Crystallography

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1st Asia Oceania Synchrotron School

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Crystallography

- What are crystals and crystallography?

- The basics of X-ray diffraction (what are we measuring?)

- Bragg's Law and structure factors (what do we do with the data?)

- Laboratories vs. synchrotrons

- Why are synchrotrons better?

Crystals

To understand crystallography, we first need to understand what we mean by a crystal.

*A **crystal** or **crystalline solid** is a solid material whose constituents (such as atoms, molecules, or ions) are arranged in a highly ordered microscopic structure, forming a crystal lattice that extends in all directions*

Crystals

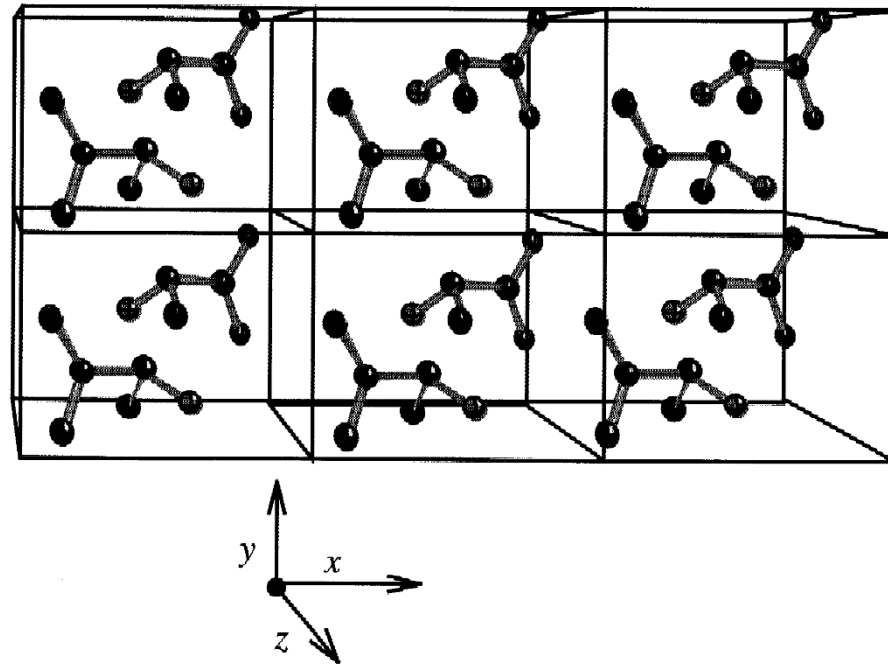For example, diamond is a regular arrangement of carbon atoms.
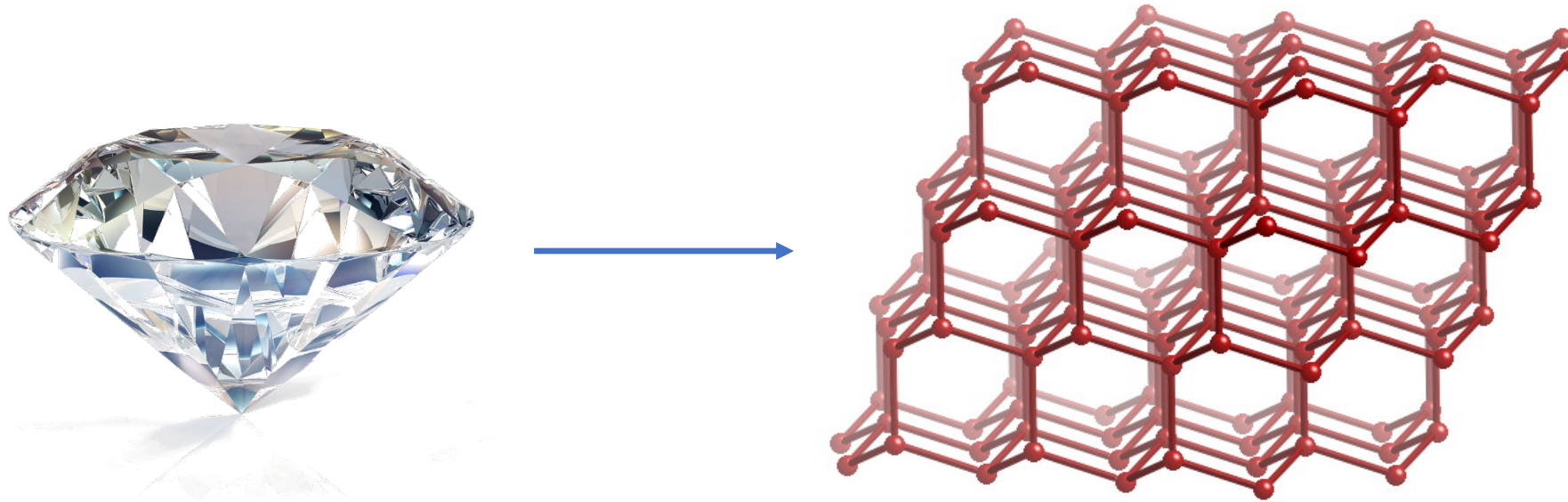
It is this regular arrangement, or periodicity, that allows X-rays to be used to determine the structure of crystalline materials.

Crystals

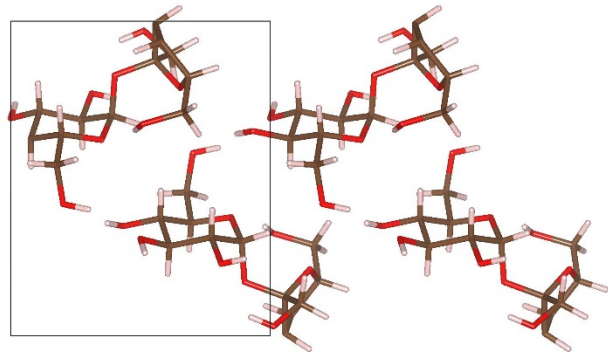Crystals comprise a unit that repeats through translation. This is called the unit cell.
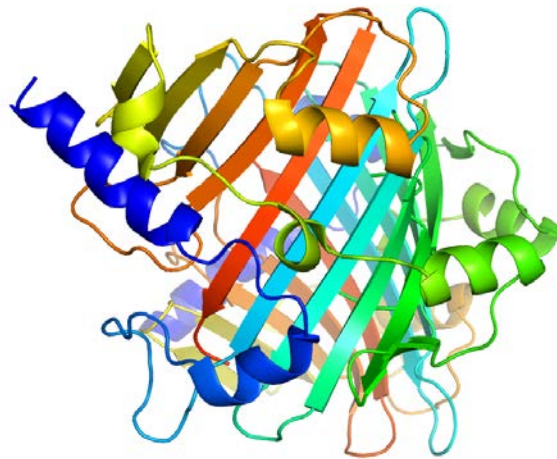
The unit cell typically contains other symmetry elements.

