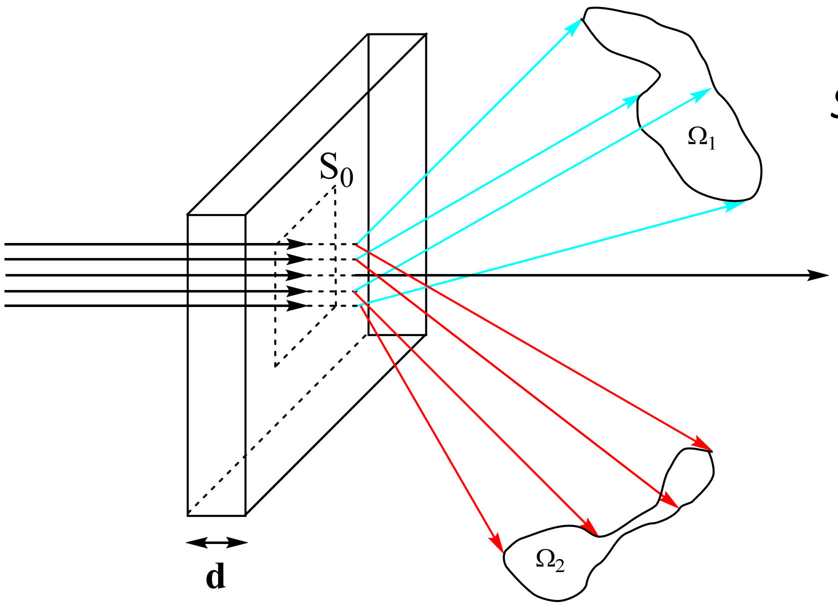
C. Roussel

Physical and Chemical Analyses of Materials

Interactions beam-matter: matter emission and beam detection

Introduction

⇨ The principal beam-matter interactions with matter are depicted below:



$\overrightarrow{\mathbf{k_0}}, \mathbf{I_0}, \mathbf{E_0}$

Primary beam

$\overrightarrow{\mathbf{k_1}}, \mathbf{I_1}, \mathbf{E_1}$

Strongly modified primary beam

scattering

$\overrightarrow{\mathbf{k_0}}, \mathbf{I_0'}, \mathbf{E_0}$

Slightly modified primary beam

absorption

$\overrightarrow{\mathbf{k_2}}, \mathbf{I_2}, \mathbf{E_2}$

Secondary beam

emission

⇨ In material analysis, the use of X-Rays and electrons as exciting beams generally causes the ionisation of the matter.

Interactions beam-matter: matter emission and beam detection

The principal photon-matter interactions with matter and their applications

beam	target	excitation	ejection	emission type	application
IR	nuclei	vibration	none	heat	**IR-S**
IR	nuclei	scattering	none	heat	**RAMAN-S**
UV-Vis	valence electrons	transition	none	UV-Vis	**UV-Vis-S**
UV-Vis	valence electrons	ionisation	electron	photoelectron	**UPS**
X-Rays	whole electrons	diffraction	none	X-Ray	**XRD / SAXS / WAXS**
X-Rays	core electrons	transition	none	X-Ray	**EXAFS / XANES**
X-Rays	core electrons	ionisation	electron	photoelectron	**XPS**
				X-Rays	**XRFS**
				Auger electron	**AES**

IR-S: Infrared Spectroscopy / **RAMAN-S**: RAMAN Spectroscopy / **UV-Vis-S**: Ultraviolet-Visible Spectroscopy / **UPS**: Ultraviolet Photoelectron Spectrometry / **XRD**: X-Ray Diffraction / **SAXS**: Small Angle X-Ray Scattering / **WAXS**: Wide Angle X-Ray Scattering / **EXAFS**: Extended X-Ray Absorption Fine Structure / **XANES**: X-Ray Absorption Near Edge Structure / **XPS**: X-Ray Photoelectron Spectrometry / **XRFS**: X-Ray Fluorescence Spectrometry / **AES**: Auger Electron Spectrometry

Interactions beam-matter: matter emission and beam detection

The principal photon-based analytical technics						
	Analysis type		**Analysis features**			
Technic	**Bulk**	**Surface**	**morphological**	**topographical**	**structural**	**chemical**
IR-S	**X**	**X**				**X**
Raman-S	**X**	**X**				**X**
UV-Vis-S	**X**	**X**				**X**
UPS		**X**				**X**
XRD	**X**				**X**	
SAXS		**X**	**X**		**X**	
WAXS	**X**				**X**	**X**
EXAFS	**X**				**X**	**X**
XANES	**X**	**X**			**X**	**X**
XPS		**X**				**X**
XRFS	**X**	**(X)**				**X**
AES		**X**				**X**

The principal electron-matter interactions with matter and their applications					
beam	**target**	**excitation**	**ejection**	**emission type**	**application**
electrons	whole atom	diffraction	none	primary electron	**LEED / RHEED**
electrons	nuclei	diffraction	none	primary electron	**TEM**
electrons	nuclei	scattering	none	primary electron	**TEM / STEM**
electrons	nuclei	backscattering	none	primary electron	**SEM / STEM**
electrons	nuclei	e^--braking	none	X-Rays (bremsstrahlung)	**X-Ray tubes**
electrons	core electrons	ionisation	electron	secondary electron	**SEM / STEM**
				X-Rays	**XRMA**
				Auger electron	**AES**

LEED: Low Energy Electron Diffraction / **RHEED**: Reflection High Energy Electron Diffraction / **TEM**: Transmission Electron Microscopy / **STEM**: Scanning Transmission Electron Microscopy / **SEM**: Scanning Electron Microscopy / **XRMA**: X-Ray Micro-Analysis / **AES**: Auger Electron Spectrometry

The principal electron-based analytical technics

	Analysis type		Analysis features			
Technic	**Bulk**	**Surface**	**morphological**	**topographical**	**structural**	**chemical**
LEED		**X**	**X**		**X**	
RHEED		**X**	**X**		**X**	
TEM	**X**	**(X)**	**X**	**(X)**	**X**	
SEM		**X**	**X**	**X**		
STEM	**X**	**X**	**X**	**X**	**X**	
XRMA	**X**	**X***				**X**
AES		**X**				**X**

*: Some authors consider XRMA as a surface analysis even if the penetration of electrons in a material is in the order of 1 µm.

