Thin Film Scattering: Epitaxial Layers

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

Tuesday, May 16 & Wednesday, May 17, 2006

- 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 sometimes we need channel analyzer
- What can we learn from reciprocal space maps
- $SrRuO_3$(110) on $SrTiO_3$(001) 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"

What we want to know about thin films?

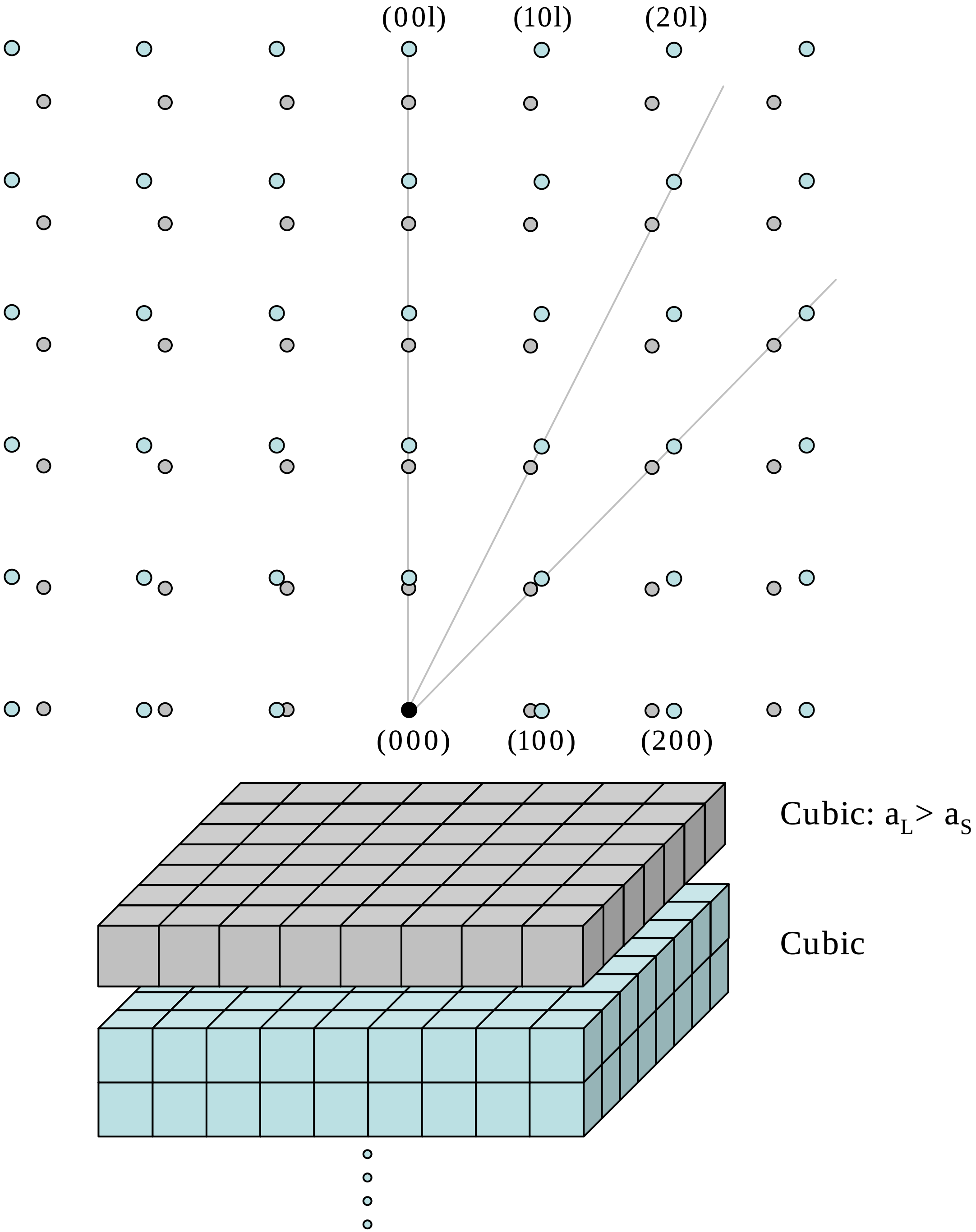
- Crystalline state of the layers:
  - Epitaxial (coherent with the substrate, relaxed)
  - Polycrystalline (random orientation, preferred orientation)
  - Amorphous
- Crystalline quality
- Strain state (fully or partially strained, fully relaxed)
- Defect structure
- Chemical composition
- Thickness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

Overview of structural parameters that characterize various thin films

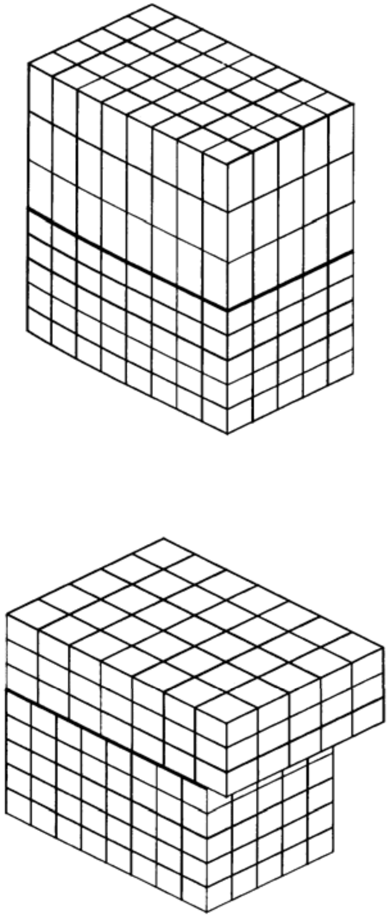
	Thickness	Composition	Relaxation	Distortion	Crystalline size	Orientation	Defects
Perfect epitaxy	×	×				×	
Nearly perfect epitaxy	×	×	?	?	?	×	×
Textured epitaxy	×	×	×	×	×	×	×
Textured polycrystalline	×	×	?	×	×	×	?
Perfect polycrystalline	×	×		×	×		?
Amorphous	×	×					

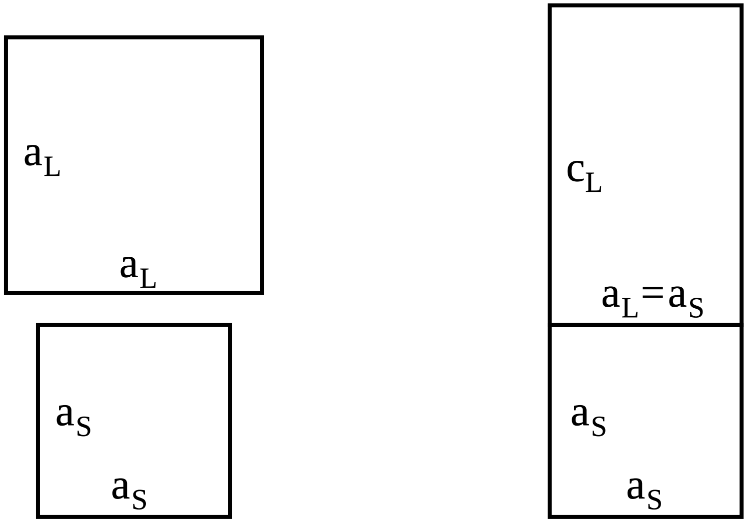
P.F. Fewster “X-ray Scattering from Semiconductors”

Relaxed Layer



Tetragonal Distortion



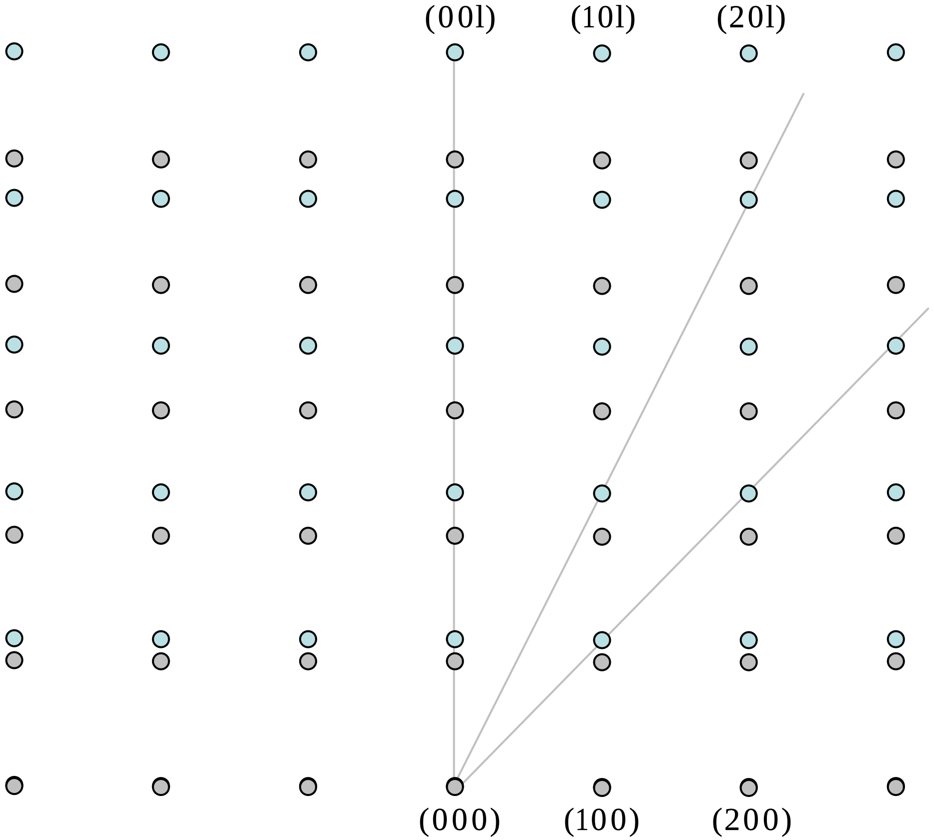


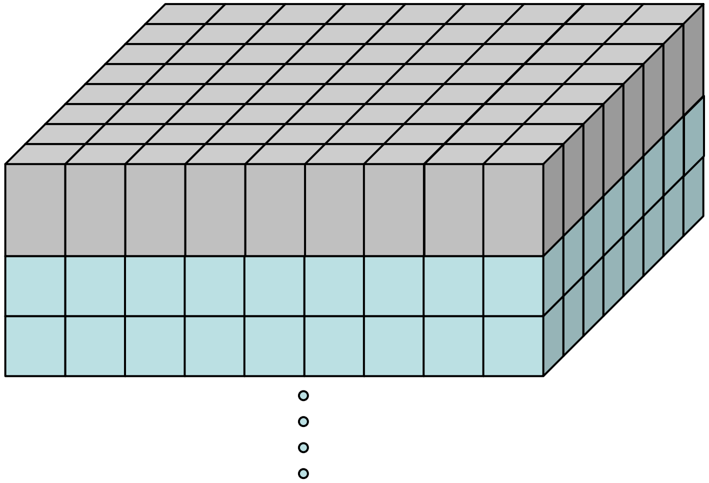
Before deposition

After deposition

$$\varepsilon_\perp = \varepsilon_{zz} = \frac{d_z^L - d_z^{L_0}}{d_z^{L_0}}$$

Strained Layer



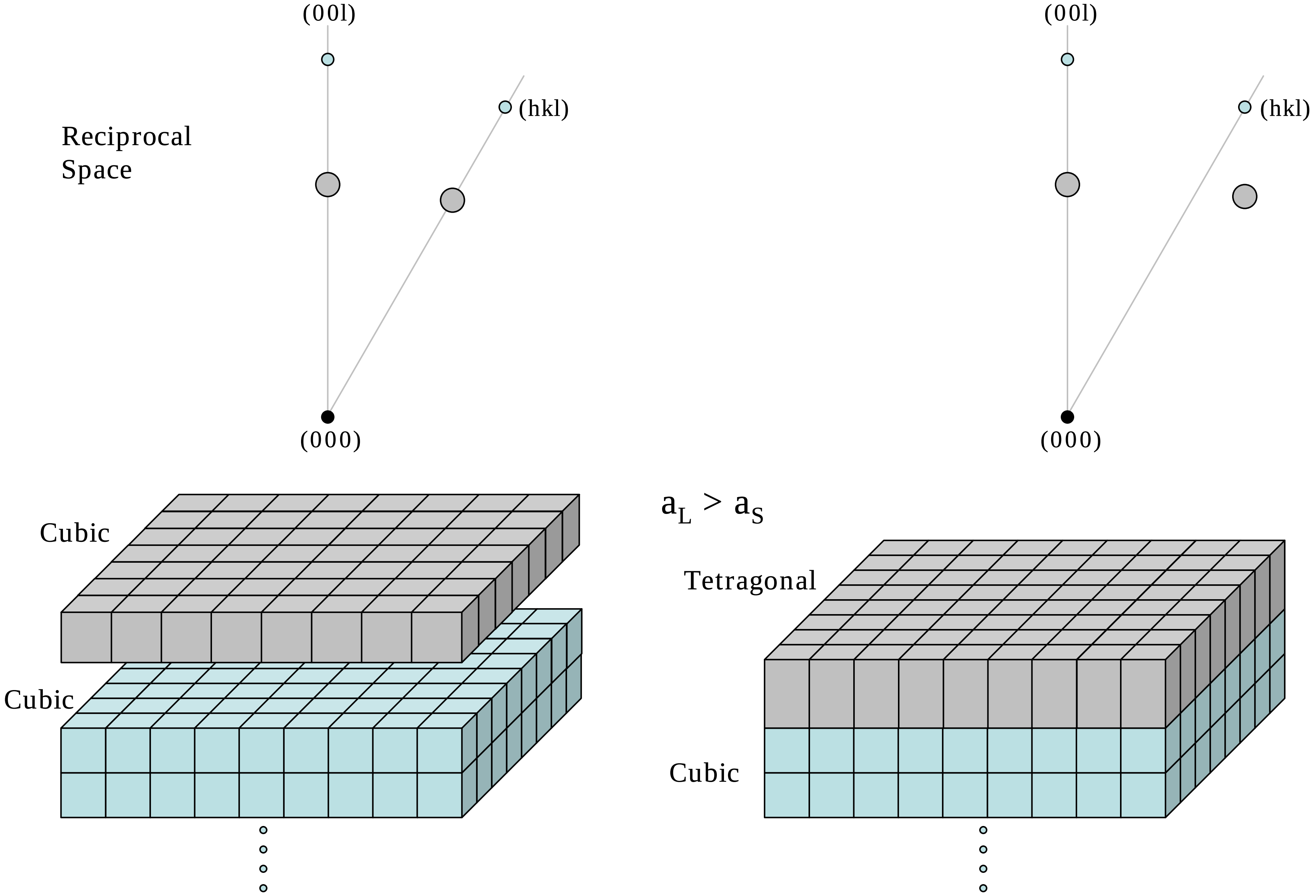


Tetragonal distortion

Tetragonal: $a^{II}_L = a_S$, $a^{\perp}_L > a_S$

Cubic

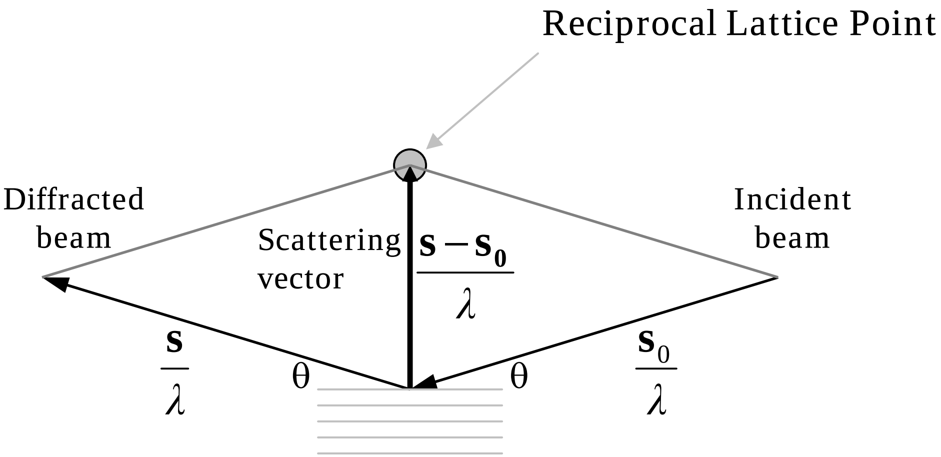
Perfect Layers: Relaxed and Strained

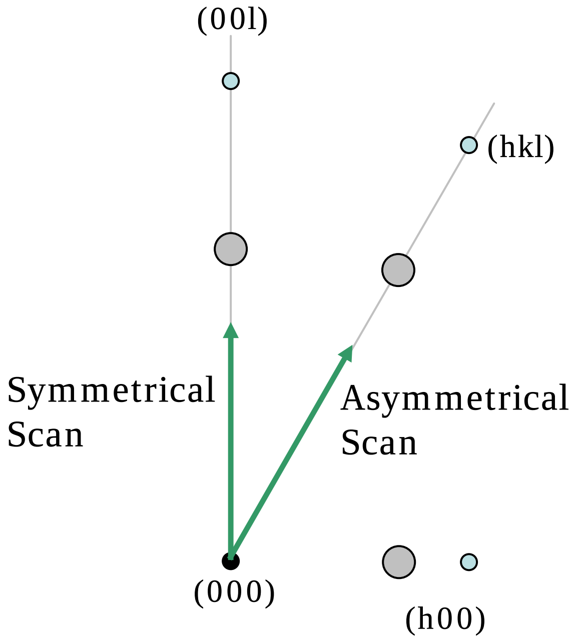


Scan Directions

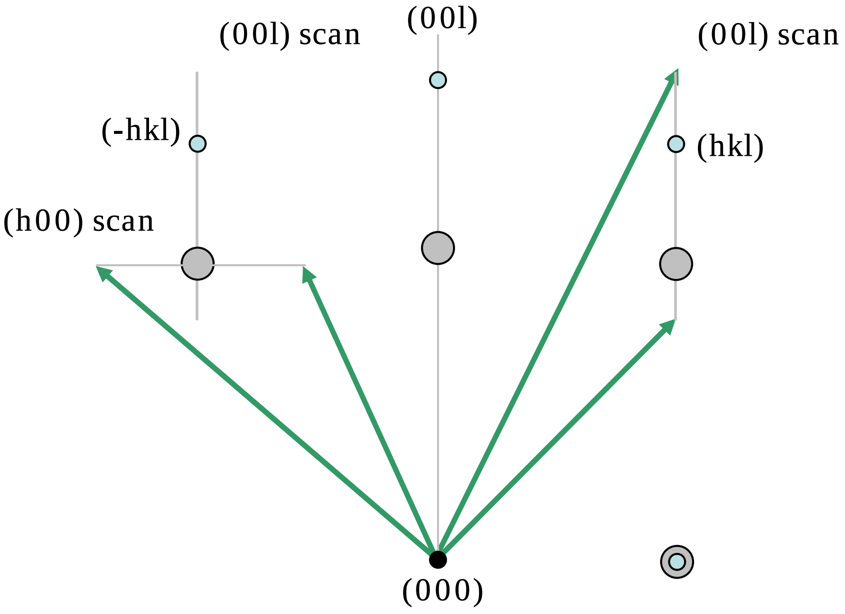
$$\left|\frac{\mathbf{s}-\mathbf{s}_0}{\lambda}\right| = \frac{2\sin\theta}{\lambda} = \left|\mathbf{d}^{*}_{hkl}\right| = \frac{1}{d_{hkl}}$$