X-Ray Crystallography

X-ray crystallography uses the interaction of X-rays with crystalline materials to determine atomic (electron) positions.
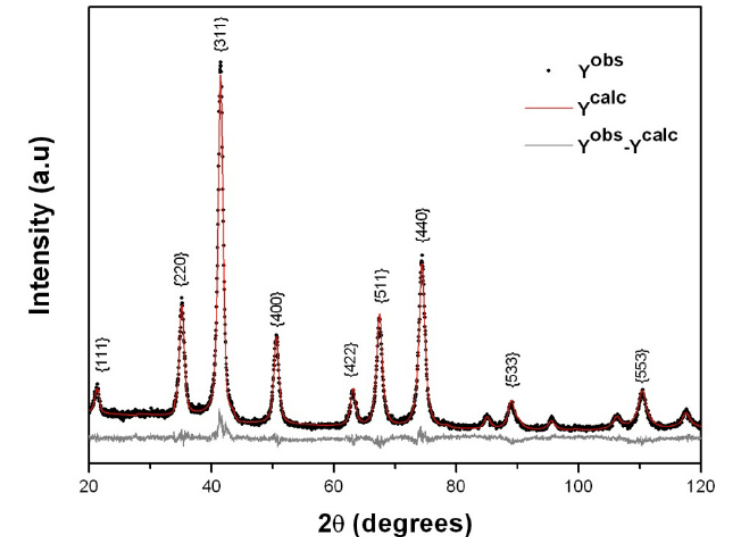
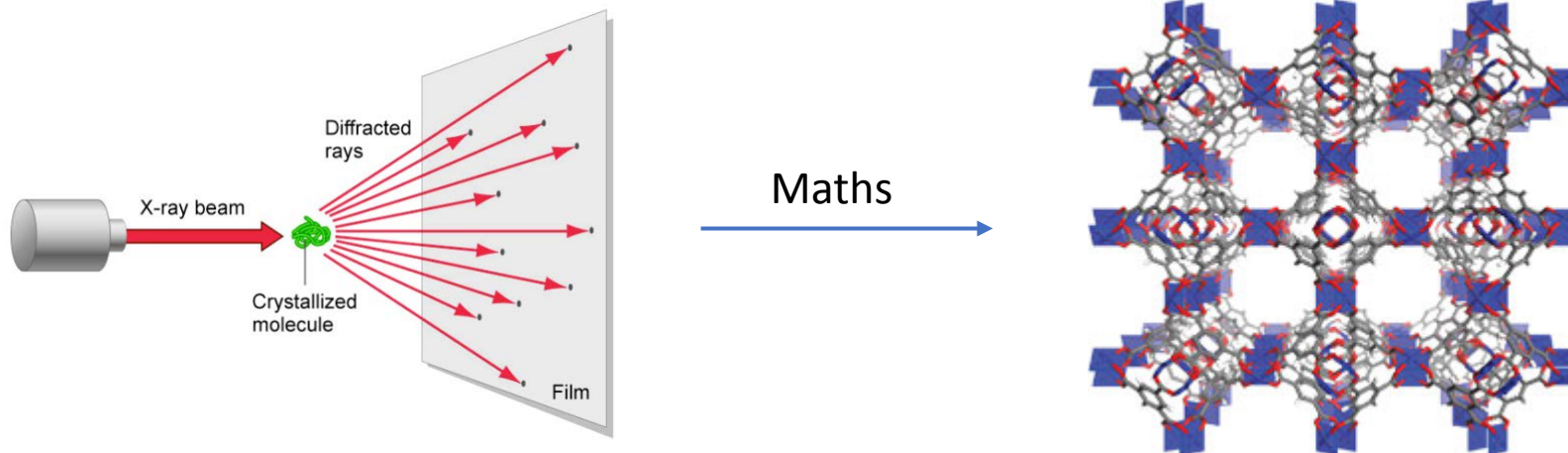**Chemical Crystallography**

Protein Crystallography

Powder Diffraction

X-Ray Diffraction

X-rays are able to interact with electrons. In a diffraction experiment, it is the positions of electron density (*i.e.* atoms) that we obtain.

X-ray crystallography allows atomic resolution of the structure to be obtained by modelling the diffraction data.
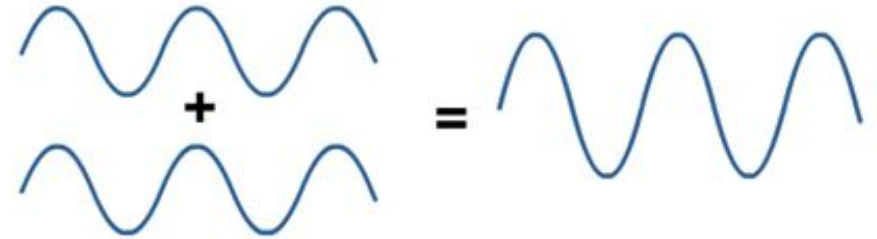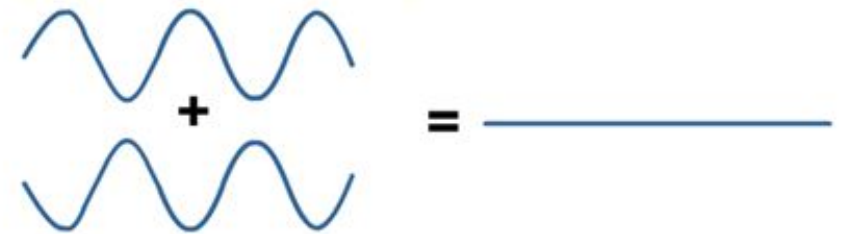
X-Ray Diffraction

Incoming X-rays produce secondary circular spherical waves when electrons are encountered.

Most emanated waves interact in a destructive manner, but the regular crystalline lattice means that in certain conditions, constructive interference occurs.
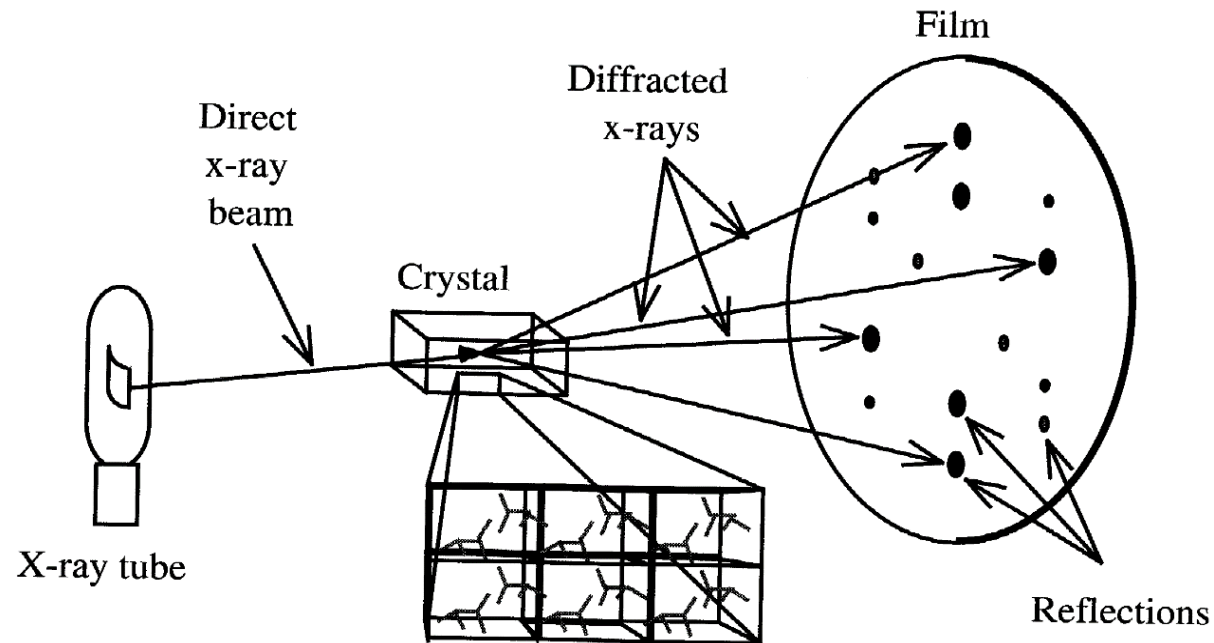
Constructive Interference

