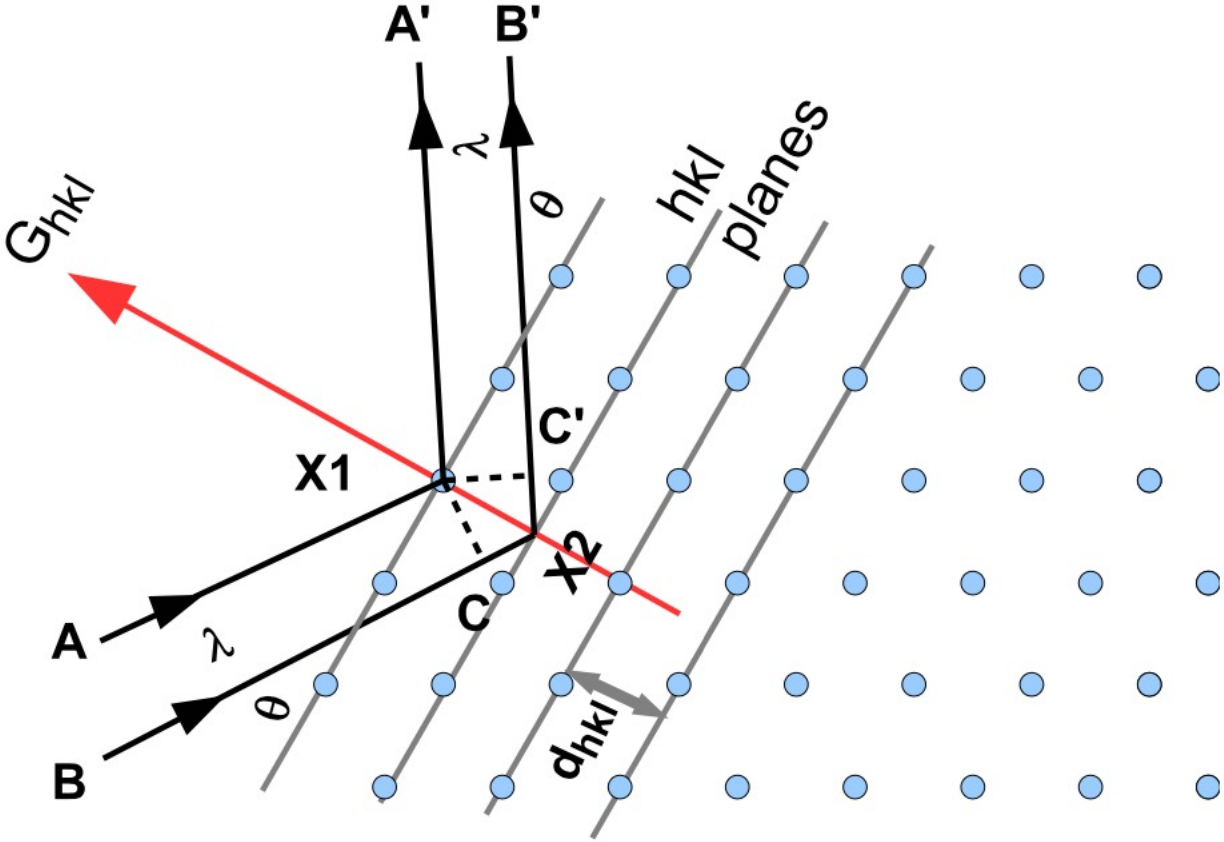
X-ray Diffraction and Reciprocal Lattice



X-ray Diffraction and Reciprocal Lattice

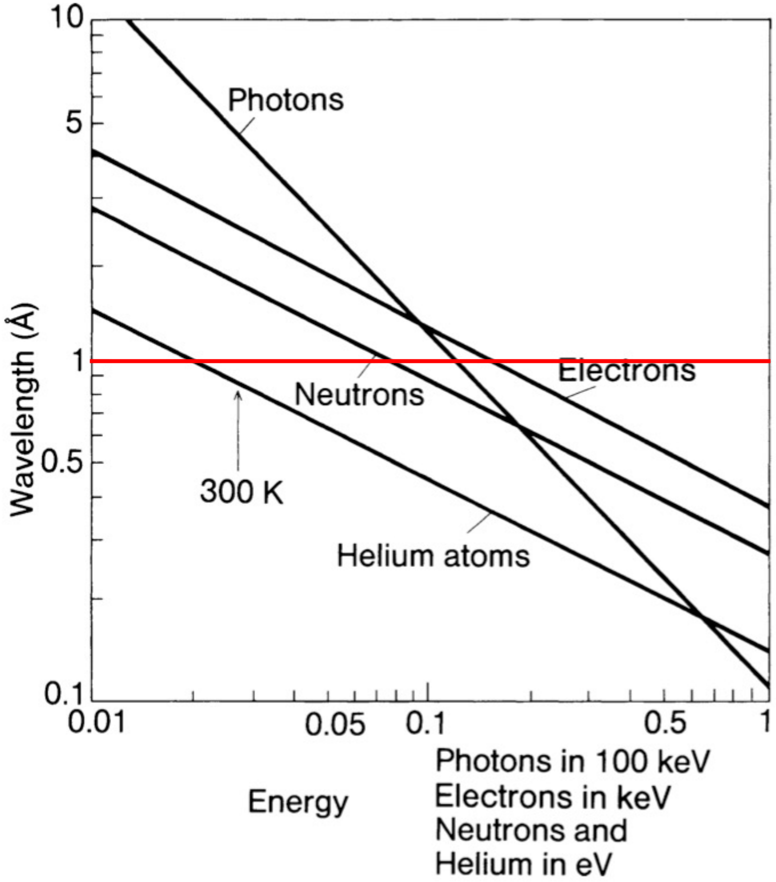
Typical interatomic distances in solid are of the order of an angstrom. Thus the typical wavelength of an electromagnetic probe of such distances must be of the order of an angstrom.

$$E = hc / \lambda \qquad \lambda\,(\text{Å}) = 12.4/E\,(\text{keV})$$

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.

