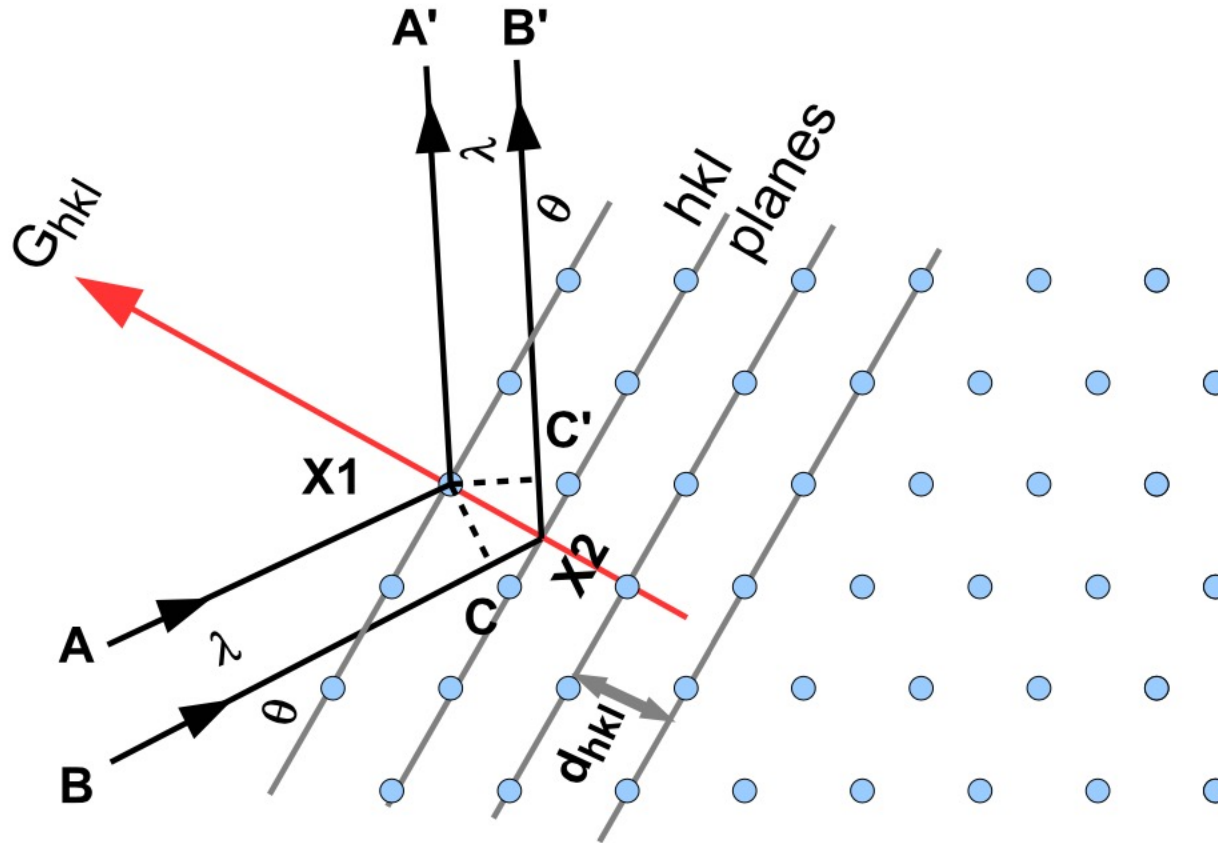


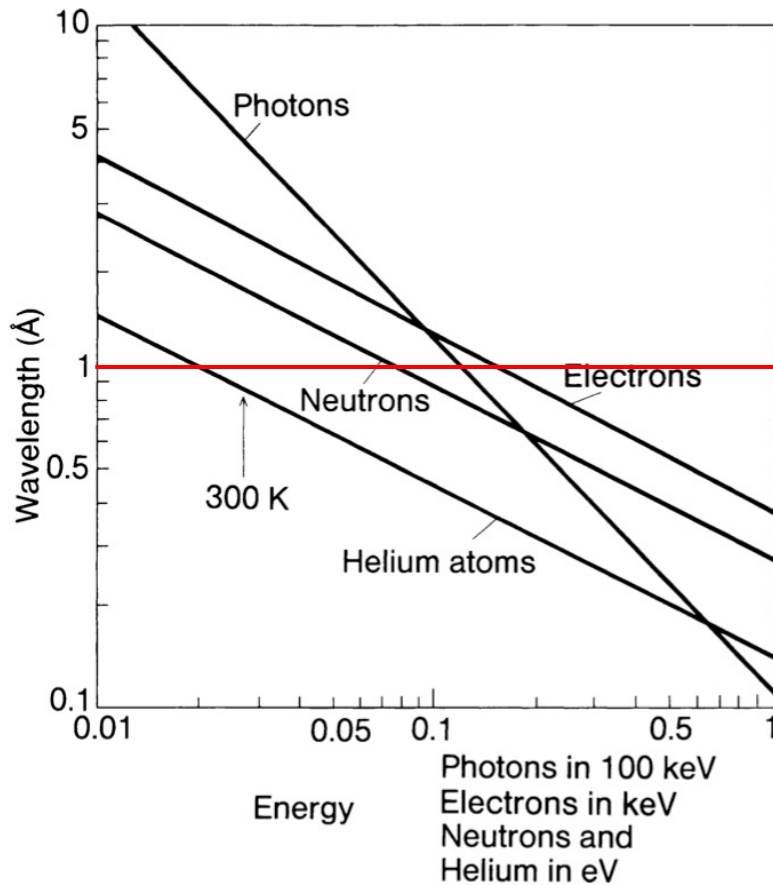
# X-ray Diffraction and Reciprocal Lattice



