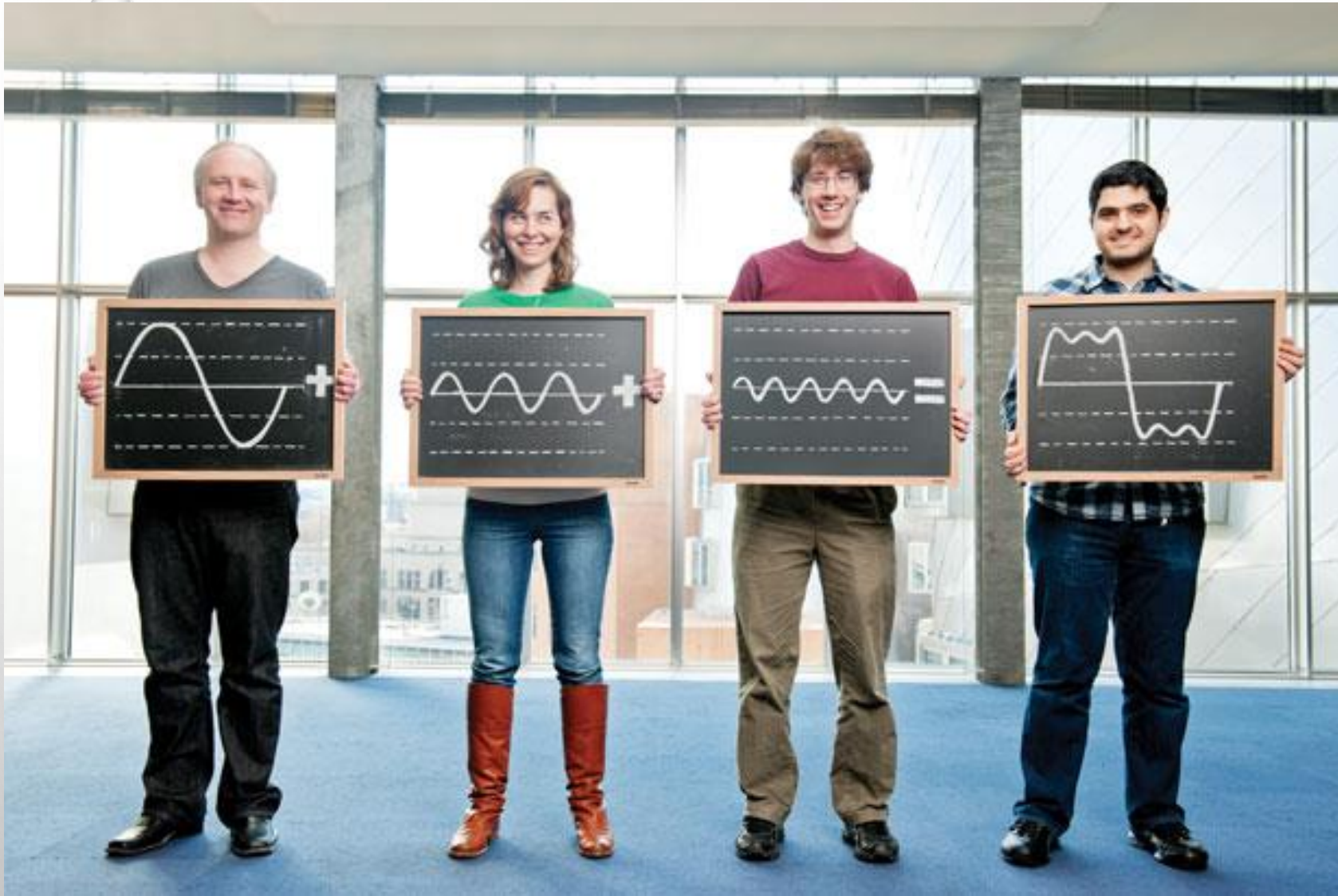


The background of the slide is a light gray gradient. It is decorated with several realistic water droplets of various sizes, some with highlights and shadows, scattered across the top and bottom edges. In the upper center, there is a faint, circular logo or watermark that appears to be a university crest or seal.

Periodic Structure and Reciprocal Lattice



Abeer Alshammari

<http://cns-alumni.bu.edu/~slehar/fourier/fourier.html>

Jean Baptiste Joseph Fourier (1768-1830)

Had crazy idea (1807):

Any periodic function can be rewritten as a weighted sum of **Sines** and **Cosines** of different frequencies.

Don't believe it?

Neither did Lagrange, Laplace, Poisson and other big wigs

Not translated into English until 1878!

But it's true!

called **Fourier Series**

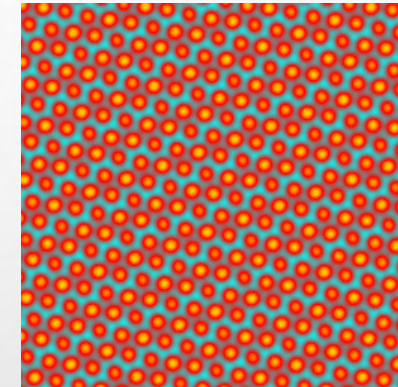
Possibly the greatest tool used in Engineering



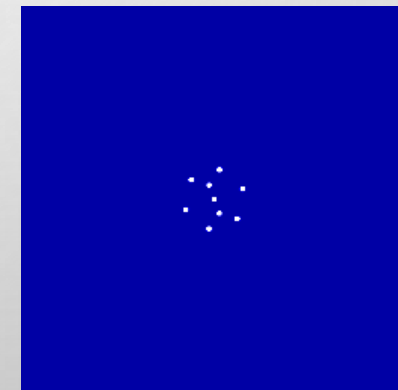
Fourier Transforms are used in

- X-ray diffraction
- Electron microscopy (and diffraction)
- NMR spectroscopy
- IR spectroscopy
- Fluorescence spectroscopy
- Image processing

This image for example looks ordered but I couldn't tell you exactly what that order is.



After taking a FT of the image it is very apparent what sort of order it has and one can determine all the distances between nearest neighbors just by taking the reciprocal of the distances between a dot and the center of the image.



Periodic Function

- any function that satisfies

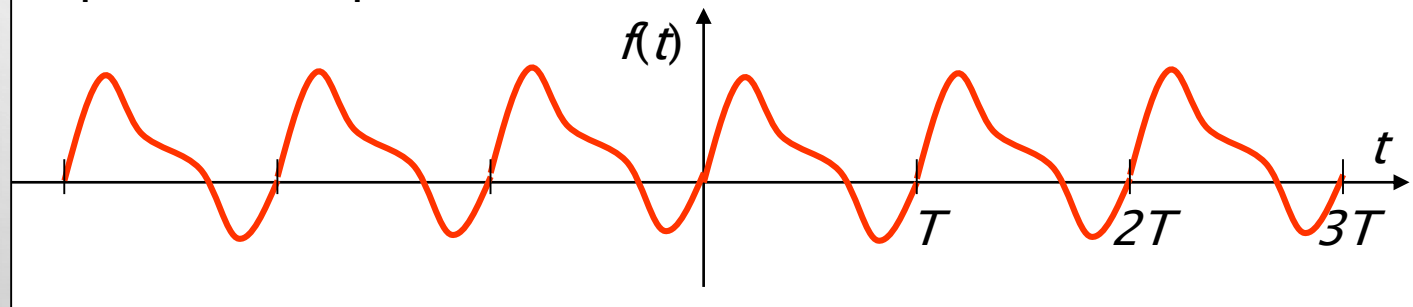
$$f(t) = f(t + T)$$

(1)

where T is a constant and is called the *period* of the function.

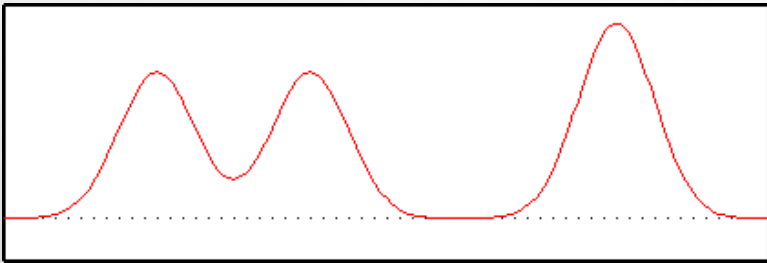
I'm calling the variable t here because I have to call it something, but the definition is general and is not meant to imply periodic functions of time.

A periodic sequence

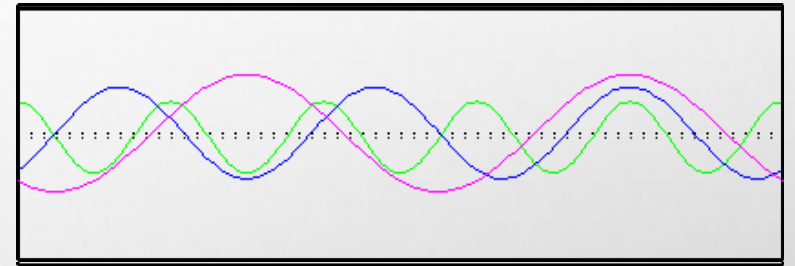


A periodic function can be described by a summation of waves with different amplitudes and phases.

So what does this mean exactly?



Can be represented by:



When you let these three waves interfere with each other you get your original wave function!

Any reasonable function can be expressed as a (infinite) linear combination of sines and cosines

$$f(t) = \underbrace{a_0}_{\text{DC Part}} + \underbrace{\sum_{n=1}^{\infty} a_n \cos \frac{2\pi n t}{T}}_{\text{Even Part}} + \underbrace{\sum_{n=1}^{\infty} b_n \sin \frac{2\pi n t}{T}}_{\text{Odd Part}} \quad (2)$$

T is a period of all the above signals

Let $\omega_0 = 2\pi/T$, the *fundamental frequency* (rad/sec) of the signal

$$f(t) = a_0 + \sum_{n=1}^{\infty} a_n \cos(n\omega_0 t) + \sum_{n=1}^{\infty} b_n \sin(n\omega_0 t) \quad (3)$$

n takes the values $(0,1,2,3,\dots)$

$$a_n = \frac{2}{T} \int_0^T f(t) \cos(n \omega_0 t) dt$$

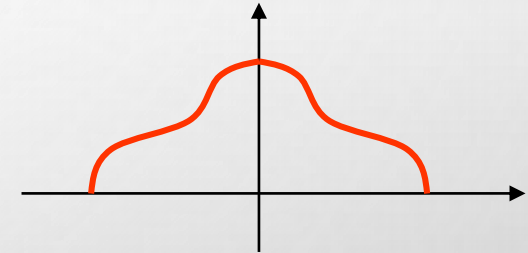
$$b_n = \frac{2}{T} \int_0^T f(t) \sin(n \omega_0 t) dt$$

$$a_0 = \frac{\int_0^T f(t) dt}{T}$$

where the constant coefficients a_n and b_n are called the Fourier coefficients of f

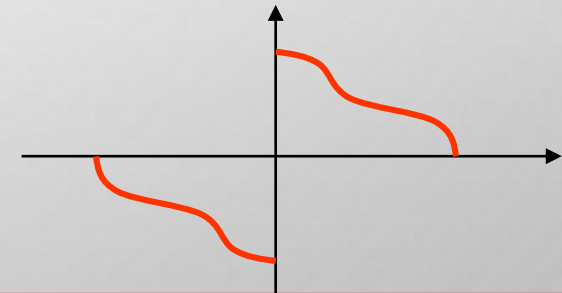
- even functions

$$f(t) = f(-t)$$



- odd functions

$$f(t) = -f(-t)$$



Dirichlet Conditions

- a periodic signal $f(t)$, has a Fourier series if it satisfies the following conditions:
 1. $f(t)$ is **absolutely integrable** over any period.
 2. $f(t)$ has only a **finite number of maxima and minima** over any period
 3. $f(t)$ has only a **finite number of discontinuities** over any period

Example: Find Fourier series of this function

$$f(x) = \begin{cases} 0, & -\pi \leq x < 0 \\ \pi, & 0 \leq x \leq \pi \end{cases}$$

We have

$$a_0 = \frac{1}{2\pi} \left(\int_{-\pi}^0 0 dx + \int_0^{\pi} \pi dx \right) = \frac{\pi}{2}, \quad a_n = \int_0^{\pi} \pi \cos(nx) dx = 0, \quad n \geq 1,$$

$$b_n = \int_0^{\pi} \pi \sin(nx) dx = \frac{1}{n} (1 - \cos(n\pi)) = \frac{1}{n} (1 - (-1)^n).$$

We obtain $b_{2n} = 0$ and $b_{2n+1} = \frac{2}{2n+1}.$

Therefore, the Fourier series of $f(x)$ is

$$f(x) \sim \frac{\pi}{2} + 2 \left(\sin(x) + \frac{\sin(3x)}{3} + \frac{\sin(5x)}{5} + \dots \right).$$

Let us then generalize the Fourier series to complex functions.

**Euler's
formula**

$$e^{i\omega t} = \cos \omega t + i \sin \omega t$$

$$e^{-i\omega t} = \cos \omega t - i \sin \omega t$$

$$\cos n\omega_0 t = \frac{1}{2} (e^{in\omega_0 t} + e^{-in\omega_0 t})$$

$$i = \sqrt{-1}$$

$$\sin n\omega_0 t = \frac{1}{2i} (e^{in\omega_0 t} - e^{-in\omega_0 t}) = -\frac{i}{2} (e^{in\omega_0 t} - e^{-in\omega_0 t})$$

Then equation (3) will be:

$$\begin{aligned} f(t) &= \frac{a_0}{2} + \frac{1}{2} \sum_{n=1}^{\infty} a_n (e^{in\omega_0 t} + e^{-in\omega_0 t}) - \frac{j}{2} \sum_{n=1}^{\infty} b_n (e^{in\omega_0 t} - e^{-in\omega_0 t}) \\ &= \frac{a_0}{2} + \sum_{n=1}^{\infty} \left[\frac{1}{2} (a_n - ib_n) e^{in\omega_0 t} + \frac{1}{2} (a_n + ib_n) e^{-in\omega_0 t} \right] \end{aligned}$$

$$\begin{aligned}
 f(t) &= c_0 + \sum_{n=1}^{\infty} \left[c_n e^{in\omega_0 t} + c_{-n} e^{-in\omega_0 t} \right] \\
 &= c_0 + \sum_{n=1}^{\infty} c_n e^{in\omega_0 t} + \sum_{n=-\infty}^{-1} c_n e^{in\omega_0 t} \\
 &= \sum_{n=-\infty}^{\infty} c_n e^{in\omega_0 t}
 \end{aligned}$$

$$\begin{aligned}
 c_0 &= \frac{a_0}{2} \\
 c_n &= \frac{1}{2}(a_n - ib_n) \\
 c_{-n} &= \frac{1}{2}(a_n + ib_n)
 \end{aligned}$$

$$c_0 = \frac{a_0}{2} = \frac{1}{T} \int_{-T/2}^{T/2} f(t) dt$$

$$c_n = \frac{1}{2}(a_n - ib_n)$$

$$= \frac{1}{T} \left[\int_{-T/2}^{T/2} f(t) \cos n\omega_0 t dt - i \int_{-T/2}^{T/2} f(t) \sin n\omega_0 t dt \right]$$

$$c_n = \frac{1}{T} \int_{-T/2}^{T/2} f(t)(\cos n\omega_0 t - i \sin n\omega_0 t) dt$$

$$= \frac{1}{T} \int_{-T/2}^{T/2} f(t) e^{-in\omega_0 t} dt$$

similarly

$$c_{-n} = \frac{1}{2}(a_n + ib_n) = \frac{1}{T} \int_{-T/2}^{T/2} f(t) e^{in\omega_0 t} dt$$

If $f(t)$ is real,

$$c_{-n} = c_n^*$$

where * denotes the complex conjugate.

$$c_n = |c_n| e^{i\phi_n}, \quad c_{-n} = c_n^* = |c_n| e^{-i\phi_n}$$

$$|c_n| = |c_{-n}| = \frac{1}{2} \sqrt{a_n^2 + b_n^2}$$

$$\phi_n = \tan^{-1} \left(-\frac{b_n}{a_n} \right)$$

$$n = \pm 1, \pm 2, \pm 3, \dots$$

$$c_0 = \frac{1}{2} a_0$$

In one dimension these points lie on a line.

What about 3D?

