Lecture 2

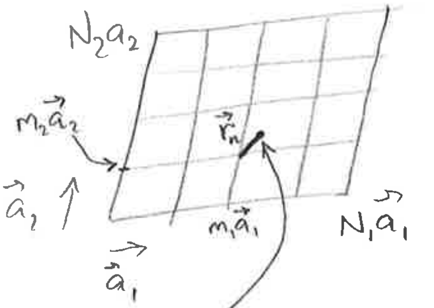
1/20/95

Integrated Intensity (Warren ch 3+4)

1. Diffraction by a crystal.

Small crystal $\left\{ \begin{array}{l} \text{immersed in the x-ray beam} \\ \text{no 'extinction' effects.} \end{array} \right.$

Extinction is the name given to loss of linearity of Intensity ∝ Size of sample because the incident beam is diminished due to being diffracted. [Not the same thing as absorption, which is linear]



Assume simple parallelapiped shape with $N_1N_2N_3$ unit cells.

Position of this atom is $m_1\vec{a}_1 + m_2\vec{a}_2 + m_3\vec{a}_3 + \vec{r}_n$

Sum over $1 \le m_j \le N_j \quad j = 1,2,3$

$1 \le n \le N_{cell}$ number of atoms in unit cell

$$E = E_0\left(\frac{e^2}{mc^2R}\right)\sum_{\substack{m_1\,m_2\\ m_3\,n}} f_n(q)\, e^{i\vec{q}\cdot(m_1\vec{a} + m_2\vec{a}_2 + m_3\vec{a}_3 + r_n)}$$

[ignoring the polarization correction for now]

Expression factorizes immediately into 4 terms

$$\sum_{m_j}^{N_j} e^{i\vec{q}\cdot m_j\vec{a}_j} = \frac{1 - e^{iN_j\vec{q}\cdot\vec{a}_j}}{1 - e^{i\vec{q}\cdot\vec{a}_j}}$$ Geometric series

$$\sum_{n}^{N_{cell}} e^{i\vec{q}\cdot\vec{r}_j} f_n(q) = F(\vec{q})$$ definition of structure factor

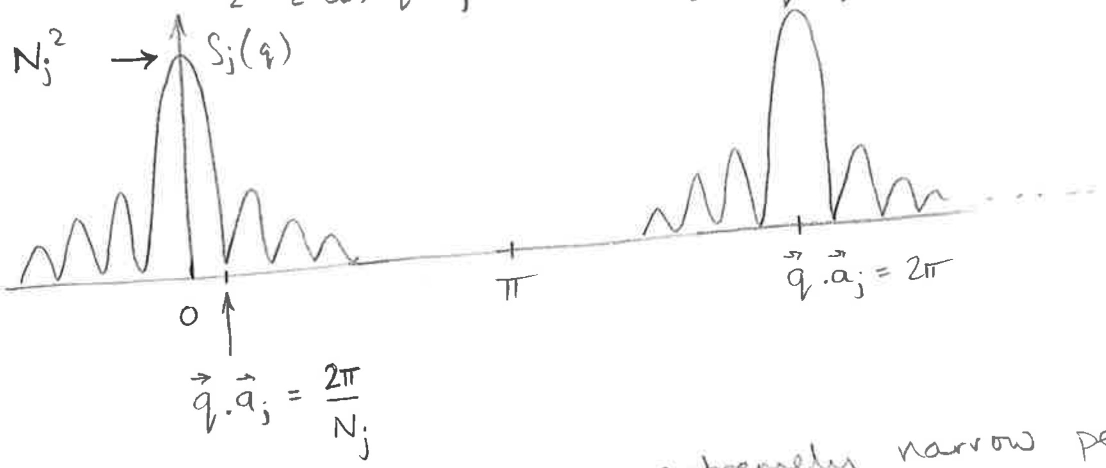
2.2

We are interested in the Intensity $I \propto |E|^2$

Take product of magnitudes of each term:

$$S_j(\vec{q}) = \left| \sum_{m_j=1}^{N_j} e^{i\vec{q}\cdot m_j\vec{a}_j} \right|^2 = \left(\frac{1-e^{iN_j\vec{q}\cdot\vec{a}_j}}{1-e^{i\vec{q}\cdot\vec{a}_j}} \right)\left(\frac{1-e^{-iN_j\vec{q}\cdot\vec{a}_j}}{1-e^{-i\vec{q}\cdot\vec{a}_j}} \right)$$

$$= \frac{2-2\cos N_j\vec{q}\cdot\vec{a}_j}{2-2\cos\vec{q}\cdot\vec{a}_j} = \frac{\sin^2 N_j\vec{q}\cdot\vec{a}_j/2}{\sin^2\vec{q}\cdot\vec{a}_j/2} \quad \text{Slit function}$$