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

# Wavelength vs particle energy

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



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

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

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

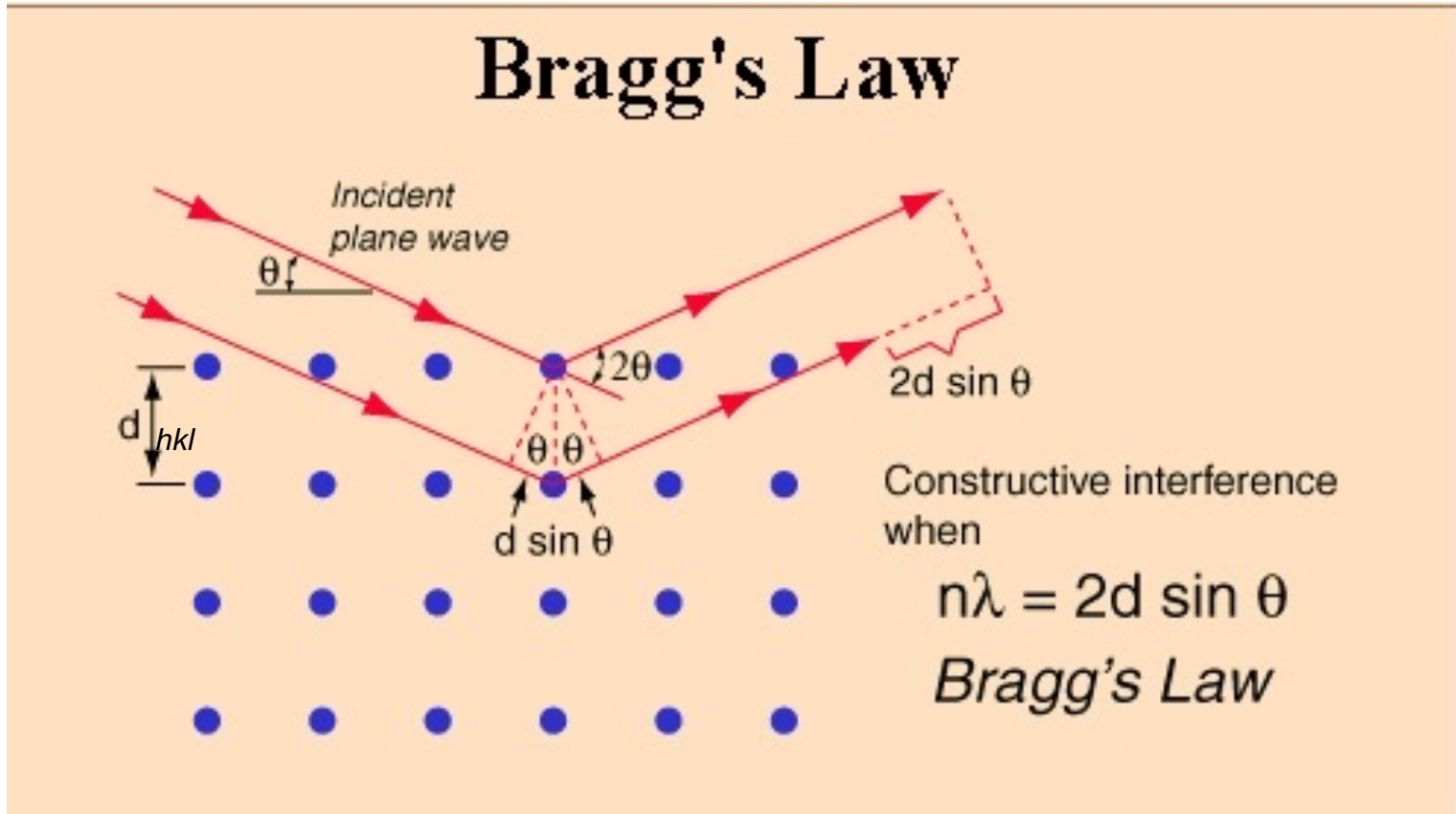
# X-ray Diffraction

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

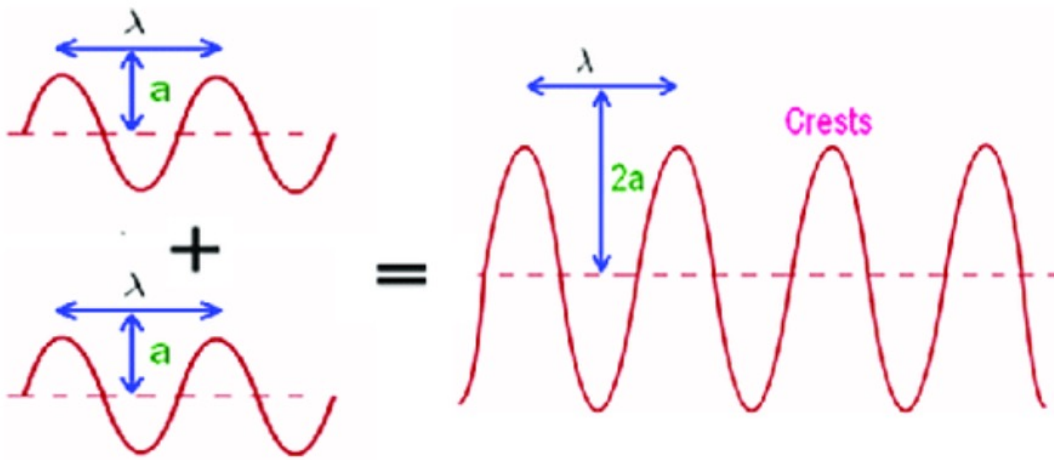


Planes with Miller index  $(hkl)$  has the interplane distance  $d_{hkl}$ :

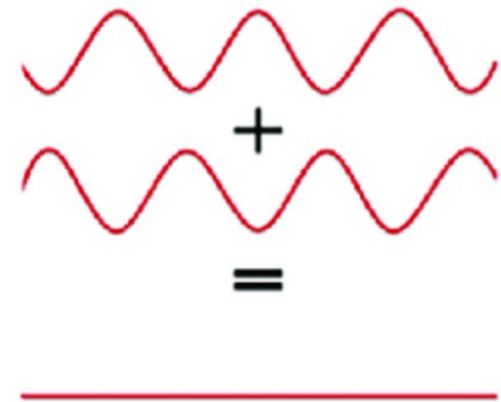
$$d_{hkl} = a / (h^2 + k^2 + l^2)^{1/2}$$