Destructive Interference

X-Ray Diffraction

Under certain conditions, constructive interference occurs which generates a series of diffraction spots or reflections.
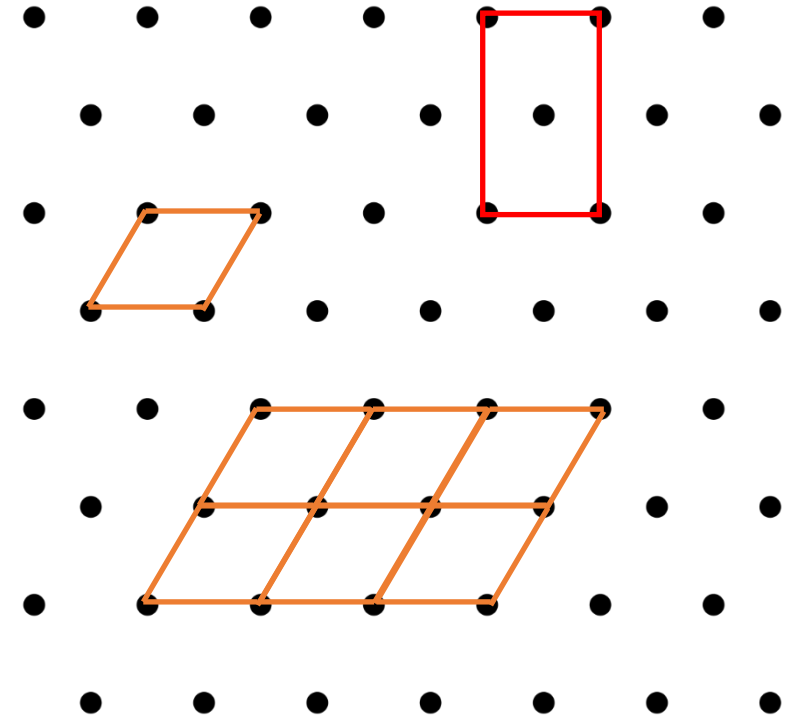
Unit Cells and Lattices

Understanding the conditions under which reflections are obtained invokes the concept of lattice points.

A lattice is an array of points, all identical in environment and orientation, related by translation.
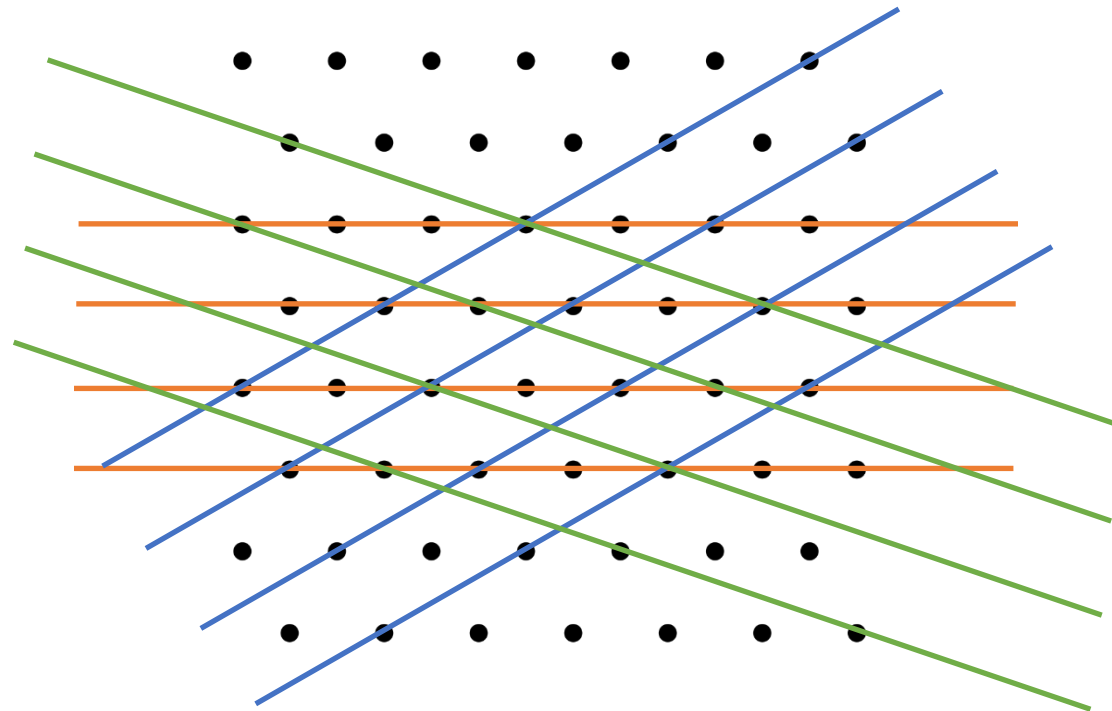
These do NOT have to be atomic positions.

Unit cells have a lattice point at each corner.

Bragg's Law

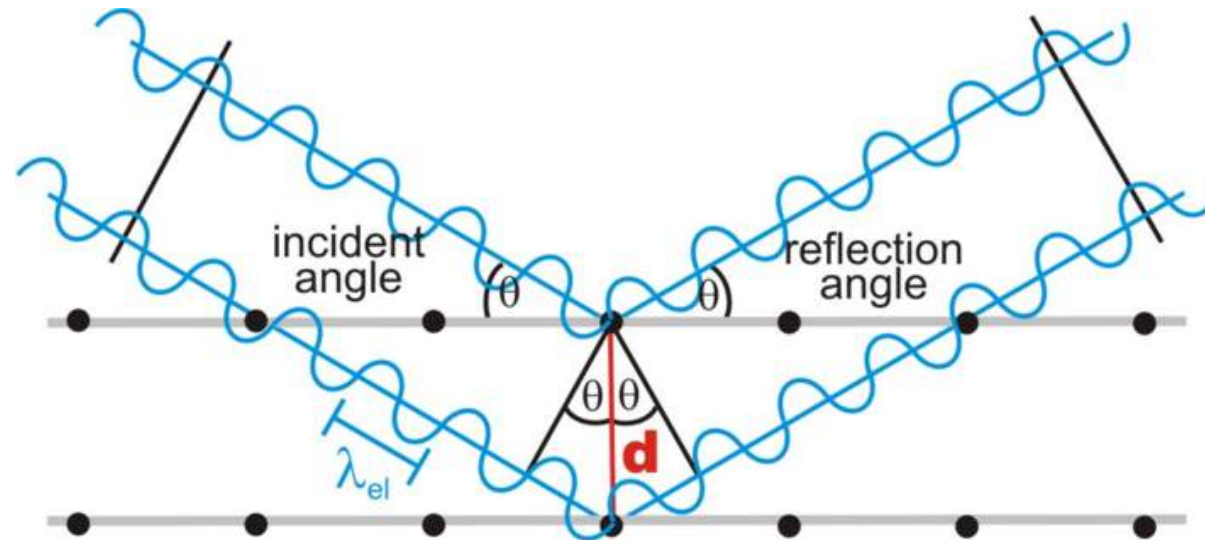A mathematical model to understand the origin of reflections is Bragg's Law.

This imagines X-rays being reflected from lattice planes through the lattice points.