Wavelength vs particle energy

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

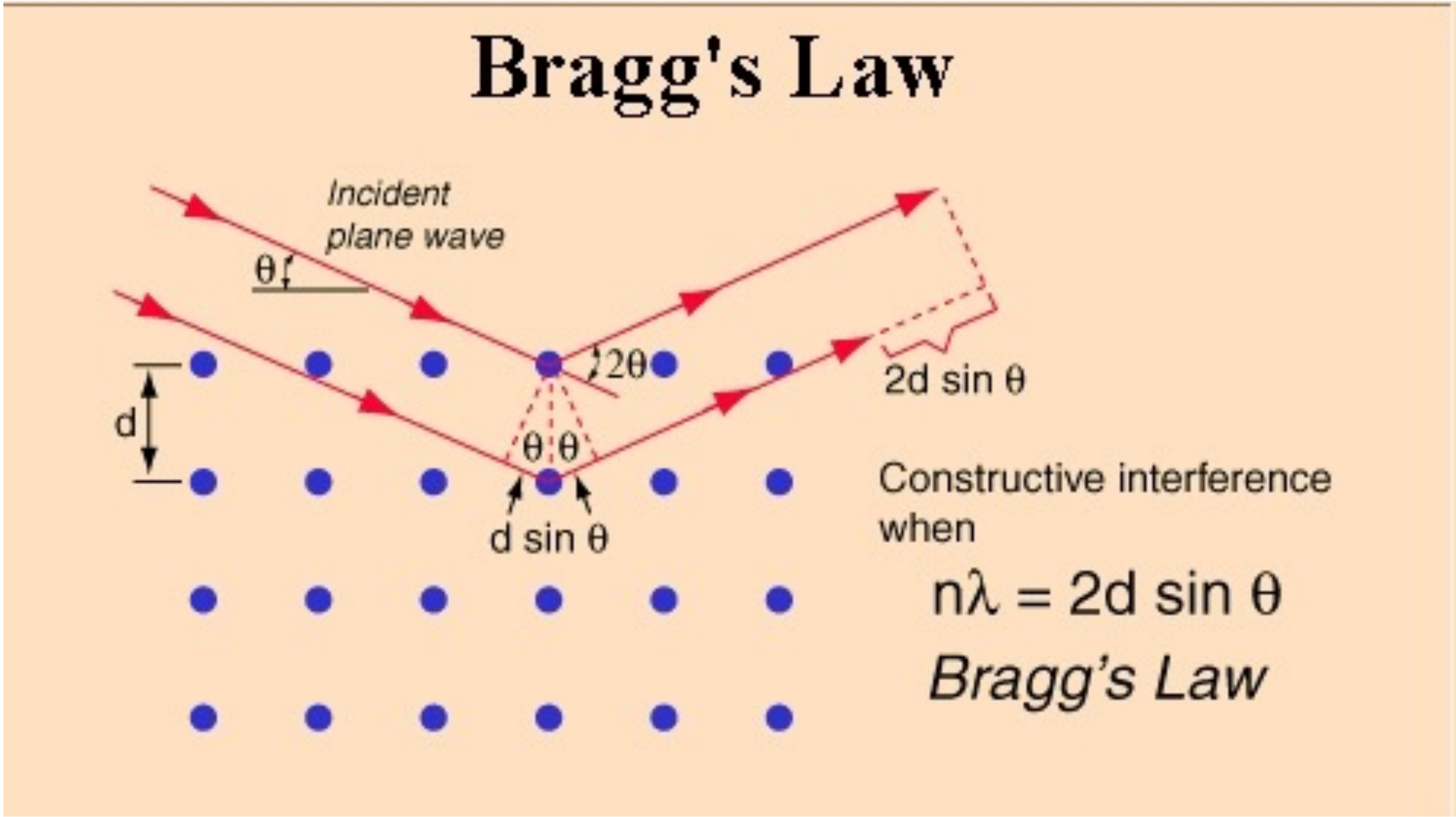


λ (Å) = 12.4/E (keV) for photon

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

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

Bragg Diffraction: Bragg’s Law

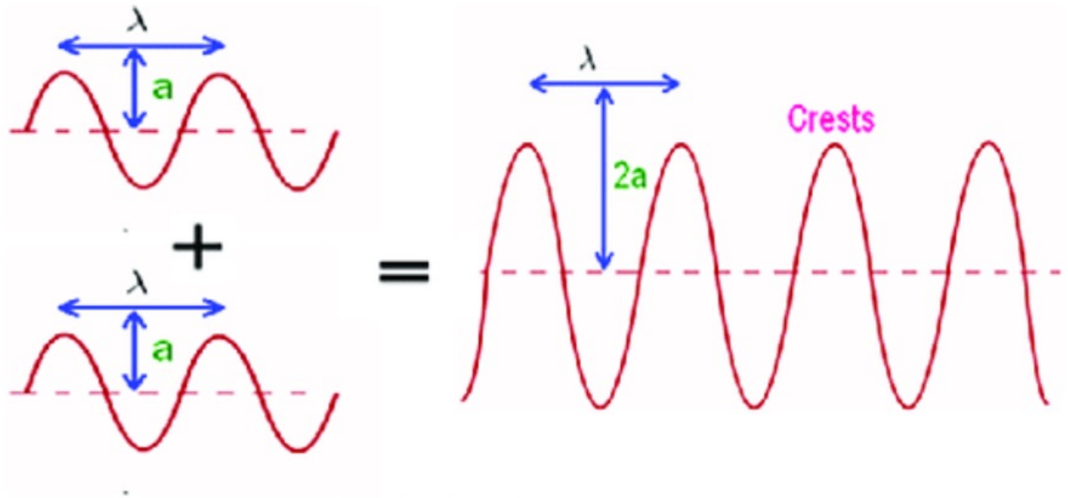


Constructive interference when

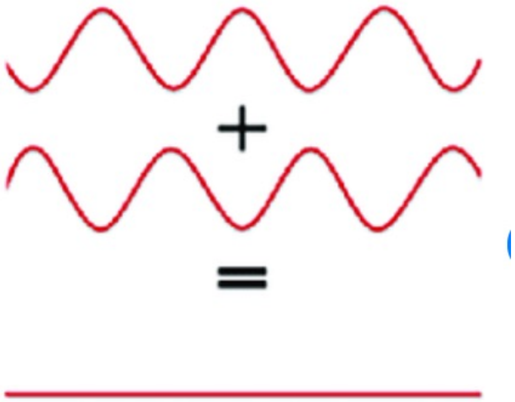
$$n\lambda = 2d \sin\theta$$

Bragg’s Law

Condition for Interferences



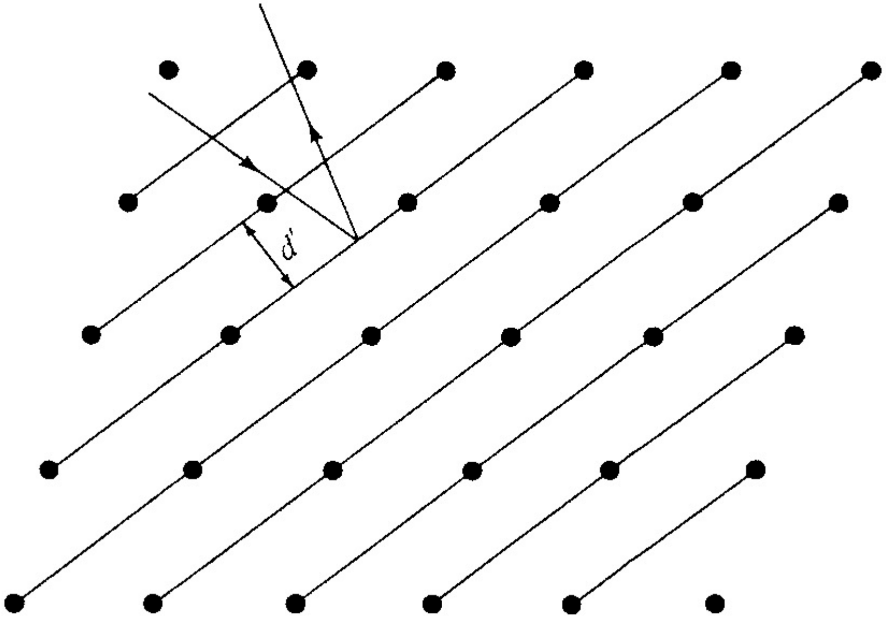
Constructive interference



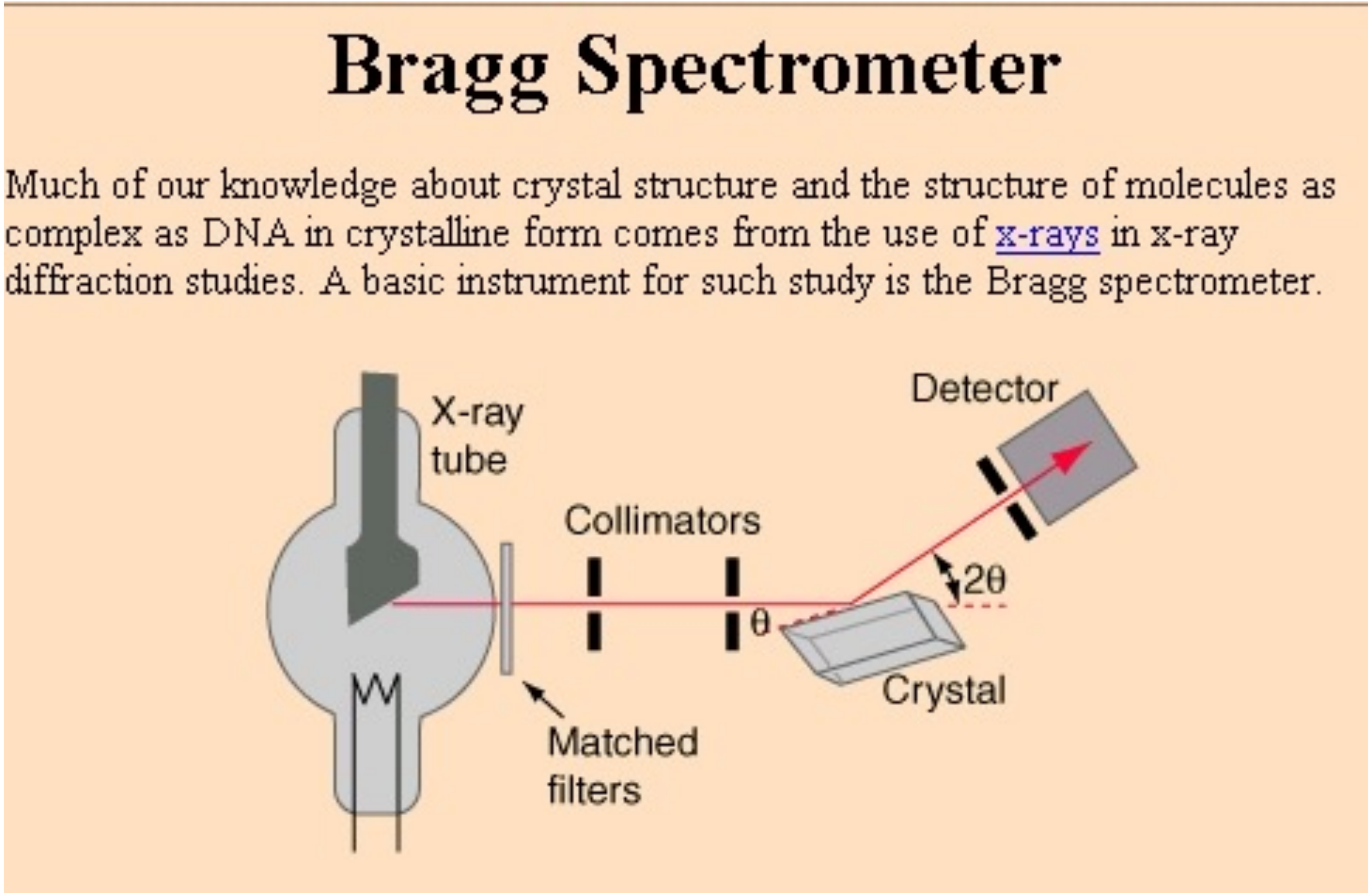
Destructive interference

Lattice planes produce Bragg diffraction

Figure 6.3
The same portion of Bravais lattice shown in Figure 6.1, with a different resolution into lattice planes indicated. The incident ray is the same as in Figure 6.1, but both the direction (shown in the figure) and wavelength (determined by the Bragg condition (6.2) with d replaced by d') of the reflected ray are different from the reflected ray in Figure 6.1. Reflections are possible, in general, for any of the infinitely many ways of resolving the lattice into planes.



