X-ray Interactions with Matter

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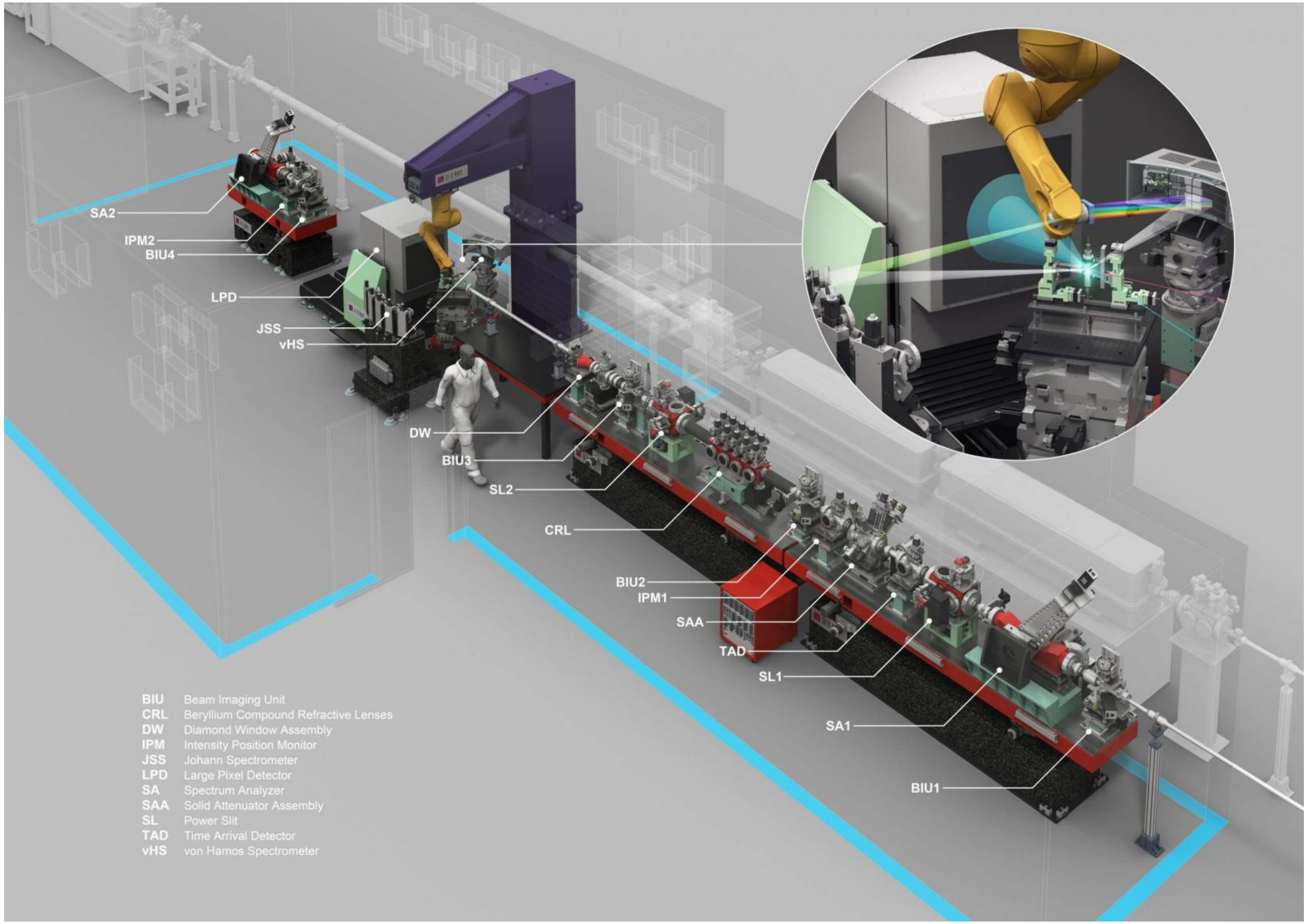
Suggested readings

[1] Attwood, D., & Sakdinawat, A. (2017). X-Rays and Extreme Ultraviolet Radiation: Principles and Applications (2nd ed.). Cambridge: Cambridge University Press.

[2] Willmott P. (2011), An introduction to synchrotron radiation: techniques and applications. John Wiley & Sons, Ltd.,

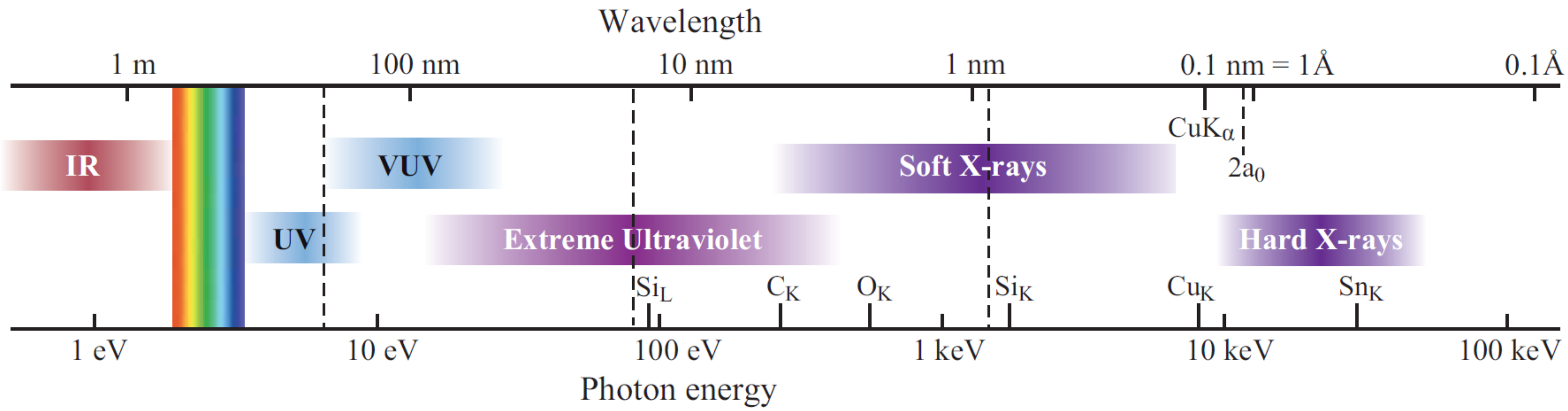
[3] Jens Als-Nielsen, Des McMorrow (2011) Elements of Modern X-ray Physics. John Wiley & Sons, Ltd.

X-ray interactions with matter



https://www.jjxray.dk/wp-content/uploads/2020/06/fxe-finala1-151127-s-1-scaled.jpg

Electromagnetic spectrum



source: [1]

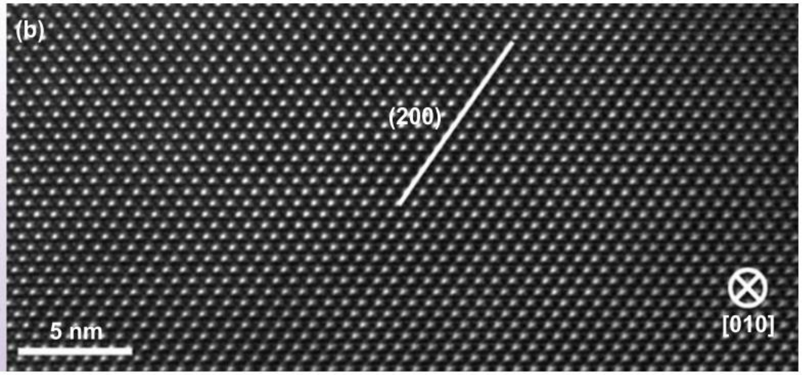
$\mathcal{E}$ – photon energy
h – Planck's constant
ω – wave frequency
c – speed of light
λ – wavelength

$$\mathcal{E} = \frac{h\omega}{2\pi} = \frac{hc}{\lambda}$$

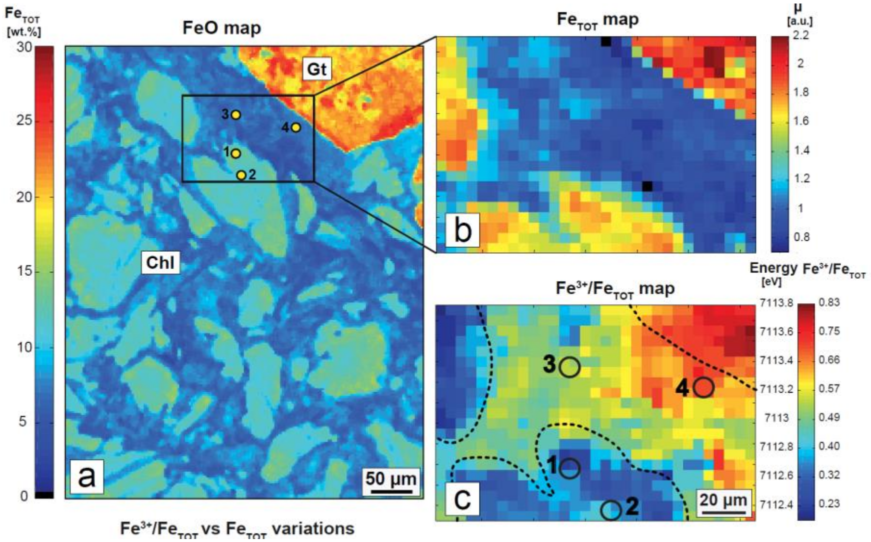
$$\lambda[\text{Å}] = \frac{hc}{\mathcal{E}} \cong \frac{12.4}{\mathcal{E}[\text{keV}]}$$

Charecteristic features of X-rays

- „See" small features (short wavelength)
- Elemental and chemical sensitivity (energy of atomic resonances)
- Penetrate visibly opaque objects (weak interaction with matter)



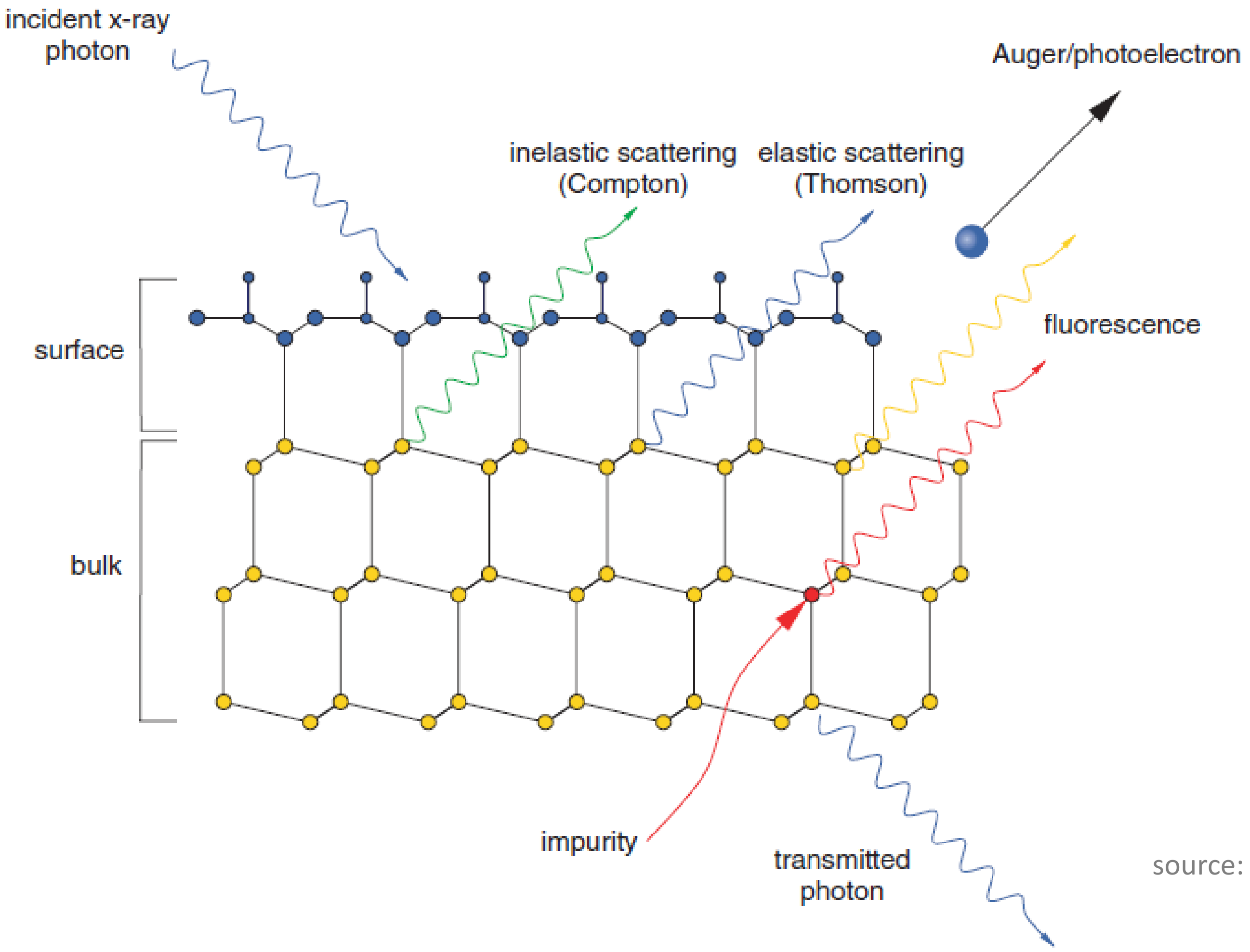
source: Y.Q. Wu, S. Gao, H. Huang, Materials Science in Semiconductor Processing, Volume 71, 2017, Pages 321-325,



source: L. Masci et al., American Mineralogist, Volume 104, pages 403–417, 2019

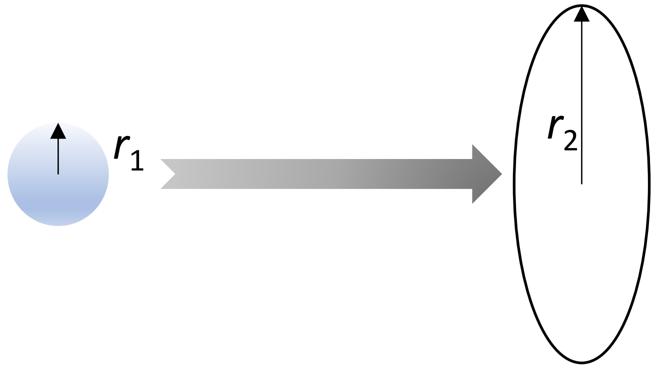
source: Wikipedia

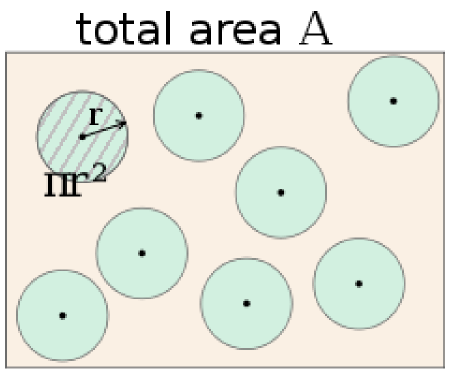
X-ray interactions mechanisms



source: [2]

Cross section



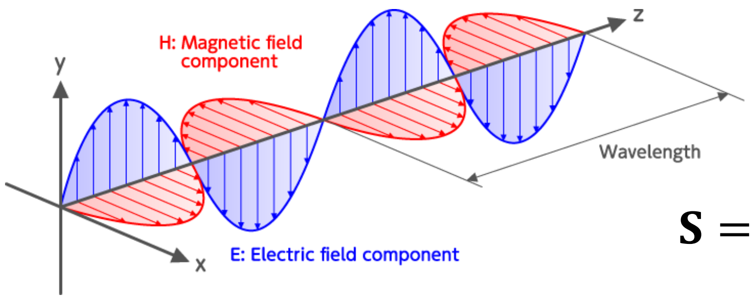


source: Wikipedia

$$\sigma = \pi(r_1 + r_2)^2 \qquad \text{probability} = \frac{n\sigma}{A}$$

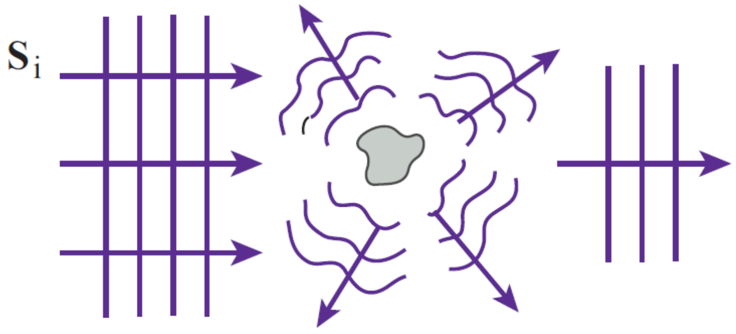
σ – **cross section** (expressed in units of area) is a measure of the probability that two particles will collide and react in a certain way.

