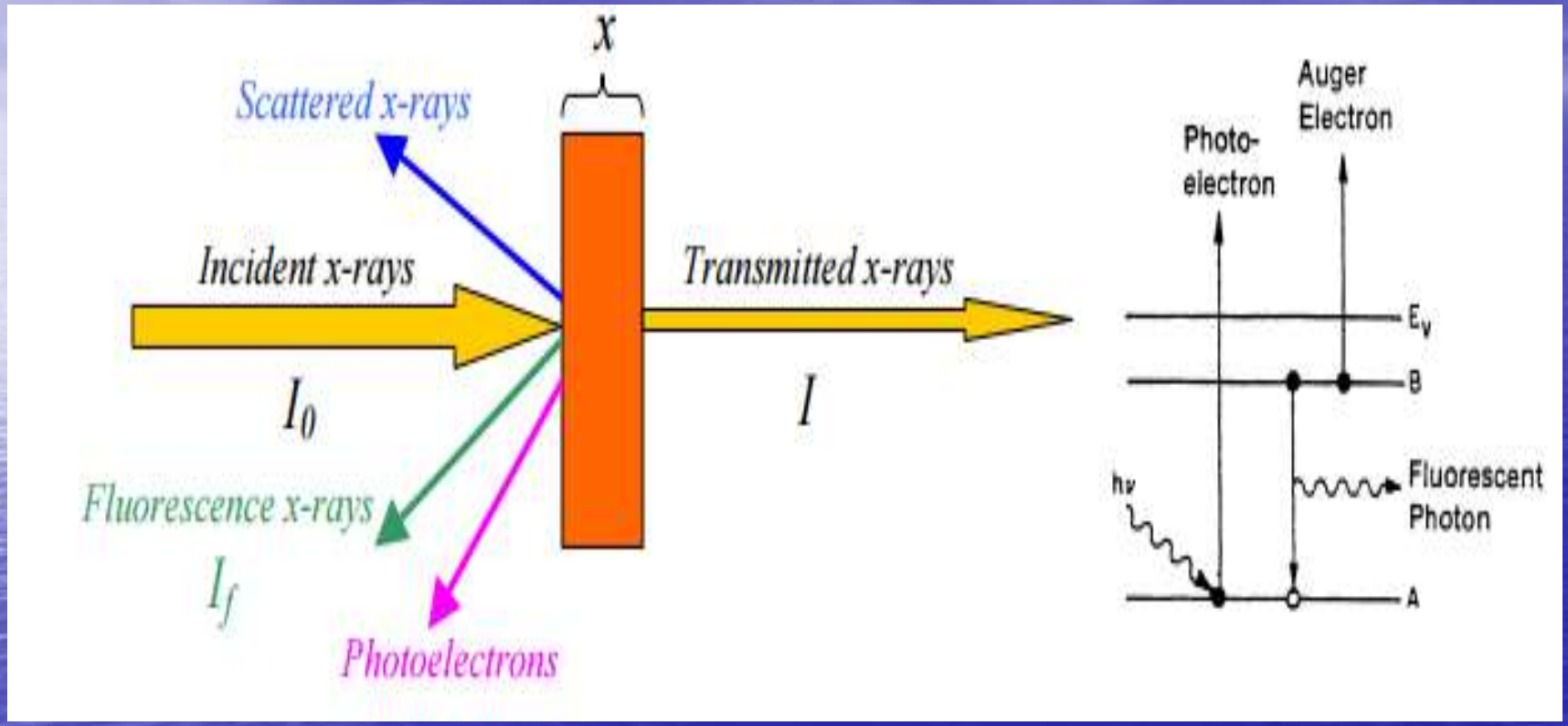
X-ray spectroscopy

is a form of optical spectroscopy that utilizes emission, absorption, scattering, fluorescence, and diffraction of X-ray radiation

1- X-ray Absorption Spectroscopy (XAS)

When the X-rays hit a sample of pure metal, the oscillating electric field of the electromagnetic radiation interacts with the electrons bound in an atom. Some of the radiation is absorbed and excite the electrons and the remainder either will be scattered by these electrons, or is transmitted.

