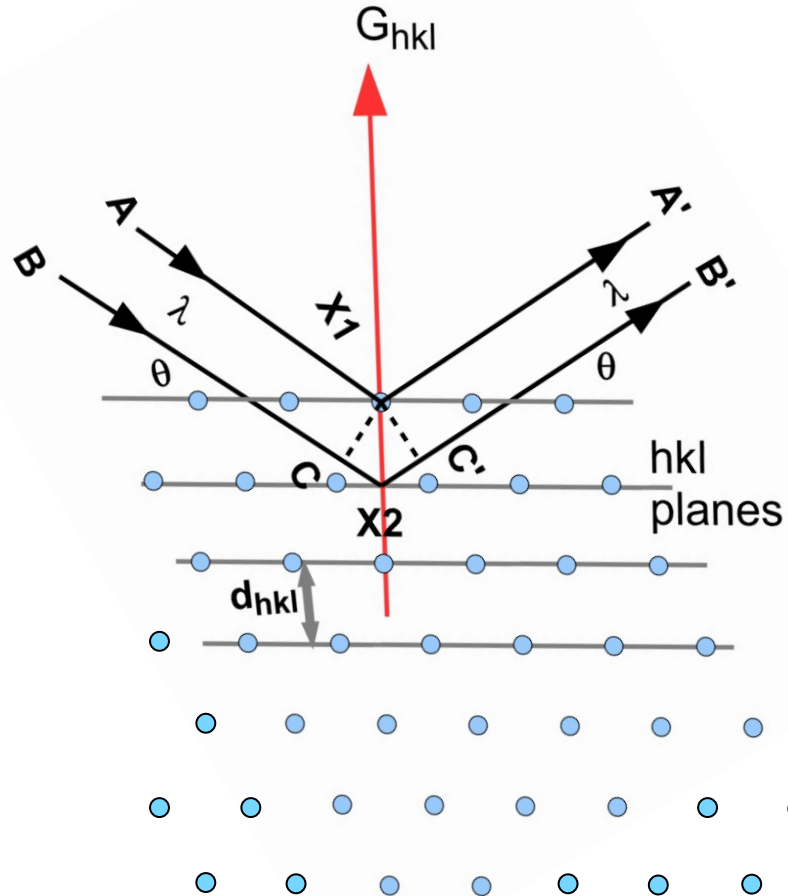


Reciprocal Lattice and X-ray Diffraction



A diffraction pattern of a crystal is a map of the reciprocal lattice of the crystal.

Reciprocal Lattice

- The reciprocal lattice is defined as the set of all wave vectors $\mathbf{K}$'s that yield plane waves with the periodicity of a given Bravais lattice.
- Let $\mathbf{R}$ denotes a Bravais lattice point; consider a plane wave $\exp(i\mathbf{k}\cdot\mathbf{r})$. This will have the periodicity of the lattice if the wave vector $\mathbf{k}=\mathbf{G}$, such that

$$\exp(i\mathbf{G}\cdot(\mathbf{r}+\mathbf{R}))=\exp(i\mathbf{G}\cdot\mathbf{r})$$

for any $\mathbf{r}$ and all $\mathbf{R}$ Bravais lattice.

- Thus the reciprocal lattice vectors $\mathbf{G}$ must satisfy
$$\exp(i\mathbf{G}\cdot\mathbf{R})=1$$

Reciprocal Lattice Vector in 1D

In one dimension with a period of a in x , we have

$$n(x+a) = n(x)$$

expand $n(x)$ in Fourier series of sines and cosines:

$$n(x) = n_0 + \sum_{p>0} [C_p \cos(2\pi p x/a) + S_p \sin(2\pi p x/a)]$$

In more compact form

$$n(x) = \sum_p n_p \exp(i2\pi p x/a)$$

To ensure that $n(x)$ is a real function, we require

$$n_{-p}^* = n_p$$

Fourier coefficient: $n_p = a^{-1} \int_0^a dx n(x) \exp(-i2\pi px/a)$

Since $n(x) = \sum_p n_p \exp(i2\pi px/a)$

$$n_p = a^{-1} \sum_{p'} n_{p'} \int_0^a dx \exp[i2\pi(p' - p)x/a]$$

If $p' \neq p$ the value of the integral is

$$\frac{a}{i2\pi(p' - p)} (e^{i2\pi(p' - p)} - 1) = 0$$

If $p' = p$, $n_p = a^{-1} n_{p'} a = n_{p'}$

We say that $2\pi p/a$ is a point in the reciprocal lattice or Fourier space of the crystal. The reciprocal lattice points tell us the allowed terms in the Fourier series, which is consistent with the periodicity of the crystal.

Reciprocal Lattice Vectors in 3D

If $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are primitive vectors of the crystal lattice, then $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ are **primitive vectors of the reciprocal lattice**.

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} ; \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} ; \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} .$$

Here

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij} \text{ where } \delta_{ij} = 1 \text{ if } i = j \text{ and } \delta_{ij} = 0 \text{ if } i \neq j.$$

Points in the reciprocal lattice are mapped by the set of vectors

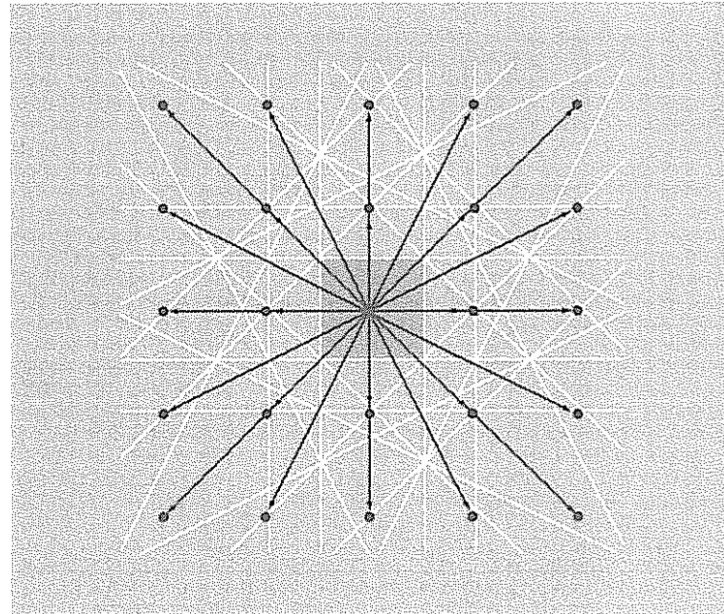
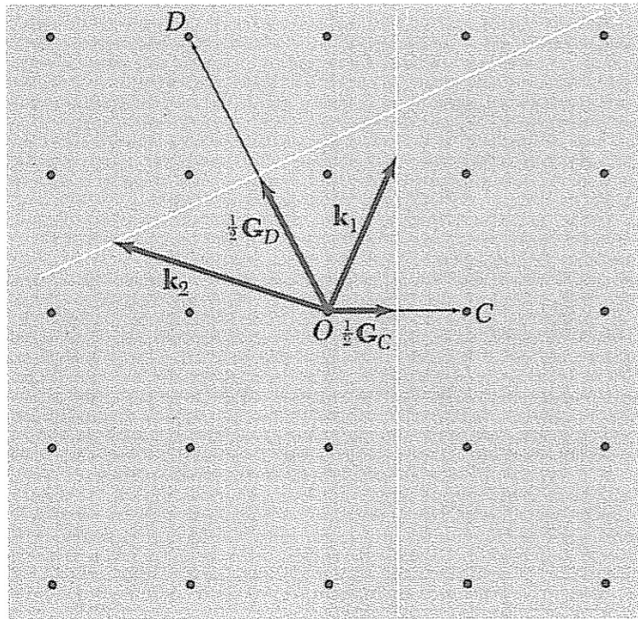
$$\mathbf{G} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3 ,$$

where v_1, v_2, v_3 are integers. A vector $\mathbf{G}$ of this form is a **reciprocal lattice vector**.

Brillouin Zone

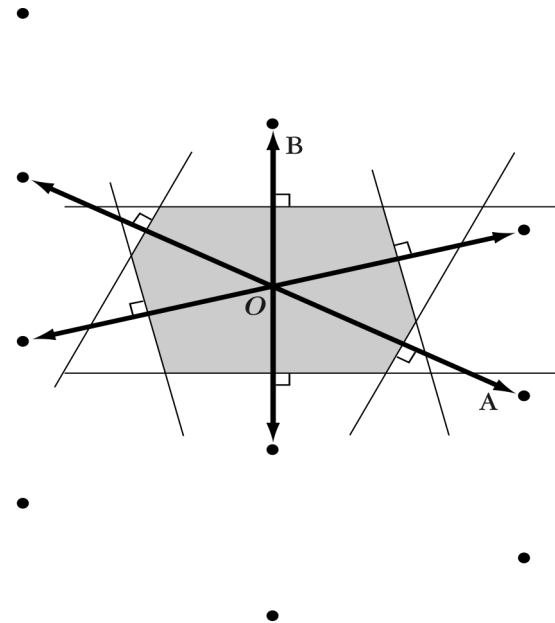
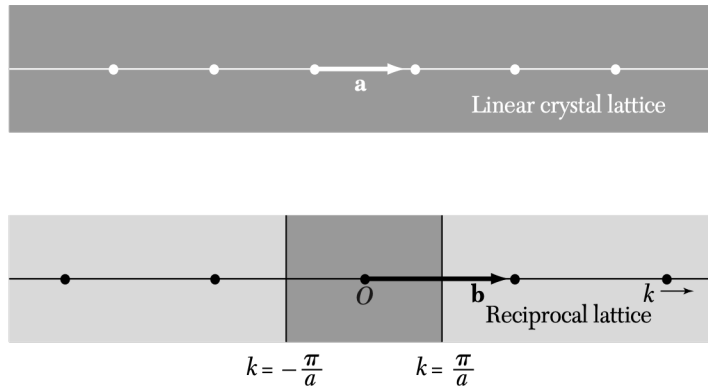
A Brillouin zone is defined as a Wigner-Seitz cell in the reciprocal lattice.

