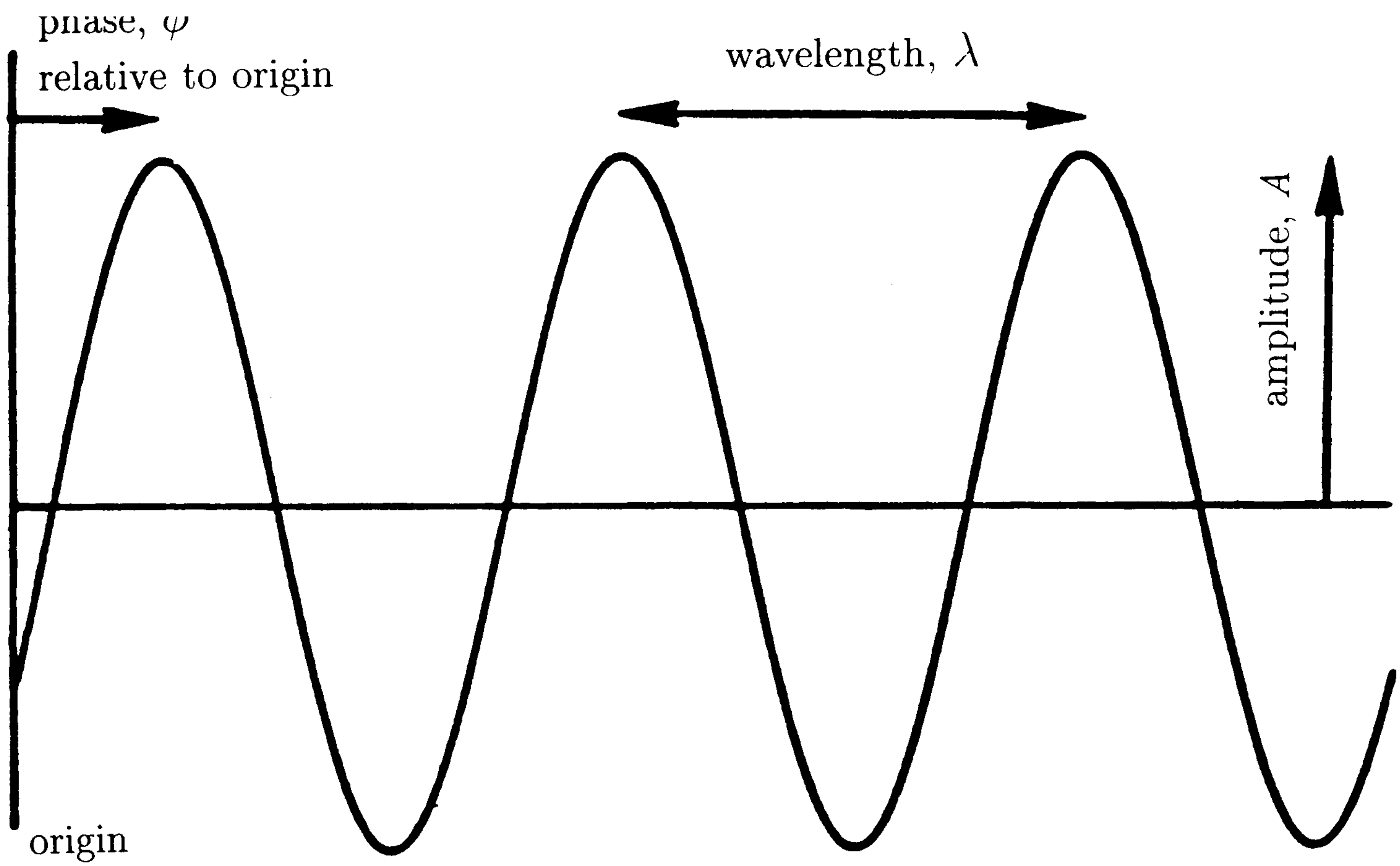
Diffraction I - Geometry

Chapter 3

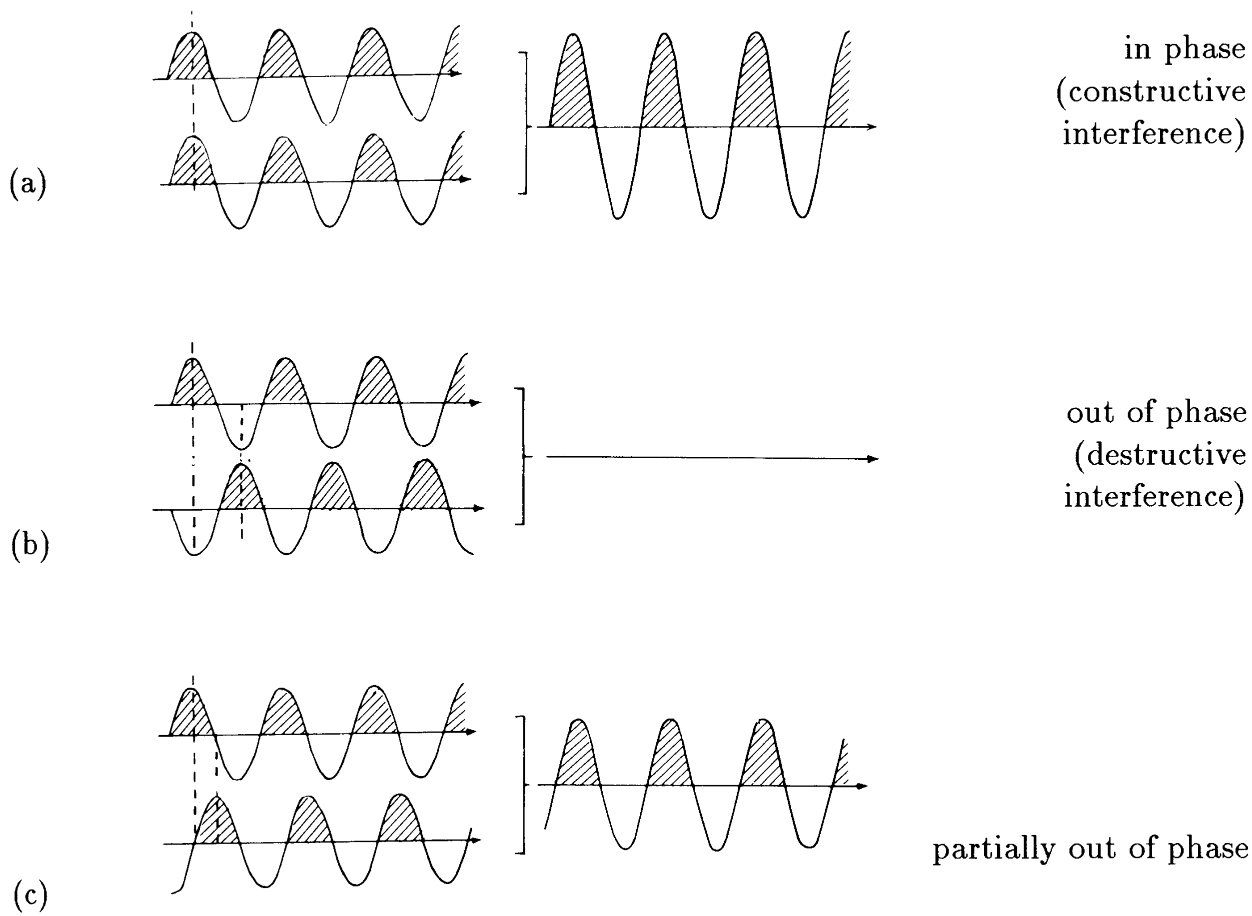
Outline

- Diffraction basics
- Braggs law
- Laue equations
- Reciprocal space and diffraction
- Units for x-ray wavelengths
- Diffraction methods
  - Laue photographs
  - Rotation photographs
  - Powder diffraction using Debye Scherrer cameras and diffractometers
- Visualization of the reciprocal lattice in a TEM

