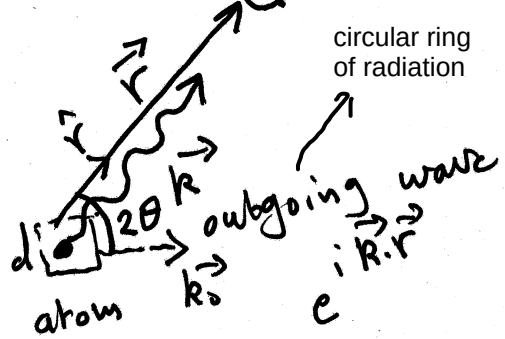
Chapter 3

Scattering and structures

The scattering experiments are performed by directing a plane wave towards a sample. The incident wave interacts with the sample and the scattered radiation is measured by a detector setting far away from the sample.

- Consider a scattering of plane wave off a crystal, where the scattering is elastic, meaning that energy is conserved, and not transfered between the wave and the crystal (incoming and outgoing waves have the same frequency)
- let us consider first, the scattering of the wave by a single atom located at the origin



Scattering angle: 2θ

Elastic scattering

$|\vec{k_0}| = |\vec{k}|$

i.e $\omega_0 = \omega'$

$|k_0| = \frac{2\pi}{\lambda}$

λ: wavelength of incident wave

$\varphi_{inc} = e^{i\vec{k_0}\cdot\vec{r}}$

$\vec{r} = r\hat{r}$; $\vec{k} = k\hat{r}$ $= k_0\hat{r}$

$r >> d$ ↓ size of the atom

$\psi_{inc} = A e^{i\vec{k_0}\cdot\vec{r}}$; for simplicity take $A=1$

- now when the incident wave collides with the atom, an outgoing spherical wave is produced that takes the form

$$\psi_{sc}(\vec{r}) = f(\vec{k},\vec{k_0})\frac{e^{ikr}}{r} \quad ; \quad \{f(\vec{k},\vec{k_0}) = f(\theta,\phi) \equiv f(\hat{r})$$ is the scattering amplitude (or the form factor). it contains info about interaction between the incident wave and the scatterer.

$$= f(\hat{r})\frac{e^{ik_0 r}}{r} \quad ; \text{ as } |k| = |k_0| \text{ for elastic scattering}$$

now the total wavefunction at the position of the detector is a superposition of ψ_{inc} and ψ_{sc}

$$\Rightarrow \psi(\vec{r}) \approx \psi_{inc}(\vec{r}) + \psi_{sc}(\vec{r}) \quad \text{for away from the scatterer i.e } r \gg d$$

$$\approx e^{-i\omega t}\left[e^{i\vec{k_0}\cdot\vec{r}} + f(\hat{r})\frac{e^{ikr}}{r}\right\} \quad \text{---- (1)}$$

↓ incident plane wave

↳ scattered spherical wave

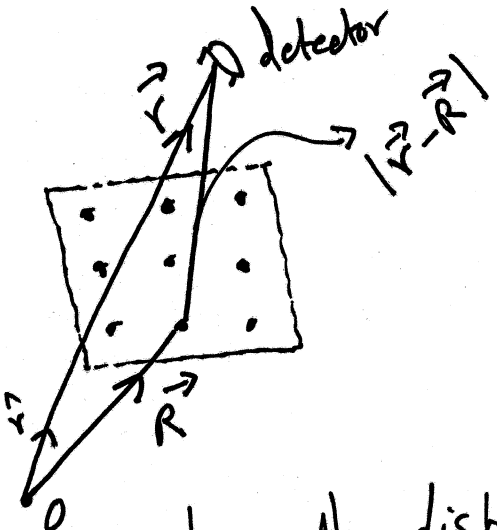
the form factor is related to the differential cross section by $I_{atom} = \frac{d\sigma}{d\Omega_{atom}} = |f(\hat{r})|^2$; $[f] \equiv$ length

$\left[\frac{d\sigma}{d\Omega}\right] \equiv$ area

and the intensity of the scattered wave at a solid angle $d\Omega$ at a distance r from the scatterer is

$$d\Omega \frac{I_{atom}}{r^2} = d\Omega \frac{|f(\hat{r})|^2}{r^2}$$

Now ask how eq^{n} (1) changes when the same incoming wave scatters off a particle located at $\vec{R}$ rather than at the origin; This shift causes the scattered wave to acquire extra phase $e^{i\vec{k}_0\cdot\vec{R}}$ with respect to the incident wave, i.e



$\vec{k}_0$

$$\psi(\vec{r}) \approx e^{-i\omega t}\left[e^{i\vec{k}_0\cdot\vec{r}} + e^{i\vec{k}_0\cdot\vec{R}}\,\frac{f(\hat{r})\,e^{ik_0|\vec{r}-\vec{R}|}}{|\vec{r}-\vec{R}|}\right]$$

$e^{i\vec{k}_0\cdot\vec{R}}$ ↓ extra phase

; where the distance travelled by the scattered wave now reads $|\vec{r}-\vec{R}|$

for sufficiently large r ($r \gg R$);

$$|\vec{r}-\vec{R}| = \left[r^2 - 2\vec{r}\cdot\vec{R} + R^2\right]^{1/2} = r\left[1 - \frac{2\vec{r}\cdot\vec{R}}{r^2} + \frac{R^2}{r^2}\right]^{1/2}$$

(R^2/r^2: small)

, $(1-x)^n = 1-nx$ for $x \ll 1$

$$= r\left[1 - \frac{\vec{r}\cdot\vec{R}}{r^2}\right] = r - \frac{\vec{r}}{r}\cdot\vec{R} = r - \hat{r}\cdot\vec{R}$$

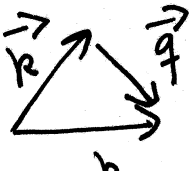
$$\Rightarrow k_0|\vec{r}-\vec{R}| = k_0 r - k_0\,\hat{r}\cdot\vec{R}$$

so $$\psi(\vec{r}) \sim e^{-i\omega t}\left[e^{i\vec{k}_0\cdot\vec{r}} + \frac{e^{ik_0 r - ik_0\hat{r}\cdot\vec{R}}}{r} f(\hat{r})\, e^{i\vec{k}_0\cdot\vec{R}}\right]$$

$\vec{k} = k_0\hat{r}$

$$\psi(\vec{r}) \sim e^{-i\omega t}\left\{e^{i\vec{k}_0\cdot\vec{r}} + \frac{f(\hat{r})}{r} e^{ik_0 r}\, e^{i(\vec{k}_0-\vec{k})\cdot\vec{R}}\right\}$$

define $\vec{q} = \vec{k}_0 - \vec{k}$



$\vec{q} = \Delta\vec{k} = \vec{k}_0 - \vec{k}$

q: difference in momenta of the incoming and outgoing waves $\Delta\vec{k}$

$$\psi(\vec{r}) \sim e^{-i\omega t}\left[e^{i\vec{k}_0\cdot\vec{r}} + \frac{f(\hat{r})}{r} e^{ikr}\, e^{i\vec{q}\cdot\vec{R}} \right} \quad \text{..... (2)}$$

Recall that

$$\vec{q} = \vec{k}_0 - \vec{k} \Rightarrow q^2 = \vec{q}\cdot\vec{q} = (\vec{k}_0 - \vec{k})\cdot(\vec{k}_0 - \vec{k})$$

$$\Rightarrow q^2 = k_0^2 + k^2 - 2\vec{k}_0\cdot\vec{k} \quad ; \text{ using } \vec{k}_0\cdot\vec{k} = k_0^2\cos(2\theta)$$

when $|k_0| = |k|$

$$= 2k_0^2 - 2k_0^2\cos 2\theta$$

$$= 2k_0^2(1 - \cos 2\theta) \quad ; \text{ using } \sin^2\theta = \frac{1-\cos 2\theta}{2}$$

$$= 4k_0^2\sin^2\theta$$

$$\Rightarrow q = 2k_0\sin\theta$$

- Now let us consider the scattering from a large collection of identical scatterers. The total intensity of the radiation arrived at the detector will be simply sum of radiation coming from each scatterer. ignoring the multiply scattering and assuming only elastic scattering, one has for ψ

$$\psi \sim e^{-i\omega t}\left[e^{i\vec{k}_0\cdot\vec{r}} + \sum_l f_l(\hat{r})\frac{e^{ikr + i\vec{q}\cdot\vec{R}_l}}{r} \right} \quad \text{---(3)}$$

↳ run over all lattice vectors

This term represents the incoming beam that also exists the sample in the forward direction ($\theta = 0$). now since we are interested in nonzero scattering angles ($\theta \neq 0$); this term can be neglected. This term is important only for very small scattering angles ($\theta \to 0$), creating bright spot in this direction

$$\Rightarrow \psi \sim e^{-i\omega t} \frac{e^{ikr}}{r} \sum_l f_l(\hat{r})\, e^{i\vec{q}\cdot\vec{R}_l} \quad \text{---} \quad (4)$$

now the intensity at the position of the detector per unit solid angle divided by the intensity $|A|^2$ of the incoming beam $I = |\psi|^2 \frac{r^2}{A^2}$ is then ; where $|\psi|^2 = \psi\psi^*$

$$I = \sum_{ll'} f_l f_{l'}^* \, e^{i\vec{q}\cdot(\vec{R}_l - \vec{R}_{l'})} \quad ; \text{ when } I \text{ used } \left|\sum_l C_l\right|^2 = \sum_{ll'} C_l C_{l'}^*$$

- Lattice sums

now since all scatterers are identical and arranged in Bravais lattice, then f is the same for all atoms, so

$$I = |f(\hat{r})|^2 \sum_{ll'} e^{i\vec{q}\cdot(\vec{R}_l - \vec{R}_{l'})} = I_{atom} \left| \sum_l e^{i\vec{q}\cdot\vec{R}_l} \right|^2 \quad \text{---} (5)$$

↓ scattering cross section for one atom

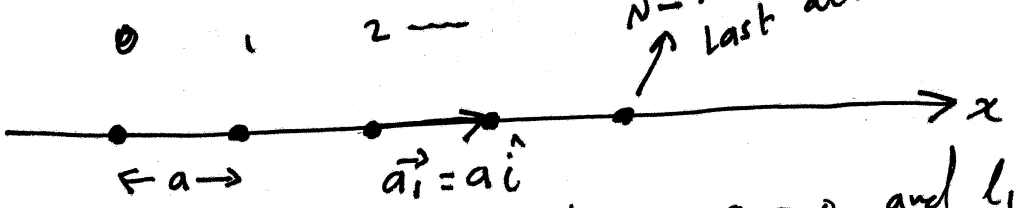
now by inspecting eq^n (5), one would ask a bout the optimal values of $\vec{q}$ that leads to intensity maxima (strong scattering). by choosing $\vec{q}$ such that $e^{i\vec{q}\cdot\vec{R}_l} = 1$ for all $\vec{R}_l$, then all terms in eq^n (5) would be one, and summing them would produce a large final result. otherwise, one might expect terms in eq^n (5) to alternate in sign and hence cancel out on average.

so the sum Σ in eq^n (5) determines the behavior of any wave interacting with a periodic lattice. The mathematics is best explained in one dimension, and then generalized to 3D.

