

Moderní experimentální metody

Rentgenová a elektronová spektroskopie III

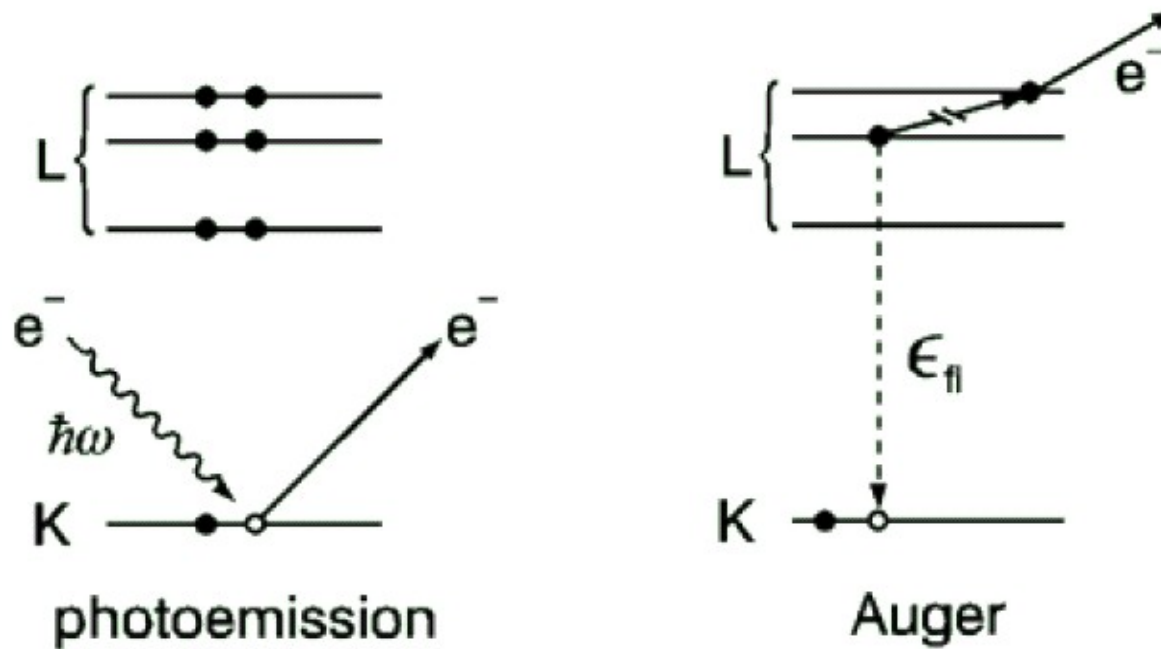
Fotoelektronová spektroskopie

- Fotoelektronová spektroskopie (XPS) a spektroskopie Augerových elektronů (AES)
- Experimentální aspekty
 - Zdroje: ARPES, ARUPS
 - Detektory
 - Příprava vzorků
- Úhlově rozlišená fotoelektronová spektroskopie (ARPES)

Fotoemise a Augerův jev

Fotoelektrony – přímo vyražené fotonem

Augerovy elektrony – sekundární emise – alternativní proces ke vzniku charakteristického rtg záření.

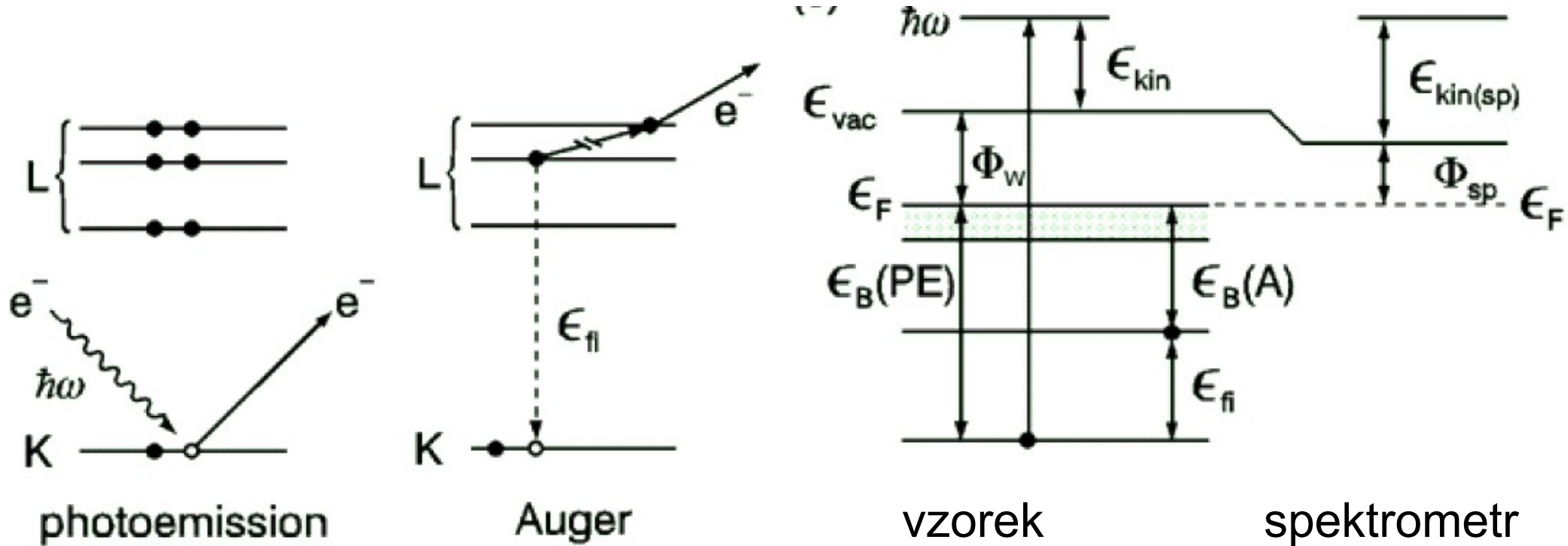


Elektronová spektroskopie měří kinetickou energii elektronů.

Fotoemise a Augerův jev

Fotoelektrony – přímo vyražené fotonem

Augerovy elektrony – sekundární emise – alternativní proces ke vzniku charakteristického rtg záření.



XPS – ESCA

Electron spectroscopy for chemical analysis

- All elements above $Z \geq 3$, Li
- Sensitivity – 1 permille
- Surface sensitivity – surface contamination
- Chemical state of surface
- Profiles along surface
- Depth profiling with ion beam

Fotoelektronová spektroskopie

Experiment:

Photon energy: 6eV to 2000eV

Laboratory sources:

- He discharge 21 eV
- Mg x-ray tube 1254 eV
- Al x-ray tube 1486 eV
- Laser 6eV (4x1.5eV)

Synchrotron – variable source

Ultra high vacuum (maximal pressure 10^{-6} Pa)

High quality surfaces needed

Optical elements – only in reflection geometry – mirrors, diffraction gratings, no windows!

Penetration depth 10^0 – 10^1 nm

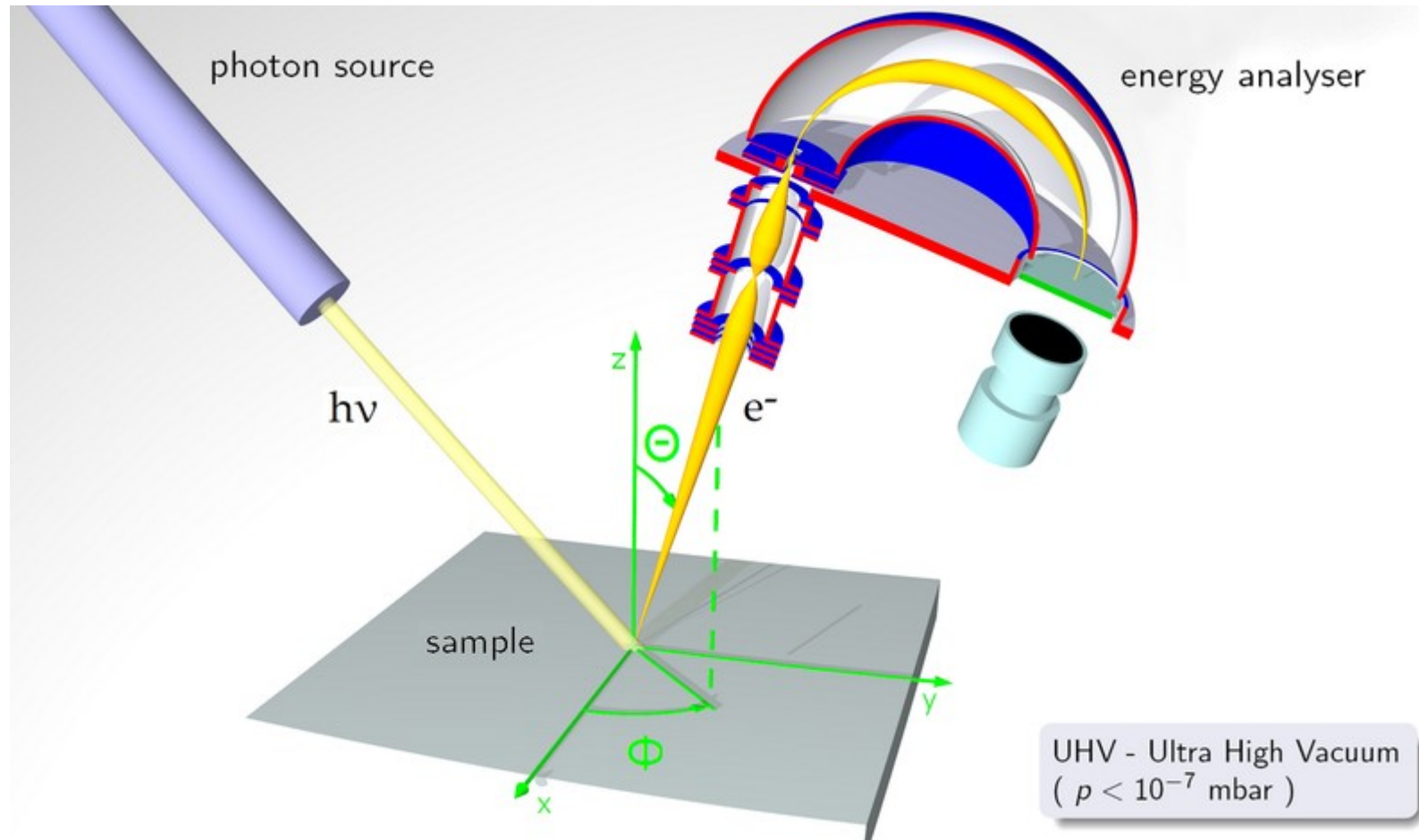
XPS

Sample preparation

Atomically clean and smooth surface

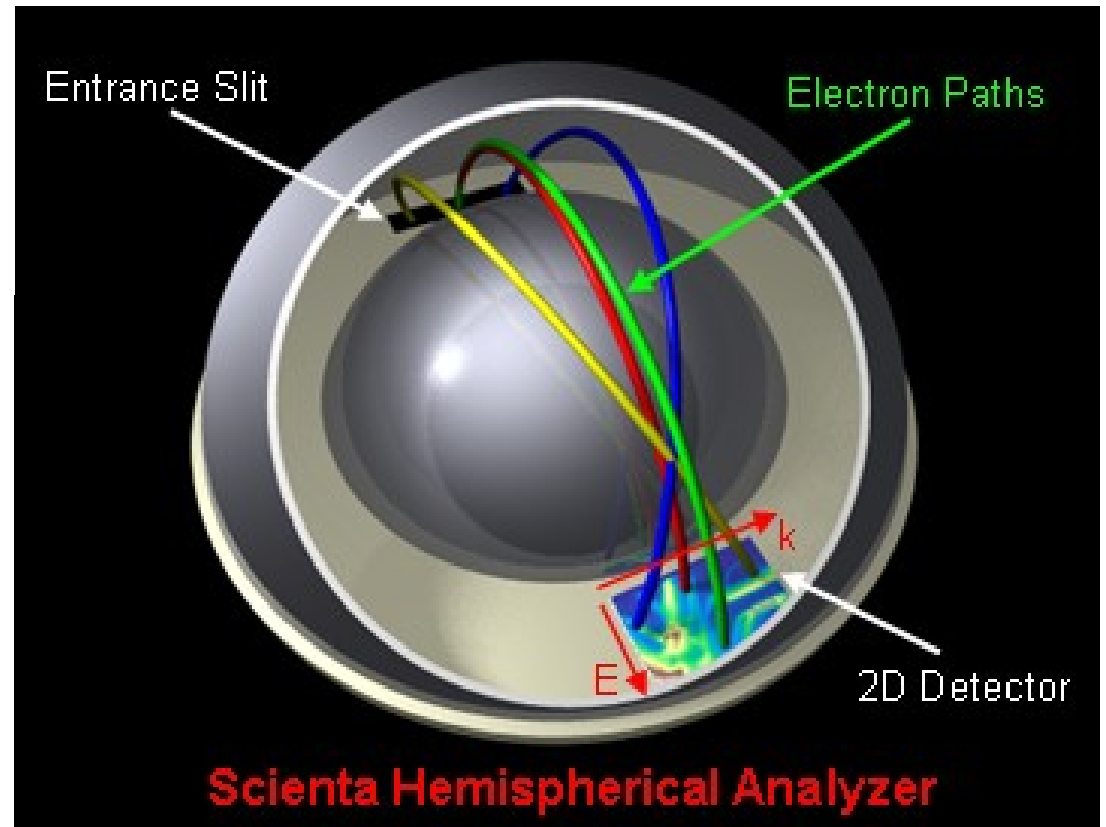
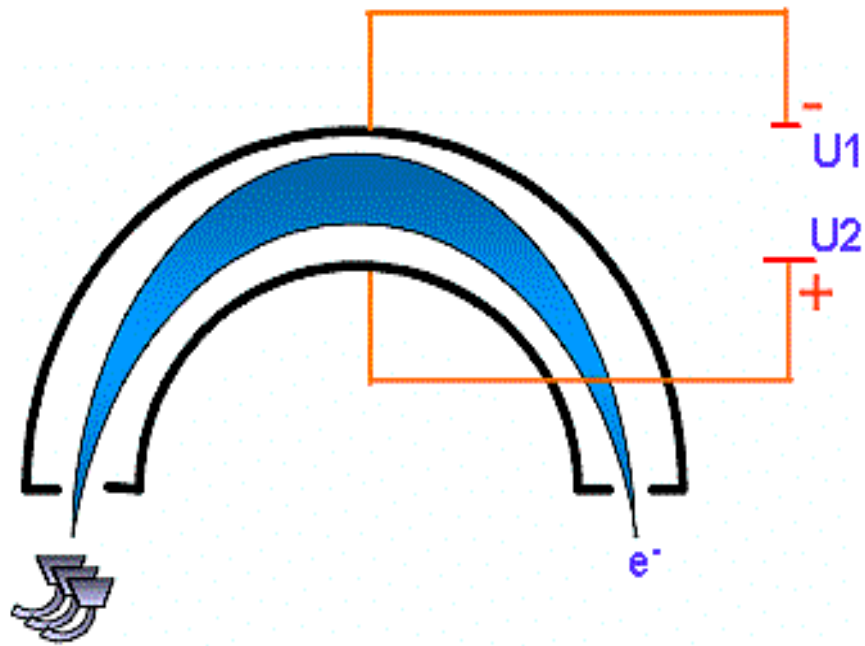
- Cleaving in vacuum
- Deposition chamber connected to XPS chamber
- Vacuum suitcase
- Protecting layers
- Ion sputtering
- heating

XPS



ARPES

Hemisférický analyzátor + CCD



Hemisférický analyzátor

$$V(r) = - \left[\frac{(V_2 - V_1)}{(R_2 - R_1)} \right] \cdot \frac{(R_1 R_2)}{r} + \text{const.}$$

$$|E(r)| = - \left[\frac{(V_2 - V_1)}{(R_2 - R_1)} \right] \cdot \frac{(R_1 R_2)}{r^2}$$

$$V(r) = \left(\frac{V_0 R_0}{r} \right) + \text{const.}$$

$$R_0 = (R_1 + R_2)/2$$

$$E_0 = |e|V_0$$

$$V_2 - V_1 = V_0 \left(\frac{R_2}{R_1} - \frac{R_1}{R_2} \right)$$

ARPES

Hemisférický analyzátor VG Scienta R4000

Scienta R4000 Spectromicroscopy Performance Optics:

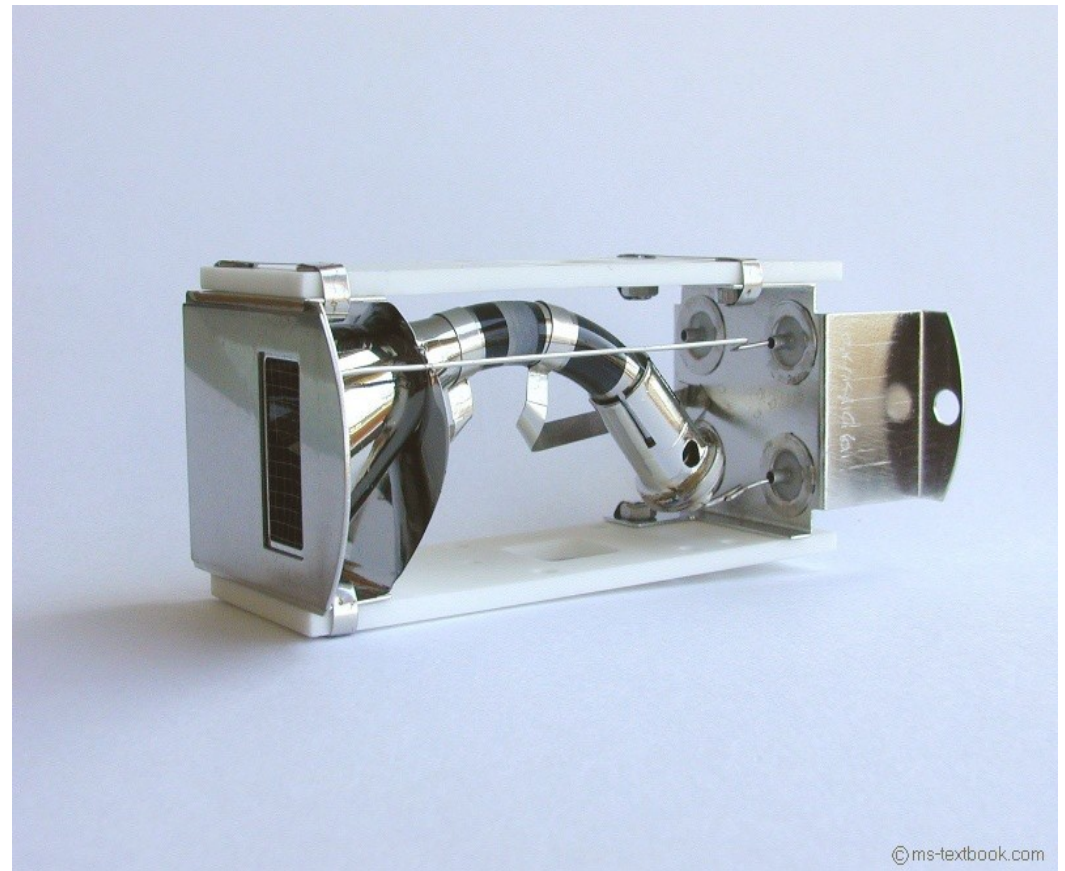
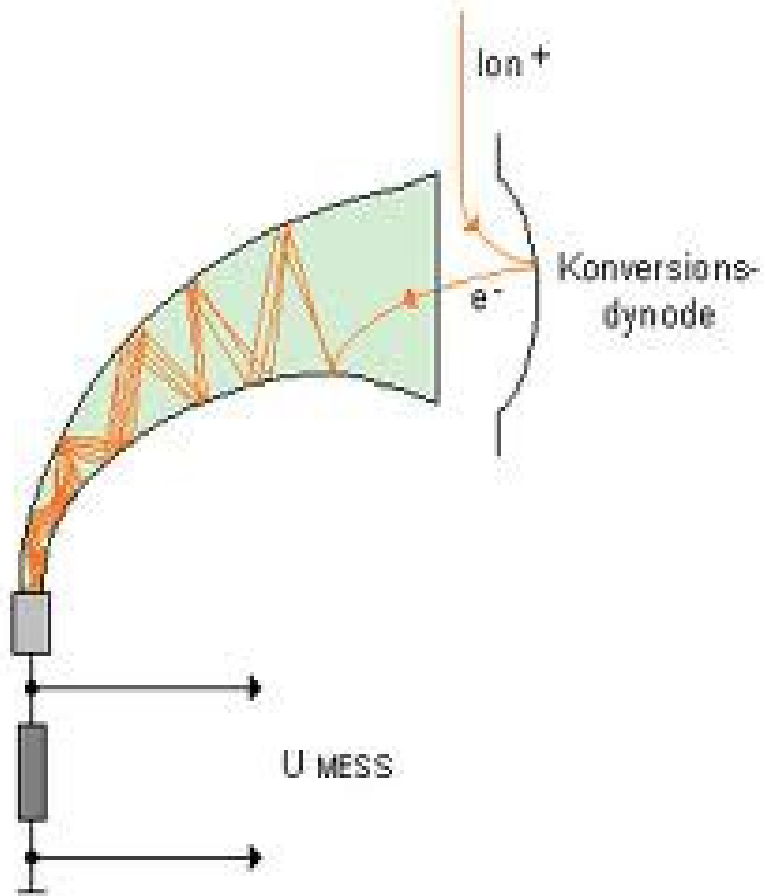
Energy resolution:	$< 2 \text{ meV}$
Theoretical resolving power using 0.2 mm entrance slit:	2000
Kinetic energy range:	0.2 - 1500 eV
Spatial resolution:	$< 10 \text{ }\mu\text{m}$
Magnification:	
<i>Imaging Mode</i>	10x, 20x, 40x
<i>Transmission Mode</i>	5x
Ultimate angular resolution:	$< 0.1 \text{ degrees}$
Widest angular range for multiplexed angle recordings:	$> 10 \text{ degrees}$



