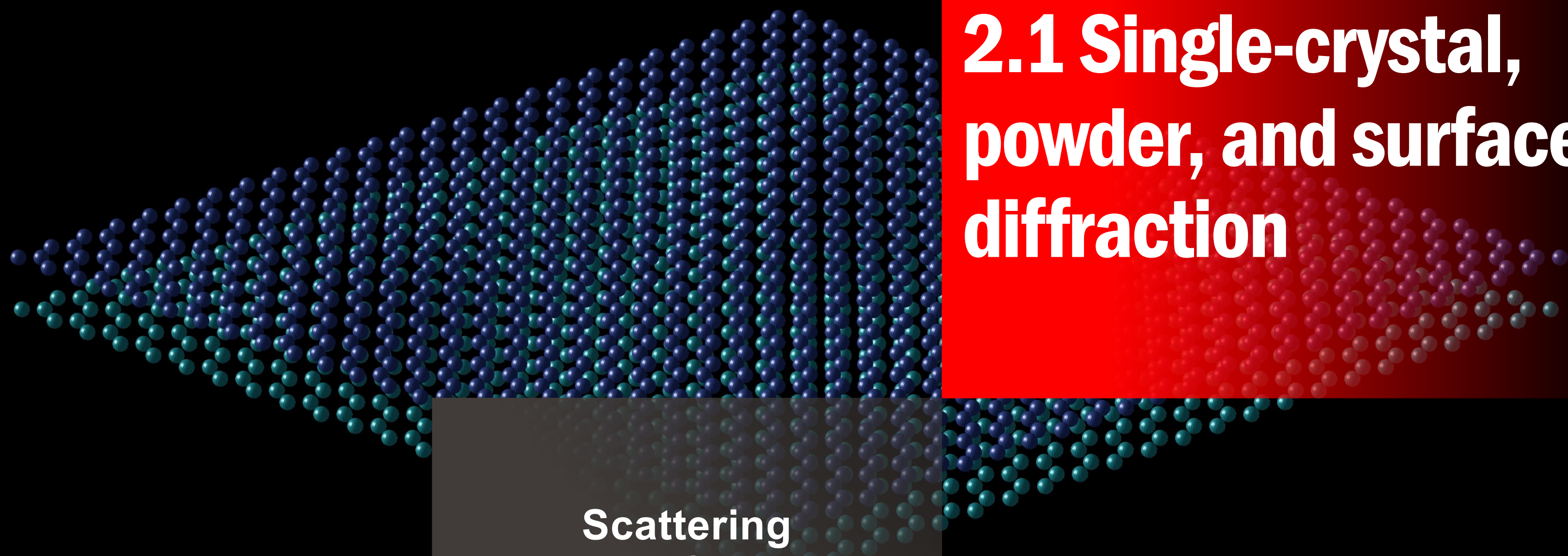
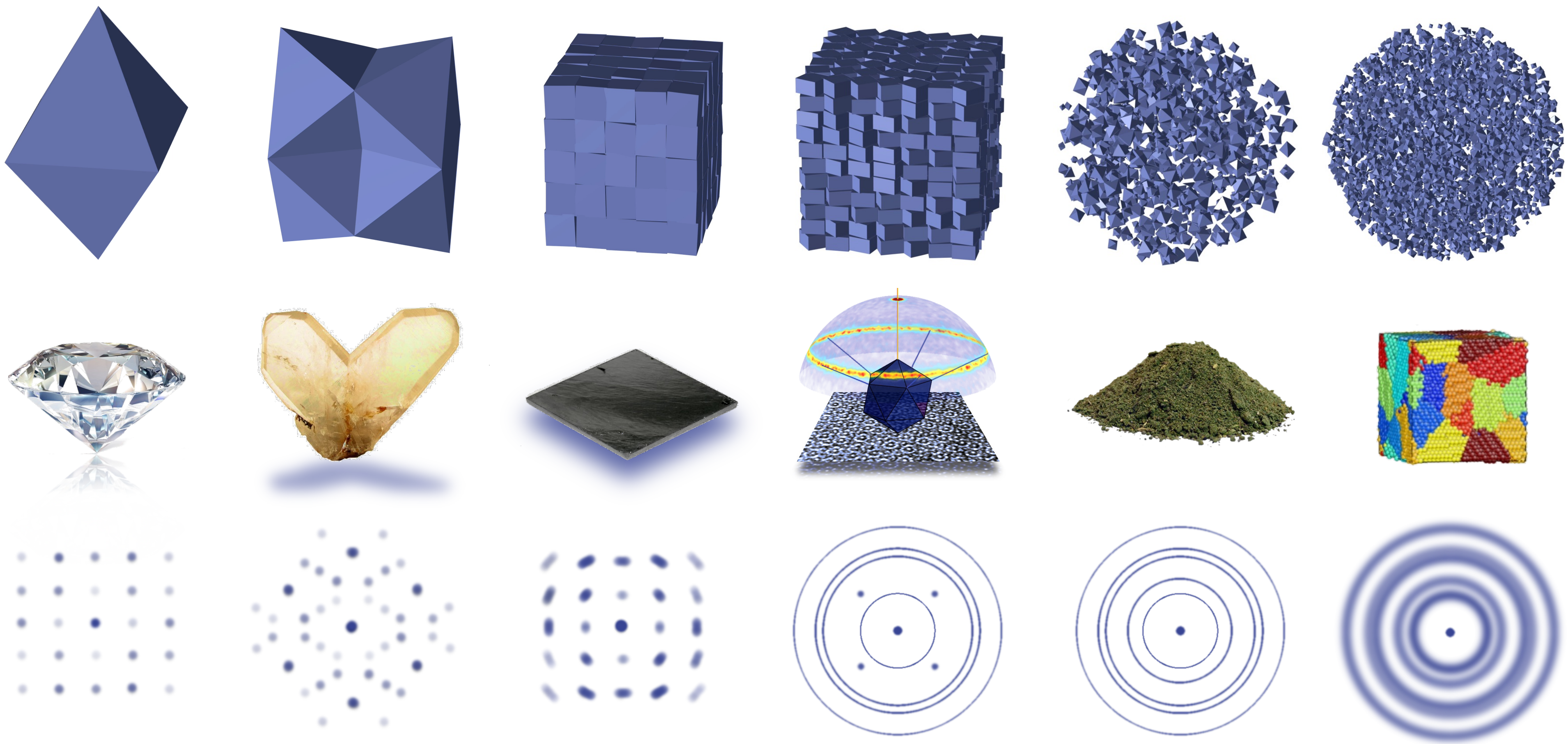
2.1 Single-crystal, powder, and surface diffraction



Scattering
Block Course
12.-13.02.2024

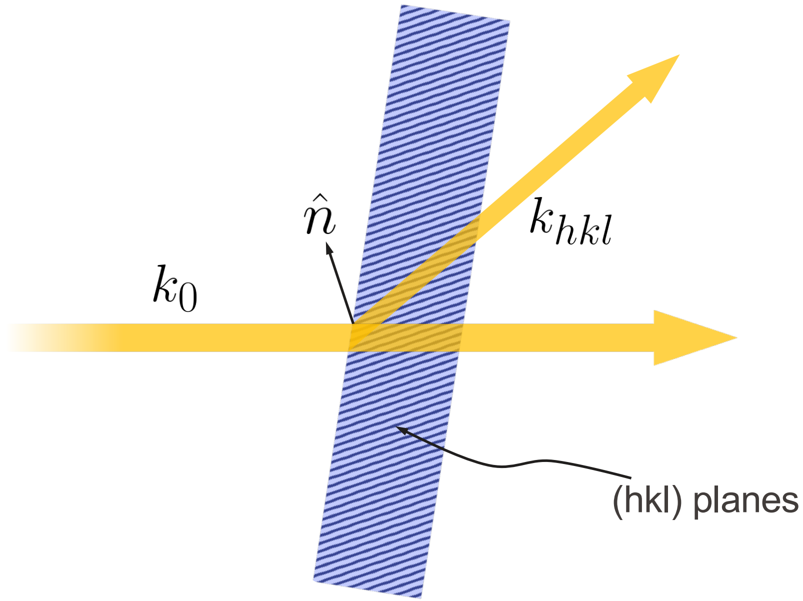
Prof. Philip Willmott

Types of crystalline samples

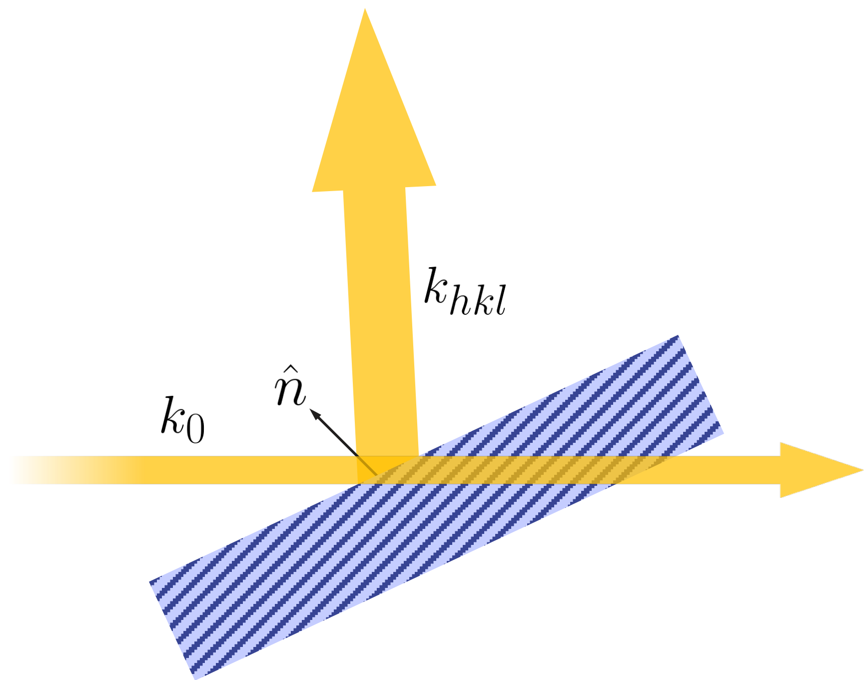


Images: Creative Commons

Laue and Bragg diffraction geometries



Laue (transmission) geometry



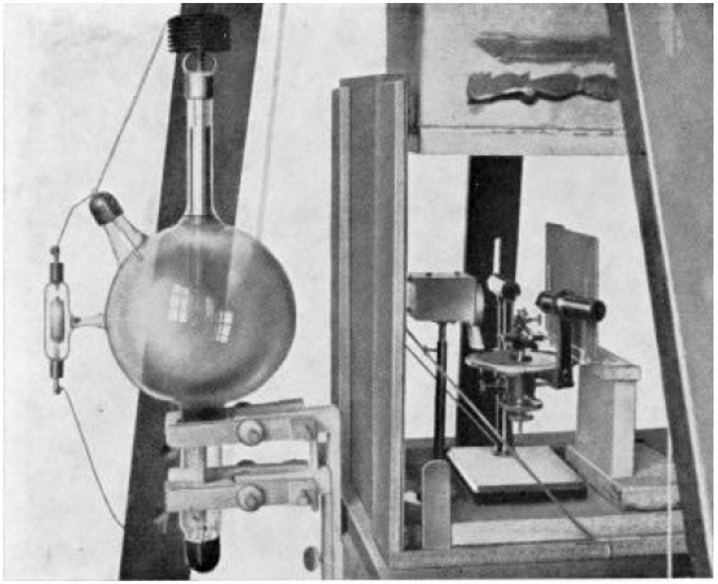
Bragg (reflection) geometry

(Bragg-Brentano geometry: $\hat{n}$ perpendicular to sample surface)

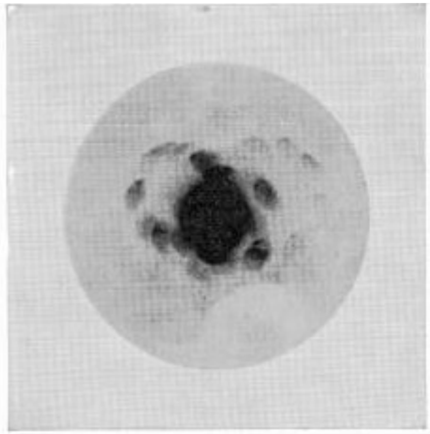
Single-crystal diffraction – the Laue method

Laue diffraction

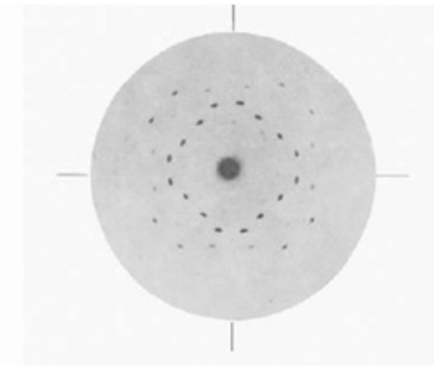
Max von Laue



Friedrich and Knipping's setup



copper sulfate pentahydrate

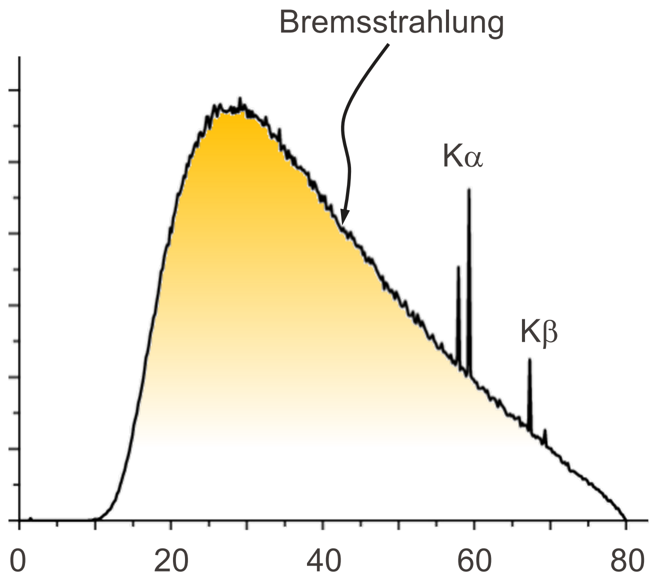


zinc sulfide

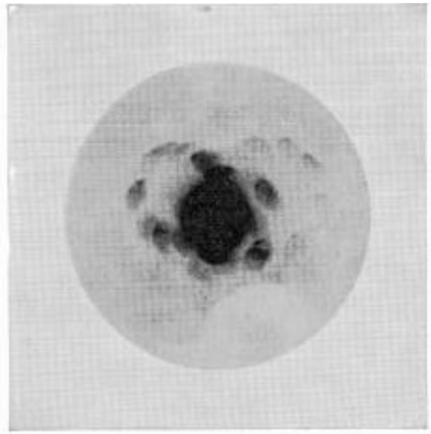
See also: https://www.iucr.org/__data/assets/pdf_file/0010/721/chap4.pdf
and https://onlinelibrary.wiley.com/doi/epdf/10.1002/andp.19133461004

Laue diffraction

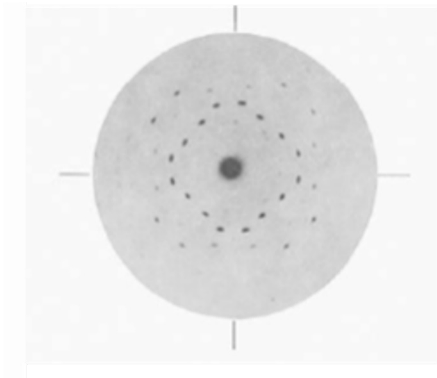
Max von Laue



Tungsten x-ray spectrum



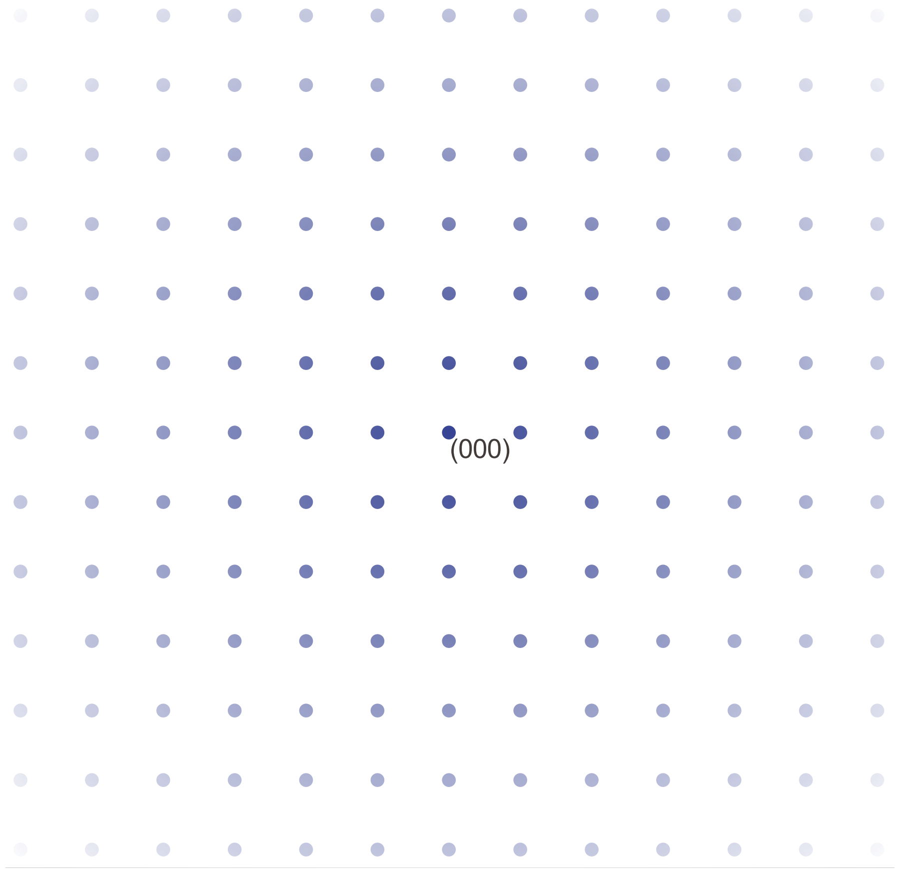
copper sulfate pentahydrate



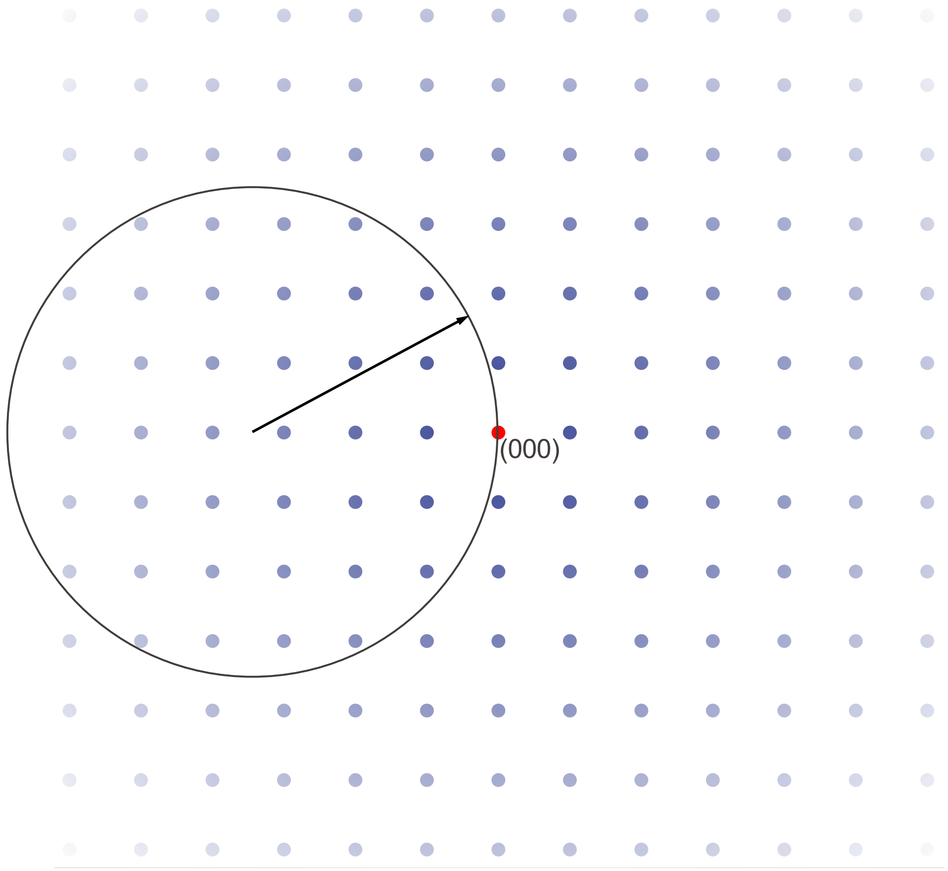
zinc sulfide

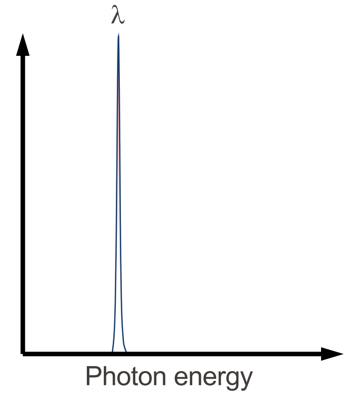
See also: https://www.iucr.org/__data/assets/pdf_file/0010/721/chap4.pdf
and https://onlinelibrary.wiley.com/doi/epdf/10.1002/andp.19133461004

