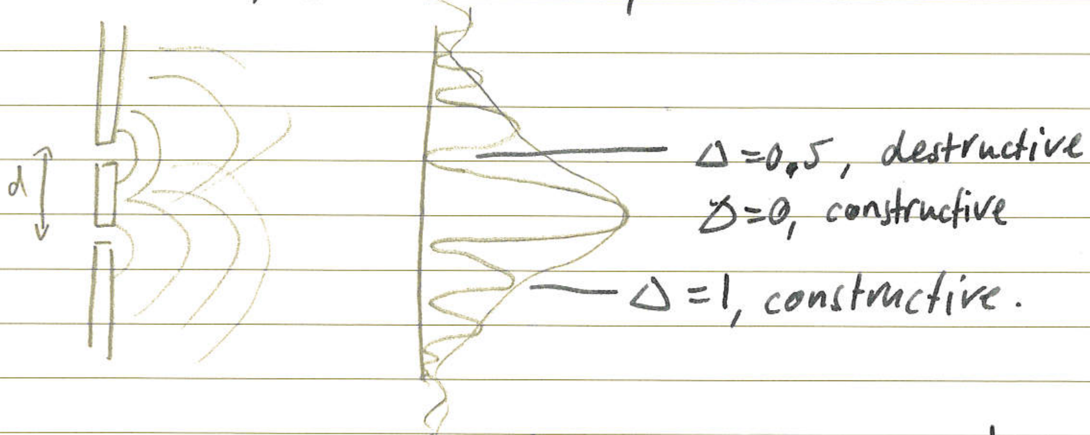
No. V0

Date 20 . 11 . 18

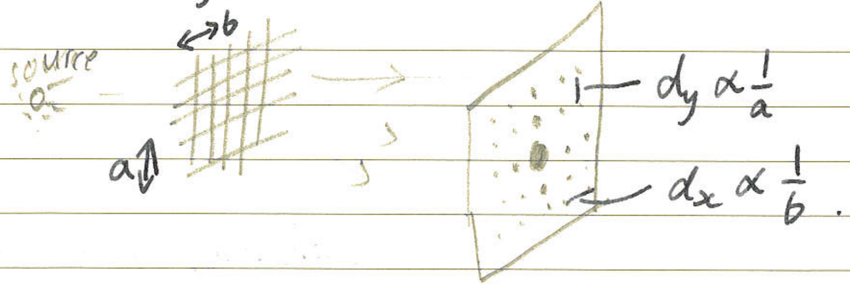
C. Diffraction

Optical Diffraction

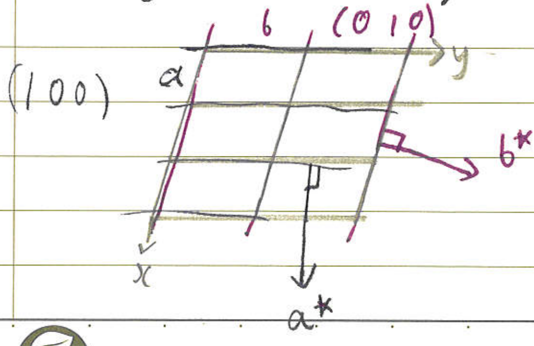
- Diffraction through a slit can be analysed with the Huygens-Fresnel principle, in which a wave can be described as an infinite line of sources.
- With 2 slits, an interference pattern forms

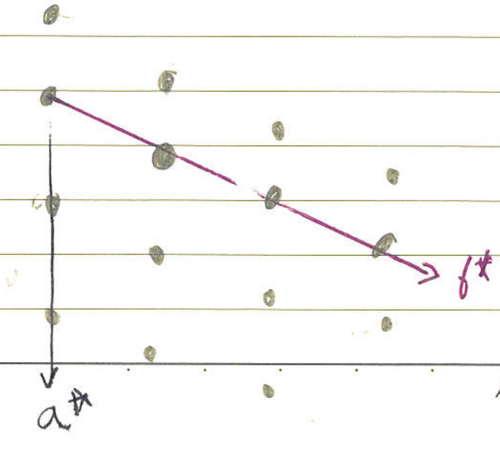


- Young's experiment found that peak spacing $\propto 1/d$.
- For many slits, the maxima become sharp, tending toward δ functions.
  ↳ i.e destructive interference everywhere except $\Delta = n\lambda$.
- A 2D diffraction grating behaves like two 1D gratings at cross angles

