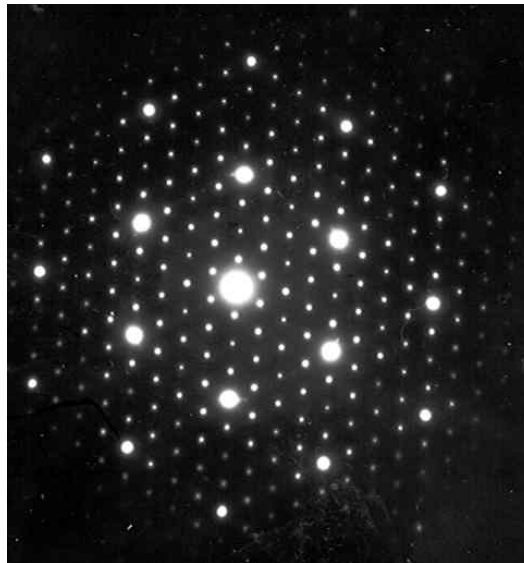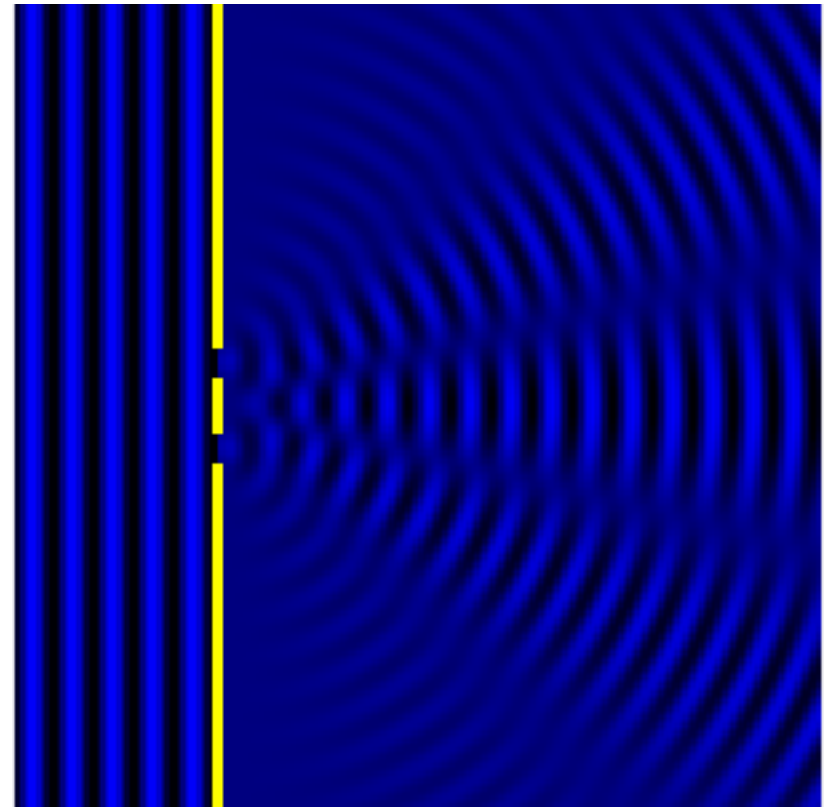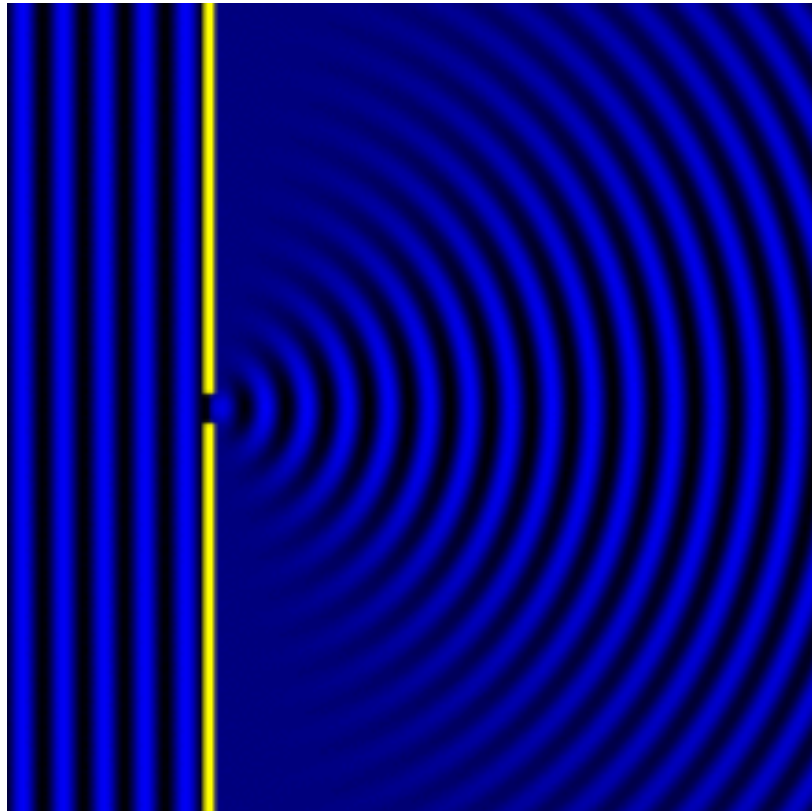# Diffraction basics

Diffraction

Diffraction refers to the phenomena exhibited by radiation when it interacts with barriers and obstacles (scattering).

Interference of waves

Diffraction is constructive interference of light rays or other types of radiation

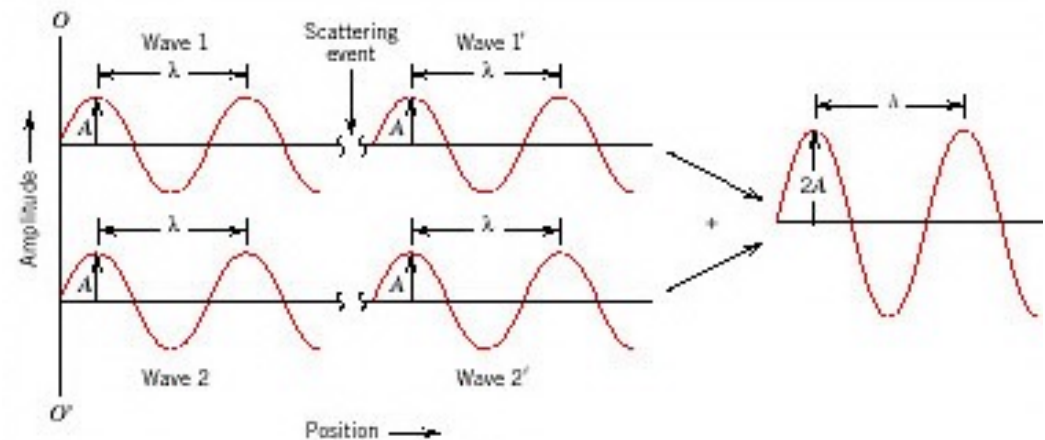Constructive interference: mutual reinforcement of the scattered rays

- Difference in distances travelled by various parallel beams are a multiple of wavelength: $\Delta d = n*\lambda$

Destructive interference: scattered beams are out of phase and cancel each other.

- Difference in distances travelled by various parallel beams are a multiple of wavelength: $\Delta d = n*\lambda/2$

So?

3
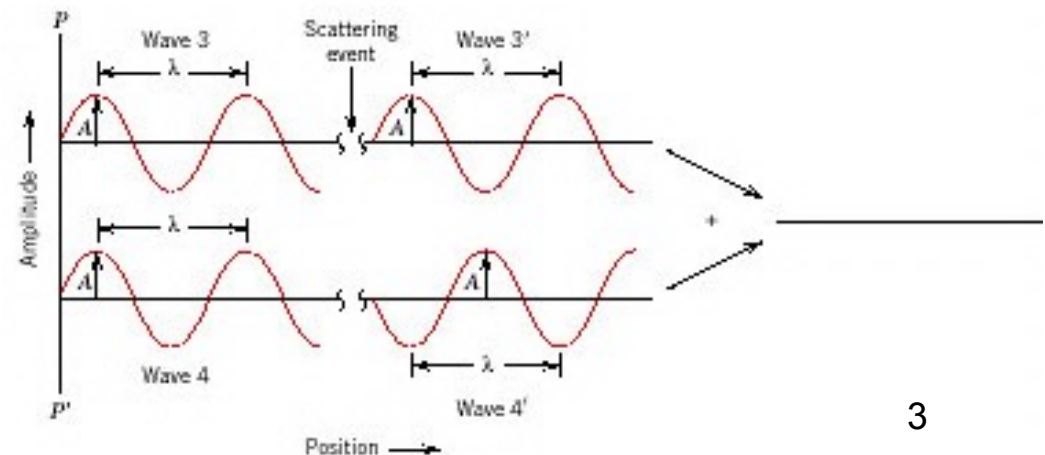
Interference vs diffraction

Feynman "Lectures on Physics" Ch. 30. Diffraction

This chapter is a direct continuation of the previous one, although the name has been changed from Interference to Diffraction. **No one has ever been able to define the difference between interference and diffraction satisfactorily.** It is just a question of usage, and there is no specific, important physical difference between them. The best we can do, roughly speaking, is to say that **when there are only a few sources, say two, interfering, then the result is usually called interference,** but if **there is a large number of them, it seems that the word diffraction is more often used.** So, we shall not worry about whether it is interference or diffraction, but continue directly from where we left off in the middle of the subject in the last chapter.

Huygen's principle

Every point on a propagating wavefront serves as the source of spherical secondary wavelets, such that the wavefront at a later time is the envelope of these wavefronts.

The wavelets advance with a speed and frequency equal to those of the primary wave at each point in space.

The image shows a wavefront, as well as a number of spherical secondary wavelets, which after a time t, have propagated out to a radius of vt. The envelop of all these wavelets is then asserted to correspond to the advanced primary wave.

Propagation of a wavefront according to Huygens's principle: **consistent with diffraction**


5
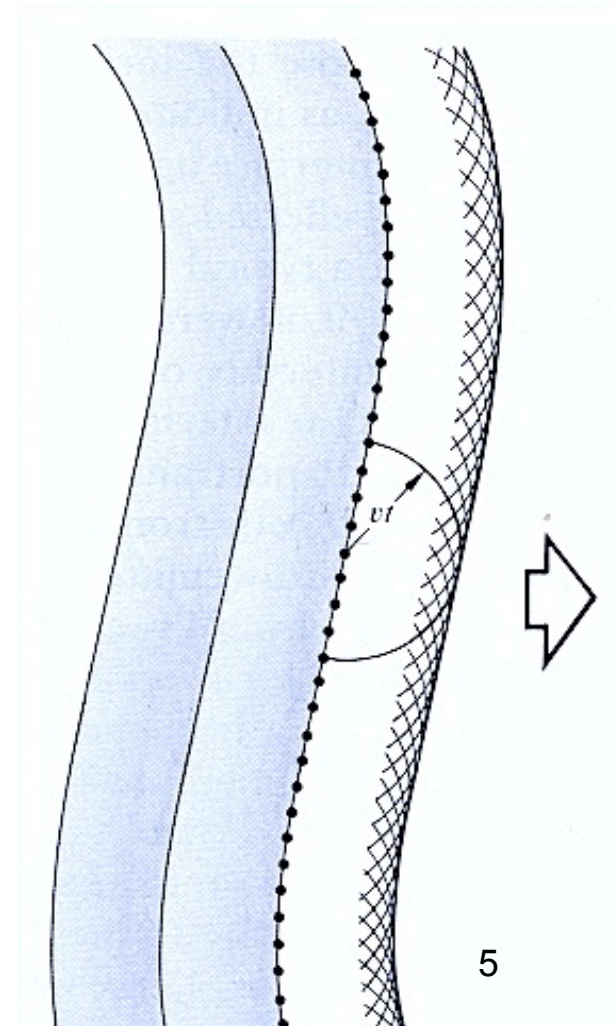
Diffraction geometry
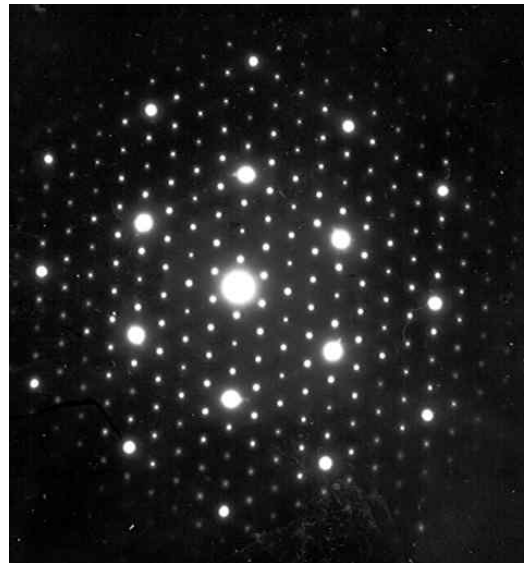
What can be said about the symmetry of this diffraction pattern?

Geometry of diffraction patterns

A diffraction pattern results from diffraction (scattering) followed by interference between the diffracted (scattered) beams.

Interference is constructive only if the radiation is coherent.

Diagram of a distant light source emitting coherent wavetrains. When one of these strikes a screen with adjacent slits, the slits act as secondary sources of light according to Huygen's principle, which then meet and interfere.

max
min
max
min
max
min
max
min
max

S₁
S₂

Barrier

Viewing screen
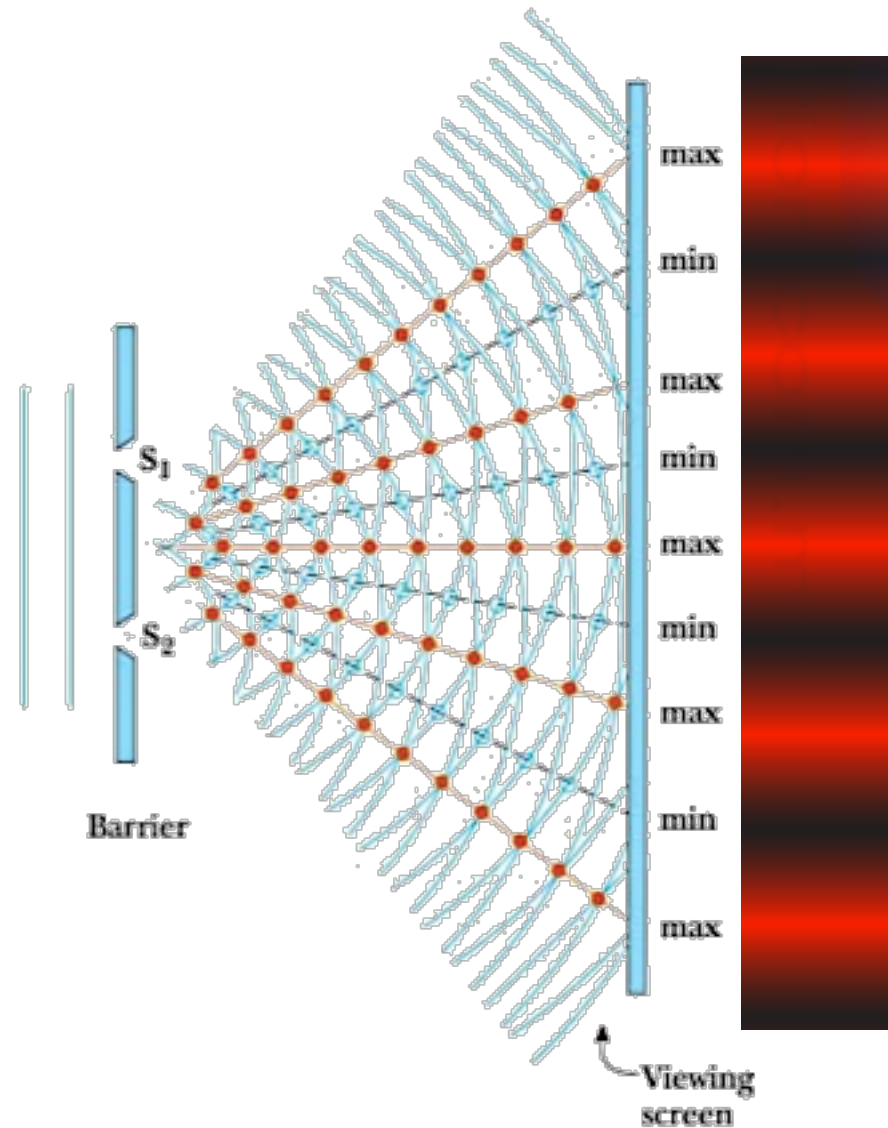
Geometry of diffraction patterns
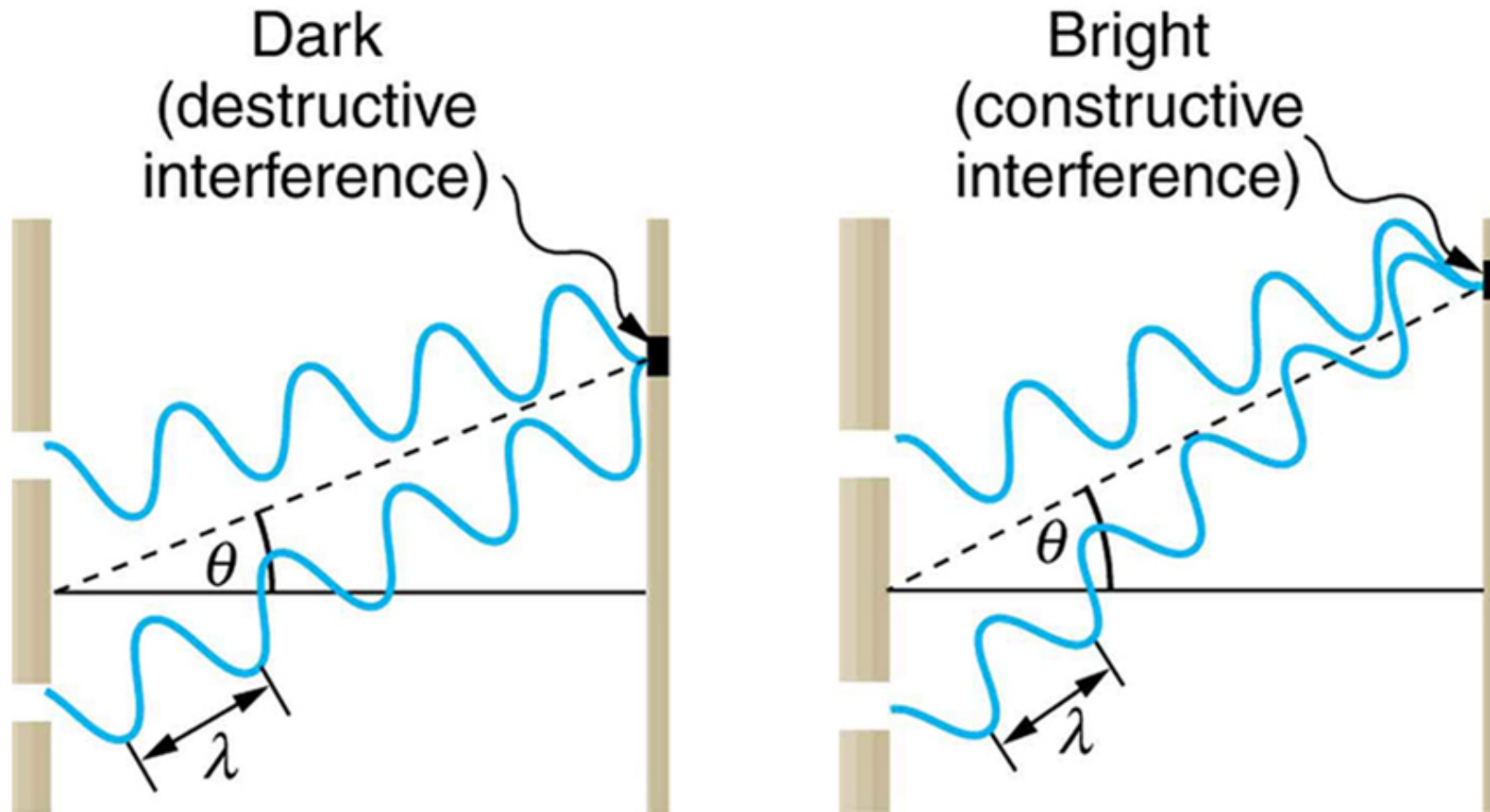
Diffraction at a wide slit (aperture)

Two slits
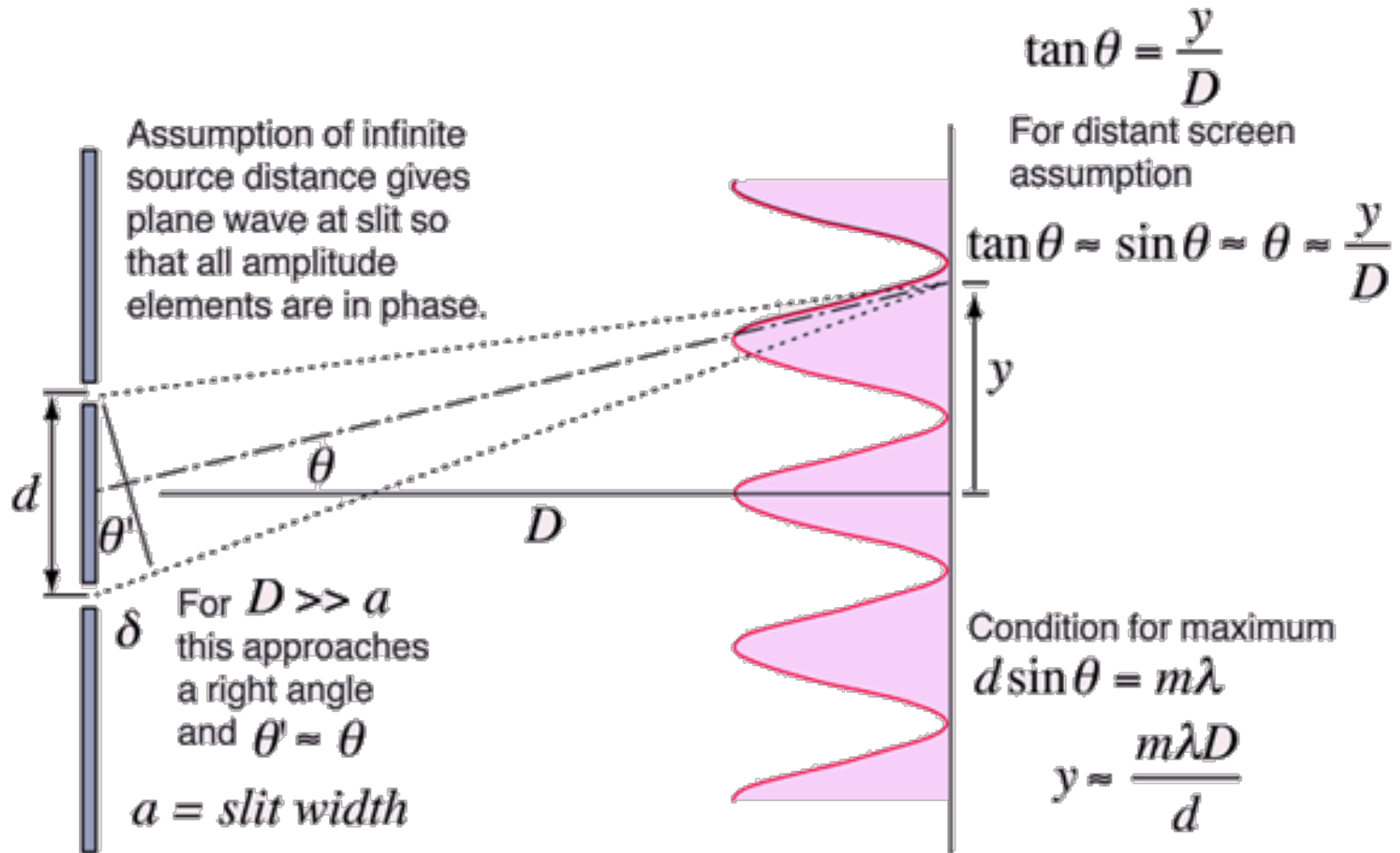
$$\tan\theta = \frac{y}{D}$$

For distant screen assumption

$$\tan\theta \approx \sin\theta \approx \theta \approx \frac{y}{D}$$

Assumption of infinite source distance gives plane wave at slit so that all amplitude elements are in phase.

