Auger electron spectroscopy (AES) and modulation techniques

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FHI-Berlin, 29.10.2004

Literature - AES:

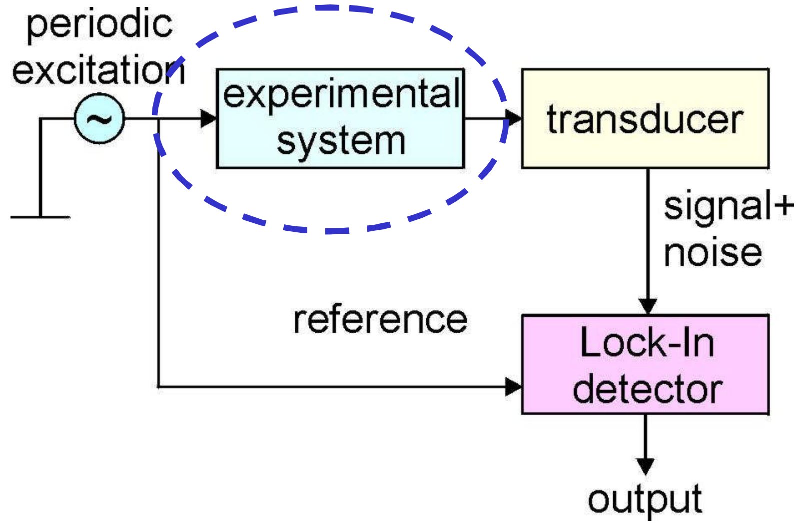
G. Ertl, J. Küppers, Low Energy Electrons and Surface Chemistry, VCH, Weinheim (1985).
J.W. Niemantsverdriet, Spectroscopy in Catalysis, Wiley-VCH, Weinheim (2000).
G.E. McGuire, Auger Electron Spectroscopy Reference Manual, Plenum Press, New York (1979).
L.E. Davis et al., Handbook of Auger Electron Spectroscopy, Physical Electronics Ind. Inc., Eden Prairie (1976).

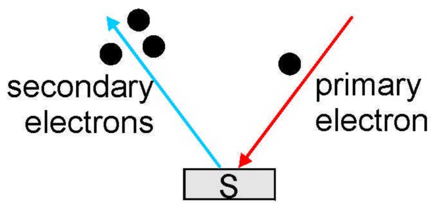
Literature - Lock-In, Modulation techniques:

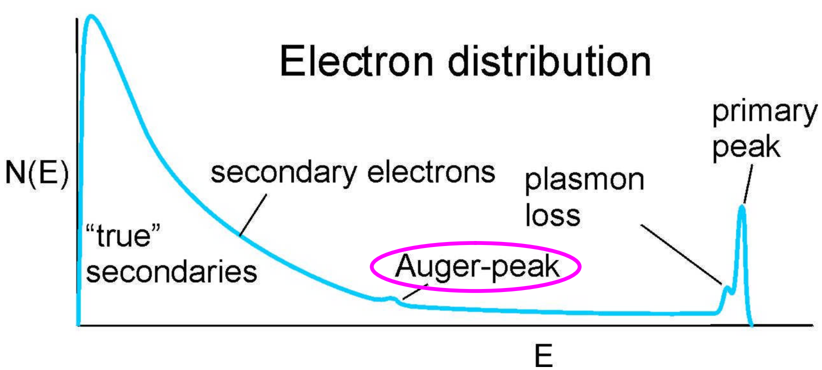
M.L. Meade, Lock-In Amplifiers: Principle and Applications, Peter Peregrinus Ltd., London (1983).
R.K. Willardson, A.C. Beer (eds.), Semiconductors and Semimetals, Vol. 9: Modulation Techniques, Academic Press, New York (1972).

Wikipedia English: http://en.wikipedia.org
German: http://de.wikipedia.org

AES - basics





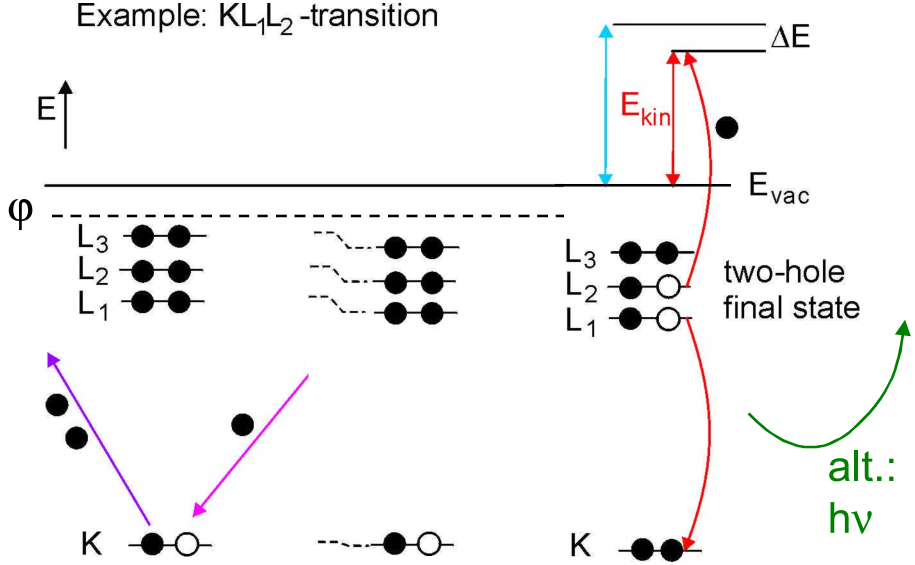


Excitation:
Primary electrons, 1-10 kV.
easy to create.
(Also possible: X-rays, see XPS).
easy to focus (< 1µm):
Scanning-Auger.
high intensity:
fast measurement,
damage (esp. adsorbates!)

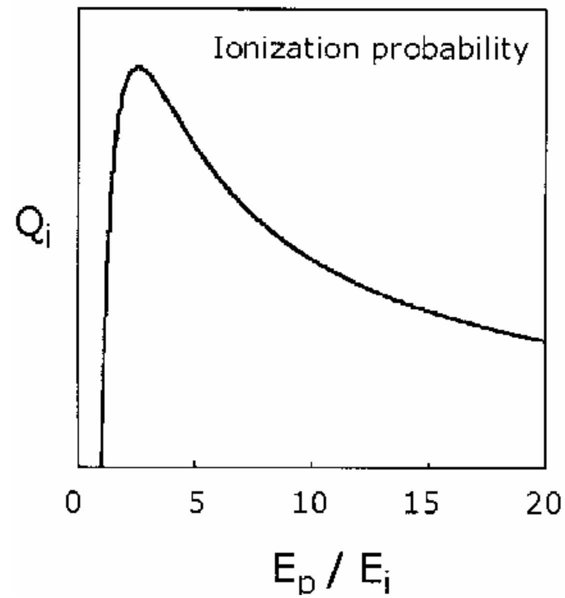
Secondary electron spectrum:
Auger-e^- are special
secondary electrons.

AES - basics

Auger process (P. Auger, 1923)



excitation)* relaxation Auger decay



Prob. of core hole creation
E_i e^- binding E
E_p e^- impact E (prim. E)

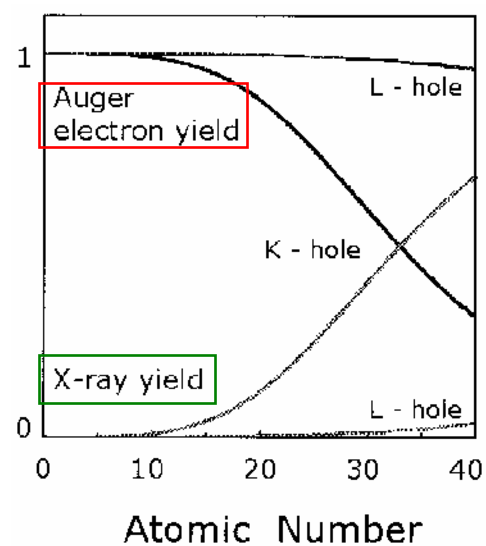
E_{KLM} is <u>independent</u> of E_p.

1st approx.:

$E_{KLM} = E_K - E_L - E_M - \Delta E - \varphi$

E_{KLM}	kin. energy of Auger electron
E_K	binding energy of K-electron etc.
φ	work function
ΔE	relaxation shift

)* core ionization may also occur by X-ray photoionization (=> XPS)



Auger decay preferred for light elements, X-ray decay preferred for heavy elements

AES - basics

Nomenclature:

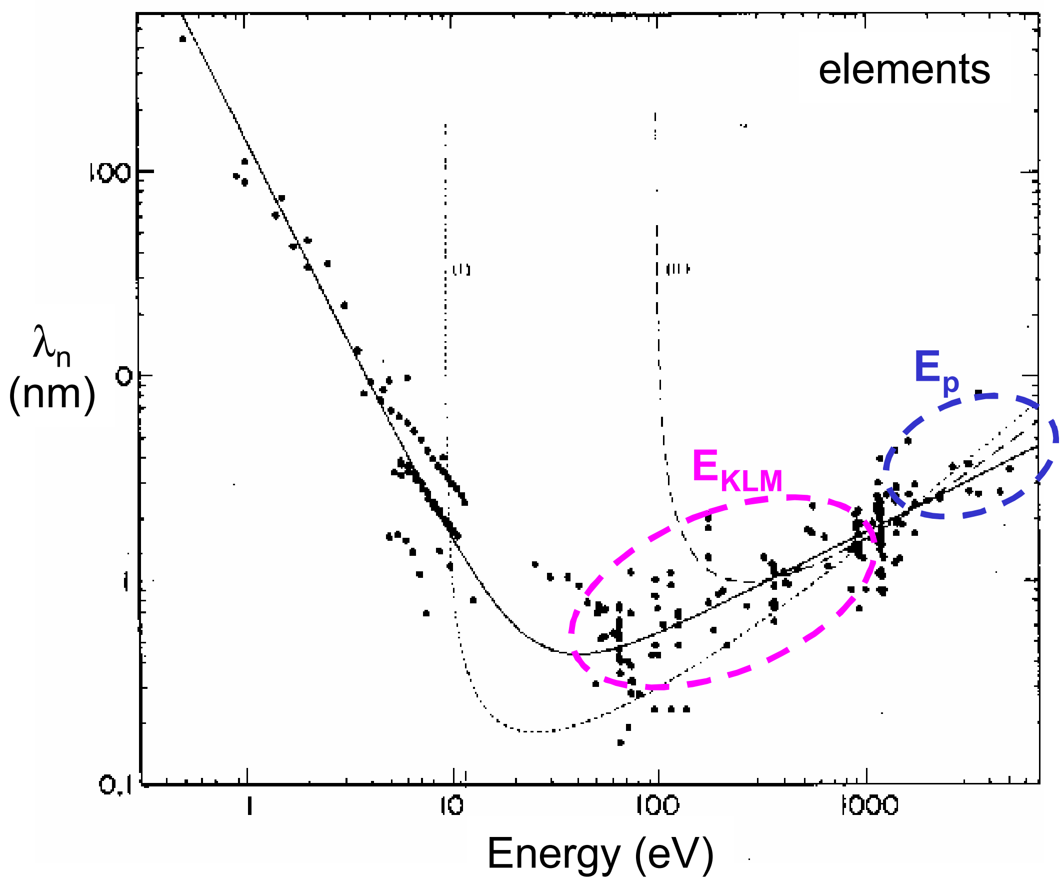
1s	K	
2s	L_1	↑
$2p_{1/2}$	L_2	
$2p_{3/2}$	L_3	
3s	M_1	or V if valence band
$3p_{1/2}$	M_2	
$3p_{3/2}$	M_3	
$3d_{3/2}$	M_4	
$3d_{5/2}$	M_5	↓