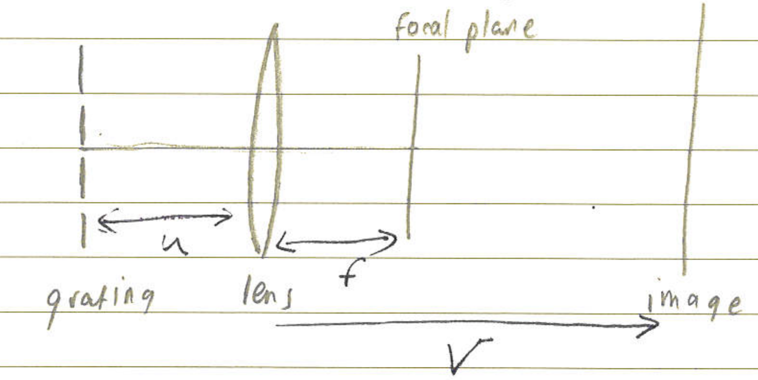


- Diffraction is always perpendicular to the set of slits
  e.g for non-orthogonal axes.





Optical microscopes and resolution

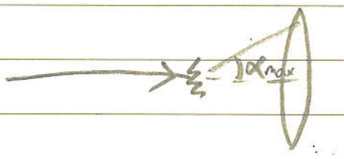


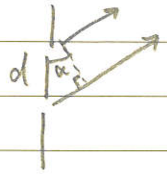
Focal length equation:

$$\frac{1}{f} = \frac{1}{u} + \frac{1}{v}$$

$$\text{Magnification} = \frac{v}{u}$$

- Abbe's Theorem states that resolving a grating with separation d requires two beams (direct and first order) to enter the lens.



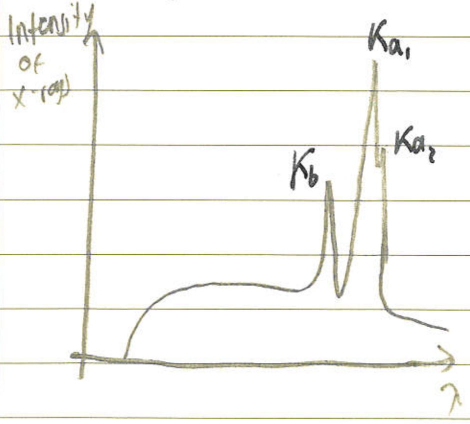


$$d = \frac{\lambda}{\sin\alpha} \rightarrow d_{min} = \frac{\lambda}{\sin\alpha_{max}}$$

- Resolution can actually be improved by a factor of 2 because light is scattered above and below: $d_{min} = \frac{\lambda}{2\sin\alpha_{max}}$

X-ray Diffraction

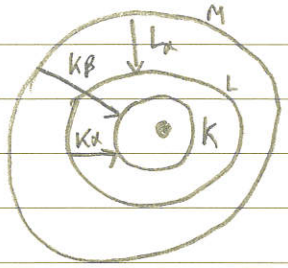
- Lattice spacing $\approx 1\,A^\circ \approx \lambda$ of X-rays.
- X-rays generated by bombarding a copper target with energetic thermionic electrons.
- The spectrum obtained has two parts: continuous, characteristic

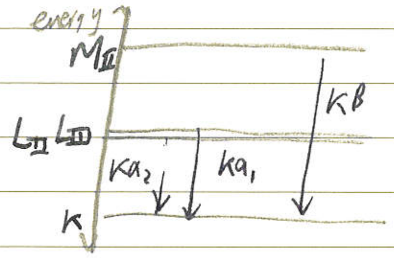


- The cont. spectrum comes from deceleration of electrons, which happens at a different rate for each electron:

$$\lambda = \frac{hc}{\Delta E}.$$

- Characteristic peaks are formed when incident e^- excites inner shell e^-. When other e^- drop into the shell, an X-ray is released.

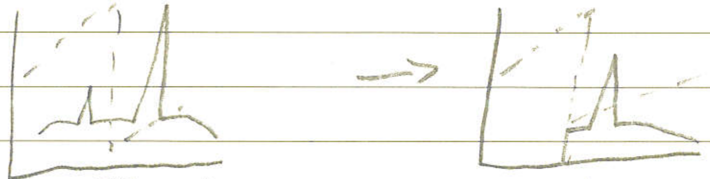




3 — tiny split due to QM

- Transitions from L_{II} and L_{III} are equally likely, but L_{III} has $4e^-$ vs $2e^-$ in L_{II}, so $K\alpha_1$ intensity double $K\alpha_2$.
- K_β transitions less likely.

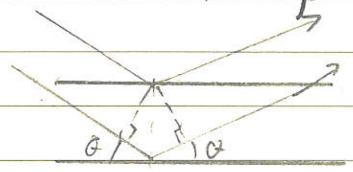
- In order to produce X-rays of one wavelength, a nickel filter can be used, with an absorption edge around 1.5Å.


unfiltered filtered

← results in (purer) copper-Kα radiation.

