

Moderní experimentální metody

Rentgenová a elektronová spektroskopie III

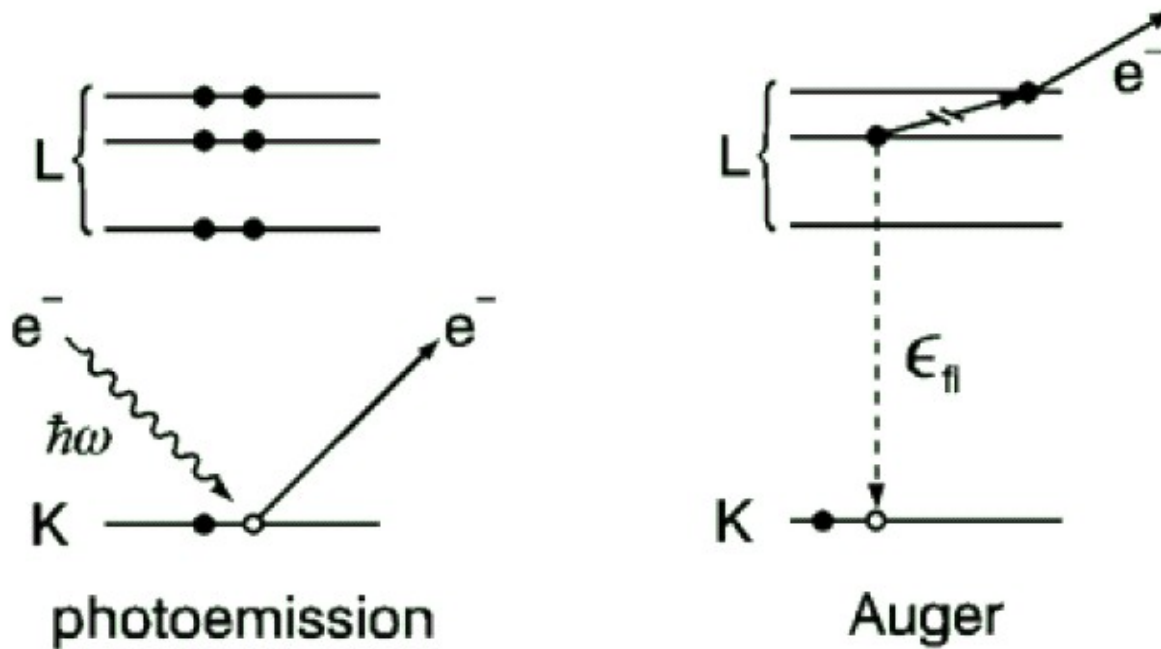
Fotoelektronová spektroskopie

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

Fotoemise a Augerův jev

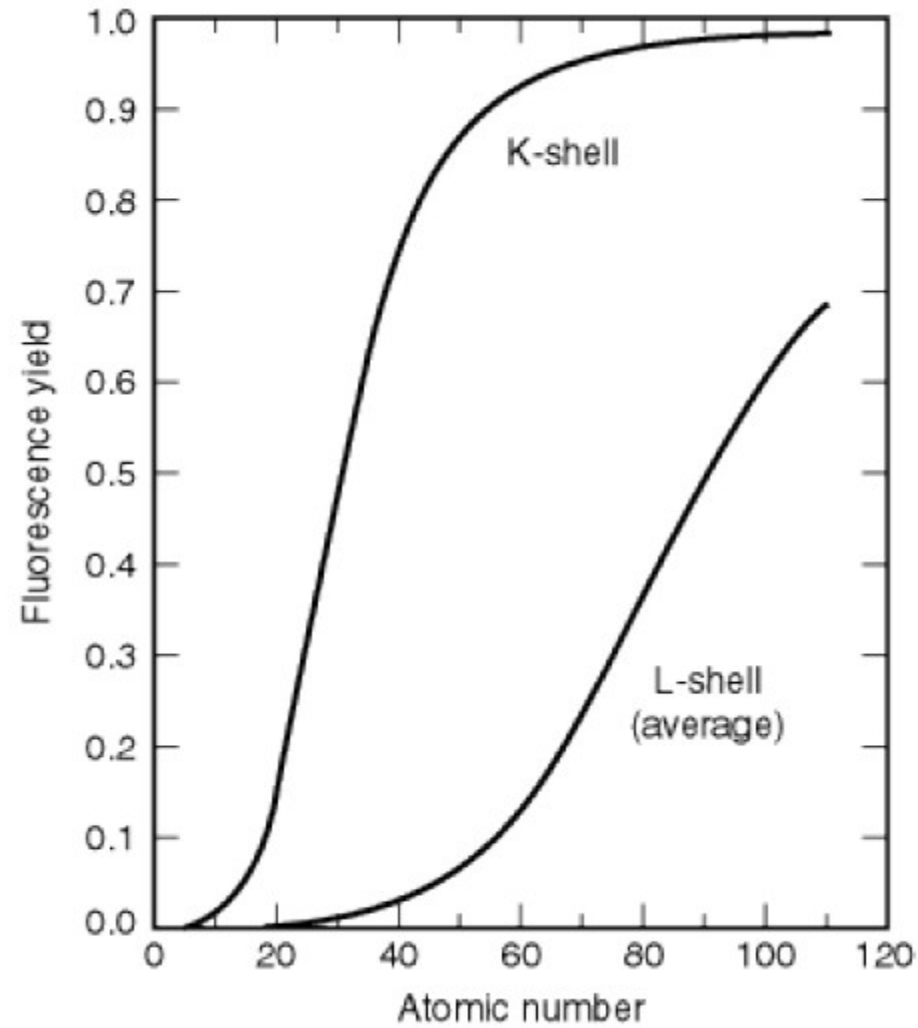
Fotoelektrony – přímo vyražené fotonem

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



Elektronová spektroskopie měří kinetickou energii elektronů.

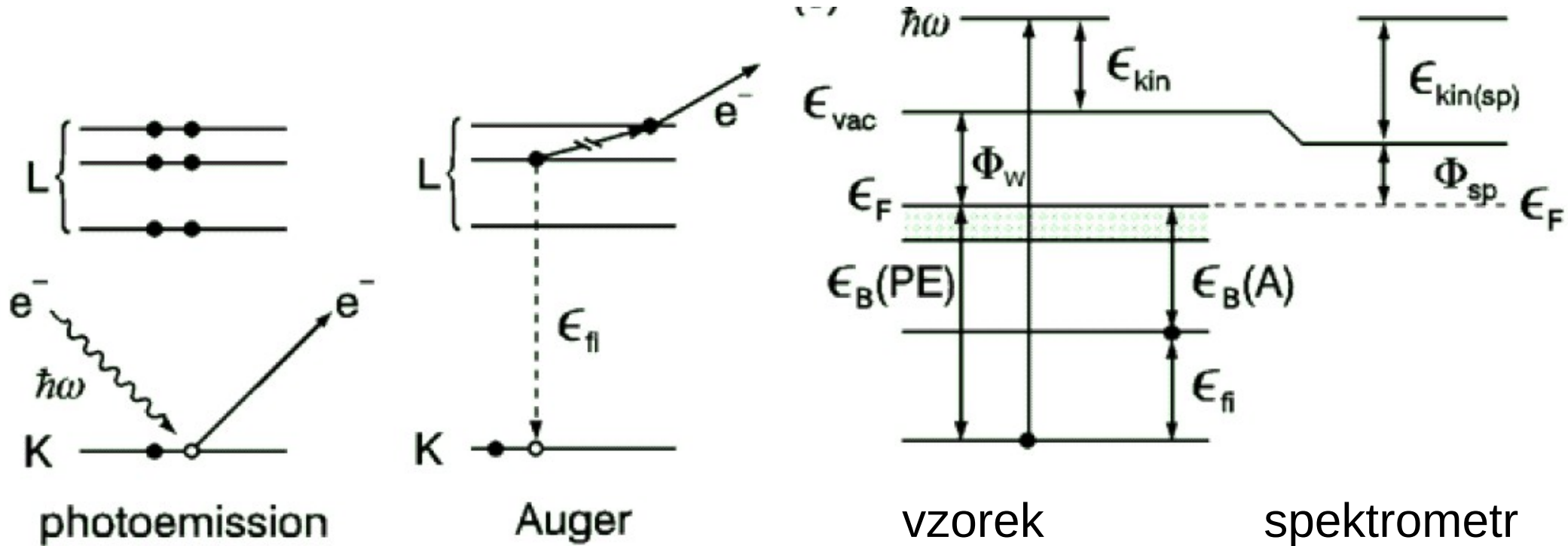
Charakteristické rtg záření



Fotoemise a Augerův jev

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XPS – ESCA

Electron spectroscopy for chemical analysis

- Reálně všechny prvky pro $Z \geq 3$, od Li
- Citlivost – jednotky promile
- Povrchová citlivost – povrchová kontaminace
- Chemický stav povrchu
- Profily podél povrchu
- Do hloubky při kombinaci s iontovým svazkem

Fotoelektronová spektroskopie

Podmínky experimentu:

Energie fotonů: 10 až 2000eV

Laboratorní zdroje:

- He výbojka 21 eV
- Mg lampa 1254 eV
- Al lampa 1486 eV

Synchrotron – laditelný zdroj

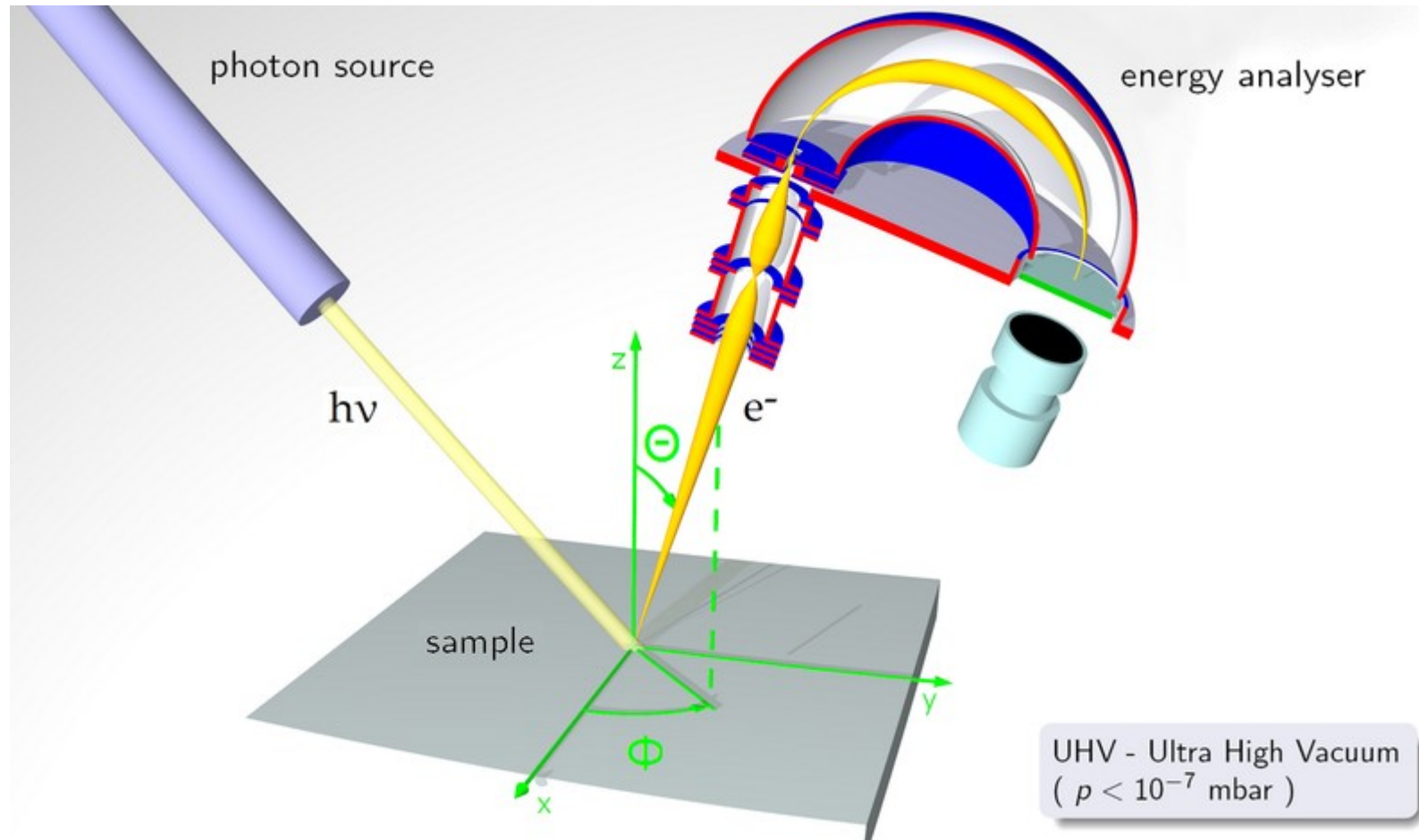
Vysoké vakuum (tlak max 10^{-6} Pa)

Vysoká kvalita a čistota povrchu vzorků

Optika – jen na odraz – zrcadla, difrakční mřížky, žádná okénka!