- Absorption varies with atomic weight


x
Scattered x-rays
Incident x-rays
Transmitted x-rays
I_0
I
Fluorescence x-rays
I_f
Photoelectrons
Auger
Electron
Photo-
electron
E_V
B
hν
Fluorescent
Photon
A

A narrow parallel monochromatic X-ray beam of intensity I_0 passing through a sample of thickness x will get a reduced intensity I according to the expression:

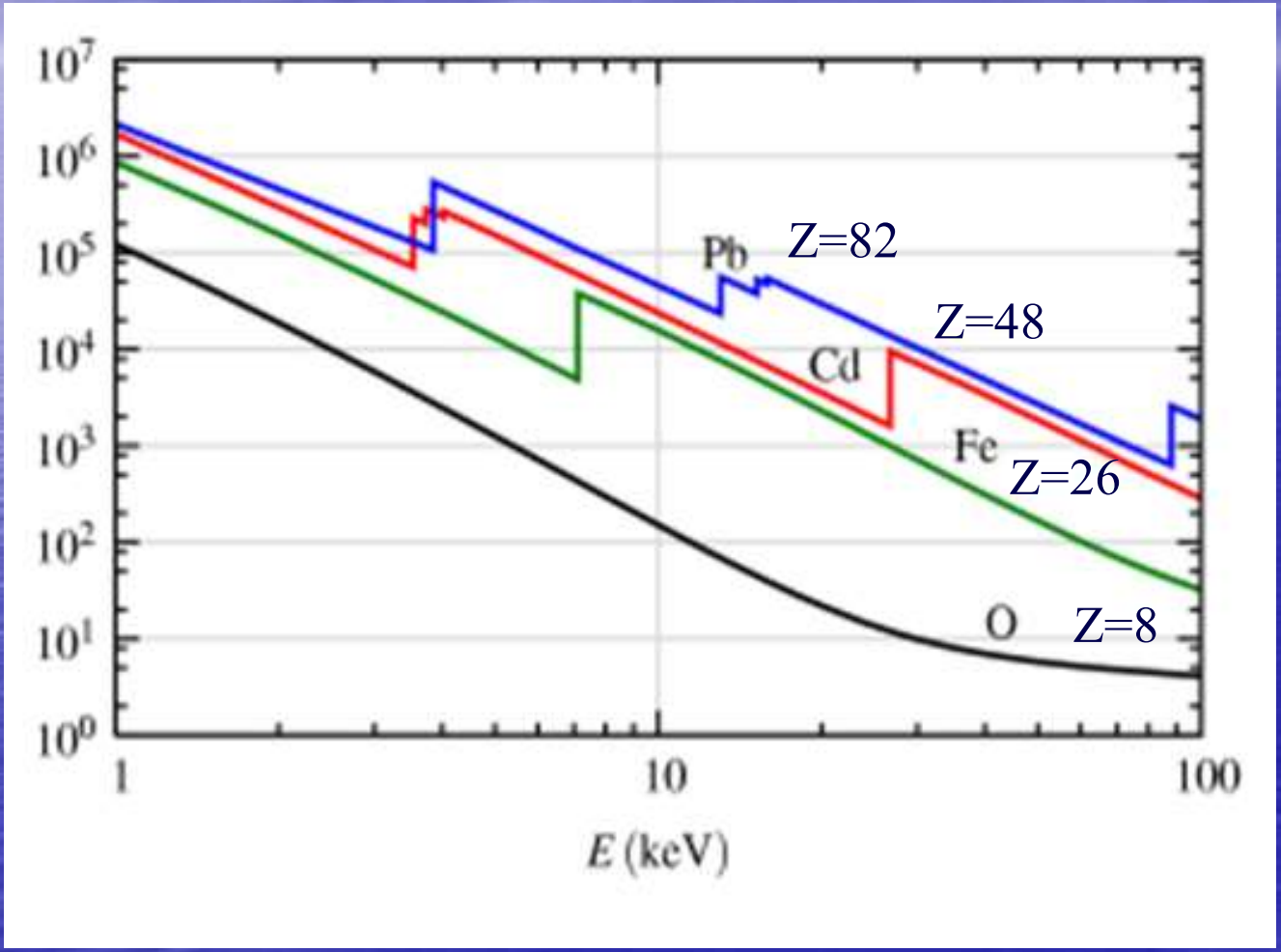
$$\ln (I_0 / I) = \mu x$$

The absorption coefficient μ, depends strongly on:

1- the X-ray energy E
2- the atomic number of the absorbing atoms Z,
3- the density ρ,
4- atomic mass m

μ increases with atomic number Z (more electrons)

μ



From Beer's Law

$$I(\lambda) = I_o(\lambda)e^{-\mu_m \rho x}$$

$I(\lambda)$ = transmitted intensity at wavelength λ

$I_o(\lambda)$ = incident intensity at wavelength λ

μ_m = mass absorption coefficient (cm^2/g)

ρ = density of sample (g/cm^3)

x = sample thickness (cm)

Q1: What would be the intensity of the transmitted beam (I_t) of Cu Kα radiation if the Be foil was 1 mm thick and the mass absorption coefficient was 1.11 cm2/g and density was 1.85 g/cm3

Sol.:

$$I_t = I_0 e^{-\mu_m \rho x}$$

$$I_t = 100 * e^{-1.11 \cdot 1.85 \cdot 0.1}$$

$$\boxed{I_t = 81.4\%}$$

Q2: What thickness of Be foil would be required to attenuate a Cu Kα radiation by 50 % if you know that the mass absorption coefficient of Be for Cu Kα X-ray beam is 1.11 cm2/g and density is 1.85 g/cm3

Sol.:

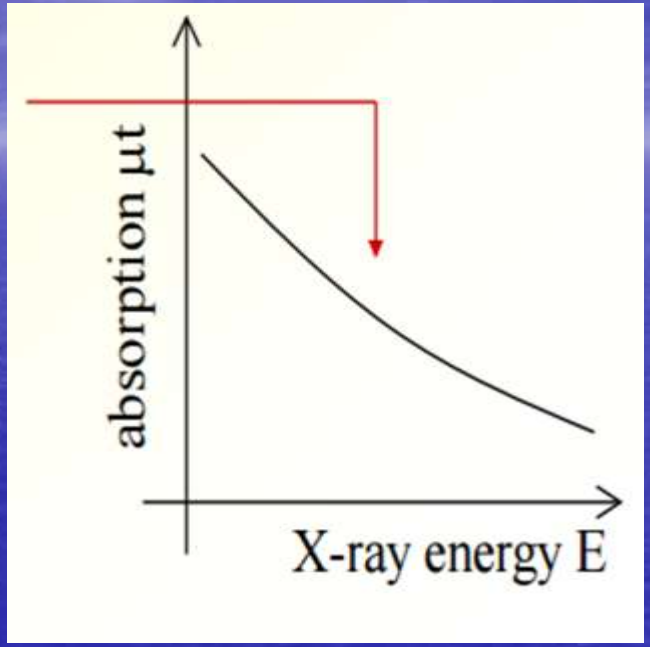
$$I_t = I_0 e^{-\mu_m \rho x}$$

$$\frac{I_t}{I_0} = 0.5 = exp - (1.11 \times 1.85 \times x)$$

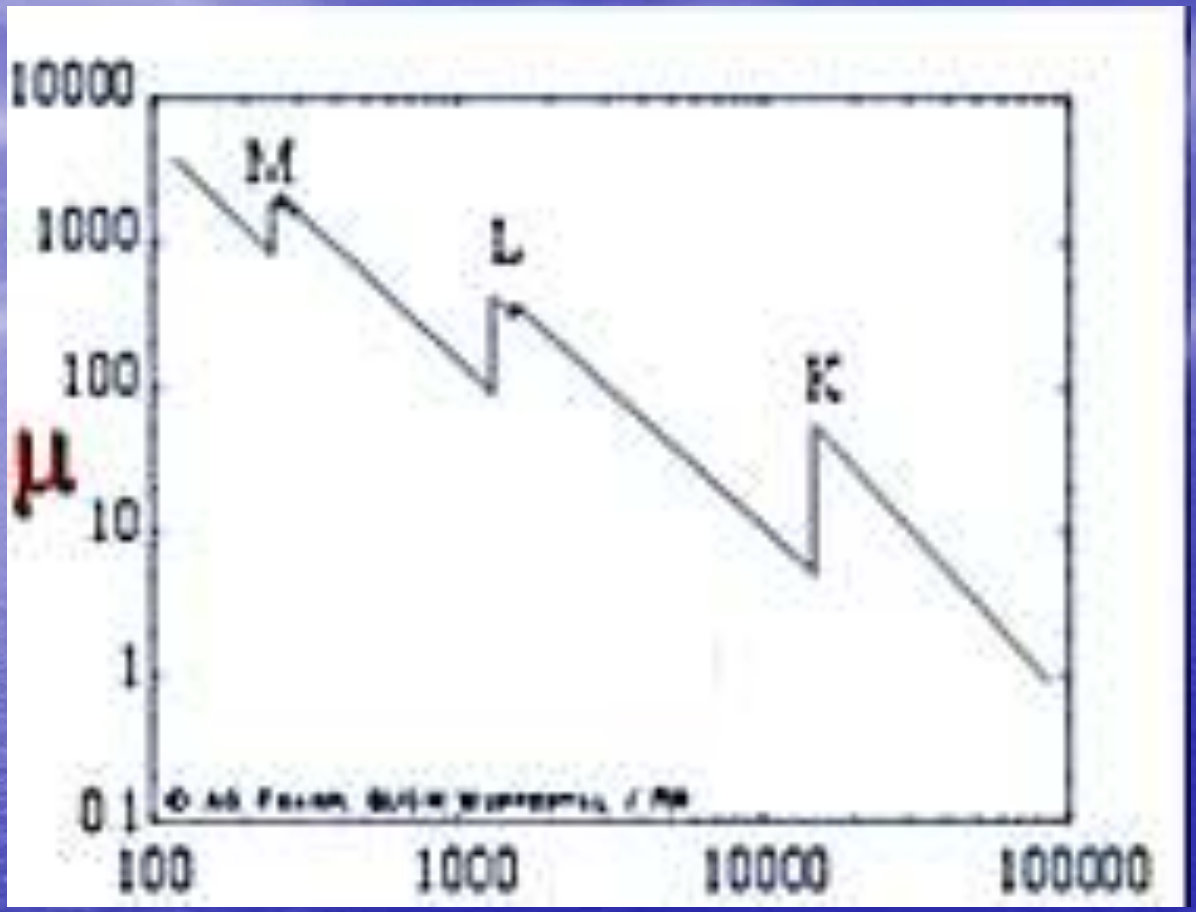
$$ln 0.5 = -2.054 \times x$$

$$x = 0.337 \text{ cm}$$

- Absorption spectroscopy: measure μ as a function of energy E
  - μ decreases with E increasing (X-ray more penetrating)
  - Longer λ are more readily absorbed than shorter λ
  - Amount of absorbed light increases with increasing λ
  - Absorption spectrum is unique for each element



At certain energies where the absorption increases drastically, and gives rise to an absorption edge. Each such edge occurs when the energy of the incident photons is just sufficient to cause excitation of a core electron of the absorbing atom, i.e. to produce a photoelectron. Thus, the energies of the absorbed radiation at these edges correspond to the binding energies of electrons in the K, L, M, etc, shells of the absorbing elements.



