Lecture 3

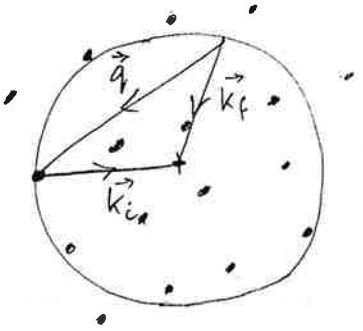
Crystallographic Experimental Methods (5-7)

1. Ewald construction.

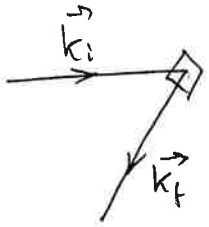
Fundamental equations for observing diffraction

$$\vec{q} = \vec{k}_f - \vec{k}_i$$

$$\vec{q} = 2\pi \vec{H}_{hkl} \text{ in rec. lattice.}$$



corresponds to



A way to construct which reflections will appear:

i) draw sphere $r = |k|$ passing through origin of R-space

ii) all R-lattice points touching surface of sphere are active diffraction points; can construct $\vec{k}_f$.

Immediately see that in general case no reflection will be hit exactly. Need to move something to get diffraction:

i) vary $\lambda = 2\pi/|k|$ by using range of values
= Laue method.

ii) rotate crystal = rotation method

iii) use powdered sample with sufficient no. of grains.

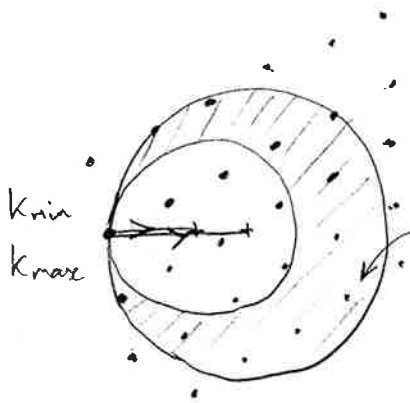
2. Laue method.

Use range of wavelengths:

Difficult to control λ-spectrum accurately.

Absorption strong function of λ.

Hence not good quantitative technique.



All reflections between the two spheres will be active.

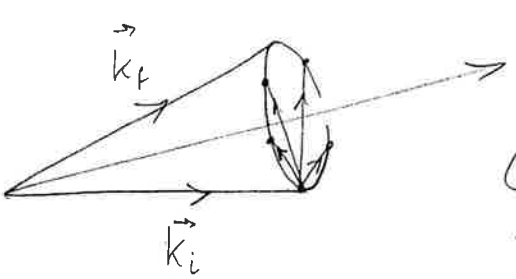
Two basic varieties : back-reflection
transmission.

i) 'back reflection' very useful for aligning crystals for cutting to a known orientation. Can locate high symmetry direction by comparing with a standard chart.

ii) 'transmission' method, described as obsolete in 1968 in coming back into popularity for protein crystallography. Quantitative problems can be solved by brute force (spectrum, absorption all well understood.
Advantage is all data in single shot
One big disadvantage is superposition of low-index refls by multiples : 111, 222, 333 all superimposed.

3. Zone axis.
Just as we said each R-lattice vector is the perpendicular of a plane in real space, each real vector $u\vec{a}_1 + v\vec{a}_2 + w\vec{a}_3$ is the perpendicular of a plane of Recip-space points = Bragg reflections.
[obvious in cubic system, but true in general]

$\vec{A}(uvw) = u\vec{a}_1 + v\vec{a}_2 + w\vec{a}_3$ = Zone axis vector representing Zone uvw