Diffraction angles

- Assume X-rays reflected by planes of atoms

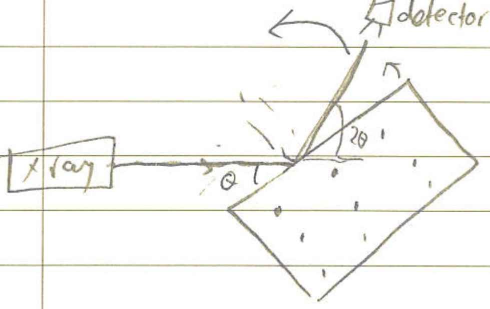


There will be a sharp peak due to constructive interference when $\Delta = n\lambda$

i.e $\lambda = 2d\sin\theta$ (Bragg's Law)

- The hkl reflection is the reflection from (hkl) planes.
- We will in general be able to see reflections from empty space e.g (2 0 0) planes between layers
  - ↳ these are actually 2^{nd} order peaks from (1 0 0) planes.

- Interplanar spacing can thus be found by rotating a source and detector to find the angles corresponding to peaks



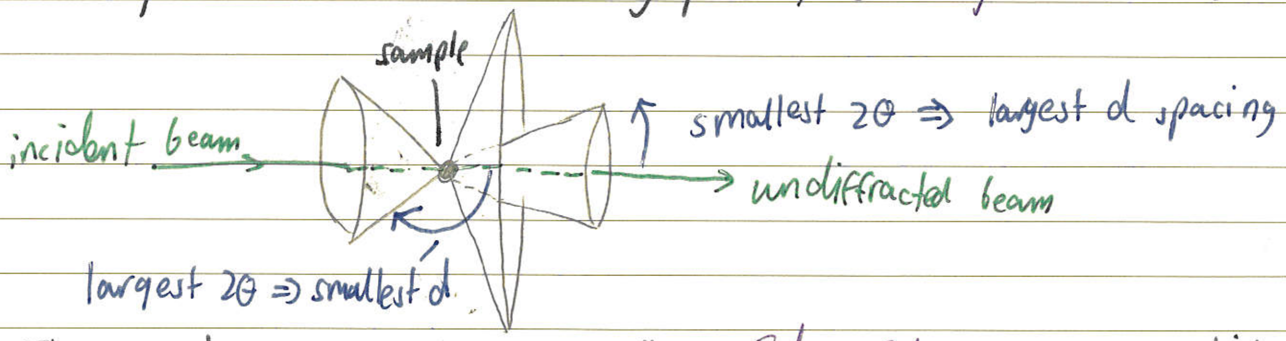
← detector must rotate at twice the rate of the sample.

- Conversely, if we want to calculate the diffraction angles for some planes, we need the spacing:

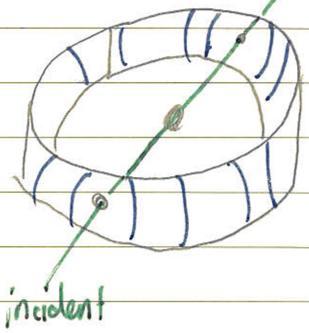
$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$ for an orthogonal basis set.

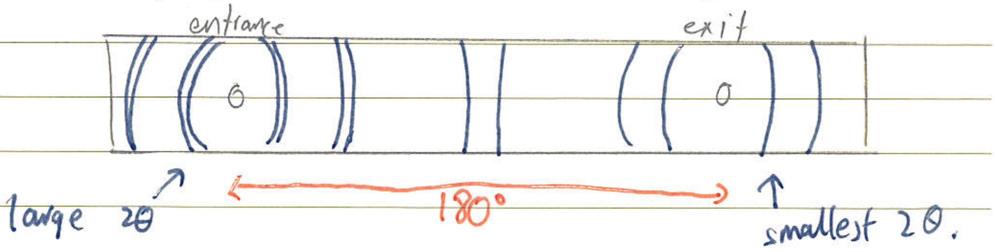
Powder diffraction

- If we use a polycrystalline sample, there will be many orientations of crystals so we will see many peaks, as Debye-Scherrer Cones



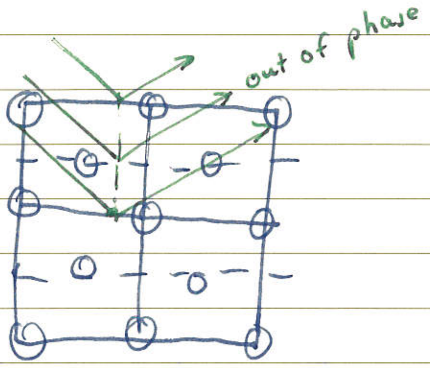
- These angles can be measured with a Debye-Scherrer camera, which wraps a ribbon of photographic film around the sample





- Around the entrance, there may be pairs of peaks from the same d, because of the $K\alpha_1/K\alpha_2$ split.

