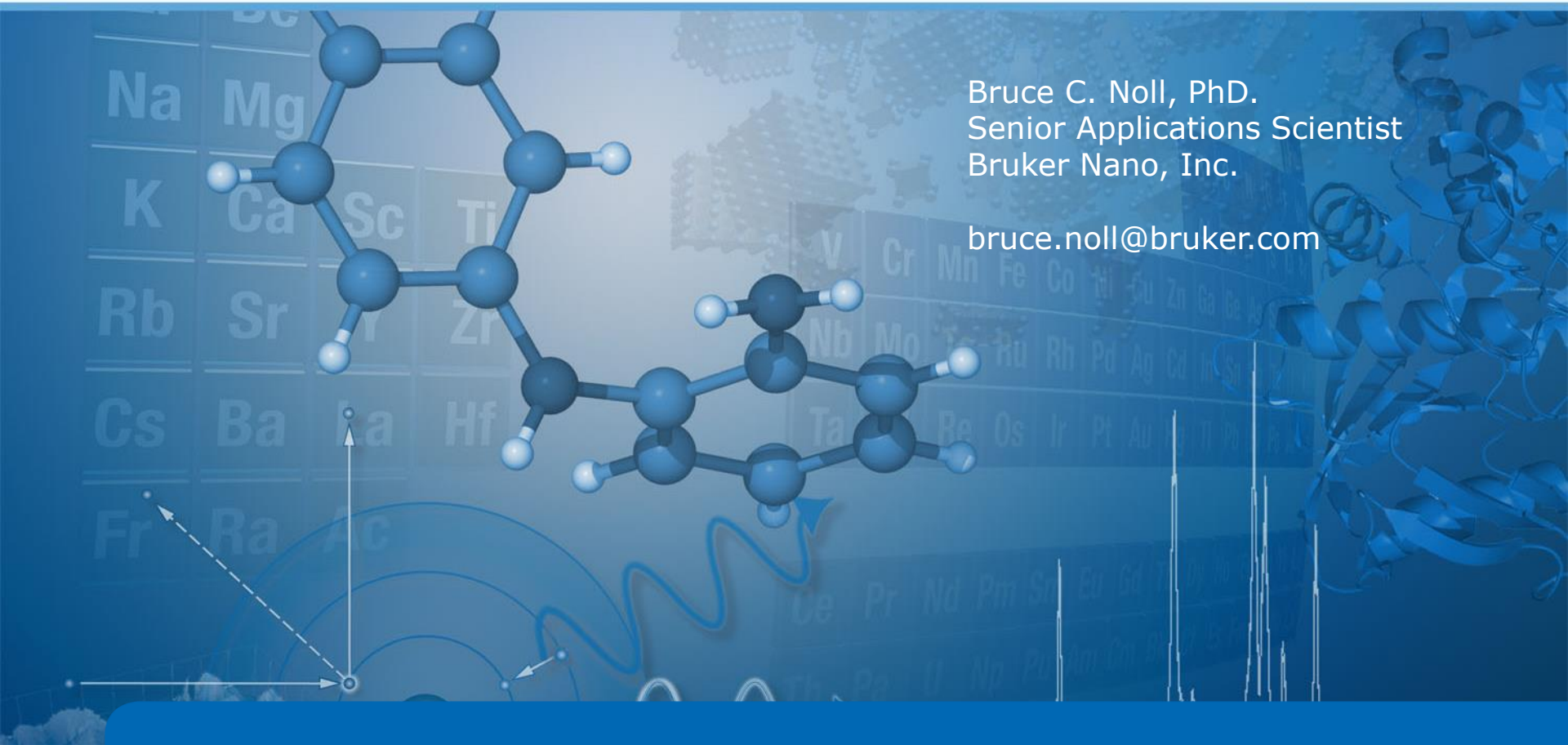
Bragg's Law



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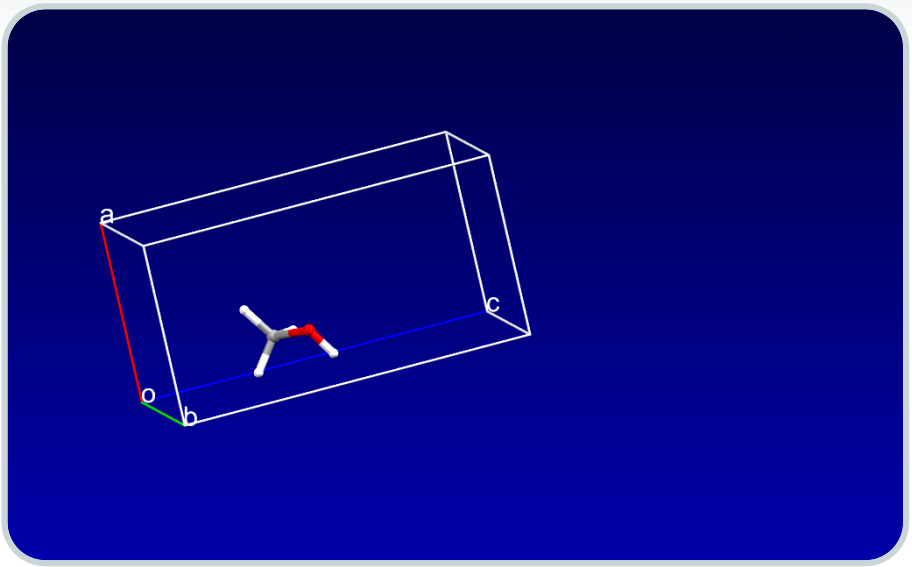
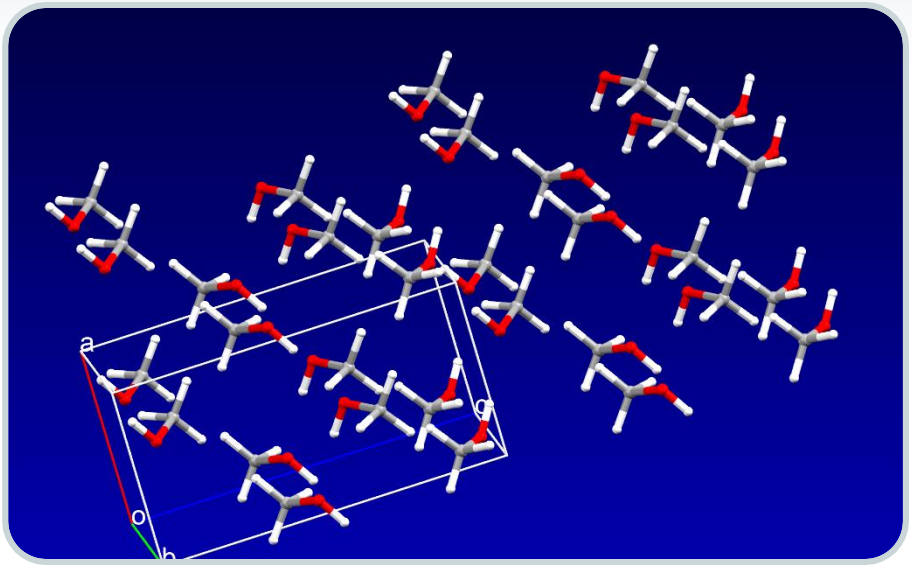
What is a Crystal?

- a body that is formed by the solidification of a chemical element, a compound, or a mixture and has a regularly repeating internal arrangement of its atoms and often external plane faces—*Merriam Webster*

Crystal Structure of Methanol





Methanol	
Orthorhombic	$P2_12_12_1$, Z=4
a= 4.647(<1) Å	σ= β= γ= 90°
b= 4.929(1) Å	
c= 9.040(1) Å	
M.T.Kirchner, D.Das, R.Boese,(2008) Cryst.Growth Des. ***8****, 763*	

Miller indices

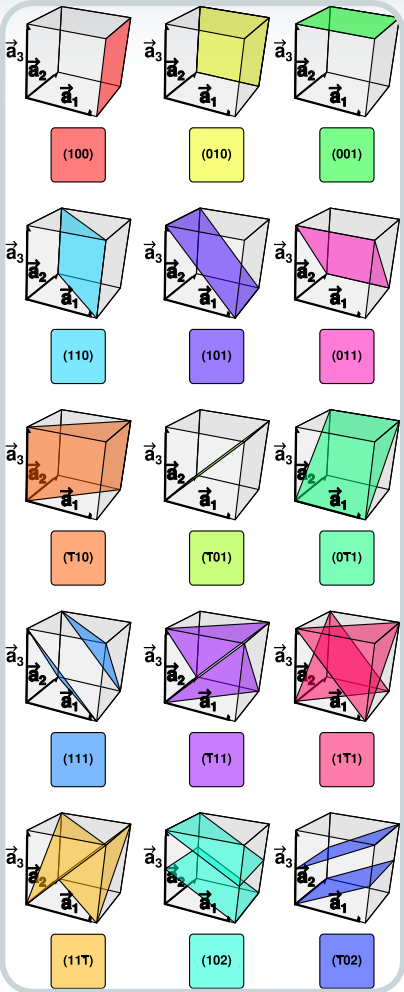
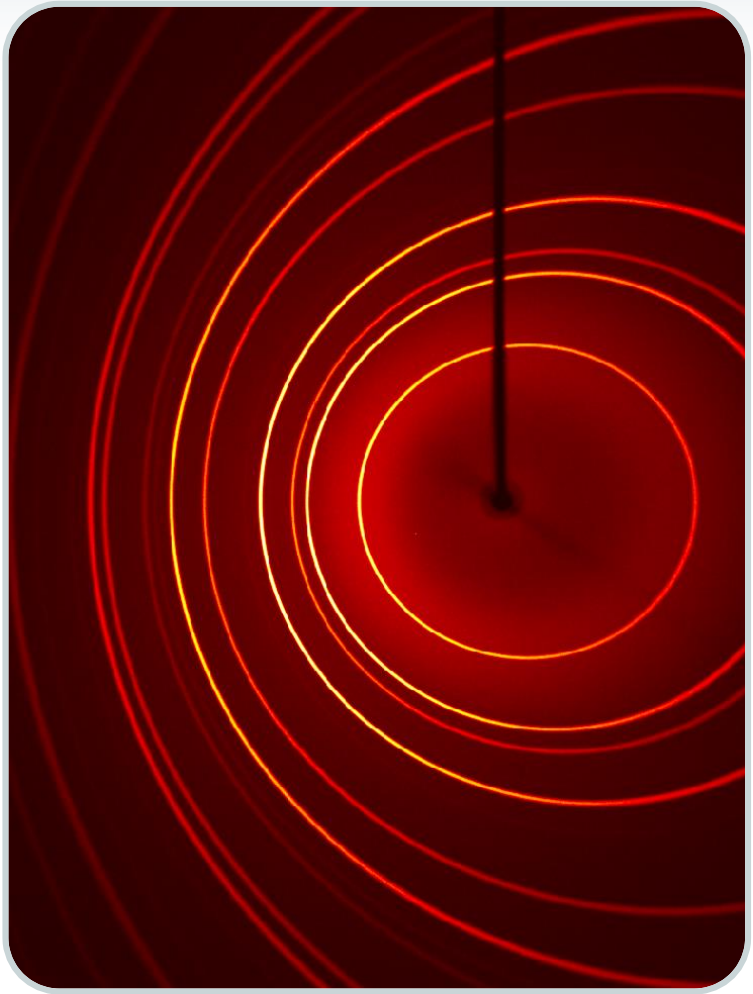
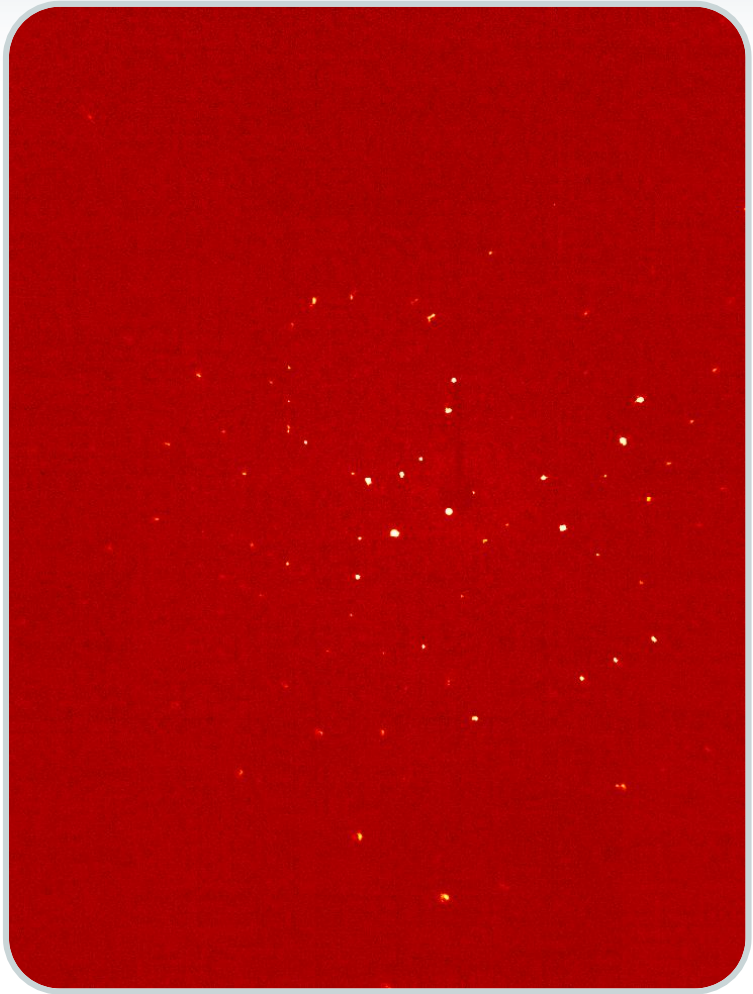