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

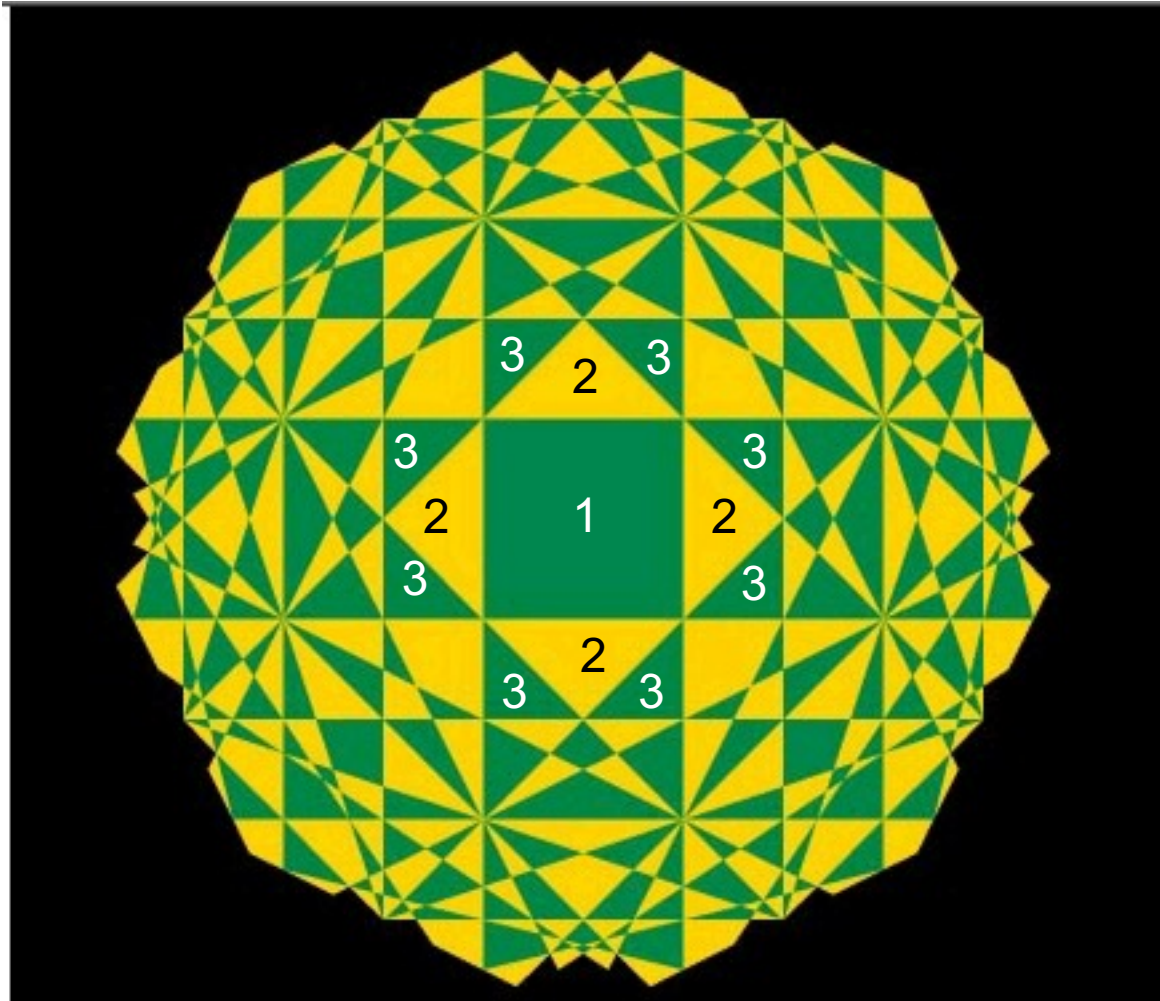


Brillouin Zone in 1D and 2D

The central cell in the reciprocal lattice is of special importance in the theory of solids, and we call it the first Brillouin zone. *The first Brillouin zone is the smallest volume entirely enclosed by planes that are the perpendicular bisectors of the reciprocal lattice vectors drawn from the origin.*



All Brillouin Zones: Square Lattice



Reciprocal Lattice to bcc Lattice

$$\mathbf{a}_1 = \frac{1}{2}a(-\hat{x} + \hat{y} + \hat{z}) ; \quad \mathbf{a}_2 = \frac{1}{2}a(\hat{x} - \hat{y} + \hat{z}) ; \quad \mathbf{a}_3 = \frac{1}{2}a(\hat{x} + \hat{y} - \hat{z})$$

$$\mathbf{b}_1 = (2\pi/a)(\hat{y} + \hat{z}) ; \quad \mathbf{b}_2 = (2\pi/a)(\hat{x} + \hat{z}) ; \quad \mathbf{b}_3 = (2\pi/a)(\hat{x} + \hat{y})$$

An fcc lattice is the reciprocal lattice of the bcc lattice.

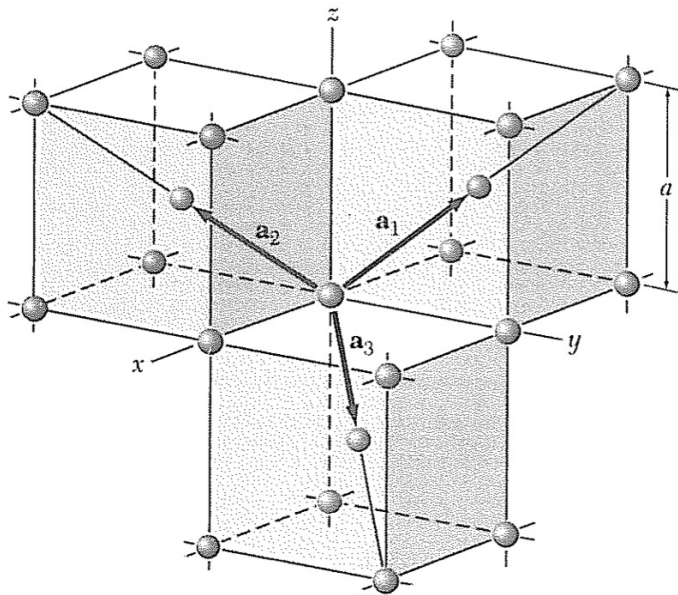


Figure 12 Primitive basis vectors of the body-centered cubic lattice.

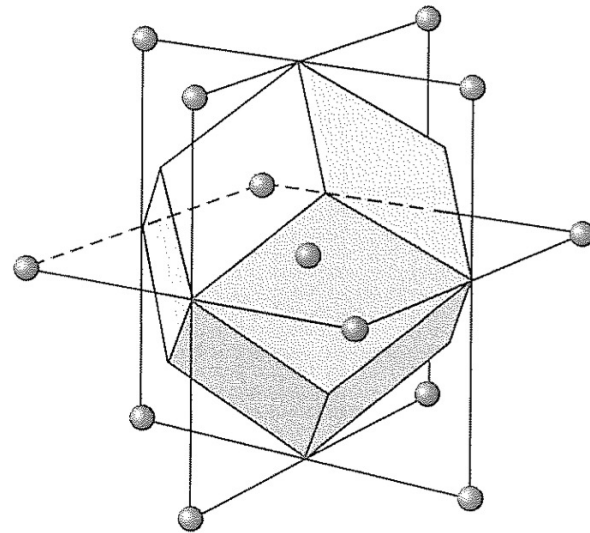


Figure 13 First Brillouin zone of the body-centered cubic lattice. The figure is a regular rhombic dodecahedron.

Reciprocal Lattice to fcc Lattice

$$\mathbf{a}_1 = \frac{1}{2}a(\hat{\mathbf{y}} + \hat{\mathbf{z}}) ; \quad \mathbf{a}_2 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{z}}) ; \quad \mathbf{a}_3 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}}) .$$

$$\mathbf{b}_1 = (2\pi/a)(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) ; \quad \mathbf{b}_2 = (2\pi/a)(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}) ;$$

$$\mathbf{b}_3 = (2\pi/a)(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) .$$

A bcc lattice is the reciprocal lattice of the fcc lattice.

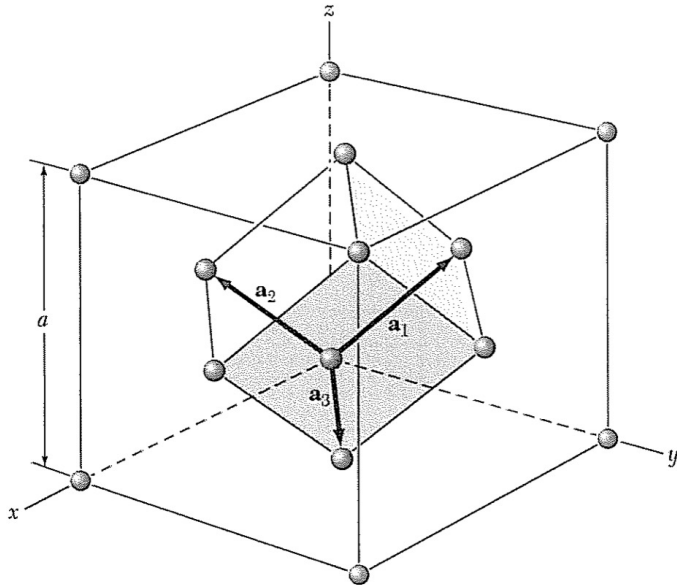


Figure 14 Primitive basis vectors of the face-centered cubic lattice.

