



Analytical Methods for Materials

Lesson 6

Production & Properties of X-rays

Suggested Reading

Chapter 1 in Waseda et al.

Section 2.1 in Leng

Other Reference

B.D. Cullity and S.R. Stock, *Elements of X-ray Diffraction, 3rd Edition* (Prentice Hall, 2001) Ch. 1

Electromagnetic Spectrum

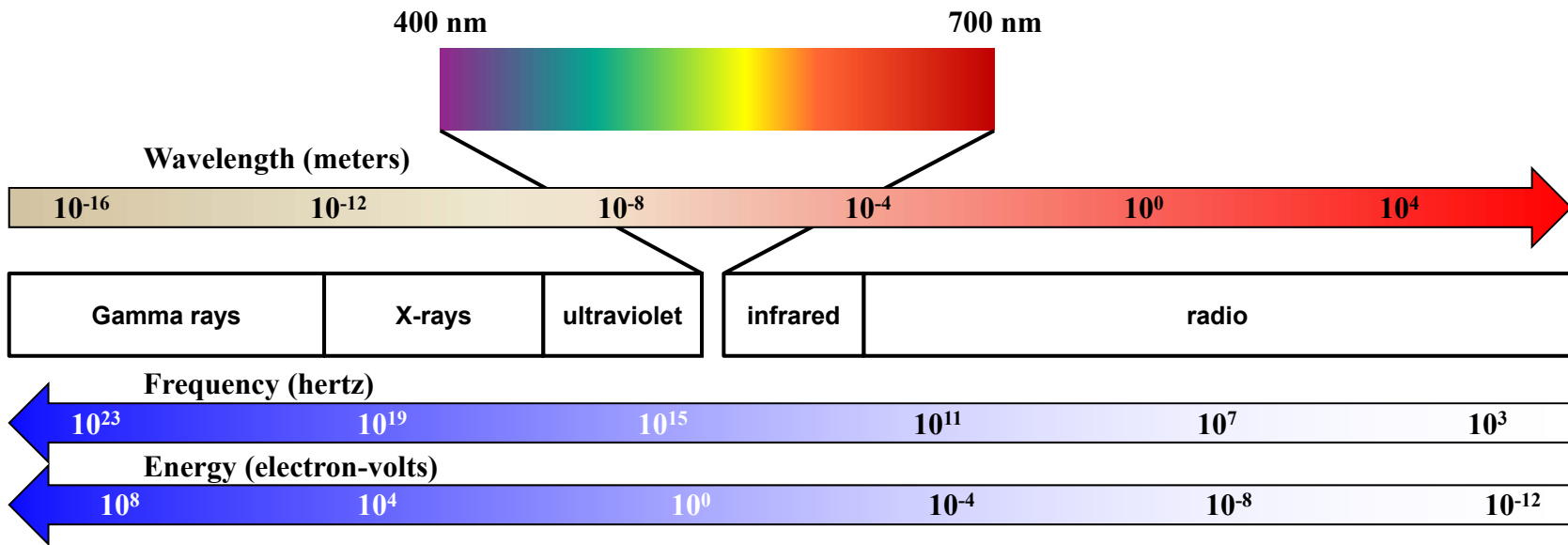
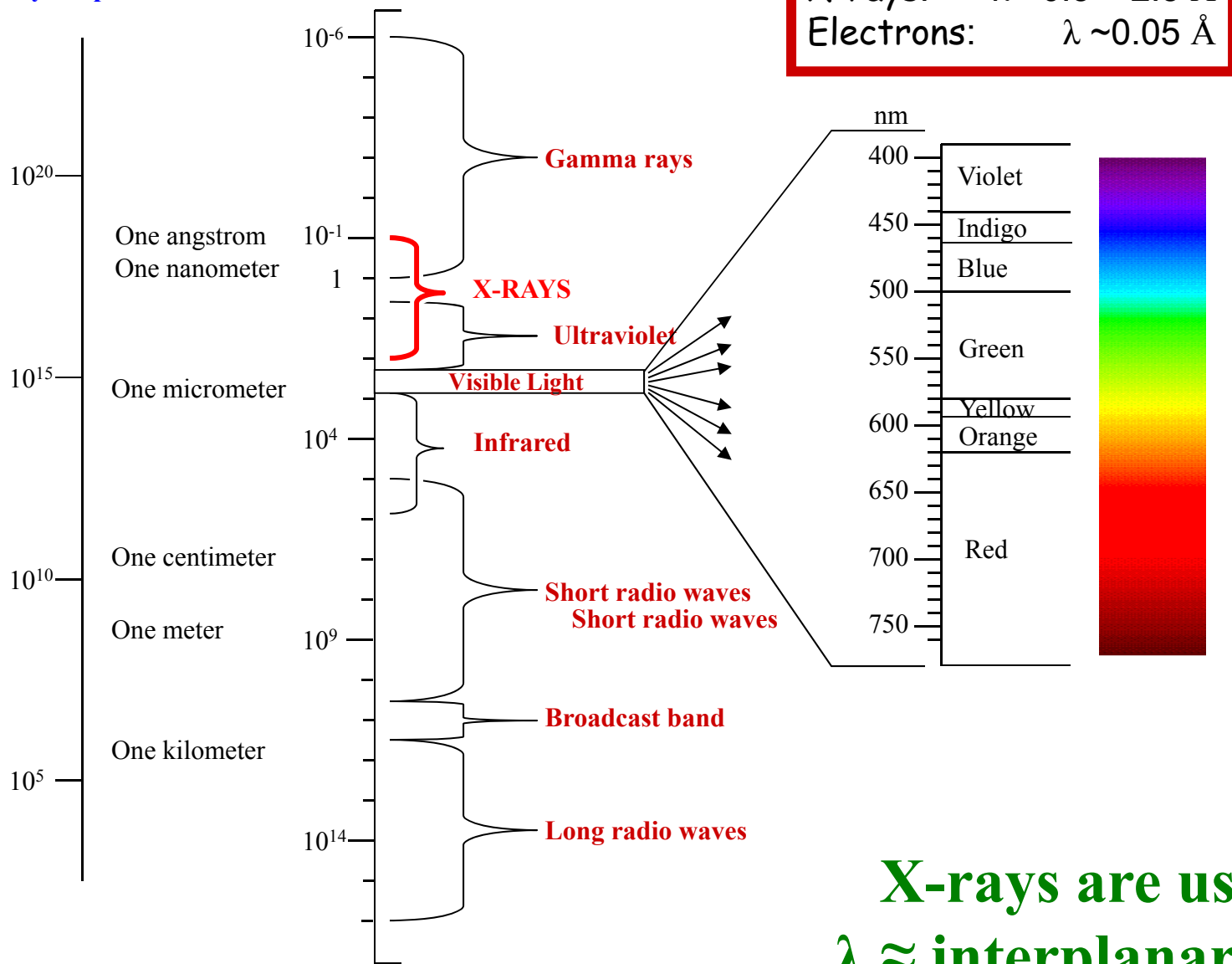


