Frithjof Nolting :: Head of LSC :: Paul Scherrer Institut

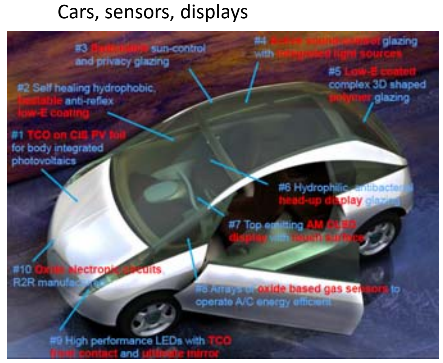
Photoemission spectroscopy

PSI Master School 2017

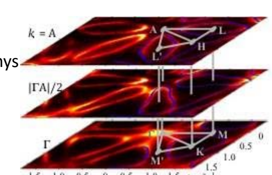
Basic research – electronic devices

Hard disc

Cars, sensors, displays



Modern communication devices are full of fascinating phys
materials

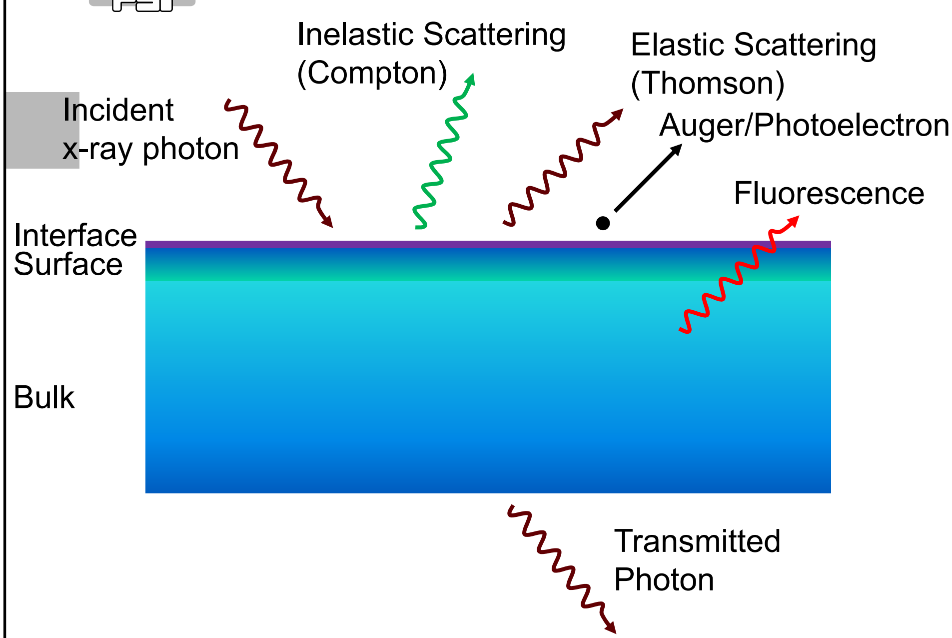


Aim of the lecture

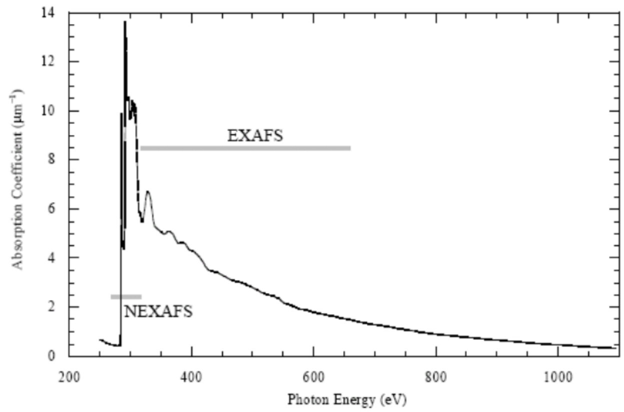
Basic concepts of Photoemission spectroscopy

- How to probe the occupied states
- Einstein and the Photoelectric effect
- Photoemission process
- XPS, X-ray photoelectron spectroscopy
- Comparison XAS and XPS
- ARPES, Angle resolved Photoemission Spectroscopy
- Ambient pressure XPS
- XPD, X-ray Photoelectron Diffraction

Key Phenomena



Absorption of Photons in the Soft X-ray Range



Near Edge X-ray Absorption Fine Structure

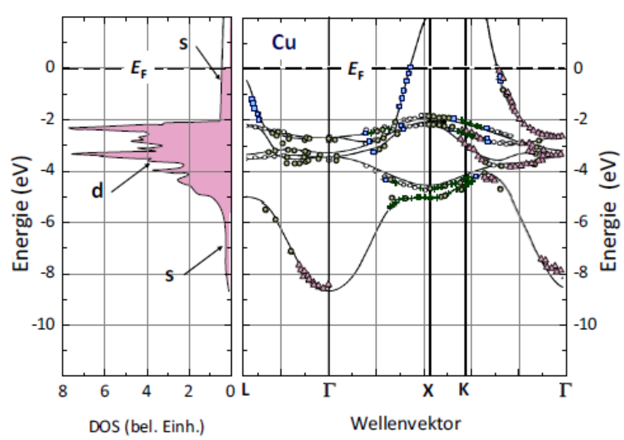
reflects density of unoccupied states

Also called XANES

Extended X-ray Absorption Fine Structure

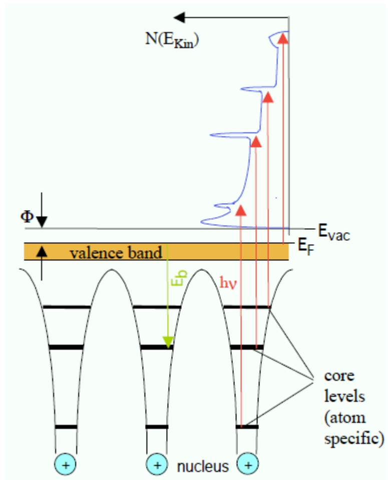
reflects spatial location of neighboring atoms

How can we probe the occupied states?