Scattering cross-section for EM radiation



$$\mathbf{S} = \mathbf{E}(\mathbf{r}, t) \times \mathbf{H}(\mathbf{r}, t)$$

source: https://i.stack.imgur.com/27cRJ.png



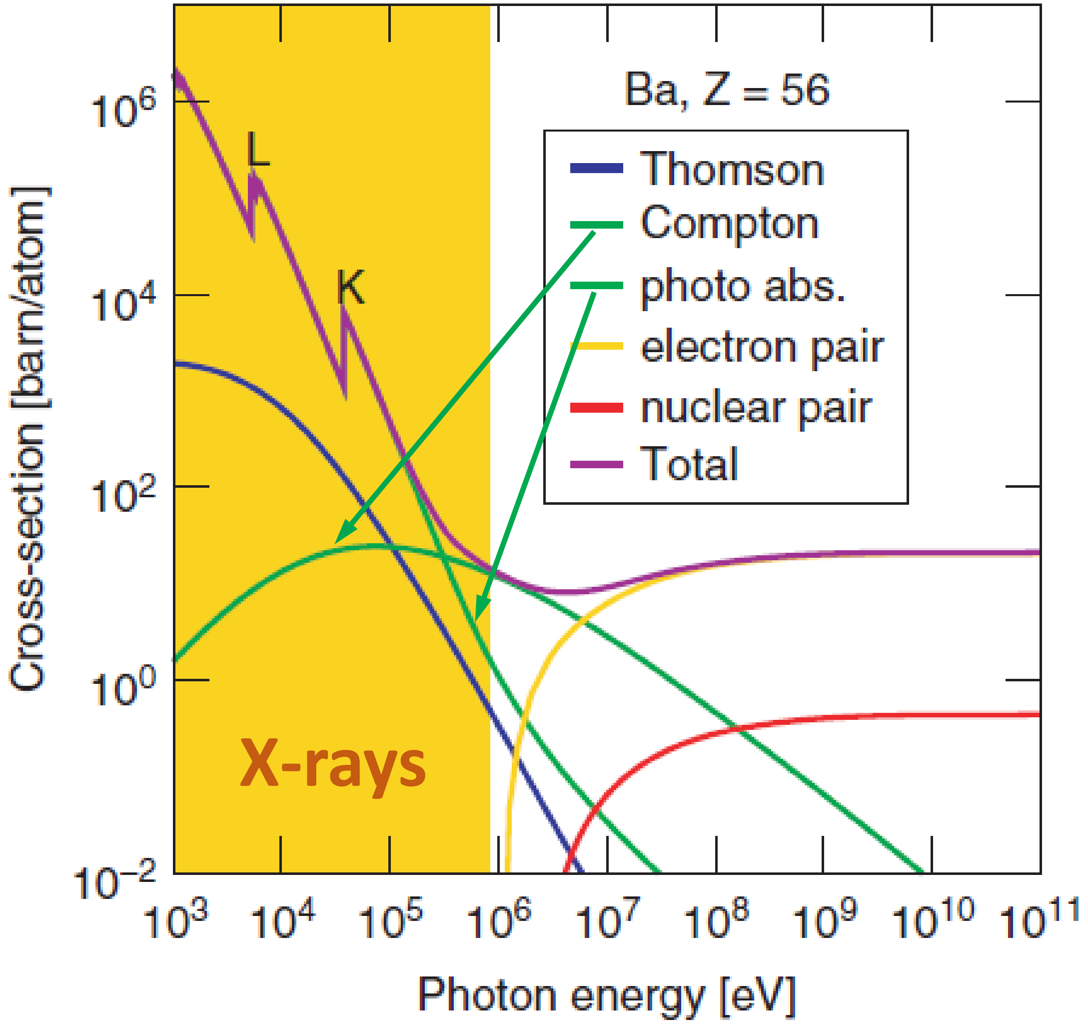
source: [1]

$$\sigma_e \overset{\text{def}}{=} \frac{\bar{P}_{\text{scatt.}}}{|\bar{\mathbf{S}}_i|}$$

average radiated power

average incident power per unit area

Cross section for X-ray generated processes



source: [2]

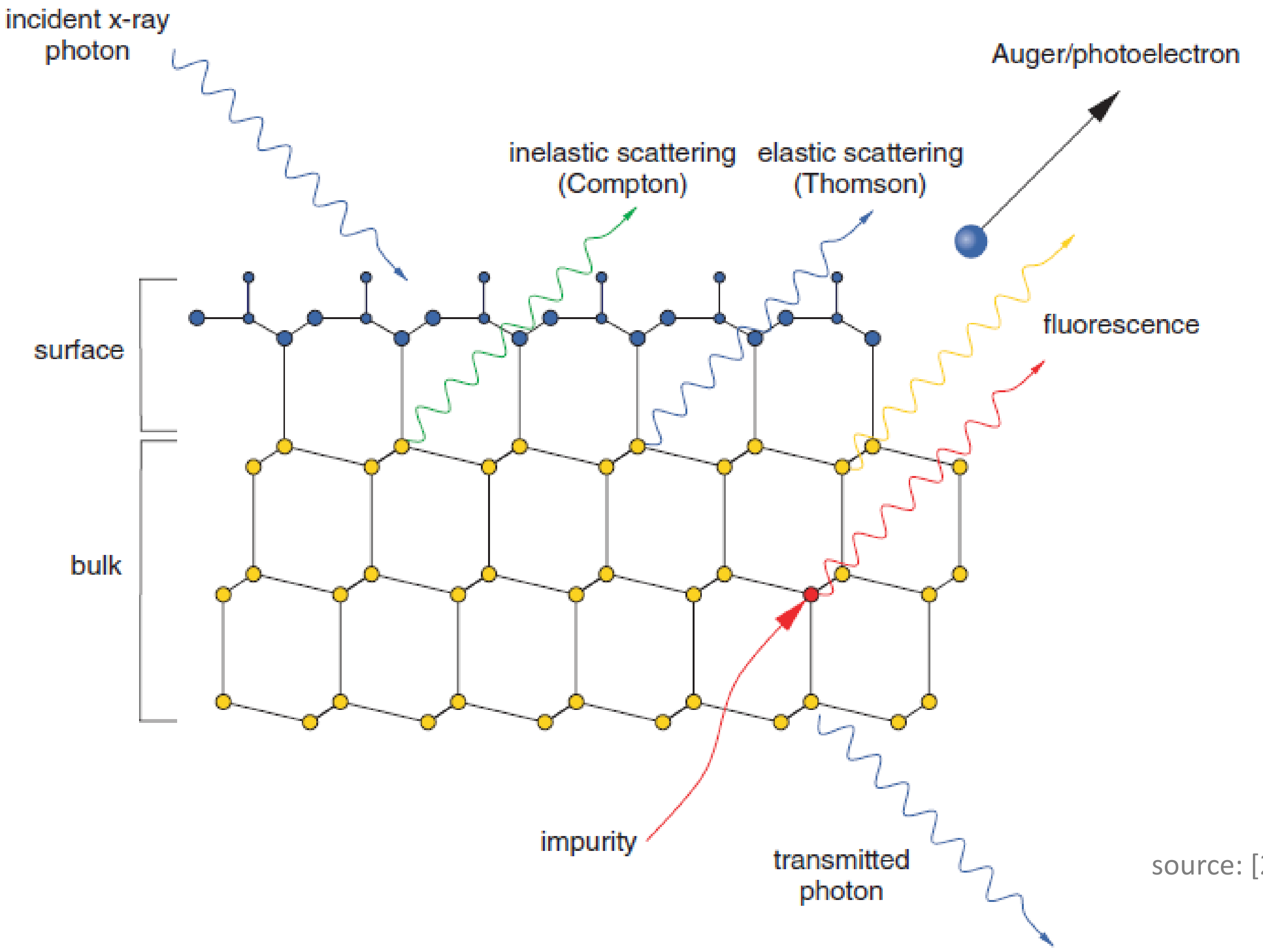
1 barn = 100 fm^2 = 10^{-28} m^2

Cross section for X-ray generated processes

source: https://www.dental-design.com.pl/

The total scattering cross section for X-rays is generally small.

X-ray interactions mechanisms

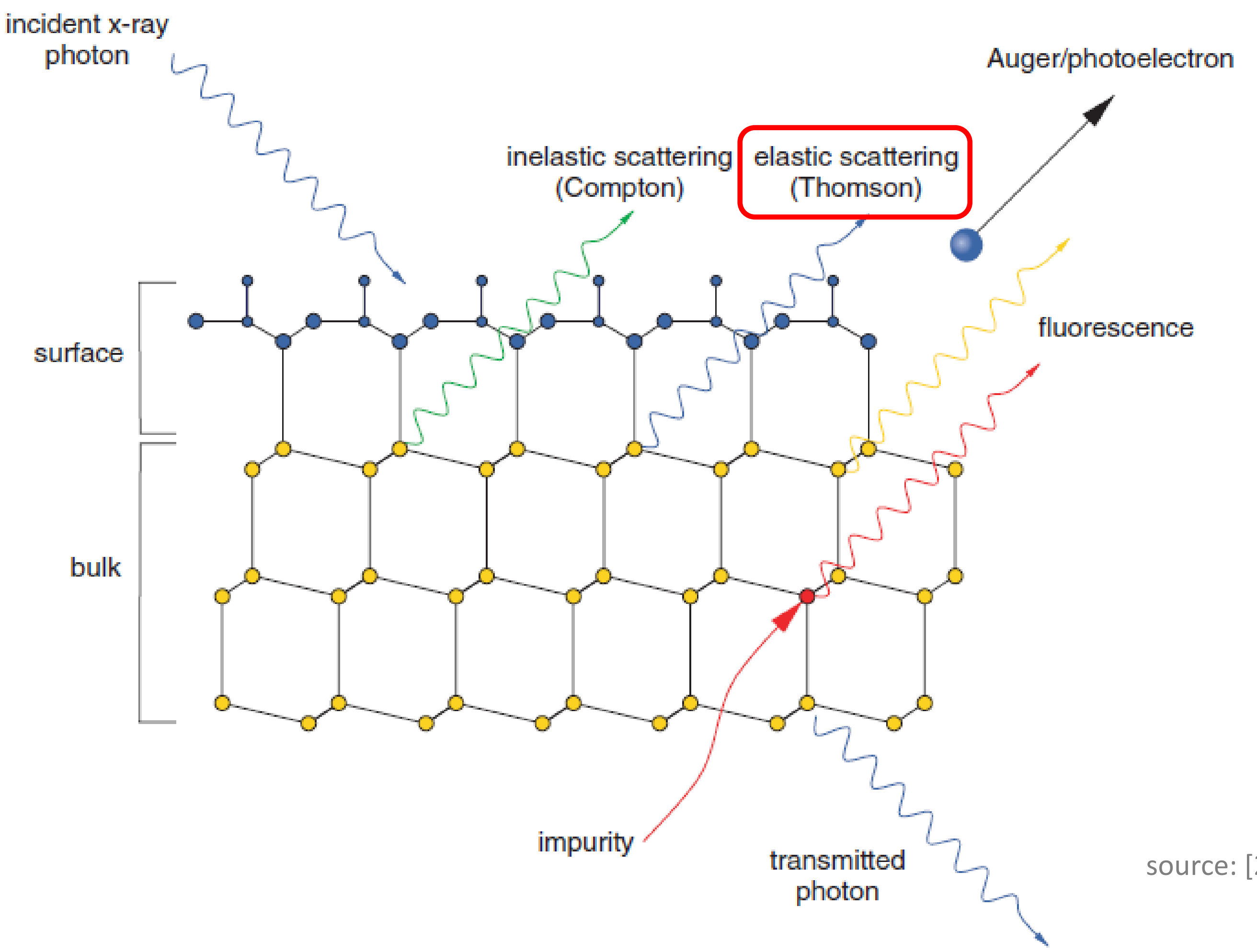


source: [2]

Scattering by electrons

- Scattering by a single, free (non-bound) electron
- Scattering by many free electrons (electron cloud of an atom)
- Scattering by bound electrons (electrons occupying discrete energy levels in an atom)

X-ray interactions mechanisms



source: [2]

Scattering by a free electron

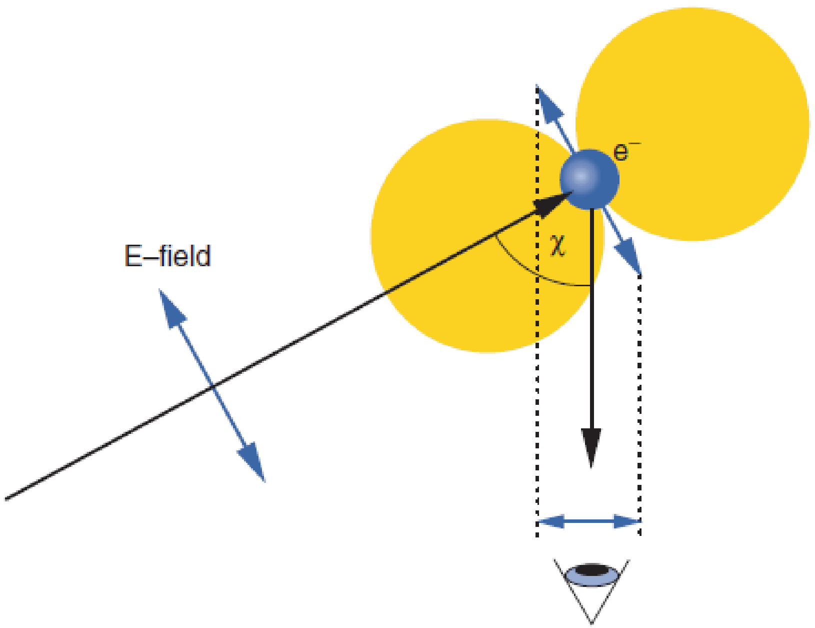
Equation of motion of a free electron: $m\mathbf{a} = -e\left[\mathbf{E}_i + \mathbf{v} \times \mathbf{B}_i\right]$

Oscillations impressed by a incident electric field: $\mathbf{E}_i = \mathbf{E}e^{-i\omega t}$

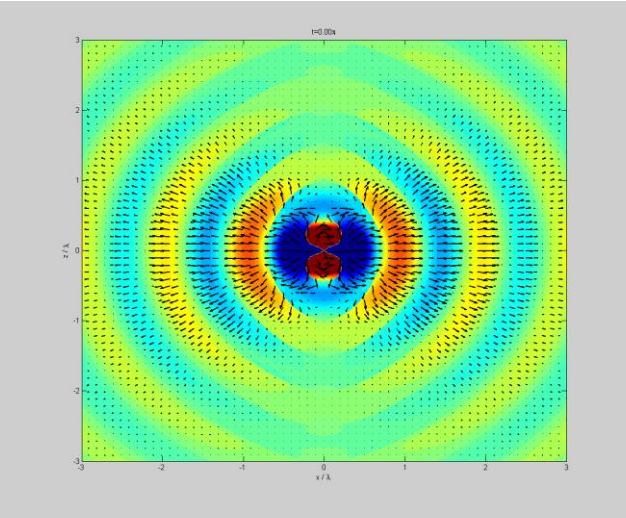
For non-relativistic oscillation velocities: $\mathbf{a}(\mathbf{r}, t) = -\frac{e}{m}\mathbf{E}_i(\mathbf{r}, t)$

The frequency of oscillations of a free electron is **the same** as that of the incident electric field.