Hloubka vniku 10^0 – 10^1 nm

XPS

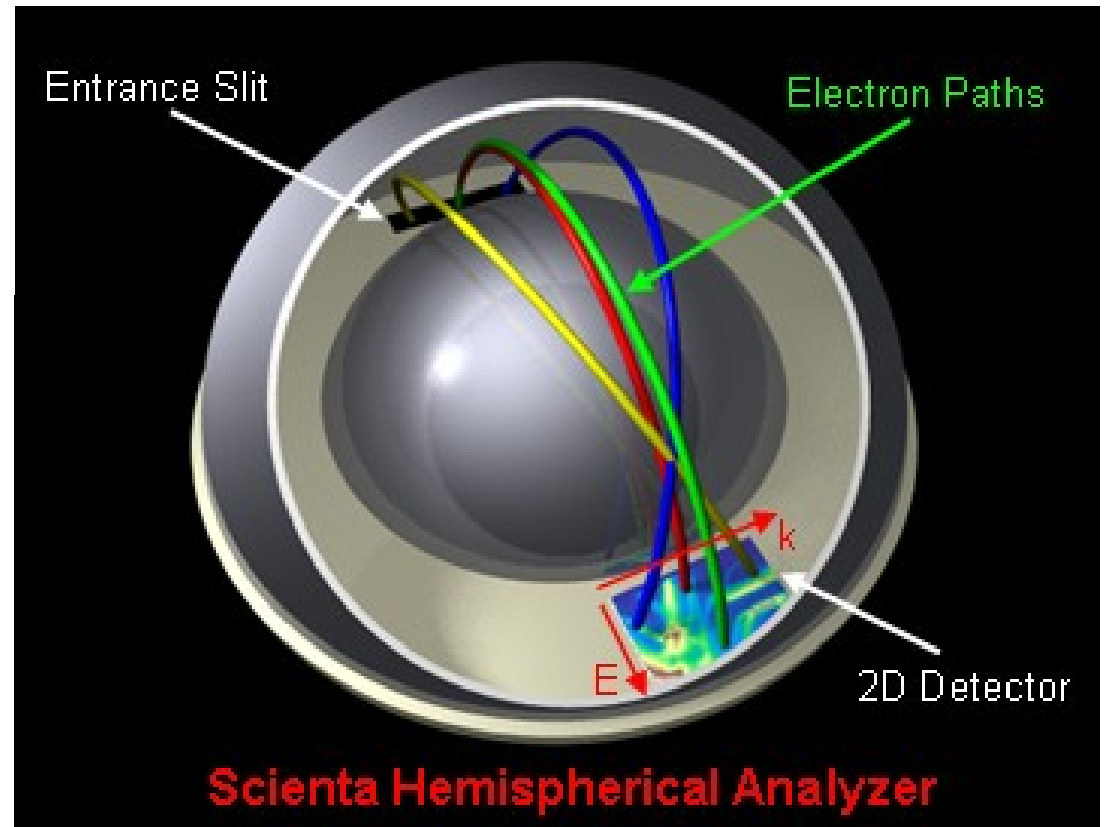
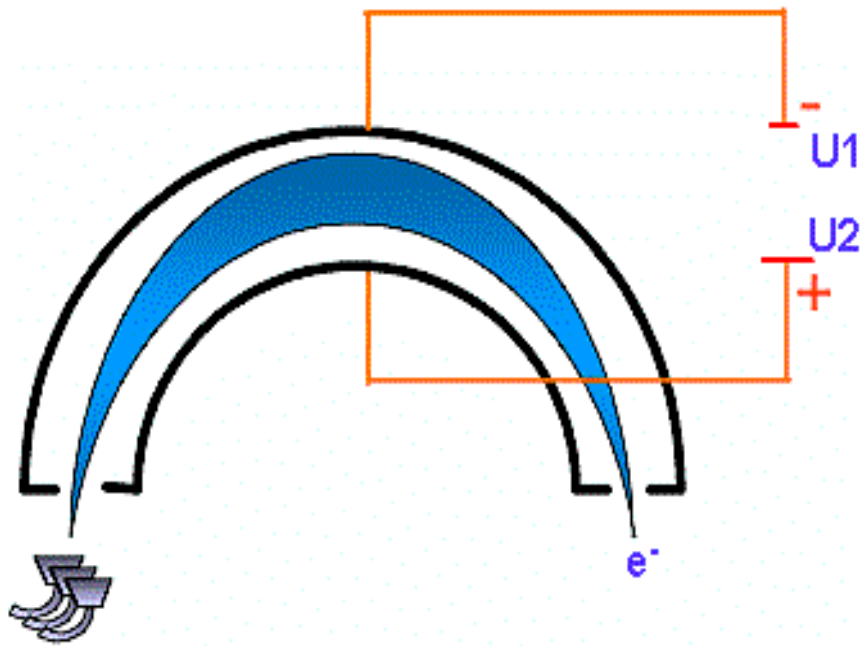


Fotoelektronová spektroskopie

Gas	Emission Line	Energy (eV)	Wavelength (nm)	Relative Intensity (%)
H	Lyman α	10.20	121.57	100
	Lyman β	12.09	102.57	10
He	1 α	21.22	58.43	100
	1 β	23.09	53.70	approx 1.5
	1 γ	23.74	52.22	0.5
	2 α	40.81	30.38	100
	2 β	48.37	25.63	<10
	2 γ	51.02	24.30	negligible
	Ne	1 α	16.67	74.37
1 α		16.85	73.62	100
1 β		19.69	62.97	< 1
1 β		19.78	62.68	< 1
2 α		26.81	46.24	100
2 α		26.91	46.07	100
2 β		27.69	44.79	20
2 β		27.76	44.66	20
2 β		27.78	44.63	20
2 β		27.86	44.51	20
2 γ		30.45	40.71	20
2 γ		30.55	40.58	20
Ar		1	11.62	106.70
	1	11.83	104.80	50
	2	13.30	93.22	30
	2	13.48	91.84	15

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:

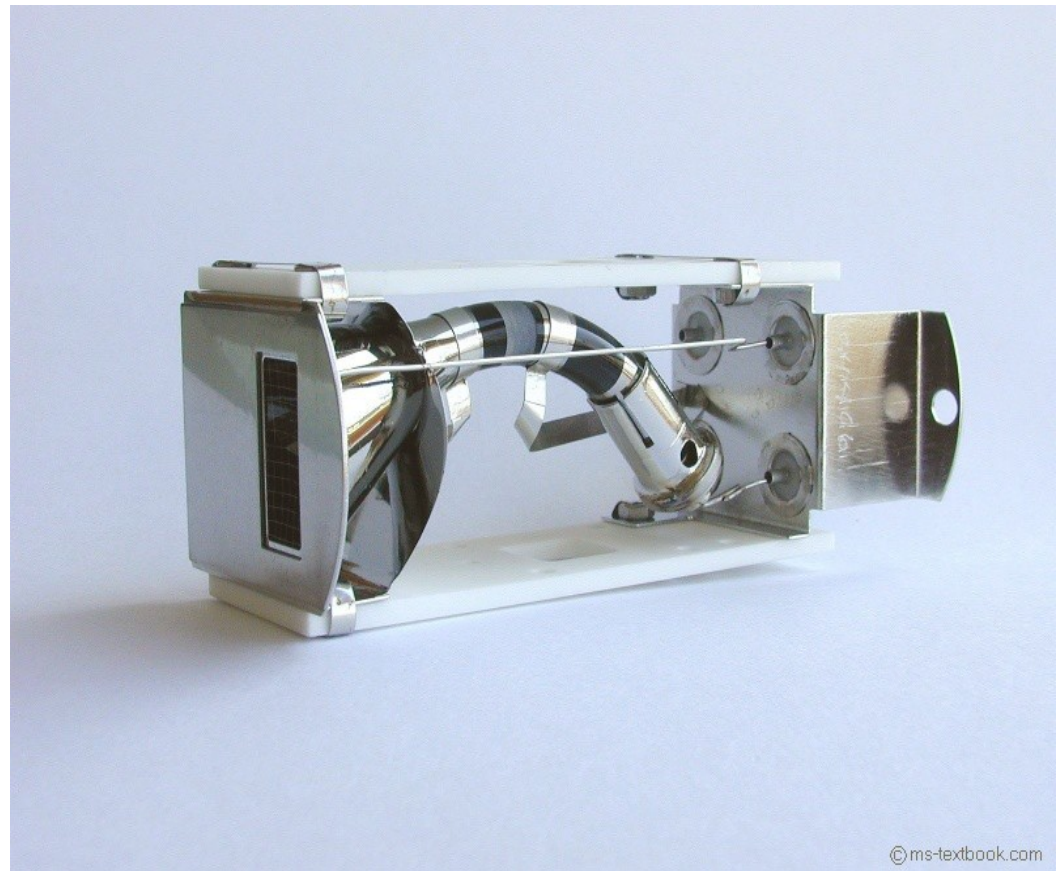
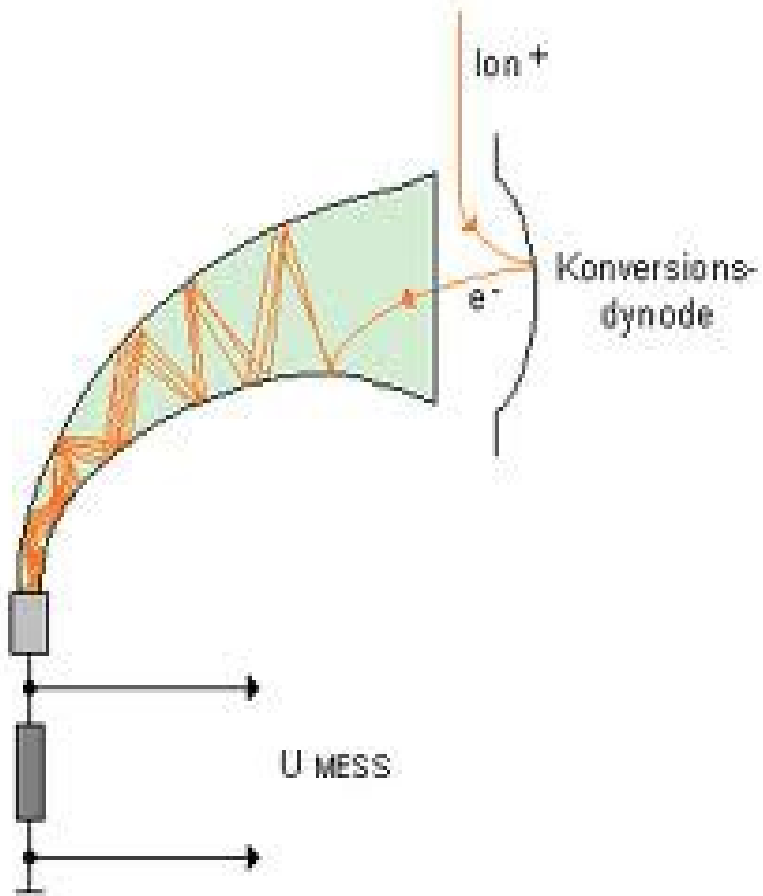
Energy resolution:	$< 2 \text{ meV}$
Theoretical resolving power using 0.2 mm entrance slit:	2000
Kinetic energy range:	0.2 - 1500 eV
Spatial resolution:	$< 10 \text{ }\mu\text{m}$
Magnification:	
<i>Imaging Mode</i>	10x, 20x, 40x
<i>Transmission Mode</i>	5x
Ultimate angular resolution:	$< 0.1 \text{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



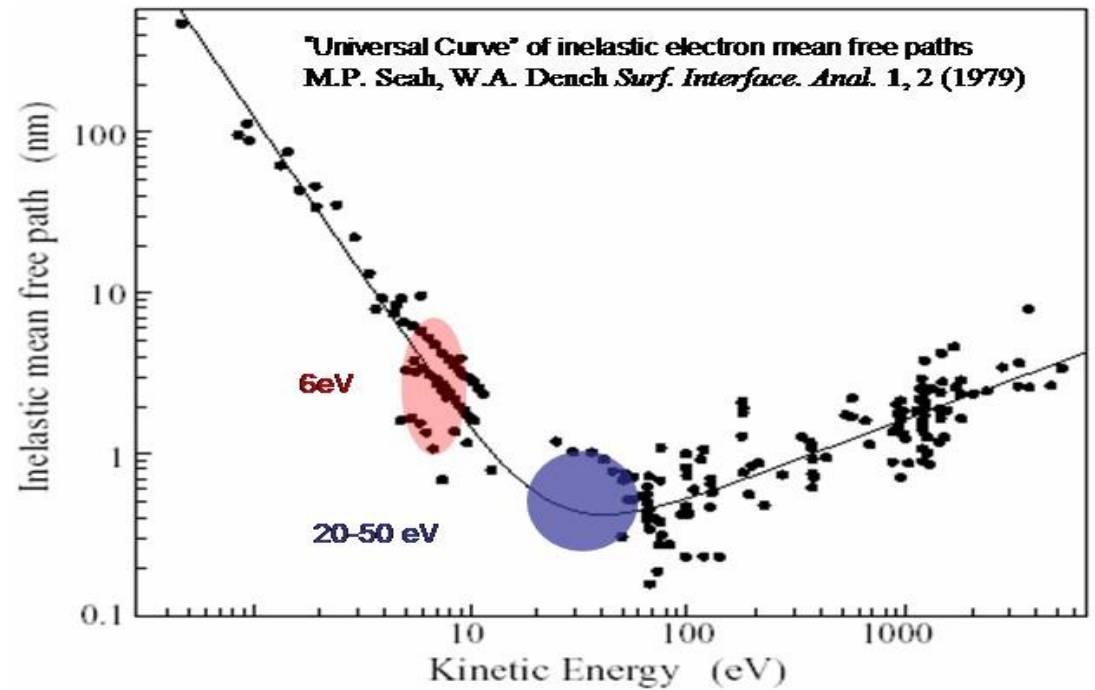
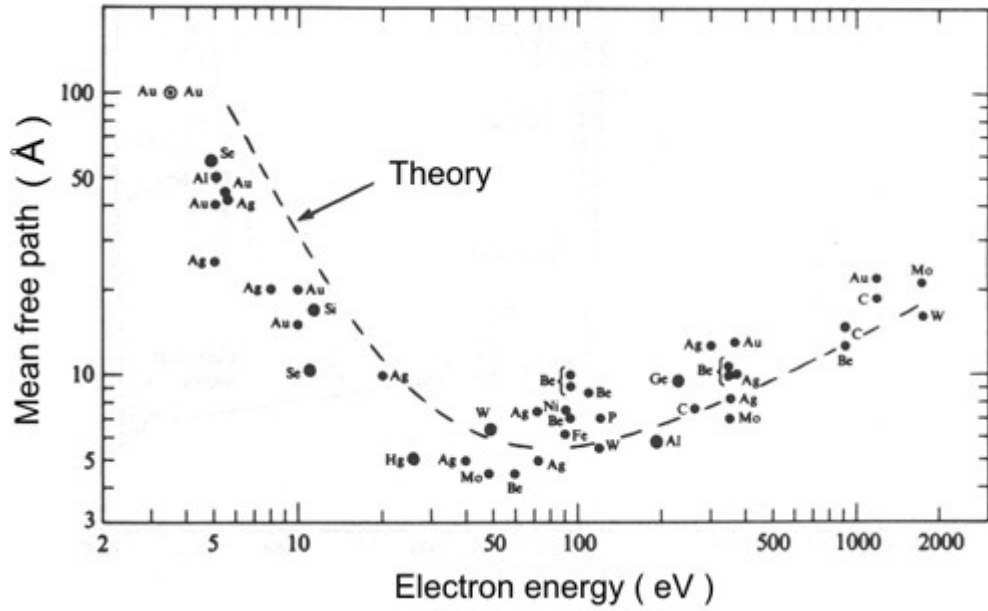
R4000 Spectrometer

