Thin Film Scattering: Epitaxial Layers

6th Annual SSRL Workshop on Synchrotron X-ray Scattering Techniques in Materials and Environmental Sciences: Theory and Application

May 29 - 31, 2012

- Thin films. Epitaxial thin films
- What basic information we can obtain from x-ray diffraction
- Reciprocal space and epitaxial thin films
- Scan directions – reciprocal vs. real space scenarios
- Mismatch, strain, mosaicity, thickness
- How to choose right scans for your measurements
- Mosaicity vs. lateral correlation length
- SiGe(001) layers on Si(001) example
- Why we need channel analyzer
- What can we learn from reciprocal space maps
- $SrRuO_3$ and $La_{0.67}Sr_{0.33}MnO_3$ films example
- Summary

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.

Homoepitaxial layer
the layer and substrate are the same material and possess the same lattice parameters.

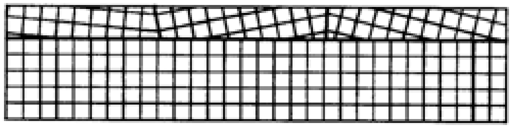
Heteroepitaxial layer
the layer material is different than the substrate and usually has different lattice parameters.

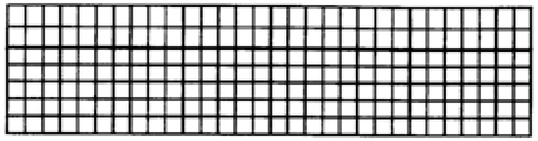
Thin films structural types

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.

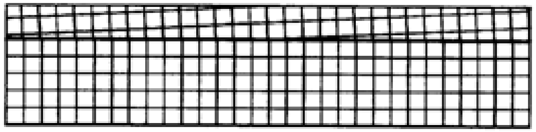
P.F. Fewster "X-ray Scattering from Semiconductors"

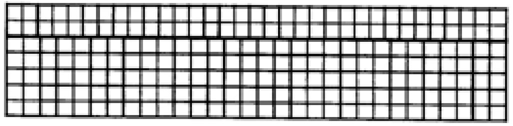
Thin films structural properties

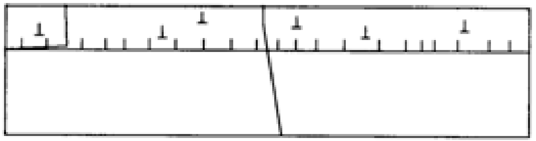

Mosaic spread

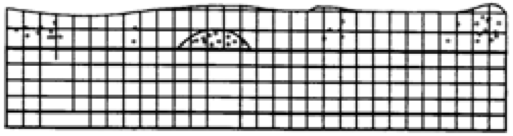

Mismatch


Curvature


Misorientation


Relaxation


Dislocation content


Inhomogeneity

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

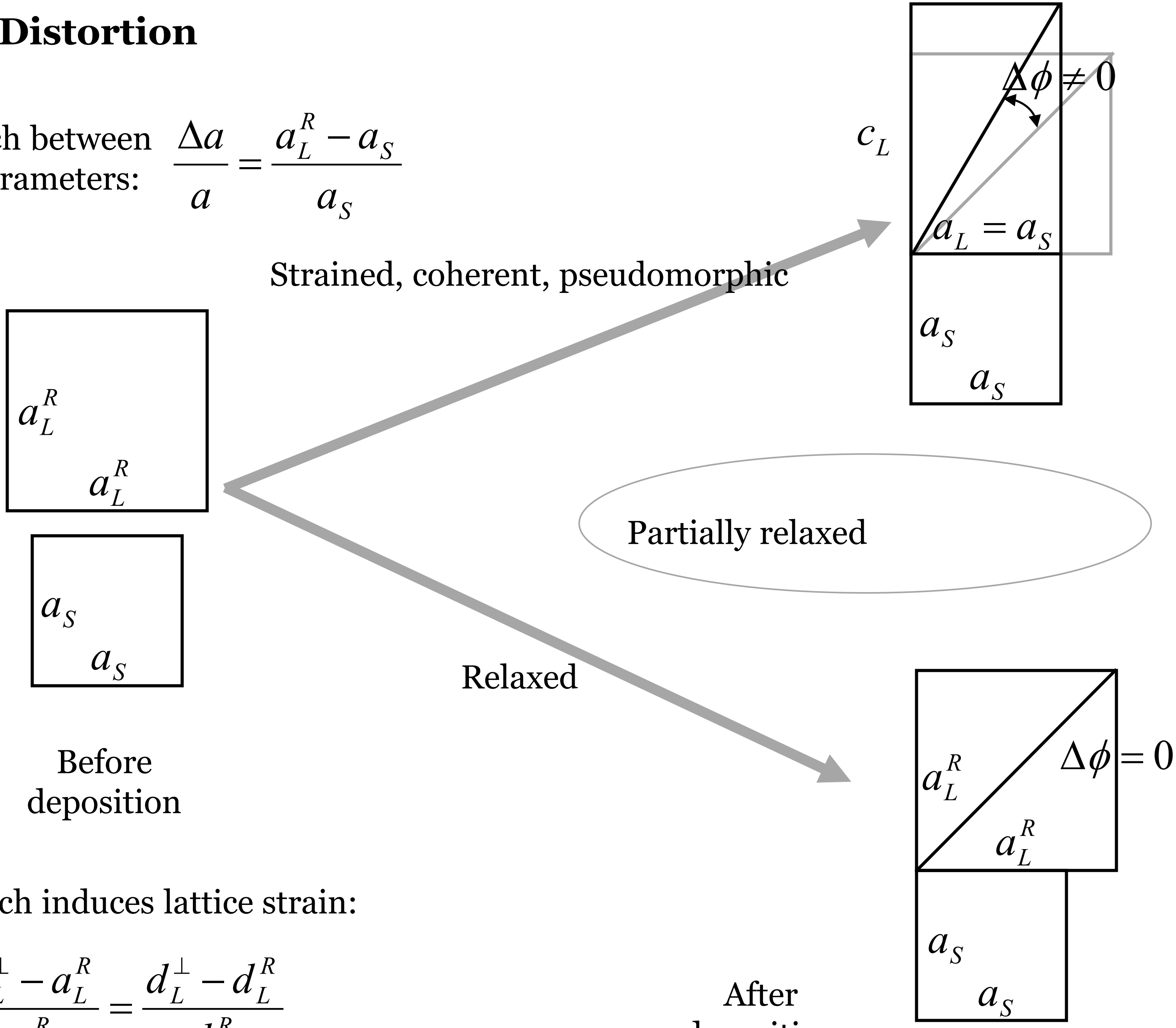
Overview of structural parameters that characterize various thin films

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

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

Tetragonal Distortion

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



Strained, coherent, pseudomorphic

Partially relaxed

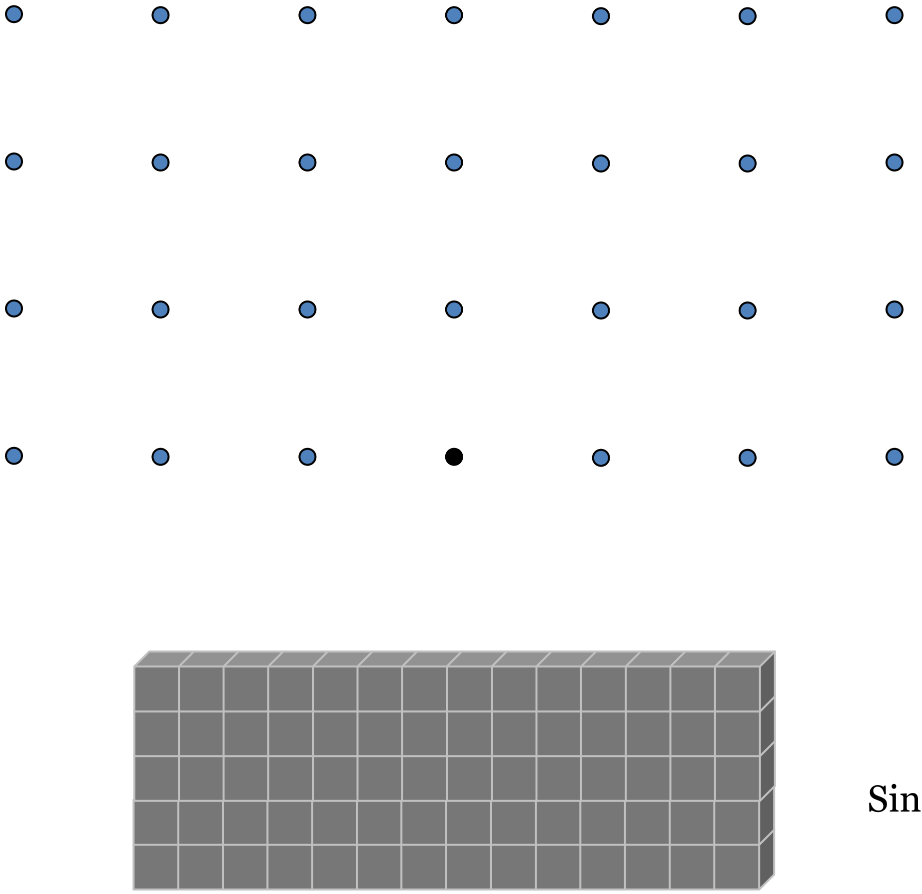
Relaxed

Before deposition

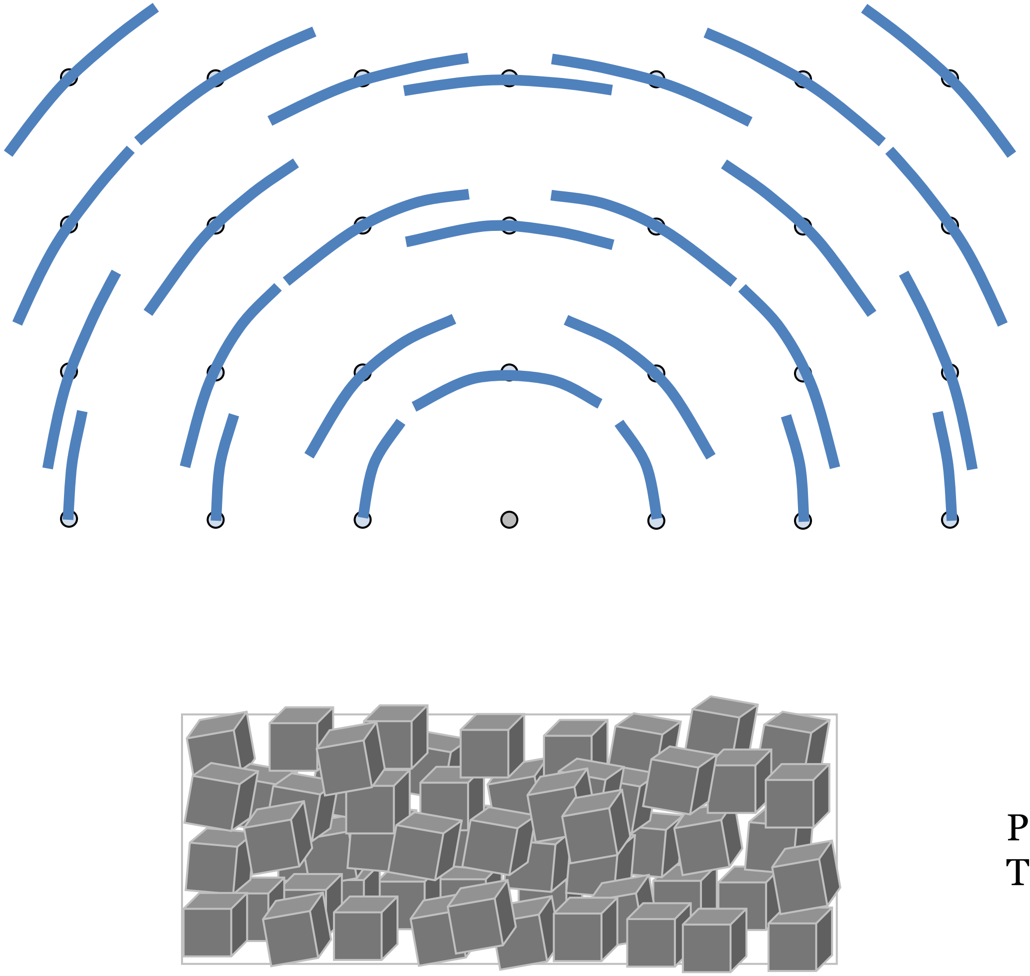
After deposition

Lattice mismatch induces lattice strain:

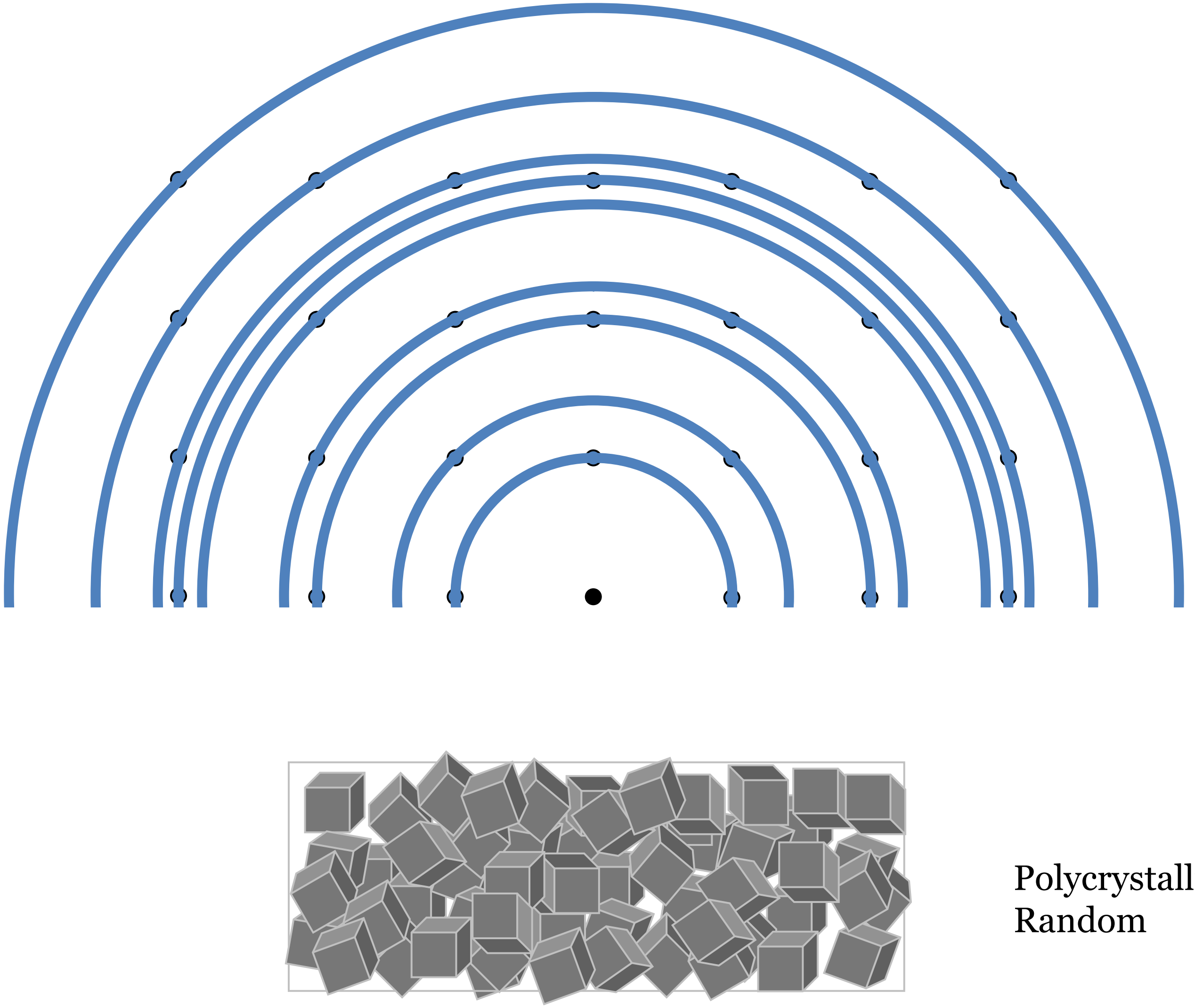
$$\varepsilon_\perp = \varepsilon_{zz} = \frac{a_L^\perp - a_L^R}{a_L^R} = \frac{d_L^\perp - d_L^R}{d_L^R}$$



