MCH – 204: Spectroscopy-II & Diffraction Methods
UNIT-III: X-ray Diffraction-I
Lecture 2:
Lattice & Lattice planes, Miller Indices, Reciprocal Lattice, Bragg equation, Diffraction by crystals, Diffraction patterns

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Ideal Crystal

- An ideal crystal is a **periodic array** of structural units, such as atoms or molecules.
- It can be constructed by the infinite repetition of these identical structural units in space.
- Structure can be described in terms of a **lattice,** with a group of atoms attached to each lattice point. The group of atoms is the **basis.**

Bravais Lattice

- An infinite array of discrete points with an arrangement and orientation that appears **exactly the same,** from any of the points the array is viewed from.
- A three dimensional Bravais lattice consists of all points with position vectors **R** that can be written as a linear combination of *primitive vectors.* The expansion coefficients must be **integers.**

Crystal lattice: Proteins

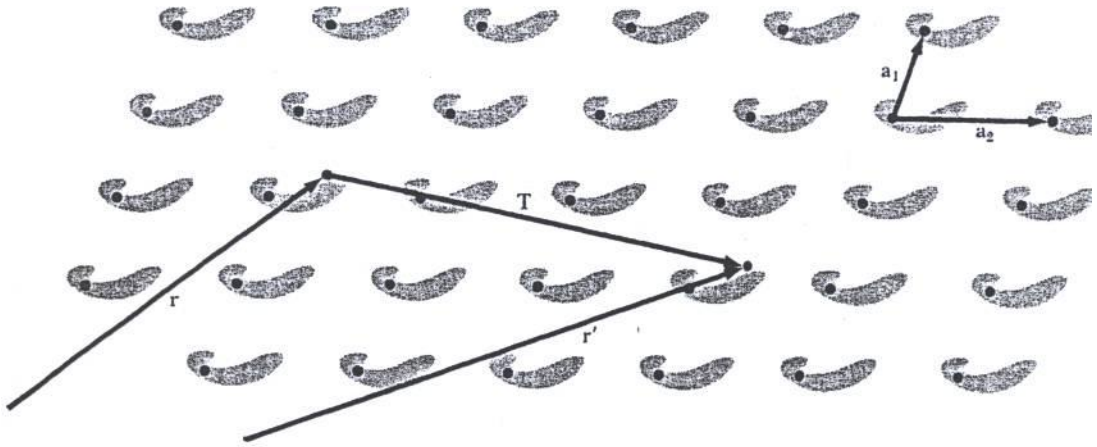


Figure 2 Portion of a crystal of an imaginary protein molecule, in a two-dimensional world. (We picked a protein molecule because it is not likely to have a special symmetry of its own.) The atomic arrangement in the crystal looks exactly the same to an observer at $\mathbf{r}'$ as to an observer at $\mathbf{r}$, provided that the vector $\mathbf{T}$ which connects $\mathbf{r}'$ and $\mathbf{r}$ may be expressed as an integral multiple of the vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. In this illustration, $\mathbf{T} = -\mathbf{a}_1 + 3\mathbf{a}_2$. The vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are primitive transla-

Crystal Structure

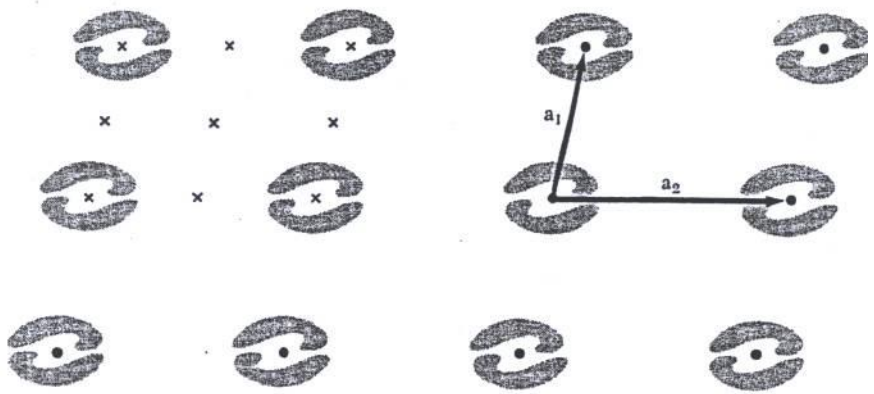


Figure 3 Similar to Fig. 2, but with protein molecules associated in pairs. The crystal translation vectors are $\mathbf{a}_1$ and $\mathbf{a}_2$. A rotation of π radians about any point marked × will carry the crystal into itself. This occurs also for equivalent points in other cells, but we have marked the points × only

Honeycomb: NOT Bravais

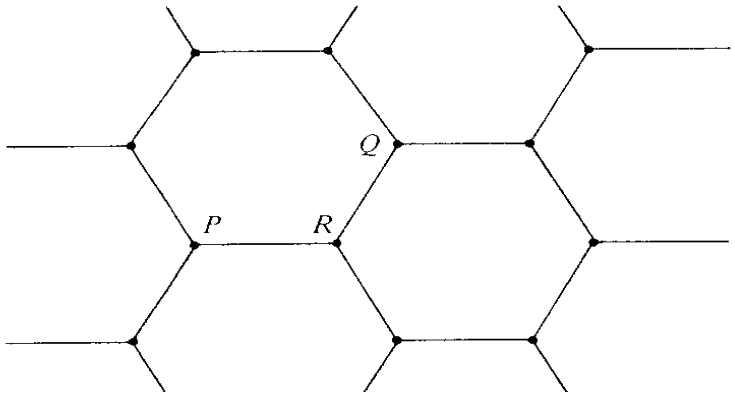


Figure 4.3
The vertices of a two-dimensional honeycomb do *not* form a Bravais lattice. The array of points has the same appearance whether viewed from point P or point Q. However, the view from point R is rotated through 180°.

Honeycomb net: Bravais lattice with **two point basis**

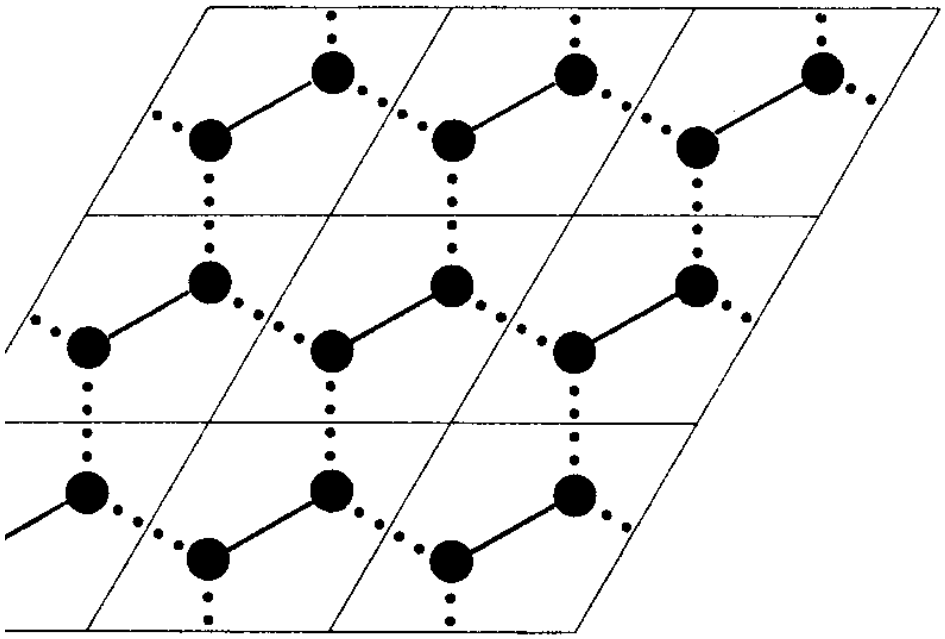


Figure 4.17
The honeycomb net, drawn so as to emphasize that it is a Bravais lattice with a two-point basis. The pairs of points joined by heavy solid lines are identically placed in the primitive cells (parallelograms) of the underlying Bravais lattice.