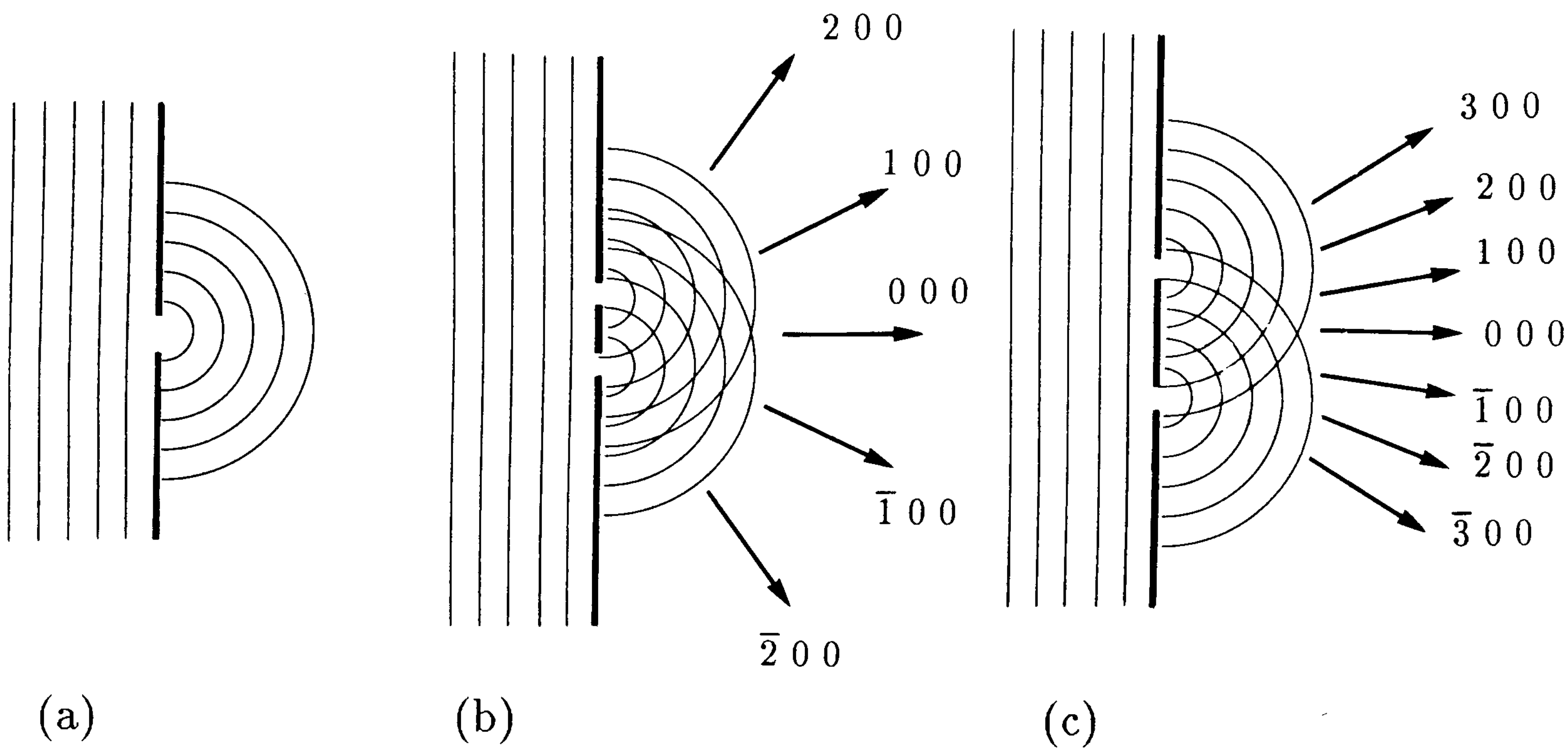
Wave characteristics



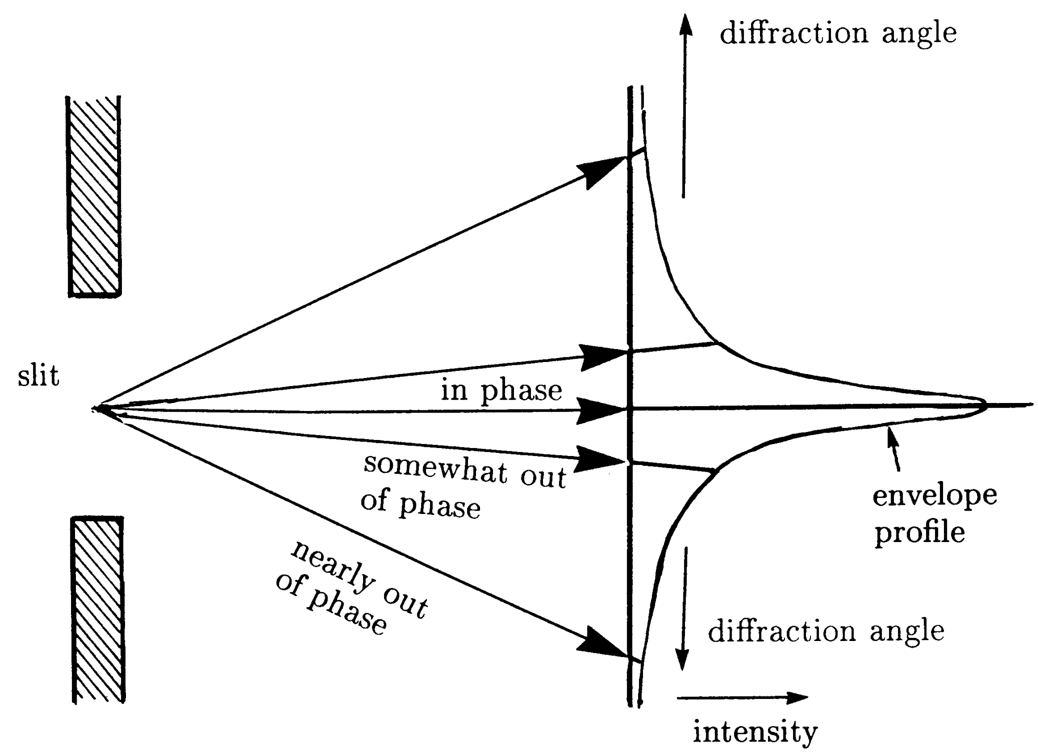
Interference between waves



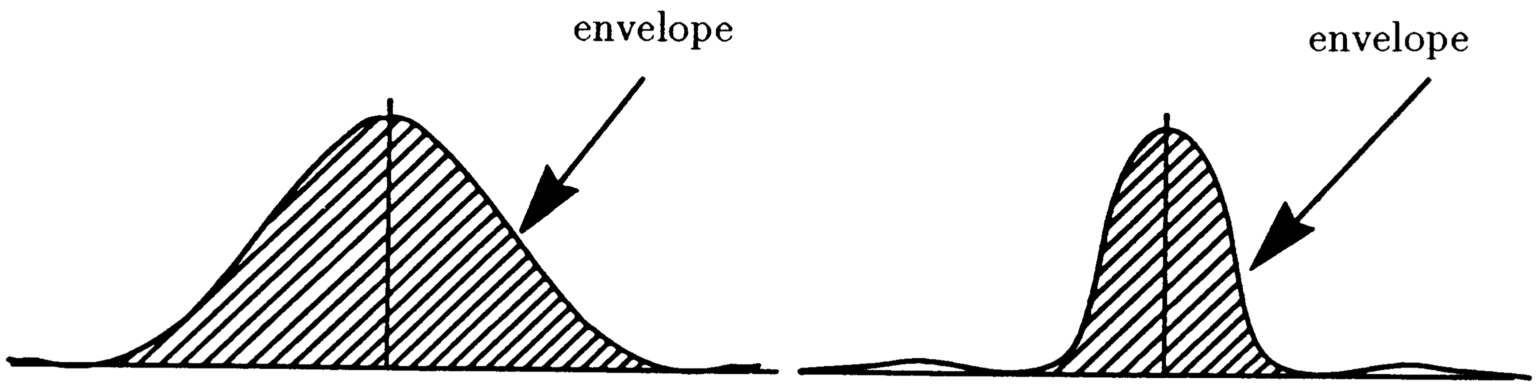
Double slit experiment



Diffraction at a single slit

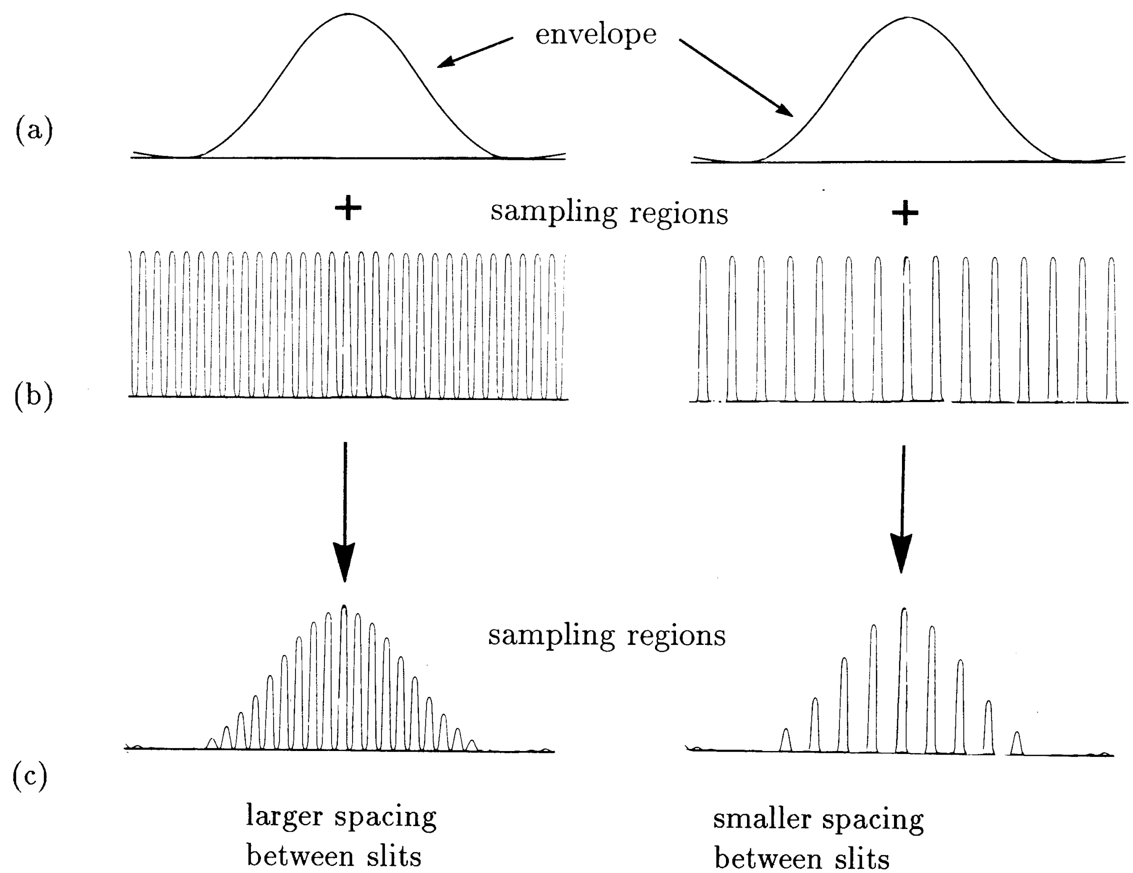


The envelope function



(a) narrow slit (b) wide slit

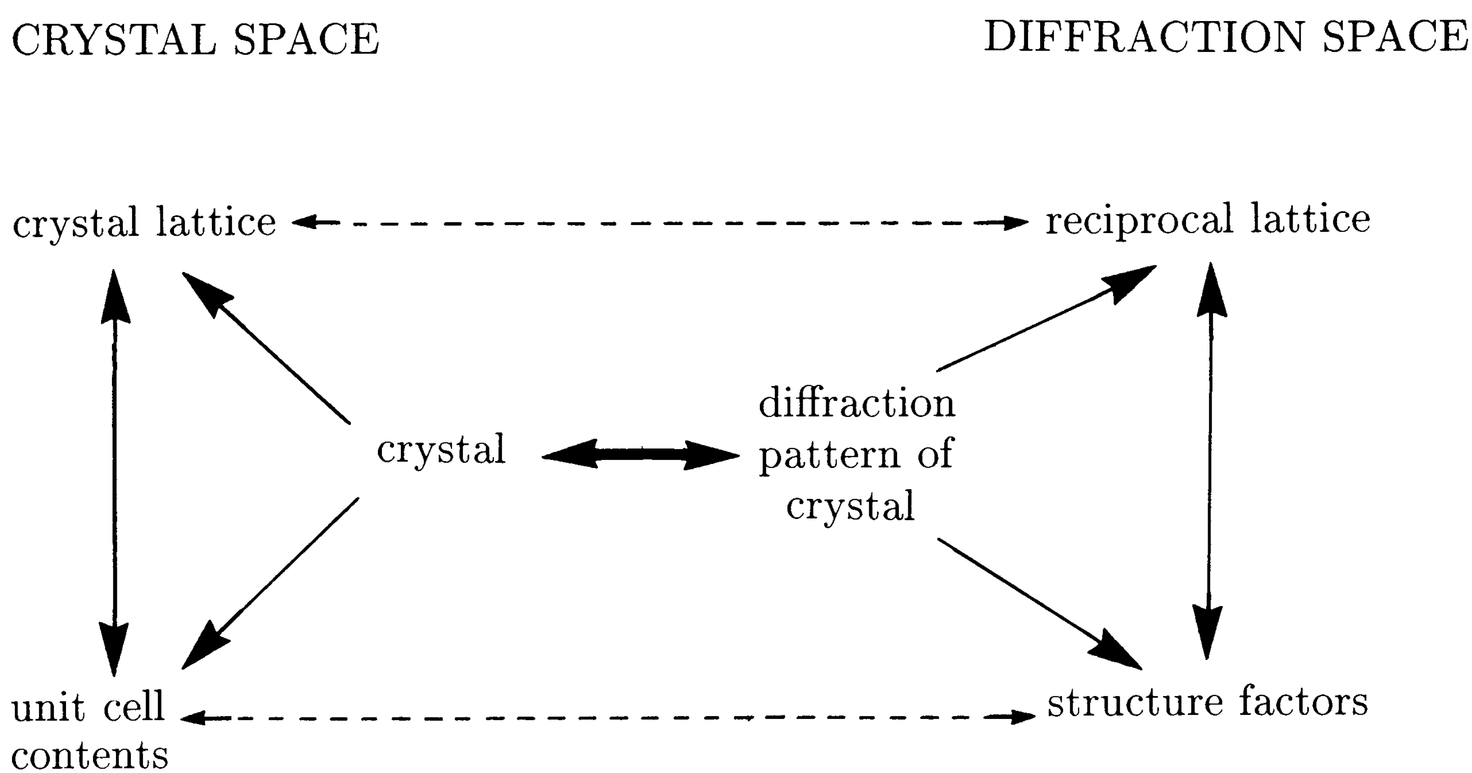
Diffraction and sampling



Diffraction from crystals

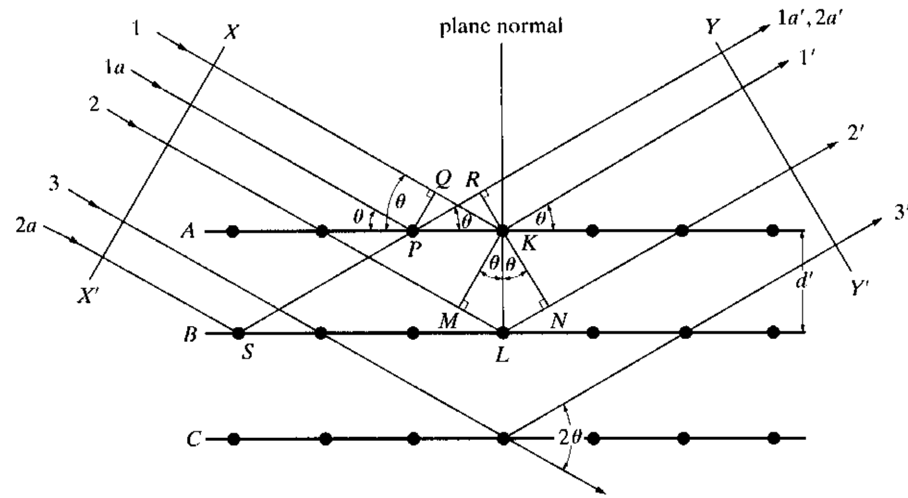
- A crystal is a three dimensional diffraction grating
- The lattice periodicity of the crystal determines the sampling regions of the diffraction pattern
  - Where the peaks appear
- The unit cell contents give you the envelope function
  - The intensity of the peaks

Real space and reciprocal space



Diffraction from ordered atoms

- Consider a 3D array of atoms arranged on planes
- Get constructive interference between x-rays scattered from atoms P and K in same plane when there is no path difference for the scattered rays



  - Need to have symmetrical diffraction so that QK-PR = PKCosθ –PKCosθ = 0
- Get constructive interference between x-rays scattered from atoms in different planes when the path length is a multiple of λ. Consider atoms K and L.
  - ML + LN = d'sinθ + d'sinθ = 2d'sinθ = nλ
- 2dsinθ = nλ is Bragg's law

Bragg "reflection"

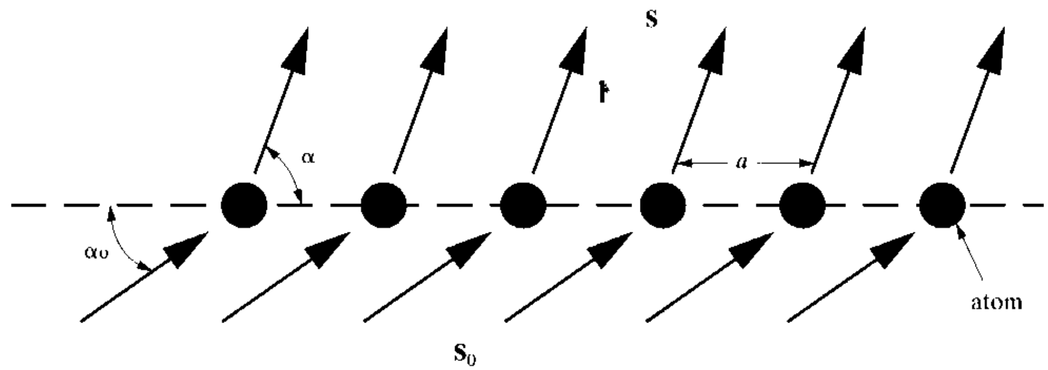
- Bragg equation is
  - $2d\sin\theta = n\lambda$
    - » n is the order of diffraction
    - » Typically we treat all higher orders of diffraction as coming from planes with spacing d/n
      - So second order diffraction from (100) can be though of as first order from (200) planes