Single crystal

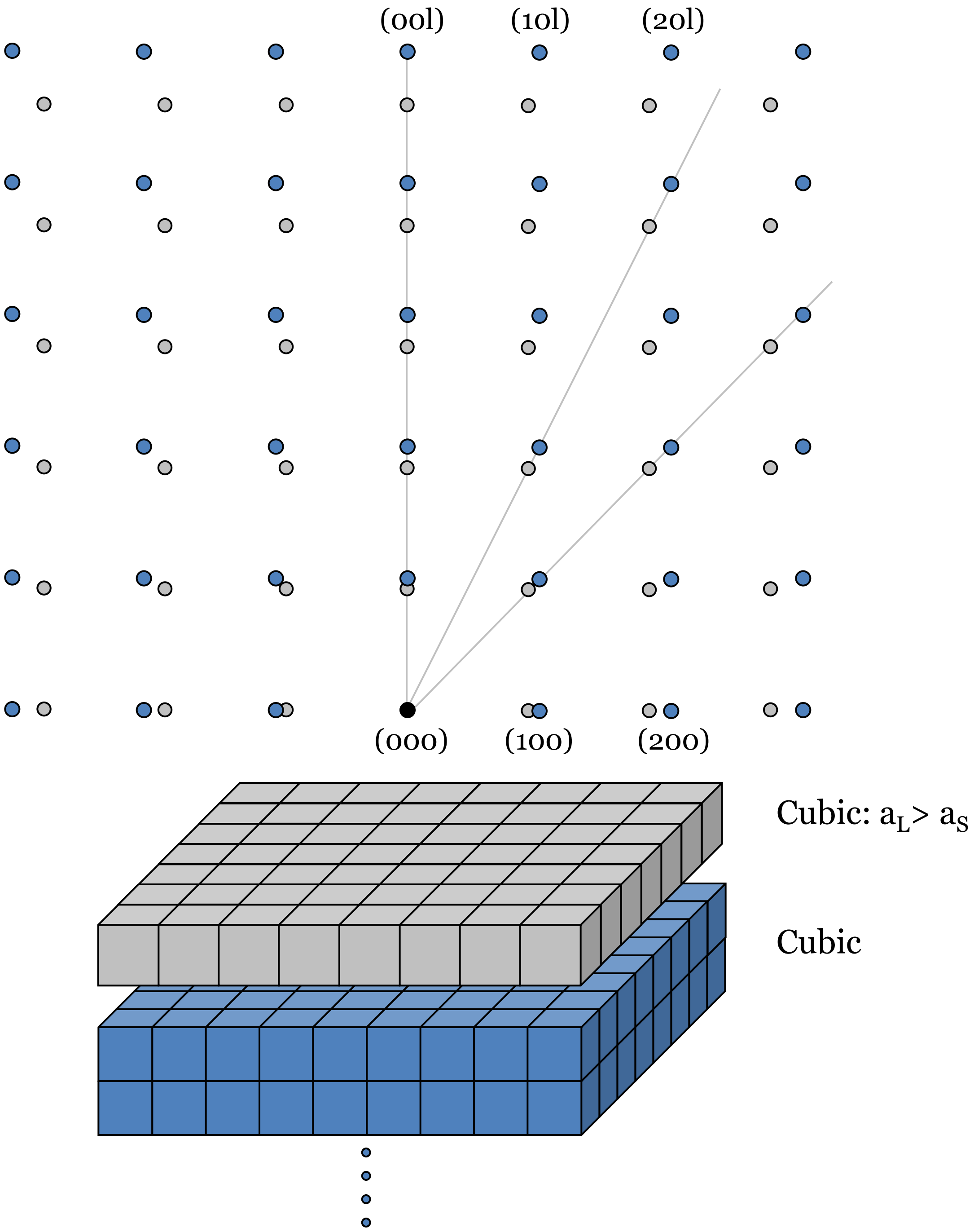


Polycrystalline
Textured



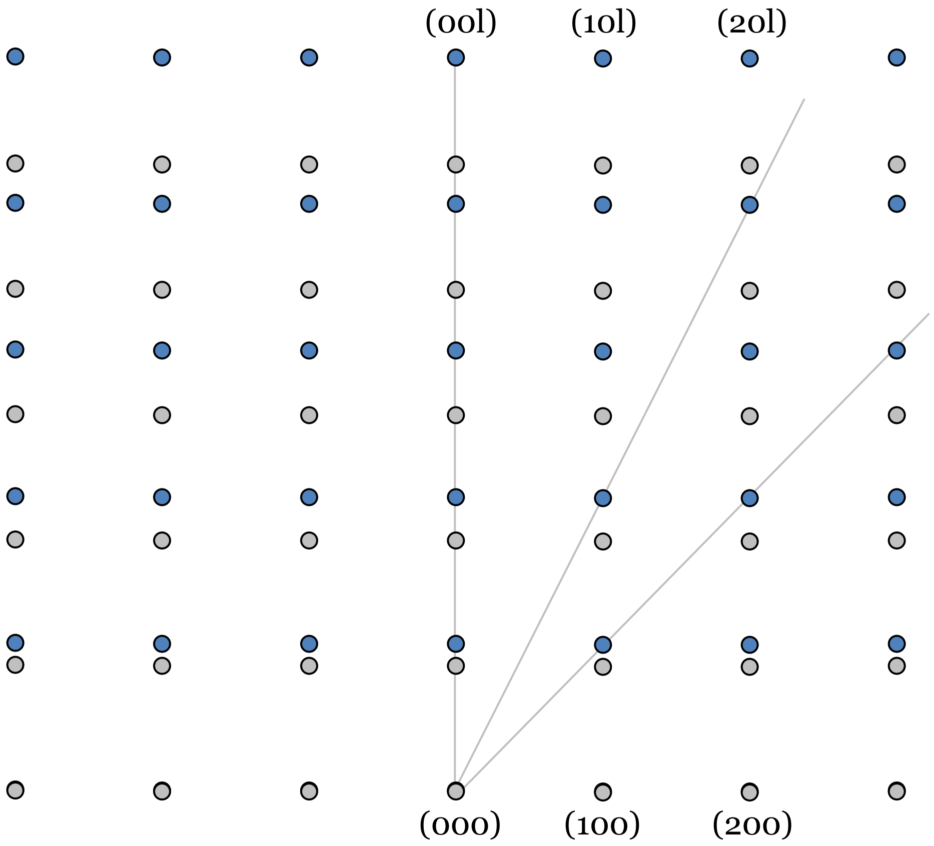
Polycrystalline
Random

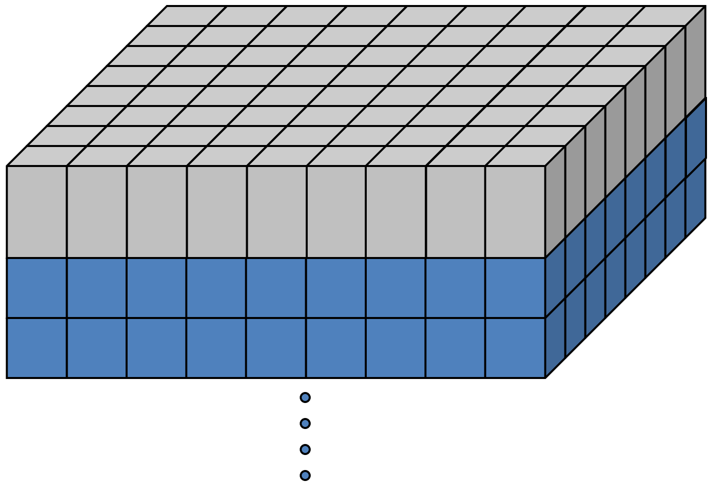
Relaxed Layer



Strained Layer

Compressive strain



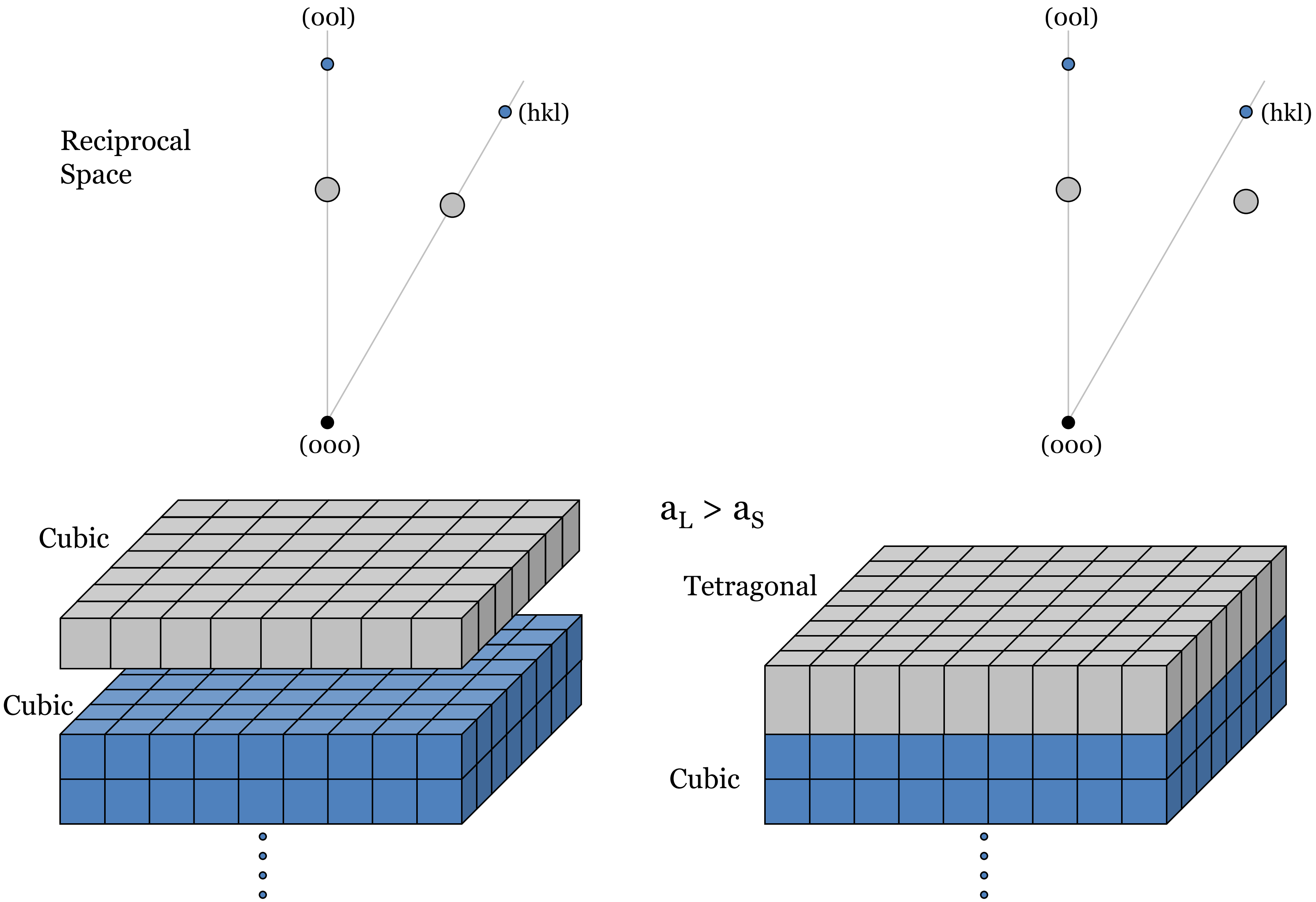


Tetragonal distortion

Tetragonal:
$$a_L^{II} = a_S$$
$$a_L^{\perp} > a_S$$

Cubic

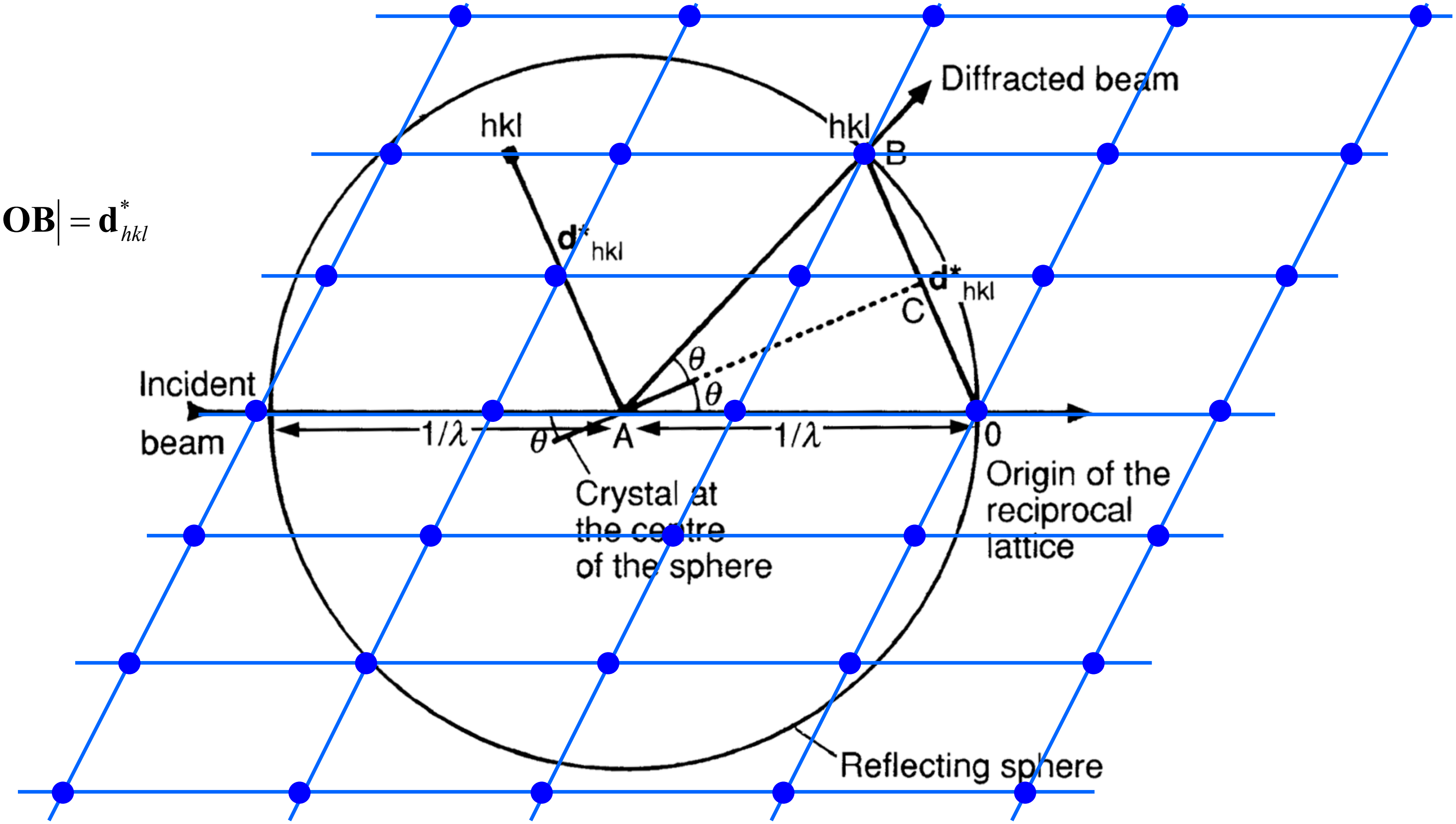
Perfect Layers: Relaxed and Strained



Reciprocal space – Ewald sphere

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

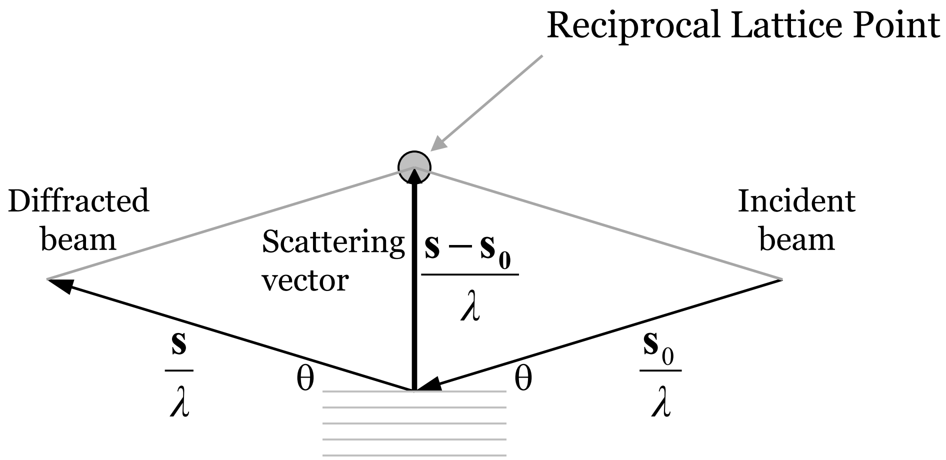
$$|\mathbf{OB}| = \mathbf{d}^*_{hkl}$$

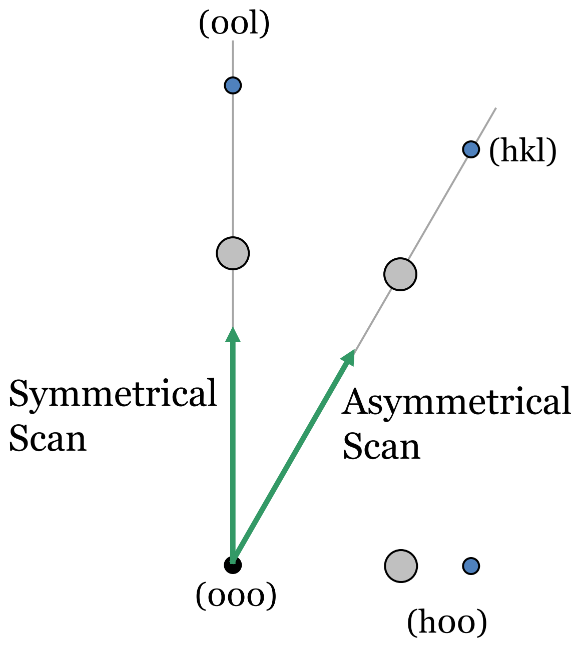


Reciprocal space – Scattering vector

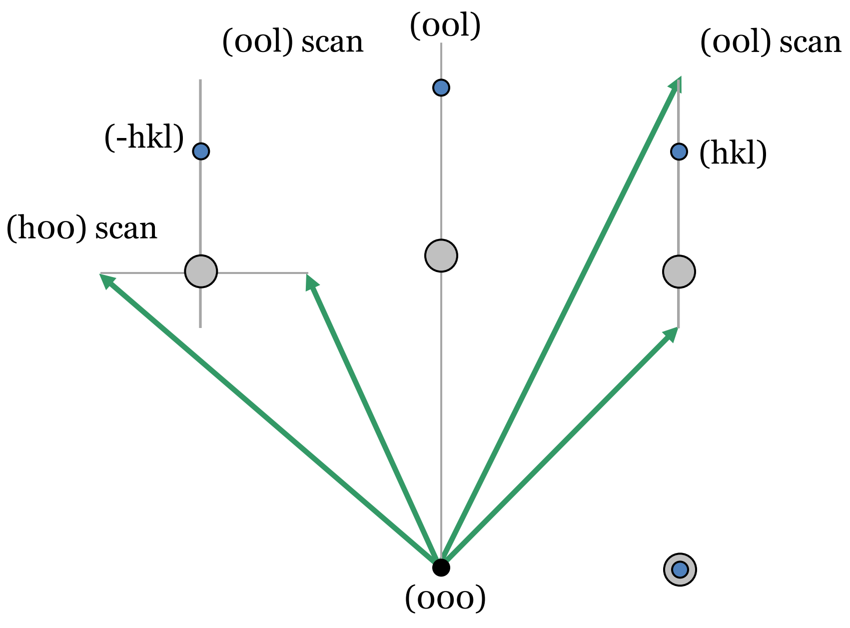
$$\left|\frac{\mathbf{s}-\mathbf{s}_0}{\lambda}\right| = \frac{2\sin\theta}{\lambda} = \left|\mathbf{d}^*_{hkl}\right| = \frac{1}{d_{hkl}}$$