Elastic (Thomson) X-ray scattering



source: [2]



source: Wikipedia

Elastic scattering: the frequency of the incident and the scattered EM wave are equal.

average power per unit area radiated by an oscillating electron:

$$\bar{P}_{\text{scatt.}} = \frac{4\pi}{3}\left(\frac{e^4|\mathbf{E}_i|^2}{16\pi^2\epsilon_0 m_e^2 c^3}\right)$$

average power per unit area carried by the incident electromagnetic wave (intensity):

$$\bar{\mathbf{S}}_i = \frac{1}{2}\sqrt{\frac{\epsilon_0}{\mu_0}}|\mathbf{E}_i|^2\mathbf{k}_0$$

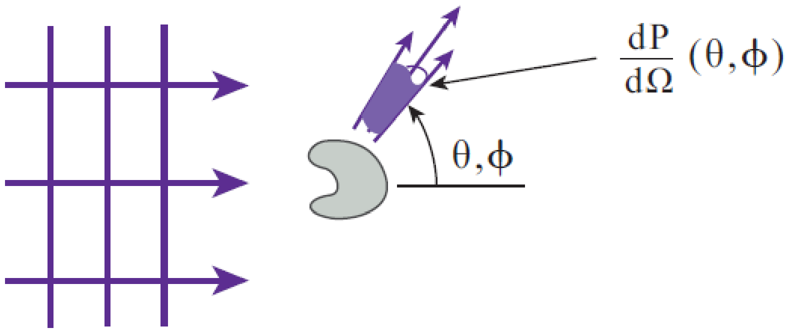
Scattering cross-section for a free electron

Thomson cross-section: $\sigma_e \overset{\text{def}}{=} \dfrac{\bar{P}_{\text{scatt.}}}{|\bar{\mathbf{S}}_i|} = \dfrac{8\pi}{3} r_e^2$

$$r_e = \frac{e^2}{4\pi\epsilon_0 m_e^2 c^2}$$

r_e - **classical electron radius** defined by equating the electrostatic energy of a uniform sphere of radius *r* and charge *e* to its rest energy $m_e c^2$.

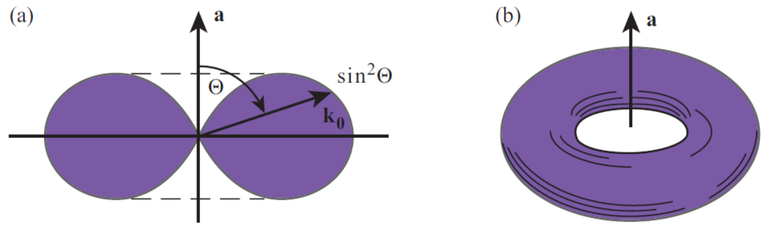
$$r_e = 2.818 \times 10^{-15}\ \mathrm{m}$$
$$\sigma_e = 6.652 \times 10^{-27}\ \mathrm{m}^2$$



source: [1]

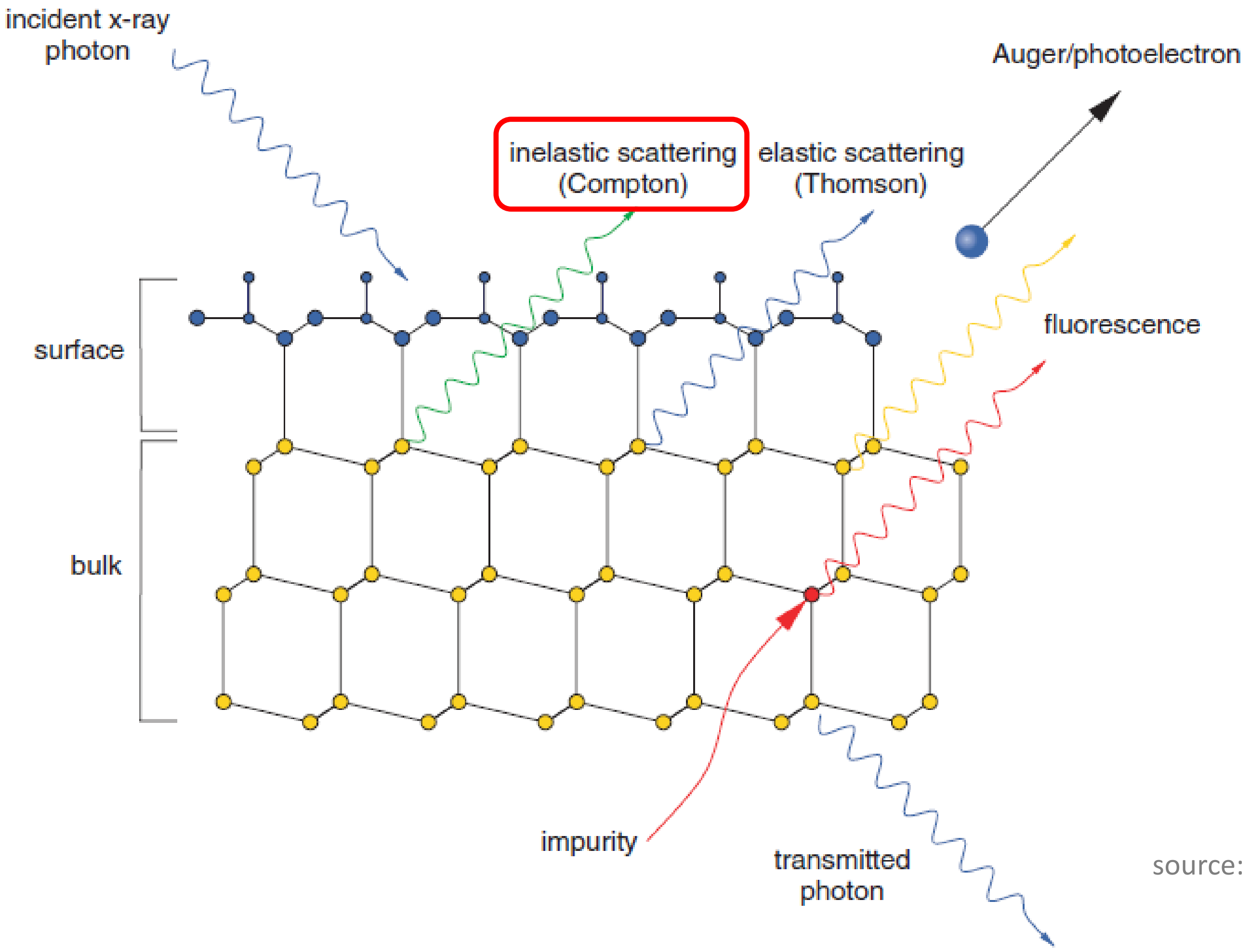
Differential Thomson scattering cross-section:

$$\frac{d\sigma_e}{d\Omega} = r_e^2 \sin^2\theta$$



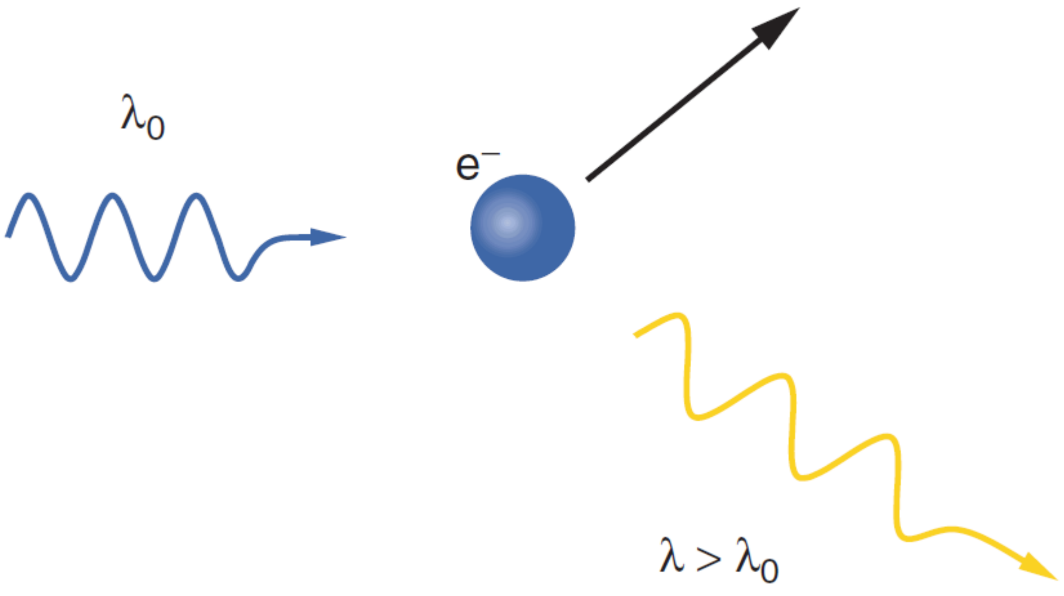
source: [1]

X-ray interactions mechanisms



source: [2]

Inelastic (Compton) X-ray scattering



source: [2]

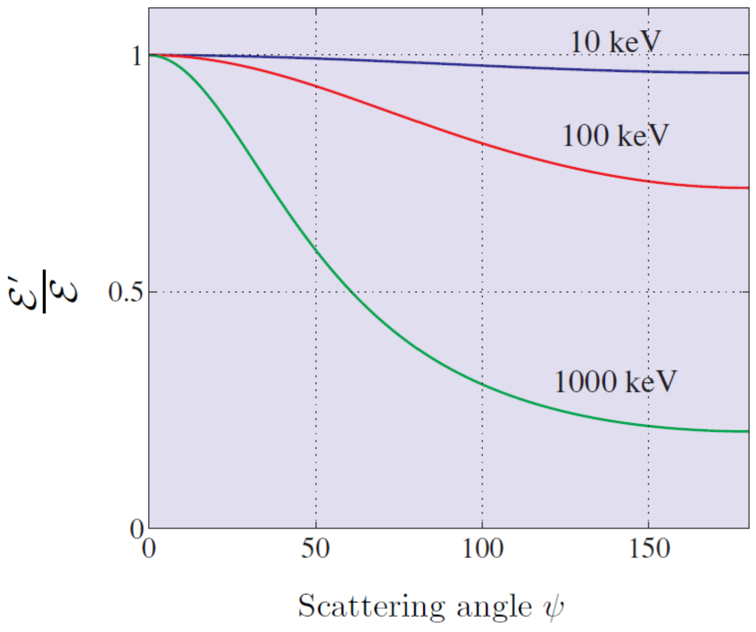
The energy loss in Compton scattering can be determined by applying the conservation of (relativistic) energy and (relativistic) momentum.

$$\Delta\lambda = \lambda - \lambda_0 = \frac{h}{m_e c}(1 - \cos\theta)$$

$$\boxed{\lambda_C = \frac{h}{m_e c} \cong 2.43 \times 10^{-12}\ \mathrm{m}}$$

λ_C - **Compton wavelength** of an electron is a property of an electron, defined as the wavelength of a photon whose energy is the same as the electron's rest energy.

Inelastic vs elastic X-ray scattering



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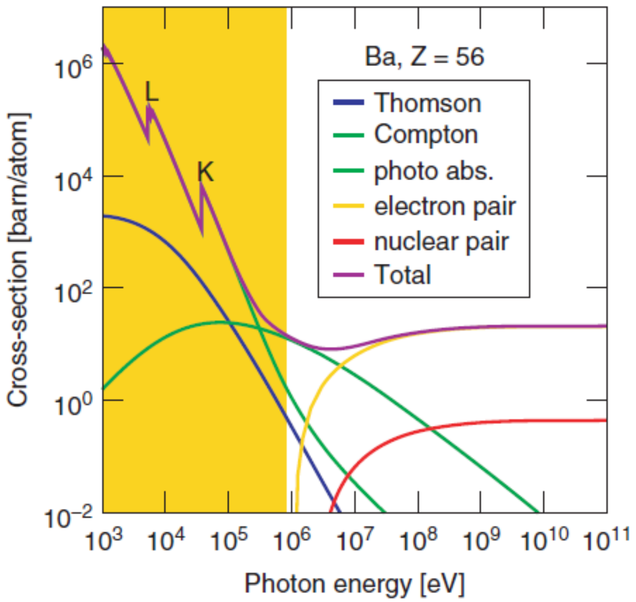


source: [2]

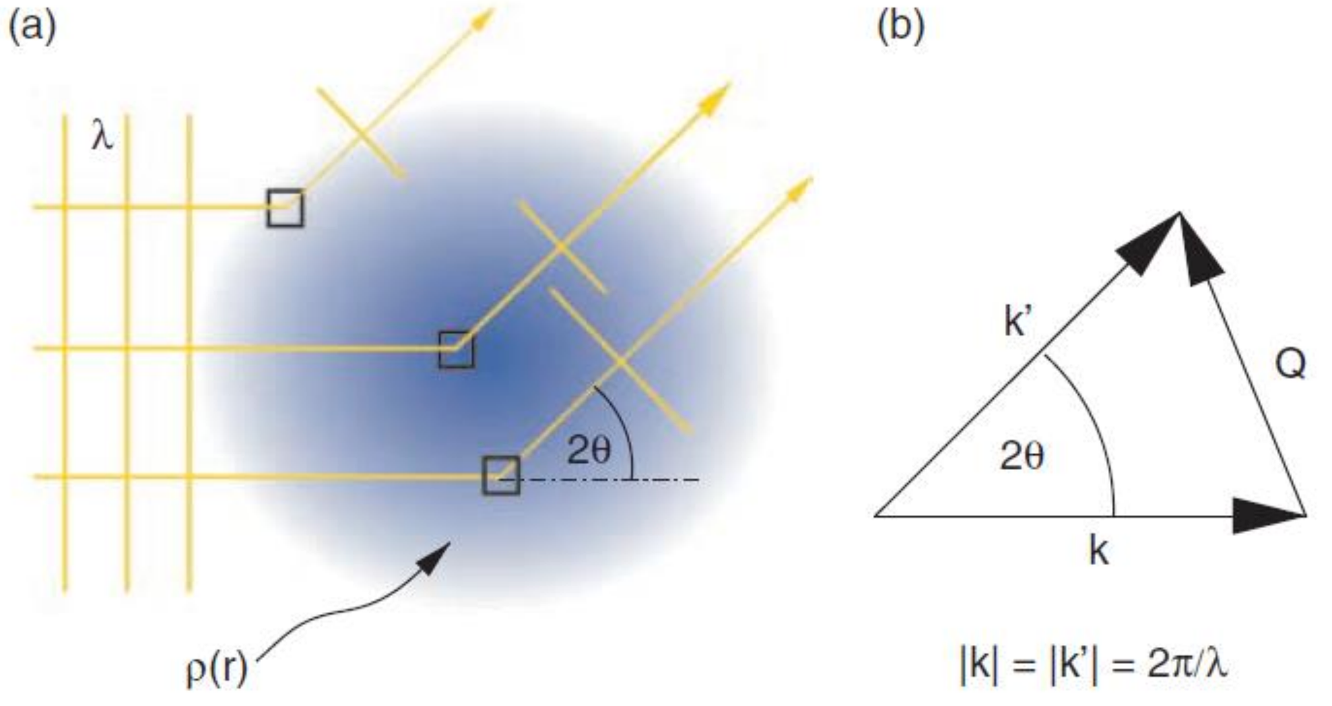
The ratio of the energy ε' of the scattered photon to the energy ε of the incident one as function of scattering angle.

fine-structure constant:

$$\alpha = \frac{r_e}{\lambda_C} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{\hbar c} \cong \frac{1}{137}$$

Do not confuse Compton scattering with photoabsorption!