In the reciprocal lattice
$$n(\underline{r}) = \sum_{\underline{G}} n_{\underline{G}} e^{i \underline{G} \cdot \underline{r}}$$

The electron number density $n(\underline{r})$ is a periodic function of \underline{r} ,

translational invariance of $n(\underline{r})$ with respect to lattice vector $\underline{r}_n = n_1 \underline{a}_1 + n_2 \underline{a}_2 + n_3 \underline{a}_3$

$$n(\underline{r} + \underline{r}_n) = n(\underline{r})$$

$$\underline{G} \cdot \underline{r}_n = 2\pi m$$



Reciprocal lattice vectors

Reciprocal Lattice

For an infinite three dimensional lattice, defined by its primitive vectors, its reciprocal lattice can be determined by generating its three reciprocal primitive vectors, through the formulae

$$\underline{G} = h \underline{b}_1 + k \underline{b}_2 + l \underline{b}_3$$

with h, k, l integers

The basis vectors $\underline{b}_1, \underline{b}_2, \underline{b}_3$ of the reciprocal lattice are determined by:

$$\underline{b}_1 = \underline{a}_1^* = 2\pi \frac{\underline{a}_2 \times \underline{a}_3}{\underline{a}_1 \cdot (\underline{a}_2 \times \underline{a}_3)}$$

$$\underline{b}_2 = \underline{a}_2^* = 2\pi \frac{\underline{a}_3 \times \underline{a}_1}{\underline{a}_1 \cdot (\underline{a}_2 \times \underline{a}_3)}$$

$$\underline{b}_3 = \underline{a}_3^* = 2\pi \frac{\underline{a}_1 \times \underline{a}_2}{\underline{a}_1 \cdot (\underline{a}_2 \times \underline{a}_3)}$$

These \underline{b}_i fulfill the condition $\underline{b}_i \cdot \underline{a}_j = 2\pi\delta_{ij}$

$$\delta_{ij} \quad \text{Kronecker delta}$$
$$\delta_{ij} = \begin{cases} 0 & i \neq j \\ 1 & i = j \end{cases}$$

G is the reciprocal lattice vector

$$\underline{G} = h \underline{b}_1 + k \underline{b}_2 + l \underline{b}_3 \quad h, k, l: \text{integer, Miller indices}$$

G must be invariant when we do translation T

$$\underline{T} = u \underline{a} + v \underline{b} + w \underline{c} \quad u, v, w: \text{integer}$$

$$n(r + T) = \sum_G n_G e^{iG(r+T)}$$

$$n(r + T) = n(r) \quad \text{This is valid only when } e^{iG.T} = e^{2\pi i s} = 1$$

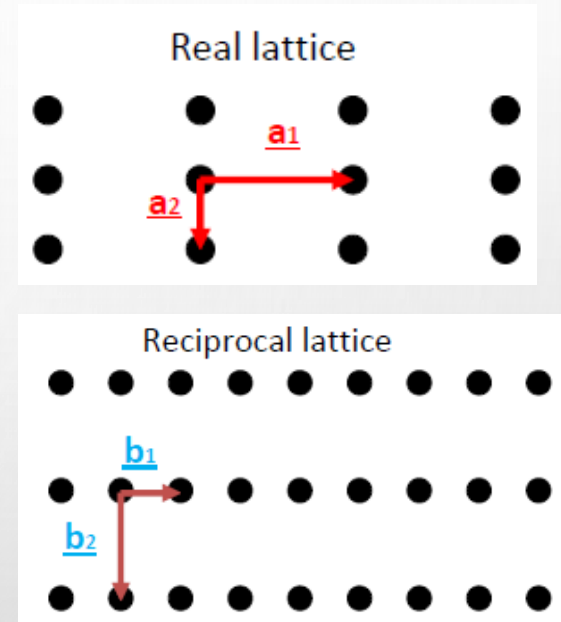
Where $s = hu + kv + lw$

Reciprocal Lattice

For every real lattice there is an equivalent reciprocal lattice. A two dimension (2-D) real lattice is defined by two unit cell vectors, say \vec{a}_1 and \vec{a}_2 inclined at an angle.

The equivalent reciprocal lattice in reciprocal space is defined by two reciprocal vectors, say \vec{b}_1 and \vec{b}_2 .

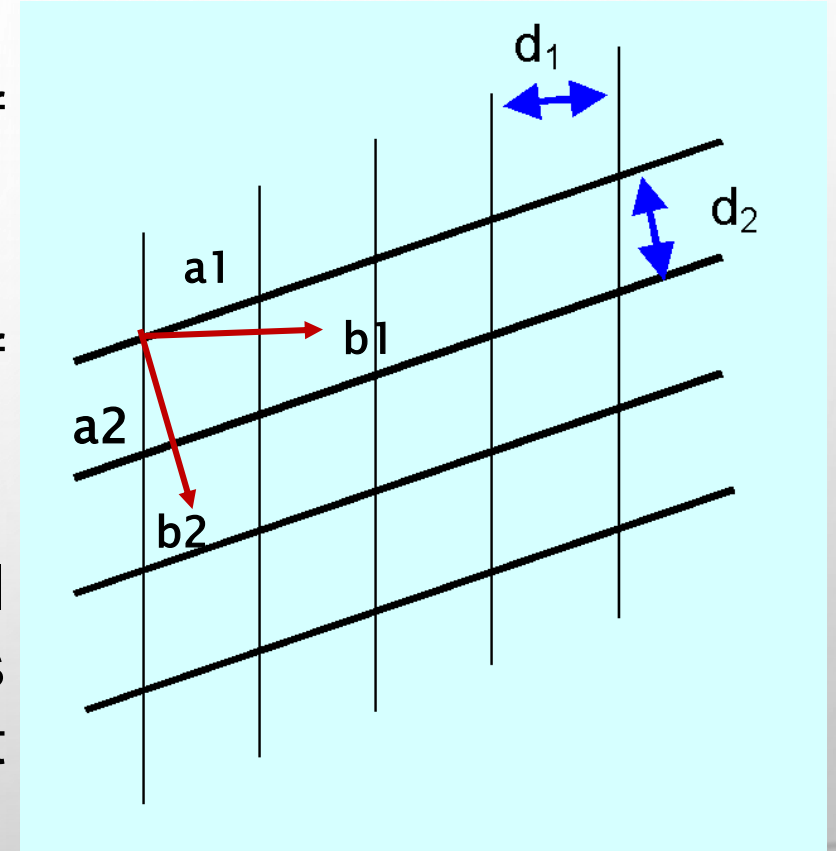
Each point represents *all* parallel crystal planes. *Eg.*, *all* planes parallel to the a-c plane are captured by (010) spot.



Reciprocal Lattice

The reciprocal vectors are defined as follows:

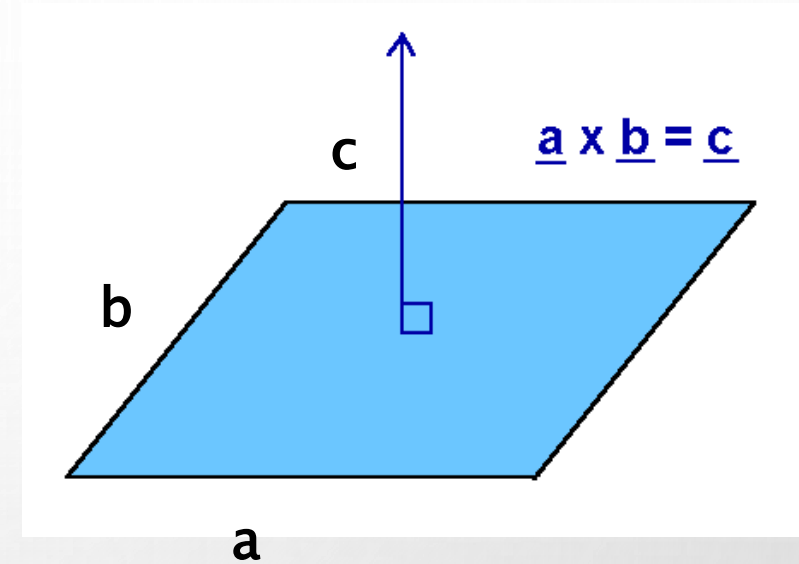
- \vec{b}_1 is of magnitude $1/d_1$ where d_1 is the spacing of the vertical planes, and is perpendicular to \vec{a}_2
- \vec{b}_2 is of magnitude $1/d_2$ where d_2 is the spacing of the horizontal planes, and is perpendicular to \vec{a}_1 .
- A reciprocal lattice can be built using reciprocal vectors. Both the real and reciprocal constructions show the same lattice, using different but equivalent descriptions.



Any set of planes can be defined by:

- (1) their orientation in the crystal (hkl)
- (2) their d-spacing

The orientation of a plane is defined by the direction of a normal (vector product)



Miller Indices Of lattice Planes

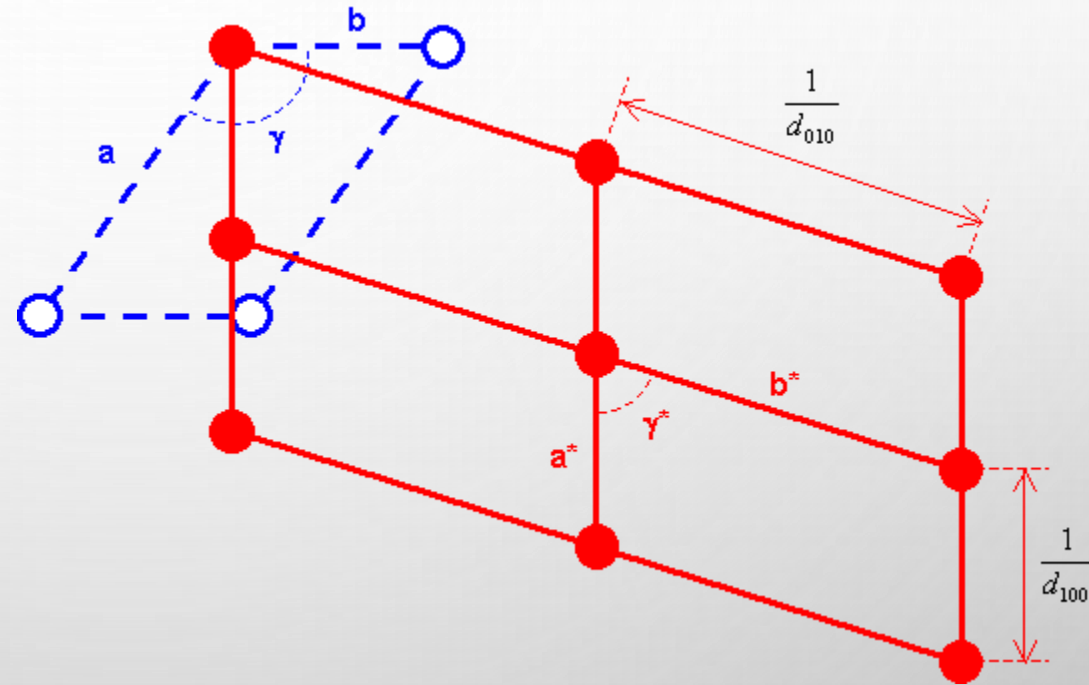
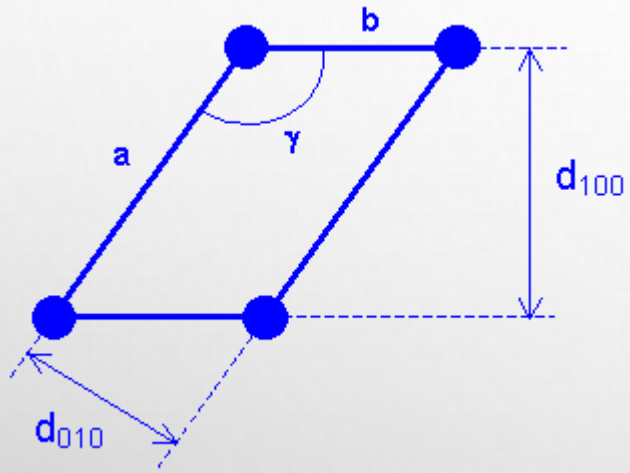
In general we describe the orientation of a lattice plane by giving a vector normal to that plane.

- There are reciprocal lattice vectors normal to any family of planes, we pick a reciprocal lattice vector to represent the normal.
- To make the choice we should use the shortest such reciprocal lattice vector.

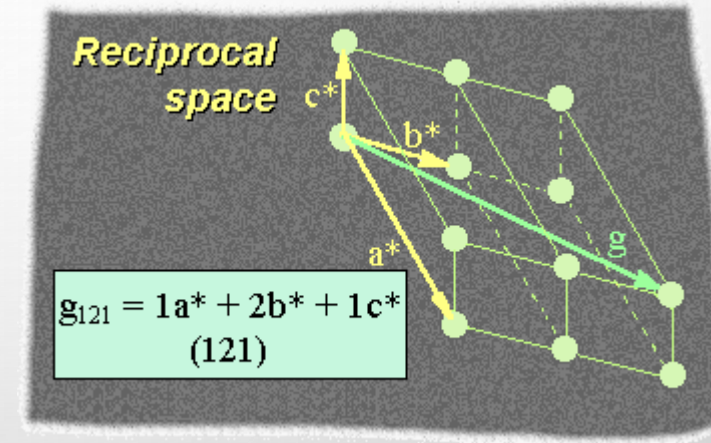
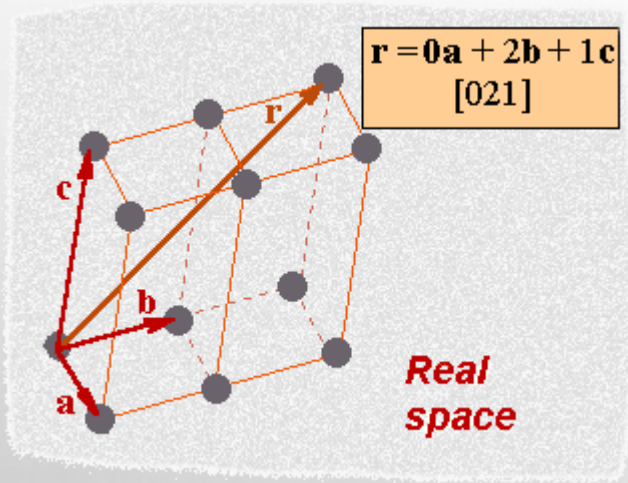
In this way we arrive at the Miller indices of the plane.

- Miller indices of a lattice plane are the coordinates of the shortest reciprocal lattice vectors normal to that plane, with respect to the specified set of primitive reciprocal lattice vectors.
- A plane with Miller indices h, k, l is normal to the reciprocal lattice vector $h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$
- h, k, l are integers.
- They have no common factor.
- They depend on particular choice of primitive vectors.

In 2D



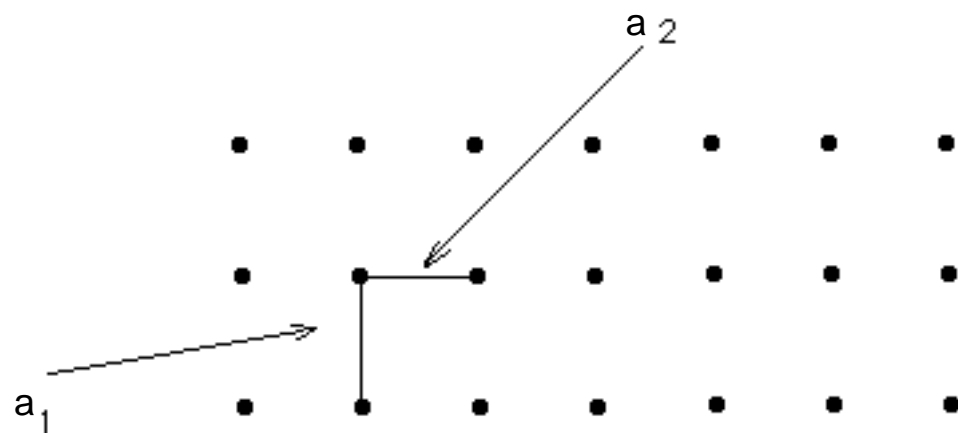
In 3D



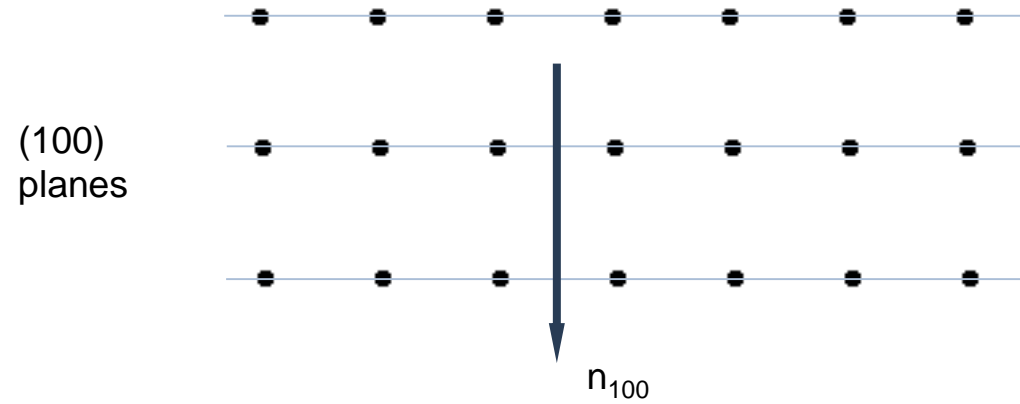
How To Build The Reciprocal Lattice

- A **lattice point** is taken as **common origin**.
- From the common origin, draw a **normal** to each plane.
- Place a point on the normal to each plane ($h\ k\ l$) at a distance from the origin equal to $1/d$.
- Such points form a periodic array called reciprocal lattice.