Matter emission from the ionisation of core electrons

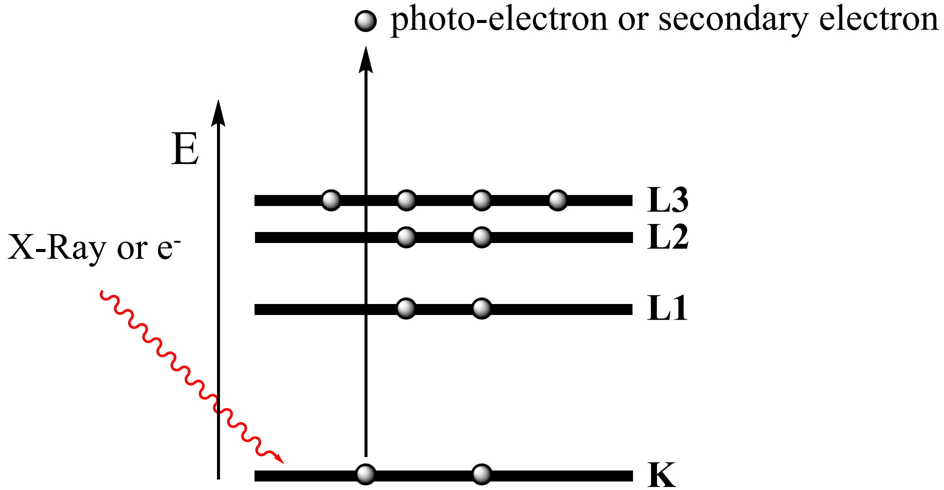
Matter ionisation by X-Rays and electrons

⇨ To describe the inelastic interactions that take place between a beam and core electrons one has to consider the electronic structure of poly-electronic atoms:

shell	n	subshell	l	m_l	j	states	energy level	notation
K	1	s	0	0	1/2	2	1s	K
L	2	s	0	0	1/2	2	2s	L1
		p	1	-1, 0, 1	1/2 3/2	2 4	$2p^{1/2}$ $2p^{3/2}$	L2 L3
M	3	s	0	0	1/2	2	3s	M1
		p	1	-1, 0, 1	1/2 3/2	2 4	$3p^{1/2}$ $3p^{3/2}$	M2 M3
		d	2	-2, -1, 0, 1, 2	3/2 5/2	4 6	$3d^{3/2}$ $3d^{5/2}$	M4 M5

$$\vec{\mathbf{J}} = \vec{\mathbf{L}} + \vec{\mathbf{S}} \quad \Rightarrow \quad \mathbf{j} = \mathbf{l} \pm \mathbf{s} \quad \Rightarrow \quad \mathbf{j} > 0 \quad \Rightarrow \quad 2\mathbf{j}+1 \ \ \textbf{states}$$

⇨ The inelastic interactions between a beam and core electrons can be described at the atomic level as:



↳ According to the energy of the primary beam, the interactions core electron-beam generally lead to the ionisation of the target atom.

↳ For X-Rays primary beams, the ejected electron is called a photo-electron.

↳ For electrons primary beams, the ejected electron is called a secondary electron (SE).

⇨ The life time of such an ionised state is about 10^{-16} s. Afterwards, the matter relaxes. The matter relaxation can lead to either X-Rays or to an Auger electrons emission.

Interactions beam-matter: matter emission and beam detection

⇨ The characteristic kinetic energy $\mathbf{Ec_0}$ of the photo-electron depends on the energy $\mathbf{E_0} = \mathbf{h\nu_0}$ of the exciting photon and on the binding energy $\mathbf{W_x}$ of the target core electron **X**:

$$\mathbf{Ec_0 = h\nu_0 - W_x = E_0 - W_x}$$

↳ After ejection, the photo-electron must migrate from the bulk material to its surface. During this travelling, it can bump other electrons through elastic and inelastic interactions with the surrounding matter.

↳ To leave the material, the photo-electron must also counteract the potential barrier **Φ** at the surface corresponding to the extraction energy **eΦ**.

↳ The kinetic energy **Ec** of the photo-electron when leaving the material is lower than its characteristic kinetic energy $\mathbf{Ec_0}$:

$$\mathbf{Ec = E_0 - W_x - e\Phi}$$

↳ The maximal value $\mathbf{Ec_0}$ is observed for photo-electrons coming from a superficial layer of thickness lower than their free mean path **l**.

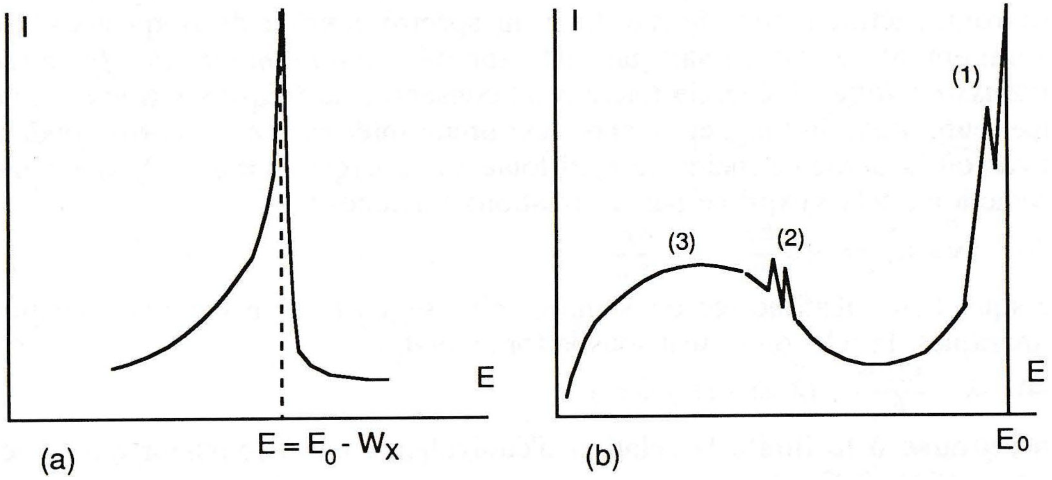
↳ The measurement of a photo-electron kinetic energy gives rise to the determination of the chemical nature of its emitting element.