For $D \gg a$ this approaches a right angle and $\theta' \approx \theta$

$a = slit\ width$

Condition for maximum

$$d\sin\theta = m\lambda$$

$$y \approx \frac{m\lambda D}{d}$$

Diffraction at a wide slit (aperture)

Slit width (*a*) several times the wavelength (λ):
Locate the first minima

M. Cagnet, M. Francon, and J. C. Thierr
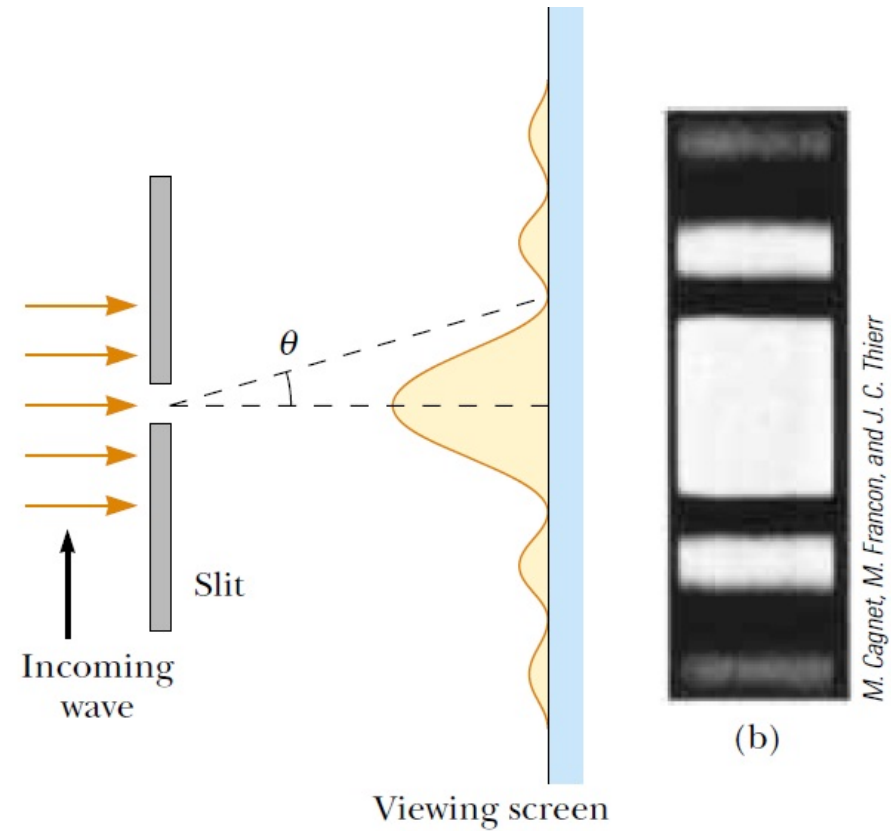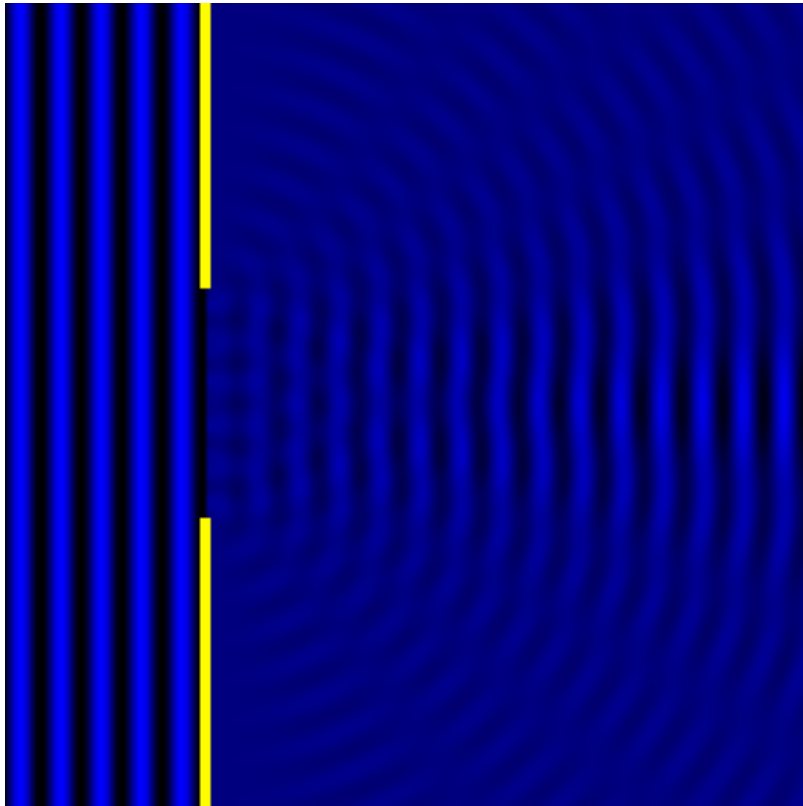
Diffraction at a wide slit (aperture)

Slit width (*a*) several times the wavelength (λ):
Locate the first minima

Virtual point sources

$$\tan\theta = \frac{y}{D}$$

$$\tan\theta \approx \sin\theta \approx \theta \approx \frac{y}{D}$$

$$\theta' \approx \theta$$

Condition for minimum

$$a\sin\theta = m\lambda$$

$$y \approx \frac{m\lambda D}{a}$$
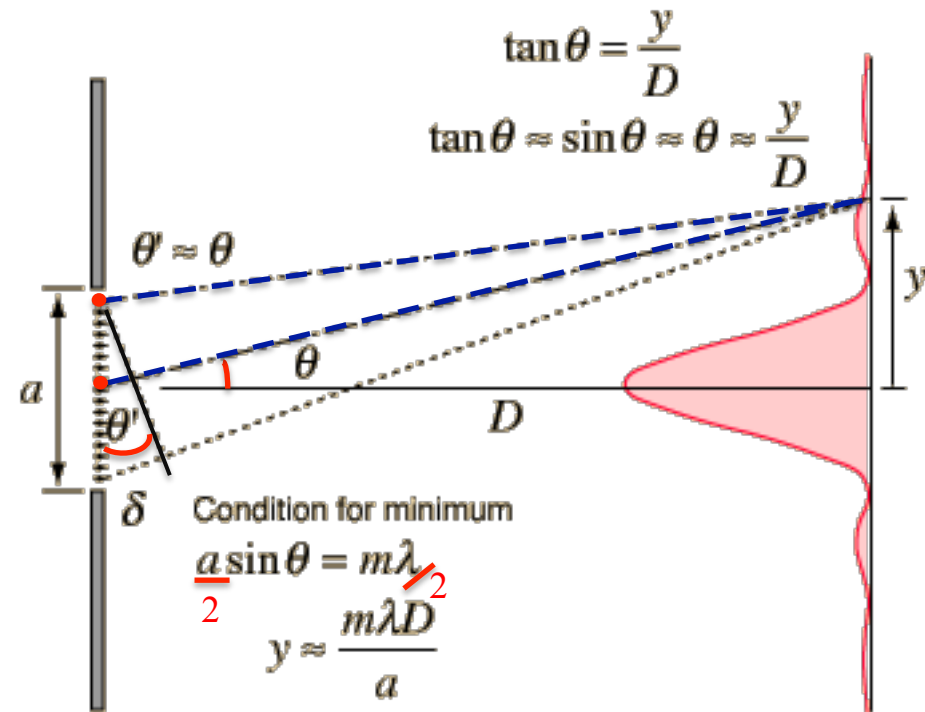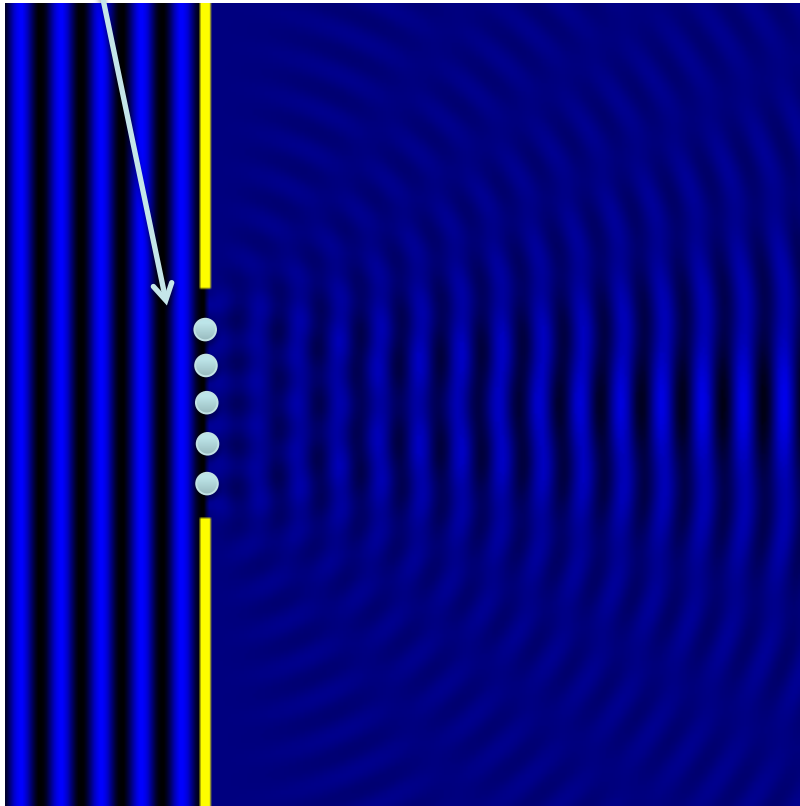
Geometry of diffraction patterns

Side view of a diffraction grating. The slit separation is d and the path difference between adjacent slits is $d \sin\theta$.
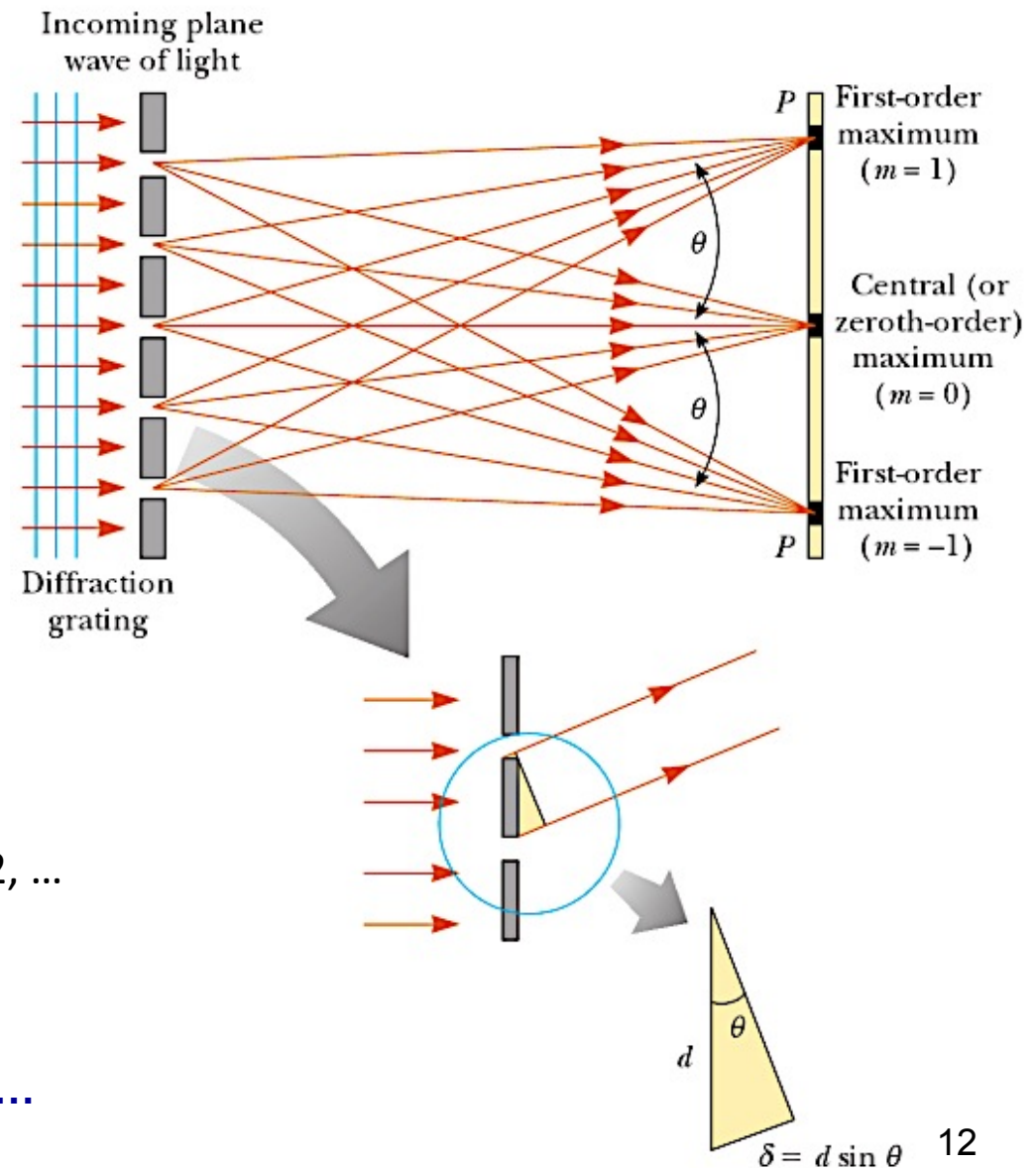
Condition for maxima in the interference plane:

$m\lambda = d \sin\theta$ with m = 0, ±1, ±2, …

m is the order of diffraction.

Reciprocal relation between θ and d…

Incoming plane wave of light

P First-order maximum ($m = 1$)

θ

Central (or zeroth-order) maximum ($m = 0$)

θ

First-order maximum ($m = -1$)

P

Diffraction grating

θ

d

$\delta = d \sin\theta$

12

Geometry of diffraction patterns

Observations of diffraction of light using a laser as a coherent light source. As the aperture size decreases the diameter of the diffracted disk and rings increases (reciprocal relation...)

(a)   (b)   (c)   (d)   (e)
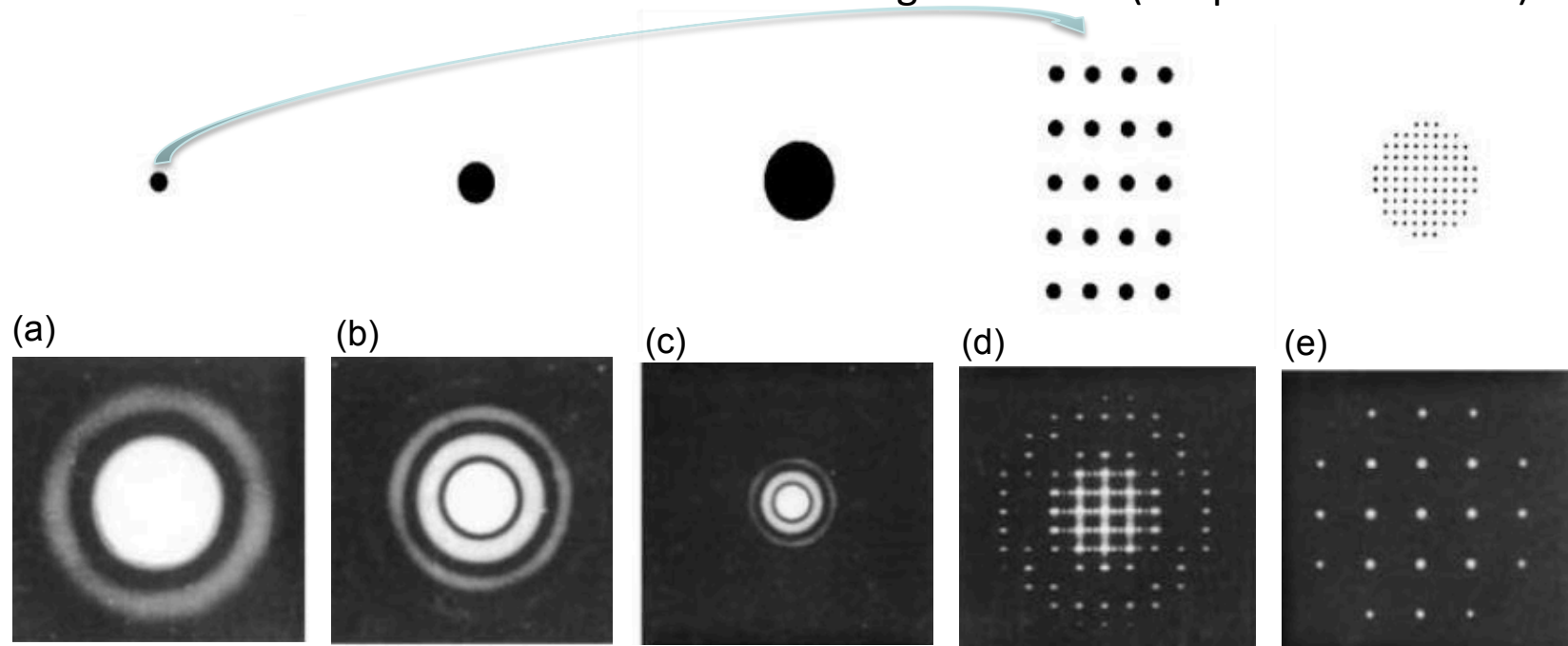
Diffracting apertures (reproduced as black dots on a white background) (left) and their corresponding diffraction patterns (or optical transforms) (right) taken using a laser, (a), (b) and (c) show the diffraction patterns (Airy discs and surrounding haloes or rings) from circular apertures of increasing diameters, (d) shows the diffraction pattern from a 4 × 5 net of small apertures (as in (a)). Note the reciprocal relationship between the net and the diffraction pattern, the 2 × 3 number of subsidiary peaks in each direction and the overall variation in intensity of the diffraction pattern in accordance with that for a single aperture (a), (e) shows that for a net of many apertures the subsidiary maxima are not discernible. (From *Atlas of Optical Transforms* by G. Harburn, C. A. Taylor and T. R. Welberry, Bell and Hyman, 1983, an imprint of HarperCollins.)

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Reciprocal lattice

The reciprocal lattice is a set of imaginary points so that the direction of a vector from one point to another coincides with the normal to a family of real space planes. The absolute value of the vector is given by the reciprocal of the real interplanar distance.

Designations:
- Real space
- Direct space
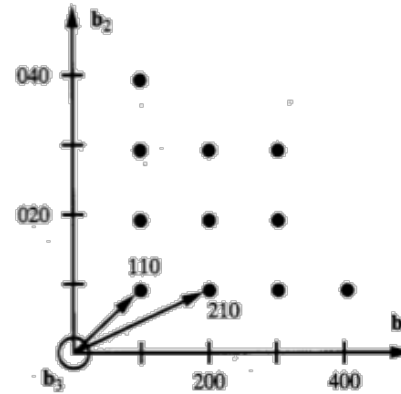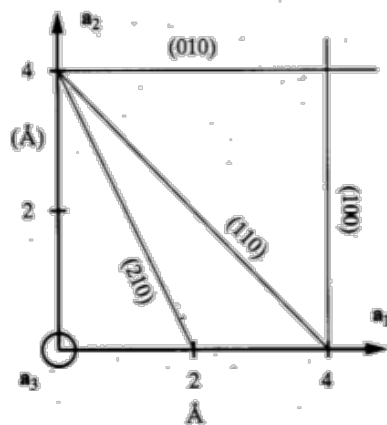
Designations:
- Reciprocal space
- Fourier space
- K-space
- Frequency space (spatial not temporal)
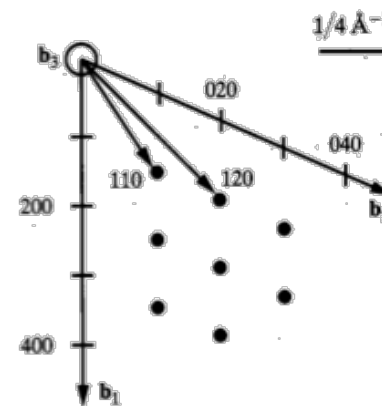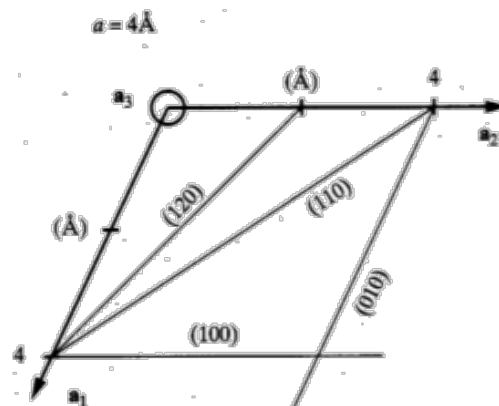
**A whole family of planes in real space is represented by a single point in reciprocal space**

Any point of the reciprocal lattice can be specified by a vector: $\mathbf{d_{hkl}}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$
This vector is perpendicular to the plane in real space with Miller indices (hkl). The length of this vector $|\mathbf{d_{hkl}}^*| = 1/d_{hkl}$ where d_{hkl} is the interplanar spacing in real space.

