X-ray Diffraction

Callister Chapter 3 p. 66-71

Maxwell's Equations

E

the E & H vectors
pulsate 90° out of phase from each other.
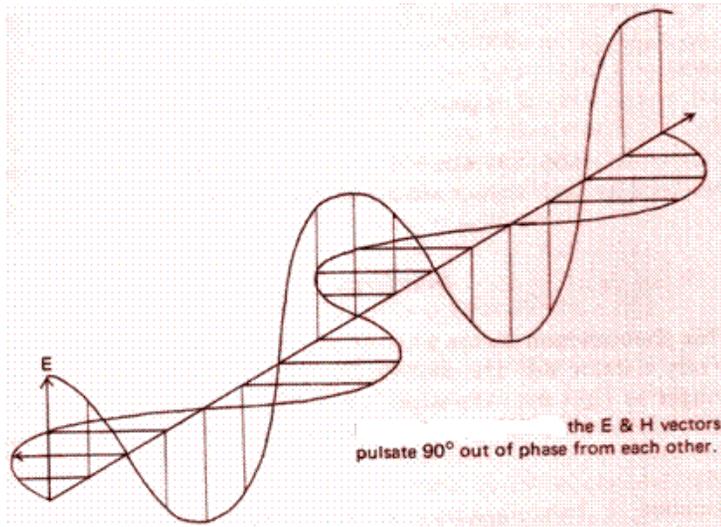
X-rays are short wavelength electro-magnetic waves. (electromagnetic spectrum link)

1) We have all seen electro-magnets which are made of a coil of wire and which display a magnetic field when electricity flows through the coil. This magnetic field is described by one of Maxwell's laws know as the generalized Ampere Law:

$$\oint_{line} \underline{B} \bullet \underline{dl} = \varepsilon_0 \mu_0 \left(\frac{d\phi_E}{dt} \right) \qquad \phi_E = EA \sim q$$

Line integral

Here a changing electric field associated with current is related to an associated magnetic field. The direction of the magnetic field is perpendicular to the direction of the electric field. For a sinusoidally oscillating electric field the magnetic field is out of phase by 90°, i.e. the magnetic field reaches a maximum when the electric field reaches a minimum.

2) Electrical generators involve the motion of a magnet on a shaft which creates an electric field and current in a surrounding coil by Faraday's law:

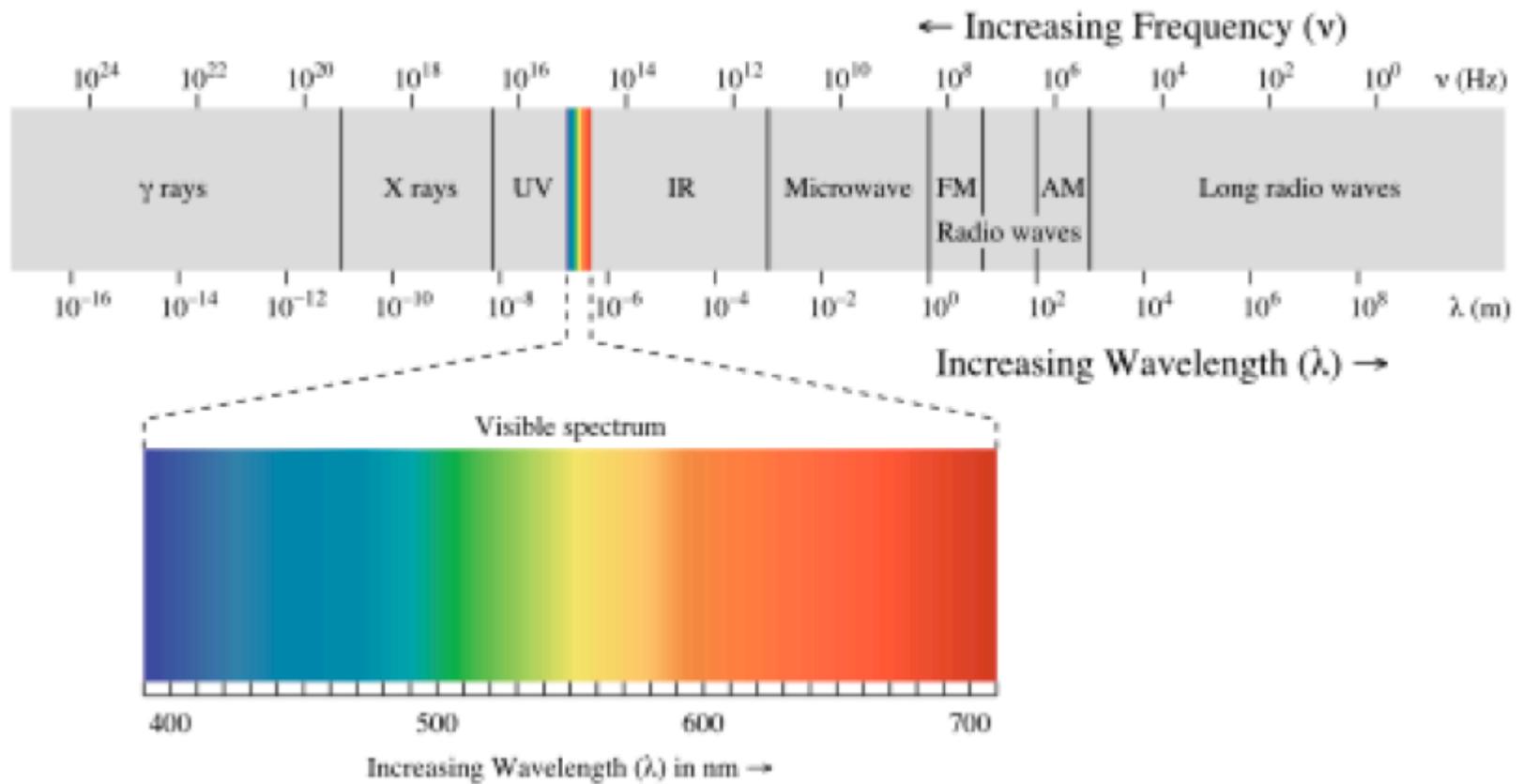$$\oint_{line} \underline{E} \bullet \underline{dl} = - \left(\frac{d\phi_B}{dt} \right) \qquad \phi_E = BA$$

Line integral

A changing magnetic field is associated with the creation of an electric field. The electric field is perpendicular to the magnetic field and is out of phase by 90°.
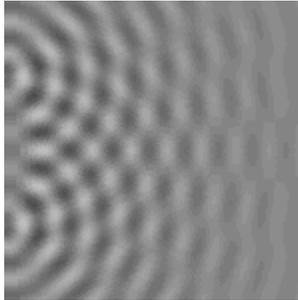
3) Any *disturbance* in electo/magnetic space can create an electro-magnetic wave just as a physical disturbance in a pool of water can create a mechanical wave where kinetic and potential energies are converted. A wave in a pool of water has an associated energy which is stored in the oscillation between kinetic and potential energies. Similarly, an electromagnetic wave has an associated energy. Some typical disturbances in order of increasing energy are: oscillating charge in an antenna (radiowave), current flow through a tightly coiled, thin wire (light/heat), change in momentum of a charged particle at high velocity (x-rays).