etc.

Two-hole final state: no Auger peaks from H, He. 

Insulating samples: charging problems.

AES – surface sensitivity



Inelastic electron mean free path λ for elements („universal curve").

full curve:

$l_n = A_n/E^2 + B_n E^{1/2}$

elements:
$A_n = 143$, $B_n = 0.054$

inorg. compounds:
$A_n = 641$, $B_n = 0.096$

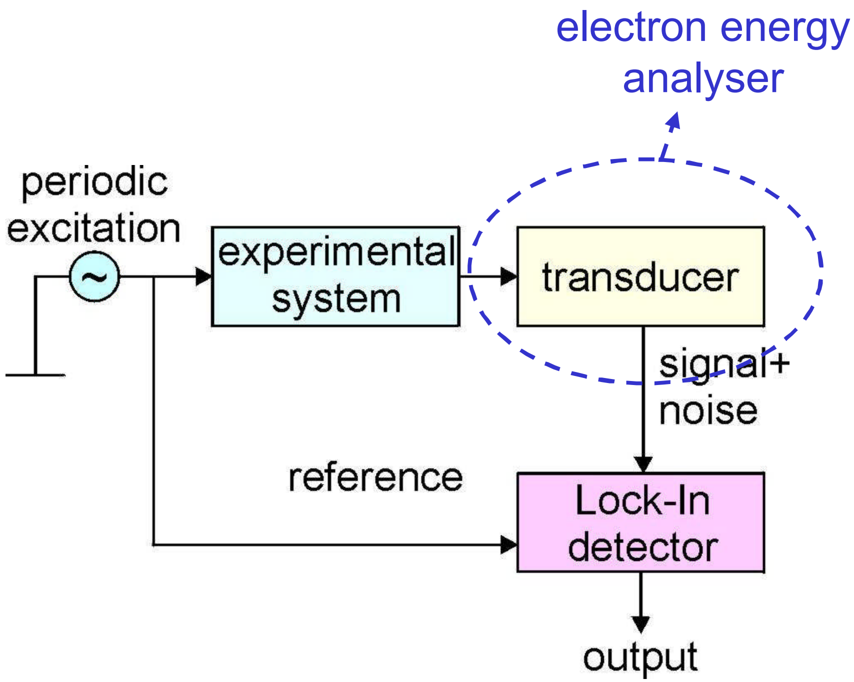
org. compounds:
$A_n = 31$, $B_n = 0.087$

[M.P. Seah, W.A. Dench
Surf. Interf. Anal. 1, 1 (1979).]

Surface sensitivity:

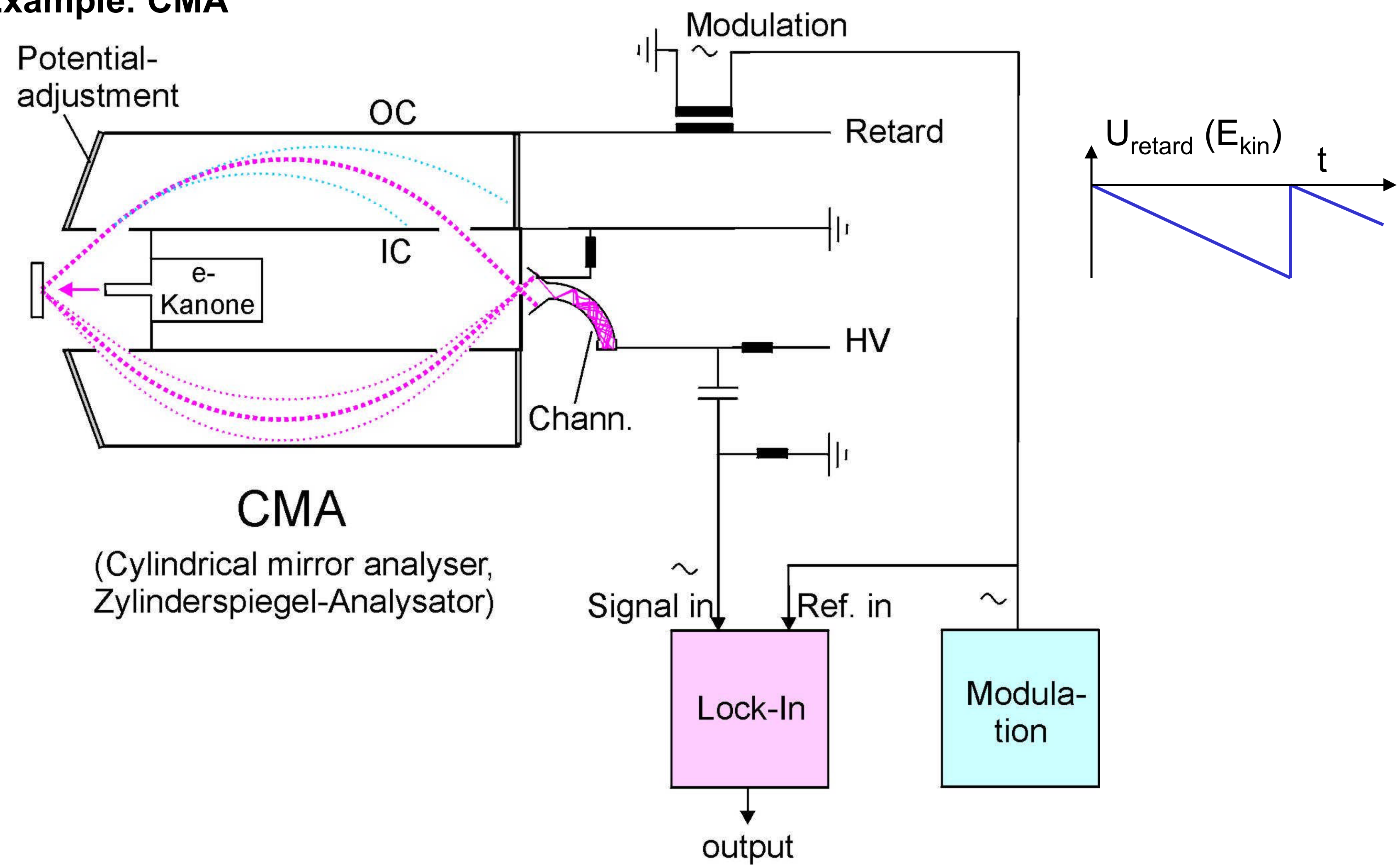
- limited penetration depth of e_{p},
- limited escape depth of e_{KLM}, only ~0.5 nm at 100 eV (~2-3 ML)
- even higher surface sensitivity for grazing incidence / escape

