Basic Crystallography: Reciprocal Space (a Gentle Introduction)

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Introduction

- Notions of **reciprocal space** and the **reciprocal lattice** are indispensable for understanding X-ray Crystallography
- Diffraction by a lattice gives a lattice as a diffraction pattern
- There is a precise mathematical relationship between the original diffracting lattice and the resulting pattern
- However, this is a (mostly) non-mathematical introduction to help you qualitatively understand the concepts of reciprocal space and the reciprocal lattice

Direct Space & Reciprocal Space

- We live in direct space
- Distances and orientations between isolated objects
- Reciprocal space is a “spatial frequency” space (e.g. number of Tim Horton’s per kilometre)
- In NMR time and frequency are related by a Fourier transform (units:time t and frequency t^{-1})
- In X-ray Crystallography direct space and reciprocal space are related by Fourier transform (units: distance Å and spatial frequency $Å^{-1}$)

Bragg's Law

- $n\lambda = 2d\sin\theta$
- Rewrite as:
- $\sin\theta = 0.5n\lambda(1/d)$
- Reciprocal relationship between diffraction angle, θ, and the d spacing
- The smaller the d spacing, the higher the diffraction angle

Reciprocal Quantities

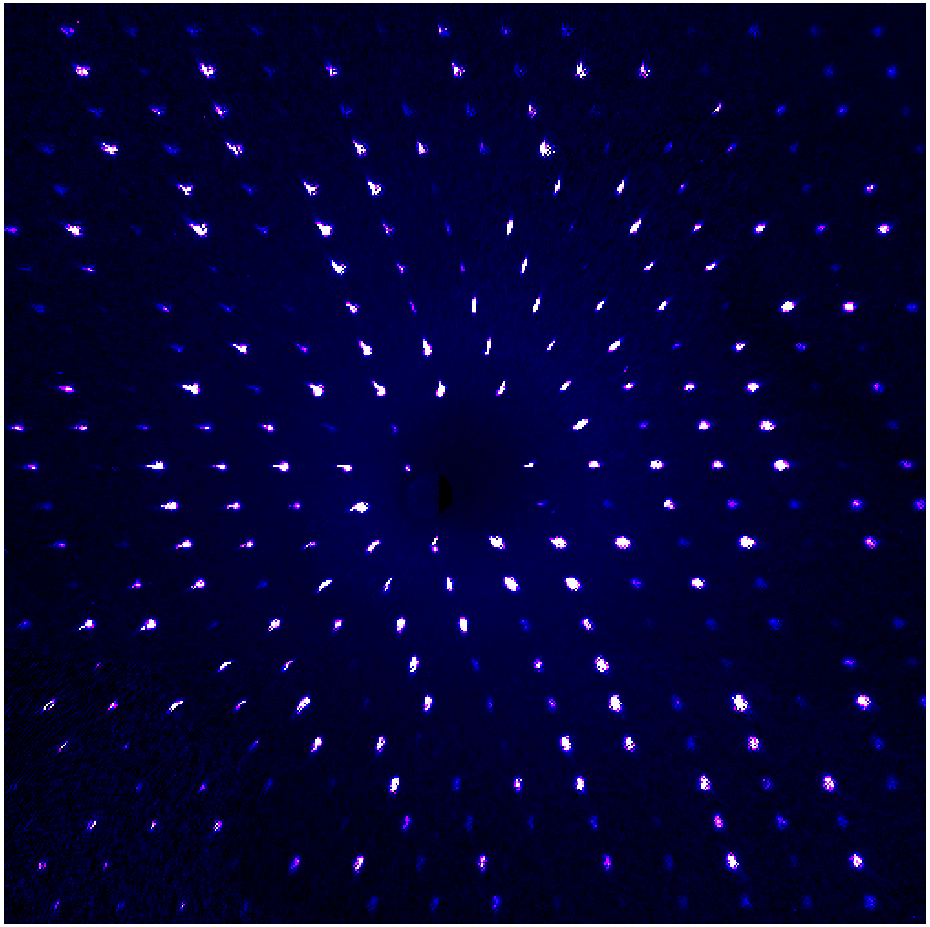
- $1/d = d^*$
- d^* is a reciprocal quantity and typically has units of $Å^{-1}$
- The '*' in general means a reciprocal space quantity
- A direct space unit cell with parameters a, b, c, α, β, γ has a corresponding reciprocal unit cell: a^*, b^*, c^*, α^*, β^*, γ^*
- There are exact mathematical relationships which relate the direct space and reciprocal space unit cell parameters