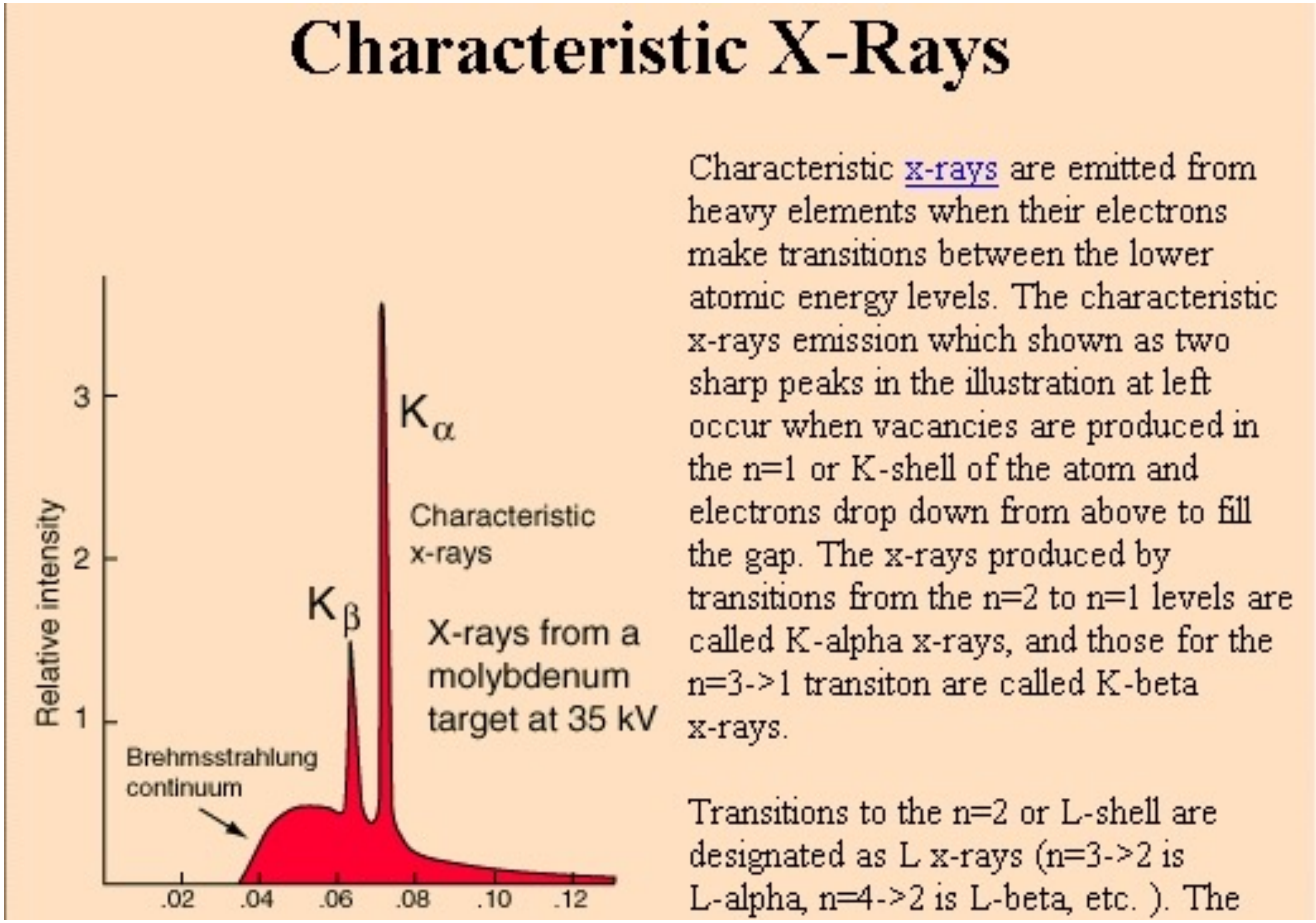
Bragg Spectrometer



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

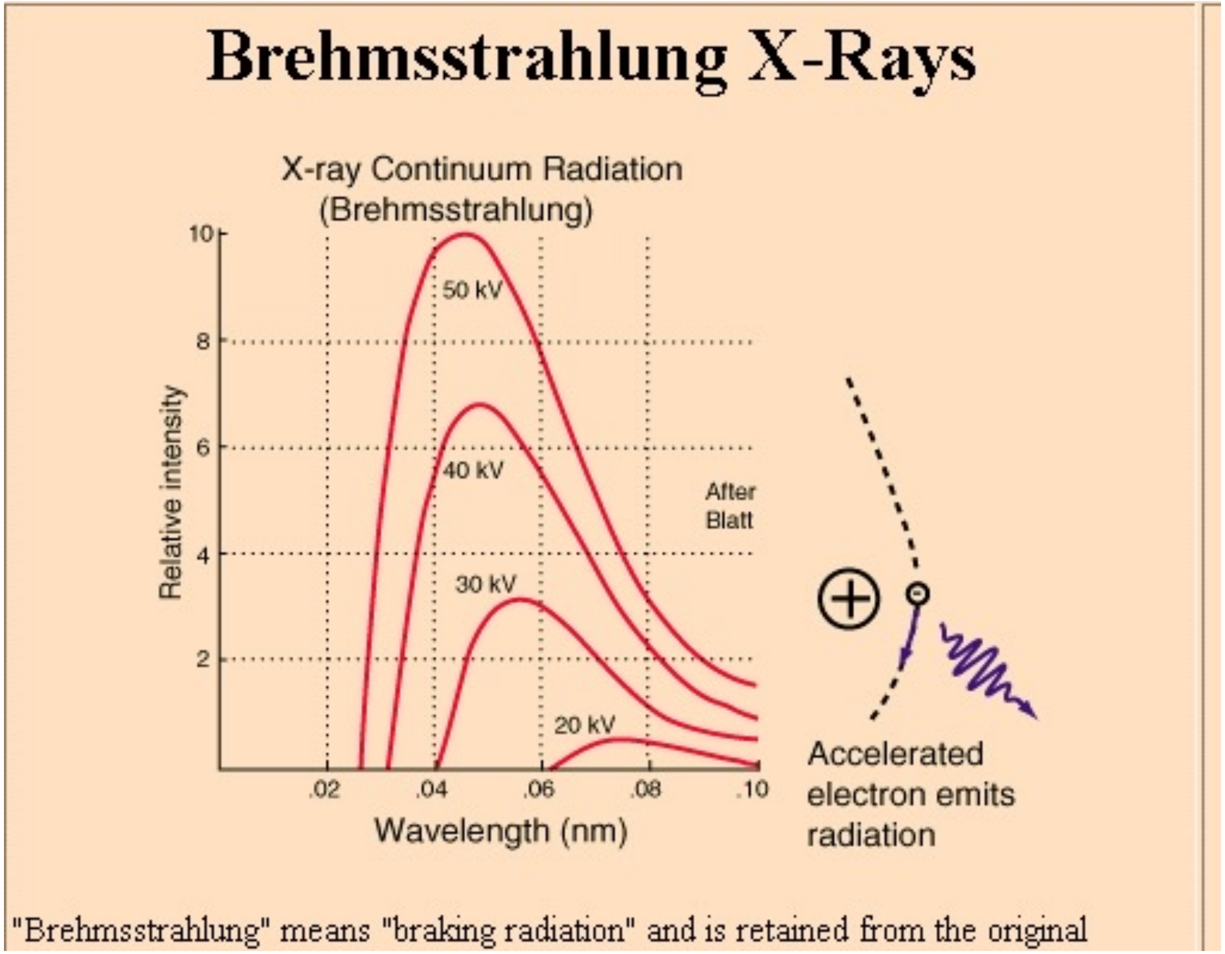


Characteristic X-Rays

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->1 transiton are called K-beta x-rays.

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

Brehmsstrahlung X-Rays



Brehmsstrahlung X-Rays

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

Bragg Peaks

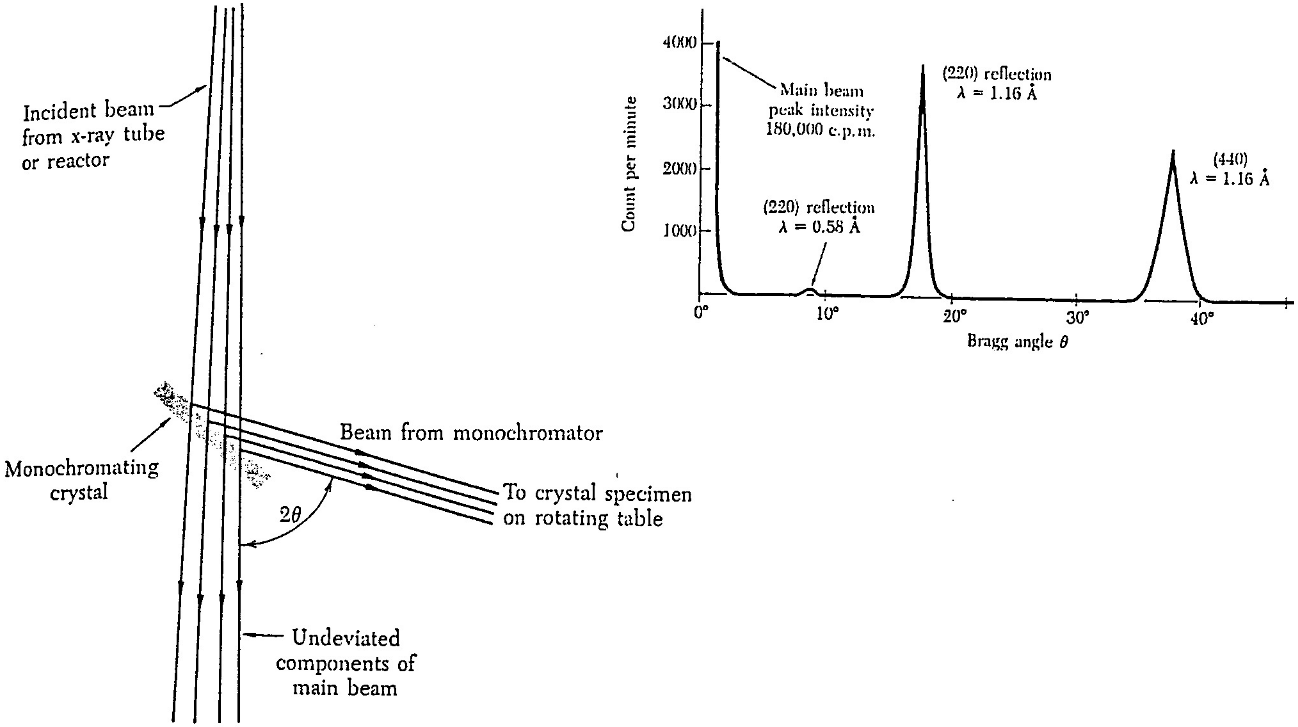
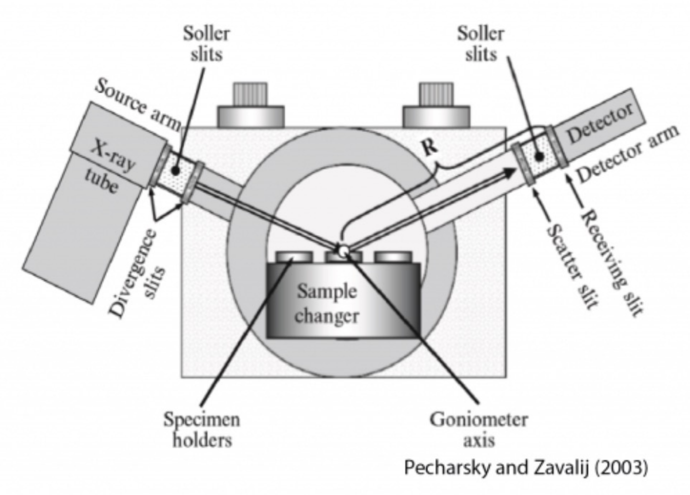
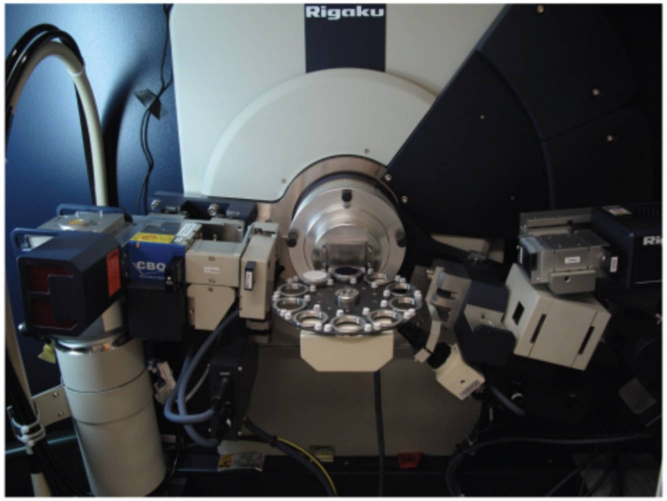


Figure 3 Sketch of a monochromator which by Bragg reflection selects a narrow spectrum of x-ray or neutron wavelengths from a broad spectrum incident beam. The upper part of the figure shows the analysis (obtained by reflection from a second crystal) of the purity of a 1.16 Å beam of neutrons from a calcium fluoride crystal monochromator. The main beam is that not reflected from the second crystal. (After G. Bacon.)

X-ray Diffractometer



Pecharsky and Zavalij (2003)



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

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

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

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

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

In more compact form

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

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

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

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 **K** that yield plane waves with the periodicity of a given Bravais lattice.
- Let 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 **r** and all **R** Bravais lattice.
- Thus the reciprocal lattice vectors **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**.