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

# Condition for Interferences



Constructive interference

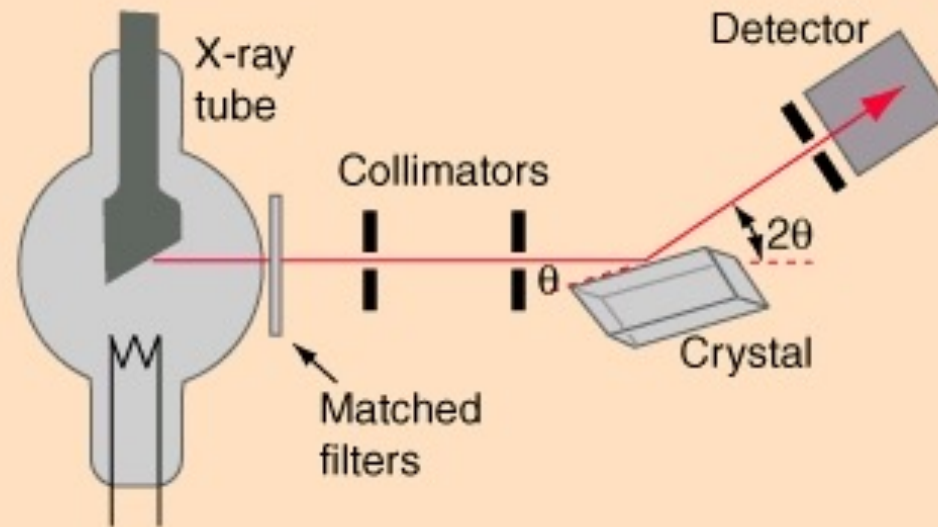


Destructive interference

# Bragg Spectrometer

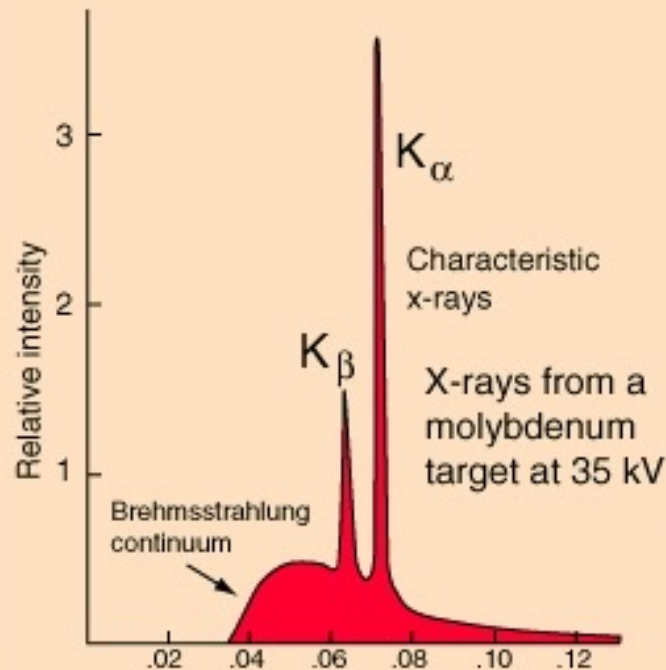
## Bragg Spectrometer

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

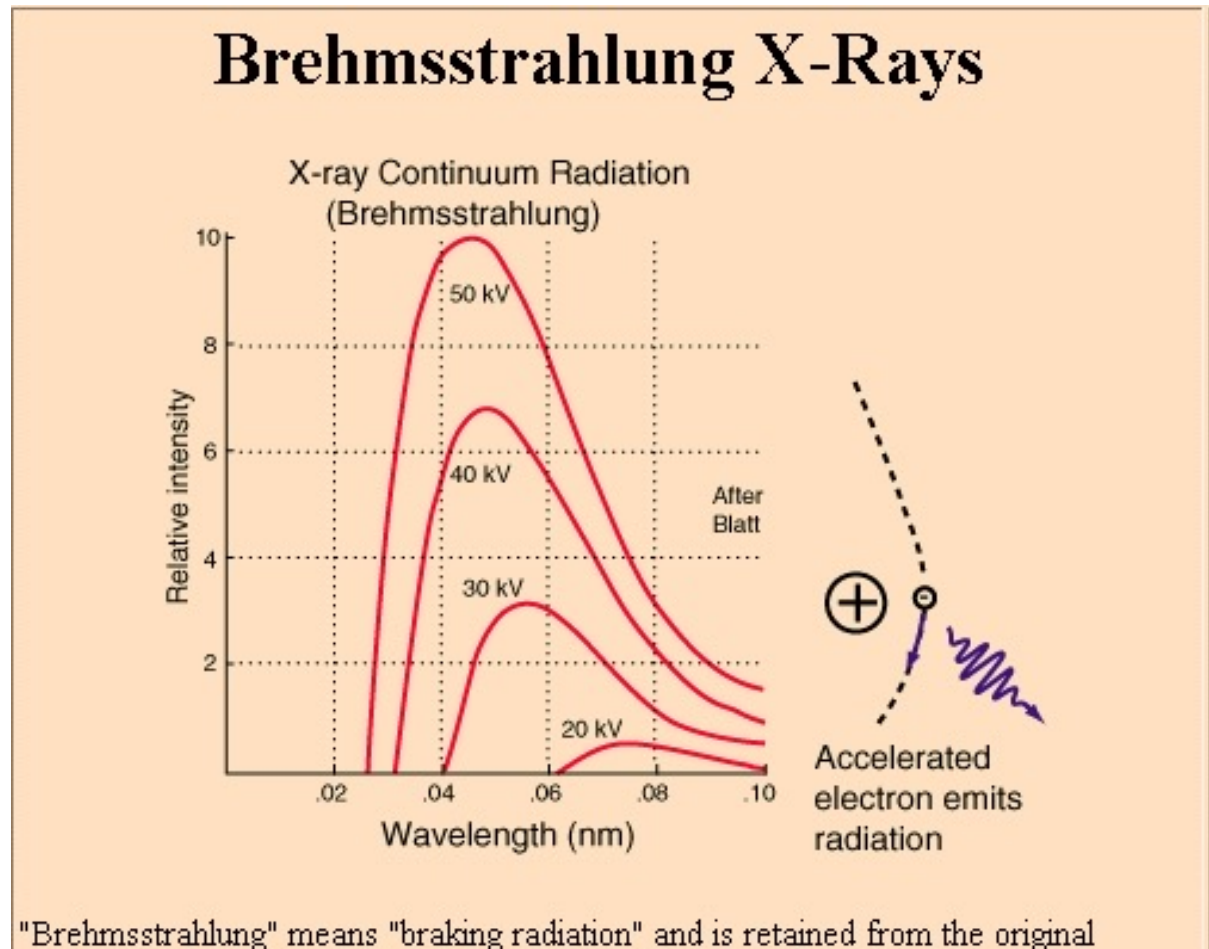
## Characteristic X-Rays



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

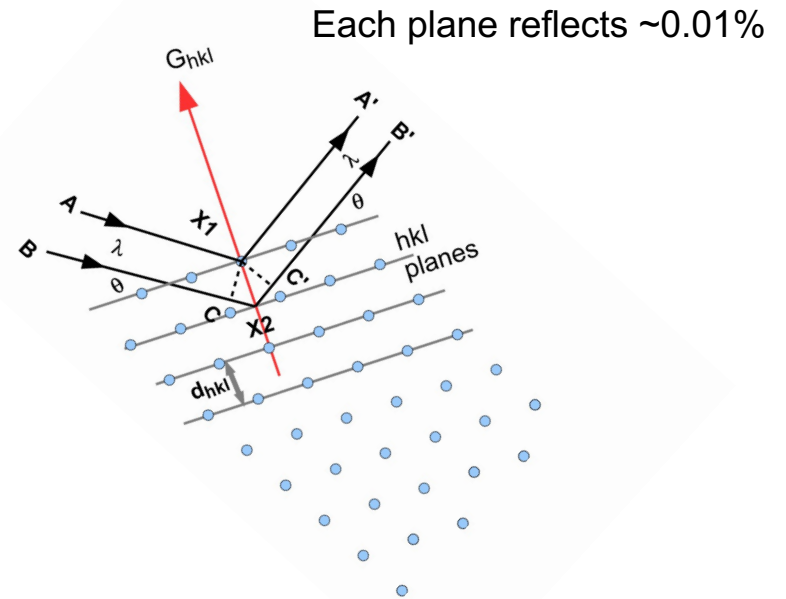
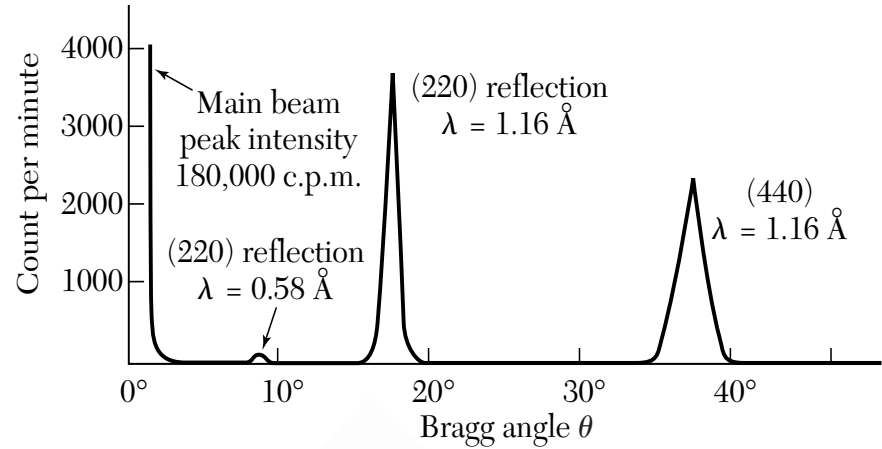
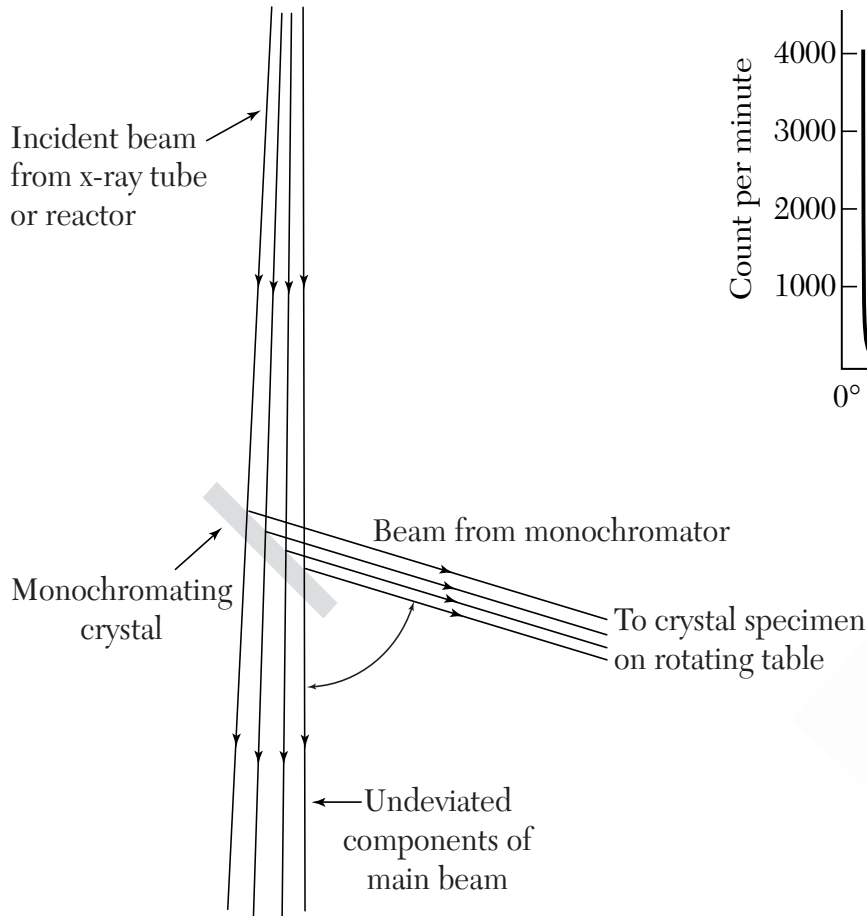
# Bremsstrahlung X-Rays