Bragg's Law

Bragg's Law supposes reflection of the incoming X-rays from these lattice planes.
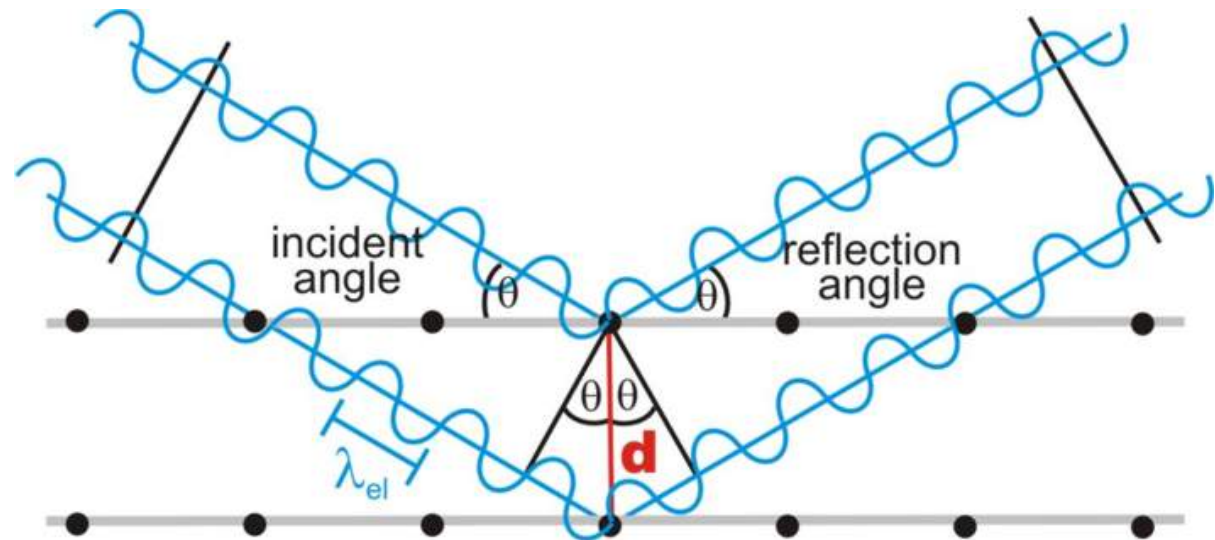
$$n\lambda = 2d \sin \theta$$

Bragg's Law

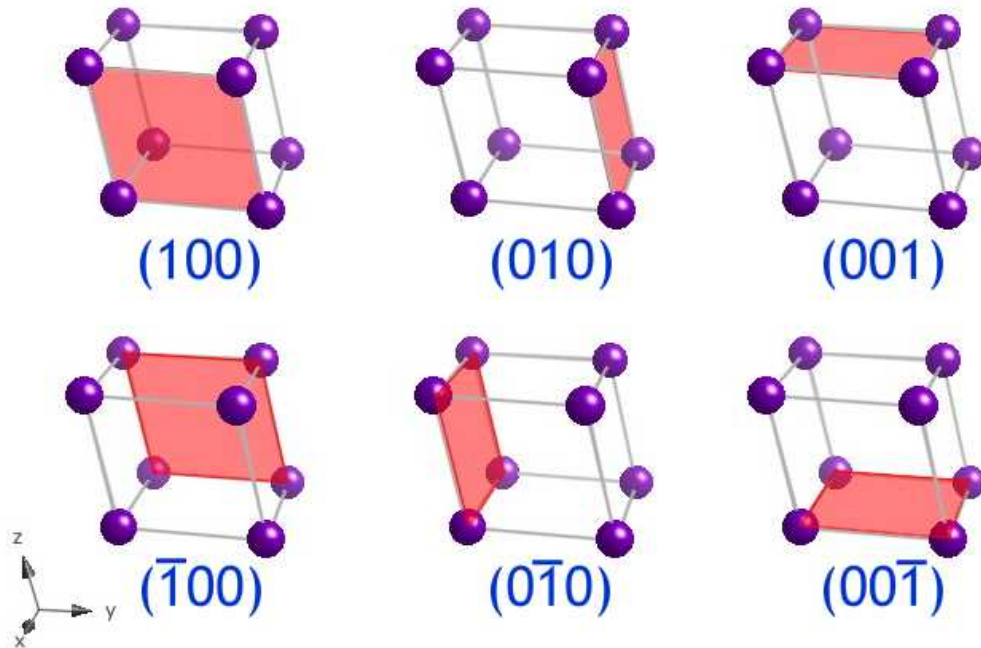An integer (n) difference in path length gives constructive interference.

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

λ = wavelength
d = lattice spacing
θ = incident angle

Lattice Planes (hkl)

The Miller indices, (hkl), are numbers defining the lattice planes in terms of how they intersect the unit cell. Each measured reflection is assigned to an hkl plane.
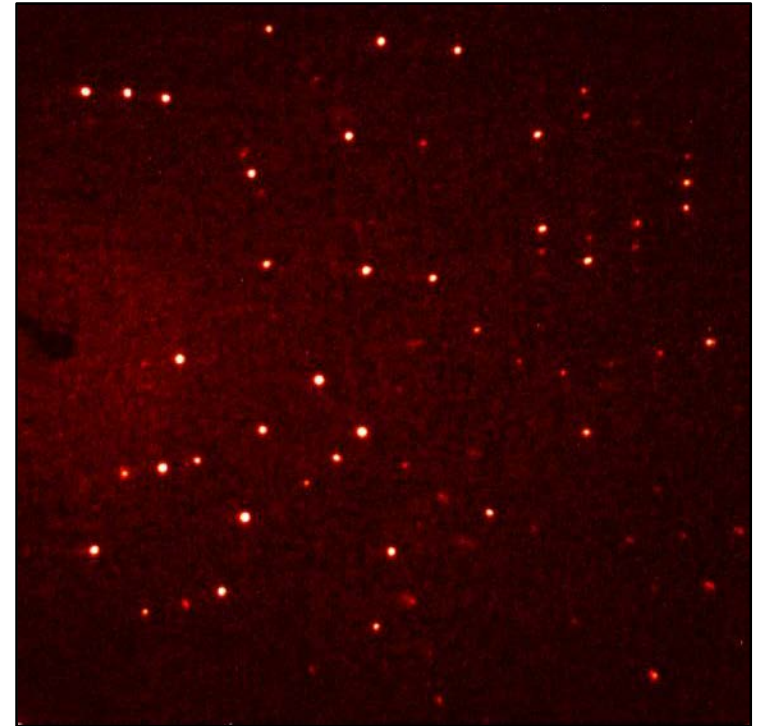

(100) (010) (001)

($\bar{1}$00) (0$\bar{1}$0) (00$\bar{1}$)

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

Diffraction Patterns

Experimentally we measure the reflections in terms of their position and intensity.

Position: Gives size/geometry of lattice (i.e. Information about the unit cell)

Intensity: Gives internal symmetry of cell and electron density (i.e. Information about the contents)

Warning

Equations ahead . . .

Structure Factors

Each reflection will have an amplitude and phase that is the sum of contributions from all the atoms in the unit cell, expressed as the structure factor, F_{hkl} (a complicated wavefunction).

$$F_{hkl} = |F_{hkl}| \cdot e^{[i\alpha_{hkl}]}$$

The amplitude $|F_{hkl}|$ is related to the measurable intensity of the reflections. The phase α_{hkl} cannot be measured and must be 'solved'.