image: Felix Kling

- Notation introduced by William Hallowes Miller in 1839
- Miller indices indicate family of lattice planes. In typical crystals, these are integers, *h,k,l.* For quasicrystals, these indices may be irrational. The indices correspond to the directions of reciprocal lattice of the crystal. A value of 0 for any index indicates that the lattice plane does not intersect that vector.
- Example 1: (100) is a plane parallel to the b and c lattice vectors, intersecting the a-axis at one unit length.
- Example 2: (020) is a plane that runs parallel to a and c, intersecting the b-axs at $\frac{1}{2}$ unit length.

X-ray Diffraction





Diffraction of X-rays by Crystals

- Von Laue discovers diffraction of X-rays by crystals in 1912
- Awarded Nobel Prize in Physics in 1914

Max Theodor Felix von Laue (1879 – 1960)

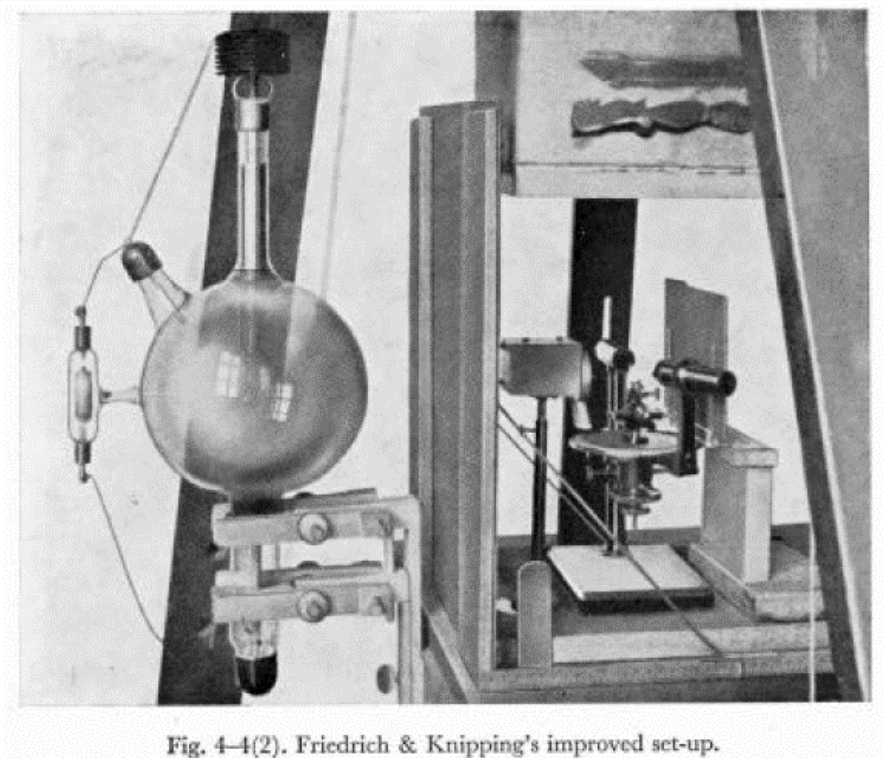
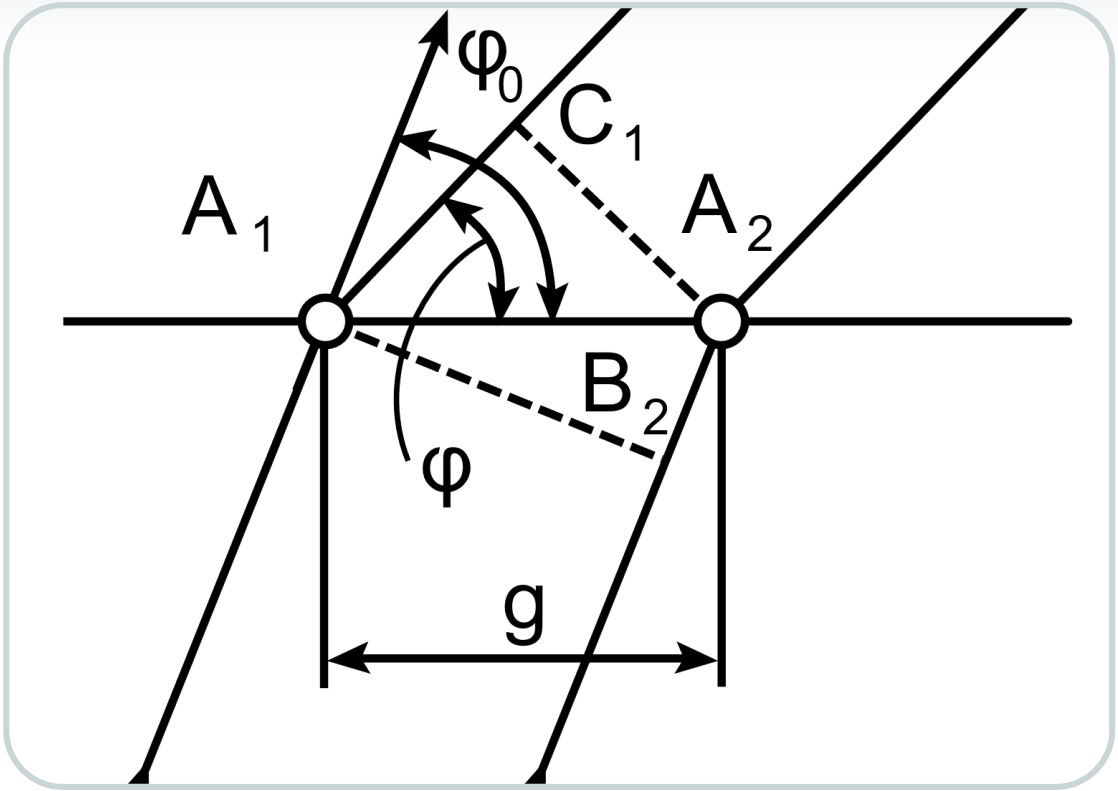


Fig. 4–4(2). Friedrich & Knipping's improved set-up.

https://www.sas.upenn.edu/~mhayden/mcep/chem507/project/history/history.html

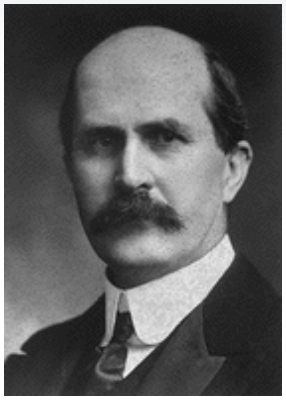
Laue Equations



- Laue equations
  - $\mathrm{a} \cdot \Delta\mathrm{k} = 2\pi h$
  - $\mathrm{b} \cdot \Delta\mathrm{k} = 2\pi k$
  - $\mathrm{c} \cdot \Delta\mathrm{k} = 2\pi l$
- a,b,c are primitive vectors of crystal lattice
- $\Delta\mathrm{k} = \mathrm{k}_{in} - \mathrm{k}_{out}$
- $\Delta\mathrm{k} =$ scattering vector
- For diffraction, (*h,k,l*) must be integers

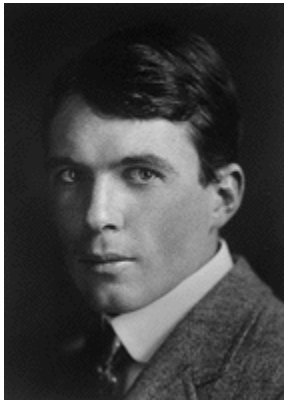
Diffraction of X-rays by Crystals

After Von Laue's pioneering research, the field developed rapidly, most notably by physicists William Lawrence Bragg and his father William Henry Bragg.