Crystal structure: basis

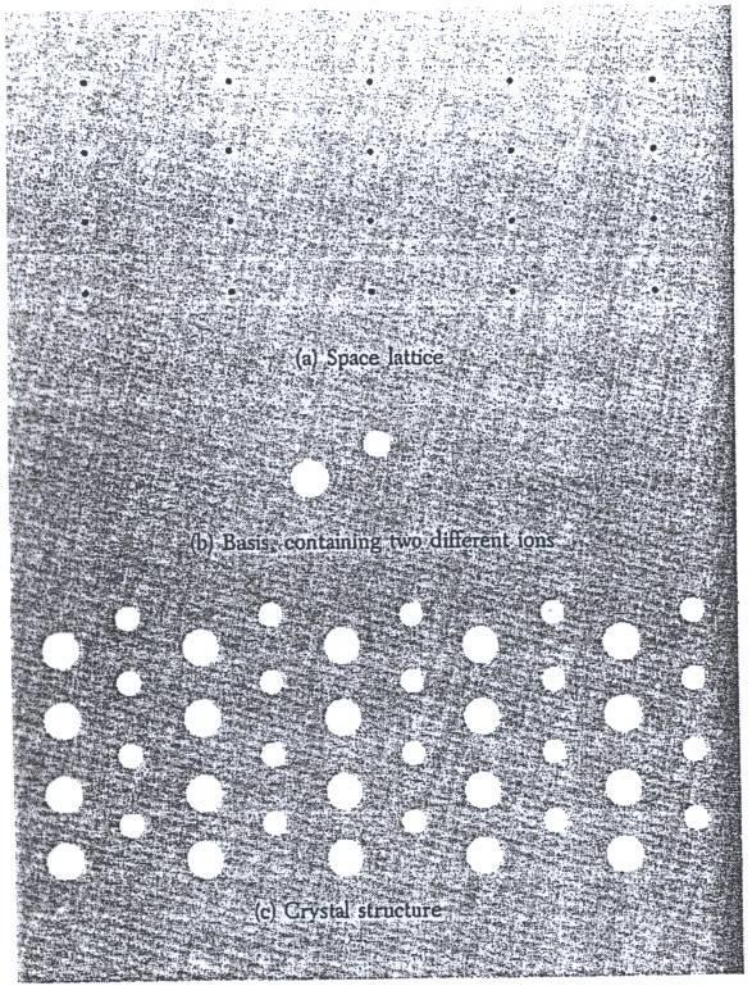


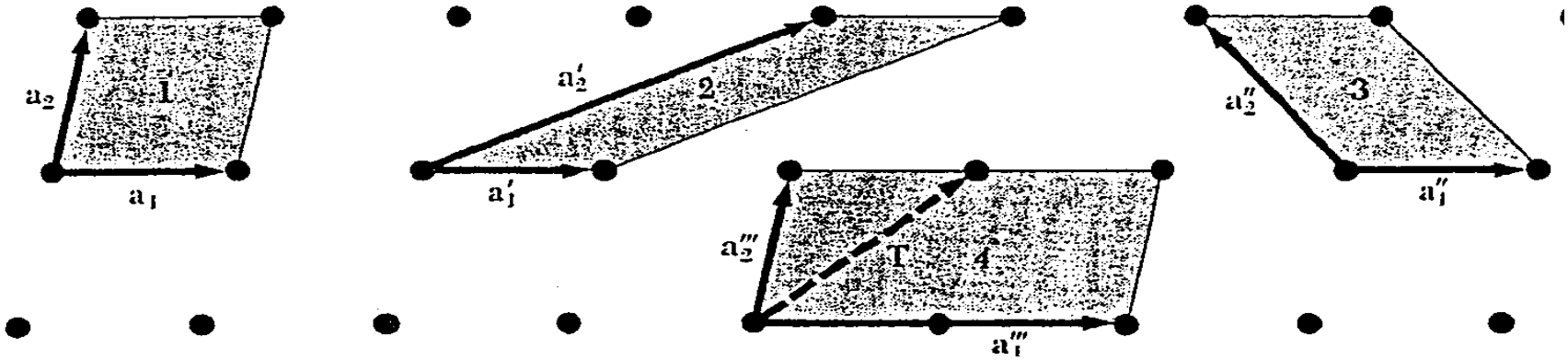
Figure 4 The crystal structure is formed by the addition of the basis (b) to every lattice point of the lattice (a). By looking at (c), you can recognize the basis and then you can abstract the space lattice. It does not matter where the basis is put in relation to a lattice point.

Translation Vector **T**

$$\mathbf{T} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3 \ .$$

Any two lattice points are connected by a vector of this form.

Translation(a1,a2), Nontranslation Vectors(a1’’’,a2’’’)



Miller indices of lattice plane

- The indices of a crystal plane (h,k,l) are defined to be a set of **integers** with no common factors, inversely proportional to the intercepts of the crystal plane along the crystal axes:

$$h:k:l = \frac{1}{x_1} : \frac{1}{x_2} : \frac{1}{x_3}$$

Indices of Crystal Plane

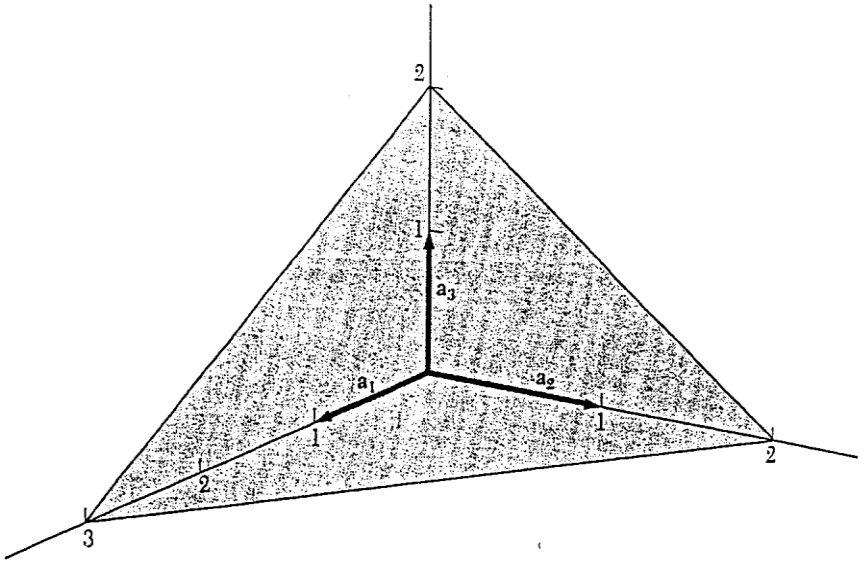


Figure 15 This plane intercepts the a_1, a_2, a_3 axes at $3a_1$, $2a_2$, $2a_3$. The reciprocals of these numbers are $\frac{1}{3}$, $\frac{1}{2}$, $\frac{1}{2}$. The smallest three integers having the same ratio are 2, 3, 3, and thus the indices of the plane are (233).