- <u>one-dimensional sum:</u>

The lattice points are located at la, where l is an integer and a is the lattice spacing; there are N lattice points

N atoms



so $\vec{R_L} = l_1\vec{a_1} + l_2\vec{a_2} + l_3\vec{a_3}$; set $a_2 = a_3 = 0$ and $l_1 = l$

$= la\hat{i}$

so the relevant sum in eq^n (5) $\Sigma_q = \sum_l e^{i\vec{q}\cdot\vec{R_L}}$ becomes

$$\Sigma_q = \sum_{l=0}^{N-1} e^{ilaq} = \sum_{l=0}^{N-1} \left[e^{iqa}\right]^l$$

Note that $\sum_{l=1}^{N} \Leftrightarrow \sum_{l=0}^{N-1}$

Finite geometric series

$$\sum_{l=0}^{N-1} x^l = \frac{1-x^N}{1-x}$$

Note also that

$\vec{q} = q_x\hat{i} + q_y\hat{j} + q_z\hat{k}$

$\Rightarrow \vec{q}\cdot\vec{R} = q_x al$

$\Rightarrow$ set $q_x = q$

$\Rightarrow \vec{q}\cdot\vec{R} = qal$

$\vec{q}$ is the scattering vector $\vec{q} = \Delta\vec{k} = \vec{k_0} - \vec{k}$

$$\Rightarrow \sum_q = \frac{1-e^{iqaN}}{1-e^{iqa}}$$

$$\text{now } |\Sigma_q|^2 = \Sigma_q \Sigma_q^*$$

$$= \frac{1-e^{iqaN}}{1-e^{iqa}} \times \frac{1-e^{-iqaN}}{1-e^{-iqa}}$$

$$\Rightarrow |\mathcal{E}_q|^2 = \frac{1 - e^{-iqaN} - e^{iqaN} + 1}{1 - e^{-iqa} - e^{iqa} + 1} = \frac{2 - (e^{iqaN} + e^{-iqaN})}{2 - (e^{iqa} + e^{-iqa})}$$

using $\cos x = \frac{e^{ix} + e^{-ix}}{2}$

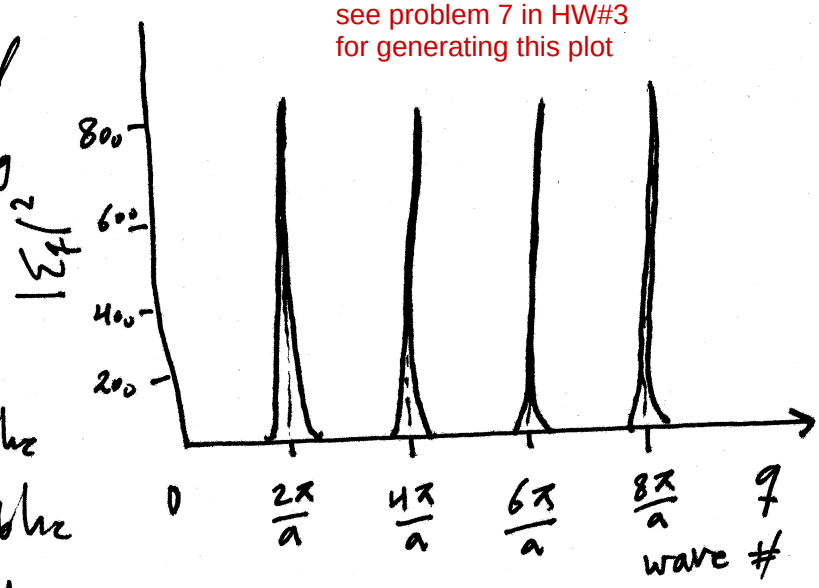
$$|\mathcal{E}_q|^2 = \frac{2 - 2\cos(qaN)}{2 - 2\cos(qa)} = \frac{1 - \cos(qaN)}{1 - \cos(qa)} \quad ; \text{ now using } \sin^2\theta = \frac{1 - \cos 2\theta}{2}$$

$$= \frac{2\sin^2(qaN/2)}{2\sin^2(qa/2)} = \frac{\sin^2(qaN/2)}{\sin^2(qa/2)} \quad \text{---- (6)}$$

a plot of eq^n (6) is shown below for the case $N = 30$

the graph contains a number of very sharp peaks, separated by regions where the scattering intensity is nearly zero.

see problem 7 in HW#3 for generating this plot



The location of the peaks are determined by searching for the points (q values) at which the denominator of eq^n (6) vanishes.

This occurs when $\sin\left(\frac{qa}{2}\right) = 0 \Rightarrow \frac{qa}{2} = l\pi$

$\Rightarrow q = \frac{2\pi}{a} l$; when l is an integer

we see that the peaks in the sum correspond exactly to the choices of q such that all terms in the sum

equal to 1 and thus add coherently (instructive interference) . for any other choice of q, the terms in the sum add with different phases and signs, giving almost vanishing intensity (destructive interference).

Because the peaks are so sharp, it is natural to represent $\sum_q$ as a sum of delta functions

$$\sum_{l=0}^{N-1} e^{ilqa} = \sum_{l'=-\infty}^{\infty} N \frac{2\pi}{L} \delta\left(q - \frac{2\pi l'}{a}\right)$$; L is the length of the lattice $L = Na$

See A.1 and A.2 Appendices

- now Returning to eq^n(5), we found that

$e^{i\vec{q}.\vec{R}} = 1 \rightarrow \vec{q}.\vec{R} = 2\pi l$ for all $\vec{R}$ in the Bravais lattice

l: integer

so only those values of qs that fulfil the above condition will produce Bragg peaks. these scattering vectors that fulfill the above condition will be denoted by $\vec{\Gamma}$ i.e $e^{i\vec{\Gamma}.\vec{R}} = 1$ or $\vec{\Gamma}.\vec{R} = 2\pi l$

the collections of scattering vectors $\vec{\Gamma}$ satisfying the above condition is called Reciprocal lattice. $\vec{\Gamma}$ is also called Reciprocal lattice vector

↳ cos (K.R)+i sin (K.R)=1, equating real parts gives cos (K.R) =1, that results in K.R = 2 Pi L

Relationship between Direct lattice and Reciprocal lattice

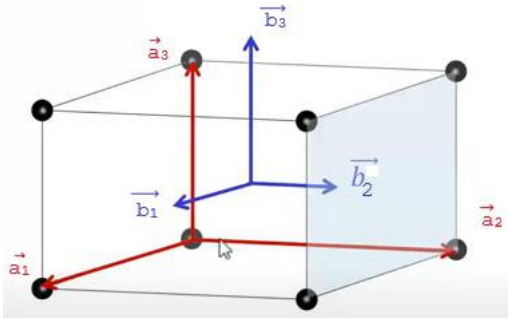
direct lattice primitive vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$; $[a]=L$

reciprocal " " = $\vec{b}_1, \vec{b}_2, \vec{b}_3$; $[b]=\frac{1}{L}$

where

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \; ; \; \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \; ; \; \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

note that $|\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|$ is the volume of the primitive cell in the direct space. in addition the quantity $|\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)|$ represents the volume of the primitive cell in the reciprocal space (k-space).



- Some properties:

- $\vec{a}_1 \cdot \vec{b}_1 = \vec{a}_2 \cdot \vec{b}_2 = \vec{a}_3 \cdot \vec{b}_3 = 2\pi$

- $\vec{a}_1 \cdot \vec{b}_2 = 2\pi \frac{\vec{a}_1 \cdot (\vec{a}_3 \times \vec{a}_1)}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = 0$ as $\vec{a}_1 \perp \vec{a}_3 \times \vec{a}_1$

similarly for other cases $\Rightarrow \vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$

- $V_K = \frac{(2\pi)^3}{\Omega_c}$; V_K : volume in reciprocal space, Ω_c : " " ; direct space

for proof, see problem 2 in HW # 3

- the reciprocal lattice of the reciprocal lattice is the direct lattice.

- Reciprocal lattice vectors are defined as

$\vec{K} = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3$; m_1, m_2, m_3 : integers $0, \pm 1, \pm 2, \cdots$

↘ translational vector in reciprocal space similar to (T or R) translational vector in direct space

The head of these lattice vectors form the points in the reciprocal lattice.