Interactions beam-matter: matter emission and beam detection

⇨ Secondary electrons are produced with a widespread energy because the energy loss by the primary electrons is not quantified.

↳ Before being able to leave the material, they undergo many elastic and inelastic interactions with the surrounding matter. Secondary electrons reach the surface when emitted from a superficial layer of thickness lower than their free mean path **l**.

↳ In contrast with photo-electrons, one can not precisely correlate the kinetic energy of these secondary electrons to the chemical nature of their emitting elements. There are not used for chemical analysis.

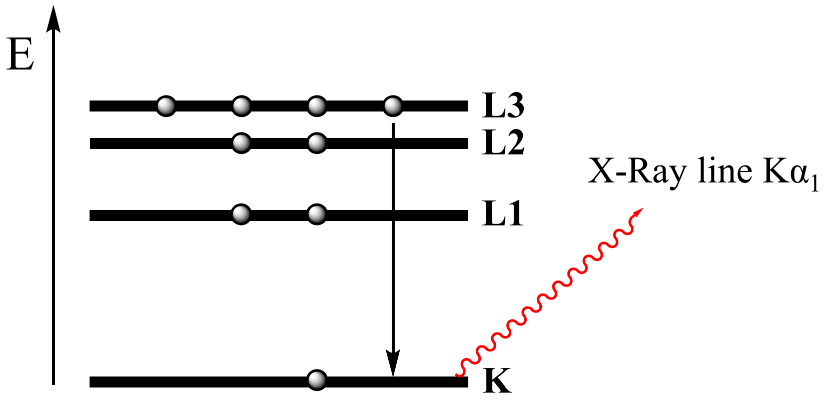


↳ After several interactions, the primary electrons loose energy and so increase their probability to be involved in elastic scattering events.

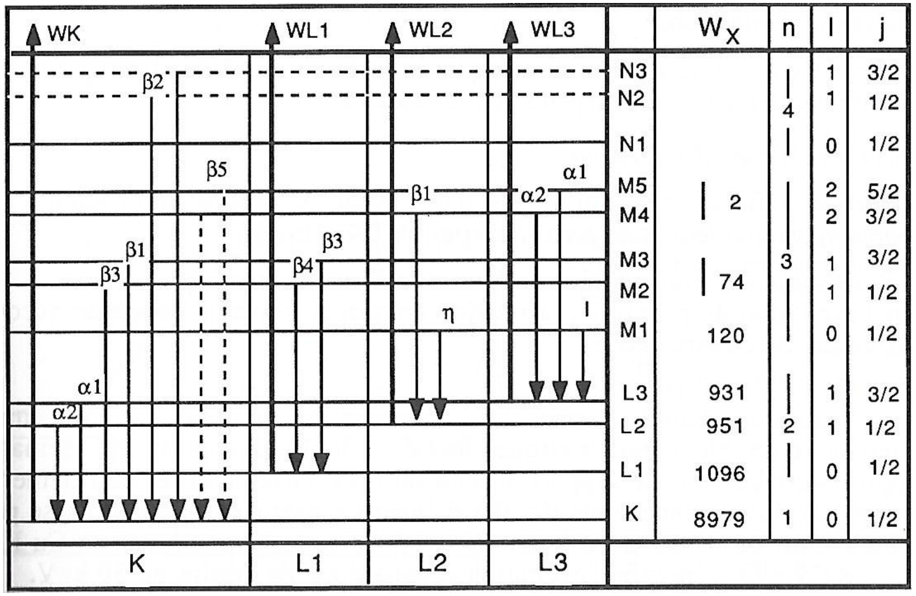
Emission electron spectra (intensity as a function of the energy) for photo-electrons from X-rays excitation (**a**) and secondary electrons from primary electrons excitation (**b**). 1: elastic scattering and plasmons, 2: Auger electrons, 3: secondary electrons.

Ionised matter relaxation by X-Rays emission

⇨ The matter relaxation can lead to the emission of an X-Ray photon:



electronic transitions are allowed for: $|\Delta n| \geq 1$; $\Delta l = \pm 1$; $\Delta j = 0, \pm 1$.



↳ Above is gathered the emission lines for copper. W_x relates to the ionisation energies for a level **X**. The notation Kα1; Kβ… relates to the Siegbahn notation. For a transition **KL3** the emission line is called Kα_1.

↳ The excitation of the matter being localised at an atomic deep level, the X-Ray lines are not affected by the chemical bonds.

⇨ The Moseley law, which correlates the emission frequency **ν** to the atomic number **Z** of the emitting atom can be used:

$$\sqrt{\nu} = k_1 (Z - k_2)$$

↳ In this equation, **k_1** and **k_2** are two constants defined for each line.

⇨ The intensity of the emission depends on different factors: the cross-section of excitation, the relaxation probability through an X-ray emission and the probability of transitions.

⇨ The cross-section of excitation **σ_X** of an atomic shell **X**, depends on the nature of the primary beam and on the excitation rate **$U_X = E_0 / W_X$**.

↳ For the excitation of the shell **K** by electrons, the cross-section of excitation **σ_K**, where **k** and **k'** are some constants, is given by:

$$\sigma_K = k(E_0 - W_K)^{1.7} = k'(U_K - 1)^{1.7}$$

↳ For the excitation of a shell **X** by X-Rays photons, the cross-section of excitation **σ_X** is maximal for **$E_0 > W_X$**.

⇨ the relaxation probability through an X-rays emission is in competition with the emission of Auger electrons.

↳ For elements with an atomic number greater than 40, the probability of the emission of X-Rays is bigger than the probability of emission of Auger electrons (see after).

⇨ The probability of transition is grasped by the relative intensities of the different lines.

↳ In general, the probability for the emission of **K** lines is 10 times higher than the probability for the emission of **L** lines.

