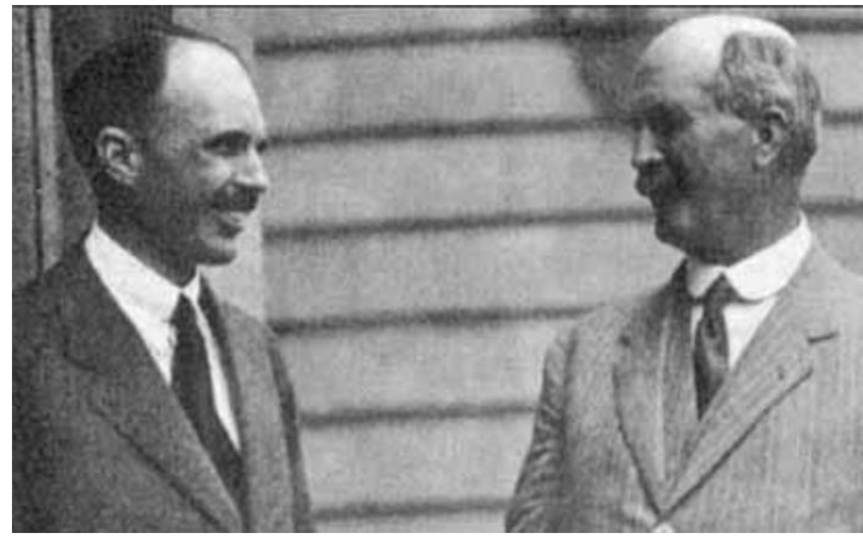
1. Fundamental physics of X-rays

1.1 Brief history of X-ray

Wilhelm Röntgen
(Find X-rays)

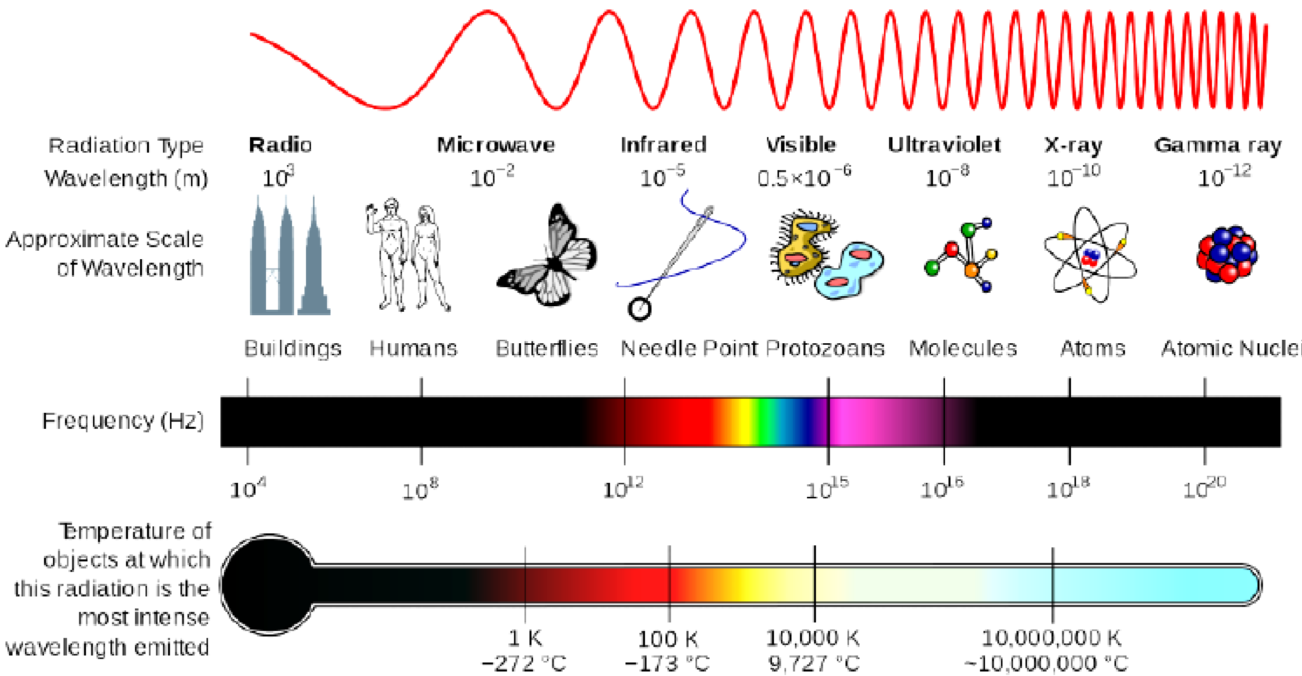
Max von Laue
(Find X-rays diffraction)



William Henry Bragg
William Lawrence Bragg
(Use of X-rays)

1.2 Nature of X-rays

The nature of X-rays is basically the same as visible light and infrared rays, which are electromagnetic waves or electromagnetic radiation.



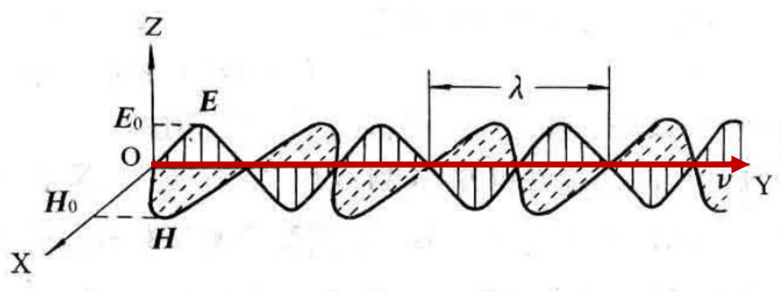
"Hard" X-rays (wavelength < 0.5 nm): high energy, strong penetration that can be used to Suitable for non-destructive testing of metal parts and metal phase analysis.

"Soft" X-rays (wavelength > 0.5 nm): longer wavelengths have lower energy and weak penetration that can be used for the analysis of non-metals.

1.2 Nature of X-rays

Wave-particle duality

- Wave properties



When X-rays propagate along the y direction, they have both electric field intensity E and magnetic field intensity H. These two vectors always vibrate periodically in two mutually perpendicular planes with the same phase and are perpendicular to the y direction. The speed of propagation is equal to the speed of light.

$$\vec{E} = \vec{E}_0 \exp[2\pi i(\frac{y}{\lambda} - \frac{t}{T} - \frac{\varphi}{2\pi})]$$

$$\vec{H} = \vec{H}_0 \exp[2\pi i(\frac{y}{\lambda} - \frac{t}{T} - \frac{\varphi}{2\pi})]$$

$$|\vec{H}| = c\varepsilon_0 |\vec{E}|$$

y - distance
t - time
T - period
c - light speed

λ - wavelength
ϕ - Initial phase angle
ε_0 - Vacuum permittivity

In X-ray analysis we normally record the physical effects caused by the electric field strength vector E. Therefore, only the change of E is discussed, and the influence of the magnetic field intensity vector H is not considered.