Laue diffraction

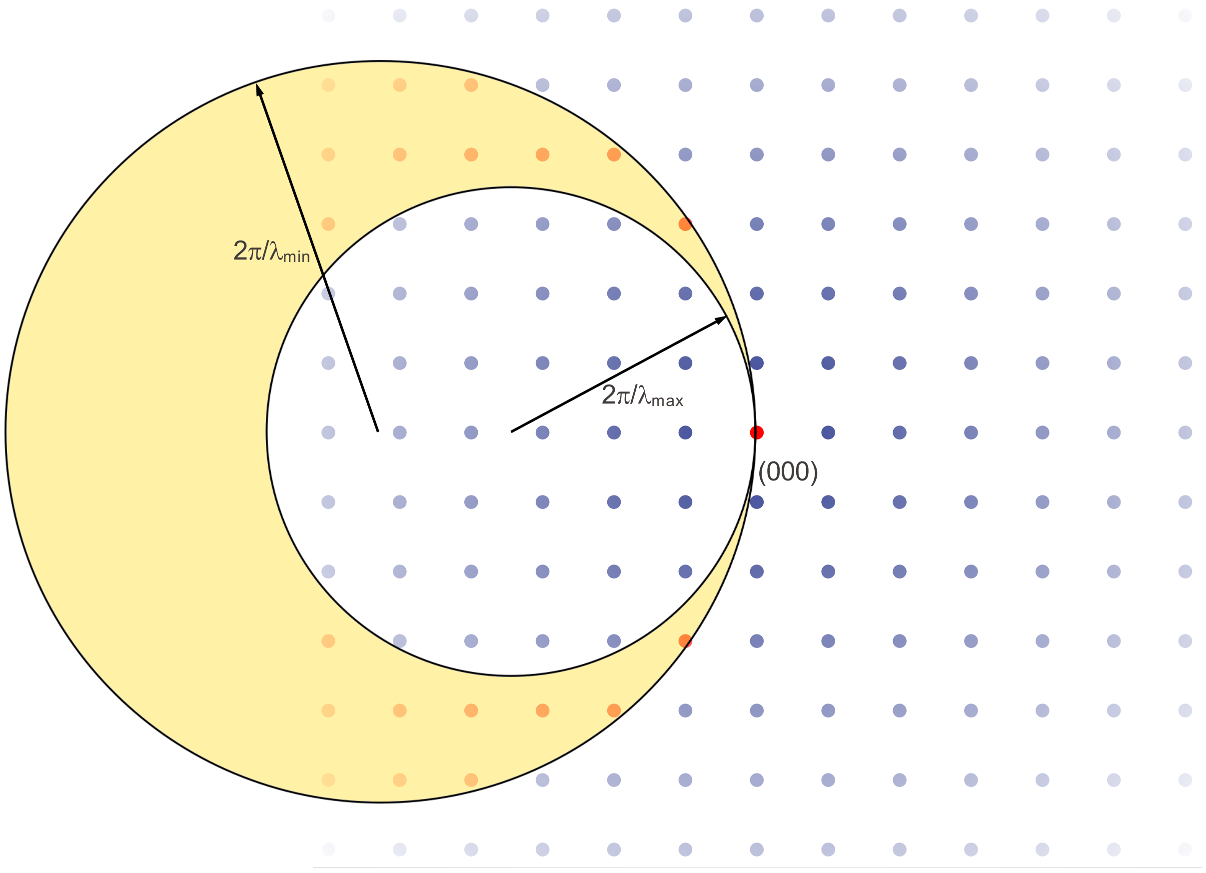


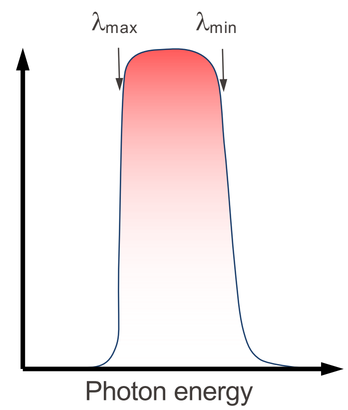
Laue diffraction



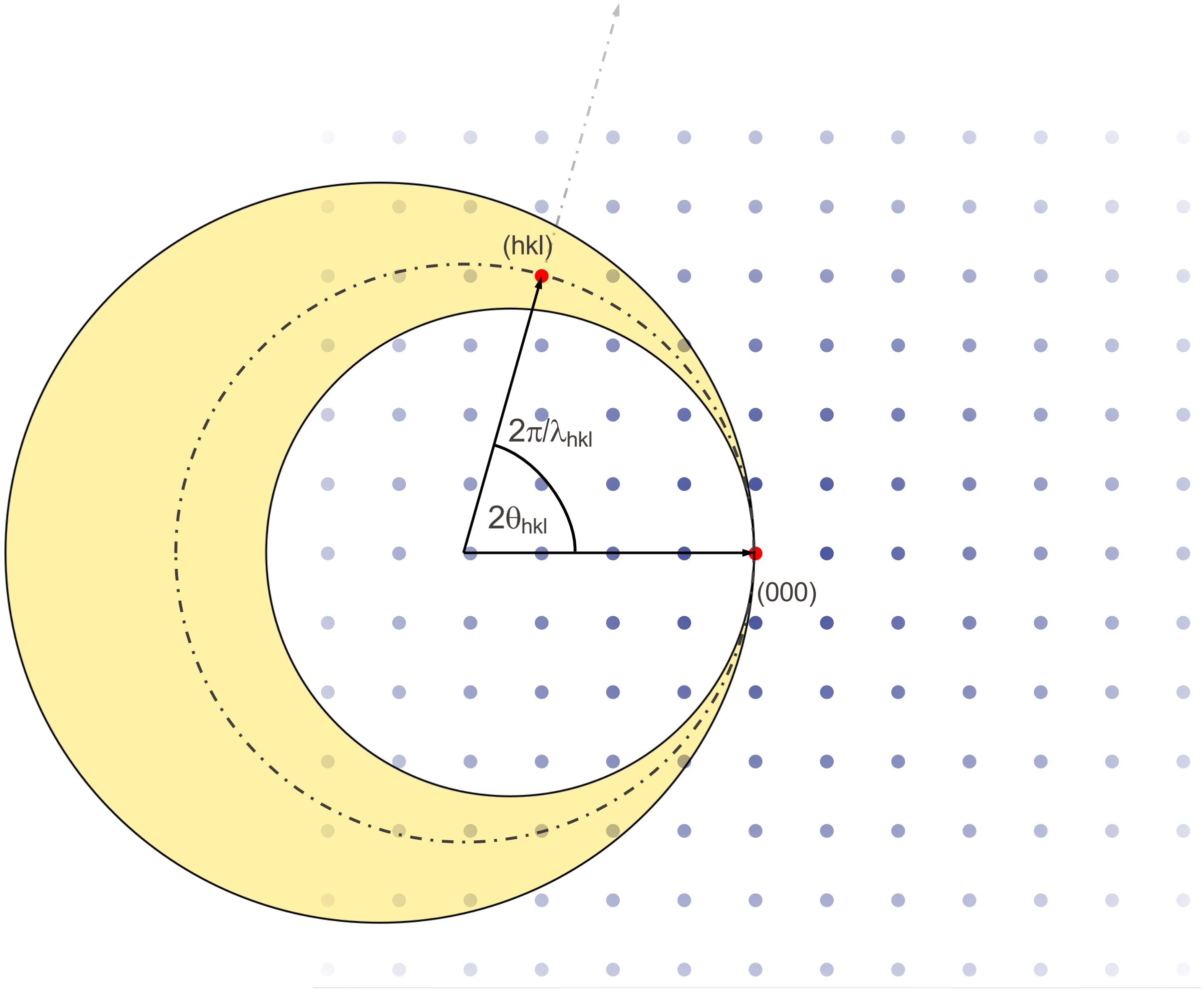


Laue diffraction



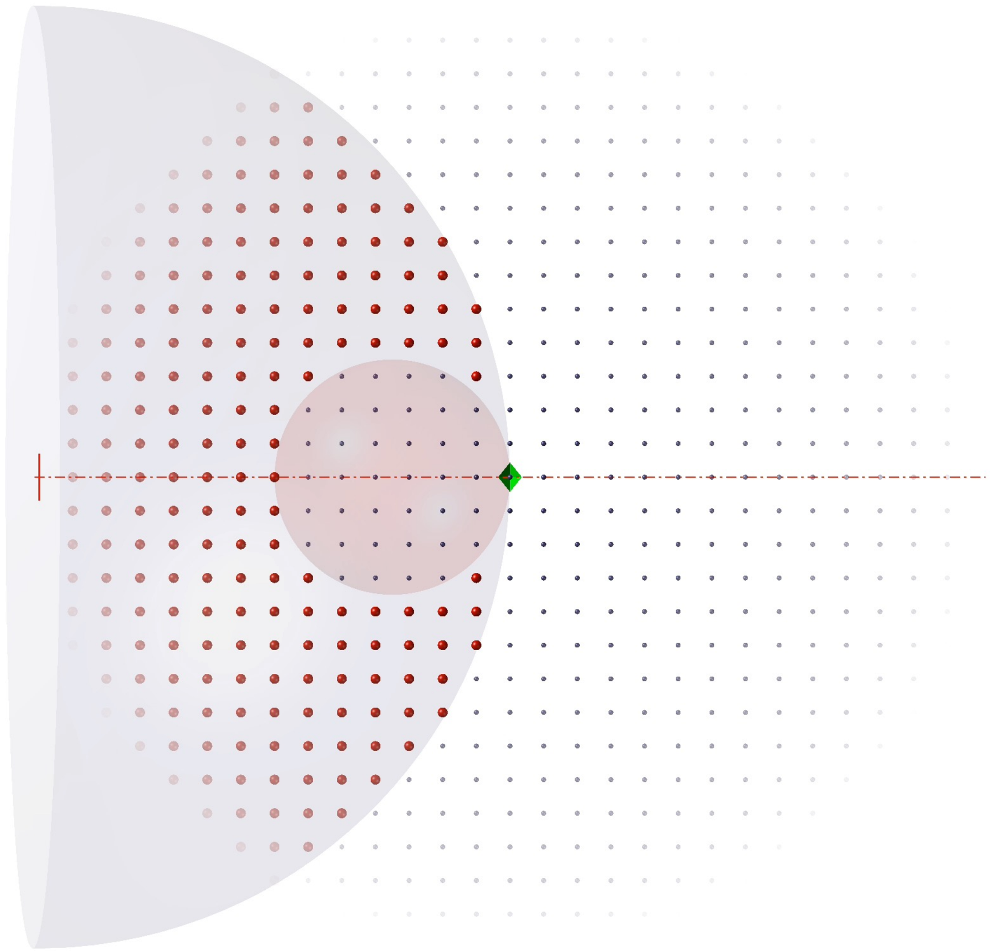


Laue diffraction

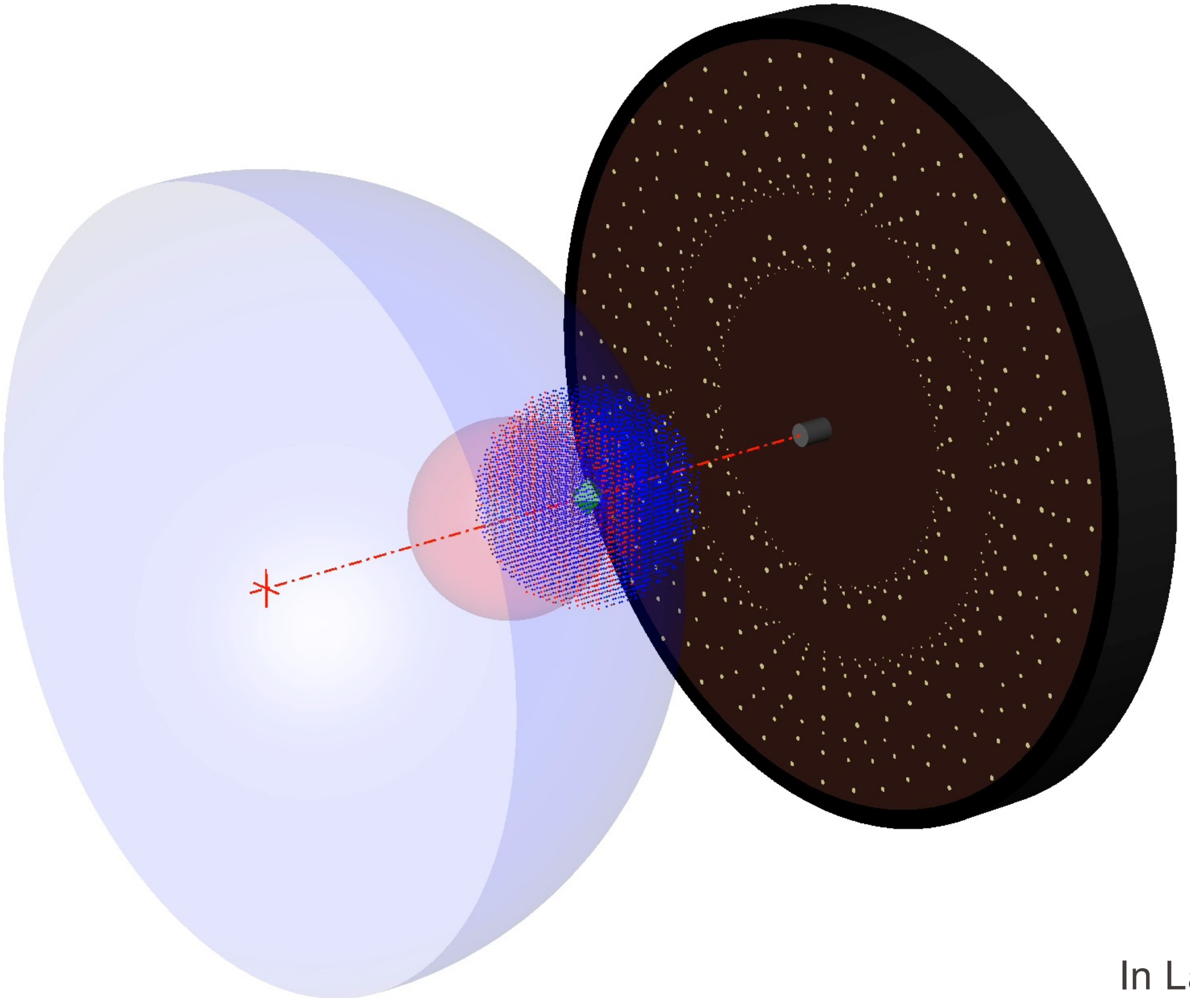


$$\lambda_{hkl} = 2d_{hkl}\sin\theta_{hkl}$$

Laue diffraction



Laue diffraction in 3D

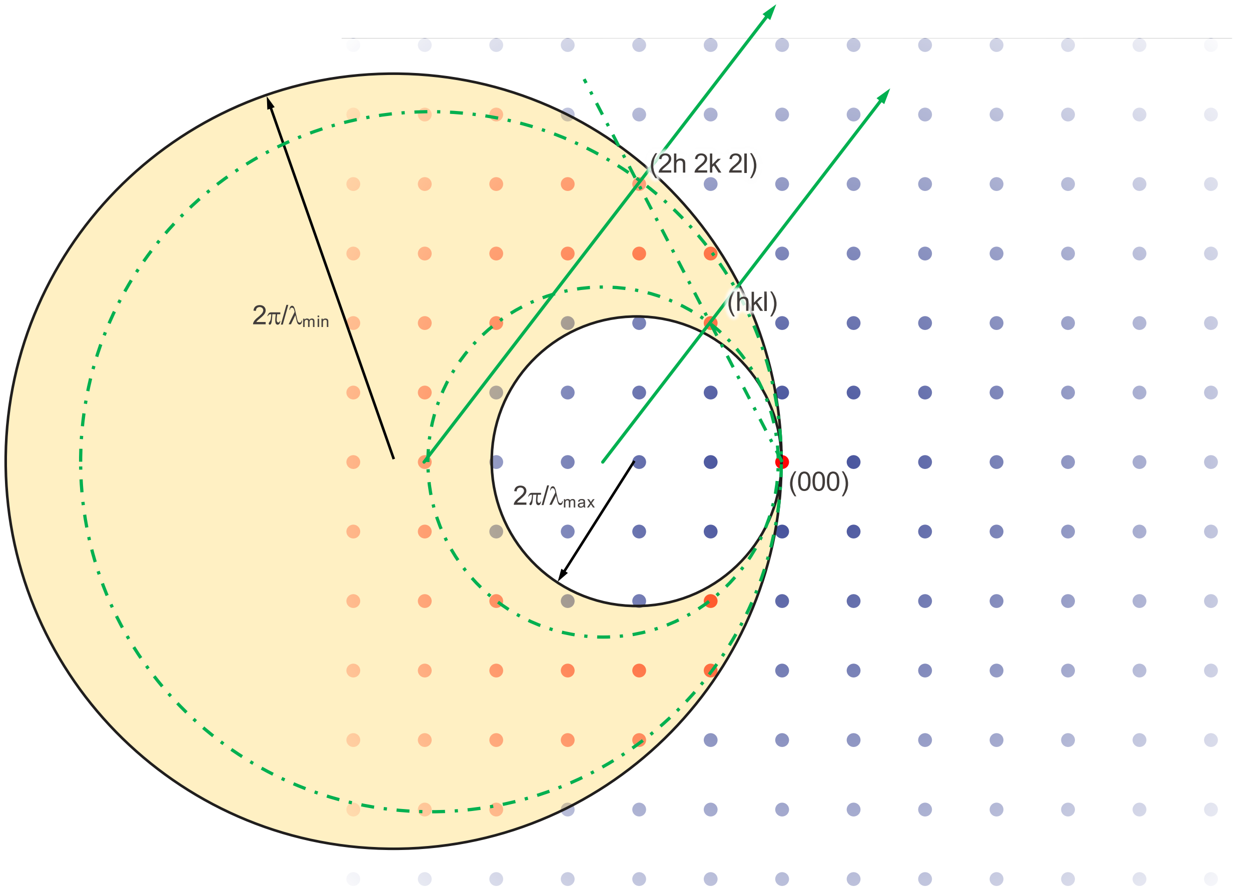


$$n_{\mathrm{Laue}} = \frac{\frac{4}{3}\pi\left(k_{\mathrm{max}}^3 - k_{\mathrm{min}}^3\right)}{8\pi^3/V}$$

$$= \frac{4\pi V}{3}\left(\frac{\lambda_{\mathrm{max}}^3 - \lambda_{\mathrm{min}}^3}{(\lambda_{\mathrm{max}}\lambda_{\mathrm{min}})^3}\right)$$

In Laue (forward-scattering) geometry

Laue diffraction and the overlap problem

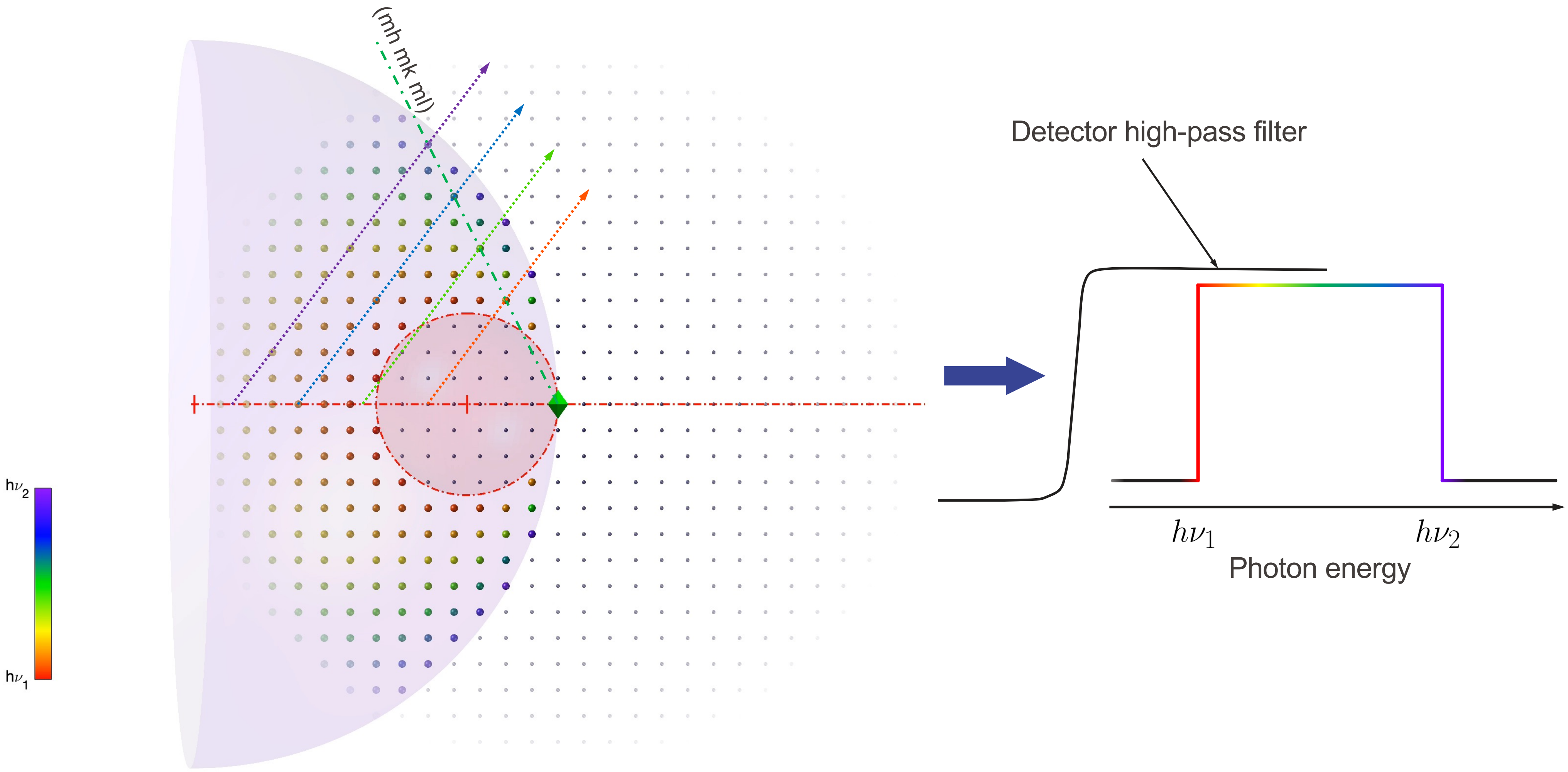


$$\lambda_{hkl} = 2d_{hkl}\sin\theta_{hkl}$$

Families (mh mk ml) for integral m that lie within the Ewald volume will precisely overlap on a detector

How does one extract their individual Bragg-peak intensities?

Laue diffraction and modern detectors



Applications of Laue diffraction

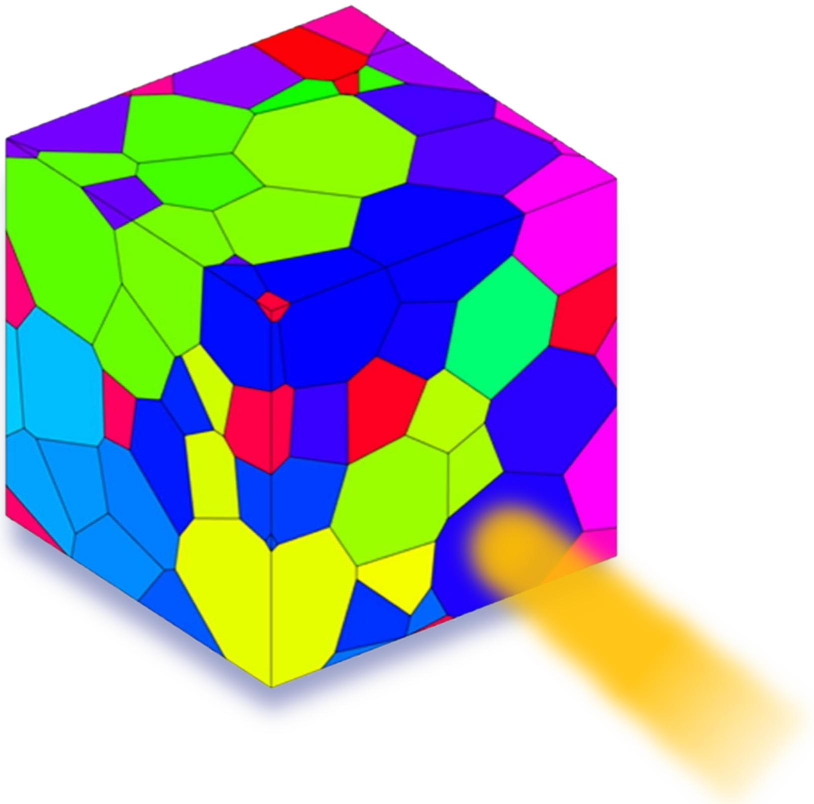
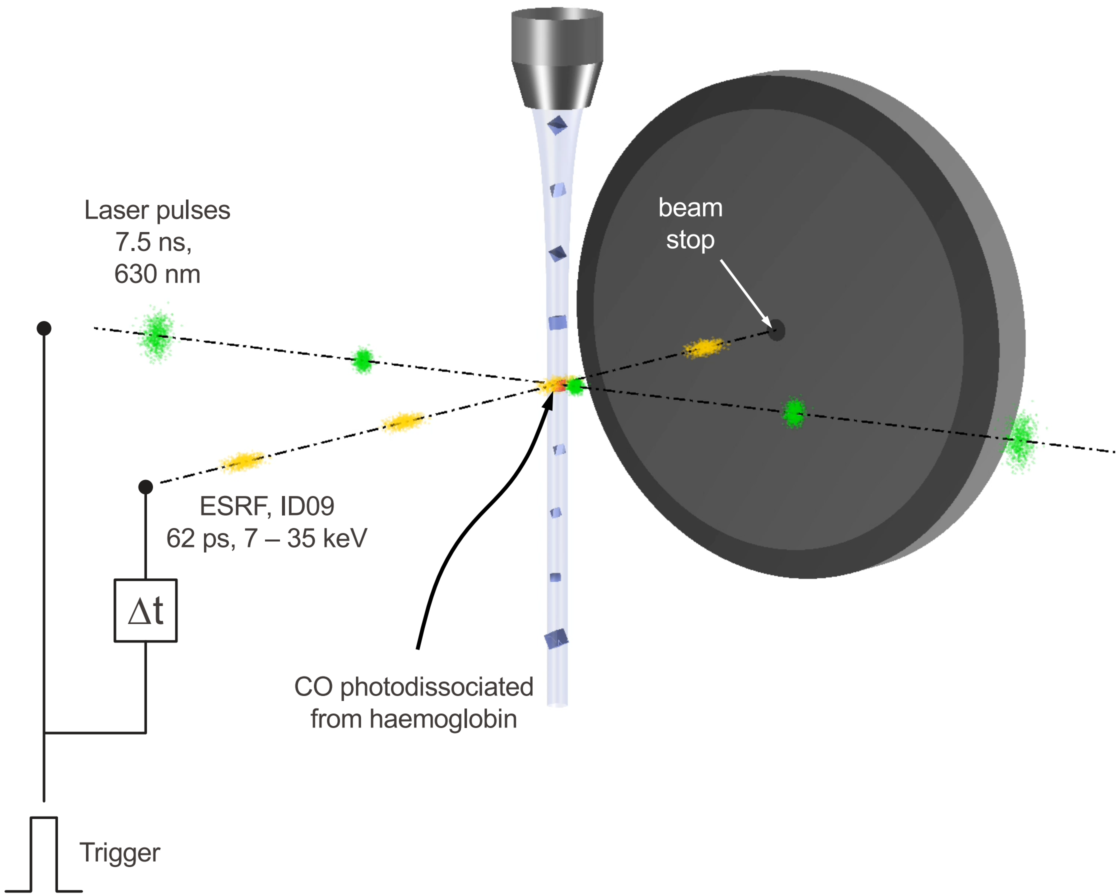


