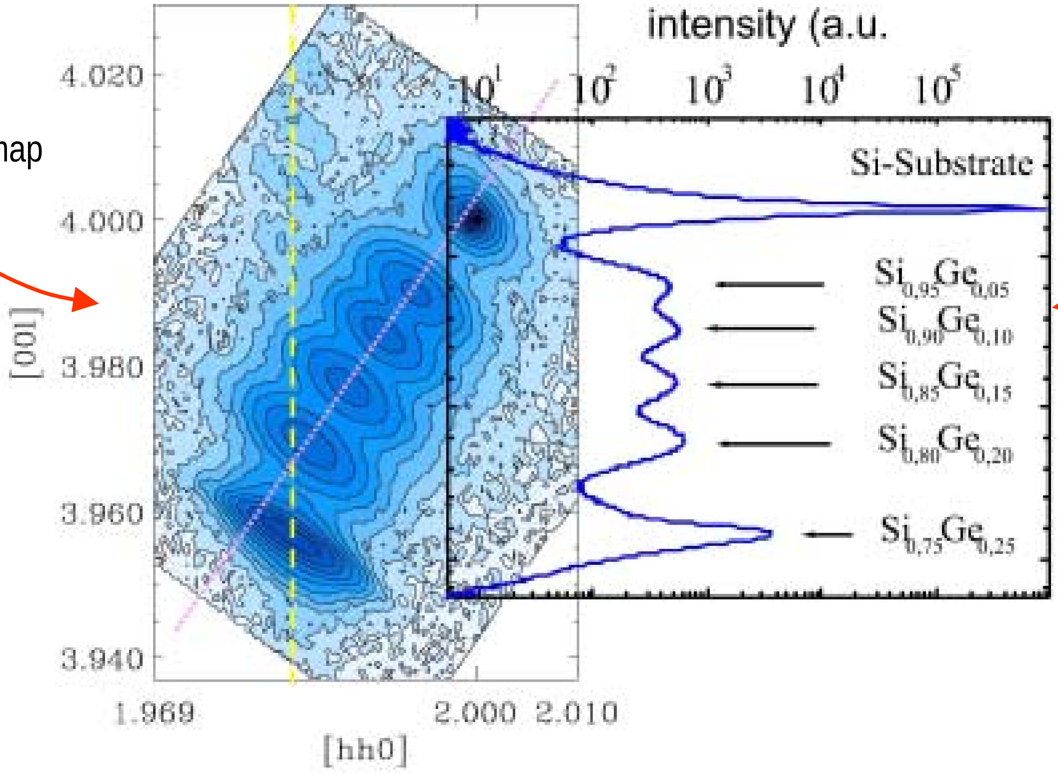
A ZnSe 310 nm layer on GaAs measured in symmetric 004 and asymmetric 115 diffractions