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

Here

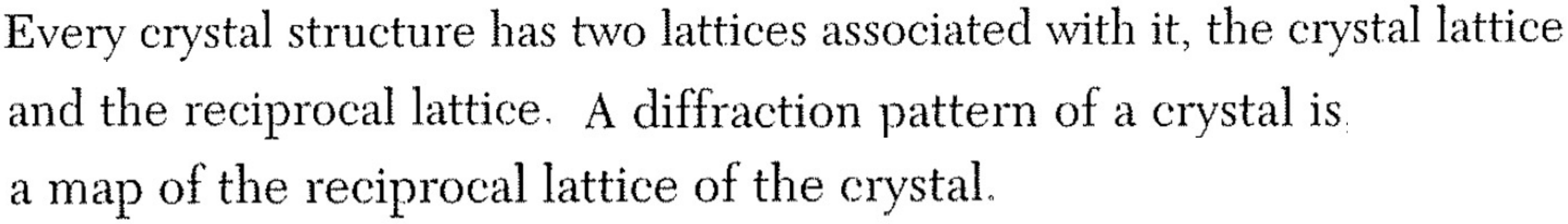
$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij} \quad \text{where } \delta_{ij} = 1 \text{ if } i = j \text{ and } \delta_{ij} = 0 \text{ if } i \neq j.$$

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

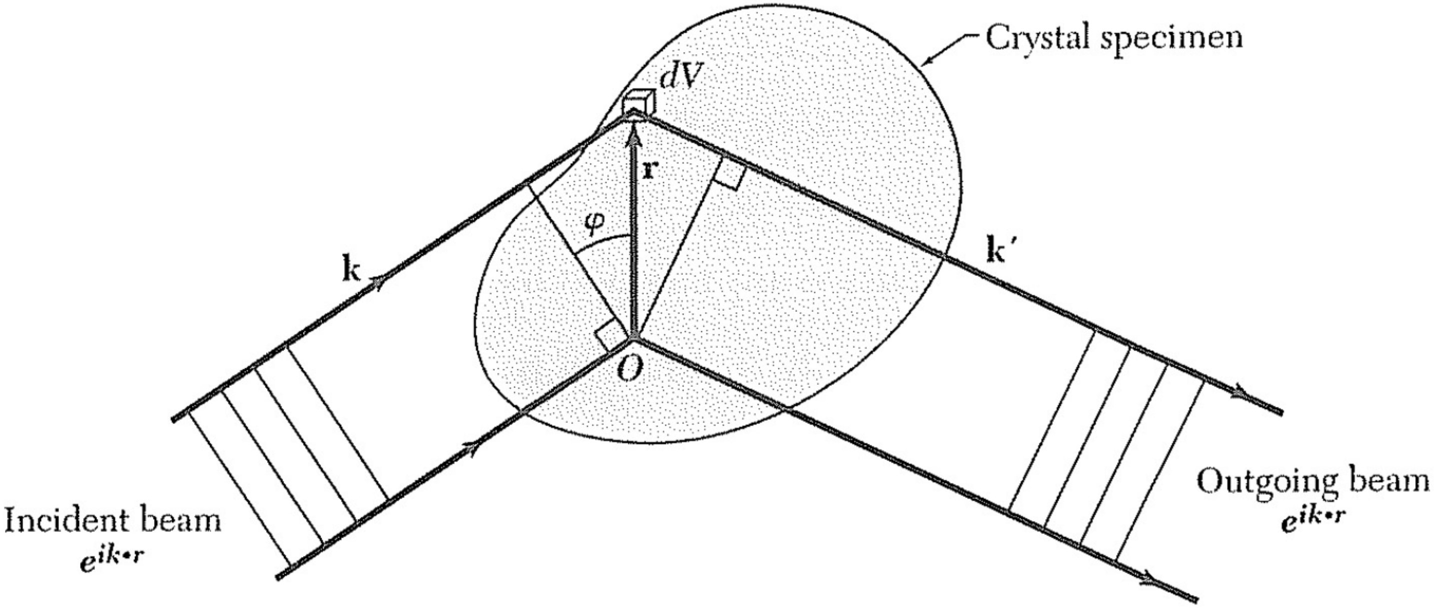


Every crystal structure has two lattices associated with it, the crystal lattice and the reciprocal lattice. A diffraction pattern of a crystal is a map of the reciprocal lattice of the crystal.

Theorem: The set of reciprocal lattice vectors **G** determines the possible x-ray reflections.

Scattering Amplitude of X-Ray Diffraction

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



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

$n(\mathbf{r})$: 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,

$\Delta\mathbf{k} = \mathbf{k}' - \mathbf{k}$ $\qquad$ $\Delta\mathbf{k}=\mathbf{G}$,

the argument of the exponential vanishes and $F = Vn_G$.

The diffraction condition is **k’ = k + G.**

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

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

or

$$2\mathbf{k} \cdot \mathbf{G} = G^2 .$$

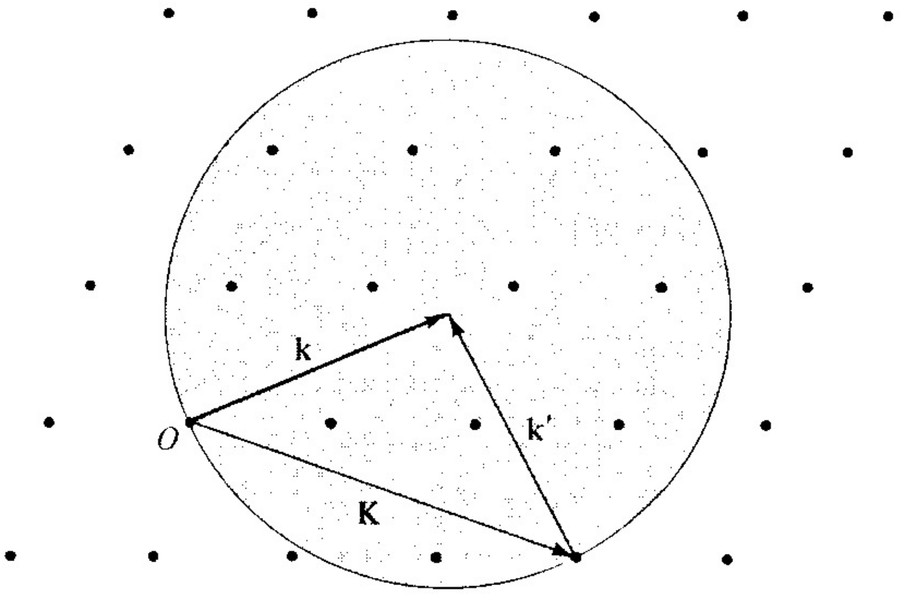
which is another statement of the Bragg condition.

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

Bragg's Law

Ewald Construction

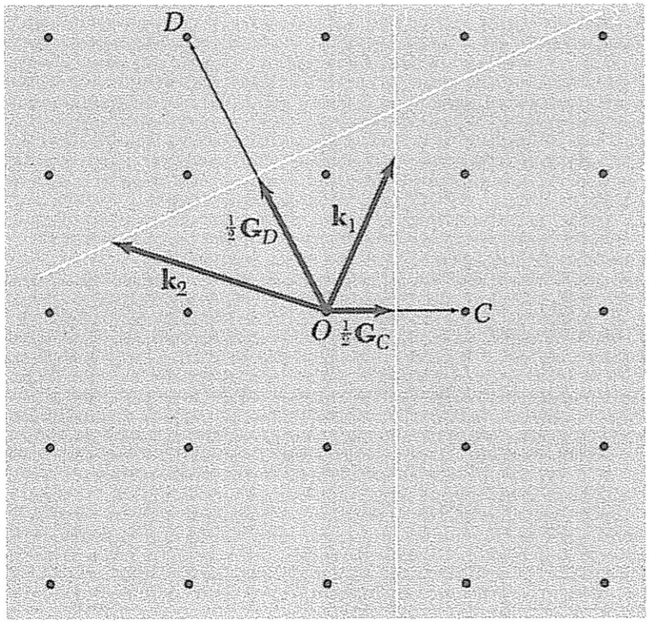
Figure 6.7
The Ewald construction. Given the incident wave vector **k**, a sphere of radius k is drawn about the point **k**. Diffraction peaks corresponding to reciprocal lattice vectors **K** will be observed only if **K** gives a reciprocal lattice point on the surface of the sphere. Such a reciprocal lattice vector is indicated in the figure, together with the wave vector **k**′ of the Bragg reflected ray.