Structure Factors

Contribution from all atoms means that each reflection gives information about the whole crystal structure, giving the structure factor equation expressed as the sum of atomic contributions.

$$F_{hkl} = \sum_{j}^{N} f_j \cdot e^{\left[2\pi \cdot i(hx_j + ky_j + lz_j)\right]}$$

f_j = atomic scattering factor of atom j
x_j, y_j, z_j = coordinates of atom j

Structure Factors

The structure factor equation can be expressed in terms of electron density.

$$F_{hkl} = \int_{cell} \rho(x,y,z) \cdot e^{[2\pi \cdot i(hx+ky+lz)]} dV$$

Where ρ(x,y,z) is the electron density at those coordinates. Integration is over the whole cell for each reflection.

Structure factors are the Fourier transform of electron density in cell.

Structure Factors

The structure factor equation gives us the relationship:

$$|F_{hkl}|^2 \text{ is proportional to } I_{hkl}$$

i.e. The amplitude of the structure factor is related to the intensity of the reflection.

Whilst we can determine $|F_{hkl}|$ we cannot measure α_{hkl} and this is known as the phase problem.

The Phase Problem

Solving the phase problem is the essence of obtaining a crystal structure from diffraction data.

Solution methods are beyond the scope of today.

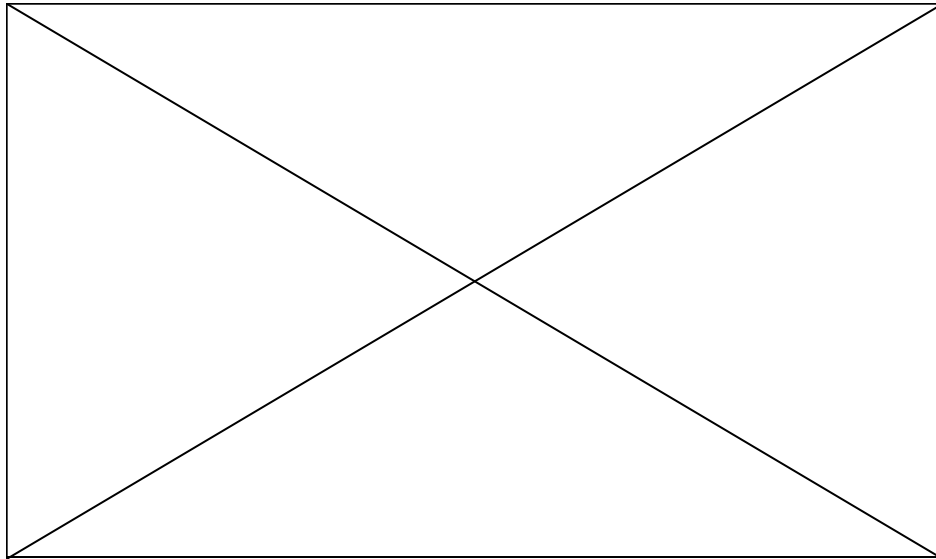Generally provides an initial 'guess' of relative phases before these are refined.

$|F_{Linda}| \cdot \alpha_{Rick}$

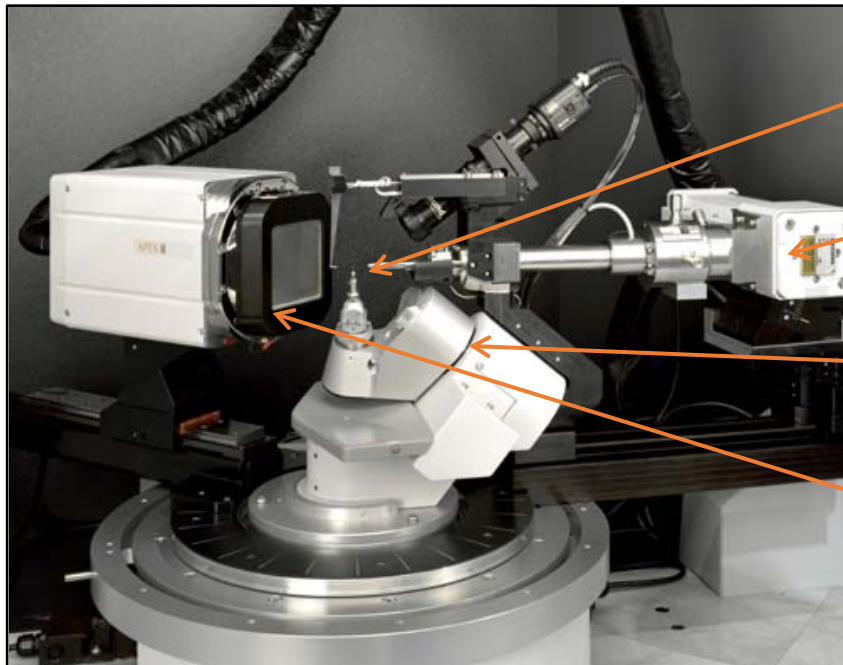$|F_{Rick}| \cdot \alpha_{Linda}$

A Diffraction Experiment

A single crystal diffraction experiment aims to collect reflections for each of the unique planes of the crystal structure.
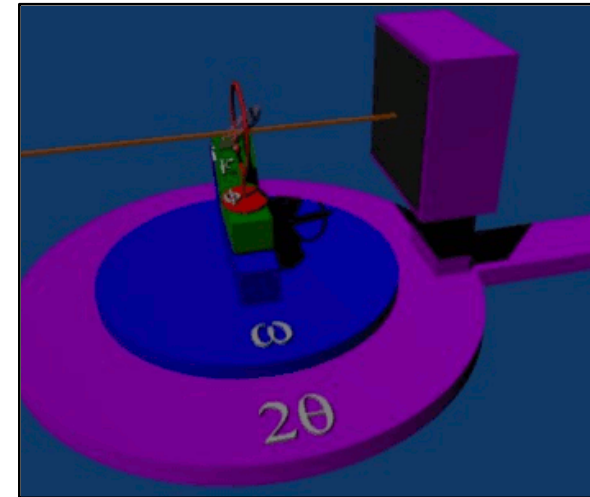
The sample is rotated in order to collect all of the unique reflections.