⇨ Although the spectrum resulting from **K** lines is simple, the one from **L** lines is more complicated.

↳ When possible, one will preferably base its study on the spectrum resulting from **K** lines. Nevertheless, for heavy elements, one has to focus on the spectrum resulting from **L** lines as the energy needed to ionise the **K** level of these elements is to high (e.g. 115.6 keV for $_{92}$U).

⇨ The Moseley law constitutes a first approach. Actually, the presence of the chemical bonds in which an element is involved induces a shift of its energy levels.

↳ Therefore the ionisation energy of the shell **X** incorporates a new term $\boldsymbol{\delta W_X}$ called the chemical shift.

- The energy needed to ionise the shell **X** is then: $\mathbf{W_X' = W_X + \delta W_X}$

- For an allowed transition between shells **X** and **Y**, we have then:

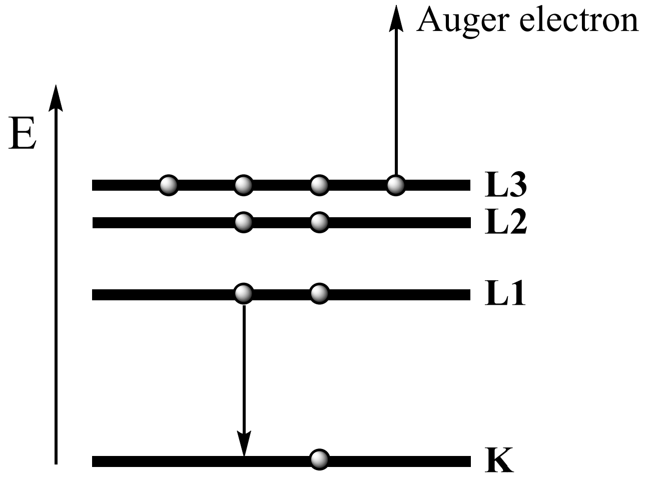
- Free atom: $\mathbf{E = W_x - W_Y}$

- Bonded atom: $\mathbf{E' = E + (\delta W_X - \delta W_Y)}$

- Sometimes the two chemical shifts compensates leading to the expected transition energy.

Ionised matter relaxation by Auger electrons emission

- The energy emitted by the relaxation of an ionised atom can be used to eject an Auger electron:



- The energy associated to the transition **L1 → K** is communicated to an electron **L3**.

- As the ionisation energy of this electron is lower than the transition energy **KL1**, this electron is ejected with a noticeable kinetic energy.

- The Auger transition is called **KL1L3**.

⇨ For a transition **XYY'**, the kinetic energy of the Auger electron depends on the energy of the **XY** transition and on the ionisation energy of the Auger electron **Y'**.

↳ For a **XYY'** transition, when the Auger electron does not undergo any interaction with the surrounding matter, its characteristic energy for an element of atomic number **Z** is:

$$\mathbf{Ec_0(Z) = W_X(Z) - W_Y(Z) - W_{Y'}(Z+1)}$$

↳ **$W_{Y'}$ (Z+1)** is introduced for tacking into account that the Auger electron is ejected from an ionised atom.

↳ As for the photo-electron, to leave the material, the Auger electron must also counteract the potential barrier **Φ** of the surface corresponding to an extraction energy **eΦ**. If no interaction occurs between the Auger electron and the surrounding matter, its kinetic energy will be:

$$\mathbf{Ec = W_X(Z) - W_Y(Z) - W_{Y'}(Z+1) - e\Phi}$$

↳ After ejection, the Auger electron must migrate from the bulk material to its surface. During this travelling, it can bump other electrons through elastic and inelastic interactions with the surrounding matter. In this case, the detected Auger electron will have a kinetic energy lower than **Ec**.

⇨ The selection rules for the Auger electron emission are the following:

↳ A transition **XYY'** is allowed if $\mathbf{W_{Y'} < W_X - W_Y}$: $\mathbf{Ec_0 > 0}$.

↳ Some Auger transition with $\Delta\mathbf{n} = \mathbf{0}$ are allowed like **L1L2M1** or **L1L3M1** for example. These transitions are named Koster – Kronig transitions.

↳ For particular atoms, the $\mathbf{Ec_0 > 0}$ condition can not be satisfied. So some transitions like **L1L3M5** are forbidden for atoms with an atomic number **Z** included in the range: $\mathbf{40 < Z < 73}$.

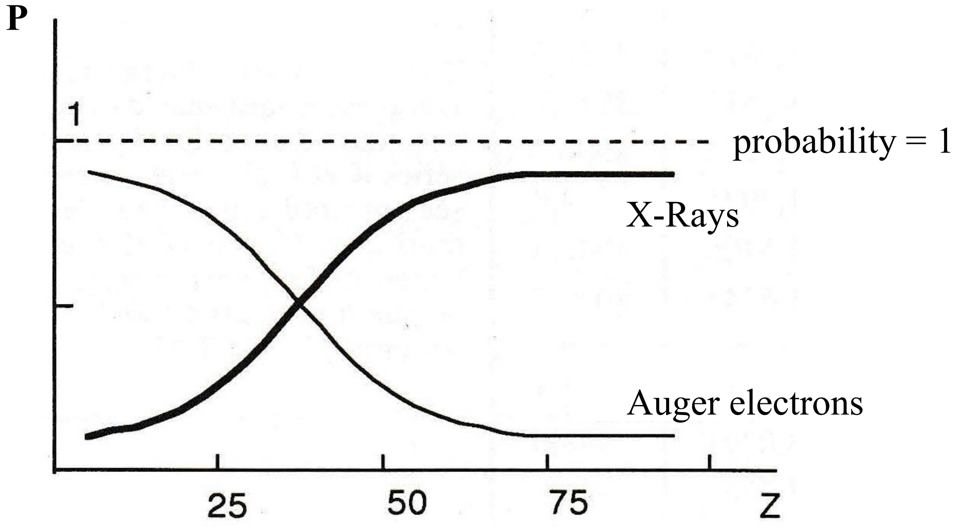
↳ Experimental data showed that Auger transitions caused by the primary ionisation of **s** electrons are favoured.

