Elektronové spektroskopie
Electron Spectroscopies

(NEVF113)

Viktor Johánek
viktor.johanek@mff.cuni.cz

1. **Základní principy a přístrojové vybavení**
2. **Transport elektronu pevnou látkou**
3. **Spektroskopie Augerových elektronů: *AES***
4. **Spektroskopie charakteristických ztrát: *EELS, HREELS***
5. **Fotoelektronová spektroskopie: *XPS, UPS, synchrotronové metody, IPE***
6. **Přídavek** (starší metody, nejnovější metody a moderní podoby klasických metod)

Electron spectroscopies

Basic definition and classification

Electron spectroscopy:
- surface analytical method using detection of emitted electrons => electronic structure and its dynamics
- excitation source (primary probe) of any type: photons, electrons, ions, elmg. field

Electron spectroscopy classes

1) Externally induced emission of electrons
   AES, XPS/UPS/PES, APS, FES
2) Modification of electron energy upon interaction with surface
   EELS, EPES, DAPS

Detection methods

- Dispersive spectroscopy – energetic distribution of emitted electrons
  AES, XPS/UPS/PES, EELS, EPES, FES
- Appearance spectroscopy – changes of total output electron signal
  APS

Not all methods using electrons belong to electron spectroscopy: **diffraction** and **microscopy**

Basic characteristics of surface spectroscopy technique:

- Surface sensitivity / specificity – true surf. specificity = signal only from surface (e.g. LEIS)
  - surface signal is distinguishable from bulk signal (e.g. shift)
  - surface signal is large compared to bulk signal

  } or (ideally) both
- Detection limit – lowest quantity of a given component that can be distinguished
  (can vary greatly depending on a particular element)

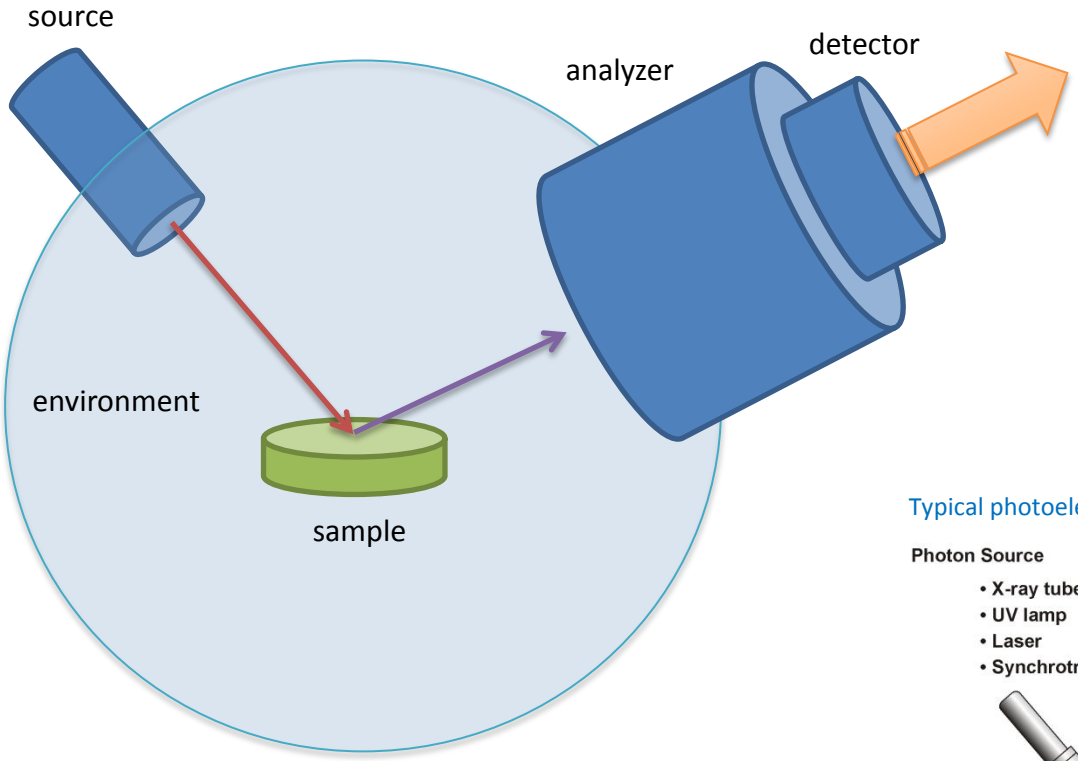
Electron spectroscopies

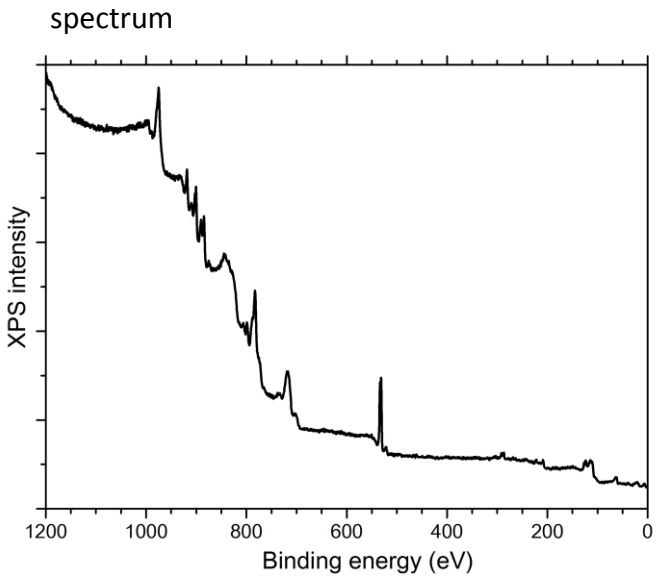
Overview of methods

Physical principle	Primary probe	Typical primary energy range (eV)	Output	Electronic levels, information content	Surface sensitivity (nm)	Technique	Acronym
Auger transition	Electron	10-10000	Electron	Filled states	high	Auger electron spectroscopy	AES
Photoemission	Photon	0-20	Electron	Filled valence states, adsorbates	high	Ultraviolet photoelectron spectroscopy	UPS
		50-2000		Filled core states, chemical sensitivity	mid	X-ray Photoelectron Spectroscopy	XPS
		0-10000		Filled valence and core states	high-mid	(Synchrotron radiation) Photoelectron Spectroscopy	(SR)PES
		1000-20000		Filled core states (bulk composition, burried structures)	low	Hard X-ray Photoelectron Spectroscopy	HAXPES
		0-5		Dispersion of filled states near EF	high	Angle resolved Ultraviolet photoelectron spectroscopy	ARUPS
		0-20		Dispersion of filled valence states	high	Angle resolved Photoelectron Spectroscopy	ARPES
Photoemission	2 photons	5-20	Electron	Electron dynamics, electron transfer through interfaces	mid	Two-photon photoemission spectroscopy	2PPE
Internal photoemission	Photon		Electron	Electronic structure of solid interfaces	low	Internal Photoemission Spectroscopy	IPE
Inverse photoemission	Electron	100-1000	Photon	Empty and image states	very high	Inverse photoemission spectroscopy	IPS (IPES)
Electron energy loss	Electron	10-100	Electron	Plasmons, valence levels	high	Electron energy loss spectroscopy	EELS
		50-2000		Core levels + fine structure	mid	Energy-loss near edge structure	ELNES
		50-2000			mid	Extended energy-loss fine structure	EXELFS
		5-10		Vibrational transitions, adsorbates	very high	High resolution electron energy loss spectroscopy	HREELS
Electron elastic scattering	Electron	100-3000	Electron	Elemental info, IMPF determination	high	Elastic peak electron spectroscopy	EPES
Core excitation threshold	Electron	50-2000	Electron	Empty states, adsorbates	high	Appearance potential spectroscopy	APS, LEAPS, HEAPS
			Electron		high	Auger electron appearance potential spectroscopy	AEAPS
			Photon		mid	Soft X-ray appearance potential spectroscopy	SXAPS

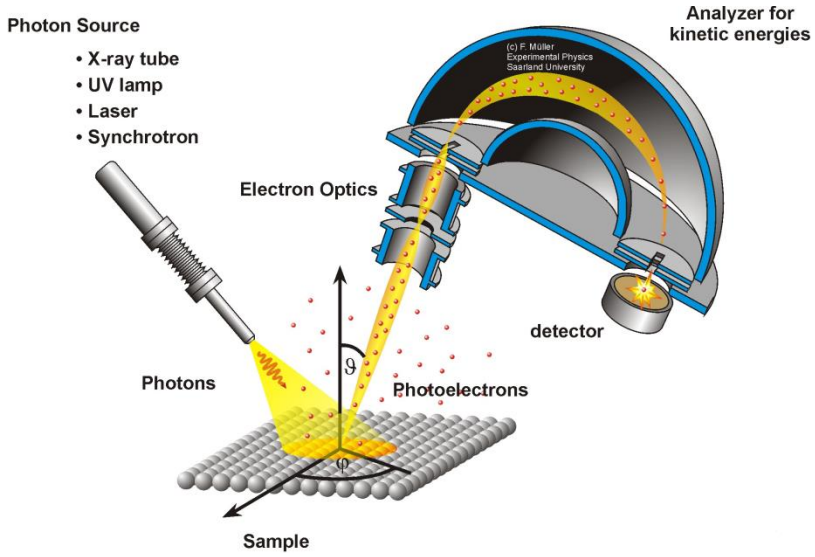
Basic principles

Experimental arrangement





Typical photoelectron spectroscopy setup



Electron optics

Basic principles

Analogy of electron and classical (photon) optics

- Law of refraction (Snell's law)
- Law of reflection
- Fermat's principle (of least action)

$$\frac{\sin \alpha_1}{\sin \alpha_2} = \frac{n_2}{n_1}$$

Determination of trajectory based on equipotentials
„index of refraction "

$$n \propto \sqrt{V}$$

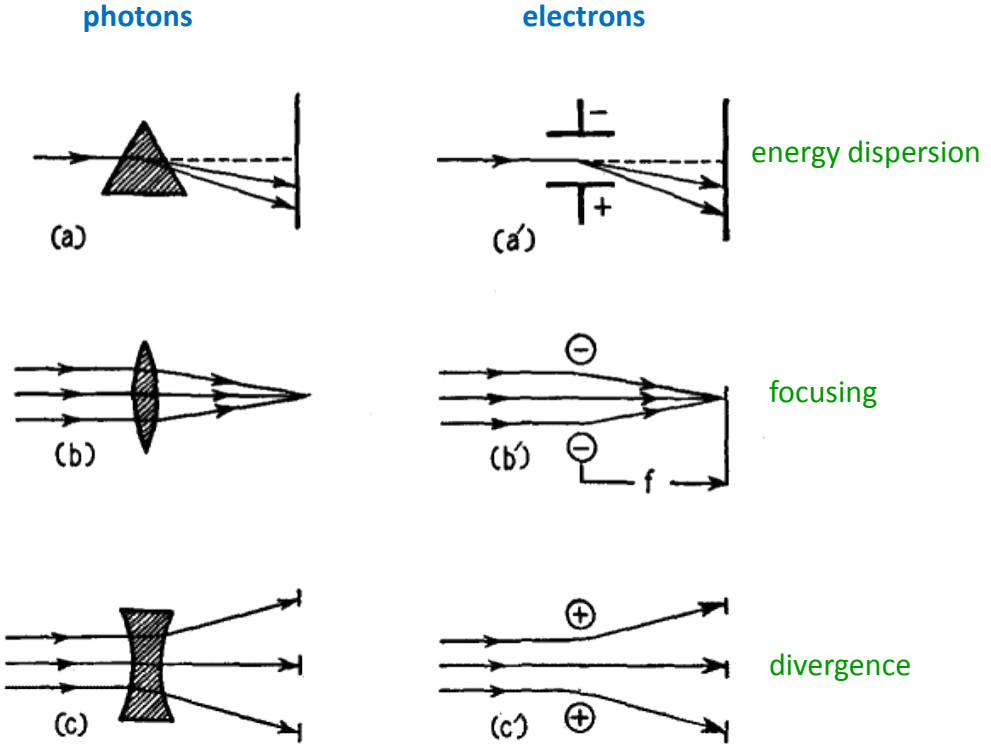
relatively slow electrons (no relativistic effects)

Analogy limitations

- No independence of rays (space charge)
- Non-zero inertia (no abrupt changes possible)
- Energy and momentum continuously variable

Other differences

- Limited choice of refracting media: electric and magnetic field only
- Vacuum required
- Abberation cannot be completely eliminated
- Much higher flexibility (n>1000 possible)
- Interaction with matter usually irreversible (S increase)
- Special phenomena available by el. pulsing (e.g., el. bunching in klystron)
- Almost all lenses in practical el. optics convergent



applies to all charged particles

	Photon	Electron
Charge	0	$-e$
Mass	$h\nu/c^2$	$m = m_0[1 - (v/c)^2]^{-1/2}$
Rest mass	0	m_0
Momentum	$p = h\nu/c$	$p = mv$
Energy	$W = h\nu = cp$	$W = mv^2/2 \quad c(m_0^2c^2 + p^2)^{1/2}$
Wavelength	$\lambda = c/n\nu$	$\lambda = h/mv$
Wave equation	Solution real	Solution complex
Statistics	Bose	Fermi
Index of refraction	$n = c/c' = c/\lambda\nu$	$n = \lambda_0/\lambda = (m/m_0)(v/c)$
Shape of refractive elements	Arbitrary	Limited by Laplace's equation
Optical components	Static	Static and dynamic

[a] Here, h is Planck's constant, 6.624×10^{-34} J-sec; ν is the frequency.

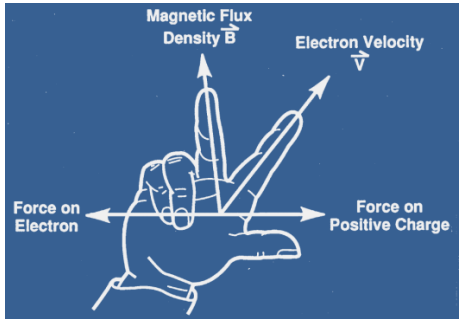
Electron optics

Basic principles

Electrostatic (Coulomb) force $\overrightarrow{F_E} = q\vec{E}$

Magnetic (Lorentz) force $\overrightarrow{F_B} = q(\vec{v} \times \vec{B})$

„right hand rule“



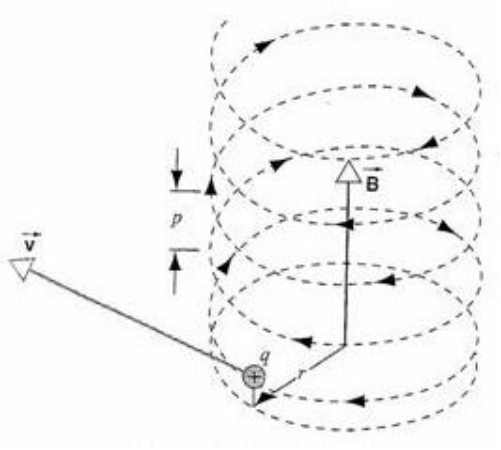
Elements of electron optics
(electrostatic or magnetic)

- Lenses – (de)focusing, magnification, switching between image and diffraction
- Deflectors – shifting or tilting beam, beam blanking/limiting
- Stigmators – correction of deficiencies of lenses

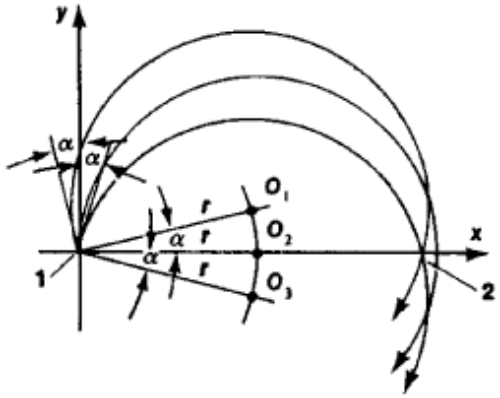
Electron optics systems in spectroscopy

- static (slow changes of E, B)
- dynamic (time-scale of changes comparable to time of flight of a particle)

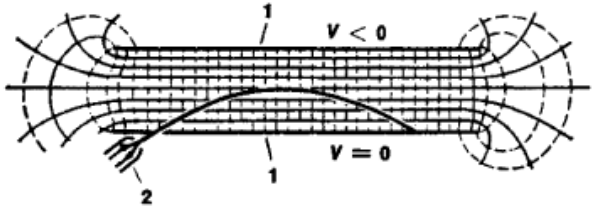
Helical path of charged particle in a uniform magnetic field



Deflection and focusing of a beam of charged particles by a uniform magnetic field



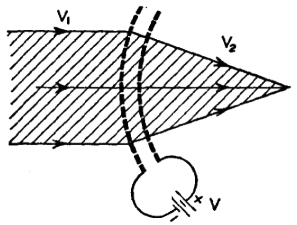
Deflection of electron beam in the uniform field of a parallel-plate capacitor



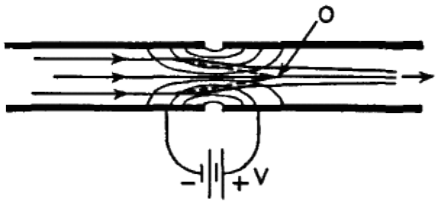
Electron optics

Basic elements of electron optics – lenses

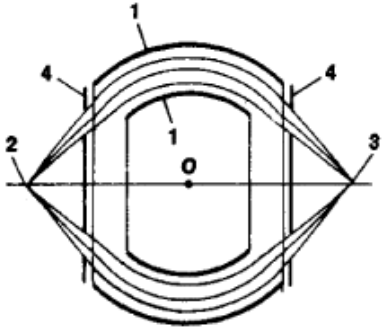
double-gauze electron lens



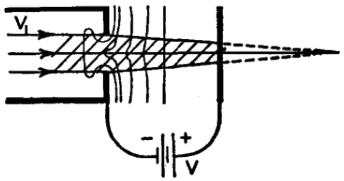
double-cylinder (Einzel) lens



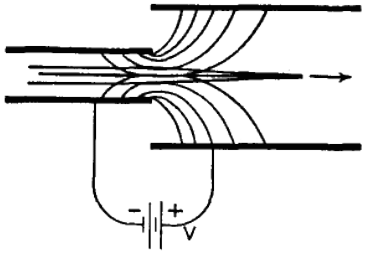
electrostatic focusing (spherical capacitor)



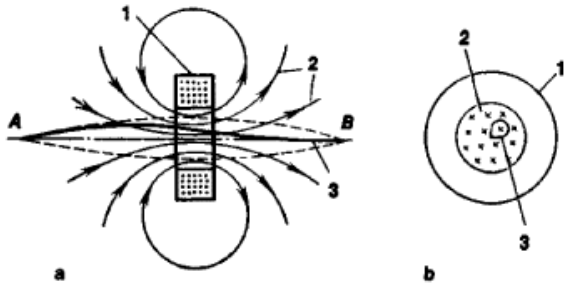
single-aperture lens



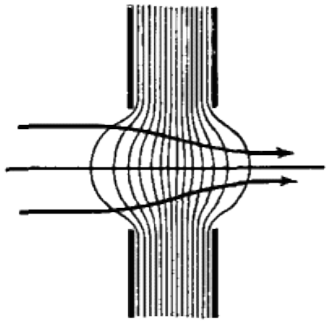
short-focus double-cylinder lens

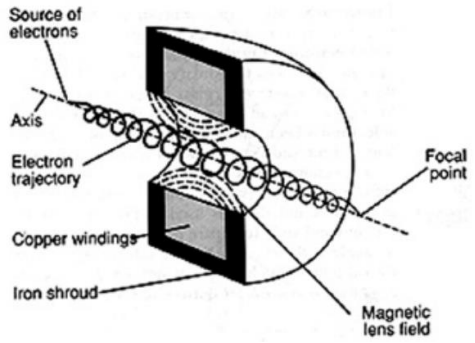


magnetic toroidal coil lens



two-aperture lens

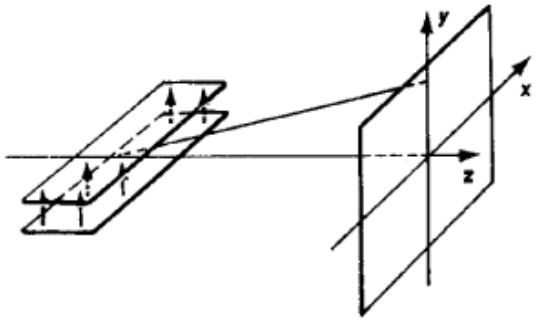




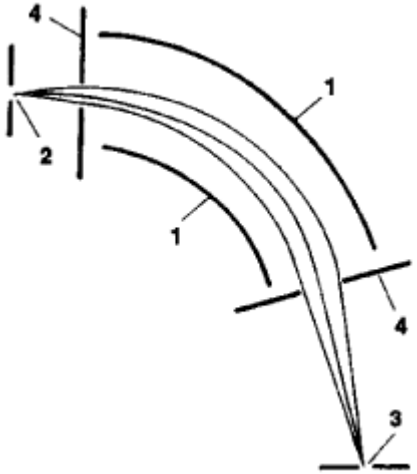
Electron optics

Basic elements of electron optics – deflectors

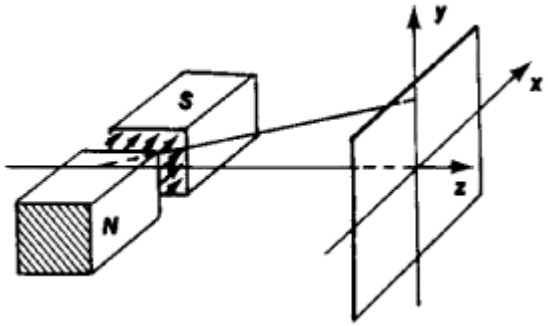
electrostatic deflector (parallel-plate capacitor)



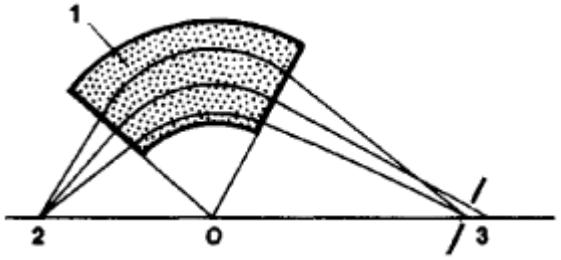
electrostatic deflector and focusor (sectional tubular capacitor)



magnetic deflector (transverse magnetic field)



magnetic deflector and focusor (sectoral magnetic field)



Applications:

- Beam scanning
- Beam alignment
- Particle filtering

Sources of charged particles

Electron sources (guns)

Essential components

- electron source (gun)
- electronic optics system - focusing, scanning, filtering

Methods of electron generation

by emission mechanism

- Thermoemission (Richardson–Dushman effect), enhanced by field (Schottky effect)
- Field emission (cold emission - tunneling) – F>10^8 V/m
- Photoemisson (photoelectric effect)
- Plasma generation

Richardson

$$I = AGT^2 e^{-\frac{W}{kT}}$$

by type of electric field

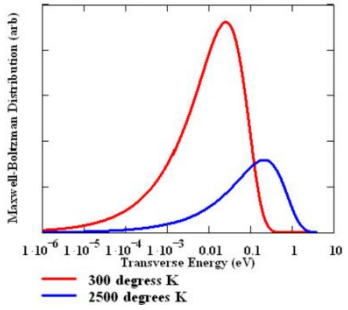
- DC
- RF

Electron source properies

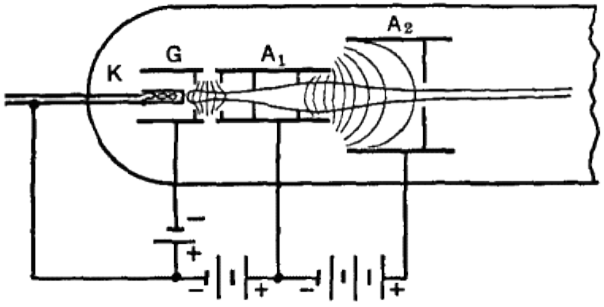
- Spot (source) size
- Brightness (spatial coherence) [per area and space angle]
- Mean energy
- Energy spread

Filament	ΔE [eV]
W	2.5
LaB_6	1.5
FEG	0.25

thermoelectron energy distribution



electron gun (emitter)

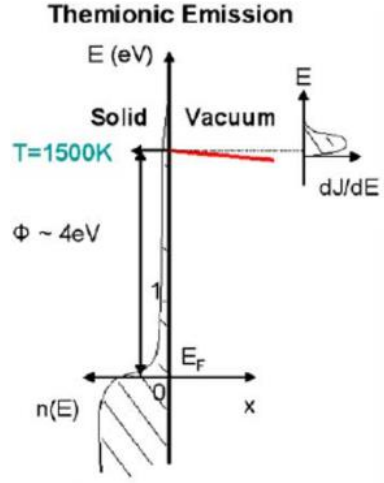


Directly heated hot cathode **filament material:**

- W, Re (~2500 K)
- Ta (~2200 K)
- ThO_2 on W, Mo, Ta (~1800-2000 K)
- LaB_6, CeB_6 on Ta (~1200 K)

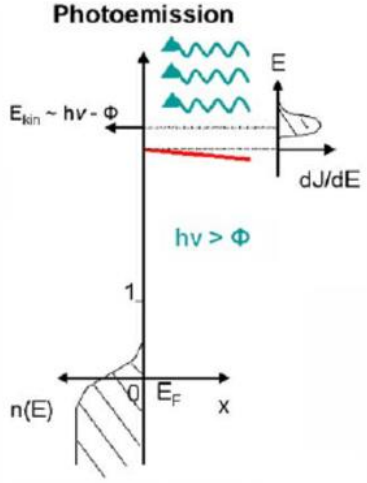
potential energy diagram

mean kin. energy



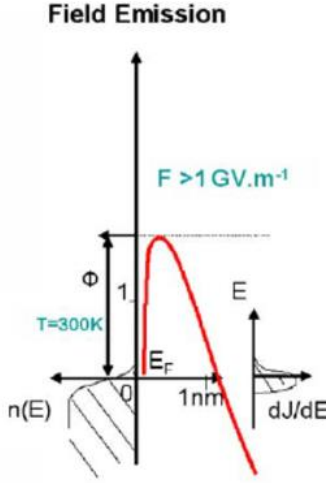
$$E_{kin} \sim \frac{3}{2} kT_{Solid}$$

$J < 10^6\ A.m^{-2}$



$$E_{kin} \sim h\nu - \Phi + e\sqrt{\frac{eF}{4\pi\varepsilon_0}}$$

$J < 10^9\ A.m^{-2}$



$$E_{kin} \sim 4kT_{Solid}$$

$J < 10^{12}\ A.m^{-2}$

Sources of charged particles

Ion sources (guns)

Methods of ion generation

- Thermal ionization
- Discharge (plasma, RF, arc, ...)
- Spark ionization

atomic ions

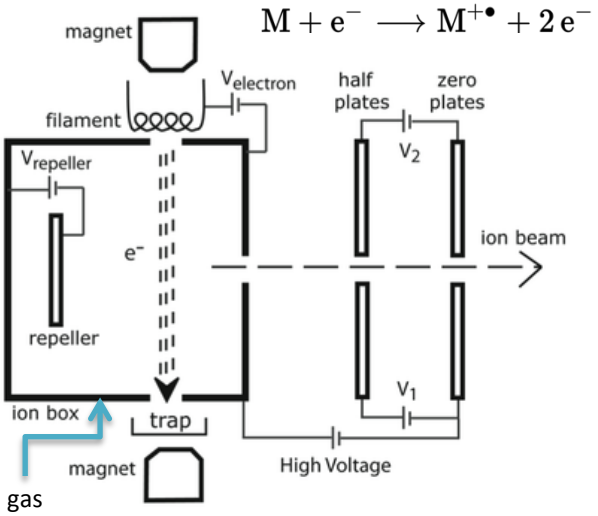
- Electron beam ionization
- Photoionozation (laser, X-ray, UV, ...)
- Chemical ionization
- Electron capture ionization
- Field ionization

molecular ions from volatile compounds

- Electrospray
- Field desorption
- High-energy particle impact
- Secondary ionization (by primary ions)
- Laser desorption/ionization

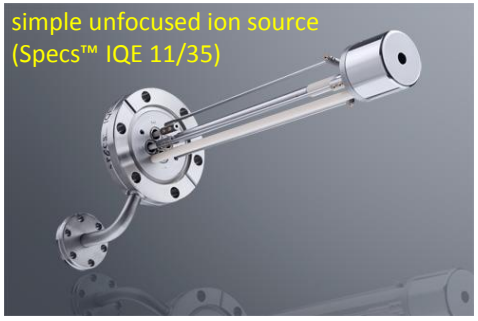
molecular ions from non-volatile compounds

ion gun with electron beam ionization



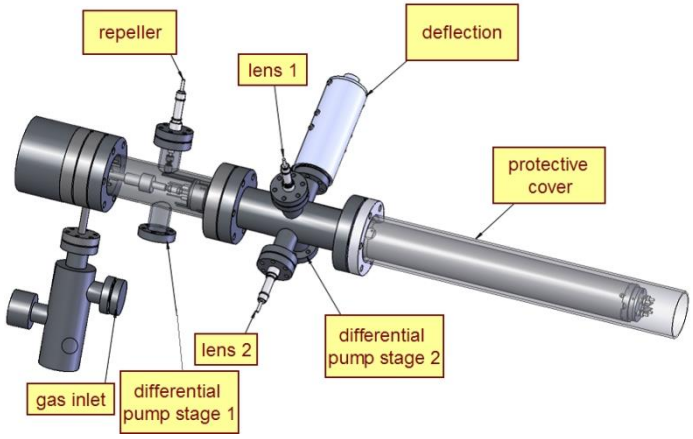
Ion source properties

- Ion type (+/-, at. mass)
- Spot size
- Beam divergence
- Brightness (current)
- Mean energy
- Energy spread
- Stability



+ high currents
+ simple and small design
- unfocused
- high pressure operation

differentially pumped focused ion source



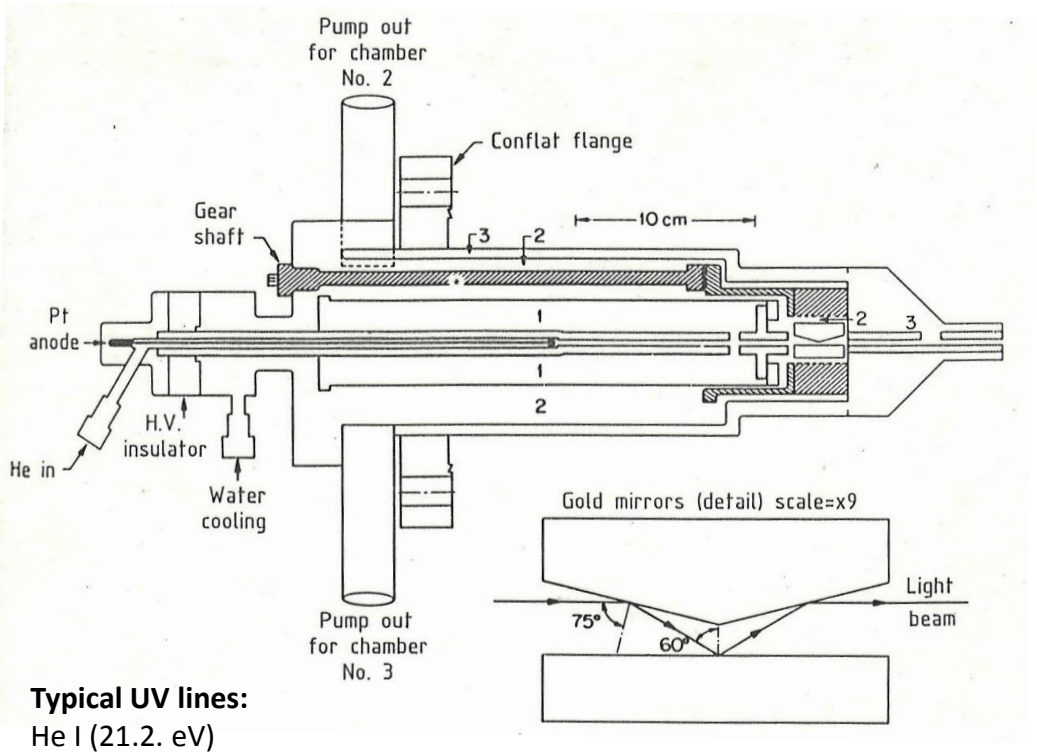
+ beam scanning feature
+ low pressure (typ. by 2-3 orders)

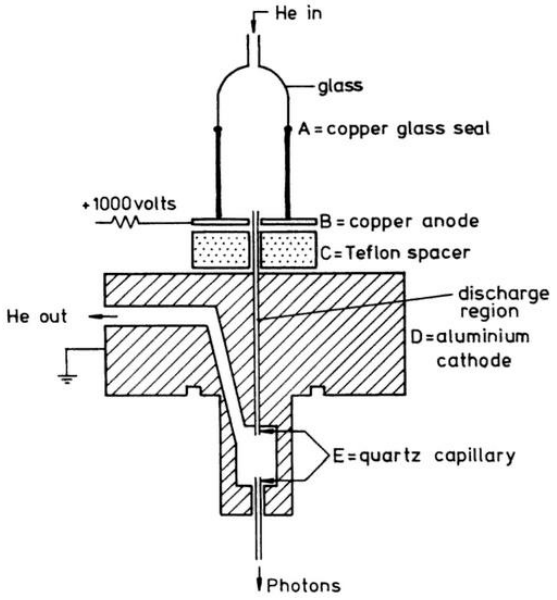
Radiation sources

Photon sources for photoelectron spectroscopy

UPS – UV vacuum source

cold cathode capillary discharge:
excitation in discharge → decay back to ground state



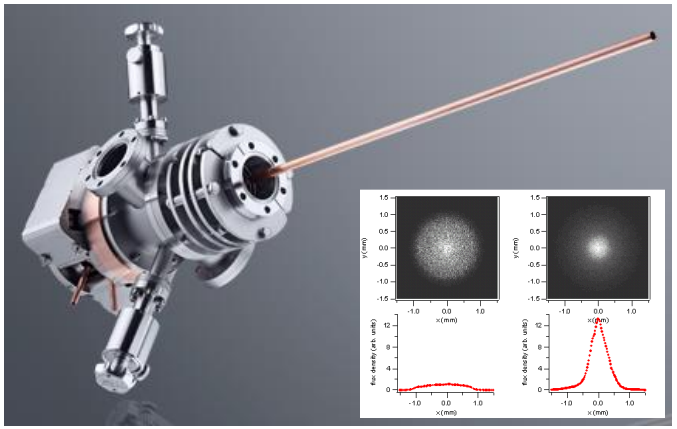


Typical UV lines:
He I (21.2. eV)
He II (40.8 eV)
Ne I (16.6 eV)
Ne II (26.8 eV)

I - light emitted from neutral atoms
II - light emitted by singly ionized atoms

(+Ar, Kr, Xe)

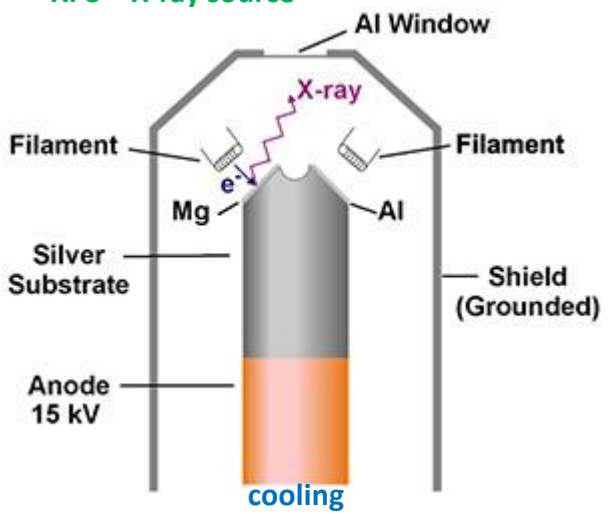
Specs™ Ultraviolet Source UVS 300

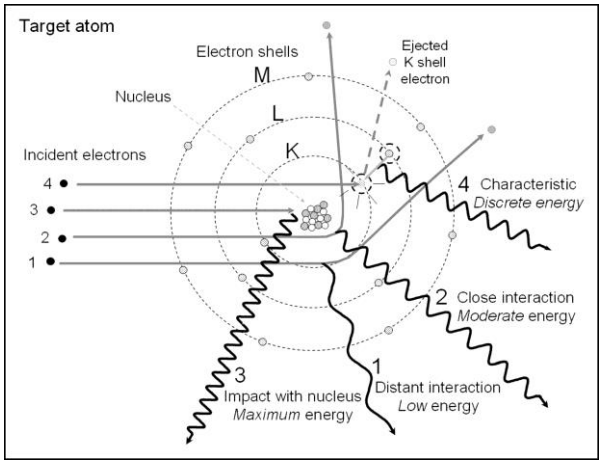


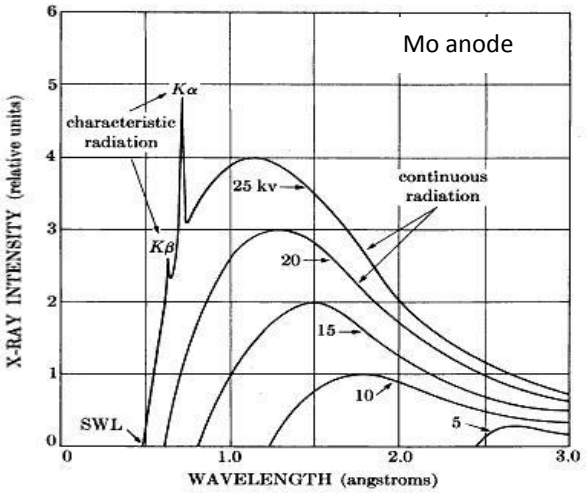
Radiation sources

Photon sources for photoelectron spectroscopy

XPS – X-ray source



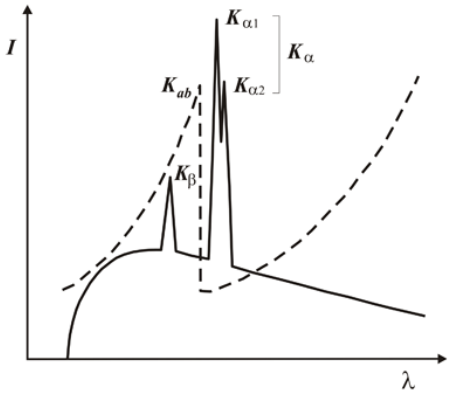




Typical dual („twin-anode“)source:

- Mg Kα line (1253.6 eV)
- Al Kα line (1486.6 eV)

(+ Ag, Mo, Cu, Si, Zr, …)



Metal (Al) filter (~µm thick window)

- shielding electrons from X-ray gun out and from the sample in
- filtering out low energy photons

(elimination of signal “cross-talks” and ghost spectral features)

Radiation sources

Photon sources for photoelectron spectroscopy

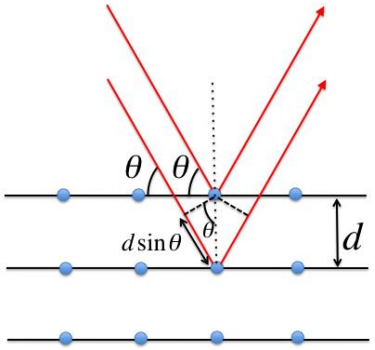
X-ray monochromator → HR-XPS

- narrower energy distribution
- lower spectral background
- elimination of unwanted x-rays from satellites and anode impurities (elimination of PE peak satellites)
- elimination of Bremsstrahlung and thermal radiation (reduction of x-ray induced damage)

Al Kα: quartz (SiO_2) with <1010> orientation => 1486.7 eV

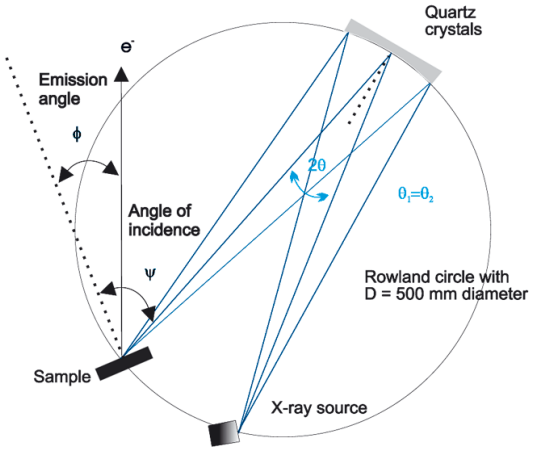
Al Kα	Intrinsic FWHM [eV]	Monochromatized FWHM [eV]
Source	0.43	0.16
Broadening in el. analyzer	0.6-0.8	0.21-0.3

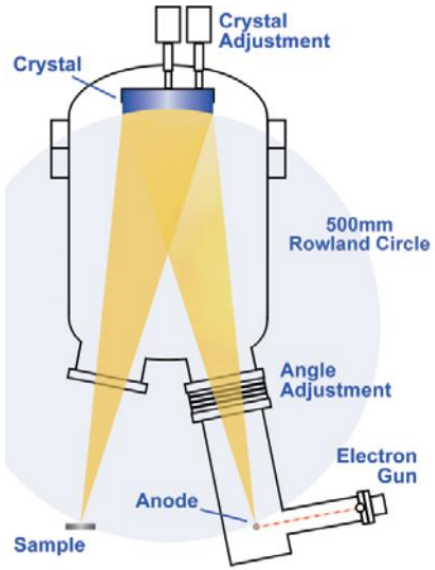
Other materials:
LiF, SiO_2, InSb, Si, Ge, PET, ADP, Beryl, TlAP, RbAP, KAP, CsAP, …



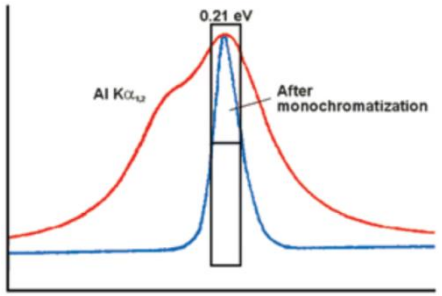
Bragg's law: constructive interference

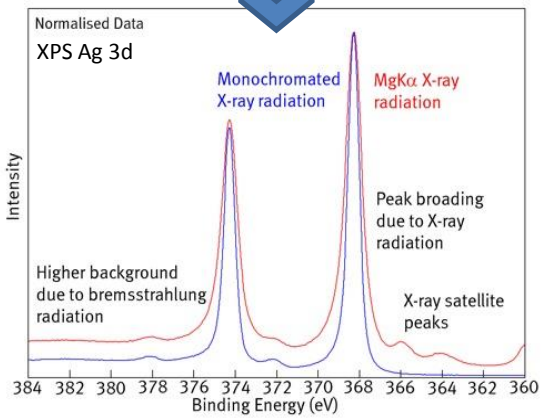
$$n\lambda = 2\,d\,\sin\Theta$$





Thermo Scientific XR5 X-ray monochromator



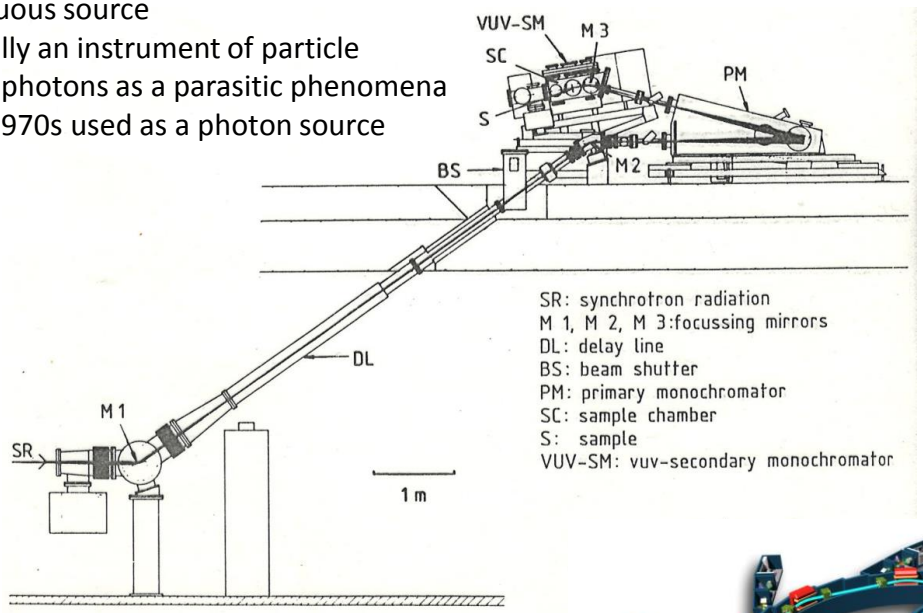


Radiation sources

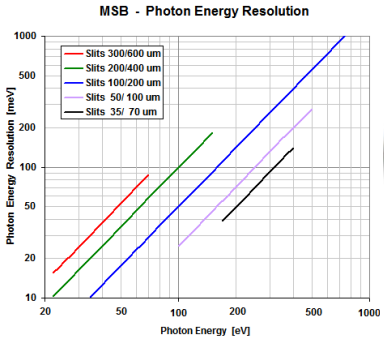
Photon sources for photoelectron spectroscopy

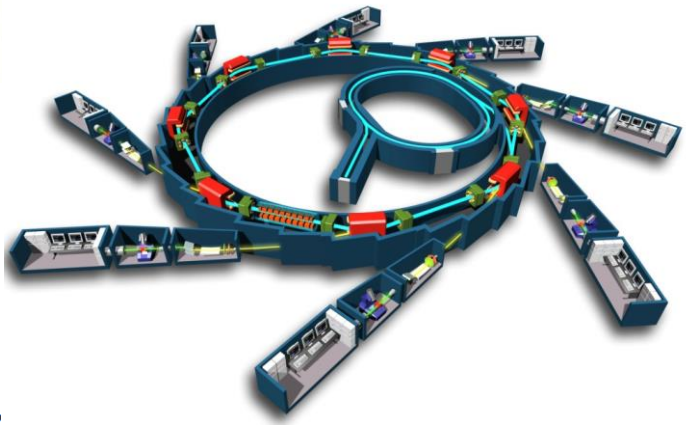
PES - Synchrotron radiation source

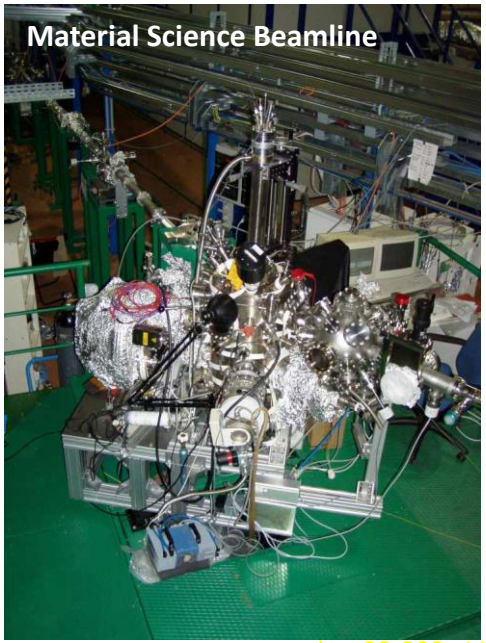
- continuous source
- originally an instrument of particle physics, photons as a parasitic phenomena
- since 1970s used as a photon source



Elettra synchrotron (Trieste, Italy)







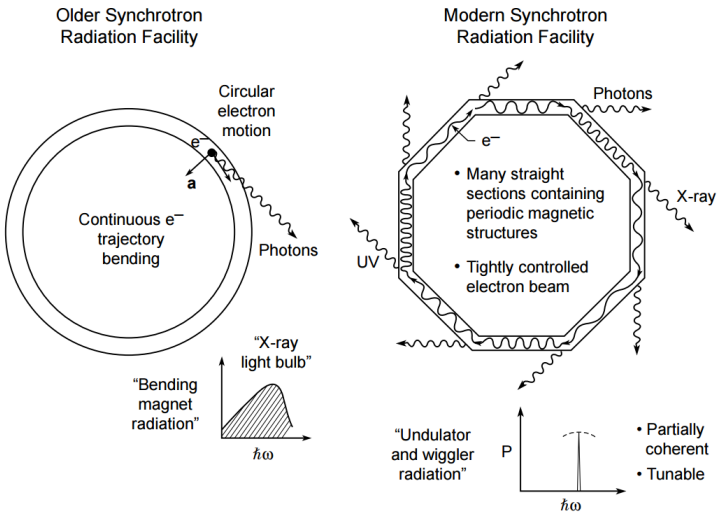
Advantages:

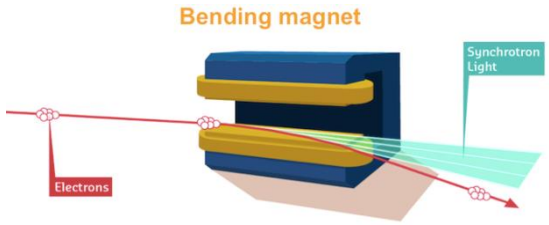
- tunable energy
- high energy resolution
- high luminosity (brilliance) – typ. 10^{11}-10^{19} fot.s^{-1}.mm^{-2}.mrad^{-2} (X-ray gun 10^{6}-10^{10})
- collimated beam
- polarized light

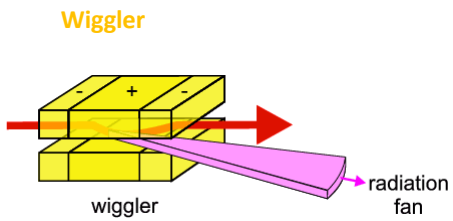
hν=20-900 eV

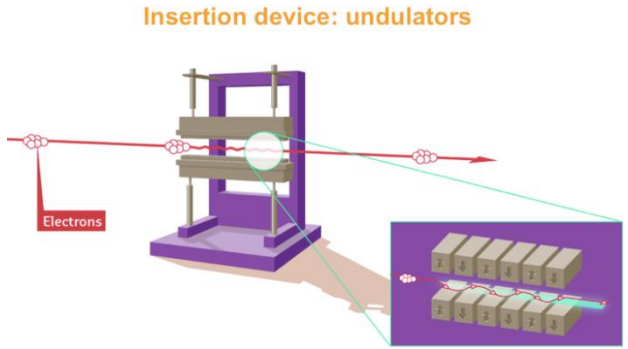
Photon sources

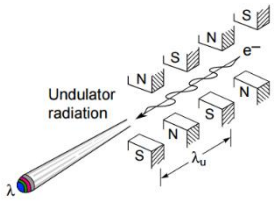
Synchrotron radiation source





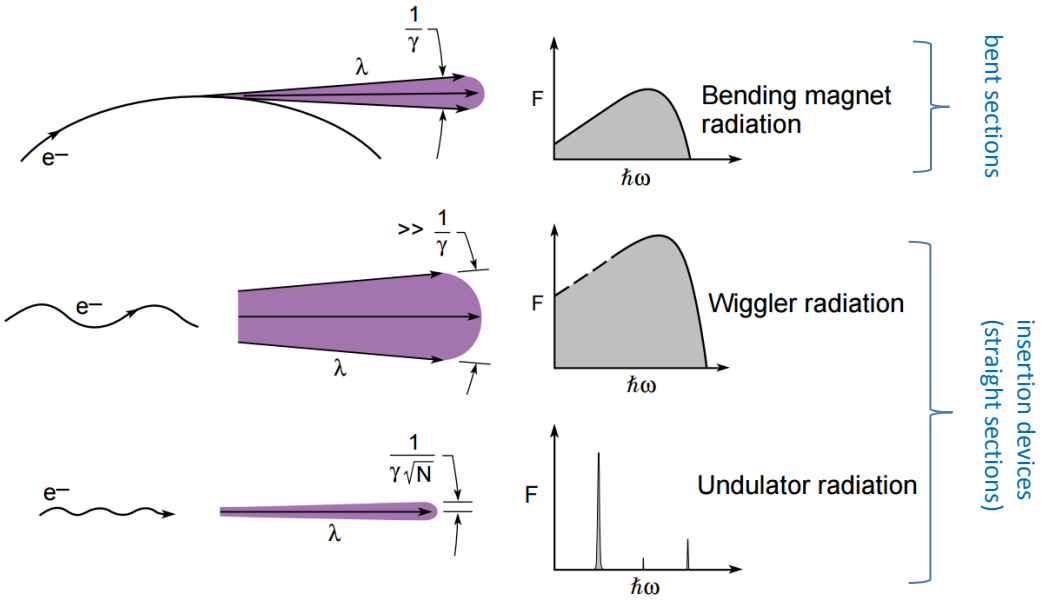


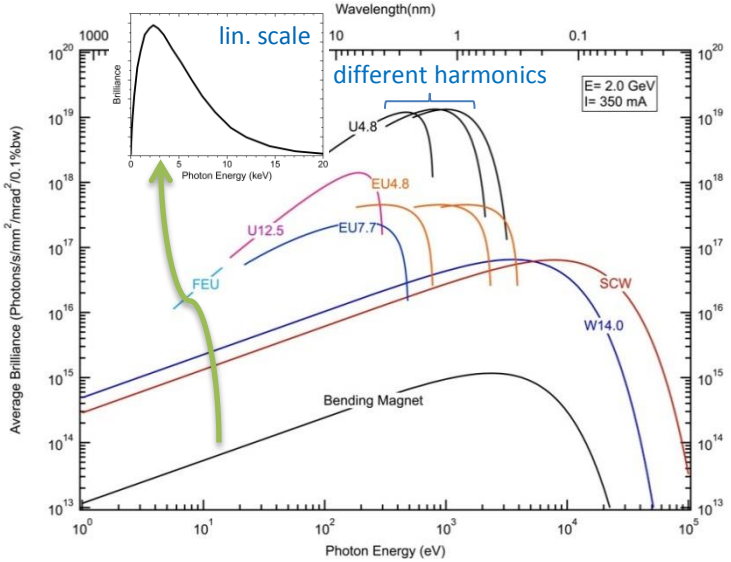




interference

Forms of synchrotron radiation





Analyzers

Basics

Role of electron analyzer

- filtering of specific particles (*E, m, q*)
- beam focusing (usually)

Types of electron analyzers

Static

- Parallel-plate analyzer
- Cylindrical mirror analyzer
- Radial (127°) cylindrical analyzer
- Hemispherical analyzer
- Magnet sector analyzer

Dynamic

- Quadrupole
- Time-of-flight
- Cyclotron resonance cell
- …

Main parameters

Energy resolution

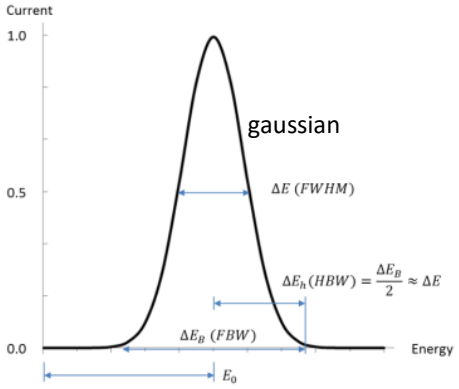
- ability to resolve adjacent peaks
- general formula:

$$\frac{\Delta E}{E} = aw + b\Delta\alpha^2 + c\Delta\beta^2$$

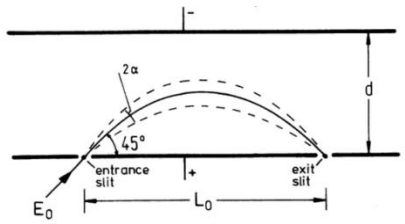
ΔE … energy passband
w … entrance and exit slit width
Δα … angular deviation of el. beam in the plane of deflection
Δβ … angular deviation of el. beam in the perpendicular plane

Transmission function

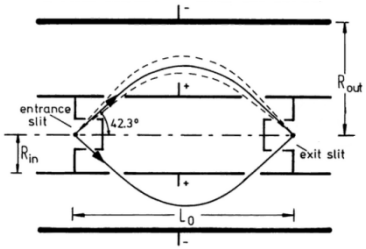
- efficiency of electron transmission
- depends of E_k and analyzer settings



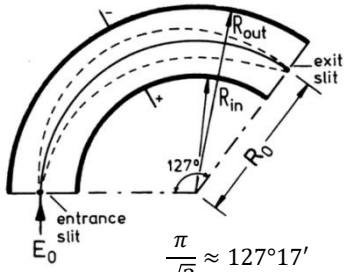
Parallel-plate analyzer



Cylindrical mirror analyzer

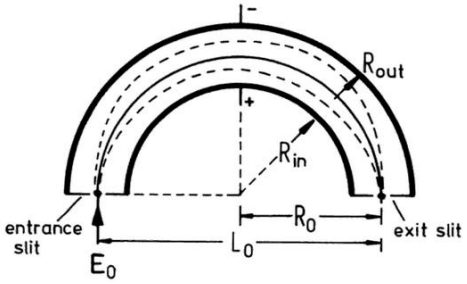


Radial (127°) cylindrical analyzer

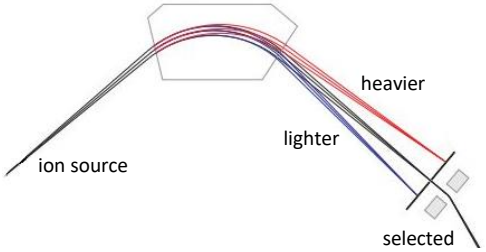


$$\frac{\pi}{\sqrt{2}} \approx 127°17'$$

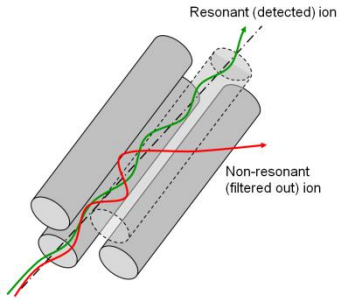
Hemispherical analyzer



Magnet sector analyzer



Quadrupole

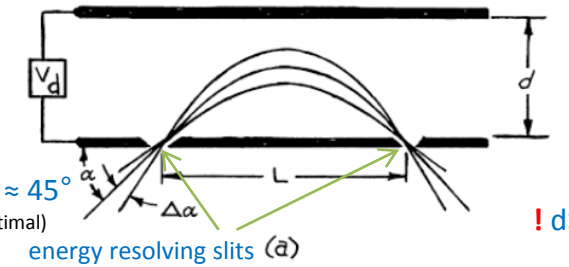


Special: **Energy-dispersive analyzer**
– broadband analyzer + position-sensitive detector
Output electron beam carries complete information

Analyzers

Parallel-plate Analyzer

(also called Plane Mirror Analyzer, PMA)



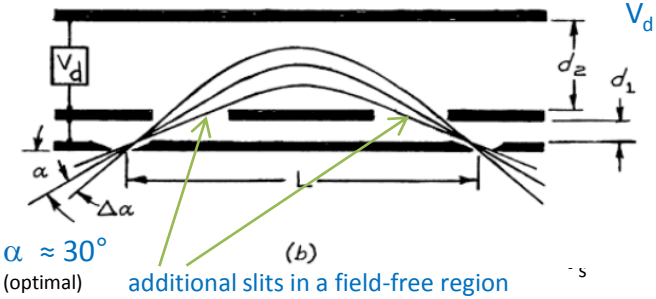
$V_d = V\ 2d/L$

($V=E_k/q$)

α ≈ 45°
(optimal)

energy resolving slits (a)

! d>L/2 to prevent striking the back plate



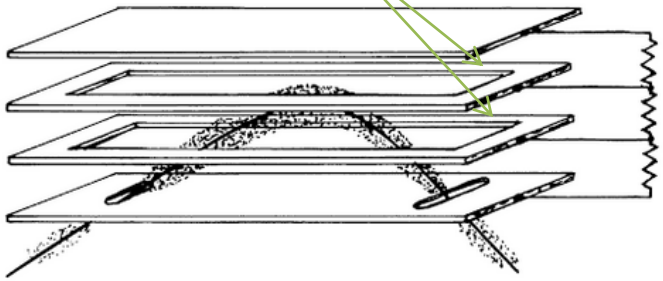
$V_d = V\ 2.6\ d_2/L$

α ≈ 30°
(optimal)

(b)

additional slits in a field-free region

guard electrodes – eliminate distortion of the field caused by fringing



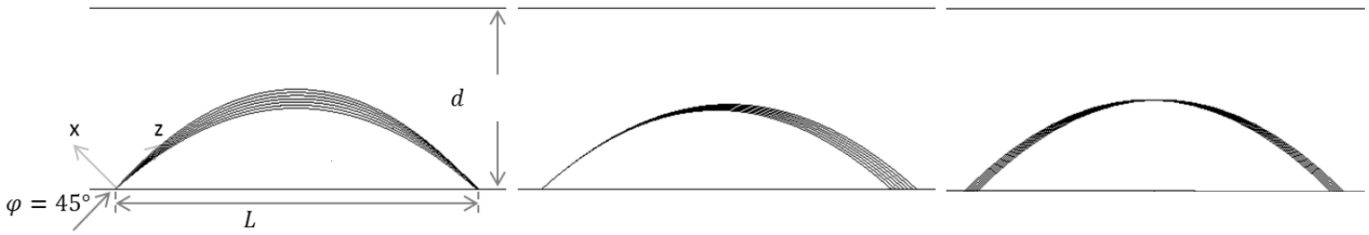
+ simplest electron analyzer
- relatively low transmission
- field distortion near slits => aberrations (can be suppressed by mesh)
- field distortions near edges (can be eliminated by guard electrodes)
- strong field needed (=> shielding necessary)

Energy resolution
(2-plate arrangement)

$$\frac{\Delta E}{E} = \frac{w}{L} + \alpha_{in}^2 + \frac{1}{2}\Delta\beta_{in}^2$$

$\Delta\alpha_{in}$, $\Delta\beta_{in}$ ... input angular divergences

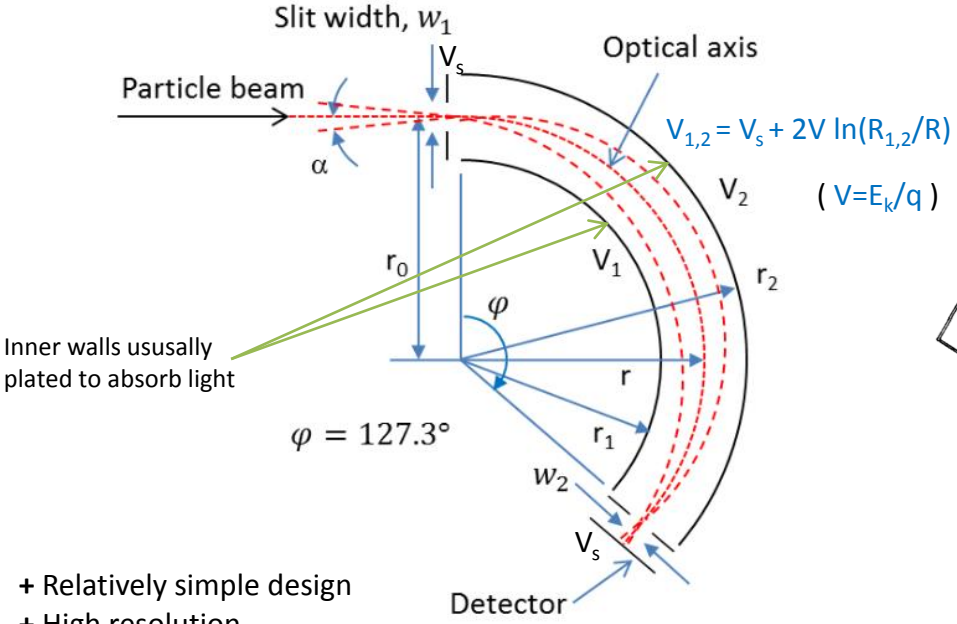
Particle trajectories through a 45° parallel-plate mirror analyzer with angular, energy, and positional variation



