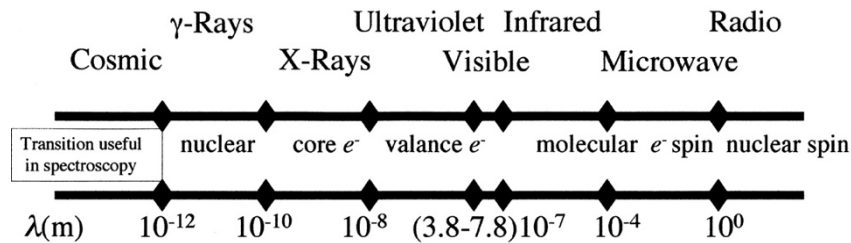# 9 - Lecture notes for GEOL3010

X-ray Crystallography

The electromagnetic (EM) spectrum.

EMspectrum.jpeg

The production of X-rays - In practice, X-rays are produced by streaming electrons across an extremely high voltage potential (15-50 Kv). The voltage is applied to a filament (typically a tungsten cathode) in a vacuum. The electrons are then accelerated into a metal target (typically a copper anode). The energy released results in two types of X-radiation.

The first type is known as **white radiation** and consists of a broad, continuous spectrum containing many wavelengths of radiation. It is a result of the very rapid deceleration of electrons as they encounter the strong electric fields of target metal. As the electrons collide they lose energy (often designated ΔE) and that energy goes into making X-ray photons. That energy, ΔE is related to the frequency of the X-ray radiation by Planck's Constant,

$$\Delta E = h \, \nu$$

- h = planck's constant ($h = 6.6 \times 10^{-34}$ kg·m^2·s^{-1},)
- ν = frequency of the X-ray radiation

Also recall that,
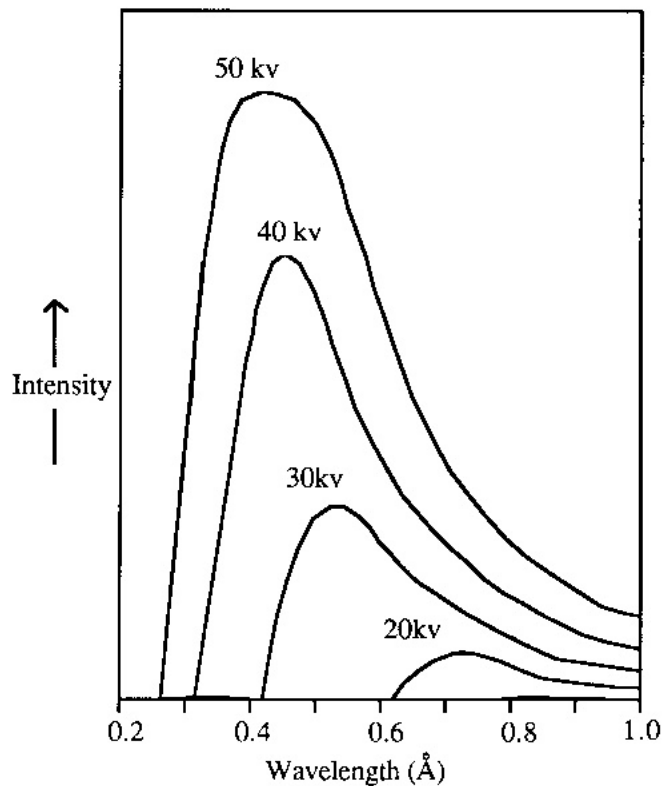
$$\nu = c \, / \, \lambda$$