Image courtesy of S. Falco *et al.*,
Comp. Mat. Sci. **136** 20-28 (2017)

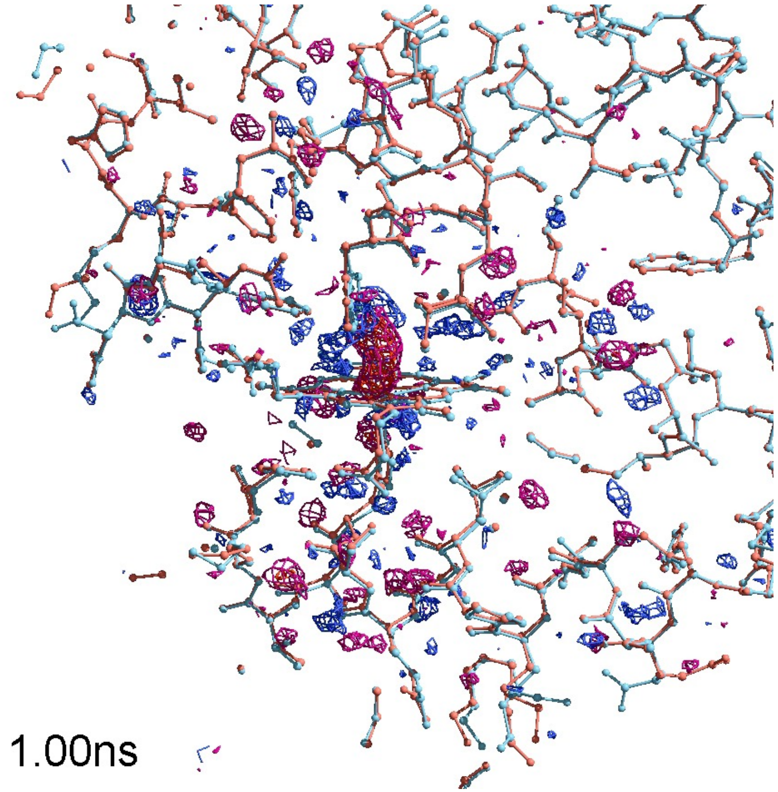
- Laue diffraction traditionally for single crystals, unsuitable for powder samples
  - Many randomly oriented crystallites simultaneously illuminated ⇒ extremely dense ring pattern: unsolvable
- DLSRs: focus can be made to be smaller than crystallites (limit ~ 100 nm)
  - Scan and rotate sample ⇒ diffraction tomogram "µLaue diffraction tomography", e.g. @ BM32 beamline, ESRF

https://www.esrf.fr/UsersAndScience/Experiments/CRG/BM32/Microdiffraction
http://scripts.iucr.org/cgi-bin/paper?S1600576715002447

Applications of Laue diffraction



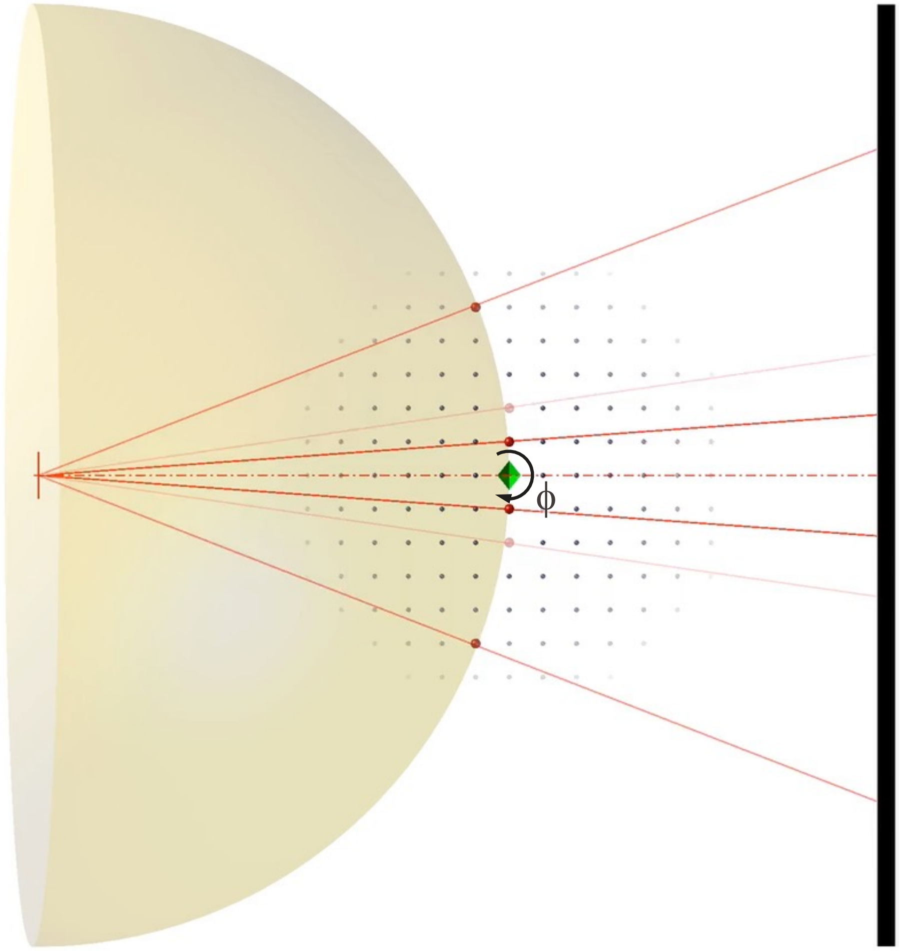
Time-Resolved Photolysis of CO-Haemoglobin
V. Šrajer *et al*., Biochemistry **40** 13802 (2001)



Courtesy American Chemical Society

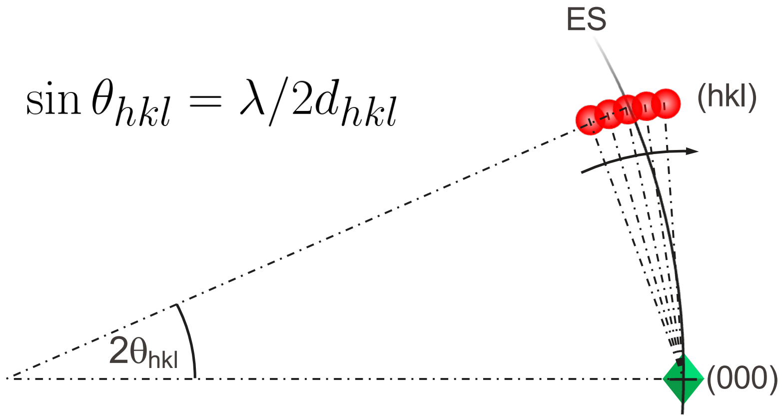
Single-crystal diffraction – the rotation method

The rotation method



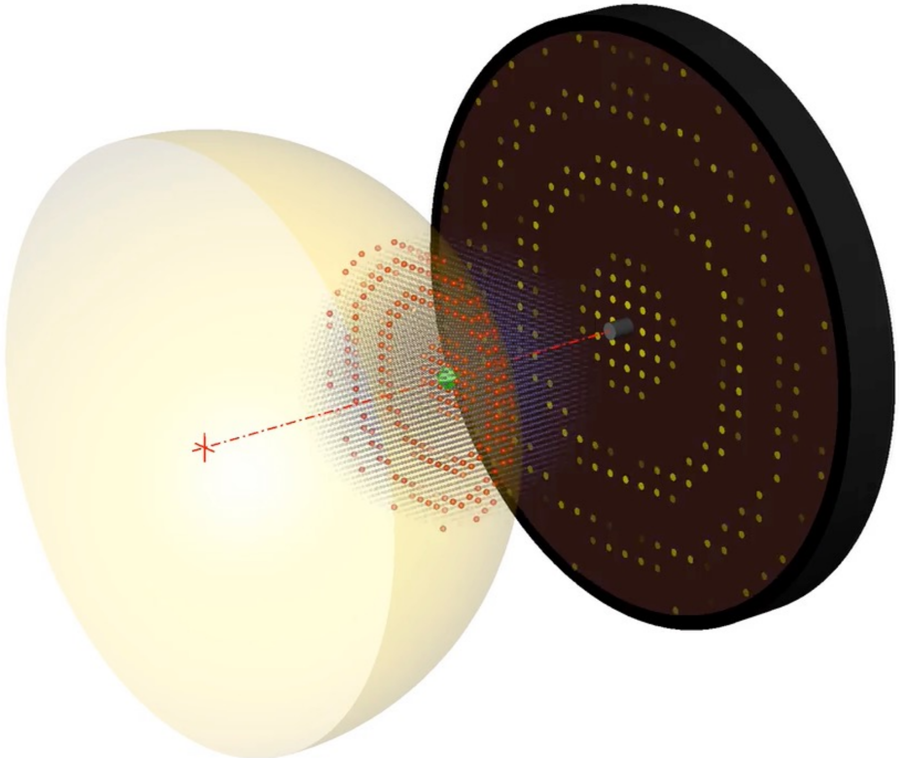
- Monochromatic radiation
- Rotate sample
  - Signal lights up as Bragg peaks pass through the Ewald sphere
  - Signal at angle 2θ relative to direct beam (000)
  - Record at high frame rates ("fine phi-slicing") to capture passage of Bragg peak through Ewald sphere ⇒ obtain Bragg-peak profile

$$\sin \theta_{hkl} = \lambda / 2d_{hkl}$$



M. Müller *et al.*, https://doi.org/10.1107/S0907444911049833

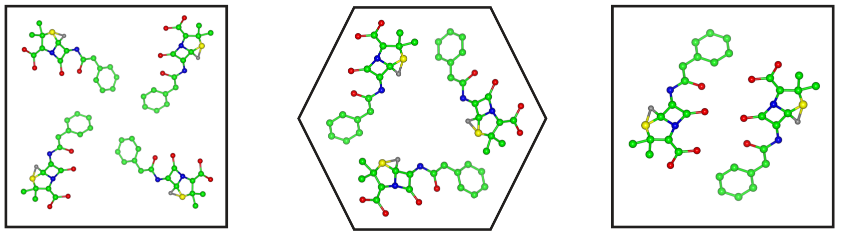
The rotation method

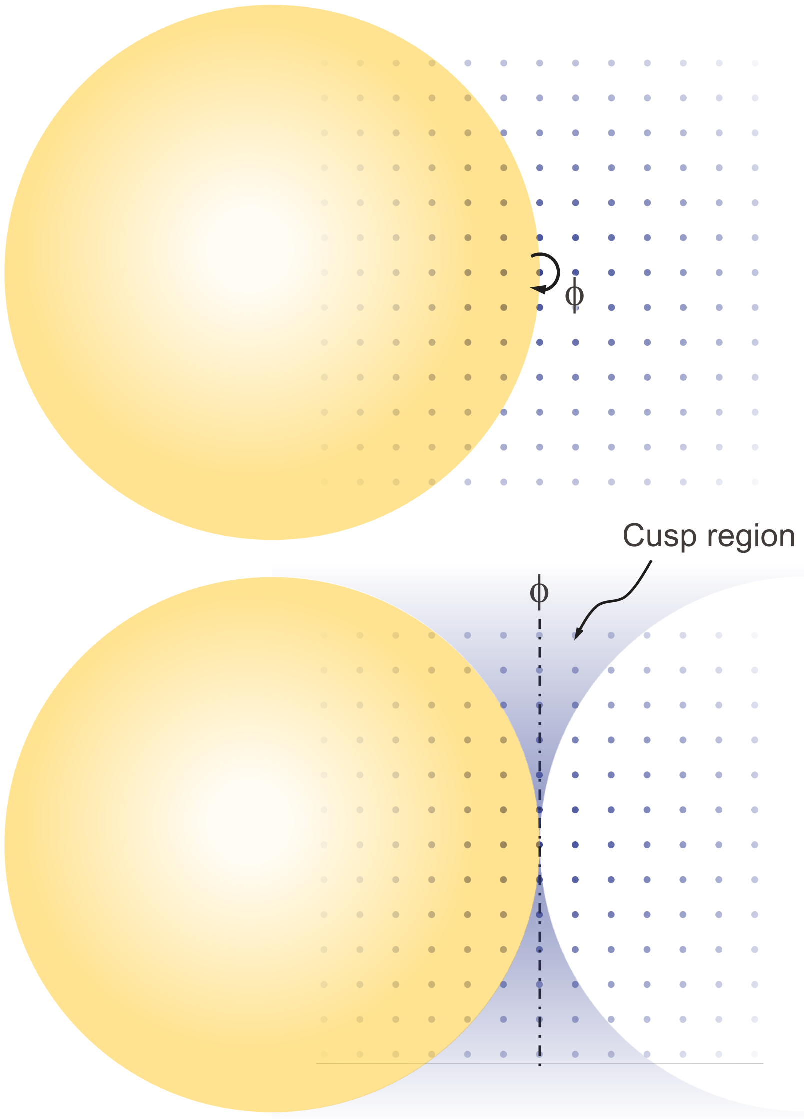


The rotation method

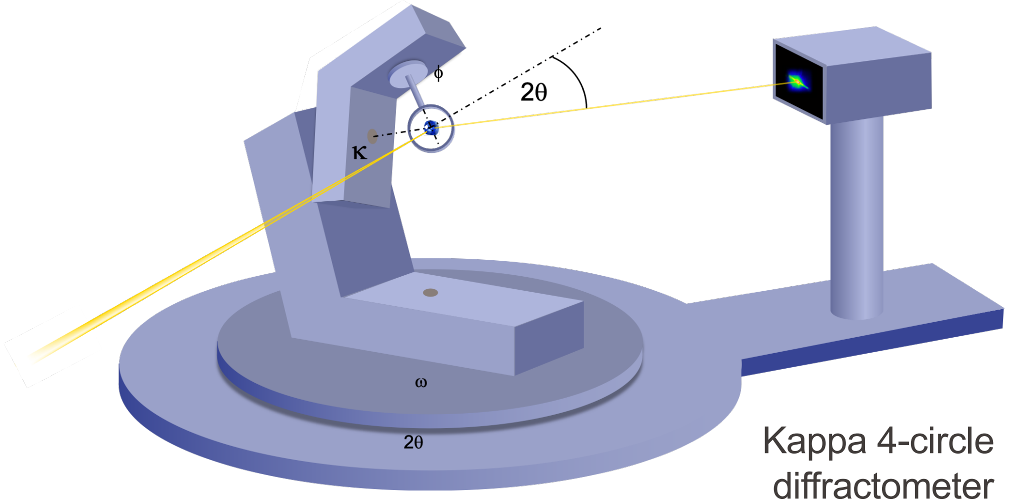
- Rotate around ϕ
- Data close to ϕ-axis (“cusp”, or “blind” region) not recorded
- Rotate ϕ (normally through 90º) to capture this missing data

- High-symmetry unit cells require reduced range of ϕ-rotation (90º, 120º, 180º)

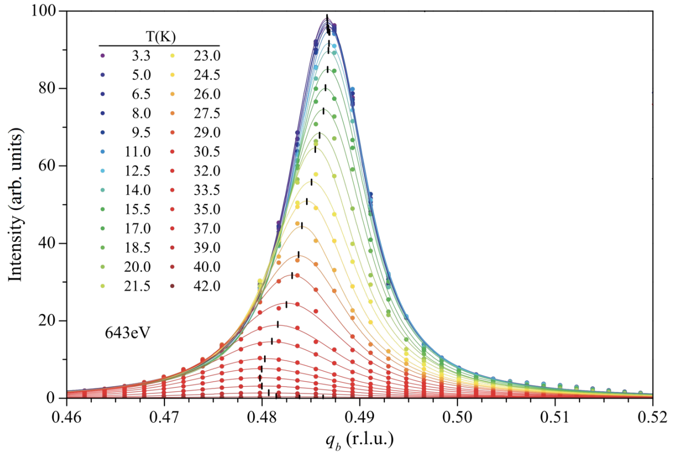




The selected Bragg peak method



Kappa 4-circle diffractometer

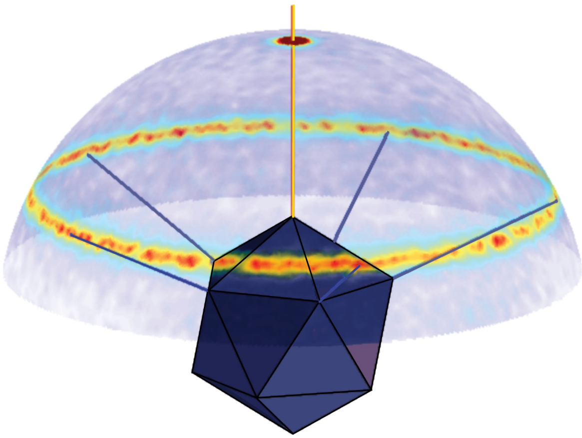


Magnetic order in multiferroic $LuMnO_3$ produces a weak Bragg peak close to (0 ½ 0), enhanced using 643-eV radiation tuned to the L-edge of Mn

Y.W. Windsor *et al.*, Phys. Rev. Lett. **113** 167202 (2014)

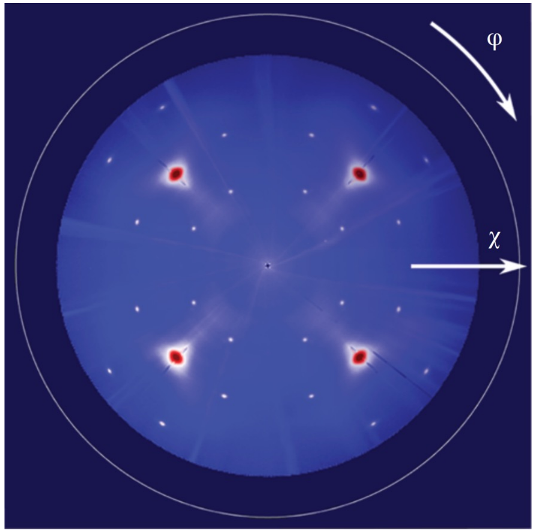
- Follow specific Bragg points
  - Observe physical phenomena through structural changes
  - e.g., change in symmetry and/or unit cell dimensions with…
    - temperature
    - pressure
    - applied magnetic field
    - …
- Signal often weak
- SR needed
- Used in
  - resonant soft x-ray scattering
  - surface x-ray diffraction

Pole figures



Pole figure of an icosahedral Ti-Ni-Zr quasicrystal film grown on Al_2O_3(0001) mapped on a spherical surface. A fivefold symmetry axis points perpendicularly out of the film, while the five other fivefold axes at 63.435" relative to each other and the out-of-plane axis, produce the ring feature. This texturing is induced by the 5-fold planes having the lowest surface energy

P.R. Willmott *et al.*,
Phys. Rev. B
71 094203 (2005)



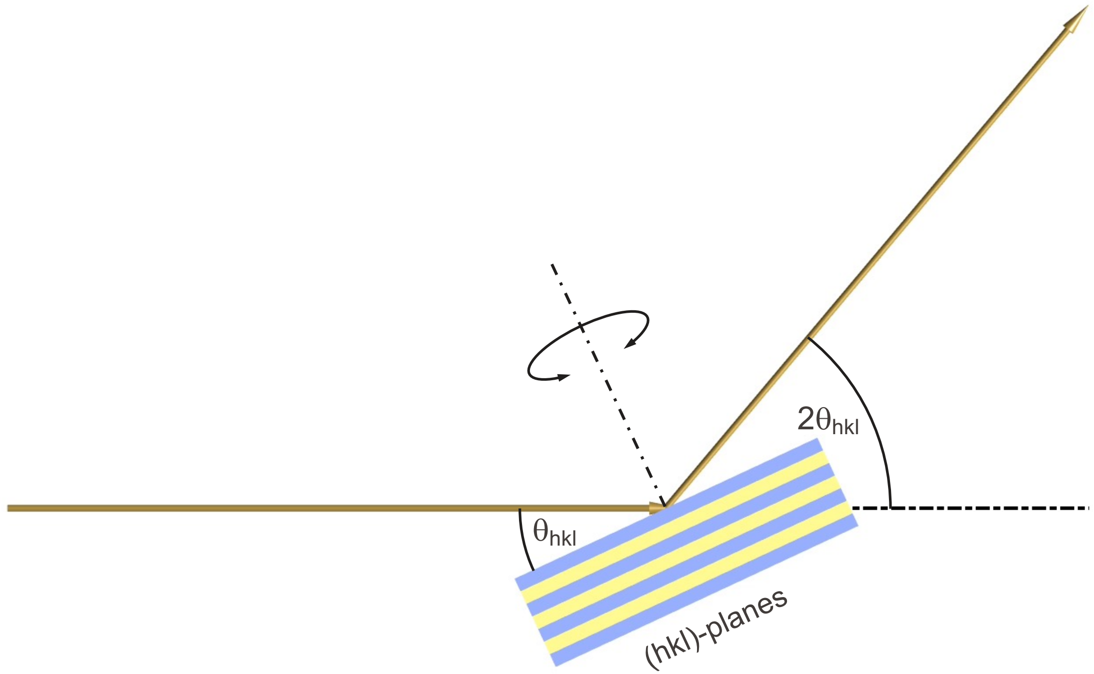
Pole figure acquired over a range of Q = 2.25 to 2.35 $Å^{-1}$ and at a photon energy of 16.49 keV of heteroepitaxial β-Fe_2O_3 thin film. The pattern encompasses three families of reflections associated with the film.