Reciprocal Relationships

- The relationships between the direct axes and reciprocal axes is strictly reciprocal
- Any statement about the two lattices remains true if you simply replace all starred (*) quantities by unstarred quantities and vice-versa
- $a^* \perp bc$(face) and $a \perp b^*c^*$(face)
- Any direct axis has as family of reciprocal lattice planes which are perpendicular to that axis
- Conversely, any reciprocal axis has a family of direct lattice planes which are perpendicular to that axis

X-ray Diffraction Patterns

- The X-ray diffraction pattern is the reciprocal lattice of a crystal's direct lattice
- Referred to as the **intensity weighted reciprocal lattice**
- Diffraction maxima are reciprocal lattice points
- Intensity distribution of diffraction pattern is related to the electron density distribution in the crystal

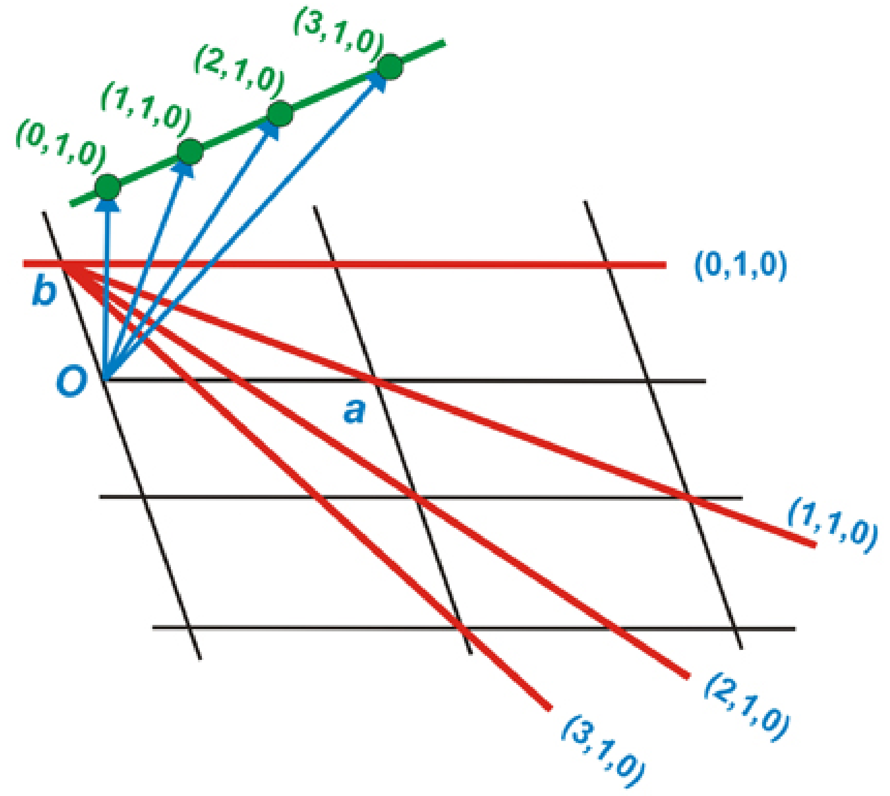


Reciprocal Lattice Points

- Are designated by their Miller index, hkl
- Assigning hkl values to the reciprocal lattice points is called ***indexing the crystal*** or ***indexing the diffraction pattern***
- Reciprocal lattice points represent the diffraction from a **set of planes** designated by the hkl value and have a corresponding d* value
- Normal to the set of planes and therefore represent a direction in reciprocal space