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



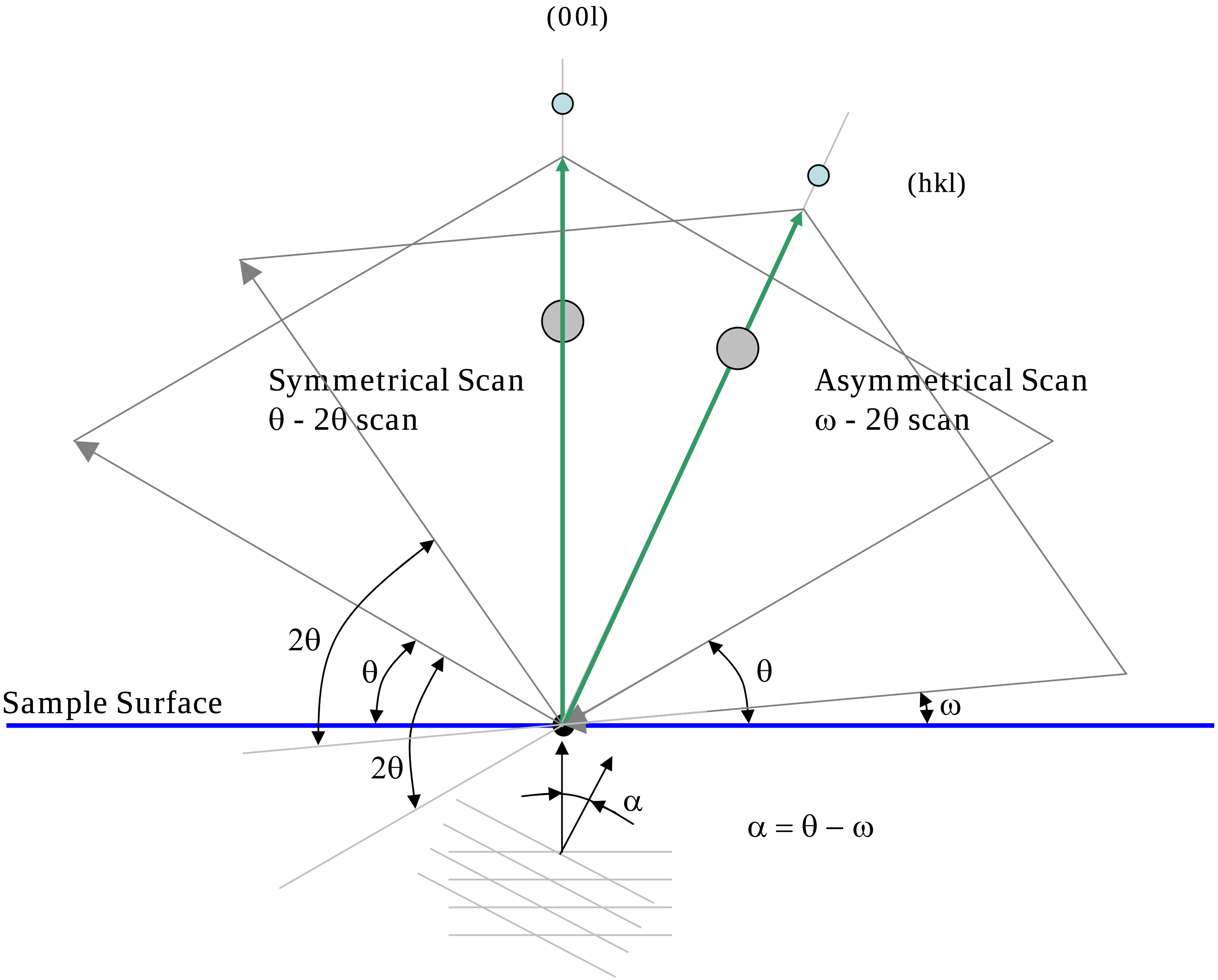


Relaxed Layer



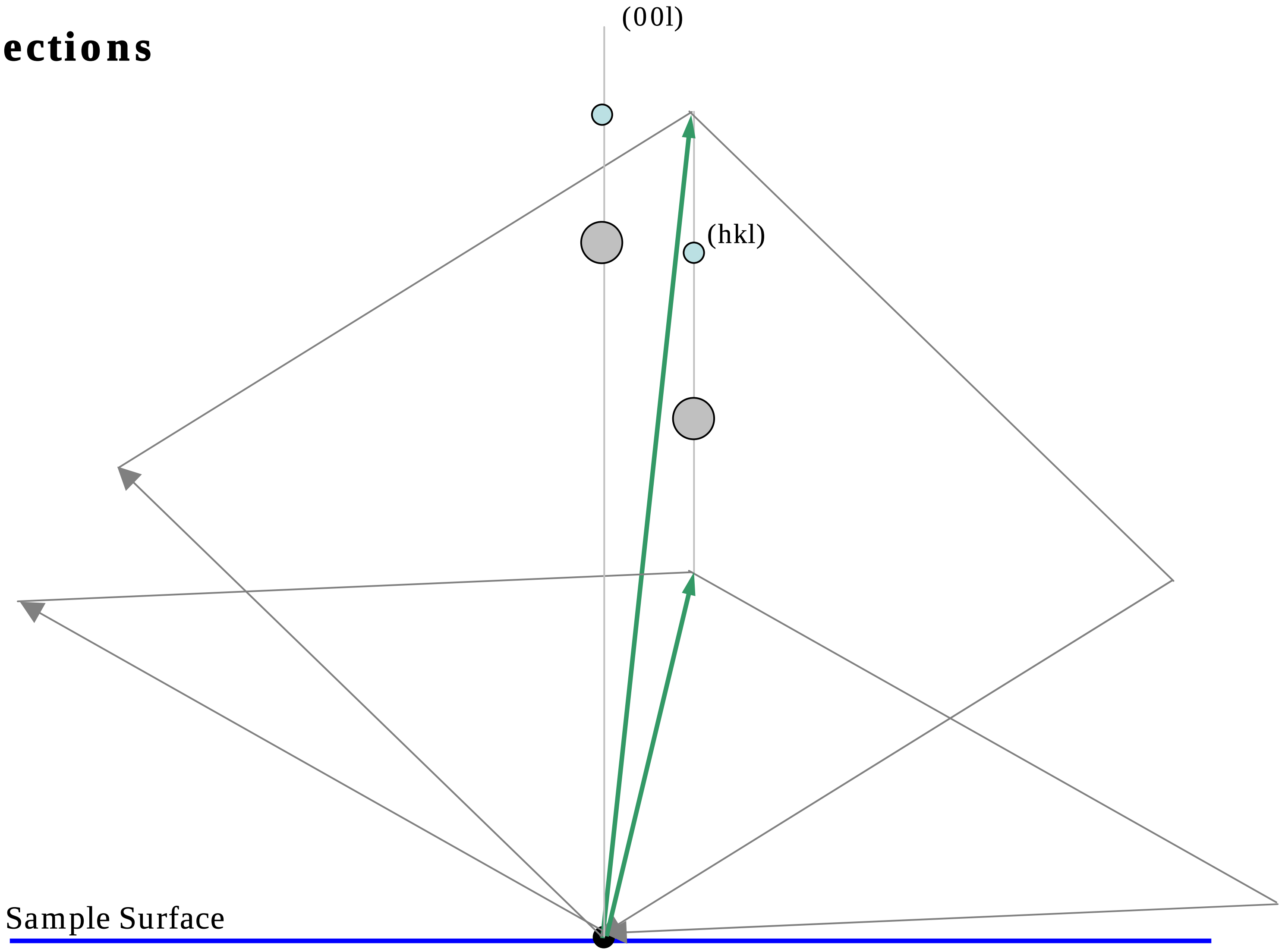
Strained Layer

Scan Directions

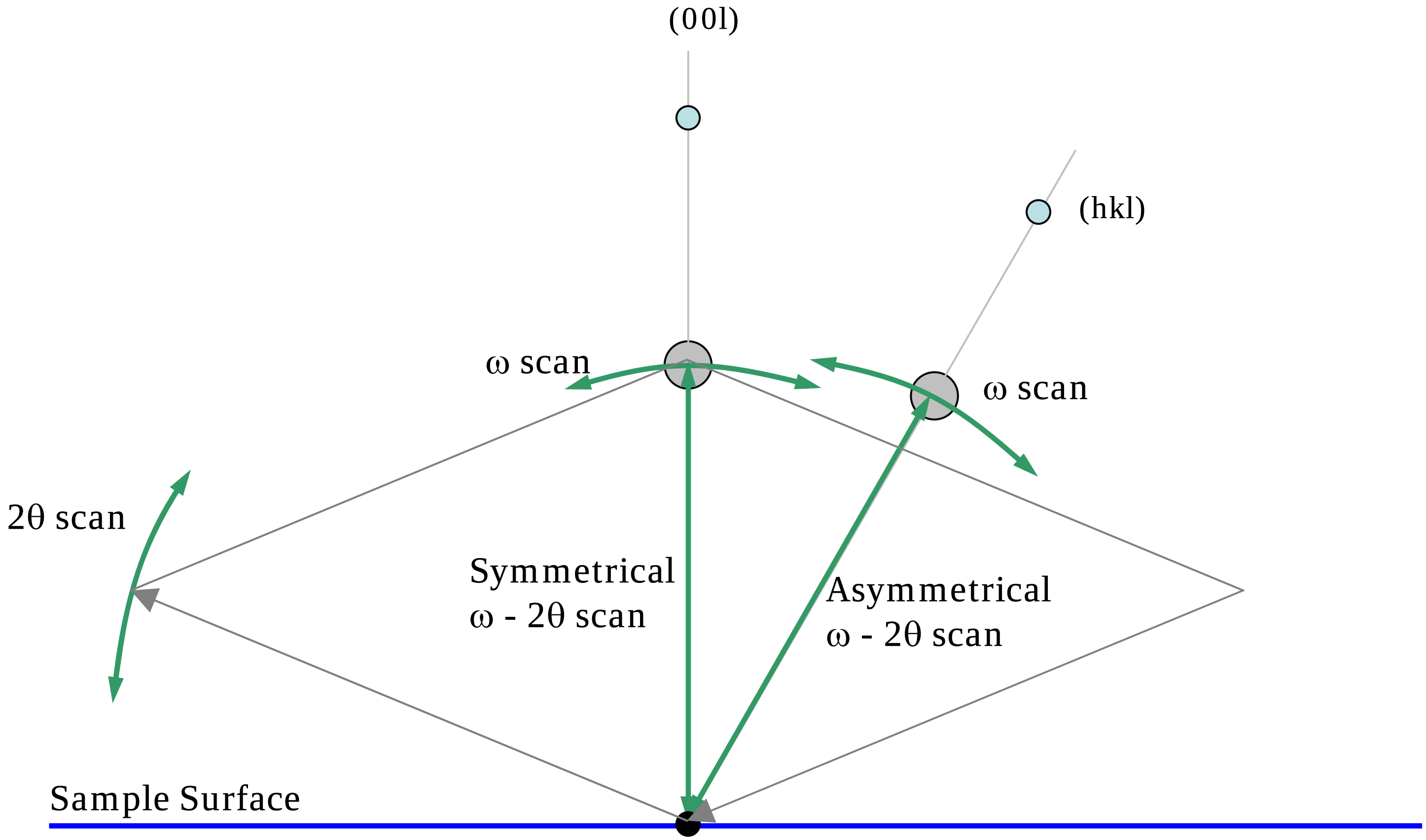


$\alpha = \theta - \omega$

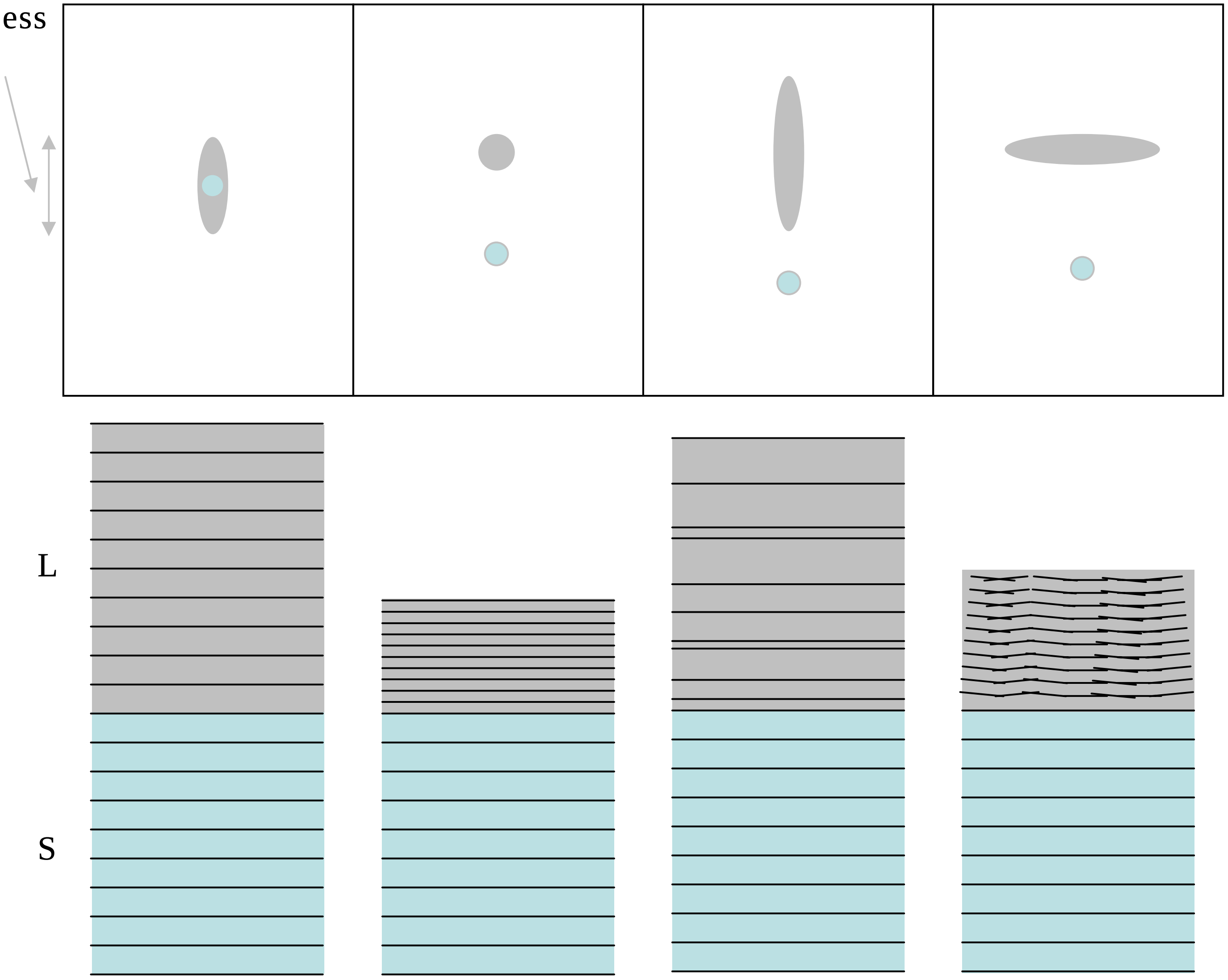
Scan Directions



Scan directions



Real RLP shapes



$c_L < a_S$

Finite thickness effect

L

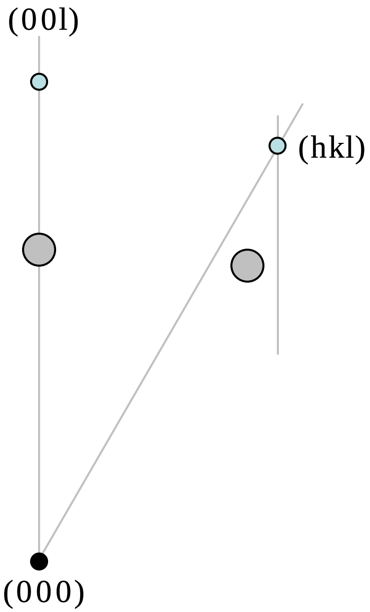
S

Homoepitaxy

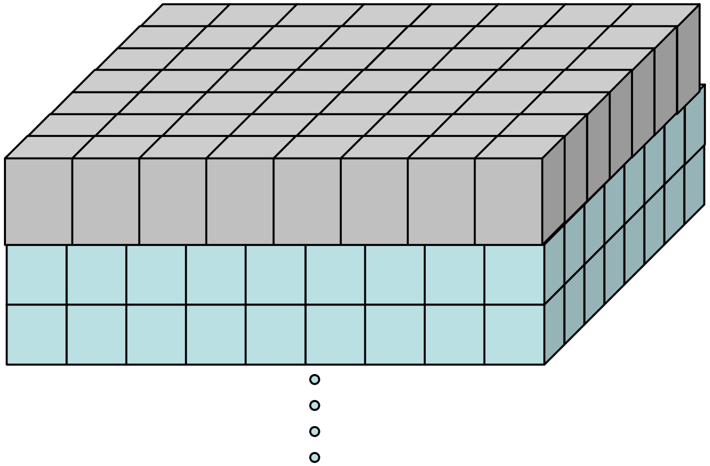
Heteroepitaxy
Tensile stress

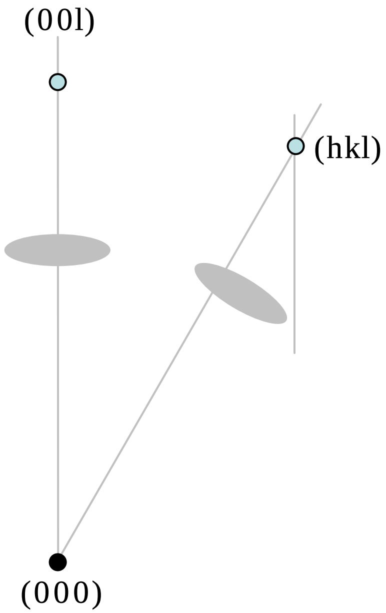
Heteroepitaxy
d-spacing variation

Heteroepitaxy
Mosaicity

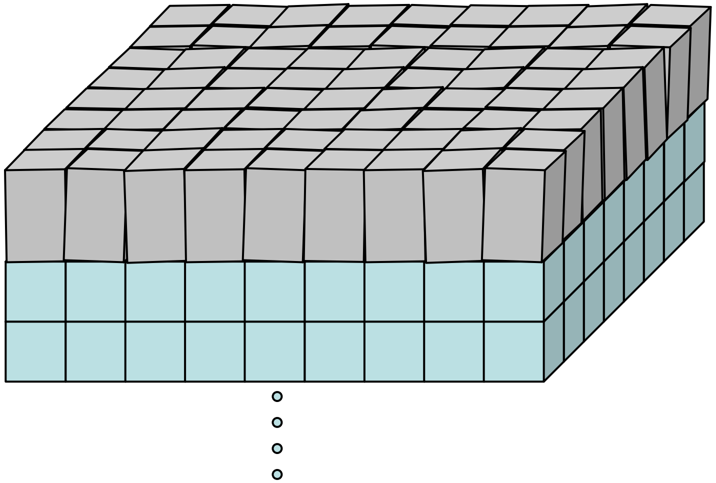


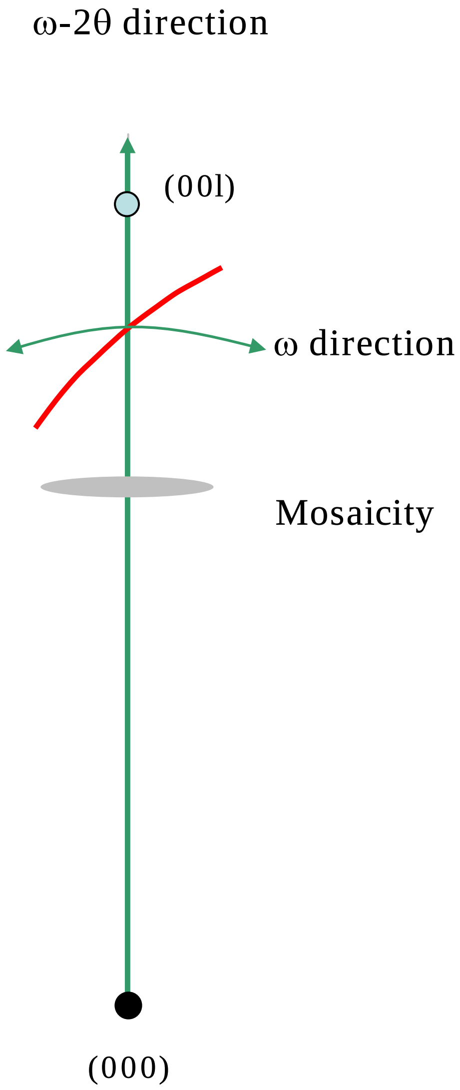
Partially Relaxed





Partially
Relaxed + Mosaicity





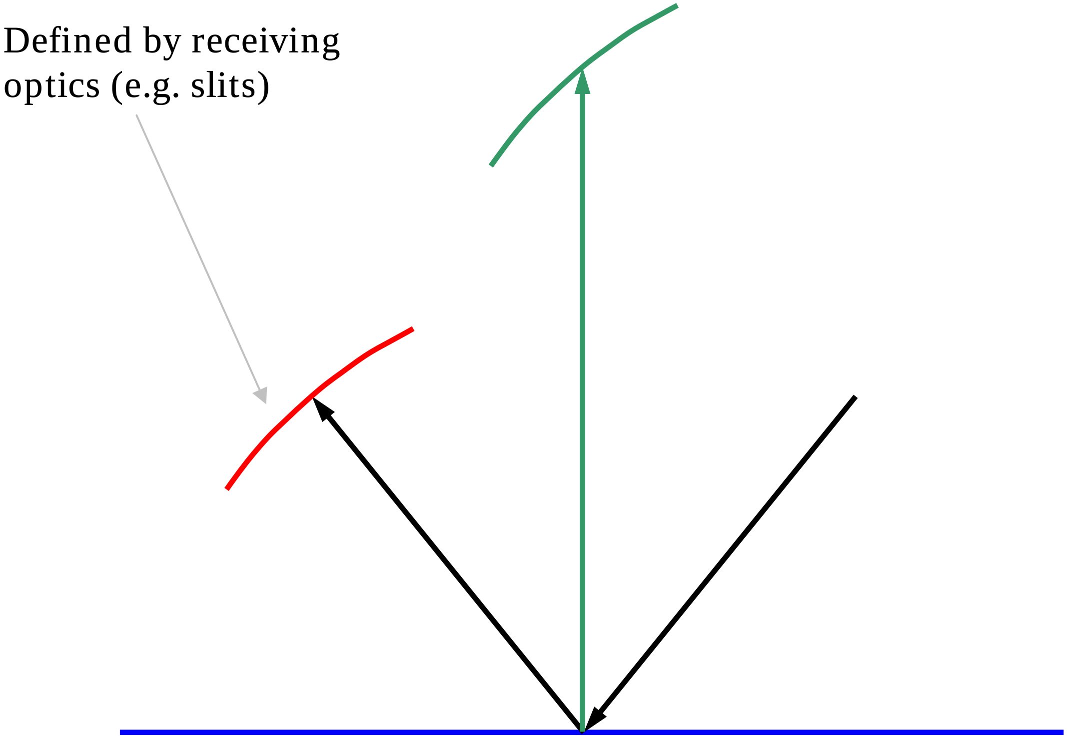
ω-2θ direction

(00l)

ω direction

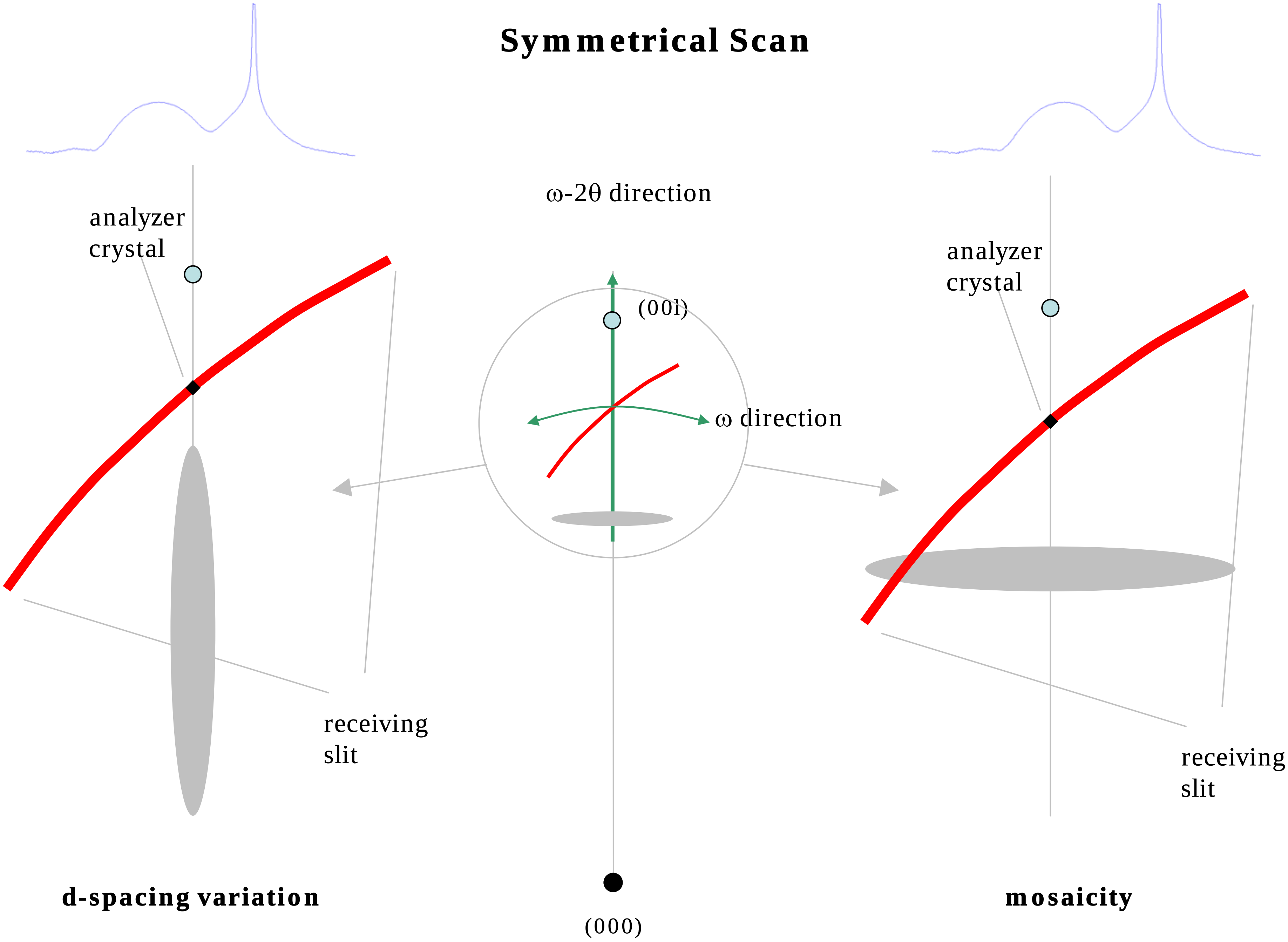
