Scattering Techniques and Geometries: SSRL Beamlines

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2018 SSRL X-Ray Scattering School

Motivation

- X-Rays are an excellent tool for studying the properties of a material.
- Intrinsic material properties are not always sufficient
  - Texture
  - Micro- or nano-scale morphology
  - Material properties/structure may change depending on the system into which they are incorporated

Need to design the experiment to the sample

Goal: Encourage careful thought regarding experimental design

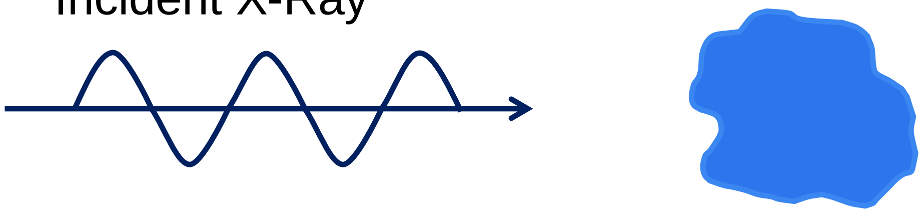
Outline

- The Basic Scattering Experiment
- Small Angle Scattering
- Reflectivity
- Powder Diffraction
- Thin Film Diffraction

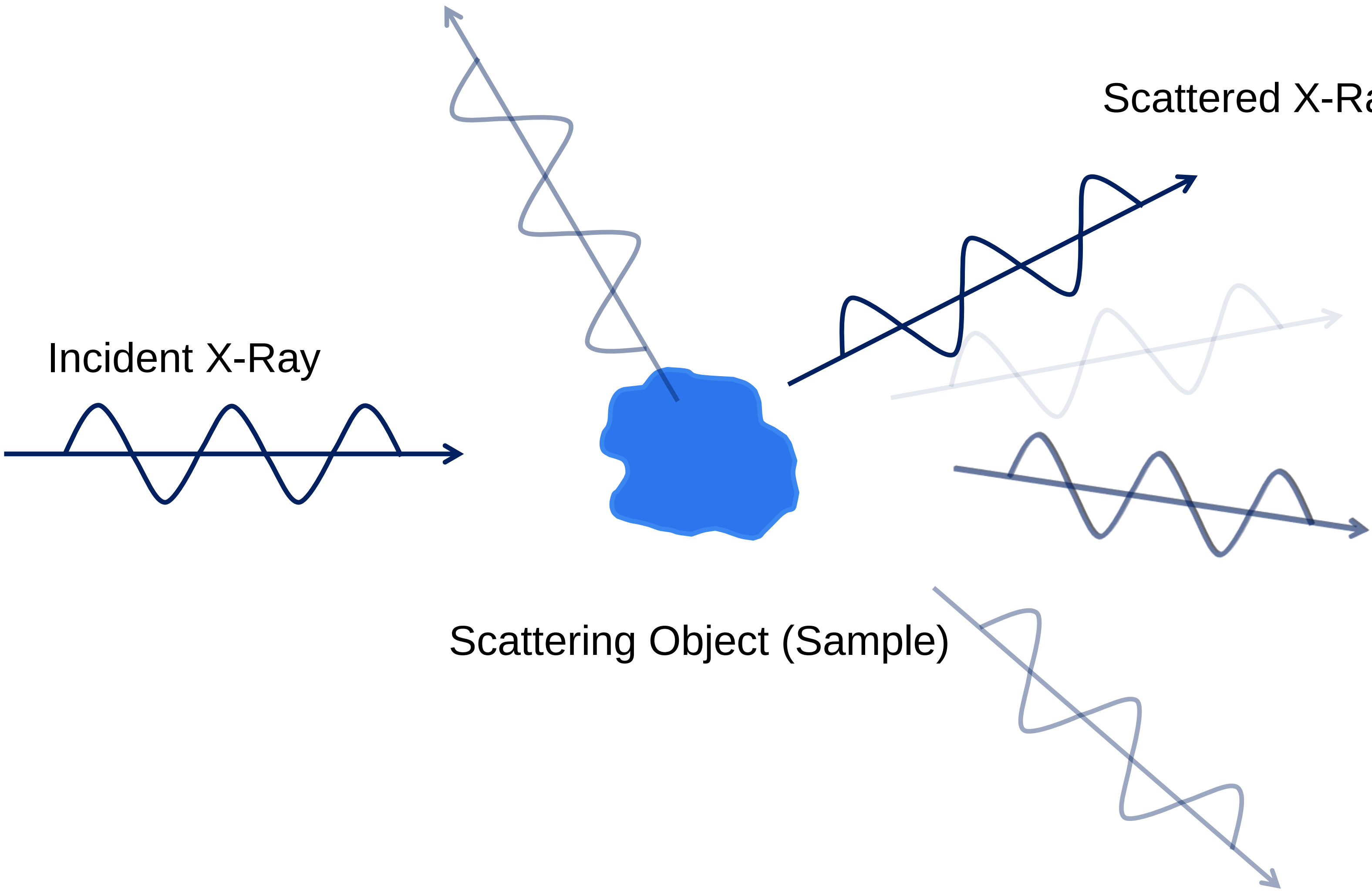
Basic Scattering Experiment

Scattering Object (Sample)

Basic Scattering Experiment

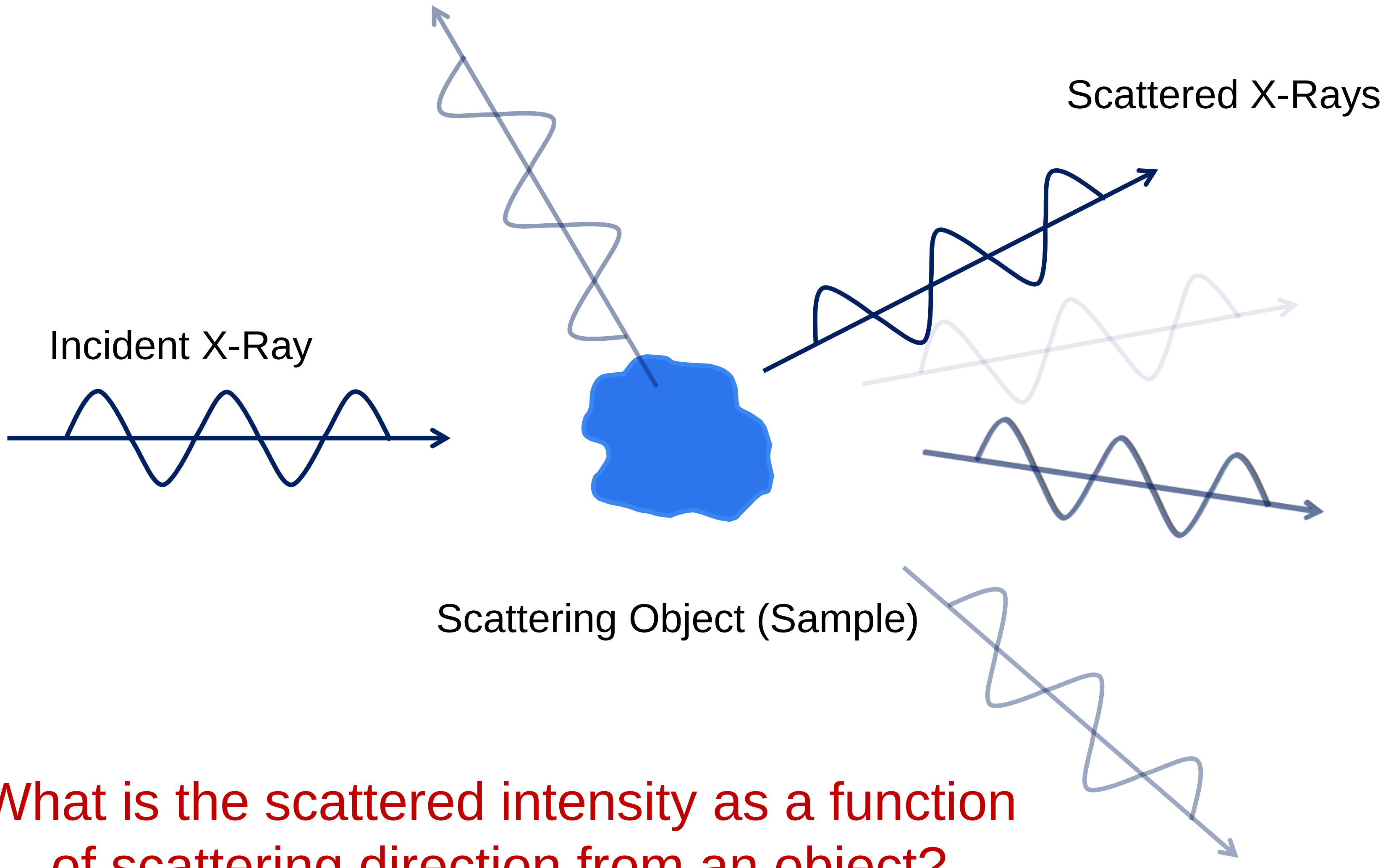


Basic Scattering Experiment



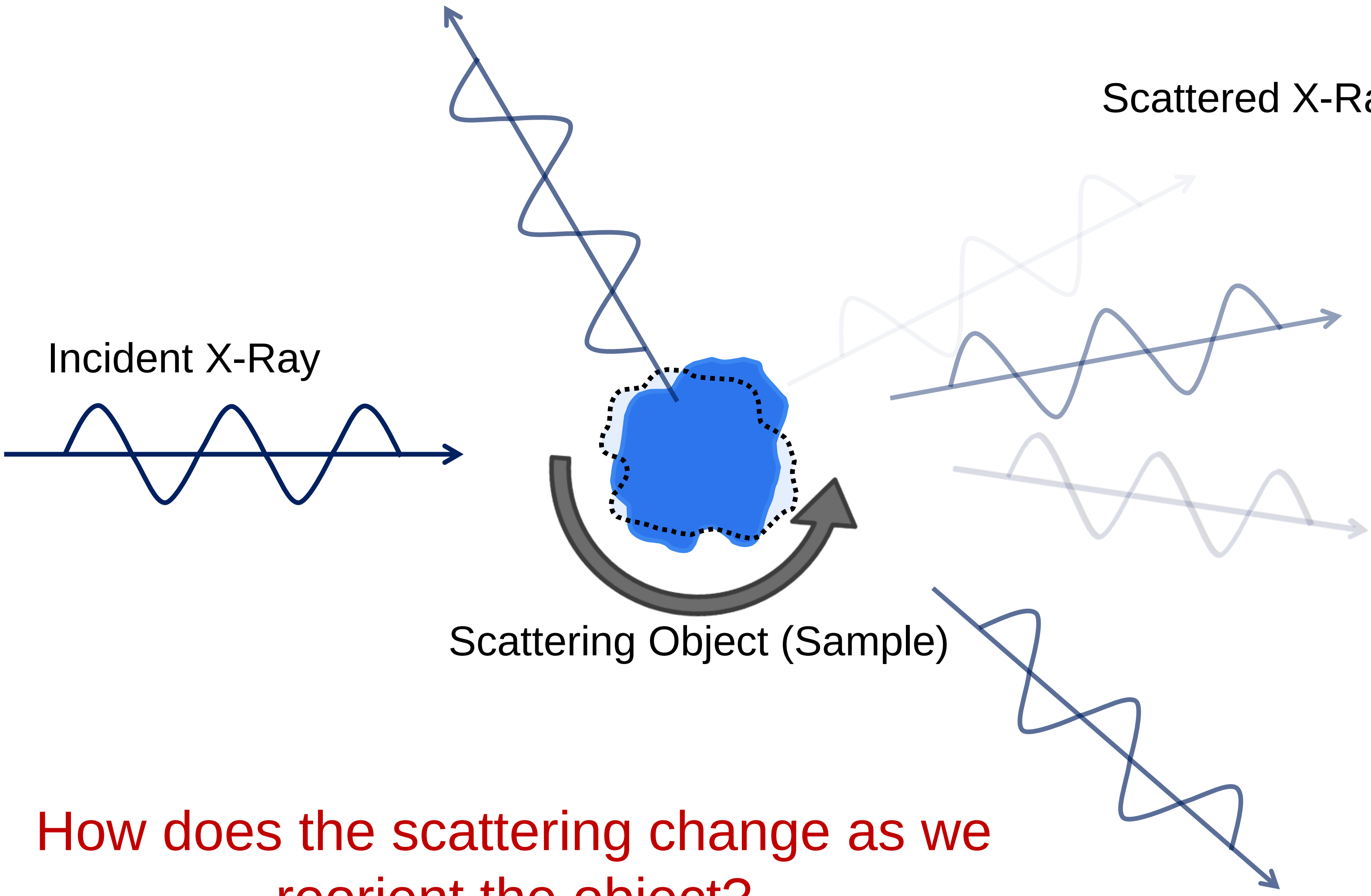
Basic Scattering Experiment

SLAC



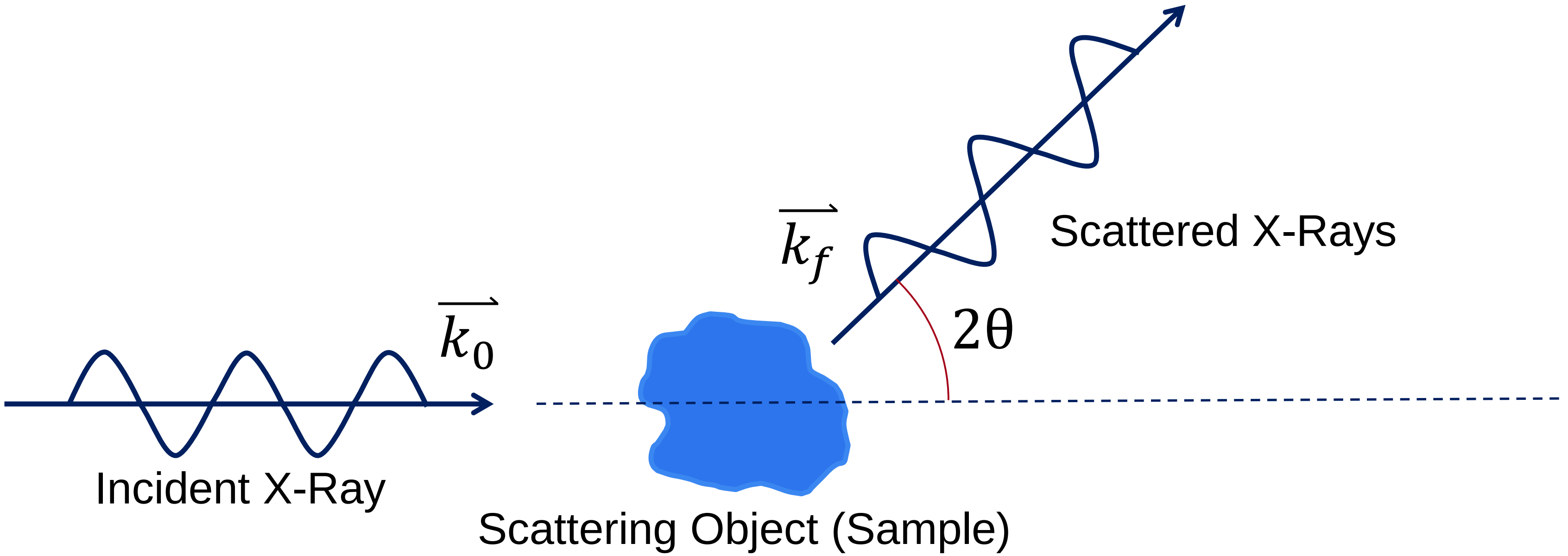
What is the scattered intensity as a function of scattering direction from an object?

Basic Scattering Experiment



How does the scattering change as we reorient the object?

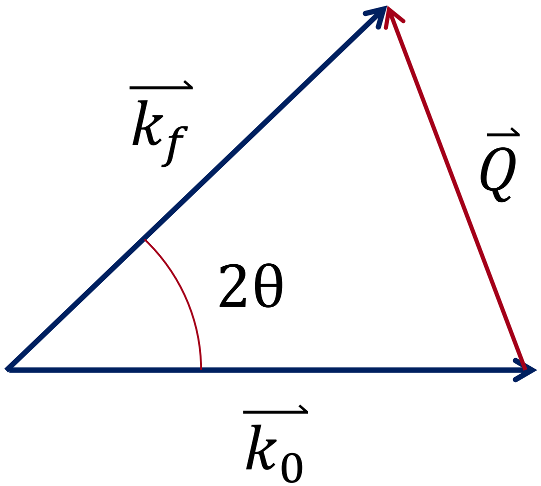
Basic Scattering Experiment

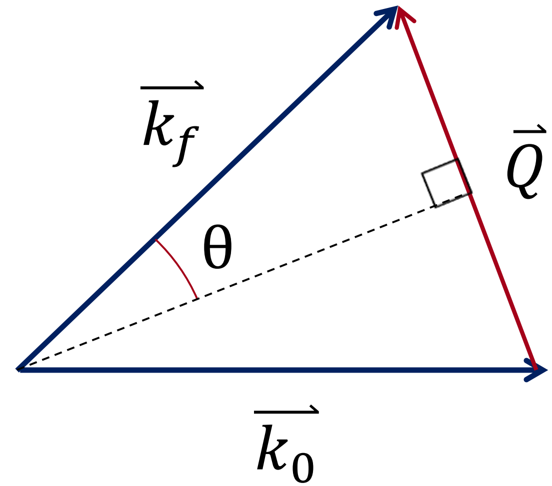


Momentum Transfer:

$$\vec{Q} = \overrightarrow{k_f} - \overrightarrow{k_0}$$

Basic Scattering Experiment





$$\sin\theta = \frac{1}{2}Q \div k_f$$

$$\sin\theta = \frac{1}{2}Q \div \frac{2\pi}{\lambda}$$

Momentum Transfer:

$$\vec{Q} = \overrightarrow{k_f} - \overrightarrow{k_0}$$

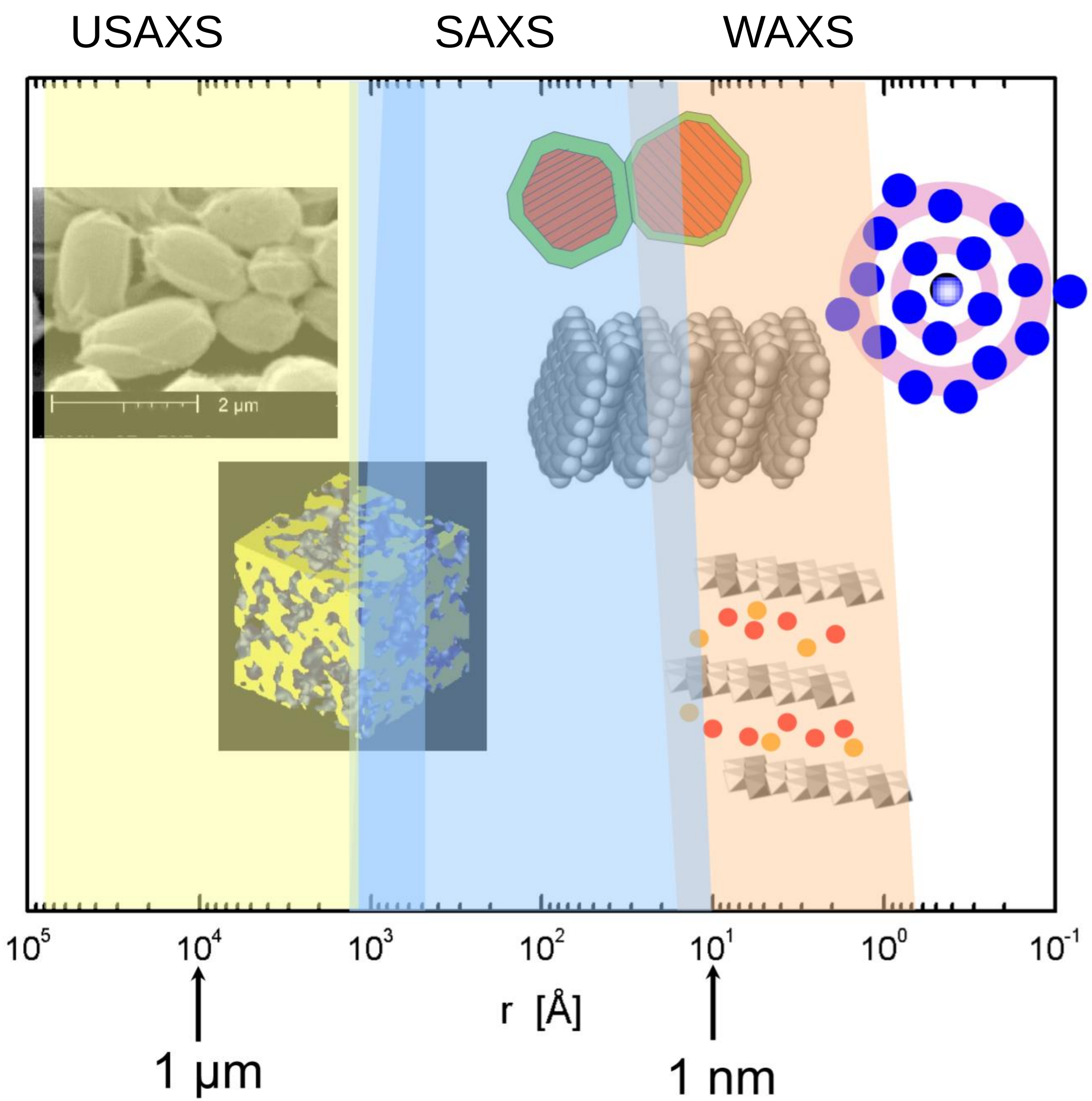
$$\left|\vec{k}\right| = \frac{2\pi}{\lambda}$$

$$\sin\theta = \frac{1}{2}Q \times \frac{\lambda}{2\pi}$$

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

All we care about is $I(\vec{Q})$

Choosing the Appropriate Length Scale



Q is inversely proportional to the length scale being probed.

Start by asking at what length scale do we want to study our sample?

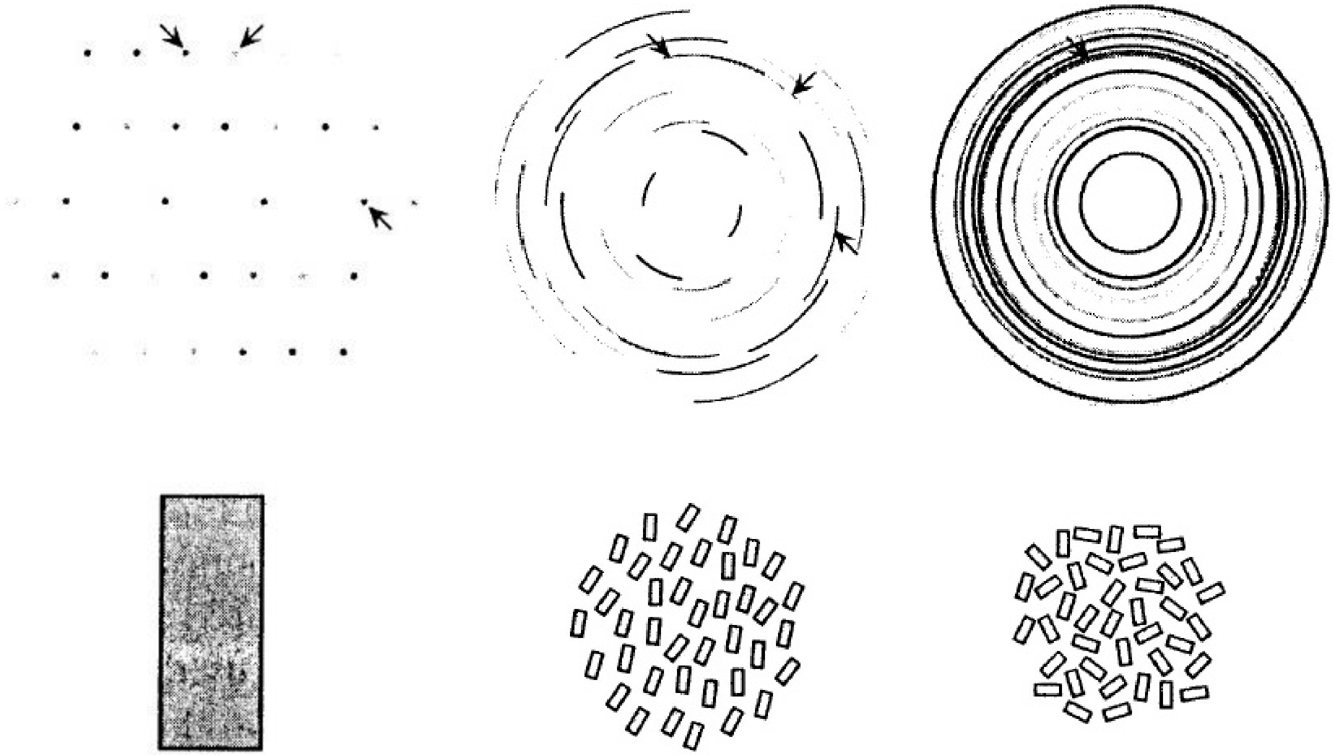
Choosing the Appropriate Geometry

SLAC

Sample Preparation:

Diffraction:

Sample:



Single Crystals

Multiply Twinned or Strongly Oriented Crystallites

Polycrystalline (Powder) Sample

David, W. I. F.; Shankland, K.; McCusker, L. B.; Baerlocher, C. *Structure Determination from Powder Diffraction Data*; IUCr, Oxford Science Publications, (2002).

Choosing the Appropriate Technique

- Small Angle X-Ray Scattering (SAXS)
  - Probes structure at the length scale of 1-100nm
- Reflectivity
  - Probes layered structure at the length scale of Å to nm's
- Powder Diffraction (WAXS)
  - Probes structure at atomic length scales (Å)
- Thin Film Diffraction
  - Polycrystalline
    - Probes structure at atomic length scales
  - Epitaxial
    - Probes structure at atomic length scales, including surface and interfacial structures

Terminology can be somewhat fluid…

Choosing the Appropriate Beamline

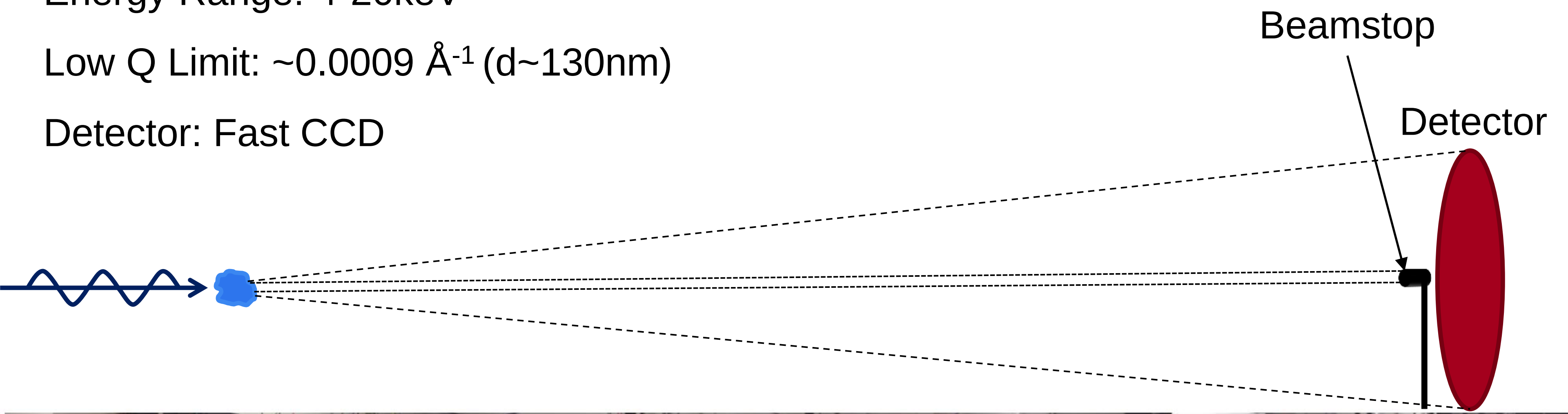
Beamline	BL1-5	BL2-1	BL7-2, BL10-2	BL11-3
Methods	•Thin Films •Real Time Experiments •Solution Phase •Transmission	•Powders •Thin Films •Reflectivity •θ-2θ •Anomalous diffraction	•Single crystals •Grazing-incidence •Anomalous diffraction •Surface studies	•Thin films •Texture •Real time experiments •Polycrystalline, small grains
Detectors	Area	Area, Point	Area, Point	Area
Advantages	•Fast measurement •Looks at large features •Variable Energy •Lowest Background	•High resolution •Accurate peak position and shape •Weak peaks •Variable energy	•High resolution •Accurate peak position and shape •Weak peaks •Variable energy •6/4 degrees of motion	•Fast measurement •Collect (nearly) whole pattern
Disadvantages	•Small q range •Background Sensitive •Difficult Interpretation	•Small q range •Background Sensitive •Difficult Interpretation	•Slow •Can be difficult to find textured peaks •Complicated	•Fixed wavelength •Low resolution •Peak shape and position less accurate •Weak peaks difficult

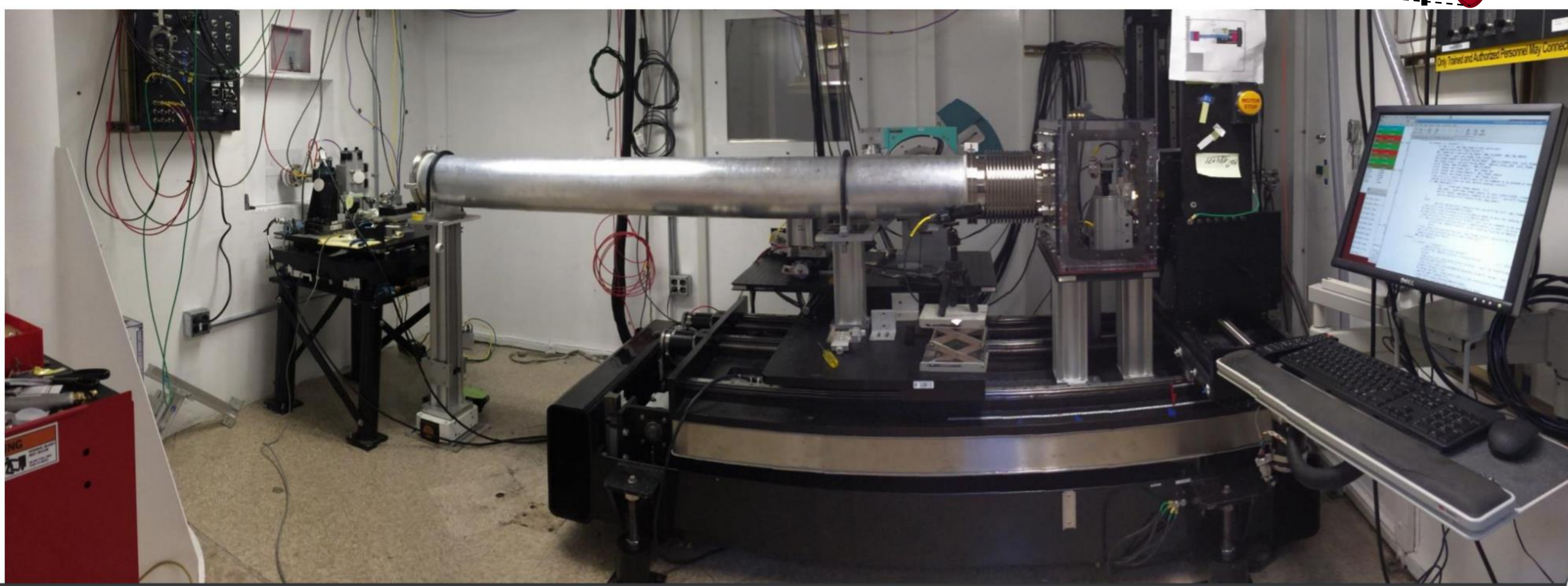
Beamline 1-5

Energy Range: 4-20keV

Low Q Limit: ~0.0009 Å^{-1} (d~130nm)

Detector: Fast CCD



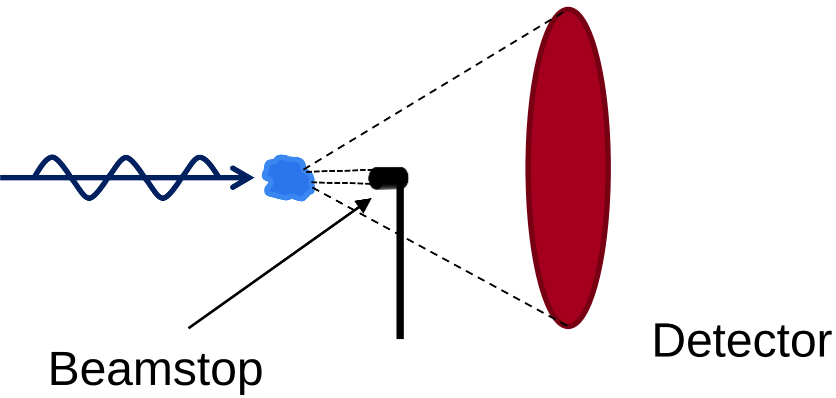


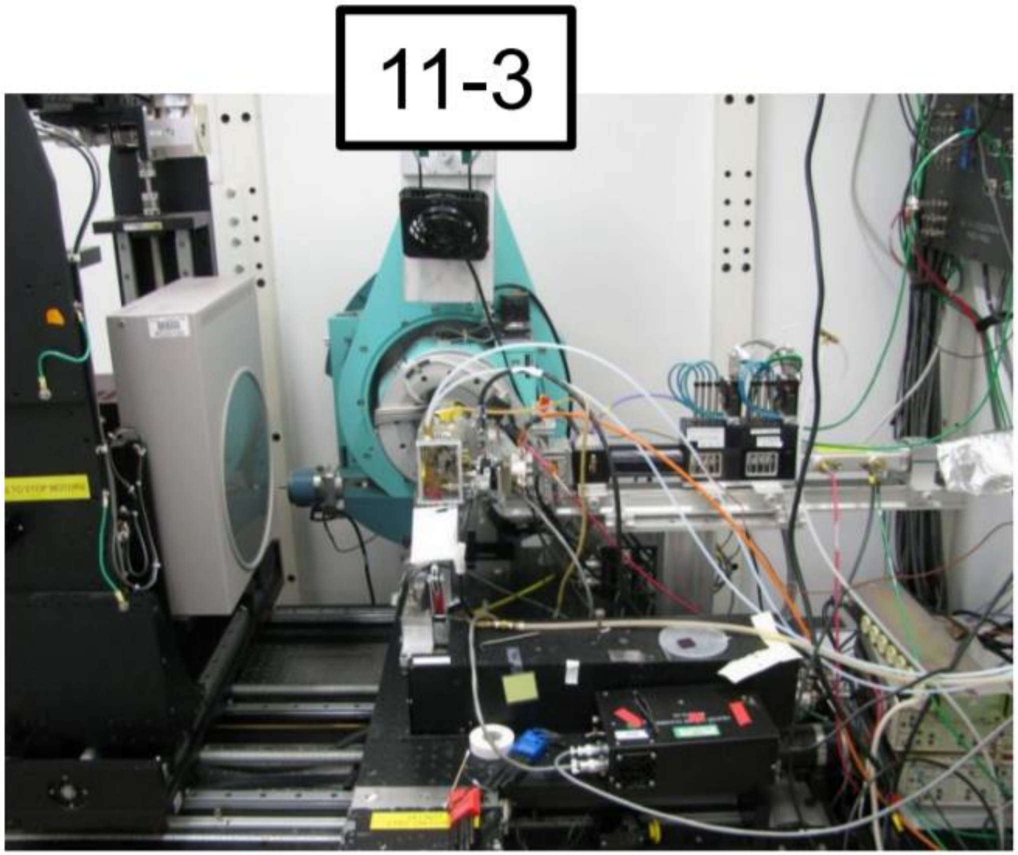
Beamline 11-3

Energy Range: 12.7keV (fixed energy)

Detector: Fast CCD

Sample-Detector Distance: 150-400mm





Beamstop is positioned close to the sample

Gives low background scattering at cost of lowest angles

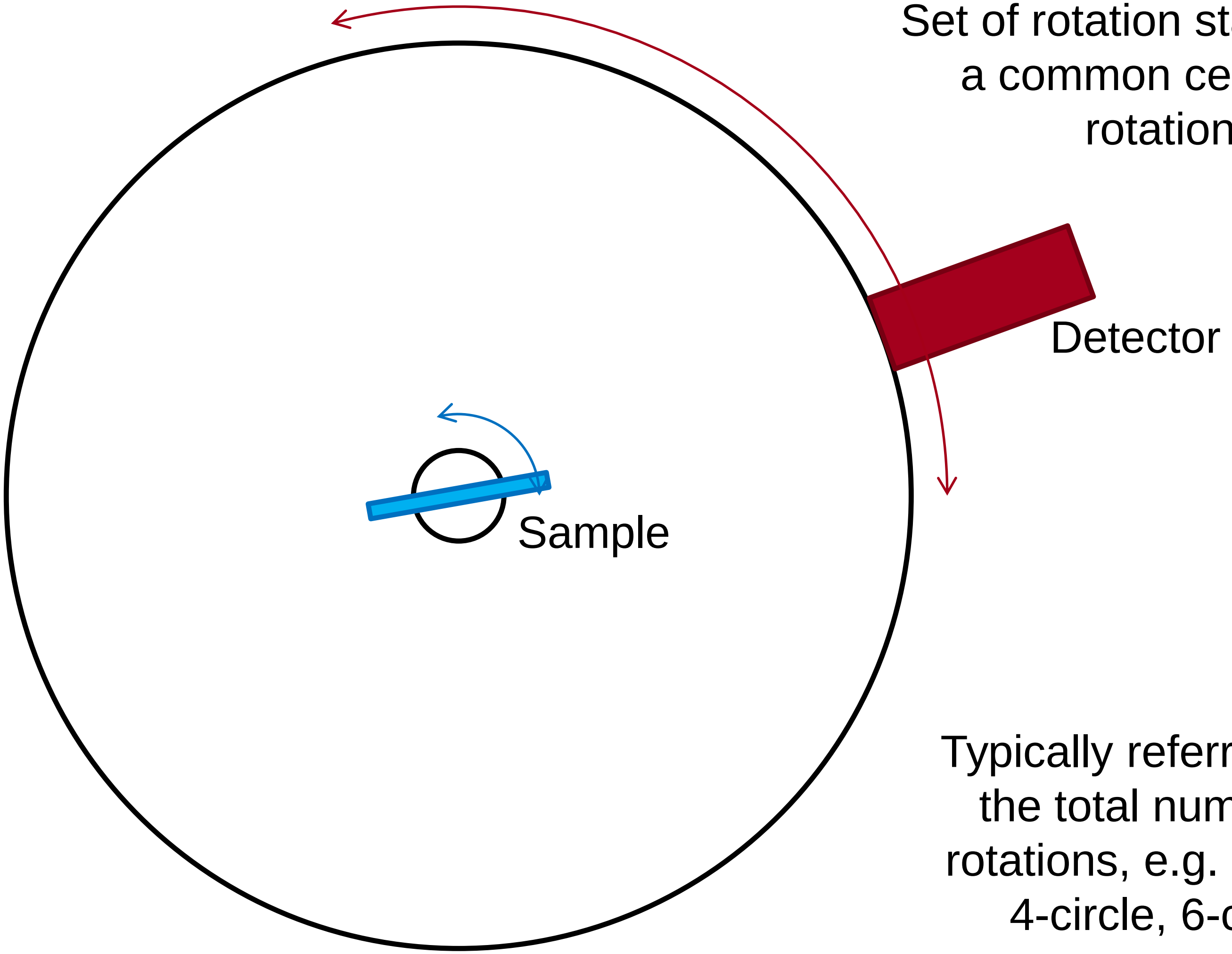
Diffractometer Beamlines (2-1, 7-2, 10-2)

https://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/x-ray-diffraction/d8-advance/eco.html

Set of rotation stages with a common center of rotation

Diffractometer Beamlines (2-1, 7-2, 10-2)

SLAC

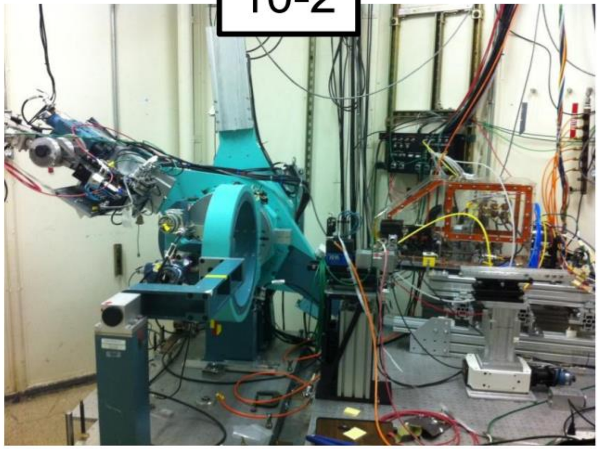


Set of rotation stages with a common center of rotation

Typically referred to by the total number of rotations, e.g. 2-circle, 4-circle, 6-circle

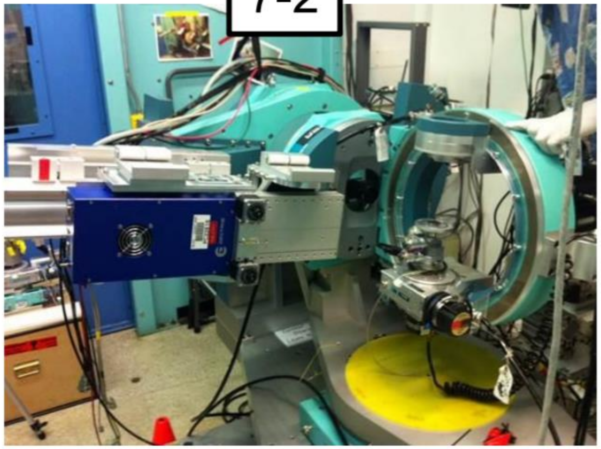
Diffractometer Beamlines (2-1, 7-2, 10-2)

10-2



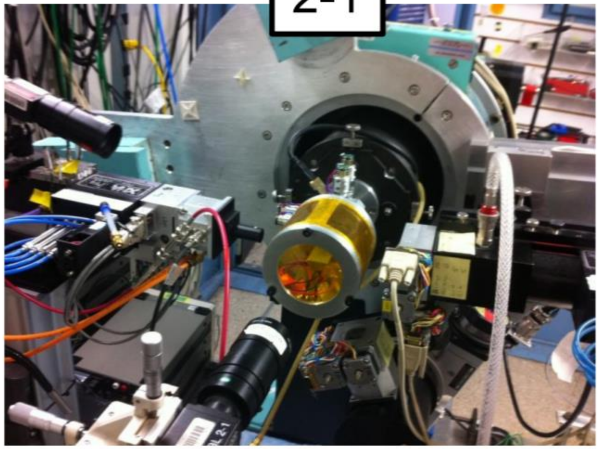
4-circle
5-30keV energy range

7-2



6-circle
5-18keV energy range

2-1



2-circle
5-17keV energy range

Can be configured with either a point detector (PMT with analyzer crystal or Vortex) or small area detectors (Pilatus 100K or 300K-W)

Number of *in-situ* chambers are compatible with all instruments, some are more beamline specific

Practical Considerations – Data Collection

Beamline Configuration:

Small Area Detector (Pilatus):
- Reduced angular resolution (~0.01º)
- Strong signal
- Fast, parallel detection (many pixels)
- Images need to be stitched together and integrated
- No background discrimination, can have very high backgrounds

Low Resolution (Soller Slits):
- Reduced angular resolution (~0.01°)
- Strong signal into detector
- No background discrimination (reduces signal to background)
- Choice of PMT or Vortex detector

High Resolution (Analyzer Crystal):
- Highest angular resolution
- Reduced signal into detector
- Good signal to background (can compensate for reduced total signal)
- Use PMT detector only

Practical Considerations – Data Collection

SLAC

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Small Area Detector (Pilatus):

- Reduced angular resolution (~0.01º)
- Strong
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Measures Position

Low Resolution (Soller Slits):

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Measures Angle

High Resolution (Analyzer Crystal):

- Highest angular resolution
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Measures Angle

Practical Considerations – Data Collection

Resolution:

What is the time tradeoff?