http://www.eng.uc.edu/~gbeaucag/Classes/XRD/Chapter1html/Chapter1.html

← Increasing Frequency (ν)

10^{24} 10^{22} 10^{20} 10^{18} 10^{16} 10^{14} 10^{12} 10^{10} 10^{8} 10^{6} 10^{4} 10^{2} 10^{0} ν (Hz)

γ rays   X rays   UV   IR   Microwave   FM   AM   Long radio waves
                                                                Radio waves

10^{-16} 10^{-14} 10^{-12} 10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2} 10^{0} 10^{2} 10^{4} 10^{6} 10^{8} λ (m)

Increasing Wavelength (λ) →

Visible spectrum

400   500   600   700

Increasing Wavelength (λ) in nm →

Electromagnetic spectrum with light highlighted

The Binary Scattering Event

$$I(2\theta) = N \, n_e^2$$

n_e Reflects the density of a
Point generating waves

N is total number of points

Why would N and n_e change with (2θ)?
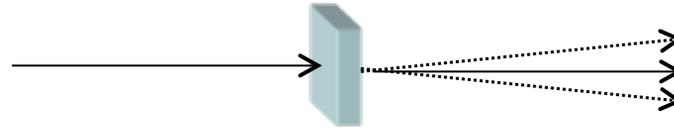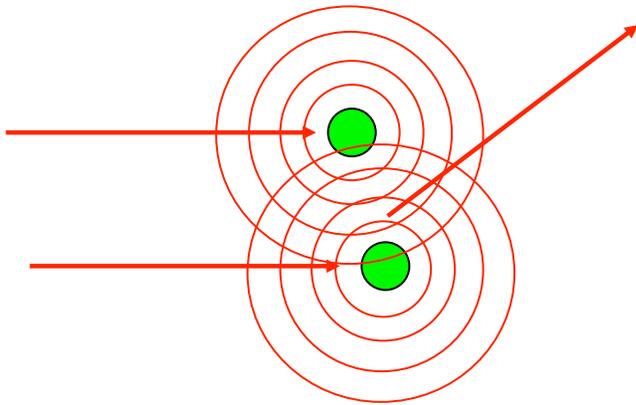
Binary Interference Yields Scattering Pattern.

-Consider that a wave scattered at an angle 2θ was in phase
with the incident wave at the source of scattering

-This can occur for points separated by **r** such that

$$r = \frac{\lambda}{2\sin(\theta)}$$

r is called the scattering vector and the scattering elements (atoms) must be located
at the ends of the scattering vector for a diffraction event to occur

The length of r changes with 2θ
The minimum of r is λ/2 and the maximum is ∞
r points in a direction normal to θ
This means that crystallographic planes must be arranged at the angle θ for diffraction to occur
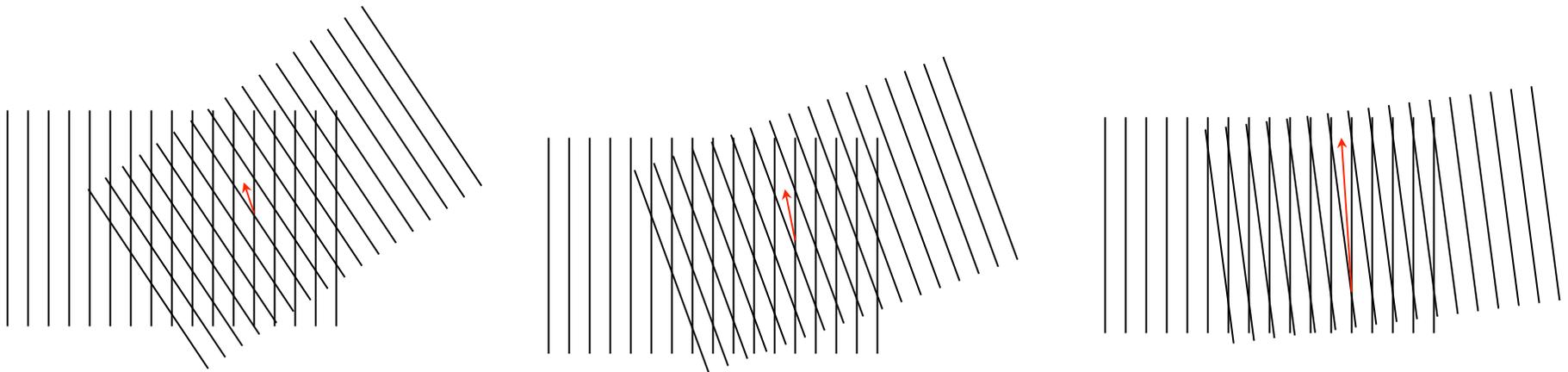
Small 2θ yields large r
Large 2θ yields small r

r has a direction roughly normal to the propagating beam (it bisects 2θ)
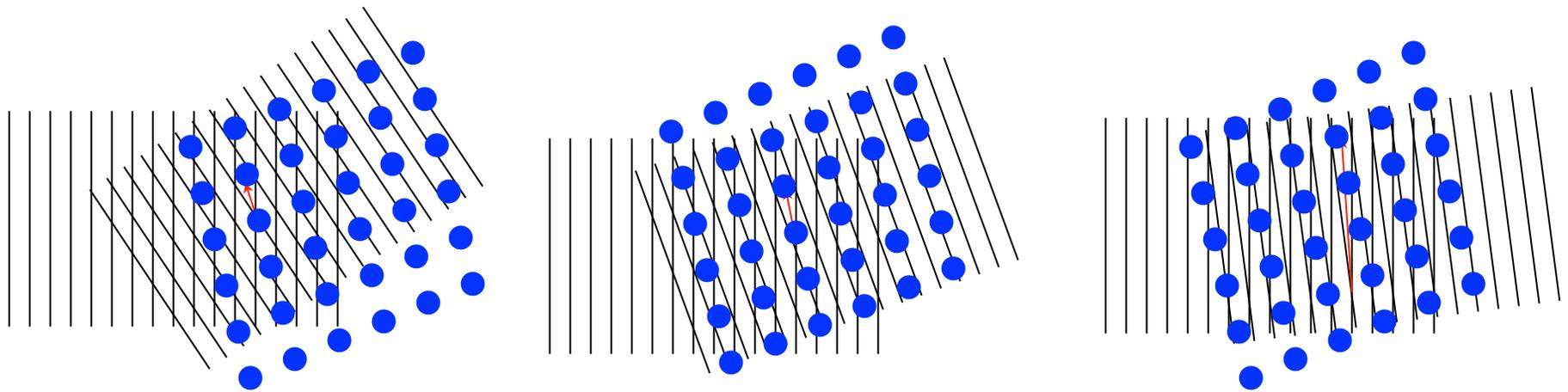
For a lattice that matches r in size and orientation we get a diffraction event

r points in a direction normal to θ
This means that crystallographic planes must be arranged at the angle θ for diffraction to occur