Indices of Planes: Cubic Crystal

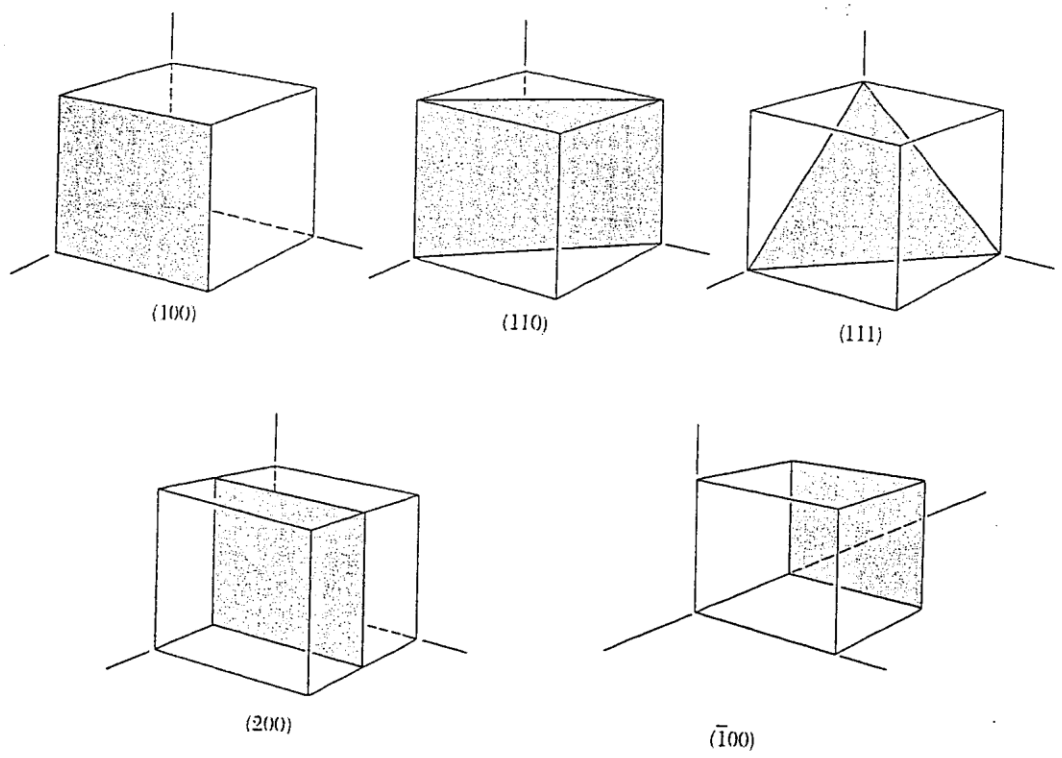
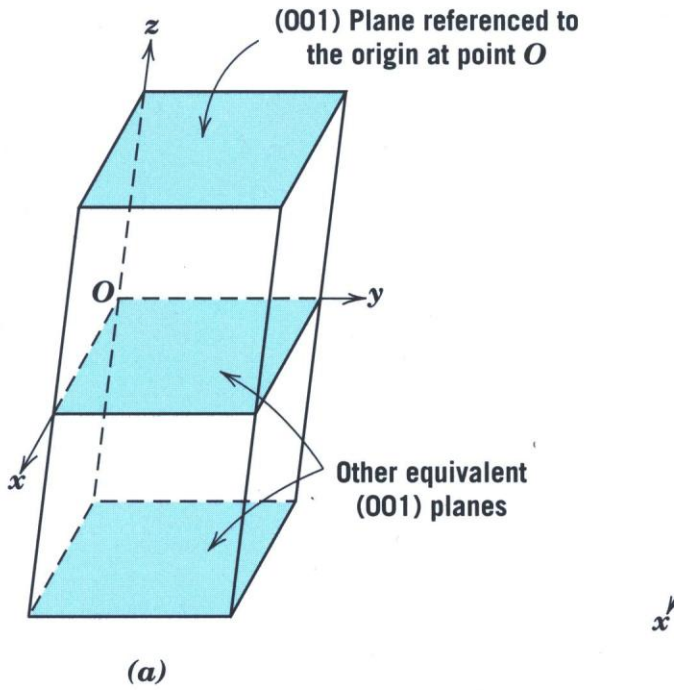
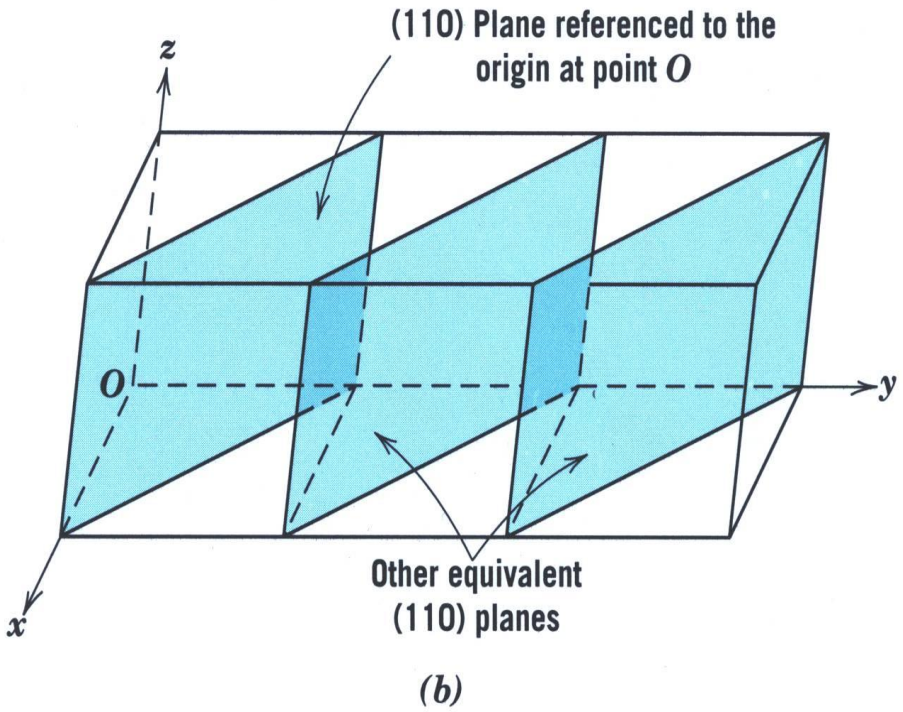


Figure 16 Indices of important planes in a cubic crystal. The plane (200) is parallel to (100) and to (1̄00).

001 Plane

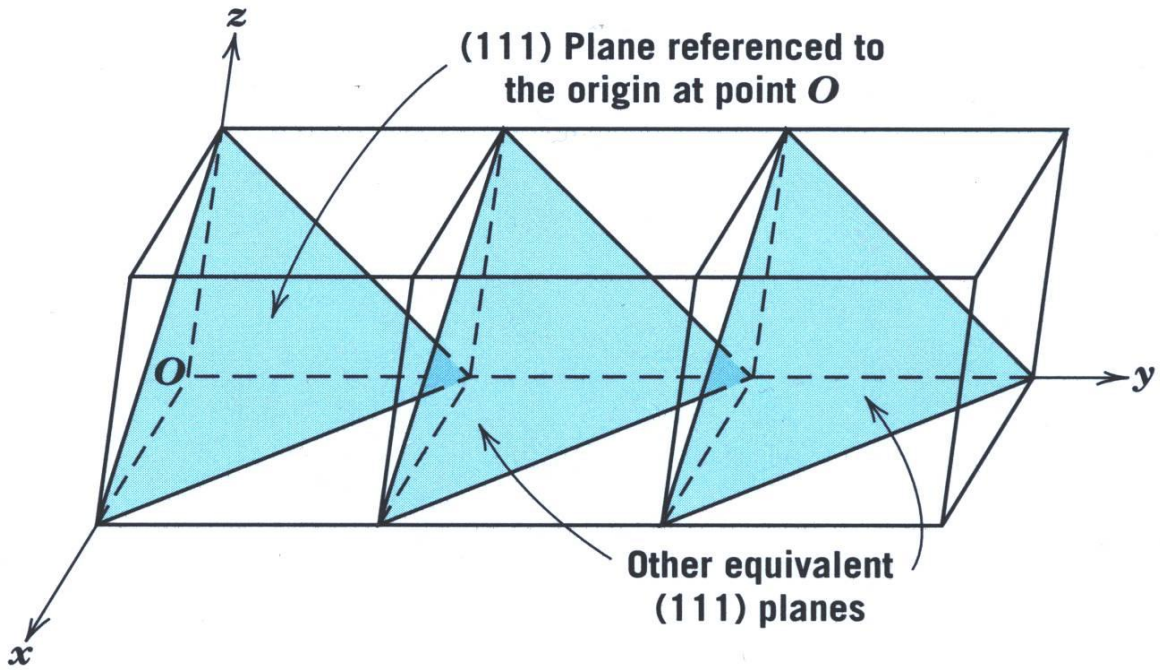

z
(001) Plane referenced to
the origin at point O
O
y
x
Other equivalent
(001) planes
x'
(a)

