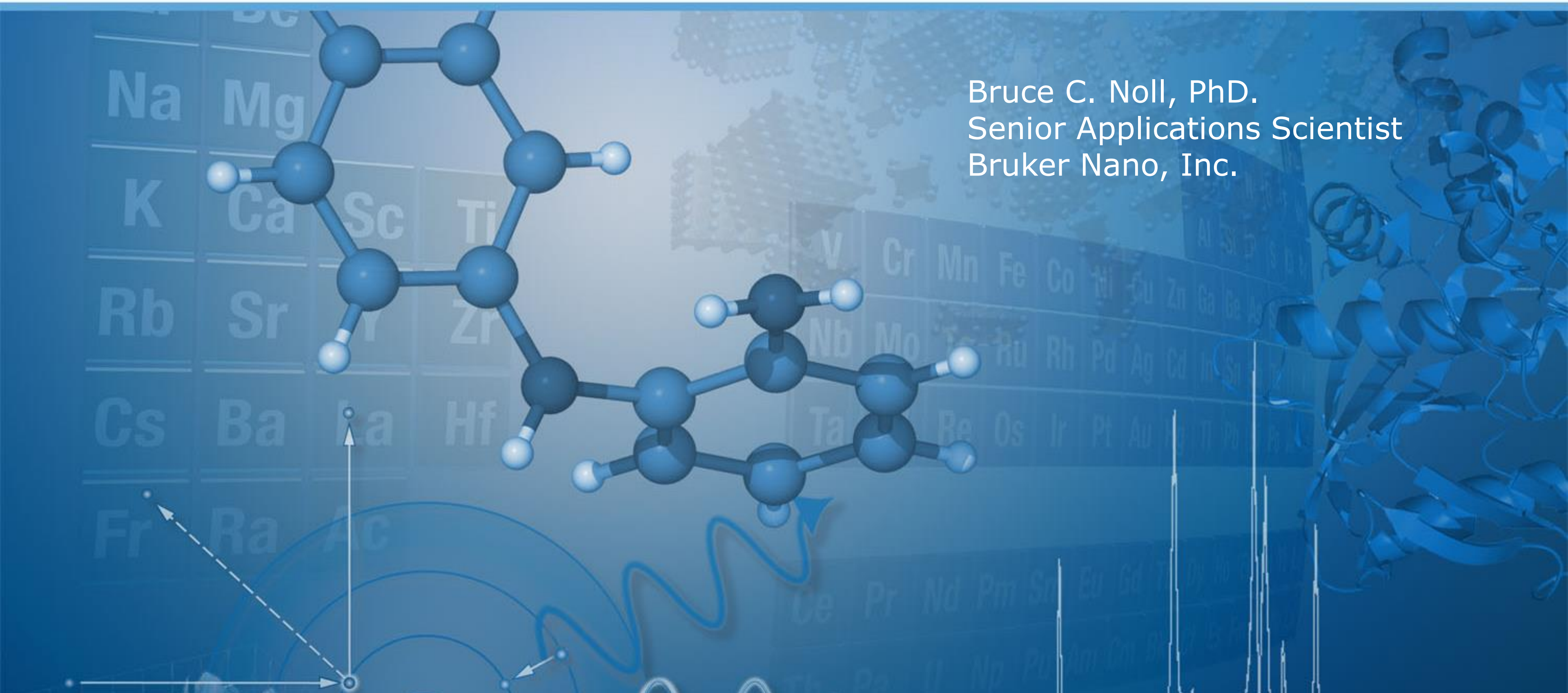
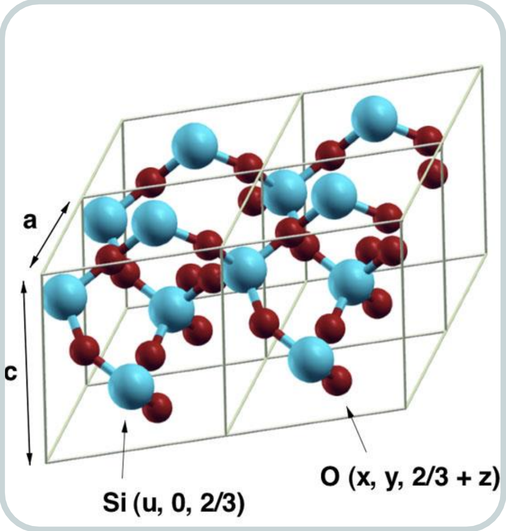
Basic Crystallography



Bruce C. Noll, PhD.
Senior Applications Scientist
Bruker Nano, Inc.

Introduction



- Crystals and Crystallography
- Crystal Lattices and Unit Cells
- Diffraction
- Bragg's Law and Reciprocal Space
- X-ray Diffraction Patterns from Crystals

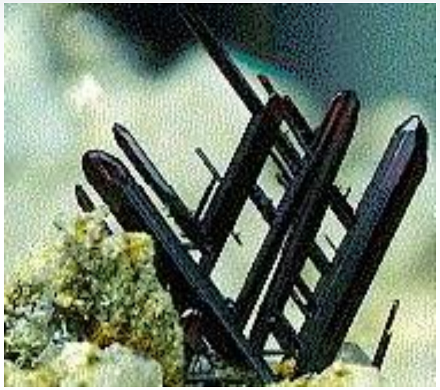
Top: JJ Harrison (https://www.jjharrison.com.au/)
Bottom: http://www.sunnyray.org/Quartz.htm

What is a Crystal?

From Merriam Webster:

- *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
- *Glass:* any of various amorphous materials formed from a melt by cooling to rigidity without crystallization