from the position of the layer peak, the value $r \approx 0.1$ follows

H. Heinke et al., J. Cryst. Growth **135**, 41 (1994).

Reciprocal space map of a graded multilayer in asymmetric 224 diffraction



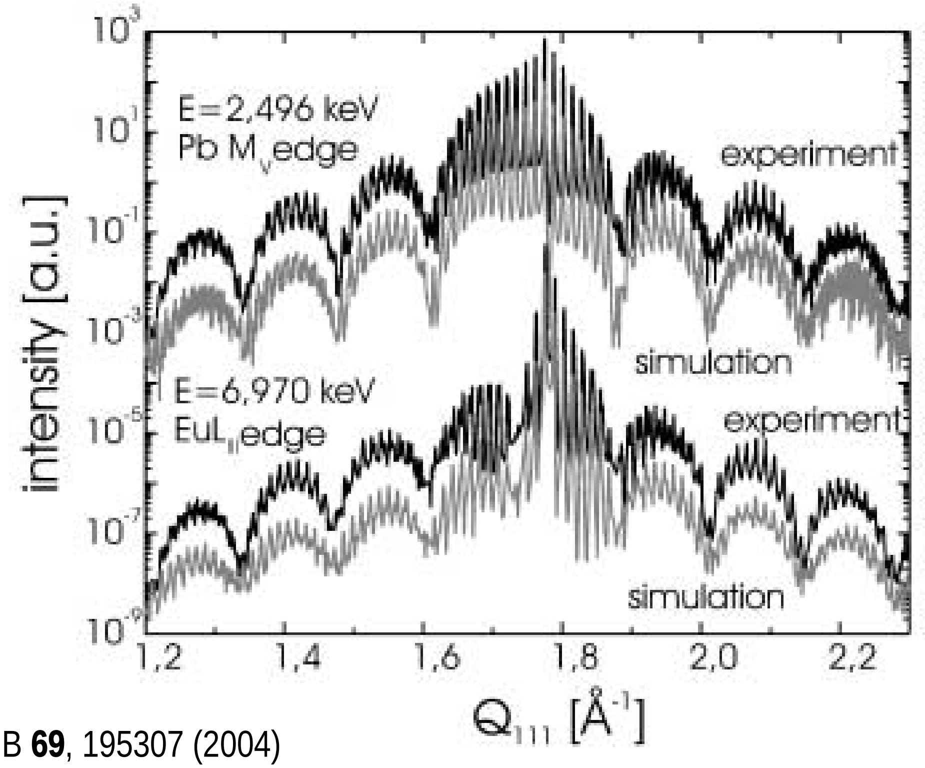
reciprocal space map

a double-crystal diffraction curve

The first 4 layers are relaxed, the 5th layer is nearly pseudomorph with respect to the 4th one

Anomalous scattering effects – using a steep dependence of the atomic scattering factor close to an absorption edge

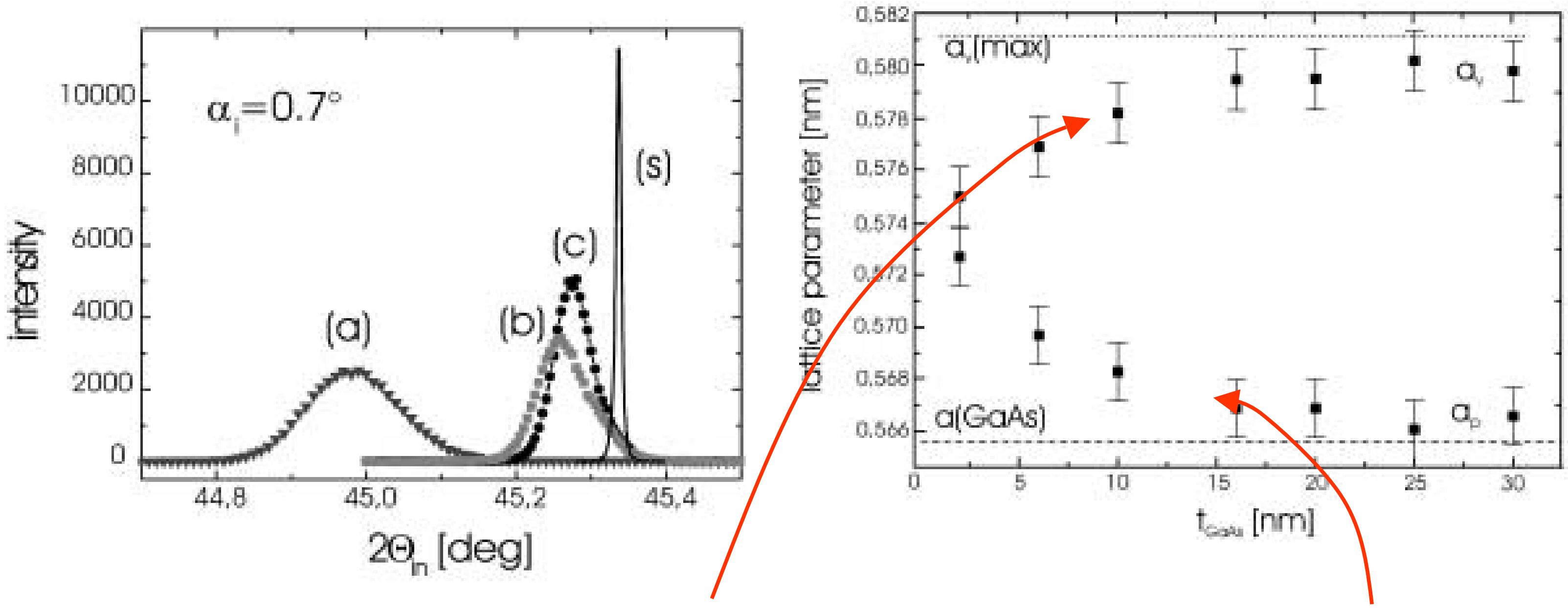
a 100-period multilayer of $(PbSe)_{123}/(EuSe)_{13}$ on PbTe (111), weak 111 diffraction.
At the Pb-edge, the PbSe layers are suppressed – the intensity stems mainly from EuSe (positive mismatch).
At the Eu-edge, the EuSe layers are suppressed, the PbSe layers are visible (negative mismatch to PbTe).