XPS

Detekce:
CCD
Channeltron



XPS



XPS

Příprava vzorků

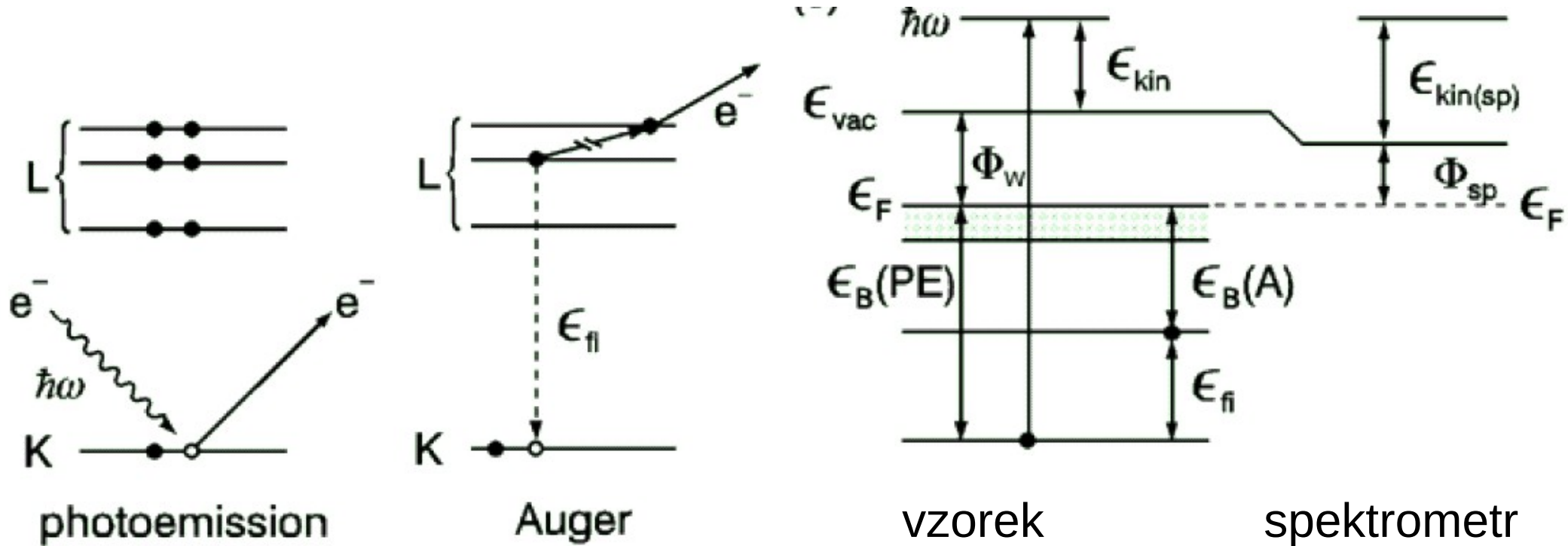
Atomárně čistý povrch a hladký povrch

- Štípání ve vakuu
- Depoziční aparatura v UHV propojená s XPS komorou
- Vakuový kufřík
- Ochranné vrstvy

Fotoemise a Augerův jev

Fotoelektrony – přímo vyražené fotonem

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



XPS

Rentgenová fotoelektronová spektroskopie

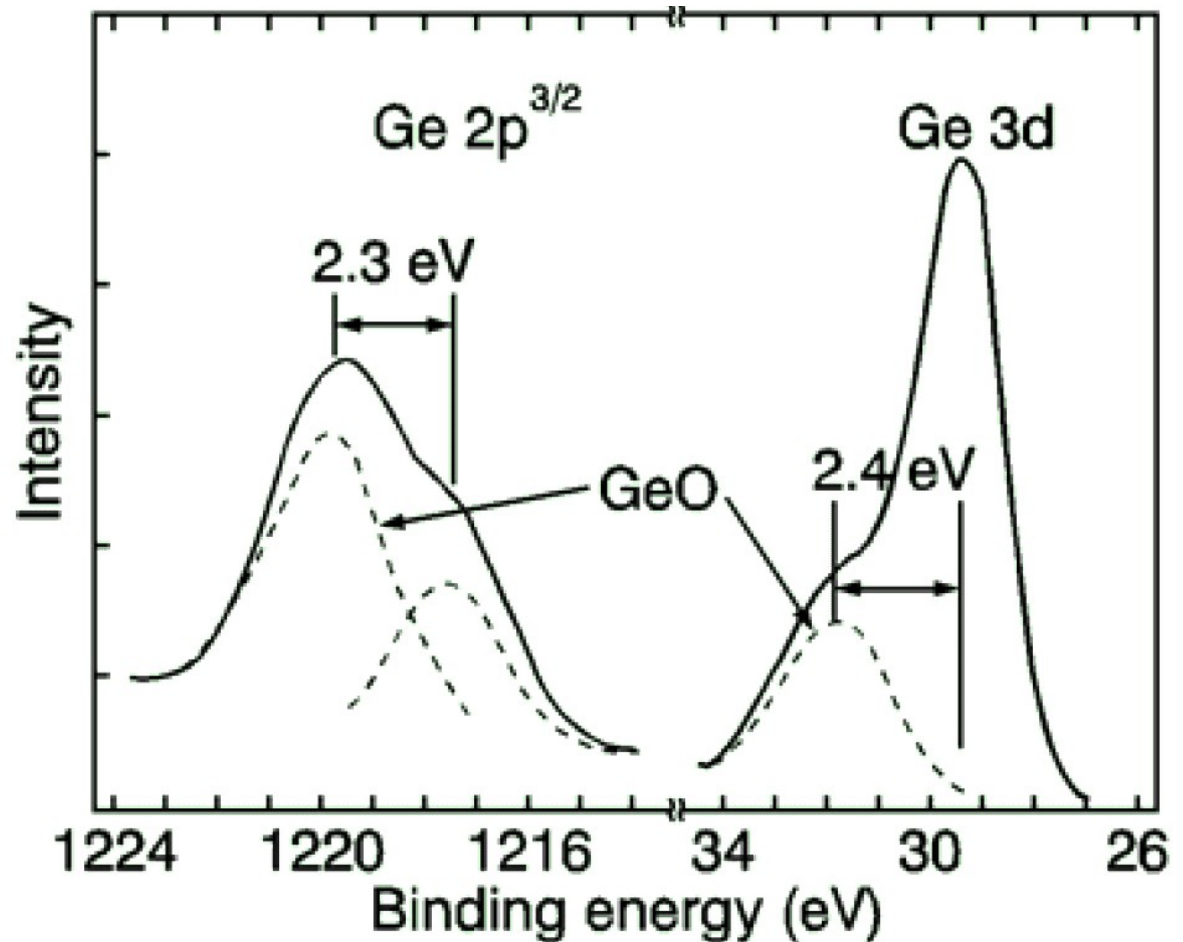
X-ray Photoelectron Spectroscopy – XPS, PES

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

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

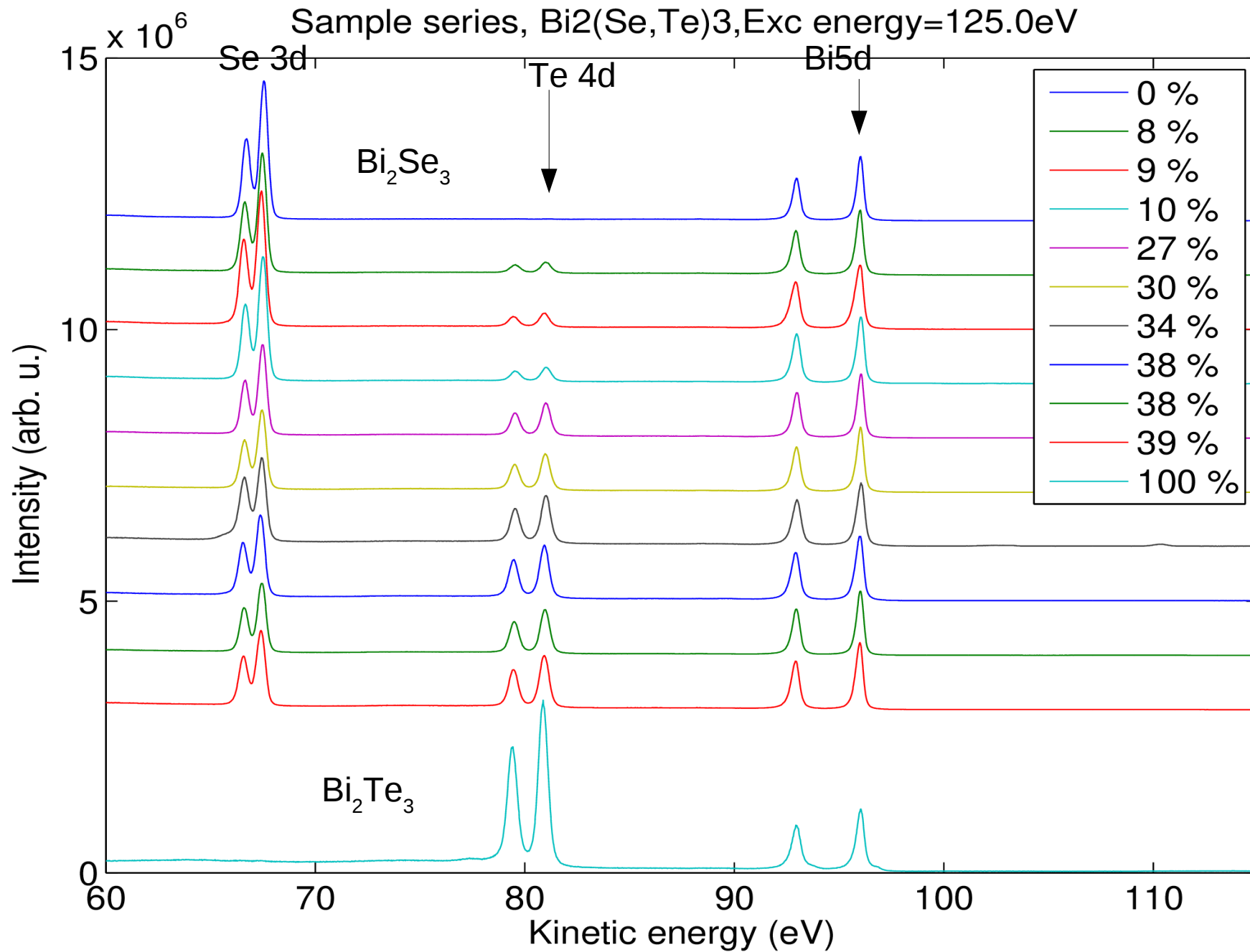
Umožňuje detekovat změny vazebné energie chemickým stavem atomu.

XPS na germaniu s velmi tenkou oxidovou vrstvou.



XPS

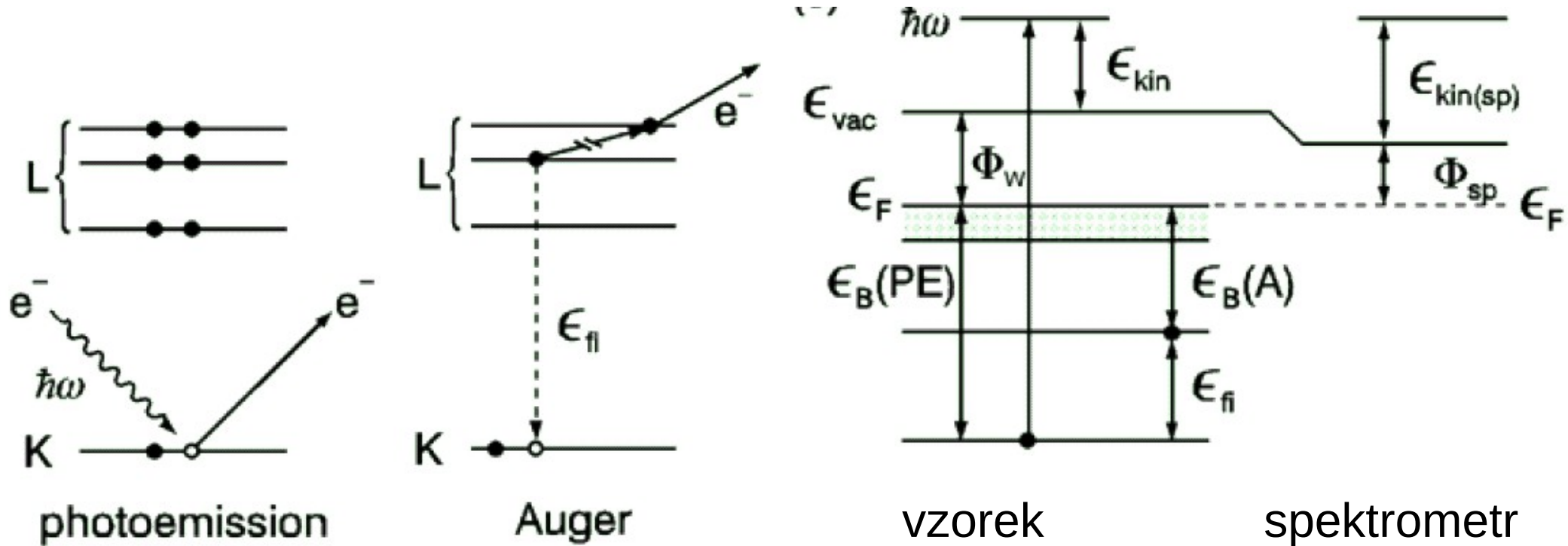
Příklad: $\text{Bi}_2(\text{Se},\text{Te})_3$ excitace 125 eV.



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.

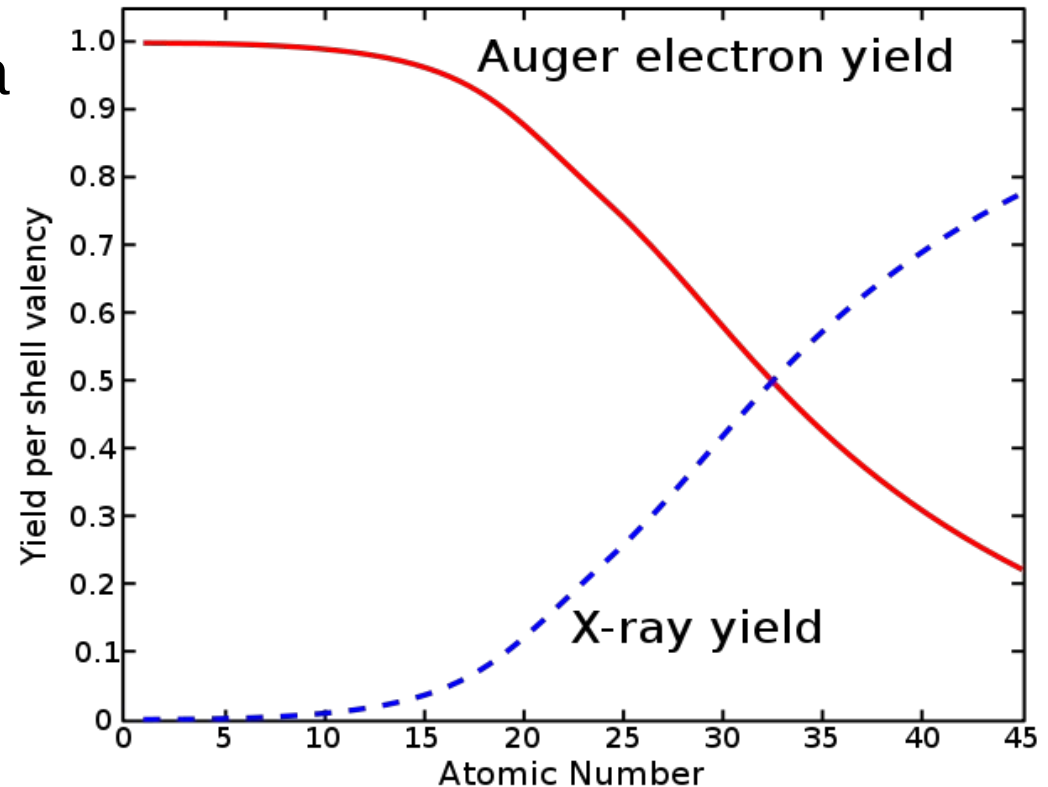
$$\epsilon_{\text{Aug}} = \epsilon_{\text{fi}} - [\epsilon_{\text{B}}(A) + \Phi_{\text{sp}}]$$

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.

