High-Resolution XRD

What is thin film/layer?

- **Material so thin that its characteristics are dominated primarily by two dimensional effects and are mostly different than its bulk properties**
  Source: semiconductorglossary.com

- **Material which dimension in the out-of-plane direction is much smaller than in the in-plane direction.**

- **A thin layer of something on a surface**
  Source: encarta.msn.com

Epitaxial Layer

- **A single crystal layer that has been deposited or grown on a crystalline substrate having the same structural arrangement.**
  Source: photonics.com

- **A crystalline layer of a particular orientation on top of another crystal, where the orientation is determined by the underlying crystal.**

<u>Homoepitaxial layer</u>
the layer and substrate are the same material and possess the same lattice parameters.

<u>Heteroepitaxial layer</u>
the layer material is different than the substrate and usually has different lattice parameters.

Accessible Information to X-ray Diffraction

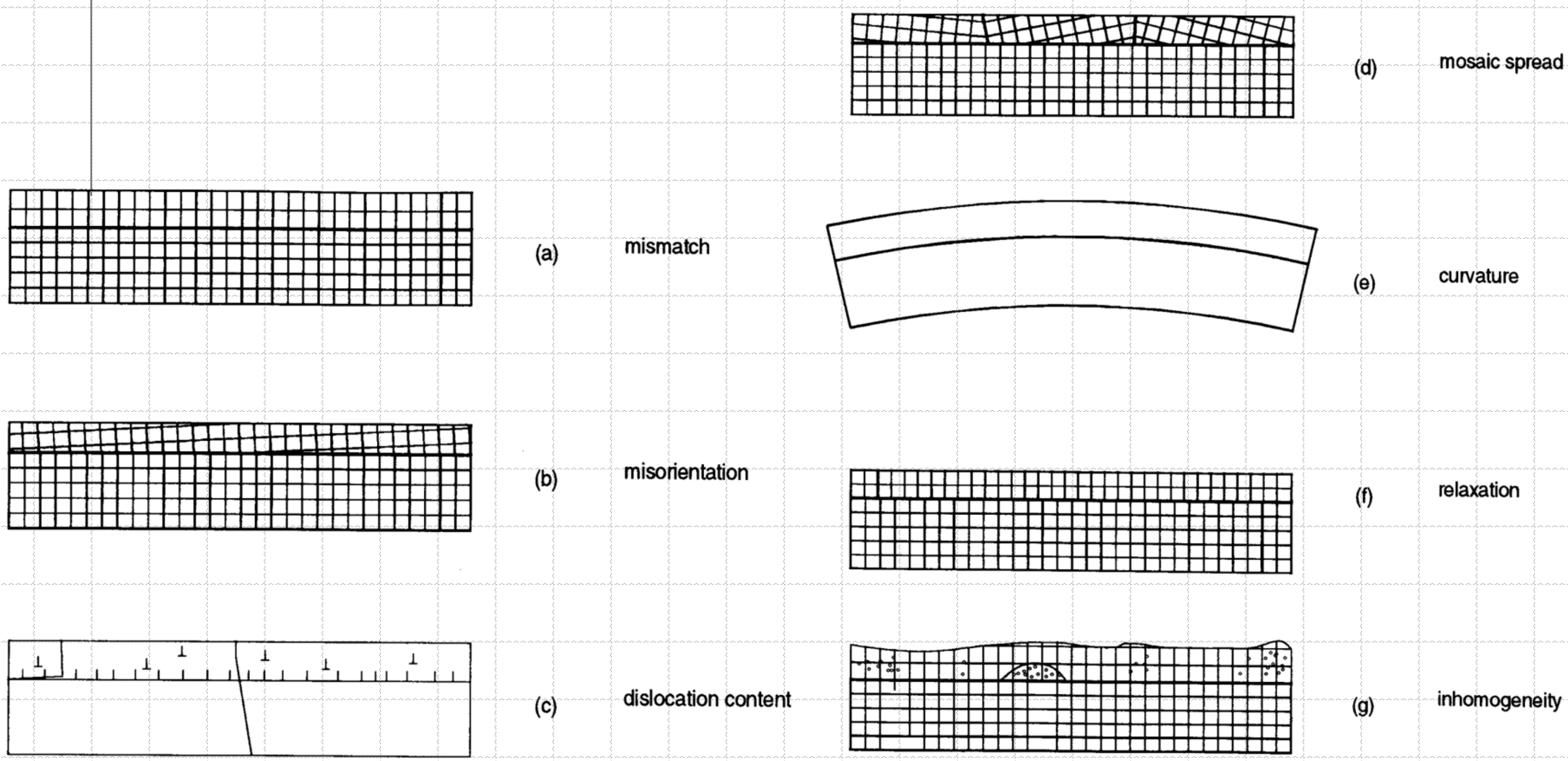
- Definition for structural types

Structure Type	Definition
Perfect epitaxial	Single crystal in perfect registry with the substrate that is also perfect.
Nearly perfect epitaxial	Single crystal in nearly perfect registry with the substrate that is also nearly perfect.
Textured epitaxial	Layer orientation is close to registry with the substrate in both in-plane and out-of-plane directions. Layer consists of mosaic blocks.
Textured polycrystalline	Crystalline grains are preferentially oriented out-of-plane but random in-plane. Grain size distribution.
Perfect polycrystalline	Randomly oriented crystallites similar in size and shape.
Amorphous	Strong interatomic bonds but no long range order.

P.F. Fewster "X-ray Scattering from Semiconductors"

Accessible Information to X-ray Diffraction

- Defects that are common in epilayer structures



What we want to know about thin films?

- Crystalline state of the layers:
- Epitaxial (coherent with the substrate, relaxed)
- Polycrystalline (random orientation, preferred orientation)
- Amorphous
- Crystalline quality
- Strain state (fully or partially strained, fully relaxed)
- Defect structure
- Chemical composition
- Thickness
- Surface and/or interface roughness

Accessible Information to X-ray Diffraction

- Structural parameters that characterize various material types

	Thickness	Composition	Relaxation	Distortion	Crystalline size	Orientation	Defects
Perfect epitaxy	×	×				×	
Nearly perfect epitaxy	×	×	?	?	?	×	×
Textured epitaxy	×	×	×	×	×	×	×
Textured polycrystalline	×	×	?	×	×	×	?
Perfect polycrystalline	×	×		×	×		?
Amorphous	×	×					

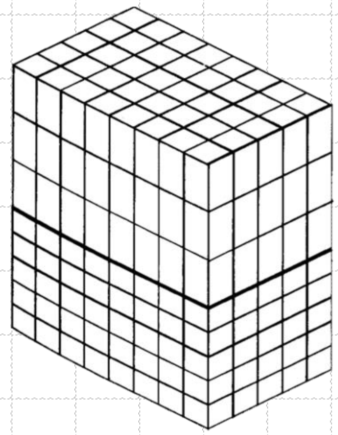
× – parameters that have meaning
? – parameters that could have meaning

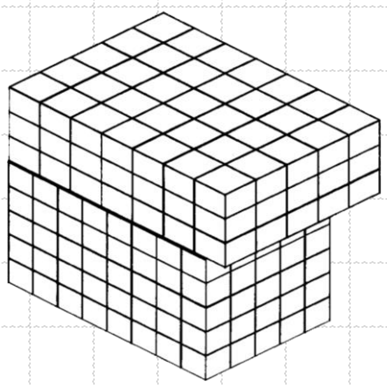
Accessible Information to X-ray Diffraction

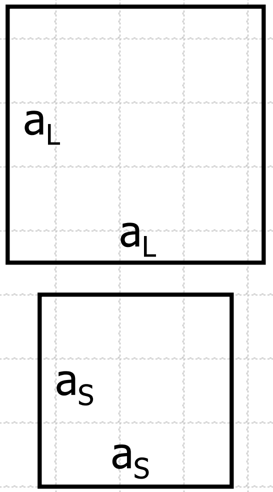
Material parameter	Effect on rocking curve	Distinguishing features
Mismatch	Splitting of layer and substrate peak	Invariant with sample rotation
Misorientation	Splitting of layer and substrate peak	Changes sign with sample rotation
Dislocation content	Broadens peak	Broadening invariant with beam size No shift of peak with beam position on sample
Mosaic spread	Broadens peak	Broadening may increase with beam size, up to mosaic cell size No shift of peak with beam position on sample
Curvature	Broadens peak	Broadening increases linearly with beam size Peak shifts systematically with beam position on sample
Relaxation	Changes splitting	Different effect on symmetrical and asymmetrical reflections
Thickness	Affects intensity of peak	Integrated intensity increases with layer thickness, up to a limit
	Introduces interference fringes	Fringe period controlled by thickness
Inhomogeneity	Effects vary with position on sample	Individual characteristics may be mapped

Mismatch

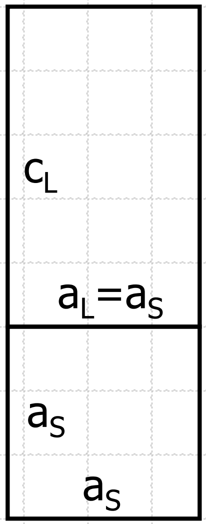
- Consider two materials with the same space group, same atomic arrangements, but slightly different lattice parameters and elastic parameters.





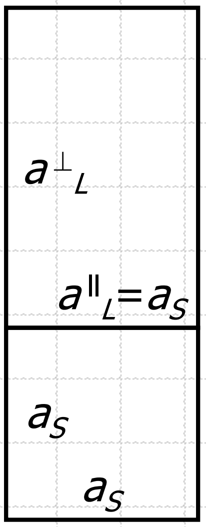


Before deposition



After deposition

Mismatch



True lattice mismatch is: $m = \dfrac{a_L^R - a_s}{a_s}$

The peak separation between substrate and layer is related to the change of interplanar spacing **<u>normal</u>** to the substrate.

If it is 00L reflection then the "experimental x-ray mismatch":

$$m^* = \frac{\Delta a^{\perp}}{a^{\perp}} = \frac{\Delta d^{\perp}}{d^{\perp}} = \frac{d_L^{\perp} - d_S^{\perp}}{d_S^{\perp}}$$

Relationship:

$$m = m^* \left\{ \frac{1-\nu}{1+\nu} \right\}$$

ν – Poisson ratio

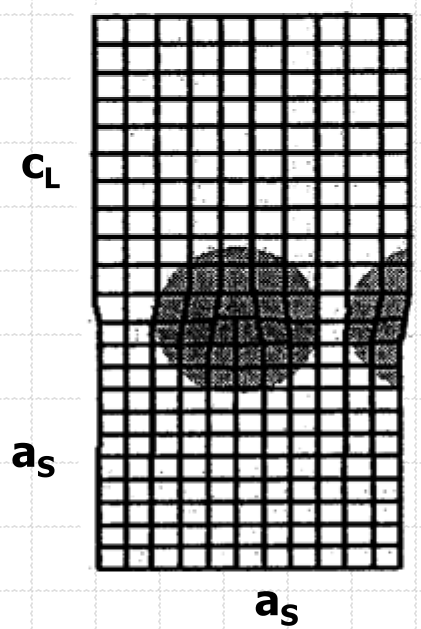
$$\nu \approx \frac{1}{3}$$

$$m \approx \frac{m^*}{2}$$

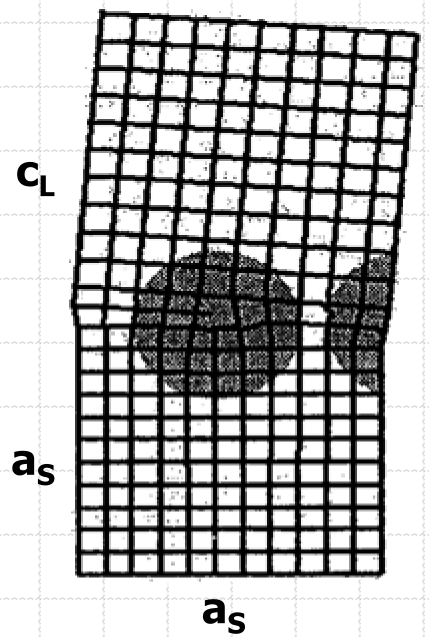
Relaxation

- The problems occur when the elastic parameters are incapable of accommodating the distortions necessary for perfect epitaxy.

Fully or partially relaxed

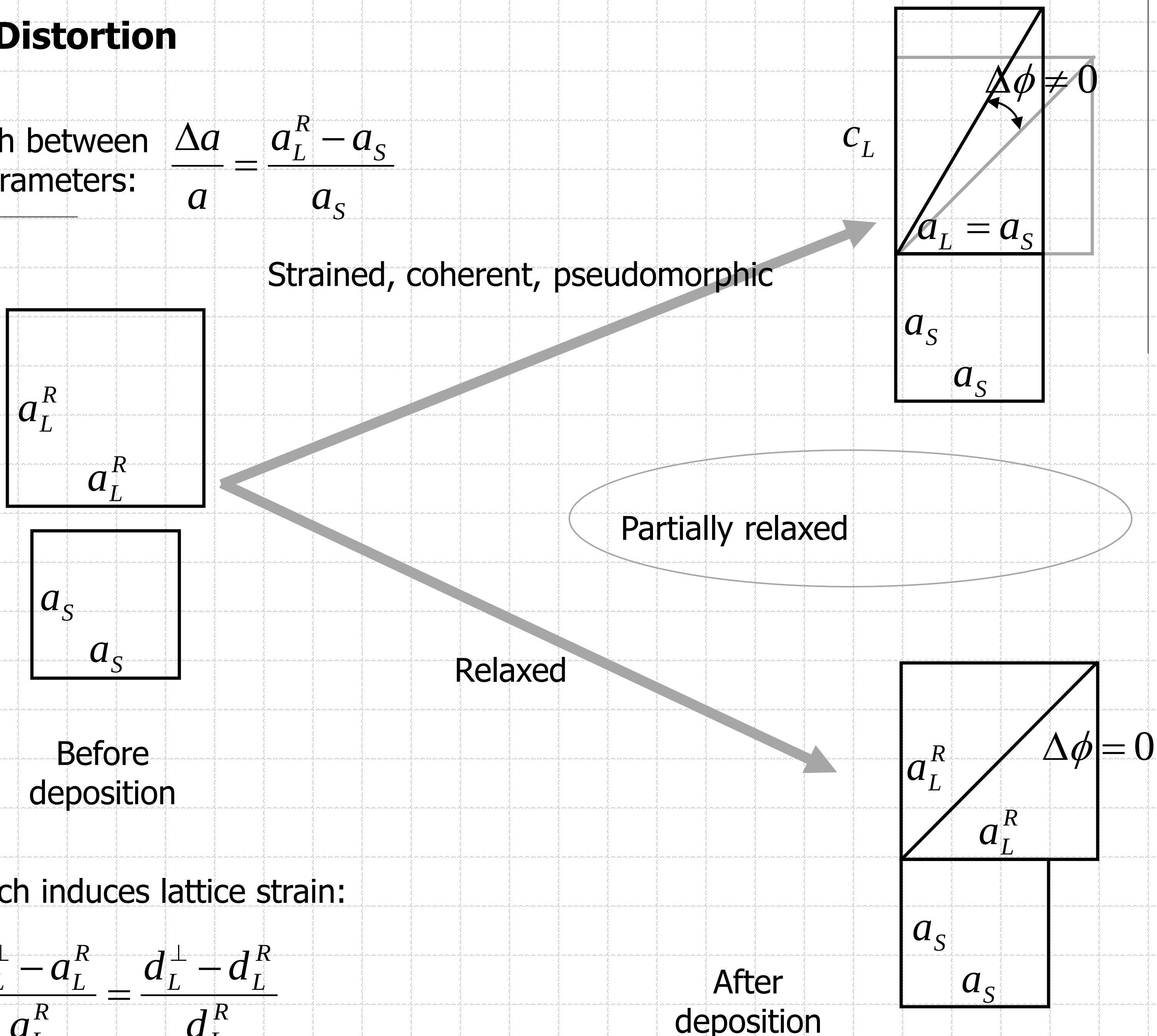


Fully or partially relaxed and tilted



Tetragonal Distortion

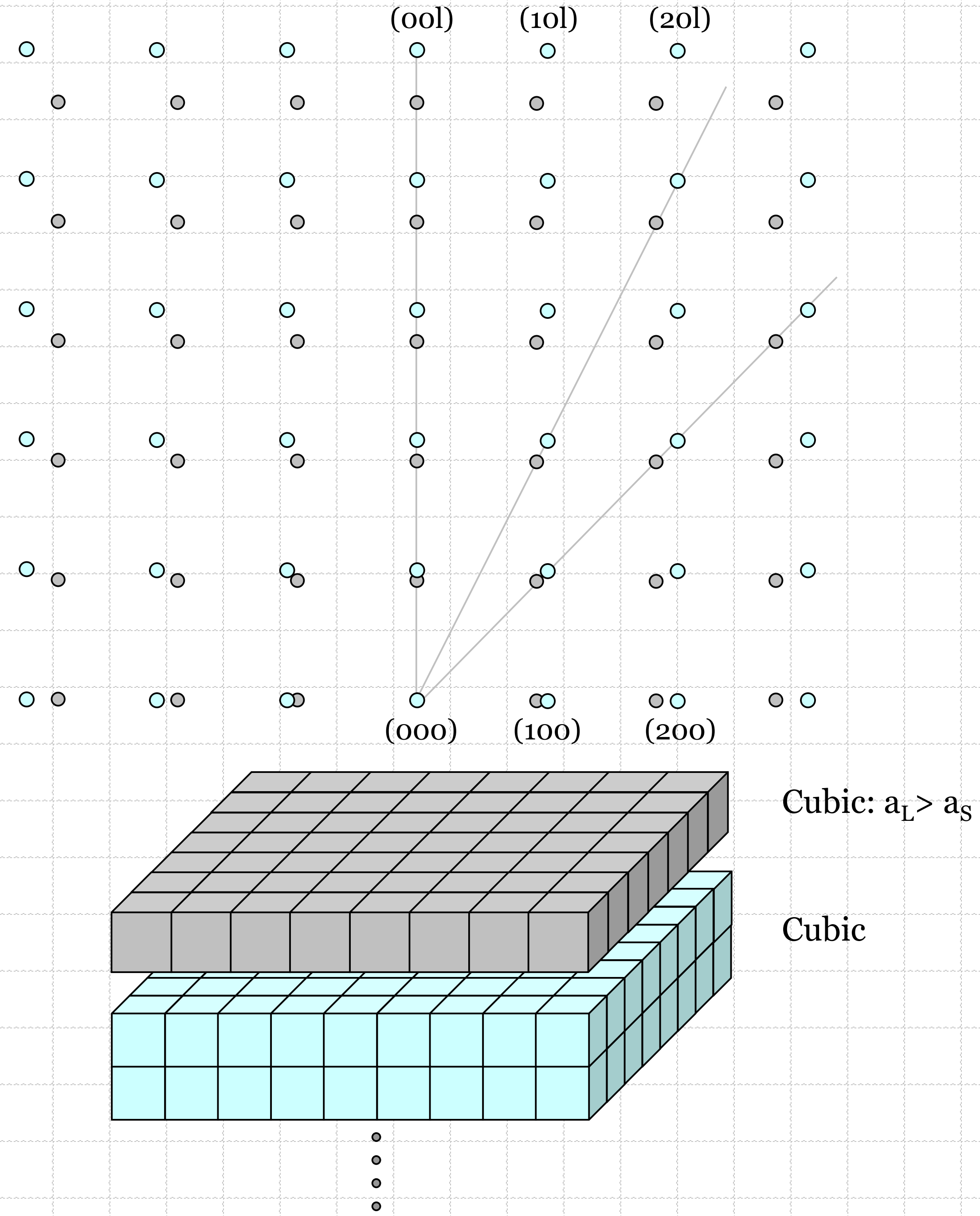
Lattice mismatch between cubic lattice parameters: $\dfrac{\Delta a}{a} = \dfrac{a_L^R - a_S}{a_S}$