P. Willmott, Intro to Synchr. Rad.

Measure energy of Photoelectron



Note: to be precise, we measure the properties of the photohole

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Photoelectric effect

Einstein's Photoelectric Equation

The electron leaves the body with energy

$$\frac{1}{2}mv^2 = hv - P,$$

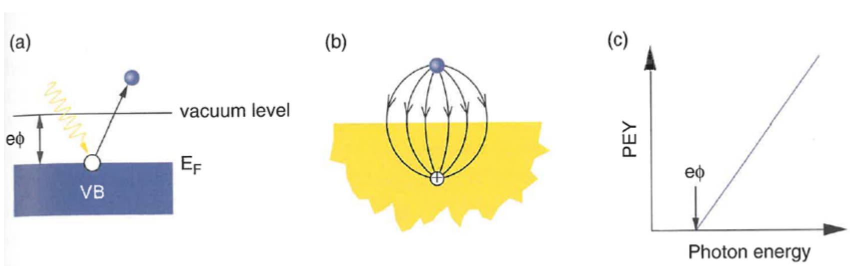
where h is Planck's constant, v is the light frequency and P is the work the electron has to do in leaving the body.

$E_e = h\nu - E_B - e\Phi$

E_B: Binding energy
$e\Phi$: workfunction

Albert Einstein, 1905

Origin of Workfunction



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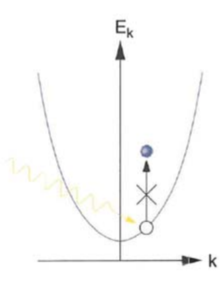
Conservation laws

Energy conservation: ($E_e = h\nu - E_B - e\Phi$)

Momentum conservation: $k_{initial} + k_{h\nu} = k_{final}$
(but momentum of electron is high, momentum of photon is small, e.g. ≈0 at UV energies)

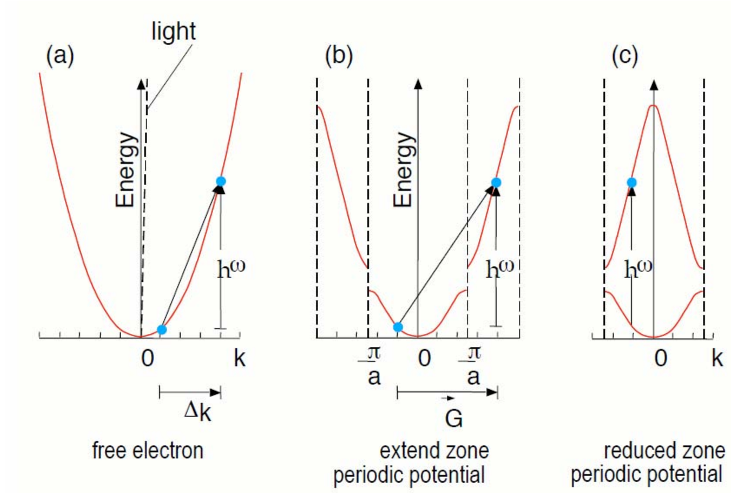
$$k_{photon} = p_{photon} / \hbar = E_{photon} / \hbar c \approx 10^8 \, \mathrm{m}^{-1}$$

