XPS

X-ray

Photoelectron

Spectroscopy

Contents

- Information conveyed by XPS
- Instrumentation
  - vacuum, sample preparation, detector
- Ingredients
  - X-rays, photoelectrons, spectrum
- Extensions
  - XPD, ARPES, SRPES, PEEM
- Conclusion

Information

gives

- Elemental
- Chemical info

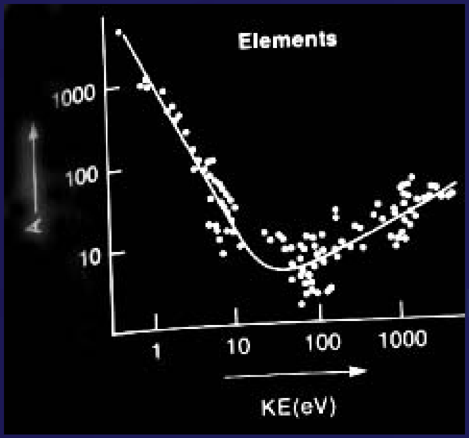
does not

- structure
- images / spatial resolution
- defects , phase

A bit of history

- Time line
  - Hertz 1887: photo-electricity
    - UV on -ve electrode facilitate the spark between two electrodes
  - Thompson1897: discovery of electron & e/m
  - Einstein 1905: quantum energetics
    - $h\nu = (KE)_e + (KE)_{atom} + (E_o - E_+) \cong (KE)_e + \Phi + (BE)_e$
  - Siegban's & Robison 1960s: technique
- Early days
  - collect photo electric current vs. retarding potential
  - differentiate

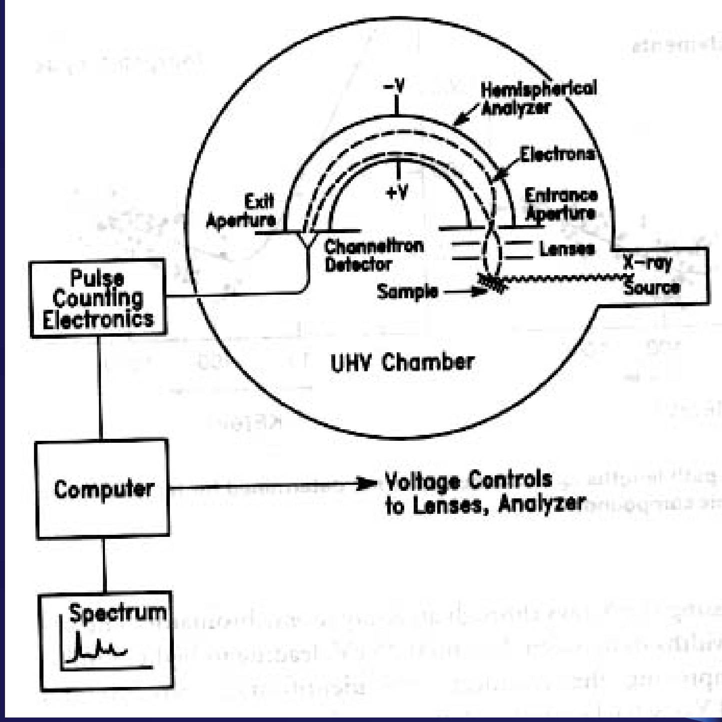
Instrumentation

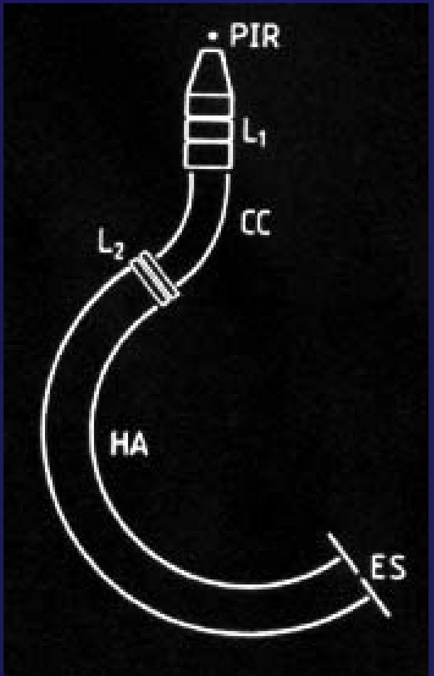


- Charged electrons: reactive with atoms
  - to the analyzer (min. p. 10^-6 bar)
  - on the solid => surface technique (5-20A)
  - surface cleanness
  - adsorbate layer (min. 10^-9bar /UHV)
- cleaning surface:
  - cleaving or scratching under vacuum,
  - ion etching, annealing