Some back of the envelope calculations:

Measured 2-theta range: 5 – 65
Assuming we count for 1 second per point, how long will this take with different step sizes?

Step Size	Total Count Time
4 (Pilatus)	15sec
0.01	1hr 40min
0.005	3hr 20min
0.002	8hr 20min
0.001 (minimum feasible)	16hr 40min

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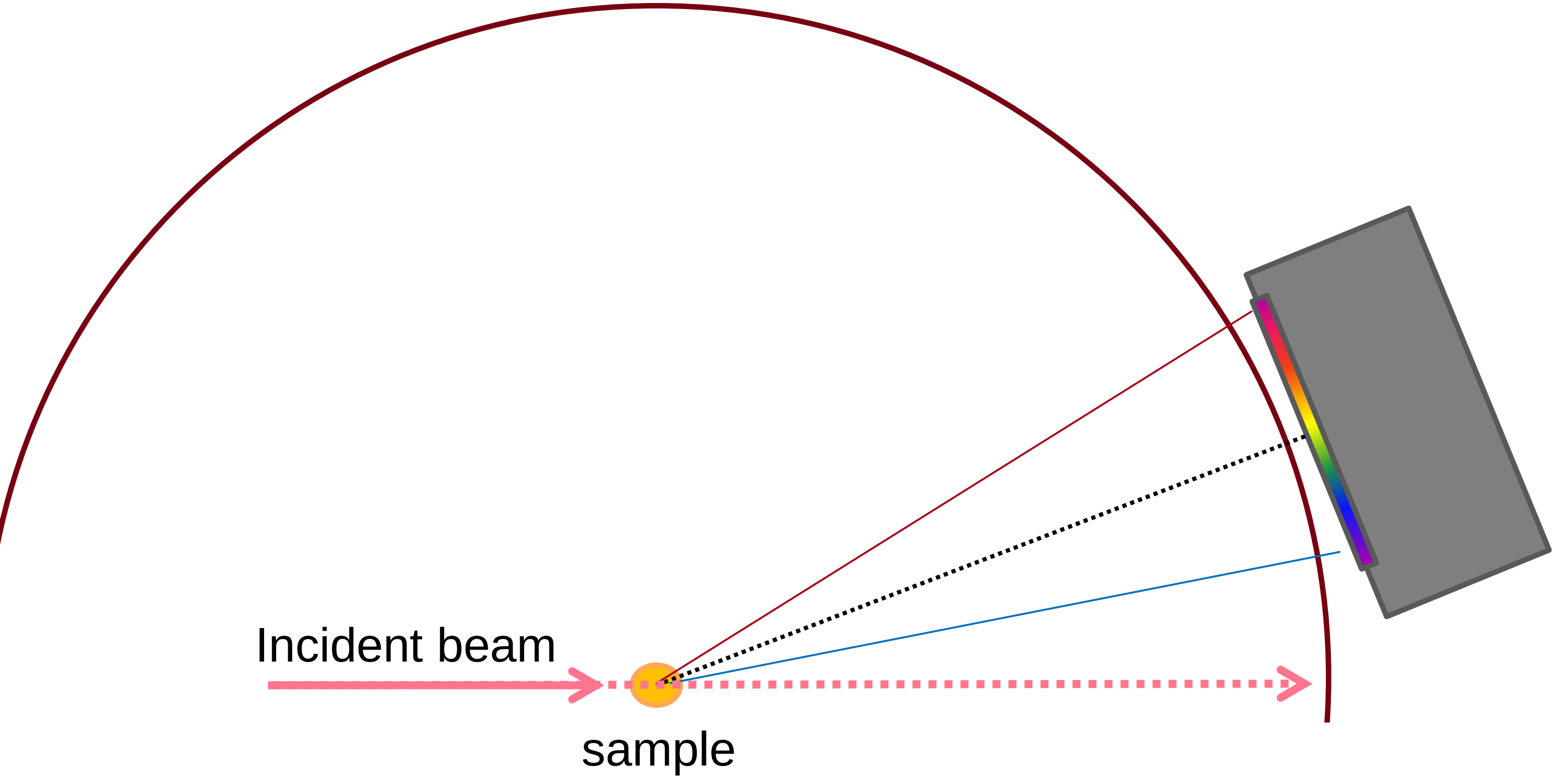
Why not always use the Pilatus?

Pilatus Issues

- Measures position, not angle
  - subject to alignment errors
- No energy discrimination
  - subject to high fluorescence backgrounds
- Hard to have a constant measurement geometry
  - steplike changes in both resolution and signal/background
- Limited resolution
  - Increased peak overlap at high angles

Pilatus Issues

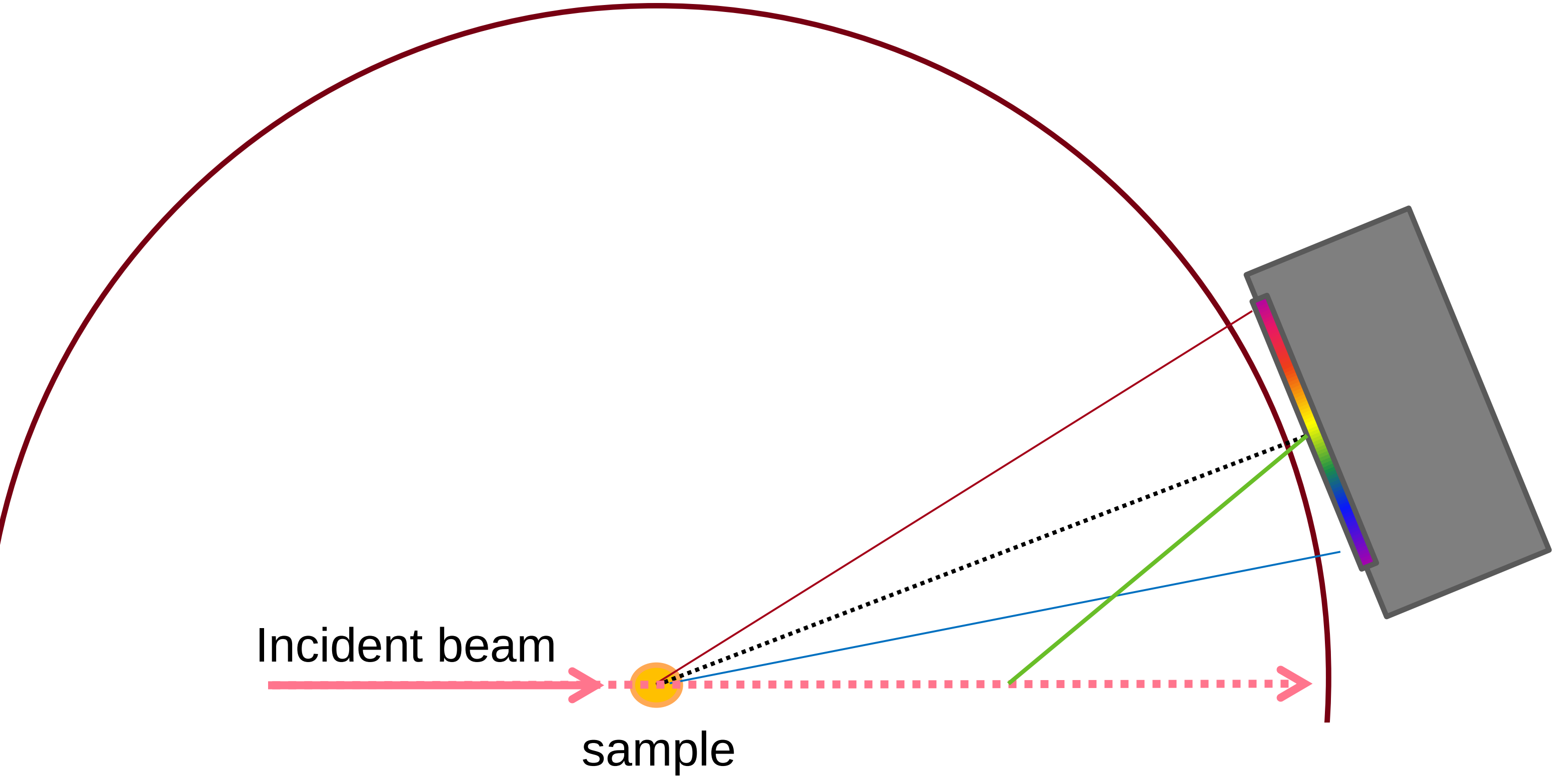
Ideally, each pixel on the detector will correspond to the scattered x-rays at a given angle from the sample position.



Pilatus Issues

Ideally, each pixel on the detector will correspond to the scattered x-rays at a given angle from the sample position.

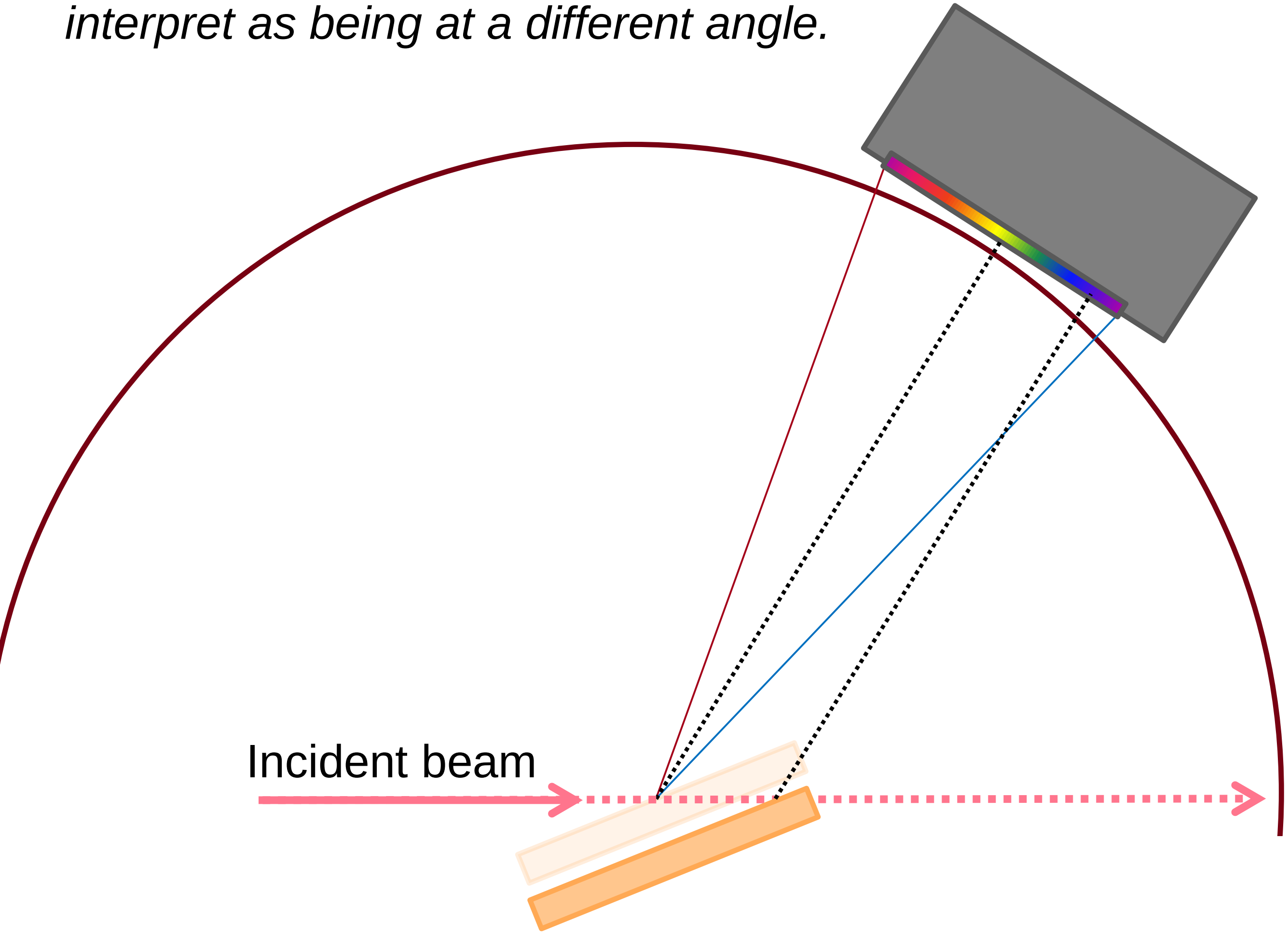
But the detector will see scattering from anywhere, which may lead to intensity at a pixel from another angle and position…



Pilatus Issues

What happens we have a flat sample which is misaligned?

Scattering at the same angle hits at a different point on the detector, *we interpret as being at a different angle.*



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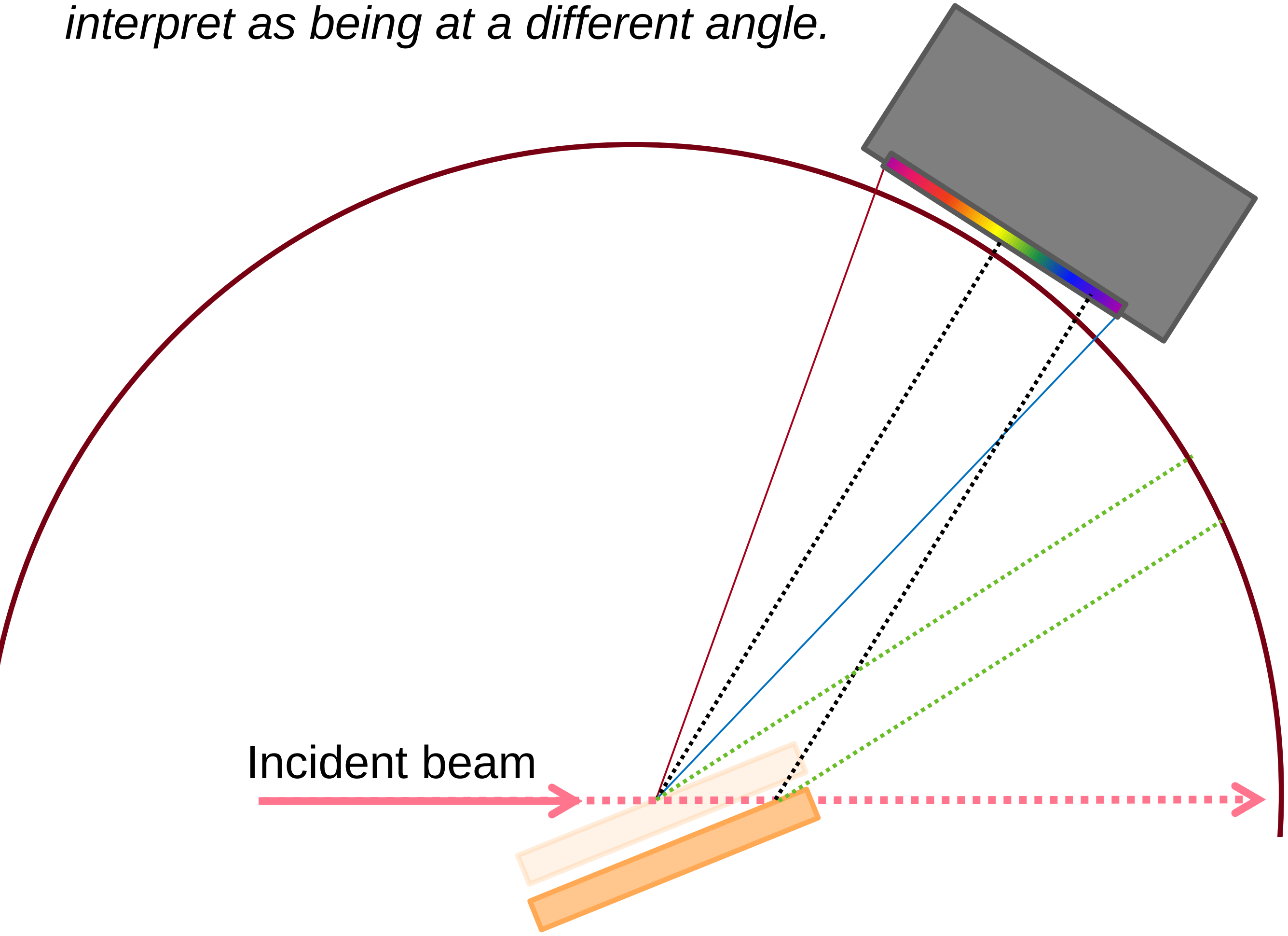


This is not a constant offset in all angles, the error will be a function of scattering angle.

Thin Film Geometries

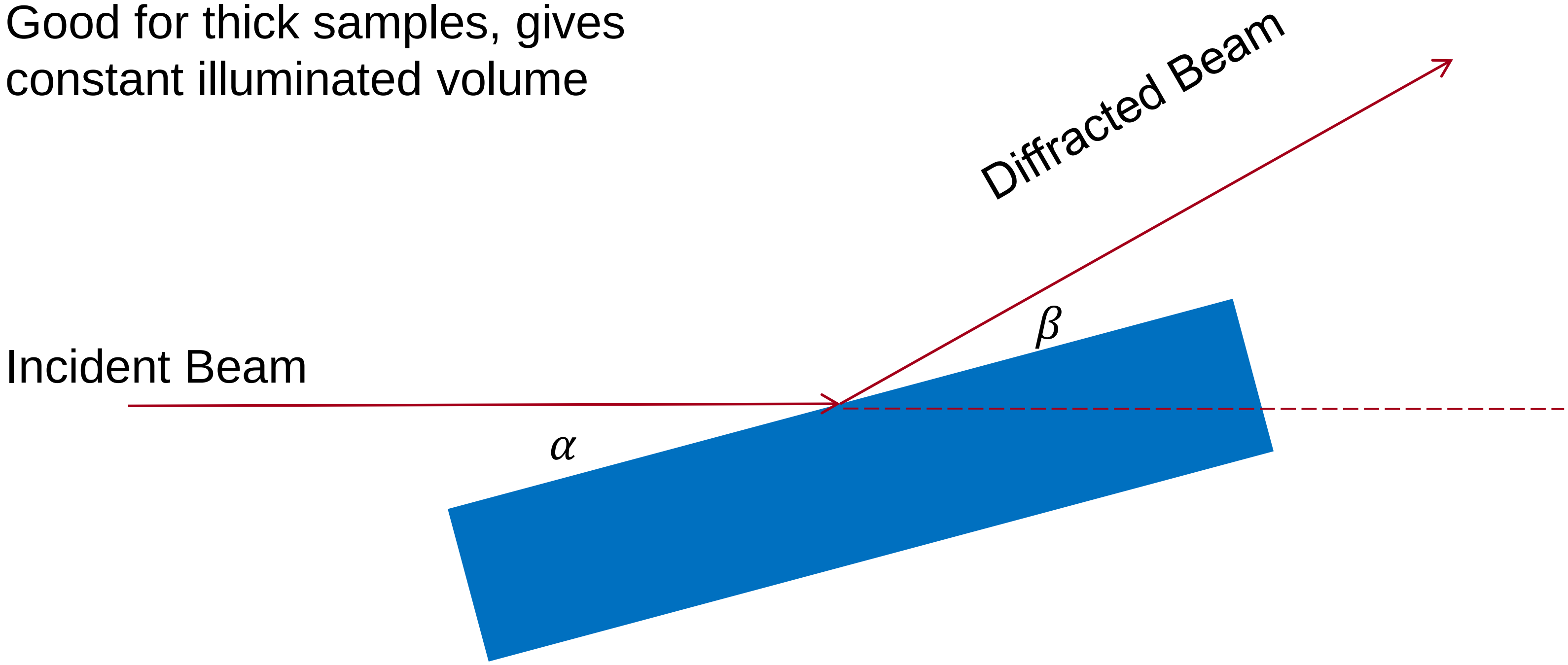
Sample Preparation:

Cannot satisfy this geometry for all points on an area detector simulaneously

Symmetric geometry sometimes called Bragg-Brentano geometry

$$\alpha = \beta$$

Good for thick samples, gives constant illuminated volume



Thin Film Geometries

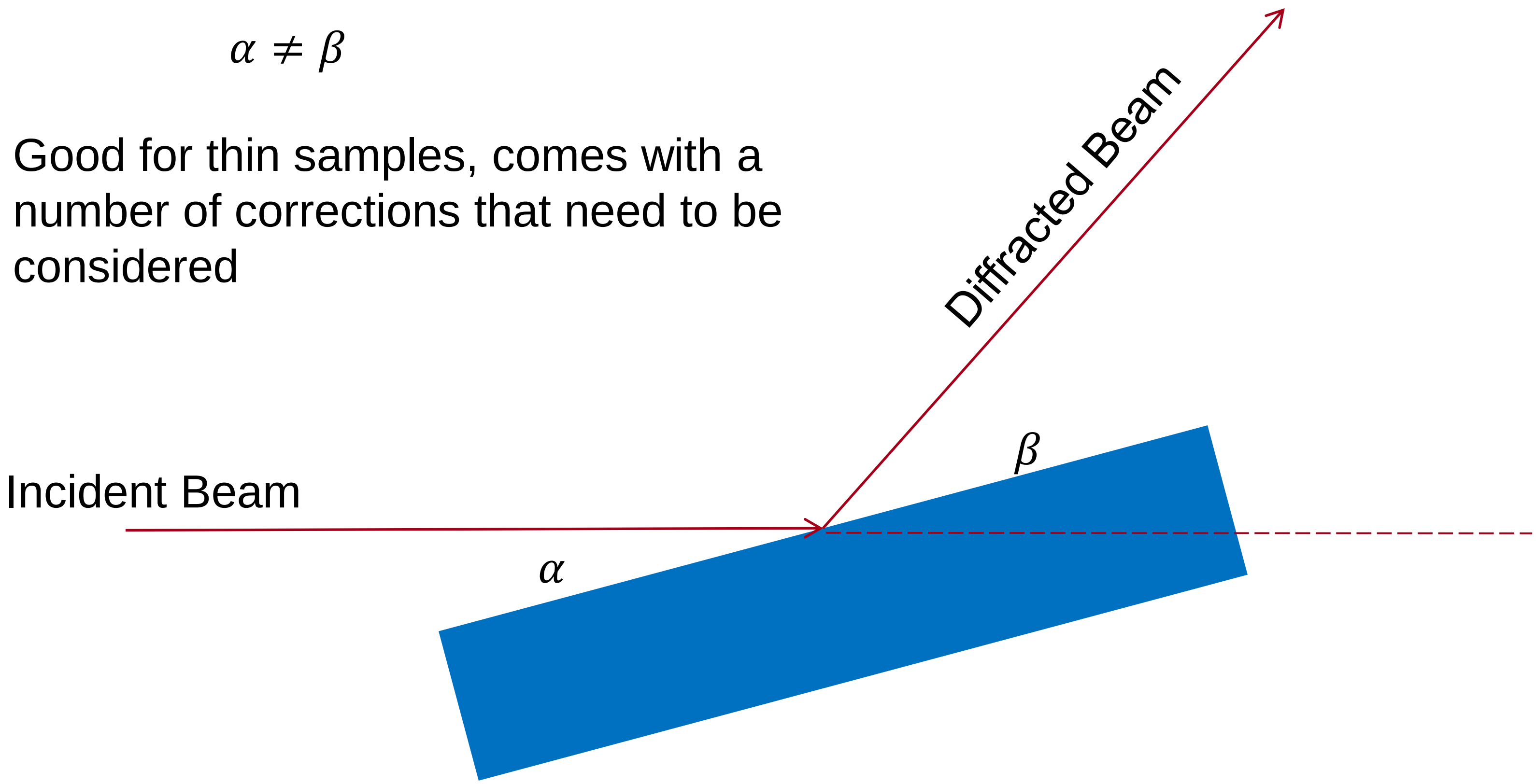
Sample Preparation:

Asymmetric geometry sometimes called grazing incidence geometry

$$\alpha \neq \beta$$

Good for thin samples, comes with a number of corrections that need to be considered

$$I_{calc} \propto \frac{2 \cdot \sin \beta}{\sin \beta + \sin \alpha}$$



Thin Film Geometries

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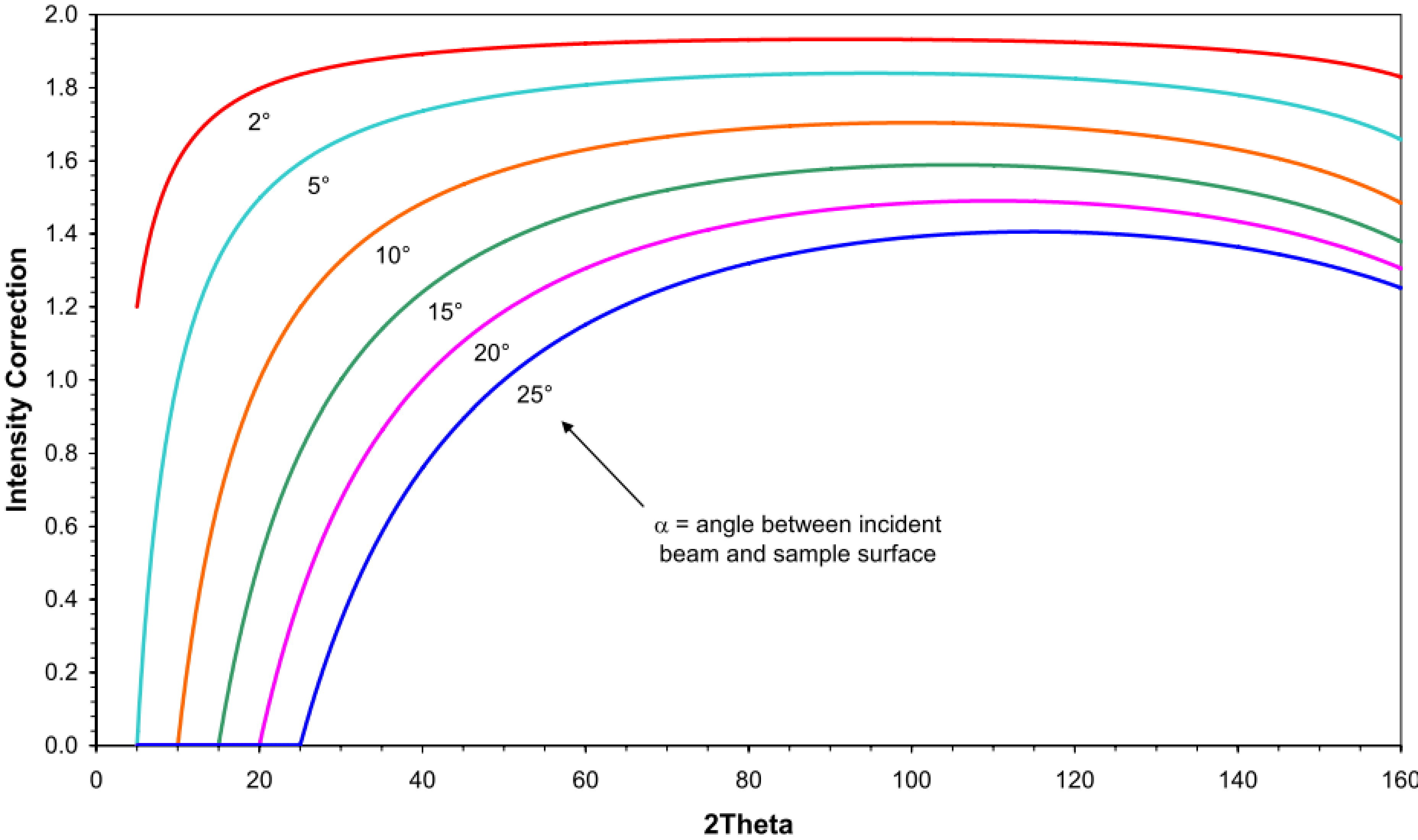
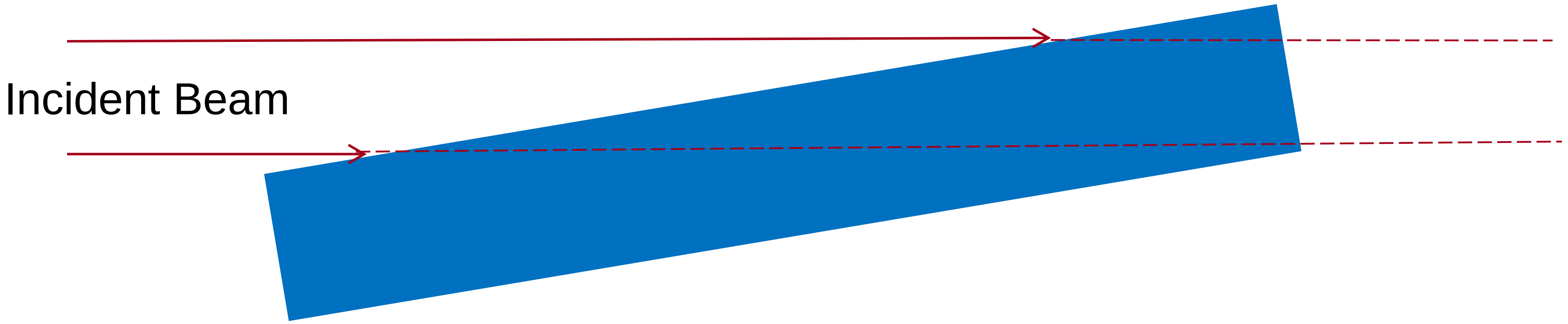


Thin Film Geometries

Grazing incidence geometry is typically used
Increases volume of sample illuminated → Increases scattering signal

- Large beam footprint (even if tightly focused beam is used)
- Limited penetration into (and thus scattering from) the substrate → Reduced background
- Can isolate scattering from just the film by operating near the critical angle or above the critical angle of the substrate



Thin Film Geometries

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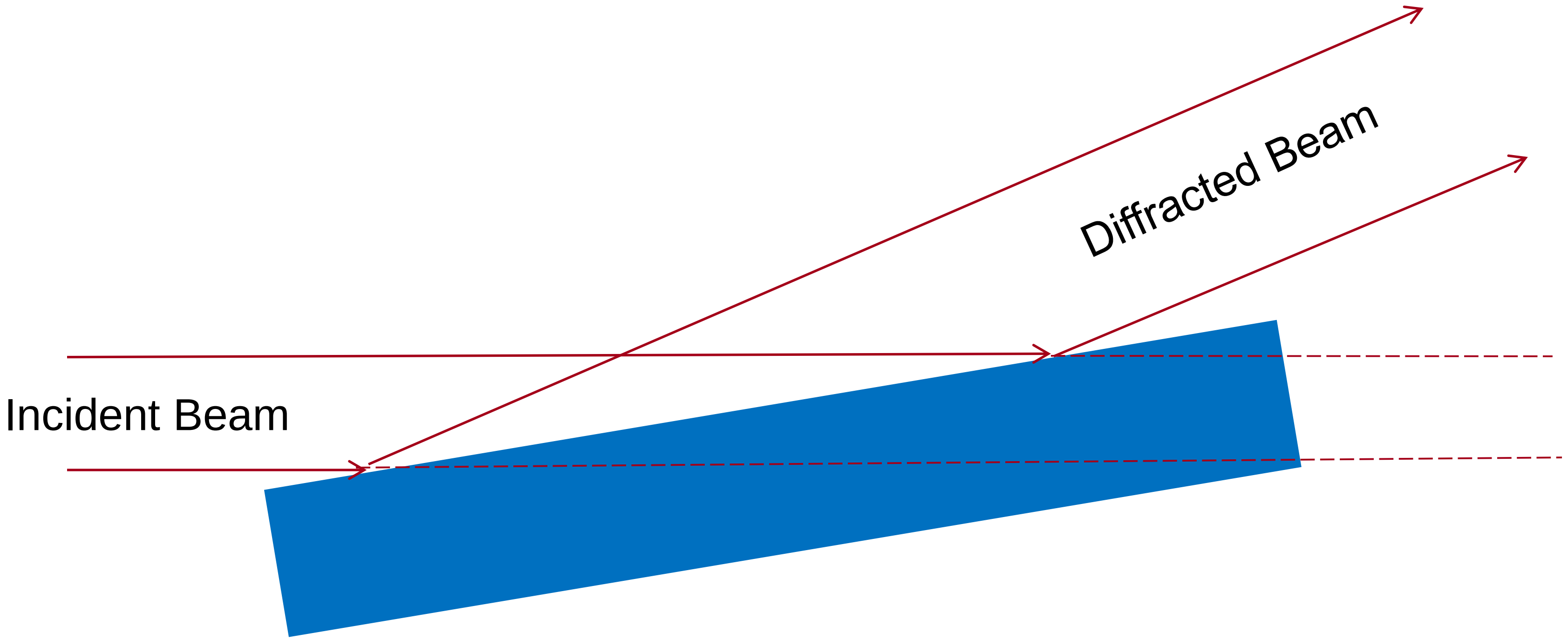
Increases volume of sample illuminated → Increases scattering signal

- Large beam footprint (even if tightly focused beam is used)
- Footprint is projected onto the detector → gives poor scattering resolution that changes with scattering angle