- We often refer to peaks in a diffraction pattern as reflections. However, the process is not one of reflection it is one of diffraction
  - There are strict conditions on the angles at which diffraction can occur and the bulk of the crystal is responsible for scattering not just the surface
  - True reflection of x-rays only occurs at very low angles

Laue equations

- The Bragg equation does not explicitly tell us about the directions in which diffraction occurs
  - We have to remember that the line bisecting the incoming and outgoing beams is always perpendicular to the planes responsible for diffraction
- Laue equations make the directionality of the process more obvious as we have a set of three equations, one for each crystallographic axis that must be simultaneously satisfied

Derivation of Laue equations

- Consider a row of atoms scattering x-rays
  - S_0 is a vector describing the incoming x-ray beam and S describes the scattered beam

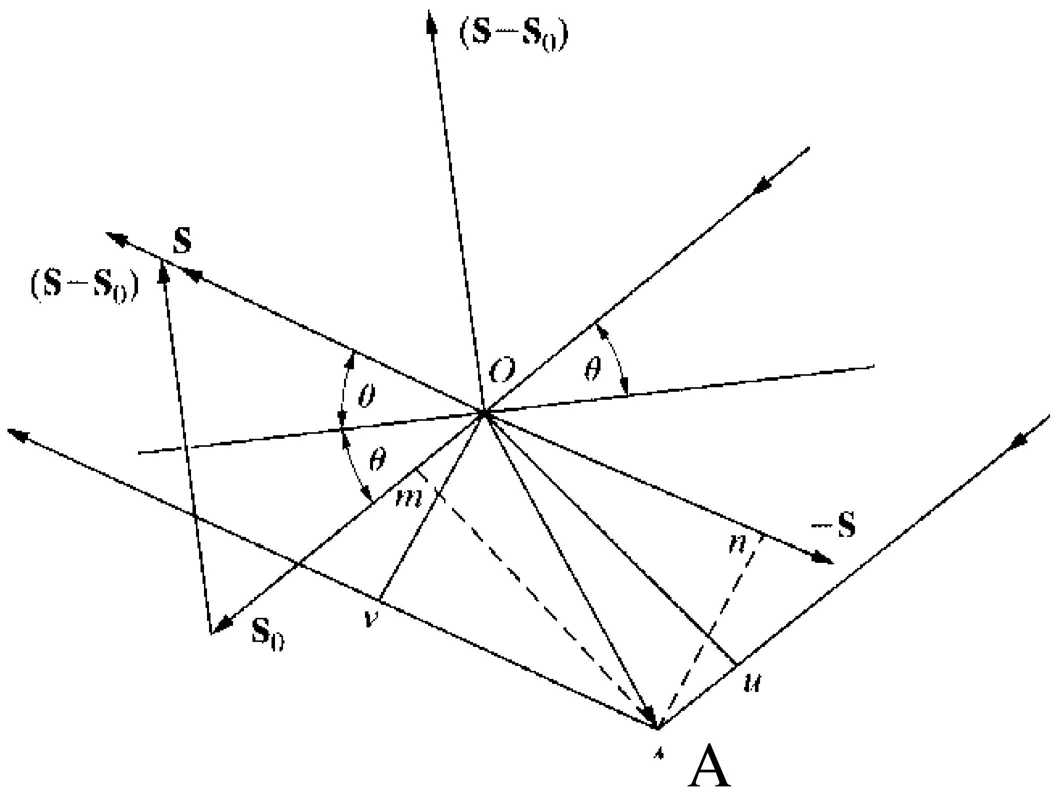


- To get constructive interference between the x-rays scattered from each atom
  - $a(\cos\alpha - \cos\alpha_0) = h\lambda$ where h is an integer
- If we have a 2D periodic array of atoms we also have to satisfy
  - $b(\cos\beta - \cos\beta_0) = k\lambda$ where k is an integer
- If we have a 3D periodic array of atoms we also have to satisfy
  - $c(\cos\gamma - \cos\gamma_0) = l\lambda$ where l is an integer

Reciprocal space and diffraction

- In thinking about diffraction we often resort to constructions, such as the Ewald sphere, in reciprocal space
  - Why is reciprocal space important?
- To see diffraction, the diffraction vector must lie on a reciprocal lattice point