- c = speed of light
- λ = wavelength

Therefore,

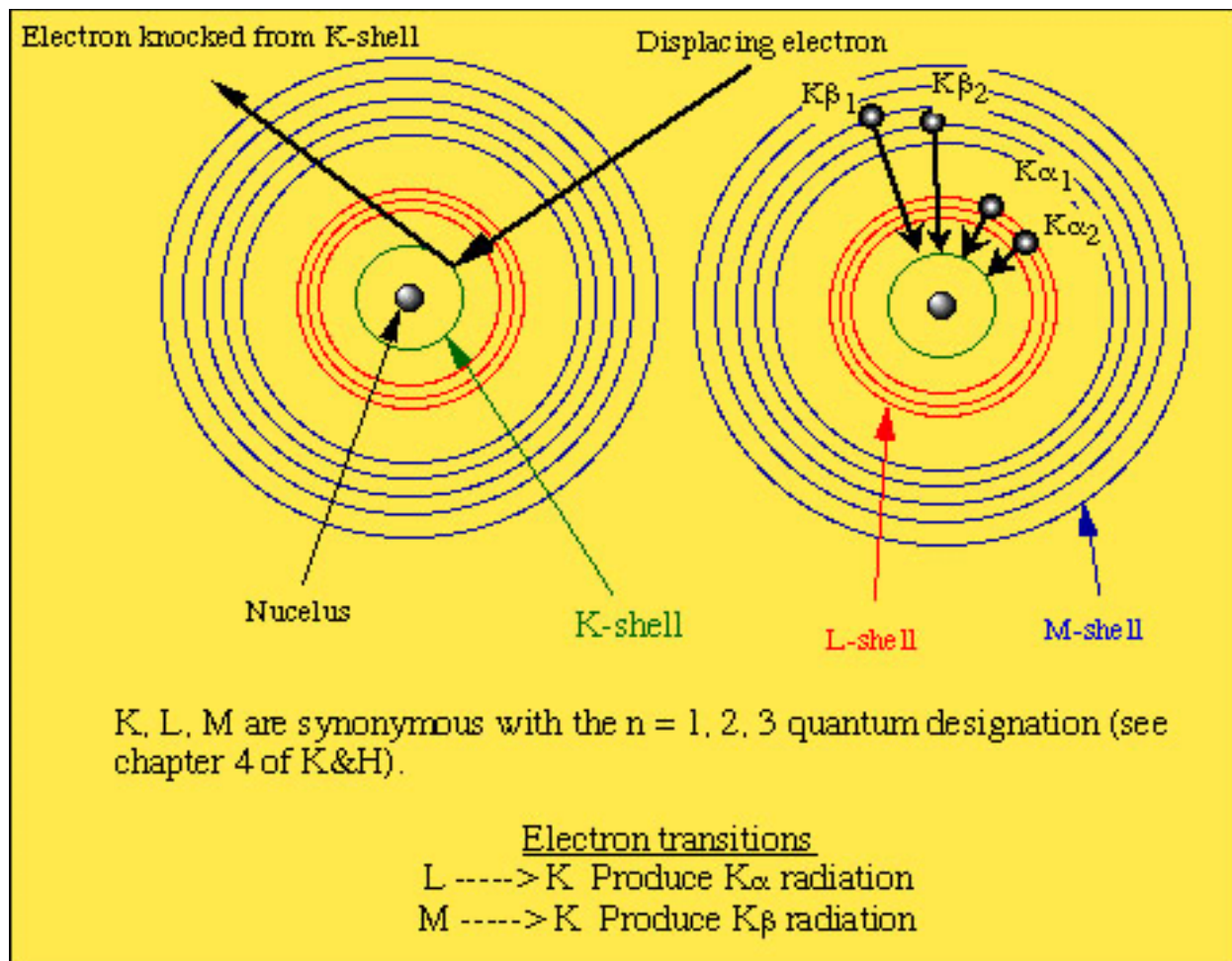$$\Delta E = h \, c \, / \, \lambda$$

The inverse relationship between energy and wavelength indicates that the wavelength of radiation becomes smaller with larger energy transitions.

White radiation intensity as a function of energy potential (voltage)

The other type of X-radiation is termed **characteristic radiation** which is characteristic of the metal target.

Recall electrons orbiting close to the nucleus are tightly bound. When source electrons strike these core shell/orbital electrons, the electrons get bounced out of position (in other words the electrons undergo an energy transition). This event is immediately followed by another electron dropping back toward the nucleus. Much like dropping a book on the desk, the release in energy appears as an emitted photon with a distinct or characteristic frequency.

Electron knocked from K-shell

Displacing electron

$K\beta_1$ $K\beta_2$

$K\alpha_1$ $K\alpha_2$

Nucelus

K-shell

L-shell

M-shell

K, L, M are synonymous with the n = 1, 2, 3 quantum designation (see chapter 4 of K&H).