Detectors

- Combination of retardation and deflection analyzers with electron multiplier or a multi channel plate at the end
- low current:
  - sweeping/stability,
  - speed

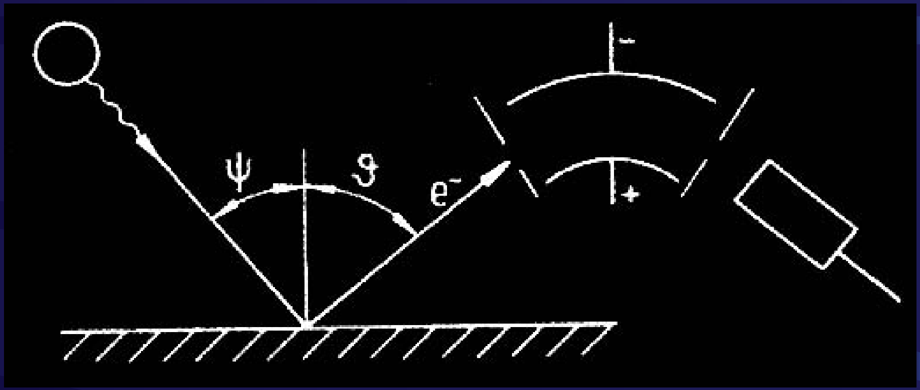


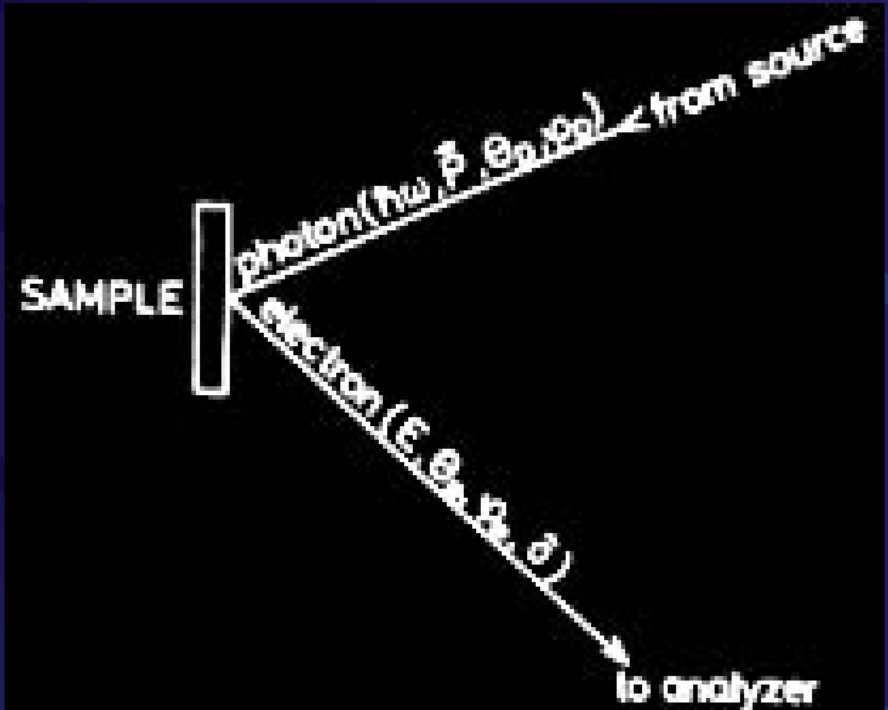


Ingredients

Ingredients

- Incoming radiation:x.rays
- Outcoming: photoelectrons
- EDC by the analyzer





X-Rays

- Parameters:energy,polarization , intensity, spot size, angle
- UPS: He lamb (pressure to choose from 21.22-52.2415)
- XPS: x-ray tube , 12-15KeV electrons hit a cooled target:
  - Y,Mξ (132,.5) Ti,Mξ (452) Mg,Kα(1253,.7) Al,Kα(1486.7,.8) SiKα(1740,.9) CuKα(8047.8,2.5)
  - secondary lines or satalites + bremsstrahlung background
- Monochromate by crystal diffraction ($2d\sin\theta=n\lambda$)
- Monochromaticity vs. brightness