1.2 Nature of X-rays

Wave-particle duality

- Particle properties

X-rays are made of streams of particles called light quanta or photons. Each light quantum has energy ε and momentum p.

$$\varepsilon = h\nu = \frac{hc}{\lambda}$$

$$p = \frac{h}{\lambda}$$

h - Planck constant 6.63×10^{-34} m^2 kg/s

c - light speed 2.998×10^{8} m/s

λ - wavelength of X-rays

ν - frequency of X-rays

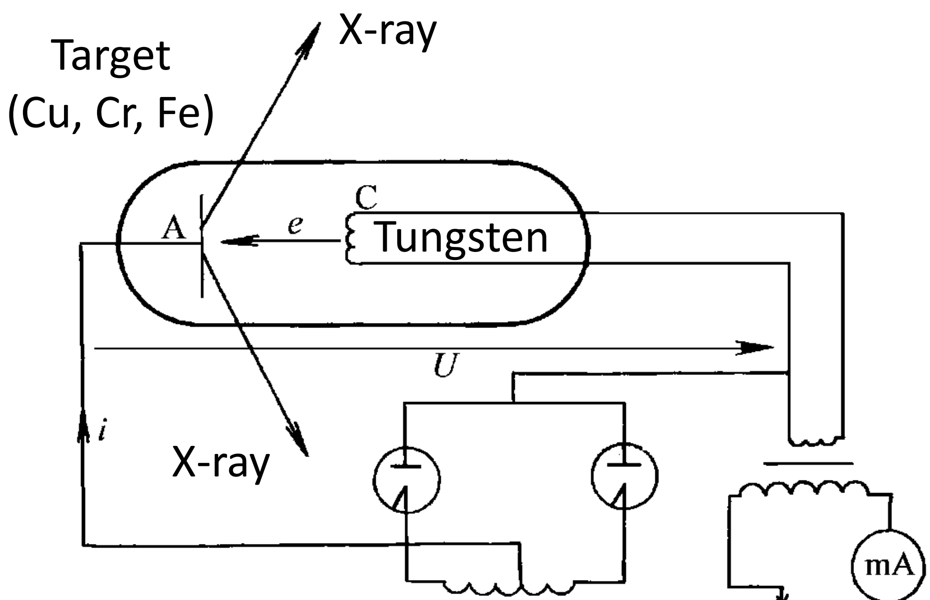
The intensity of X-rays is described from a particle perspective:
The product of photon number and photon energy (unit area perpendicular to the propagation direction per unit time)

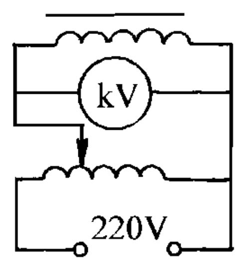
Wave-particle duality is an objective property of X-rays:

- “Wave” is reflected in the continuity of material motion, and phenomena such as interference and diffraction can occur during the propagation process.
- “Particle” characteristics are prominently manifested in the interaction of matter and the mutual exchange of energy.

X-rays
- “Wave” → It propagates in space with a certain frequency and wavelength.
- “Particle” → Consists of a large number of discontinuous particle streams.

1.3 Generation of X-rays and X-ray tubes





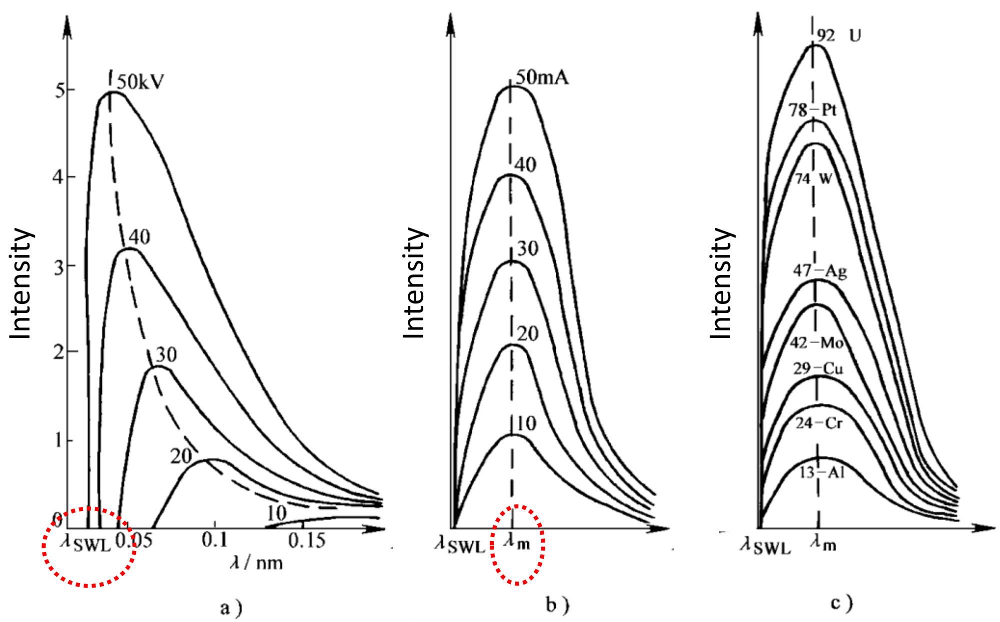
- It mainly consists of a cathode (Tungsten) and an anode (target) made of pure metals such as (Cu, Cr, Fe, Mo).
- The cathode is heated by electricity, and DC high voltage (approximately tens of thousands of volts) is applied between the cathode and anode.
- A large number of electrons emitted from the cathode fly towards the anode at high speed and collide with the anode to produce X-rays.

1.4 X-ray spectroscopy

- Continuous X-ray Spectroscopy

The spectral line whose intensity varies continuously with wavelength is called continuous X-ray spectrum.

The characteristic of the continuous X-ray spectrum is that the wavelength of the X-ray has a minimum value λ_{SWL}, and its intensity has a maximum value at λ_m.



Influence of tube voltage (a), tube current (b) and anode target atomic number (c).

a). Tube voltage ***U*** ↑ Intensity ↑
λ_{SWL} ↓ λ_m ↓

b). Tube current ***i*** ↑ Intensity ↑
λ_{SWL} — λ_m —

c). Atomic number ***Z*** ↑ Intensity ↑
λ_{SWL} — λ_m —

1.4 X-ray spectroscopy

- Continuous X-ray Spectroscopy

Why does the continuous X-ray spectrum have a short wavelength limit λ_{SWL}? Quantum theory can be used to explain the continuum spectrum and the short-wave limit. If the tube voltage is U, the kinetic energy of the electrons reaching the anode target is eU. When the electrons convert all the energy into a light quantum in a collision, the maximum energy $h\nu_{max}$ can be obtained. The wavelength is λ_{SWL}.

$$\nu_{\mathbf{max}} = eU/h = c/\lambda_{\mathbf{SWL}}$$

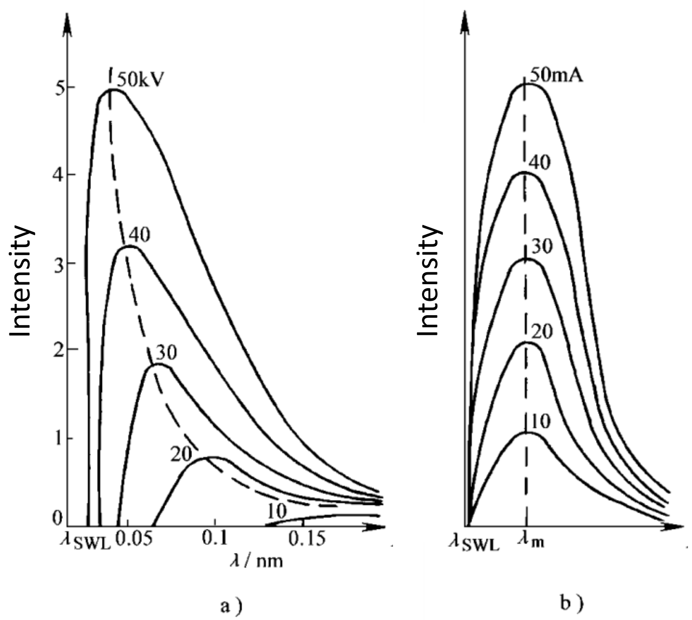
$$\lambda_{\mathbf{SWL}} = (hc)/(eU) = \frac{6.626\times10^{-34}\,\mathrm{J\cdot s}\times2.998\times10^{8}\,\mathrm{m\cdot s^{-1}}}{1.602\times10^{-19}\,\mathrm{C\cdot U}} = \frac{1240\mathrm{nm}}{\mathrm{U}}$$

Most of the electrons reach the anode target and consume their energy through multiple collisions. Due to the different energy consumption each time, X-rays of different wavelengths larger than λ_{SWL} are produced, forming a continuous spectrum.