R4000 Spectrometer

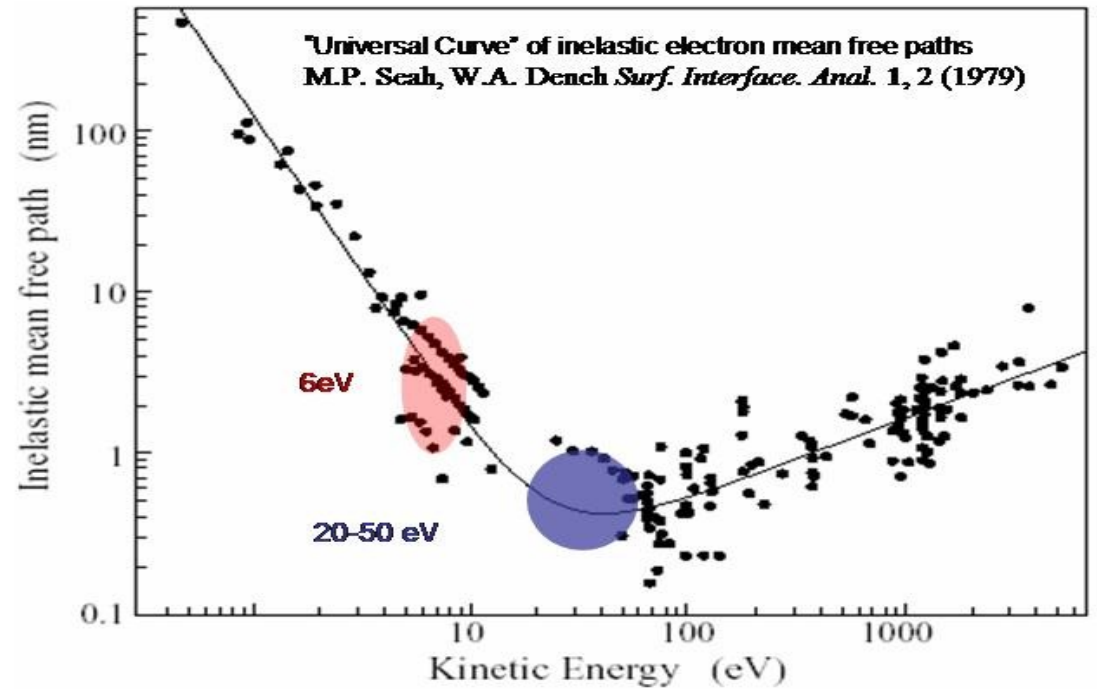
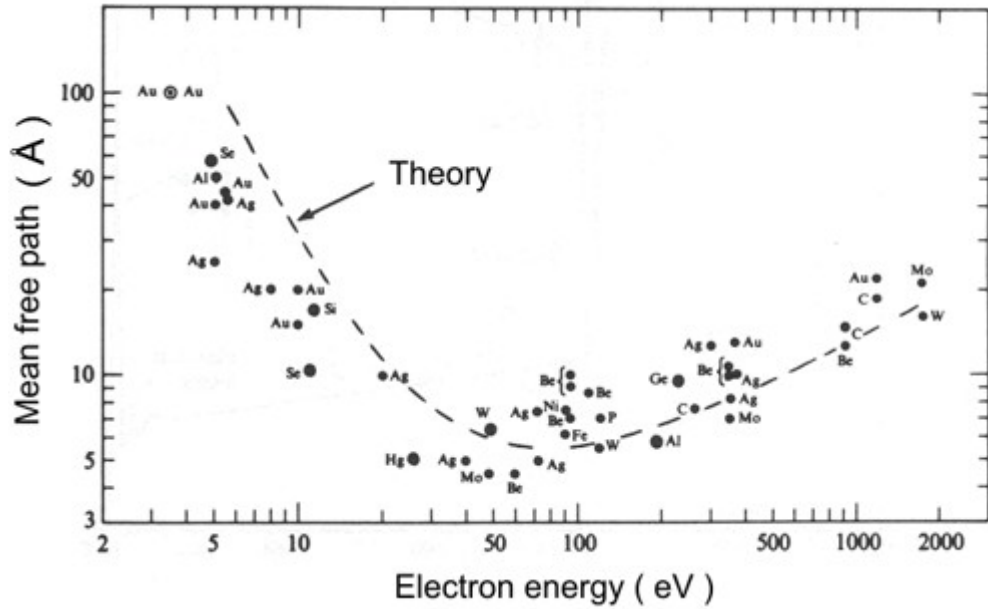
XPS

Detekce:
CCD
Channeltron



XPS

Electron escape depth



XPS

Rentgenová fotoelektronová spektroskopie

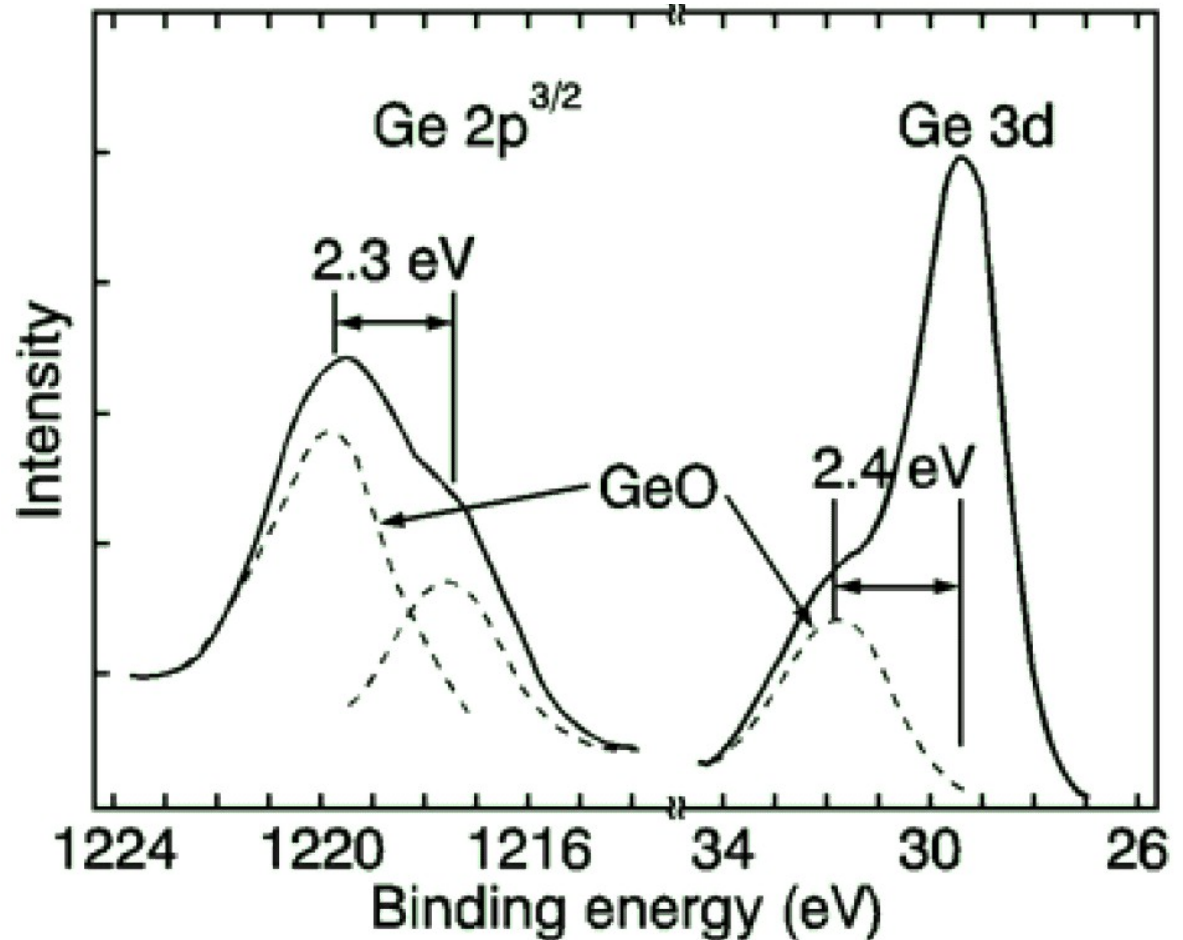
X-ray Photoelectron Spectroscopy – XPS, PES

Kinetická energie elektronu odpovídá rozdílu energie fotonu a ionizační energie slupky.

$$\epsilon_{\text{kin}} = \hbar\omega - [\epsilon_{\text{B}}(\text{PE}) + \Phi_{\text{sp}}]$$

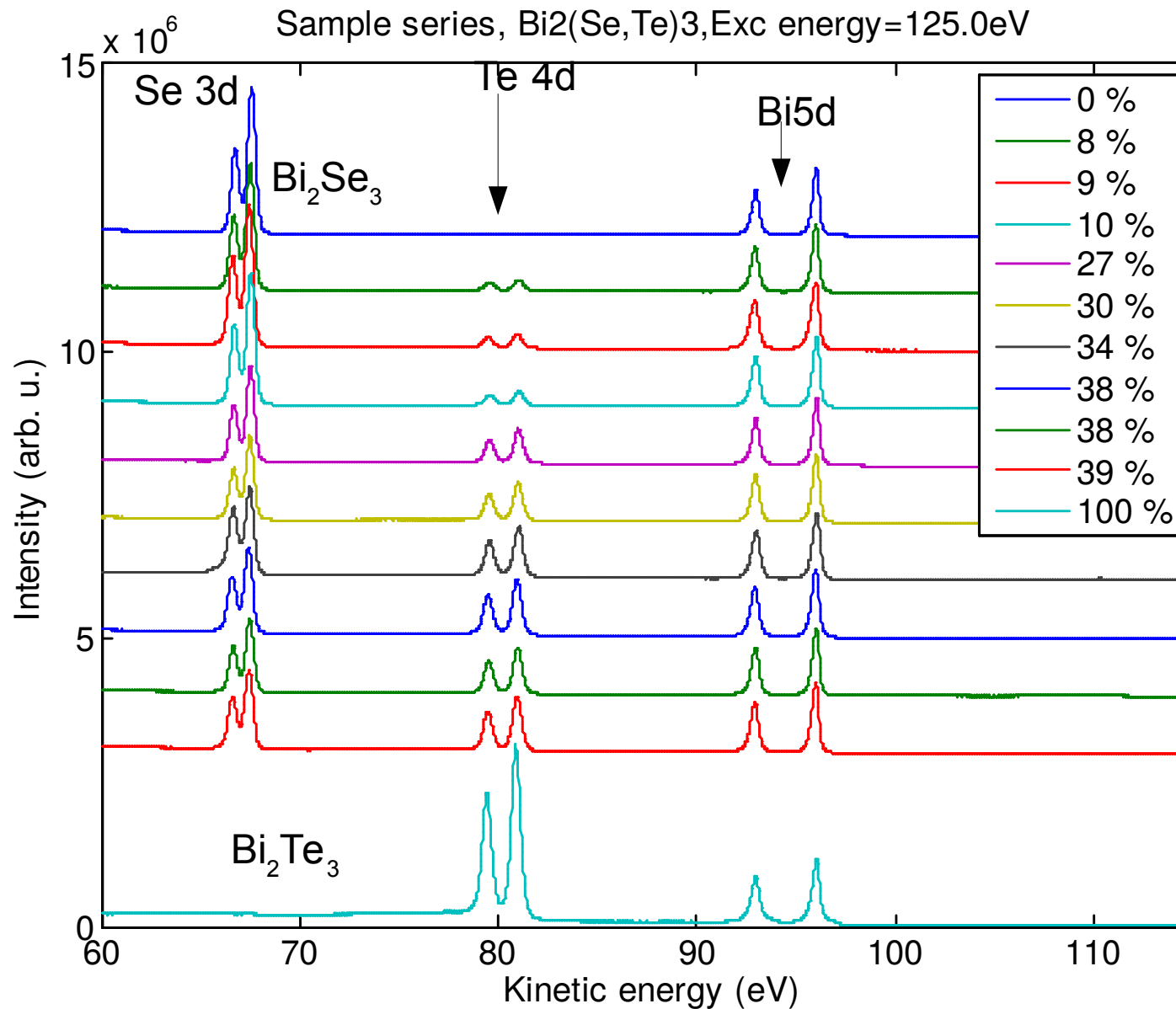
Umožňuje detekovat změny vazebné energie chemickým stavem atomu.

XPS na germaniu s velmi tenkou oxidovou vrstvou.

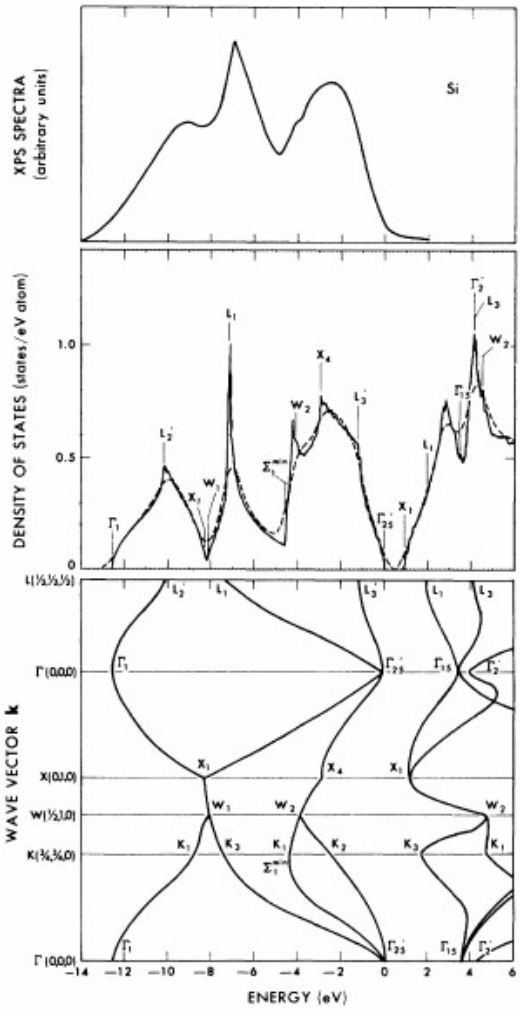


XPS

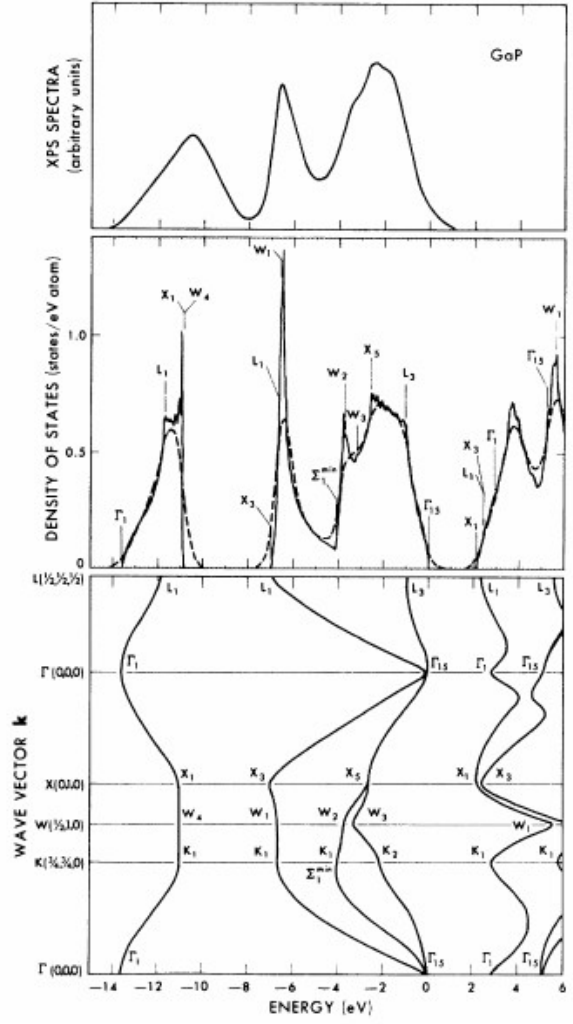
Příklad: $\text{Bi}_2(\text{Se},\text{Te})_3$ excitace 125 eV.