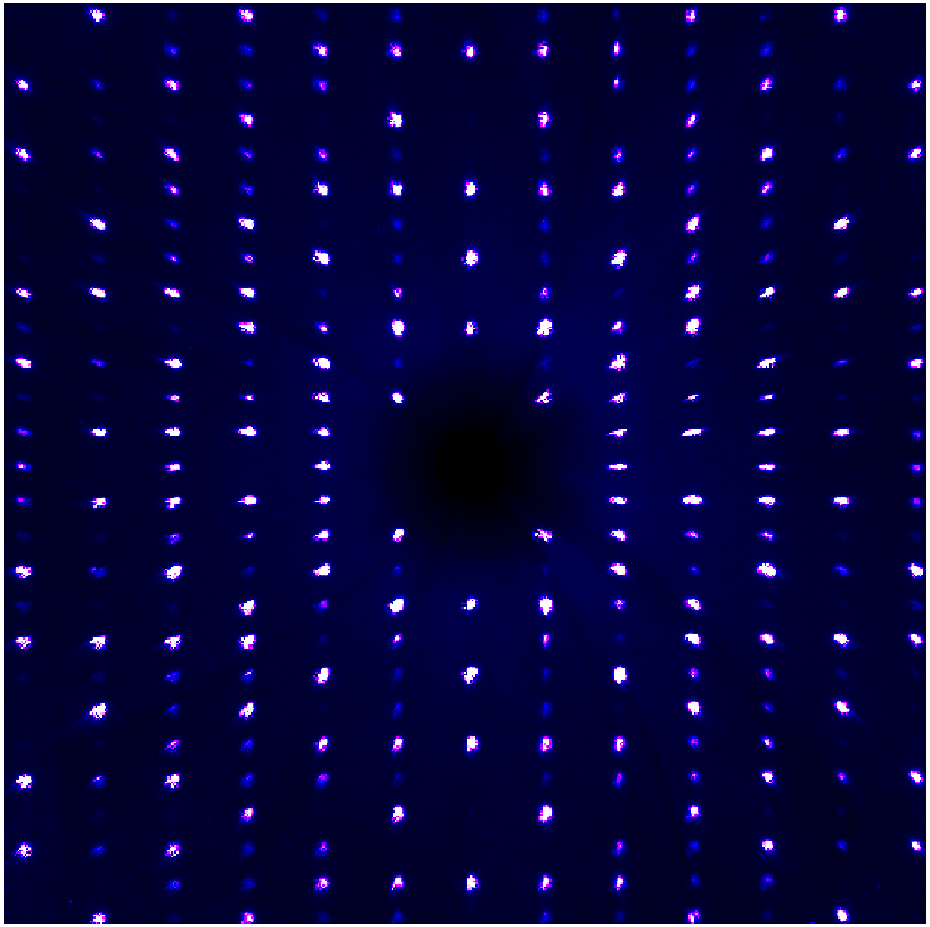
Graphical Construction of Reciprocal Lattice from Direct Space Lattice

- For a set of planes in direct space, we draw a vector normal to these planes
- Terminate the vector at a distance 1/d
- For a given lattice row:
- d*(nh,nk,nl) = nd*(hkl)
- Graphic: http://www.xtal.iqfr.csic.es/Cristalografia/parte_04-en.html



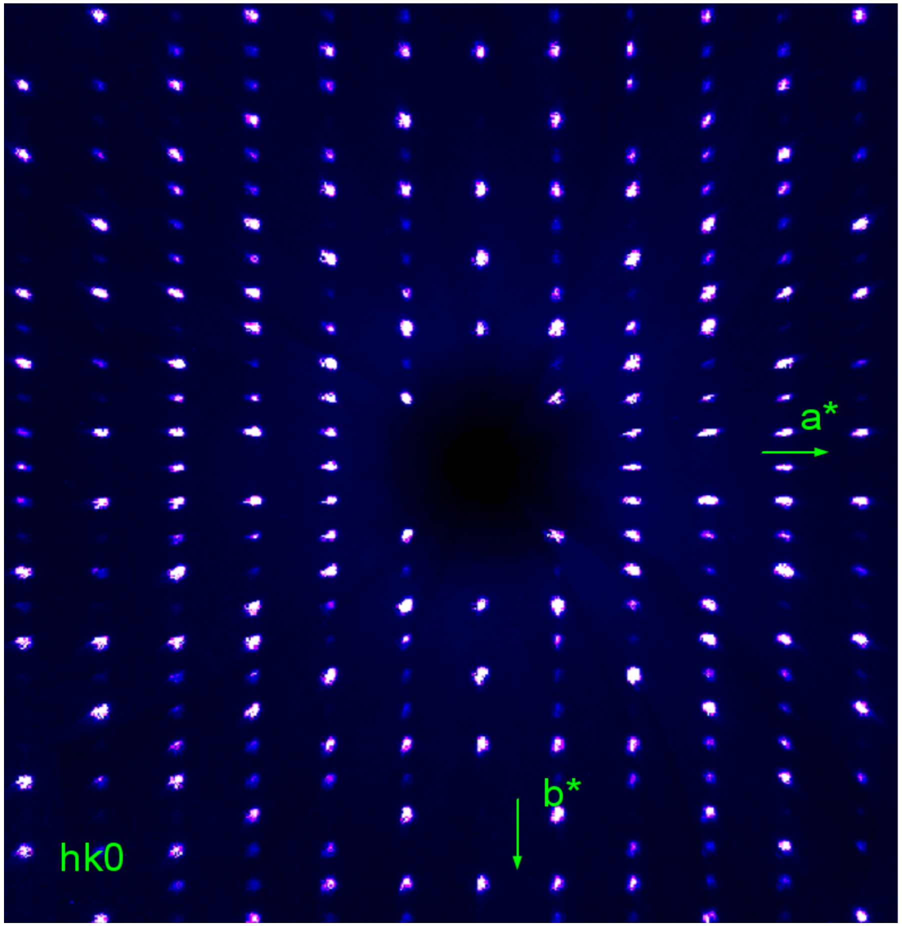
Indexing a Diffraction Pattern

- Synthesized reciprocal lattice layer (hk0) from an actual crystal
- Vertical axis has closer packed reciprocal lattice points
- Vertical axis has larger direct space unit cell parameter