This is called the specular (mirror-like) analogy, the plane seems to act like a mirror
(*the plane is not a mirror and there is no reflection, this is an interference phenomena*)
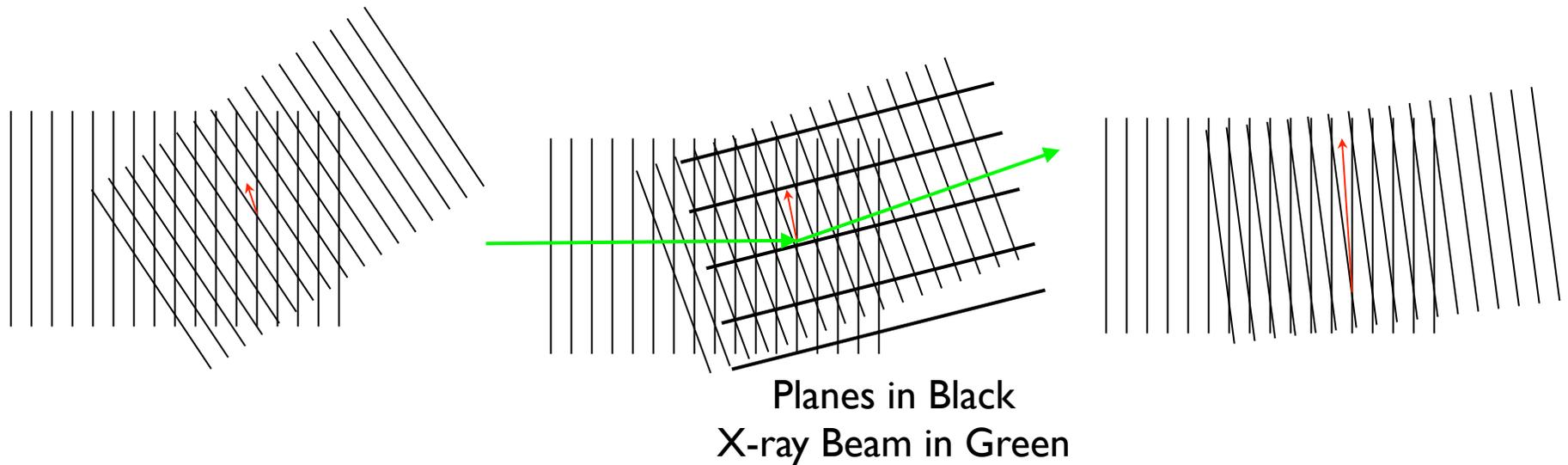
Planes in Black
X-ray Beam in Green

Small 2θ yields large r
Large 2θ yields small r

r has a direction roughly normal to the propagating beam (it bisects 2θ)

Bragg's Law defines the angle 2θ of diffraction for a plane with d-spacing d(hkl)

λ/2 is the smallest size that can be measured
At small angle d goes to ∞
The function depends on θ not 2θ

Since d is inverse to the sin of the angle we call the diffraction space "inverse space"
it is also called momentum space (for other reasons)
In a 2D or 1D diffraction pattern large distances from the beam center correspond to small "d" and large distances correspond to large "d"

$$d = \frac{\lambda}{2\sin(\theta)}$$

Another feature in inverse space are the Miller Indices
Large unit cell indices correspond to small unit cell distances
Small indices correspond to large unit cell distances

The Miller Indices are vectors in inverse space.
(i.e. in the diffraction pattern)

Also, directions are orthogonal (right angles)
We will look at this later

Derive Bragg's Law Following the Specular Analogy

Planes in Black
X-ray Beam in Green

Add Bisector

Add Normal to Beam to get Extra distance traveled
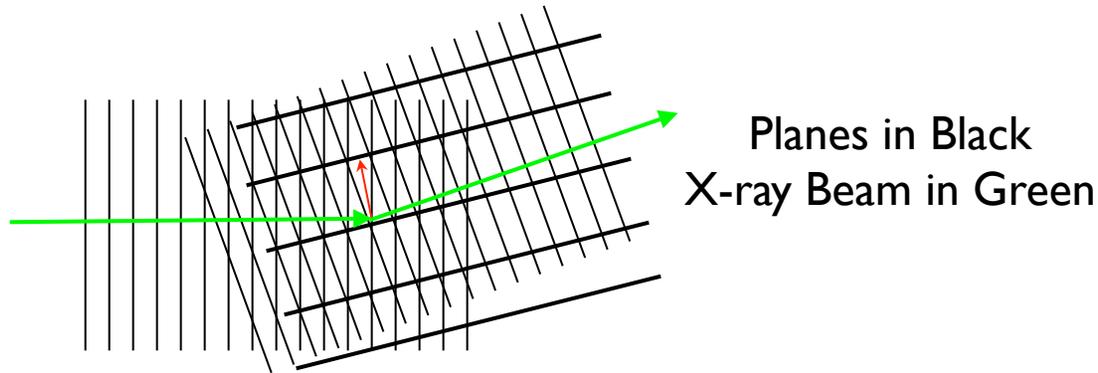
For constructive interference the extra distance traveled must equal a multiple of λ

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

n = 1 for x-ray diffraction from 3d crystals

$$d = \frac{\lambda}{2\sin(\theta)}$$
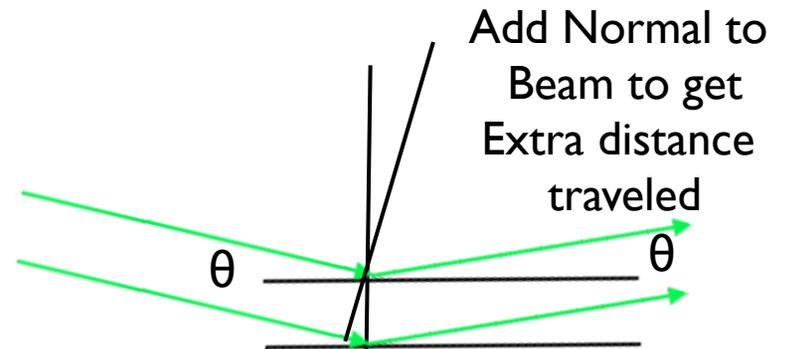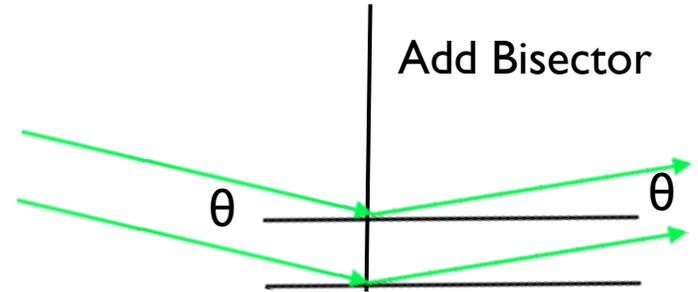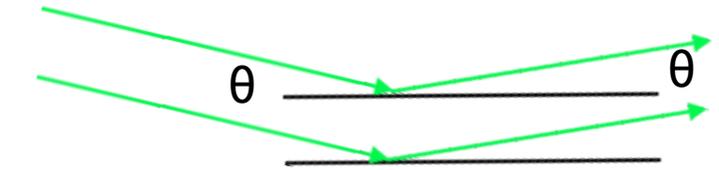
Extract Right Triangle and Solve for Distance

$$\Delta x = d \sin \theta$$

The total extra distance is twice this: 2 d sin θ

What is needed to get an x-ray peak:

1) 2θ, λ and d_{hkl} must meet Bragg's Condition
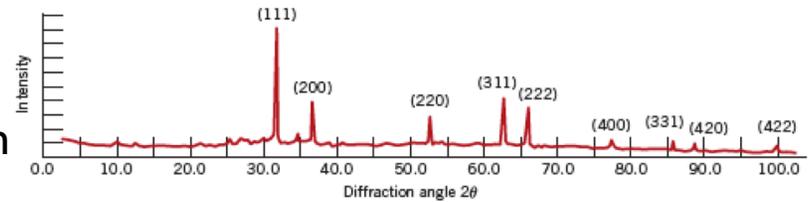
2) (hkl) plane must be aligned in the specular condition
   Plane that meets (1) must be at an angle θ to the incident beam

3) The plane must be oriented in the aziumthal angle so that
   the diffraction peak falls on the detector (for a single channel detector)
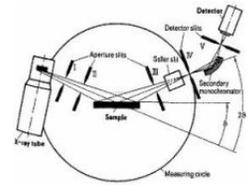
**Normally for a single crystal with a monchromatic source it
is unlikely that all three of these conditions will be met**
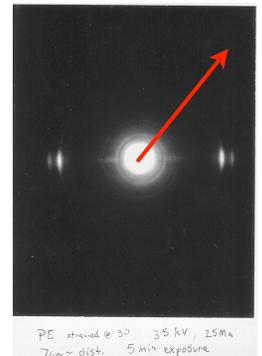
There are two common ways to overcome this limitation

1) Grind the single crystal into a powder so that all possible orientations will be present
Overcoming 2) and 3)
Used for grainy metals, polymers, most diffraction experiments in Materials Science.

2) Use polychromatic radiation so that most reflections will be observed
Overcoming 1)
Laue Pattern/Laue Method (Used for Protein Crystals/Silicon Alignment/Gem Stones)

Diffraction from a perfect crystal (Laue Method)

Polychromatic

Laue Method
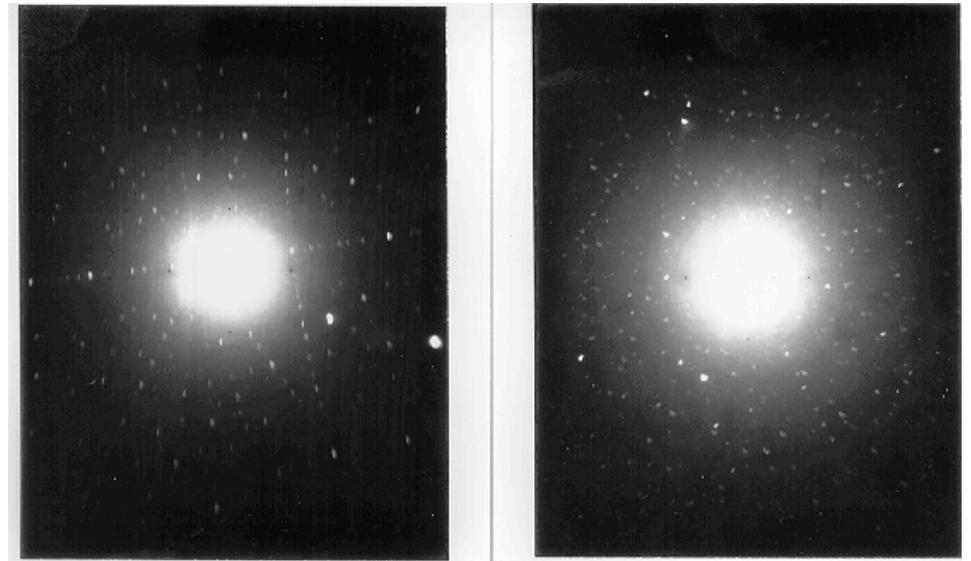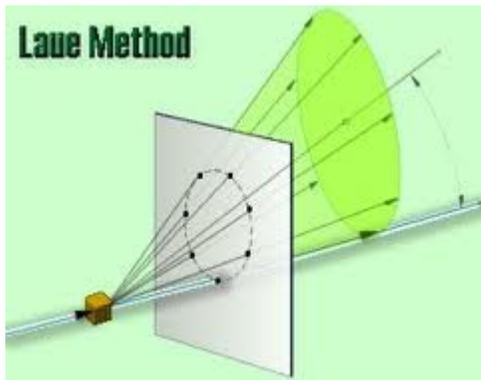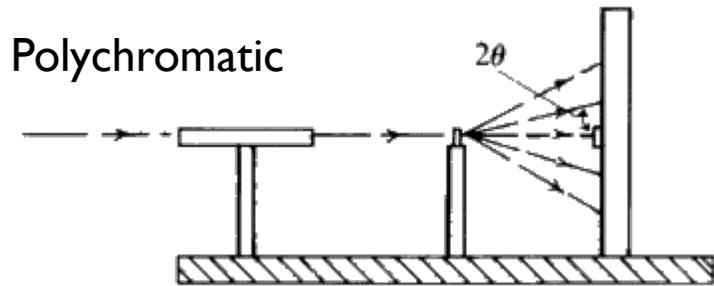
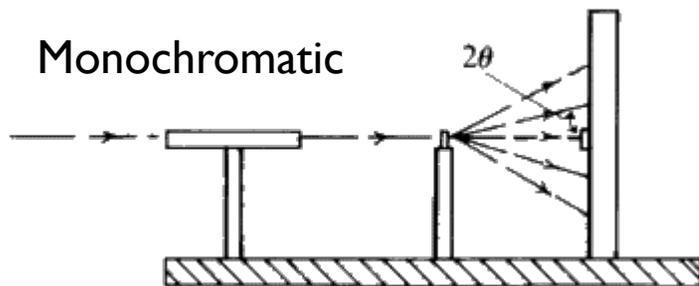Si   15min   3cm   40kv
Back reflection