Example: SC lattice

$\vec{a_1} = a\hat{i}$, $\vec{a_2} = a\hat{j}$, $\vec{a_3} = a\hat{k}$

$$\Rightarrow \vec{b_1} = 2\pi \frac{\vec{a_2}\times\vec{a_3}}{\vec{a_1}\cdot(\vec{a_2}\times\vec{a_3})} = 2\pi \frac{a^2\hat{i}}{a^3} = \frac{2\pi}{a}\hat{i}$$

$$\vec{b_2} = \frac{2\pi}{a}\hat{j} \quad \text{and} \quad \vec{b_3} = \frac{2\pi}{a}\hat{k}$$

$$V_\Gamma = \frac{(2\pi)^3}{\Omega_c} = \frac{(2\pi)^3}{a^3}$$

we see that the reciprocal lattice of the SC (in direct space) is also a SC lattice.

the reciprocal lattice vectors are given by

$$\vec{\Gamma} = m_1\vec{b_1} + m_2\vec{b_2} + m_3\vec{b_3} \quad ; \quad \vec{b_1} = \frac{2\pi}{a^3}\vec{a_2}\times\vec{a_3} = \frac{2\pi}{a}\hat{i}$$

$$= \frac{2\pi}{a}m_1\hat{i} + \frac{2\pi}{a}m_2\hat{j} + \frac{2\pi}{a}m_3\hat{k}$$

$$\vec{\Gamma} = \frac{2\pi}{a}(m_1\hat{i} + m_2\hat{j} + m_3\hat{k}) \quad ; \quad |\vec{\Gamma}| = \frac{2\pi}{a}\sqrt{m_1^2+m_2^2+m_3^2}$$

as shown above

- Separation between adjacent planes in the direct lattice is given by

$$d = \frac{2\pi}{|\vec{\Gamma}|} = \frac{2\pi}{\frac{2\pi}{a}\sqrt{m_1^2+m_2^2+m_3^2}} = \frac{a}{\sqrt{m_1^2+m_2^2+m_3^2}}$$

in other textbooks m_1, m_2, m_3 are called miller indices and labeled as $hkl \Rightarrow d(hkl) = a/\sqrt{h^2+k^2+l^2}$

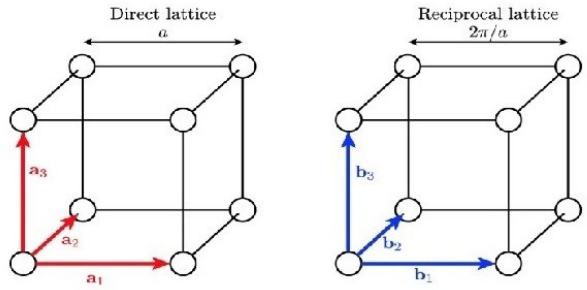
Lattice	Lattice Spacing	Primitive Vectors	Reciprocal Lattice Spacing	Reciprocal Lattice Primitive Vectors	V_C	$(V_P)_{dir}$	$(V_P)_{rec}$
sc	a	$(1\,0\,0)$ $(0\,1\,0)$ $(0\,0\,1)$	$\frac{2\pi}{a}$	$(1\,0\,0)$ $(0\,1\,0)$ $(0\,0\,1)$	a^3	a^3	$\left(\frac{2\pi}{a}\right)^3$
fcc	a	a1 $(\frac{1}{2}\ \frac{1}{2}\ 0)$ a2 $(\frac{1}{2}\ 0\ \frac{1}{2})$ a3 $(0\ \frac{1}{2}\ \frac{1}{2})$	$\frac{4\pi}{a}$	b1 $(\frac{1}{2}\ \frac{1}{2}\ -\frac{1}{2})$ b3 $(-\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ b2 $(\frac{1}{2}\ -\frac{1}{2}\ \frac{1}{2})$	a^3	$a^3/4$	$4\left(\frac{2\pi}{a}\right)^3$
bcc	a	a1 $(\frac{1}{2}\ \frac{1}{2}\ -\frac{1}{2})$ a2 $(-\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ a3 $(\frac{1}{2}\ -\frac{1}{2}\ \frac{1}{2})$	$\frac{4\pi}{a}$	b1 $(\frac{1}{2}\ \frac{1}{2}\ 0)$ b3 $(\frac{1}{2}\ 0\ \frac{1}{2})$ b2 $(0\ \frac{1}{2}\ \frac{1}{2})$	a^3	$a^3/2$	$2\left(\frac{2\pi}{a}\right)^3$
Hex (simple and hcp)	a, c	$(\frac{1}{2}\ \frac{\sqrt{3}}{2}\ 0)$ $(-\frac{1}{2}\ \frac{\sqrt{3}}{2}\ 0)$ $(0\ 0\ 1)$	$\frac{4\pi}{\sqrt{3}a}, \frac{2\pi}{c}$	$(\frac{\sqrt{3}}{2}\ \frac{1}{2}\ 0)$ $(\frac{\sqrt{3}}{2}\ -\frac{1}{2}\ 0)$ $(0\ 0\ 1)$	$\frac{\sqrt{3}}{2}a^2 c$		$\frac{(2\pi)^3}{\frac{\sqrt{3}}{2}a^2 c}$

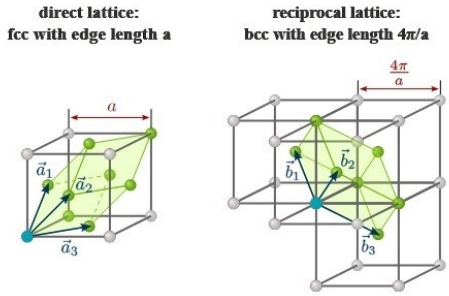
note that b2 and b3 are switched in the table for both fcc and bcc

should be $(-\frac{\sqrt{3}}{2}, \frac{1}{2}, 0)$

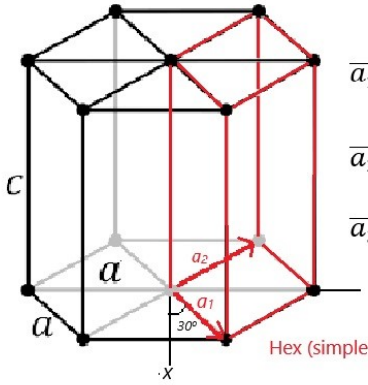
$(V_P)_{rec} = (2\pi)^3 / (V_P)_{dir}$

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$
$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_2 \cdot \vec{a}_3 \times \vec{a}_1}$$
$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_3 \cdot \vec{a}_1 \times \vec{a}_2}$$





$$\vec{b_1} = \frac{4\pi}{a}\left(\frac{\hat{\imath}}{2} + \frac{\hat{\jmath}}{2} - \frac{\hat{k}}{2}\right)$$
$$\vec{b_2} = \frac{4\pi}{a}\left(-\frac{\hat{\imath}}{2} + \frac{\hat{\jmath}}{2} + \frac{\hat{k}}{2}\right)$$
$$\vec{b_3} = \frac{4\pi}{a}\left(\frac{\hat{\imath}}{2} - \frac{\hat{\jmath}}{2} + \frac{\hat{k}}{2}\right)$$



$$\vec{a_1} = \frac{\sqrt{3}}{2}\,a\,\hat{\imath} + \frac{1}{2}\,a\,\hat{\jmath}$$
$$\vec{a_2} = -\frac{\sqrt{3}}{2}\,a\,\hat{\imath} + \frac{1}{2}\,a\,\hat{\jmath}$$
$$\vec{a_3} = c\,\hat{k}$$

$$\vec{b_1} = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}\,\hat{\imath} + \hat{\jmath}\right) = \frac{4\pi}{\sqrt{3}a}\left(\frac{1}{2}\,\hat{\imath} + \frac{\sqrt{3}}{2}\,\hat{\jmath}\right)$$
$$\vec{b_2} = \frac{2\pi}{a}\left(-\frac{1}{\sqrt{3}}\,\hat{\imath} + \hat{\jmath}\right) = \frac{4\pi}{\sqrt{3}a}\left(-\frac{1}{2}\,\hat{\imath} + \frac{\sqrt{3}}{2}\,\hat{\jmath}\right)$$
$$\vec{b_3} = \frac{\pi}{a}\sqrt{\frac{3}{2}}\,\hat{k} = \frac{2\pi}{c}\,\hat{k}\text{, where } \frac{c}{a} = \sqrt{8/3}$$

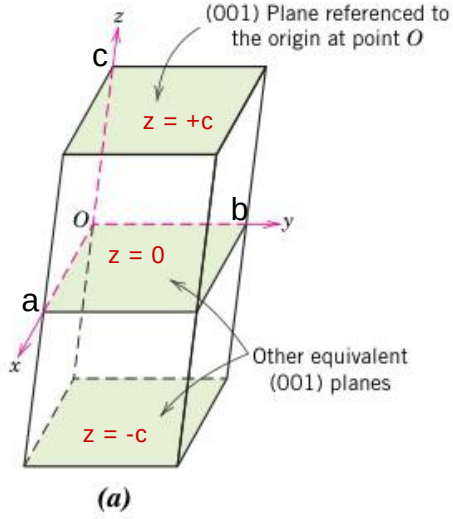
Hex (simple and hcp)

primitive vectors for hcp are the same as primitive vectors for simple hexagonal

3.2.6 CRYSTALLOGRAPHIC PLANES (Miller indices as (hkl))

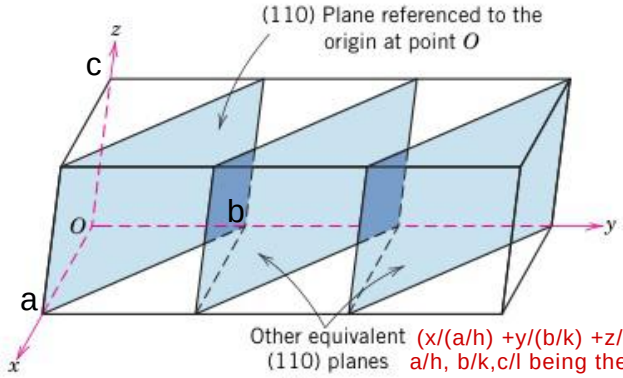
The orientations of planes for a crystal structure are represented in a similar manner. Any two planes parallel to each other are equivalent and have identical indices. The procedure used to determine the h, k, and l index numbers is as follows:

1. If the plane passes through the selected origin, either another parallel plane must be constructed within the unit cell by an appropriate translation, or a new origin must be established at the corner of another unit cell.



(a)

equation of a plane is hx+ky+lz=d. if a plane passes through origin, then d=0, and hence hx+ky+lz=0, where (h,k,l) are Miller indices that represent the vector normal to plane. The last equation can be written as N.r = 0, with N=(h,k,l) and r=(x,y,z)



(b)

if primitive lattice vectors (a,b,c) are known, then the equation of a plane takes the form below

(x/(a/h) +y/(b/k) +z/(c/l) = 1, with a/h, b/k,c/l being the intercepts with the three axes). for the (110) plane, we get x/a + y/b = 1 (or bx+ay=ab). for a cube a=b=c , then x+y=a

2. The plane either intersects or parallels each of the three axes. The coordinate for the intersection of the plane with each of the axes is determined (referenced to the origin of the coordinate system). If a plane does not intersect an axis, we take the intersection at infinity. (∞)

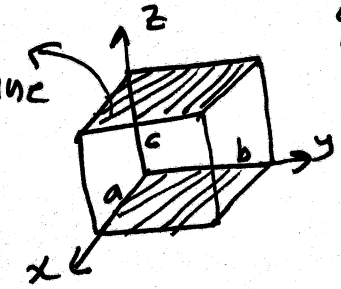
3. The reciprocals of these numbers are taken, and if necessary , these numbers are multiplied or divided by the smallest integer to normalize them in terms of their respective a, b, and c lattice parameters

4. Finally, the integer indices, not separated by commas, are enclosed within parentheses, thus: (hkl).

An intercept on the negative side of the origin is indicated by a bar or minus sign positioned over the appropriate index.