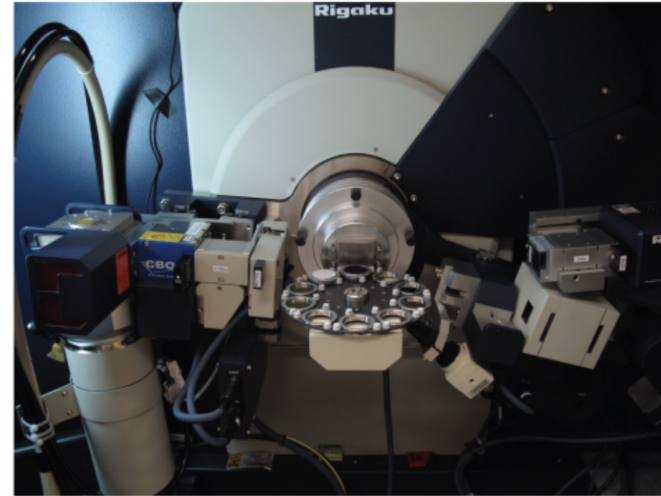
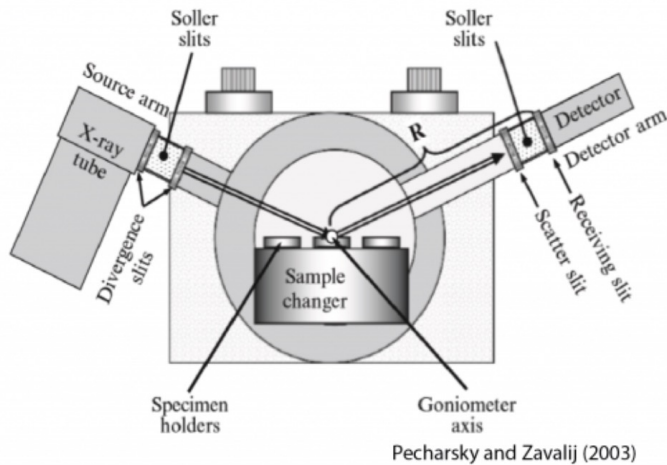
"Bremsstrahlung" means "braking radiation" and is retained from the original



# 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  $\varphi$ ,  $\kappa$ ,  $\omega$  and  $2\theta$  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](file:///Users/mac/Downloads/Kappa_goniometer_animation.ogv.360p.webm)

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:

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

In more compact form

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

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

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.

# Reciprocal Lattice

- The reciprocal lattice is defined as the set of all wave vectors  $\mathbf{K}$  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 Vectors

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

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

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**.

# Diffraction Conditions

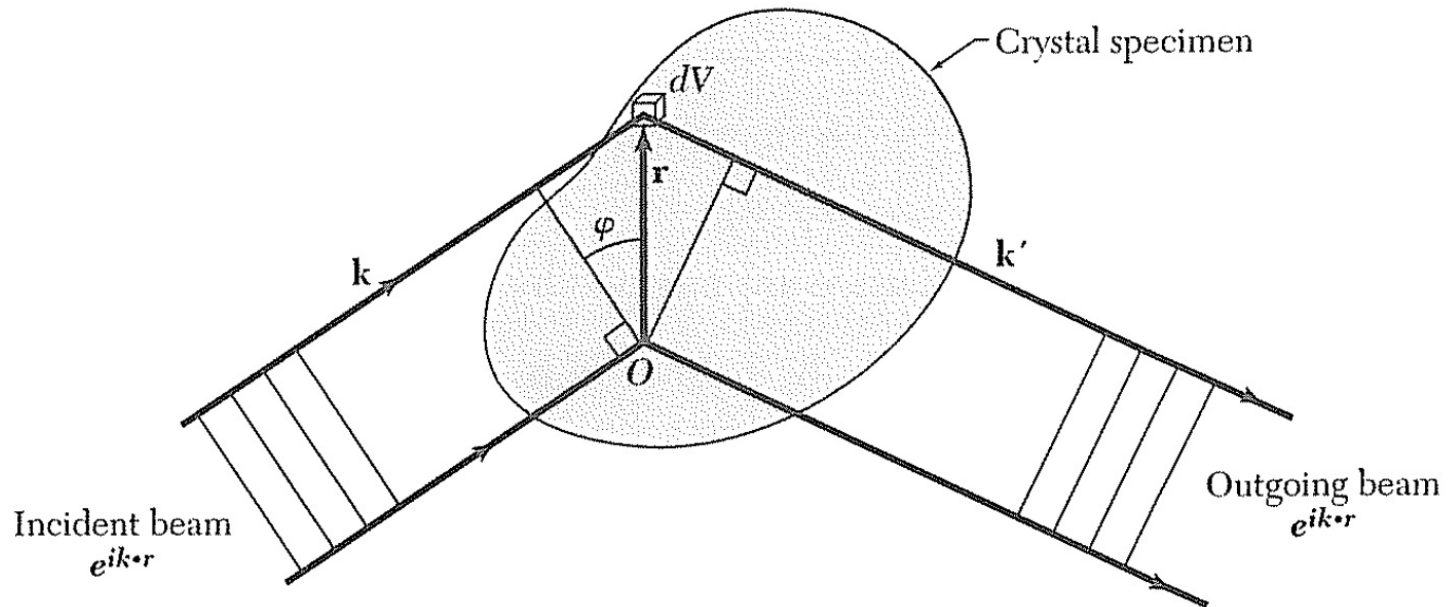
Every crystal structure has two lattices associated with it, the crystal lattice and the reciprocal lattice. A diffraction pattern of a crystal is a map of the reciprocal lattice of the crystal.

*Theorem:* The set of reciprocal lattice vectors  $\mathbf{G}$  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

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

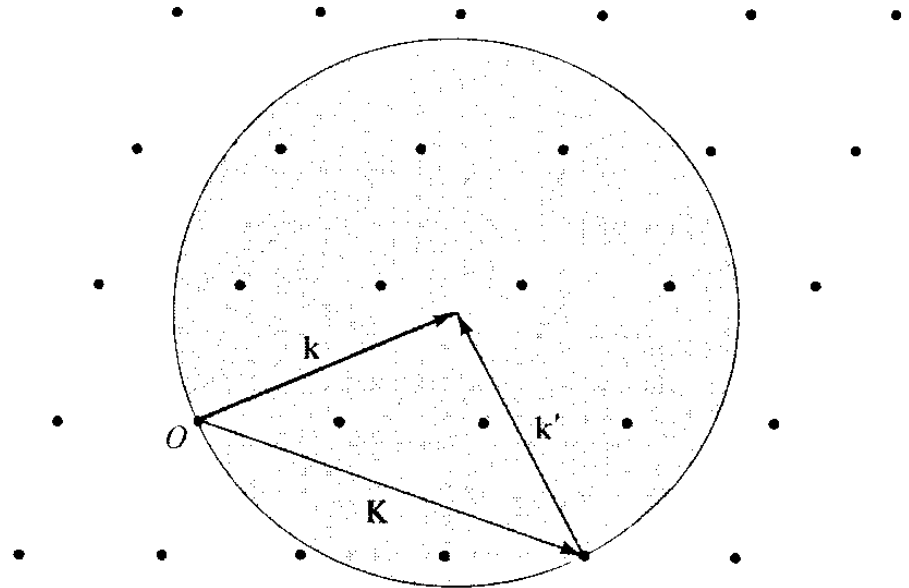
which is another statement of the Bragg condition.