X-ray scattering by a cloud of free electrons



source: [2]

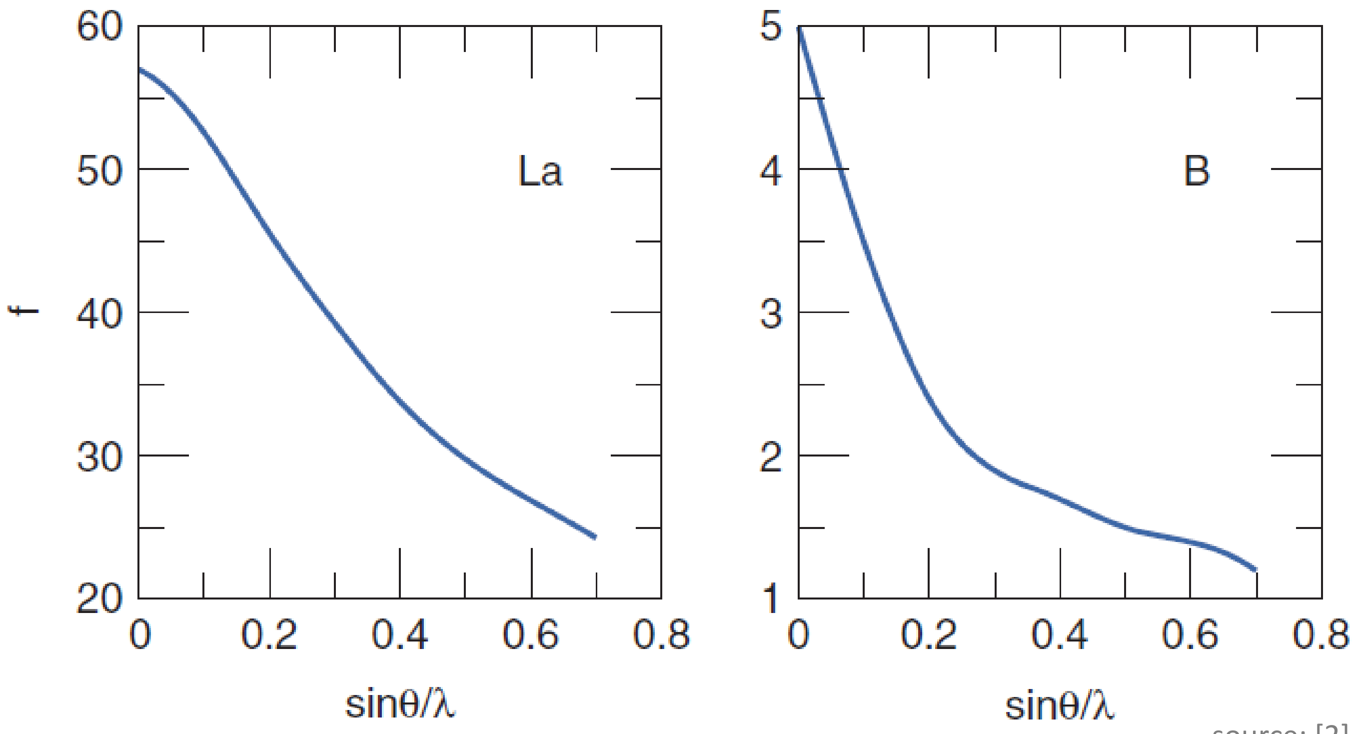
$$\mathbf{Q} = \mathbf{k} - \mathbf{k}'$$

$$\boxed{Q = \frac{4\pi}{\lambda}\sin\theta}$$

$\mathbf{Q}$ – scattering vector

Atomic scattering factor

$$f\,(\mathbf{Q}) = \int \rho(\mathbf{r})\, e^{i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{r} = \begin{cases} Z & \text{for } \mathbf{Q} \to 0 \\ 0 & \text{for } \mathbf{Q} \to \infty \end{cases}$$



source: [2]

Atomic scattering (form) factor involves a Fourier transform of a spatial charge distribution from real space to momentum (Q) space.

Scattering by a bound electron

Equation of motion of a bound electron:

$$\underbrace{m\frac{d^2\mathbf{x}}{dt^2}}_{\text{acceleration}} + \underbrace{m\gamma\frac{d\mathbf{x}}{dt}}_{\text{dissipative force}} + \underbrace{m\omega_s^2\mathbf{x}}_{\text{restoring force}} = \underbrace{-e(\mathbf{E}_i + \underbrace{\mathbf{v}\times\mathbf{B}_i}_{\simeq 0})}_{\text{Lorentz force}}$$

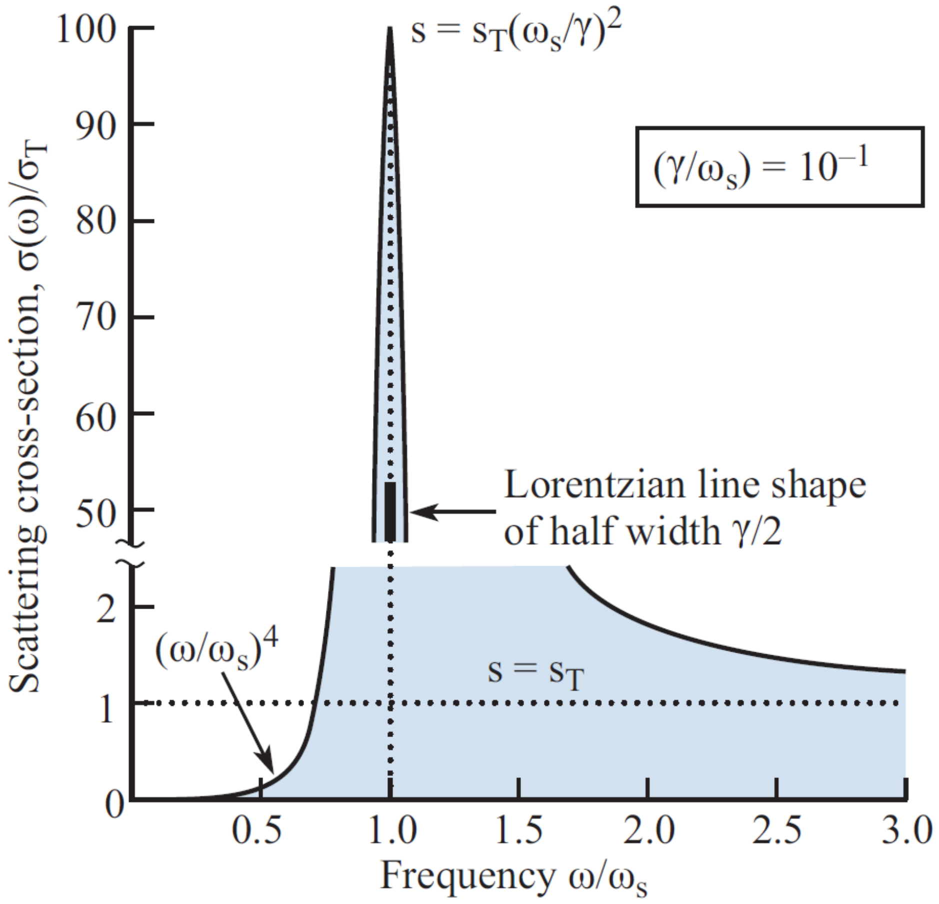
Oscillations impressed by a incident electric field: $\mathbf{E}_i = \mathbf{E}e^{-i\omega t}$

Acceleration of a bound electron: $\mathbf{a} = \dfrac{-\omega^2}{\omega^2 - \omega_s^2 + i\gamma\omega}\dfrac{e\mathbf{E}_i}{m}$

Scattering cross-section for a bound electron of resonant frequency ω_s:

$$\boxed{\sigma = \frac{8\pi}{3}r_e^2\frac{\omega^4}{\left(\omega^2-\omega_s^2\right)^2+(\gamma\omega)^2}}$$

Scattering by a bound electron



source: [1]

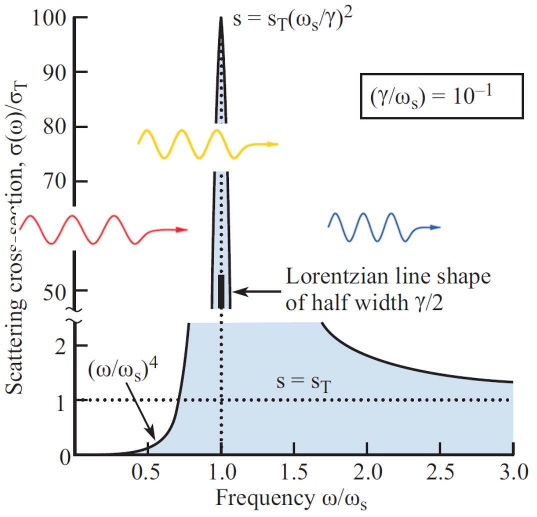
$$\sigma = \frac{8\pi}{3} r_e^2 \frac{\omega^4}{\left(\omega^2 - \omega_s^2\right)^2 + (\gamma\omega)^2}$$

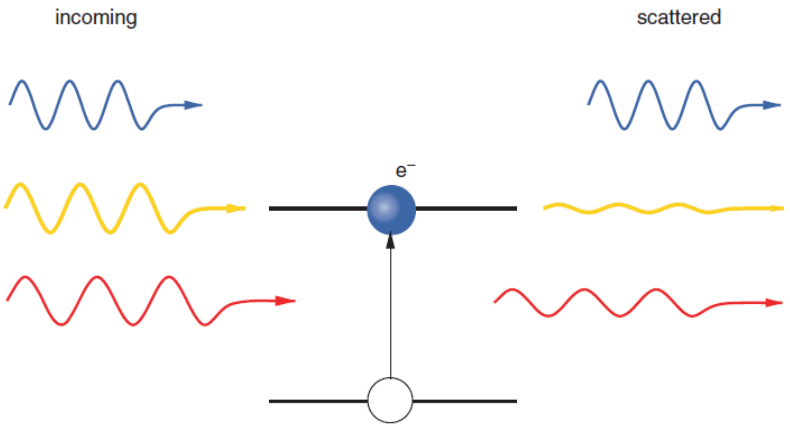
Unlike for a free electron, the scattering cross-section for a bound electron is **strongly frequency dependent**, especially near the resonance.

Scattering by a bound electron

$$\boxed{f_1 = f - f'}$$

scattering from a bound electron	=	scattering from a free electron	-	damping





The amplitude of the scattered EM wave decreases as the energy of the incident radiation approaches the electron binding energy (the resonance).

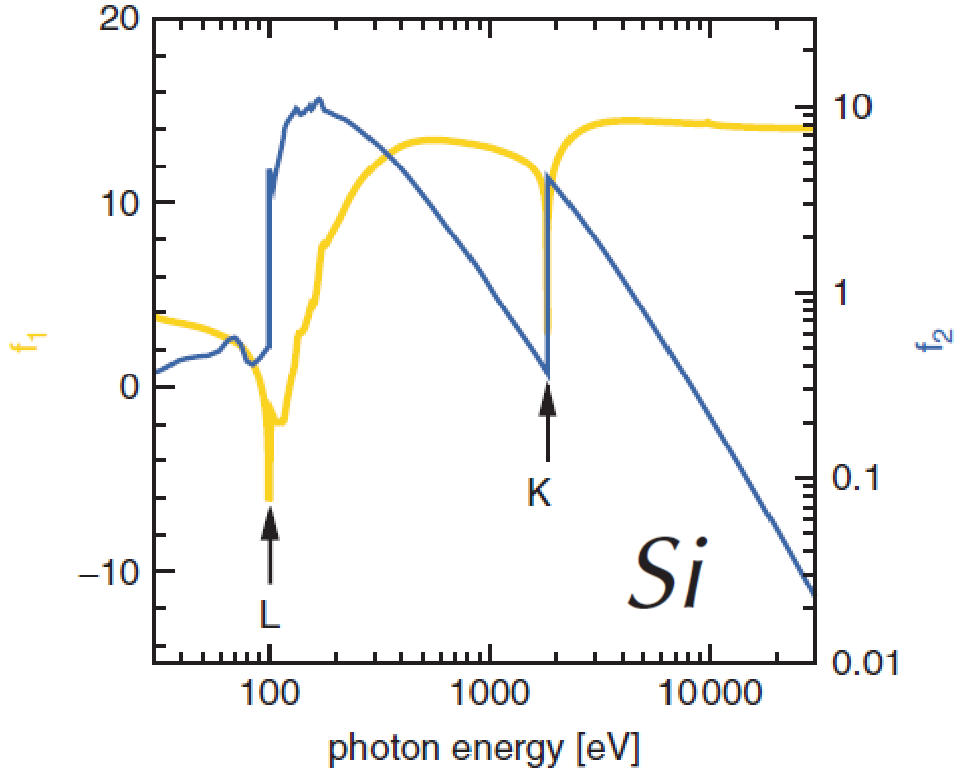
Complex atomic scattering factor

The interference between the incoming and emitted radiation causes energy loss (i.e. absorption), and the additional (damping) term is imaginary.

$$f = f_1 + i f_2$$

$$f_1 = f - f'$$

$$\boxed{f_2 \propto \varepsilon^{-2}}$$



source: [2]

Index of refraction

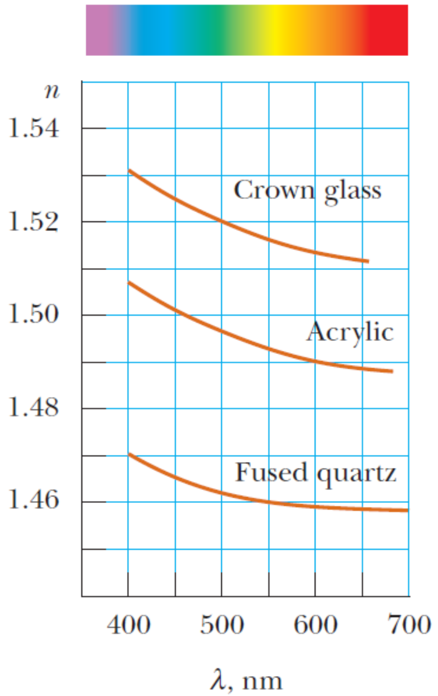
The index of refraction n is a complex quantity describing the response of electrons in matter to electromagnetic radiation of a wavelength λ.

$$n = n_{Re} + i n_{Im}$$

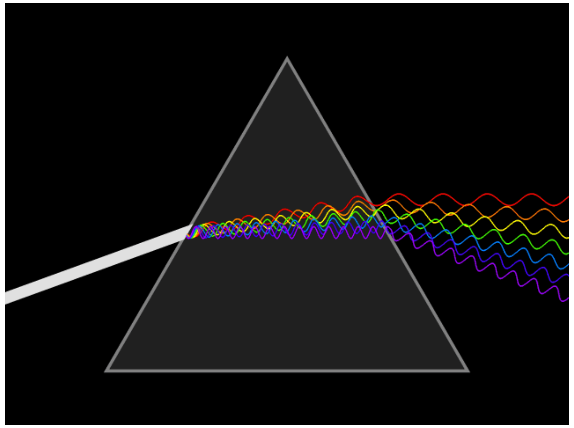
$$n = 1 - \frac{r_e}{2\pi}\lambda^2 \sum_i N_i f_i^0$$

N_i - number of atoms of type i
f_i^0 - complex atomic scattering factor in a forward direction