Figure modeled after

http://mrbarlow.files.wordpress.com/2007/09/em_spectrum.jpg

Frequency in
cycles per second

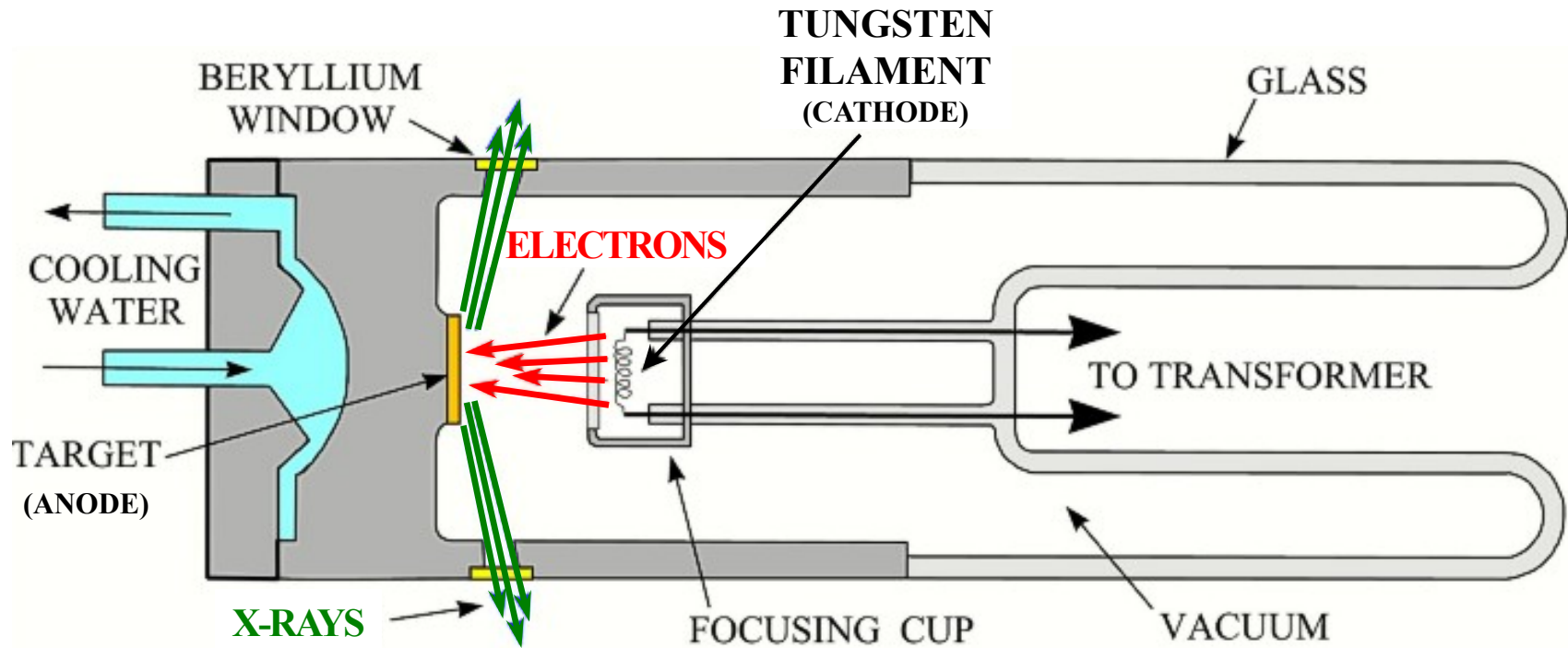
Wavelength
in nm



**X-rays are useful b/c
 $\lambda \approx$ interplanar spacings**

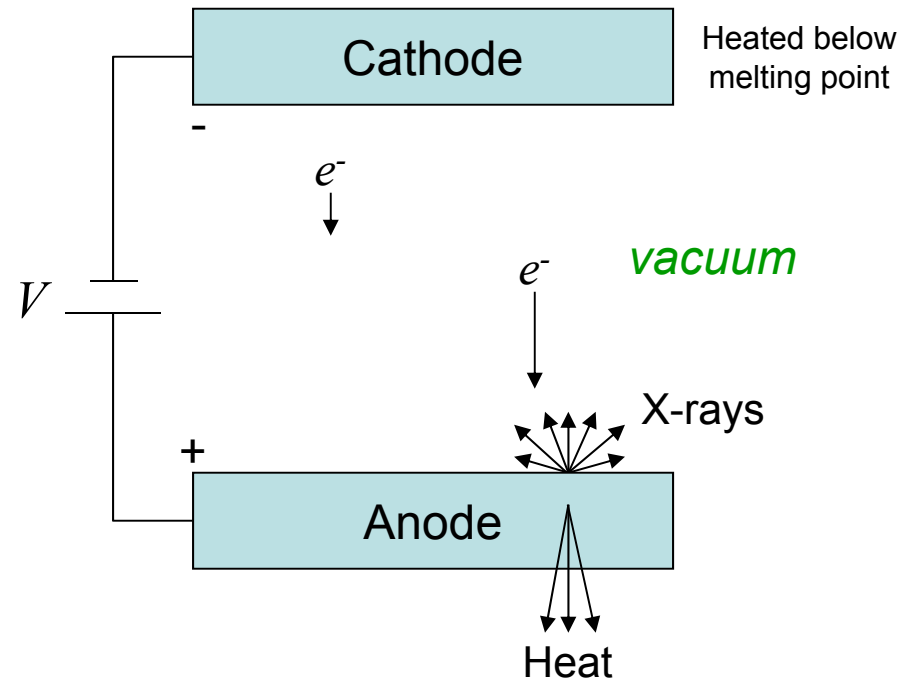
**Spectrum of electromagnetic radiation as a
function of frequency (s^{-1}) and wavelength (nm).**

X-ray Tube



X-ray Production

- Heat a suitable cathode to a high temperature and apply a voltage, V , between the cathode and anode.
- The electric field ($E = V/x$, where x is the spacing between the electrodes) pulls electrons with the highest energies out of the cathode and accelerates them towards the anode.
- The electrons rapidly decelerate when they strike the anode.



X-ray Production – cont'd

- Potential energy of electron: $E = eV$
- At the anode, electron is accelerated to maximum velocity (v^*). Potential energy is converted to kinetic energy. $E = eV = \frac{1}{2}m[v^*]^2$
- Electrons will either lose some or all of their energy at impact with the anode (target).
- 1% of the kinetic energy is transferred to atomic and conduction electrons which are excited into higher energy levels. When they revert back to their original energy levels, they emit X-rays.

X-ray Production – cont'd

- If electrons lose all energy at impact (elastic collision), an X-ray of minimum wavelength is generated:

$$E = eV = h\nu = \frac{hc}{\lambda}$$

$$E_{\max} = \frac{hc}{\lambda_{\min}} = \frac{1}{2}m[v^*]^2 = e_e V$$

∴

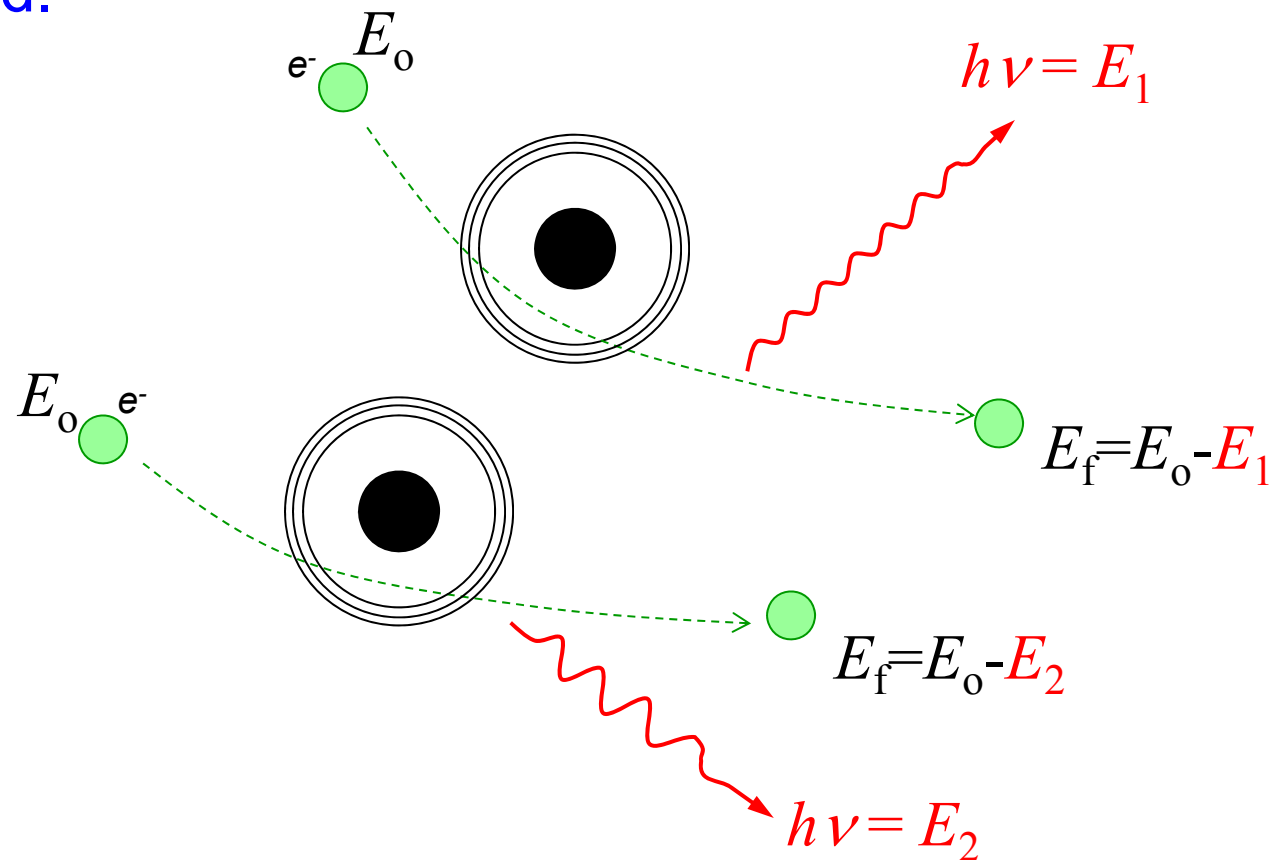
$$\lambda_{\min} = \boxed{\lambda_{SWL}} = \frac{hc}{e_e V} = \frac{(6.626 \times 10^{-34})(3 \times 10^8)}{(1.6022 \times 10^{-19})V} \cong \boxed{\frac{12.43}{V} \text{ (}\overset{\circ}{\text{A}}\text{)}}$$

- This is called the short wavelength limit!

(kV)

X-ray Production – cont'd

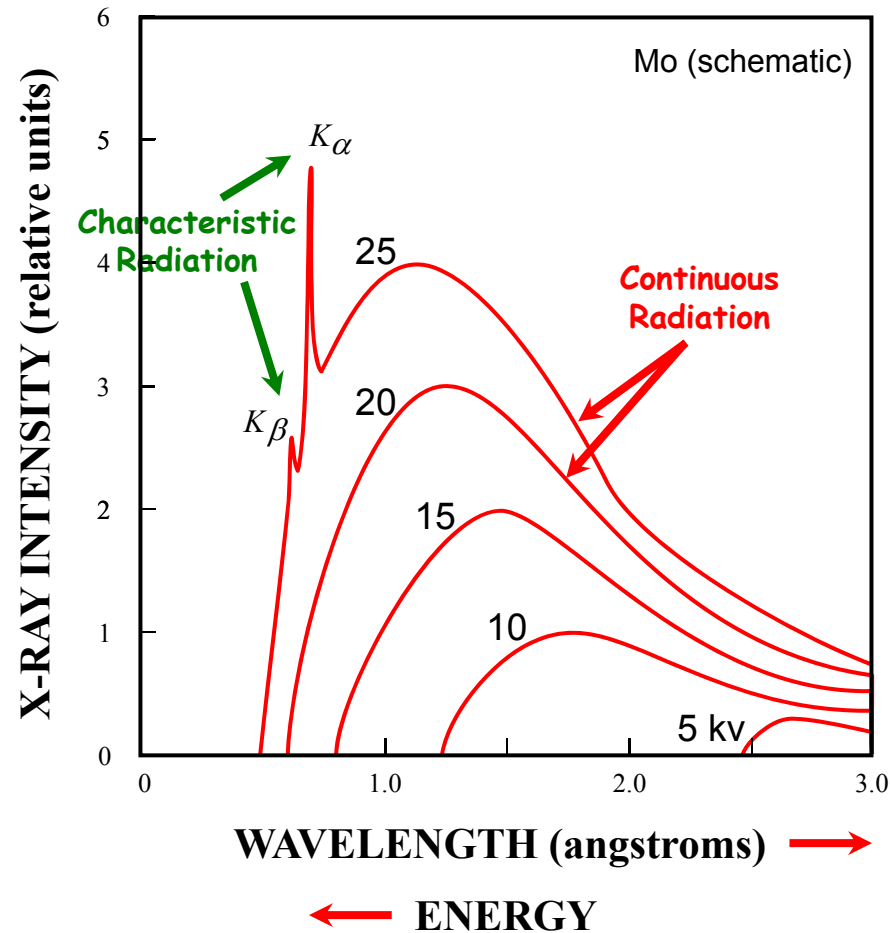
- When an incident electron loses a fraction of its energy as opposed to all energy, an X-ray of longer wavelength ($\lambda > \lambda_{\text{SWL}}$) is produced.



- This is known as white or continuous radiation!