Diffraction intensities



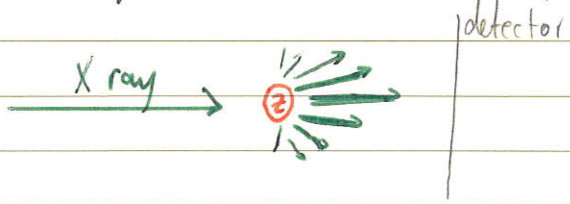
- For a bcc crystal, reflections from the intermediate planes will destructively interfere with the 100 reflection
  - ↳ systematic absence
  - ↳ we only see {2 0 0} planes etc.
- However, 110 is present because no intermediate layers have been introduced.
- 111 absent.

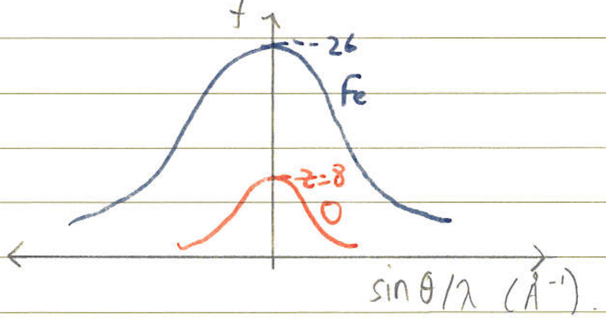
- A similar analysis for cubic F shows that only 111 is present.

- For any given atom, X-rays are scattered by the electrons. The amount of scattering from an individual atom is described by the scattering factor, f.

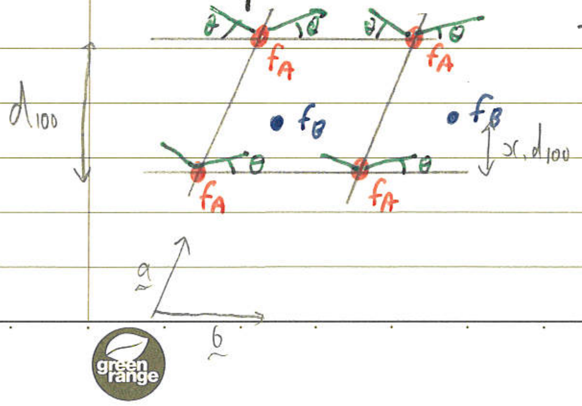
$$f = \frac{\text{atom's overall scattering}}{\text{single } e^- \text{ scattering}}$$

  - because there are Z electrons in an atom, we would expect $f = Z$.
  - this is only true for constructive interference when the scattering angle is zero. As this angle ↑, there is more destructive interference.





- For multiple atoms we can't just add the scattering factor because of phase



  - In the A lattice, X-rays incident at the Bragg angle will be in phase (by definition)
  - Consider B atoms some fraction x_1 of the distance between the {100} A planes.

path diff = $x_1 \lambda$ ∴ $\phi_{1,x} = 2\pi x_1$

- In general, the phase difference ~~for~~ of the nth atom is:

$$\boxed{\phi_n = 2\pi(hx_n + ky_n + lz_n)}$$

- We define the Structure factor F as

$$\hat{\vec{F}} = \frac{\text{crystal's overall scattering}}{\text{single } e^- \text{ scattering}} = \sum f_i \text{ (incl phase)}$$

- We should treat~~a~~ scattering as a complex quantity:

$$\hat{f}_n = f_n e^{i\phi_n} \Rightarrow \boxed{\hat{F}_{hkl} = \sum_{n=1}^{N} f_n \exp(2\pi i(hx_n+ky_n+lz_n))}$$

- To get the intensity, we take the modulus:

$$I_{hkl} \propto |\hat{F}_{hkl}|^2$$

- Using this analysis, we can reclassify systematic absences.

	Present	Absent
P	all	none
I	h+k+l even	h+k+l odd
F	hkl all even/odd	hkl mixed.