T. U. Schuelli et al., Phys. Rev. B **69**, 195307 (2004)

Grazing-incidence diffraction – determining the lateral lattice parameter

A series of $In_{0.8}Ga_{0.2}As$(18nm)/GaAs superlattices with various GaAs thicknesses, 200 GID diffraction:



the mean vertical lattice parameter increases with increasing thickness of GaAs

the common in-plane lattice parameter decreases with increasing thickness of GaAs

D. Rose et al., Physica B **198**, 256 (1994).

1. High-resolution x-ray scattering – how it works
2. High-resolution x-ray scattering – what it can do
3. **2D layers and multilayers:**
    3.1. thicknesses of layers
    3.2. strains in layers
    3.3. **interface roughness**
4. What else can be done
5. High-resolution x-ray scattering – what it cannot do

Interface roughness in x-ray reflection:

- decreases the intensity of the specularly reflected rays
- gives rise to diffuse x-ray scattering

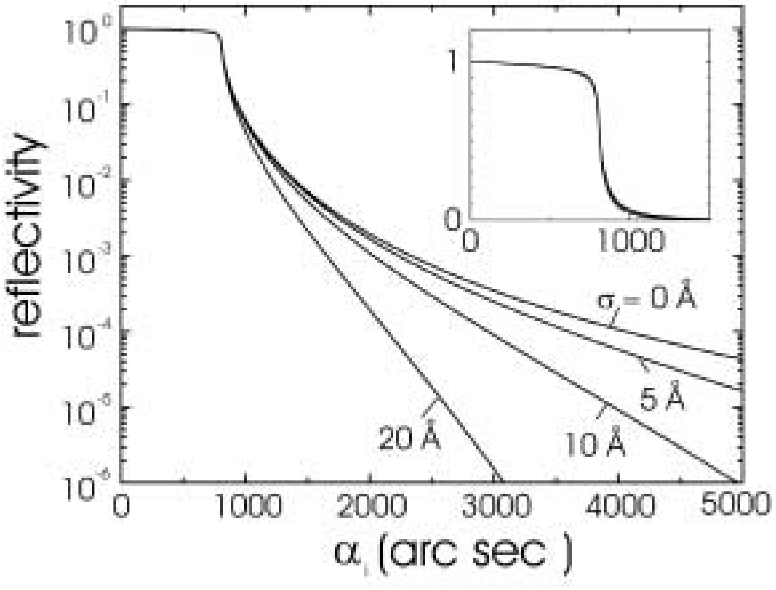
Decrease of the specular intensity – the Fresnel reflectivity coefficient of an interface is multiplied by the attenuation factor

rms roughness of the interface

$$\exp(-Q_z Q_{zT} \sigma^2 / 2)$$

the vertical component of the scattering vector above the interface

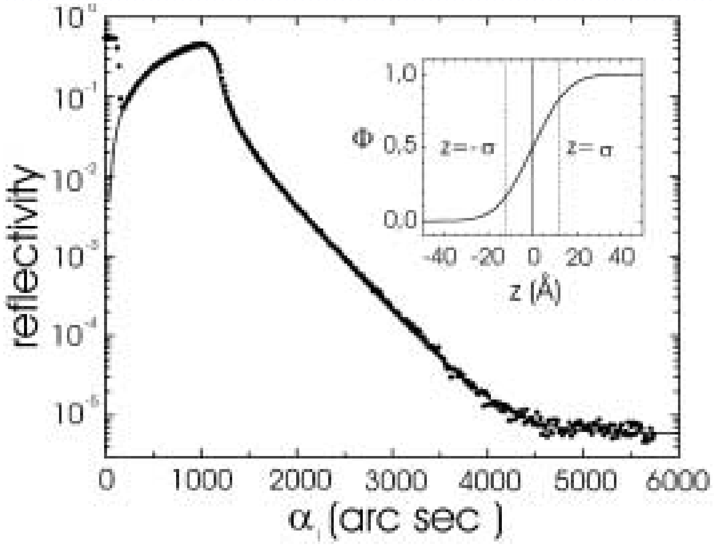
the vertical component of the scattering vector below the interface



specular reflectivity of a Si surface calculated for various roughnesses

Examples of specular reflectivity results:

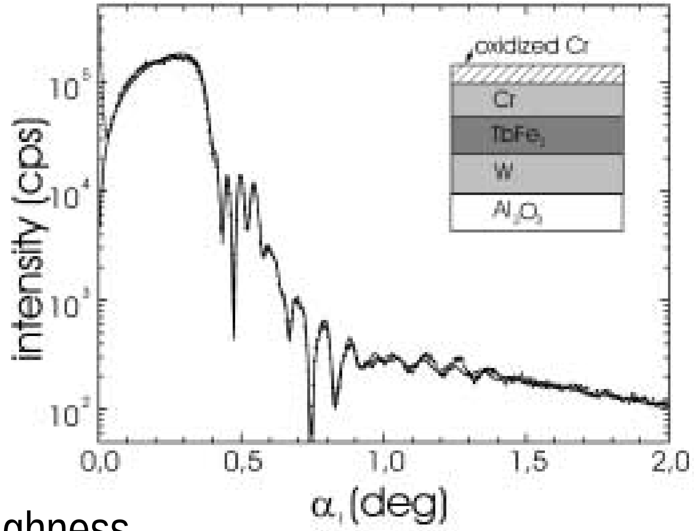
measured and fitted specular reflectivity
of a rough GaAs surface



measured and fitted specular reflectivity
of a metallic sandwich, rms roughnesses:

$$\sigma_{Al_2O_3} = (0.2 \pm 0.05)\ \text{nm}, \sigma_{TbFe_2} = (9.4 \pm 0.5)\ \text{nm},$$

$$\sigma_{Cr} = (2.2 \pm 0.3)\ \text{nm}$$

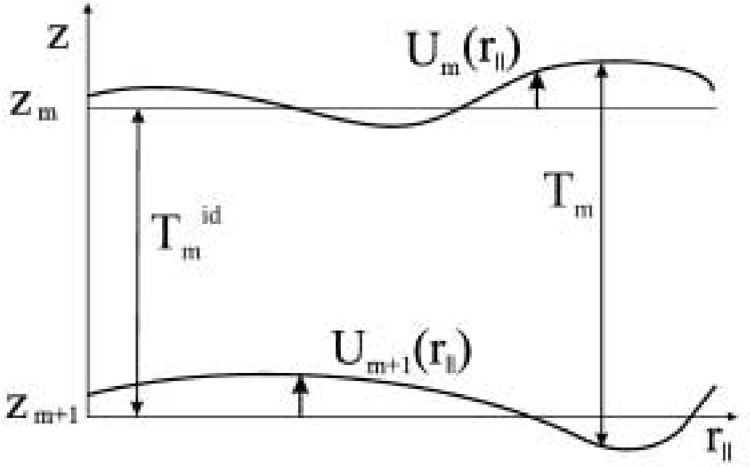


The specular reflectivity is sensitive to the rms roughness
but **not to the roughness correlation length**