Mosaicity

(000)



Defined by receiving optics (e.g. slits)

Symmetrical Scan



ω-2θ direction

analyzer
crystal

(00l)

ω direction

analyzer
crystal

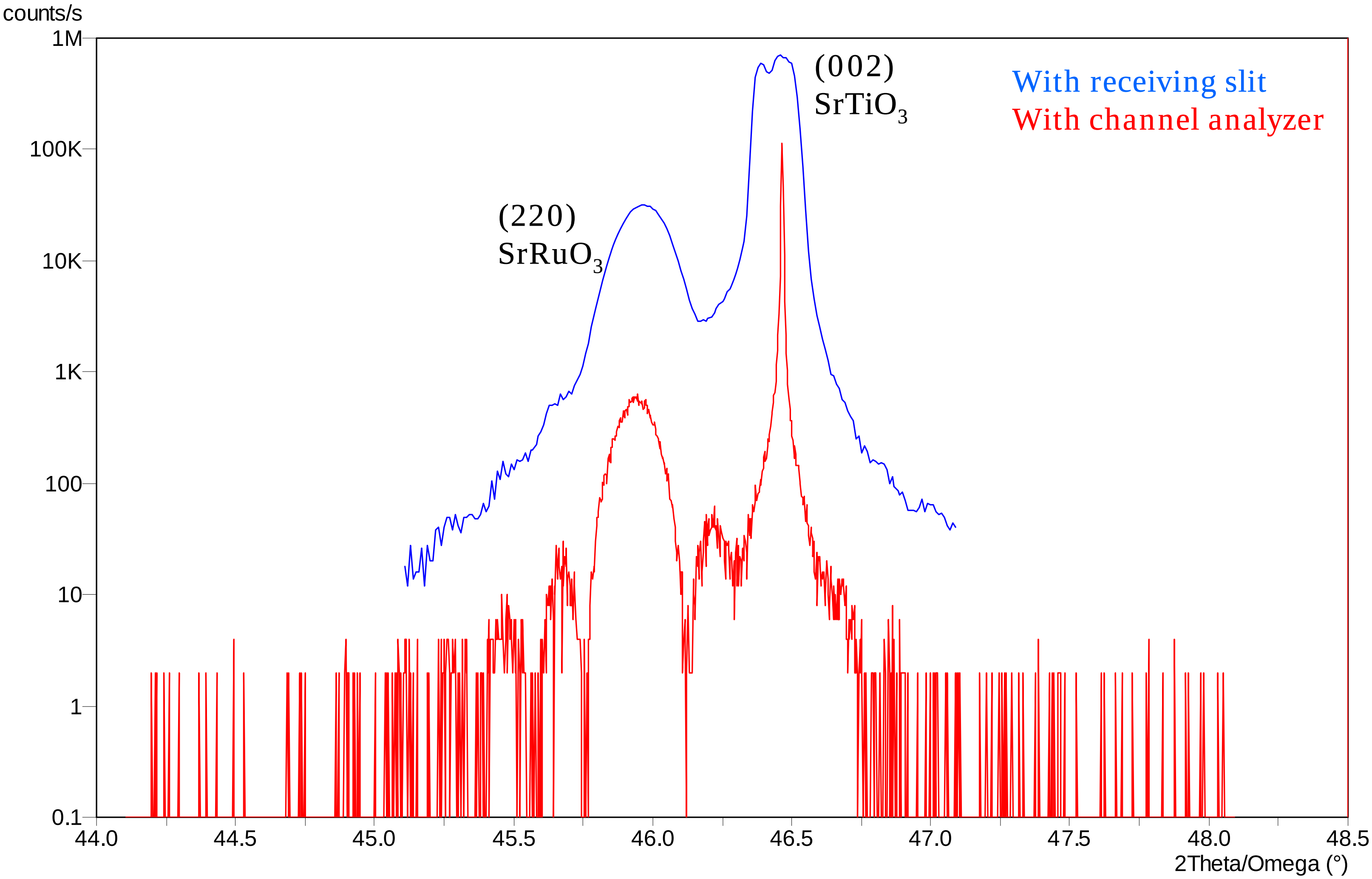
receiving
slit

receiving
slit

d-spacing variation

(000)

mosaicity


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)
$SrRuO_3$
(002)
$SrTiO_3$
With receiving slit
With channel analyzer

Mismatch

True lattice mismatch is: $$\boxed{m = \frac{a_L - a_S}{a_S}}$$

The peak separation between substrate and layer is related to the change of interplanar spacing normal to the substrate through the equation:

$$\frac{\delta d}{d} = -\delta\theta \cot\theta$$

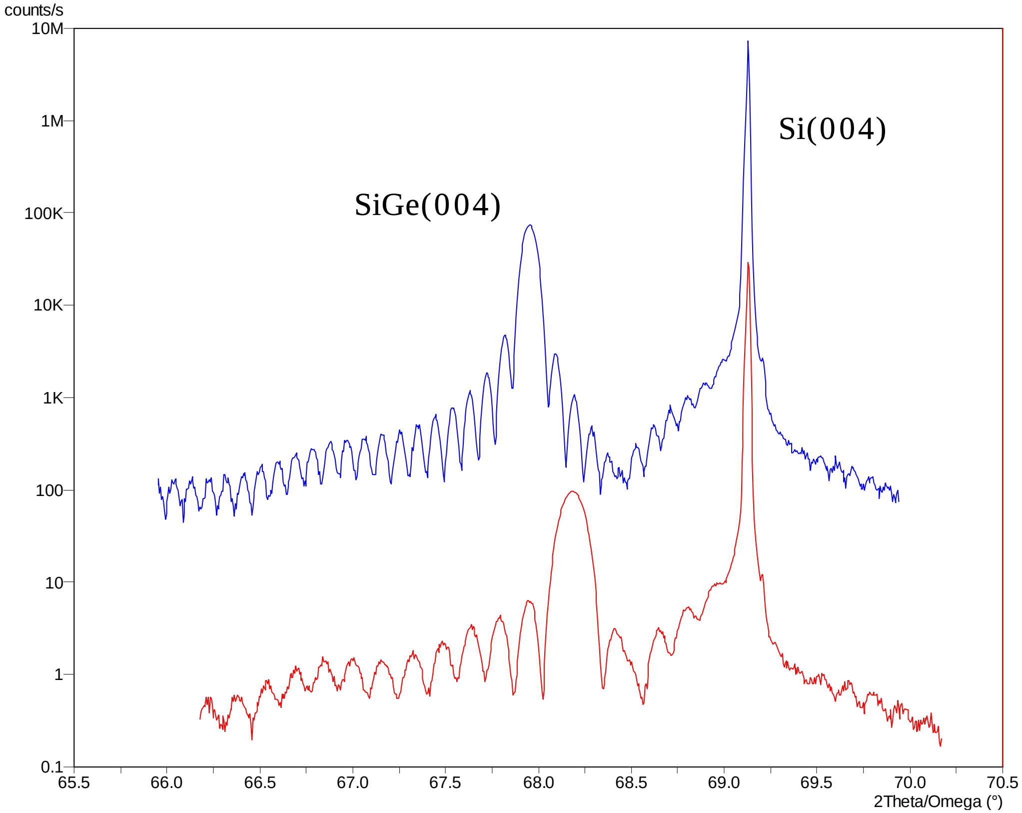
If it is (00l) reflection then the "experimental x-ray mismatch":

$$m^* = \frac{\delta a}{a} = \frac{\delta d}{d}$$

And true mismatch can be obtained through:

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

where: ν – Poisson ratio

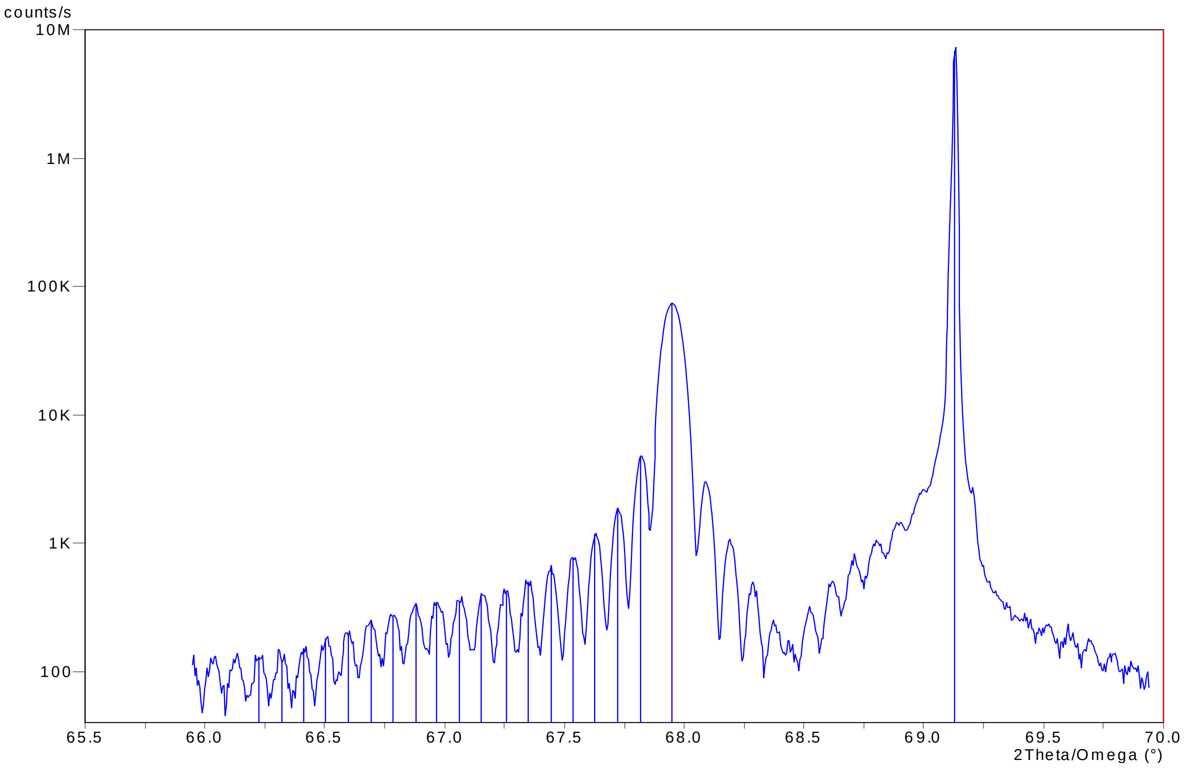


$$\boxed{\begin{array}{l} \nu \approx \dfrac{1}{3} \\ m \approx \dfrac{m^*}{2} \end{array}}$$

Layer Thickness

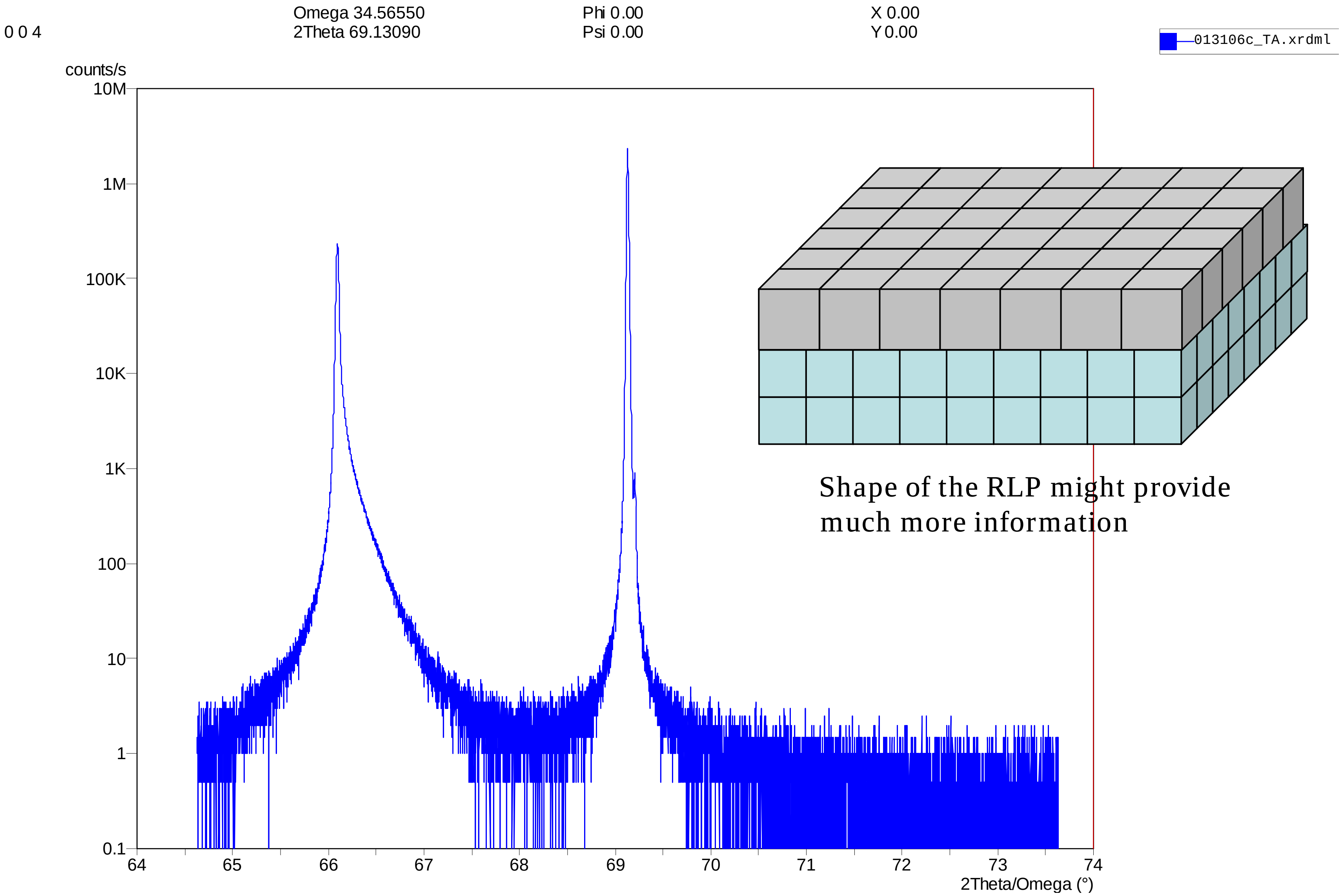
Interference fringes observed in the scattering pattern, due to different optical paths of the x-rays, are related to the thickness of the layers

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

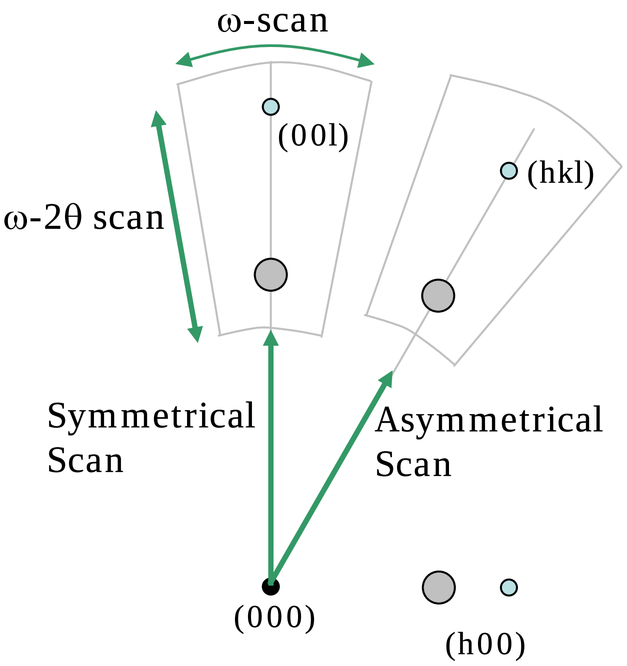


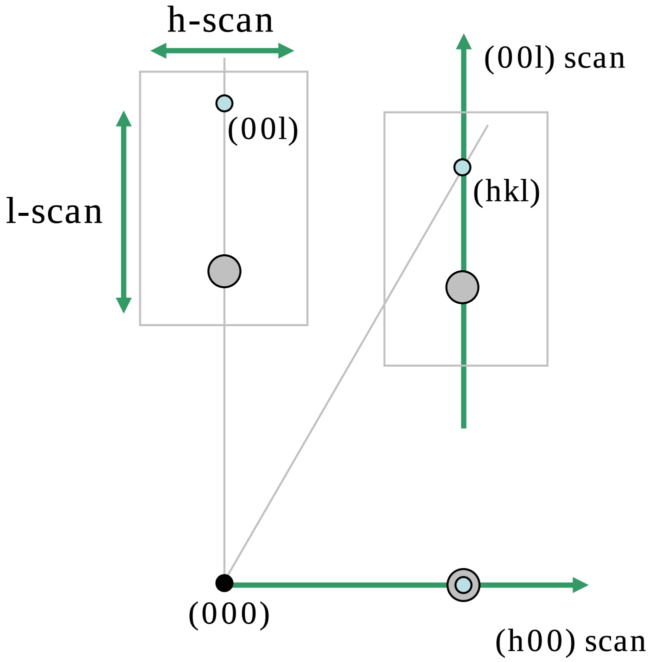
```
Substrate Layer Separation
S-peak:                  L-peak:                  Separation:
Omega(°)    34.5649      Omega(°)    33.9748      Omega(°)    0.59017
2Theta(°)   69.1298      2Theta(°)   67.9495      2Theta(°)   1.18034

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
```

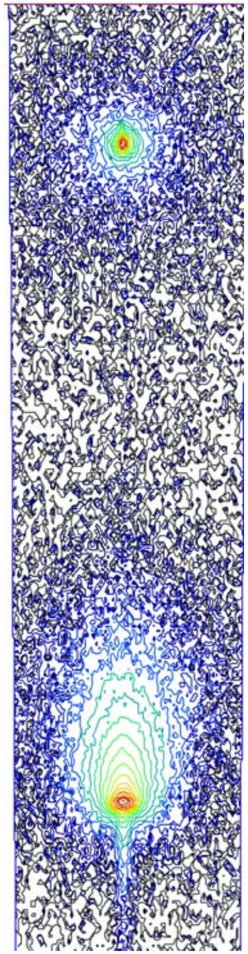
Relaxed SiGe on Si(001)

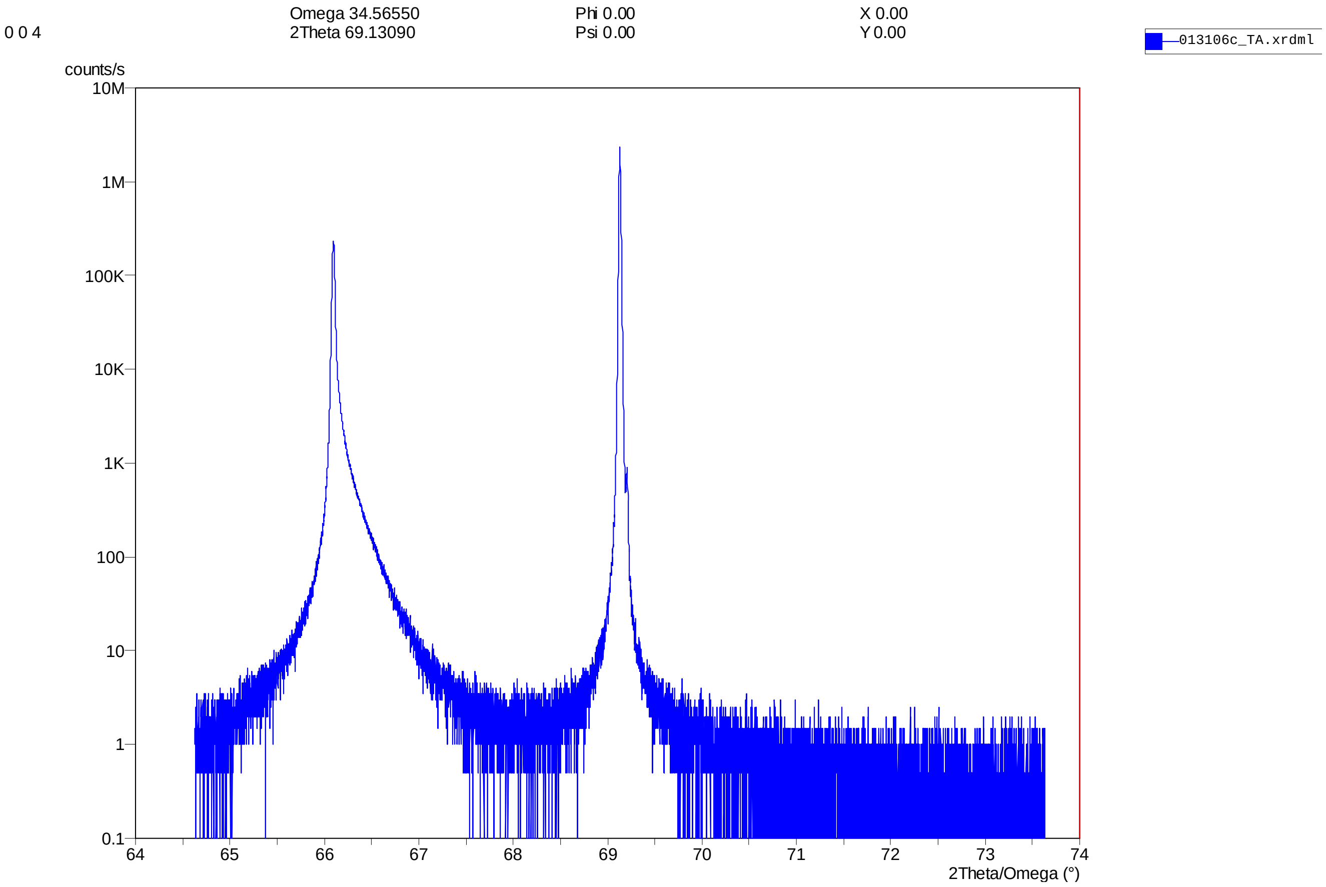


Shape of the RLP might provide much more information


ω-scan
ω-2θ scan
(00l)
(hkl)
Symmetrical Scan
Asymmetrical Scan
(000)
(h00)


h-scan
(00l) scan
(00l)
l-scan
(hkl)
(000)
(h00) scan

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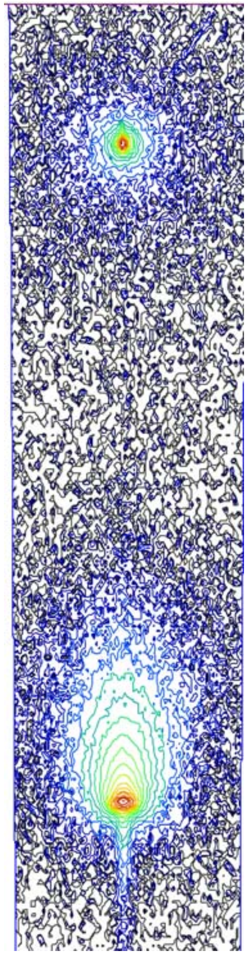
2Theta 69.13090
Phi 0.00
Psi 0.00
X 0.00
Y 0.00
013106c_TA.xrdml
counts/s
10M
1M
100K
10K
1K
100
10
1
0.1
64
65
66
67
68
69
70
71
72
73
74
2Theta/Omega (°)