AES – electron energy analysis



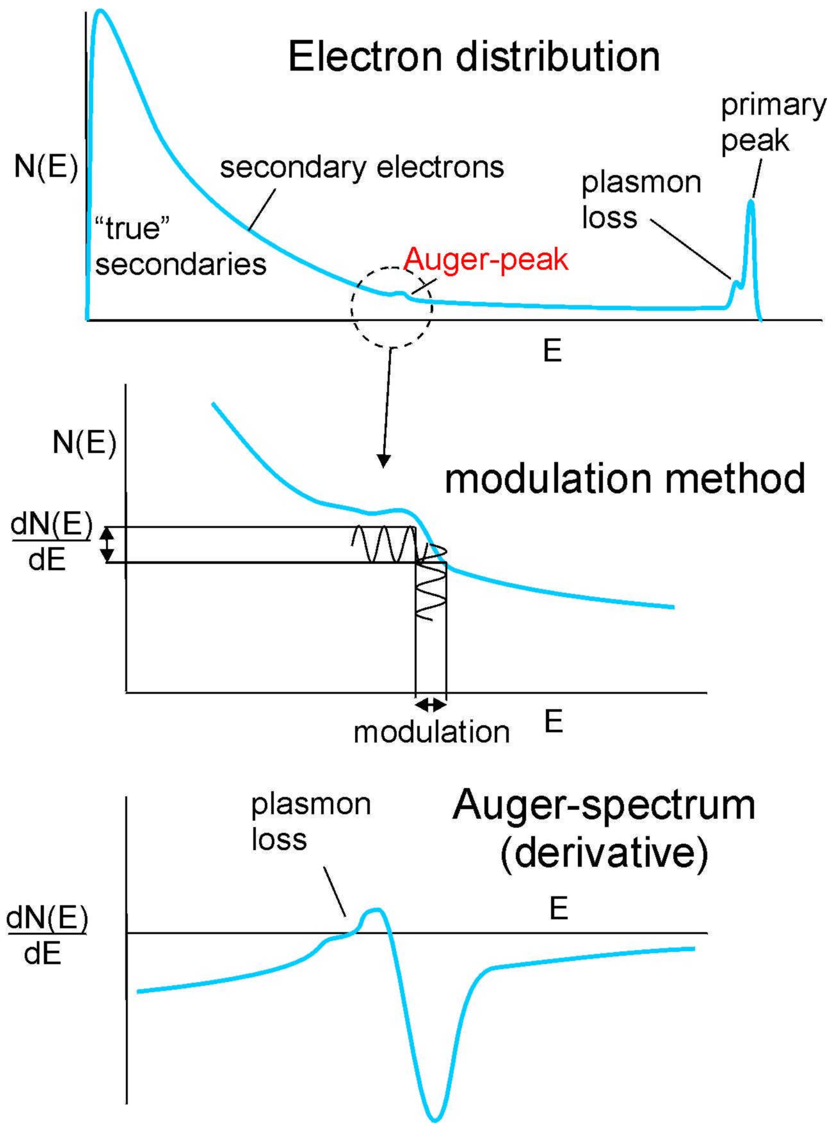
AES – electron energy analysis

Example: CMA

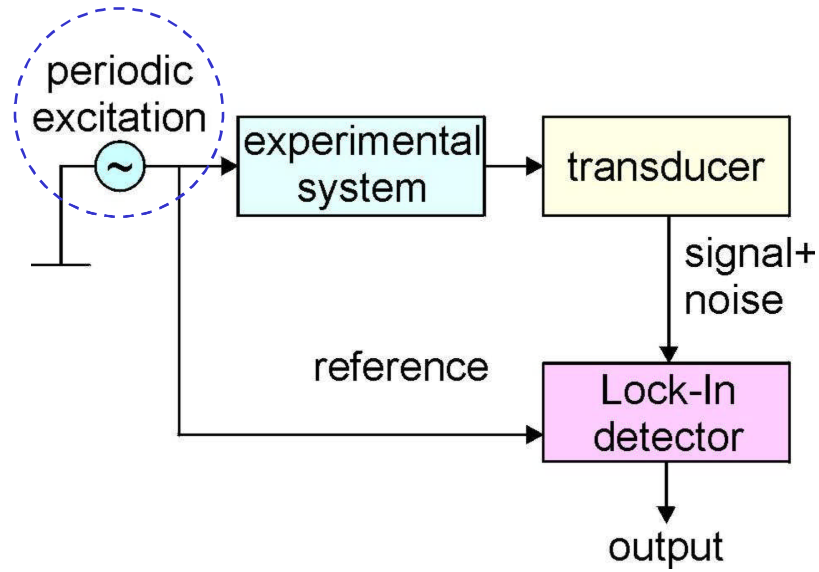


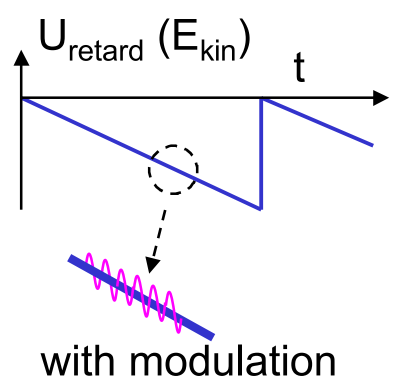
Other analyser types:	Hemispherical analyser Cylindrical sector analyser, Retarding field analyser (LEED optics)

AES – modulation method

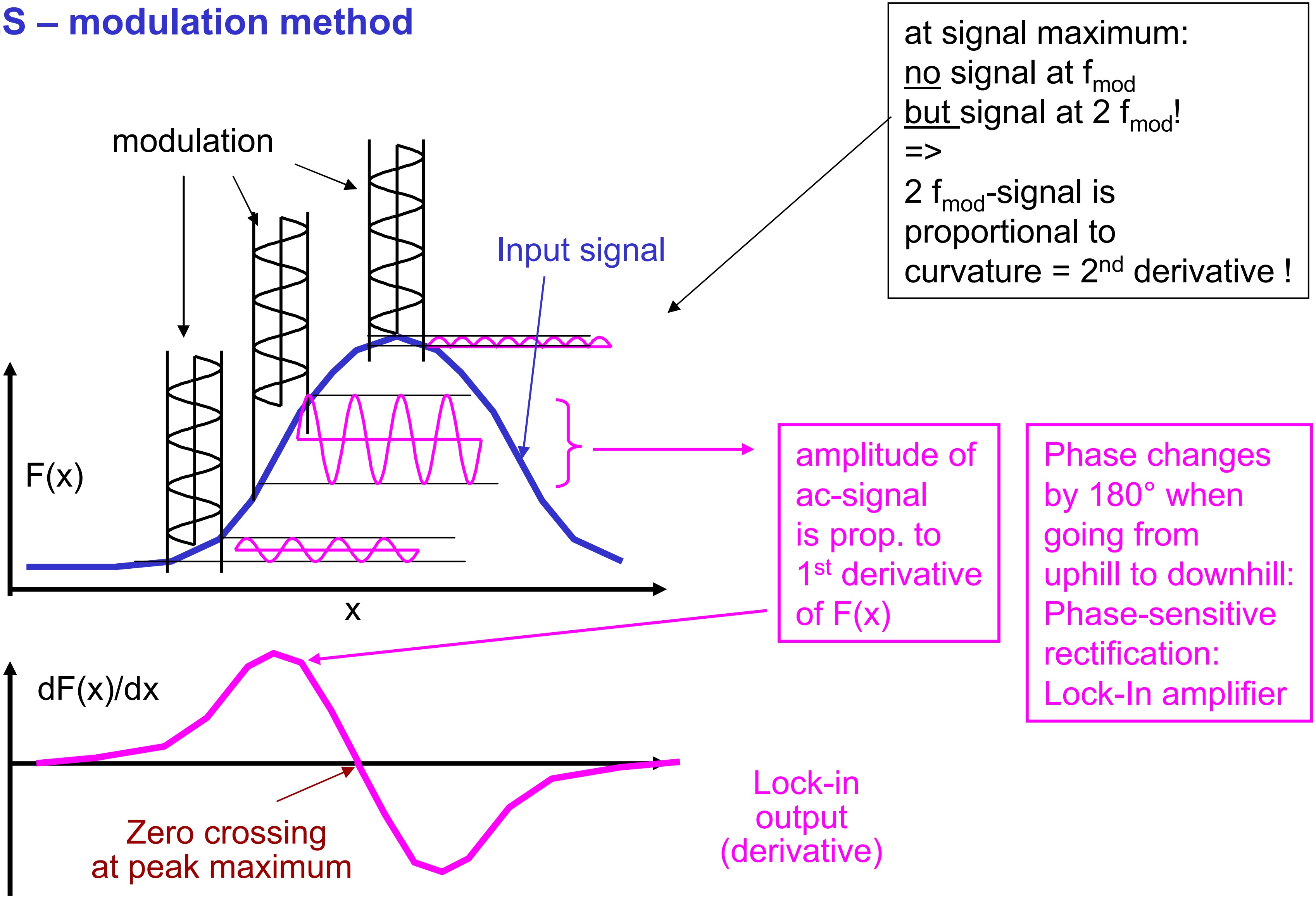


Problem: small signal on high background, noise ~sqrt(N)