1.4 X-ray spectroscopy

- Continuous X-ray Spectroscopy

The area under the continuum intensity distribution curve is the total intensity of the continuum X-ray spectrum, which depends on the three factors of X-ray tube ***U***, ***i***, and ***Z***.



$$I_c = \int_{\lambda_{SWL}}^{\infty} I(\lambda)d\lambda = K_1 iZU^2$$

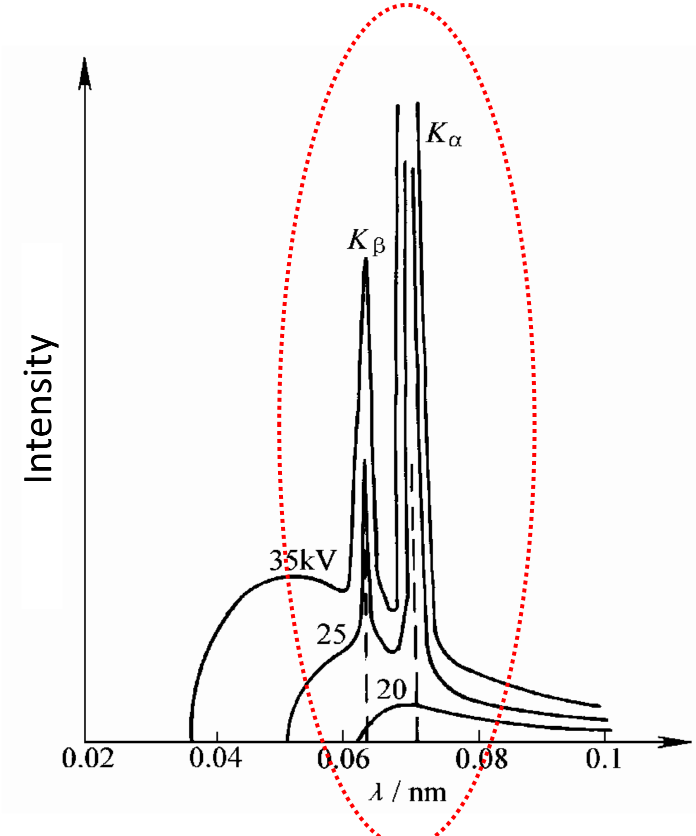
$\eta = I_c / iU = K_1 ZU$ Efficiency ($\eta \approx 1\%$)

$K_1 = (1.1 \sim 1.4) \times 10^{-9}$

It can be seen that the higher the tube voltage of the X-ray tube and the larger the atomic number of the anode target, the higher the efficiency of the X-ray tube. Because K_1 is $(1.1 \sim 1.4) \times 10^{-9}$, even with tungsten anode (Z = 74), tube voltage 100 kV, $\eta \approx 1\%$, the efficiency is very low. Most of the energy consumed during electronic target shooting causes the target to heat up.

1.4 X-ray spectroscopy

- Characteristic X-ray spectrum



When the X-ray tube voltage is higher than a critical value U_K of the target, a series of linear spectra with very high intensity and narrow wavelength range will appear at certain specific wavelength positions, called characteristic spectra. The wavelength has a certain relationship with the anode target atomic number:

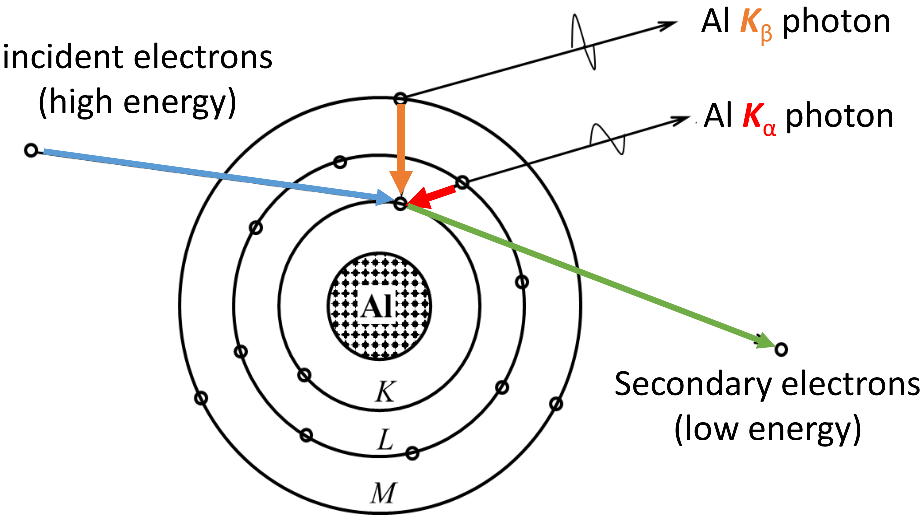
$$\sqrt{\frac{1}{\lambda}} = K_2(Z-\sigma)$$

K₂*, *σ constants

Atomic number ***Z*** ↑ Wavelength ***λ*** ↓

1.4 X-ray spectroscopy

- Characteristic X-ray spectrum



If the incident electrons (enough energy) rushing toward the anode (target), they will knock out the inner electrons and become free electrons. At this time, the atoms are in a high-energy unstable state and must spontaneously transition to a stable state. If the ***L*** layer electron jumps to the ***K*** layer to fill the vacancy, the atom changes from the ***K*** excited state to the ***L*** excited state, and the energy difference is released in the form of X rays, which are characteristic X rays, called K_α rays.

If M-layer electrons replenish K-layer vacancies, K_β rays with shorter wavelengths will be emitted.

Energy of electron at different layers (K, L, M…)

$$E_n = -\frac{2\pi^2 m e^4}{h^2 n^2}(Z-\sigma)^2$$

E_n: Energy of electron with the main quantum number n;

n is the main quantum number; m is the electron mass.