$$k_{electron} \approx 10^{10} \, \mathrm{m}^{-1}$$

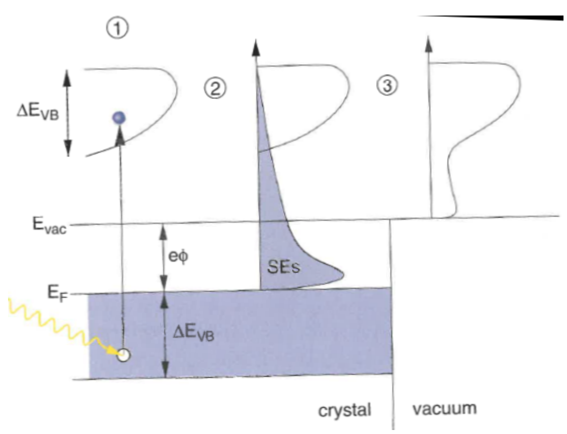


free electron

Conservation laws – electron in a crystal



Three step model

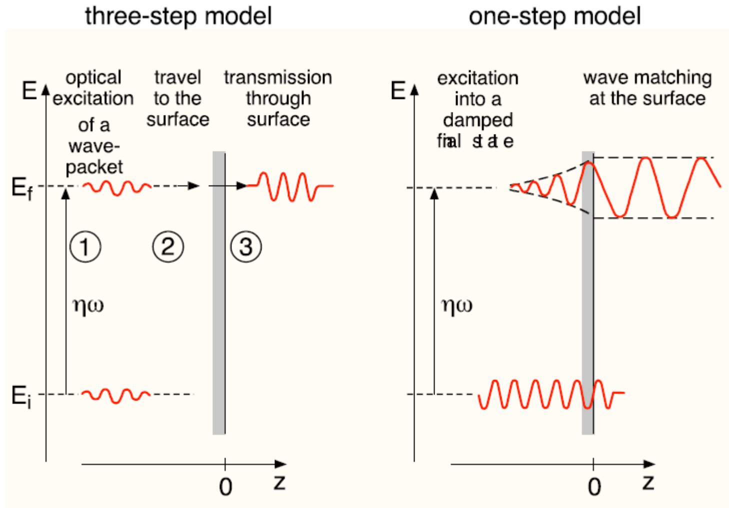


1) Creating of photoelectron
2) Travel to surface
3) Penetrate surface

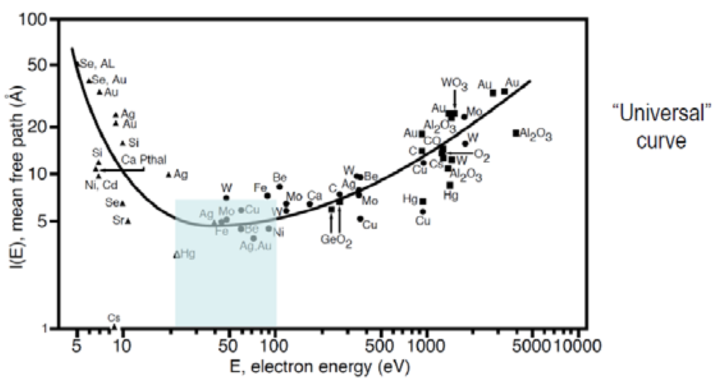
Note: this is a simplified model

P. Willmott, Intro to Synchr. Rad.

One-Step Model

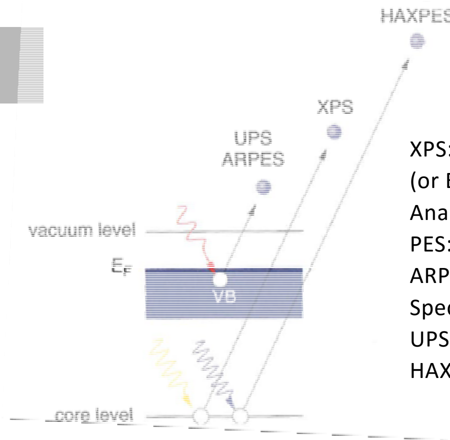


Universal curve



- Number of electrons reaching the surface is reduced by electron-electron scattering
- Only sensitive to first couple of atomic layers!!
- Clean surface and UHV needed
- Background of scattered electrons with lower kinetic energies (secondaries)

UPS, XPS, HAXPES



XPS: X-ray Photoelectron Spectroscopy
(or ESCA: Electron Spectroscopy for Chemical Analysis)
PES: Photoelectron Spectroscopy
ARPES: Angle resolved Photoemission Spectroscopy
UPS: ultraviolet Photoelectron Spectroscopy
HAXPES: hard X-ray PES

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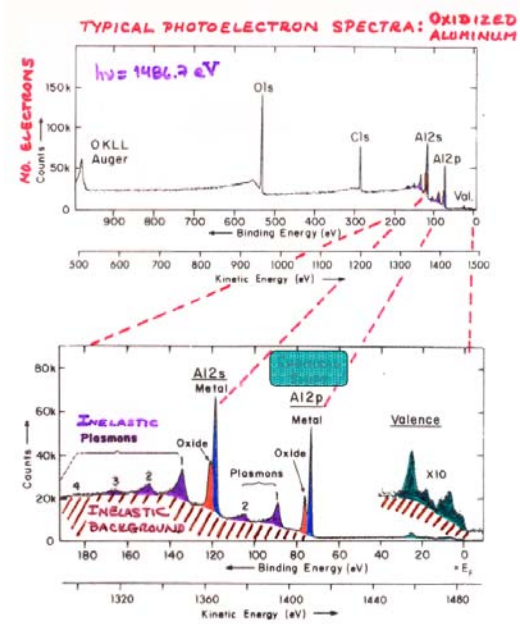
XPS – fingerprinting of elements



XPS - fingerprinting of valence

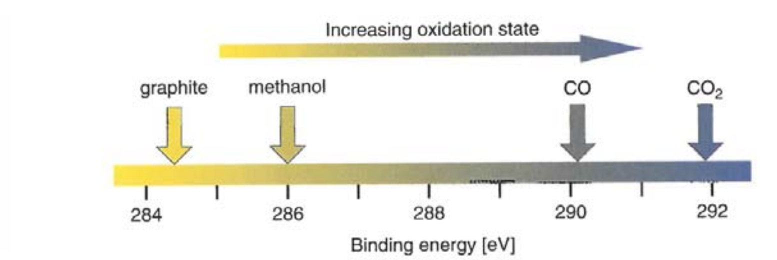


Figure 6.56 *A plot of the shift in binding energies of the C 1s core electron in different carbon-containing compounds.*

Rule of thumb: elements in a higher oxidation state have electrons with higher binding energies