photon energy

- energy of absorption edge E_0 is unique for each element

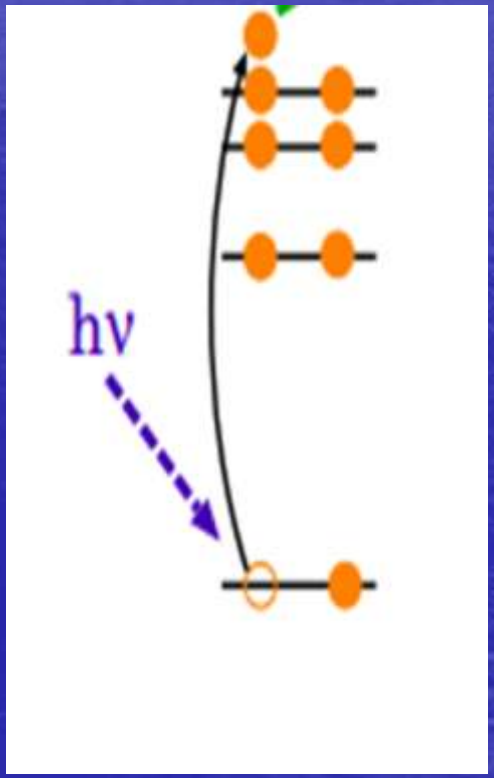
2- X-RAY FLUORESCENCE (XRF)

-X-ray is absorbed by an atom

-Energy is transferred to a core electron

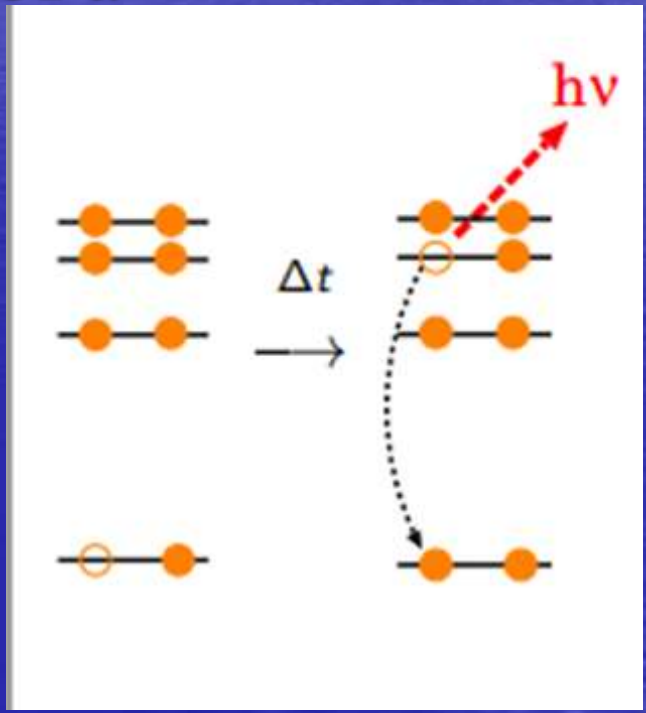
- Electron become excited

- Ion remains with a core-hole



-An ion with a core-hole is quite unstable After a short time ($\approx 10^{-15}$s) a higher level electron will drop down in energy to fill the core hole

- Energy is liberated in the form of a fluorescence photon



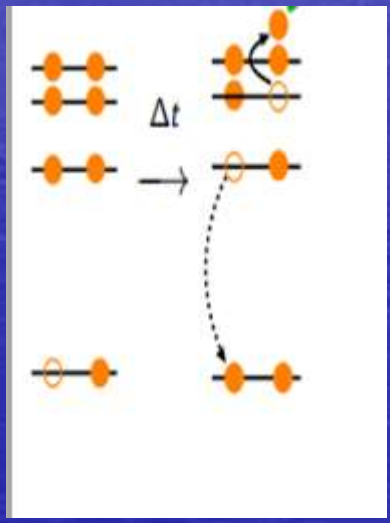
This leaves a second hole (not core) which is then filled from an higher shell . The result is a cascade of fluorescence photons which are characteristic of the absorbing atom

3- Auger Electron Spectroscopy(AES)

The emitted X-ray photon from the target atom can eject another electron of the same atom called Auger electron.

