Crystal structure from x-ray Diffraction

How wave scatter off crystals?

First way to determine the crystal structure by scattering was described by Fermi known as the Fermi-golden rule.

Think wave as a particle (?!) scattering off the potential $V(\bar{r})$. The transition rate is

$$\Gamma(\bar{k}', \bar{k}) = \frac{2\pi}{\hbar} |\langle \bar{k}' | V(\bar{r}) | \bar{k} \rangle|^2 \delta(E_{k'} - E_k)$$

where $\langle k' | V(r) | k \rangle = \int d\bar{r} \frac{e^{-i\bar{k}'\cdot\bar{r}}}{\sqrt{L^3}} V(\bar{r}) \frac{e^{i\bar{k}\cdot\bar{r}}}{\sqrt{L^3}} =$

$= \frac{1}{L^3} \int d\bar{r}\, e^{-i(\bar{k}'-\bar{k})\cdot\bar{r}} V(\bar{r})$ which is just the FT. of the crystal.

Intriguing, for the crystal $k' - k = G$ ← is a reciprocal lattice vector!

Proof: Lets write $\bar{r} = \bar{R} + \bar{x}$

↑ lattice vector | position w. in U.C. ↖

$$\langle k' | V | k \rangle = \frac{1}{L^3} \int d\bar{r}\, e^{-i(\bar{k}-\bar{k})\cdot\bar{r}} V(\bar{r}) = \sum_{U.C.} \sum_{R} e^{-i(\bar{k}'-\bar{k})\cdot\bar{R}} \cdot \int_{UC} d\bar{x}\, e^{-i(\bar{k}'-\bar{k})\cdot\bar{x}} \cdot V(\bar{x})$$

$$= \begin{cases} 0 & \text{if } k' = k + \bar{G} \end{cases}$$

in other words: $\boxed{\bar{k}' - \bar{k} = \bar{G}}$ known as the Laue equation or the Laue condition

Other way to say this

$k' - k = G$ is the conservation of crystal momentum

When the wave is out of the crystal

$k' = k$ ⇐ elastic scattering.

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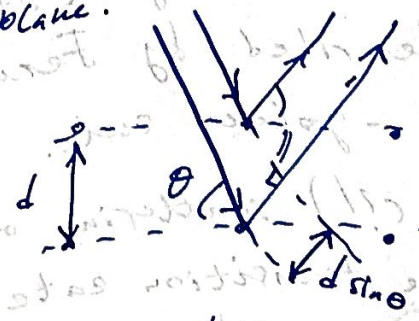
DIFFRACTION LIMIT

Laue condition = scattering conditions

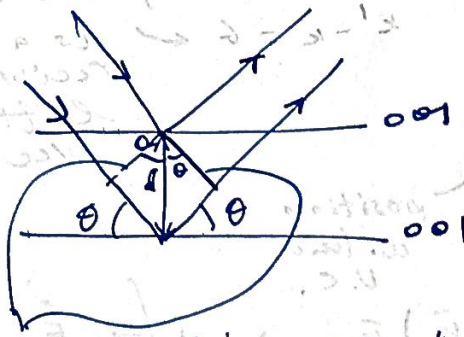
But 1st lets look at the scattering off a plane:

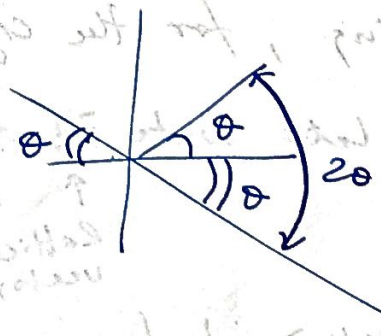


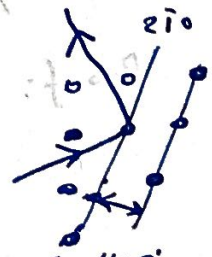
to scatter off is equivalent to saying the outgoing wave have interfered constractively.

extra distance for travel $= 2d\sin\theta$. should contain the integer number of λs

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



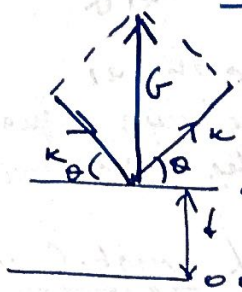




$d\sin\theta + d\sin\theta = n\lambda$. $n = 1, 2, 3, 4 \ldots$

This is very visual but in reality very inconvinient since scattering occurs in the momentum space, e.g. the Fermi golden rule.