Electron transitions
L -----> K Produce $K\alpha$ radiation
M -----> K Produce $K\beta$ radiation

The energy difference between electron levels are quantum amounts and the amount released will depend upon the number of protons and neutrons in the nucleus and the shell from which the electron was displaced.

In geology labs, the most common targets used are copper and cobalt.

Since there are only two possible sites in the L shell (quantum number $n = 2s$) of a copper atom, we have two slightly different energy transitions (i.e. L --> K or $2s$ --> $1s$) : $K\alpha_1$, from the outer most L shell and $K\alpha_2$.

The result is the production of very intense monochromatic radiation. This is the radiation that we take advantage of when doing X-ray crystallography.
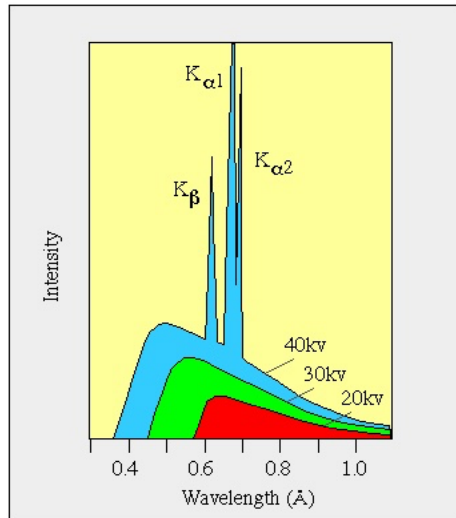
Diffraction Effects

What are some common examples of diffraction effects?

1. rainbow from the film of oil on water

2. intersection of ripples on a pond.

The essential feature for the diffraction phenomenon is that the distances between the scattering points is of the same magnitude as the wavelength of the waves being scattered.

What is the typical repeat distance for a crystal unit cell? (about 5-10 Å).

Wavelength of $Cu\alpha_1$ = 1.54059 Å

When a monochromatic X-ray strikes a crystal, the X-rays are scattered by the electron clouds of the atoms in the crystal.

There are three ways in which the scattering (*i.e.*, the re-radiation of electrons) is modified;

1. The type of atom (*e.g.*, Fe verses Mg)

2. Thermal vibrations of the atom center (blurs the atoms as scattering centers).

3. The arrangement of atoms.

Scattering - The incident beam (λ) interacts with the vibrating atom. Characteristic radiation is re-radiated in all directions as a spherical wave front.
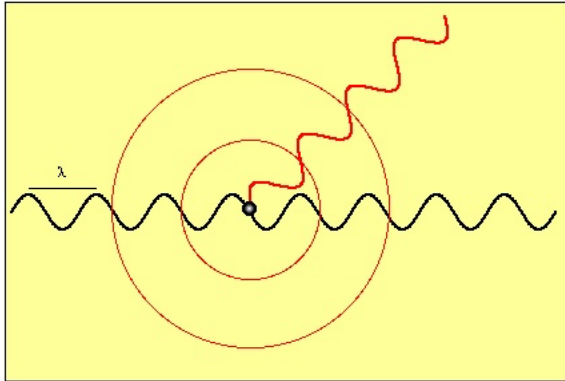
When the re-radiated waves are in resonance with the incident radiation then they are reinforced. This is termed coherent scattering.

Incoherent scattering occurs when the wavelengths (λ) of the wave fronts are different from the incident λ.
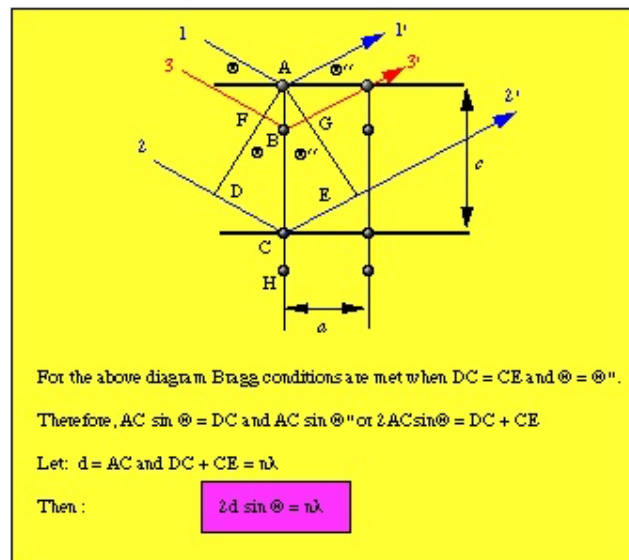