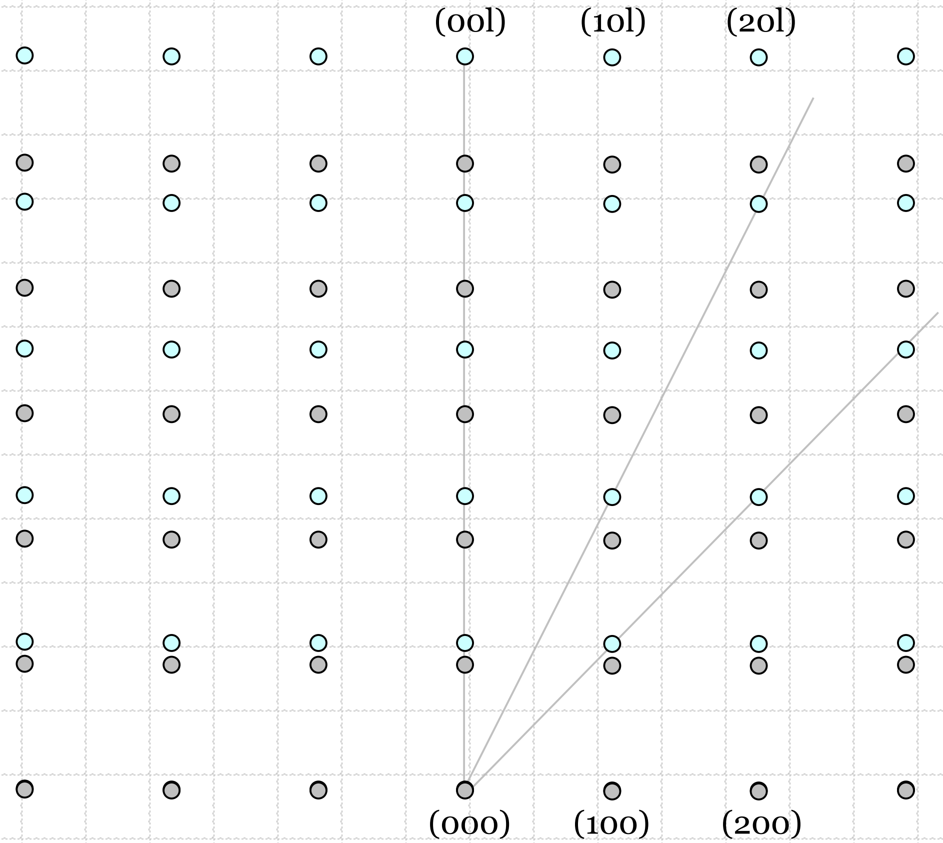
Lattice mismatch induces lattice strain:

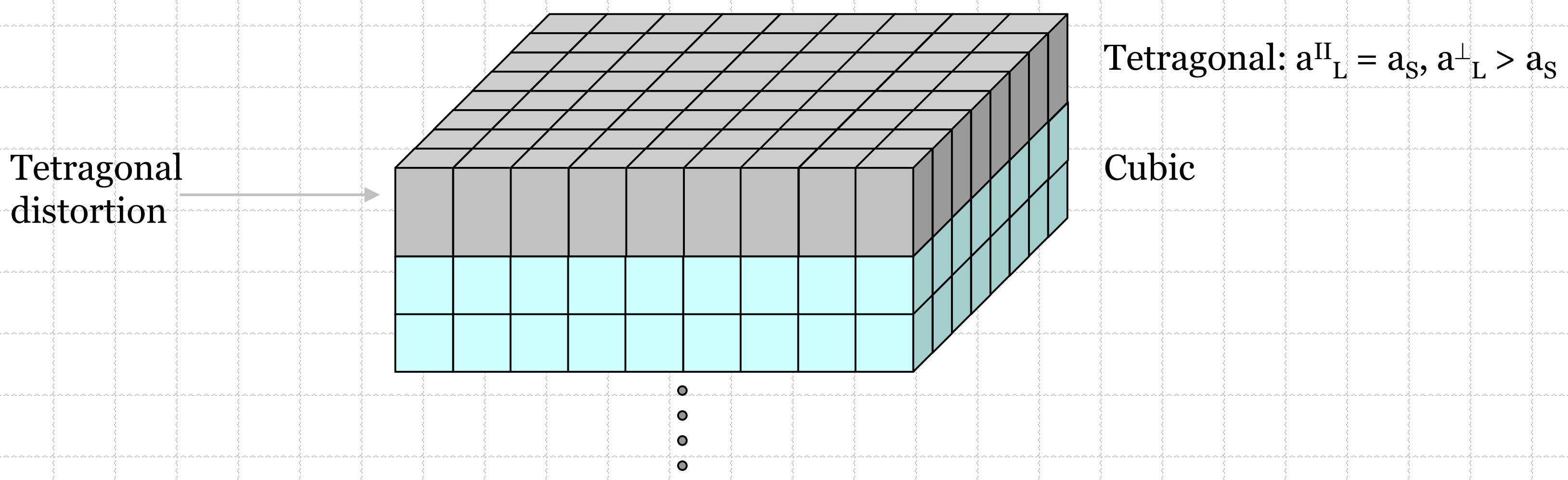
$$\varepsilon_{\perp} = \varepsilon_{zz} = \frac{a_L^{\perp} - a_L^R}{a_L^R} = \frac{d_L^{\perp} - d_L^R}{d_L^R}$$

Relaxed Layer

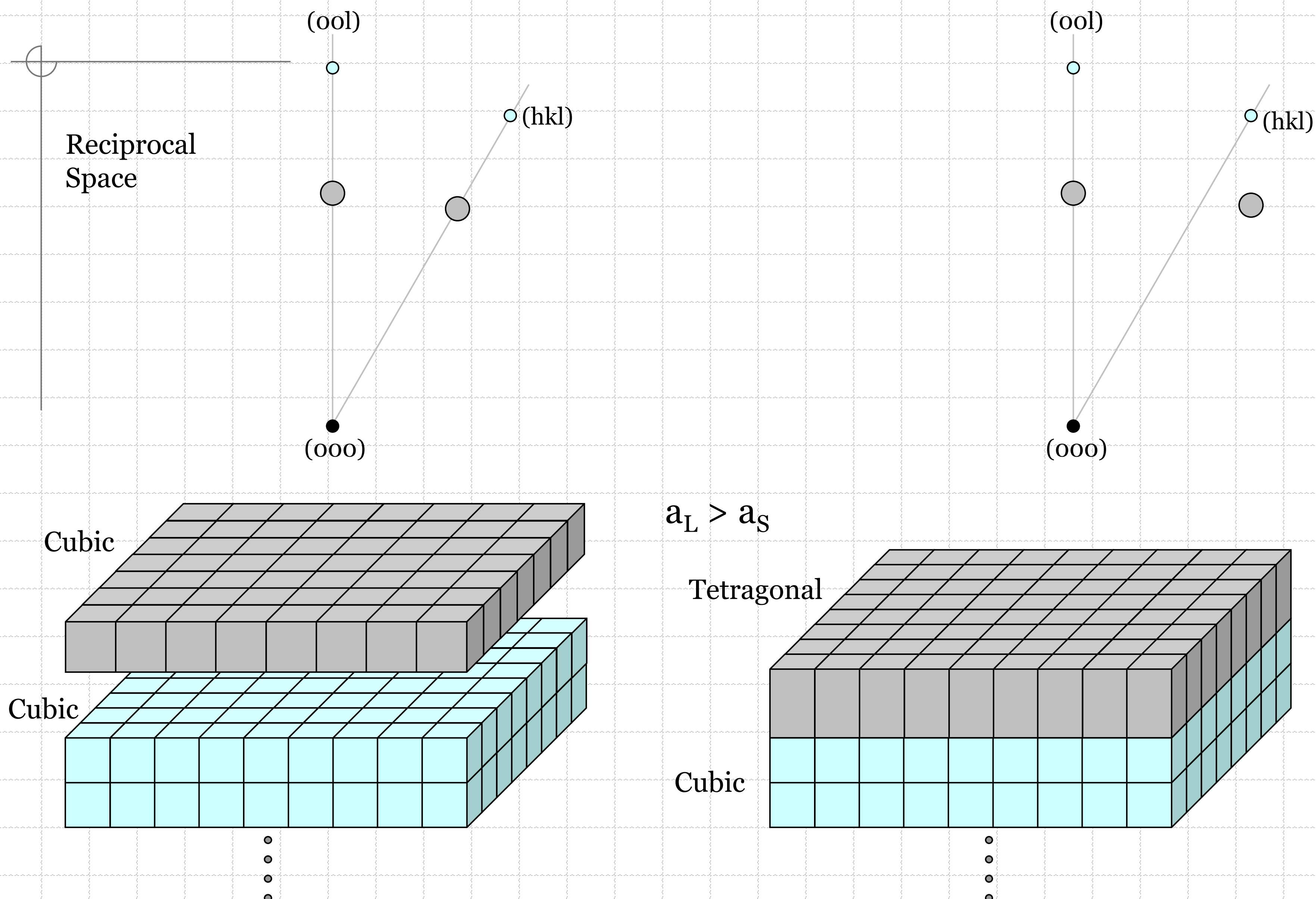


Strained Layer





Perfect Layers: Relaxed and Strained



Strain

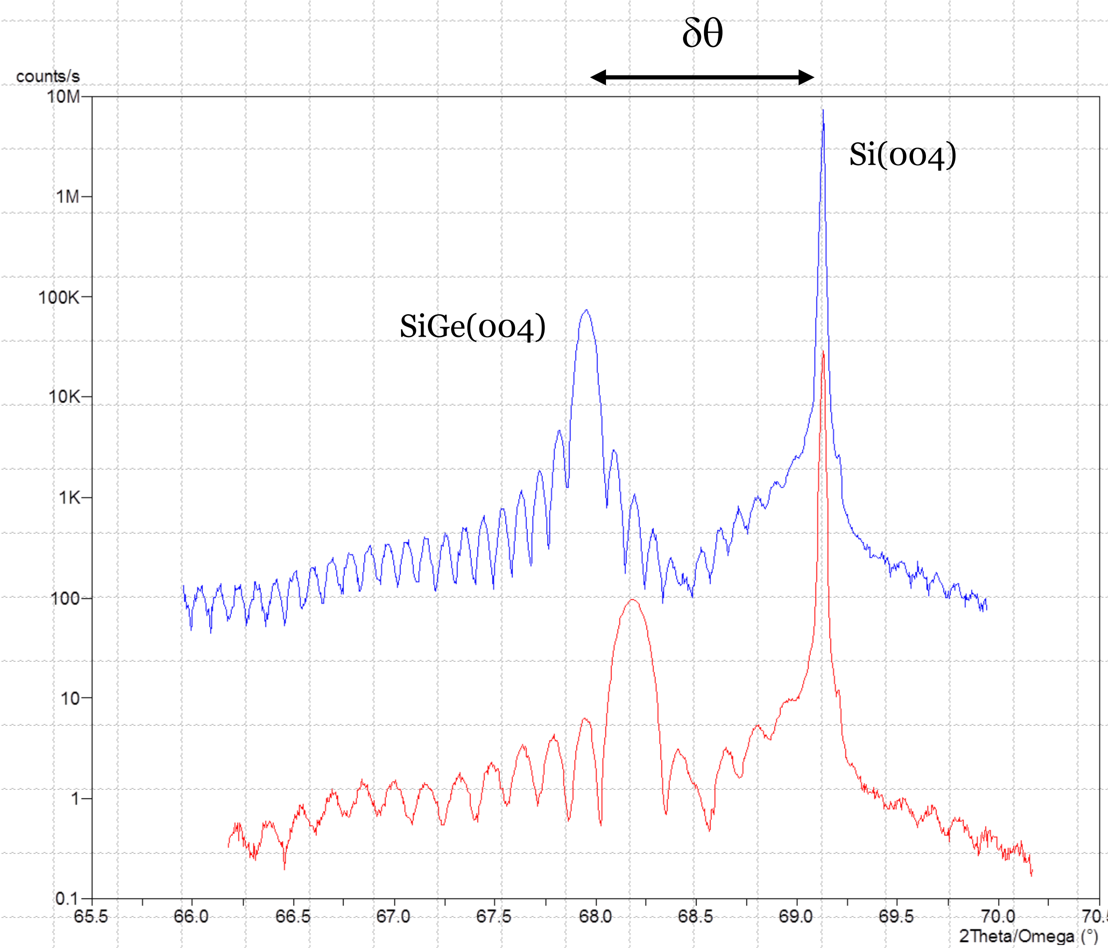
$$\varepsilon_{zz} = \frac{d_L^z - d_{L_R}^z}{d_{L_R}^z}$$

$$\varepsilon_{xx} = \frac{d_L^x - d_{L_R}^x}{d_{L_R}^x}$$

$$\varepsilon_{yy} = \frac{d_L^y - d_{L_R}^y}{d_{L_R}^y}$$

$$\varepsilon_{zz} = -\frac{\nu}{1-\nu}\left(\varepsilon_{xx} + \varepsilon_{yy}\right)$$

$$\varepsilon_{zz} = -\frac{2\nu}{1-\nu}\varepsilon_{ave}$$

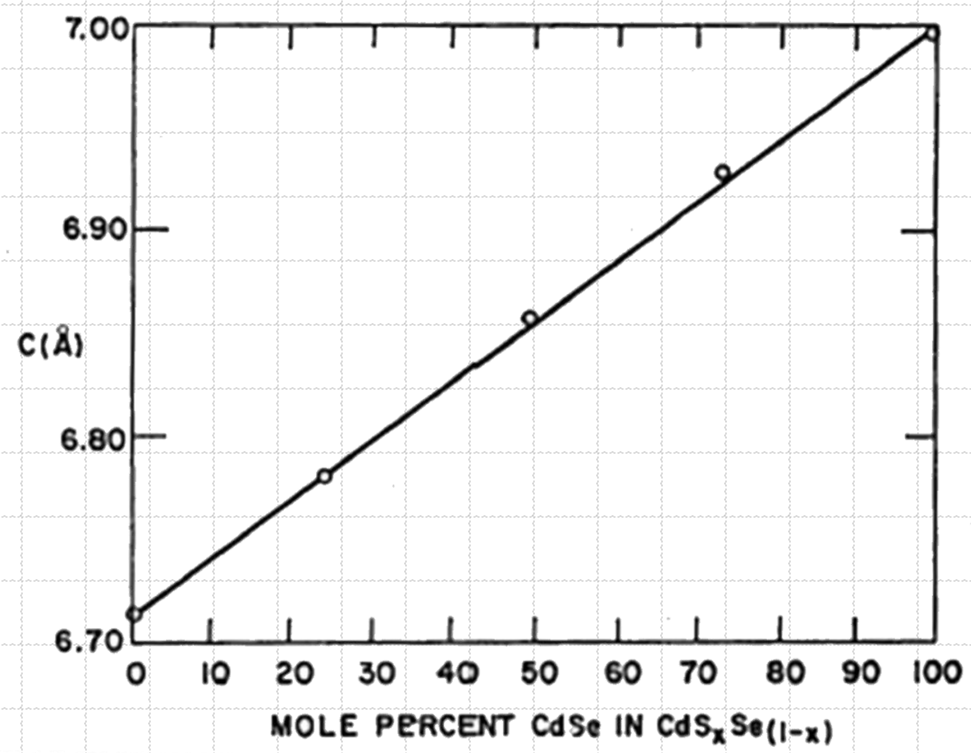


F. C. Frank and J. H. van der Merwe, Proc. R. Soc. London, Ser. A ***198****, 216 (1949).*

Composition

- **Vegard's law**
  - Vegard's law states that the lattice parameter of substitutional solid solution varies linearly between the lattice parameter values for the components. The composition is expressed in atomic percentage.