Analyzers

Radial (127°) Cylindrical Analyzer

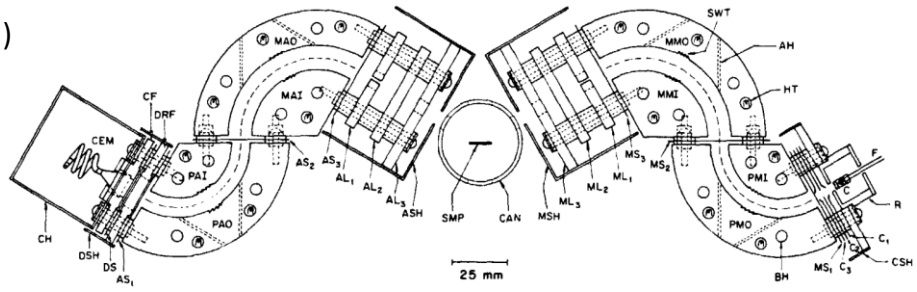
(also called Cylindrical Deflector Analyzer, CDA)



$V_{1,2} = V_s + 2V \ln(R_{1,2}/R)$

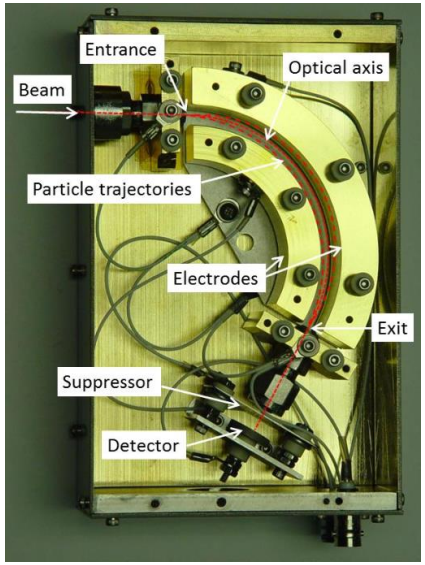
($V=E_k/q$)

Double-pass HREELS based on 127° cylindrical deflectors

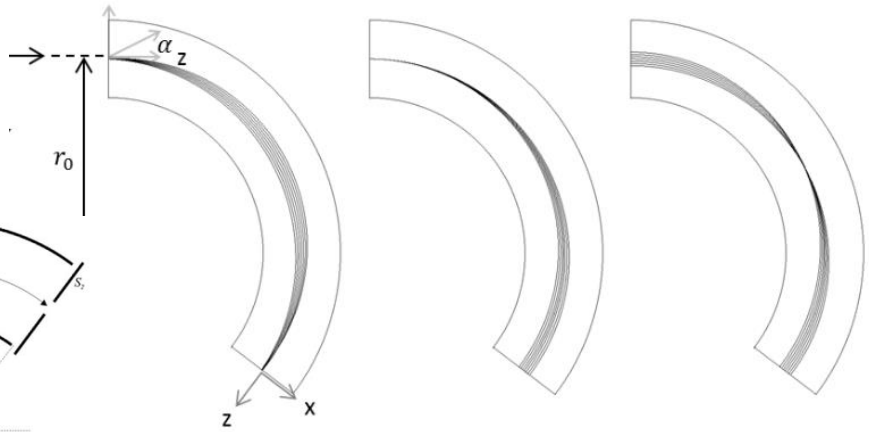


\+ Relatively simple design
\+ High resolution
\- Low transmission
\- Only radial component of velocity affected

Plasma Controls™ radial cylindrical analyzer



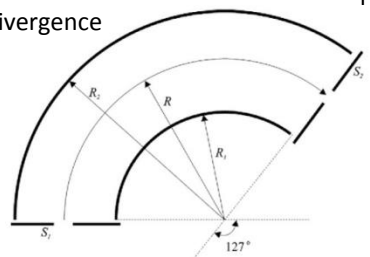
Particle trajectories through a radial cylindrical analyzer with angular, energy, and positional variation



Energy resolution

$$\frac{\Delta E}{E} = 2\frac{w}{R} + \frac{4}{3}\Delta\alpha_{in}^2$$

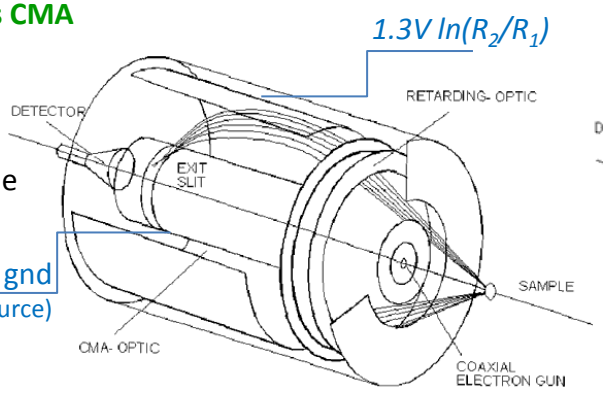
$\Delta\alpha_{in}$ ... input angular divergence



Electron analyzers

Cylindrical Mirror Analyzer (CMA)

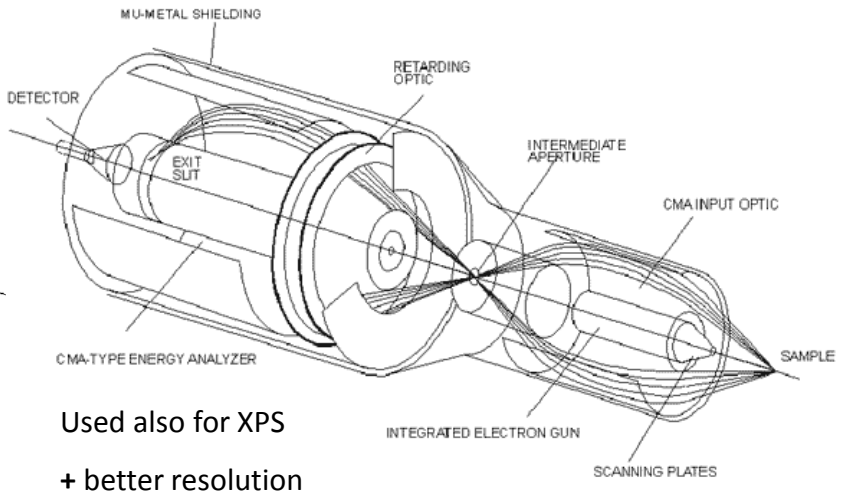
Single pass CMA



Used for AES, ELS, UPS

+ axial symmetry with room for integrated el. source
+ high sensitivity
- relatively low resolution

Double pass CMA



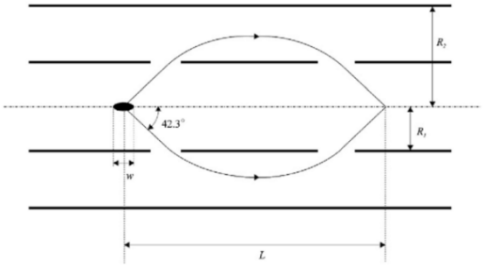
Used also for XPS

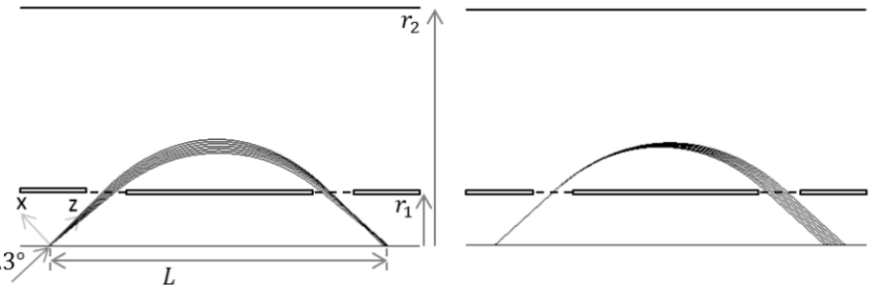
+ better resolution
- less sensitivity

Energy resolution

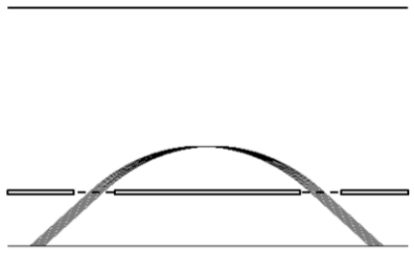
$$\frac{\Delta E}{E} \approx 1.09 \frac{w}{L}$$

L ... source-detector distance
w ... axial extent of the source





Particle trajectories through a cylindrical mirror analyzer with angular, energy, and positional variation



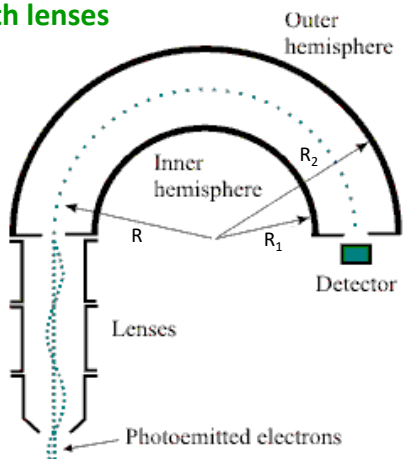
Staib™ single pass CMA ESA 100

Electron analyzers

Hemispherical (Deflection) Analyzer (HDA)

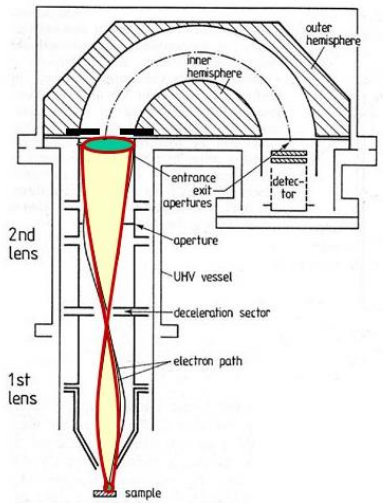
(also called Spherical Deflector Analyzer, SDA)

Hemispherical electron analyzer with lenses

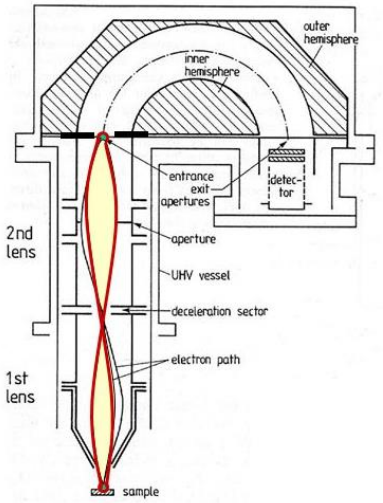


$V_{1,2} = V\,(2\,R/R_{1,2} - 1)$

Resolution—Intensity tradeoff



Small E_{pass} ←→ Large E_{retard}
High resolution
Low throughput (low count rates)



Large E_{pass} ←→ Small E_{retard}
Low resolution
High throughput (high count rates)

Energy resolution of the analyzer

Factors:

- energy of photoelectrons
- pass energy
- analyzer radius (R)
- slit width (w)
- transfer optics quality ($\Delta\alpha$)

$$\frac{\Delta E}{E} = \frac{w_{in} + w_{out}}{2R} + \frac{1}{4}\Delta\alpha_{in}^{\,2}$$

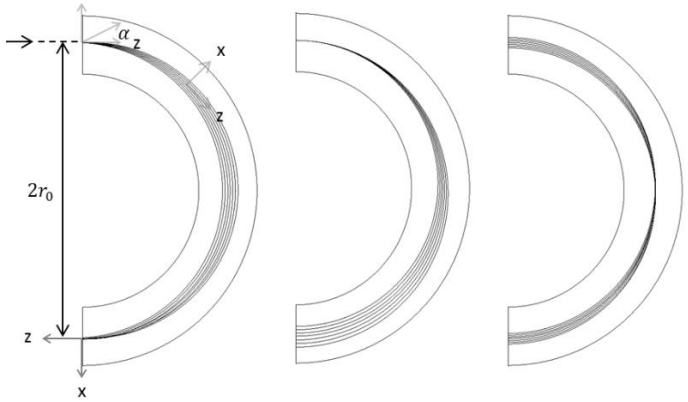
Pass energy

- original E_k is lowered to get higher energy resolution
- the retarding lens system also focuses electrons

Operation modes

- Constant Analyzer Transmission (CAT)
  (or Constant Analyzer Pass Energy, CAE/CPE)
  - constant pass energy => fixed resolution
  - discriminates lower KE electrons (most are backscattered)
- Constant Retarding Ratio (CRR) – not used for XPS

Particle trajectories through a hemispherical analyzer with angular, energy, and positional variation



Omicron™ Hemispherical Energy Analyser EA 125

Detectors

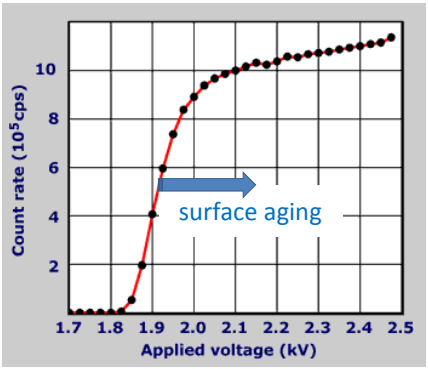
Detection of charged particles

Detectors of charged particles
→ conversion of electron/ion flux to current

- Faraday cup
- Electron multiplier: γ_e >>1 (typ. 3-10)
  - dynode(s)
  - channeltron
  - microchannel plate (MCP)

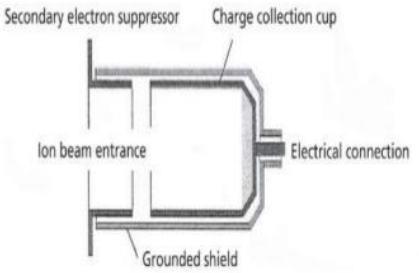
Ion detection: requires conversion electrode (-> e^-)

- CCD (charge coupled devices) or MCP+CCD
  (position sensitive analyzer)

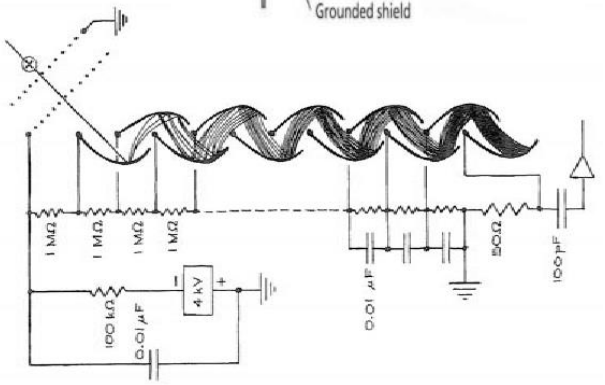


typical parameters:
voltage ≈1-3 kV
amplification 10^6-10^9

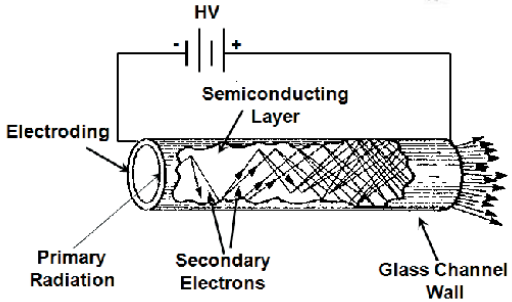
Faraday cup



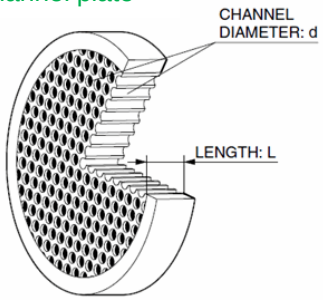
dynode

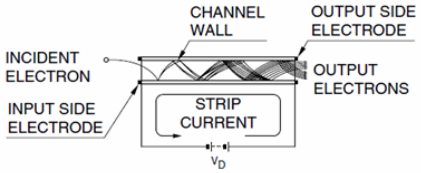


channeltron

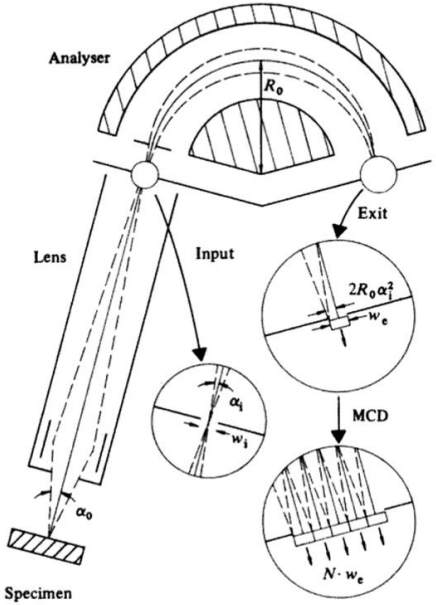


microchannel plate





Multichannel detection



Specs™ extended-range channel electron multiplier (CEM)

Environment for electron specroscopy

What is needed for a spectrometer to work

General requirements

- low pressure (vacuum)
- no (or low) electromagnetic interference (EMI)

Why vacuum?

1) Avoid scattering of electrons and/or photons
2) Ensure surface cleanliness

Typical pressure 10^{-6}-10^{-8} Pa (ultra-high vacuum)

Not available until 1960s

Mean free path in gas phase
(ideal gas, hard spheres)

$$\lambda = \frac{k_B T}{\sqrt{2}\pi d^2 P}$$

σ ... (effective) cross section

Rule of thumb: MFP at 1 Pa air ~6 mm

Electrons: *more complicated and E_k dependent, but similar magnitude ($\sigma \approx 10^{-19}$-10^{-20} m^2)*

Reduction of elmg. interference (noise)

- magnetic shielding (mu-metal)
- electric shielding (metal plate, mesh, ...)
- active field cancellation (on the scale of instrument or room)
- elimination of sources of elmg. radiation
- proper grounding

More critical for microscopic methods

Samples for electron spectroscopy

Types of samples and their treatment

Solids

Most common, best vacuum compatibility

Liquids **Gases**

differential pumping required

Issues to be aware of

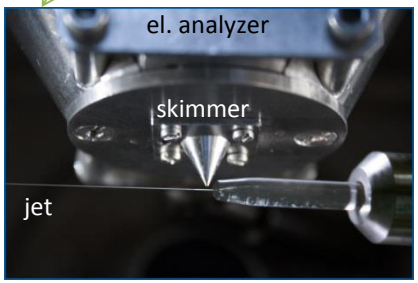
- Electrical conduction should be guaranteed (especially for AES) – problem for powders and isolators
- Sources of degradation or alteration
  - surface-environment processes (adsorption, desorption, vaporization, corrosion, …)
  - surface-bulk processes (segregation, relaxation, restructuring, …)

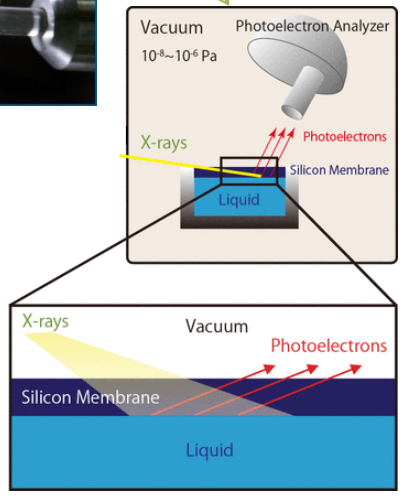
Solid sample preparation methods (*vacuum, in situ*)

- ion sputtering
- desorption
- surface reaction
- annealing
- material deposition
- cleavage

- Precipitate on a solid
- Beam-jet crossing
- Separating membrane

- atoms, molecules, clusters, ions, …
- can be mixed with calibration gas (typ. Ar, He)



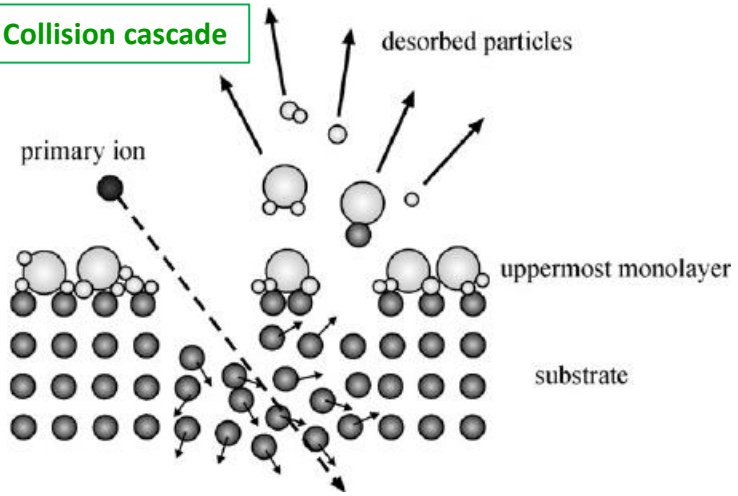


Sample treatment for electron spectroscopy

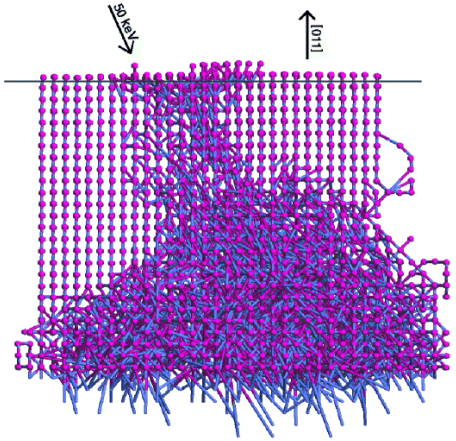
Ion sputtering

Ion sputtering
- most versatile vacuum-compatible method:
  many types of solids, highly tunable (E, Z, Θ, t, F, T)

Collision cascade

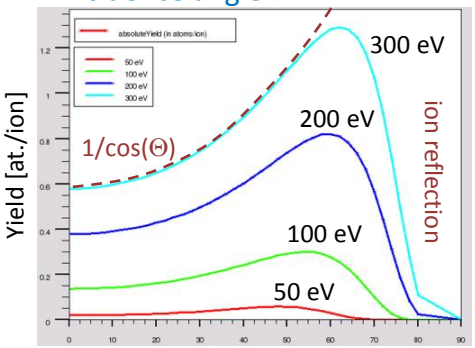


Higher energy, lighter ions: bulk more affected

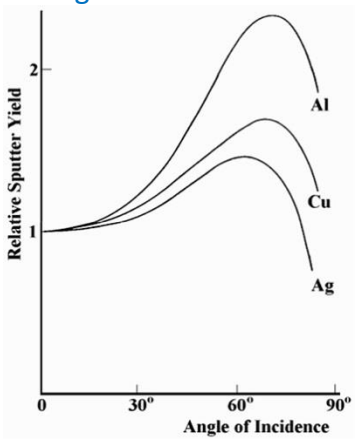


Ion sputtering yield
Depends on:
- target material
- ion energy
- ion mass
- incidence angle
- nature of the primary ion (inert/reactive)

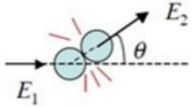
incidence angle



target material



Elastic energy transfer



$$\frac{E_2}{E_1} \propto \frac{4M_1M_2}{(M_1+M_2)^2} cos^2\theta$$

(Inelastic collision → second. electrons)

Sputtering yield

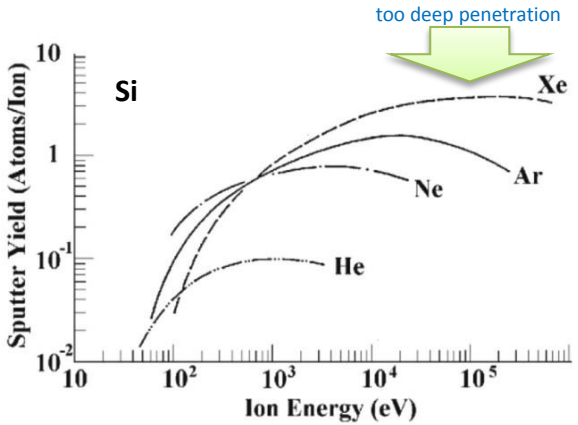
$$\gamma = \alpha \frac{M_i M_t}{(Mi+Mt)^2} \frac{E_p}{E_{bond}}$$

! $E_p > E_{threshold}$ (≈ heat of vaporization)

E_s≈3-10 eV (=> energy efficiency ~0.01-0.1)

For ~100-1000 eV typical yield ~0.05-1

ion mass and energy



Sample treatment for electron spectroscopy

Ion sputtering

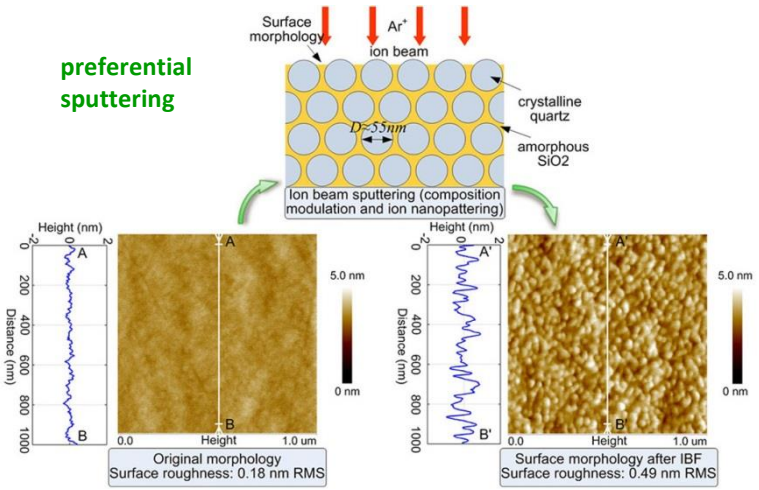
Potential pitfalls of ion sputtering:

- preferential sputtering
- structurally-dependent sputtering (channeling)
- surface roughening
- ion implantation
- ion-induced defects (surface, bulk)
- ion-induced intermixing (multi-comp. samples)
- ion-induced chemistry

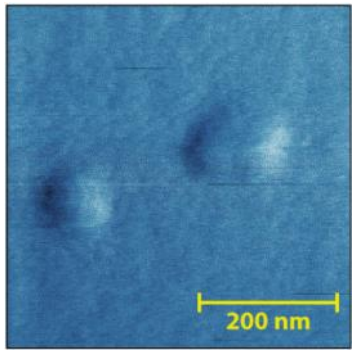
⇒ for harmless surface cleaning:

- optimal incidence angle (~60-70°)
- optimal surface temperature
- heavier ions (less penetration)
- moderate ion flux
- cyclic annealing (surface „healing“)

preferential sputtering

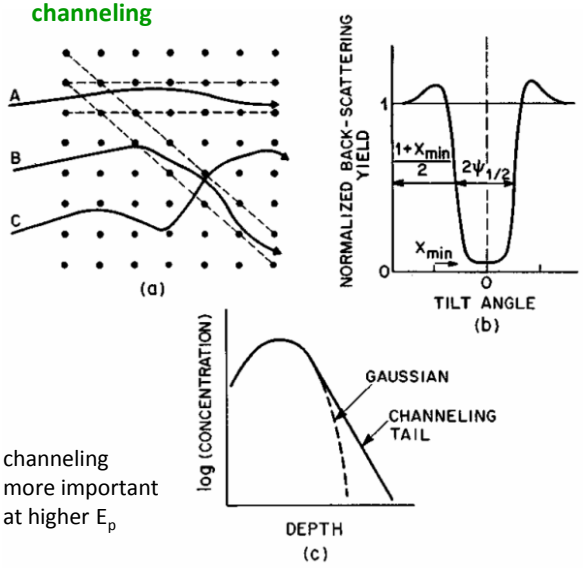


ion implantation



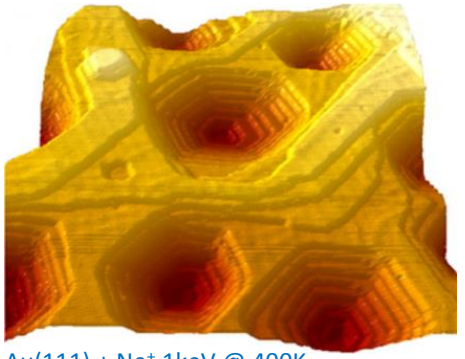
takes part also on the atomic level

channeling



channeling more important at higher E_p

surface roughening



Au(111) + Ne^+ 1keV @ 400K

Impact of irradiation on sample

Vlivy dopadajícího záření na složení a strukturu povrchu a možnosti jejich eliminace

Processes

Charging

-work function change
-coulombic repulsion/attraction
-differential charging

can be of **local** character

Electron beam damage

-e-beam heating (generation of phonons)
-electron stimulated reaction
-electron stimulated desorption
-electron stimulated adsorption
-sputtering

Photon beam (radiation) damage

-radiative heating
-photochemistry
-ionization

Consequences

-energy shifts in spectra
-intensity changes in spectra
-structural changes
-spectra instability
-change of NP disperision (precipitation, coalescence, disintegration, ...)

mostly temporary

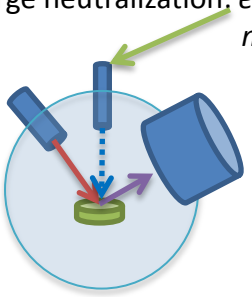
-melting
-structural changes (lattice, grains, defects, amorphization, crystalization, segregation, ...)
-phase transitions or separations
-composition changes
-changes of chemical structure
-surface reactions
-surface desorption
-surface contamination

mostly permanent

Energy and time dependent. Generally more damaging:
Mid E (~1 keV) or higher E (~100 keV) for sputtering
Lower E (~10-100 eV) and near absorption edge

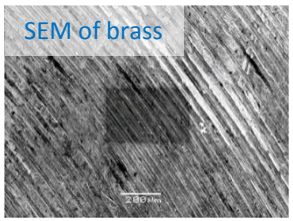
Elimination methods

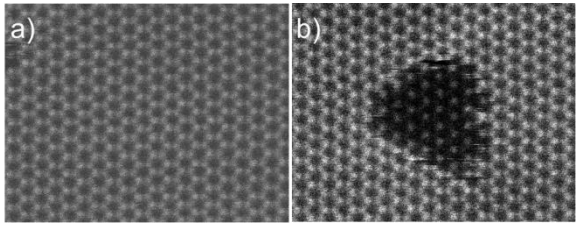
-reference line to correct E_B
-charge neutralization: *electron flood gun (1-20 eV)*
magnetic lens system



-short exposure
-monochromatization
-change of beam position
-clean environment (UHV)

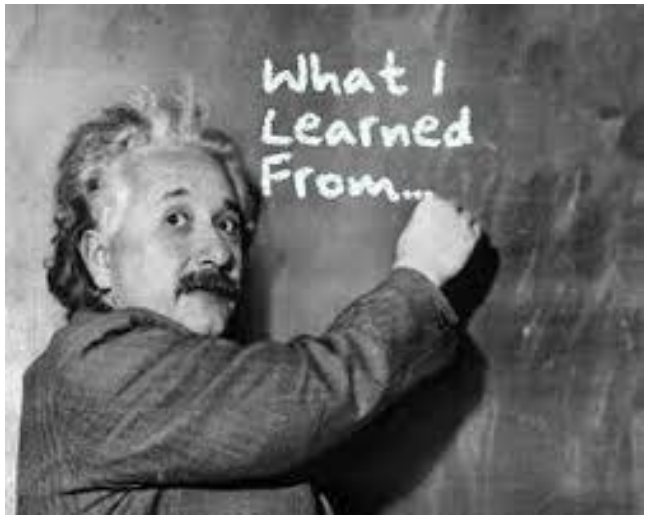
Example of e-beam damage of graphene





Experimental systems for electron spectroscopy

Take-home Messages



Hold your gun

Quality primary source essential

The wide, the short, … the ugly

Electron analyzer resolution $\frac{\Delta E}{E} \propto \frac{aperture\ size}{analyzer\ size}$

There's no gain without pain

Resolution × Sensitivity

You can do something only in the middle of nothing

Vacuum needed

Gentleman's rule: Observe, touch, but don't hurt

Minimize beam damage

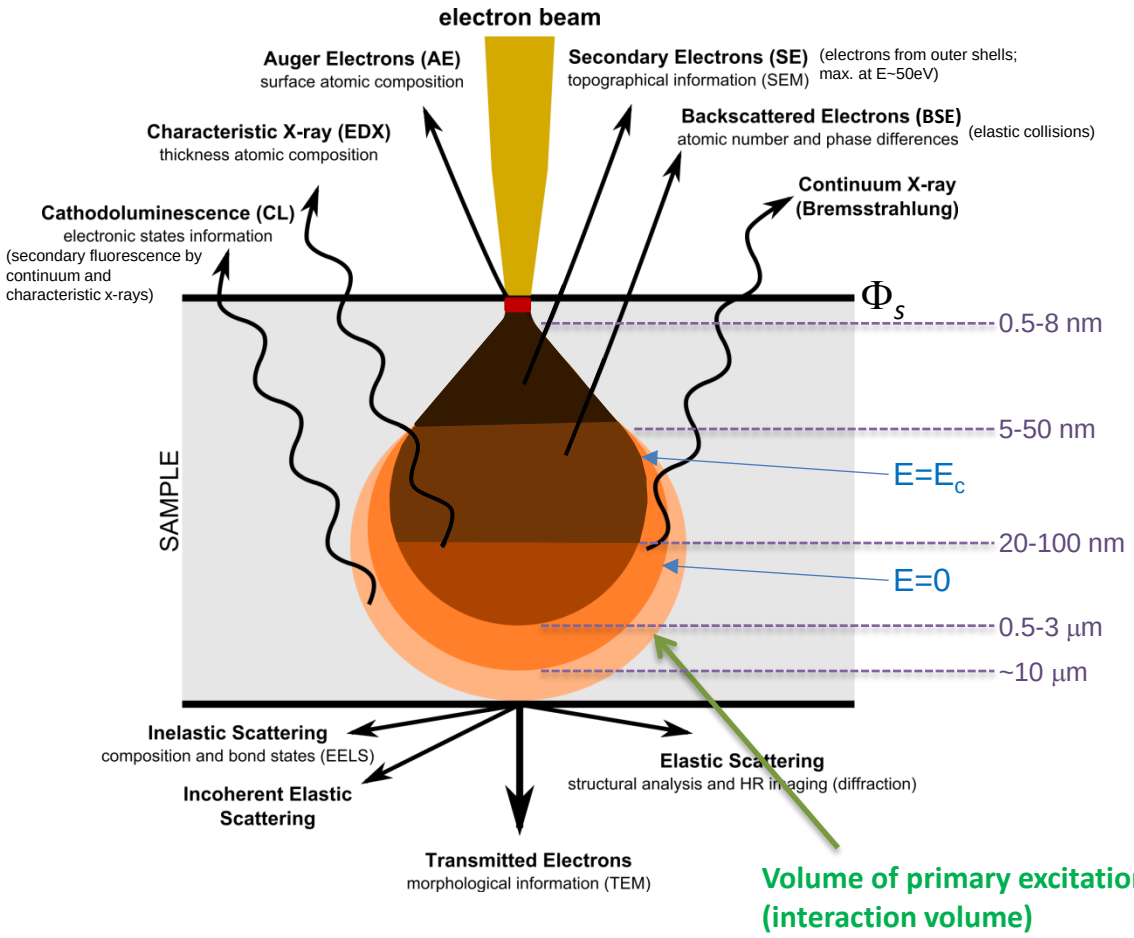
Bumpy is fun, but flat makes it done

Surface sensitive methods: Planar and clean samples preferred

Interaction of electrons with matter

Elementary processes

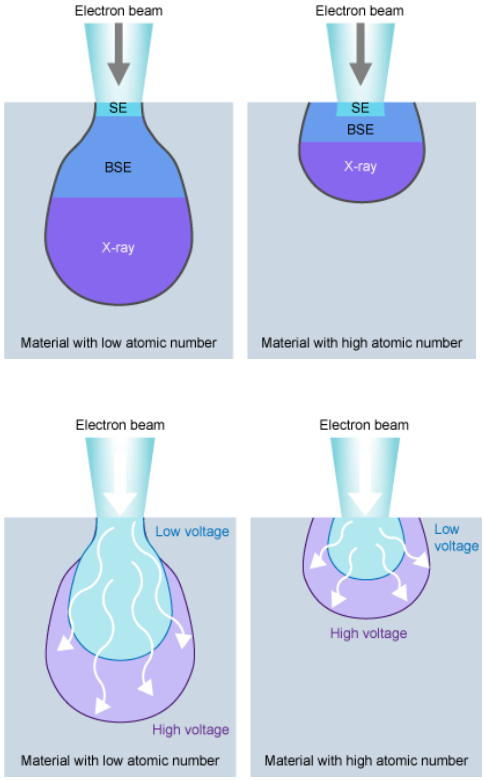
Primary processes



Work function Φ_s

- surface dipole layer due to spillout of electrons to vacuum
  => depletion of electrons below surface

Influence of electron energy and atomic number



Diameter of the interaction **larger** than the electron spot
- important in microscopy (=> resolution)

Electron transport in solids

Elementary processes

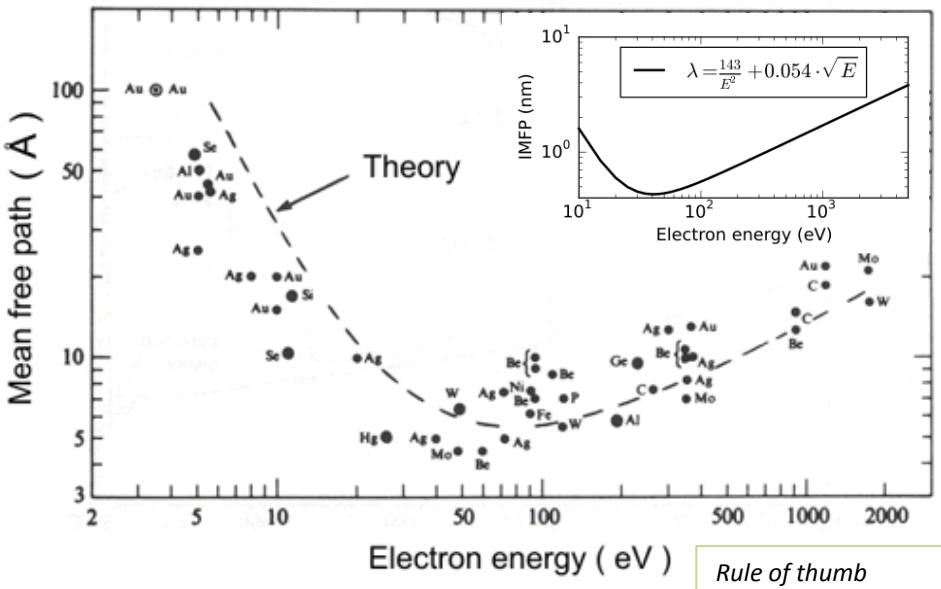
Electron scattering

Elastic – the electron trajectory within the specimen changes, but its kinetic energy and velocity remains essentially constant.
The result is generation of backscattered electrons (BSE).

Inelastic – the incident electron trajectory is only slightly perturbed, but energy is lost through the transfer of energy to the specimen. The result is the generation of:
•phonon excitation (heating)
•cathodoluminescence (visible light fluorescence)
•continuum radiation (bremsstrahlung)
•characteristic x-ray radiation
•plasmon production (secondary electrons)
•Auger electrons (ejection of outer shell electrons)

Multiple scattering – elastic, inelastic

Inelastic mean free path of electron in elements "Universal IMFP curve"



Quasi-universal nature of the curve for different materials is due to the fact that the major interaction mechanism between the electrons and the solid is the excitation of plasmon waves whose energy is determined by the electron density in the solid

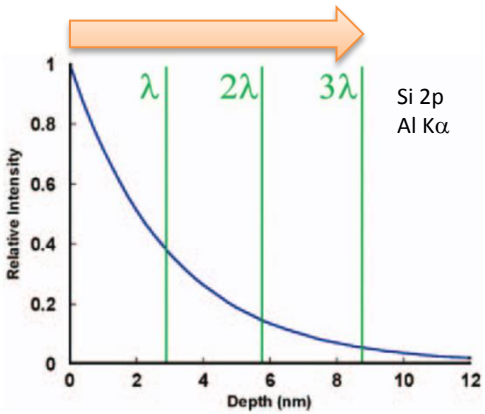
Rule of thumb
at hν =1000 eV
λ = 5-10 Å … metals
15-40 Å … oxides
15-30 Å … polymers

Photoelectron probe (sampling) depth

Contribution of atom id depth d:

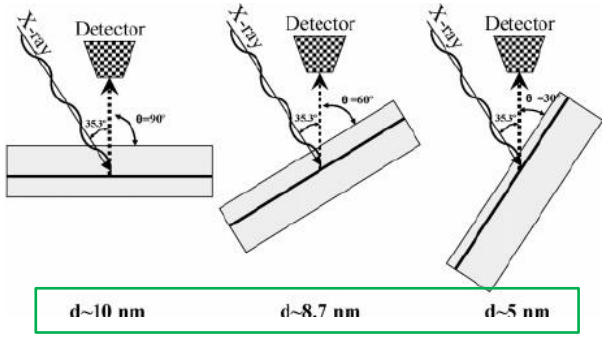
$$I \propto I_o e^{-d/\lambda \cos\theta}$$

=> 95% of the signal comes from atoms within **3λ** depth



In some cases the information depth is determined by **probe penetration depth** (INS, grazing incidence angles, …)

Angular dependence

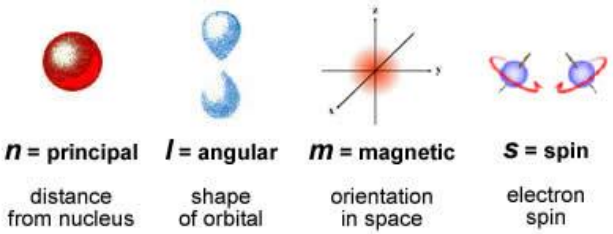


Atomic structure

Quantum numbers

Quantum numbers

Symbol	Name	Values	Defines	Notes
n	principal	Positive integers (1, 2, 3 ...)	Electron shell (1=K, 2=L, 3=M, etc.)	Principle binding energy
l	azimuthal	Integers from 0 to $(n-1)$	Electron cloud shape (0=sphere, 1=dumbbell, etc.)	Orbital angular momentum. Chemists follow optical spectroscopy conventions using letters rather than numbers: **s**harp ($l=0$), **p**rinciple ($l=1$), **d**iffuse ($l=2$), **f**undamental ($l=3$)
m	magnetic	$-l$ to $+l$	Electron orientation in magnetic field	Not significant in the absence of an external magnetic field
s	spin	±½	Electron spin direction	Clockwise or counterclockwise (↑ or ↓)
$\bar{j}$	inner precession (spin-orbit interaction)	$l \pm ½$	Total angular momentum vector	Determines permissible transitions between electron shells. For s orbitals ($l=0$), $\bar{j}$ can only be +½ (vector sum must be positive)



Subshell	# of orbitals
s	1
p	3
d	5
f	7

Smart People Don't Fail

max. $2(2l+1)$ electrons per subshell
max. $2n^2$ electrons per shell

Arrangement of electrons in atoms

Pauli exclusion principle

"No two electrons in an atom (or a molecule) can have the same set of quantum numbers simultaneously." (i.e., electrons are fermions)

	K	L_I	L_{II}	L_{III}	M_I	M_{II}	M_{III}	M_{IV}	M_V	N_I	N_{II}	N_{III}	N_{IV}	N_V	N_{VI}	N_{VII}
n	1	2	2	2	3	3	3	3	3	4	4	4	4	4	4	4
l	0	0	1	1	0	1	1	2	2	0	1	1	2	2	3	3
s	+½	+½	-½	+½	+½	-½	+½	-½	+½	+½	-½	+½	-½	+½	-½	+½
$\bar{j}$	½	½	½	1½	½	½	1½	1½	2½	½	½	1½	1½	2½	2½	3½

1s singlet — *2p* doublet — *3p* doublet — *3d* doublet — *4p* doublet — *4d* doublet — *4f* doublet

Spin-orbit splitting (coupling)
- interaction between electron spin (intrinsic magnetic momentum) and its motion (magnetic field generated by orbit)
(Internal Zeeman effect)

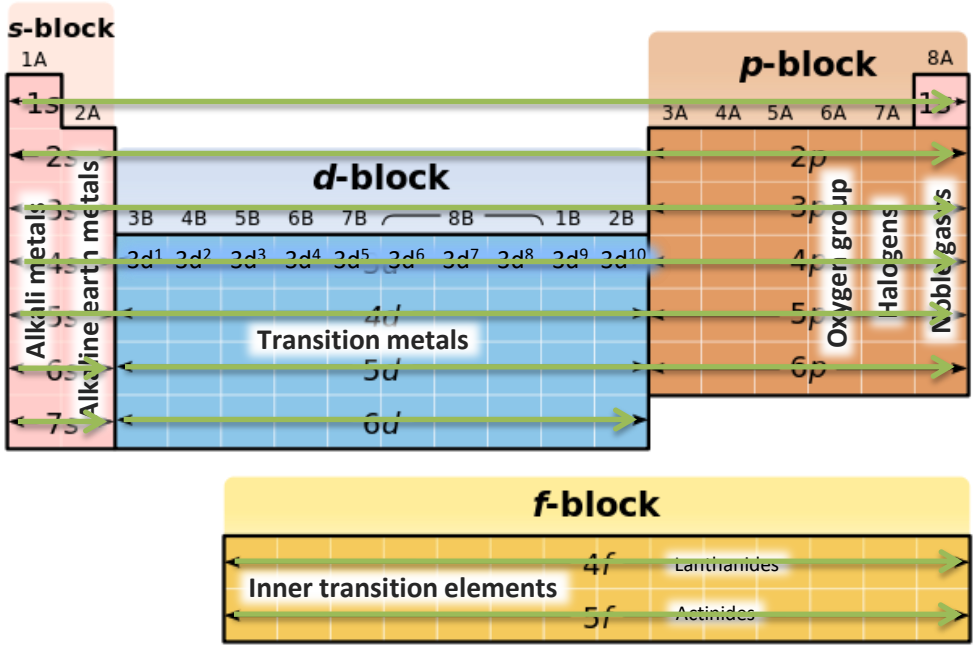
Transitions between electron shells

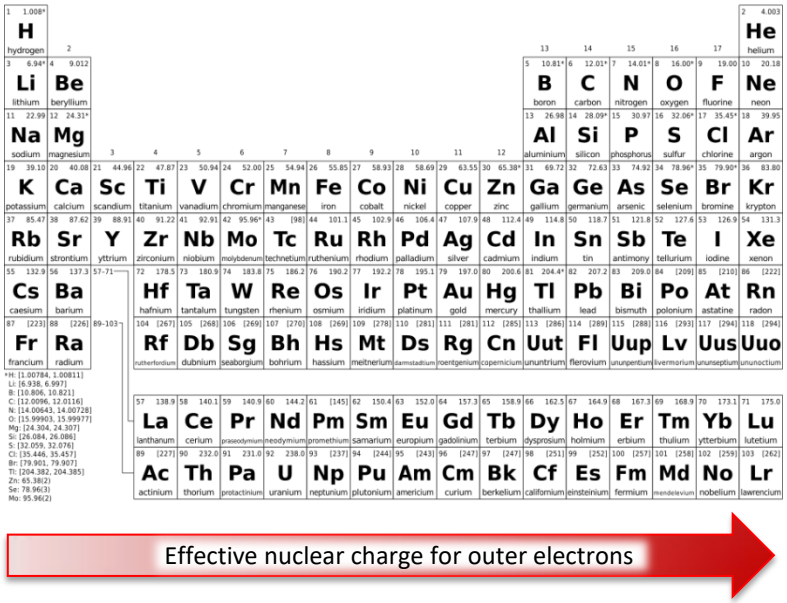
Quantum selection rules

1) The change in ***n*** must be ≥ 1 ($\Delta n \neq 0$)
2) The change in ***l*** can only be ±1
3) The change in ***j*** can only be ±1 or 0

Atomic structure

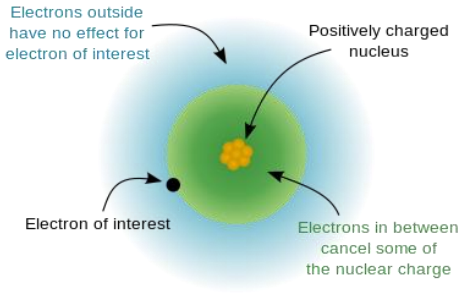
Orbitals and periodic table





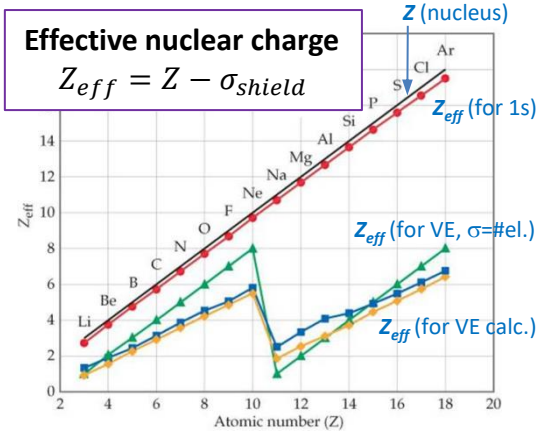
Occupation of subshells (by energy) – works for most elements
1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d

Electron shielding (screening)

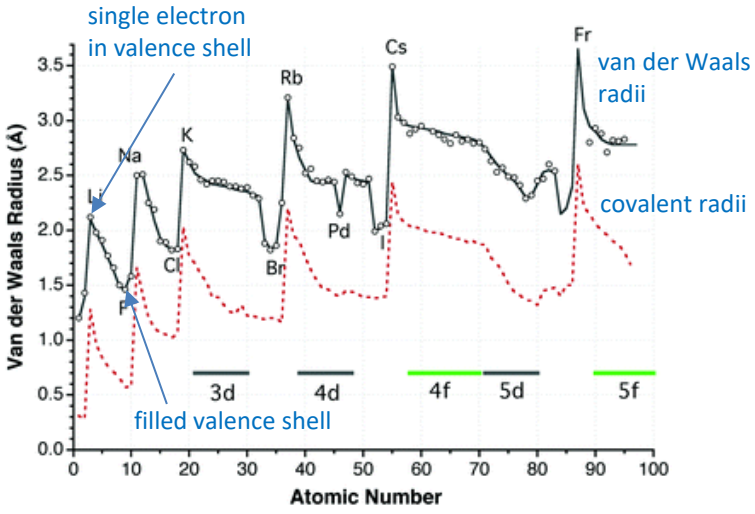


Effective nuclear charge

$$Z_{eff} = Z - \sigma_{shield}$$



Atomic radii trend

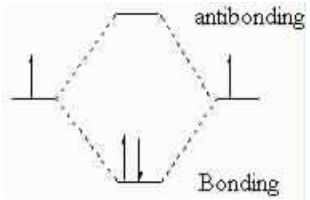


Atomic structure

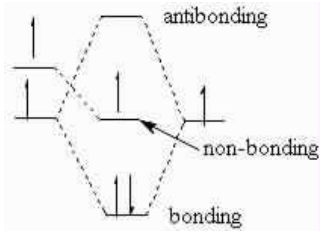
Band theory of solids

Origin of an electron band

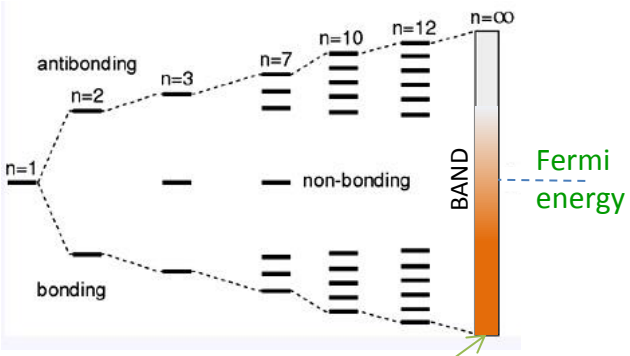
Homonuclear molecule
with 2 atomic orbitals



with 3 atomic orbitals



From single atom to solid



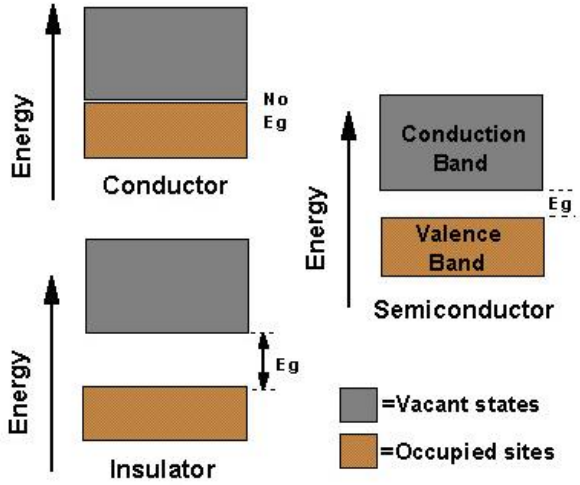
electron occupation at T>0K
(half-full band originating from single-electron orbitals)

Conductors, semi-conductors, insulators

Defined by relationship between

valence band - low energy electrons
&
conduction band - higher energy electrons

- insulator – large energy gap
- semi-conductor – small energy gap (~eV)
- conductor – VB&CB overlap (no energy gap)



Auger electron spectroscopy

History and fundamentals

Brief history

1925: Discovery of slow electron emission upon irradiation of solid matter by electron beam by *Pierre Auger* (independently also by *Lise Meitner* in 1923)
1930s-1950s: Auger transitions considered just a nuisance in standard spectroscopies
1953: First use for study of surface impurities (but still remained difficult mainly due to small peaks on large background)
1968: Measurement of differential energy distribution – demonstrated usefulness of AES (using LEED optics)
1969: Invention of CMA – great speed and sensitivity improvement
1969: Depth profiling using AES and ion sputtering
1980s: Implementation of Schottky field emitters as electron sources (spatial resolution ~20nm)
1990s: Use of hemispherical analyzers (along with CMA)

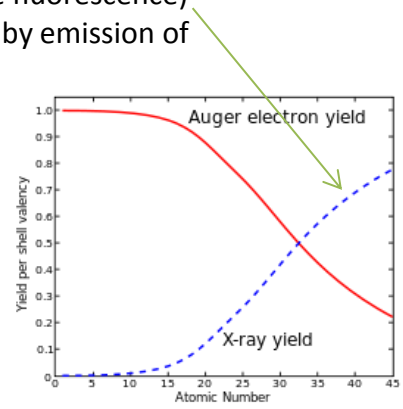
Auger phenomenon

- non-irradiative electron de-excitation process (competitive relaxation process to irradiative fluorescence)
- occurs by Coulombic interaction: energy loss by emission of one or more electrons (**Auger electron**)
- initial excitation of any type: electron (→ AES), photon, ion, proton, …

Solids vs. isolated atoms

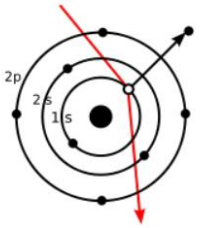
- diff. electronic structure (delocalized bands)
- primary beam alteration
- alteration of AEs (transport through solid)
- work function
- valence band

→ E_A diff. up to ~15-20 eV

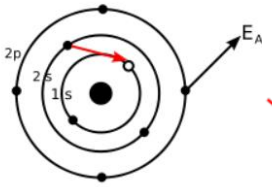


relative yields for K-shell

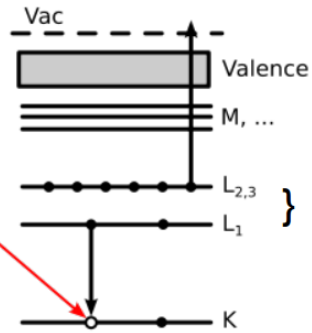
Scheme of Auger process



Electron collision



Auger electron emission

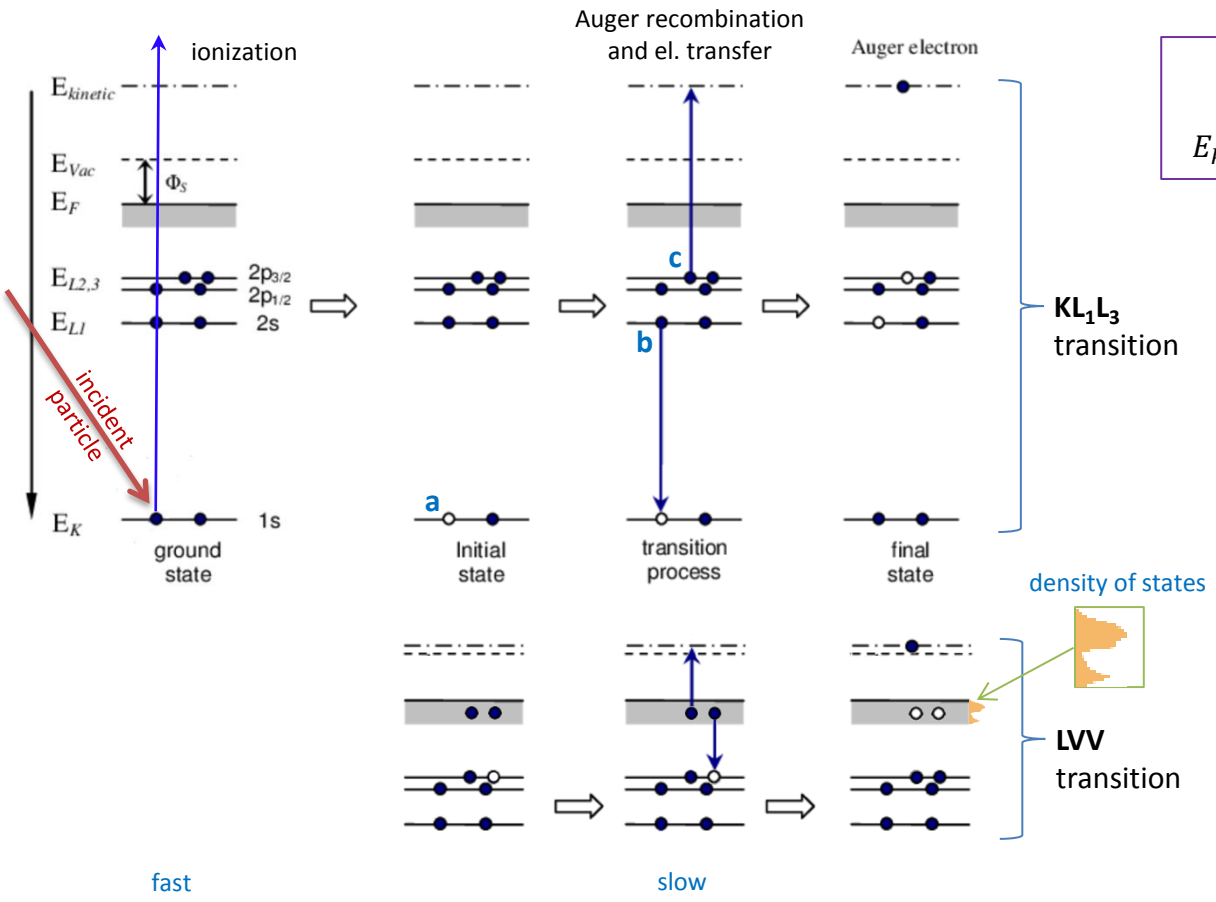


AEs are „slow“ ⇒ short mean free path ⇒ very **surface sensitive** technique

Provides information (chemical composition) from very thin layer (ca. 1 nm)

Auger electron spectroscopy

Auger process in solids



$$A(0) + h\nu \rightarrow A^{+}(a) + e^{-} \qquad A^{+}(a) \rightarrow A^{++}(b,c) + e_A^{-}$$

There is **no** real photon intermediating the transition (not an internal photoemission)

Conservation laws

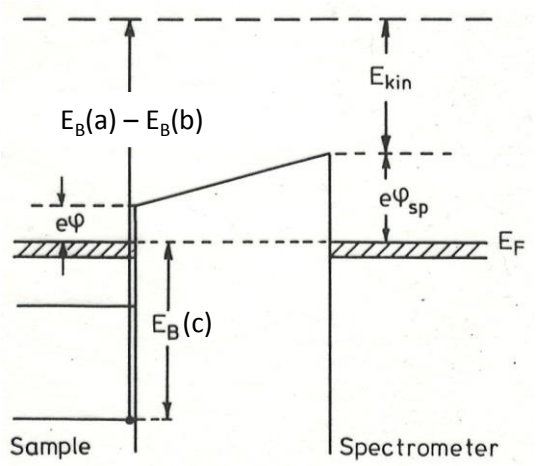
$$E_B(a) = \varepsilon_f(N-1) - \varepsilon_i(N)$$

$$E_{kin}(a,b,c) = E_B(a) - E_B(b) - E_B(c) - U_f(b,c)$$

Final state energy difference
change of potential due to

- hole-hole (*a*-*b*) and el.-el. interaction in the final state (h-h repulsion, el. screening, ...)
- relaxation energies

Spectrometer reference



$$E_{kin,sp}(a,b,c) = E_B(a) - E_B(b) - E_B(c) - U_f(b,c) - \Phi_{sp}$$

AE energy is **independent** of primary beam energy

Auger electron spectroscopy

Nomenclature

Naming of electronic levels in Auger transition

- conventionally X-ray type (**K, L, M, N, O**) + **V** (valence band) e.g.: **LMM**
- for energetically well distinguishable electronic levels: sub-indices e.g.: **$L_1M_3M_4$, M_5VV**
- group of Auger transitions: sub-indices omitted

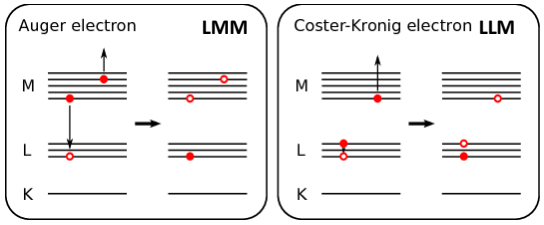
Nomenclature											
X-ray type (AES)		K	L_1	L_2	L_3	M_1	M_2	M_3	M_4	M_5	N_1	…
Spectroscopy (XPS)		1s	2s	$2p_{1/2}$	$2p_{3/2}$	3s	$3p_{1/2}$	$3p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$	4s	…
Quantum numbers	n	1	2	2	2	3	3	3	3	3	4	…
	l	0	0	1	1	0	1	1	2	2	0	…
	s	+½	+½	-½	+½	+½	-½	+½	-½	+½	+½	…
	j	1/2	1/2	1/2	3/2	1/2	1/2	3/2	3/2	5/2	1/2	…

Coster–Kronig transition

- special case of Auger transition: vacancy is filled by an electron from a higher subshell of the same shell

$$X_pX_qY_r$$

- fast => wider peak (Uncertainity principle: $\delta E \delta t \approx \hbar$)
- observed for some elements only



Super Coster-Kronig: $X_pX_qX_r$

- very fast => usually dominant transition

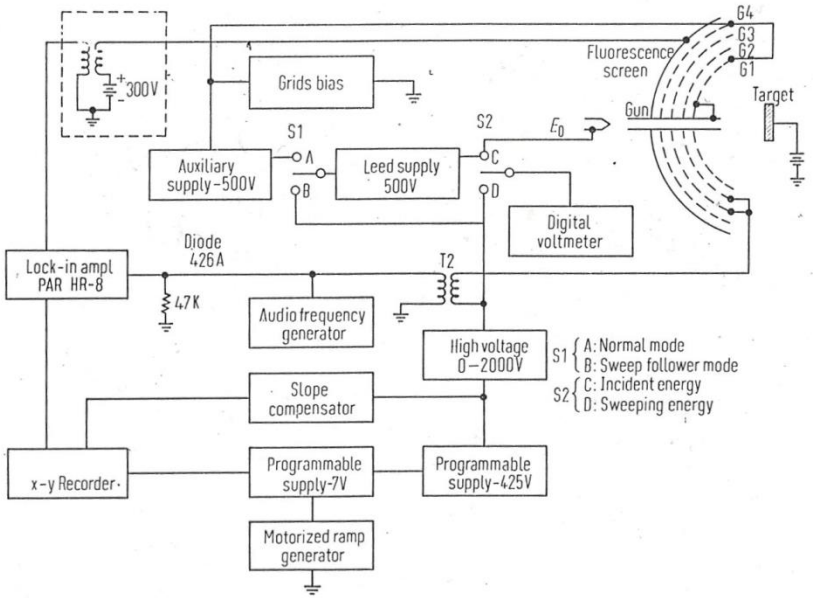
Most common excitations

initial level	*element*
K	3 (Li) – 13 (Al)
L	11 (Na) – 35 (Br)
M	19 (K) – 70 (Yb)
N	39 (V) – 94 (Pr)