X-ray Emission Spectrum

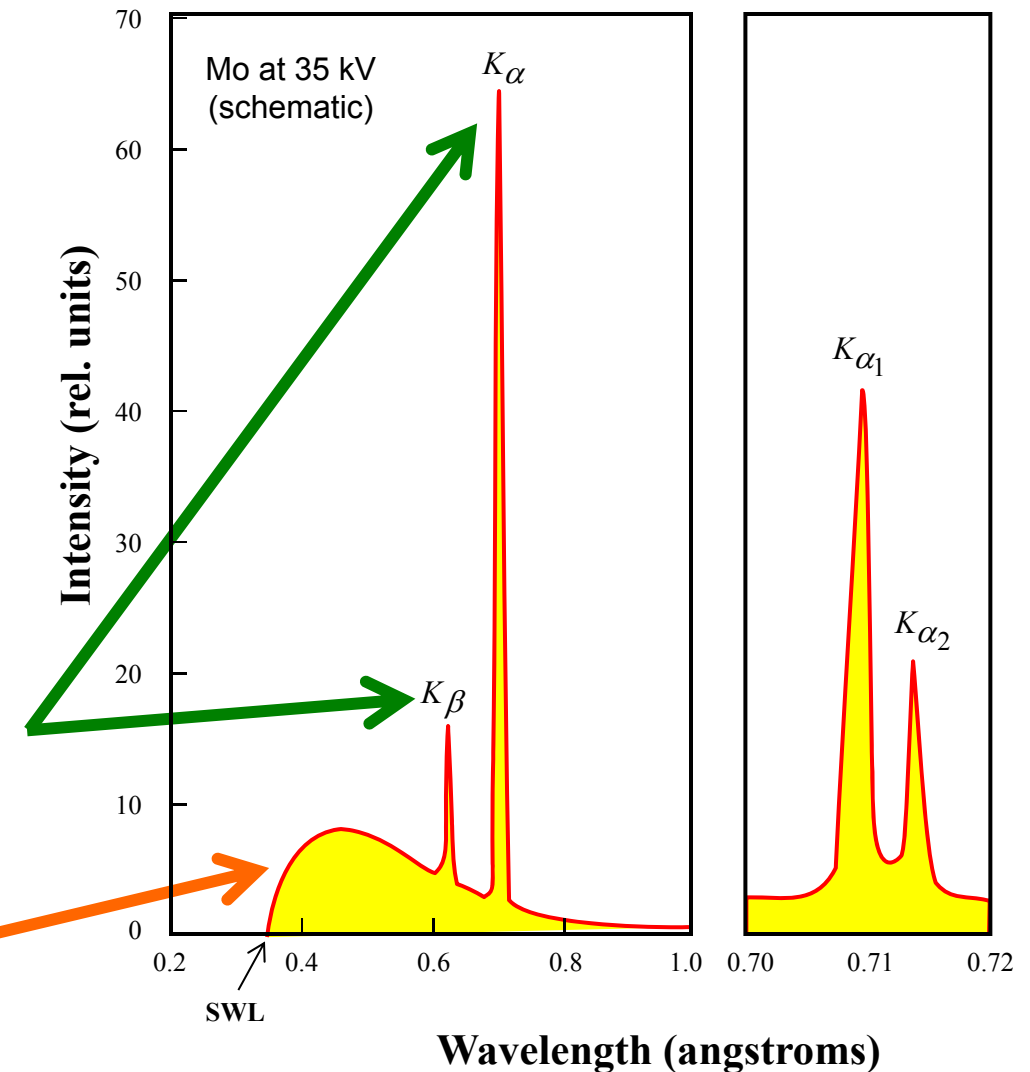


$$\lambda_{SWL} = \frac{hc}{e_e V}$$

- All features vary with incident energy (*i.e.*, accelerating voltage) and target material.

X-ray Spectrum

- X-rays result from fast electron irradiation of metal targets (Cu, Co, Cr, Mo) under vacuum.
- Types of X-rays:
 - **Characteristic**: X-rays from core-level ionization.
 - **Continuous / Bremsstrahlung**: “white” or “braking” radiation from deceleration of electrons.



Continuous Spectrum

- Recap:
 - Different electrons lose energy in different ways.
 - Some lose all of their energy in one collision
 - Some will be deflected and lose some of their total energy until all is used up.
- Result:
 - X-rays can be produced with a wide range of energies and wavelengths.
- The broad hump occurs where there is the most probable energy loss.

Intensity of the Continuous Spectrum from Target

$$I_{cs} = AiZV^m$$

where,

$A, m =$ constants

$i =$ current

$Z =$ atomic number

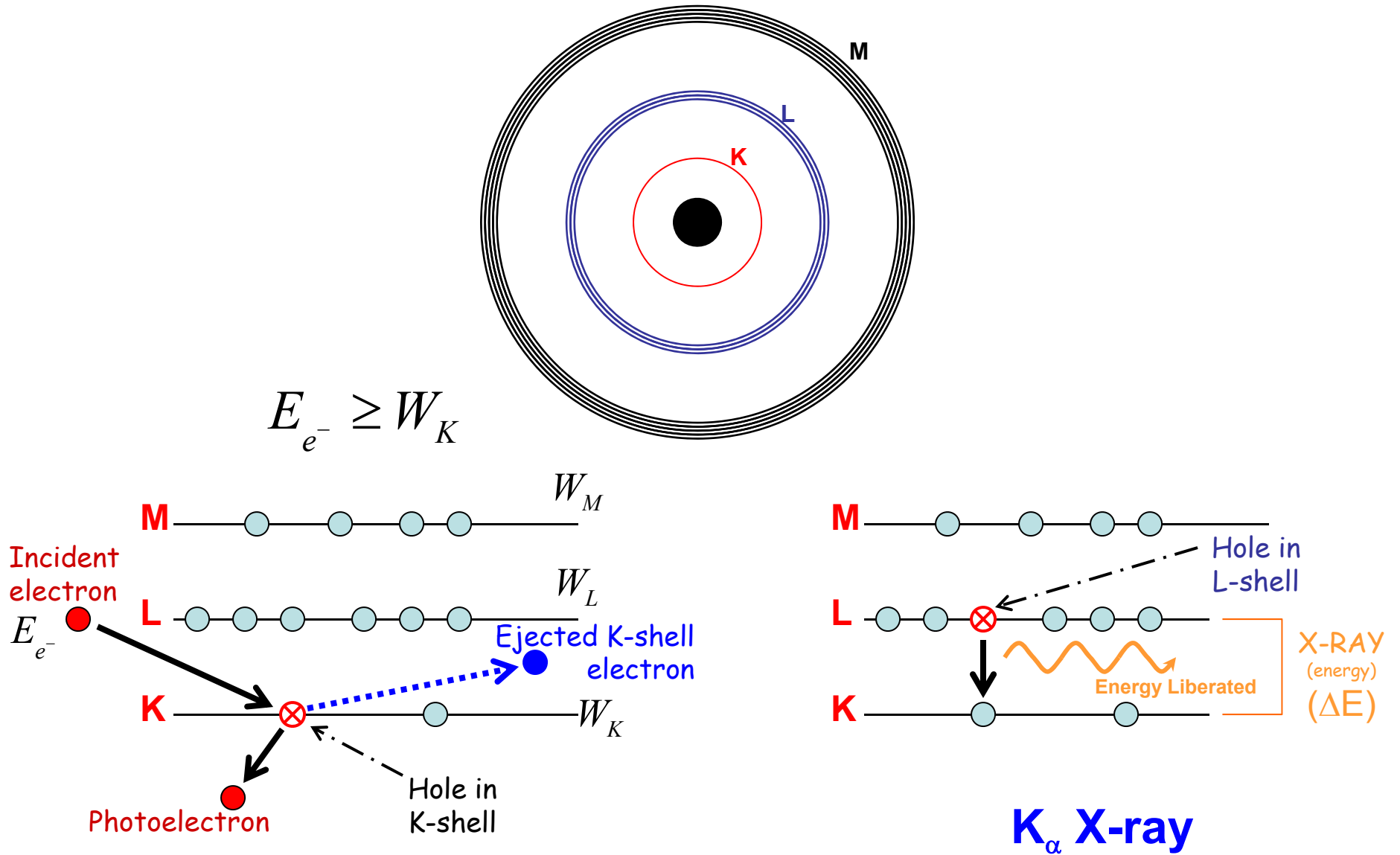
$V =$ accelerating voltage

Higher atomic number (Z) elements and high voltages are required to generate high intensity X-rays

The Characteristic Spectrum

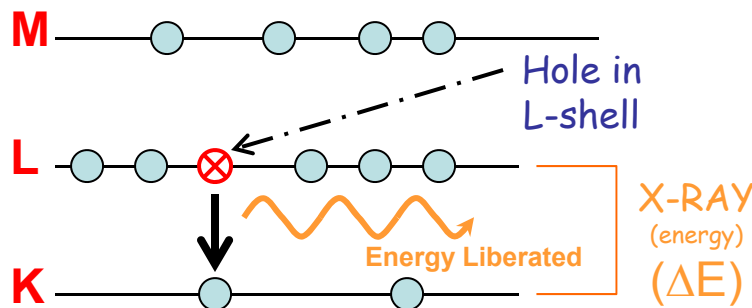
- What if incident e^- 's have enough energy to knock inner shell electrons from their orbits (*i.e.*, to cause core-level ionization)?
- This leaves the atom in an excited state.
- An electron from a higher energy level can fall into the lower energy state emitting an X-ray with a characteristic energy/wavelength.

Origin of the Characteristic Spectrum



X-ray Energy

- Equal to the difference between the energy of the incident electron and the binding energy of the electrons in their shells/orbitals.