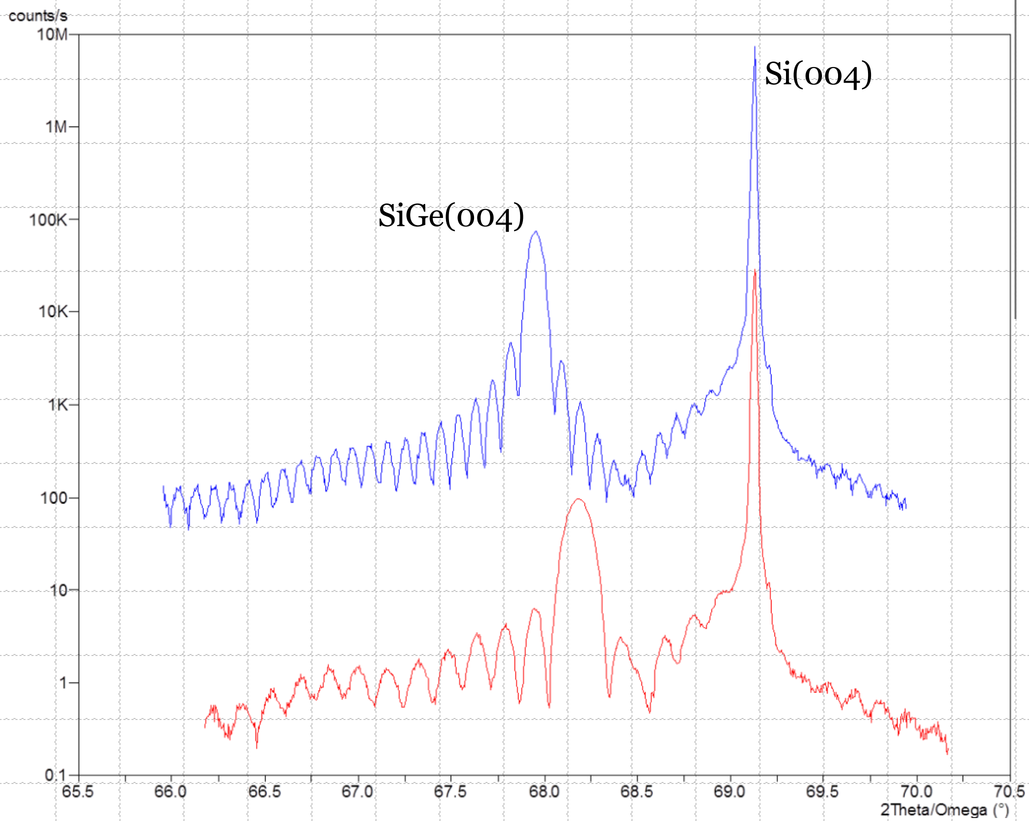
$$a^R_{A_x B_{1-x}} = x a^R_A + (1-x) a^R_B$$



Composition

$$a^R_{A_xB_{1-x}} = xa^R_A + (1-x)a^R_B$$

$$x = \frac{a^R_{A_xB_{1-x}} - a^R_B}{a^R_A - a^R_B}$$



$$m = \frac{a^R_L - a_S}{a_S} = m^* \frac{1-\nu}{1+\nu}$$

$$m^* = \frac{a_\perp - a_S}{a_S} = \frac{d^z_L - d^z_S}{d^z_S} = \frac{\sin\theta_S - \sin(\theta_S + \Delta\theta)}{\sin(\theta_S + \Delta\theta)}$$

For $Si_{1-x}Ge_x$: $a_{Ge_xSi_{1-x}} = xa_{Ge} + (1-x)a_{Si} + 0.007[(2x-1)^2 - 1]$

Bragg's law:

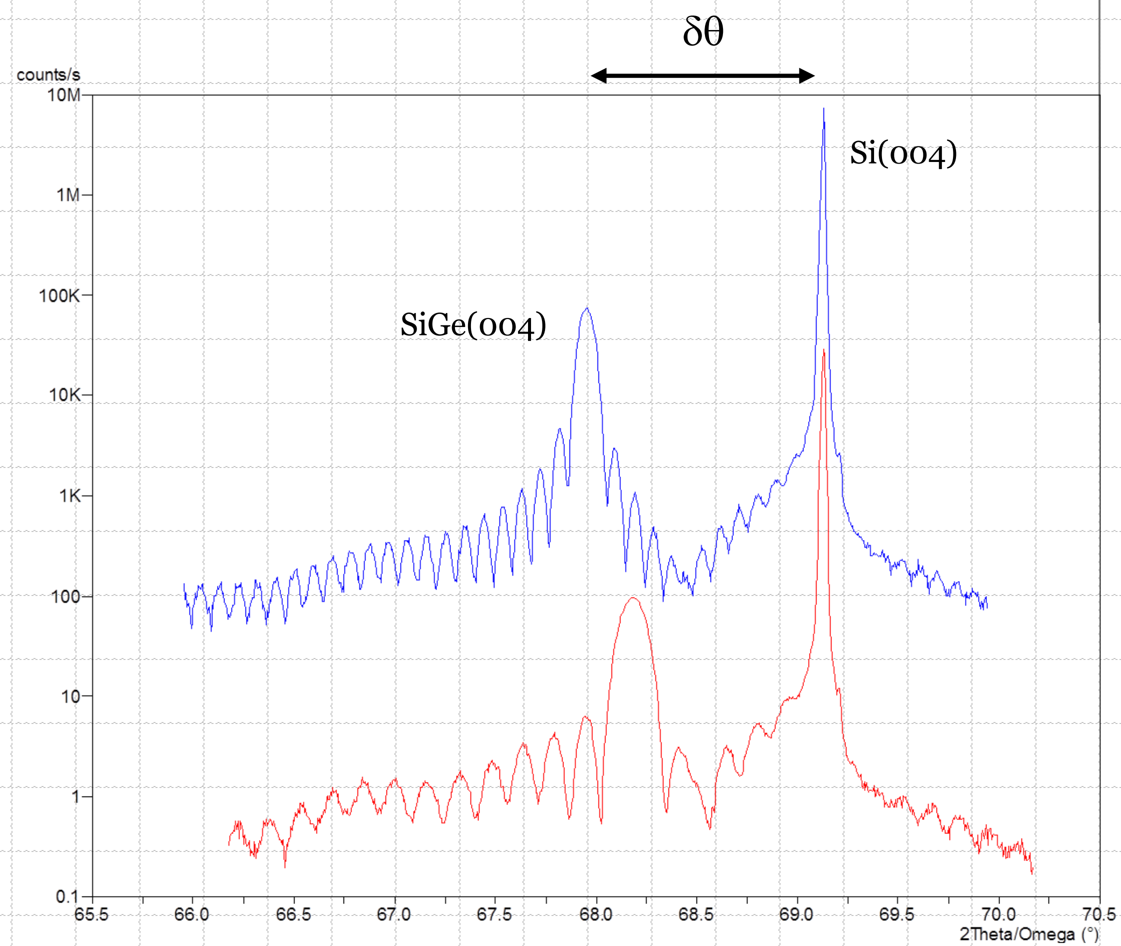
$$2d\sin\theta = \lambda$$

For out-of-plane lattice parameter:

$$c_L = l d_{hkl}$$

$$d_{hkl} = \frac{\lambda}{2\sin\theta_L}$$

$$\theta_L = \theta_S + \Delta\theta$$



θ_S can be calculated from Bragg's law knowing $a_S = 5.431$ Å

Layer Tilt

- If the layer is tilted relative to the substrate then this will result in a shift of the layer peak relative to that of the substrate.
- This is not connected with the composition.

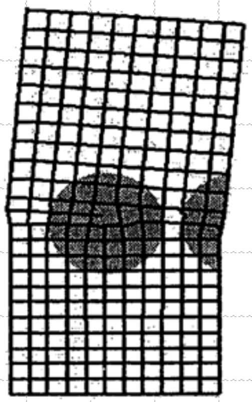
The resulting layer peak splitting $\Delta\theta$ will depend on:

- mismatch peak splitting $\delta\theta$
- α – tilt angle
- φ – rotation angle

If specimen is rotated by angle φ about its normal the layer peak will be displaced by: $\alpha cos\varphi$

$$\Delta\theta_0 = \delta\theta + \alpha\cos\varphi_0$$

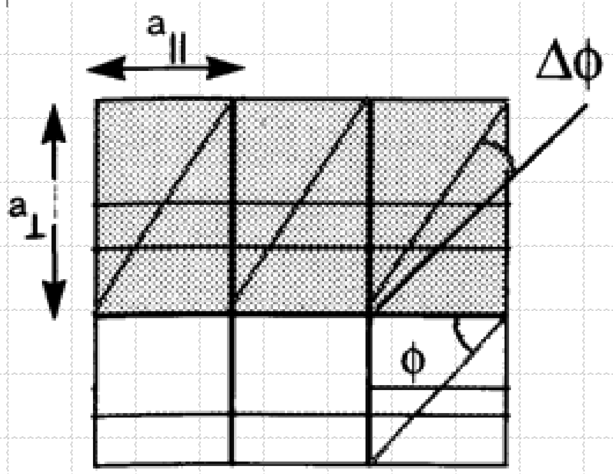
$$\Delta\theta_{180} = \delta\theta + \alpha\cos\varphi_{180}$$



Then true splitting mismatch: $\delta\theta = \dfrac{(\Delta\theta_0 + \Delta\theta_{180})}{2}$

Layer Relaxation

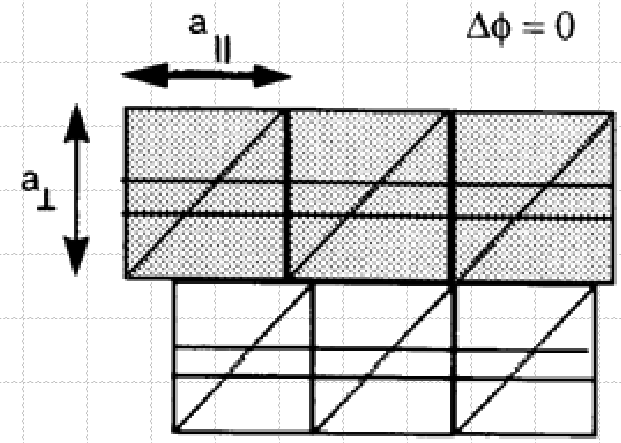
- Our layer is completely coherent.
  - In this case it is enough to measure misfit only along (00*l*) direction.
- Partially or fully relaxed layers.
  - We need to measure misfit parallel to the interface as well as perpendicular.
  - For this we need an asymmetric reflection (e.g. 224, 113).



Fully Strained

Epilayer

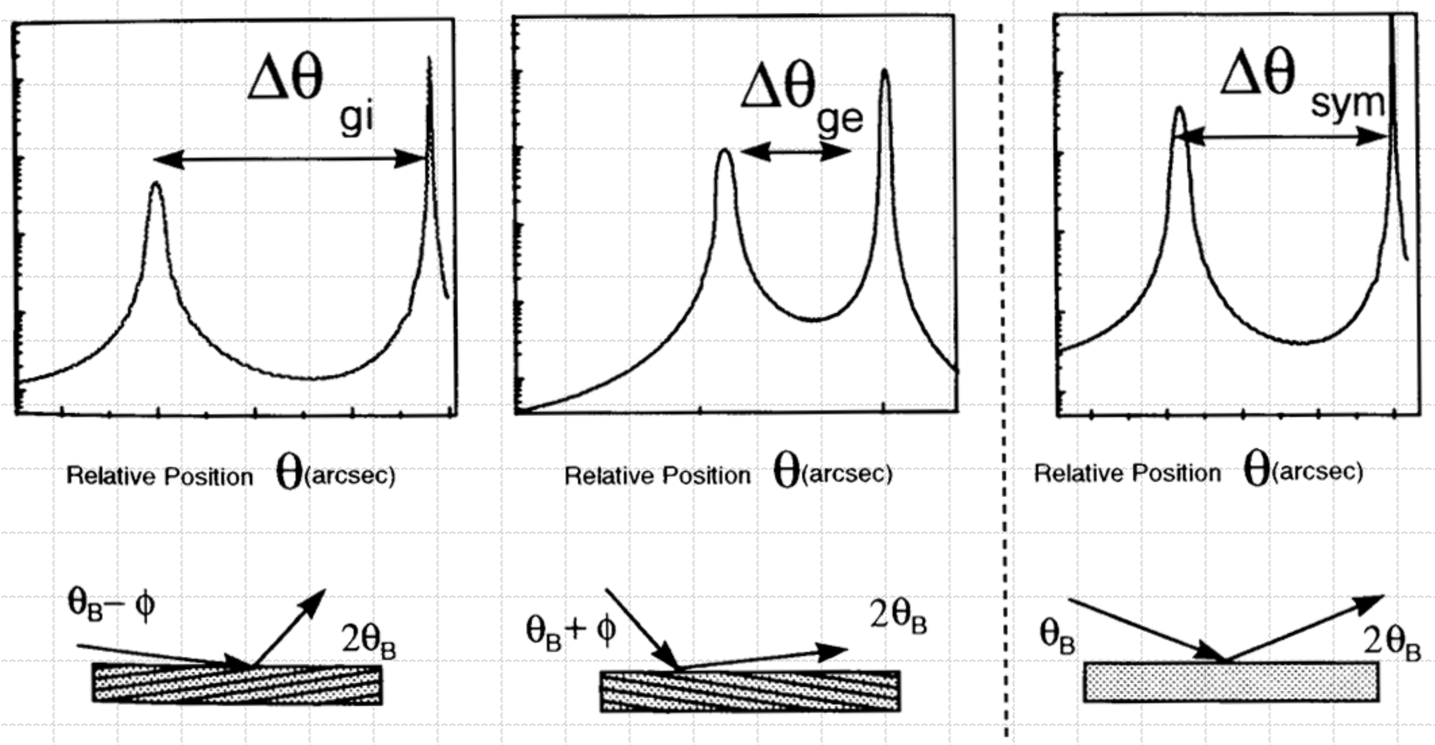
Substrate



Fully Relaxed

Layer Relaxation

- The effect of tilt on the peak splitting is reversed if the specimen is rotated by 180° about its surface normal.
- The splitting due to mismatch will not be affected by such rotation.
- We can make grazing incidence or grazing exit measurements to separate the tilt from the true splitting.



Relaxation

- The resulting measured splittings are now different between these two geometries:

$$\Delta\theta_{gi} = \delta\theta - \Delta\phi \quad \text{– grazing incidence}$$

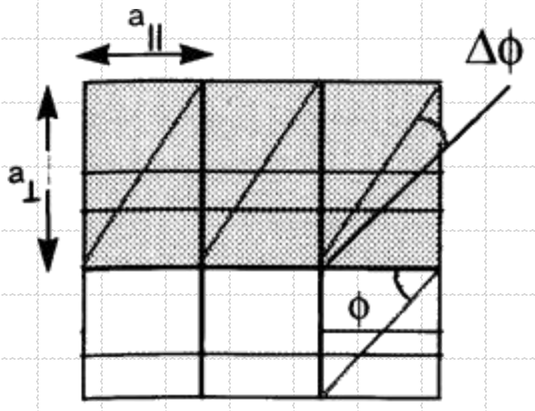
$$\Delta\theta_{ge} = \delta\theta + \Delta\phi \quad \text{– grazing exit}$$

We need to know the lattice parameter of the layer parallel and perpendicular to the substrate: a_L, b_L, and c_L. From these we may calculate the relaxation and the fully relaxed lattice parameter a_S.

Consider $a_L = b_L$ (tetragonal distortion).

$$\theta_L = \theta_S + \delta\theta$$

$$\phi_L = \phi_S + \Delta\phi$$



ϕ – angle between reflecting plane and the surface

Relaxation

- Using interplanar spacing equation and Bragg law:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a_L^2} + \frac{l^2}{c_L^2}$$

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

we obtain cell constants for the layer (001 oriented):

$$c_L = \frac{l\lambda}{2\sin\theta_L \cos\phi_L}$$

$$a_L = \frac{l\lambda}{2\sin\theta_L \sin\phi_L}\sqrt{\frac{h^2 + k^2}{l^2}}$$

Relaxation

- The relaxation is defined as:

$$R = \frac{a_{L_x} - a_{S_x}}{a_{L_x}^R - a_{S_x}} \times 100$$

$a_{L_x}^R$ – the fully relaxed in-plane lattice parameter of the epilayer.