For large N, there is an extremely narrow peak around each lattice point, defined by:

$$\left.\begin{aligned} \vec{q}\cdot\vec{a}_1 &= 2\pi h' \\ \vec{q}\cdot\vec{a}_2 &= 2\pi k' \\ \vec{q}\cdot\vec{a}_3 &= 2\pi l' \end{aligned}\right\} \quad \text{Laue equations}$$

Solution of these equations is $\vec{q} = 2\pi(h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3)$
$= 2\pi\, H_{hkl}$

provided $h=h'$ $k=k'$ $l=l'$

hence sharp peak whenever $\vec{q} = 2\pi$ (a recip lattice vector)

Same condition we saw last time for Bragg reflection from planes of crystal.

Reassembling the intensity (with polarization corr.)

$$I = I_0 \left(\frac{e^2}{mc^2 R}\right)^2 \left(\frac{1+\cos^2 2\theta}{2}\right) |F(\vec{q})|^2 S_1(\vec{q})\, S_2(\vec{q})\, S_3(\vec{q})$$

2. Examples of structure factor.

Division into unit cell and lattice is not unique.

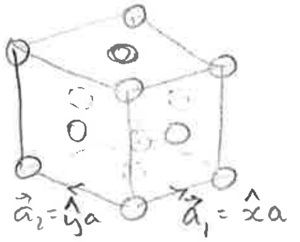
Can always take double-sized unit cell + 2x sparse lattice.

Often choose a 'convenient' lattice for ease of handling

eg cubic lattice has orthogonal $\vec{a}_j$'s

FCC Lattice in cubic coordinate frame:

Lattice points at $m_1 a\hat{x} + m_2 a\hat{y} + m_3 a\hat{z}$



$m_1 m_2 m_3$
0 0 0
½ ½ 0
½ 0 ½
0 ½ ½

Can generate FCC structure in SC coords so long as every atom gets replaced by 4.

Single atom basis:

$$F(\vec{q}) = \sum_n f(q)\, e^{i\vec{q}\cdot\vec{r}_n} = f(q)\left[1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)}\right]$$

$$\left.\begin{aligned} \vec{q} &= 2\pi\left(h\frac{1}{a}\hat{x} + k\frac{1}{a}\hat{y} + l\frac{1}{a}\hat{z}\right) \\ \vec{r}_n &= m_1 a\hat{x} + m_2 a\hat{y} + m_3 a\hat{z} \end{aligned}\right\} \quad \vec{q}\cdot\vec{r}_n = 2\pi(hm_1 + km_2 + lm_3)$$

Thus, in the cubic coordinate frame, any crystal with FCC structure will have two classes of reflections

$F(\vec{q}) = 4f(q)$ hkl unmixed 111 200 220 etc.

absent reflection $F(\vec{q}) = 0$ hkl mixed 100 110 123 etc

The allowed reflections are the only ones that appear in the RL of FCC if the primitive choice of $\vec{a}_1 \vec{a}_2 \vec{a}_3$ had been made.

3. Second example of structure factors.

NaCl with 2 atoms per primitive cell in FCC Bravais lat

Na	Cl
000	00½
½½0	½½½
½0½	½01
0½½	0½1

$\xrightarrow{}$ add (00½)

Displacement vector causes SF sum to factorize:

$$F(\vec{q}) = \left[1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(h+l)}\right] \cdot \left[f_{Na}(q) + f_{Cl}(q)\, e^{\pi i l}\right]$$

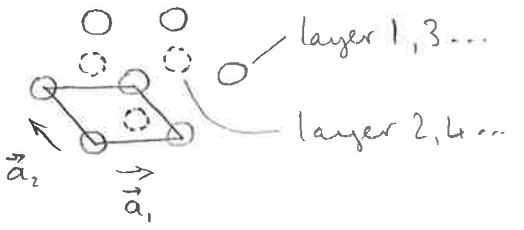
First [ ] gives usual systematic absences.