PES and DOS examples: when the nature is nice



Si

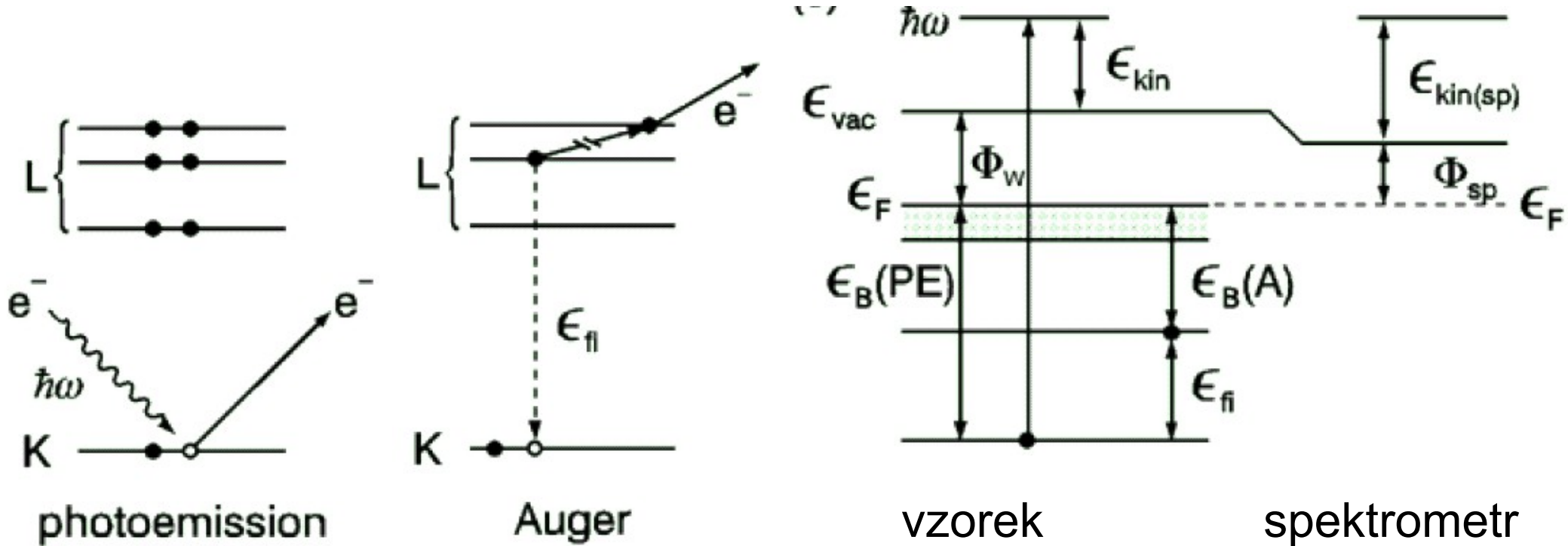


GaP

Fotoemise a Augerův jev

Fotoelektrony – přímo vyražené fotonem

Augerovy elektrony – sekundární emise – alternativní proces ke vzniku charakteristického rtg záření.



AES

Spektroskopie Augerových elektronů

Auger Electron Spectroscopy – AES

Energie elektronu při přechodu na uvolněnou hladinu se může předat Augerovu elektronu.

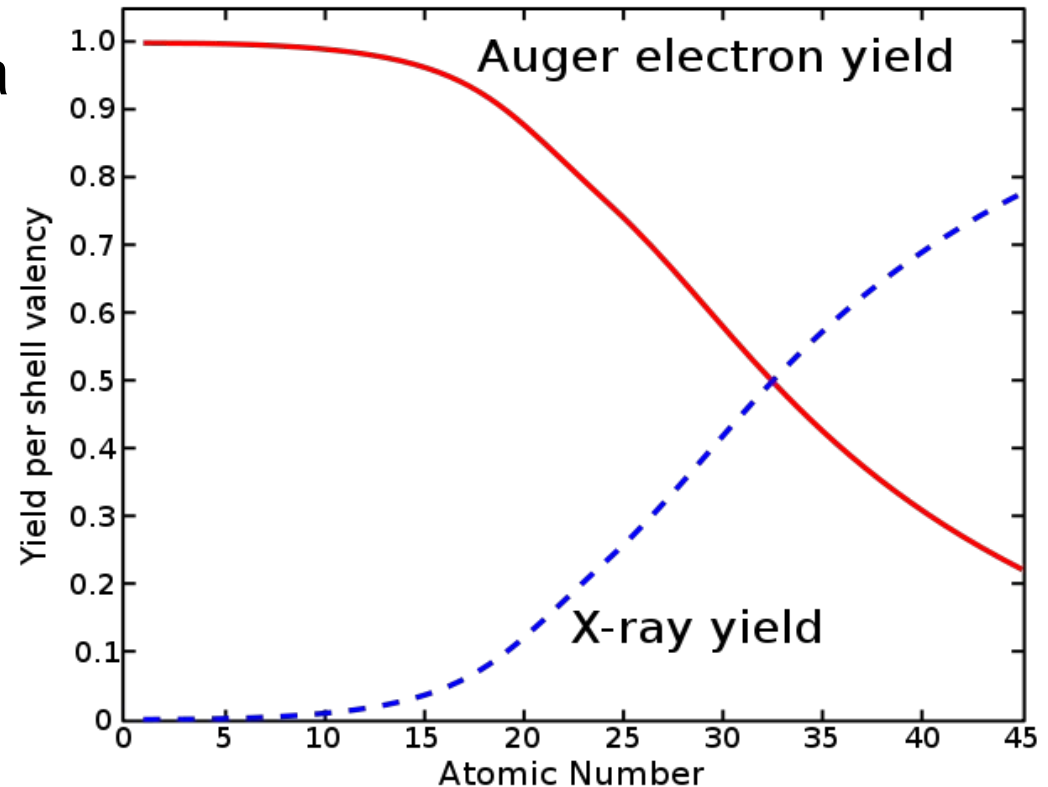
$$\epsilon_{\text{Aug}} = \epsilon_{\text{fi}} - [\epsilon_{\text{B}}(A) + \Phi_{\text{sp}}]$$

Charakteristické energie se značí FIB. Přechod I→F, ionizuje se B.

Pravděpodobnost emise Augerova elektronu a rtg záření závisí na protonovém čísle.

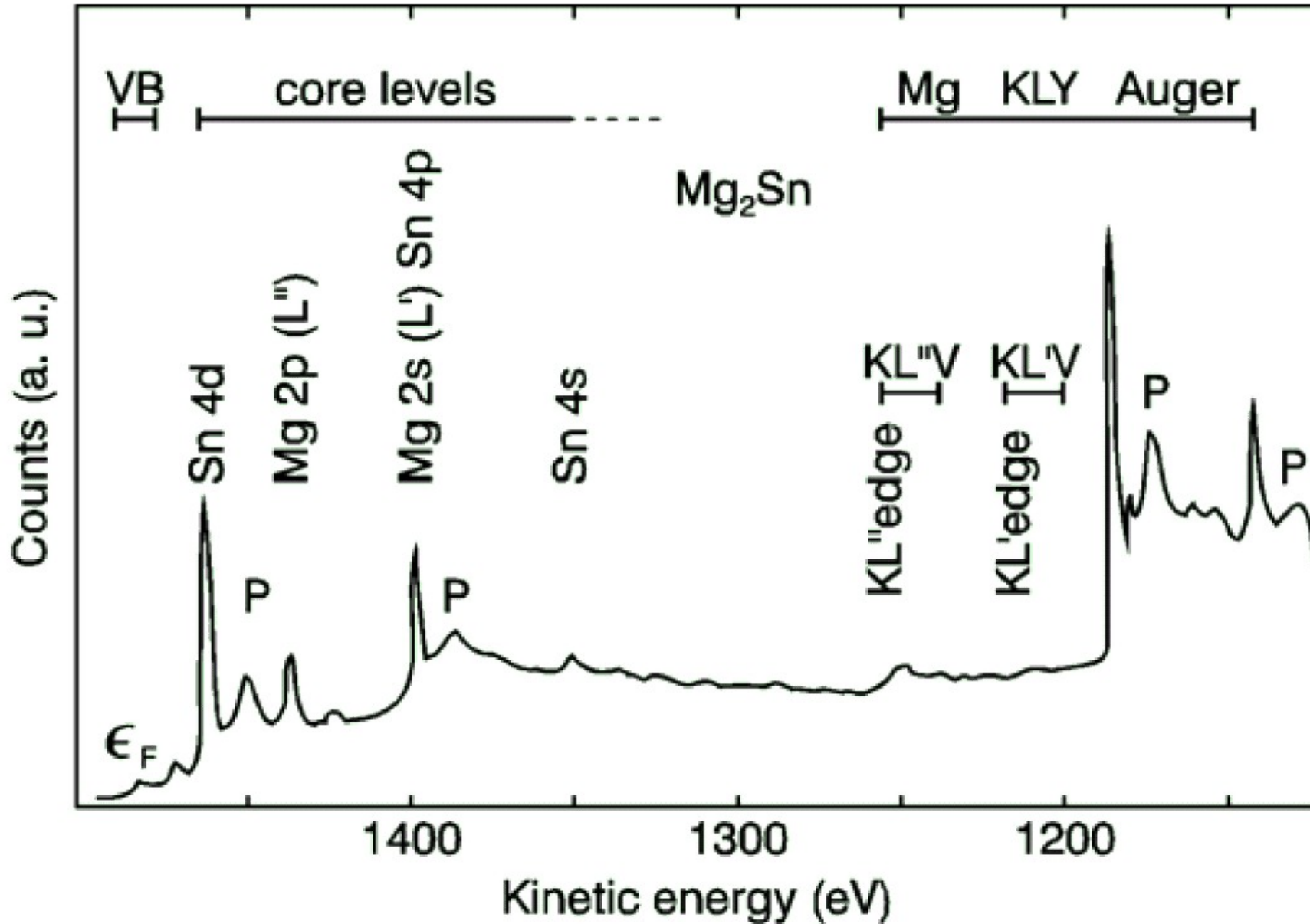
Augerova spektroskopie je nejcitlivější na lehké prvky.

Často se měří v kombinaci s XPS, používá se v elektronové mikroskopii.



XPS + AES

Fotoelektronová a Augerova spektroskopie na Mg_2Sn .
Budící rtg svazek 1486 eV – čára Al $K\alpha$



Angle-Resolved Photoemission spectroscopy overview

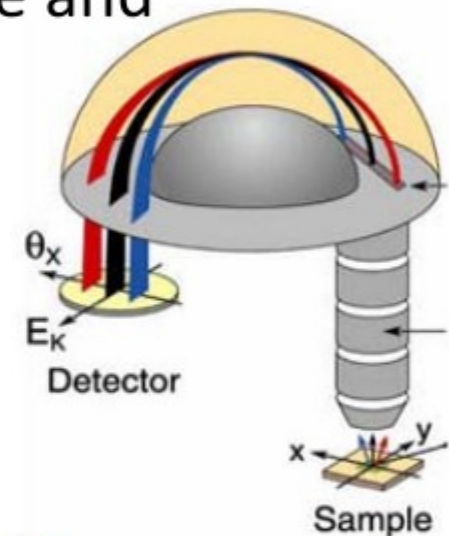
- Purpose: measure electronic band structure and interactions
- Photoelectric effect, conservation laws

$$E_{kin} = h\nu - \phi - |E_B|$$

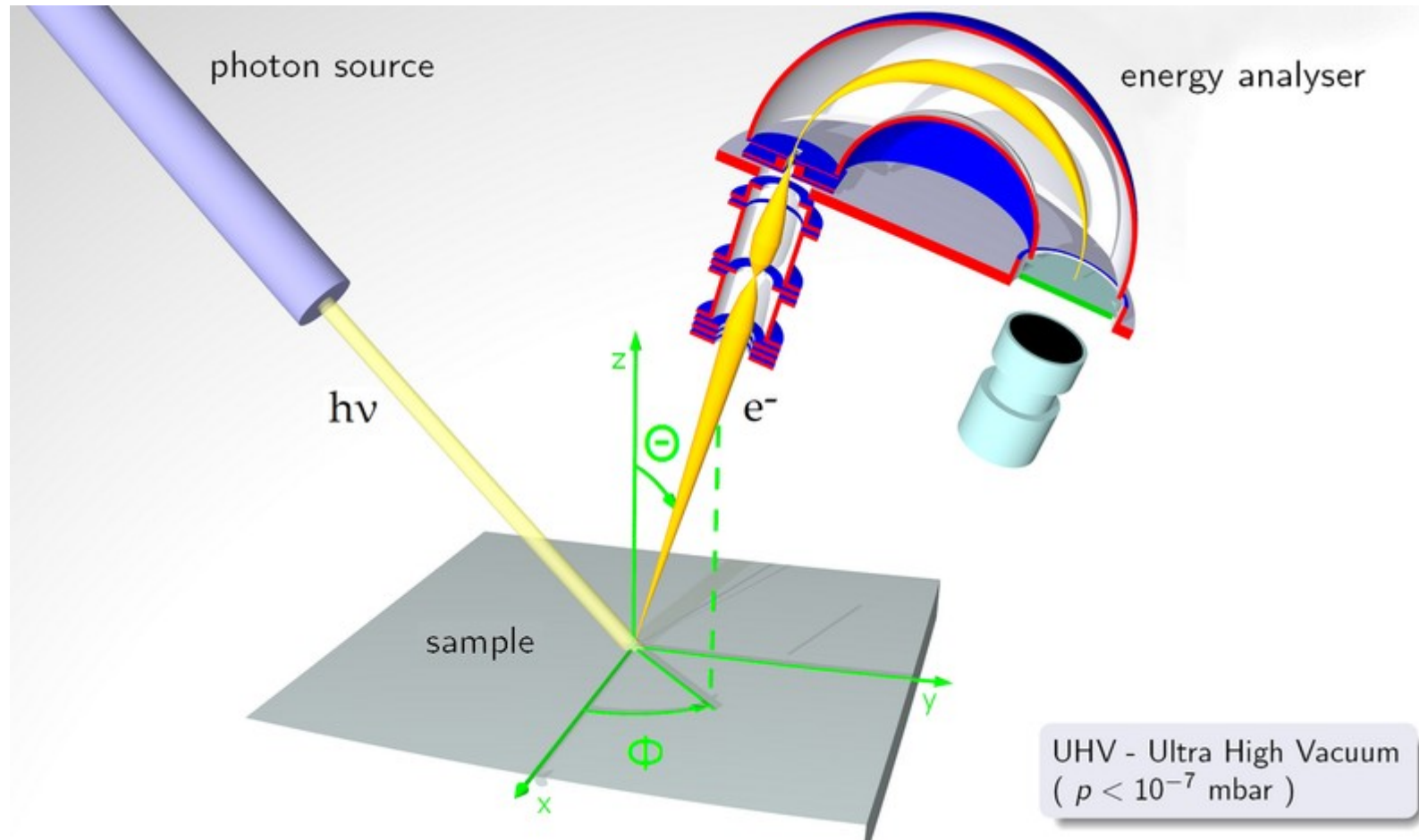
$$\mathbf{p}_{||} = \hbar \mathbf{k}_{||} = \sqrt{2mE_{kin}} \cdot \sin \vartheta$$

Definitions:

- E_{kin} = kinetic energy of photoelectron **measure**
 $h\nu$ = photon energy **Know (6-200 eV this lecture)**
 ϕ = work function **know/measure (~ 4 eV)**
- E_B = electron binding energy inside material, relative to Fermi level **want**
 $k_{||}$ = crystal momentum, parallel to sample surface plane **want**
 m = mass of free electron **know**
 ϑ = emission angle of photoelectron **measure**



ARPES - úhlově rozlišená



ARPES

Zákony zachování

- Kvaziimpulz – zachovává se tečná složka

$$\hbar\vec{k}_{\text{foton},\parallel} + \hbar\vec{k}_{i,\parallel} = \hbar\vec{k}_{f,\parallel}$$

$$\hbar\vec{k}_{i,\parallel} \approx \hbar\vec{k}_{f,\parallel} = \sqrt{2mE} \sin \theta$$

$$\hbar\vec{k}_x = \sqrt{2mE} \sin \theta \cos \phi$$

$$\hbar\vec{k}_y = \sqrt{2mE} \sin \theta \sin \phi$$

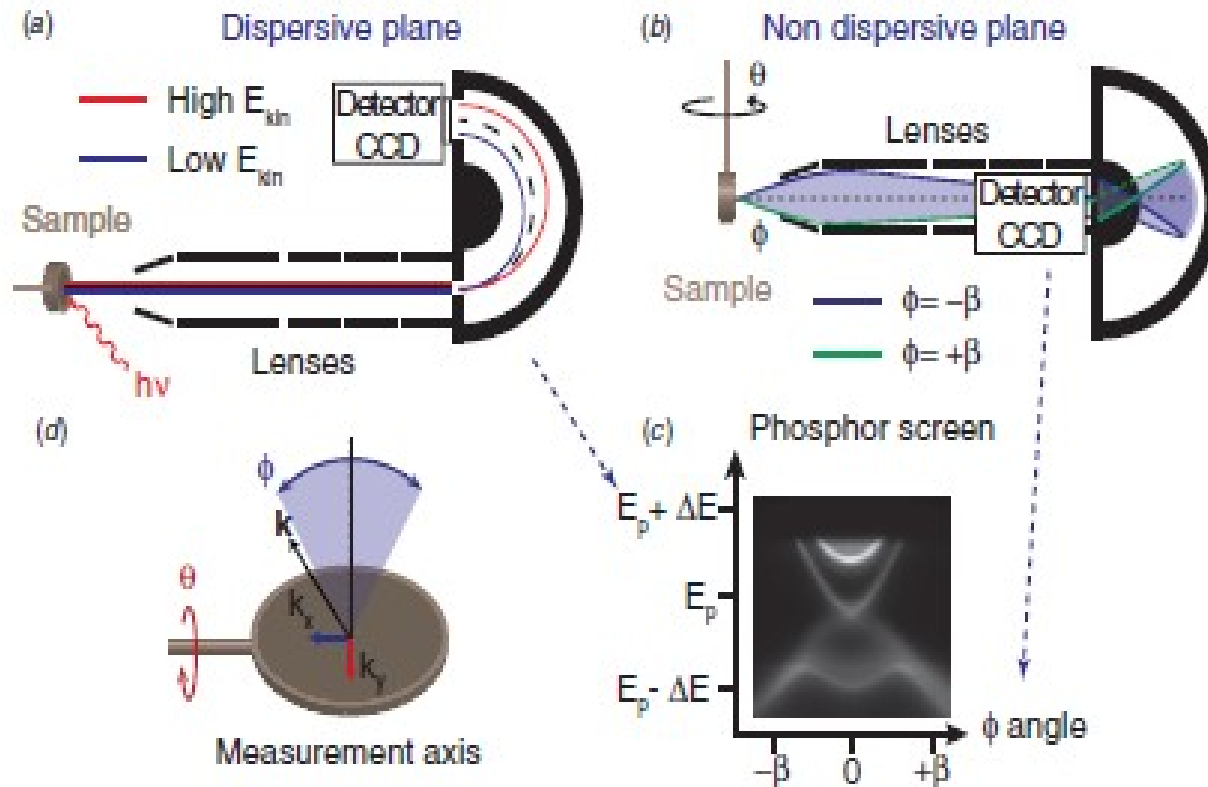
$$\hbar\vec{k}_z = \sqrt{2mE} \cos \theta$$

- energie

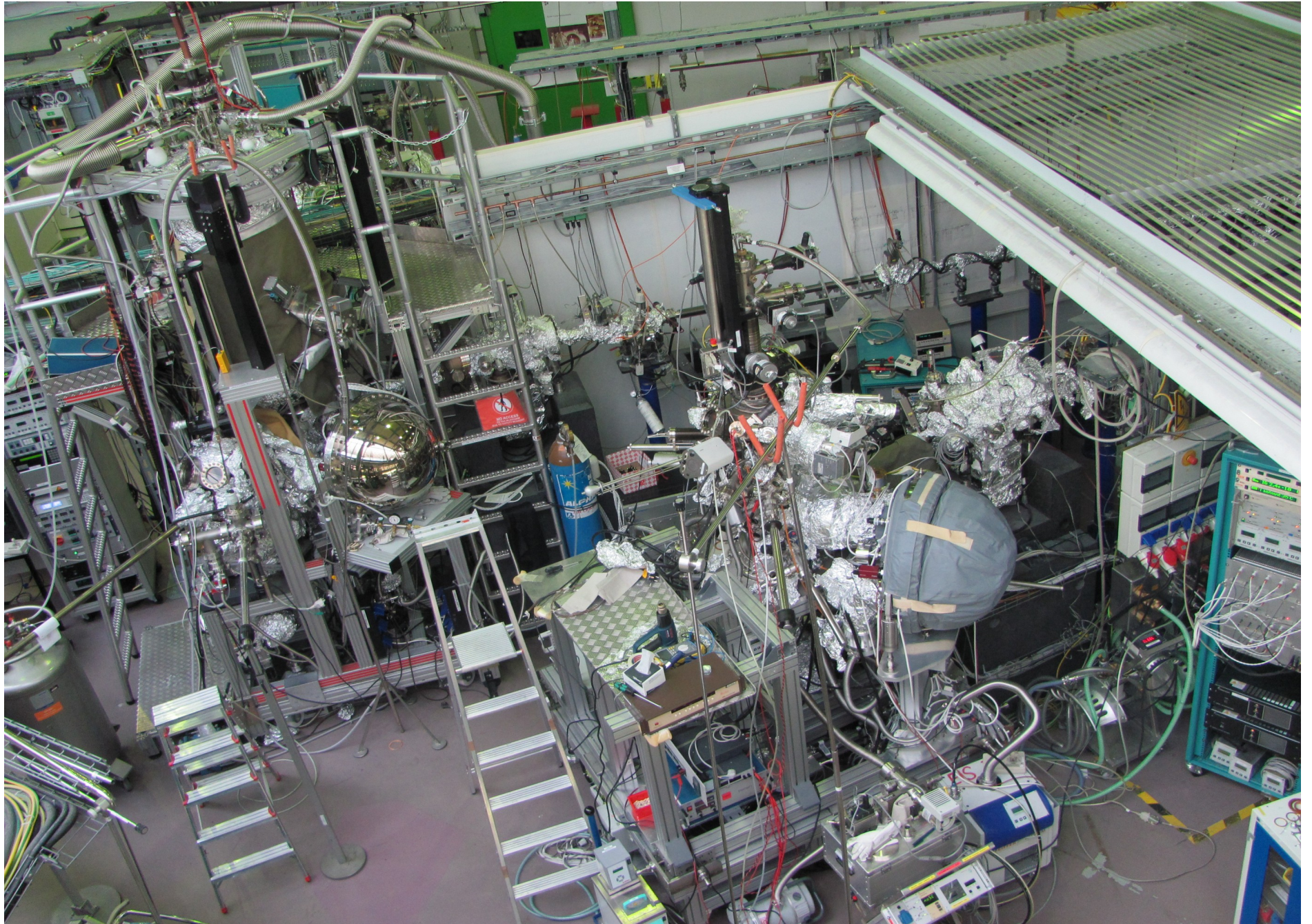
$$E_{\text{bound}} = \hbar\omega_i - E_{\text{kin,elektron}} - \varphi$$

$$\mathbf{k}_{\parallel} = (\sin(\phi)\hat{\mathbf{x}} + \cos(\phi)\sin(\theta)\hat{\mathbf{y}}) \cdot \sqrt{\frac{2m_e E_{\text{kin}}}{\hbar^2}},$$

$$k_z = \sqrt{2m_e / \hbar^2 (V_0 + E_{\text{kin}} \cos(\theta))}.$$



ARPES at BESSY



What is actually being measured by ARPES?