LAUE CONDITION ≟ Bragg condition.



the spacing between the planes $d = 2\pi/|G|$

From this fig.

$\bar{k}\cdot\bar{G} = \sin\theta = -\bar{k}'\cdot\bar{G}$ if $k - k' = G$ and $|k| = |k'| = \frac{2\pi}{\lambda}$

if the L. condition is satisfied $k - k' = G$

we can write down:

$\frac{2\pi}{\lambda}(\hat{k} - \hat{k}') = G$ where $\hat{k}$ and $\hat{k}'$ are the unit vectors

$\hat{G} \cdot \frac{2\pi}{\lambda}(\hat{k} - \hat{k}') = G \cdot G \Rightarrow \frac{2\pi}{\lambda}\left[\underbrace{\hat{G}\cdot\hat{k}}_{\sin\theta} - \hat{G}\hat{k}'\right] =$

$= |G|$ $\quad\quad -\sin\theta'$

$\Rightarrow \frac{2\pi}{\lambda} \cdot 2\sin\theta = |G| \Rightarrow \lambda = \underbrace{\frac{2\pi}{|G|}}_{d}\, 2\sin\theta \Rightarrow$

$\lambda = 2d\sin\theta$ which is the Bragg cond.

h is missing because we consider 2 closest planes.

> Bragg = interference is constructive
> Laue = crystal momentum is conserved

Scattering amplitudes

Lets start with the Fermi golden rule

$\Gamma(k, k') = \frac{2\pi}{\hbar} |\langle k'|V(x)|k\rangle|^2 \delta(E_{k'} - E_k)$

where $\langle k'|V|k\rangle = \left[\frac{1}{V_B}\sum_R e^{-i\underbrace{(k'-k)}_{=G}R}\right] \cdot \underbrace{\int_{U.C.} dx\, e^{-i(k-k')\cdot x} V(x)}_{\text{structure factor } S(G)}$

$\Rightarrow$ Scattering intensity $I_{hkl} \sim |S_{hkl}|^2$

also we can assume that $V(x) = \sum_{atoms\, j} V_j(x - x_j)$ scattering fact. of individual atoms.

Examples of scatt. factors

Neutrons vs. Xrays.

neutrons are neutral and carry only dipolar magnetic moment. The scattering potential is VERY SHORT range, so we can assume:

$$V(x) = \sum_j f_j \, \delta(x - x_j)$$

↑ the atomic form factor a.f.f. tabulated e.g. google "NIST atomic form factors"

a.f.f is proportional to the nuclear scattering length b_j, i.e. $f_j = \frac{2\pi\hbar^2}{m_{neutron}} b_j$

So $S(\bar{G}) = \int_{u.c.} dx \, e^{i\bar{G}\cdot\bar{x}} \frac{2\pi\hbar^2}{m} b_j \cdot \delta(\bar{x} - \bar{x}_j)$

$= \frac{2\pi\hbar^2}{m} \sum_j b_j e^{i\bar{G}\cdot x_j}$

X-rays

Now lets compare those to x-rays.

$$V_j(x - x_j) = Z_j \, g_j(x - x_j)$$

So the V_j is prop. to the electron charge density

here Z_j is the atomic number of atom j (i.e. the number of electrons).

$\frac{\sum}{k \uparrow k'}$ $(p + eA)^2/2m$

So $S(\bar{G}) = \sum_j f_j(\bar{G}) e^{i\bar{G}\cdot\bar{x}_j}$

here f_j is almost $\sim Z_j$ but some dependence on $\bar{G}$

$f_j(G) = \int dx \, e^{iG\cdot x} V_j(x)$

the integral over all crystal not u.c.

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Neutrons vs. X-rays.

- for X-rays $f_j \sim Z_j$ X-rays scatter very strongly off heavy ions. and very hard to see light atoms e.g. H, Li etc.
  Hart to separate elok in Z atoms

- Nuclear scatt. length for neutrons b_j varies very strongly from atom to atom

  Hydrogen is no problem
  Atoms with similar Z are no problem

- The form factor for neutrons is constant with θ.

  For X-rays it is complicated.

(+) Neutrons can easily detect spin of electrons and the choice for studying magnetic orders.

Examples.