↳ The number of possible **XYY'** transitions increases a lot with the atomic number of an element that complicates the Auger spectra and so their interpretations. Below is given a short list of possible Auger transitions: **KL1L1**, **KL1L2**, **KL1L3**, **KL2L2**, **KL2L3**, **KL3L3**, **KL1M1**,…, **L1M1M1**,…

Competition between Auger electrons and X-Rays emission

⇨ The Auger electrons and X-Rays emissions are in competition, depending on the atomic number of the emitting element.

⇨ The intensities of the Auger transitions are complementary to the X-Ray transition ones and depend on the atomic number of the considered element:



$$\mathbf{I}_{\mathbf{Auger}} = \mathbf{v}\frac{\mathbf{P}_{\mathbf{Auger}}}{\mathbf{P}_{\mathbf{Auger}} + \mathbf{P}_{\mathbf{X-Ray}}}$$

↳ **v** is the rate of ionisation of the primary energy level, $\mathbf{P}_{\mathbf{Auger}}$ and $\mathbf{P}_{\mathbf{X-Ray}}$ are related to the probabilities of these emissions.

↳ The Auger effect disturbs the X-Ray emissions: modification of the relative intensity of the lines of different series, displacement of the energy levels which causes the appearance of satellites lines.

↳ The presence of Auger transitions broadens the X-Ray lines, especially for light elements.

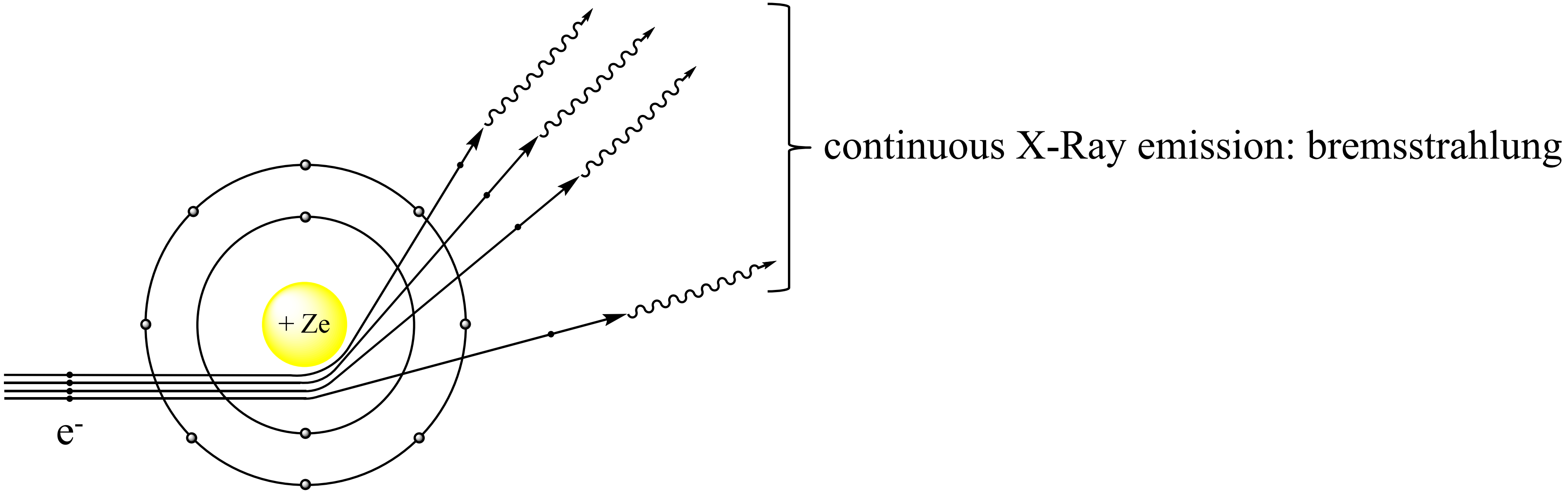
↳ The chemical shift for Auger transitions is more important that for X-Ray transitions. It is more pronounced for light elements and for transitions in which valence band electrons are involved.

Matter emission from electron's braking

⇨ The interaction electron-nucleus gives rise to an electron braking with a trajectory deviation.

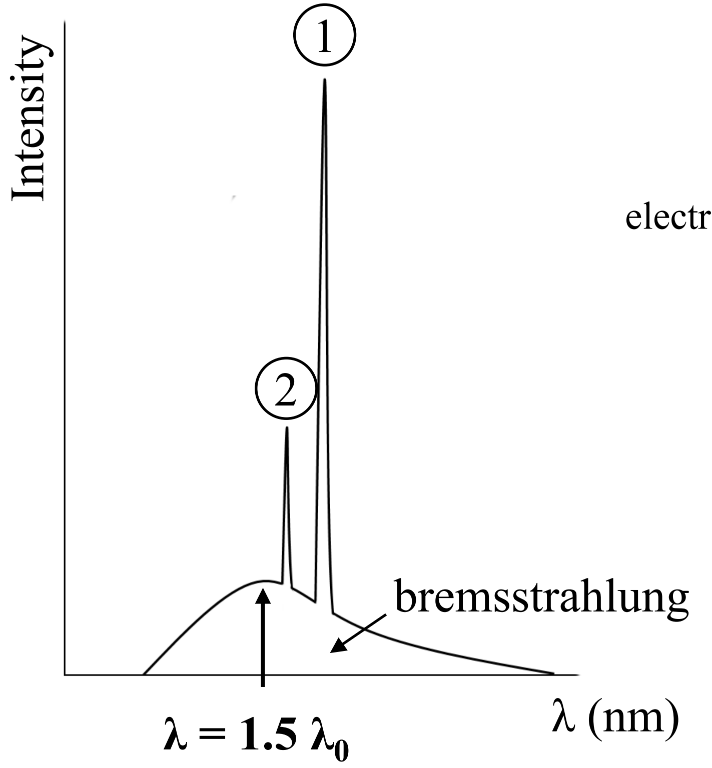
⇘ The electron trajectory deviation depends on the distance between the incoming electron and the target nucleus. The closer trajectory to the nucleus, the greater electron braking and so, the higher energy loss. The energy loss is qualified by the **LET**.