Auger electron spectroscopy

Instrumentation

RFA (LEED) setup

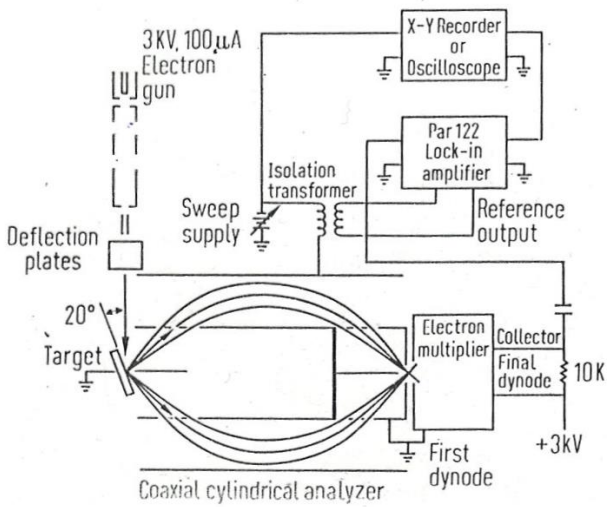


LEED-AES device by Chang

The sweep follower mode eliminates all energy loss peaks from the spectrum

spherical symmetry => integrated signal

CMA setup



AES using CMA and glancing angle primary electron gun (from Palmberg et al.)

cylidrical symmetry => azimutally integrated signal

Primary source

- most commonly electron beam: much higher intensity than std. X-ray
- X-rays: lower background, less beam damage

Electron beam angle

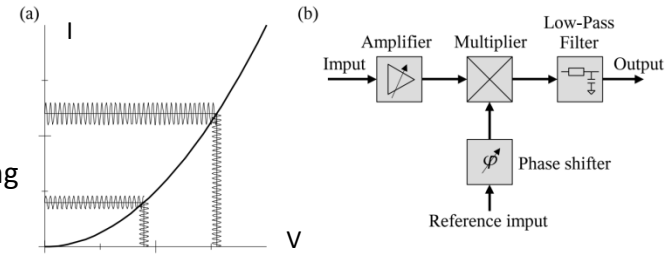
- optimally grazing incidence (~84°)
  - Auger electrons have low escape depth (at higher angle the intensity drops due to roughness)

Analyzer

- most commonly CMA
- RFA and HSA: angle integrated, no diffraction effects

Lock-in detection

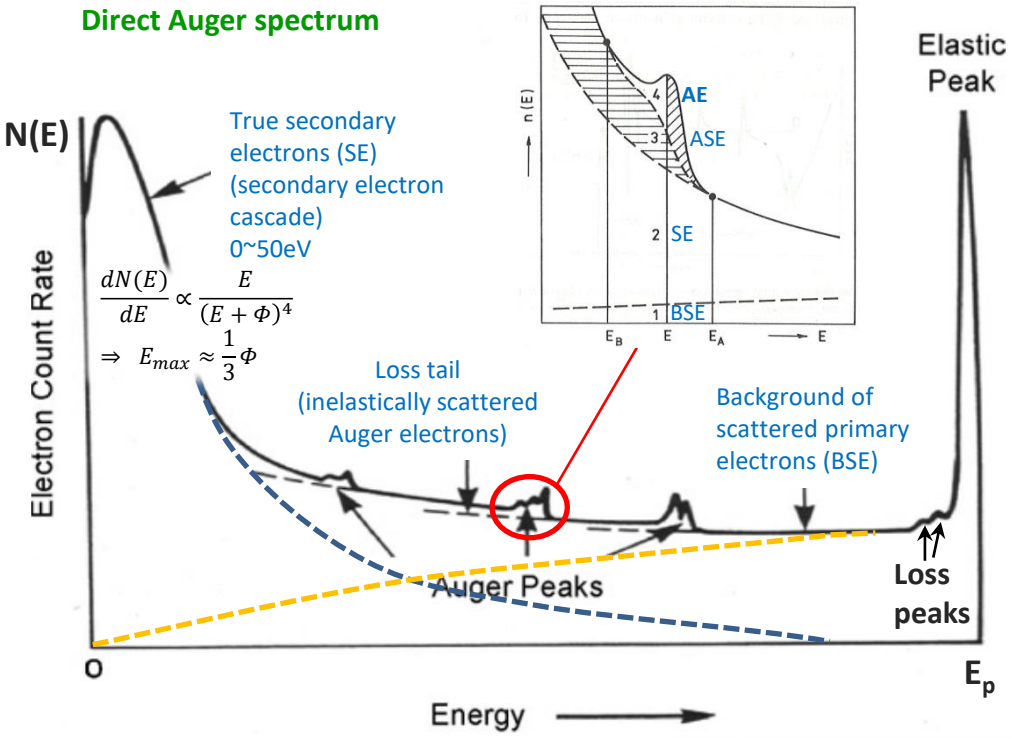
- produces differential spectra
  → suppression of the slowly-varying background



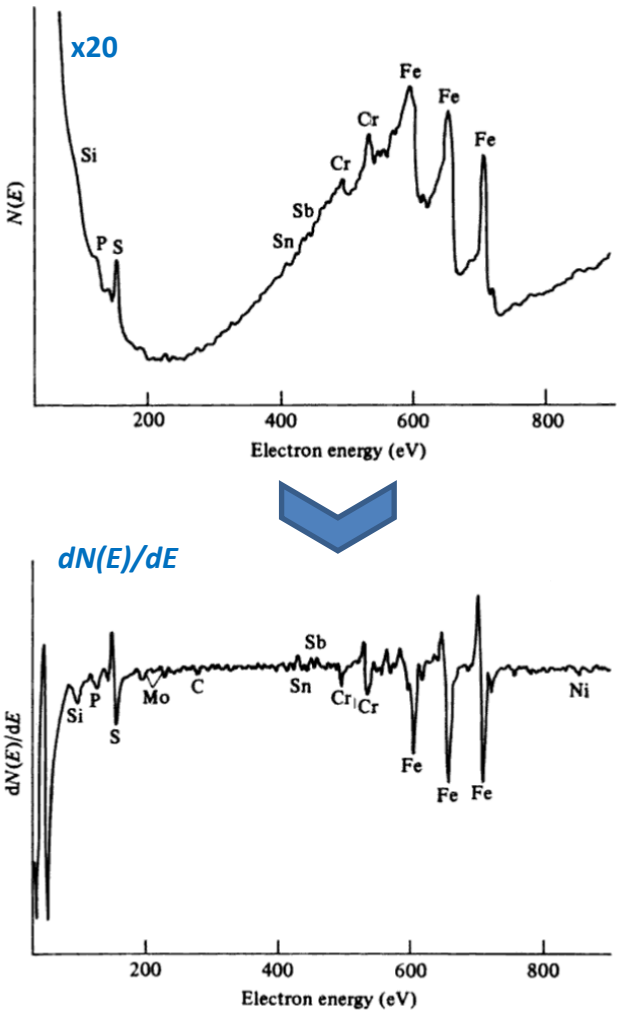
Auger electron spectroscopy

Auger electron spectrum of solids

Direct Auger spectrum



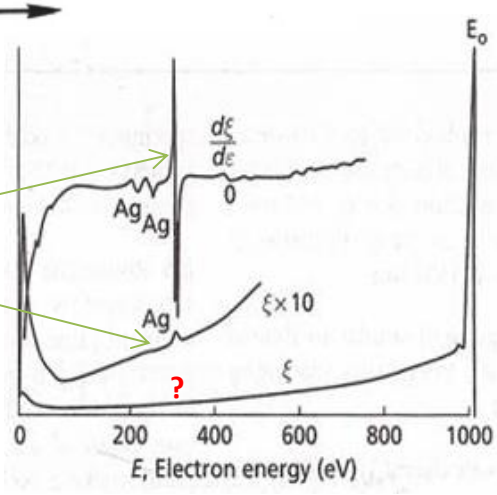
Differential Auger spectrum



Very high background & low efficiency of Auger process => **small peaks**

→ amplification

→ derivation

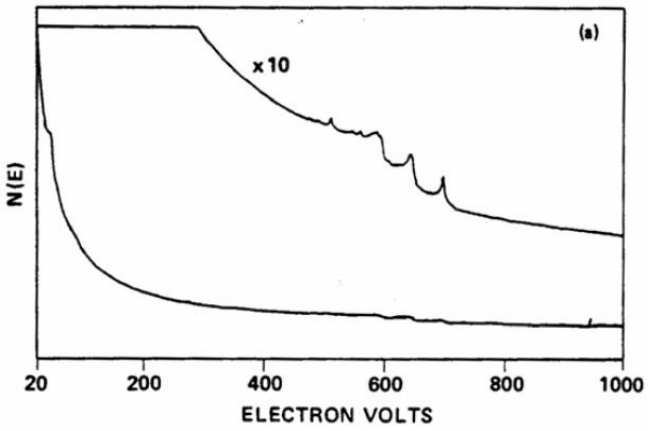


Auger electron spectroscopy

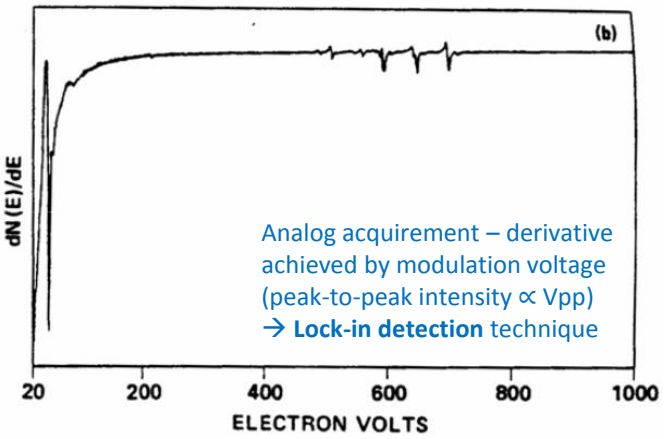
Auger electron spectrum

4 display modes of Auger spectra

N(E) vs E

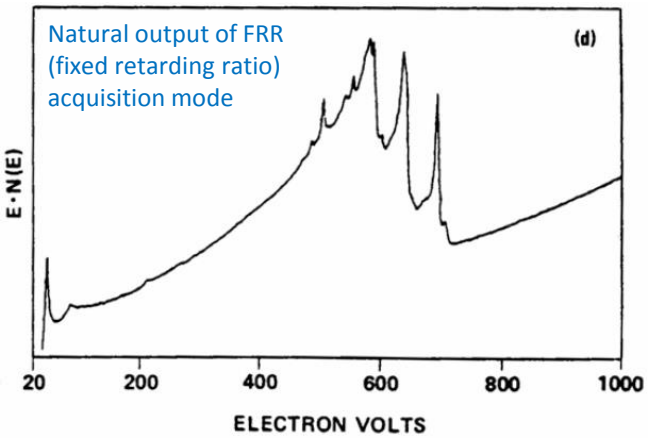


dN(E)/dE vs E

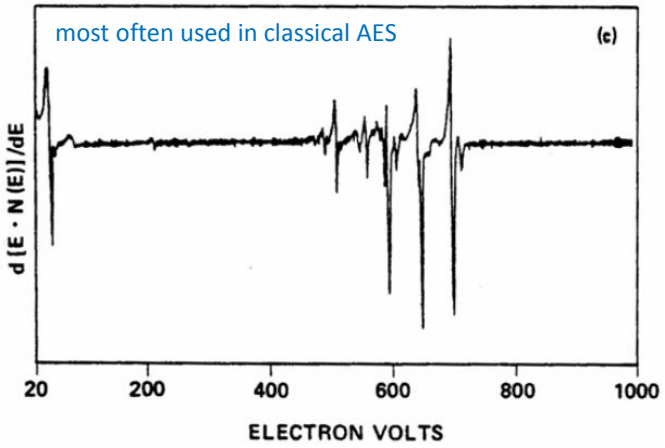


Analog acquirement – derivative achieved by modulation voltage (peak-to-peak intensity ∝ Vpp)
→ **Lock-in detection** technique

N(E)·E vs E



d[N(E)·E]/dE vs E



Current state-of-the-art technology: high sensitivity, digital acquirement
=> **direct** APS measured

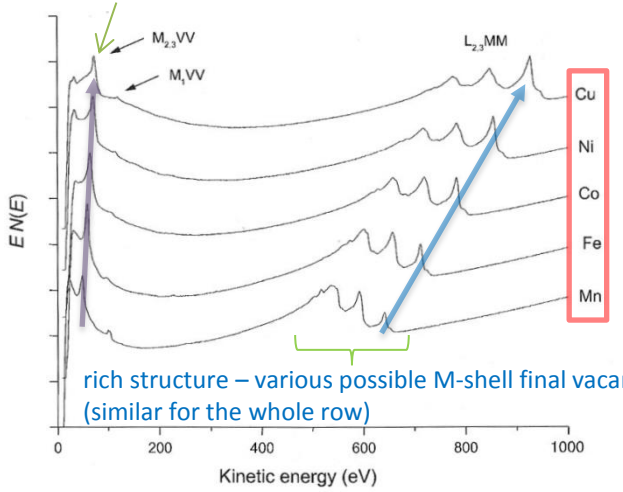
(can be derived later numerically)

Auger electron spectroscopy

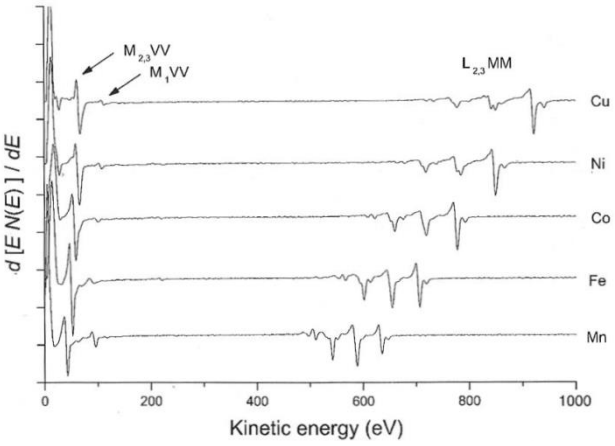
Qualitative analysis

1st row transition metals

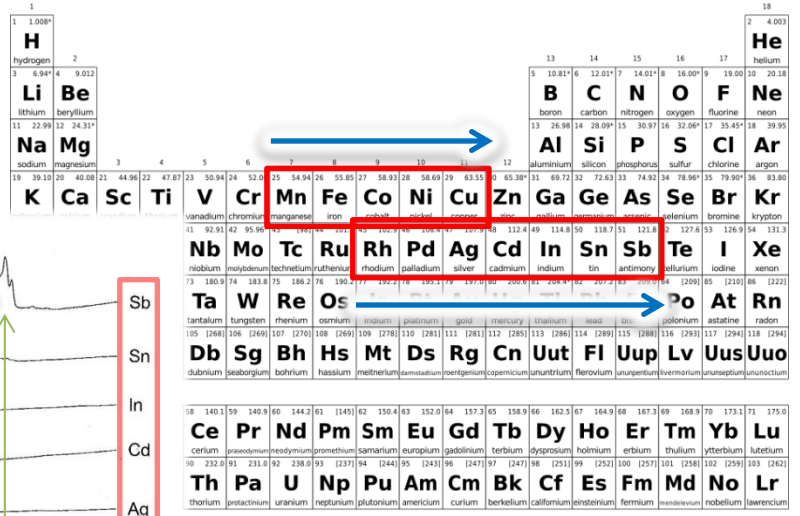
Small energy differences
=> usually not used in analysis due to overlaps

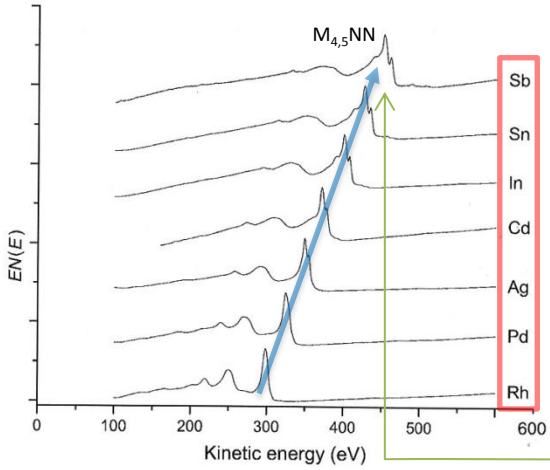


rich structure – various possible M-shell final vacancies
(similar for the whole row)

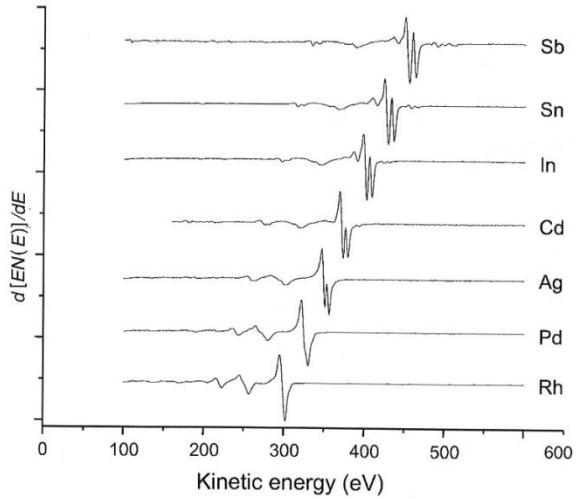


2nd row transition metals





doublet
(not resolved for lighter elements)



Auger electron spectroscopy

Qualitative analysis – basic identification

Basic elemental analysis

– identification by **peak position** (Auger electron energy)
– often more Auger lines present → cross-check using relative intensities

start with most intensive line

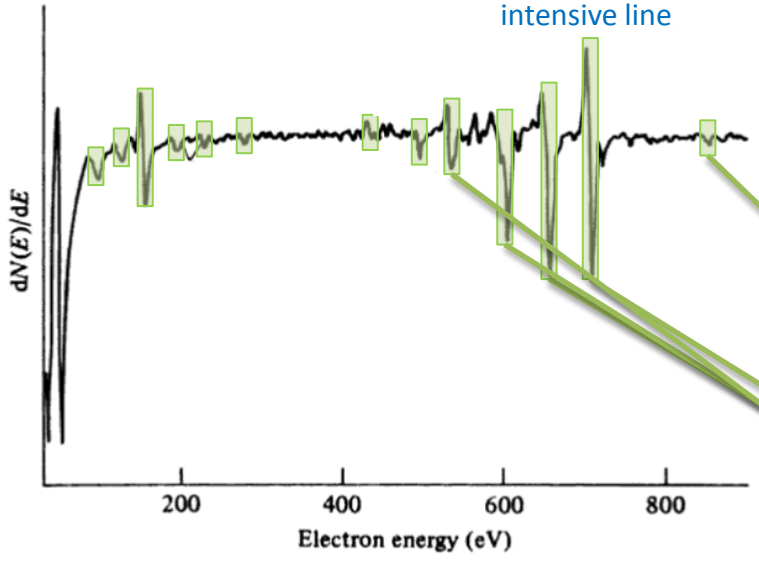
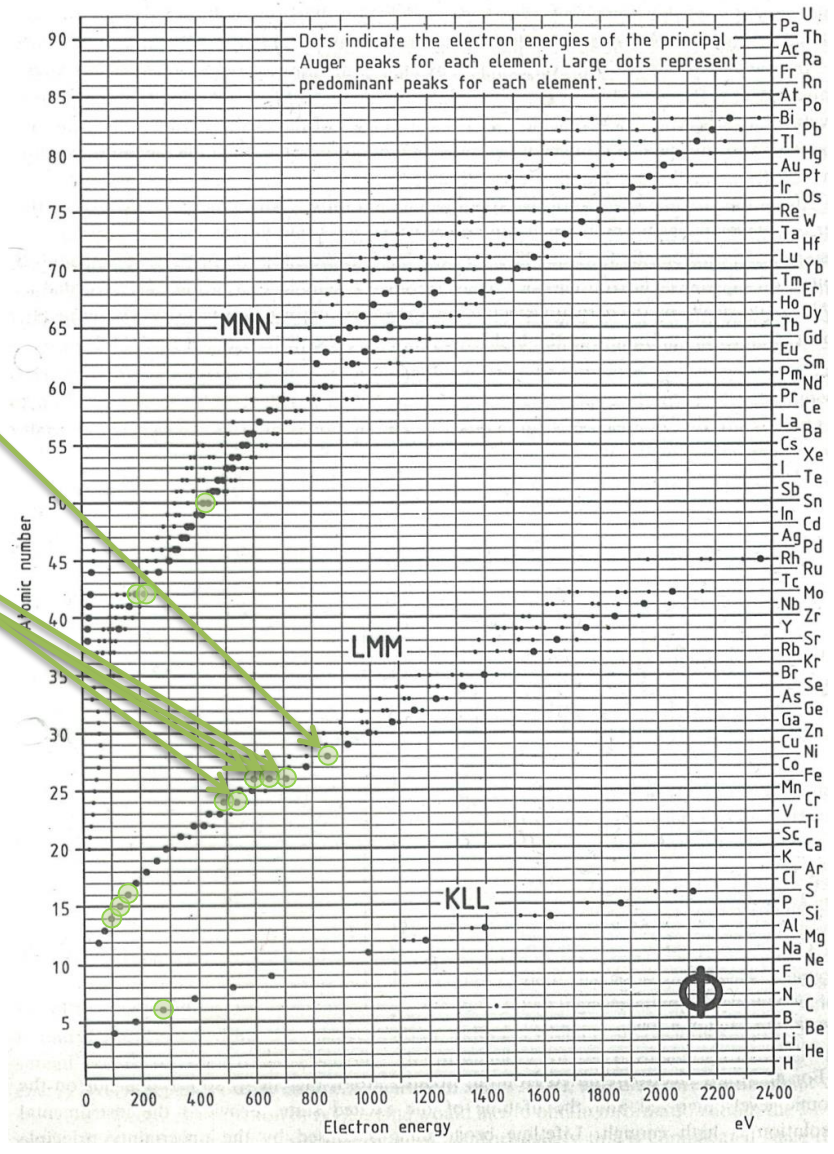


Chart of principle Auger electron energies



Static charging issue

Total electron yield

> 1 – positive charging (→ higher EB) – identification remains possible
< 1 – negative charging (→ lower EB) – analysis often impossible

Elimination

- lower E_p (→ fewer secondary electrons)
- glancing incidence beam

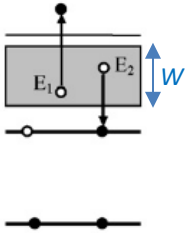
Auger electron spectroscopy

Qualitative analysis – chemical and structural effects

Main spectral features:

peak shape (lineshape) and **peak position shift**

- contain information on the nature of the environment: (reflect changes in initial electronic structure, screening, and relaxation process)
- peak width due to:
  - excited state lifetime
  - XVV: valence band width ($\Delta E_k^{XVV} = 2W$)
  - energy losses of escaping AE in solid
  - instrument (analyzer, not source: $\tau_{ioniz} \ll \tau_{Auger}$)



Chemical effects due to:

- chemical bond → charge transfer → shifts of electronic levels
- changes in valence band electronic structure
- modification of loss processes
- new states possible in XVV: cross-transitions between different atoms (interatomic transitions)

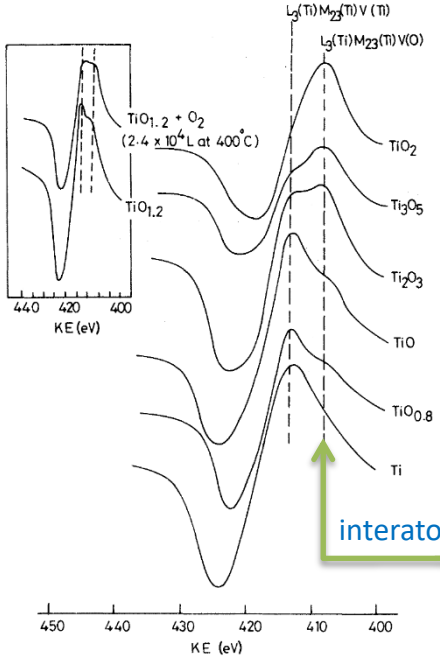
What can be detected:

- chemical state in compounds (oxidation state, stoichiometry, …)
- substrate-particle interactions (supported nanoparticles)
- adsorbates
- structurally-induced electron density redistribution (coordination, crystallography)
- charge transfer in alloys (but usually weak shifts)

Theoretical modeling difficult
=> in practice spectra of standard samples are often used ("fingerprint method")

Typical chemical shifts due to oxidation

- ~8-15 eV for *p*-group elements (Al, Si, …)
- ~4-5 eV for *d*-group (transition metals)
- always to lower E_k – charge shift towards electronegative oxygen



AES of Ti and Ti oxides (LMV Auger line)

interatomic $L_3(Ti)M_{23}(Ti)V(O)$ line

Better than AES to study

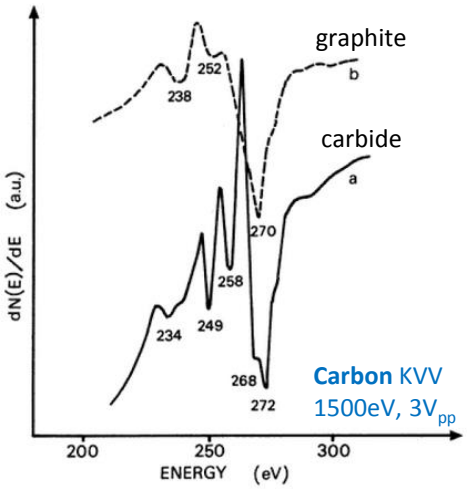
- core-shell chemical shifts – XPS
- valence band structure changes – UPS

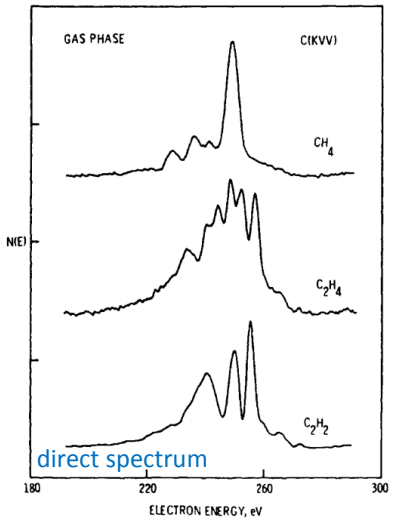
Photoemission = single-electron process => easier interpretation

Auger electron spectroscopy

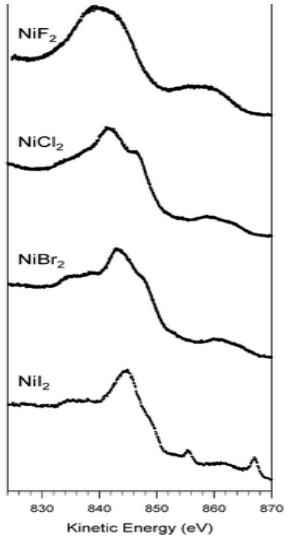
Qualitative analysis – chemical and structural effects – examples

Differences in the line shape and peak position for the C Auger (KVV) in clean carbon and different C_xH_y compounds

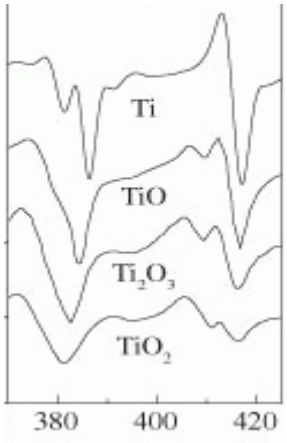




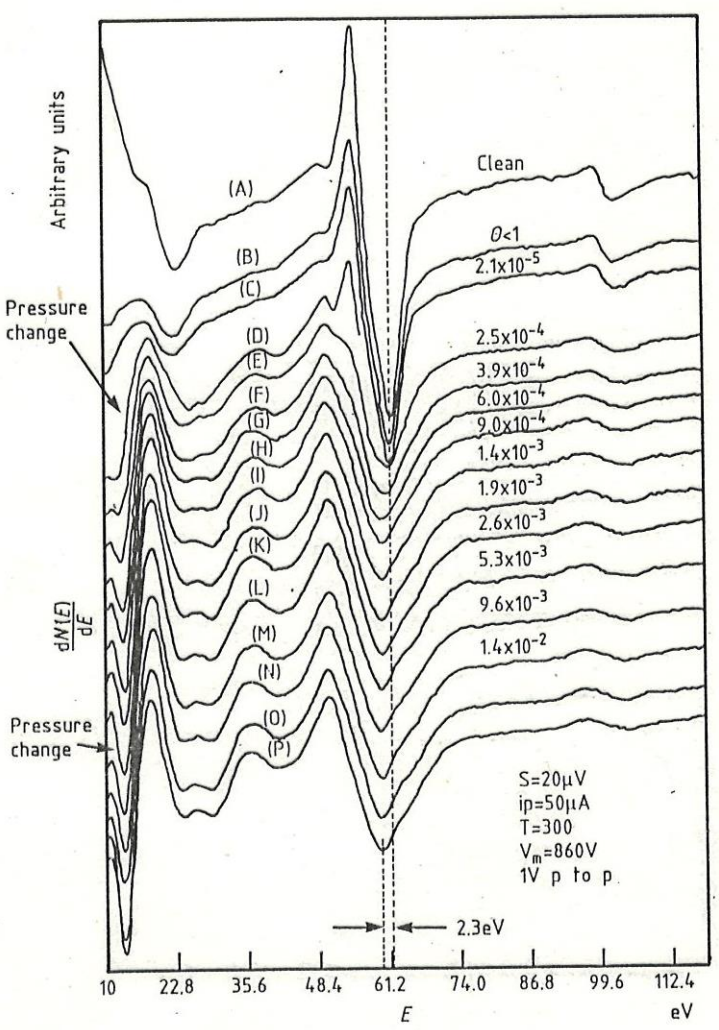
AES of nickel halides
(Ni LMM Auger line)



Ti oxides (LMM line)
- different stoichiometries

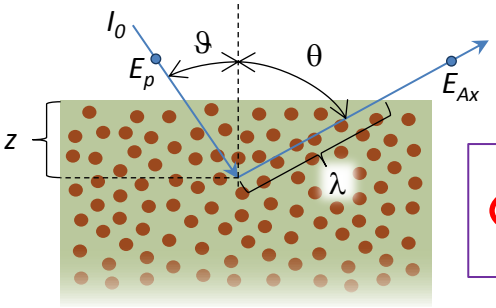


Gradual oxidation of nickel



Auger electron spectroscopy

Quantitative analysis



m … matrix
x … analyzed element

Auger line intensity

$$I_x(X,Y,Z) = I_0 \cos(\vartheta) A\, \sigma_x(E_p) \chi_x(X,Y,Z) T(E_{Ax}) D(E_{Ax}) [1 + r_m(E_{Ax}, \alpha)] \int_0^\infty N_x(z) e^{-z/\lambda_m(E_{Ax}) \cos\theta} dz$$

source | atom | measurement | solid matter (AE attenuation)

Determining factors

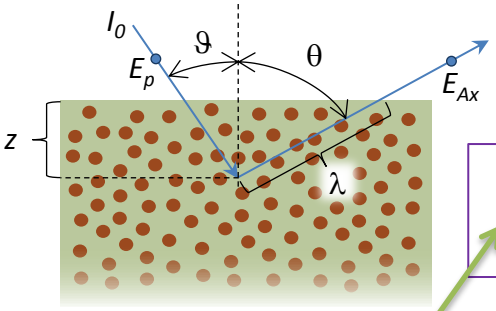
Sample dependent terms
- ionization cross section
- Auger transition probability
- secondary ionization coefficient
- concentration profile of an element
- inelastic mean free path of AE

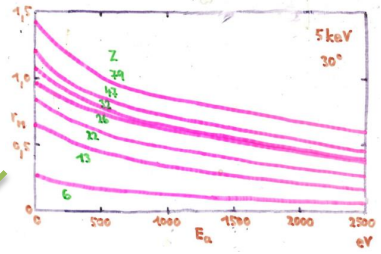
Instrument dependent terms
- primary beam intensity and angle
- analysis area
- analyzer transmission function
- detector sensitivity
- Auger emission angle

Solids vs. isolated atoms
- diff. electronic structure (delocalized bands)
- primary beam alteration
- alteration of AEs (transport through solid)
- work function
- existence of valence band

Auger electron spectroscopy

Quantitative analysis





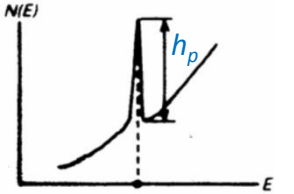
Auger line intensity

$$I_x(X,Y,Z) = I_0 \cos(\vartheta) A\, \sigma_x(E_p) \chi_x(X,Y,Z) T(E_{Ax}) D(E_{Ax}) [1 + r_m(E_{Ax}, \alpha)] \int_0^{\infty} N_x(z) e^{-z/\lambda_m(E_{Ax}) \cos\theta} dz$$

m … matrix
x … analyzed element

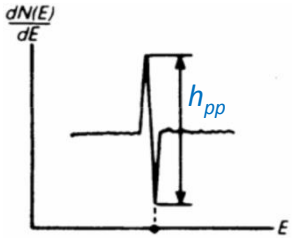
Peak intensity determination

Peak-to-background



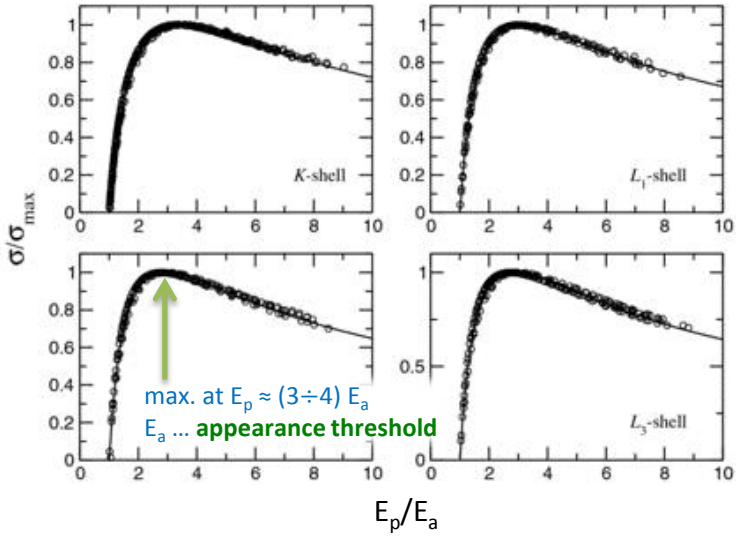
Direct spectra: often after background subtraction

Peak-to-peak



Assumption: Gaussian shape
=> $I \propto h_{p(p)}$

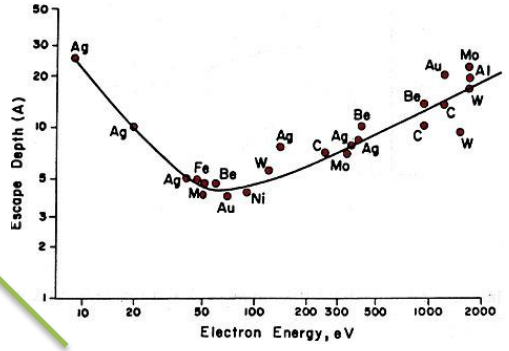
Ionization cross section $\sigma \approx 10^{-20}$ cm^2



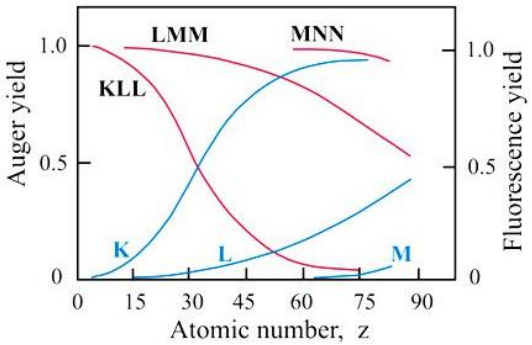
Primary energy dependence for ionizing K and L levels by electron impact
Quite universal curve for different levels and elements

E_p choice trade-off: max. σ, min λ

Electron IMFP



Auger transition yield

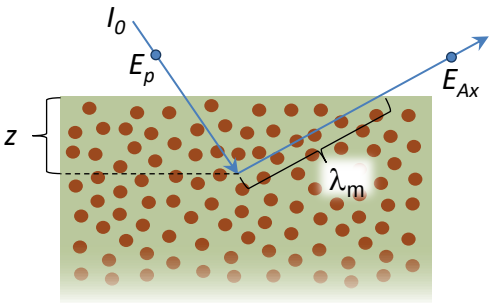


Relative yields for Auger emission and fluorescence from K, L, and shells

=> X-ray can be neglected for low *z* and E_p

Auger electron spectroscopy

Quantitative analysis



a … 1st element (matrix)
b … 2nd element

Semi-quantitative approach

Quantification analysis using **first principle**: possible but rarely done
(mainly due the large differences between coupling schemes that govern the Auger transitions in a multi ionized atom)

=> use of **standard spectra** or **relative sensitivity factors** derived from pure materials

Method of standards

Assumptions:
- the same instrument and settings (I_0, φ, θ, *T*, *D*)
- homogeneous sample:
  - no depth dependence
  - no anisotropy

The atomic factors (σ, χ) are cancelled-out

$$\frac{I_a/I_a^0}{I_b/I_b^0} = \frac{[1+r_{ab}(E_{Aa})]}{[1+r_{ab}(E_{Ab})]}\frac{N_a}{N_b}\frac{\lambda_{ab}(E_{Aa})}{\lambda_{ab}(E_{Ab})}\frac{[1+r_b(E_{Ab})]}{[1+r_a(E_{Aa})]}\frac{N_b^0}{N_a^0}\frac{\lambda_b(E_{Ab})}{\lambda_a(E_{Aa})}$$

from standards

$N_x^0 = R_x^{-3}$ … atom density of pure element *x*
$N_a = R_{ab}^{-3} X_a$ … atom density of element *a* in compound *ab*

X_x … relative atom. concentration
R_x … atom. radius

$$\frac{N_a}{N_b}\frac{N_b^0}{N_a^0} = \frac{X_a}{X_b}\left(\frac{R_a}{R_b}\right)^3$$

$\lambda \cong 0.41 R^{1.5}\sqrt{E}$ ([nm], [eV]; approx. by Powell)

$$\frac{X_a}{X_b} = F_{ab}^A \frac{I_a/I_a^0}{I_b/I_b^0}$$

F_{ab}^A … matrix coefficient (factor):

$$F_{ab}^A = \frac{[1+r_{ab}(E_{Ab})]}{[1+r_{ab}(E_{Aa})]}\frac{[1+r_a(E_{Aa})]}{[1+r_b(E_{Ab})]}\left(\frac{R_b}{R_a}\right)^{1.5}$$

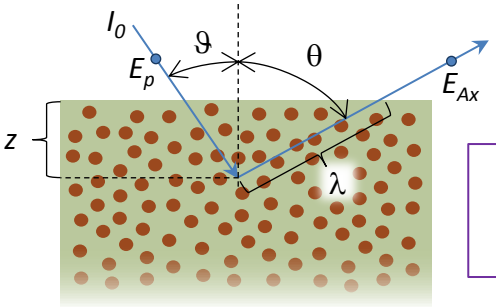
$$F_{ab}^A \xrightarrow[X_b \to 0]{} \frac{[1+r_a(E_{Ab})]}{[1+r_b(E_{Ab})]}\left(\frac{R_b}{R_a}\right)^{1.5}$$

⇒ constant for a given matrix type, does not depend on the concentrations of *a*, *b*

similar *r*, *R*: $F_{ab}^A \approx 1$ $\quad X_a = \frac{I_a/I_a^0}{I_b/I_b^0}$

Auger electron spectroscopy

Quantitative analysis



m … matrix
x … analyzed element

Auger line intensity

$$I_x(X,Y,Z) = I_0 \cos(\vartheta) A\, \sigma_x(E_p) \chi_x(X,Y,Z) T(E_{Ax}) D(E_{Ax}) [1 + r_m(E_{Ax}, \alpha)] \int_0^\infty N_x(z) e^{-z/\lambda_m(E_{Ax}) \cos\theta} dz$$

independent values

$S_x(E_p, X, Y, Z)$ **sensitivity factor**

(determined theoretically or experimentally for each *z*, E_p and *X,Y,Z*)

constant

Simplification: **Homogeneous sample**

$$N_x(z) = N_x$$

$$\int_0^\infty N_x(z) e^{-z/\lambda_m(E_{Ax}) \cos\theta} dz$$

$$= N_x \int_0^\infty e^{-z/\lambda_m(E_{Ax}) \cos\theta} dz = {}^{N_x}/_{\lambda}$$

- λ and r_m usually hard to determine
  => assumed constant
- anisotropy (azim. angle dependence) not considered
  (otherwise I_x should be angle-integrated)

Handle with care: lot of imprecision and assumptions, should be used judiciously.

$$N_x = N \frac{{}^{I_x}/_{S_x}}{\sum_i {}^{I_i}/_{S_i}}$$

Auger electron spectroscopy

Quantitative analysis

Relative sensitivity method

- sensitivity determined for pure elemental standards

- most accurate for alloys with similar *z* (=> similar σ, χ, r, λ => linearization conditions obeyed)

Alternative:

Reference spectra method

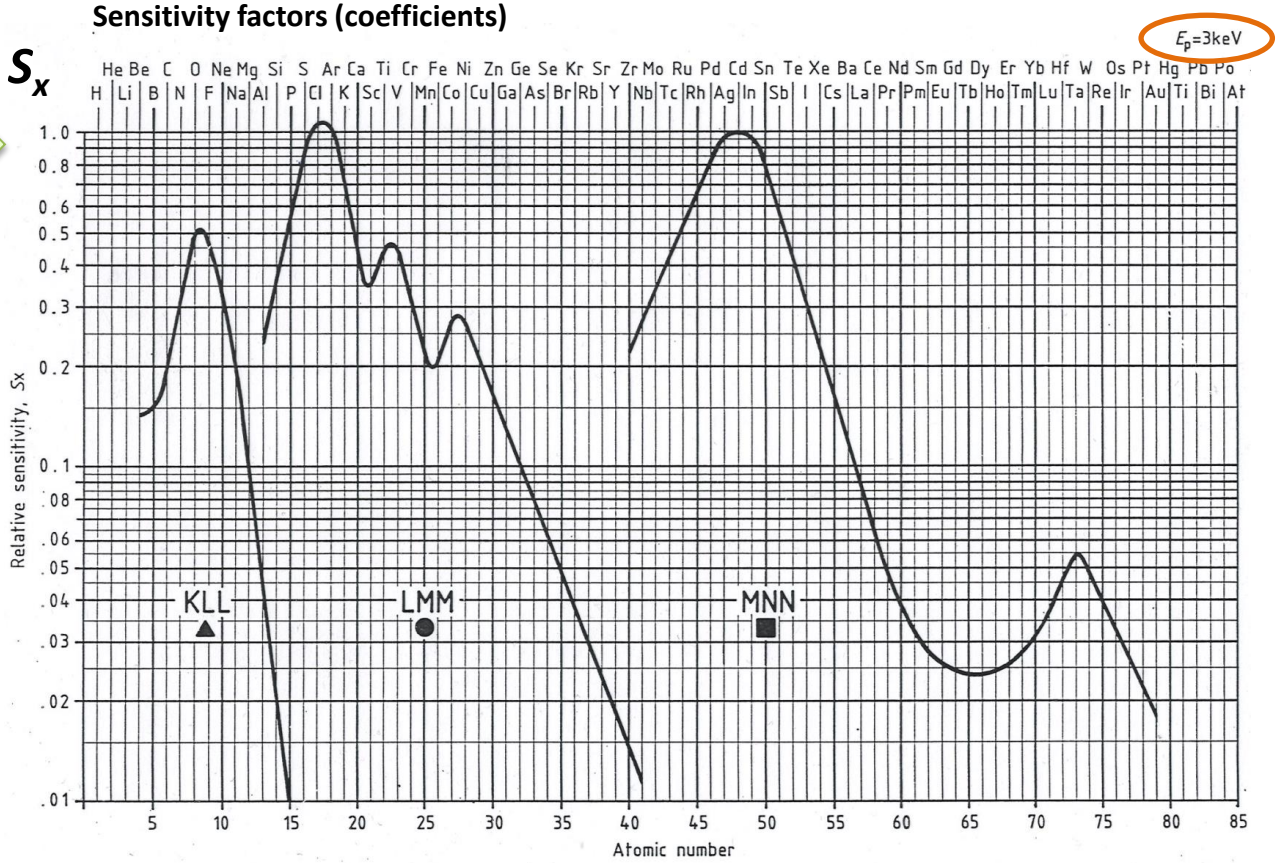
- uses library of ref. spectra taken under constant conditions
- best matching linear combination of spectra is found

Non-homogeneous samples

- combination with numerical models
- complementary input required (XPS, STM, SIMS, ...)

→ will be discussed later (XPS, PES)

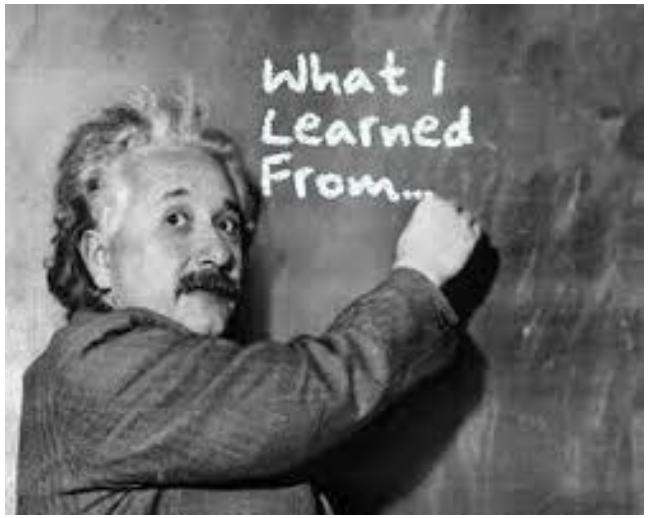
Sensitivity factors (coefficients)



Relative sensitivity factors obtained from standard samples (pure elements)

Auger electron spectroscopy

Take-home Messages



- Auger transition = non-irradiative electron de-excitation process *(no photon generated)*
- Surface sensitive (~1 nm) – *good for adsorbates*
- AE energy independent of primary energy

Main indicators

peak position
- elemental identification *(cross-check all transitions)*

peak intensity
- elemental concentration

peak shift
- charge transfer *(chemistry)*
- local structure *(coordination)*
- interatomic transitions

peak width
- excitation lifetime
- losses
- valence band width

peak shape
- changes in DOS
- loss processes

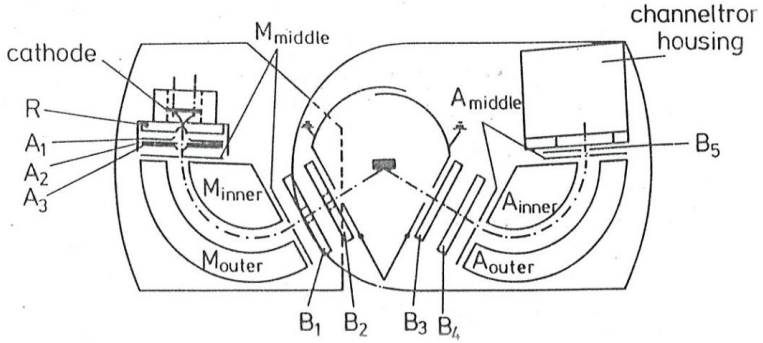
Electron energy loss spectroscopy

History, basic classification, instrumentation

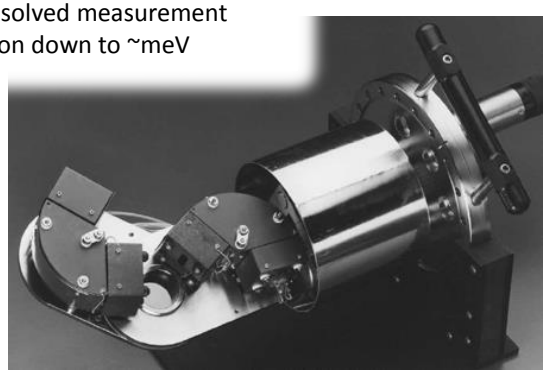
Brief history

1940s (mid): EELS developed by *James Hillier* and *R.F. Baker*
1967: Mapping of small molecules on W(100)
1970s: Further development - HREELS (*H. Ibach*)
1990s: Widespread in research due to advances in instrumentation

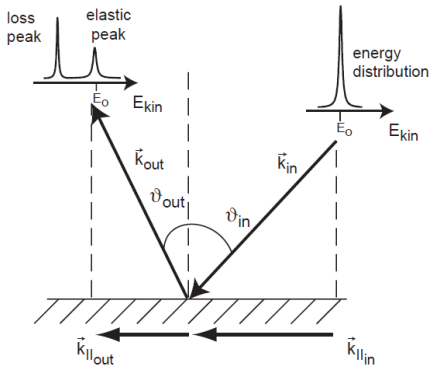
Instrumentation



- resolution determined mainly by el. source
- usually large impact angle
- AREELS – angle resolved measurement
- HREELS – resolution down to ~meV



Electron energy loss spectroscopy
- based on characteristic energy losses due to inelastic scattering



EELS
- plasmons, inter- and intra-band transitions – ~10^0-10^1 eV
- surface sensitive – small primary beam penetration (typical E_p≈10^1-10^2 eV)
- => spectroscopy of transitions from occupied to unoccupied states
  => interpretation less straight-forward that in XPS

HREELS
- adsorbate vibrations and surface phonons – ~10^1-10^2 meV
- vibrational spectroscopy

ELNES/EXELFS
- absorption edges and related fine structures at higher energy loss region (≳ 100 eV)
- core-levels

TEM-EELS
- excitation of bulk plasmons, inner-shell ionizations, interband transitions – E_p≈10^2 keV
- high spatial resolution (~10^{-1}-10^0 nm)
- penetration depth ~μm
- most common EELS variant nowadays
- complementary to XPS (inner-shell electrons → elemental analysis, chemical sensitivity) – absorption edges instead of peaks

Electron energy loss spectroscopy

Fundamentals

Characteristic energy loss

energy loss = **primary** interaction event (affects primary electron)

energy

- vibrational excitation (~10^1–10^2 meV) (→ HREELS)
- single valence electron excitation (3–20 eV) to
  - the same shell – intraband transition
  - a different shell – interband transition
  - an adsorbate state
- collective valence electron excitation (plasmon) (5–50 eV)

„classic" EELS

- inner-shell ionization (~10^2 eV) + extended fine structure at the edge for core electron excitation (→ ELNES, EXELFS)
- deeper inner-shell ionization (10^2–10^3 eV) – usually glancing angle to be surface sensitive (→ REELS)

Zero-loss (primary) peak

- in EELS used for energy scale (E_0) and intensity (I_0) calibration (utilized directly in diffraction methods or in EPES)
- width ∝ energy spread of primary source
- typically 10^3-10^4 × intensity of low-loss signal

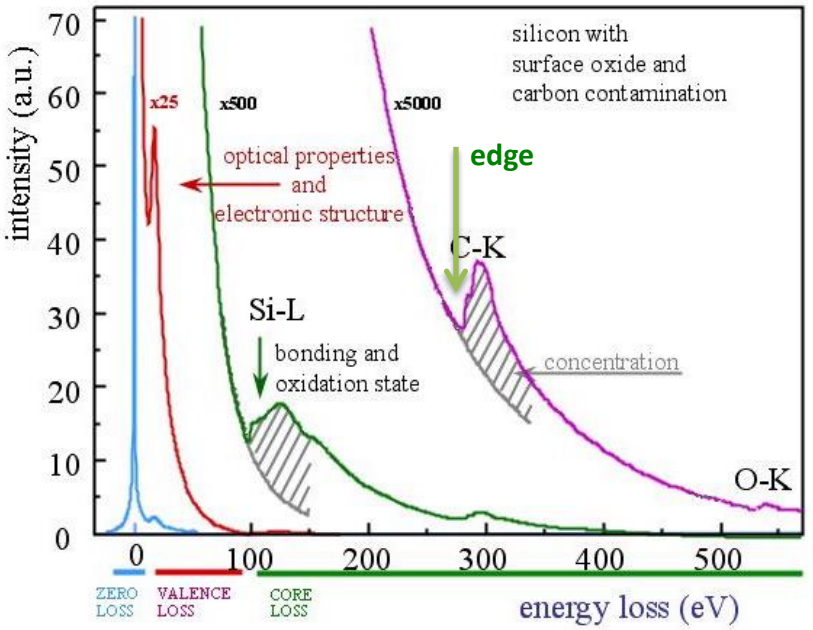
Basic EELS interpretation

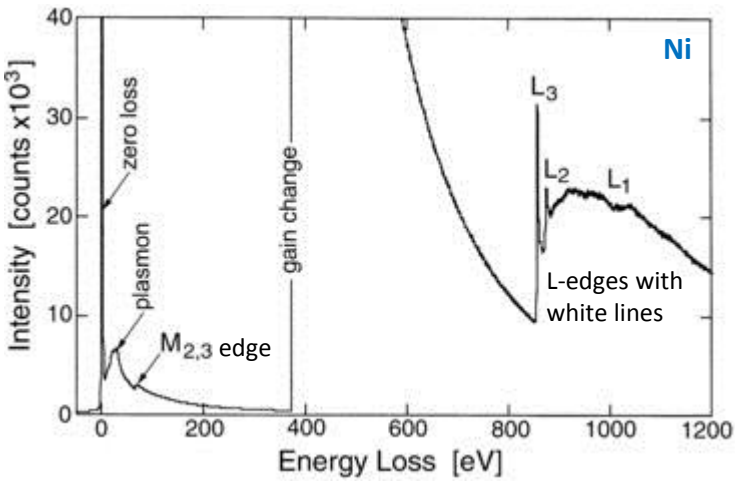
- losses appear as peaks or edges
- very small features on large background

- sharp initial state (e.g. *d* band) => EELS represents DOS vs. E of the final state
- both initial and final state broad – more complicated interpretation

- possible angular effects

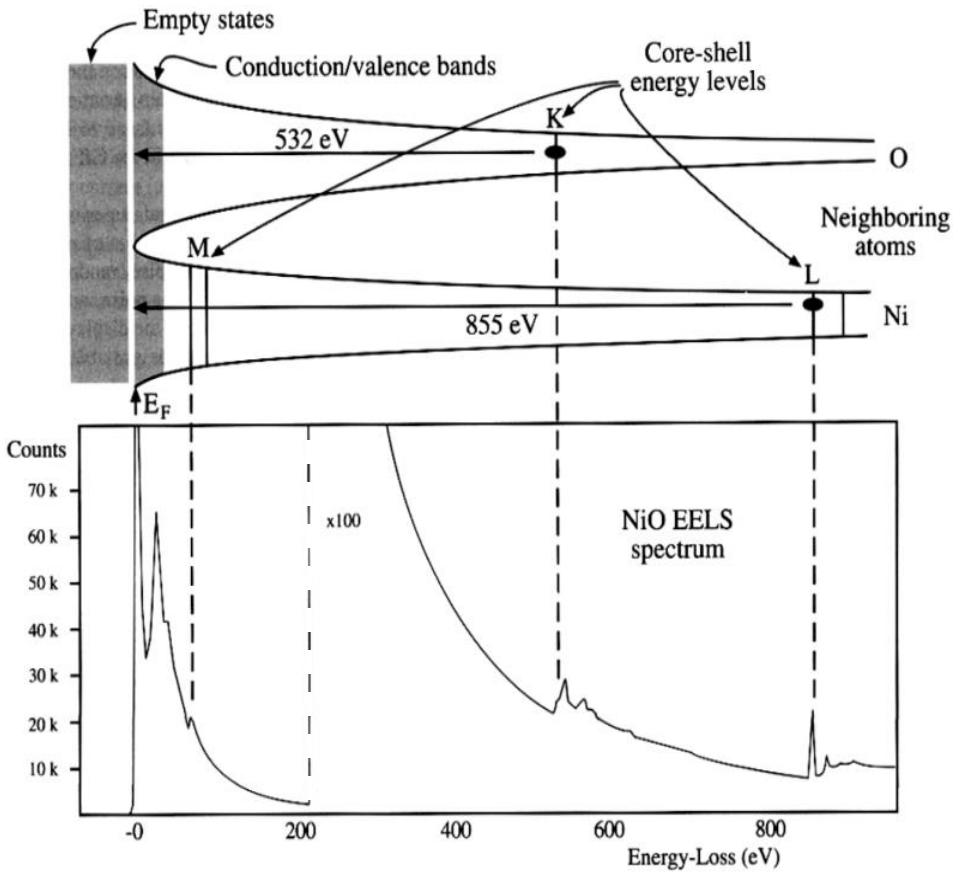
Electron energy loss spectrum





Electron energy loss spectroscopy

EELS vs. band structure



Dipole selection rule

Δl between initial and final state = **±1**

=> just some transitions allowed

Inelastic collision of electron

= excitation of another electron from initial state with wave function ψ_i to final wave function ψ_f in the coulombic potential $V(\vec{k})$

Cross section calculation (from Fermi's golden rule of QM)

$$\frac{d\sigma_f}{d\Omega} = \frac{4\pi^2 m^2}{h^2} \left| \langle \psi_f | V(\vec{k}) | \psi_i \rangle \right|^2$$

Nomenclature and quantum numbers of electronic transitions in EELS

Observed edges		Initial state	Initial state quantum number n	l	j	Final state
K		$1s^{1/2}$	1	0	1/2	p
L_1		$2s^{1/2}$	2	0	1/2	p
L_2	$L_{2,3}$	$2p^{1/2}$	2	1	1/2	s or d
L_3		$2p^{3/2}$	2	1	3/2	s or d
M_1		$3s^{1/2}$	3	0	1/2	p
M_2	$M_{2,3}$	$3p^{1/2}$	3	1	1/2	s or d
M_3		$3p^{3/2}$	3	1	3/2	s or d
M_4	$M_{4,5}$	$3d^{3/2}$	3	2	3/2	p or f
M_5		$3d^{5/2}$	3	2	5/2	p or f
N_1		$4s^{1/2}$	4	0	1/2	p
N_2	$N_{2,3}$	$4p^{1/2}$	4	1	1/2	s or d
N_3		$4p^{3/2}$	4	1	3/2	s or d
N_4	$N_{4,5}$	$4d^{3/2}$	4	2	3/2	p or f
N_5		$4d^{5/2}$	4	2	5/2	p or f
N_6	$N_{6,7}$	$4f^{5/2}$	4	3	5/2	d
N_7		$4f^{7/2}$	4	3	7/2	d

Electron energy loss spectroscopy

Loss mechanisms – plasmons

Plasmons

- quantum of plasma oscillation (collective phenomena)
- solids: longitudinal wavelike oscillations of quasi-free (weakly bound – VB, CB) electrons in the array of positively charged nuclei
- quasi-particle with $E \equiv E(\vec{k})$ and plasmon frequency ω_p ($E_p = \hbar\omega_p$)

→ Plasmon types

- bulk plasmon: $\vec{k}_\perp \neq 0$
- surface plasmon: $\vec{k}_\perp = 0$

Simple case: harmonic undamped oscillations of free-electron gas within rigid lattice

$$\omega_p = \sqrt{\frac{4\pi n_e e^2}{m_e}}$$

m_e … electron weight
n_e … density of electrons

- plasmons decay in phonons or photons
- short lifetime $\tau \approx 10^{-15}$ s (dumping via short range el.-el. interaction or plasmon-electron interaction)
- localized to <10 nm
- typical energy loss $\Delta E \approx$ 5-30 eV (UV range, $n_e \approx 10^{23}$ cm^{-3})
  (small ΔE => strongly forward-scattered – good in transmission setup)
- multiple losses often detectable

$$\omega_{p(s)} = \omega_{p(p)} \frac{1}{\sqrt{1+\varepsilon}}$$

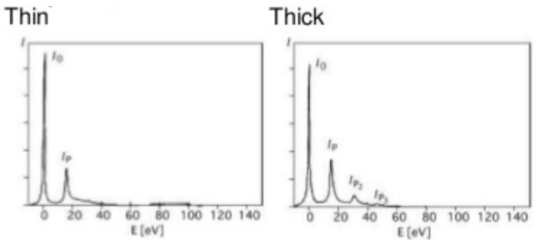
ε … relative permittivity (dielectric constant)

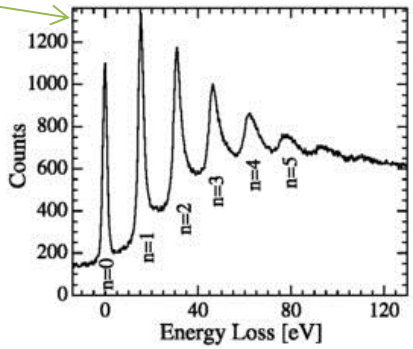
=> vacuum (no adsorbate):

$$\omega_{p(s)} = \omega_{p(p)} \frac{1}{\sqrt{2}}$$

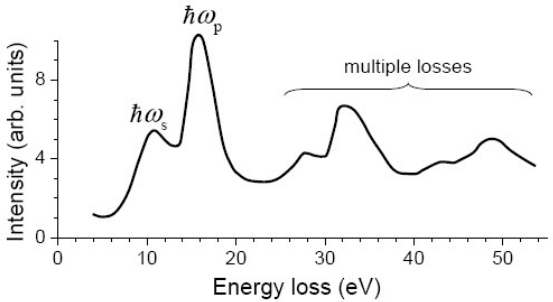
Information carried by plasmons

- reflect (quasi)free-electron density ($\omega_p \propto \sqrt{n_e}$)
- chemical effects (bonding)
- surface effects (surface states, adsorption)
- sample thickness (*in transmission*)





Low-loss spectrum taken from a thick sample of ~120 nm Al metal on C using 120 keV electrons and β=100 mrad

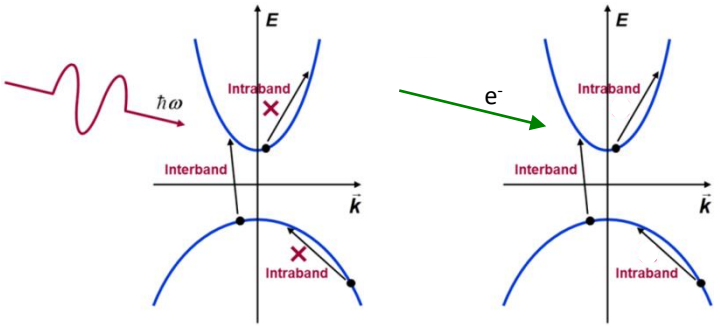


Electron energy loss spectroscopy

Loss mechanisms – inter- and intra-band transitions

Electronic transitions

- **Intraband**
  - within the same shell (typically valence or conduction band)
  - optically forbidden in metals (photon momentum << electron momentum), but can be facilitated by phonons (T>0K) or surface states
- **Interband**
  - between different shells (core electron-hole interaction)
  - not forbidden in metals



Interband transition threshold (ITT)

- minimum energy required for interband transition
- material-specific value

- semiconductors and insulators: ITT = band gap
- metals: more complicated – bands overlap near E_F
  (=> electron-phonon scattering dominant source of electrical and thermal resistance in metals)

Energy conservation

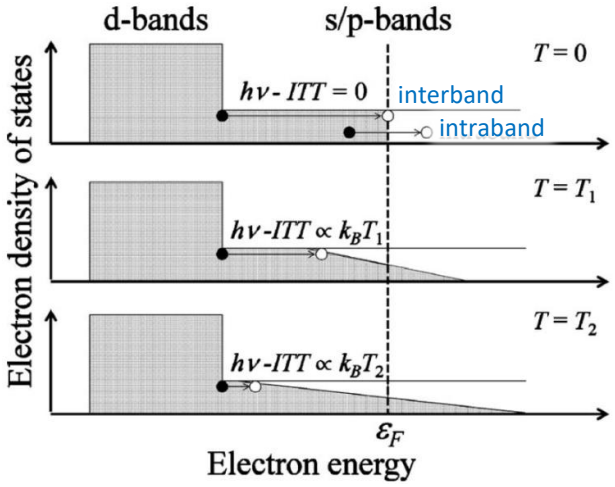
$$E_m(\vec{k}_f) = E_n(\vec{k}_i) + \hbar\omega$$