For cubic lattice: $\varepsilon_{zz} = -\frac{\nu}{1-\nu}\left(\varepsilon_{xx} + \varepsilon_{yy}\right)$ and $\varepsilon_{xx} = \varepsilon_{yy} = \frac{a_L^R - a_{L_x}}{a_L^R}$ $\varepsilon_{zz} = \frac{a_L^R - a_{L_z}}{a_L^R}$

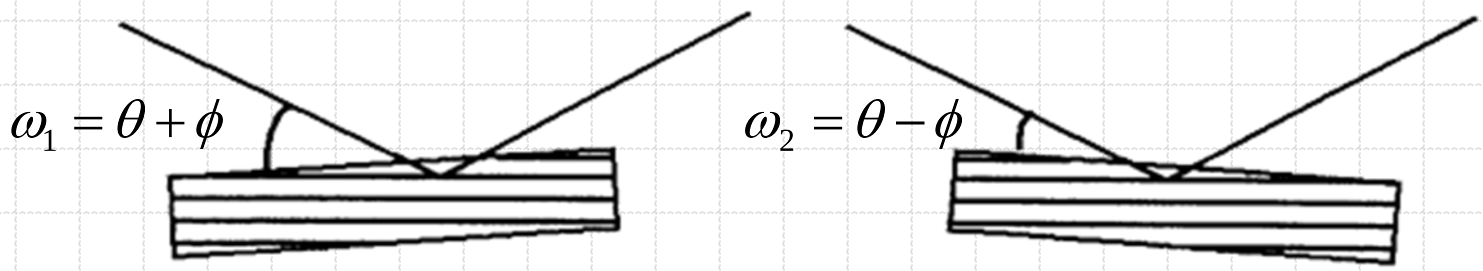
Then:

$$a_{L_z} = a_{L_x}^R \left[1 - \frac{2\left(a_{L_x}^R - a_{L_x}\right)}{a_{L_x}^R} \frac{\nu}{1-\nu}\right] \qquad a_{L_x}^R = \frac{a_{L_z} - 2a_{L_x}\left(\frac{\nu}{1-\nu}\right)}{1-2\left(\frac{\nu}{1-\nu}\right)}$$

$a_{L_x}^R$ is the value that is used in Vegard's law to find the composition of the epilayer.

Substrate misorientation

- Substrates are often specified at some angle from (001) or (111).
- This may need to be verified.



Rotation of the surface plane through 180° between measurements

$$\phi = \frac{\omega_1 - \omega_2}{2}$$

If we do measurements at 0° and 180° to get ϕ_0 and at 90° and 270° to get ϕ_{90}, then maximum φ_{max} is given by:

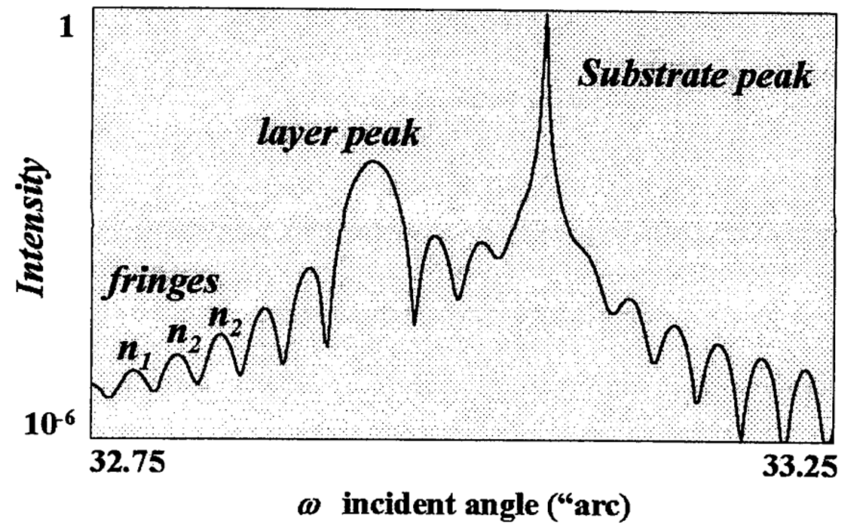
$$\phi_{\max} = \arctan \sqrt{\tan^2 \phi_0 + \tan^2 \phi_{90}}$$

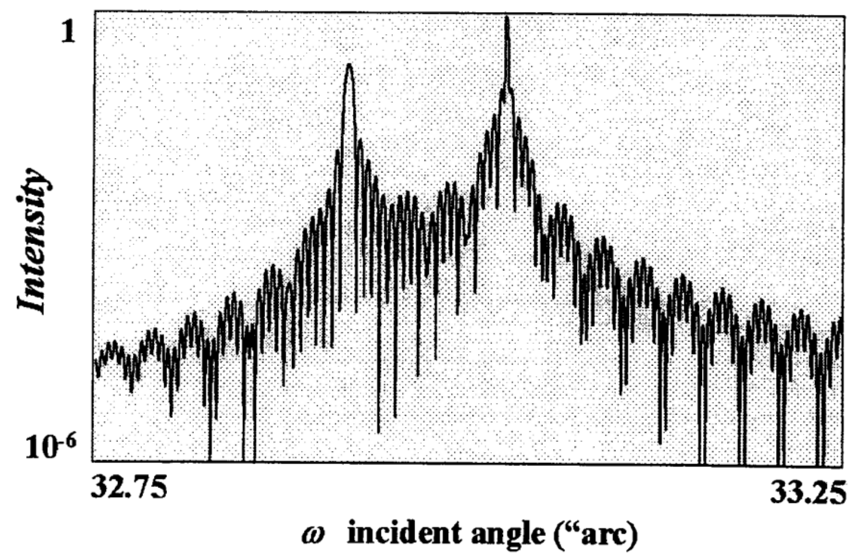
$$\varphi_{\max} = \arctan \left(\frac{\tan \phi_{90}}{\tan \phi_0} \right)$$

Determination of Thickness

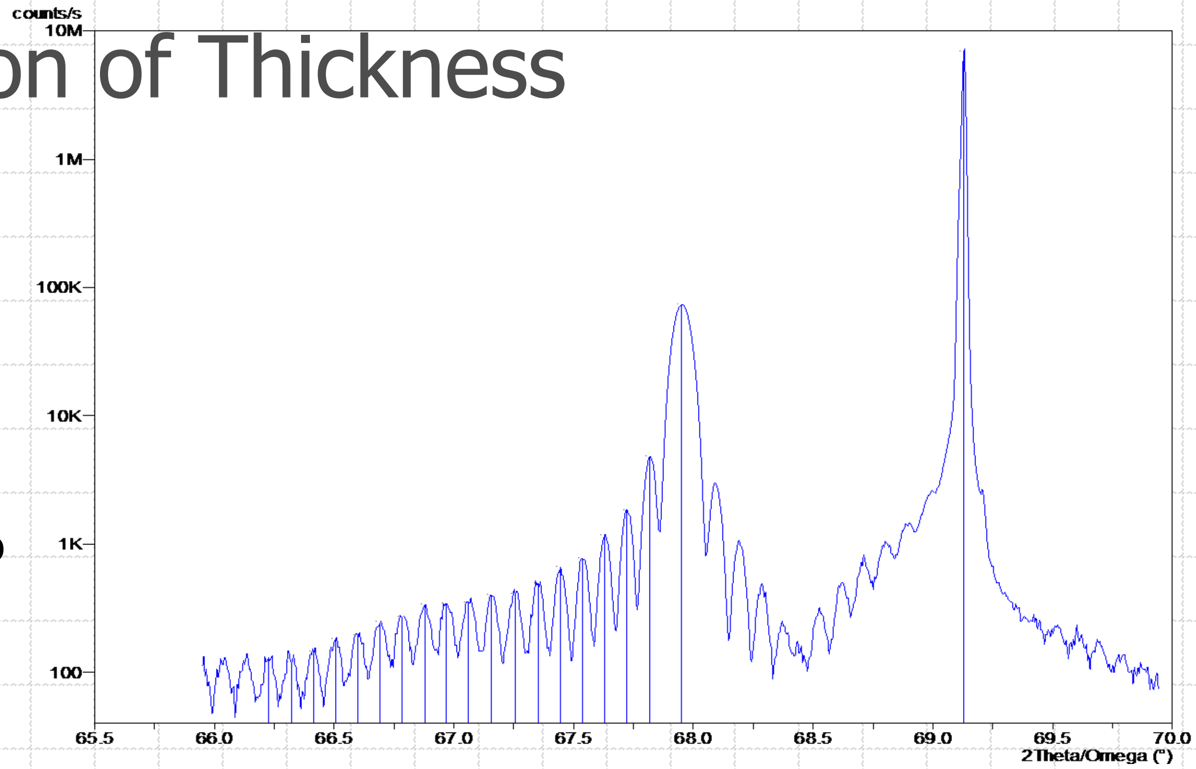
- Interference fringes observed in the scattering pattern, due to different optical paths of the x-rays, are related to the thickness of the layers.

$$t = \frac{(n_1 - n_2)\lambda}{2(\sin\omega_1 - \sin\omega_2)} \sim \frac{(n_1 - n_2)\lambda}{2\Delta\omega\cos\omega_1}$$





Determination of Thickness



- Interference fringes observed in the scattering pattern, due to different optical paths of the x-rays, are related to the thickness of the layers.

$$t = \frac{(n_1 - n_2)\lambda}{2(\sin\omega_1 - \sin\omega_2)}$$

Substrate Layer Separation

S-peak:		L-peak:		Separation:	
Omega(°)	34.5649	Omega(°)	33.9748	Omega(°)	0.59017
2Theta(°)	69.1298	2Theta(°)	67.9495	2Theta(°)	1.18034

Layer Thickness

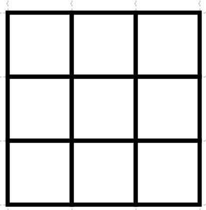
Mean fringe period (°): 0.09368

Mean thickness (um): 0.113 ± 0.003

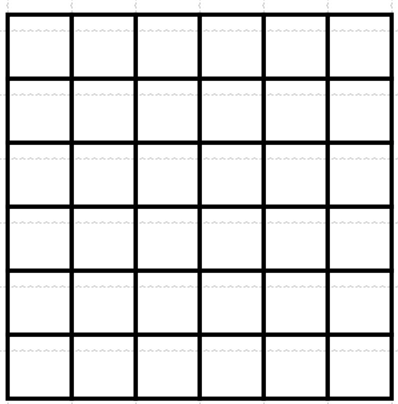
2Theta/Omega (°)	Fringe Period (°)	Thickness (um)
66.22698 - 66.32140	0.09442	0.111637
66.32140 - 66.41430	0.09290	0.113528
66.41430 - 66.50568	0.09138	0.115481
66.50568 - 66.59858	0.09290	0.113648
66.59858 - 66.69300	0.09442	0.111878
66.69300 - 66.78327	0.09027	0.117079

Area Homogeneity

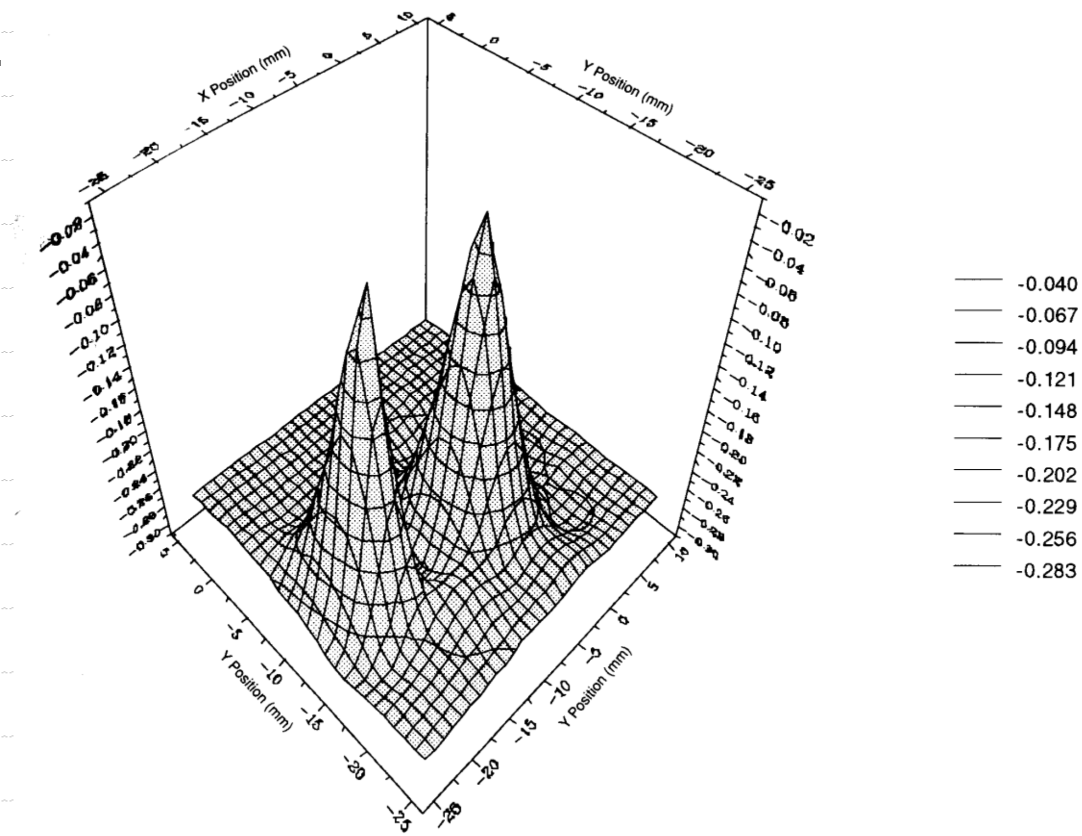
- Whatever the crystal growers claim, epitaxial layers are not uniform across their area.
  - 1% consistency is good.