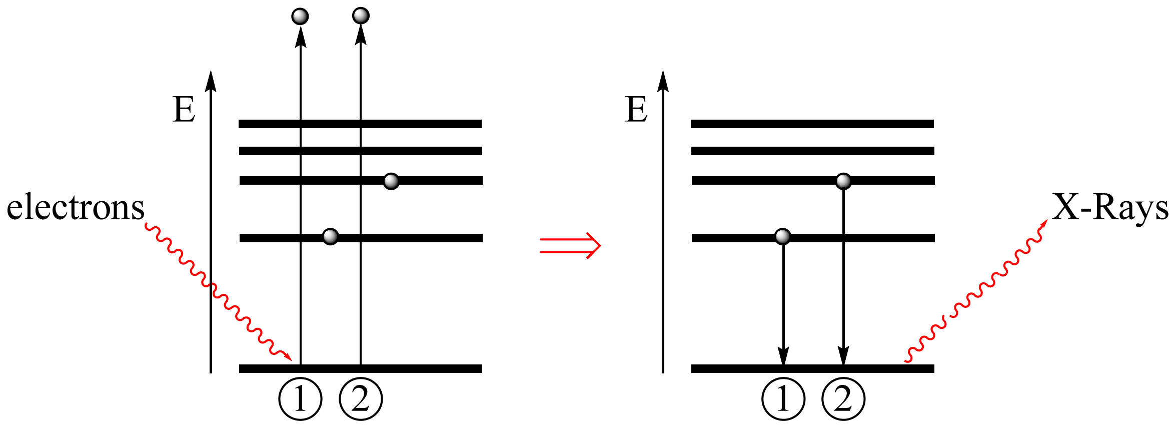
⇘ The energy lost by an electron when braking is transformed into an X-Ray emission.



- As all the trajectory deviations are allowed and so all the energy losses, it leads to the emission of a continuous X-Rays spectrum called "bremsstrahlung".

- Below is represented a typical X-Rays emission including the ionisation of the target material. The ionisation of the core electrons of the material gives rise to the emission of specific lines (1 and 2).





- λ_0 is given by: $\lambda_0 = \frac{hc}{E_0}$

- E_0 corresponds to the energy of the electrons of the primary beam

Detectors for the analysis of X-Rays and electrons emissions

General features

⇨ A detector provides the measurement of a beam intensity and energy.

↳ The beam intensity measurement consists in counting the number of photons or electrons entering the detector.

↳ The beam energy measurement consists in determining the energy of photons or electrons entering the detector.

⇨ A detector must be qualified as a function of:

↳ Its dead time $\mathbf{t_0}$: fraction of time needed to observe two consecutive events

↳ Its count rate: number of events counted per time unit

↳ Its maximum count rate: maximal number of events counted per second ($\mathbf{1 / t_0}$)

↳ Its background noise: defined by the signal over noise ratio

↳ Its efficiency **ε**: defined by the measured intensity over the incident intensity, $\boldsymbol{\varepsilon} = \mathbf{I_m / I_0}$

- Its detection threshold $\mathbf{W_m}$: minimum events needed to trigger a response (many often minimum energy required)
- Its energy resolution $\boldsymbol{\delta E}$: the capacity of distinguishing two events based on their energies
- Its relative energy resolution: for a event of energy $\mathbf{E_0}$, the relative energy resolution is defined as $\boldsymbol{\delta E / E_0}$
- Its transmission factor $\boldsymbol{\tau}$ for a detection solid angle $\boldsymbol{\Omega}$: $\boldsymbol{\tau = \varepsilon\Omega / 4\pi}$
- Its lifetime: maximum number of events that can be detected

X-Ray detectors

Fluorescent screen

- A fluorescent screen is a qualitative but not a quantitative detector.
- This detector cannot be used for spectrometric purposes.

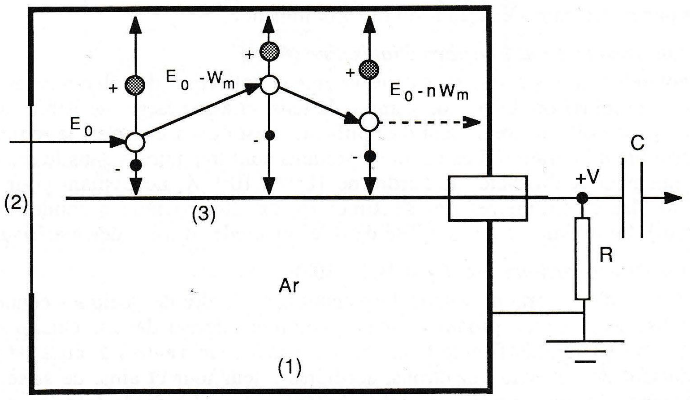
Gas detectors

⇨ The principle of these detectors relies on the ionisation of a gaz.

↳ The incoming X-ray photons produce a cascade of electron-ion pairs.

↳ When applying a voltage between an anode and a cathode, the electrons are collected at the anode and the ions from the ionised gas being reduced at the cathode. The generated current relates to the number of produced electron-ion pairs.

⇨ Below is depicted the scheme of an Ar detector for an incoming photon of energy $\mathbf{E_0}$. The detection threshold of the detector is $\mathbf{W_m}$:



1: gas chamber, 2: entering window, 3: collecting anode

↳ Each incoming photon generates $\mathbf{E_0}$ / $\mathbf{W_m}$ electron-ion pairs, mainly by Compton effect.