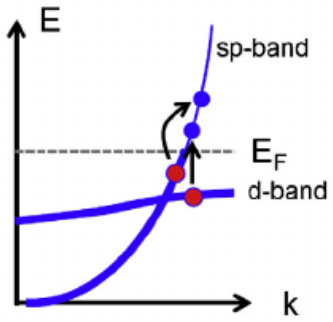
Momentum conservation

$$\vec{k}_f = \vec{k}_i + \vec{q}$$

$$|\vec{q}| \ll |\vec{k}_f|, |\vec{k}_i| \qquad |\vec{k}_e| \sim |\vec{k}_f|, |\vec{k}_i|$$

Noble metals





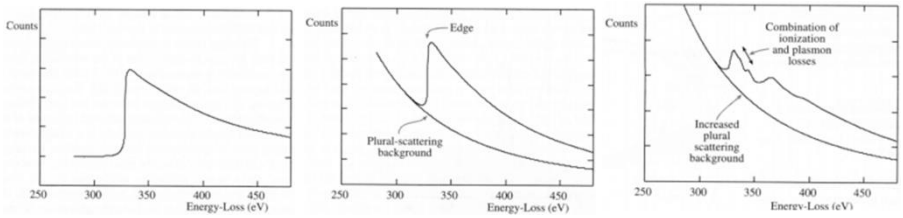
Electron energy loss spectroscopy

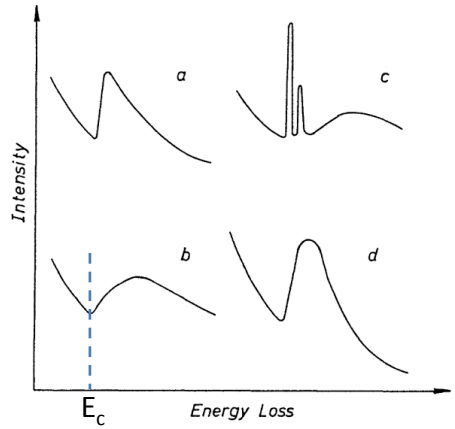
Loss mechanisms – inner-shell ionization

Inner-shell (core-shell) ionization
- high-energy loss due to core-electron emission
- appears as triangular edge in EELS

Absorption edge

E_c … critical ionization energy – main indicator (→ elemental analysis)
- edge height ∝ absorption intensity ∝ differential cross section
- intrinsically sharper than AES (2 vs. 3-level process)
- easier interpretation (rare ovelaps) but weaker features
- shape depends on electronic structure
  - changes significantly with filled/empty states
  - is affected by bonding
- background – multiple inelastic electron scattering

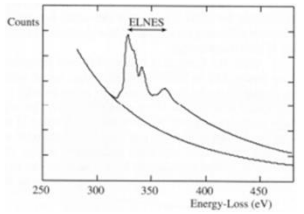




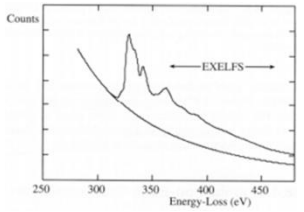
4 main families of edge shape
a) saw tooth profile
b) delayed edge
c) edge with white lines
d) low-loss plasmon-like edges

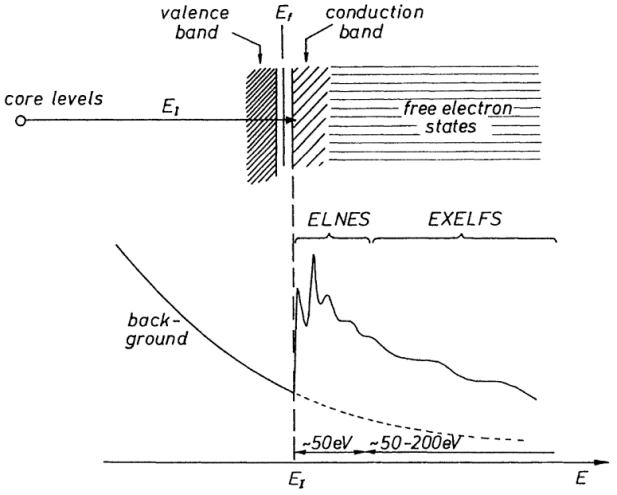
Additional features
- effects of further low-loss events of ionization-loss electrons

ELNES (energy-loss near edge structure)
- spectral features with $\Delta E \lesssim E_c + 50$ eV
- contains information on local density of empty states, oxidation state



EXELFS (extended energy-loss fine structure)
- spectral features with $\Delta E \gtrsim E_c + 50$ eV at the tail of an edge
- contains information on **local** coordination of the respective atom (no long-order needed => even for polycrystals)
- typically ~100x smaller than low-loss features





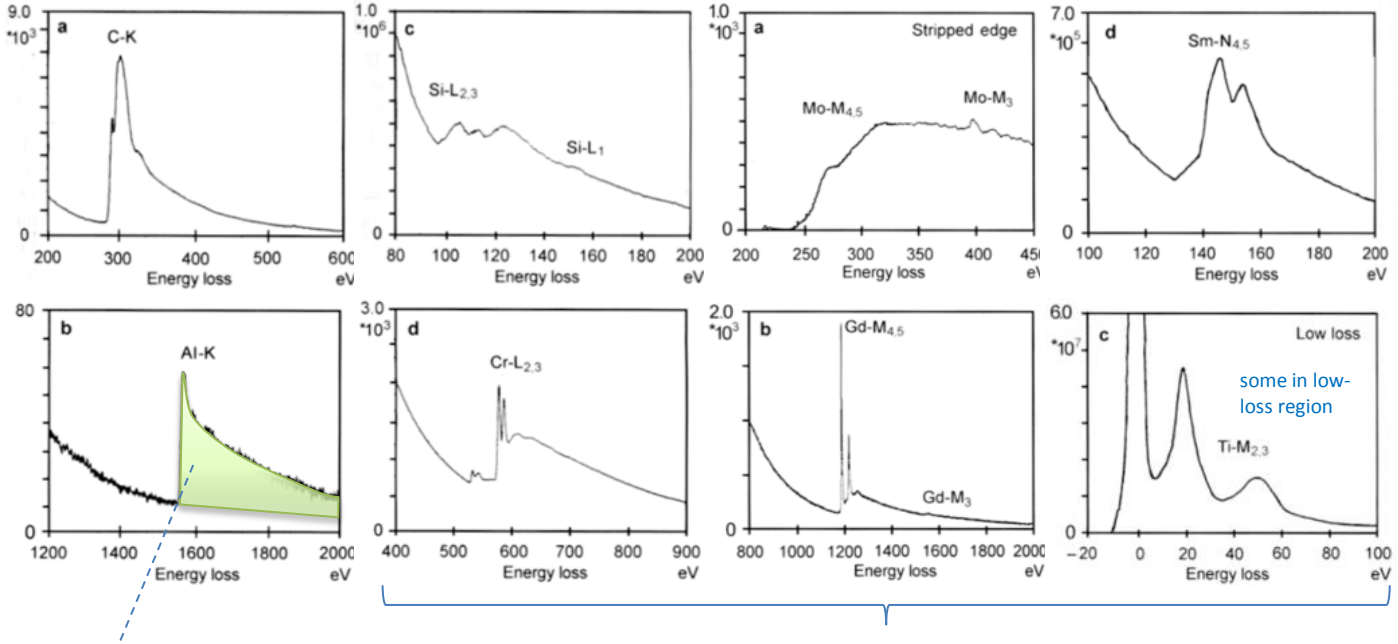
Scheme of core-loss excitation

Electron energy loss spectroscopy

Loss mechanisms – inner-shell ionization

ELNES fingerprints

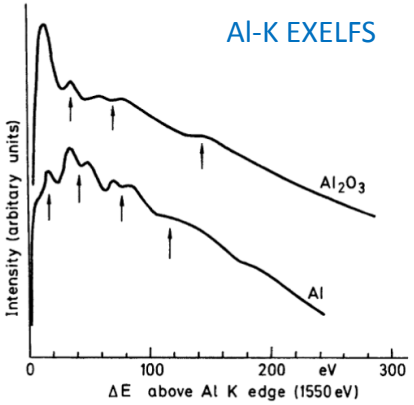
K edges **L edges** **M edges** **N edges**



sharp onsets

broader; separate subshells often resolved

Chemical sensitivity



Redistribution of valence charge
=> altered core-level screening
=> energy if core states change
=> shift of edge thresholds

Edge intensity ∝ differential cross section

=> ELNES can be used to calculate **energy distribution of empty states** directly:

- K excitation probes *p*-like unoccupied DOS
- L_{23} probes both *s*-like and *d*-like states
- M_{45} probes *p*-like and *f*-like states
- …

} allowed transitions: $\Delta l = \pm 1$

ELNES can be **orientation dependent**

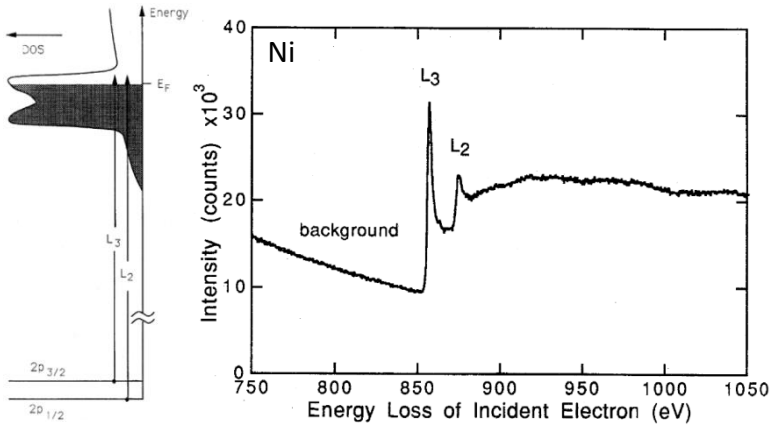
(anisotropic crystals: ELNES changes with the alignment of the momentum transfer along different crystallographic directions)

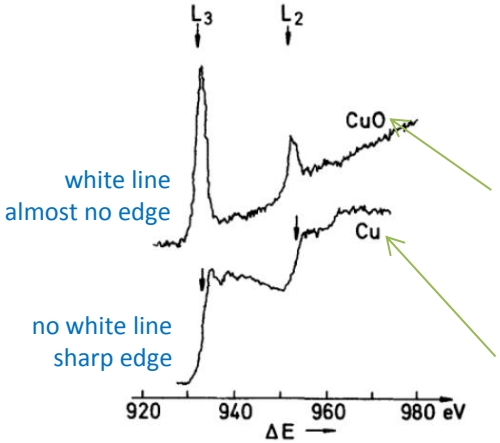
Electron energy loss spectroscopy

Loss mechanisms – inner-shell ionization

"**White line**"
- peak sometimes detected at the onsets of L or M shells
- arises from excitation of a deeper core electron to unoccupied outer states

3d and 4d transition metals and alloys
- L_2 and L_3 white line: excitation 2p → d state





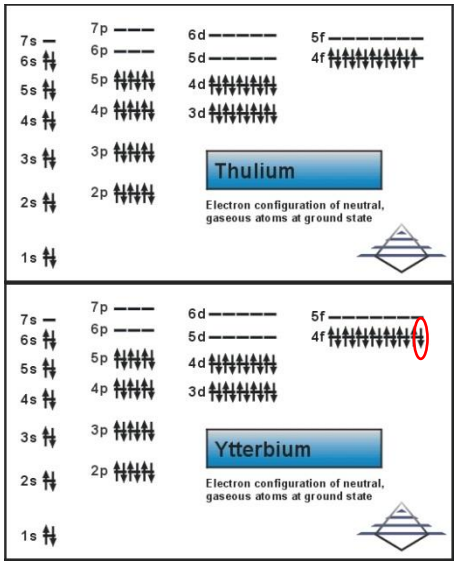
white line
almost no edge

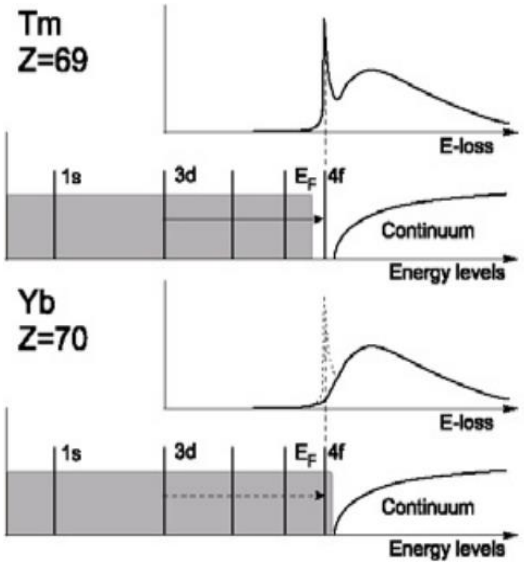
no white line
sharp edge

electron exchange between Cu and O
→ vacant states in the *3d* band
→ Fermi level shifts to *3d* band
→ white lines

filled *3d* band

4f and 5f inner transition elements
- M_4 and M_5 white line: excitation 3d → f state





For Yb (*z*=70) and higher *z*, the f-shell is completely filled => white lines cannot occur

Electron energy loss spectroscopy

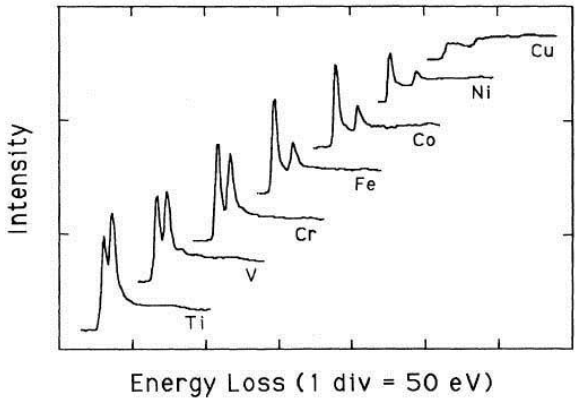
Qualitative analysis – elemental and chemical information

Most frequent use of **EELS in qualitative analysis**

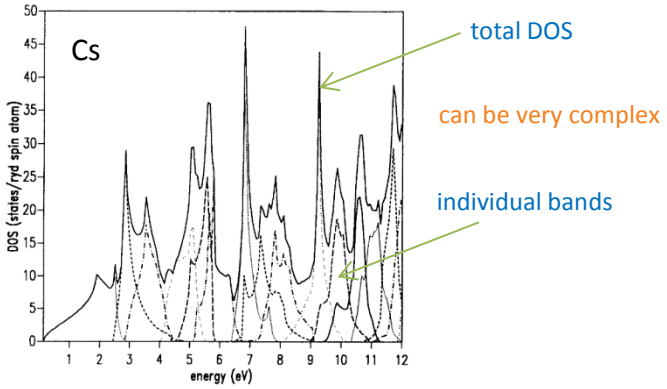
- composition of surface precipitates containing light elements
- surface adsorption
- oxides, carbides, nitrides, carbo-nitrides, hydrides, …

- easier interpretation (rare overlaps) but weaker features than AES

Inner-shell ionization used for **elemental analysis** – edge position



Plasmon losses used mainly for **VB DOS** and **surface analysis**



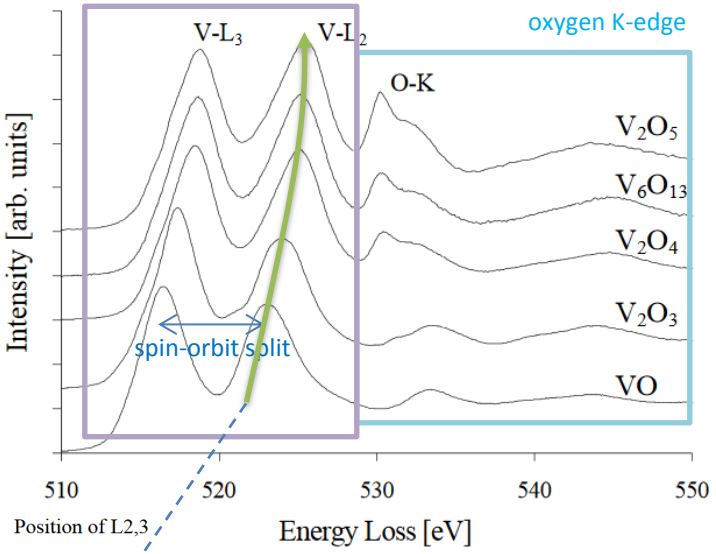
Chemical effect indicators

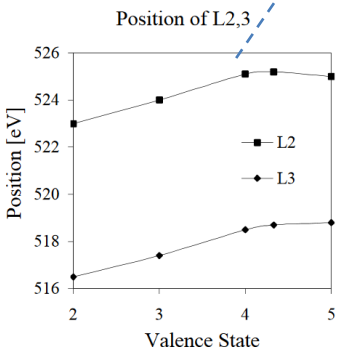
- chemical shifts: chemical surrounding of atom → charge distribution of its valence band measured as edge (E_c) shift
- plasmon-loss structure changes
- presence and intensity of white lines
- edge fine structure

} „**chemical fingerprint**“ or QM calculation (DFT)

Vanadium oxides

vanadium L-edge





Changes in the oxidation state of vanadium reflected by

- variation of the O-K edge **shape**
- varying **intensity ratio** of 2 white lines at V-L edges (due to changes in valence state).

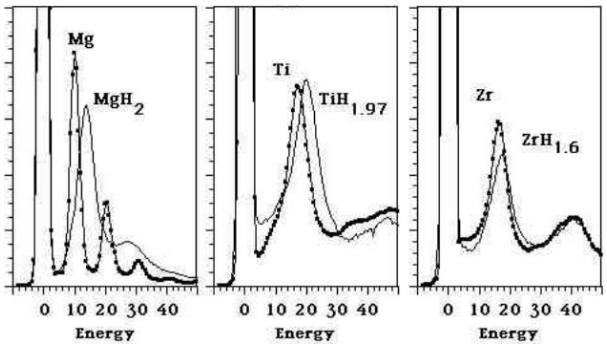
Shift results from a **reduced screening** of the positively charged nucleus with decreasing *3d* occupancy

Electron energy loss spectroscopy

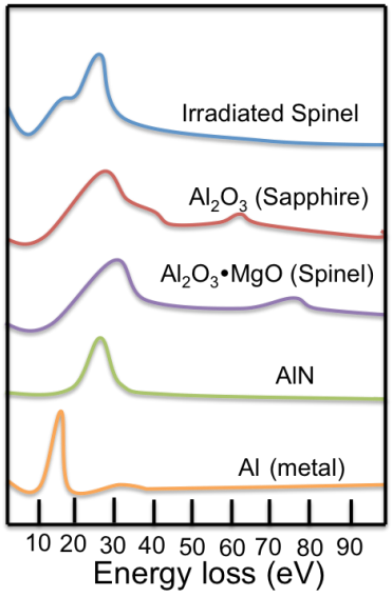
Qualitative analysis – examples

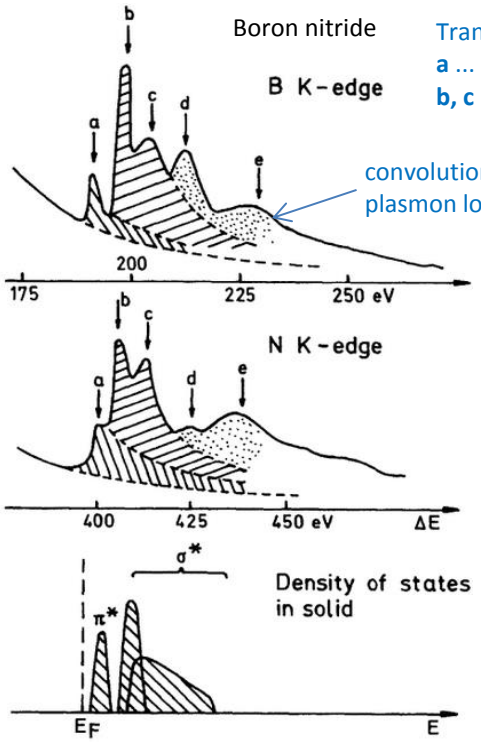
Solids

Plasmon losses – effect of hydrogen in metals



Plasmon losses of Al compounds

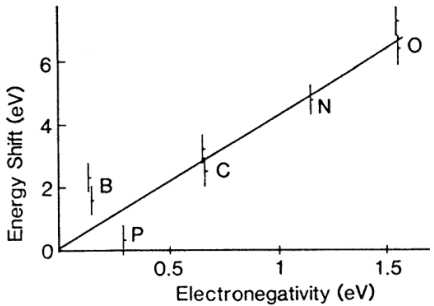




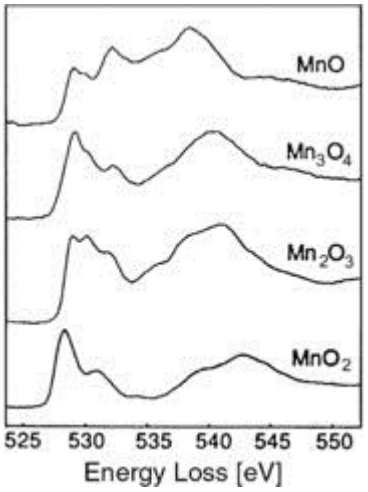
Transitions to
a ... π* bands
b, c ... σ* bands

convolution due to plasmon losses

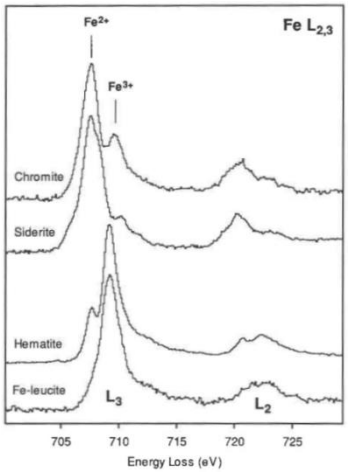
Chemical shift of the first peak in Si L_{23} ELNES of amorphous silicon alloys



Oxygen K-edges from various manganese oxides, showing a variety of ELNES spectral features



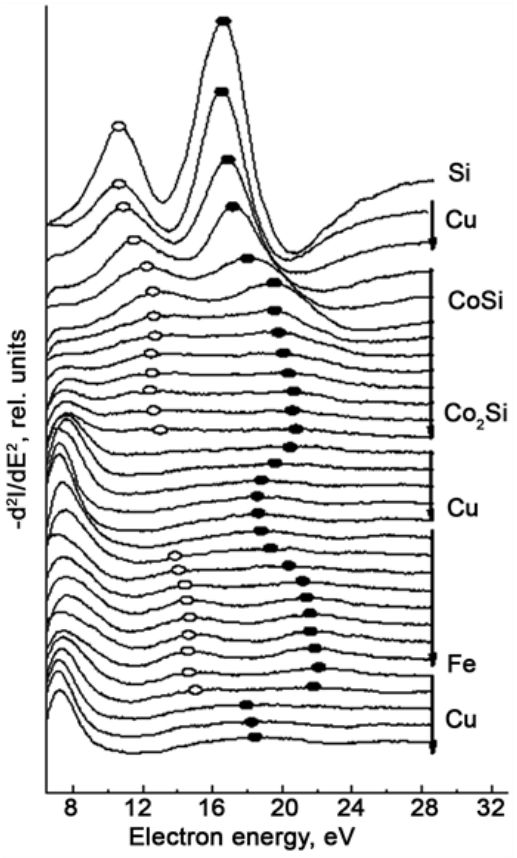
Fe L-edges of different iron compounds



Electron energy loss spectroscopy

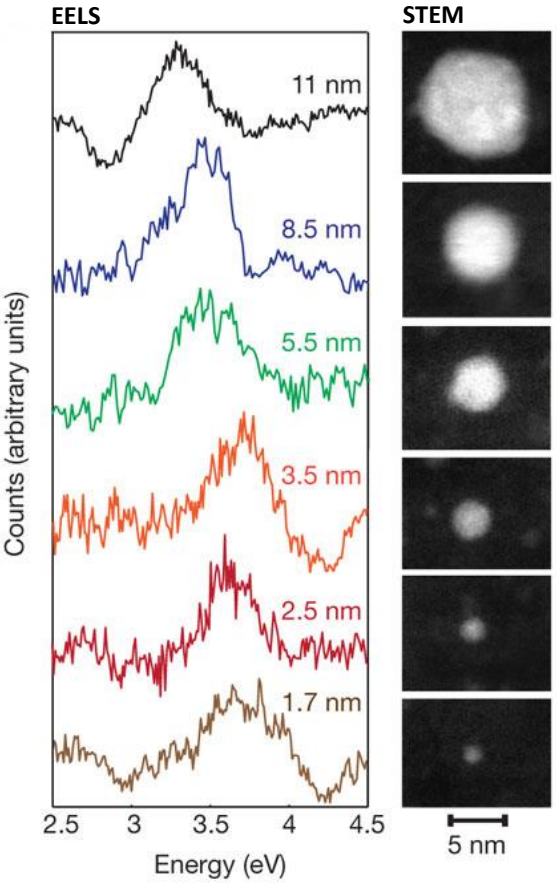
Qualitative analysis – examples

Thin films



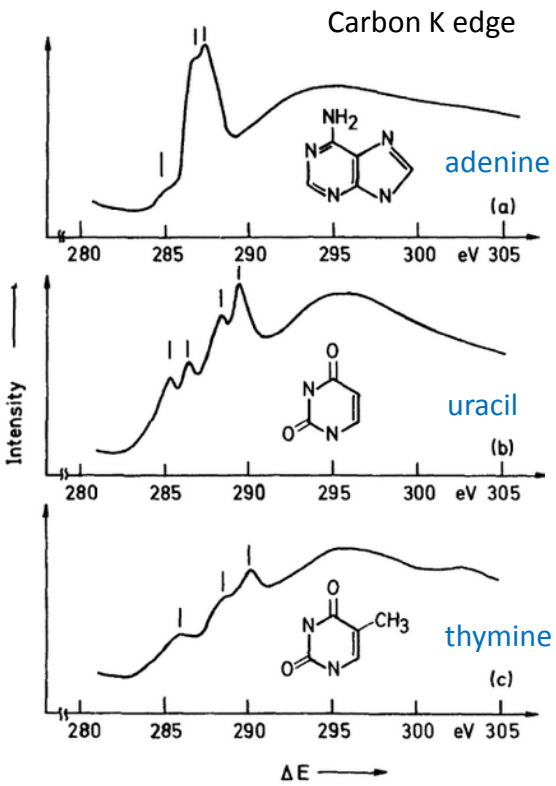
Low-loss EELS during the growth of Cu/Fe/Co/Cu multilayer film on Si(001)

Nanoparticles



Set of normalized, deconvoluted low-loss EELS spectra from quantum-sized Ag particles

Molecules



Core-level EELS of different nucleobases

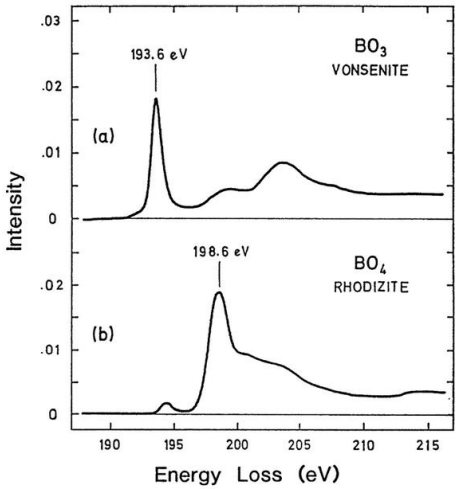
Electron energy loss spectroscopy

Qualitative analysis – structural information

Structural sensitivity

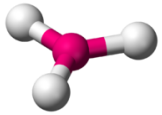
ELNES can exhibit a structure specific to the arrangement and type of atoms in the first coordination shell (and local electronic structure) – "**coordination fingerprint**"
→ bonding information

- changes possible in both edge position and fine structure
- small variations in the fingerprint structure can reflect changes in bond lengths and bond angles
- the choice of a scattering vector allows selection of particular final crystal orbitals for the transitions in question

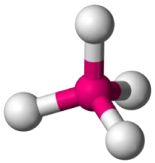


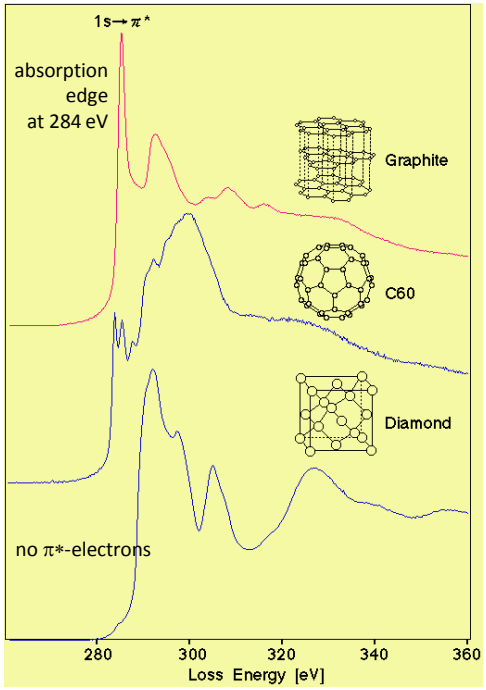
Boron K edge

Trigonal-planar oxygen coordination (vonsenite)



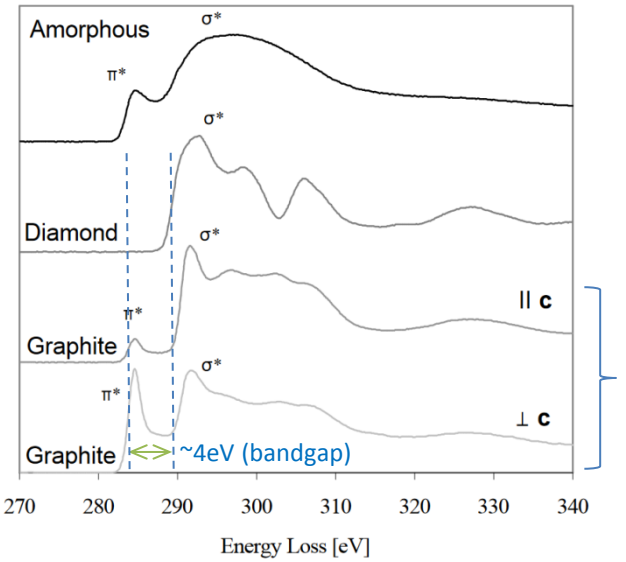
Tetrahedral oxygen coordination (rhodizite)

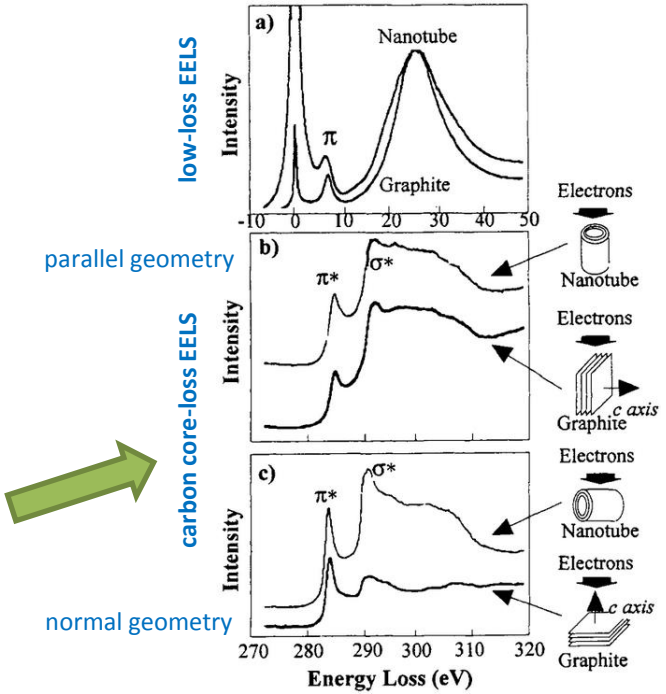




Carbon K-edge – fine structure

exitation of carbon K-shell electron (*1s* electron) to empty anti-bonding π*-orbital



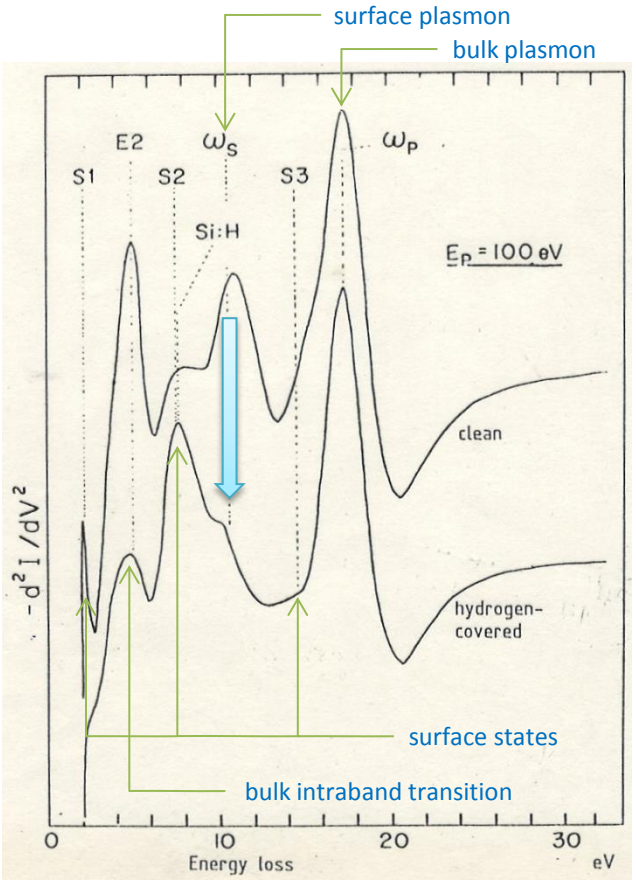


Electron energy loss spectroscopy

Qualitative analysis – adsorbate induced losses

Plasmons

Si(100) + H_2

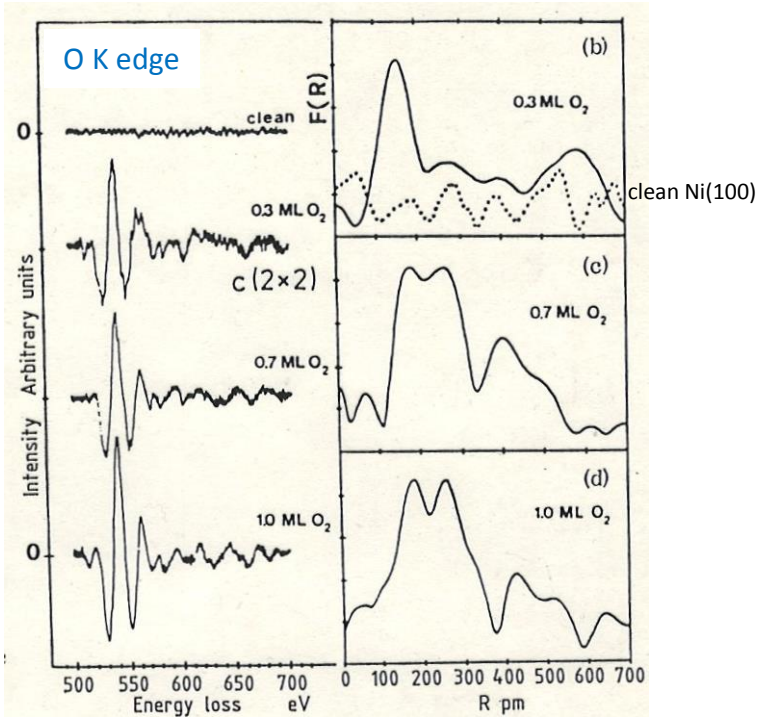


Fine structure

Ni(100) + O_2

Deriv. EXELFS spectrum

Fourier transformation: local spatial information



Most surface-related features within $\Delta E \approx 30$ eV

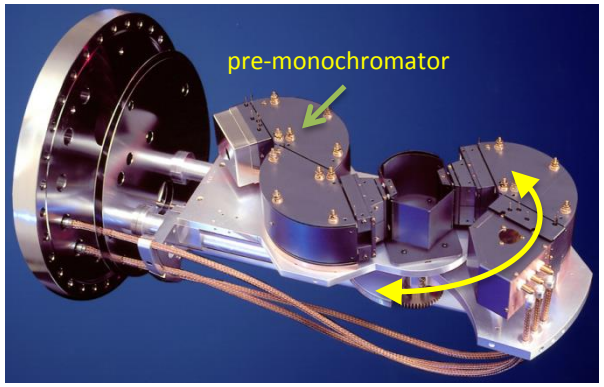
Better method to observe adsorbates: **HREELS** →

Electron energy loss spectroscopy

HREELS

High resolution EELS

- vibrational excitations (=> sibling of IRAS): E_{vibr} ≈ 6–500 meV (~50–4000 cm^{-1})
- E_p ≈ 5-10 eV
- standard resolution ΔE ≈ 3-4 meV, 0.25 meV in modern instruments (UHREELS)
- extreme surface and absolute sensitivity (<10^{-2}-10^{-4} ML depending on molecule)
  => mainly for characterization of gas-solid interfaces (adsorbates) and thin films
- usually angle-resolved

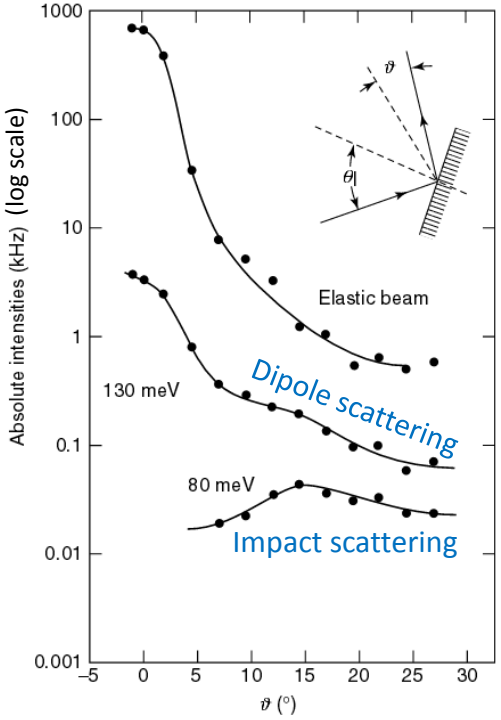


Scattering mechanisms

1) **Dipole scattering**
- electron behavior similar to IR elmg. wave – interaction with oscillating dipoles created by vibrations of species at surface
- long-range interaction
- IR selection rules apply:
  - only fundamental transitions allowed
  - only vibrations accompanied by a change in dipole moment observed

  + on metal surfaces:
  - only vibrations perpendicular to surface are HREELS active (image charge effect)
  - intensity maximal at specular reflection

2) **Impact scattering**
- involves penetration of incident electron to the adsorbed molecule
- very fast energy transfer, vibrational mode excited while electron still inside the molecule
- more complex process
- dipole-scattering selection rules do not apply
- „propensity rules“:
  - vanishes in the specular direction
  - dominant process at higher vibrational energies
  - strong dipole scaterers are weak impact scaterrers and vice versa



Electron energy loss spectroscopy

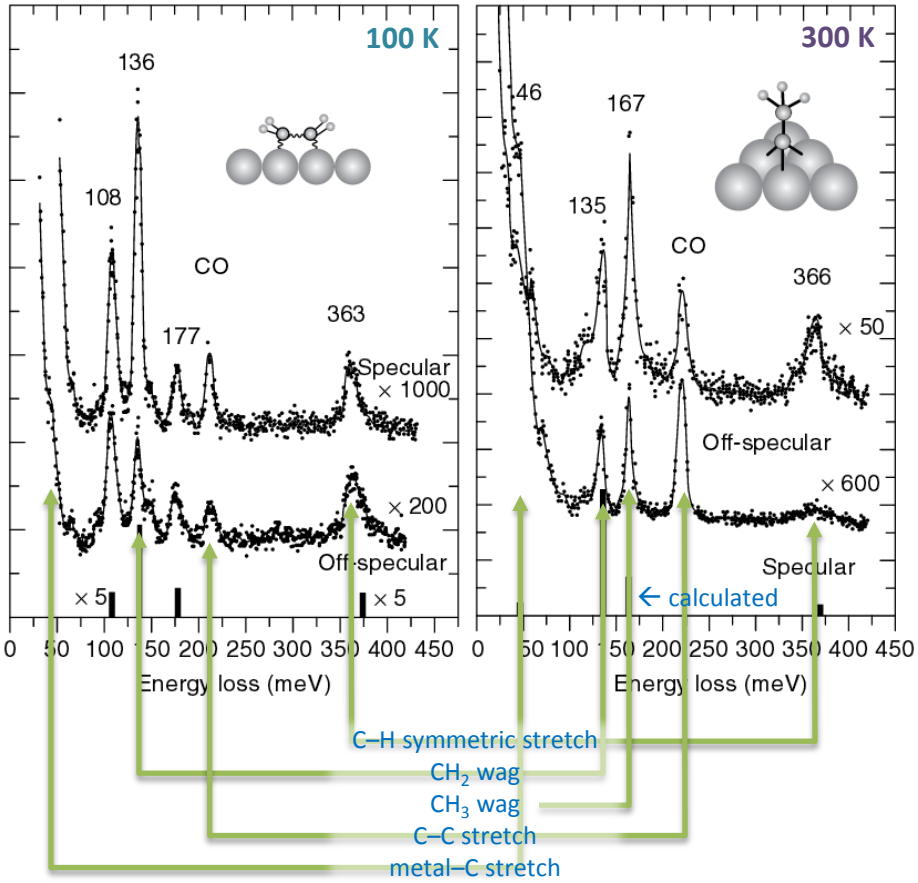
HREELS – examples

Adsorbates

Ethylene on Pd(111)

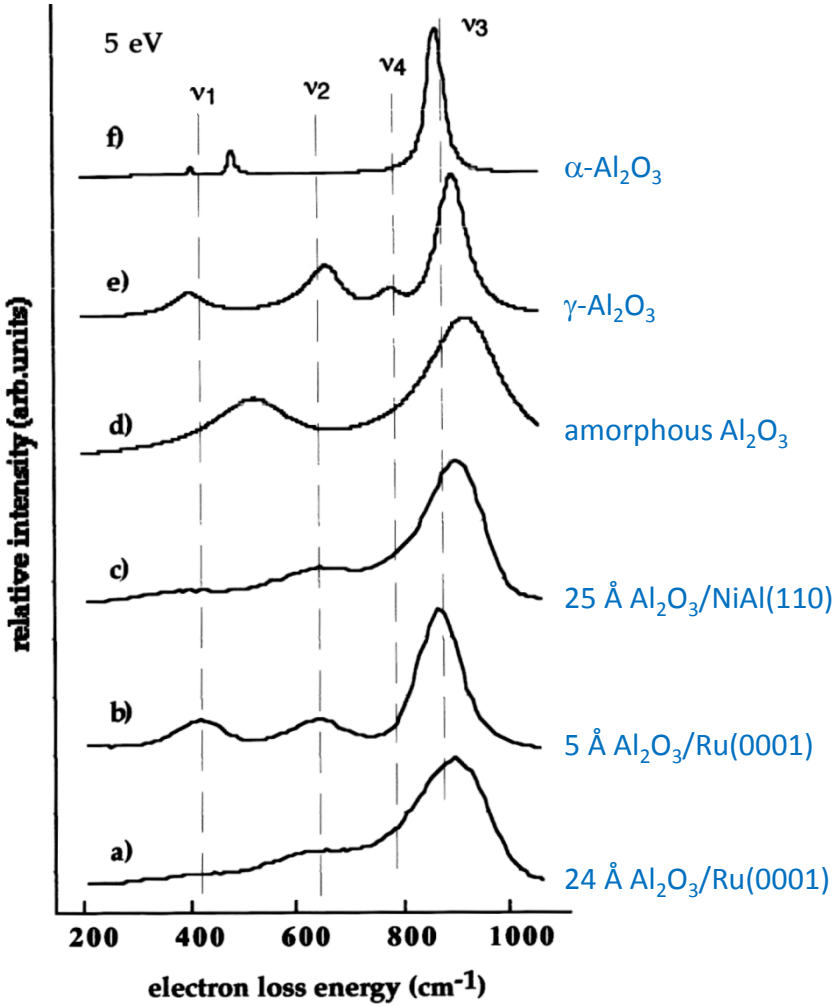
di-σ bonded ethylene
vibr. spectrum characteristic of aliphatic (sp^3-hybridized) compounds

π-bonded ethylidyne
vibrational modes of C_{3v} symmetry



Solids

Aluminum oxides – thin films



Electron energy loss spectroscopy

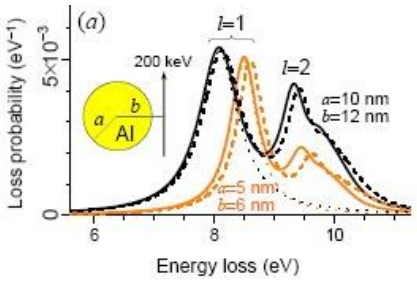
Quantitative analysis

Quantitative indicators

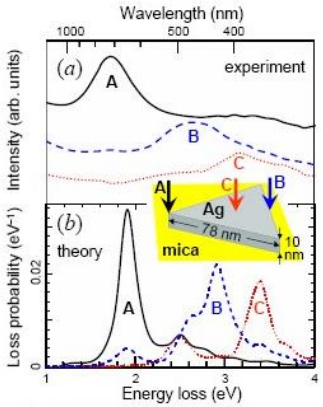
- **Plasmons**

Valence electron density (occupied states): $E_p \propto \sqrt{n_e}$

- adsorbates, nanoparticles, thin films, surface compounds, …



Plasmon losses in Al nanospheres

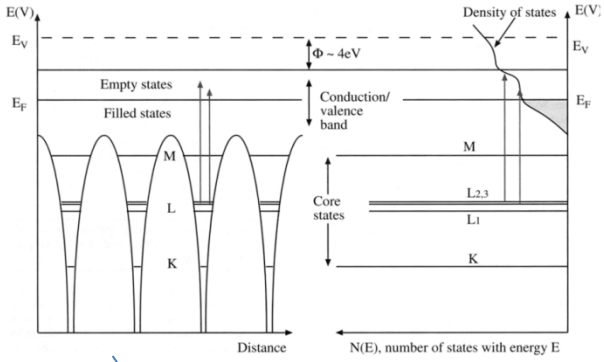


Plasmon modes in an individual Ag triangular nanoprism supported on mica

- **Core-level edge**

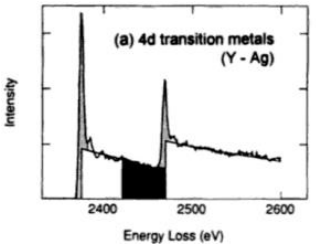
Edge intensity ∝ differential cross section
=> **energy distribution of empty states** (mainly *s, p* or molecular bands)

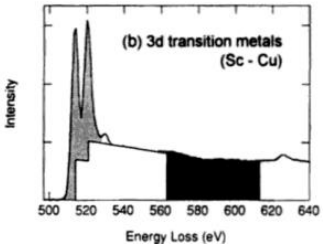
Originates from electron transitions from core orbitals to unoccupied bands
=> In first-order aproximation it images projection of the unoccupied DOS

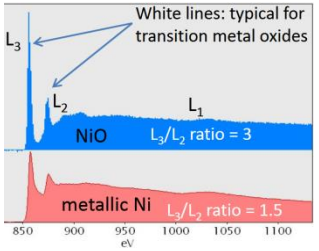


- **White line**

intensities reflect number of electrons in in the **final-state** *d* or *f* band
=> the doublet ratio does not necessarily follow the ratio of degeneracy of ground state



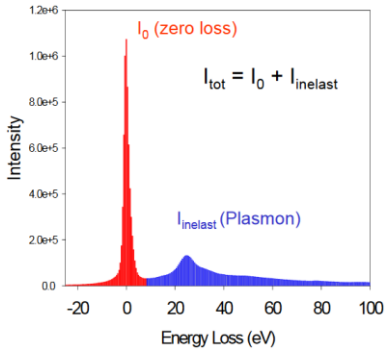




=> white line ratio can reflect oxidation state

Transmission experiment

- plasmon or edge intensity can be used to calculate thickness (relative or absolute) or IMFP



$$d = \lambda \ln\left({I_{tot}}/{I_0}\right)$$

$$\lambda \equiv \lambda(E_0, z)$$

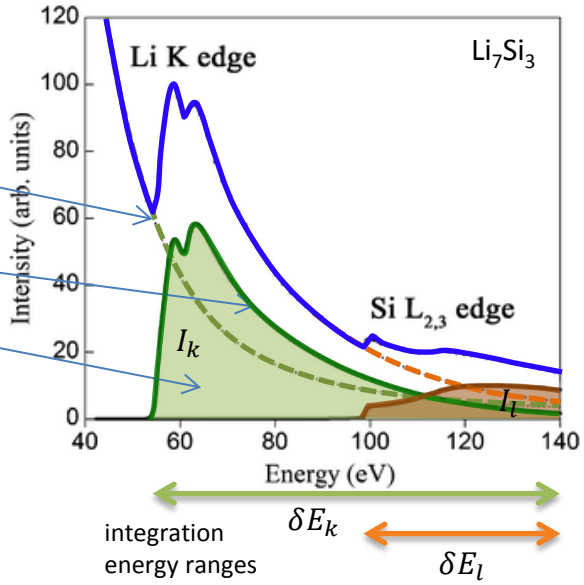
Electron energy loss spectroscopy

Quantitative analysis – edges

Steps of quantitative analysis

1) removal of background (below peak or from beneath the edge)
2) deconvolution of features
3) integration of area (within the peak or edge)
4) determination of composition

$I_{bg} = aE^{-b}$



$$I_k = I_0 \wp_k$$
$$\wp_k = N\sigma_k$$
$$N = \frac{I_k}{I_0 \sigma_k}$$

$\wp_k$ … probability of excitation of *k*-th shell
N … areal density (concentration) of analyzed element
σ_k … ionization cross-section for *k*-th shell

Applicable to any single edge

Assump. : most electrons in zero-loss peak
(=> total beam integral = I_0)
– We can instead use I_{low} … low-loss intensity integrated up to the energy loss

In general, the core-loss intensity is measured across finite energy and angle region
=> we have to consider partial I and σ: $I(\delta E, \alpha, \beta)$, $\sigma(\delta E, \alpha, \beta)$
α … incident beam convergence angle
β … collection angle

If low-loss distribution or absolute σ_i's not available:

Ratio method

$$\frac{I_k}{I_l} = \frac{\sigma_k}{\sigma_l}\frac{X_k}{X_l}$$

X_i … relative concentration

(intensities from the same spectra; if possible, also the same edge type)

Edges of all components needed

j edges measured → *j-1* equations

&

$$\sum_{i=1}^{j} X_i = 1$$

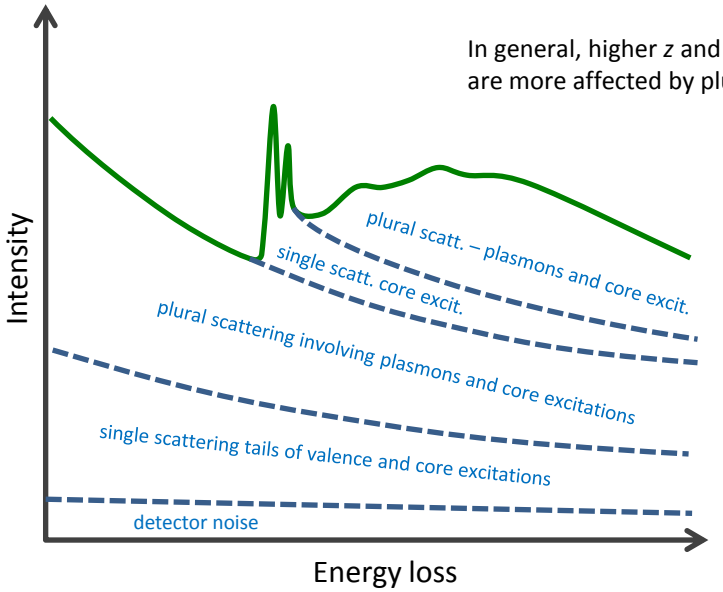
j unknowns & *j* equations → X_i

Electron energy loss spectroscopy

Quantitative analysis – multiple scattering issue

Effects of multiple (plural) scattering

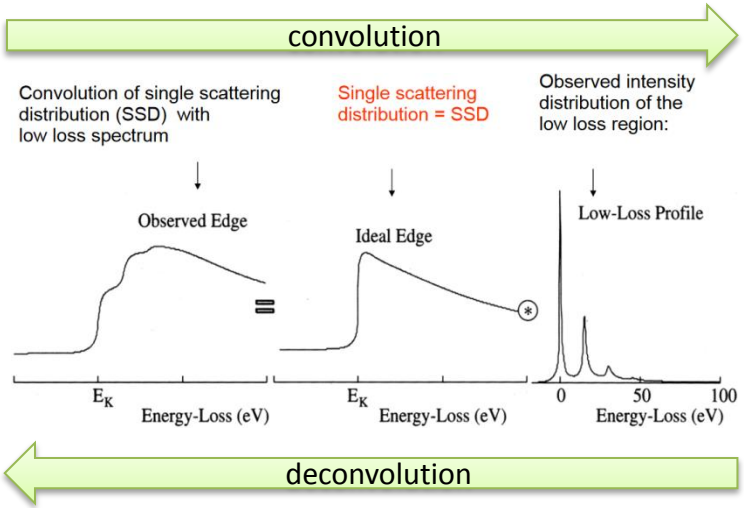
- Redistribution of core-loss intensity – due to convolution of the edge shape and low-loss spectrum
- Alteration of the edge shape and intensity, additional features



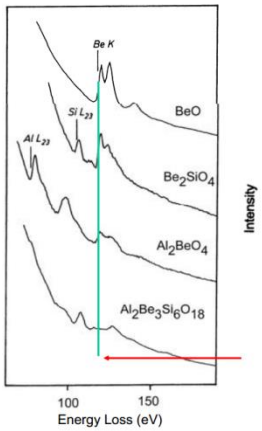
Numerical treatment methods

Fourier space: convolution → product

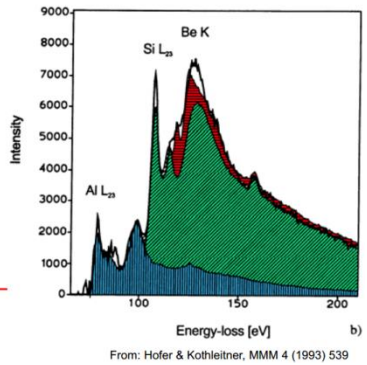
- Deconvolution (Fourier-based methods)
- Incorpotate into quantification (direct calculation, modeling)



Complicated example: overlapping edges

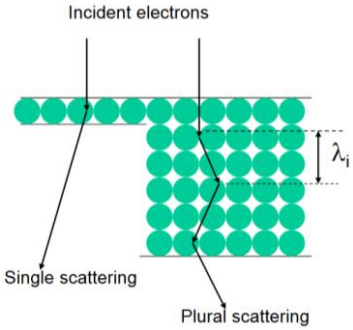


Fourier-log deconvolution from reference spectra



From: Hofer & Kothleitner, MMM 4 (1993) 539

Consideration of multiple inelastic scattering in transmission experiment



$$\lambda_i = \frac{1}{N\sigma_i}$$

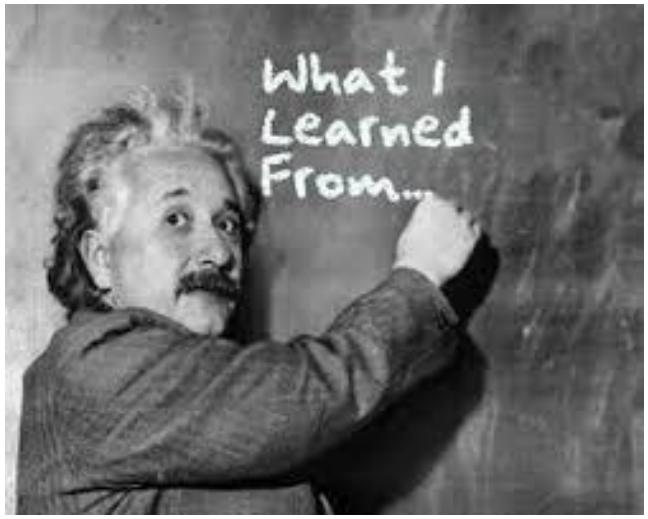
Probability for n-times scattering:

$$\wp_n = \left(\frac{d}{\lambda_i}\right)^2 e^{\frac{1}{n!}\frac{d}{\lambda_i}}$$

(Poisson distribution)

Electron energy loss spectroscopy

Take-home Messages



- Monochromatic source crucial
- One of the best methods to characterize adsorbates (especially HREELS)
- Very wide energy range (vibrations to core-levels)

Main indicators

plasmon intensity
- occupied valence band DOS

edge position
- core level position
  (effective charge on an atom – composition, valence)

edge intensity
- empty states DOS

white line intensity (or ratio)
- occupation of outer *d* or *f* bands

near edge loss structure
- local coordination

orientation dependence of ELNES
- crystallographic information
- anisotropy in the chemical bonding and band structure

Photon-excited methods equivalents

electrons	*photons*
HREELS	IRAS
ELNES	XANES
EXELFS	NEXAFS

Photoelectron spectroscopy

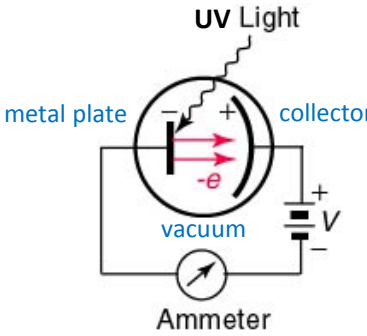
Brief history and fundamentals

Brief history

1887: Discovery of photoelectric effect (*H. Hertz*)
1895: Discovery of X-rays (*W. Röntgen*)
1899: Discovery and identification of the electron (*J.J. Thompson*)
1900: Discovery of energy quanta (black body radiation) (*M. Planck*)
1905: Quantum theory (photoelectric eff. explanation) (*A. Einstein*)
1958: UPS spectra (*W.E. Spicer*)
1967: ESCA (XPS) (*K. Siegbahn*)
Originally, ESCA was meant to provide bulk or gas-phase information; soon its surface sensitivity was discovered.
1969: First commercial XPS (HP)
1970s: First applications of synchrotron radiation
1970s+: Development of UHV instrumentation, investigation of λ of electrons

Photoelectric effect

Experiment (discovery)



Hertz:
light → charged particles

Thompson:
charged particles = electrons

Explanation (theory)

Planck, Einstein:
light is emitted and absorbed in **quanta of energy**

$$E = h\nu$$

→ electron absorbs a single quantum to leave the material

$$E_k^{max} = h(\nu - \nu_0)$$

$$E_k^{max} = h\nu - W$$

h … Planck's constant
W … work function

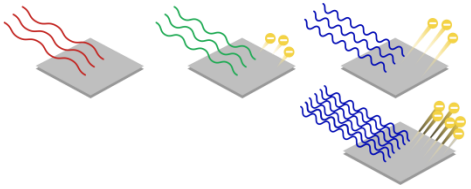
Millikan:
further verified in subsequent experiments

Classical expectations

1) Force on electrons ∝ electric field of light
$$\vec{F} = -e\vec{E}$$
=> E_k of electrons should increase with $|\vec{E}|$
2) Electron should be emitted independent of light frequency ν for sufficiently large $\vec{E}$
3) For very low light intensity: lag between exposure and el. emission (needed to absorb enough energy)

Actual results

1) Maximum E_k independent of intensity, but depends on ν.
2) Minimal cut-off frequency ν_0 required for emission
3) No time lag. Light intensity determines emission rate.