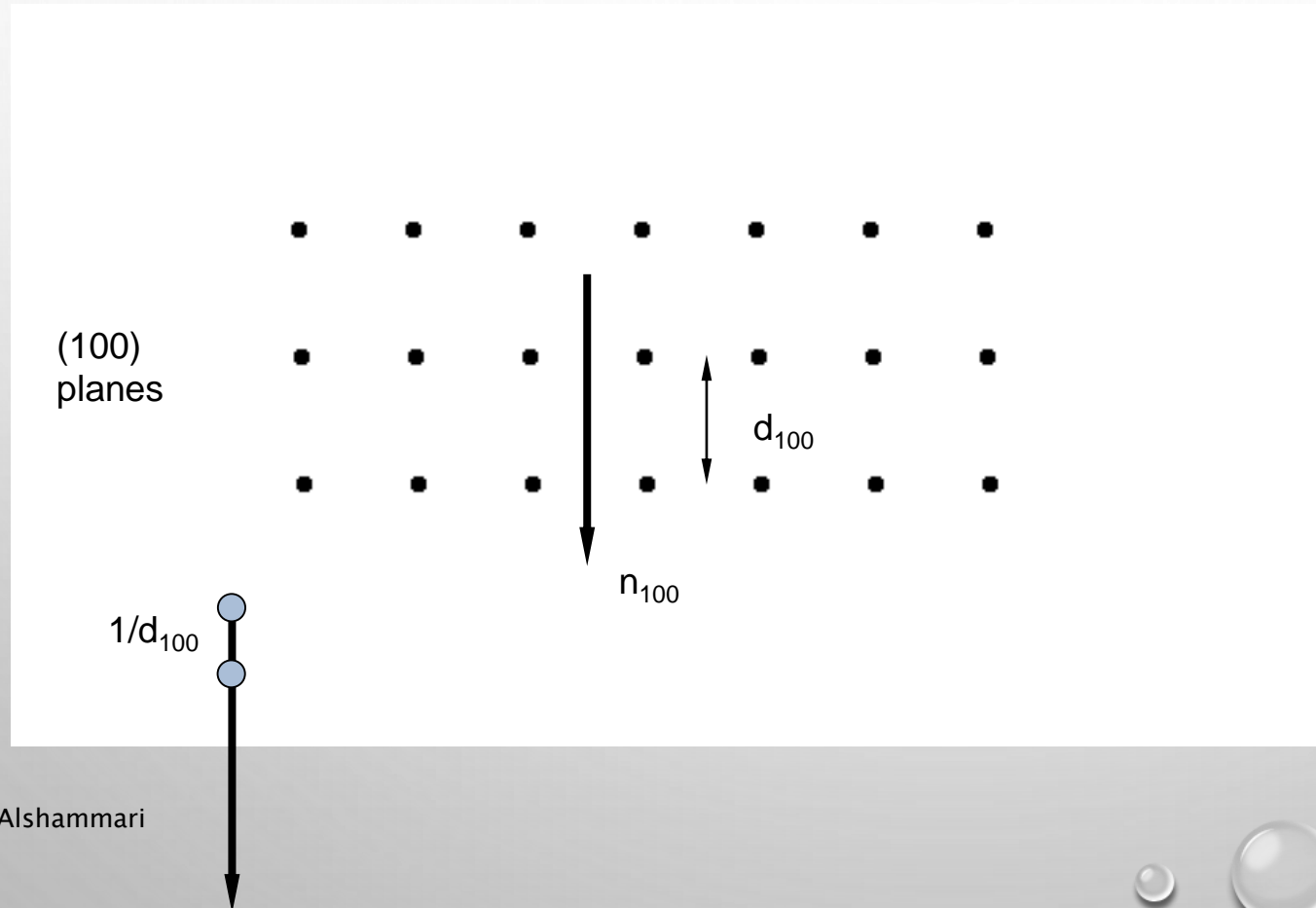
Real space lattice - basis vectors

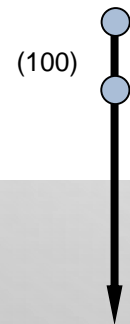
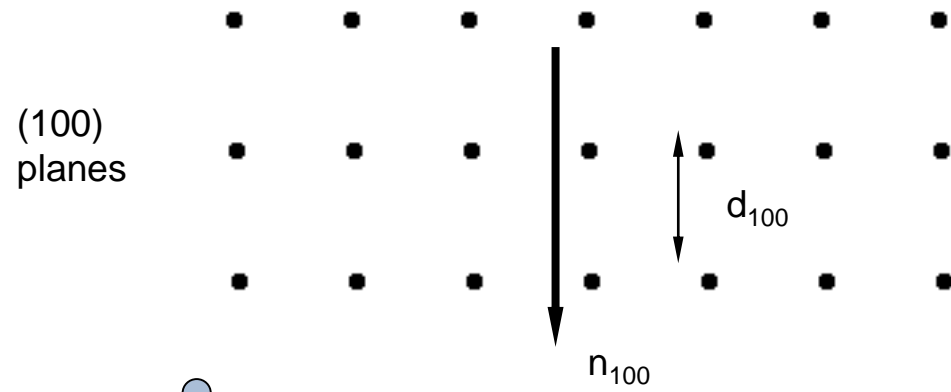


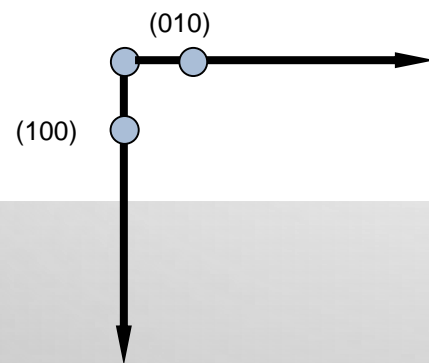
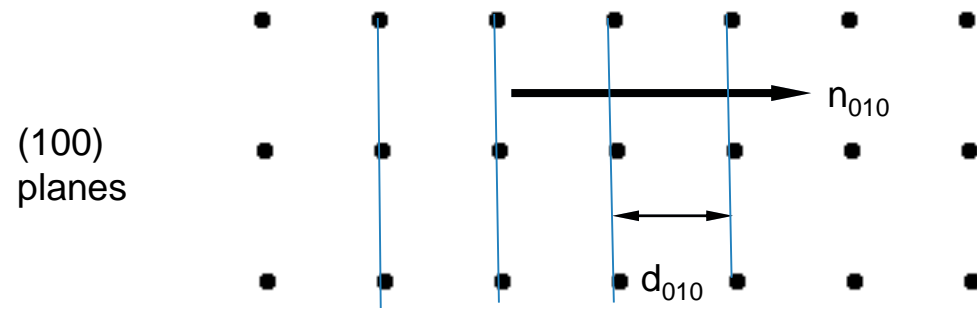
Real space lattice - choose set of planes

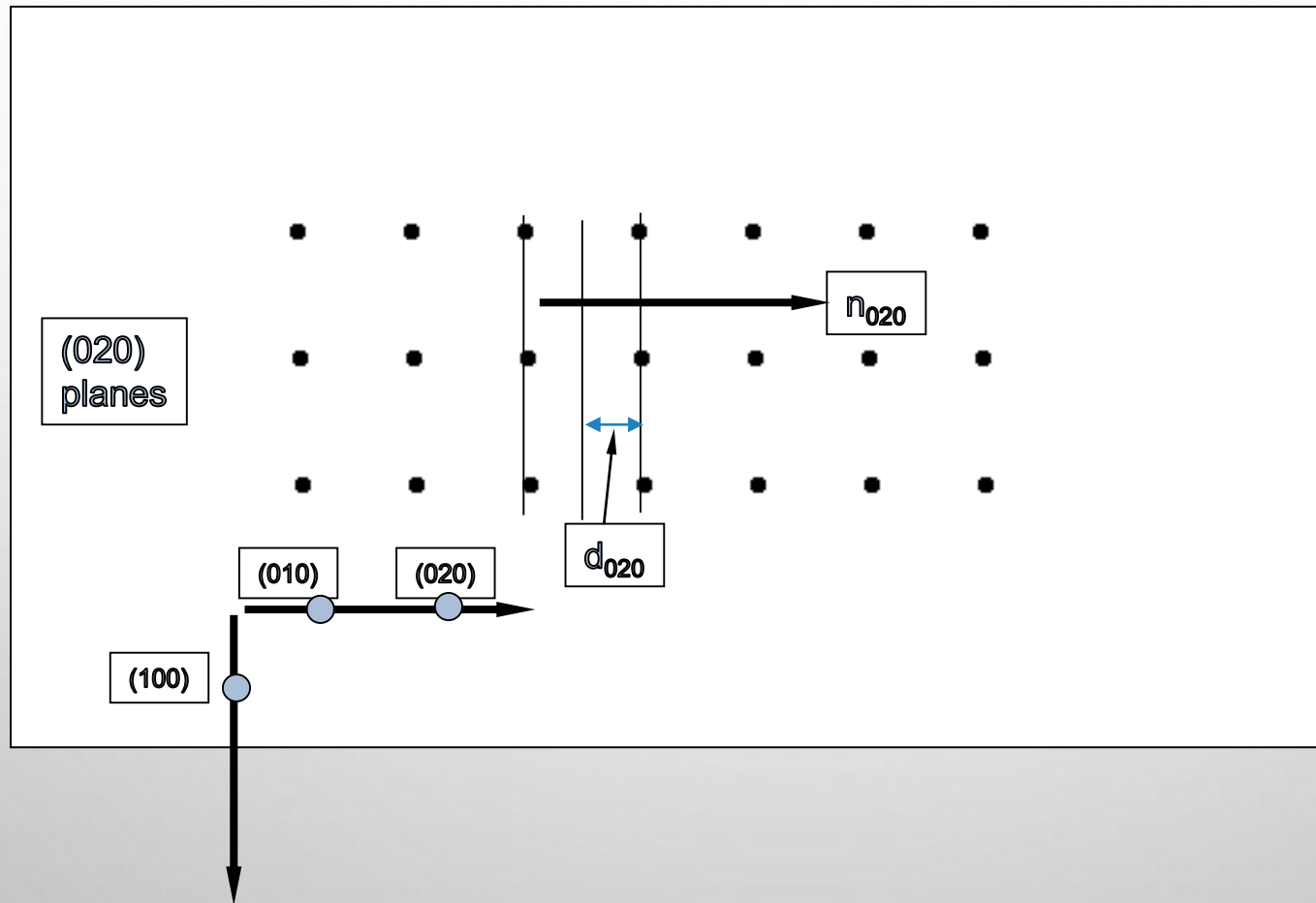


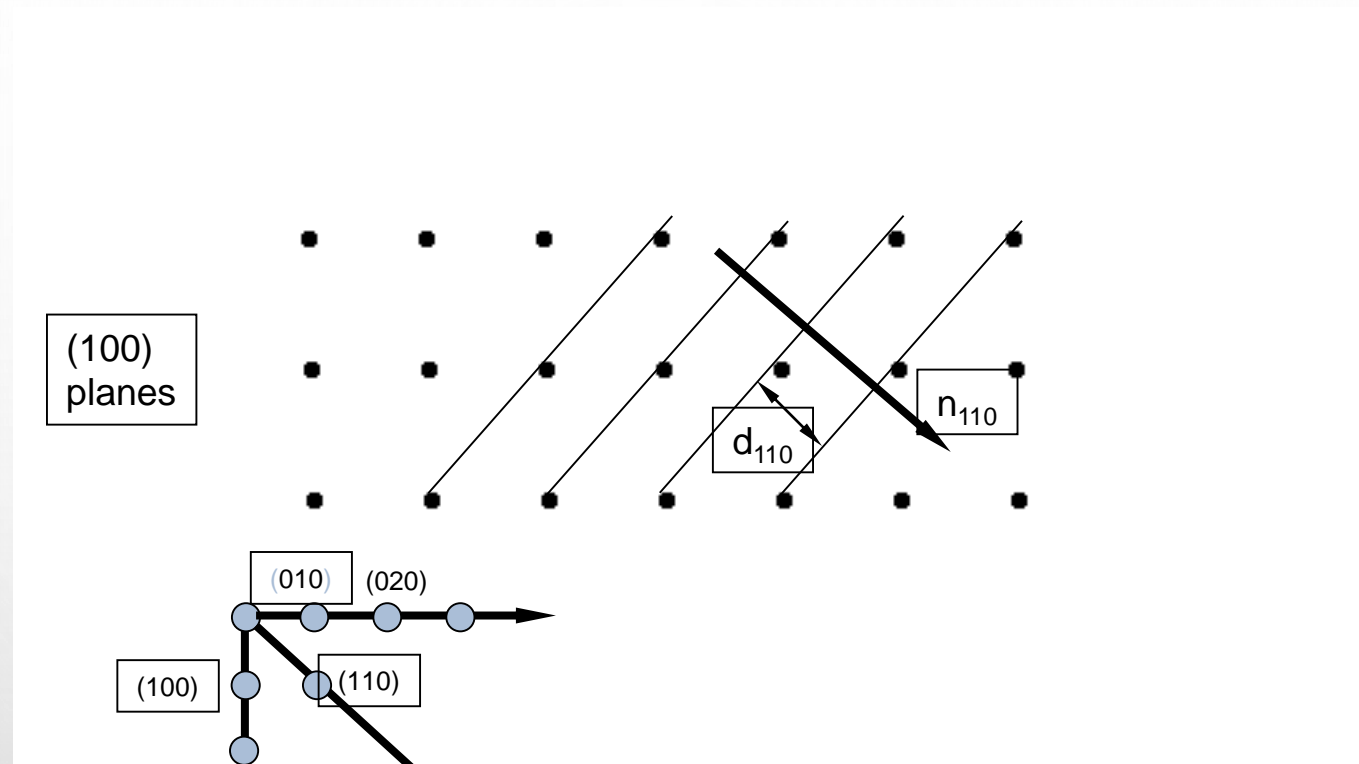
Real space lattice - interplanar spacing d











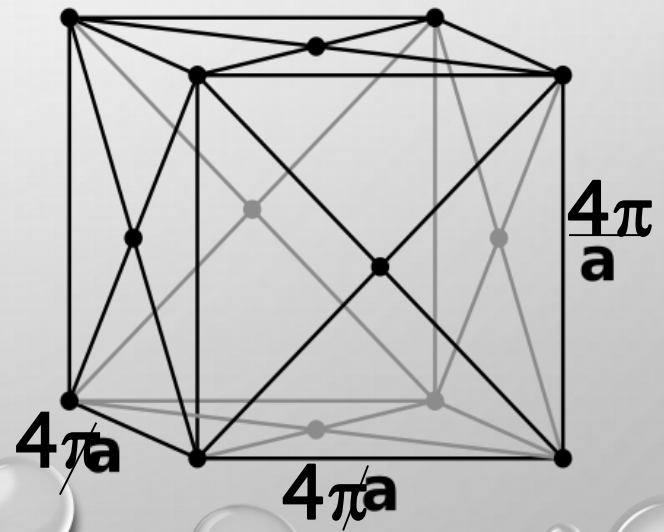
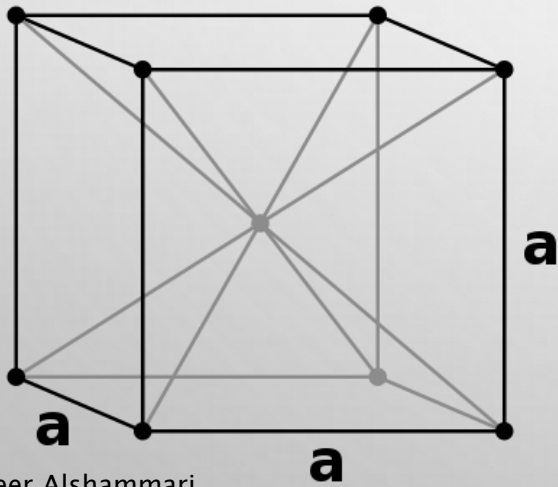
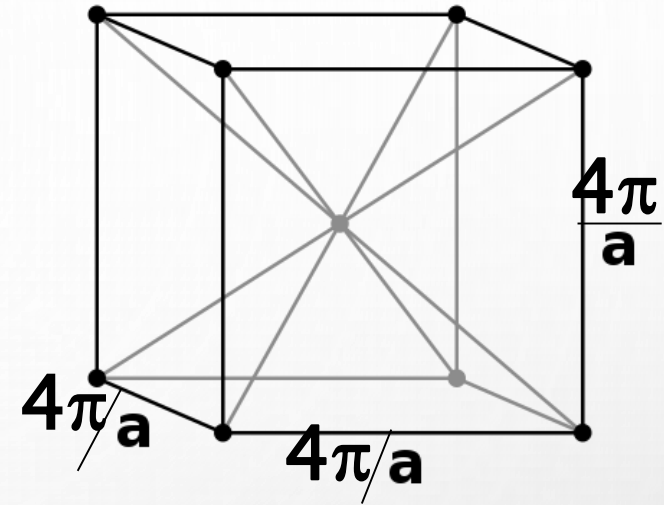
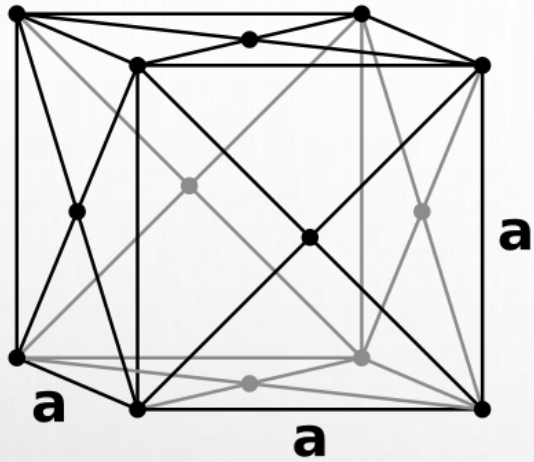
Reciprocal Lattice properties

- ❑ Direct lattice is a lattice in ordinary space whereas the reciprocal lattice is a lattice in the Fourier space.
- ❑ The \underline{b}_i vectors in reciprocal lattice has the dimensions of $(\text{length})^{-1}$ whereas the primitive vectors of the direct lattice have the dimensions of length
- ❑ A diffraction pattern of a crystal is a map of the reciprocal lattice of the crystal whereas a microscopic image is a map of direct lattice
- ❑ When we rotate a crystal, both direct and reciprocal lattice rotates
- ❑ Each point in the reciprocal lattice represents a set of parallel planes of the crystal lattice
- ❑ If the coordinates of reciprocal vector \underline{G} have no common factor, then \underline{G} is inversely proportional to the spacing of the lattice planes normal to \underline{G}
- ❑ The volume of unit cell of the reciprocal lattice is inversely proportional to the volume of unit cell of the direct lattice
- ❑ The direct lattice is the reciprocal of its own reciprocal lattice

The reciprocal lattice of a simple cubic lattice with primitive cell side a is again a simple cubic lattice, but with cell side $2\pi/a$.