P. Willmott, Intro to Synchr. Rad.

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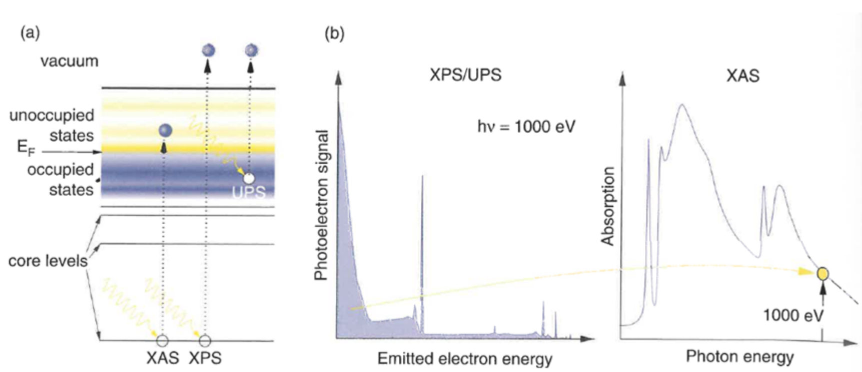
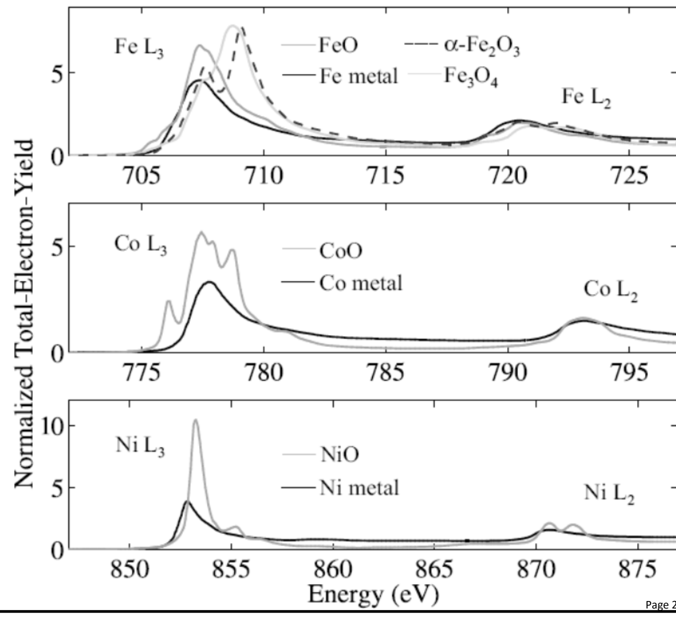
Comparison XPS and XAS

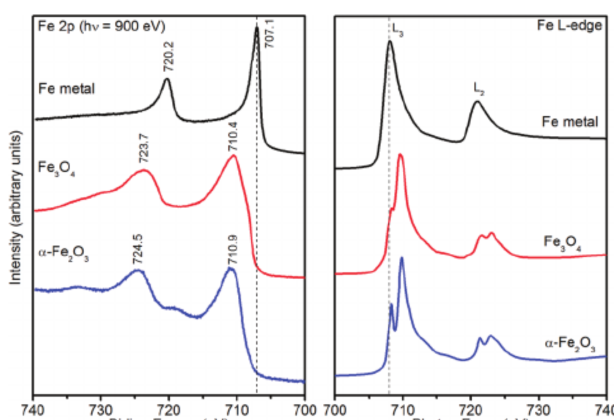


P. Willmott, Intro to Synchr. Rad.

Comparison XPS and XAS



Comparison XPS and XAS



Leveneur, Jérôme & Waterhouse, Geoffrey & Kennedy, John & Metson, James & Mitchell, David. (2011). Nucleation and growth of Fe nanoparticles in SiO2: A TEM, XPS, and Fe L-Edge XANES investigation. The Journal of Physical Chemistry C. 115. 20978-20985. 10.1021/jp206357c.

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From binding energy to density of states

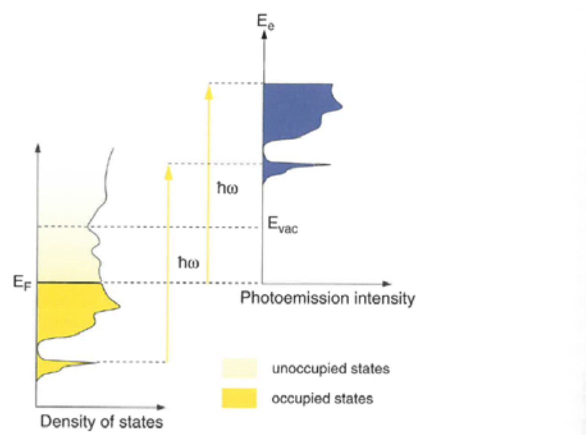
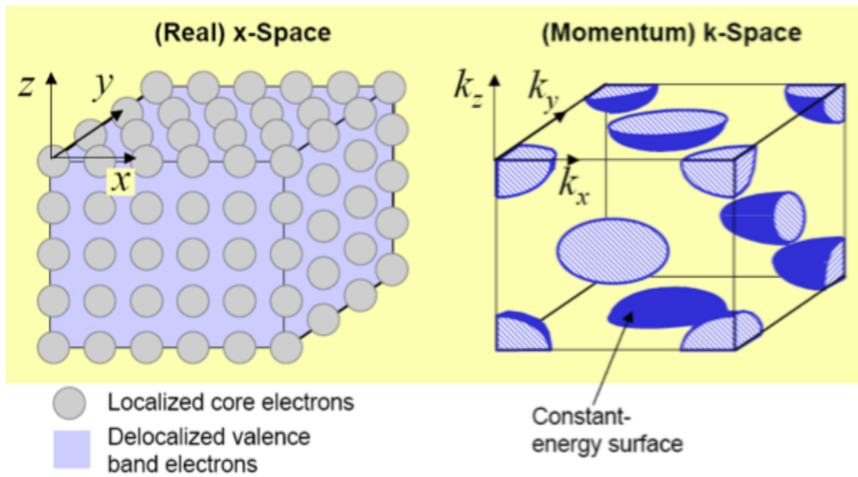