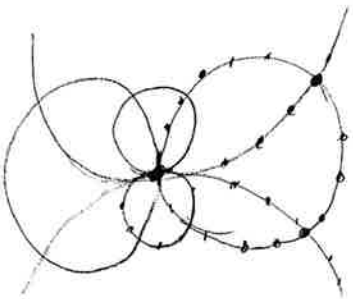


Consider circle of points in recip. space perpendicular to $\vec{A}$

Any $\vec{q} = 2\pi \vec{H}_{hkl}$ in that circle necessarily satisfies $\vec{H}_{hkl} \cdot \vec{A} = 0$ (since perpendicular) $\Rightarrow \vec{H}_{hkl}$ is in zone uvw

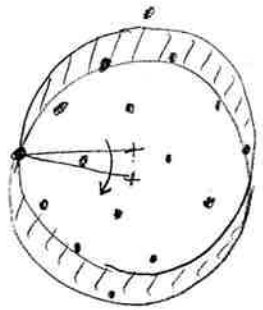
Let length of $\vec{k}_i$ vary; $\vec{k}_f$'s always on same cone.

Proves that Laue pattern is made up of rings (strictly ellipses on flat film)



Most pronounced circles are the lower-index zones,

4. Rotation method.

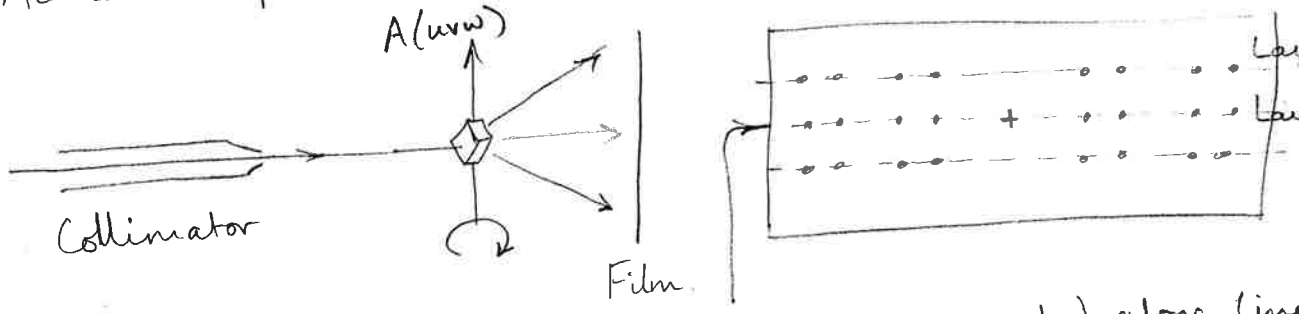


Rotating crystal is the same as rotating the Ewald sphere. All reflections passed through will be observed (shaded region). If rotation is uniform then accurate integration of intensity is obtained (see lecture 2).

i) View shown is down a zone axis of the xtal (perpendicular to a plane of rec. space points. A 180° rotation will generate full set of measurements on a single line of the detector. (Or use Weissenberg method to spread out in 2D)

ii) Monochromatic beam ⇒ well defined absorption ⇒ best quantitative results. Only LP correction is needed.

iii) Actual experiment using film or 2D detector.



Layer 0 satisfies $\vec{A}(uvw) \cdot \vec{H}_{hkl} = 0$

$(u\vec{a}_1 + v\vec{a}_2 + w\vec{a}_3) \cdot (h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3) = uh + vk + wl = 0$

Layer 1 satisfies $uh + vk + wl = 1$ etc ...

Usually choose low-index zone, like 001 (along $\vec{a}_3$)

then Layer 0 has $l = 0$, all h, k.

" " 1 " $l = 1$, all h, k.

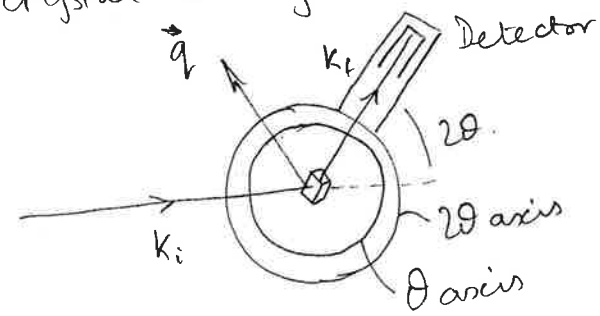
5. 2-circle diffractometer.

