# X-Ray Diffractometry

The determination of crystal structure

The identification of unknown phases

The visualisation of a **crystals** internal atomic arrangement

The concept of **diffraction** is the bending of a wave or beam due to the elements in the target material; however, unlike with refraction, there is no speed change in the beam

This concept holds true for beams of light, x-rays, or electrons

The patterns that are generated by diffraction of a beam is directly related to the crystal structure of the material that is targeted

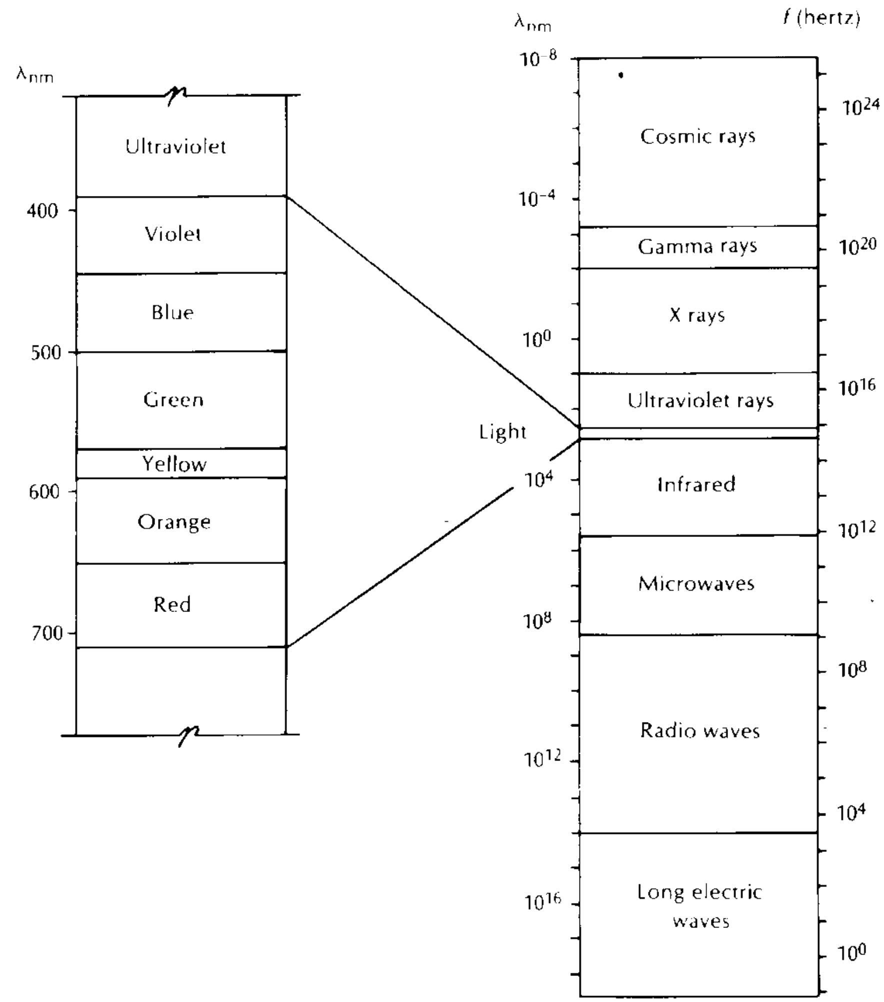
At the atomic scale:

Diffraction patterns appear as a series of peaks
Spacing between peaks is related to sizes of structures
Intensities of peaks relate to concentration of atoms in a structure