- Electrons live in bands
- Interactions (electron-electron, electron-phonon, etc) can change band dispersions and quasiparticle lifetimes
- Single particle spectral function captures these interactions

Single particle spectral function: $A(\mathbf{k}, \omega) = -\frac{1}{\pi} \frac{\Sigma''(\mathbf{k}, \omega)}{[\omega - \varepsilon_{\mathbf{k}} - \Sigma'(\mathbf{k}, \omega)]^2 + [\Sigma''(\mathbf{k}, \omega)]^2}$

Bare band: $\varepsilon_{\mathbf{k}}$

Self Energy: $\Sigma(\mathbf{k}, \omega) = \Sigma'(\mathbf{k}, \omega) + i\Sigma''(\mathbf{k}, \omega)$

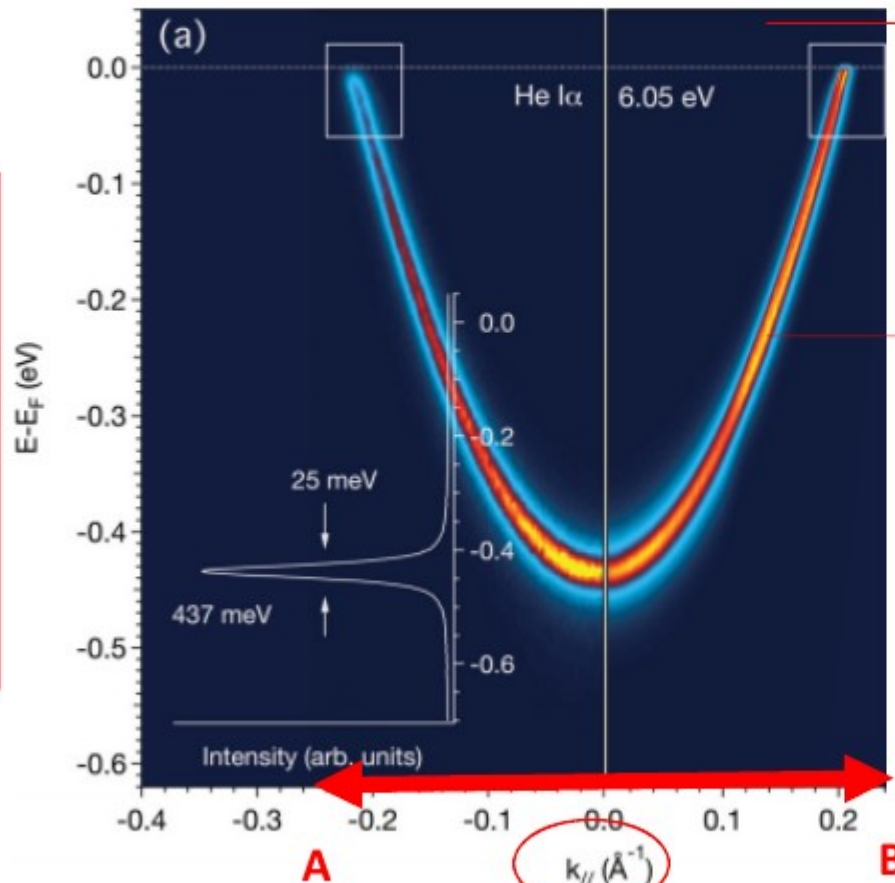
Band position

Linewidth or lifetime

Band structure
+
Interactions

Band structure: simple metal (Cu 111 surface)

Electron binding energy
 $|E_B| = E - E_F$

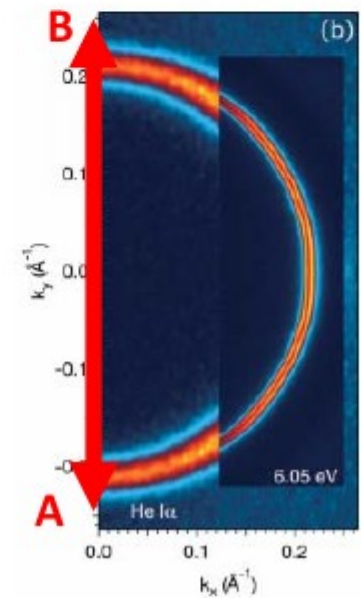


In-plane momentum

Fermi-Dirac cutoff

$$F(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1}$$

$$\epsilon_k = E(k) = \frac{\hbar^2 k^2}{2m^*}$$



Fermi surface map is (usually) produced by pasting adjacent slices together

Photoemission basics: 3 step model

$$E_{kin} = h\nu - \phi - |E_B|$$

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

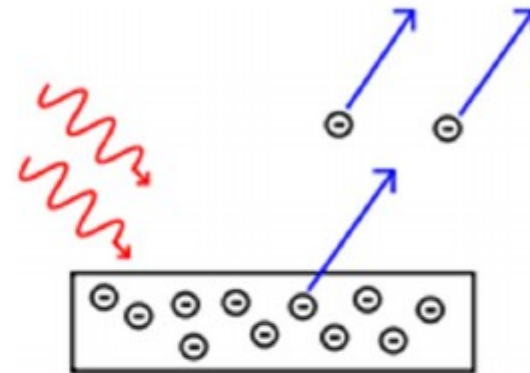


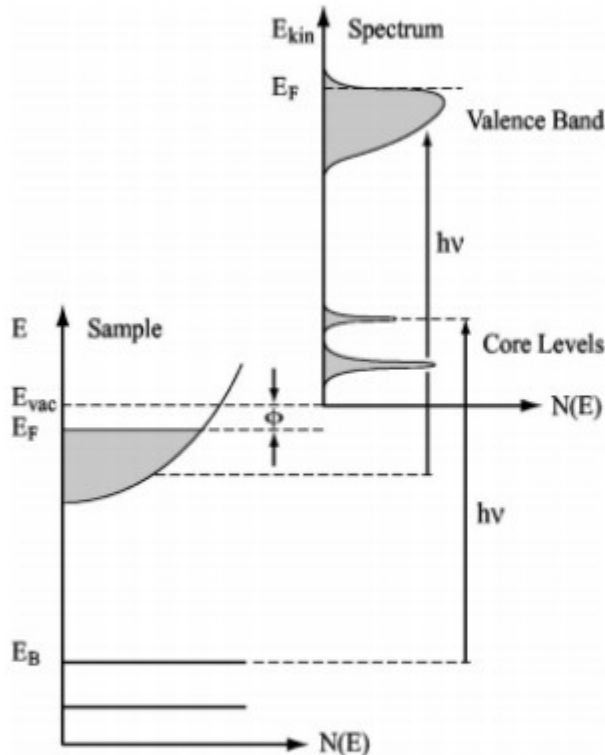
Image:

https://en.wikipedia.org/wiki/Photoelectric_effect

1. Optical excitation of electron in the bulk
2. Travel of excited electron to the surface
3. Escape of photoelectrons into vacuum

Photoemission intensity is given by product of these three processes (and some other stuff)

1. Optical excitation of electron in bulk



Hufner. *Photoelectron Spectroscopy* (2003)

- Start: electron in occupied state of N-electron wavefunction, Ψ_i^N
- End (of this step): electron in unoccupied state of N electron wavefunction, Ψ_f^N
- **Sudden Approximation:** no interaction between photoelectron and electron system left behind

Probability of transition related to Fermi's golden rule:

$$w_{fi} = \frac{2\pi}{\hbar} \left| \langle \Psi_f^N | -\frac{e}{mc} \mathbf{A} \cdot \mathbf{p} | \Psi_i^N \rangle \right|^2 \delta(E_f^N - E_i^N - h\nu)$$

\mathbf{p} =electron momentum

\mathbf{A} =vector potential of photon (points in direction of polarization)

Express as antisymmetric product of 1-electron state and N-1 electron state

$$\text{e.g.: } \Psi_f^N = \mathcal{A} \phi_f^k \Psi_f^{N-1}$$

1. Optical excitation of electron in bulk (continued)

$$\langle \Psi_f^N | -\frac{e}{mc} \mathbf{A} \cdot \mathbf{p} | \Psi_i^N \rangle = \langle \phi_f^k | -\frac{e}{mc} \mathbf{A} \cdot \mathbf{p} | \phi_i^k \rangle \langle \Psi_m^{N-1} | \Psi_i^{N-1} \rangle$$
$$\equiv M_{f,i}^k \langle \Psi_m^{N-1} | \Psi_i^{N-1} \rangle$$

$M_{f,i}^k$ = 'ARPES matrix elements'

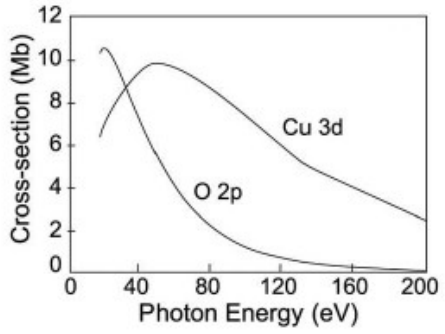
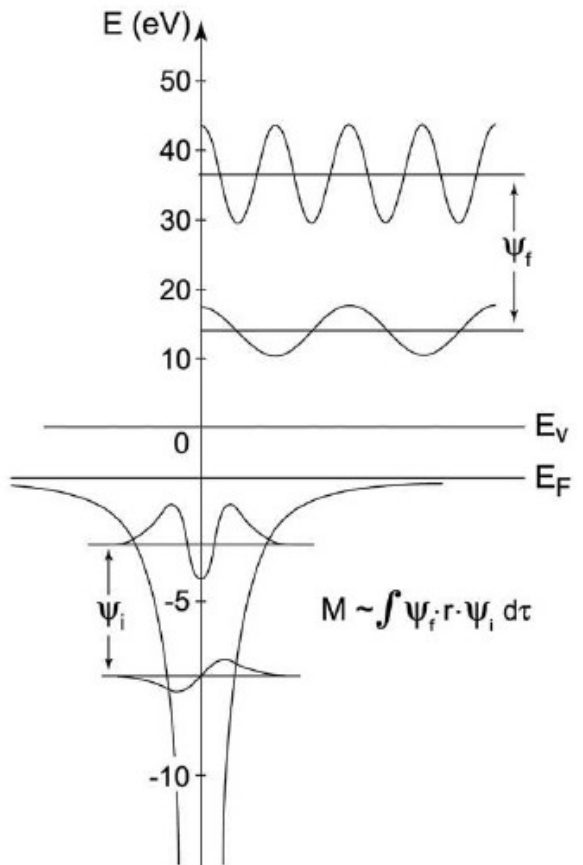
m = index given to $N-1$ -electron **excited** state

Total photoemission intensity originating from this step:

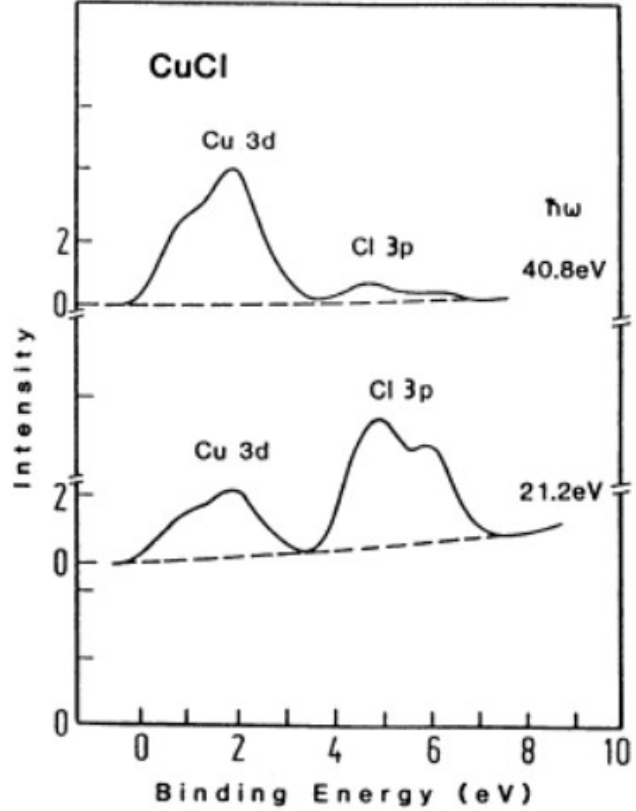
$$I(\mathbf{k}, E_{kin}) = \sum_{f,i} W_{f,i}$$
$$= \sum_{f,i} |M_{f,i}^k|^2 \sum_m | \langle \Psi_m^{N-1} | \Psi_i^{N-1} \rangle |^2 \delta(E_{kin} + E_m^{N-1} - E_i^N - h\nu)$$

Consequences of step 1: Observed band intensity is a function of experimental geometry, photon energy, photon polarization
"Matrix element effects"

Photoemission spectra: Matrix elements effect



Phys. Scr. **T109**, 61 (2004)



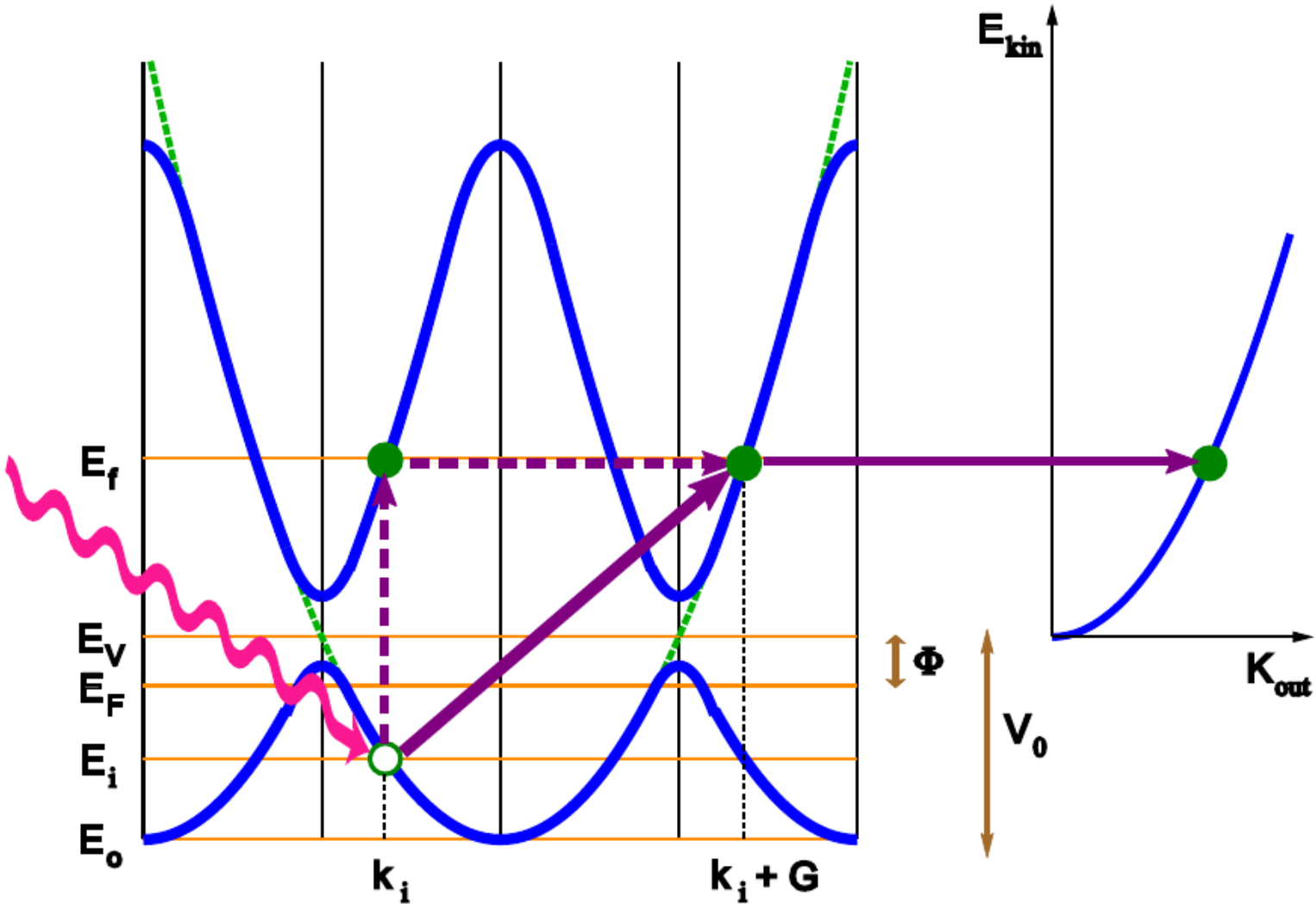
PRB **8**, 2786 (1973)

By varying $\hbar\omega$ we can put emphasis on one element or another.