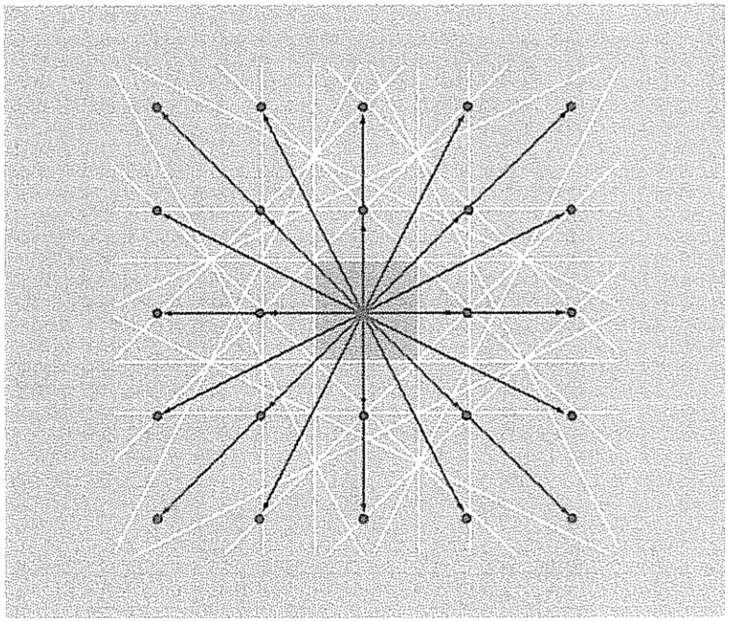


Brillouin Zone

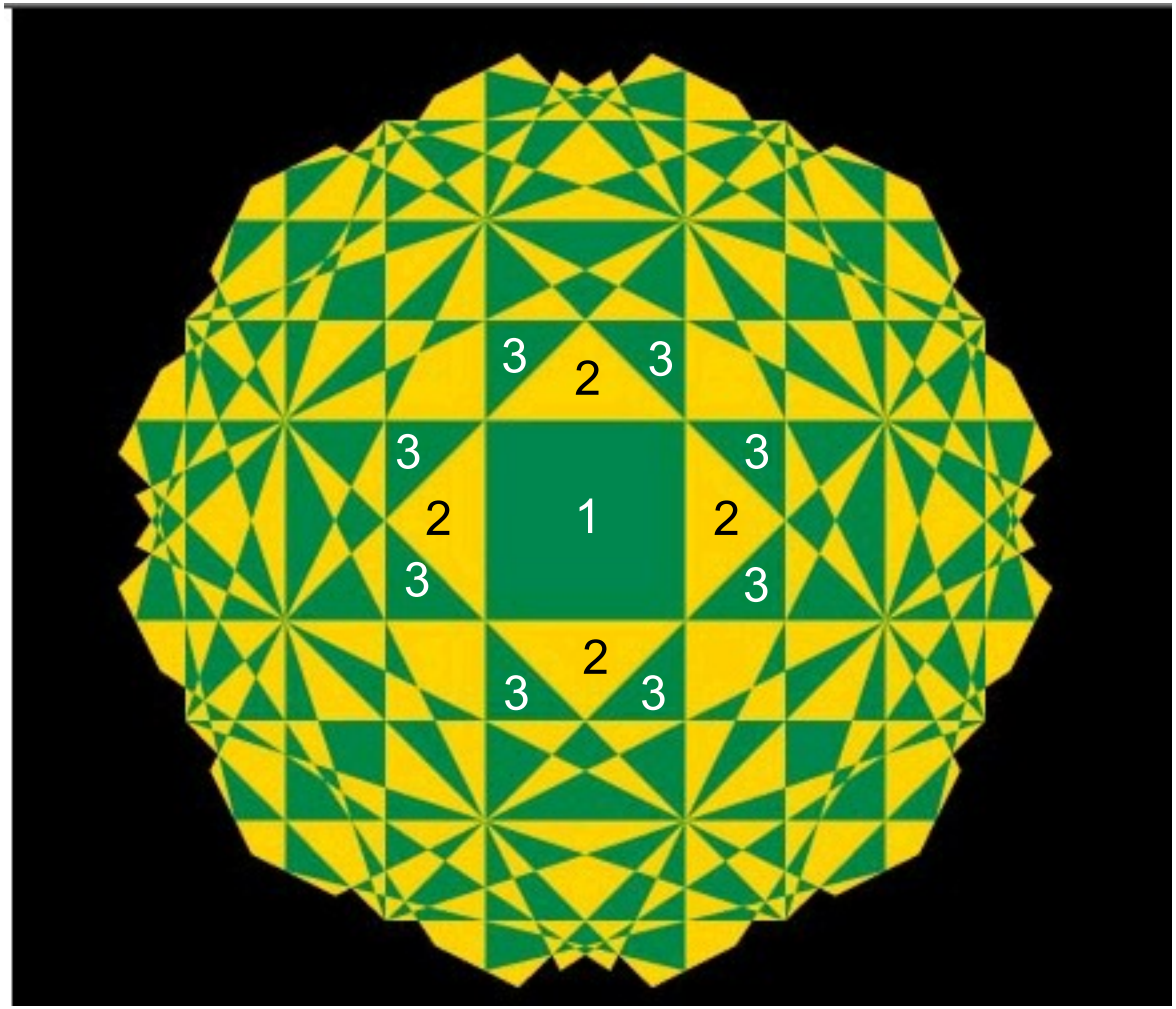
A Brillouin zone is defined as a Wigner-Seitz cell in the reciprocal lattice.

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





All Brillouin Zones: Square Lattice



Reciprocal Lattice to bcc Lattice

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

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

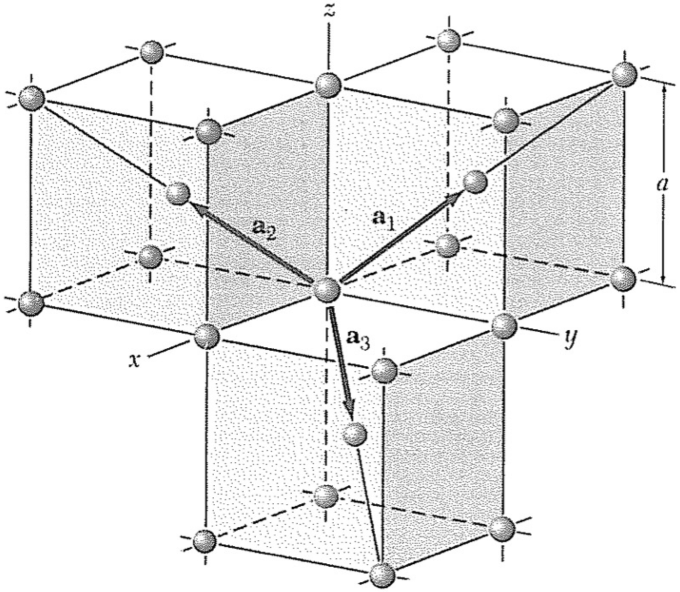


Figure 12 Primitive basis vectors of the body-centered cubic lattice.