110 Planes


(110) Plane referenced to the origin at point O
z
O
y
x
Other equivalent (110) planes

(b)

111 Planes


z
(111) Plane referenced to
the origin at point O
O
y
x
Other equivalent
(111) planes

(c)

Symmetry planes

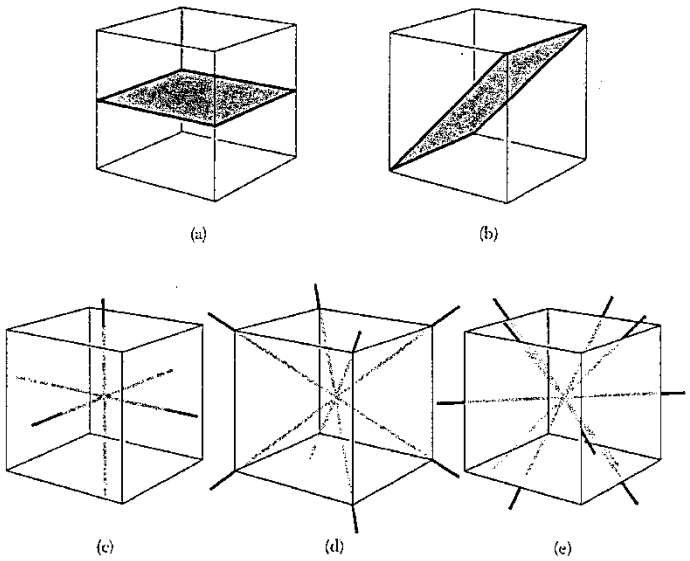


Figure 8 (a) A plane of symmetry parallel to the faces of a cube. (b) A diagonal plane of symmetry in a cube. (c) The three tetrad axes of a cube. (d) The four triad axes of a cube. (e) The six diad axes of a cube.

Bravais Lattice: Two Definitions

(a) A Bravais lattice is an infinite array of discrete points with an arrangement and orientation that appears *exactly* the same, from whichever of the points the array is viewed.

(b) A (three-dimensional) Bravais lattice consists of all points with position vectors $\mathbf{R}$ of the form

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, \qquad (4.1)$$

The expansion coefficients n1, n2, n3 must be **integers.** The vectors **a1,a2,a3** are **primitive vectors** and span the lattice.

Reciprocal Lattice

- Every periodic structure has two lattices associated with it. The first is the real space lattice, and this describes the periodic structure. The second is the reciprocal lattice, and this determines how the periodic structure interacts with waves. This section outlines how to find the basis vectors for the reciprocal lattice from the basis vectors of the real space lattice.

In real space we have:
$a, b, c, \alpha, \beta, \gamma$

While in reciprocal space we have:
$a^*, b^*, c^*, \alpha^*, \beta^*, \gamma^*$

In the simple case of the orthorhombic tetragonal and cubic systems where $\alpha, \beta, \gamma = 90°$
A* = 1/a; b* = 1/b; c* = 1/c and
α, β, γ *and* $\alpha^*, \beta^*, \gamma^* = 90°$

However:

In the triclinic system:

TABLE 2.3 Triclinic Direct and Reciprocal Relationships

$$a^* = \frac{bc \sin \alpha}{V} \qquad a = \frac{b^* c^* \sin \alpha^*}{V^*}$$

$$b^* = \frac{ac \sin \beta}{V} \qquad b = \frac{a^* c^* \sin \beta^*}{V^*}$$

$$c^* = \frac{ab \sin \gamma}{V} \qquad c = \frac{a^* b^* \sin \gamma^*}{V^*}$$

$$V = \frac{1}{V^*} = abc\sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$$

$$V^* = \frac{1}{V} = a^* b^* c^* \sqrt{1 - \cos^2 \alpha^* - \cos^2 \beta^* - \cos^2 \gamma^* + 2 \cos \alpha^* \cos \beta^* \cos \gamma^*}$$

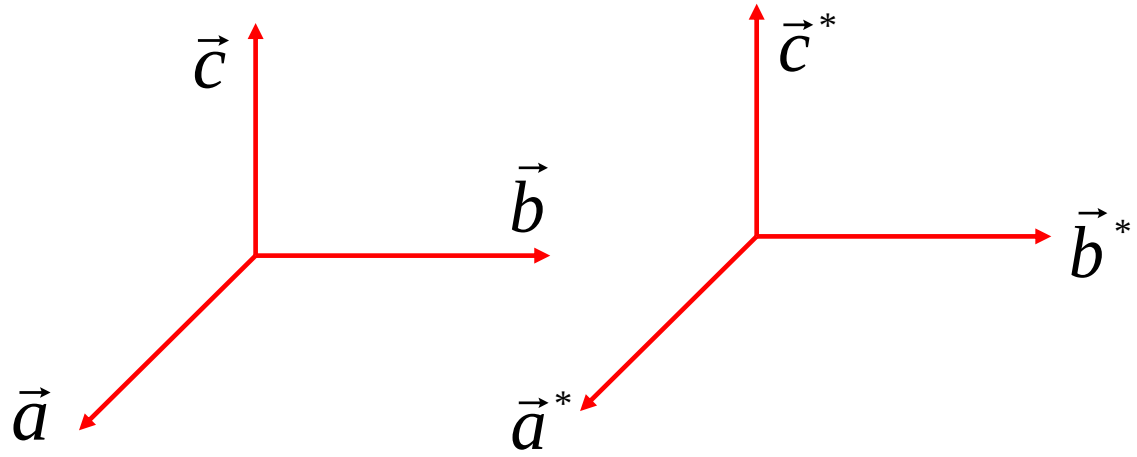
$$\cos \alpha^* = \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma} \qquad \cos \alpha = \frac{\cos \beta^* \cos \gamma^* - \cos \alpha^*}{\sin \beta^* \sin \gamma^*}$$

$$\cos \beta^* = \frac{\cos \alpha \cos \gamma - \cos \beta}{\sin \alpha \sin \gamma} \qquad \cos \beta = \frac{\cos \alpha^* \cos \gamma^* - \cos \beta^*}{\sin \alpha^* \sin \gamma^*}$$