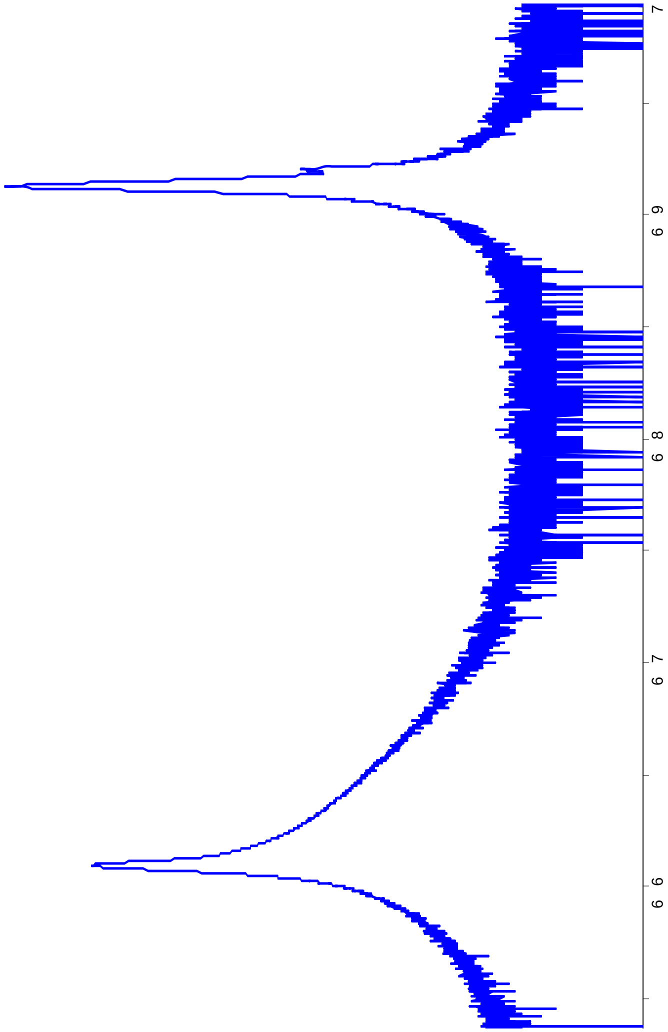
Relaxed SiGe on Si(001)

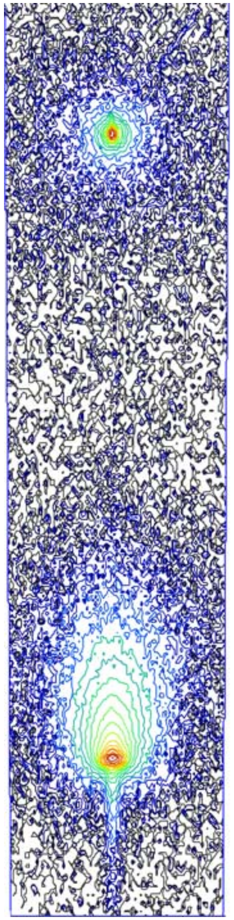
(oo4) RLM

Si(004)

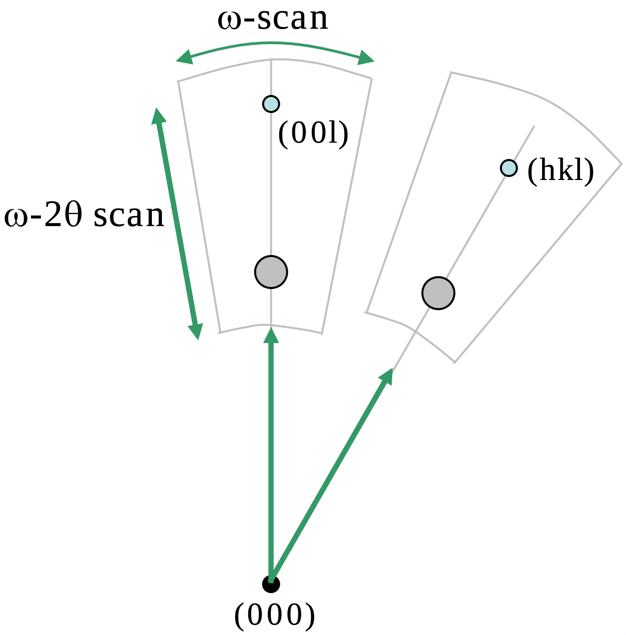
SiGe(004)

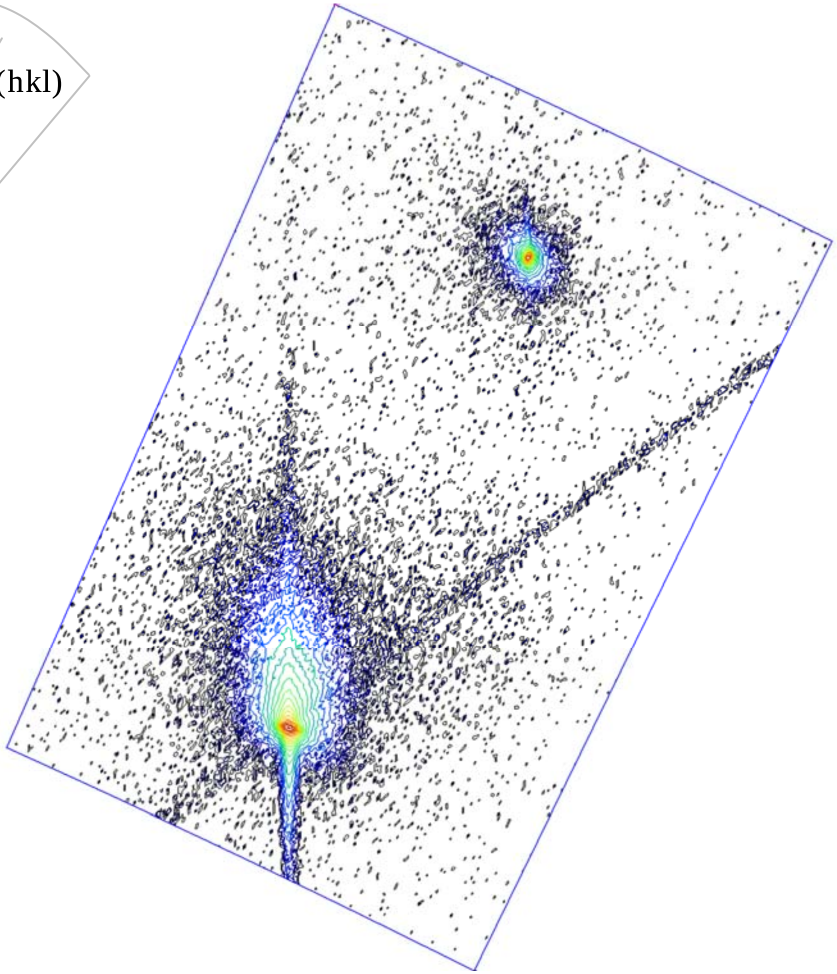






(004)





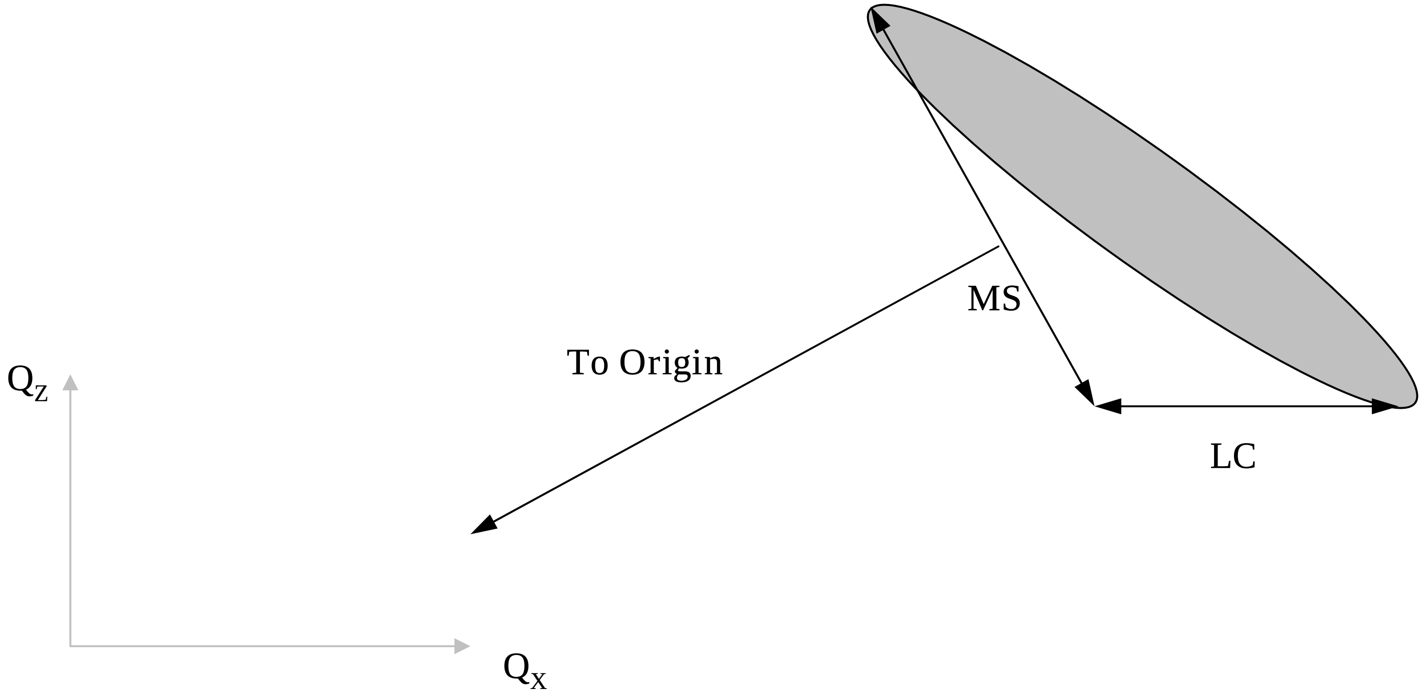
(113)

Mosaic Spread and Lateral Correlation Length

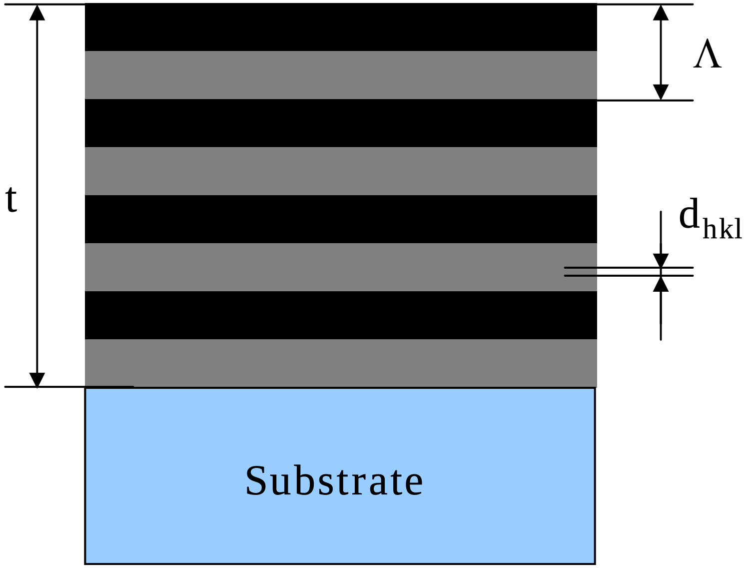
The Mosaic Spread and Lateral Correlation Length functionality derives information from the shape of a layer peak in a diffraction space map recorded using an asymmetrical reflection

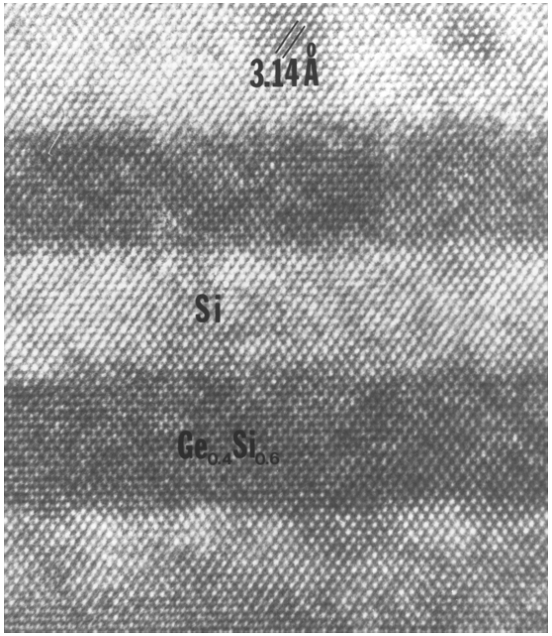
The mosaic spread of the layer is calculated from the angle that the layer peak subtends at the origin of reciprocal space measured perpendicular to the reflecting plane normal.

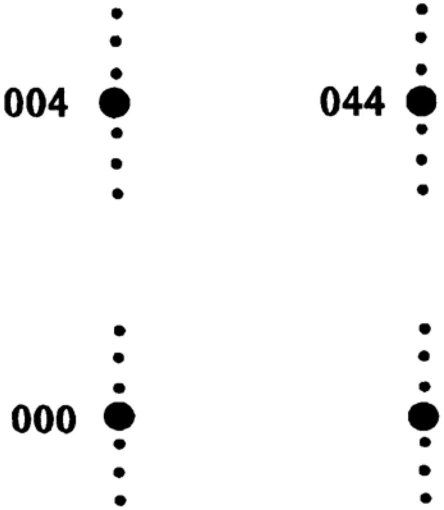
The lateral correlation length of the layer is calculated from the reciprocal of the FWHM of the peak measured parallel to the interface.