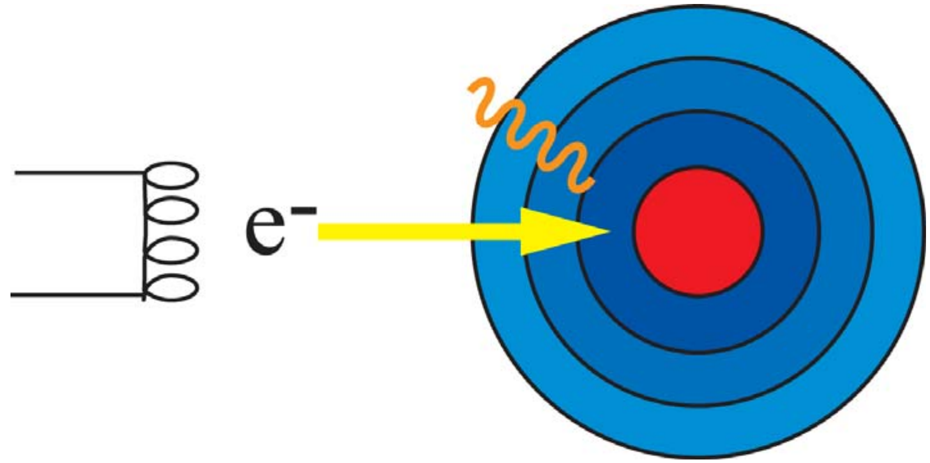
# The nature of X-rays

- X-rays are short wavelength, high-energy emissions generated when electrons travelling at high speed collide with atoms.
- The properties of the resultant X-rays are unique to specific target atoms.
- The number of X-rays (intensity) is proportional to the number of electrons colliding with the target.

Spectrum of energy…. UV-vis, IR, X-ray

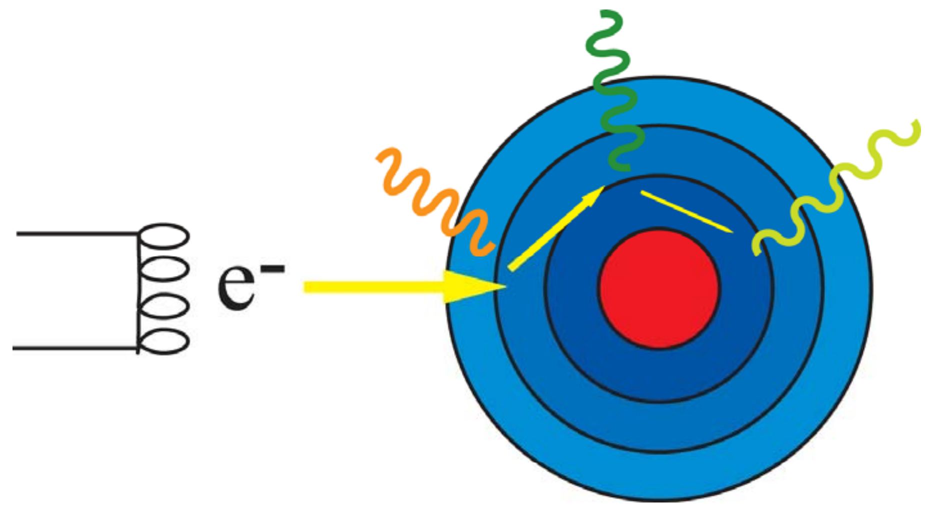


When the electron enters the electric field of an atom it loses some energy. This energy is "released" as a quantum of X-radiation.

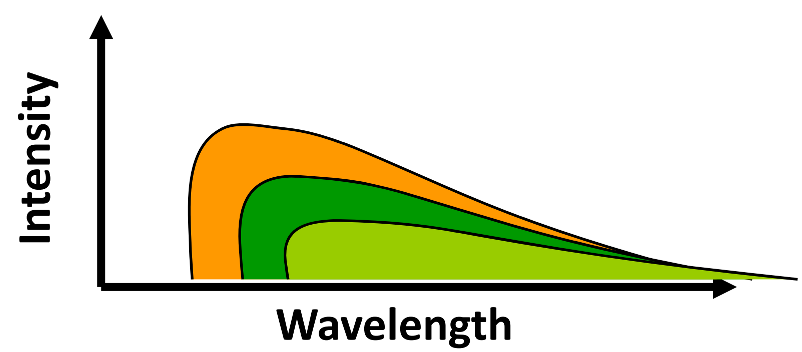



Its energy is inversely proportional to is wavelength ($E = hc/\lambda$)

Normally the energy of an electron is lost stepwise giving rise to several X-ray quanta, each with increasing wave-length and decreasing energy.