Case for atoms in a lattice - Now imagine a row of atoms centers scattering X-rays. Note: coherent scattering only exists in integral numbers of wavelengths (nλ). i.e., 1 λ, 2 λ, 3 λ, 4 λ ....
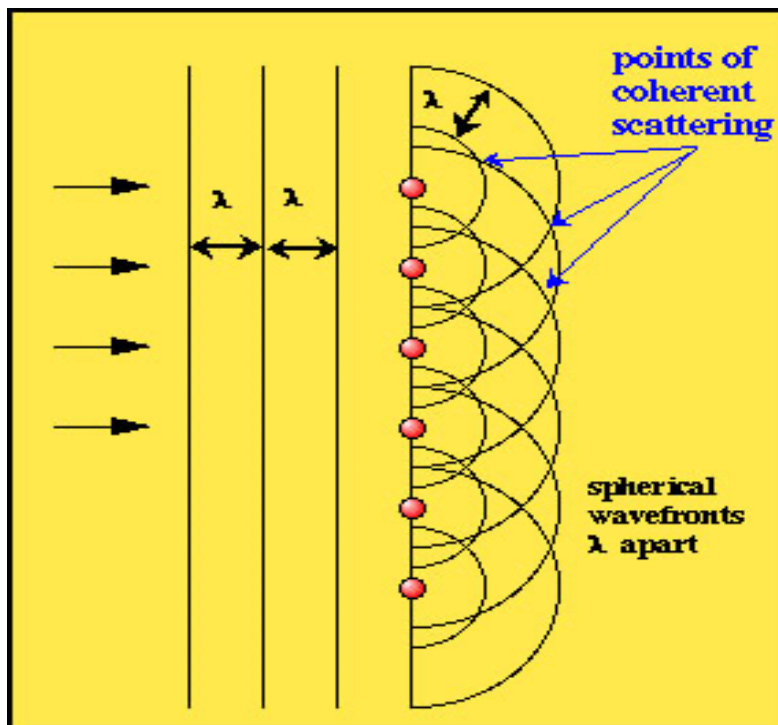
For each unit cell there is an incident beam that is diffracted and emanates from the cell. The conditions for diffraction call for constructive interference only at points that an integral number of the wavelength.

Bragg's Law

If we consider an incident beam approaching scattering centers at some angle (θ), it can be shown that the only place the scattered beam will be in phase is at the same or "reflected" angle that leaves the scattering points.

For the above diagram Bragg conditions are met when DC = CE and Ө = Ө".

Therefore, AC sin Ө = DC and AC sin Ө" or 2ACsinӨ = DC + CE

Let: d = AC and DC + CE = nλ

Then: 2d sin Ө = nλ

Geometrically, the conditions of constructive interference are met only when DC = CE therefore,

θ = θ' and AC = DC sin θ.

Under these conditions there is zero path length difference between rays 1 and 2.

Unlike light, which can be reflected at all angles, X-rays are "reflected" only at specific angles.

The wave fronts that pass through a crystal must have path-length-differences exactly 1,2,3...n integers away or they will destructively interfere.

Compare Rays 1 and 3.

Note path length difference into the plane of atoms is the distance FB + BG.

This additional distance must be equal to some integer distance (i.e., FB + BG = nλ), but it does not.

Note that the distance AC is the interplanar d-spacing.

Under "reflecting" conditions then $\theta = \theta'$ and $\sin \theta = \underline{AC} / \underline{DC}$ and $\sin \theta' = \underline{AE} / \underline{CE}$

Let: $d = AC$ and $n\lambda = \underline{DC} + \underline{CE}$

then: $2AC \sin \theta = \underline{DC} + \underline{CE}$

By substitution, we get Bragg's law.

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