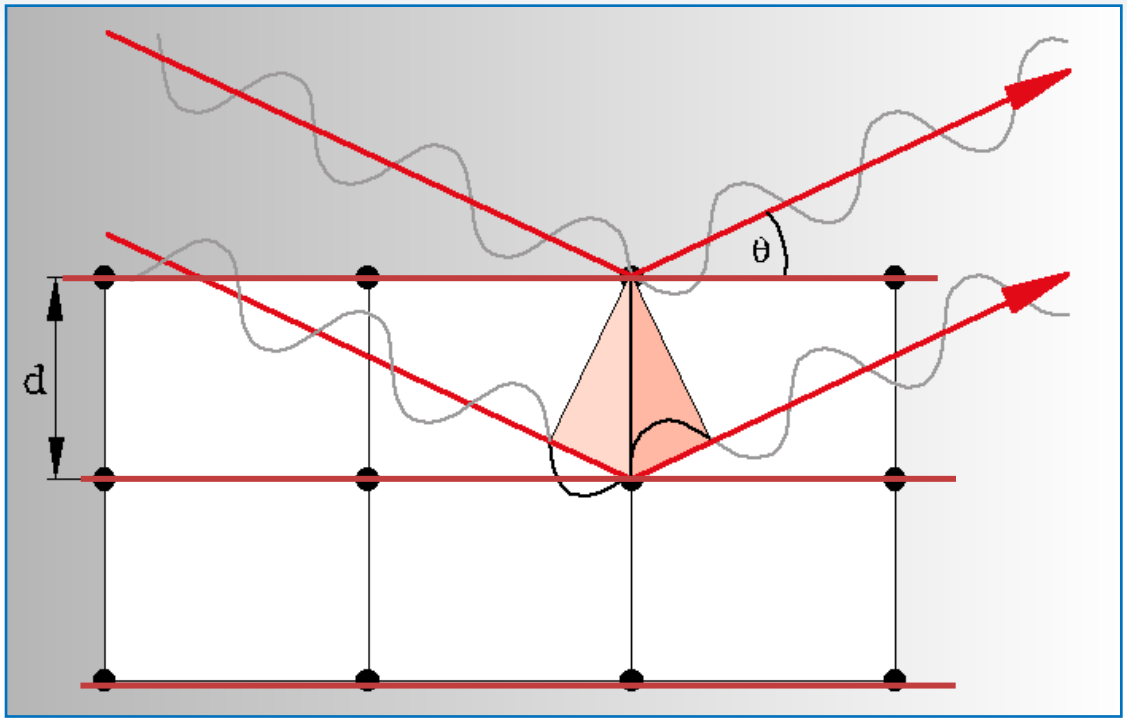
William Henry Bragg

In 1912-1913, the younger Bragg developed Bragg's law, which connects the observed scattering with reflections from evenly-spaced planes within the crystal.



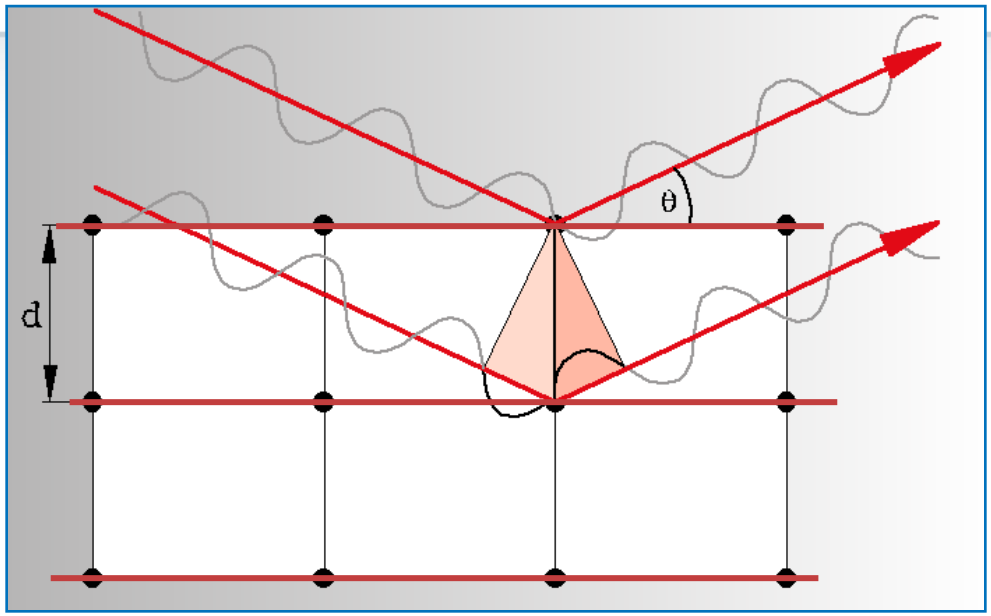
William Lawrence Bragg

Bragg's Law

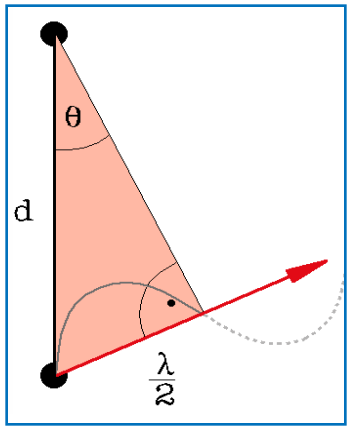


- X-rays scattering coherently from 2 of the parallel planes separated by a distance d.
- Incident angle and reflected (diffracted angle) are given by θ.

Bragg's Law



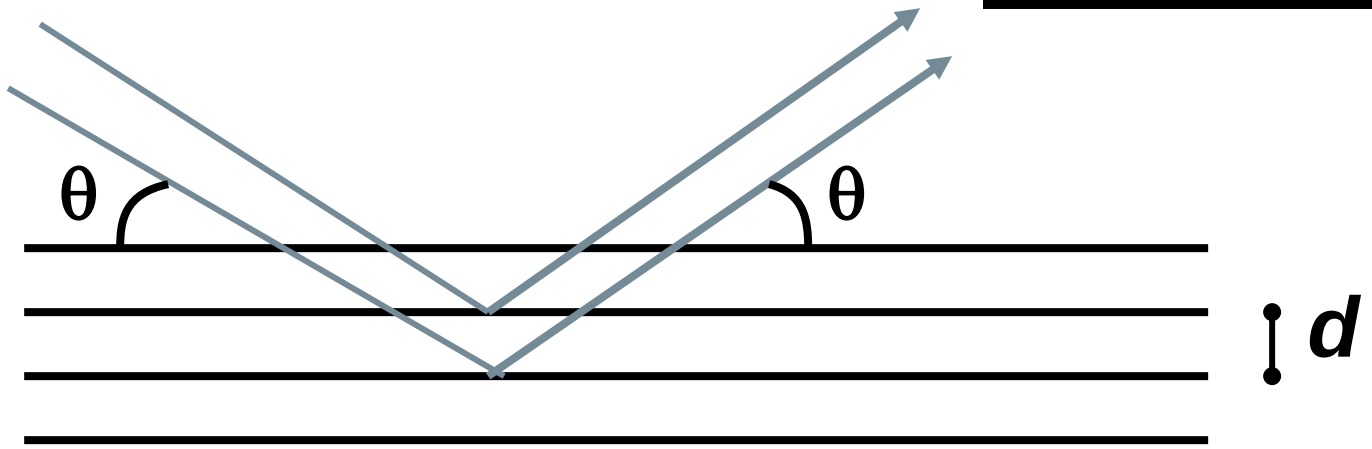
- The condition for constructive interference is that the path difference leads to an integer number of wavelengths.
- Bragg condition → concerted constructive interference from periodically-arranged scatterers.
- This occurs ONLY for a very specific geometric condition.



$$\frac{\lambda}{2} = d \cdot \sin\theta \longrightarrow n\lambda = 2d\sin\theta$$

Bragg's Law

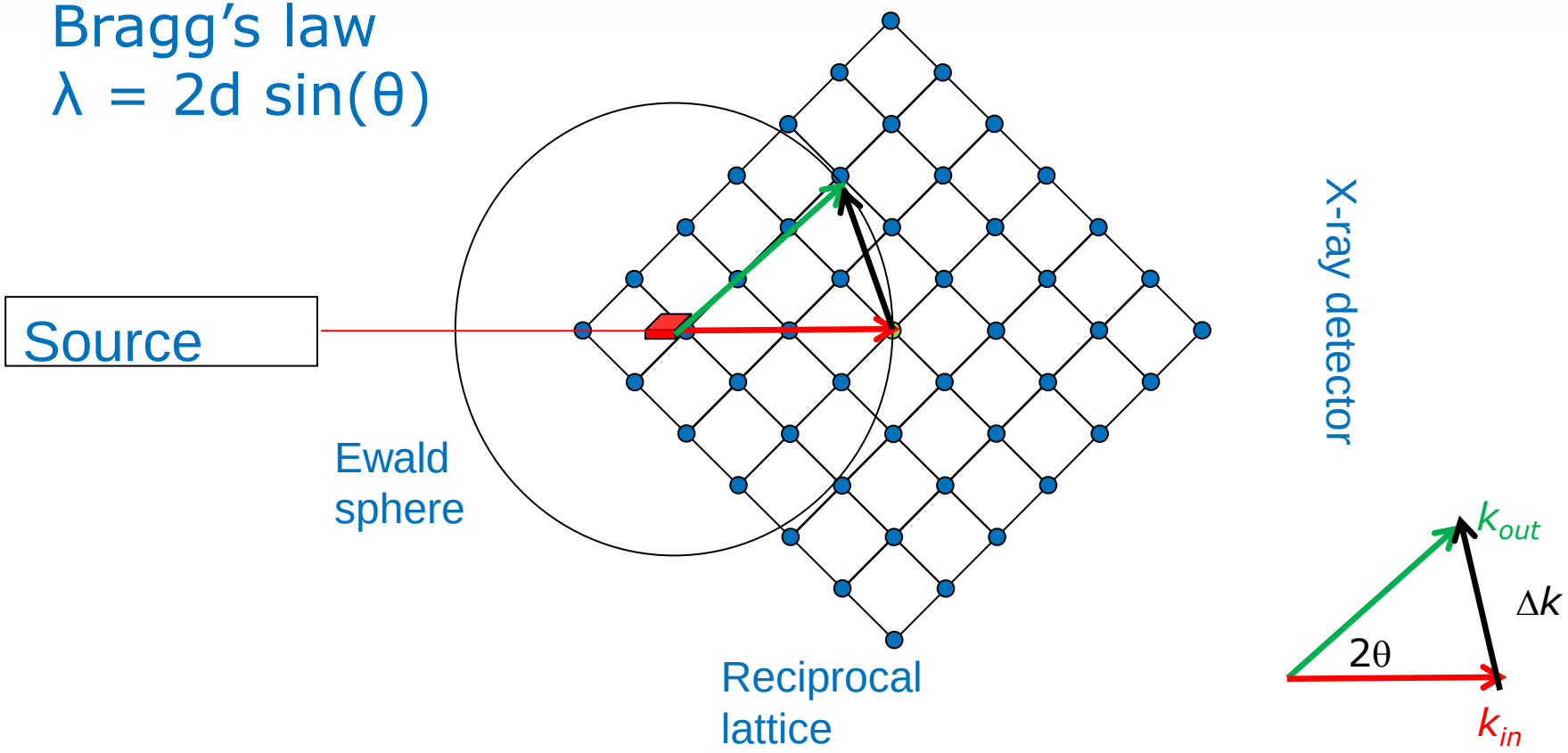
$$n\lambda = 2d \sin(\theta)$$



We can think of diffraction as reflection at sets of planes running through the crystal. Only at certain angles 2θ are the waves diffracted from different planes a whole number of wavelengths apart (i.e., in phase). At other angles, the waves reflected from different planes are out of phase and cancel one another out.