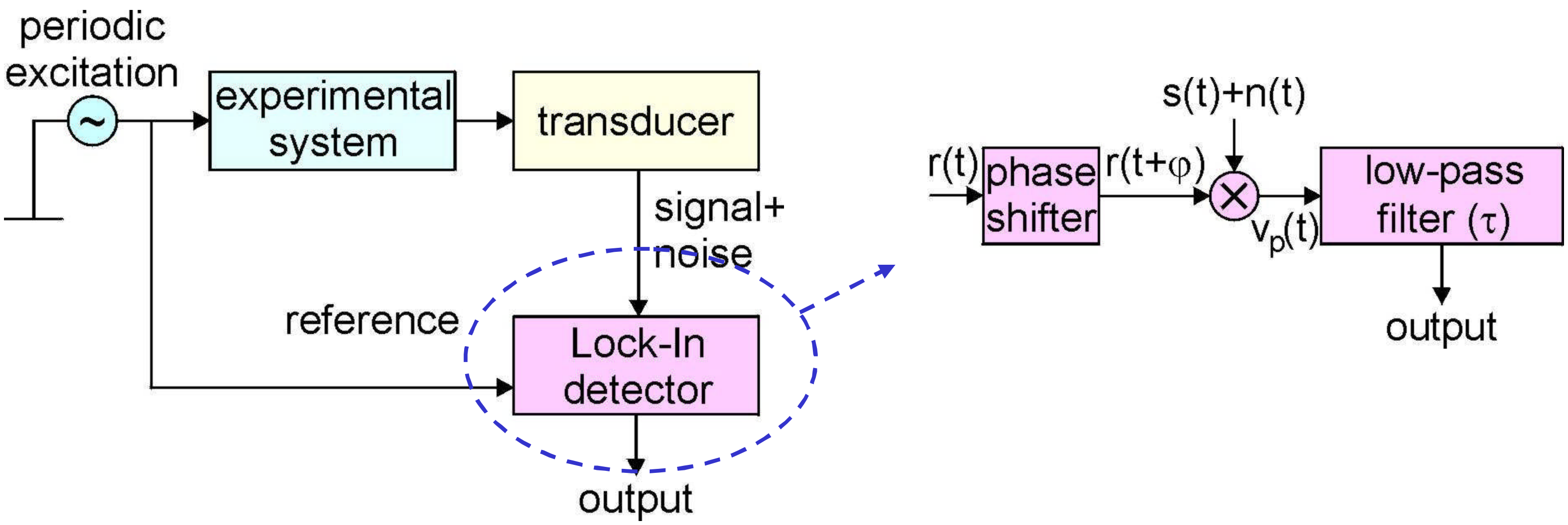




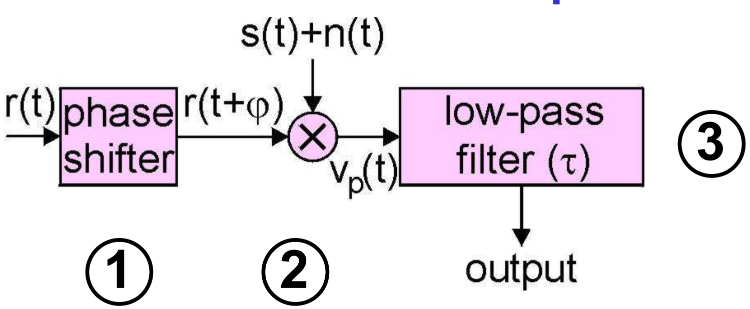
AES – modulation method

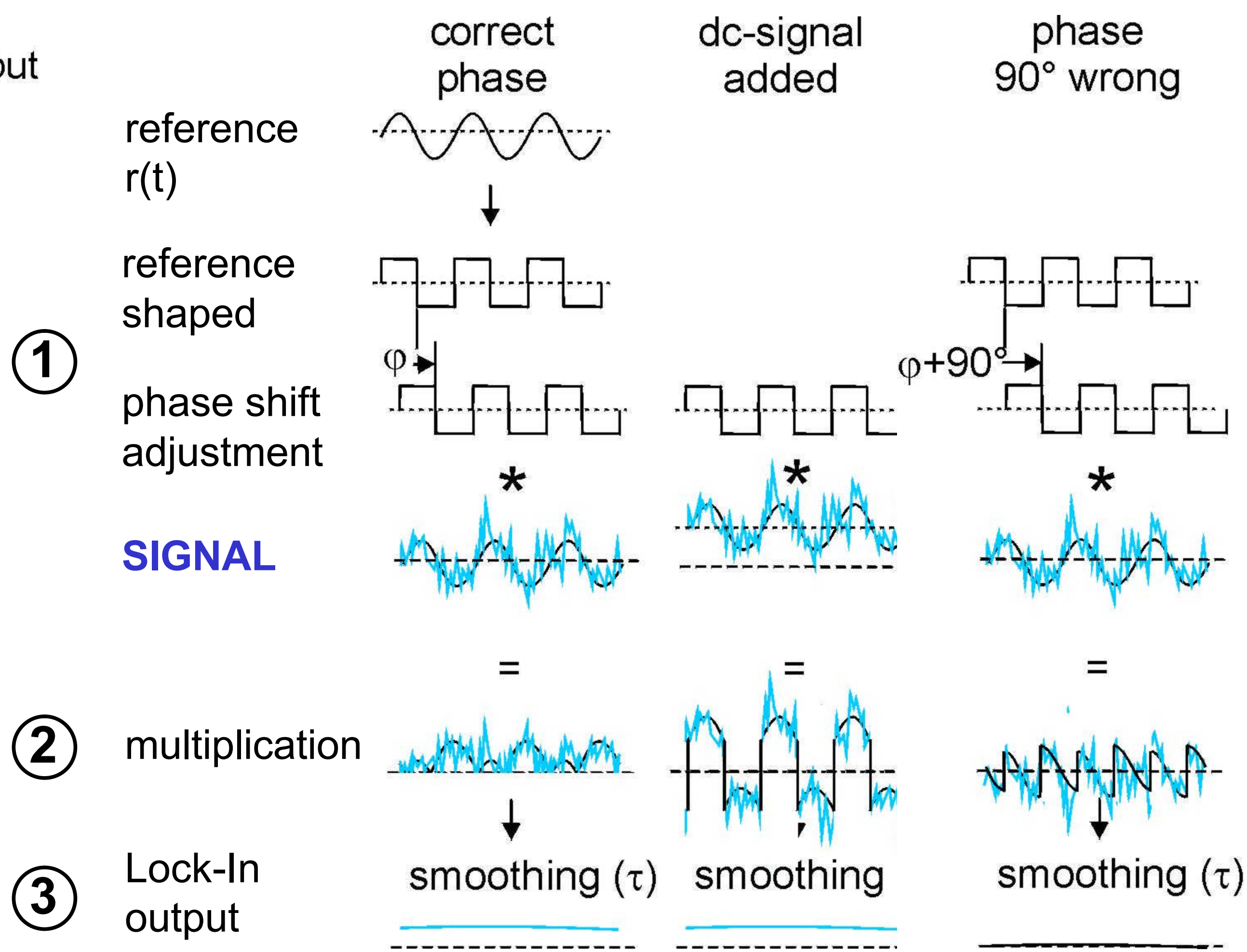


AES – Lock-In technique



AES – Lock-In technique



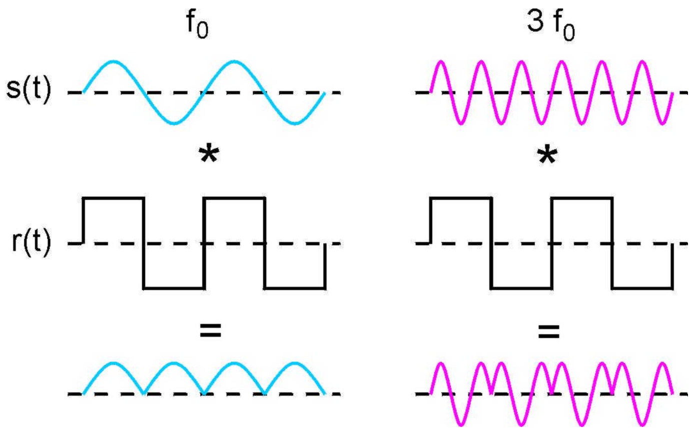


This example:
S/N~1

Possible:
up to
S/N~1/1000

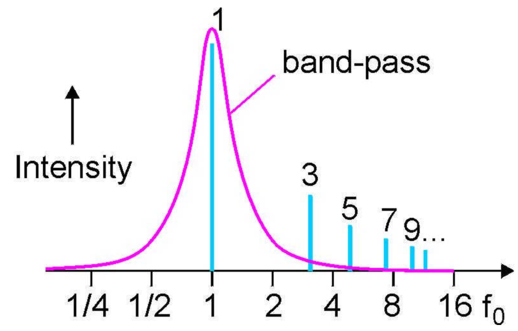
AES – Lock-In technique

Lock-In:
Amplification of
odd harmonics



I_0 $\qquad$ $1/3\ I_0$

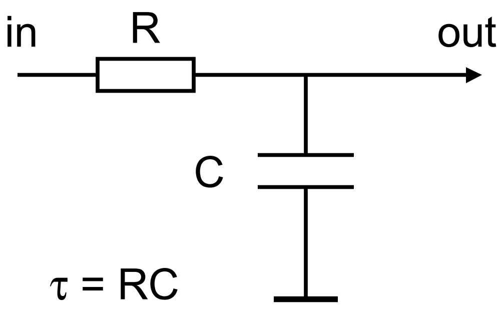
Suppression
of odd harmonics
by band-pass
filter at LI-input