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



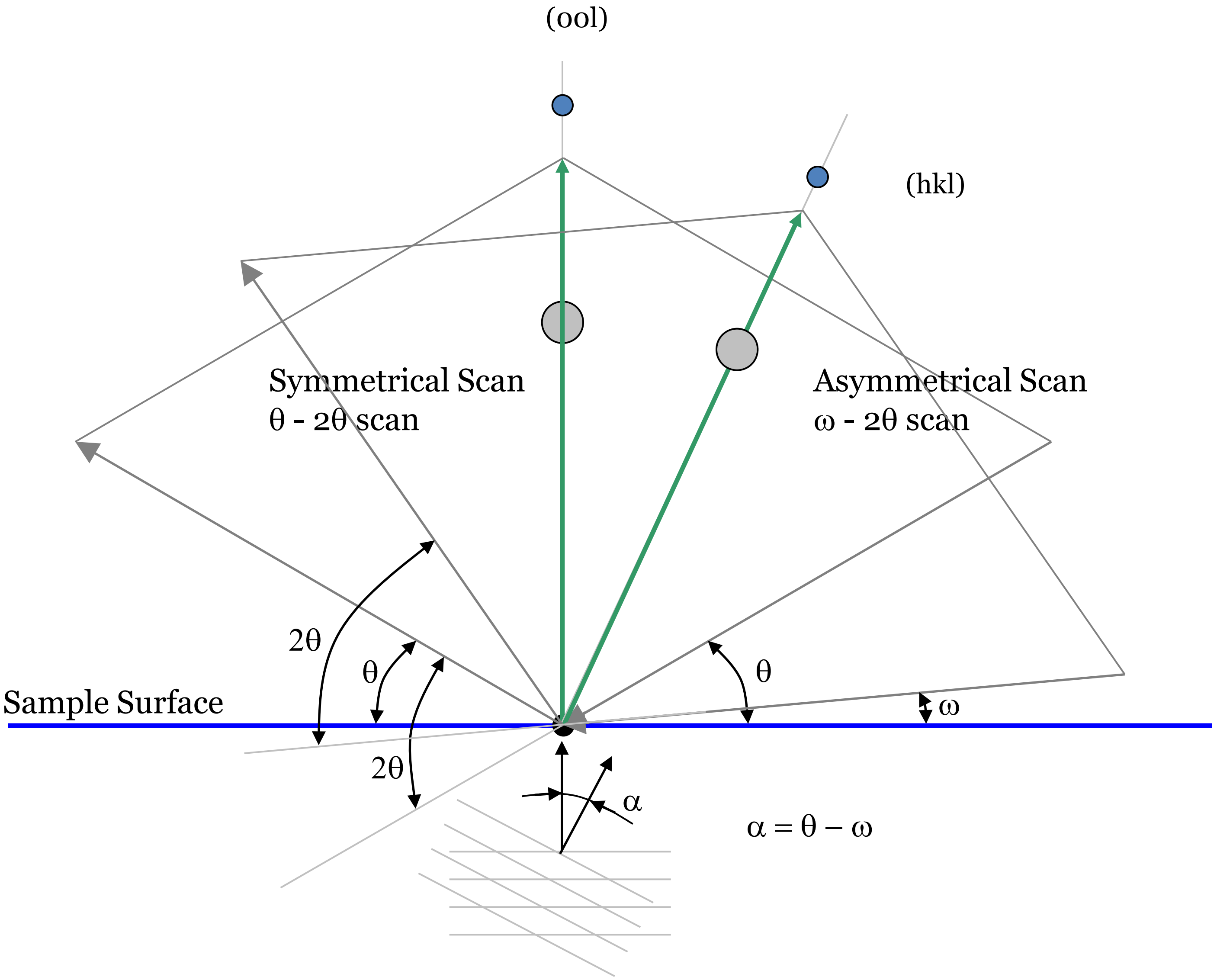


Relaxed Layer

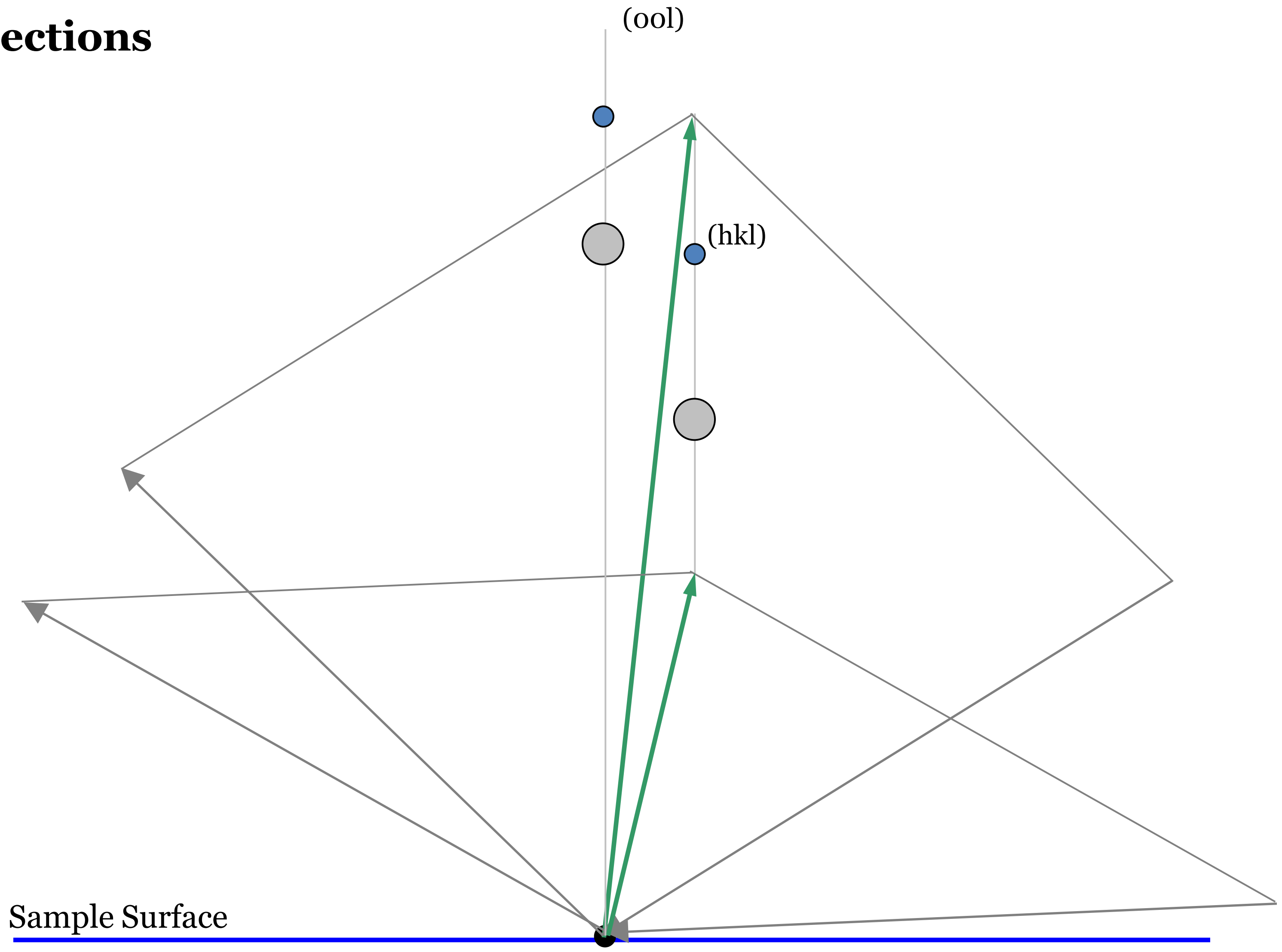


Strained Layer

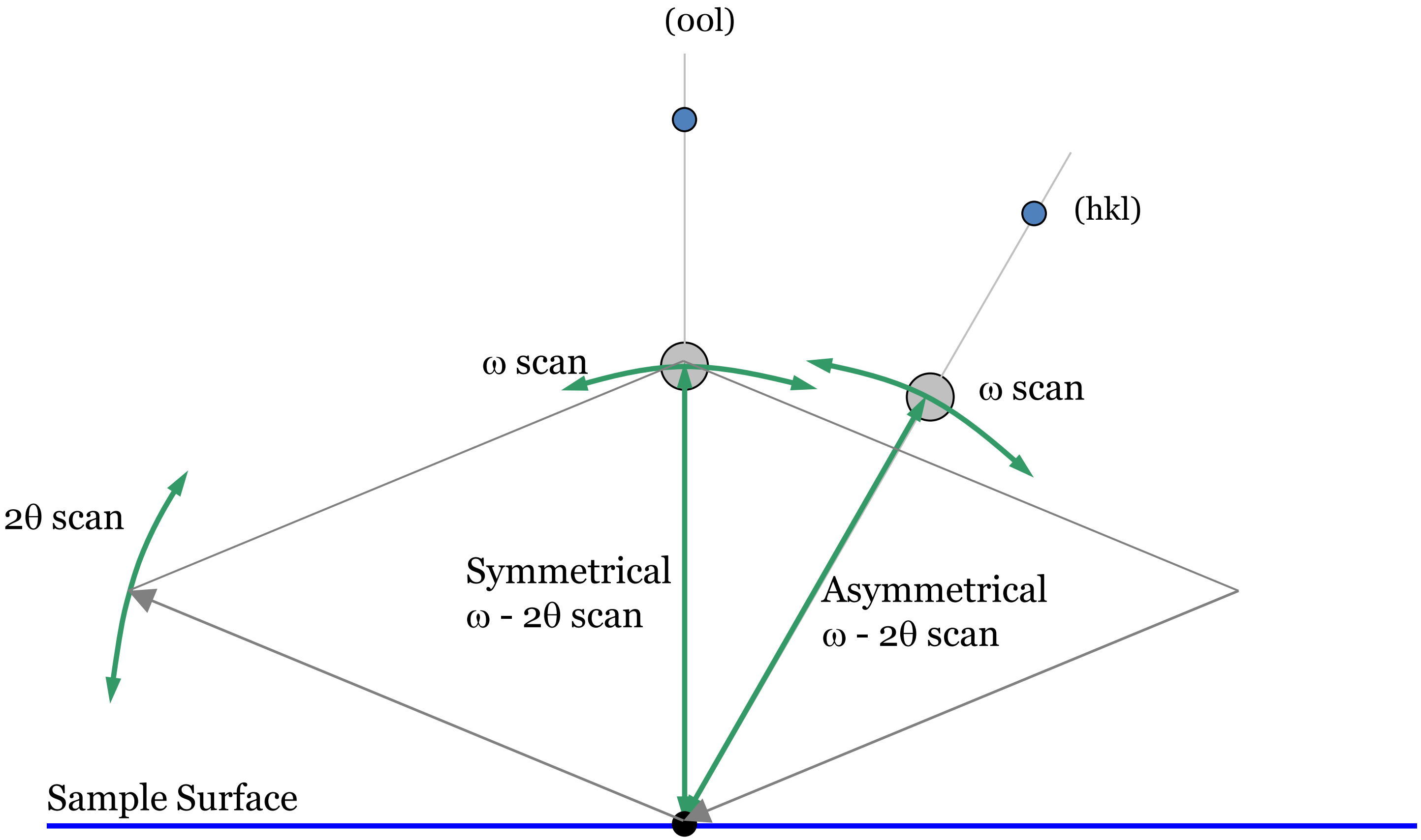
Scan Directions



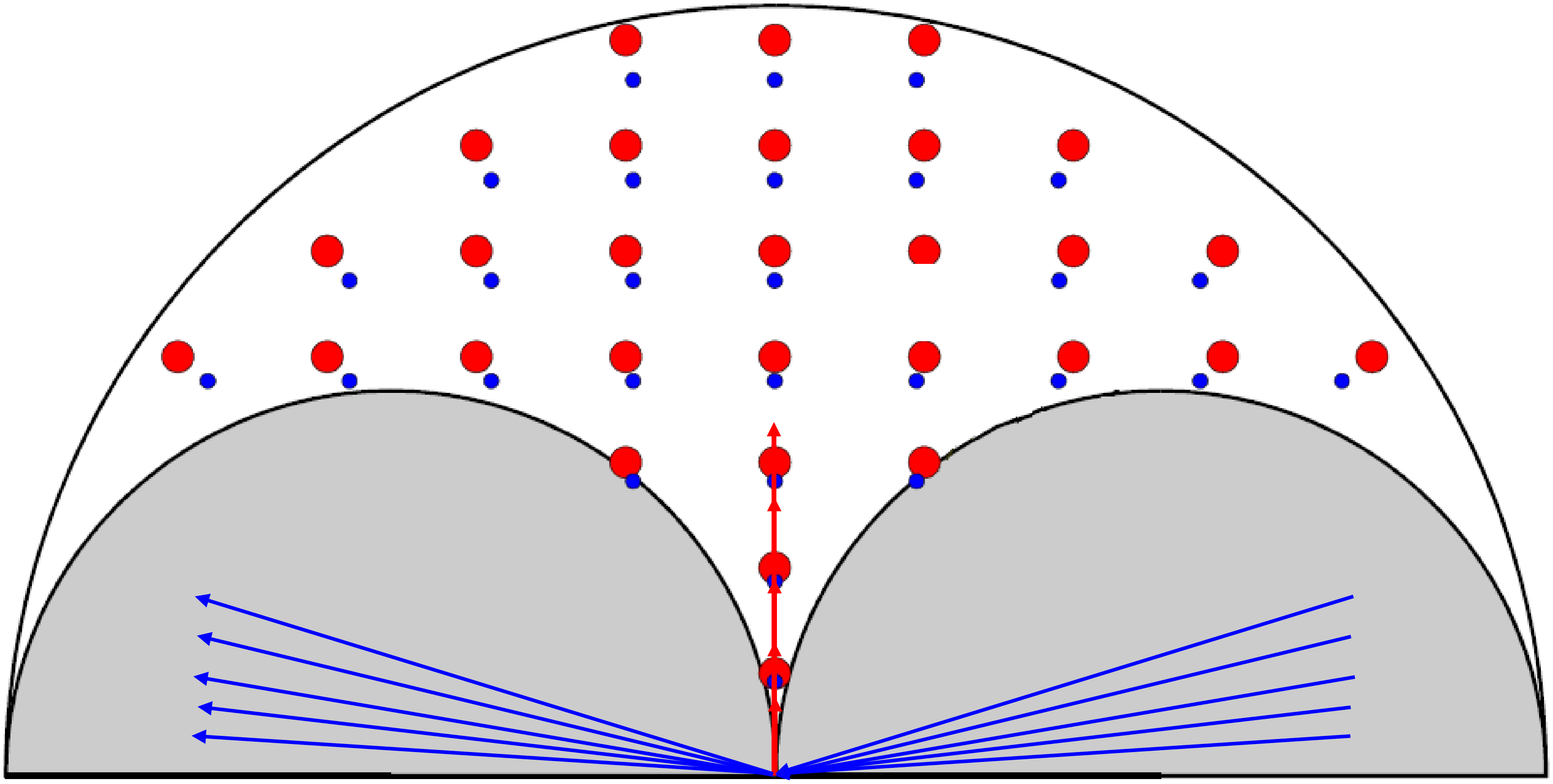
Scan Directions



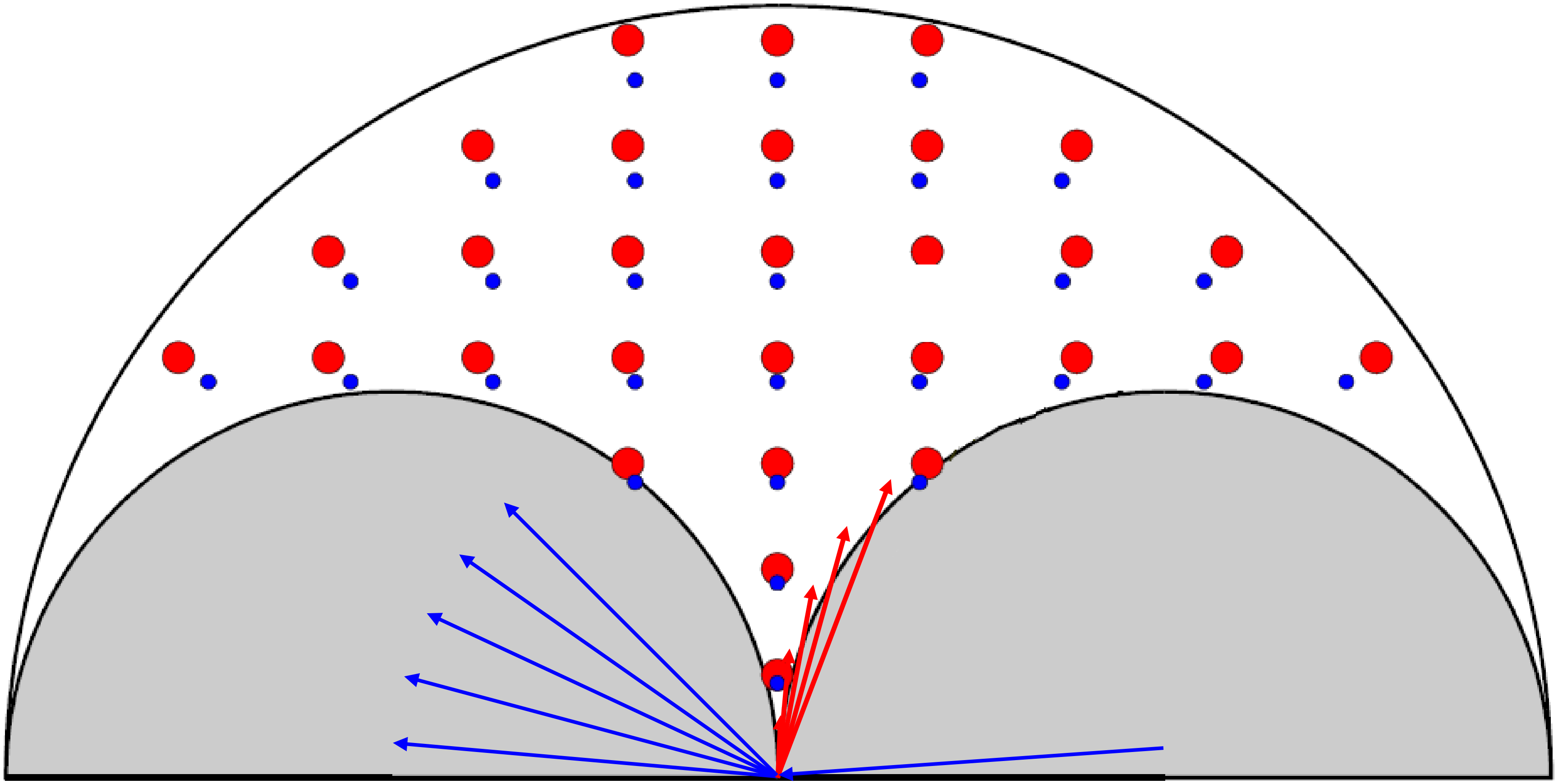
Scan Directions



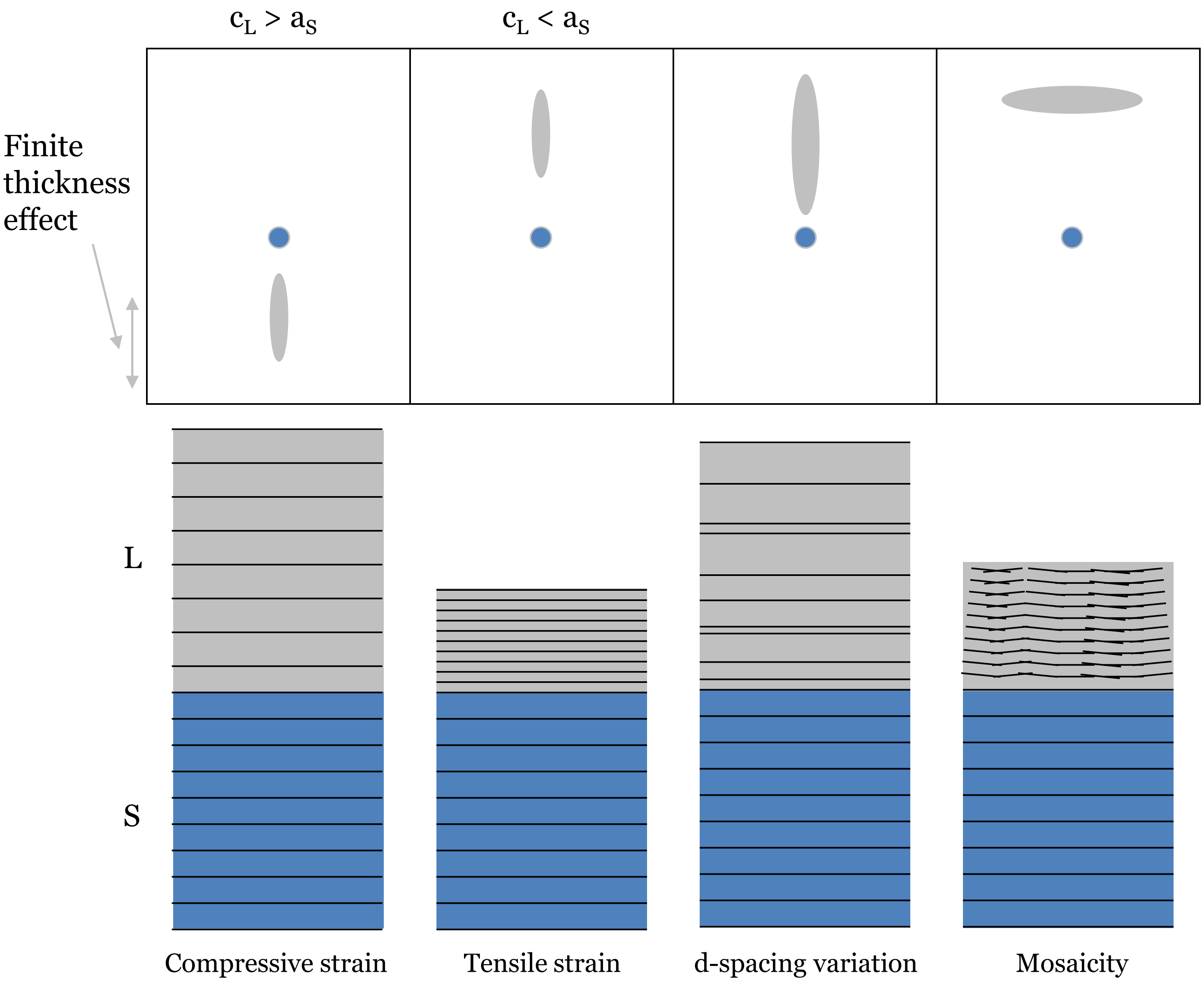
Symmetrical Scan



Grazing Incidence Diffraction



Real RLP shapes



Mismatch

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

For cubic (001) oriented material the experimentally measured normal component of the mismatch:

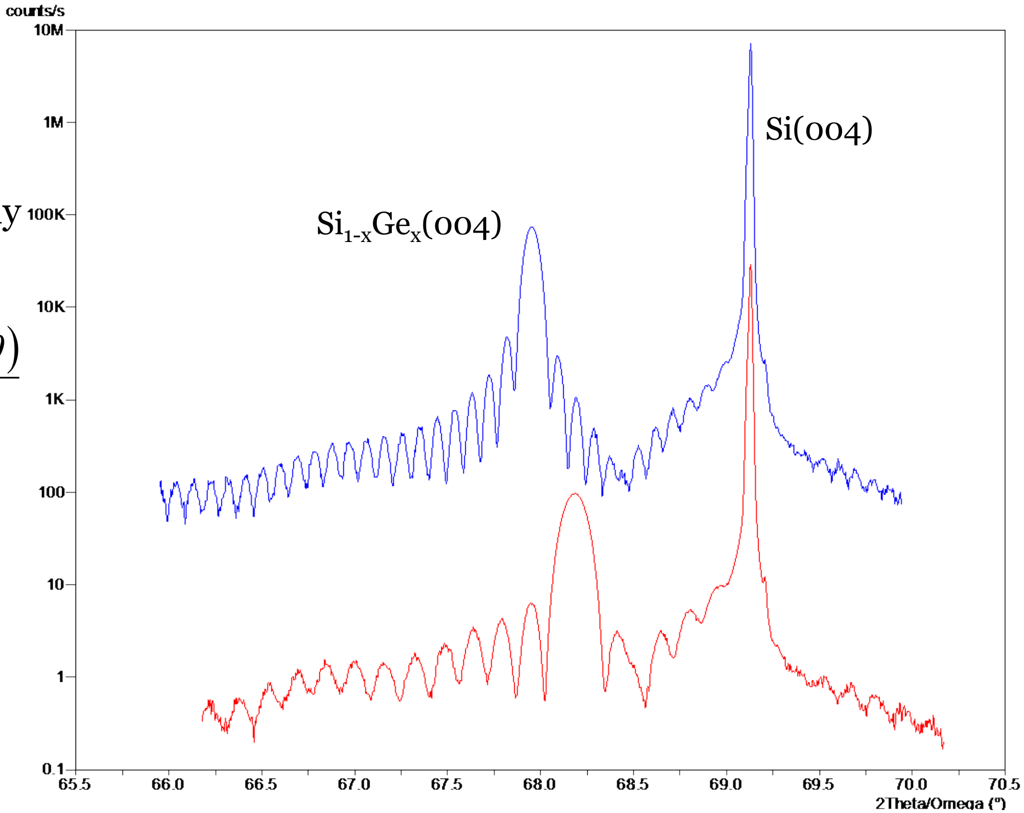
$$m_\perp = \frac{a_\perp - a_S}{a_S} = \left(\frac{\Delta a}{a}\right)_\perp = \left(\frac{\Delta d}{d}\right) = \frac{\sin\theta_S - \sin(\theta_S + \Delta\theta)}{\sin(\theta_S + \Delta\theta)}$$

The experimental mismatch, $m_\perp$, can be related to the mismatch through the equation:

$$m = \frac{a_L^R - a_S}{a_S} = \frac{1-\nu}{1+\nu} m_\perp$$

where ν is Poisson ratio.
For Si, ν = 0.28

$$\boxed{\begin{array}{l} \nu \approx \dfrac{1}{3} \\ m \approx \dfrac{m^*}{2} \end{array}}$$



The composition of the $A_{1-x}B_x$ alloy can be calculated from Vegard's law:

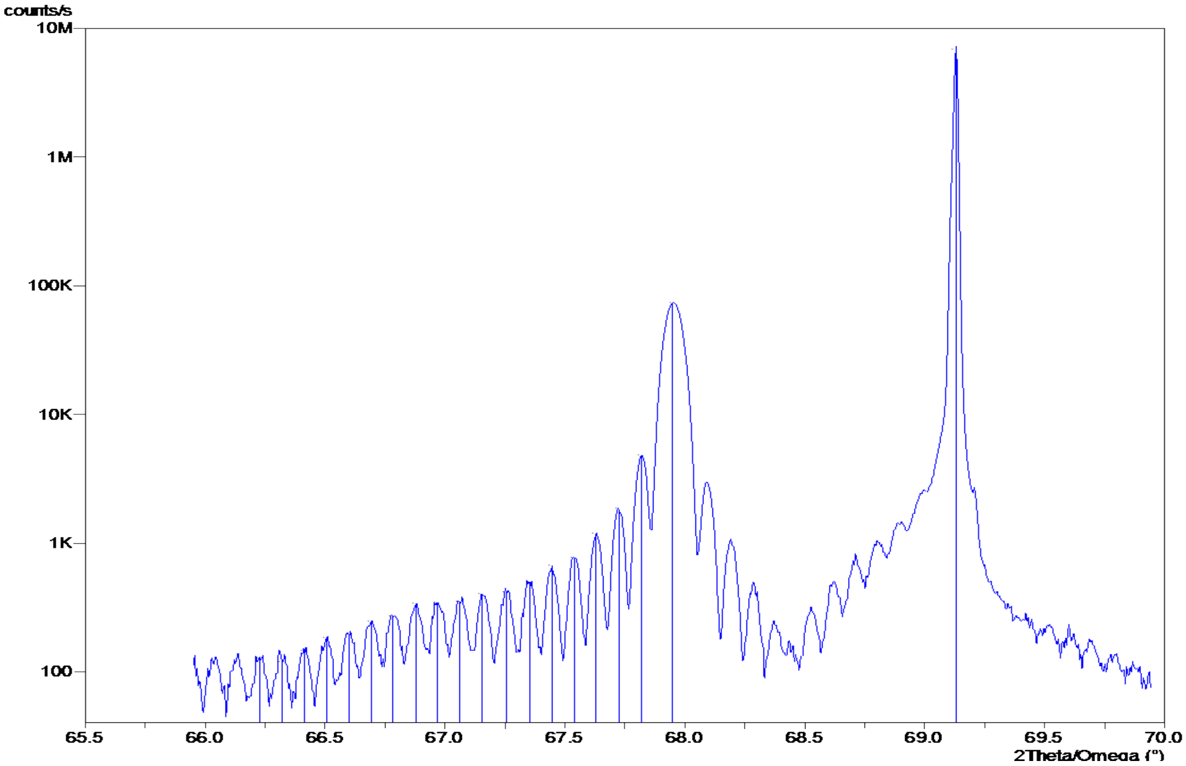
$$a_L^R(x) = (1-x)a_A + xa_B$$

$$x = m\frac{a_A}{a_B - a_A}$$

Layer Thickness

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

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



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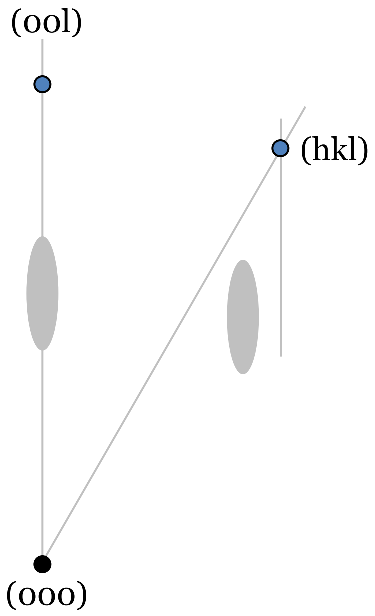
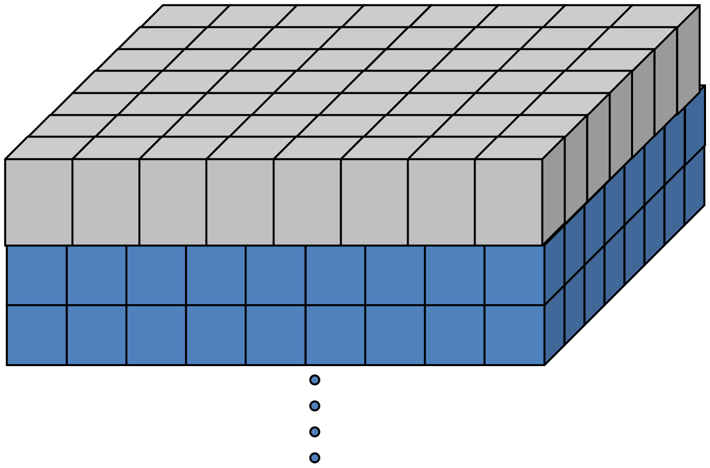
Substrate Layer Separation
S-peak:                L-peak:                Separation:
Omega(°)    34.5649    Omega(°)    33.9748    Omega(°)    0.59017
2Theta(°)   69.1298    2Theta(°)   67.9495    2Theta(°)   1.18034