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

# Ewald Construction

Figure 6.7

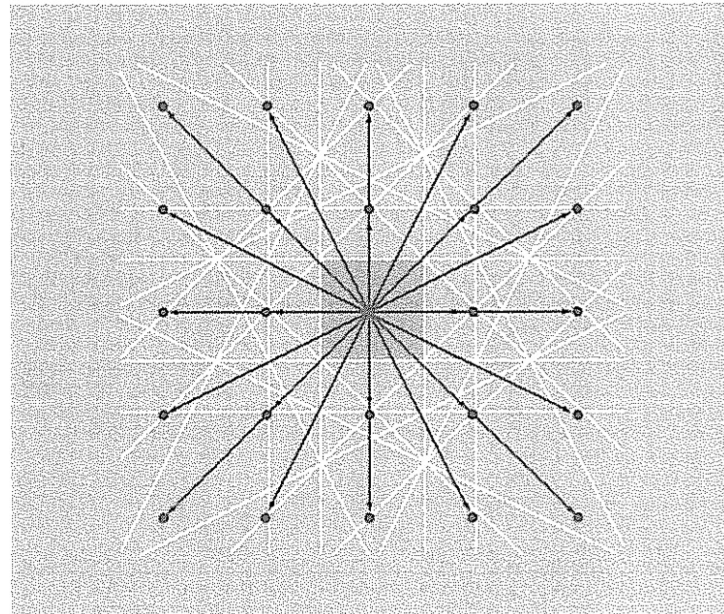
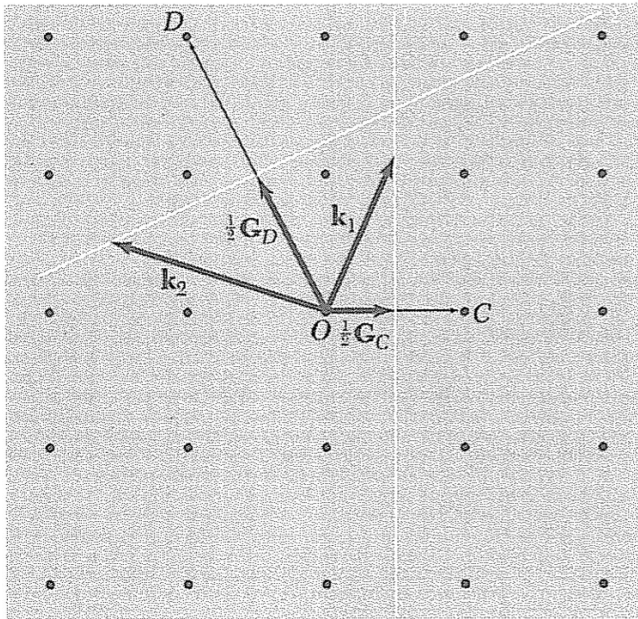
The Ewald construction. Given the incident wave vector  $\mathbf{k}$ , a sphere of radius  $k$  is drawn about the point  $\mathbf{k}$ . Diffraction peaks corresponding to reciprocal lattice vectors  $\mathbf{K}$  will be observed only if  $\mathbf{K}$  gives a reciprocal lattice point on the surface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



# Brillouin Zone

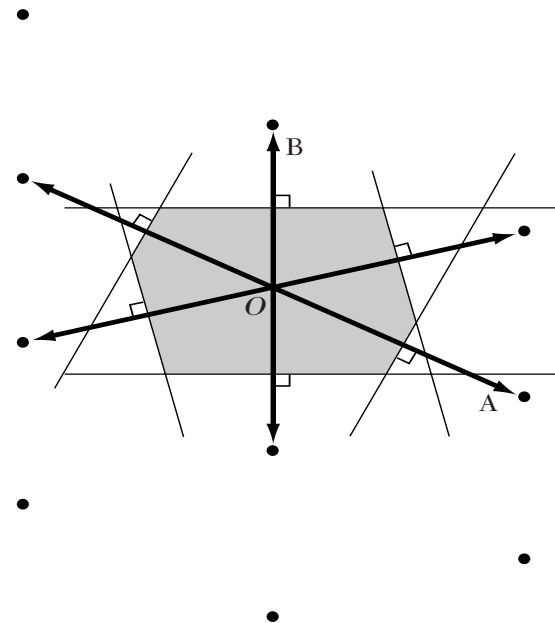
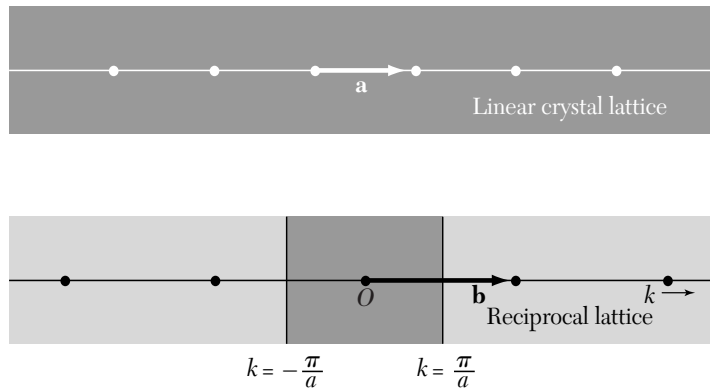
A Brillouin zone is defined as a Wigner-Seitz cell in the reciprocal lattice.