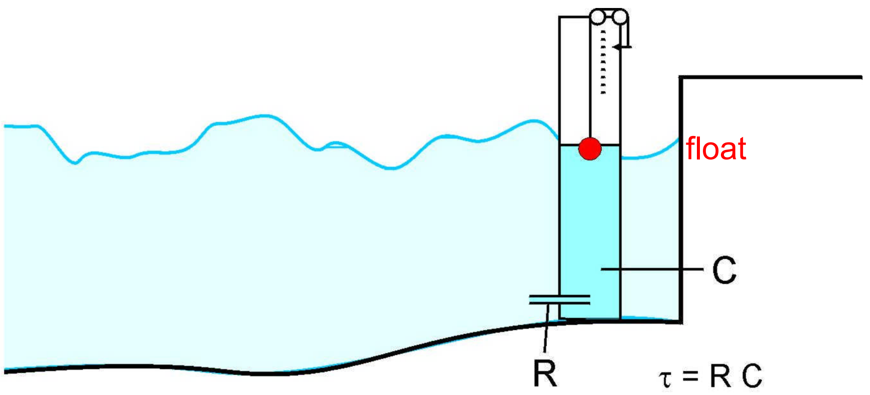


6 db or 12 db
per octave

AES – signal smoothing

Low-pass filter



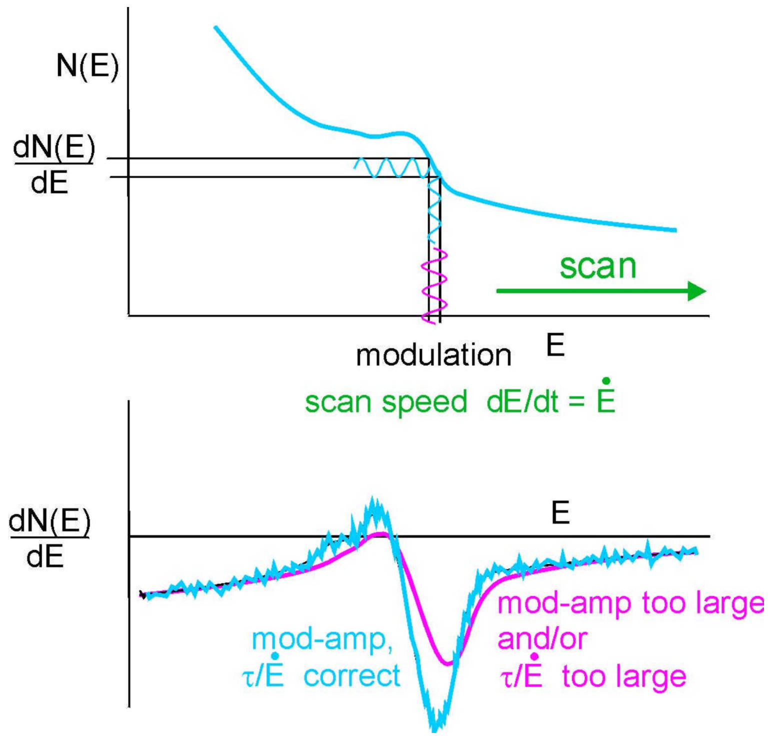


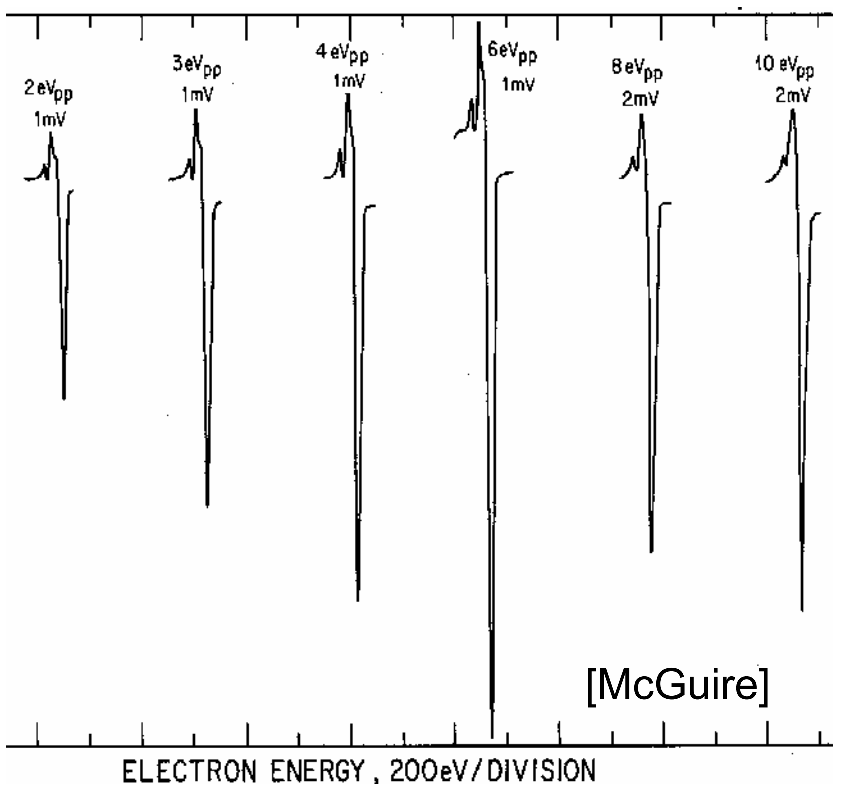
tide-gauge

smoothed signal

- always lags behind (by τ)
- cannot follow changes faster than $1/\tau$

AES – signal smearing





S/N ratio ~ τ
For too high τ:
smearing of structures

For low enough mod.-amp.:
output ~ mod.-amp.
Then: smearing of structures

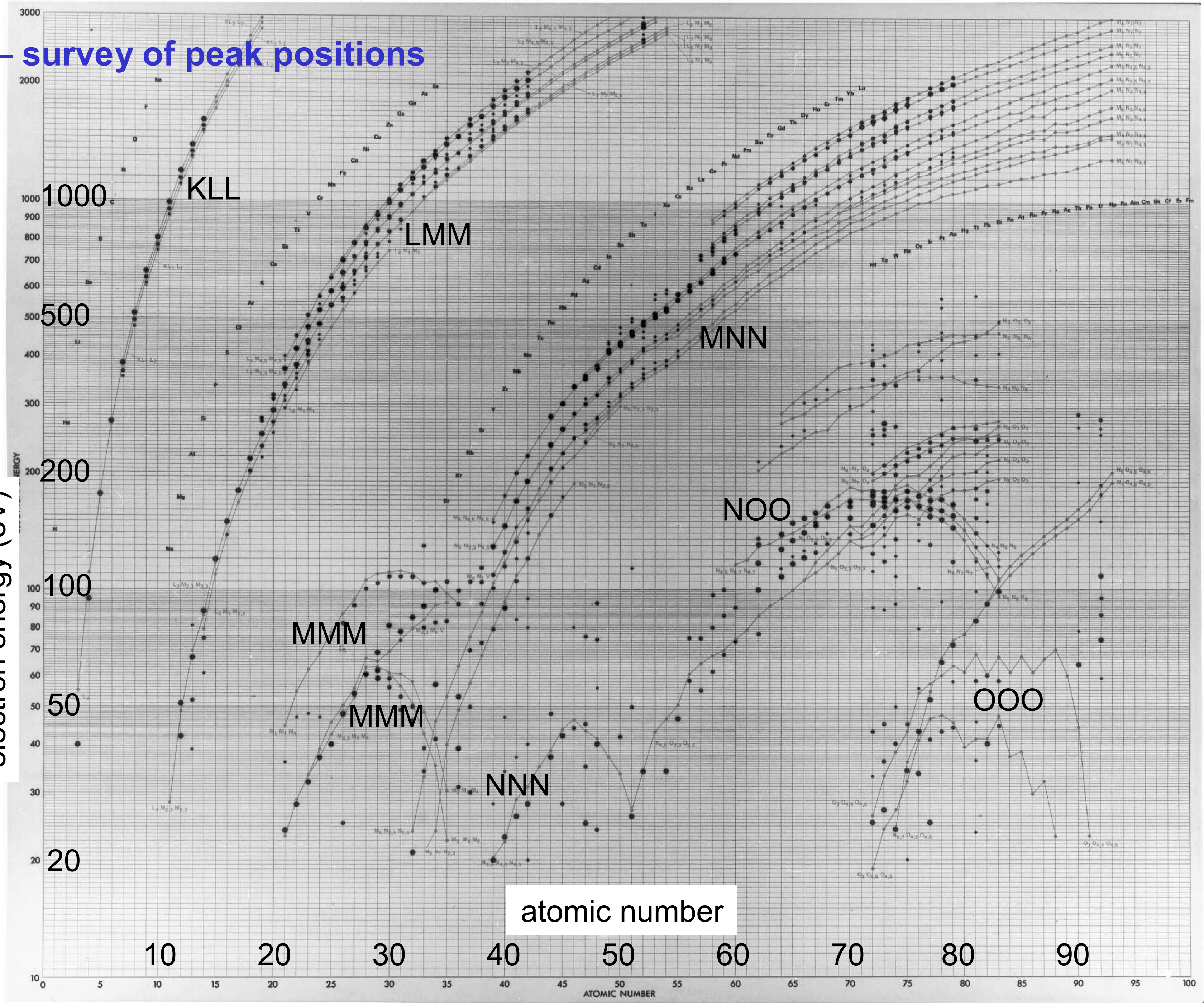
Energy:
Position of (neg.) minimum in 1st derivative spectrum (easy to determine)

Find best compromise: peak width : mod.-amp.
S/N : τ vs. dE/dt

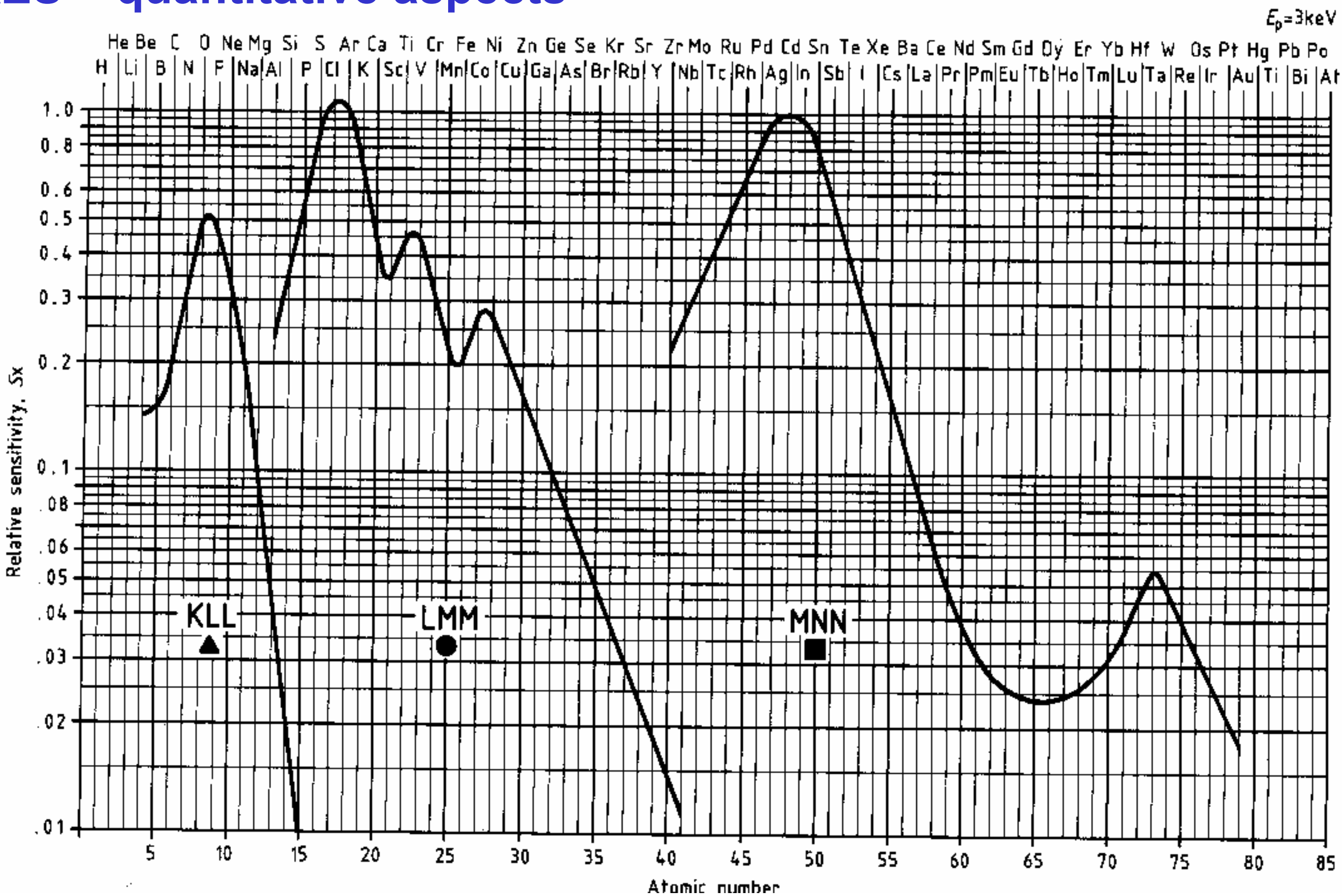
Intensity:
Often peak-to-peak intensity
Better minimum-to-zero-line intensity (less dependent on loss structure)

AES – survey of peak positions

All 🙂 elements have intense peaks between ~50 eV and ~1500 eV



AES – quantitative aspects



The sensitivity of peaks from all elements does not differ by more than a factor of 10 – 50. ☺