Reciprocal space and diffraction 2



- Consider x-rays scattered from two lattice points O and A
  - $\mathbf{S_0}$ is a unit vector parallel to the incoming beam and $\mathbf{S}$ is a unit vector parallel to the scattered beam,

Reciprocal space and diffraction 3

Path difference between x-rays scattered from O and A is

$\delta = uA + Av = Om + On = \mathbf{S_0}.\mathbf{OA} + (\mathbf{-S}).\mathbf{OA}$

$= - \mathbf{OA}.(\mathbf{S}\text{-}\mathbf{S_0})$

So the phase difference is

$\phi = 2\pi\delta/\lambda = 2\pi(\mathbf{S}\text{-}\mathbf{S_0}).\mathbf{OA})/\lambda = -2\pi.\mathbf{H}.\mathbf{OA}$

where $\mathbf{H} = (\mathbf{S}\text{-}\mathbf{S_0})/\lambda = h'\mathbf{b_1} + k'\,\mathbf{b_2} + l'\mathbf{b_3}$ is the scattering vector and has been defined in reciprocal space

OA is real space lattice vector $p\mathbf{a_1} + q\mathbf{a_2} + r\mathbf{a_3}$, where p,q and r are integers

So $\phi = 2\pi\ (h'\mathbf{b_1} + k'\,\mathbf{b_2} + l'\mathbf{b_3}).\ (p\mathbf{a_1} + q\mathbf{a_2} + r\mathbf{a_3})$

$= 2\pi\ (ph'+qk'+rl')$

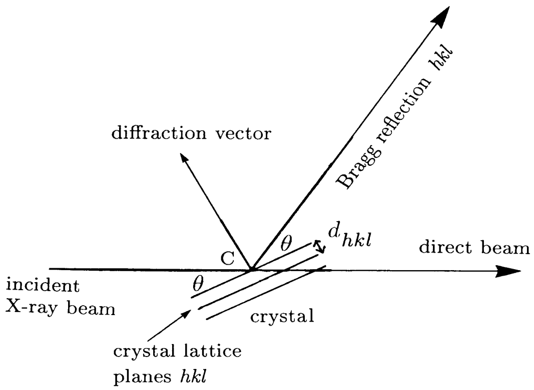
For constructive interference ϕ must be a multiple of 2π this can only occur when h', k' and l' are all integers'

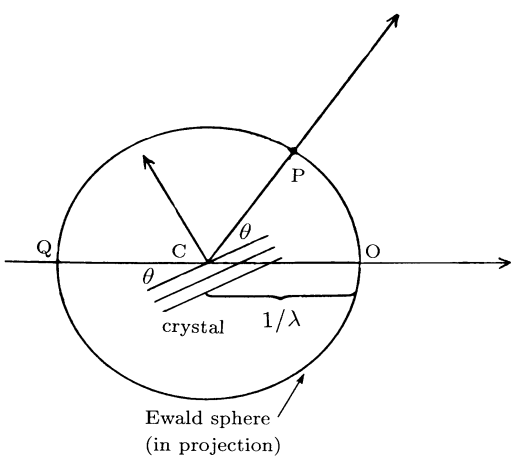
You only get diffraction when the diffraction vector coincides with a reciprocal lattice point

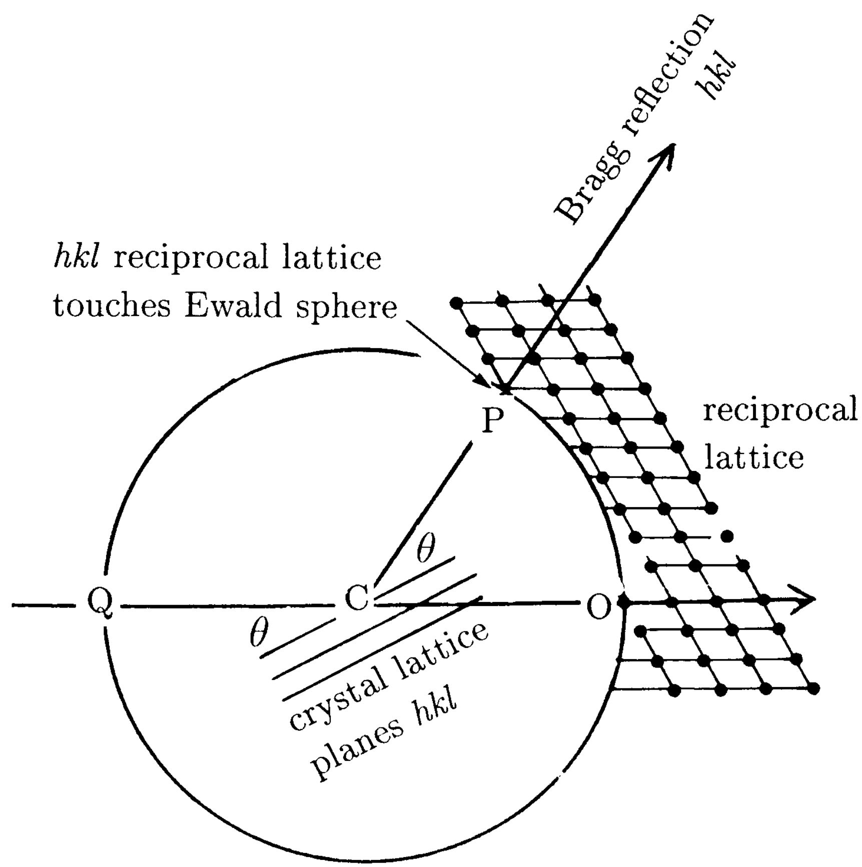
Ewald construction

- We can express the requirement that the scattering vector lies on a reciprocal lattice point geometrically. This is done in the Ewald construction
  - Draw the reciprocal lattice. Draw a sphere of radius $1/\lambda$ with one point on the sphere touching the origin of reciprocal space (this is the Ewald sphere).
  - The line joining the sphere center to the origin of reciprocal space is parallel to the incoming x-ray beam
  - Any <u>**re**</u>ciprocal <u>**l**</u>attice <u>**p**</u>oint (<u>**relp**</u>) touching the surface of the sphere is in the diffraction condition and the diffracted beam will travel in the direction of the line joining the sphere center to a relp on the surface of the sphere
  - We can rotate the crystal and hence the reciprocal lattice to bring other relps into the diffraction condition

Ewald construction



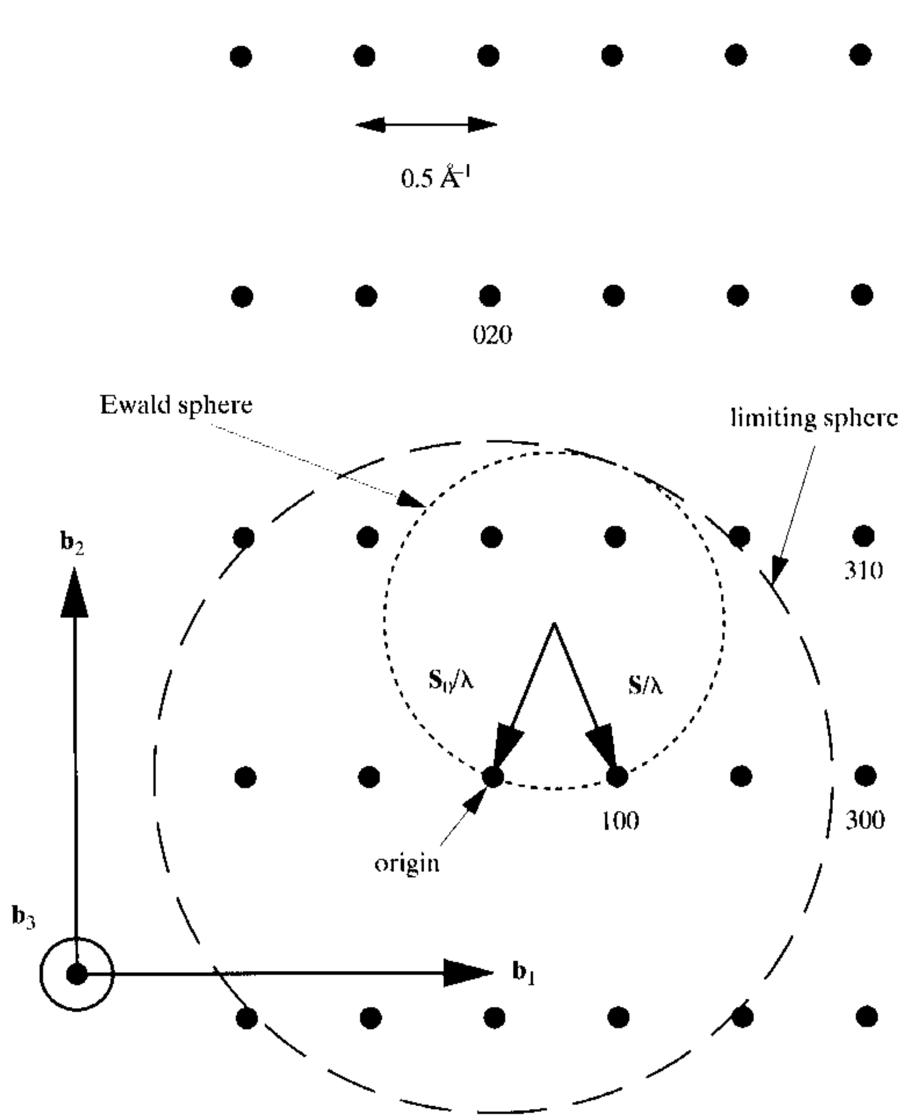




Using the Ewald construction

- The Ewald construction allows you to see what direction a diffracted beam will travel in.
  - Note that a crystal in a random orientation in the X-ray beam will not necessarily give any diffraction as no relp may lie on the Ewald sphere
  - Rotation of the crystal or the use of polychromatic radiation will lead to the observation of several spots
- We can predict which diffracted beams are observable with a given wavelength by rotating the sphere around the origin or reciprocal space. This rotation marks out a larger so called limiting sphere
  - Only those relps that lie within the surface of the limiting sphere can ever be observed

Limiting sphere



Calculating diffraction angles

- The angle between the incident x-ray direction and the diffracted beam is referred to as the Bragg angle 2θ
- It can be calculated by combining Braggs law with the equation relating d-spacing (interplanar spacing) and lattice constants/Miller indices
- $2d\sin\theta = \lambda$
- For a crystal with orthogonal axes