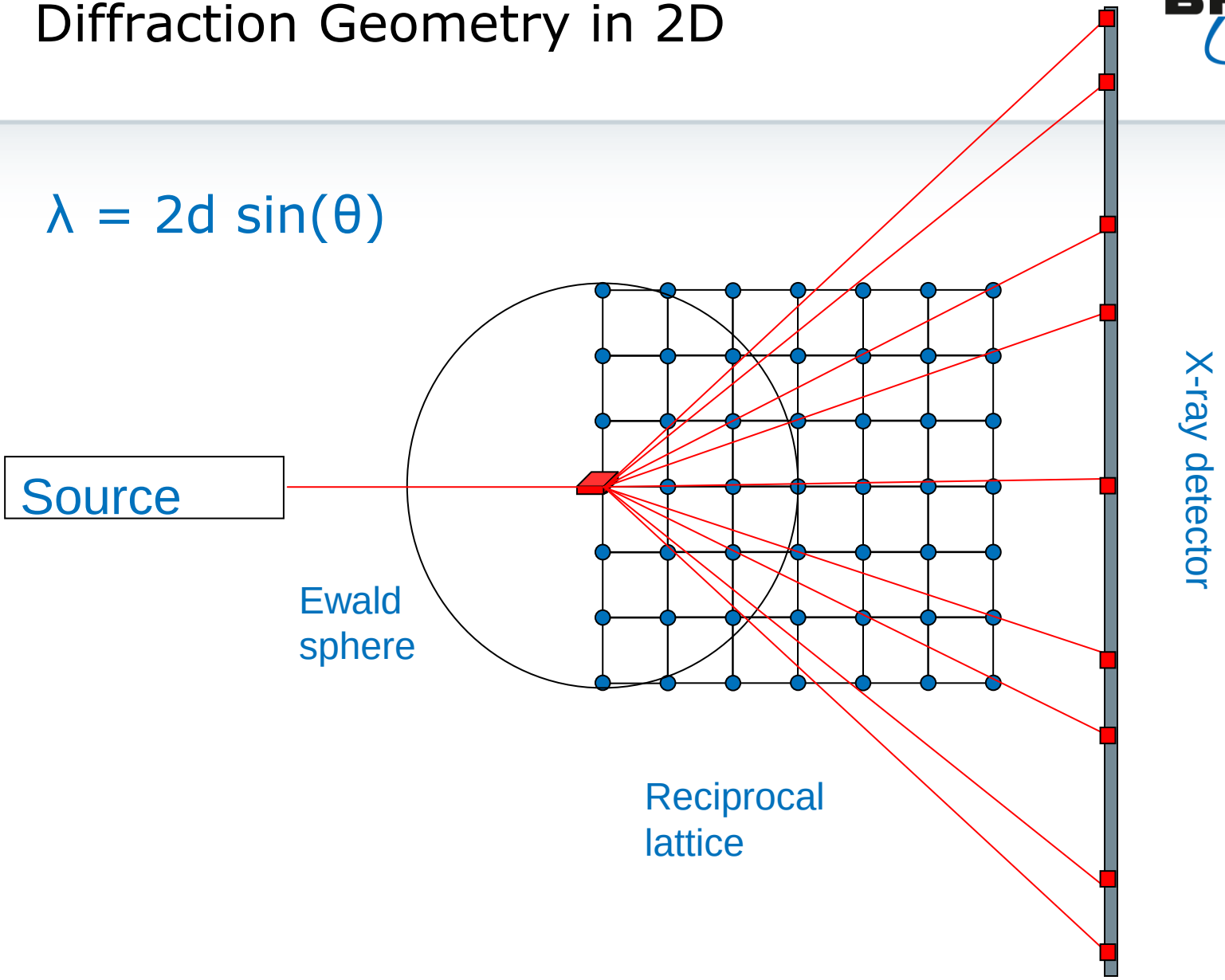
Diffraction Geometry in 2D

Bragg's law
$\lambda = 2d \sin(\theta)$

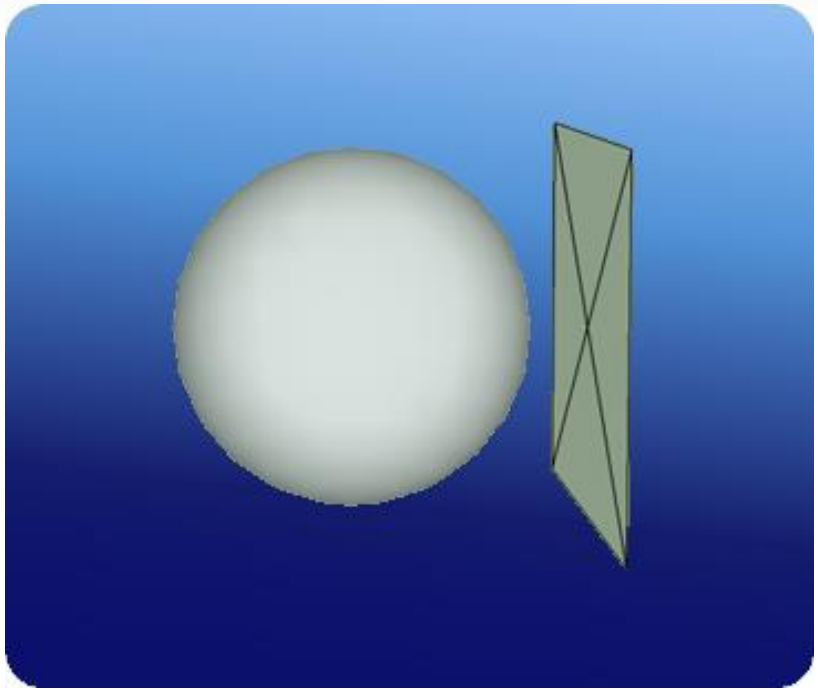


Diffraction Geometry in 2D

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



Detection area in 3D, square detector

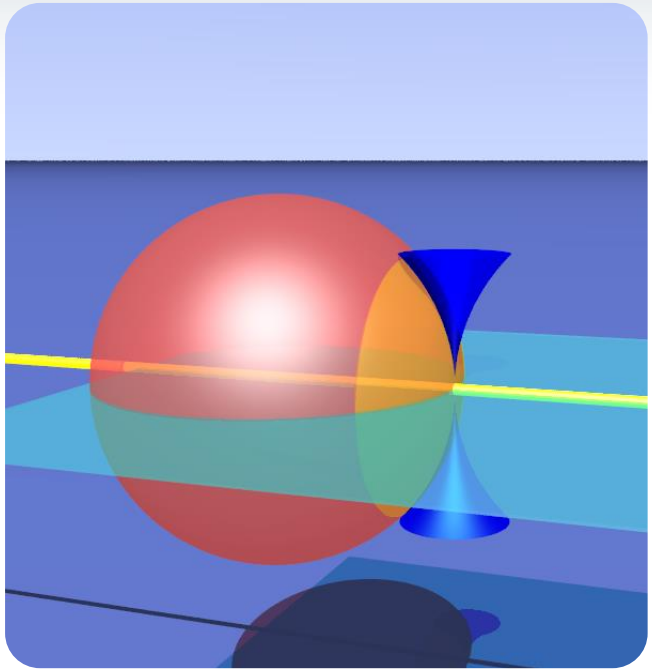


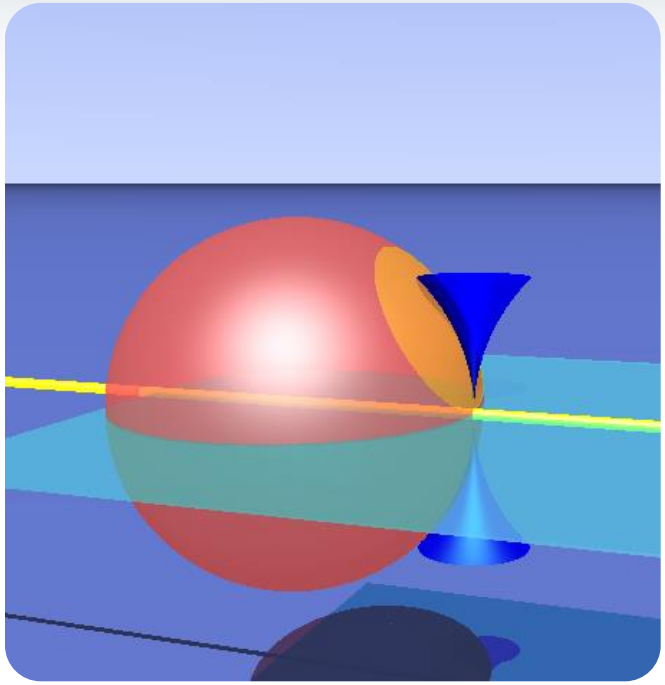
- The detection area of a detector is the projection of the (square) detector onto the surface of the Ewald sphere

Detection area in 3D, square detector

- The size of the detection area depends on the detector's size and its distance from the sample
- The position of detection area depends on the 2θ swing angle of the detector