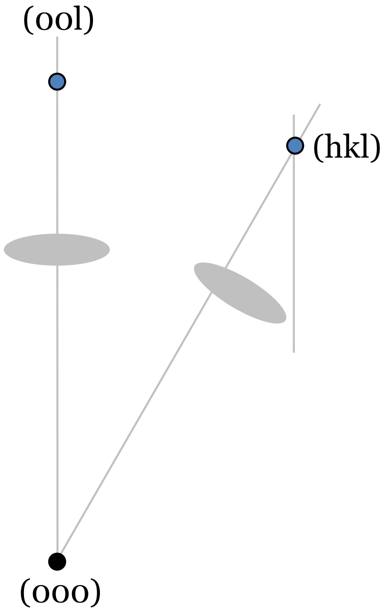
Layer Thickness
Mean fringe period (°): 0.09368
Mean thickness (um): 0.113 ± 0.003

 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
```

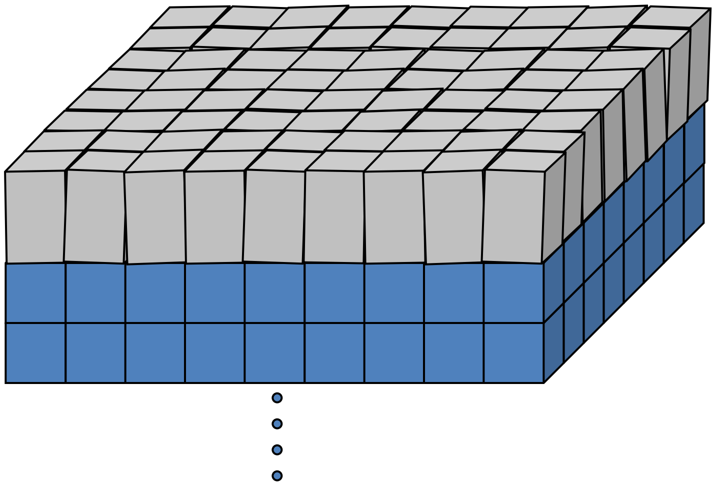


Partially Relaxed + Thin

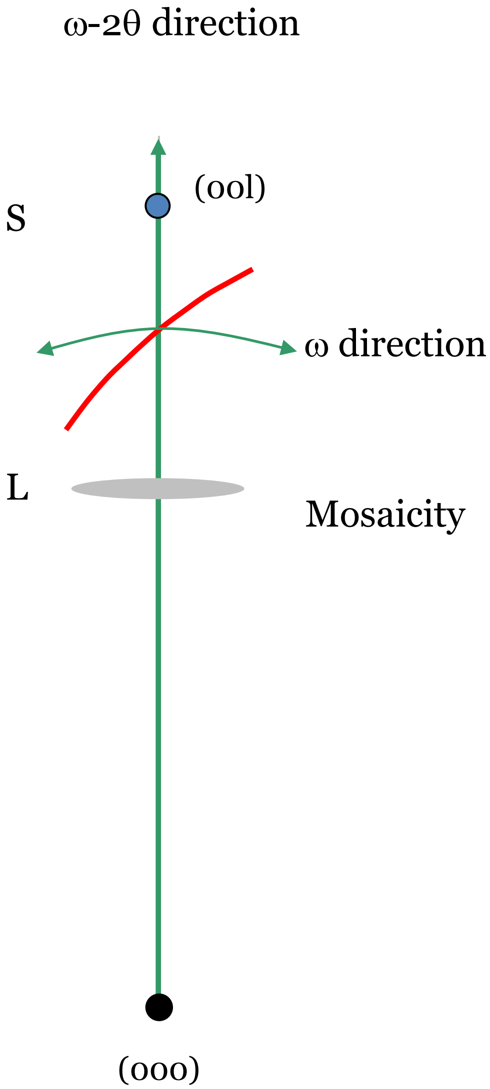




Partially Relaxed + Mosaicity



Symmetrical scan



ω-2θ direction

S

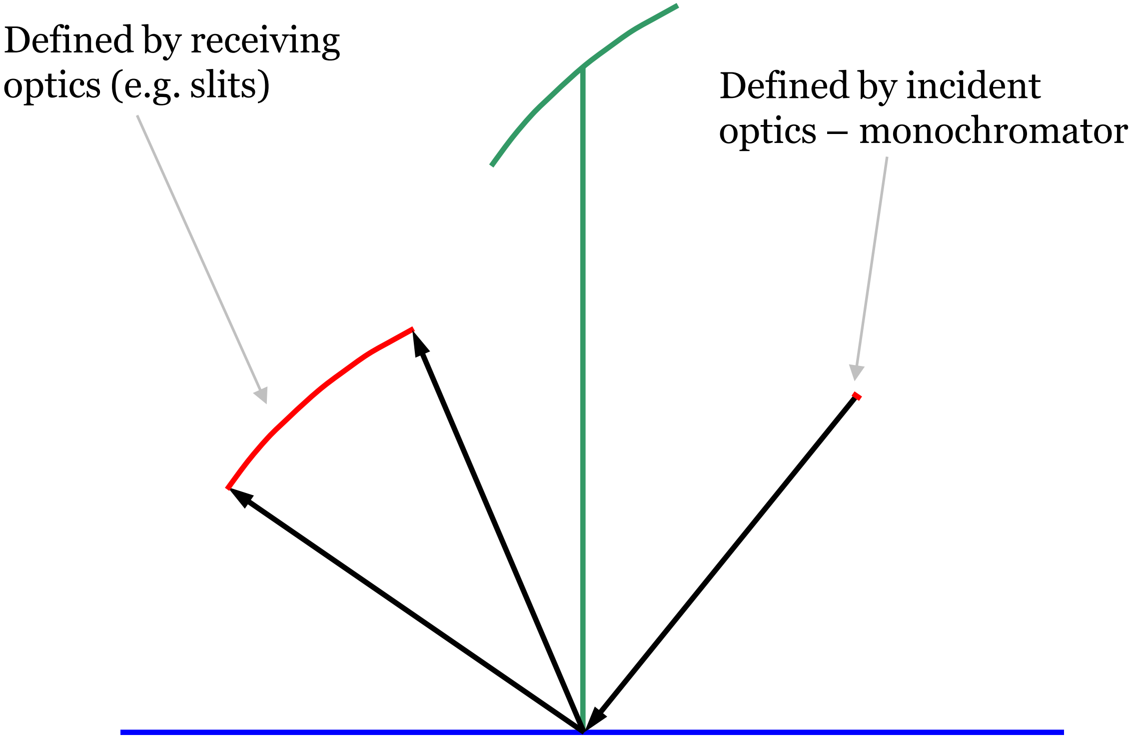
(00l)

ω direction

L

Mosaicity

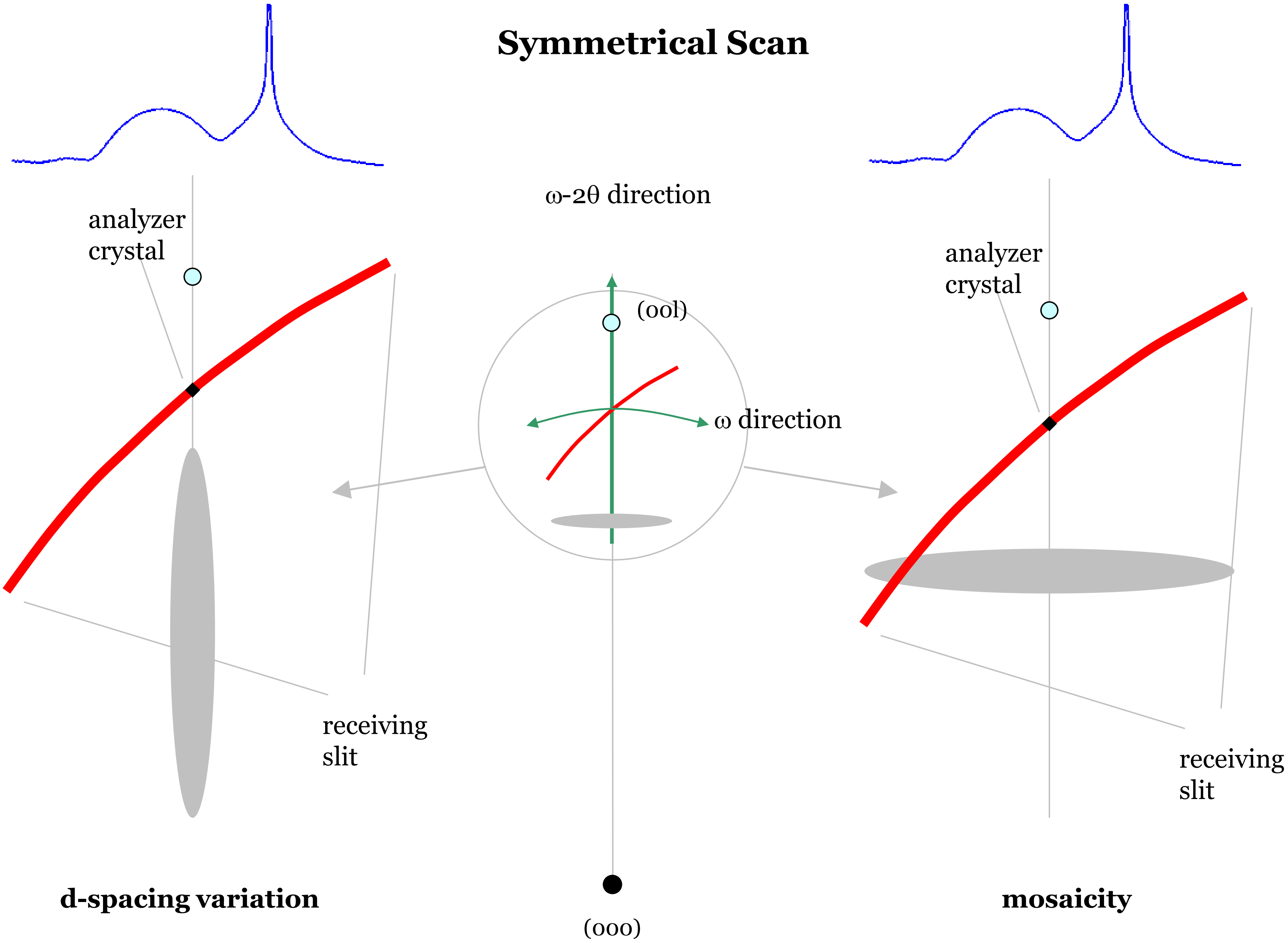
(000)



Defined by receiving optics (e.g. slits)

Defined by incident optics – monochromator

Symmetrical Scan



ω-2θ direction

analyzer crystal

(00l)

ω direction

receiving slit

analyzer crystal

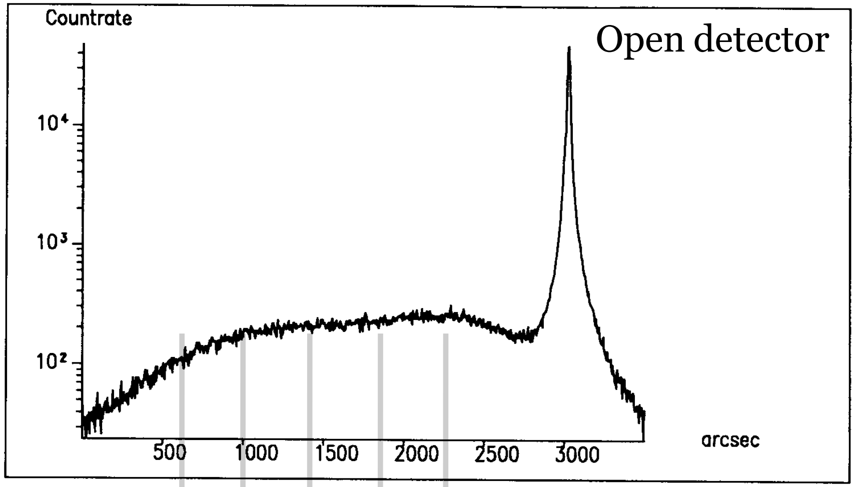
receiving slit

d-spacing variation

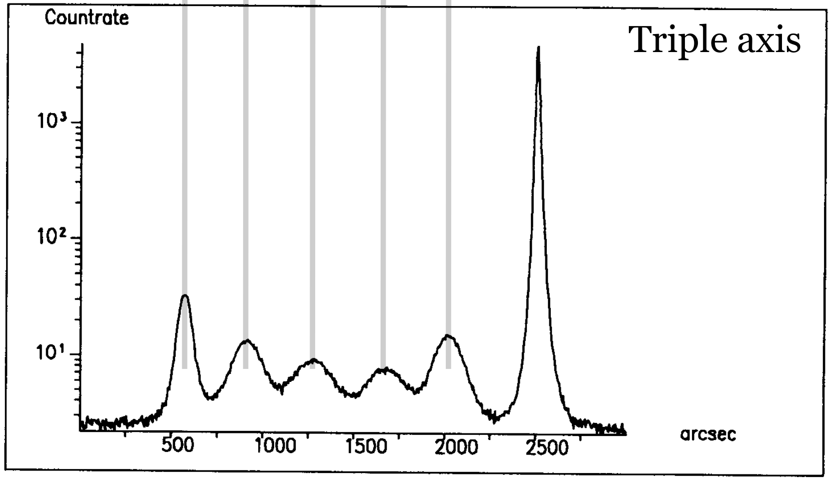
(000)

mosaicity

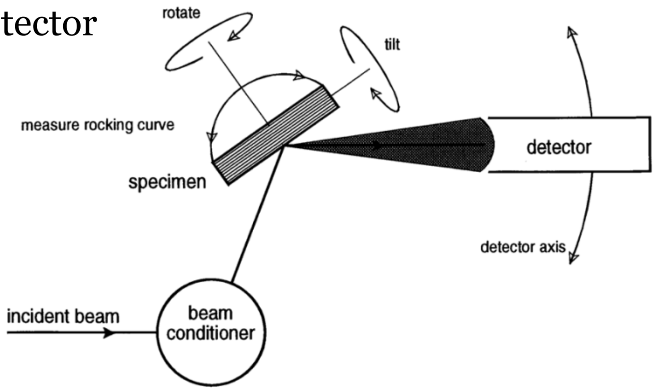
Triple axis diffractometry



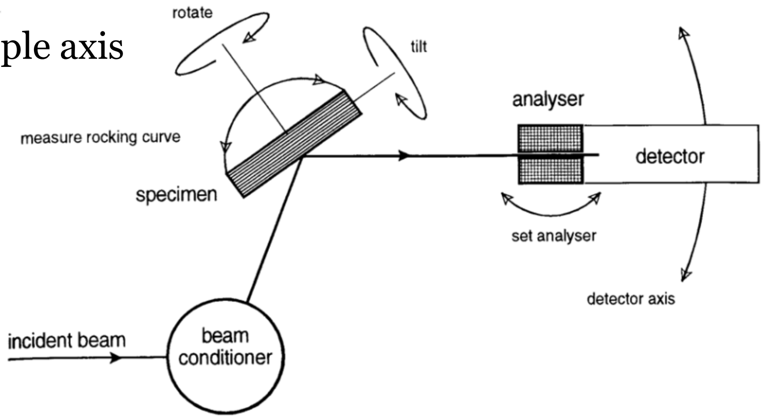
Ge content: 50% 40% 30% 20% 10%

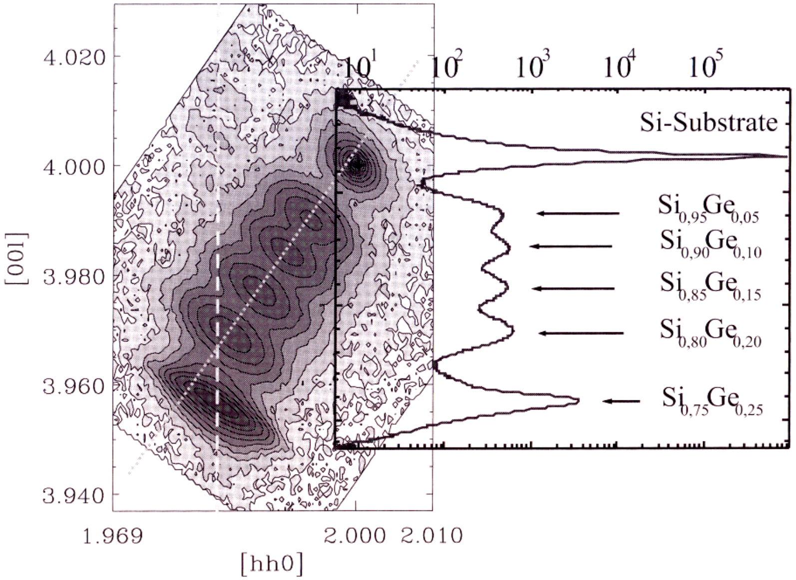


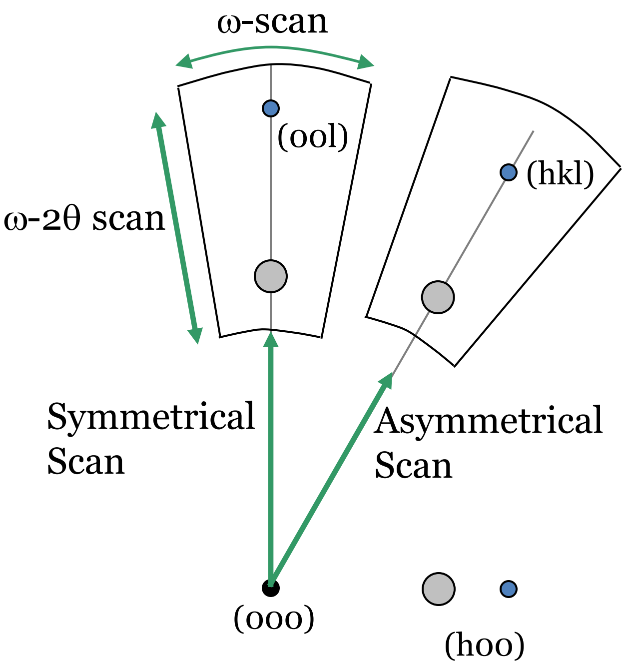
Open detector

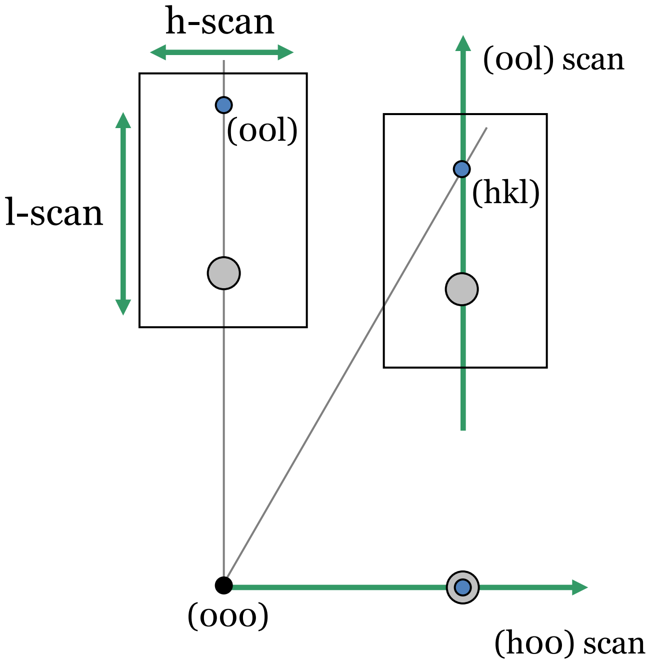


Triple axis

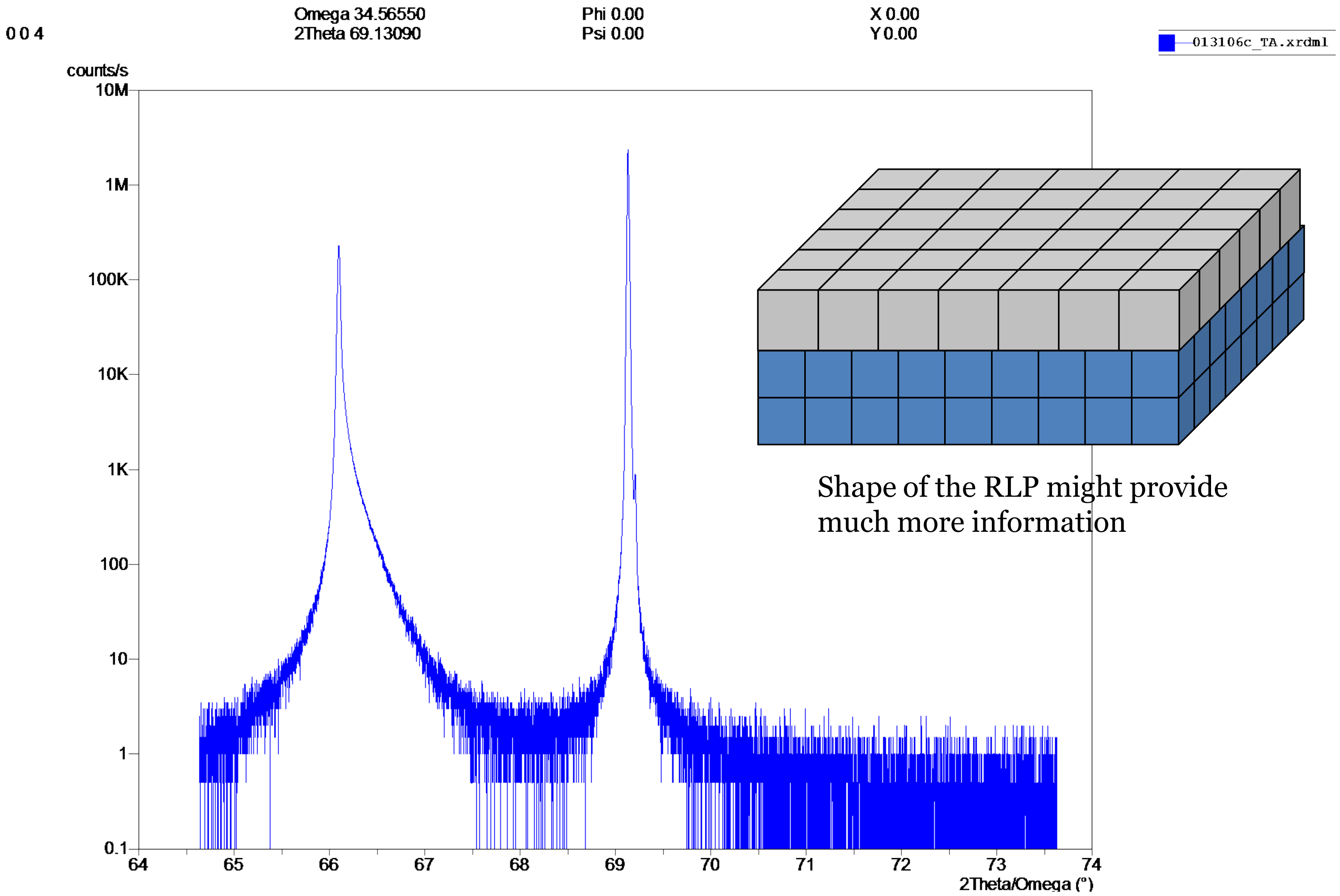





ω-scan
(ool)
(hkl)
ω-2θ scan
Symmetrical Scan
Asymmetrical Scan
(ooo)
(hoo)


h-scan
(ool) scan
(ool)
l-scan
(hkl)
(ooo)
(hoo) scan

Relaxed SiGe on Si(001)



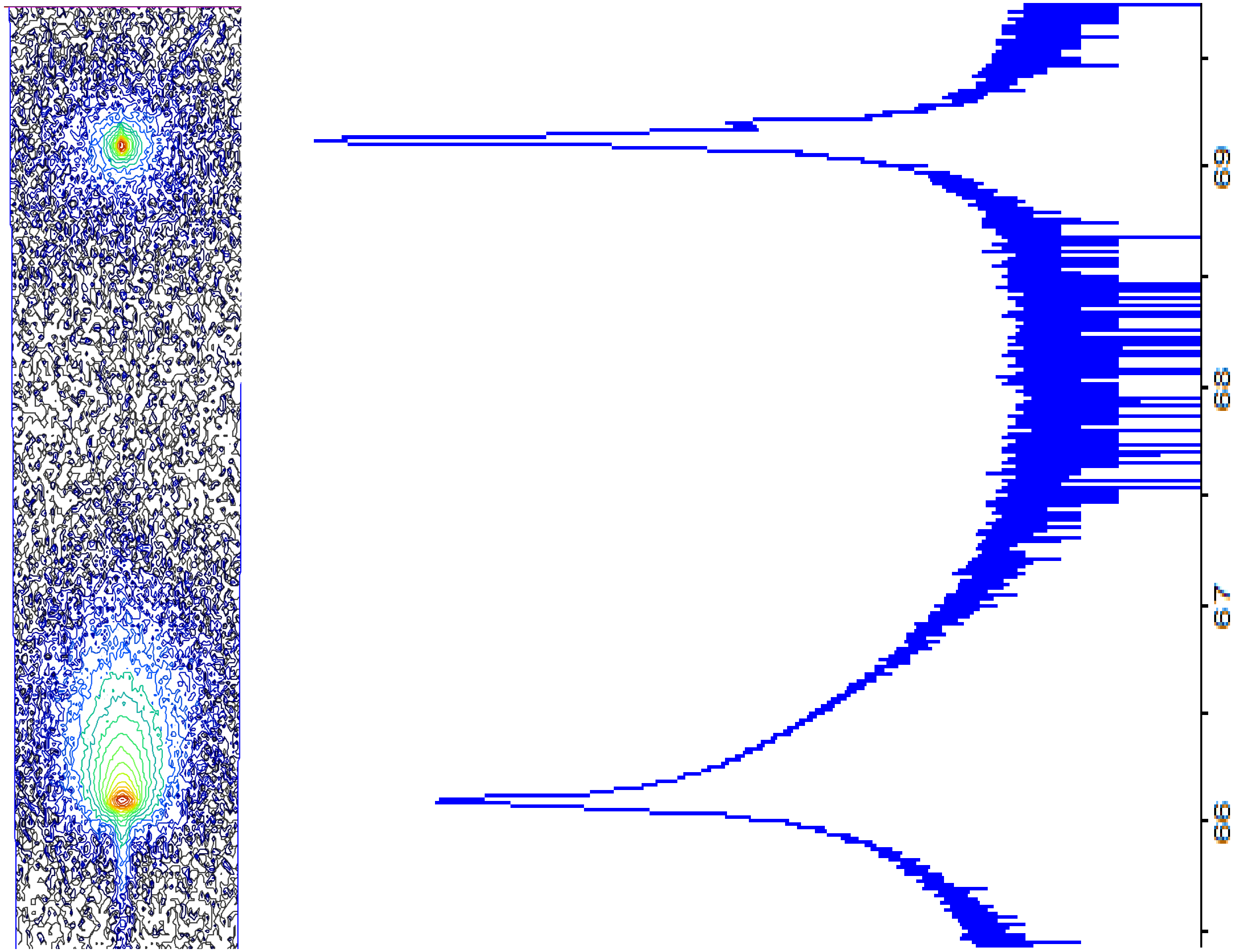
Shape of the RLP might provide much more information

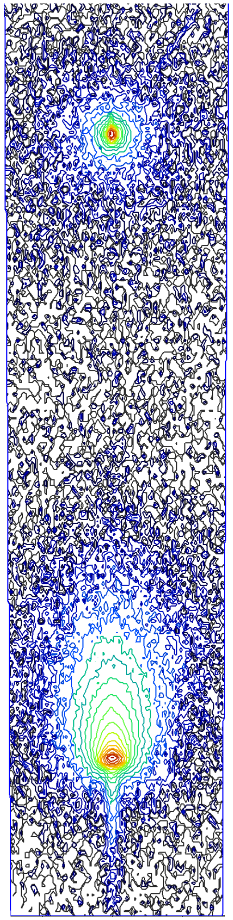