Examples of Crystals

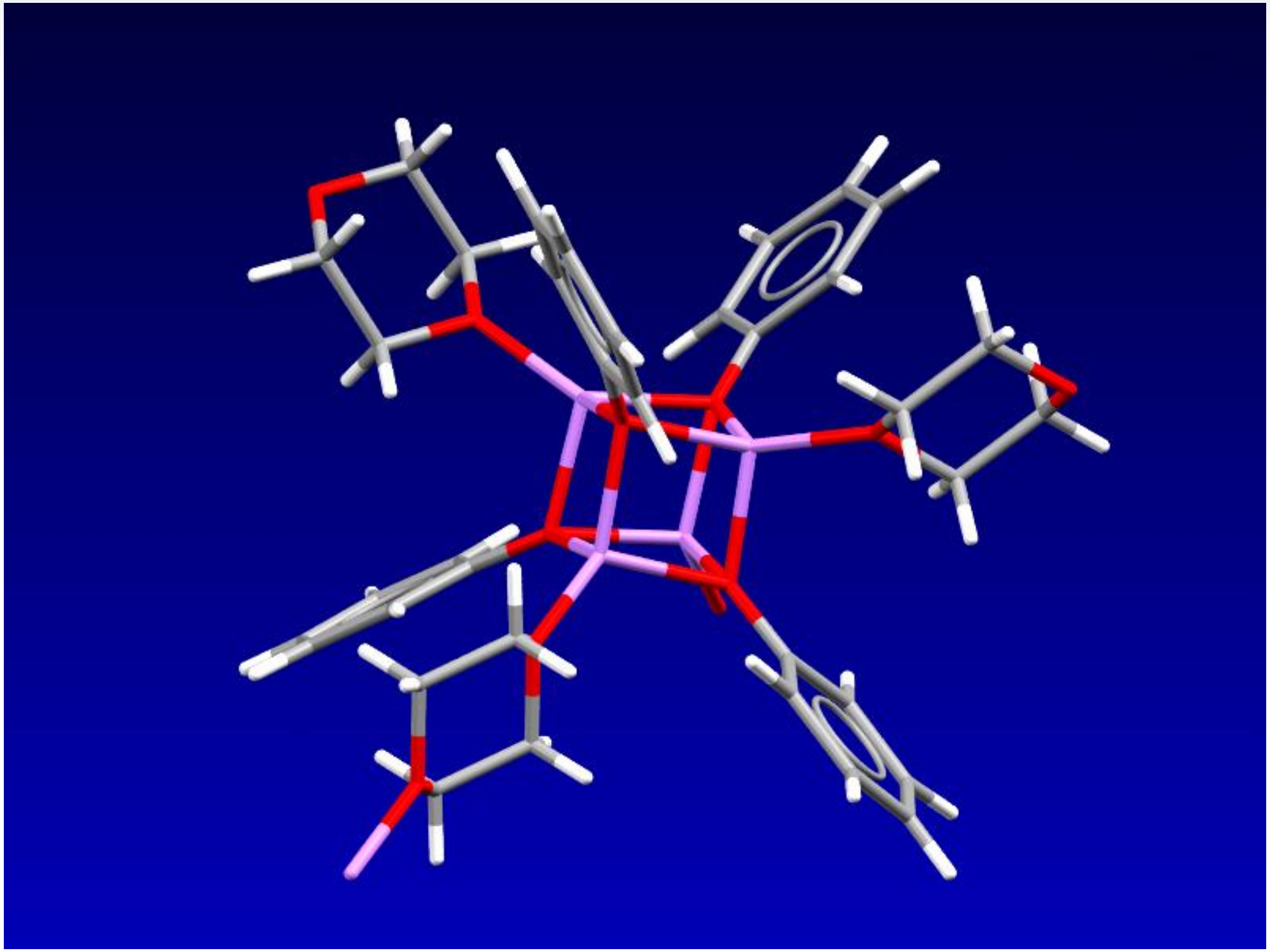





Foundations of Crystallography

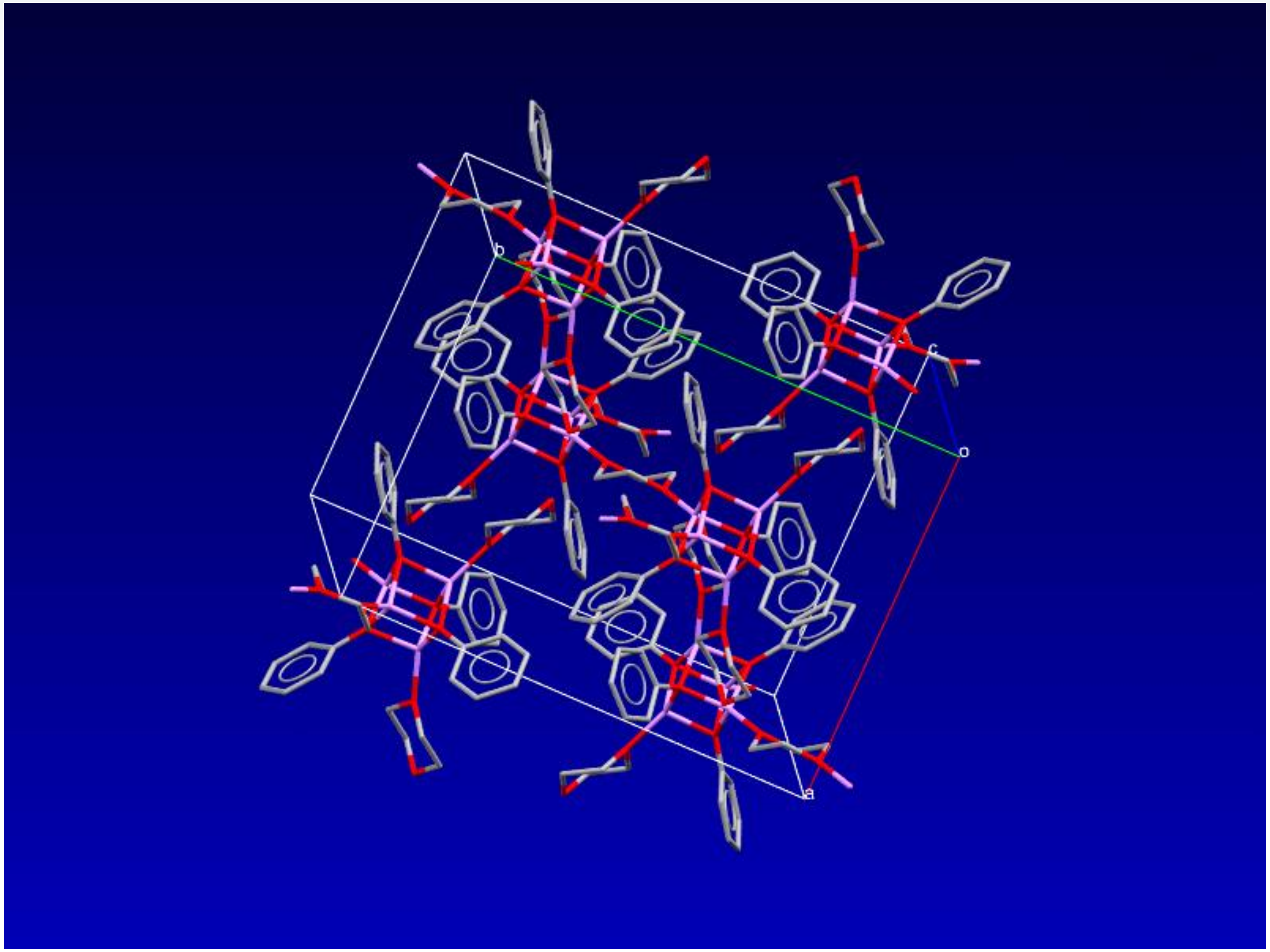
- *Crystallography* is the study of crystals.
- Scientists who specialize in the study of crystals are called *crystallographers*.
- Early studies of crystals were carried out by mineralogists who studied the symmetries and shapes (*morphology*) of naturally-occurring mineral specimens.
- This led to the correct idea that crystals are regular three-dimensional arrays (*Bravais lattices*) of atoms and molecules; a single *unit cell* is repeated indefinitely along three principal directions that are not necessarily perpendicular.