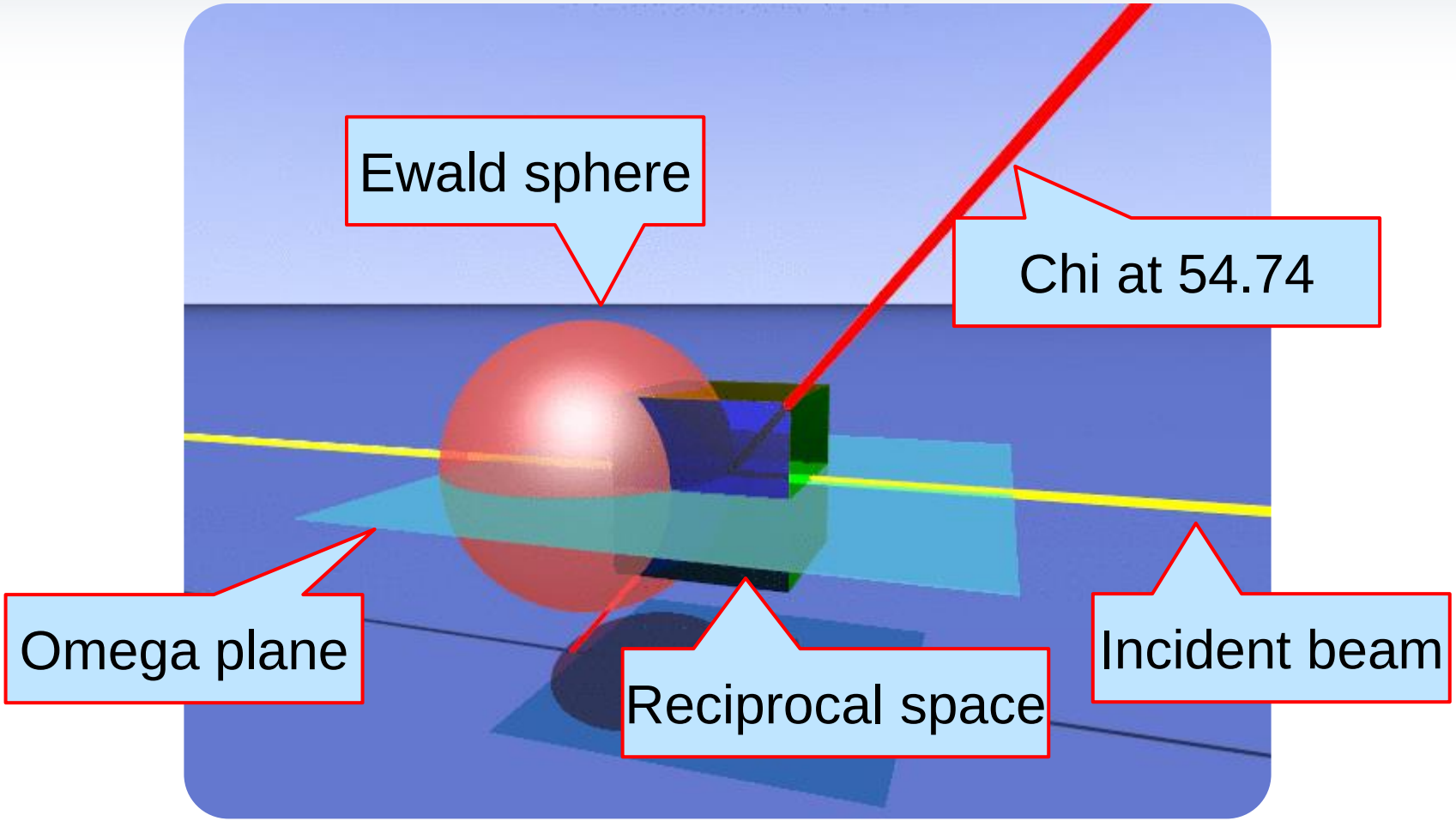
Cusp area



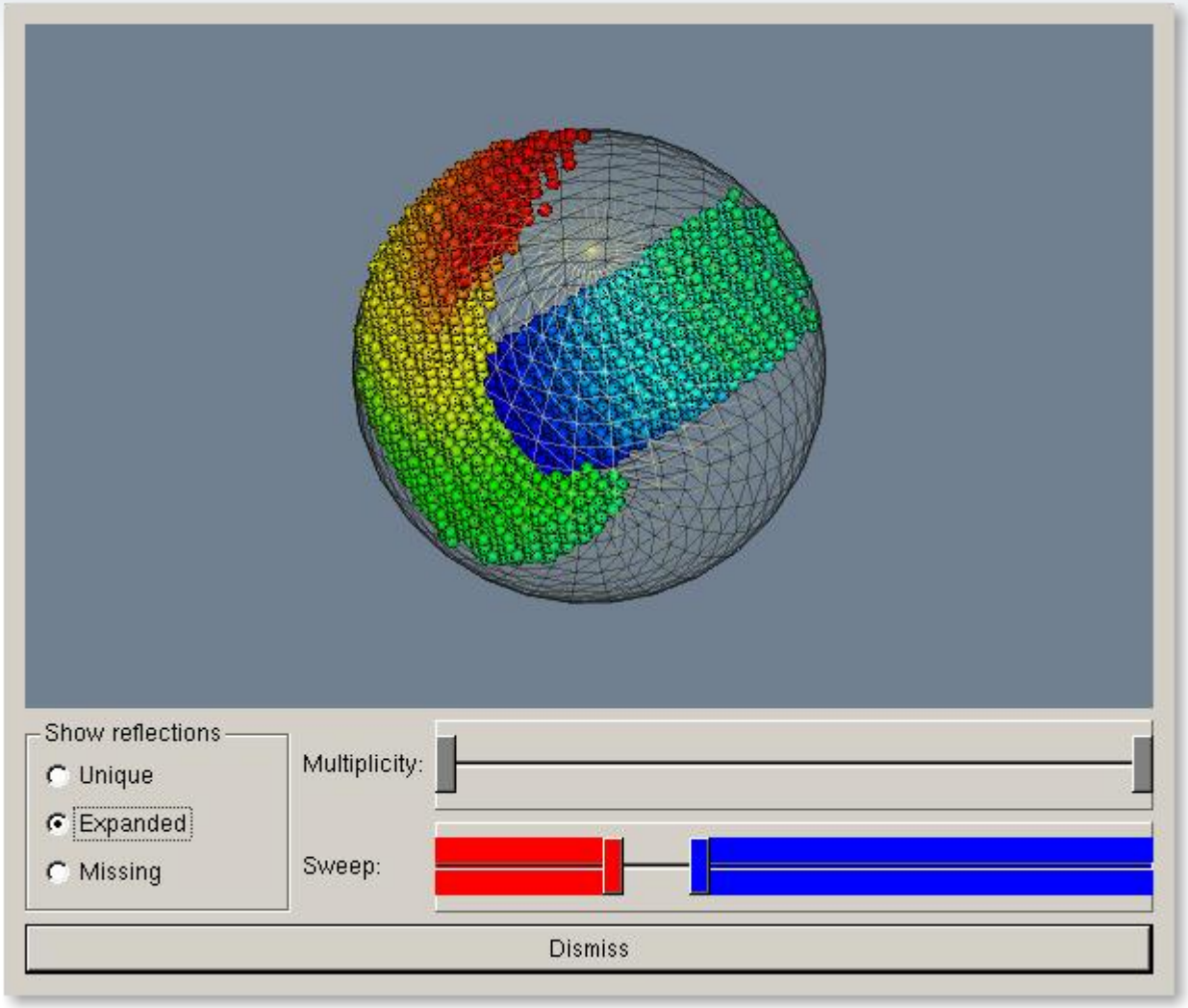


- One single scan will miss the cusp and will not be sufficient to collect true multiplicity
- Changing the crystal's orientation using one axis and scanning using another axis will allow the acquisition of missing data and
- Provide redundant data