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

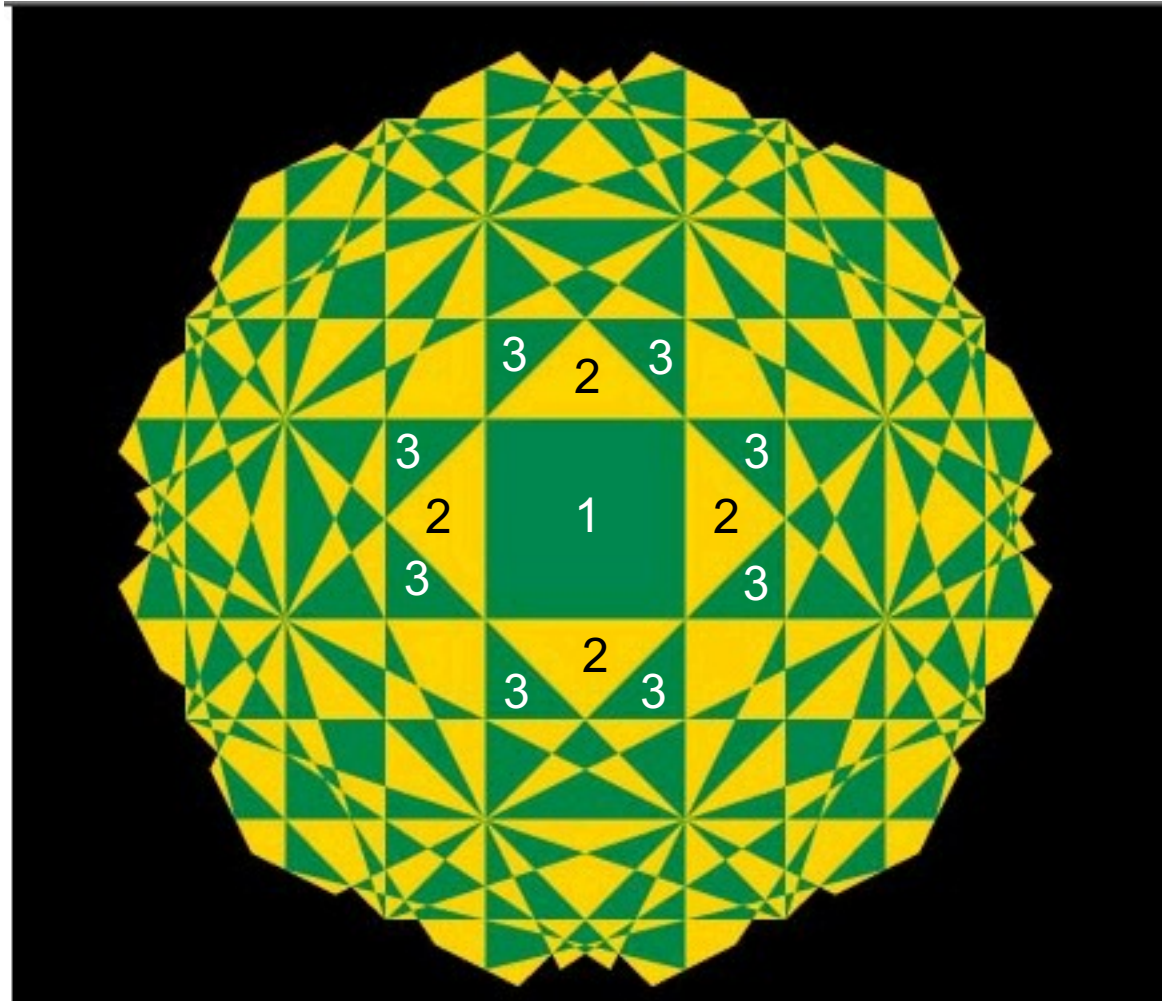


# Brillouin Zone in 1D and 2D

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

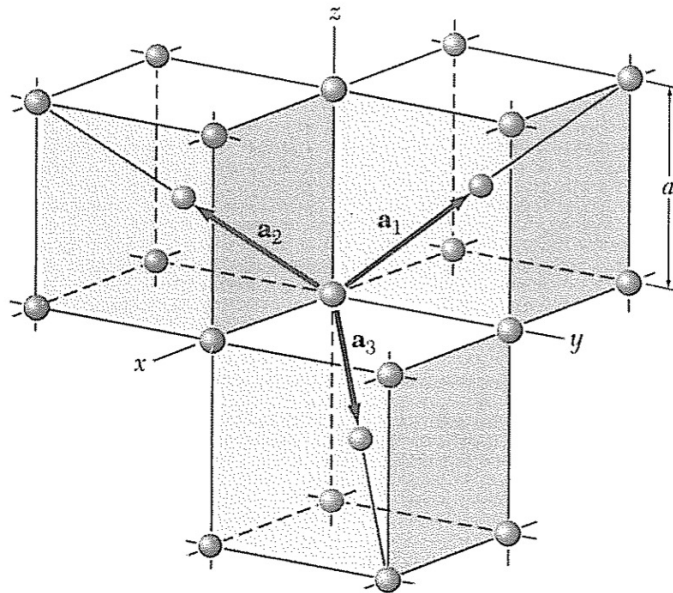


# Reciprocal Lattice to bcc Lattice

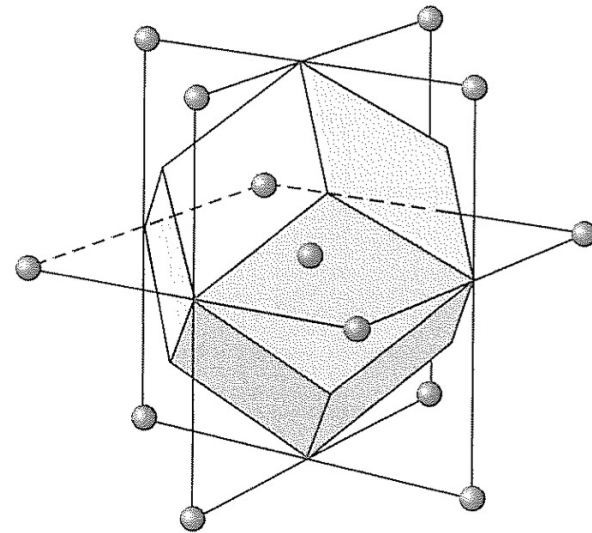
$$\mathbf{a}_1 = \frac{1}{2}a(-\hat{x} + \hat{y} + \hat{z}) ; \quad \mathbf{a}_2 = \frac{1}{2}a(\hat{x} - \hat{y} + \hat{z}) ; \quad \mathbf{a}_3 = \frac{1}{2}a(\hat{x} + \hat{y} - \hat{z})$$

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

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



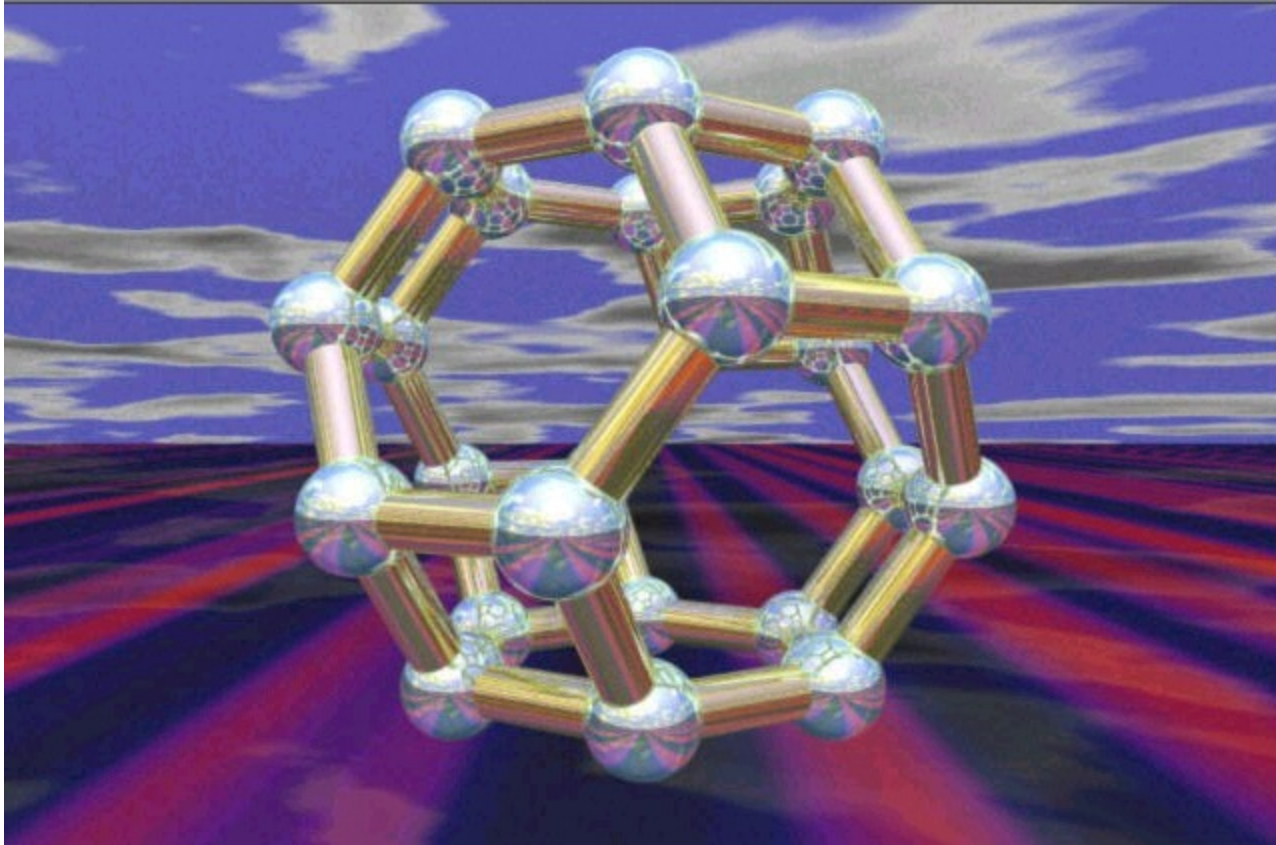
**Figure 12** Primitive basis vectors of the body-centered cubic lattice.