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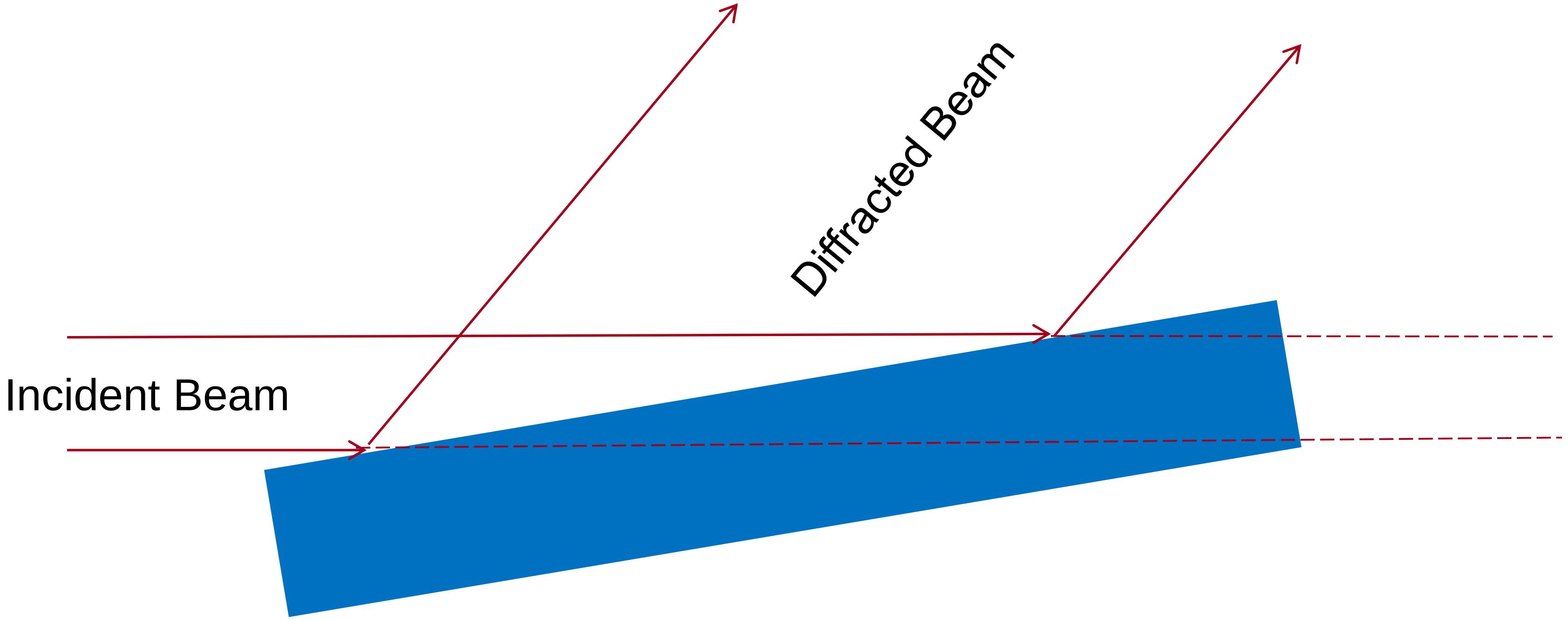
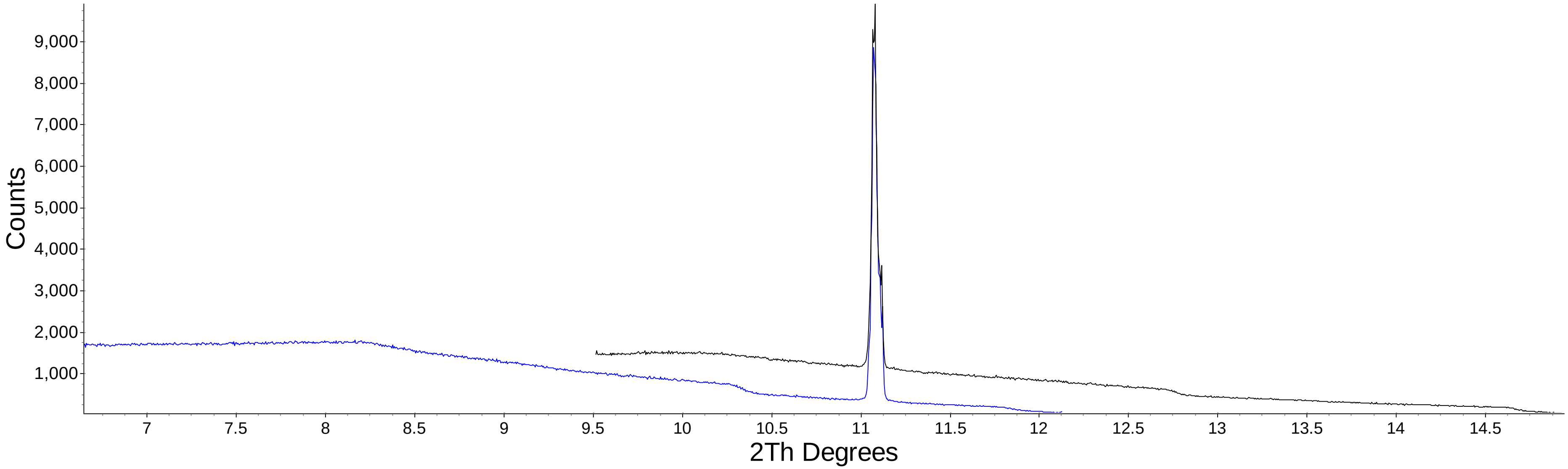
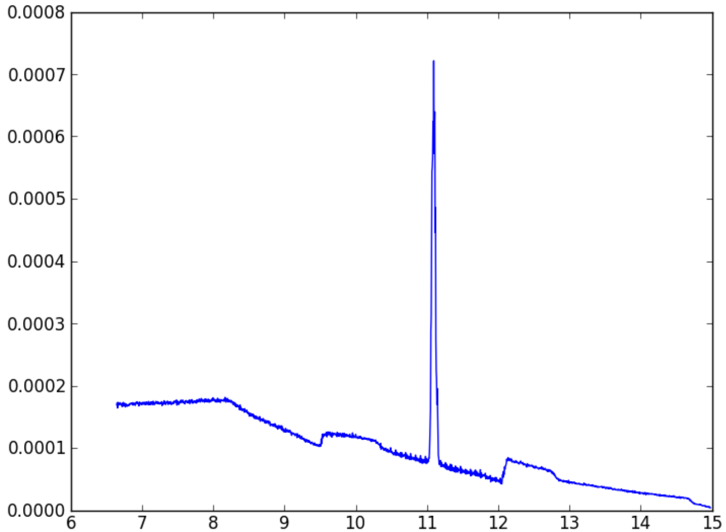


Some Pilatus Data Examples…

LaB6 standard plate – 2 sequential images integrated and compared

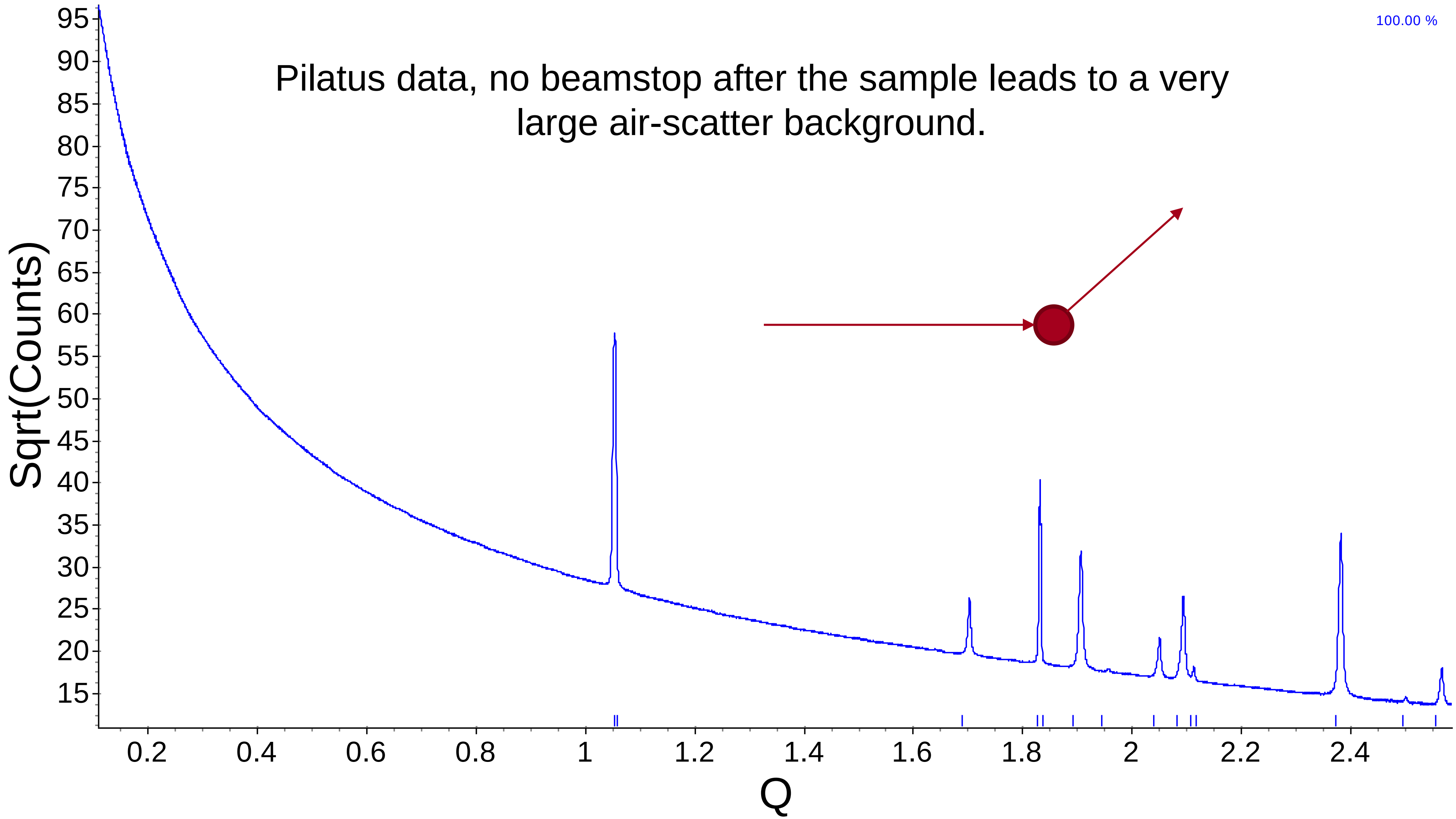


Leads to steps in the background, this will be very difficult to properly fit or account for in a refinement.



Some Pilatus Data Examples…

Sample for structure solution, capillary geometry (cylindrical symmetry)

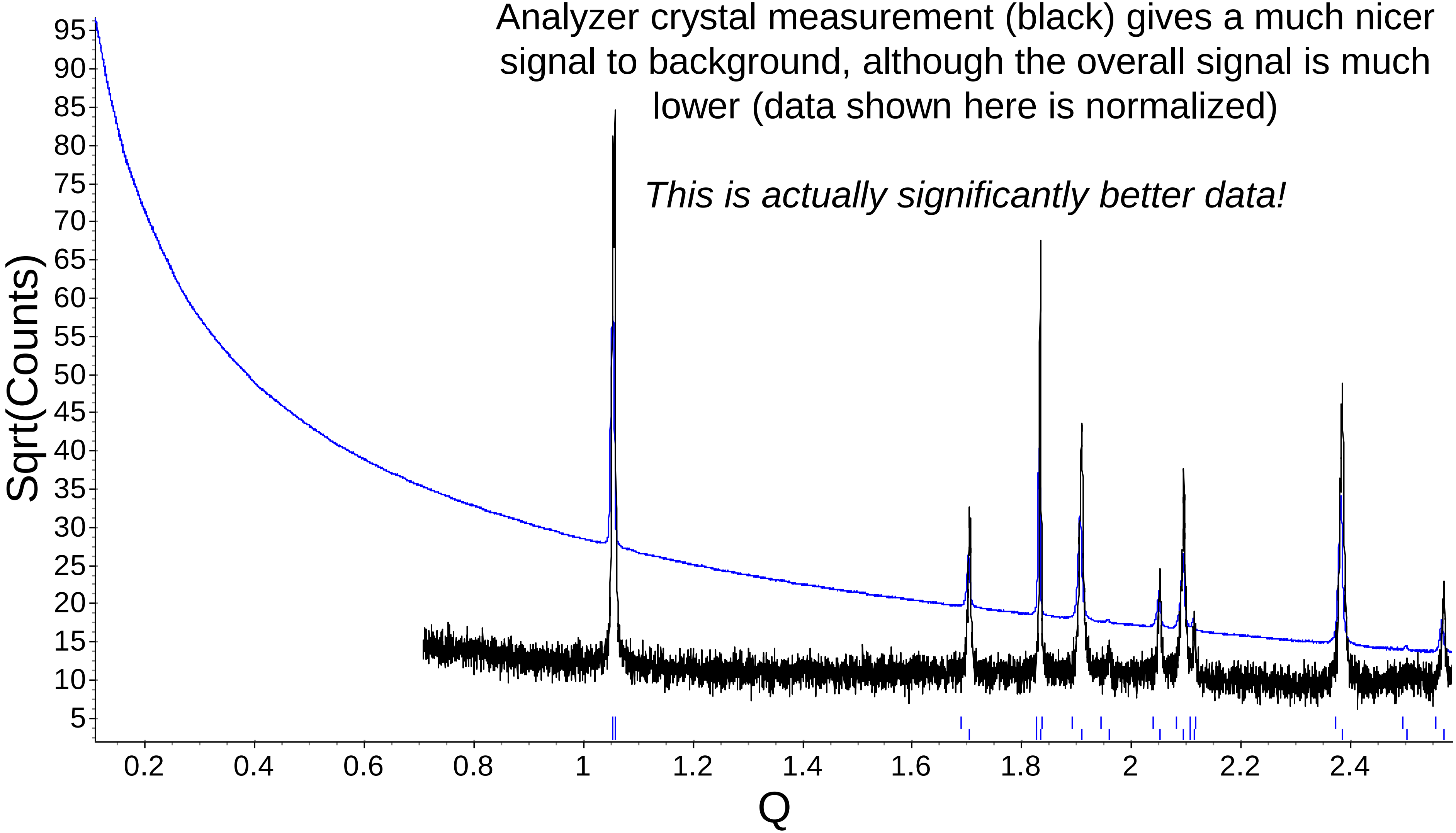


Some Pilatus Data Examples…

Sample for structure solution, capillary geometry

Analyzer crystal measurement (black) gives a much nicer signal to background, although the overall signal is much lower (data shown here is normalized)

This is actually significantly better data!



Some Pilatus Data Examples…

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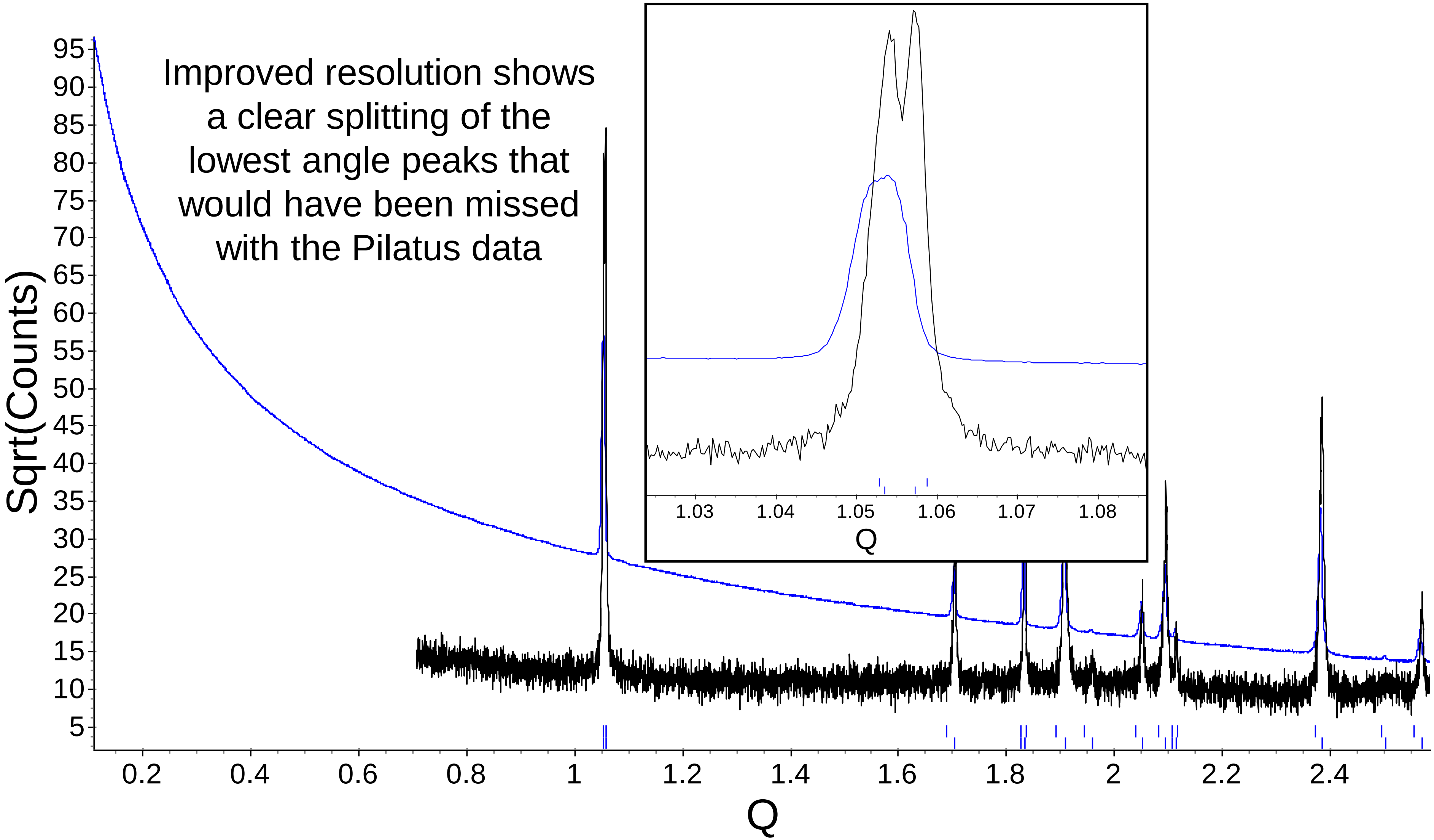


Analyzer Crystal

- Measures angle
  - Not subject to alignment errors
- Accepts only a single energy
  - Eliminates high fluorescence backgrounds
- Highest possible resolution
  - Separate closely spaced peaks
  - Increases information from high angle (overlapped) peaks
- Point detector
  - Collecting full data is slow

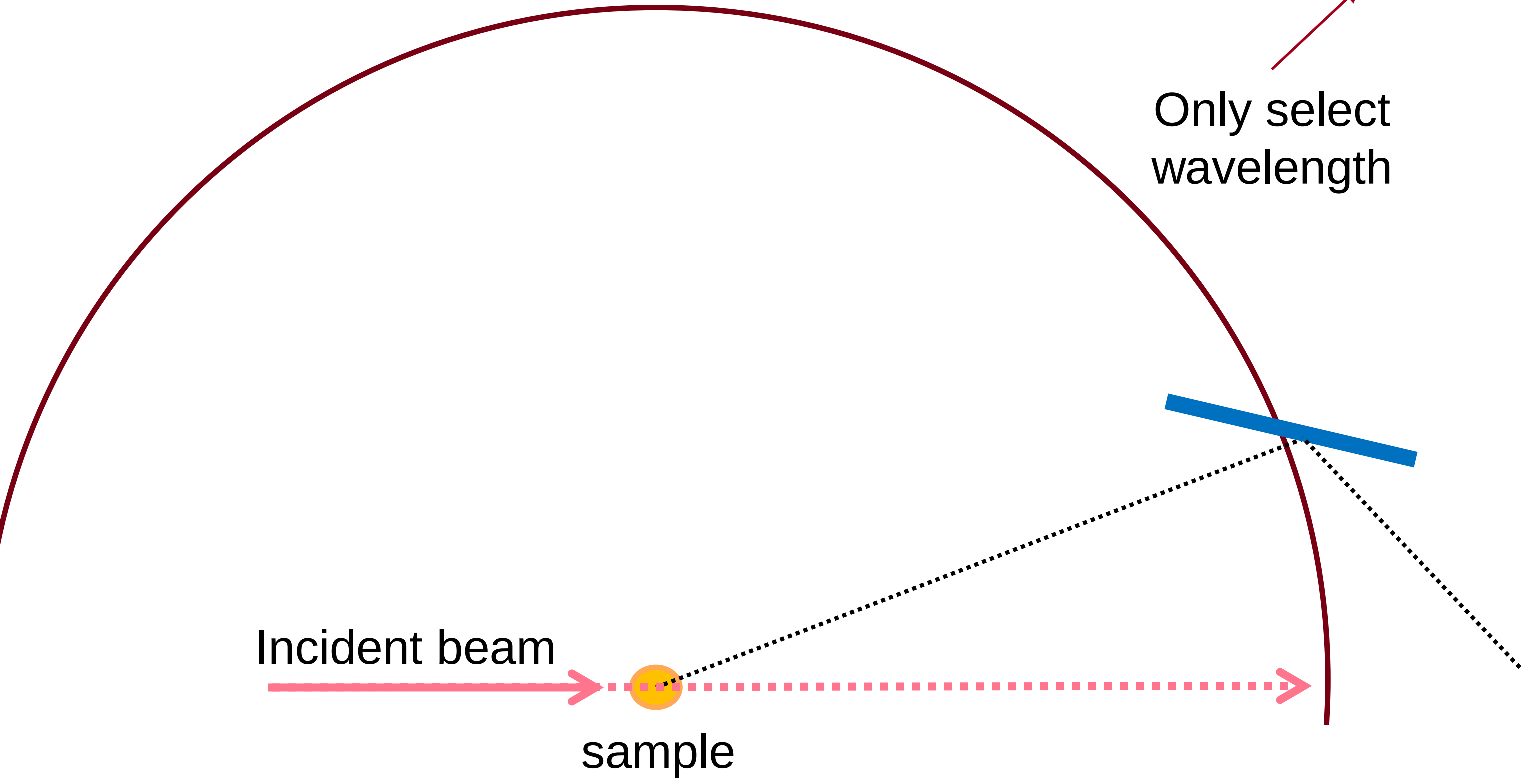
Analyzer Crystal

Only x-rays that are incident on the analyzer at an angle/energy that satisfies the Bragg condition will diffract to scatter into the detector.

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

Only select wavelength

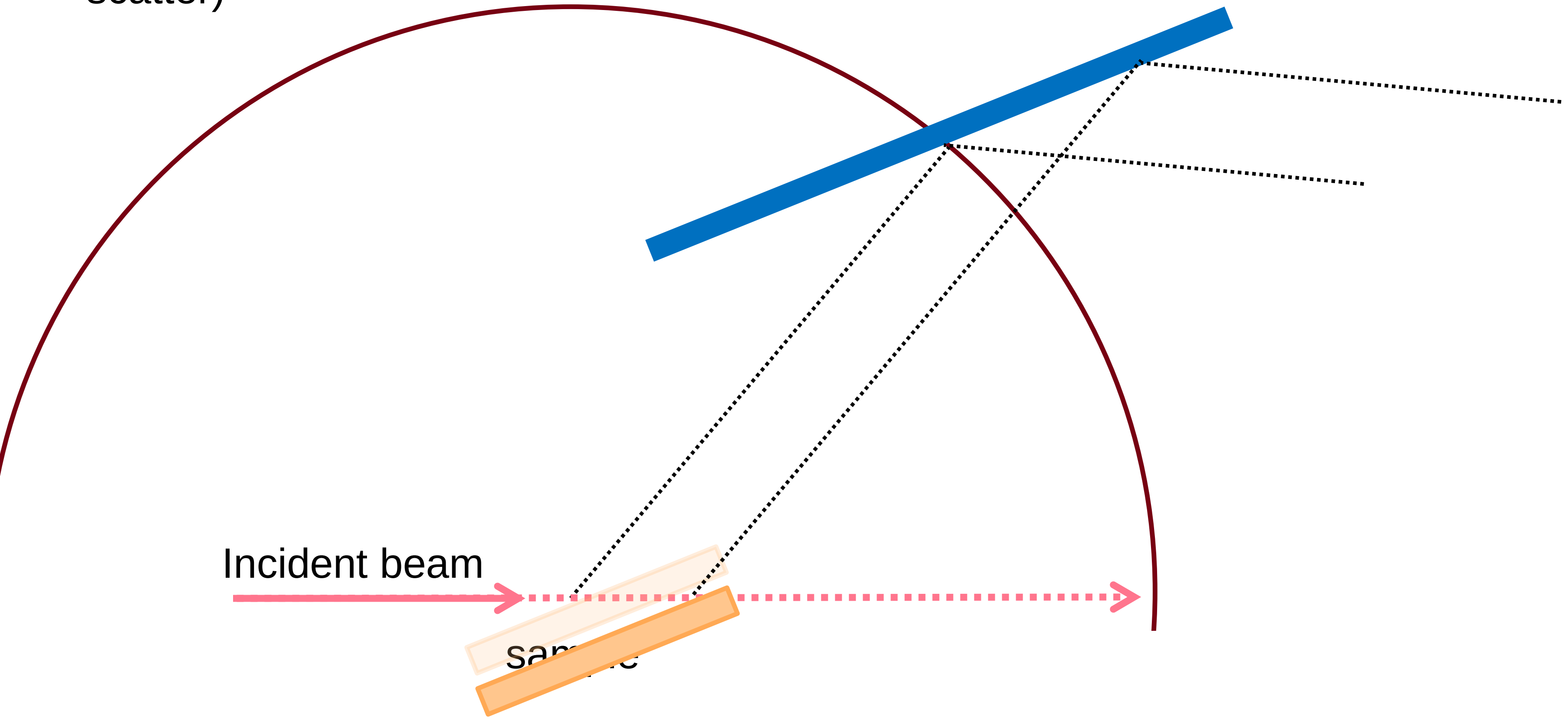
Only select angle



Analyzer Crystal

Fairly insensitive to misalignment – just hits a different spot on the analyzer and is diffracted into a different area on the detector

Can use slits to limit the accepted volume if desired (can cut down on air scatter)



Analyzer Crystal

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<u>What determines the resolution?</u>

- Rocking (Darwin) width of the crystal
  - Use perfectly imperfect crystals
  - Can move to higher order peaks to increase resolution

- Energy resolution of the monochromator
  - Typically on the order of 10^{-4} for double bounce Si (111)
  - Minimize vertical divergence in the optics
  - Can use higher order peaks

- Divergence of the incident x-ray beam
  - Want a parallel beam geometry
  - Minimize vertical divergence
  - Can use paired slits to make the beam more parallel at the cost of intensity

Powder XRD Conclusions and Q&A

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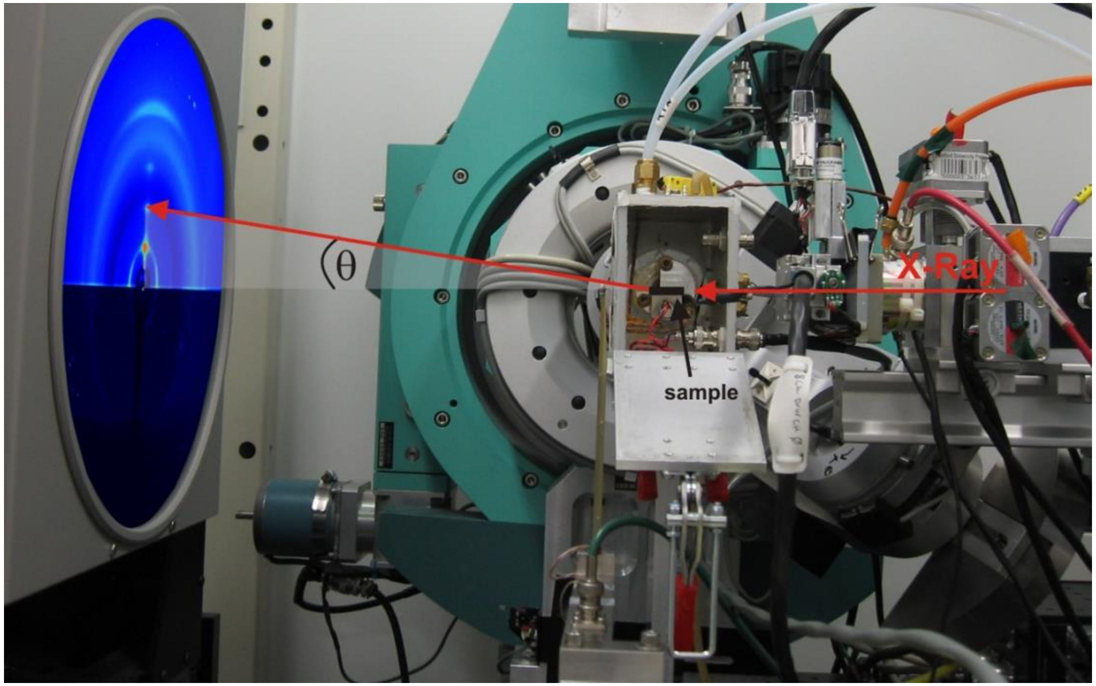
Think carefully about your experiment to determine the correct setup.

Analyzer Crystal data is the gold standard, but often too slow or unnecessary for many experiments

Sample geometry can have a large impact on data quality when using an area detector

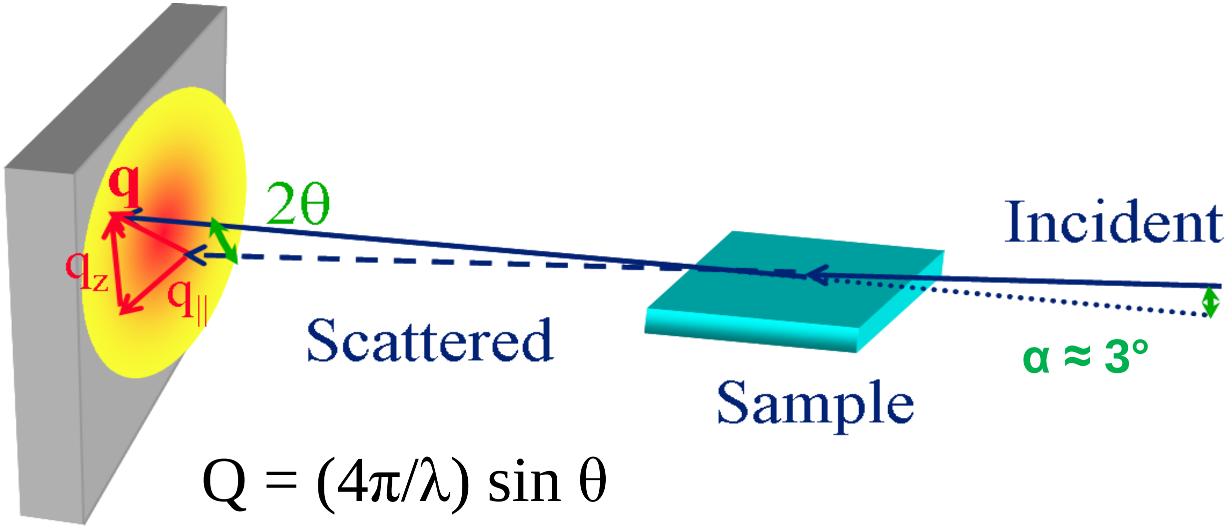
Discuss with your beamline scientist!

Grazing Incidence – the "Missing Wedge"



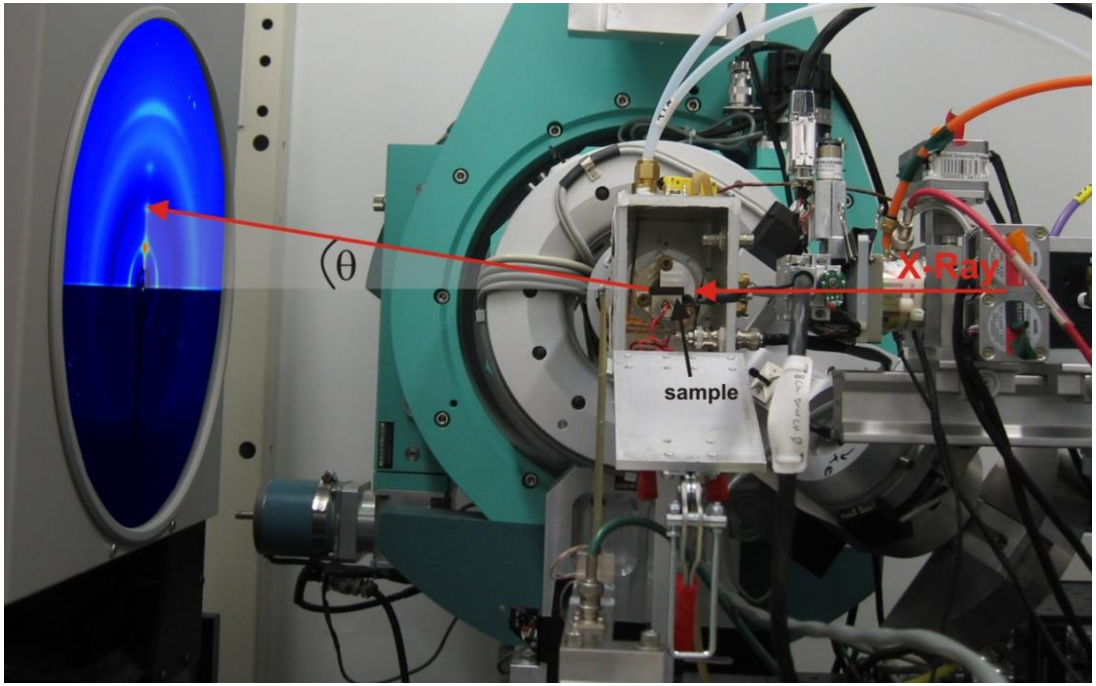
This is SSRL Beamline 11-3

Grazing incidence chamber couple with a large area detector to collect as much of the complete scattering solid angle as possible.



$$Q = (4\pi/\lambda) \sin \theta$$

Grazing Incidence – the "Missing Wedge"



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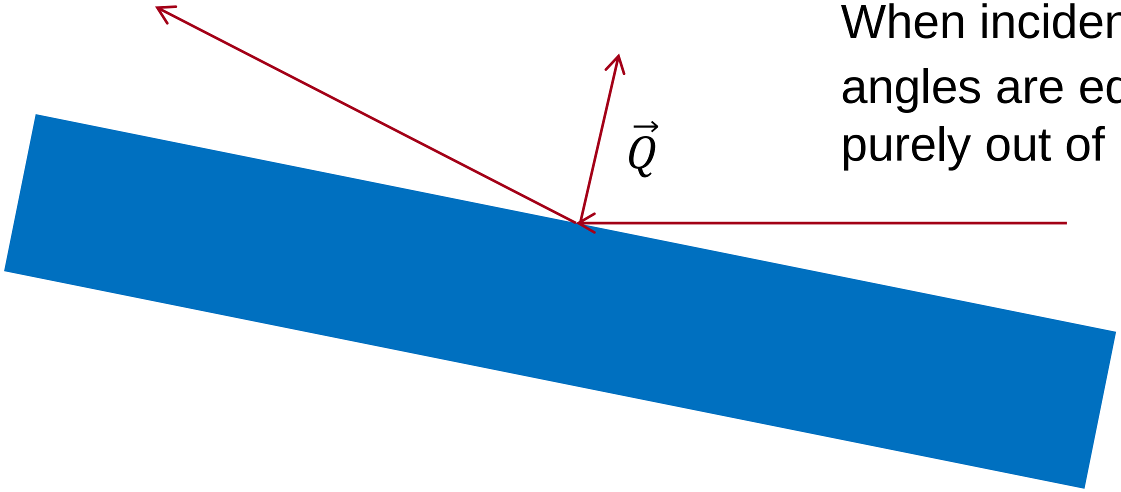
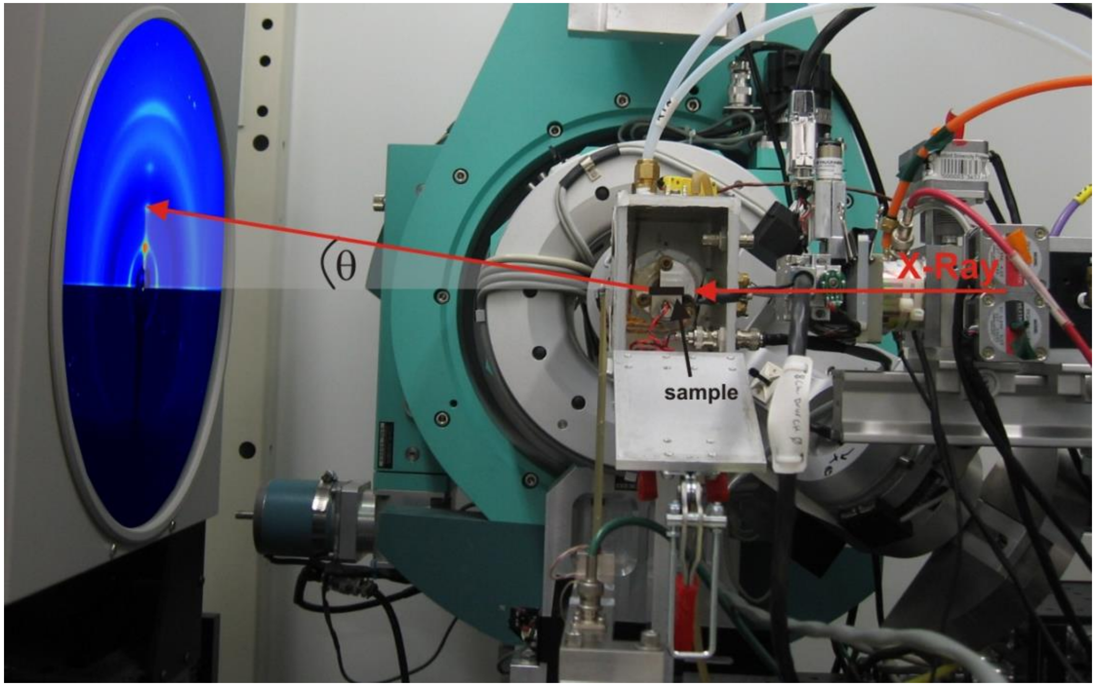


When incidence and exit angles are equivalent, $\vec{Q}$ is purely out of plane (Q_z)

Grazing Incidence – the "Missing Wedge"