Making a Crystal:
the asymmetric unit

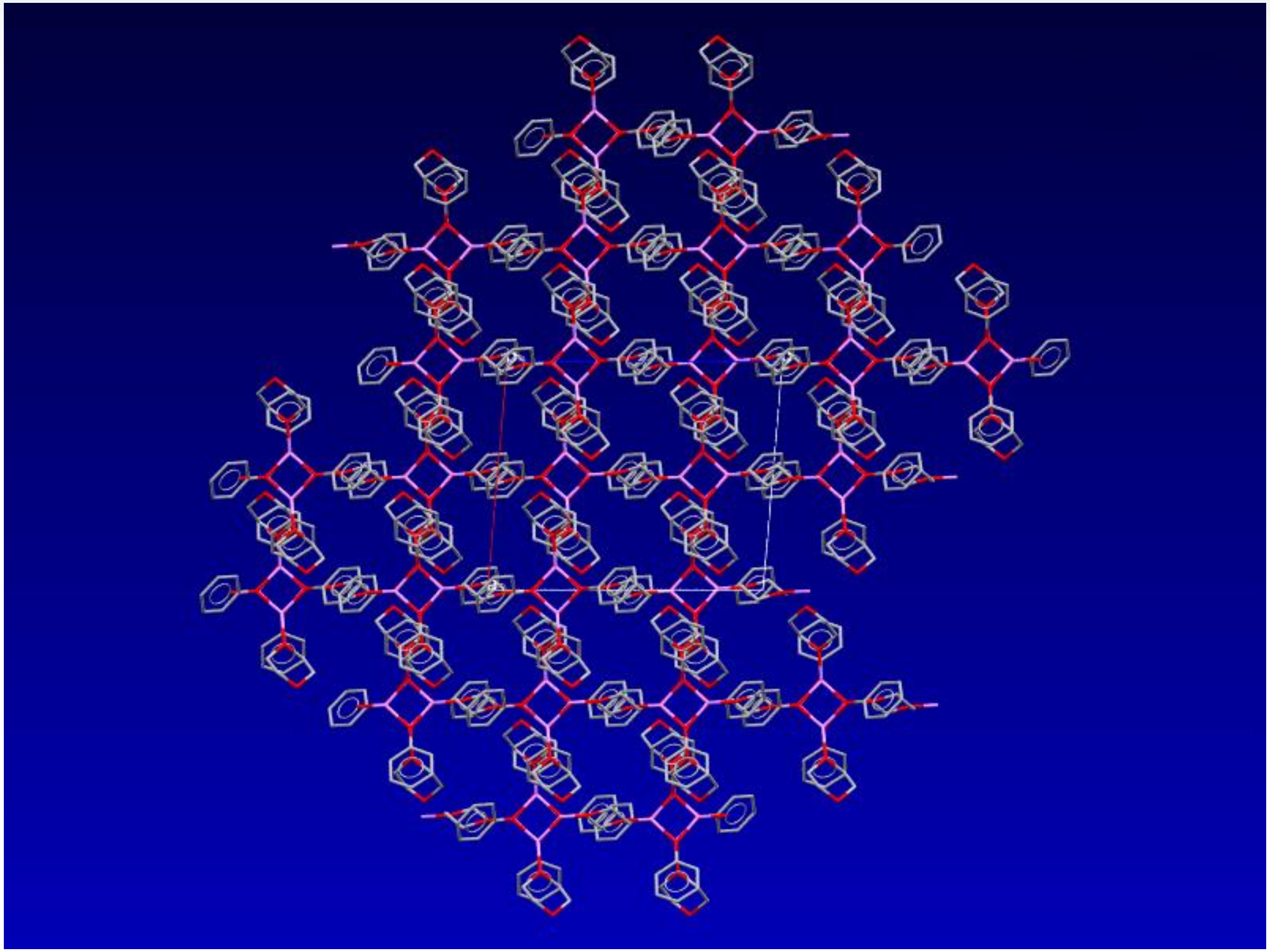


D.J. MacDougall et al, doi:10.1039/b413434f

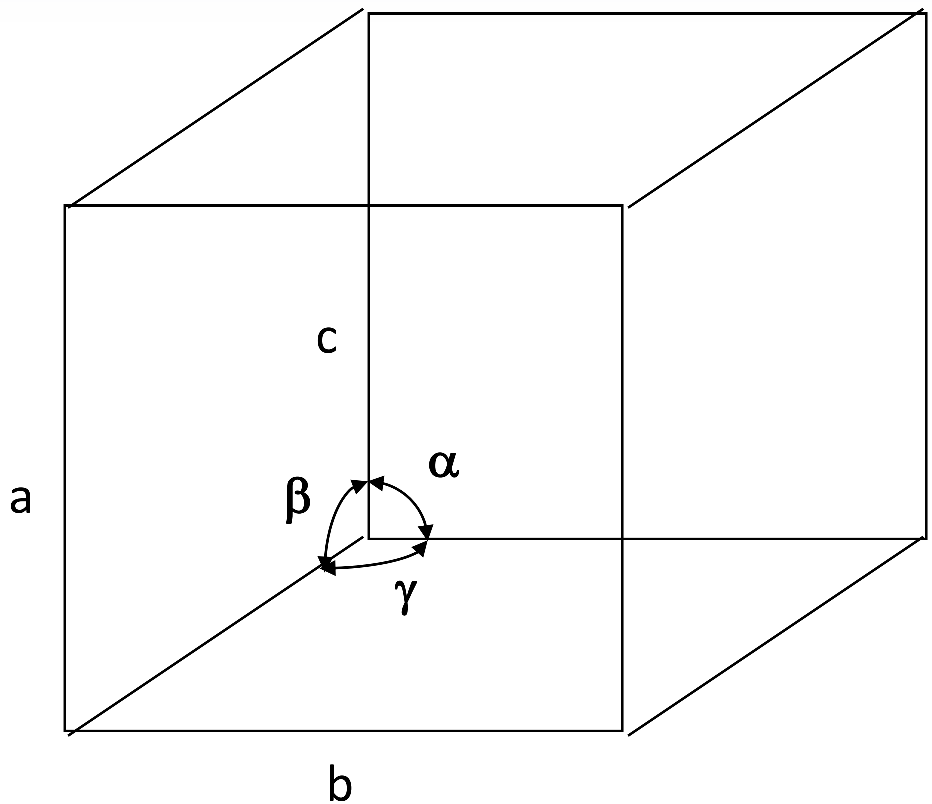
Making a Crystal: the unit cell



Making a Crystal: the extended structure

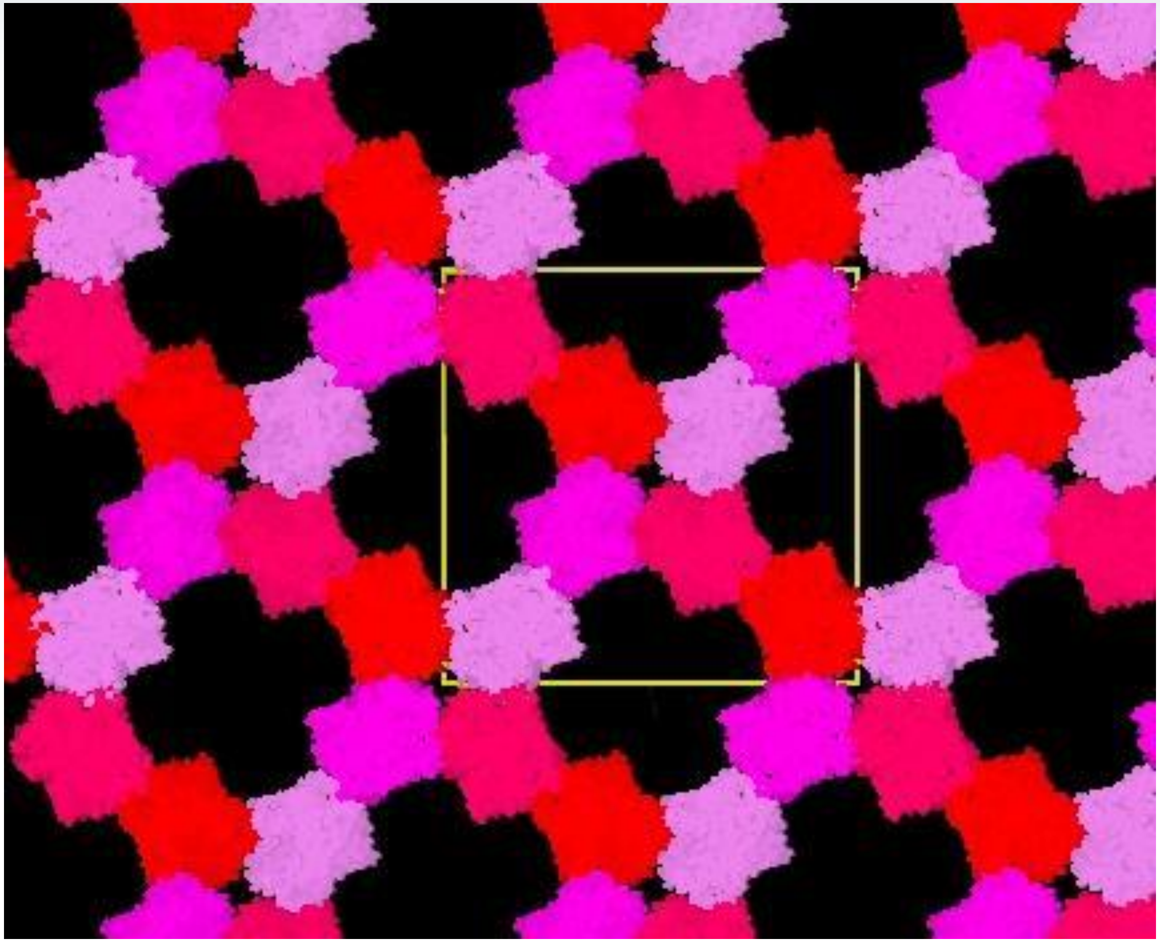


Unit Cell Description in terms of Lattice Parameters



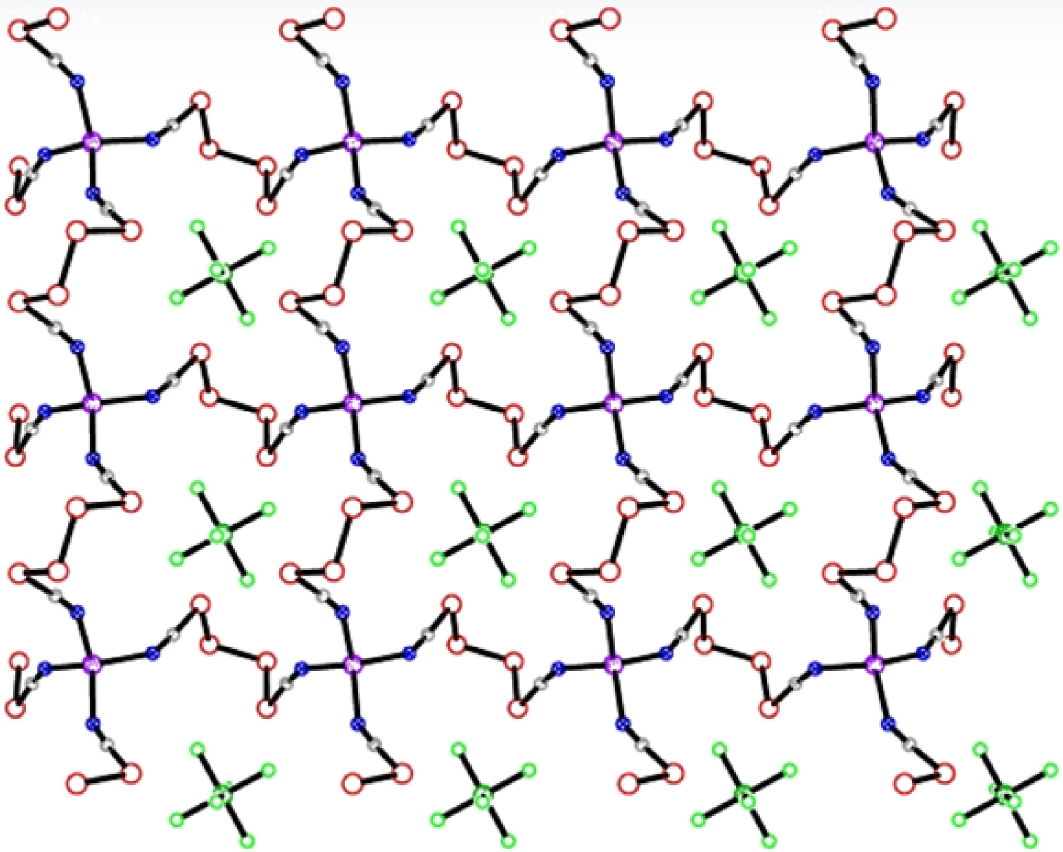
- a ,b, and c define the edge lengths and are referred to as the crystallographic axes.
- α, β, and γ give the angles between these axes.
- Lattice parameters → dimensions of the unit cell.