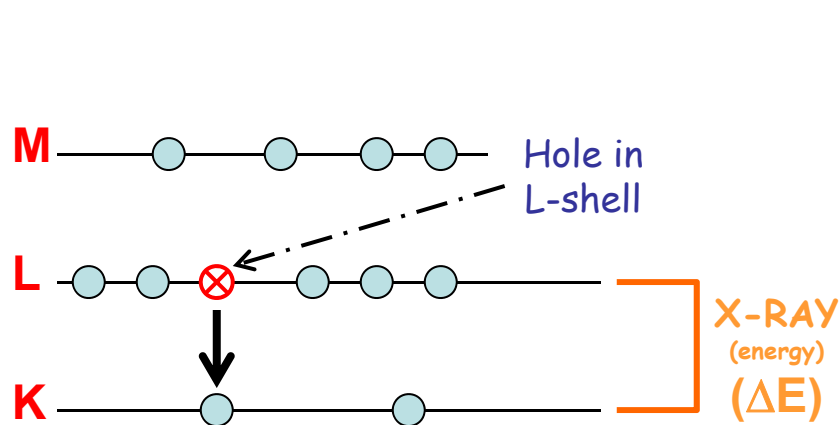


Characteristic X-ray Emission

$$E_{x\text{-ray}} = W_L - W_K$$

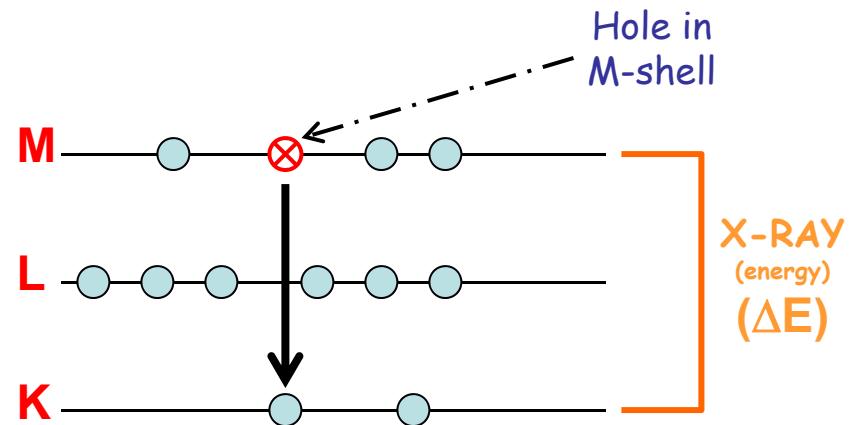
Type of X-ray will depend upon orbitals

K_{α} and K_{β} Radiation



K_{α} X-ray

$L \rightarrow K$



K_{β} X-ray

$M \rightarrow K$

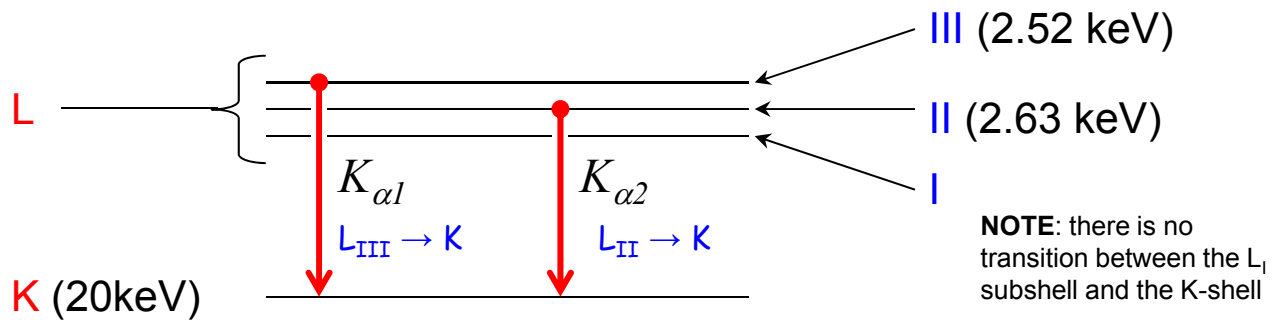
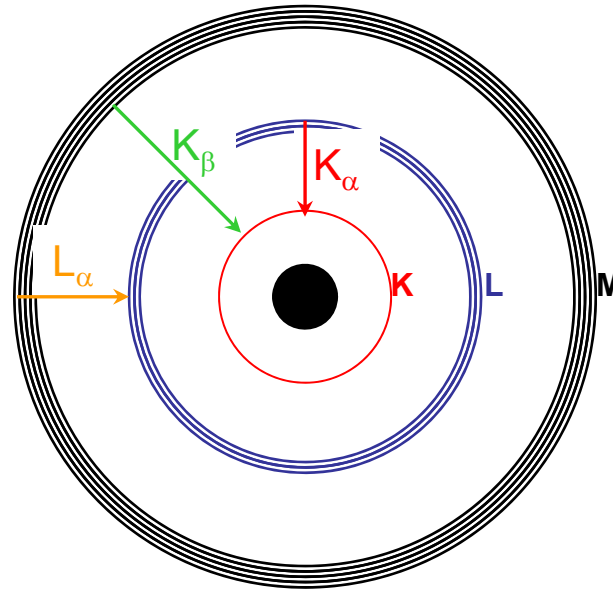
X-ray radiation is *characteristic* of the energy liberated during the electron transition

The Characteristic Spectrum

Shells and sub-shells have different energy levels

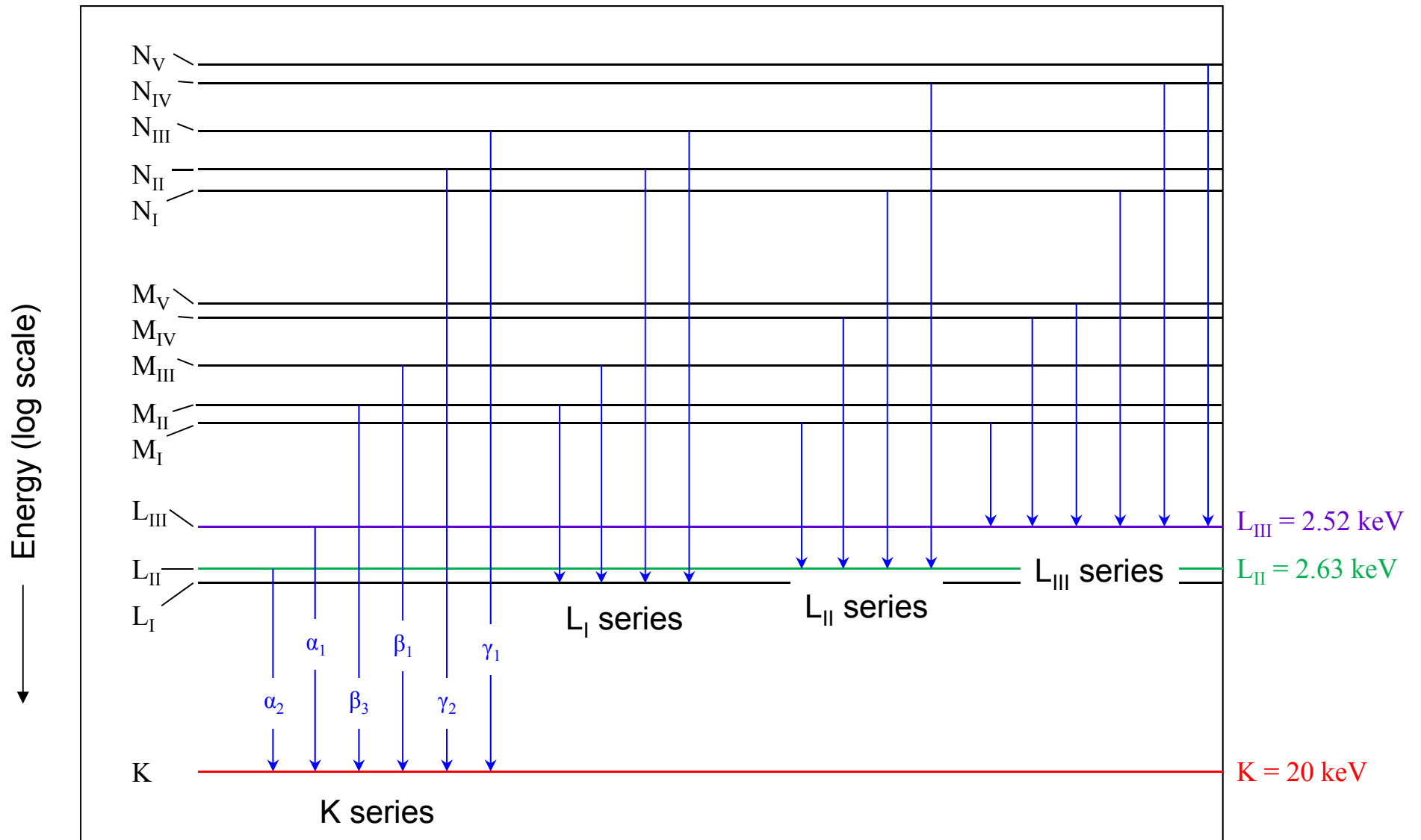


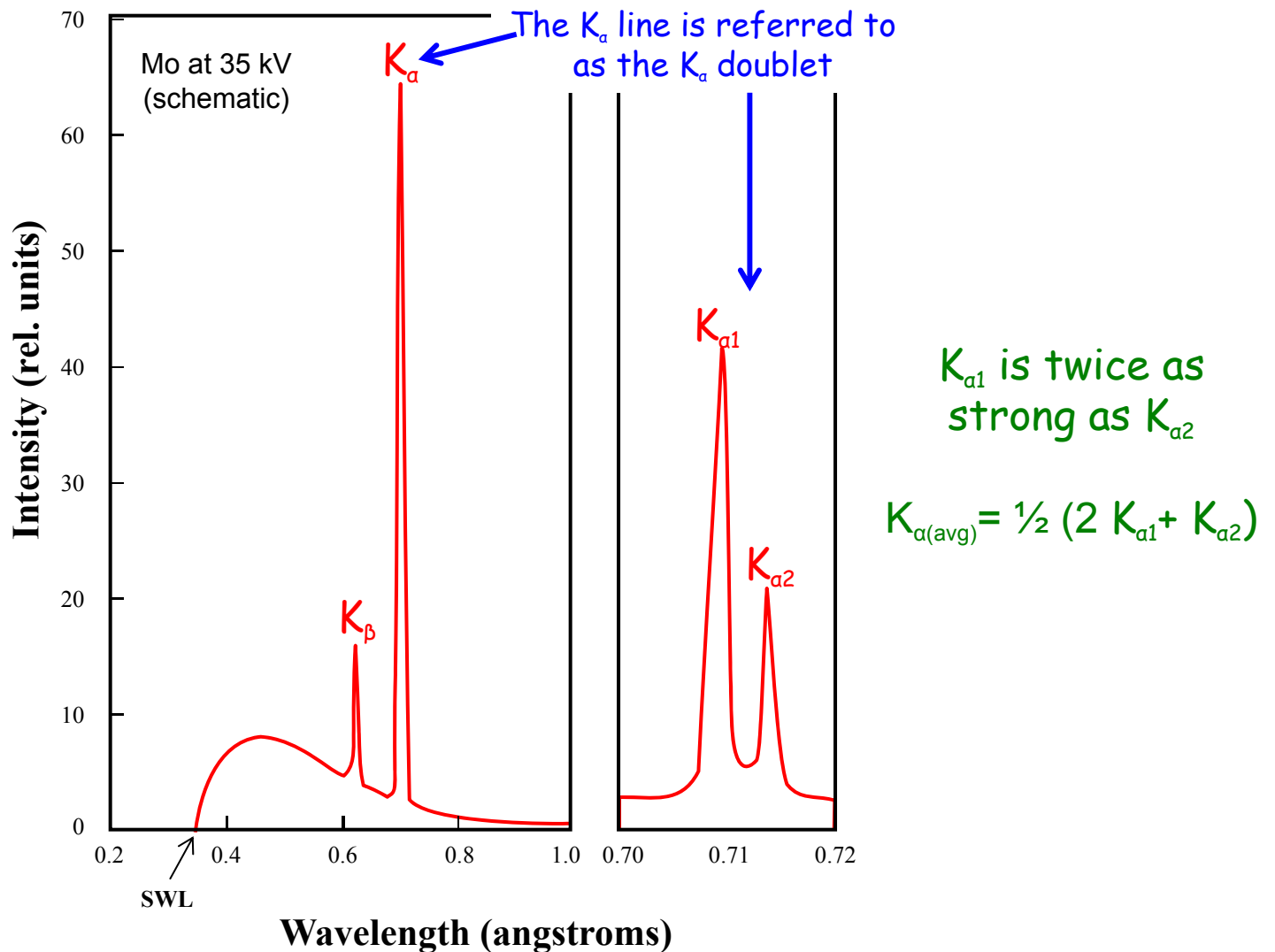
Different types of characteristic radiation!



$K_{\alpha 1}$, $K_{\alpha 2}$, $K_{\beta 1}$, the strongest of the K set, are typically used for diffraction.