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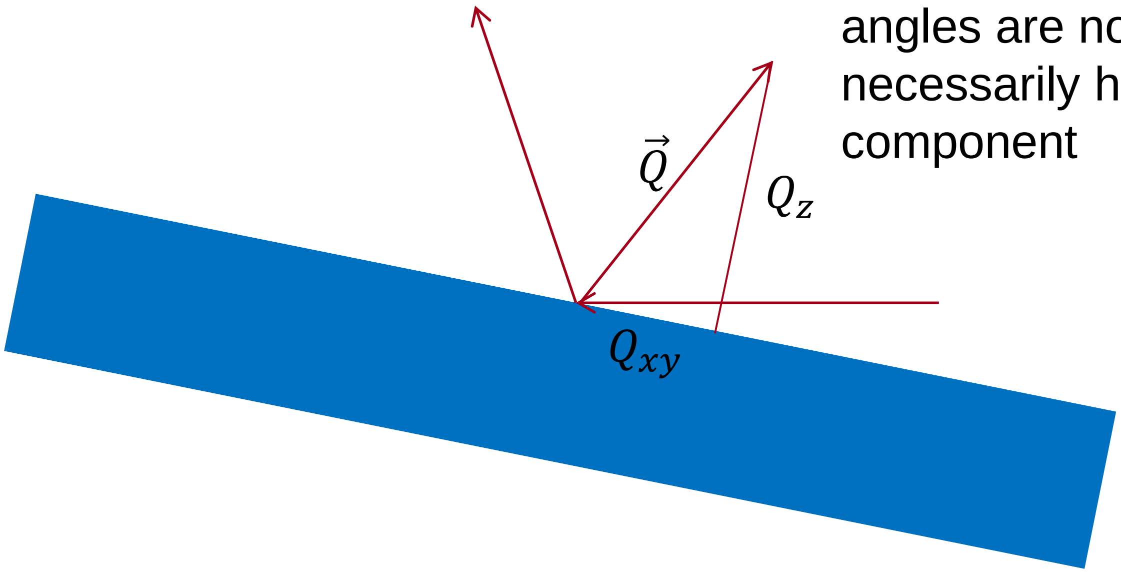
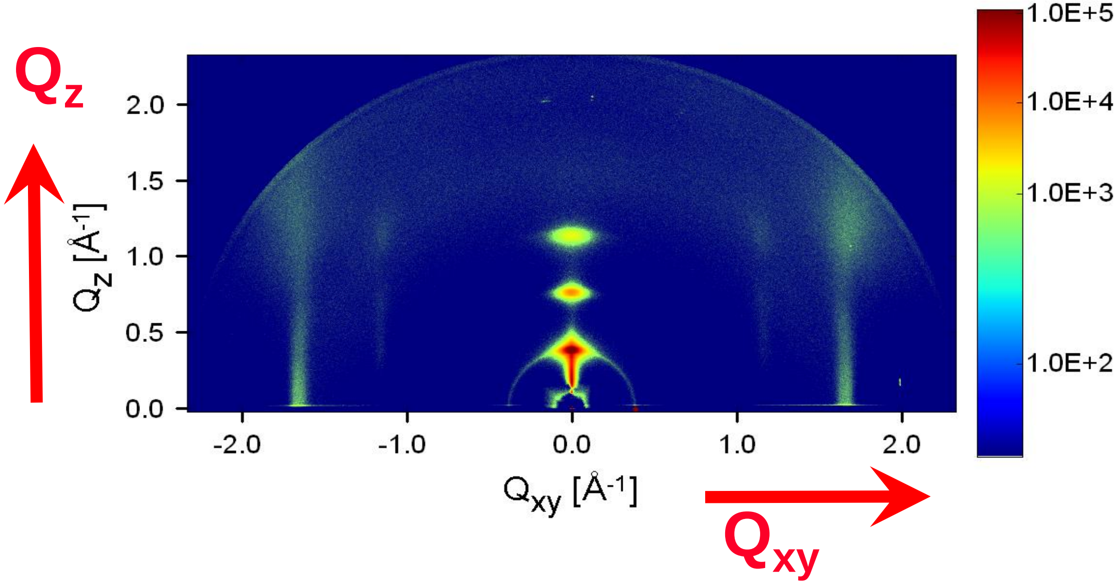
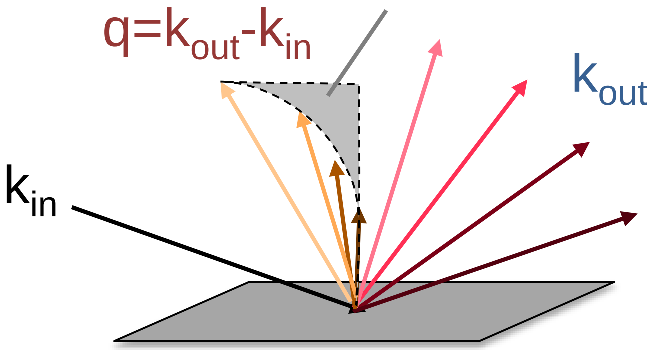


When incidence and exit angles are not equivalent, $\vec{Q}$ necessarily has some in-plane component

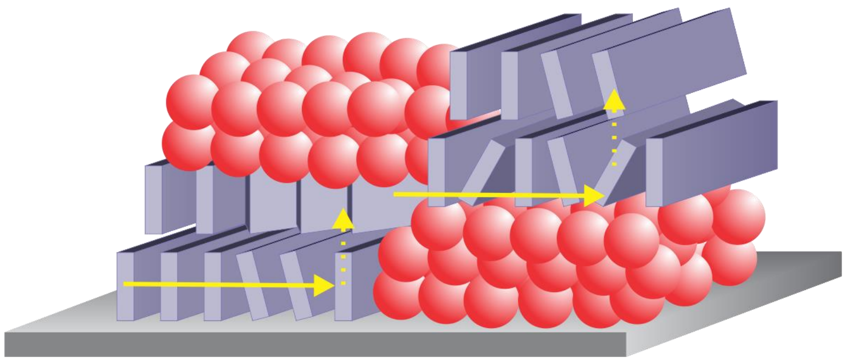
Grazing Incidence – the "Missing Wedge"



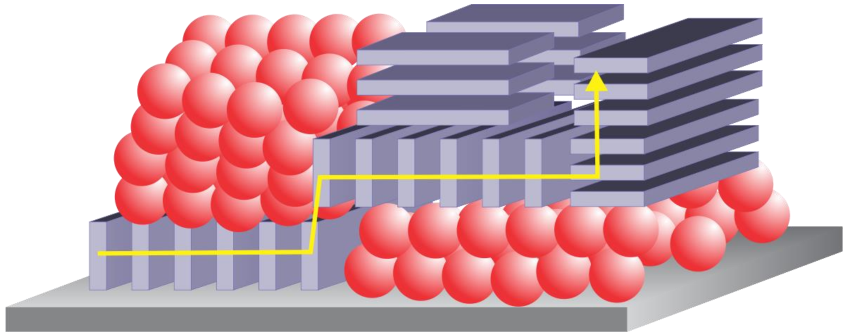


Baker et al., *Langmuir* 2010, 26, 9146

Rivnay, Salleo, Toney, *Chem Revs* **112**, 5488 (2012)

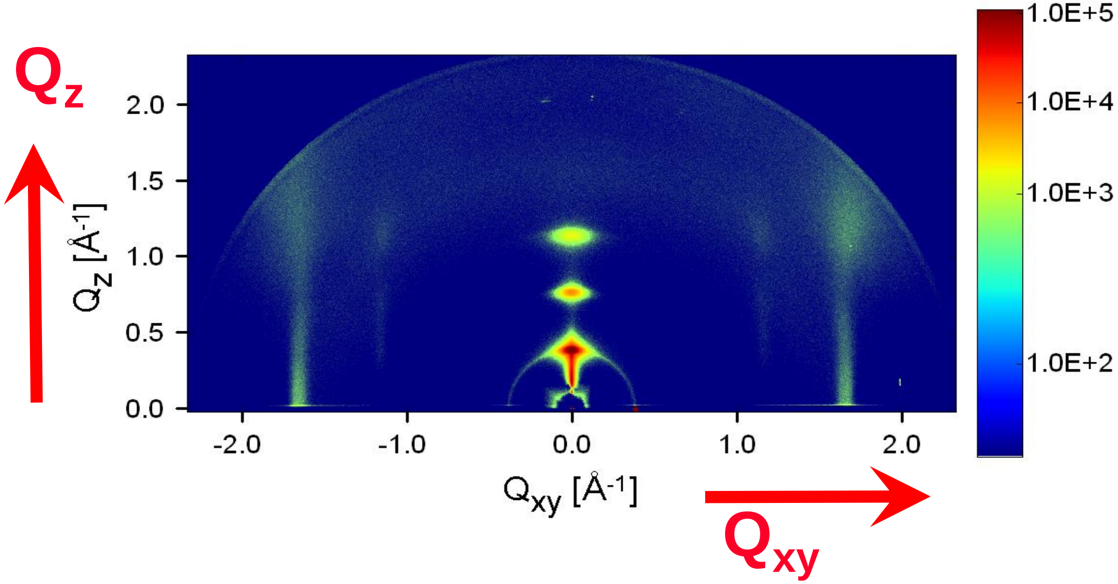


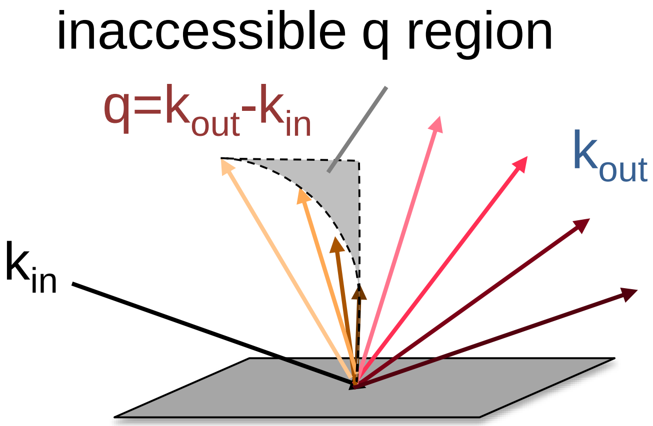
mainly edge-on



mixed orientation

Grazing Incidence – the "Missing Wedge"



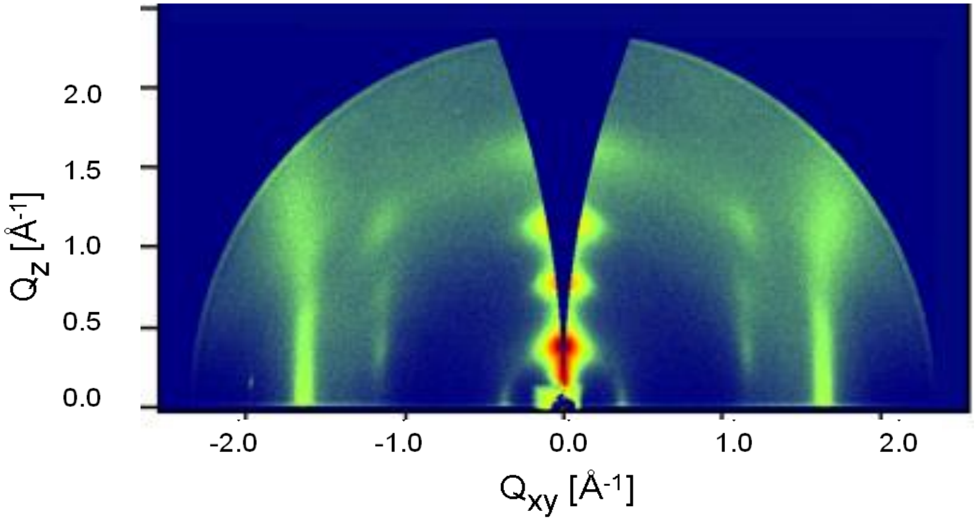


Baker et al., *Langmuir* 2010, 26, 9146

Rivnay, Salleo, Toney, *Chem Revs* **112**, 5488 (2012)

Grazing incidence geometry will always have an inaccessible region in Q-space

Specular measurements are needed to fill in this missing area



Thin Film Geometries

General Considerations:

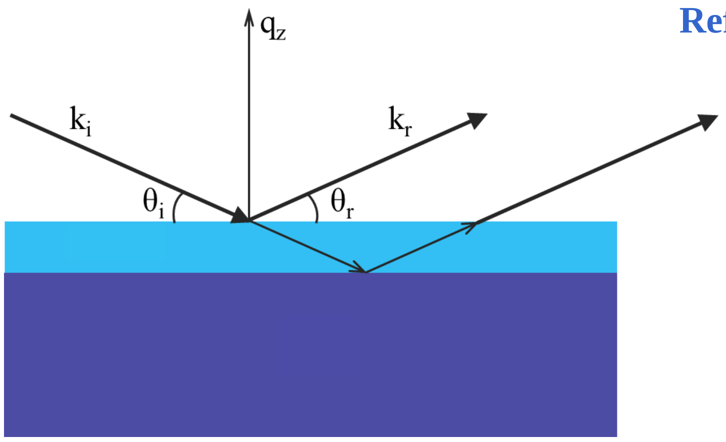
- Weakly scattering or extremely thin films
  - Work at very grazing incidence to enhance film signal and reduce substrate signal
  - Typically near critical angle, ~0.1º incidence angle
- Strongly scattering or thicker films
  - Work at moderate incidence angles to balance resolution and signal/background ratio
  - Typically incidence angle of a couple degrees

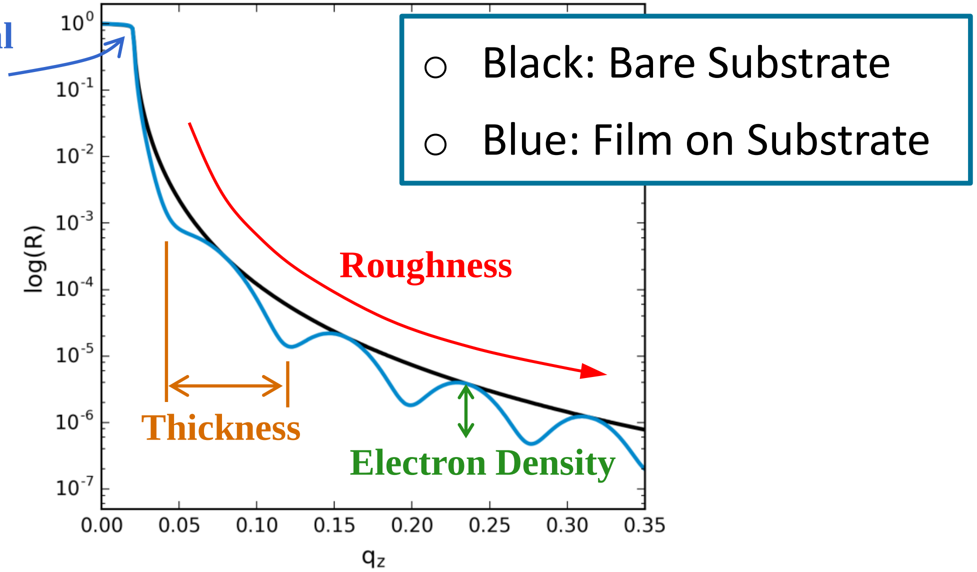
Decide what is best for your samples and what you are trying to learn

May need to measure at multiple incidence angles or include a specular measurement to fill in the "missing wedge"

X-ray Reflectivity

X-ray Reflectivity (XRR): surface-sensitive technique to characterize surfaces, thin films and multilayers.

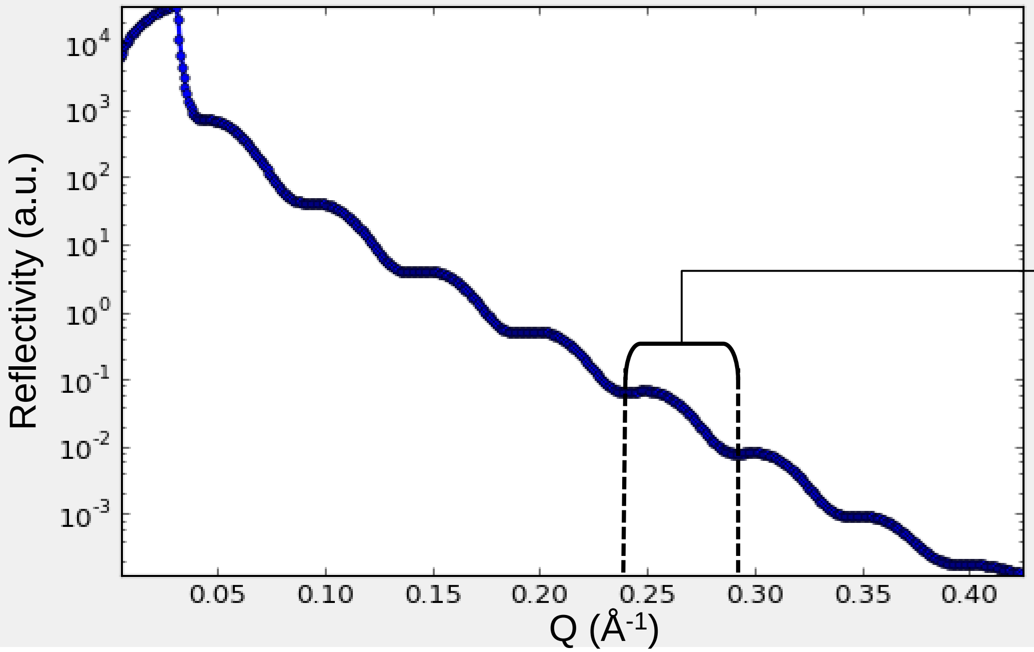




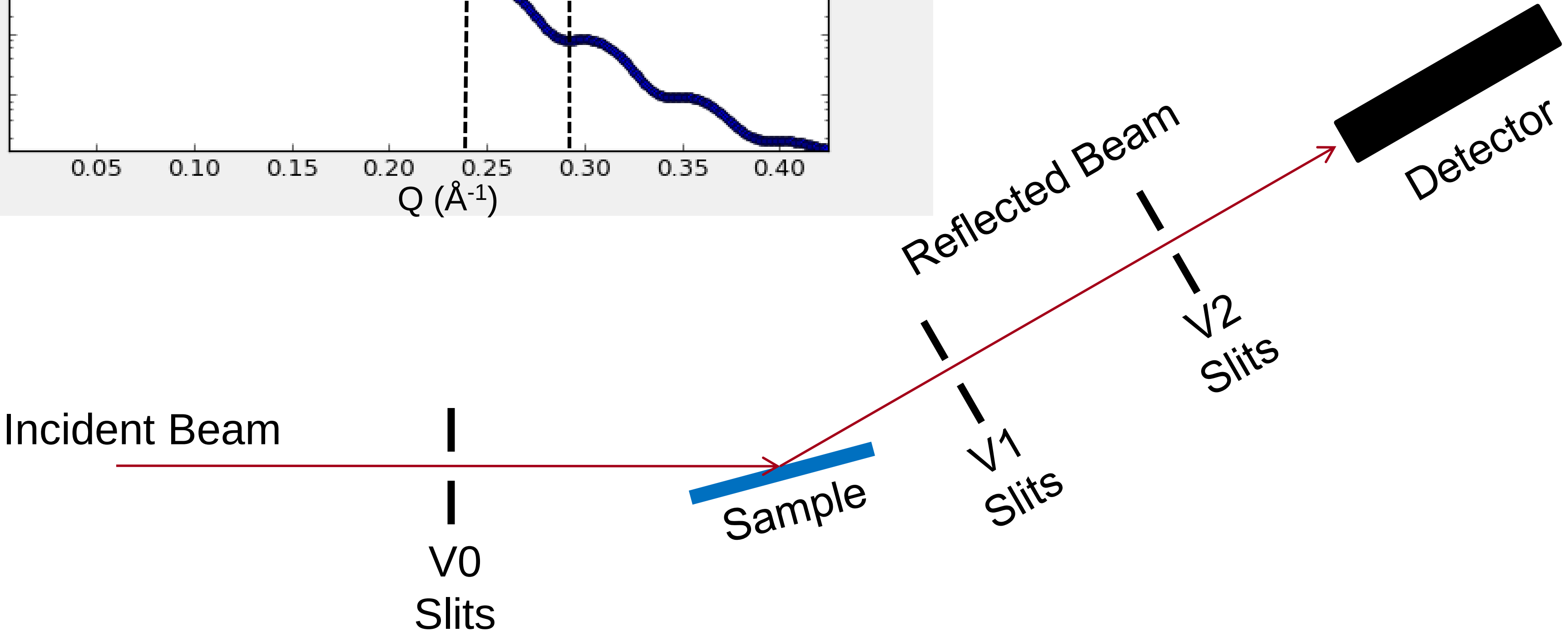
$$\theta_i = \theta_r = \theta \qquad q_z = k_r - k_i = \frac{4\pi}{\lambda}\sin\theta$$

$$R(q_z) = \frac{I(\theta)}{I_0}$$

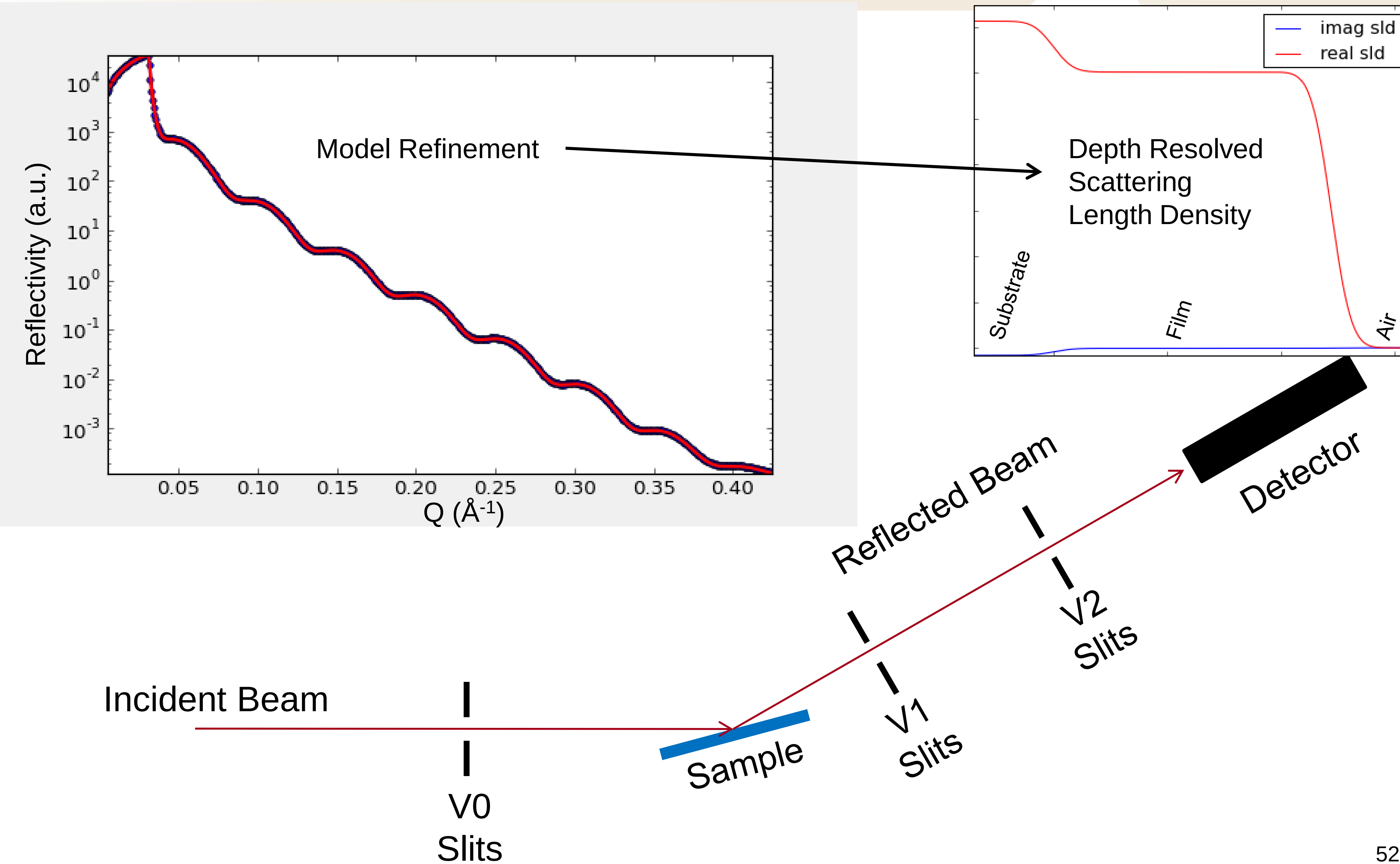
Reflectivity



$$\Delta Q = \frac{2\pi}{d}$$



Reflectivity



Reflectivity

Reflectivity is used to characterize out-of-plane structure in layered materials

Can give very accurate thicknesses and good estimate of interface roughness

- Cannot distinguish between conformal roughness and interdiffusion

Requires highly smooth and flat samples, typically with lengths along the beam direction of a few mm or more

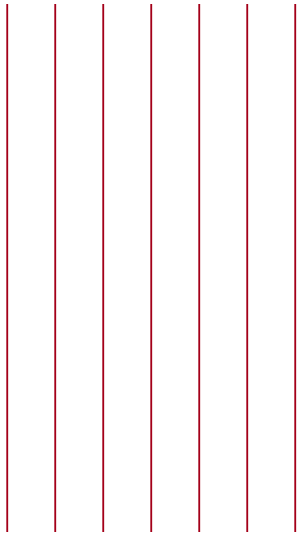
If the sample does not look mirrorlike, it is unlikely to work for XRR

CTR – Basic Diffraction Theory

Consider the scattering of x-rays from an isolated electron:

<u>Incident Plane Wave</u>

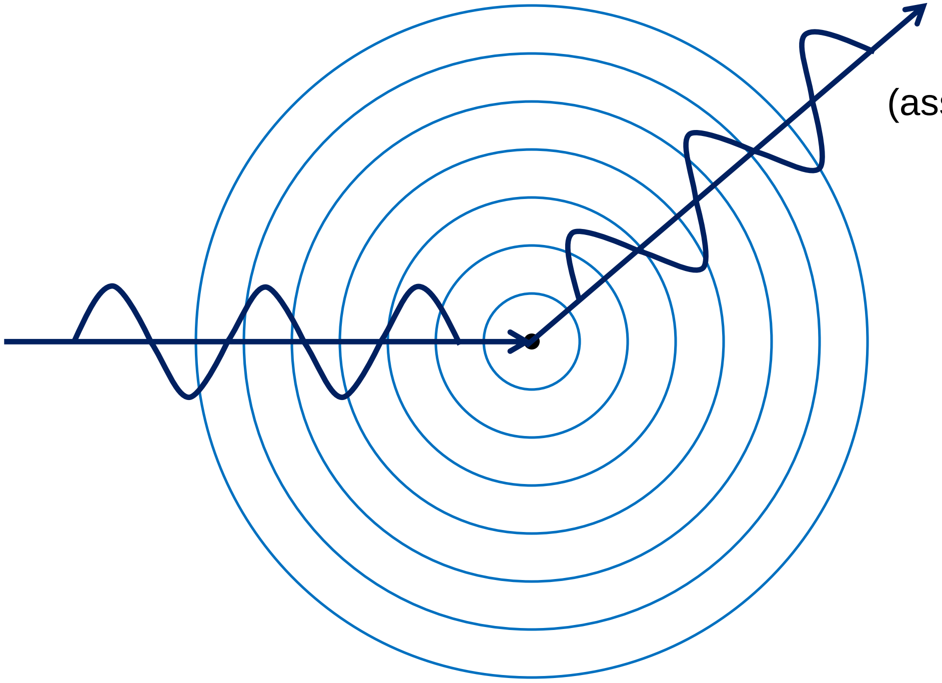
$$E = E_0 e^{i(\overrightarrow{k_0}\cdot\vec{x} - \omega t)}$$



<u>“Spherically Symmetric” Scattered Wave</u>

$$E = \frac{q^2 E_0}{mc^2 R} e^{i(\overrightarrow{k_0}\cdot\vec{R} - \omega t)}$$

(assuming σ-polarization)

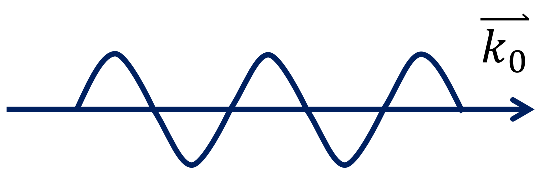


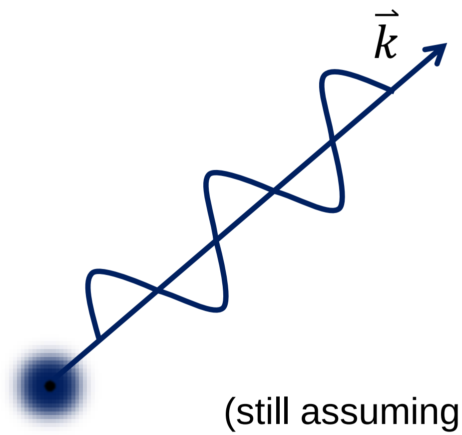
CTR – Basic Diffraction Theory

Consider the scattering of x-rays from a collection of electrons, e.g. an atom:

<u>Incident Plane Wave</u>

$$E = E_0 e^{i(\overrightarrow{k_0}\cdot\vec{x} - \omega t)}$$





(still assuming σ-polarization)

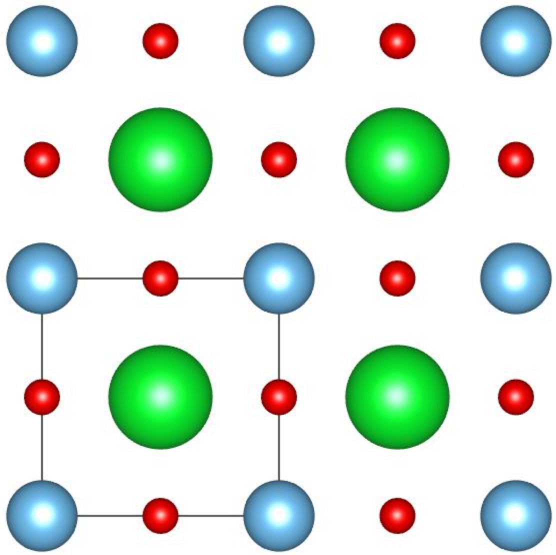
$$E = \frac{q^2 E_0}{mc^2 R} e^{i(\overrightarrow{k_0}\cdot\vec{R} - \omega t)} \int e^{\left(2\pi i/\lambda\right)(\vec{k}-\overrightarrow{k_0})\cdot\vec{r}} \rho(\vec{r})\, dV$$

Distribution of charge within the atom $\equiv f$

CTR – Basic Diffraction Theory

Consider a 2-D plane of regularly spaced atoms

Generalize to a non-trivial unit cell



$$E = \frac{q^2 E_0}{mc^2 R} e^{-i\omega t} e^{i\overrightarrow{k_0}\cdot\vec{R}} \underbrace{\sum_j f_j e^{-i\vec{Q}\cdot\overrightarrow{r_j}}}$$

Sum over atoms in unit cell

CTR – Basic Diffraction Theory

Consider a 2-D plane of regularly spaced atoms

$$E = \frac{q^2 E_0}{mc^2 R} e^{-i\omega t} e^{i\overrightarrow{k_0}\cdot\vec{R}} \sum_j f_j e^{-i\vec{Q}\cdot\overrightarrow{r_j}} \sum_{n_1=0}^{N_1} e^{-i\vec{Q}\cdot n_1\vec{a}} \sum_{n_2=0}^{N_2} e^{-i\vec{Q}\cdot n_2\vec{b}} \sum_{n_3=0}^{N_3} e^{-i\vec{Q}\cdot n_3\vec{c}}$$

Sum over atoms in unit cell

Sum over unit cells along lattice directions

⇕

Structure Factor - F

CTR – Basic Diffraction Theory

Consider a 2-D plane of regularly spaced atoms

$$E = \frac{q^2 E_0}{mc^2 R} e^{-i\omega t} e^{i\overrightarrow{k_0}\cdot\vec{R}} \sum_j f_j e^{-i\vec{Q}\cdot\overrightarrow{r_j}} \sum_{n_1=0}^{N_1} e^{-i\vec{Q}\cdot n_1 \vec{a}} \sum_{n_2=0}^{N_2} e^{-i\vec{Q}\cdot n_2 \vec{b}}$$

Sum over atoms in unit cell

Sum over unit cells in the plane

Sums over lattice directions take the form of a geometric sum:

$$S = \sum_{k=0}^{N} ar^k = a + ar + ar^2 + \cdots = a\frac{1 - r^{N+1}}{1 - r}$$

CTR – Basic Diffraction Theory

Consider a 2-D plane of regularly spaced atoms

$$\sum_{n_1=0}^{N_1} e^{-i\vec{Q}\cdot n_1\vec{a}} \rightarrow \sum_{n_1=0}^{N_1} [e^{-i\vec{Q}\cdot\vec{a}}]^{n_1} \rightarrow \frac{1}{1-e^{-i\vec{Q}\cdot\vec{a}}}$$

Sums over lattice directions take the form of a geometric sum:

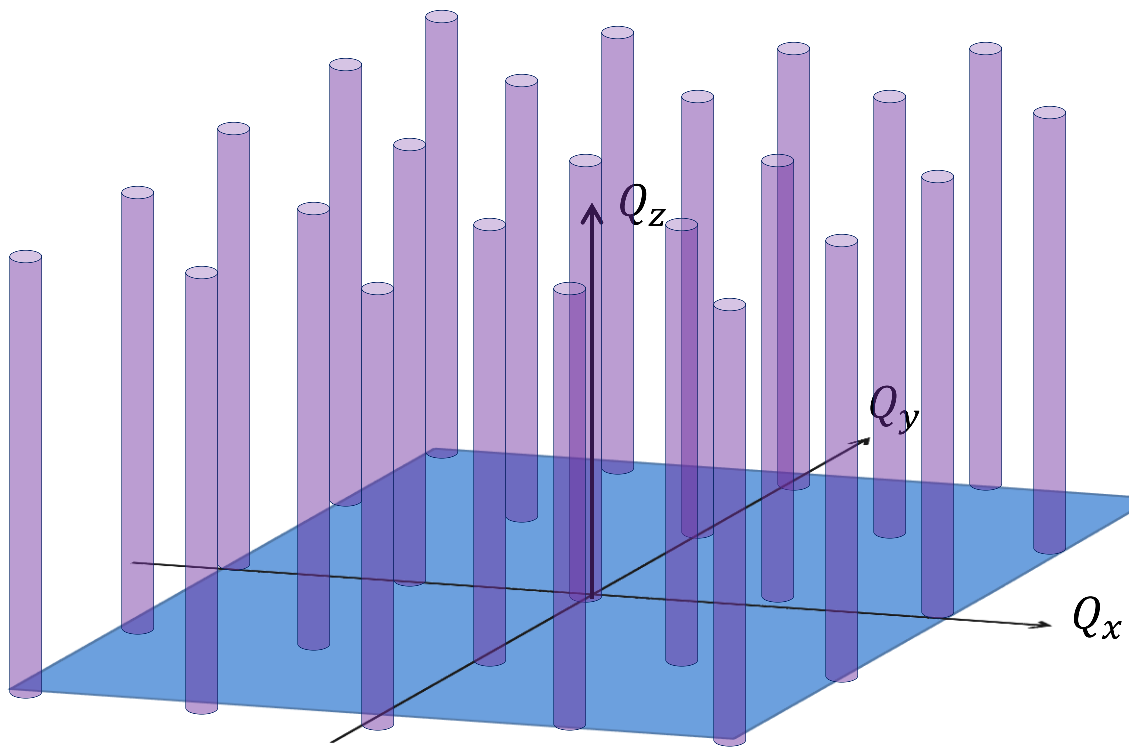
$$S = \sum_{k=0}^{N} ar^k = a + ar + ar^2 + \cdots = a\frac{1-r^{N+1}}{1-r}$$

$$\lim_{N\to\infty} a\frac{1-r^{N+1}}{1-r} = \frac{a}{1-r}$$

CTR – Basic Diffraction Theory

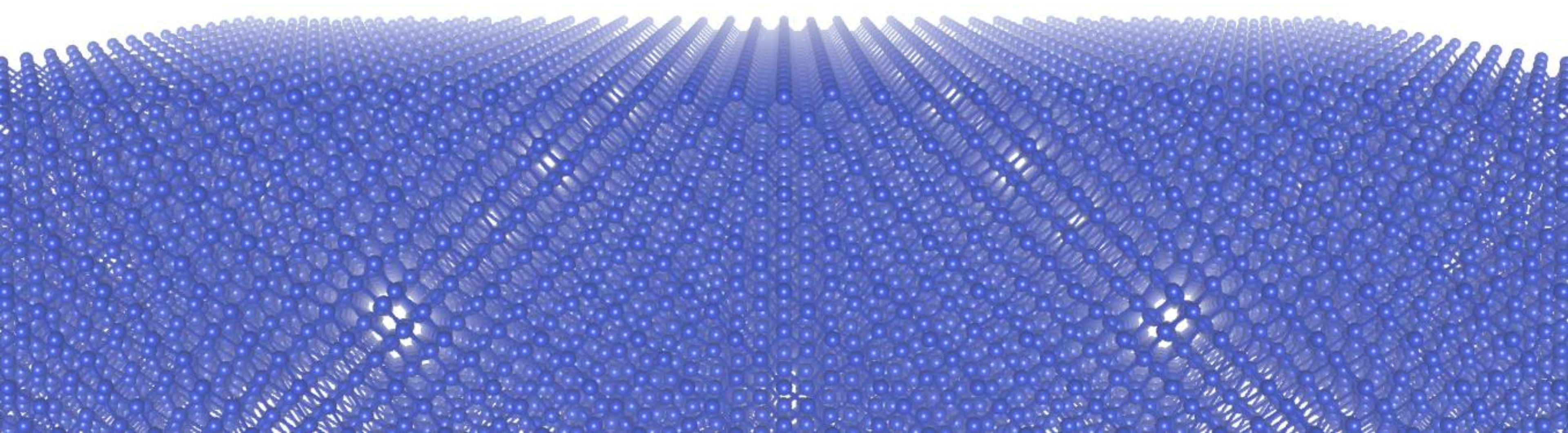
Consider a 2-D plane of regularly spaced atoms

$$E = \frac{q^2 E_0}{mc^2 R} e^{-i\omega t} e^{i\overrightarrow{k_0}\cdot\vec{R}} \sum_j f_j e^{-i\vec{Q}\cdot\vec{r_j}} \times \frac{1}{1 - e^{-i\vec{Q}\cdot\vec{a}}} \times \frac{1}{1 - e^{-i\vec{Q}\cdot\vec{b}}}$$



CTR – Basic Diffraction Theory

$$E = \frac{q^2 E_0}{mc^2 R} e^{-i\omega t} e^{i\overrightarrow{k_0}\cdot\vec{R}} \sum_j f_j e^{-i\vec{Q}\cdot\overrightarrow{r_j}} \times \frac{1}{1 - e^{-i\vec{Q}\cdot\vec{a}}} \times \frac{1}{1 - e^{-i\vec{Q}\cdot\vec{b}}} \times \frac{1}{1 - e^{-i\vec{Q}\cdot\vec{c}}}$$