For example, Auger electron eject from M shell by Kα photon , in this case the electron has kinetic energy equal to :

$E_{Auger} = h\upsilon K\alpha - E_M$

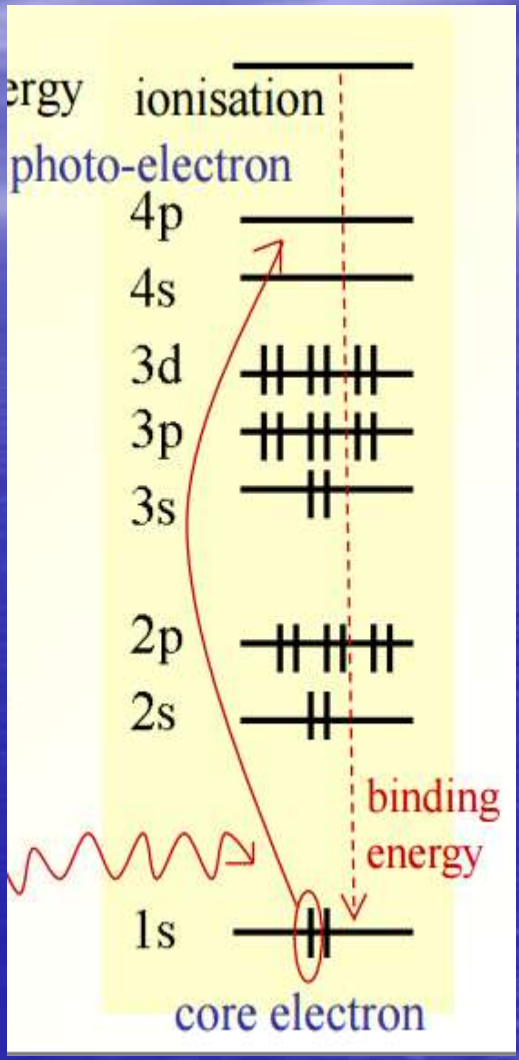


For light materials (small atomic numbers than 70), there is competition between the X-ray emission and Auger electron emission . While heavy materials (large atomic number greater than 70), the effect of Auger is neglected.

By the measurement of the intensity of Auger electrons that result as a function of the Auger energy , the resulting spectra can be used to determine the identity of the emitting atoms and some information about their environment such as the percentage of impurities in materials.

4- X-ray photoelectron spectroscopy (XPS)

Because X-rays are higher in frequency and energy than UV rays, hitting them on a sample can provide enough energy to eject core electrons. Core electrons are inner-shell electrons that are closer to the nucleus, and thus require more energy to remove compared to valence electrons .Once electrons are ejected from the sample, a detector is able to calculate the kinetic energies of the electrons