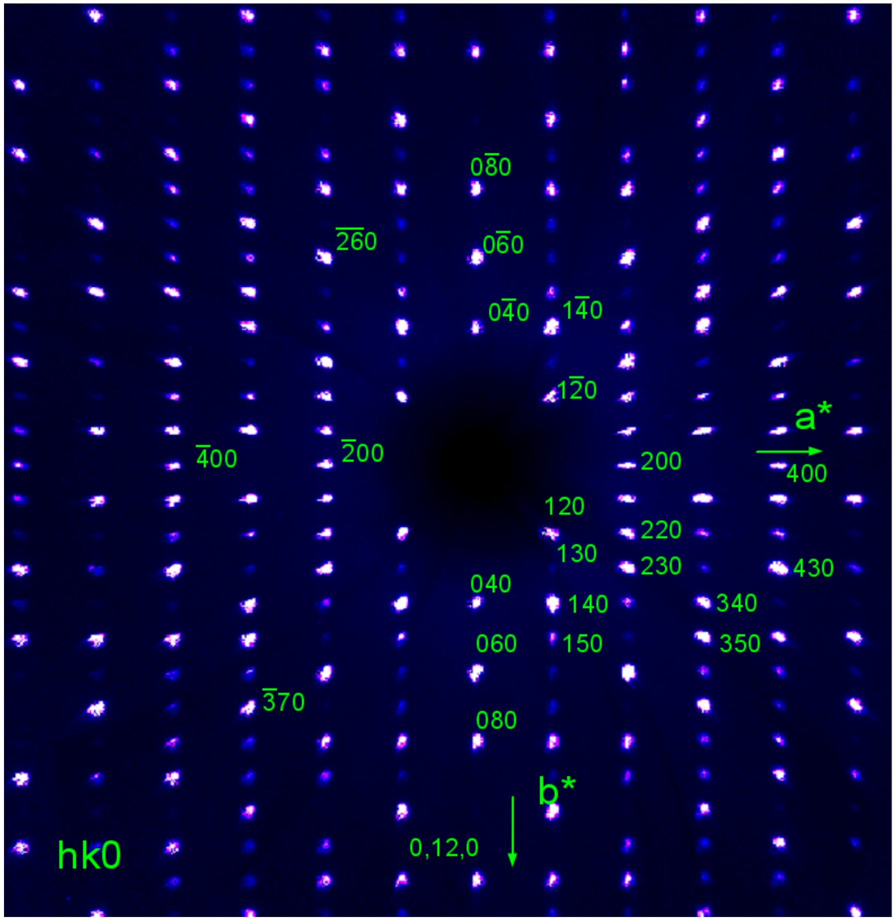
Indexing a Diffraction Pattern

- First assign the lattice directions
- Notice there are systematic absences along the h00 and 0k0 reciprocal axes
- Indicative of two screw axes (translational symmetry elements)