Energy-level diagram for molybdenum showing all allowed electron transitions





$$E_{L_{III} \rightarrow K} = 20 - 2.52 = 17.48 \text{ keV}, \quad \underline{\underline{\lambda_{K\alpha 1} = 0.709 \text{ \AA}}}$$

$$E_{L_{II} \rightarrow K} = 20 - 2.63 = 17.37 \text{ keV}, \quad \underline{\underline{\lambda_{K\alpha 2} = 0.714 \text{ \AA}}}$$

Intensity of the Characteristic Spectrum from the Target

$$I = Bi(V - V_K)^n$$

where

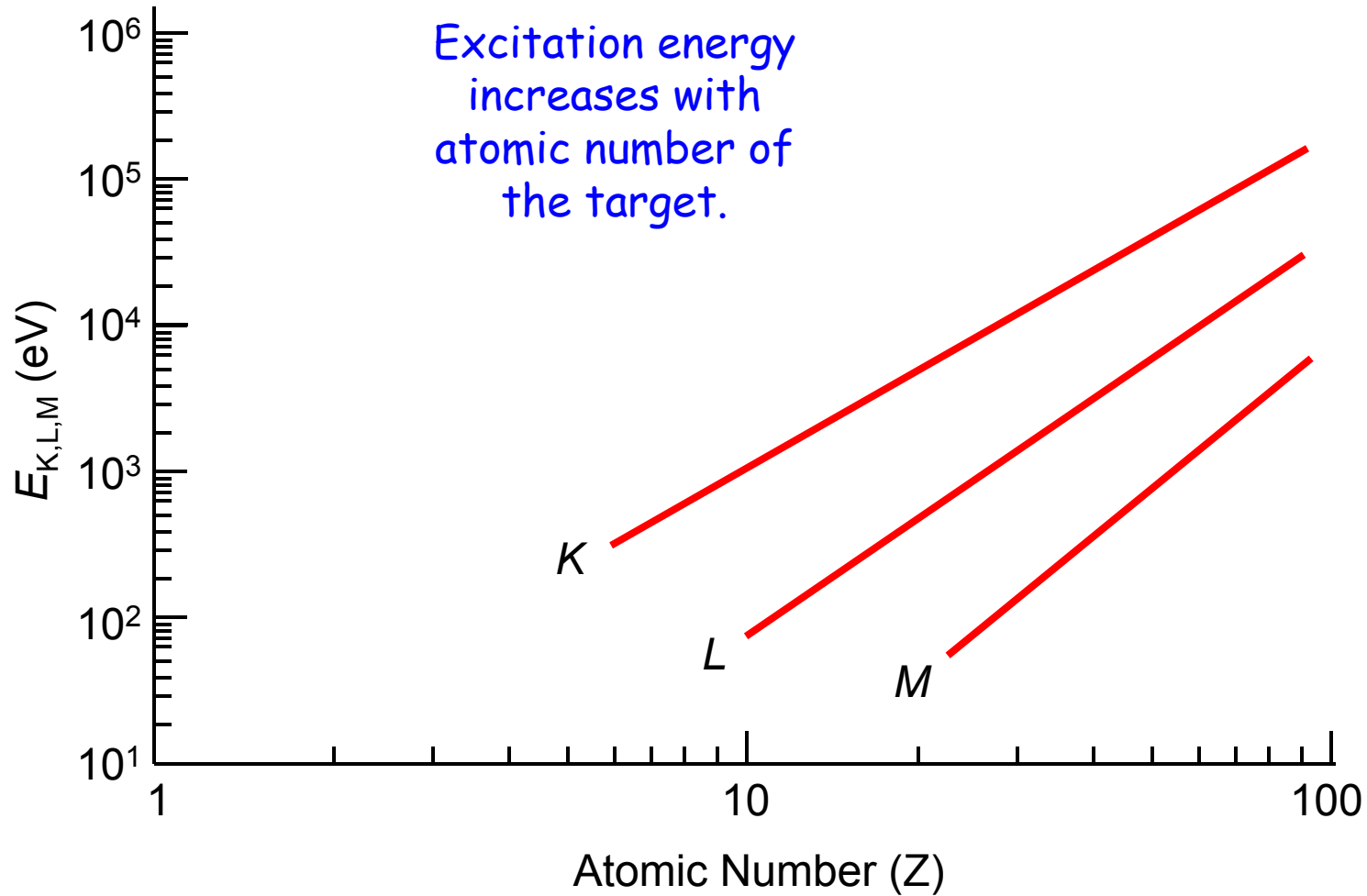
I = intensity

i = tube current

V = applied voltage

V_K = voltage to eject K-shell electrons

n = constant $\cong 1.6$



Variation of excitation energy to eject electrons from inner shells with atomic number.

Commonly Used X-ray Wavelengths

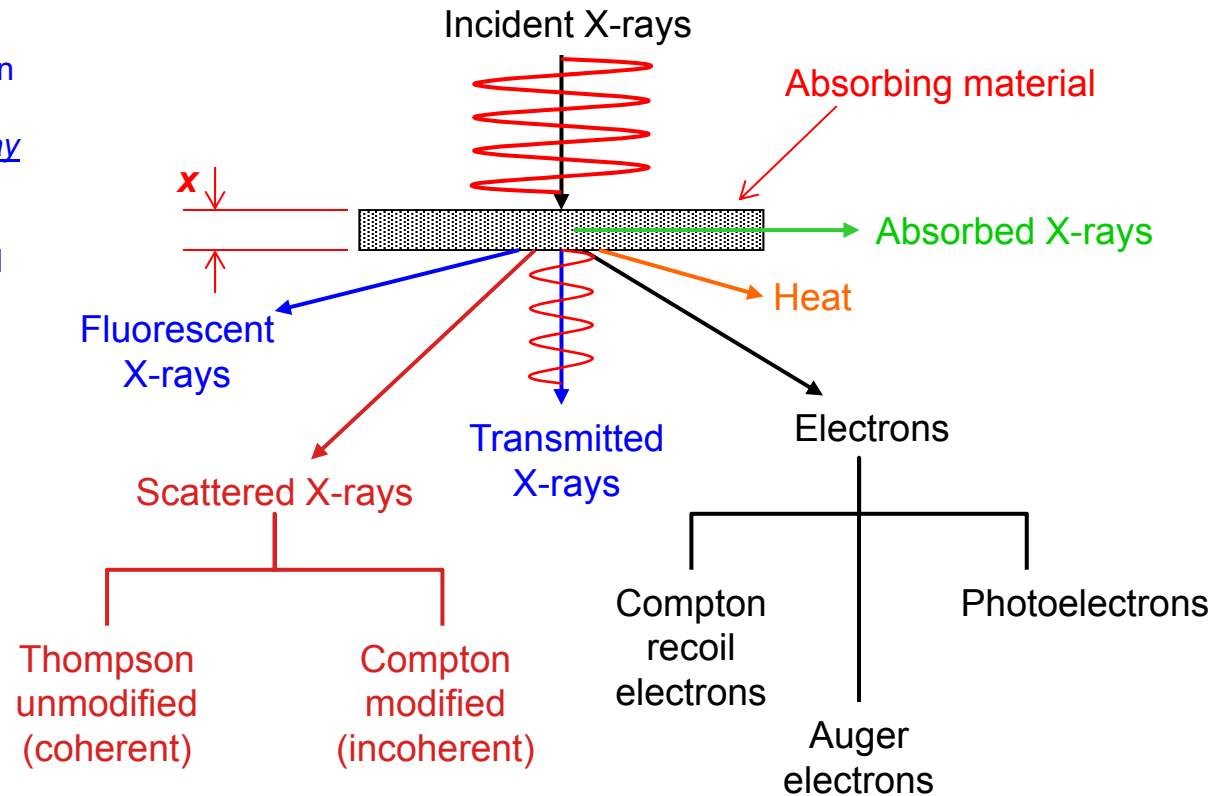
(THIS IS IMPORTANT!)

Copper Anodes	Bearden (1967)	Holzer et al. (1997)	Cobalt Anodes	Bearden (1967)	Holzer et al. (1997)
Cu K _{α1}	1.54056Å	1.540598 Å	Co K _{α1}	1.788965Å	1.789010 Å
Cu K _{α2}	1.54439Å	1.544426 Å	Co K _{α2}	1.792850Å	1.792900 Å
Cu K _{β1}	1.39220Å	1.392250 Å	Co K _{β1}	1.62079Å	1.620830 Å
Molybdenum Anodes	Bearden (1967)	Holzer et al. (1997)	Chromium Anodes	Bearden (1967)	Holzer et al. (1997)
Mo K _{α1}	0.709300Å	0.709319 Å	Cr K _{α1}	2.28970Å	2.289760 Å
Mo K _{α2}	0.713590Å	0.713609 Å	Cr K _{α2}	2.293606Å	2.293663 Å
Mo K _{β1}	0.632288Å	0.632305 Å	Cr K _{β1}	2.08487Å	2.084920 Å

- Values from Cullity (1956) and Bearden [*Rev. Mod. Phys.* **39** (1967) 78-124] usually quoted. However, they are incorrect.
 - Bearden's values (1967) are reprinted in *International Tables for X-Ray Crystallography* and most XRD textbooks.
- The most recent values are from Hölzer et al. [*Phys. Rev. A* **56** (1997) 4554-4568].

What happens when x-rays encounter matter?

Adapted from Fig. 4-7 in
B.D. Cullity and S.R.
Stock, *Elements of X-ray
Diffraction, 3rd Edition*,
Prentice Hall, Upper
Saddle River, NJ, 2001



X-rays are **attenuated**

Part of incident X-ray energy is lost as they travel through a material

Modes of X-ray Attenuation

- Absorption

- Caused by electronic transitions within an atom.
- X-rays transfer their energy to the material, requiring re-emission of a new X-ray (just like electron beams).

- Scattering

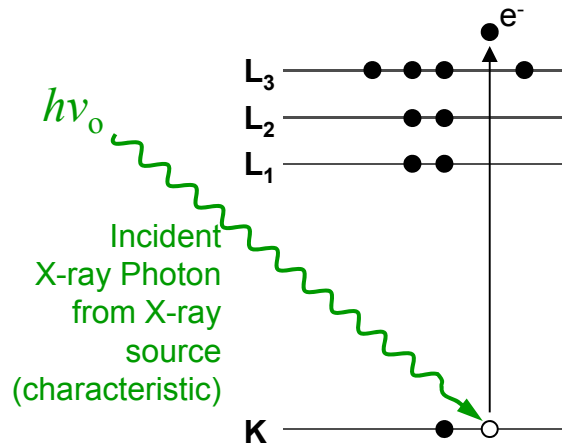
- X-ray is deflected from its original path with or without energy loss.
- Scattering occurs in all directions; thus, energy in the scattered beams does not appear in the transmitted beam.