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Notes on reciprocal lattice

Construction of reciprocal lattice
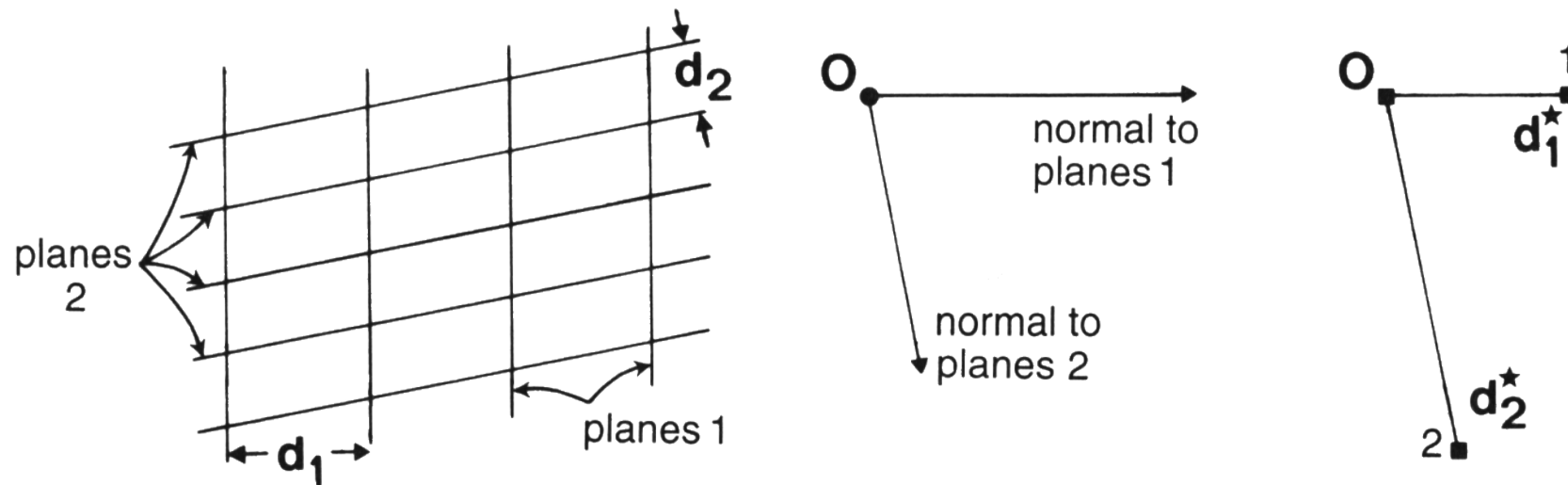
1. Identify the basic planes in the direct space lattice, *i.e. (001), (010), and (001).*

2. Draw normals to these planes from the origin.

3. Mark distances from the origin along these normals proportional to the **inverse** of the distance from the origin to the direct space planes.

Notes on reciprocal lattice

- The points of the direct and reciprocal lattices have the same meaning as the points defined in geometry: mathematical entities.

- The **direct-space lattice** can be used to indicate the location of **real objects (atoms)** and has dimensions of m, whereas the **reciprocal lattice** can be used to indicate the position of **diffracted light/radiation spots** and has dimensions of m^{-1}.

- Reciprocal space is also called Fourier space, **k**-space $(2\pi/\lambda)$ or frequency space, in contrast to real space or direct space.

- The diffraction patterns are visual representations or images of the object (crystal) Fourier transforms.

- The results of diffraction experiments can be easily interpreted using the reciprocal lattice. Useful information about the internal structure of crystalline matter can be obtained through the **Ewald construction in reciprocal space** (see below).

- The geometry of the diffraction pattern is determined by the crystal lattice, but the diffracted intensity at each reciprocal point is determined by the motive or base.

Notes on reciprocal lattice

The reciprocal lattice is related to the real space lattice by:

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a}.(\mathbf{b} \times \mathbf{c})} \qquad \mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a}.(\mathbf{b} \times \mathbf{c})} \qquad \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a}.(\mathbf{b} \times \mathbf{c})}$$

- **a**, **b**, **c** are the vectors of the real space lattice and **a***, **b***, **c*** are the vectors of the reciprocal lattice.

- Note $V = \mathbf{a}.(\mathbf{b}^* \times \mathbf{c}^*)$ (unit cell volume)

- These relations are symmetrical and show that the reciprocal lattice of the reciprocal lattice is the direct lattice.

Notes on reciprocal latticec

- The points of the direct and reciprocal lattices have the same meaning as the points defined in geometry: mathematical entities.

- The **direct-space lattice** can be used to indicate the location of **real objects (atoms)** and has dimensions of m, whereas the **reciprocal lattice** can be used to indicate the position of **diffracted light spots** and has dimensions of m^{-1}.

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- The geometry of the diffraction pattern is determined by the crystal lattice, but the diffracted intensity at each reciprocal point is determined by the motive or base.

Optical Fourier transform

- Frequency = 1/period = $1/d_{hkl}$
  (in this context the period refers to interplanar distance, not time)
- **K** are the diffraction vectors
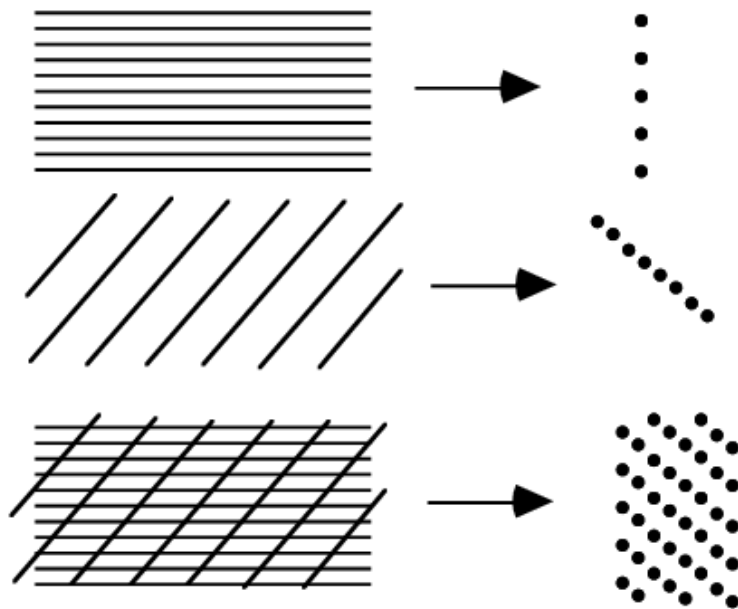
- One set of closely-spaced horizontal lines gives rise to a widely-spaced vertical row of points.

- A second set of more widely-space diagonal lines gives rise to a more closely-spaced row of points perpendicular to these lines.

- If one multiplies one set of lines by another, this will give an array of points at the intersections of the lines in the bottom part of the figure.

- The Fourier transform of this lattice of points, which was obtained by multiplying two sets of lines, is the convolution of the two individual transforms (*i.e.* rows of points) , which generates a reciprocal lattice.

Optical Fourier transform

Both spaces are periodic and with the same symmetry, so:

$$F(u) = \int_{\infty}^{-\infty} f(x) e^{-i2\pi ux} dx.$$
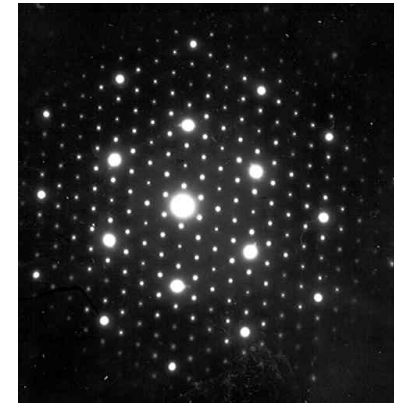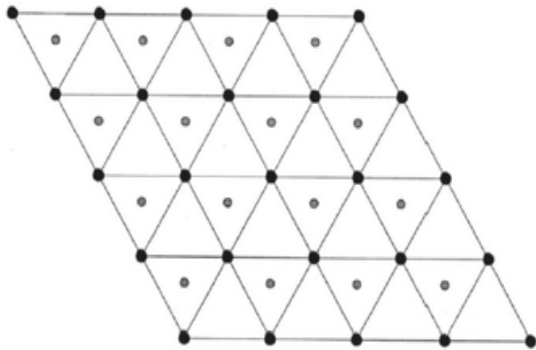
$$f(x) = \int_{\infty}^{-\infty} F(u) e^{i2\pi ux} du$$

Spatial frequency
(position in the diffraction pattern)

Amplitude
(measure of intensity at each point in recirpocal space))

Euler's formula
$$e^{i\varphi} = cos\varphi + i\, sin\varphi$$

Summations of sinudoisal functions!

Bragg's Interpretation

W. H. Bragg examined Laue's photographs and noticed that the spots were elongated. He surmised that this elongation arose from specular reflection of the x-rays off of "planes" of regularly arranged atoms. Incident beams are 'reflected' in phase if the path difference between them equals an integer multiple of the wavelength:
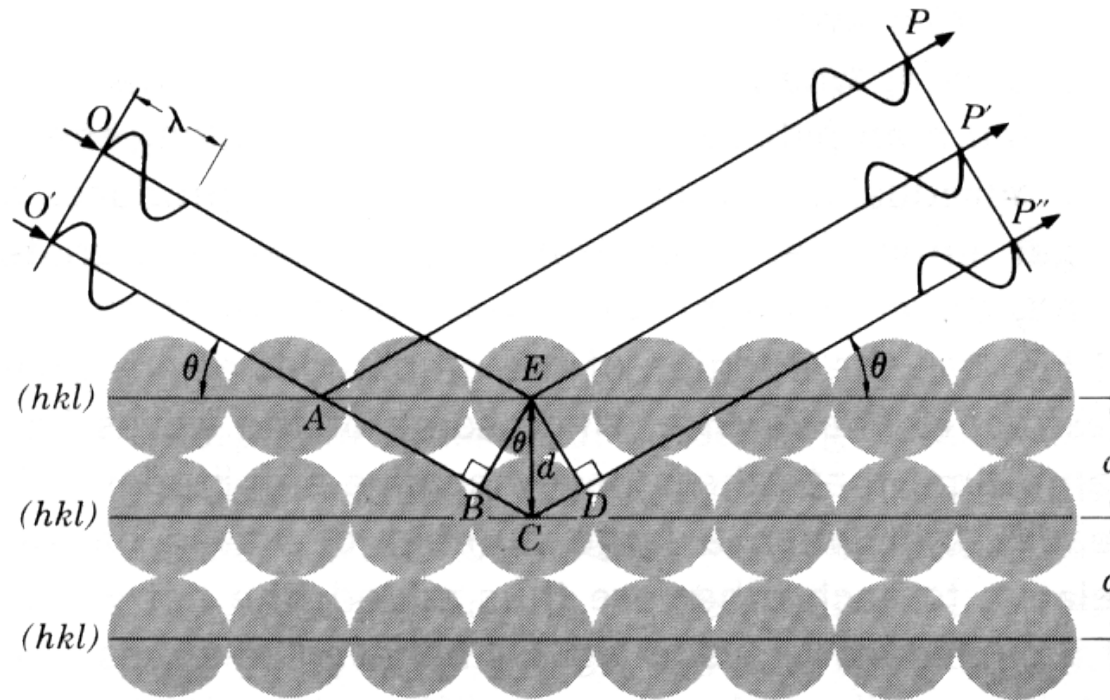
$$BC = d\sin\theta \qquad CD = d\sin\theta$$

$$BC + CD = \text{ path difference} = n\lambda$$

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

Vectorial form of Bragg's law (Ewald or reflecting sphere)

$$d^*_{hkl} = \frac{S - S_o}{\lambda}$$

Postulate:
- a sphere of radius $1/\lambda$,
- intersecting the origin of the reciprocal lattice,
- with the starting point of the incident (or direct) beam vector at the sphere center,
- and unitary incident and diffracted vectors S_0 and S: Then:
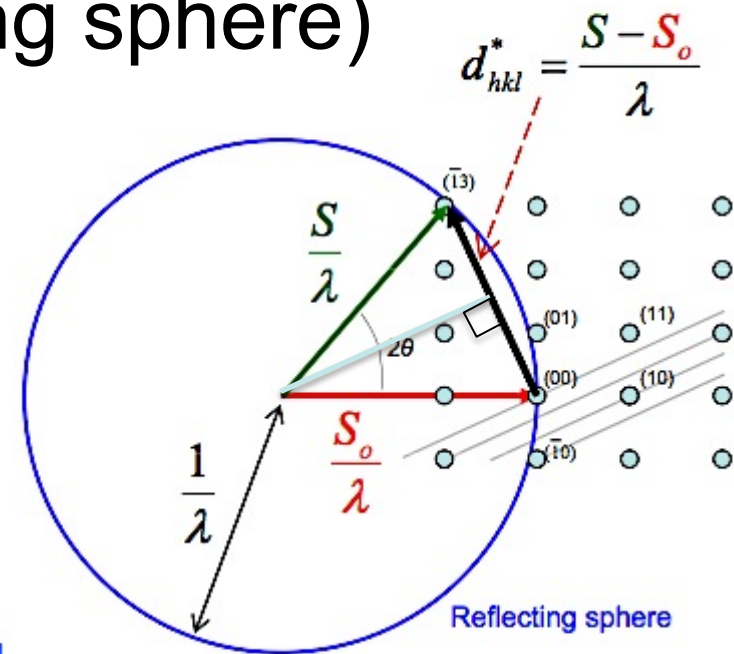
$$|S - S_0| = 2\,R\,\sin\theta = 2\sin\theta\,/\lambda$$

Only when $S - S_0$ coincides with a **re**ciprocal **la**ttice **p**oint (i.e. when $|S - S_0| = |d^*_{hkl}| = 1/d_{hkl}$) is Bragg's law satisfied:
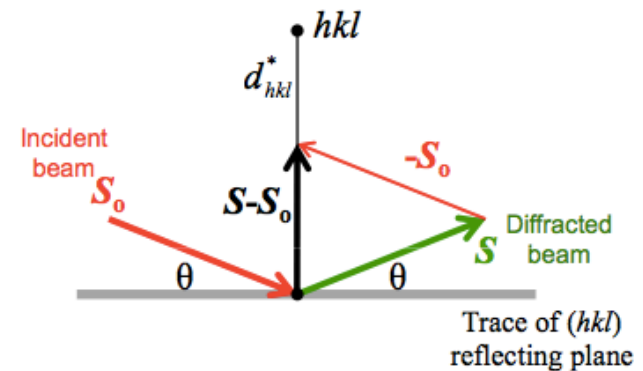
$$2\sin\theta\,/\lambda = 1/d_{hkl}$$

Therefore constructive interference occurs when $S - S_0$ coincides with the reciprocal vector of the reflecting planes!

For this incident angle there is no diffracted intensity !
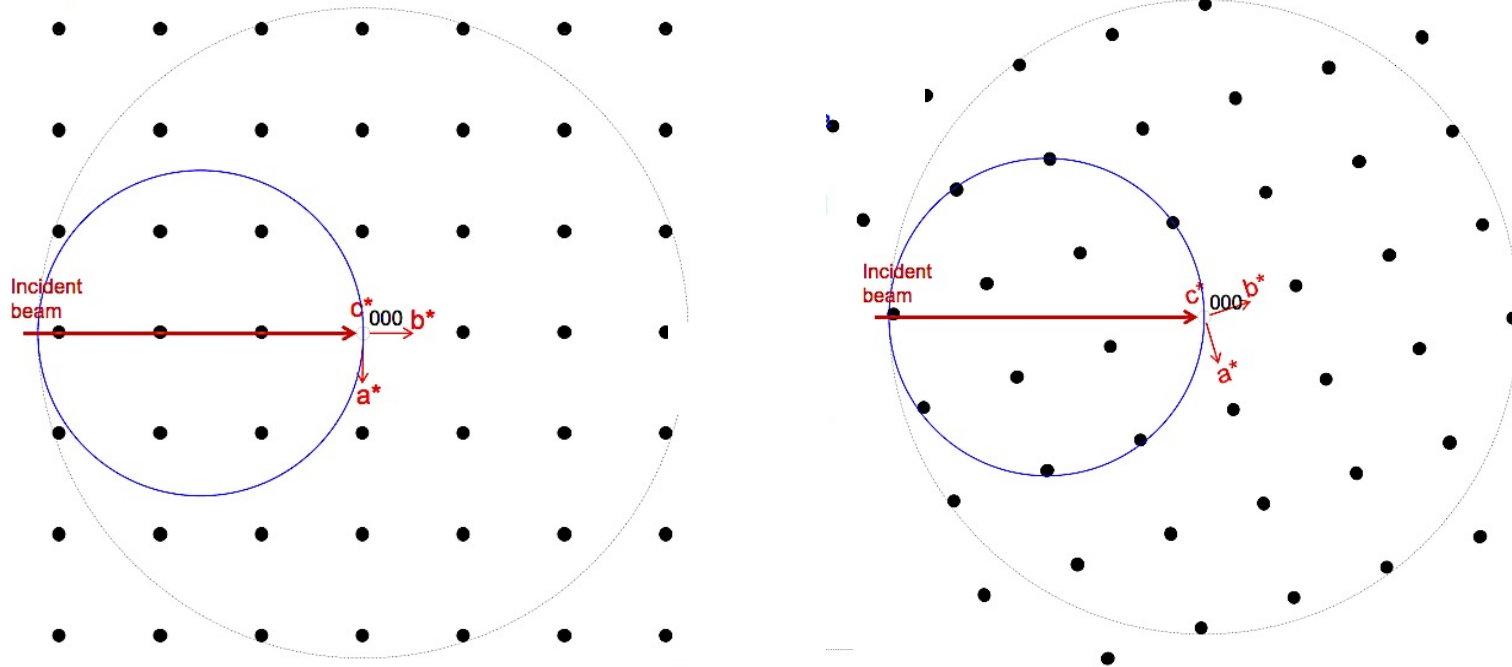
Notation: $d^*_{hkl} = g_{hkl}$

Reflecting sphere

Vectorial form of Bragg's law
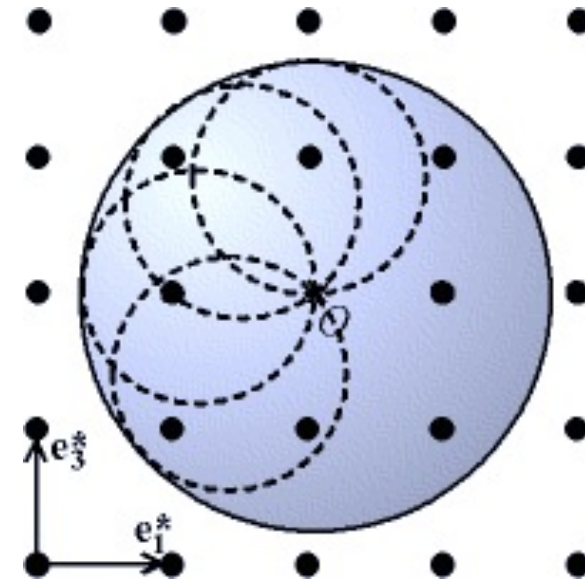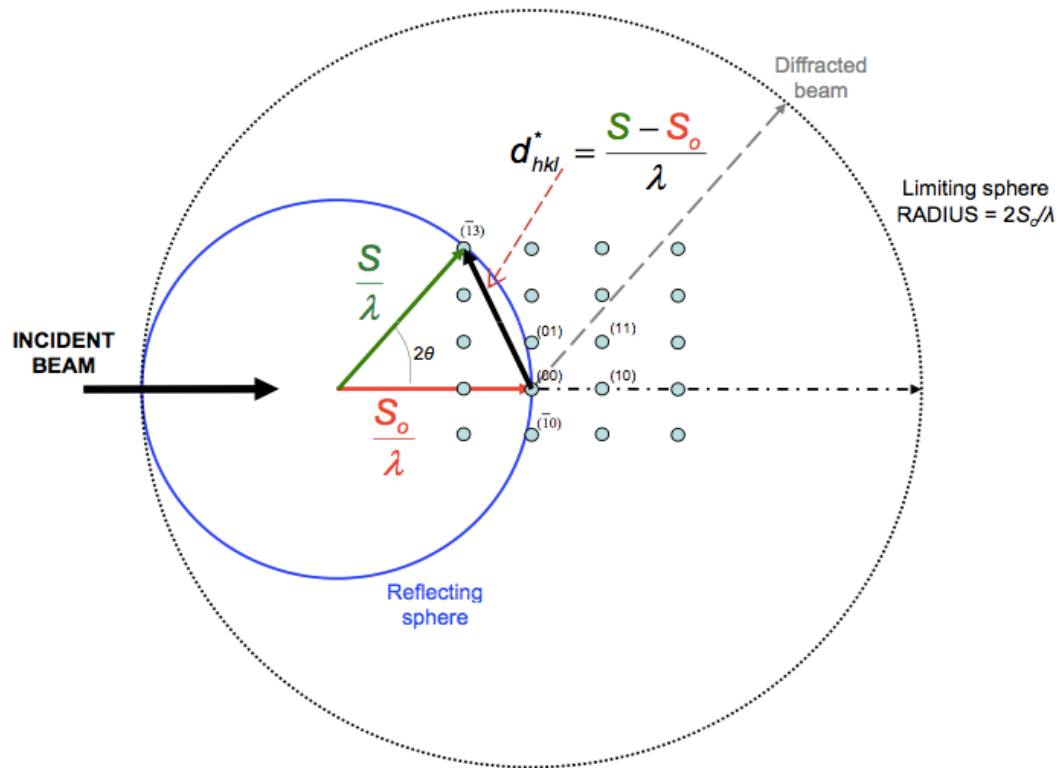# Ewald or reflecting sphere

A change in the orientation of the incident beam relative to the crystal changes the orientation of the reflecting sphere.

Eventually a condition where diffraction occurs.

A change in λ changes the sphere radius and may also be used to satisfy Bragg's law.