Relaxed SiGe on Si(001)

(004) RLM

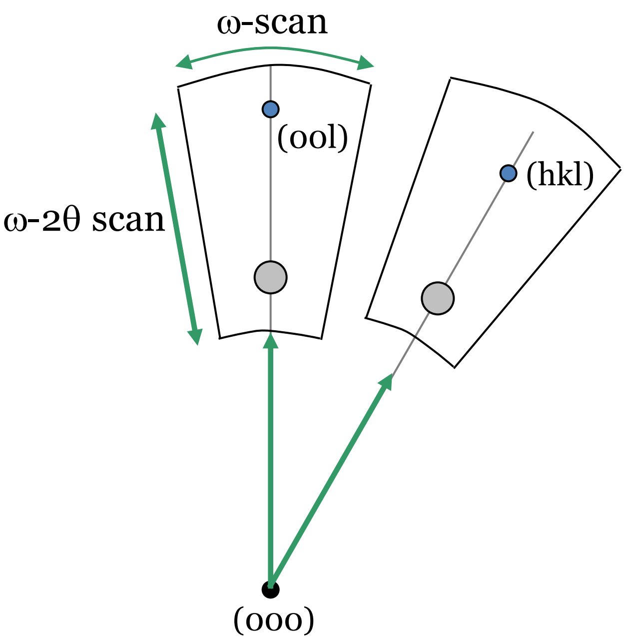
Si(004)

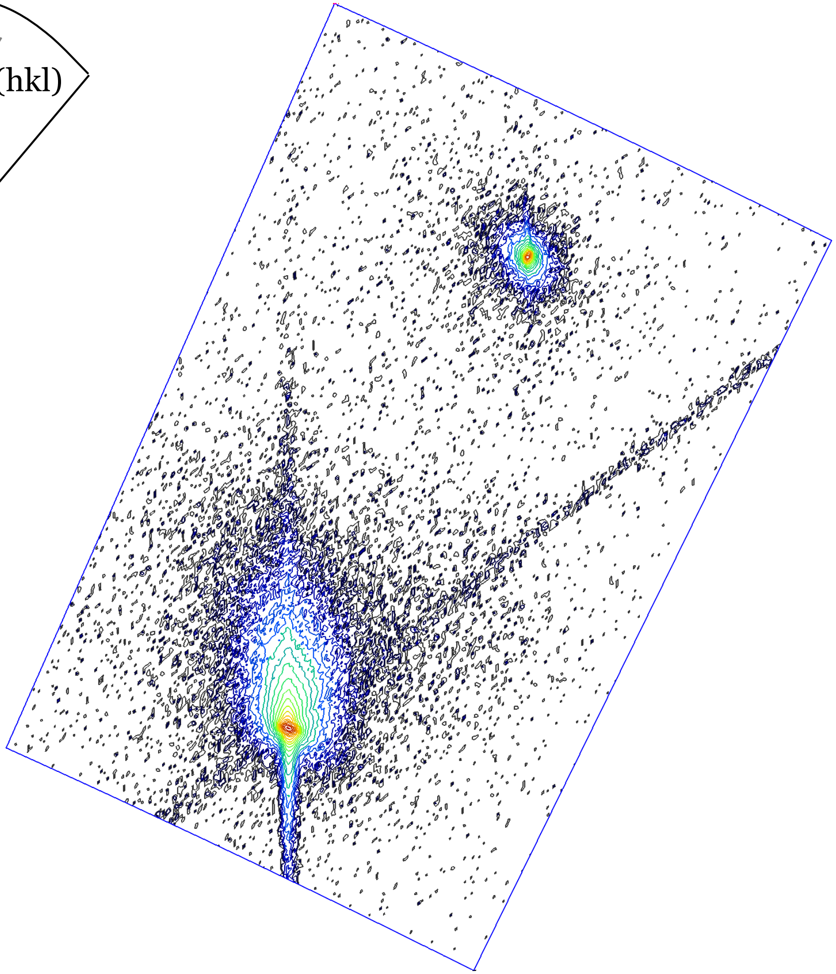
SiGe(004)





(004)





(113)

Relaxation

The relaxation is defined as:

$$R = \frac{a_L - a_S}{a_L^R - a_S} \times 100$$

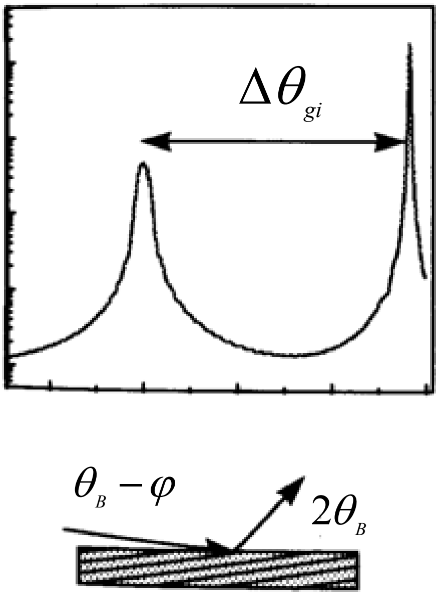
To separate the layer tilt from the true splitting we can make grazing incidence and grazing exit measurements:

- 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

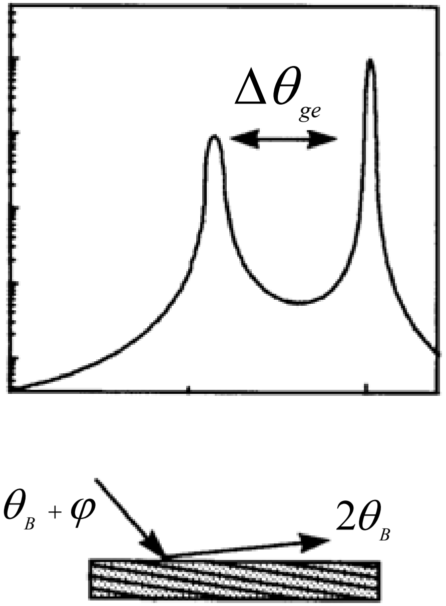
$$\Delta\theta_{gi} = \Delta\theta + \Delta\varphi \quad - \text{ grazing incidence}$$

$$\Delta\theta_{ge} = \Delta\theta - \Delta\varphi \quad - \text{ grazing exit}$$

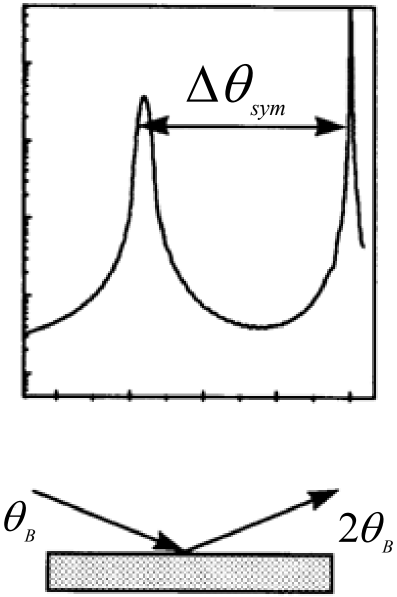
Grazing incidence



Grazing exit

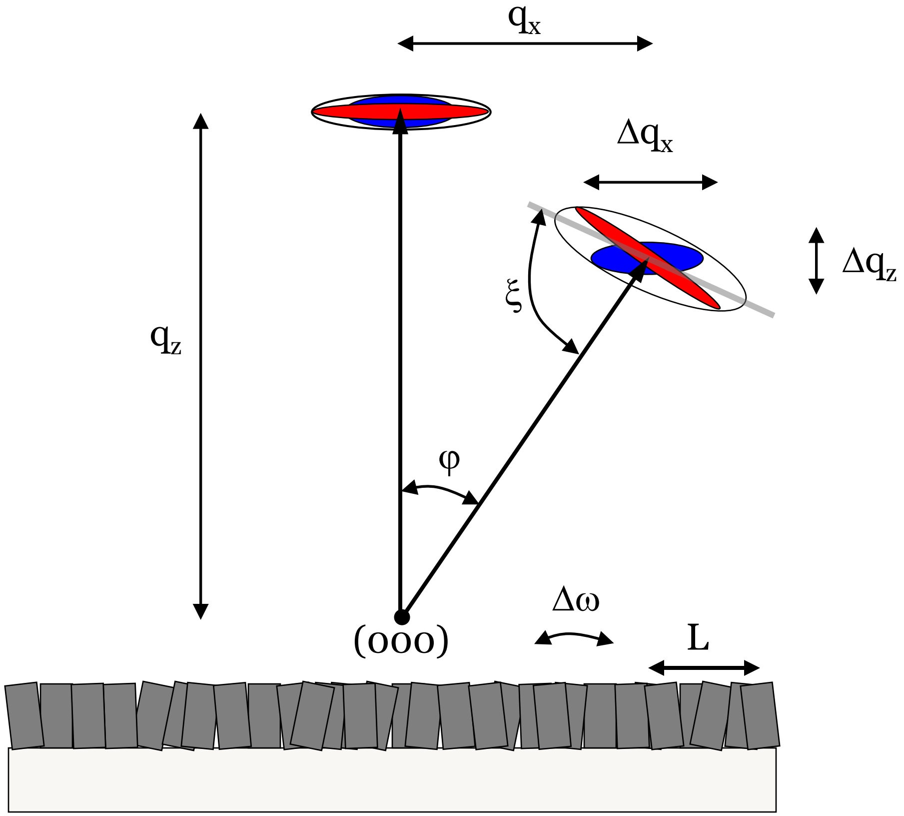


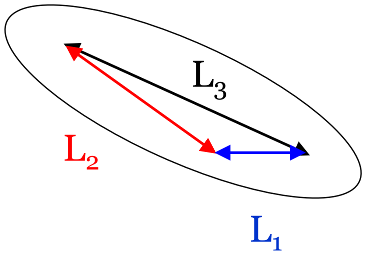
Symmetrical scan



Analysis of Laterally Inhomogeneous Layers

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

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

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

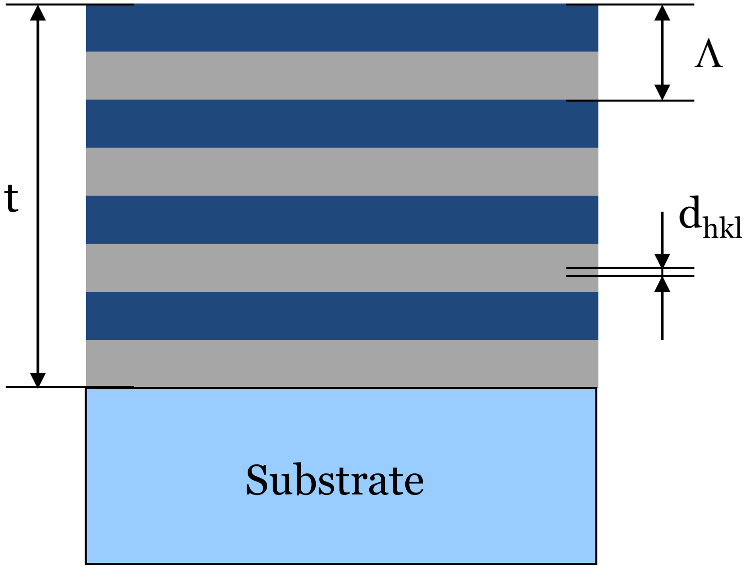
$$\frac{L_1}{L_2} = -\frac{\cos\xi}{\cos(\varphi+\xi)}$$

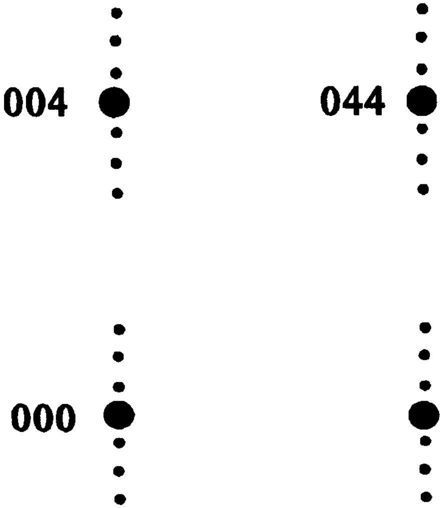
$$\frac{L_3}{L_2} = -\frac{\sin\varphi}{\cos\xi}$$

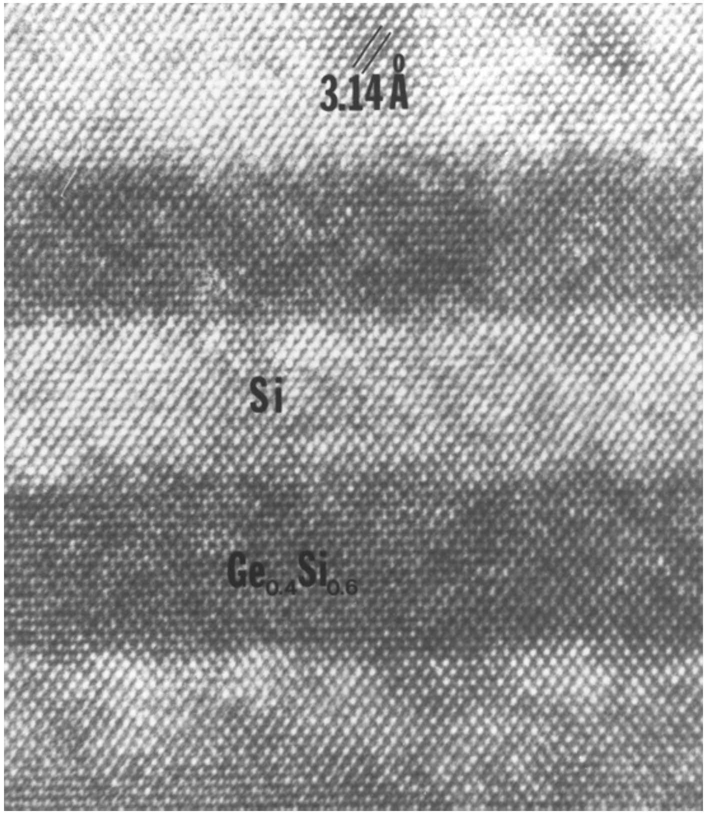
Lateral correlation length $= \frac{1}{L_1}$

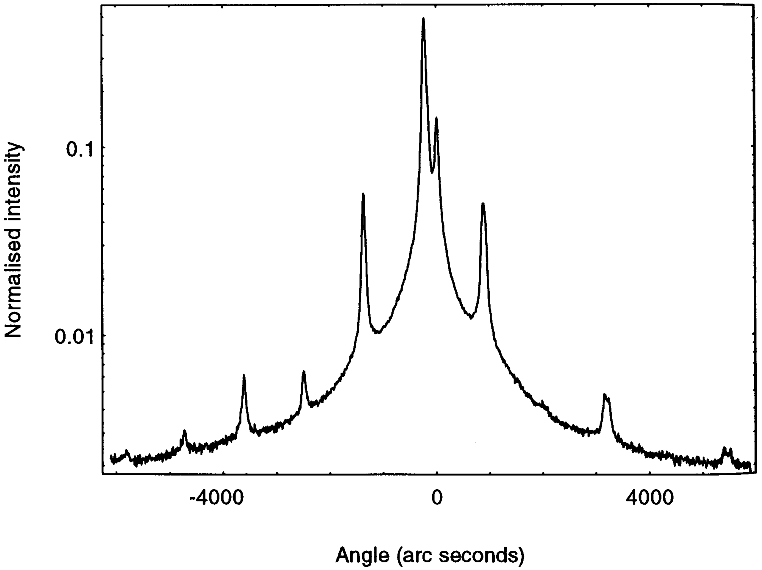
Microscopic tilt $= \frac{L_2}{\sqrt{q_x^2 + q_z^2}}$