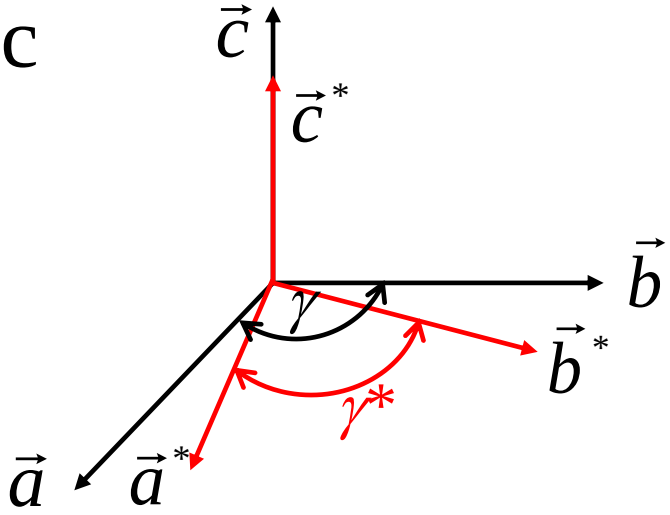
$$\cos \gamma^* = \frac{\cos \alpha \cos \beta - \cos \gamma}{\sin \alpha \sin \beta} \qquad \cos \gamma = \frac{\cos \alpha^* \cos \beta^* - \cos \gamma^*}{\sin \alpha^* \sin \beta^*}$$

Reciprocal lattices corresponding to crystal systems in real space

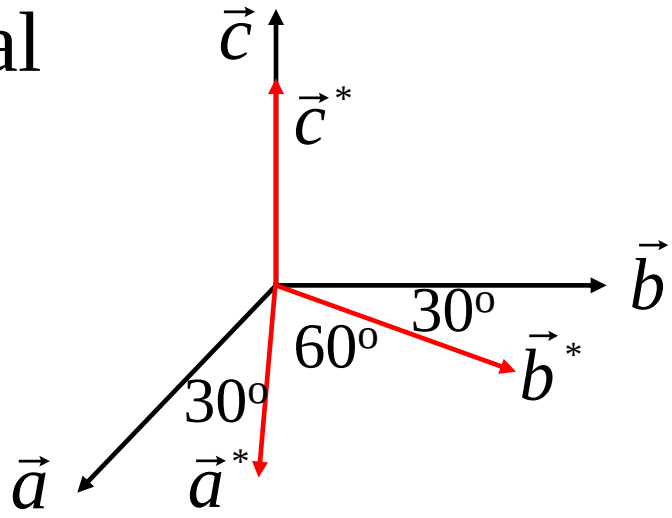
(i) Orthorhombic ,tetragonal ,cubic

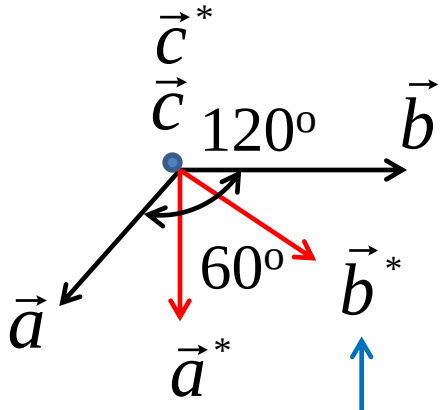


(ii) Monoclinic



(iii) Hexagonal





We deal with reciprocal lattice
Transformation in Miller indices.

$\vec{a}^* \perp \vec{b}; \quad \vec{a}^* \perp \vec{c}$

$\vec{b}^* \perp \vec{a}; \quad \vec{b}^* \perp \vec{c}$

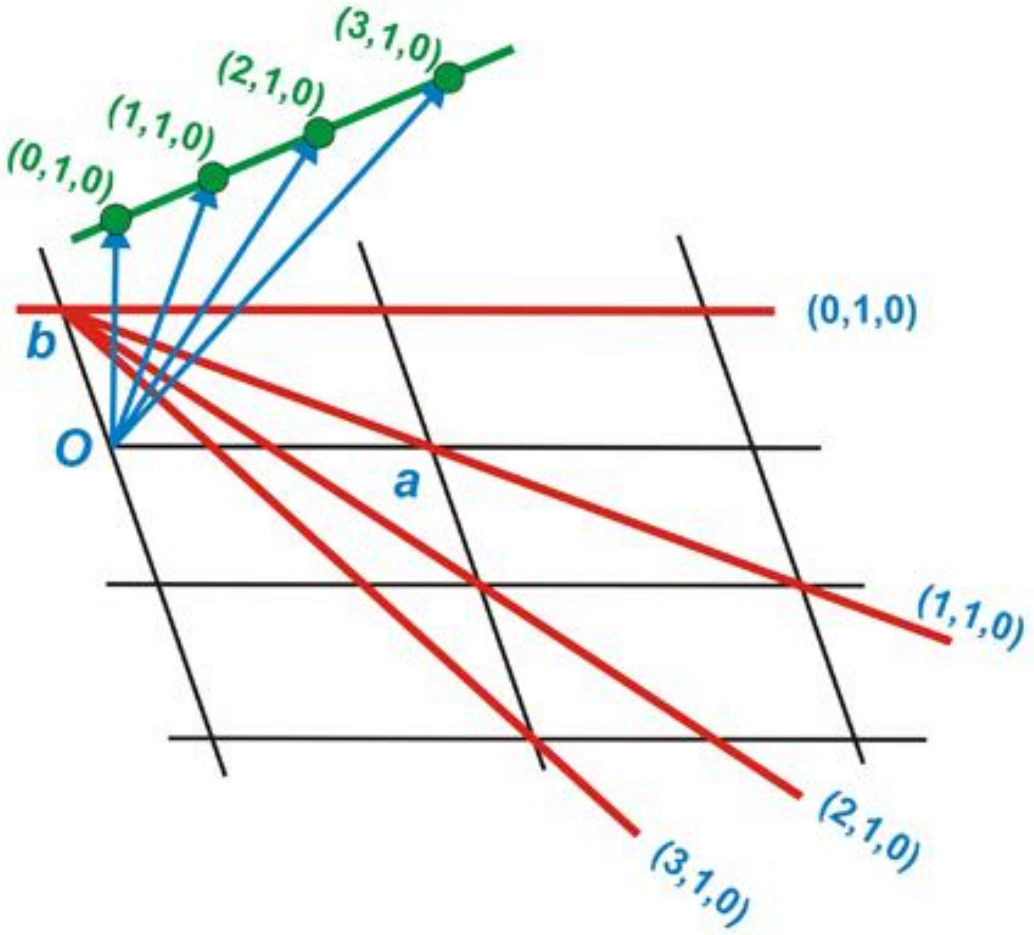
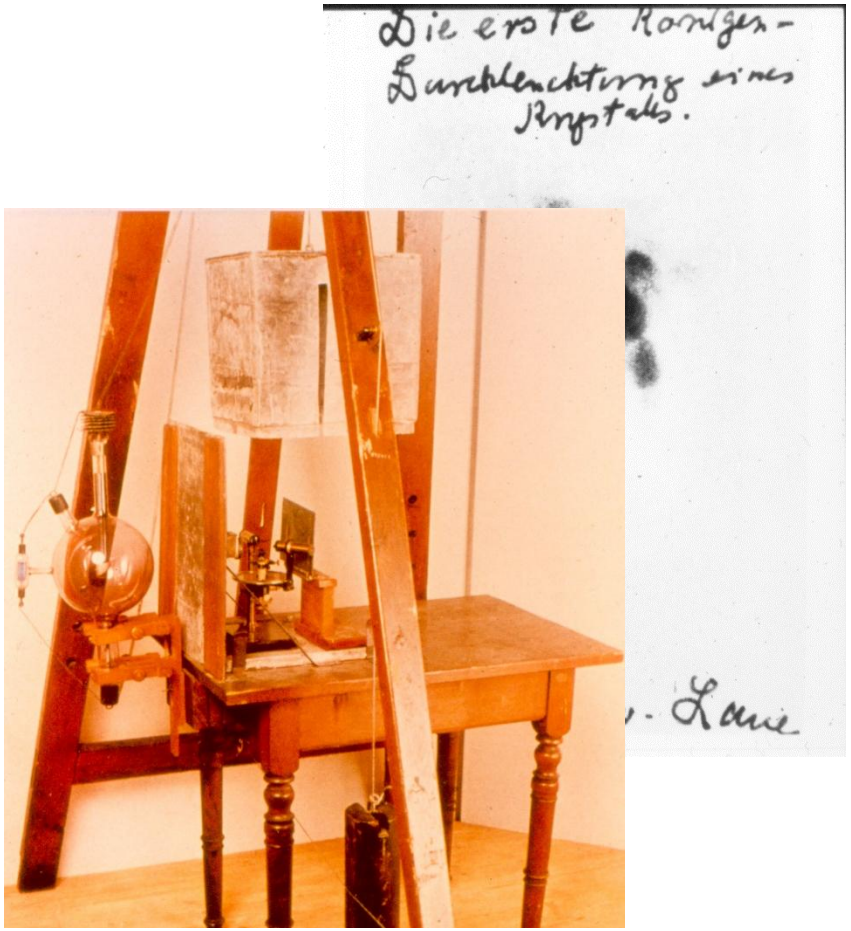