Vectorial form of Bragg's law
The limiting sphere

The limiting sphere is obtained by the rotation around the origin of the reflection (Ewald) sphere. Defines the possible 'reflections' in a diffractogram, which depend only on the wavelength (radius of Ewald shpere is $1/\lambda$ since S and S_0 are unitary): **planes with $1/d > 2/\lambda$ cannot scatter radiation with λ wavelength due to too small interplanar distances…**

Bragg 'reflection'

physically wrong but geometrically right

In fact…
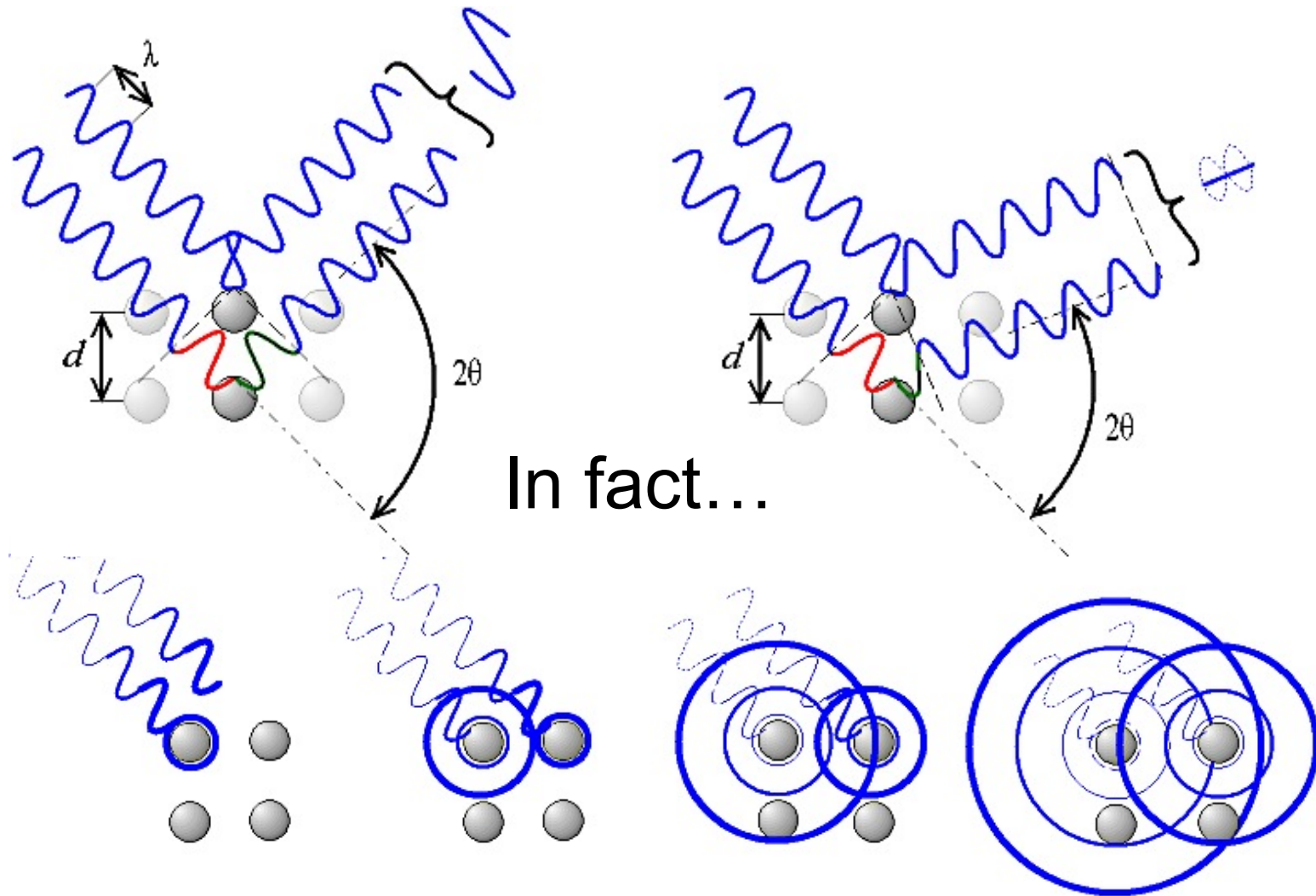
Very useful but not a correct description!

Derivation of Laue equations

Assume a row of scatterers separated by constant repeat, a. Radiation of wavelength λ is incident on this row at an angle α_o. Examine the the scatter from this row at an angle α_n.
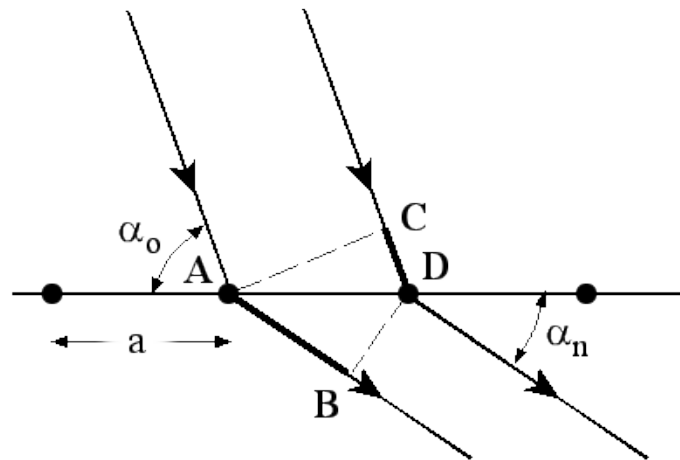
The path difference of rays scattering from points A and D is just AB-CD. If the incoming rays are in phase, the path difference must be some integer multiple of the wavelength for constructive interference to occur.
This leads to the first **Laue equation:**

$$AB - CD = a(\cos\alpha_n - \cos\alpha_0) = n_x\lambda$$

Derivation of Laue equations

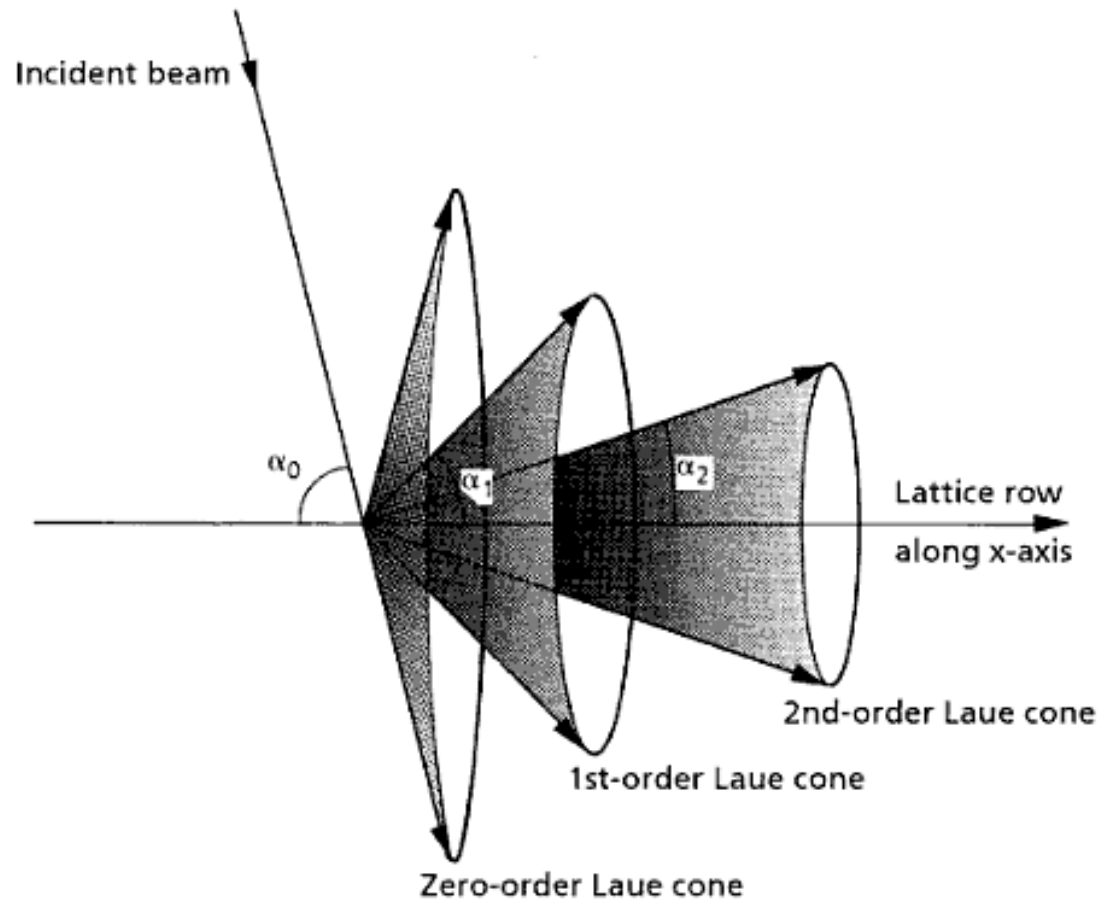In reality the angle α_n does not need to be measured only as θ in Bragg's law illustrations. In fact, the diffracted beams of the same order form a conical surface (α_n in constant on the conical surface).


Three Laue cones representing the directions of the diffracted beams from a lattice row along the x-axis with $0\lambda(n_x = 0)$, $1\lambda(n_x = 1)$ and $2\lambda(n_x = 2)$ path differences. The corresponding Laue cones for $n_x = -1$, $n_x = -2$ etc. lie to the left of the zero order Laue cone.

Derivation of Laue equations

Next consider another row of scatterers at some angle, to the first with repeat distance, b. A second Laue equation can be written for this direction. The incident rays will make angle β_0 to this row and the scattered rays β_n. This equation must also result in some integer multiple of the wavelength, n_y, for constructive interference to occur.

$$AB - CD = b(\cos\beta_n - \cos\beta_0) = n_y\lambda$$

Diffracted
rays

S

S

b

a

S₀

Incident ray
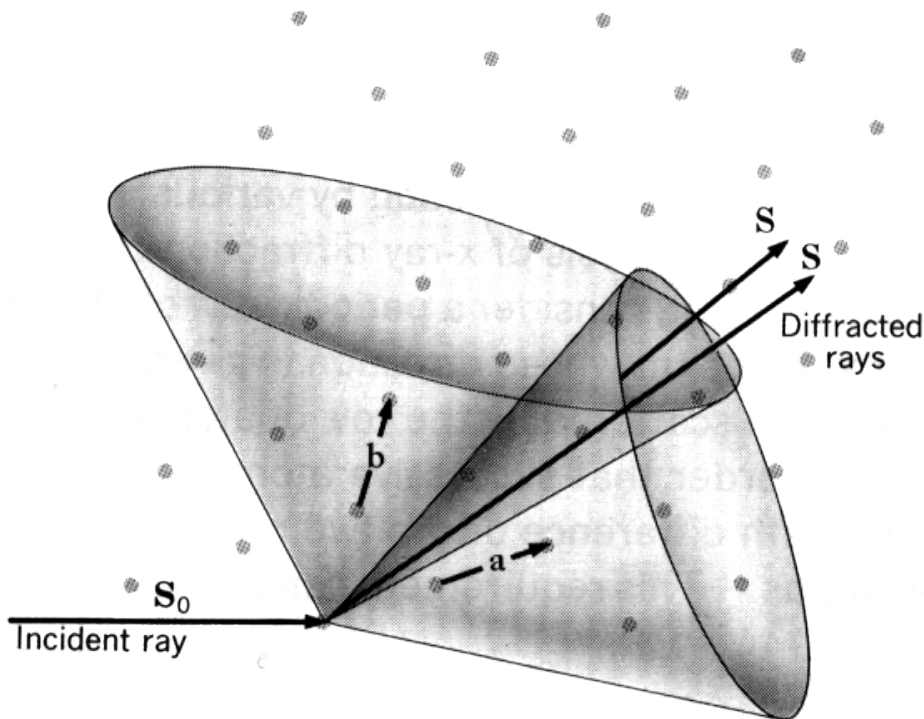
Laue's remarkable idea was that this equation must have a simultaneous solution with the equation written for the x direction (and the z direction as well). The solution to this second equation also forms a cone except this time about **b**. The simultaneous solution to these two equations can be viewed as the intersection of the two cones originating at a common apex and which intersect along two lines.

Derivation of Laue equations

Adding scatterers in a third direction to form a 3D lattice gives the third Laue equation. This results in a set of equations with one simultaneous solution. By analogy with the previous results this solution will be a single vector lying at the intersection of three cones sharing a common apex.

$$AB - CD = a(\cos\alpha_n - \cos\alpha_0) = n_x\lambda$$

$$AB - CD = b(\cos\beta_n - \cos\beta_0) = n_y\lambda$$

$$AB - CD = c(\cos\gamma_n - \cos\gamma_0) = n_z\lambda$$
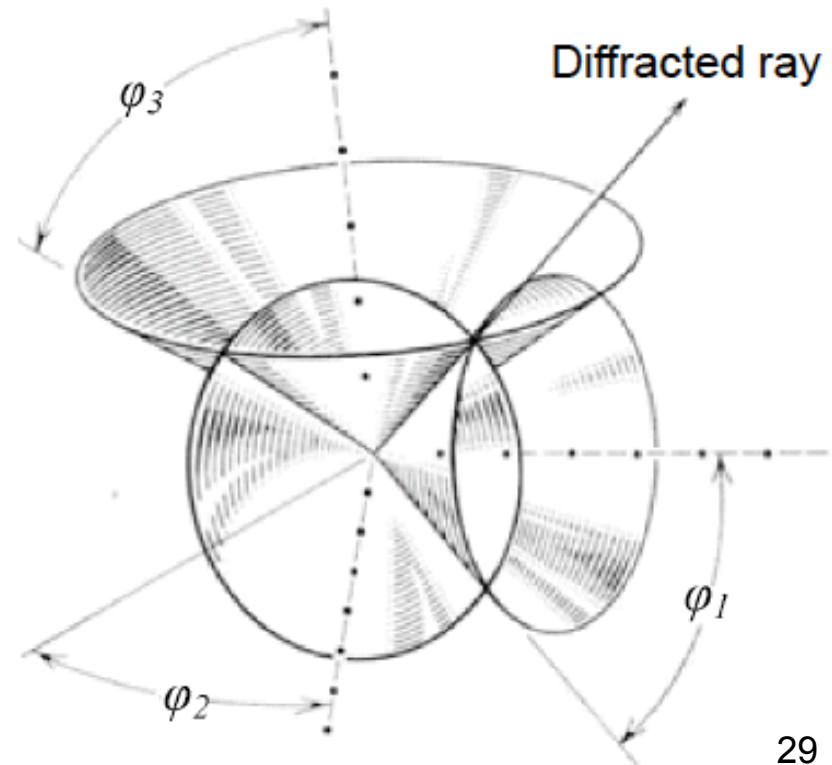
Vectorial form of Laue equations

The first Laue equation is valid for any scattered ray that makes an angle α_n with the unit cell axis. Thus the Laue condition is consistent with a cone of scattered rays centered about the a axis.

This equation can be restated in vector terms. The repeat distance a, becomes a unit cell vector **a**. Define a unit vector parallel to the incoming ray, **S$_0$**, and a unit vector parallel to the scattered ray, **S**. Then:
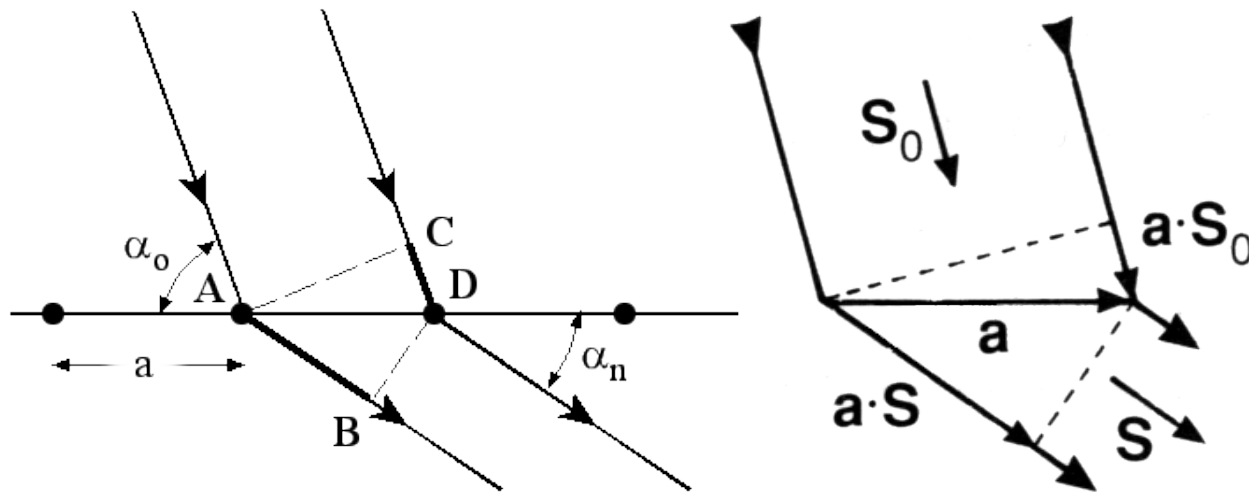
$$\mathbf{a} \bullet \mathbf{S} = a(\cos\alpha_n)$$

$$\mathbf{a} \bullet \mathbf{S_0} = a(\cos\alpha_0)$$

$$\mathbf{a} \bullet (\mathbf{S} - \mathbf{S_0}) = n_x\lambda$$

Ewald sphere: vectorial form of Laue equations

Look at first Laue condition in vector form $\quad \mathbf{a} \bullet \dfrac{(\mathbf{S} - \mathbf{S_0})}{\lambda} = n_x$

Postulate that $\mathbf{S}$-$\mathbf{S_0}\backslash\lambda$ represents any vector $\mathbf{g}$ in reciprocal space.

$$\mathbf{g} = \left(\frac{\mathbf{S} - \mathbf{S_0}}{\lambda} \right) = p\mathbf{a}^* + q\mathbf{b}^* + r\mathbf{c}^*$$

1st Laue eq.: $\quad \mathbf{a} \bullet \mathbf{g} = p\mathbf{a} \bullet \mathbf{a}^* + q\mathbf{a} \bullet \mathbf{b}^* + r\mathbf{a} \bullet \mathbf{c}^* = p \; = n_x$

2nd Laue eq.: $\quad \mathbf{b} \bullet \mathbf{g} = p\mathbf{b} \bullet \mathbf{a}^* + q\mathbf{b} \bullet \mathbf{b}^* + r\mathbf{b} \bullet \mathbf{c}^* = q \; = n_y$

3rd Laue eq.: $\quad \mathbf{c} \bullet \mathbf{g} = p\mathbf{c} \bullet \mathbf{a}^* + q\mathbf{c} \bullet \mathbf{b}^* + r\mathbf{c} \bullet \mathbf{c}^* = r \; = n_z$

The Laue conditions require that p, q, r be integers (n_x, n_y, n_z). So they are the just Miller indices, h, k, and l! Hence the Laue equations are consistent with the concept of reciprocal lattice vector.

Ewald sphere: vectorial form of Laue equations

So there is diffraction when the scattering vector **g** equals a reciprocal lattice vector **d***:

$$\mathbf{g} = \left(\frac{\mathbf{S} - \mathbf{S_0}}{\lambda} \right) = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* = \mathbf{d}^*_{hkl}$$

Ewald was responsible for first interpreting Laue's results in terms of reciprocal lattices. He devised a simple geometric construction that demonstrates the relationship in quite elegant but simple way.

$$\mathbf{g} = \left(\frac{\mathbf{S} - \mathbf{S_0}}{\lambda} \right) = \mathbf{d}^*_{hkl} = \frac{1}{d_{hkl}} = \frac{2}{\lambda}\sin\theta$$

$$\lambda = 2d_{hkl}\sin\theta$$

Consistent with Bragg's law too!

X-ray diffraction methods

In XRD the Ewald sphere radius is short so the **coincidence between reciprocal lattice points and the sphere is rare**.

In order to record a diffraction pattern some reciprocal lattice points must lie on or pass through the Ewald sphere. This can be achieved in several different ways:

- Use "white" radiation and a single crystal: **Laue method**

- Use monochromatic radiation and rotate a single crystal: **Rotation method** and similar techniques

- Use monochromatic radiation and a sample containing crystals with many different orientations (a powder): **Powder diffraction**

The Laue method (single crystal diffraction)

As in Laue's original experiment:

- Using "white" Bremsstrahlung radiation from an X-ray tube so that many different wavelengths are scattered by the sample

- Many reflections will simultaneously satisfy Bragg's law without rotating the crystal