Superlattices and Multilayers

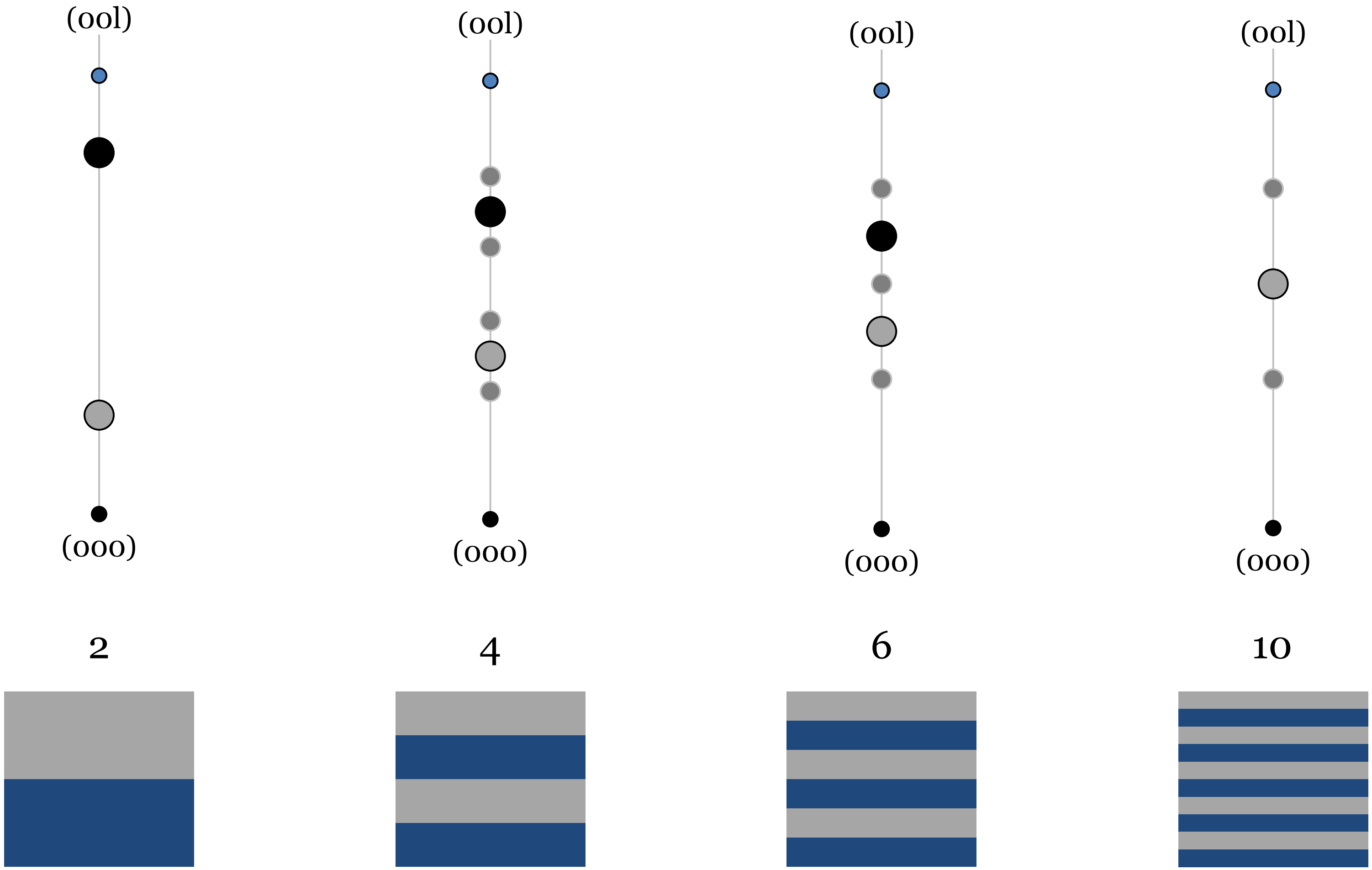


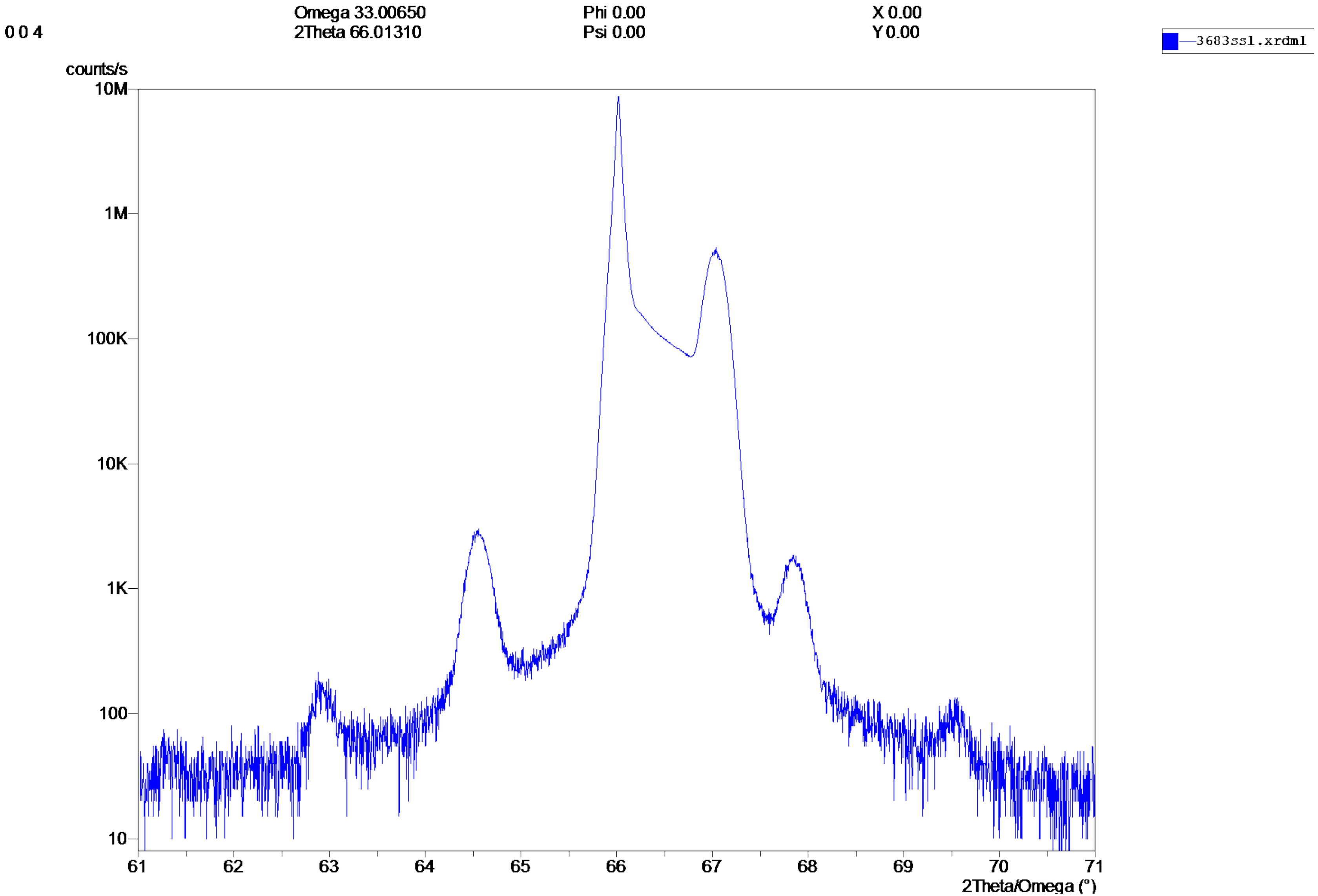






Superlattices and Multilayers

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2Theta 66.01310
Phi 0.00
Psi 0.00
X 0.00
Y 0.00
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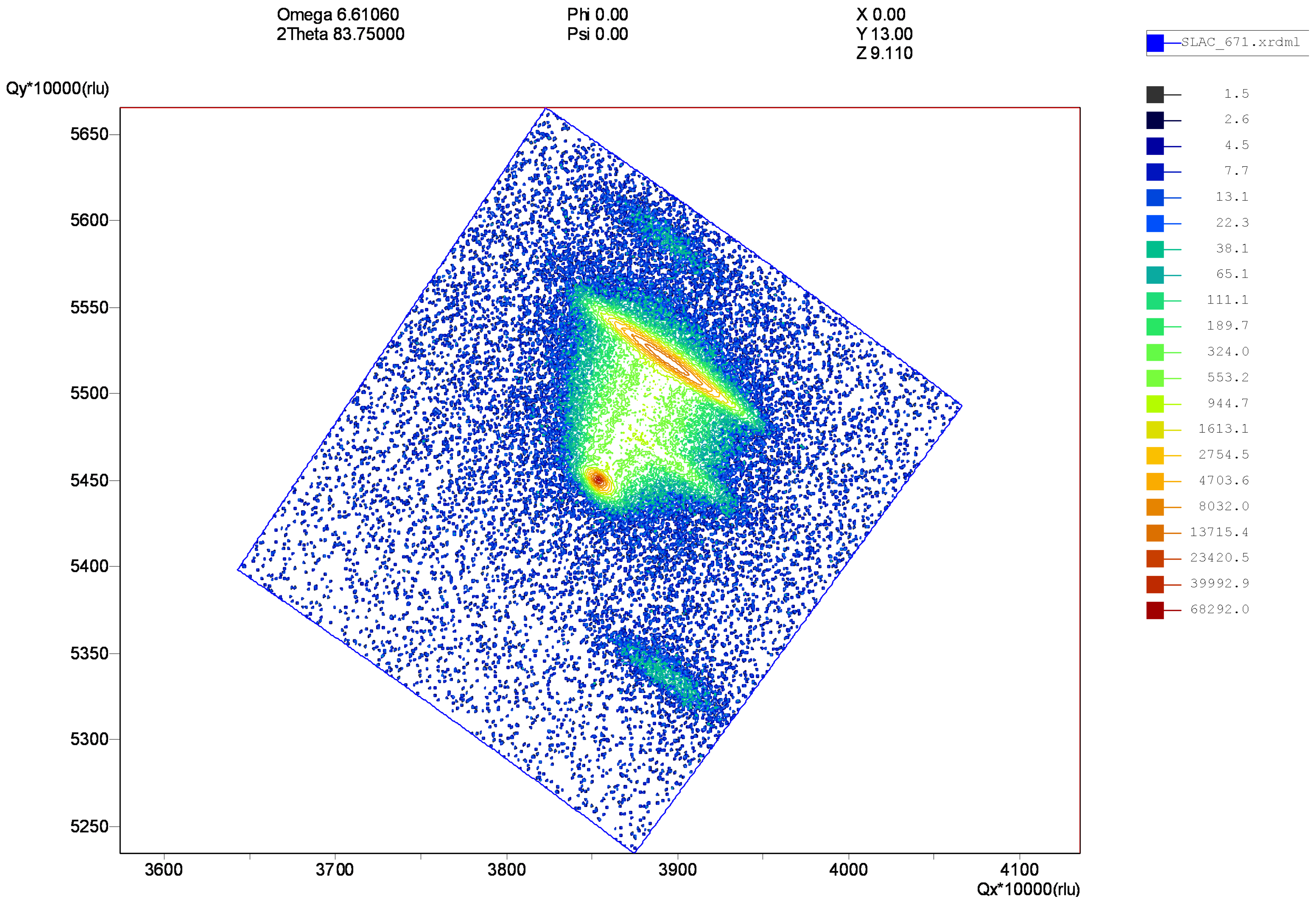
counts/s
10M
1M
100K
10K
1K
100
10
61
62
63
64
65
66
67
68
69
70
71
2Theta/Omega (°)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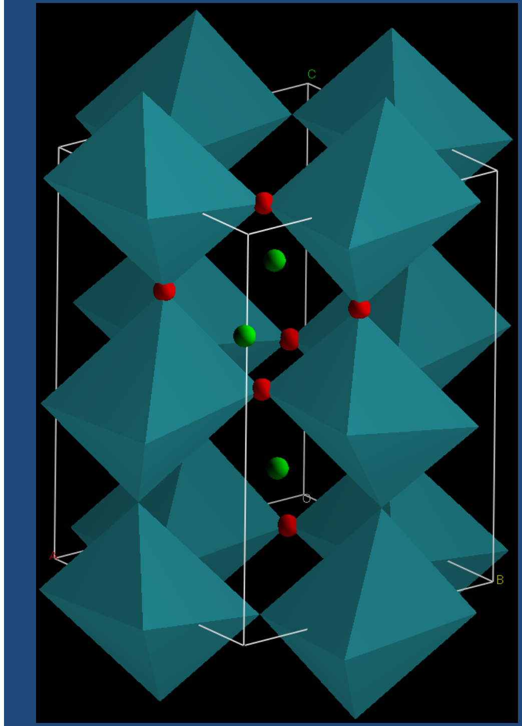
5650
5600
5550
5500
5450
5400
5350
5300
5250
3600
3700
3800
3900
4000
4100
Qx*10000(rlu)
1.5
2.6
4.5
7.7
13.1
22.3
38.1
65.1
111.1
189.7
324.0
553.2
944.7
1613.1
2754.5
4703.6
8032.0
13715.4
23420.5
39992.9
68292.0

Structure of $SrRuO_3$

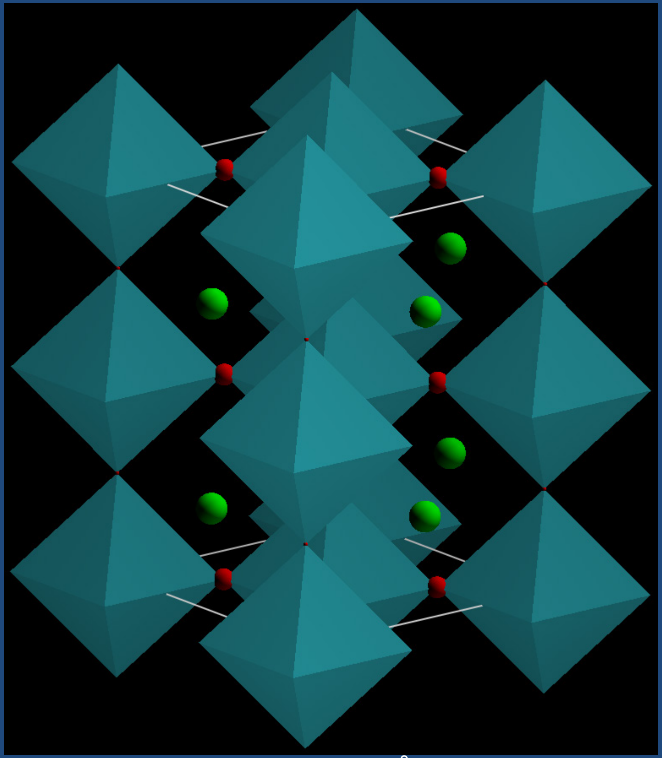
Orthorhombic



a = 5.586 Å
b = 5.555 Å
c = 7.865 Å

→ 275-550 °C

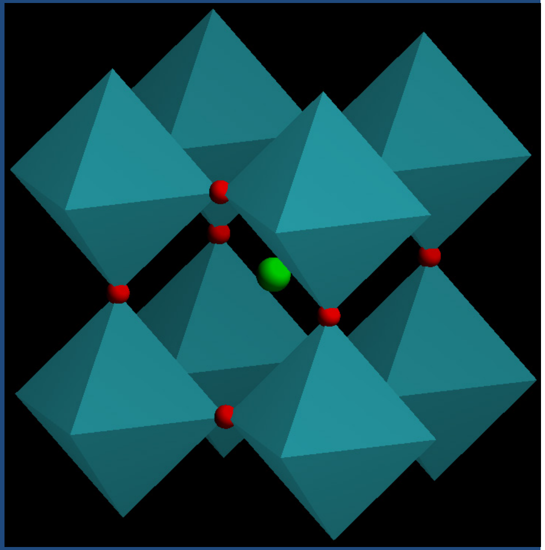
Tetragonal



a = 5.578 Å
c = 7.908 Å

→ 510-702 °C

Cubic



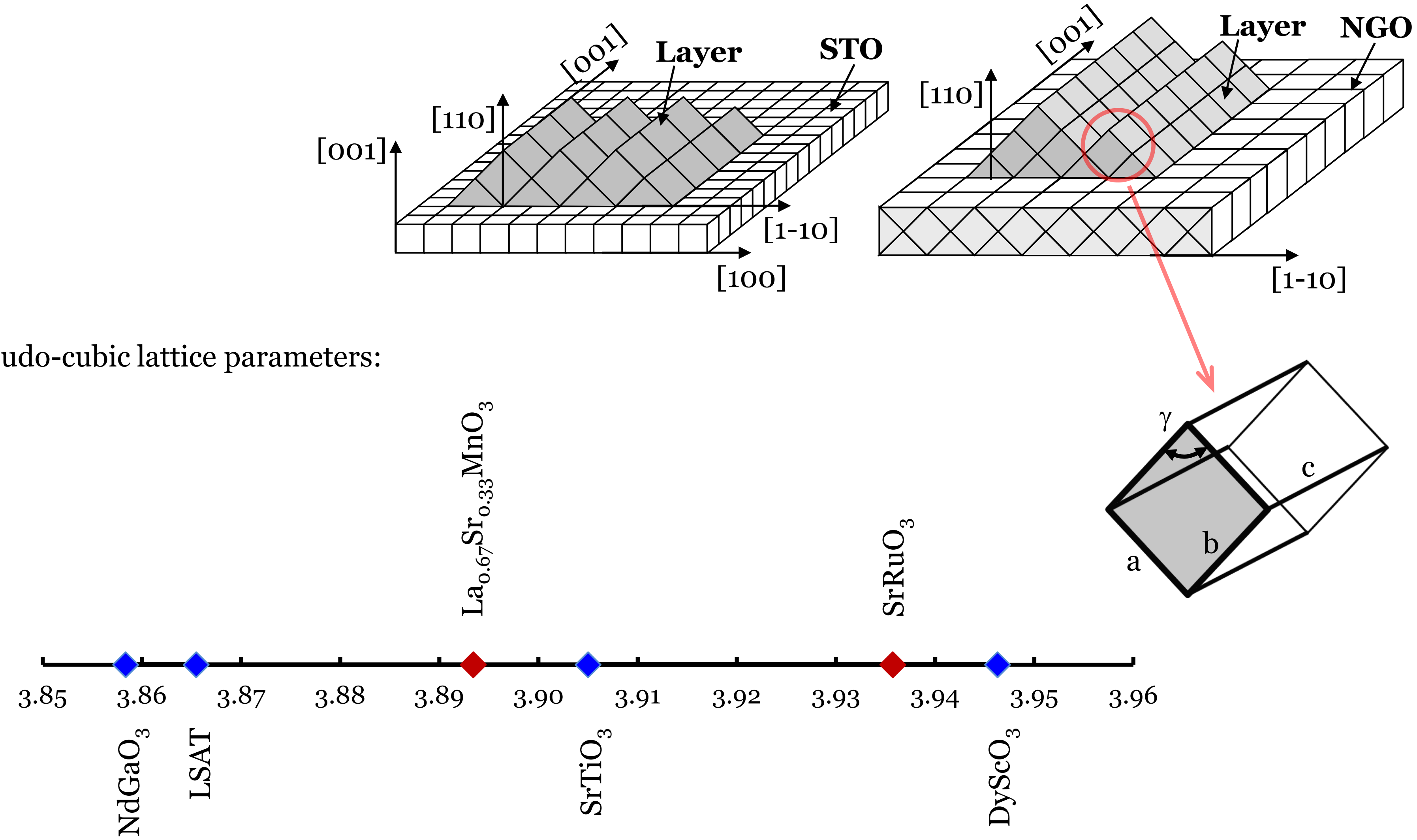
a = 3.956 Å

Samples:

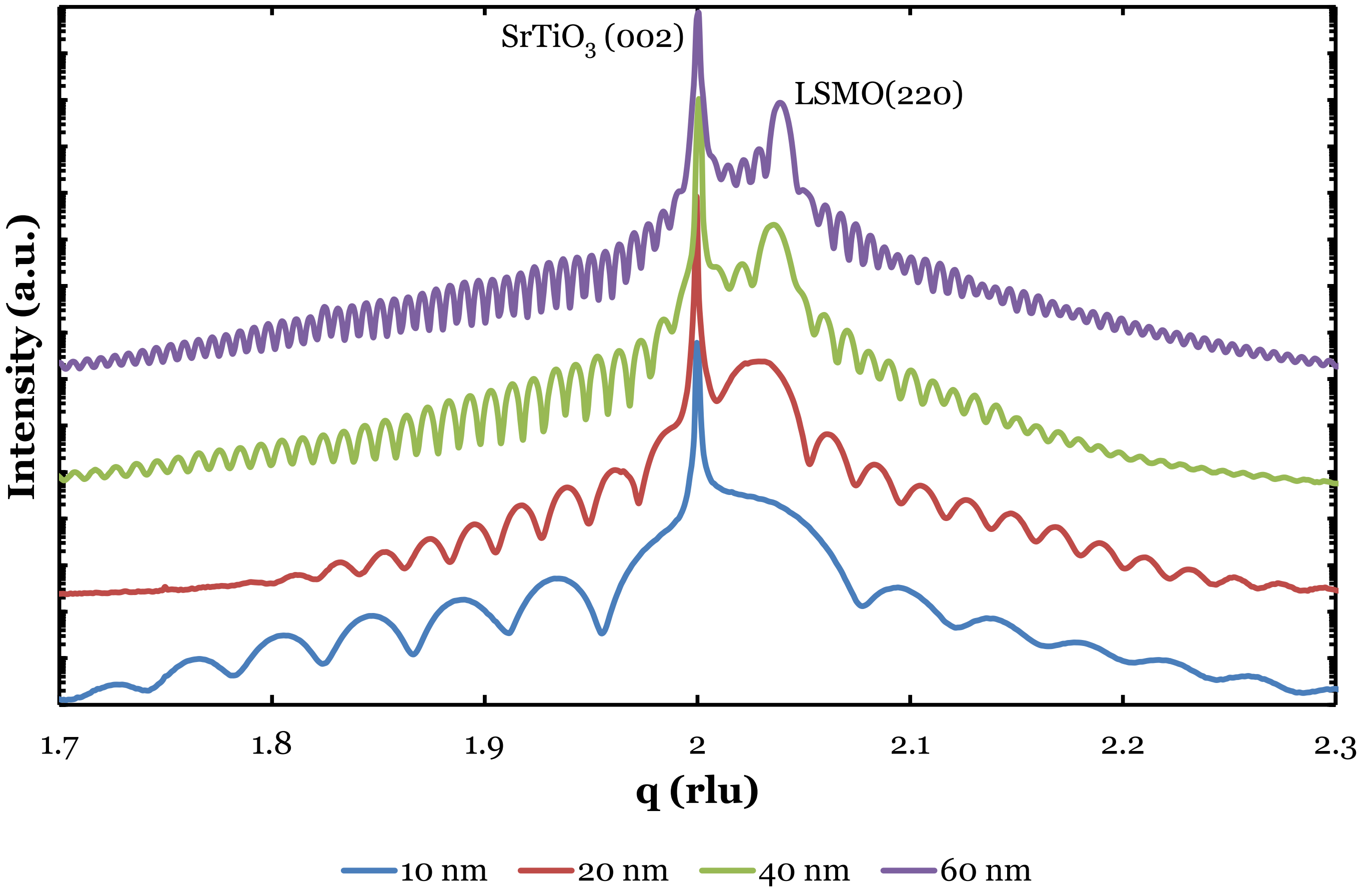
$SrRuO_3$ on $SrTiO_3$ and $DyScO_3$

$La_{0.67}Sr_{0.33}MnO_3$ on $NdGaO_3$, LSAT, $SrTiO_3$ and $DyScO_3$

Pseudo-cubic lattice parameters:

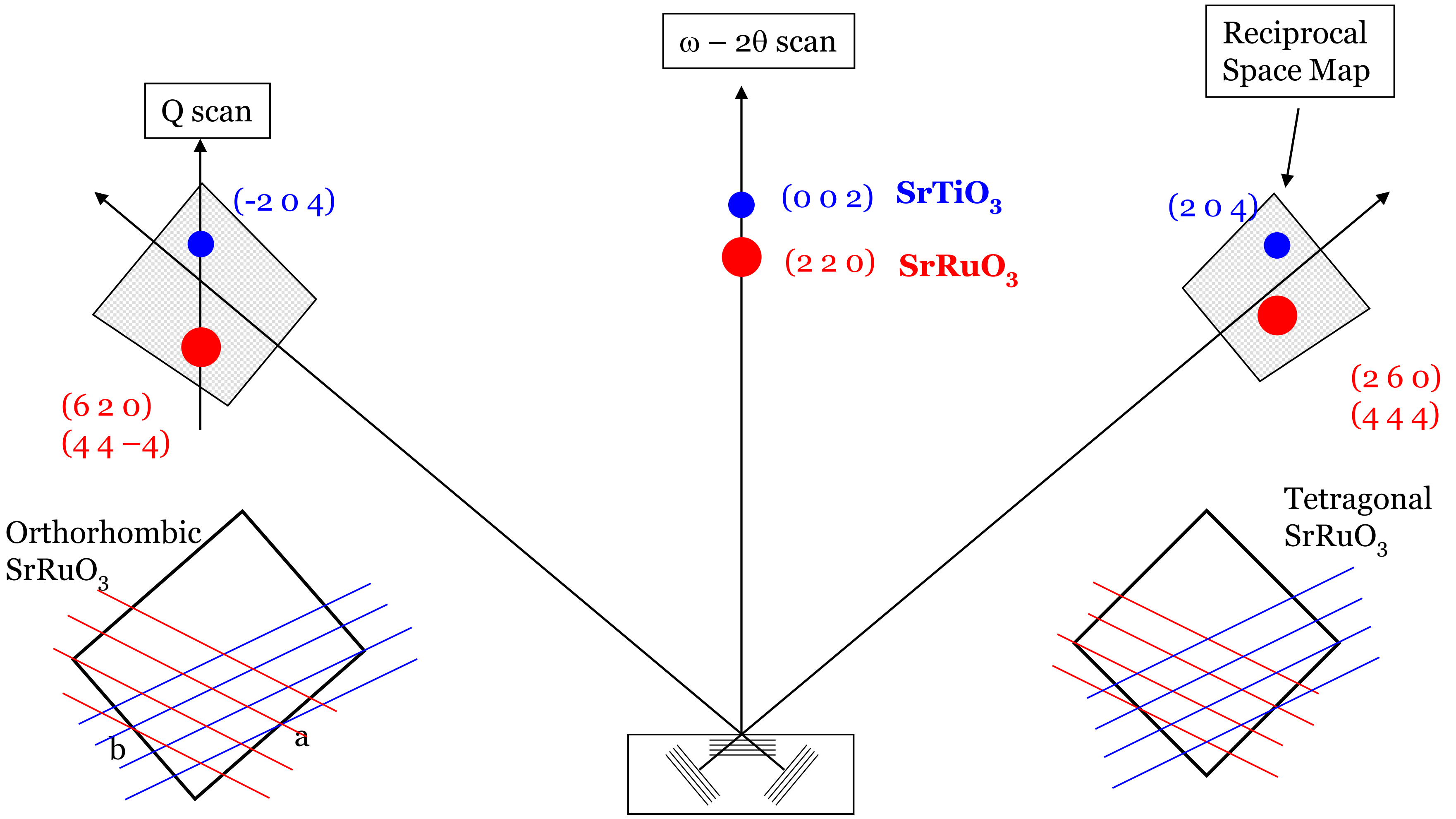


Symmetrical scans along STO[001] direction



Finite thickness fringes around the Bragg peak indicate very good structural quality throughout the film