Nice explanation of absorption & fluorescence

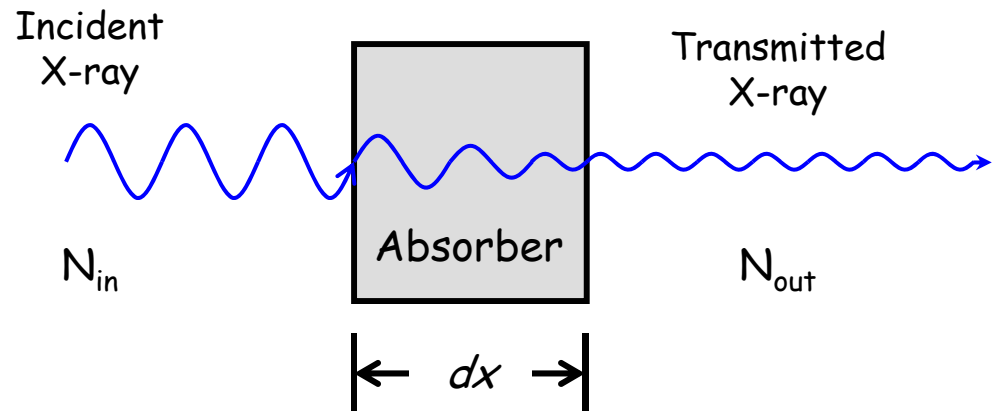
<http://www.youtube.com/watch?v=1v3bmO1wdqE>

Absorption - 1

- When a photon comes in, is 'destroyed,' and an electron is excited from a lower energy level to a higher energy level.



Absorption of a photon

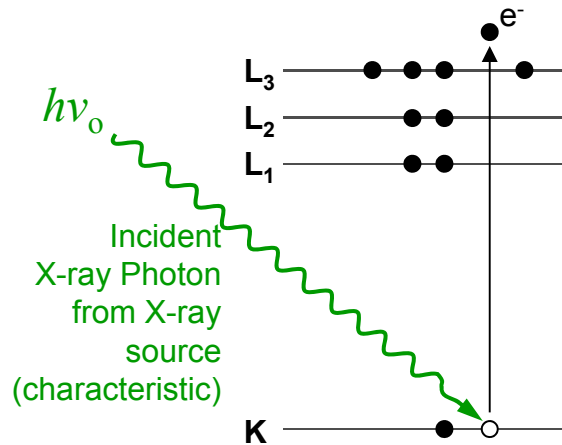


C = conc. of electrons/cm³ that will be excited by x-rays

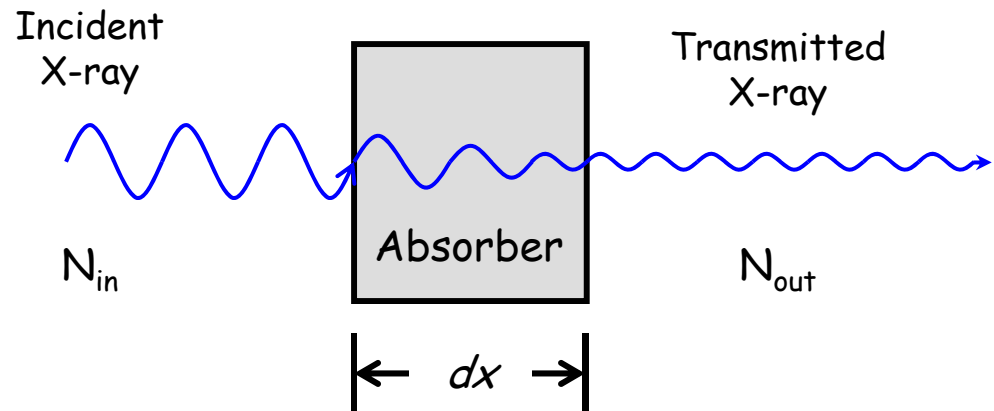
k = const. of proportionality related to probability of excitement

Absorption - 2

- When a photon comes in, is 'destroyed,' and an electron is excited from a lower energy level to a higher energy level.



Absorption of a photon



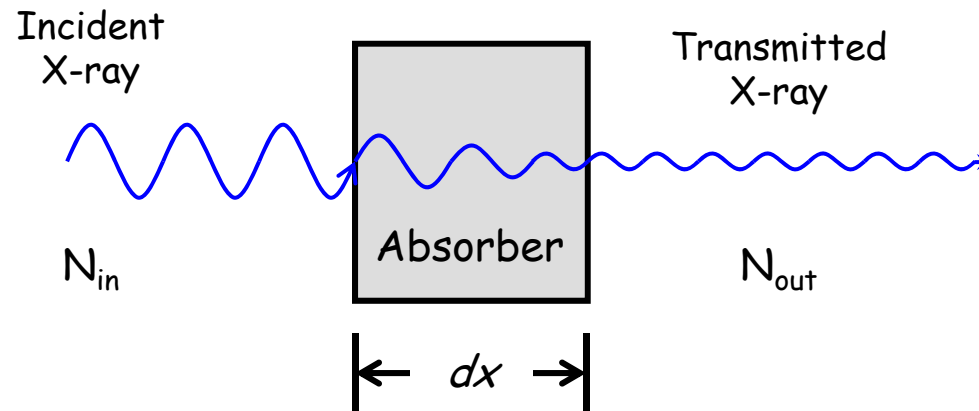
Let $\alpha =$ probability of absorption $= Ck$

$$N = \# \text{ photons} = (\# \text{ electrons/gram}) \times \rho \times dV$$

$$dV = \text{volume of absorber} = 1 \times 1 \times dx$$

$\rho =$ density of absorber

Absorption - 3



N_{in} = # photons entering absorber = N

N_{out} = # photons exiting absorber = $N - \alpha N dx$

\therefore

$$\Delta N = N_{out} - N_{in} = N - \alpha N dx - N = -\alpha N dx$$

$$dx \rightarrow 0; \Delta N \rightarrow dN$$

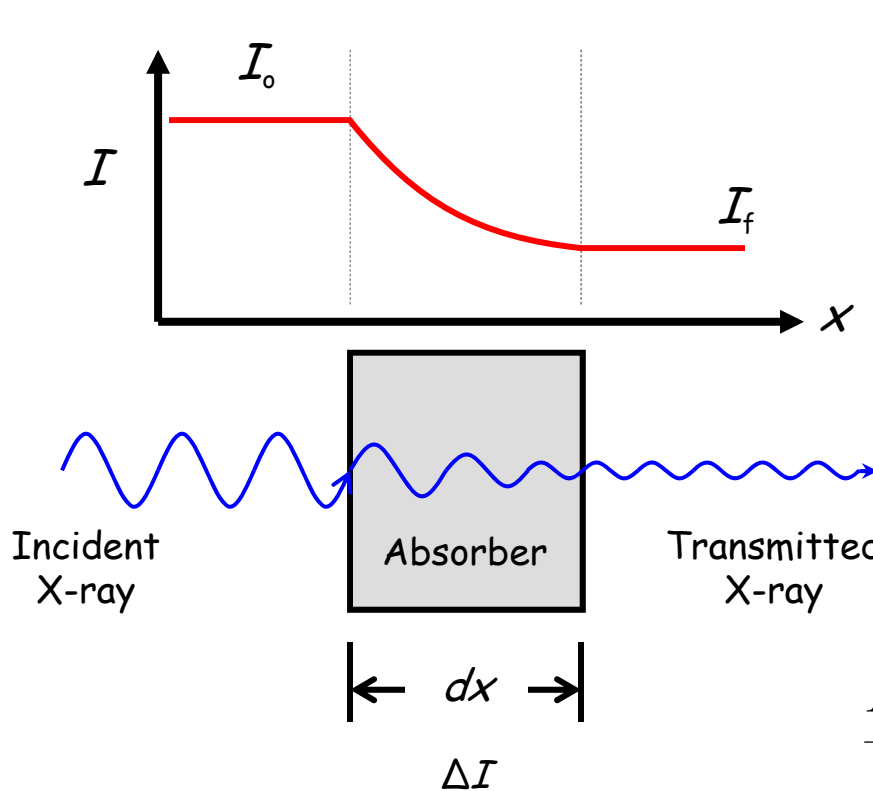
$$dN = -\alpha N dx$$

$$\frac{dN}{dx} = -\alpha N \quad \rightarrow \quad \boxed{N \approx e^{-\alpha x}}$$

Says how # photons changes as they pass through an absorber. Assumes α is proportional to N and dx .

Absorption - 4

- Now consider an absorbing material with a proportionality constant $\alpha = \mu$.



- How does I_f depend on I_0 ?

$$I_f = e^{-\mu x} I_0$$

- How can we use this?

- Recall, inside of absorber:

$$\mu = F(\lambda, \rho) \propto \text{concentration, } C$$

$$\frac{I_f}{I_0} = e^{-\mu x}$$

$$\ln\left(\frac{I_f}{I_0}\right) = -\mu(\lambda, \rho)x$$

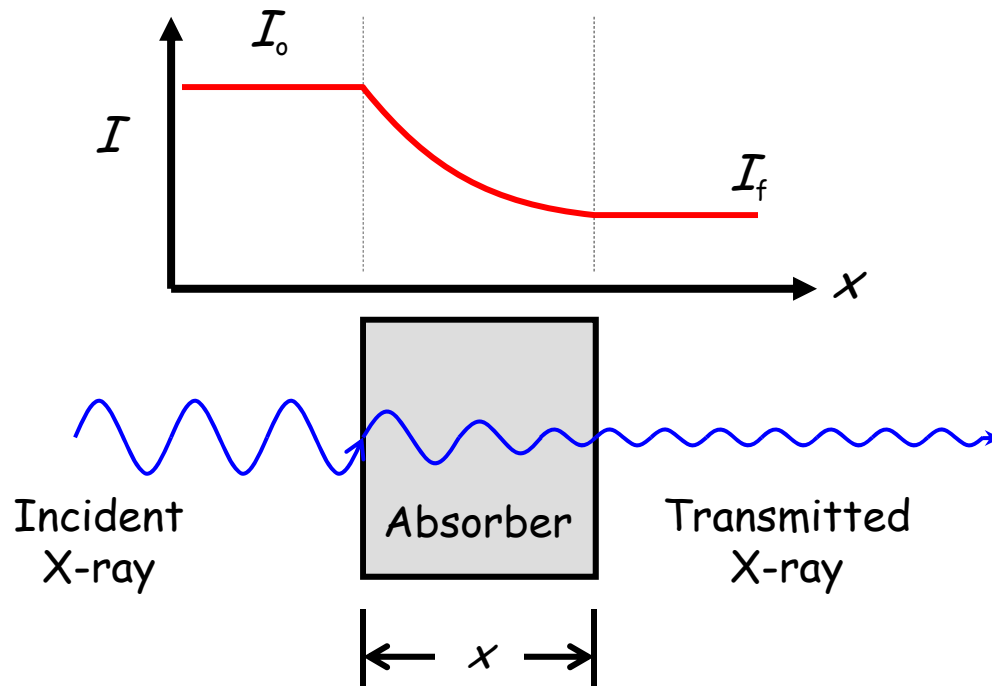
Example:

We can use this principle to ID a material.

Expose it to radiation with a variety of λ 's; to determine μ , and conc.

Absorption - 5

Change in X-ray intensity caused by absorption



$$\boxed{-\frac{dI}{I} = \mu dx}$$

μ = linear absorption coeff.
It is a function of ρ and λ .