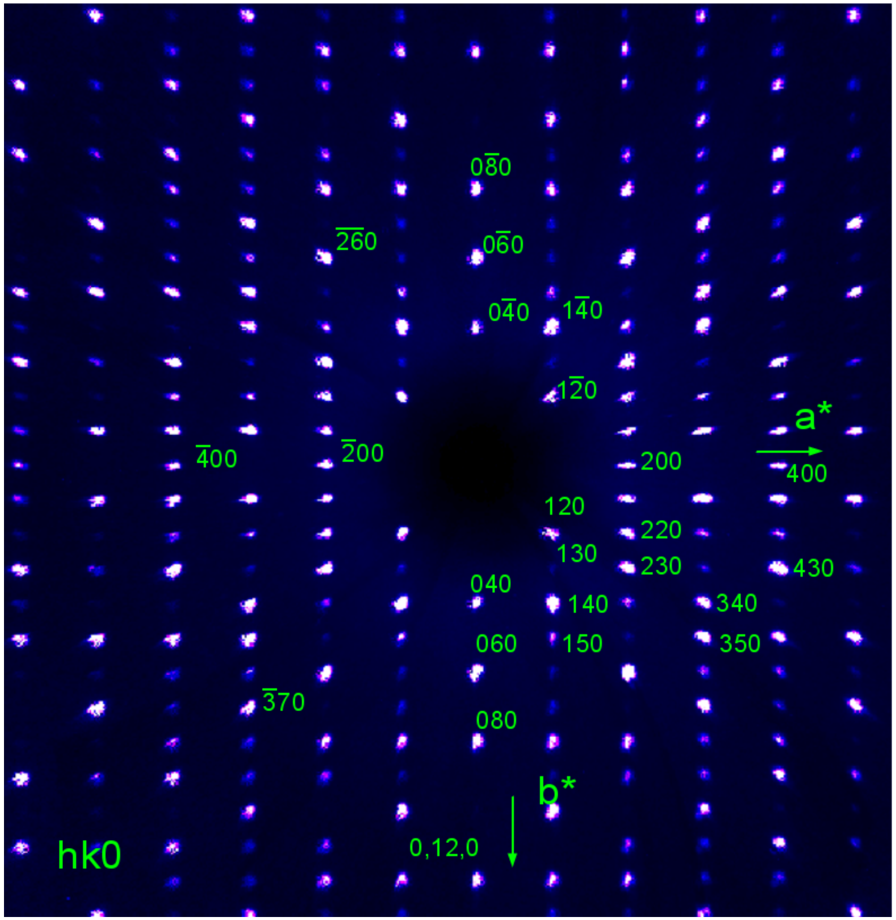
Indexing a Diffraction Pattern

- Assign hkl values to each reciprocal lattice point
- Use Bragg's Law to calculate the interplanar spacing associated with each reciprocal lattice point
- Measure angle between a* and b* to obtain γ*
- Repeat process with other zero layers (0kl and h0l)



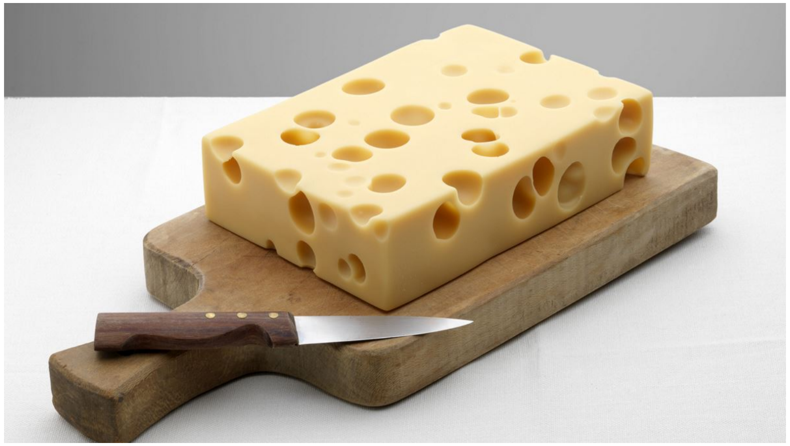
How to think about this

- Each reciprocal lattice point represents both a direction and d spacing
- With each reciprocal lattice point measured, we are "sampling" the electron density with certain spatial frequency in a given direction



The Swiss Cheese Analogy

- We want to map where all the holes are in a block of Swiss cheese
- We (virtually) slice the block using various thicknesses and at various orientations
- We then take these slices and use them to map the size and shapes of the all the holes in the block