The Unit Cell Concept

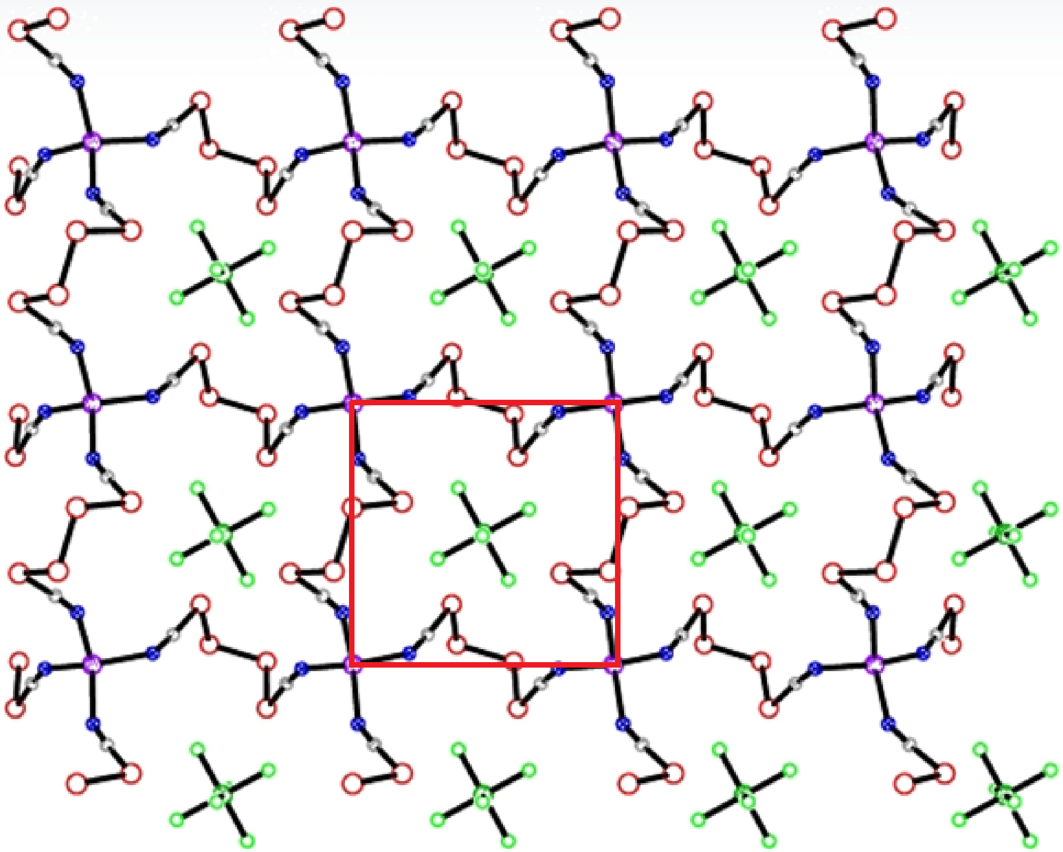


Ralph Krätzner

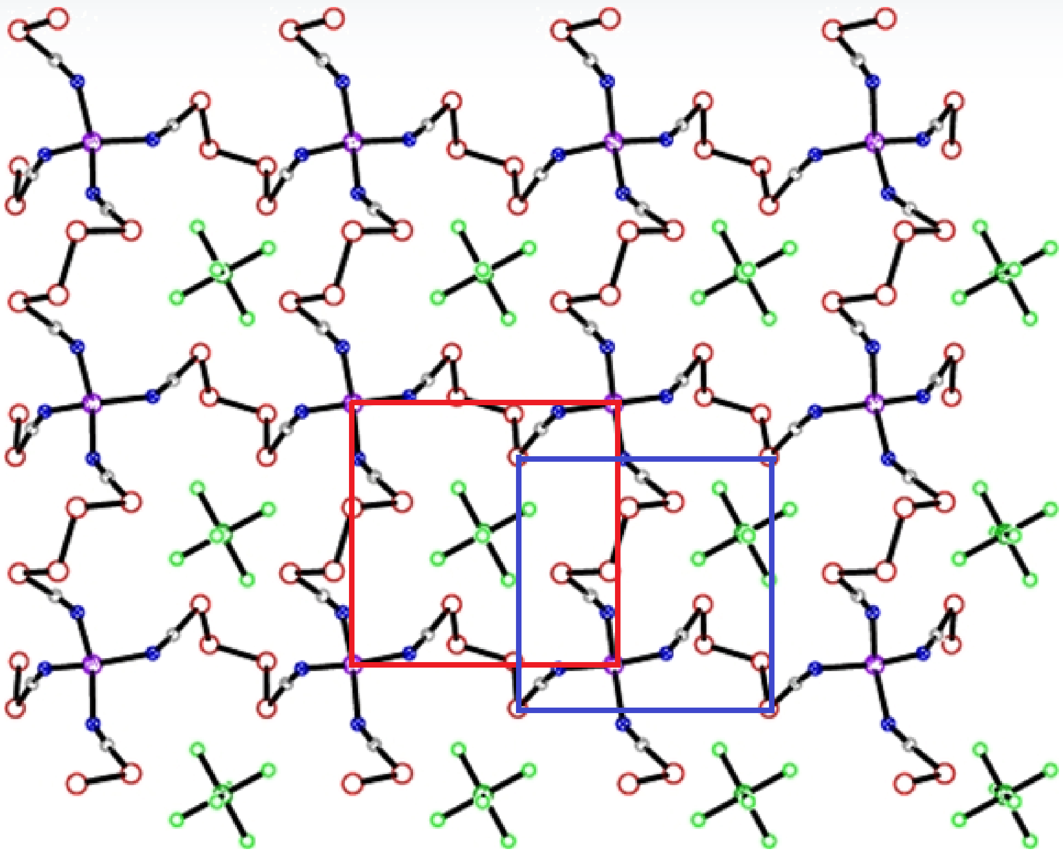
Choice of the Unit Cell



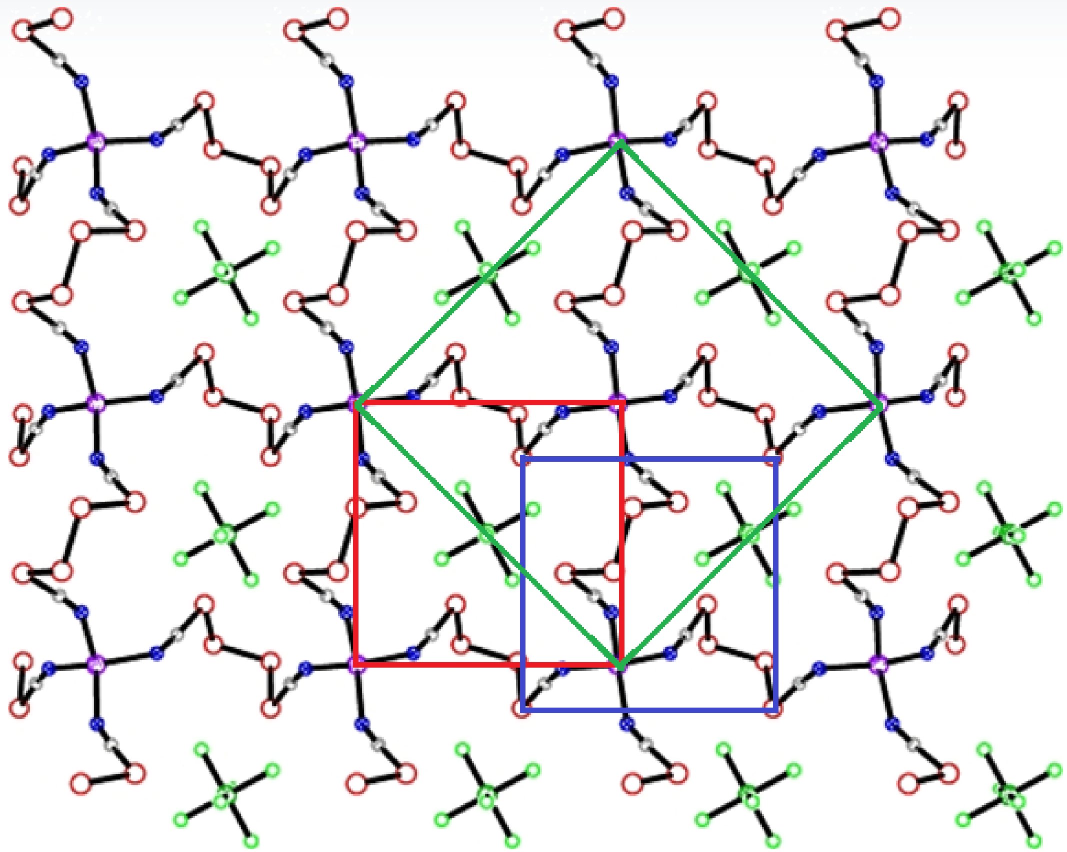
Choice of the Unit Cell



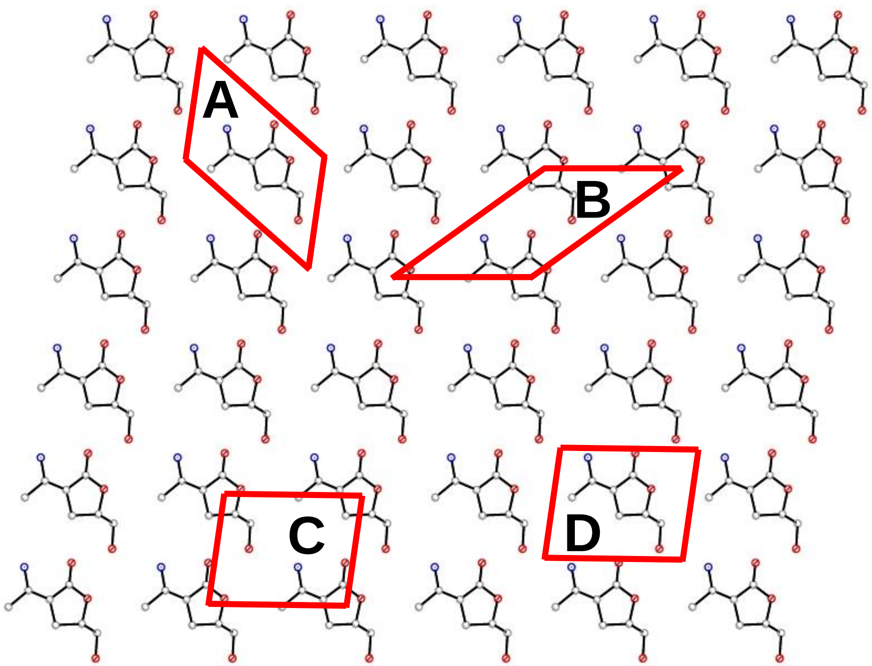
Choice of the Unit Cell



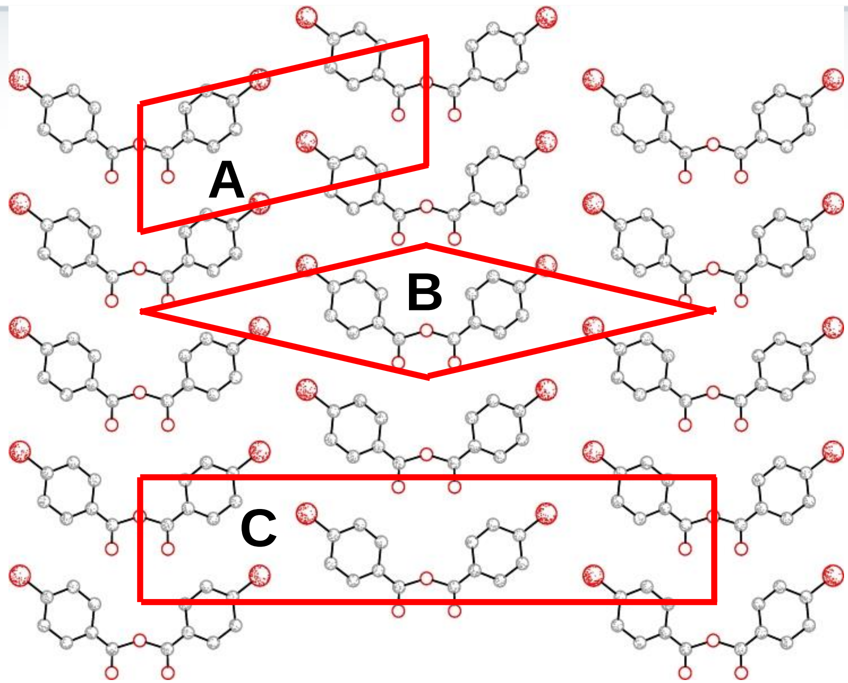
Choice of the Unit Cell



Choice of the Unit Cell

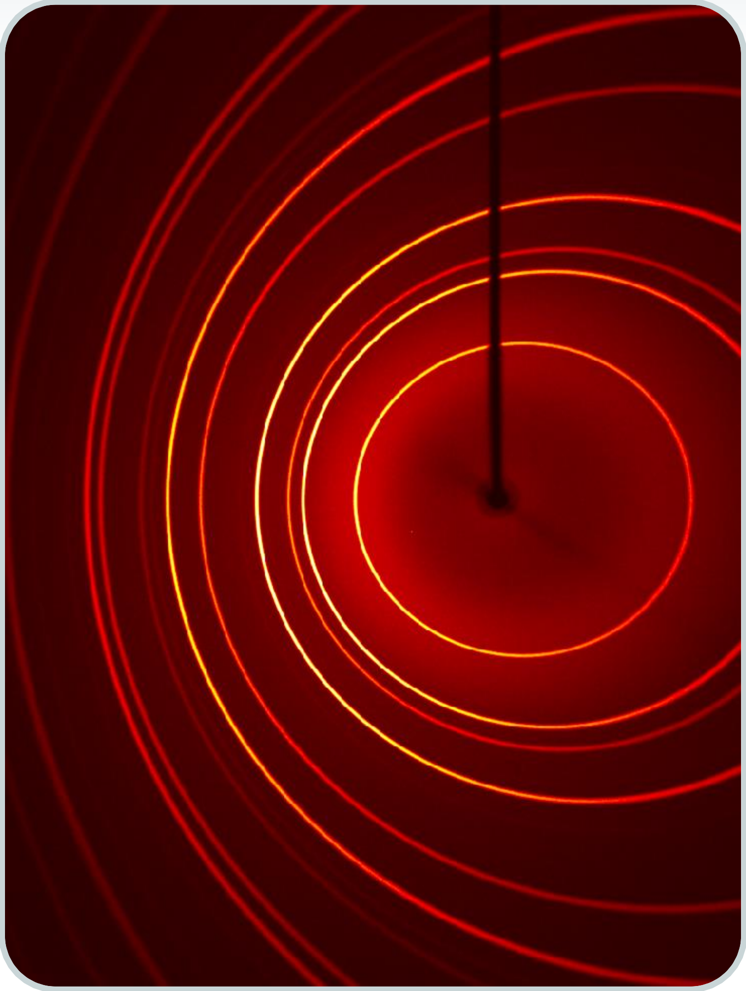


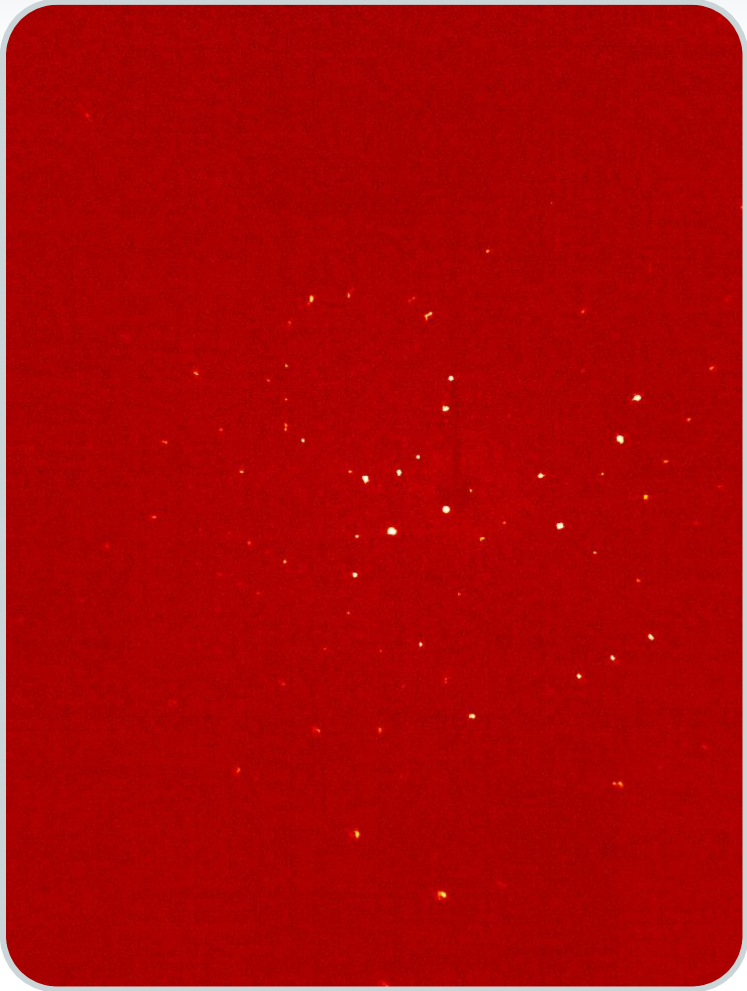
No symmetry - many possible unit cells. A primitive cell with angles close to 90º (C or D) is preferable.



The conventional C-centered cell (C) has 90º angles, but one of the primitive cells (B) has two equal sides.

X-ray Diffraction





Diffraction of X-rays by Crystals

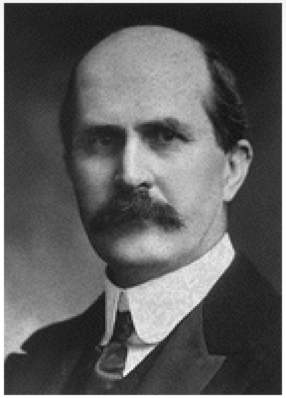
- The science of X-ray crystallography originated in 1912 with the theory by Max von Laue that crystals diffract X-rays.
- Walter Friedrich and Paul Knipping performed experiments to prove Laue’s theory

Max Theodor Felix von Laue (1879 – 1960)