Synchrotron radiation

- Tunable bright energy
  - 20-5000ev
  - utilize ionization cross section
- without loss of signal you can:
  - monchormatize
  - collimate / focus
- Polarized
- controllable time pulsation

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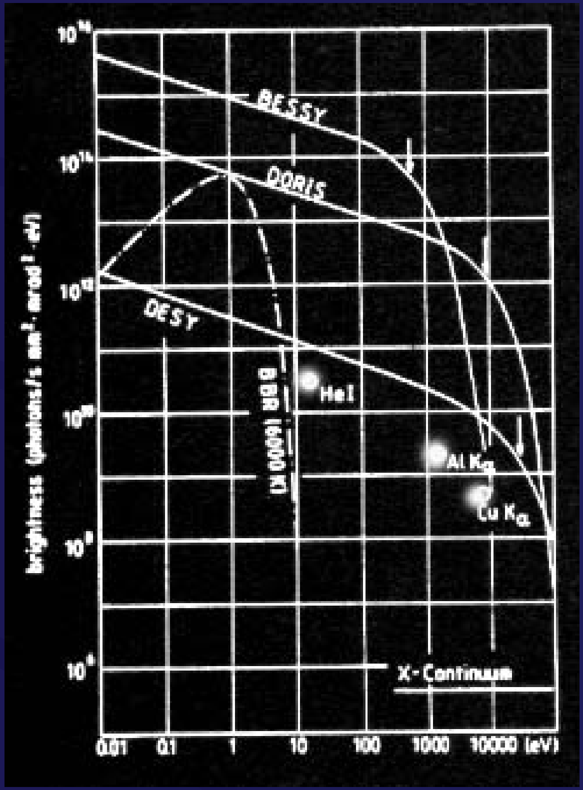
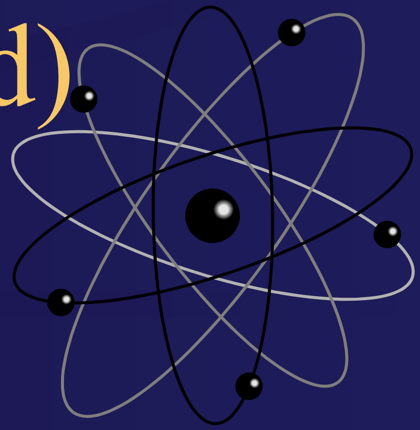


PhotoElectrons (bound)



- <u>While bound</u>
  - Fully characterized by four quantum numbers: (principal, angular, magnetic, and spin)
  - negotiated by QM/Coulomb interactions with all all parties including: the nucleus, other electrons and the immediate chemical environment
  - Observed: n, l, and LS-coupling for unpaired electrons
- Some theories tries to predict BE for all lines

PhotoElectrons (leaving)