J.D. Emery *et al.*,
ACS Appl. Mater. Interf. **6**, 21894–21900 (2014)

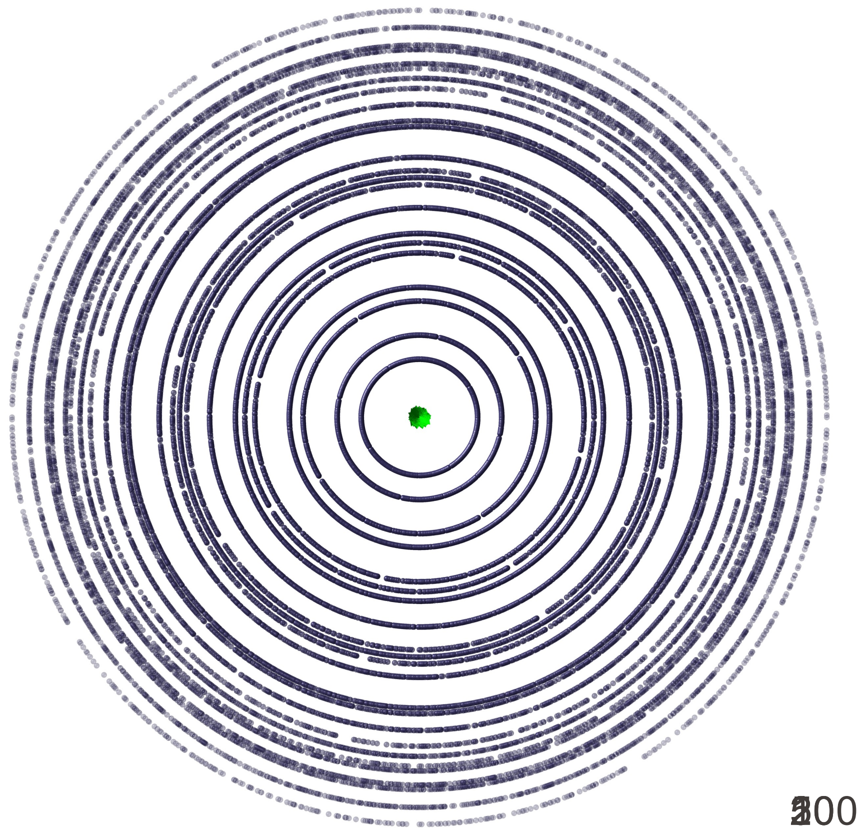
- Fix θ-2θ
- Rotate sample
  - azimuthally (ϕ) by up to 2π
  - polar coordinate (χ) up to π
- Modern detectors can record range of 2θ
  - Vary θ and obtain multiple pole figures in one image
- Suitable for single-crystal and some textured samples

Powder diffraction

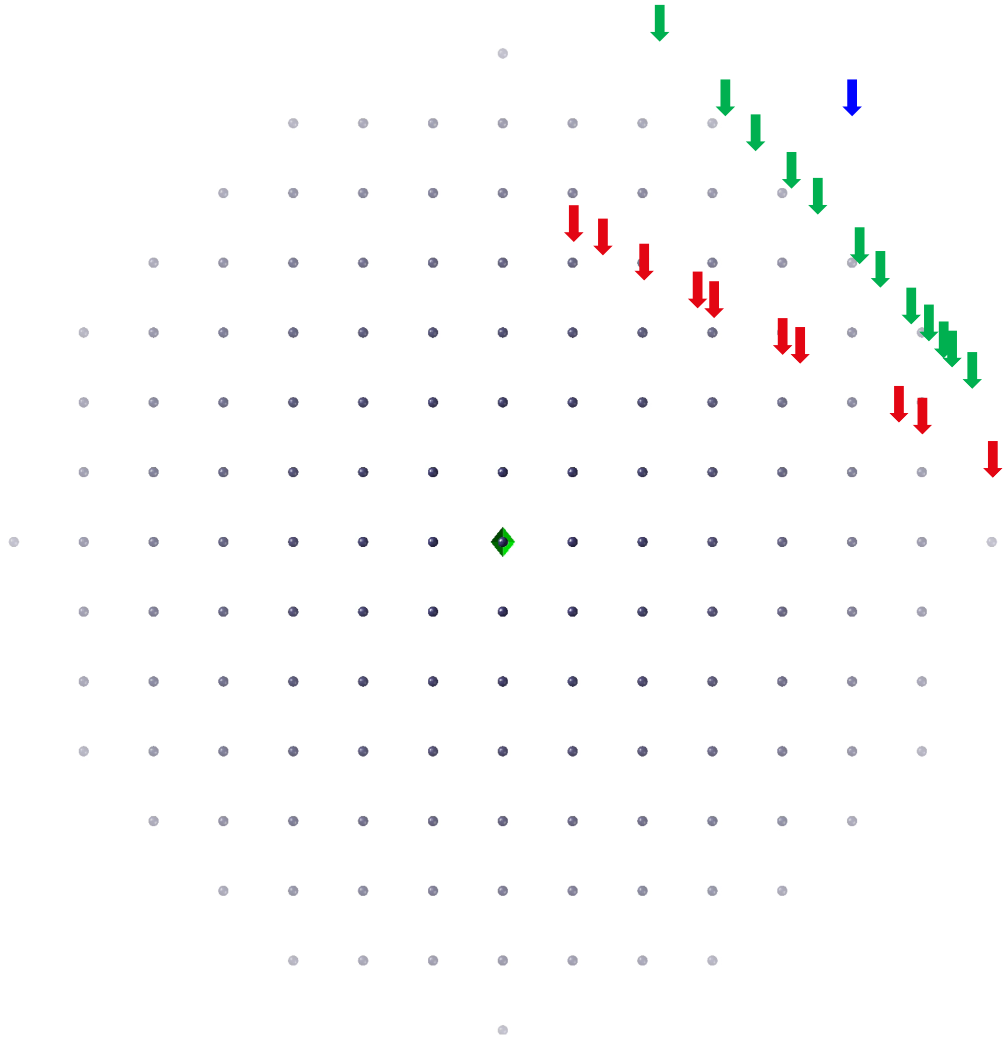
Symmetry axis of the Bragg condition



Generating Debye-Scherrer rings

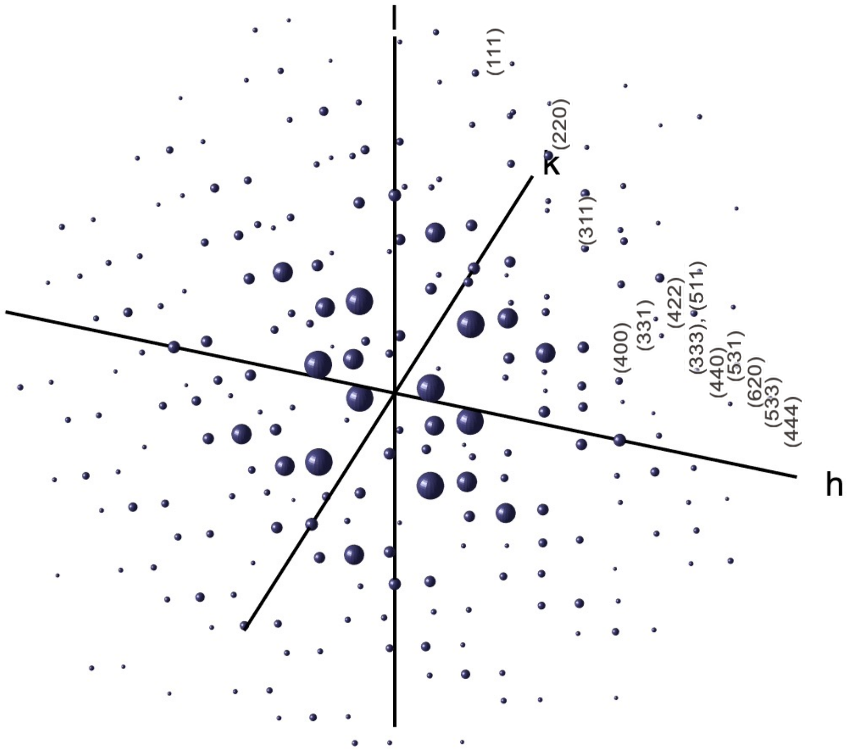


Generating Debye-Scherrer rings



- h or k = 0, h = k: M = 4
- h ≠ k ≠ 0: M = 8
- (hk) = (50) and (43) have same $d_{hk} = d_{10}/5$, M = 12

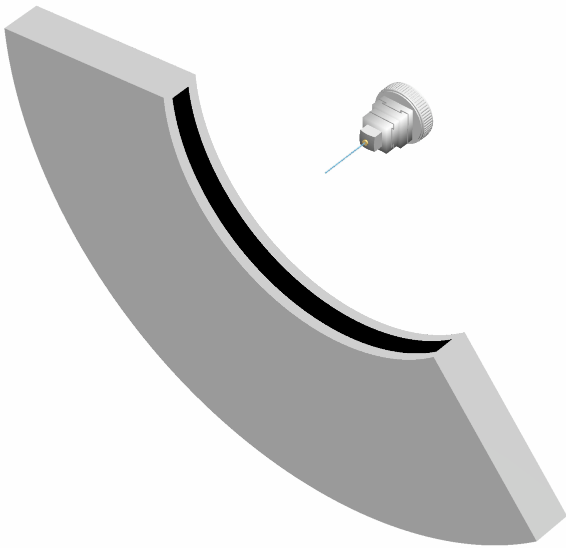
Powder diffraction – the whys and wherefores



Silicon single crystal to powder pattern

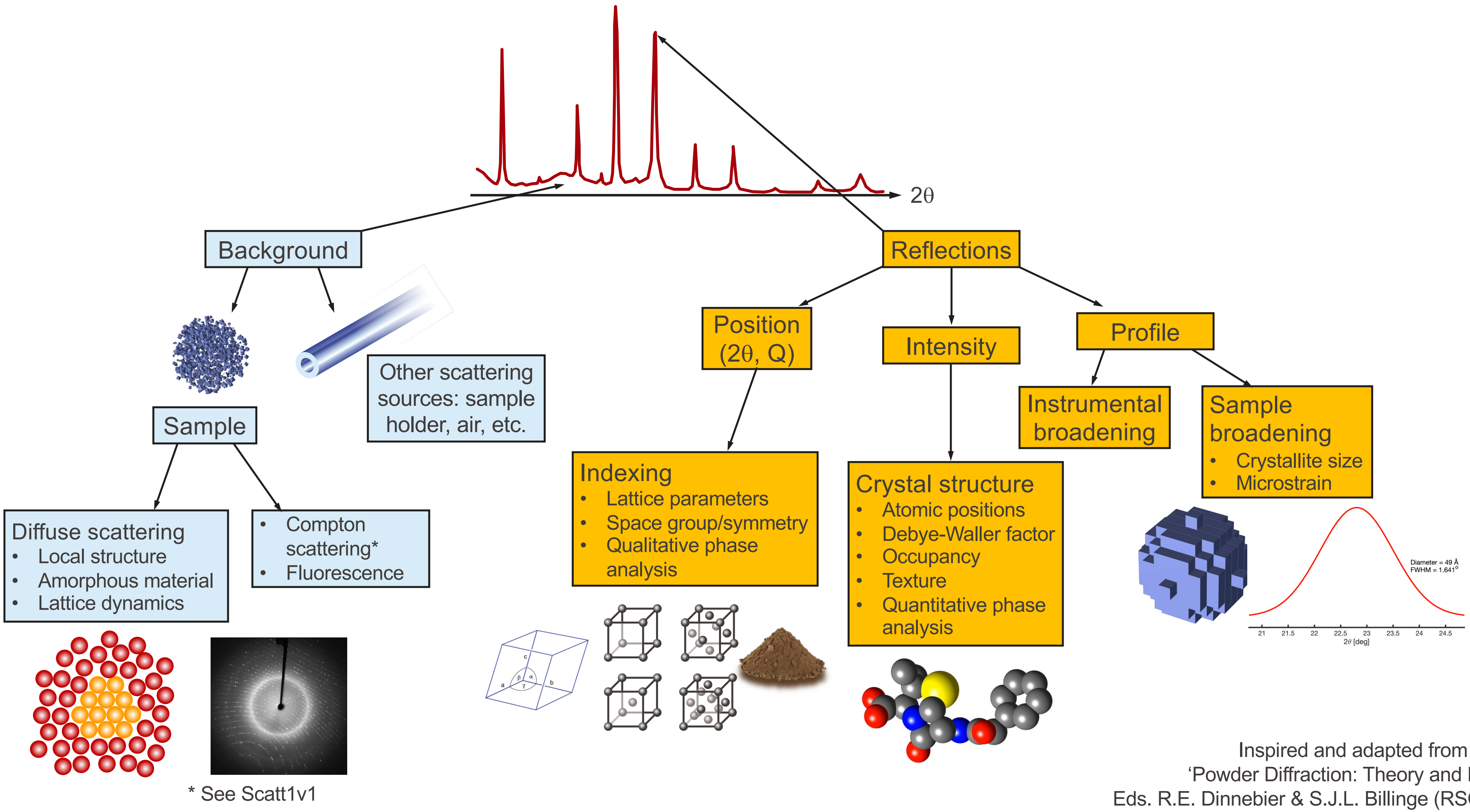
- 3D information collapsed to 1D
  - e.g. silicon single crystal
    - $(h^2 + k^2 + l^2)^{1/2} \le 7$
      246 Bragg peaks in 3D reduced to 12 in 1D
  - Rapid data acquisition ✓
    - Time-resolved studies even down to μs regime
    - Reduced radiation damage
  - Overlapping signal ✗
    - Density of peaks increases with decreasing symmetry (unit cell, basis)

Powder diffraction – the whys and wherefores



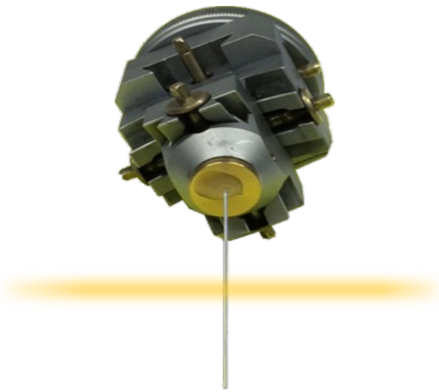
- Materials that only produce micro- or nanocrystals of sufficient quality – PXRD!
- Identification of composite parts in multicomponent mixtures – PXRD!
  - Pharmaceuticals, earth sciences, minerology, archaeology, catalysis…
- Extreme environmental studies, phase changes as function of temperature and/or pressure – PXRD!
  - Information often only extractable from powder samples
    - Microcrystallites' large surface area-to-volume ratio accommodates phase changes by relaxation and propagation of crystallographic faults to surface

Information content from powder diffraction data

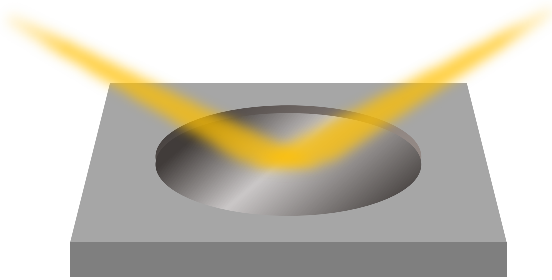


Inspired and adapted from figure in
'Powder Diffraction: Theory and Practice'
Eds. R.E. Dinnebier & S.J.L. Billinge (RSC, 2008)

Common sample configurations

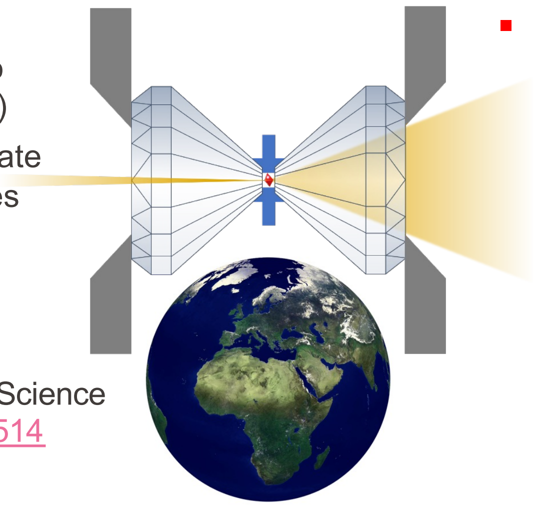


- Capillary
  - Transmission (Debye-Scherrer) geometry
  - Diameter typically between 0.2 and 1 mm
  - Requires good transmission
  - Quartz, sapphire capillaries
  - Normally true powder/randomly oriented crystallites
  - Option to spin capillary

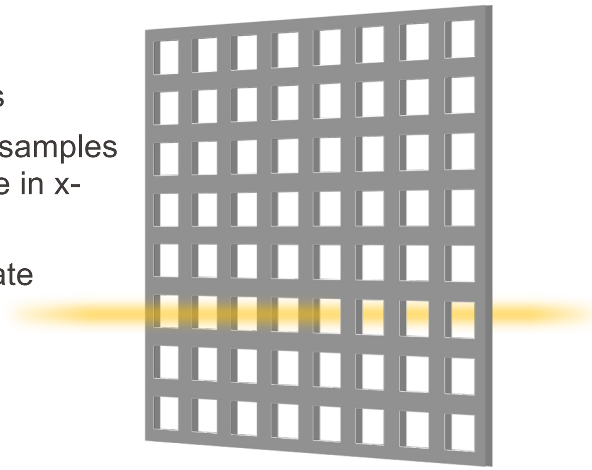


- Flat plate
  - Reflection geometry
  - Often Bragg-Brentano geometry $(\theta-2\theta)$
  - Often high-Z materials
  - Thin heteroepitaxial films
  - Often textured sample
  - Option to spin plate around sample normal

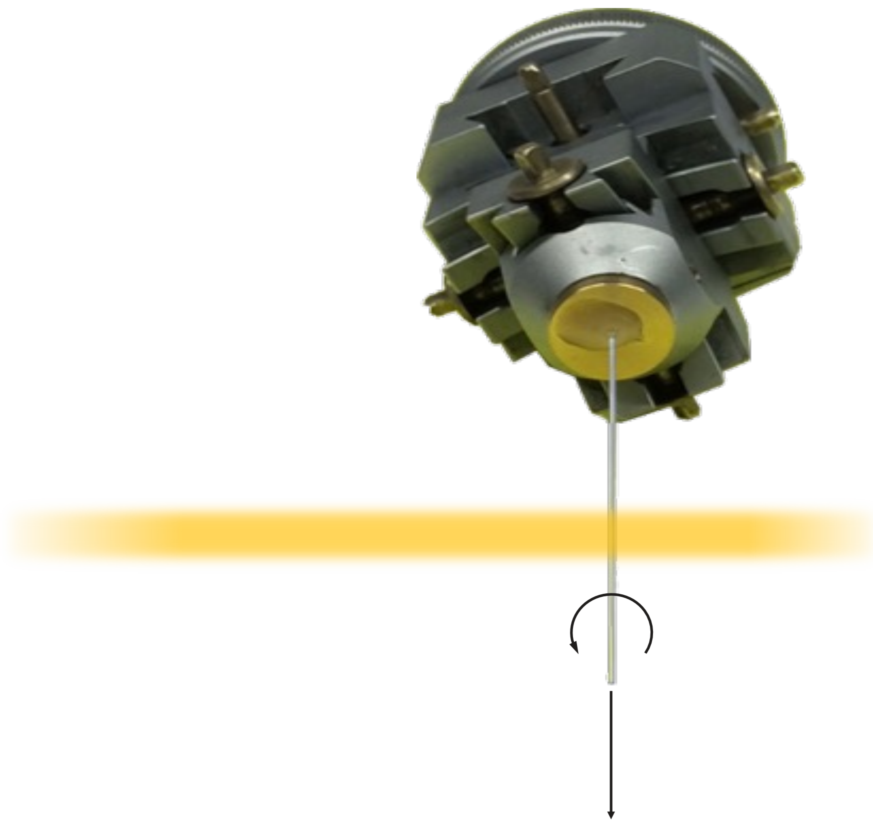
- Diamond anvil cell
  - High-pressure experiments up to 200 GPa (2 million atmospheres)
  - Insert small ruby crystal to calibrate pressure via its fluorescence lines
  - Geology/deep-earth simulations
    - Up to 600 GPa, 5000 K
    - Inner core conditions
    - See e.g., S. Anzellini *et al.*, Science DOI: 10.1126/science.1233514



- Multisample plate
  - Survey experiments
  - Rapid exchange of samples via rastering of plate in x- and y-directions
  - 100s of samples/plate possible



Typical sample sizes

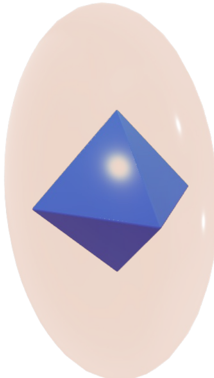


- u.c. linear dimensions ~ 10 Å
- 1000 u.c./μm; 10^9/μm^3
  - SR @ DLSRs: $\ell_c^{(l)}$ ~ 10 μm, $\ell_c^{(t)}$ ~ 100 μm
  - ⇒ linear crystallite size ~ 5 μm should be coherently illuminated ≡ 10^{11} u.c.
- Take 0.5-mm ϕ ID capillary, illuminate 2-mm length
  - ~ 10^6 crystallites illuminated
  - Spin sample to get larger fraction of these in Bragg condition
    - Factor = 2π/(BP width) ~ 2 x 10^4
- Radiation damage?
  - Shift capillary along its own axis

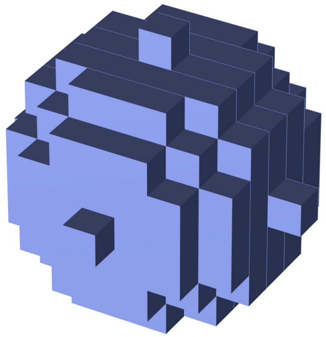
The Scherrer equation

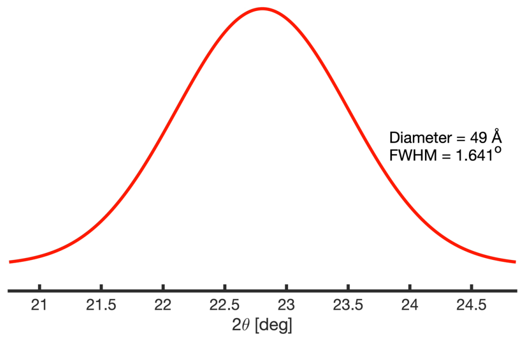
$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

- Only valid if crystallite size < coherence volume $\ell_c^{(l)} \cdot \ell_c^{(t,x)} \cdot \ell_c^{(t,y)}$ and quasi monodisperse
- 3rd generation: crystallites ~ 0.1 μm
  - Scherrer eqn. unsuitable for single-crystal diffraction
- DLSRs: 1 – 5 μm



- τ = crystallite size (same units as λ)
- K = form factor $\simeq$ unity
- λ = x-ray wavelength
- β = 2θ-FWHM of Bragg peak in radians
- θ = Bragg angle

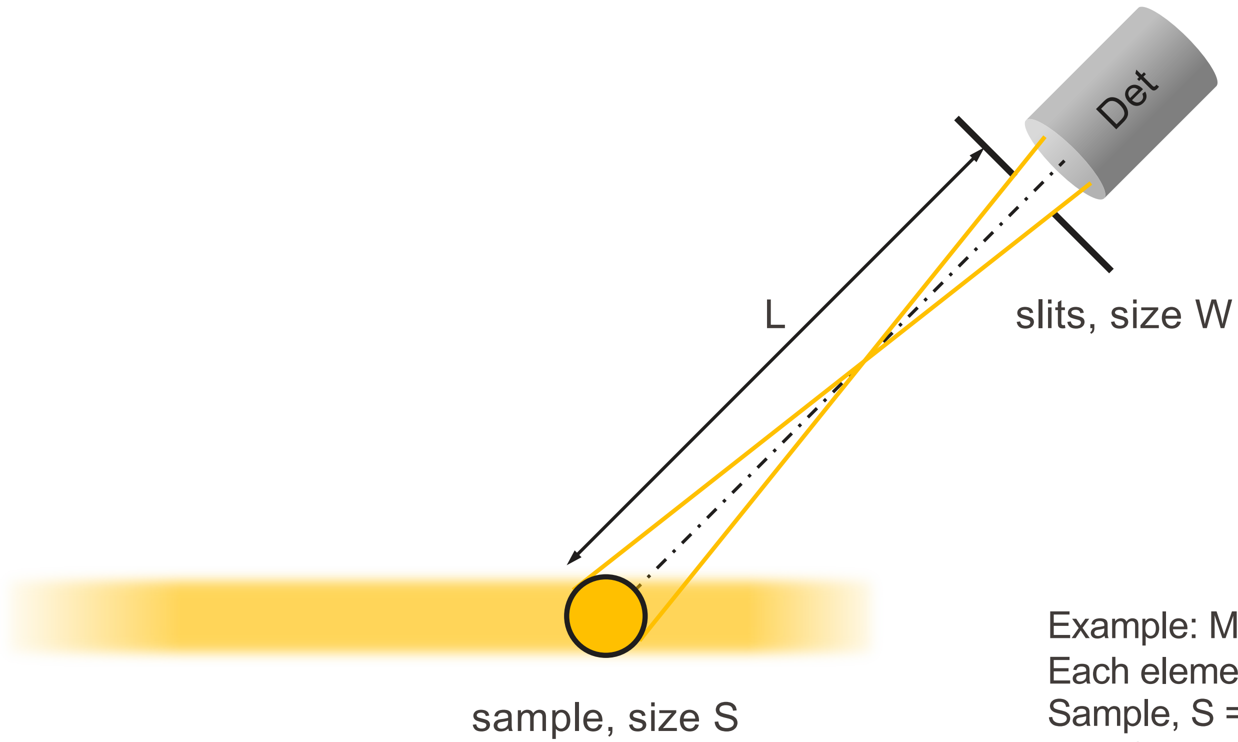




Intrinsic Si(111) peak @ 10 keV for spherical crystallites between 9 and 201 unit-cell diameter