Interaction of photons with matter

Photoionization process

Photoionization

Ionization of atom (molecule, solid) by photon

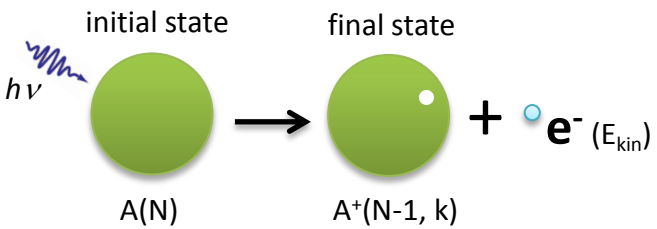
Koopmans' theorem (frozen orbital approximation)

The negative of the **HOMO energy = ionization potential**

… or: Energy required to add an electron to an excited state is eigenvalue of H_{HF} (Hartree-Fock hamiltonian)

Originally for closed-shell systems but applicable also to open-shell systems

HF approximation: orbitals of ion are identical to neutral atom (molecule) "frozen orbitals" – no orbital relaxation considered



Final state lifetime very short ($\tau \approx 10^{-15} – 10^{-14}$ s)

excited electron level

$$A(N) + h\nu \rightarrow A^+(N-1,k) + e^-$$

Energy conservation

$$\varepsilon_i(N) + h\nu = \varepsilon_f(N-1,k) + E_{kin}$$

$$E_{kin} = h\nu - \left[\varepsilon_f(N-1,k) - \varepsilon_i(N)\right]$$

$$E_B(k) = -\varepsilon_k^{HF} - \varepsilon_{relax} - \varepsilon_{correl} - \varepsilon_{rel}$$

binding energy
referenced to vacuum level

relativistic energy

correlation energy

usually very small contributions

relaxation energy

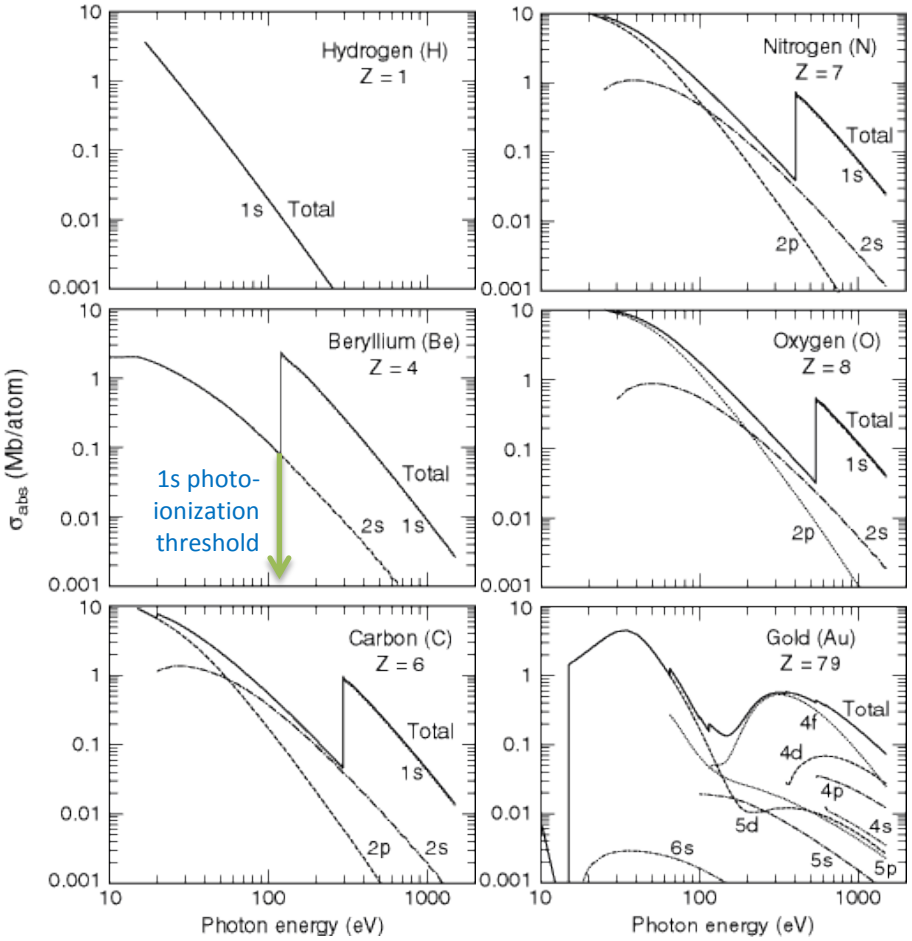
k-th orbital energy by HF first approximation calculation

Interaction of photons with matter

Photoionization process

Photoionization cross-section

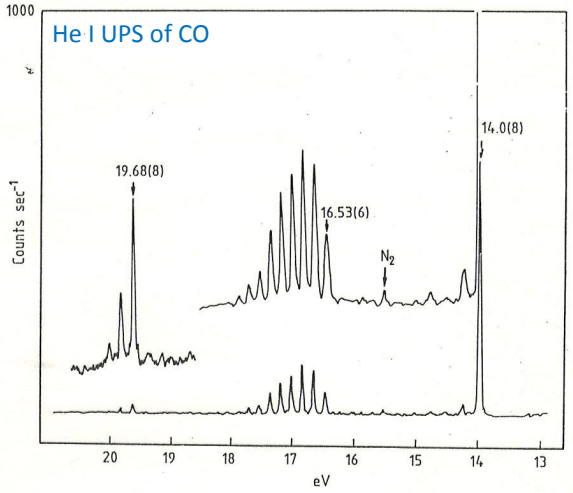
- probability of a photoionization
- quantum effect: minimal threshold $h\nu$ required
- analytical solution of $\sigma(E)$ only for H atom (z>1: numerical methods)



Numerically calculated values for isolated atoms

Photoionization of molecules

- more degrees of freedom
  => add. contribution to total energy:
  - translational and rotational E:
    too small to be resolved
  - vibrational E: fine structure (UPS)
- orientation dependent



Multi-electron system: shared e-e interactions
=> shielding of an electron has smaller impact on other electrons

Interaction of photons with matter

Photoemission process in solids

Photoemission from a solid

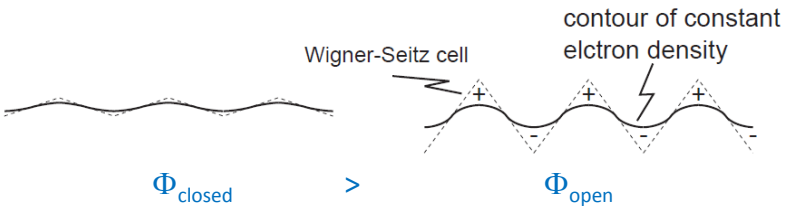
New phenomena:

- Band structure (valence electrons)
- Surface states
- Electron transport through solid => surface sensitivity (λ)
- Electrostatic surface potential (work function)
- Photon momentum has to be considered (=>dispersion/angular effects)
- Quasiparticle (manybody) effects (plasmons, phonons)

Work function

- reflects surface **charge distribution**

Surface orientation dependence (~100 meV)

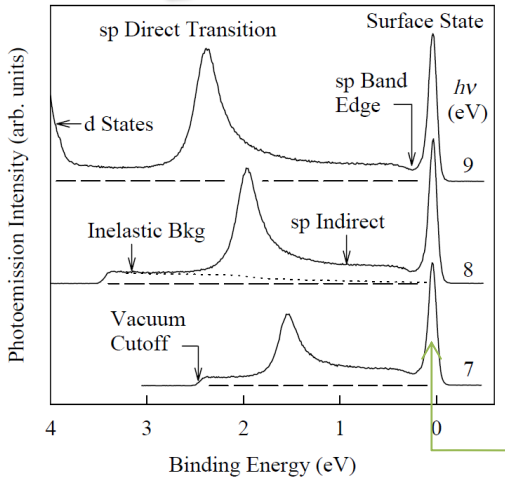


closed-packed

open- surface: charge smooting
(Smoluchowski effect)

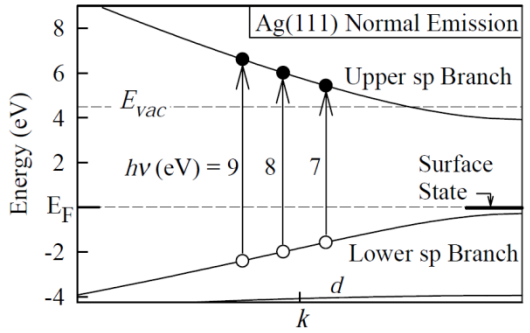
Φ change due to **adsorption** - additional dipole moment (+ or -)

spectrum



no dispersion

band diagram

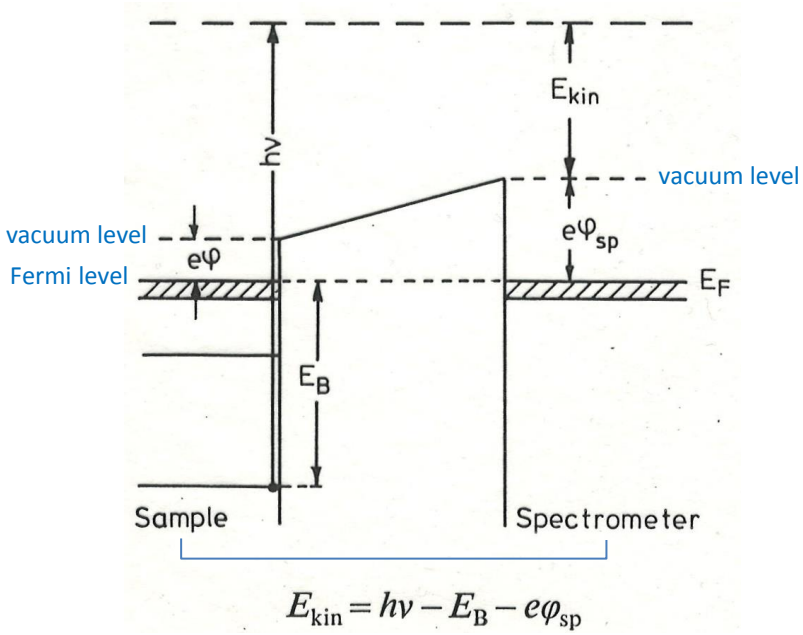


Photoelectron spectroscopy

Fundamentals

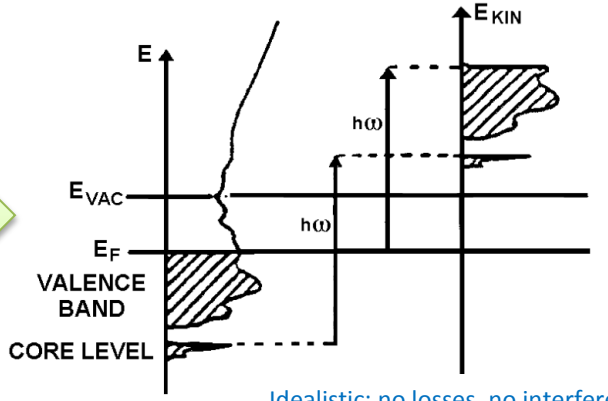
Photoelectron spectroscopy
- mapping of **occupied** electronic states up to Fermi level
  (empty states → Inverse photoemission spectroscopy)

Energy diagram of photoemission process

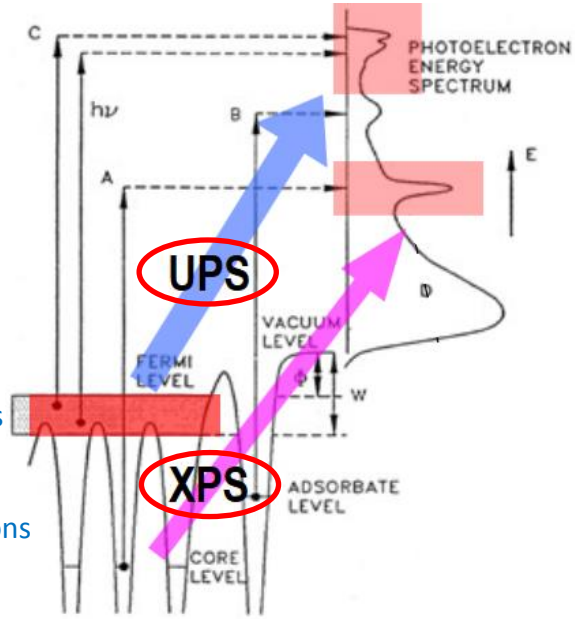


$$E_{kin} = h\nu - E_B - e\varphi_{sp}$$

Schematic representation of the density of occupied states (DOS) in the photoemission process



Idealistic: no losses, no interferences



valence electrons

core-shell electrons

Photoemission in a solid – 3-step model
1) Probability of absorption of photon by electron and its excitation
2) Probability of photelectron scattering on its path to surface
3) Probability of photoelectron transmission through surface

Often not well separable (the steps can interfere)
→ one-step model – more accurate

X-ray photoelectron spectroscopy

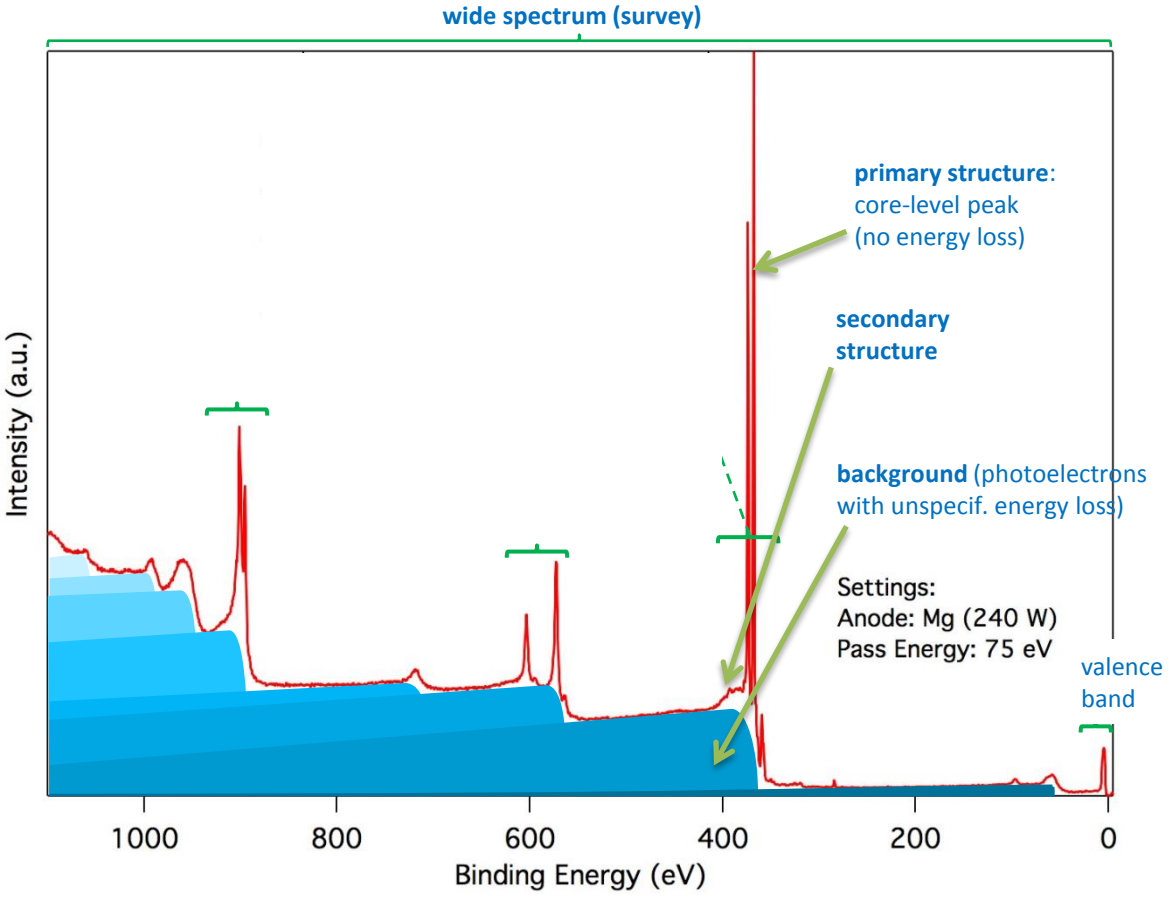
Qualitative analysis – basic identification

Basic elemental analysis

– identification by **peak positions** (element-specific core-level photoelectron energies)
– often more levels present → cross-check using relative peak intensities
– doublets wherever applicable (p, d, f) - spin-orbit splitting
→ ΔE_{split} and peaks area ratio almost invariant of environment
– take Auger peaks into account too (E_A is E_p independent)

– be aware of source-related satellite peaks (non-monochromatic sources)

z		K 1s	L-I 2s	L-II 2p1/2	L-III 2p3/2	M-I 3s	M-II 3p1/2	M-III 3p3/2	M-IV 3d3/2	M-V 3d5/2	N-I 4s	N-II 4p1/2	N-III 4p3/2	N-IV 4d3/2	N-V 4d5/2
1	H	13.6													
2	He	24.6													
3	Li	54.7													
4	Be	111.5													
5	B	188													
6	C	284.2													
7	N	409.9	37.3												
8	O	543.1	41.6												
9	F	696.7													
10	Ne	870.2	48.5	21.7	21.6										
11	Na	1070.8	63.5	30.4	30.5										
12	Mg	1303	88.6	49.6	49.21										
13	Al	1559	117.8	72.9	72.5										
14	Si	1839	149.7	99.8	99.2										
15	P	2145.5	189	136	135										
16	S	2472	230.9	163.6	162.5										
17	Cl	2822	270	202	200										
18	Ar	3205.9	326.3	250.6	248.4	29.3	15.9	15.7							
19	K	3608.4	378.6	297.3	294.6	34.8	18.3	18.3							
20	Ca	4038.5	438.4	349.7	346.2	44.3	25.4	25.4							
21	Sc	4492	498.0	403.6	398.7	51.1	28.3	28.3							
22	Ti	4966	560.9	460.2	453.8	58.7	32.6	32.6							
23	V	5465	626.7	519.8	512.1	66.3	37.2	37.2							
24	Cr	5989	696	583.8	574.1	74.1	42.2	42.2							
25	Mn	6539	769.1	649.9	638.7	82.3	47.2	47.2							
26	Fe	7112	844.6	719.9	706.8	91.3	52.7	52.7							
27	Co	7709	925.1	793.2	778.1	101	58.9	59.9							
28	Ni	8333	1008.6	870	852.7	110.8	68	66.2							
29	Cu	8979	1096.7	952.3	932.7	122.5	77.3	75.1							
30	Zn	9659	1196.2	1044.9	1021.8	139.8	91.4	88.6	10.2	10.1					
31	Ga	10367	1299.0	1143.2	1116.4	159.51	103.5	100	18.7	18.7					
32	Ge	11103	1414.6	1248.1	1217.0	180.1	124.9	120.8	29.8	29.2					
33	As	11867	1527.0	1359.1	1323.6	204.7	146.2	141.2	41.7	41.7					
34	Se	12658	1652.0	1474.3	1433.9	229.6	166.5	160.7	55.5	54.6					
35	Br	13474	1782	1596	1550	257	189	182	70	69					
36	Kr	14326	1921	1730.9	1678.4	292.8	222.2	214.4	95.0	93.8	27.5	14.1	14.1		
37	Rb	15200	2065	1864	1804	326.7	248.7	239.1	113.0	112	30.5	16.3	15.3		
38	Sr	16105	2216	2007	1940	358.7	280.3	270	136	134.2	38.9	21.6	20.1		
39	Y	17038	2373	2156	2080	392.0	310.6	298.8	157.7	155.8	43.8	24.4	23.1		
40	Zr	17998	2532	2307	2223	430.3	343.5	329.8	181.1	178.8	50.6	28.5	27.1		
41	Nb	18986	2698	2465	2371	466.6	376.1	360.6	205	202.3	56.4	32.6	30.8		
42	Mo	20000	2866	2625	2520	506.3	411.6	394	231.1	227.9	63.2	37.6	35.5		
43	Tc	21044	3043	2793	2677	544	447.6	417.7	257.6	253.9	69.5	42.3	39.9		
44	Ru	22117	3224	2967	2838	586.1	483.3	461.5	284.2	280	75	46.3	43.2		
45	Rh	23220	3412	3146	3004	628.1	521.3	496.5	311.9	307.2	81.4	50.5	47.3		
46	Pd	24350	3604	3330	3173	671.6	559.9	532.3	340.5	335.2	87.1	55.7	50.9		
47	Ag	25514	3806	3524	3351	719	603.8	573	374	368.3	97	63.7	58.3		
48	Cd	26711	4018	3727	3538	772	652.6	618.4	411.9	405.2	109.8	63.9	63.9	11.7	10.7
49	In	27940	4238	3938	3730	827.2	703.2	665.3	451.4	443.9	122.9	73.5	73.5	17.7	16.9
50	Sn	29200	4465	4156	3929	884.7	756.5	714.6	4g3.2	484.9	137.1	83.6	83.6	24.9	23.9



XPS also called:
Electron spectroscopy for chemical analysis (ESCA)

X-ray photoelectron spectroscopy

Resolution and surface sensitivity

Photoelectron energy resolution

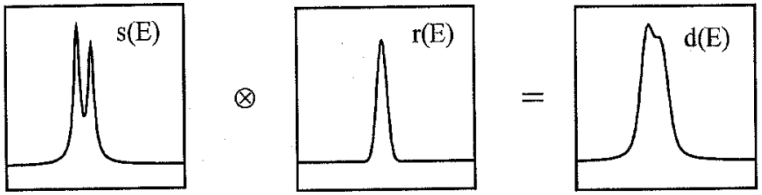
$$\Delta E_{total} = \sqrt{\Delta E_s^2 + \Delta E_x^2 + \Delta E_{an}^2}$$

ΔE_s … inherent energy linewidth of the PE production event (Lorenzian shape)
- lifetime dependent (lifetime of the core hole state) $\propto 2\hbar/\tau$
- temperature dependent (thermal broadening) $\propto {}^3/_2\, kT$

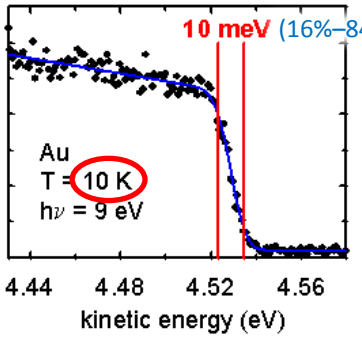
ΔE_x … exciting (x-ray) line width (modelled as a Gaussian)

ΔE_{an} … analyzer resolution (modelled as a "box" function or Gaussian)

Convolution of inherent signal with instrumental function



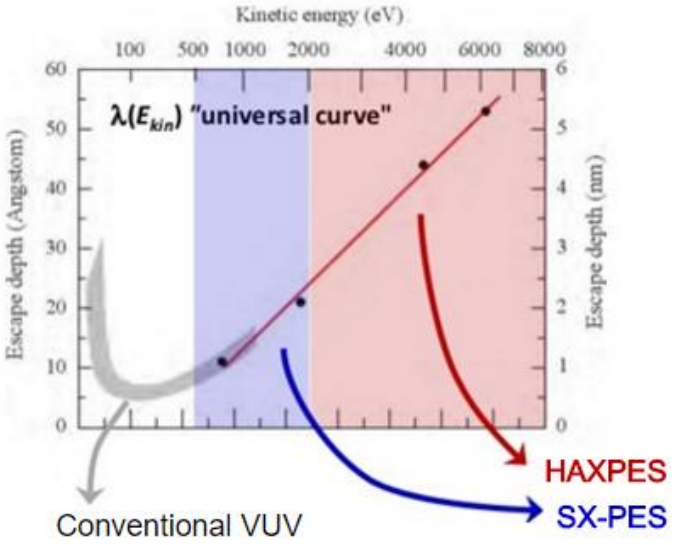
Practical measurement of total resolution



Problematic determination for
- semiconductors – E_F within gap
- insulators – additional problem of charging

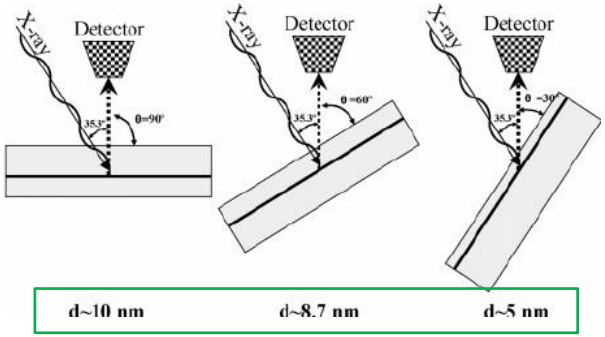
→ Some good reference core-level peak can be used (usually C 1s)

Information depth



For XPS: $3\lambda_{IMPF} \approx 2$–$10$ nm

Angular dependence



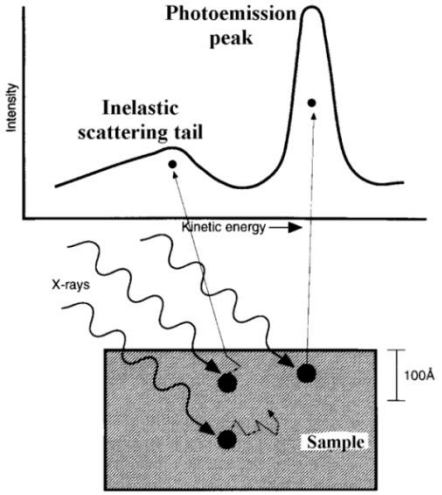
X-ray photoelectron spectroscopy

Energy loss background

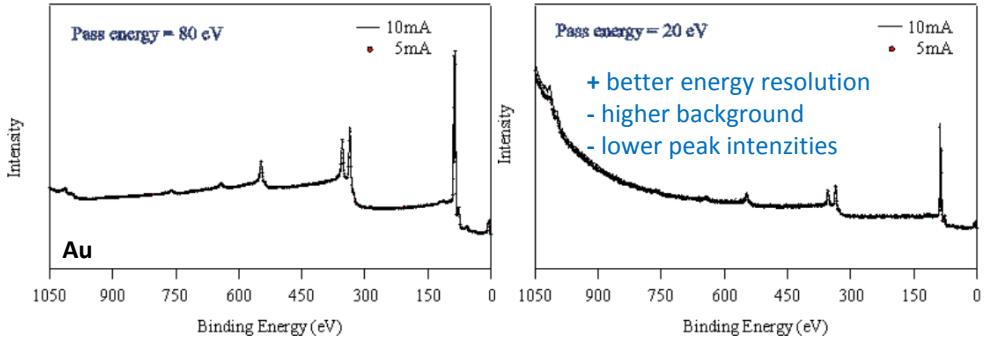
XPS background origin

Extrinsic losses

- electron-phonon events
- inelastic scattering (**photoemission non-specific** electron energy losses – a **part of electron transport process**)



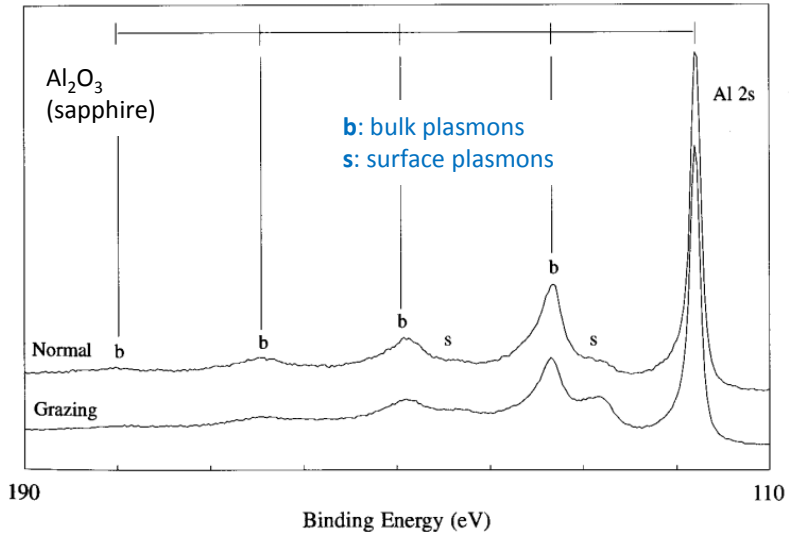
Character of background depends also on transmission function (affected by E_{pass})



vs. **Intrinsic losses**

- electron-electron events
- alternative final states (a **part of photoemission process)**

Intrinsic loss example: plasmon losses



Some photoelectrons can excite multiple modes
(equivalent to multiple loss events in an extrinsic plasmon process)

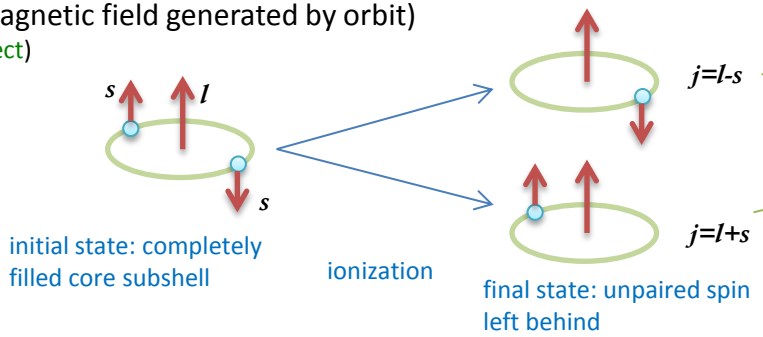
Sometimes hard to separate

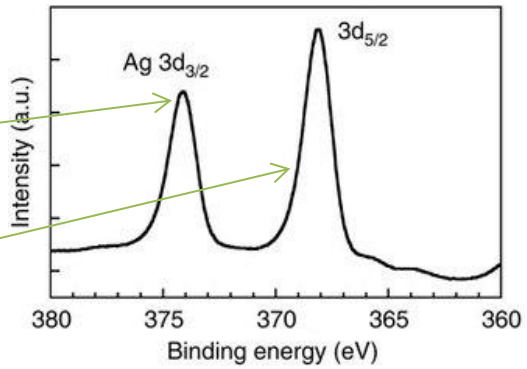
- similar timescale => extrinsic and intrinsic processes interfere coherently
- similar energy magnitude

X-ray photoelectron spectroscopy

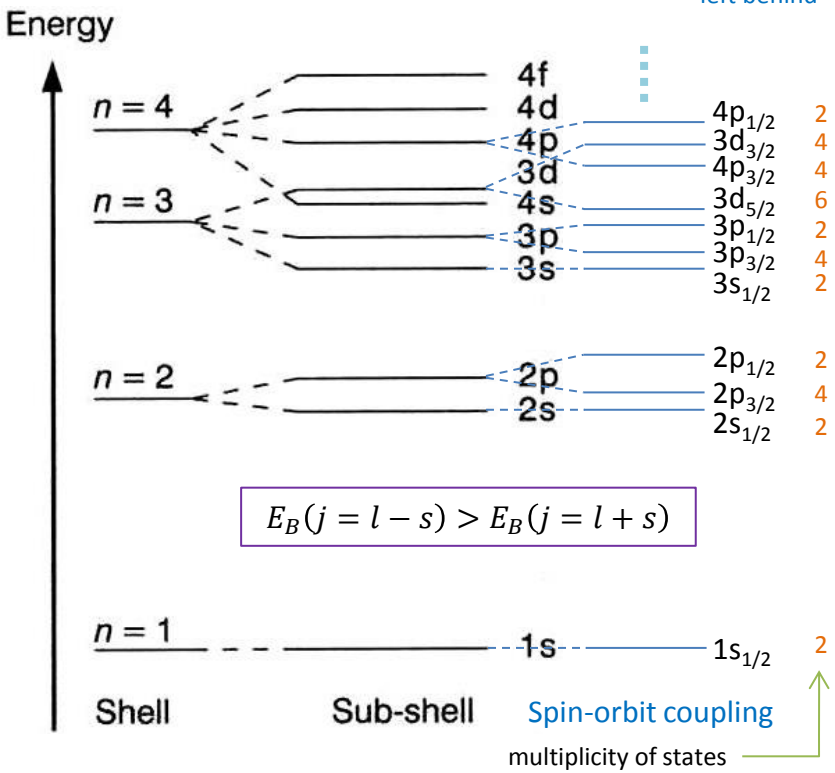
Spin-orbit splitting

Spin-orbit splitting (coupling) or **LS coupling**
- interaction between electron spin (intrinsic magnetic momentum) and its motion (magnetic field generated by orbit)
(Internal Zeeman effect)





Ag 3d: $(3d)^{10} + h\nu \rightarrow (3d)^9 + e^-$
n = 3, l = 2, s = 1/2, j = l+/-s = **5/2**, **3/2**
degeneracy: $3d_{5/2}$: 2x(5/2)+1=**6**
$3d_{3/2}$: 2x(3/2)+1=**4**



$$E_B(j = l - s) > E_B(j = l + s)$$

Intensity (branching) ratio = ratio of spin-orbit component multiplicities

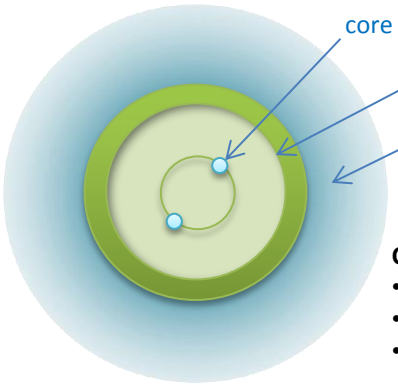
$$r = \frac{2j^+ + 1}{2j^- + 1} = \frac{2l + 2}{2l} = 1 + \frac{1}{l}$$

Subshell (*l*)	Total angular momentum (*j*) components	Ratio of the degeneracies ($g^{+/-} = 2j^{+/-} + 1$)
s (0)	1/2	---
p (1)	3/2, 1/2	4/2
d (2)	5/2, 3/2	6/4
f (3)	7/2, 5/2	8/6

X-ray photoelectron spectroscopy

Chemical shifts

Origin of chemical shift

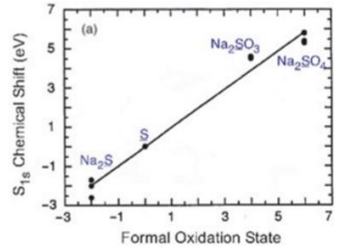


Chemical environment factors
- oxidation state
- electronegativity of neighboring atoms
- coordination number

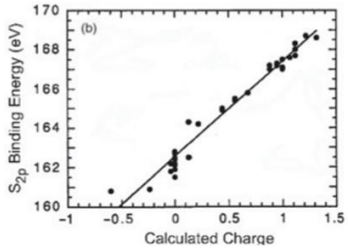
2 identical atoms in different chemical environments

$\Delta E_B = a\Delta q_i + e\Delta V_i$

Atomic and molecular solids (covalent bonds, dispersion forces, dipole-dipole forces, H bonds)
$j \approx$ atoms bound to atom i
=> ΔV_i small
=> electronegativity effects dominate q_i
=> $\Delta E_B \propto \Delta q_i$



Ionic solids (ionic bonds)
V_i summed over the whole solid
=> ΔV_i can be $\gtrsim \Delta q_i$
=> shifts can be very small even for oxidation states change (ΔV_i and Δq_i can even cancel out)



Charge potential model

$$E_B = E_B^0 + aq_i + eV_i \qquad V_i = \sum_{j \neq i} {}^{q_j}/_{r_{ij}}$$

aq_i, eV_i: contributions from surrounding atoms (→ polarizability)

${}^{q_i}/_{r_v}$ … classical potential inside hollow sphere (→ electronegativity)

E_B^0 … reference energy (neutral atom)
i, j … atom designations
r_v … average valence orbital radius

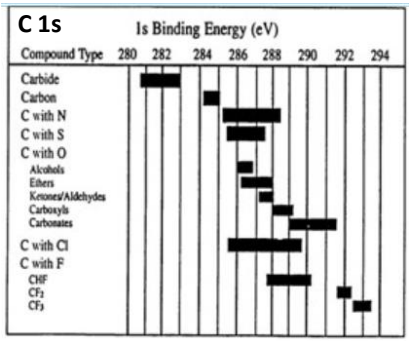
=> All core level undergo the same chem. shift (*approx.*)

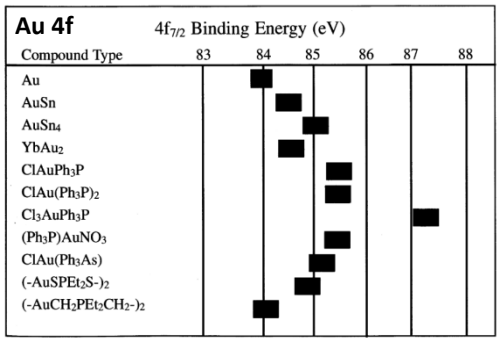
For equivalent compounds ΔE_B decrease down a periodic table column (r_j ↑)

True chemical shift is an **initial state effect**

References:
- handbooks of instrument manufacturers
- NIST database
- pure samples
- literature data

Simple assignment often impossible – tabulated values vary widely



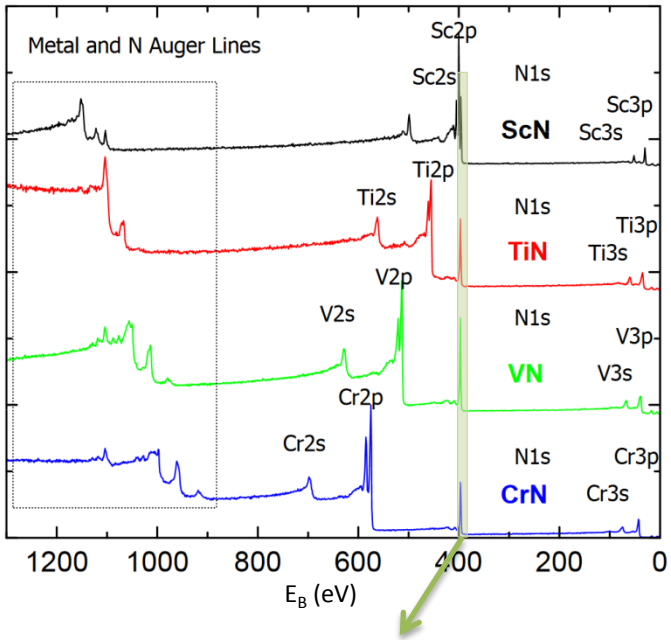


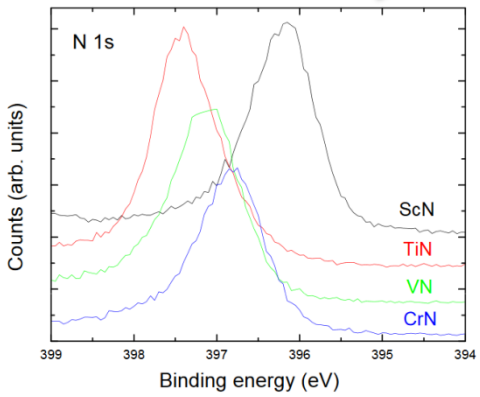
X-ray photoelectron spectroscopy

Chemical shifts – examples

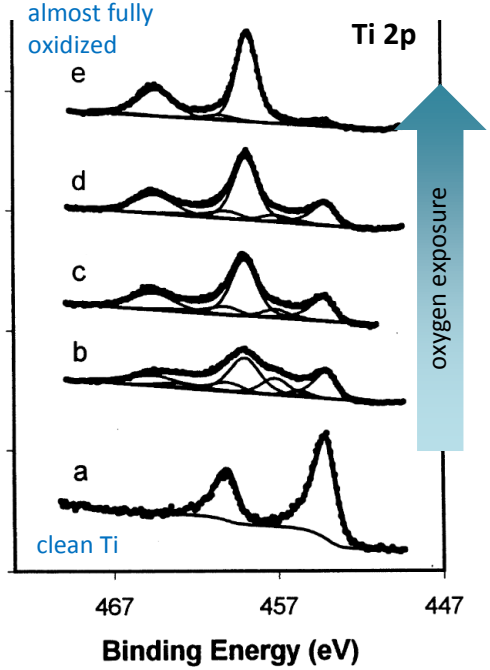
Nitride – different base metals

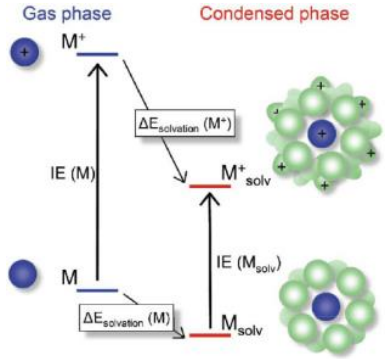
First-Row Transition Metal Nitrides (ScN, TiN, VN, and CrN)





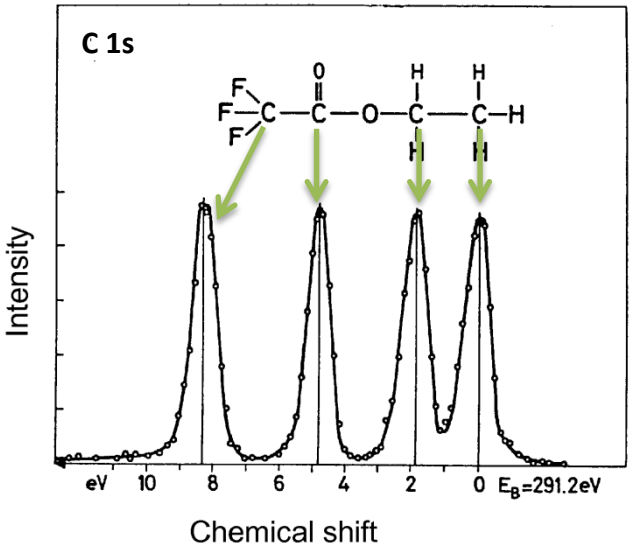
Oxide – different level of oxidation

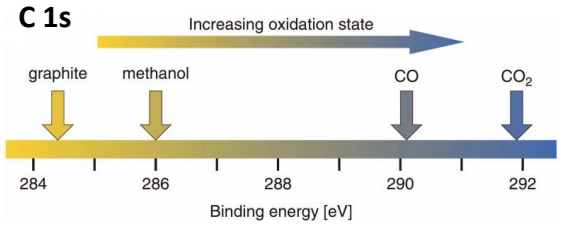




Organic molecule – different atom position

Ethyl trifluoroacetate

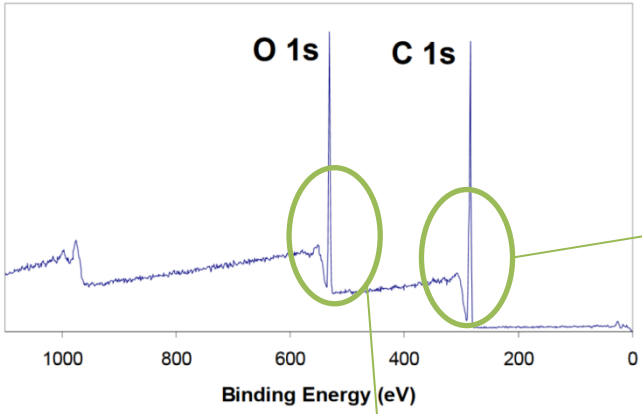


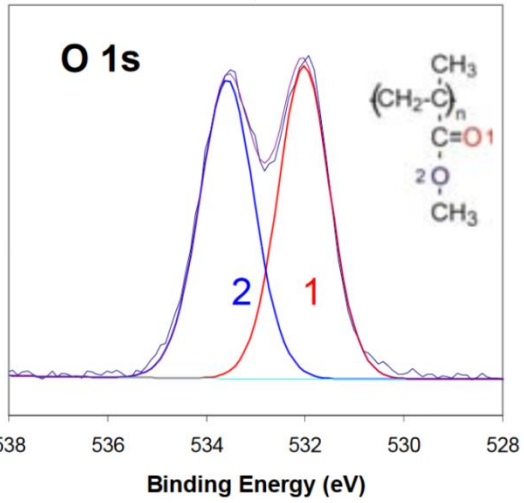


X-ray photoelectron spectroscopy

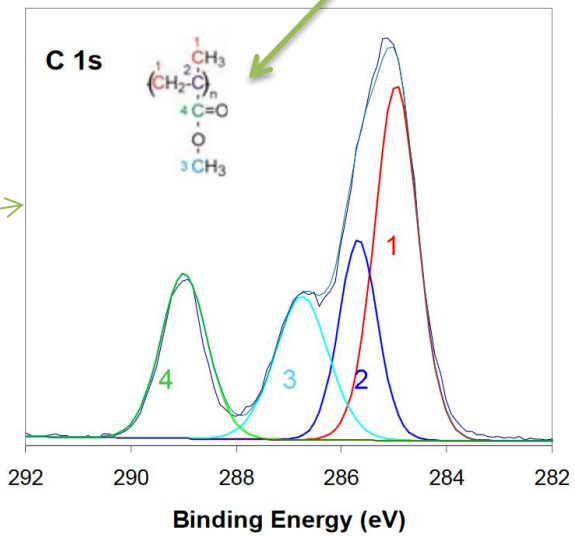
Chemical shifts – range of the effect

XPS of polymethylmethacrylate

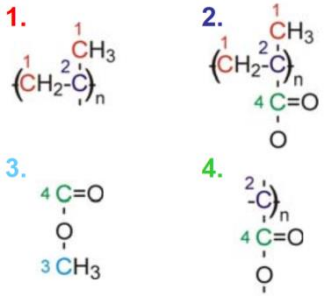




what we have…



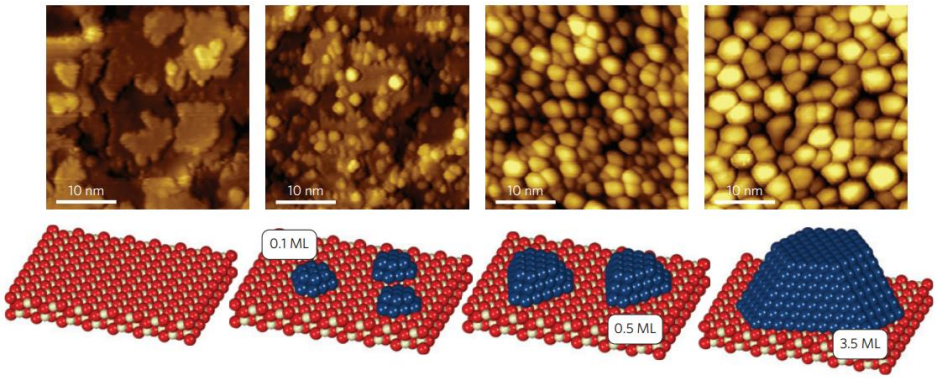
… what we actually see



Sensitivity to chemical structures with XPS is **short-ranged**.
=> Additional information or the use of complimentary methods is essential.

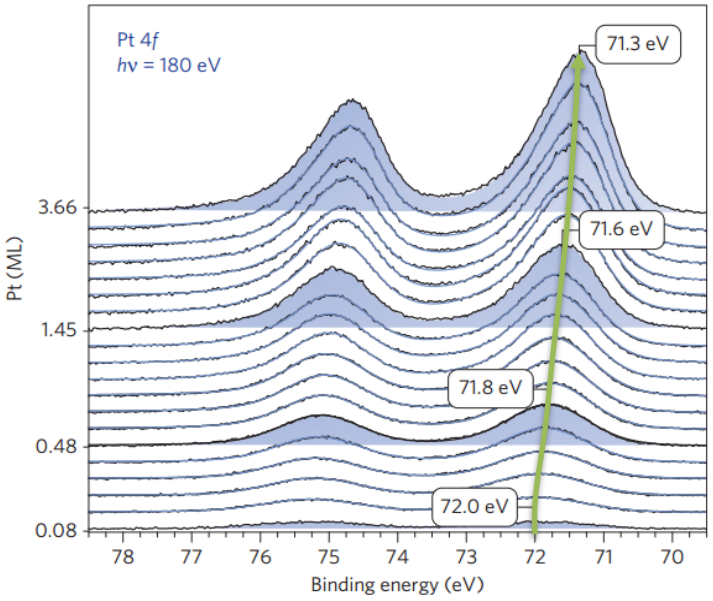
X-ray photoelectron spectroscopy

Particle size effect

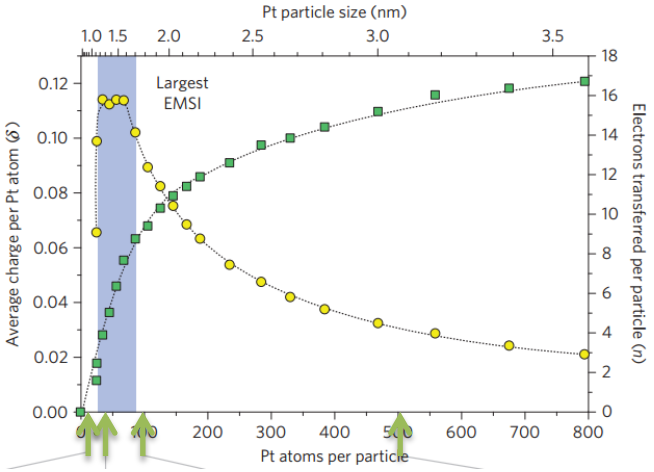


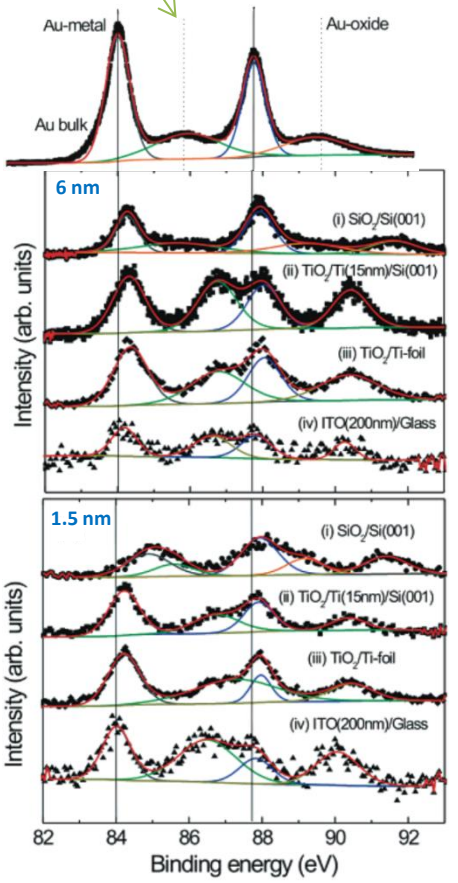
Shift of BE due to

- Intrinsic („true“): different electronic structure of NP vs bulk metal
  (atoms with different coordination numbers
  => can also depend on fine structure of particle)
- MSI: size-dependent charge transfer between NP and support
  (=> can be also very substrate-dependent)



we can even measure the charge transfer



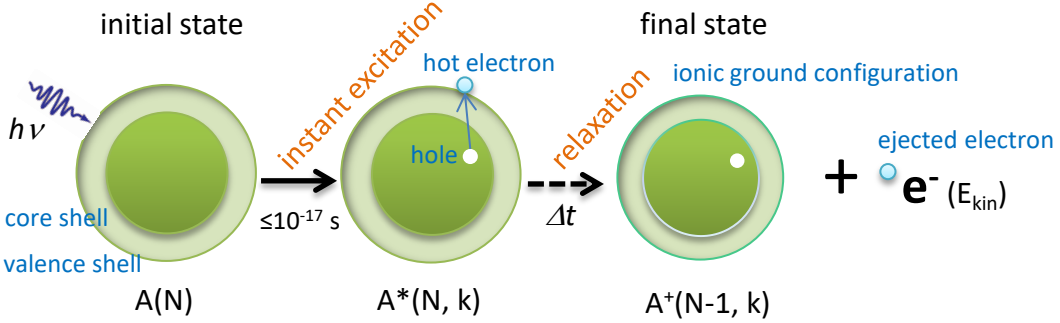


Lykhach Y., Kozlov S.M., Skála T., Tovt A., Stetsovych V., Tsud N., Dvořák F., Johánek V., Neitzel A., Mysliveček J., Fabris S., Matolín V., Neyman K.M., Libuda J.: *Counting Electrons on Catalyst Nanoparticles*, **Nature Mater.** 15(3) (2016) pp. 284-289

X-ray photoelectron spectroscopy

Final state effects

Final state consideration



$$A(N) + h\nu \;\rightarrow\; A^*(N,k) + e^- \;\rightarrow\; A^+(N-1,k) + e^-$$

Effects due to final state

- relaxation effect
- multiplet splitting
- multielectron excitations
  - shake-up, shake-off, shake-down → satellites
  - electron-hole excitation → continuous satellite (asymmetric line shape)
- (plasmon loss peaks)
- vibrational effects (UPS/VB-PES)

Ionic ground state → "parent" (main) peak
Unrelaxed states → final state must be considered

Energy conservation

$$\varepsilon_i(N) + h\nu = \varepsilon_f(N-1,k) + E_{kin}$$

$$E_{kin} = h\nu - \left[\varepsilon_f(N-1,k) - \varepsilon_i(N)\right]$$

often $\varepsilon_{relax} \approx \delta\varepsilon_{correl}$ ⇒ Koopmans' theorem good approximation

$$\ldots + \delta\varepsilon_{correl} = \varepsilon_{correl}(N-1,k) - \varepsilon_{correl}(N) > 0$$

$$E_B(k) = -\varepsilon_k^{HF} - \varepsilon_{relax} - \left[\varepsilon_{correl}(N) - \varepsilon_{correl}(N-1,k)\right] - \delta\varepsilon_{rel}$$

- $\delta\varepsilon_{rel}$ → relativistic energy term
- $\left[\varepsilon_{correl}(N) - \varepsilon_{correl}(N-1,k)\right]$ → correlation energies – must be considered for both initial and final state
- ε_{relax} → **relaxation energy**
- ε_k^{HF} → k-th **orbital energy** by HF first approximation calculation
- $E_B(k)$ → experimentally determined binding energy *referenced to vacuum level*

Improvement over Koopman's theorem: **relaxation** considered

→ lowers apparent E_B (by ~1-10 eV)

X-ray photoelectron spectroscopy

Final state effects – relaxation effect

Electron screening

- dynamic screening of the generated hole (quasiparticle) by remaining electrons

=> weaker coulombic interaction
=> higher E_k

Previous scheme: adiabatic approximation

✖

In reality: diabatic process – electron is removed quickly
=> the final state is not necessarily the ground state
(consideration of hole decay time → dynamics)

$t - t_{excit}$

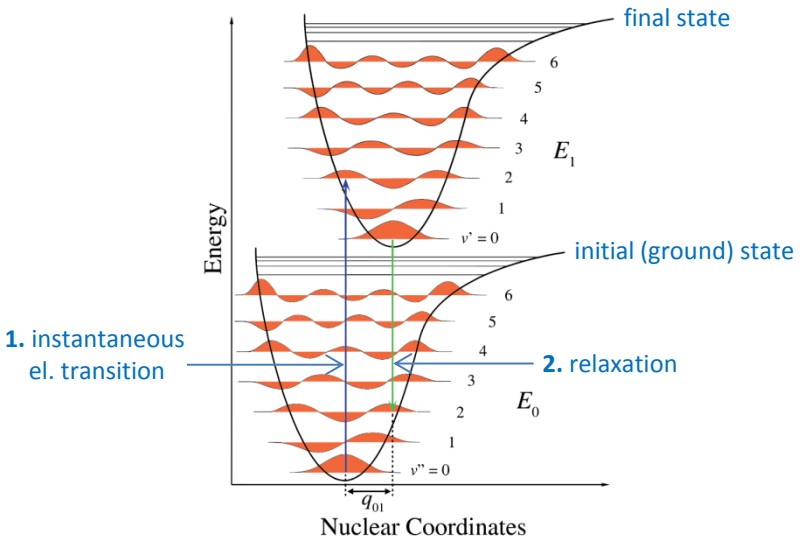
Relaxation energy → $\Delta E_B(\delta t) = h\nu - E_{kin} - \varepsilon_{relax}(\delta t) + \phi$

Relaxation time → intrinsic peak width ($\Delta E \Delta t \geq \hbar/2$)

Localized screening 10^{-16} ~10^{-15} s ⟵ Screening response time ⟶ Delocalized screening 10^{-13} ~10^{-12} s

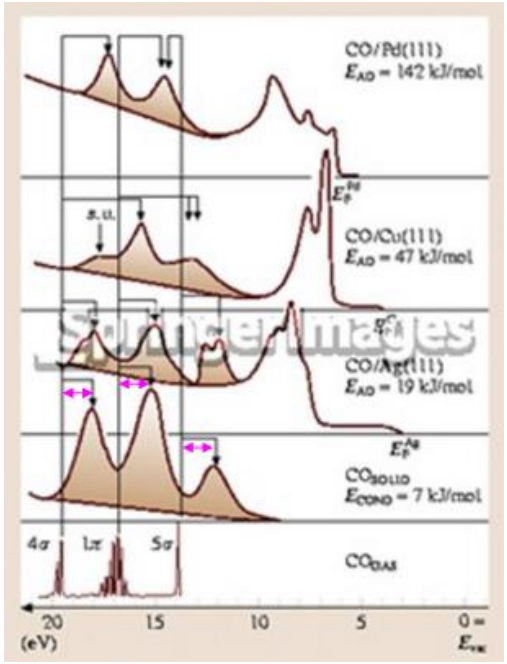
Atomic relaxation (gas phase)

Franck-Condon principle: electrons move much faster than nuclei, transition probability ∝ (overlap integral between $\psi_{initial}$ & ψ_{final})^2



Extra-atomic relaxation (solid phase)

- final state relaxation dependent on chemical environment
- many-body process



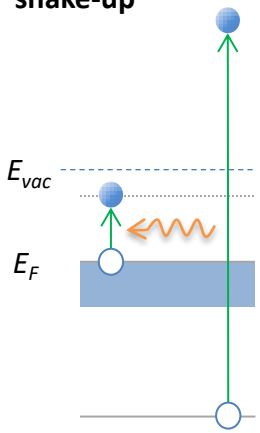
X-ray photoelectron spectroscopy

Final state effects – multielectron excitations

Shake-up and shake-off

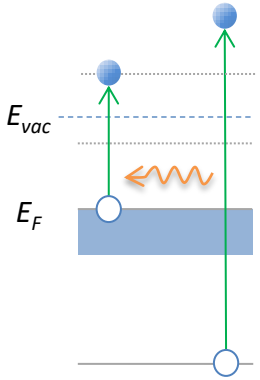
- relaxation ΔE → excitation of a valence electron
=> loss of E_k → Satellite at higher EB

shake-up



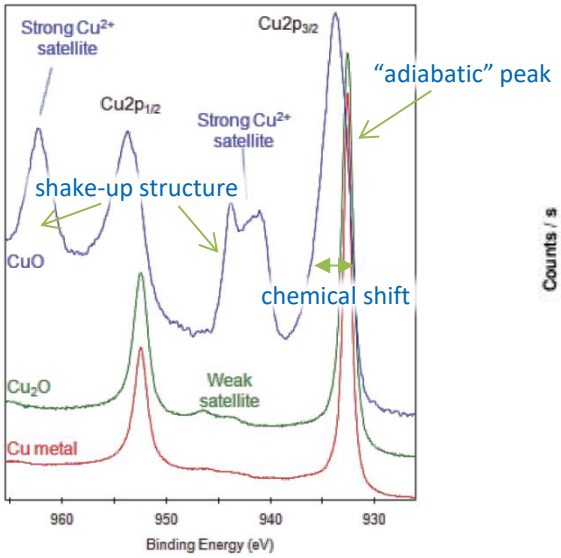
excitation to unoccupied **bound** states

shake-off



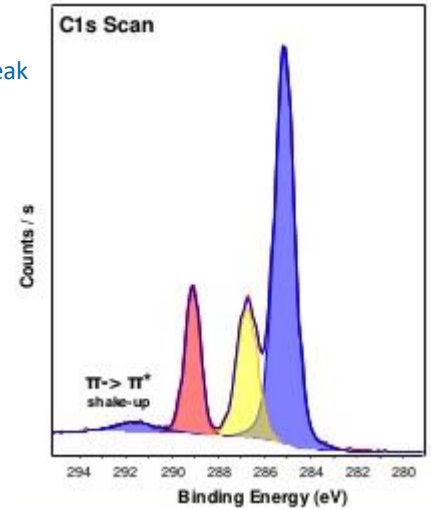
excitation to unoccupied **unbound** states
(rarely results in peaks)

Inorganics
manily transition metals and rare earths
with unpaired electrons in 3d / 4f shells



Organics

Poly(ethylene terephthalate)



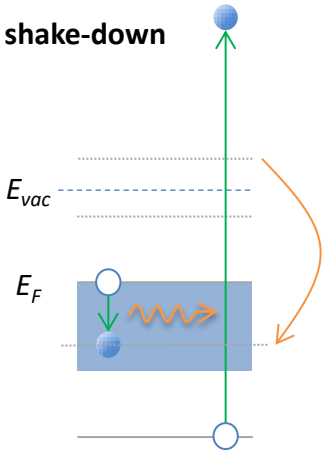
Shake-down

- electron from occupied valence state → empty state
(down-shifted by reduced screening)
=> E_k gain → Satellite at lower EB

- Usually interatomic screening-relaxation effect
(e.g. transition *O 2p* → *M 4f* in metal oxide affecting emission from *3d*)

- Relatively rare, but typical for rare-earth elements

shake-down



(Kotani-Toyozawa model)

Relaxation of an empty state
due to reduced screening

=> re-increased screening => E_k gain

Both intraatomic and interatomic interactions possible

X-ray photoelectron spectroscopy

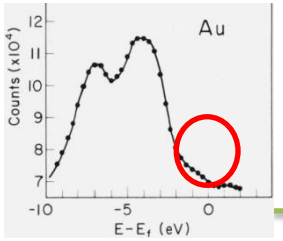
Final state effects – multielectron excitations

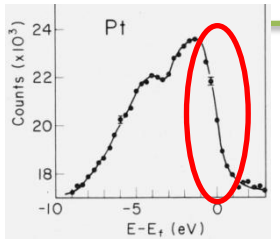
Electron-hole excitation

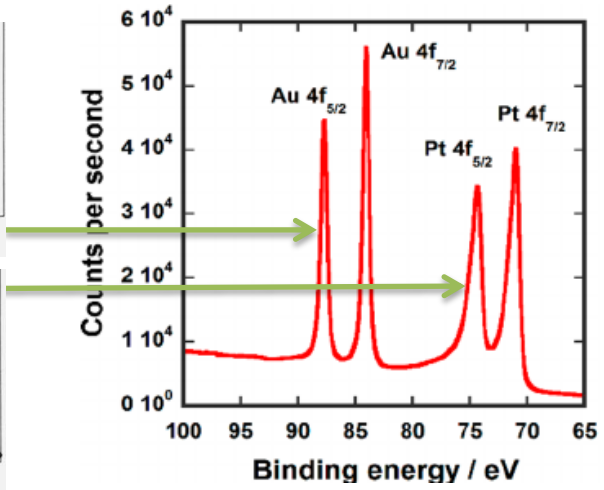
- metals: **many-body** response of a Fermi liquid to a sudden creation of a core hole
(core hole acts as potential scattering conduction electrons)

- shake-up like event within unfilled el. levels above E_F
=> high-EB **tail** – asymmetric shape, no discrete peaks

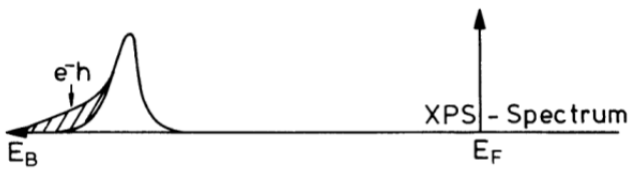
- intensity ∝ DOS at Fermi level
(=> significant for transition metals)



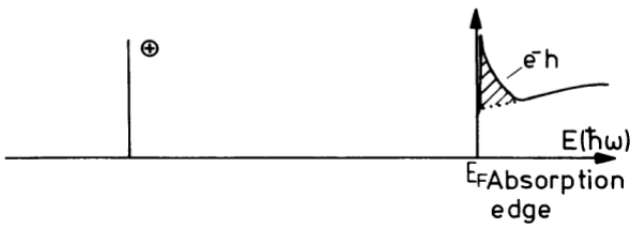




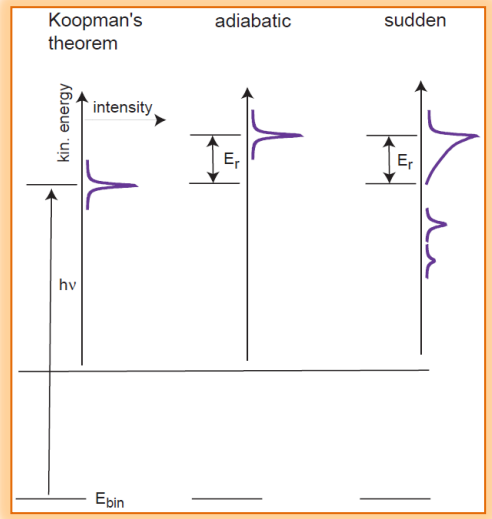
→ Doniach-Sunjic line shape



XPS



X-ray absorption



X-ray photoelectron spectroscopy

Final state effects – multiplet interactions

Multiplet splitting (exchange splitting, electrostatic splitting)

- in presence of unpaired valence electrons
- coupling between the unpaired core electron (after photoionization) with the unpaired electrons in the outer shell
- different energies for parallel and anti-parallel spins of the interacting levels

→ usually observed as an envelope of multiple structures

Multiplet Interaction

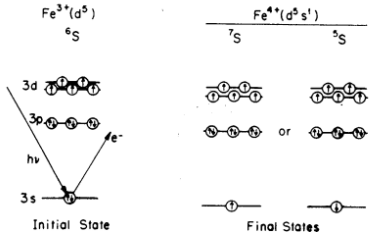


FIGURE 5.24. Schematic of multiplet splitting following photoionization in Fe^{3+}.

S level interaction

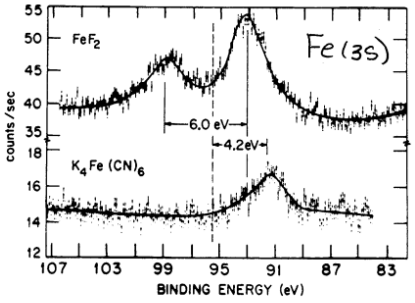
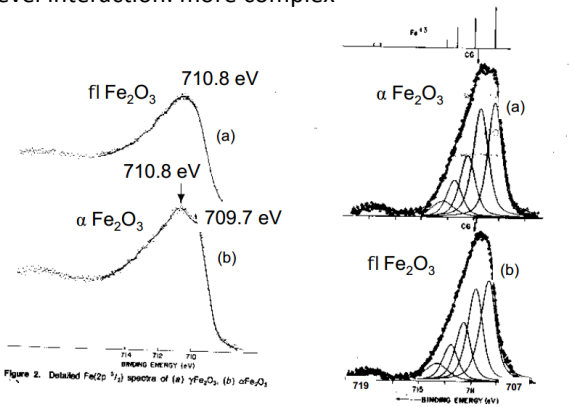


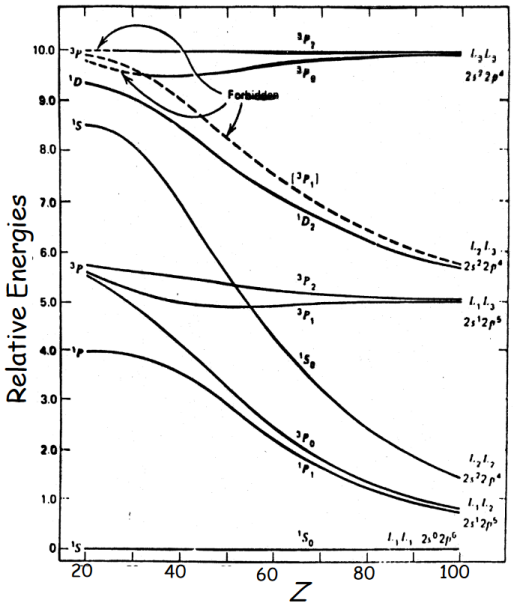
FIGURE 5.25. Photoelectron spectra of 3s shell in some transition metal compounds showing effect of multiplet splitting. [Reproduced from Carver *et al.*,[117] Figure 2.]