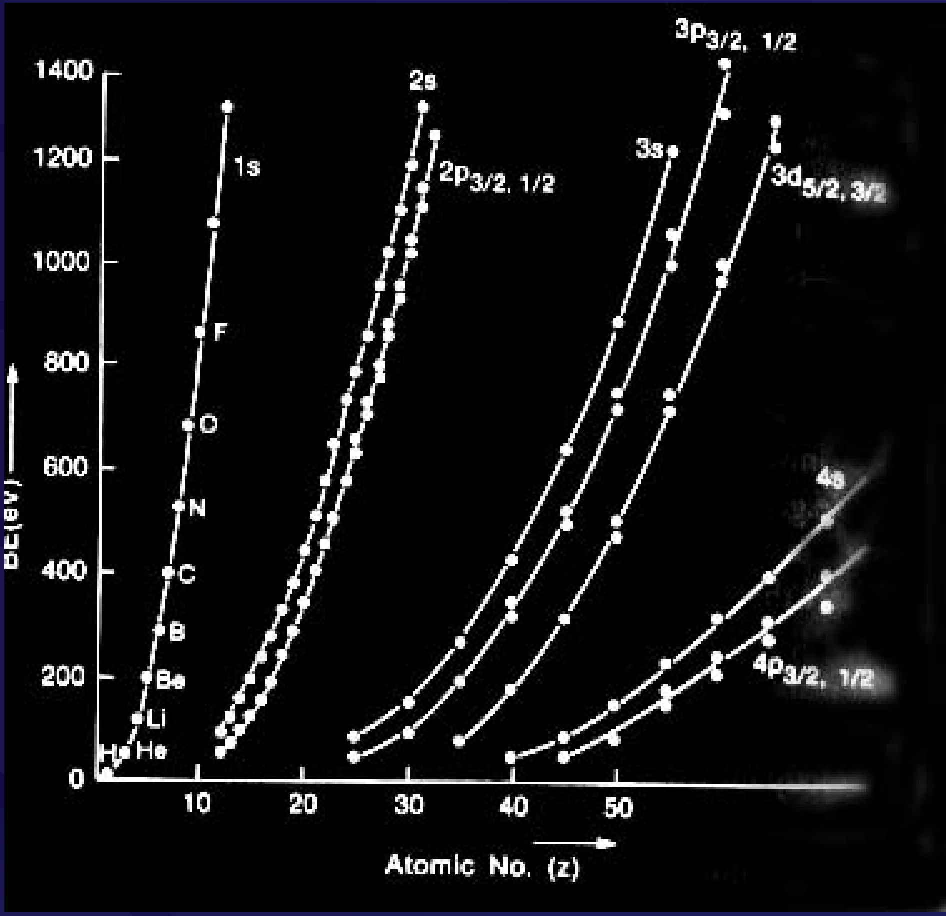
- Some electrons leave the sample intact and form XPS lines
- While leaving the sample: charged,energetic interacting with:
  - collective oscillation of electron (plasmons ≅ bulk 10, Surface < 10eV)
  - surface charge (global effect)
  - bound e-h pair (exciton)
  - crystal vibrations (phonons ≅.1eV)
  - spin waves / magnons

PhotoElectrons (as a beam)

- As a beam out of the sample
  - beam with direction (polar, azimuthal)
  - beam out of a certain sized spot
  - intensity distributed particles over a range of K.E
- XPS is angle integrated and wide area (cm2) analysis