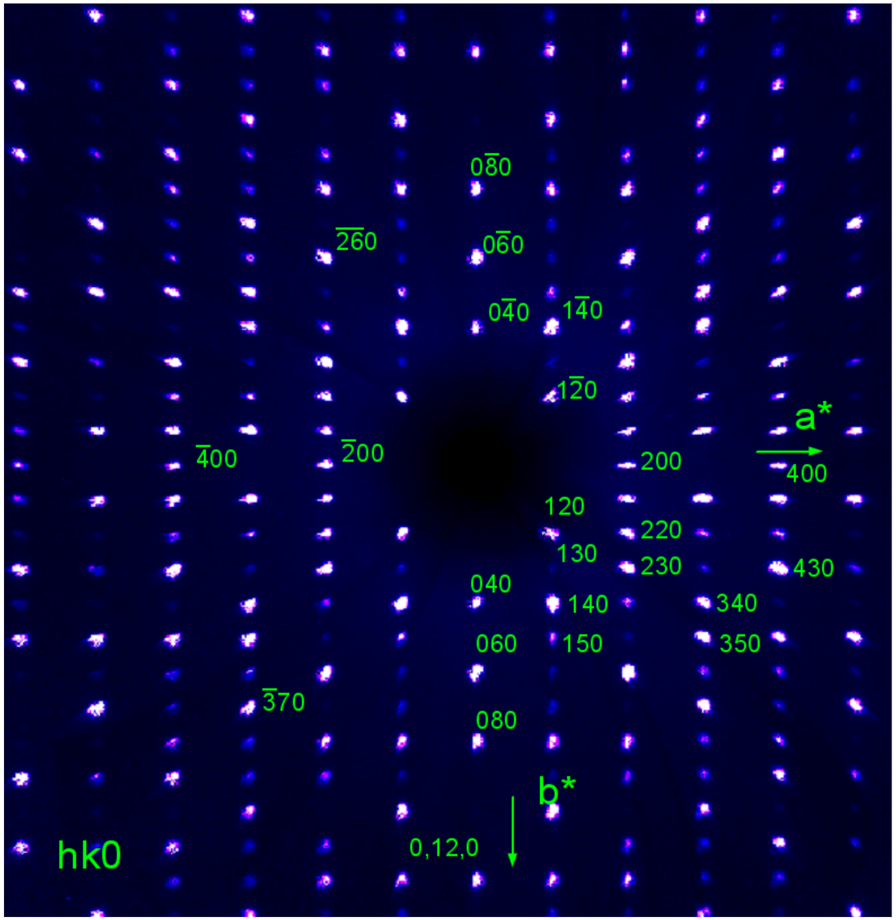
Resolution of Our Mapping

- Slicing our cheese every 10 mm will cause us to miss some of the smaller holes in the cheese
- We make finer and finer slices to map even the smaller holes within the cheese
- Why not just use all fine slices rather than both low and high resolution slices?
- Analogy breaks down at this point
- In X-ray we need both the low resolution data and high resolution data

Slice Width	**Reciprocal Units**	Low Resolution
Every 10.0 mm	**1/10 or 0.1 mm^{-1}**	$\downarrow$
Every 5.0 mm	**1/5 or 0.2 mm^{-1}**	$\downarrow$
Every 2.0 mm	**1/2 or 0.5 mm^{-1}**	$\downarrow$
Every 1.0 mm	**1/1 or 1 mm^{-1}**	$\downarrow$
Every 0.5 mm	**1/(1/2) or 2.0 mm^{-1}**	High Resolution

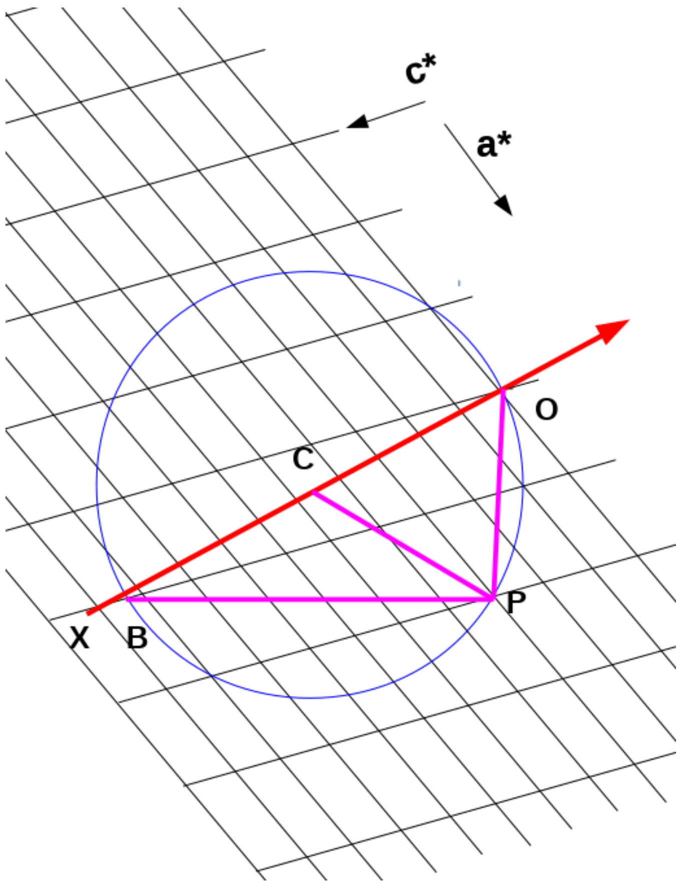
Resolution in Reciprocal Space

- The higher the diffraction angle, the finer the slice we are using to sample our crystal's electron density
- Diffraction condition only allows us to sample the electron density distribution at certain spatial frequencies (Bragg's Law)
- We need to collect both high and low resolution data