Diffraction Geometry in 3D phi and omega scans

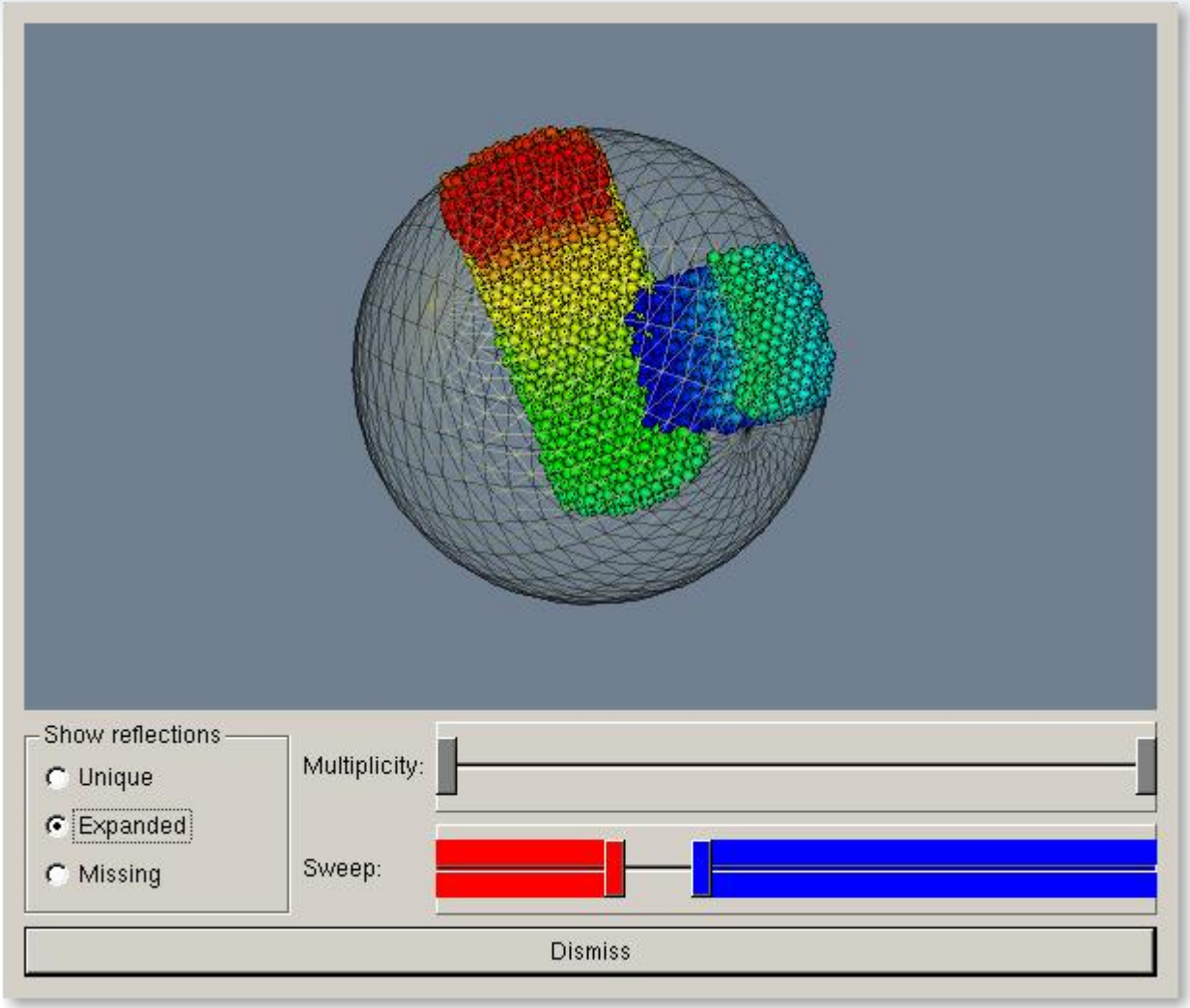


Omega scans



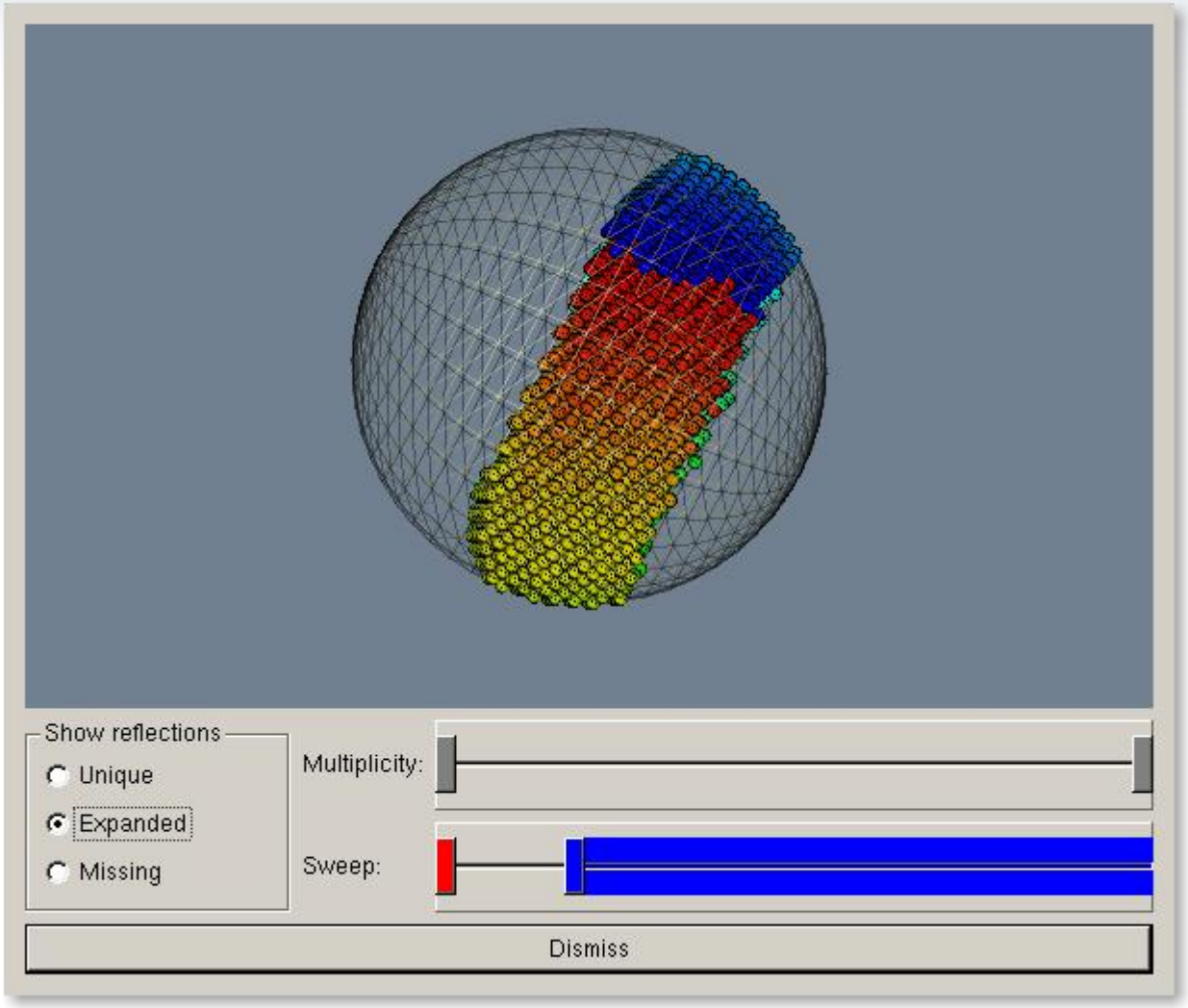
- omega scans are geometrically very flexible
- A combination of omega scans can cover reciprocal space very effectively

Omega scans



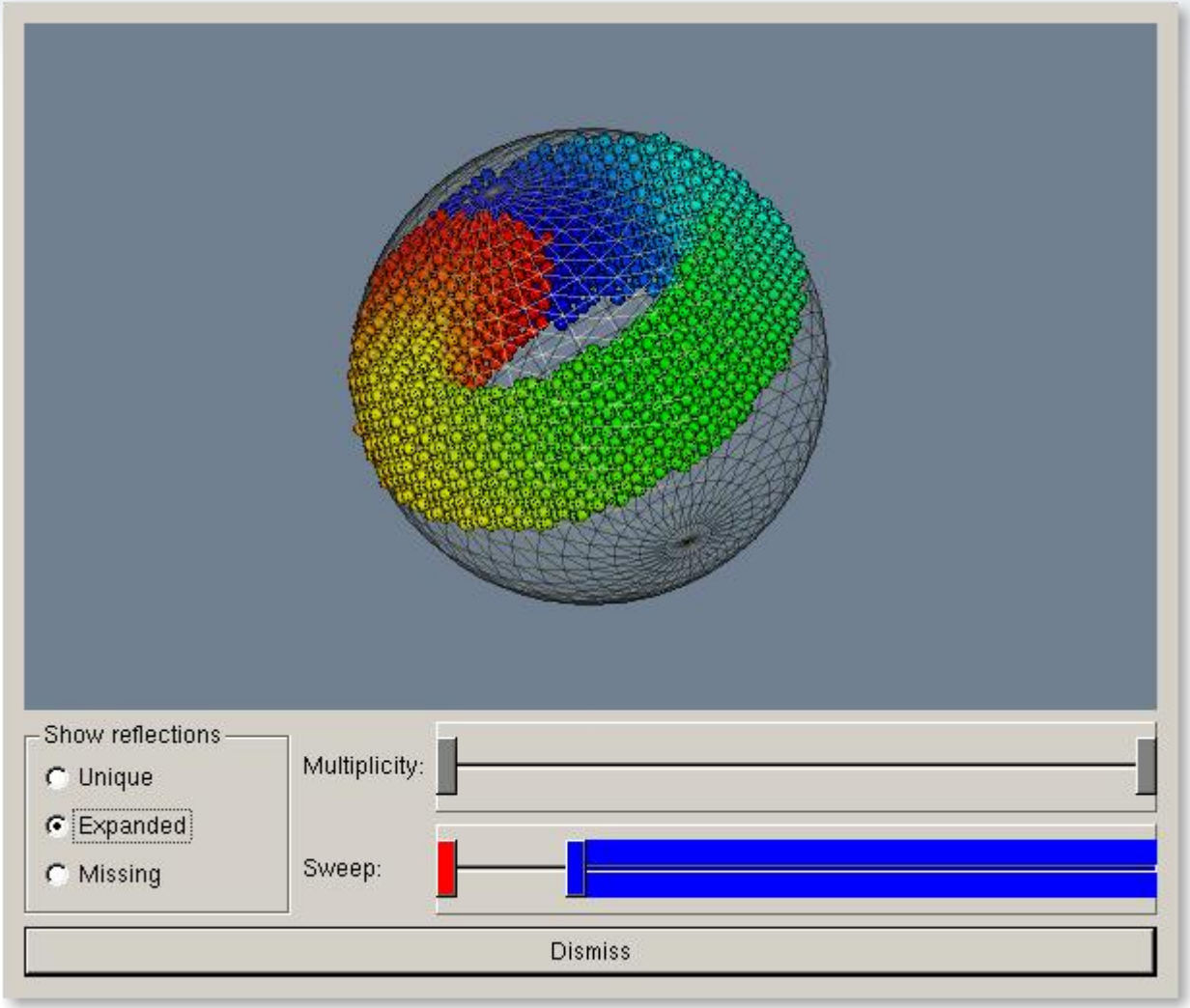
- omega scans are geometrically very flexible
- A combination of omega scans can cover reciprocal space very effectively

Phi Scan



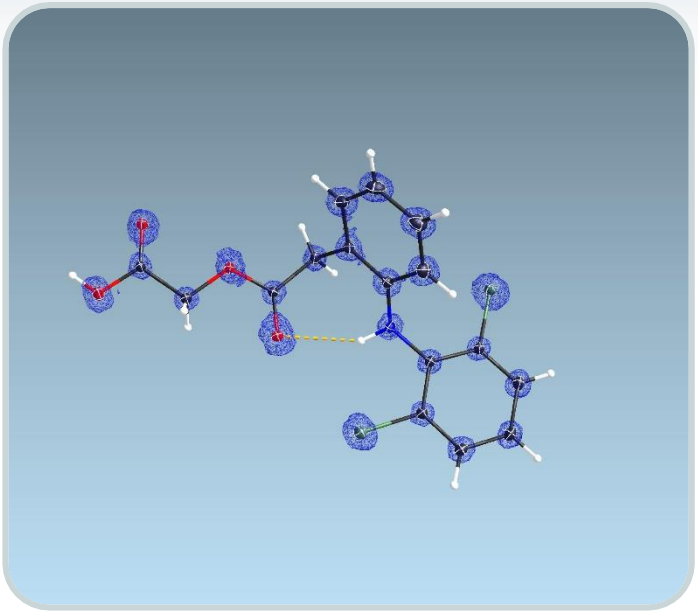
- Phi scans are always oriented along the phi spindle axis
- They are most efficient if they are perpen-dicular to the beam

Phi Scan



- Phi scans are always oriented along the phi spindle axis
- They are most efficient if they are perpen-dicular to the beam

Resolution

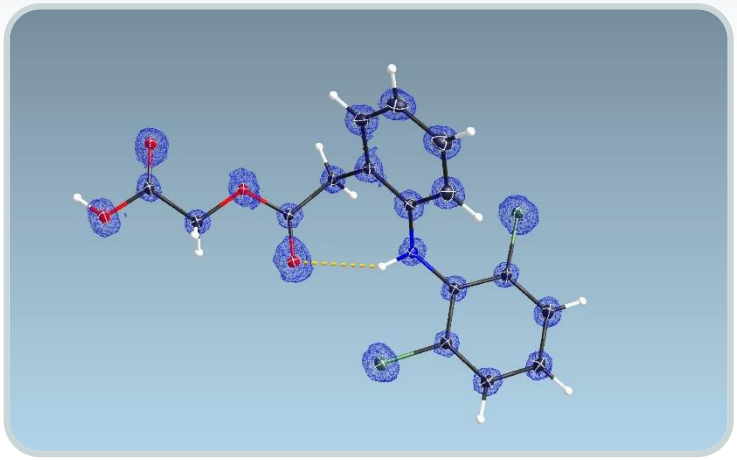


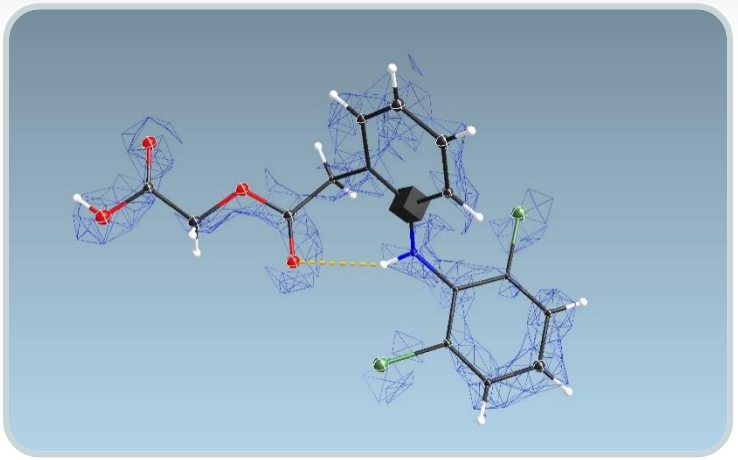
- Higher resolution provides better determination of atomic positions and more accurate values for derived geometry
- Resolution is limited by wavelength of radiation and by instrument geometry
- Maximum resolution is given by Bragg's Law. Solve for d:

$$d = \frac{\lambda}{2\sin(\theta)}$$

- Highest resolution will be at $\sin(\theta)=1$, so $d = \frac{\lambda}{2}$
- For Cu Kα (1.54178 Å) d_{max}= 0.77 Å;
- For Mo Kα (0.71073 Å) d_{max}= 0.36 Å