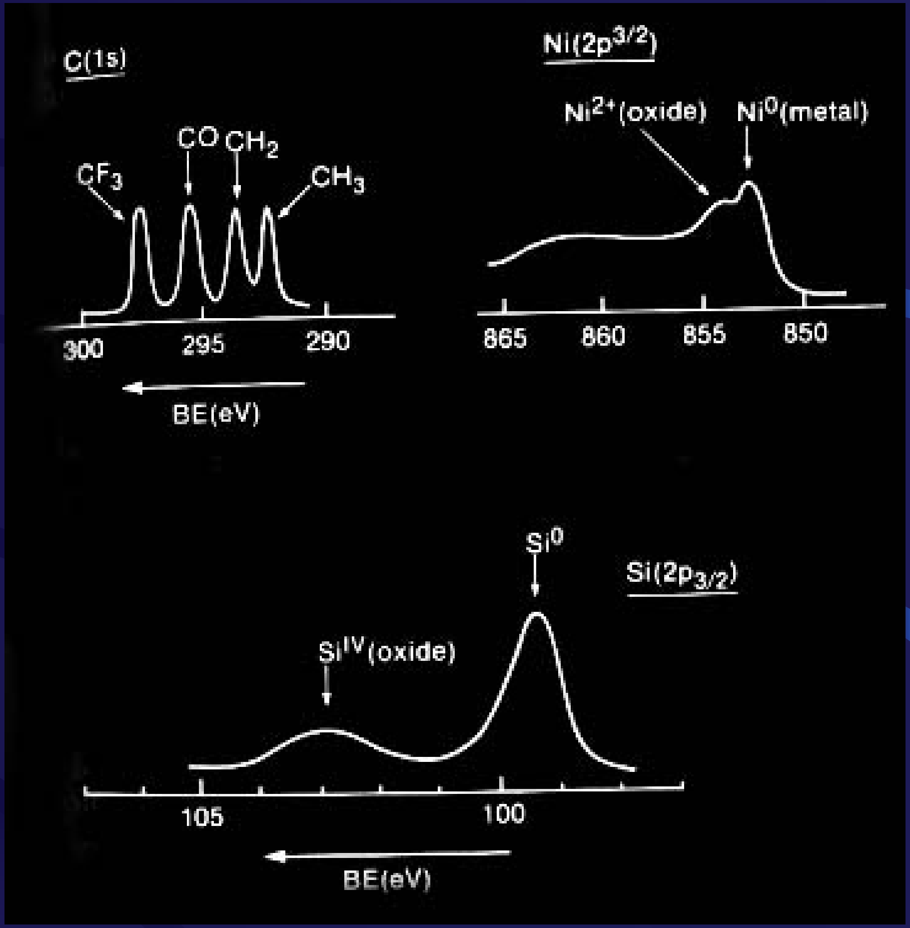
Elemental Info

- Well tabulated
- different lines will make it sure in case of confusion
- n, l, LS