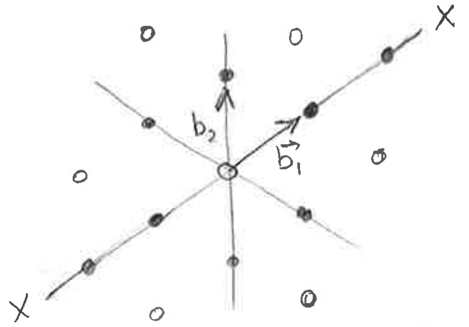
Second [ ] gives different classes of allowed S.Fs:

$$F(q) = \begin{cases} 4(f_{Na}(q) + f_{Cl}(q)) & l \text{ even} \quad 200 \ 220 \ 220 \text{ etc} \\ 4(f_{Na}(q) - f_{Cl}(q)) & l \text{ odd} \quad 111 \ 311 \ 113 \text{ etc} \end{cases}$$

4. Third example of structure factor

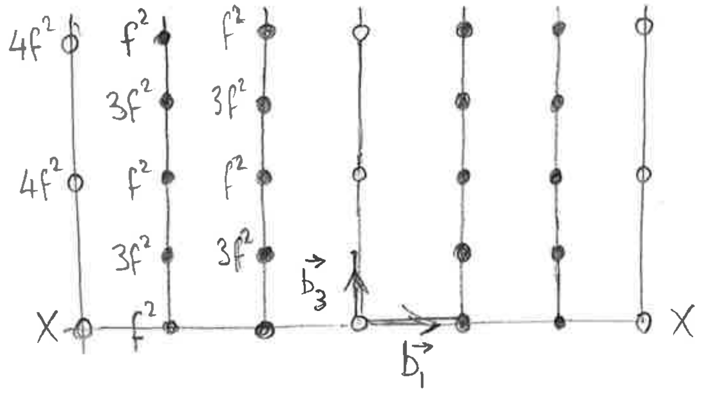
Zn = HCP . 2 atoms / cell in hexagonal Bravais lattic





●○ are two kinds of rows of reflections

The pattern of weak and strong intensities is characteristic of each structure. Interpretation is the ultimate goal.



5. Naming of crystal structures.

i) Correct convention is to name parent compound.
eg 'Rocksalt' for NaCl and all cubic structures the same
'Zincblende' for ZnS, Wurtzite, Perovskite ... (minerals)
'Diamond' 'Copper' 'Tungsten' etc.

ii) Strictly incorrect, but common to use name of (Bravais) lattice FCC BCC HCP etc
Only an element can have structure = Bravais lattice.

6. Integrated intensity.
Small crystal i) completely illuminated
ii) no absorption.

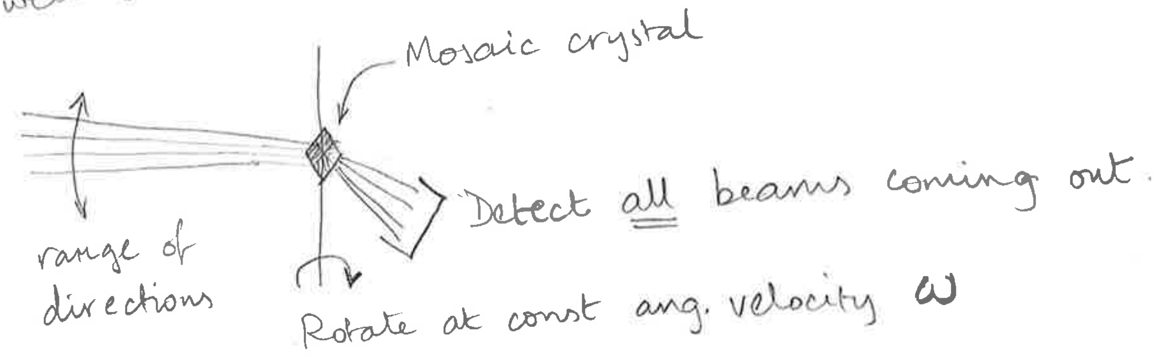
$$I_{max} = I_0 \left(\frac{e^2}{mc^2 R}\right)^2 |F(\vec{q})|^2 N_1^2 N_2^2 N_3^2$$

In principle, we could measure $|F(q)|$ this way.
But we have to hit the maximum perfectly.
Real situation is impossible because:

i) real beam imperfectly collimated → range of directions
ii) real detector " " " " "
iii) real crystal is not always perfect, containing a range of orientations:

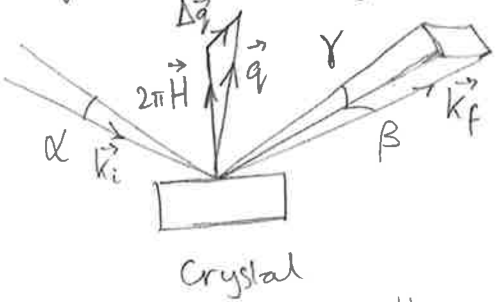
$$E = \int I(\vec{q})\, d^3\vec{q} \text{ over peak.}$$

Integrated intensity is well defined both experimentally and theoretically



2.6

Easier to consider crystal stationary and imagine rotating the incident beam.