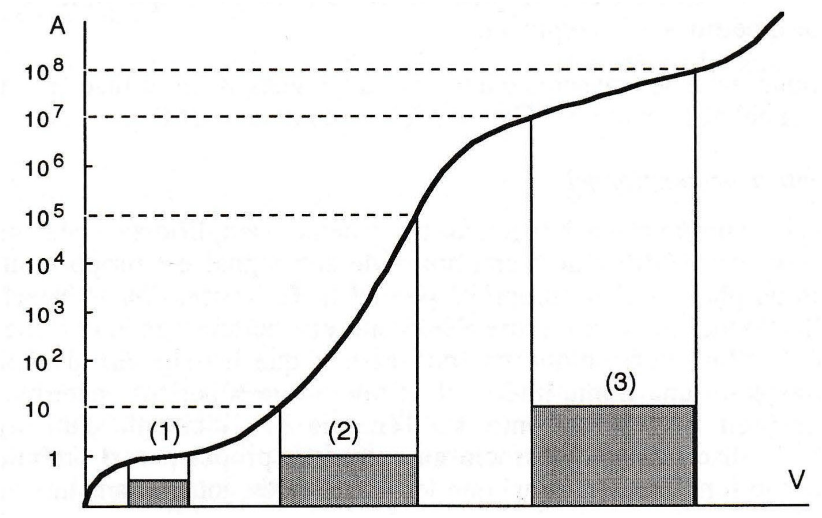
↳ When the incoming photon energy is greater that the ionisation of the deep energy levels of the rare gas, the photo-electric effect occurs as well.

↳ The excitation of the rare gas can give rise to an X-Rays fluorescence which is not detected (signal loss).

⇳ The efficiency is maximum when each incoming photon leads to an electron-ion pair.

⇳ To achieve this goal, the incoming window must be made of a thin plate of beryllium or mylar (organic polymer).

⇨ Below is depicted the different operating domains of such a detector represented by the coefficient of amplification **A** of the signal as a function of the applied tension **V** at the detector:



⇳ Region (**1**): A part of electron-ion pairs recombines (**0 < A< 1**). When **A = 1**, **V** is just enough to ensure the collection of the pairs.

⇳ Region (**2**): the electron cascade occurs close to the anode. One photon induces one cascade of electrons, this is the working domain (**10^2 < A < 10^5**).

⇳ Region (**3**): Geiger-Muller detector. There is no proportionality. This region is used to qualitatively detect weak emissions.

↳ In the region (**2**), the amplitude of the detector signal is proportional to the incoming photon energy. In this region, the detector provides an energy discrimination.

↳ In the region (**2**) one can associate a filter with a given energy width to gain in sensibility for a given photon energy domain.

⇨ To improve the lifetime of the detector, and halogen gas with a reversible electrochemical oxidation (Br_2 or Cl_2) is added to help the reduction of the rare gas used for the detection.

Scintillation solid detectors

⇨ The active part of the detector is the scintillator made of sodium iodide activated by some thallium: NaI(Tl).

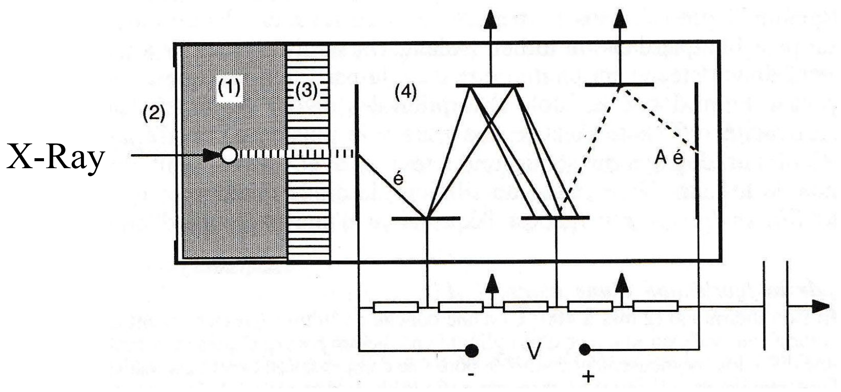
↳ This material absorbs a wide range of X-Rays and is transparent to its own scintillations.

↳ An incoming X-Ray photon generates some electron-hole pairs ($\mathbf{E_0} / \mathbf{W_m}$) in NaI(Tl), that is some electrons are promoted from the valence band to the conducting band of the scintillator.

↳ The electrons located in the conducting band migrate to a Tl atom and are relaxed at its contact.

➪ The relaxation leads to photons, converted into a photo-electrons at the beginning of the photomultiplier then further transformed into a cascade of electrons by a series of dynodes.

⇨ Below is depicted the scheme of such detector:



1: scintillator NaI(Tl)
2: beryllium window
3: wave guide
4: photomultiplier made of dynodes
A: coefficient of amplification
○: hole

Semiconductor solid detectors

⇨ Theses detectors are based on a semiconductor device.

➪ For a photon energy up to 30 keV, the semiconductor is usually based on silicon doped with some lithium (Si(Li)) which constitutes a PIN junction. For higher energies, a semiconductor of hyper pure germanium is required.

➪ Other detectors based on GaAs, CdTe or CdZnTe are also available.

⇨ The operating mode of such detector is as follows:

↳ An incoming X-ray photon can generate a photo-electron inside the semiconductor by a photo-electric effect. The generated photo-electron will then interact with the valence band electrons to create some electron-holes pairs, some electrons are promoted to the conducting band of the semiconductor.

↳ The number of created electron-hole pairs is related to the energy of the detected photon ($\mathbf{E_0} / \mathbf{W_m}$).

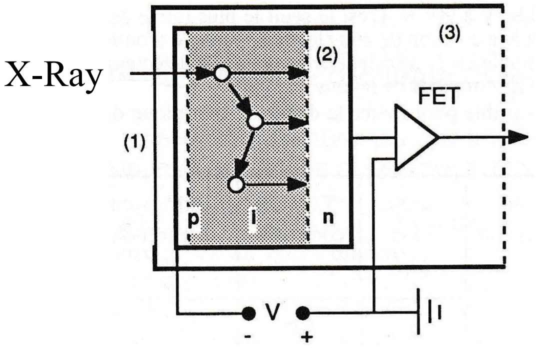
↳ An incoming X-ray photon can also generate electron-hole pairs by means of a Compton effect. In general the X-Rays beam/semiconductor interaction proceeds mainly by a photo-electric effect, the Compton effect being effective for X-Ray photons of high energy.

↳ The created electron-hole pairs are stabilised thanks to the tension applied at the semiconductor and the electrons promoted to the conducting band are driven into an electrical circuit. Hence, a current impulsion is generated which constitutes the detector signal (see chemical analyses: spectrometry).