Same as rotation method, constrained to Layer 0

i) Replace film by electronic detector.

ii) Measure one reflection (in scattering plane) at a time

iii) Move from one zone to the next by reorienting crystal on goniometer. Usually under computer control.



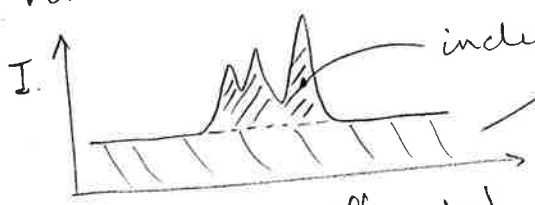
Can set any reflection within current zone using combination of θ & 2θ

Measure integrated intensi with smooth scan of θ.

6. 3-circle diffractometer.
Keep θ & 2θ fixed (mechanically) in 1:2 ratio
Set 2θ for Bragg angle for h,k,l desired.
Bring desired reflection $2\pi \vec{H}_{hkl} = \vec{q}$ using two degrees of freedom to orient crystal. (ϕ, χ)

4-circle diffractometer.
Same as 3-circle with independent θ and 2θ.
Will operate as 2-circle or 3-circle defined above.
Very widely used instrument

7. Integrated intensity.
All these instruments use the integrated-intensity method met last time. [Sin 2θ = Lorentz factor.]
Reminder of necessary conditions:
i) rotate reflection entirely and smoothly through $\vec{q}=2$



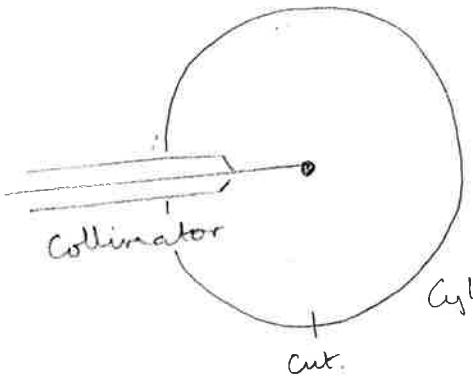
ii) collect all diffracted beam; no slits allowed.

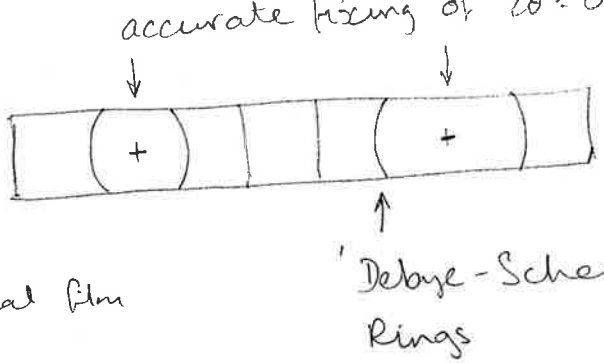
Other methods are possible:
eg define incident and exit beam directions so tightly that every point in $I(q)$ resolved. (good for measuring sha
Find I_{max} = peak (same mosaic!) } of peak etc)
or evaluate $\int I(\vec{q})\, d^3\vec{q}$ numerically }
Either way, a correction for the 'resolution function' will be needed, different for each hkl, depending on slits e
Only way to avoid this is to work with the exptal. integrated intensity above.