Transmission Laue

Back reflection Laue
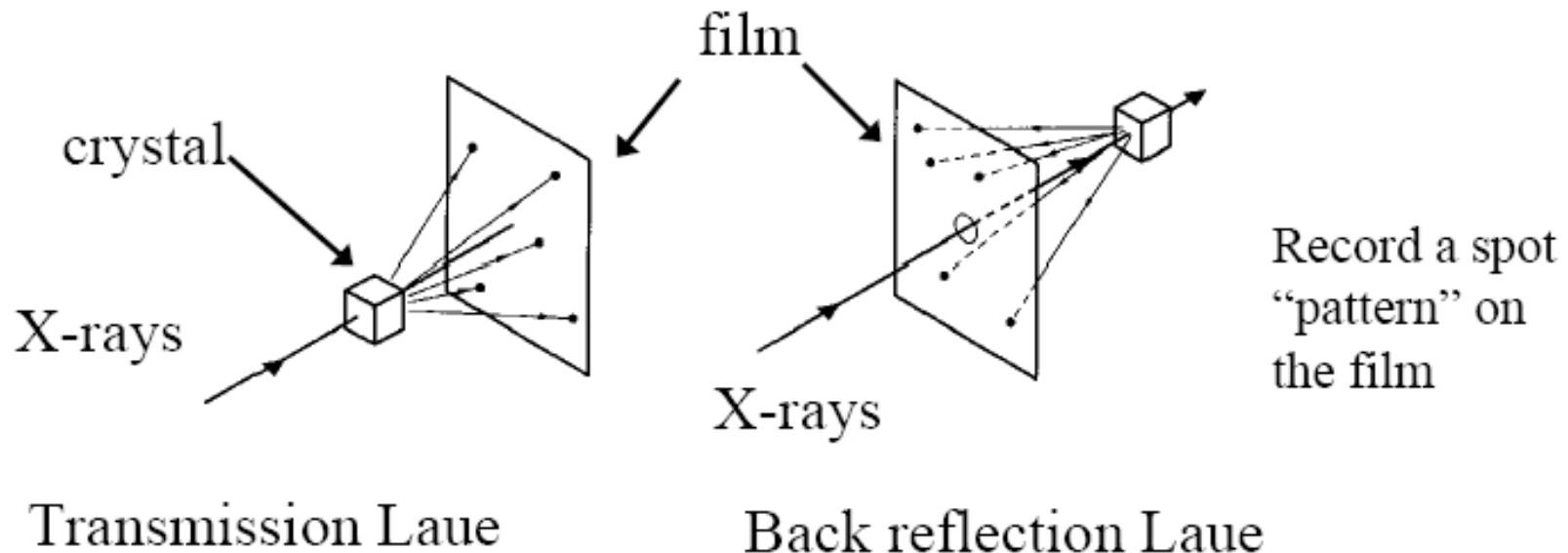
Appearance of Laue diffractograms
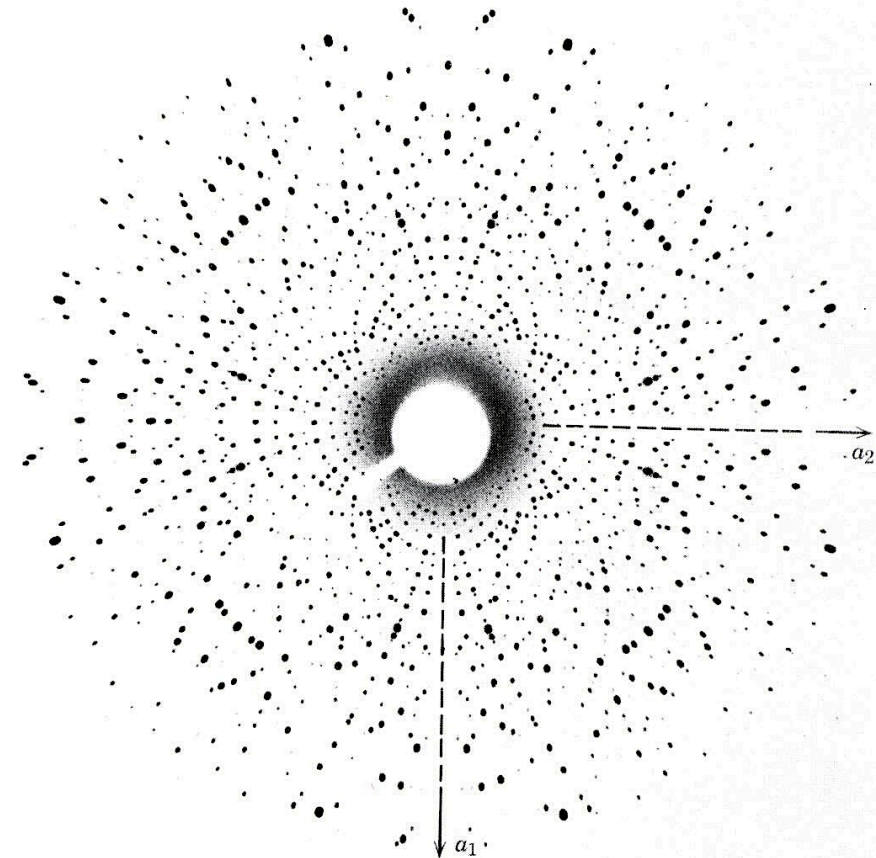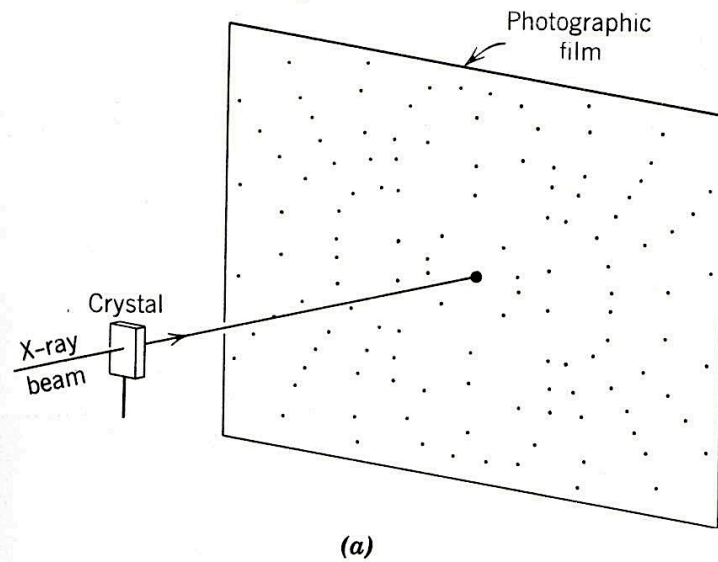
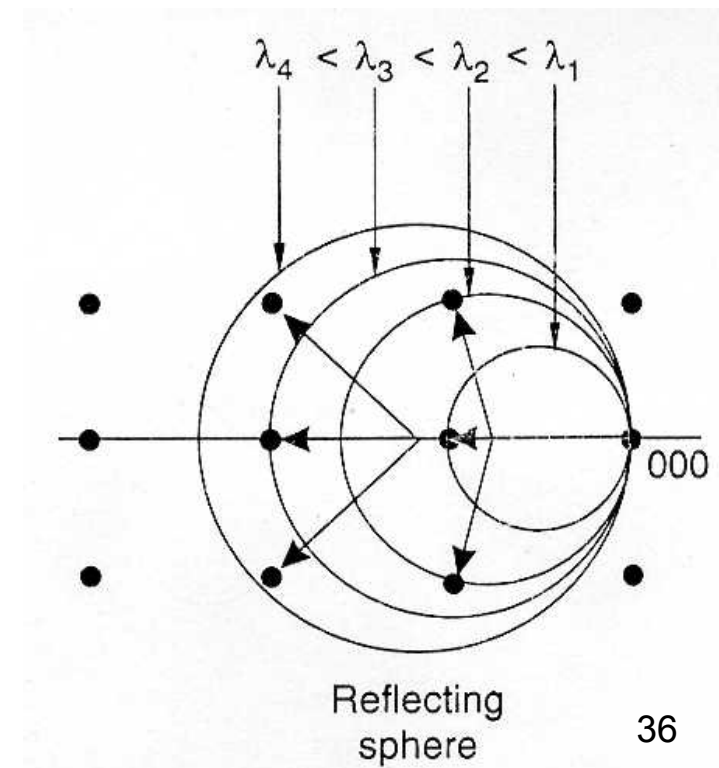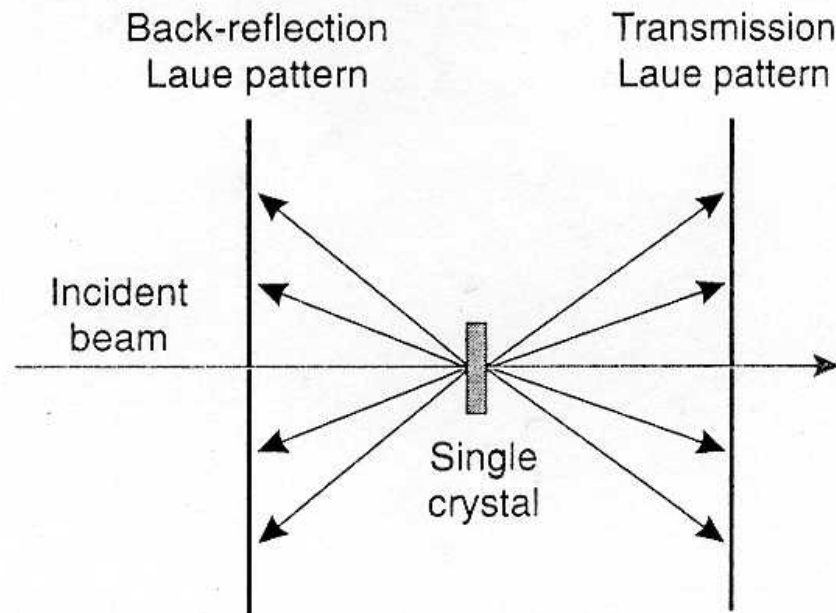(a) Obtaining a Laue photograph with a stationary crystal. (b) Laue photograph of vesuvianite with point group symmetry $4/m2/m2/m$. The photograph was taken along the fourfold rotation axis (c axis) of vesuvianite, thus revealing fourfold symmetry and mirrors in the arrangement of diffraction spots. The axial directions, a_1 and a_2, were inked onto the photograph after it had been developed.

Ewald construction for Laue method

Back-reflection
Laue pattern

Transmission
Laue pattern

Incident
beam

Single
crystal

$\lambda_4 < \lambda_3 < \lambda_2 < \lambda_1$

000

Reflecting
sphere
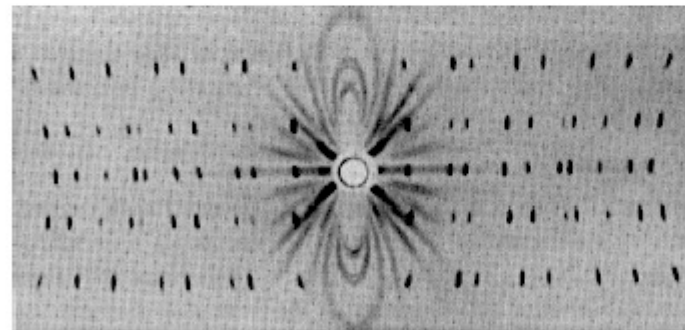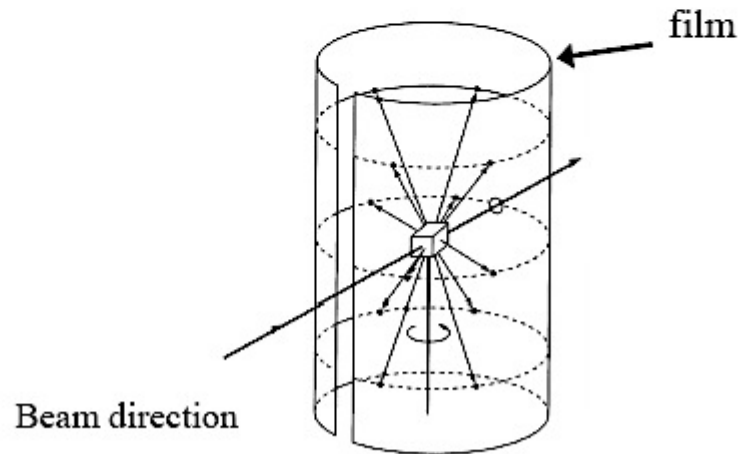
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Rotating crystal method (single crystal method)

Aligned crystal is rotated around one axis so relps pass through the Ewald sphere:

- Produces spots lying on lines

Rotation photograph of quart showing spots on layer lines

relps = reciprocal lattice points

Ewald construction for rotating crystal method
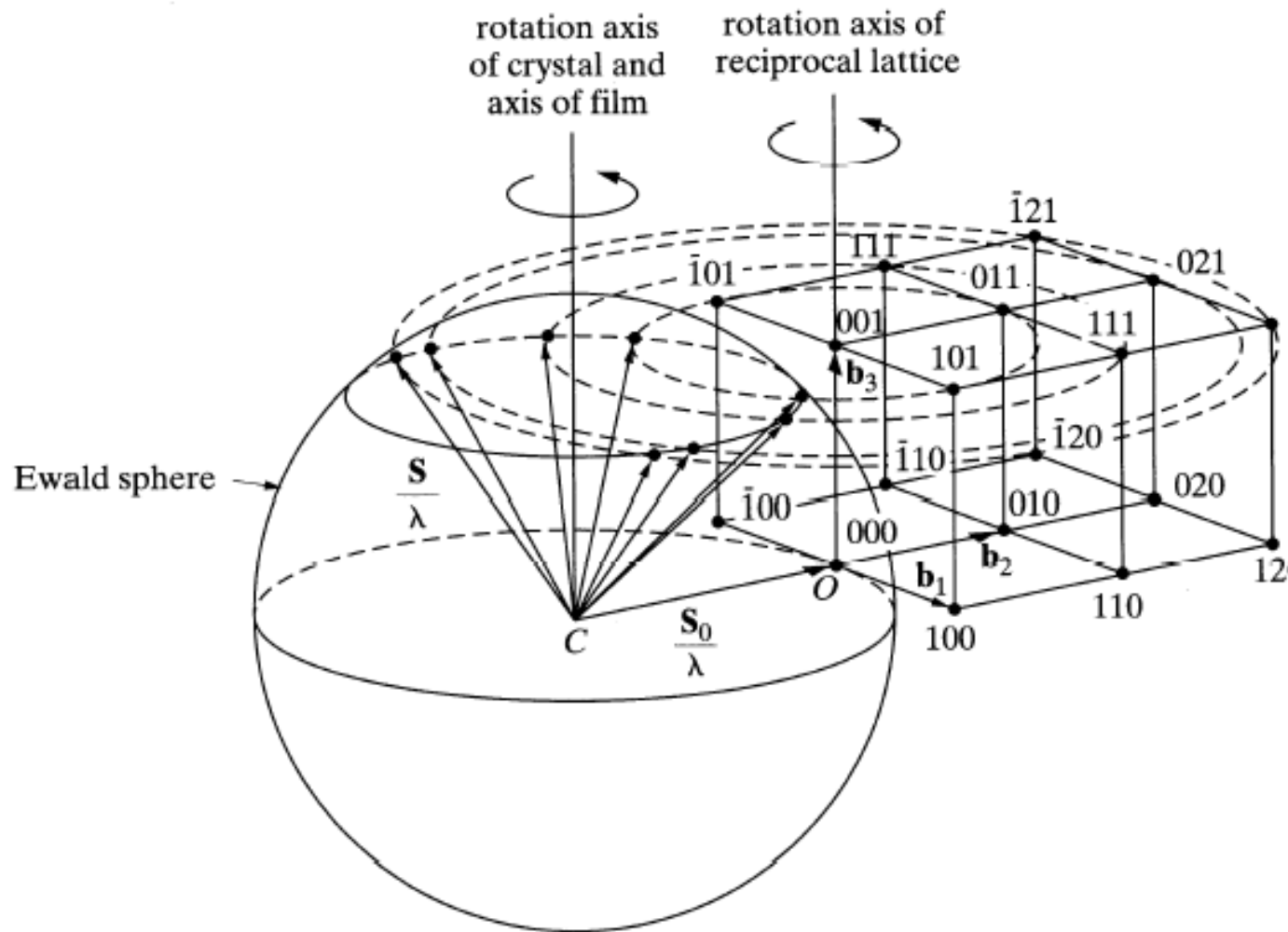
Powder diffraction method
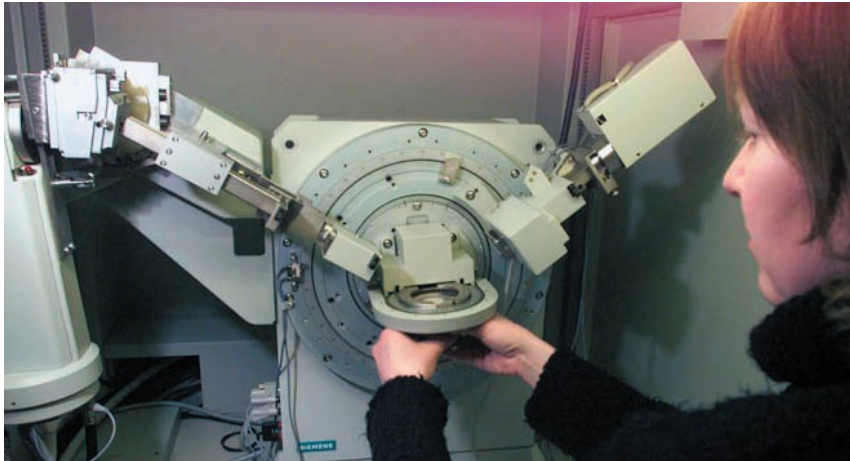
Bragg-Brentano-geometry

Diffractometer
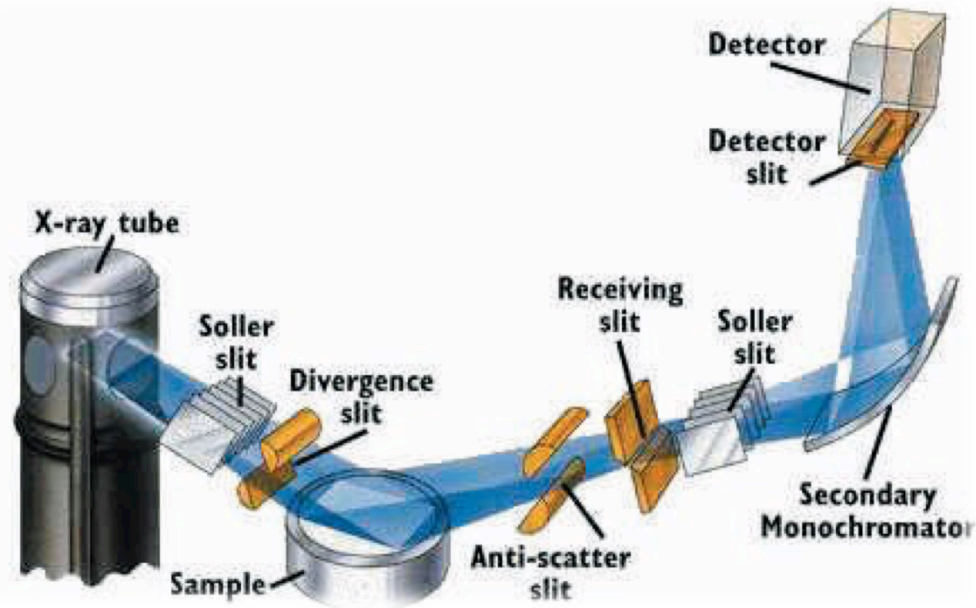
Reciprocal lattice of a powder

In a powder we have a large number of crystals all at different orientations

The reciprocal space no longer has one set of points, but many sets of points at different orientations. All of these points lie on the surface of spheres or shells.

– **R**eciprocal **l**attice shells – **rel** shells

Ewald construction for powder

Ewald's Sphere

Diffraction Cone

Debye Ring

Incident Beam

2θ

s

d^*_{hkl}

s_o

s

Detector

- In powder diffraction you generate an infinite number of randomly oriented, but identical, reciprocal lattice vectors.

- They form circles with their ends placed on the surface of Ewald's sphere.

- They produce powder diffraction cones at different Bragg angles

$$|R^*| = |g| = d^*_{hkl} = \frac{1}{d_{hkl}}$$

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Ewald construction for powder

Figure 8.2

Ewald's sphere

Incident Beam

$\left|d^*_{hkl}\right| = \dfrac{1}{d_{hkl}}$

2θ

S_0

2θ

2θ

024
133
004
222   113
022
002
111

A diffracted cone is formed every time Bragg's law is satisfied. We may use a photographic film (Debye-Sherrer camera in the old days) or a revolving detector (Bragg-Brentano diffractometer) to record the diffracted intensity.

The powder rotates (θ) to increase the probably of diffraction and the detector rotates (2θ) to intersect the diffracting cones.

Electron diffraction (TEM) of single crystal

Fourier transforms again:

Crystal

Thin disc

Real space

X

multiplication

FT

FT

Reciprocal space

⊗

convolution

"Relrod"

=

2 lengths scales in reciprocal space!
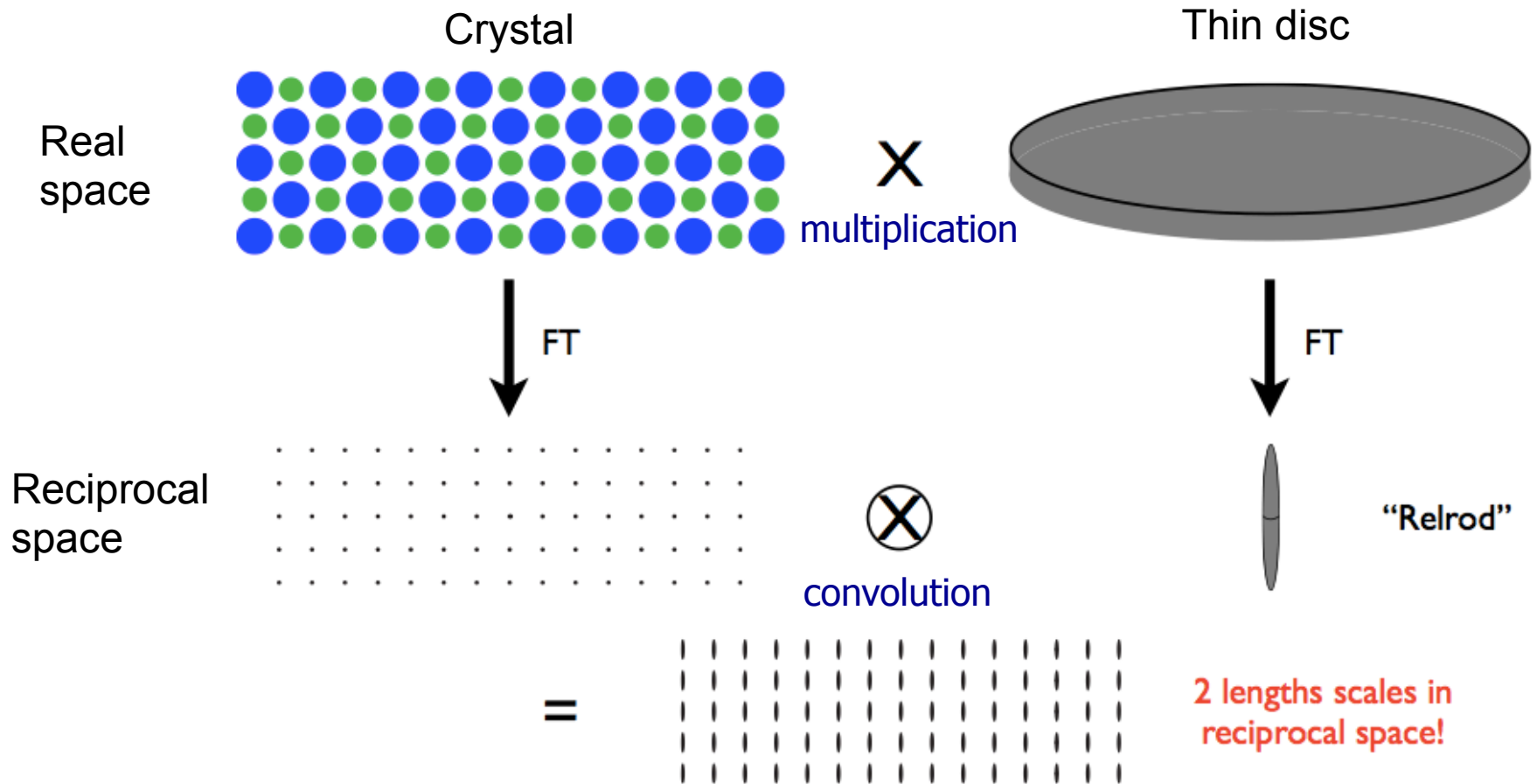
Reciprocal lattice scales: small parallel to the plane of the disc (almost infinite in atomic scale) and larger perpendicular to the disc due to finite and small thickness

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Diffraction from a single crystal (TEM)
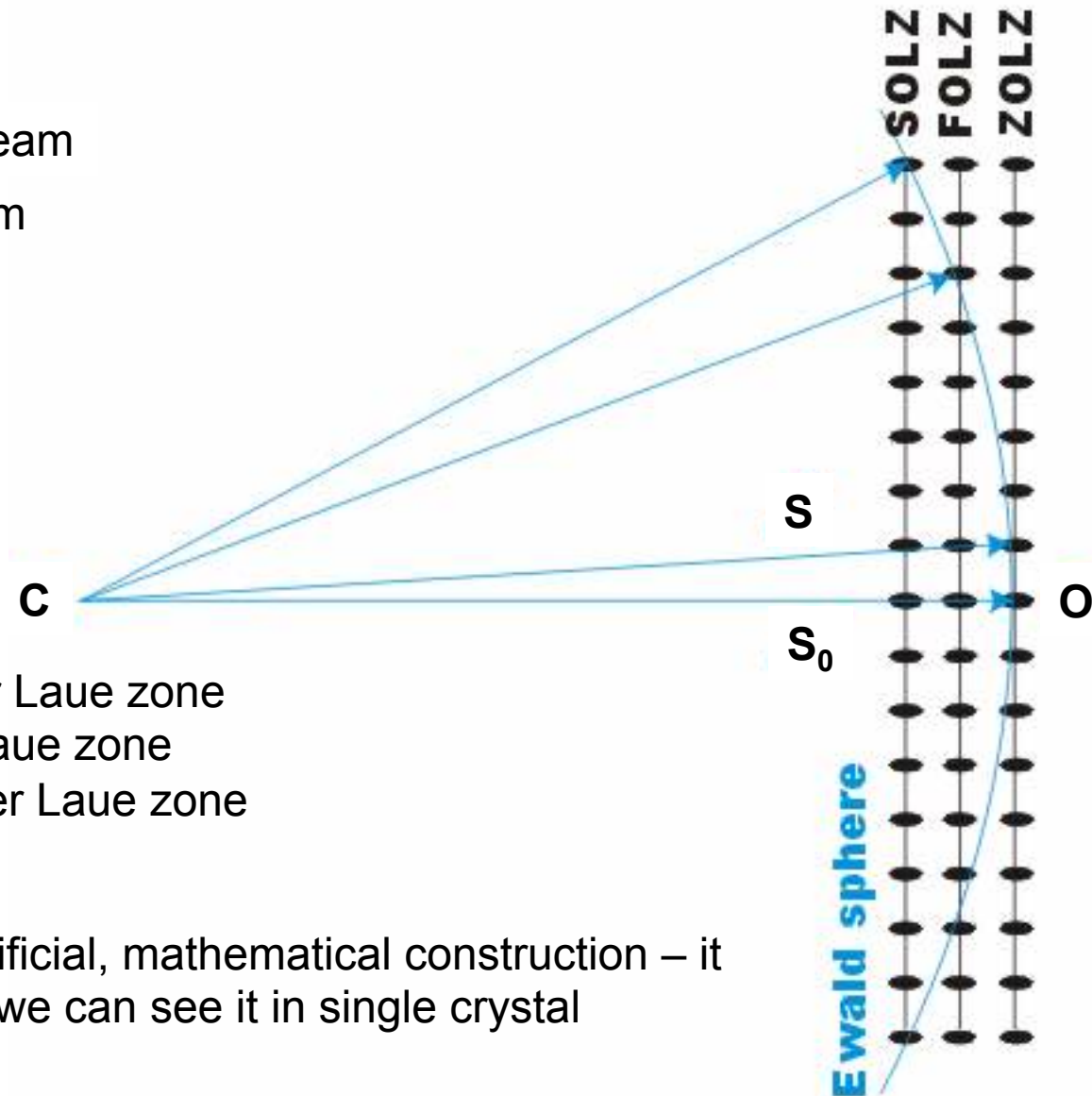
S_0 is the transmitted beam

S is the diffracted beam

ZOLZ is the zeroth order Laue zone
FOLZ is the first order Laue zone
SOLZ is the second order Laue zone

The reciprocal space is an artificial, mathematical construction – it doesn't really exist; however, we can see it in single crystal diffraction.