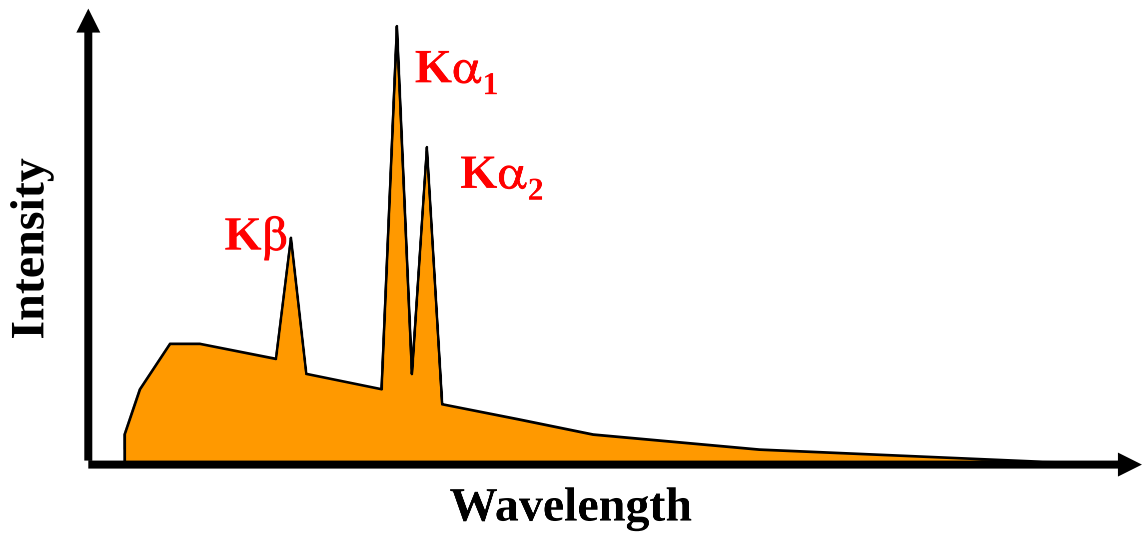

So, with a continuous stream of electrons you produce a continuous stream of X-rays with across a range known as the continuous spectrum.



# Characteristic Line Spectra

At a critical accelerating voltage there will be a marked intensity of X-rays of element specific wavelengths.

These X-rays are generated by interaction between the accelerated electrons and the **orbital** electrons of the target and are known as the **characteristic line spectra.**

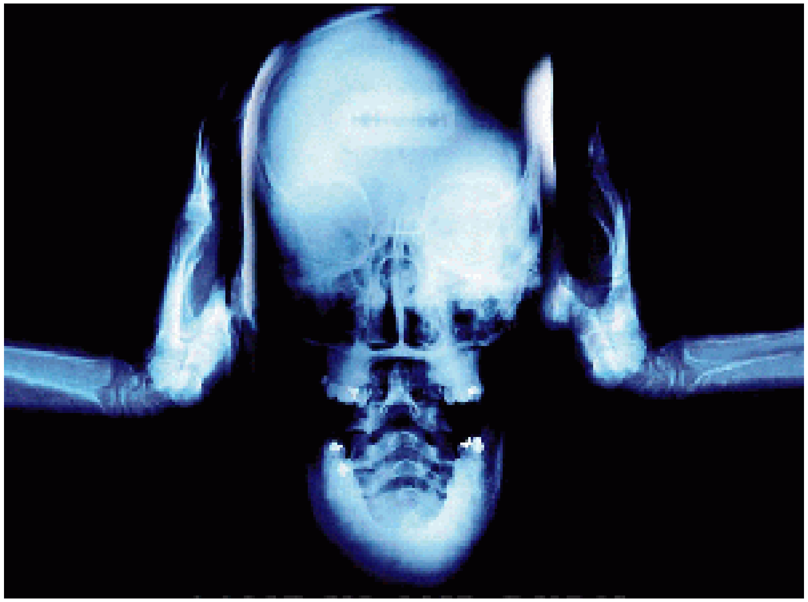



The lines occur in groups called the **K, L, M and N-series.**

A K-series spectrum is shown above. It will look very similar for all X-ray sources. These are the most important for diffraction – lower energy X-rays are absorbed.