8. Powder diffraction.

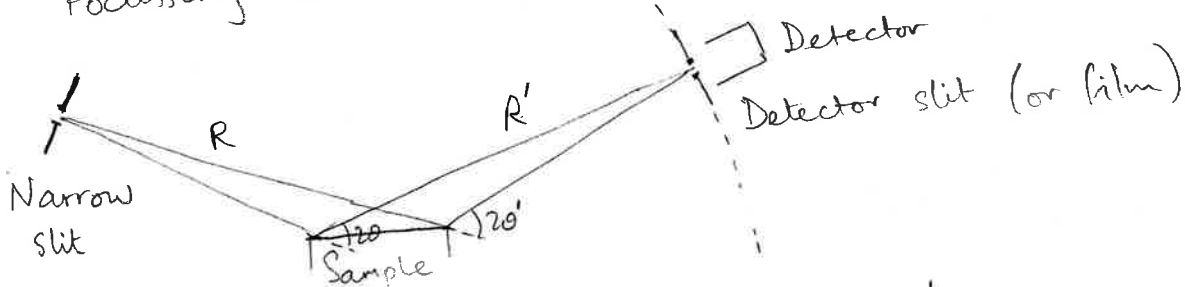
Assume distribution of small mosaic grains is totally rando
(often needs work – very fine grinding)

Simplest (film) method.





Focussing method (film or detector).



- Set $R = R' \gg$ sample size, then $2\theta = 2\theta'$ everywhere on sample diffracting grains are at different angles in different places but that is ok for a powder.
- Sample must bisect slits, so can't use a wide film with fixed sample. Otherwise use $\theta = 2\theta/2$ as on single crystal diffractometer (can use same instrument).
- Source may be divergent; often use X-ray tube directly with no slit.
- Drive motors continuously; record peaks on chart recorder.
- Only error is due to finite extent of slit out of plane of page (see Warren p 72).

9. Steps in structure determination with powder diffraction

i) Measure data:
Integrated area of peaks, best estimate of 2θ.

ii) Apply corrections to intensity (LP)
Convert 2θ to units of $1/d = q/2\pi = 2\sin\theta/\lambda$

iii) Search data bank for these reflections (eg CD-Rom)
List in order from strongest to weakest.

iv) Harder cases are mixtures of compounds.

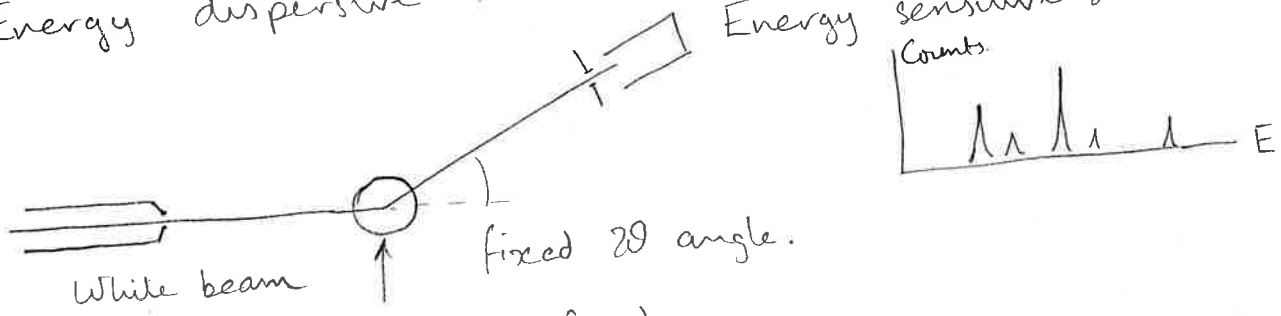
10. Manual 'indexing' method for orthorhombic case

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}, \quad \frac{h^2+k^2}{a^2} + \frac{l^2}{b^2}, \quad \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Cubic Tetragonal Orthorhombic

List $1/d^2$ for all observed reflections
Look for spacings as integer multiples of 1, 2 or 3 constants
→ lattice params. (1, 3, 4, 5, 8 ...) $1/a^2$ should occur.
Simple example NaCl (p55 & 57) = cubic.