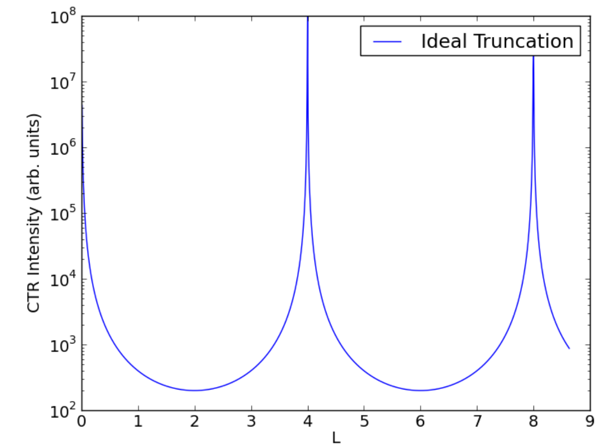


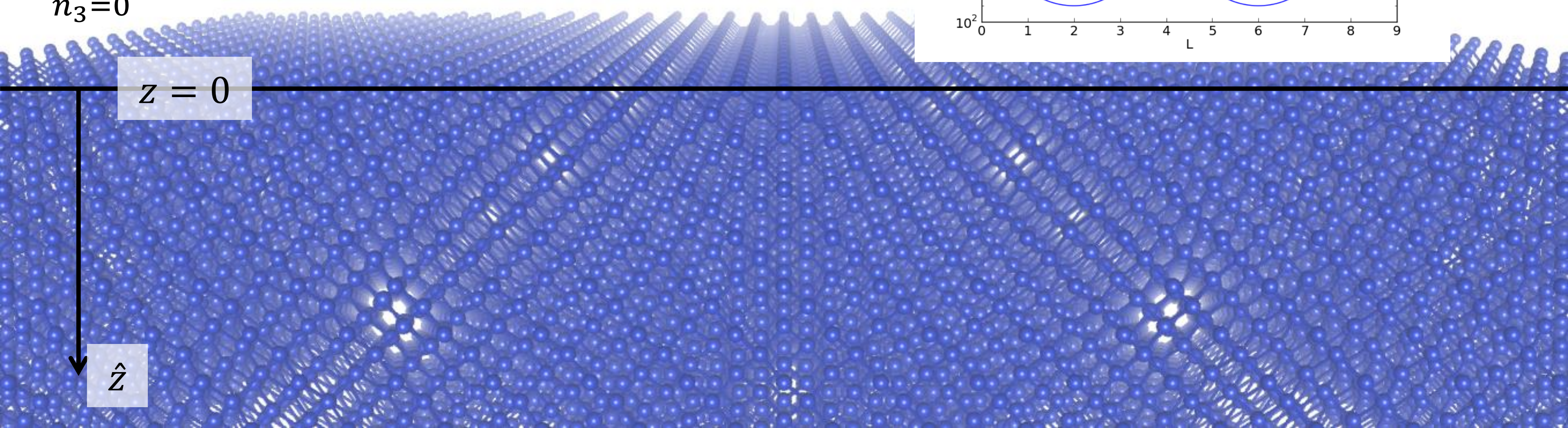
CTR – Basic Diffraction Theory

$$E = \frac{q^2 E_0}{mc^2 R} e^{-i\omega t} e^{i\vec{k_0}\cdot\vec{R}} \sum_j f_j e^{-i\vec{Q}\cdot\vec{r_j}} \times \frac{1}{1 - e^{-i\vec{Q}\cdot\vec{a}}} \times \frac{1}{1 - e^{-i\vec{Q}\cdot\vec{b}}} \times \frac{1}{1 - e^{-i\vec{Q}\cdot\vec{c}}}$$

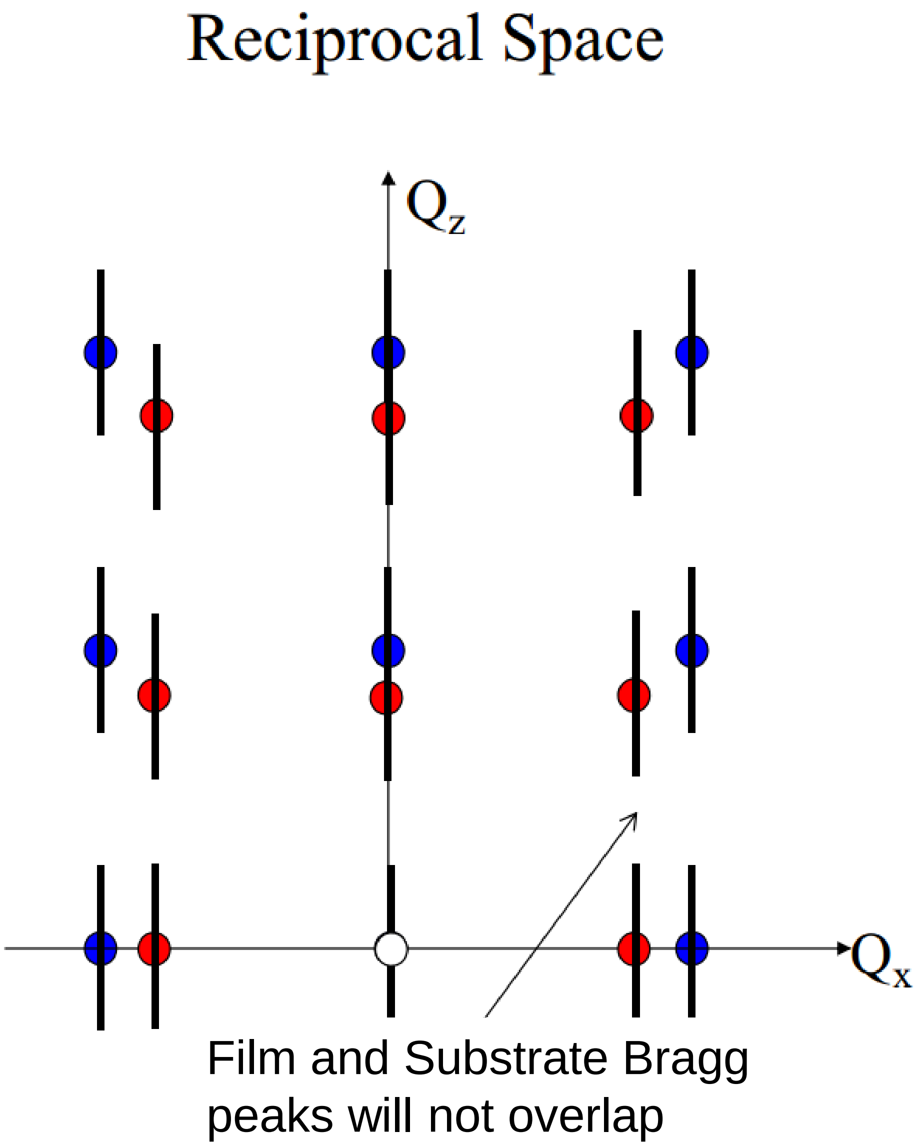
$$\sum_{n_3=0}^{N_3} e^{-i\vec{Q}\cdot n_3 \vec{c}}$$

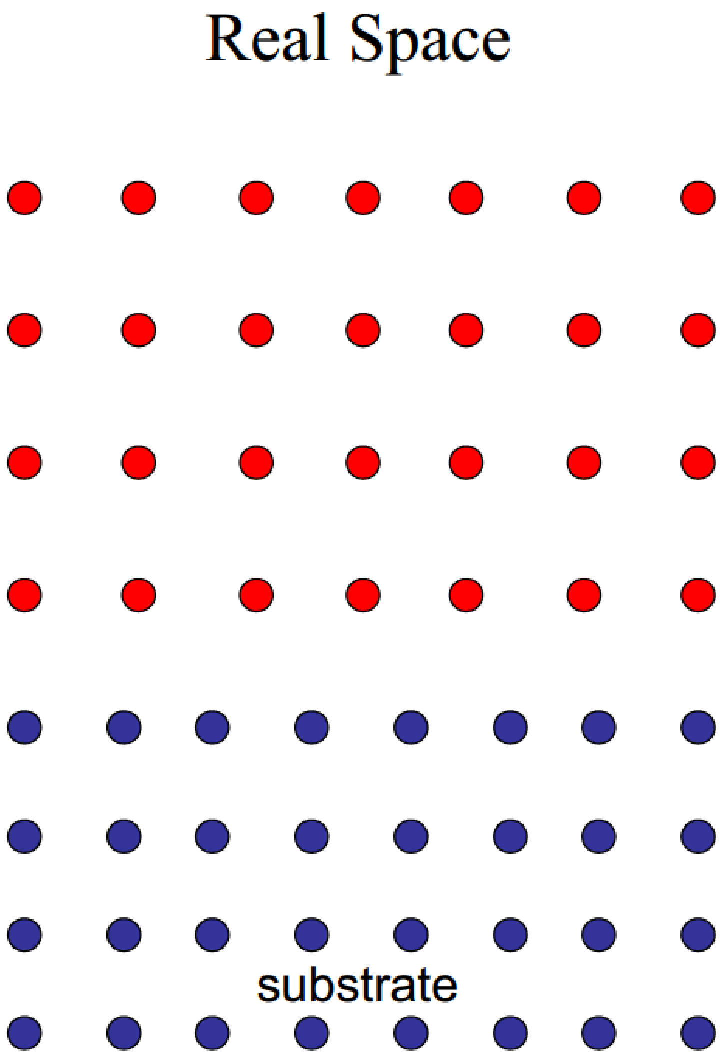
$$E \propto F_{u.c.} \frac{1}{1 - e^{-i\vec{Q}\cdot\vec{c}}}$$





Thin Film Diffraction (Single Crystal)

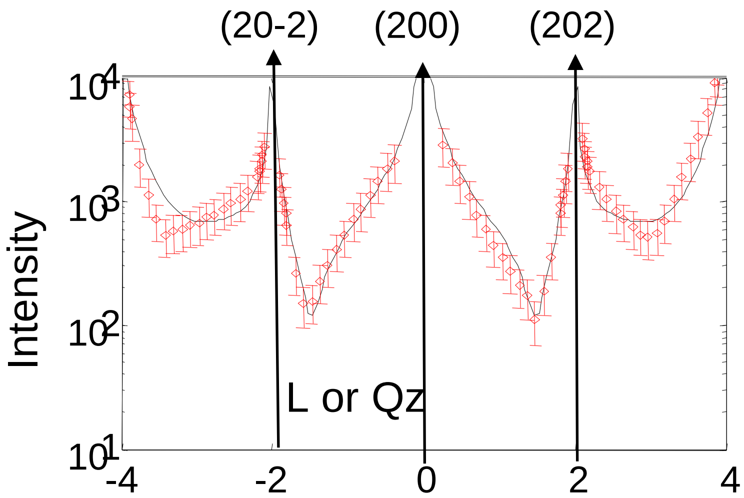


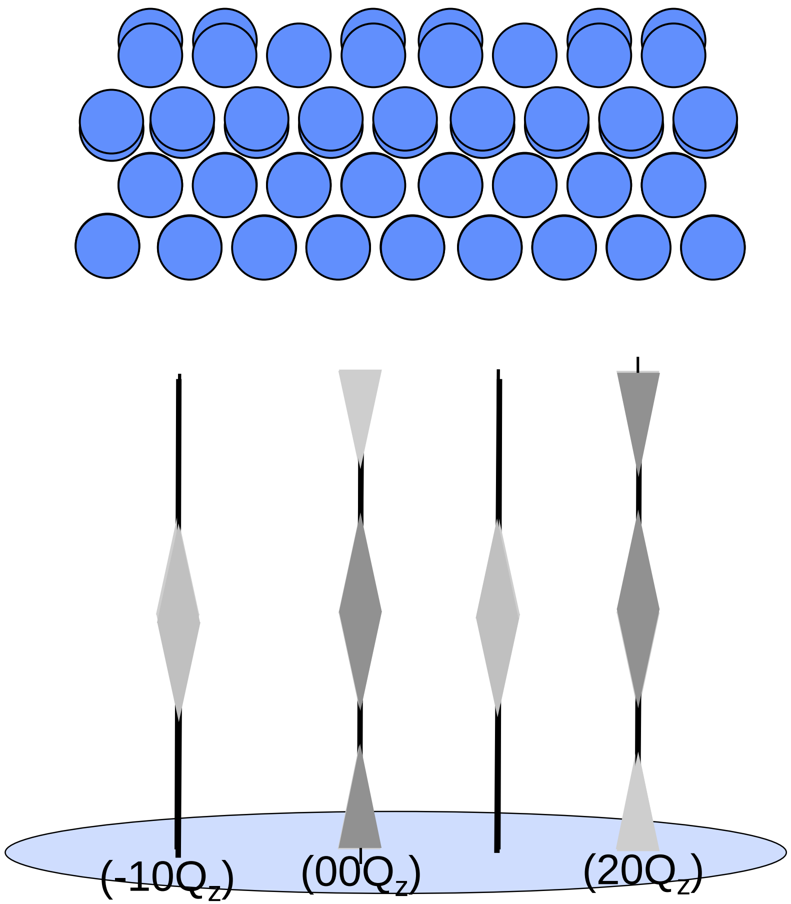


CTR – What We Can Learn

Crystal truncation rod (CTR):

Scattering that arises between bulk Bragg peaks due to the presence of a sharp termination of a crystal (a surface). The scattering is perpendicular to the surface and is a sensitive function of surface/interface structure.

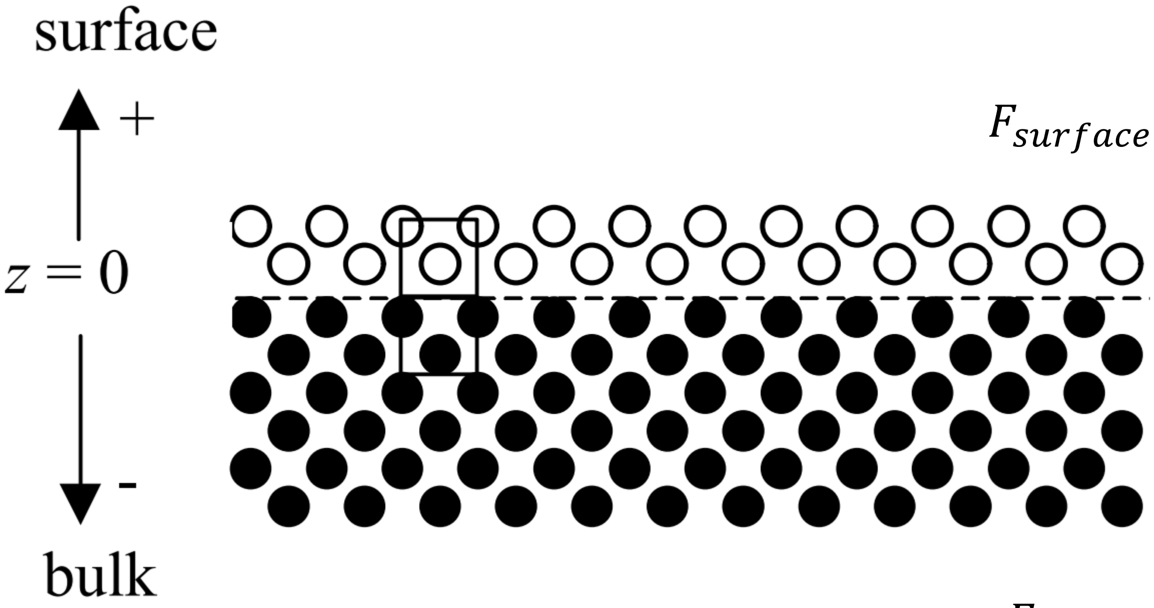




Robinson PRB **33**, 3830 (1986)

CTR – Practical Calculations

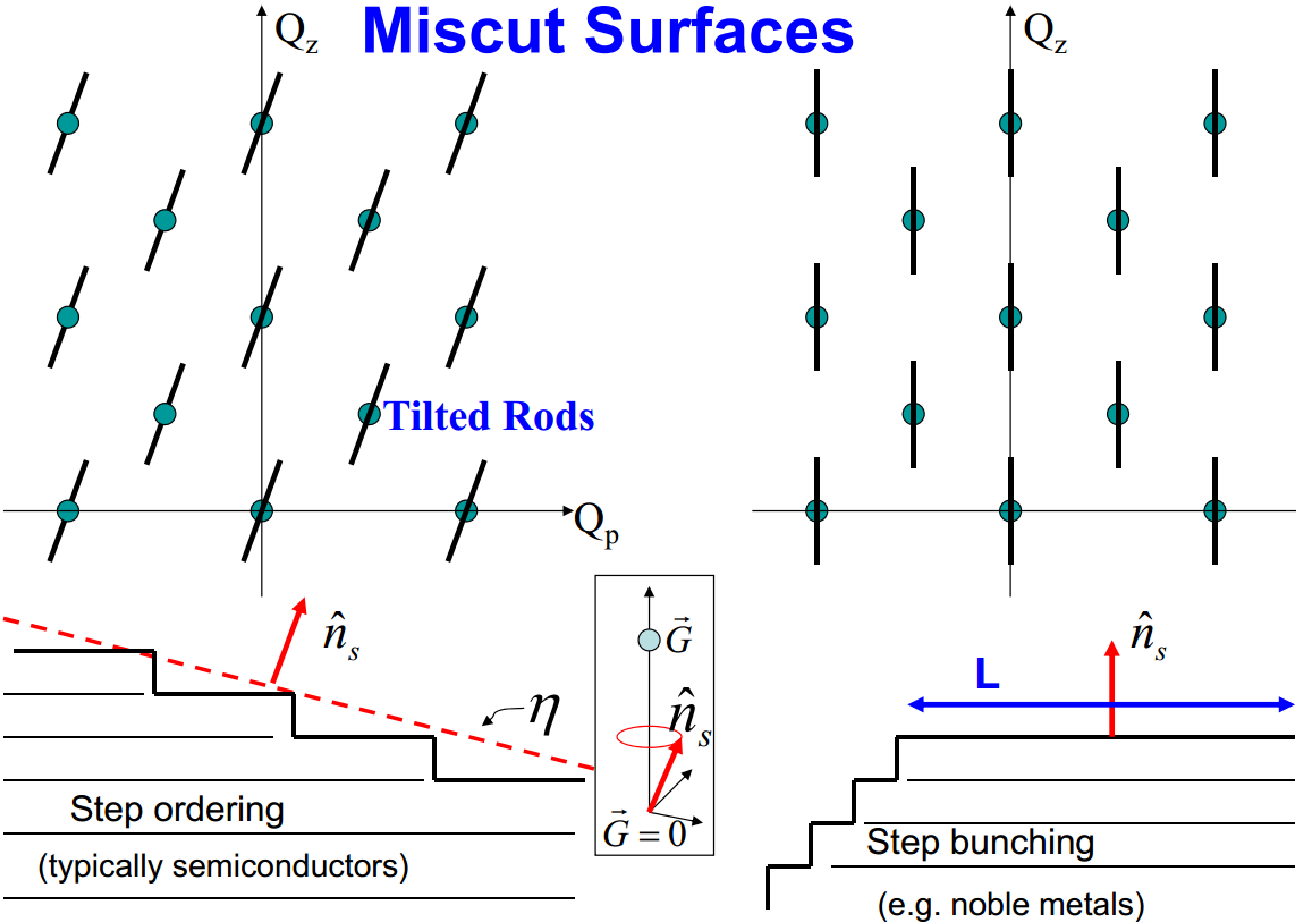
$$F_{CTR} = F_{surface} + F_{bulk}$$



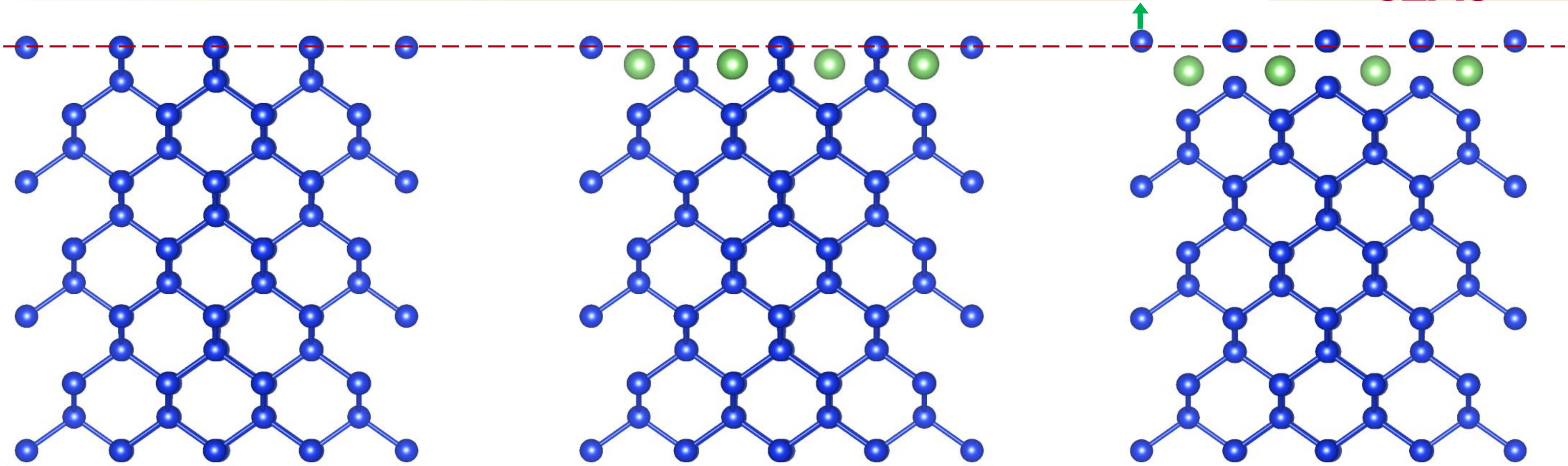
$$F_{surface} = \sum_{j}^{surface\ U.C.} f_j \Theta_j e^{i2\pi(hx_j + ky_j + lz_j)}$$

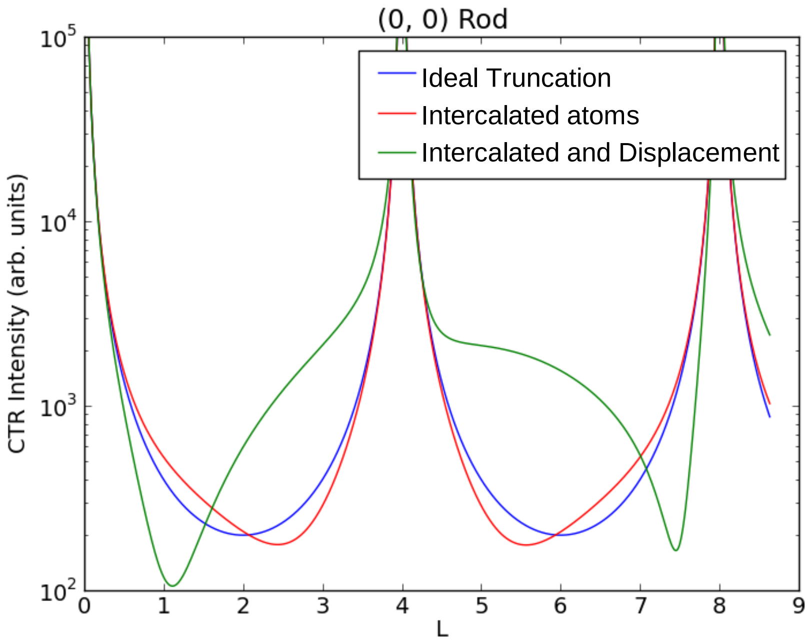
$$F_{bulk} = F_{u.c.} \frac{1}{1 - e^{i2\pi l}}$$

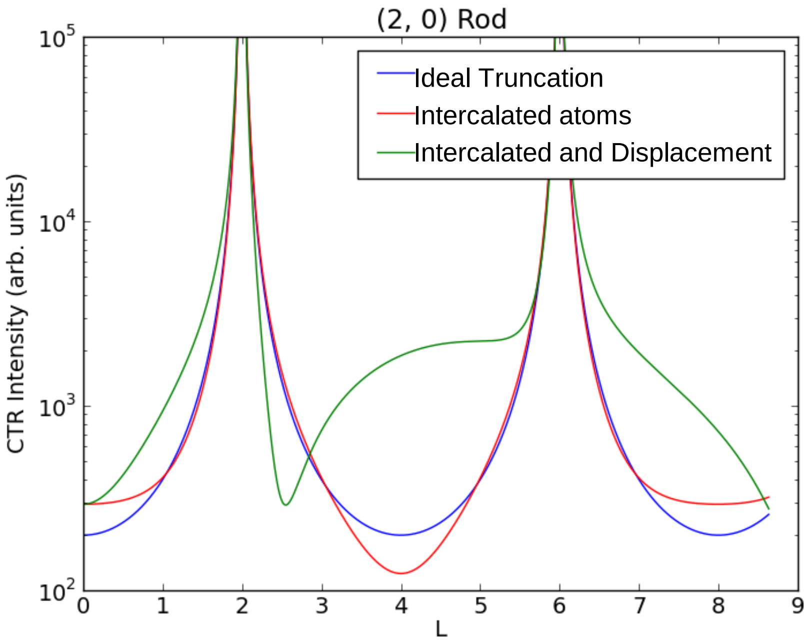
Miscut Surfaces



Crystal Truncation Rod Modelling

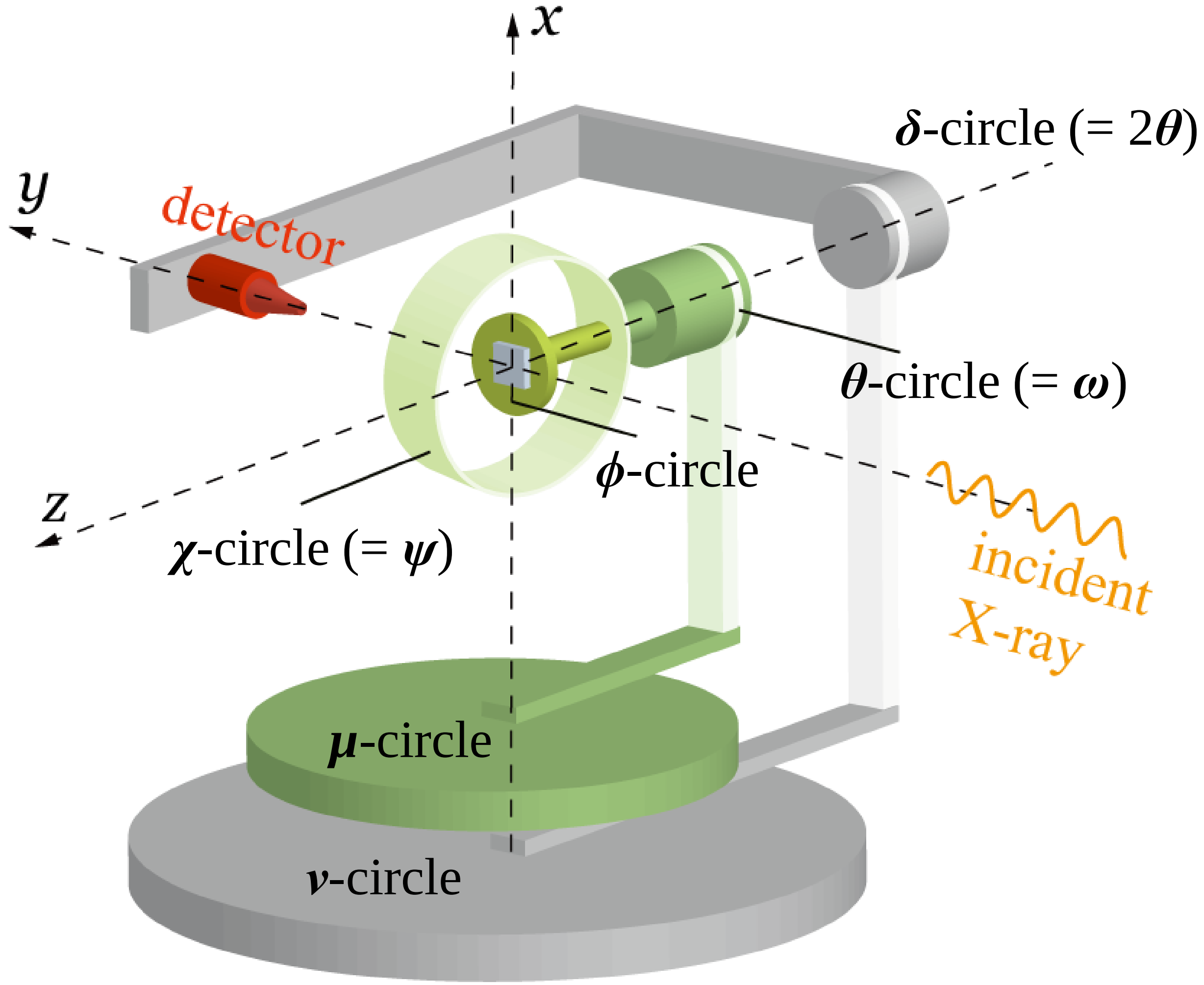




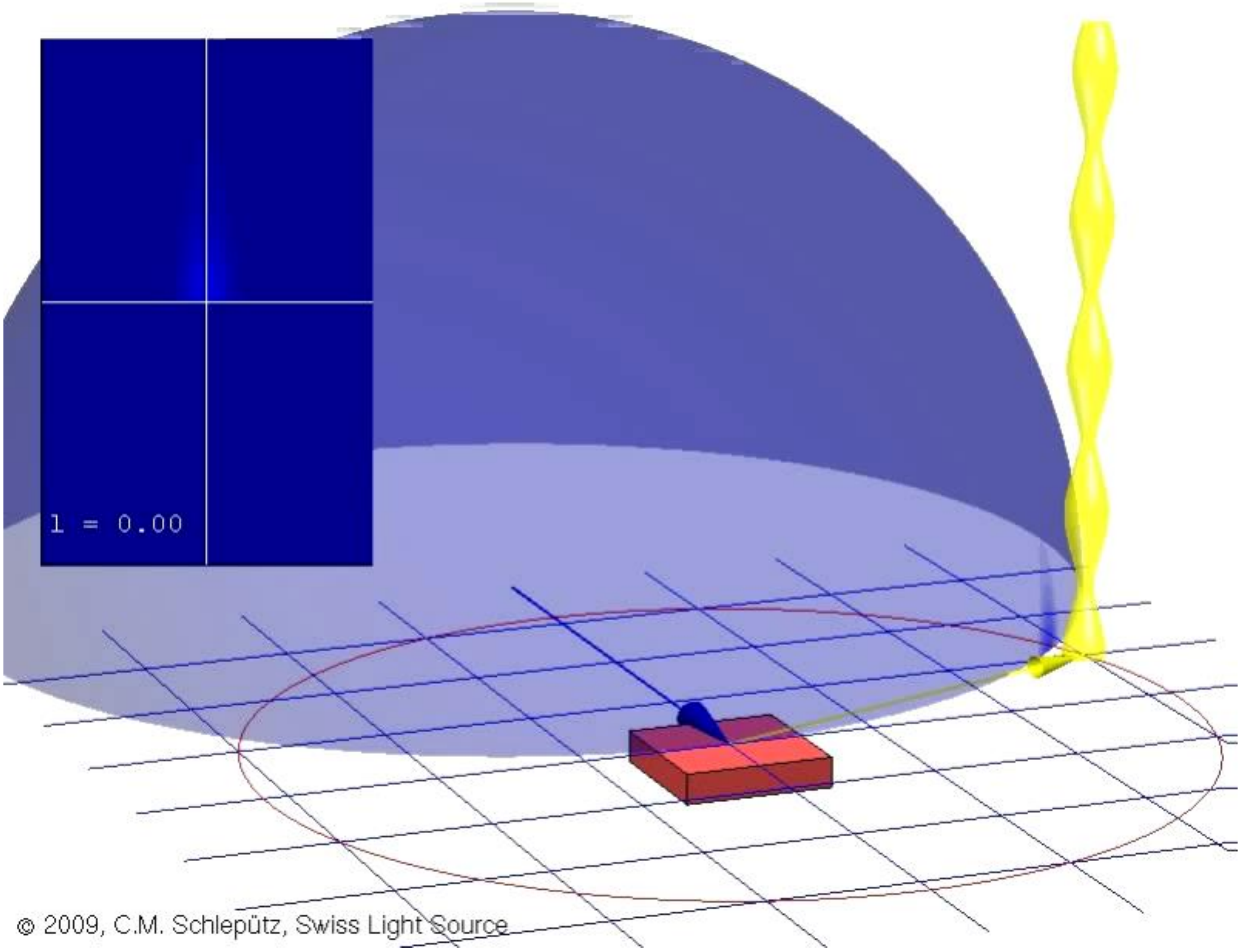


CTR and Films – How to Measure

4-circle (or more)
Small area detectors are now common

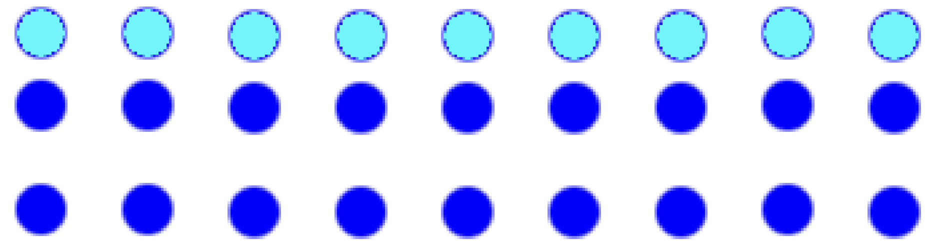


CTR- How to Measure



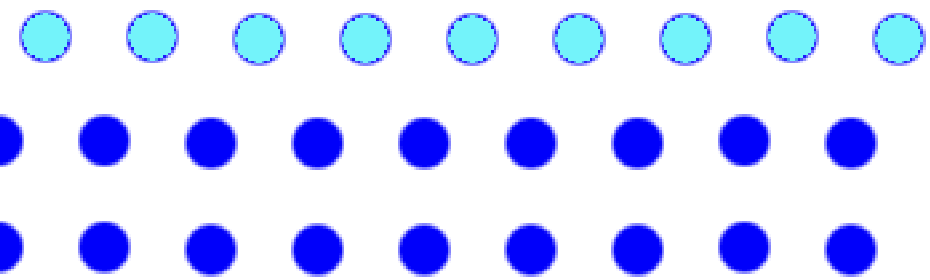
Examples of CTR Features

Out of plane spacing changes at the surface



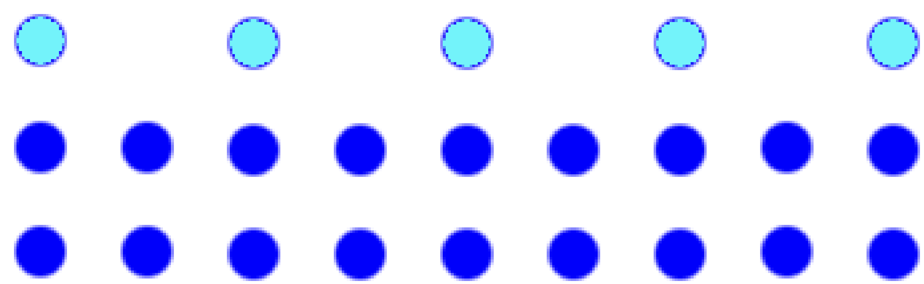
Normal relaxation

In plane spacing changes at the surface



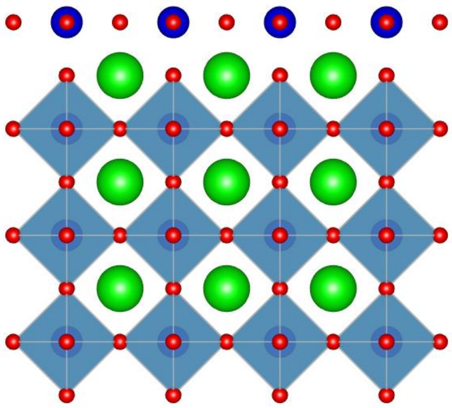
Lateral relaxation

Periodicity changes at the surface

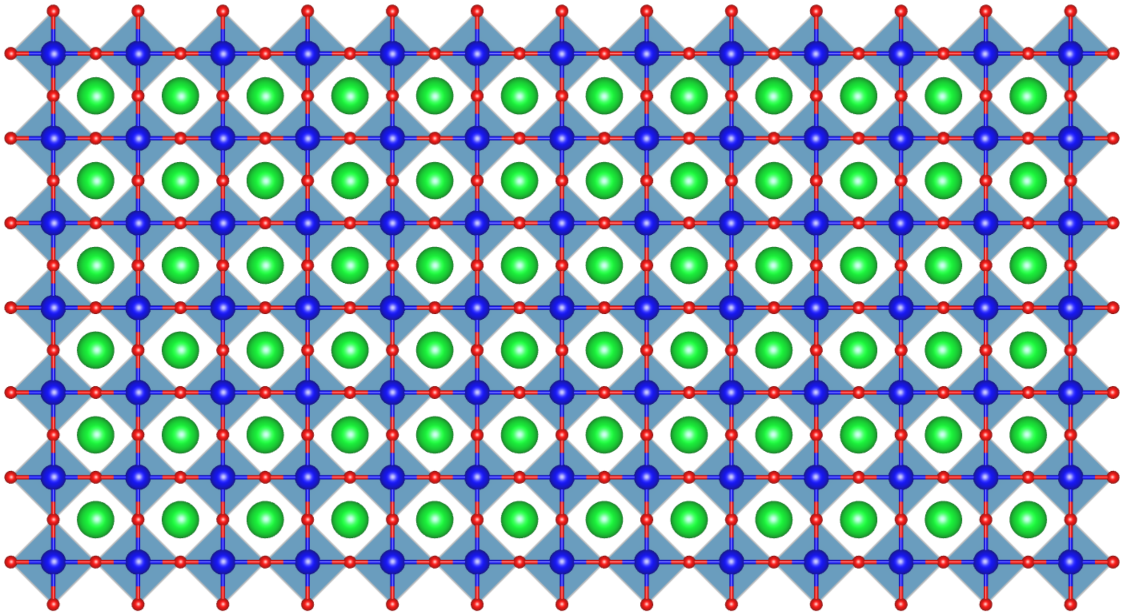


Example Reconstruction

Surface Reconstructions



Cross section view



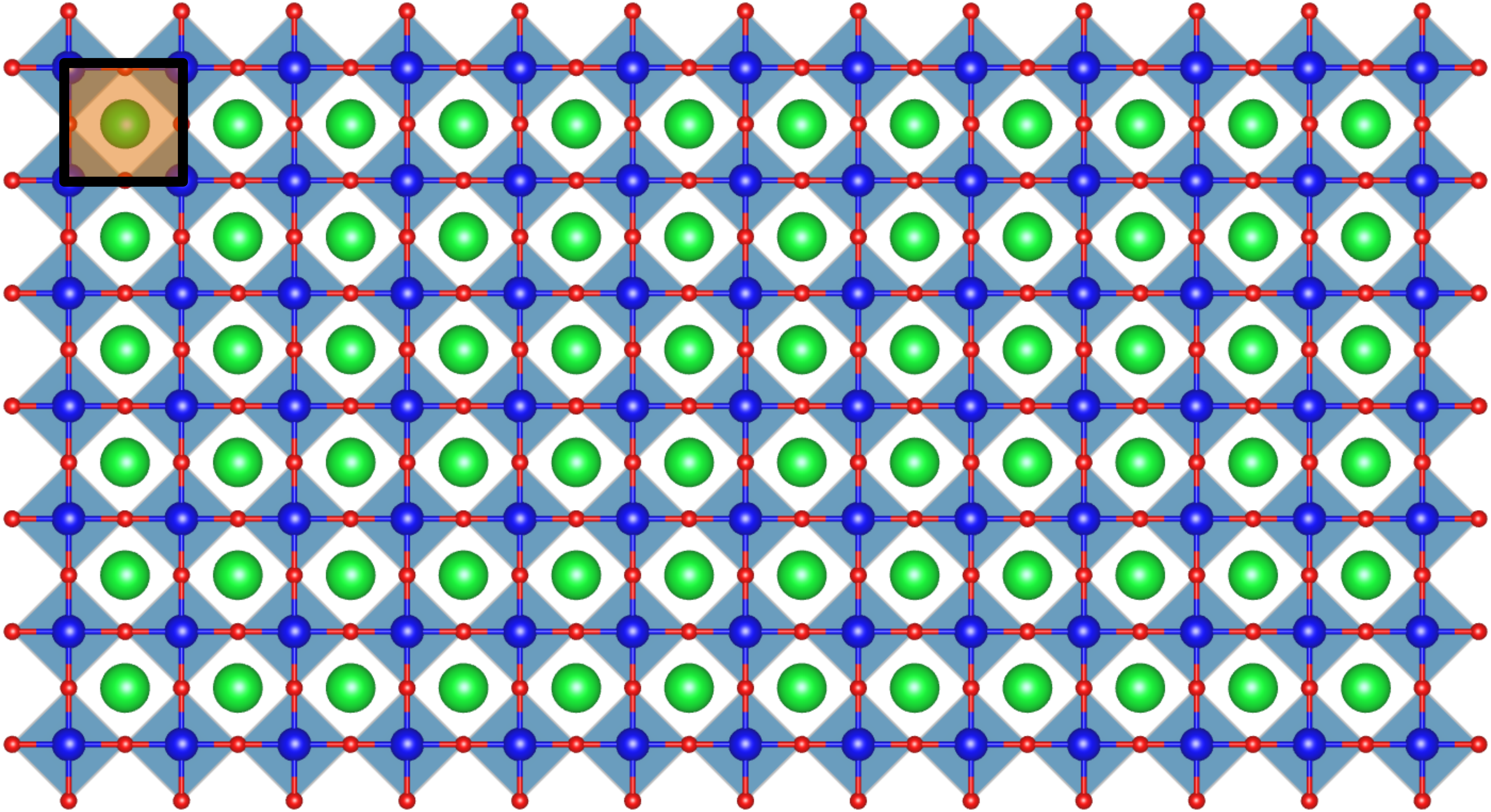
Top down view

For viewing reconstructions, we will consider the top down view.