Diagram showing 4 Miller planes and how these are used to derive the equivalent reciprocal points, one for each set of Miller

Max von Laue

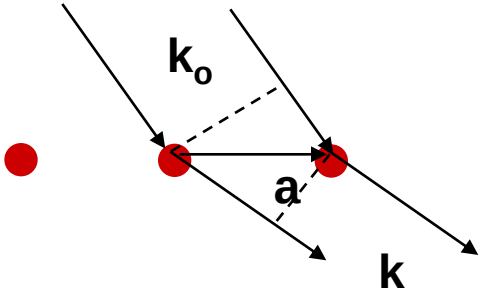
- The periodicity and interatomic spacing of crystals had been deduced earlier (e.g. Auguste Bravais).
- von Laue realized that if X-rays were waves with short wavelength, interference phenomena should be observed like in Young's double slit experiment.
- Experiment in 1912, Nobel Prize in 1914



Laue conditions

$$\Psi(\vec{r}) = Ae^{2\pi i\vec{k}\cdot\vec{r}} \qquad k = \frac{1}{\lambda}$$

*Scattering from a periodic distribution of scatters along the **a** axis*



The scattered wave will be in phase and constructive interference will occur if the phase difference is 2π.

$\Phi = 2\pi\mathbf{a}\cdot(\mathbf{k}-\mathbf{k_o}) = 2\pi\mathbf{a}\cdot\mathbf{g} = 2\pi h$, similar for ***b*** and ***c***

$$\vec{g}_{hkl} = h\vec{a^*} + k\vec{b^*} + l\vec{c^*}$$

Note the use of reciprocal values for ***a***, ***b***, and ***c***

The Laue equations

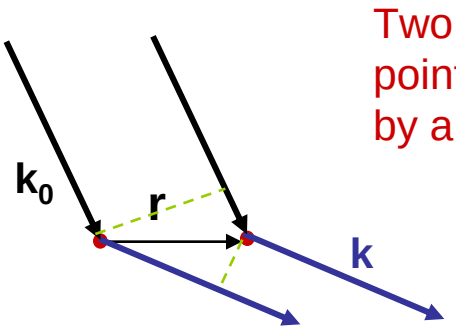
The **Laue equations** give three conditions for incident waves to be diffracted by a crystal lattice

- Waves scattered from two lattice points separated by a vector **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 **r** on **k** and the projection of **r** on $\mathbf{k_0}$, $\boldsymbol{\varphi} = 2\pi \mathbf{r}\cdot(\mathbf{k}-\mathbf{k_0})$

If $(\mathbf{k}-\mathbf{k_0}) = \mathbf{r^*}$, then $\boldsymbol{\varphi} = 2\pi n$

$\mathbf{r^*} = h\mathbf{a^*}+k\mathbf{b^*}+l\mathbf{c^*}$

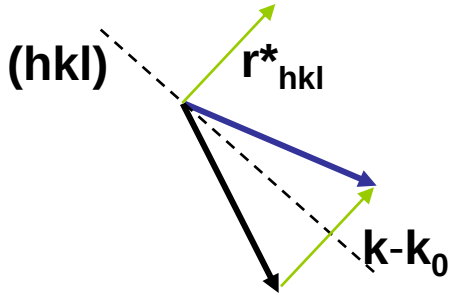
$\Delta = \mathbf{r}\cdot(\mathbf{k}-\mathbf{k_0})$



$\Delta = \mathbf{a}\cdot(\mathbf{k}-\mathbf{k_o}) = h$

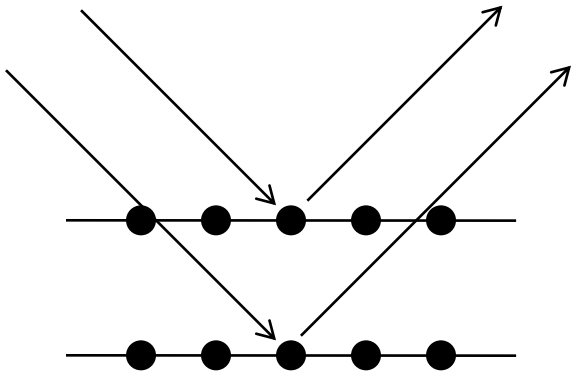
$\Delta = \mathbf{b}\cdot(\mathbf{k}-\mathbf{k_o}) = k$

$\Delta = \mathbf{c}\cdot(\mathbf{k}-\mathbf{k_o}) = l$



Bragg's law

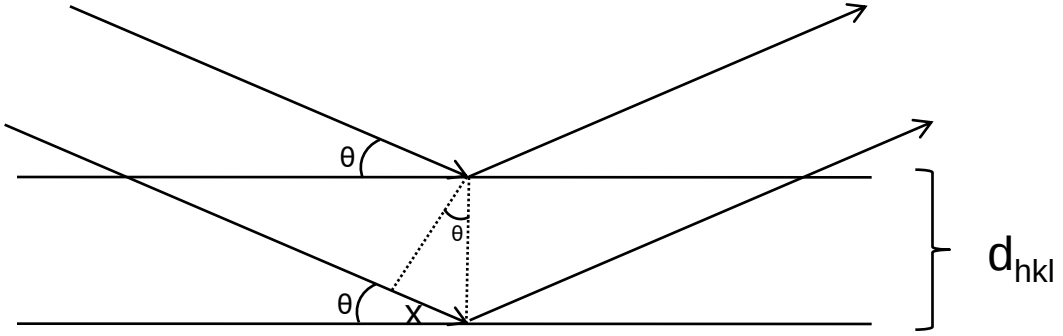
• William Henry and William Lawrence Bragg (father and son) found a simple interpretation of von Laue's experiment
• Consider a crystal as a periodic arrangement of atoms, this gives crystal planes
• Assume that each crystal plane reflects radiation as a mirror
• Analyze this situation for cases of constructive and destructive interference
• Nobel prize in 1915



Derivation of Bragg's law

$$\sin(\theta) = \frac{x}{d_{hkl}}$$

$$\Rightarrow x = d_{hkl}\sin(\theta)$$



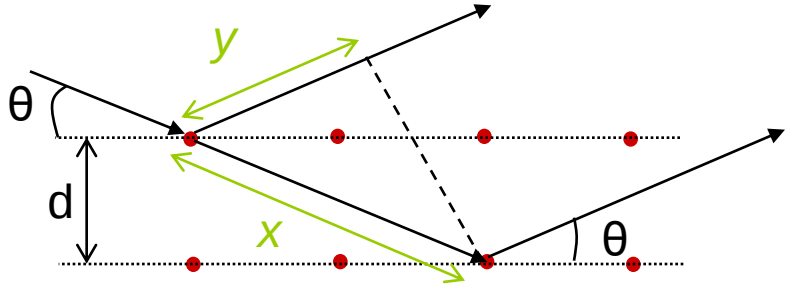
Path difference Δ= 2x => phase shift
Constructive interference if Δ=nλ
This gives the criterion for constructive interference:

$$\Rightarrow \Delta = 2d_{hkl}\sin(\theta) = n\lambda$$

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

Bragg's law

- $n\lambda = 2d\sin\theta$
  - Planes of atoms responsible for a diffraction peak behave as a mirror