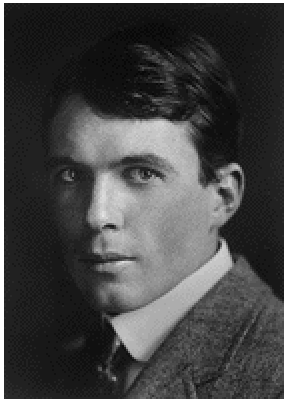
Diffraction of X-rays by Crystals

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

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

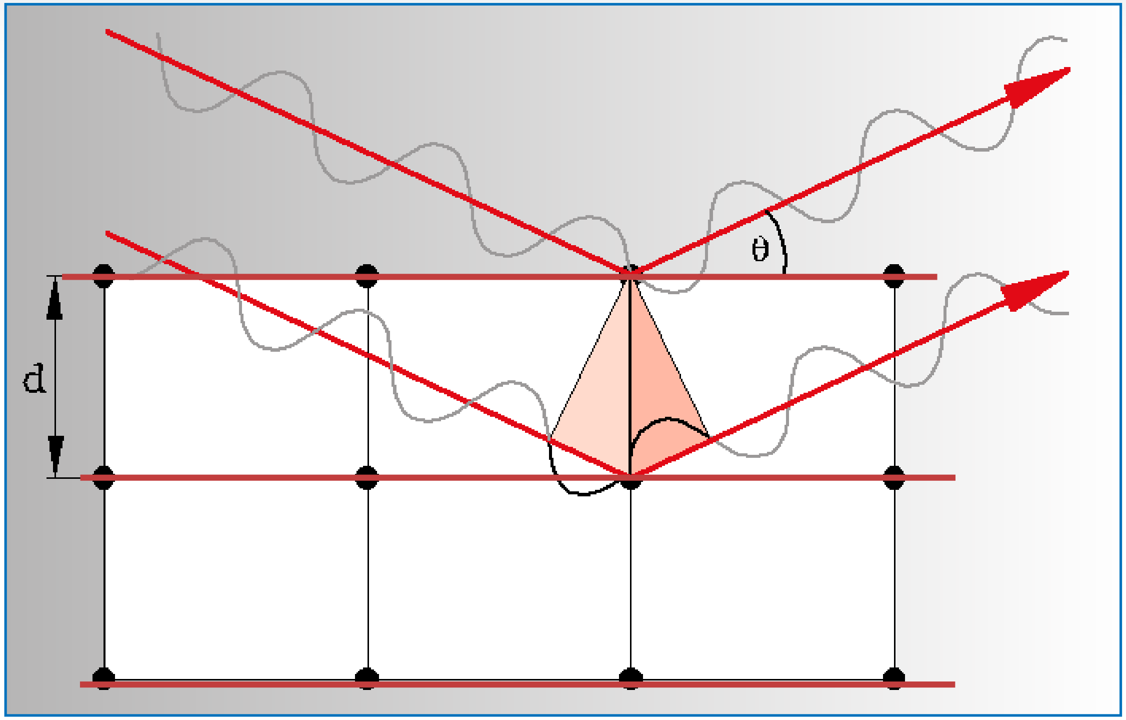


William Henry Bragg



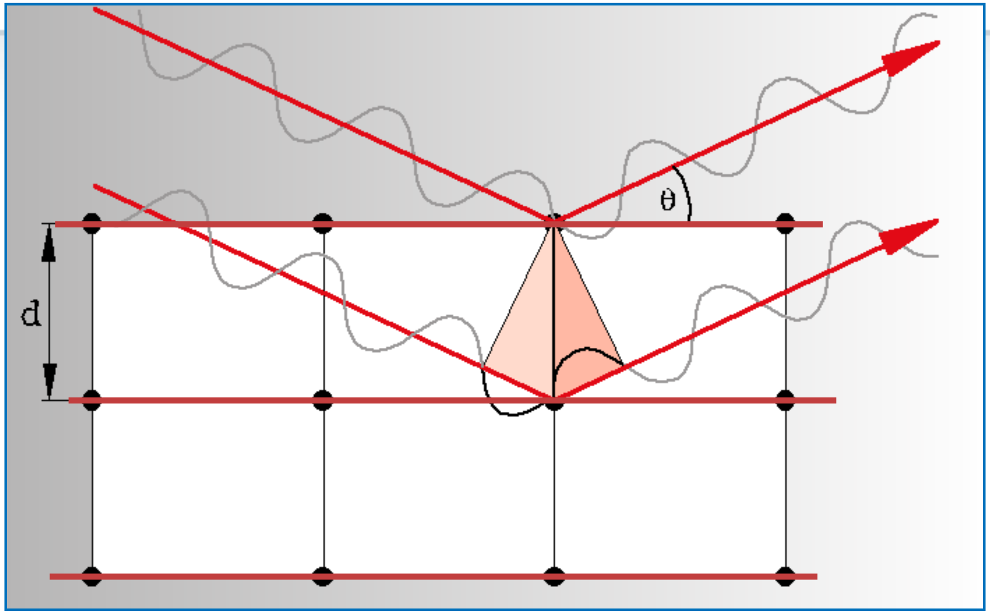
William Lawrence Bragg

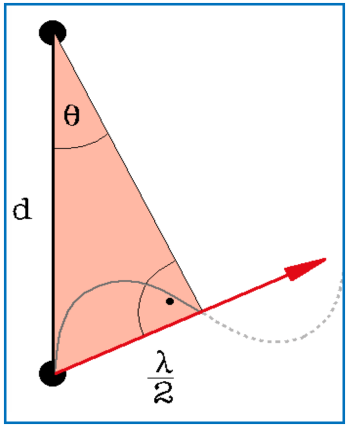
Bragg's Law



- 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



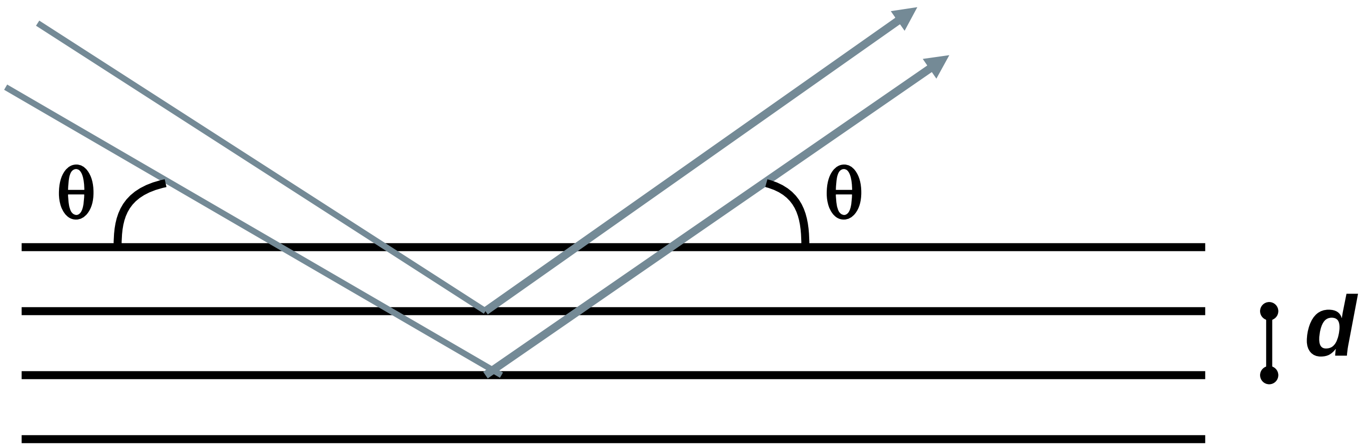


- The condition for constructive interference is that the path difference leads to an integer number of wavelengths.
- Bragg condition → concerted constructive interference from periodically-arranged scatterers.
- This occurs ONLY for a very specific geometric condition.

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

Bragg's Law

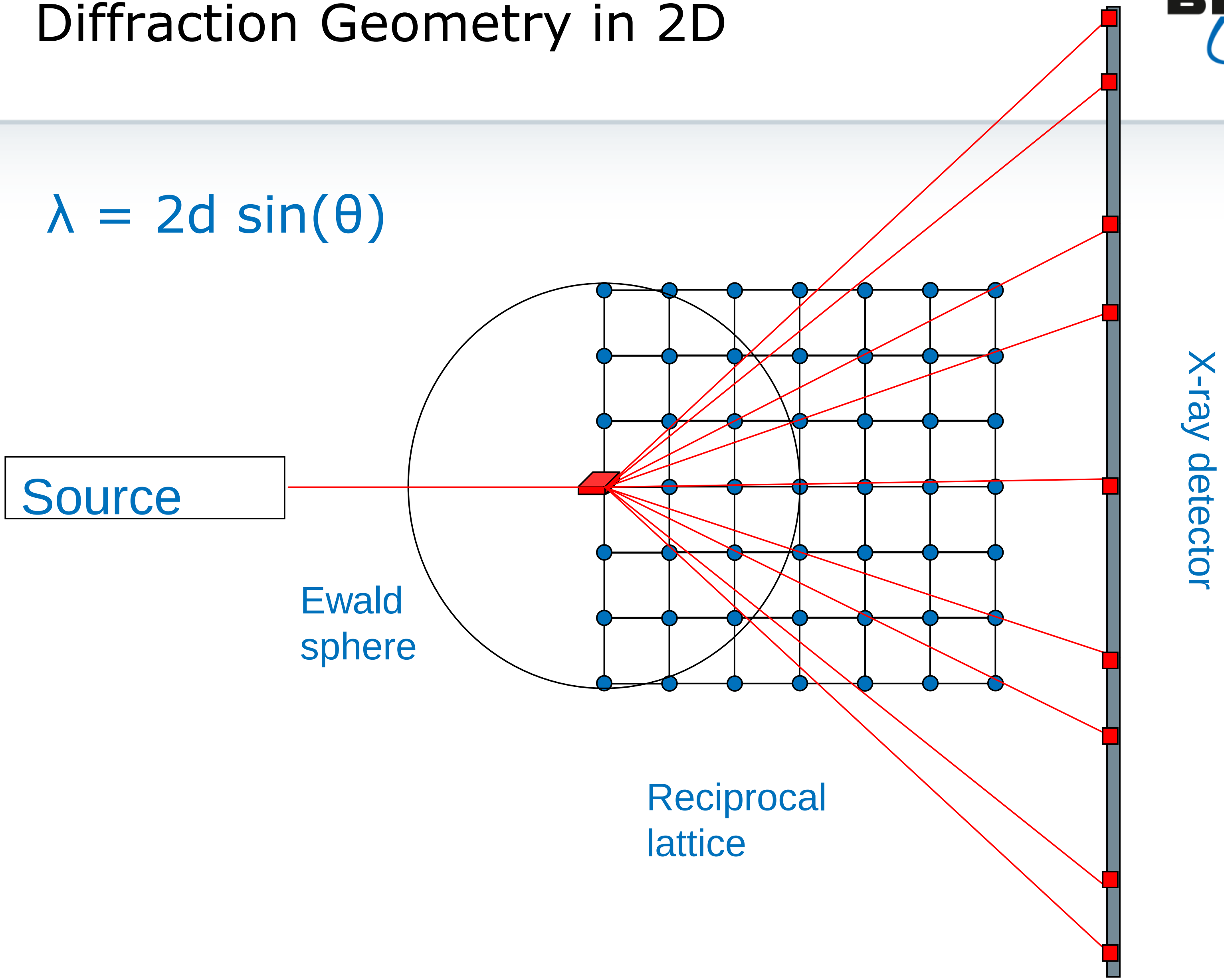
$$n\lambda = 2d \sin(\theta)$$



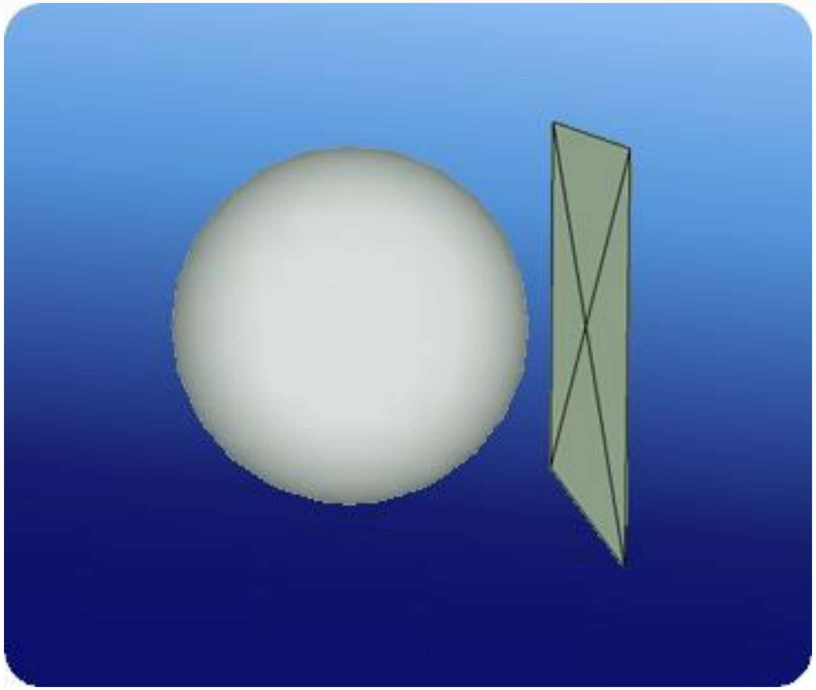
We can think of diffraction as reflection at sets of planes running through the crystal. Only at certain angles 2θ are the waves diffracted from different planes a whole number of wavelengths apart (i.e., in phase). At other angles, the waves reflected from different planes are out of phase and cancel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