- The reciprocal lattice of an fcc Bravais lattice with conventional cubic cell side a is a bcc lattice with conventional cubic cell side $4\pi/a$.
- The reciprocal lattice of an bcc lattice with conventional cell side a is similarly an fcc lattice with conventional cell side $4\pi/a$.
- The reciprocal lattice on a simple hexagonal Bravais lattice with lattice constants a and c is also a simple hexagonal lattice but with lattice constants $4\pi/\sqrt{3}a$ and $2\pi/c$, and rotated 30° around the c -axis.
- The volume v_g of the reciprocal lattice primitive cell is $v_g = (2\pi)^3/v_c$, where v_c is the volume of the direct lattice primitive cell. The cell volumes can be obtained from the corresponding primitive vectors by taking $v_c = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$ and $v_g = \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)$.

FCC and BCC



❑ Reciprocal Lattices to SC, FCC and BCC

	<u>Direct lattice</u>	<u>Reciprocal lattice</u>	<u>Volume</u>
<u>SC</u>	$\begin{cases} \mathbf{a}_1 = a\mathbf{x} \\ \mathbf{a}_2 = a\mathbf{y} \\ \mathbf{a}_3 = a\mathbf{z} \end{cases}$	$\begin{cases} \mathbf{b}_1 = (2\pi/a)\mathbf{x} \\ \mathbf{b}_2 = (2\pi/a)\mathbf{y} \\ \mathbf{b}_3 = (2\pi/a)\mathbf{z} \end{cases}$	$(2\pi/a)^3$
<u>FCC</u>	$\begin{cases} \mathbf{a}_1 = \frac{1}{2}a(\mathbf{x} + \mathbf{y}) \\ \mathbf{a}_2 = \frac{1}{2}a(\mathbf{y} + \mathbf{z}) \\ \mathbf{a}_3 = \frac{1}{2}a(\mathbf{z} + \mathbf{x}) \end{cases}$	$\begin{cases} \mathbf{b}_1 = \frac{2\pi}{a}(-\mathbf{x} + \mathbf{y} - \mathbf{z}) \\ \mathbf{b}_2 = \frac{2\pi}{a}(\mathbf{x} - \mathbf{y} + \mathbf{z}) \\ \mathbf{b}_3 = \frac{2\pi}{a}(\mathbf{x} + \mathbf{y} - \mathbf{z}) \end{cases}$	$2(2\pi/a)^3$
<u>BCC</u>	$\begin{cases} \mathbf{a}_1 = \frac{1}{2}a(\mathbf{x} + \mathbf{y} - \mathbf{z}) \\ \mathbf{a}_2 = \frac{1}{2}a(-\mathbf{x} + \mathbf{y} + \mathbf{z}) \\ \mathbf{a}_3 = \frac{1}{2}a(\mathbf{x} - \mathbf{y} + \mathbf{z}) \end{cases}$	$\begin{cases} \mathbf{b}_1 = \frac{2\pi}{a}(\mathbf{y} + \mathbf{z}) \\ \mathbf{b}_2 = \frac{2\pi}{a}(\mathbf{x} + \mathbf{z}) \\ \mathbf{b}_3 = \frac{2\pi}{a}(\mathbf{x} + \mathbf{y}) \end{cases}$	$4(2\pi/a)^3$

FCC to BCC

$$\vec{a} = \frac{a}{2}(\hat{x} + \hat{z}) \quad \vec{b} = \frac{a}{2}(\hat{x} + \hat{y}) \quad \vec{c} = \frac{a}{2}(\hat{y} + \hat{z})$$

$$V = \vec{a} \cdot (\vec{b} \times \vec{c}) = \frac{a}{2}(\hat{x} + \hat{z}) \cdot \left[\frac{a}{2}(\hat{x} + \hat{y}) \times \frac{a}{2}(\hat{y} + \hat{z}) \right]$$

$$\left[\frac{a}{2}(\hat{x} + \hat{y}) \times \frac{a}{2}(\hat{y} + \hat{z}) \right] = \frac{a^2}{4}(\hat{z} + (-\hat{y}) + \hat{x})$$

$$\underline{V} = \vec{a} \cdot (\vec{b} \times \vec{c}) = \frac{a}{2}(\hat{x} + \hat{z}) \cdot \frac{a^2}{4}(\hat{x} - \hat{y} + \hat{z}) = \frac{a^3}{8} \times 2 = \underline{\frac{a^3}{4}}$$

Volume of F.C.C. is a^3 . There are four atoms per unit cell! → the volume for the primitive of a F.C.C. structure is ? _____

$$\begin{aligned}
 \underline{\vec{a}^*} &= \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot (\vec{b} \times \vec{c})} = \frac{\frac{a}{2}(\hat{x} + \hat{y}) \times \frac{a}{2}(\hat{y} + \hat{z})}{a^3/4} \\
 &= \frac{\frac{a^2}{4}(\hat{x} + \hat{y}) \times (\hat{y} + \hat{z})}{a^3/4} = \frac{(\hat{x} + \hat{y}) \times (\hat{y} + \hat{z})}{a} \\
 &= \frac{\hat{z} + (-\hat{y}) + \hat{x}}{a} = \underline{\frac{\hat{x} - \hat{y} + \hat{z}}{a}}
 \end{aligned}$$

Similarly,

$$\vec{b}^* = \frac{\hat{x} + \hat{y} - \hat{z}}{a} \qquad \vec{c}^* = \frac{-\hat{x} + \hat{y} + \hat{z}}{a}$$

$$\frac{\hat{x} - \hat{y} + \hat{z}}{a}, \frac{\hat{x} + \hat{y} - \hat{z}}{a}, \frac{-\hat{x} + \hat{y} + \hat{z}}{a} \rightarrow \text{B.C.C.}$$

BCC to FCC

$$\mathbf{a} = \frac{1}{2}a(-\hat{x} + \hat{y} + \hat{z}); \mathbf{b} = \frac{1}{2}a(\hat{x} - \hat{y} + \hat{z}); \mathbf{c} = \frac{1}{2}a(\hat{x} + \hat{y} - \hat{z})$$

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{V}$$

$$\begin{aligned} \hat{x} \times \hat{y} &= \hat{z} & \hat{y} \times \hat{z} &= \hat{x} \\ \hat{z} \times \hat{x} &= \hat{y} \end{aligned}$$

$$\mathbf{b} \times \mathbf{c} = \frac{1}{2}a(\hat{x} - \hat{y} + \hat{z}) \times \frac{1}{2}a(\hat{x} + \hat{y} - \hat{z}) = \frac{a^2}{4}(2\hat{y} + 2\hat{z}) \quad ; \quad V = a^3 / 2$$

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{V} = \frac{1}{a}(\hat{y} + \hat{z})$$

$$\mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{V} = \frac{1}{a}(\hat{x} + \hat{z}) \quad \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{V} = \frac{1}{a}(\hat{x} + \hat{y})$$

The vector set is the same as the FCC primitive translation vector.

Unit of the reciprocal lattice is 1/length.

Interplanar distances in reciprocal lattice

If we take the vector \underline{u} and unit vector of the reciprocal lattice \hat{G}

$$\underline{G} = h\underline{A} + k\underline{B} + l\underline{C}$$

$$d(hkl) = \underline{u} \cdot \frac{\underline{G}}{|\underline{G}|}$$

$$d(hkl) = \underline{u} \cdot \frac{h\underline{A} + k\underline{B} + l\underline{C}}{|\underline{G}|}$$

$$d(hkl) = \underline{u} \cdot \frac{a \cdot \underline{A}}{|\underline{G}|} = \frac{2\pi}{|\underline{G}|}$$

Example: calculate d spacing in the simple cubic lattice, a,b,c are all perpendicular and identical in length=a ,also A,B, C are all perpendicular and identical in length= $2\pi/a$

$$|\underline{G}| = \sqrt{h^2 A^2 + k^2 B^2 + l^2 C^2}$$

$$d(hkl) = ua. \frac{\underline{G}}{|\underline{G}|}$$

$$d(hkl) = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Interaction of X-rays and Matter

Scattering.

coherent, incoherent
elastic (Thomson), inelastic (Compton)

Absorption.

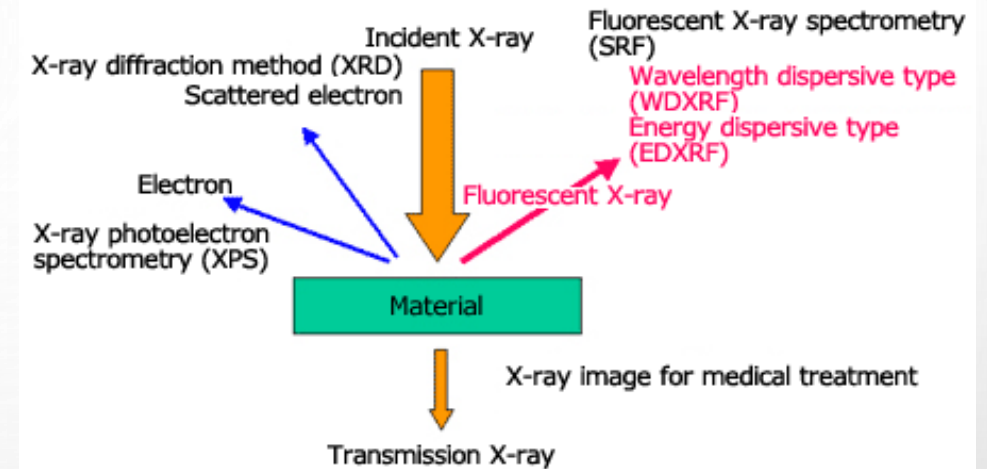
atoms: can then be emitted as fluorescence, photoelectrons, Auger electrons

molecules: can emit fluorescence, phosphorescence, transfer heat, (stimulated emission)

Diffraction. The bending of waves due to obstructions and small apertures, as with crystals.

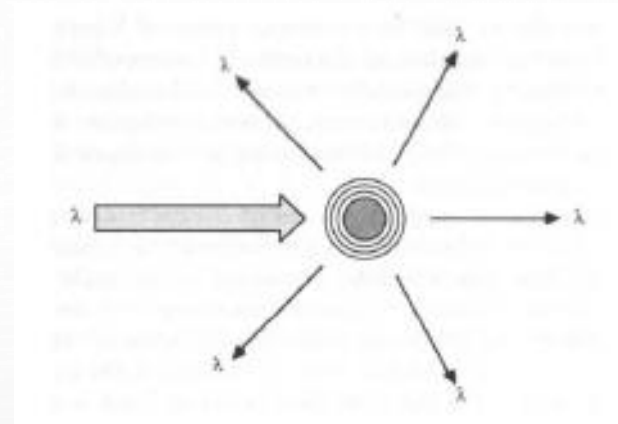
Refraction. The bending of a wave as it passes from one medium to another

Reflection. Radiation bouncing back from one medium to the original medium, where the wavelength \ll size of the object.



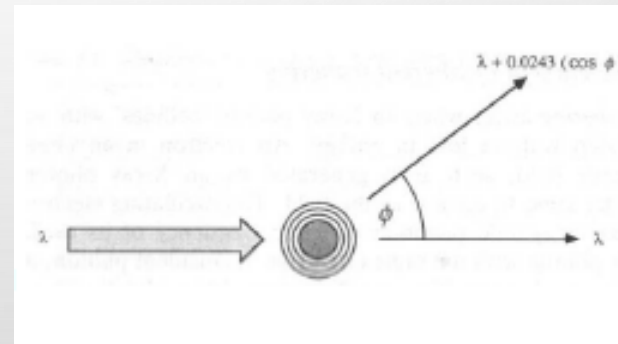
X-ray Scattering

Coherent scattering occurs when the X-ray particle collides with an atom and deviates without a loss in energy.



Coherent

Incoherent scattering is where the incident X-ray loses some of its energy to the scattering electron. As total momentum is preserved, the wavelength of the scattered photon is increased.



Incoherent

Scattering and Diffraction

- ❑ Diffraction is the special case of scattering. One sees diffraction as a result of coherence of scattered waves i.e. when there is periodicity.
- ❑ Scattering is the phenomenon that is seen when any radiation interacts with particles.
- ❑ Scattering will happen at all angles while diffraction is possible only at angles which satisfies Bragg's equation.
- ❑ Scattering is a kind of particle behavior, but diffraction is a kind of wave behavior. Of course every matter have wave-particle duality, so if one particle interacted with another, both of the scattering and diffraction will happen.
- ❑ Scattering may change the wavelength(energy) of the particle, like Raman scattering, but diffraction often do not involve the energy change, but more referred to wavelength dispersion (spatial dispersion), like diffraction from grating, or X-ray diffraction from crystals.

- For electromagnetic radiation to be diffracted the spacing in the grating should be of the same order as the wavelength
- In crystals the typical interatomic spacing $\sim 2\text{-}3 \text{ \AA}$ so the suitable radiation is X-rays
- Hence, X-rays can be used for the study of crystal structures



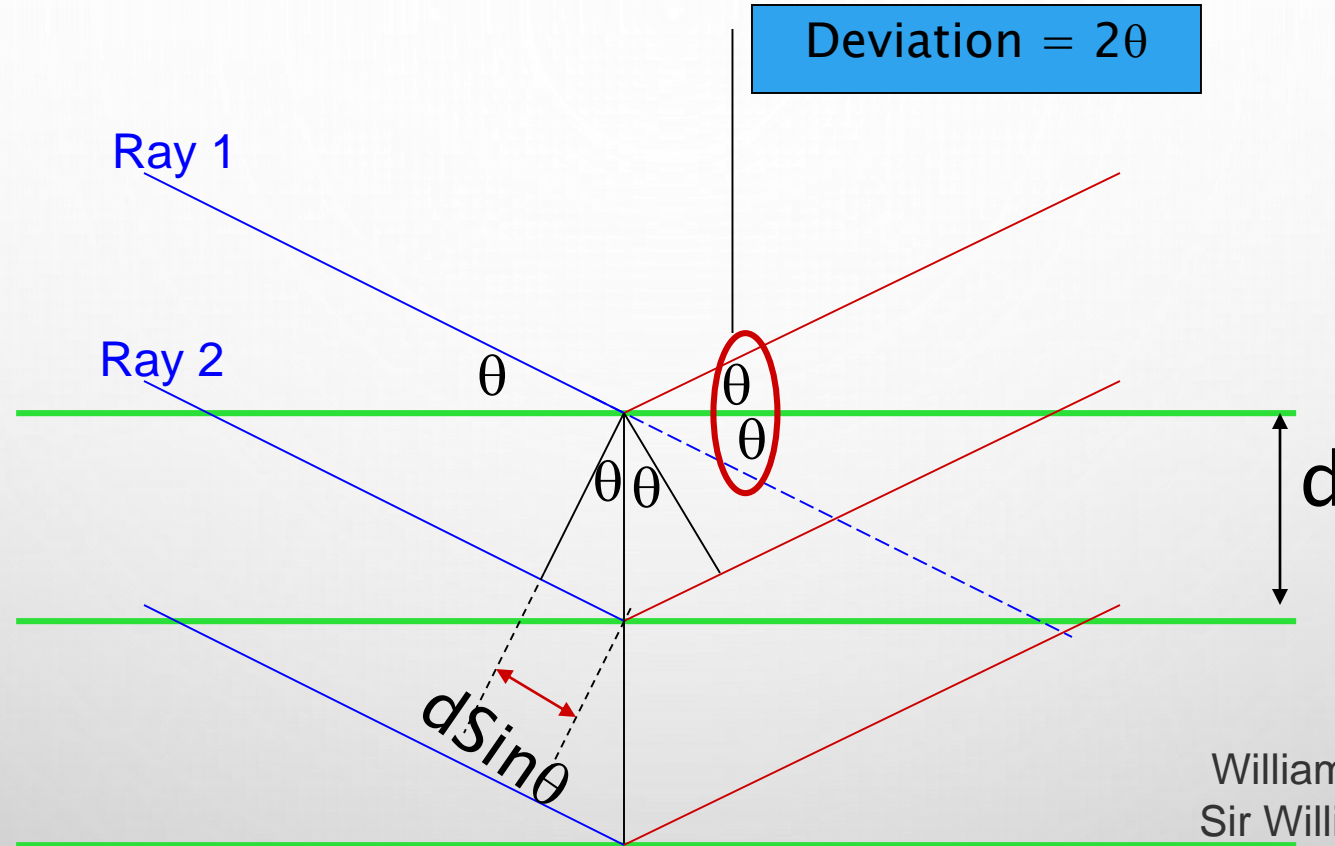
To investigate atomic/molecular structure, we use X-rays, electrons, and neutrons, since they can have wavelengths about the sizes of atoms.