Recall $I_{hkl} \sim |S_{hkl}|^2$

if our lattice vectors are orthogonal we get

$$S_{hkl} = \sum_j f_j \, e^{2\pi i (hx_j + ky_j + lz_j)}$$

where $[x_j\ y_j\ z_j]$ are the coordinates of an atom j within the u.c.

Cs^+Cl^-

Simple cubic with basis:

Cs	[0 0 0]
Cl	[1/2 1/2 1/2]

$$S_{hkl} = \sum_j \ldots = f_{Cs} \underbrace{e^{2\pi i (\ldots 0 \ldots)}}_{1} + f_{Cl} \, e^{2\pi i (h \cdot 1/2 + k\,1/2 + l\,1/2)} = f_{Cs} + f_{Cl} (-1)^{h+k+l}$$

and $I_{hkl} \sim |S|^2$

Systematic Absences in Scattering

Caesium bcc:

bcc is simple cubic with basis

Cs	0 0 0
Cs	1/2 1/2 1/2

and by analogy to CsCl we get:

$$S_{hkl} = f_{Cs} + f_{Cs} \, e^{2\pi i (\ldots)} = f_{Cs} + f_{Cs} (-1)^{h+k+l}$$

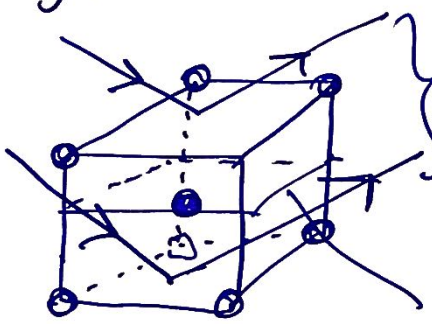
$$= f_{Cs} \left[1 + (-1)^{h+k+l}\right]$$

if $h+k+l = 2n+1$, $n = 0, 1, 2 \ldots$

the $S_{hkl} = 0$!!

This phenomenon is known as the <u>systematic absence</u>.

Why?



Consider e.g. (001) planes

they scatter constructively

BUT

this plane scatters off

destructively so there

is no intensity.

Copper fcc

fcc is simple cubic with a basis of 4 ~~atoms~~ lattice points

$(0\,0\,0)$ $(1/2\ 1/2\ 0)(1/2\ 0\ 1/2)$ $(0\ 1/2\ 1/2)$

so now

$$S_{hkl} = f_{Cu}\left[1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + \right.$$

if all h k l are odd e iπ(k+l) e

or h k l are all even

then it is OK, otherwise $S_{hkl} = 0$

Sometimes these systematic absences are called <u>the selection rules</u>

they occur for any Bravais lattice

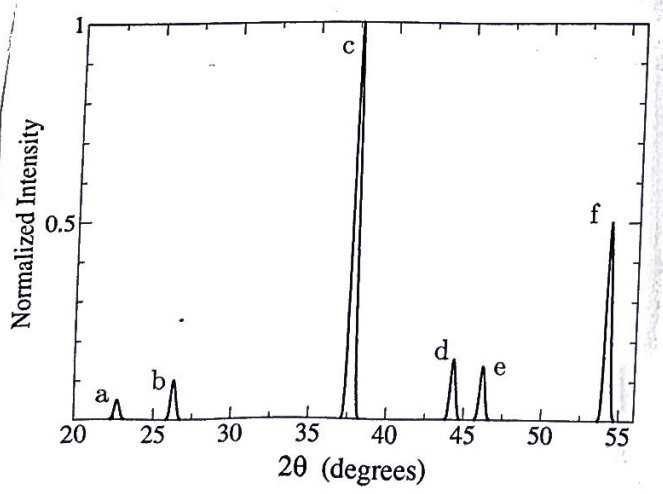
EXAMPLE L11

Let me work out for you a real-world example, e.g. for scattering off PrO_2 i.e. Given the following diffraction pattern obtained by neutrons with $\lambda = 0.123$ nm obtain the lattice size and the crystal structure type.