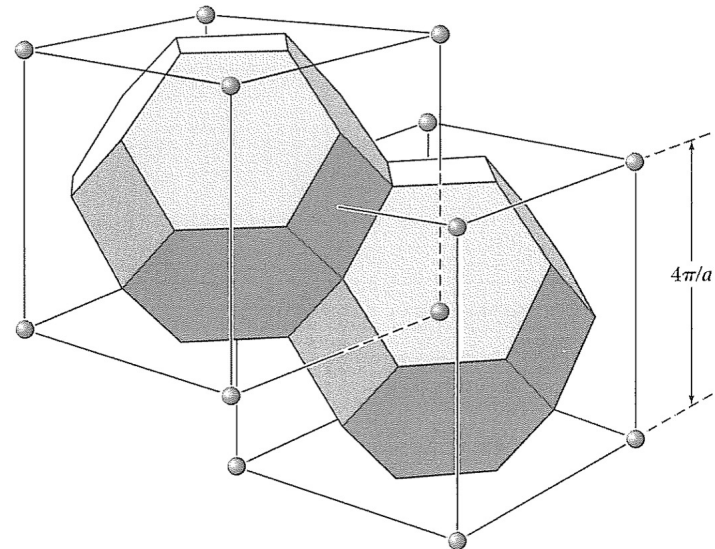
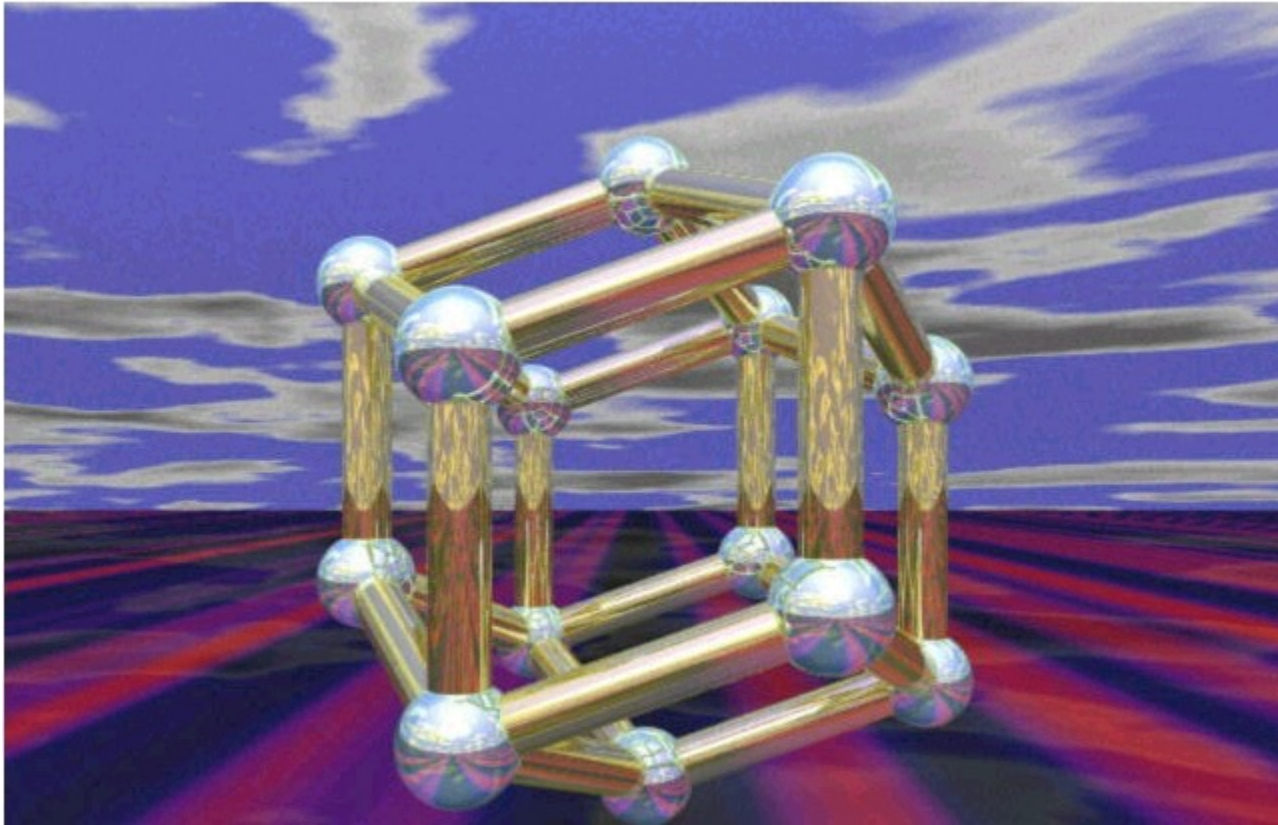
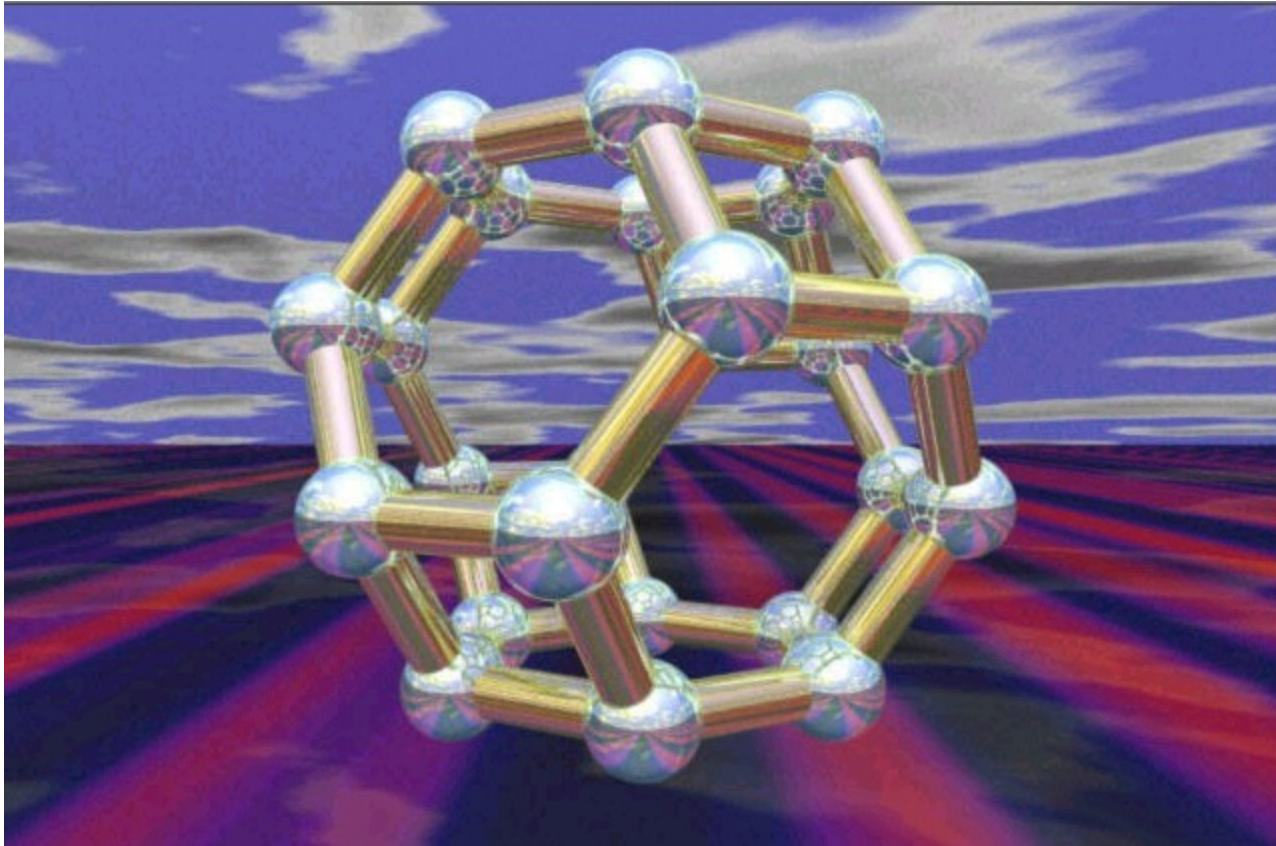


Figure 15 Brillouin zones of the face-centered cubic lattice.