See also e.g.: http://prism.mit.edu/XRAY/oldsite/CrystalSizeAnalysis.pdf

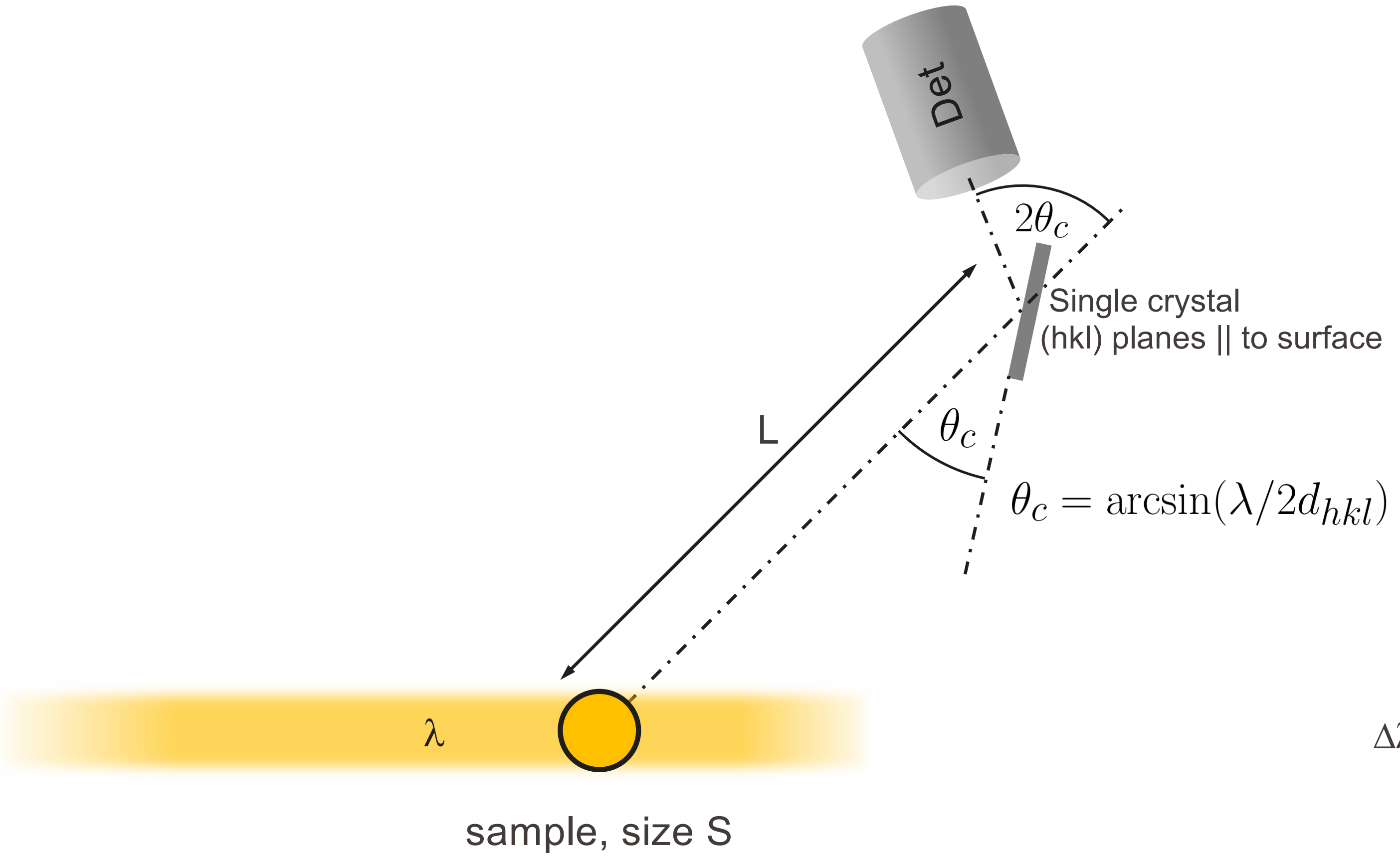
Angular resolution in powder diffraction

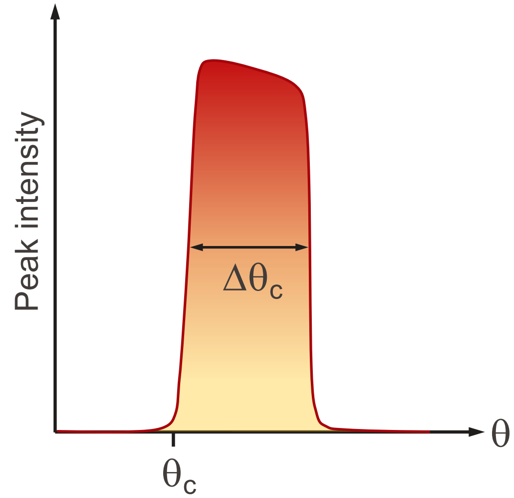


$$\text{Resolution } (2\theta, \text{ radians}) = \frac{S+W}{L}$$

Example: Mythen microstrip detector
Each element has a width (≡ slit width, W) = 50 μm (0.05 mm)
Sample, S = 0.5-mm capillary.
L = 70 cm
Resolution = (0.5+0.05)/700 = 7.9×10^{-4} rad (0.045^{o})

Crystal analyzers – getting the best angular resolution





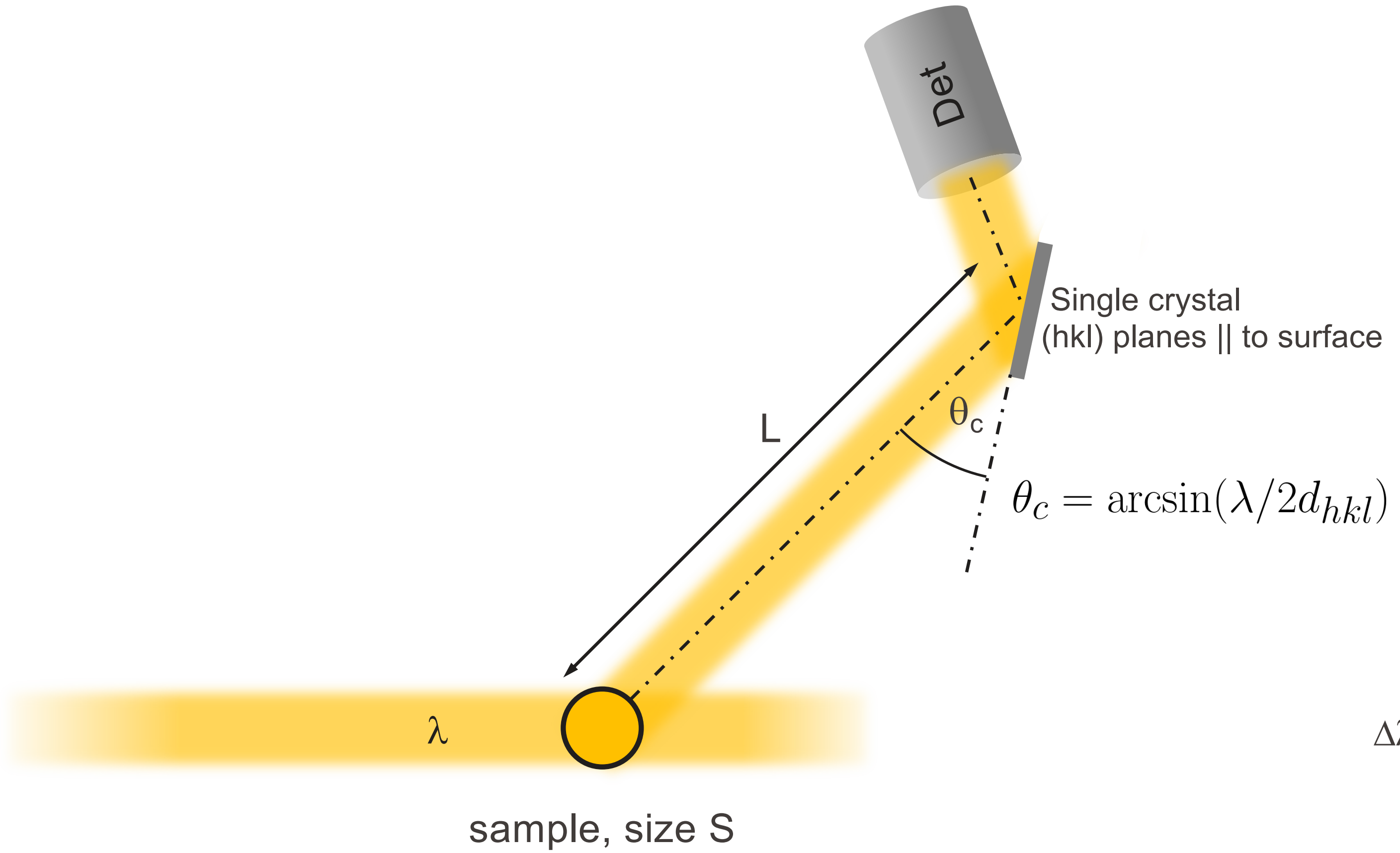
$\Delta\theta_c = (\Delta\lambda/\lambda) \tan \theta_c$

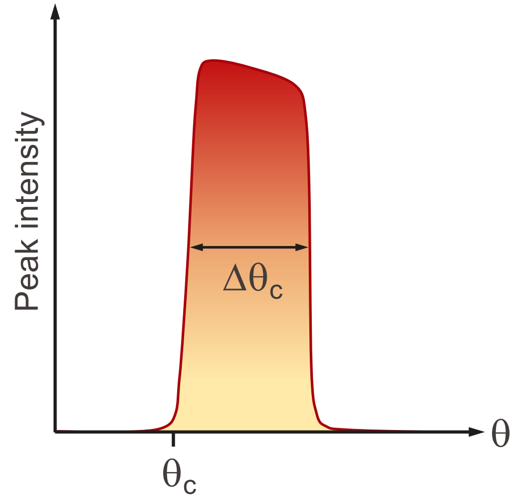
$\Delta\lambda/\lambda$ = const = 1.31×10^{-4} for Si(111)

$\Delta\theta_c = 2.64 \times 10^{-5}$ rad @ 10 keV
≡ slit width of 18 μm for an infinitely small sample size S, and L = 700 mm

See also: https://www.chess.cornell.edu/users/calculators/x-ray-calculations-darwin-width

Crystal analyzers – Nature's slits





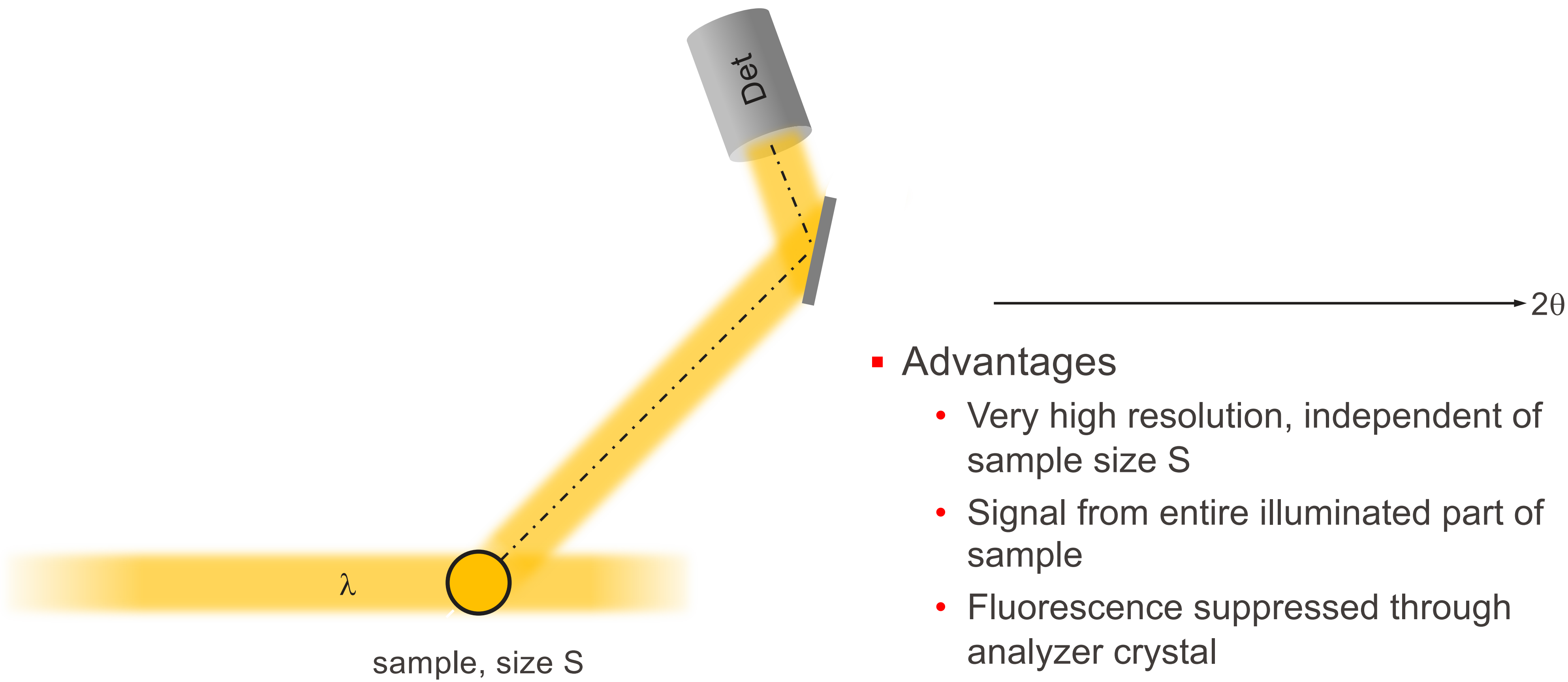
$\Delta\theta_c = (\Delta\lambda/\lambda) \tan \theta_c$

$\Delta\lambda/\lambda$ = const = 1.31×10^{-4} for Si(111)

$\Delta\theta_c = 2.64 \times 10^{-5}$ rad @ 10 keV
≡ slit width of 18 μm for an infinitely small
sample size S, and L = 700 mm

See also: https://www.chess.cornell.edu/users/calculators/x-ray-calculations-darwin-width

Crystal analyzers – nice but slow

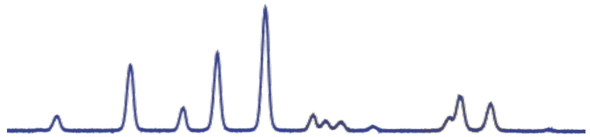


- Advantages
  - Very high resolution, independent of sample size S
  - Signal from entire illuminated part of sample
  - Fluorescence suppressed through analyzer crystal
- Disadvantages
  - Very slow! Minutes to hours

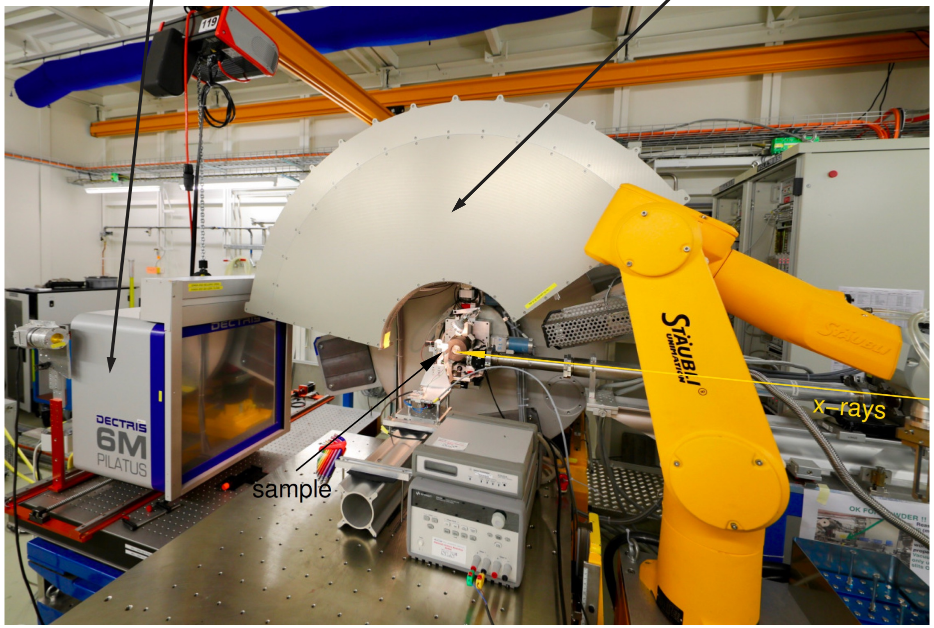
Powder diffraction – 1-D and 2-D detectors

"Pilatus" 6M 2-D HPAD
2463 x 2527 pixels
172 μm pixel size
Best suited for ultrafast experiments

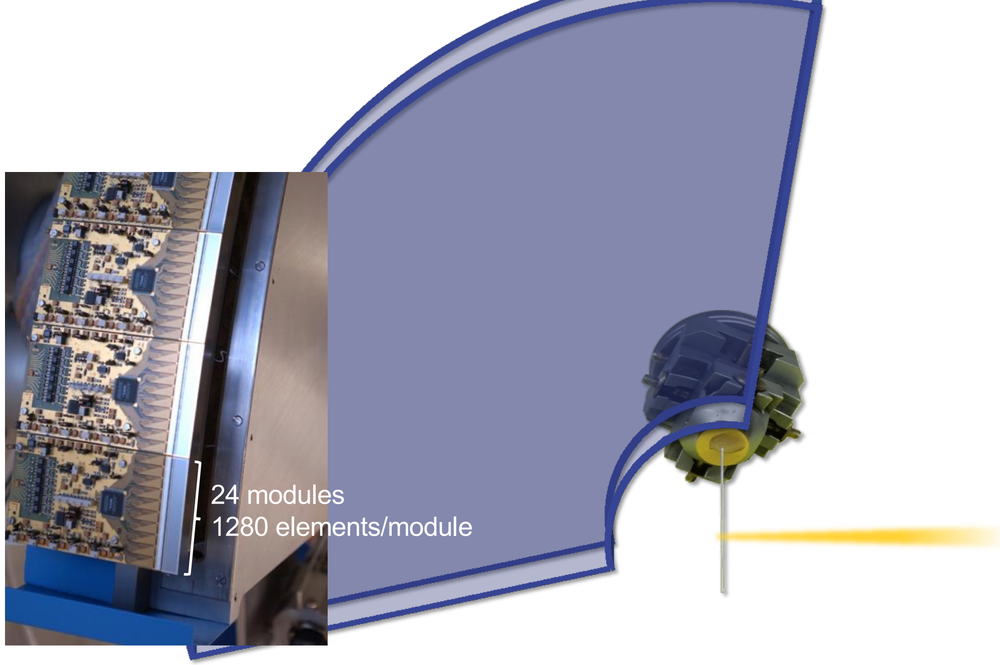
"Mythen" 1-D strip detector
30720 elements over 120°
50 μm element width
Best suited for high-Q experiments



Parallel acquisition
~ seconds or shorter



Materials Science beamline, SLS



See B. Schmitt *et al*., https://doi.org/10.1016/S0168-9002(02)02045-4

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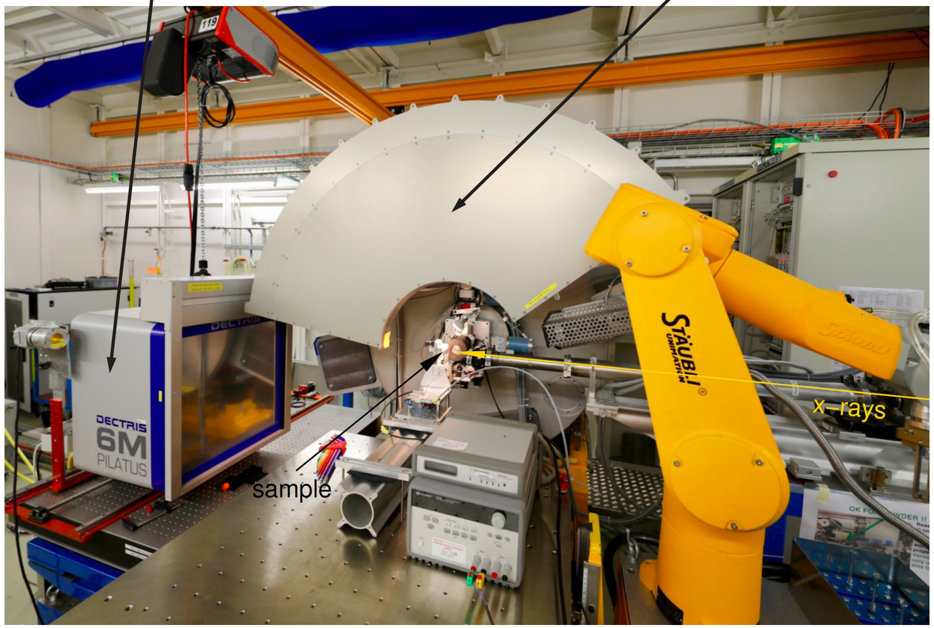
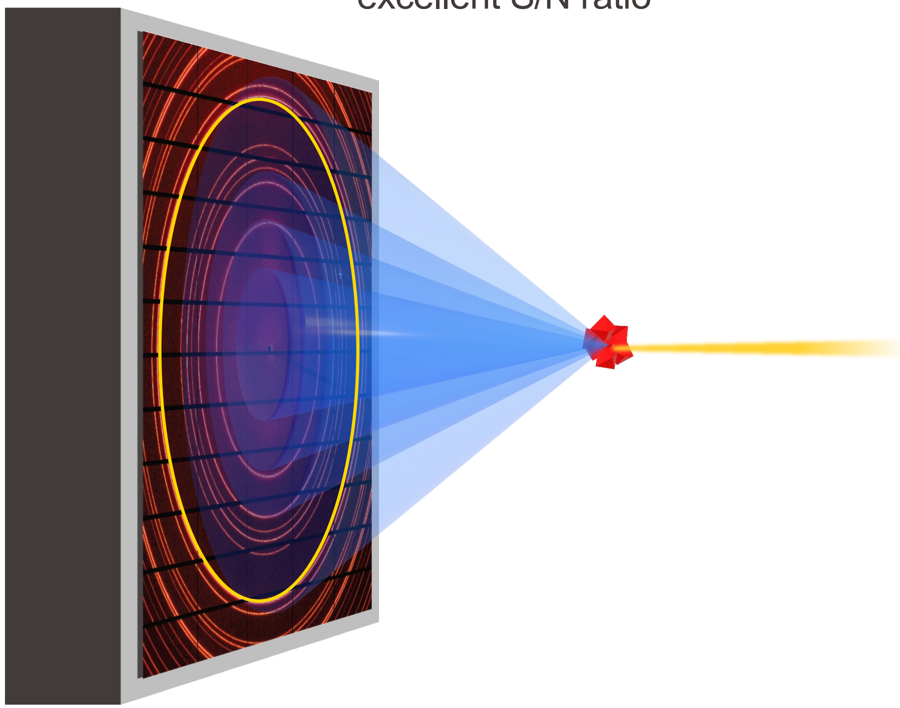
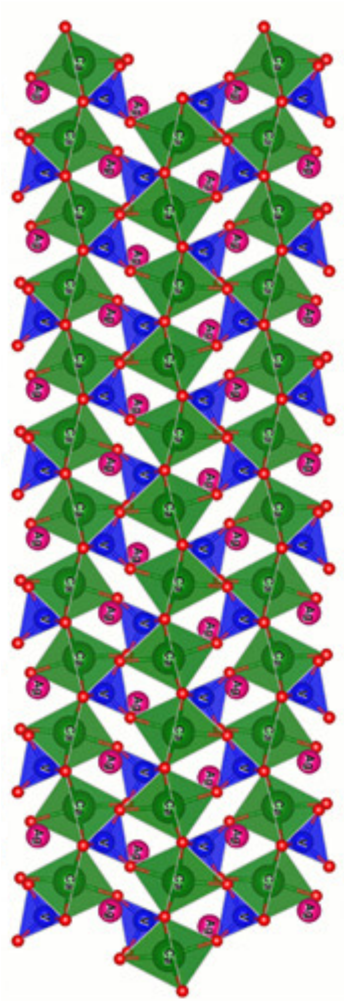