Here is the experimental data for <u>powder diffraction</u> from PrO_2, $\lambda = 0.123$

First read the angle data as precise as posible. For clarity use a tableform

Expt. data for PrO_2



crystal structure of PrO_2

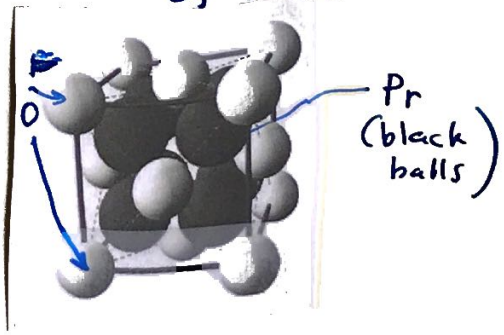


Table for analysis

peak	2θ	$d = \lambda/(2\sin\theta)$	d_a^2/d^2	$3d_a^2/d^2$	$N = h^2+k^2+l^2$	$\{hkl\}$	$a = d\sqrt{h^2+k^2+l^2}$
a	22.7°	0.313 nm	1	3	3	111	.542 nm
b	26.3°	0.270 nm	1.33	3.99	4	200	.540 nm
c	37.7°	0.190 nm	2.69	8.07	8	220	.537 nm
d	44.3°	0.163 nm	3.67	11.01	11	311	.541 nm
e	46.2°	0.157 nm	3.97	11.91	12	222	.544 nm
f	54.2°	0.135 nm	5.35	16.05	16	400	.540 nm

Comments to the obtained result presented in the Table.

- First you must remember we measure 2Θ not ~~Θ~~
- Given the wave length λ we calculate the lattice spacing $d_{hkl} = \frac{\lambda}{2\sin\Theta}$
- Next I assume some pseudo cubic type of lattice for Pr_2O_2 and based on this we calculate

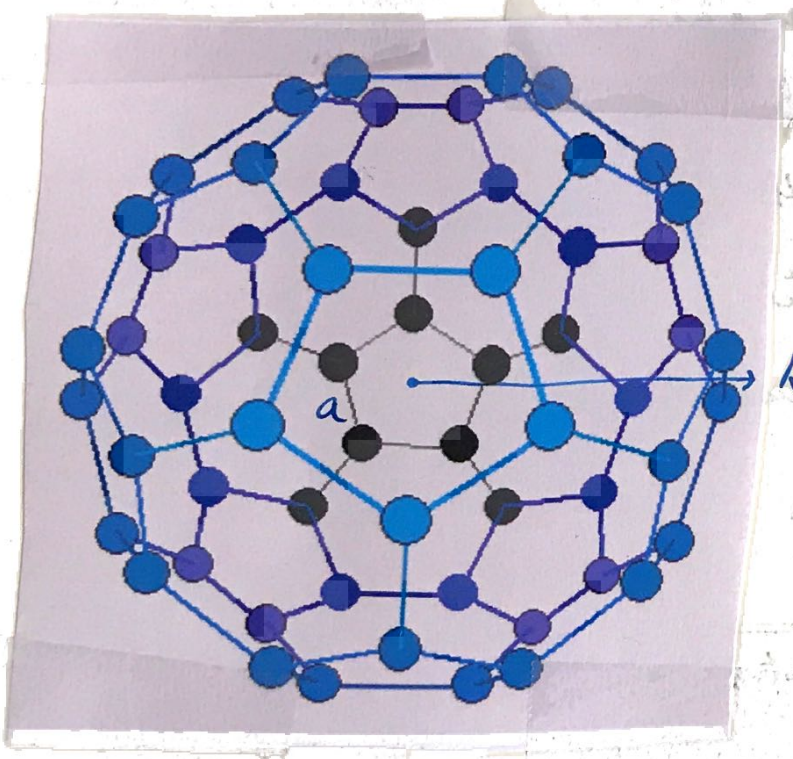
$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} \Rightarrow \frac{a^2}{d^2_{hkl}} = h^2+k^2+l^2 \equiv N$$

- next we can normalize the positions of the lattice planes to the value calculated for the first peak labeled as a.