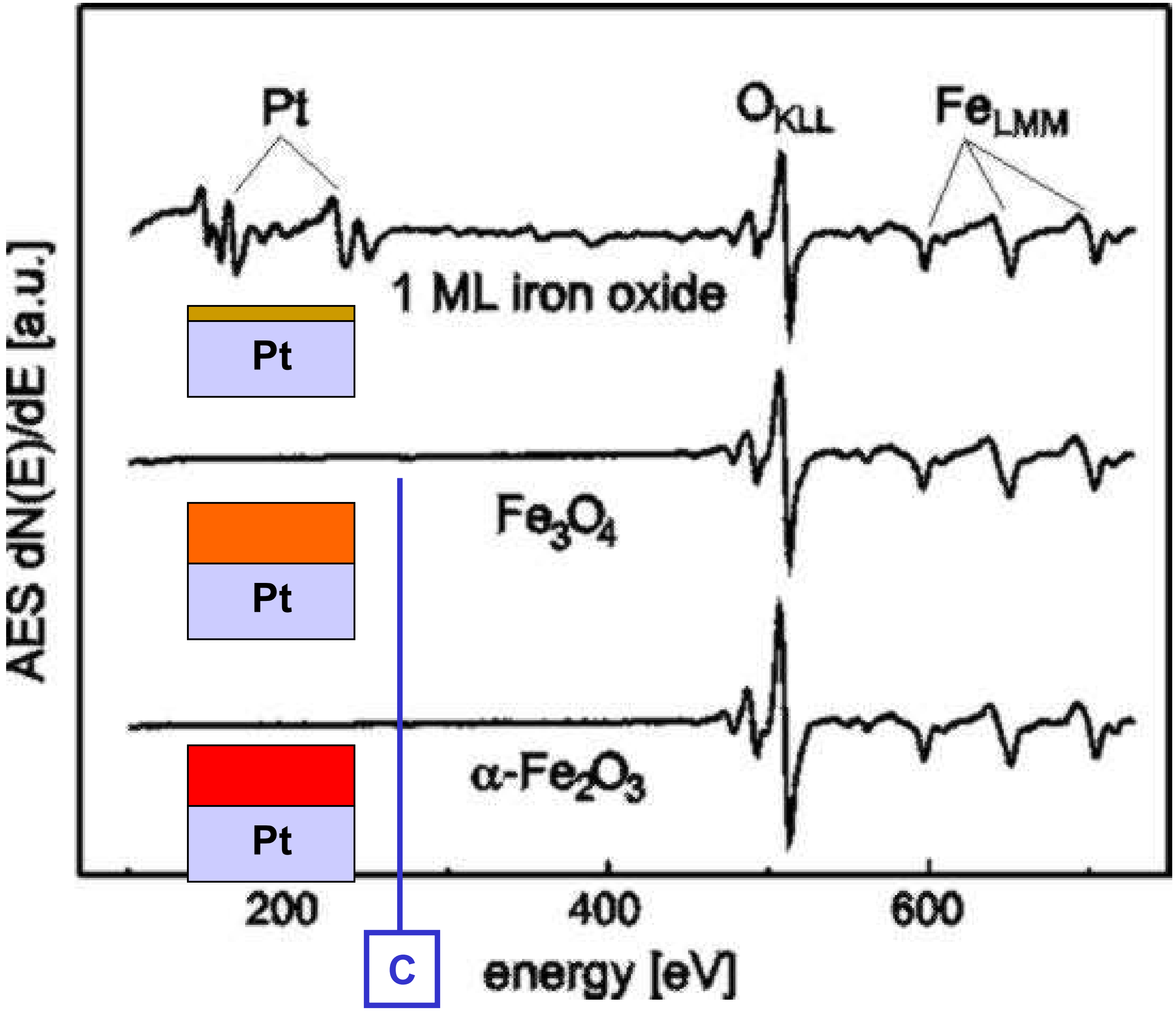
Relative sensitivity factors; attention: valid for certain experimental setup [Davis]

Two components:

$$x_A/x_B \approx \frac{J_A/J_{A0}}{J_B/J_{B0}} = \frac{J_A/S_A}{J_B/S_B}$$

x_i molar fractions
J_i measured intensities
J_{i0} intensity of component alone
S_i rel. sensitivity factors

AES – quantitative aspects



meas. J_{Fe}/J_O	bulk compos. x_{Fe}/x_O	derived S_{Fe}/S_O
0.30	1	0.3
	„too high“ O-signal explanation: O-terminated	
0.28	0.75	0.37
0.25	0.67	0.37
		Handbook: 0.4

„Auger-clean“

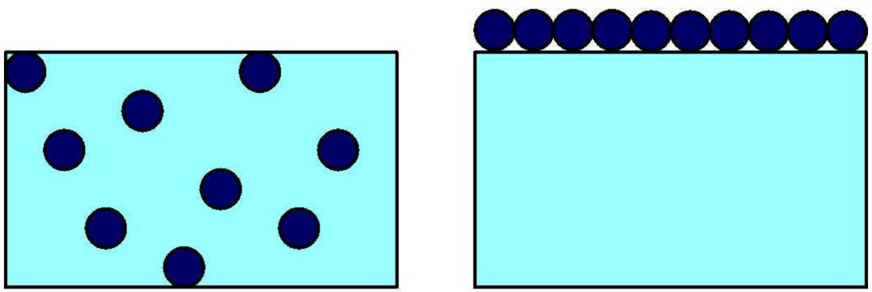
Spectrum appears free of **C**-peak.
Actually: noise ≈ 3% of O-peak intensity
→ $J_C \leq 3\%$ of J_O or ~6% of (J_O+J_{Fe})

Measure with high S/N, (slow speed)

AES – quantitative aspects

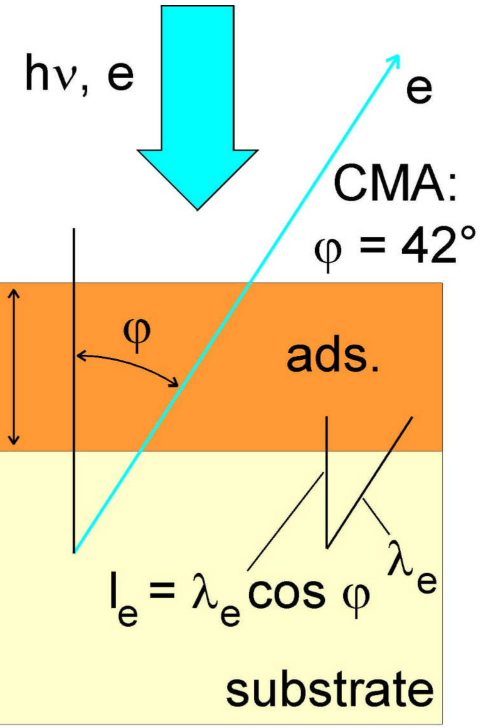
example: oxygen

Same signal for



bulk content 15 %   1 ML

Continuous layer



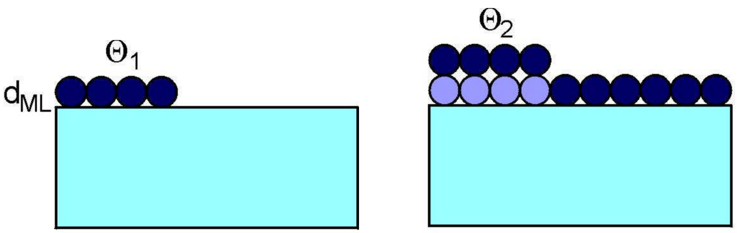
$$J_{sub} = J_{0,sub} \exp(-d/l_{e,sub})$$

$$J_{ad} = J_{0,ad} \left(1 - \exp(-d/l_{e,ad})\right)$$

(extinction law)