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Units for x-ray wavelengths

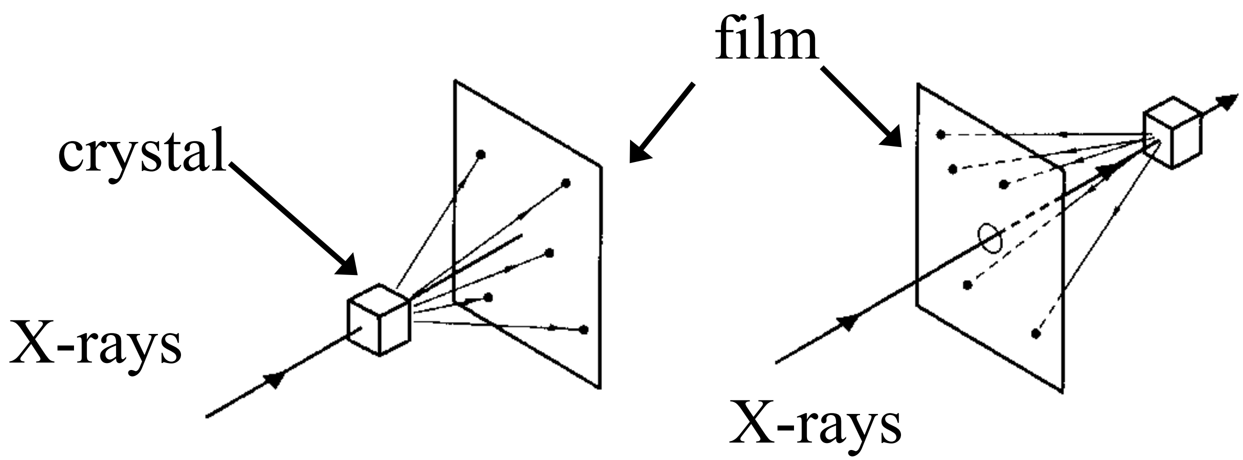
- The wavelengths of x-ray emission lines are usually determined by measuring Bragg angles
  - To do this you have to know the lattice spacing for the crystal you are using
    - » In early studies this was determined using density measurements that were of limited accuracy
  - a precise value for the lattice spacing was assumed and used as the basis for a new length unit, the XU
    - » XU ~ 0.001Å
  - Later work has enabled more accurate determinations of lattice spacings. This has led to the conversion of old wavelength values in XU or kX (1000XU) to "corrected" values in Å
    - » Be careful regarding the units for any wavelength values that you use as they may be in XU or they may have been corrected more or less accurately to give values in Angstroms.

Diffraction methods

- 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 all different orientations (a powder)
      - Powder diffraction

The Laue method

- As used in Laue's original experiment
  - Use the "white" Bremsstrahlung radiation from the tube so that many different wavelengths are incident on the sample
    - » Many reflections will simultaneously satisfy Bragg's law without rotating the crystal



Record a spot "pattern" on the film

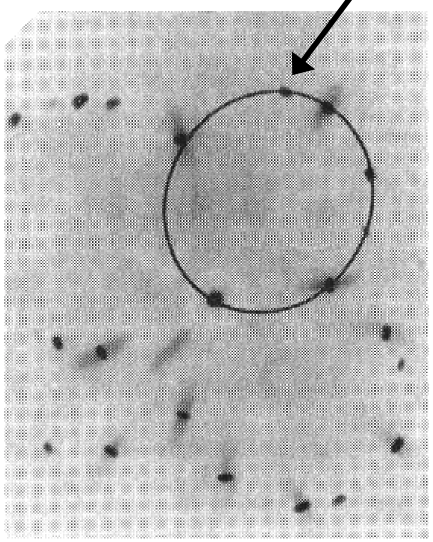
Transmission Laue

Back reflection Laue

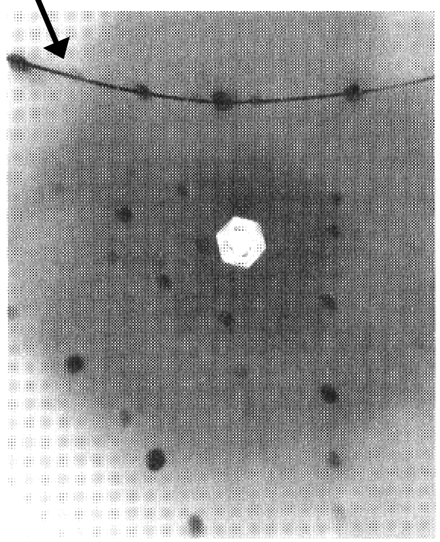
Appearance of Laue photos

- Spots appear on ellipses or hyperbola. The spots lying on these lines belong to a common zone

All reflections on common zone

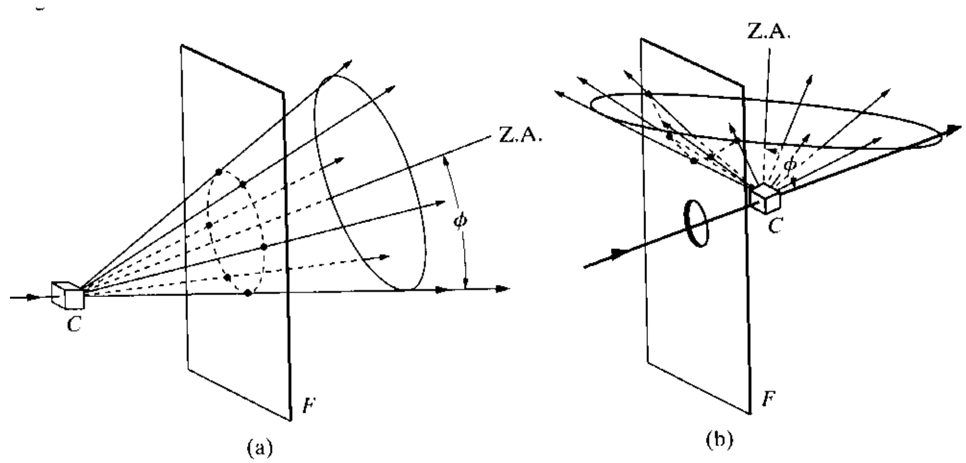


Transmission



Back reflection

Transmission Reflection

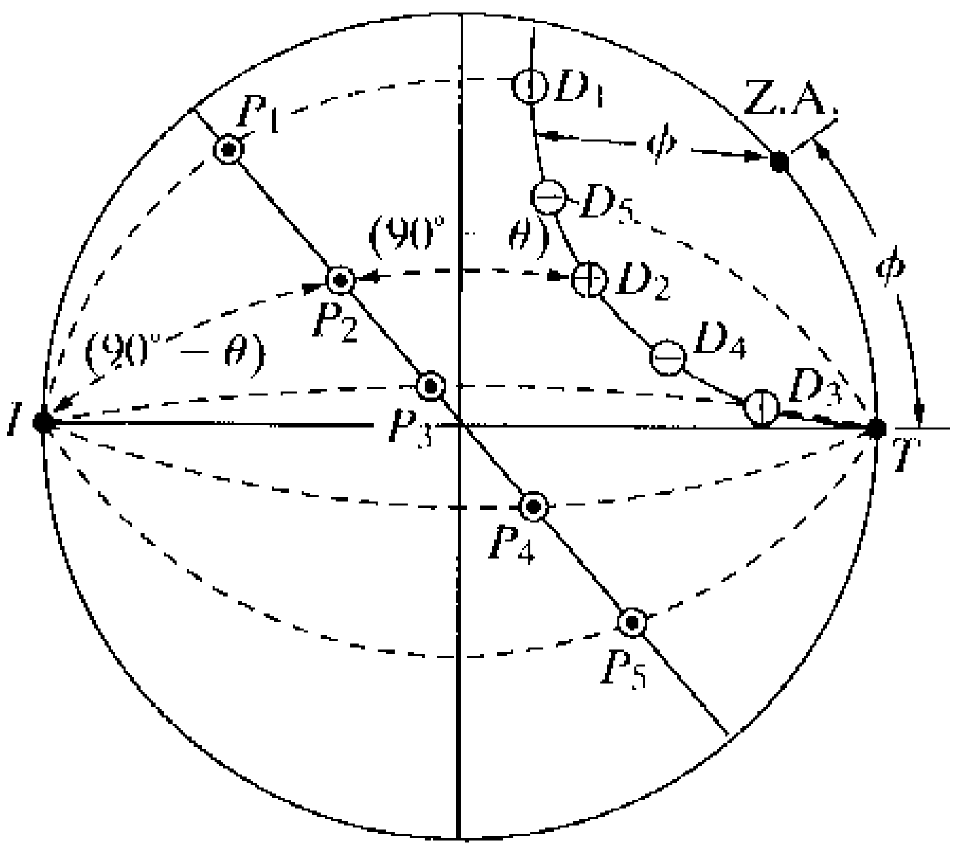


Diffracted beams for reflections in a zone fall on a cone centered around the zone axis

Proving reflections fall on a cone

- Can represent Laue diffraction using a stereographic projection
  - Arrange projection so that zone axis falls on the basic circle
    - » By definition all poles in the zone are at 90 degrees to this axis
  - The pole (normal to diffraction planes), the diffracted beam and incident and transmitted beams must be coplanar
    - » So diffracted beam lies on the same great circle as the pole and the points where the incident and transmitted beams cut the basic circle. Also the diffracted beam must make the same angle to the pole as the pole does to the incident beam.
      - This uniquely locates the diffracted beam direction on the pole figure.
  - We can do this for all the poles in zone
    - » Find that all diffracted beams lie on a small circle defined by the intersection of the sphere of projection and a cone with semi-apex angle ϕ