Example 1:

Top plane

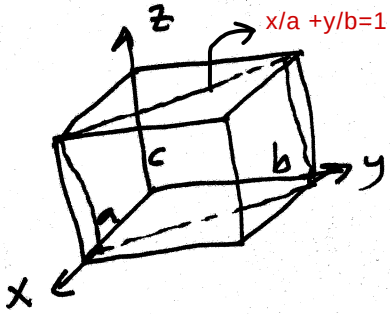


The two planes z=0 and z=c are equivalent and have the same Miller indices

intersections	x	y	z
	∞	∞	c
reciprocal	$\frac{1}{\infty}$	$\frac{1}{\infty}$	$\frac{1}{c}$
	0	0	$\frac{1}{c}$
normalize	a x 0	b x 0	c x $\frac{1}{c}$
	0	0	1

(hkl) = (0 0 1)

Example 2!



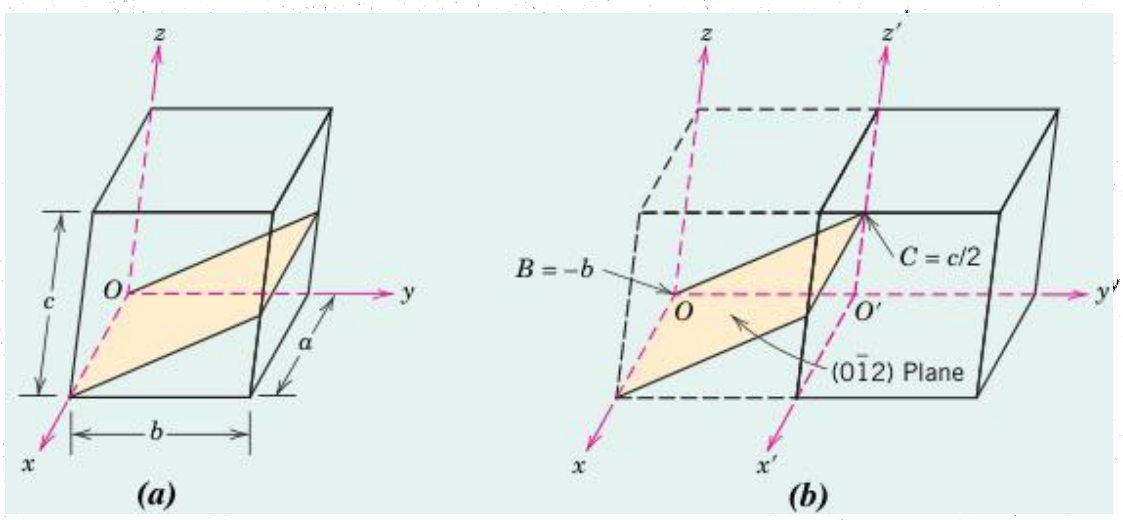
	x	y	z
	a	b	∞
	$\frac{1}{a}$	$\frac{1}{b}$	$\frac{1}{\infty}$
	a x $\frac{1}{a}$	b x $\frac{1}{b}$	c x $\frac{1}{\infty}$
	1	1	0

(hkl) = ($\frac{1}{h}$ $\frac{1}{k}$ 0)

A "family" of planes contains all planes that are crystallographically equivalentthat is, having the same atomic packing; a family is designated by indices enclosed in braces. For example, in cubic crystals, the (111), $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}\bar{1}1)$, $(11\bar{1})$, $(1\bar{1}\bar{1})$, $(\bar{1}1\bar{1})$, $(\bar{1}\bar{1}1)$, -- all belong to the {111} family

EXAMPLE

Determine the Miller indices for the plane shown in the accompanying sketch (a).



Because the plane passes through the selected origin O, a new origin must be chosen at the corner of an adjacent unit cell. In choosing this new unit cell, we move one unit-cell distance parallel to the y-axis, as shown in sketch (b)

intersections x' y' z'

∞ $-b$ $\frac{c}{2}$

reciprocal $\frac{1}{\infty}$ $\frac{1}{-b}$ $\frac{2}{c}$

normalize $a \times \frac{1}{\infty}$ $b \times \frac{1}{-b}$ $c \times \frac{2}{c}$

0 -1 2

$(0\ -1\ 2)$

$(0\ \bar{1}\ 2)$

h k l

the equation of the plane is
(x/(a/h) +y/(b/k) +z/(c/l) = 1 or
(h/a) x +(k/b) y +(l/c) z =1,
with (h,k,l)=(0,-1,2). Hence we get

-y/b +2z/c =1

Table 3.1 in textbook records the reciprocal lattices of SC, bcc, fcc, and hexagonal. As shown in the table the reciprocal lattice of a bcc lattice of spacing a is an fcc lattice of spacing $4\pi/a$. The reciprocal lattice of an fcc lattice of spacing a is a bcc lattice of spacing $4\pi/a$.

- scattering from a lattice with a basis

we found that the intensity of the scattered radiation from an identical monoatomic lattice is given by

$$I = |f(\vec{r})|^2 \left| \sum_l e^{i\vec{q}\cdot\vec{R}_l} \right|^2$$

(lattice with a basis)

Now for non Bravais lattice (lattice with a basis) the vector $\vec{R}_l$ is modified as

$\vec{R}_l \to \vec{R}_l + \vec{v}_{l'}$, where $\vec{R}_l$: specify the position of the unit cell in the lattice

l: sum over all unit cells

l': " " " atoms in unit cell

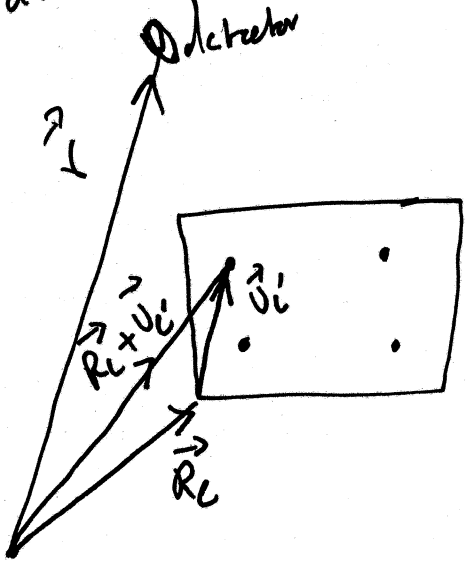
$\vec{v}_{l'}$: specify the position of the atoms inside the unit cell

$$\sum_{\text{all atoms}} \to \sum_{R_l} \sum_{v_{l'}}$$

$$\to \sum_{l} \sum_{l'}$$

l: over unit cells

l': sum over the basis in unit cell



so $\sum_q = \sum_l e^{i\vec{q}\cdot\vec{R}_l} \rightarrow \sum_{l,l'} e^{i\vec{q}\cdot(\vec{R}_l+\vec{U}_{l'})}$

$$= \left(\sum_l e^{i\vec{q}\cdot\vec{R}_l}\right)\left(\sum_{l'} f_{l'} e^{i\vec{q}\cdot\vec{U}_{l'}}\right)$$

$\sum_l e^{i\vec{q}\cdot\vec{R}_l}$ ← geometrical lattice sum (sum over reciprocal lattice vectors)

$\sum_{l'} f_{l'} e^{i\vec{q}\cdot\vec{U}_{l'}}$ → sum over all basis in unit cell called structure factor of the basis $S(\vec{q})$

so $I \propto \left|\sum_q\right|^2 \propto \left|\sum_l e^{i\vec{q}\cdot\vec{R}_l}\right|^2 \left|\sum_{l'} f_{l'} e^{i\vec{q}\cdot\vec{U}_{l'}}\right|^2$

$\therefore S(\vec{q}) = \sum_{l'} f_{l'} e^{i\vec{q}\cdot\vec{U}_{l'}}$, $F_q = |S(q)|^2$ modulation factor

Note that $I \neq 0$ only when $\left|\sum_l e^{i\vec{q}\cdot\vec{R}_l}\right|^2 \neq 0$

and $\left|\sum_{l'} f_{l'} e^{i\vec{q}\cdot\vec{U}_{l'}}\right|^2 \neq 0$

the first sum (geometrical terms) does not vanish only for those q values that satisfy the condition $\vec{q}\cdot\vec{R}_l = 2\pi l$; l : integer

or $\vec{K}\cdot\vec{R}_l = 2\pi l$, meaning q has to be a reciprocal lattice vector

so the first sum determines the position of Bragg peaks and the second sum modulates the intensity of these peaks.

$$\therefore S(\vec{q}) = S(\vec{H}) = \sum_{i'} f_{i'} e^{i \vec{H} \cdot \vec{U}_{i'}}$$

but $\vec{H} = l_1 \vec{b_1} + l_2 \vec{b_2} + l_3 \vec{b_3}$ and $\vec{U_{i'}} = x_{i'} \vec{a_1} + y_{i'} \vec{a_2} + z_{i'} \vec{a_3}$

$$\Rightarrow \vec{H} \cdot \vec{U_{i'}} = 2\pi l_1 x_{i'} + 2\pi l_2 y_{i'} + 2\pi l_3 z_{i'} \text{ ; where } \vec{b_i} \vec{a_j} = 2\pi \delta_{ij}$$

$$= 2\pi (l_1 x_{i'} + l_2 y_{i'} + l_3 z_{i'})$$

$$\Rightarrow S(\vec{q}) = \sum_{i'} f_{i'} e^{2\pi i (l_1 x_{i'} + l_2 y_{i'} + l_3 z_{i'})}$$

when i' run over the basis in the unit cell.
note that $(x_{i'}, y_{i'}, z_{i'})$ are non cartesian coordinates, they refer to multiples of the primitive vectors

Examples:

① SC lattice: got one basis at $(0,0,0)$ $i'=1$

$\Rightarrow S(q) = f_1$; all reflections are allowed

so interms of miller indices (hkl) or $(l_1 l_2 l_3)$ in Marder

we have for the allowed reflections

$(100), (110), (111), (200), (210), (211), (220), (221),$

$(300), (310), (311), (320), (321), (322), (330), (331)$

$(332),$,---------

{hkl} families ← Note that (100), (010), (001) are equivalent
- and (111), (222), (333), are equivalent too
- (210), (201), (021) are also equivalent