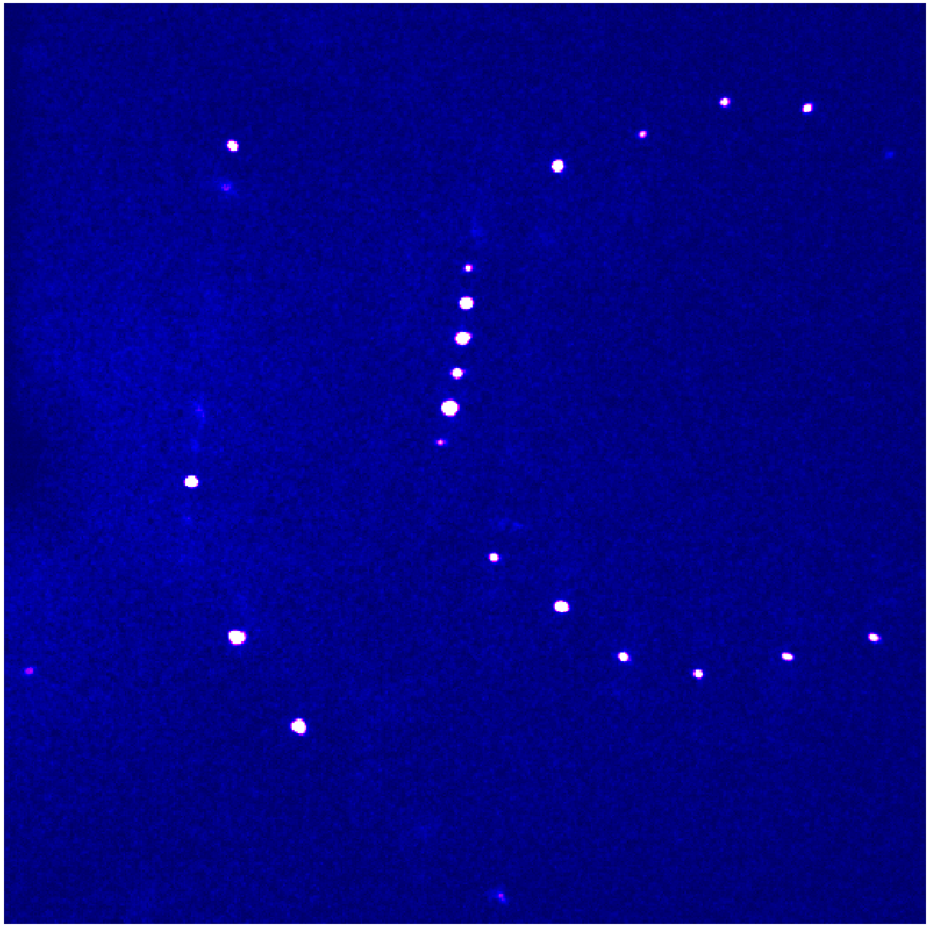
Ewald Construction

- Graphical depiction of Bragg's Law
- Circle has radius of 1/λ, centre at C such that origin of reciprocal lattice, O, lies on circumference
- XO is the X-ray beam, P is the reciprocal lattice point (in this case the 202 reflection)
- OP is the reciprocal lattice vector (**d***) and is normal to the (202) set of planes [aka the Scattering Vector]
- Angle OBP is θ, the Bragg angle
- Angle OCP is 2θ
- CP is the direction of the diffracted beam
- BP is parallel to the set of (202) planes
- **Any time a reciprocal lattice point falls on the circumference, Bragg's Law is fulfilled**



Ewald Sphere

- 2D Ewald construction can be generalized to 3D to generate the “Ewald Sphere” (also called the “Sphere of Reflection”)
- Anytime a reciprocal lattice point is on the surface of the sphere Bragg’s Law is fulfilled
- Experimentally, we rotate the crystal (lattice) to bring a greater number of reciprocal lattice points pass through the surface of the sphere
- Image shows the detector slicing through part of the Ewald sphere and all the lattice points which were laying on the surface of the sphere



Ewald Spheres and Limiting Spheres

- Ewald sphere has a diameter of $2/\lambda$
- Every reciprocal lattice point within that distance can be brought into diffracting position
- Limiting sphere has a radius of $2/\lambda$
- The total number of reciprocal lattice points within the limiting sphere is approximated by
- $N \approx 33.5(V_{cell} / \lambda^3)$

Limiting Spheres of Common Radiations

- $N_{MoK\alpha} \approx 33.5V_{cell} / 0.71073^3 = 93.3V_{cell}$
- $N_{CuK\alpha} \approx 33.5V_{cell} / 1.54178^3 = 9.14V_{cell}$
- Normally, we don't collect all reflections within the limiting sphere. In practice, we pick some maximum value of θ
- $N_{\theta(max)} \approx (33.5 / \lambda^3) V_{cell} \sin^3\theta_{max}$
- You will always get more data with a shorter wavelength