X-ray diffraction scan types for [110] growth



Q scan

$\omega - 2\theta$ scan

Reciprocal Space Map

(-2 0 4)

(0 0 2) **$SrTiO_3$**

(2 2 0) **$SrRuO_3$**

(2 0 4)

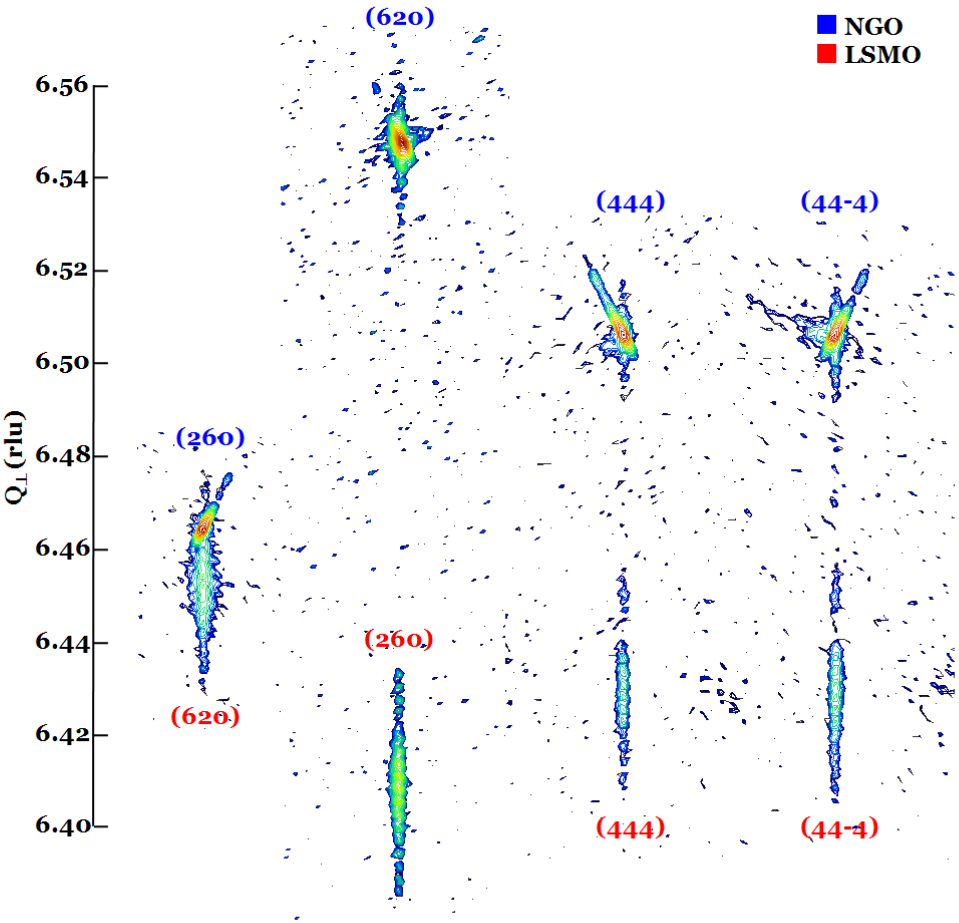
(6 2 0)
(4 4 −4)

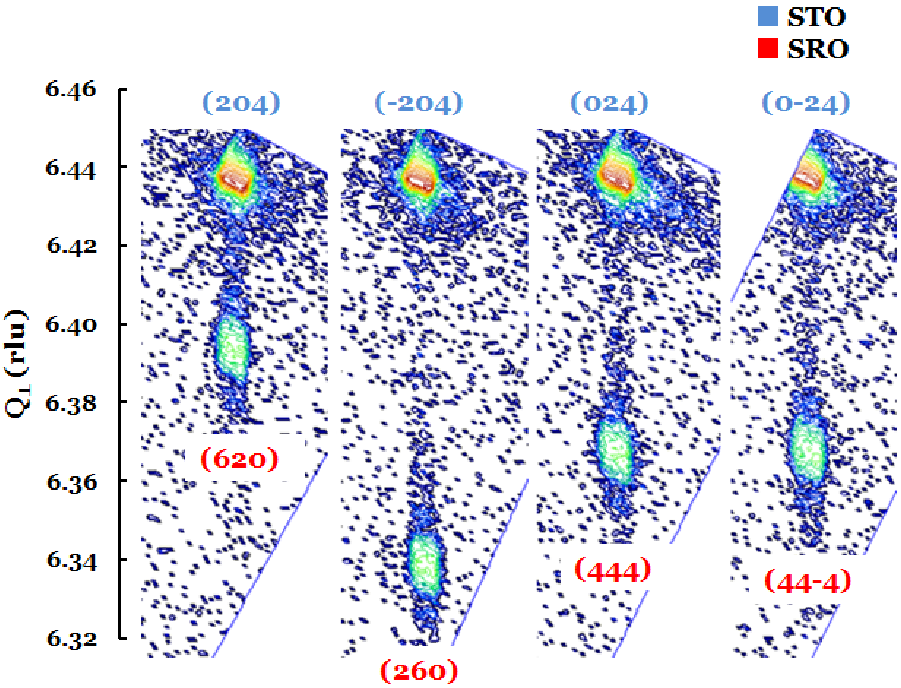
(2 6 0)
(4 4 4)

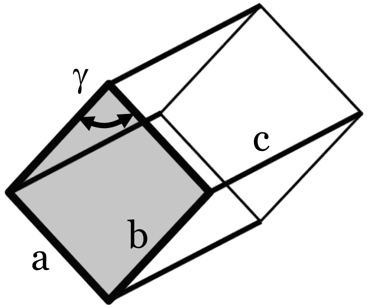
Orthorhombic $SrRuO_3$

Tetragonal $SrRuO_3$

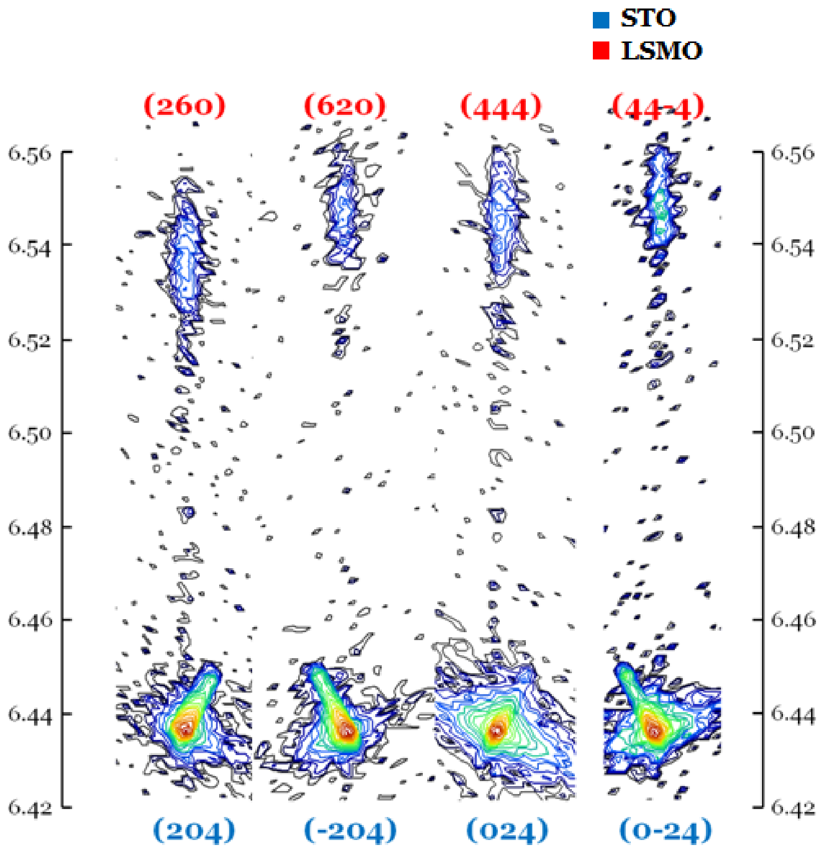
Compressive Stress $\xrightarrow{a \neq b}$ Unit cell is orthorhombic

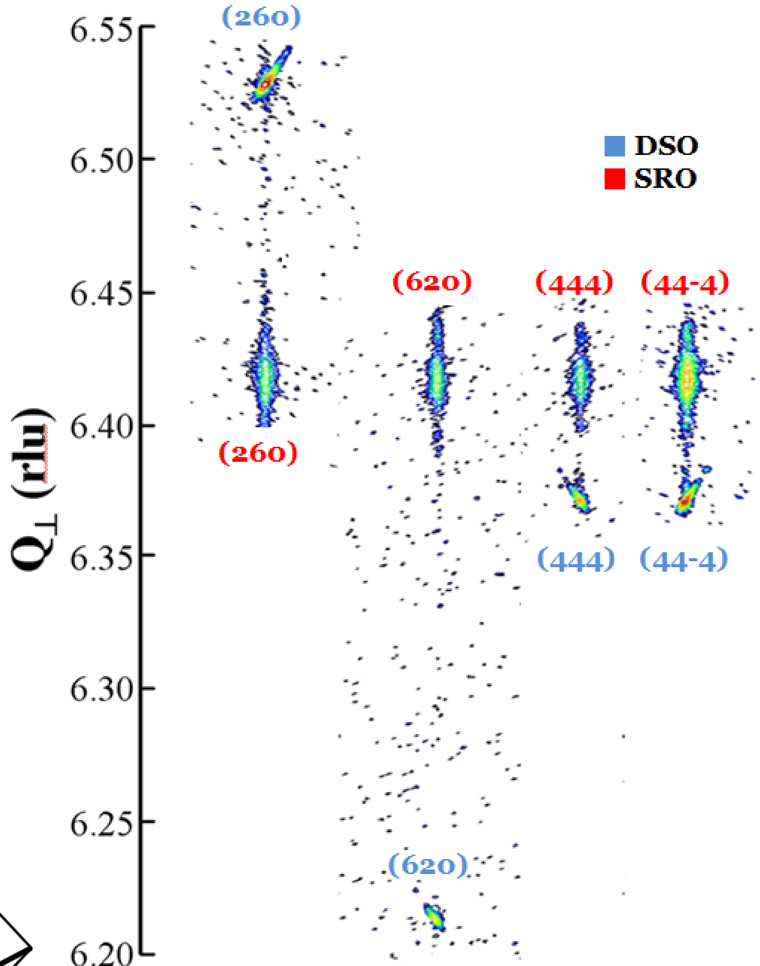


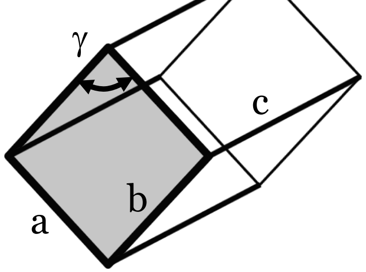




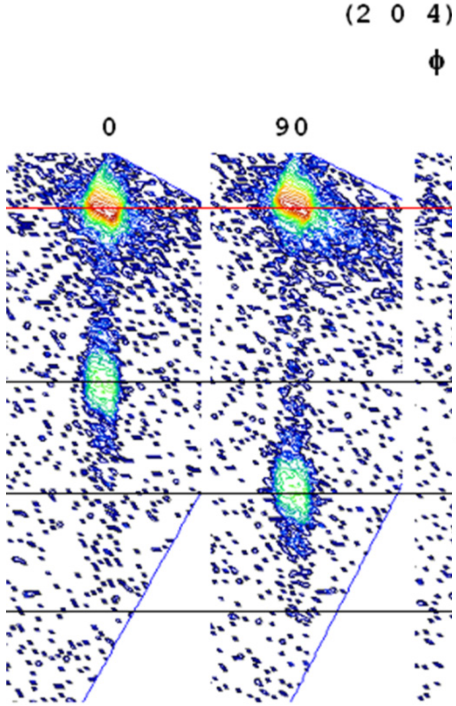
Tensile Stress → a = b → Unit cell is tetragonal

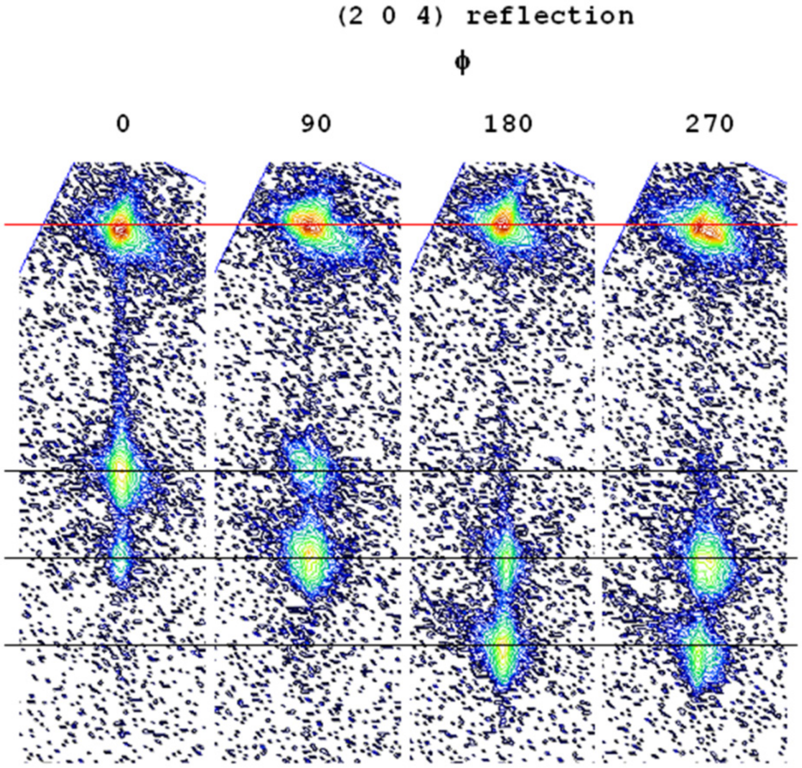


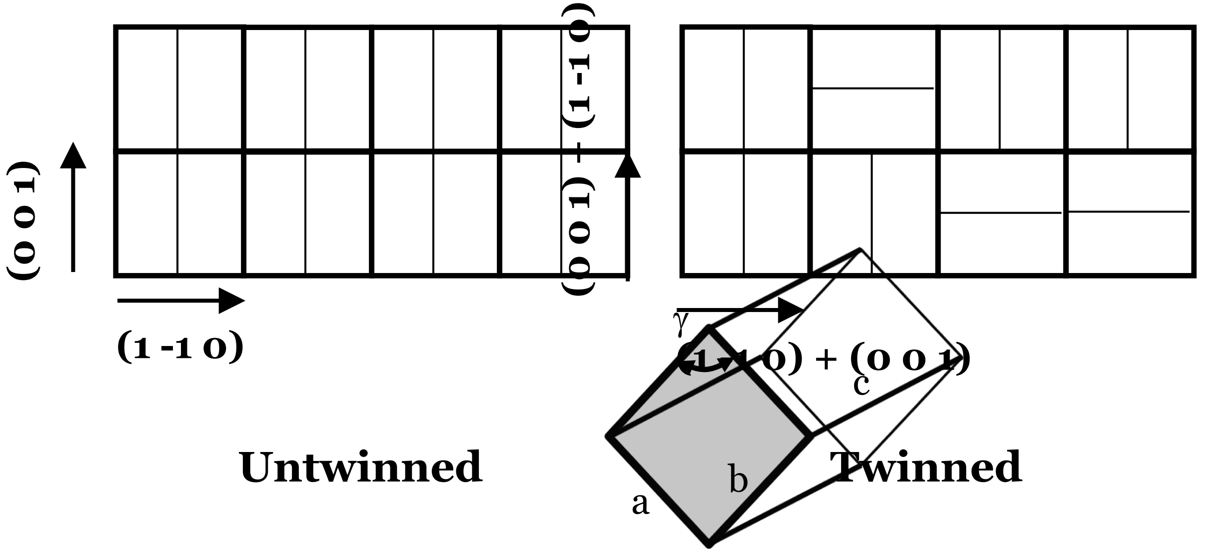




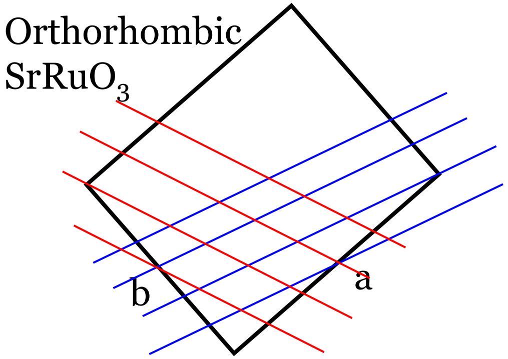
Twinning in $SrRuO_3/SrTiO_3$

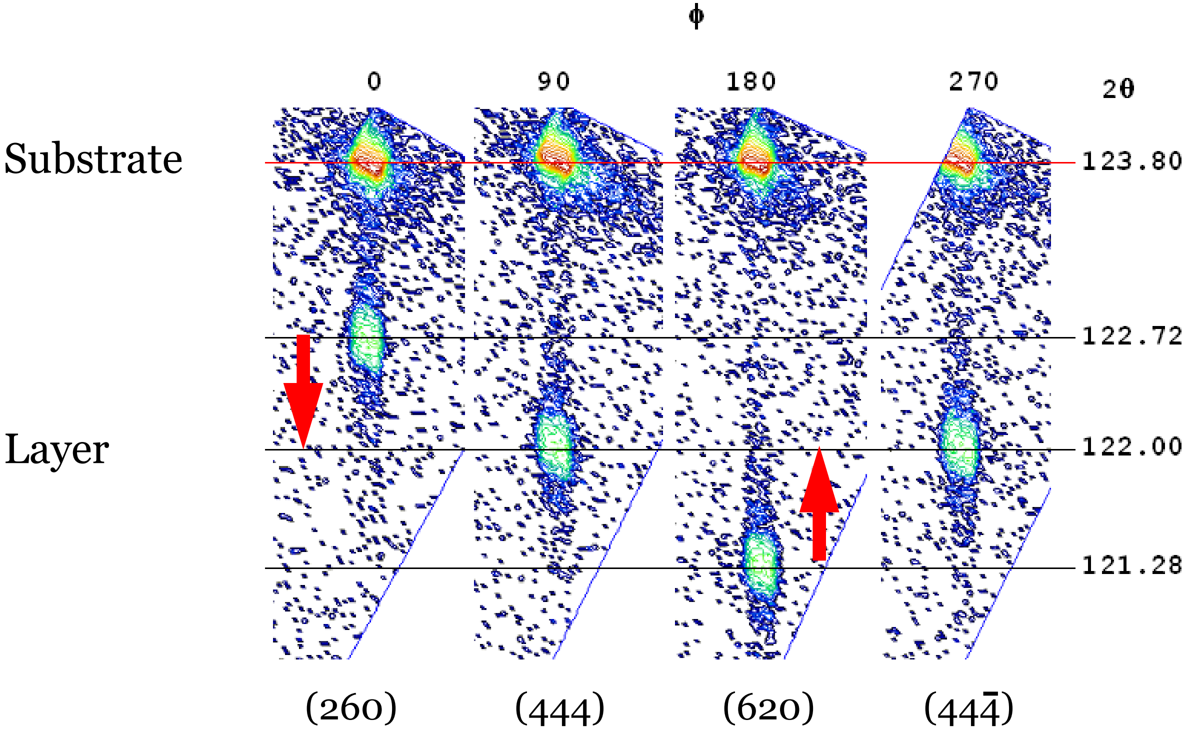






High-Resolution Reciprocal Area Mapping

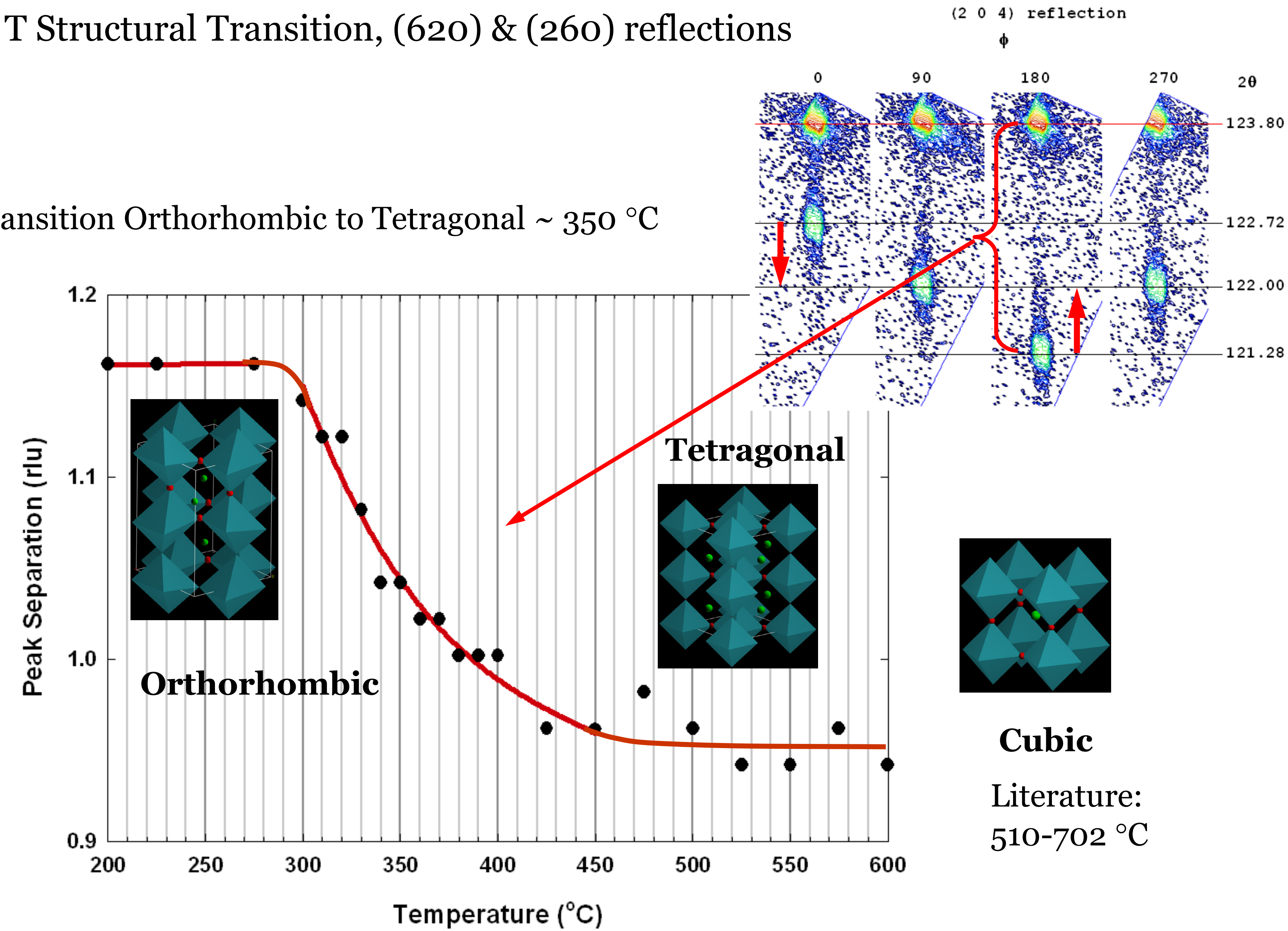




Orthorhombic to Tetragonal Transition

O – T Structural Transition, (620) & (260) reflections

Transition Orthorhombic to Tetragonal ~ 350 °C



Orthorhombic

Tetragonal

Cubic

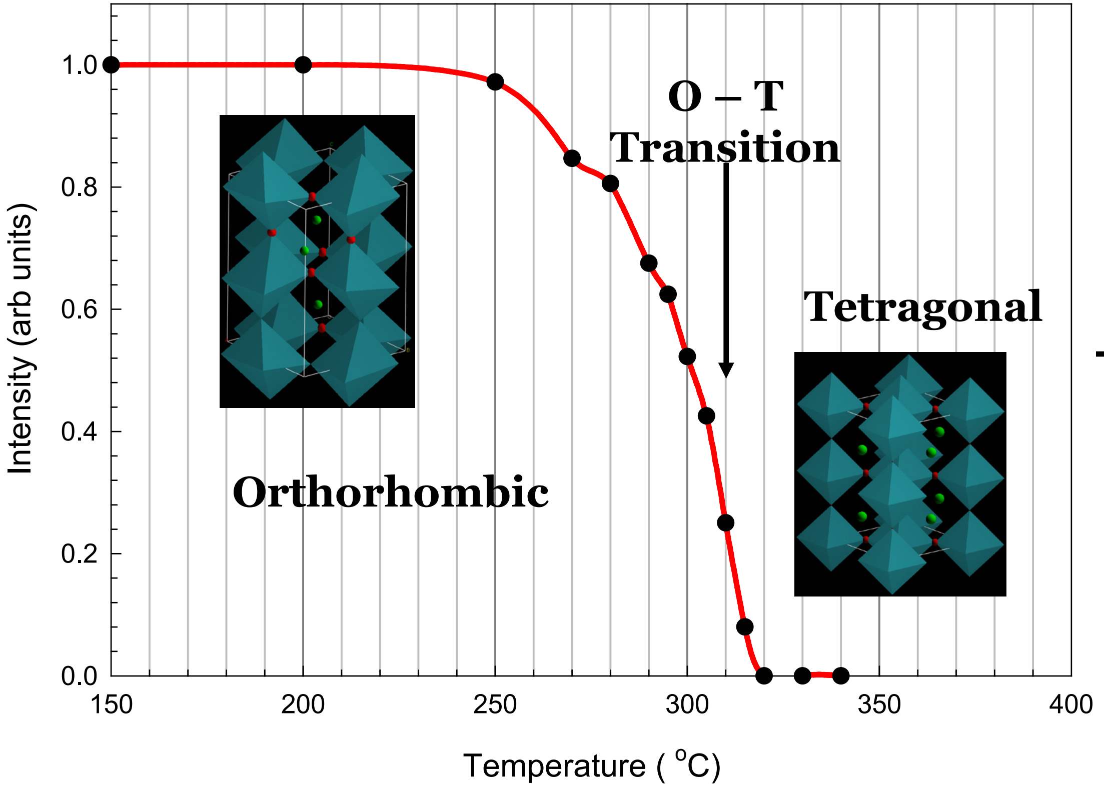
Literature:
510-702 °C

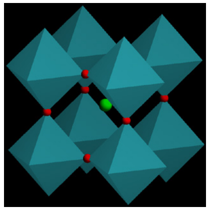
Appl. Phys. Lett. **91**, 071907 (2007)

O – T Structural Transition, (221) reflection

(221) Peak	
Orthorhombic	**Present**
Tetragonal	**Absent**

Transition Orthorhombic to Tetragonal ~ 310 °C

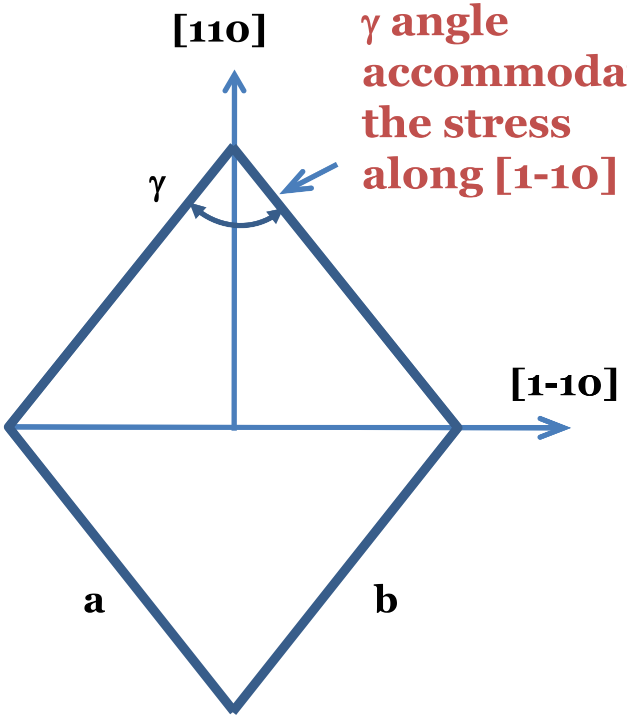