1.4 X-ray spectroscopy

- Characteristic X-ray spectrum

The frequency of characteristic X-rays can be calculated by the following:

$$h\nu = W_{n2} - W_{n1} = (-E_{n2}) - (-E_{n1})$$

$$E_n = -\frac{2\pi^2 m e^4}{h^2 n^2}(Z-\sigma)^2$$

$\boldsymbol{W_{n2}}$ and $\boldsymbol{W_{n1}}$ are the atomic excited state energies before and after the electron transition respectively, and $\boldsymbol{E_{n2}}$ and $\boldsymbol{E_{n1}}$ are the electron energies in the shell. According to the classical atomic model, the electrons in the atom are distributed on a series of shells, and the innermost shell (***K*** shell) has the lowest energy, increasing in the order of ***L***, ***M***, ***N***.

$$h\nu = \frac{2\pi^2 m e^4}{h^2}(Z-\sigma)^2\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

If $n_2 = 1$ (***K*** layer), $n_1 = 2$ (***L*** layer), the emitted K_α wavelength $\lambda_{K\alpha}$

$$\sqrt{\frac{1}{\lambda_{K_\alpha}}} = K_2(Z-\sigma) \qquad K_2 = \sqrt{\frac{me^4}{8\varepsilon_0^2 h^3 c}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)} = \sqrt{R\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)}$$

1.4 X-ray spectroscopy

- Characteristic X-ray spectrum

In the K excited state, the probability of the ***L*** layer electron transitioning to the ***K*** layer is much greater than the probability of the ***M*** layer transition, so the intensity of the K_α is 5 times higher than K_β; the relationship between the $K_{\alpha1}$ and $K_{\alpha2}$ spectral lines is $\lambda_{K\alpha1} < \lambda_{K\alpha2}$, $I_{K\alpha1} \approx 2I_{K\alpha2}$. The characteristic wavelengths of several elements and the excitation voltages of ***K*** family spectral lines are shown in the table:

Target	Z	*Characteristic wavelength of K family* /0.1nm				K Absorption limit λ_K/0.1nm	U_K /kV	U_o /kV
		$K_{\alpha1}$	$K_{\alpha2}$	K_α	K_β			
Cr	24	2.28970	2.29361	2.29100	2.08487	2.07020	5.43	20~25
Fe	26	1.93604	1.93998	1.93736	1.75661	1.74346	6.40	25~30
Co	27	1.78897	1.79285	1.79026	1.72079	1.60815	6.93	30
Ni	28	1.65791	1.66175	1.65919	1.50014	1.48807	7.47	30~35
Cu	29	1.54056	1.54439	1.54184	1.39222	1.28059	8.04	35~40
Mo	42	0.70930	0.71359	0.71730	0.63229	0.61978	17.44	50~55

$$\lambda_{K\alpha} = (2\lambda_{K\alpha1} + \lambda_{K\alpha2}) / 3$$

1.4 X-ray spectroscopy

- Characteristic X-ray spectrum

Target	*Z*	*Characteristic wavelength of K series* /0.1nm				*K* Absorption limit λ_K/0.1nm	U_K /kV	U_o /kV
		$K_{\alpha1}$	$K_{\alpha2}$	K_{α}	K_{β}			
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To obtain characteristic X-rays with shorter wavelengths, a material with a larger atomic number needs to be used as the anode. U_K in the table is the critical excitation voltage of the *K* series characteristic spectrum. The larger the atomic number of the anode target, the higher the critical excitation voltage required. The intensity of the characteristic spectrum increases as the tube voltage U and tube current i increase. In order to improve the intensity of the characteristic spectrum, a higher tube voltage should be used.

1.5 Interaction of X-rays with Matter

The interaction between X-rays and matter is a complex process. In terms of energy conversion, when a beam of X-rays passes through matter, it can be divided into three parts:

- part of it is scattered
- part of it is absorbed
- Part of it passes through the material and continues to propagate in the original direction

1.5 Interaction of X-rays with Matter

- Scattering of X-rays

The scattering of X-rays by matter is mainly the result of the interaction between electrons and X-rays.

Scattering of X-rays
- Coherent scattering: Diffraction effect produced by incident X-rays interacting with tightly bound electrons in atomic nuclei in matter.
- Incoherent scattering: The diffraction effect caused by the interaction between incident X-rays and loosely bound electrons in the nuclei of substances.

1.5 Interaction of X-rays with Matter

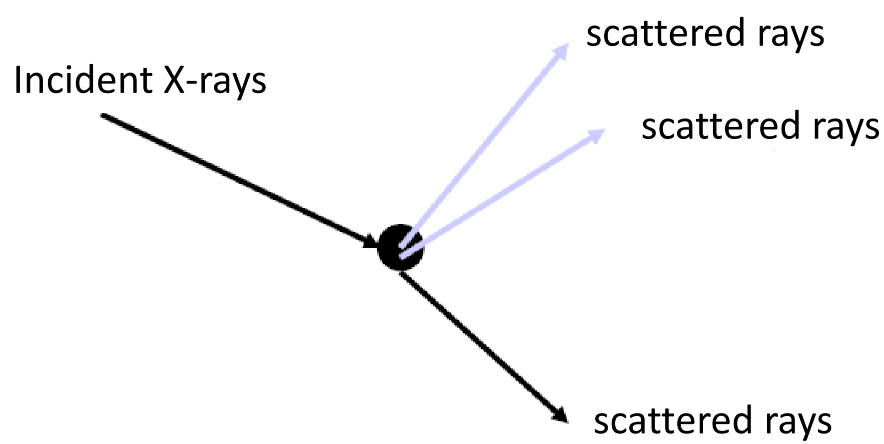
- Coherent scattering

When the incident X-ray meets the electrons that are tightly bound by the atomic nucleus, the electrons are forced to vibrate under the action of the X-ray alternating electric field, and radiate radiation with the same wavelength as the incident X-ray to the surroundings.

Because the X-rays scattered by each electron have the same wavelength and a constant phase lag, they may interfere with each other, so it is called coherent scattering.

The scattering of X-rays by matter can be regarded as only the scattering of electrons.

Coherently scattered waves account for only a tiny fraction of the incident energy.

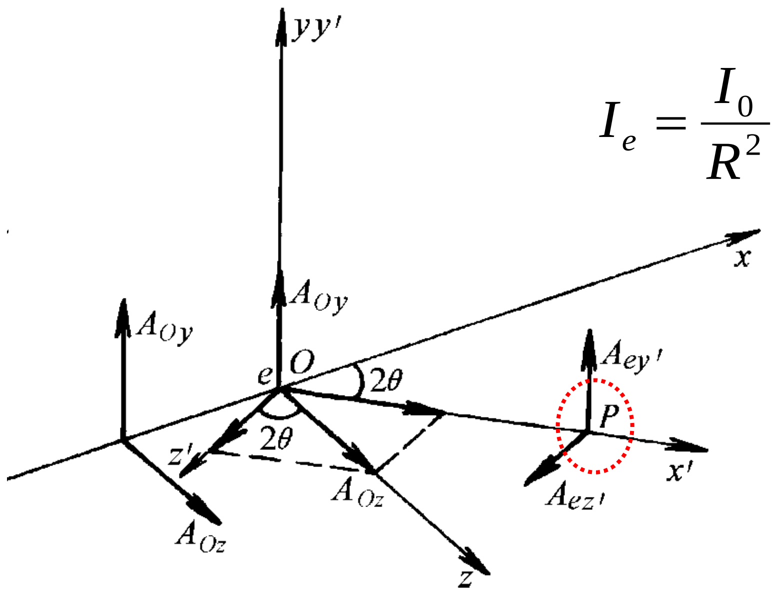


1.5 Interaction of X-rays with Matter

- Coherent scattering

Coherent scattering intensity of an electron at point P (I_e):

$$I_e = \frac{I_0}{R^2}\left(\frac{\mu_0}{4\pi}\right)^2\left(\frac{e^2}{mc}\right)^2\frac{1+\cos^2 2\theta}{2} = \frac{I_0}{R^2} f_e^{\,2}\,\frac{1+\cos^2 2\theta}{2}$$