First Brillouin Zone for fcc

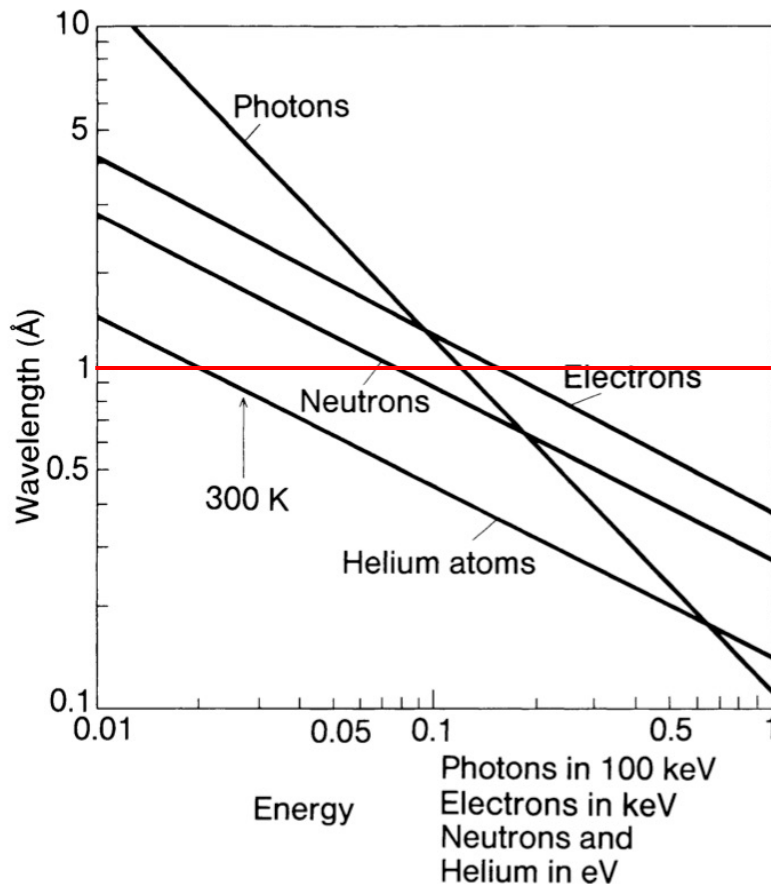


First Brillouin Zone for bcc



Wavelength vs particle energy

de Broglie wavelength $\lambda = h/P = h/(2mE)^{1/2}$



$$\lambda (\text{\AA}) = 12.4/E (\text{keV}) \text{ for photon}$$

$$\lambda (\text{\AA}) = [150/E (\text{eV})]^{1/2} \text{ for electron}$$

$$\lambda (\text{\AA}) = [82/E (\text{meV})]^{1/2} \text{ for neutron}$$

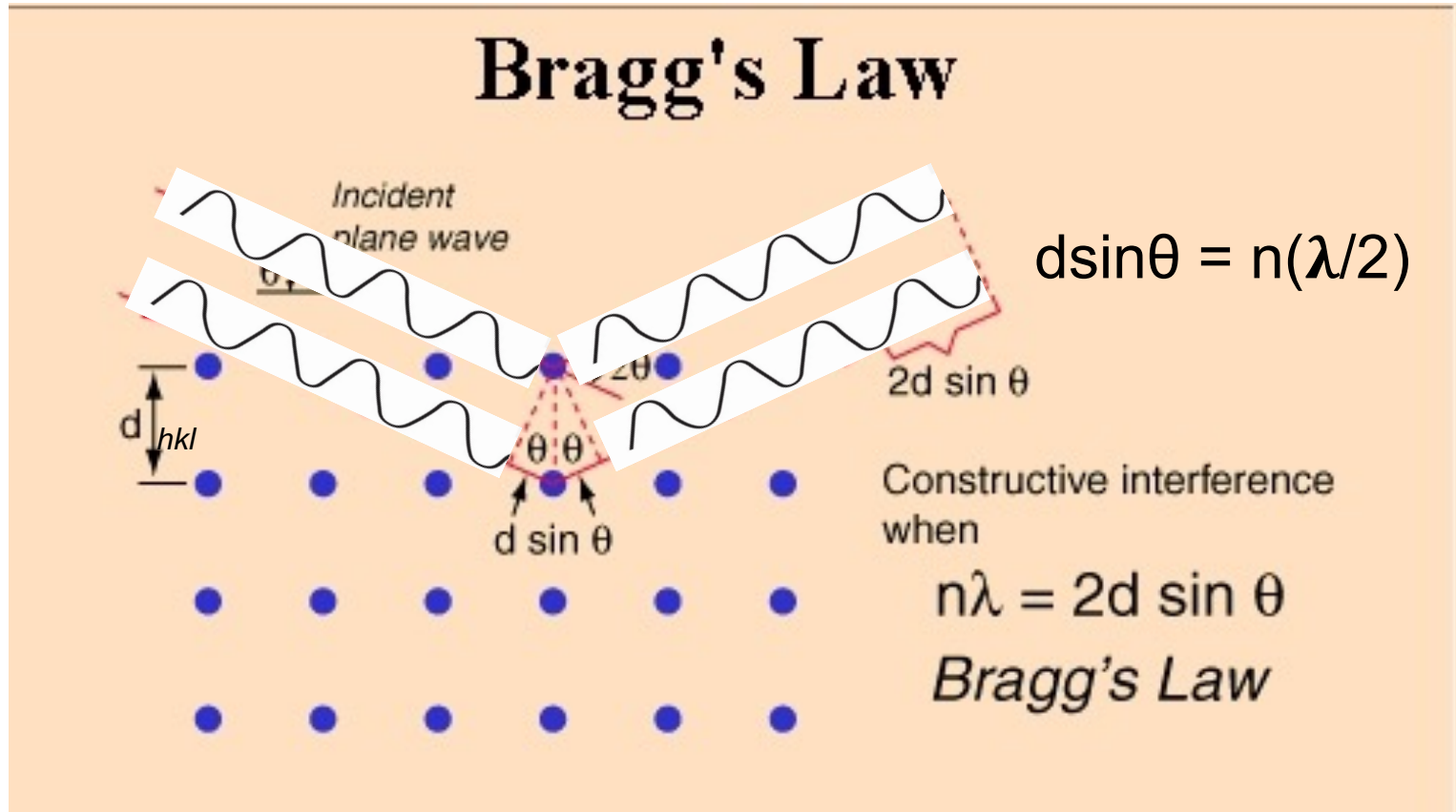
X-ray Diffraction

Typical interatomic distances in solid are of the order of an angstrom. Thus the typical wavelength of an electromagnetic probe of such distances must be of the order of an angstrom.

$$E = hc / \lambda \quad \lambda \text{ (\AA)} = 12.4/E \text{ (keV)}$$

Upon substituting this value for the wavelength into the energy equation, we find that E is of the order of 12 thousand eV, which is a typical X-ray energy. Thus X-ray diffraction of crystals is a standard probe.

Bragg Diffraction: Bragg's Law

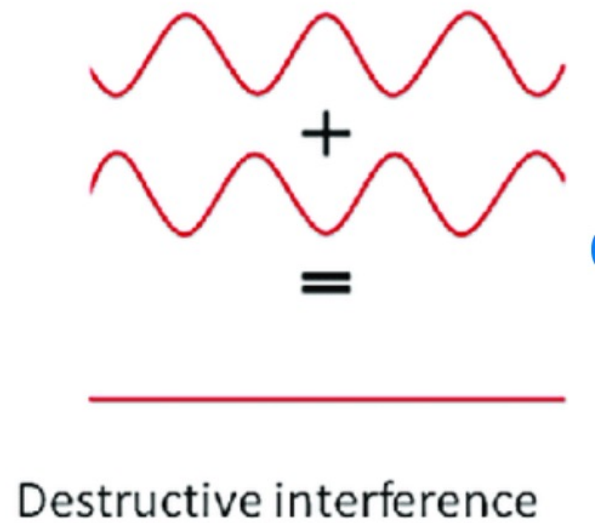
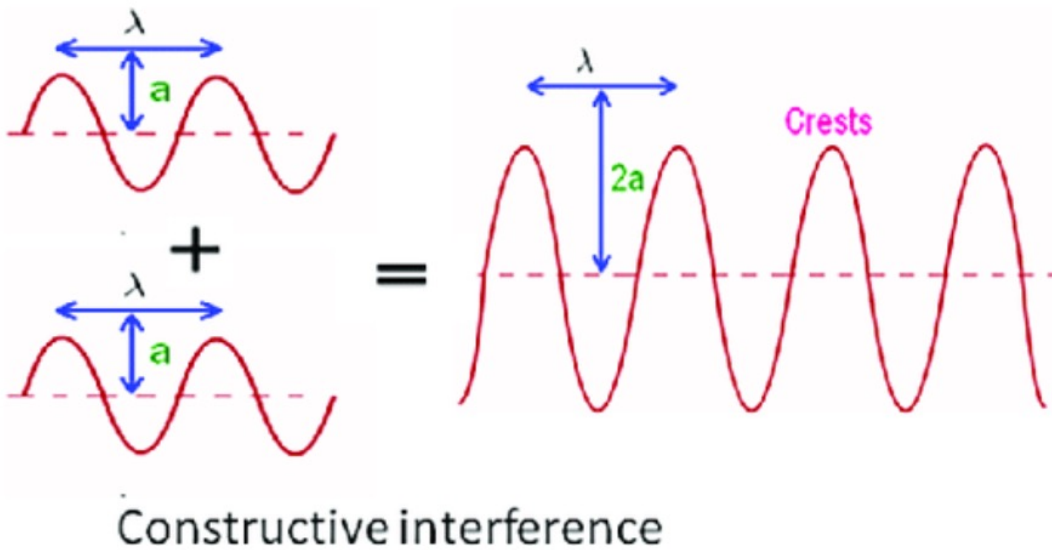


Planes with Miller index (hkl) has the interplane distance d_{hkl} :

$$d_{hkl} = a/(h^2+k^2+l^2)^{1/2}$$

$$n\lambda = 2d_{hkl} \sin \theta_{hkl}$$

Condition for Interferences



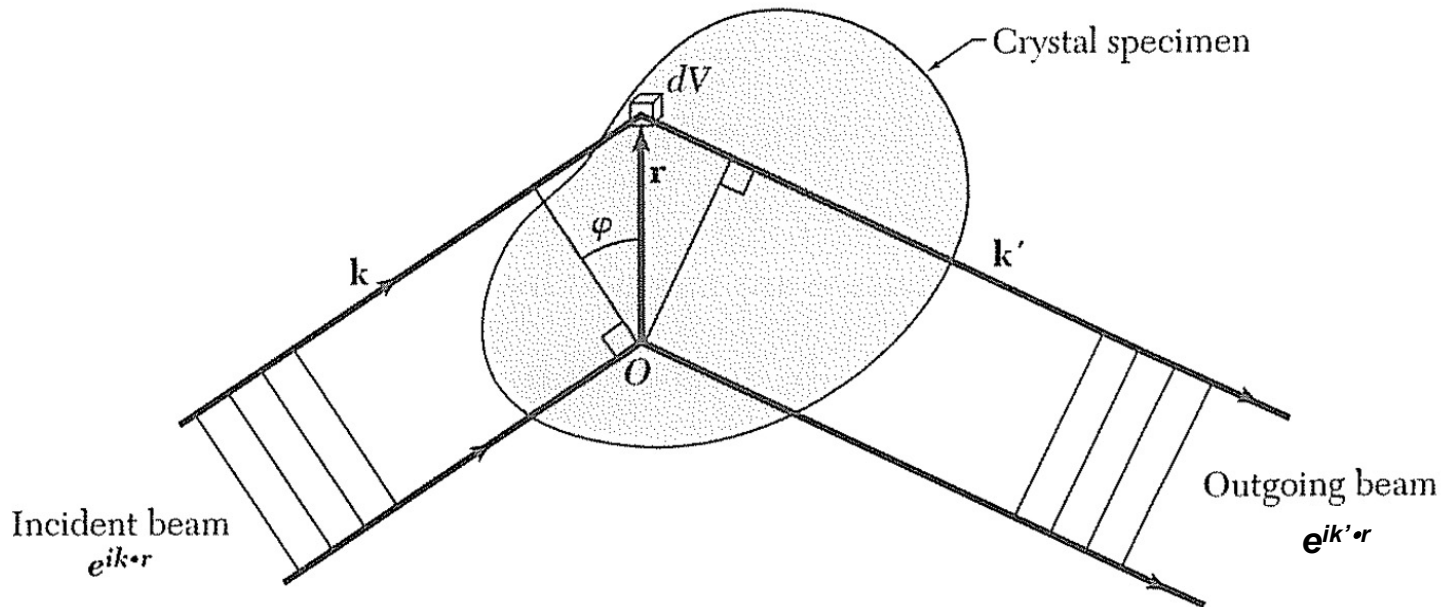
Diffraction Conditions

Every crystal structure has two lattices associated with it, the crystal lattice and the reciprocal lattice. A diffraction pattern of a crystal is a map of the reciprocal lattice of the crystal.

Theorem: The set of reciprocal lattice vectors $\mathbf{G}$ s determines the possible x-ray reflections.

Scattering Amplitude of X-Ray Diffraction

$$F = \int dV n(\mathbf{r}) \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}] = \int dV n(\mathbf{r}) \exp(-i\Delta\mathbf{k} \cdot \mathbf{r}) ,$$



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

$n(\mathbf{r})$: Electron number density at $\mathbf{r}$

The periodic function of electron number density $n(\mathbf{r})$ can be expressed as

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r})$$

the scattering amplitude

$$F = \sum_{\mathbf{G}} \int dV n_{\mathbf{G}} \exp[i(\mathbf{G} - \Delta\mathbf{k}) \cdot \mathbf{r}]$$

When the scattering vector $\Delta\mathbf{k}$ is equal to a particular reciprocal lattice vector,

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

$$\Delta\mathbf{k} = \mathbf{G} ,$$

the argument of the exponential vanishes and $F = Vn_{\mathbf{G}}$.

The diffraction condition is $\mathbf{k}' = \mathbf{k} + \mathbf{G}$.