② **bcc** : SC lattice with 2 basis $(0,0,0)$, $(1/2,1/2,1/2)$

$$S(q) = \sum_{i'=1}^{2} f_{i'}\, e^{2\pi i (l_1 x_{i'} + l_2 y_{i'} + l_3 z_{i'})}$$

$$= f_1 + f_2\, e^{+i\pi(l_1+l_2+l_3)} \quad ; \text{ but } f_1 = f_2 \text{ same type of atoms}$$

$$= f\left[1 + e^{i\pi(l_1+l_2+l_3)}\right]$$

$$= \begin{cases} 0 \; ; \text{ if } l_1+l_2+l_3 = \text{odd} \; ; \text{ No diffraction occurs} \\ 2f \; ; \text{ if } l_1+l_2+l_3 = \text{even} \end{cases}$$

(called extinction)

some important relations: $e^{ix} = \cos x + i\sin x$; $e^{-ix} = \cos x - i\sin x$

$\Rightarrow e^{ix} + e^{-ix} = 2\cos x$; $e^{n\pi i} = (-1)^n$

Typical allowed reflections (110), (200), (211), (220), (310), (222), (321), (400), (411), (330), … smaller sum comes first in l1+l2+l3=even

note that (400) and (200) are not equivalent

③ **fcc** : SC lattice with 4 basis located at $(0,0,0)$, $(1/2,1/2,0)$, $(1/2,0,1/2)$, $(0,1/2,1/2)$; $f_1 = f_2 = f_3 = f_4 \equiv f$

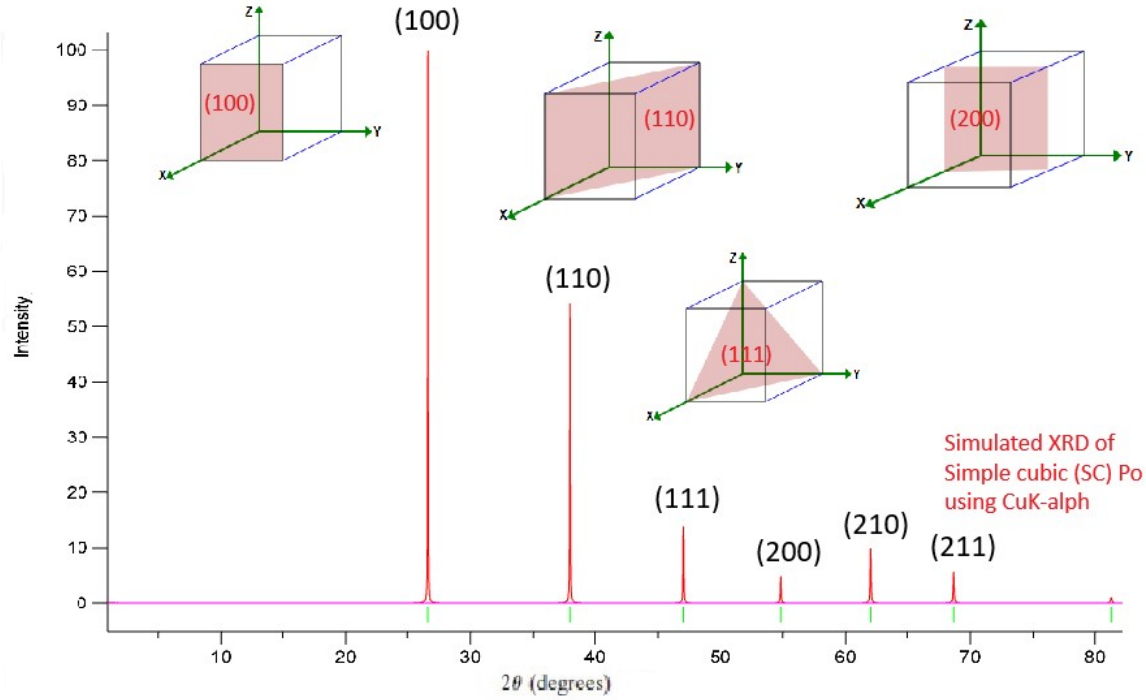
$$S(q) = \sum_{i'=1}^{4} f_{i'}\, e^{2\pi i (l_1 x_{i'} + l_2 y_{i'} + l_3 z_{i'})}$$

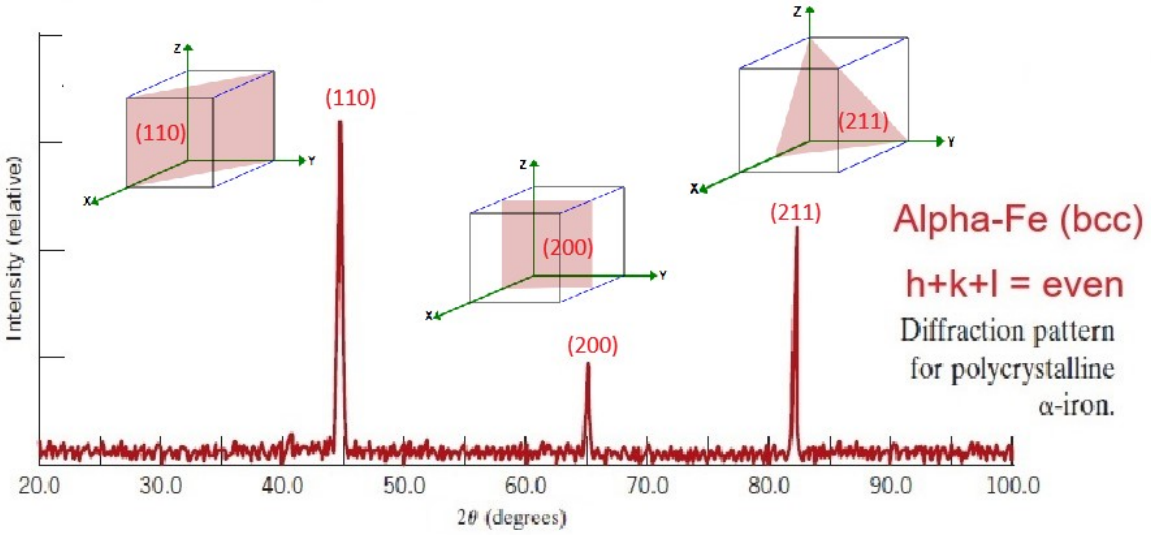
$$= f\left[1 + e^{i\pi(l_2+l_3)} + e^{i\pi(l_1+l_3)} + e^{i\pi(l_1+l_2)}\right]$$

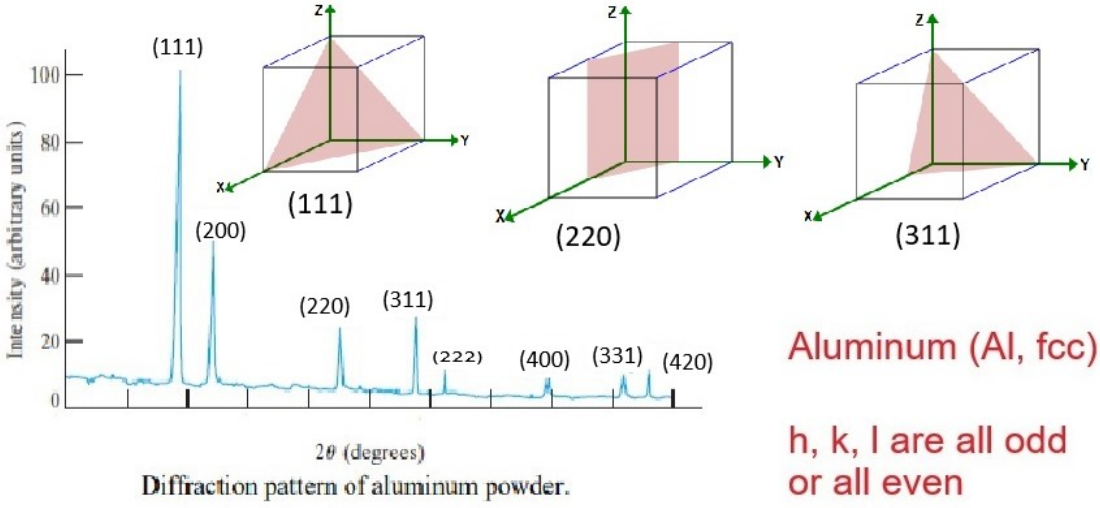
$$= \begin{cases} 0 \; ; \text{ for mixed indices odd and even} \rightarrow \text{such as } (1,1,2) \\ 4f \; ; \text{ unmixed } \leftarrow \text{(all even or all odd!)} \; ; \; (111), (220) \end{cases}$$

zero is even

allowed reflections : (111), (200), (220), (311), (222), (400), (331), (333), ----

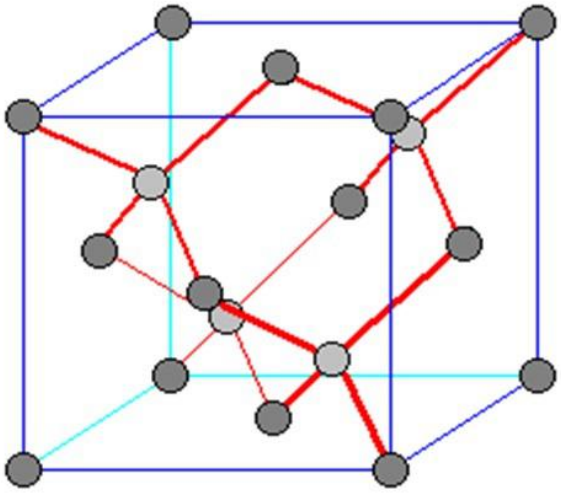

(100)
(110)
(111)
(200)
(210)
(211)
Intensity
2θ (degrees)
Simulated XRD of
Simple cubic (SC) Po
using CuK-alph


(110)
(200)
(211)
Intensity (relative)
2θ (degrees)
Alpha-Fe (bcc)
h+k+l = even
Diffraction pattern
for polycrystalline
α-iron.