Diffractometers

Equipment for single-crystal diffraction is very similar in a lab and a synchrotron.
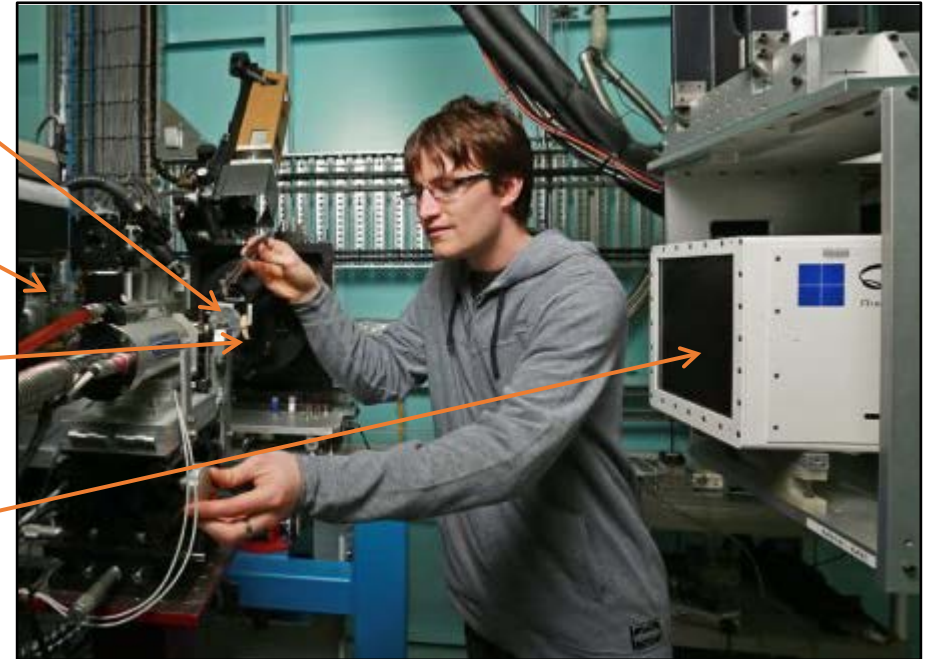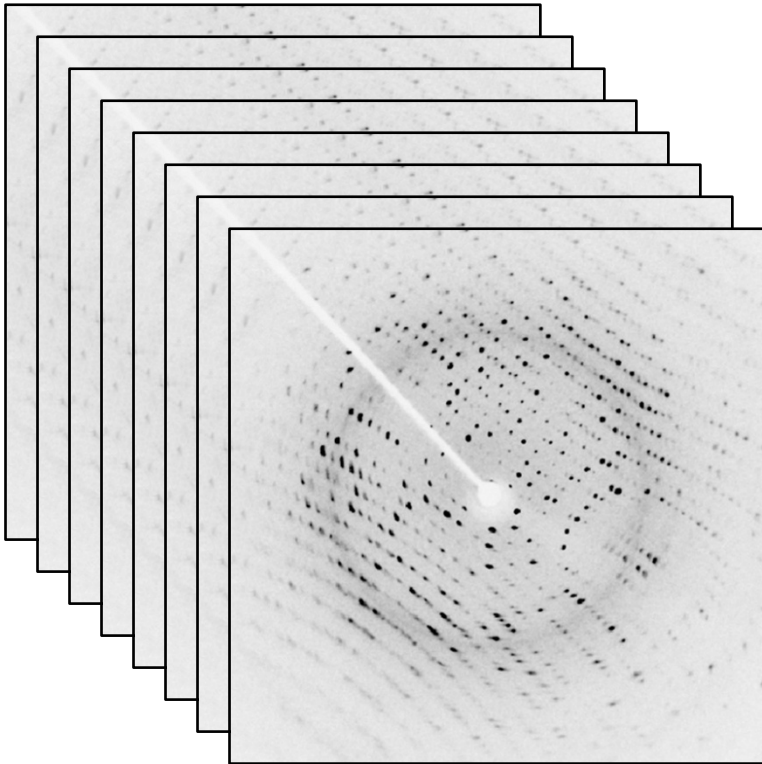

Sample

Source

Rotation stage

Detector

After the Collection

At the end of a data collection, we have hundreds (thousands) of raw image files.

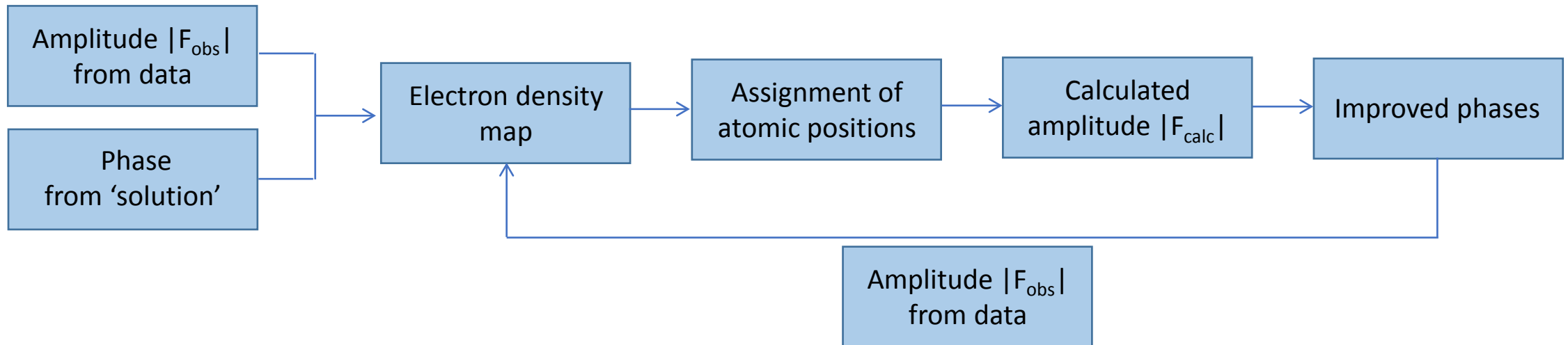Positions of reflections (h,k,l)

Intensity of reflections ($|F_{hkl}|$)

Crystallographic Refinement

Structural refinement improves the phases by comparing a model (made by you) to the data.

A cyclic process until best agreement between F_{obs} and F_{calc} is reached.

Advantages of Synchrotrons

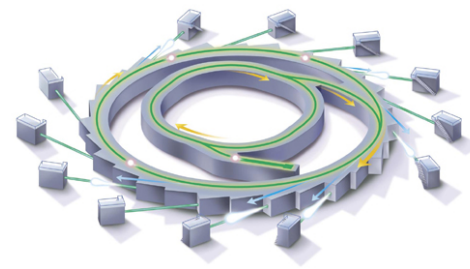**"Anything you can do, I can do better"**
(Irving Berlin)

Diffraction intensity is a combination of two main components:

(i) Scattering power of sample.

   Bigger crystals, heavier elements – more electrons to scatter X-rays.

(ii) Intensity of radiation.

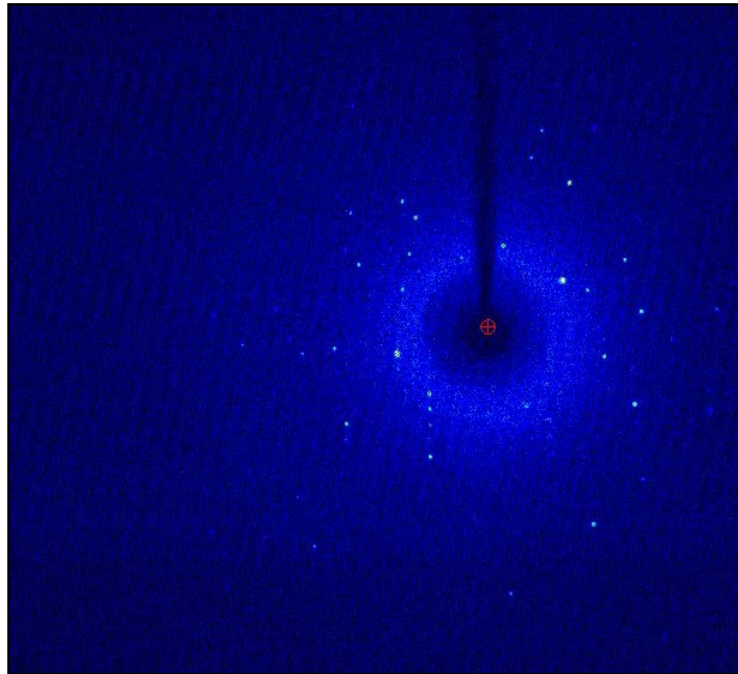   More incident radiation gives more scattered radiation.

Advantages of Synchrotrons

In practice it is hard to get bigger crystals.