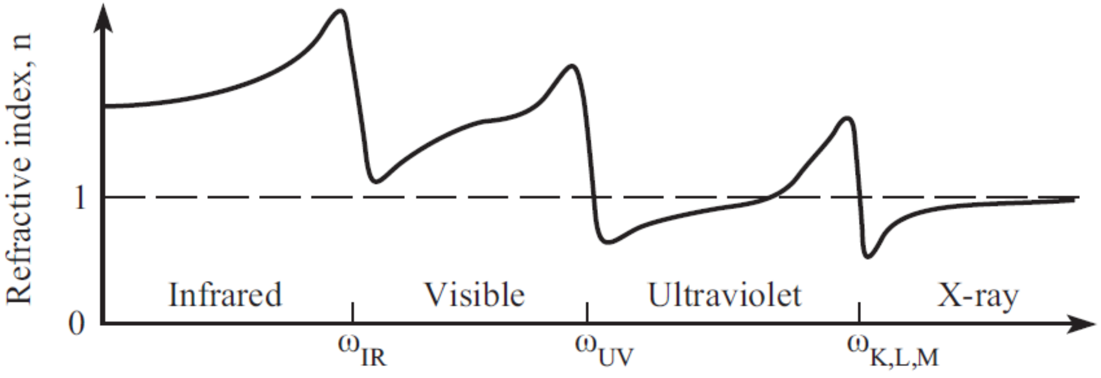
Anomalous dispersion



source: Halliday, Resnick & Walker – Fundamentals of Physics



source: Wikipedia



source: [1]

$$n = 1 - \delta + i\beta$$
$$n_{Re} = 1 - \delta$$
$$n_{Im} = \beta$$

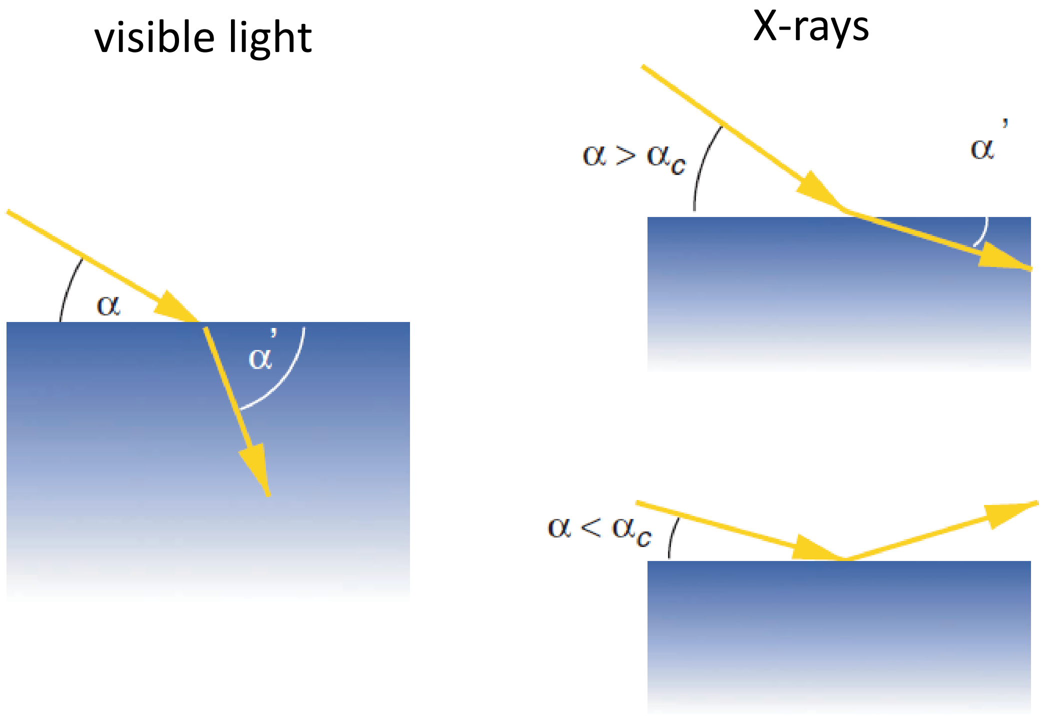
$$\delta = \frac{n_a r_e \lambda^2}{2\pi} f_1^0(\omega)$$
$$\beta = \frac{n_a r_e \lambda^2}{2\pi} f_2^0(\omega)$$

n_a - atomic density

eg. for Si in the X-ray regime:
$\delta \approx 5 \times 10^{-6}$

For X-rays, n_{Re} is only slightly less than unity.

Total external reflection of X-rays



source: [2]

For X-rays, at grazing angles less than the critical angle, total **external** reflection will occur.

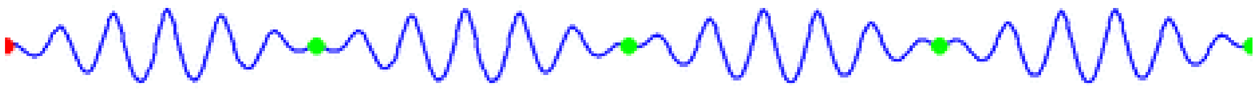
$$n_{Re} = \frac{\cos\alpha}{\cos\alpha\prime} < 1$$

$$\alpha_c \approx \sqrt{2\delta}$$

typical values of α_c:
a few milliradians/tenths of a degree

Phase velocity of X-rays in matter

$$\text{phase velocity} = \frac{v}{n_{Re}} > c$$

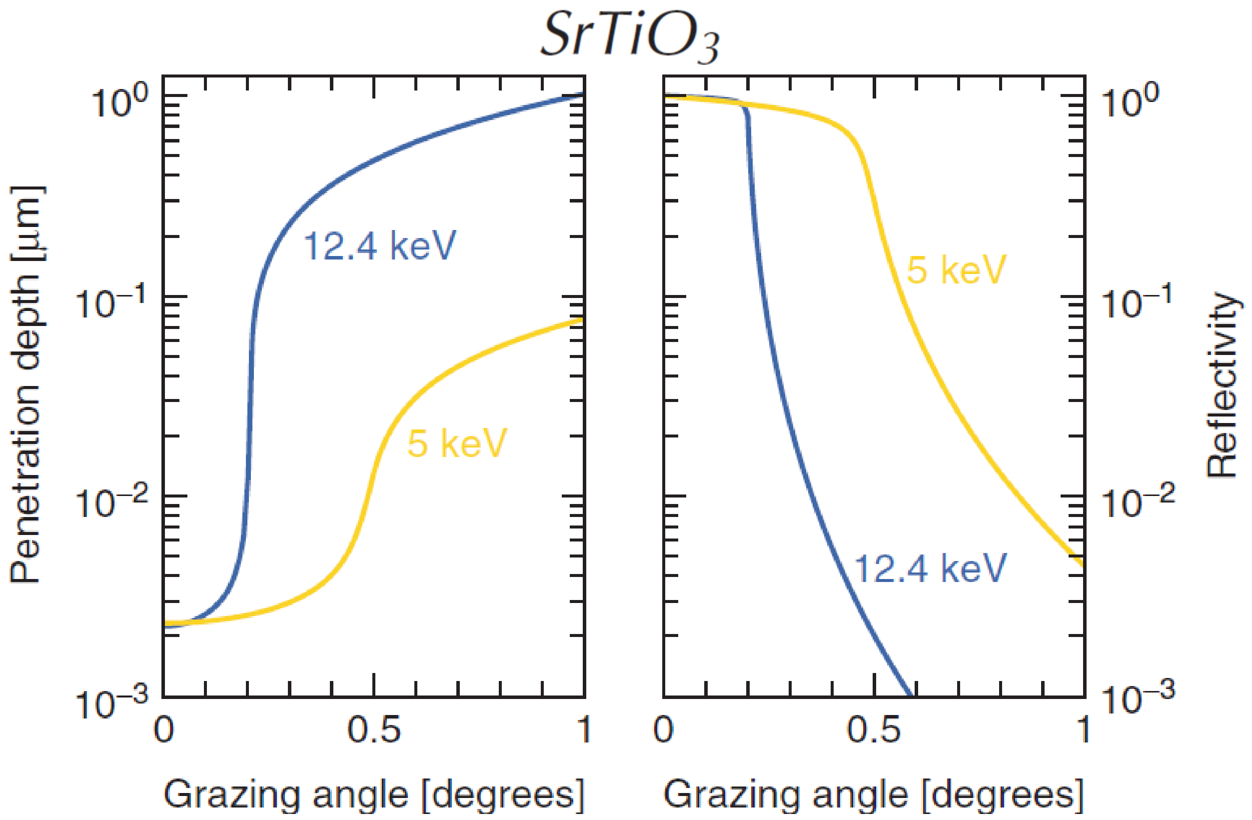


source: Wikipedia

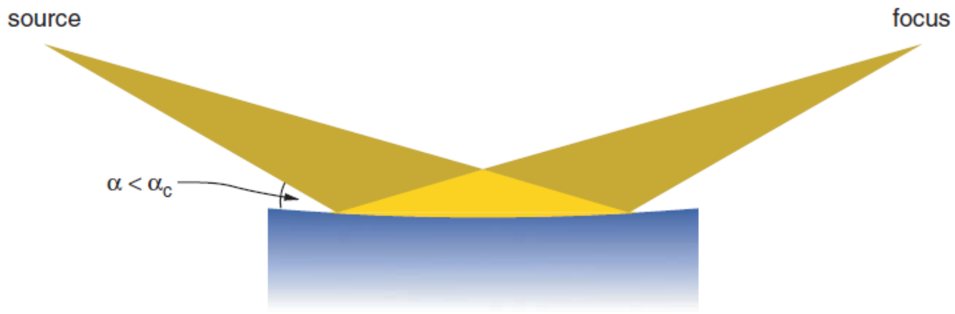
source: przegladsportowy.pl

RED point moves at **phase velocity**
GREEN point moves at **group velocity**
It is the **group velocity** that carries energy/information.

Total external reflection of X-rays



source: [2]



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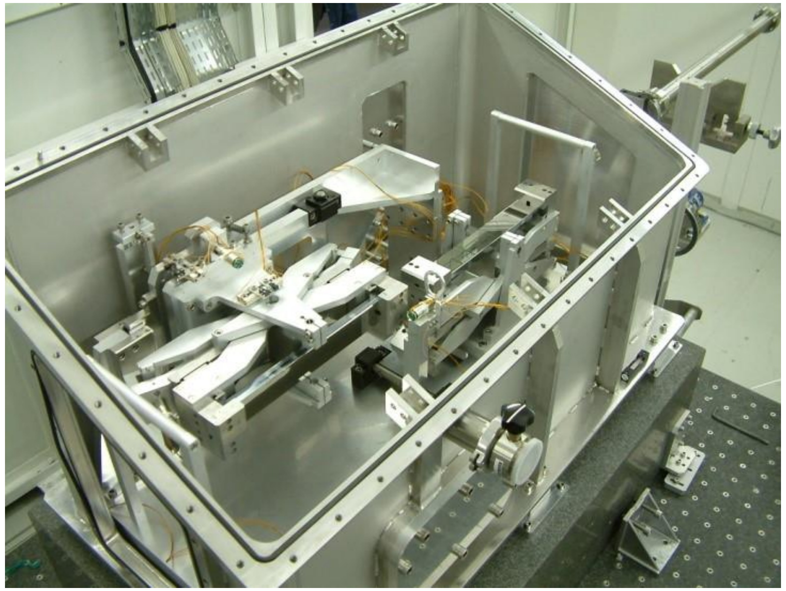
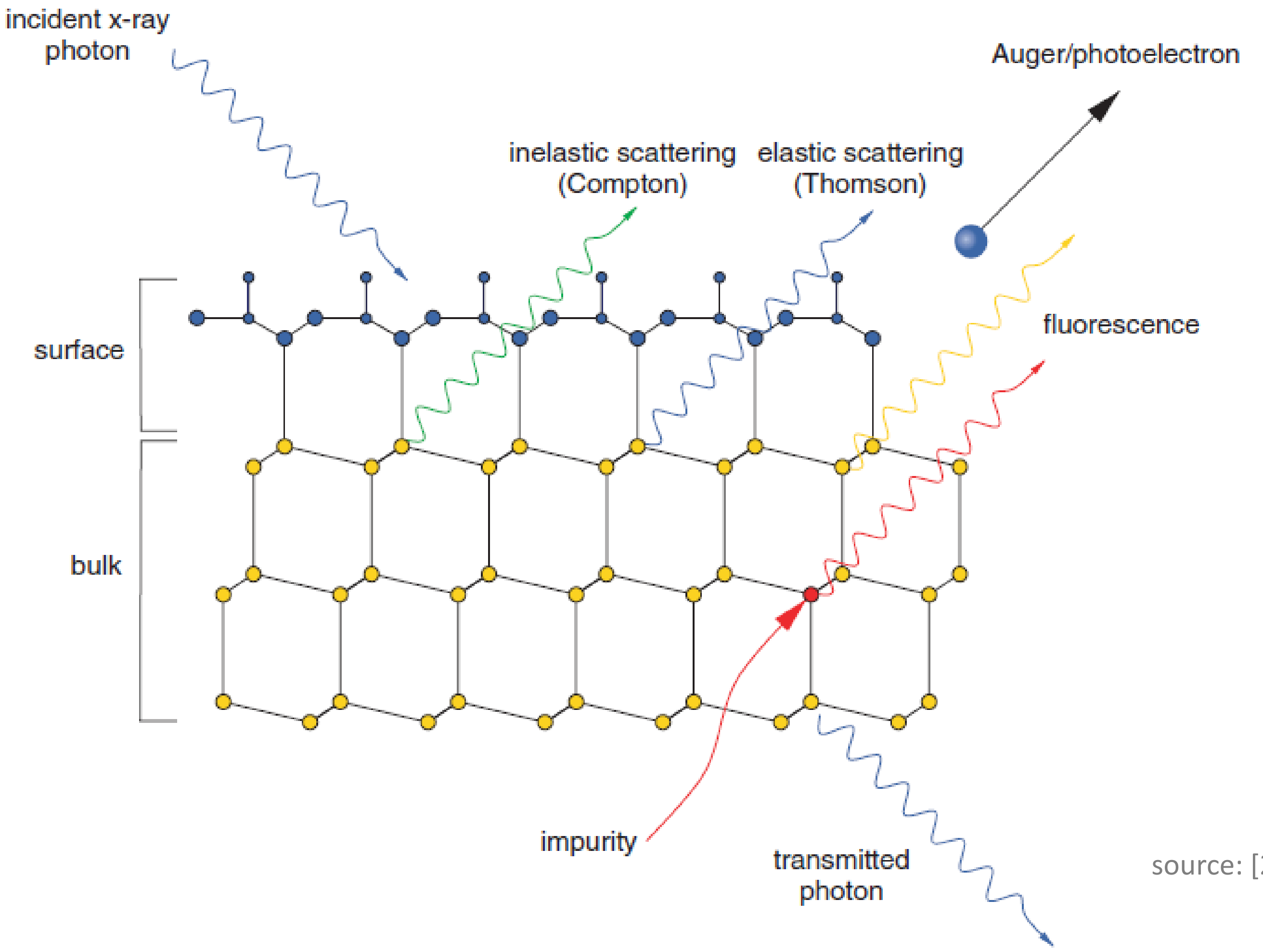