2p level interaction: more complex



Detailed Fe(2p$^{3/2}$) spectra of (a) flFe_2O_3 , (b) αFe_2O_3

Origin of the multiplets



L-S coupling
(normally in the final state)
(coulomb >> spin-orbit)

j-j coupling (spin-orbit interaction)
(normally for the initial state)
(spin-orbit >> coulomb)

Stark effect

Zeeman effect

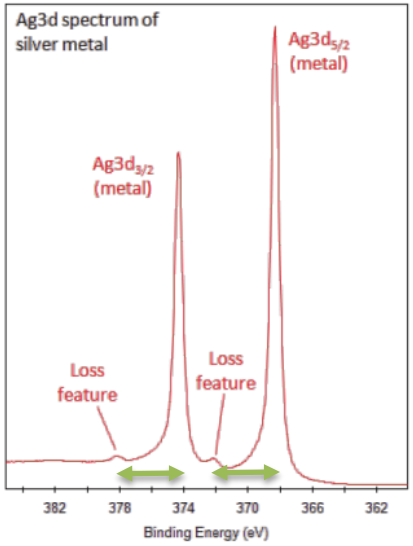
intermediate coupling
(spin-orbit ≈ coulomb)

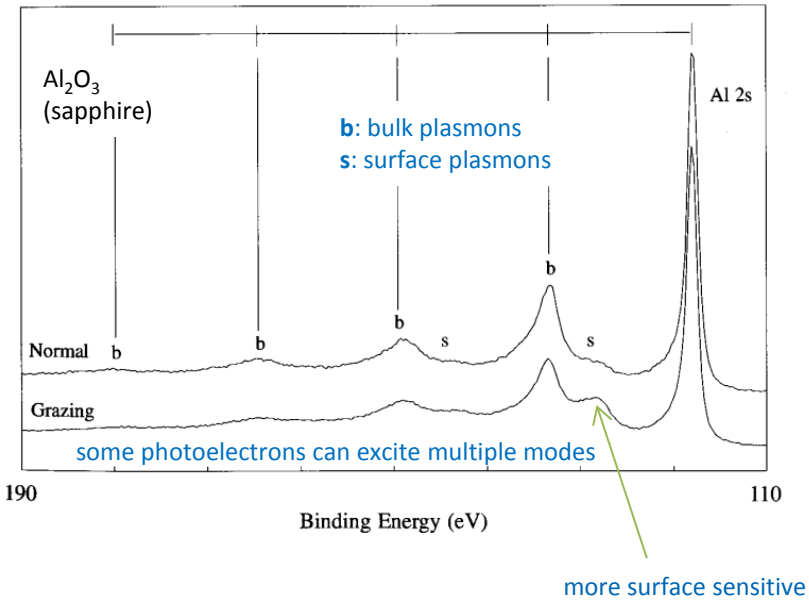
X-ray photoelectron spectroscopy

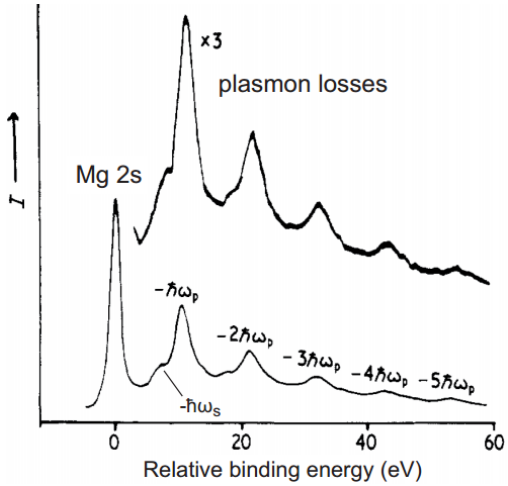
Final state effects – plasmon losses and vibrational effects

(Intrinsic) plasmon losses

Screening of core hole potential by collective oscillations of valence electrons
-bulk plasmons, sufrace plasmons
-higher modes possible







Vibrational fine structure

- solids with significant vibrational structure
- e.g. polymers – C 1s peak asymmetry mainly due to C-H stretch vibration

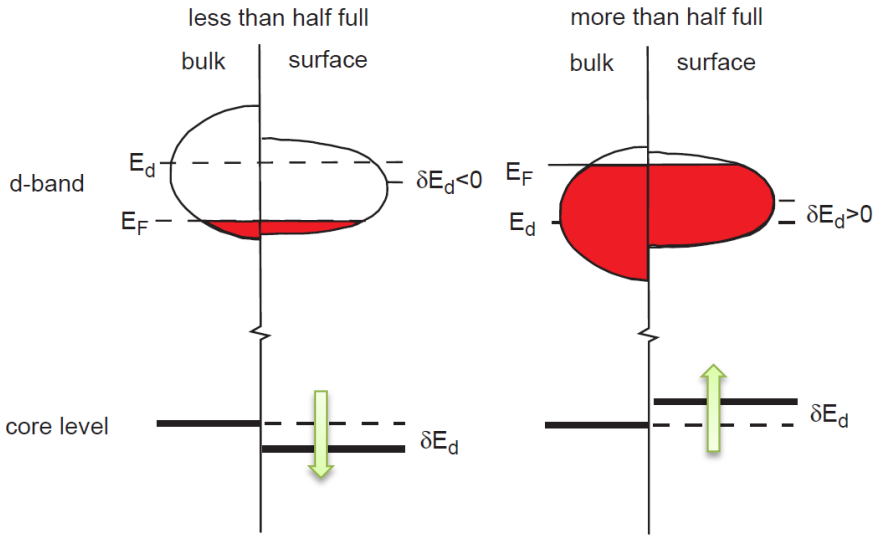
X-ray photoelectron spectroscopy

Surface core level shifts

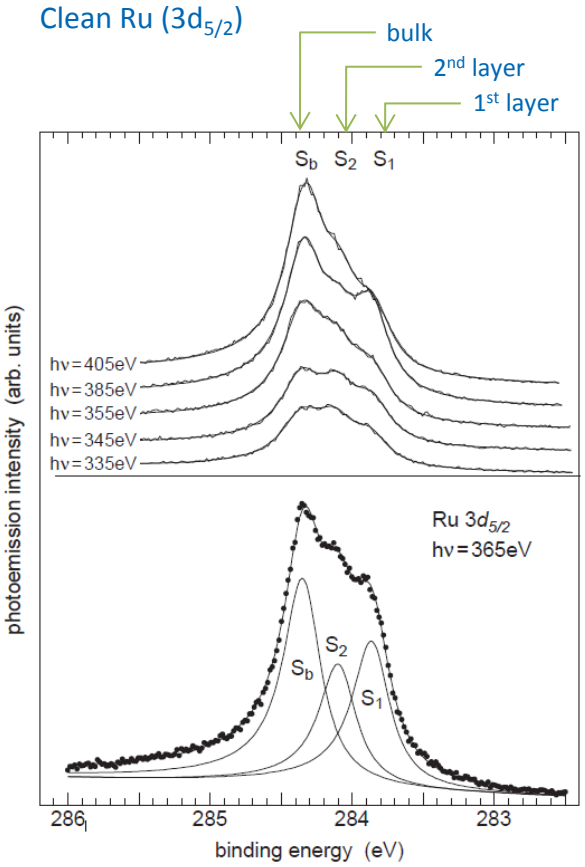
Surface core level shift (SCLS)

-related to the different surroundings of the surface and bulk atoms
-usually smaller extent than CLS => high resolution PES usually required

Surface band **narrowing** due to smaller number of nearest neighbors
→ shift of binding energy



charge neutrality => electrostatic shift

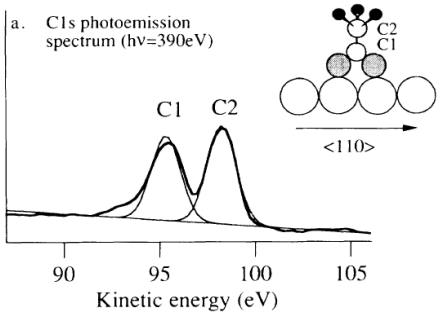


X-ray photoelectron spectroscopy

Resolution of local structures

XPS = integral method, but local-type phenomena often detectable

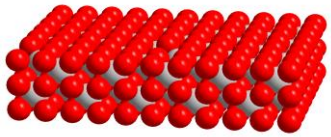
Adsorbate

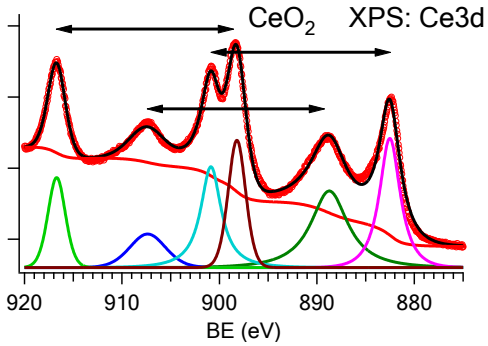


$OOCCH_3/Cu(110)$

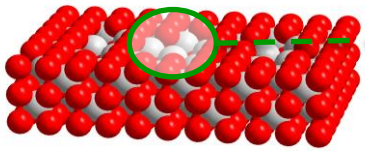
Local stoichiometry

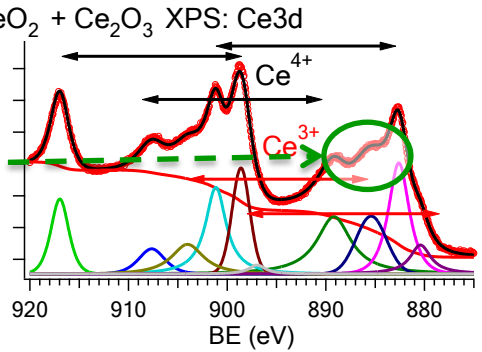
CeO_2 (100)



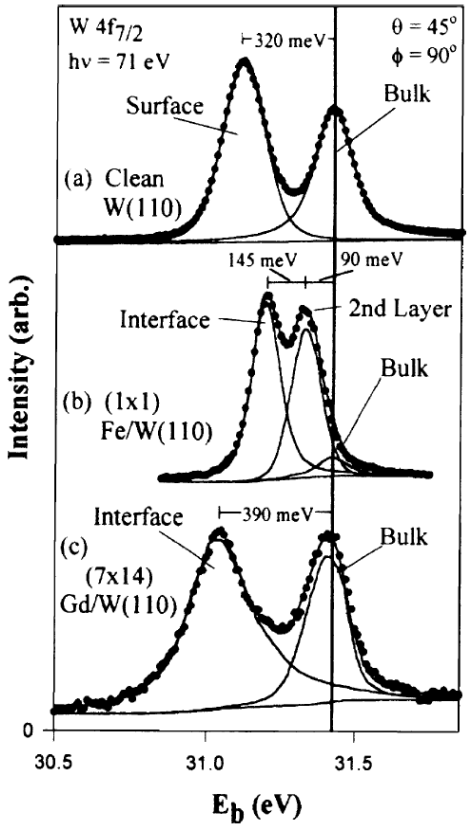


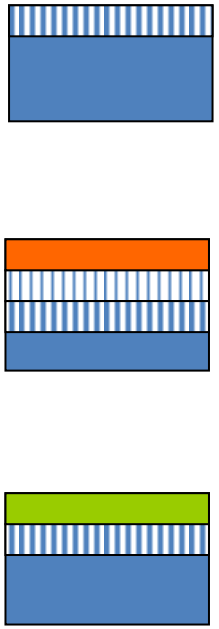
CeO_2 (100) +
Ce^{3+} oxygen vacancy





Surface and interface



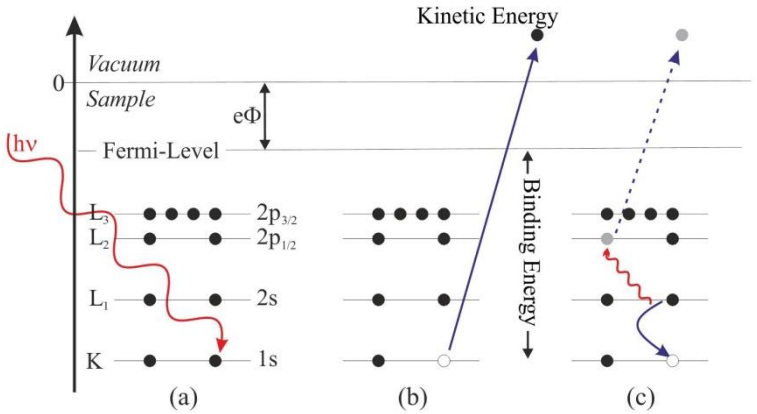


X-ray photoelectron spectroscopy

Auger features in XPS

Auger transition of photoexcited atom

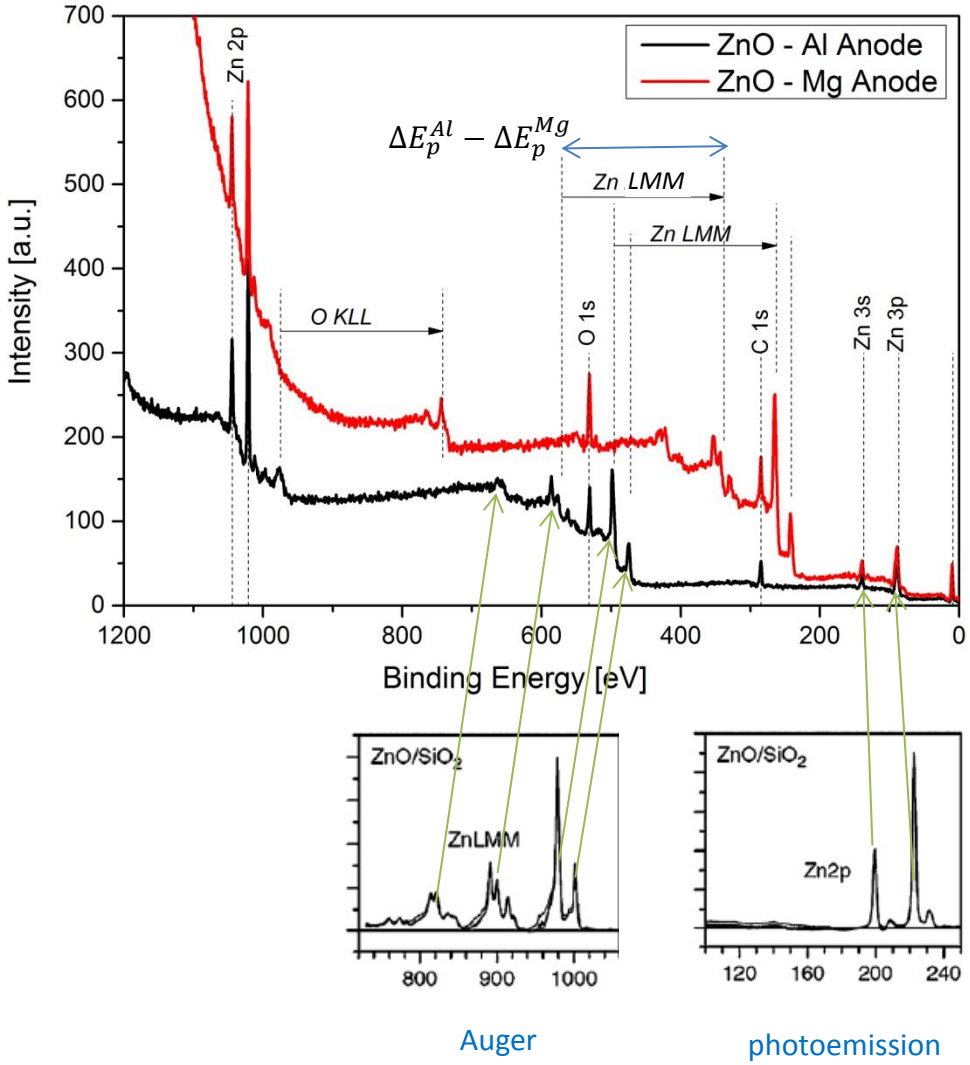
E_k independent of primary photon energy
=> distinction from PE features



Chemical effects on X-ray induced Auger peaks

Ionization -> change in
- atomic core potential
- valence charge
- charge distribution around atom
- final state – doubly-ionized system

-> affect: AE energies, lineshapes, intensity ratios
(+ satellite structure via local unoccupied DOS)



X-ray photoelectron spectroscopy

Auger parameter

Auger parameter

(def. by *Wagner*)
- primarily for prominent lines (core –level states)

$$\alpha = E_k(C_1, C_2, C_3) - E_k(C)$$

$$E_k(C_1, C_2, C_3) \approx E_b(C_1) - E_b(C_2) - E_b(C_3)$$
$$E_k(C) \approx h\nu - E_b(C)$$

Usually $C \in \{C_1, C_2, C_3\}$

1) Fixed difference between Auger and photoelectron line of the same element in a given chemical state
2) Charge shifts eliminated (are cancelled out)
3) Work function doesn't need to be considered

- Especially useful for insulators and semiconductors
- can be negative
- $\Delta\alpha \propto$ polarisability of chemical environment of core-ionized atom

(Modified) Auger parameter

$$\alpha' = E_k(C_1, C_2, C_3) + E_b(C)$$

$$\alpha' = E_k(C_1, C_2, C_3) - E_k(C) + h\nu$$

- no primary energy dependence
- used nowadays instead of α
- always positive

Auger parameter shift

Positions of compounds indicate both relaxation energy and initial state effects

$$\Delta\alpha' = \Delta E_k(C_1, C_2, C_3) + \Delta E_b(C)$$

$$\Delta E_b \approx -\Delta\varepsilon - \Delta R$$
$$\Delta E_k \approx \Delta\varepsilon + 3\Delta R$$

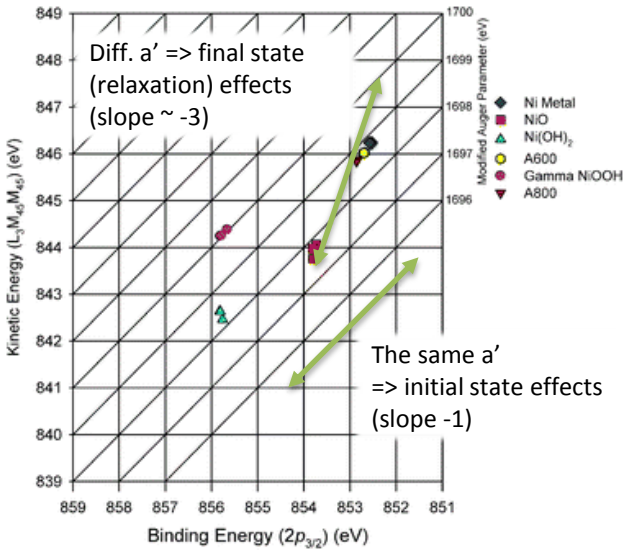
$\Delta\varepsilon$ … initial state effects (chemical shift)
ΔR … relaxation energy

=> $\Delta\alpha' \approx 2\Delta R$

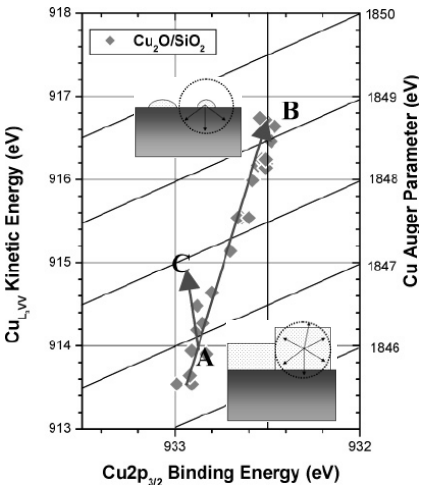
Wagner plot

= chemical state plot (diagram)

- correlation between PE and AE energies
- for most intense core PE and core-core-core AE features
- positions of compounds indicate both relax. energy and initial state effects



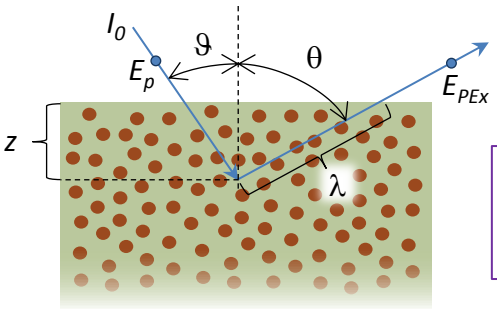
Ni $2p_{3/2}$–Ni LMM Wagner plot for Ni metal, Ni alloys, NiO, $Ni(OH)_2$ and NiOOH.x



$\Delta\alpha'$ due to polarization contribution of the support to ΔR

X-ray photoelectron spectroscopy

Quantitative analysis – homogeneous solids



m … matrix
x … analyzed element

Photoelectron line intensity

$$I_x(C) = I_0 \cos(\vartheta) A\, \sigma_x(E_p) T(E_{PEx}) D(E_{PEx}) \int_0^{\infty} N_x(z)\, e^{-z/\lambda_m(E_{PEx})\cos\theta}\, dz$$

source | atom | measurement | solid matter (PE attenuation)

Determining factors

Sample dependent terms
- photionization cross section
- concentration profile of an element
- inelastic mean free path of AE

Instrument dependent terms
- primary photon beam intensity and angle
- analysis area
- analyzer transmission function
- detector sensitivity
- photoelectron emission angle

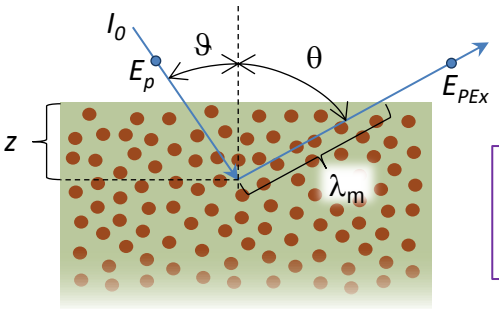
Sources of quantitative information
- primary spectral features
- inelastically-scattered electron background
- secondary electron cascade background (low $E_k \lesssim$250eV, usually ignored in XPS – low intensity and only few levels, but essential for AES)

AES and XPS quantification similar…
… but AES a bit more complex:
- more levels involved (→ *Auger transition probability*)
- secondary ionization coefficient
- inelastically scattered primary electrons => strong background

$I_x(C)$… pure PE intensities (without background)
If not angle-integrated – to be considered:
- analyzer acceptance space-angle
- angular dependence of sigma

X-ray photoelectron spectroscopy

Quantitative analysis – homogeneous solids



m … matrix
x … analyzed element

Photoelectron line intensity

$$I_x(C) = I_0 \cos(\vartheta) A\, \sigma_x(E_p) T(E_{PEx}) D(E_{PEx}) \int_0^\infty N_x(z) e^{-z/\lambda_m(E_{PEx}) \cos\theta} dz$$

independent values

$S_x(E_p, C)$

sensitivity factor

(determined theoretically or experimentally for each *z*, E_p and *X*)

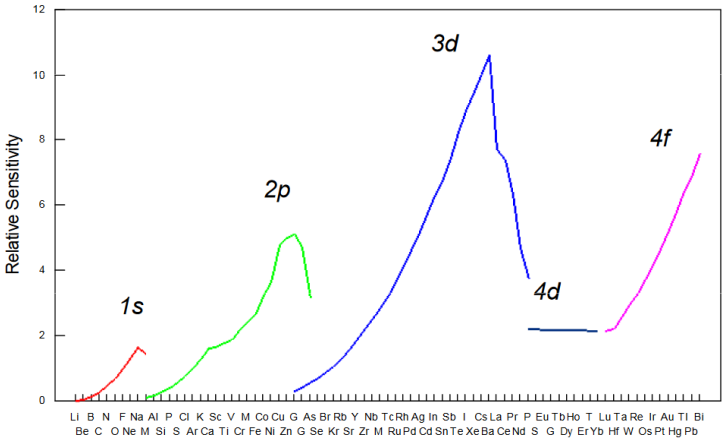
Simplification: **Homogeneous sample**

$$N_x(z) = N_x$$

$$\int_0^\infty N_x(z) e^{-z/\lambda_m(E_{PEx}) \cos\theta} dz$$

$$= N_x \int_0^\infty e^{-z/\lambda_m(E_{PEx}) \cos\theta} dz = N_x \lambda$$

- λ usually hard to determine
  => assumed constant
- anisotropy (azim. angle dependence) not considered
  (otherwise I_x should be angle-integrated)



$$N_x = N \frac{I_x / S_x}{\sum_i I_i / S_i}$$

S incorporates σ
=> angle dependent

X-ray photoelectron spectroscopy

Quantitative analysis – layer thickness

Thin layer (single-layer model)

- Thickness calculated from layer signal relative to bulk

Assumptions
- planar geometry
- homogeneous sample: $N_x(z) = const.$
- normal incidence: $\theta = 0$

"Indefinitely" thick sample (≳10-100 nm in practice)

$$I_x^{\infty}(C) = K_{instr} N_x \sigma_x(E_p) \int_0^{\infty} e^{-z/\lambda_x(E_x)}\, dz$$

Thin layer

$$I_x^{d}(C) = K_{instr} N_x \sigma_x(E_p) \int_0^{d} e^{-z/\lambda_x(E_x)}\, dz$$

=>

$$I_x^{d}(C) = I_x^{\infty}\,(C)\left(1 - e^{-d/\lambda_x(E_x)}\right)$$

=>

$$d = \lambda_x(E_x)\, ln \frac{I_x^{\infty}}{I_x^{\infty} - I_x^{d}}$$

$\theta \neq 0$:

$$d = \lambda_x(E_x)\, ln \frac{I_x^{\infty}}{I_x^{\infty} - I_x^{d}} \cos\theta$$

$\lambda(E)$ in XPS = attenuation length at photoelectron energy E: both inelastic and elastic collisions considered
$\Rightarrow \lambda > \lambda_{IMFP}$
Similar for small angles ($\theta \lesssim 50°$)

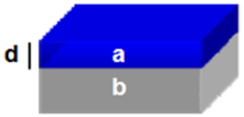
Thin overlayer (two-layer model)

- Thickness calculated from under-layer signal attenuation

Assumptions
- planar geometry
- homogeneous layers: $N_a(z) = const.$, $N_b(z) = const.$
- under-layer thick ($\gg \lambda$)

$$d = \lambda_a(E_b)\, ln \frac{I_b^{\infty}}{I_b^{att}} \cos\theta$$

$\lambda_a(E_b)$ … attenuation length of photoelectrons with kin. energy E_b in the matter a



If $d < 1$ monolayer (ML) → coverage $\Theta \approx d/d_{ML}$

If we don't know I_b^{∞} (layer a is already present)
=> determination from XPS intensities of both compounds:

$$I_a^{d} = kS_a\left(1 - e^{-d/\lambda_a(E_a)}\right)$$
$$I_b^{\infty} = kS_b e^{-d/\lambda_a(E_b)}$$

=>

$\lambda_a(E_a) \approx \lambda_a(E_b) \equiv \lambda_a$:

$$d = \lambda_a\, ln\left(1 + \frac{I_a/S_a}{I_b/S_b}\right) \cos\theta$$

Energy dependence of λ considered → numerical solution

X-ray photoelectron spectroscopy

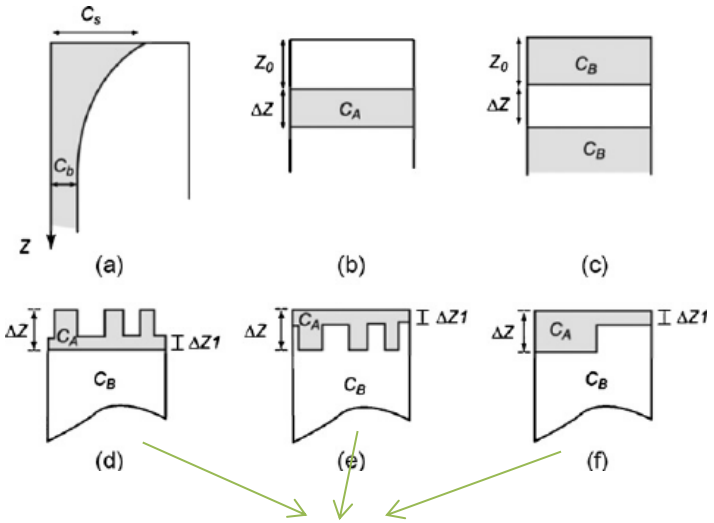
Quantitative analysis – disambiguity and use of energy losses

Traditional XPS quantification assumes
- sample surface (detected depth) is homogeneous
- surface concentrations are directly proportional to peak intensities

Non-homogeneous samples
– more complicated and sometimes disambiguous

More accurate quantification should include
- peak intensity
- peak shape
- background signal

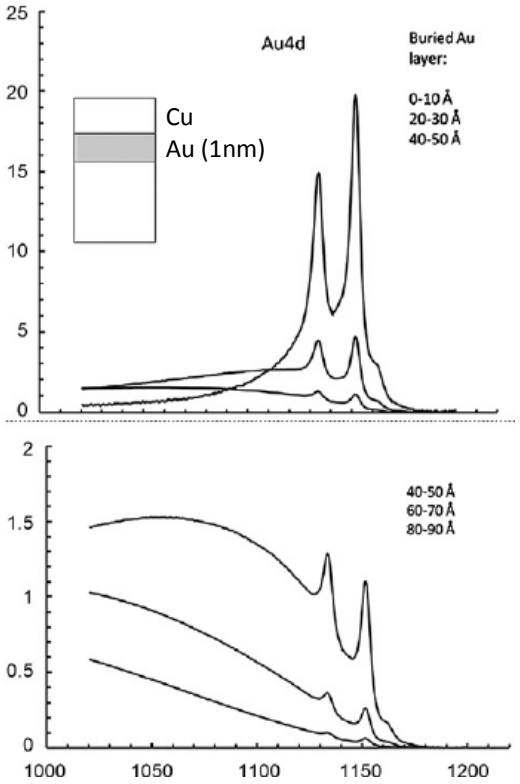
Examples of in-depth profiles



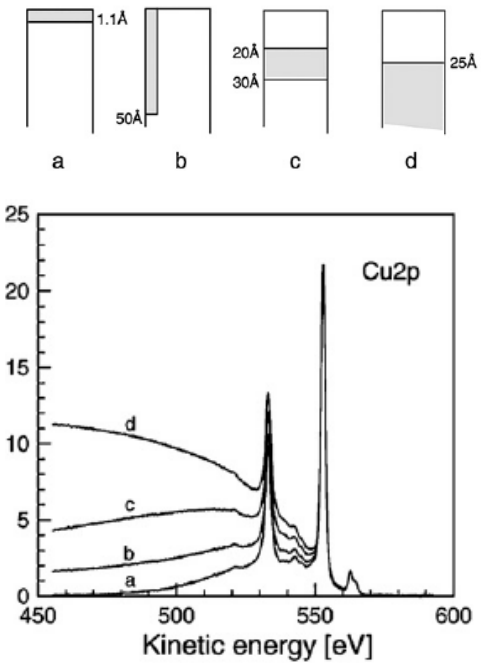
Give identical spectra

Tougaard's method (software *Quases*)
– fitting of inelastic scattering tail (background)

Different peak intensities (and known structure)



The same peak intensities



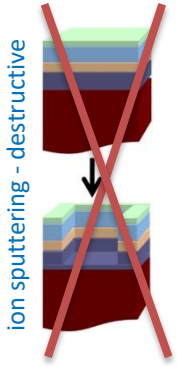
Angle resolved XPS

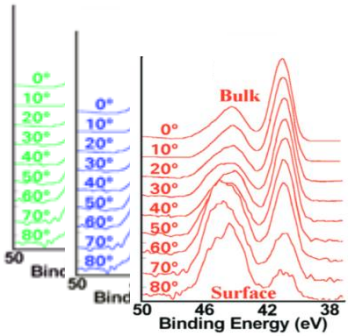
Depth profiling

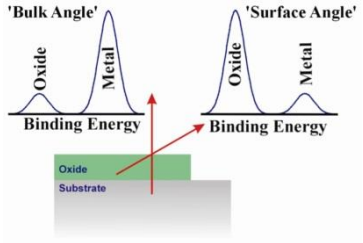
Conventional (serial) ARXPS

1) slit limiting angular acceptance
2) step-wise sample tilting
3) scanning through electron energies

Surface sensitivity ∝ detection angle
=> non-destructive depth profiling

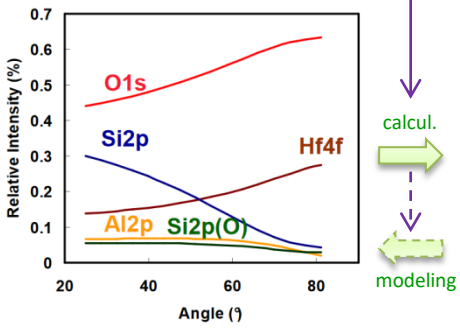






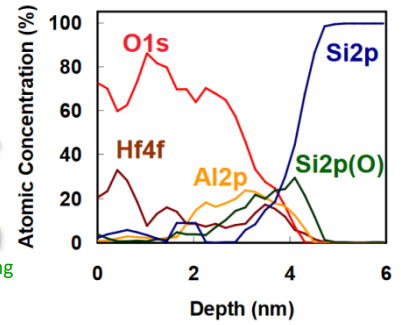
Beer-Lambert

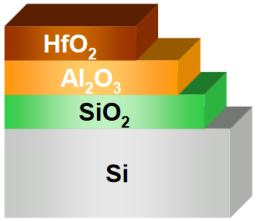
$$I_a(\theta) \propto \int_0^{\infty} c_a(z) e^{-z/\lambda_a \cos(\theta)}\, dz$$



calcul.

modeling

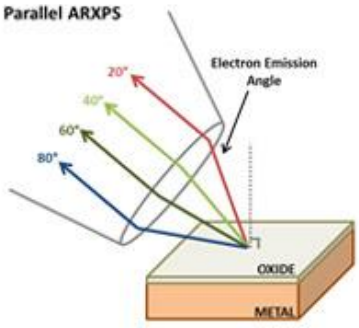


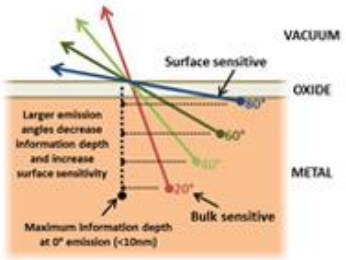


relative depth profile (RDP)

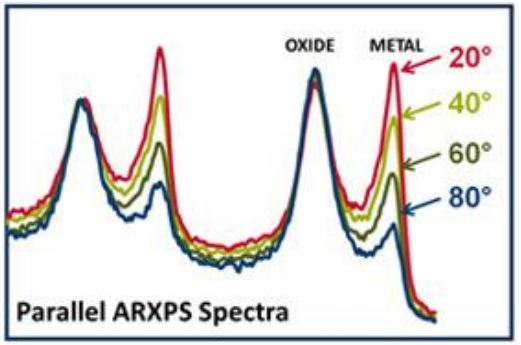
Parallel ARXPS

- additional el. optics and multi-channel detector
- no sample tilting needed
- with **2D detector**: energy dispersion measured directly (no energy scanning needed)





Spectra set obtained in a “single-shot”!



Ultraviolet photoelectron spectroscopy

Basics

Basic properties and applications

- mapping of valence electrons for both substrate and adsorbate
- study of chemisorption (determination of bonding orbital, bond strength, …)
- vibrational states accessible (higher resolution)
- most common sources: He (*21.2, 40.8 eV*) and Ne (*16.8, 28.6 eV*), synchrotron radiation (*tunable*)

UPS quantification

- valence orbital energies (& compar. to QM theory)
- interaction strengths and bond energies
- adsorbate coverage
- work function determination

Three-step model

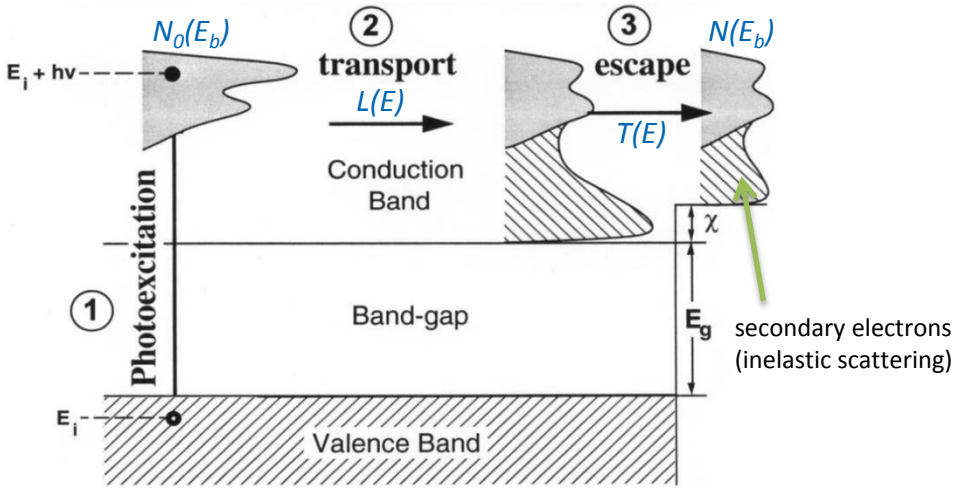
Energy distribution:

$$N(E_b) = AN_0(E_b)L(E_k)T(E_k)$$

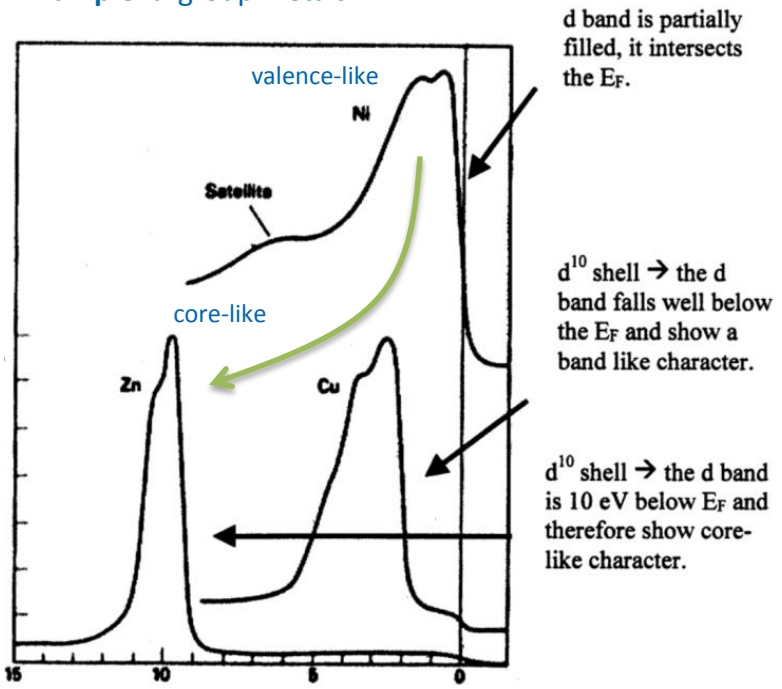
$$L(E_k) \approx \frac{\lambda(E_k)}{\alpha(h\nu)}$$

α … light absorption coefficient

T … smooth „cut-off“ function – doesn’t introduce any structure to spectra



Example: *d*-group metals

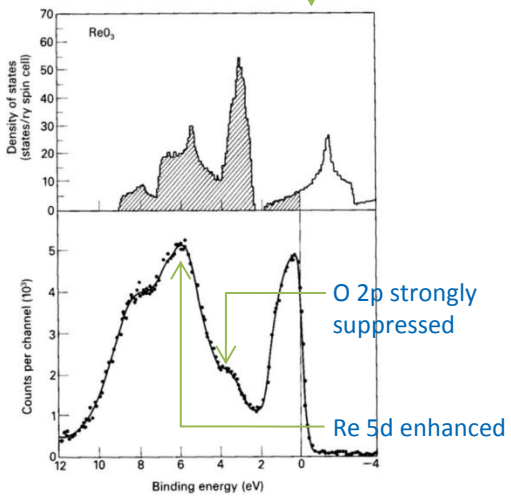


Ultraviolet photoelectron spectroscopy

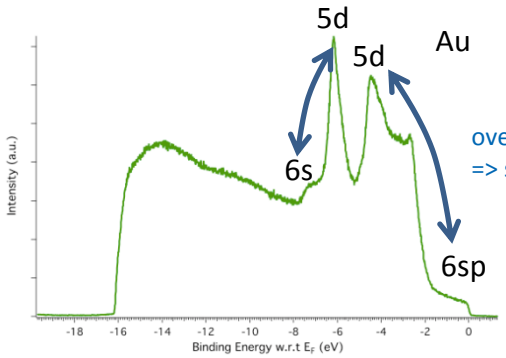
General issues

- There is no well-defined boundary between **valence** and **core-level** electrons (up to ~10-15 eV) => overlaps possible

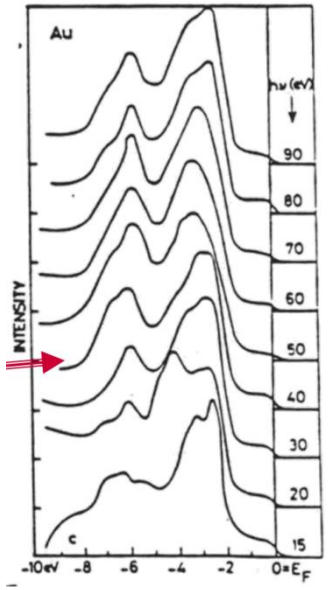
- **Photoelectron spectrum ≠ DOS**
- hole-lifetime broadening ($\propto E_b$)
- cross-section differences
- multi-electron excitations (e.g., resonances)
  – peaks possible in empty parts of DOS



- Unlike XPS, UPS also sensitive to empty DOS
- Low $h\nu$ => Spectrum distortion due to high SE background
- Hybridization effects



- Strong dependence of VB spectra on photon energy (esp. low $h\nu$)



- Selection rules (k conservation) in solids
  – direct/indirect transitions

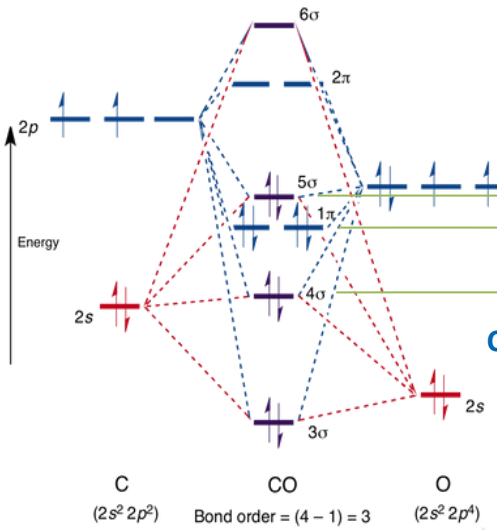
Ultraviolet photoelectron spectroscopy

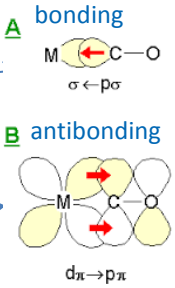
Adsorption on solids

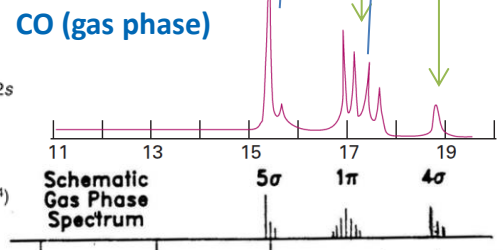
Chemisorption studies by UPS

- based upon comparison of **gas phase** and **chemisorbed** spectra

- energy level positions
  → orbital identification
- energy level shifts and shape changes
  → nature of bonding, charge transfer across interface
- polarization and photon energy dependence
  → orientation (structural information)



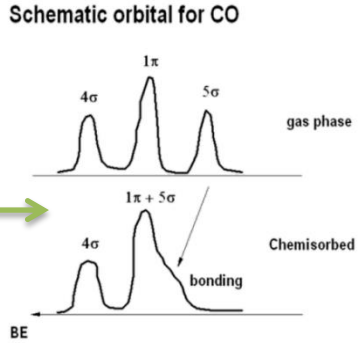




Adsorbate vs. gas phase

- Superimposition
- Overlap of substrate and molecular levels

- Selective intensity change
- charge transfer (donation/acceptance)

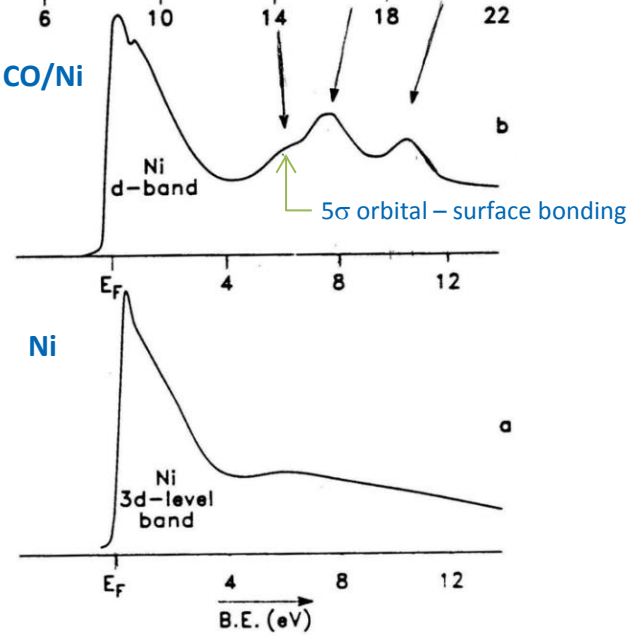


- Broadening

– initial state effect: coupling of adsorbate levels and surface bands
– final state effects: inelastic processes, reduce lifiteme of excitation

- Shifts

-work function of adsorbate level
-chemical shift (initial state effect)
-extramolecular screening (final state effect)



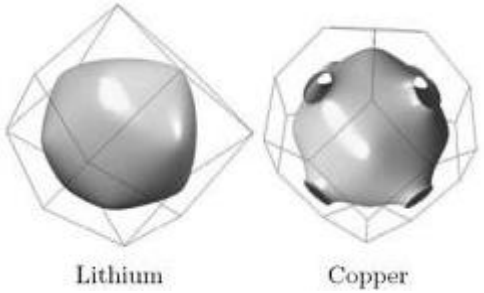
Angle resolved UPS

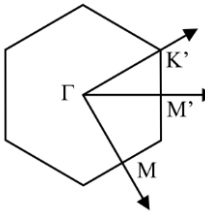
Fermi surface scans

Fermi surface
- Abstract boundary between ccupied and unoccupied electronic levels
- Changes shape upon bonding
- Many implications for transport (thermal, electrical), optical, magnetic, and equilibrium properties

Fermi surface scan (mapping)
- Setting the energy windows to a small interval around E_F ($dE_b \approx E_F$)
- Accumulating the data over the crystal hemisphere (azimuthal and polar angles)

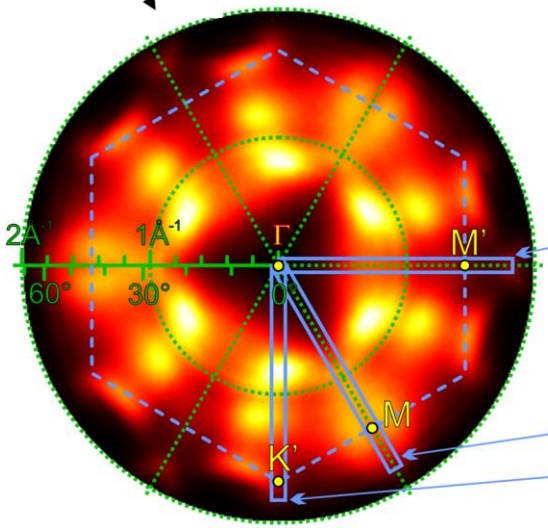
FS simplest case: **Li**
- atom: spherical between *2s* and *2p*
- lattice: spherical symmetry broken

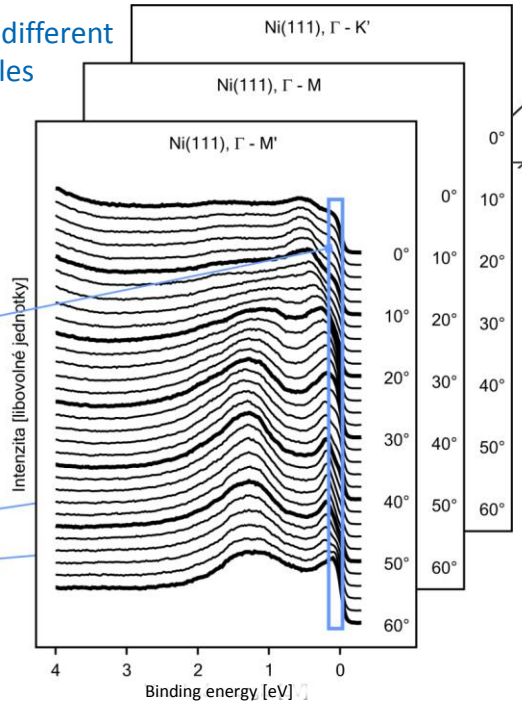


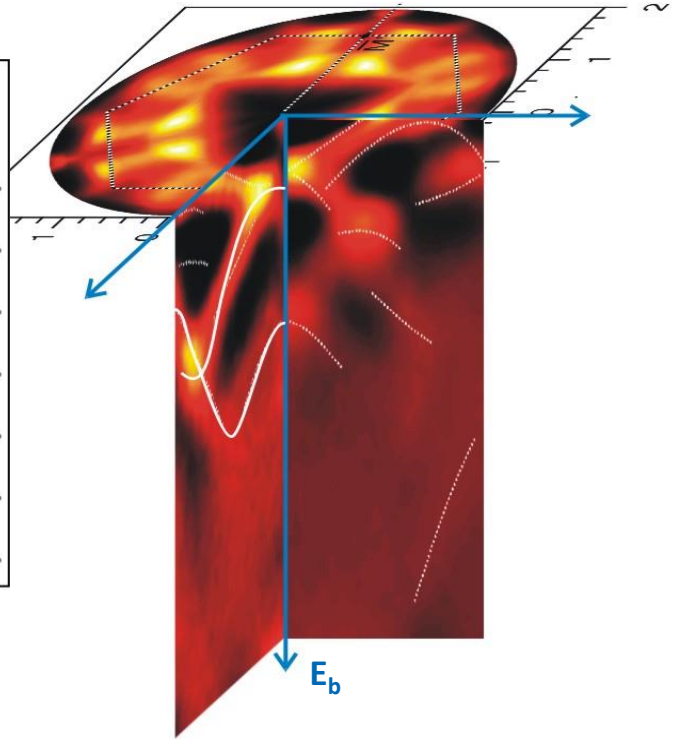


Surface Brillouin zone

Polar scans at different azimuthal angles







Photoemission spectroscopy

Synchrotron radiation photoemission spectroscopy

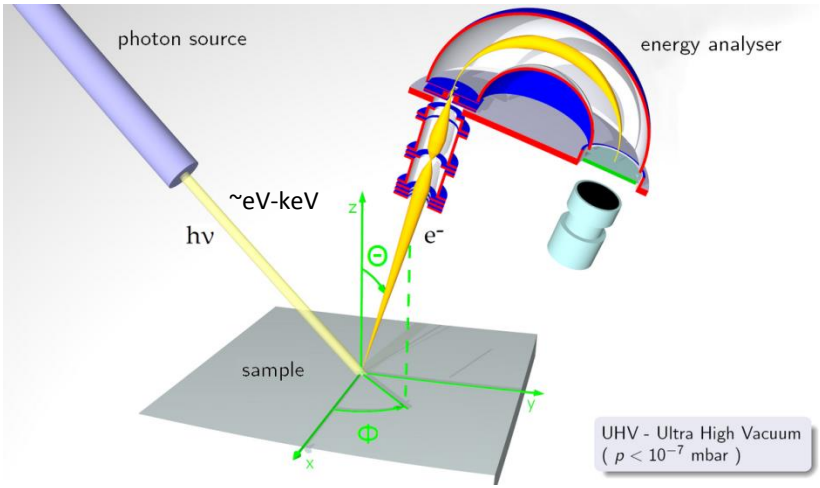
Synchrotron radiation photoemission spectroscopy (SRPES)

Synchrotron light source

- high monochromaticity
- controllable polarization
- high luminosity
- high spatial coherence (→ microscopy)

Benefits of tunable energy

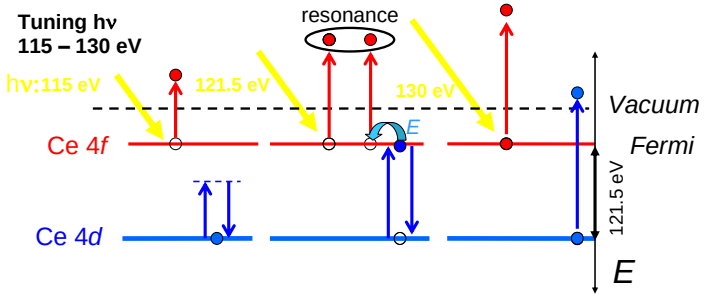
- covers all energy ranges (UPS, XPS, HXPES)
- variable probing depth (→ depth profiling)
- high resolution
- mapping of band dispersion (→ ARPES)
- resonance effects (→ RPES)



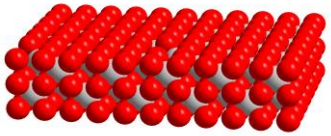
Photoemission spectroscopy

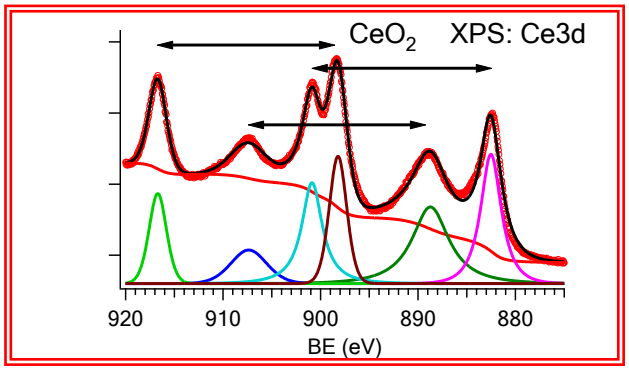
Resonant photoemission

Synchrotron Radiation Resonance Photoemission: Ce

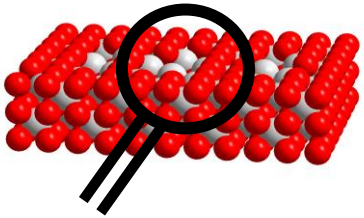


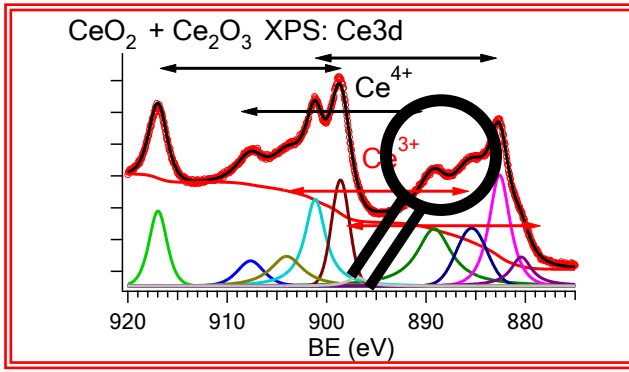
CeO_2 (100)



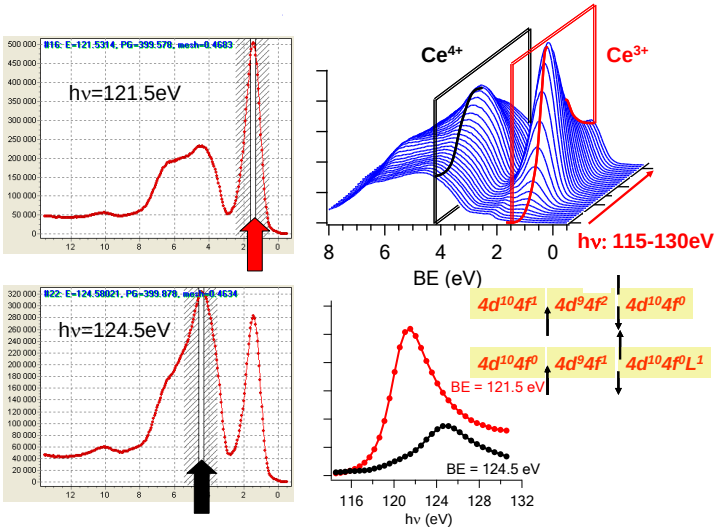


CeO_2 (100) + Ce^{3+} oxygen vacancy



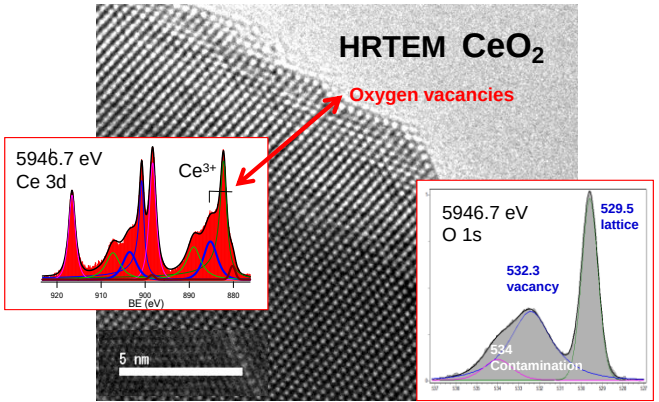


Resonance Photoemission: CeO_x



High Energy HX-SRPES

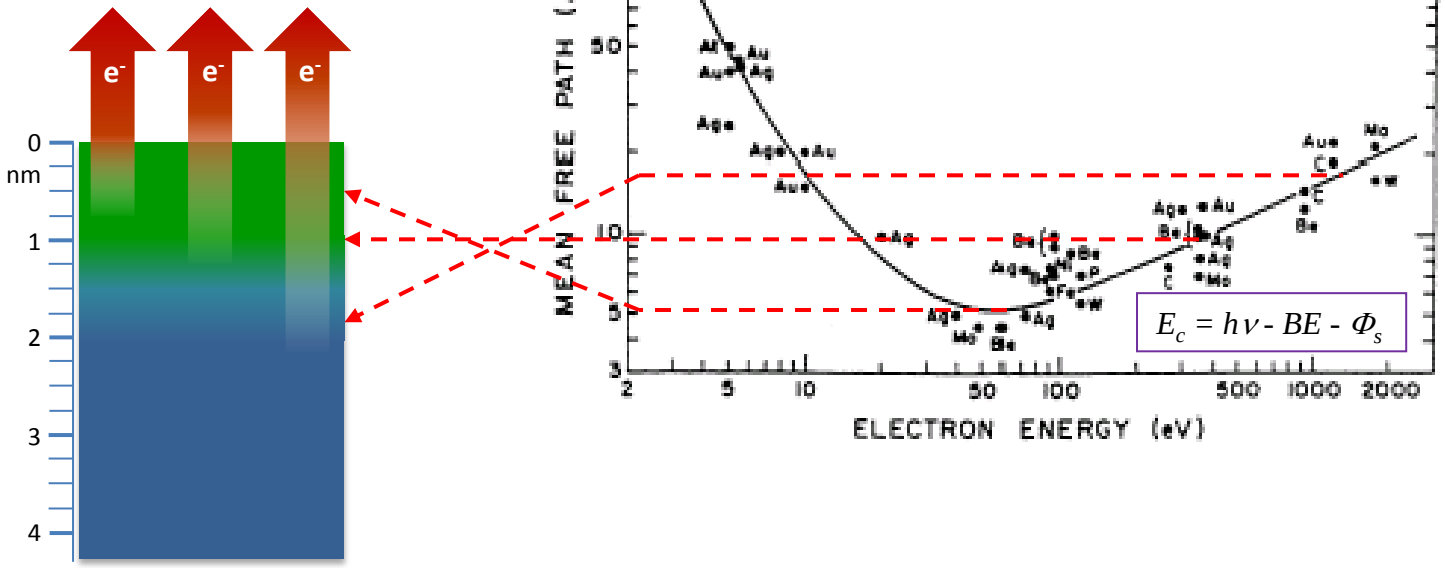
6 keV – 7 nm information depth, low contamination sensitivity – well suitable for nanocatalyst PES study



Photoemission spectroscopy

SRPES depth profiling

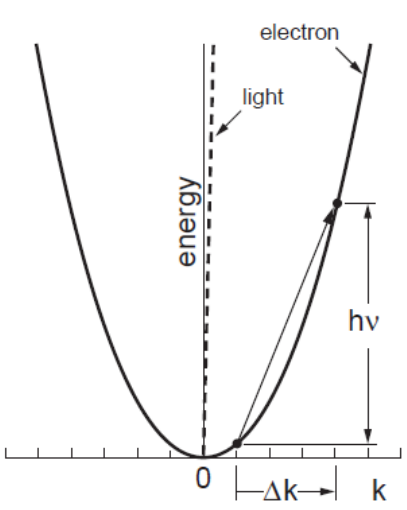
Depth sensitivity through $\lambda(E_k)$ by variation of $h\nu$
- non-destructive



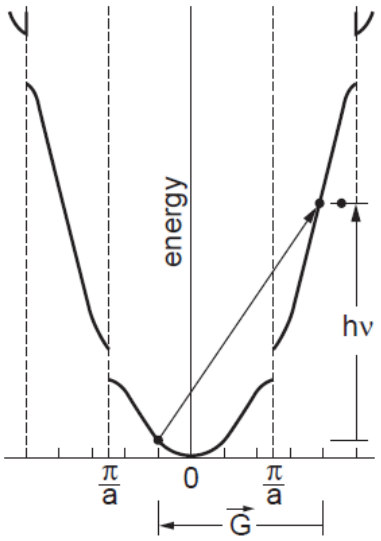
Angle resolved PES

ARPES Fundamentals

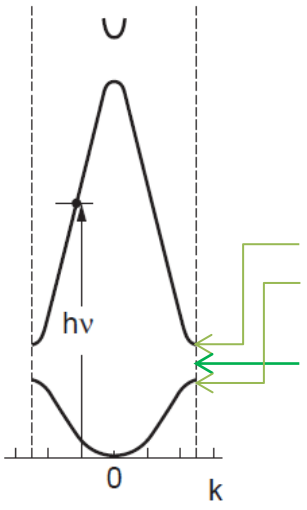
Photoexcitation in a periodic potential



free electron/
constant potential



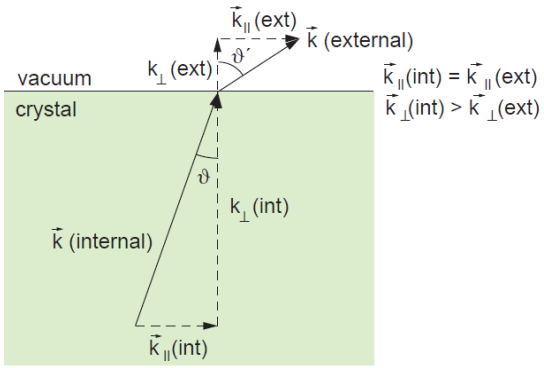
extended zone
periodic potential



reduced zone
periodic potential

At the Brillouin zone boundary, the gradient of the energy is parallel to the boundary

Band gaps open at zone boundary



Energy conservation

$$E_f(\vec{k}_f) = E_i(\vec{k}_i) + \hbar\omega$$

Momentum conservation (*k*-selection rule)

$$\vec{k_f} = \vec{k_i} + \vec{G} + \cancel{\vec{k}_{photon}}$$

$\vec{G}$... reciprocal lattice vector

low E_p => only "vertical" transitions

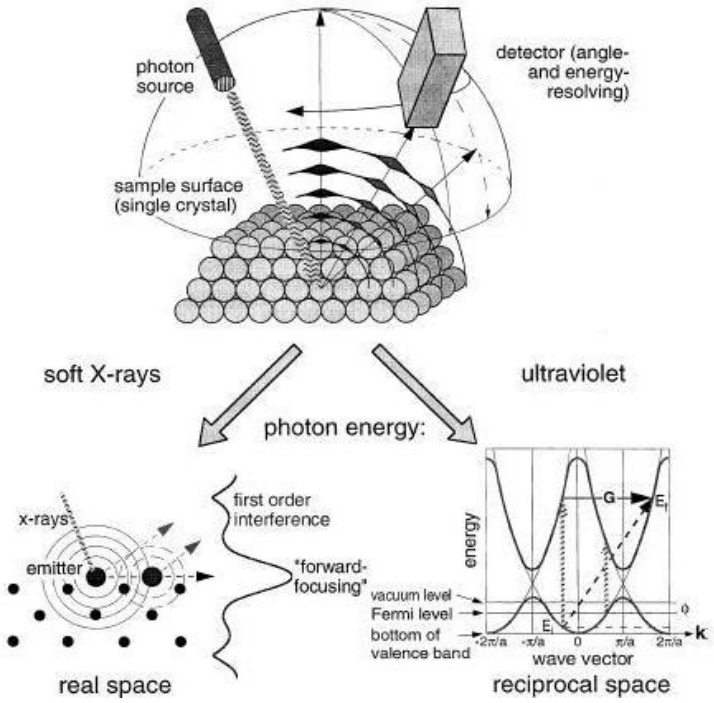
✖

high E_p => suppression of direct (near k-conserving) transitions

Band structure mapping: determination of $E_i(\vec{k_i})$

Angle resolved PES

Direct mapping of electronic state dispersion



Final state energy referenced to the vacuum level

$$E_f(\vec{k}) = \frac{\hbar^2}{2m}\left(k_\parallel^2 + k_\perp^2\right) + e\Phi - V_0$$