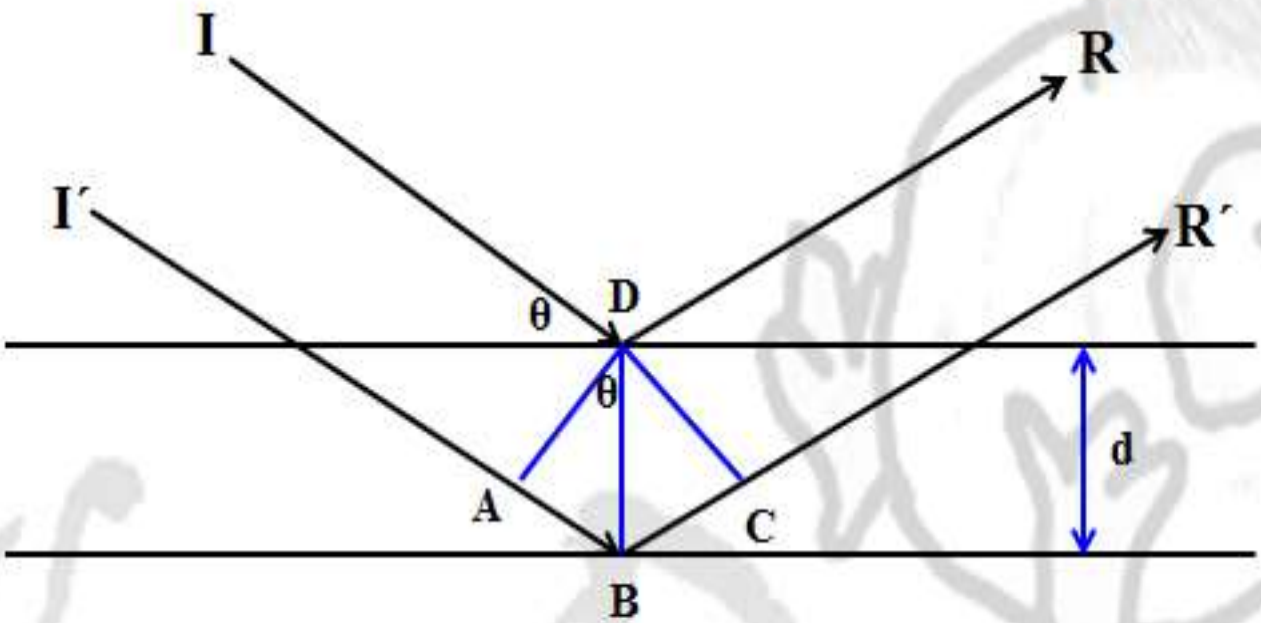


The frequency and energy of incident photons can be used to calculate the binding energy of the ejected electron using the following equation: $BE = hv - KE_{electron}$, as well as the relative number of electrons with that kinetic energy. We can use this information to calculate the minimum energy required to remove electrons from different subshells within an atom. This is called the binding energy of the electron, and the binding energies depend on the chemical structure and elemental composition of a sample

5- X-RAY DIFFRACTION (XRD)

- Basis is diffraction of X-rays by crystals
- Depends on the crystal properties of solids
- Just like how light is diffracted by diffraction grating
- Diffraction pattern can be used to determine atomic spacing in crystals
- Used for the determination of the arrangement of atoms in crystals (that is the crystal structure; X-ray crystallography)
- Useful for solid crystalline materials (alloys, polymers, metals)

Diffraction of X-rays by a crystal



- θ = angle of incidence

- d = distance between lattice planes (interplanar distance)
- Incident waves (I and I′) are in phase with each other

- Reflected waves (R and R′) should also be in phase with each other
- The waves interfere destructively if they are out of phase

- A beam of X-ray is reflected at each layer in a crystal if the spacing between the planes (d) equals the λ of radiation

- The wave I′ travels an extra distance AB + BC

- AB + BC must be a whole number (n) of wavelengths for the waves R and R′ to be in phase (for reinforcement to take place)

- Distance AB + BC = $n\lambda$

$AB + BC = 2AB$

$AB = BD\sin\theta = d\sin\theta$

$n\lambda = 2d\sin\theta$ (called the Bragg Equation)

Q1: The second order diffraction for a certain crystal was 18.4 degrees using X-rays with a wavelength of 1.42 A°.What is the interplanar spacing of atoms in this crystal?

Sol.

1 A° = 1× 10^{-10} m = 100 pm

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

$$d = \frac{n\lambda}{2\sin\theta} = \frac{2(1.42\text{A°})}{2\sin(18.4°)}$$

= 4.50 A°

= 450 PM

Q2:The spacing between planes of atoms in crystal ABC was found to be 1.28 A° using an X-ray wavelength of 122 pm .Assuming second order diffraction, what should be the angle at which the X-rays will be reflected across the surface of the crystal?

Sol.:

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

$$\text{Sin}\,\theta = \frac{n\lambda}{2d} = \frac{2(122)}{2(128)} = 0.9531$$

$$\theta = \sin^{-1}(0.9531)$$

$$= 72.38°$$