(111)
(200)
(220)
(311)
(222)
(400)
(331)
(420)
Intensity (arbitrary units)
2θ (degrees)
Diffraction pattern of aluminum powder.
Aluminum (Al, fcc)
h, k, l are all odd
or all even

(4) Diamond Lattice: There are two ways to calculate the structure factor. The first is to consider Diamond lattice as a simple cube with 8 basis (8 atoms / primitive cell). So the sum in this case goes over all 8 atoms. The proof is lengthy.

The second way is to consider Diamond as an fcc lattice with two basis located at $(0,0,0)$ and $(1/4, 1/4, 1/4)$. $\Rightarrow$



Diamond lattice

$$S(q) = \sum_{i'=1}^{2} f_{i'} e^{2\pi i (l_1 x_{i'} + l_2 y_{i'} + l_3 z_{i'})}$$

$$= f_1 + f_2 e^{2\pi i \left(\frac{l_1}{4} + \frac{l_2}{4} + \frac{l_3}{4}\right)}$$

but $f_1 = f_2$ (same type of atoms)

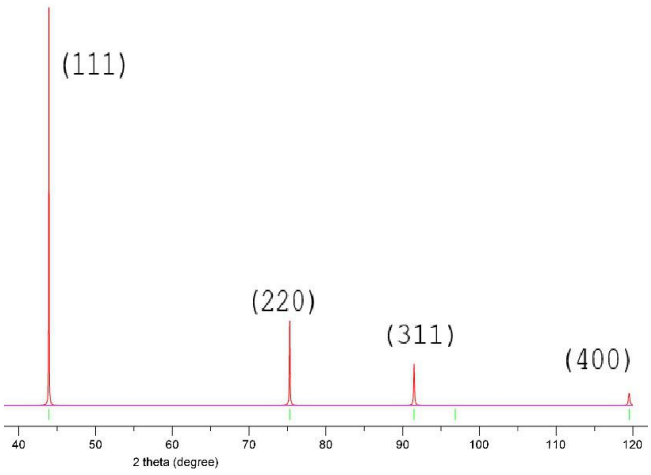
$$= f\left[1 + e^{i\frac{\pi}{2}(l_1 + l_2 + l_3)}\right]$$

using $e^{i\pi/2} = i$, $e^{i\frac{3\pi}{2}} = -i$,

$e^{(\text{odd})\, i\pi} = -1$, $e^{(\text{even})\, i\pi} = +1$

$$= \begin{cases} 0, & \text{if } l_1 + l_2 + l_3 = 2, 6, 10, 14, \cdots \\ 2f, & \text{if } l_1 + l_2 + l_3 = 4, 8, 12, 16, \cdots \\ f[1+i]; & \text{if } l_1 + l_2 + l_3 = 1, 5, 9, \cdots \\ f[1-i]; & \text{if } l_1 + l_2 + l_3 = 3, 7, 11, \cdots \end{cases}$$

simulated XRD of Diamond



Now the modulation factor F_K reads

$$F_K = |S(q)|^2 = \begin{cases} 0, & l_1+l_2+l_3 = 2,6,10,14,\ldots \text{ even and not multiple of 4 (extinctions)} \\ 4f^2, & l_1+l_2+l_3 = 4,8,12,16,\ldots \text{ even and multiple of 4} \\ 2f^2, & l_1+l_2+l_3 = \text{odd} \end{cases}$$

See that peaks such as (200) and (222) that appear in fcc with 4 atoms/primitive cell disappear here in diamond with 8 atoms/primitive cell. This is called extinction.

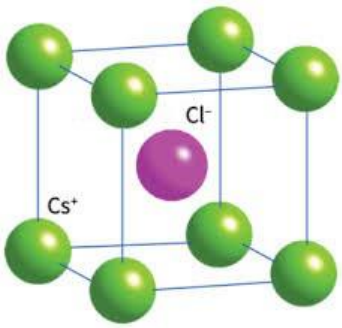
(5) CsCl lattice: simple cube with two basis

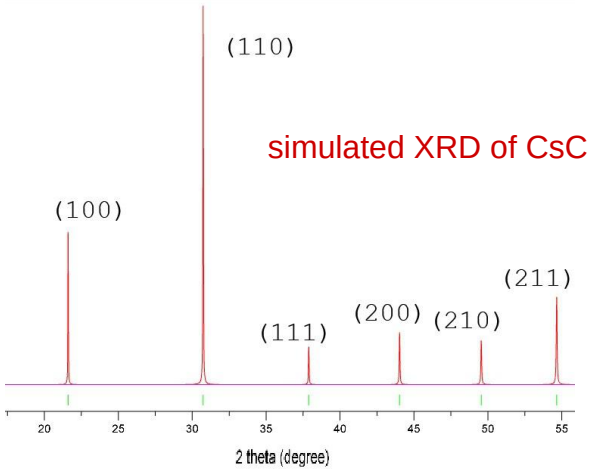
Cs(0,0,0) and Cl(1/2,1/2,1/2).

$$S(q) = f_{Cs} + f_{Cl}\, e^{2\pi i\left(\frac{l_1}{2}+\frac{l_2}{2}+\frac{l_3}{2}\right)}$$

$$= f_{Cs} + f_{Cl}\, e^{\pi i(l_1+l_2+l_3)}$$

$$= \begin{cases} f_{Cs}+f_{Cl}; & l_1+l_2+l_3 = \text{even} \\ f_{Cs}-f_{Cl}; & l_1+l_2+l_3 = \text{odd} \end{cases}$$





simulated XRD of CsCl

(6) NaCl lattice

See problem 6 in HW #3

Experimental Methods:

XRD is widely used to determine crystal structure of solids, using Bragg law $2d\sin\theta = n\lambda$. i.e diffraction occurs for those values of λ, θ, d which satisfy the Bragg's law. There are 3 experimental methods to determine crystal structure of solids using XRD:

(1) **Laue method:** widely used to determine symmetry of a single crystals.

here a continuous spectrum of x-ray wavelengths is incident on a crystal while holding θ fixed. So some particular wavelengths are reflected by appropriate planes satisfying Bragg condition, and hence producing Bragg peaks. in principle, a flat photographic films are placed around the crystal. the diffracted beams generate a pattern of spots on the film that reflects the symmetry of the reciprocal lattice and hence the direct lattice.

- Ewald construction is a good technique to understand and analyze patterns obtained by Laue methods

procedure:

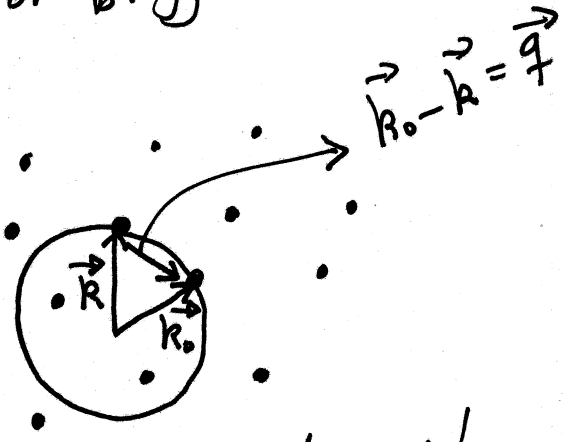
i) draw the vector $\vec{k_0}$ so that it ends on a reciprocal lattice point

ii) draw a sphere of radius k_0

iii) if the sphere touches other reciprocal lattice points, then it gives the direction of $\vec{K}$

that the condition $\Delta\vec{k} = \vec{k_0} - \vec{k} = \vec{q} = \vec{H}$ is satisfied.
(iii) if there are no points on the sphere, then the Laue condition is not satisfied for that particular $k_0 = \frac{2\pi}{\lambda}$; i.e so this specific λ, there is no θ that satisfies the Laue condition (or Bragg condition)

so there has to be at least two lattice points on the spherical surface to satisfy Laue condition



2D rep of Ewald construction

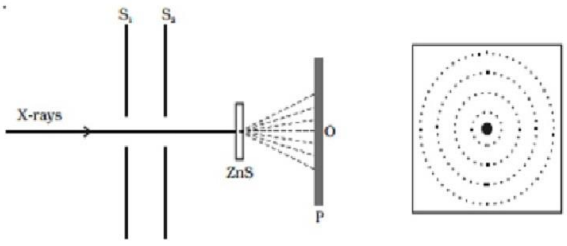
(2) Rotating crystal method

here single wavelength is incident on a crystal. The Bragg condition is unlikely to be satisfied. now by rotating the crystal, then we can scan over θ (i.e scan over different sets of planes) and then some planes will satisfy the diffraction condition. this method is also used to study and analyze single crystals. Again here, the diffracted beams are recorded on a cylindrical photograph films that map the reciprocal lattice of the crystal.

Laue Method and Rotating Crystal Method map reflections in reciprocal space

Laue method

source: X-ray with distribution of wavelengths



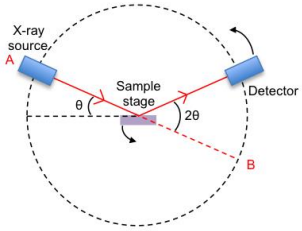
(a) Laue experimental set up *(b) Laue spot*

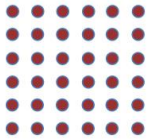
X–rays from the X–ray tube is collimated into a fine beam by two slits S1 and S2. The beam is now allowed to pass through a zinc sulphide (ZnS) crystal. The emergent rays are made to fall on a photographic plate P. The diffraction patten so obtained consists of a central spot at O and a series of spots arranged in a definite pattern about O as shown in figure. The central spot is due to the direct beam, whereas the regularly arranged spots are due to the diffraction pattern from the atoms of the various crystal planes. These spots are known as Laue spots.