Reconstructions will deal with the 2-dimensional plane groups.

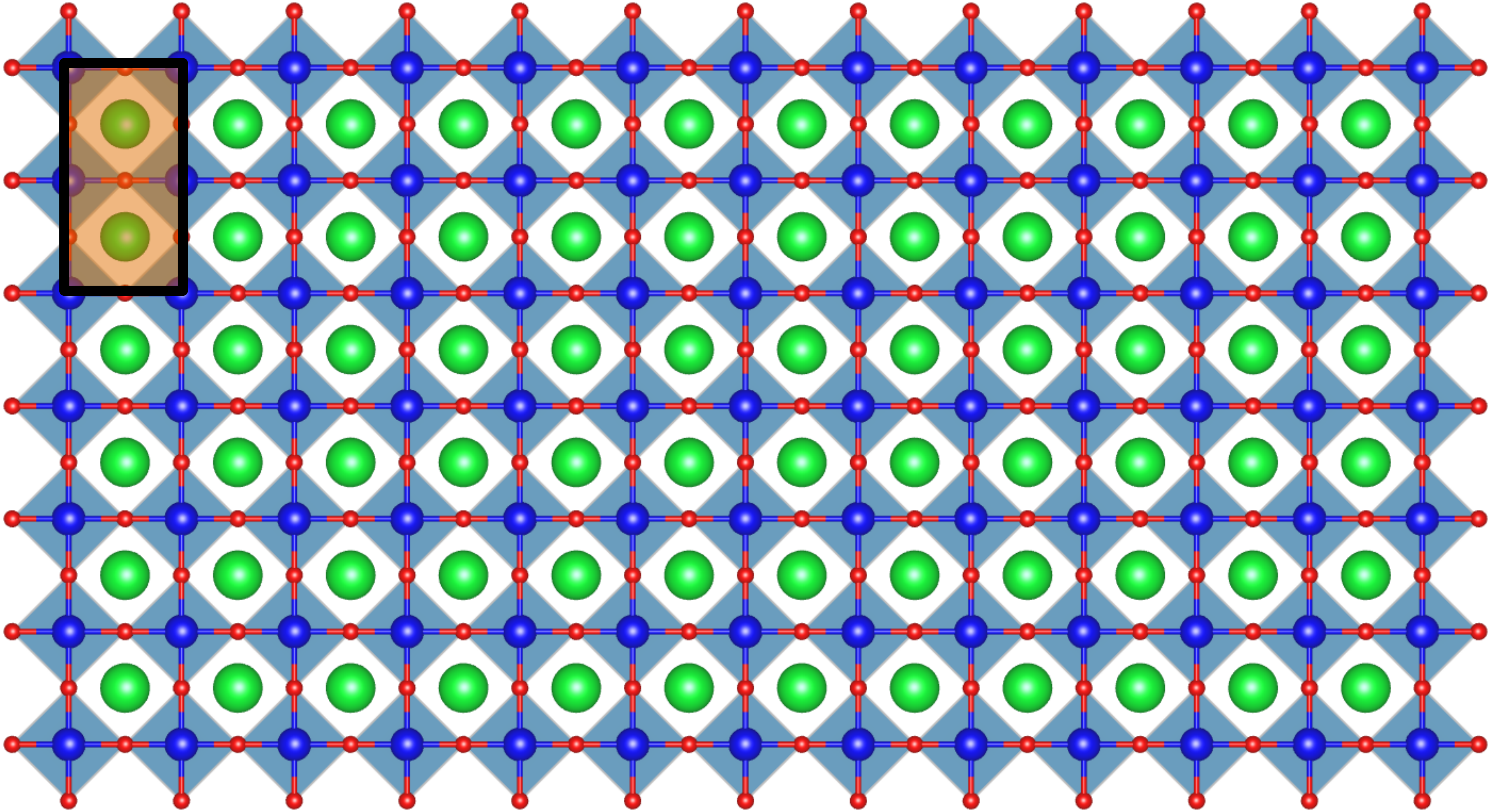
Surface Reconstructions

(1 x 1) surface reconstruction



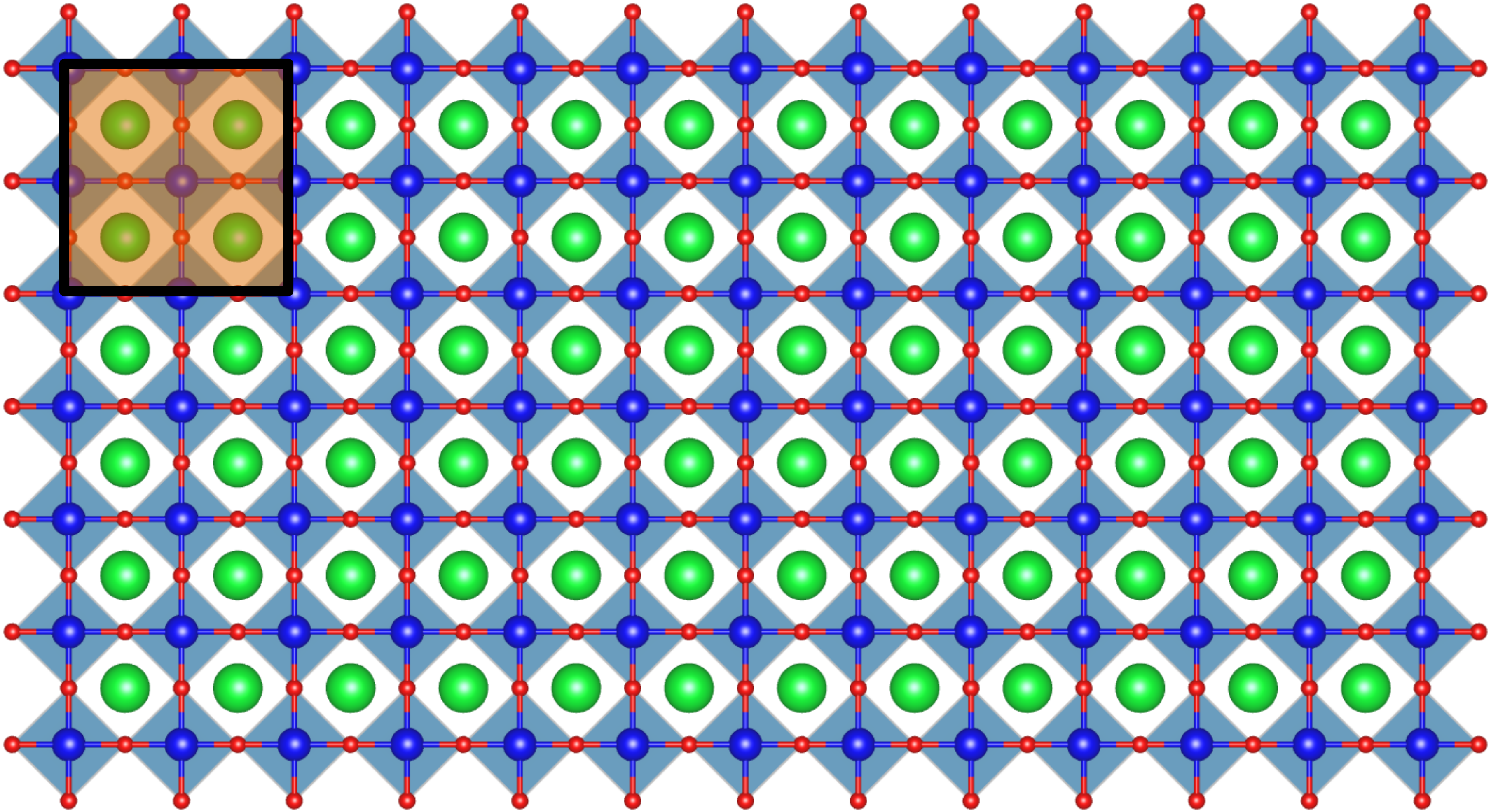
Surface Reconstructions

(2 x 1) surface reconstruction



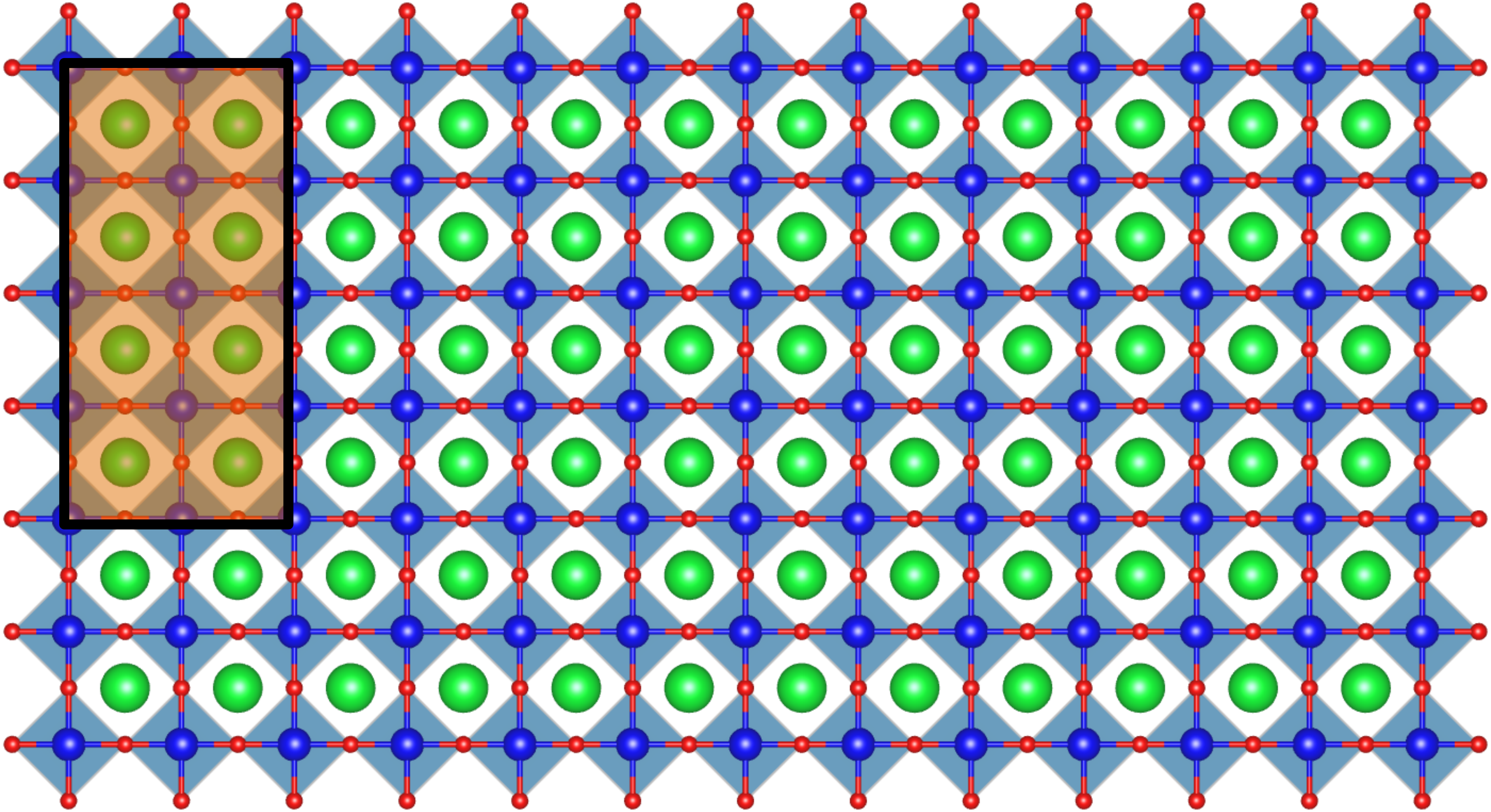
Surface Reconstructions

(2 x 2) surface reconstruction



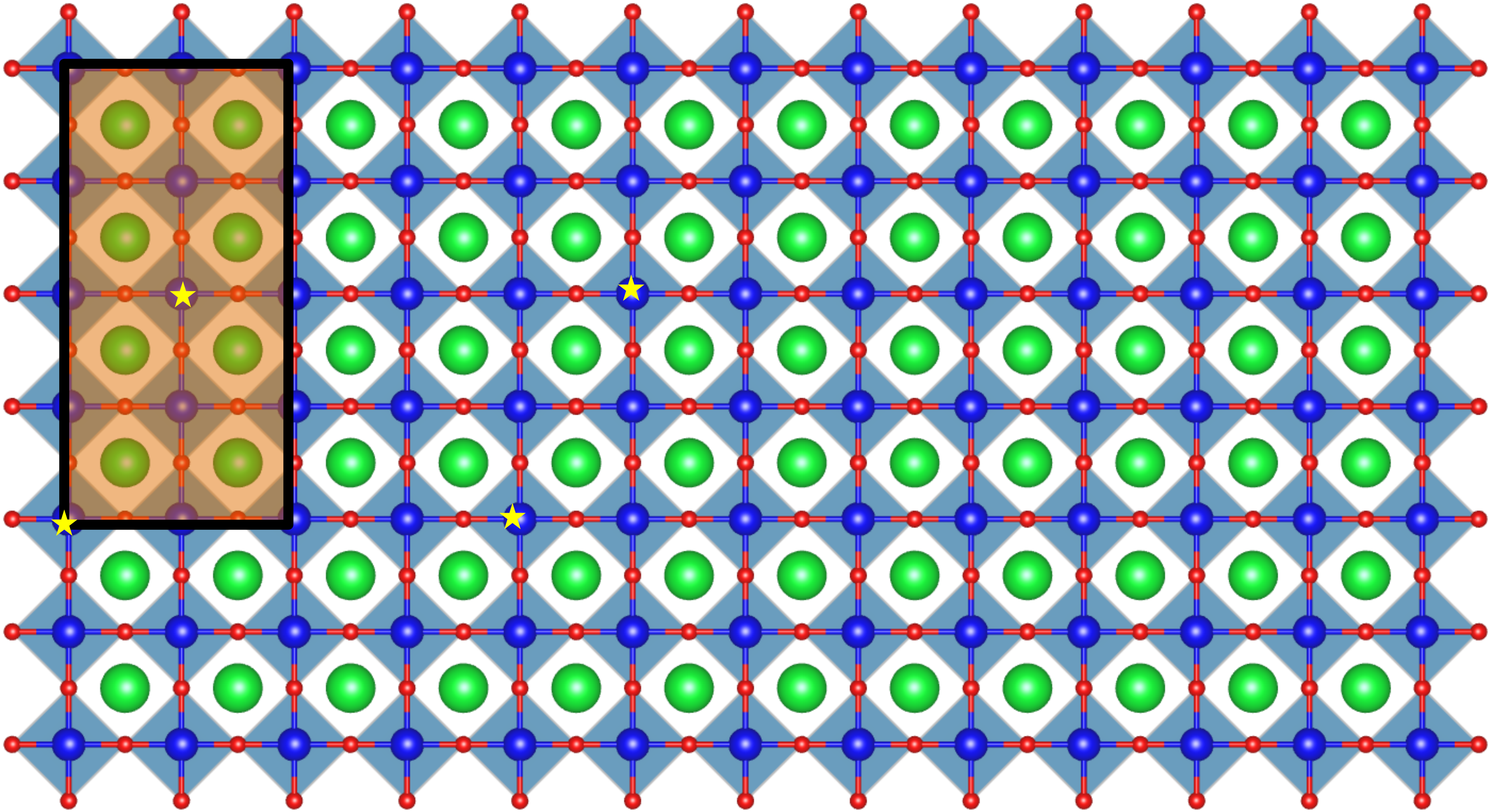
Surface Reconstructions

c(4 x 2) surface reconstruction



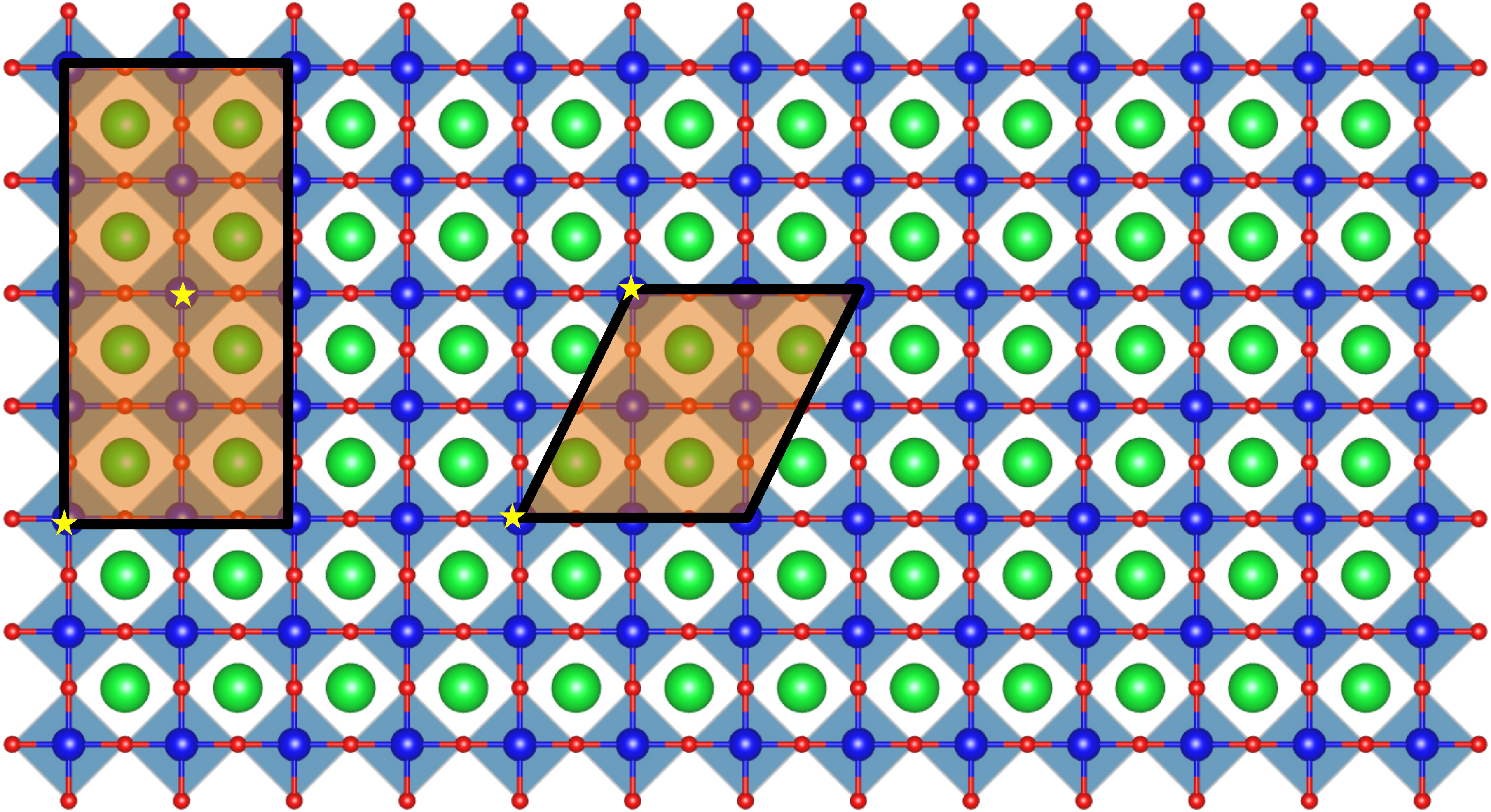
Surface Reconstructions

c(4 x 2) surface reconstruction



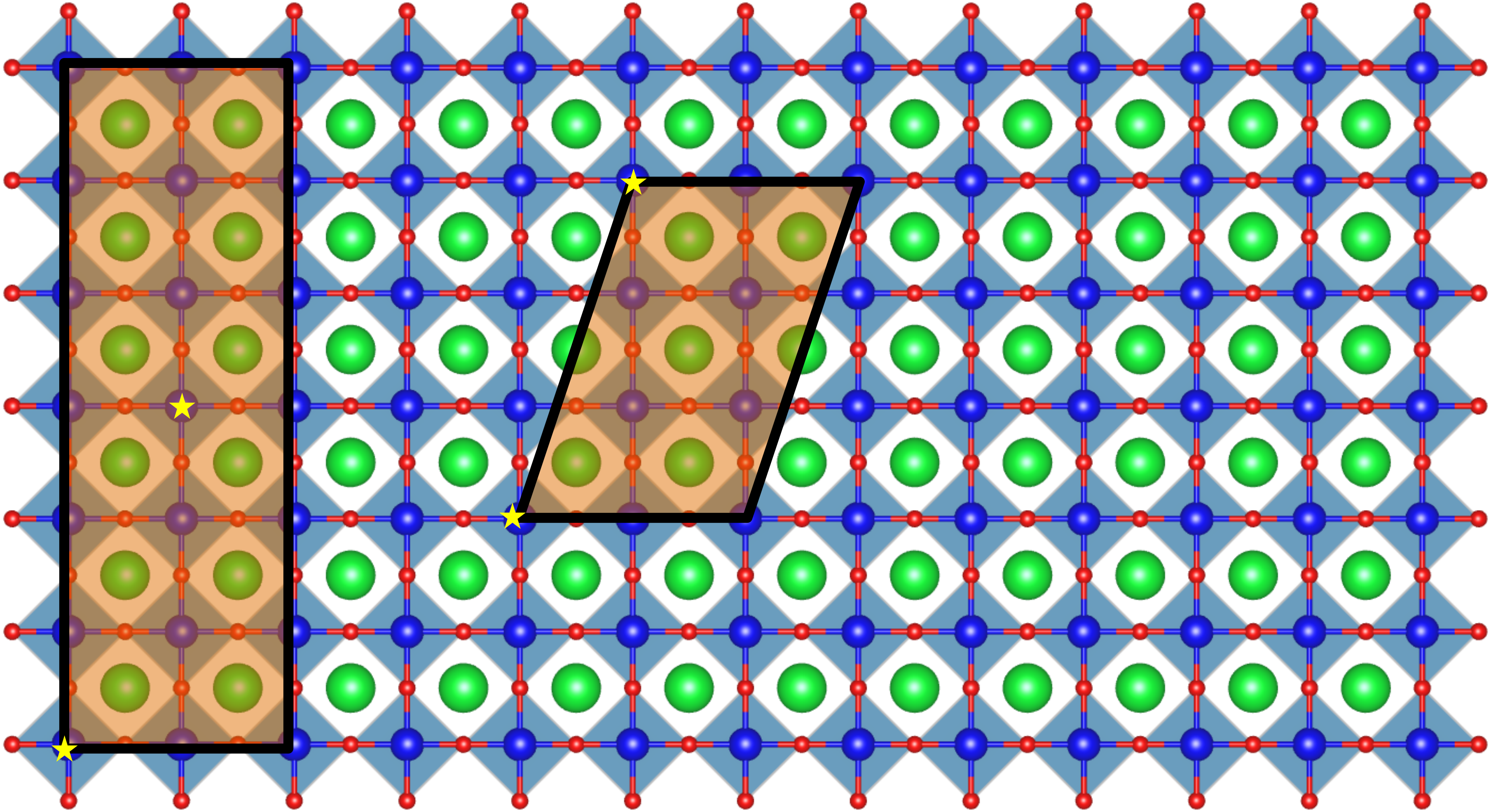
Surface Reconstructions

c(4 x 2) surface reconstruction



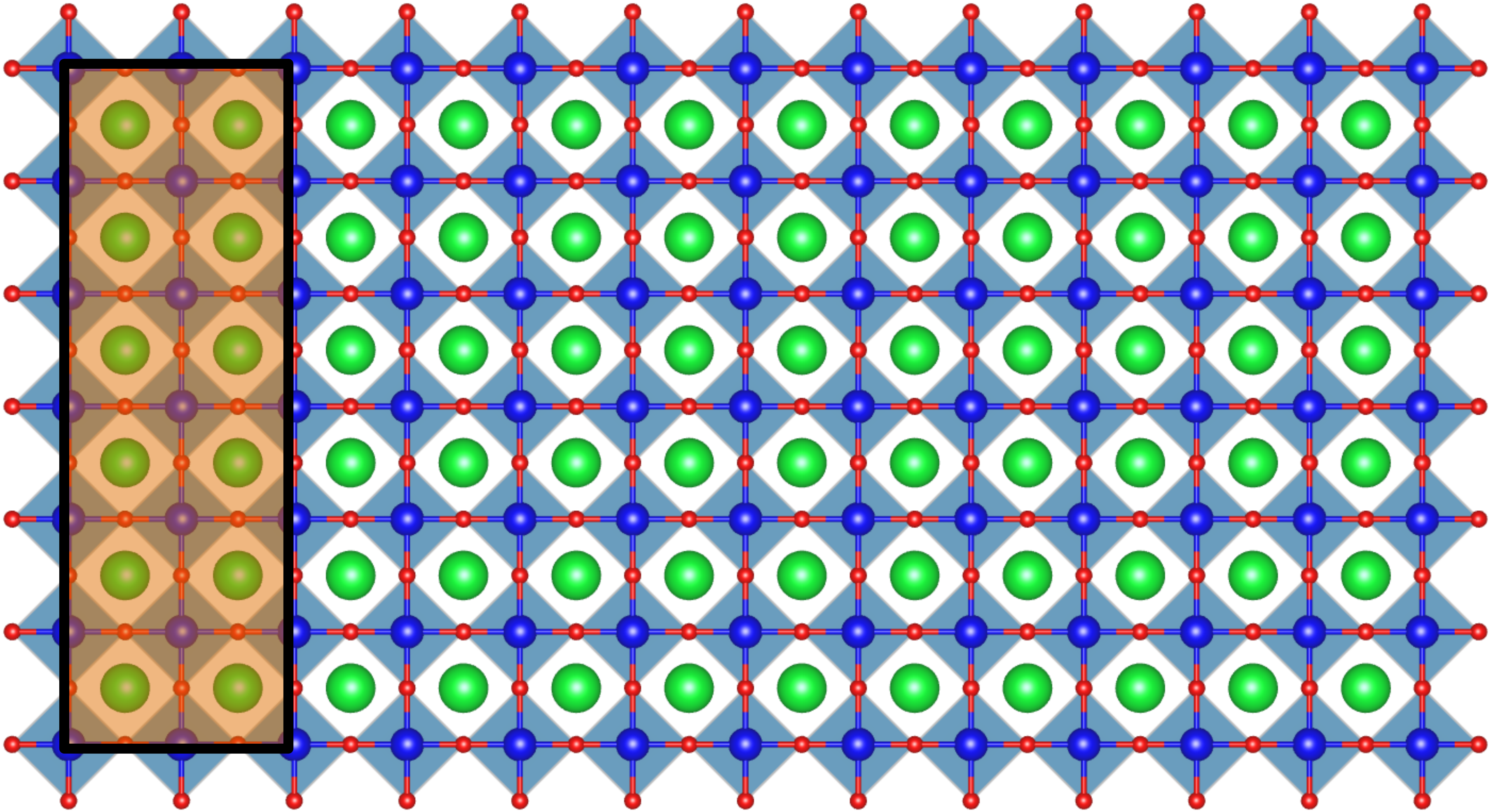
Surface Reconstructions

c(6 x 2) surface reconstruction



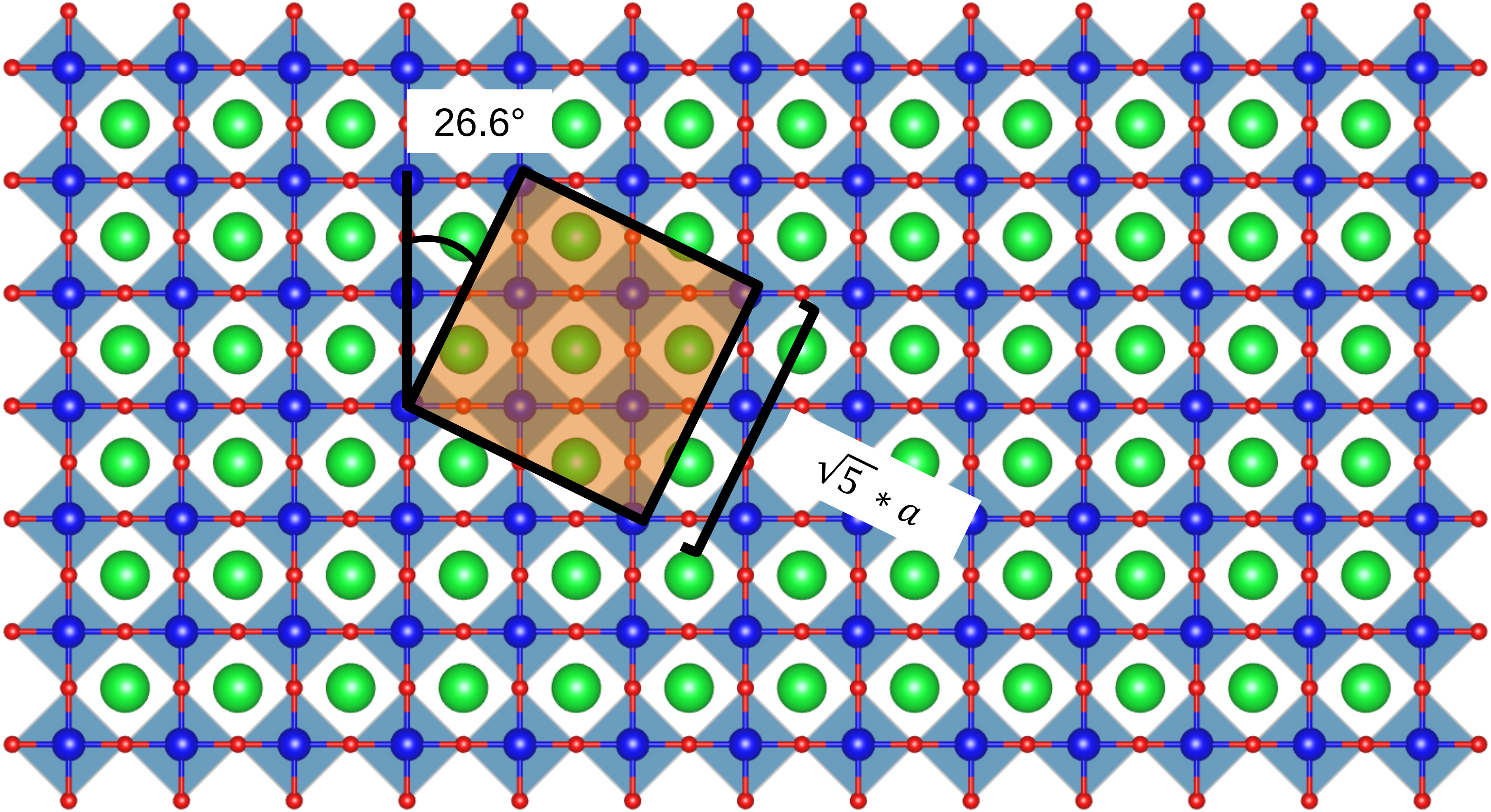
Surface Reconstructions

(6 x 2) surface reconstruction

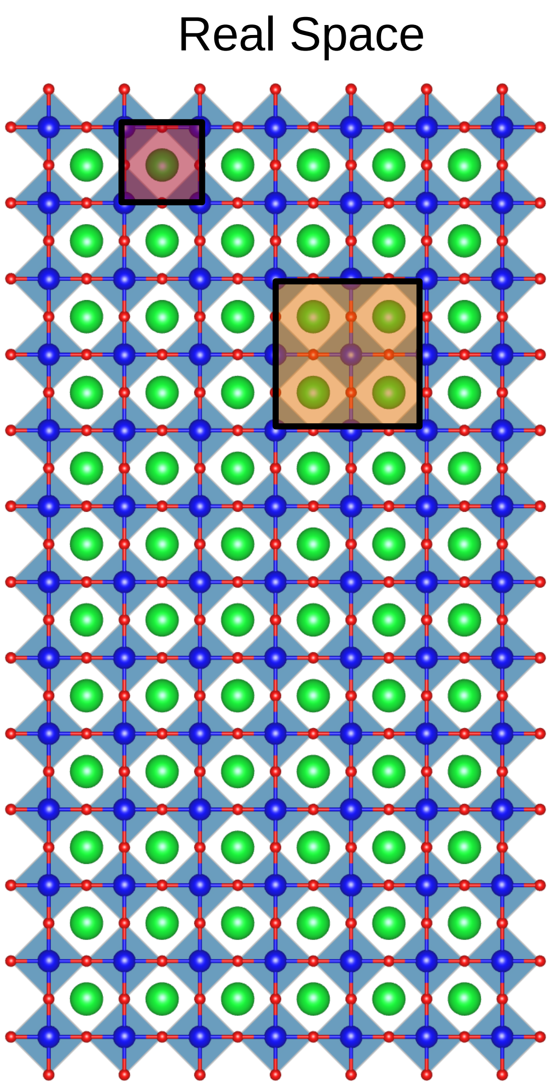


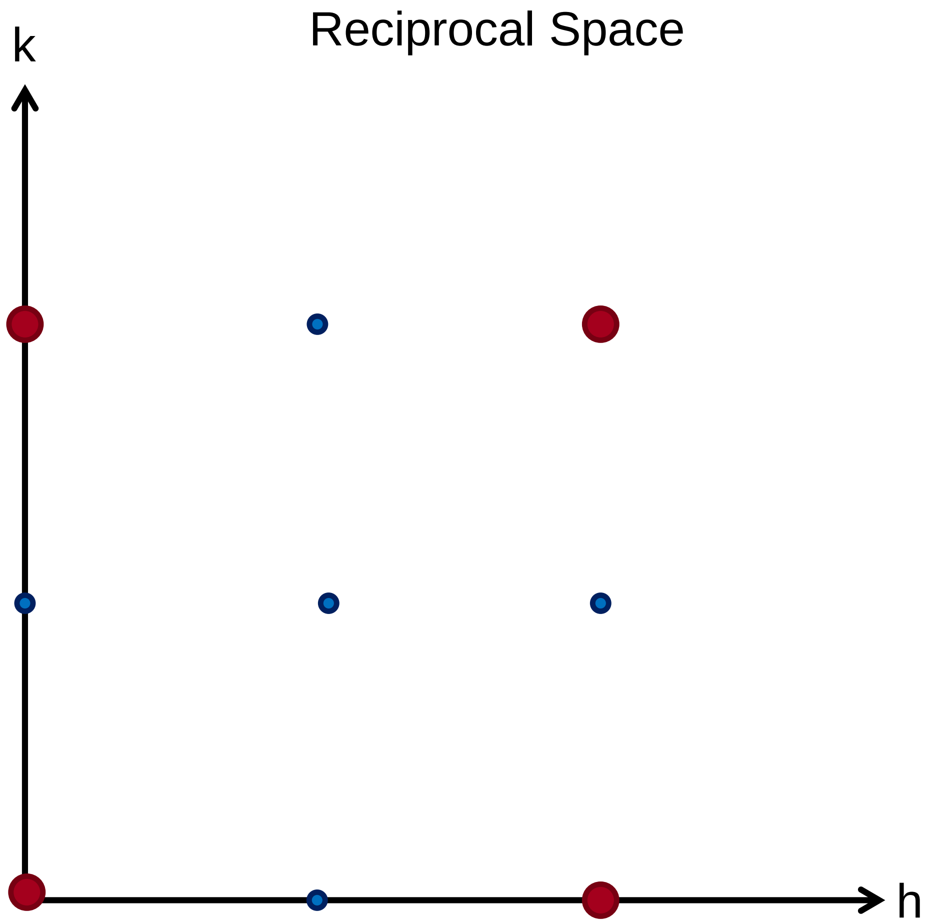
Surface Reconstructions

$(\sqrt{5} \times \sqrt{5})$R26.6° surface reconstruction



Identifying Surface Reconstructions or Film Superlattices





Surface reconstructions or film superlattices give rise to scattering at half order positions, e.g. (½, ½, ½)

Thin Film Diffraction and CTR

General Considerations:

- Very sensitive technique for exploring structure in epitaxial films (or relaxed films) or surface structure of crystals or films
- Requires high quality samples on crystalline substrates
- Alignment is very demanding, do not take shortcuts at this stage
- Surface structures are very sensitive, these should be measured under inert atmosphere and care should be taken to avoid beam damage
- Should always survey for fractional order rods to confirm presence or absence of a surface reconstruction

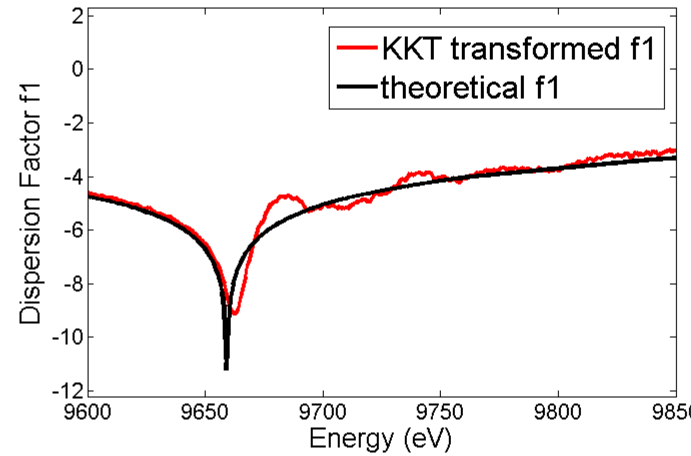
Other Experimental Approaches and Techniques