Figure 6.49 *Energy distribution curves. EDCs are generated by recording the photoelectron intensity as a function of photoelectron kinetic energy for a fixed photon energy and detector angle. Assuming a constant transition probability, the intensity at a kinetic energy* $\mathcal{E}_e = h\nu - e\phi - E_B$ *is proportional to the local density of states at* E_B *having the in-plane wavevector* $k_\parallel$ *selected by the detector orientation. In this schematic, the photoemission intensity has been plotted as a function of* $\mathcal{E}_e$ *for didactical reasons. More commonly, however, it is plotted as a function of* E_B.

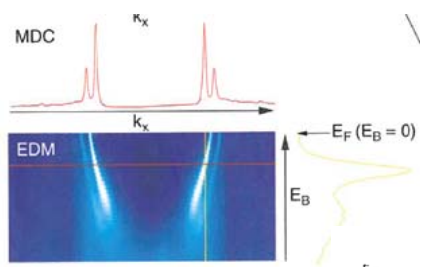
P. Willmott, Intro to Synchr. Rad.

To band maps

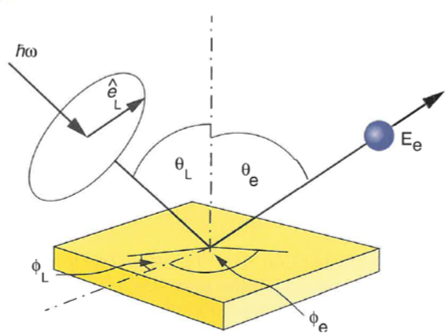
Angle-resolved photoelectron spectroscopy (ARPES)



To band maps



EDM: Energy Distribution Map
MDC: Momentum Distribution Curve
EDC: Energy Distribution Curve



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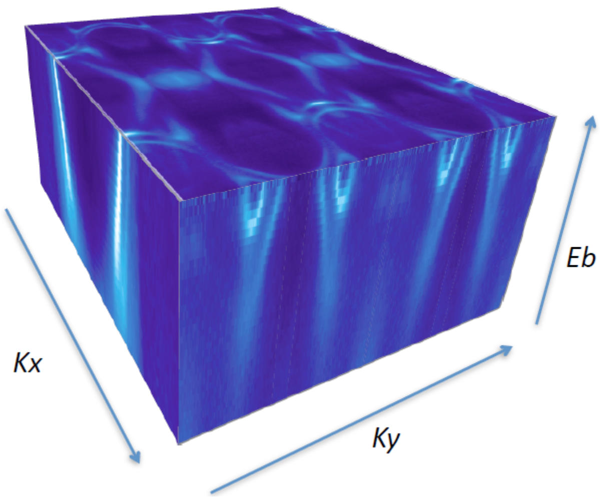
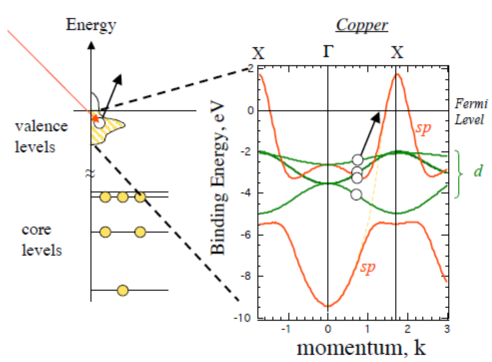
Ni(110)

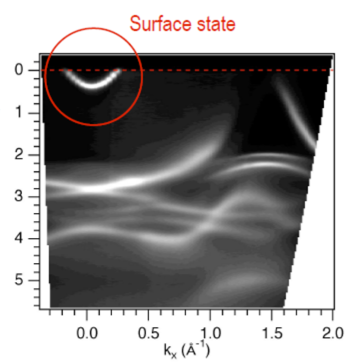


SIS beamline at SLS

X.Y. Cui et al, Phys Rev B 81 (201) 245118

APRES from Cu(111)





scanning of E_i *and* θ:

Band structure along curved line in 3D k - space

Analyzer

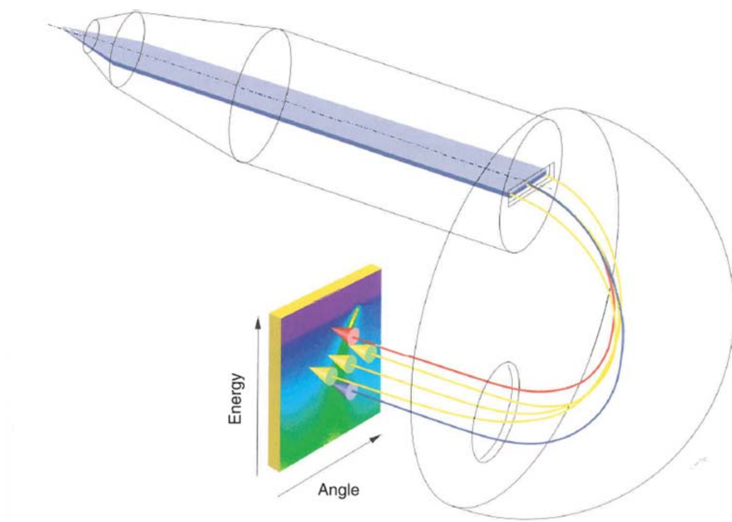
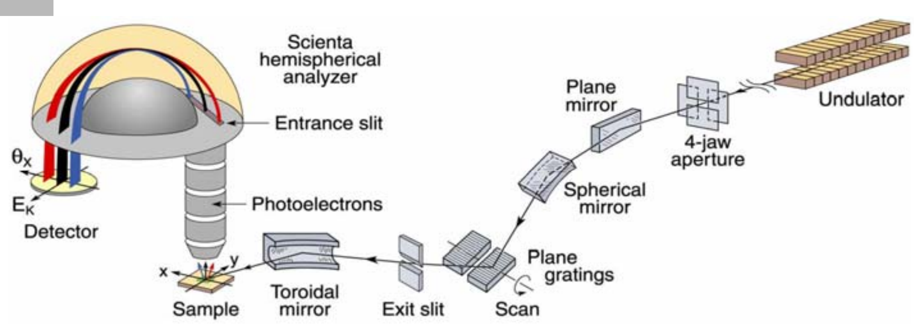


Figure 4.44 *Data spanning different electron kinetic energies and trajectories can be simultaneously recorded using a multichannel plate and CCD camera as the detector system in a CHA.*

P. Willmott, Intro to Synchr. Rad.

ARPES beamline

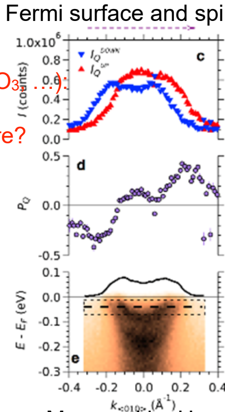


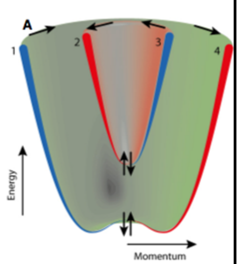
Spin-resolved ARPES at COPHEE

Courtesy Hugo Dil

Results:
- Topological insulators: first ever verification of spin-momentum locking of surface state. Bi_2Se_3, Bi_2Te_3, $PbBi_4Te_7$, $TlBiSe_2$, Bi(114), α-Sn, TCI, thin films, …
- Spin structure of SmB_6 as topological Kondo insulator
- Rashba systems: quantum well states, 2D, 1D, spin-orbit density wave
- Bulk Rashba systems: measurement of 3D Fermi surface and spin structure (BiTeI, BiTeCl, GeTe …)
- 2DEG on transition metal oxides (e.g. $SrTiO_3$ …):
  -combination of Rashba and magnetism
  -influence of ferroelectricity on spin structure?

Capabilities:
- Spin vector in 3D for any point in k-space
- Use photon-energy and -polarisation to study correlation effects
- Resonant effects ("XMCD above Curie", singlet-triplet distinction)
- In-situ sample preparation

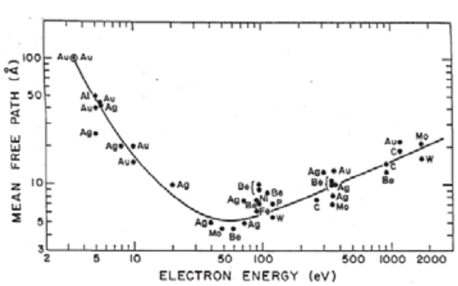


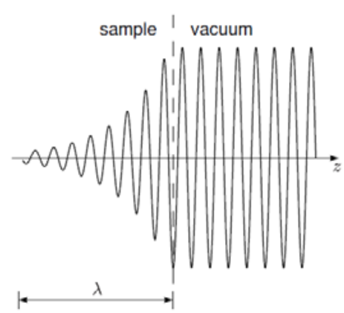


$SrTiO_3$(001)

Managed by Hugo Dil (EPFL and PSI)

Soft-X-Ray ARPES





- Larger mean free path increases probing depth (main signal still from surface region)
- Increased damping distance enhances k_z resolution ($\Delta k_z = \lambda^{-1}$): large problem at low hv
- High kinetic energies mean final state feels less of crystal potential: more free electron-like