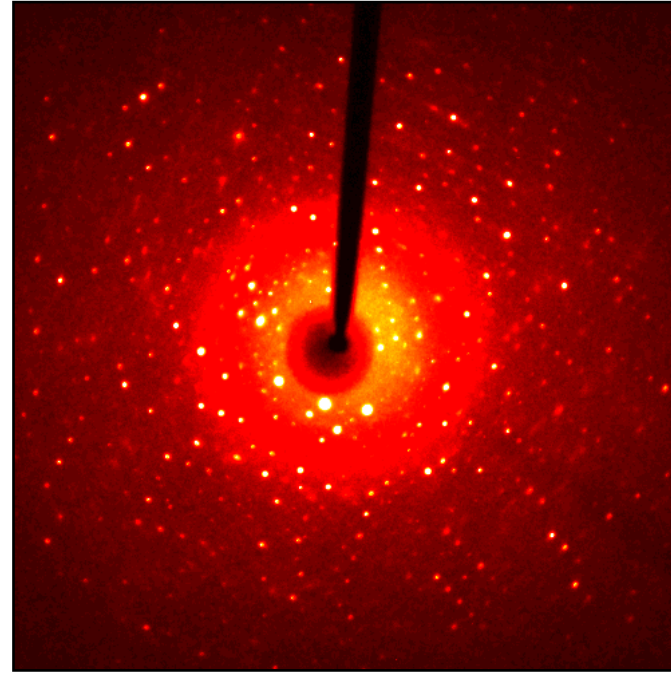Synchrotron sources provide very intense radiation, enhances diffraction.

Lab source

90 seconds

Synchrotron

1 second

Brighter Light, Smaller Crystals

Routine collections on crystals < 50 μm (0.05 mm).

Slightly less routine collections ~ 2 μm.

Diffraction from samples this size would either be impossible or require <u>many</u> days on a laboratory source.

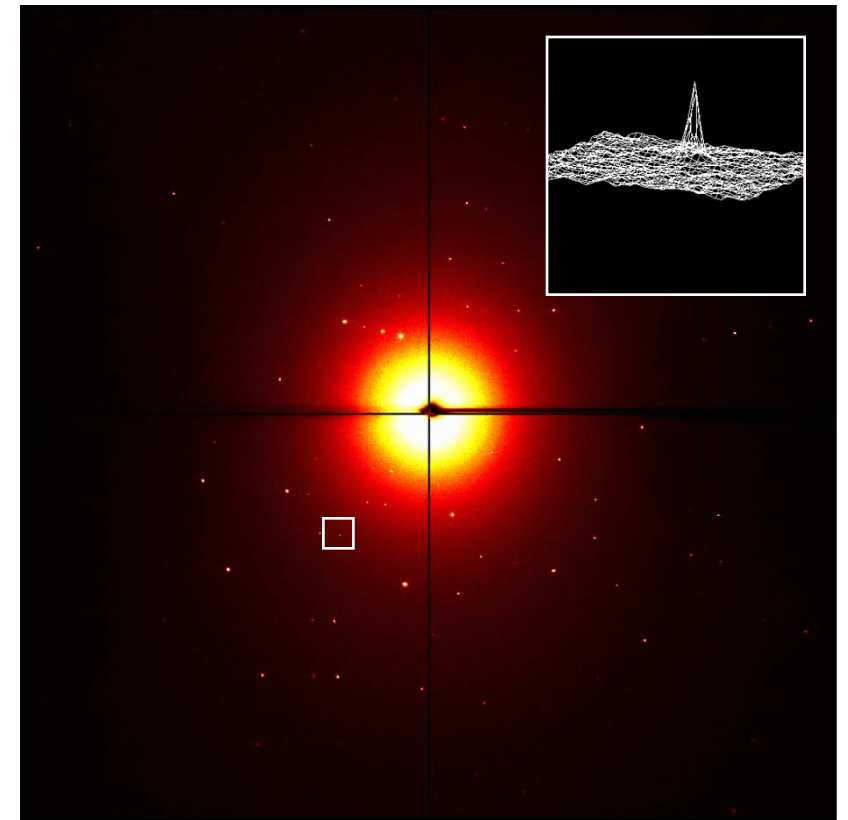Can make 'impossible' crystals possible and speed up 'routine' samples for high throughput.

Brighter Light, Smaller Crystals

The high intensity, and sensitive detectors, give better data quality.
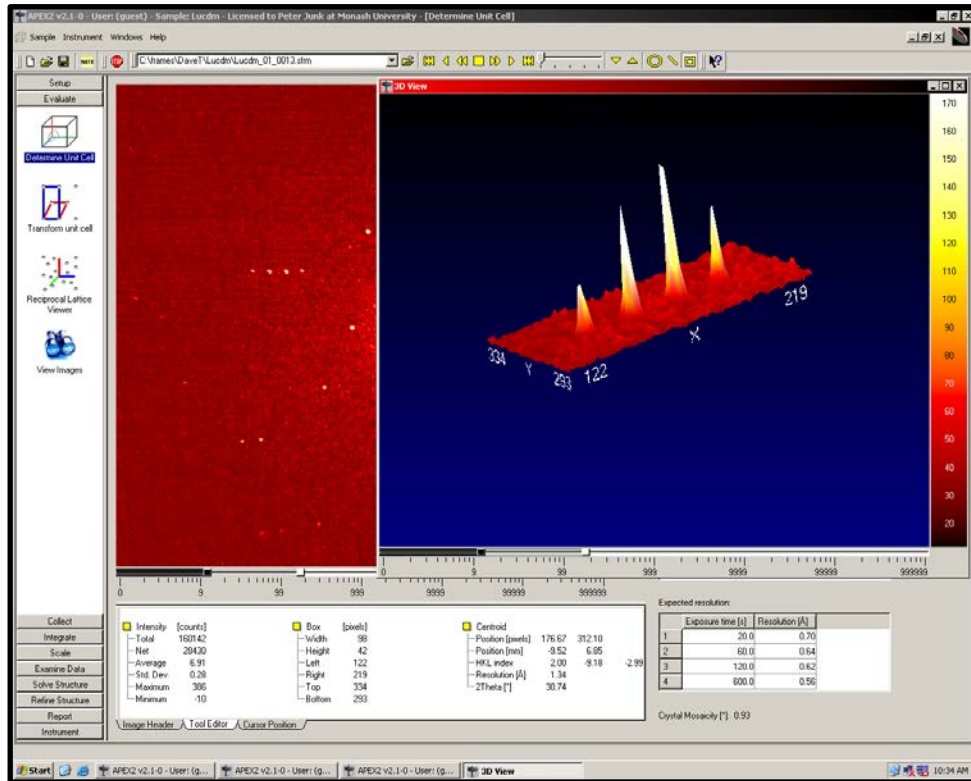
Lab

**Reduced background and improved signal-to-noise increases data quality**

Synchrotron

Enhanced Resolution

Intensity of reflections decreases as a function of 2θ.

However, high angle data corresponds to smaller d-spacings and is therefore higher resolution data.