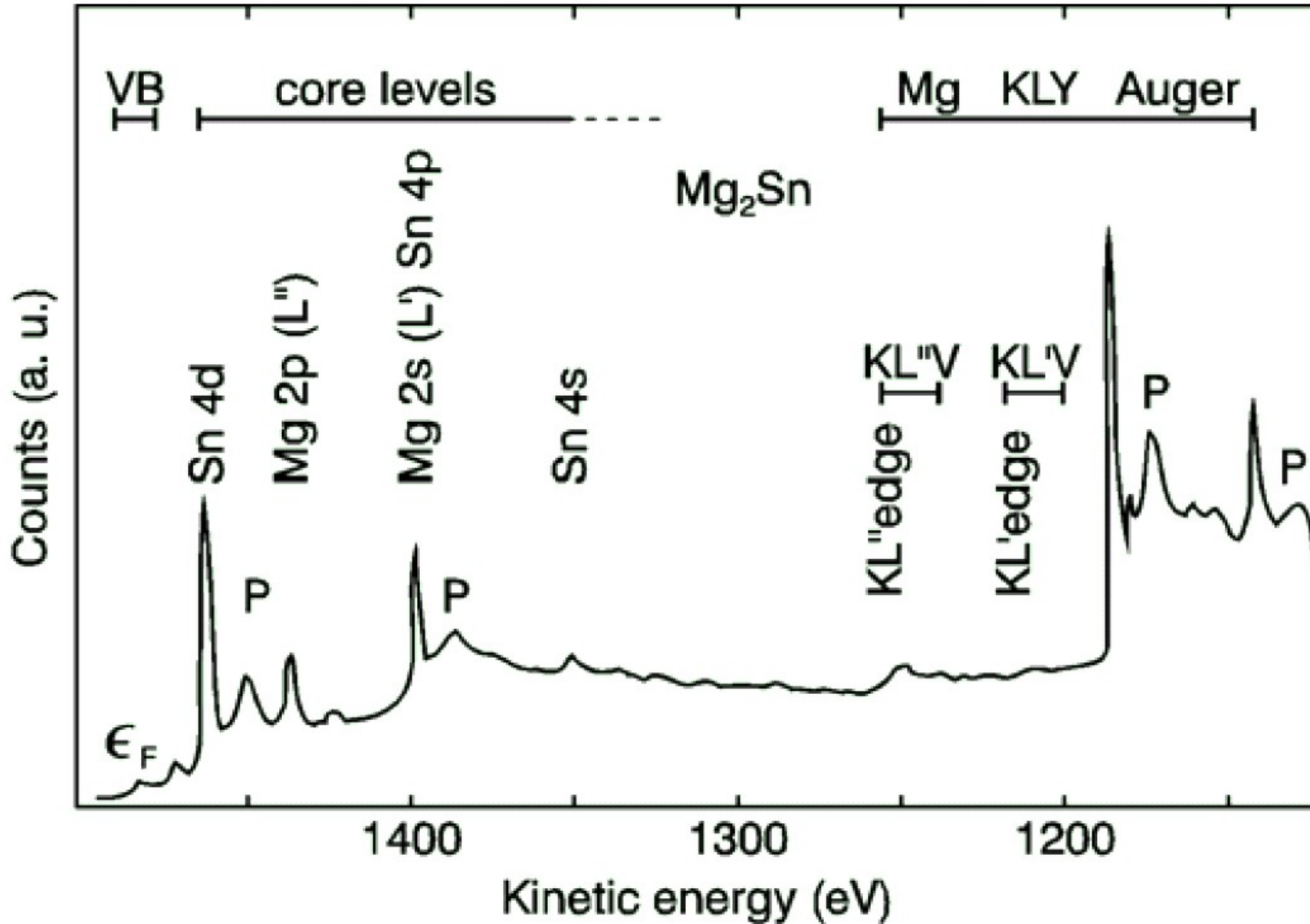
Často se měří v kombinaci s XPS, používá se v elektronové mikroskopii.



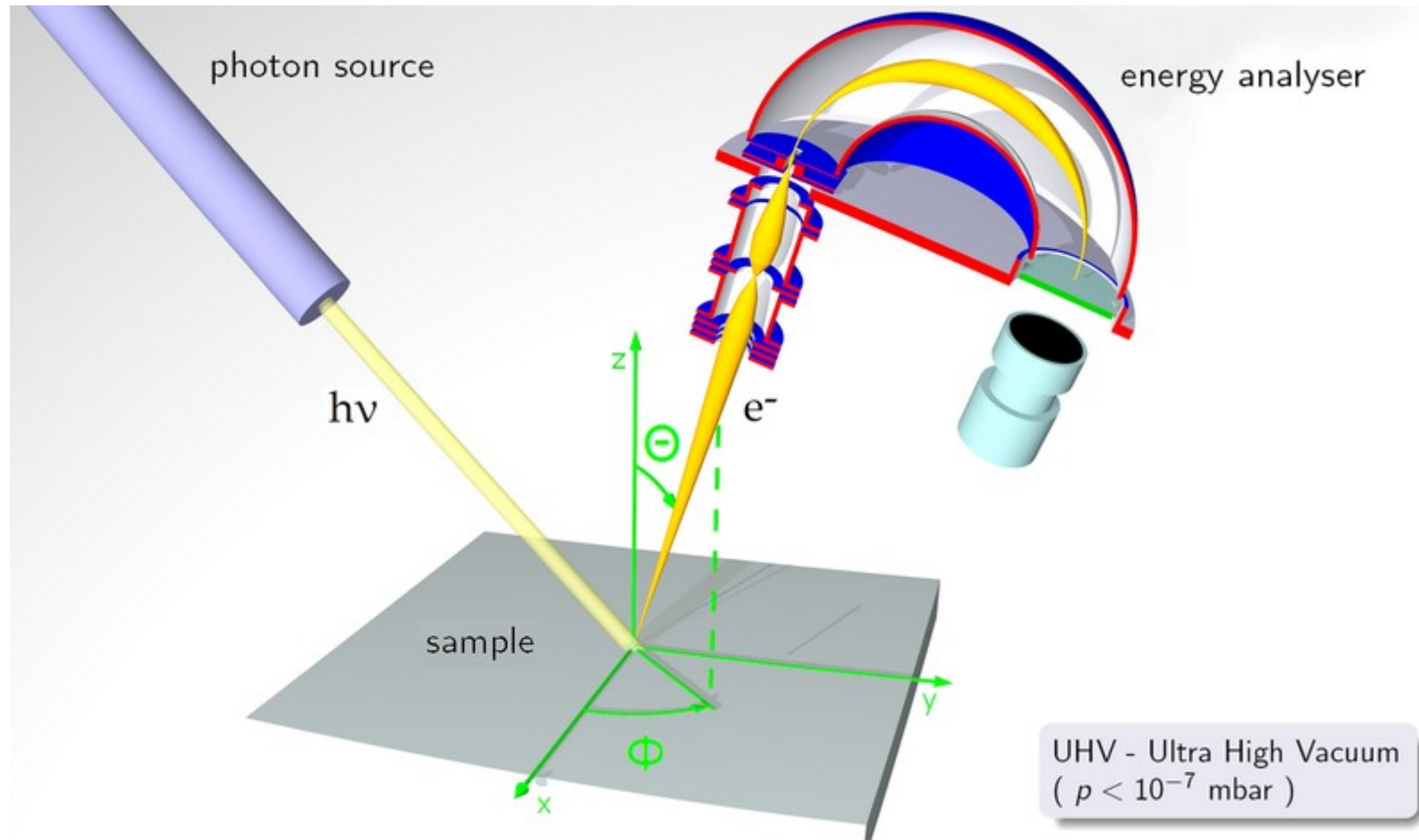
XPS + AES

Fotoelektronová a Augerova spektroskopie na Mg_2Sn .

Budící rtg svazek 1486 eV – čára Al $K\alpha$



ARPES - úhlově rozlišená



ARPES

Zákony zachování

- Kvaziimpulz – zachovává se tečná složka

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

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

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

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

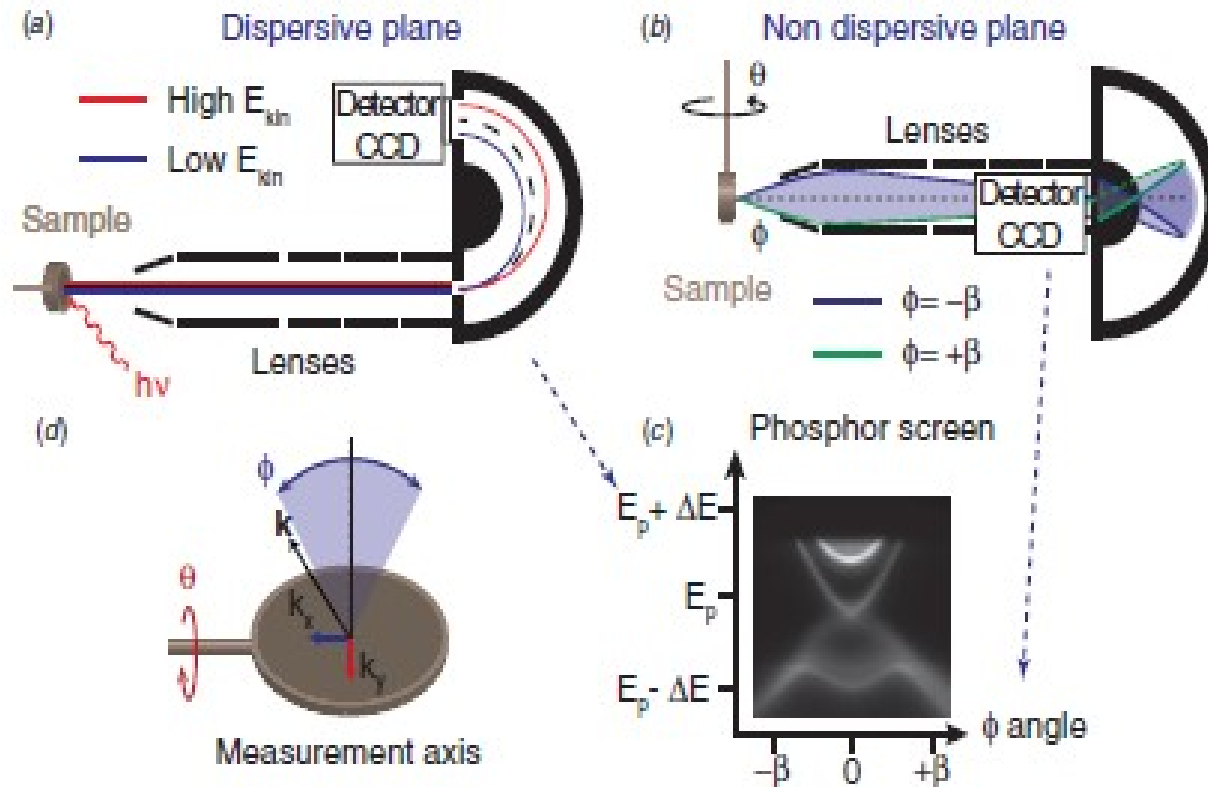
$$\hbar \vec{k}_z = \sqrt{2mE} \cos \theta$$

- energie

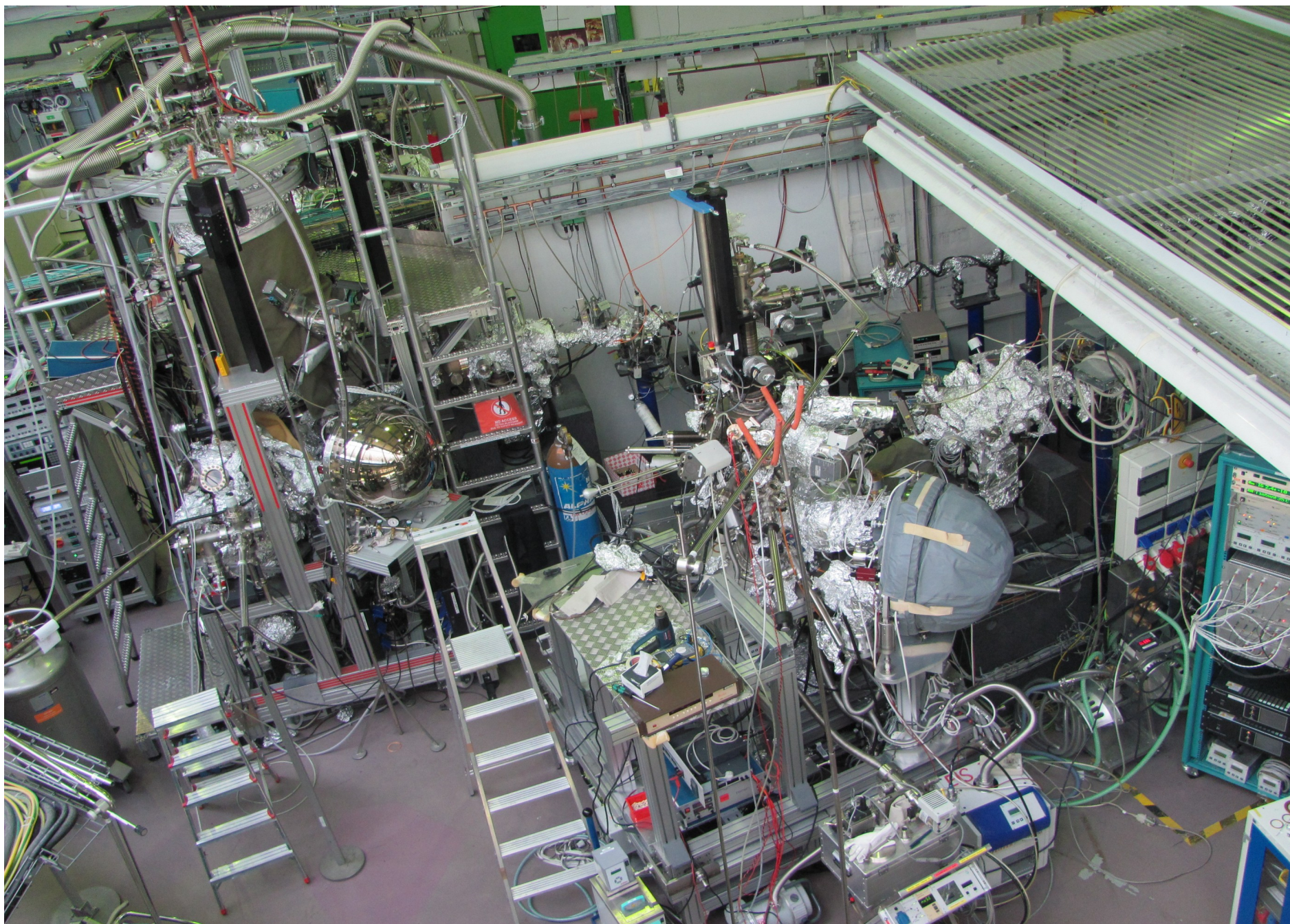
$$E_{\text{bound}} = \hbar \omega_i - E_{\text{kin,elektron}} - \varphi$$