Materials Science beamline, SLS

Integrate along entire ring –
excellent S/N ratio

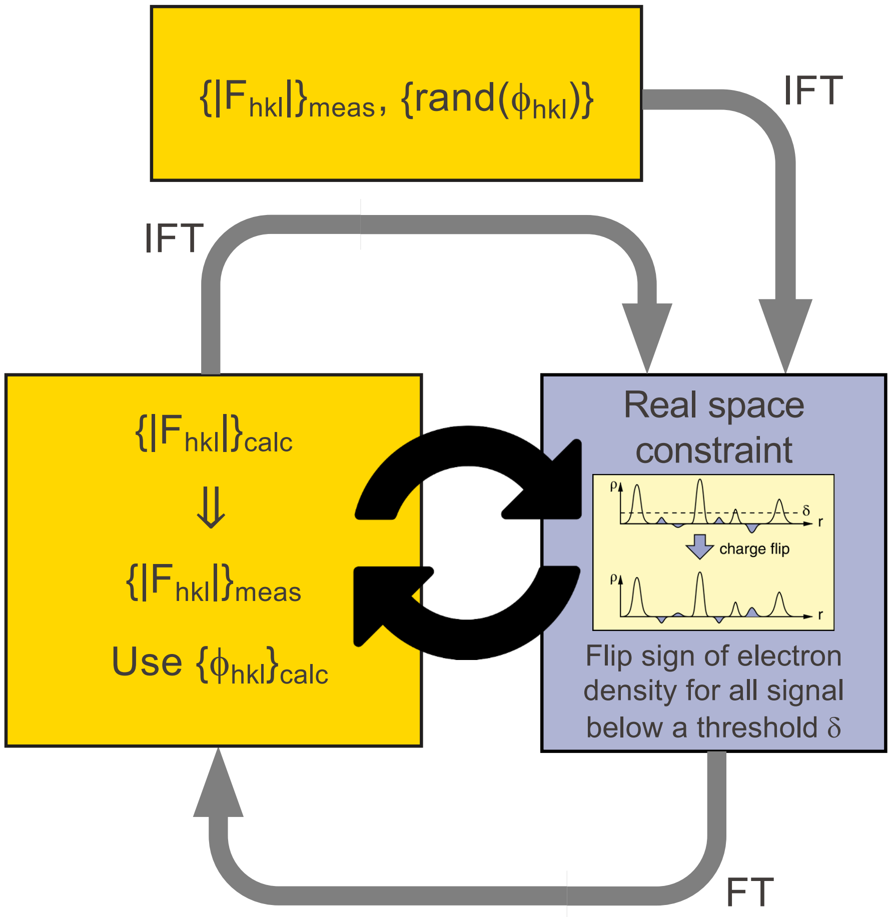


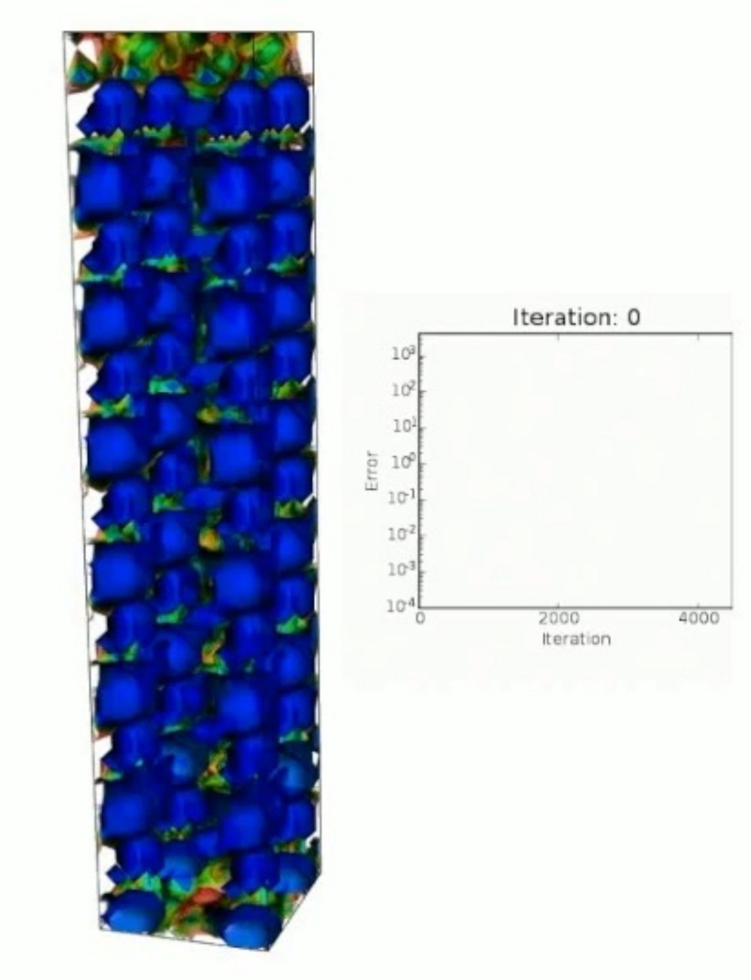
Solving the structure in PXRD – model building



- Indexing yields
  - Lattice constants
  - Space group symmetry
- Stoichiometry normally known
  - Apply constraint of physical bond lengths and volume typically occupied by an atom
- Other physical properties
  - e.g. piezoelectric ⇒ noncentrosymmetric
- Known motifs?
  - e.g. oxygen octahedra
  - Apply rigid-body translations and rotations
- Simulated annealing
- Rietveld refinement

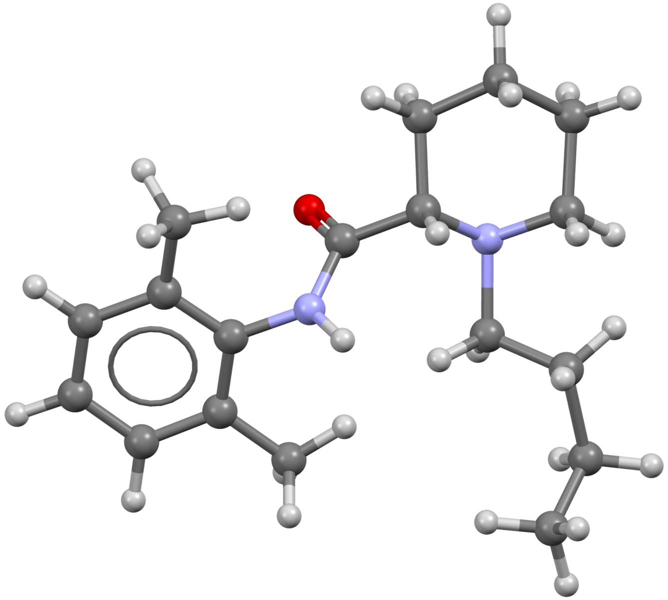
Charge flipping





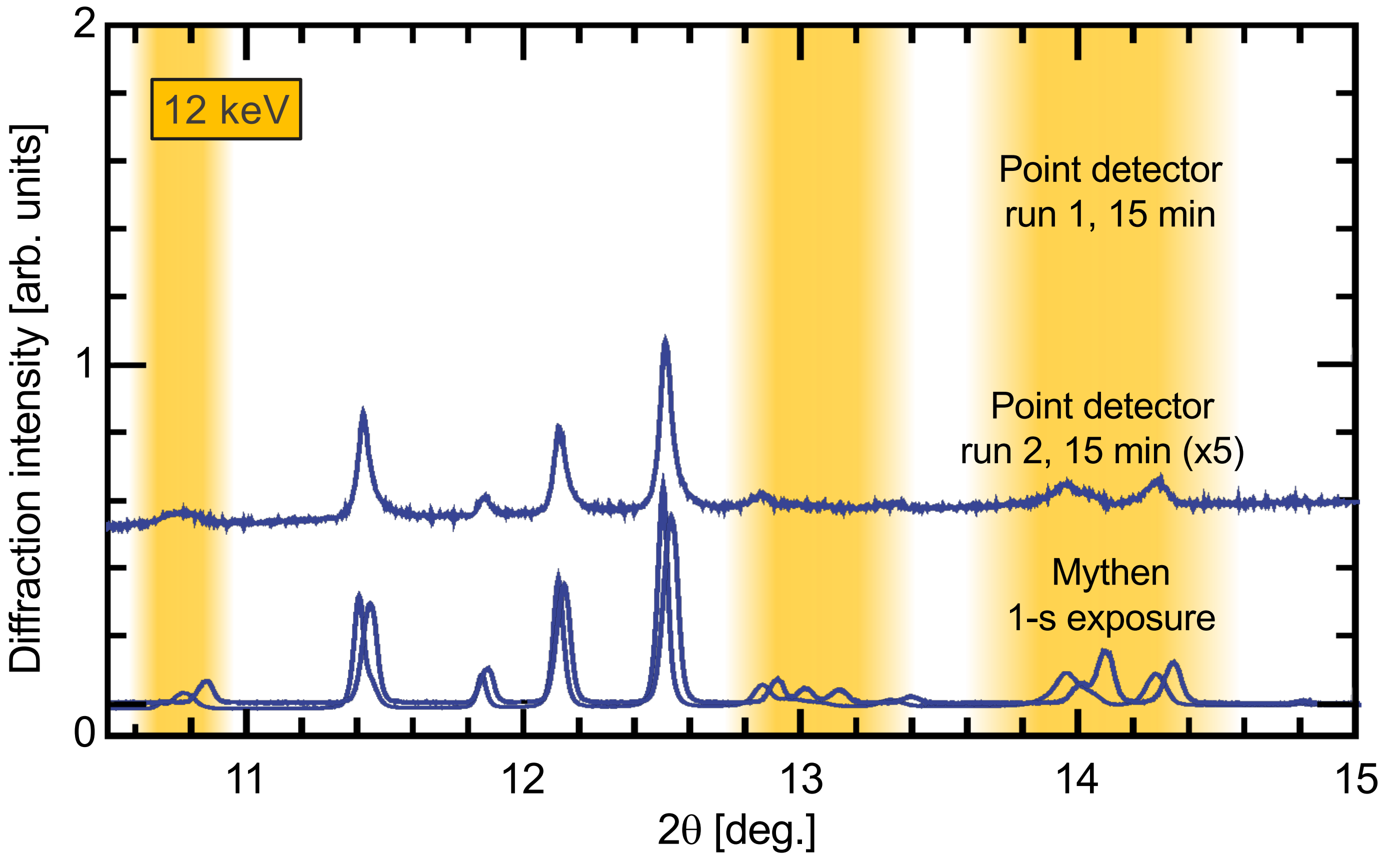
See also: http://www.crystal.mat.ethz.ch/research/ZeolitesPowderDiffraction/ChargeFlipping.html

Example I – radiation damage testing pharmaceuticals



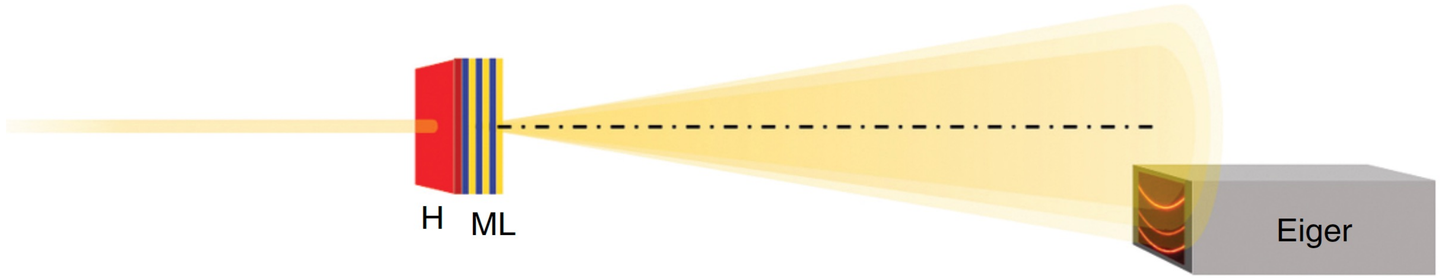
Bupivacaine – anaesthetic drug
R-enantiomer (chiral)
[S-enantiomer more vasoconstrictive]

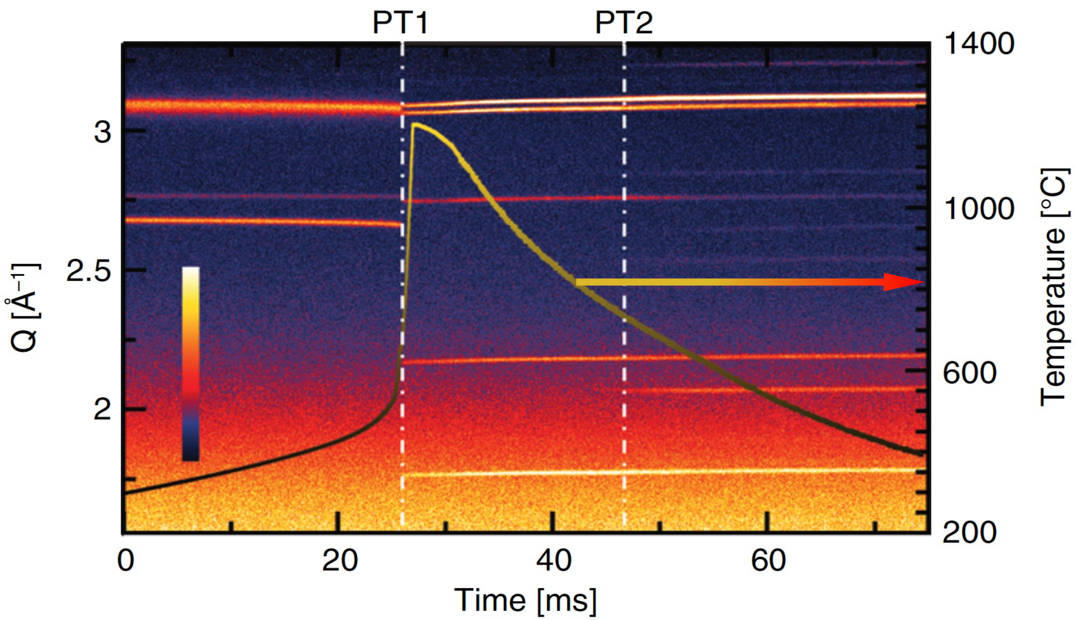
(Courtesy Creative Commons)



See also: A. Bergamaschi *et al*., https://doi.org/10.1107/S0909049510026051

Example II – Ultrafast diffraction in real time



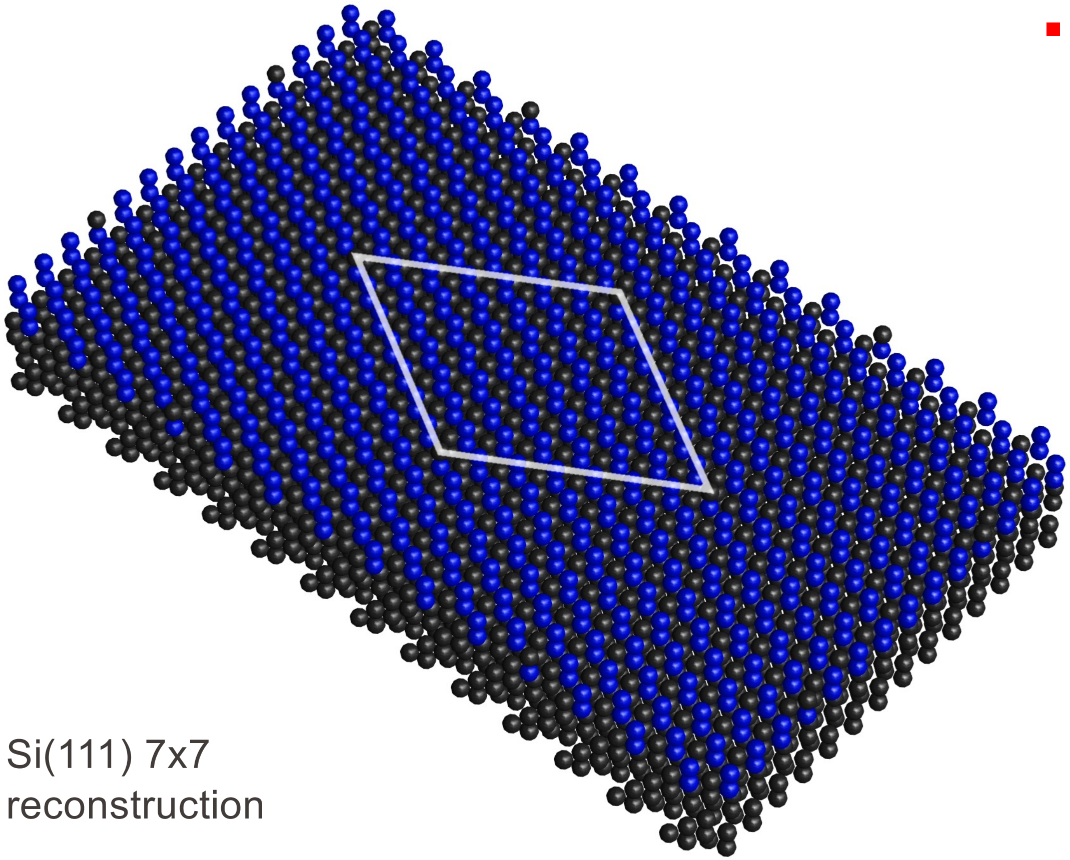


- Runaway exothermic alloying reaction in Al/Ni multilayers
  - H: 10'000 K/s heat rate up to 500°C
  - Ignition occurs @ ~ 400 – 500°C
  - Runaway reaction up to 10^6 K/s takes over
  - Experiment ca. 0.1 s long!
- Eiger 500k detector
  - 4-bit/pixel ⇒ accelerated frame rate
  - 20 kHz frame rate (50 µs exposure – 4 µs dead time)
  - Max $2\theta \simeq 30°$
  - Integrate Debye-Scherrer ring signals azimuthally

See also: T. Neuhauser *et al.*, https://doi.org/10.1016/j.actamat.2020.05.035

Surface diffraction

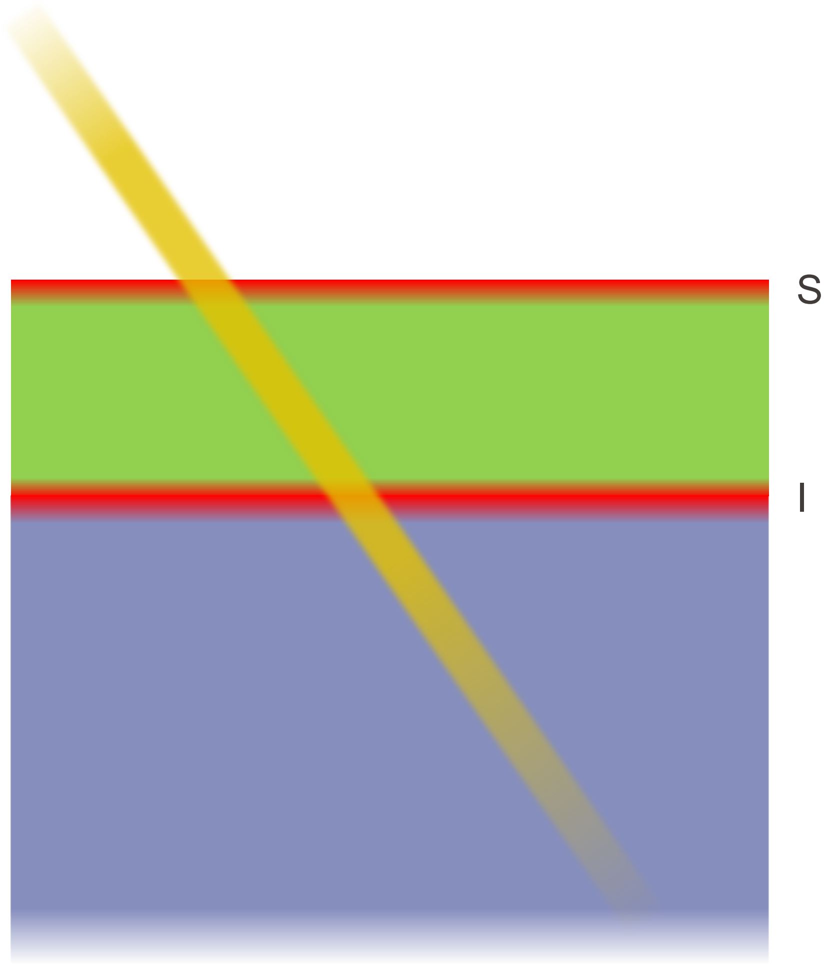
Goals of SXRD



Si(111) 7x7
reconstruction

- Study of crystalline surfaces *and* interfaces
  - Surfaces/interfaces different from bulk
  - “Dangling” bonds
  - Polar discontinuities
  - Surface energy minimization – relaxations and reconstructions
  - Interesting and unexpected new physical properties
    - See e.g., $LaAlO_3/SrTiO_3$ interface
      S.A. Pauli *et al.*,
      DOI:10.1103/PhysRevLett.106.036101

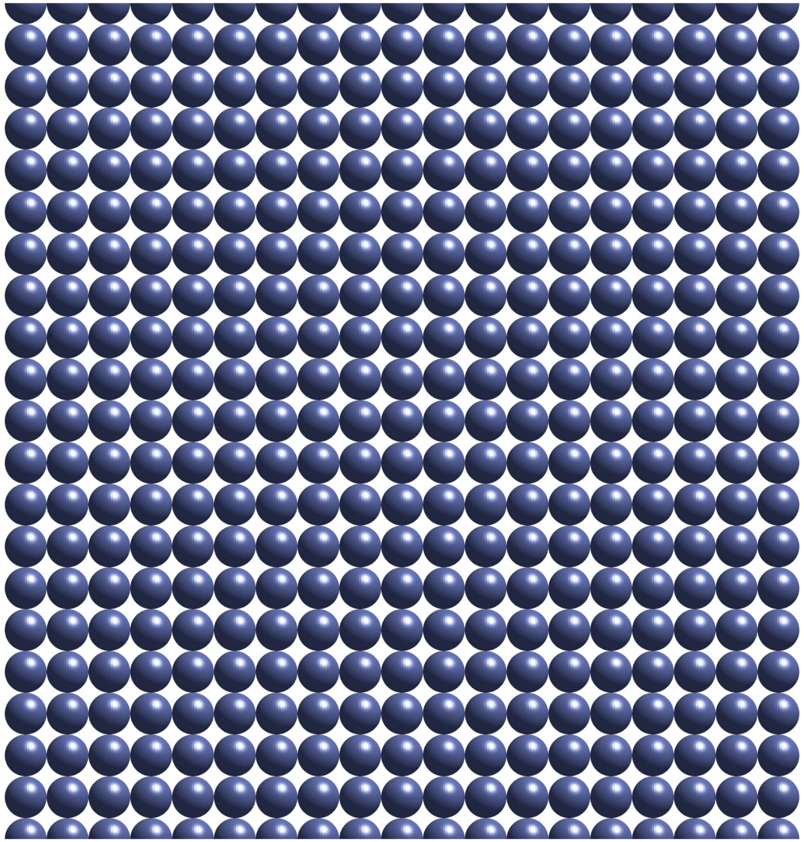
Signal from surfaces or interfaces



- How does one find out the structure of a surface or interface using scattering methods?
- Surfaces and interfaces different from bulk
- Very small scattering volume
  - ~ 1 – 5 ML, or 1 – 5 nm depth
  - c.f. extinction length ~ 10 μm
- Go to positions in reciprocal space where bulk signal is weak…
- Let's discuss this in more detail

Crystal truncation rods – the signal that keeps on giving

- The “LEED/RHEED” explanation



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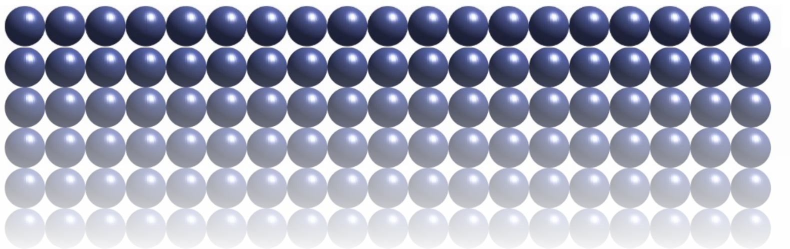