3×3 grid

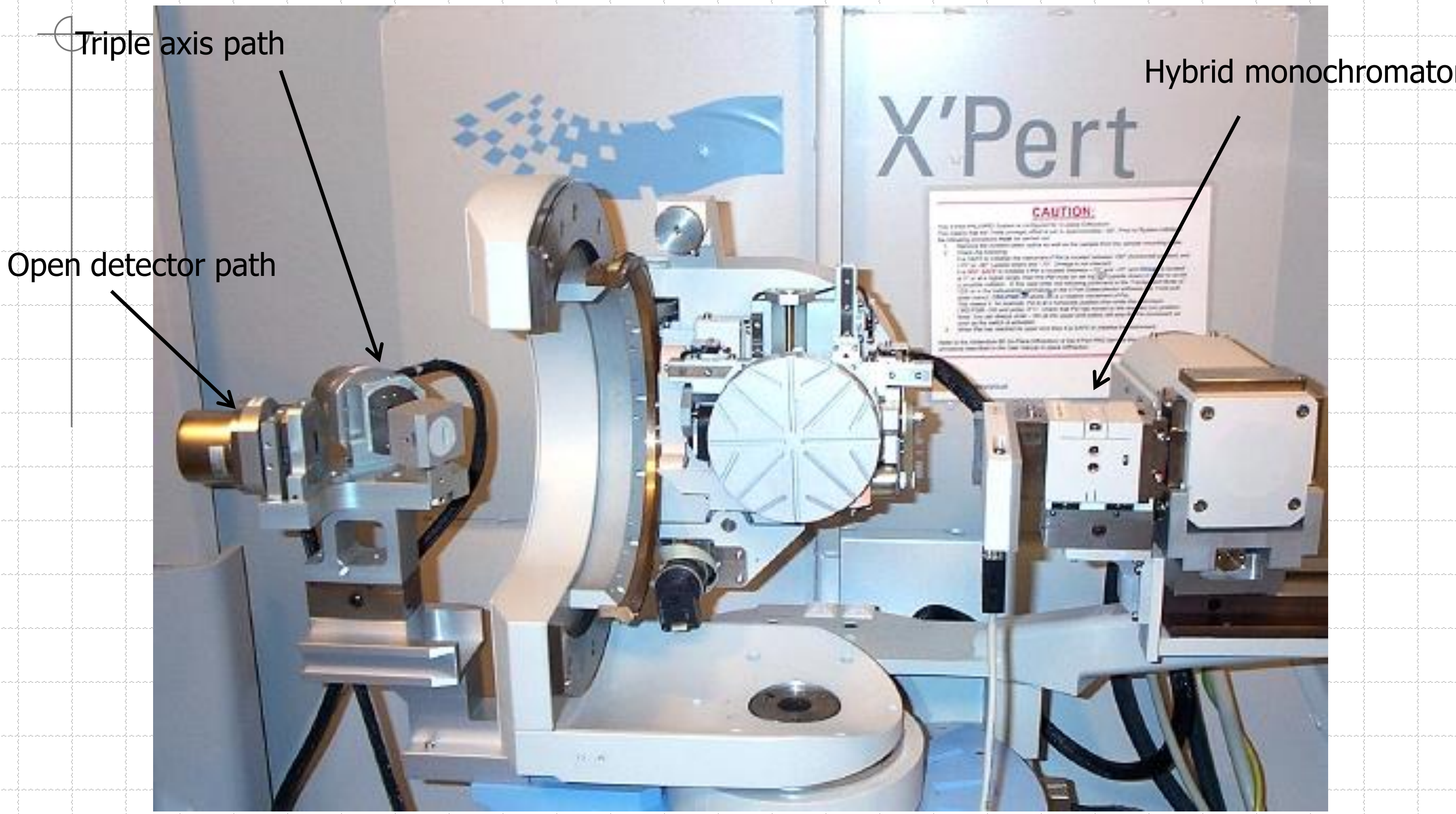


9×9 grid

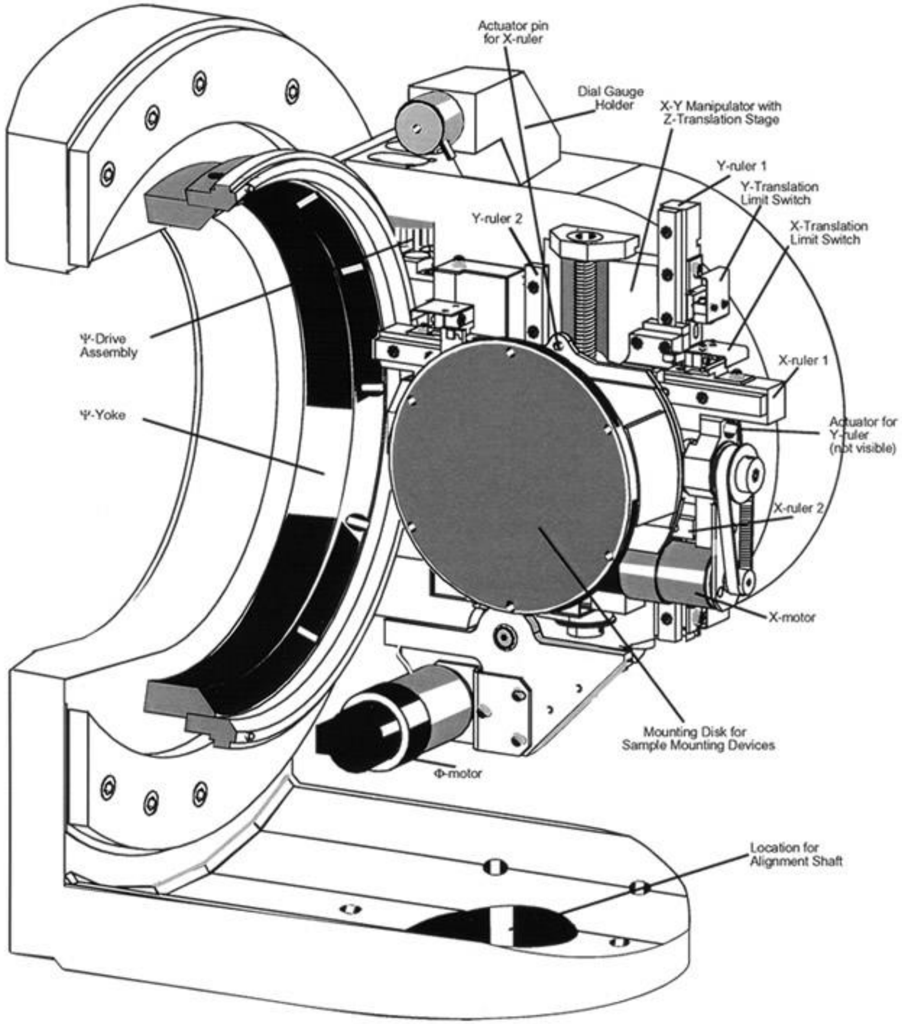


Surface mesh plot showing the variation of In content in an InAlAs layer on GaAs

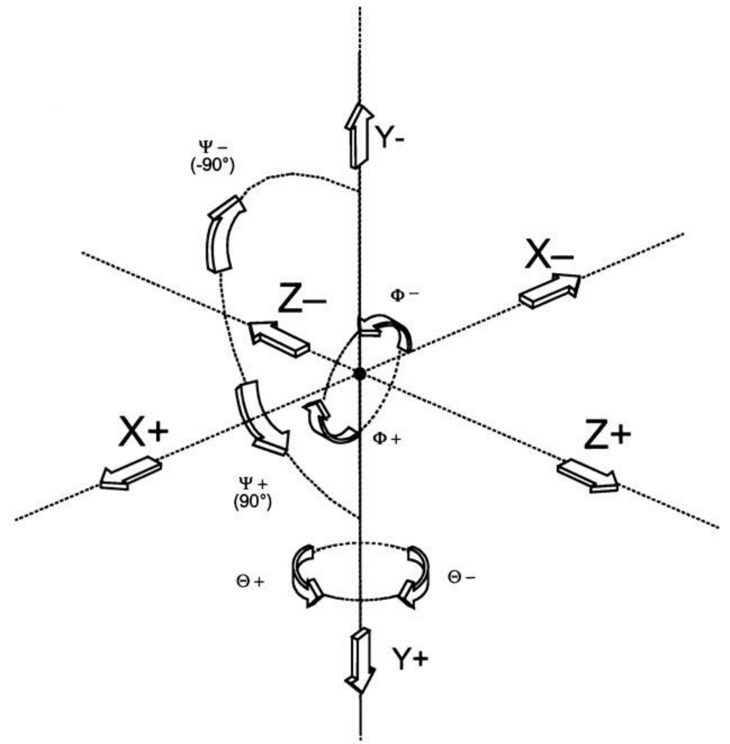
Materials Research Diffractometer



Materials Research Diffractometer

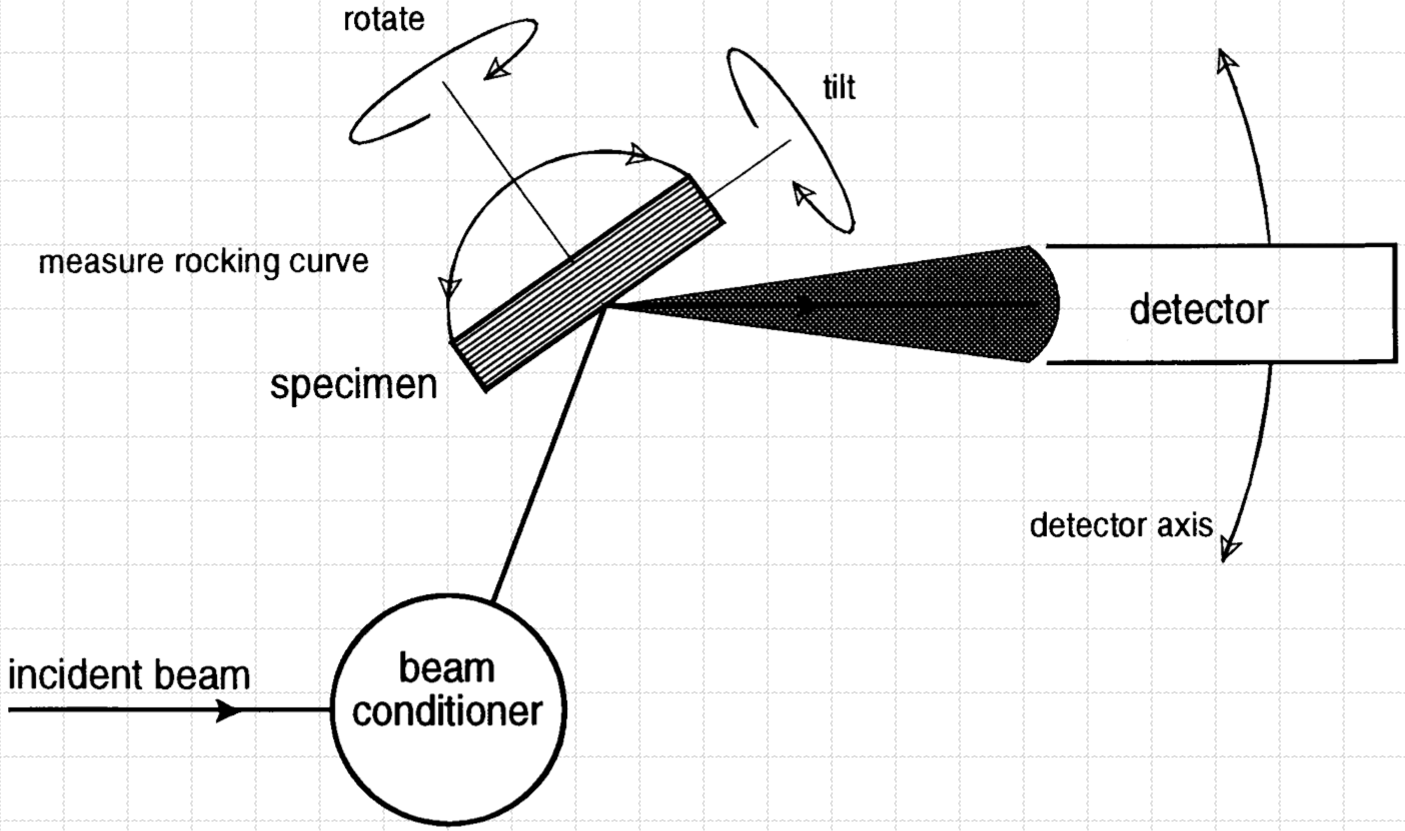


Six Motorized Movements of MRD Cradle



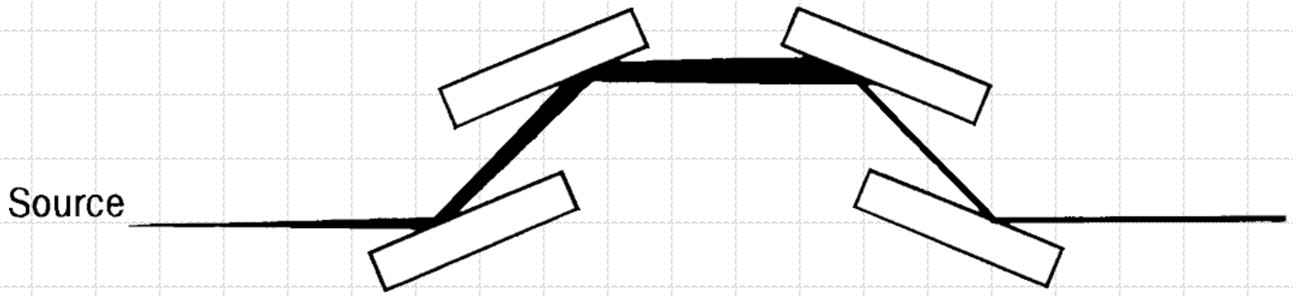
High-Resolution Diffractometry

- Schematic of high resolution double-axis instrument



High-Resolution Diffractometry

- Bartels



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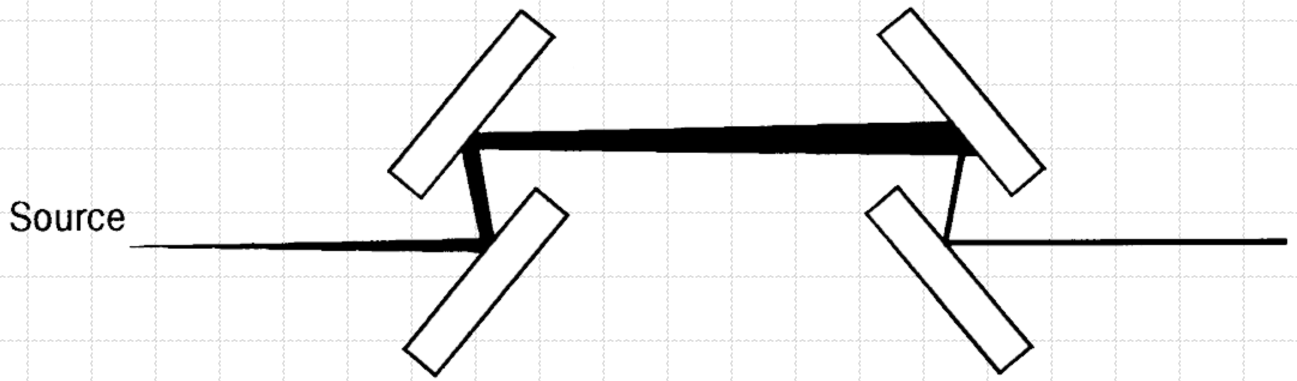
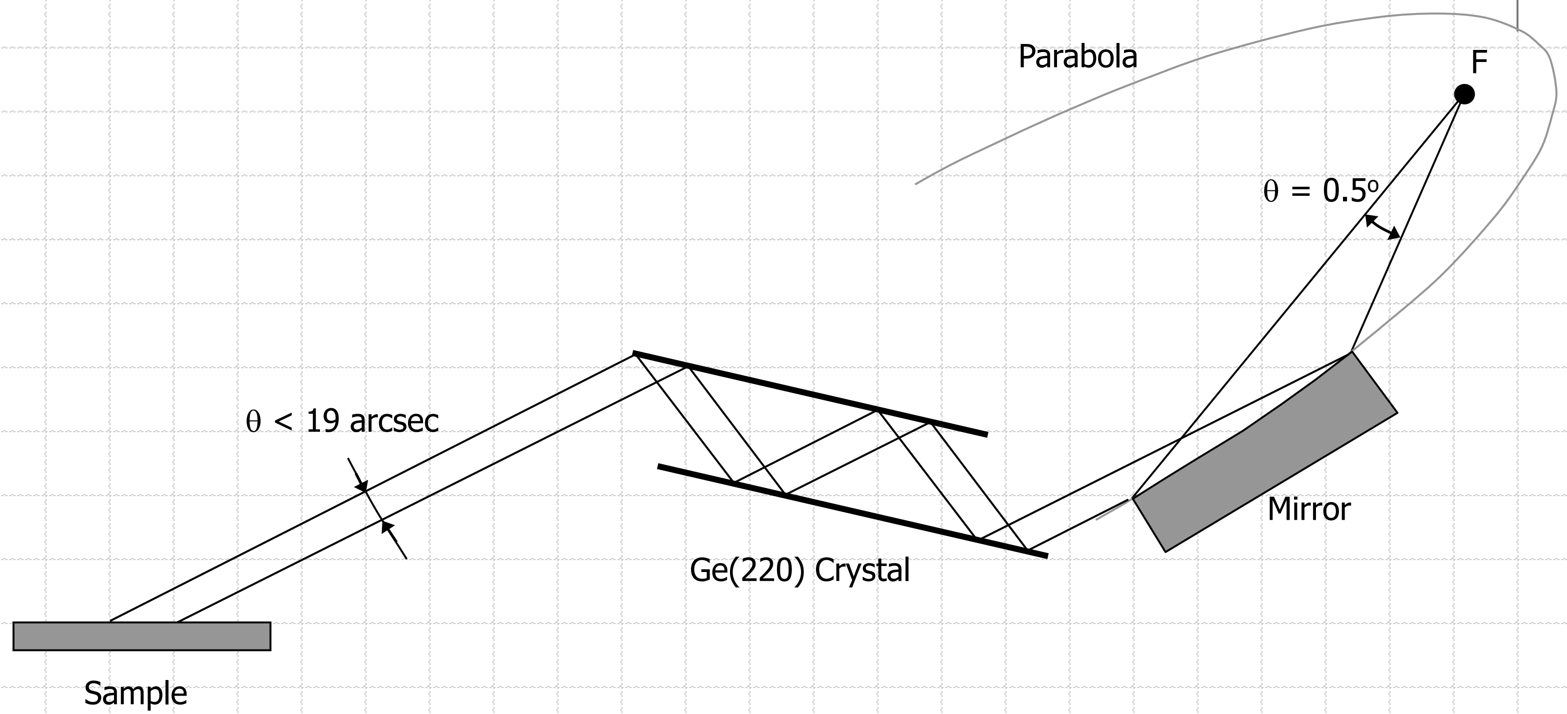


440

High Resolution Geometry

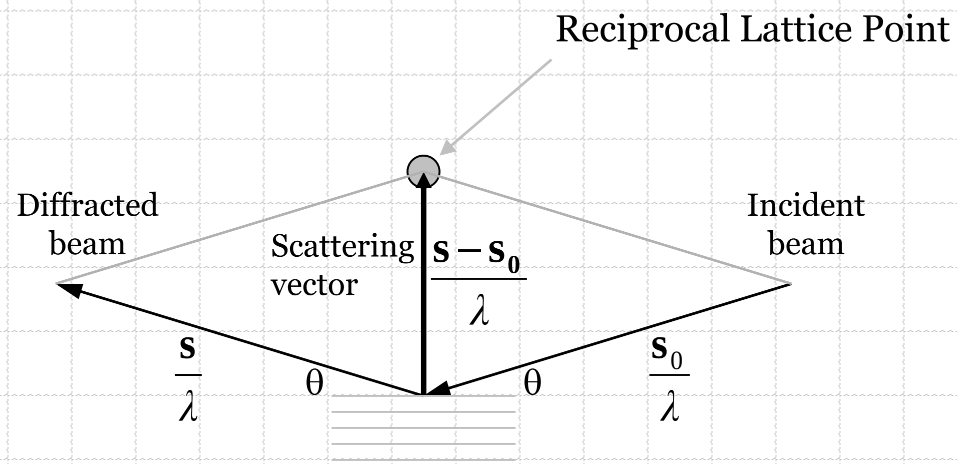
- Incident Beam:
  - X-ray Hybrid Monochromator