Stereographic projection examining Laue diffraction

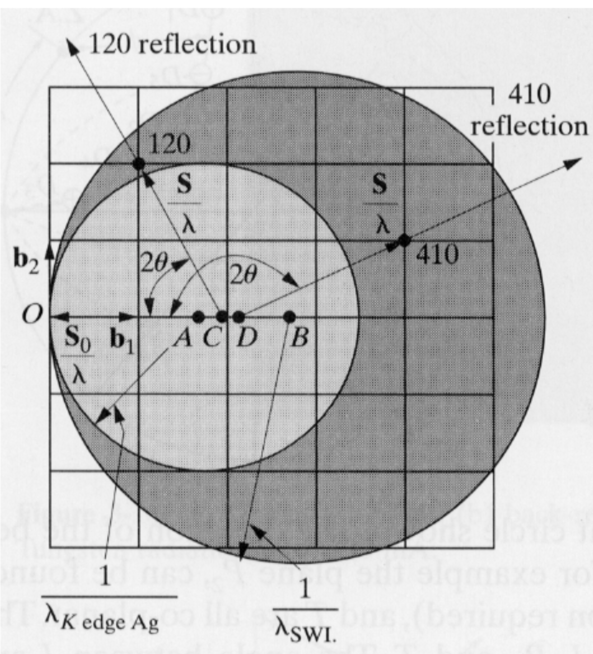


All diffracted beams belonging to a zone lie on the surface of a cone

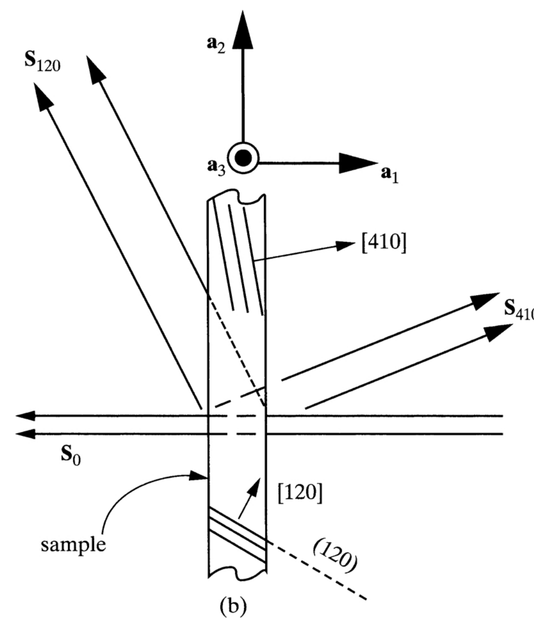
Z.A. – zone axis
P_n – pole belonging to zone
D_n – diffracted beam corresponding to the pole n
I – incident beam direction
T – transmitted beam direction

Ewald construction for Laue method

- In practice, no x-ray beam is truly “white”, it is only useable over a finite wavelength range
  - Can represent this range by drawing Ewald spheres corresponding to the wavelength limits

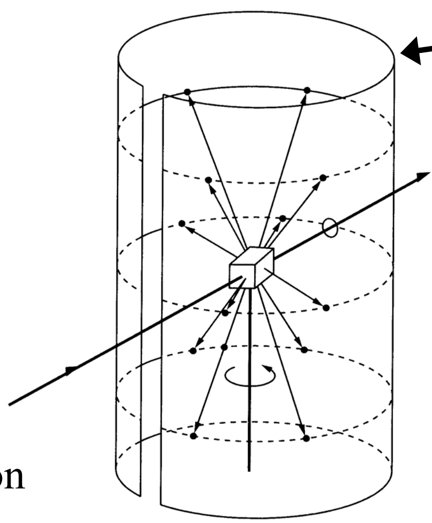


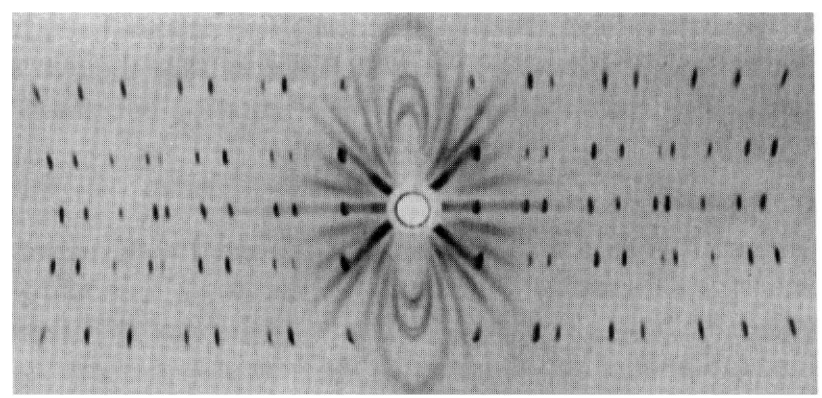
All relps lying in the dark shaded area will give diffracted beams



Rotation photography

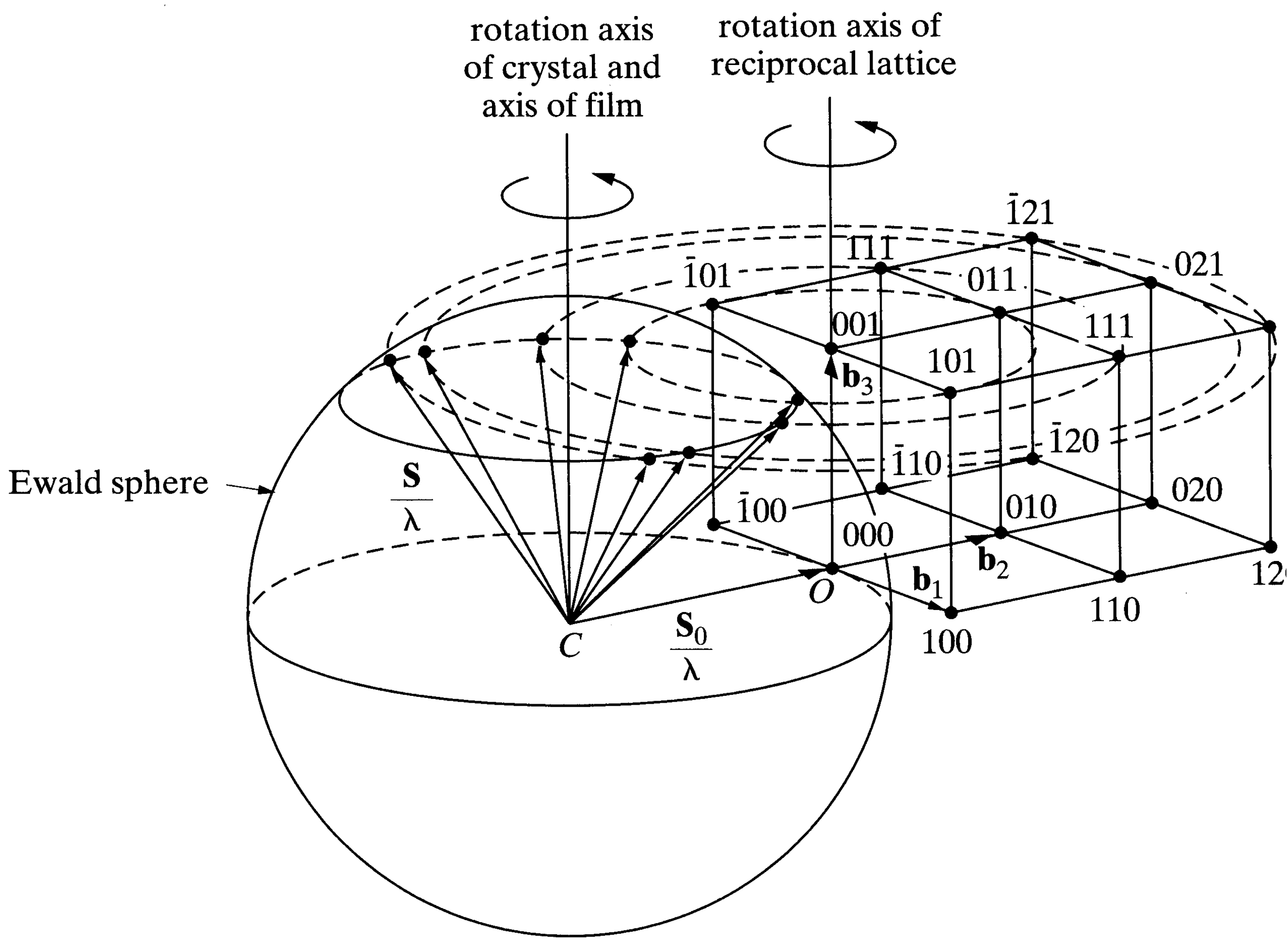
- Aligned crystal is rotated around one axis so relps pass through the Ewald sphere
  - Produces spots lying on layer lines





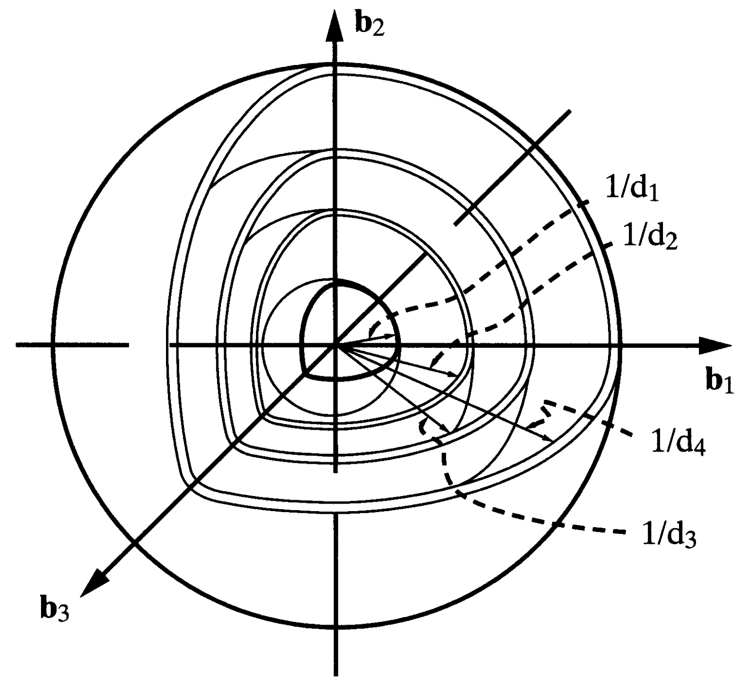
Rotation photograph of quart showing spots on layer lines