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



# First Brillouin Zone for bcc



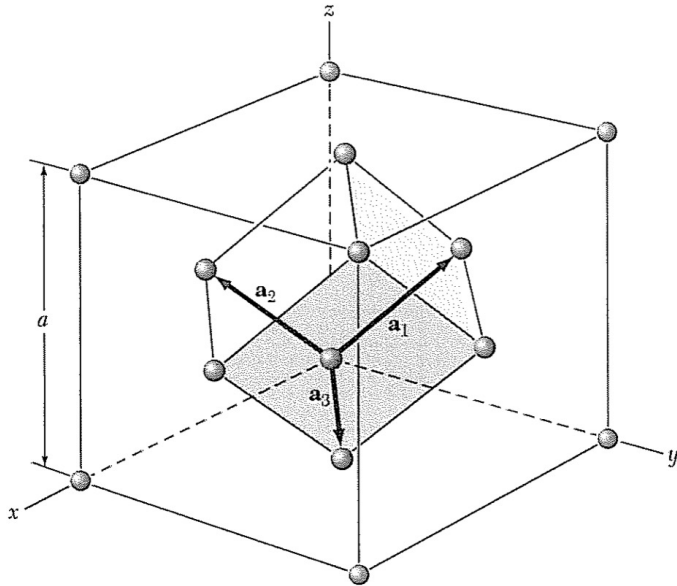
# Reciprocal Lattice to fcc Lattice

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

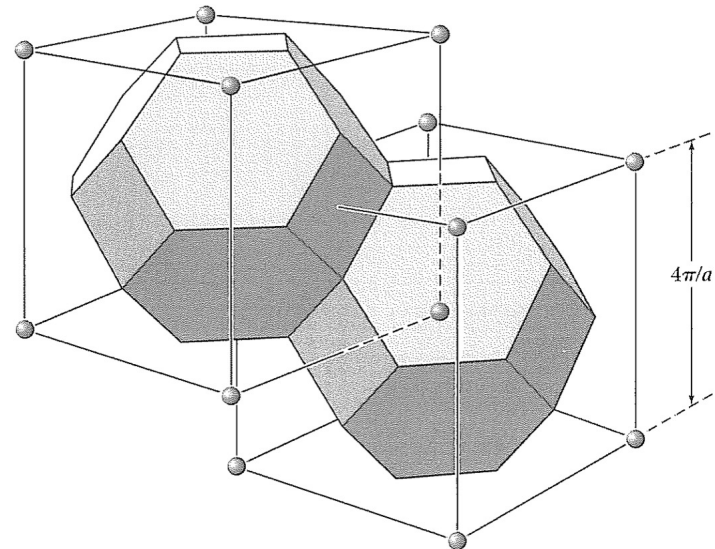
$$\mathbf{b}_1 = (2\pi/a)(-\hat{x} + \hat{y} + \hat{z}) ; \quad \mathbf{b}_2 = (2\pi/a)(\hat{x} - \hat{y} + \hat{z}) ;$$