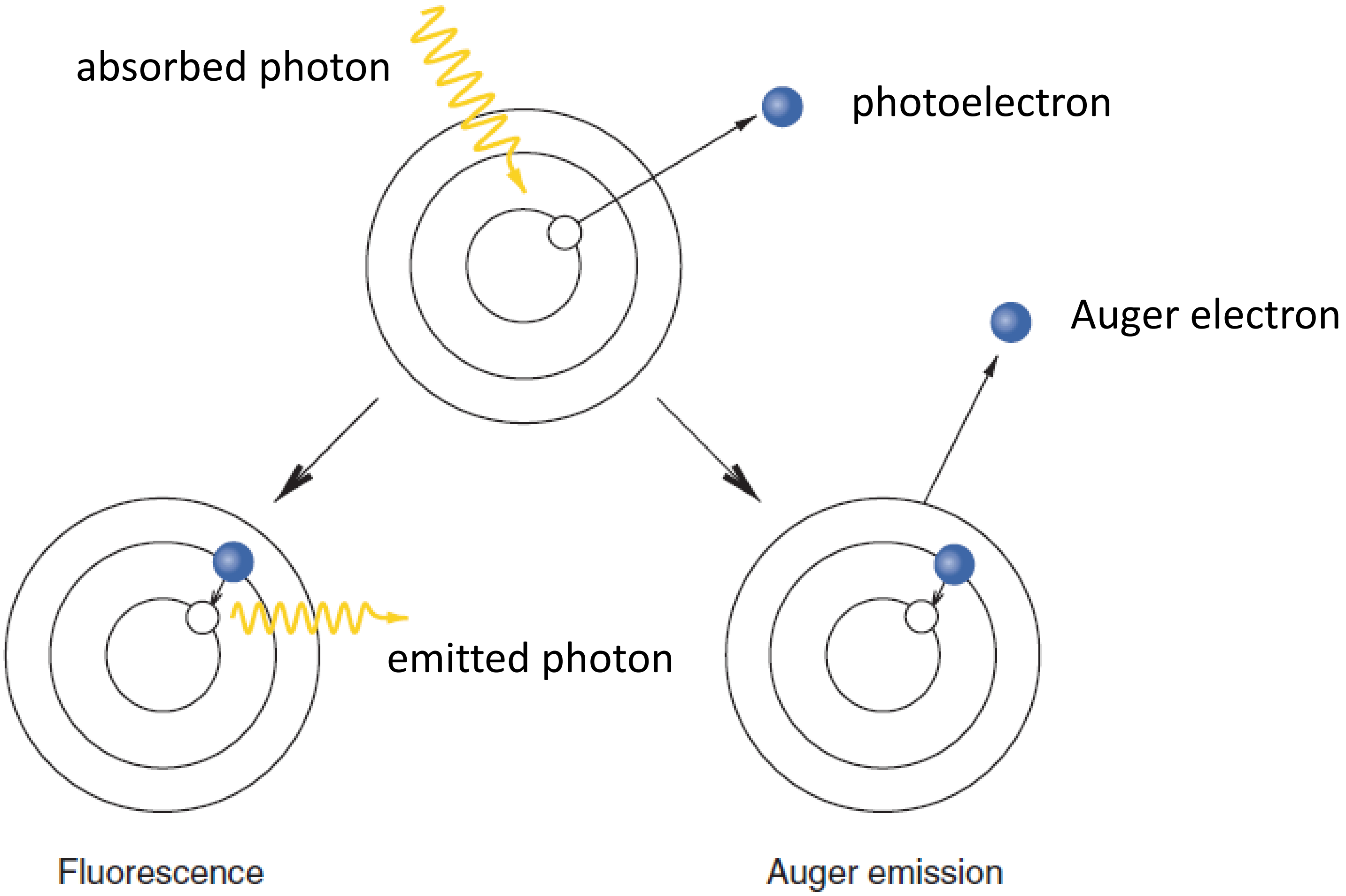
source: esrf.fr

X-ray interactions mechanisms



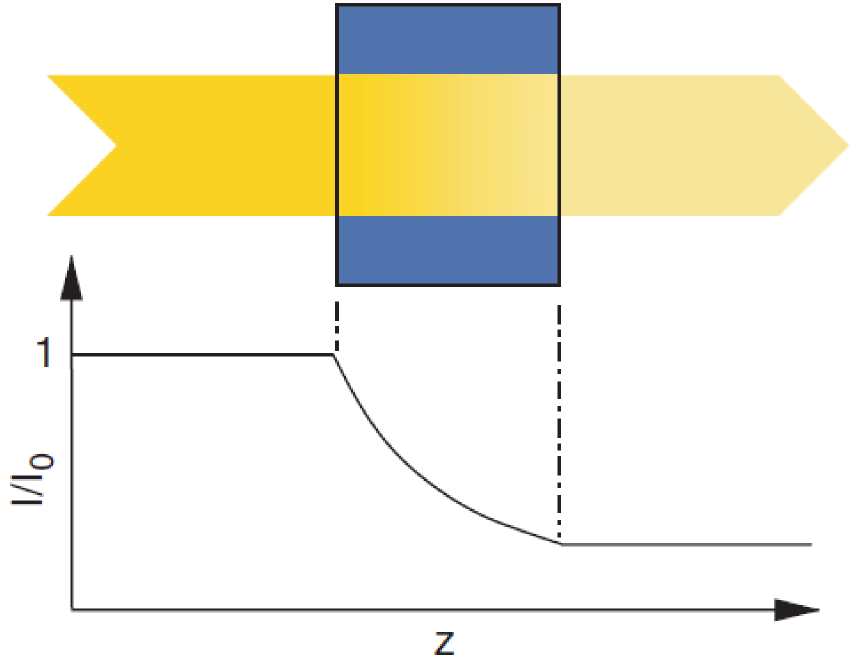
source: [2]

Basic absorption and emission processes



source: [2]

Absorption coefficent



source: [2]

$$I \sim E^2 = E_0 \exp(-2n_{Im}k_0 z)$$

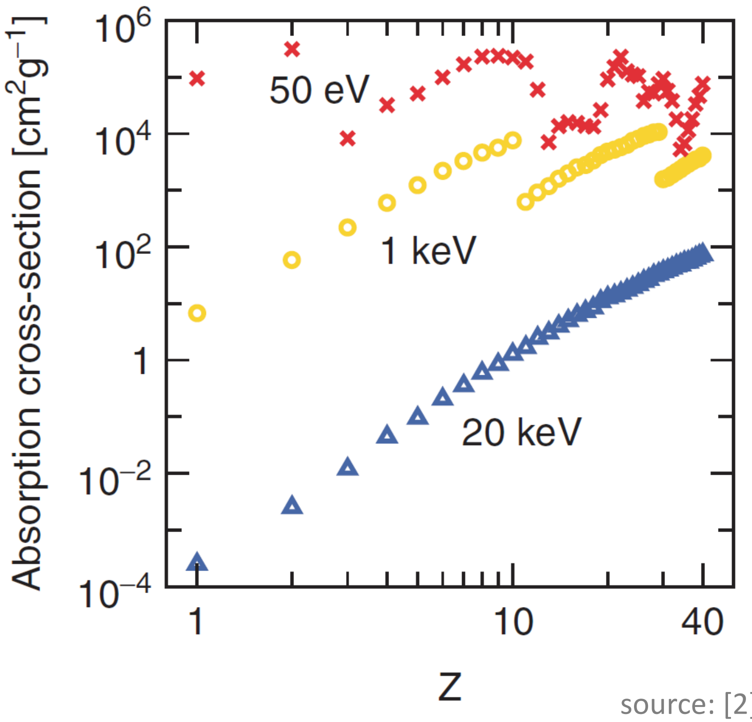
Beer–Lambert equation for linear absorption:

$$\boxed{\frac{I(z)}{I_0} = \exp(-\mu z)}$$

$$\boxed{\mu = 2n_{Im}k_0}$$

Absorption coefficient μ is defined as the reciprocal of the thickness d of the material which is needed to reduce the intensity of an incident beam by a factor of $1/e$.

Absorption coefficent



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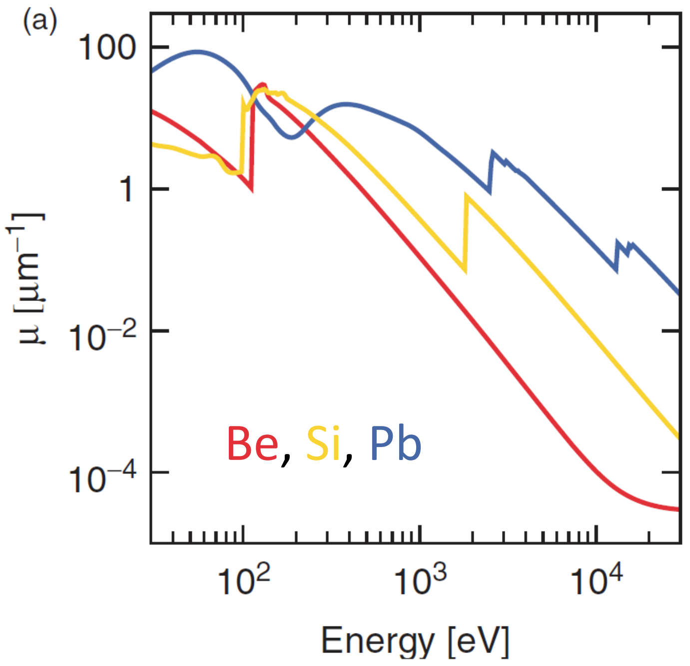
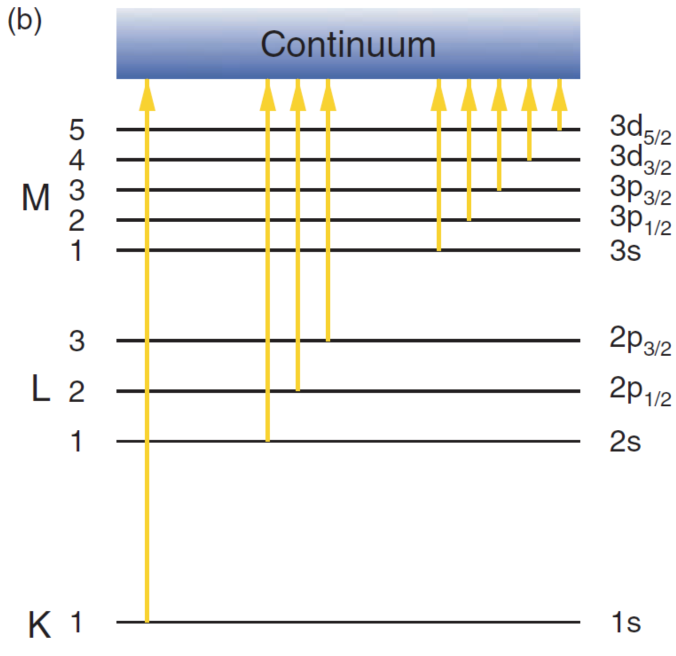




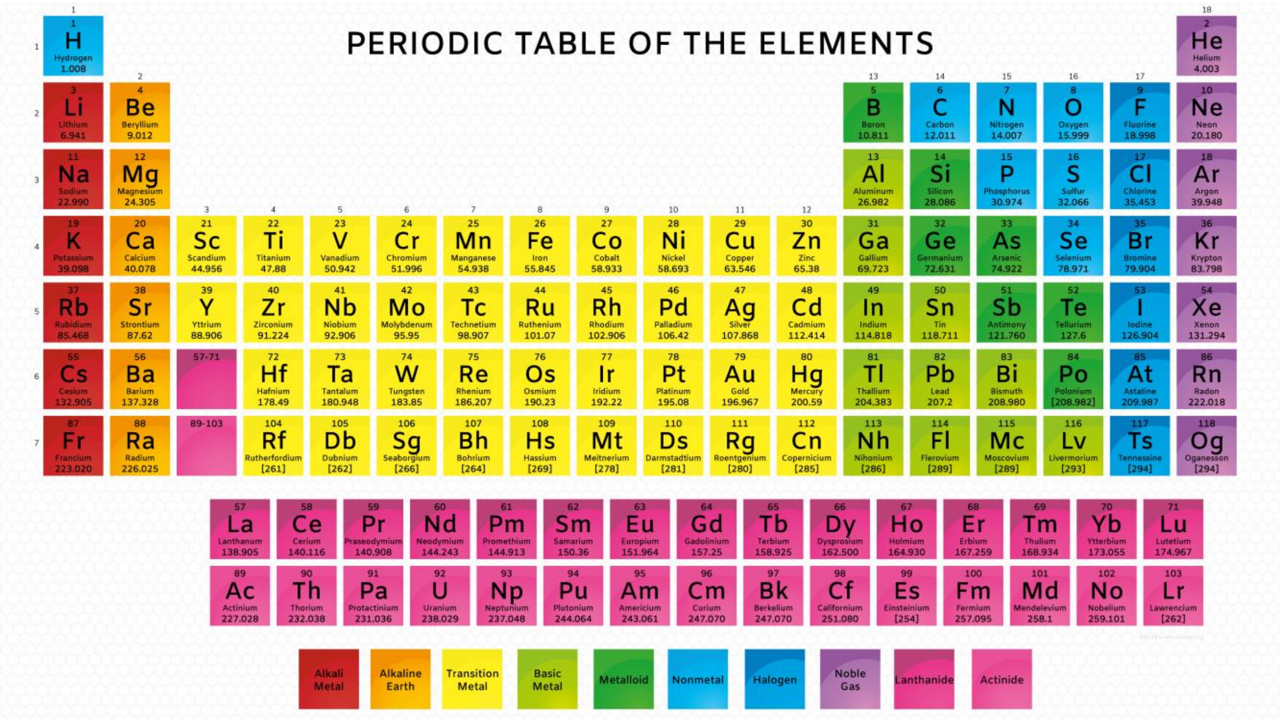
source: [2]

$$\mu = \rho_{at}\sigma_a \propto Z^4$$

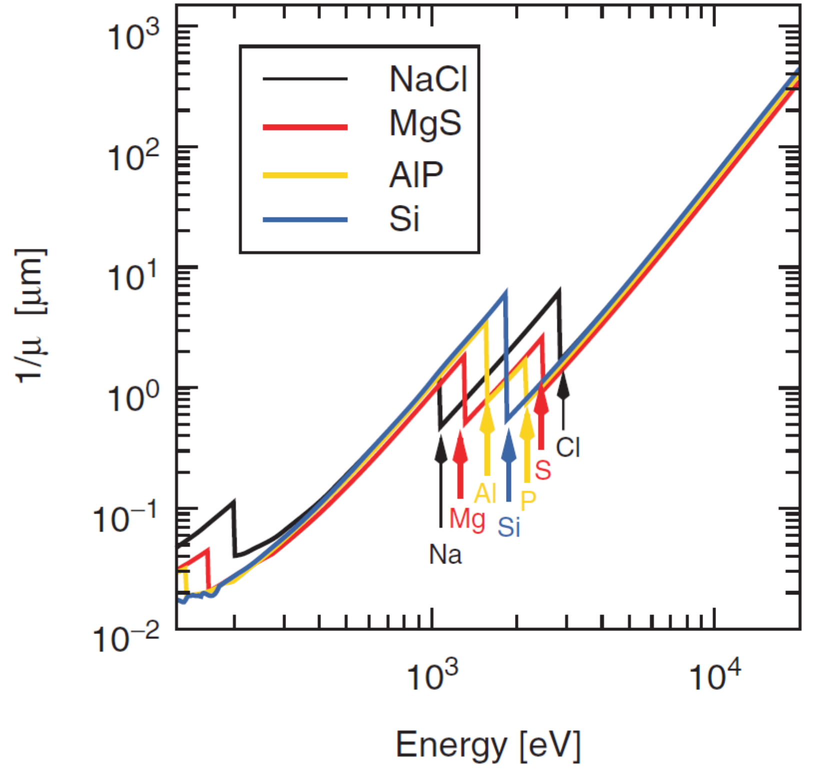
$$\mu \propto \varepsilon^{-3}$$

Absorption edges

XFEL HUB-POLAND



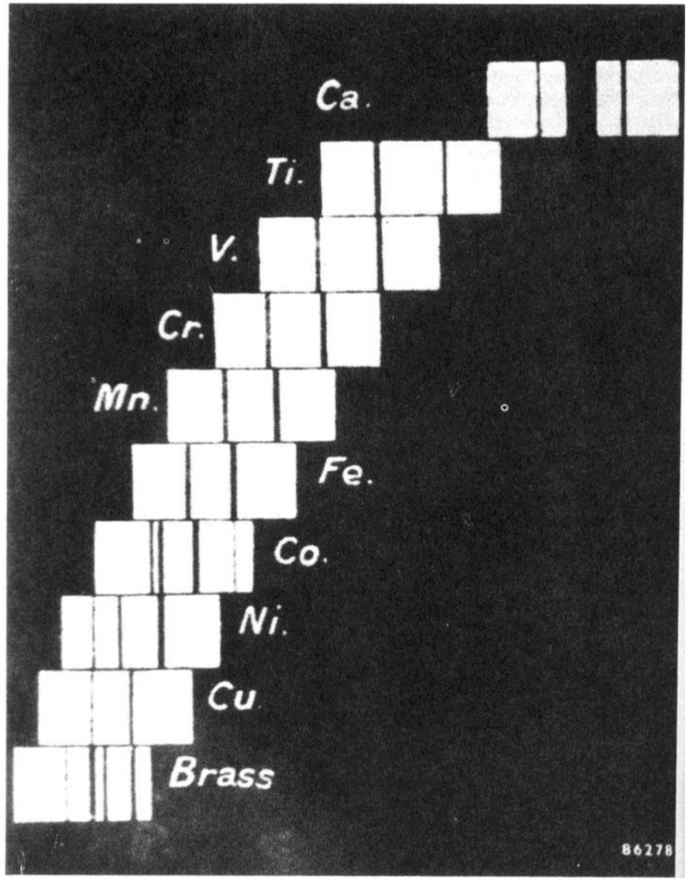
source: sciencenotes.org

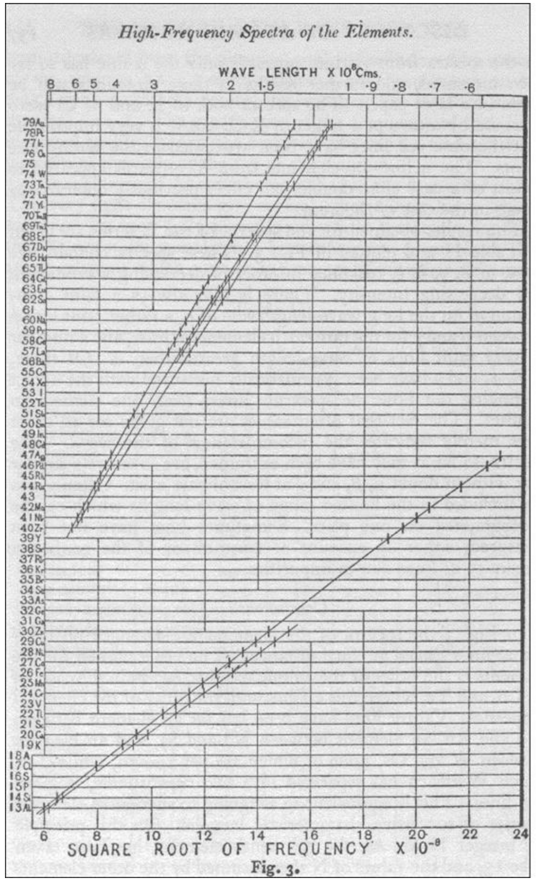


source: [2]