# Using X-rays to our advantage

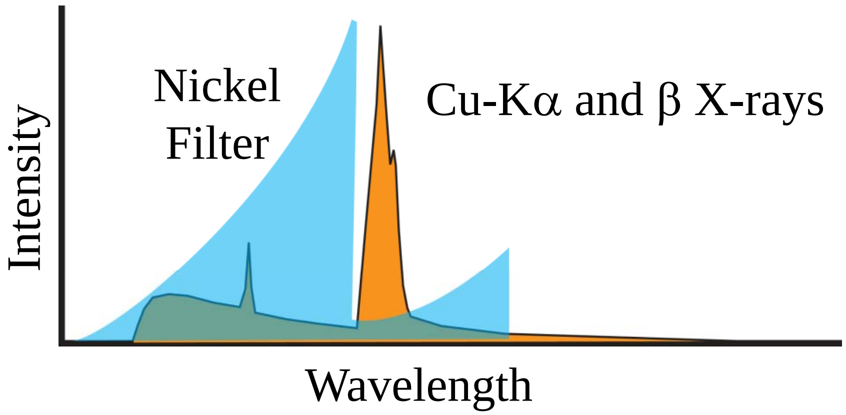
The high energy of X-rays enables them to pass through many substances – a property that has been put to good use for medical purposes for many years.



Mineralogists require one extra step.

The line spectra contains many X-rays of different wavelengths. For diffraction studies, we need monochromatic X-rays.

We apply a filter to remove the Kb lines (as well as any others that are not absorbed by the studied mineral).



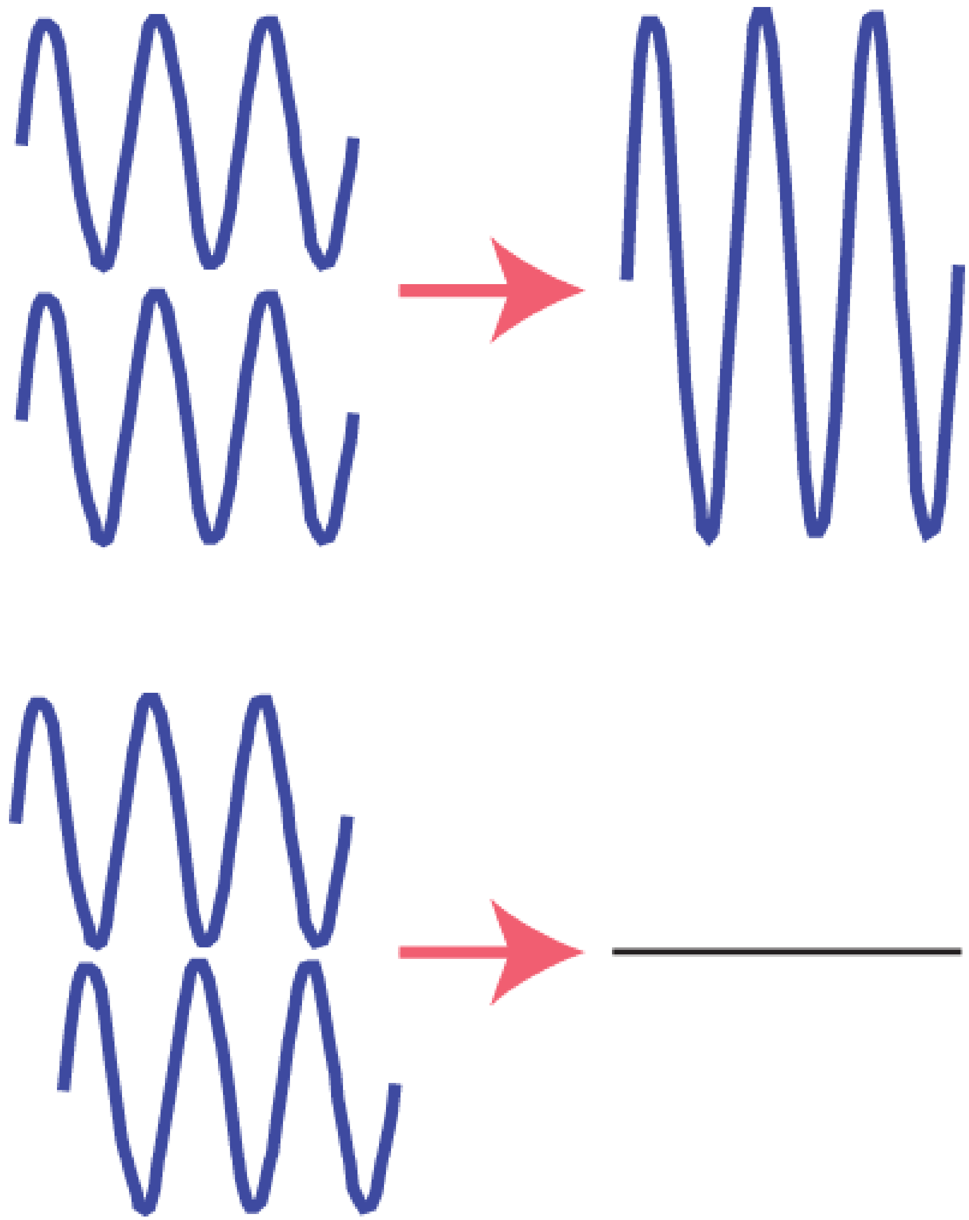
X-rays interact with materials in a wide variety of ways.