Reciprocal space representation of a rotation photograph



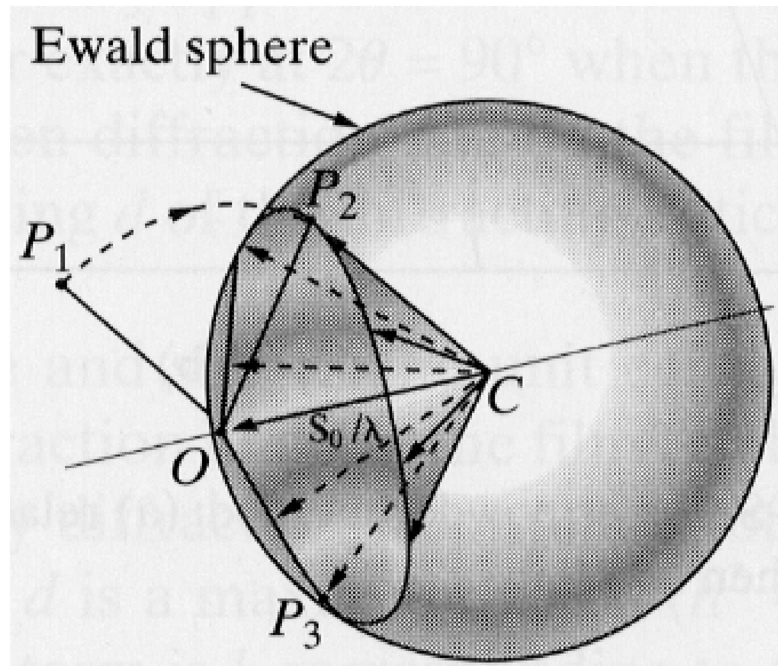
Powder diffraction

- In a powder we have a large number of crystals all at different orientations
- In reciprocal space we no longer have one set of points, but many sets of points at different orientations. All of these points lie on the surface of spheres or shells.
  - Reciprocal lattice shells – rel shells



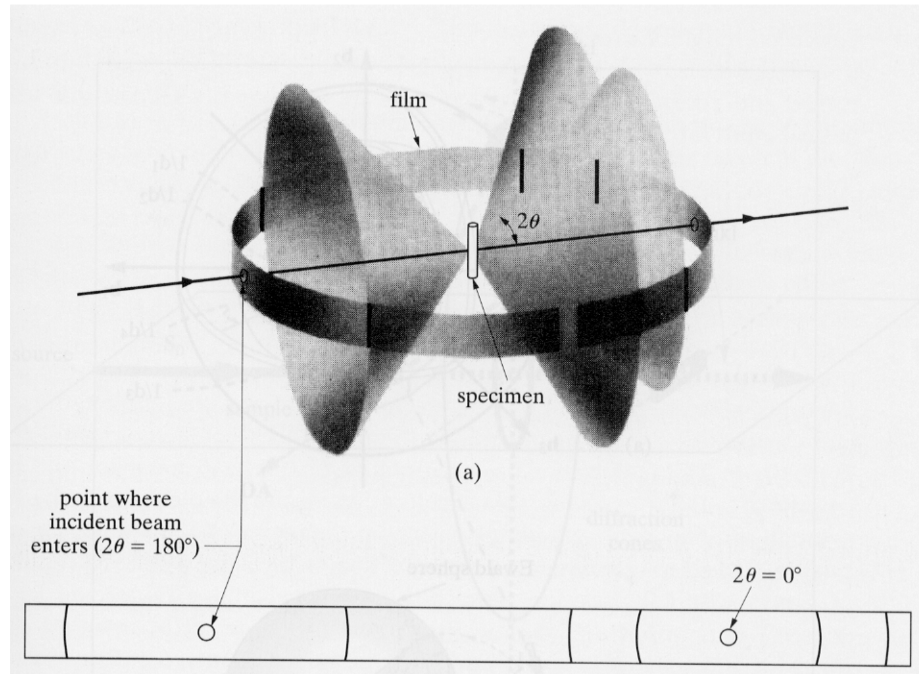
Reciprocal space representation of powder diffraction

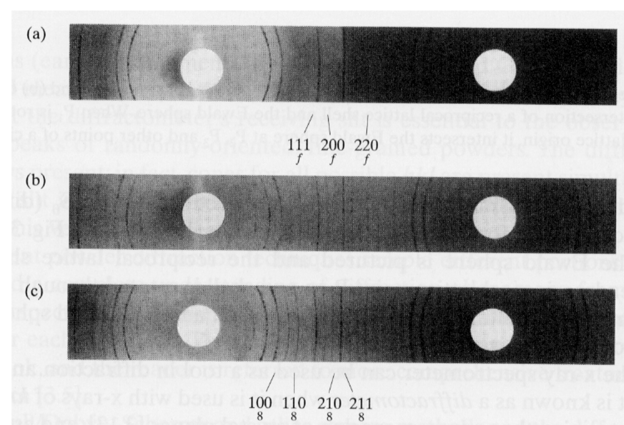
- Reciprocal lattice shells of the powder intersect with the Ewald sphere to form circles
- All the diffracted beams from a powder sample lie on the surface of cones



Debye-Scherrer camera

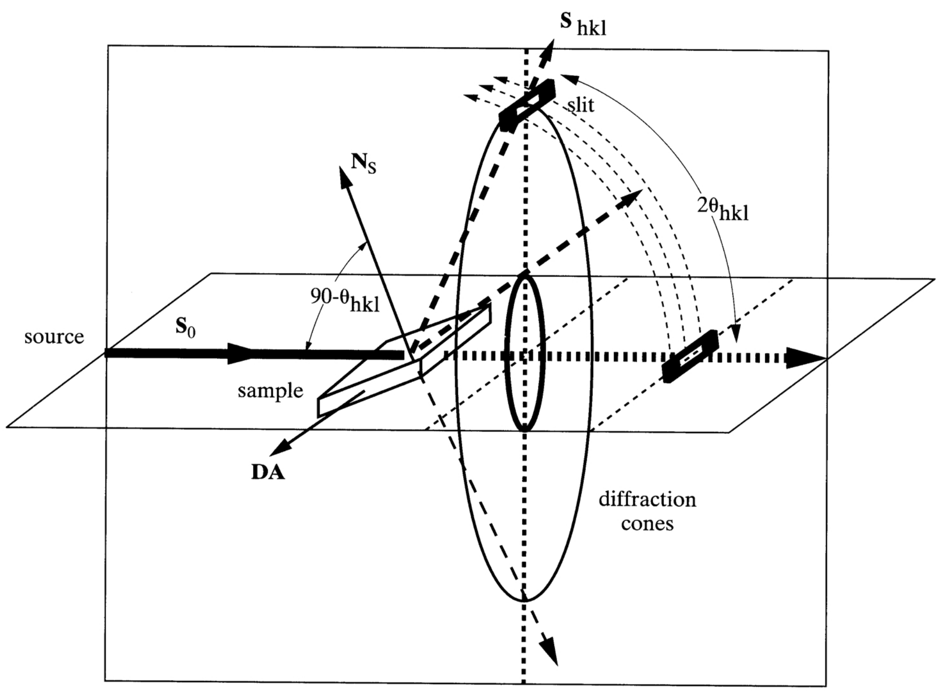
- Can record sections on these cones on film or some other x-ray detector
  - Simplest way of doing this is to surround a capillary sample with a strip of film
  - Can covert line positions on film to angles and intensities by electronically scanning film or measuring positions using a ruler and guessing the relative intensities using a "by eye" comparison



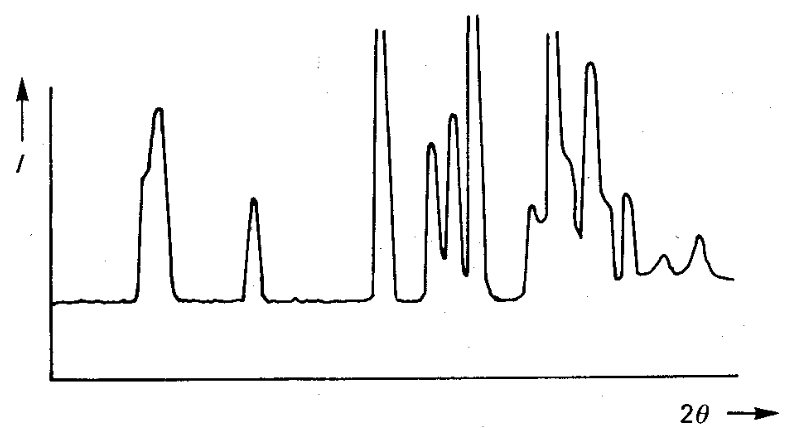


Powder diffractometer

- Alternatively, you can intercept sections of the cones using an electronic detector



Slit is moved to different 2θs. The x-rays passing through the slit are recorder electronically giving a powder pattern