SOLZ FOLZ ZOLZ

C

S

S_0

O

Ewald sphere

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Geometry of diffraction patterns

grating

Fresnel diffraction
(also called near-field)

Fraunhofer diffraction
(also called far-field)

+1

0

-1
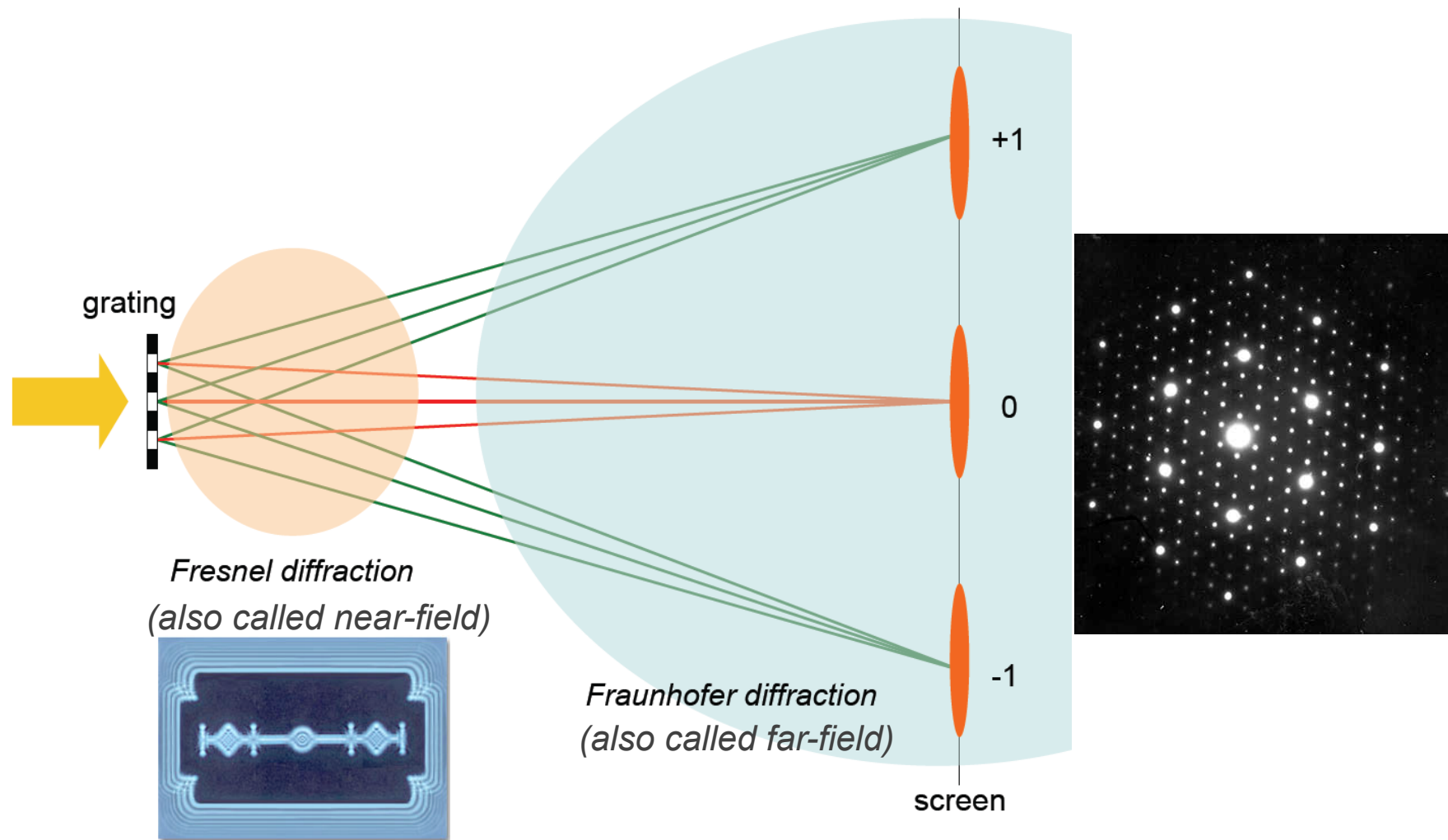
screen

Fraunhofer diffraction pattern: the rays leave the diffracting object in parallel directions:
- Screen very far from the object
- Converging lenses may be used to make the rays converge in smaller distances

Geometry of diffraction patterns
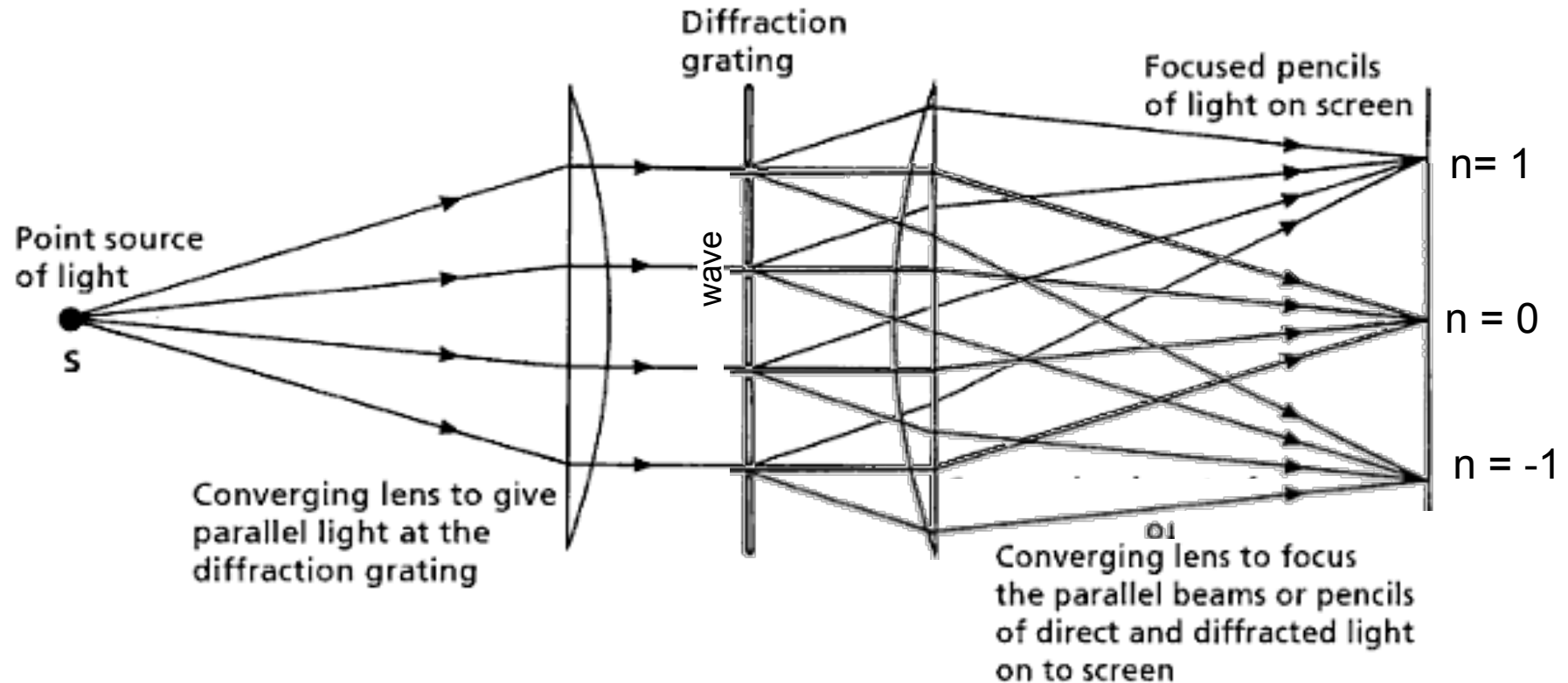
A plane wavefront (parallel light) incident upon a grating may be achieved by inserting a lens (left) with the point source at its focus. Conversely, the parallel 'pencils' of the direct and diffracted light may be sharply focused onto a screen or photographic plate by inserting another lens

Diffraction intensity
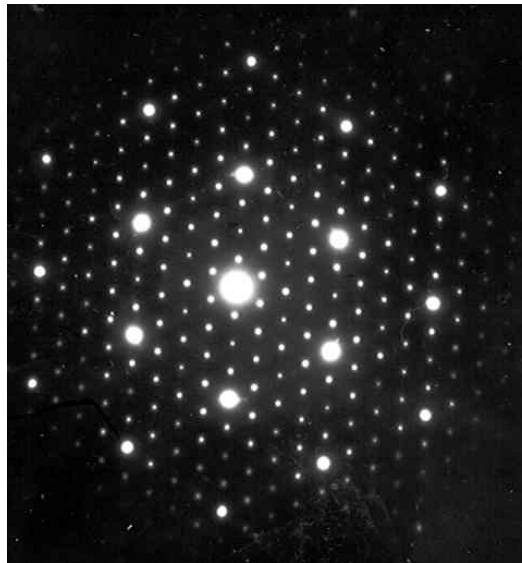
What can be said about the intensity of the "reflections" in this diffraction pattern?

Scattering by electrons

- Electrons and other charged particles scatter X-rays.
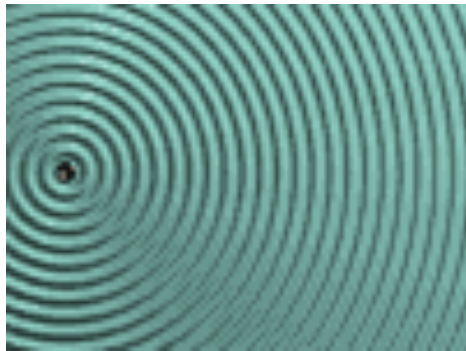
Interaction of a X-ray front with an isolated electron, which becomes a new X-ray source, producing the X-rays waves in a spherical mode.
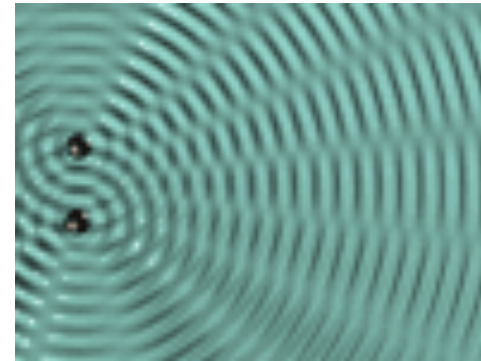
The spherical waves produced by two electrons interact with each other, producing positive and negative interferences.

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Scattering by an electron

(λ_0, ν_0)

Sets electron into oscillation

Emission in 'all' directions

Coherent
(definite phase relationship)

(λ_0, ν_0) *Scattered beams*
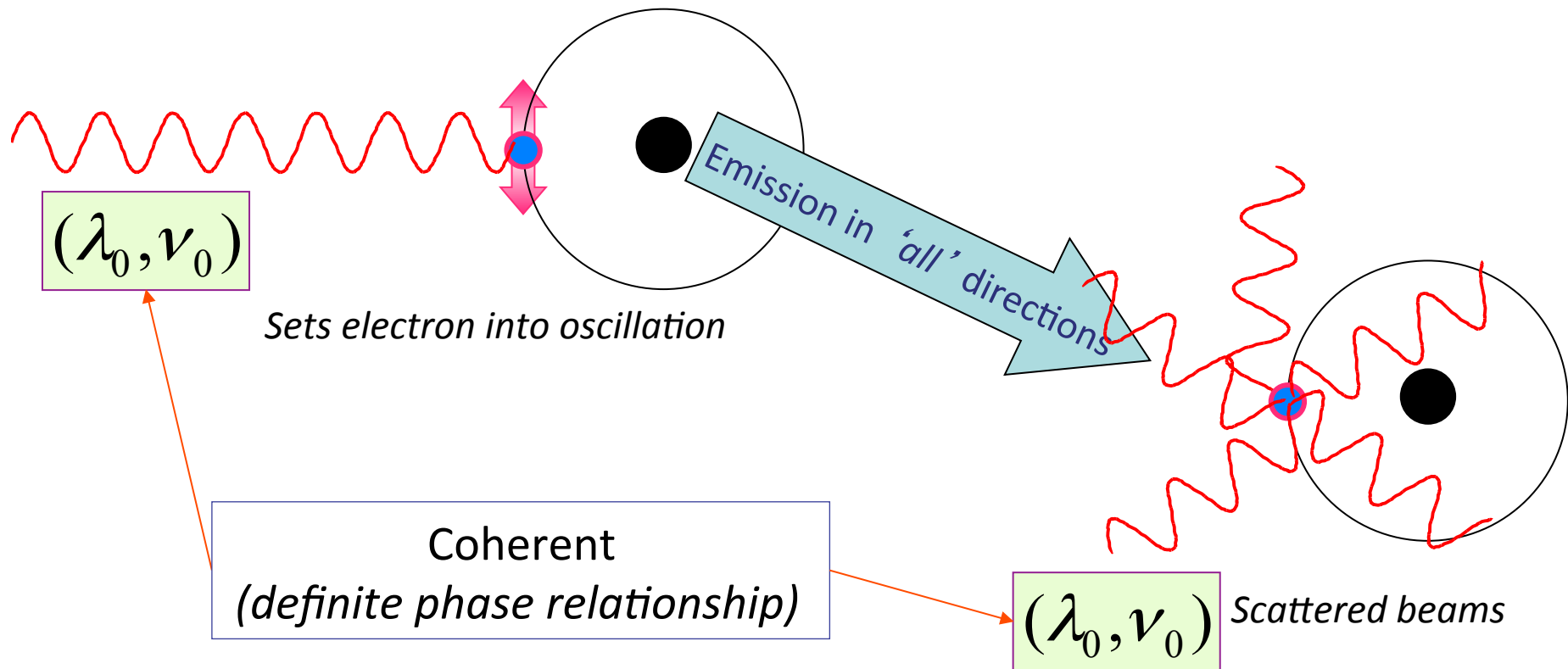
- The electric field **(E)** is the main cause for the acceleration of the electron
- The moving particle radiates most strongly **in a direction perpendicular to its motion**
- The radiation will be polarized along the direction of its motion

Scattering by an electron

For a wave oscillating in z direction

z

P

r

θ

x
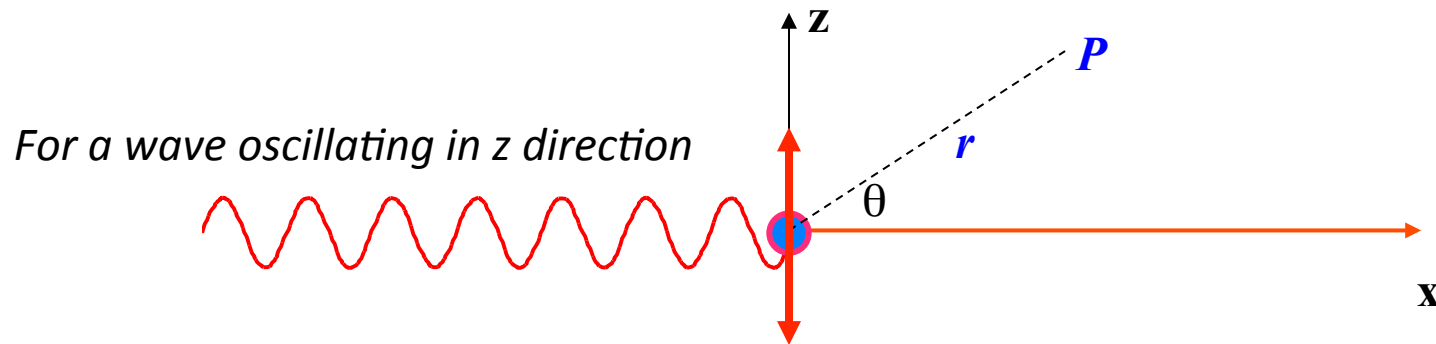
Intensity of the scattered beam due to an electron at a point P such that $r \gg \lambda$