Displace $\vec{k_i}$ by α.

Displace $\vec{k_f}$ by β & γ

$\Rightarrow$ displace $\vec{q} = \vec{k_f} - \vec{k_i}$ by $\Delta\vec{q}$

integrate $\Delta\vec{q}$ in all recip. space directions around $\vec{q} = 2\pi\vec{H}$.

Observation is of integrated intensity

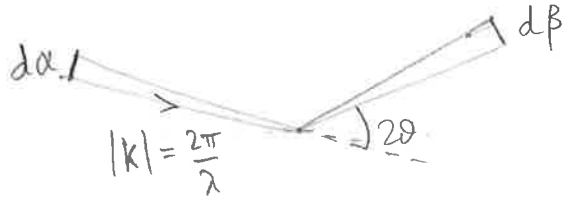
i) over Area of detector

ii) over time as crystal is rotating.

$$E = \int I(q)\, dA\, dt = \int I(q)\, R^2 d\beta\, d\gamma\, \frac{d\alpha}{\omega}$$

Evaluate reciprocal space volume element 2 ways:

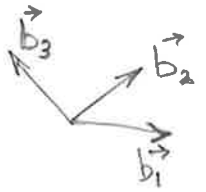
i)



($d\gamma$ is out of plane)

$$dV = d\alpha\, d\beta\, d\gamma \sin 2\theta \left(\frac{2\pi}{\lambda}\right)^3$$

ii)



These are the 3 directions in which we must resolve $\vec{q} = p_1\vec{b_1} + p_2\vec{b_2} + p_3\vec{b_3}$

$$d\vec{q} = dp_1\,\vec{b_1} + dp_2\,\vec{b_2} + dp_3\,\vec{b_3}$$

then
$$\left.\begin{aligned} \vec{q}\cdot\vec{a_1} &= p_1 \\ \vec{q}\cdot\vec{a_2} &= p_2 \\ \vec{q}\cdot\vec{a_3} &= p_3 \end{aligned}\right\} \text{by orthogonality}$$

$$dV = (2\pi)^3 dp_1\,\vec{b_1}\cdot dp_2\,\vec{b_2}\times dp_3\,\vec{b_3} = (2\pi)^3 V_b\, dp_1\, dp_2\, dp_3 \quad \text{(vol. of recip ce}$$
$$= \frac{(2\pi)^3}{V_a}\, dp_1\, dp_2\, dp_3 \quad \text{(vol. of cell)}$$

Equating these: $d\alpha\, d\beta\, d\gamma = \dfrac{\lambda^3}{V_a \sin 2\theta}\, dp_1\, dp_2\, dp_3$

$$E = \int I(q)\, R^2/\omega \; \lambda^3 \frac{1}{V_a \sin 2\theta}\, dp_1\, dp_2\, dp_3$$

$$I(\vec{q}) = I_0 \left(\frac{e^2}{mc^2 R}\right)^2 |F(\vec{q})|^2\, S_1(\vec{q})\, S_2(\vec{q})\, S_3(\vec{q})$$

$$S_1(\vec{q}) = \frac{\sin^2 N_1 \vec{q}\cdot\vec{a}_1}{\sin^2 \vec{q}\cdot\vec{a}_1} = \frac{\sin^2 N_1 p_1}{\sin^2 p_1} \Rightarrow \text{Integral factorizes}$$

$$\int_{\text{peak}} S_1(\vec{q})\, dp_1 = \int_{\text{peak}} \frac{\sin^2 N_1 p_1}{\sin^2 p_1}\, dp_1 \simeq \int_{-\infty}^{\infty} \frac{\sin^2 N_1 p_1}{p_1^2}\, dp_1 = N_1$$

Hence $E = I_0 \left(\frac{e^2}{mc^2 R}\right)^2 \frac{R^2}{\omega} \frac{\lambda^3}{V_a \sin 2\theta} N_1 N_2 N_3 |F(q)|^2$

Simplify using $N_1 N_2 N_3 V_a = V$ volume of sample.

$$E = \frac{I_0}{\omega}\left(\frac{e^2}{mc^2}\right)^2 \frac{\lambda^3 V}{V_a^2 \sin 2\theta} |F(\vec{q})|^2 \quad \propto V, \text{ not } V^2$$

