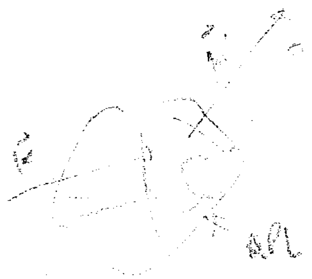
day 5 pg 5

back to our case



$$F \propto \int_{\text{volume}} e^{i\Delta\phi}\, dV$$

before $\Delta\phi = 2\pi \frac{\Delta PL}{\lambda}$

Now $\Delta\phi = \vec{k}\cdot\vec{r} - \vec{k}'\cdot\vec{r}$

$= -\Delta\vec{k}\cdot\vec{r}$

$\Delta\vec{k} = \vec{k}' - \vec{k}$

But x-rays scatter due to electron density, so need to weight by $n(\vec{r})$:

$$F = \int_{\substack{\text{volume}\\ \text{of}\\ \text{crystal}}} n(\vec{r})\, e^{-i\Delta\vec{k}\cdot\vec{r}}\, dV$$

scattering amplitude $\propto F$

Plug in Fourier representation of $n(\vec{r})$:

$$F = \int_{\substack{\text{vol of}\\ \text{xtal}}} \left(\sum_{\vec{G}} n_{\vec{G}}\, e^{i\vec{G}\cdot\vec{r}}\right) e^{-i\Delta\vec{k}\cdot\vec{r}}\, dV$$

$$= \sum_{\vec{G}} \int_{\substack{\text{vol of}\\ \text{xtal}}} n_{\vec{G}}\, e^{i(\vec{G}-\Delta\vec{k})\cdot\vec{r}}\, dV$$

this $= 0$ unless $\boxed{\Delta\vec{k} = \vec{G}}$!

(HW problem)

(due to oscillations)

day 6 pg 1

That's a huge part of the reason why those RLVs are useful

One step further: magnitude of k is not changing, only direction, so $k = k'$

$\vec{k}' - \vec{k} = \vec{G} \rightarrow \vec{k}' = \vec{G} + \vec{k}$

$\vec{k}'\cdot\vec{k}' = (\vec{G}+\vec{k})\cdot(\vec{G}+\vec{k})$

$\cancel{k^2} = G^2 + 2\vec{k}\cdot\vec{G} + \cancel{k^2}$

$G^2 + 2\vec{k}\cdot\vec{G} = 0$

if $\vec{G}$ is recip. lattice vector then so is $-\vec{G}$, so

$$-2\vec{k}\cdot\vec{G} + G^2 = 0$$

$$\boxed{2\vec{k}\cdot\vec{G} = G^2}$$

Bragg's Law! (obvious? ☺)

[illegible] recip lattice superimposed [illegible]

$$2k\cancel{G}\sin\theta = G^{\cancel{2}}$$

G from plane

magn of G? $G = \frac{2\pi}{d}$ for [illegible]

$$2\left(\frac{2\pi}{\lambda}\right)\sin\theta = \frac{2\pi}{d}$$

[illegible] of planes representing same hkl spacing (HW 2-1)

hkl = (222)

↓

write as (111) but has ½ the spacing

introduces factor of n

$$2\left(\frac{2\pi}{\lambda}\right)\sin\theta = \left(\frac{2\pi}{d/n}\right)$$

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

Laue Eqns
Ewald construction } on your own

skip Brillouin Zone for now, jump to

$\boxed{\text{Fourier Analysis of the Basis}}$

Back to $F = \int_{\text{volume of crystal}} n(\vec{r})\, e^{-i(\vec{\delta k}\cdot\vec{r})}\, dV$

Note: 1) all cells contribute same amount
2) $\vec{\delta k}$ must $= \vec{G}$ for it to be non zero

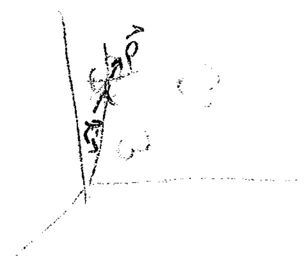
$$F = N \int_{\text{unit cell}} n(\vec{r}) \cdot e^{-i\vec{G}\cdot\vec{r}}\, dV$$

Note 3) Assume $n(\vec{r})$ only nonzero close to each nucleus

write $\vec{r} = \vec{r}_j + \vec{\rho}$

$\vec{r}_j$: vector pointing to jth nucleus

$\vec{\rho}$: vector pointing to electron charge density surrounding nucleus (horrible symbol!) not density!