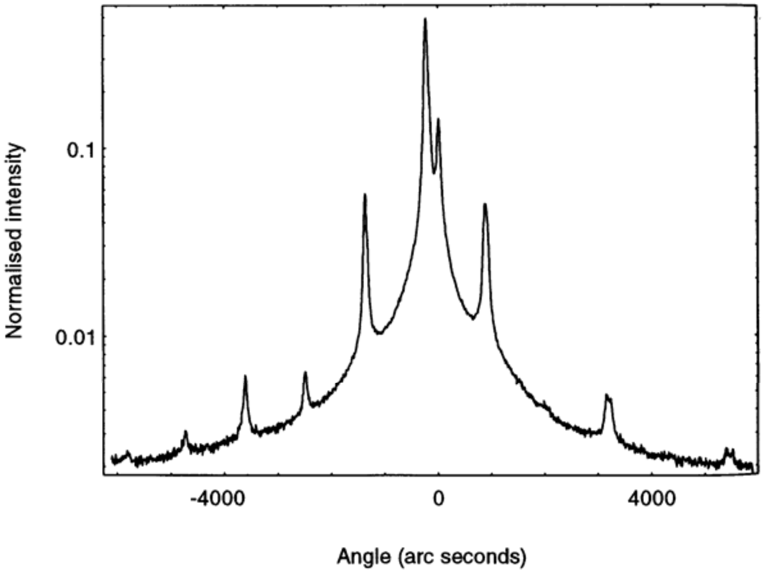


Superlattices and Multilayers

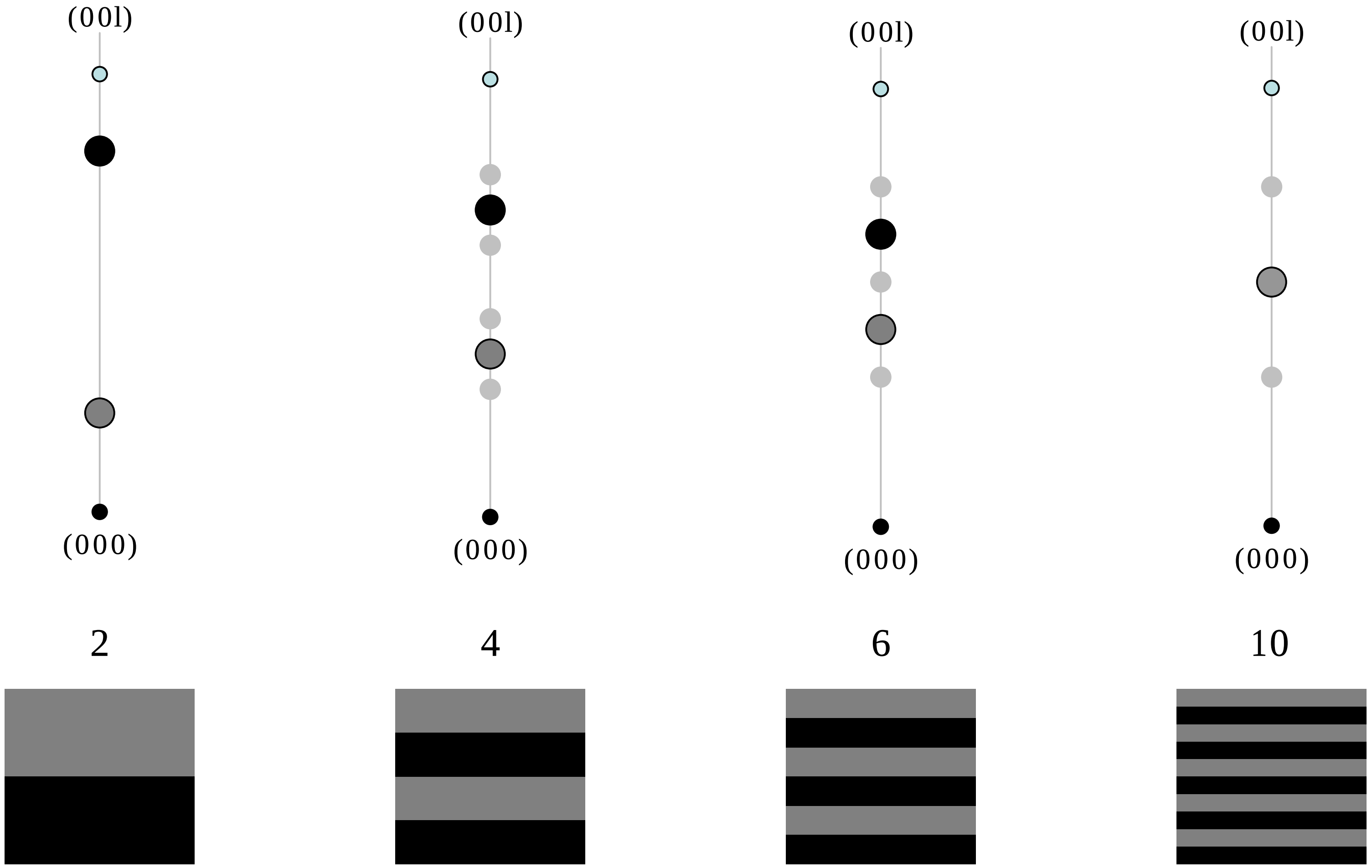


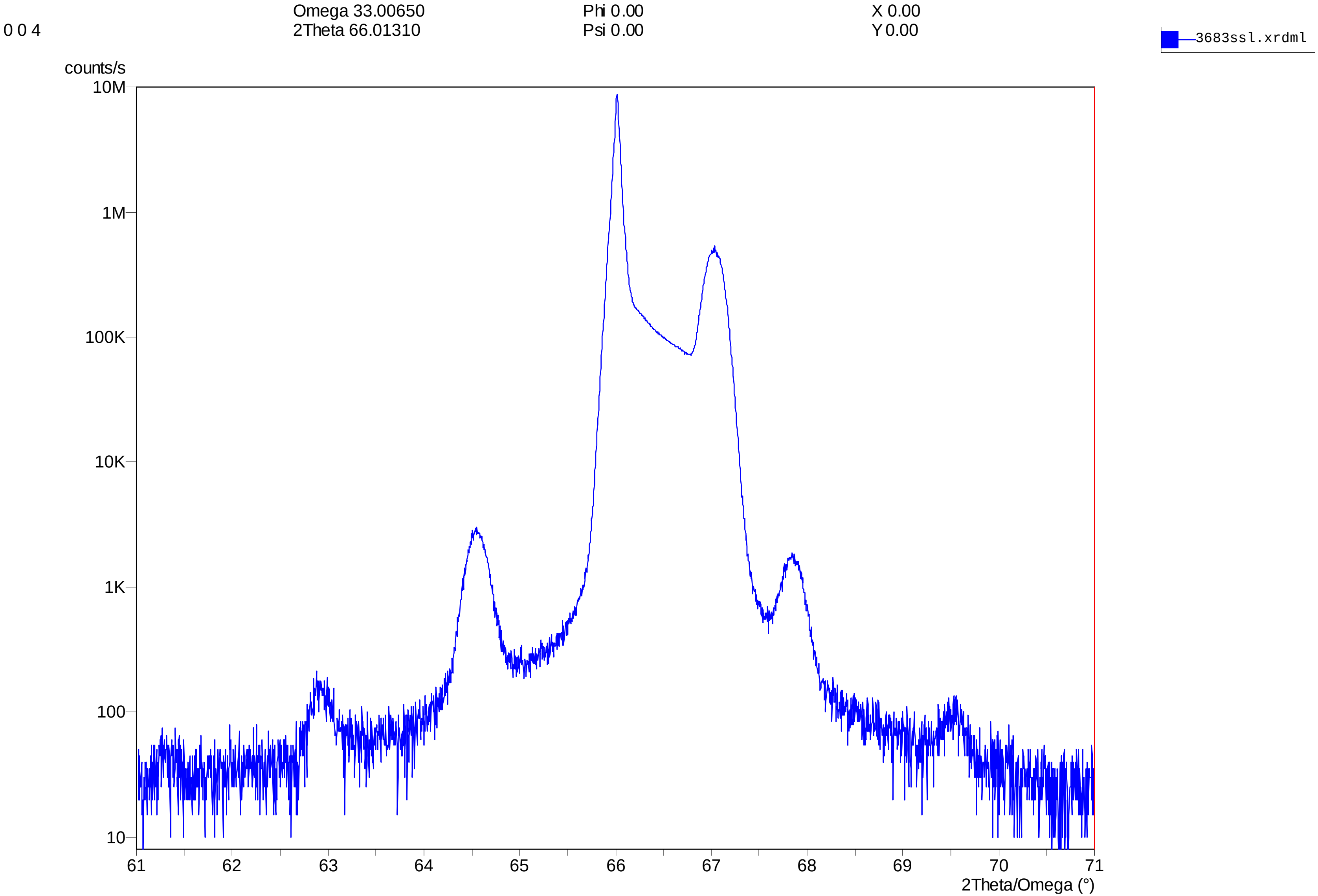






Superlattices and Multilayers

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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
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1M
100K
10K
1K
100
10
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63
64
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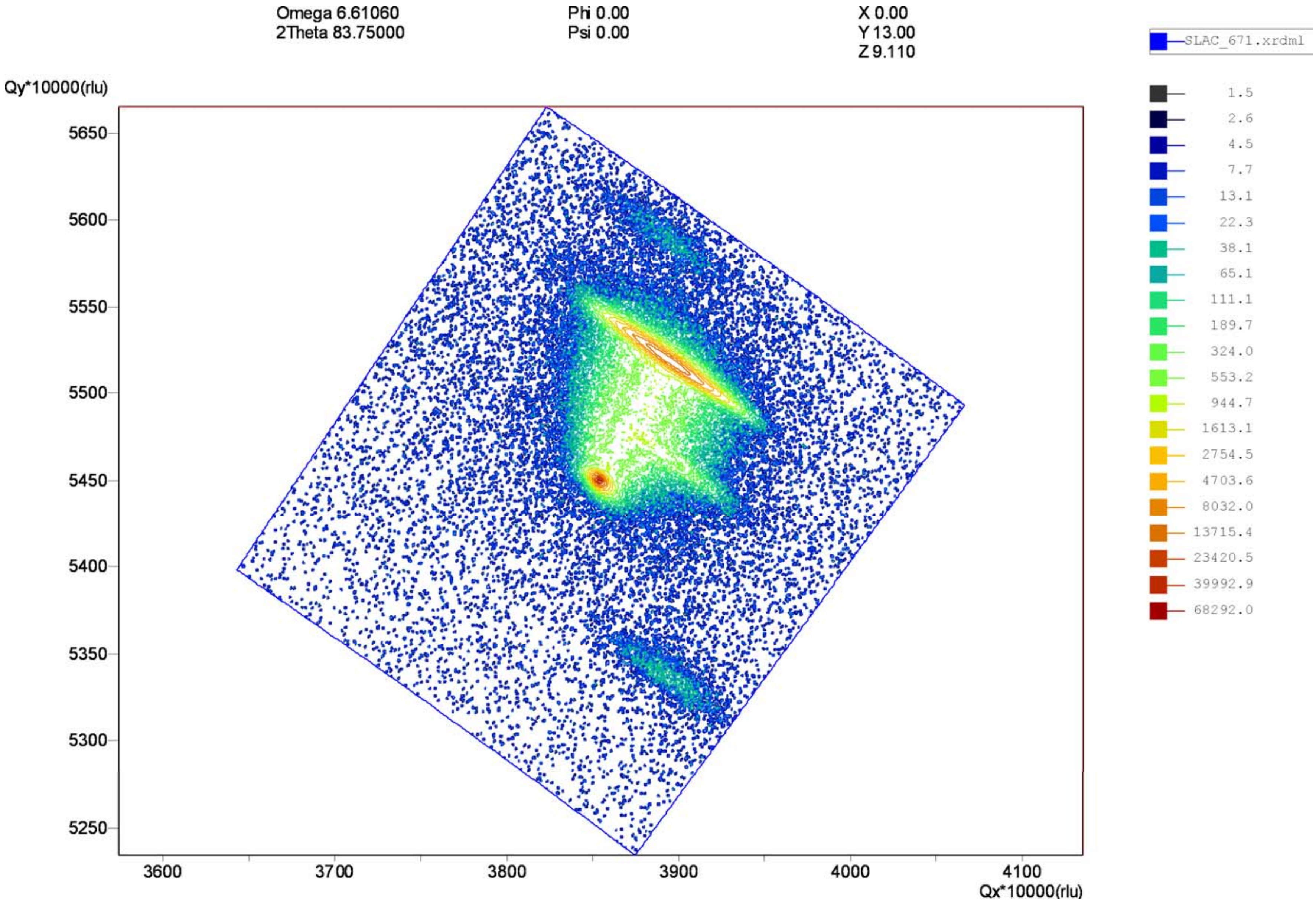
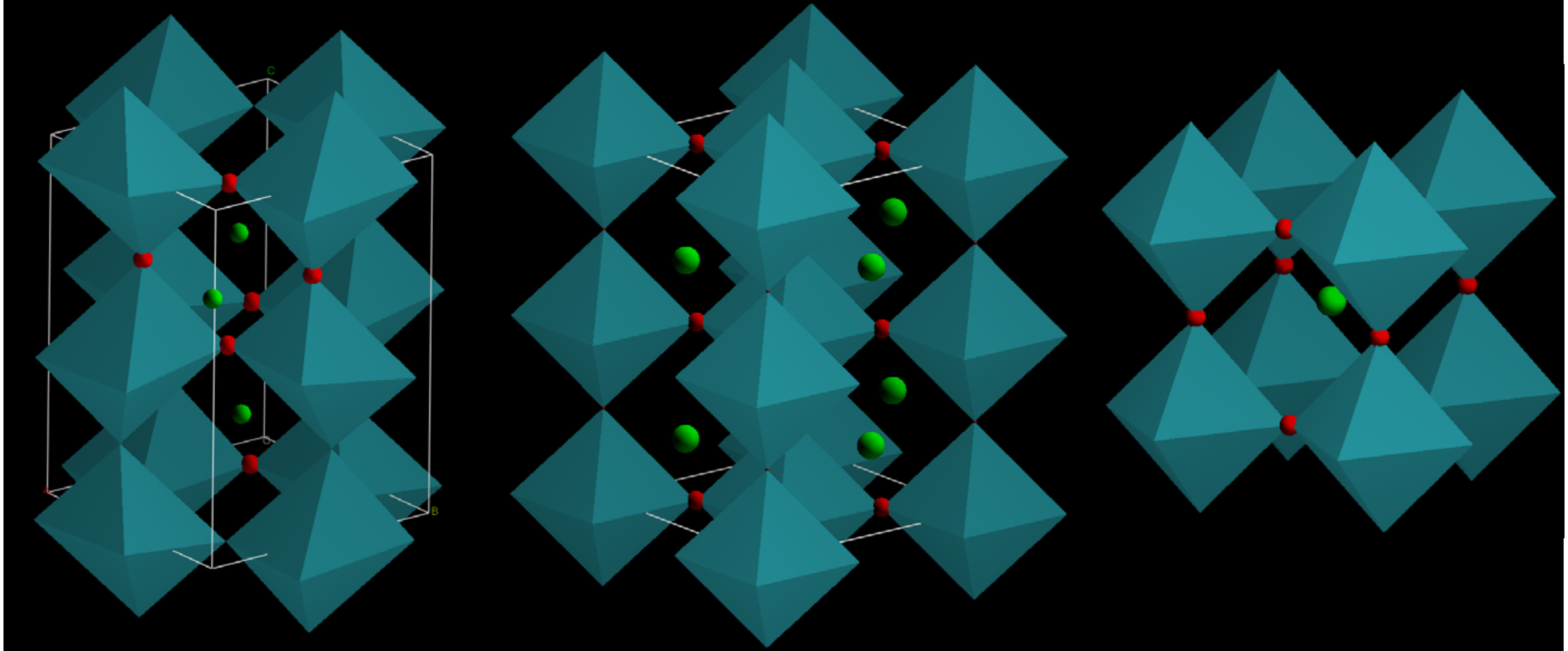
66
67
68
69
70
71
2Theta/Omega (°)


Omega 6.61060
2Theta 83.75000
Phi 0.00
Psi 0.00
X 0.00
Y 13.00
Z 9.110
SLAC_671.xrdml
Qy*10000(rlu)
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

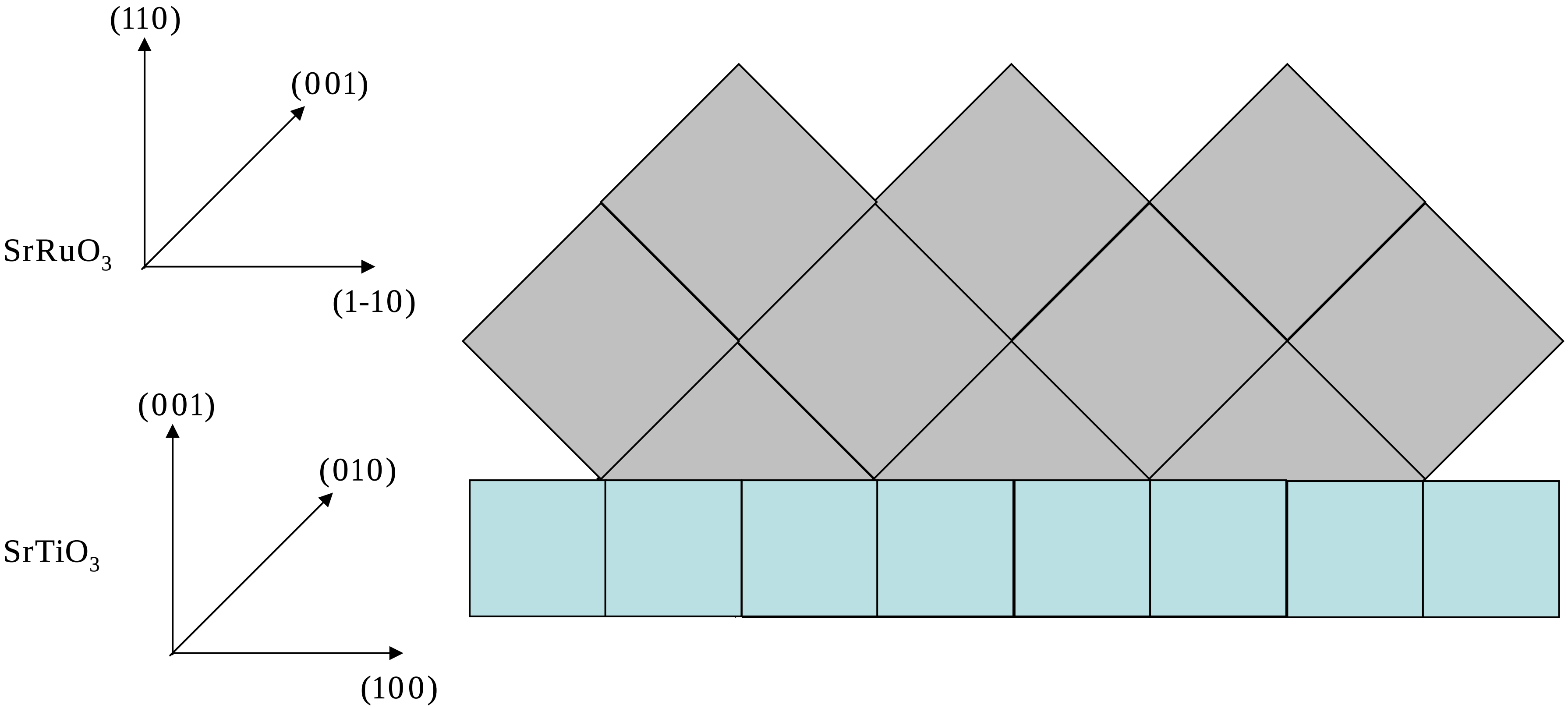
Tetragonal

a = 5.578 Å
c = 7.908 Å

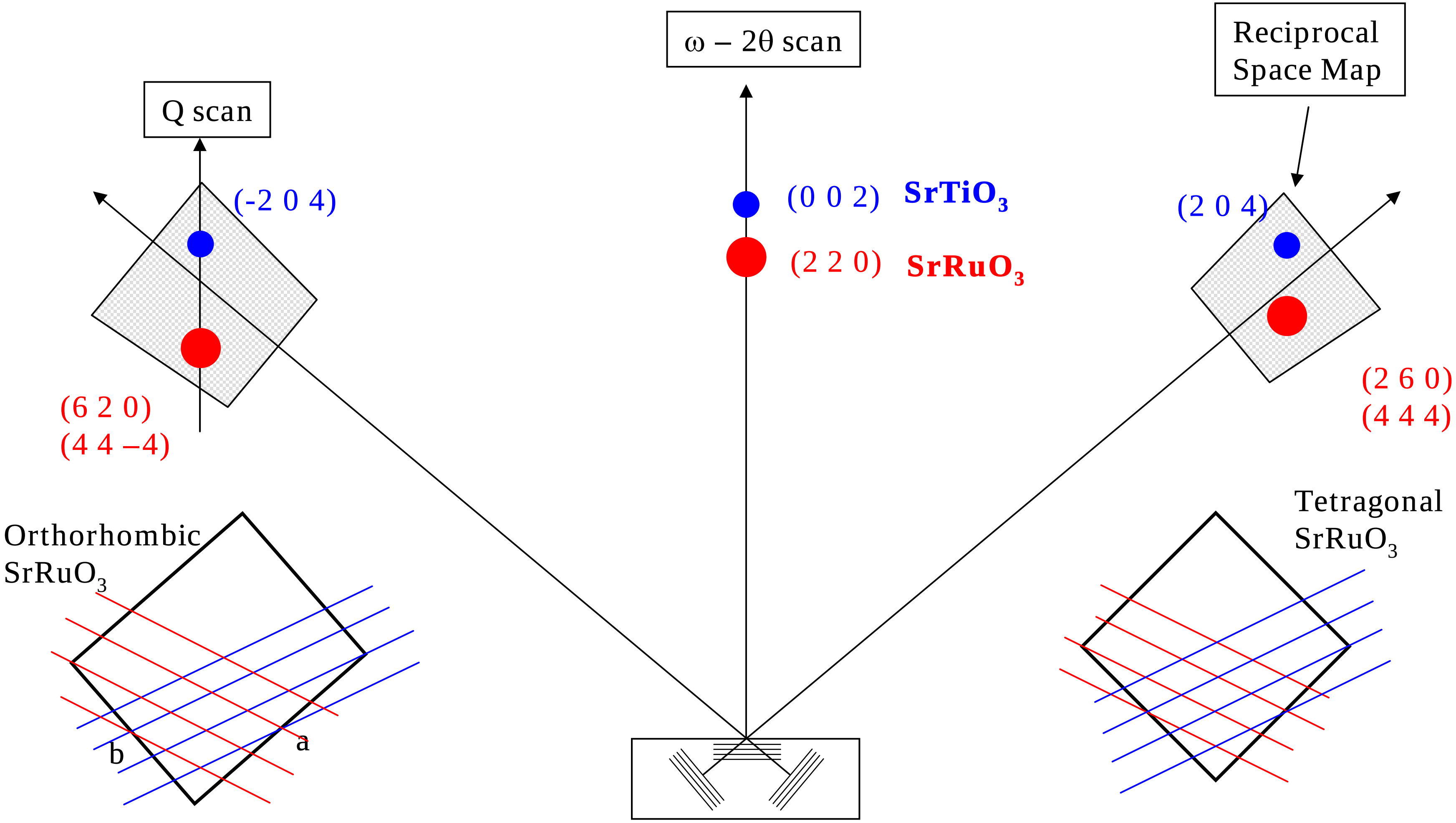
→ 510-702 °C

Cubic

a = 3.956 Å


(110)
(001)
$SrRuO_3$
(1-10)
(001)
(010)
$SrTiO_3$
(100)