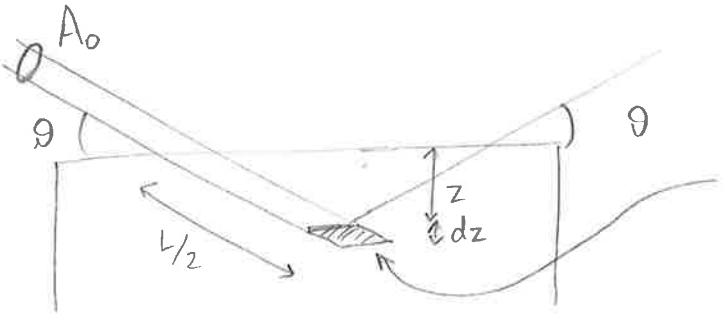
- Factor of $\sin 2\theta$ is called the Lorentz factor for the rotation method.
- Crystal which is not a parallelopiped can be decomposed into blocks which are; then sum E's.

7. Extended face imperfect crystal.

"Ideally imperfect" means sufficiently mosaic to remove extinction. Mosaics each diffract as above.

- Need to include apsorption so $I \propto I_0 e^{-\mu L}$ at distance
  μ = linear apsorption coefficient.
- Beam now smaller than sample; its cross sectional area is A_0.

(2.8)



# of mosaics in volume $A_0\,dz/\sin\vartheta$ is $A_0\,dz/V\sin\vartheta$

$$E' = E\int_{z=0}^{\infty} \underbrace{e^{-2\mu z/\sin\vartheta}}_{\mu L} \frac{A_0\,dz}{V\sin\vartheta} = \frac{A_0}{2V\mu}E$$

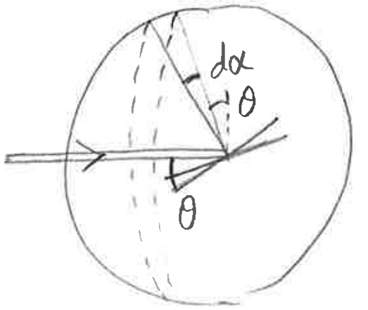
$$= \frac{P_0}{\omega}\left(\frac{e^2}{mc^2}\right)^2 \frac{\lambda^3}{V_a^2\,2\mu\sin 2\vartheta}\left|F(\vec{q})\right|^2 \quad \text{where } P_0 = I_0 A_0$$

8. Powder sample with esctended face.
Powder is identical sample to above (small mosaics)
except the mosaic distribution is totally random in rec. space
⇒ $\vec{H}_{hkl}$ vector distributed uniformly over surface of sphere
In <u>high-symmetry</u> crystal structures more than one reflection lies on the same sphere

eg cubic $\pm1\ \pm1\ 0$, $0\ \pm1\ \pm1$, $\pm1\ 0\ \pm1$ 12 perms
$\pm1\ \pm1\ \pm1$ 8 perms

m_{hkl} is the 'multiplicity' of the reflection $m_{110} = 12$

Assume sample contains M crystals each of volume V, and they all contribute equally (ie no absorption)
There will be Mm_{hkl} vectors on the sphere in reciprocal space.



a given range of incidence angles dα will illuminate the ring of reflections shown

$$dM = \frac{d\alpha \cos\theta . 2\pi}{4\pi} \times M m_{hkl}$$

$$= \frac{M m_{hkl} \cos\theta}{2} d\alpha$$

β & γ integration is the same as before

Integrated intensity $P = \int I(\vec{q}) \frac{M m_{hkl} \cos\theta}{2} d\alpha \; R^2 d\beta d\gamma$

$$= I_0 \left(\frac{e^2}{mc^2}\right)^2 \frac{MV \lambda^3 m_{hkl}}{4 V_a^2 \sin\theta} |F(\vec{q})|^2$$

MV is the total volume of the sample

$\sin 2\theta = 2 \sin\theta \cos\theta$ has become $\sin\theta$ now.

9. Extended-face powder sample

$P' = \frac{P}{2\pi R \sin 2\theta}$ = observed intensity per unit length around ring

$$= \frac{P_0}{16\pi R} \left(\frac{e^2}{mc^2}\right)^2 \frac{\lambda^3 m_{hkl}}{2\mu V_a^2} \left(\frac{1 + \cos^2 2\theta}{\sin\theta \; \sin 2\theta}\right)$$

most useful result for real experiments

Powder diffractometer with fixed slit measures fixed length of powder line.