The reason we are able to neglect scattering from the protons in the nucleus

$$I = I_0 \frac{e^4}{m^2 c^4}\left(\frac{sin^2\theta}{r^2}\right)$$

Scattering by atoms

- The atom can be considered to be a collection of electrons. This electron density scatters radiation.
- For radiation to remain coherent the interference between x-rays scattered from different points within the atom has to be considered.
- **This leads to a strong angle dependence of the scattering.**
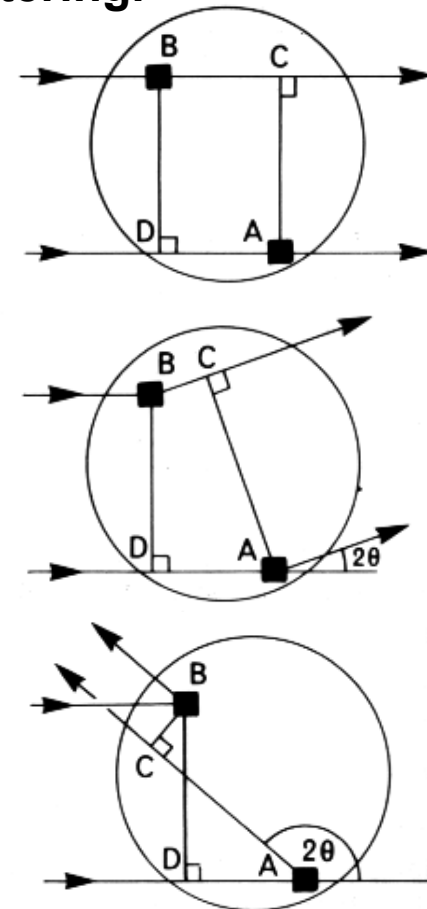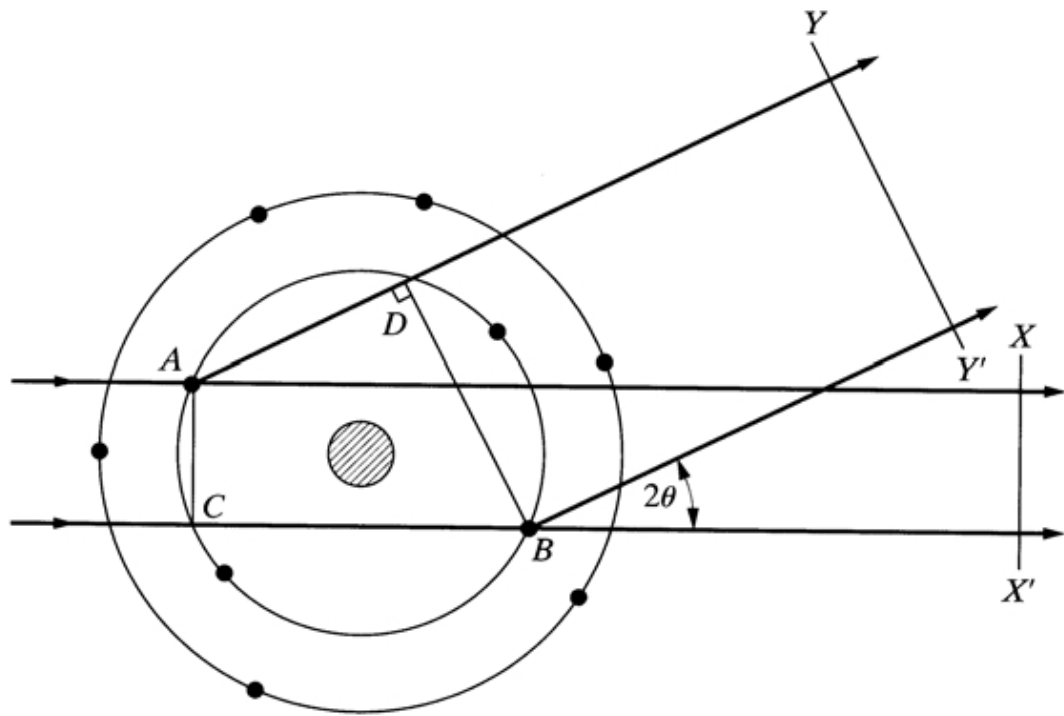
Scattering by atoms
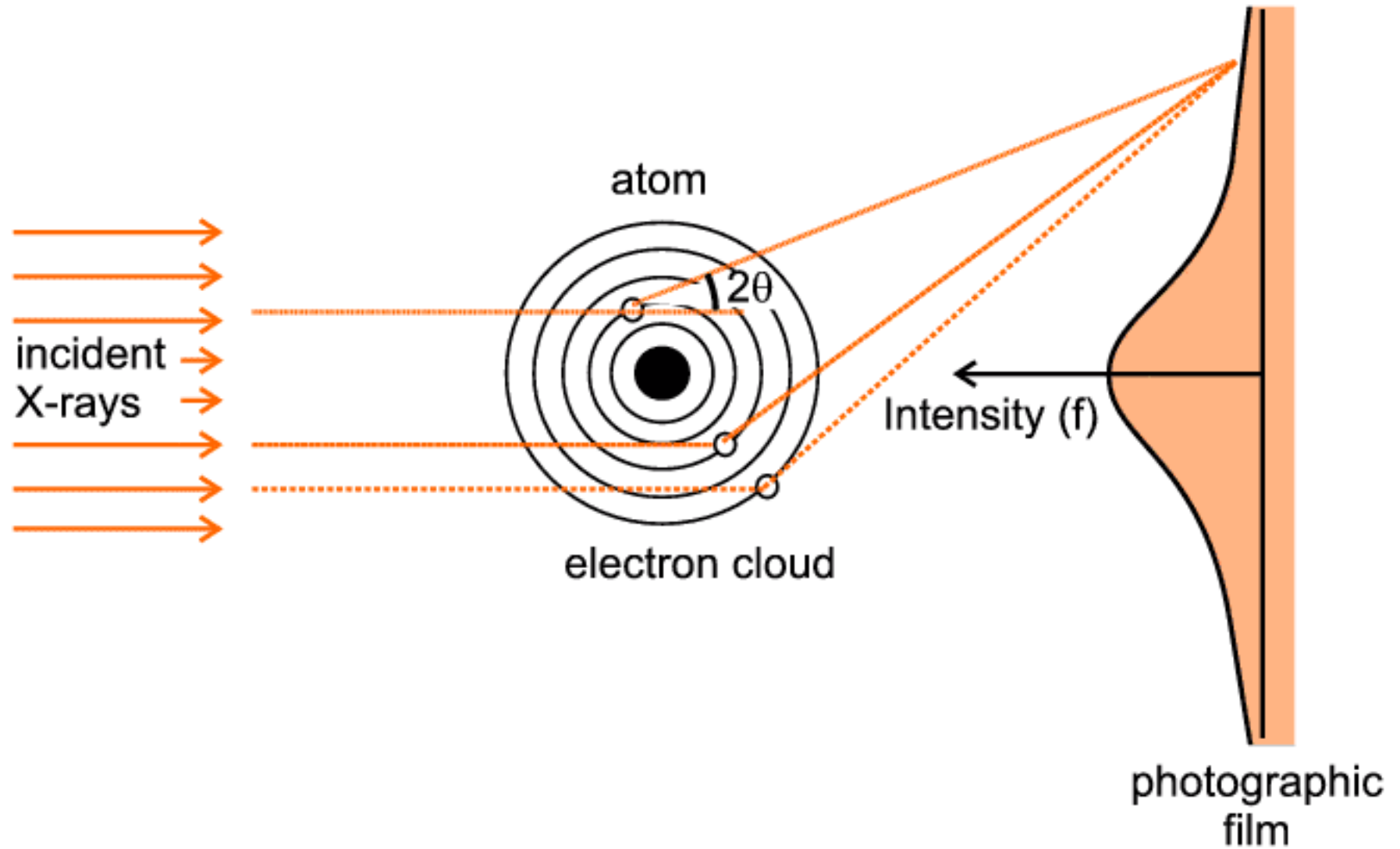
Scattering by atoms

The scattering power of an atom is given by the atomic form factor (f): ratio of scattering from the atom to what would be observed from a single electron
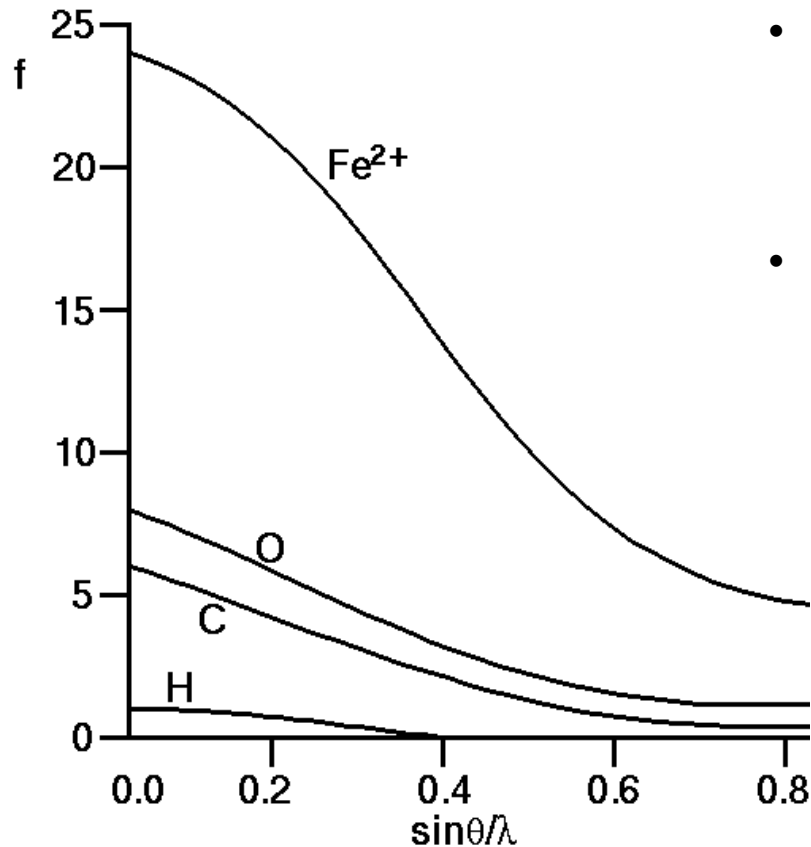
- Form factor is expressed as a function of $(\sin\theta)/\lambda$ as the interference depends on both λ and the scattering angle

- Form factor is equivalent to the atomic number at low angles, but it drops rapidly at high $(\sin\theta)/\lambda$

*Atomic scattering factors calculated for atoms and ions with different numbers of electrons. Note that the single electron of the hydrogen atom (**H**) scatters very little as compared with other elements, especially with increasing **θ**. Hydrogen will therefore be "**difficult to see**" ..*

Coherent scattering from crystals

Extinctions from centered cells or different atoms in the unit cell

- Due to crystal periodicity scattering from atoms in one unit cell can be used to determine the intensities of the diffracted beams
- The positions of the atoms in a unit cell determine the intensities of the reflections.
- Consider diffraction from (001) planes in body centered cells:

Diffraction from (001) planes
(a)   (b)
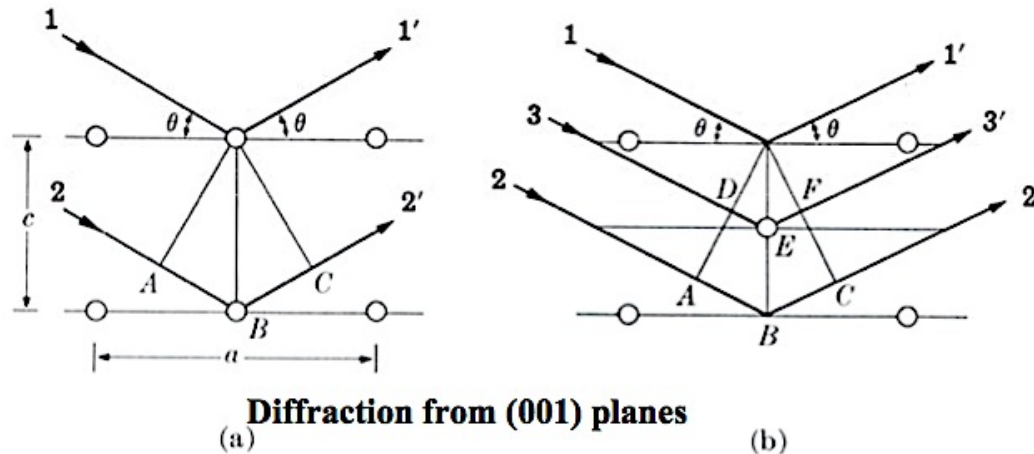
These (001) planes diffract?

(a) If the path length between rays 1 and 2 differs by λ, the diffraction angle is satisfied and the diffracted intensity corresponds to that of 1 atom (in primitive cells we have 1 atom/cell).

(b) For the centred cell, in the same configuration, the path length between rays 1 and 3 will differ by $\lambda/2$ and destructive interference in (b) will lead to **NO** diffracted intensity for (001) in any body-centered (BC) lattice (I-cubic, I- tetragonal, or I-orthorhombic).

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Coherent scattering from crystals

Extinctions from centered cells and/or

- Unit Cell (UC) is representative of the crystal structure
- Scattered waves from various atoms in the UC interfere to create the diffraction pattern
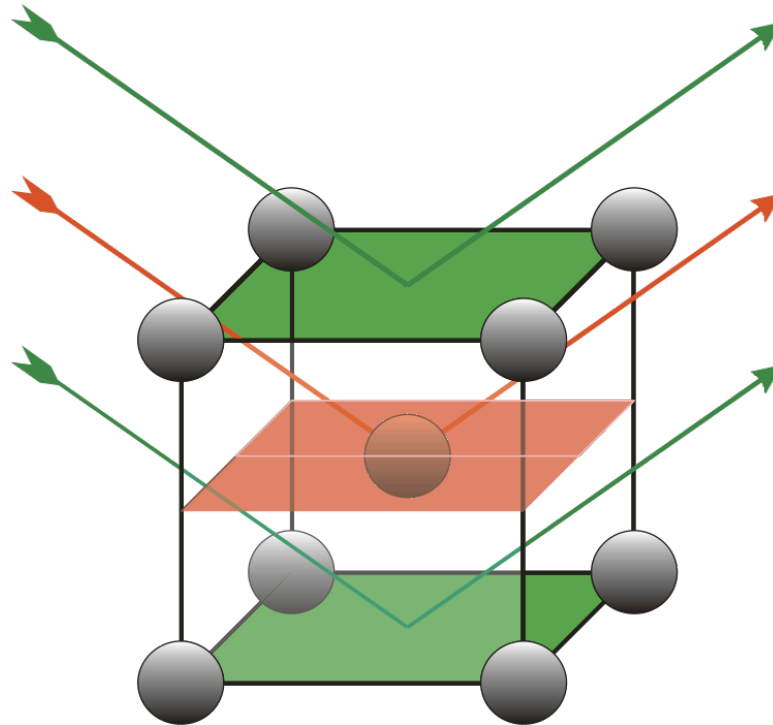
The wave scattered from the middle plane is out of phase with the ones scattered from top and bottom planes

Change in phase due to atoms in fractional coordinates (revisiting the structure factor concept)

Change in phase due to atoms in fractional coordinates
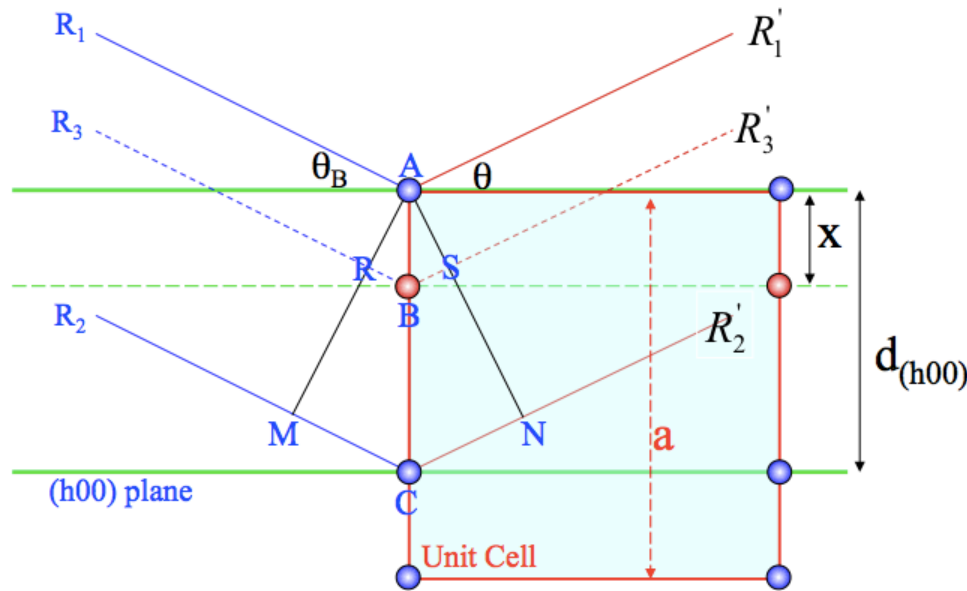
$$AC = d_{h00} = \frac{a}{h}$$

$$MCN :: AC = d_{h00}$$

$$RBS :: AB = x$$

$$\frac{AB}{AC} = \frac{x}{d_{h00}} = \frac{x}{a/h}$$

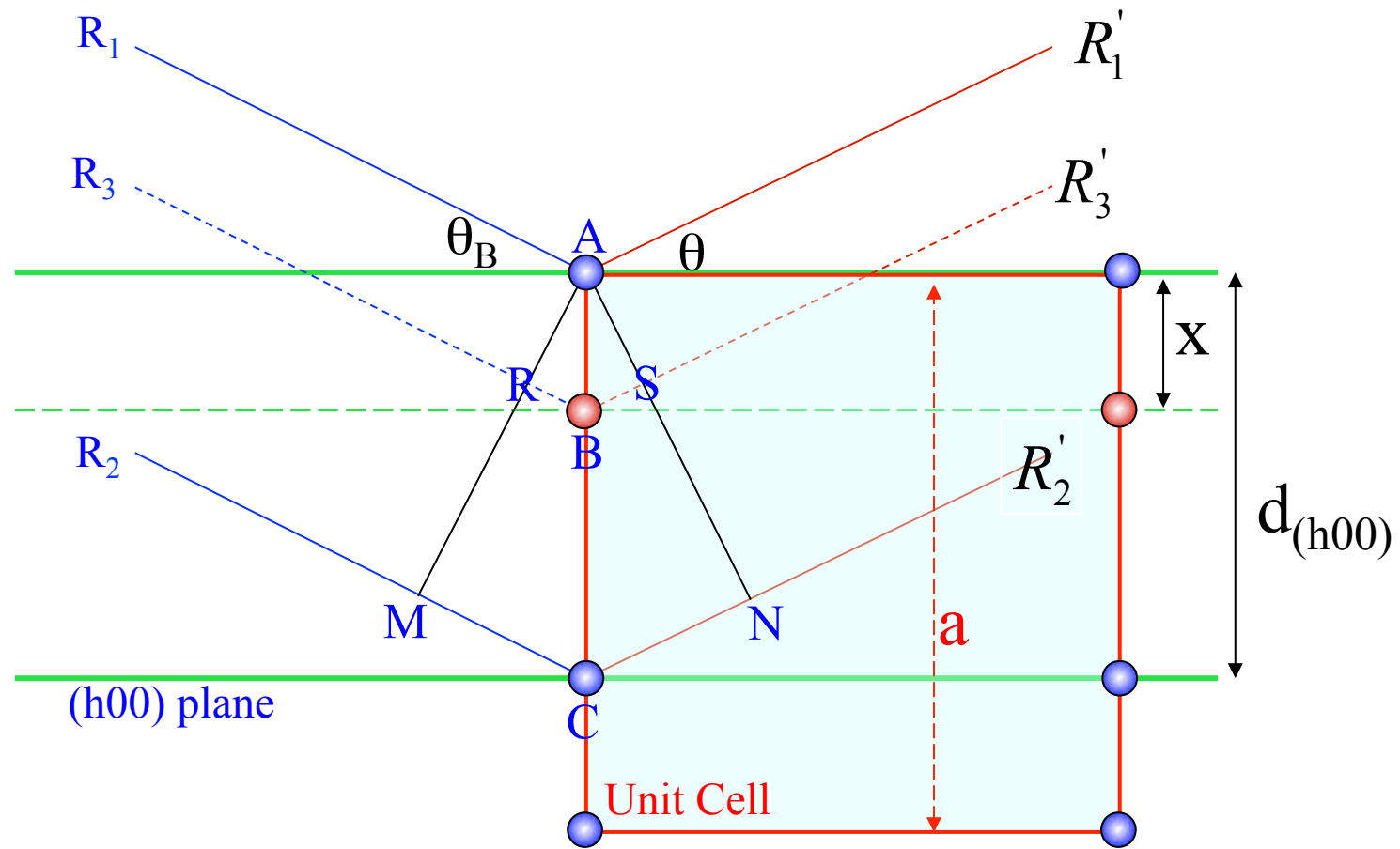*Note: R_1 corresponds to corner atoms and R_3 to from atoms in additional positions in the Unit Cell (UC)*

$$\delta_{R_1 R_2} = MCN = 2d_{h00} \sin(\theta) = \lambda$$

$$\delta_{R_1 R_3} = RBS = \frac{AB}{AC} MCN = \frac{AB}{AC} \lambda = \frac{x}{a/h} \lambda$$

$$\varphi = \frac{2\pi}{\lambda} \delta$$

$$\varphi_{R_1 R_3} = \frac{2\pi}{\lambda} \frac{x}{a/h} \lambda = 2\pi h \frac{x}{a} \quad \frac{x}{a} \rightarrow fractional\ coordinate \rightarrow x' \qquad \boxed{\varphi_{R_1 R_3} = 2\pi h x'}$$

Extending to 3D $\quad \boxed{\varphi = 2\pi(h x' + k y' + l z')} \longrightarrow$ *Independent of the shape of UC*

Revisiting the complex notation

The phase difference between rays scattered from the origin and rays scattered from an atom at fraction coordinates (x'v'w') is:

$$\varphi = 2\pi(h\,x' + k\,y' + l\,z')$$

- Each atom within the unit cell may produce a scattered wave of different amplitude.
- The amplitude is given by the form factor *f* for the atom.
- All of the scattered waves from individual atoms sum together to produce a wave whose amplitude can be measured (the phase is more difficult to retrieve).

Tool to handle the summation of waves scattered from different atoms:
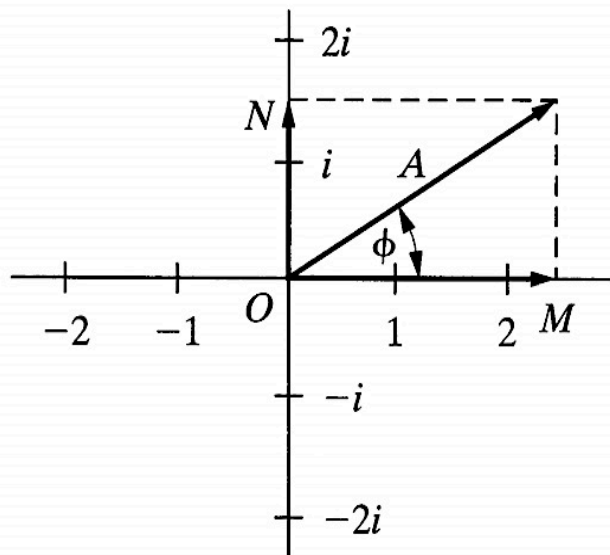
The most convenient way to represent the amplitude and phase of a scattered wave is by a vector in the complex plane.