3. Escape of photoelectrons into vacuum

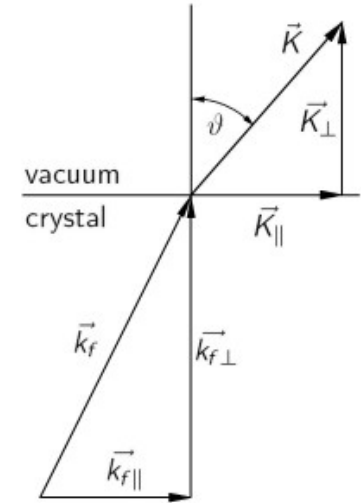
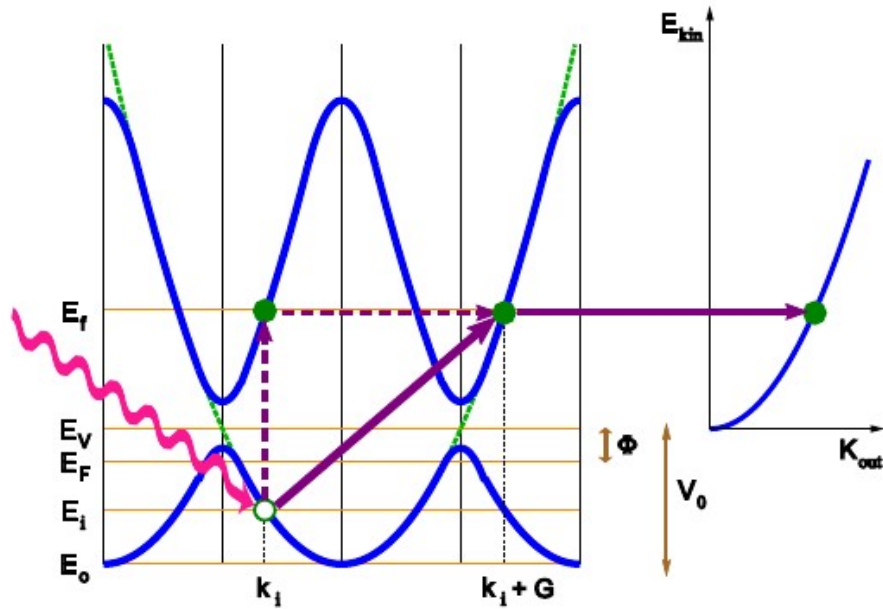
- Electron loses work function (Φ) worth of energy
- Transmission probability through surface depends on energy of excited electron and Φ

Recovering ε_k^n and \mathbf{k} (1)



Conservation of energy: $E_{kin} = \hbar\omega - \Phi - (E_F - E_i)$

Recovering $\varepsilon_{\mathbf{k}}^n$ and \mathbf{k} (2)

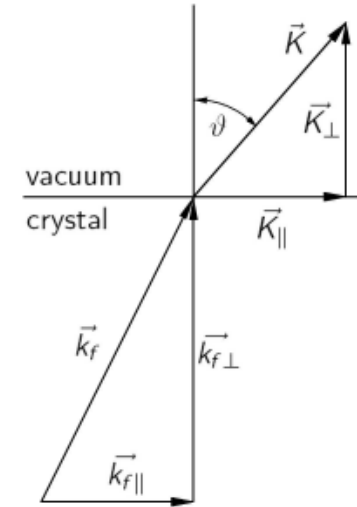
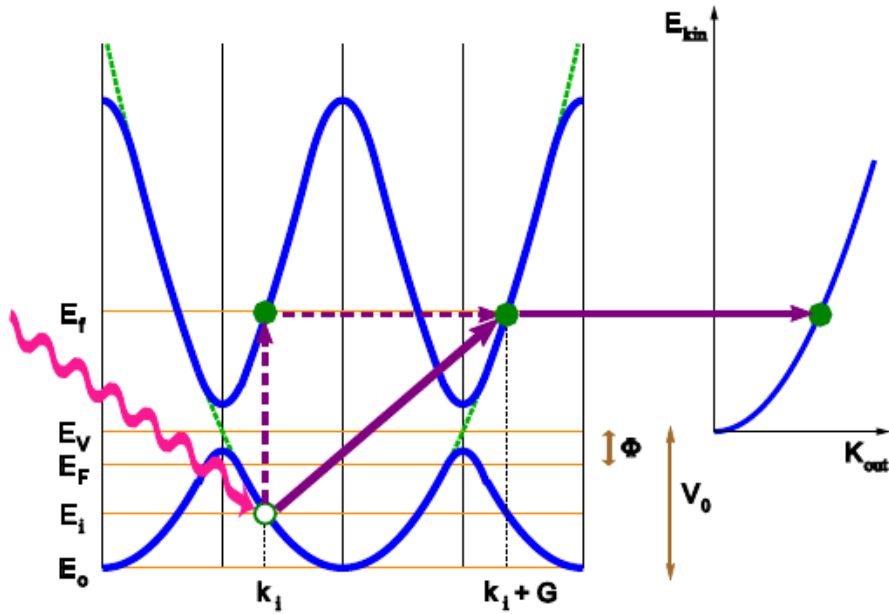


Momentum:

Parallel component \mathbf{k}_{\parallel} is conserved up to a reciprocal lattice vector:

$$\mathbf{k}_{\parallel} = \mathbf{K}_{\text{out},\parallel} - \mathbf{G}_{\parallel} .$$

Recovering $\varepsilon_{\mathbf{k}}^n$ and \mathbf{k} (3)

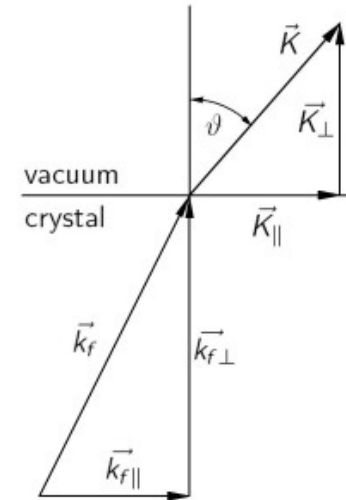
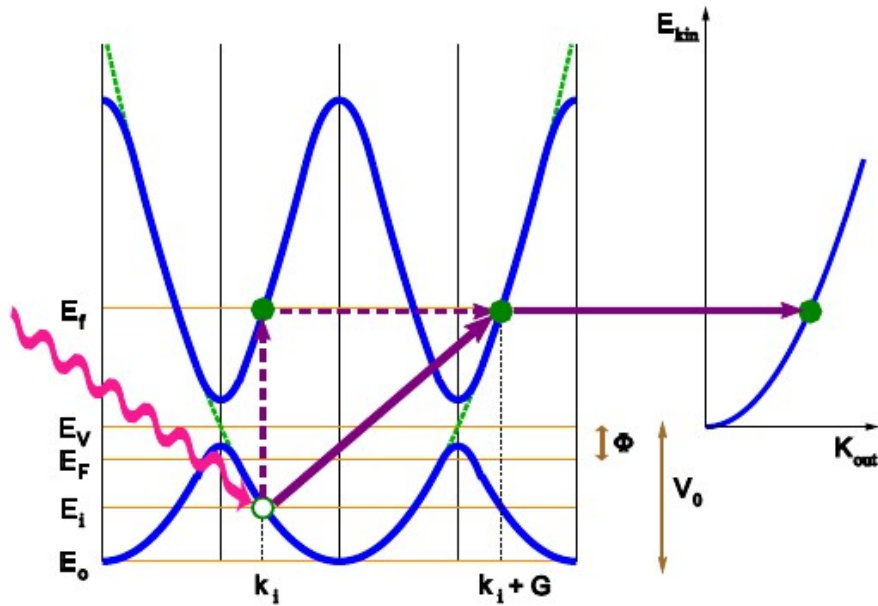


Perpendicular component can be recovered if assumptions about the bulk final state (in the solid) are made.

Assuming the **free-electron-like character** of the final state, one gets (in the extended zone scheme):

$$E_f - E_0 = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left[(k_{\perp} + G_{\perp})^2 + (\mathbf{k}_{\parallel} + \mathbf{G}_{\parallel})^2 \right] .$$

Recovering $\varepsilon_{\mathbf{k}}^n$ and \mathbf{k} (4)



Energy balance:

$$E_f - E_0 = E_{\text{kin}} + (E_V - E_0)$$

Free-electron approx.:

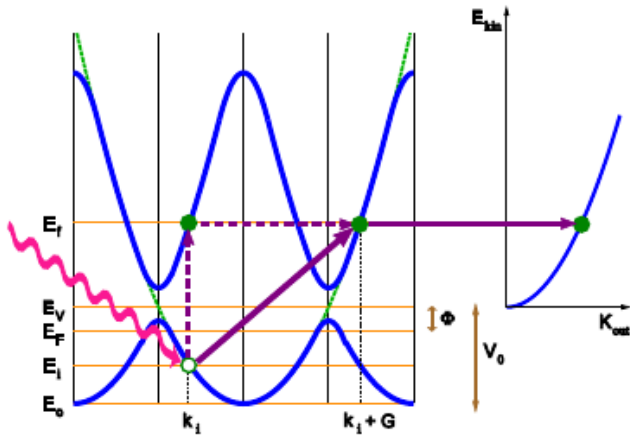
$$E_f - E_0 = \frac{\hbar^2}{2m} [(k_{\perp} + G_{\perp})^2 + (\mathbf{k}_{\parallel} + \mathbf{G}_{\parallel})^2] .$$

Recovering $\varepsilon_{\mathbf{k}}^n$ and \mathbf{k} (5)

$$\frac{\hbar^2}{2m} [(k_{\perp} + \mathbf{G}_{\perp})^2 + (\mathbf{k}_{\parallel} + \mathbf{G}_{\parallel})^2] = E_{\text{kin}} + (E_V - E_0)$$

$$\begin{aligned} k_{\perp} + \mathbf{G}_{\perp} &= \sqrt{\frac{2m}{\hbar^2} [E_{\text{kin}} + (E_V - E_0)] - K_{\text{out},\parallel}^2} \\ &= \sqrt{\frac{2m}{\hbar^2} [E_{\text{kin}} + (E_V - E_0) - E_{\text{kin}} \sin^2 \theta]} \\ &= \sqrt{\frac{2m}{\hbar^2} [E_{\text{kin}} \cos^2 \theta + (E_V - E_0)]} \\ &= \sqrt{\frac{2m}{\hbar^2} [E_{\text{kin}} \cos^2 \theta + V_0]} \end{aligned}$$

Few more notes



$$k_{\perp} + G_{\perp} = \sqrt{\frac{2m}{\hbar^2} [E_{\text{kin}} \cos^2 \theta + V_0]}$$

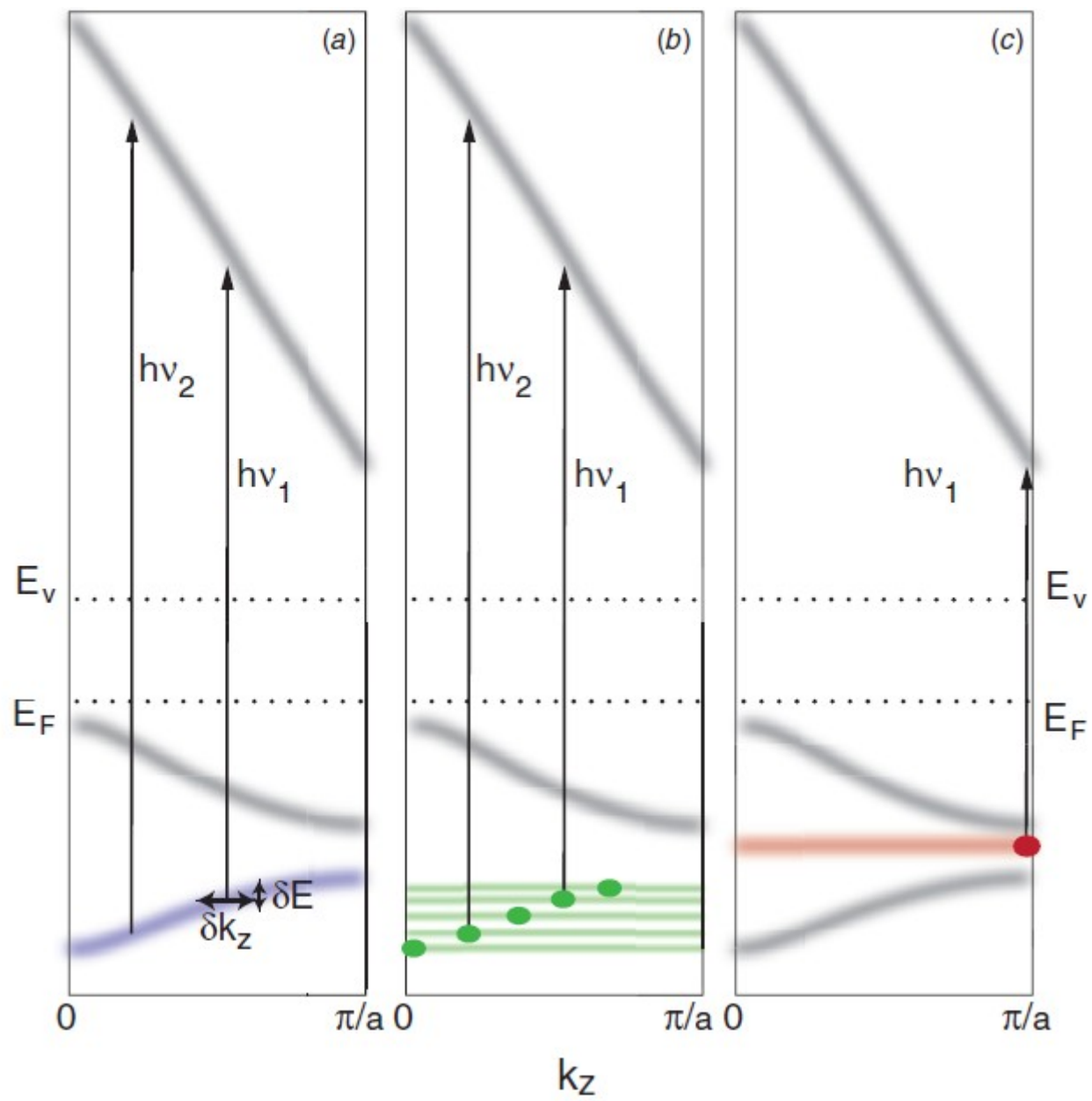
The **inner potential** V_0 has to be determined by an educated guess (by fitting it so that experiment matches the theory or by imposing symmetry requirements — to make the bands have the symmetry of the solid).

Weak point:

Nearly-free electron approximation for the final bulk states will work well only for “nice” materials (such as alkali or simple metals) and/or for high energies.

Surface states vers. bulk states

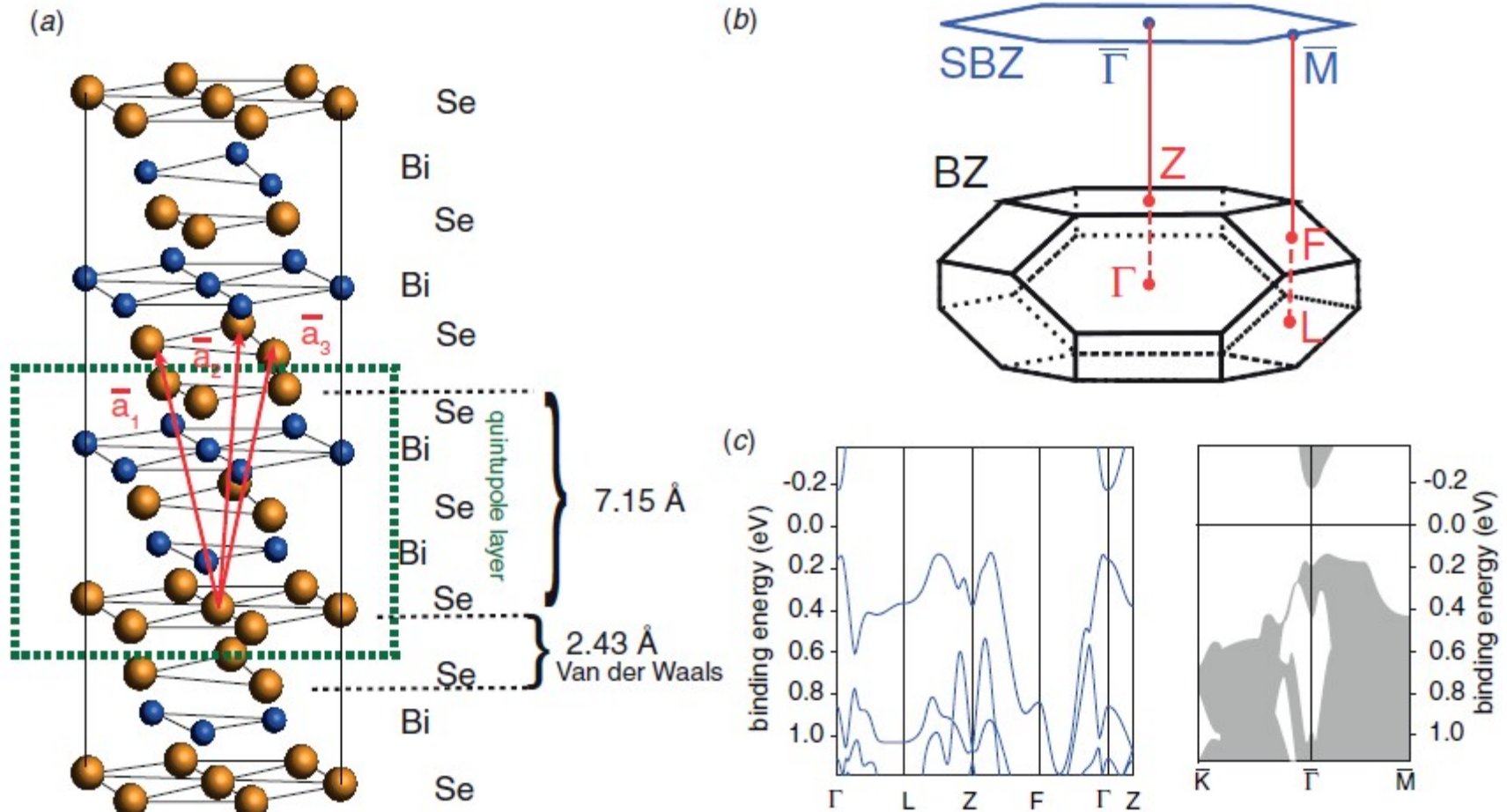
- ▶ Surface states have no dispersion along k_{\perp} .
- ▶ Energies and momenta of surface and bulk states cannot overlap (otherwise, it would be a bulk state. . .)
- ▶ Surface state have sharper linewidths (DOS in surface layers in more atomic-like).