- This leads to a simplification in the structure factor formula: we can factorise out the contribution from the lattice:

$$P: \quad \hat{F}_{hkl} = (\quad)\sum_{\text{motif}} f_n \exp(2\pi i(hx_n+ky_n+lz_n))$$

$$I: \quad \hat{F}_{hkl} = \left(1+(-1)^{h+k+l}\right)\sum_{\text{motif}} (\dots)$$

$$F: \quad \hat{F}_{hkl} = \left(1+(-1)^{h+k}+(-1)^{h+l}+(-1)^{k+l}\right)\sum_{\text{motif}} (\dots)$$

$$\text{i.e. } \hat{F}_{hkl} = \left(\begin{matrix}\text{sum over lattice}\\ \text{NO ATOMS}\end{matrix}\right) \times \sum_{\text{motif}} \dots$$

- The intensity also scales with multiplicity m_{hkl}: having more of a particular plane increases intensity.
- Also depends on geometric factors, e.g. a much smaller fraction of the cone will be captured by the camera when $2\theta \approx 90°$

- Thus for powder diffraction the intensity is given by:

$$\boxed{I_{hkl} \propto M_{hkl} |\hat{F}_{hkl}|^2 g(\theta)}$$

↳ in reality, factors like absorption / temp will affect I
↳ any preferred grain orientation can have a significant effect.

Indexing powder diffraction patterns

- For cubic crystals : $d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} = \frac{a}{\sqrt{N}}$.

↳ But $\lambda = 2 d_{hkl} \sin\theta \implies \boxed{\frac{\sin^2\theta}{N} = \frac{\lambda^2}{4a^2} = \text{constant}}$

↳ i.e $\frac{\sin^2\theta_1}{N_1} = \frac{\sin^2\theta_2}{N_2} = \dots = \frac{\sin^2\theta_n}{N_n} \implies \boxed{\frac{N_n}{N_1} = \frac{\sin^2\theta_n}{\sin^2\theta_1}}$

- From this, we use the following procedure:

1. Find $\sin^2\theta/\sin^2\theta_1$ for each peak and tabulate
2. Multiply this by an integer if the values aren't already ints
   ↳ this gives N for each peak
3. Find 3 numbers whose squares add to N, giving hkl.

- There cannot be N=7 because no three squares add to 7.
  ↳ P lattices skip N=7 and N=15
  ↳ if there appears to be N=7, multiply everything by 2 so this is N=14 (i.e 321 reflections), giving an I lattice.
- This method assumes we know all the peaks, and does not tell us about the motif: this info is in the intensities.

Cubic P : evenly spaced with N=7 and N=15 missing
Cubic I : evenly spaced, N = 2, 4, 6, 8, ...
Cubic F : N = 3, 4, 8, 11, 12 (i.e h, k, l all odd or all even).

- Some positions have two peaks, e.g N=9 has 300 and 221.

- There is an upper limit to the number of peaks:

$$N_{max} = \frac{a^2}{d_{hkl}^2} = \frac{4a^2}{\lambda^2} \quad \text{because } \sin\theta < 1$$

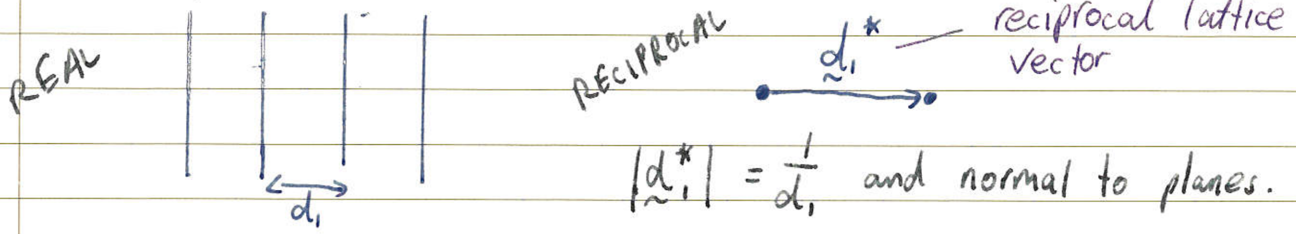
- We will have more accurate results if we use higher 2θ:

$$d = \frac{\lambda}{2\sin\theta} \Rightarrow d'(\theta) = -\frac{d}{\tan\theta} \Rightarrow \frac{\delta d}{d} = -\frac{\delta\theta}{\tan\theta}$$

↳ thus higher $\theta \Rightarrow$ lower $\delta d / d$
↳ must use radians
↳ eventually, error in λ may become important