Diffraction Geometry in 2D

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



Detection area in 3D, square detector

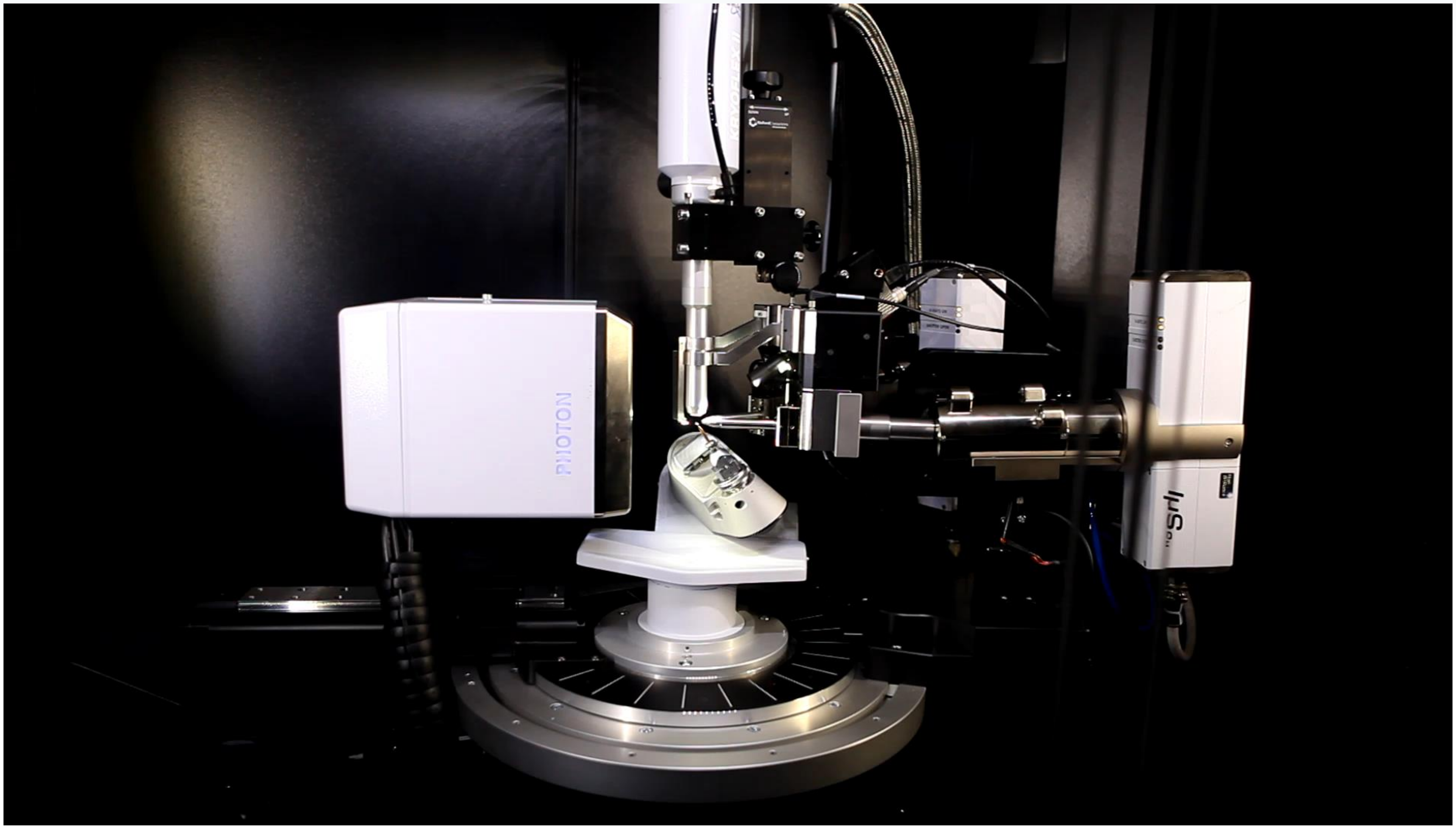


- The detection area of a detector is the projection of the (square) detector onto the surface of the EWALD sphere