In elastic scattering $k'^2 = k^2$, so the diffraction condition can be written as

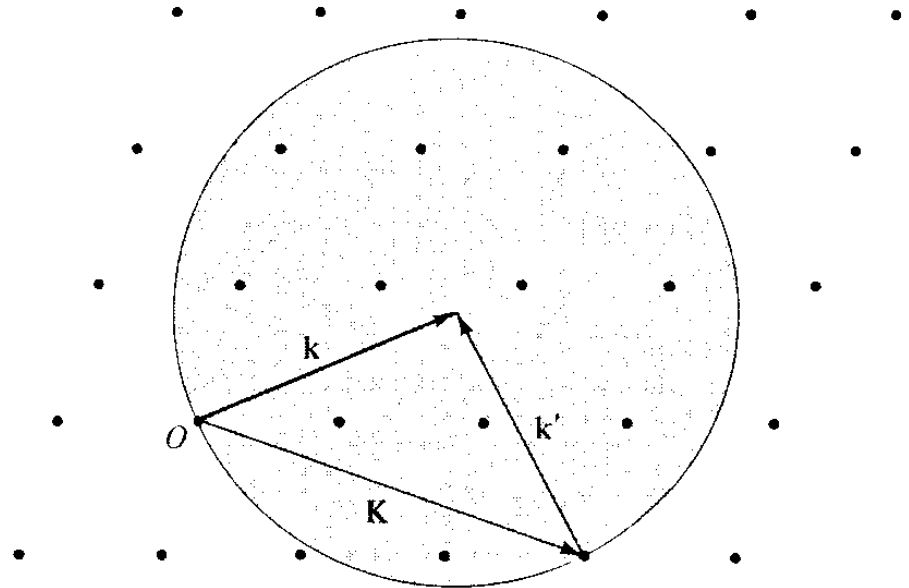
$$2\mathbf{k} \cdot \mathbf{G} + G^2 = 0 \quad \text{or} \quad 2\mathbf{k} \cdot \mathbf{G} = G^2$$

which is another statement of the Bragg condition.

$$n\lambda = 2d \sin \theta \quad \text{Bragg's Law}$$

Ewald Construction

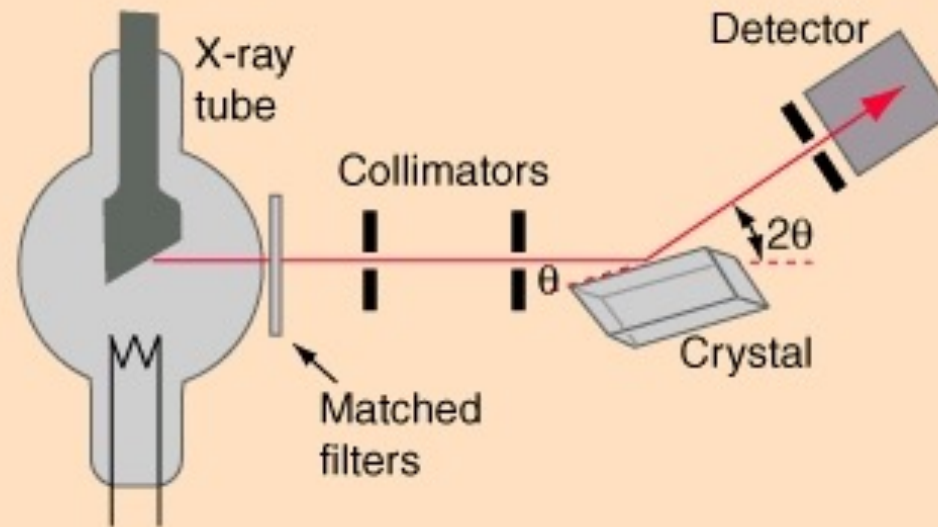
The Ewald construction. Given the incident wave vector $\mathbf{k}$, a sphere of radius k is drawn about the point $\mathbf{k}$. Diffraction peaks corresponding to reciprocal lattice vectors $\mathbf{K}$ will be observed only if $\mathbf{K}$ gives a reciprocal lattice point on the surface of the sphere. Such a reciprocal lattice vector is indicated in the figure, together with the wave vector $\mathbf{k}'$ of the Bragg reflected ray.



Bragg Spectrometer

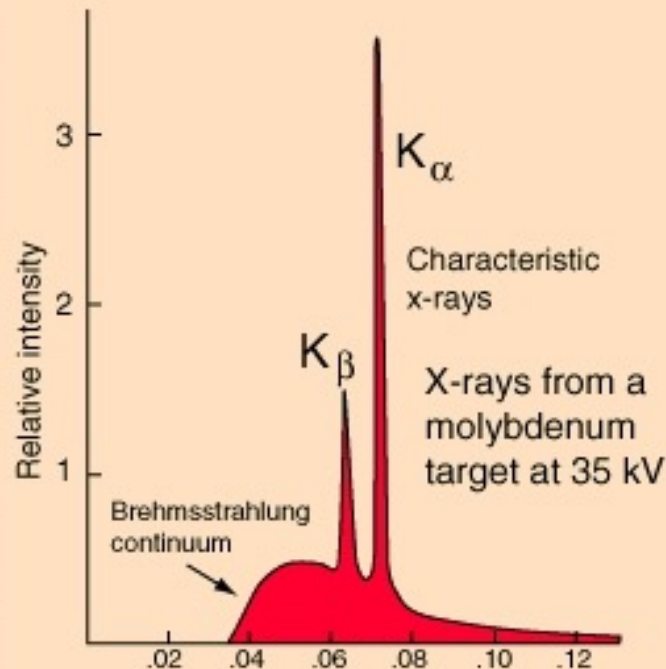
Bragg Spectrometer

Much of our knowledge about crystal structure and the structure of molecules as complex as DNA in crystalline form comes from the use of [x-rays](#) in x-ray diffraction studies. A basic instrument for such study is the Bragg spectrometer.



Characteristic X-Rays

Characteristic X-Rays



Characteristic x-rays are emitted from heavy elements when their electrons make transitions between the lower atomic energy levels. The characteristic x-rays emission which shown as two sharp peaks in the illustration at left occur when vacancies are produced in the $n=1$ or K-shell of the atom and electrons drop down from above to fill the gap. The x-rays produced by transitions from the $n=2$ to $n=1$ levels are called K-alpha x-rays, and those for the $n=3 \rightarrow 1$ transition are called K-beta x-rays.

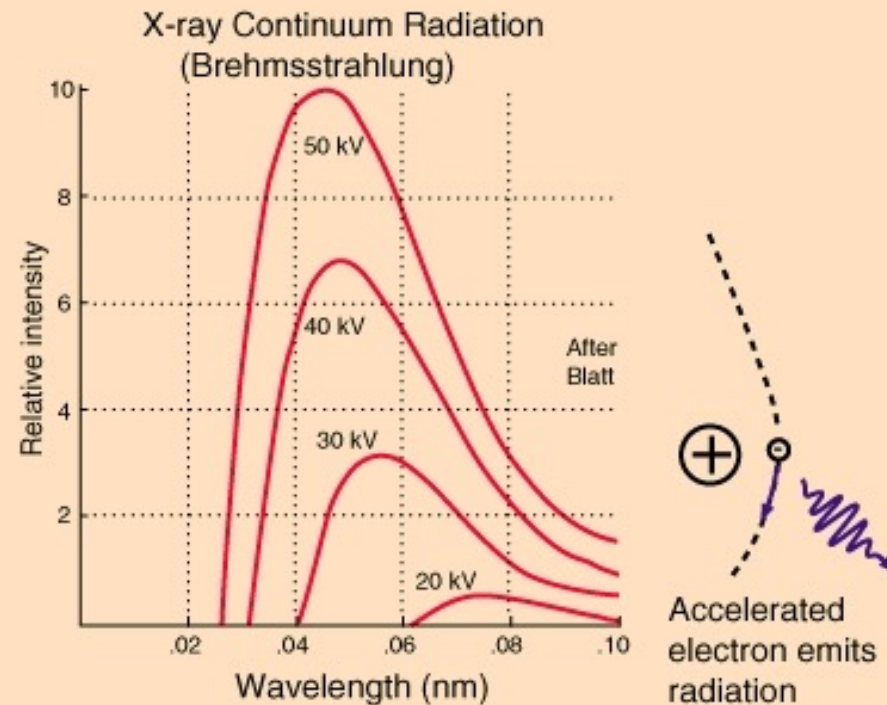
Transitions to the $n=2$ or L-shell are designated as L x-rays ($n=3 \rightarrow 2$ is L-alpha, $n=4 \rightarrow 2$ is L-beta, etc.). The

Wavelengths for X-Radiation

Copper Anodes	Bearden (1967)	Holzer et al. (1997)		Cobalt Anodes	Bearden (1967)	Holzer et al. (1997)
Cu K α 1	1.54056Å	1.540598 Å		Co K α 1	1.788965Å	1.789010 Å
Cu K α 2	1.54439Å	1.544426 Å		Co K α 2	1.792850Å	1.792900 Å
Cu K β	1.39220Å	1.392250 Å		Co K β	1.62079Å	1.620830 Å
Molybdenum Anodes				Chromium Anodes		
Mo K α 1	0.709300Å	0.709319 Å		Cr K α 1	2.28970Å	2.289760 Å
Mo K α 2	0.713590Å	0.713609 Å		Cr K α 2	2.293606Å	2.293663 Å
Mo K β	0.632288Å	0.632305 Å		Cr K β	2.08487Å	2.084920 Å