Reciprocal Lattices

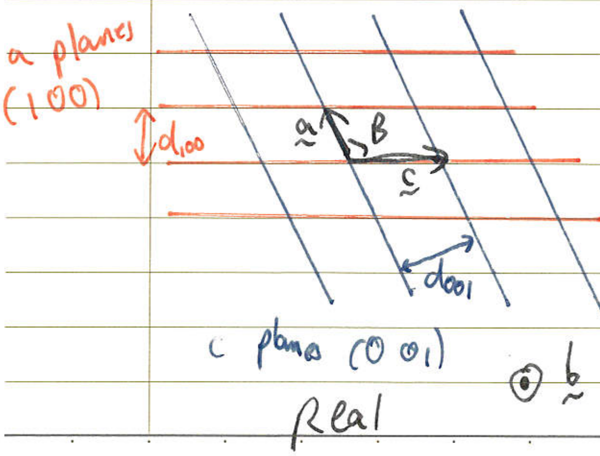
- A reciprocal lattice represents a real lattice in inverse space.
  ↳ periodic features become points

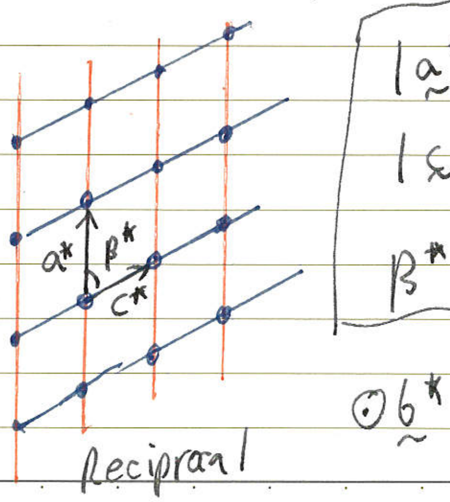


$|\underset{\sim}{d}_1^*| = \frac{1}{d_1}$ and normal to planes.

↳ thus the reciprocal lattice vector encodes all the info for a set of planes.

- For a primitive monoclinic lattice viewed parallel to [010]:





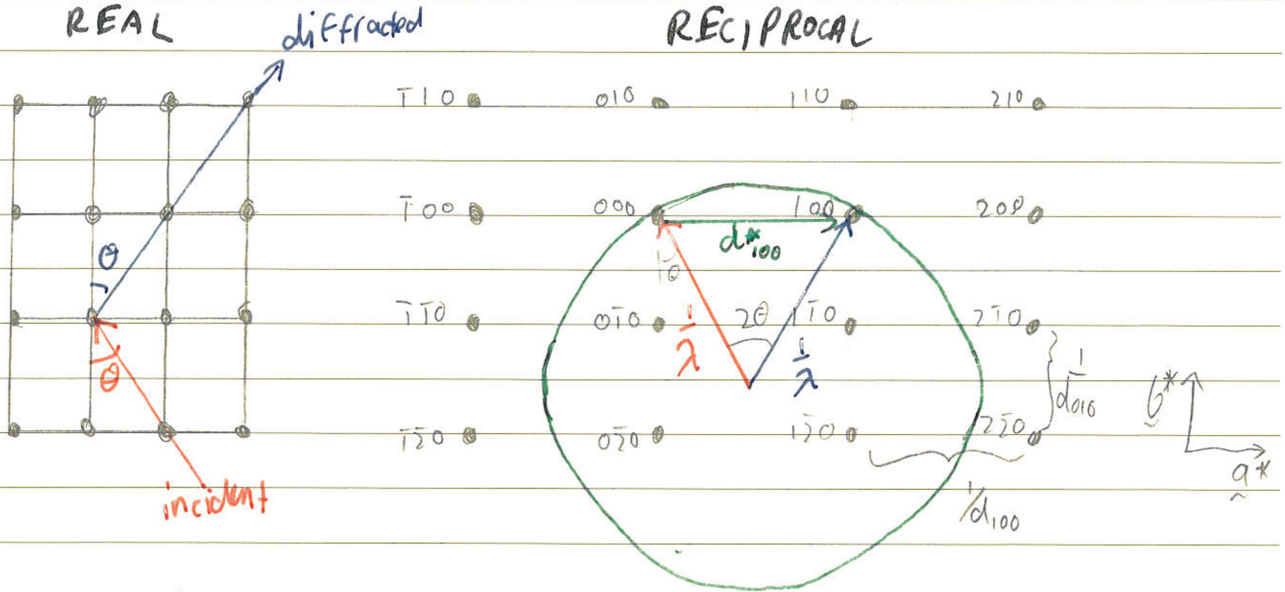
$$\boxed{\begin{aligned} |\underset{\sim}{a}^*| &= \frac{1}{d_{100}} \\ |\underset{\sim}{c}^*| &= \frac{1}{d_{001}} \\ \beta^* &= 180° - \beta \end{aligned}}$$

- The reciprocal lattice for a cubic P real lattice is also cubic P.
- However, systematic absences lead to the following result:

real I lattice ⟷ reciprocal F lattice
real F lattice ⟷ reciprocal I lattice

The Ewald sphere

1. Draw the reciprocal lattice
2. Draw a vector representing an incoming X-ray. It will point to the origin and have length $1/\lambda$
3. Draw a circle/sphere centred on the start of that vector.