This is a result of their electromagnetic properties.

For crystallographic (and mineralogical) purposes we are most interested in their scattering by **layers of atoms**.

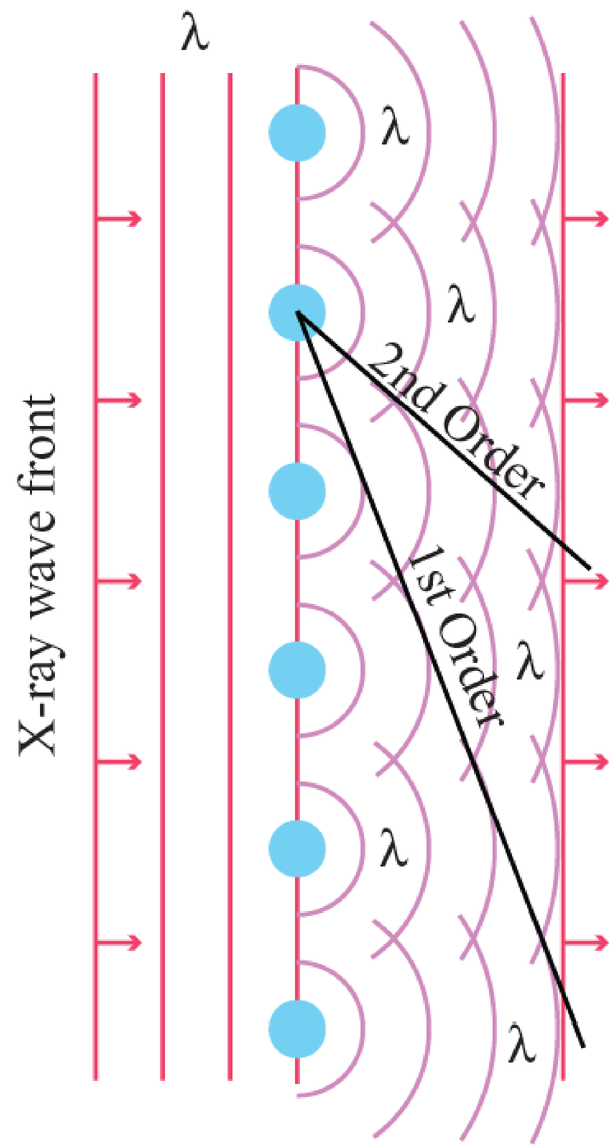
To understand the nature of the incident X-ray beam and that of the X-rays which are emitted and their value to mineralogy we must first look at the *constructive* versus *destructive* nature of "**waves**".