Interference

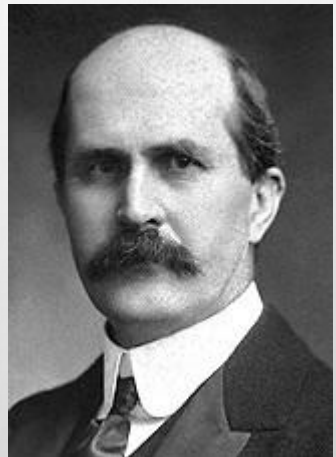
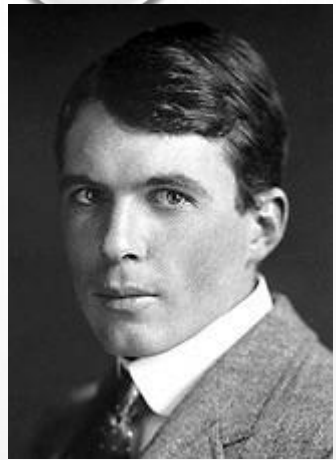
- For waves with the same frequency and amplitude, we see *constructive interference* when two waves have a phase difference of $n\lambda$, where ($n \in \mathbb{Z}$)
 - called “in phase”
- *Destructive interference* is observed for a phase difference of $(n + \frac{1}{2})\lambda$, where ($n \in \mathbb{Z}$)
 - called “out of phase”
- A phase difference can result from a path difference
 - happens in slit experiments
 - the same thing happens when X-rays are diffracted by a crystal
 - The X-rays penetrate deeply and many layers contribute to the reflected intensity
 - The diffracted peak intensities are therefore very sharp (in angle)
 - The physics of the lattice planes is totally obscure!

BRAGG'S EQUATION

Bragg's law tells you at which angle θ to expect maximum diffracted intensity for a particular family of crystal planes. For large crystals, all other angles give zero intensity.



- The path difference between ray 1 and ray 2 = $2d \sin \theta$
- For constructive interference: $n\lambda = 2d \sin \theta$



William Lawrence Bragg and his father, Sir William Henry Bragg, were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS, and diamond.

Bragg's Law can easily be derived by considering the conditions necessary to make the phases of the beams coincide when the incident angle equals the reflecting angle.

The rays of the incident beam are always in phase and parallel up to the point at which the top beam strikes the top layer at atom z (Fig. 1). The second beam continues to the next layer where it is scattered by atom B. The second beam must travel the extra distance $AB + BC$ if the two beams are to continue traveling adjacent and parallel. This extra distance must be an integral (n) multiple of the wavelength (λ) for the phases of the two beams to be the same: $n\lambda = AB + BC$ (2).

Recognizing d as the hypotenuse of the right triangle Abz , we can use trigonometry to relate d and θ to the distance $(AB + BC)$. The distance AB is opposite θ so,

$$AB = d \sin\theta \quad (3).$$

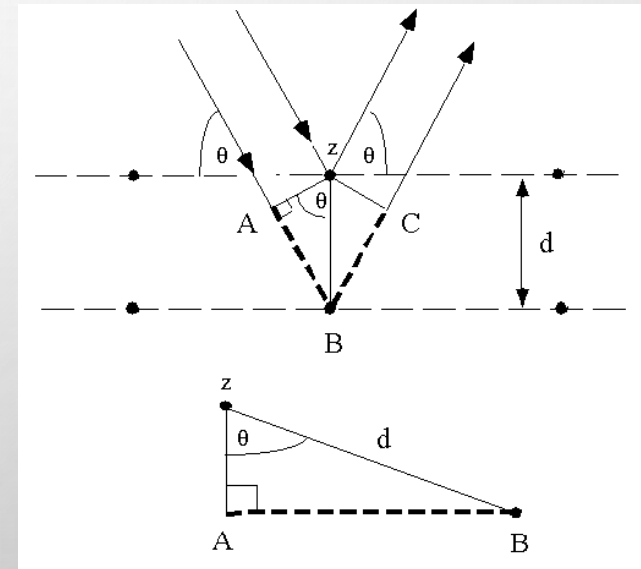
Because $AB = BC$ eq. (2) becomes,

$$n\lambda = 2AB \quad (4)$$

Substituting eq. (3) in eq. (4) we have,

$$n\lambda = 2 d \sin\theta, \quad (1)$$

and Bragg's Law has been derived. The location of the surface does not change the derivation of Bragg's Law.



Von Laue Diffraction Theory In Crystals

- The periodicity and interatomic spacing of crystals had been deduced earlier.
- Von laue realized that if x-rays were waves with short wavelength, interference phenomena should be observed like in young's double slit experiment.
- experiment in 1912, nobel prize in 1914

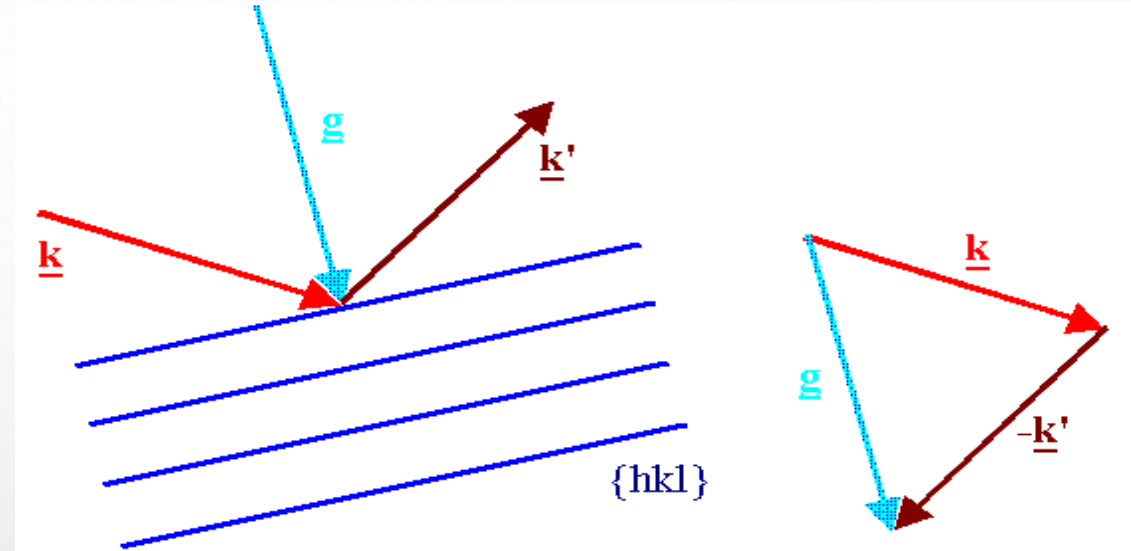
Laue's diffraction condition

$$\mathbf{k}' = \mathbf{k} + \mathbf{G}_{hkl}$$

- Given an incident \mathbf{k} , want to find a \mathbf{k}' that satisfies this condition
(under the constraint $|\mathbf{k}'|=|\mathbf{k}|=2\pi/\lambda$)

Graphical Laue

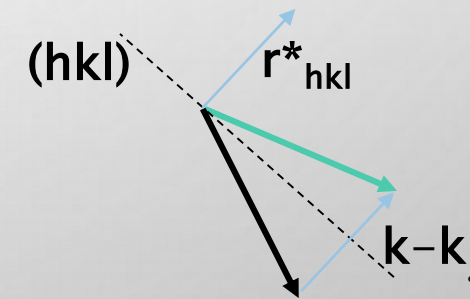
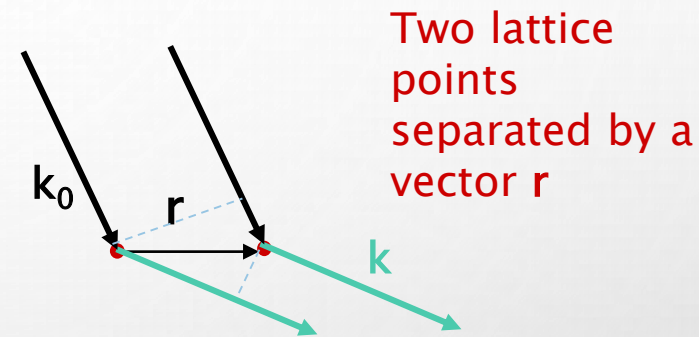
- If, and only if the three vectors involved form a **closed triangle**, is the Laue condition met. If the Laue condition is **not** met, the incoming wave just moves through the lattice and emerges on the other side of the crystal (**neglecting absorption**).



The Laue Equations

The **Laue equations** give three conditions for incident waves to be diffracted by a crystal lattice

- waves scattered from two lattice points separated by a vector \mathbf{r} will have a path difference in a given direction.
- the scattered waves will be in phase and constructive interference will occur if the phase difference is 2π .
- the path difference is the difference between the projection of \mathbf{r} on \mathbf{k} and the projection of \mathbf{r} on \mathbf{k}_0 ,



Von Laue Diffraction Theory in crystals

Amplitude of plane wave

$$A_p = A e^{-i\omega t} e^{ik \cdot r}$$

k wave vector

ω angular momentum

$k = 2\pi/\lambda$

λ wavelength

Only fraction γ of the amplitude will be scattered to the observation point B described by vector R

$$A_B = \gamma A_p \frac{e^{ik \cdot \varrho}}{|\varrho|}$$

ϱ is a vector describing B w.r.t the scattering center.

$$\varrho = R - r$$

We suppose elastic scattering

$$|k| = |k'| = 2\pi/\lambda$$

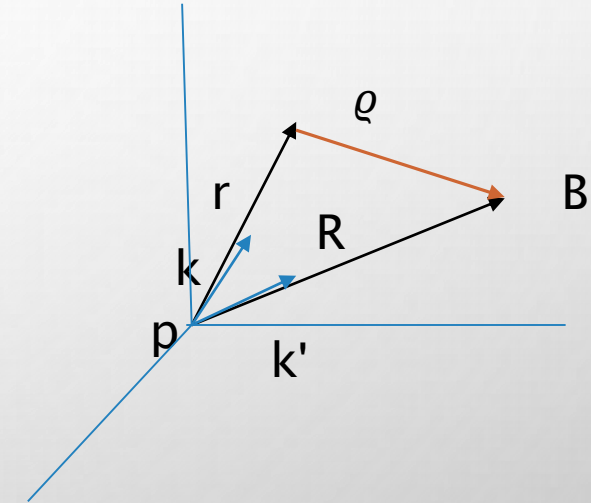
$$|r| \ll |R|$$

R parallel to ϱ

$$|\varrho| \approx |R|$$

Scattering center p

It is an atom



$$\begin{aligned}
 A_B &= \frac{\gamma}{R} A e^{-i\omega t} e^{ik.r} e^{ik.(\vec{R}-r)} \\
 &= \frac{A}{R} e^{-i\omega t} e^{ik.\vec{R}} \gamma e^{[(k-\vec{k}).r]} \\
 &= A_o \gamma e^{[\Delta k.r]}
 \end{aligned}$$

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

$$A_o = \frac{A}{R} e^{-i\omega t} e^{ik.\vec{R}}$$

$$r = u\vec{a} + v\vec{b} + w\vec{c}$$

$$\begin{aligned}
 A_{tot} &= \sum_{u,v,w} A_B \\
 &= A_o \gamma \sum_{u,v,w} e^{i[\Delta k.(u\vec{a}+v\vec{b}+w\vec{c})]}
 \end{aligned}$$

The maximum amplitude will at
 $u(\Delta k.a) + v(\Delta k.b) + w(\Delta k.c) = 2\pi m$

$$e^{i2\pi m} = 1$$

Laue conditions

$$\Delta k.a = 2\pi m_1, \Delta k.b = 2\pi m_2, \Delta k.c = 2\pi m_3$$

G satisfy these relations

$$\Delta k = G$$

The wavevectors of the incoming and outgoing beams are k and k' . We suppose that the amplitude of the wave scattered from a volume element is proportional to the local electron concentration $n(r)$. The total amplitude of the scattered wave in the direction of k' is proportional to the integral over the crystal of $n(r) dV$ times the phase factor $\exp[i(k - k') \cdot r]$.

The total scattering amplitude:

$$F = \int dV n(r) e^{i(\Delta k \cdot r)}$$

$$F = \int_G dV n_G e^{-iG \cdot r} e^{i\Delta k \cdot r}$$

$$F = \int_G dV n_G e^{-i(G - \Delta k) \cdot r}$$

This scattering is maximum when $(G - \Delta k) \cdot r \approx 0$

When the scattering vector Δk is equal to a particular reciprocal lattice vector

$$G = \Delta k$$

Bragg law in vector form

The diffraction condition is written as

$$k + G = \hat{k}$$

Using elastic scattering : $|k| = |\hat{k}|$

$$(k + G)^2 = k^2$$

$$k^2 + 2kG + G^2 = k^2$$

$$-2k \cdot G = G^2$$

$$2|k| \cdot |G| \cos\left(\frac{\pi}{2} - \theta\right) = |G|^2$$

Here θ is the angle between the incident beam and the crystal plane

$$d = \frac{2\pi}{|G|} \quad , \quad |k| = \frac{2\pi}{\lambda}$$

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

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

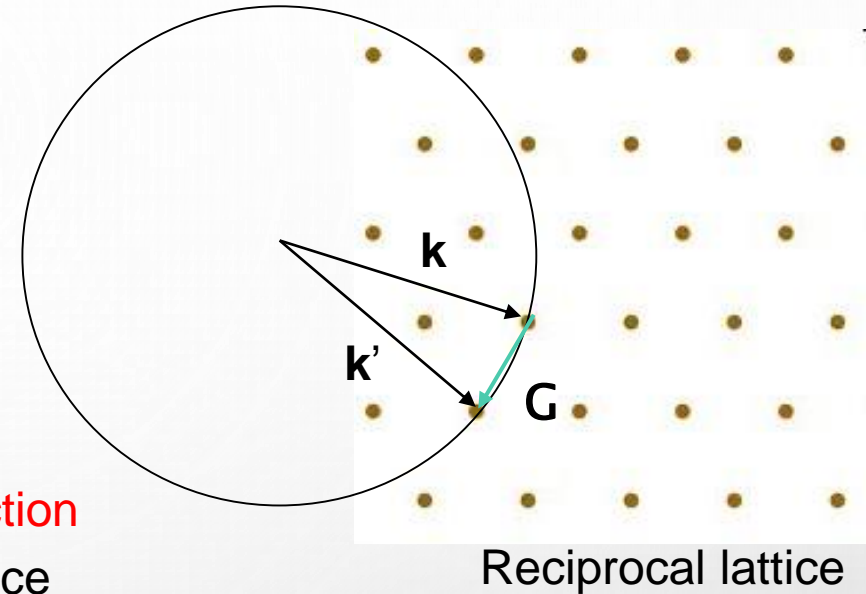
Bragg law

The Ewald construction

- vector representation of Bragg law
- $|\mathbf{k}| = |\mathbf{k}_0| = 2\pi/\lambda$

- One problem: there are infinitely many \mathbf{G}_{hkl} 's.
- It's convenient to solve it graphically using **the Ewald construction**

The observed diffraction pattern is the part of the reciprocal lattice that is intersected by the Ewald sphere



We draw a sphere of radius $k = 2\pi/\lambda$ about the origin of \mathbf{k} .

A diffracted beam will be formed if this sphere intersects any other point in the reciprocal lattice.

The sphere as drawn intercepts a point connected with the end of \mathbf{k} by a reciprocal lattice vector \mathbf{G} .

The diffracted x-ray beam is in the direction $\mathbf{k}' = \mathbf{k} + \mathbf{G}$.

<http://www.chembio.uoguelph.ca/educmat/chm729/recip/ewindex.htm>

Brillouin Zone

A Brillouin zone is defined as a Wigner-Seitz primitive cell in the reciprocal lattice

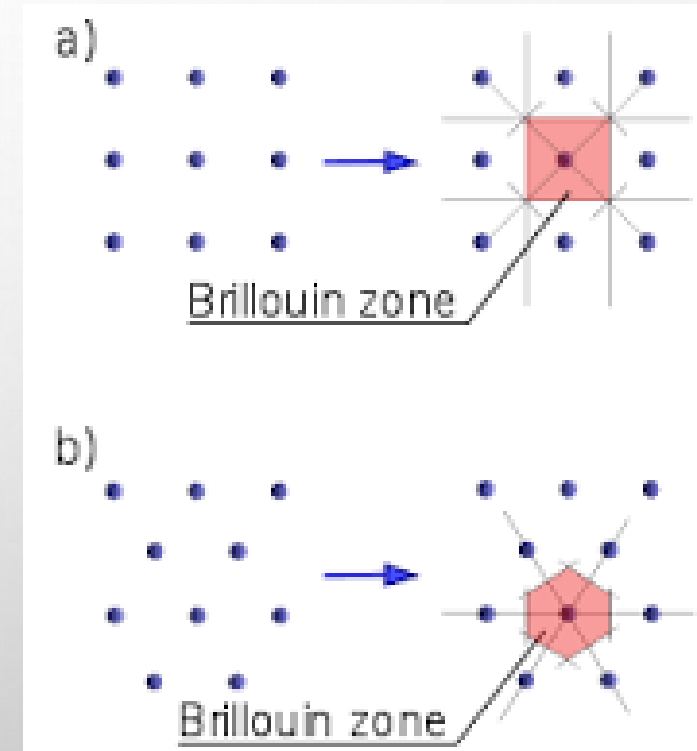
The Brillouin zone gives a vivid geometrical interpretation of the diffraction condition

$$2k \cdot G = G^2$$

÷ 4 both sides

$$k \cdot \left(\frac{1}{2} G \right) = \left| \frac{1}{2} G \right|^2$$

- The Brillouin construction exhibits all wavevectors k that can be Bragg reflected by the crystal.
- The constructions divide the Fourier space into fragments, out of which the first Brillouin zone is of greatest importance.