Silicon   3cm   40 KV
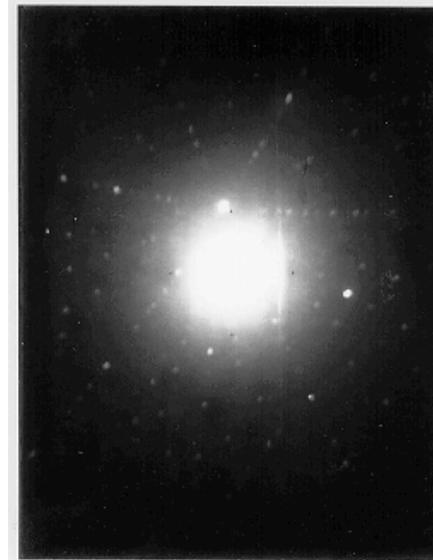
Ge at 3cm back Reflection. 40kv
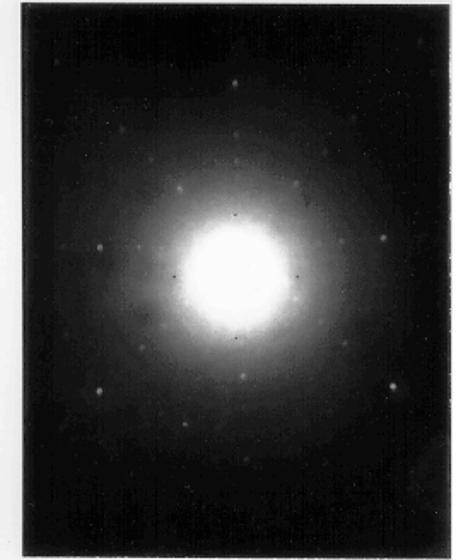
NaCl   20min   40kV 3cm

Diffraction from a Powder
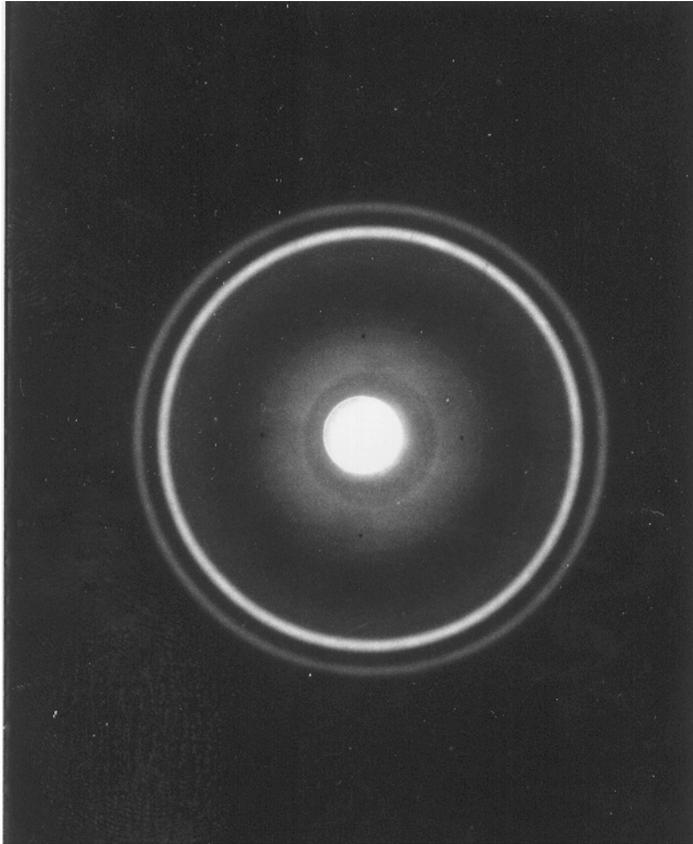## Powder Pattern (Debye-Scherrer Method)

Monochromatic

2θ
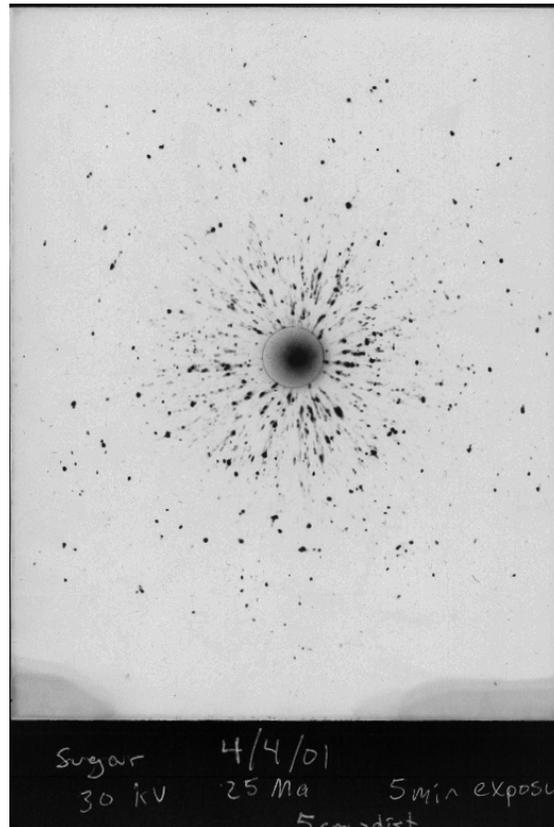
Sugar

Ground up Sugar
(Debye-Scherrer Rings)

Sugar   4/4/01
30 kV   25 Ma   5 min exposur
5 cm dist

Sugar II (ground up)   4/4/01
35 kV, 25 Ma   5 cm -dist.
5 min. exposure

Orientation (Polyethylene)