It is all about synchronisation.



**Crystals consist of a long-range ordered three-dimensional structure.**

When our **filtered X-ray beam** strikes the atoms of the lattice the electrons in its path vibrate with the frequency of the incident X-radiation, absorbing some energy and acting as **a source for new X-ray energy….**



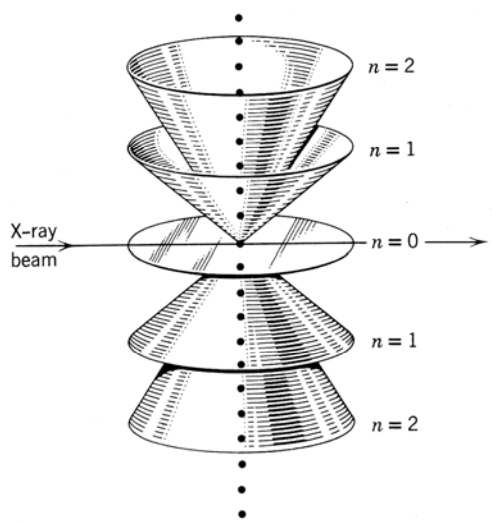

## …. of the same wavelength.

In this diagram the X-rays are scattered in two dimensions through the lattice where many of them interact destructively.

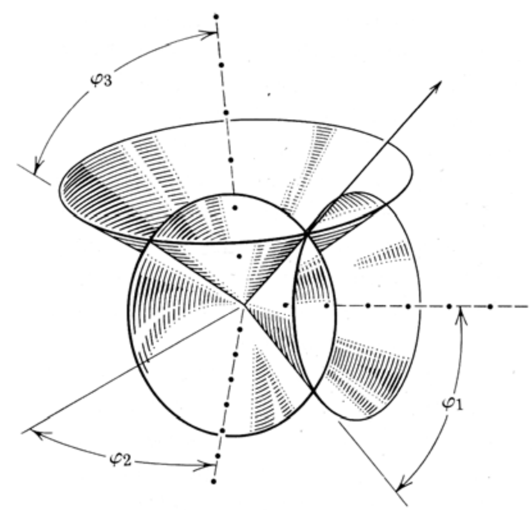
However, at each integral number of wavelengths (n) the X-rays are inphase, reinforcing one another, producing diffracted X-rays.

# What happens when this is image is expanded to 3-dimensions?

For a line of atoms the scattering creates cones.




For a 3-dimensional distribution of atoms, we see three cones.




Identifying the geometry of the cones is a complex affair requiring the solving of simultaneous (Laue) equations.

These cones create waves that are essentially destructive, except along linear features where all cones intersect.

l1

By solving the Laue equations it is possible to determine the spacing between atoms in all three dimensions.

Fortunately, shortly after Laue’s discovery W.L. Bragg pointed out that diffraction can be thought of in terms of “reflectance”.

However, unlike light, the X-rays are not “reflected” continuously, but rather when a specific set of conditions is met for a specific plane of parallel atoms in the minerals structure.