The path difference: x-y

$Y = x\cos 2\theta$ and $x\sin\theta = d$

$\cos 2\theta = 1 - 2\sin^2\theta$

2.4. BRAGG'S LAW IN RECIPROCAL SPACE

In X-ray crystallography the most important property of the reciprocal lattice is that it allows a simple visualization of Bragg's law that is much more convenient in practice than the one used in the derivation above. Imagine a crystal in a beam of X-rays of wavelength λ, and consider the a^*c^* section of its reciprocal lattice (Fig. 2.21*a*). Assuming that the crystal is oriented so that the X-ray beam is parallel to this a^*c^* plane, draw a line XO in the direction of the beam and passing through the r.l. origin O. Finally, describe a circle of radius $1/\lambda$ with its center C on XO and located so that O falls on its circumference.

Now consider the properties of an r.l. point P lying on this circle. The

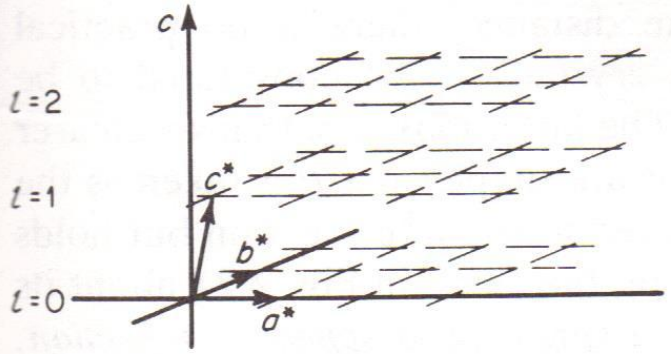


Figure 2.20. Reciprocal lattice levels a^*b^* perpendicular to a direct axis c.

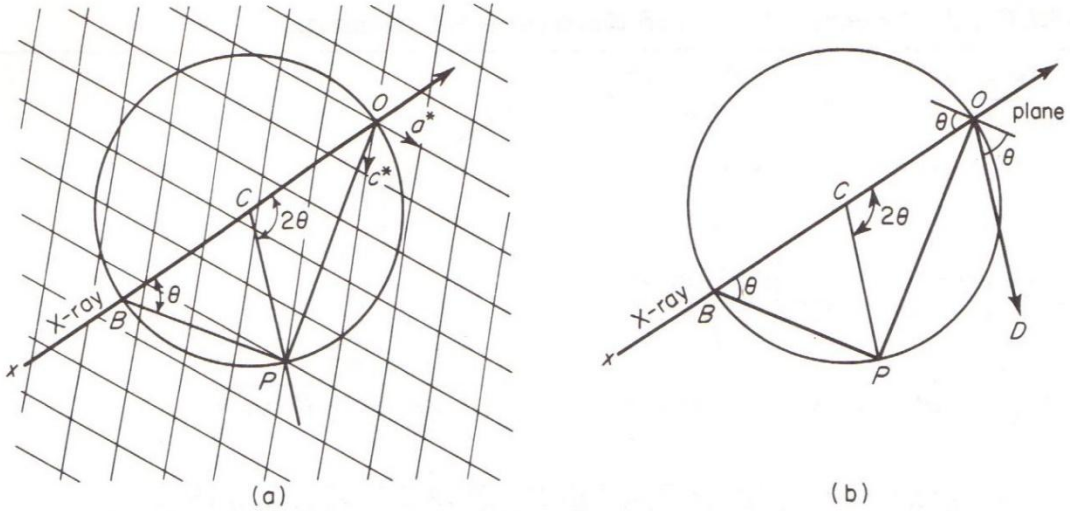


Figure 2.21. Diffraction in terms of the reciprocal lattice. (*a*) The reciprocal lattice and the sphere of reflection; (*b*) the direct plane and the reflected ray.

angle OPB is inscribed in a semicircle and thus is a right angle. Therefore,

$$\sin OBP = \sin \theta = \frac{OP}{OB} = \frac{OP}{2/\lambda} \tag{2.16}$$

$$\sin \theta = (OP/2)\lambda \tag{2.17}$$

But since P is a reciprocal lattice point, the length of OP is by definition equal to $1/d_{hkl}$. Substituting gives