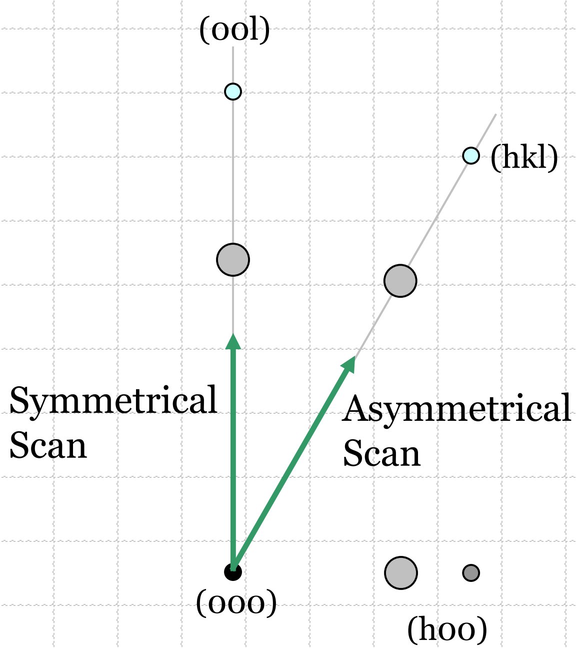


Scan Directions

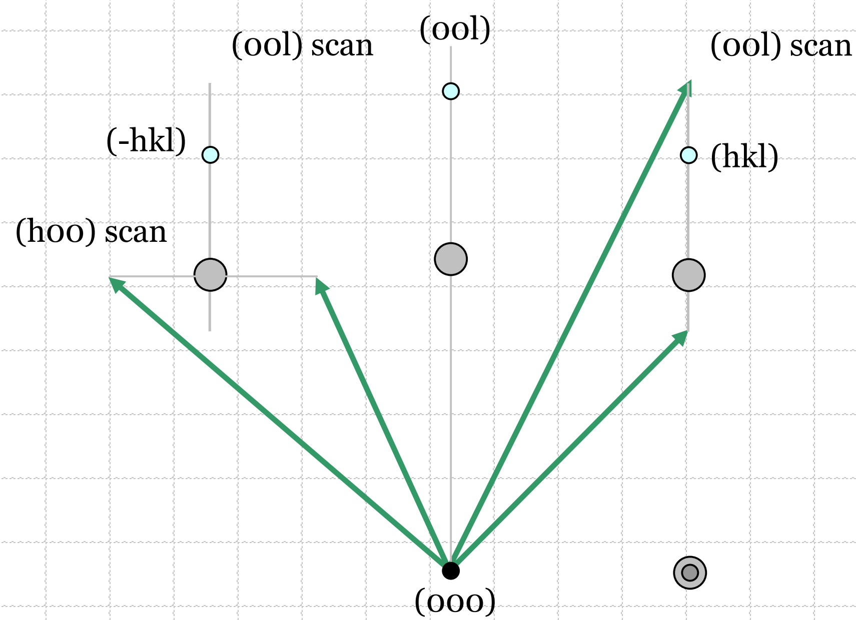
$$\left|\frac{\mathbf{s}-\mathbf{s_0}}{\lambda}\right| = \frac{2\sin\theta}{\lambda} = \left|\mathbf{d}^*_{hkl}\right| = \frac{1}{d_{hkl}}$$

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



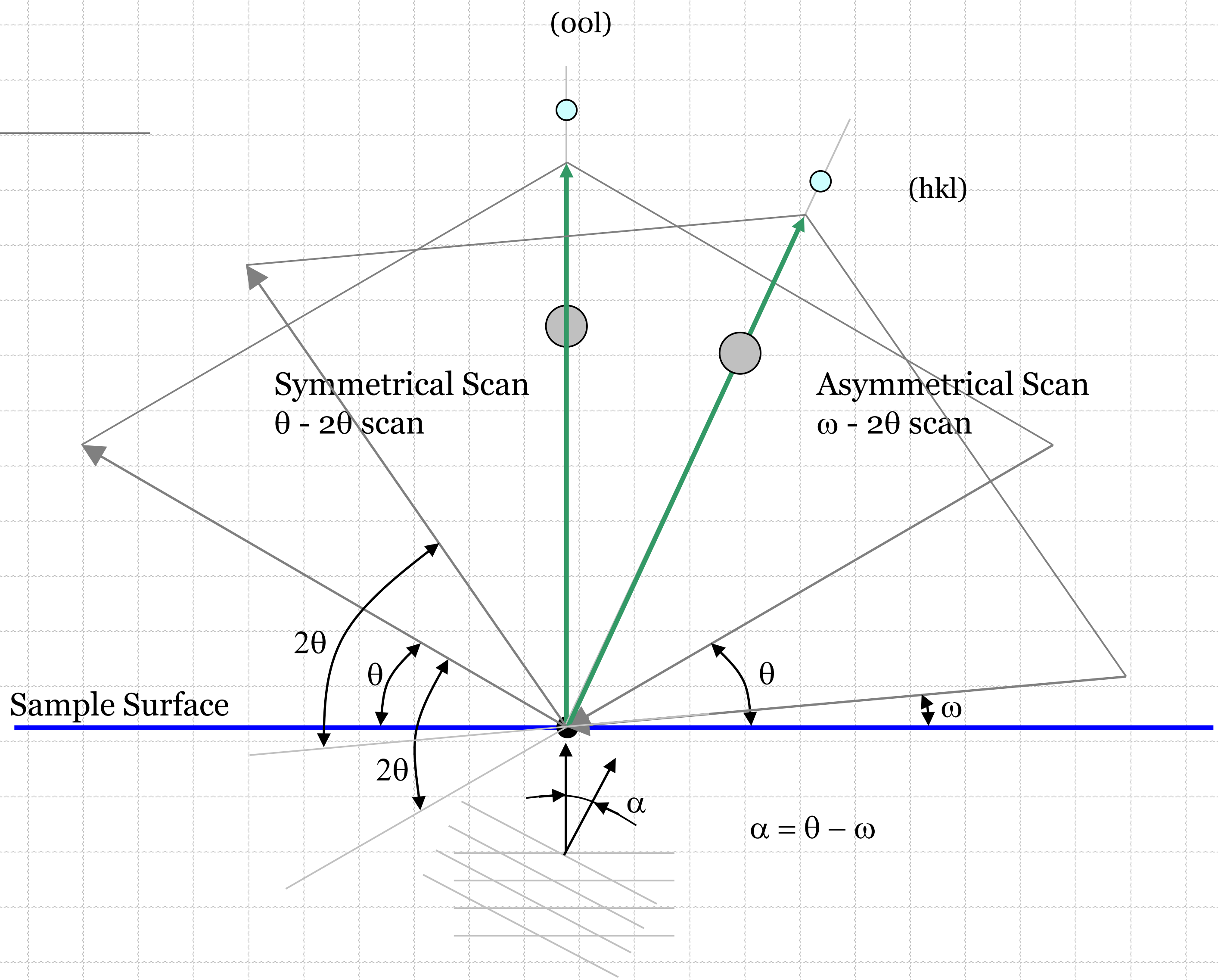


Relaxed Layer

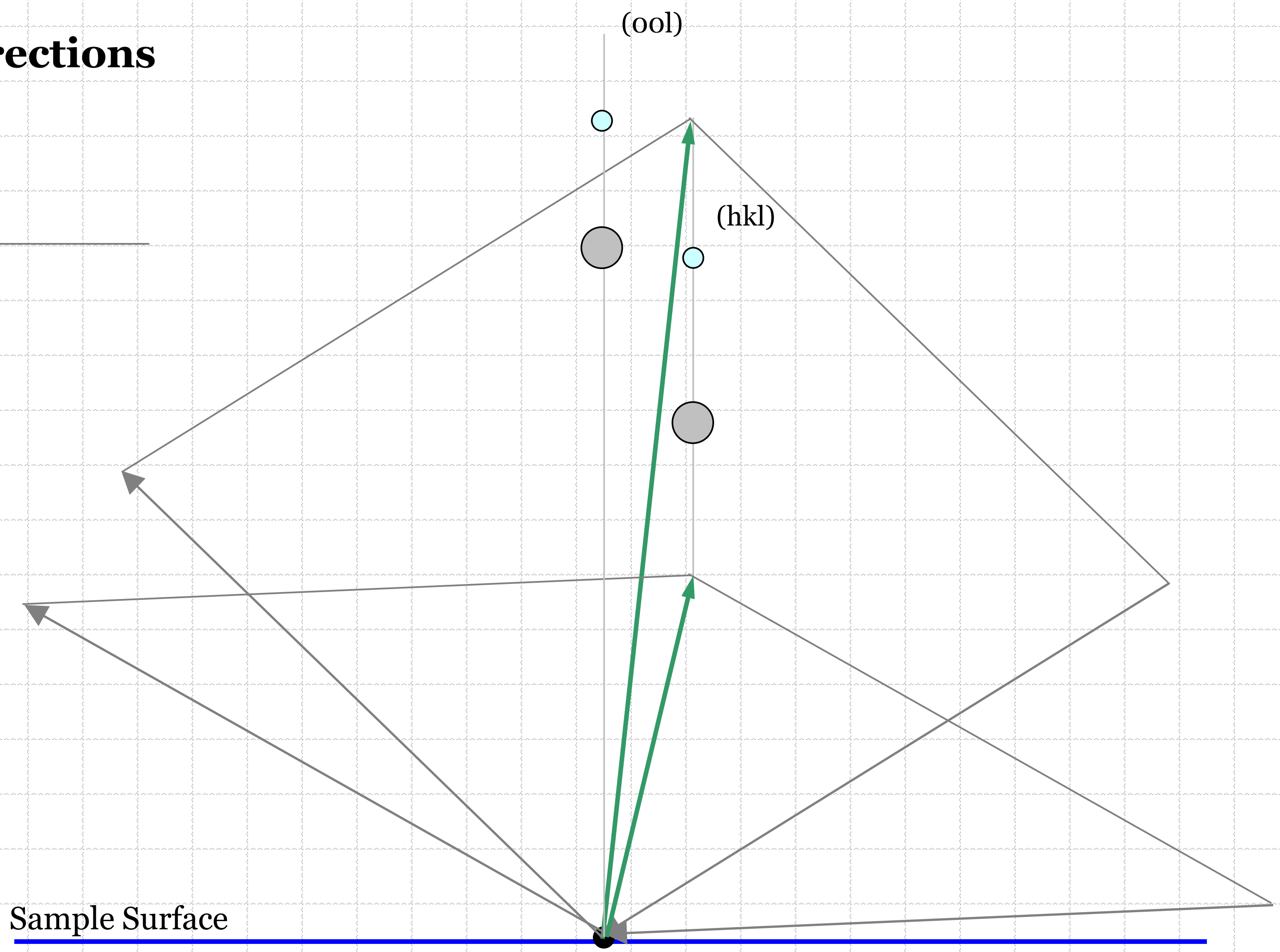


Strained Layer

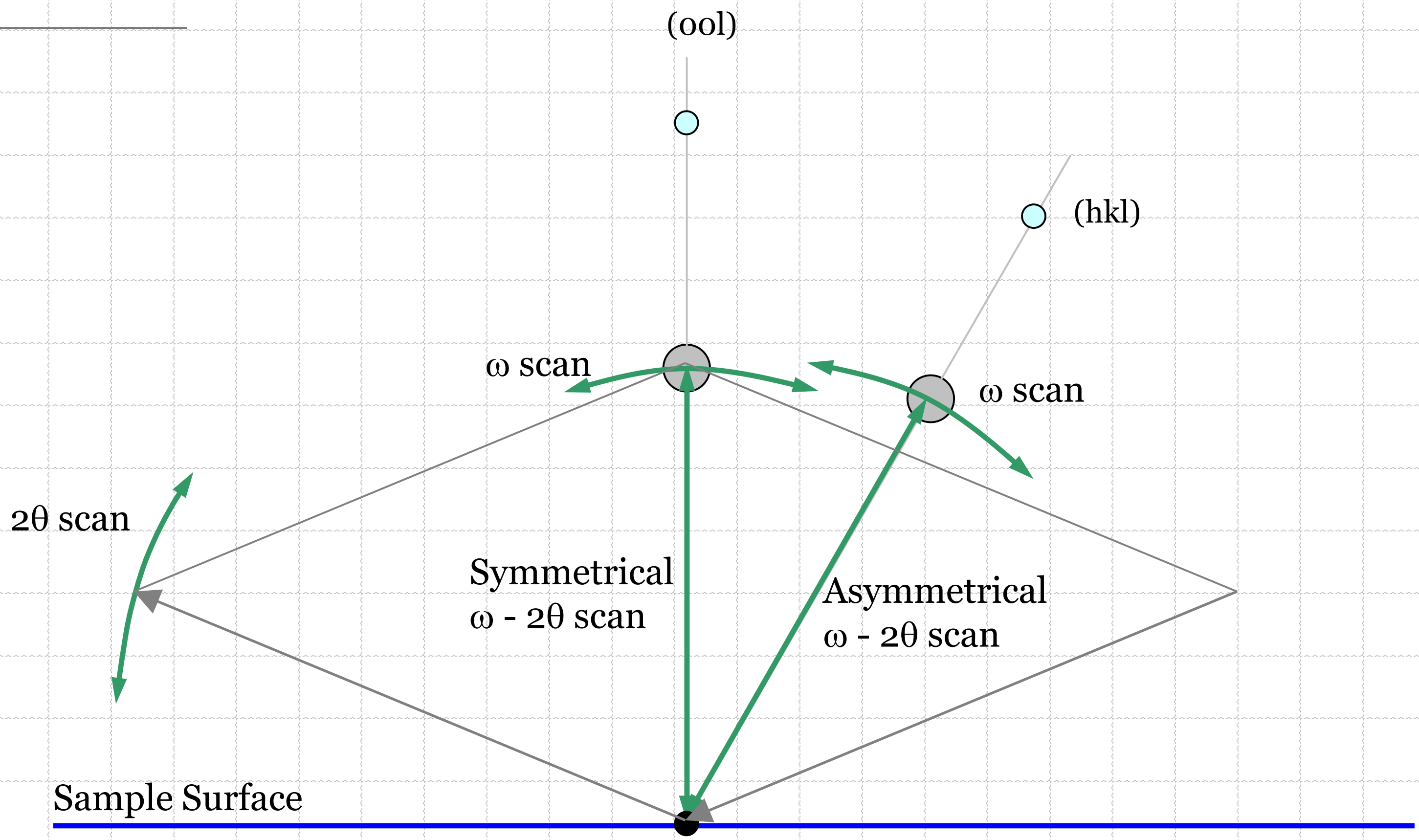
Scan Directions



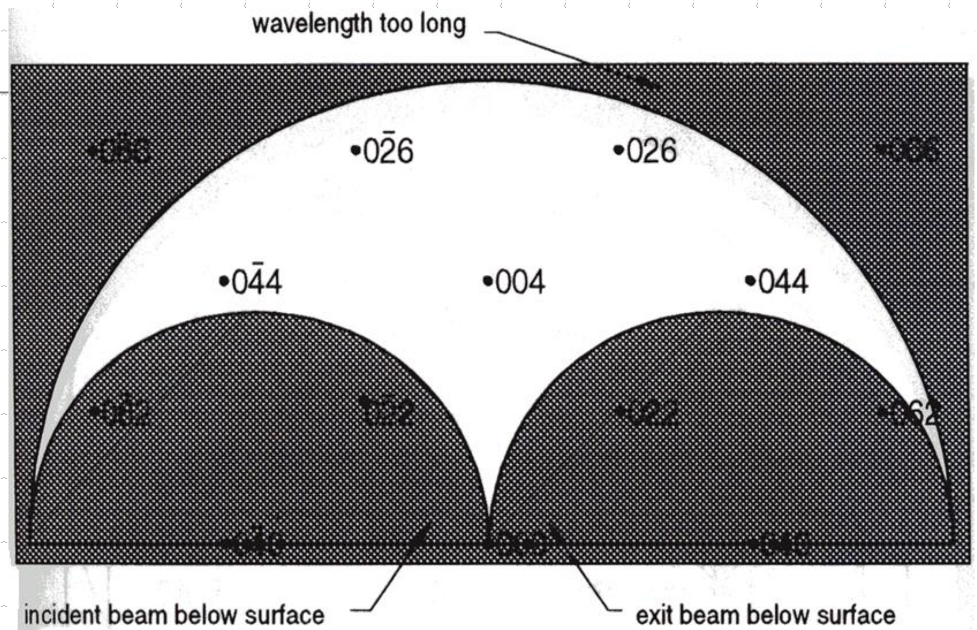
Scan Directions



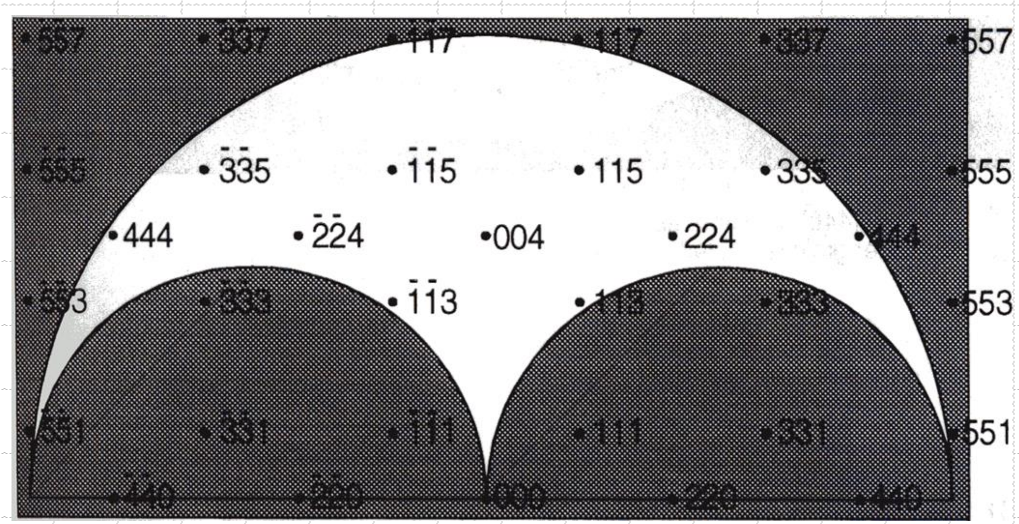
Scan directions



Reciprocal Space for Si(001)