Wave of amplitude A and phase φ:
$$Ae^{i\varphi} = A(\cos\varphi + i\,\sin\varphi)$$

- Real when φ is multiple of 2π
- 1 for even multiples
- -1 for odd multiples

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Change in phase due to atoms in fractional coordinates

$$\varphi = 2\pi(h\,x' + k\,y' + l\,z') \xrightarrow[\text{complex notation}]{\text{wave equation in}} E = Ae^{i\varphi} = fe^{i[2\pi(h\,x'+k\,y'+l\,z')]}$$

- *If atom B is different from atom A → 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 is the scattering factor for the unit cell*
- *The unit cell scattering factor is called the **Structure Factor (F)***

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

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

for n atoms in the UC:
$$F_{hkl} = \sum_{j=1}^{n} f_j \, e^{i\varphi j} = \sum_{j=1}^{n} f_j \, e^{i\left[2\pi\left(h\,x'_j + k\,y'_j + l\,z'_j\right)\right]}$$

Intensity of the diffracted wave:
$$I \propto F_{hkl}^{2}$$

*The structure factor is independent of the **shape** and **size** of the unit cell !!!*

Structure factor calculations

Simple cubic

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

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

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

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

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

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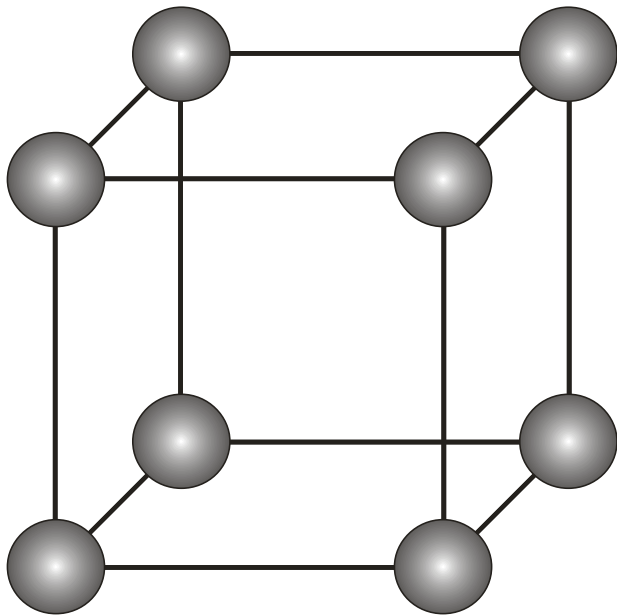
$$F = f_j\ e^{i\varphi_j} = f_j\ e^{i[2\pi(h\ x'_j + k\ y'_j + l\ z'_j)]}$$

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

$$F^2 = f^2 \qquad \Rightarrow F \text{ is independent of the scattering plane (h k l)}$$

Structure factor calculations

C centered orthorhombic

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

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

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

$$= f \ e^0 + f \ e^{i[2\pi(\frac{h+k}{2})]} = f[1 + \underbrace{e^{i\pi(h+k)}}]$$
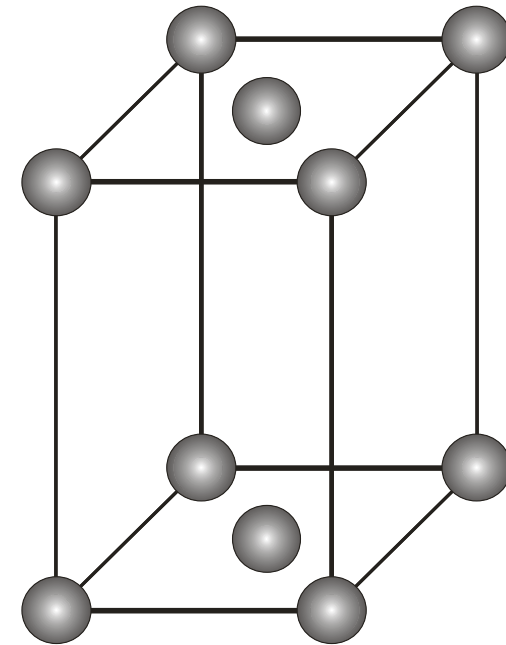
Real

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

(h + k) even
Both even or both odd $\rightarrow$ $F = 2f \longrightarrow F^2 = 4f^2$

e.g. (001), (110), (112); (021), (022), (023)

Mixture of odd and even
(h + k) odd $\rightarrow$ $F = 0 \longrightarrow F^2 = 0$

$\Rightarrow F$ *is independent of the* '*l*' *index*

e.g. (100), (101), (102); (031), (032), (033)

Structure factor calculations

C centered orthorhombic

Simple Orthorhombic lattice [001] projection
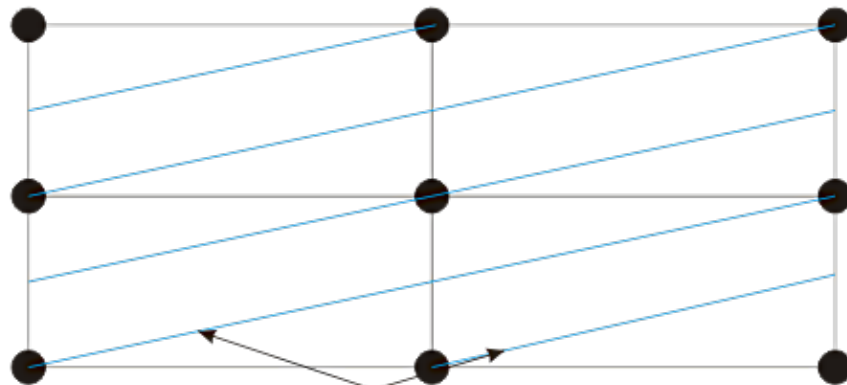
Trace of (210) planes

These (210) planes form a translationally equivalent set: pass through all lattice points

C-Centred Orthorhombic lattice [001] projection

To form a translationally equivalent set of planes (passing through all lattice points) the red set of planes have to be drawn

- If the blue planes are scattering in phase then on C- centering the red planes will scatter out of phase (with the blue planes - as they bisect their normal) and hence the (210) reflection will become extinct
- This analysis is consistent with the extinction rules: (h + k) odd is absent

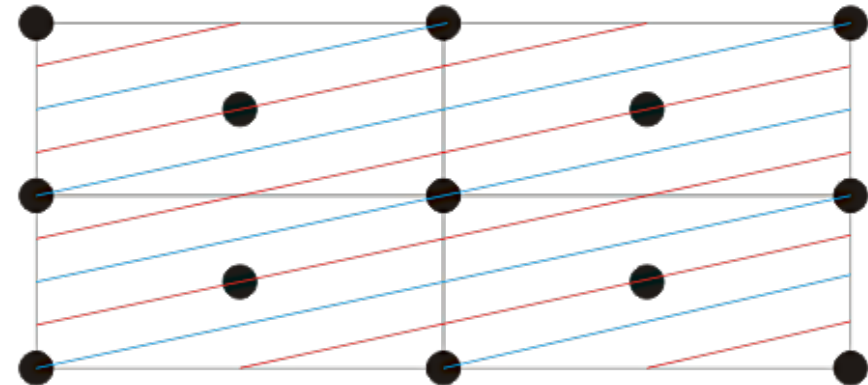# Structure factor calculations

C centered orthorhombic

Simple Orthorhombic lattice [001] projection

Trace of (310) planes

These (310) planes form a translationally equivalent set:
pass through all lattice points
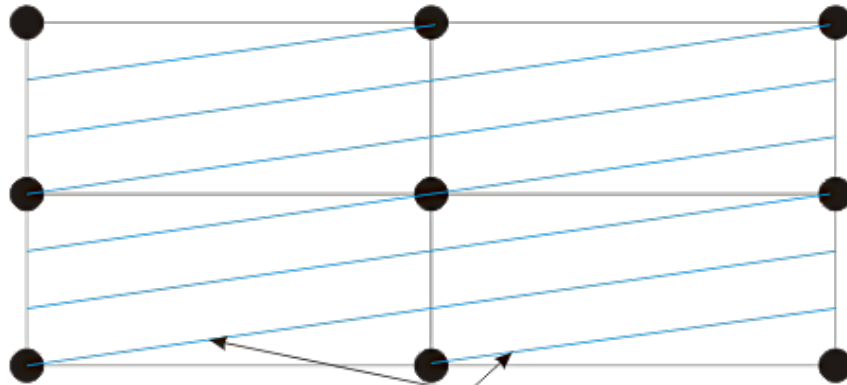
C-Centred Orthorhombic lattice [001] projection

No new planes are to be added to form a
translationally equivalent set of planes on C-centering

- In case of the (310) planes no new translationally equivalent planes are added on lattice centering ⇒ this reflection cannot go missing.
- This analysis is consistent with the extinction rules: (h + k) even is present

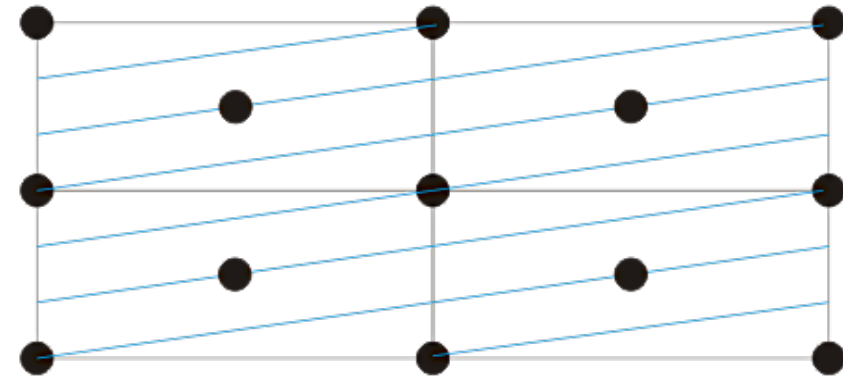# Structure factor calculations

Body centered orthorhombic

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

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

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

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

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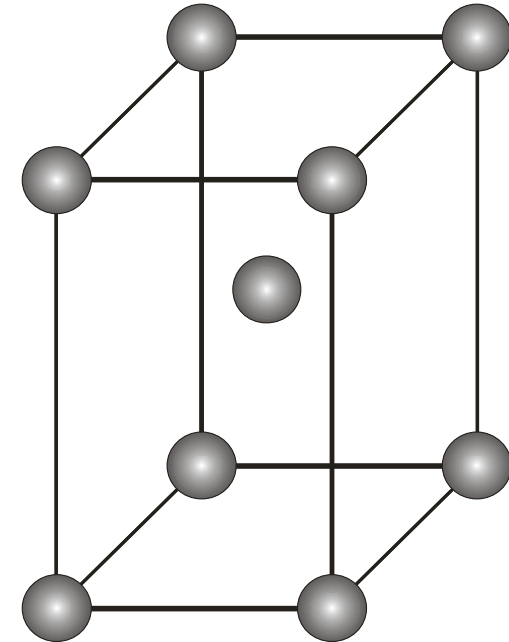
$$F = f[1 + e^{i\pi(h+k+l)}]$$

$(h + k + l)$ even → $F = 2f \longrightarrow F^2 = 4f^2$

e.g. (110), (200), (211); (220), (022), (310)

$(h + k + l)$ odd → $F = 0 \longrightarrow F^2 = 0$

e.g. (100), (001), (111); (210), (032), (133)

Structure factor calculations

Face centred cubic

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

(½, ½, 0), (½, 0, ½), (0, ½, ½)

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

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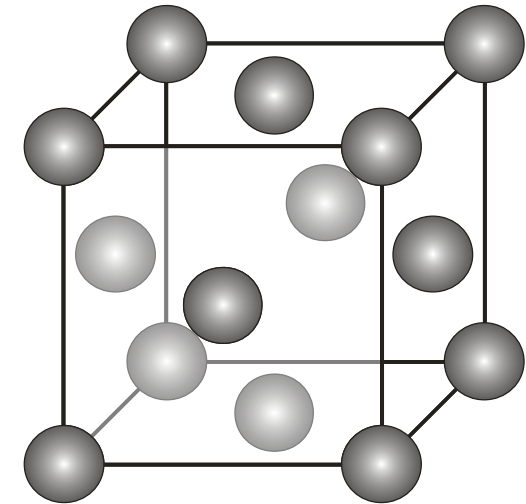
$$= f[1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}] \longrightarrow \boxed{\text{Real}}$$

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

(h, k, l) unmixed $\longrightarrow$ $F = 4f \longrightarrow F^2 = 16f^2$

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

(h, k, l) mixed $\longrightarrow$ $F = 0 \longrightarrow F^2 = 0$

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

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

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

Mixed indices	CASE	h	k	l
	A	o	o	e
	B	o	e	e

CASE A: $[1 + e^{i\pi(e)} + e^{i\pi(o)} + e^{i\pi(o)}] = [1 + 1 - 1 - 1] = 0$

CASE B: $[1 + e^{i\pi(o)} + e^{i\pi(e)} + e^{i\pi(o)}] = [1 - 1 + 1 - 1] = 0$

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

Unmixed indices *All odd (e.g. 111); all even (e.g. 222)*

Unmixed indices	CASE	h	k	l
	A	o	o	o
	B	e	e	e

CASE A: $[1 + e^{i\pi(e)} + e^{i\pi(e)} + e^{i\pi(e)}] = [1 + 1 + 1 + 1] = 4$

CASE B: $[1 + e^{i\pi(e)} + e^{i\pi(e)} + e^{i\pi(e)}] = [1 + 1 + 1 + 1] = 4$

(h, k, l) unmixed $\Longrightarrow$ $F = 4f \longrightarrow F^2 = 16f^2$

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

Structure factor calculations

NaCl
Face Centered Cubic

Na$^+$ at (0,0,0) + Face Centering Translations → (½, ½, 0), (½, 0, ½), (0, ½, ½)
Cl$^-$ at (½, 0, 0) + FCT → (0, ½, 0), (0, 0, ½), (½, ½, ½)

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

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

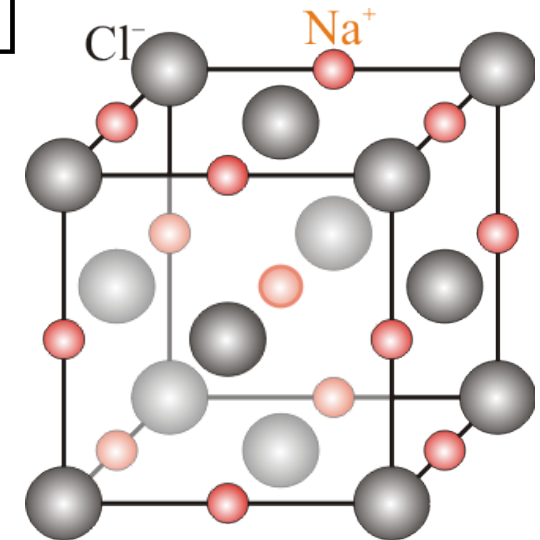$$F = f_{Na^+} [1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}] +$$

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

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

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

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

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

$$F = factor1 \cdot factor2$$

Zero for mixed indices

Mixed indices

Mixed indices	CASE	h	k	l
	A	o	o	e
	B	o	e	e

CASE A : $factor2 = [1 + e^{i\pi(e)} + e^{i\pi(o)} + e^{i\pi(o)}] = [1 + 1 - 1 - 1] = 0$

CASE B : $factor2 = [1 + e^{i\pi(o)} + e^{i\pi(e)} + e^{i\pi(o)}] = [1 - 1 + 1 - 1] = 0$
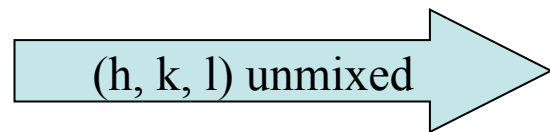
(h, k, l) mixed $\longrightarrow$ $F = 0 \longrightarrow F^2 = 0$ $\quad$ *e.g. (100), (211); (210), (032), (033)*

Unmixed indices

Unmixed indices	CASE	h	k	l
	A	o	o	o
	B	e	e	e

CASE A : $factor\,2 = [1 + e^{i\pi(e)} + e^{i\pi(e)} + e^{i\pi(e)}] = [1+1+1+1] = 4$

CASE B : $factor\,2 = [1 + e^{i\pi(e)} + e^{i\pi(e)} + e^{i\pi(e)}] = [1+1+1+1] = 4$

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

e.g. (111), (222); (133), (244)

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

e.g. (222),(244)

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

e.g. (111), (133)

Extinctions due to centering and/or different atomic form factors

Crystal Type	Bravais Lattice	Reflections Present	Reflections Absent
Simple	Primitive, P	Any h,k,l	None
Body-centered	Body centered, I	$h+k+l$ = even	$h+k+l$ = odd
Face-centered	Face-centered, F	h,k,l unmixed	h,k,l mixed
NaCl	FCC	h,k,l unmixed	h,k,l mixed
Zincblende	FCC	Same as FCC, but if all even and $h+k+l\neq 4N$ then absent	h,k,l mixed and if all even and $h+k+l\neq 4N$ then absent
Base-centered	Base-centered	h,k both even or both odd	h,k mixed
Hexagonal close-packed	Hexagonal	$h+2k=3N$ with l even $h+2k=3N\pm 1$ with l odd $h+2k=3N\pm 1$ with l even	$h+2k=3N$ with l odd

Scattering by a unit cell
Generic case? Consult the Tables of Crystallography

No. 14 $P2_1/c$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3)

Positions

Multiplicity, Wyckoff letter, Site symmetry		Coordinates				Reflection conditions
4	e	1	(1) x,y,z	(2) $\bar{x}, y+\frac{1}{2}, \bar{z}+\frac{1}{2}$	(3) $\bar{x}, \bar{y}, \bar{z}$	(4) $x, \bar{y}+\frac{1}{2}, z+\frac{1}{2}$

General:

$h0l : l = 2n$
$0k0 : k = 2n$
$00l : l = 2n$

Special: as above, plus

2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	$hkl : k+l = 2n$
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$	$hkl : k+l = 2n$
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$hkl : k+l = 2n$
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$	$hkl : k+l = 2n$

Symmetry of special projections

Along [001] $p2gm$
$a' = a_p$ $b' = b$
Origin at $0,0,z$

Along [100] $p2gg$
$a' = b$ $b' = c_p$
Origin at $x,0,0$

Along [010] $p2$
$a' = \frac{1}{2}c$ $b' = a$
Origin at $0,y,0$

Reciprocal space and intensities

The scattered intensity distribution in reciprocal space is sometimes represented by weighting the points of a reciprocal lattice drawing:
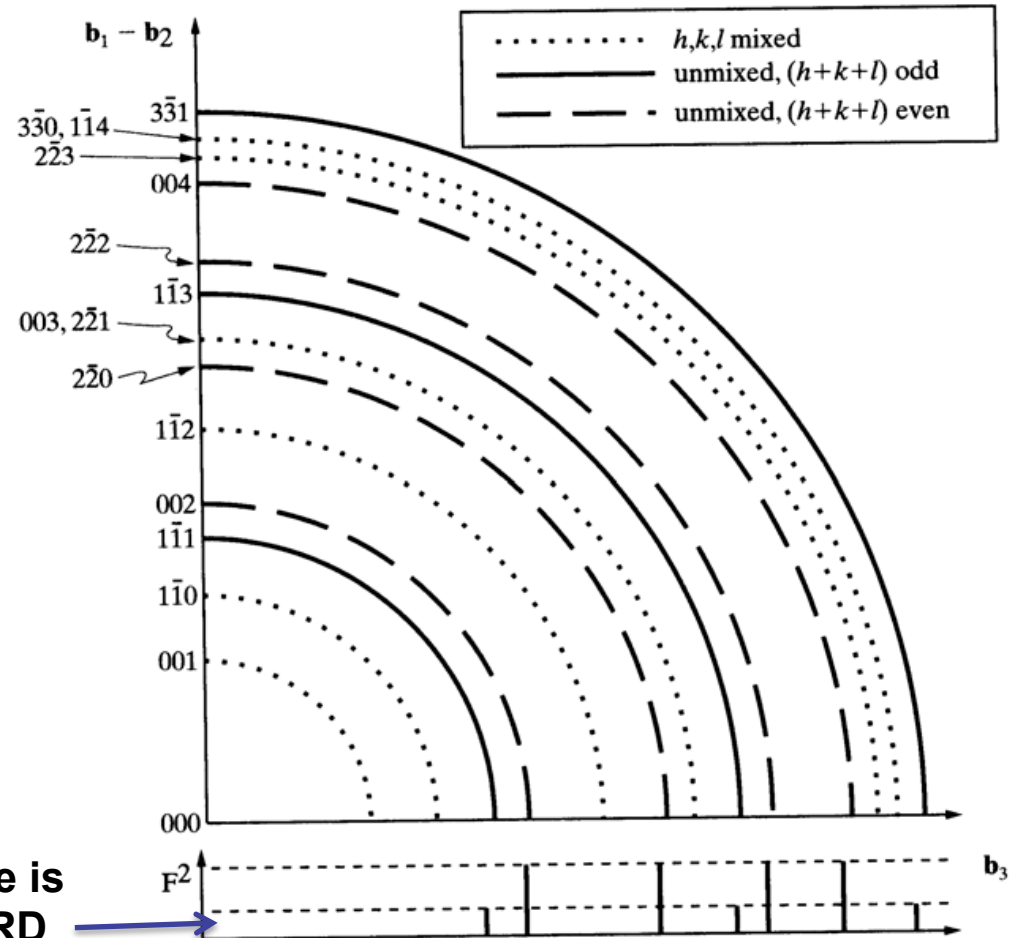
- Larger points indicate higher intensity
- Crosses indicate absences or extinctions

Section of weighted reciprocal space for NaCl
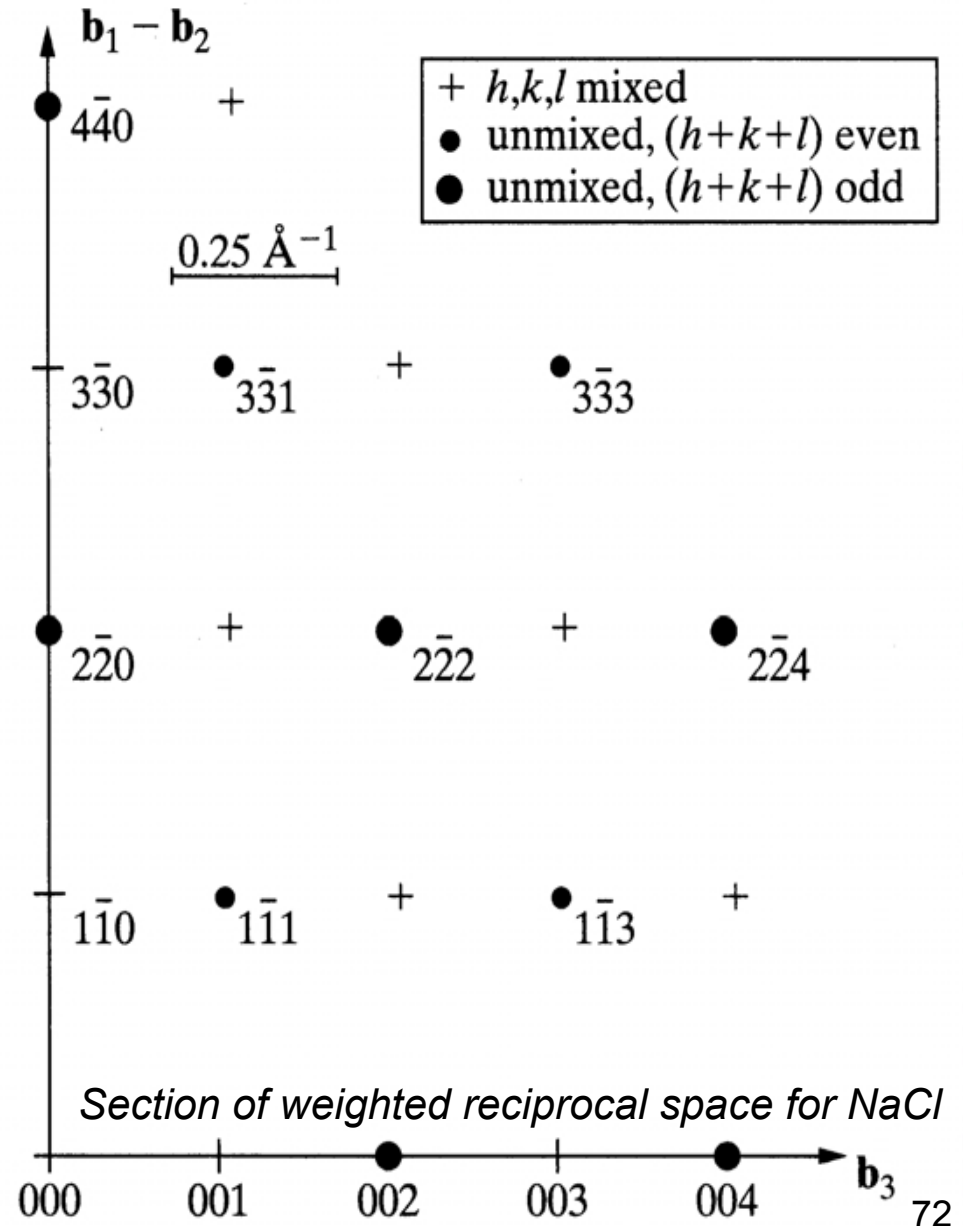
Reciprocal space of a powder with intensities

- Rel shells for powders

- Representation of the scattered intensity for a powder in reciprocal space

A radial profile is similar to a XRD diffraction pattern

Section of weighted reciprocal space for a NaCl powder showing the reciprocal lattice shells (rel shells)