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

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



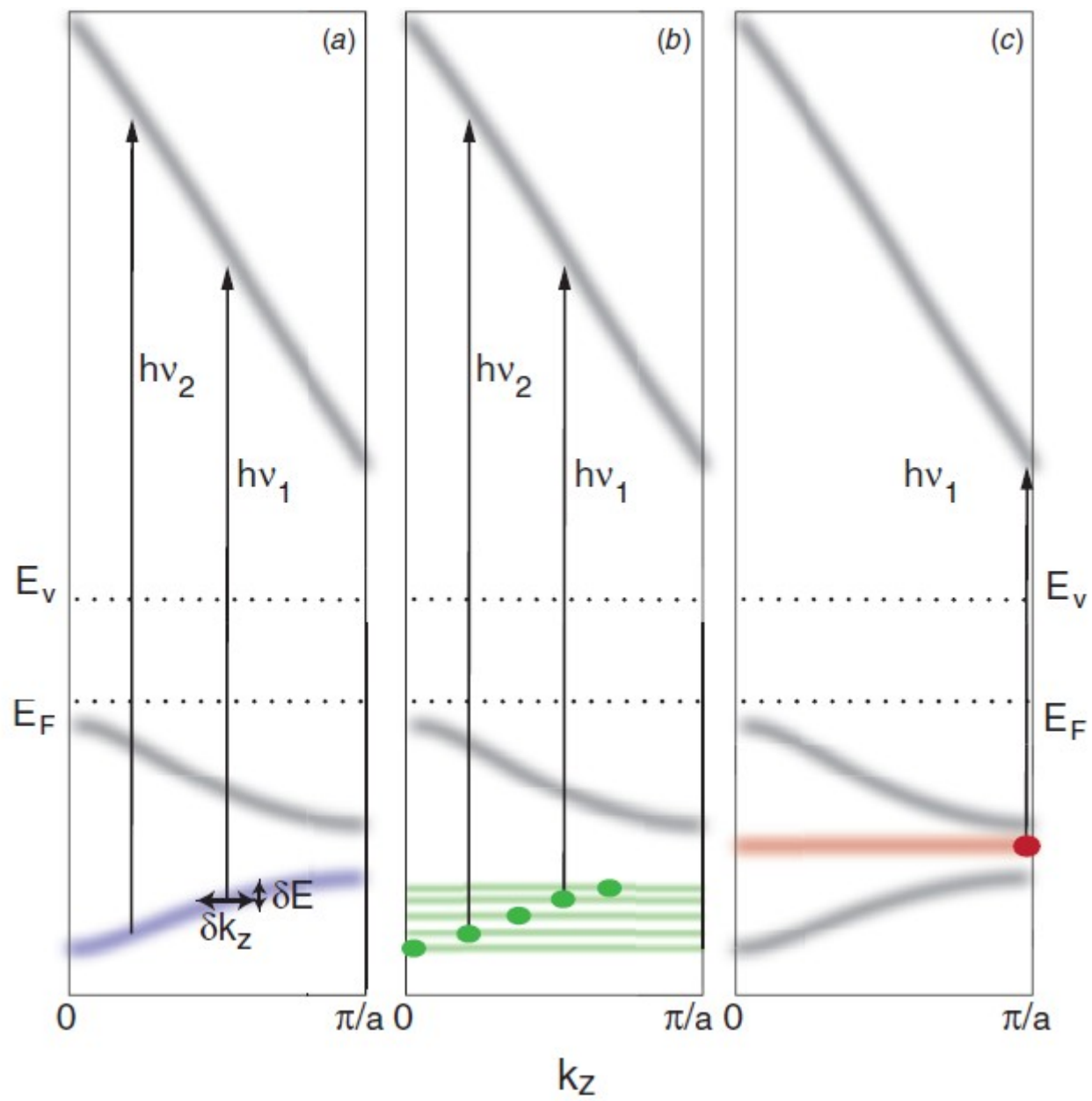
ARPES at BESSY



$$I(E_{\text{kin}}, \mathbf{k}) \propto |M_{fi}(\mathbf{k}_f, \mathbf{k}_i)|^2 f(h\nu - E_{\text{kin}} - \Phi, T) \int \mathcal{A}(h\nu - E_{\text{kin}} - \Phi, \mathbf{k}) \mathcal{L}(k_z, k_z^0) dk_z,$$

where \mathbf{k}_i and \mathbf{k}_f are the three-dimensional wave vectors for the initial and final states in the solid, \mathbf{k} is the wave vector for the free electron outside the solid, $h\nu$ is the photon energy, f is the Fermi distribution, Φ is the work function, \mathcal{A} is the hole spectral function and \mathcal{L} is a Lorentzian distribution to account for the real-space damping of the outgoing electron wave, with k_z^0 being the perpendicular wave vector for the un-damped final state wave. M_{fi} is the matrix element for the photoemission process. The integration is over all possible perpendicular wave vector components k_z . For QWS or surface states, this integration becomes irrelevant.

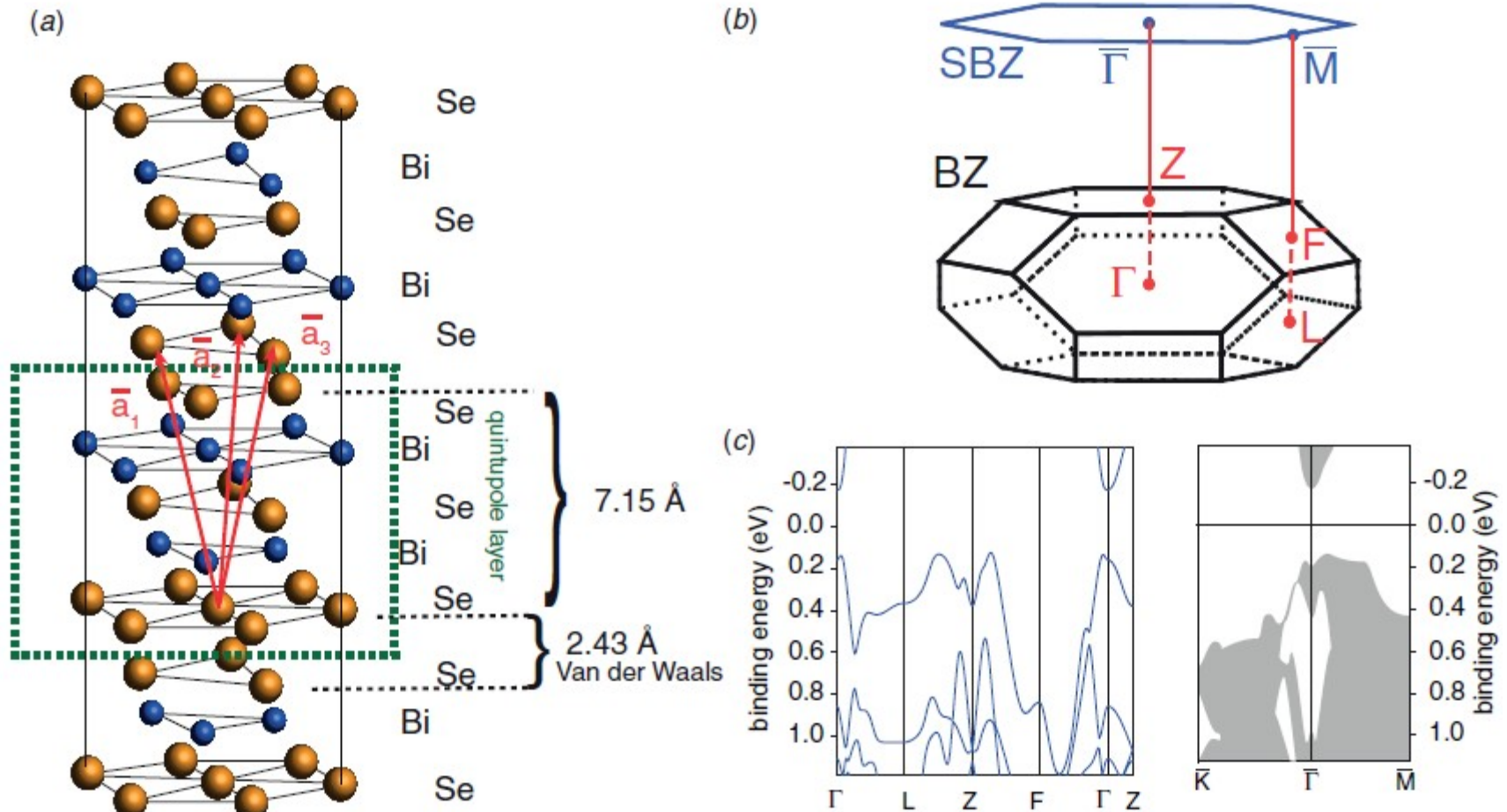
The quantity of most interest is often the spectral function \mathcal{A} . In simple terms, this is a measure of finding an electron with a certain energy and crystal momentum, i.e. an image of the band structure, including lifetime broadening effects. For two-dimensional systems such as surface states and QWS, the photoemission intensity is directly proportional to \mathcal{A} , as no final state broadening has to be considered. For a detailed further analysis, it is only necessary to assume that the matrix element does not depend strongly on the binding energy or the wave vector.

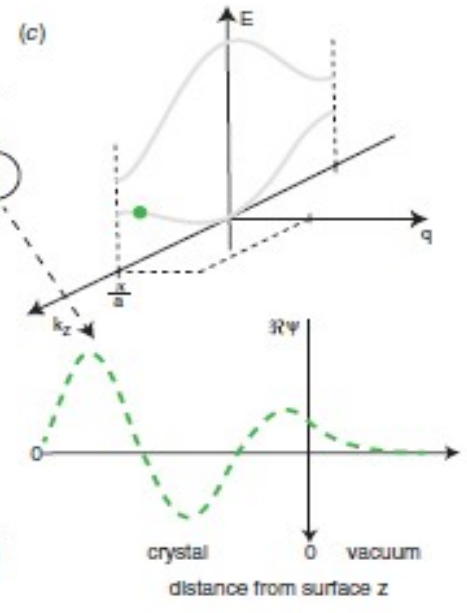
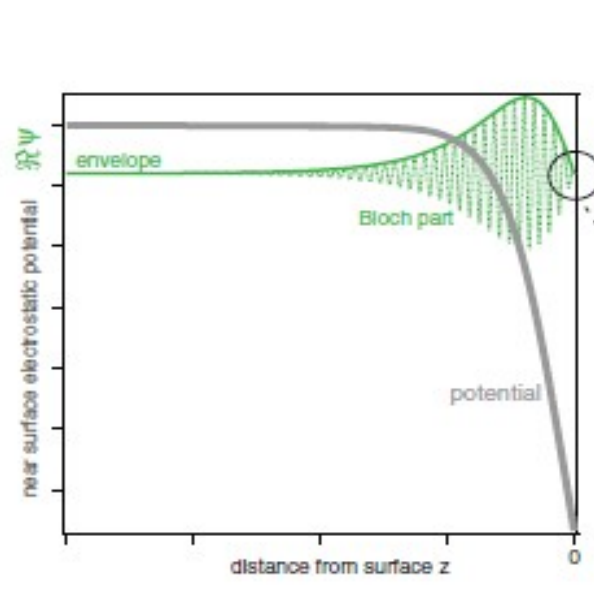
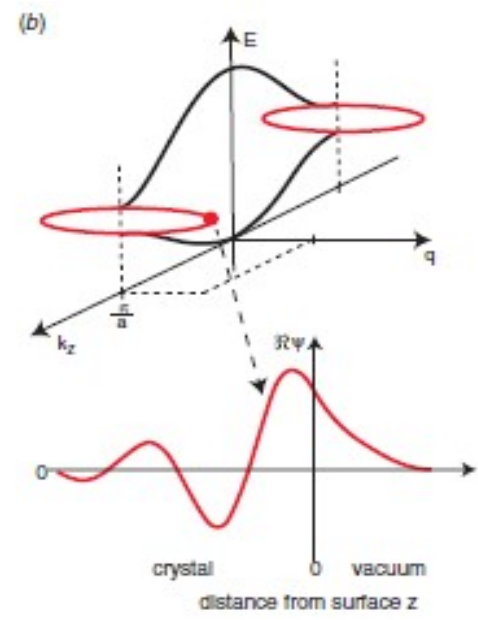
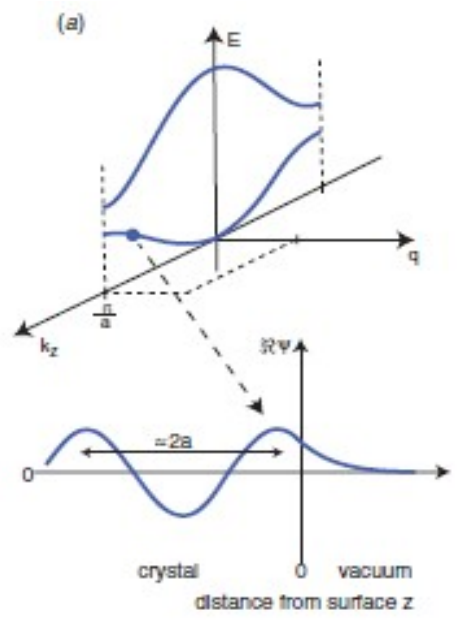