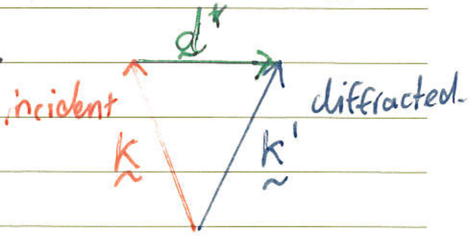
- The 100 point lies on the surface of the sphere. We can say.

$$\sin\theta = \frac{\frac{1}{2}|d_{100}^*|}{1/\lambda} = \frac{\lambda}{2d_{100}} \Rightarrow \lambda = 2d_{100}\sin\theta$$

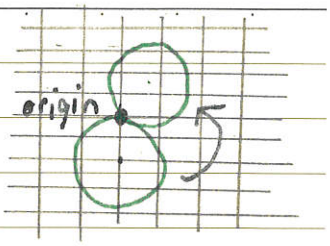
- This shows that:

$$\boxed{\text{Bragg condition satisfied} \Longleftrightarrow d^*_{hkl} \text{ on Ewald sphere}}$$

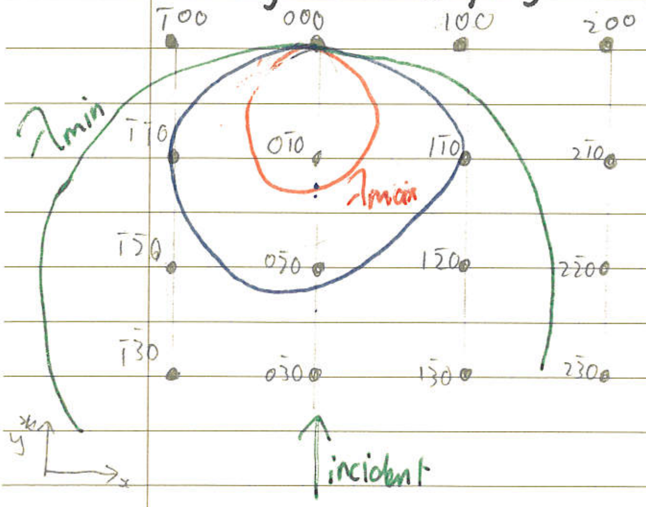
- The vectors in reciprocal space are wavevectors, satisfying $\underset{\sim}{k}' = \underset{\sim}{k} + \underset{\sim}{d}^*$
- The Ewald sphere always passes through the origin of reciprocal space



- If we want to measure a particular reflection with λ constant, we imagine rotating the sphere (pinned to the origin) until it intersects



- Alternatively, we can fix the direction and vary λ (e.g by using 'white' X-rays).



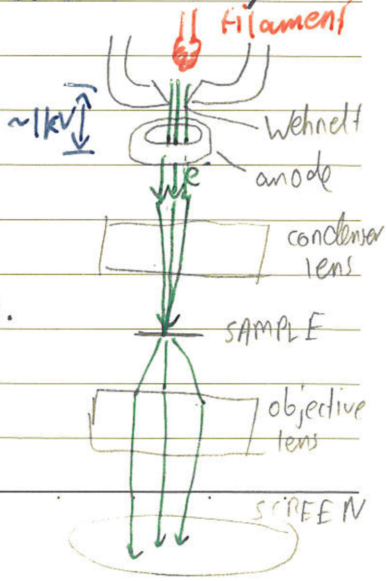
- Within the range of λ_{min} to λ_{max}, there will be ~~eife~~ spheres intersecting different points, corresponding to different diffractions
- e.g there is some sphere passing through $0\bar{3}0$, i.e diffraction straight back to the source.

Electron Microscopy

- It is difficult to focus diffracted X-rays into an image. However, with electrons, we can just use electromagnets.
- Additionally, they can have very small wavelengths

$$\lambda = \frac{h}{p} \quad \text{and} \quad E = \frac{p^2}{2m} \implies \lambda = \frac{h}{\sqrt{2mE}}$$ (needs relativistic correction for high E).

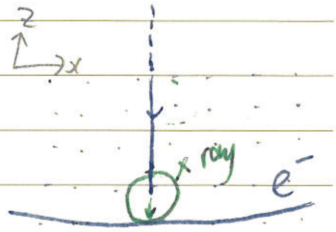
- A transmission electron microscope (TEM) passes electrons through a thin sample.
  - electrons generated by thermionic emission from a hot tungsten filament through a ~~Wehelt~~ Wehnelt
  - condenser lenses produce a focused beam
  - after scattering, the objective lenses (movable) focus the pattern onto a screen (e.g CCD or film).
    - ↳ because they are electromagnetic lenses, the focal length can be adjusted.