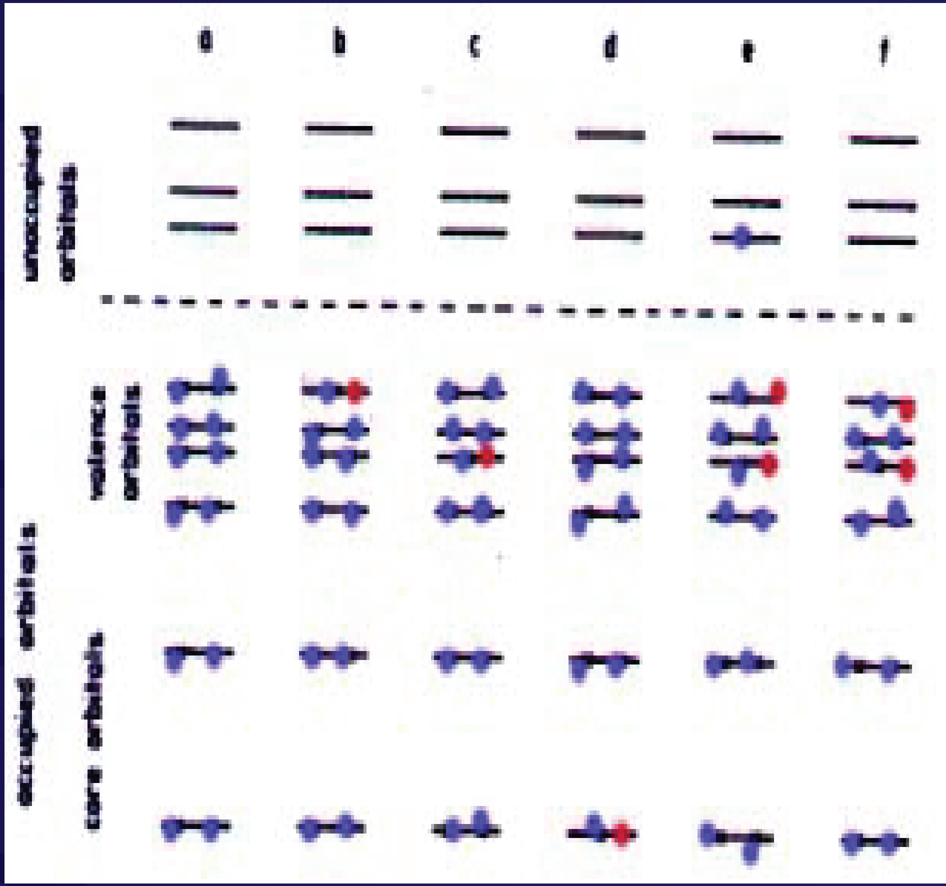


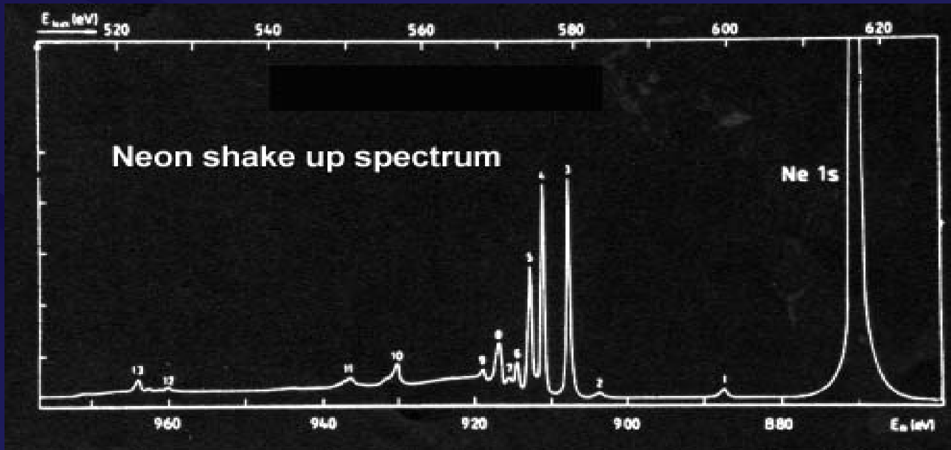
Chemical Info

- Not all lines are sensitive
- shifts are towards higher BE
- area ratios -> relative concentration



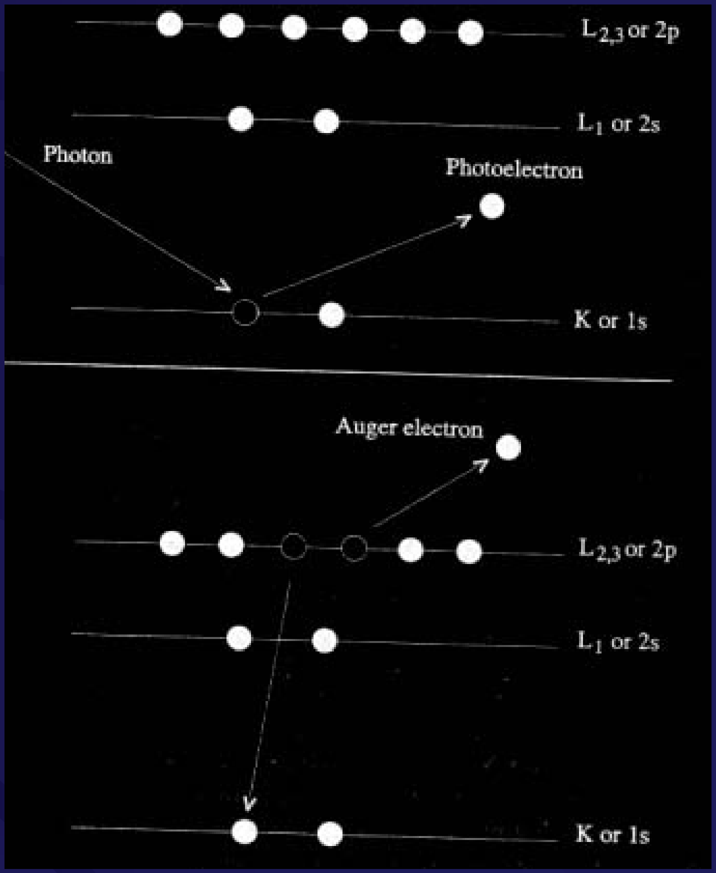
- Shake up/off lines:
- weak / unfavorable (more than one e)





Auger process

- 3 electrons are involved
- KE of Auger is not hν dependant
- broad peak



The spectrum (E)