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

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

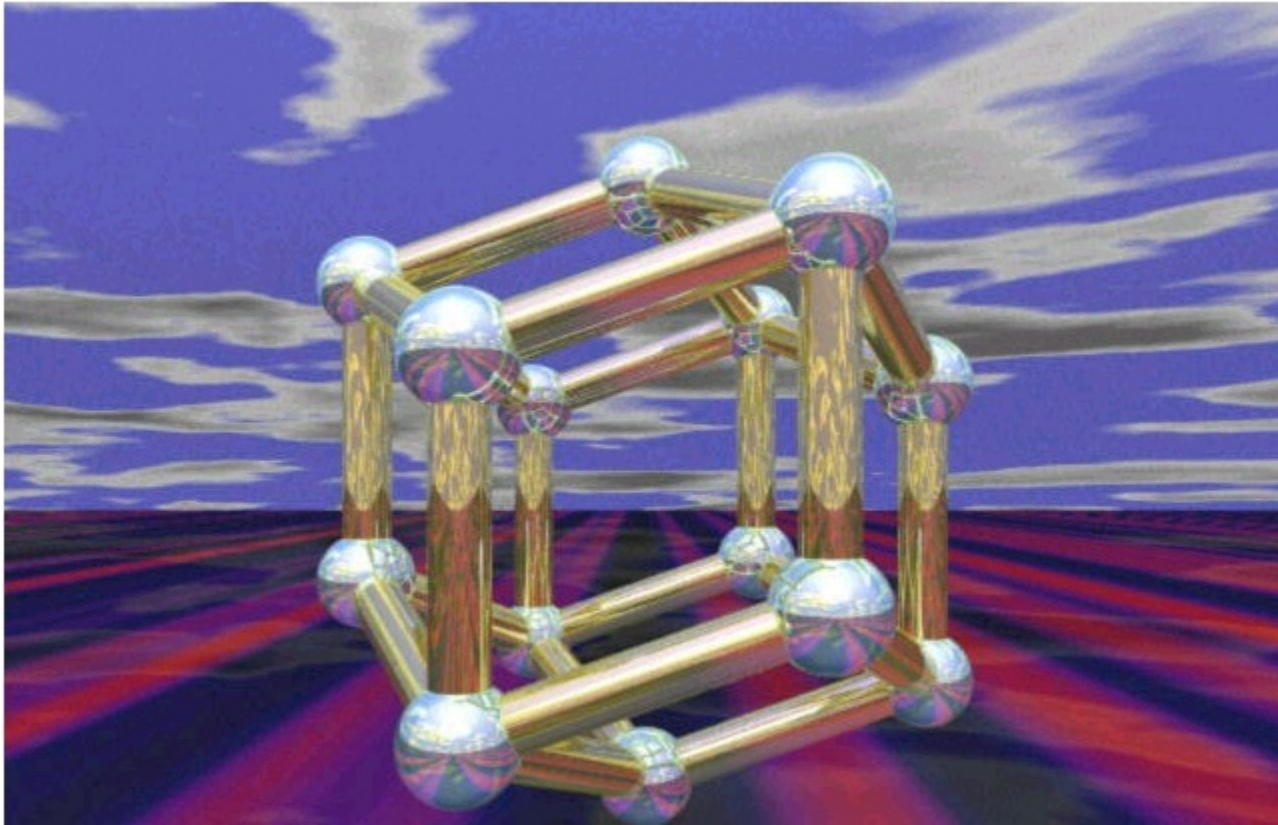


**Figure 14** Primitive basis vectors of the face-centered cubic lattice.



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

# First Brillouin Zone for fcc



# Fourier Analysis of the Basis

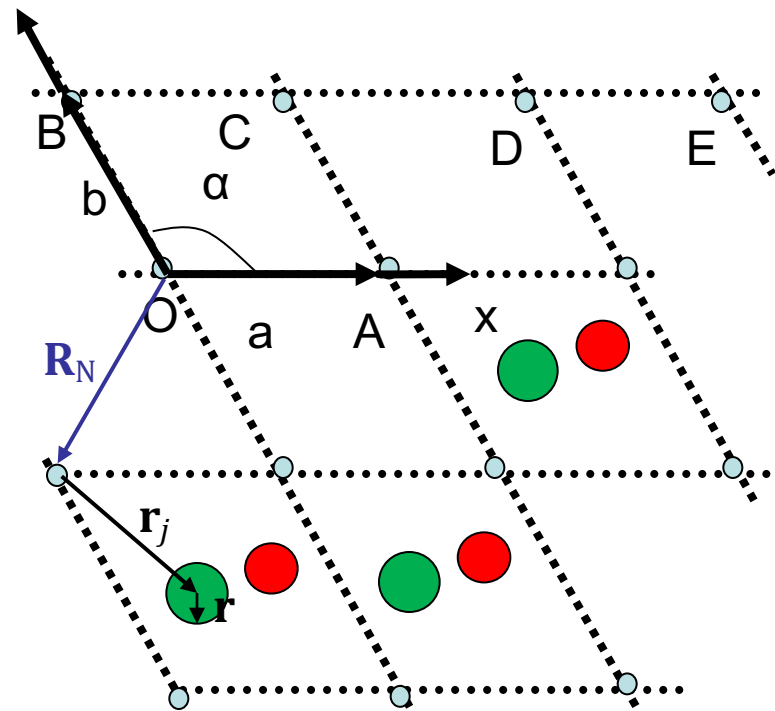
When the diffraction condition,  $\Delta\mathbf{k} = \mathbf{G}$ , is satisfied, the scattering amplitude for a crystal of  $N$  cells may be written as

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

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,

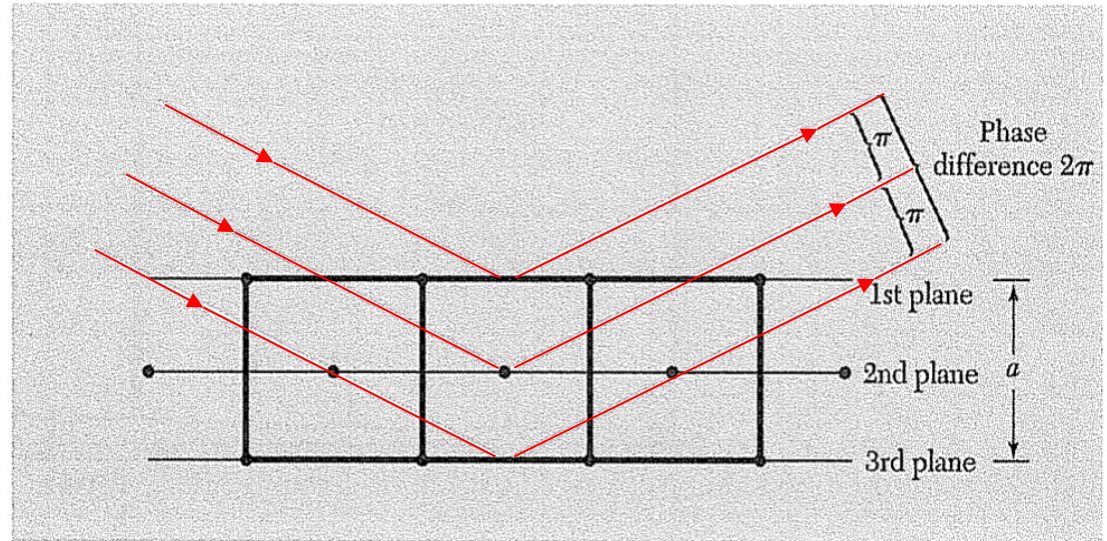
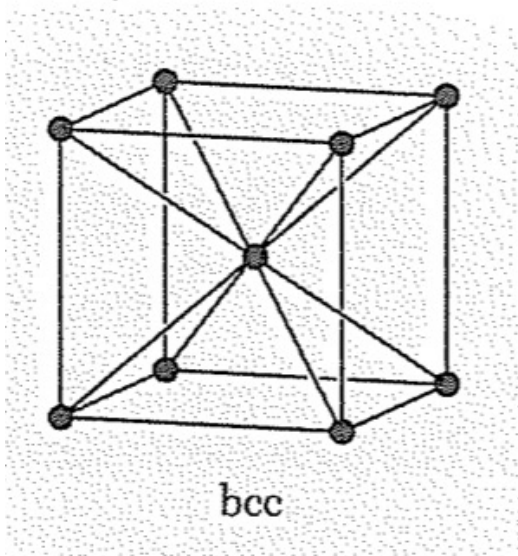
$$S(v_1 v_2 v_3) = f \{1 + \exp[-i\pi(v_1 + v_2 + v_3)]\}$$

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.



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

# Structure Factor of the fcc Lattice

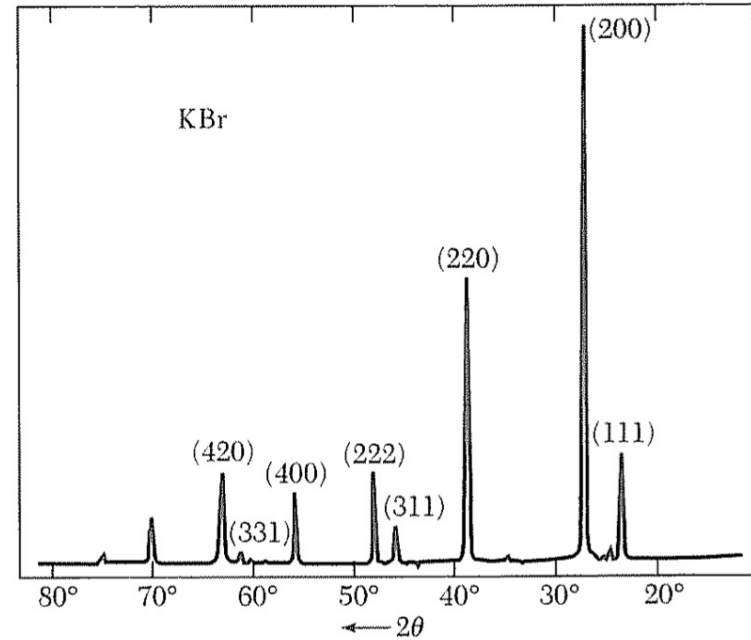
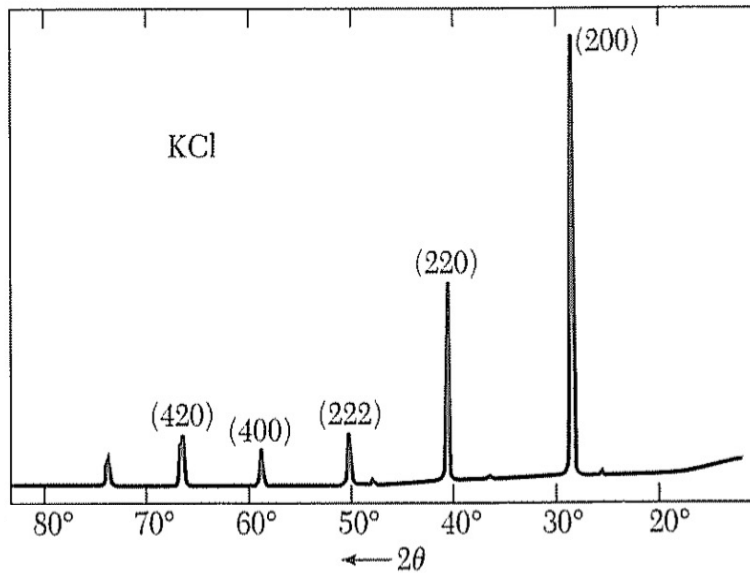
The basis of the fcc structure referred to the cubic cell has identical atoms at  $000$ ;  $0\frac{11}{22}$ ;  $\frac{1}{2}0\frac{1}{2}$ ;  $\frac{11}{22}0$ . Thus

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

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.



# X-ray Reflections from KCl and KBr Powders



Both KCl and KBr have an fcc lattice but different form factors.

# 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.