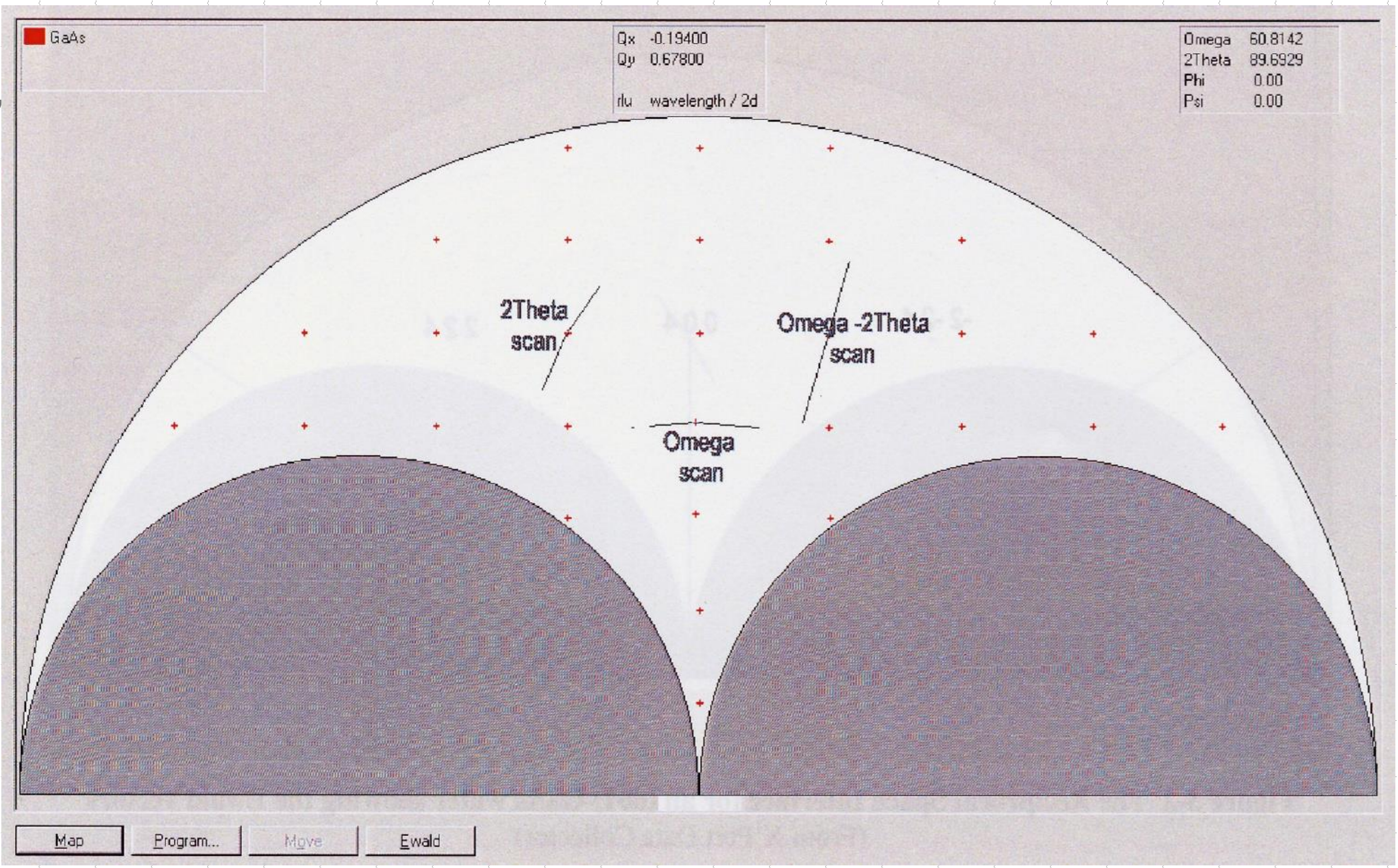


Along Si[100]



Along Si[110]

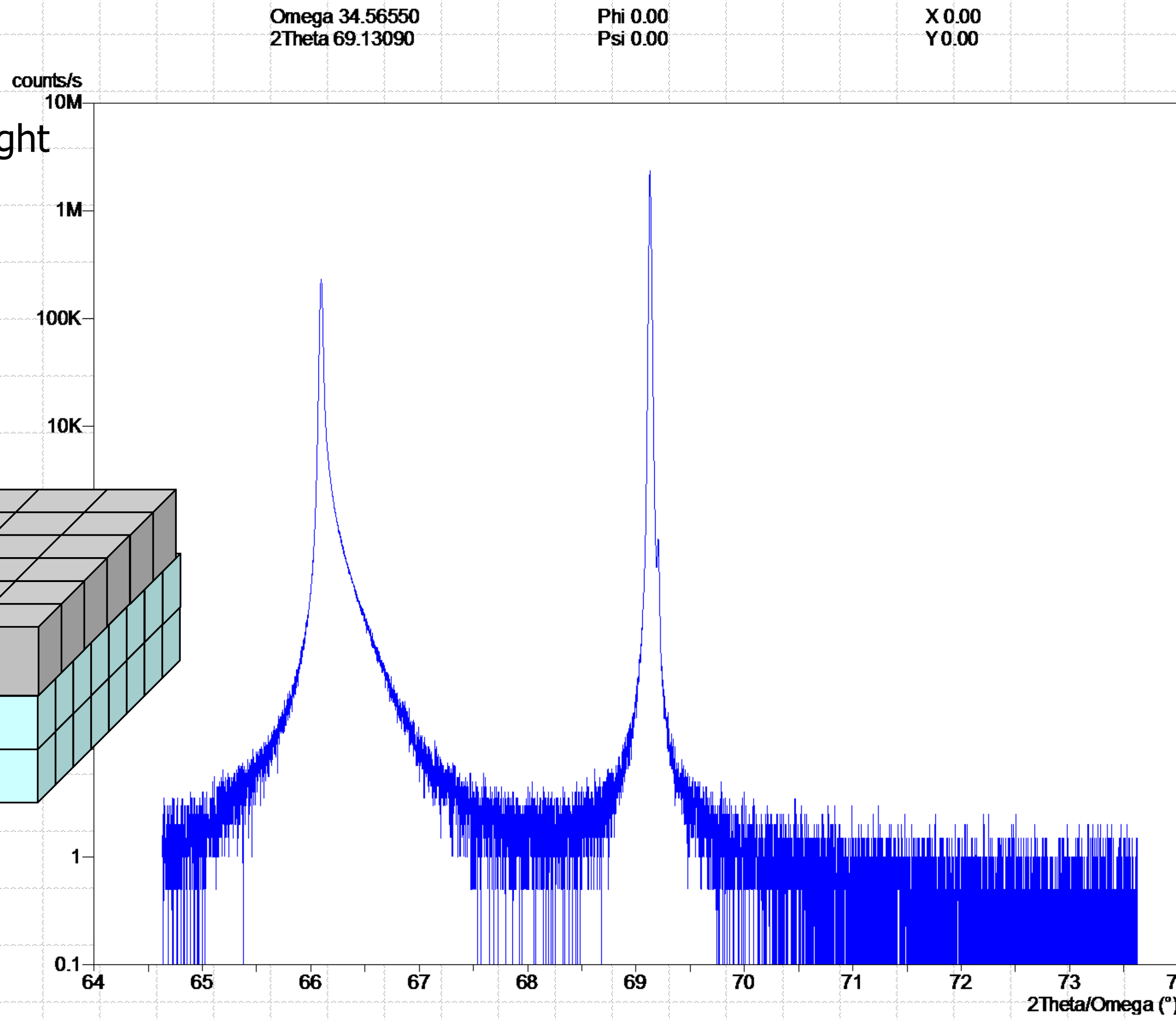
Reciprocal Space

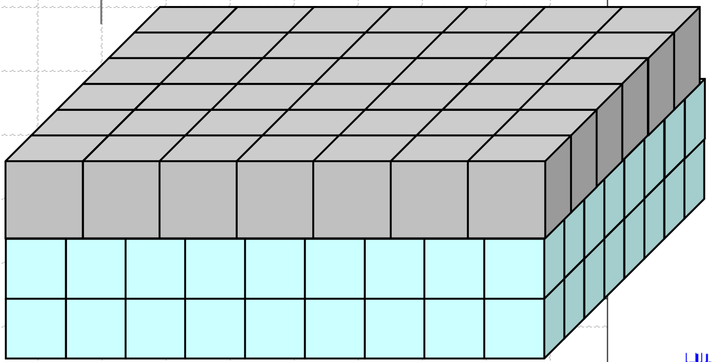


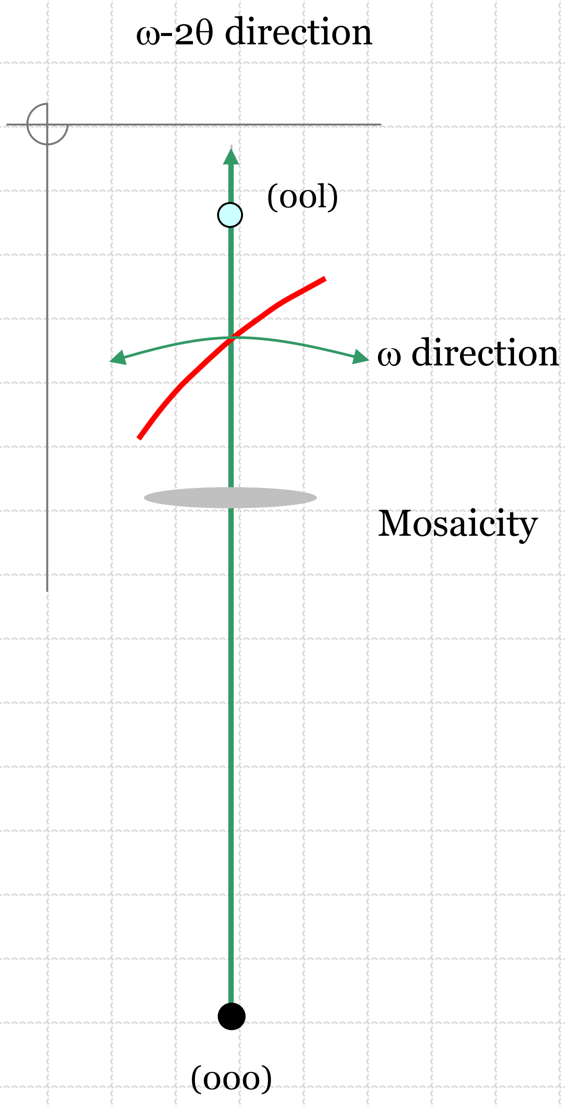
ω-scan is in the direction of an arc centered on the origin
2θ-scan is an arc along Ewald sphere circumference
ω-2θ scan is always strait line pointing away from the origin of the reciprocal space

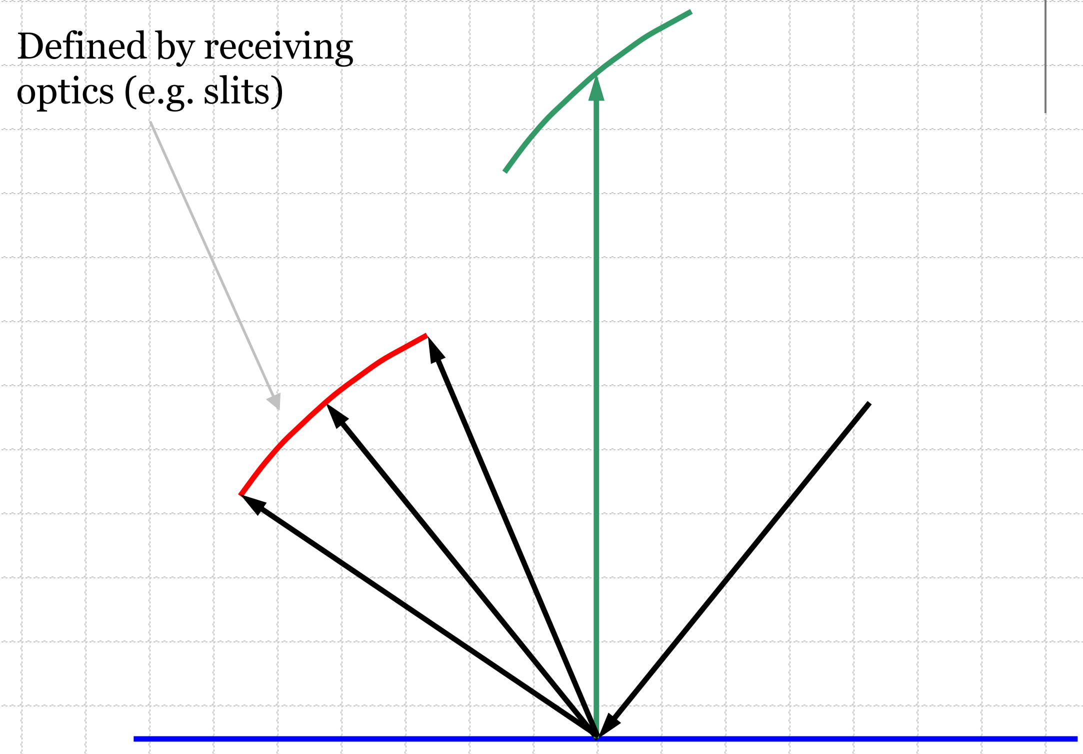
Relaxed SiGe on Si(001)