ΔI

a portion of the incident beam is removed

$$-\int_{I_0}^I \frac{dI}{I} = \int \mu dx$$

$$-\ln I = \mu x + C$$

at $x = 0$, $I = I_0$, thus $C = -\ln I_0$

$$I(x) = I_0 e^{-\mu x} \quad \leftarrow \text{(Beer's law)}$$

If a beam of X-rays travels a distance $x=1/\mu$ through a solid, intensity will be decreased to 36.78% of its original value.

Since μ depends upon ρ and λ , we can re-write this relationship as:

$$I = I_0 e^{-(\mu/\rho)\rho x}$$

μ/ρ is a constant known as the *mass absorption coefficient*.

There are tabulated μ/ρ values for each element.

For alloys or compounds

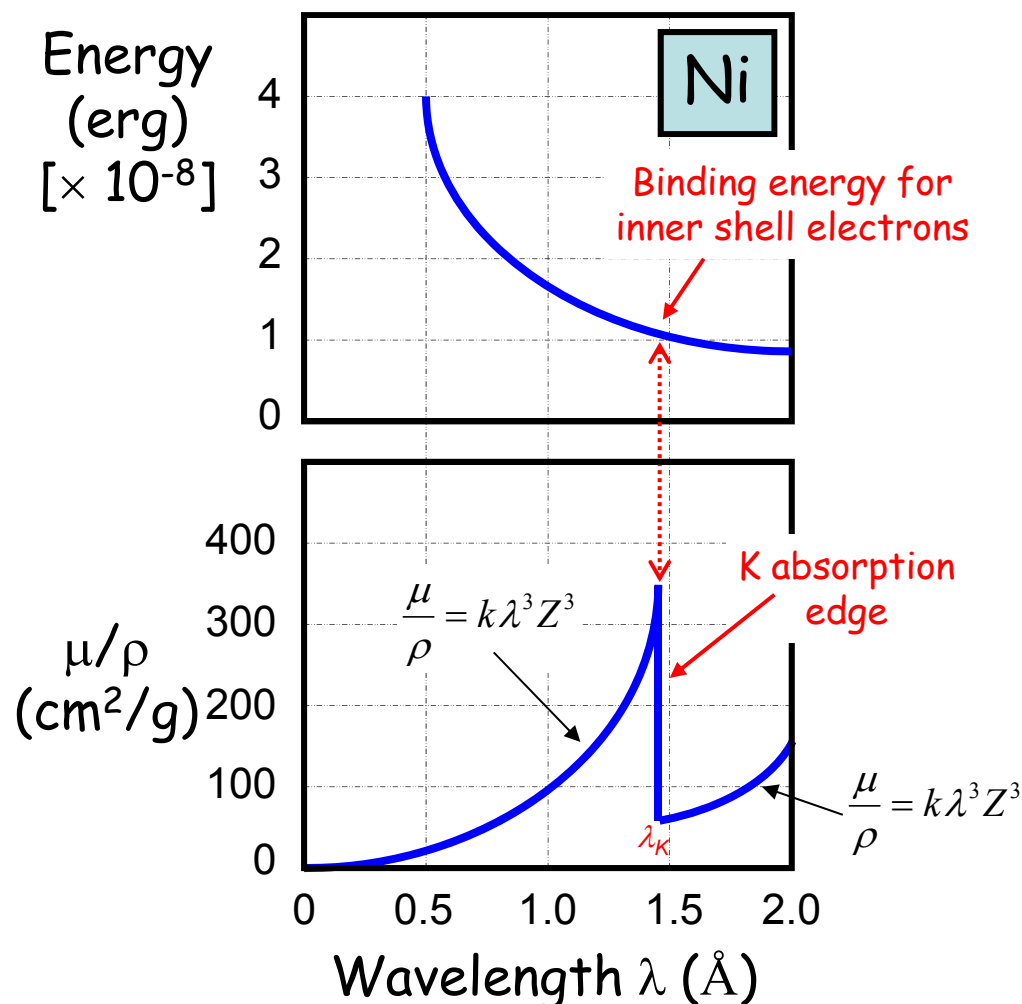
$$\frac{\mu}{\rho} = w_1 \left(\frac{\mu}{\rho} \right)_1 + w_2 \left(\frac{\mu}{\rho} \right)_2 + \cdots + w_n \left(\frac{\mu}{\rho} \right)_n$$

where:

w_x = weight fractions of elements
 $(\mu/\rho)_x$ = elemental mass absorption coefficients

ALL MATERIALS ABSORB

Wavelength dependence of μ/ρ



$$\frac{\mu}{\rho} = k\lambda^3 Z^3$$

If X-ray photon energy is high enough to eject an inner shell electron, μ/ρ will suddenly increase.

This is the **absorption edge**

UP TO THE ABS. EDGE

Long λ (low E) X-rays are easily absorbed

Short λ (high E) X-rays penetrate deeply and are not easily absorbed

There are many absorption edges

Absorption edges correspond to the binding energies for different types of inner shell electrons

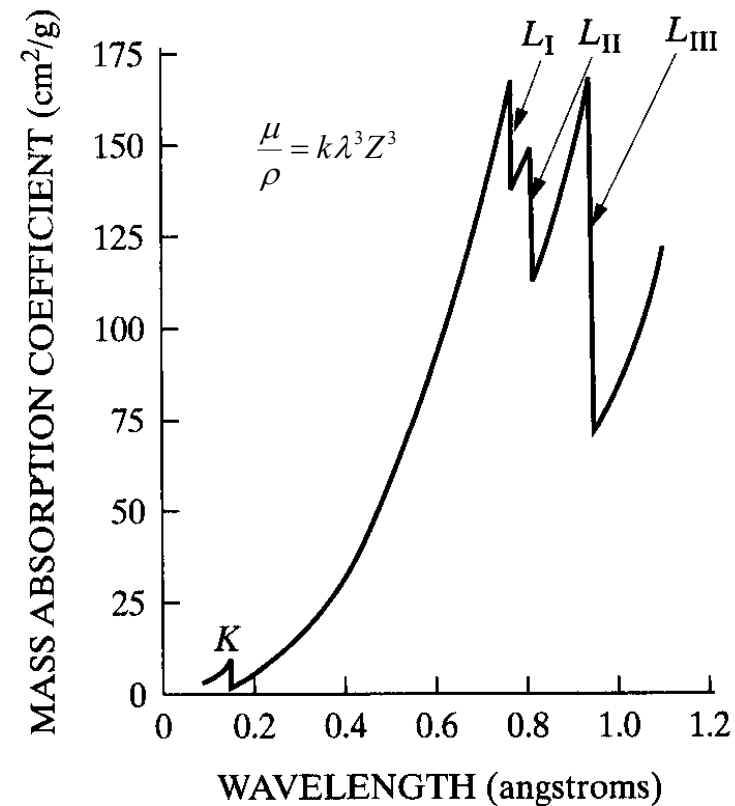


Figure 1-10 Absorption coefficients of lead, showing *K* and *L* absorption edges [1.6].

B.D. Cullity and S.R. Stock, *Elements of X-ray Diffraction, 3rd Edition*, Prentice Hall, Upper Saddle River, NJ, 2001

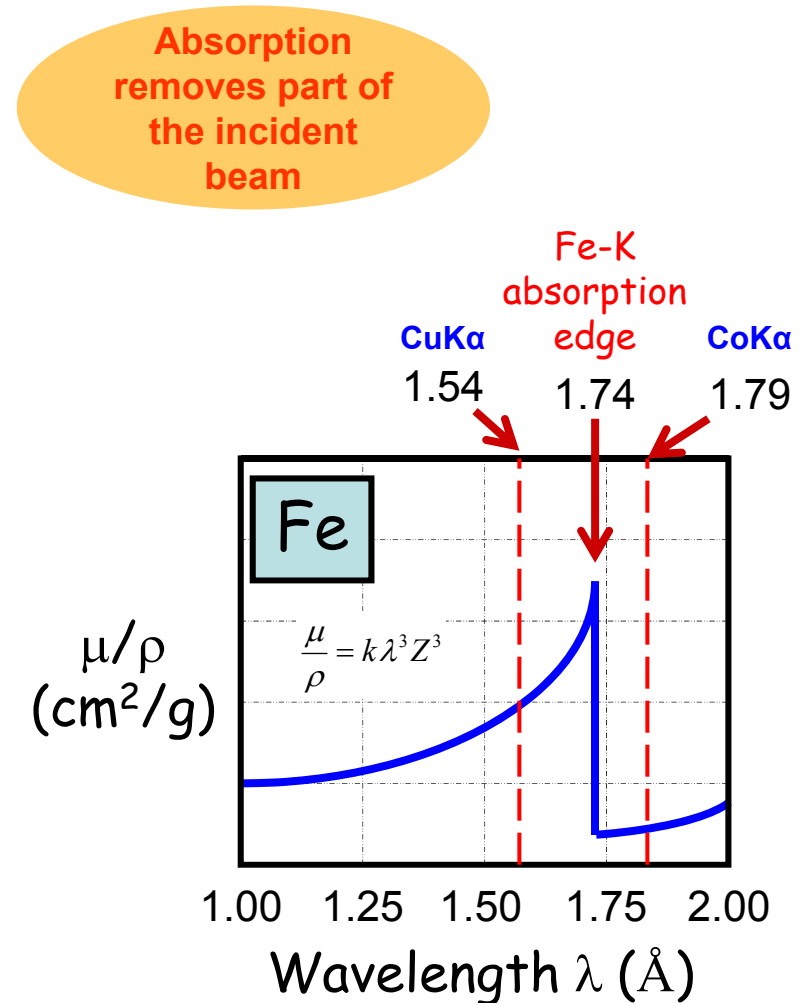
Significance of Absorption

- Absorption limits the sample thickness and x-ray wavelengths that can be used.