Resonant X-Ray Diffraction

X-Ray Diffraction and Crystallography

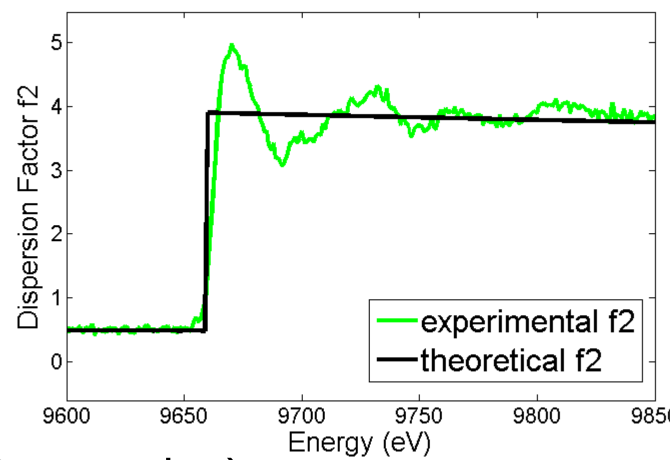
- Lattice; unit cell size & strain; crystallite orientation
- Phase identification & quantify
- Where are the atoms: atomic/crystal structure
- Grain/crystallite size; defects & disorder

$$f = f_o + f_1(E) + i f_2(E)$$



Resonant Diffraction

- Element specific (Cu, Zn, Sn, Se)
- Change in atomic scattering power
- Distinguishes between kesterite and stannite phases
- Quantify anti-site disorder and stoichiometry



$$I(Q,E) = \left| \sum_i x_i f_i(Q,E) \cdot e^{2\pi i(hx+ky+lz)} \right|^2$$

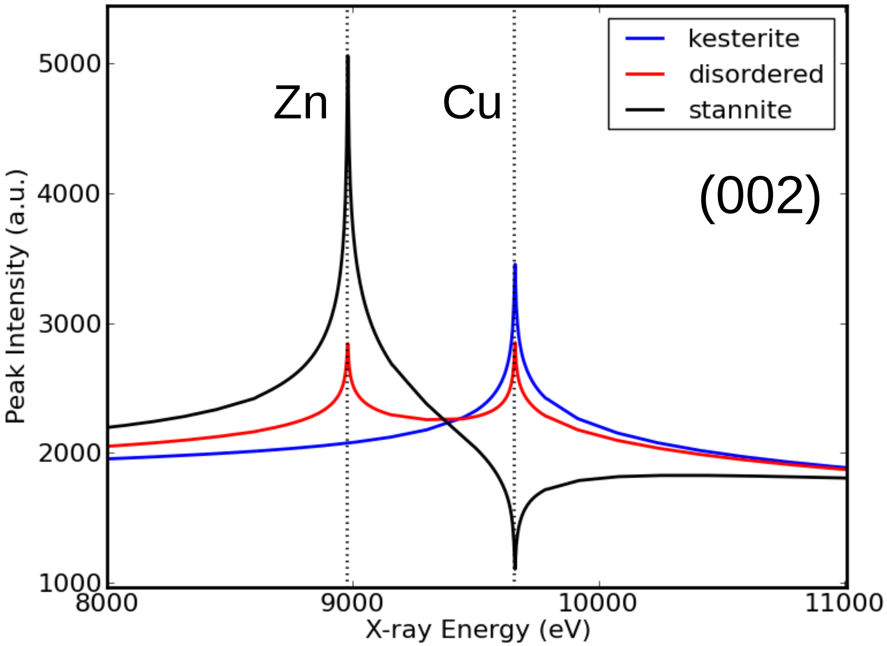
element selectivity — Site selection

Y. Shi *et al.* (In Preparation)

Resonant Diffraction

Phase Identification - CZTSSe

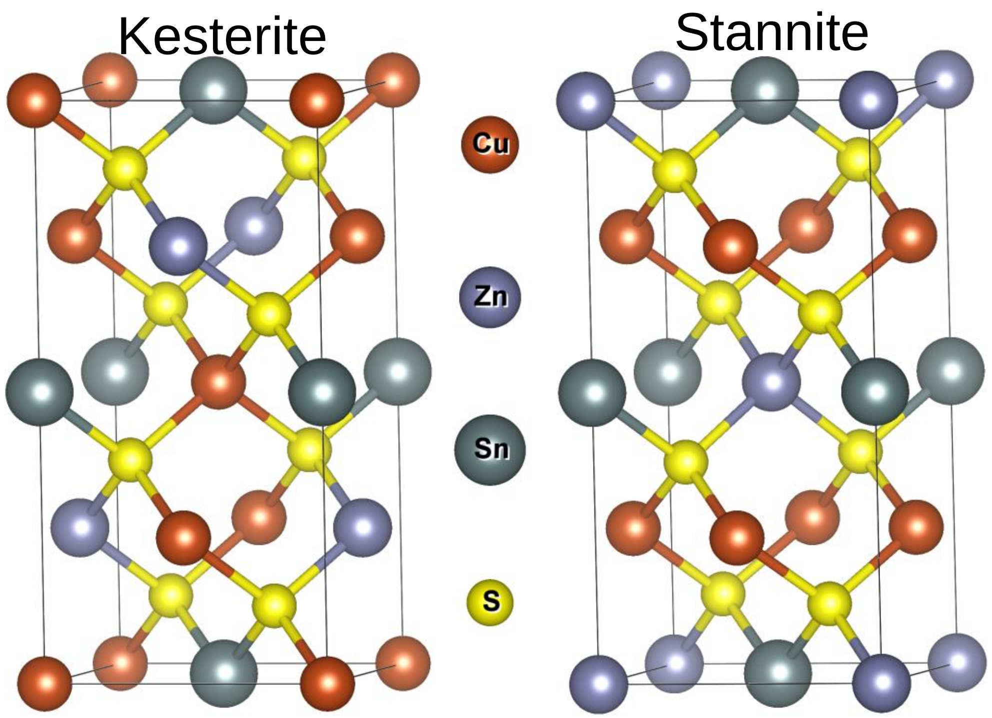
Resonant elastic X-ray diffraction



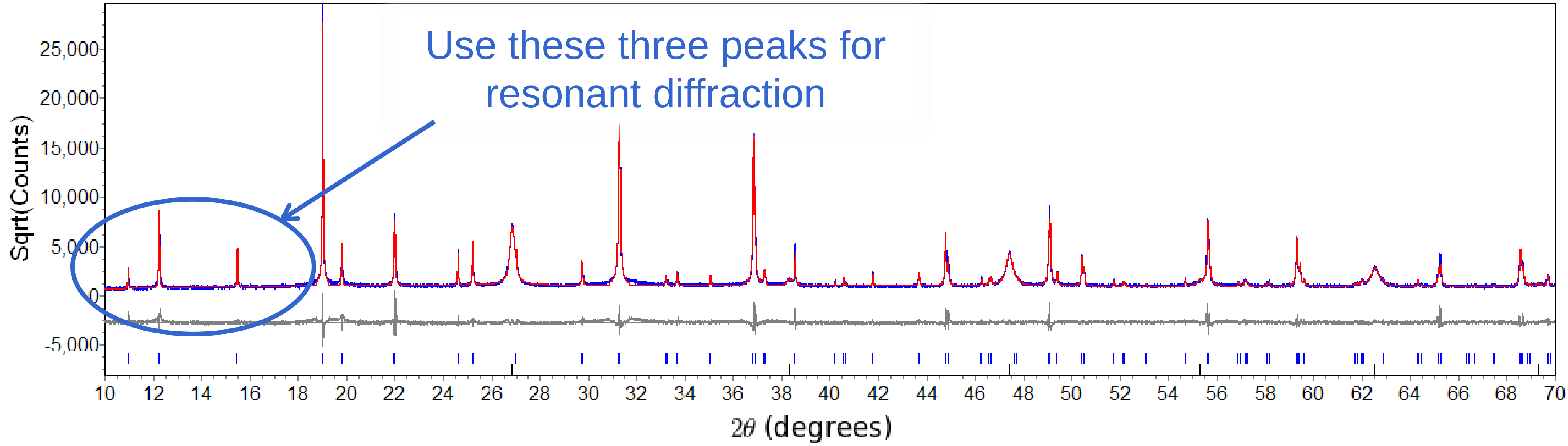
$$I(Q,E) = \left| \sum_i x_i f_i(Q,E) \cdot e^{2\pi i(hx+ky+lz)} \right|^2$$

element selectivity   Site selection

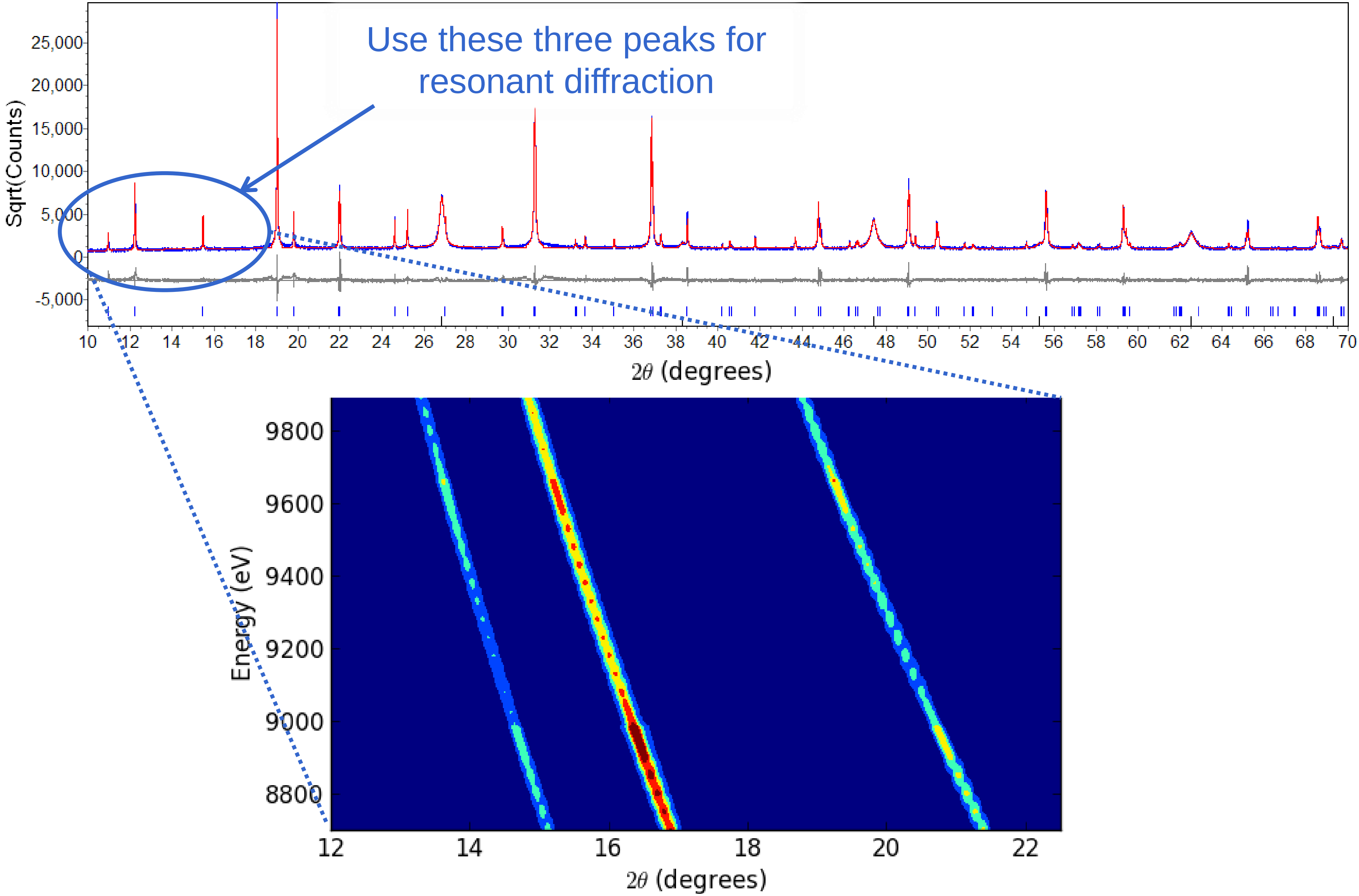
Qualitatively Different Resonant Behavior for Different Phases.



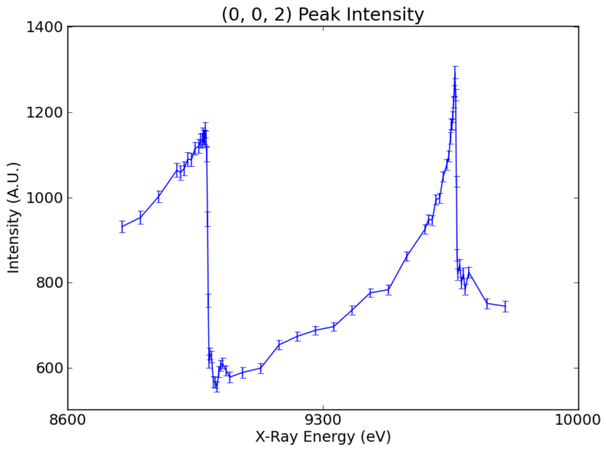
Resonant X-Ray Diffraction

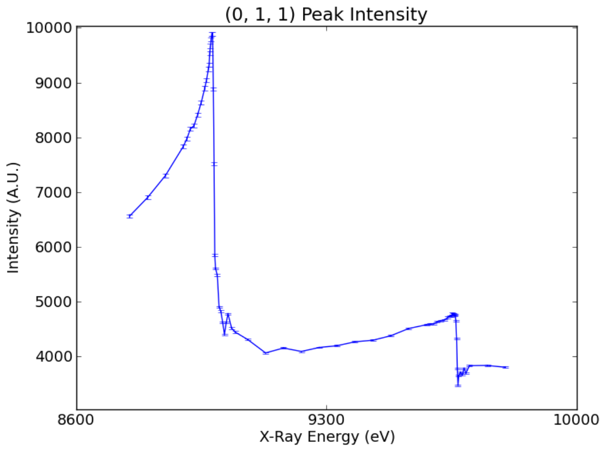


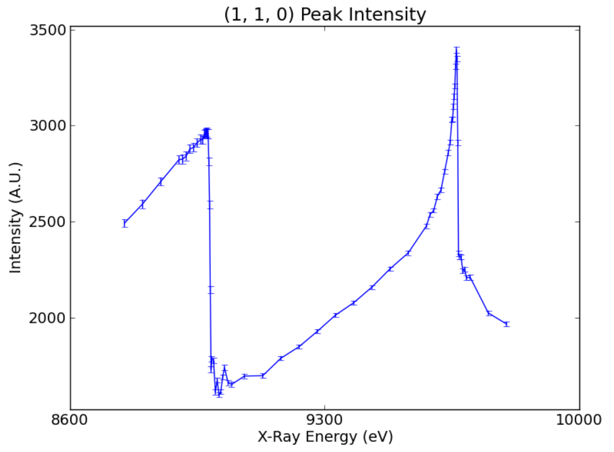
Resonant X-Ray Diffraction

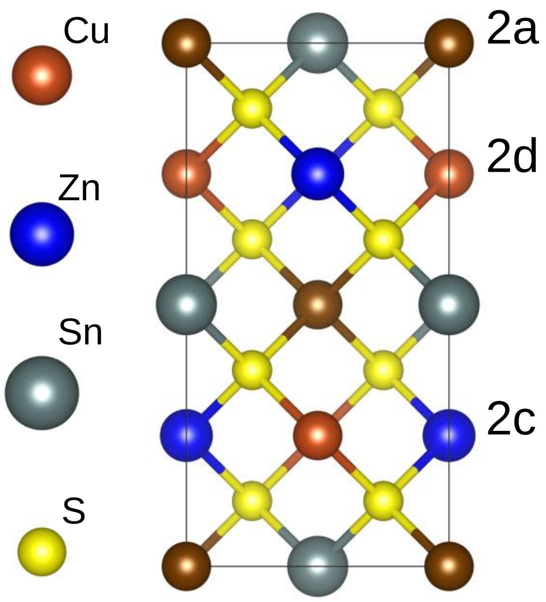


Resonant X-Ray Diffraction Model



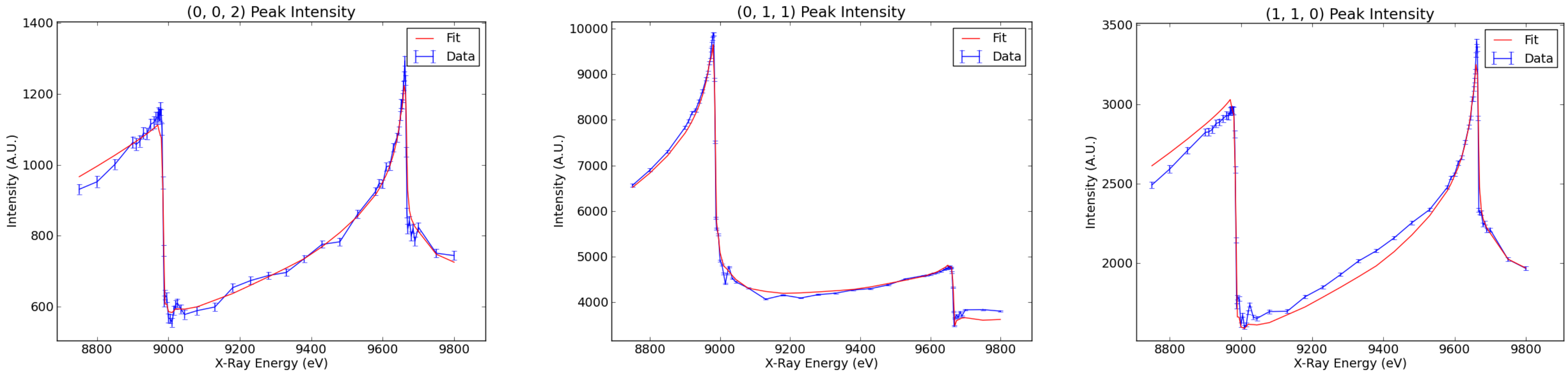


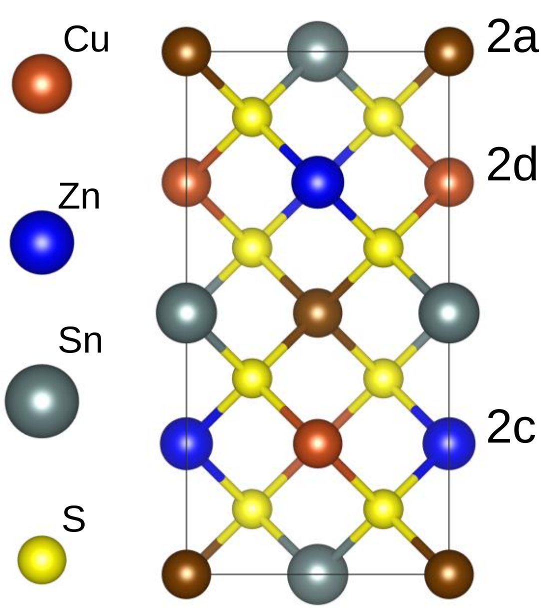




2a → Cu + Zn ≤ 1
2d → Cu + Zn ≤ 1
2c → Cu + Zn ≤ 1
Interstitial → Cu + Zn + Sn ≤ 1

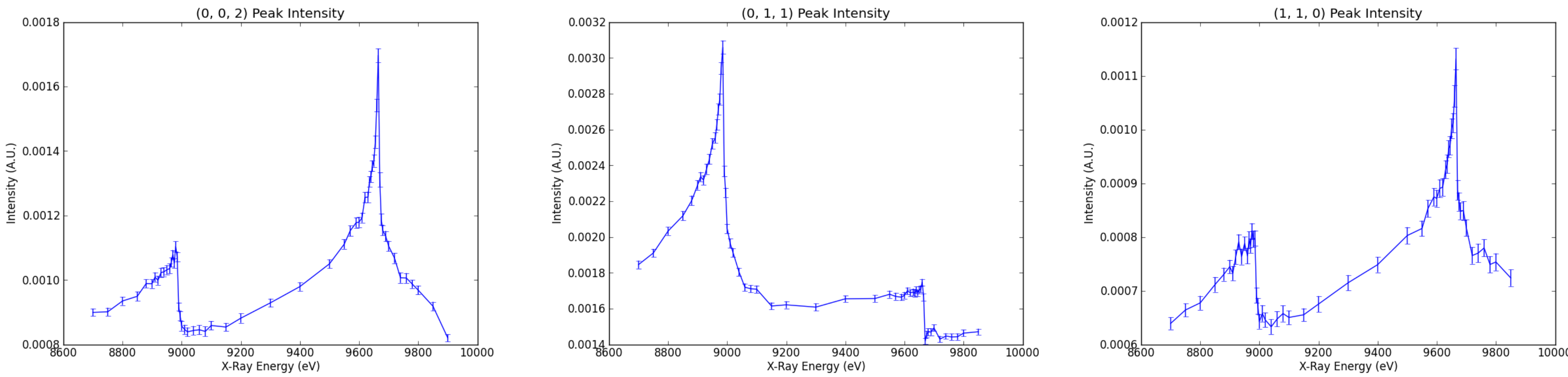
Resonant X-Ray Diffraction Model

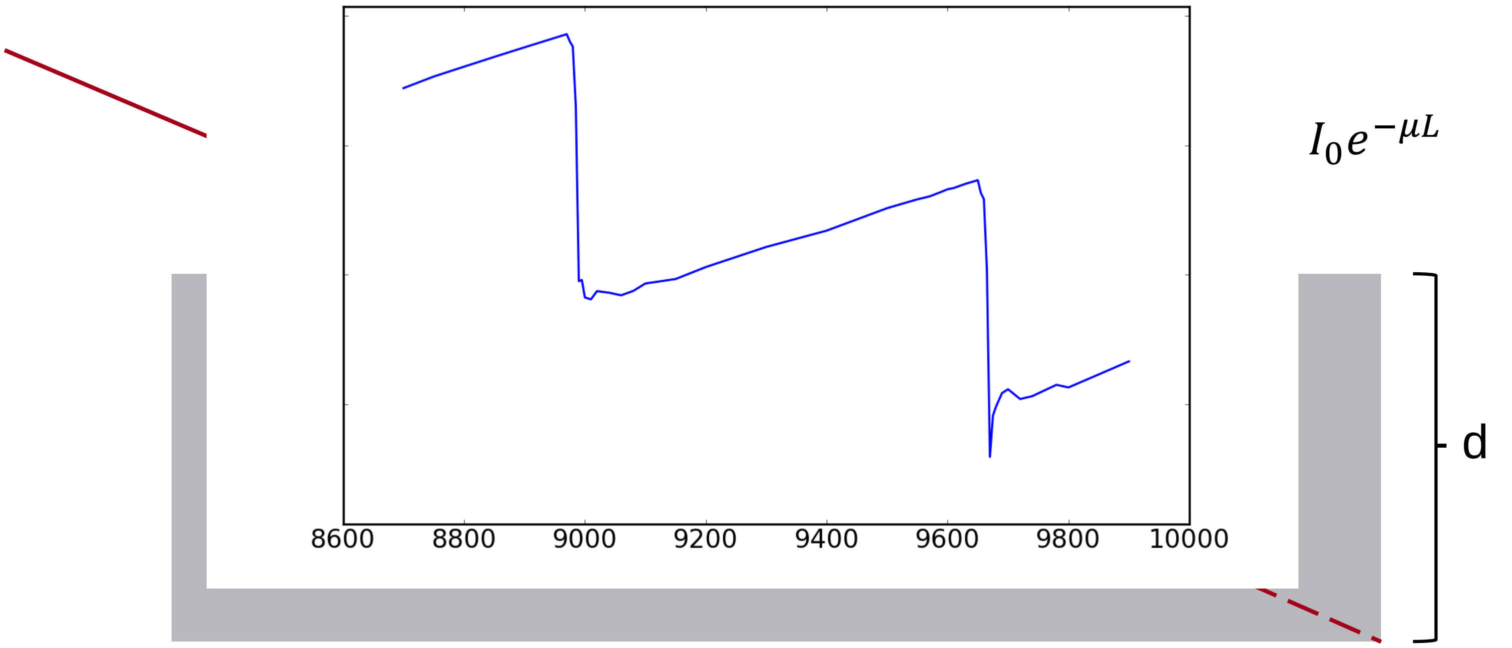




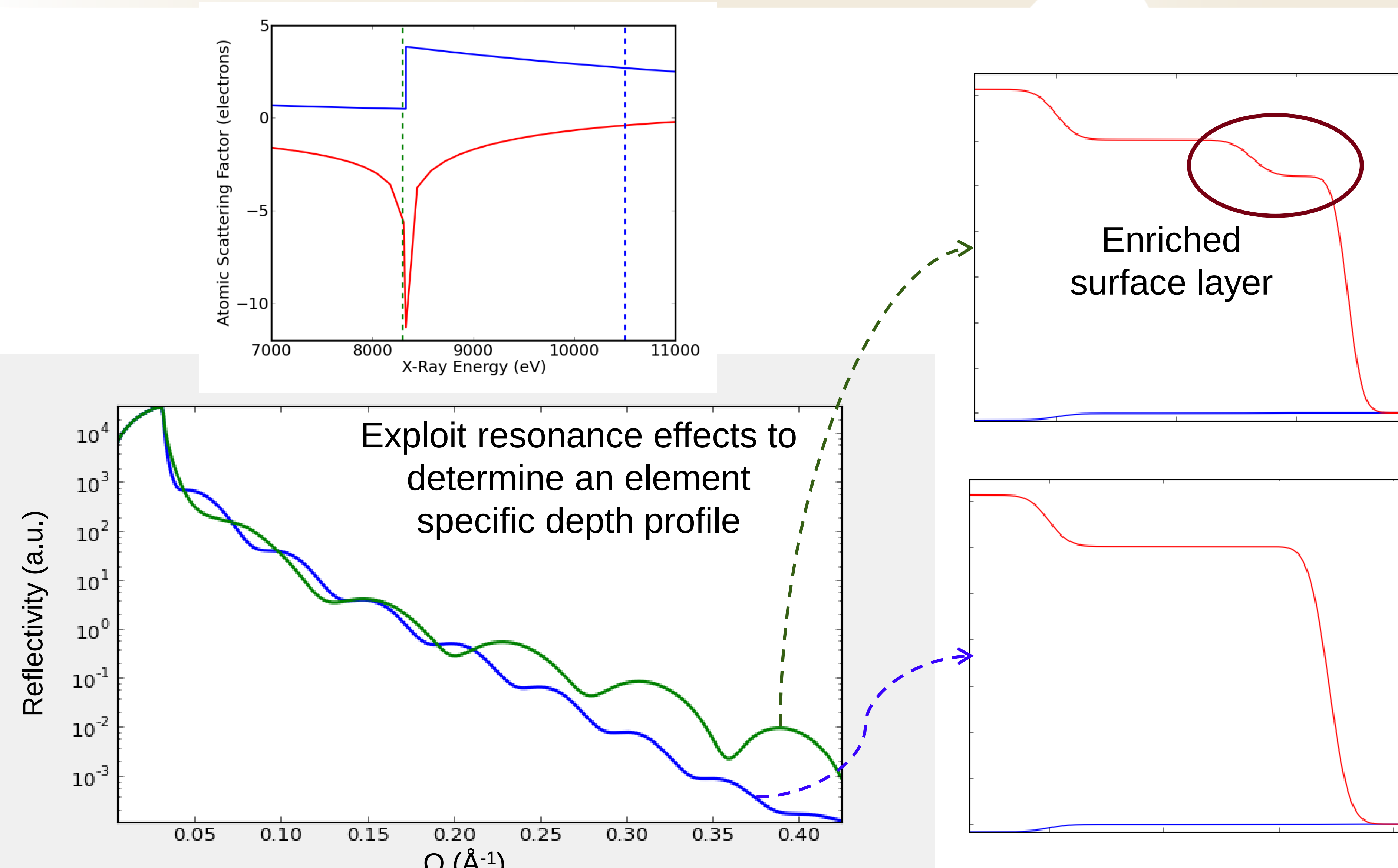
Position	Cu Occupancy	Zn Occupancy	Vacancy
2a $(0, 0, 0)$	0.90	0.10	0.00
2d $(0, {}^1/_2, {}^1/_4)$	0.50	0.45	0.05
2c $(0, {}^1/_2, {}^3/_4)$	0.45	0.48	0.07
interstitial $({}^3/_4, {}^1/_4, {}^1/_8)$	0.06	0.12	0.82

Resonant X-Ray Diffraction Absorption





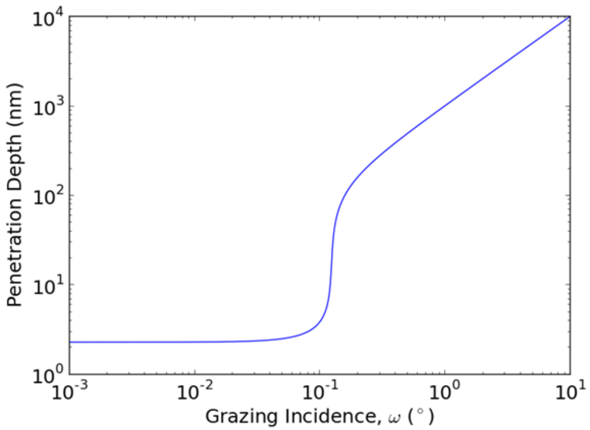
Resonant Reflectivity

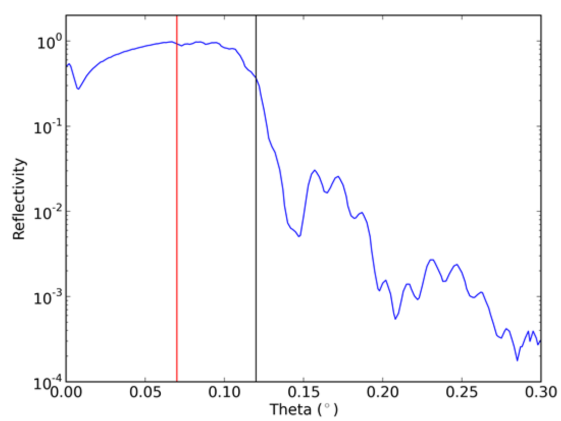


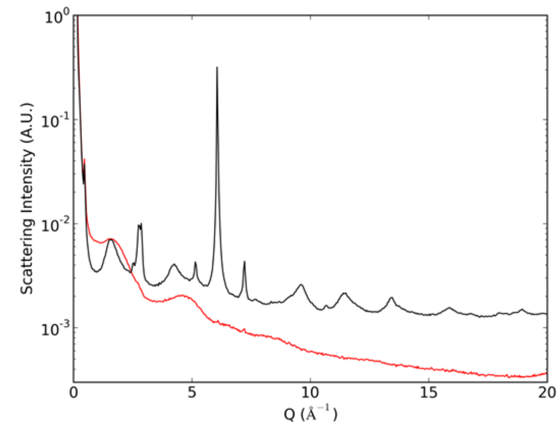
Depth Profiling

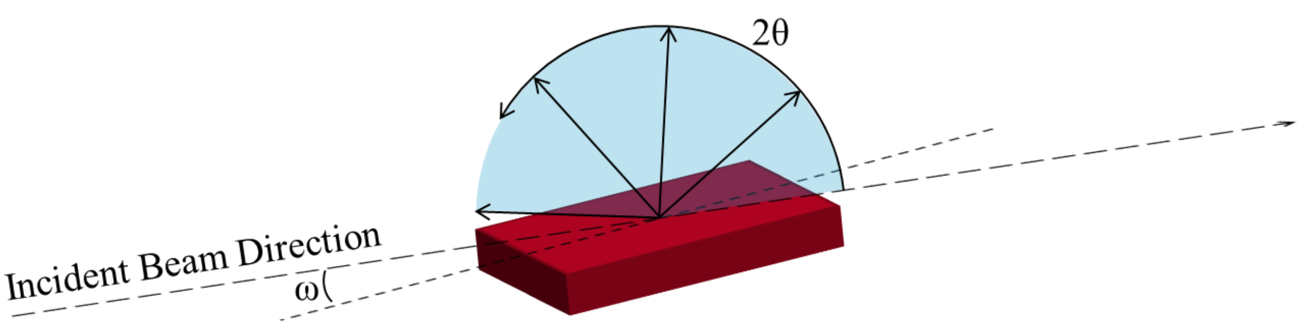
Control over the incidence angle can give control over the depth of the x-ray probe
This is especially powerful if you can work near or below the critical angle

However, this is quite tricky and should be done carefully!









In-situ and *Operando* Techniques

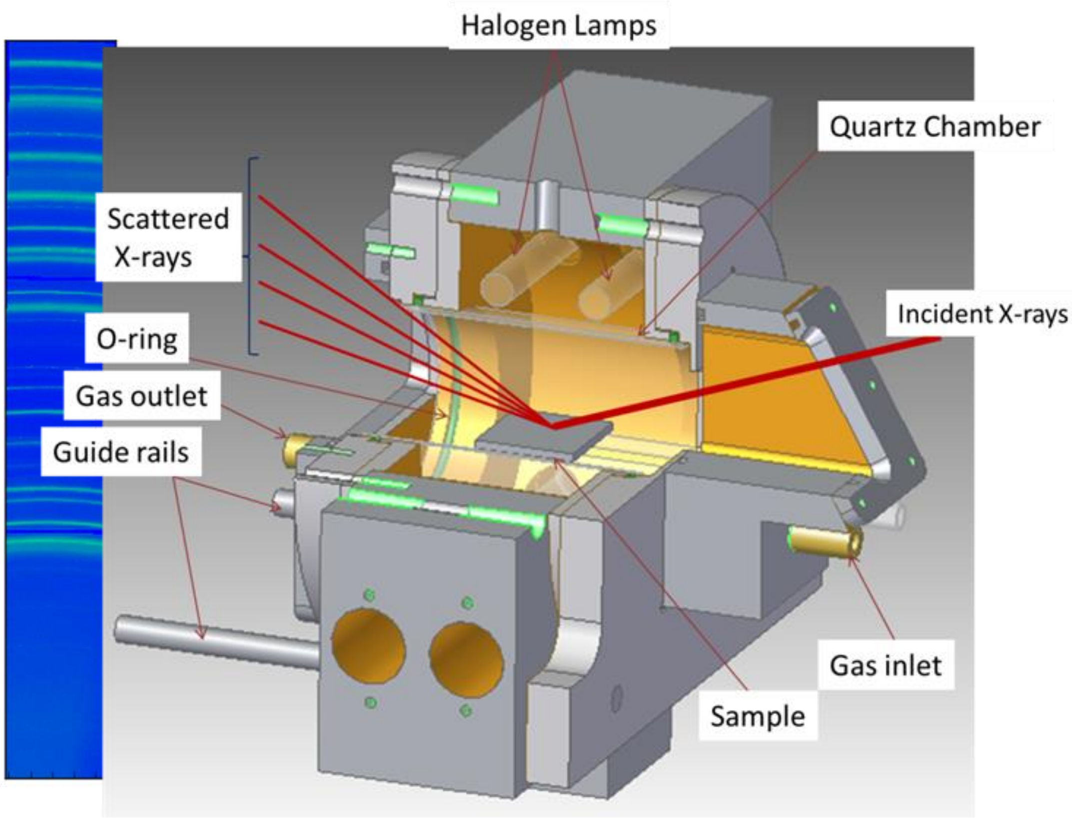
Often we want to characterize a material under a certain set of conditions or as part of a device while operating

Rapid Thermal Processing for PV applications

Our implementation gives all of the functionality available in commercial RTP systems without compromise for use on a beamline

Can ramp up to ~1200ºC at >100ºC per second

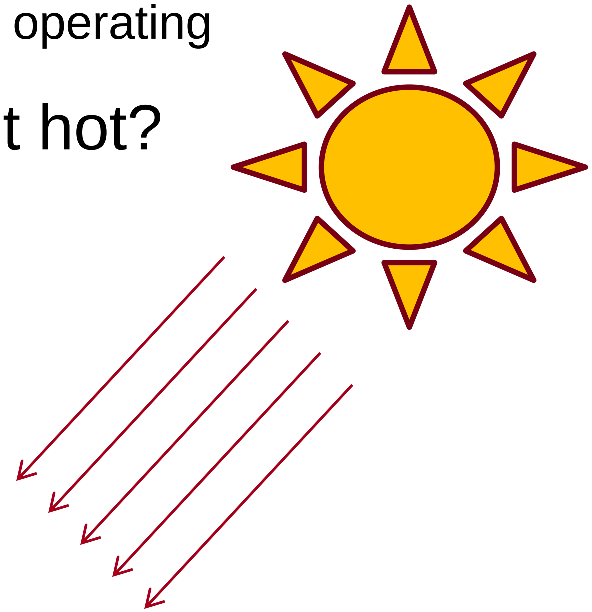
Coupled to a fast area detector (Pilatus) for collection of XRD data



In-situ and *Operando* Techniques

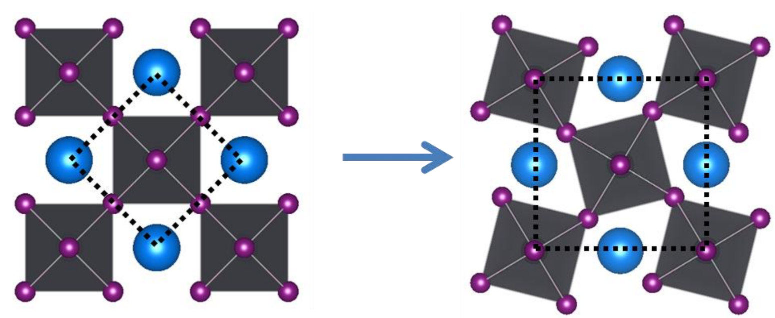
Often we want to characterize a material under a certain set of conditions or as part of a device while operating

What happens when solar cells get hot?