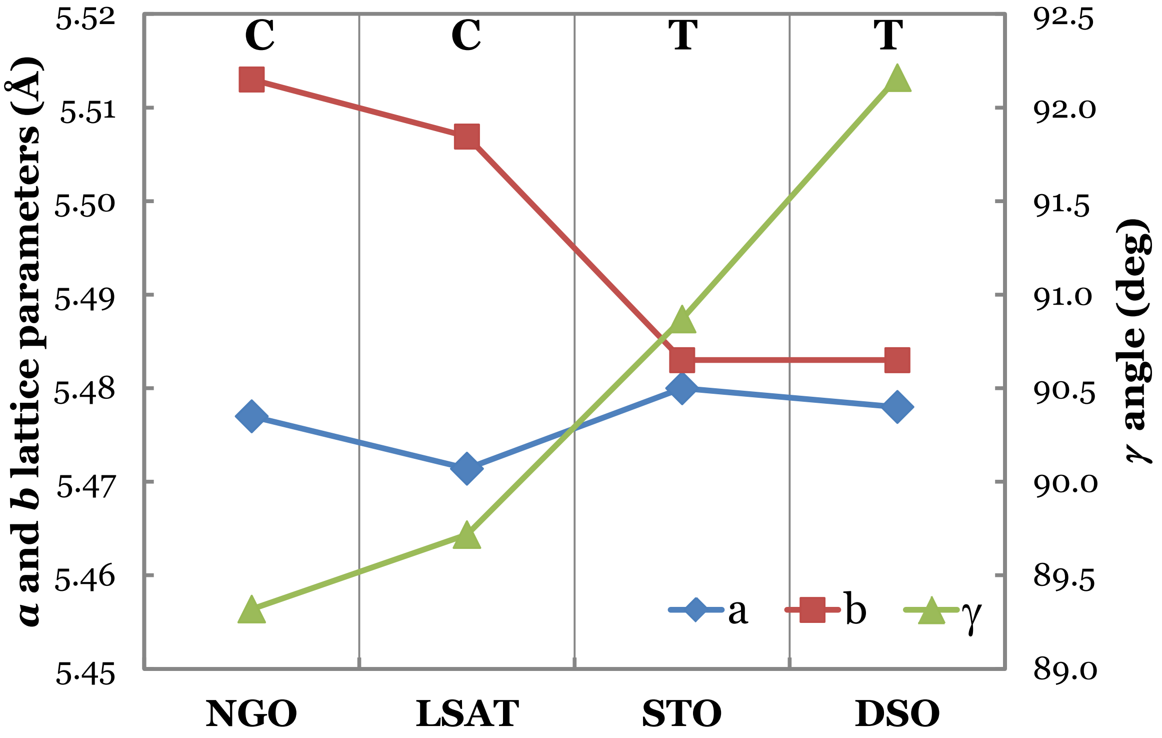
Cubic

Literature:
510-702 °C

Appl. Phys. Lett. **91**, 071907 (2007)

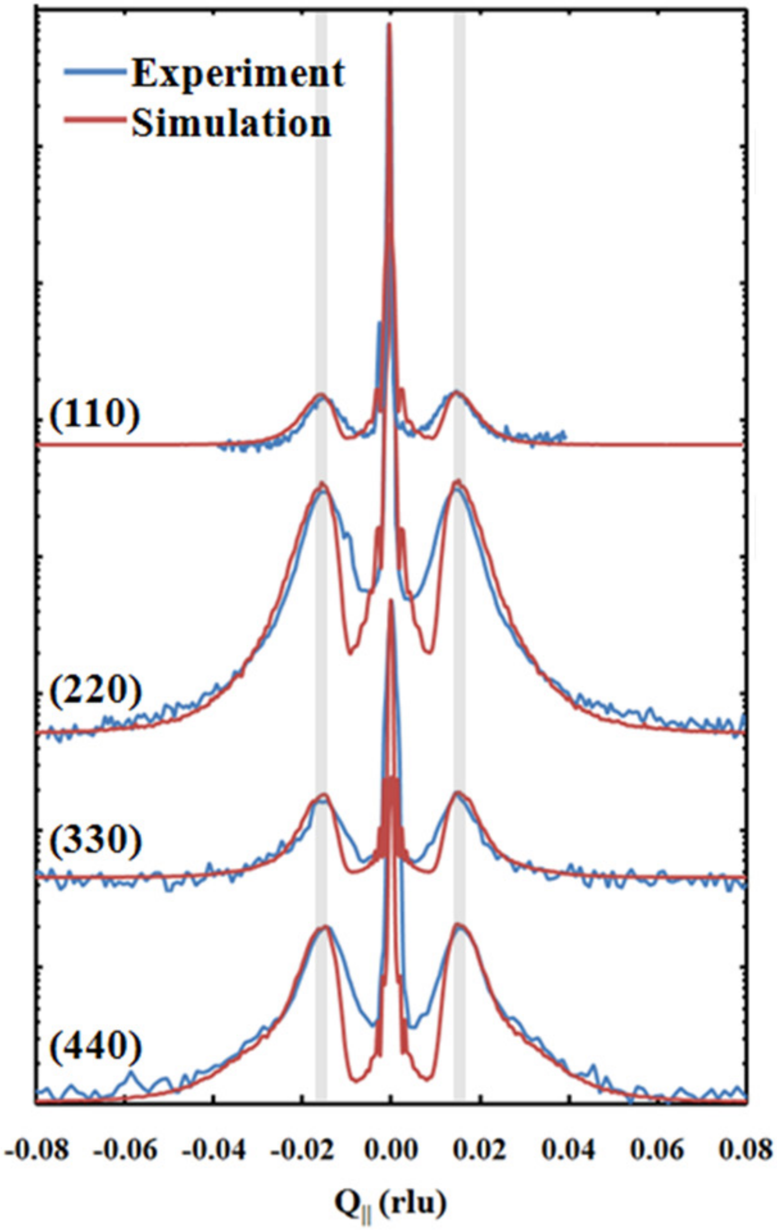


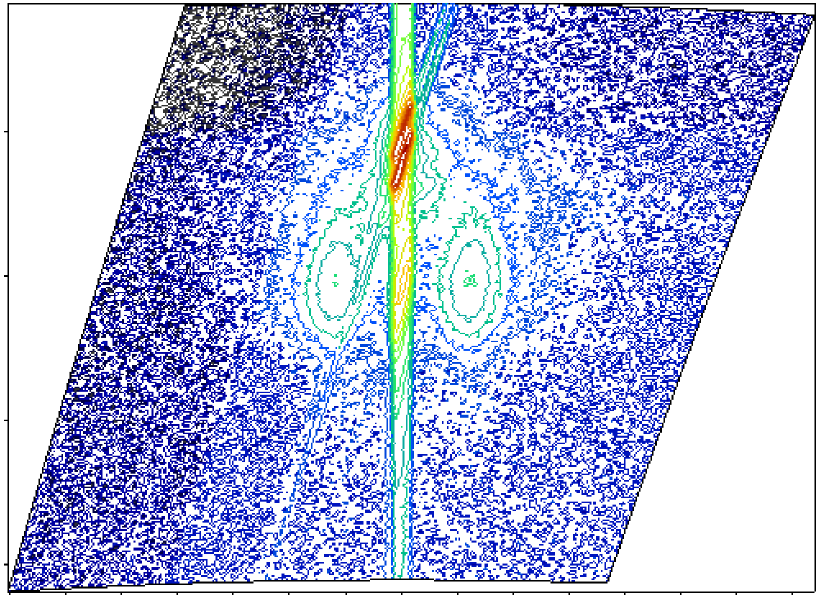
γ angle accommodates the stress along [1-10]

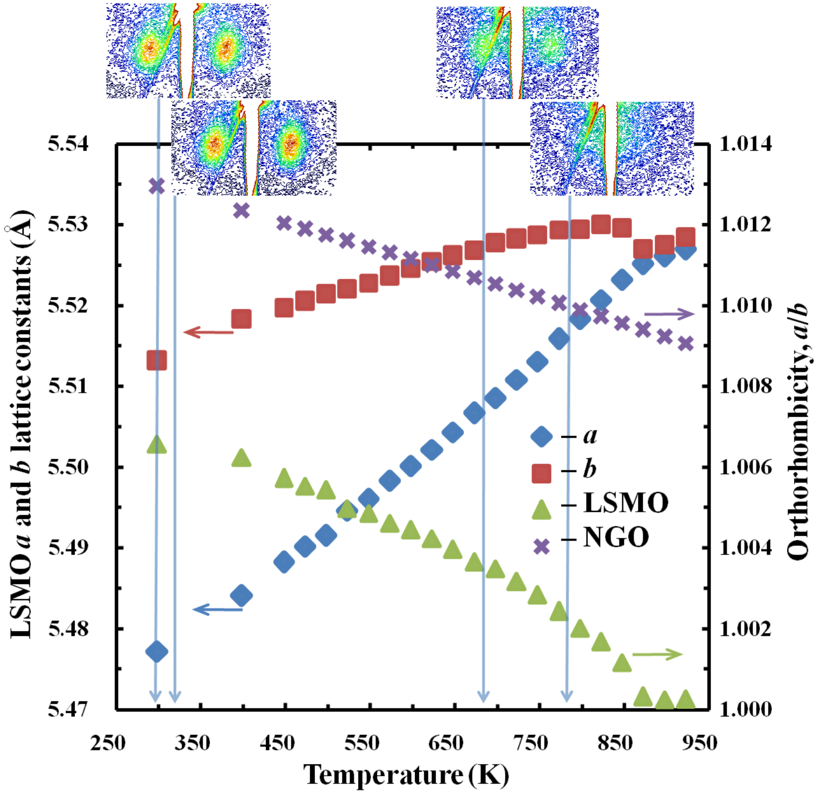


Substrate	a (Å)	b (Å)	ab (Å)	c (Å)	Layer	a (Å)	b (Å)	ab (Å)	c (Å)	γ (°)
$NdGaO_3$	5.428	5.498	7.726	7.708	LSMO/NGO	5.477	5.513	7.725	7.707	89.32
LSAT	5.476	5.476	7.744	7.740	LSMO/LSAT	5.471	5.507	7.744	7.740	89.72
$SrTiO_3$	3.905				LSMO/STO	5.480	5.483	7.809	7.809	90.87
$DyScO_3$	5.444	5.721	7.897	7.904	LSMO/DSO	5.478	5.483	7.895	7.902	92.16
LSMO (O)	5.488	5.524	7.762	7.787						

Strain (%)			
$NdGaO_3$	LSAT	$SrTiO_3$	$DyScO_3$
along ab = -0.79 along c = -1.02	along ab = -0.55 along c = -0.60	along ab = 0.28 along c = 0.28	along ab = 1.39 along c = 1.48



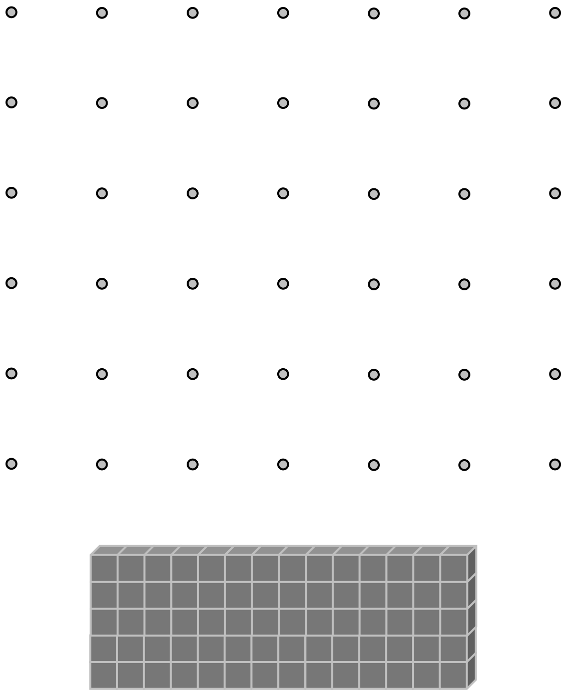




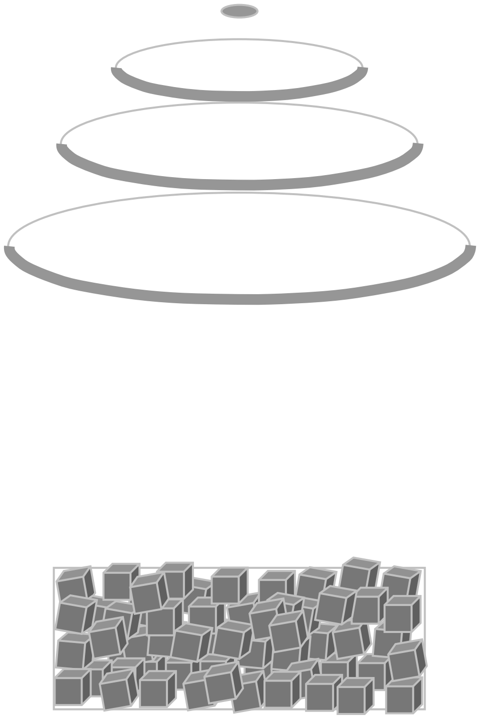
Appl. Phys. Lett. **95**, 152508 (2009)

Summary

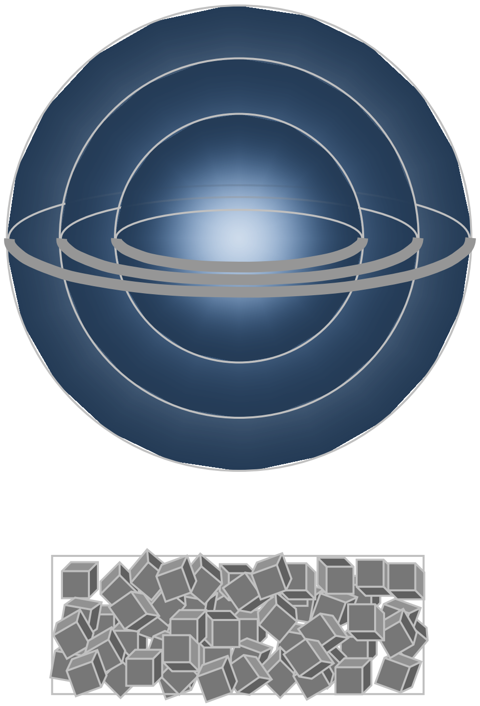
- Reciprocal space for epitaxial thin films is very rich.
- Shape and positions of reciprocal lattice points with respect to the substrate reveal information about:
  - Mismatch
  - Strain state
  - Relaxation
  - Mosaicity
  - Composition
  - Thickness ….
- Diffractometer instrumental resolution has to be understood before measurements are performed.



Single crystal



Preferred orientation



Polycrystalline