Then $$F = N \sum_j \int n(\vec{\rho})\, e^{-i\vec{G}\cdot(\vec{r}_j+\vec{\rho})}\, dV_\rho$$

dV_ρ → integrating over x y z coords that represent ρ

$$= N \sum_j e^{-i\vec{G}\cdot\vec{r}_j} \underbrace{\int n(\vec{\rho})\, e^{-i\vec{G}\cdot\vec{\rho}}\, dV_\rho}_{f_j}$$

f_j "atomic form factor" of j^{th} atom
only an atomic property!

structure factor

$$\frac{F}{N} = \boxed{S_{\vec{G}} = \sum_j e^{-i\vec{G}\cdot\vec{r}_j} \cdot f_j}$$

$$\boxed{S_{\vec G} = \sum_j f_j e^{-i\vec G\cdot\vec r_j}}$$

with $f_j = \int_{\text{all space}} n_j(\vec r) e^{-i\vec G\cdot\vec r}$

only depends on atom j. No info about structure! (Look up in table)

Note $\vec G\cdot\vec r = (v_1\vec b_1 + v_2\vec b_2 + v_3\vec b_3)\cdot(x\vec a_1 + y\vec a_2 + z\vec a_3)$

remember $\vec b_i\cdot\vec a_j = 2\pi\delta_{ij}$

$= 2\pi(v_1 x + v_2 y + v_3 z)$

Note that $\Delta\vec k = \vec G$ is necessary but not sufficient condition for a spot.
second condition $S_{\vec G} \neq 0$

bcc structure   bcc lattice, all atoms identical

conventional (cubic) unit cell.
2 atoms in basis
(0,0,0)
and $(\frac12,\frac12,\frac12)$ (a ...)

Use hkl for $v_1 v_2 v_3$?

$S_{\vec G} = f \sum_{\text{basis}} e^{-i(\vec G\cdot\vec r_j)}$

$= f\left(1 + e^{-i2\pi(v_1\frac12 + v_2\frac12 + v_3\frac12)}\right)$

$= \begin{cases} 0 & \text{if } v_1+v_2+v_3 = \text{odd} \\ 2f & \text{if } v_1+v_2+v_3 = \text{even} \end{cases}$

diffraction lines (200)(110)(222) etc ✓
(100)(300),(111) etc ✗

why no (100)? → $\boxed{\text{Fig 16 pg 41}}$

day 6 pg 5

fcc structure conventional cell

fcc lattice, all atoms same
1 atom/primitive unit cell

(000)
$(0\,\tfrac{1}{2}\,\tfrac{1}{2})$
$(\tfrac{1}{2}\,0\,\tfrac{1}{2})$
$(\tfrac{1}{2}\,\tfrac{1}{2}\,0)$

$$S_{\vec G} = f \sum_j e^{-i\vec G\cdot\vec r_j} \qquad \vec G = v_1\vec b_1 + v_2\vec b_2 + v_3\vec b_3$$

$$= f\left(1 + e^{-i2\pi\left(\frac{v_2}{2}+\frac{v_3}{2}\right)} + e^{-i2\pi\left(\frac{v_1}{2}+\frac{v_3}{2}\right)} + e^{-i2\pi\left(\frac{v_1}{2}+\frac{v_2}{2}\right)}\right)$$

v_1	v_2	v_3	S
0	0	0	4f
0	0	1	f(1+-1-1+1)=0
0	1	0	0
0	1	1	↓
1	0	0	↓
1	0	1	↓
1	1	0	↓
1	1	1	4f

0 = even
1 = odd

only diffraction spots that are all even or all odd!

day 7 pg 1

Atomic form factor revisited

$dV = r^2 \sin\theta\, dr\, d\theta\, d\phi$

$$f_j = \int_{\substack{\text{all}\\\text{space}}} n_j(\vec r)\, e^{-i\vec G\cdot\vec r}\, dV$$

align z axis with G
assume spherical symmetry for n

$$= 2\pi \int_0^\infty n_j(r)\, dr \underbrace{\int_0^\pi \sin\theta\, d\theta\; e^{-iGr\cos\theta}}\quad \times\left(\frac{+iGr}{+iGr}\right)$$

then $\int e^u\, du$

$$\frac{e^{-iGr\cos\theta}}{+iGr}\Bigg|_{\theta=0}^{\pi} = \frac{e^{iGr} - e^{-iGr}}{iGr}$$

$$= \frac{1}{Gr}\, 2\sin Gr$$

$$= 4\pi \int_0^\infty n_j(r)\, r^2\, \frac{\sin Gr}{Gr}\, dr$$

typo in book! pg 42