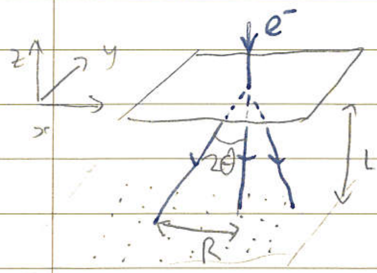
No. 6

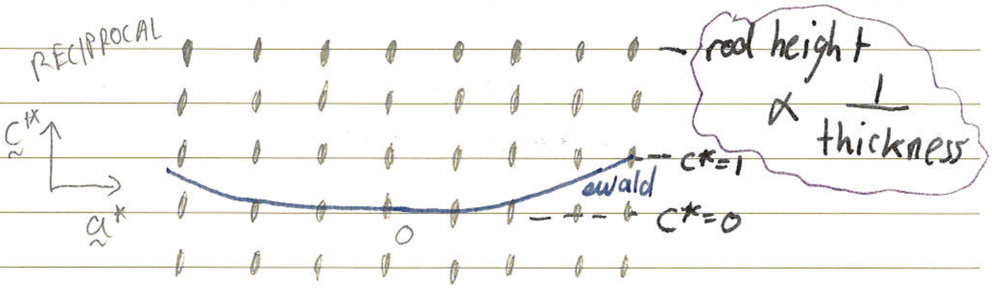
Date 30 . 12 . 18

Electron diffraction patterns



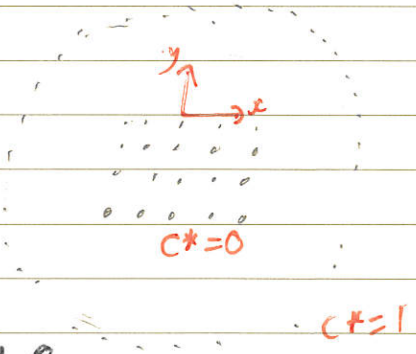
- The Ewald spheres will be much larger than in X-ray diffraction because λ much smaller.
- Because we are using a thin film, the reciprocal lattice points become rods in the direction of the normal (i.e z).





rod height $\propto \frac{1}{\text{thickness}}$

- The diffraction pattern will then be xy cross sections
- Because the Ewald sphere intersects many points in the $c^*=0$ layer, we get many spots that can be used to find the lattice parameters
- There are some $c^*=1$ reflections too.

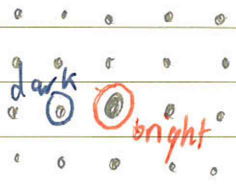


- From the geometry of the detector setup:
  - ↳ $\tan 2\theta = R/L \Rightarrow 2\theta = R/L$ for small θ.
  - ↳ $\sin\theta \approx \theta$ $\therefore$ Bragg's law: $\lambda = 2d_{hkl}\theta$

$$\therefore \boxed{d_{hkl} = \frac{\lambda L}{R}}$$ with $\lambda L \equiv$ camera constant

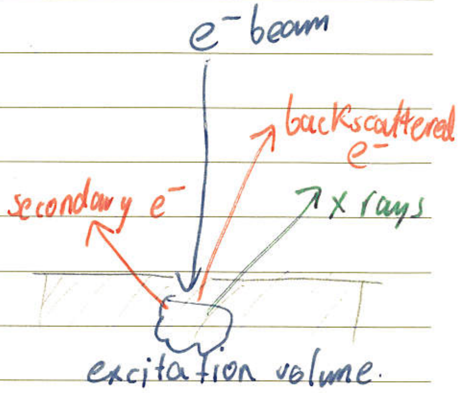
Electron microscope imaging

- Using the objective aperture, whose width and position can be varied, we can form an image from specific diffraction spots
  - ↳ a bright field image contains the central spot and illuminates many features
  - ↳ dark field images include the electrons that have interacted strongly, highlighting imperfections



- To get the highest resolution image, multiple spots should be used

Scanning electron microscopes



- Unlike the TEM, the SEM does not use diffraction.
- Focuses on inelastic scattering, leading to:
  - heat (ignored)
  - secondary electrons emitted by excited atoms
  - backscattered electrons from elastic collisions
  - X-rays / light from excited electrons dropping to ground.
- Secondary electrons are used to image the surface
- Backscattered electrons can give info about chemical composition.