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

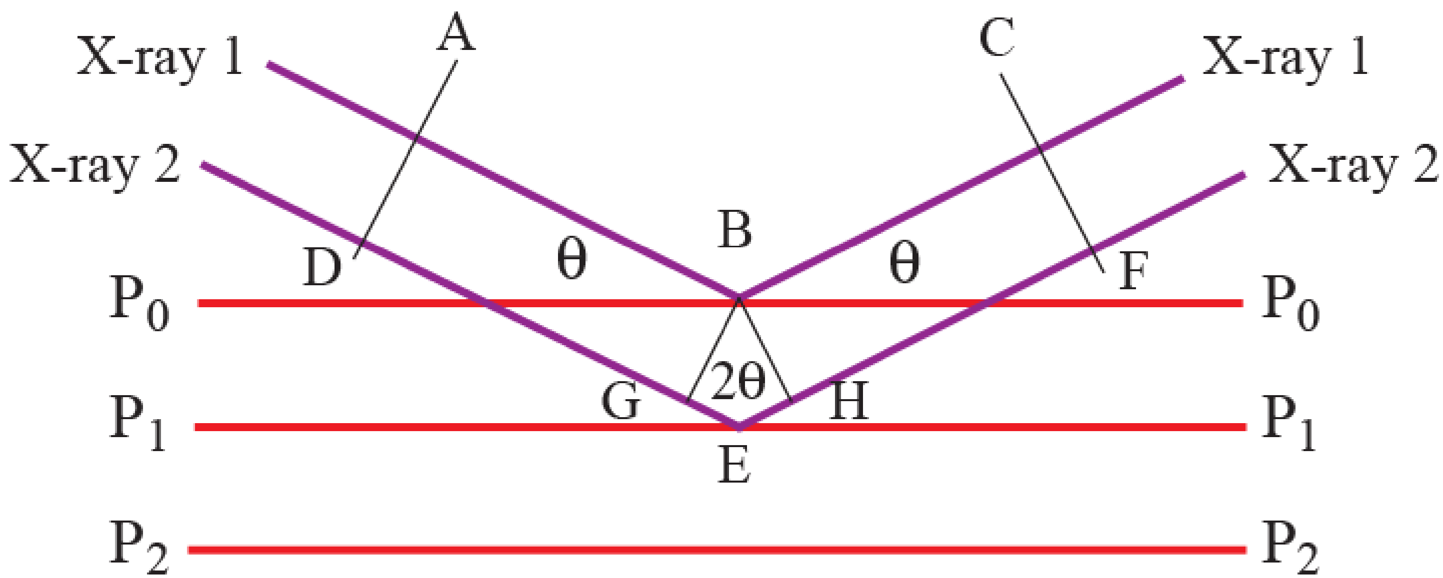
**Slide 11**

**l1**

n is an integer
l is the wavelength of X-rays
d is the distance between each parallel plane of atoms
Theta is the angle of incidence and "reflections"/diffraction
localuser, 8/4/2006

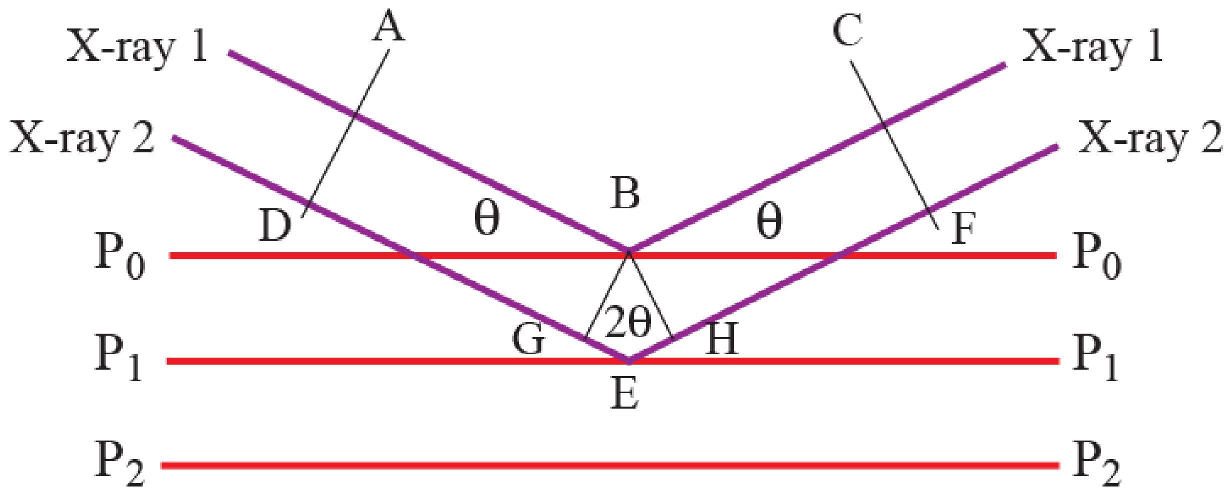
Lines $P_0P_0$, $P_1P_1$ and $P_2P_2$ represent a family of atomic planes with spacing *d*