Bragg-Brentano diffractometer

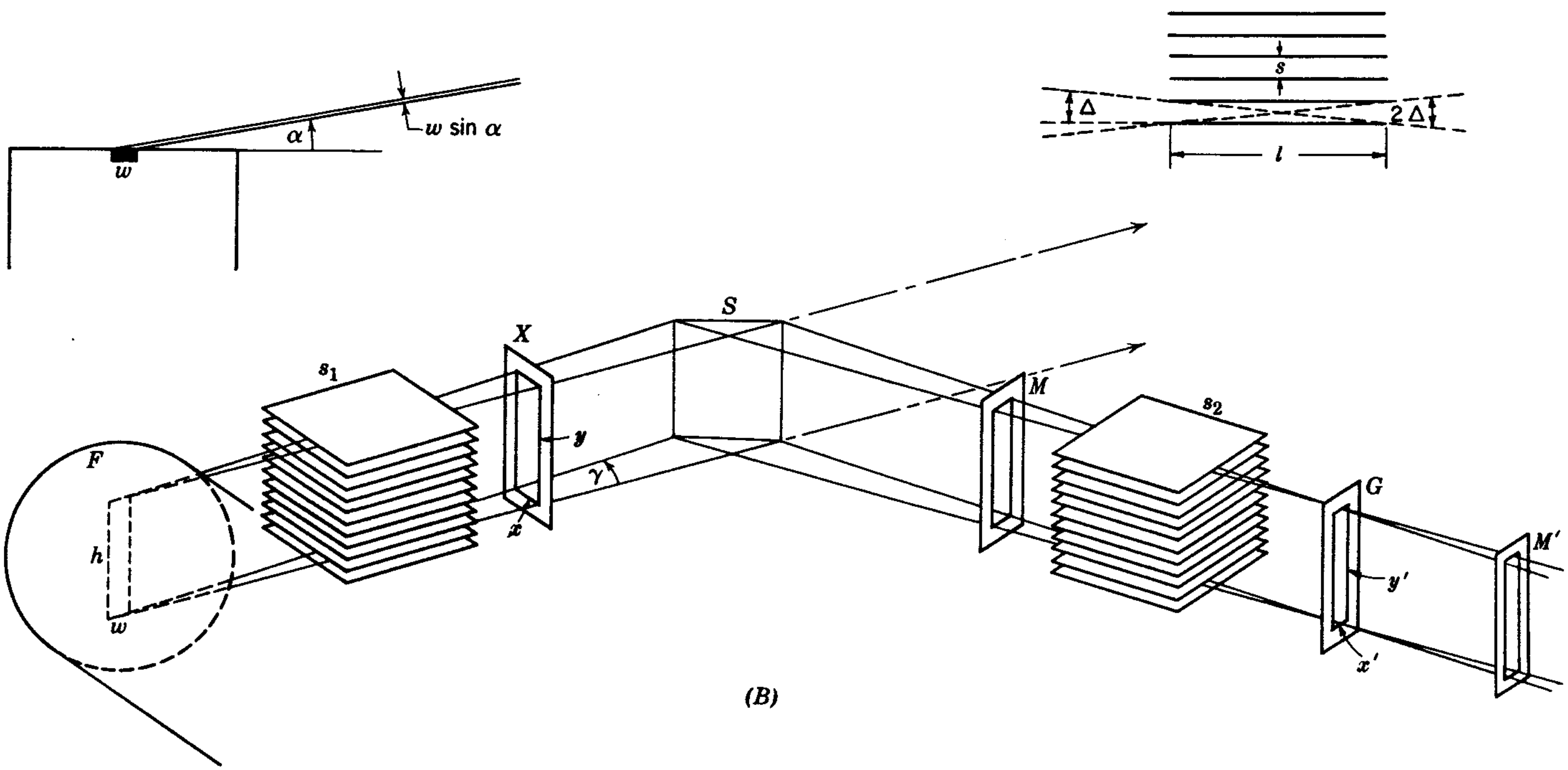
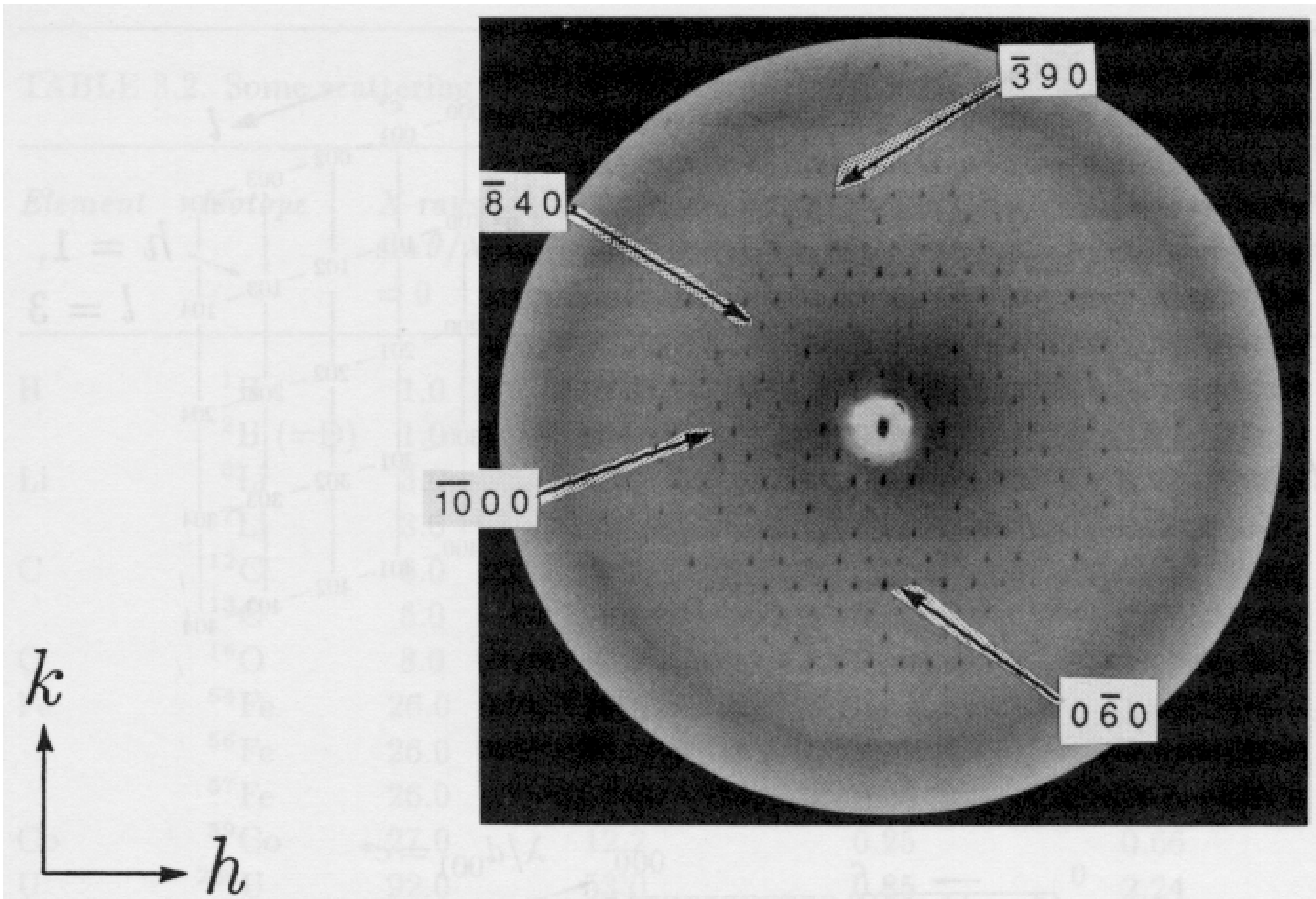


Fig. 5-4. (*A*) Optical arrangement used in early x-ray diffractometer. (*B*) Present-day optical arrangement with a "line" x-ray source and Soller slits to limit axial divergence.

Visualization of the reciprocal lattice

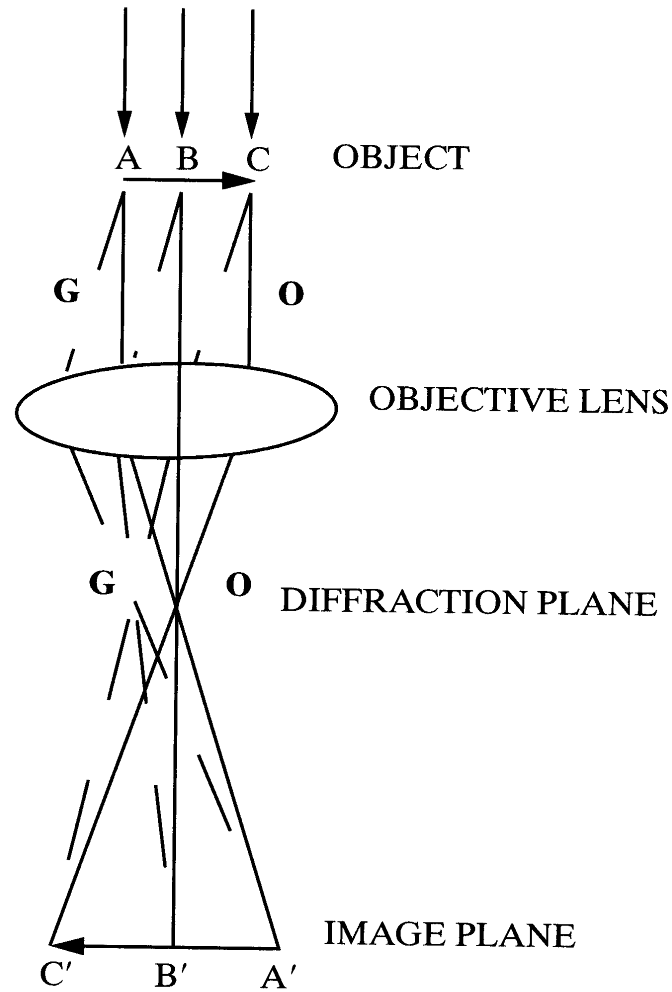
- Some techniques record diffraction patterns that are undistorted slices through reciprocal space
  - Precession photography uses a complex motion of the crystal and the x-ray film to record a diffraction pattern that can be any slice through reciprocal space
  - Electron diffraction directly records patterns that are slices through reciprocal space

A precession photograph



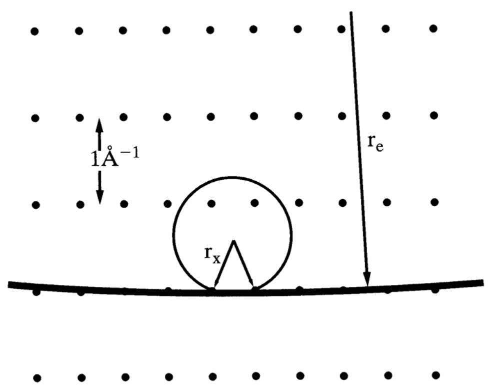
Imaging and diffraction in the TEM

- In a TEM the electron beam hits the object being studied. Some electrons are diffracted and some pass through the sample. The objective lens focuses all the beams to points in the diffraction plane. So we would see a diffraction pattern here. The diffracted beams combine in the image plane to form an image. Other lenses can be used to form magnified images of either the diffraction or image planes.

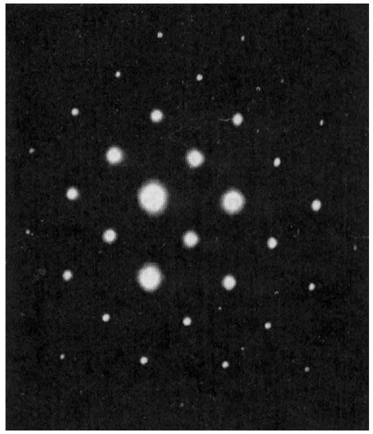


Why ED patterns have many spots

- Typically, in X-ray or neutron diffraction only one reciprocal lattice point is one the surface of the Ewald sphere at one time
- In electron diffraction the Ewald sphere is not highly curved due to the very short wavelength electrons that are used. This almost flat Ewald sphere intersects with many relps at the same time
  - In real crystals relps are not infinitely small and in a real microscope the Ewald sphere is not infinitely thin



Ewald sphere for Cu radiation is much more curved than that for electrons in an electron diffraction experiment



Electron Diffraction pattern from NiAl