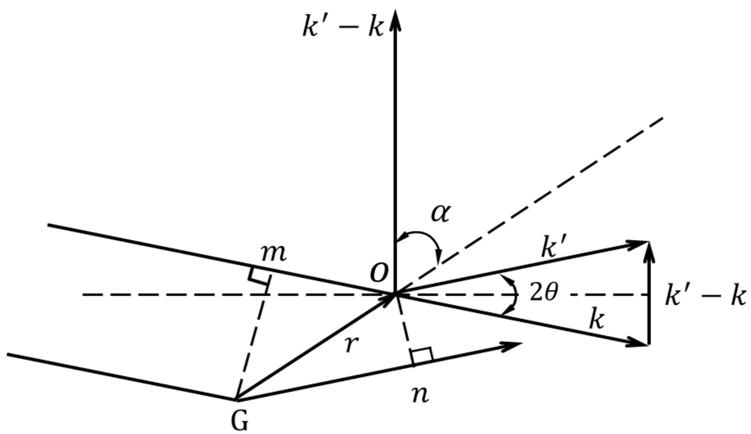


Coherent scattering of an electron

I_0 - Incident ray intensity
I_e - Coherent scattering intensity of an electron
R - The distance between an electron to a point P
2θ - Scattering angle
$f_e^2 = 7.94\times10^{-30}\mathrm{m}^2$ - Electron scattering factor

1.5 Interaction of X-rays with Matter

- Coherent scattering



Coherent scattering of all electrons in atom

The atomic scattering factor (***f***): the ratio of the combined amplitude of coherent scattered waves of all electrons in an atom to the amplitude of coherent scattered waves of one electron.

$$f = \int_V \rho(\mathbf{r}) e^{i\phi} \, dV \qquad \phi = \frac{4\pi \sin\theta}{\lambda} r \cos\alpha$$

$\rho(\mathbf{r})$ - Electron distribution density in atom
ϕ - Phase difference
$\mathbf{d}V$ - volume element
α - angle between $\mathbf{r}$ and $(\mathbf{k'}\text{-}\mathbf{k})$

Coherent scattering intensity of atoms (I_a): $\quad I_a = f^2 I_e$

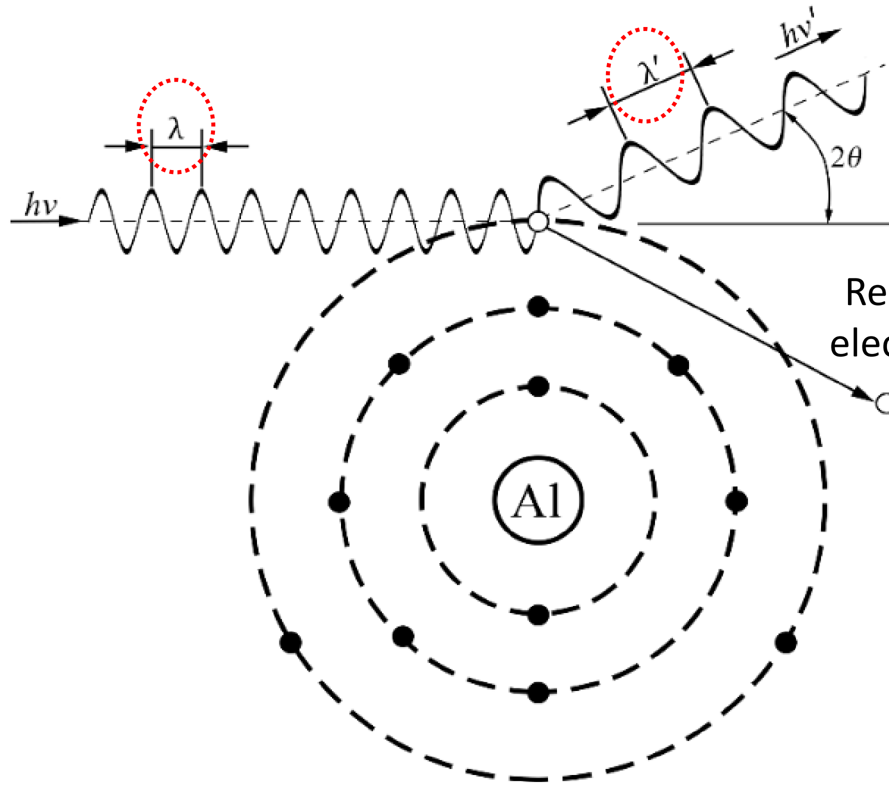
The above analysis regards electrons as free electrons, ignoring the constraints of electrons by nuclei and the repulsion of other electrons. Therefore, the atomic scattering factor needs to be corrected:

$$f_{\text{effect}} = f_0 + f' + \mathrm{i}f''$$

1.5 Interaction of X-rays with Matter

- Incoherent scattering

When X-rays collide with free electrons or electrons that are weakly bound by the nucleus, the electrons gain part of the energy and leave the nucleus and become recoil electrons. The X-ray energy is lost and incoherent scattering with longer wavelength occurs. The incoherent scattering effect was first discovered by Compton and Wu Youxun, and explained this phenomenon with the quantum theory of X-ray light quanta colliding with free electrons.



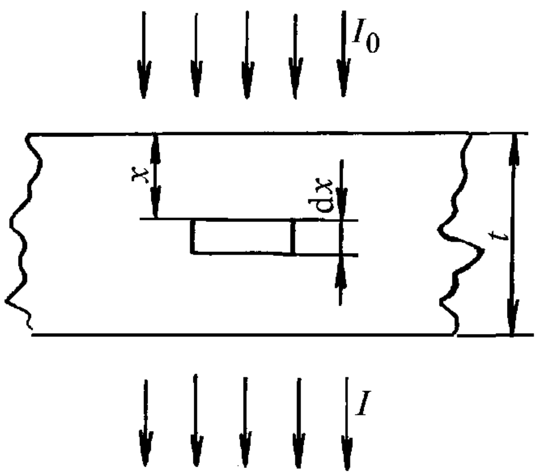
Compton effect

The wavelength change $\Delta\lambda$ caused by incoherent scattering is:

$$\Delta\lambda = \lambda' - \lambda = 0.00243(1 - \cos 2\theta) = 0.00486\sin^2\theta$$

1.5 Interaction of X-rays with Matter

- The absorption and transmission of X-rays



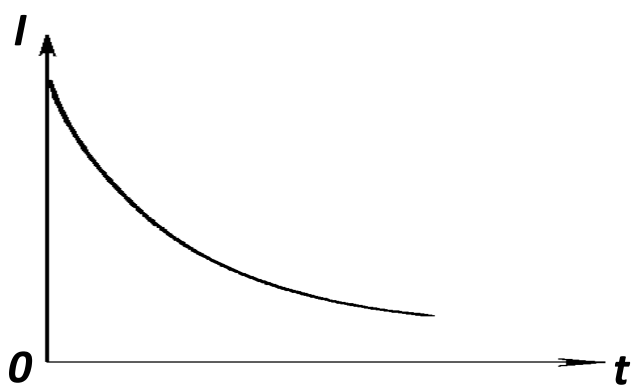
Attenuation of X-rays after passing through the matter