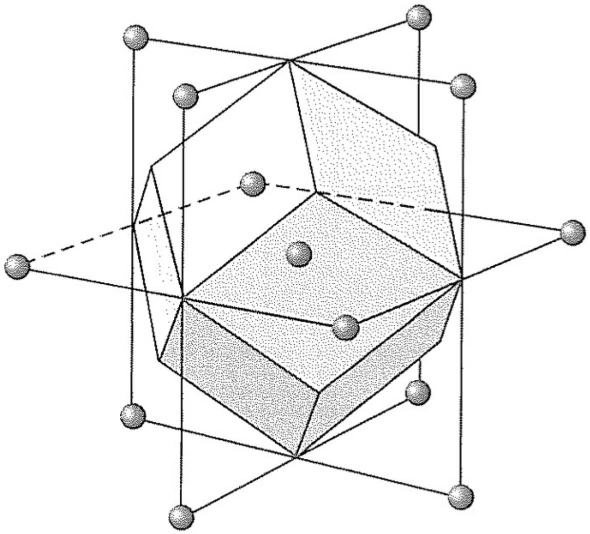
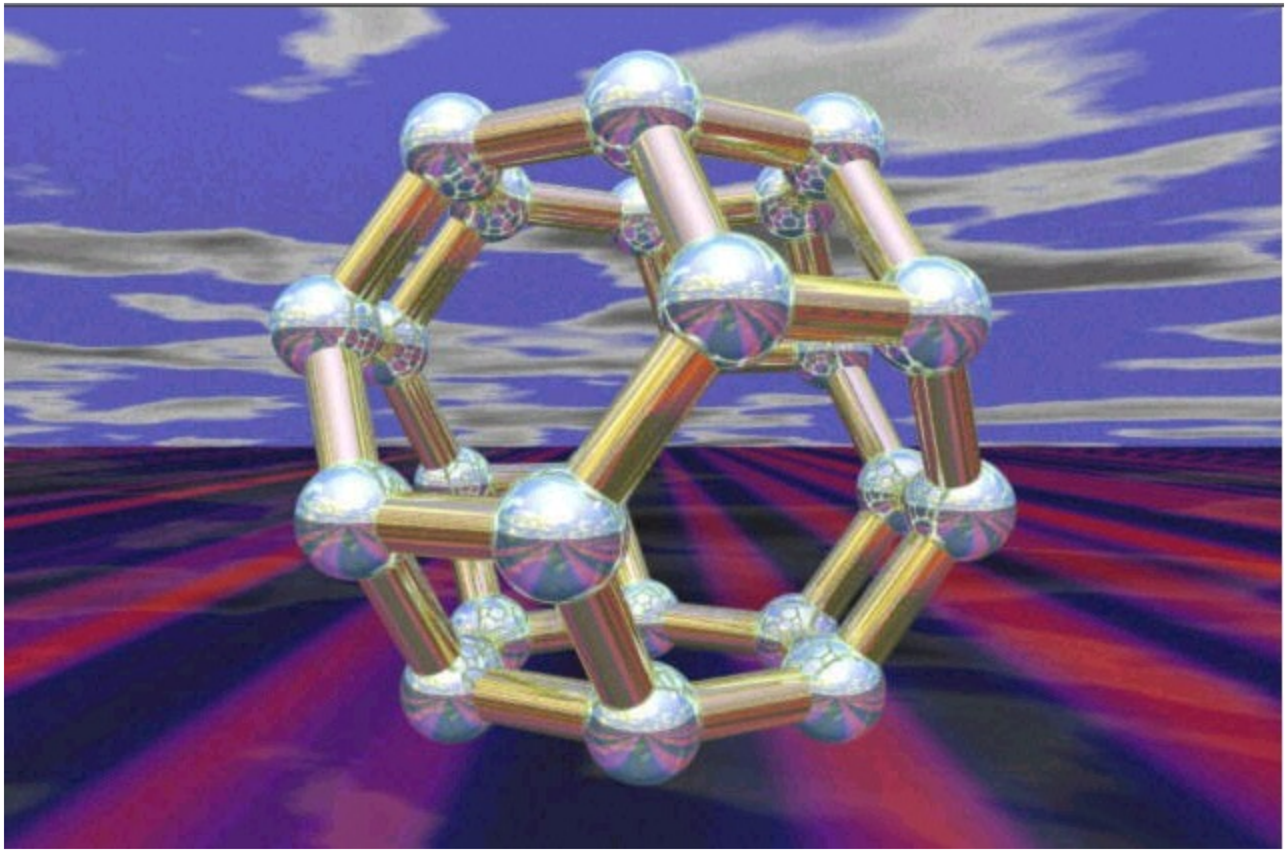


Figure 13 First Brillouin zone of the body-centered cubic lattice. The figure is a regular rhombic dodecahedron.

First Brillouin Zone for bcc



Reciprocal Lattice to fcc Lattice

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

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

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

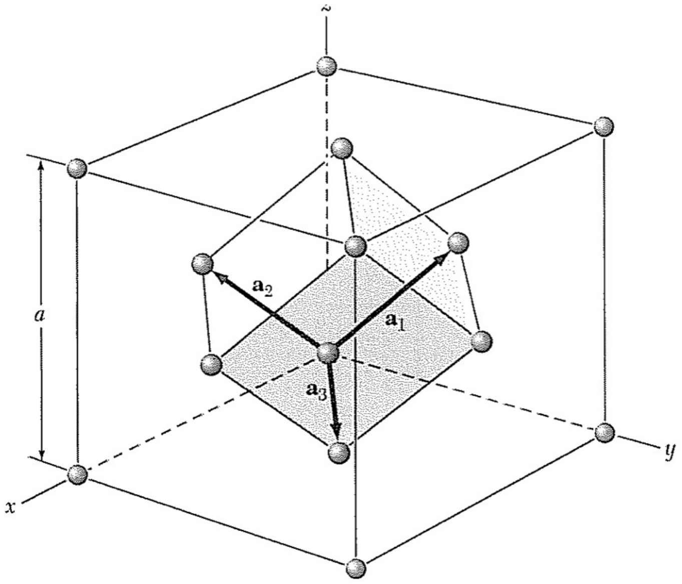


Figure 14 Primitive basis vectors of the face-centered cubic lattice.

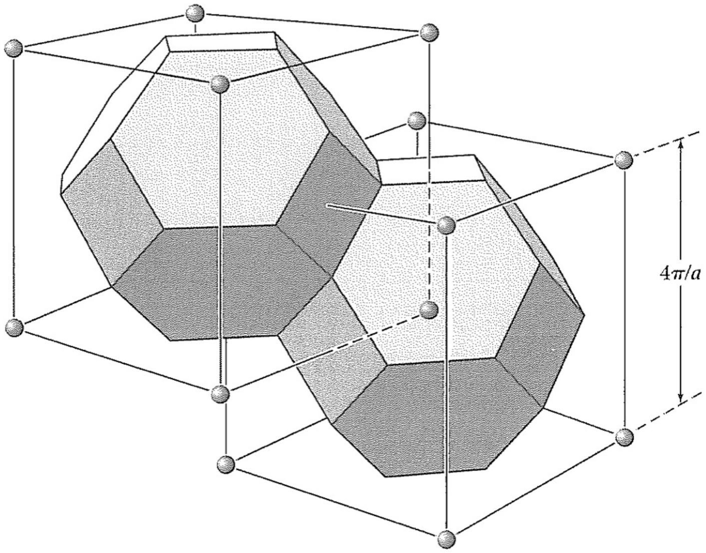
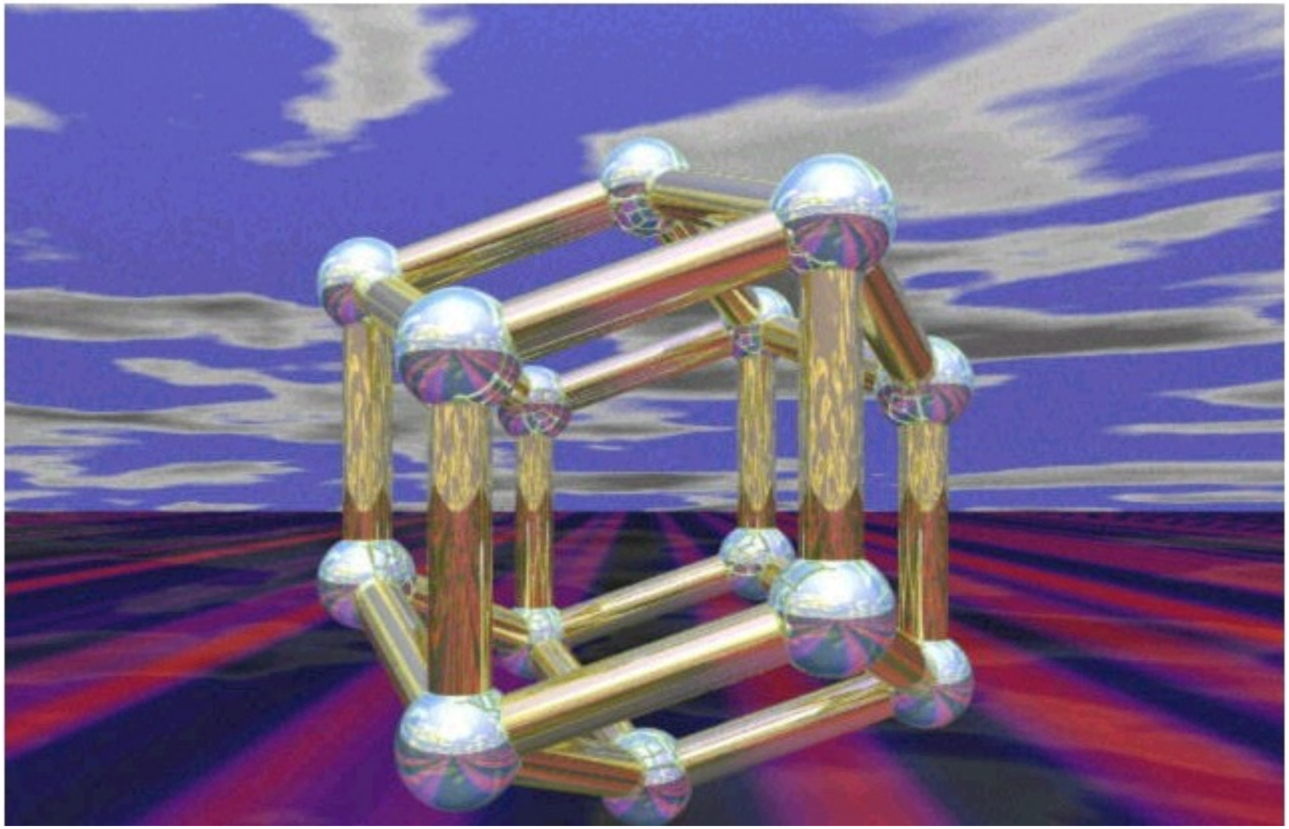


Figure 15 Brillouin zones of the face-centered cubic lattice.