↳ In contrast with gas detectors and scintillation solid detectors, there is no *in situ* amplification (cascade of electrons or photomultiplier), so the amplification coefficient **A = 1**. An electronic amplifier is used to magnify the signal.

↳ The detector is cooled with liquid nitrogen (77 K) to improve the signal other noise ratio as it is the case for all semiconductor based detectors.

⇨ The scheme of an Si(Li) detector is depicted below:



1: beryllium window
2: Si(Li) material with different domains: **p** (positive), **i** (intrinsic), **n** (negative)
3: vacuum chamber cooled with liquid nitrogen
○: holes

Electron detectors

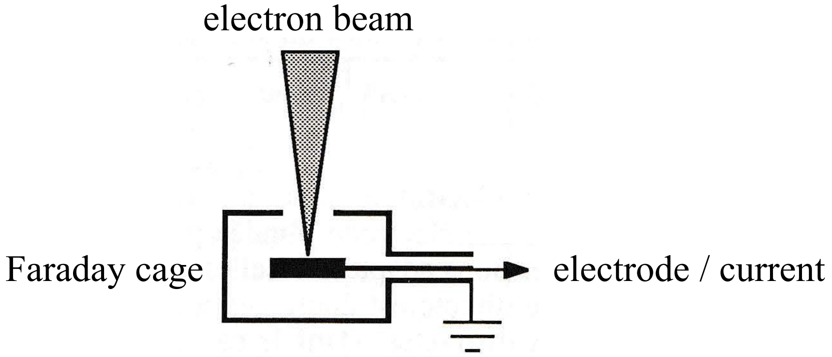
Fluorescent screen

⇨ A fluorescent screen is a qualitative but not a quantitative detector.

↳ This detector cannot be used for spectrometric purposes, it is mainly dedicated to Transmission Electron Microscopy (TEM).

Direct detectors

⇨ As a flux of electron gives rise to an electrical current, one can use an electrode shielded by a Faraday cage to collect the incoming electrons.



➥ This method is applied to the detection of weak electron beams like the diffracted electron beams detected in TEM.

Scintillation detectors

⇨ The principle is the same than the one for the detection of X-Ray photons.

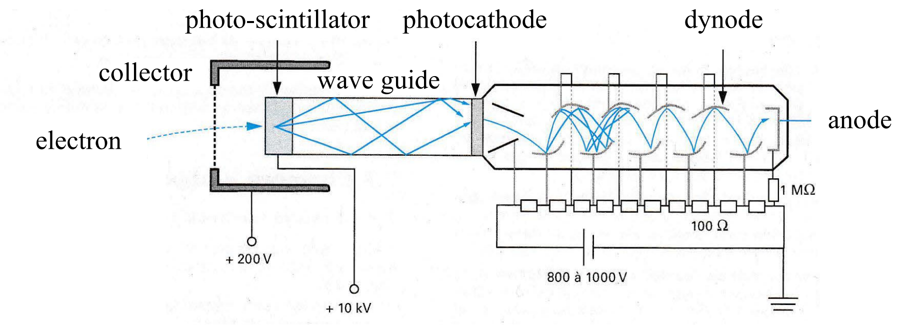
➥ The photo-scintillator can be either made of an organic resin doped with a scintillation compound (*p*-terphenyl or diphenyloxazole) or a doped mineral solid (cerium-doped yttrium silicate). Organic based photo-scintillators have a shorter lifetime.

Interactions beam-matter: matter emission and beam detection

- Organic and mineral scintillators provide a short dead time about 10^{-9}s.

- For electrons of weak energy (< 1keV), the application of an electric field is required to drive them into the detector as it is the case for SE in Scanning Electron Microscopy (SEM). They are accelerated at a few keV.

- Below is depicted the scheme of such a detector:



- The collector is positively polarised to accelerate the incoming electrons further converted into photons by the photo-scintillator.

- The produced photons are thus converted in electrons by a photocathode, multiplied by some dynodes and finally collected at an anode.

Semiconductor solid detectors

⇨ Theses detectors are based on a semiconductor device, the same than the ones used to detect X-Rays.

⇨ The main difference with an X-Ray detector remains into the thickness of the PIN device which is lower due to the greater LET of electrons compared to X-Rays.

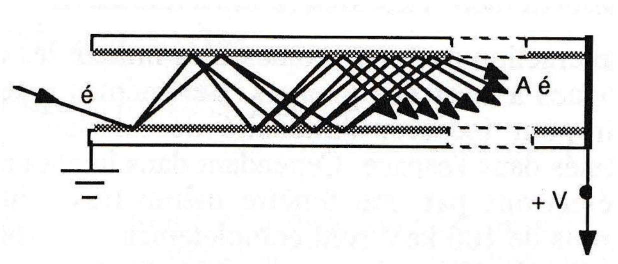
⇨ For electrons detection, a low temperature is not required, the detectors work at room temperature.

Channeltron detectors

⇨ A channeltron is an electron multiplier.

⇨ When entering the channeltron, an electron is accelerated by an electric field and then bumps the walls of the channel, generating some SE finally collected at an anode placed at the end of the channel.

⇨ Channeltrons were firstly made of oxygen treated Be-doped Cu plates (SE gain ~ 2×10^6). A high resistance semiconductor material that has a high SE emissivity is also used (SE gain ~ 2×10^7 - 2×10^8).



- A channetron can replace a photomultiplier made of dynodes for the detection of X-Ray photons as well.
- In this scheme, **A** stands for the amplification coefficient.

Comparison between the principal detectors

detector	amplification A	dead time t_0 (µS)	count rate (events /s)	detection threshold W_m (eV)
Ar	1	1	10^6	26.4
Ar-CH_4	10 - 10^5	0.5	2×10^6	26.4
scintillator	10^6	0.001 - 0.2*	5×10^6	50
semiconductor	1	1	10^6	3.8

*: 0.001 µs for organic, 0.003 – 0.008 µs for cerium-doped yttrium silicate and 0.2 µs for NaI(Tl)