Unoriented

Highly Oriented

PE strained @ 30   3 5 kV, 25Ma
7cm ~ dist.   5 min exposure
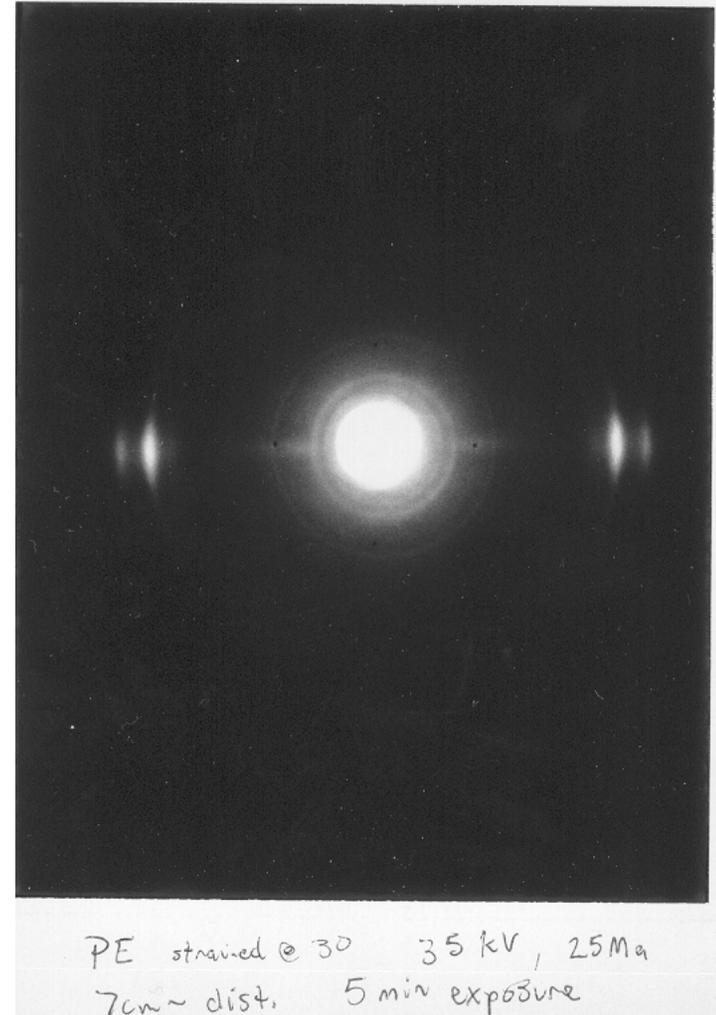
Polymers have broad Debye-Scherrer Rings
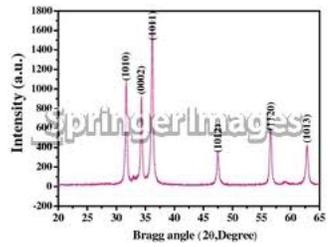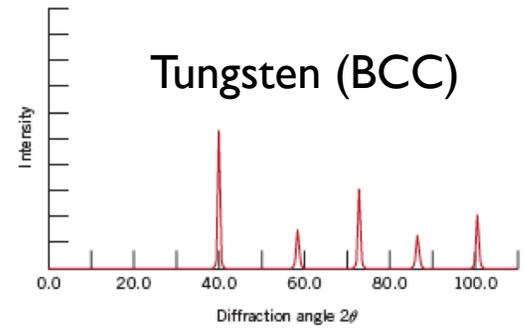
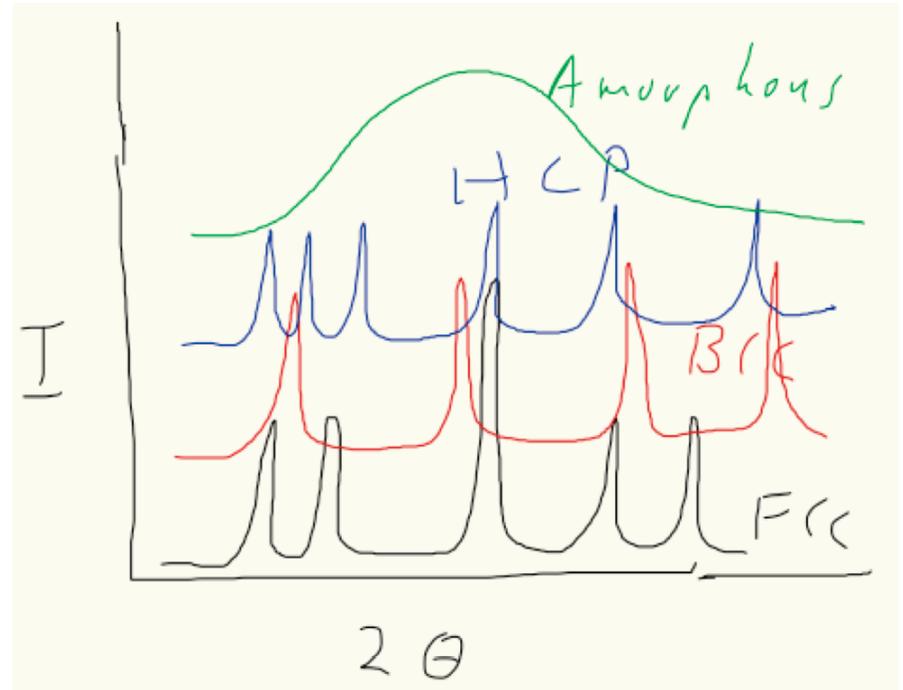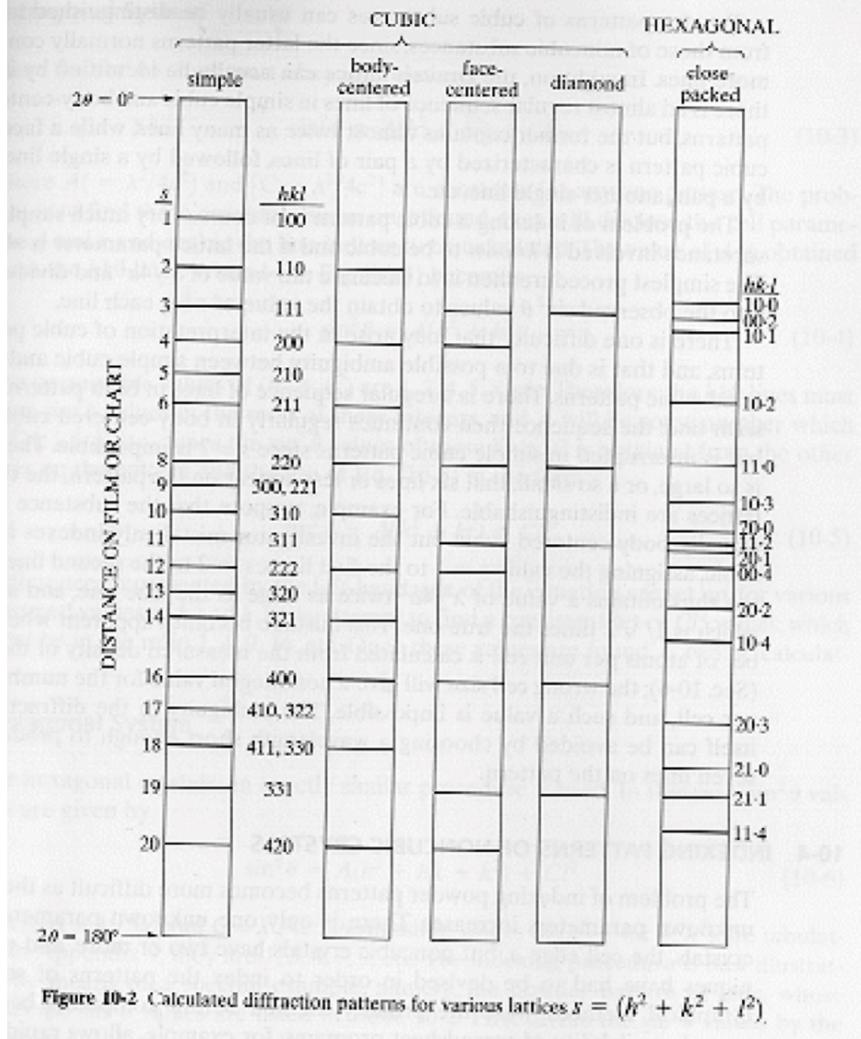# Orientation Aluminum and Graphite
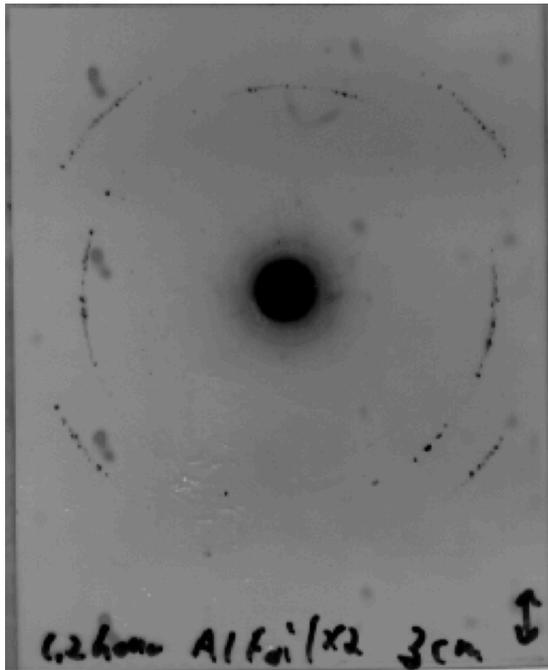
Aluminum Foil
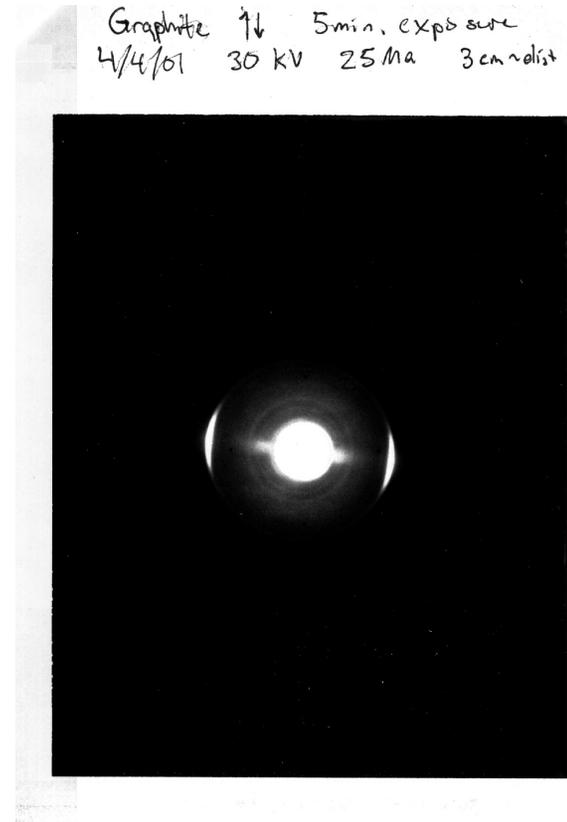
Graphite