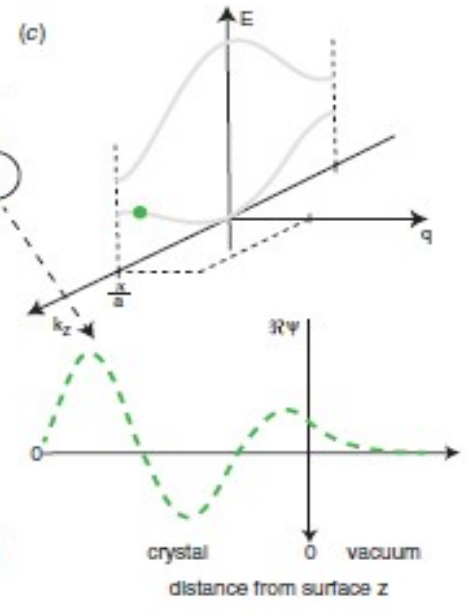
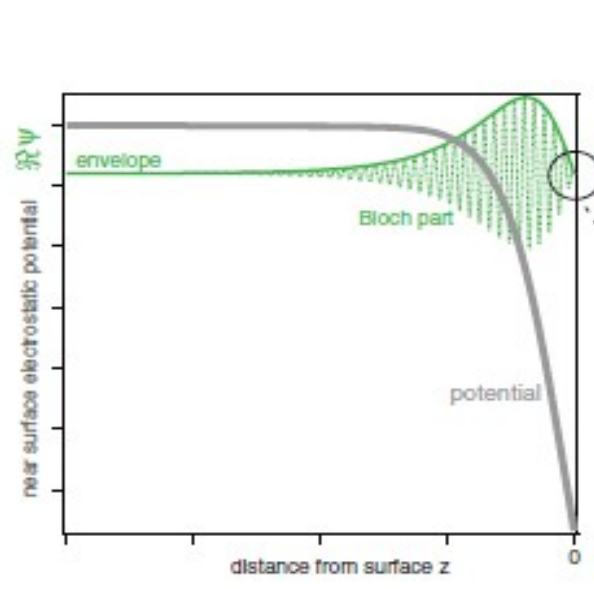
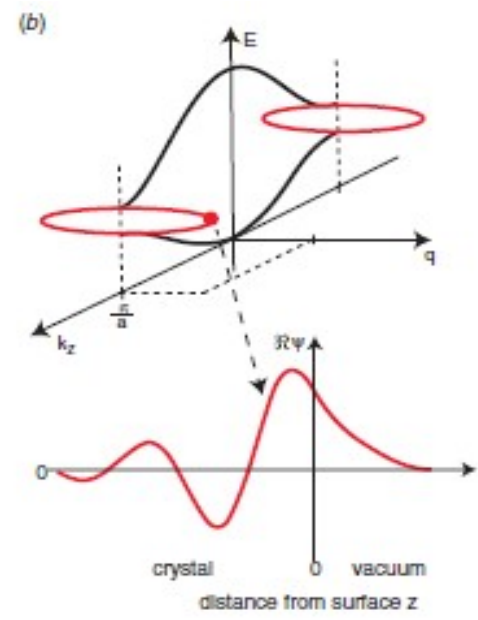
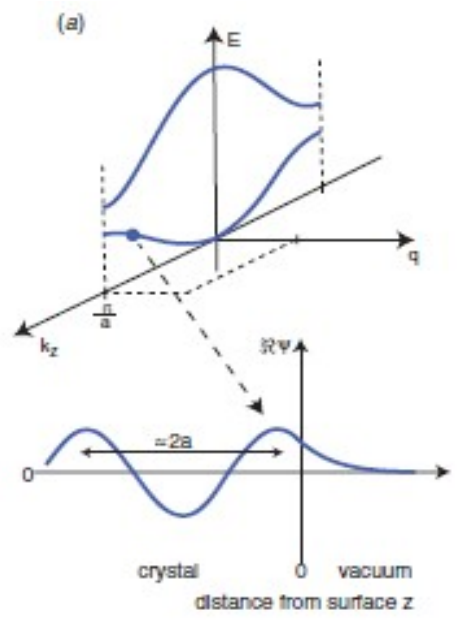


INVITED PAPER

The electronic structure of clean and adsorbate-covered Bi_2Se_3 : an angle-resolved photoemission study

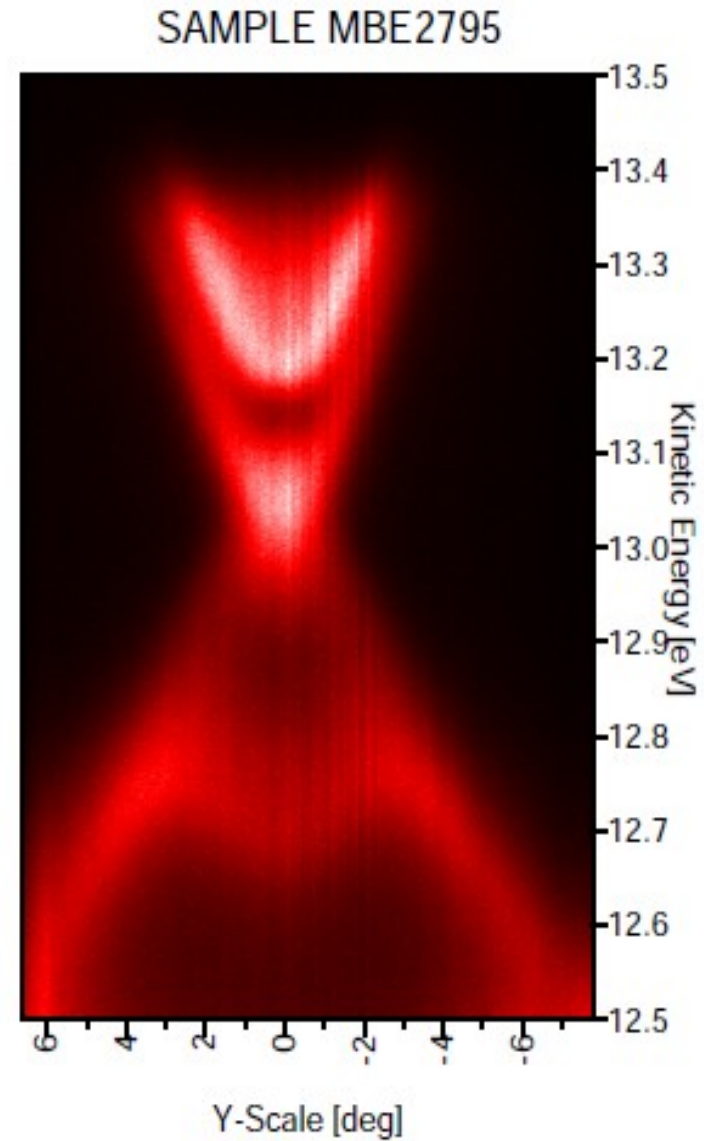
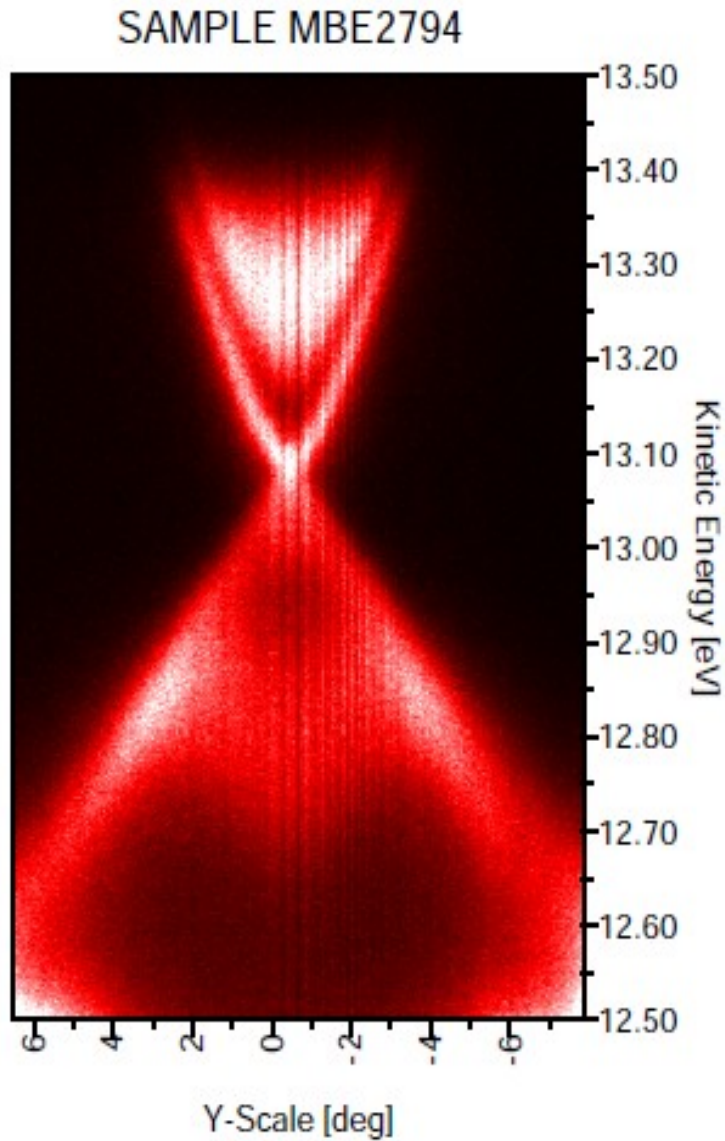
Marco Bianchi¹, Richard C Hatch¹, Dandan Guan¹, Tilo Planke¹, Jianli Mi², Bo Brummerstedt Iversen² and Philip Hofmann¹





ARPES

Příklad: pásová struktura Bi_2Se_3



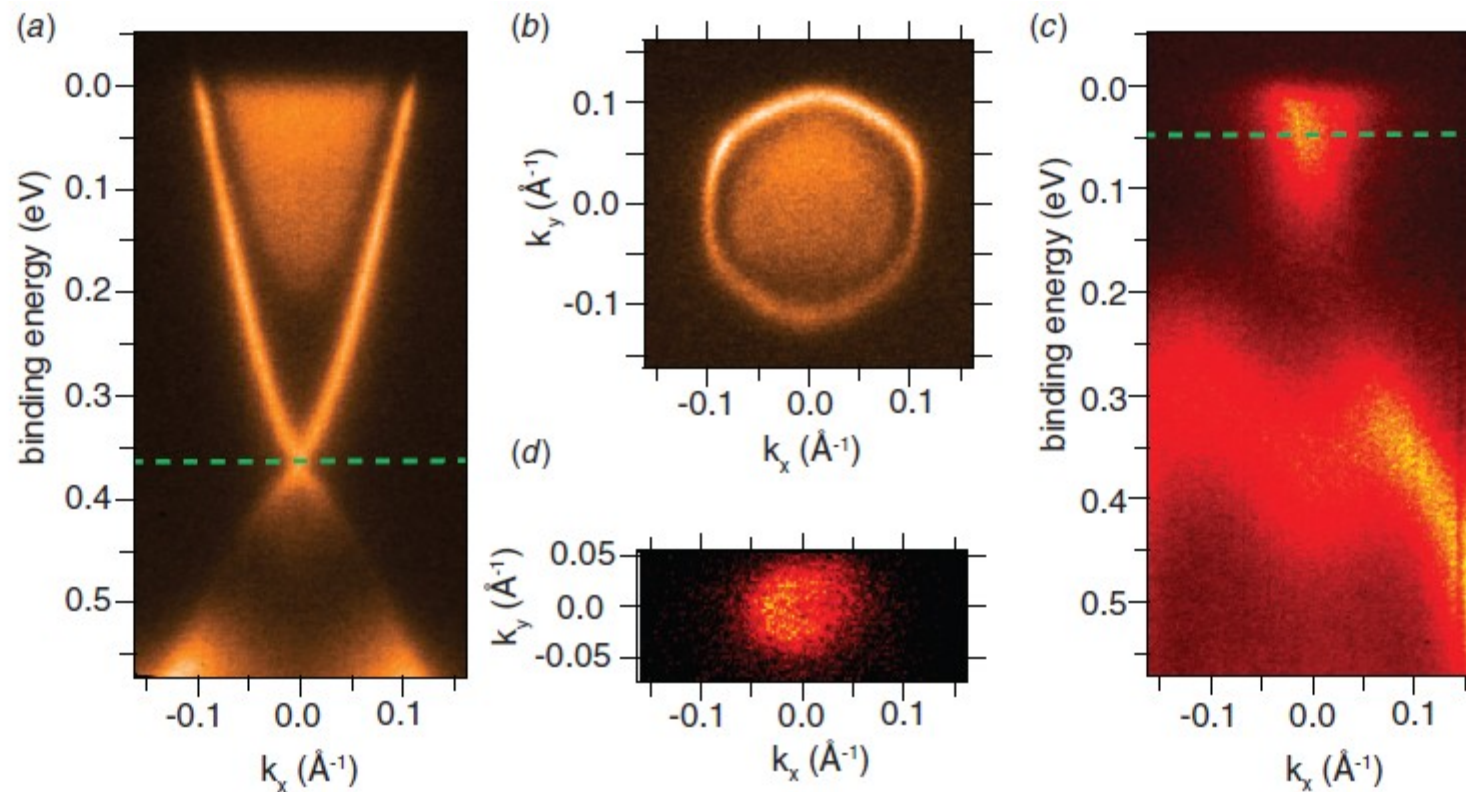


Figure 5. ARPES spectra for the pristine surface of Bi_2Se_3 . High photoemission intensity is displayed in bright. (a) Energy dispersion in the $\bar{K}\Gamma\bar{K}$ direction of the SBZ and (b) Fermi surface for the stoichiometric Bi_2Se_3 sample. (c) and (d) Energy dispersion and Fermi surface for the Ca-doped sample, respectively. The Dirac point is at a binding energy of ≈ 50 meV.

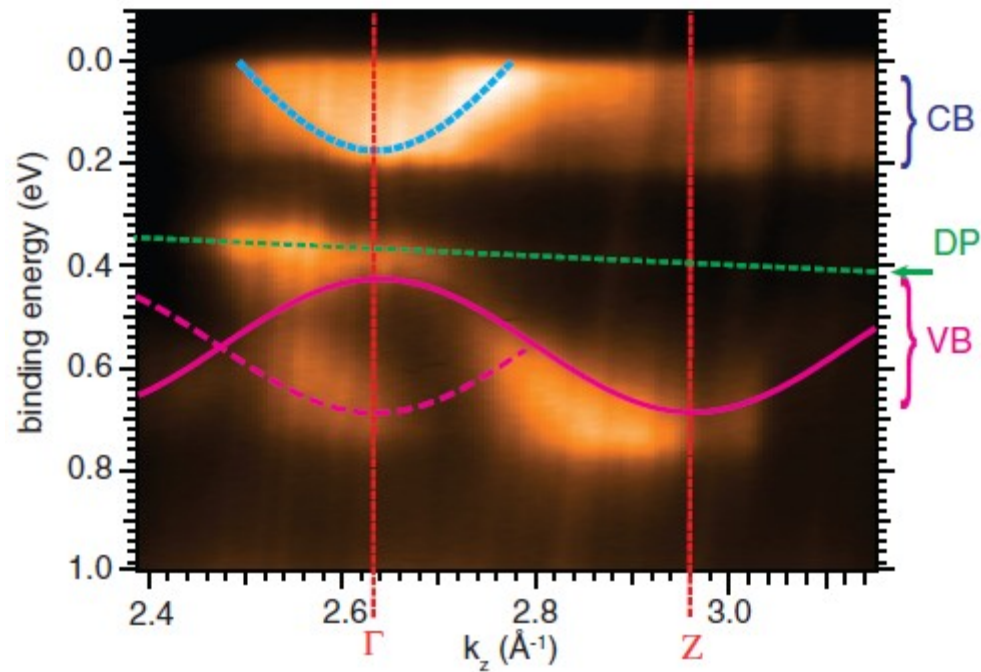


Figure 6. Photon energy scan on the pristine surface of intrinsic Bi_2Se_3 crystal illustrating the dispersion of the states at normal emission as a function of k_z . The data shown are a subset of a larger photon energy scan between $h\nu = 14$ eV and $h\nu = 32$ eV. The drift of the Dirac point with photon energy is due to the ageing effect that occurs during the scan. The CB and valence band (VB) (highlighted with blue and magenta lines as a guide to the eye) disperse, revealing the bulk Γ and Z points. The dashed magenta line is a shifted replica of the VB dispersion caused by a surface umklapp process.