- Example:

- Analysis of Fe

- $E_{\text{FeK}} = 7.109 \text{ keV}$ ($\lambda = 1.74 \text{ \AA}$)
 - CuK α X-rays ($\lambda = 1.54 \text{ \AA}$): μ/ρ is too high
 - CoK α X-rays ($\lambda = 1.79 \text{ \AA}$): μ/ρ is lower; X-rays absorbed less

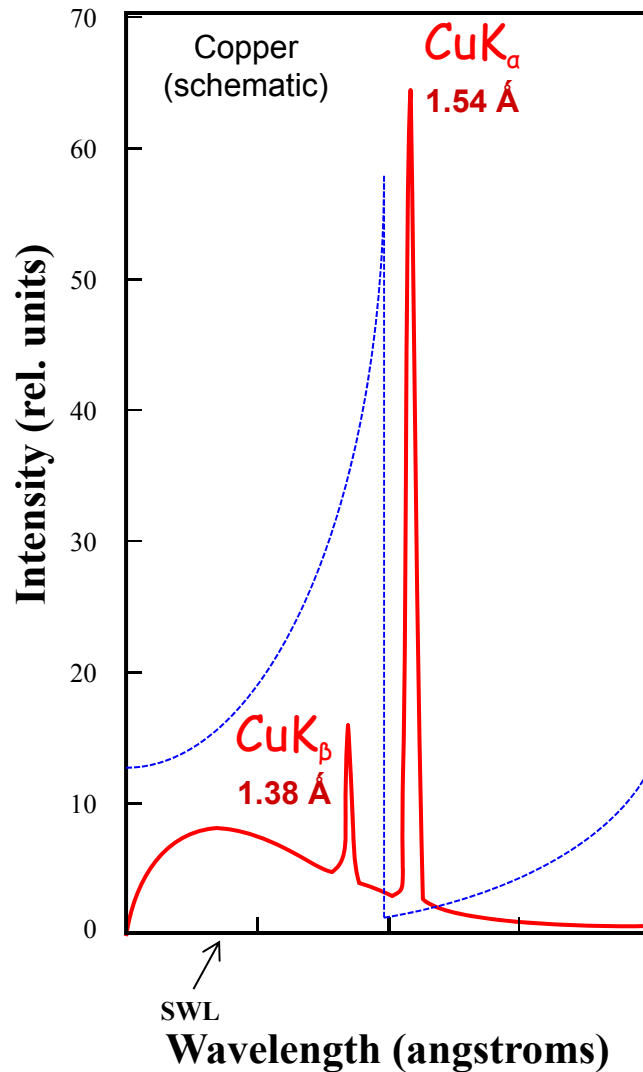


Good aspects/uses of absorption

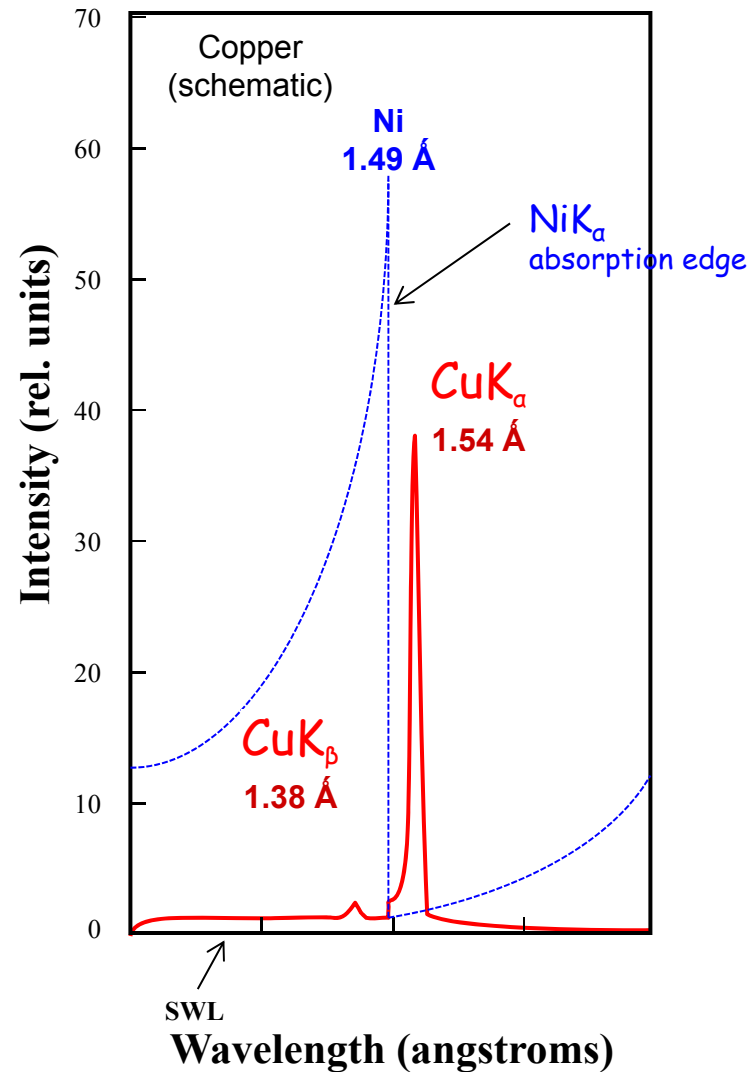
X-ray Filters

- We can conduct XRD experiments without adversely influencing our health by using X-ray absorbing shields (e.g., lead aprons, leaded glass, etc.).
- We can also utilize absorption to improve our XRD experiments...
- “Filtering” of unwanted X-rays.

NO FILTER



FILTER



In this case, the Ni filter primarily absorbs the K_β X-rays. It absorbs less K_α X-rays leaving us one kind of X-rays for analysis.

General Rules for Filtering

- If we place a thin foil with atomic number (Z-1) in a beam of X-rays generated with a target of atomic number Z,

the K_β peak of the target radiation will be almost completely absorbed and the background intensity around the K_α peak will also be attenuated (i.e., reduced).

$$\begin{array}{c} \text{BEFORE} \\ \frac{K_\alpha}{K_\beta} = \frac{7.5}{1.0} \end{array}$$

$$\begin{array}{c} \text{AFTER} \\ \frac{K_\alpha}{K_\beta} = \frac{500.0}{1.0} \end{array}$$

Filters for common target metals

Table 1. Filters to Suppress $K\beta$ Radiation.

Target	Filter	Incident Beam* $\frac{I(K\alpha)}{I(K\beta)}$	Filter thickness for a $\frac{I(K\alpha)}{I(K\beta)} = \frac{500}{1}$	
			in trans. beam $\frac{I(K\alpha) \text{ trans}}{I(K\alpha) \text{ incident}}$	mg/cm ² ; inches
Mo	Zr	5.4	77 ; 0.0046	0.29
Cu	Ni	7.5	18 ; 0.0008	0.42
Co	Fe	9.4	14 ; 0.0007	0.46
Fe	Mn	9.0	12 ; 0.0007	0.48
Cr	V	8.5	10 ; 0.0006	0.49

* Intensity ratio at the target [1]. This ratio outside the X-ray tube will be changed somewhat by the differential absorption of $K\alpha$ and $K\beta$ by the tube window.

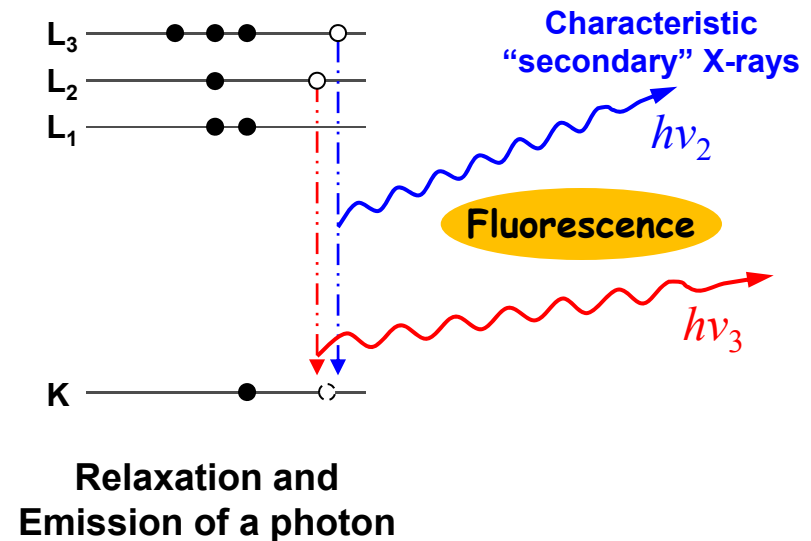
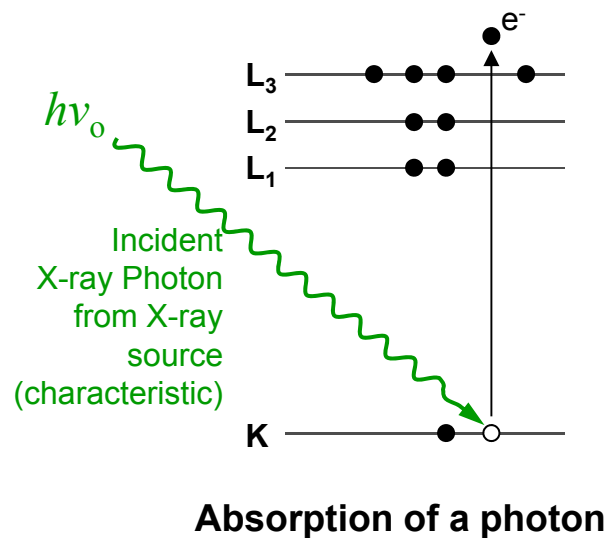
[1] International Tables for Crystallography, Ed. A.J.C. Wilson, Vol. A-C (Kluwer, 1995)

Adapted from B.D. Cullity and S.R. Stock, Elements of X-ray Diffraction, 3rd Edition, Prentice Hall, Upper Saddle River, NJ, 2001

Bad aspects/uses of absorption

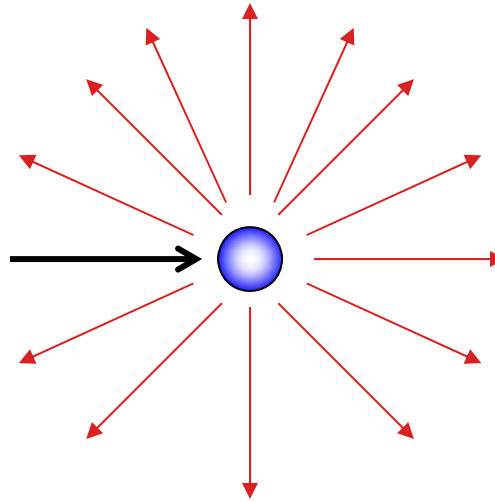
X-ray Fluorescence

- Short λ , high energy x-rays can generate secondary characteristic x-rays within the specimen/target.
(Process is identical to how electrons generate x-rays)
- Energy loss produces fluorescent X-rays with lower energies and longer λ than the characteristic radiation.



X-ray Fluorescence – cont'd

- Fluorescent x-rays radiate in all directions.



- These X-rays will be out of phase with incident x-rays; thus they will not “reinforce” the diffracted characteristic x-rays.
- Fluorescent radiation produces an undesired distributed background, which can be large enough to obscure the diffraction effects that you are after.

X-ray Fluorescence – cont'd

- Most of the loss in X-ray intensity results from fluorescent absorption.
- Want to avoid fluorescence, minimize absorption of the incident beam.
- Select X-radiation for with λ close to minimum, but on the long λ side (i.e., higher λ) of the absorption edge.

Example

- For analysis of steel:
 - CuK α x-radiation ($\lambda=1.54 \text{ \AA}$) is less than ideal for steels and other iron alloys ($E_{\text{FeK}}=7.109 \text{ keV} \equiv 1.743 \text{ \AA}$).
 - CoK α x-radiation ($\lambda=1.789 \text{ \AA}$) is just on the long λ side of the K $_{\text{Fe}}$ edge and will yield sharp fluorescence-free diffraction patterns from steel.
- What about MoK α x-radiation?

**Start reading Chapters 2 and 6
in Waseda.**