Wavelength Imposed Limits

- Maximum value of sine function = 1.0
- Imposes certain limits on the X-ray experiment
- Shorter wavelengths allow collection of more data points out to higher resolution

Quantity	**CuKα**	**MoKα**
λ	1.54178 Å	0.71073 Å
$(\sin\theta/\lambda)_{max}$	0.648 Å^{-1}	1.407 Å^{-1}
d_{min}	0.771 Å	0.355 Å
Resolution Limit ($0.92d_{min}$)	0.71 Å	0.33 Å

Practical Considerations for Data Collection

- Long axes give densely packed reciprocal lattice rows
- Integration is better if peaks aren't overlapping
- Choose minimum crystal to detector distance as:

  DX(mm) = 2 * longest primitive axis (Å) [MoKα]

  DX(mm) = 1 * longest primitive axis (Å) [CuKα]
- For non-merohedrally twinned samples, move the detector back even farther

Experimental Determination of Space Group

- Space groups are determined primarily through the examination of systematic absences in the diffraction pattern
- Systematic absences arise from the presence of translational symmetry elements
    - Non-primitive lattice centrings
    - Screw axes (rotation with translation)
    - Glide planes (reflection with translation)

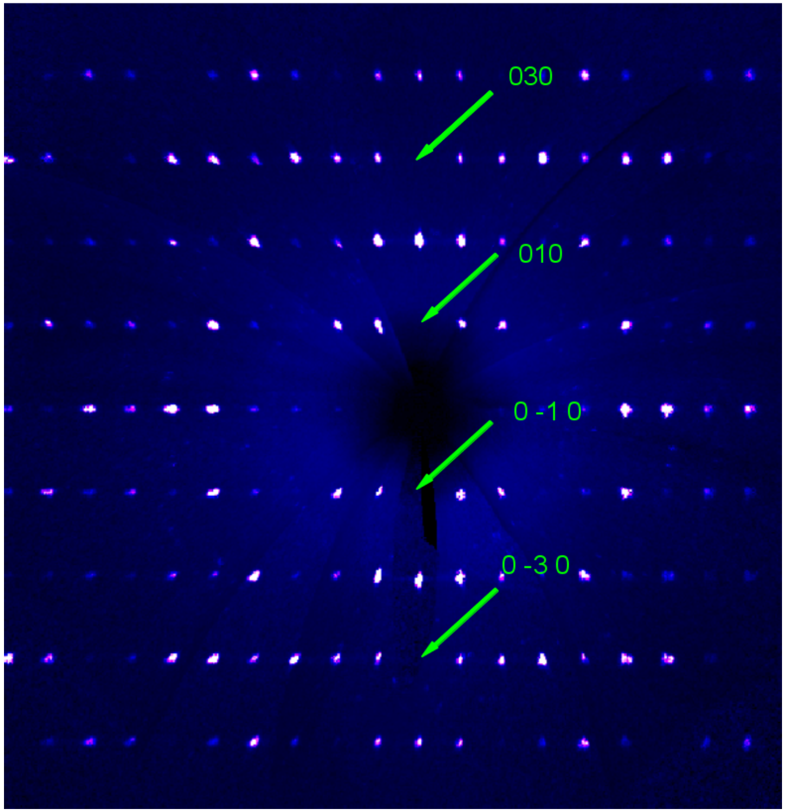
Systematic Absences due to Non-Primitive Lattices

- Non-primitive lattices exhibit systematic absences in the general hkl class of reflections

Centring	Absence Condition for hkl reflections
A	k+l = odd
B	h+l = odd
C	h+k = odd
F	k+l = odd, h+l = odd, h+k = odd
I	h+k+l = odd

Screw Axis Absences

- Screw axes affect the classes of axial reflections: h00, 0k0, and 00l
- The type of screw axis is determined by examining the pattern of the absence
- Example: In this figure there is a 2_1 axis parallel to b*
- 0k0: k = odd



Orientation of Glide Planes

- When a glide plane is present one can determine the orientation and type of glide plane present from the affected class(es) of reflections
- The 0 index of the affected layer indicates the orientation of the glide's reflection
  - 0kl: glide reflects across (100)
  - h0l: glide reflects across (010)
  - hk0: glide reflects across (001)

Identification of Glide Planes

- The translational component identifies the type of glide plane
- The translational component causes absences in along the affected axes
- 0kl:

  k = odd → b glide; l = odd → c glide; k+l = odd →n glide
- h0l:

  h = odd → a glide; l = odd → c glide; h+l = odd → n glide
- hk0:

  h = odd → a glide; k = odd → b glide; h+k = odd → n glide

Example of c glide (h0l: l = odd)