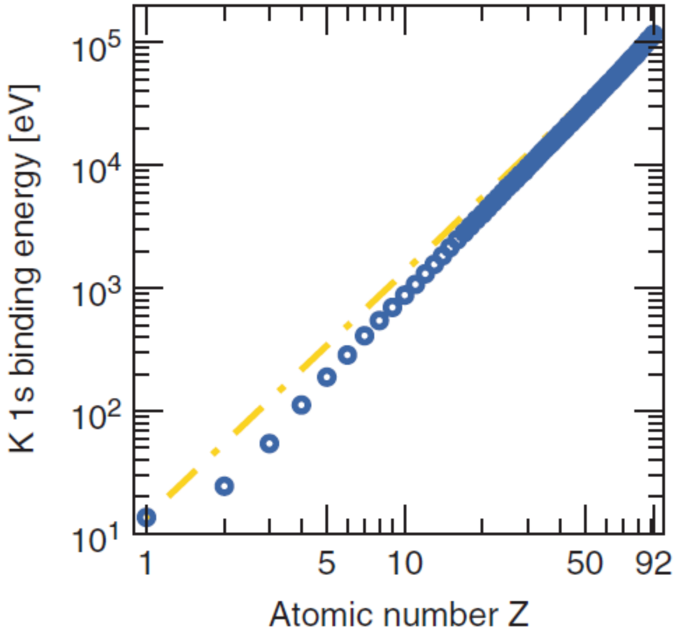
Absoption edge energy scales with the the atomc number *Z*

Moseley law





source: Wikipedia

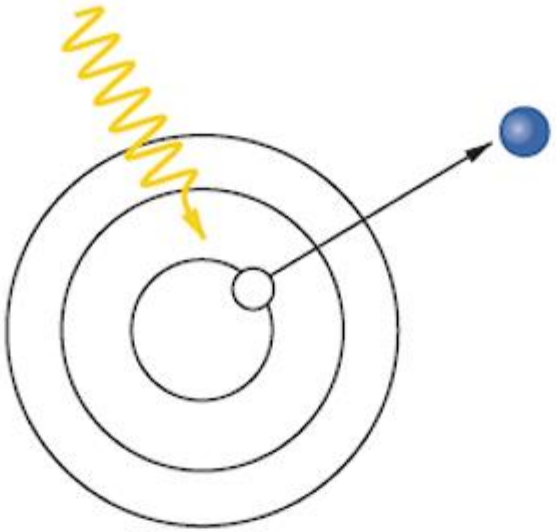


source: [2]

Bohr model: $\varepsilon_i - \varepsilon_f = \frac{m_e {q_e}^2 {q_Z}^2}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$

$$\boxed{\varepsilon_{K_\alpha} \approx 1.017 \times 10^{-2}(Z-1)^2}$$

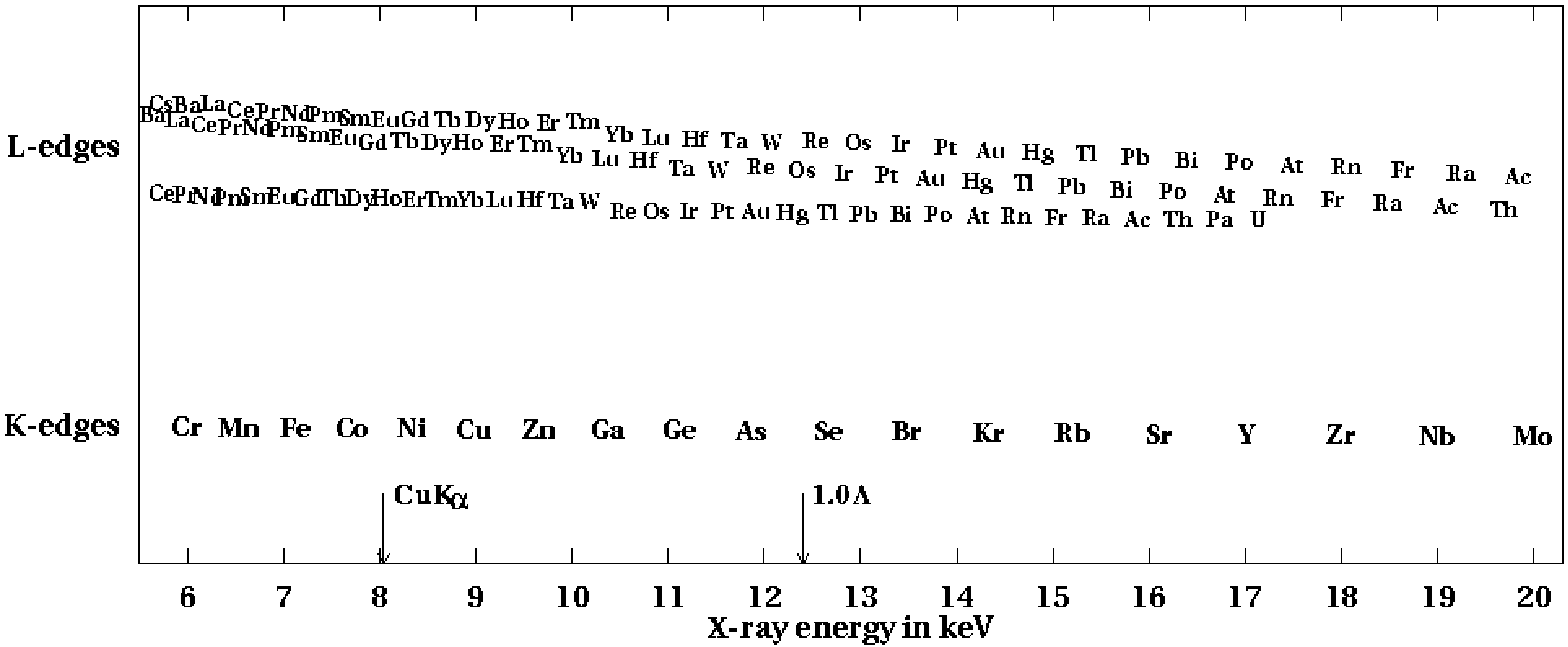
Nomenclature for absorption edges



Edge	Configuration	Edge	Configuration
K	$1s$	N_1	$4s$
L_1	$2s$	N_2	$4p_{1/2}$
L_2	$2p_{1/2}$	N_3	$4p_{3/2}$
L_3	$2p_{3/2}$	N_4	$4d_{3/2}$
M_1	$3s$	N_5	$4d_{5/2}$
M_2	$3p_{1/2}$	N_6	$4f_{5/2}$
M_3	$3p_{3/2}$	N_7	$4f_{7/2}$
M_4	$3d_{3/2}$	O_1	$5s$
M_5	$3d_{5/2}$	O_2	$5p_{1/2}$

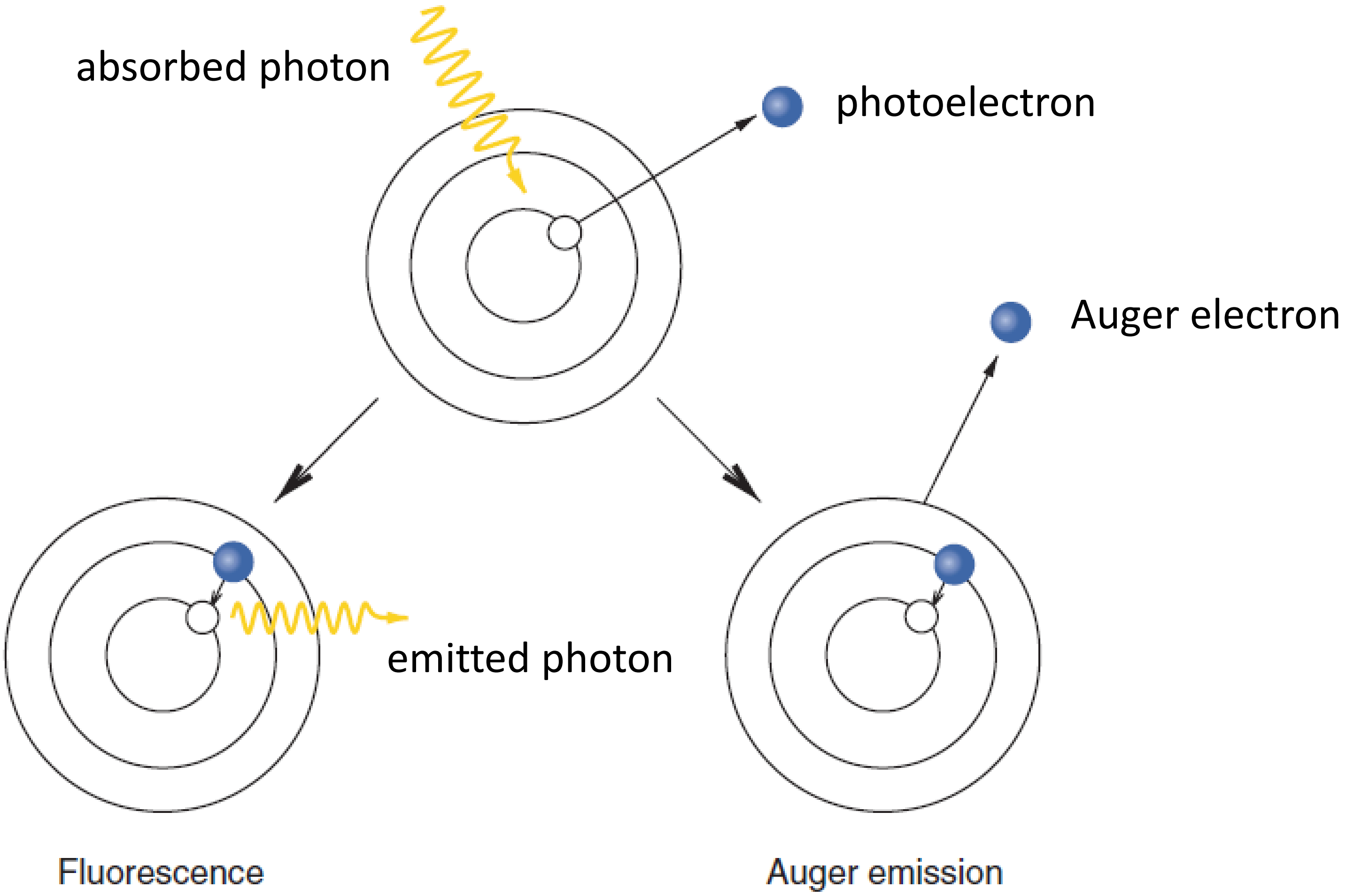
source: [2]

Absorption edges of elements



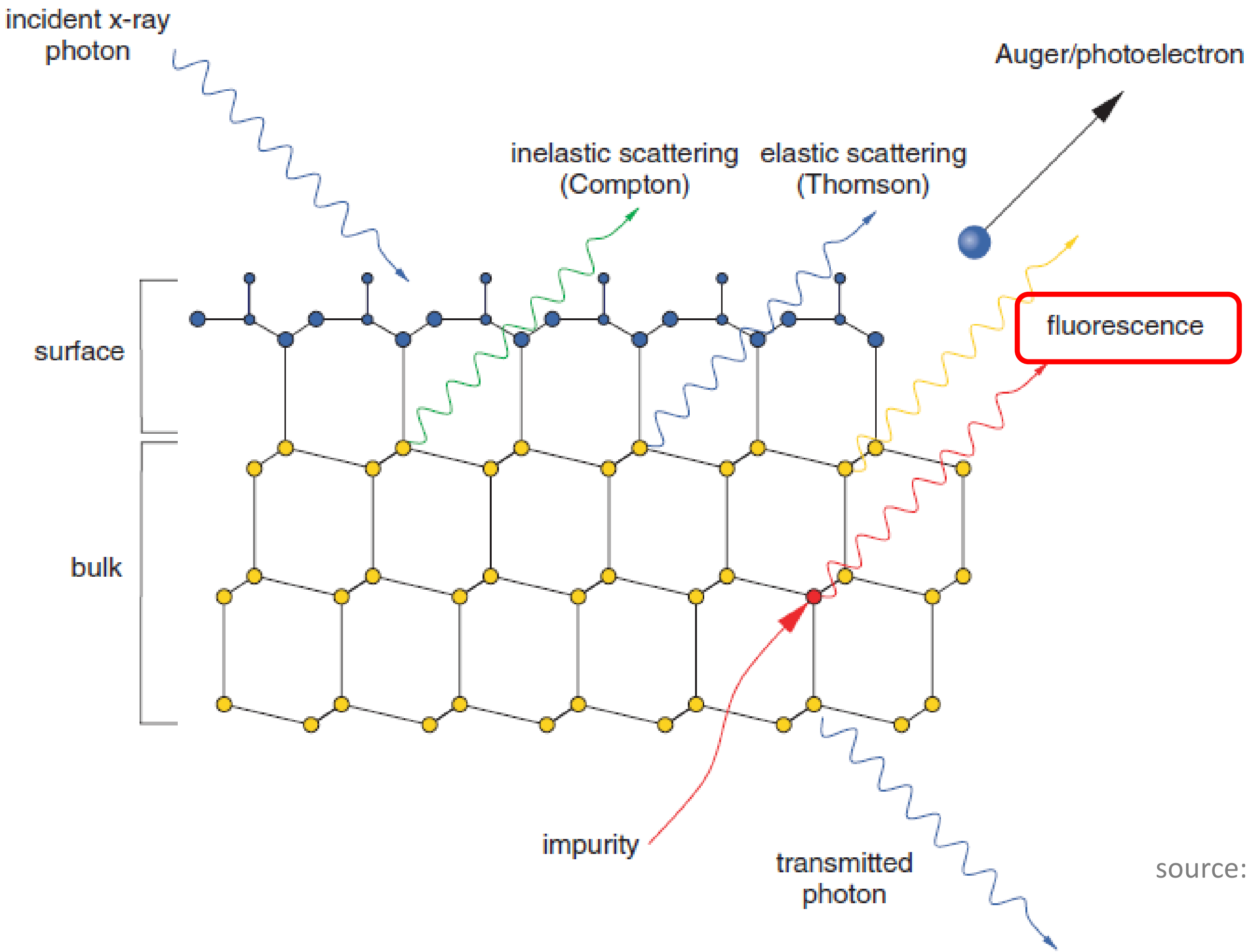
source: http://skuld.bmsc.washington.edu/scatter/AS_chart.html

X-ray fluorescense and Auger emission



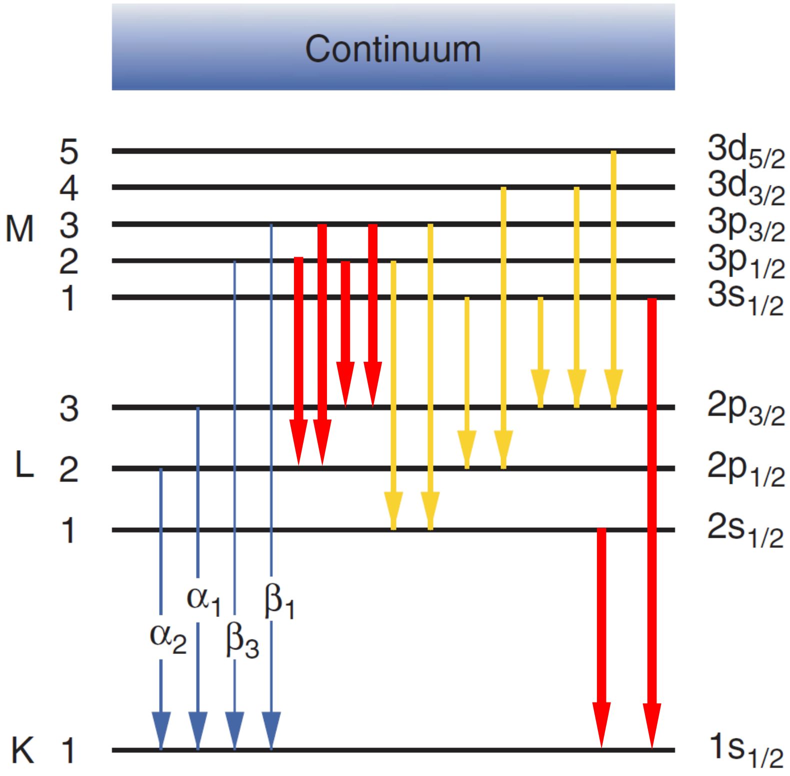
source: [2]

X-ray interactions mechanisms



source: [2]

Fluorescent X-ray emission lines



Forbidden!

source: [2]

X-ray fluorescent emission lines result from the transition of an outer-shell electron relaxing to the core-hole left behind by the ejection of the photoelectron from the atom.