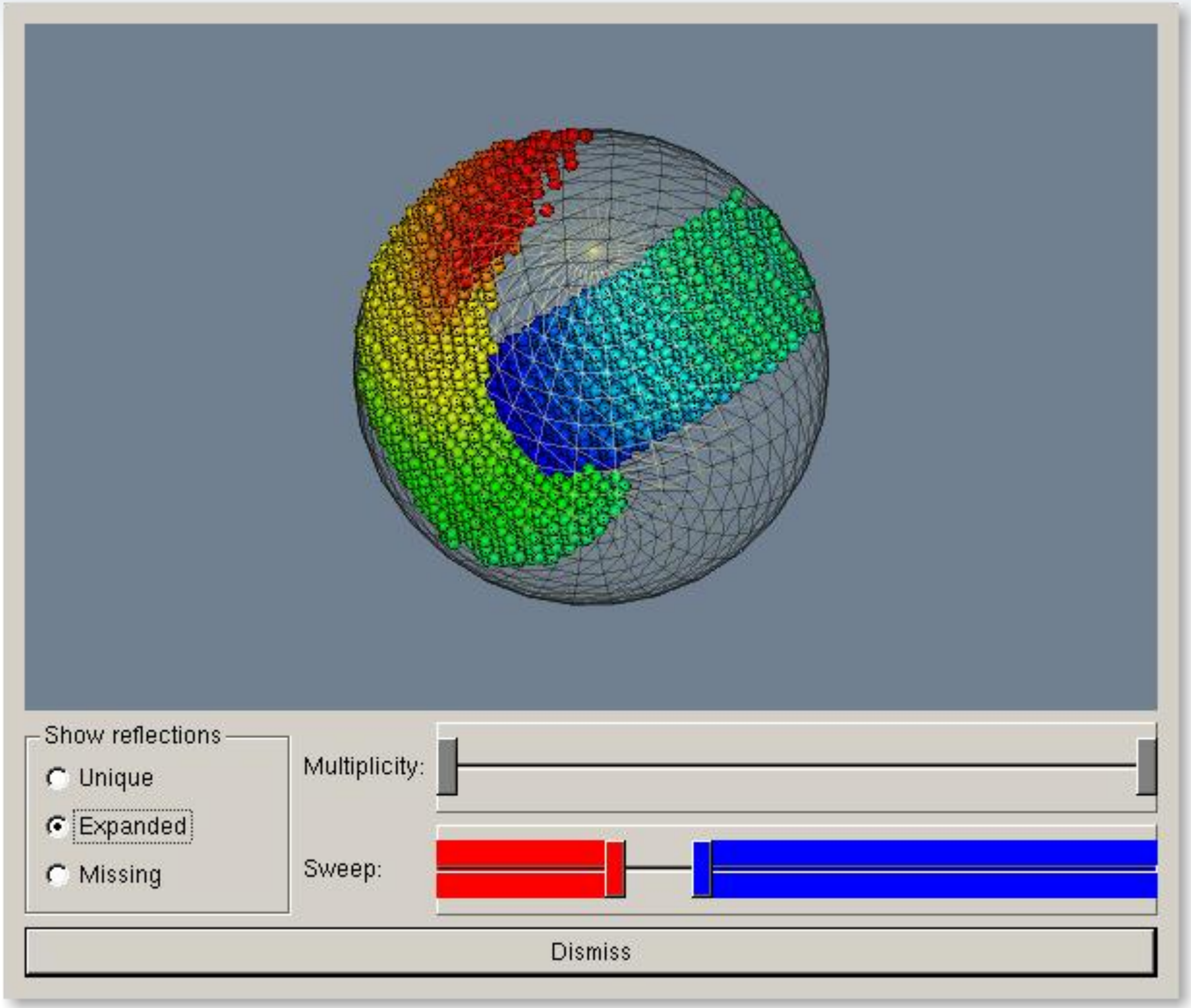
Detection area in 3D, square detector

- 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

4-circle diffractometer

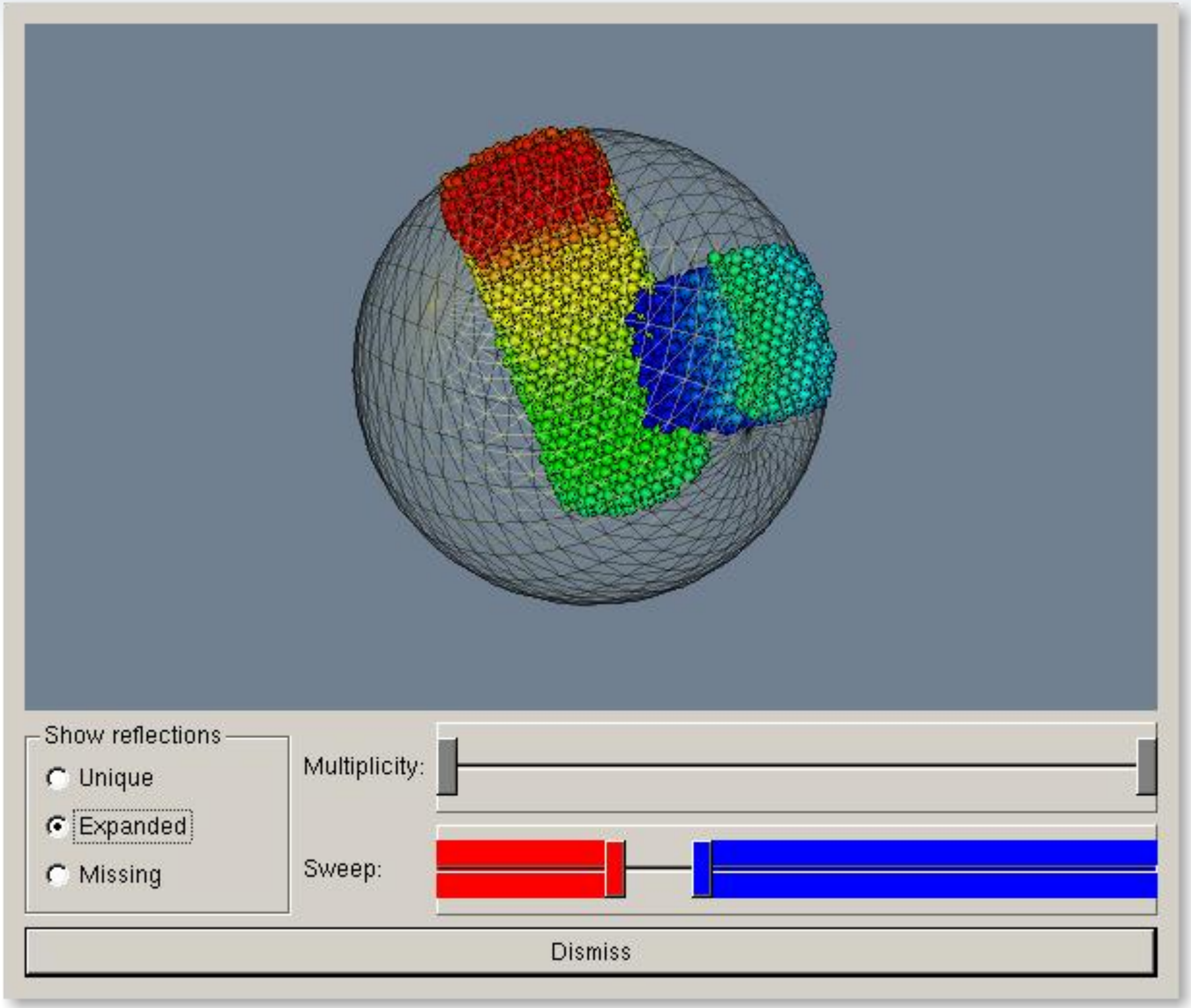


Omega scans



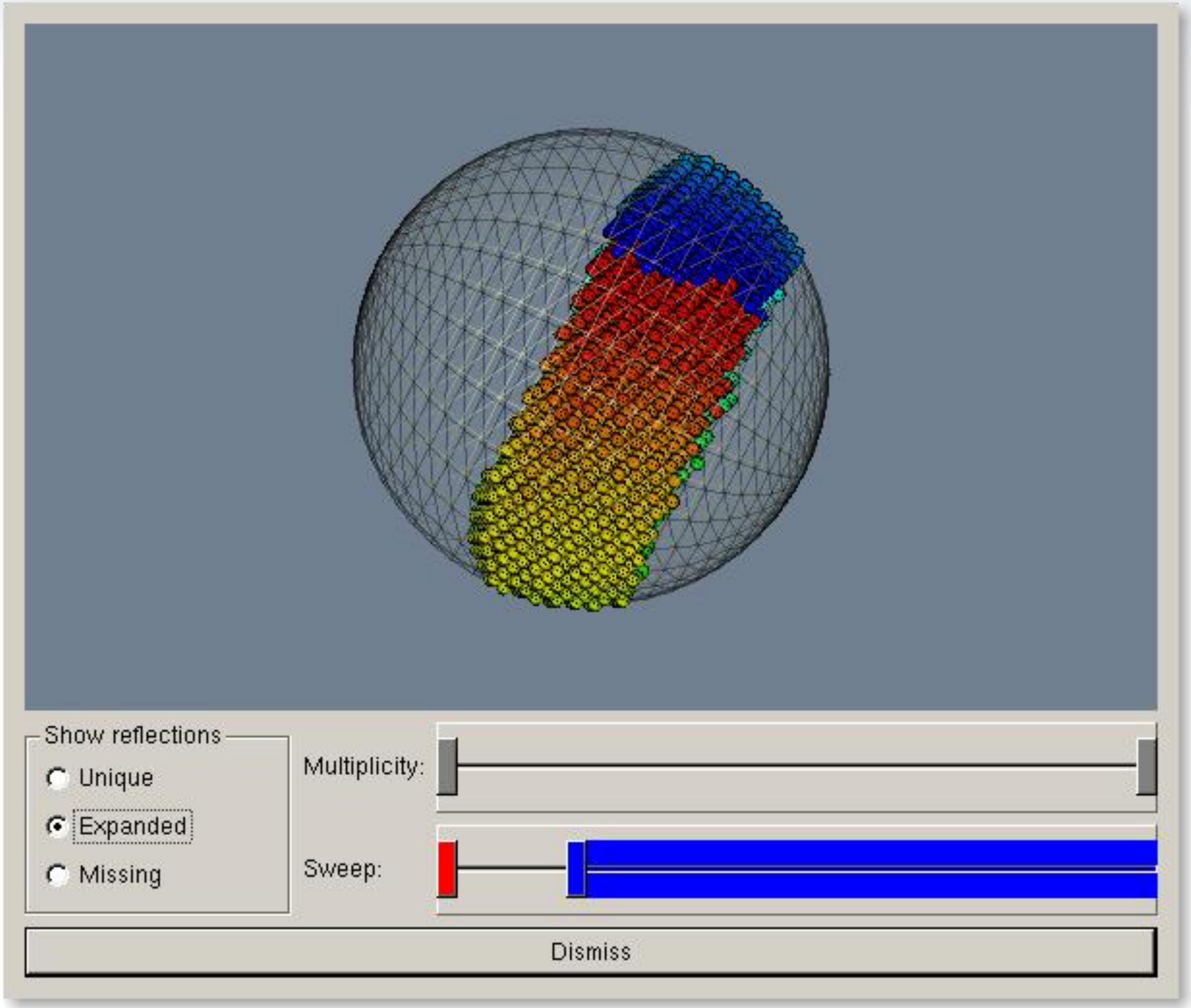
- omega scans are geometrically very flexible
- A combination of omega scans can cover reciprocal space very effectively

Omega scans



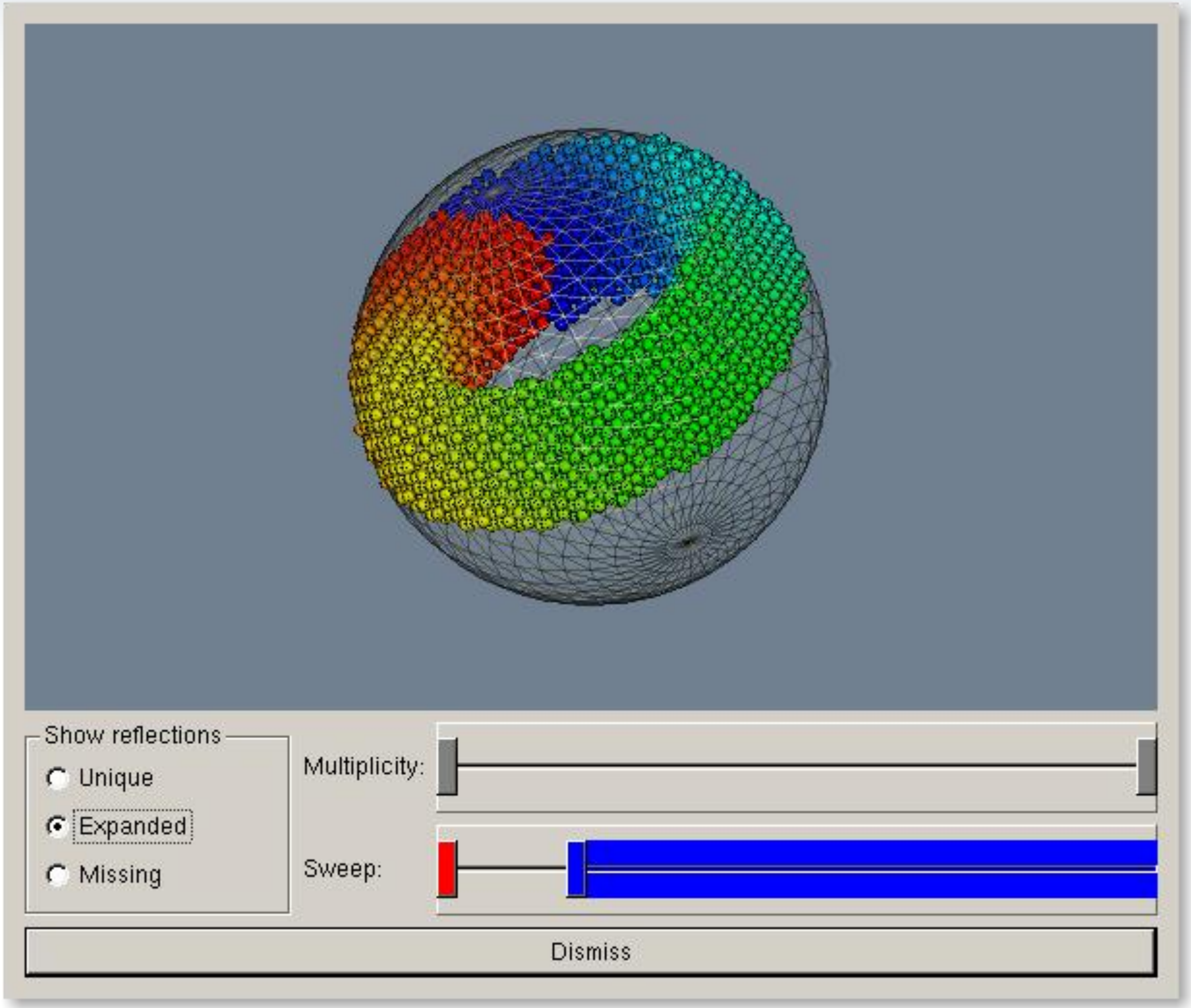
- omega scans are geometrically very flexible
- A combination of omega scans can cover reciprocal space very effectively

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

Recommended reading

- **Crystal Structure Analysis: A Primer (International Union of Crystallography Texts on Crystallography Book 14) 3rd Edition, Kindle Edition**
- by Jenny Pickworth Glusker, Kenneth N. Trueblood

- **Crystal Structure Determination 2nd ed. 2004, Corr. 5th printing 2010 Edition**
- by Werner Massa (Author), Robert O. Gould (Translator)

- **Fundamentals of Crystallography (International Union of Crystallography Texts on Crystallography)**
- by Carmelo Giacovazzo, Hugo Luis Monaco, et al. | Jun 4, 2011

BRUKER

Innovation with Integrity