X-ray Diffraction Scan Types



Q scan

ω – 2θ scan

Reciprocal
Space Map

(-2 0 4)

(6 2 0)
(4 4 –4)

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

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

(2 0 4)

(2 6 0)
(4 4 4)

Orthorhombic
$SrRuO_3$

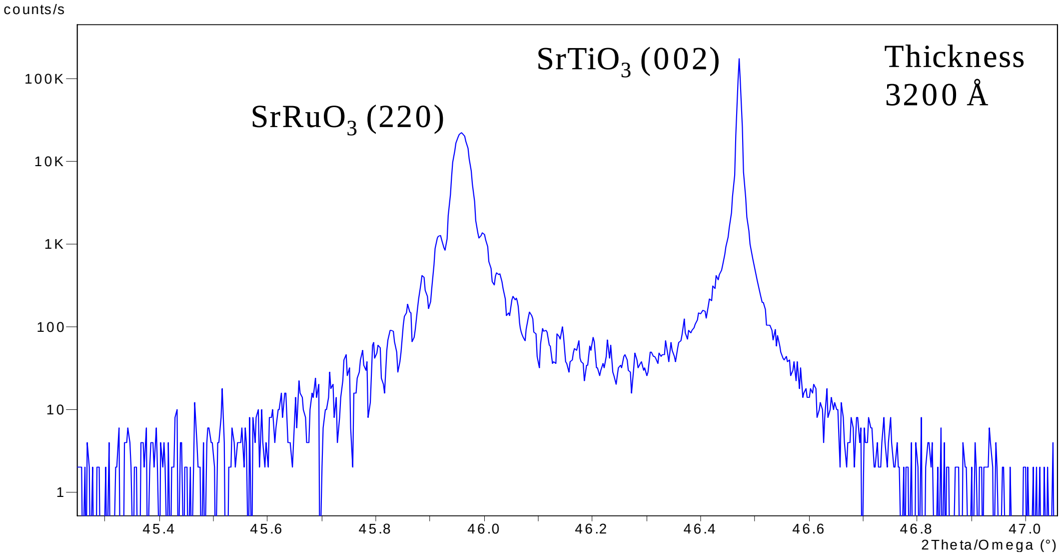
b

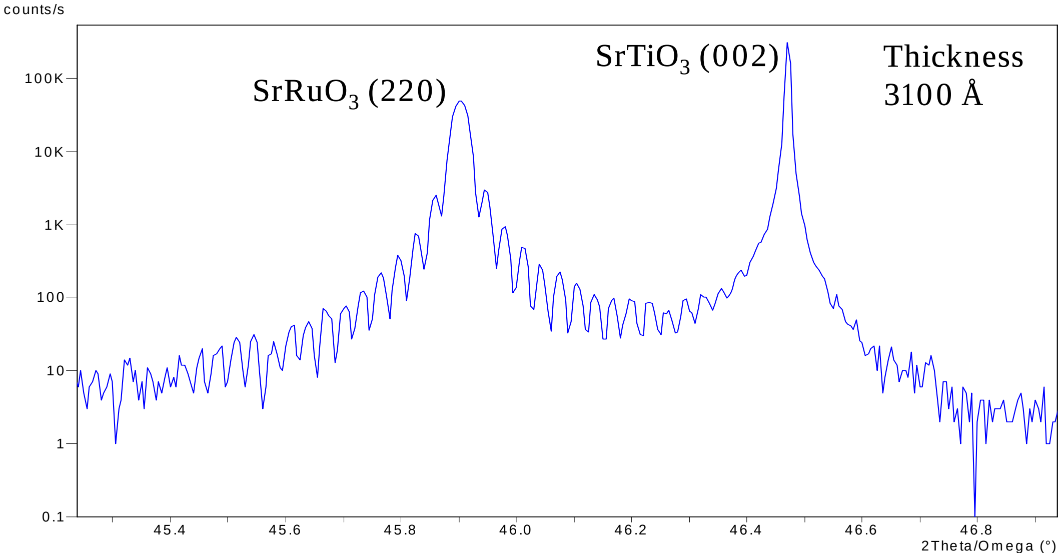
a

Tetragonal
$SrRuO_3$

ω – 2θ symmetrical scans

Finite size fringes indicate well ordered films

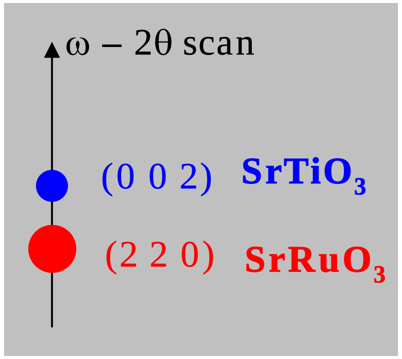


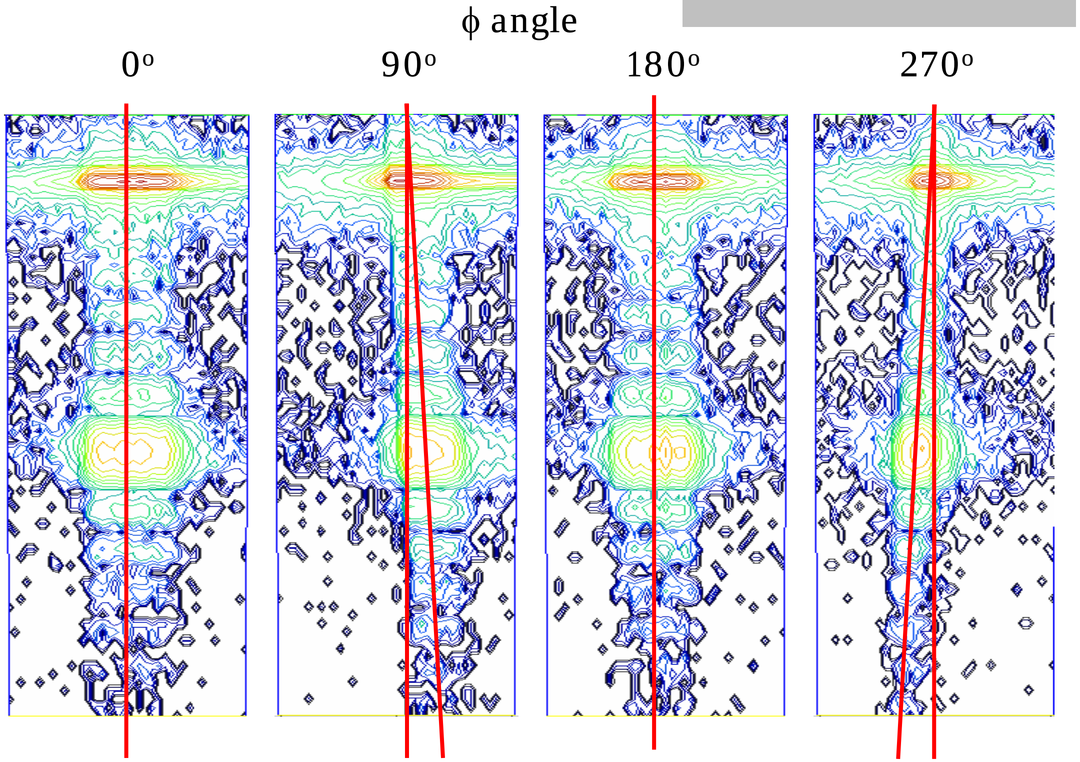


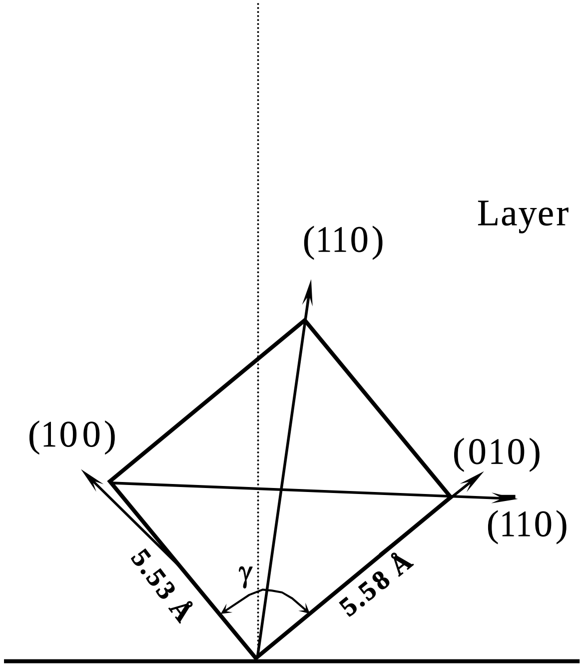
Reciprocal Lattice Map of SrRuO3 (220) and SrTiO3 (002)

Distorted perovskite structure:

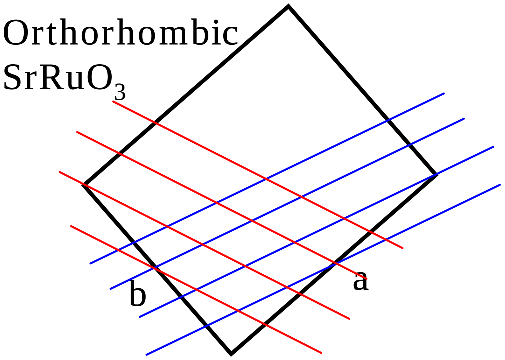
Films are slightly distorted from orthorhombic, γ = 89.1° – 89.4°