This method is used to identify crystal symmetry and not used in general to determine crystal structure

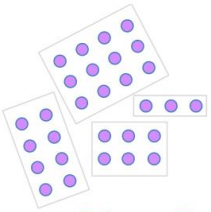
Powder method maps reflections in direct space

wavelength is fixed (monochromatic), sample is rotating (angle is changing)

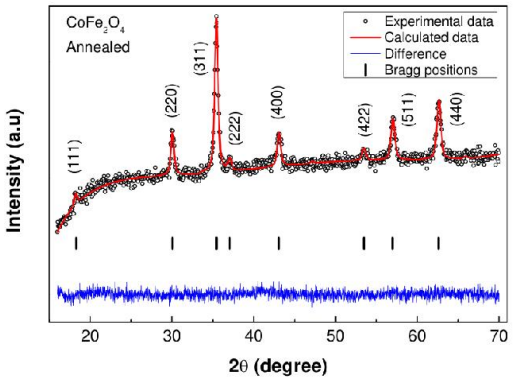




Single crystal



Polycrystalline

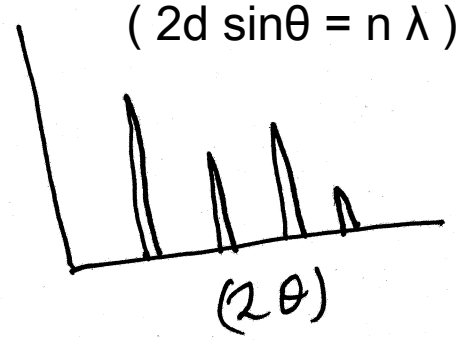


d-spacing and lattice constant are determined by Bragg's law that will be discussed next ($2d \sin\theta = n \lambda$)

③ Powder method: widely used for polycrystalline materials.

λ is fixed (monochromatic x-ray), θ is changing

The powder consists of small crystallites with different orientations. once sample is rotated, some planes in these crystallites will satisfy Bragg condition and hence produce a peak in the XRD spectrum. by continue rotating the sample, other planes may satisfy Bragg condition and hence produce a second peak and so on.



There are mainly 3 types of probes to study solid materials

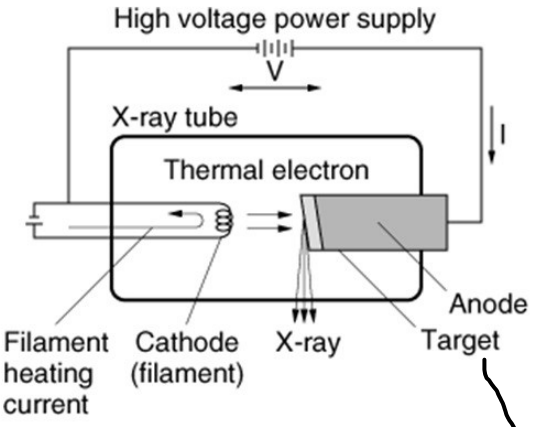
① x-ray (Electromagnetic waves) scattered by atomic electrons. used to study structure of materials

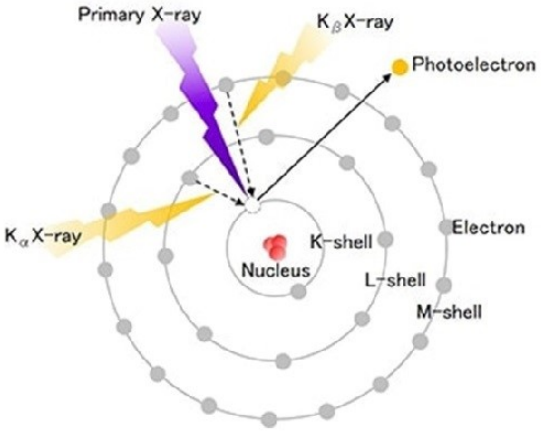
② Neutrons: They have magnetic moments. can interact with other magnetic particles (electrons and nuclei). Therfore They are used to study magnetic properties of materials.

③ Electrons: charged particles. can't penetrate deep into solid. they are used to study surfaces, films, therefore used in SEMs for collecting surface images of materials. ——

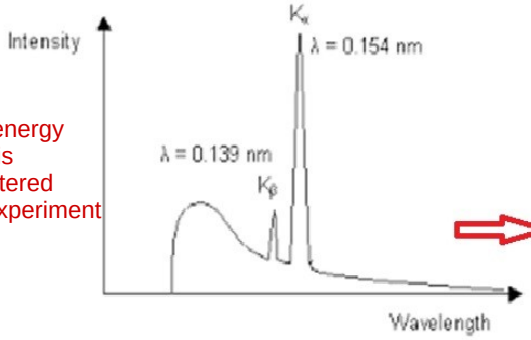
Production of X-rays

X-rays are generated when matter is irradiated by a beam of high-energy charged particles such as electrons. In the laboratory, a filament is heated to produce electrons which are then accelerated in vacuum by a high electric voltage in the range 20-60 kV towards a metal target, which being positive is called the anode. The process is extremely inefficient with 99% of the energy of the beam being dissipated as heat in the target. A typical X-ray spectrum from a copper target is shown below. In general, Kα is observed as a doublet peak (not shown in the figure) in the XRD pattern and Kβ is fileted out by a metal foil during the measurement.





The incident electron collides with another electron in the K-shell. The latter is ejected as a photoelectron, resulting in a vacancy in the K-shell. An electron from a higher shell fills the vacancy. The difference in energy is released as an x-ray photon.



The low energy line K_B is usually filtered in XRD experiment

Wavelengths of typical X-ray anode materials

Anode materials	K_α (Average)	$K_{\alpha 1}$	$K_{\alpha 2}$	K_β
Cr	2.291	2.2897	2.29361	2.08487
Fe	1.93736	1.93604	1.93998	1.75661
Co	1.79026	1.78897	1.79285	1.62079
Cu	1.54184	1.54056	1.54439	1.39222
Mo	0.71073	0.7093	0.71359	0.63229
Ag	0.56088	0.55942	0.56381	0.49708

Copper K-alpha radiation is intense, monochromatic and is of the order of the lattice spacing found in crystalline solids and it is usually used in most XRD experiments

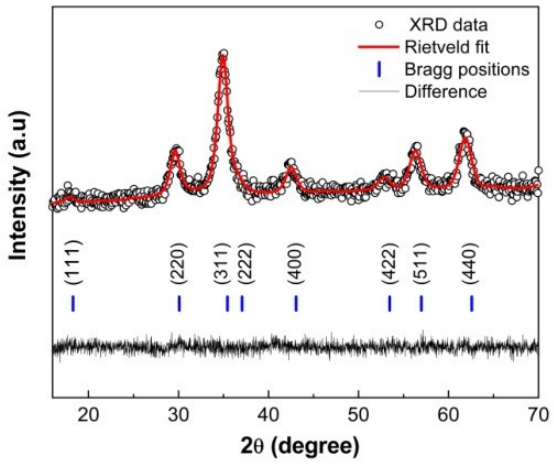
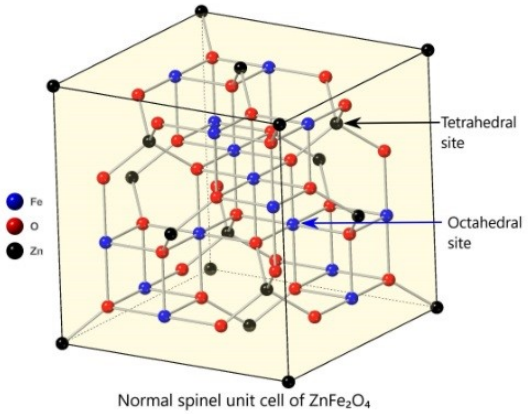


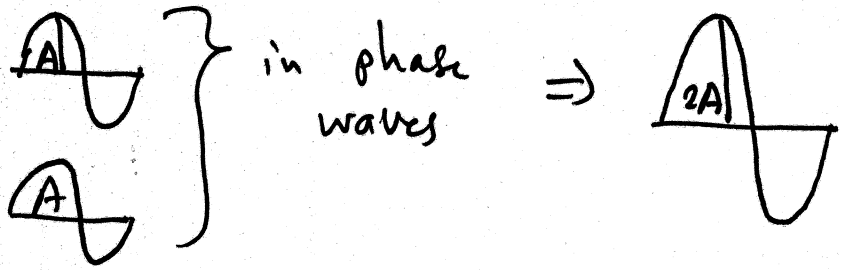
Figure 1: XRD data and Rietveld-refined fit of the as prepared $ZnFe_2O_4$ ferrite NPs.



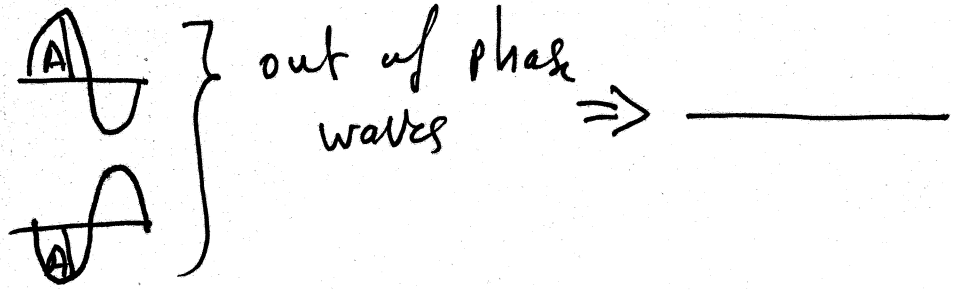
d-spacing and lattice constant are determined by Bragg's law that will be discussed next

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

when two waves meet at some point in space they interfere constructively or distructively



in phase waves ⇒ constructive interference (Instructive)

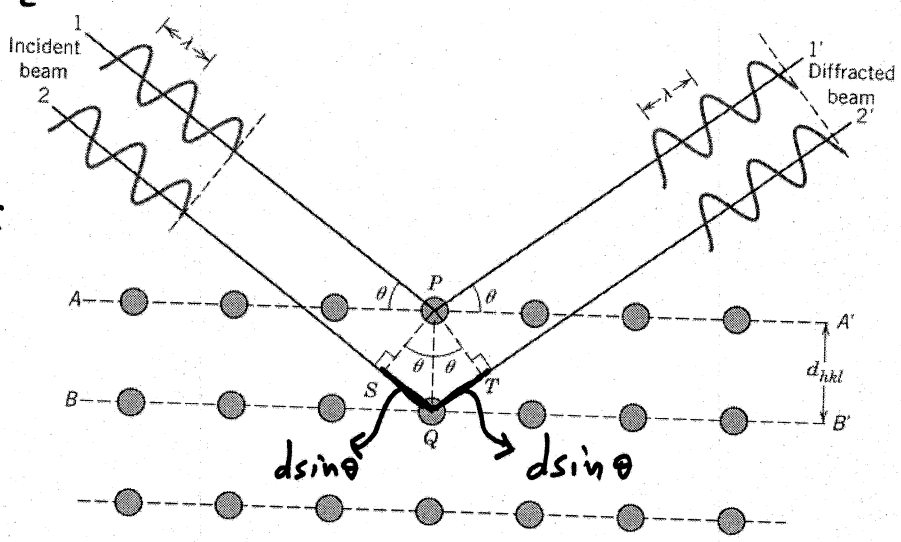


out of phase waves ⇒ ——— distructive interference

X-Ray Diffraction and Bragg's Law

Consider the two parallel planes of atoms which have the same h, k, and l Miller indices and are separated by the interplanar spacing d_{hkl} as shown in figure. Now assume that a parallel, monochromatic, and coherent (in-phase) beam of x-rays of wavelength λ is incident on these two planes at an angle θ. Two rays in this beam, labeled 1 and 2, are scattered by atoms P and Q.