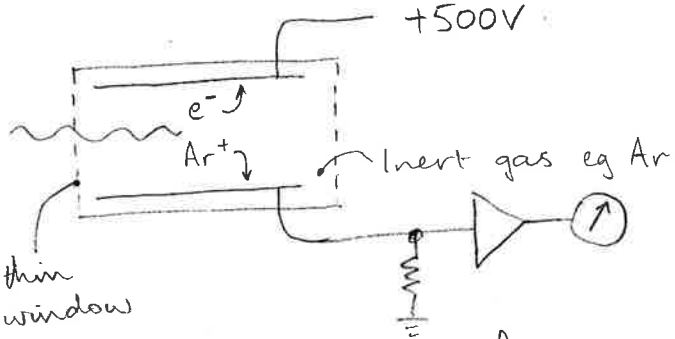
11. Energy dispersive method



Again, single shot expt, good for transient expts.

12. X-Ray Detectors

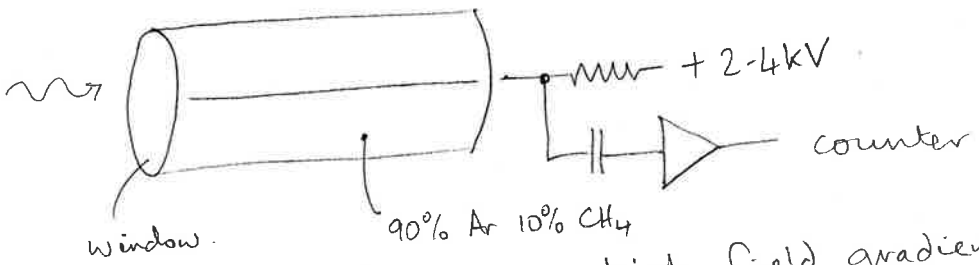
i) Ionization chamber.



Current ∝ intensity of x-rays.

- Can't see individual photons, hence will always be less accurate than counter.
- Prone to 'saturation' when too many ionizations take place they can neutralize each other
- Some x-rays pass right through

ii) Proportional counter. (Geiger counter)



Thin wire has very high field gradient, almost at point of electrical breakdown of gas.

Photon → ionizations → avalanche of 10^3-10^4 ionizations

→ Pulse → discriminator + counter.

Pulse ∝ energy of x-ray (= # ionizations generated)

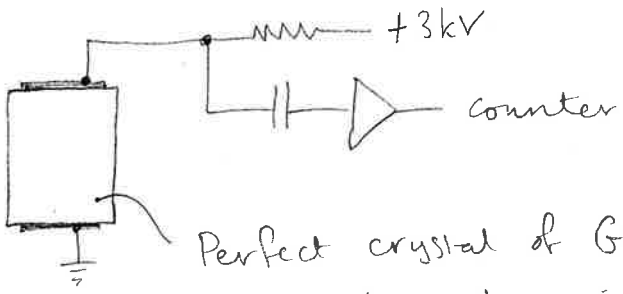
~ 10keV ÷ ⊗ Binding energy of He ~ 20eV

→ 500 ionizations <u>once absorbed</u>.

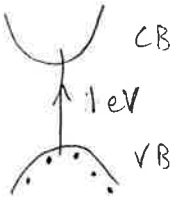
Position-reading (eg multiwire) versions possible.

Some energy resolution (~10%) useful for discriminating background (cosmic rays, lab next door etc)

iii) Solid-state detector.



Perfect crystal of Ge or Si, cooled to 77K so it is insulator.



Number of electrons promoted from VB to Conduction band (just like ionization)

Drift to terminal → pulse of current.

Excellent energy resolution ~ 100 eV out of 10 kV.

iv) Scintillation detector.

NaI is transparent to visible light
relatively opaque to X-rays (heavy elements)

Ionization of atoms → recombination → light pulse
(~ 100 light photons for 1 x-ray).

Advantage = fast (can be made very fast)
1μs 1ns

Some (~10%) energy resolution.

Demos

White beam Laue PX picture

Chart for Laue diff.

Detectors