→ Simplified matrix element and "cleaner" spectrum

Price to pay: less good resolution (40meV vs. 4meV) and lower count rate

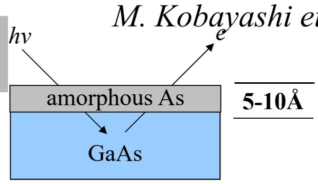
ADRESS beamline at SLS

PAUL SCHERRER INSTITUT

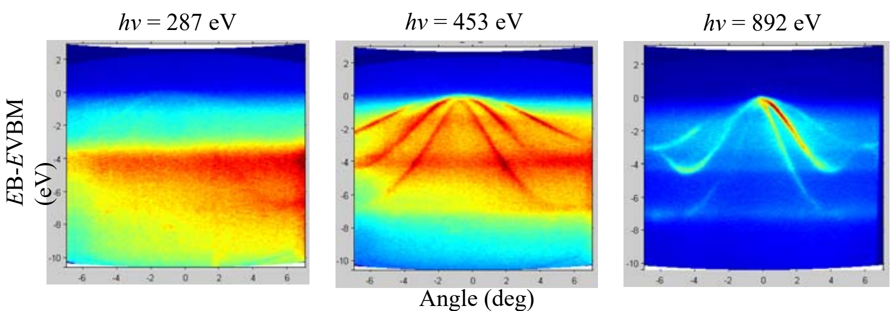
High Energies: Soft-X-Ray ARPES

Band structure of GaAs through amorphous As layer

M. Kobayashi et al (SLS); samples: Uni Tokyo



• large λ required: Soft-X-ray ARPES



• acquisition time 3 min

• GaAs signal piles up with *hv*

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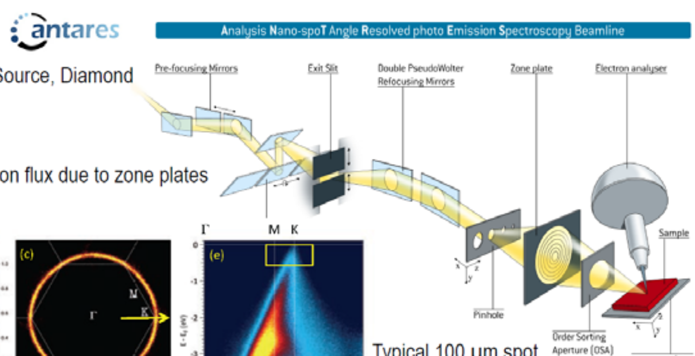
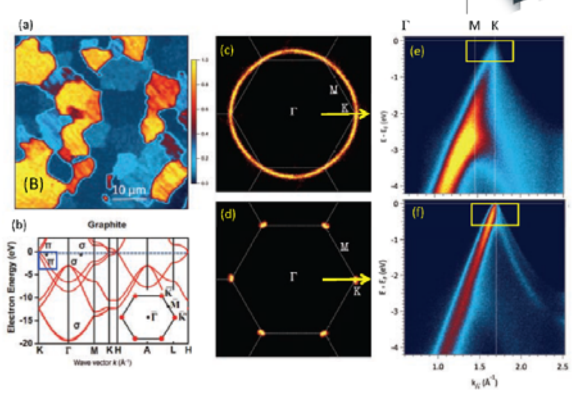
NanoARPES

Developments at:
Soleil, Advanced Light Source, Diamond



Significant loss of photon flux due to zone plates



Typical 100 µm spot

nano 200 nm spot

Different orientational domains of graphite are easily resolved

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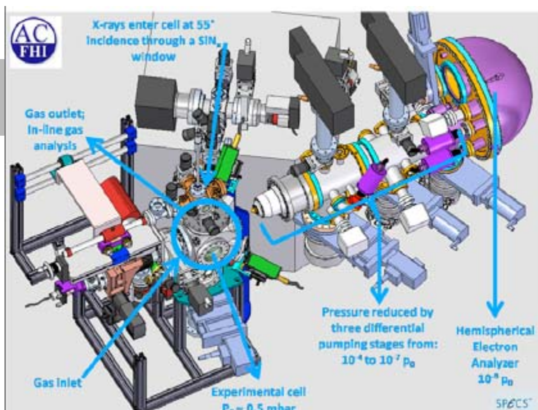
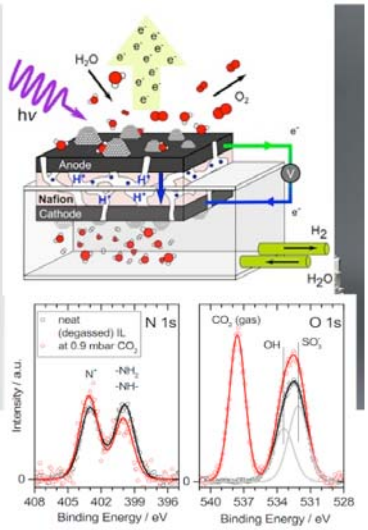
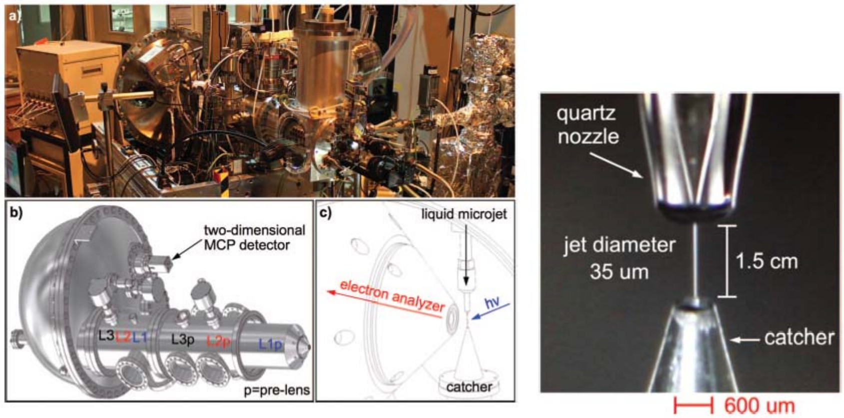
Ambient pressure XPS