AES – quantitative aspects

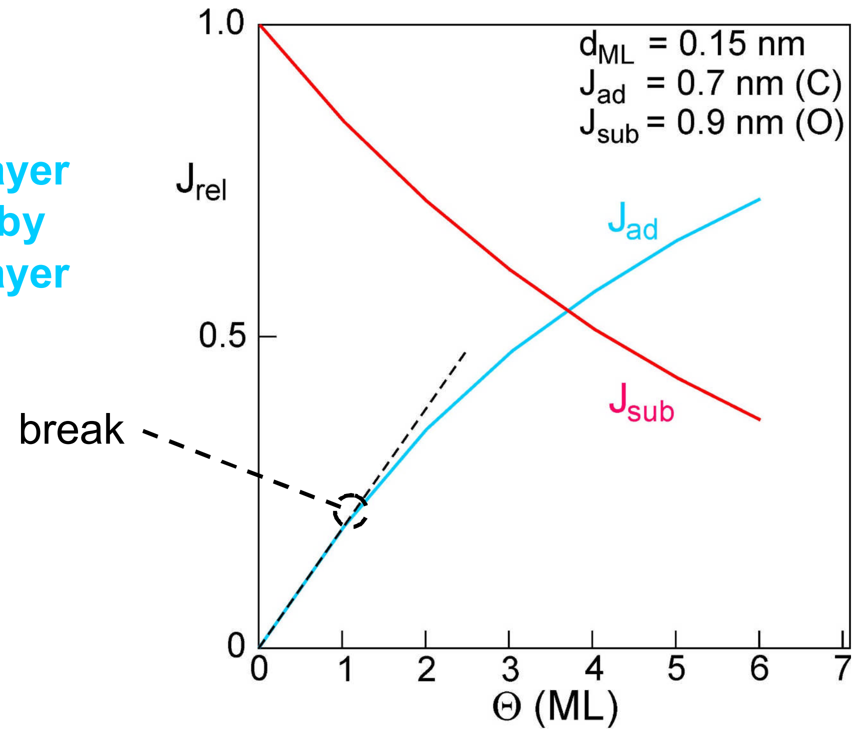
Discrete layer model



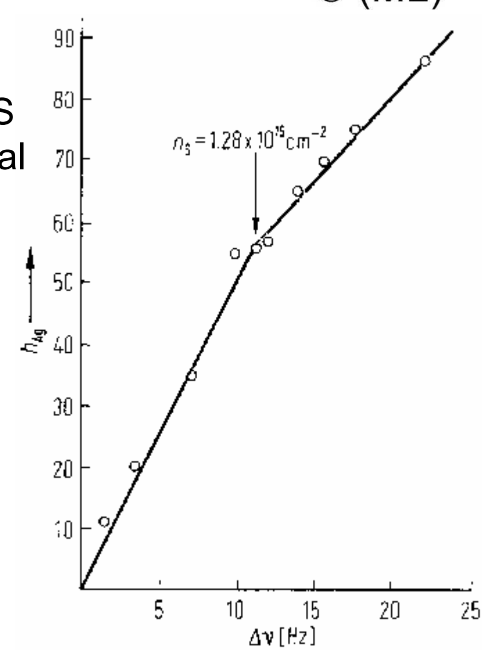
$J_{ad} = J_{0,ML}\Theta_1$

$J_{ad} = J_{0,ML}(1 + \Theta_2(\exp(-d_{ML}/l_{e,ad}))$

layer by layer



AES signal of Ag

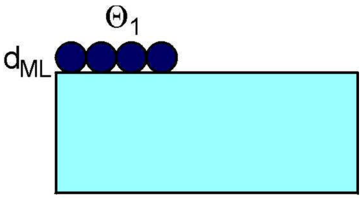


microbalance signal of Ag deposition

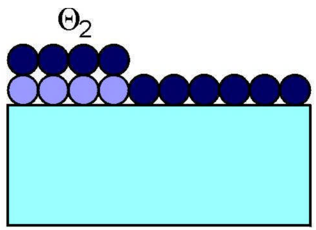
example:
Ag on W(110)
[Bauer, Poppa, Thin Solid Flms 12 (1972) 167]

AES – quantitative aspects

Discrete layer model

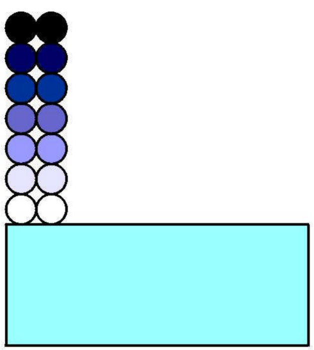


$J_{ad} = J_{0,ML}\Theta_1$

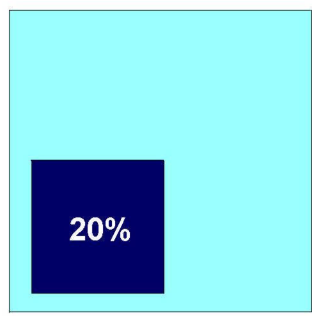


$J_{ad} = J_{0,ML}(1 + \Theta_2(\exp(-d_{ML}/l_{e,ad}))$

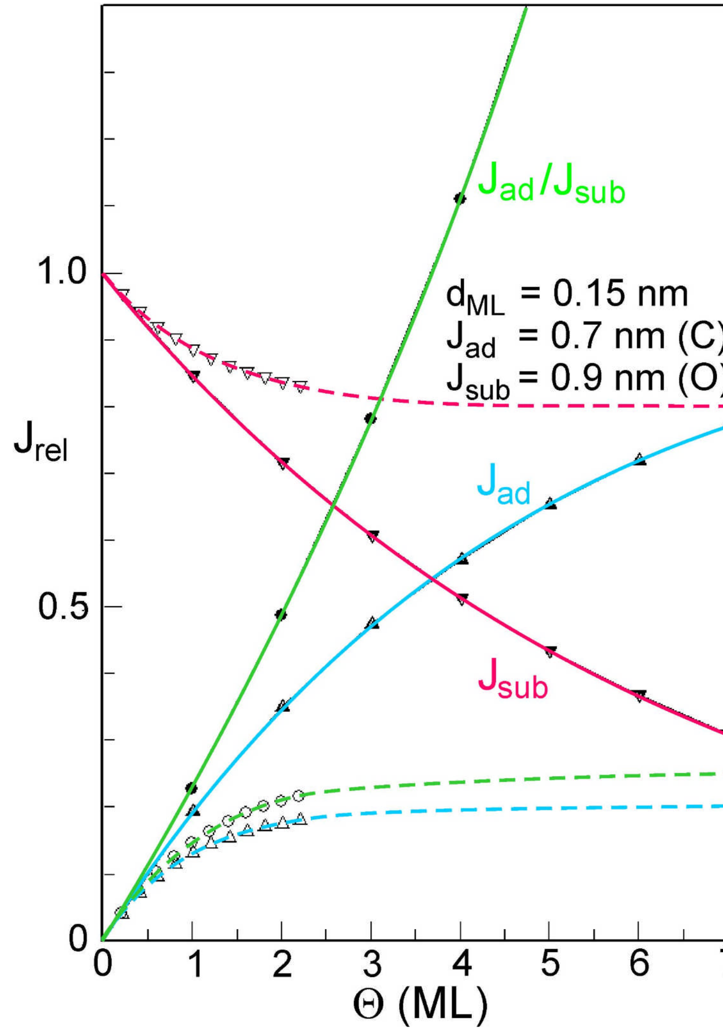
layer by layer



$J_{ad} = J_{0,ad}(\Theta_1 + \Theta_2 \exp(-d_{ML}/l_{e,ad}) + \Theta_3 \exp(-2d_{ML}/l_{e,ad}) + \ldots$



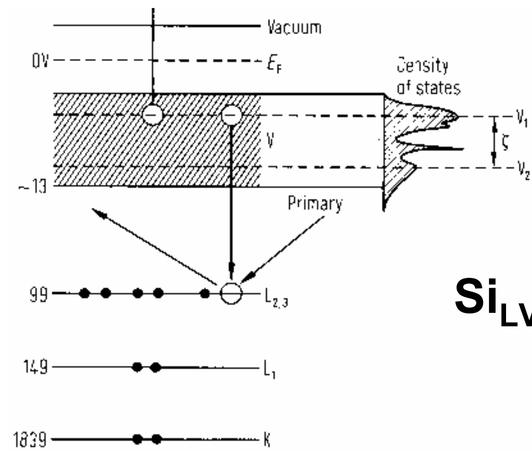
island 20% coverage



AES – Peak shapes

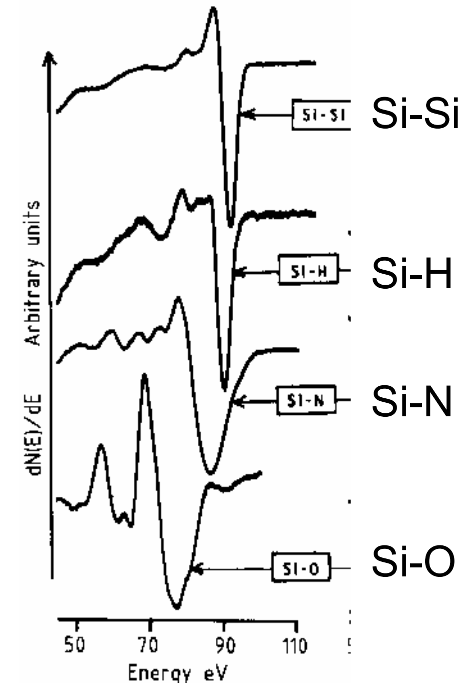
Especially if the (wide) valence band is involved, peaks are wide and contain valence band structure.

Example Si_{LVV} peak: self-folding of V-band, chemical (and relaxation?) shifts.

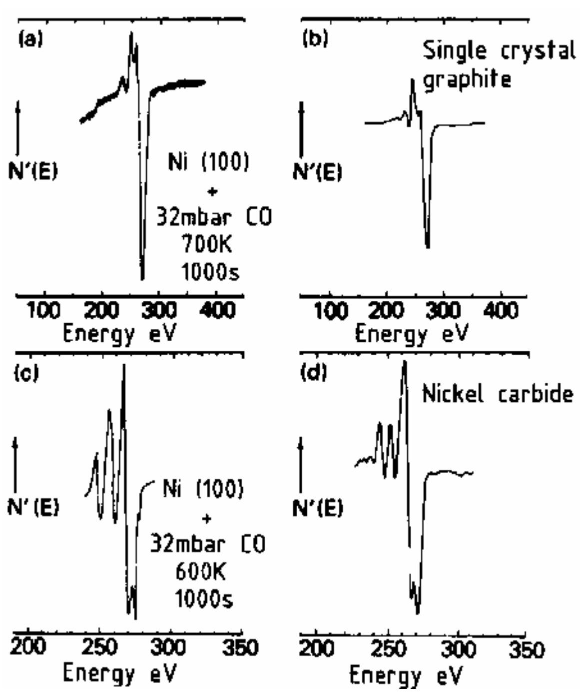


Si_{LVV}

[Ertl, Küppers, fig. 2.13]



[Ertl, Küppers, fig. 2.31]

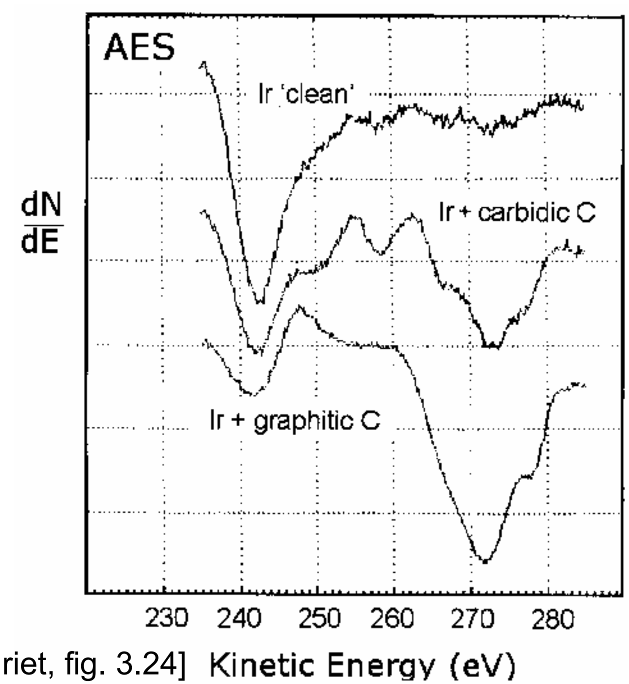


C_{KVV}

graphitic (sp^2)

carbidic (sp^3)