When an X-ray with an intensity $\boldsymbol{I_0}$ irradiates a uniform material with a thickness $\boldsymbol{t}$ and passes through a $\mathbf{d}\boldsymbol{x}$ thickness at a depth $\boldsymbol{x}$, the intensity attenuation $\mathbf{d}\boldsymbol{I_x}/\boldsymbol{I_x}$ is proportional to $\mathbf{d}\boldsymbol{x}$.

$$\frac{\mathrm{d}I_x}{I_x} = -\mu_l \,\mathrm{d}x \longrightarrow I = I_0 \,\mathrm{e}^{-\mu_l t}$$

$\boldsymbol{I} / \boldsymbol{I_0}$ is transmission coefficient

μ_l is intensity attenuation of X-rays passing through a material per unit thickness



Variation of X-ray Intensity with Penetration Depth

1.5 Interaction of X-rays with Matter

- The absorption and transmission of X-rays

The mass of a matter in a unit volume varies with its density, so for a certain matter μ_l is not a constant. In order to express the essential absorption characteristics of the matter, the mass absorption coefficient is used $\mu_m = \mu_l / \rho$ (ρ is the density of the matter).

$$I = I_0 e^{-\mu_l t} \xrightarrow{\mu_m = \mu_l / \rho} I = I_0 e^{-\mu_m \rho t} = I_0 e^{-\mu_m m}$$

μ_m avoids the influence of density and can be used as a physical quantity reflecting the X-ray absorption properties of the matter itself.

Mass absorption coefficient of complex matter

For complex matters composed of multiple elements, such as compounds and mixtures, the mass absorption coefficient depends only on the mass coefficient μ_{mi} of each component and the mass fraction w_i of each component.

$$\bar{\mu}_m = \sum_{i=1}^{n} \mu_{mi} w_i$$

1.5 Interaction of X-rays with Matter

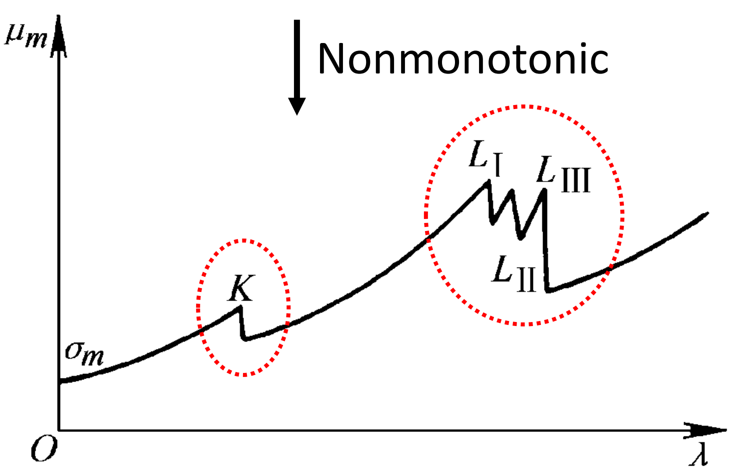
- The absorption and transmission of X-rays

The relationship between mass absorption coefficient and wavelength (λ) of X-rays, atomic number (Z) of absorb matters.

$$\mu_m \approx K_4 \lambda^3 Z^3$$

Z — λ ↓ μ_m ↓ transmission ↑

λ — Z ↑ μ_m ↑ absorption ↑



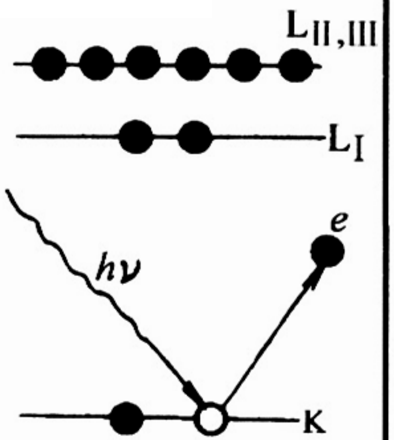
Mass absorption coefficient versus wavelength curve

The absorption coefficient suddenly increases at certain wavelengths, and the corresponding wavelength is called the absorption limit. Each substance has its specific series of absorption limits, which are characteristic quantities of absorbing elements, and this absorption coefficient curve with characteristic absorption limits is called the absorption spectrum of the substance.

1.5 Interaction of X-rays with Matter

- Photoelectric effect

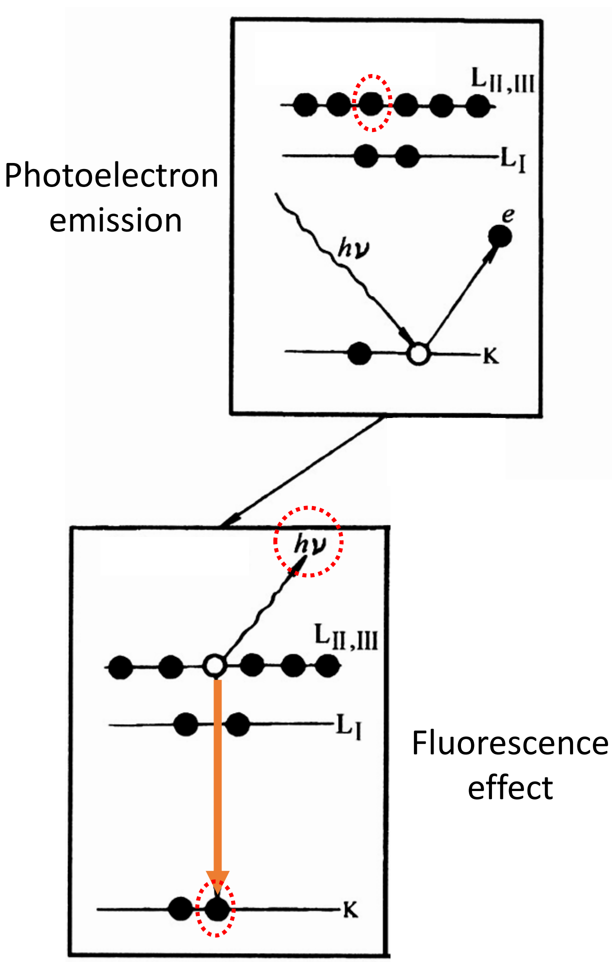
Photoelectron emission



When the energy of the incident X-ray light quantum is equal to or slightly larger than the binding energy of electrons in a certain shell of the absorber atom, the electrons can easily obtain energy and escape from the inner layer and become free electrons, called photoelectrons. This phenomenon of photons knocking out electrons is called photoelectric effect. A large amount of incident energy will be consumed, resulting in a sudden increase in the absorption coefficient, and the corresponding incident wavelength is the absorption limit.