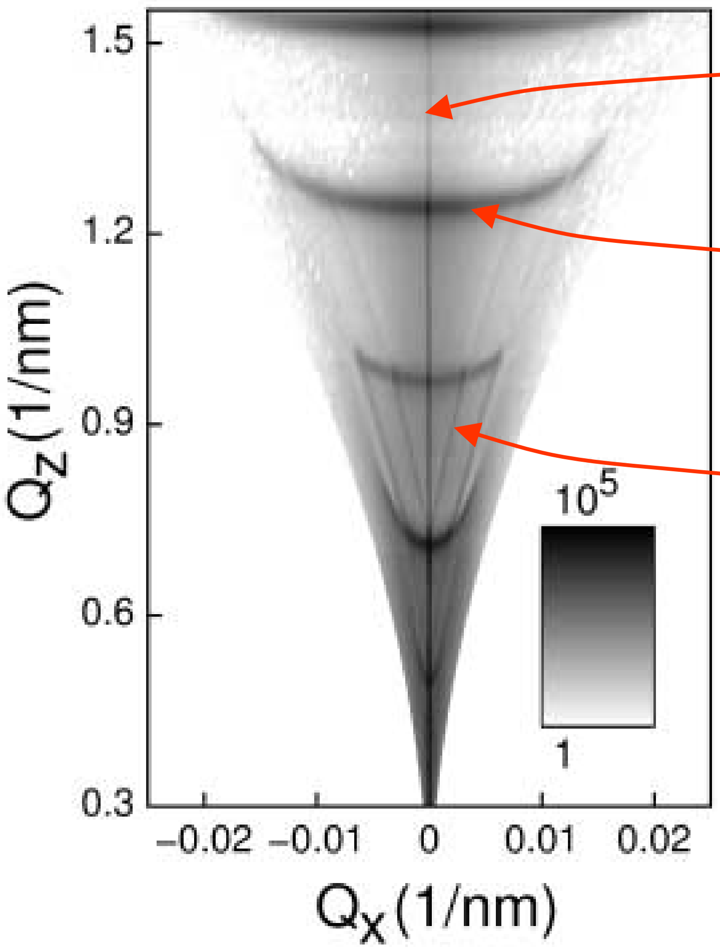
Diffusely scattered intensity distribution in reciprocal space is, roughly speaking, proportional to the Fourier transformation of the roughness correlation function

$$C_{mn}(\boldsymbol{r}-\boldsymbol{r}')=\langle U_m(\boldsymbol{r})U_n(\boldsymbol{r}')\rangle$$

sketch of the interfaces in a rough multilayer



Example: a reciprocal space map of a GaAs(15nm)/AlAs(7nm) multilayer



specular rod with superlattice satellites

diffuse scattering sheets due to the correlation of the roughness of different interfaces

umweganregung effects

V. Holý et al. Phys. Rev. B **49**, 10668 (1994)

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Volume defects in the layers:

- mosaic structure of relaxed layers
  - → size of the mosaic blocks
- misfit dislocations in relaxed layers
  - → densities of particular dislocation types
- defects in implanted layers
  - → vertical profiles of radiation defects
- precipitates, stacking faults, dislocation loops etc.
  - → types, sizes and densities of the defects

V. Holý et al., J. Appl. Cryst. **27**, 551 (1994)

V. Kaganer et al., Phys. Rev. B **55**, 1793 (1997).

M. A. Krivoglaz, *X-Ray and Neutron Diffraction in Nonideal Crystals (*Springer, Berlin, 1996)

Semiconductor nanostructures:

- etched quantum wires and dots
  - → morphology and strain
- self-organized quantum wires and dots
  - → positions, shapes and chemical compositions of non-capped and buried nanostructures

U. Pietsch et al., *High Resolution X-Ray Scattering from Thin Film and Lateral Nanostructures,* (Springer 2004).
J. Stangl et al., Rev. Mod. Phys. in print (2004)
M. Schmidbauer, *X-Ray Diffuse Scattering from Self-Organized Mesoscopic Semiconductor Structures,* (Springer 2004).

Local methods – microdiffraction (a powerful x-ray optics is necessary)

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5. **High-resolution x-ray scattering – what it cannot do**

High-resolution x-ray scattering method measures the intensity distribution **in reciprocal space** and it is not trivial to obtain real-space information (**phase problem**).

Usually, a suitable structure model must be chosen *a priori* and fitted to measured data.

Attempts to overcome the phase problem by a direct method were successful only in trivial cases
- a phase recovery of a wave diffracted from a thin layer
- coherent (i.e. phase-sensitive) small angle scattering from metallic clusters

Monographs on high-resolution x-ray scattering:

- V. Holý, U. Pietsch and T. Baumbach, *High-Resolution X-Ray Scattering From Thin Films and Multilayers*, (Springer 1999); a new edition appears in 2004
- P. F. Fewster, X-Ray Scattering From Semiconductors, (Imperial Coll. Press 2003).
- D. K. Bowen, B. K. Tanner, *High Resolution X-Ray Diffractometry Topography,* (CRC Press 1998) .

THANK YOU FOR YOUR KIND ATTENTION