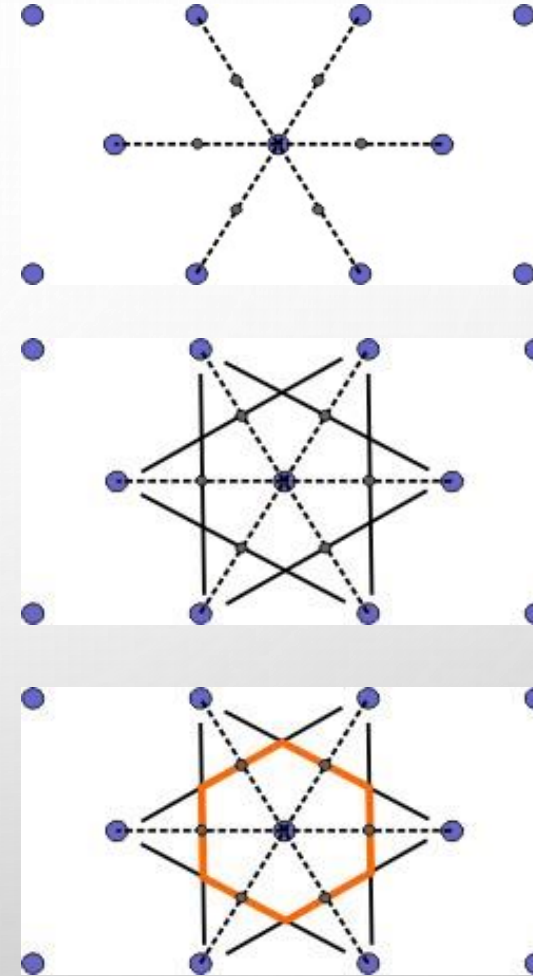


Construction of first Brillouin zone

Draw lines connecting the origin point to its nearest neighbors.

Draw perpendicular bisectors to these lines. These perpendicular bisectors are Bragg Planes.

Taking the smallest polyhedron containing the point bounded by these planes is first Brillouin zone



Higher Brillouin Zones

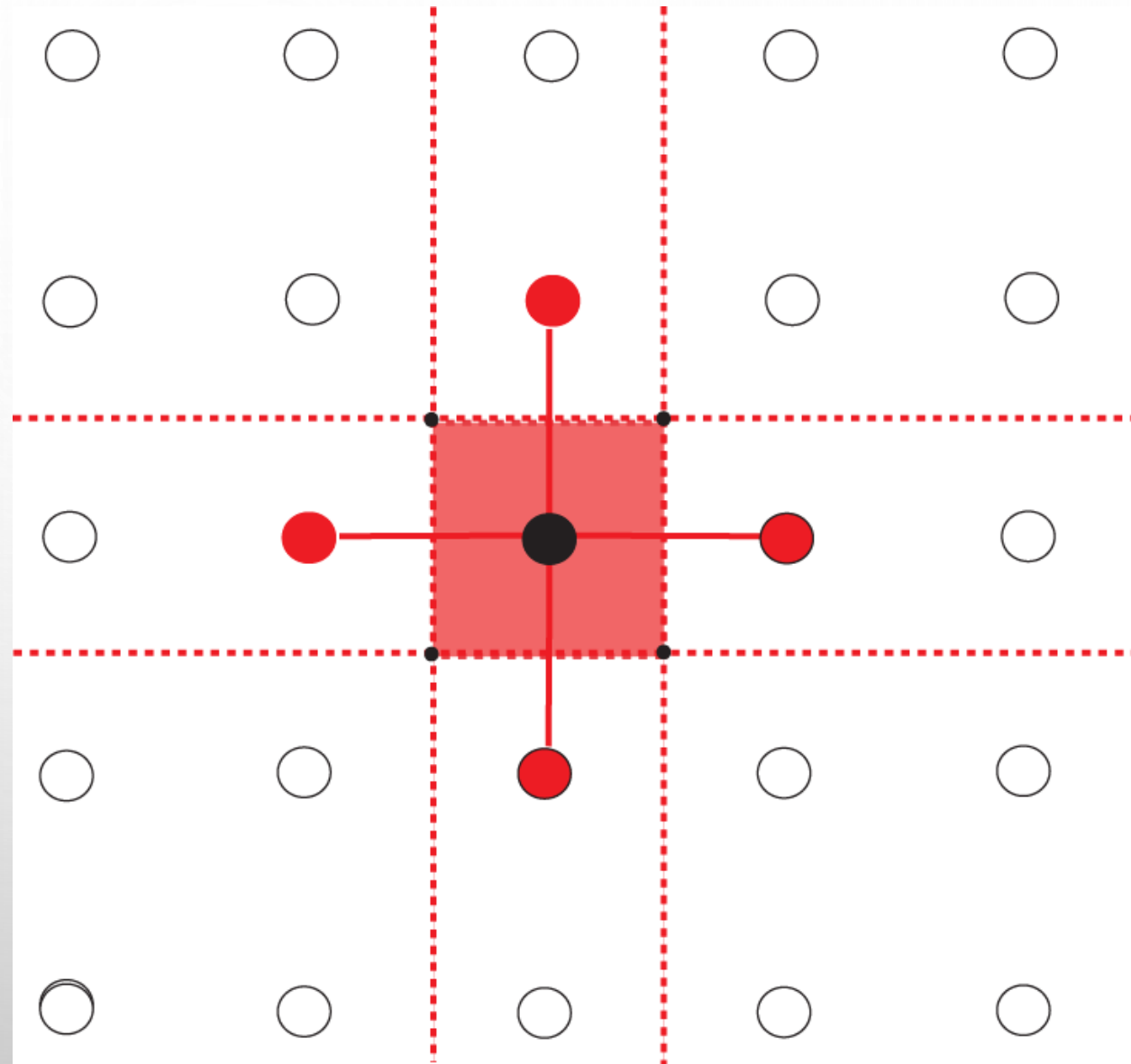
The second Brillouin zone is the set of points that can be reached from the first zone by crossing only one Bragg plane.

The $(n + 1)$ th Brillouin zone is the set of points not in the $(n - 1)$ th zone that can be reached from the n th zone by crossing $n - 1$ Bragg planes.

The n th Brillouin zone can be defined as the set of points that can be reached from the origin by crossing $n - 1$ Bragg planes, but no fewer.

The locus of points in reciprocal space that have no Bragg Planes between them and the origin defines the first Brillouin Zone.

It is equivalent to the Wigner-Seitz unit cell of the reciprocal lattice. Small black dots represent point of intersection of Bragg planes

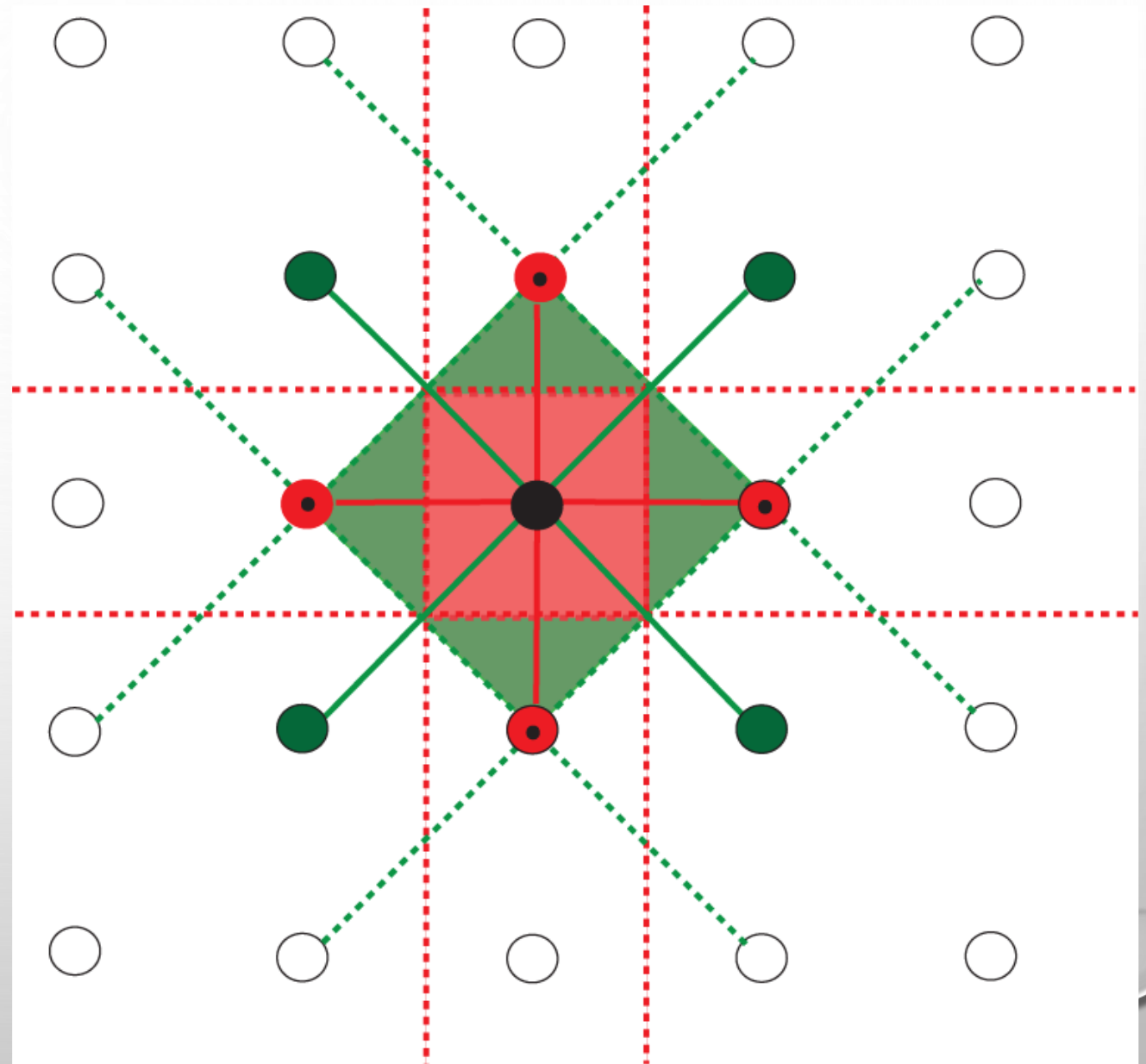


The second Brillouin Zone is the region of reciprocal space in which a point has one Bragg Plane between it and the origin.

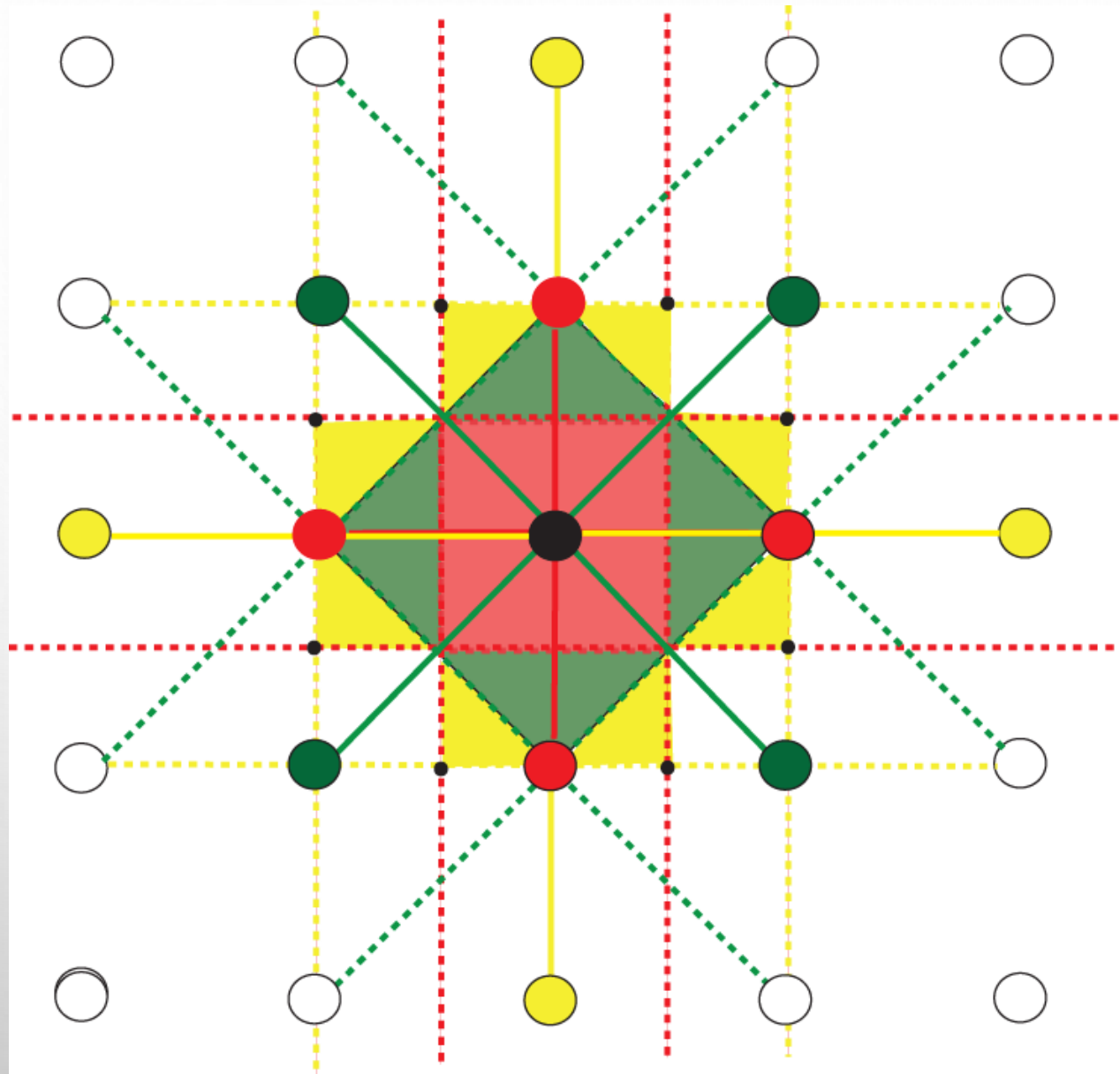
Note that the areas of the first and second Brillouin Zones are the same.

Small black dots represent point of intersection of Bragg planes

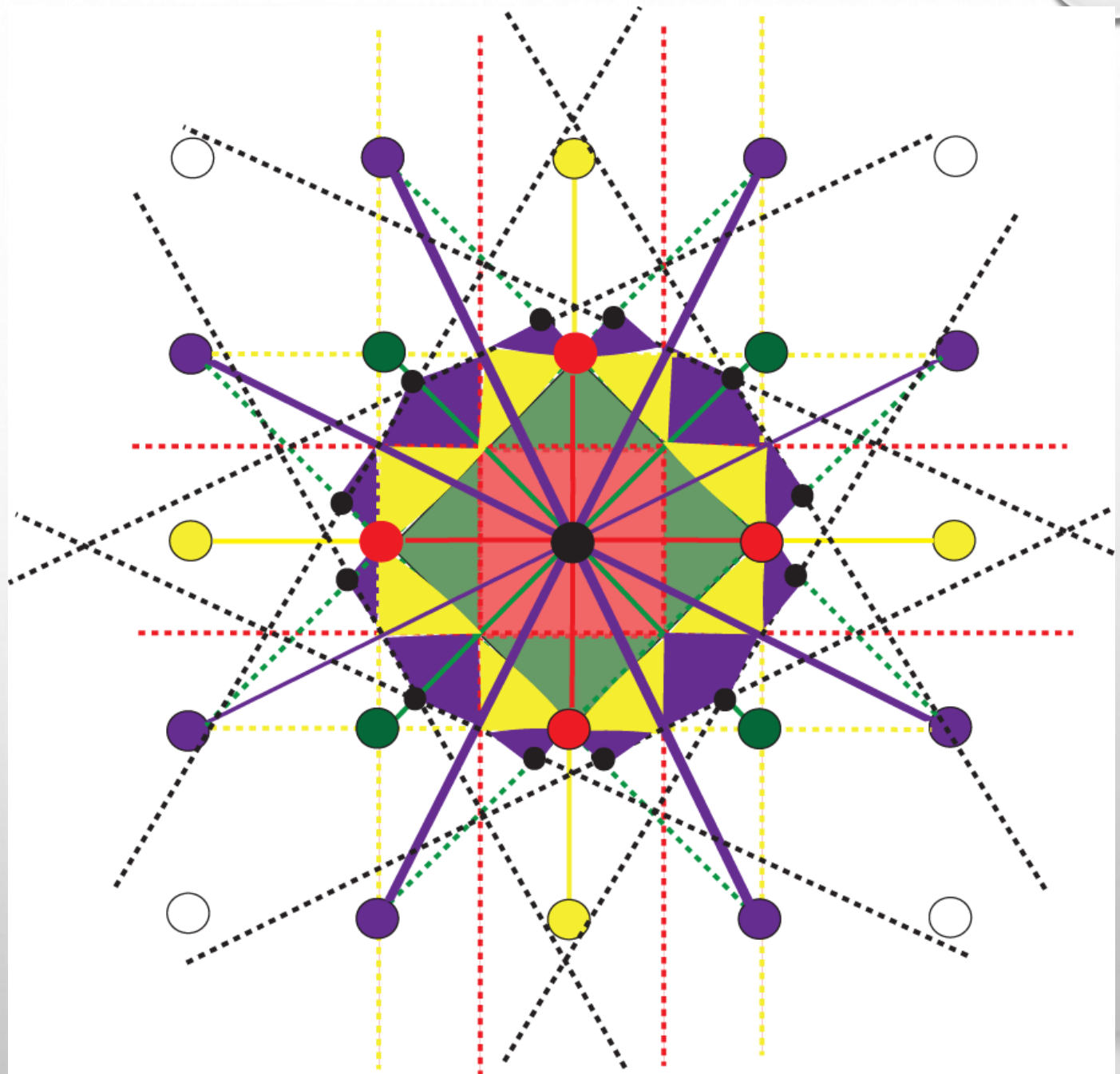
all BZs have exactly the same area/volume

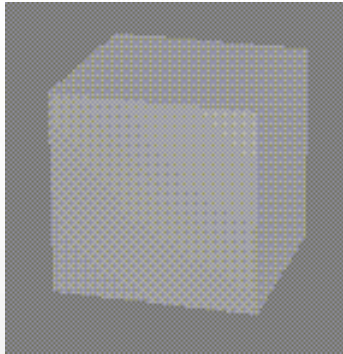


The construction can quite rapidly become complicated as you move beyond the first few zones, and it is important to be systematic so as to avoid missing out important Bragg Planes.