ARPES

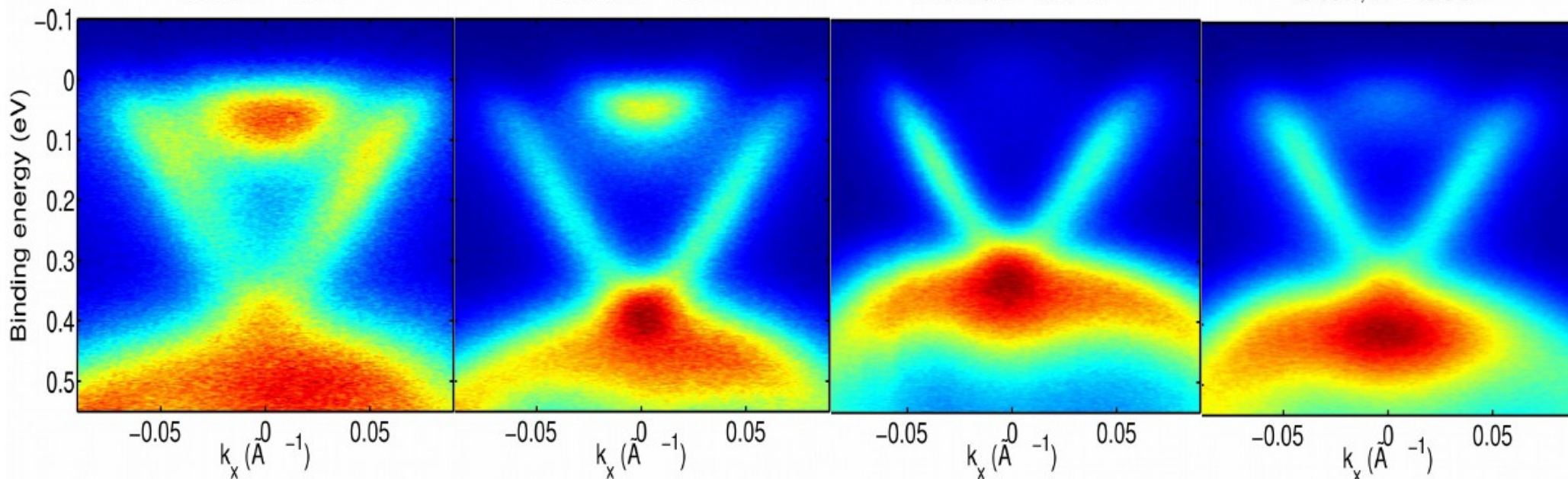
Příklad: pásová struktura Bi_2Se_3

Te 8%, $h\nu = 15.0$ eV

Te 10%, $h\nu = 15.0$ eV

Te 27%, $h\nu = 15.0$ eV

Te 30%, $h\nu = 15.0$ eV

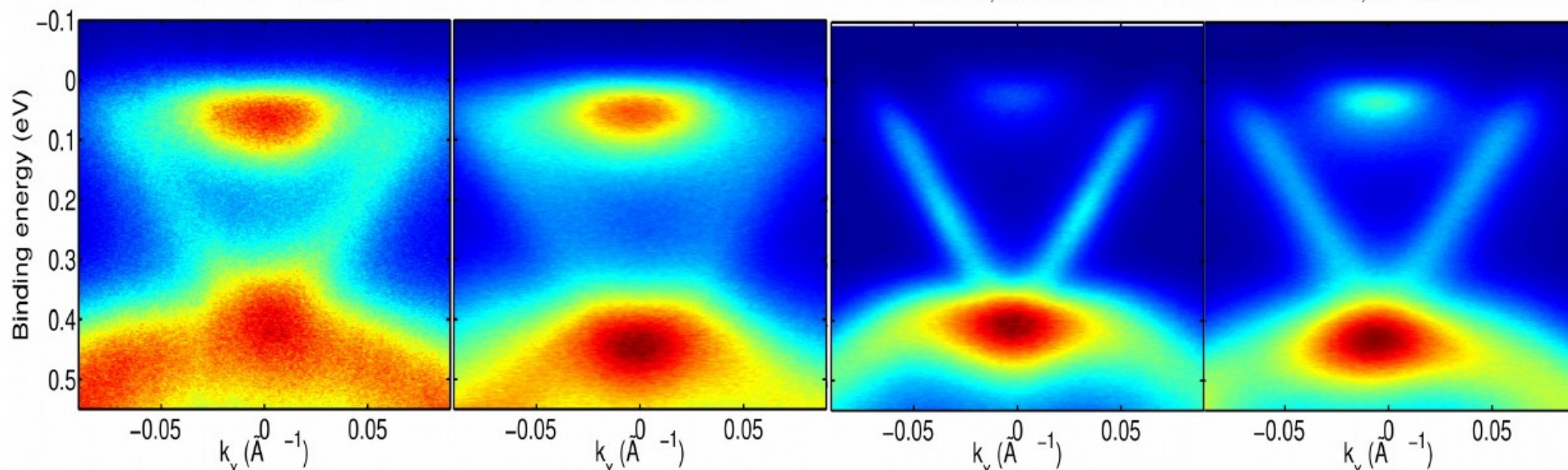


Te 34%, $h\nu = 15.0$ eV

Te 38%, $h\nu = 15.0$ eV

Te 38%, $h\nu = 15.0$ eV

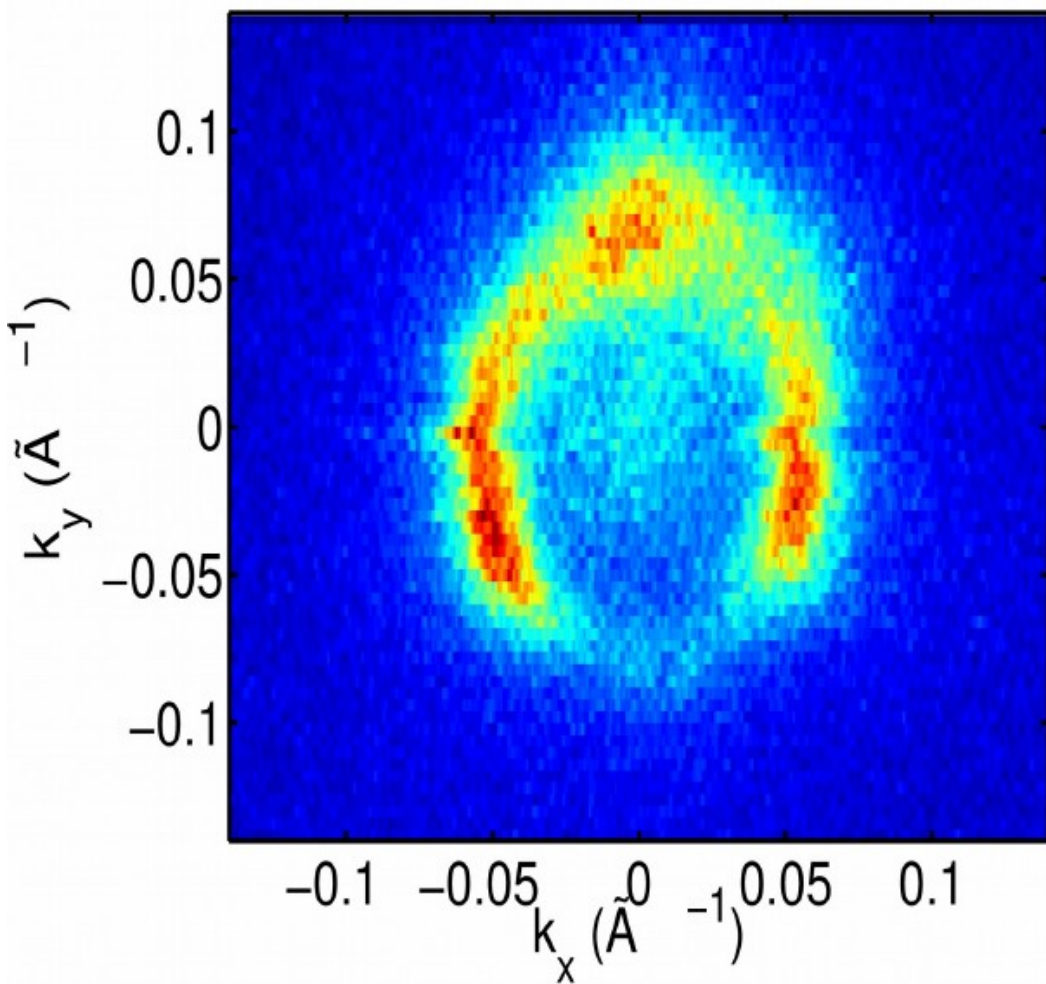
Te 39%, $h\nu = 15.0$ eV



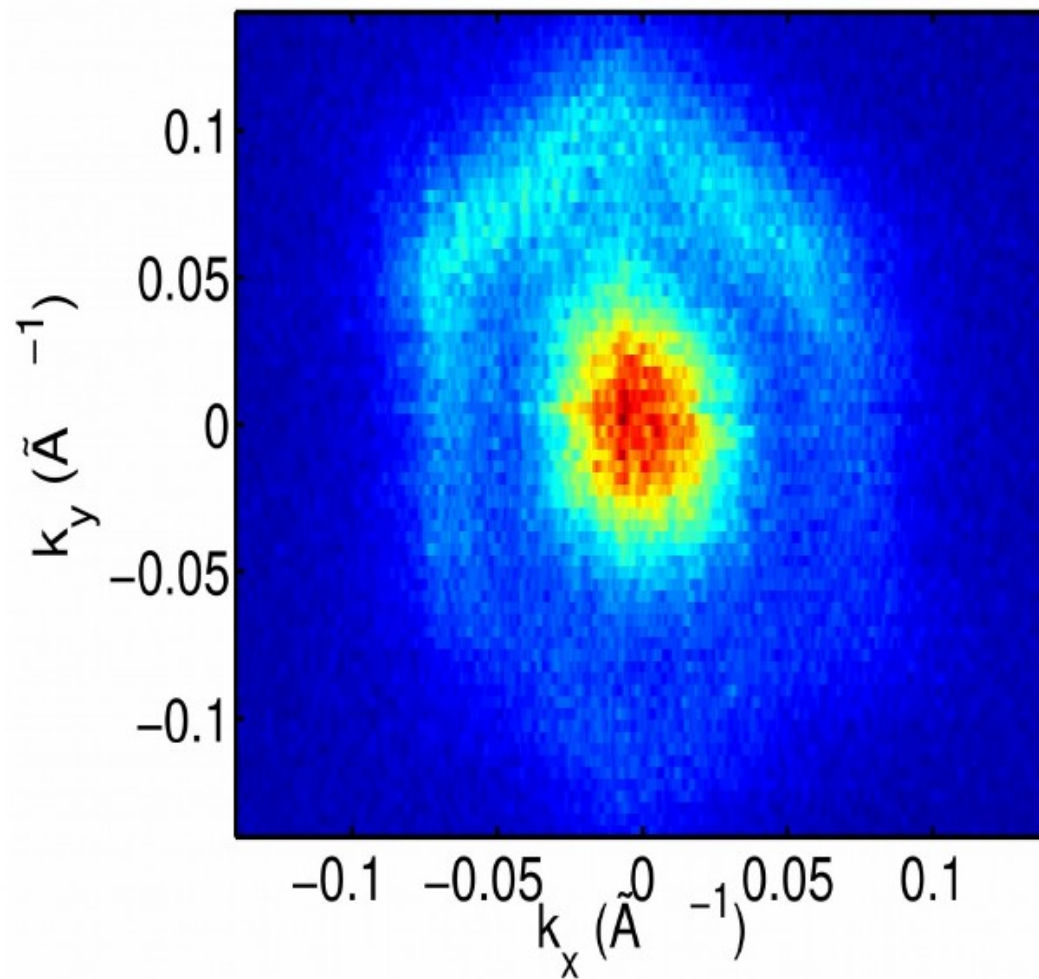
ARPES

Příklad: pásová struktura Bi_2Se_3

Te 27%, $h\nu = 15.0$ eV



Te 39%, $h\nu = 15.0$ eV



Topological crystalline insulators:

- Topological surface states (TSS) protected by point group crystal symmetry
- Band inversion is required

Materials:

(i) Rock salt SnTe and SnSe:

- Conduction and valence bands inverted
- TSS protected by (110) mirror plane symmetry

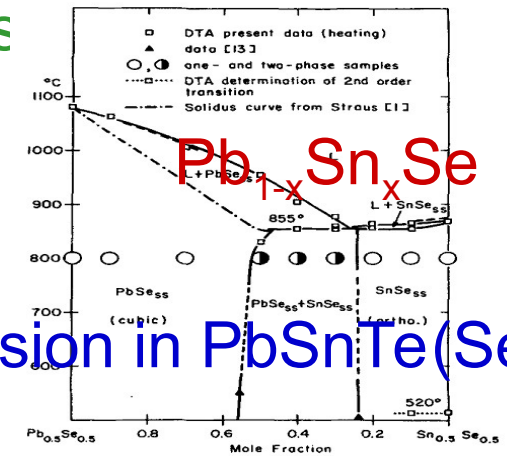
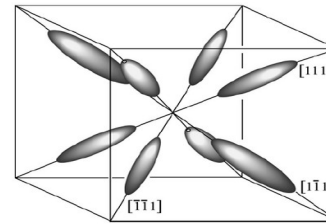
Disadvantages:

High intrinsic p-doping due to Se/Te vacancies. Thus, only valence band can be seen by ARPES. SnSe has orthorhombic lattice at normal conditions

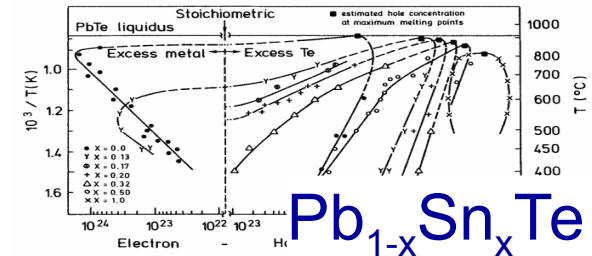
(ii) Ternary $Pb_{1-x}Sn_xTe$ and $Pb_{1-x}Sn_xSe$:

- Pseudobinary systems with rock salt structure
- Band inversion occurs for $x_{Sn} >$ critical value
- Topological transition can be tuned by temperature and Sn content
- p-type carrier concentration decreases with increasing of Pb content

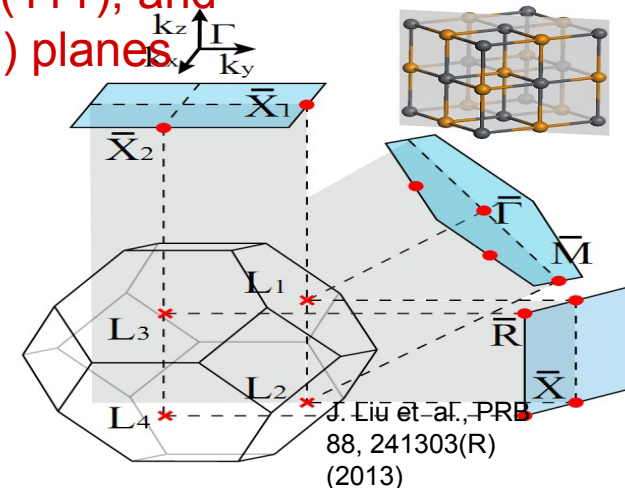
Phase diagrams



Band inversion in $PbSnTe(Se)$

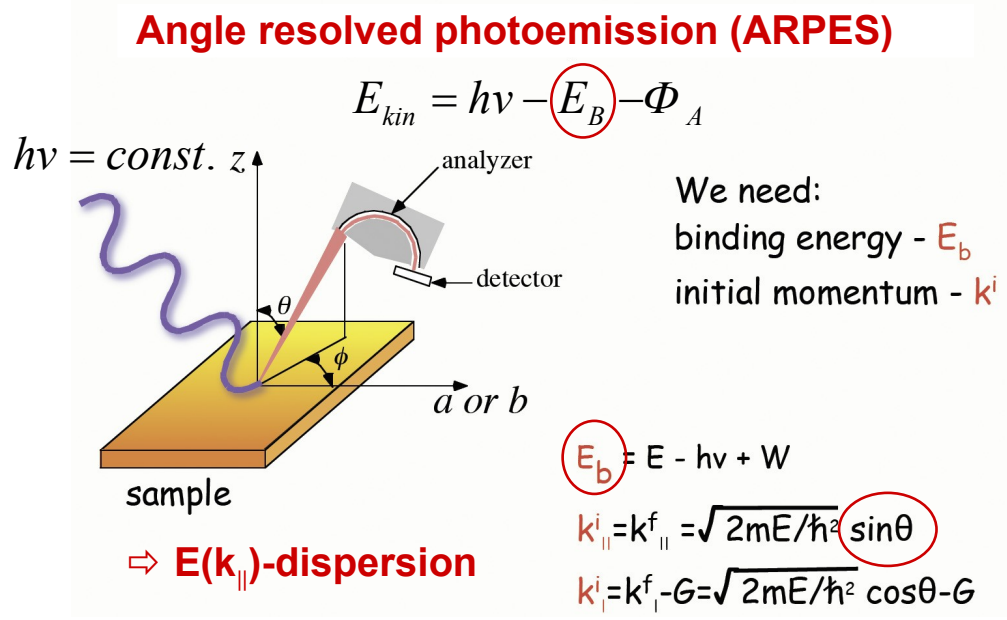
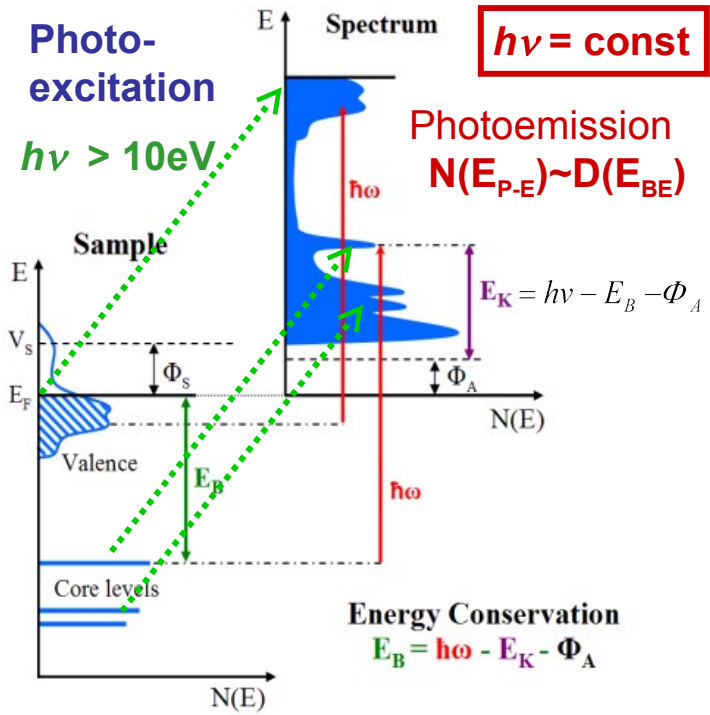


Brillouin zone projections onto (001), (111), and (110) planes

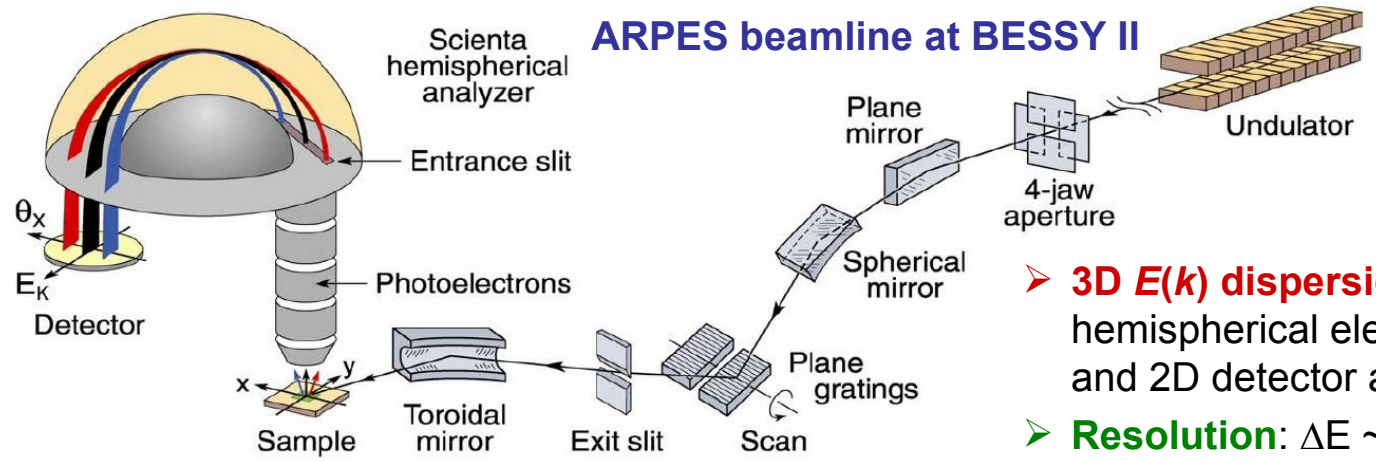


J. Liu et al., PRB 88, 241303(R) (2013)

Angle Resolved Photoemission Spectroscopy



obtained from **angular and energy** spectrum of photoexcited electrons

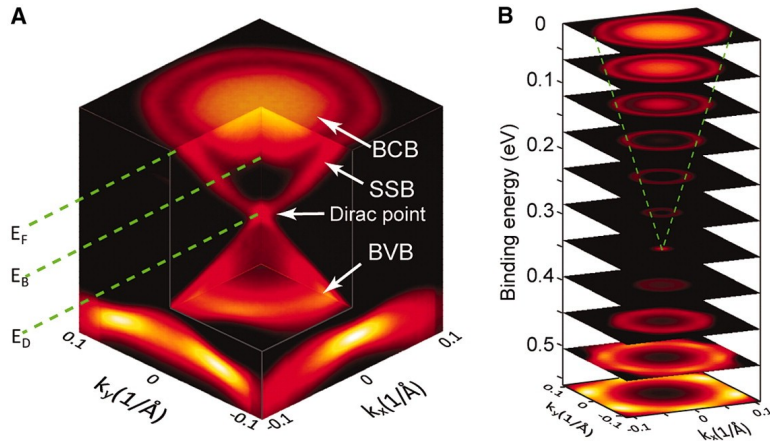


- **3D $E(k)$ dispersion** obtained by hemispherical electron analyzer and 2D detector array
- **Resolution:** $\Delta E \sim 10\text{meV}$, $\Delta\theta \sim 0.1^\circ$

Angular Resolved Photoemission: Examples

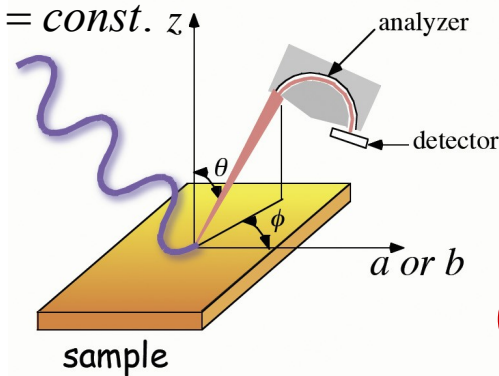
Examples:

Bi₂Se₃



ARPES experiment

$$E_{kin} = h\nu - E_B - \Phi_A$$



We need:

binding energy - E_b
initial momentum - k^i

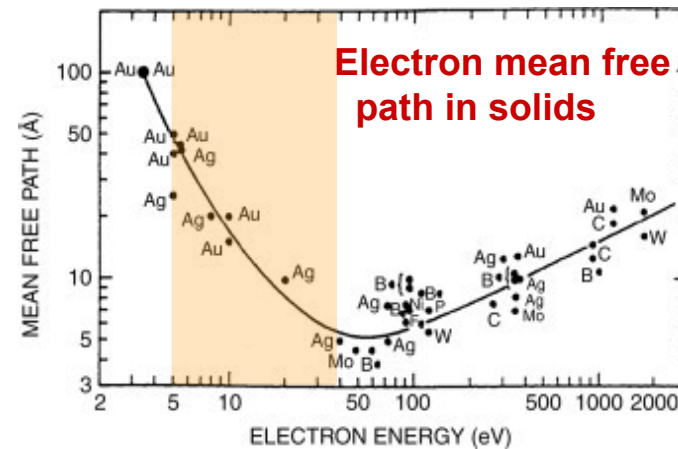
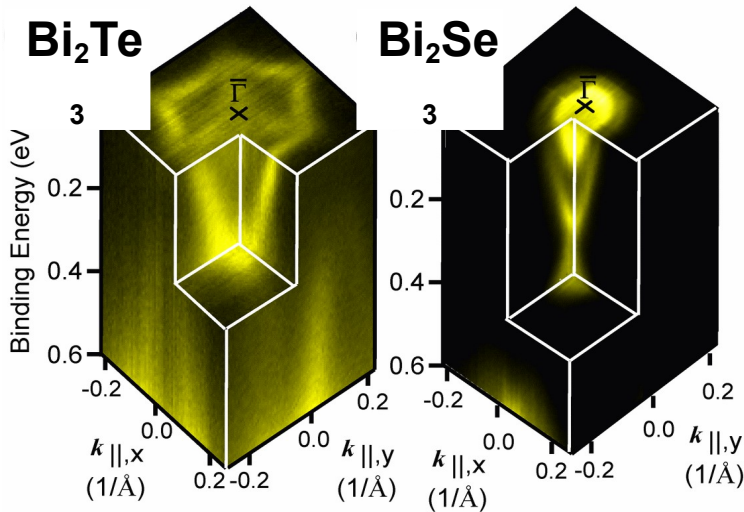
$$E_b = E - h\nu + W$$

$$k_{||}^i = k_{||}^f = \sqrt{2mE/h^2} \sin\theta$$

$$k_{\perp}^i = k_{\perp}^f - G = \sqrt{2mE/h^2} \cos\theta - G$$

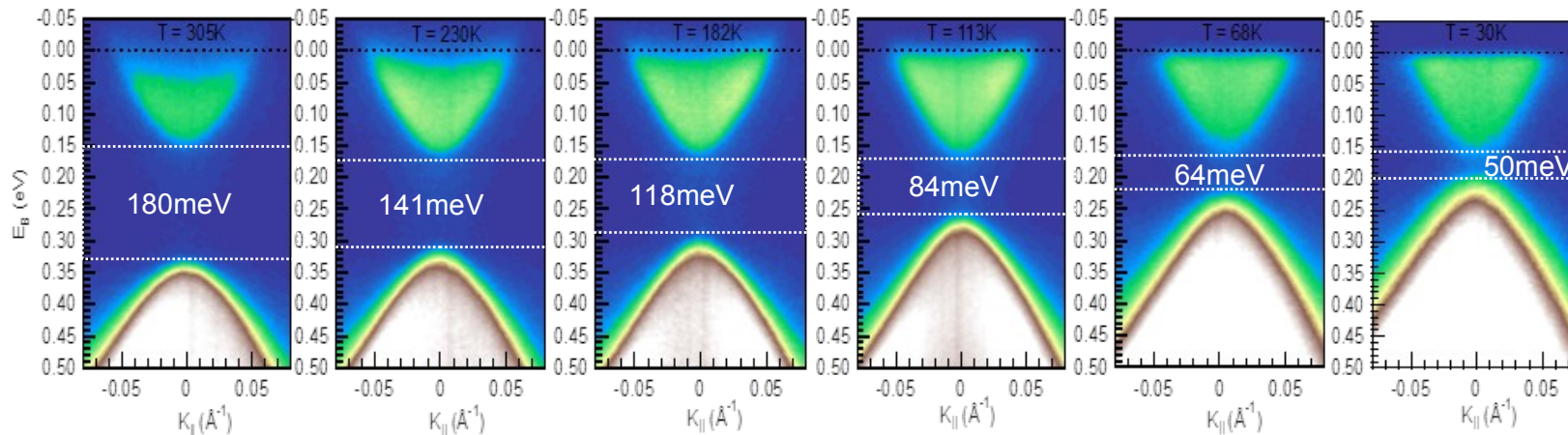
⇒ **E(k)-dispersion**

⇒ Measurement of angular dependent **energy spectrum $N(E)$** of photoexcited electrons

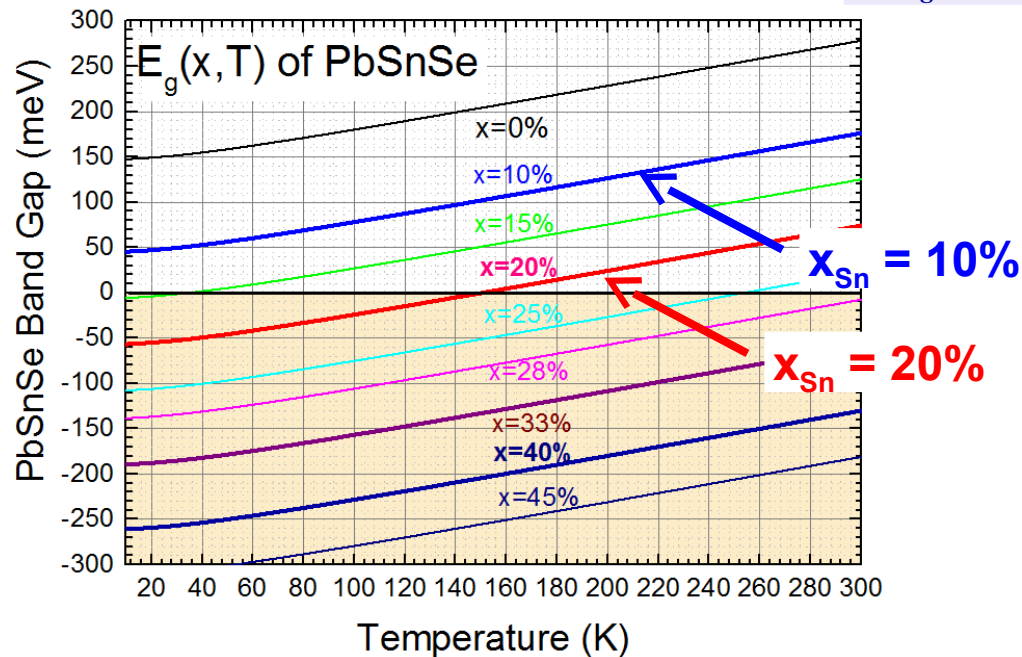


Zoom-in around the Γ -Point: PbSnSe (111) Epilayers

(a) PbSnSe with $x_{\text{Sn}} = 10\%$: Normal band structure



$$\Leftrightarrow E_g(x, T) = 125 - 1021x + (480 + 0.256 T^2)^{1/2}$$



2D Structures: TCI Surface Quantum Wells

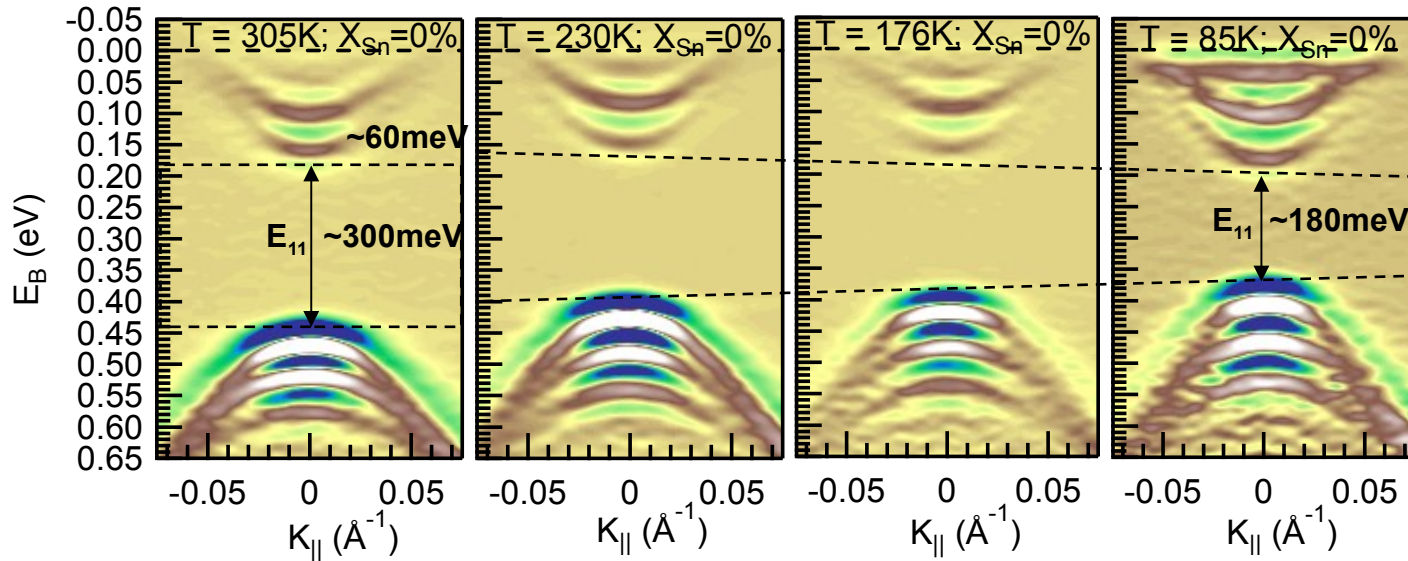
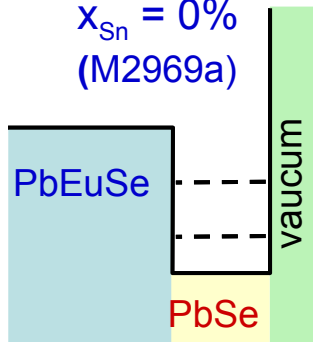
- ⇒ MBE of asymmetric quantum wells (vacuum barrier): discrete 2D QW states
- ⇒ Opening of a gap due to coupling between top & bottom topological surface state

(a) PbSe QW

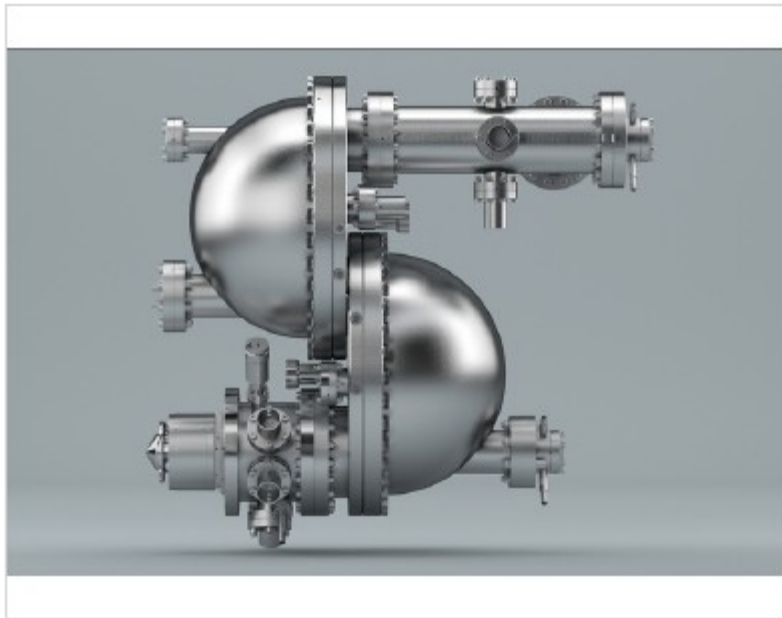
$d_{\text{QW}} = 100\text{\AA}$

$x_{\text{Sn}} = 0\%$

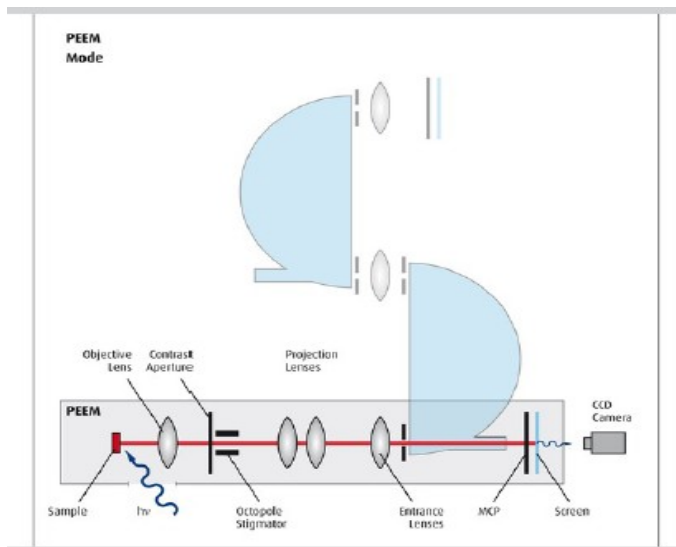
(M2969a)



NanoESCA – kombinace mikroskopie a spektroskopie



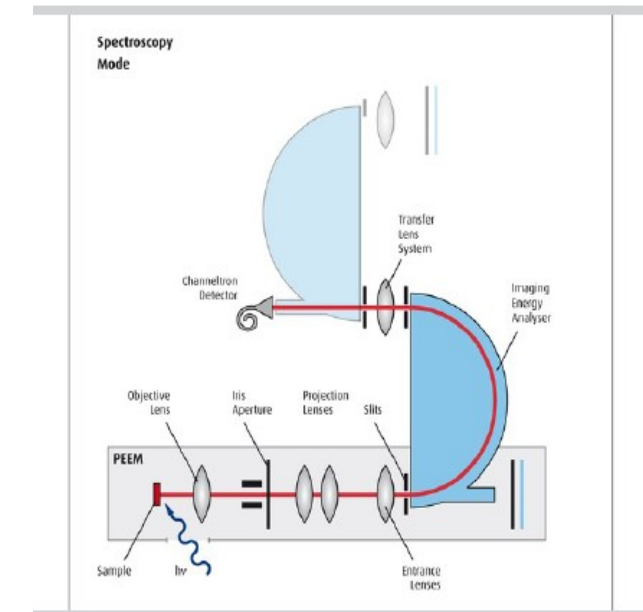
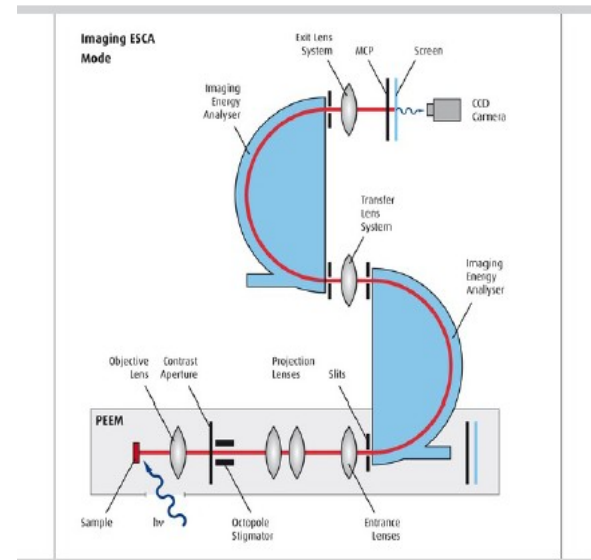
PEEM – photoelectron microscopy



Imaging ESCA –
zobrazení
jen určité
energie
elektronů

XPS

Rozlišení 50nm

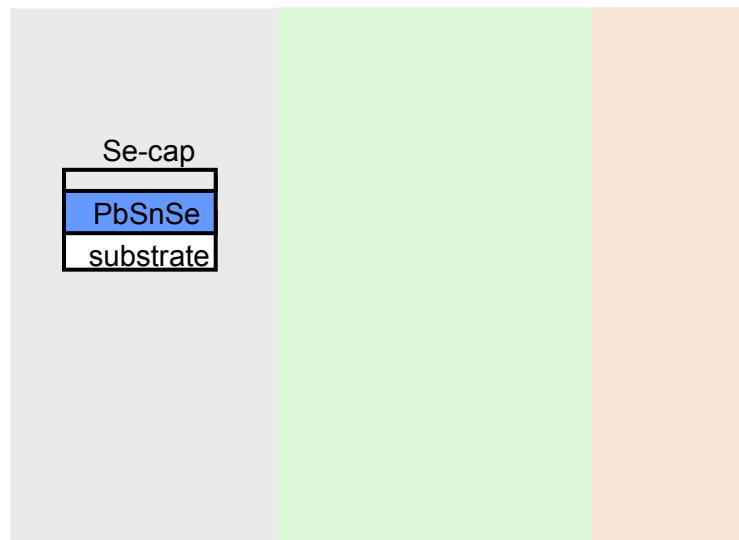


Clean Surface Preparation by Capping / Decapping

⇒ Surface needs to be protected against oxidation during transfer from MBE to ARPES in air: *Use of an easily desorbable capping layer*

I. Selenide Compounds:

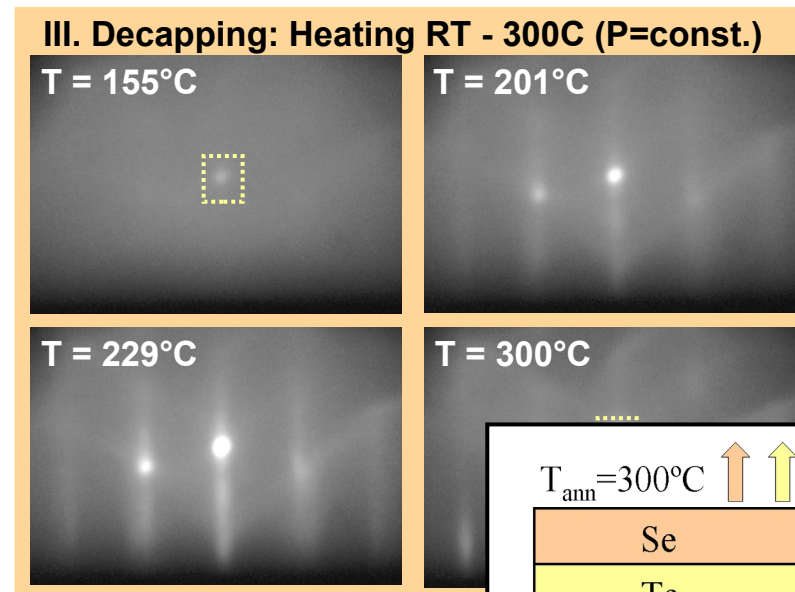
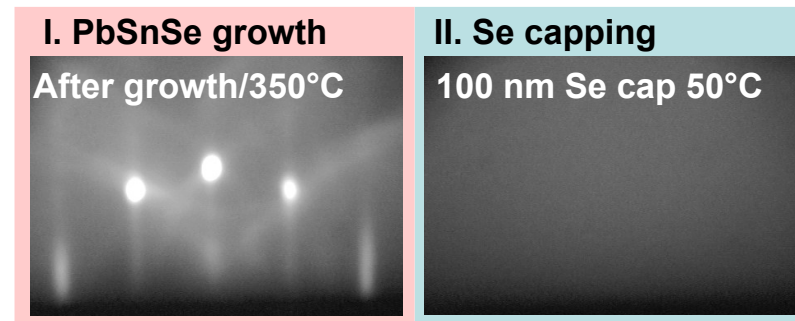
Amorphous Se cap layer (~ 100 nm) deposited at RT: Volatile surface oxide



⇒ Clean surface recovered at $T_{des} < T_{growth}$

II. Tellurides: ⇒ More difficult

Tellurium oxide is too stable for desorption & Se strongly intermixes with tellurides



⇒ Te / Se double cap layer structure used.