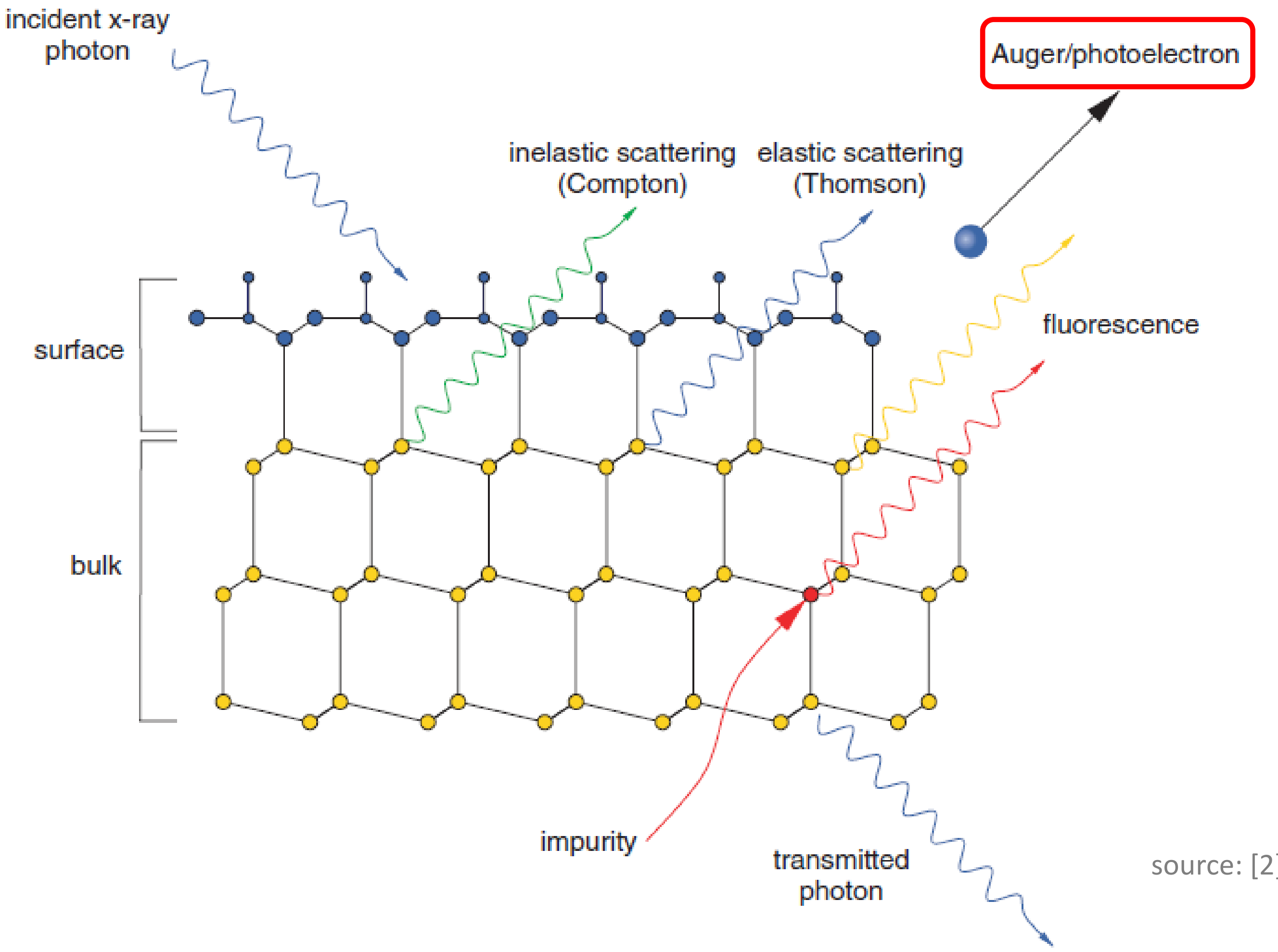
total angular momentum quantum numer (**j**) = azimuthal quantum numer (**l**) + spin quantum number (**s**)

$$\mathbf{j} = \mathbf{l} + \mathbf{s}$$

$$l = 0, 1, 2, \ldots (s, p, d, \ldots); \; s = \pm 1/2$$

Selection rules: $\Delta l = \pm 1$, $\Delta j = 0, \pm 1$ but not $0 \rightarrow 0$

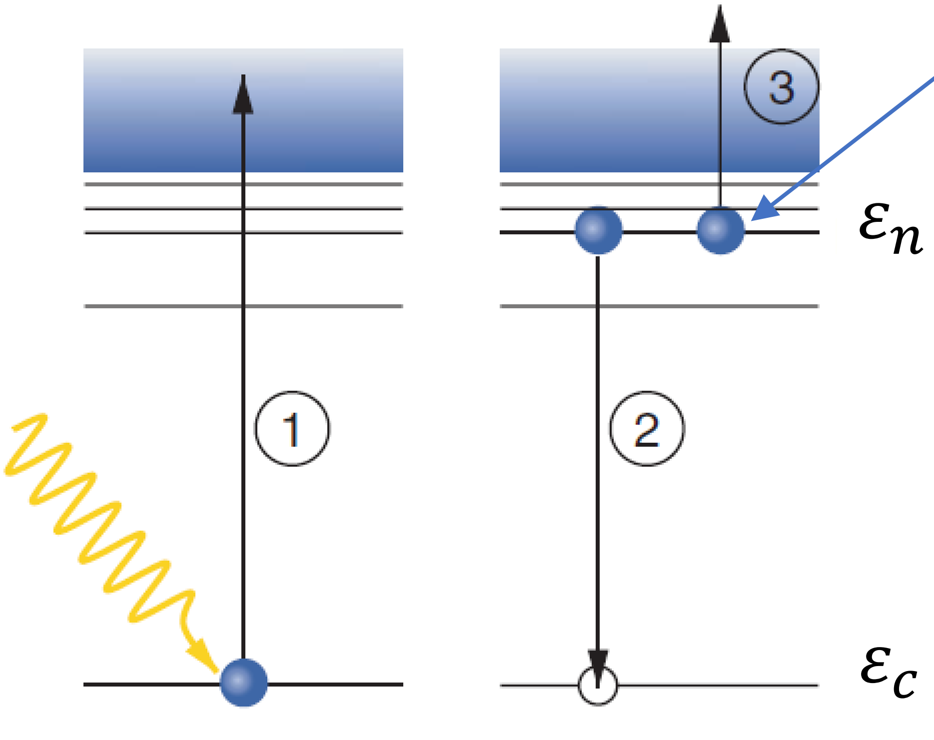
X-ray interactions mechanisms



source: [2]

Auger emission

Auger electrons are produced when an outer shell electron relaxes to the core-hole produced by the ejection of a photoelectron. The excess energy in this process is $|\varepsilon_c - \varepsilon_n - \varepsilon_n{}'|$ where ε_c is the core electron binding energy and and ε_n, $\varepsilon_n{}'$ are outer-shell binding energies of the core-hole filling and emitted eletron .



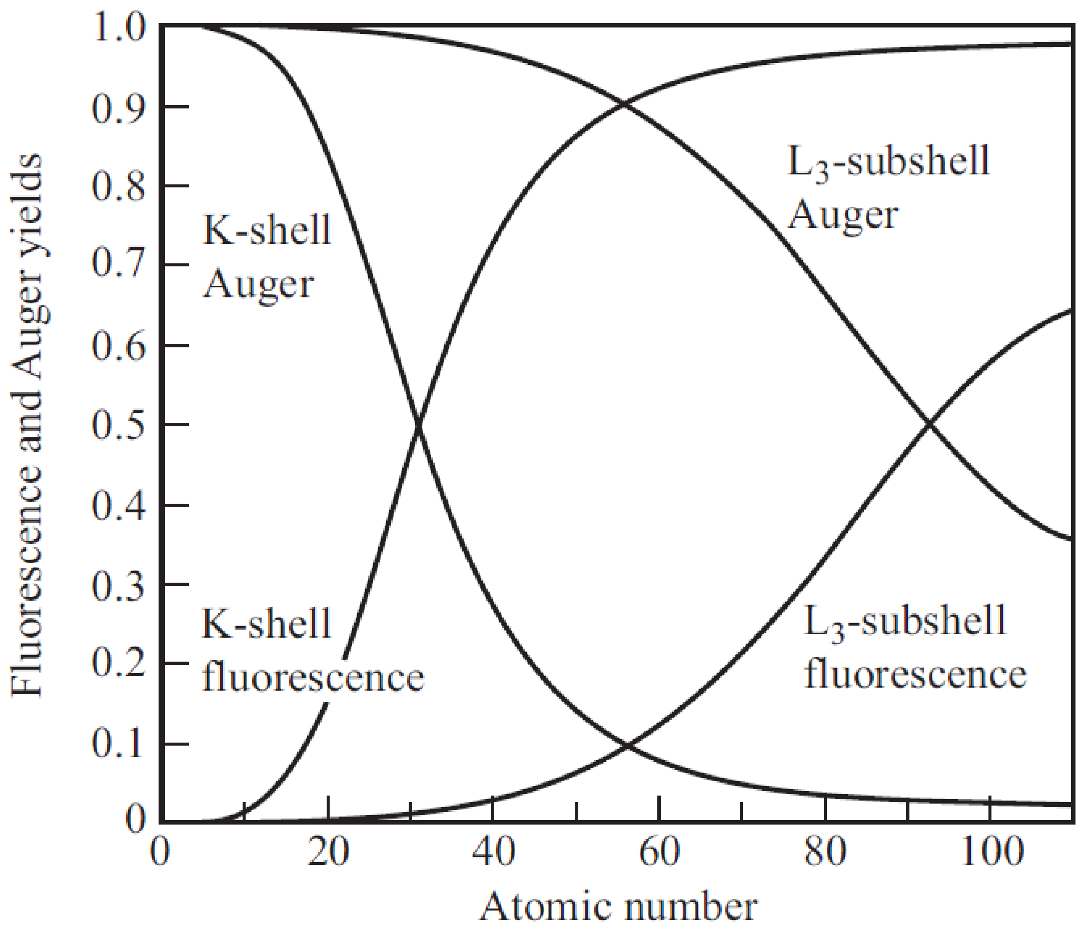
Auger electron energy: $|\varepsilon_c - 2\varepsilon_n|$

source: [2]

Nomenclature: *ABC* (eg. *KLL*)
A – photoelectron level
B – core-hole filling electron
C – emitted electron level

The energies of Auger electrons (typically: 100 – 500 eV) are **independent of the incident photon energy**. Those electrons have escape depth of a few nanometers and thus Auger spectroscopy is **surface-sensitive**.

X-ray fluorescence vs. Auger emission



source: [1]

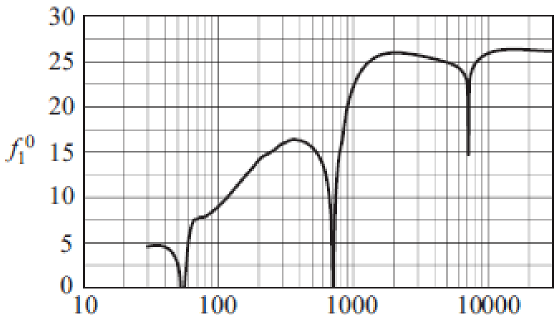
The contribution of fluorescence (radiative relaxation of the excited state) increases with the atomic number.
Auger emission (non-radiative relaxation) exhibits an opposite trend.

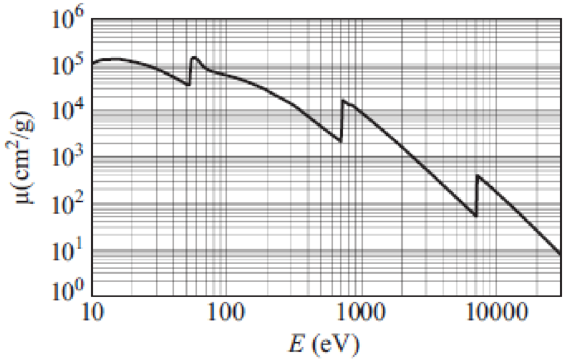
X-ray properties of elements

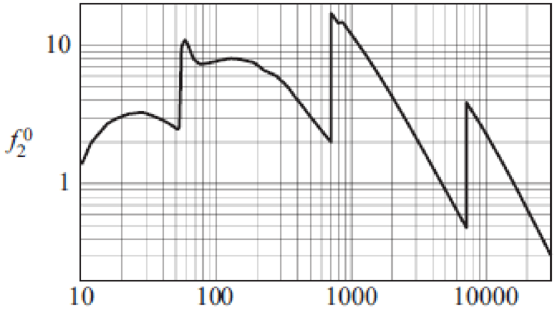
σ_a(barns/atom) = μ(cm^2/g) × 92.74
E(keV)μ(cm^2/g) = f_2^0 × 753.46

Iron (Fe)
Z = 26
Atomic weight = 55.847

Energy (eV)	f_1^0	f_2^0	μ(cm^2/g)
30	4.610	3.219	8.085E+04
70	7.664	7.727	8.318E+04
100	9.043	7.668	5.777E+04
300	15.983	5.584	1.402E+04
700	1.152	2.024	2.178E+03
1000	22.267	11.964	9.014E+03
3000	25.736	2.159	5.423E+02
7000	22.004	0.495	5.331E+01
10000	25.975	2.267	1.708E+02
30000	26.200	0.304	7.631E+00







Edge Energies:						
K	7112.0 eV	L_1	844.6 eV	M_1	91.3 eV
		L_2	719.9 eV	M_2	52.7 eV
		L_3	706.8 eV	M_3	52.7 eV

B.L. Henke, E.M. Gullikson and J.C. Davis, "X-Ray Interactions: Photoabsorption, Scattering, Transmission, and Reflection at E = 50–30,000 eV, Z = 1–92," Atomic Data and Nucl. Data Tables 54, 181 (1993). Current updates are maintained by E.M. Gullikson at http://www.cxro.LBL.gov/optical_constants

source: [1]

What happens when an X-ray photon meets an atom?

Very likely: **nothing**!

The photon is **scattered** by an electron …

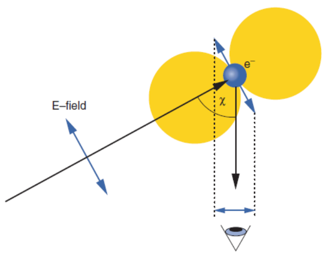
… **elastically** (no photon energy change is involved).

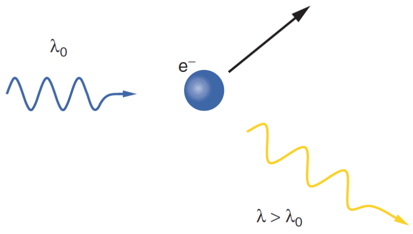
… **non-elastically** (involving photon energy loss).

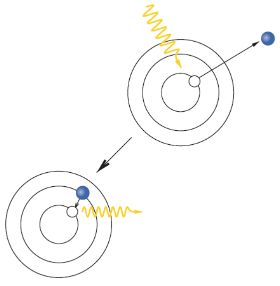
The photon is **absorbed** by an electron, the (photo)electron is ejected and…

… the outer shell electron relaxes to fill the core-hole and the **photon is emitted**.

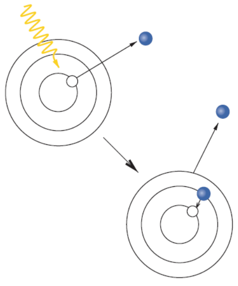
… the outer shell electron relaxes to fill the core-hole and another **electron is emitted**.







Fluorescence



Auger emission