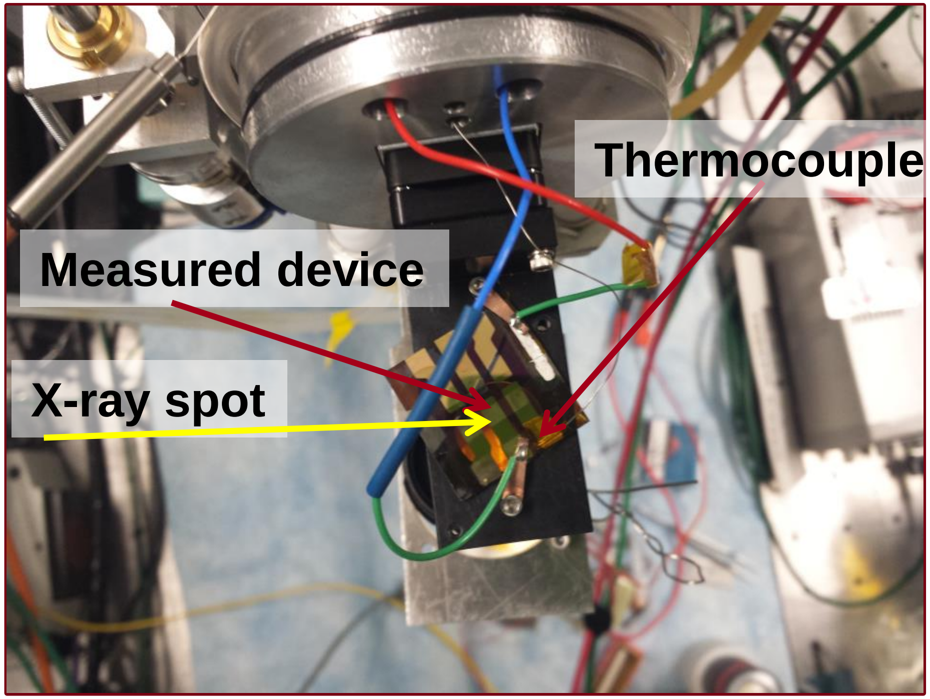


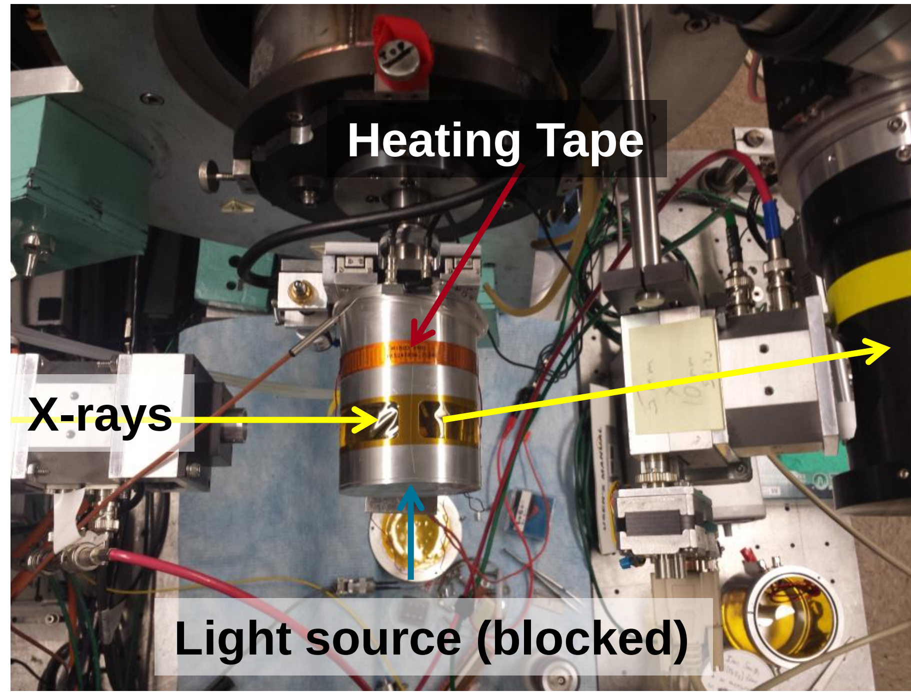
MAPbI_3 undergoes phase transitions:

- cubic for >~ **335K (60 C)**
- tetragonal **~335 K (60 C)**
- orthorhombic below **~165 K**



In-situ and *Operando* Techniques





Operando chamber:

- White LED light (~ 1 Sun)
- Kapton heating tape
- Thermocouple on top of device
- He environment
- IV curves with light
- 1D and 2D XRD at temperature

In-situ and *Operando* Techniques

Often we want to characterize a material under a certain set of conditions or as part of a device while operating

If you want to measure your sample under a specific set of conditions, talk to the beamline scientists – There is a good chance that we can help figure out how

SSRL Overview

SLAC

5 Main Scattering Beamlines for Material Science

BL1-5 SAXS/WAXS
BL2-1 Powder XRD (High Res. and Low Res. Setups), Reflectivity
BL7-2 6-Circle Diffractometer, Surface and Thin Film Diffraction, Powder Diffraction
BL10-2 4-Circle Diffractometer, Surface and Thin Film Diffraction, Powder Diffraction
BL11-3 Large Area Detector for Powder Diffraction and GI Measurements

SSRL proposals are not beamline specific. A single proposal can get you time on any of the Materials Scattering or Spectroscopy beamlines.

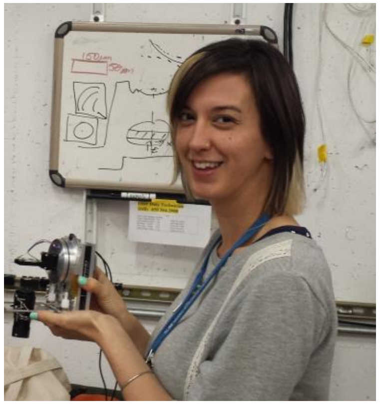
Most beamlines are easy to configure to your needs, we are happy to work with you on the best setup for your experiments.

Acknowledgements

Mike Toney and his group

Chris Tassone and his group

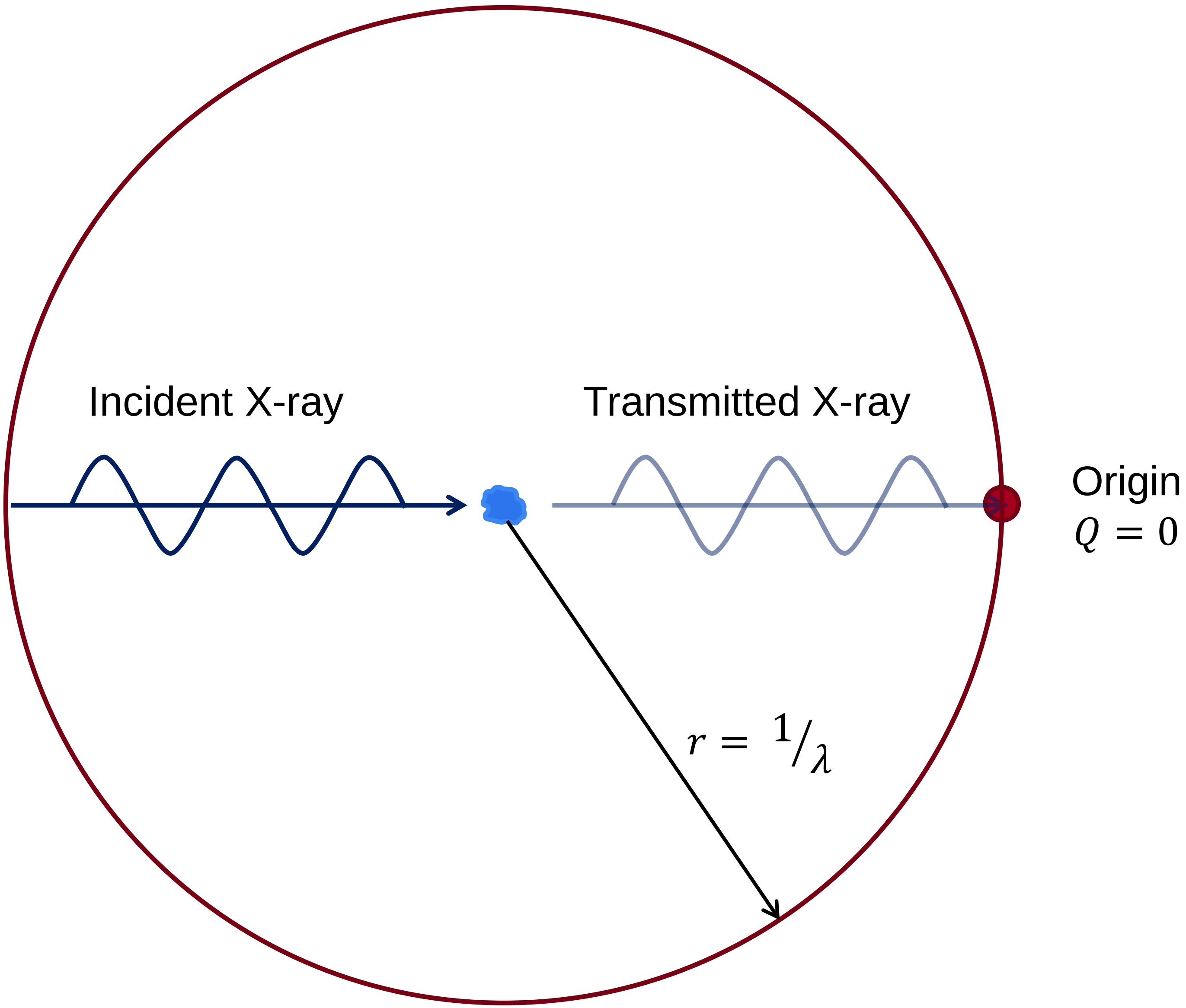
Laura Schelhas



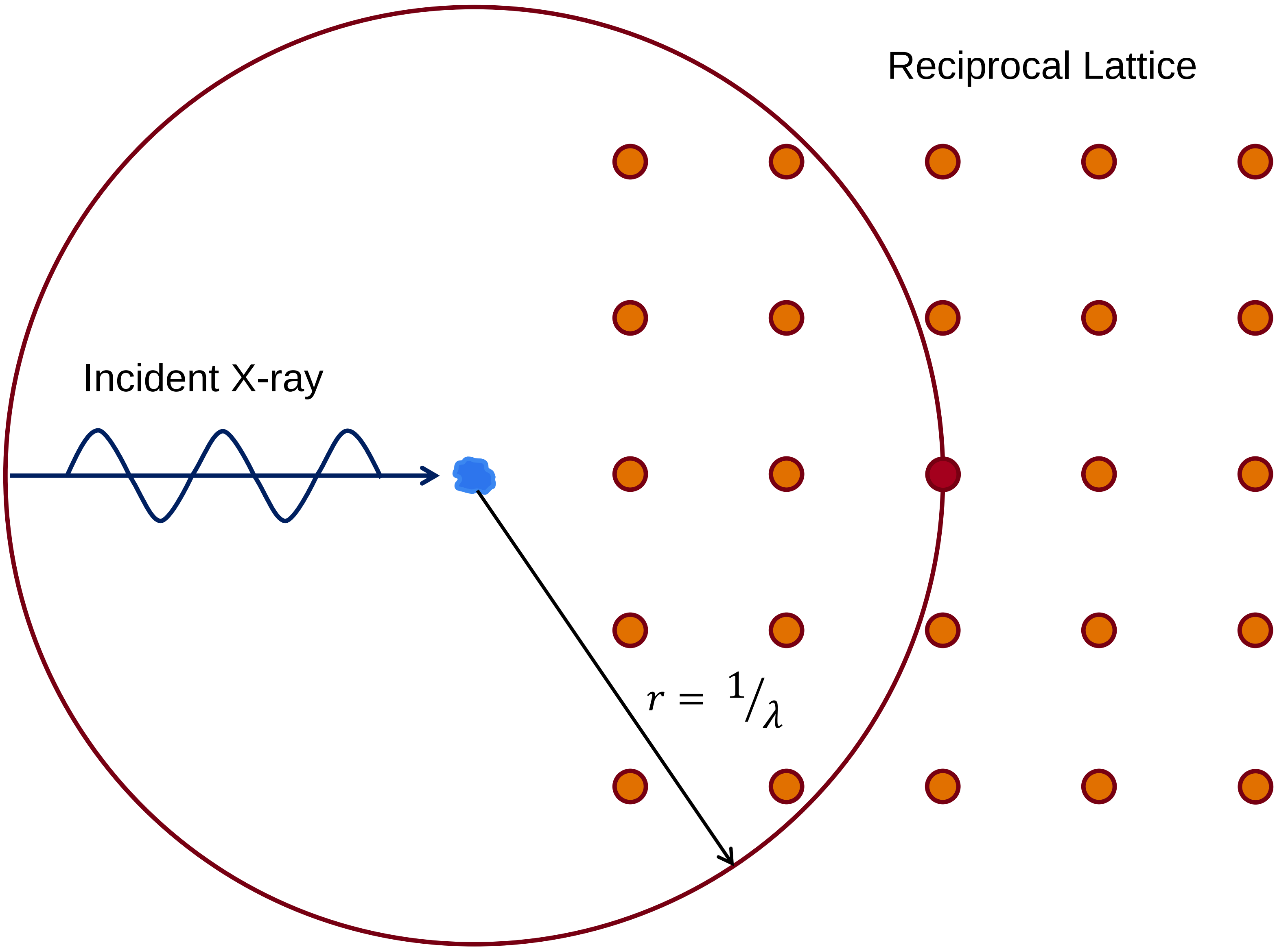
Questions

Find the measurement approach and geometry that works best for your sample, not necessarily what makes the measurement easier

Ewald Construction

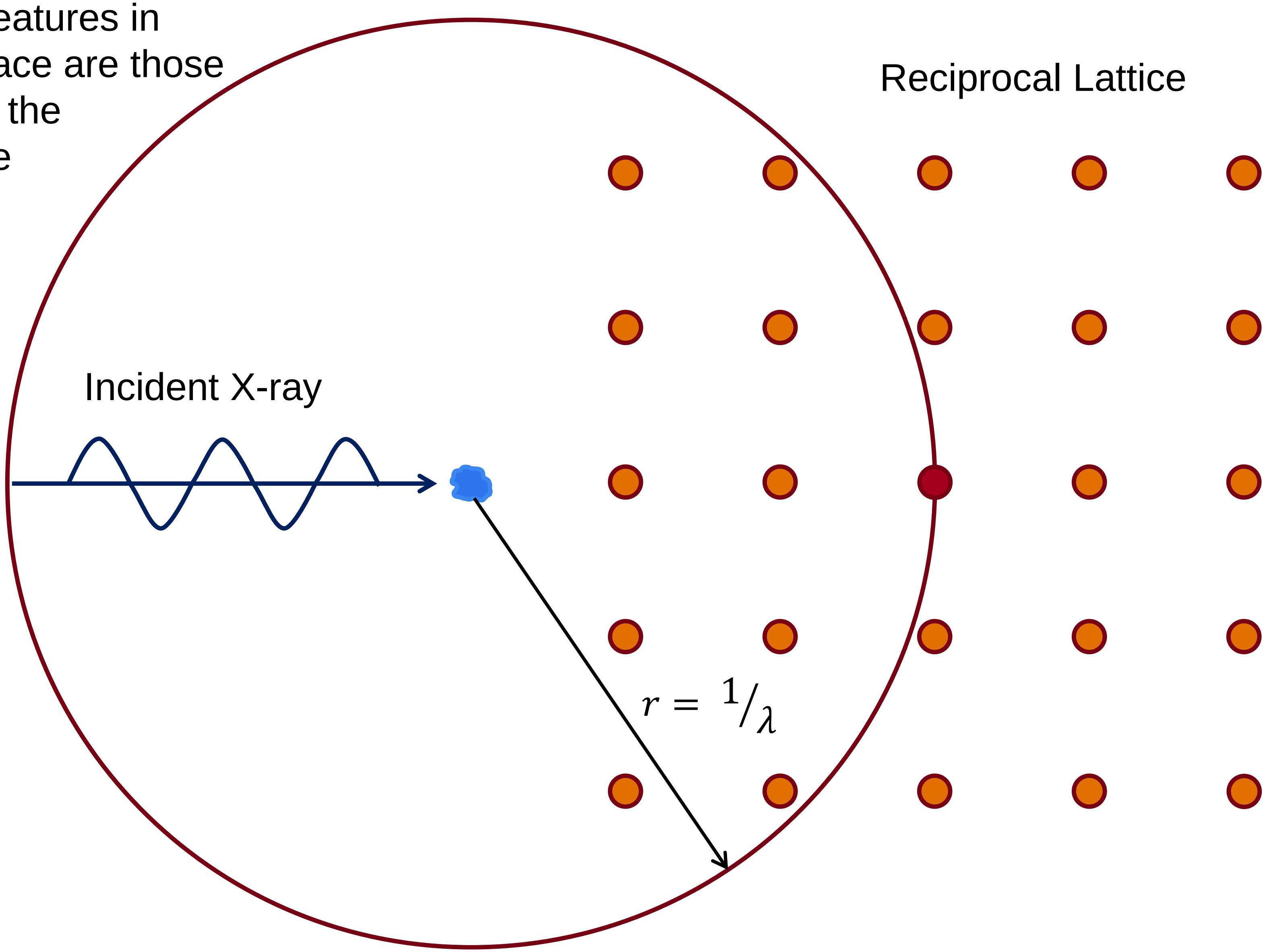


Ewald Construction



Ewald Construction

Observable features in reciprocal space are those with intersect the Ewald Sphere



Ewald Construction

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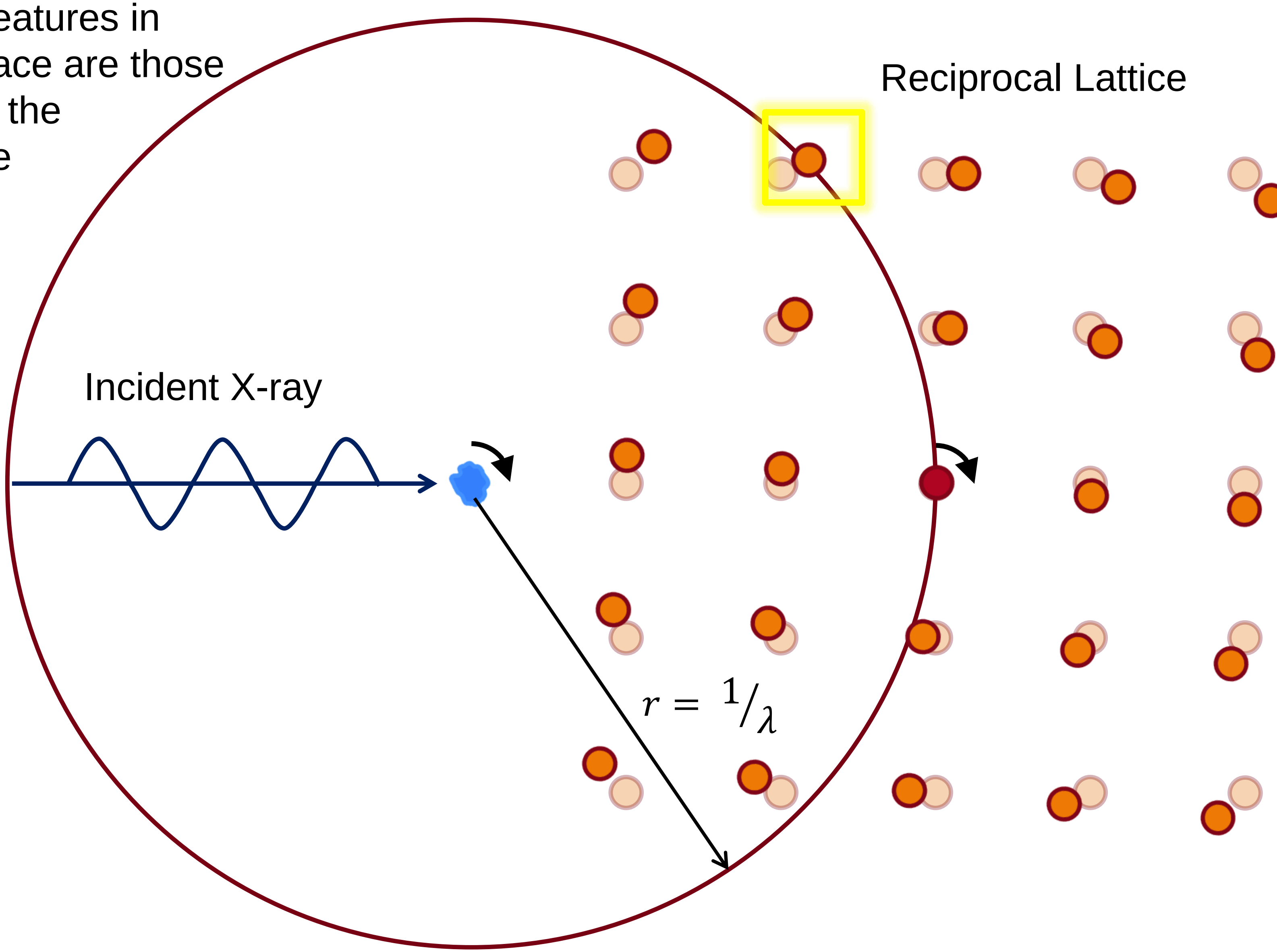

Ewald Construction

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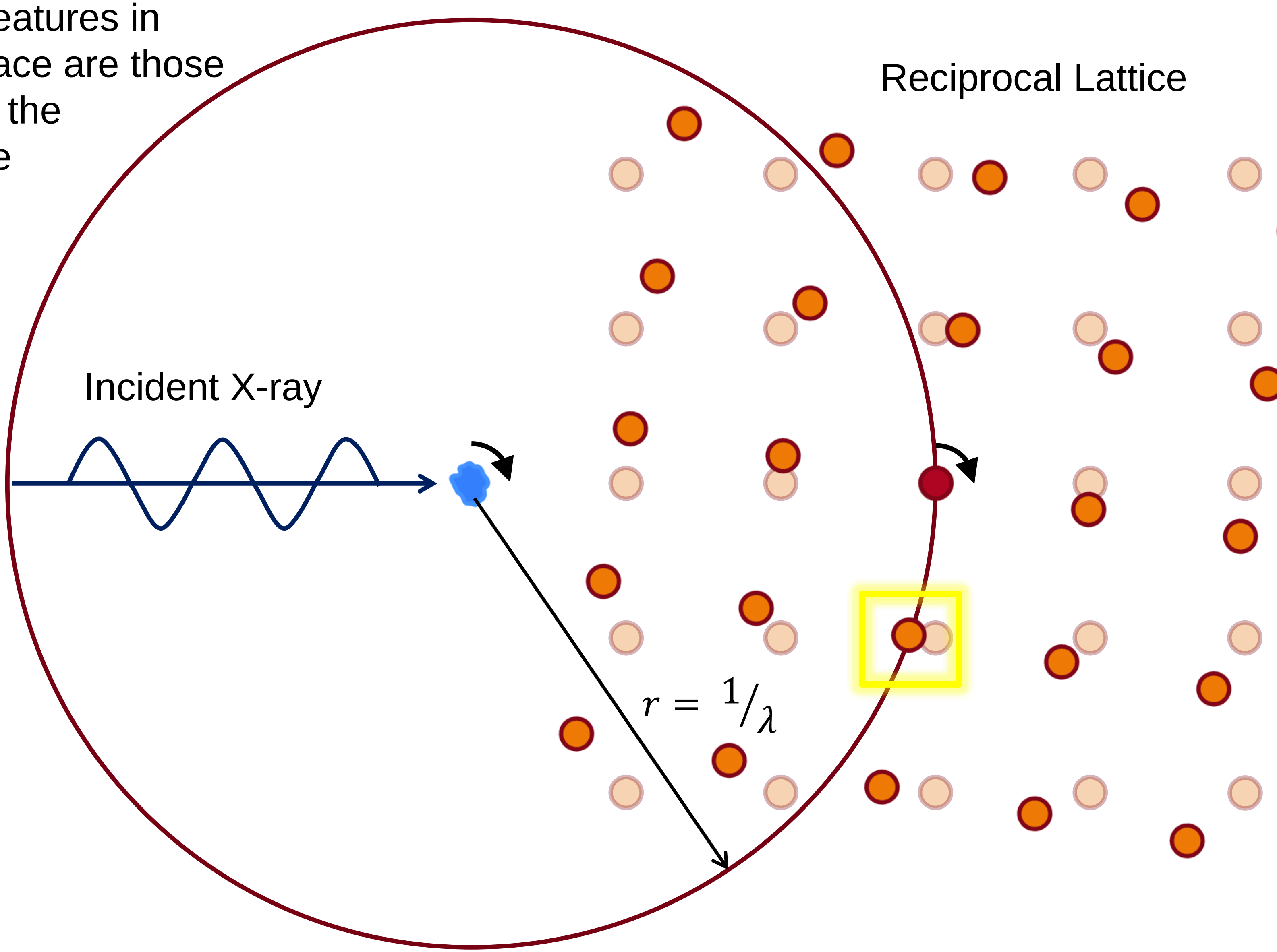

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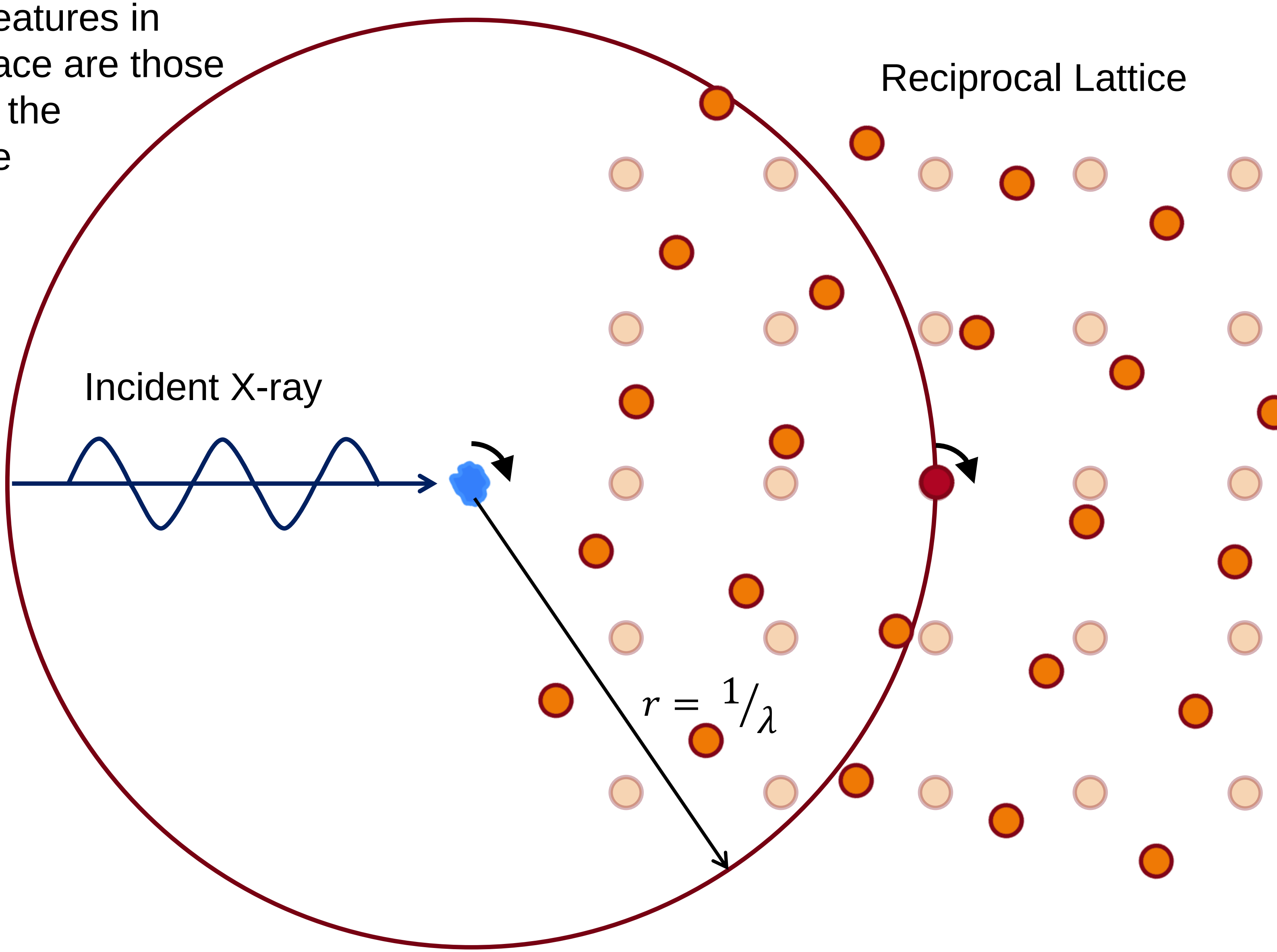

Ewald Construction

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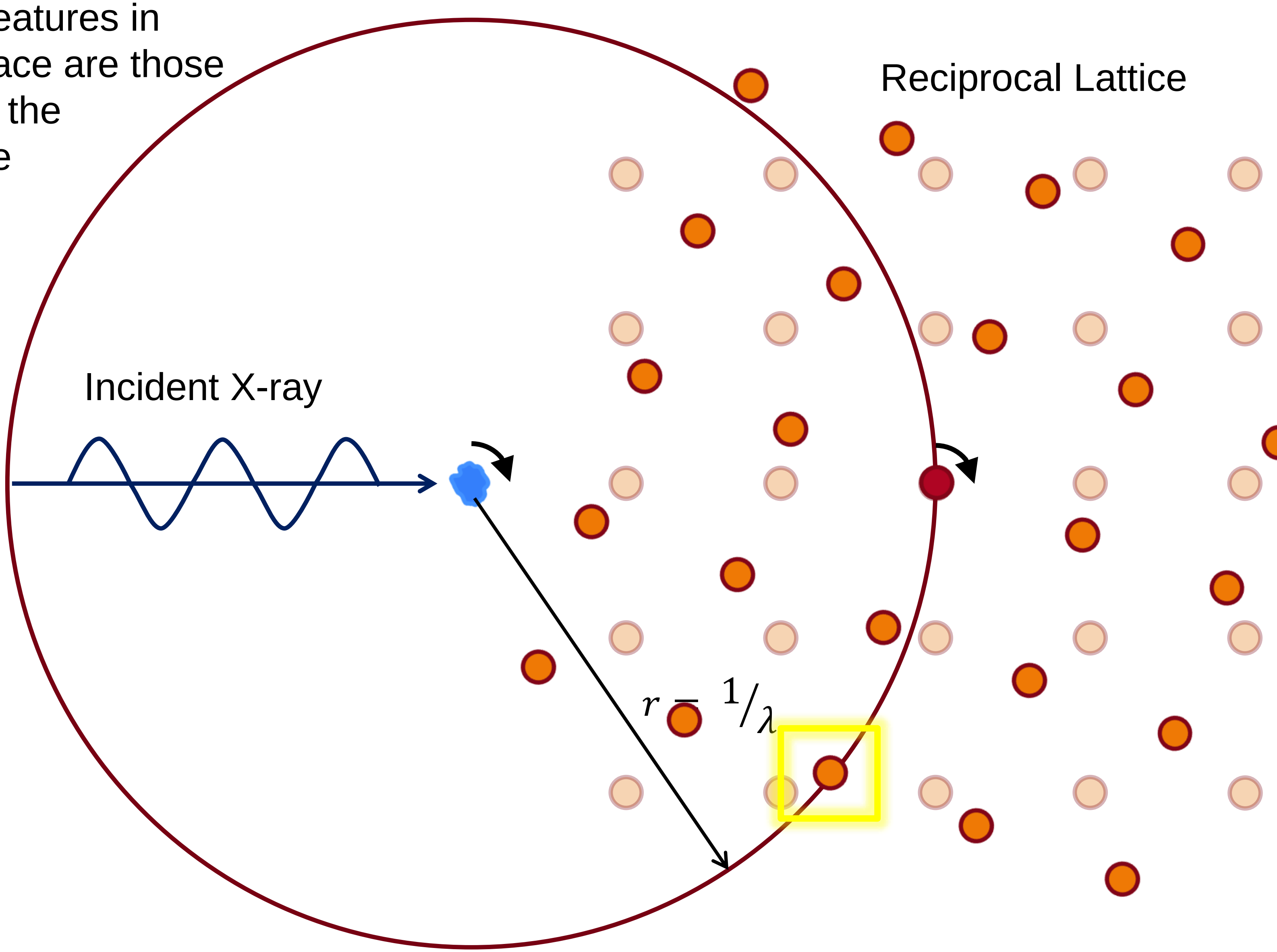
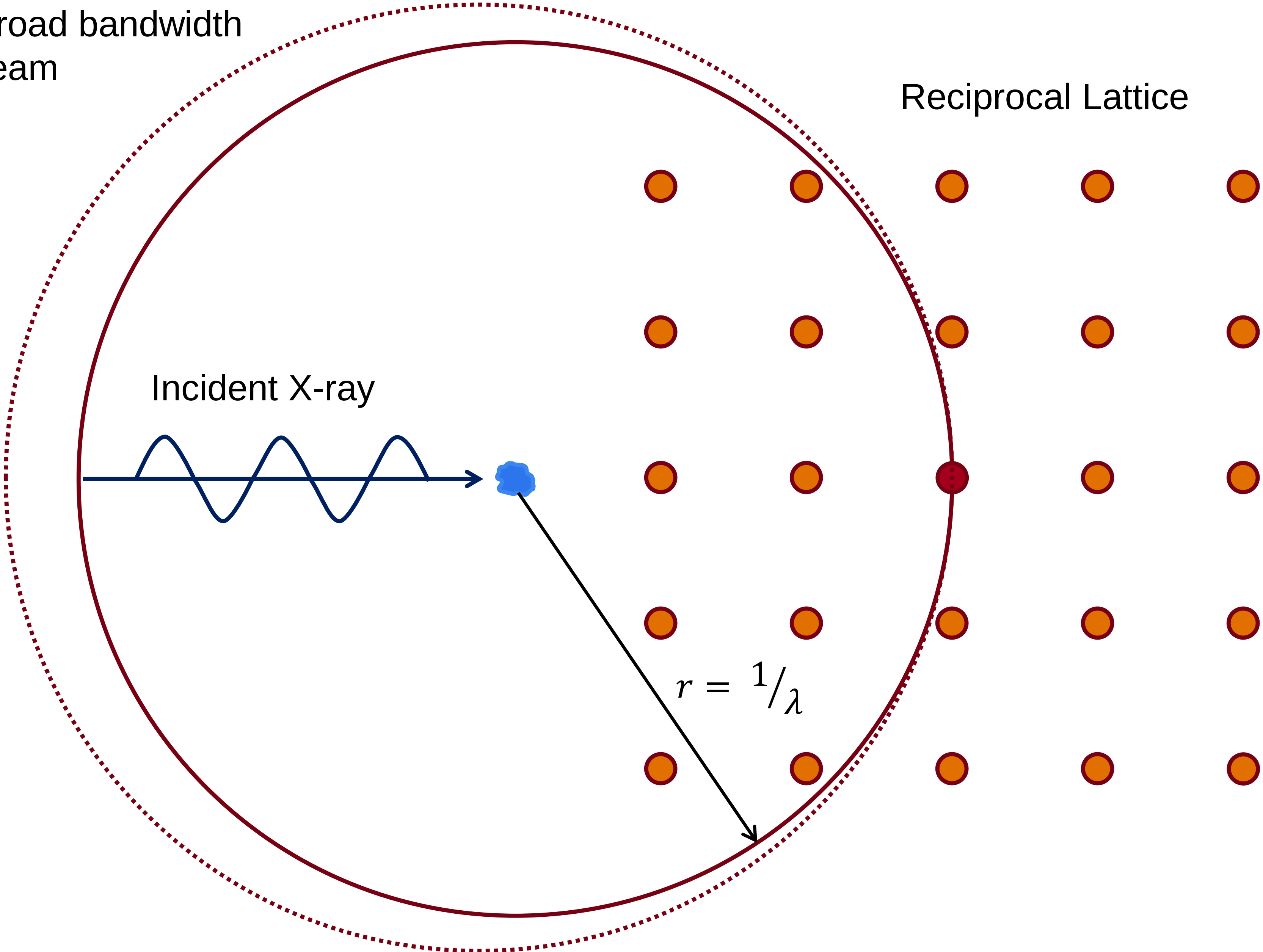
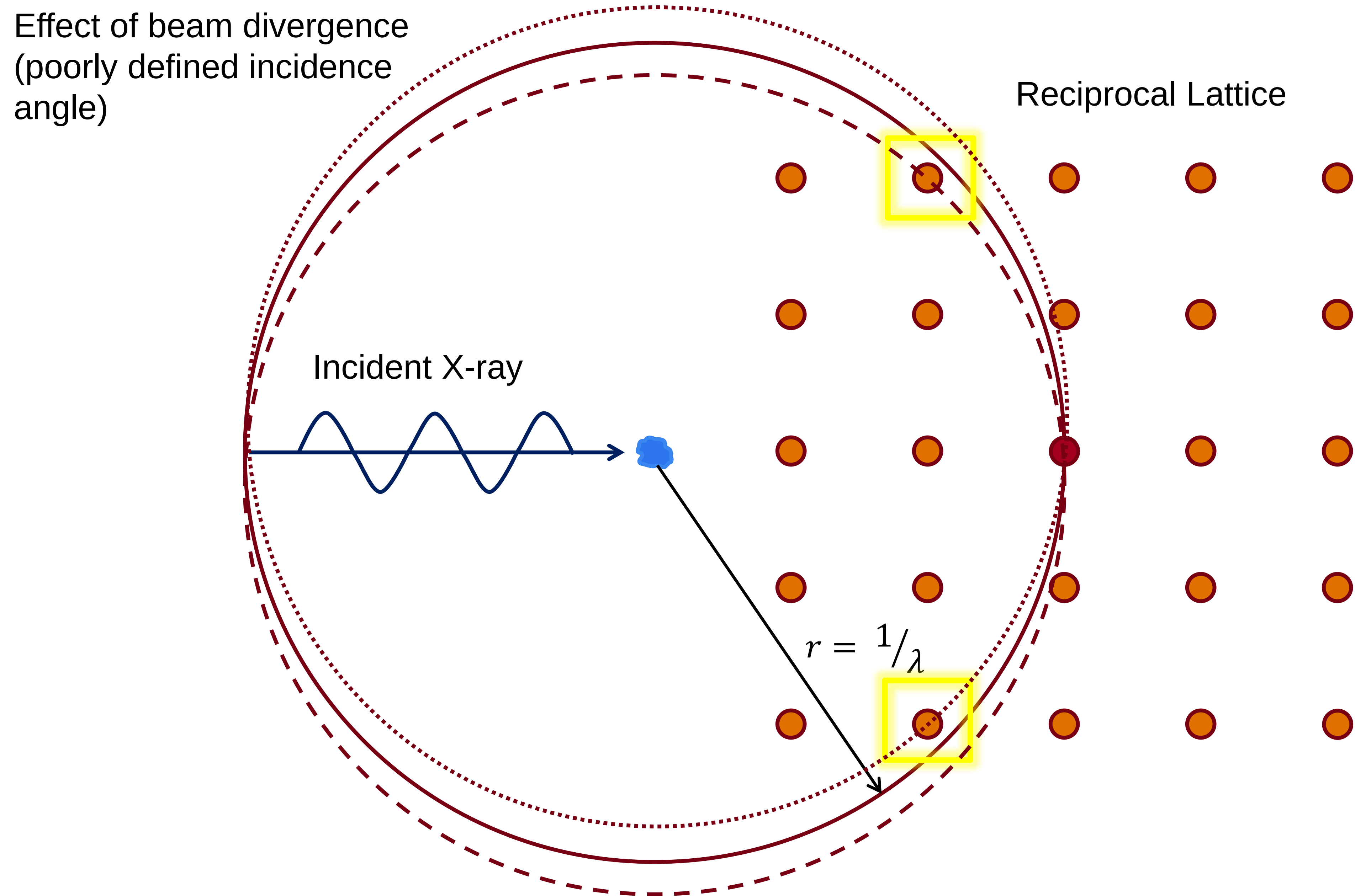


Ewald Construction

Effect of broad bandwidth incident beam



Ewald Construction



Summary

- Reciprocal space is a convenient way to think of scattering
- Miller Indices (h,k,l) allow us to orient ourselves and identify features in reciprocal space from crystalline (ordered) materials
- Ewald Sphere geometric construct for identifying which reciprocal space features are observable

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

$$Q = \frac{2\pi}{d} \qquad d = \frac{2\pi}{Q}$$