- Shape of the RLP might provide much more information

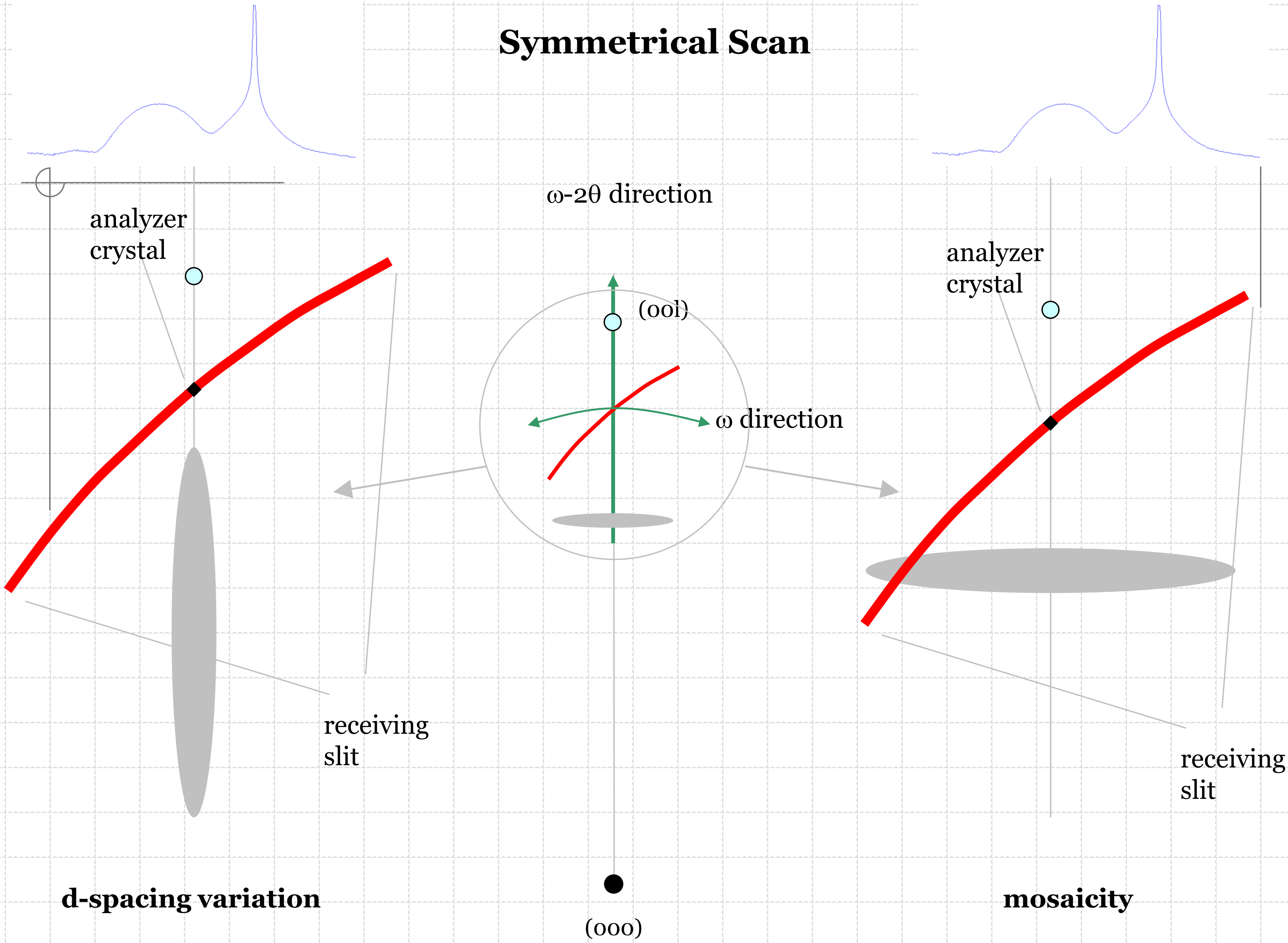


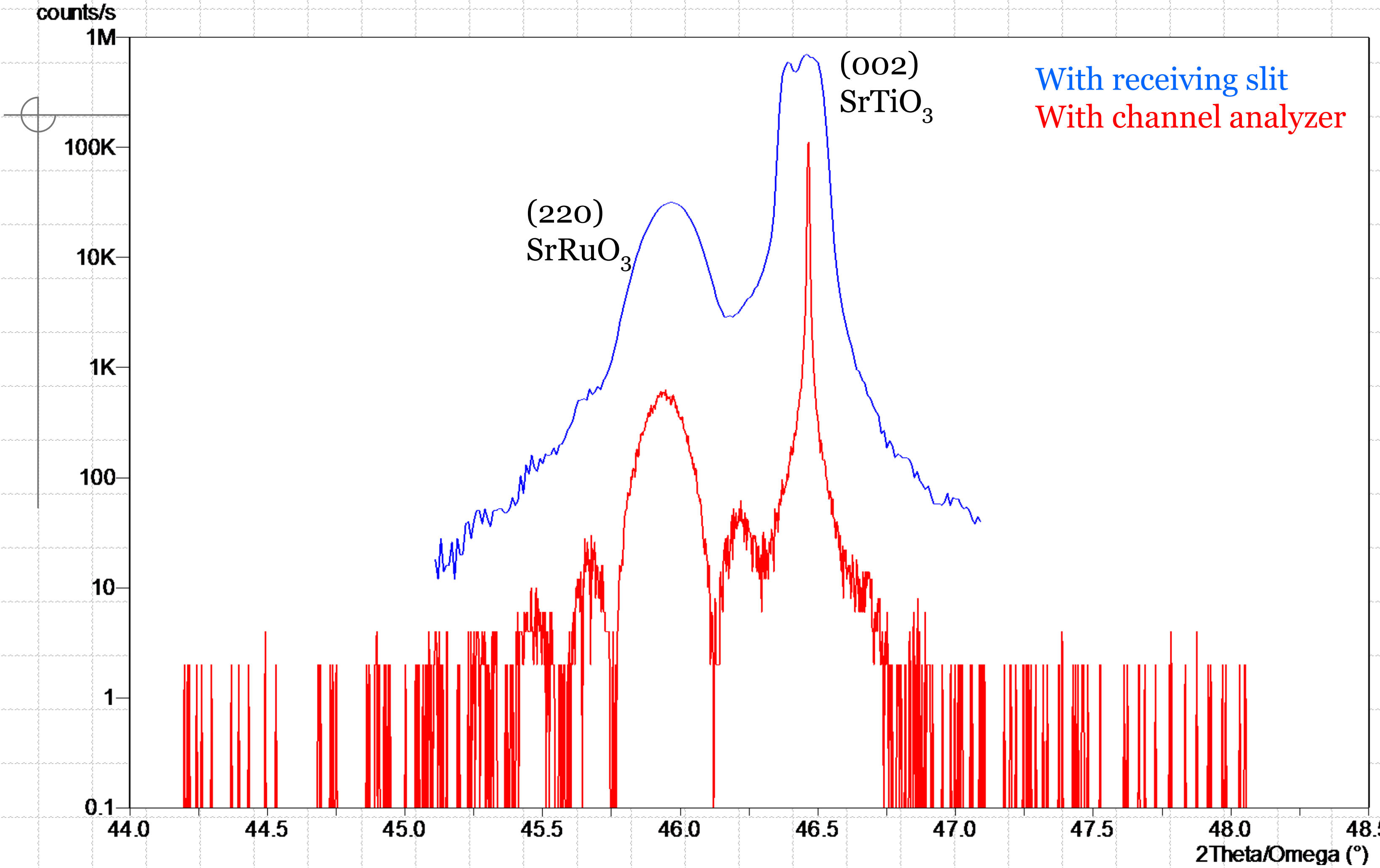



ω-2θ direction
(ool)
ω direction
Mosaicity
(ooo)

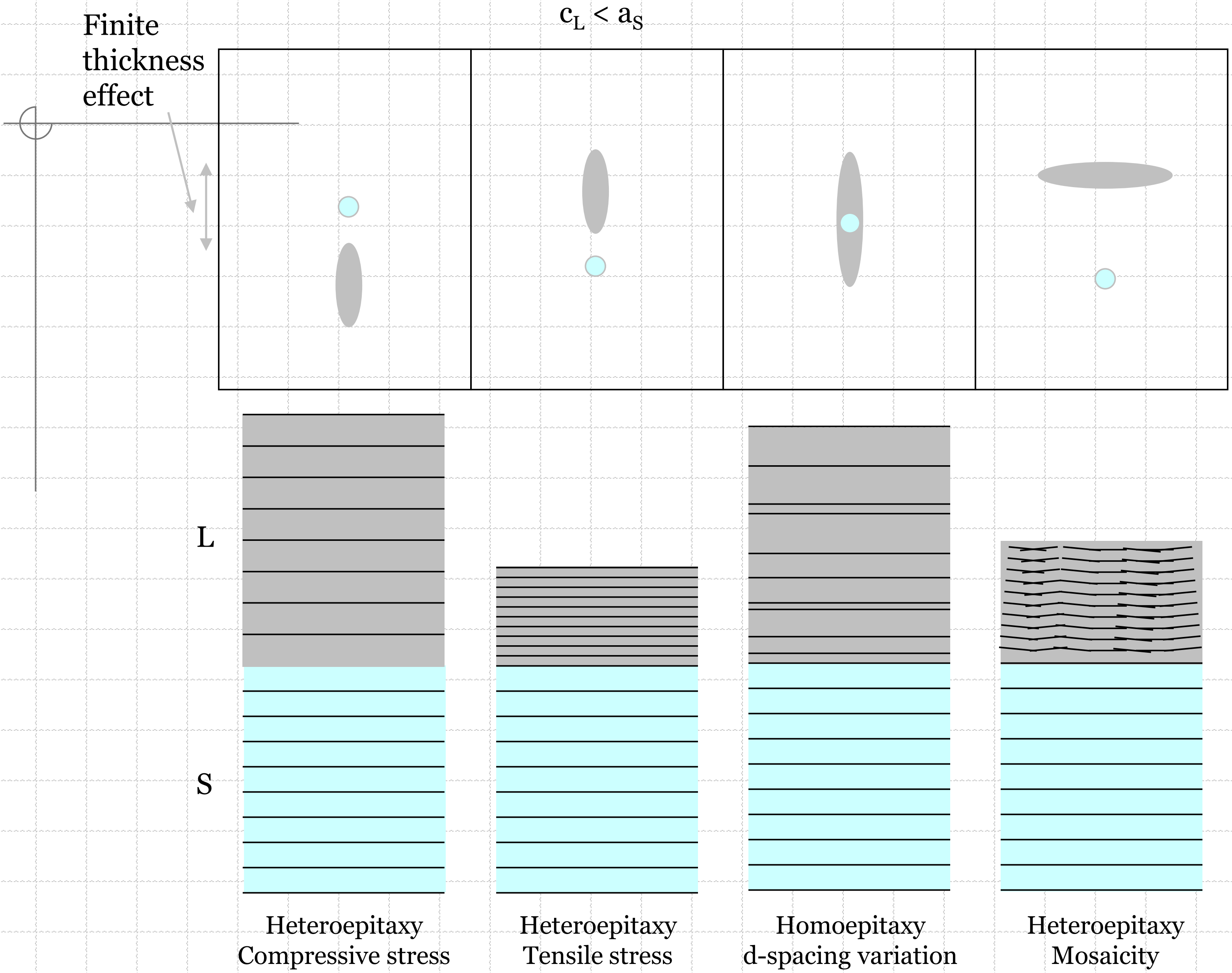

Defined by receiving
optics (e.g. slits)

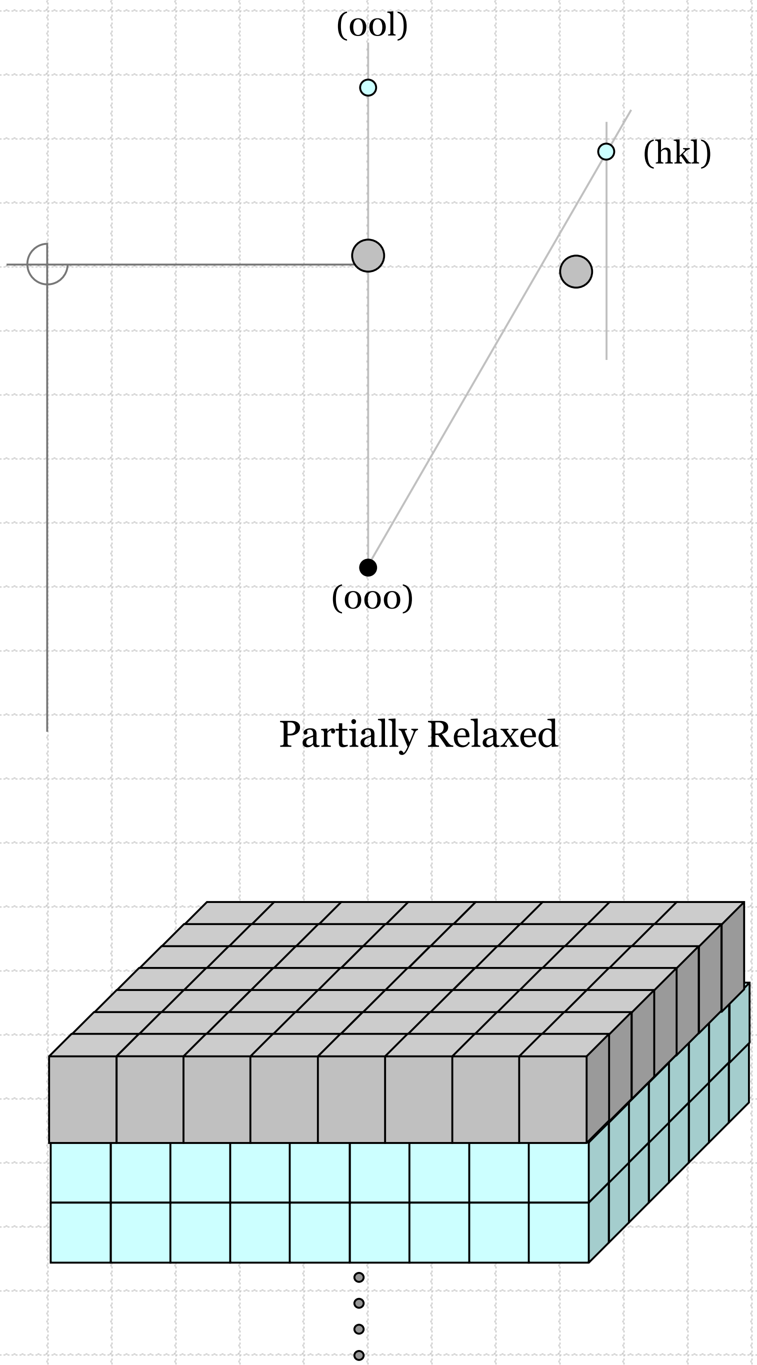
Symmetrical Scan

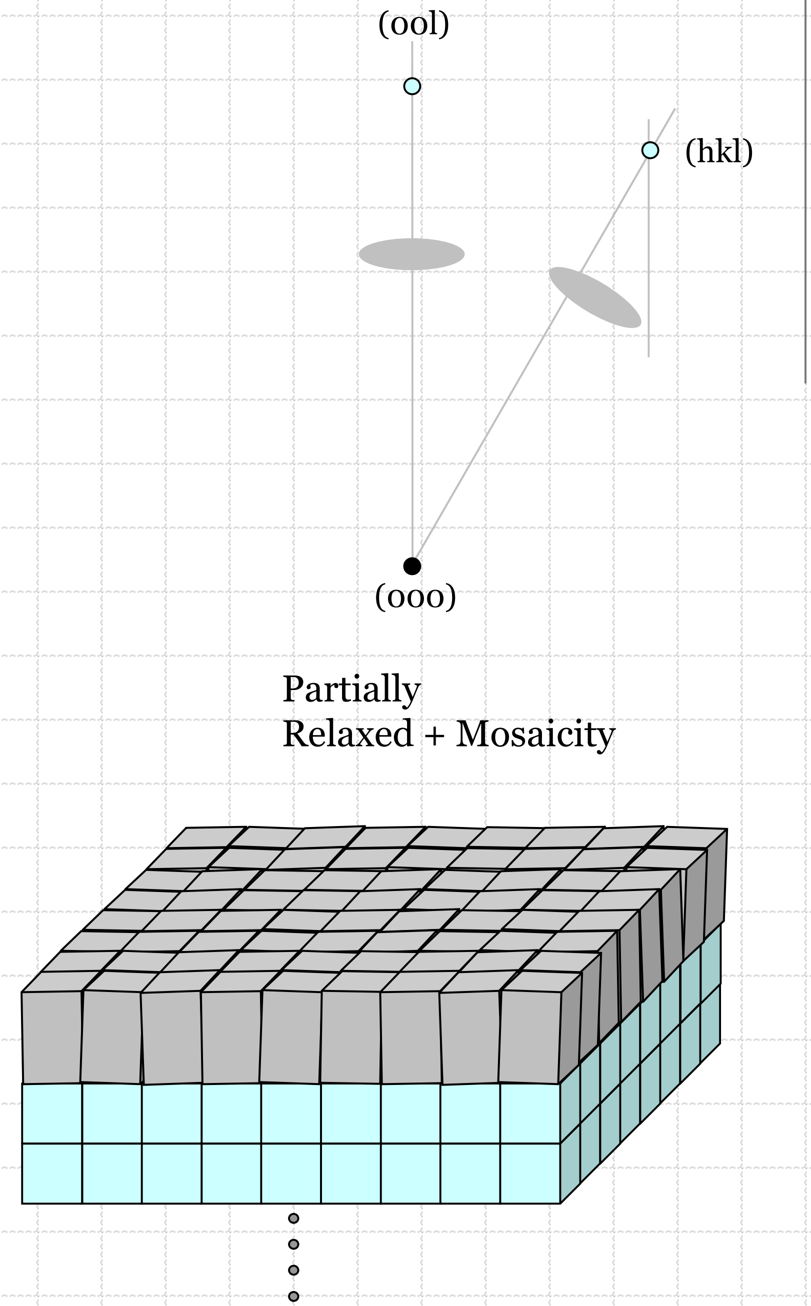



counts/s
1M
100K
10K
1K
100
10
1
0.1
44.0
44.5
45.0
45.5
46.0
46.5
47.0
47.5
48.0
48.5
2Theta/Omega (°)
(220)
SrRuO3
(002)
SrTiO3
With receiving slit
With channel analyzer

Real RLP shapes

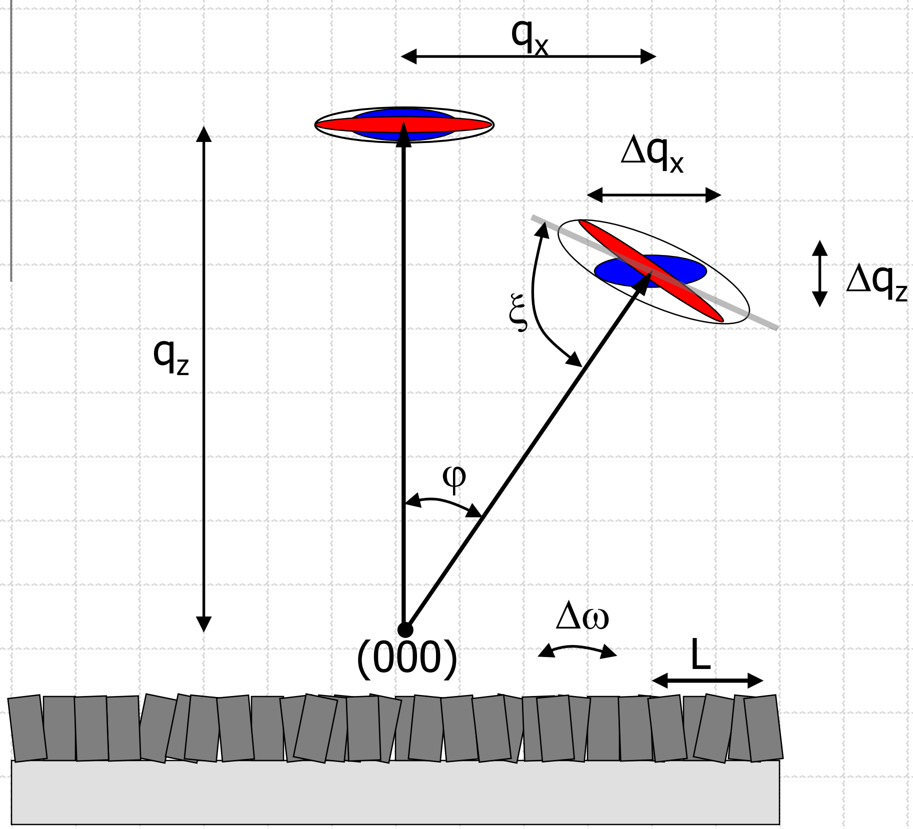


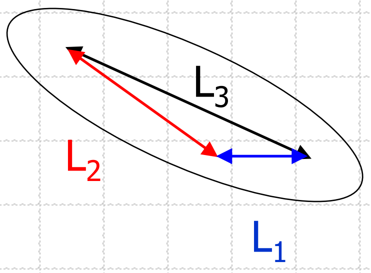

(ool)
(hkl)
(ooo)
Partially Relaxed


(ool)
(hkl)
(ooo)
Partially
Relaxed + Mosaicity

Mosaic Spread and Lateral Correlation Length

The Mosaic Spread and Lateral Correlation Length functionality derives information from the shape of a layer peak in a diffraction space map recorded using an asymmetrical reflection





$$L_3 = \sqrt{\Delta q_x^2 + \Delta q_z^2}$$

and

$$\varphi = \frac{1}{\tan\left(\frac{q_x}{q_z}\right)}$$

$$\xi = \frac{1}{\tan\left(\frac{\Delta q_x}{\Delta q_z}\right)}$$

$$\frac{L_1}{L_2} = -\frac{\cos\xi}{\cos(\varphi+\xi)}$$

$$\frac{L_3}{L_2} = -\frac{\sin\varphi}{\cos\xi}$$

Lateral correlation length $= \frac{1}{L_1}$

Microscopic tilt $= \frac{L_2}{\sqrt{q_x^2 + q_z^2}}$