Chemical shifts in XPS spectra during catalysis or operation of electrochemical cell

Liquid jet XPS



Soon at NanoXAS beamline at SLS
Already used at SIM and PHOENIX beamline

M.A. Brown et al, Rev. Sci. Instrum 84, (2013) 073904

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X-ray Photoelectron Diffraction (XPD)

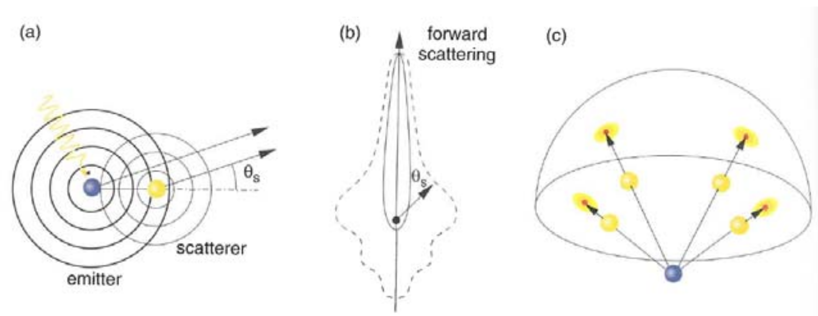

Figure 6.57 The scattering processes in x-ray photoelectron diffraction. (a) The outgoing wave of an ejected photoelectron can be either direct or be scattered elastically by neighbouring atoms. (b) Scattering has a pronounced forward contribution for electrons with energies of several hundred to several thousand eV. Towards the lower limit of this range (dashed polar distribution), forward scattering is less pronounced than at higher electron energies (solid line). (c) In a crystal, pronounced forward scattering has the effect that scattering along high-symmetry crystal axes is therefore much enhanced.

PEARL beamline at SLS

P. Willmott, Intro to Synchr. Rad.

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X-ray Photoelectron Diffraction (XPD)

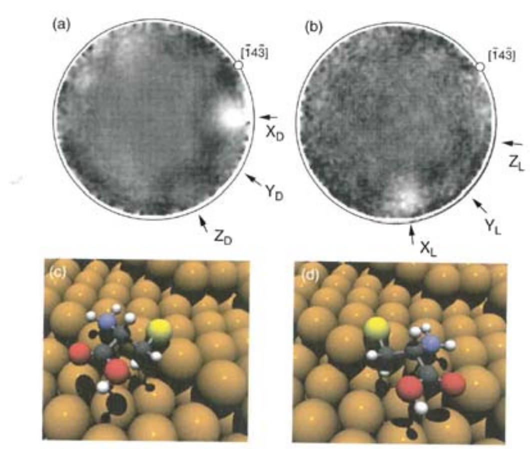

Figure 6.60 N 1s emission patterns for (a) D-cysteine and (b) L-cysteine. The patterns are dominated by the features labelled X_D and X_L, associated with forward scattering with the central carbon atom nearly in plane. The two weaker features Y and Z are due to scattering of the N 1s wave with the COOH carboxyl group. The absorption structures and orientations of (c) D-cysteine and (d) L-cysteine, determined by XPD results and theoretical calculations. Adapted from [61] with permission of the American Physical Society.

PEARL beamline at SLS

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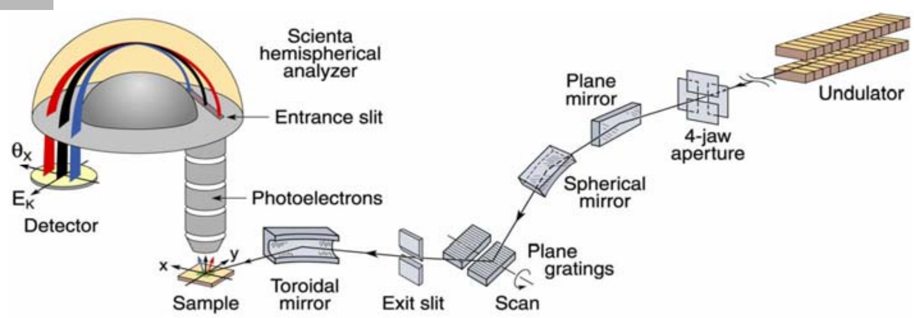
ARPES beamline

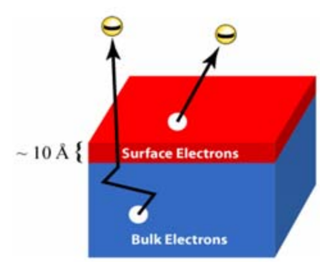


ARPES, Advantages and Limitations

Advantages

- **Direct information about the electronic states!**
- Straightforward comparison with theory - little or no modeling.
- High-resolution information about **BOTH energy** and **momentum**
- **Surface-sensitive probe**
- Sensitive to "**many-body**" effects
- Can be applied to small samples (100 μm x 100 μm x 10 nm)

Limitations



Now SX-ARPES

- **Not bulk sensitive**
- Requires clean, atomically flat surfaces in **ultra-high vacuum**
- Cannot be studied as a function of pressure or magnetic field

Courtesy of Kyle Shen