V_0 … inner potential (= energy of VB bottom rel. to E_{vac})

Energy conservation

$$E_f = E_{kin} + e\Phi$$

$$E_f(|\vec{k}|) = E_i(|\vec{k}|) + \mathrm{h}\nu$$

Direct transition => conservation of $k_\parallel$

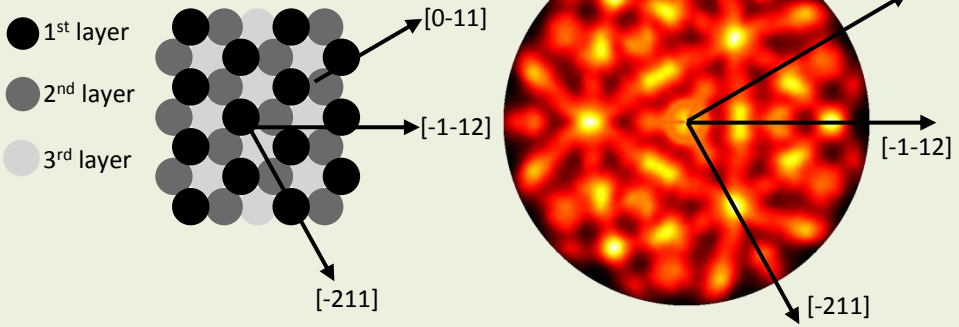
$$\hbar k_\parallel = \sqrt{2mE_{kin}}\sin\vartheta$$

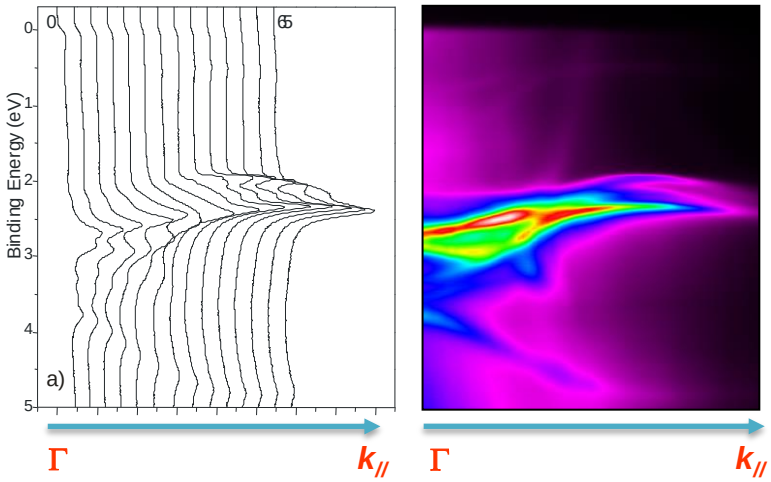
$k_\parallel$ is conserved
$k_\perp$ not conserved => cannot be mapped directly by PES

$\Rightarrow$ good for mapping 2D structures (e.g. graphene)
3D mapping accessible via variable E_p

Energetically unresolved → **XPD**

XPD (diffraction)

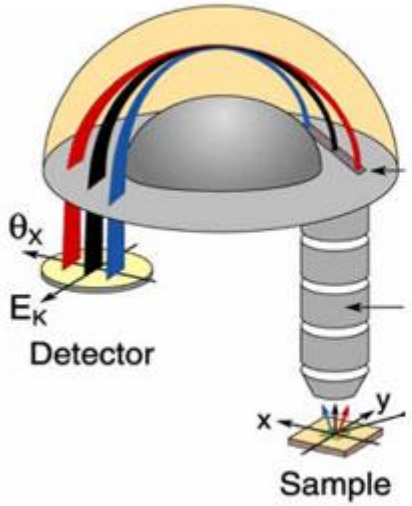


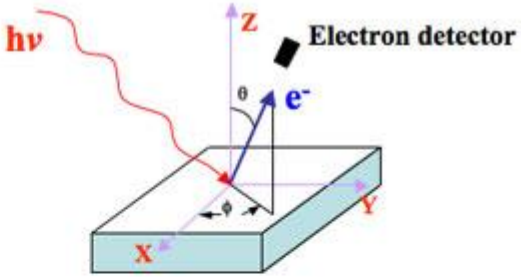


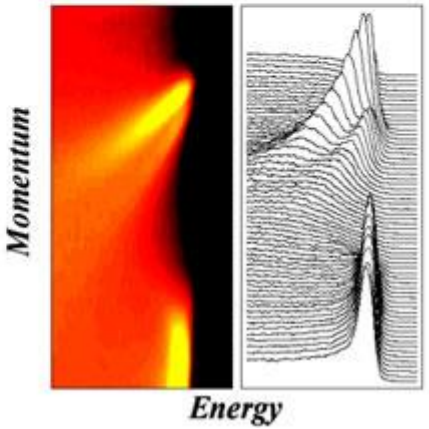
Angle resolved PES

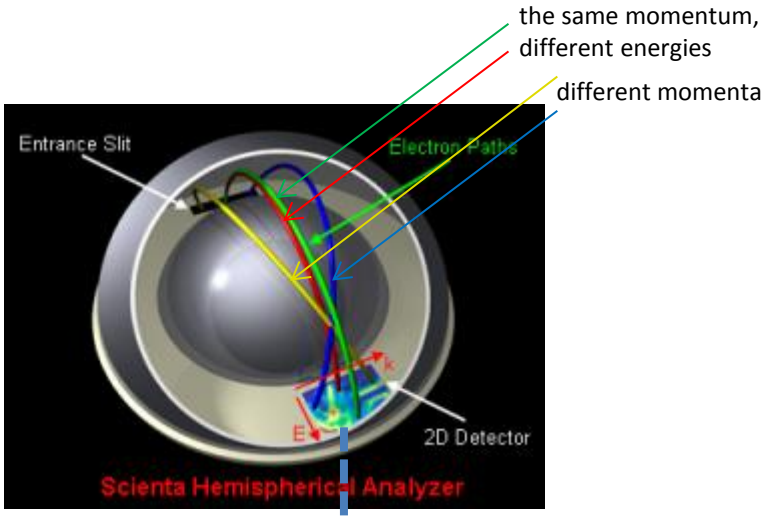
Direct mapping of electronic state dispersion

2D-detection setup



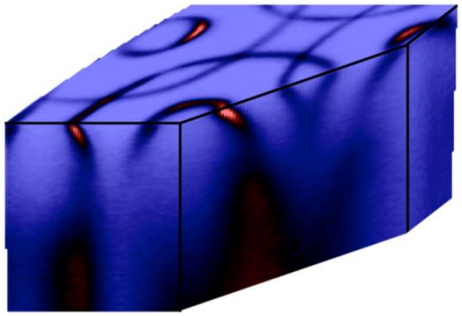


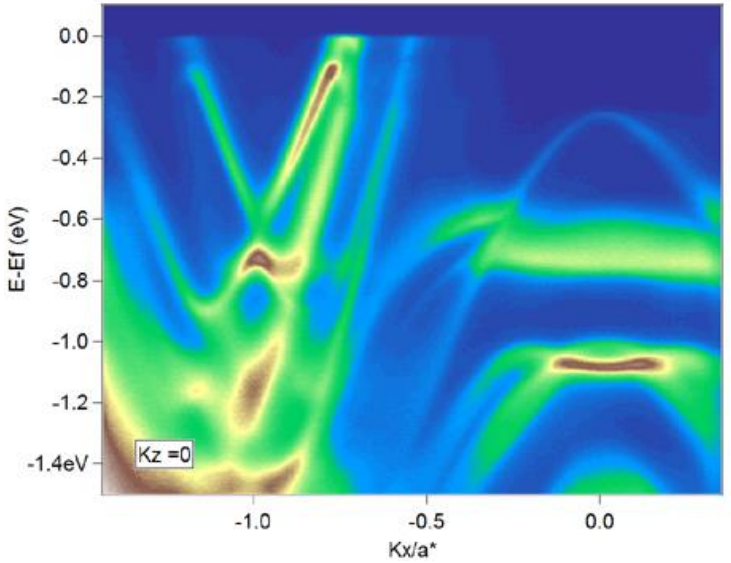




2D detector: MCP, phosphor screen, CCD

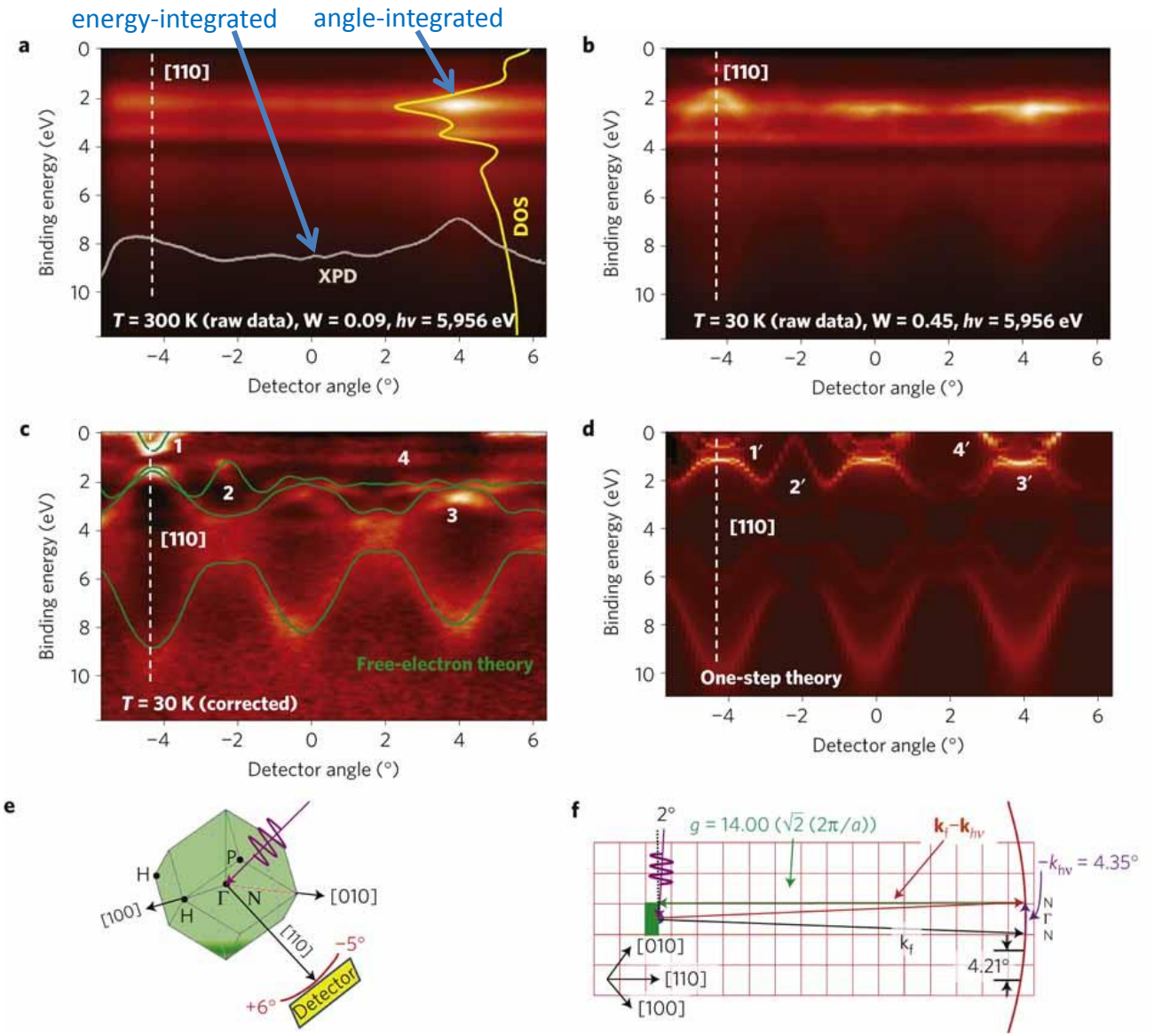
Direct resolution of electrons in energy-momentum space
=> imaging of electronic structure of solids





Angle resolved PES

Direct mapping of electronic state dispersion



A.X. Gray et al.: Nature Materials 10, 759–764 (2011)

Internal Photoemission Spectroscopy

General concept and instrumentation

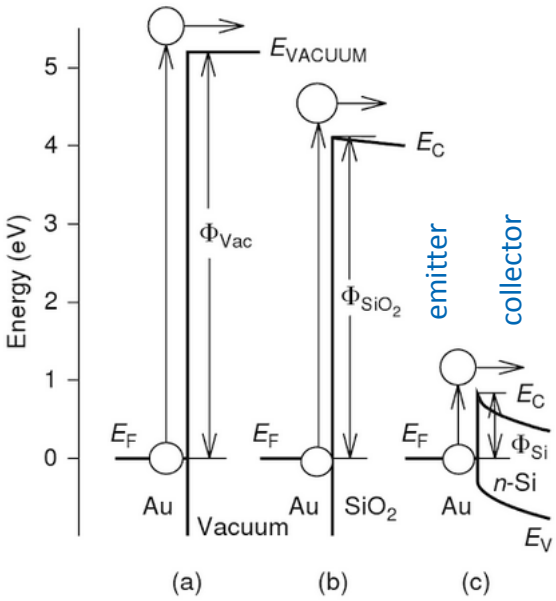
Basic principle

Optically induced transition of a mobile charge carrier (electron or hole) from one solid (emitter) into another solid (collector)
⇒ Used mainly to characterize **interfaces**

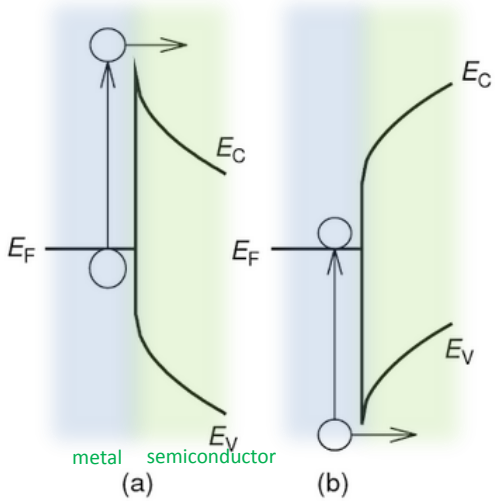
- similar to classical (external) photoemission methods, but difference in potential barriers of interface and surface
- can be combined with electric or magnetic fields

IPE mechanism

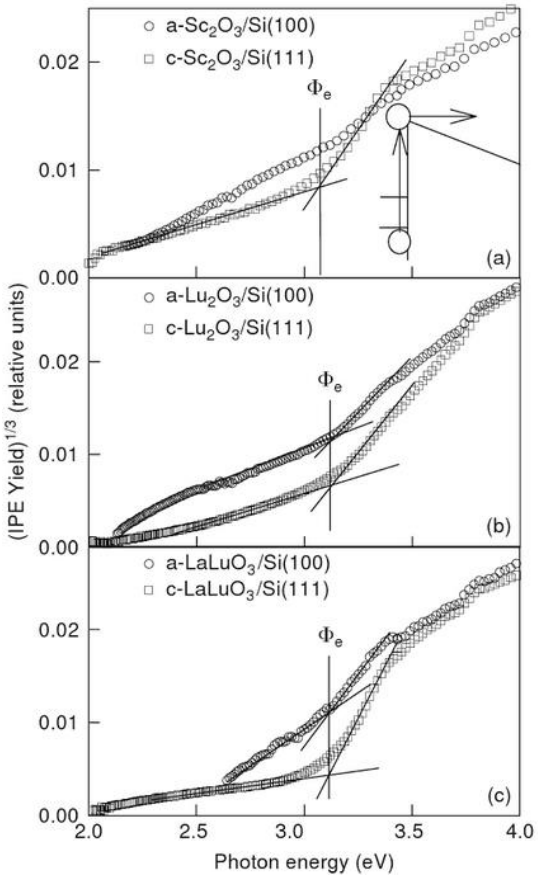
Photoemission from el. states near Fermi level to
vaccum **insulator** **semiconductor**



Optically excited electron transitions due to photoemission of
electron **hole**

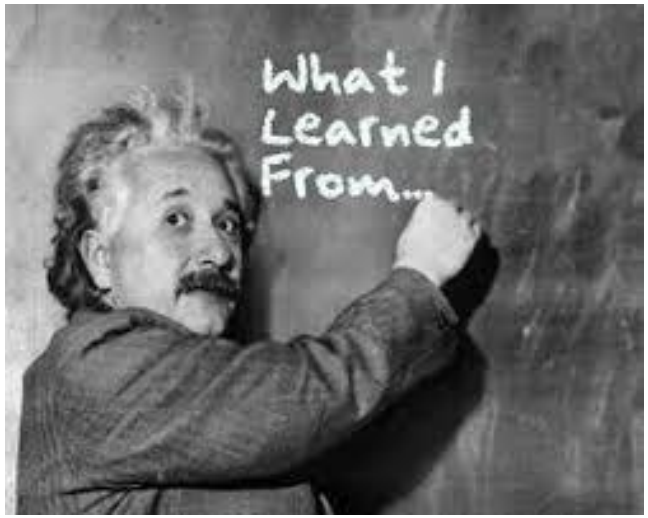


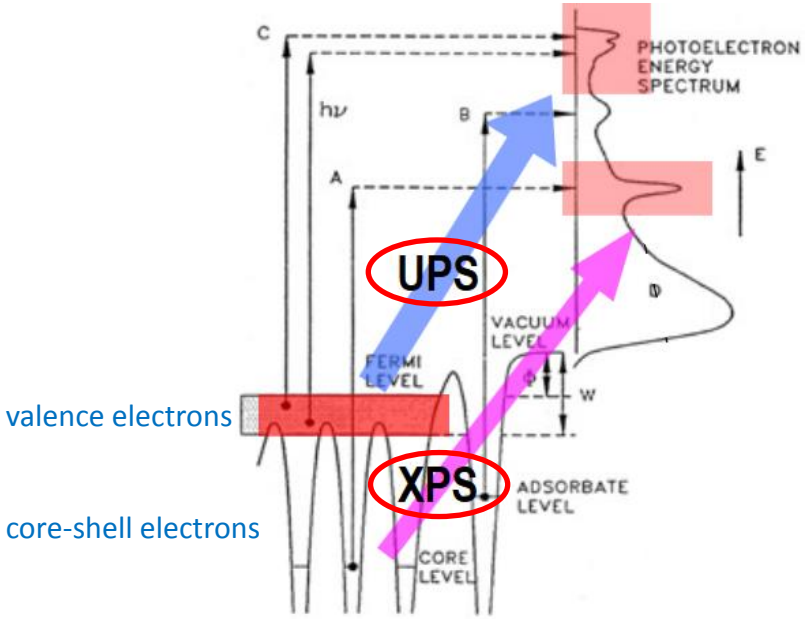
Examples of IPE spectra



Photoelectron spectroscopies

Take-home Messages





XPS

Main indicators

primary structure (initial state effects)
- elemental analysis – peak positions
- chemical state analysis – peak shifts

secondary structure (final state effects)
- multiplet splitting
- shake-up and shake-off satellites
- metal core level asymmetry
- vibrational fine structure
- plasmon loss features

UPS

- correlated with occupied DOS near FE
- sensitive to adsorbates
- band dispersion mapping: ARUPS

SRPES

Variable E =>
- depth profiling
- band dispersion mapping: ARPES
- resonance effects

ARXPS vs. **ARUPS/ARPES**
depth profile × electron structure diagram

Appearance potential spectroscopy

Fundamentals

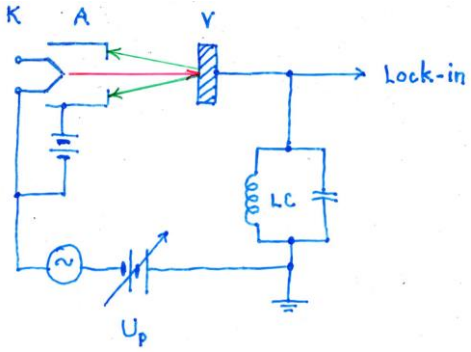
- Developed in 1970's (*R.L. Park and J.E. Houston*)
- From ~2000's replaced by XAS (X-ray Absorption spectroscopy)
  – SR available, easier interpretation

Basic principle

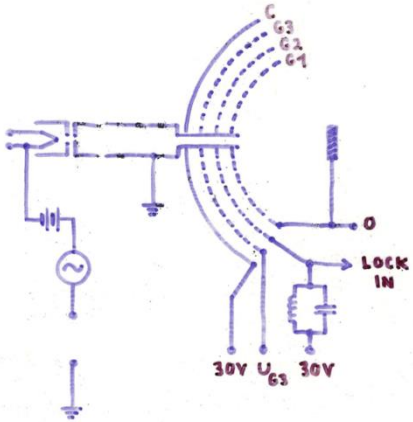
- variable E_p
- measurement of threshold energy for the creation of inner shell excited atom => probing empty states
- relaxation → emission of Auger electron or x-ray
- no energy analysis of the decay of the excited state required
  => no electron analyzer needed (but can be used)
- typical $E_p \approx$ 50-2000 eV
  => highly surface sensitive
- differential spectrum: separation of appearance features from primary and scattered electrons
- primary source = electrons => focusable to ≲nm

APS instrumentation

AEAPS basic analog set-up



LEAPS setup (LEED optics)

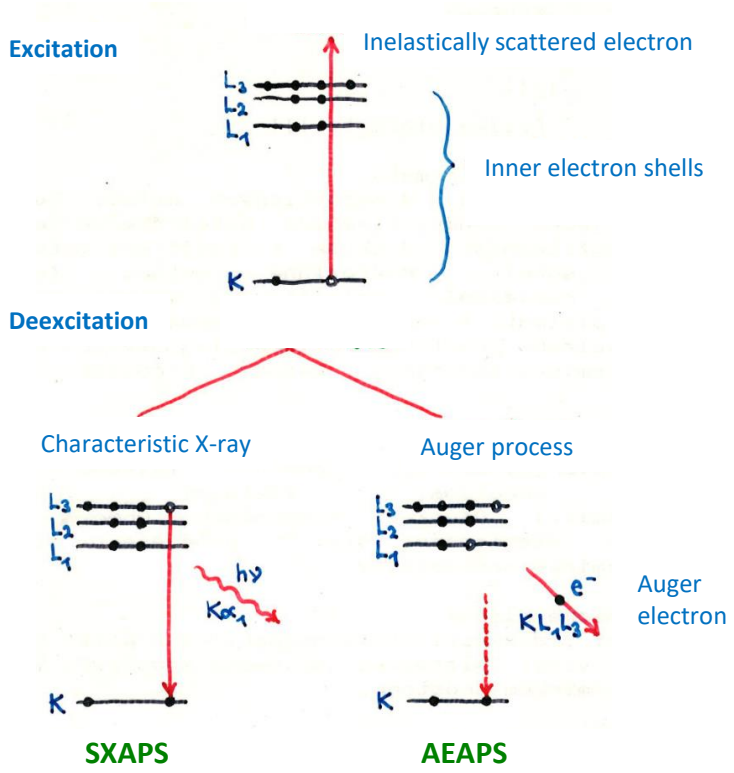


Main variants

- Soft X-Ray Appearance Potential Spectroscopy (SXAPS)
- Auger Electron Appearance Potential Spectroscopy (AEAPS)
- Disappearance Potential Spectroscopy (DAPS)
  – measurement of quasi-elastic scattered electrons (abrupt decrease upon Auger electron emission threshold); direct – no role of deexcitation

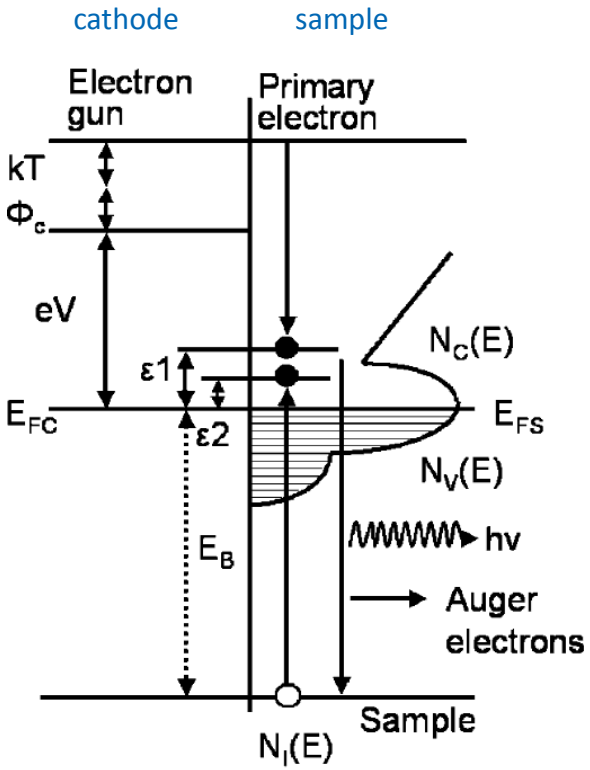
… special or newer variants

- inelastic electron tunnelling spectroscopy (down to ~0.1 eV)
- nuclear resonance capture spectroscopies (>1 MeV)



Appearance potential spectroscopy

Basic mechanism and quantification



Threshold:
- Primary electron captured in empty levels
- Core-level electron excited to empty level

=> 2 electrons in empty level + core-hole → relaxation

Energy conservation

$$\underbrace{eV + \Phi_c + kT}_{E_p} = E_b + \varepsilon_1 + \varepsilon_2$$

$\varepsilon_1 \approx 0, \varepsilon_2 \approx 0$ =>

$$E_p \approx E_b$$

Electron gun	Thermal emission	Field emission
Φ_c	~4-5 eV	0 eV
kT	~250 meV	~25 meV

$$E_p \approx eV$$

Transition rate

$$T(E) \propto \int_0^E \int_0^{E'} N_c(E'')\, N_c(E' - E'')dE'' \times N_I(E + E_b - E')dE'$$

N_c … density of empty states for one-electron
N_I … density of filled states for excited core-level

$N_I \sim \delta$-function ($\int$=1) =>

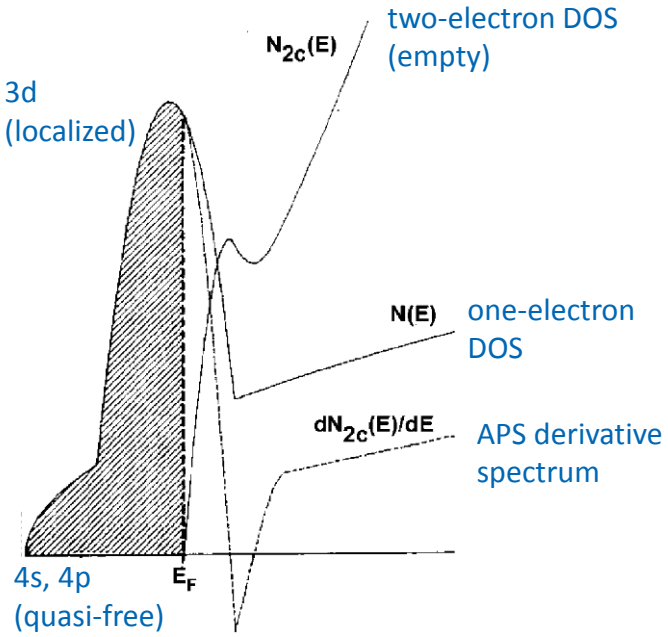
$$T(E) \propto \int_0^E N_c(E')N_c(E - E')dE'$$

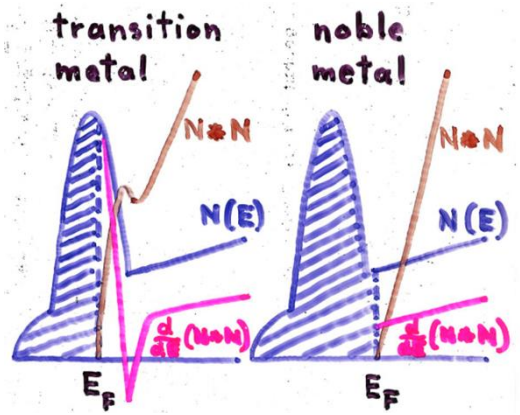
=> rate (→ spectral intensity) proportional to self-convolution of density of empty states for one-electron system (because there are 2 electrons)

Appearance potential spectroscopy

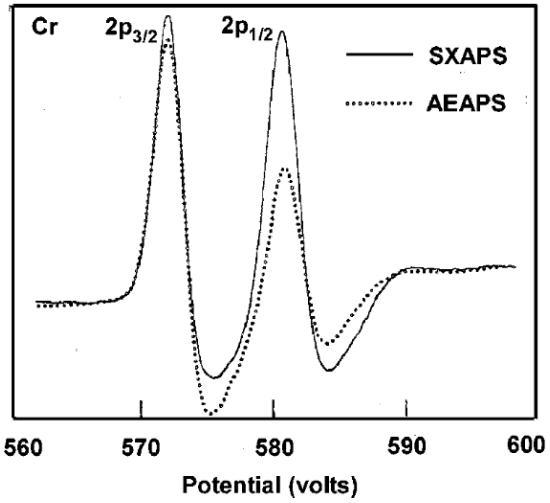
Spectrum analysis

APS schematic spectrum: 3d transition metals

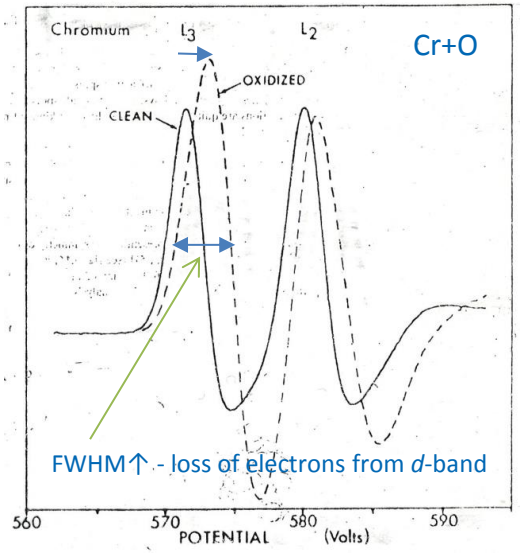




SXAPS vs. AEAPS

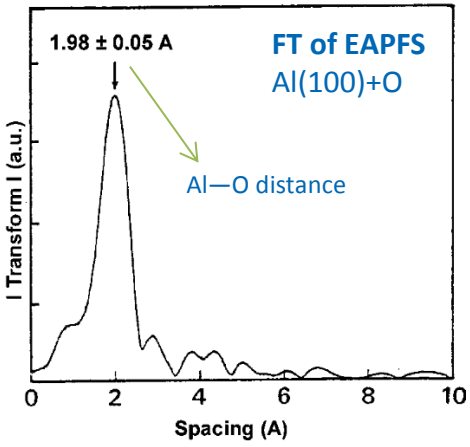


"Chemical shift" in APS



Fine structures above APS thresholds
→EAPFS (extended appearance potential fine structure)
- extends to ~100's eV

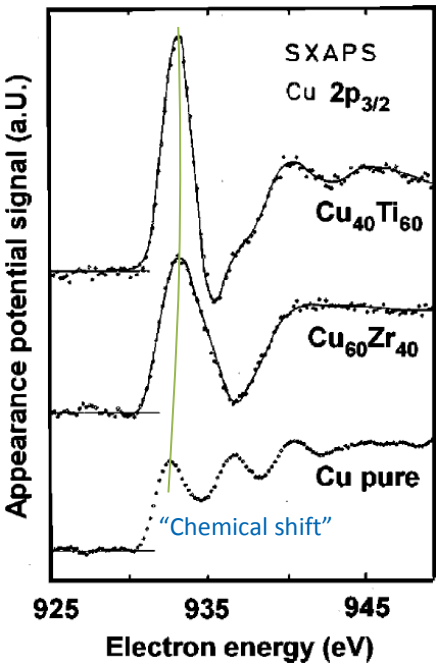
periodic features
↓ *Fourier transform*
interatomic spacings



Appearance potential spectroscopy

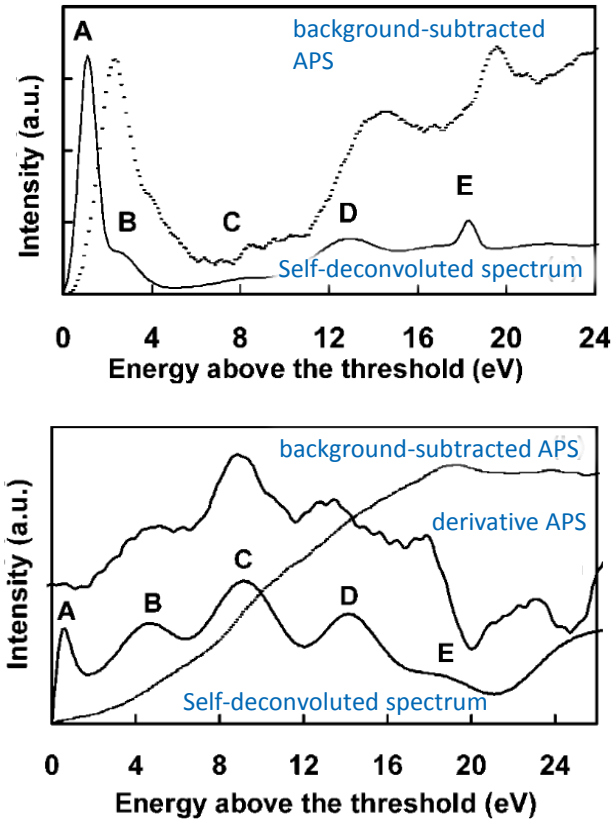
APS spectra – examples

Alloys

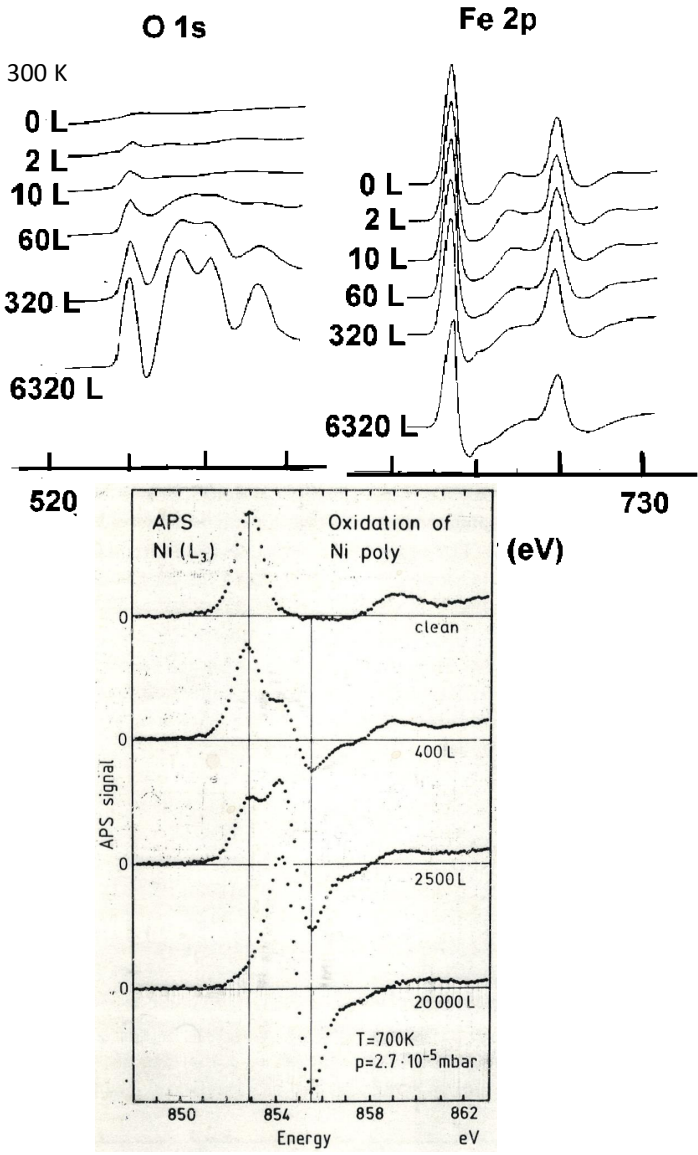


Compounds

oxides, hydrides, carbides, nitrides, borides, sulphides…



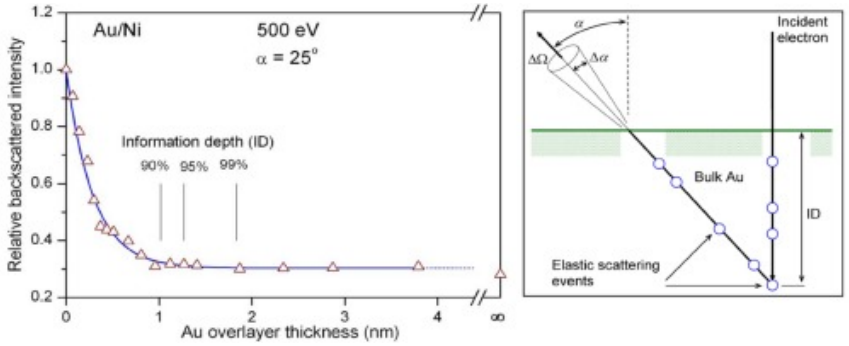
Chemisorptions and reactions



Elastic peak electron spectroscopy

Fundamentals

- based on intensity measurement of elastic peak
- typical E_p≈100-3000 eV
- until 1970's – elastic electrons only in LEED and spectral normalization & calibration
- development of quantitative analysis of el. spectroscopies => quantification of IMFP needed



Advantages
- non-destructive depth profile probe
- high surface sensitivity

Applications
- experimental IMFP determination
- depth profiling of layered structures
- thin film growth investigation

Elastic scattering probability (prob. of elastic electron reflection)

$$r_e(E_p, Z, \alpha, \vartheta, \Delta\Omega) \propto N_A(Z)\sigma_{eff}(E_p, Z)\lambda_{IMFP}(\alpha, \vartheta)$$

N_A … density of atoms
σ_{eff} … effective elastic scattering cross-section
λ_{IMFP} … inelastic mean free path
ϑ … incident electron angle
α … detection angle (solid acceptance angle of analyzer $\Delta\Omega$)

- experimental curve affected by type of analyzer (CMA, RFA, HDA…)

Angular resolved EPES (AREPES)

$$\frac{dr_e(E, \alpha, \vartheta)}{d\Omega}$$

Penetration depth distribution function (PDDF)
= probability of elastic backscattering of electron from max. depth *z*
- usually normalized to total elastic backscattering probability (over the depth *z*): $\int_0^\infty \xi(z, \alpha, \vartheta)dz = r_e(\Delta\Omega)$

Mean penetration depth (MPD)
= mean value of PDDF

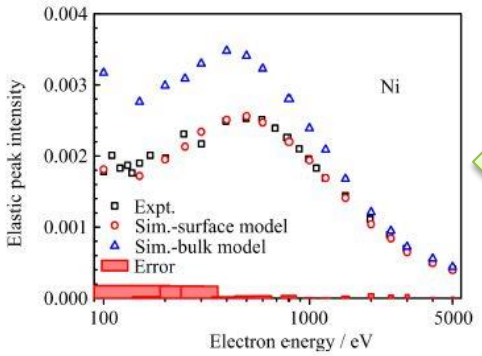
$$G = \frac{\int_0^\infty z\xi dz}{\int_0^\infty \xi dz}$$

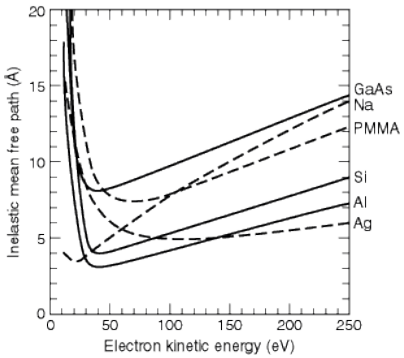
Information depth (ID)
= thickness *T* penetrated by a specified percentage (e.g. $p_{ID}^{90\%}$)

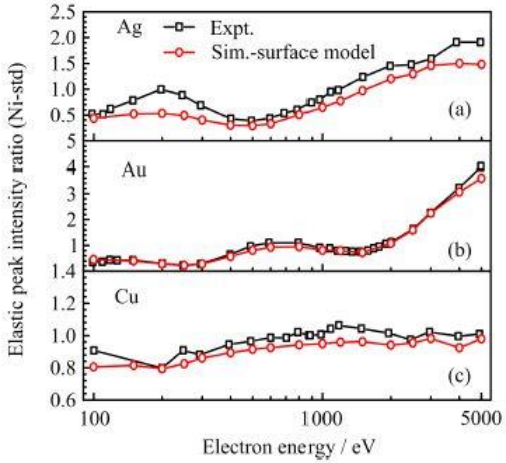
$$p_{ID}^T = \frac{\int_0^T \xi dz}{\int_0^\infty \xi dz} \quad \rightarrow T$$

Elastic peak electron spectroscopy

EPE spectra and theory

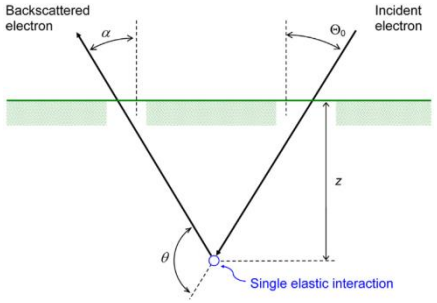




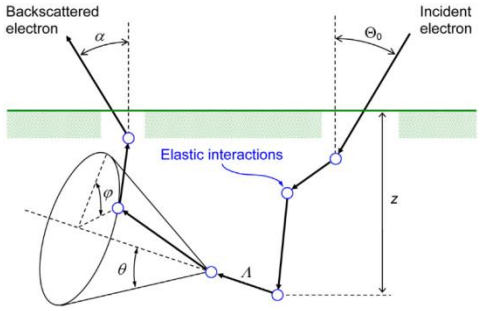


Theoretical treatment

- Single scattering approach – ordered layered systems



- Monte-Carlo (electron trajectory simulation) – more accurate, also for disordered systems

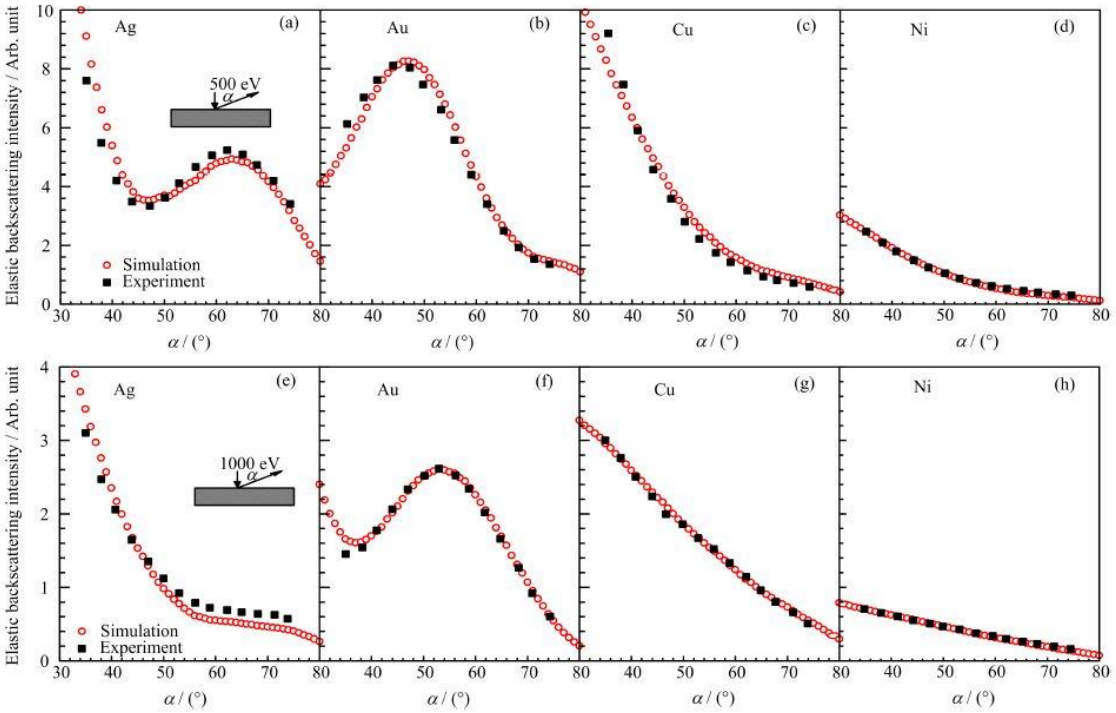


Simulation parameters
- solid (composition, structure, density)
- details of impact mechanisms
- inelastic scattering at surface (usually neglected)
- experimental geometry

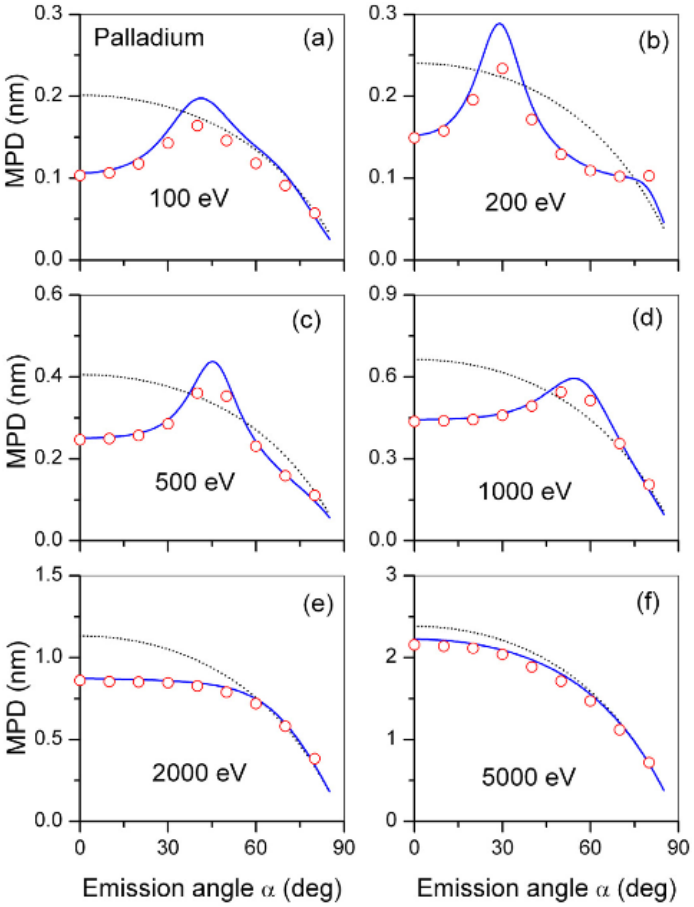
Elastic peak electron spectroscopy

Angular resolved EPES

Angular resolved EPES (AREPES)



Mean penetration depth
(mean value of PDDF)
- angular dependence



Two-photon photoemission spectroscopy

Basic principles

2-photon emission process

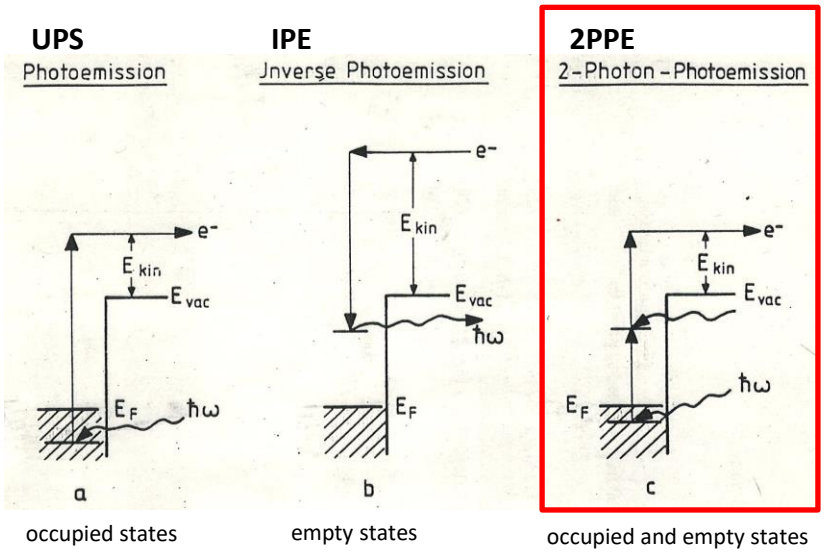
1) Photoexcitation by photon pump (~fs-ps)
2) Emission of free electron by photon probe

No time delay (t=0):

$$E_{kin} = h\nu_{pump} + h\nu_{probe} - E_b - \Phi$$
$$h\nu_{pump} < \Phi, h\nu_{pump} + h\nu_{probe} > \Phi$$

Δt>0, (partially) relaxed electron:

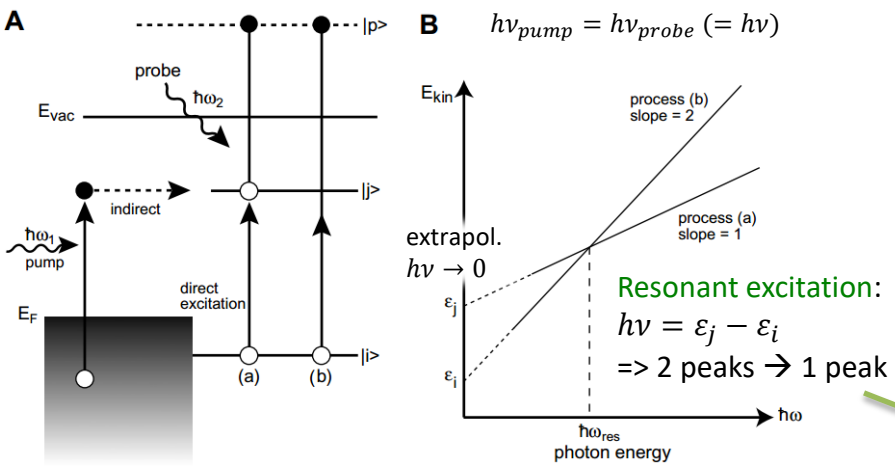
$$E_{kin}(\Delta t) = h\nu_{pump} + h\nu_{probe} - E_b(0) - \Phi - \Delta E_{rel}(\Delta t)$$



occupied states | empty states | occupied and empty states

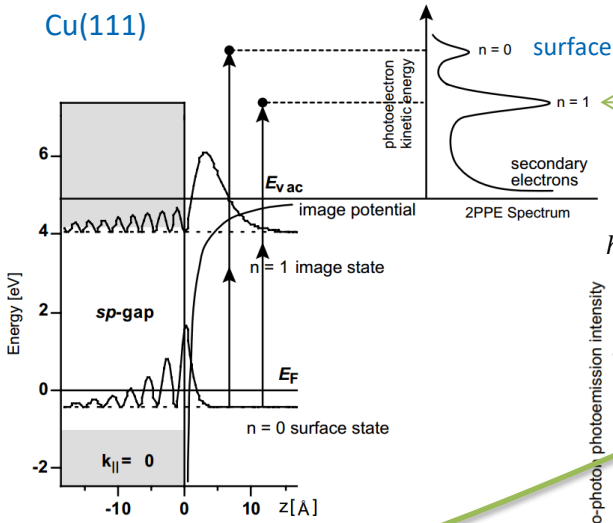
Elementary processes

a) Incoherent: step-by-step 1-photon process
(transient intermediate state + subsequent excitation from ε_j state)
b) Coherent 2-photon excitation (from ε_i state)

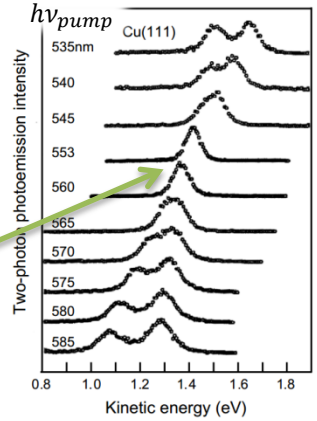


Resonant excitation:
$h\nu = \varepsilon_j - \varepsilon_i$
=> 2 peaks → 1 peak

Cu(111)



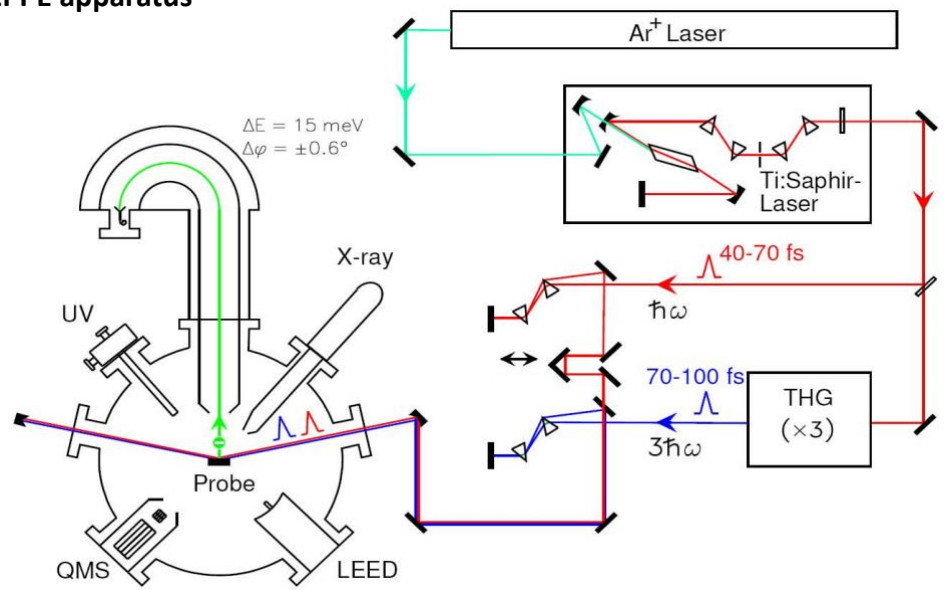
1st IPS (unoccupied image potential state)

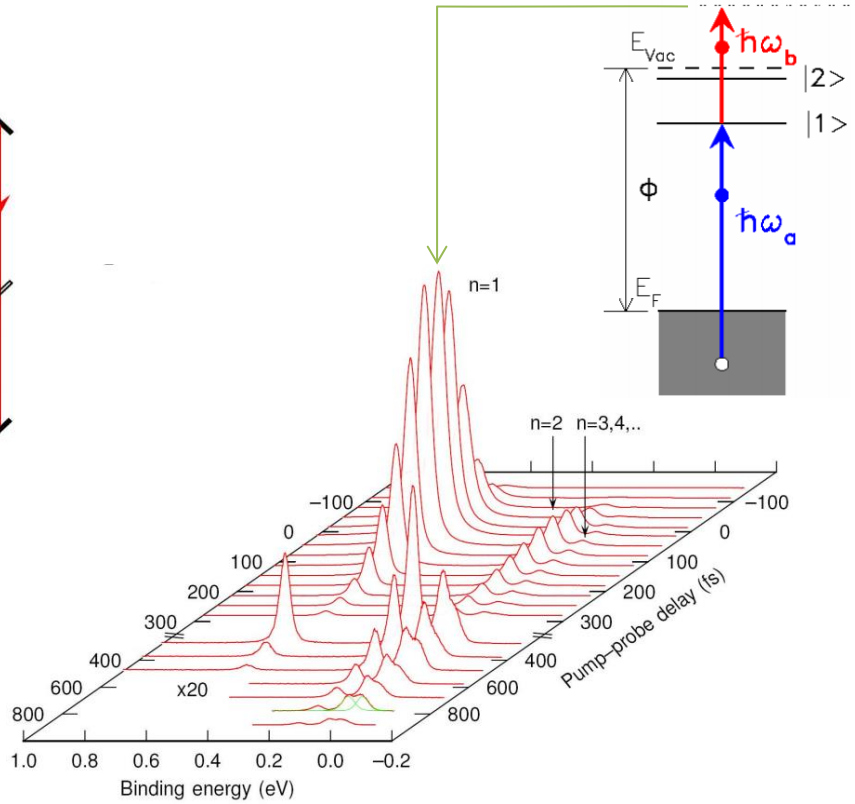


Two-photon photoemission spectroscopy

Experimental arrangement and applications

2PPE apparatus



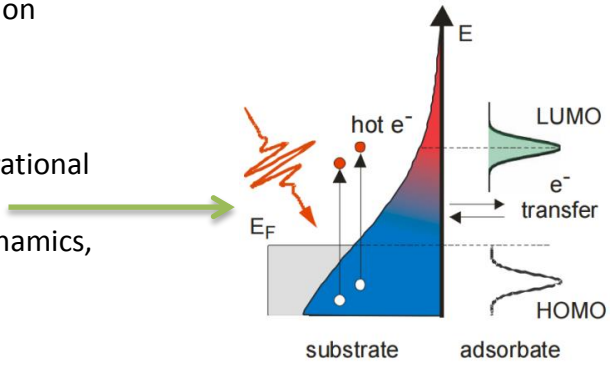


(+) Better energy resolution (almost like in UPS)
(+) Electron dynamics measurements
(-) Lifetime of the excited state has to be sufficiently long

AR measurement → momentum resolution

Used to study

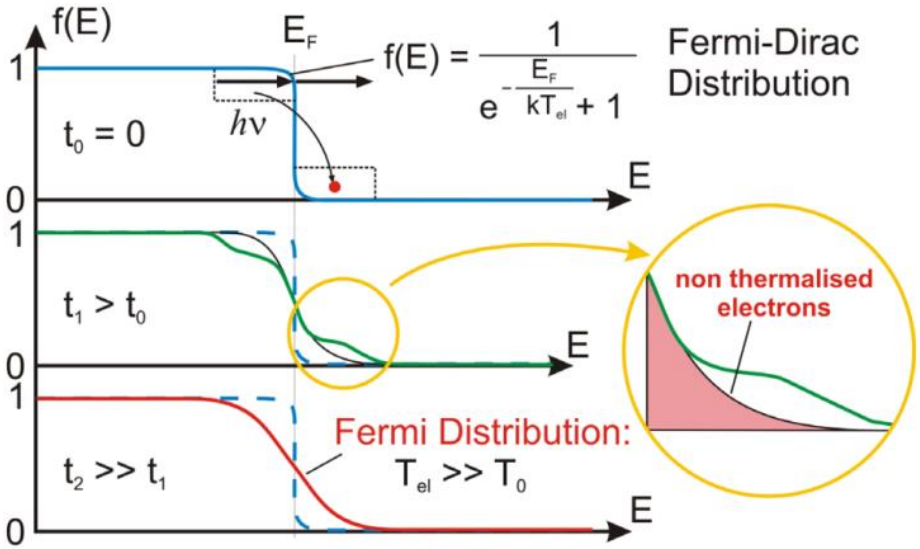
- electron transfer across interfaces
- surface dynamics (femtochemistry, vibrational energy relaxation, …)
- time-resolved 2PPE: charge transfer dynamics, decay of excited states, …



Two-photon photoemission spectroscopy

Electron dynamics measurement

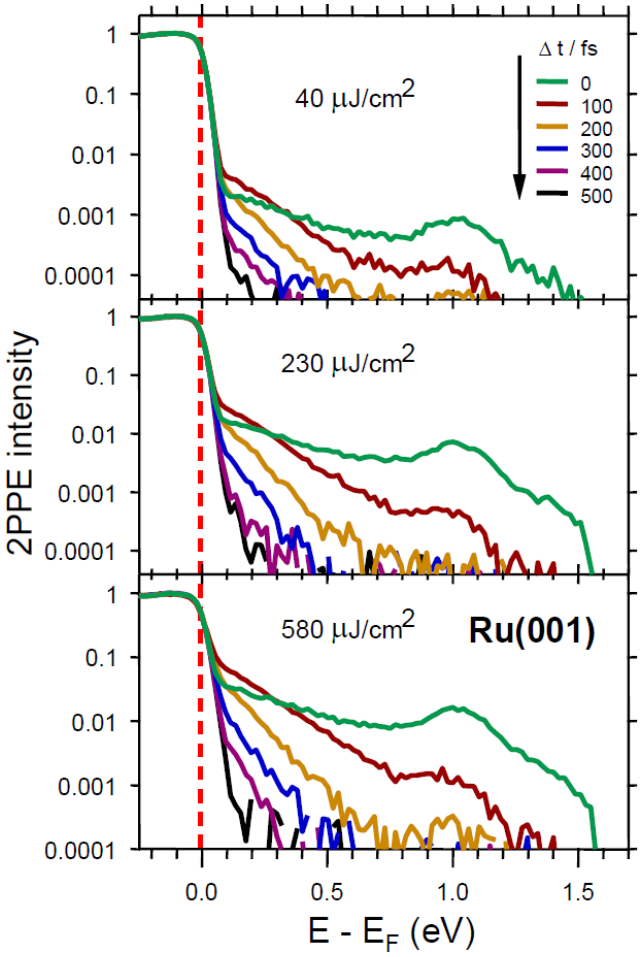
Electron dynamics in metals following optical excitation



Excitation density

- low (<10^{-4} e^-/atom): interaction with “cold” electrons
  => single quasiparticle lifetimes
- high (>10^{-4} e^-/atom): interaction with “hot” electrons
  => hot electron temperature

Cooling of photoexcited electron gas



W.S. Fann, R. Storz, H.W.K. Tom, J. Bokor: Phys Rev B 46 (1992), 13592
Lisowski et al.: Appl. Phys. A 78 (2004), 165

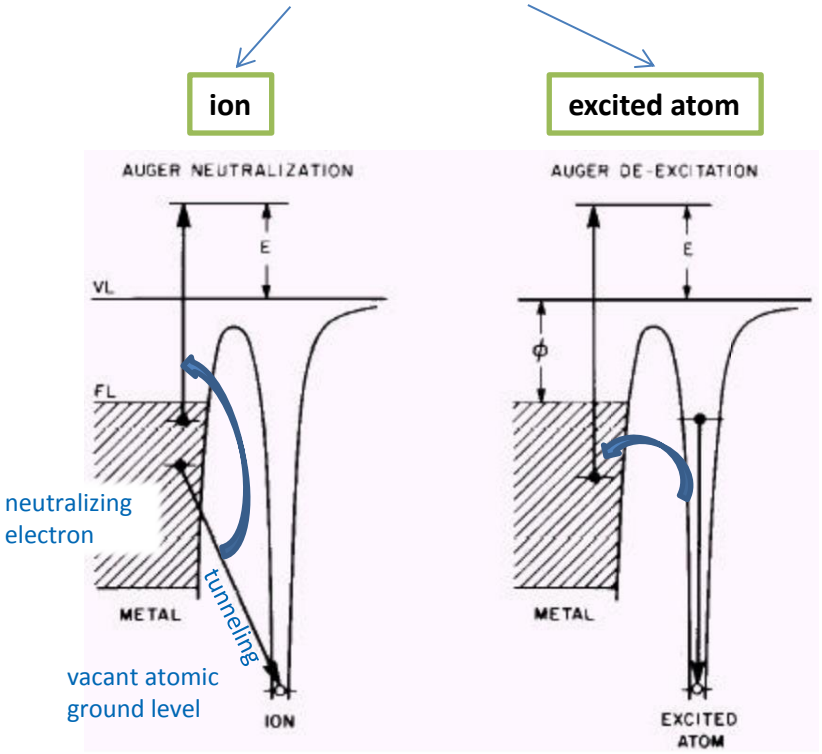
Ion neutralization spectroscopy

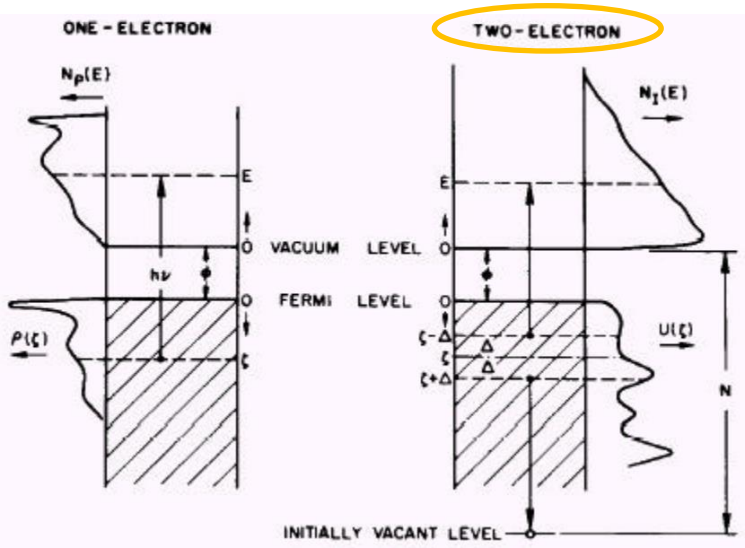
Basic principle

Ion interaction with matter producing electrons:

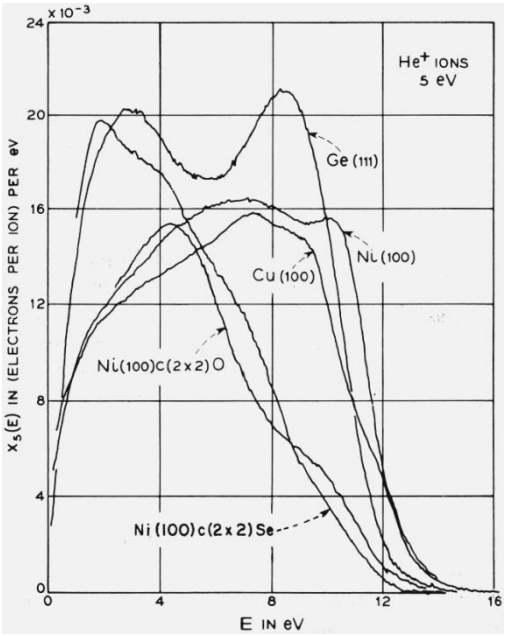
- high E (MeV): kinetic emission – ejection of electron
- low E (10-100 eV): potential emission – neutralization of ion → **INS**

Mechanism
2-electron Auger-type process induced by
low kinetic energy ion (+) or excited atom



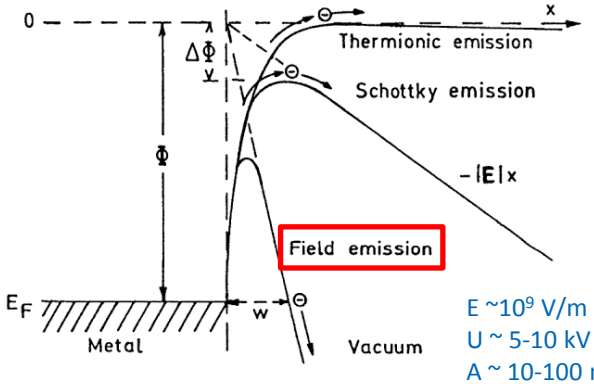


Participation of electrons from filled states valence band => energy **band** rather than specific energies



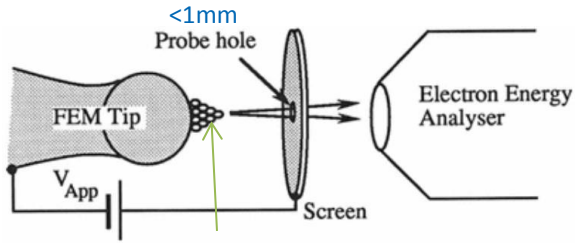
Field emission electron spectroscopy

General concept, instrumentation, spectra

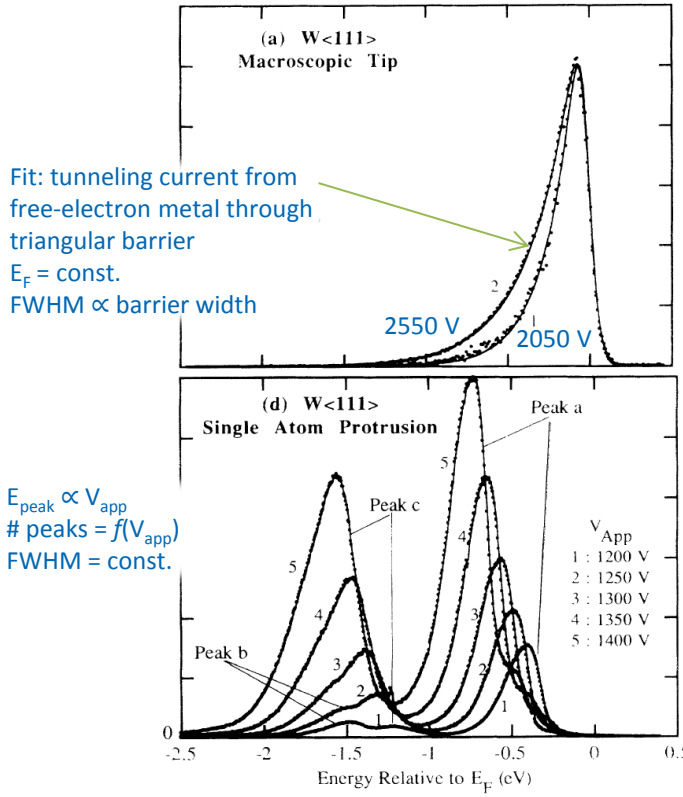


- Based on Field Emission Microscopy
  → Energy distribution from a small selected area
  => probing local DOS

E ~10^9 V/m
U ~ 5-10 kV
A ~ 10-100 nm (tip)



protrusion tip



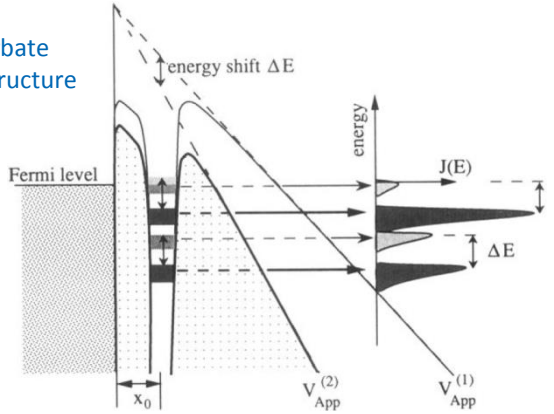
Fit: tunneling current from free-electron metal through triangular barrier
E_F = const.
FWHM ∝ barrier width

$E_{peak} \propto V_{app}$
# peaks = $f(V_{app})$
FWHM = const.