1.5 Interaction of X-rays with Matter

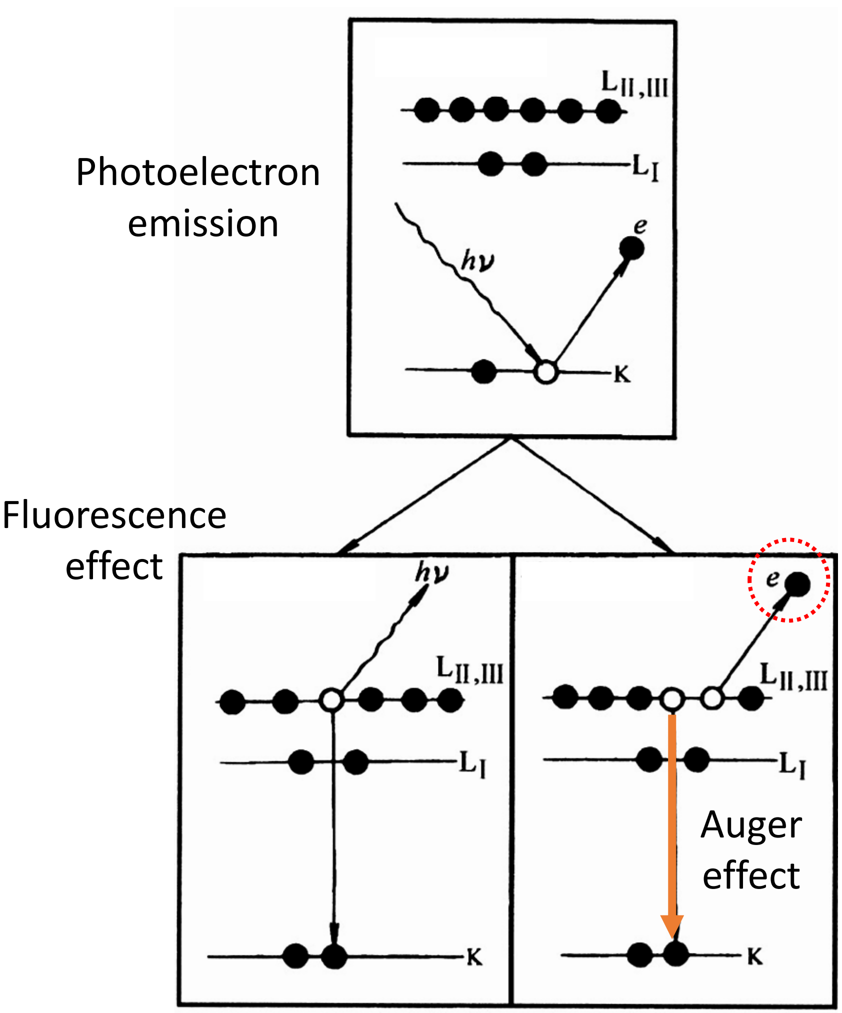
- Fluorescence effect



Atoms in the corresponding excited state due to the photoelectric effect will undergo the transition process of outer electrons to the inner, and at the same time radiate characteristic X-rays. The characteristic radiation generated by X-ray excitation is called secondary characteristic radiation. , this phenomenon of photoluminescence is called fluorescence effect.

1.5 Interaction of X-rays with Matter

- Auger effect



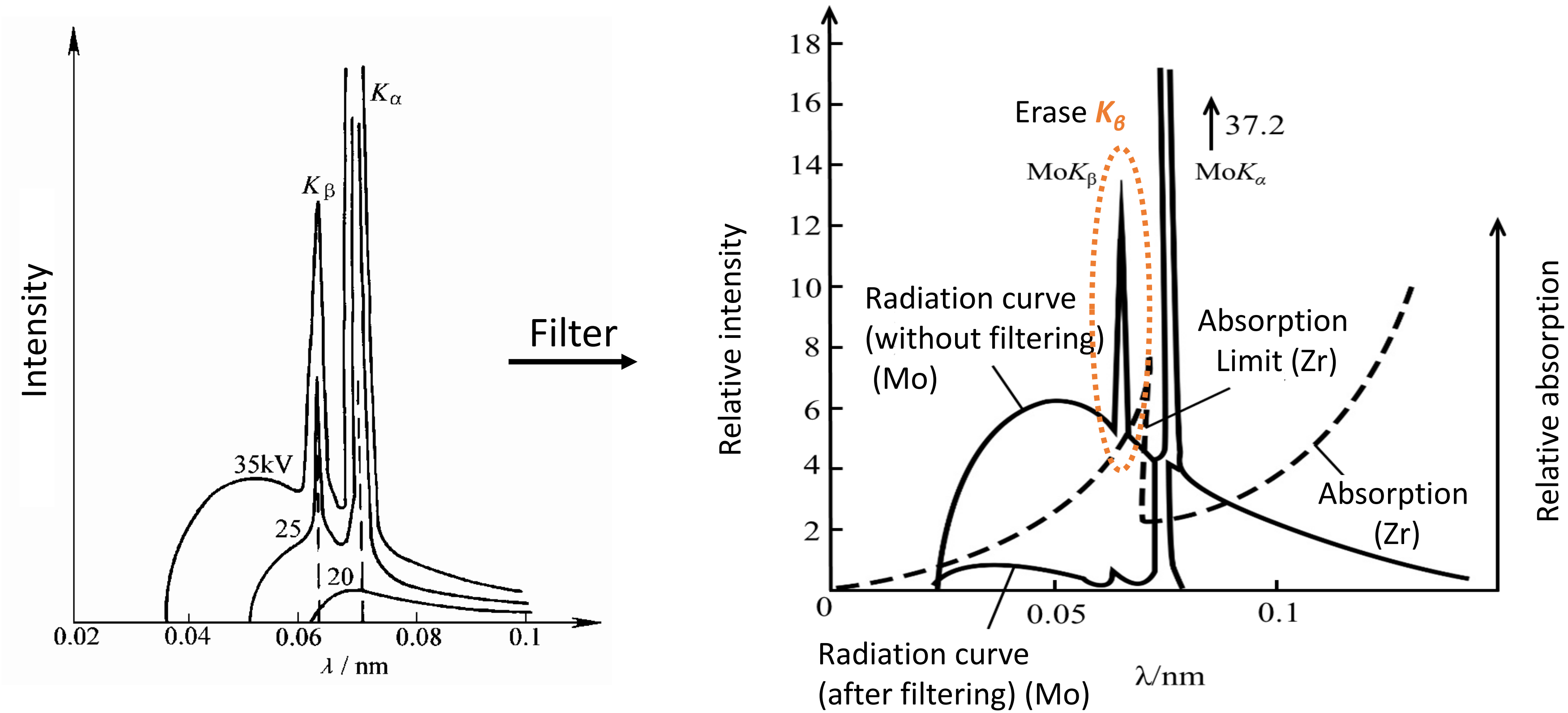
After the K-layer electrons of the atom are knocked out, an electron in the L-layer jumps into the K-layer to fill the vacancy, and another L-layer electron gains energy and escapes from the atom to become an Auger electron. This kind of K-layer vacancy is said to be replaced by two L-layer vacancies The process is the Auger effect.

Both fluorescent X-rays and Auger electrons are signals of the chemical composition of matter. Fluorescent X-rays for compositional analysis of heavy elements, Auger electrons for surface light element analysis.

1.5 Interaction of X-rays with Matter

- Applications of Absorption Limits

The phenomenon that the absorption coefficients on both sides of the absorption limit are very different can be used to select filters to absorb unnecessary radiation and obtain monochromatic X-rays.



1.5 Interaction of X-rays with Matter

- Applications of Absorption Limits

A suitable material can be selected so that its absorption limit lies exactly between the K_α and K_β wavelengths of the characteristic spectrum and is as close as possible to the K_α wavelength. Making this material into a thin sheet-filter and placing it in the incident light path will strongly absorb the K_β line and absorb very little K_α line, and essentially monochromatic radiation can be obtained.