More intense radiation at synchrotrons gives better high angle data and better resolution of the electron density.
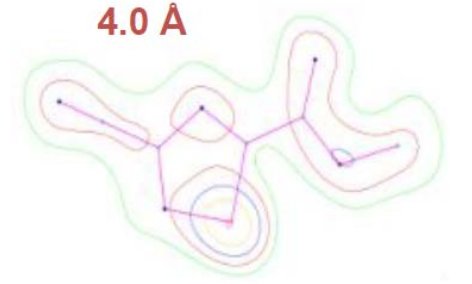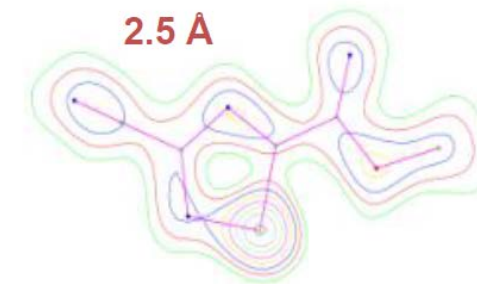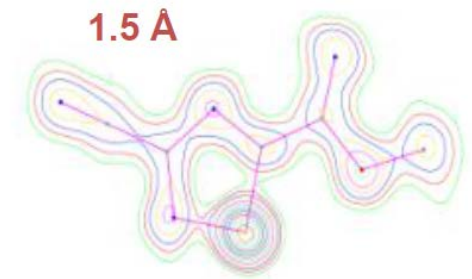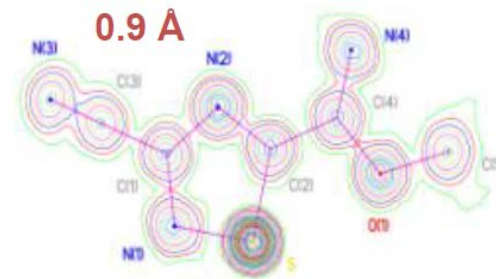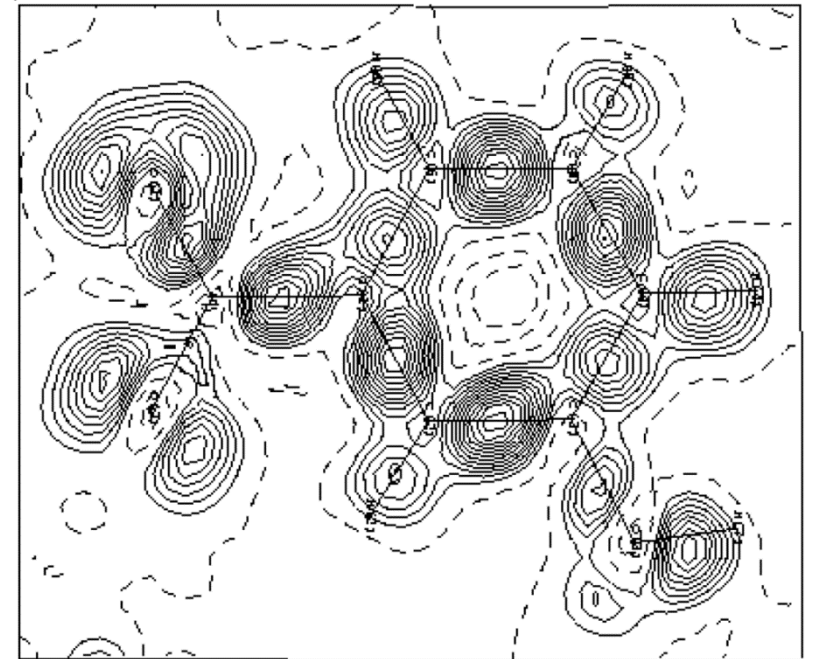
Charge Density

Very high quality, high resolution data can be used to obtain more information that using the Independent Atom Model.

Synchrotrons can capture this information with good quality data.

Allows chemical bonding to be modelling by using 'multipoles' or 'spherical harmonics'.

Diffuse Scatter

The higher intensity of the beam at a synchrotron can also reveal more information from non-Bragg reflections, diffuse scatter.

This information can be used to determine long-range order in systems that are otherwise described as 'disordered' on the unit cell scale.
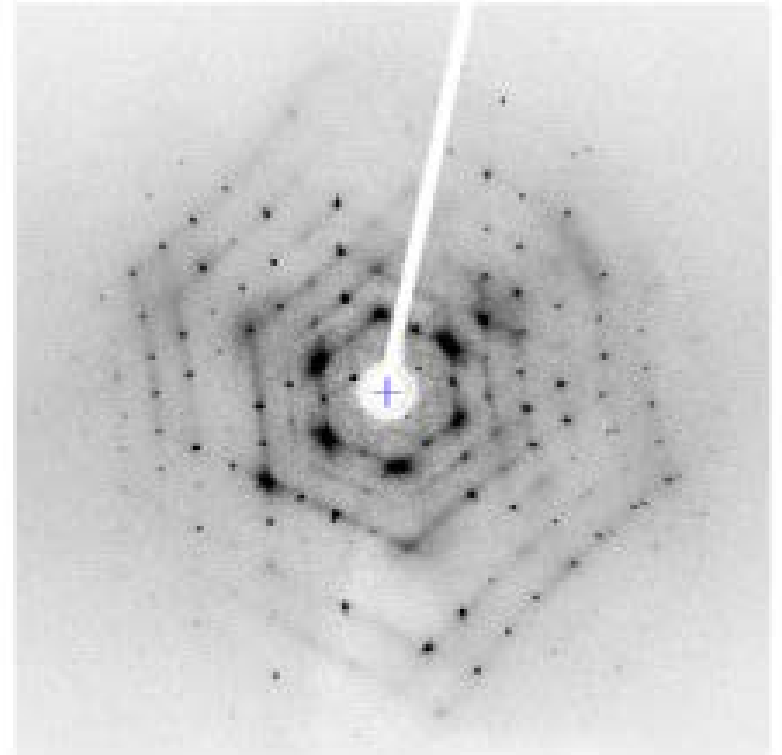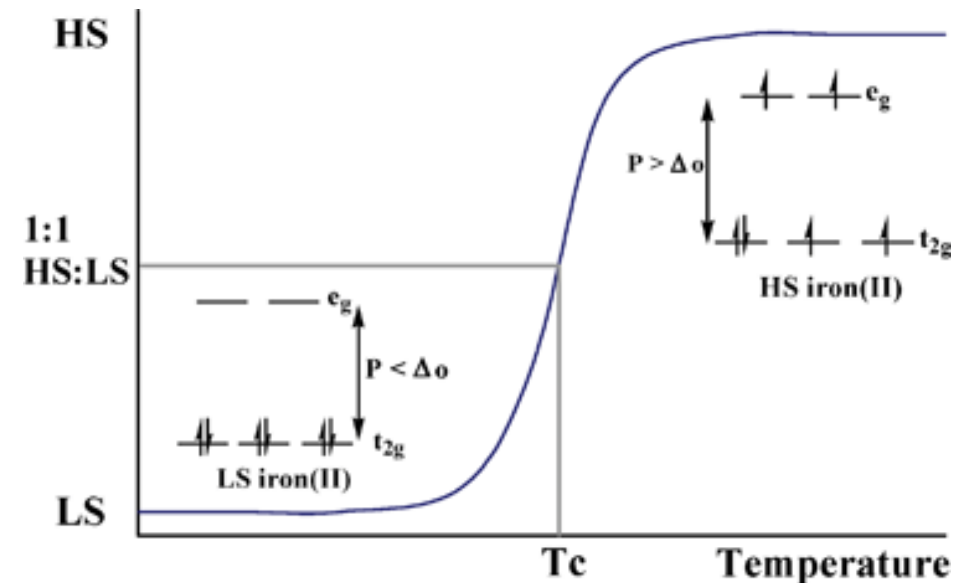
High Throughput – e.g. Temperature Scans

Many materials exhibit gradual phase transitions, *e.g.* spin crossover.

Probing structure at multiple temperatures is time consuming.

30 second data collections (MX2) makes this easier, giving full structural information at various temperatures.

Synchrotrons are Big

The scale associated with large instrument facilities allows for unconventional experiments to be conducted more easily.

- High pressure
- Heliostat (very low temperature)
- Excited state (lasers)
- Special atmospheres

Support your local synchrotron, ask them what they can do for you!