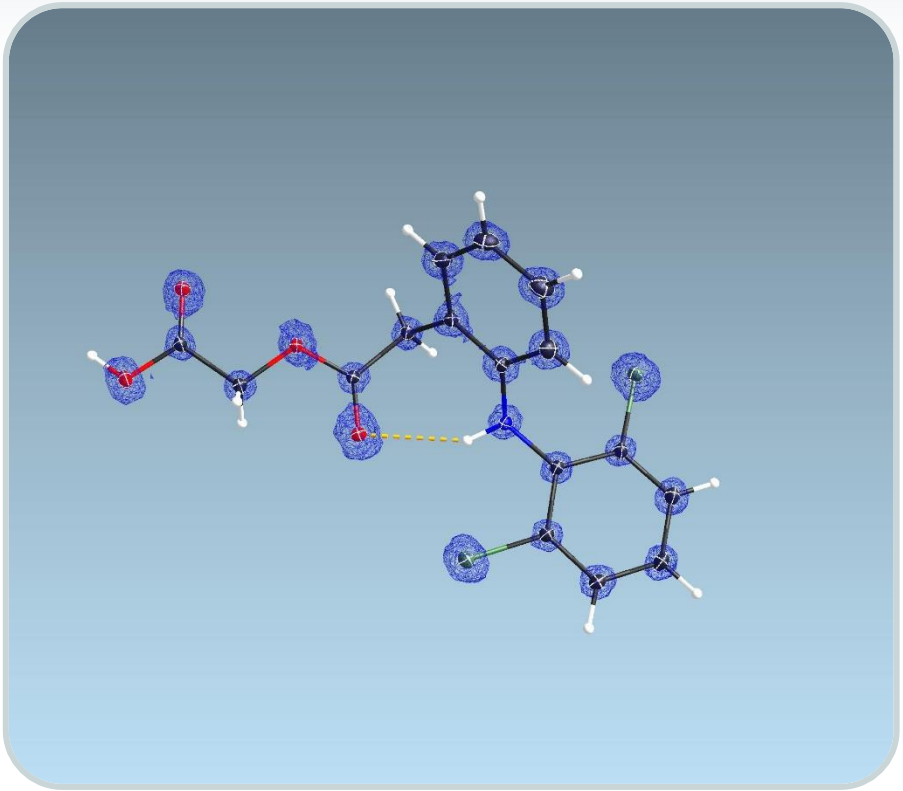
Impact of Resolution on Structure Determination





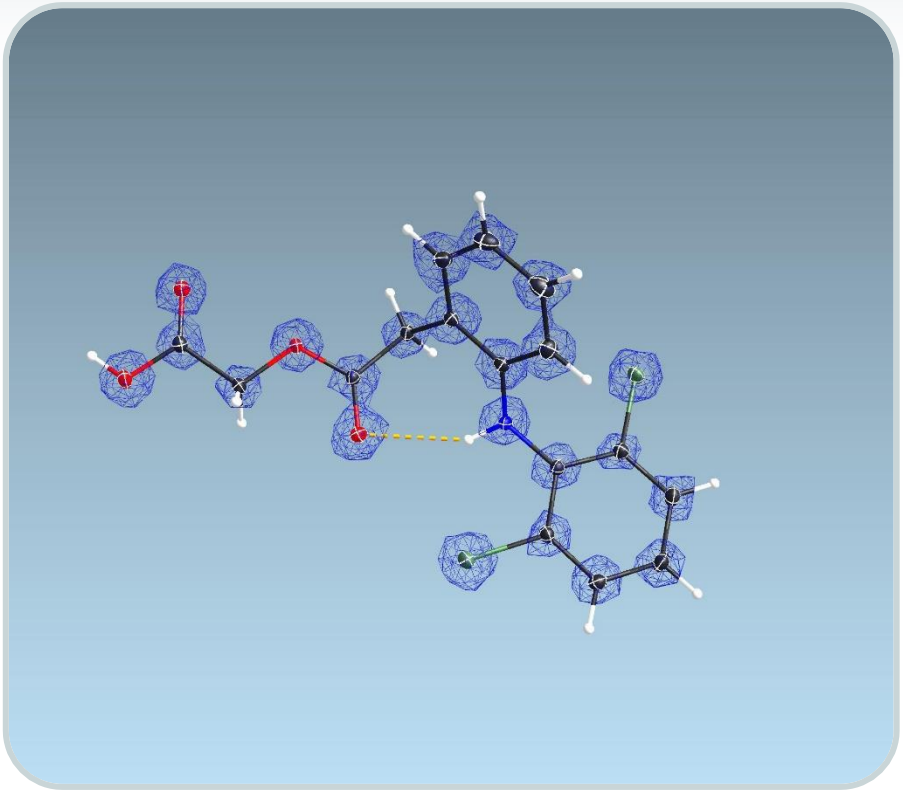
resolution/Å	data	parameters	ratio	R1	peak/e·Å³	hole/e·Å³
0.36	32178	216	149.0	0.0246	0.62	-0.65
0.60	7373	216	34.1	0.0223	0.58	-0.25
0.75	3773	216	17.5	0.0245	0.42	-0.30
0.80	3047	216	14.1	0.0241	0.33	-0.30
0.83	2787	216	12.9	0.0236	0.28	-0.31
0.95	1859	216	8.6	0.0223	0.18	-0.29
1.00	1594	216	7.4	0.0219	0.17	-0.30
1.50	474	101	4.7	0.0304	0.13	-0.22

Structure refinement to 0.36 Å



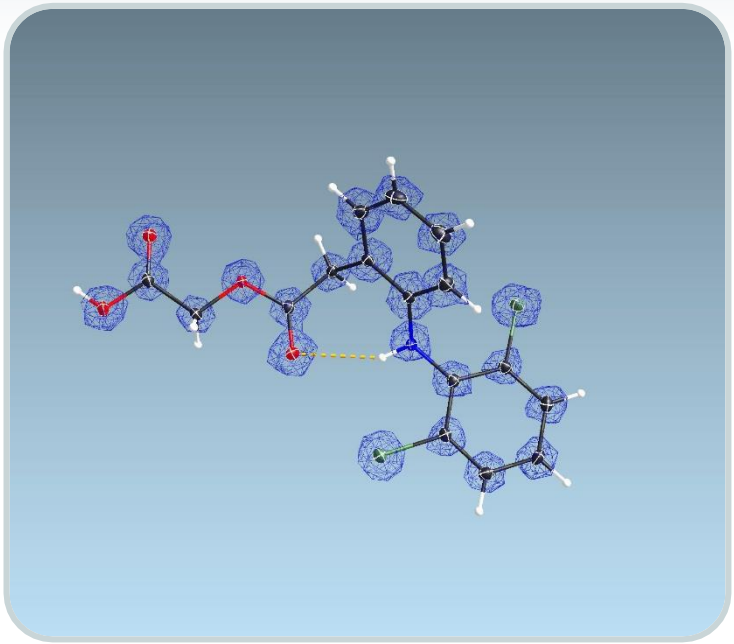
- 32178 unique data
- 149:1 data to parameter ratio
- 216 parameters
- Anisotropic refinement of thermal displacement parameters

Structure refinement to 0.75 Å

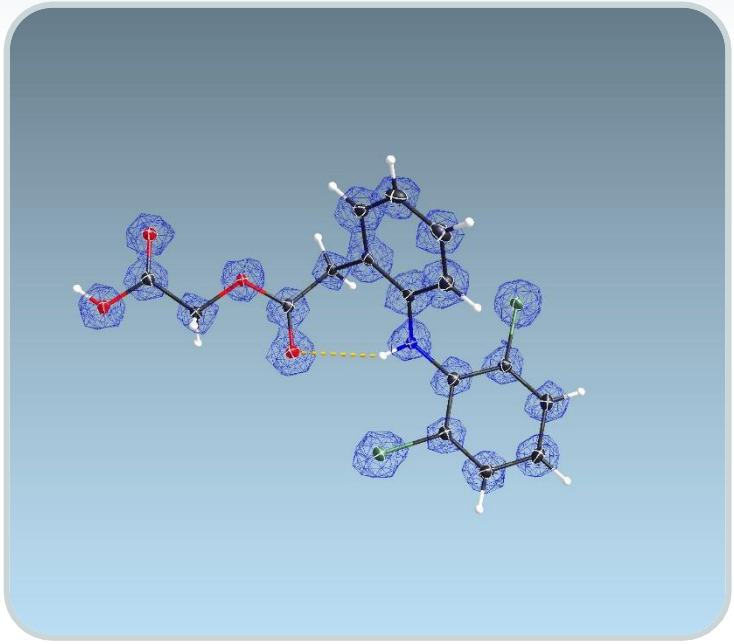


- 3773 unique data
- 17.5:1 data to parameter ratio
- 216 parameters
- Anisotropic refinement of thermal displacement parameters