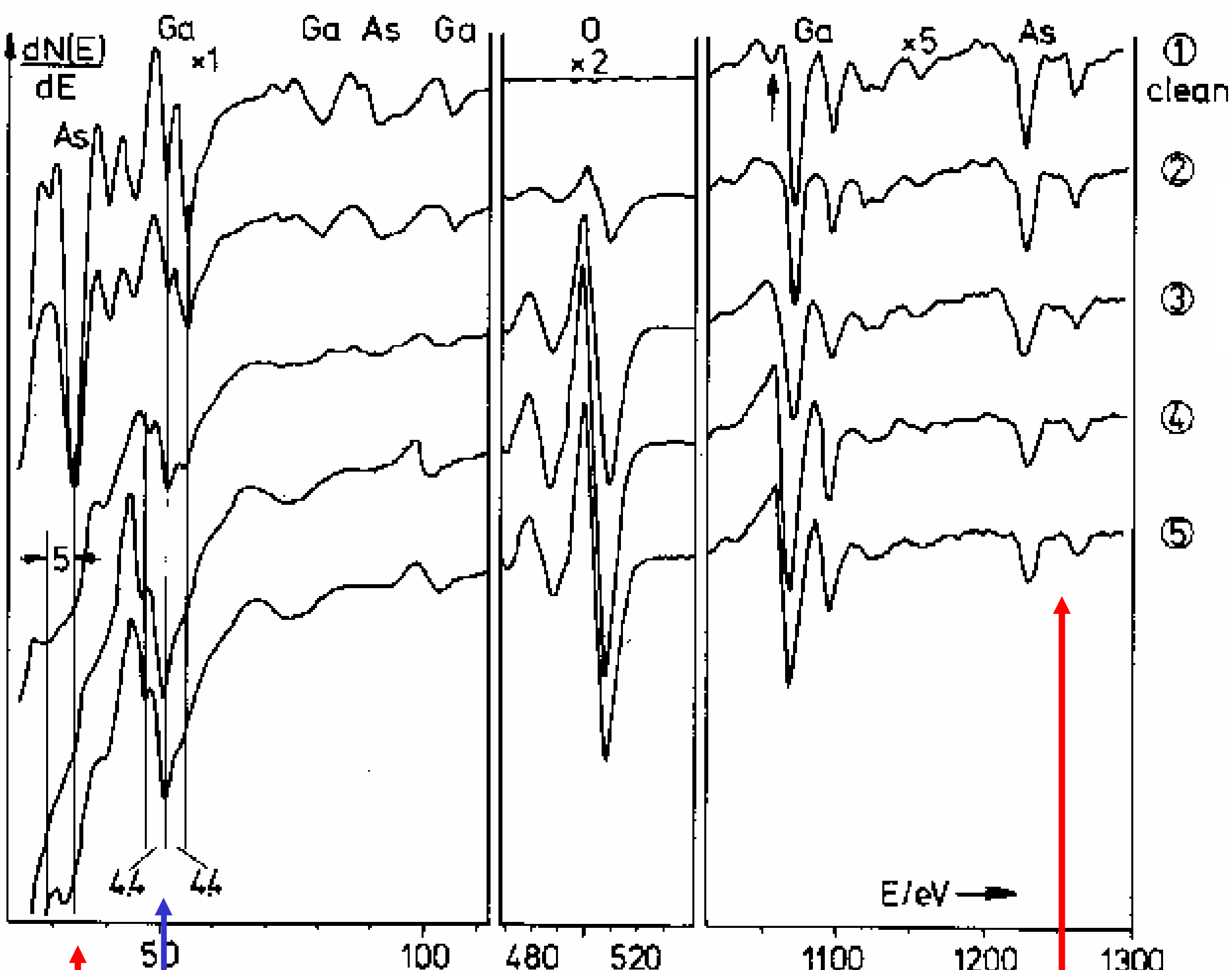
[Ertl, Küppers, fig. 2.33]



[Niemantsverdriet, fig. 3.24]

AES – Peak shapes

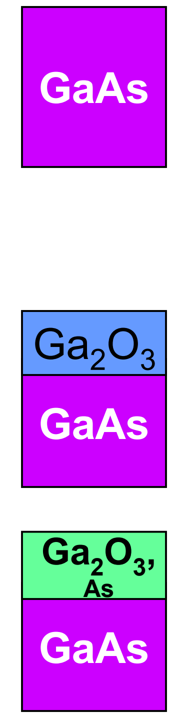
electron stimulated oxidation of GaAs



GaAs(111), clean

increasing oxidation, e^--stimulated

24 h later



chemical shift of Ga-peak

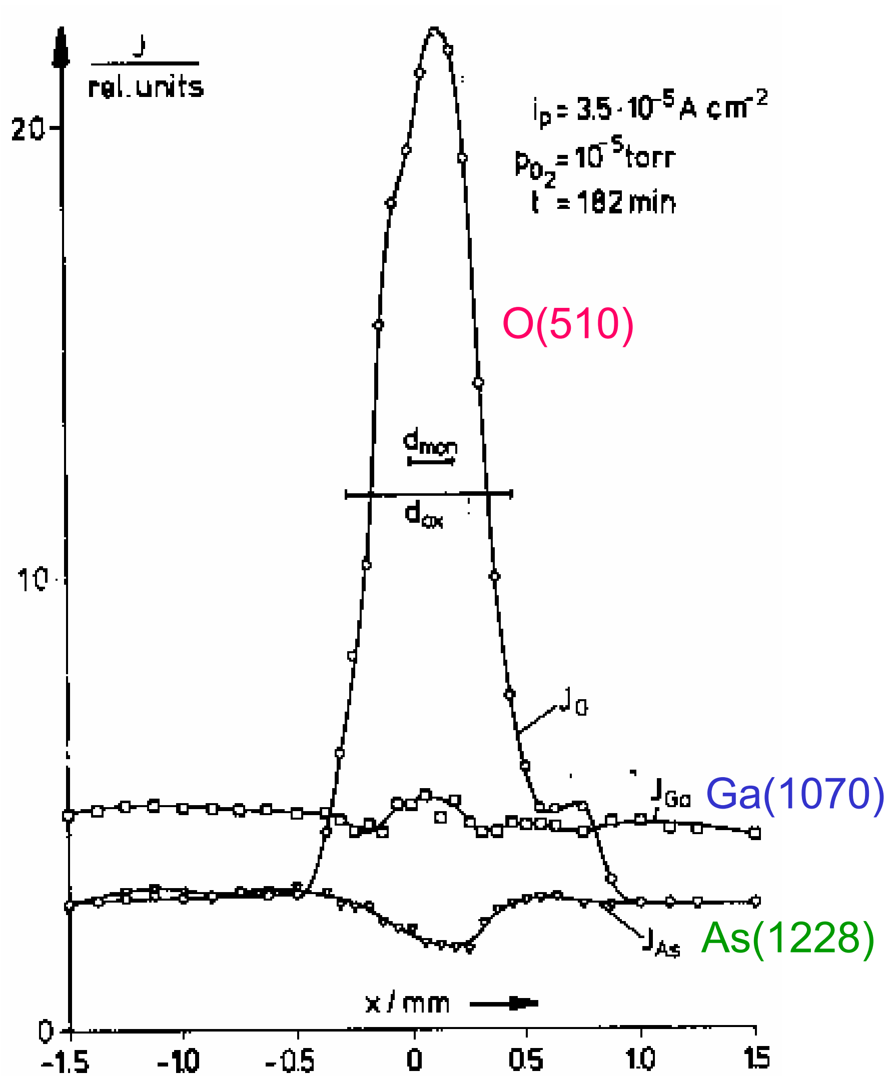
As-peak very surface sens.

As-peaks less surface sens.

As depletion at surface

[Ranke, Jacobi, Surf. Sci. 47 (1975) 525]

AES – electron beam influence



position on the sample

Example:
GaAs(111)-Ga

AES during oxygen admission causes strongly enhanced adsorption on the spot irradiated by electrons:

electron-stimulated oxidation.

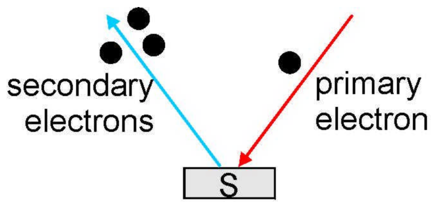
In the center of the beam,
As is depleted and Ga enriched:

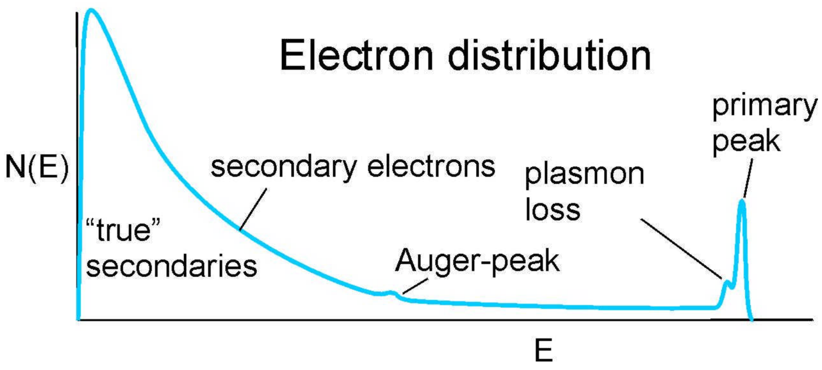
As_2O_5 desorbs (high vapor pressure)
Ga_2O_3 remains.

Probable reason:
e⁻induced dissociation of molecularly adsorbed O_2.

[Ranke, Jacobi, Surf. Sci. 47 (1975) 525]

AES – electron beam influence





Adsorbates may be
decomposed and
(partially) desorb

Affects quantitative analysis.

Substrate usually unaffected.

Responsible:
All e^- with sufficient energy,
i.e. mainly secondaries.

AES: primary e^- cause many secondaries
strongly „destructive".

XPS, UPS: primary radiation causes less secondaries
less destructive.

AES – Conclusions

- UHV-method
- elemental analysis
- comparatively simple
- independent of excitation energy
- difficult for insulating materials
- surface sensitive (0.4 – 2 nm)
- qualitative analysis simple
- quantitative analysis possible
- destructive (for molecular adsorbates)
- chemical information

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