Target (Anode)			Filters ($I_{K\beta}$ = 1/600)				I / I_0 (K_α)
Z_T	$\lambda_{K\alpha}$ /nm	$\lambda_{K\beta}$ /nm	Z_F	λ_K /nm	Thickness /mm	ρt / g·cm^{-2}	
Ag 47	0.0561	0.0497	Rh 45	0.0534	0.079	0.096	0.29
Mo 42	0.0711	0.0632	Zr 40	0.0688	0.108	0.069	0.31
Cu 29	0.1542	0.1392	Ni 28	0.1488	0.021	0.019	0.40
Co 27	0.1790	0.1621	Fe 26	0.1743	0.018	0.014	0.44
Fe 26	0.1937	0.1757	Mn 25	0.1895	0.016	0.012	0.46
Cr 24	0.2291	0.2085	V 23	0.2268	0.016	0.009	0.50

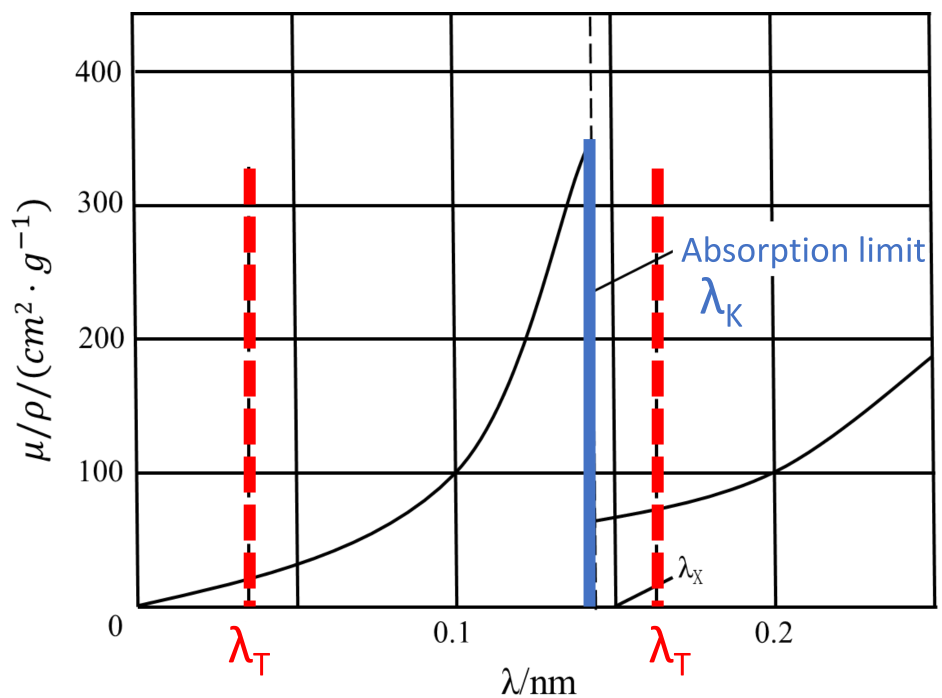
$Z_T < 40$， $Z_F = Z_T - 1$ $Z_T > 40$， $Z_F = Z_T - 2$

1.5 Interaction of X-rays with Matter

- Applications of Absorption Limits

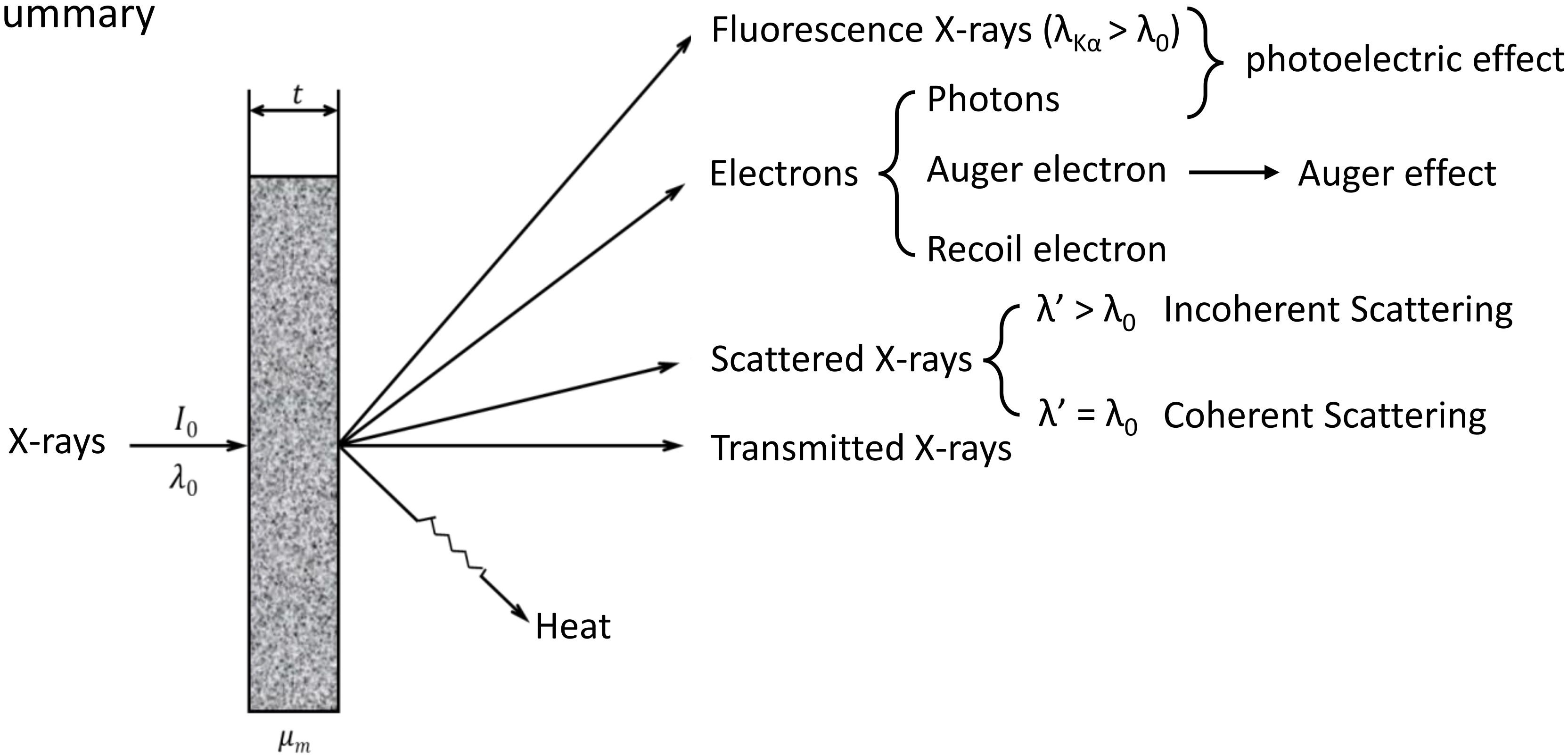
In X-ray diffraction analysis, it is better that the sample absorbs as little X-ray as possible to obtain high diffraction intensity and low background.

The incident ray wavelength λ_T is slightly larger or much smaller than the λ_K of the sample, that is, the principle of selecting the target material according to the sample is $Z_T \leq Z_S + 1$ or $Z_T >> Z_S$.



1.5 Interaction of X-rays with Matter

- Summary



- Fluorescence X-ray is the basis of qualitative and quantitative elemental chemical analysis;
- X-ray excited photoelectrons and Auger electrons are the basis for X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) analysis;
- Coherent scattering is the basis of X-ray diffraction (XRD) technology;
- Fundamentals of non-destructive testing in transmitted X-rays.