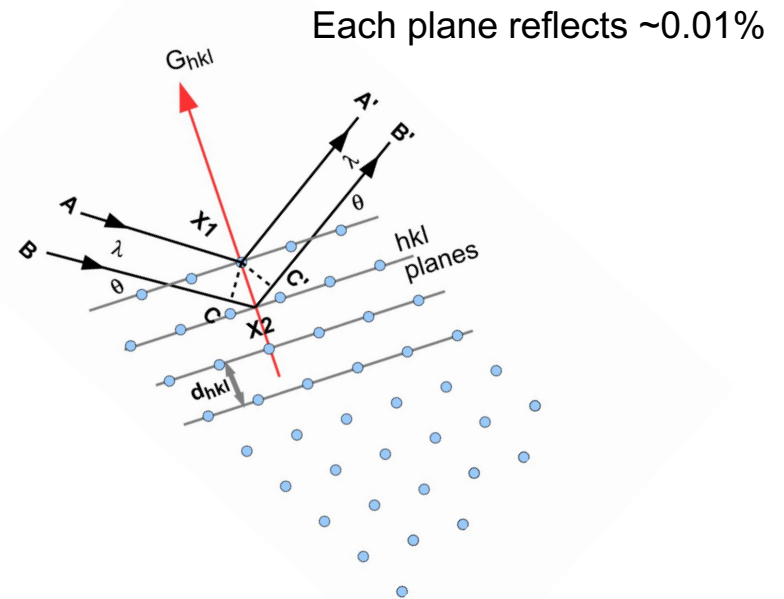
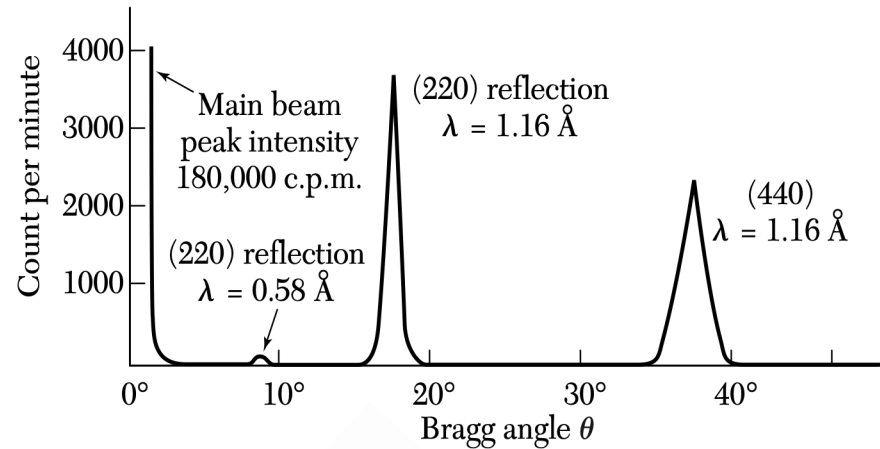
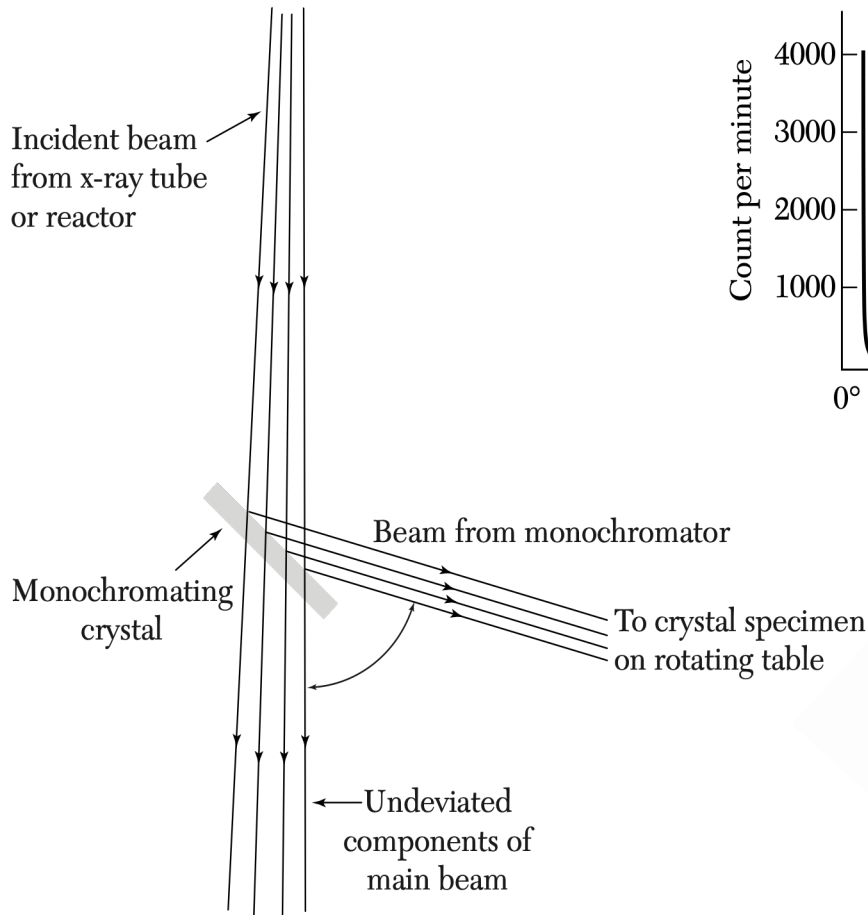
Bremsstrahlung X-Rays

Bremsstrahlung X-Rays

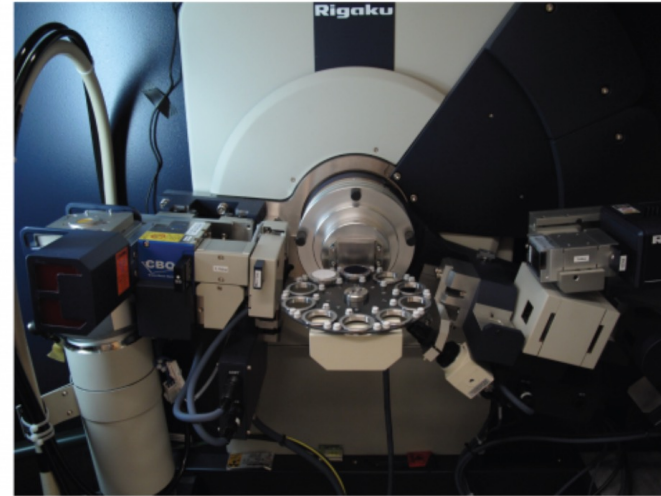
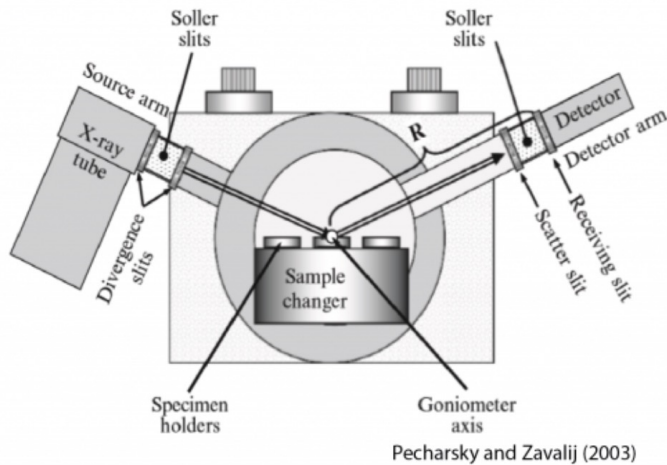