Diffractometer Scans (Single Channel Detector)

Nickel (FCC)
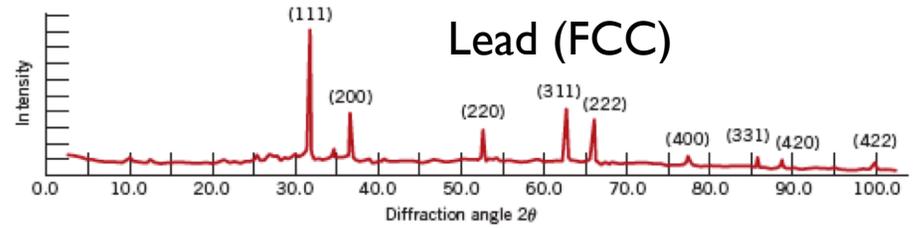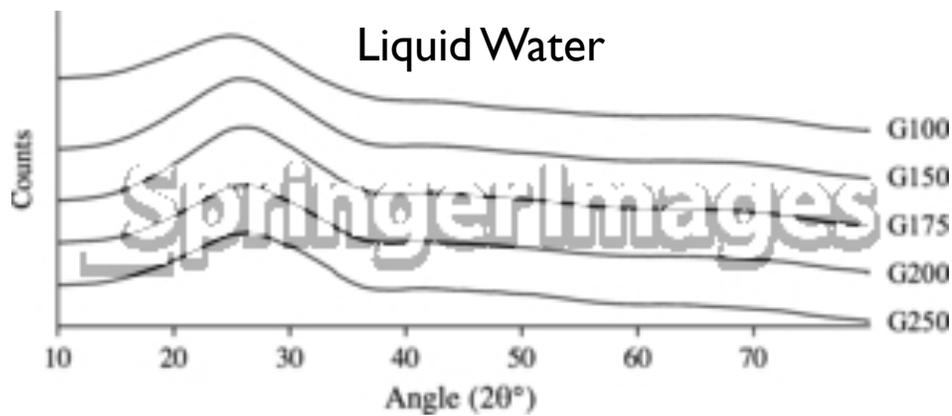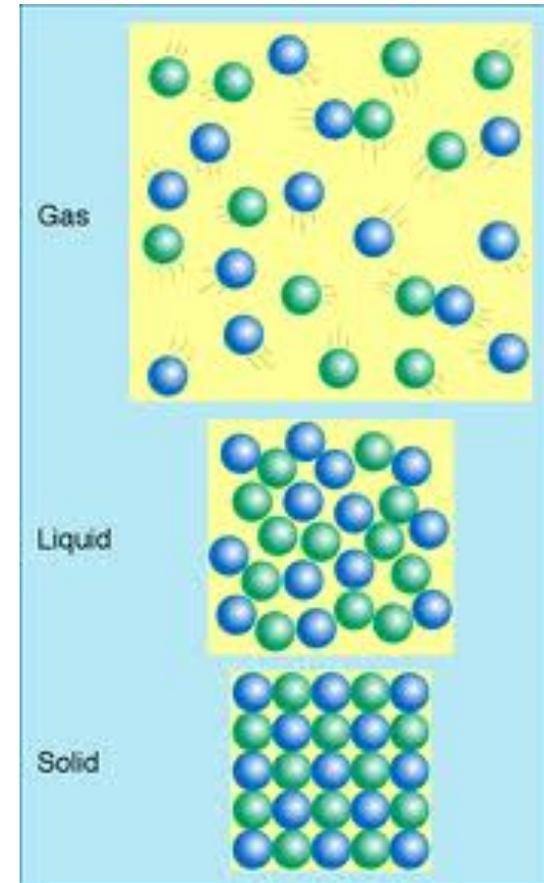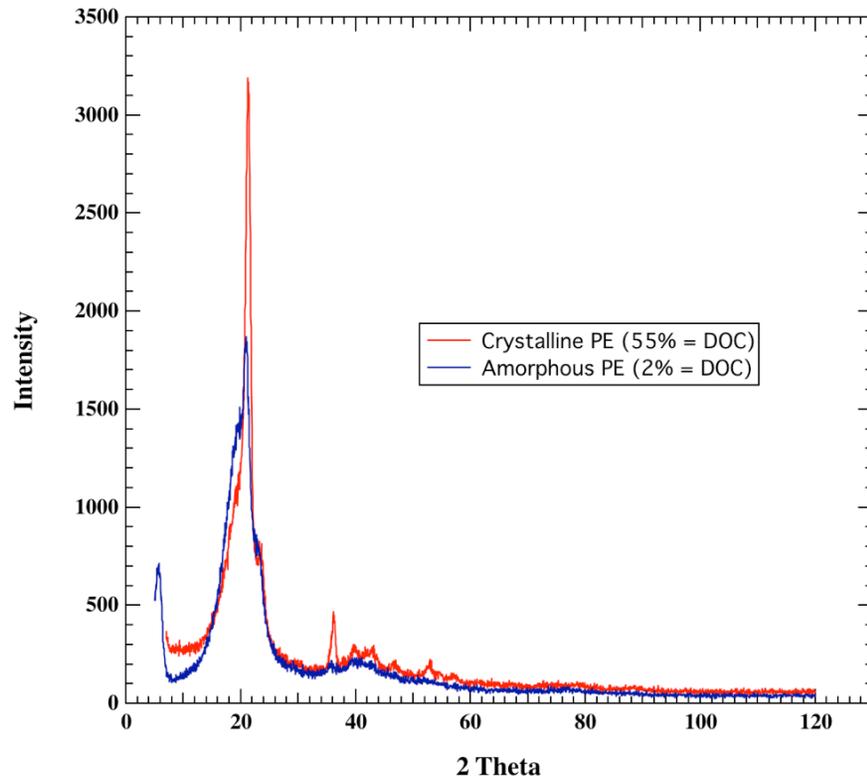
Lead (FCC)