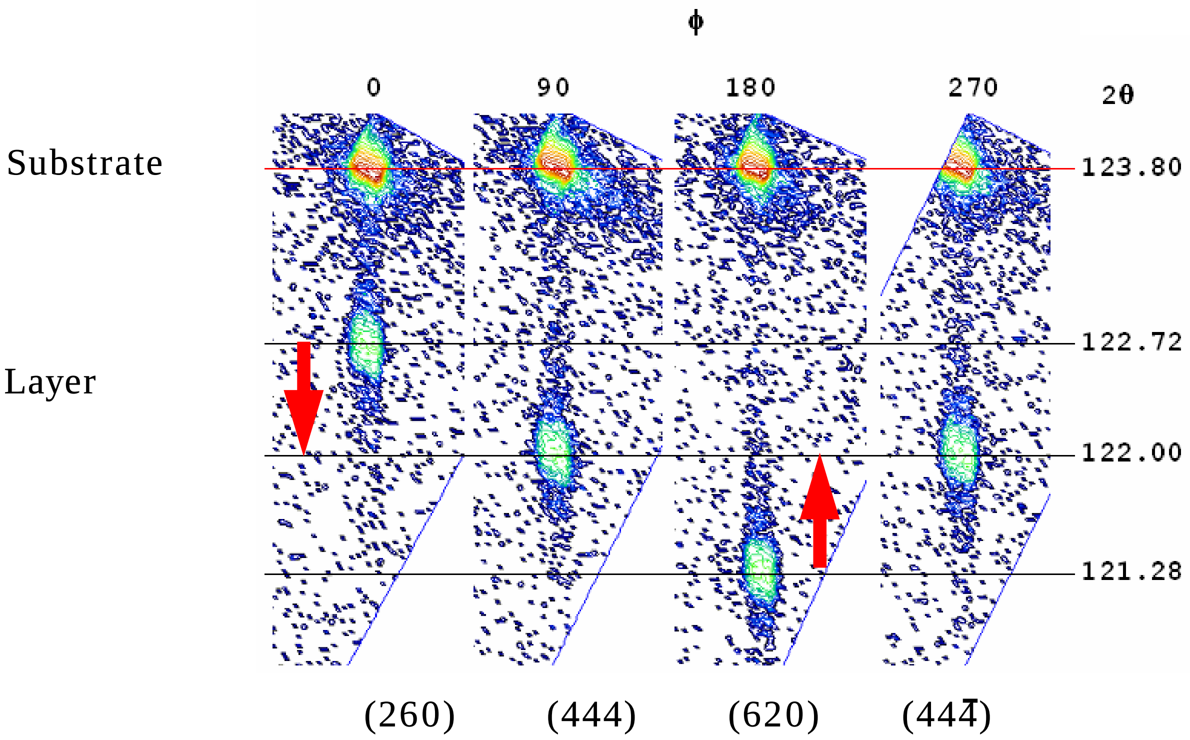




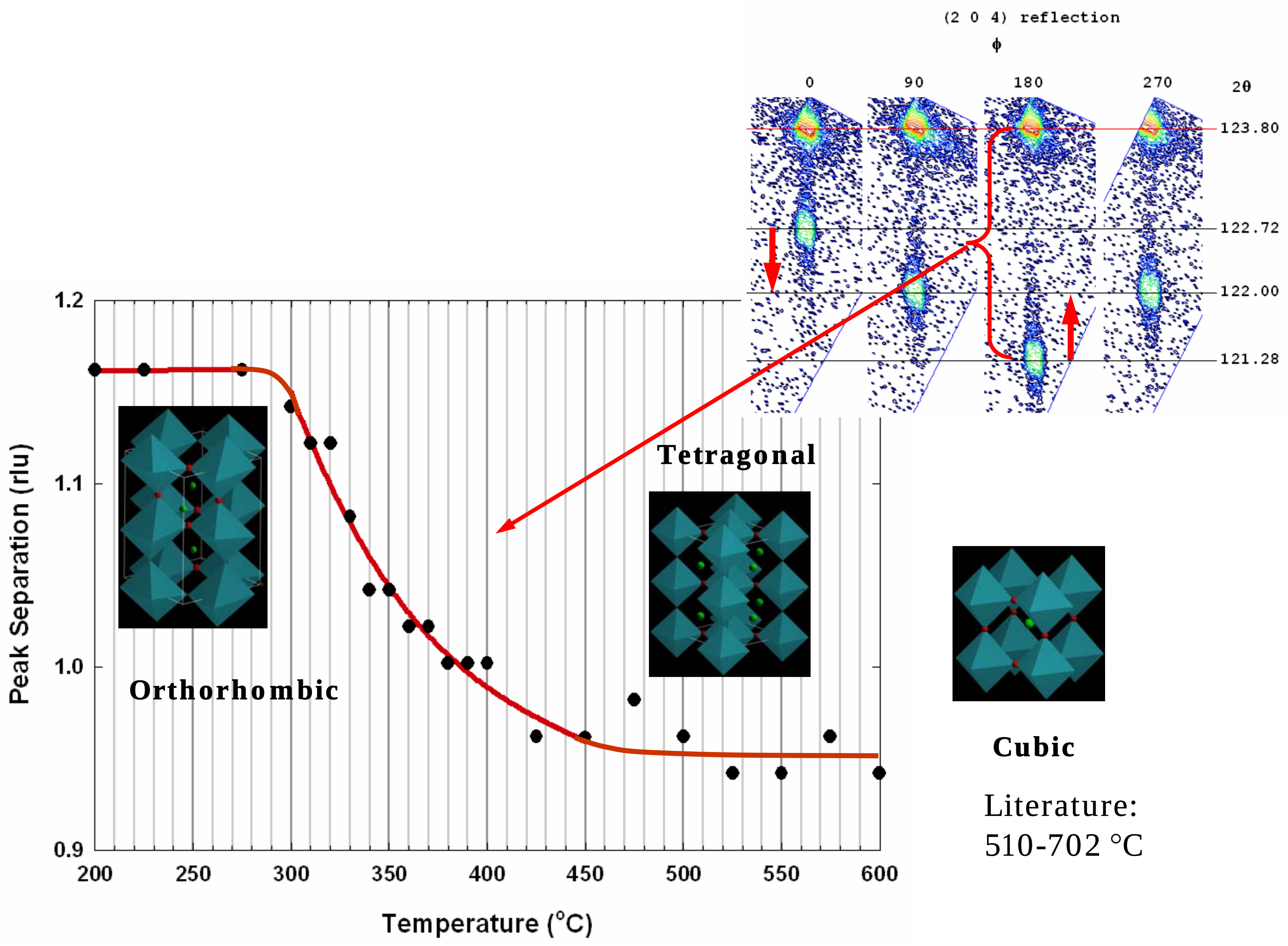


High-Resolution Reciprocal Area Mapping





Orthorombic to Tetragonal Transition

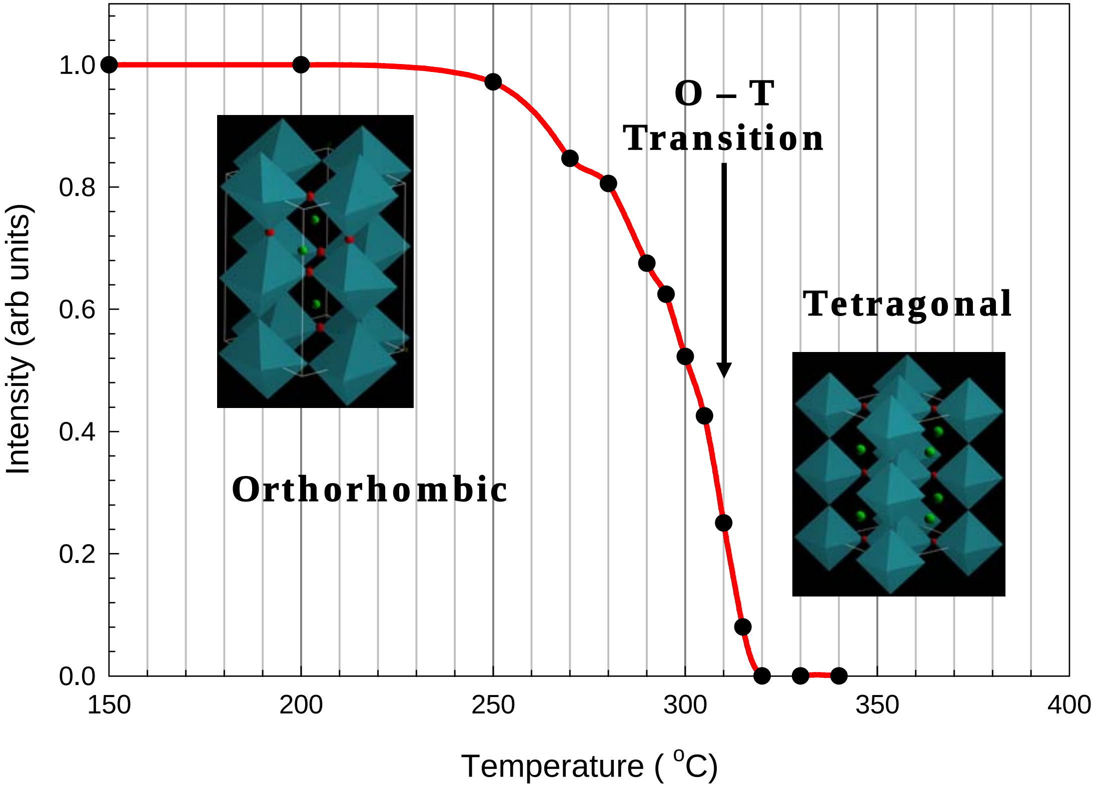


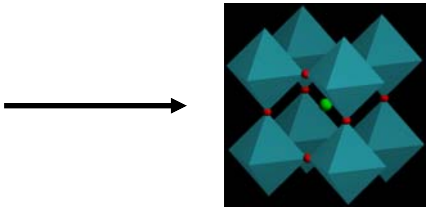
Literature:
510-702 °C

Transition Orthorhombic to Tetragonal ~ 350 °C

Structural Transition, (221) reflection

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





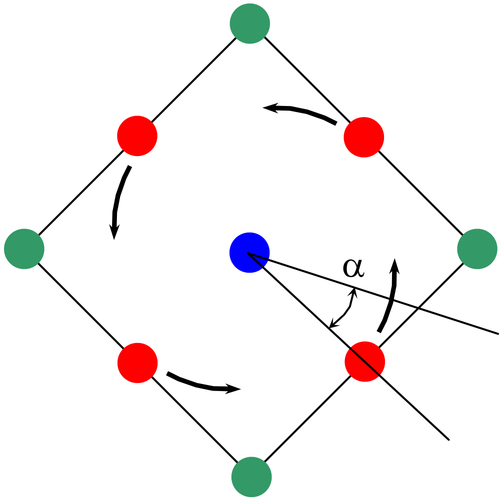
Cubic

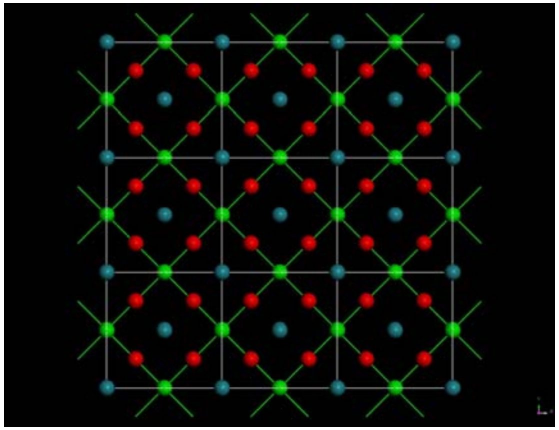
Literature:
510-702 °C

Transition Orthorhombic to Tetragonal ~ 310 °C

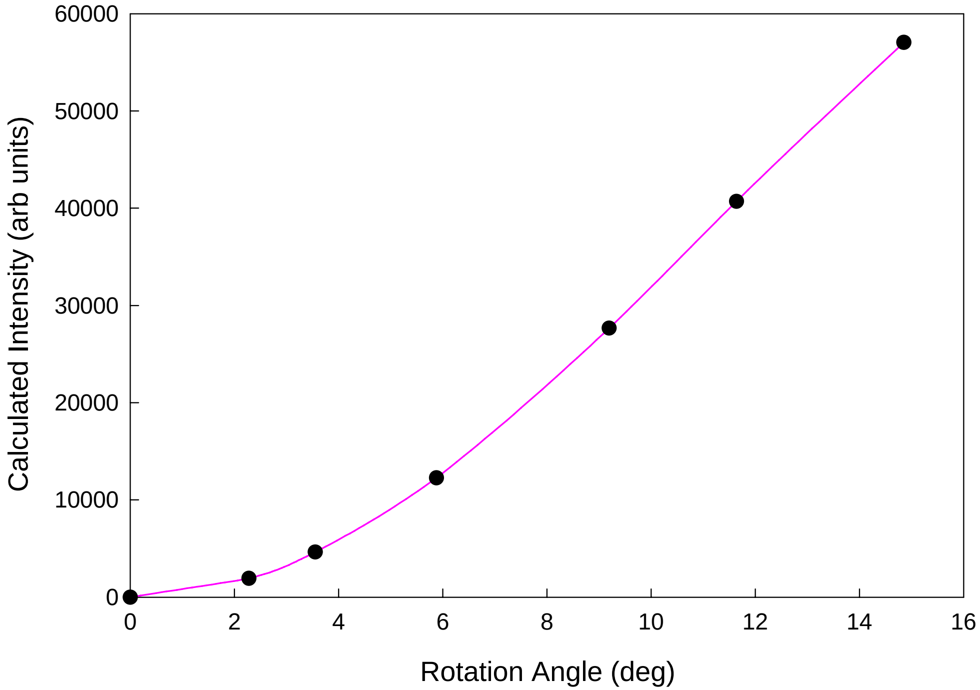
Transition Orthorhombic to Tetragonal ~ 310 °C

Structural Transition, (211) reflection



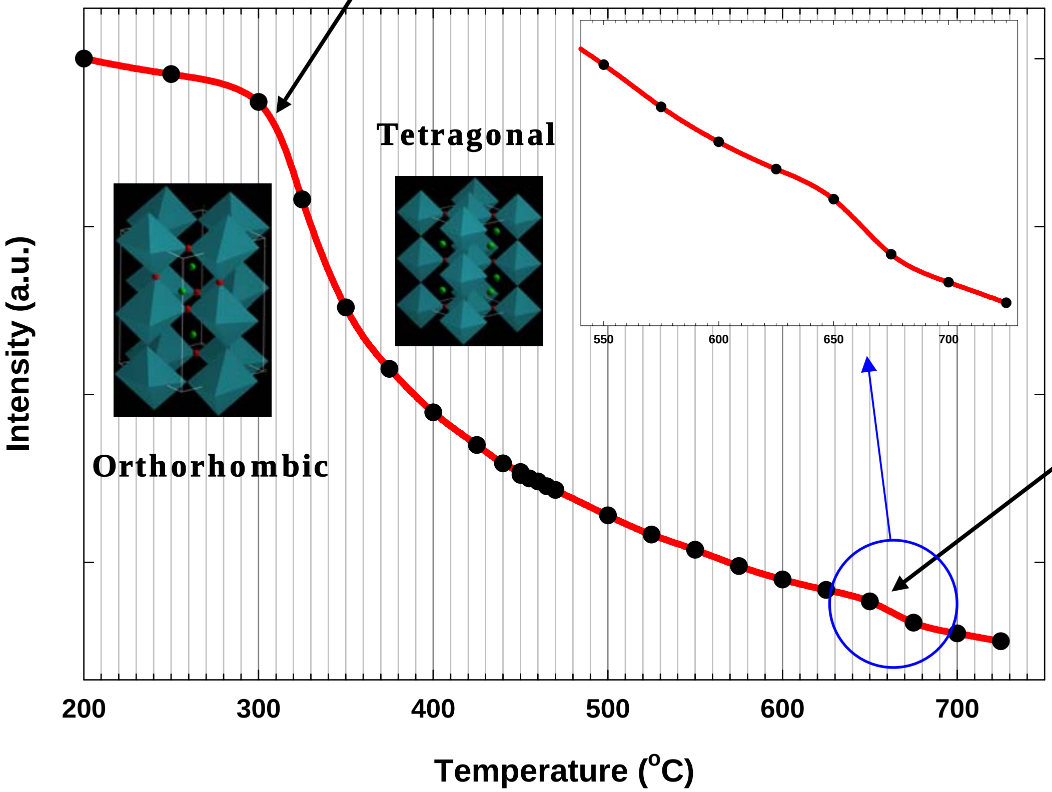


(211) peak is **absent** in cubic $SrRuO_3$

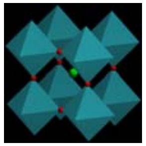


Structural Transition, (211) reflection

O – T Transition = 310 °C



Attempt for
T – C Transition ?

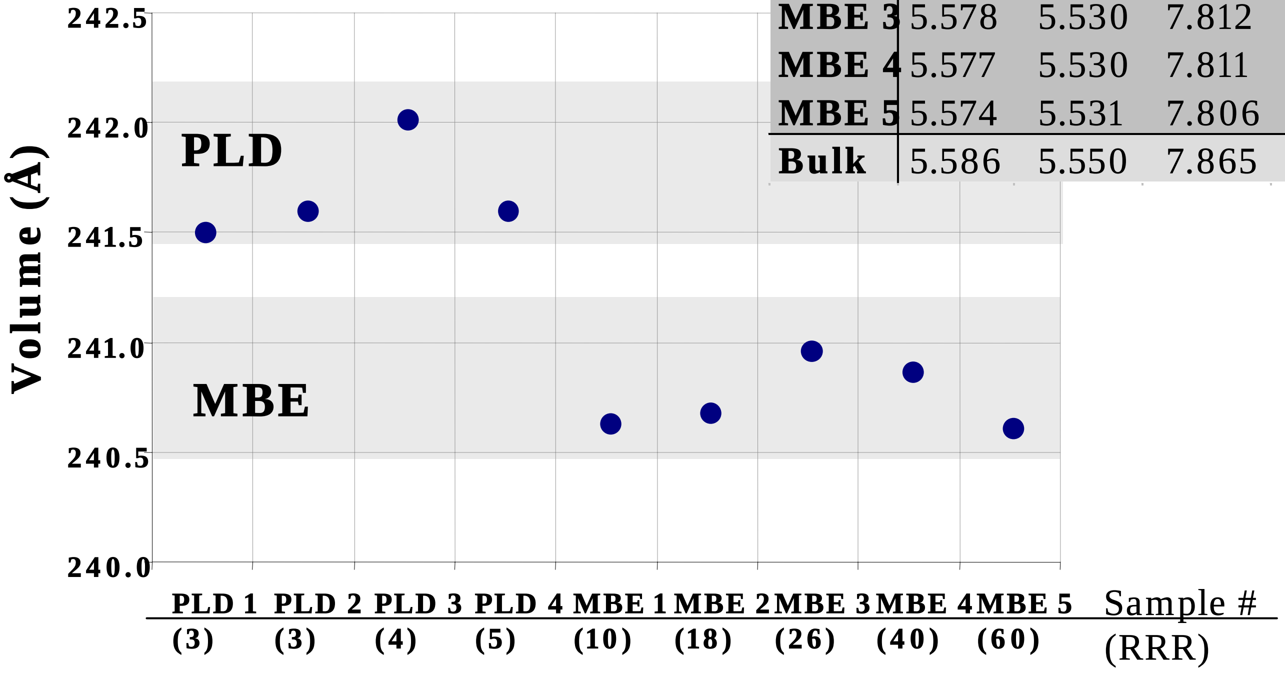


Cubic

Refined Unit Cells

We used (620), (260), (444), $(44\bar{4})$, (220) and (440) reflections for refinement

	a	b	c	a	b	g	V
PLD 1	5.583	5.541	7.807	90.0	90.0	89.2	**241.52**
PLD 2	5.583	5.541	7.811	90.0	90.0	89.2	**241.61**
PLD 3	5.590	5.544	7.809	90.0	90.0	89.1	**242.03**
PLD 4	5.583	5.541	7.810	90.0	90.0	89.2	**241.61**
MBE 1	5.572	5.534	7.804	90.0	90.0	89.4	**240.64**
MBE 2	5.577	5.528	7.808	90.0	90.0	89.4	**240.70**
MBE 3	5.578	5.530	7.812	90.0	90.0	89.4	**240.98**
MBE 4	5.577	5.530	7.811	90.0	90.0	89.4	**240.88**
MBE 5	5.574	5.531	7.806	90.1	90.1	89.4	**240.63**
Bulk	5.586	5.550	7.865	90.0	90.0	90.0	**243.85**

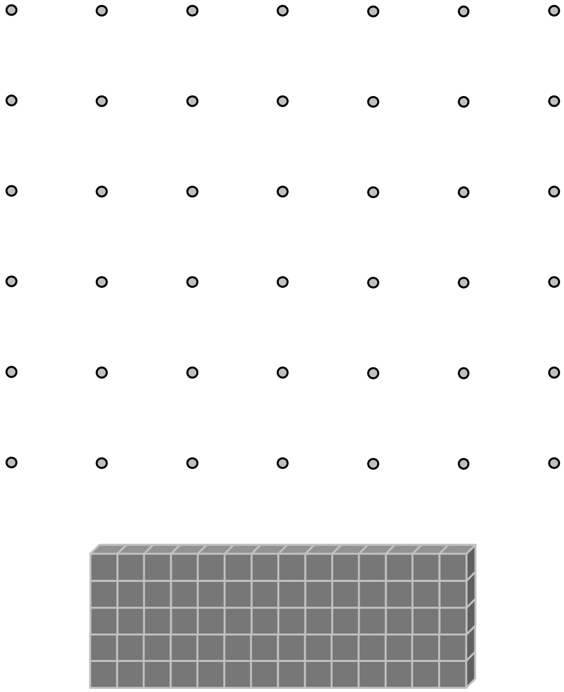


Summary

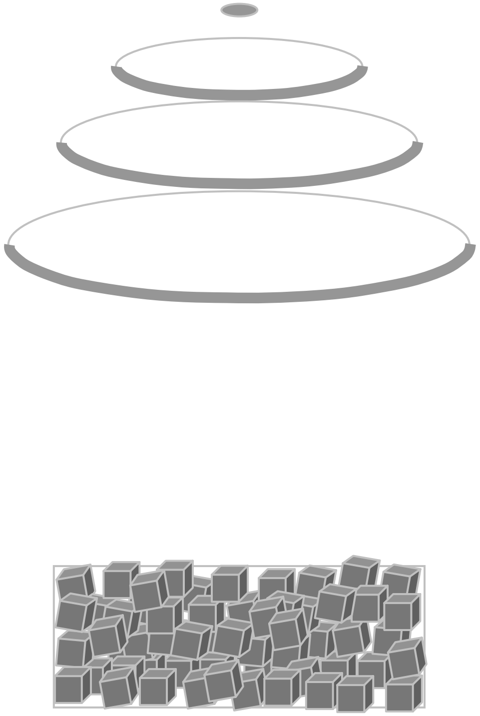
- Reciprocal space for epitaxial thin films is very rich.

- Shape and positions of reciprocal lattice points with respect to the substrate reveal information about:
    - Mismatch
    - Strain state
    - Relaxation
    - Mosaicity
    - Composition
    - Thickness ....

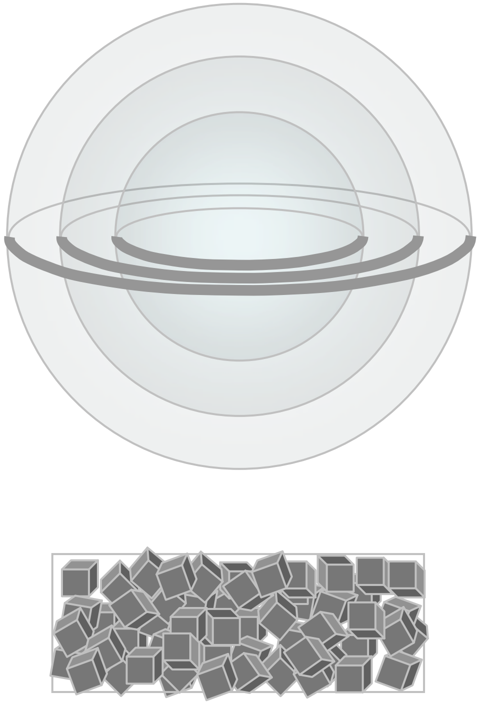
- Diffractometer instrumental resolution has to be understood before measurements are performed.



Single crystal



Preferred orientation



Polycrystalline