"Bremsstrahlung" means "braking radiation" and is retained from the original

Bragg Peaks



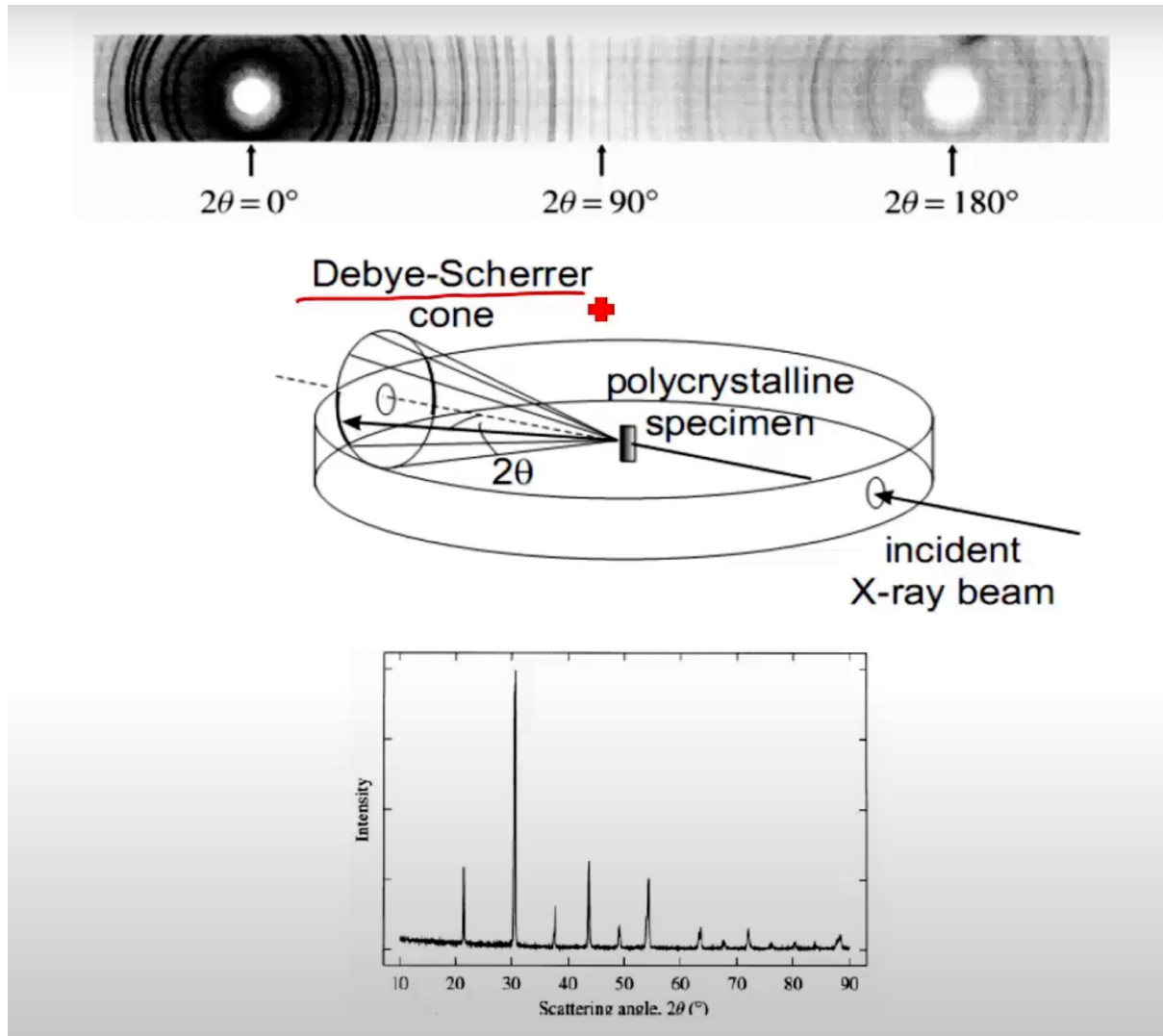
X-ray Diffractometer



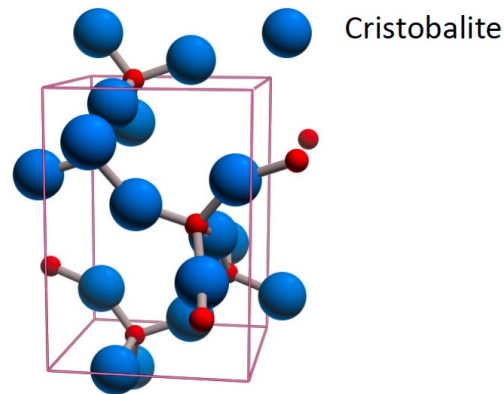
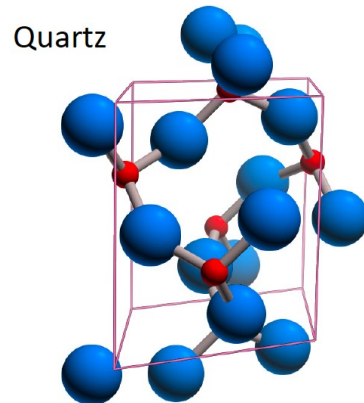
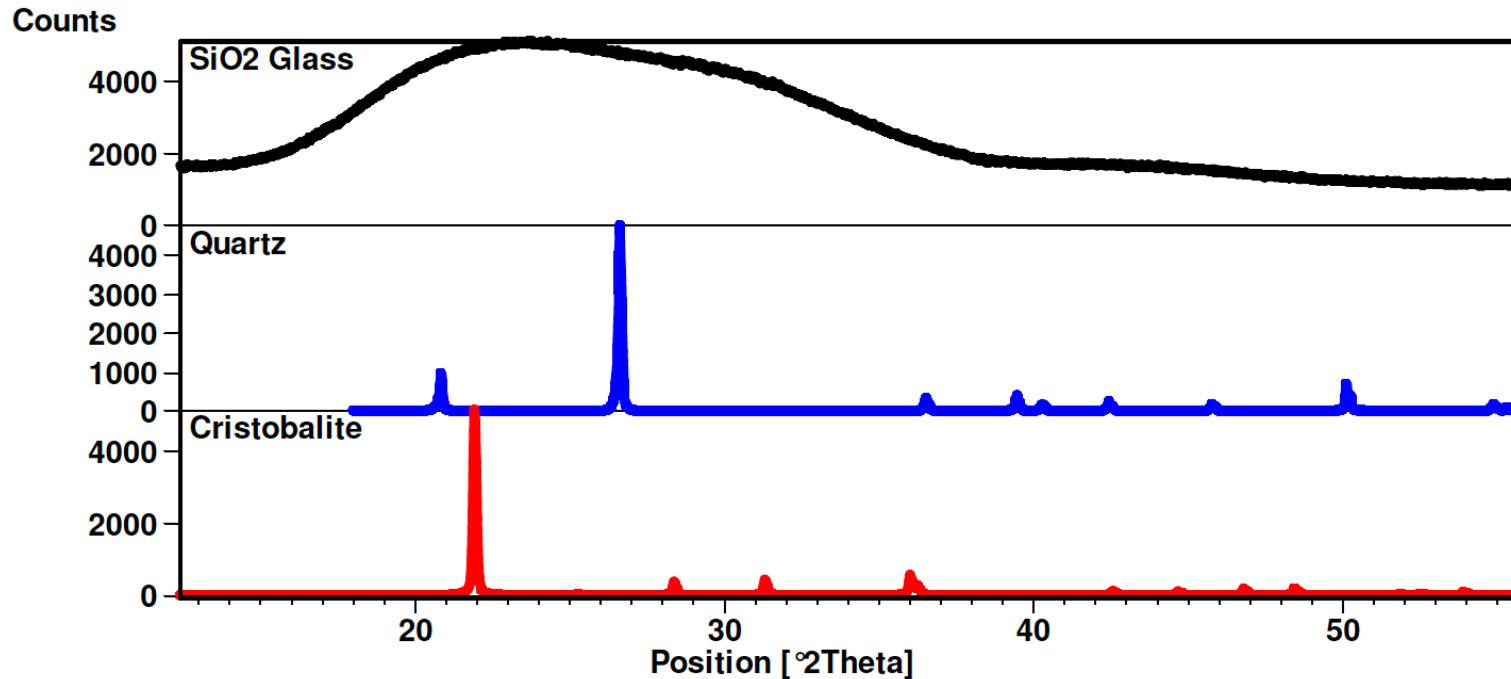
Animation showing the five motions possible with a four-circle kappa goniometer. The rotations about each of the four angles φ , κ , ω and 2θ leave the crystal within the X-ray beam, but change the crystal orientation. The detector (red box) can be slid closer or further away from the crystal, allowing higher resolution data to be taken (if closer) or better discernment of the Bragg peaks (if further away).

file:///Users/mac/Downloads/Kappa_goniometer_animation.ogv.360p.webm

X-ray Diffraction Rings from a Powder Sample



X-ray diffraction patterns from 3 different forms of SiO_2



Electron number density $n(\mathbf{r})$ is a periodic function of $\mathbf{r}$

$$n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r}) \quad \mathbf{T} = u_1 \mathbf{a}_1 + u_2 \mathbf{a}_2 + u_3 \mathbf{a}_3$$

In one dimension with a period of a in x , we expand $n(x)$ in Fourier series of sines and cosines:

$$n(x) = n_0 + \sum_{p>0} [C_p \cos(2\pi p x/a) + S_p \sin(2\pi p x/a)]$$

In more compact form

$$n(x) = \sum_p n_p \exp(i2\pi p x/a)$$

To ensure that $n(x)$ is a real function, we require

$$n_{-p}^* = n_p$$

The extension of the Fourier analysis to periodic functions $n(\mathbf{r})$ in three dimensions is straightforward. We must find a set of vectors $\mathbf{G}$ such that

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r})$$

is invariant under all crystal translations $\mathbf{T}$ that leave the crystal invariant.

$$n_{\mathbf{G}} = V_c^{-1} \int_{\text{cell}} dV n(\mathbf{r}) \exp(-i\mathbf{G} \cdot \mathbf{r})$$

Here V_c is the volume of a cell of the crystal.

Fourier Analysis of the Basis

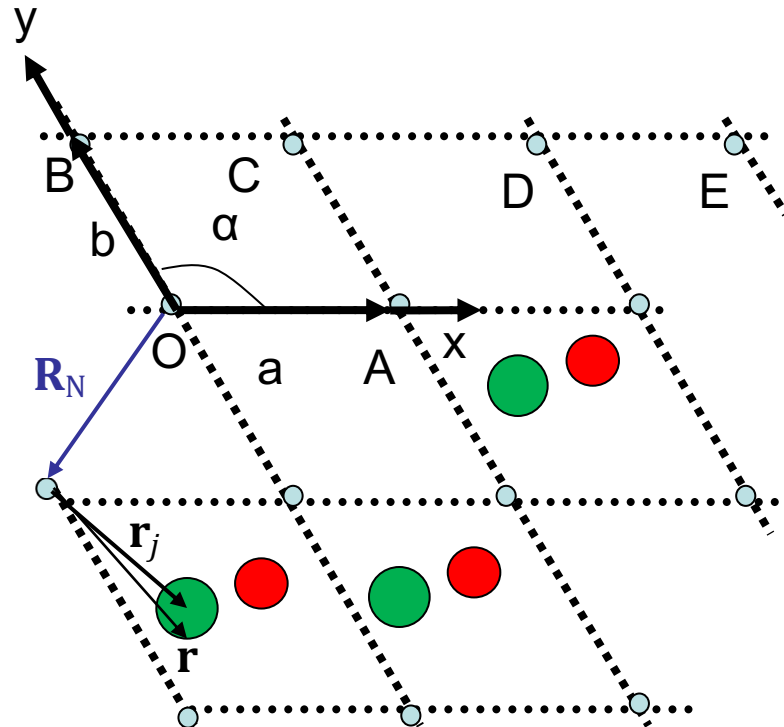
When the diffraction condition, $\Delta \mathbf{k} = \mathbf{G}$, is satisfied, the scattering amplitude for a crystal of N cells may be written as

$$F_{\mathbf{G}} = N \int_{\text{cell}} dV n(\mathbf{r}) \exp(-i\mathbf{G} \cdot \mathbf{r}) = NS_{\mathbf{G}}$$

The quantity $S_{\mathbf{G}}$ is called the **structure factor**, with $\mathbf{r} = 0$ at one corner.

If $\mathbf{r}_j$ is the vector to the center of atom j , then the function $n_j(\mathbf{r} - \mathbf{r}_j)$ defines the contribution of that atom to the electron concentration at $\mathbf{r}$. The total electron density is

$$n(\mathbf{r}) = \sum_{j=1}^s n_j(\mathbf{r} - \mathbf{r}_j)$$



The structure factor $S_{\mathbf{G}}$ may be written as

$$\begin{aligned} S_{\mathbf{G}} &= \sum_j \int dV n_j(\mathbf{r} - \mathbf{r}_j) \exp(-i\mathbf{G} \cdot \mathbf{r}) \\ &= \sum_j \exp(-i\mathbf{G} \cdot \mathbf{r}_j) \int dV n_j(\boldsymbol{\rho}) \exp(-i\mathbf{G} \cdot \boldsymbol{\rho}) \end{aligned}$$

where $\boldsymbol{\rho} = \mathbf{r} - \mathbf{r}_j$. We now define the **atomic form factor** as

$$f_j = \int dV n_j(\boldsymbol{\rho}) \exp(-i\mathbf{G} \cdot \boldsymbol{\rho}) ,$$

then

$$S_{\mathbf{G}} = \sum_j f_j \exp(-i\mathbf{G} \cdot \mathbf{r}_j)$$

Since $\mathbf{G} \cdot \mathbf{r}_j = (v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3) \cdot (x_j \mathbf{a}_1 + y_j \mathbf{a}_2 + z_j \mathbf{a}_3)$
 $= 2\pi(v_1 x_j + v_2 y_j + v_3 z_j)$, so

$$S_{\mathbf{G}}(v_1 v_2 v_3) = \sum_j f_j \exp[-i2\pi(v_1 x_j + v_2 y_j + v_3 z_j)]$$

Structure Factor of the bcc Lattice

The bcc basis referred to the cubic cell has identical atoms at

$x_1 = y_1 = z_1 = 0$, and $x_2 = y_2 = z_2 = \frac{1}{2}$. Thus,

$$S(v_1 v_2 v_3) = f \{1 + \exp[-i\pi(v_1 + v_2 + v_3)]\}$$

and

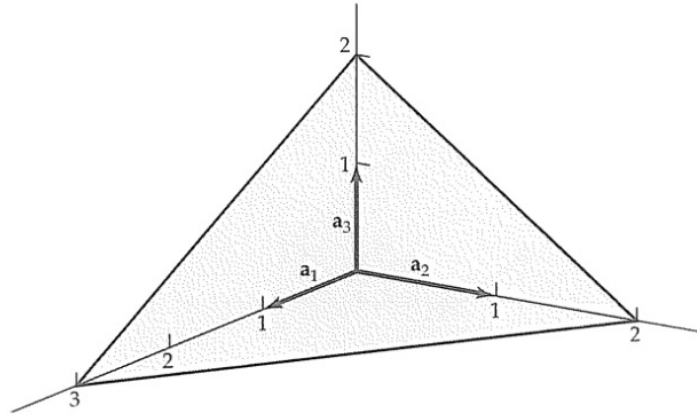
$$S = 0 \quad \text{when } v_1 + v_2 + v_3 = \text{odd integer} ;$$

$$S = 2f \quad \text{when } v_1 + v_2 + v_3 = \text{even integer}$$

Metallic sodium has a bcc structure. Its diffraction pattern does not contain lines such as (100), (300), (111) or (221), but lines such as (200), (110) and (222) will be present.