Structure refinement to 0.80 and 0.83 Å

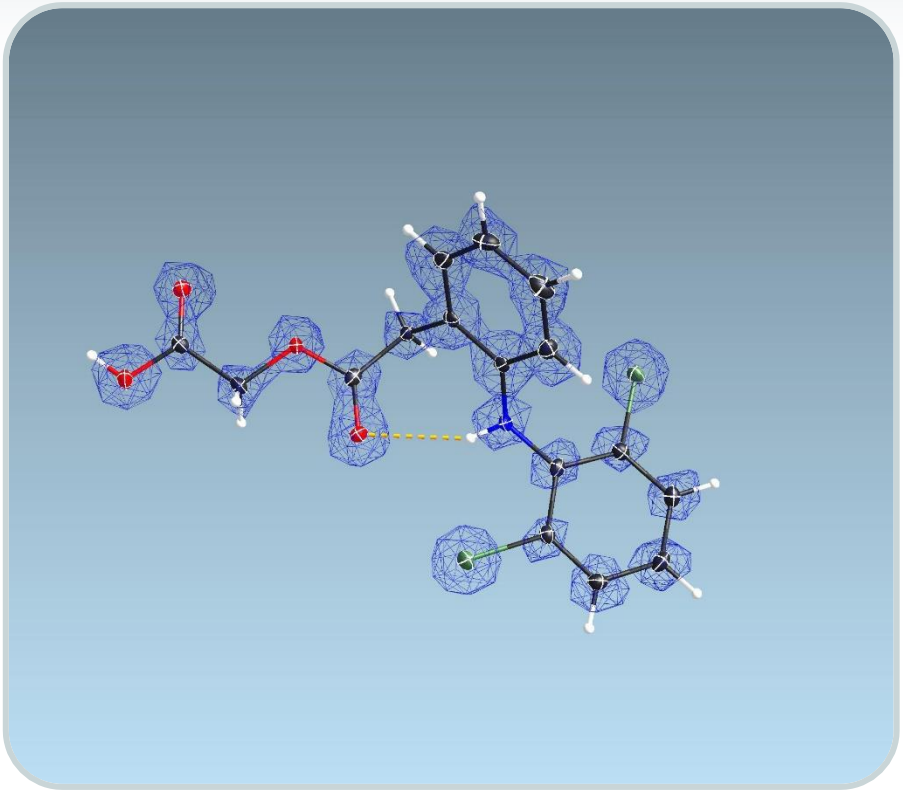


- 3047 unique data
- 216 parameters
- 14.1:1 data to parameter ratio



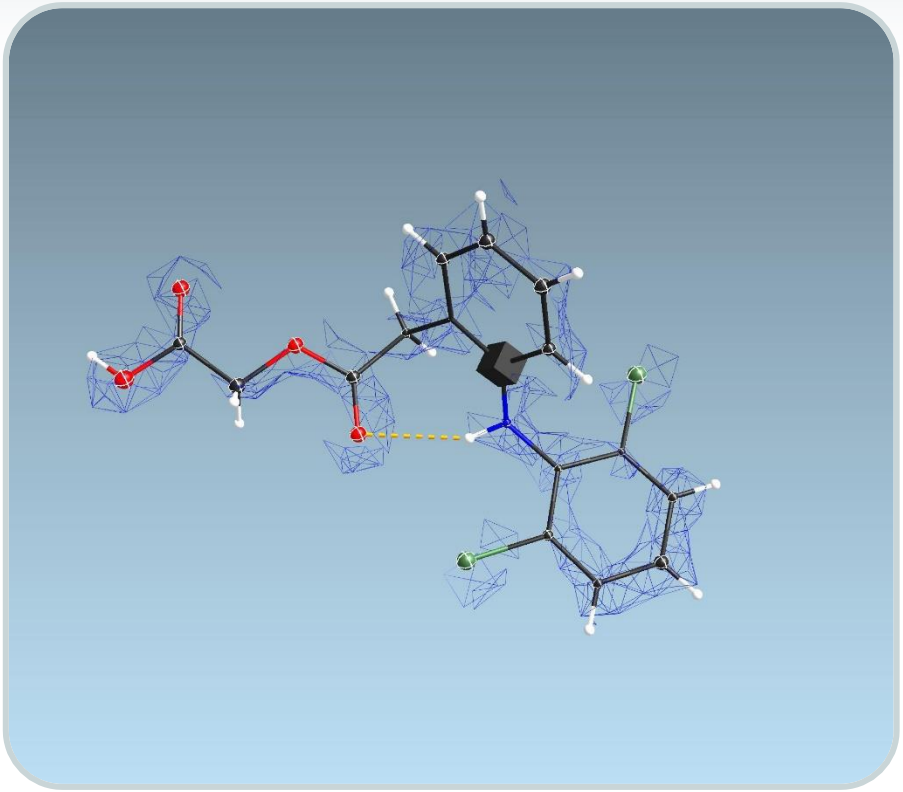
- 2787 unique data
- 216 parameters
- 12.9:1 data to parameter ratio

Structure refinement to 0.75 Å



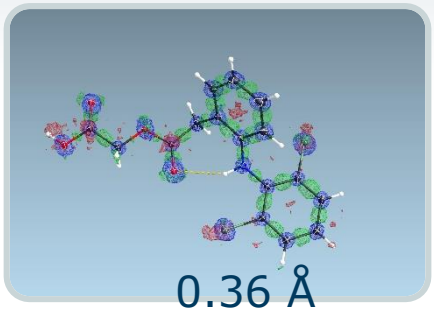
- 1594 unique data
- 7.4:1 data to parameter ratio
- 216 parameters
- Anisotropic refinement of thermal displacement parameters

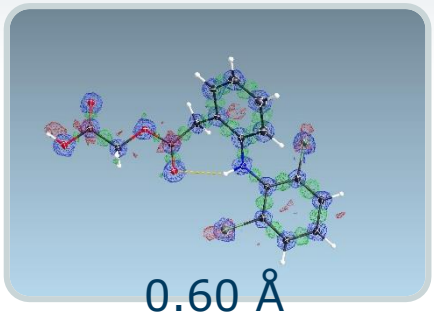
Structure refinement to 1.5 Å

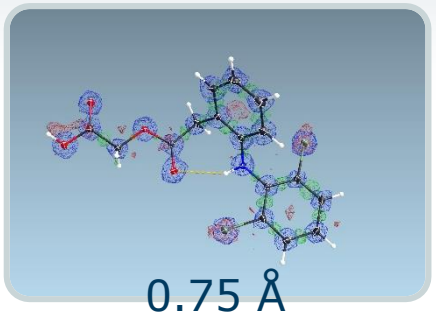


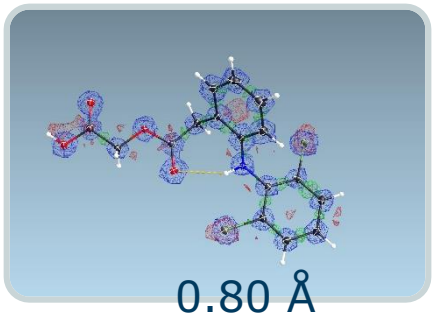
- 474 unique data
- 4.7:1 data to parameter ratio
- 101 parameters with isotropic refinement of thermal parameters
- U_{iso} cannot be modeled for one C atom

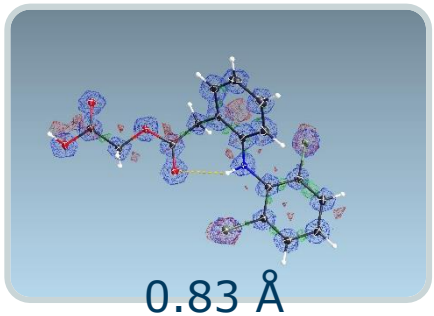
Gallery of Aceclofenac at different resolutions

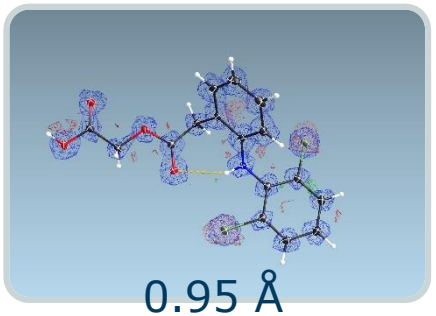


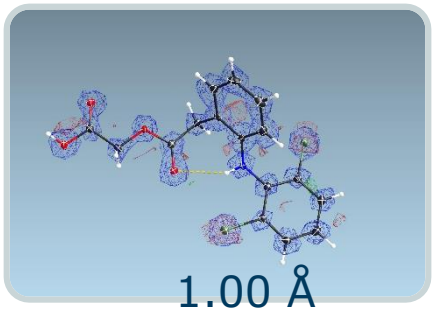


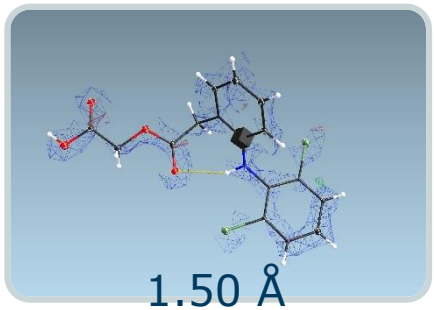








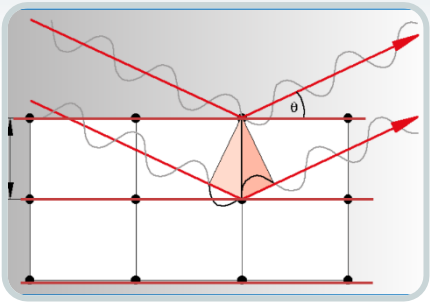


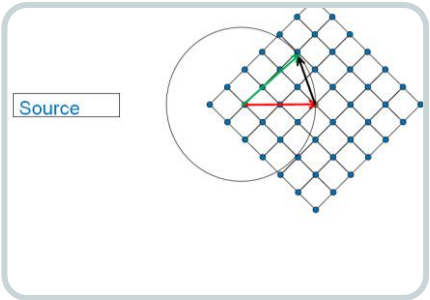


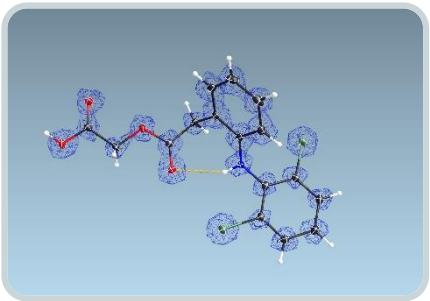
- Showing observed and difference electron density
- Mo Kα radiation

Conclusions

- Bragg's Law relates diffraction to reflection from crystallographic planes
- The Ewald construction helps to visualize the diffraction sphere and consider data collection strategy
- Acquiring data to higher resolution leads to more accurate determination of the atomic positions and more reliable derived geometric parameters

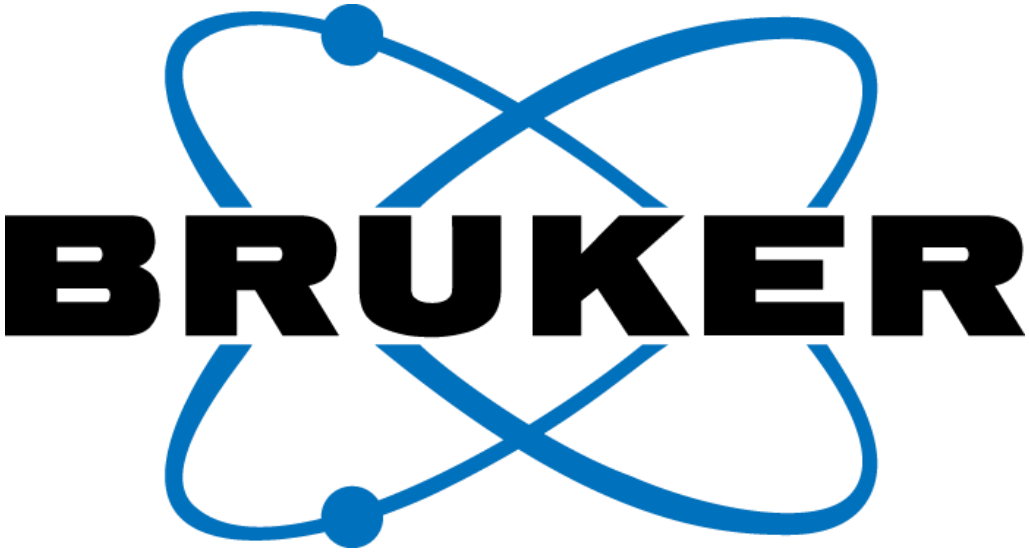






Suggested Reading

- **Crystal Structure Analysis: A Primer**
  - J. P. Glusker and K. N. Trueblood
  - Oxford ; New York : Oxford University Press, 2010.
- **Crystal structure determination**
  - W. Massa
  - Berlin Springer, 2016.
- **Fundamentals of crystallography**
  - C. Giacovazzo, et al
  - Oxford ; New York : Oxford University Press, 2009.



Innovation with Integrity