X-ray 1 striking the first atomic plane $P_0P_0$ is diffracted at incident angle q.




For the diffracted X-ray to be detected it must be reinforced by additional diffracted X-rays that are in phase.

For X-ray 2 to be in phase, the distance DEF must be an integral number (n) of wavelengths greater than ABC (i.e. GE + EH = nl).




In this case the goal is to establish the d spacing ($P_0$-$P_1$), which is also equal to the distance BE.

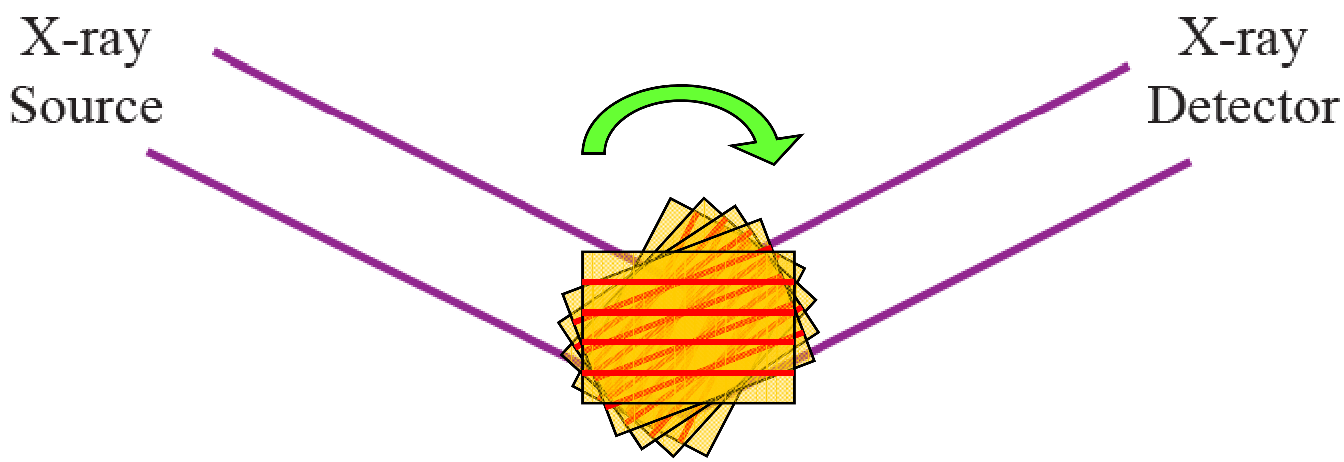
The angle GBE = $\theta$.
The distance GE + EH = $n\lambda$.

GB is parallel to AD, thereby forming a right-angle with X-ray 2.

So, from geometry: $\sin\theta$ = opposite/hypotenuse (GE/BE)
where GE is $\frac{1}{2}n\lambda$, and BE = d.

$$\sin\theta = \tfrac{1}{2}n\lambda/d$$
$$d\sin\theta = \tfrac{1}{2}n\lambda$$

$$\mathbf{2d\sin\theta = n\lambda \; (n\lambda = 2d\sin\theta)}$$




When a crystal is placed in the X-ray at an orientation that satisfies the Bragg equation (n = 1) a beam a diffracted X-rays will strike the detector.

On rotation of the crystal there will be further "reflections" detected when the Bragg equation is satisfied at certain $\theta$ angles (n = 2, 3, 4 etc).

These X-rays are all being diffracted by the same family of planes and are referred to as the 1st, 2nd, 3rd order "reflections".