INVITED PAPER

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

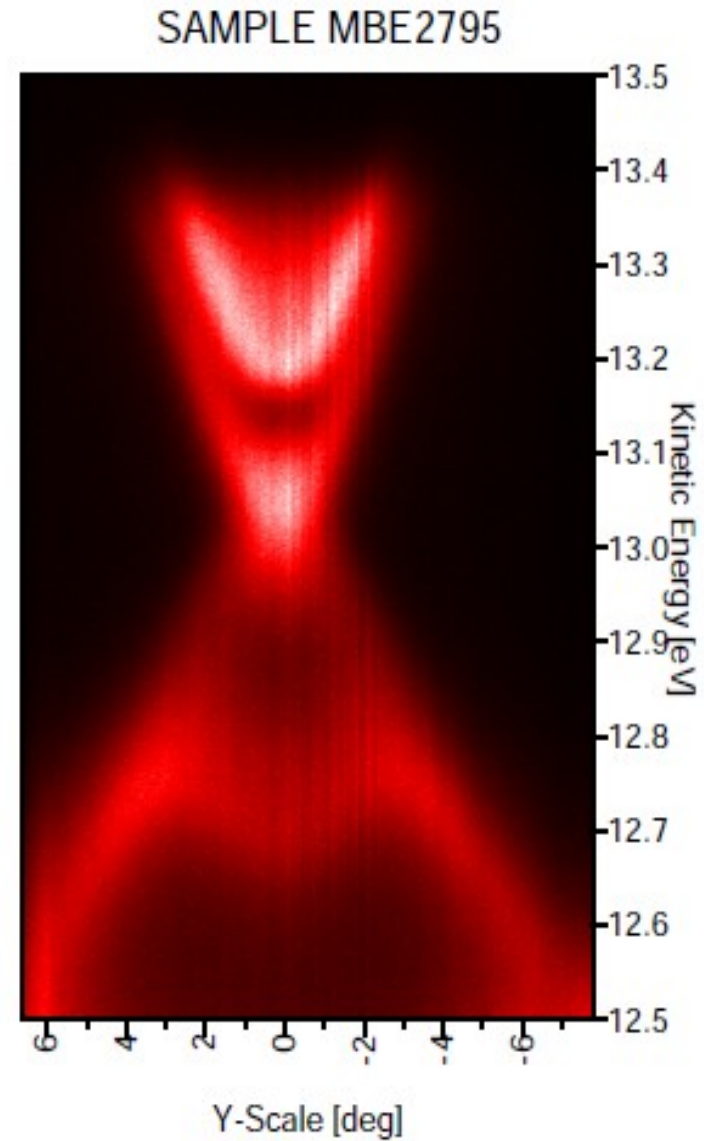
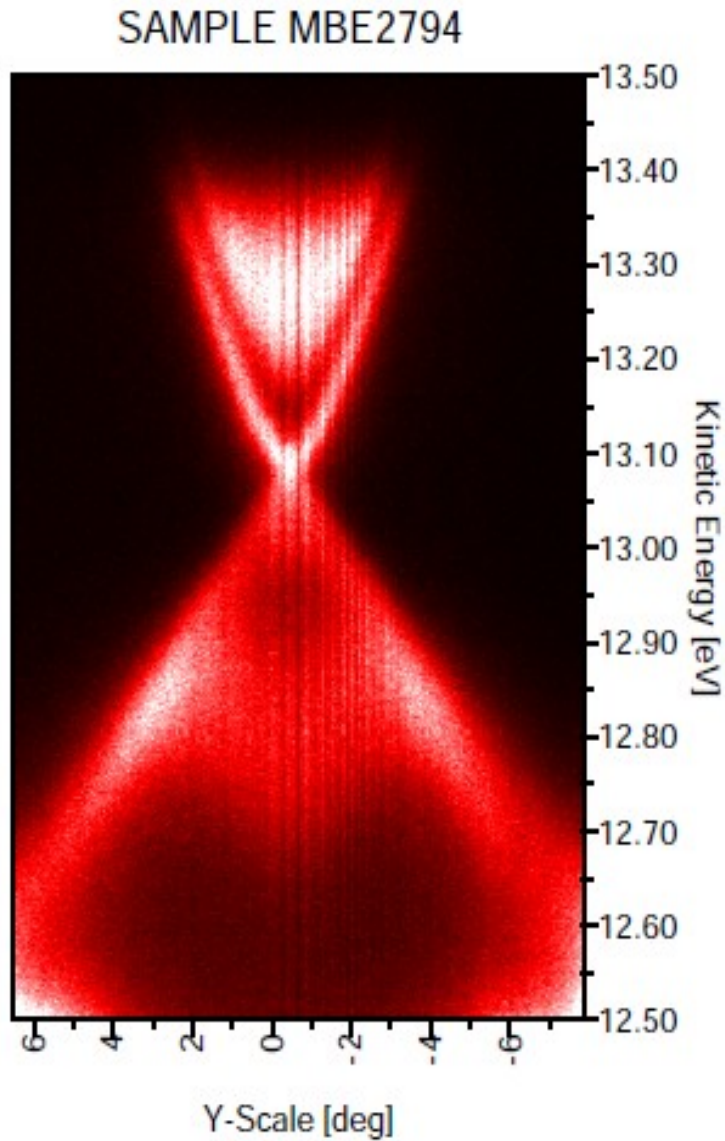
Marco Bianchi¹, Richard C Hatch¹, Dandan Guan¹, Tilo Planke¹,
Jianli Mi², Bo Brummerstedt Iversen² and Philip Hofmann¹





ARPES

Příklad: pásová struktura Bi_2Se_3



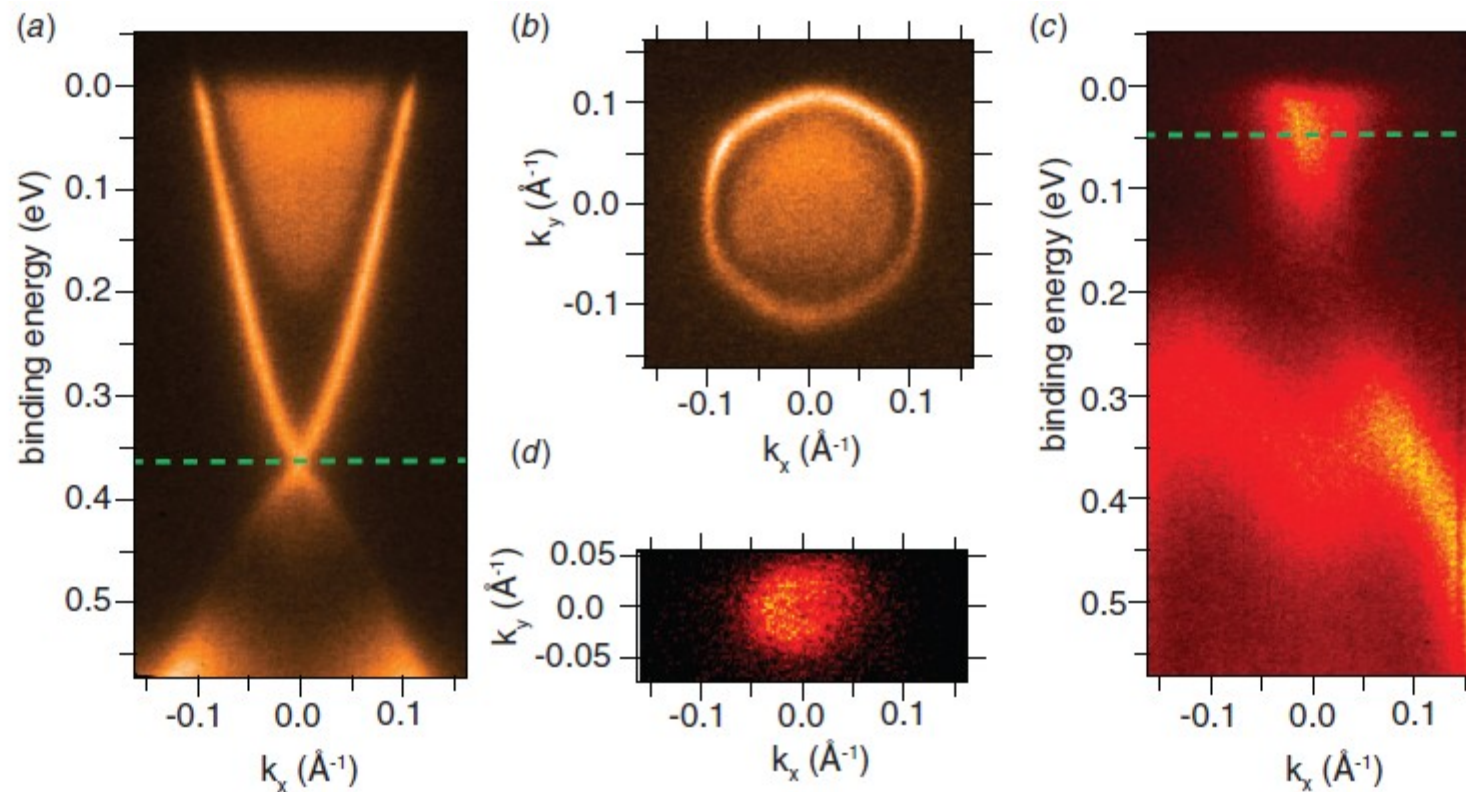


Figure 5. ARPES spectra for the pristine surface of Bi_2Se_3 . High photoemission intensity is displayed in bright. (a) Energy dispersion in the $\bar{K}\Gamma\bar{K}$ direction of the SBZ and (b) Fermi surface for the stoichiometric Bi_2Se_3 sample. (c) and (d) Energy dispersion and Fermi surface for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

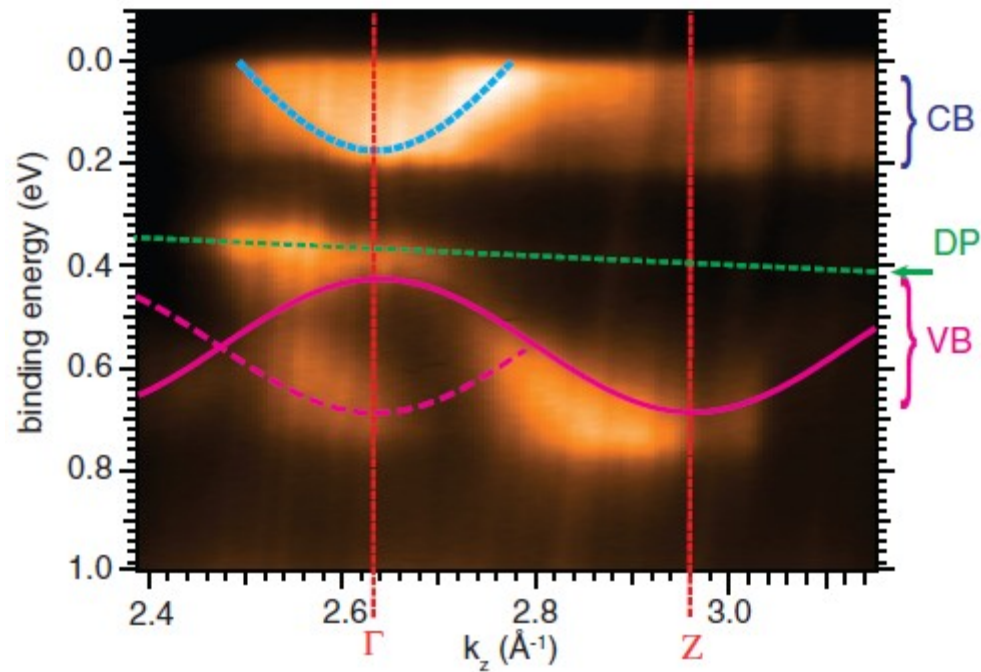


Figure 6. Photon energy scan on the pristine surface of intrinsic Bi_2Se_3 crystal illustrating the dispersion of the states at normal emission as a function of k_z . The data shown are a subset of a larger photon energy scan between $h\nu = 14$ eV and $h\nu = 32$ eV. The drift of the Dirac point with 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