Constructive interference between the scattered two rays occurs when the path difference (length) is



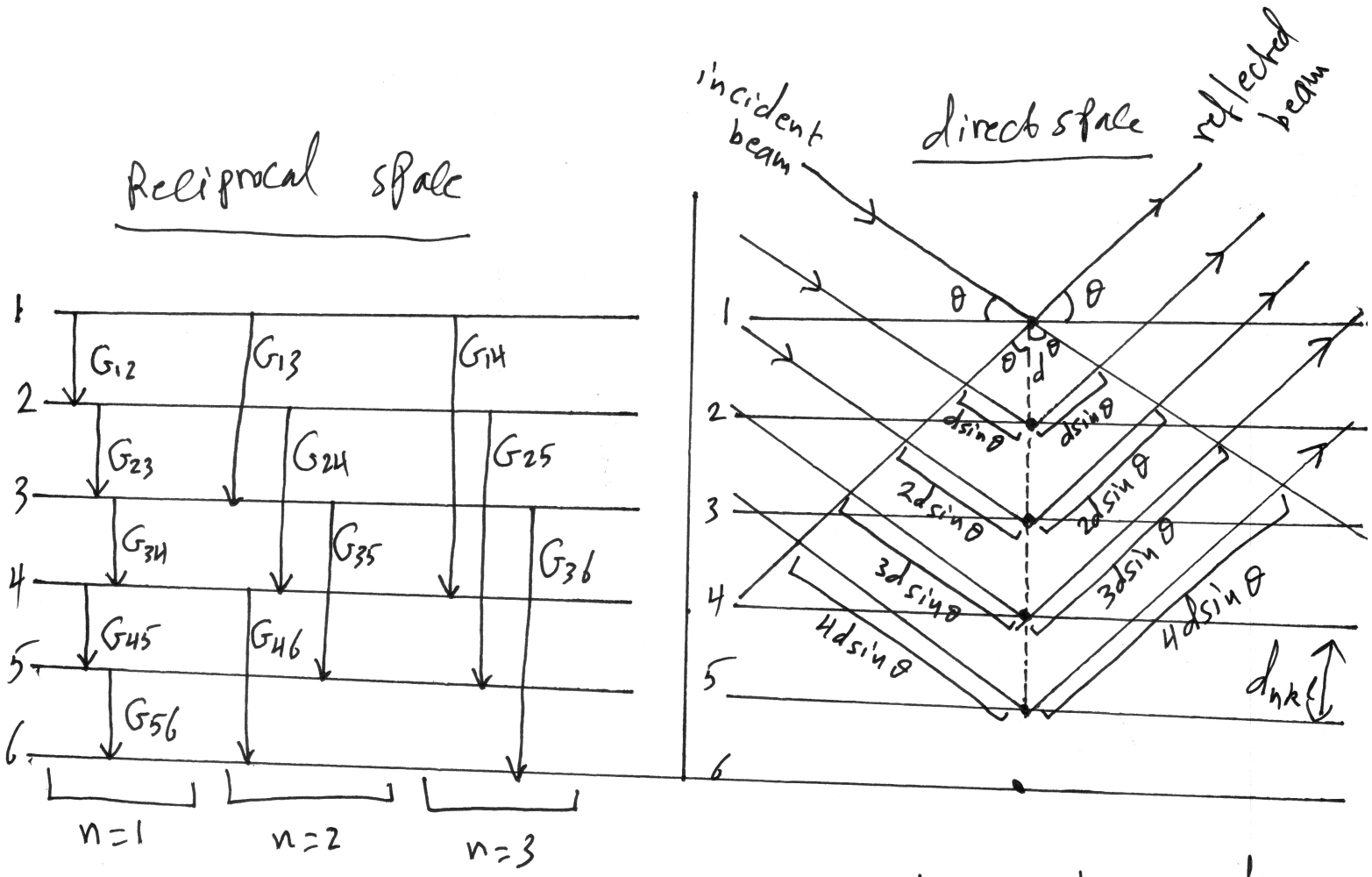
$$\overline{SQ} + \overline{QT} = n\lambda$$

$$d_{hkl}\sin\theta + d_{hkl}\sin\theta = n\lambda$$

$$\boxed{2d_{hkl}\sin\theta = n\lambda}$$ Bragg's law

n: order of reflection

if this condition is not satisfied, the interference will be distructive with a very low-intensity diffracted beam.



- 1st order diffraction ($n=1$): between any two adjacent planes such as 12, 23, 34, 45, 56

↓ for example $d\sin\theta + d\sin\theta = 1\lambda \Rightarrow 2d\sin\theta = 1\lambda$ (↓ $n=1$)

diffraction from these planes results in the shortest reciprocal lattice vector $|G_{12}| = |\vec{K}| = \frac{2\pi}{d_{hkl}}$

- 2nd order diffraction ($n=2$): between 13, 24, 35, 46

$\Rightarrow 2d\sin\theta + 2d\sin\theta = 4d\sin\theta = 2(2d\sin\theta) = 2\lambda \Rightarrow n=2$

$|G_{13}| = |K_{13}| = 2\frac{2\pi}{d_{hkl}} = 2|G_{12}|$

- 3rd order diffraction ($n=3$); between 14, 25, 36 gives

$3d\sin\theta + 3d\sin\theta = 6d\sin\theta = 3(2d\sin\theta) = 3\lambda \Rightarrow n=3$

and so on, $|G_{14}| = |K_{14}| = 3\frac{2\pi}{d_{hkl}} = 3|G_{12}|$

$\Rightarrow \vec{K}$ is an integral multiple of the shortest reciprocal lattice vector

EXAMPLE

d_{220} ↗ 2θ ↗

For BCC iron, compute (a) the interplanar spacing and (b) the diffraction angle for the (220) set of planes. The lattice parameter for Fe is 0.2866 nm. Assume that monochromatic radiation having a wavelength of 0.1790 nm is used, and the order of reflection is 1.

(a) $h=2,\ k=2,\ l=0 \Rightarrow d_{hkl} = \dfrac{a}{\sqrt{h^2+k^2+l^2}} = \dfrac{0.2866\ nm}{\sqrt{2^2+2^2+0^2}} = 0.1013 nm$ ↓ d_{220}

(b) $\sin\theta = \dfrac{n\lambda}{2d_{220}} = \dfrac{(1)(0.1790\ nm)}{(2)(0.1013\ nm)}$

$= 0.884 \Rightarrow \theta = \sin^{-1}(0.884) = 62.13^\circ$

$\Rightarrow$ Diffraction angle $= 2\theta = 124.26^\circ$

EXAMPLE

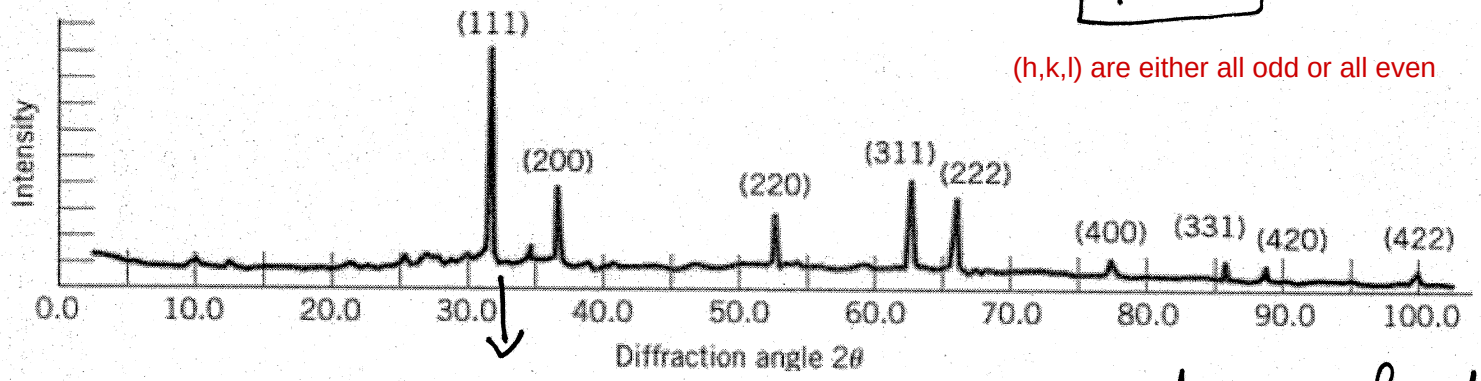
(Pb)

Figure 3.24 shows an x-ray diffraction pattern for lead taken using a diffractometer and monochromatic x-radiation having a wavelength of 0.1542 nm; each diffraction peak on the pattern has been indexed. Compute the interplanar spacing for each set of planes indexed; also, determine the lattice parameter of Pb for each of the peaks. For all peaks, assume the order of diffraction is 1.

$\lambda = 0.1542$ nm

FCC

(h,k,l) are either all odd or all even



$2\theta = 31.3^\circ$

$\Rightarrow d_{111} = \dfrac{n\lambda}{2\sin\theta} = \dfrac{(1)(0.1542\ nm)}{(2)\sin\left(\frac{31.3}{2}\right)} = 0.2858\ nm$

similar calculations for the next peaks leads to the following tabulated values of d_{hkl} and a

Peak Index	2θ	d_{hkl}(nm)	a(nm)
200	36.6	0.2455	0.4910
220	52.6	0.1740	0.4921
311	62.5	0.1486	0.4929
222	65.5	0.1425	0.4936

and

$a = d_{hkl}\sqrt{h^2+k^2+l^2}$

$= d_{111}\sqrt{1^2+1^2+1^2}$

$= (0.2858\ nm)\sqrt{3} = 0.4950\ nm$