Figure 10-2 Calculated diffraction patterns for various lattices $s = (h^2 + k^2 + l^2)$.
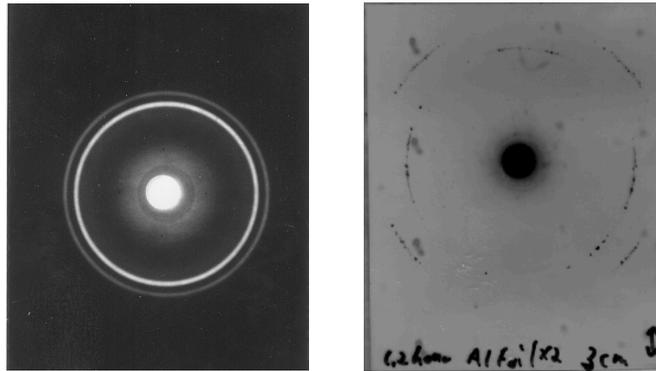

Tungsten (BCC)

Zinc (HCP)

Lead (FCC)
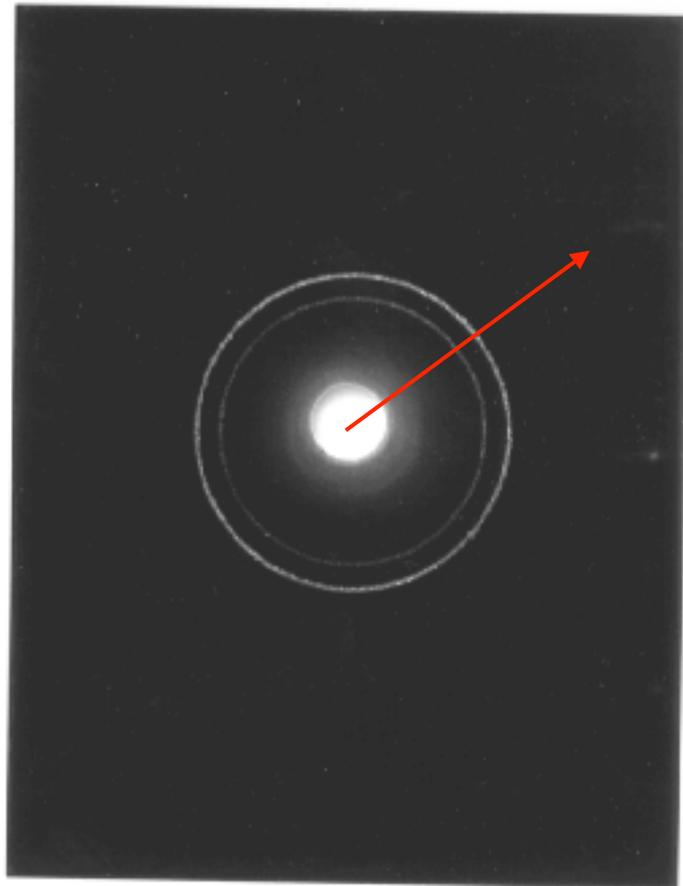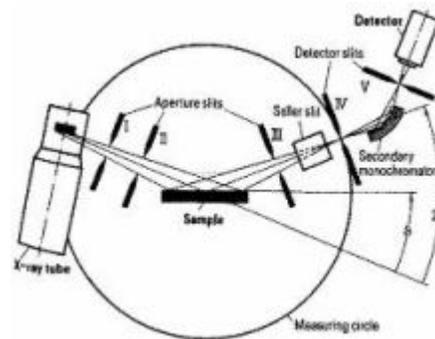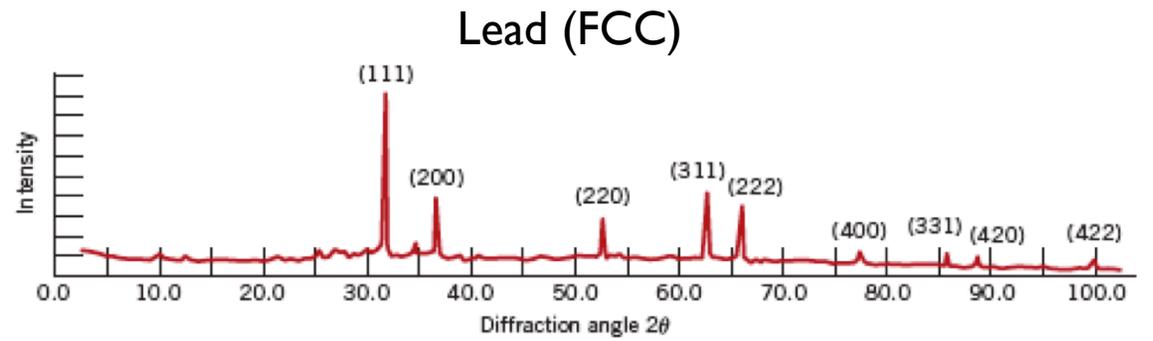
What is an Amorphous Halo?

Liquid Water

What is Scherrer Broadening?

$$t = \frac{0.9\lambda}{B\cos(\theta)}$$

Size of the crystal, t, decreases as the breadth of the peak, B, increases
(**B is in radians for this to work**)

What other kinds of peak broadening occur?

Residual Stress in the crystal causes broadening

Debye Thermal Broadening caused by thermal motion of the atoms
(Used to measure heat capacity)

What can we measure from diffraction?

Size: d-spacing, RMS distance for Amorphous

Composition: Alloys, Blends, DOC for Polymers

Grain size sub-micron scale (Nanocrystal size)

Residual Stress

Heat Capacity/Mean Free Path of Atoms

Grain size super-micron scale

Orientation of Crystals

Thermal Expansion Coefficient for Lattice Parameters

What can't we measure from diffraction?

No Picture of the Crystal

No Real-Space Image