- Originally to study el. states of tip-adsorbed atoms and molecules
- Macroscopic tips (≳ 100 nm) – sampled area ≳ 2 nm
- Nanoscale protrusions – few nm high, single-atom-ended (field-surface melting mechanism: U&T)
  → self-collimated (~4°) coherent electron beam

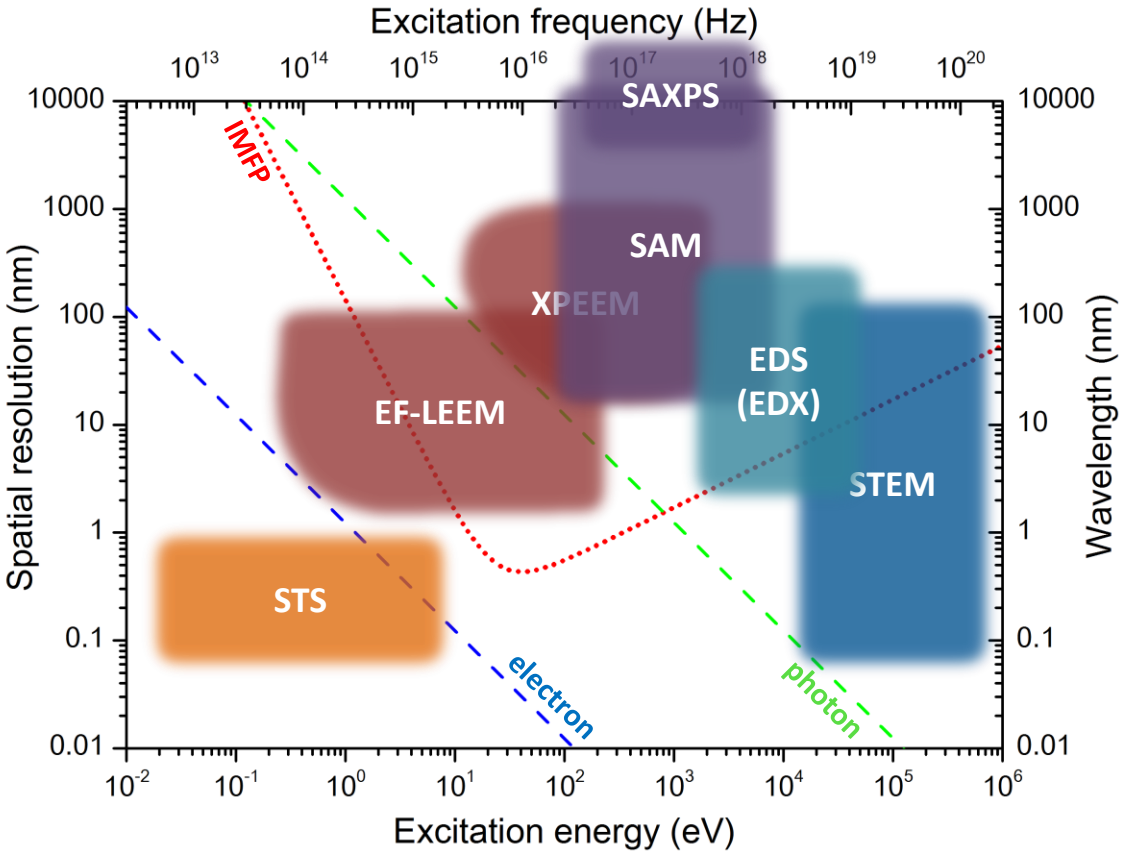
- 1966 - first theory of field emission taking into account energy-band structure
- 1970's – improvement by LEED theorists
- 1990's – incorporation to STM theories; Relevance for Scanning tunneling spectroscopy – theory of structure-dependent tunelling (+role of tip)

surface atom, adsorbate
→ localized band structure

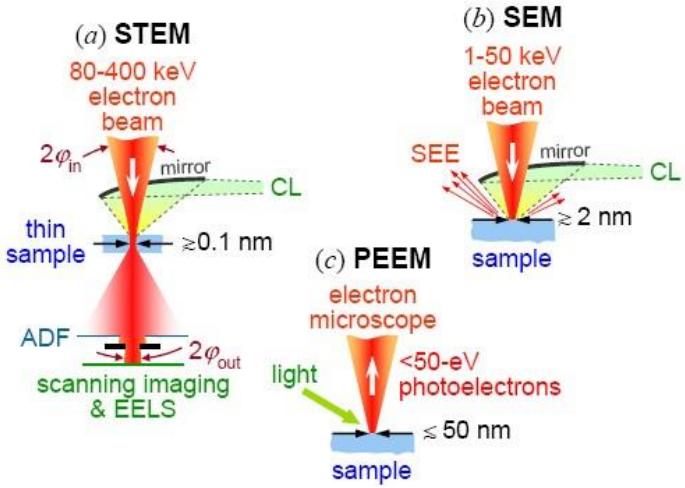


El. spectroscopy in microscopic methods

Spatially-resolved electron spectroscopies



Atlas of most common spatially-resolved electron spectroscopy techniques



Some of the electron microscopes equipped to perform electron spectroscopy

Key feature in microscopy: **contrast**
→ many different origins
→ path to spectroscopy

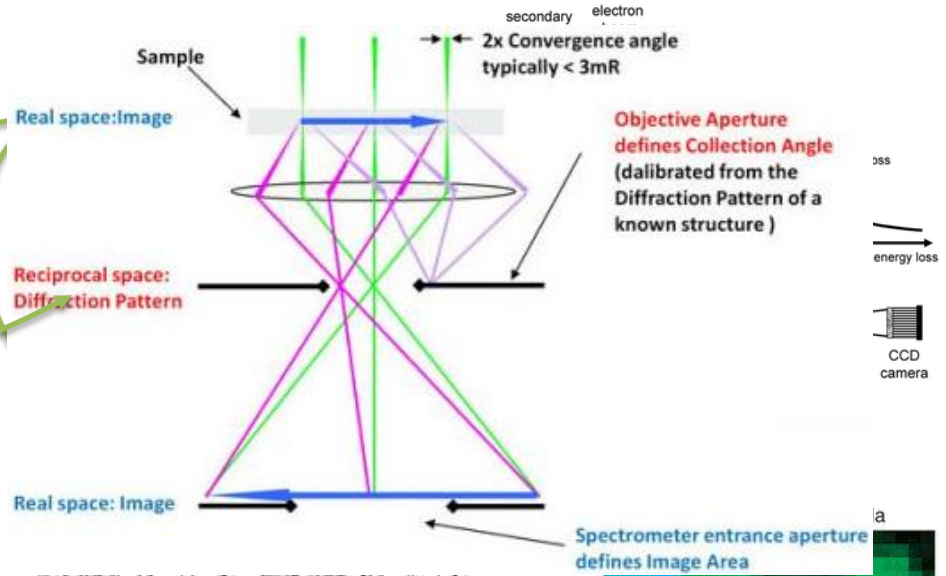
El. spectroscopy in microscopic methods

(HR)EELS in (S)TEM

- analysis of energy distribution of electrons transmitted through a thin specimen in Scanning transmission el. microscope (STEM)
- ≲100 nm thick samples
- beam focused down to <0.1 nm spot

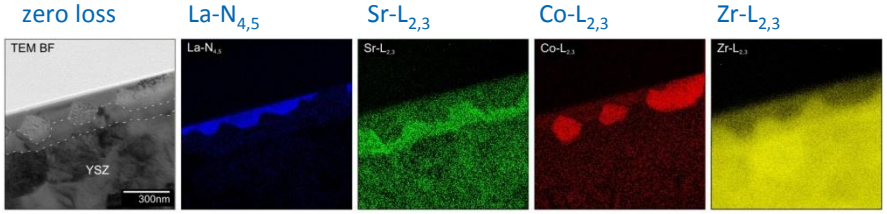
(S)TEM sources of image contrast

- bright-field – thickness & density contrast (in-axis detection)
- dark-field – diffraction contrast – scattered electrons (large-momentum transfers) → annular dark-field detector (ADF)
- cathodoluminescence (CL) light detection

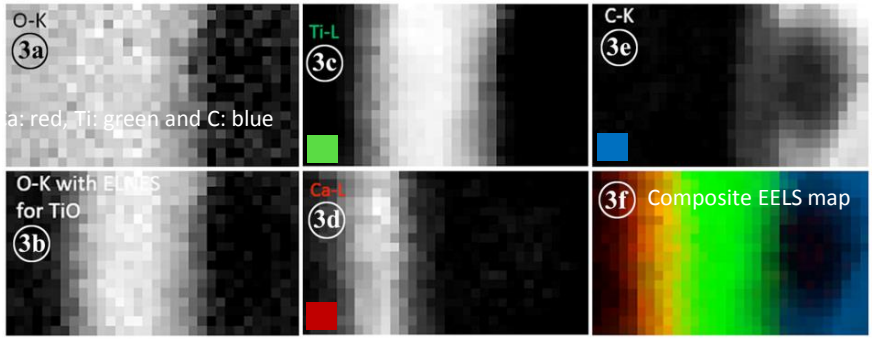


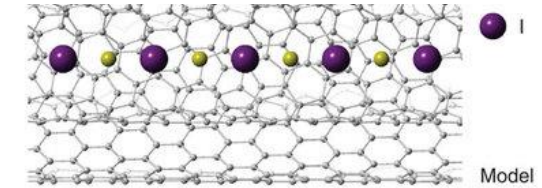
Core-level elemental mapping

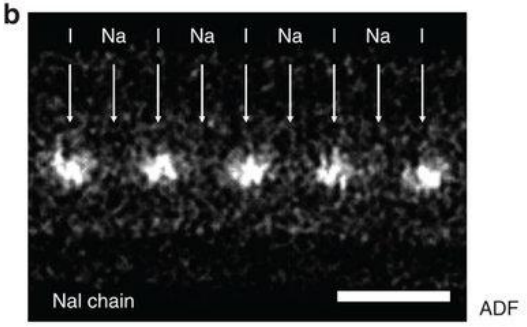
Nanocrystalline LaSrCoO layers on Yttria-stabilized Zirconia



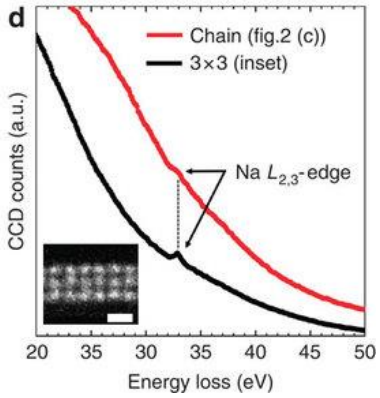
EELS mapping of Au/TiO_2 structure







imaged by TEM at 30-60 keV

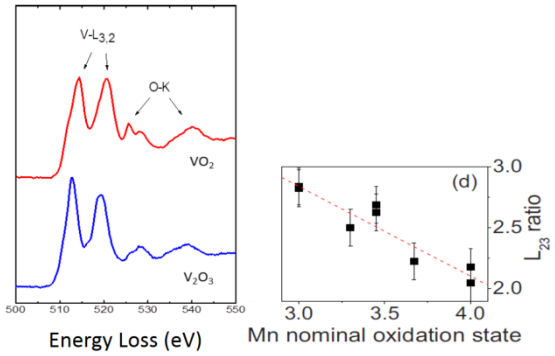


L. Dieterle et al.: J. Mat. Sci. 43 (2008), p. 3135; Adv. Energy Mat. 1 (2011), p. 249
M. Kawasaki et al., Appl. Phys. Lett. 102 (2013) 091603

Senga R. & Suenaga K.: *Single-atom electron energy loss spectroscopy of light elements*, Nat. Commun. 6 (2015), p. 7943

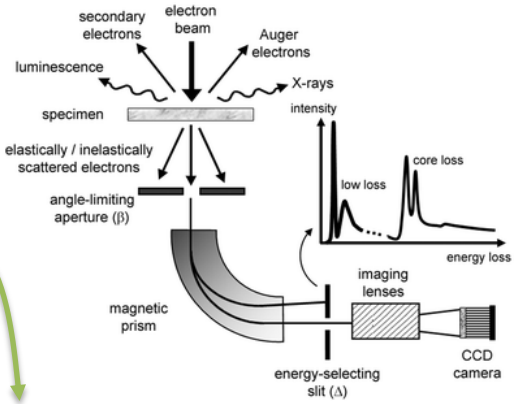
El. spectroscopy in microscopic methods

(HR)EELS in (S)TEM



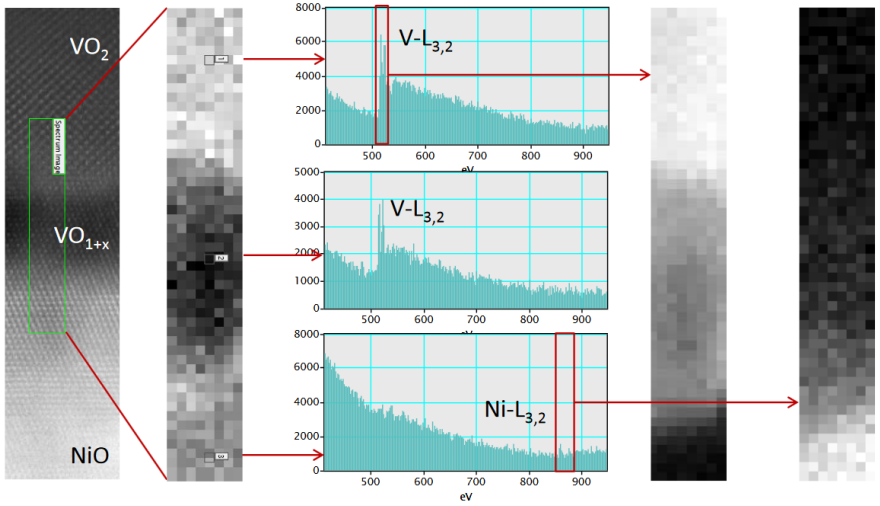
EFTEM (**Energy-filtered TEM**)

1. core-level imaging
2. white line contrast
3. plasmon imaging



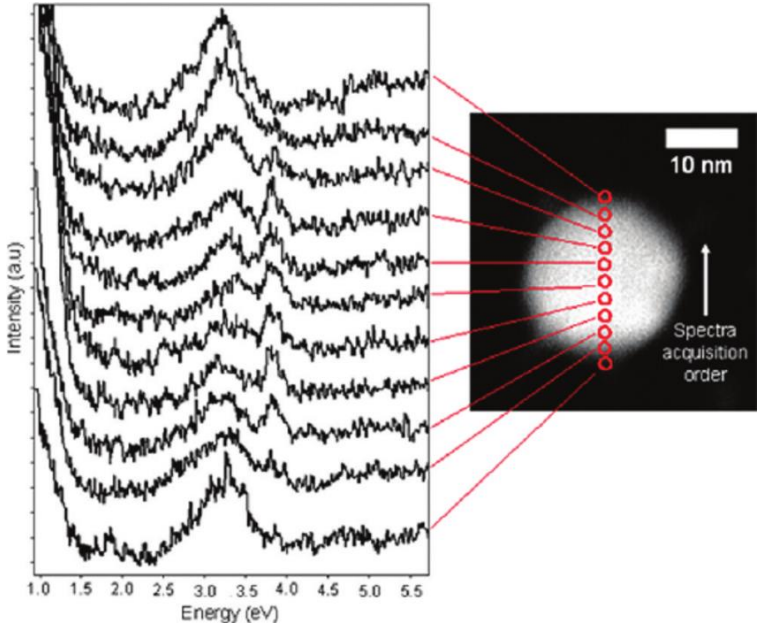
Oxidation state mapping of a thin film

STEM-EELS analysis of VO_x/NiO with VO_x oxidation state resolution



Local EEL spectroscopy of nanostructures

Set of local low-loss EELS spectra of single silver nanoparticle



← H. Zhou et al., M. Varela et al.

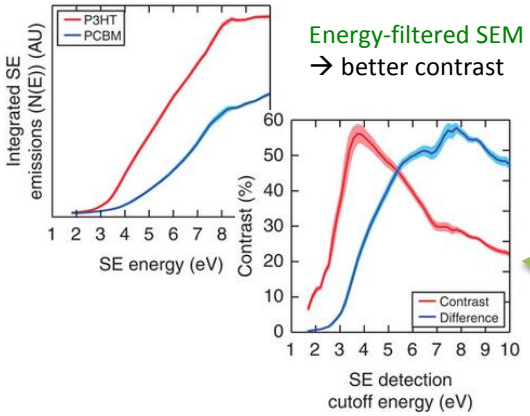
→ A.L. Kon et al.: *Electron Energy-Loss Spectroscopy (EELS) of Surface Plasmons in Single Silver Nanoparticles and Dimers: Influence of Beam Damage and Mapping of Dark Modes*, ACS Nano 3(10), 2009, 3015

El. spectroscopy in microscopic methods

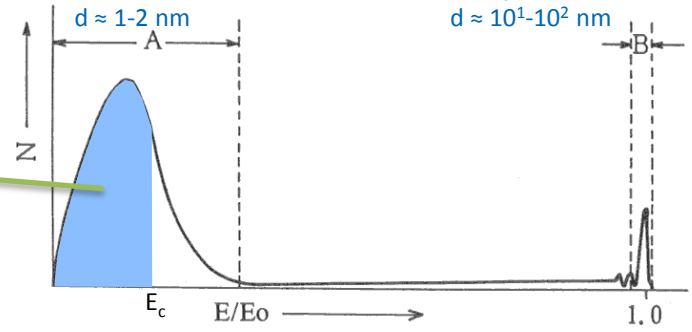
SEM basics

Scanning electron microscopy (SEM)

- **imaging**: secondary electrons (SE) or backscattered electrons (BSE)
- E_p ≈ 100eV~30keV
- spatial resolution down to ~1-2 nm

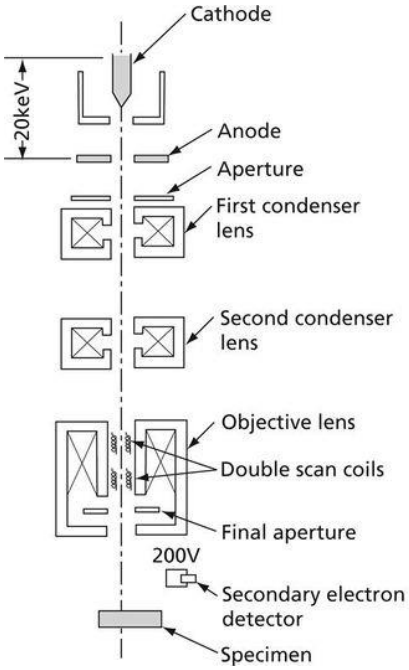


Energy-filtered SEM
→ better contrast



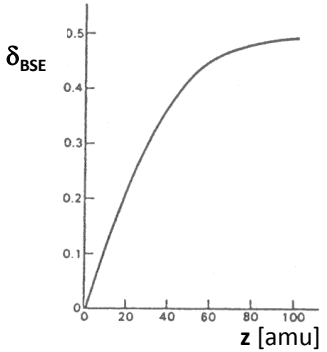
Secondary electrons
E ≈ 10^0-10^1 eV
d ≈ 1-2 nm

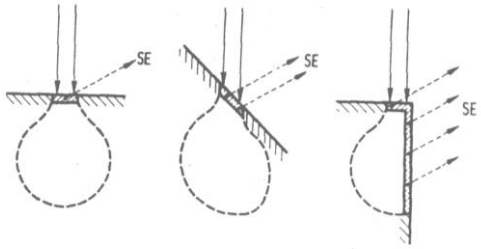
Backscattered electrons
E ≈ E_0
d ≈ 10^1-10^2 nm

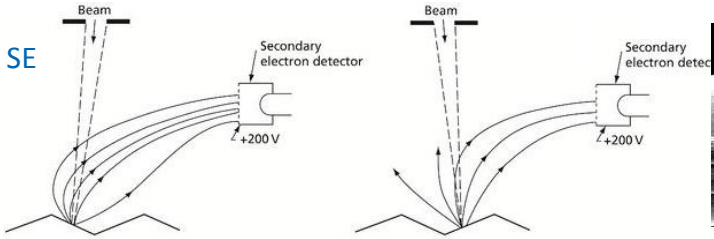


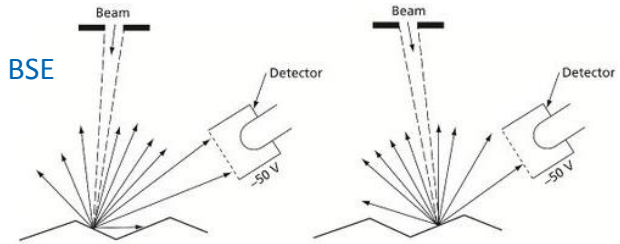
Origins of contrast in SEM

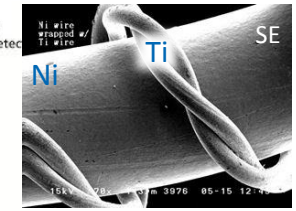
- elemental composition (local differences of BSE yields)
- structure (edge or relief effect)
  - points and edges produce more SE
  - edge orientation and angle rel. to detector (SE & BSE)
- electric or magnetic field(s)

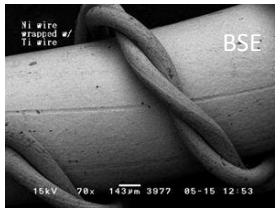












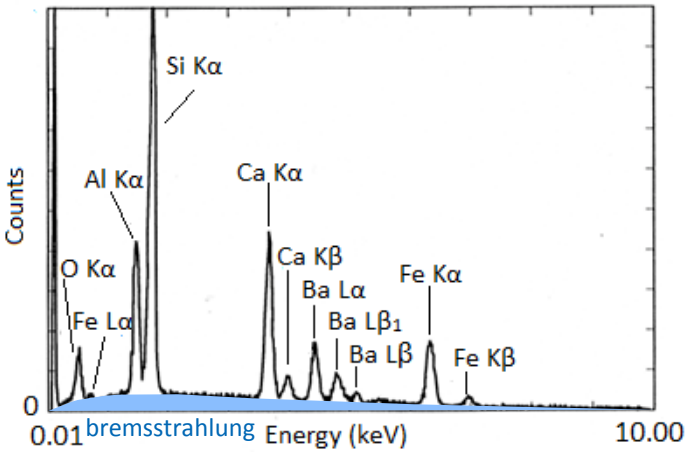
z(Ni)>z(Ti) => Ni brighter

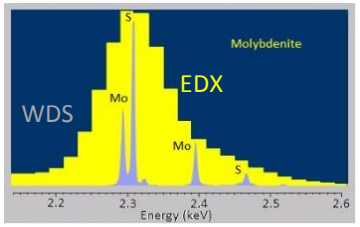
El. spectroscopy in microscopic methods

EDS in SEM – elemental mapping

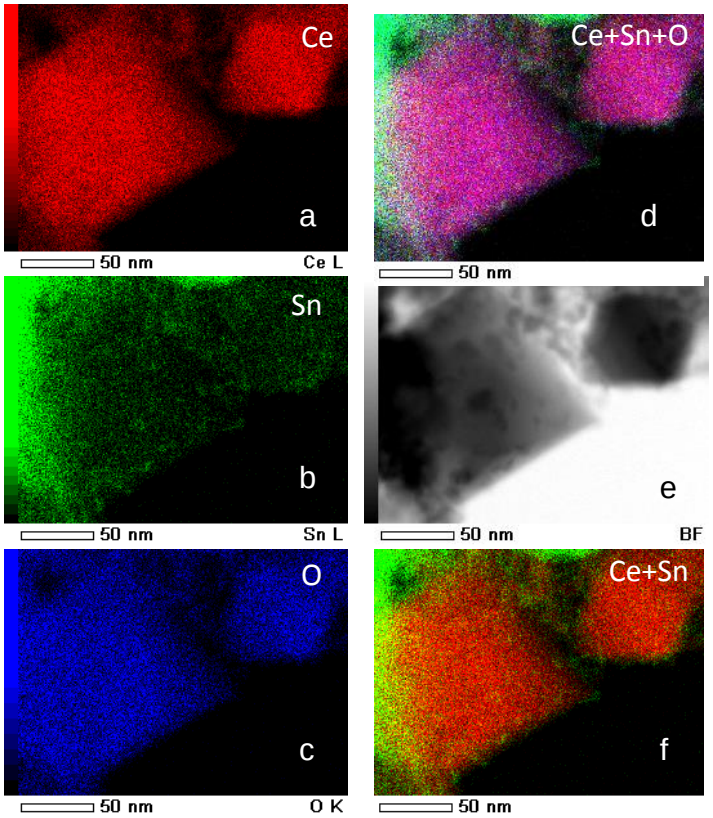
Energy dispersive x-ray spectroscopy (**EDS** or **EDX**)
- **spectroscopy**: cathodoluminiscence (CL) emission – X-rays
- „volume“ characterization (large *d*)
- spatial resolution ~μm (can be lower for thin specimens)

Wavelength EDS (**WDS**)
- **X-ray filter** => selective mapping
- slower but more sensitive (~10-100 ppm; EDX ~2000 ppm) & better resolution





Example: Elemental map of Sn/CeO_x NPs



Qualitative EDX analysis
- point analysis
- line analysis
- area analysis (2D mapping)

Quantitative EDX analysis
- X-ray intensity comparison to standards

+ corrections
  - X-ray absorption
  - secondary X-rays

Constraints and limitations
- peak-background ratio => detection limit
- peak separation > detector E-resolution
- only for boron and heavier elements (× H,He, Li, Be)

El. spectroscopy in microscopic methods

AES in SEM – elemental and chemical mapping

Scanning Auger microscopy (**SAM**)

-SEM + **electron analyzer** (mainly CMA, HDA)

a) serial acquisition – tuned to selected Auger energy; initial survey needed

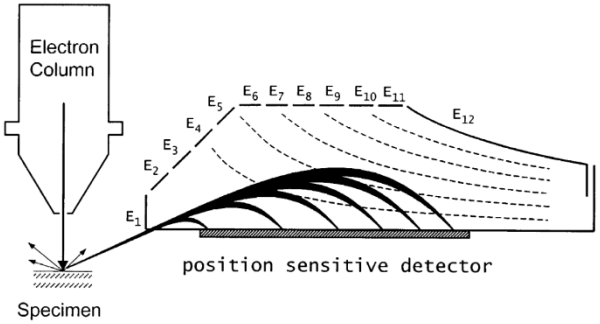
b) parallel acquisition – complete spectrum from the same spot; beam damage and drift effects minimized

-spatial resolution ~10-20 nm - defined by the primary beam size (due to high surface sensitivity)

-higher sensitivity for lighter elements

-chemical effects detectable

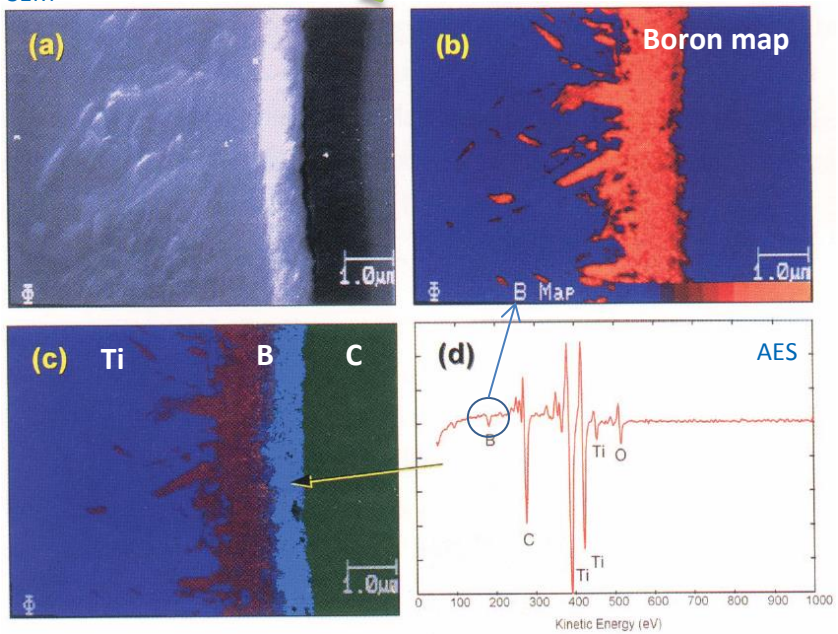
Hyperbolic field analyzer



Depth profiling – cross section or continuous sputtering

TiB_2 coating on Ti

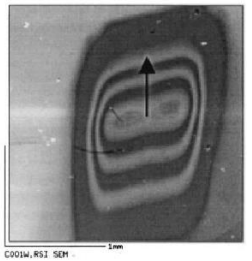
SEM



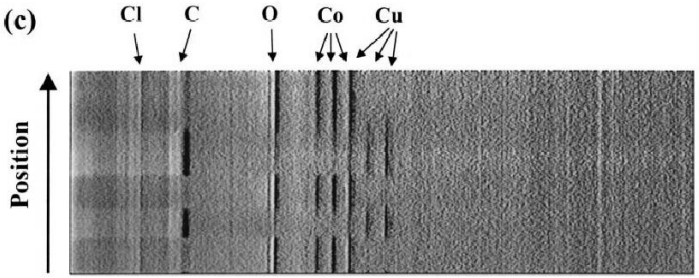
Bevelled multilayer Cu/Co structure

(a) Cross-section scheme

(b) SEM



AES line scans

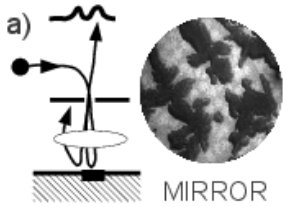


Collection rate: 5s/spectrum

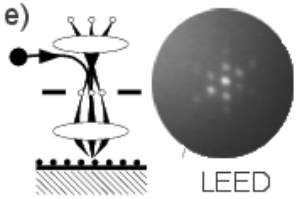
El. spectroscopy in microscopic methods

Low energy electron microscope – basics

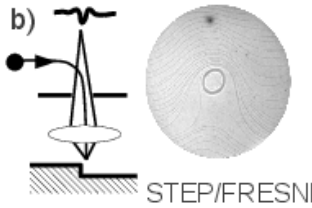
LEEM operation modes



reflection

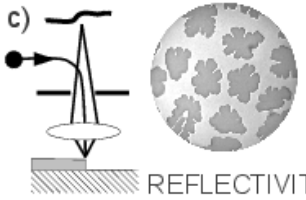


diffraction

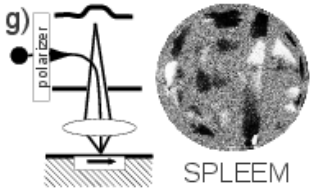


phase contrast – interference in Fresnel diffraction

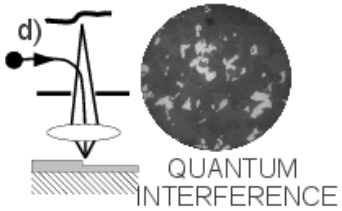
intensity of selected diffraction spot



composition (diffraction) contrast

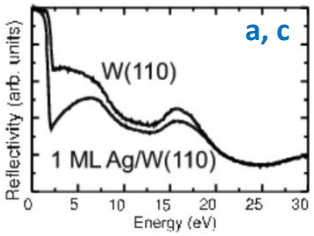


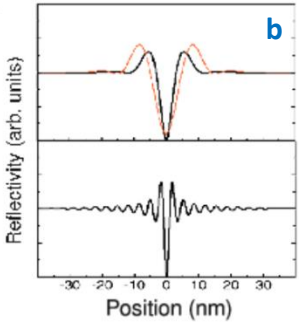
magnetic contrast of spin polarized electrons

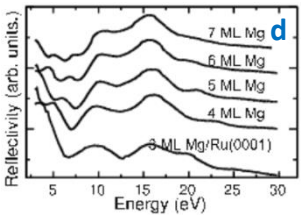


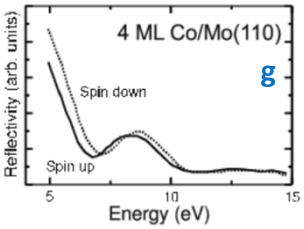
phase contrast – different thicknesses

Origins of phase contrast



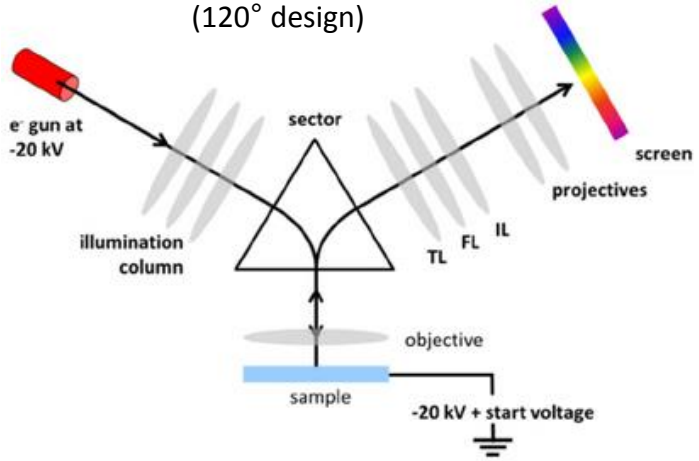




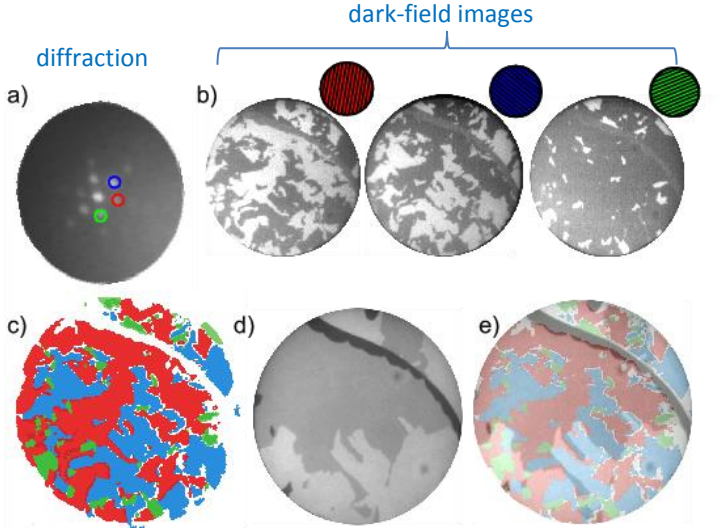


LEEM schematics

(120° design)



Composite imaging



composite dark-field + bright-field = complete image

shows both rotational and stacking domains

El. spectroscopy in microscopic methods

Spectral photoelectron low energy electron microscopy (SPELEEM)

LEEM (Low energy electron microscope)
- structural and material sensitivity
- probe: 0-500 eV electrons (5-20 keV in optics)
- ≲5 nm resolution (~20 nm for EELS)
- video-rate imaging possible

EF-LEEM
- energy filter: adds spectral resolution (≲200 meV)

→ microprobe (selected area) EELS, AES

LEEP (LEEM-IV)
- variation of E_p, no energy filter needed
- surface potential mapping

(UV-)PEEM (Photoemission electron microscope)
- chemical and electronic structure sensitivity, adsorbates
- probe: monochromatic UV light (Hg, Ar, He, ... lamp)
- ≲100 nm resolution
- video-rate imaging possible

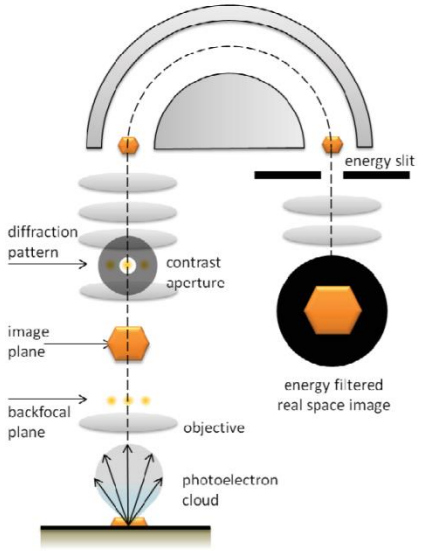
XPEEM (XAS-PEEM)
- probe: soft X-rays (50-1000 eV)
- ≲50 nm resolution

HAXPEEM (HAXPES-PEEM)
- probe: hard X-rays (~keV)
- buried layers

microscopy

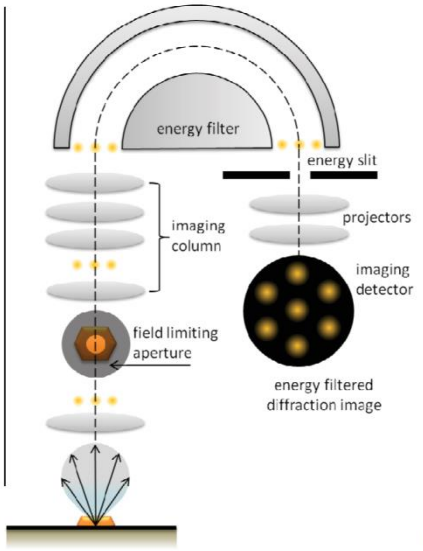
spectro-microscopy

imaging mode
EF-LEEM / XPEEM



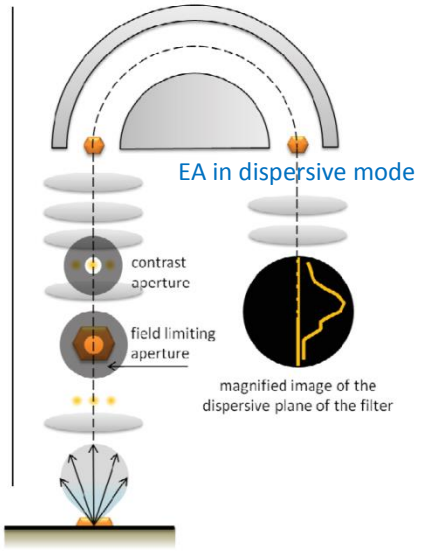
→ image for selected E
(and optionally wave vector)

diffraction mode
μLEED / μARPES



→ diffraction pattern of
selected area for selected E

spectroscopy mode
μAES, μEELS / μXPS (μPES)

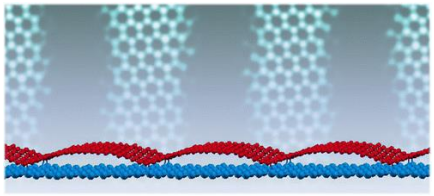


→ E spectrum for selected area
(and optionally wave vector)

El. spectroscopy in microscopic methods

(HA)XPEEM – applications

UV
DOS mapping



graphene
Ir(100)

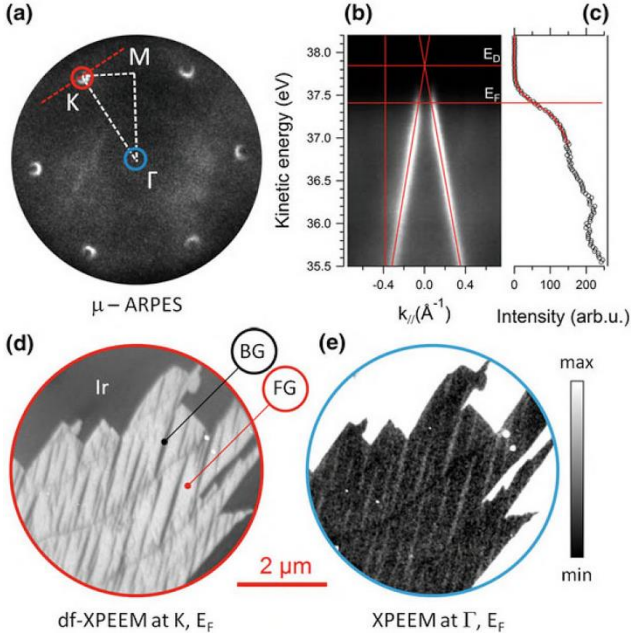
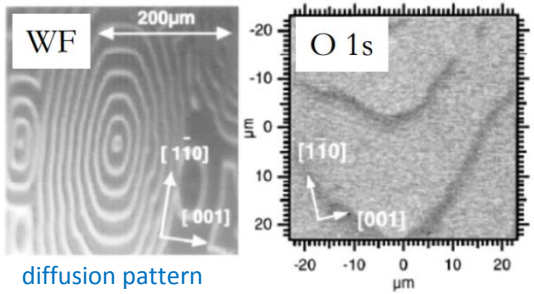


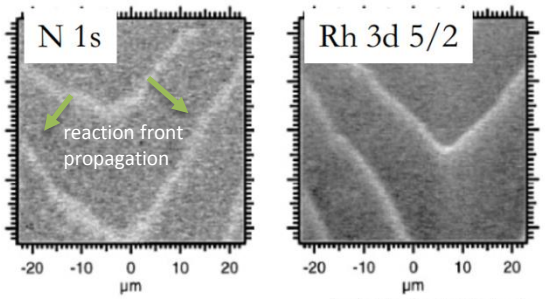
Fig. 21.5 **a** Microprobe ARPES map of flat graphene (*FG*) on Ir(100) and **b**, **c** cross section through one of the Dirac cones. **d** Dark-field PEEM image, obtained positioning the contrast aperture at the *K* point, demonstrating that flat graphene has a much higher DOS then buckled graphene (*BG*); **e** inversion of contrast in the PEEM image at the Γ reveals hybridization with Ir states in BG.

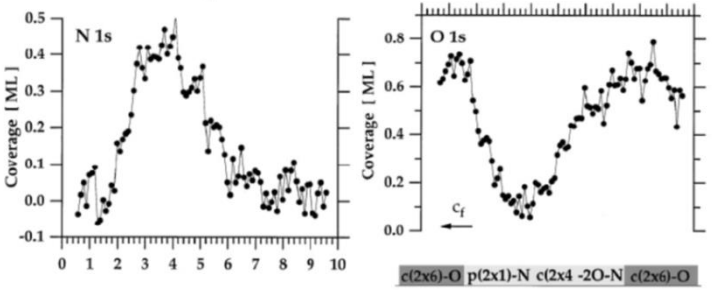
SX
Chemical imaging

$NO+H_2$ on Rh(110)
Quantitative measurement of concentration profiles during reaction

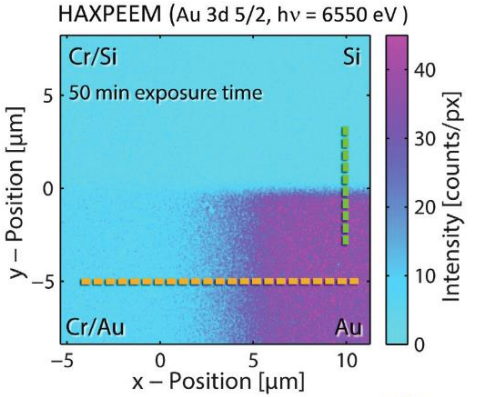


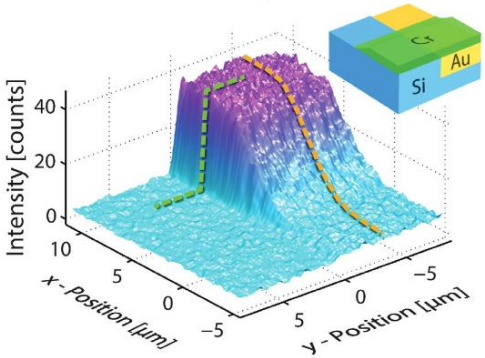
diffusion pattern





HX
Depth profiling (3D imaging)



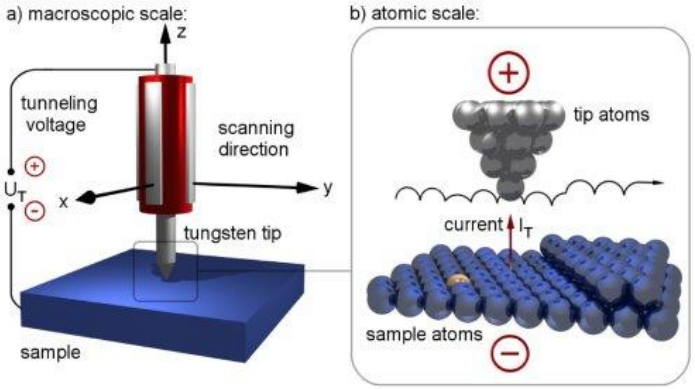


A. Locatelli et al.: *Temperature-Driven Reversible Rippling and Bonding of a Graphene Superlattice*, ACS Nano 7 (8), 2013, pp. 6955–6963
A. Schaak et al.: *Elementally Resolved Imaging of Dynamic Surface Processes: Chemical Waves in the System Rh(110)/NO+H_2*, Phys. Rev. Lett. 83, (1999), p. 1882
M.Patt et al.: *Bulk sensitive hard x-ray photoemission electron microscopy*, Rev. Sci. Instrum., 85, (2014), 113704

El. spectroscopy in microscopic methods

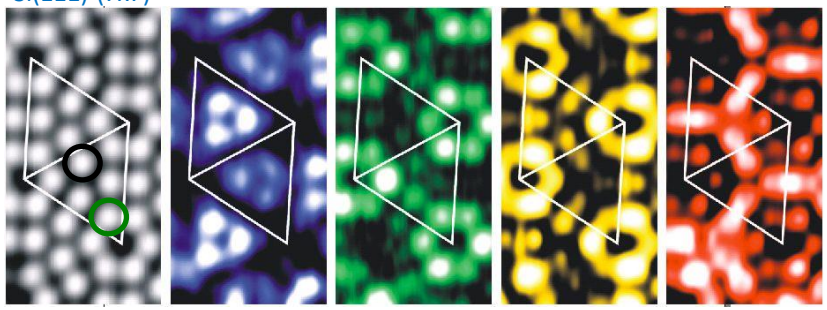
Scanning tunneling spectroscopy in STM

Scanning tunneling microscope



Spectroscopic maps in STM
- derivative (*dI/dV*) signal at various potentials

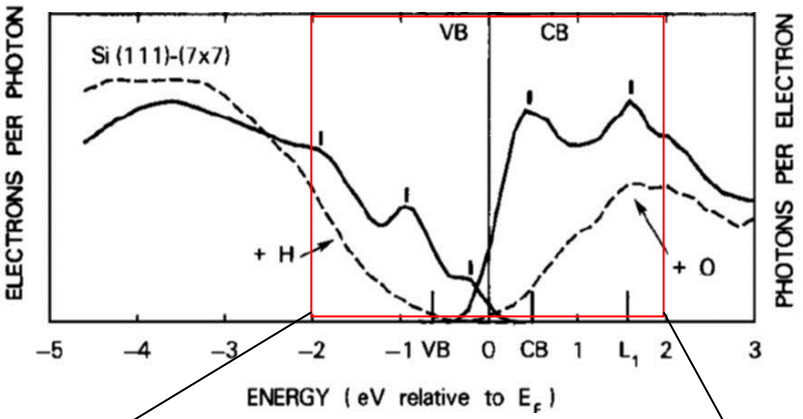
Si(111)-(7x7)



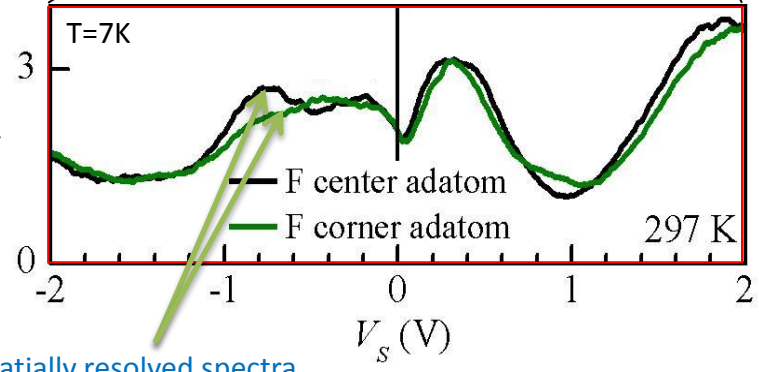
STM topography **STS**: E=-1,3eV E=-0,5eV E=+1,4eV E=+1,6eV

occupied states empty states

Occupied states – UPS Empty states – IPS



fixed position



spatially resolved spectra

Shows **both** occupied and empty states!

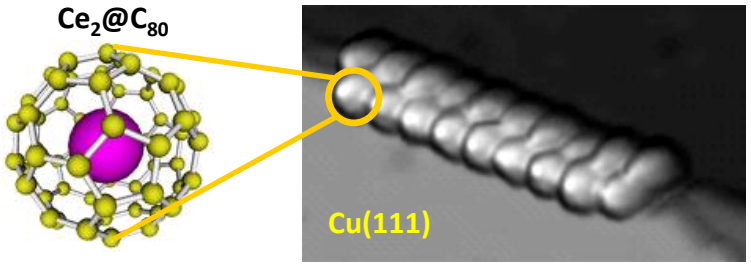
F.J. Himpsel, Th. Fauster: *Probing valence states with photoemission and inverse photoemission*, J. Vac. Sci. Technol. A2, (1984), p. 815
J. Mysliveček et al.: *Structure of the adatom electron band of the Si(111)-7x7 surface*, Phys. Rev. B, 73 (16), (2006), Art. No. 161302

El. spectroscopy in microscopic methods

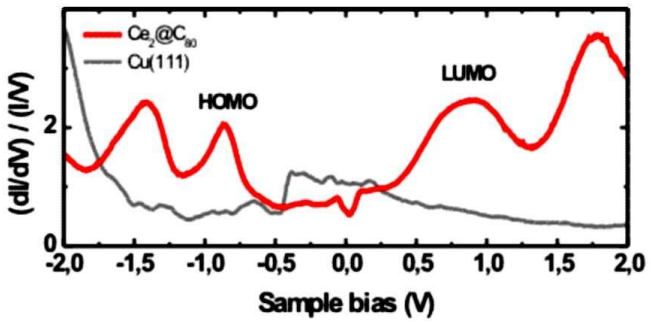
Scanning tunneling spectroscopy in STM

Single-molecule spectroscopy

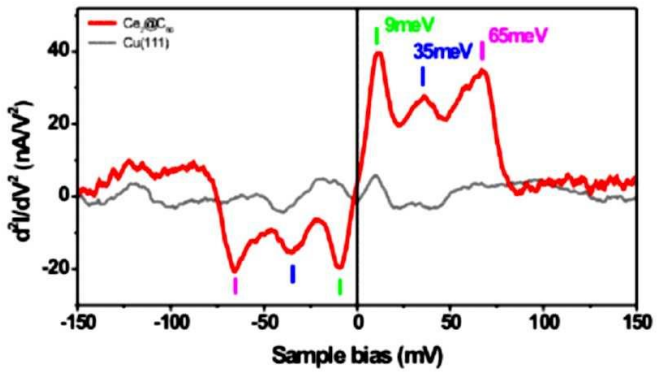
$Ce_2@C_{80}$



Electronic spectrum of $Ce_2@C_{80}$ molecule



Vibrational spectrum of $Ce_2@C_{80}$ molecule

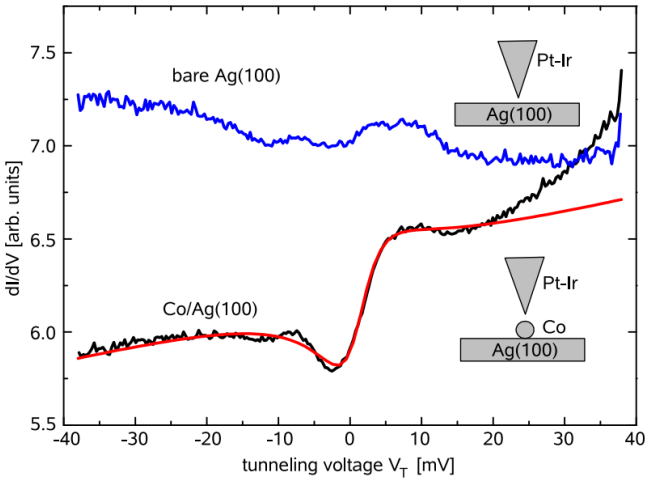


A. Stróżecka et al.

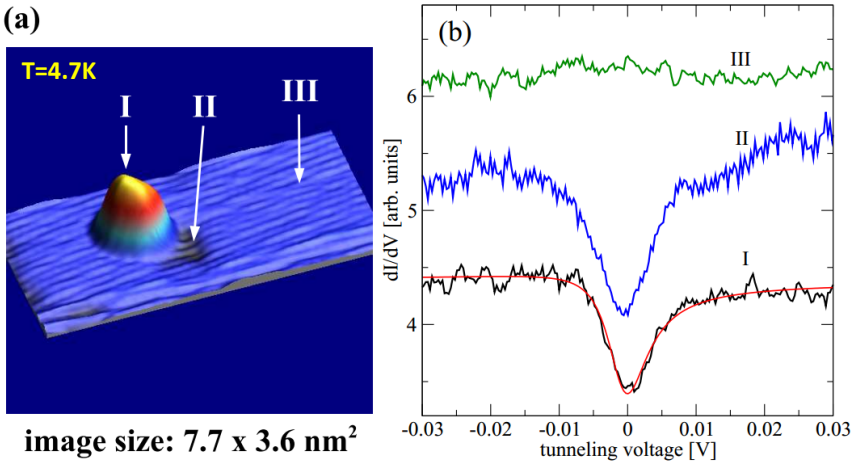
Single-atom spectroscopy

Usually very low temperatures required

Co adatom on Ag(100)



Ce adatom on Ag(100) after exposure to H_2



M. Ternes: PhD thesis, 2006

Operando photoelectron spectroscopies

NAP-XPS/PES

Operando spectroscopy studies

- high-pressure reactions
- analysis of liquids and liquid-solid or liquid-gas in
- realistic-pressure sensing
- electrochemistry
- …

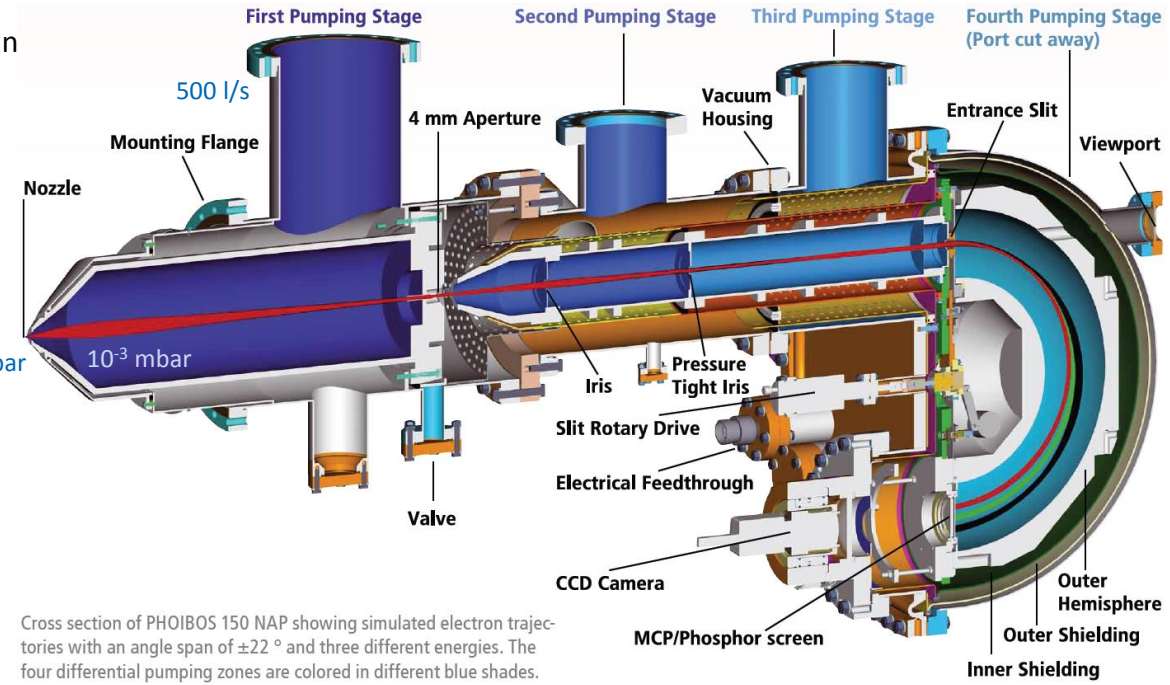
BUT

Electron spectroscopy methods require **vacuum**
=> "pressure gap"

NAP = near ambient pressure

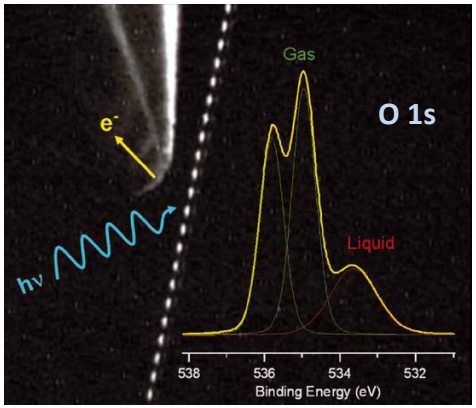
~10^0-10^1 mbar
- multistage differential pumping required

Specs Phoibos 150 NAP

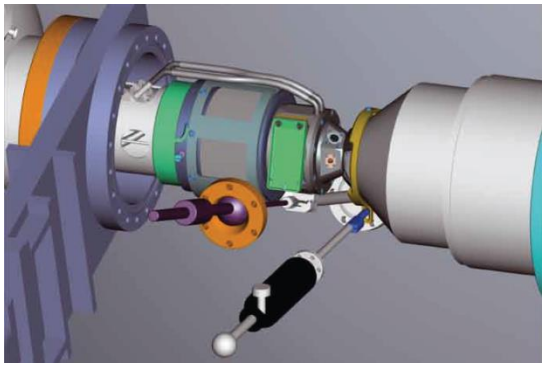


Cross section of PHOIBOS 150 NAP showing simulated electron trajectories with an angle span of ±22 ° and three different energies. The four differential pumping zones are colored in different blue shades.

Droplet jet of 40% ethanol solution



0.3 mm aperture



High-pressure cell

Exchangeable conic aperture (nozzle) (<1 mm)