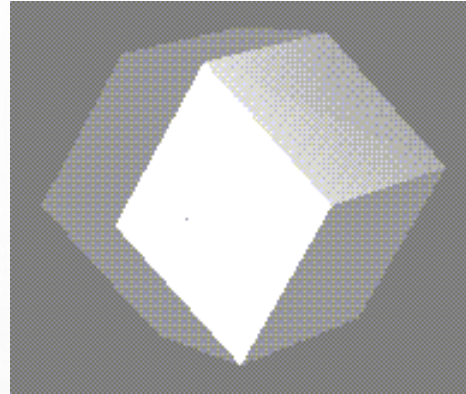


**Small black dots
represent point
of intersection of Bragg
planes**

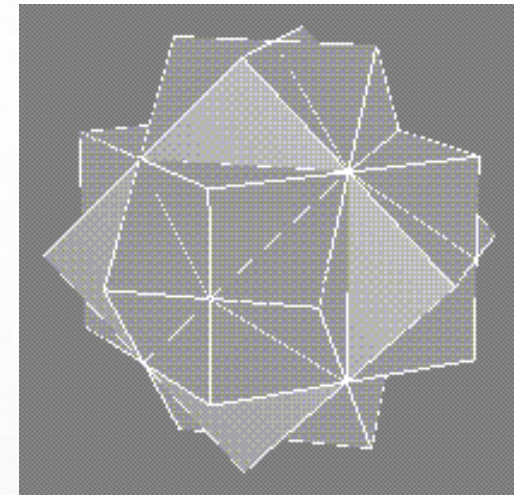




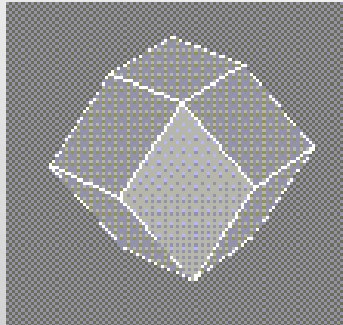
First BZ in SC



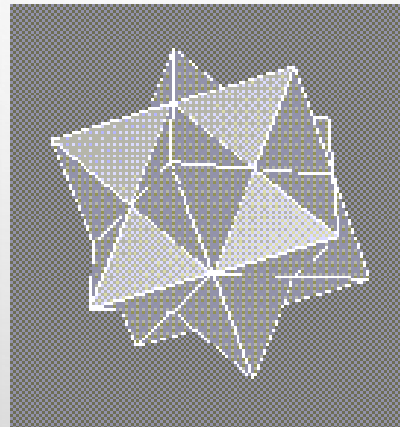
Second BZ in SC



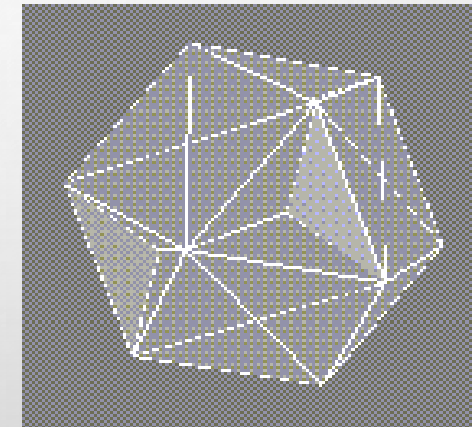
Third BZ in SC



First BZ in BCC

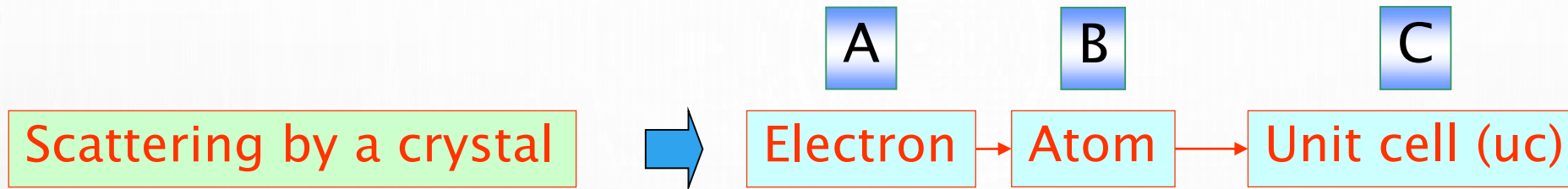


Second BZ in BCC



Second BZ in BCC

Structure Factor and Atomic Form Factor



Scattering by an atom is essentially the sum of the scattering of the electron cloud” around the nucleus.

- Because of the distance between electrons scattering within the atom and the fact that the x-ray wavelength is of the same order as the atomic dimensions, there will be path differences between the scattered waves. These differences will always be less than one wavelength, so the interference will always be partially destructive.
- This phenomenon is called the *atomic scattering factor*, described by the quantity f . At zero degrees, f will be equal to the number of electrons surrounding the atom or ion. At higher scattering angles, the factor will be less.

B

Scattering by an Atom

Scattering by an atom \propto [Atomic number, (path difference suffered by scattering from each e^- , λ)]

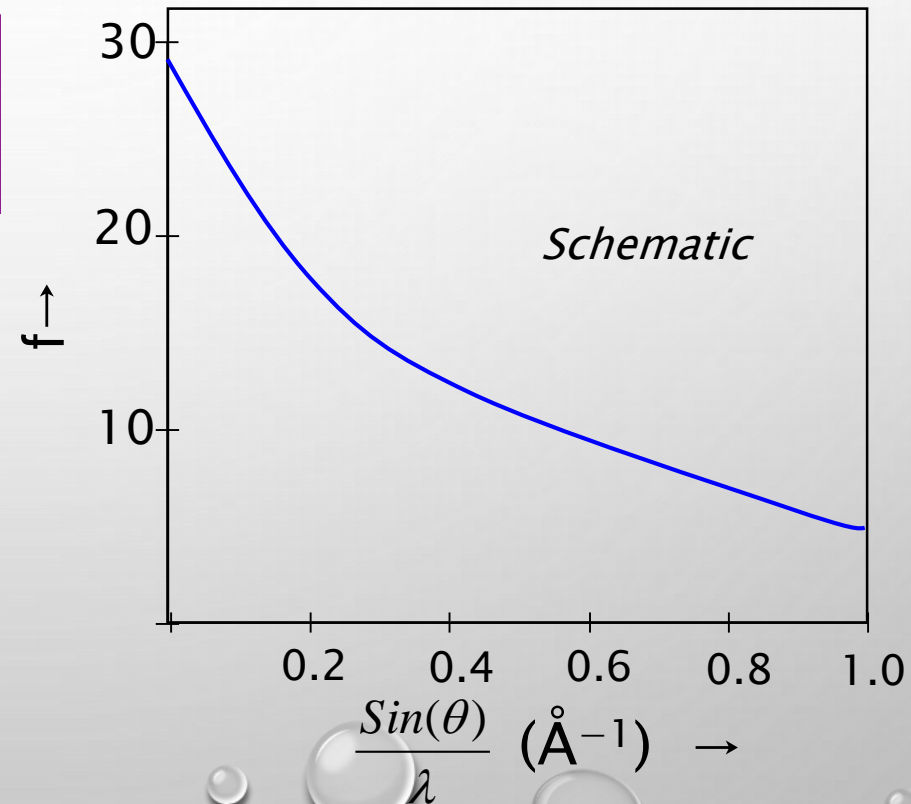
Scattering by an atom \propto [Z, (θ , λ)]

$$\frac{\sin(\theta)}{\lambda}$$

- *Angle of scattering leads to path differences*
- *In the forward direction all scattered waves are in phase*

f = Atomic Scattering Factor

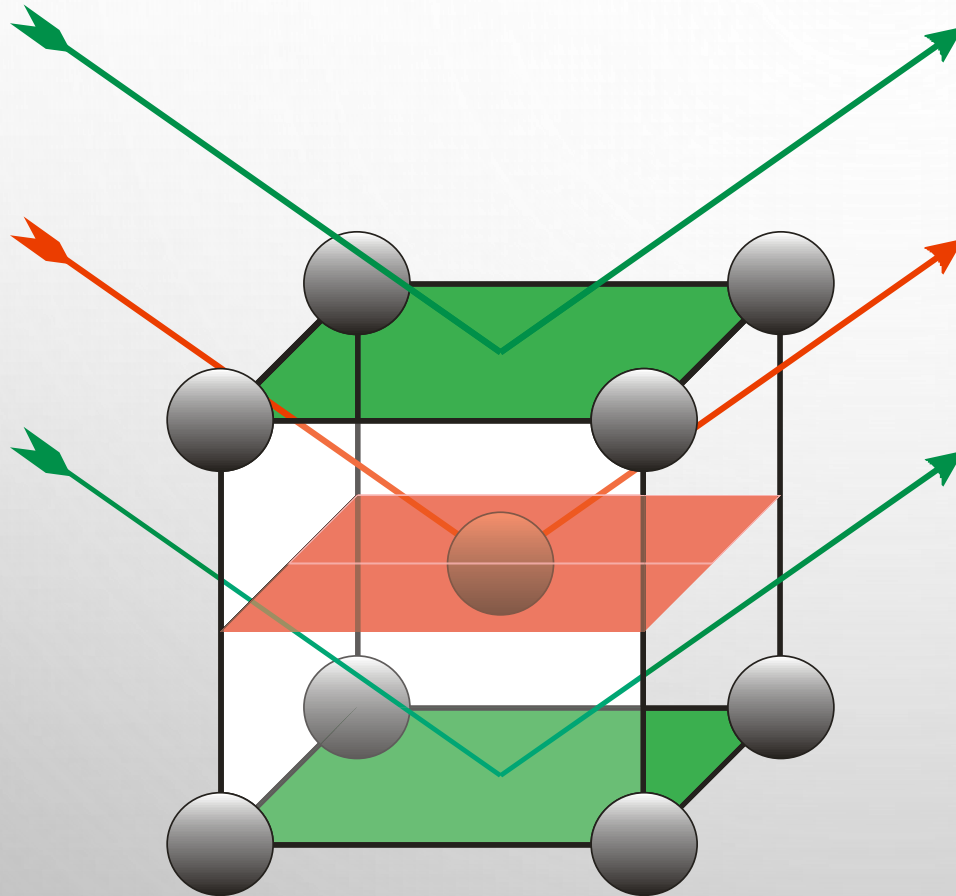
$$= \frac{\text{Amplitude of wave scattered by an atom}}{\text{Amplitude of wave scattered by an electron}}$$



C

Scattering by the Unit cell (uc)

- *Coherent Scattering*
- *Unit Cell (uc) representative of the crystal structure*
- *Scattered waves from various atoms in the uc interfere to create the diffraction pattern*



Structure Factor (F): The resultant wave scattered by all atoms of the unit cell

The wave scattered from the middle plane is out of phase with the ones scattered from top and bottom planes

- If atom B is different from atom A \rightarrow the amplitudes must be weighed by the respective atomic scattering factors (f)
- The resultant amplitude of all the waves scattered by all the atoms in the uc gives the scattering factor for the unit cell
- The unit cell scattering factor is called the **Structure Factor** (F)

Scattering by an unit cell = f(position of the atoms, atomic scattering factors)

$$F = \text{Structure Factor} = \frac{\text{Amplitude of wave scattered by all atoms in uc}}{\text{Amplitude of wave scattered by an electron}}$$

$$I \propto F^2$$

Structure factor (of the basis) \rightarrow

$$F = NS_{\vec{G}} \quad S_{\vec{G}} = \sum_j^s f_j e^{-2\pi i \vec{G} \cdot \vec{r}_j}$$

atomic form factor for the j -th atom

$$r_j = x_j \bar{a} + y_j \bar{b} + z_j \bar{c}$$

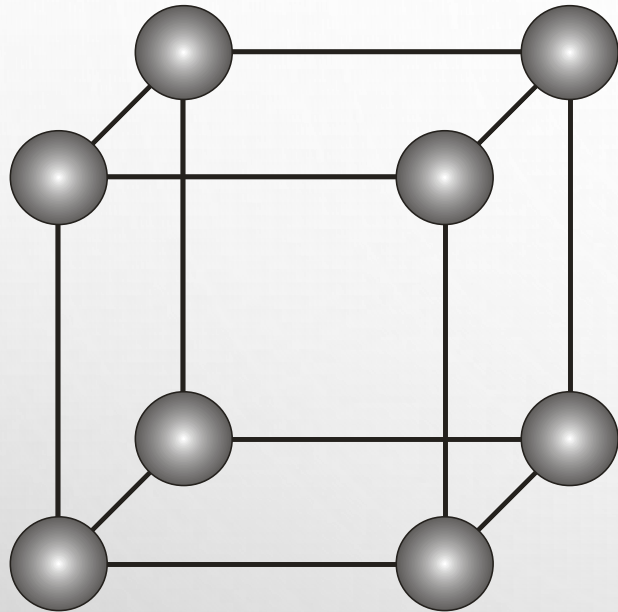
$$F_n^{hkl} = \sum_{j=1}^n f_j e^{-i[2\pi(h x'_j + k y'_j + l z'_j)]}$$

The **Structure Factor** is independent of the shape and size of the unit cell; but is dependent on the position of the atoms within the cell

Structure factor calculations

Simple Cubic

A Atom at (0,0,0) and equivalent positions



$$e^{ni\pi} = (-1)^n$$

$$e^{(odd\,n)i\pi} = -1$$

$$e^{(even\,n)i\pi} = +1$$

$$e^{ni\pi} = e^{-ni\pi}$$

$$\frac{e^{i\theta} + e^{-i\theta}}{2} = \cos(\theta)$$

$$F = f_j e^{i\varphi_j} = f_j e^{i[2\pi(h x'_j + k y'_j + h z'_j)]}$$

$$F = f e^{i[2\pi(h \cdot 0 + k \cdot 0 + h \cdot 0)]} = f e^0 = f$$

$$F^2 = f^2$$

$\Rightarrow F$ is independent of the scattering plane ($h\ k\ l$)

D Atom at (0,0,0) & (½, ½, 0) and equivalent positions

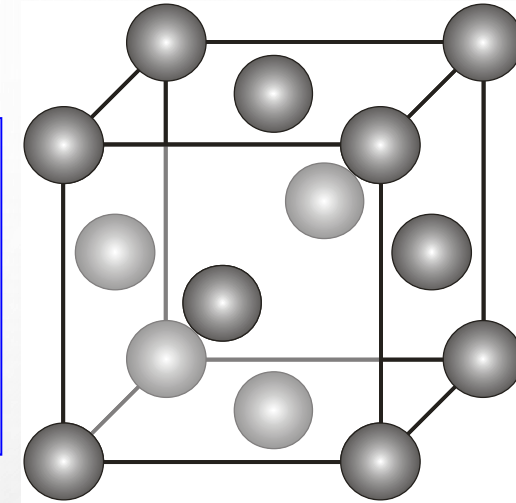
Face Centred Cubic

$$F = f_j e^{i\varphi_j} = f_j e^{i[2\pi(h x'_j + k y'_j + l z'_j)]}$$

$$F = f \left[e^{i[2\pi(0)]} + e^{i[2\pi(\frac{h+k}{2})]} + e^{i[2\pi(\frac{k+l}{2})]} + e^{i[2\pi(\frac{l+h}{2})]} \right]$$
$$= f [1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}]$$

Real

(½, ½, 0), (½, 0, ½), (0, ½, ½)



$$F = f [1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}]$$

(h, k, l) unmixed

$$F = 4f$$

$$F^2 = 16f^2$$

e.g. (111), (200), (220), (333), (420)

(h, k, l) mixed

$$F = 0$$

$$F^2 = 0$$

e.g. (100), (211); (210), (032), (033)

Two odd and one even (e.g. 112); two even and one odd (e.g. 122)

E

Na⁺ at (0,0,0) + Face Centering Translations $\rightarrow (\frac{1}{2}, \frac{1}{2}, 0), (\frac{1}{2}, 0, \frac{1}{2}), (0, \frac{1}{2}, \frac{1}{2})$
 Cl⁻ at $(\frac{1}{2}, 0, 0)$ + FCT $\rightarrow (0, \frac{1}{2}, 0), (0, 0, \frac{1}{2}), (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