Index System for Crystal Planes

Figure 13 This plane intercepts the a_1 , a_2 , a_3 axes at $3a_1$, $2a_2$, $2a_3$. The reciprocals of these numbers are $\frac{1}{3}$, $\frac{1}{2}$, $\frac{1}{2}$. The smallest three integers having the same ratio are 2, 3, 3, and thus the indices of the plane are (233).



- Find the intercepts on the axes in terms of the lattice constants a_1 , a_2 , a_3 . The axes may be those of a primitive or nonprimitive cell.
- Take the reciprocals of these numbers and then reduce to three integers having the same ratio, usually the smallest three integers. The result, enclosed in parentheses (hkl), is called the index of the plane.

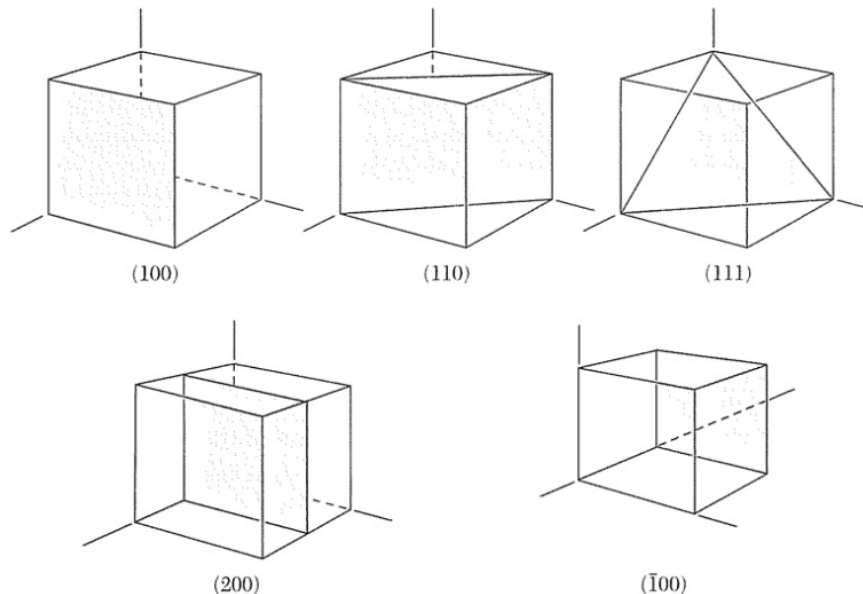


Figure 14 Indices of important planes in a cubic crystal. The plane (200) is parallel to (100) and to (100).

Diffraction from the planes of a bcc Lattice

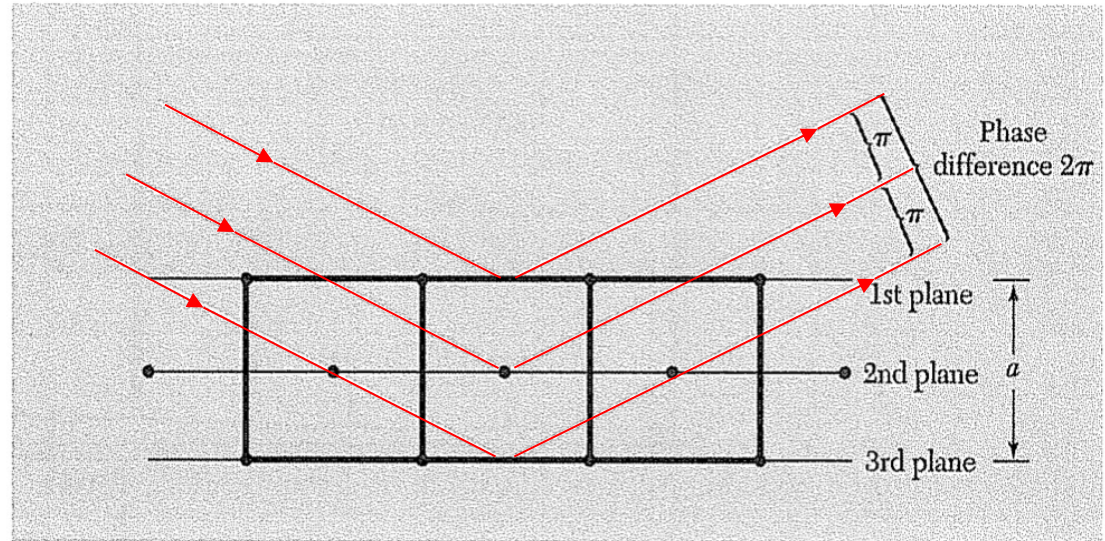
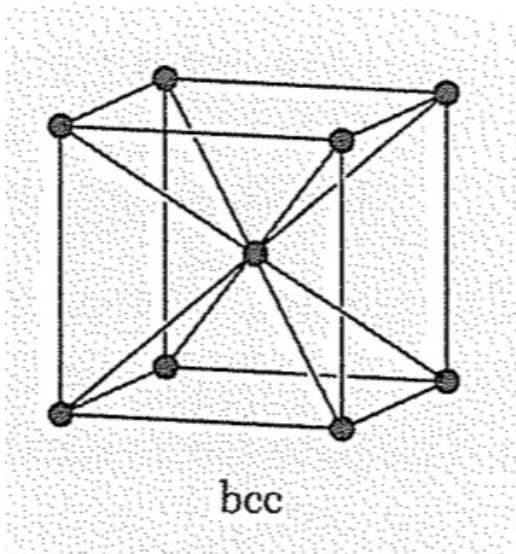


Figure 16 Explanation of the absence of a (100) reflection from a body-centered cubic lattice. The phase difference between successive planes is π , so that the reflected amplitude from two adjacent planes is $1 + e^{-i\pi} = 1 - 1 = 0$.

Structure Factor of the fcc Lattice

The basis of the fcc structure referred to the cubic cell has identical atoms at 000 ; $0\frac{11}{22}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{11}{22}0$. Thus

$$S(v_1v_2v_3) = f\{1 + \exp[-i\pi(v_2 + v_3)] + \exp[-i\pi(v_1 + v_3)] + \exp[-i\pi(v_1 + v_2)]\}$$

If all indices are even integers, $S = 4f$; similarly if all indices are odd integers. But if only one of the integers is even, two of the exponents will be odd multiples of $-i\pi$ and S will vanish. If only one of the integers is odd, the same argument applies and S will also vanish. Thus in the fcc lattice no reflections can occur for which the indices are partly even and partly odd.

Missing Diffraction Orders

- The missing orders follow rules depending on which type of lattice it is:

Simple cubic (sc):

any (hkl)

Body-centred cubic (bcc):

$h+k+l = \text{even}$

Face-centred cubic (fcc):

$h, k \text{ \& } l \text{ all odd or all even}$

Missing orders make it easier to identify a particular crystal structure – i.e. it is helpful!

Lattice Type			
Miller indices	sc	bcc	fcc
1 0 0	Y	N	N
1 1 0	Y	Y	N
1 1 1	Y	N	Y
2 0 0	Y	Y	Y
2 1 0	Y	N	N
2 1 1	Y	Y	N
2 2 0	Y	Y	Y
3 1 0	Y	Y	N
3 1 1	Y	N	Y

Atomic Form Factor

$$f_j = \int dV n_j(\mathbf{r}) \exp(-i\mathbf{G} \cdot \mathbf{r})$$

If the electron distribution is spherically symmetric about the origin, then

$$\begin{aligned} f_j &\equiv 2\pi \int dr r^2 d(\cos \alpha) n_j(r) \exp(-iGr \cos \alpha) \\ &= 2\pi \int dr r^2 n_j(r) \cdot \frac{e^{iGr} - e^{-iGr}}{iGr}, \end{aligned}$$

$$f_j = 4\pi \int dr n_j(r) r^2 \cdot \frac{\sin Gr}{Gr}$$

If the same total electron density were concentrated at $r = 0$,

$$f_j = 4\pi \int dr n_j(r) r^2 = Z : \text{ the number of atomic electrons.}$$

Problems

- 1. Interplanar separation.** Consider a plane hkl in a crystal lattice. (a) Prove that the reciprocal lattice vector $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ is perpendicular to this plane. (b) Prove that the distance between two adjacent parallel planes of the lattice is $d(hkl) = 2\pi/|\mathbf{G}|$. (c) Show for a simple cubic lattice that $d^2 = a^2/(h^2 + k^2 + l^2)$.
- 2. Structure factor of diamond.** The crystal structure of diamond is described in Chapter 1. The basis consists of eight atoms if the cell is taken as the conventional cube. (a) Find the structure factor S of this basis. (b) Find the zeros of S and show that the allowed reflections of the diamond structure satisfy $v_1 + v_2 + v_3 = 4n$, where all indices are even and n is any integer, or else all indices are odd. (Notice that h, k, l may be written for v_1, v_2, v_3 and this is often done.)
- 3.** Show that the reciprocal lattice of a two-dimensional lattice can be represented by rods. Discuss the Ewald construction for diffraction from a two-dimensional lattice and determine the diffracted beam for a particular orientation and magnitude of $\mathbf{k}_0$. Why does one observe a diffraction pattern of electrons from a surface for all values and orientations of $\mathbf{k}_0$ above a critical value? Calculate the critical energy at which the first diffracted beam appears, when the electrons are incident perpendicular to a (100) surface of a Cu crystal.