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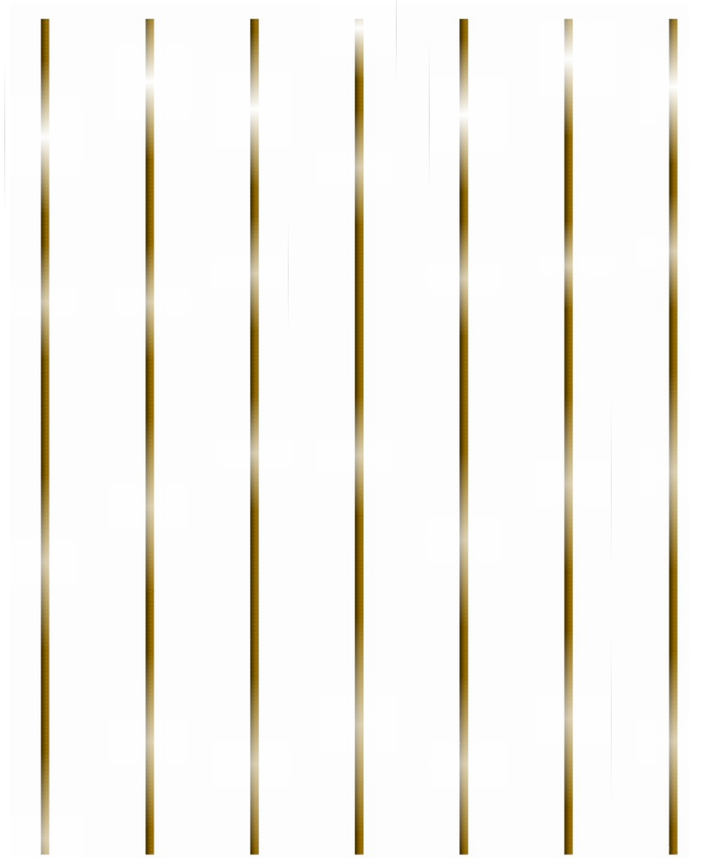
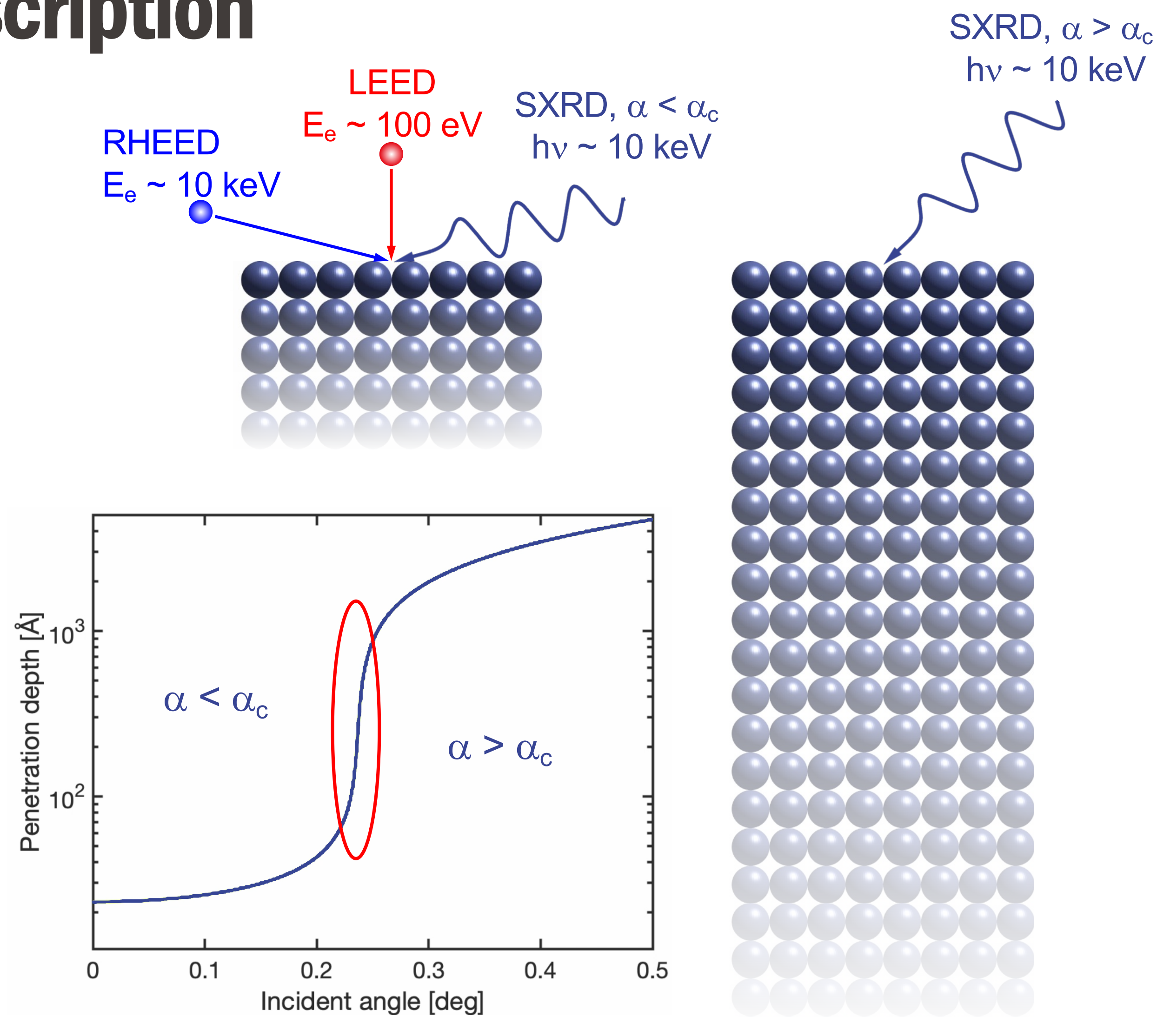


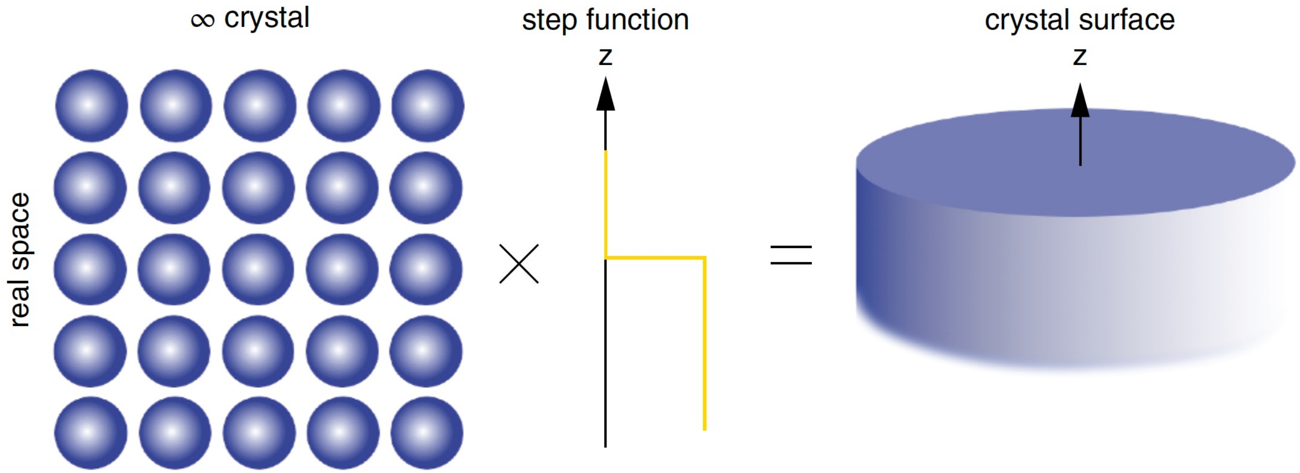
Continuous signal, but modulated

CTRs – a better description

- Why?
  - LEED, RHEED: surface sensitive (~ nm)
  - X-rays: bulk (~ 100 nm)
- X-rays
  - n < 1
  - Total external reflection
  - Evanescent standing wave below α_c
  - Enhanced surface sensitivity
  - BUT: normally $\alpha > \alpha_c$
- Why?
  - Buried interfaces
  - Experimental stability



CTRs explained via the convolution theory

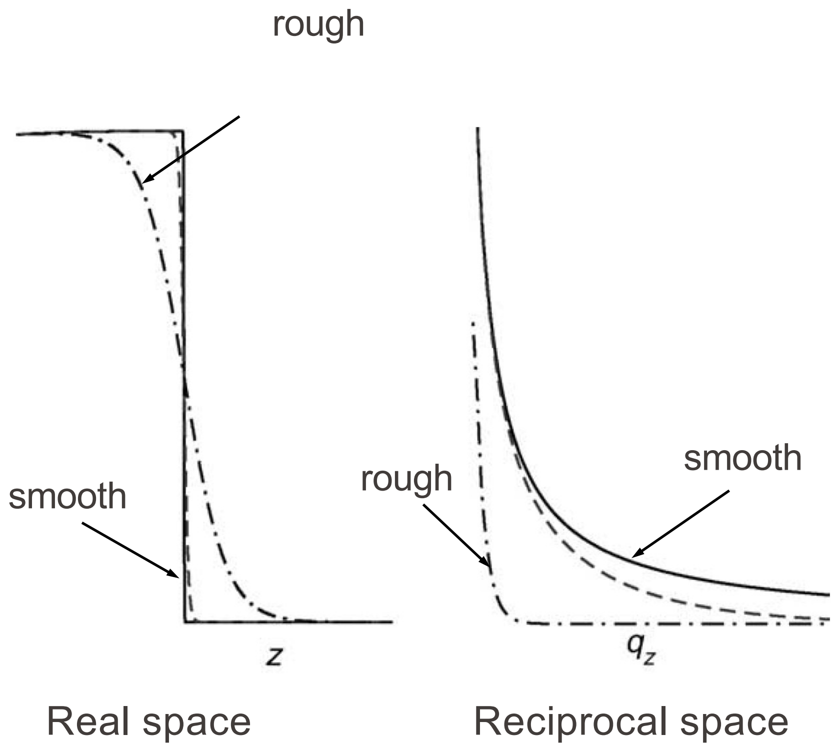


- FT(f x g) = FT(f) ⊗ FT(g)

See also: Supplementary Material
“Fourier transforms and convolutions made simple”

Why don't we see CTRs all the time?

- Why do you not always see CTRs?
  - After all, every crystal has a surface…
- But how flat is that surface?
  - Atomically flat – "shape function" quite broad in k-space
  - Rough, nobbly surface (on atomic scale)
    - Real-space: large depth variations
    - k-space: "shape function" very narrow
- Nanocrystals have CTRs with modulations that reveal their size



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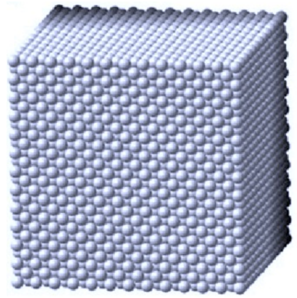
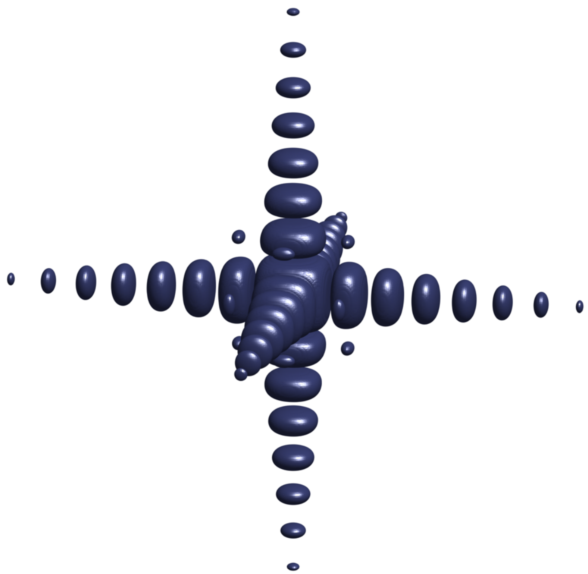
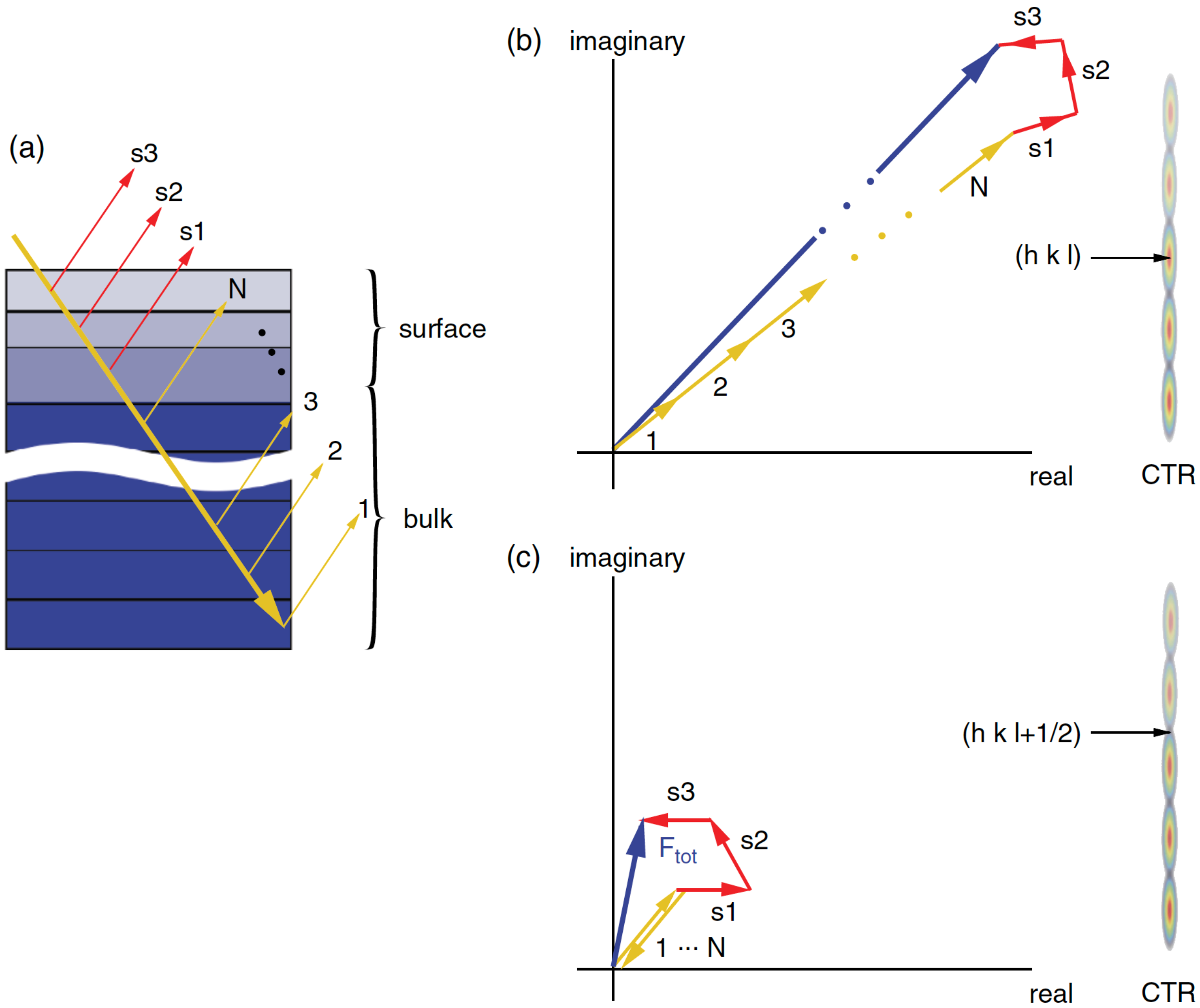




See e.g., A. Pryor Jr. *et al.*, Scientific Reports DOI:10.1038/s41598-018-26182-1

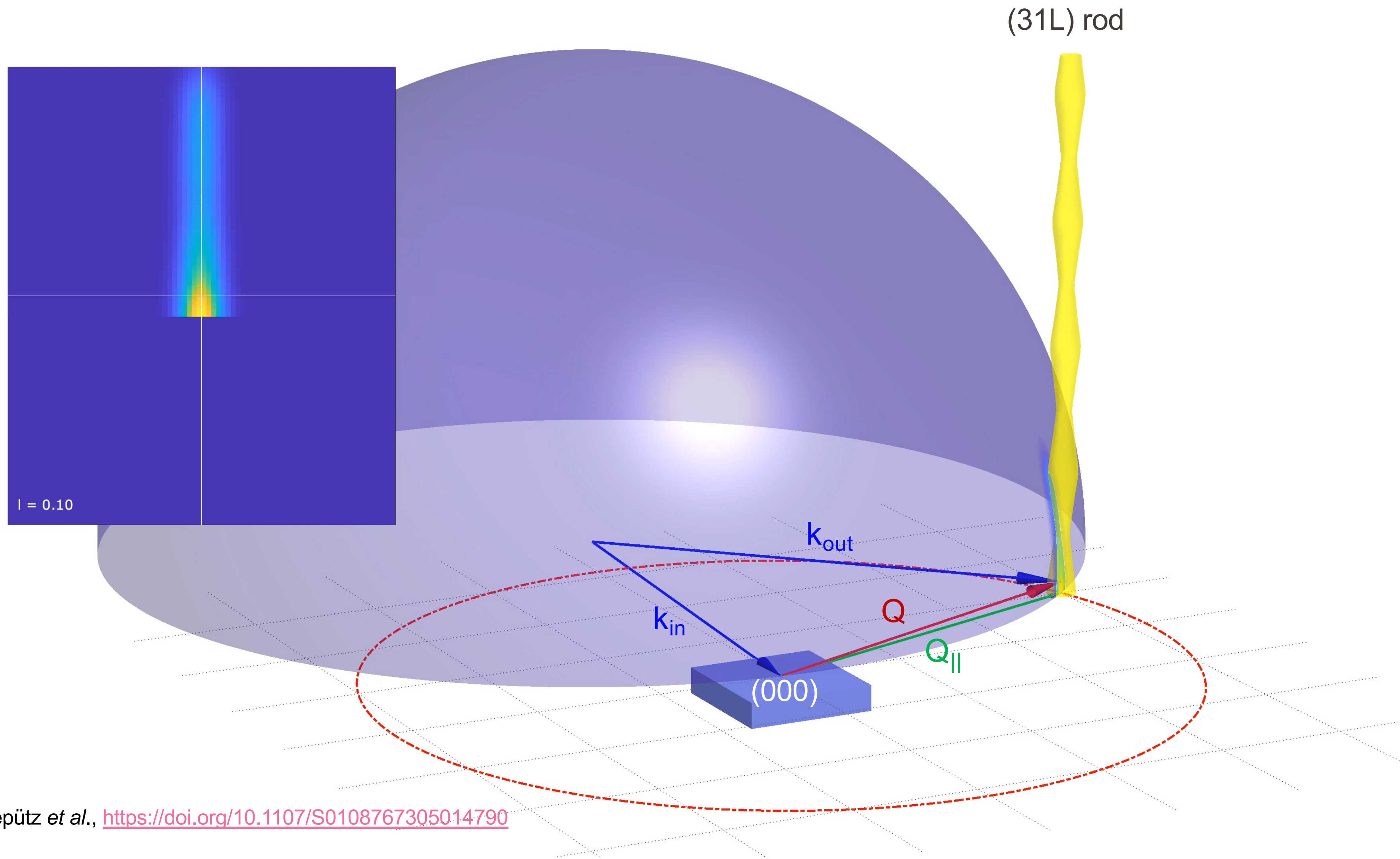
Intensity variations along CTRs



@ Bragg peak
$\phi_b = 2m\pi$

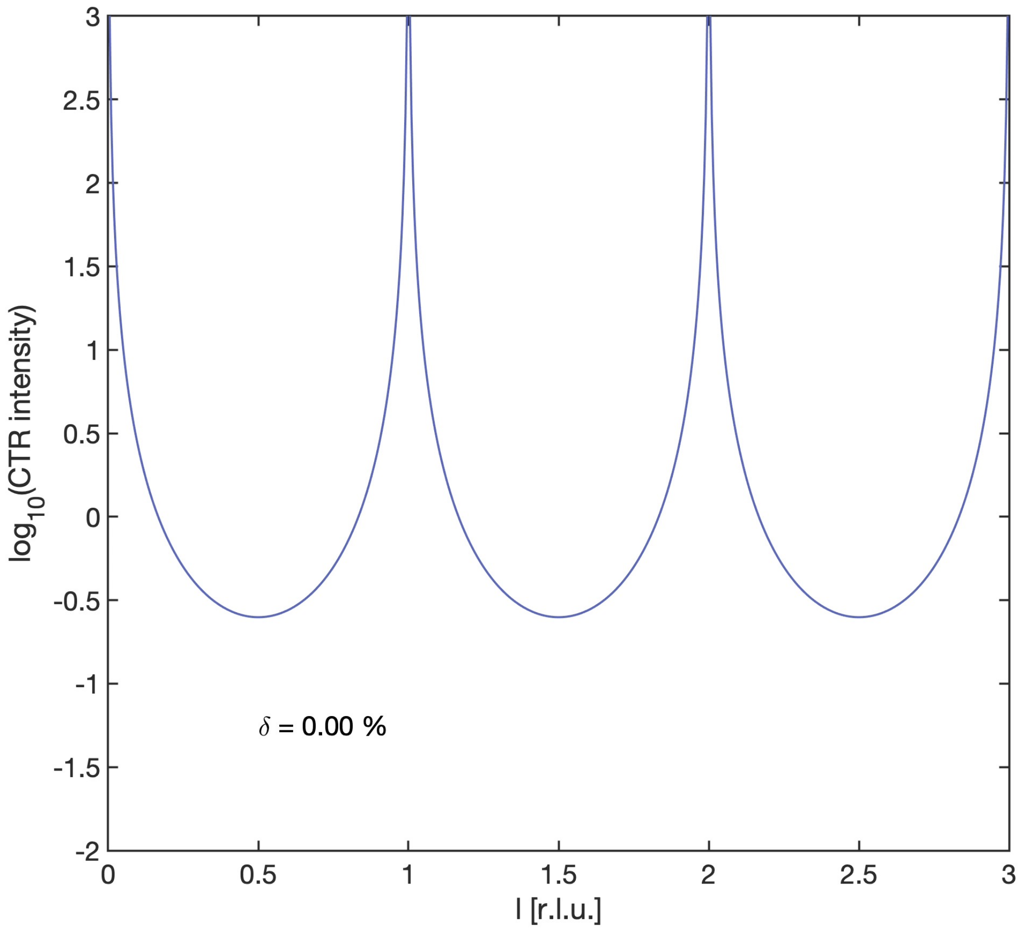
@ anti-Bragg point
$\phi_b = (2m+1)\pi$

Recording SXRD data

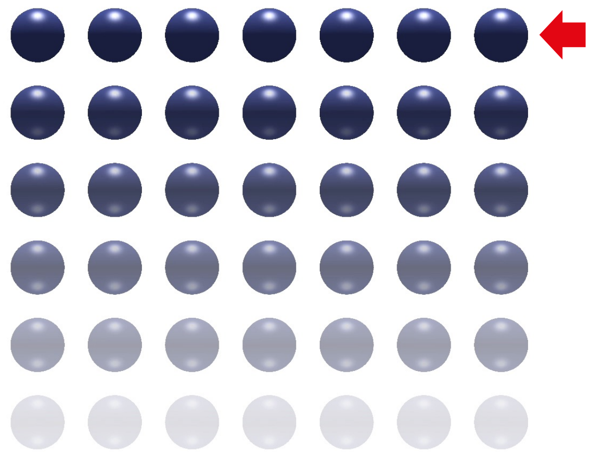


C.M. Schlepütz *et al.*, https://doi.org/10.1107/S0108767305014790

Relaxations and reconstructions



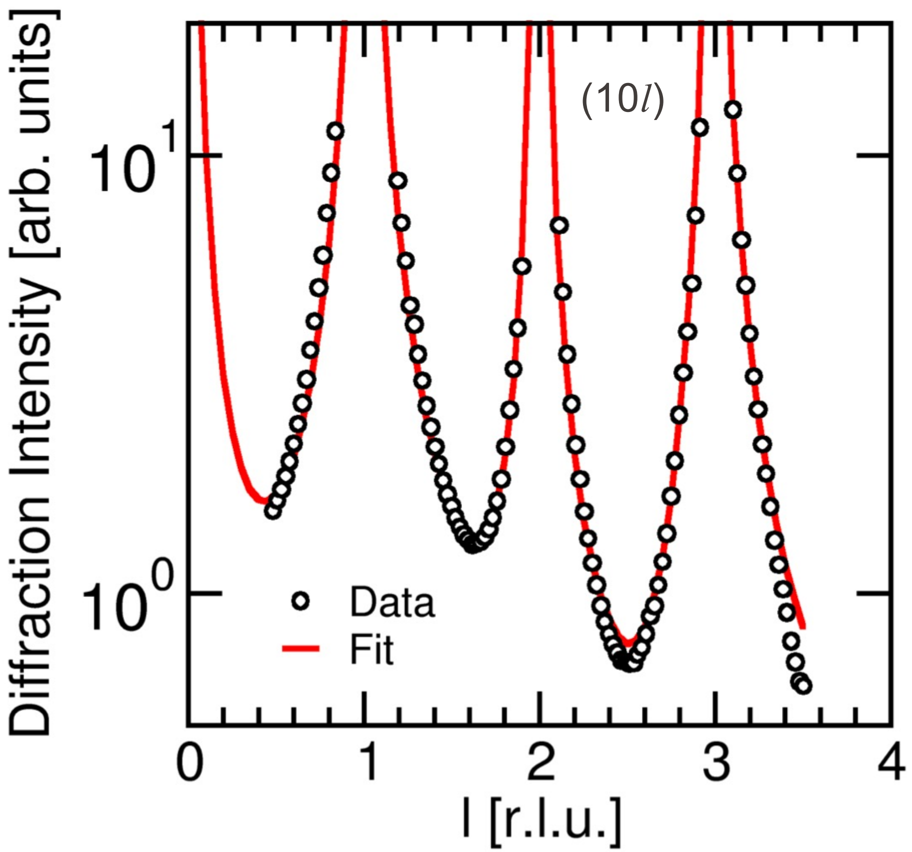
- Relaxations
  - Vertical (out-of-plane) movements only



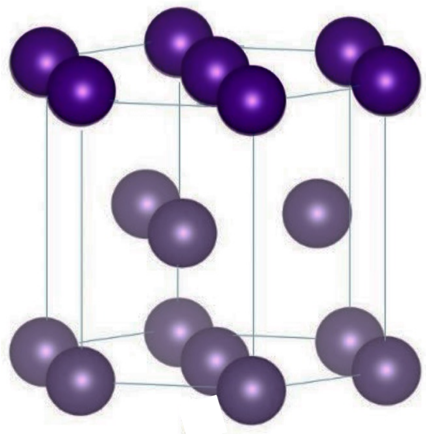
x10 exaggeration:
± 5% shifts
shown as ± 50%

$$I(l,\delta) = \left| A(Q) \left(\frac{1}{1 - e^{i2\pi l}} + e^{-i2\pi(1+\delta)l} \right) \right|^2$$