First Brillouin Zone for fcc



Fourier Analysis of the Basis

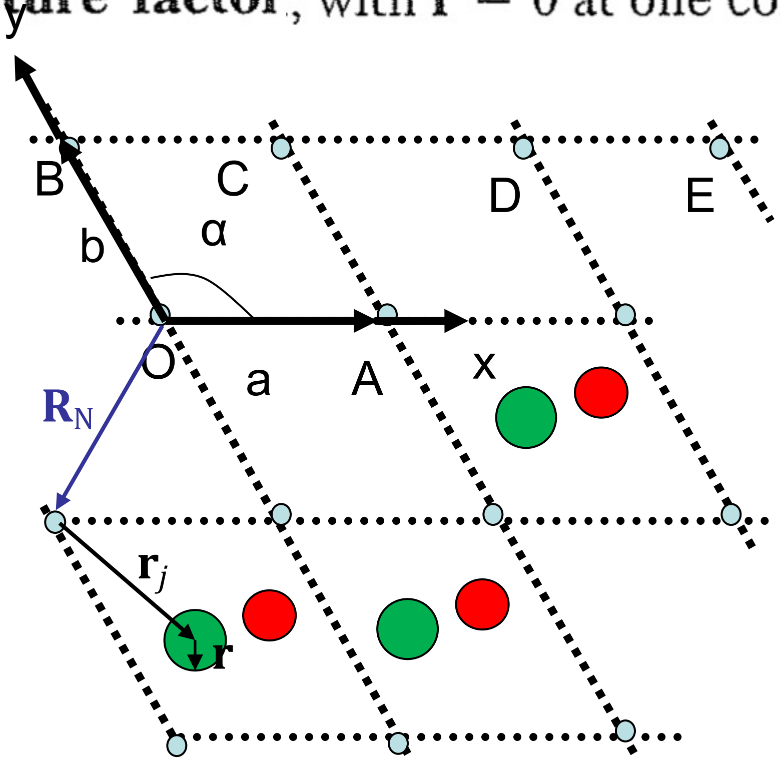
When the diffraction condition, **Δk = G**, is satisfied, the scattering amplitude for a crystal of *N* cells may be written as

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

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 **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

$$S_{\mathbf{G}} = \sum_j \int dV\, n_j(\mathbf{r} - \mathbf{r}_j) \exp(-i\mathbf{G} \cdot \mathbf{r})$$

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

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 $\mathbf{G} \cdot \mathbf{r}_j = (v_1\mathbf{b}_1 + v_2\mathbf{b}_2 + v_3\mathbf{b}_3) \cdot (x_j\mathbf{a}_1 + y_j\mathbf{a}_2 + z_j\mathbf{a}_3)$
$= 2\pi(v_1x_j + v_2y_j + v_3z_j)$, so

$$S_{\mathbf{G}}(v_1v_2v_3) = \sum_j f_j \exp[-i2\pi(v_1x_j + v_2y_j + v_3z_j)]$$

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 $x_2 = y_2 = z_2 = ½$. Thus,

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

and

$$S = 0 \qquad \text{when } v_1 + v_2 + v_3 = \text{odd integer} \;;$$
$$S = 2f \qquad \text{when } v_1 + v_2 + v_3 = \text{even integer}$$

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.

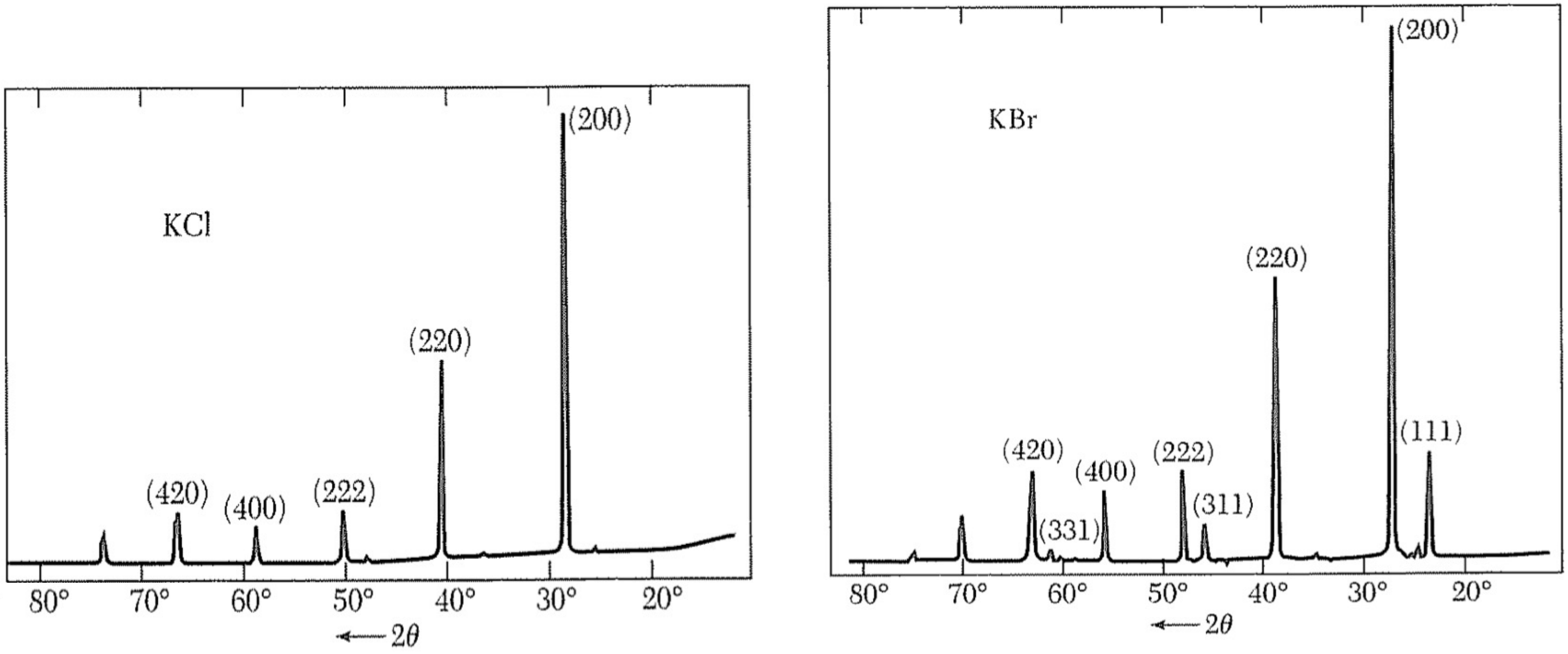
Structure Factor of the fcc Lattice

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

$$f_j \equiv 2\pi \int dr\, r^2\, d(\cos\alpha)\, n_j(r) \exp(-iGr\cos\alpha)$$

$$= 2\pi \int dr\, r^2 n_j(r) \cdot \frac{e^{iGr} - e^{-iGr}}{iGr} \; ,$$

$$f_j = 4\pi \int dr\, n_j(r) r^2 \;\mathrm{x}\; \frac{\sin Gr}{Gr} \; .$$

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

$f_j = 4\pi \int dr\, n_j(r) r^2 = Z$ **:** 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 k_0. Why does one observe a diffraction pattern of electrons from a surface for all values and orientations of 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.