- Peaks:
  - XPS lines
  - Auger
  - Others:
    - palsmons, shakeup,

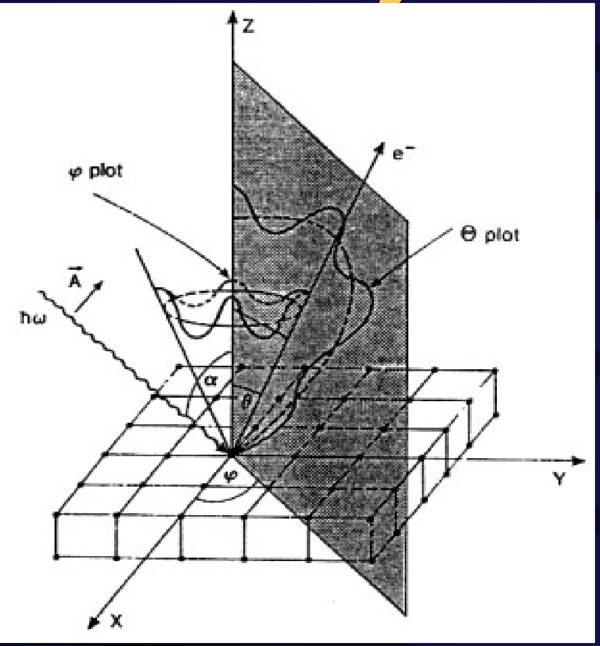
- libraries and standard's spectra and pure samples

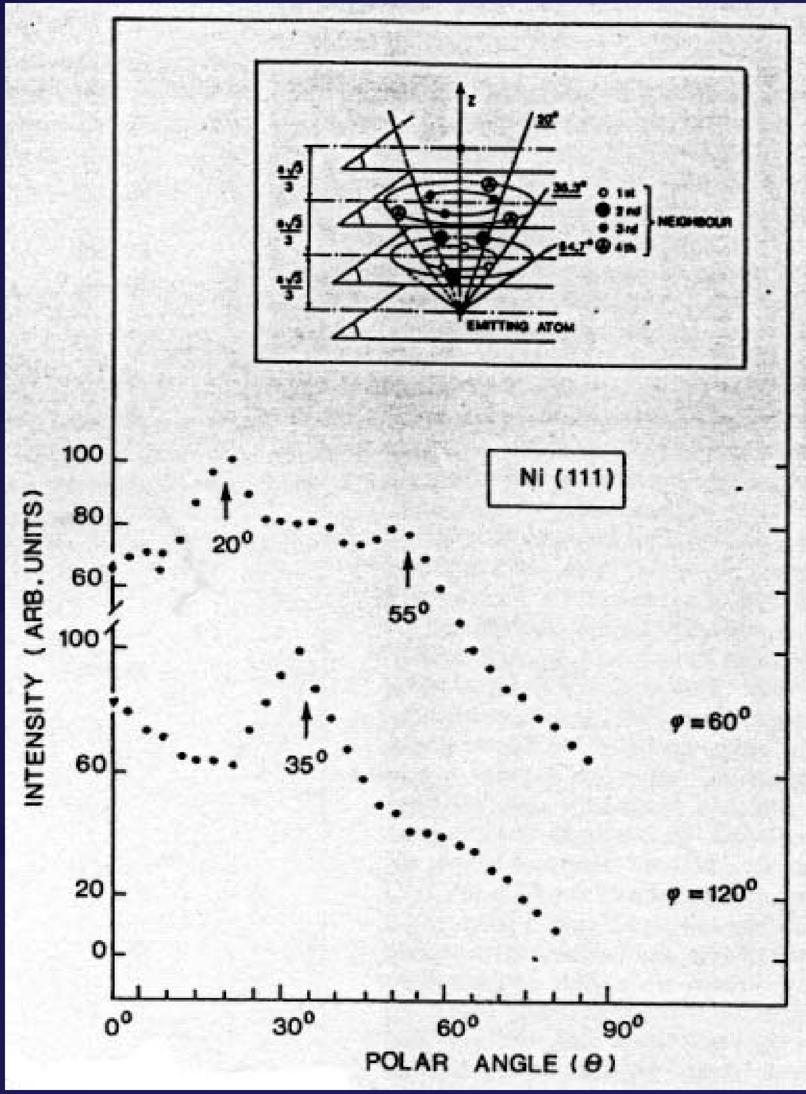
Spectrum (I)