$$\sin \theta = 1\lambda/2d_{hkl} \tag{2.18}$$

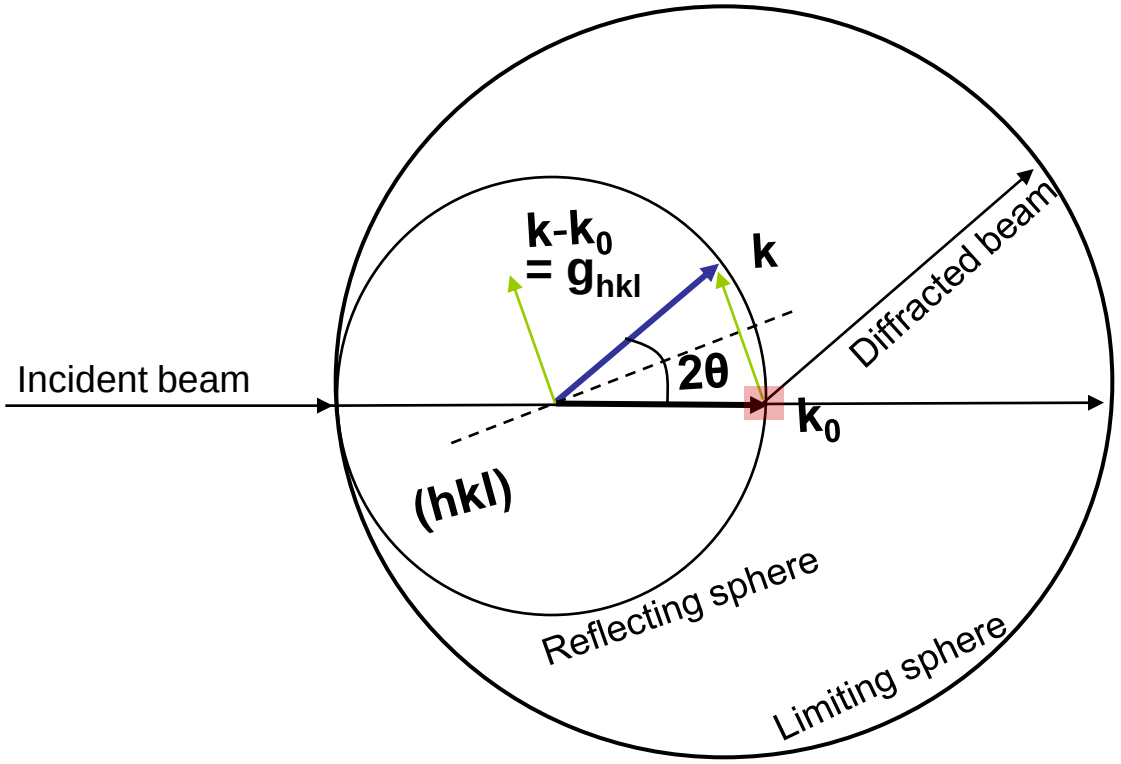
or

$$1\lambda = 2d \sin \theta \tag{2.19}$$

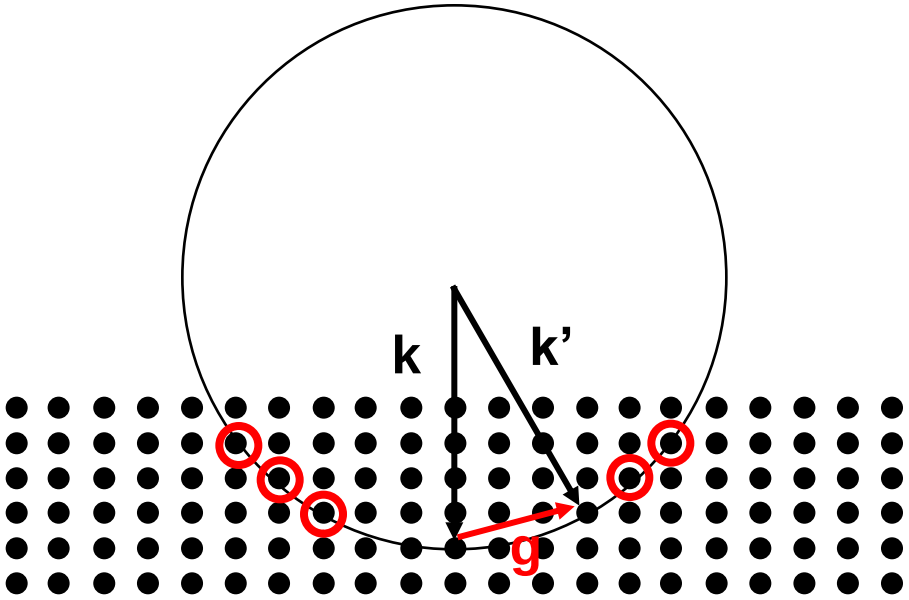
which is just Bragg's law with $n = 1$.

The limiting-sphere construction

- Vector representation of Bragg law
- $|\mathbf{k}| = |\mathbf{k_0}| = 1/\lambda$
  - $\lambda_{x\text{-rays}} >> \lambda_e$



The Ewald Sphere (’limiting sphere construction’)



Elastic scattering:

$$k = k' = \frac{1}{\lambda}$$

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

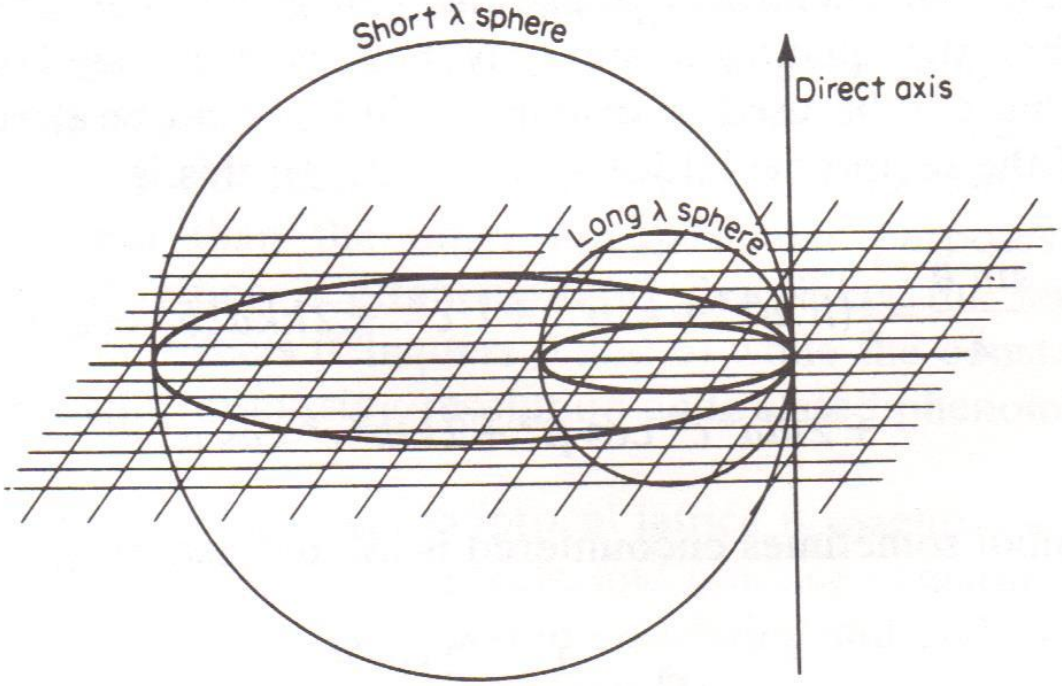
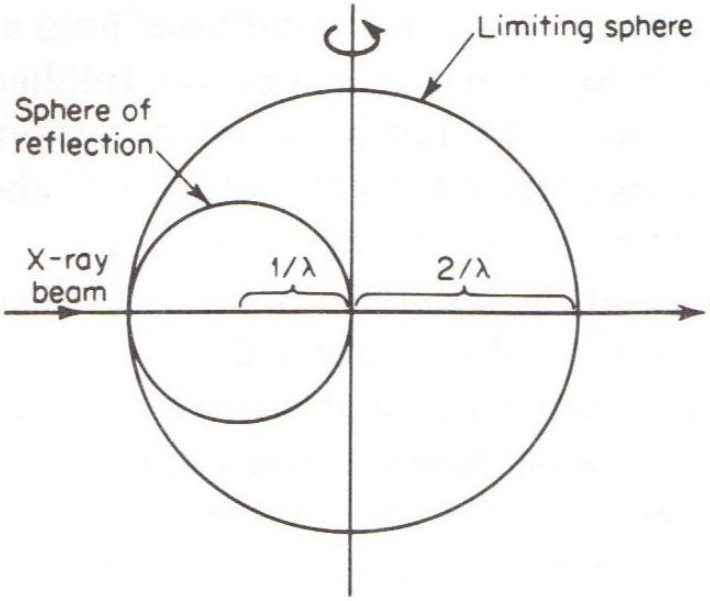
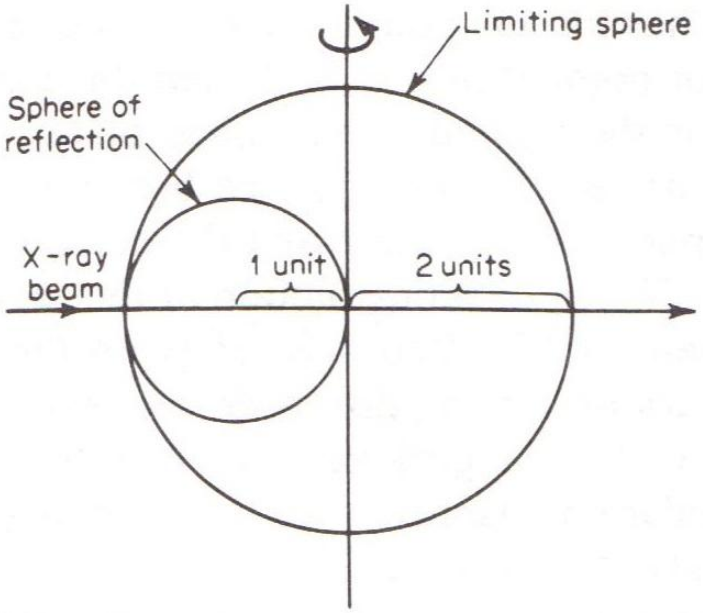


Figure 2.22. Spheres of reflection for two wavelengths.


Limiting sphere
Sphere of reflection
X-ray beam
1/λ
2/λ

(a)


Limiting sphere
Sphere of reflection
X-ray beam
1 unit
2 units

(b)

Typical X–ray diffraction pattern collected by film methods shown below.