Relaxations and reconstructions

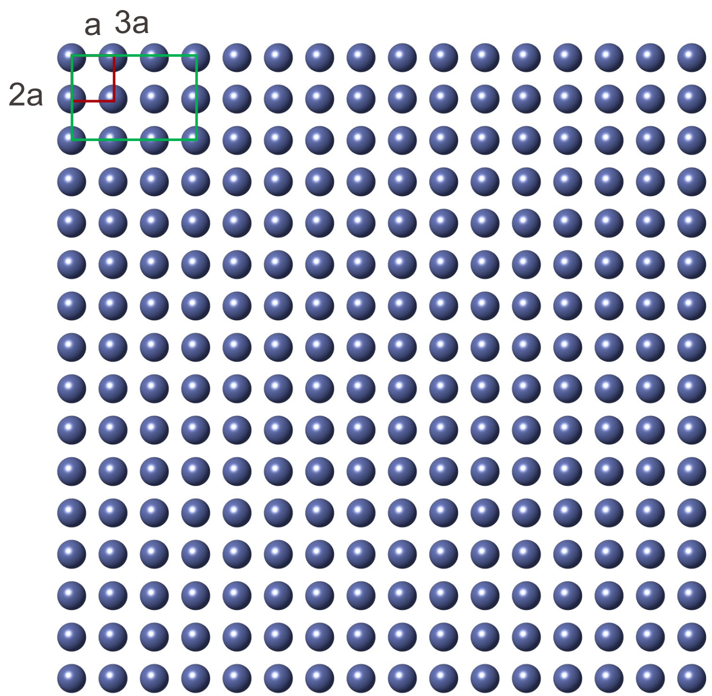


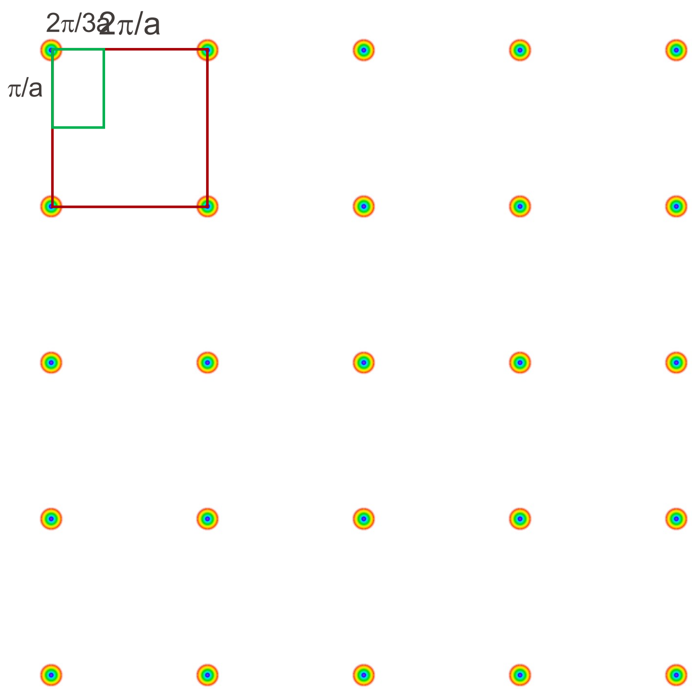
- Example: surface of Ru(0001)
  - Hexagonal close packed (hcp) u.c.
  - Bulk interatomic layer separation = 2.141 Å
  - Top layer: (2.080±0.003) Å
  - Contraction of 2.8%



See D. Martoccia *et al*., PRL (2008) DOI: 10.1103/PhysRevLett.101.126102

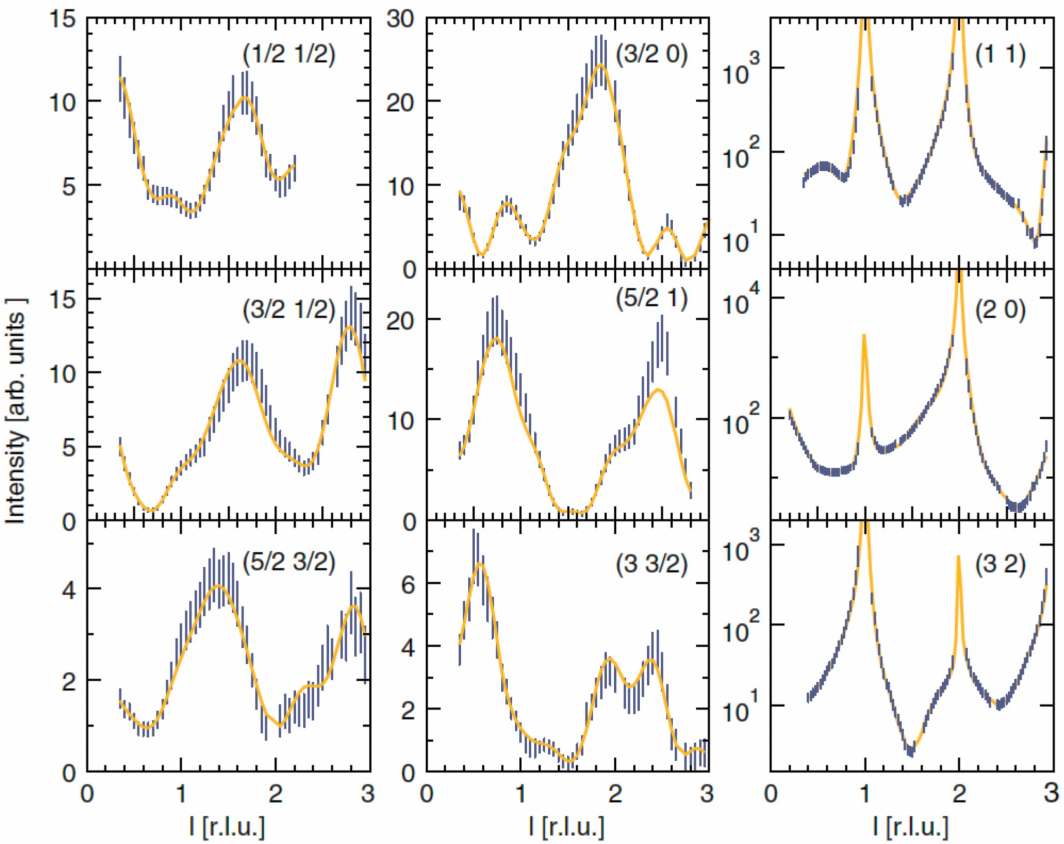
Relaxations and reconstructions

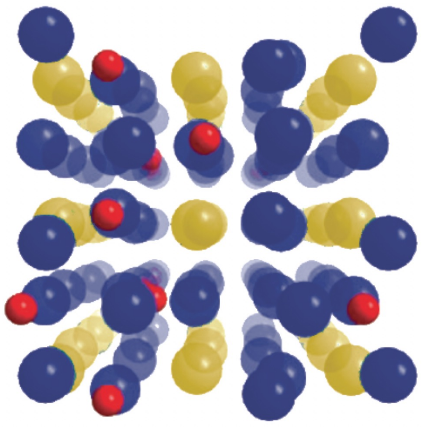




- Reconstructions
  - In-plane movements
  - Vertical (out-of-plane) movements also possible

Superstructure rods



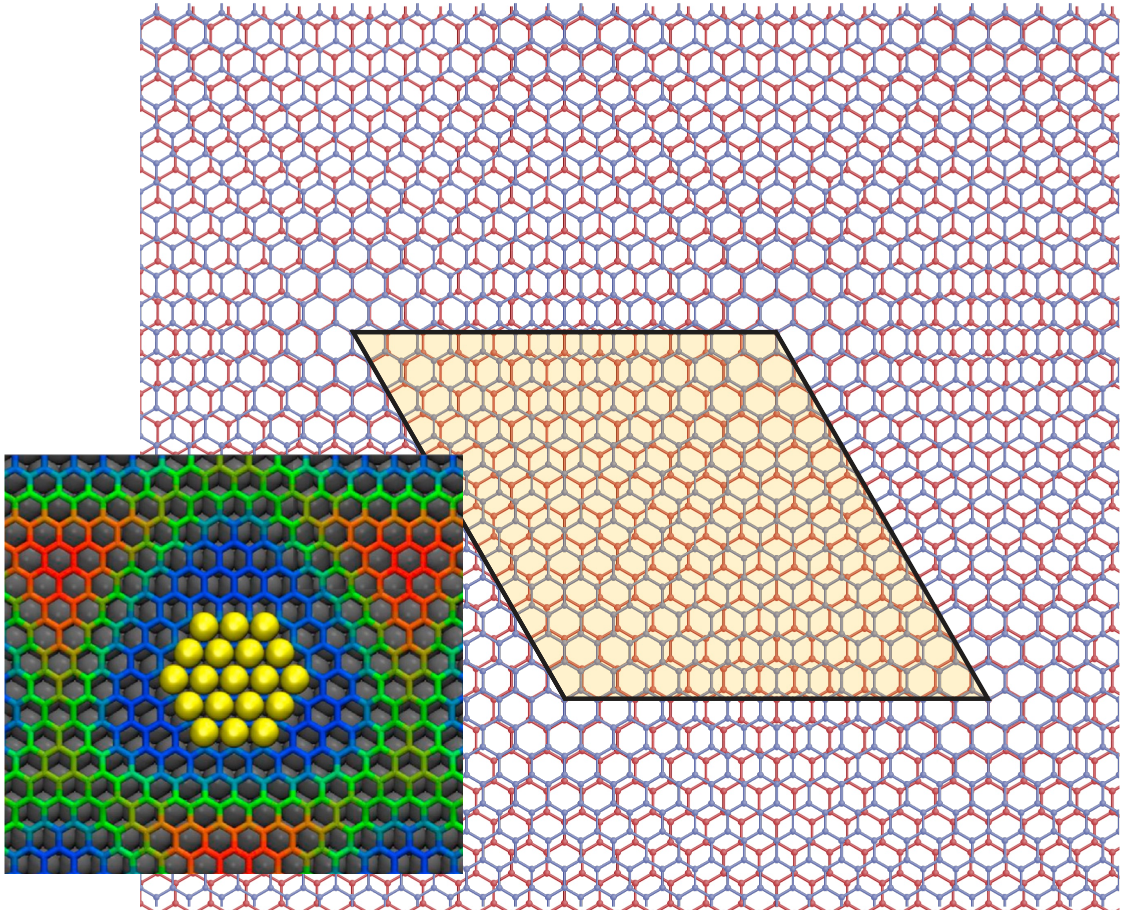


$SrTiO_3$ 2x2 surface
Ti: red, O: blue, Sr: yellow

- Sometimes called fractional-order rods
- Different in-plane periodicity than bulk structure
- No bulk contribution ⇒ no intense Bragg peaks
  - Intensities similar to minima of CTRs
- Intensity fluctuations much more modest than in CTRs
- Provide information exclusively about superstructure and not bulk

See R. Herger *et al.*, https://doi.org/10.1103/PhysRevLett.98.076102

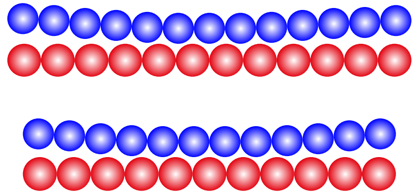
Example – graphene on ruthenium



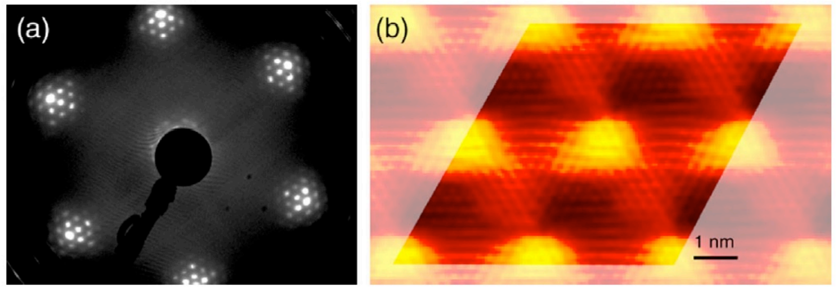
- Graphene on ruthenium(0001)
  - Corrugated moiré pattern
  - Literature 2007
    - 13x13 on 12x12?

      or

    - 12x12 on 11x11?



- LEED and STM analysis ambiguous



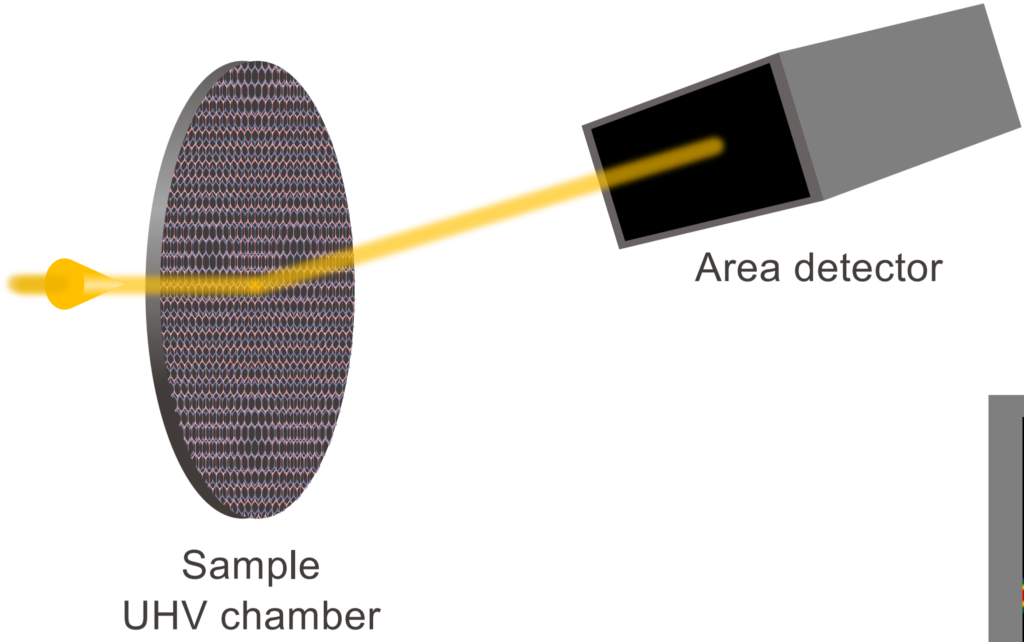
LEED STM

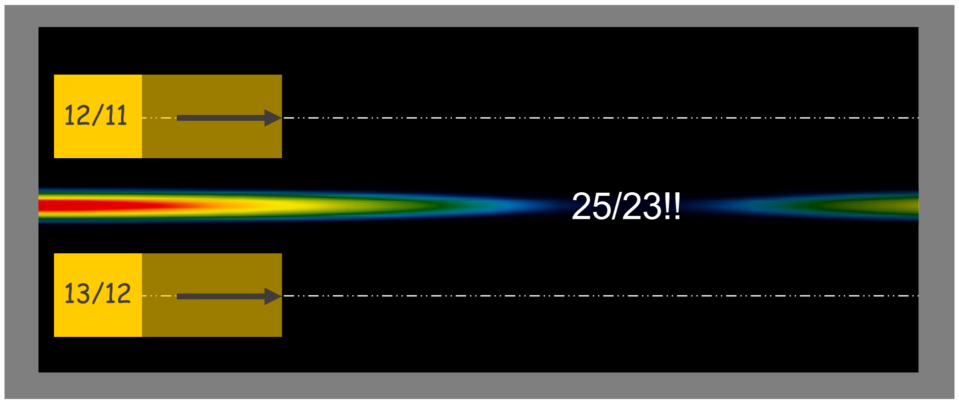
Image of nanoparticle on graphene from M. D. Jiménez-Sánchez *et al.*, Carbon https://doi.org/10.1016/j.carbon.2020.11.086

See D. Martoccia *et al.*, PRL (2008) DOI: 10.1103/PhysRevLett.101.126102

Example – graphene on ruthenium

- Experiment
  - Glancing-incident beam
  - Alignment calibrated to bulk Ru-substrate diffraction signal
    - Accuracy 0.0002 r.l.u.
  - In-plane position of superstructure rods

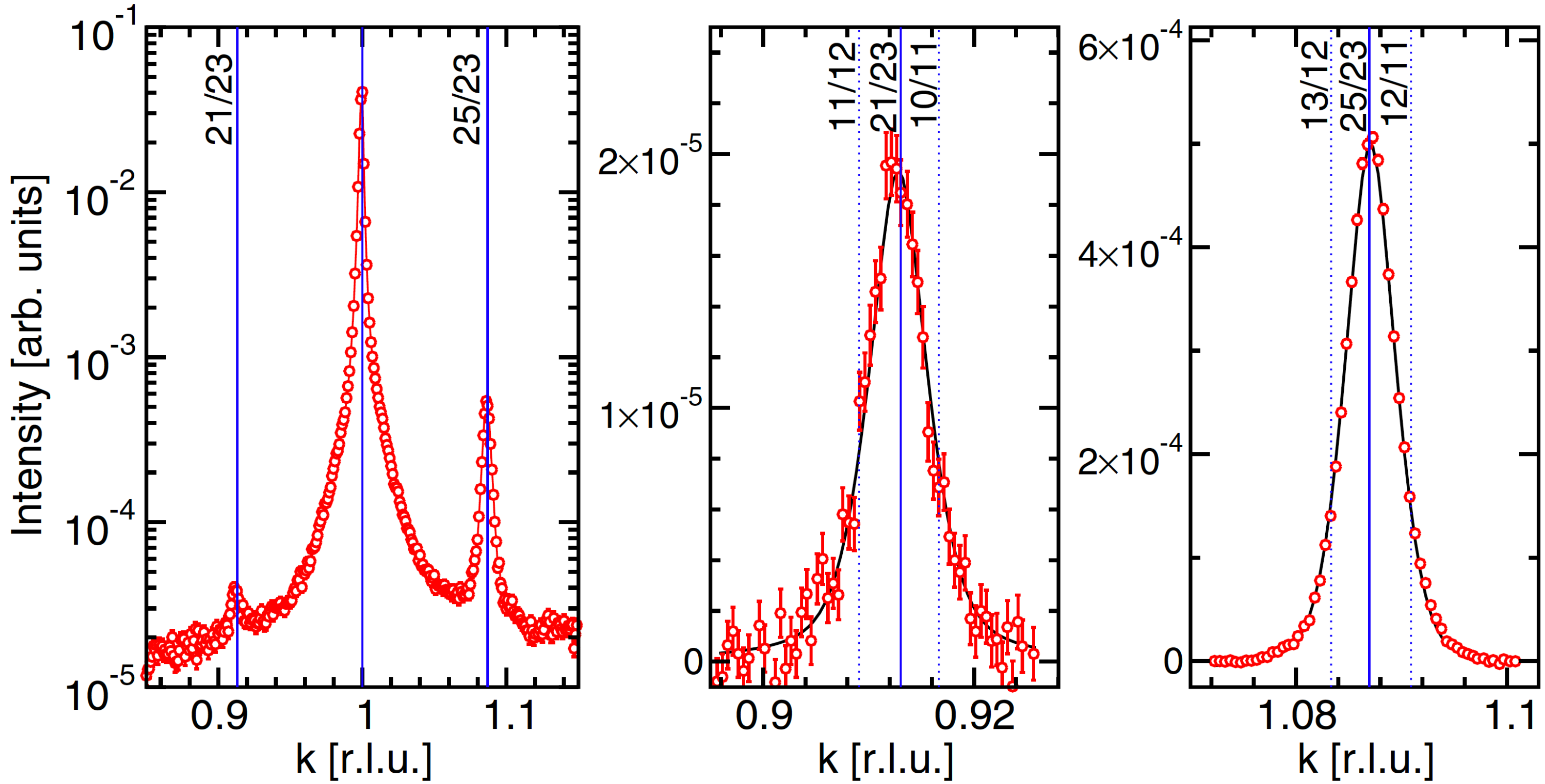




See D. Martoccia *et al*., PRL (2008) DOI: 10.1103/PhysRevLett.101.126102

Example – graphene on ruthenium

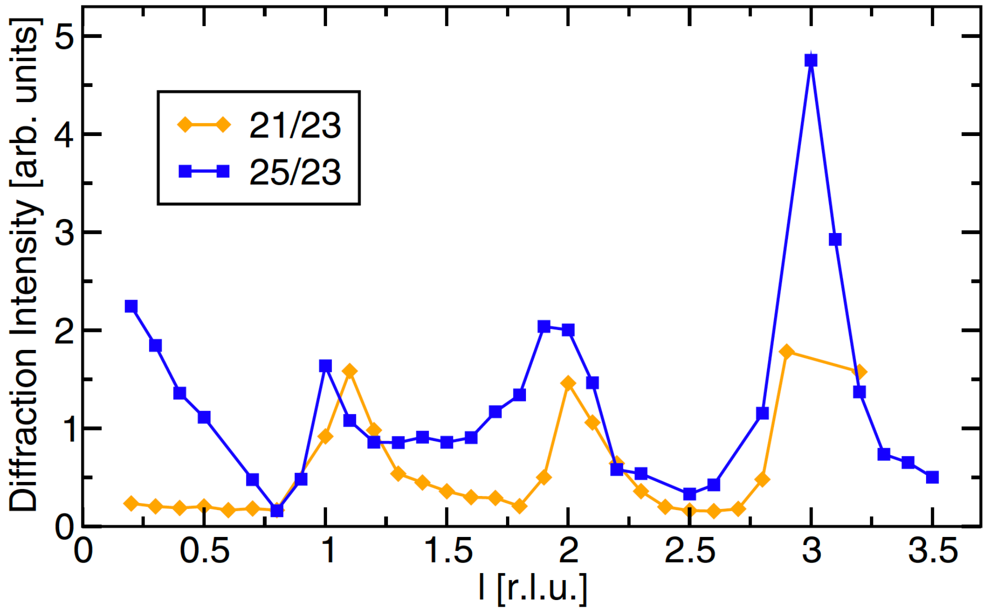
- In-plane data (scans at a constant out-of-plane scattering vector $Q_\perp$)

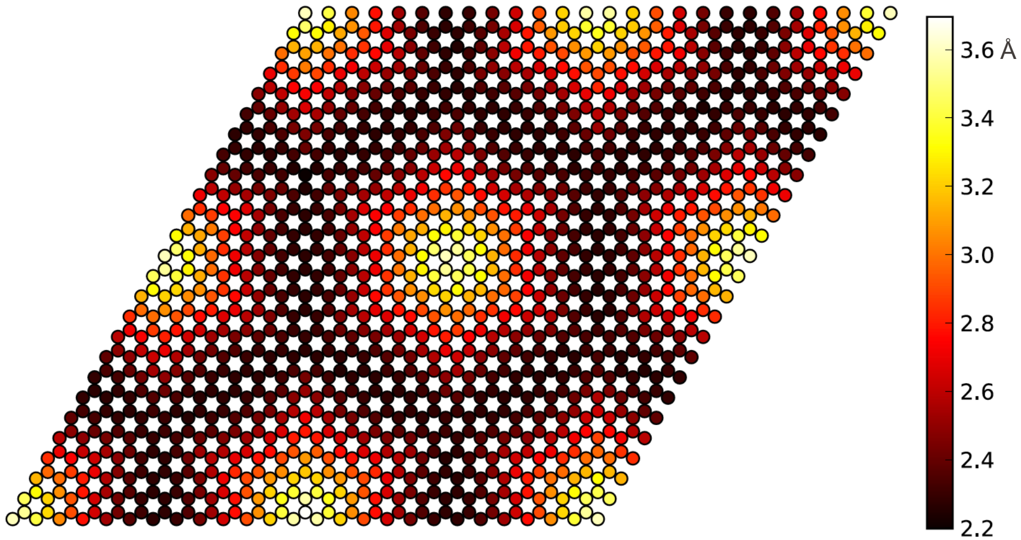


See D. Martoccia *et al.*, PRL (2008) DOI: 10.1103/PhysRevLett.101.126102

Example – graphene on ruthenium

- Out-of-plane data (scans along the l direction for fixed h and k)
  - Probes out-of-plane positions of top Ru layer and graphene
  - (0 25/23 L) and (0 21/23 L) rods
  - Model to data indicates corrugation amplitude ~ 1.4 Å





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Coming up…