- Intensity
  - atomic:
    - no. of electrons
    - photoionization cross section (hν dep.)
  - Instrumental
    - sample area
    - radiation flux
    - KE detection efficiency
    - angular detection efficiency
- ->Relative concentration using peak areas

Extended techniques

X-ray Photoelectron Diffraction (XPD)

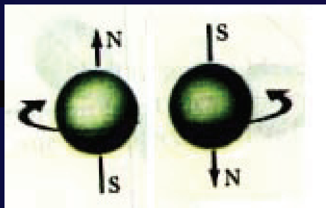




- Track angular variation of a certain peak intensity. It varies only if it belongs to the second layer

Consideration: preparation, propped depth, time

->surface structure + enhanced surface sensitivity



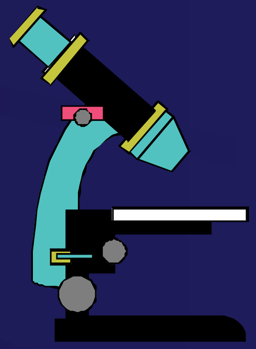
Spin resolved XPS (SRPES)

- Orientation of the spin of the photoelectron can be maintained from emission to detection
- Mott detector can tell the spin -> up/down

- Band structure of a magnetic material affects the up/down ratio
- Band structure <-- XPS

Photoelectron Emission Microscopy (PEEM)

- By focusing the x-rays only a chosen spot of the sample may contribute to the spectrum --> image
- Focusing can be done via:
  - collimating (signal↓ -> synchrotron)
  - x-ray optics (under development)



- Advantage: Element specific,chemical status
- Applications: diffusion, segregation, Shottky barrier

Conclusion

- A look back
- what does the future holds?

Information

+ve

- Elemental (but no trace analysis .01-.3%)
- Chemical info (resolution, globality)

-ve

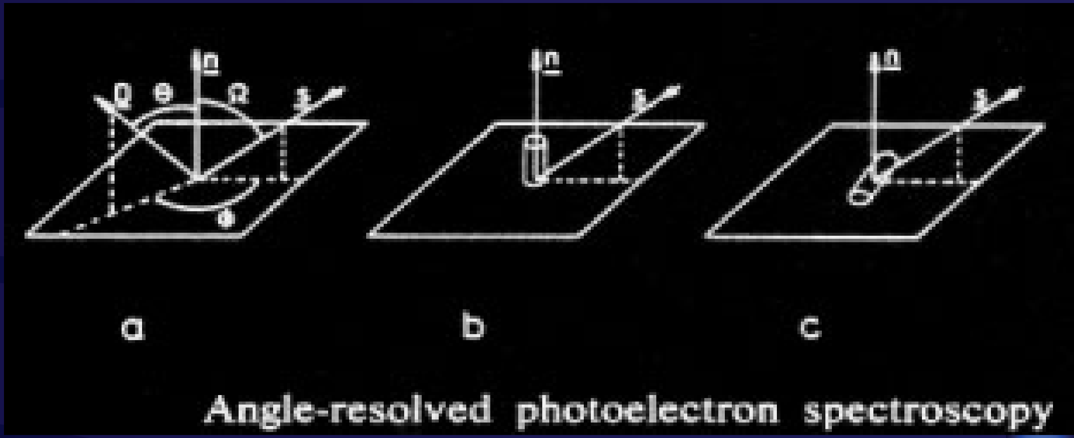
- structure (-> XPD)
- images   (-> PEEM)
- defects , phase

Future

- Wide range tunable, sharp, bright, well focused, controlled pulsed , and affordable x-ray source (synchrotron)
- High resolution, fast/efficient detectors
- automated processing

Angle resolved XPS (ARPES)

- Anisotropy of electron photo emission direction
- Function of:
  - atom, molu. orientation
  - **E,**hν of radiation



•Difference

•ARPES:molecule, atom of the crystal and adsorbate

•XPD: structure of an atomic layer