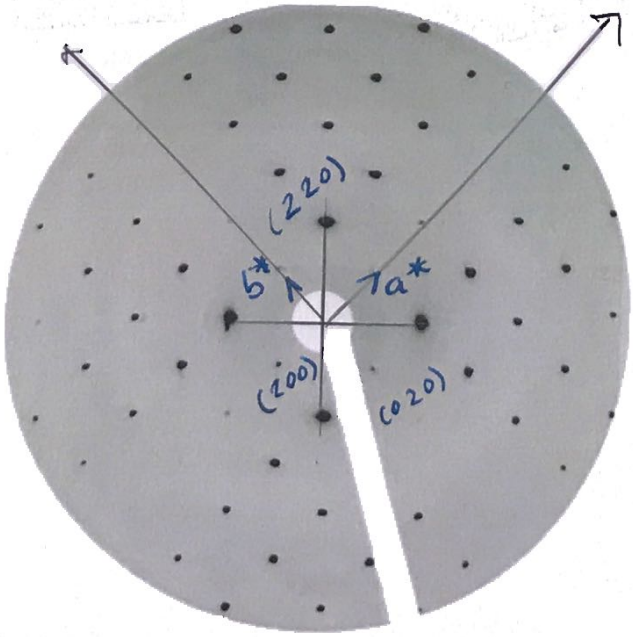
$$\frac{d^2}{da^2} \quad \text{where } d = \frac{\lambda}{2\sin\Theta}$$

- HERE IS THE "ART" MOMENT notice that $3 \times \frac{d^2}{da^2}$ gives us the almost the whole number!
- Next try to reproduce this whole numbers as the combination of $\{h,k,l\}$ to form $h^2+k^2+l^2 \equiv N$
- Verify your guess by calculating the material lattice constan $a = d\sqrt{h^2+k^2+l^2}$ it MUST be the SAME NUMBER!

— Lets try to estimate intersities and work out some interesting information. Consider C_{60}.



Assume we know the size of the primitive unit cell (fcc)
$a = 14.17 \pm 0.07 \text{ Å}$
Can we estimate the radius of the hollow sphere R from the ~~electron~~ X-ray diffraction?



X-ray diffraction pattern for a C_{60} single crystal obtained with the experimental setup known as a precession chamber. This directly visualises the Bragg spots corresponding to a plane of the reciprocal lattice of the crystal (to solve Question 2.6 one has to take into account that the actual diameter of the film in 12 cm). Image courtesy of Launois, P., Moret, R.: Laboratoire de Physique des Solides. Orsay, France

X-ray from C_{60}

By inspecting the diffraction image we notice that (h,0,0) and (0,k,0) spots are very faint., i.e about say 10^3 lower compared to (200). Lets set the charge distribution to be uniform inside the sphere, i.e.: $\rho(r) = A\,\delta(r-R)$  R

Each carbon couributes 6 electrons, so the total number of the electrons: $6\times 60 = 360\,e^-$

$$360e = \int \rho(r)\,dr^3 = A\int_0^\infty 4\pi r^2\,\delta(r-R)\,\delta r = 4\pi R^2 \cdot A \Rightarrow$$

$$A = \frac{360\,e^-}{4\pi R^2}$$

Next lets calculate the structure factor

$$S(G) = \int \rho(r)\,e^{i\,G\cdot r} = \frac{360e^-}{4\pi R^2}\int_0^\infty r^2\cdot\delta(r-R)\,dr \cdot$$

$$\int_0^{2\pi} d\varphi \int_0^{\pi} e^{i\,G\,r\cos\theta}\,\sin\theta\,d\theta = \quad \left(\frac{\sin\theta\,d\theta}{d(\cos\theta)}\right)$$

$$= \frac{1}{2\pi}$$

$$\cos\theta \equiv \beta \Rightarrow \int_{-1}^{1} e^{\beta x}\,d_{\beta x} = \frac{1}{\beta}\underbrace{\left[e^{+\beta} - e^{-\beta}\right]}_{\equiv \sin\beta\cdot 2i} =$$

$$= \frac{360\,e^-}{2R^2}\int_0^\infty 2\,\frac{\sin Gr}{Gr}\,r^2\,\delta(r-R)\,dr =$$

$$= 360\,e^-\,\frac{\sin GR}{GR}$$ and the spot intensity

$$I_{hkl} \sim \left|S(\bar{G})\right|^2 = \frac{\sin^2 GR}{(GR)^2}$$

if $GR = \pi n \Rightarrow I = 0$ means those spots are $G = n\left(\frac{4\pi}{a}\right)$ since the (h00) and (0k0) are almost gone

↑ a size of the conventional fcc. cubic

Those spots correspond to $G = \left(\frac{4\pi}{a}\right) 4$

↑ size of the side of conv. fcc

thus $\frac{\pi \cdot 4}{R} = \left(\frac{4\pi}{a}\right) 4 \rightarrow R \equiv \frac{a}{4}$

or $R = 3.54 \text{ Å}$ the size of the backyball case!