NaCl:
Face Centred Cubic

$$F = f_{Na^+} \left[e^{i[2\pi(0)]} + e^{i[2\pi(\frac{h+k}{2})]} + e^{i[2\pi(\frac{k+l}{2})]} + e^{i[2\pi(\frac{l+h}{2})]} \right] +$$

$$f_{Cl^-} \left[e^{i[2\pi(\frac{h}{2})]} + e^{i[2\pi(\frac{k}{2})]} + e^{i[2\pi(\frac{l}{2})]} + e^{i[2\pi(\frac{h+k+l}{2})]} \right]$$

$$F = f_{Na^+} [1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}] +$$

$$f_{Cl^-} [e^{i\pi(h)} + e^{i\pi(k)} + e^{i\pi(l)} + e^{i\pi(h+k+l)}]$$

$$F = f_{Na^+} [1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}] +$$

$$f_{Cl^-} e^{i\pi(h+k+l)} [e^{i\pi(-k-l)} + e^{i\pi(-l-h)} + e^{i\pi(-h-k)} + 1]$$

$$F = [f_{Na^+} + f_{Cl^-} e^{i\pi(h+k+l)}] [1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}]$$

$$F = [f_{Na^+} + f_{Cl^-} e^{i\pi(h+k+l)}] [1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}]$$

Zero for mixed indices

(h, k, l) mixed $\longrightarrow F = 0 \longrightarrow F^2 = 0$ e.g. (100), (211); (210), (032), (033)

(h, k, l) unmixed $\longrightarrow F = 4[f_{Na^+} + f_{Cl^-} e^{i\pi(h+k+l)}]$

$F = 4[f_{Na^+} + f_{Cl^-}] \longrightarrow$ If (h + k + l) is even $\longrightarrow F^2 = 16[f_{Na^+} + f_{Cl^-}]^2$

$F = 4[f_{Na^+} - f_{Cl^-}] \longrightarrow$ If (h + k + l) is odd $\longrightarrow F^2 = 16[f_{Na^+} - f_{Cl^-}]^2$

\Rightarrow Presence of additional atoms/ions/molecules in the uc (as a part of the motif) can alter the intensities of some of the reflections

Crystal structure determination

Monochromatic X-rays

Many θ s (orientations)
Powder specimen

POWDER
METHOD

Panchromatic X-rays

Single θ

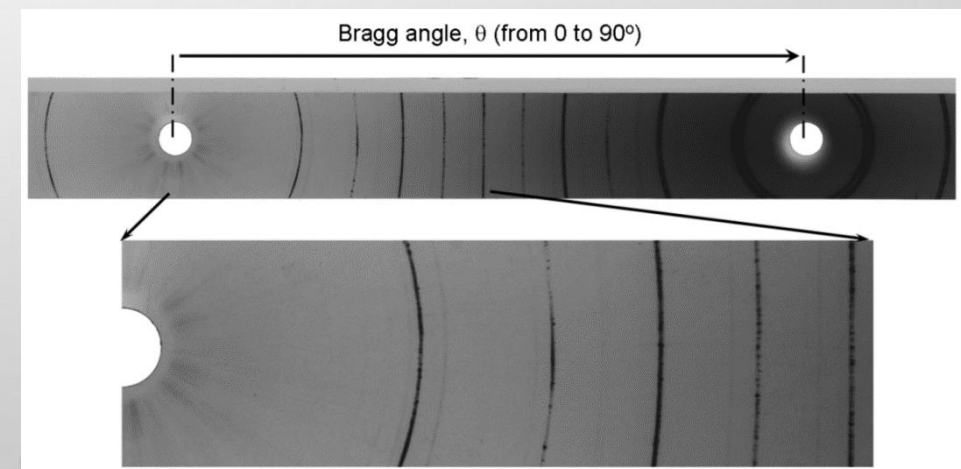
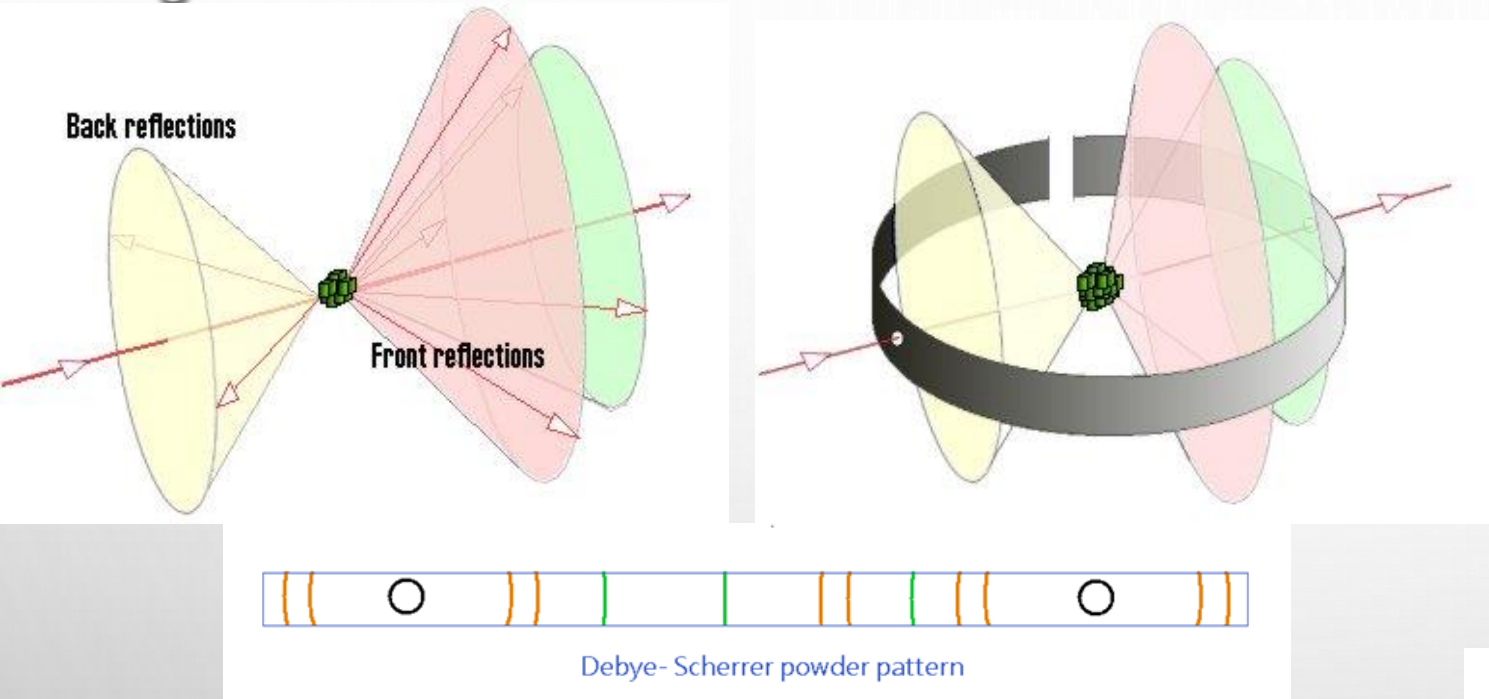
LAUE
TECHNIQUE

Monochromatic X-rays

θ Varied by rotation

ROTATING
CRYSTAL
METHOD

Powder Method (Debye-Scherrer geometry)



- If a **powdered crystal** is used, then there is *no need to rotate* it, because there will always be some small crystals at an orientation for which diffraction is permitted. here a monochromatic x-ray beam is incident on a powdered or polycrystalline sample.
- Useful for samples that are difficult to obtain in single crystal form.
- The powder method is used to determine the **lattice parameters** accurately. lattice parameters are the magnitudes of the primitive vectors **a, b and c** which define the unit cell for the crystal.
- For every set of crystal planes, by chance, one or more crystals will be in the correct orientation to give the correct Bragg angle to satisfy Bragg's equation. every crystal plane is thus capable of diffraction.
- Each diffraction line is made up of a large number of small spots, each from a separate crystal. each spot is so small as to give the appearance of a continuous line.

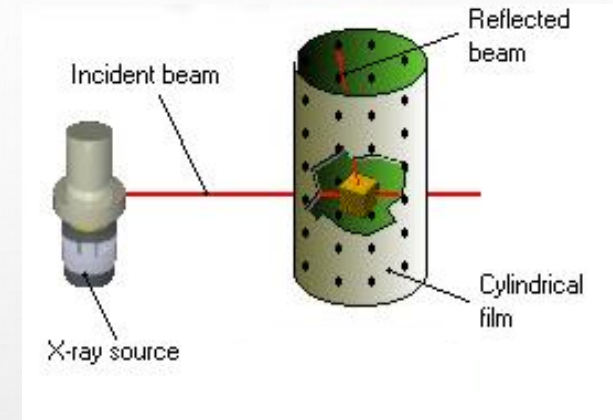
Important advantages and uses of powder diffraction:

1. The need to grow crystals is eliminated.
2. A powder diffraction pattern can be recorded very rapidly and the technique is non-destructive.
3. With special equipment very small samples may be used (1-2mg.)
4. A powder diffraction pattern may be used as a fingerprint. It is often superior to an infrared spectrum in this respect.
5. It can be used for the qualitative, and often the quantitative, determination of the **crystalline components** of a powder mixture.
6. Powder diffractometry provides an easy and fast method for the detection of crystal polymorphs. (Polymorphs are different crystal forms of the same substance.)

Rotating Crystal Method

In the rotating crystal method, a **single crystal** is mounted with an axis normal to a **monochromatic** x-ray beam. A cylindrical film is placed around it and the crystal is rotated about the chosen axis. As the crystal rotates, sets of lattice planes will at some point make the correct Bragg angle for the monochromatic incident beam, and at that point a diffracted beam will be formed.

The reflected beams are located on the surface of imaginary cones. When the film is laid out flat, the diffraction spots lie on horizontal lines.



The reflected beams are located on the surfaces of imaginary cones. By recording the diffraction patterns (both angles & intensities) for various crystal orientations, one can determine the **shape & size of unit cell** as well as the **arrangement of atoms** inside the cell.

Laue Method

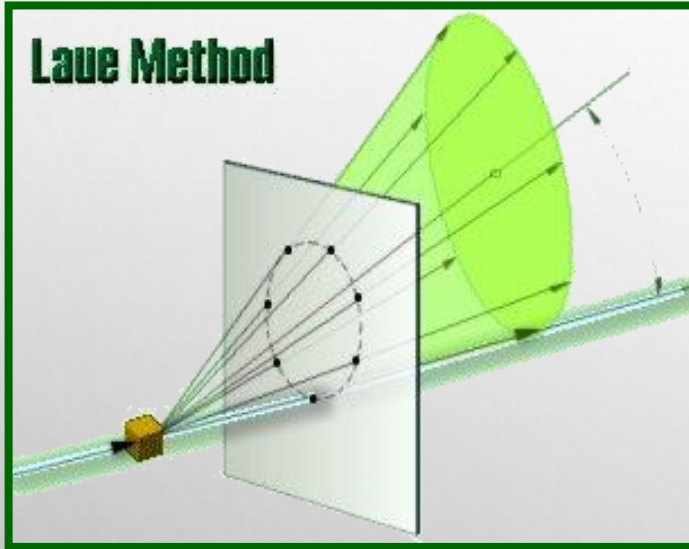
- The laue method is mainly used to **determine the orientation of large single crystals** while radiation is reflected from, or transmitted through a **fixed crystal**.
- The diffracted beams form arrays of spots, that lie on curves on the film.
- ***The Bragg angle is fixed***
for every set of planes in the crystal. each set of planes picks out & diffracts the particular wavelength from the white radiation that *satisfies the Bragg law for the values of d & θ* involved.
- The symmetry of the Laue spot pattern reflects *the symmetry of the crystal when viewed along the direction of the incident beam.*

- The Laue method is often used to determine the orientation of single crystals by illuminating the crystal with a continuous spectrum of X-Rays.

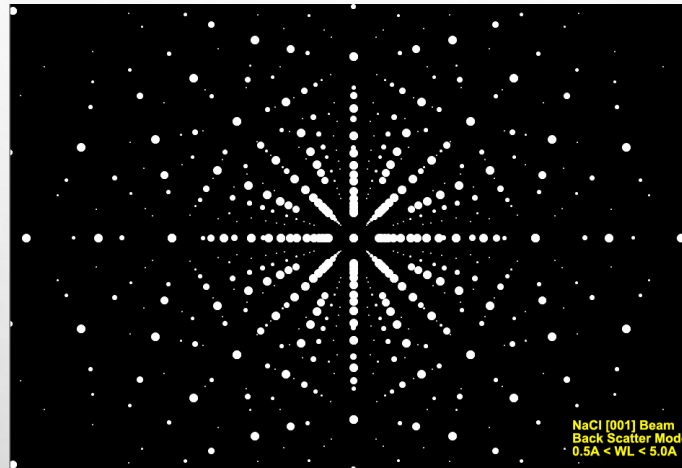
Single Crystals

Continuous Spectrum of X-Rays *Symmetry & Orientation of Crystals*

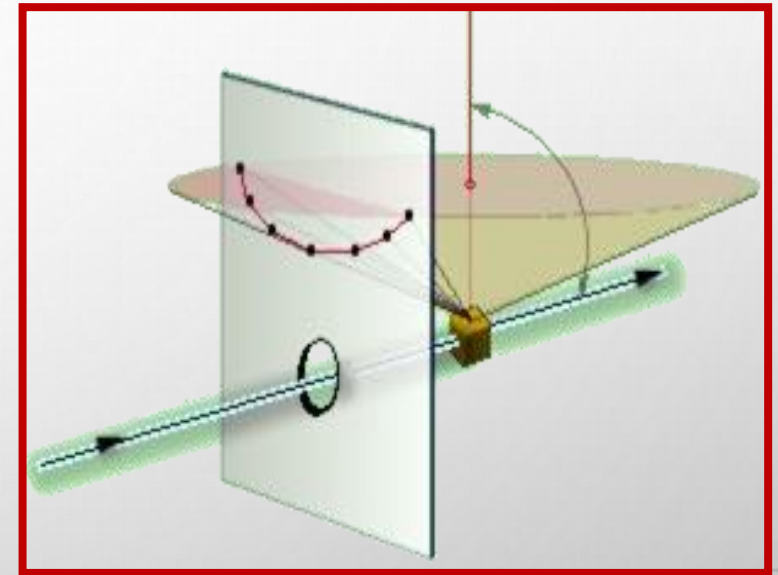
Transmission Laue Method



The film is placed behind the crystal to record beams which are transmitted through the crystal.



Back-Reflection Laue Method



The film is placed *between* the x-ray source and the crystal. the beams which are diffracted in a backward direction are recorded.

Diffraction By Electron and Neutron

- Other radiation sources than **X-Rays**, such as **neutrons** or **electrons** can also be used in crystal diffraction experiments.
- The physical basis for the diffraction of **electrons** or **neutrons** is the same as that for the diffraction of **X Rays**. The only difference is in the mechanism of scattering.

Complementarity of the three types of radiation

X-ray diffraction



- Photon energies 10keV-100keV
 - large penetration depth
 - 3D crystal structure
- scattering by electron density
 - best results for atoms with high Z

Electron diffraction



- Charged particle
 - “strong” interaction with matter
 - low penetration depth
- Study of: surfaces
thin films

Neutron diffraction



- Interaction with nuclei
 - Improved efficiency for light atoms
 - Inelastic scattering: phonons
- Magnetic moment interacts with moment of electrons
 - Magnetic scattering: Structure, magnons

Neutron Diffraction

- it is an important tool in the investigation of the magnetic ordering that occurs in some materials.
- light atoms such as **h** are better resolved in a neutron pattern because, having only a few electrons to scatter the **x-rays**, they do not contribute significantly to an **x-ray** diffraction pattern.
- because **they are neutral**, *neutrons do not interact with electrons in the crystal*. so, unlike x-rays, which are scattered entirely by electrons, neutrons are scattered entirely by nuclei.
- although uncharged, neutrons have **an intrinsic magnetic moment**, ***so they will interact strongly with atoms & ions in the crystal which also have a magnetic moment.***
- neutrons are more useful than x-rays for determining the crystal structures of solids containing light elements.
- neutron sources in the world are limited so neutron diffraction is a very special tool & is very expensive.

Electron Diffraction

It has also been used in the analysis of crystal structure. The electron, like the neutron, possesses **wave-like properties**:

Of course, electrons are **charged** & so interact strongly with all atoms. So electrons with an energy of a few eV are completely *absorbed by the crystal*.

- in order to enable an electron beam to penetrate into a crystal, it must have a very high energy (50 keV to 1 MeV). in addition, the crystal must be thin (100–1000 nm).
- If low electron energies are used, the penetration depth will be very small (only about 50 Å), & the beam will be reflected from the surface. consequently, electron diffraction is a useful technique for surface structure studies.
- Electrons are scattered strongly in air, so diffraction experiments must be carried out high vacuum. this brings complication and it is expensive as well.

Advantages & Disadvantages of XRD Compared to Other Methods

advantages

- **x-rays** are the least expensive, the most convenient & the most widely used method to determine crystal structures.
- **x-rays** are not absorbed very much by air, so the sample need not be in an evacuated chamber.

disadvantages

- **x-rays** do not interact very strongly with lighter elements.