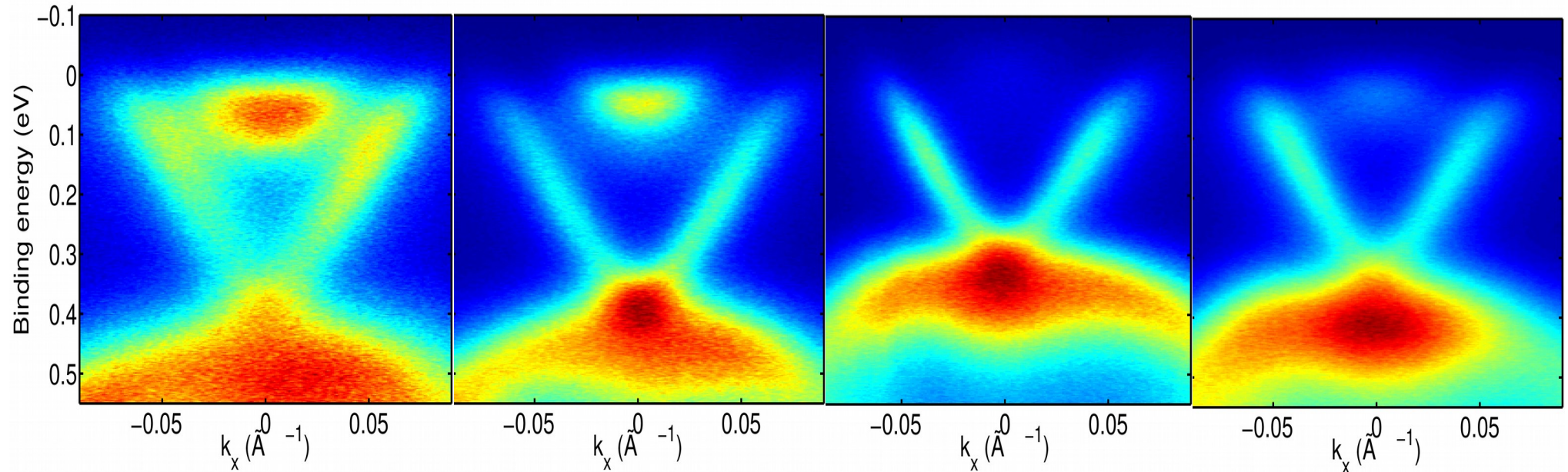
Příklad: pásová struktura Bi_2Se_3

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

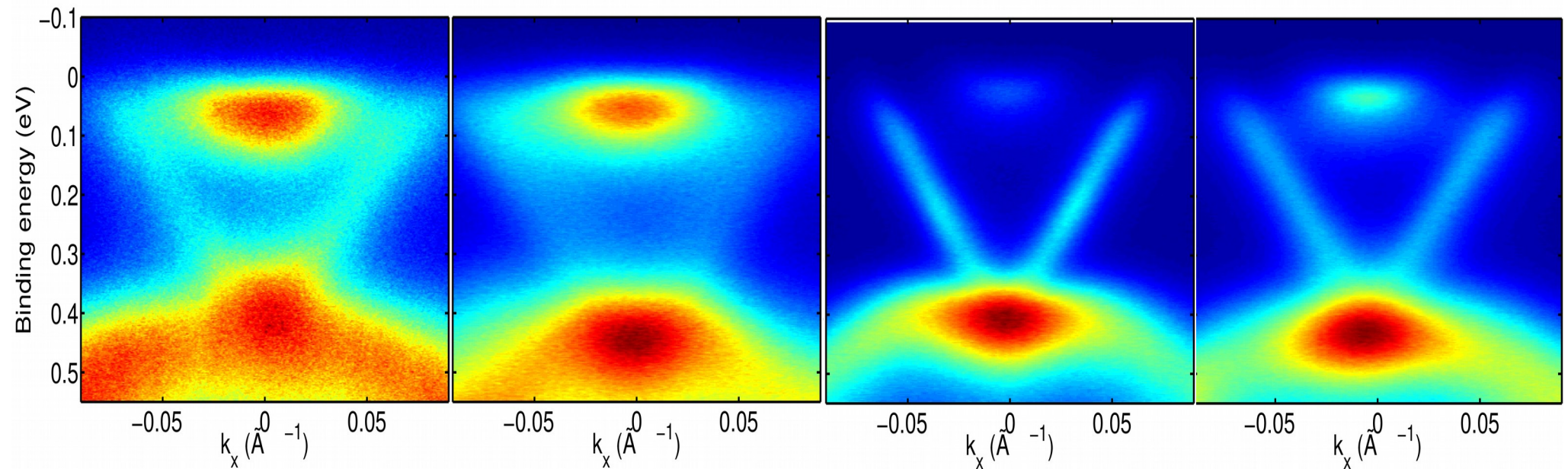


Te 34%, $h\nu = 15.0$ eV

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

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

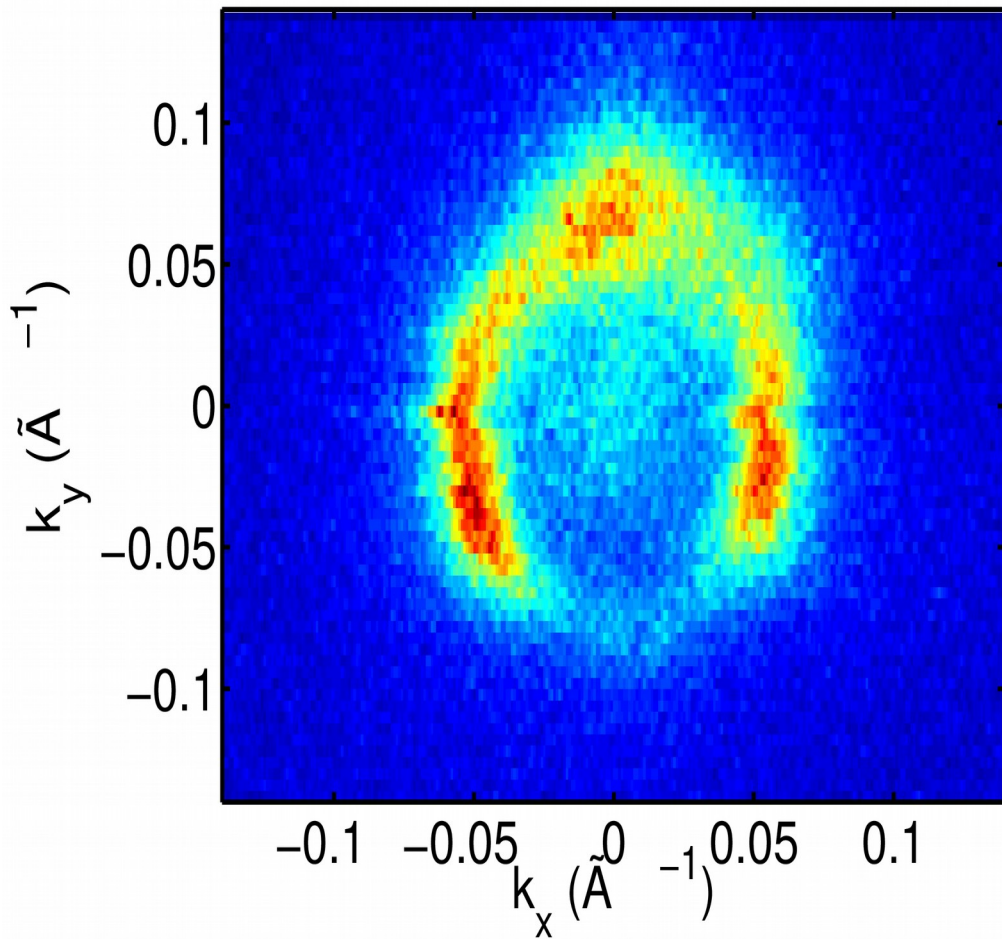
Te 39%, $h\nu = 15.0$ eV



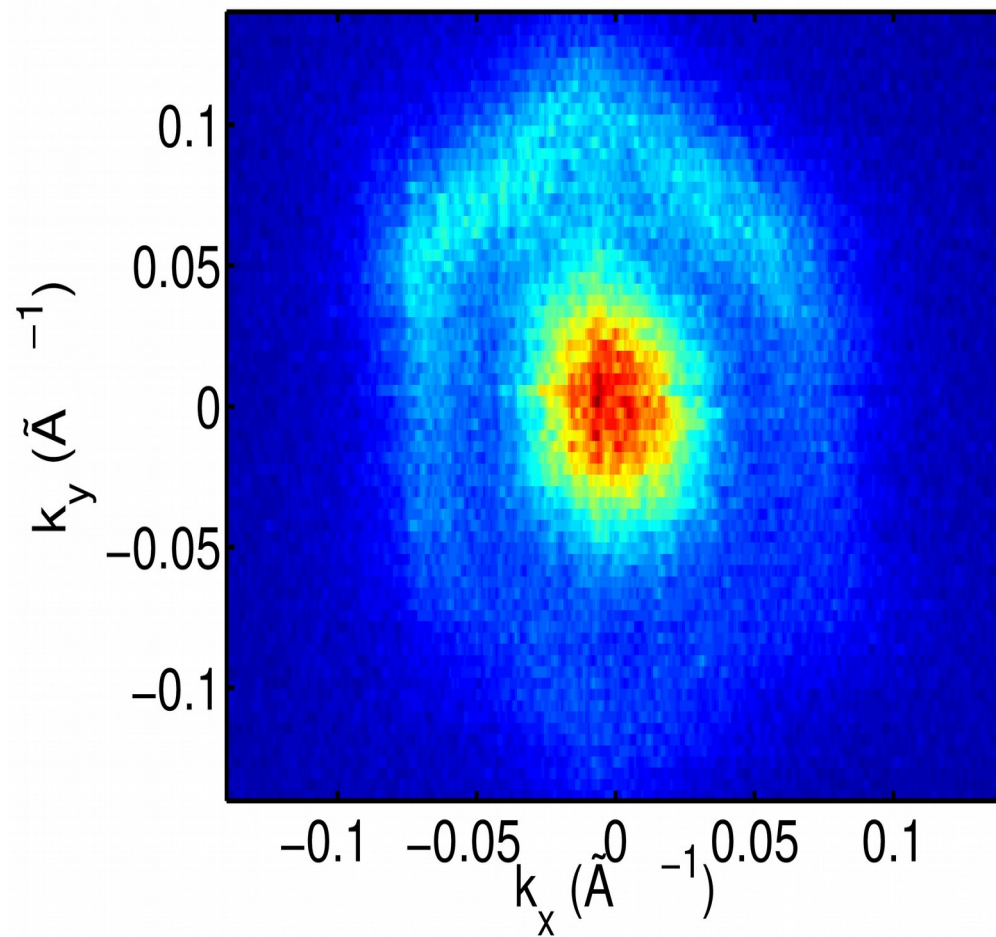
ARPES

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

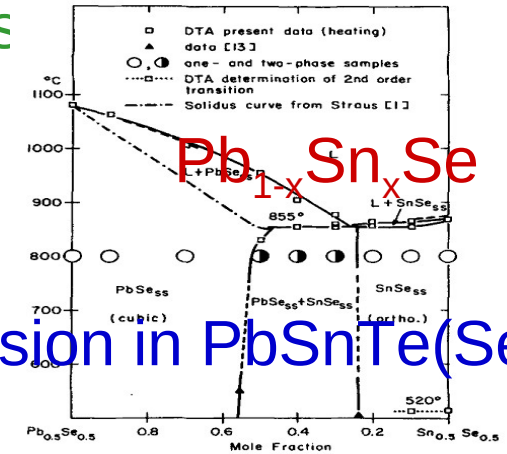
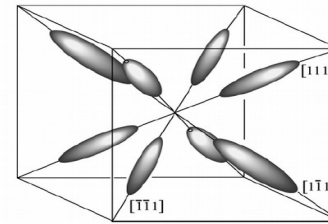
Disadvantages:

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

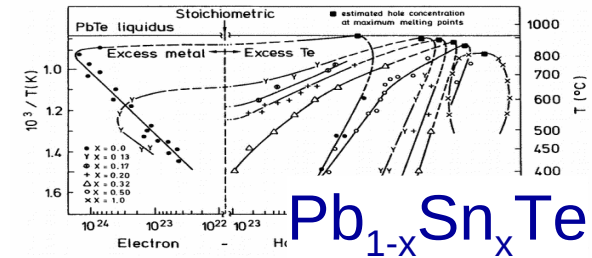
(ii) Ternary $Pb_{1-x}Sn_xTe$ and $Pb_{1-x}Sn_xSe$:

- 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

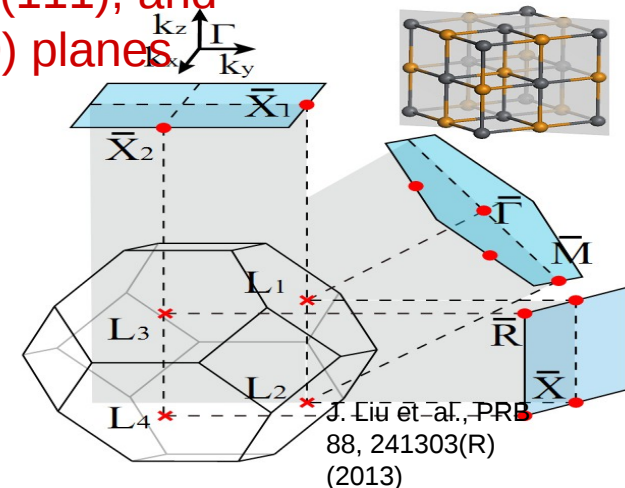
Phase diagrams



Band inversion in $PbSnTe(Se)$

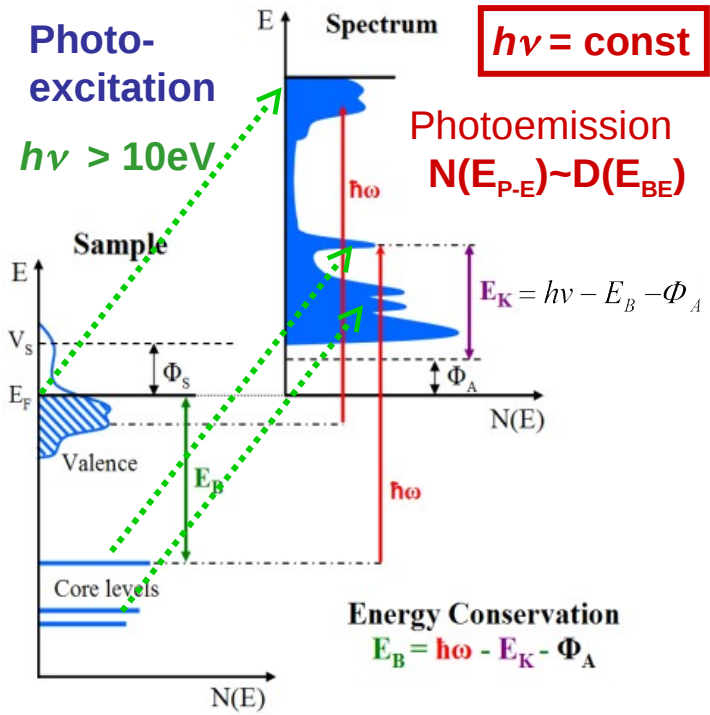


Brillouin zone projections onto (001), (111), and (110) planes



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

Angle Resolved Photoemission Spectroscopy



Angle resolved photoemission (ARPES)

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

$h\nu = \text{const.}$

We need:
 binding energy - E_b
 initial momentum - k^i

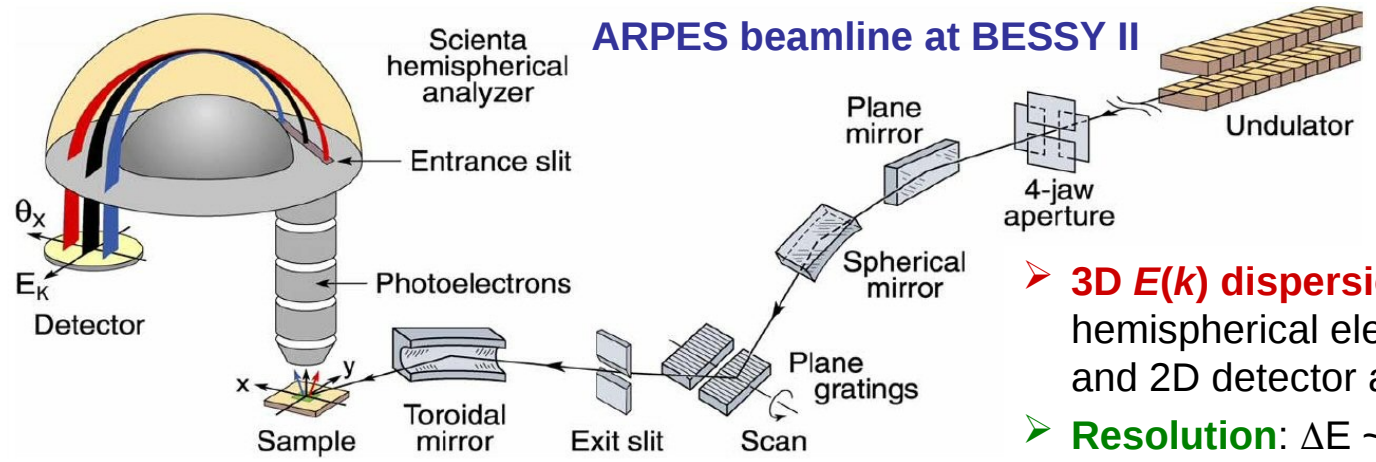
$E_b = E - h\nu + W$

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

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

$\Rightarrow E(k_{||})\text{-dispersion}$

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

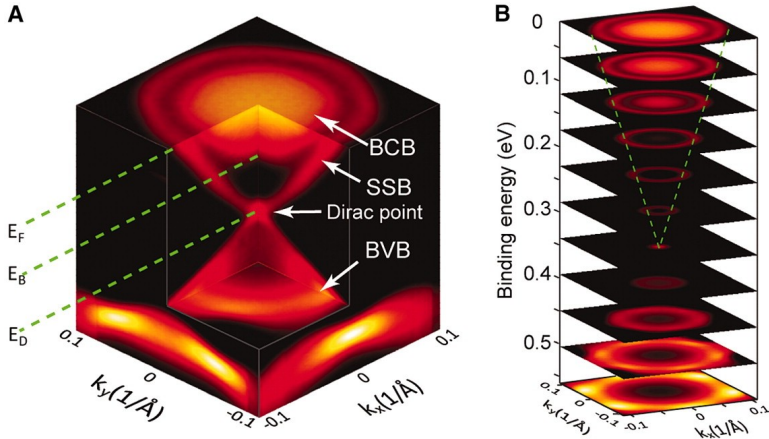


- **3D $E(k)$ dispersion** obtained by hemispherical electron analyzer and 2D detector array
- **Resolution:** $\Delta E \sim 10\text{meV}$, $\Delta\theta \sim 0.1^\circ$

Angular Resolved Photoemission: Examples

Examples:

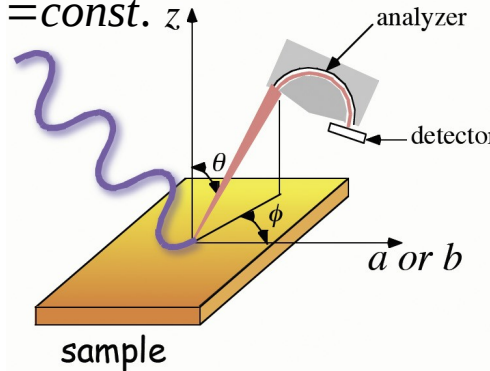
Bi₂Se₃



ARPES experiment

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

$h\nu = const.$ z



We need:

binding energy - E_b
initial momentum - k^i

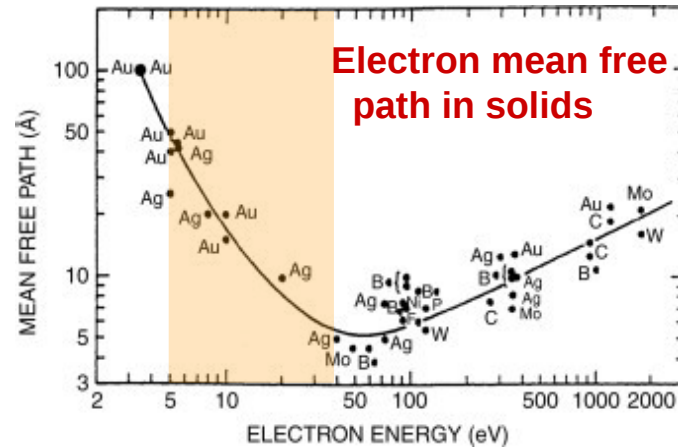
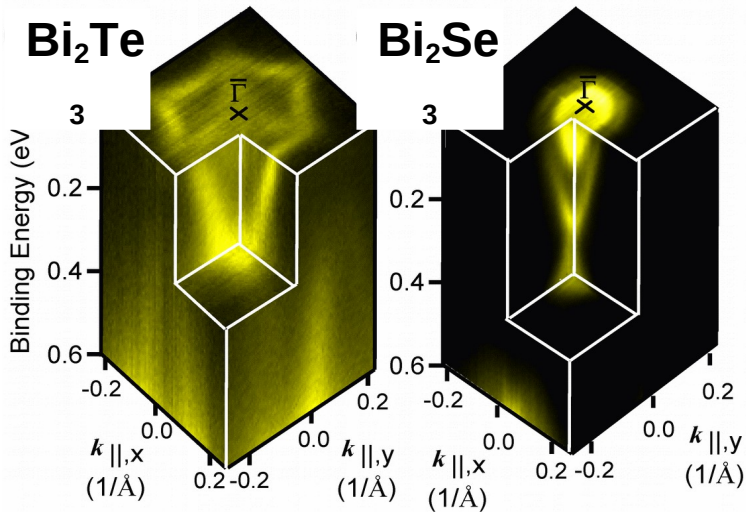
$$E_b = E - h\nu + W$$

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

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

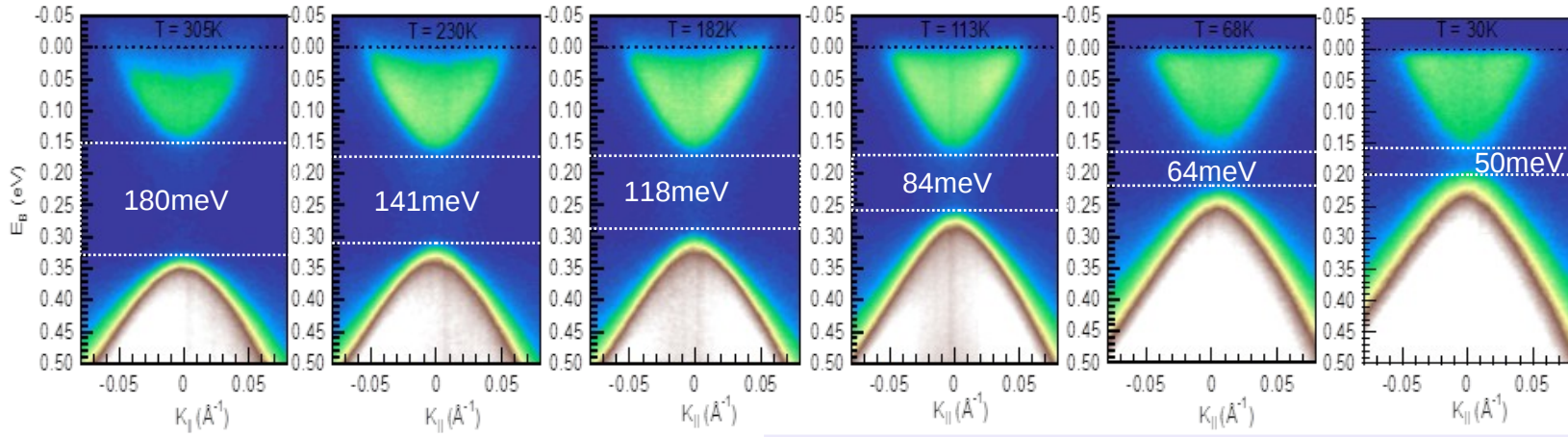
⇒ **E(k)-dispersion**

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

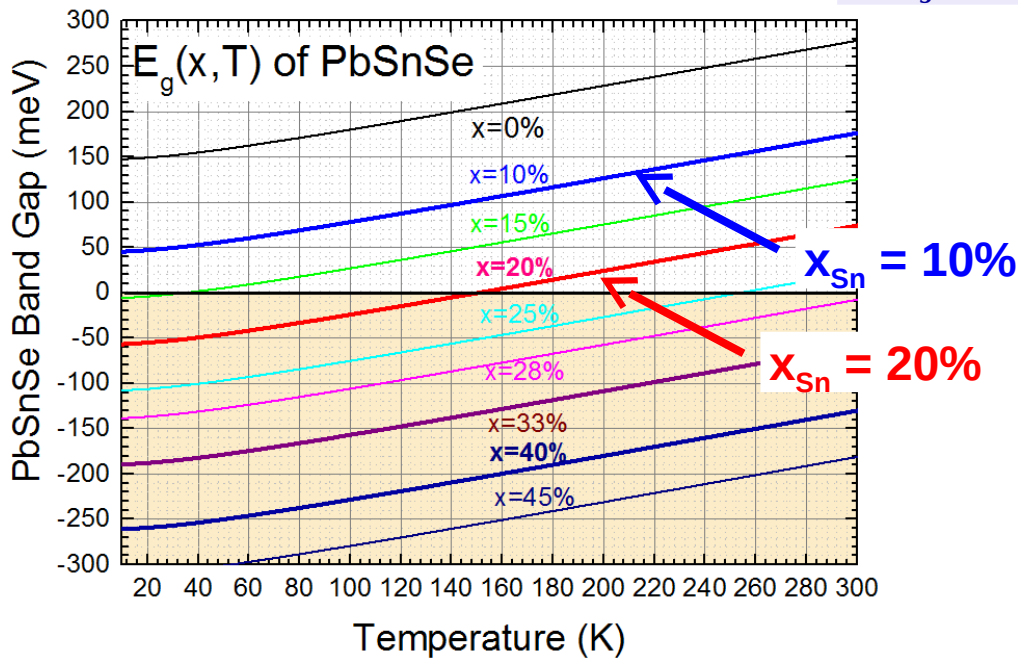


Zoom-in around the Γ – Point: PbSnSe (111) Epilayers

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



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



2D Structures: TCI Surface Quantum Wells

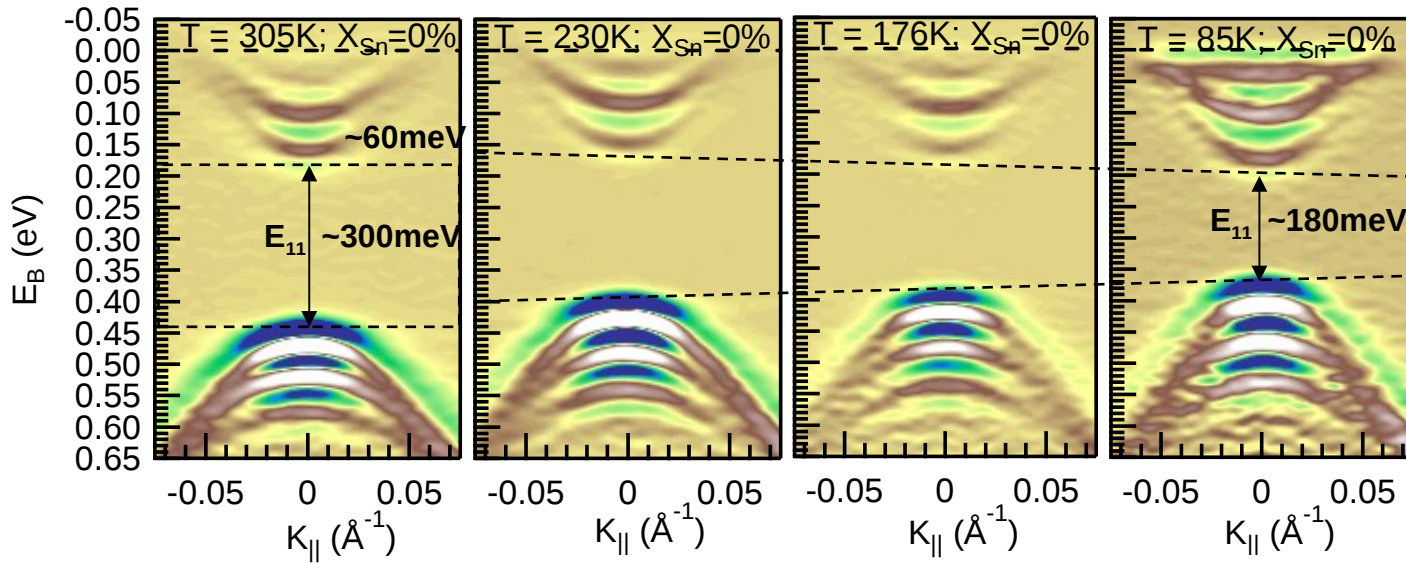
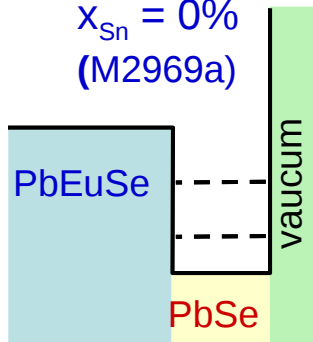
- ⇒ MBE of asymmetric quantum wells (vacuum barrier): discrete 2D QW states
- ⇒ Opening of a gap due to coupling between top & bottom topological surface state

(a) PbSe QW

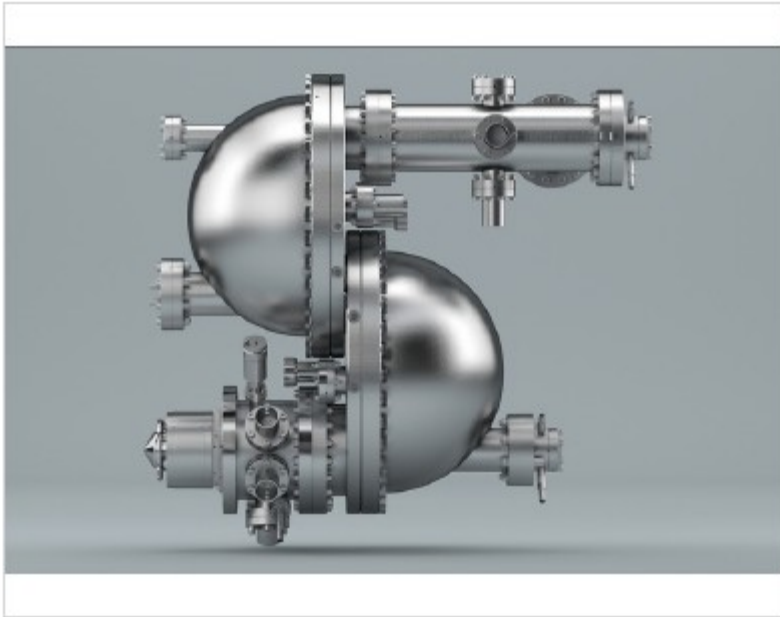
$d_{\text{QW}} = 100\text{\AA}$

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

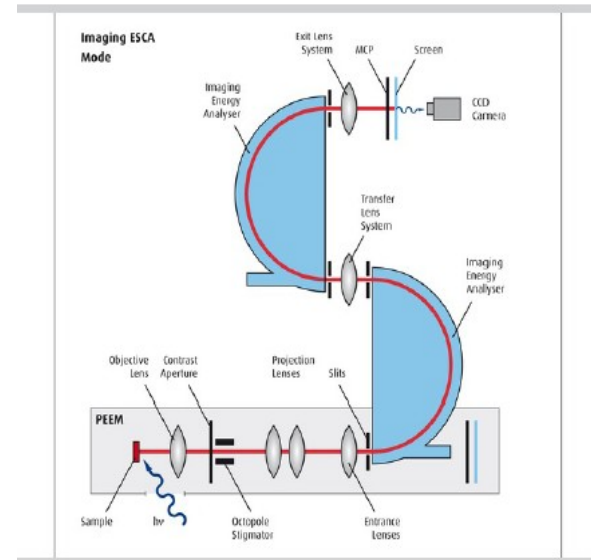
(M2969a)



NanoESCA – kombinace mikroskopie a spektroskopie

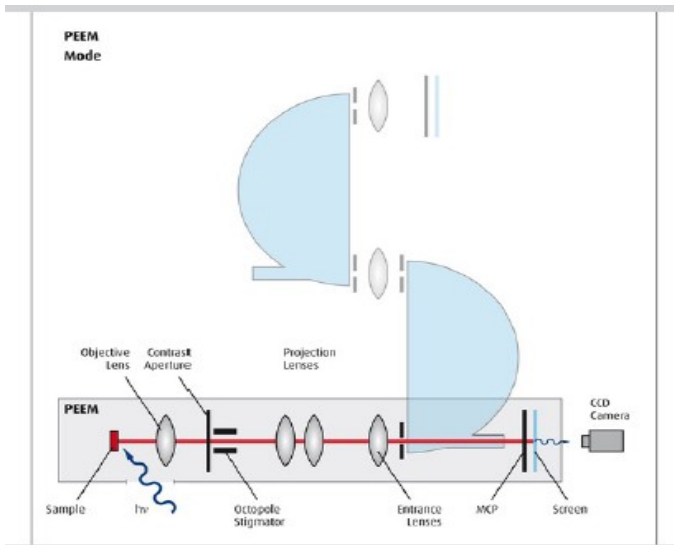
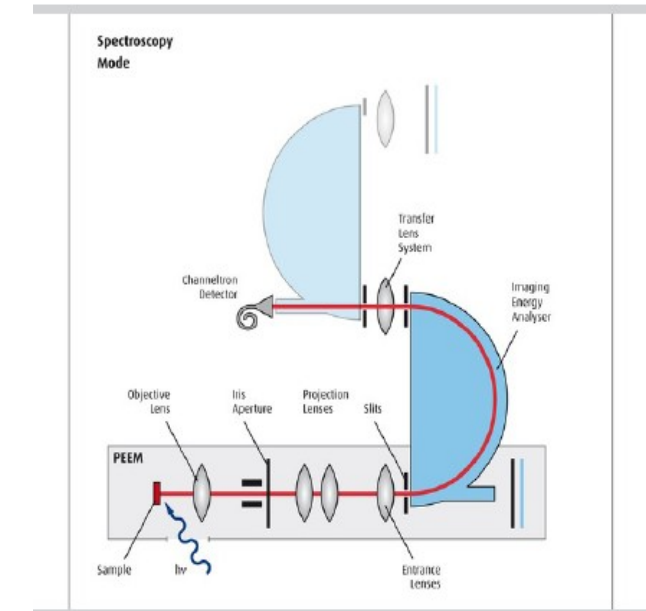


Imaging ESCA –
zobrazení
jen určité
energie
elektronů



PEEM – photoelectron
microscopy

XPS



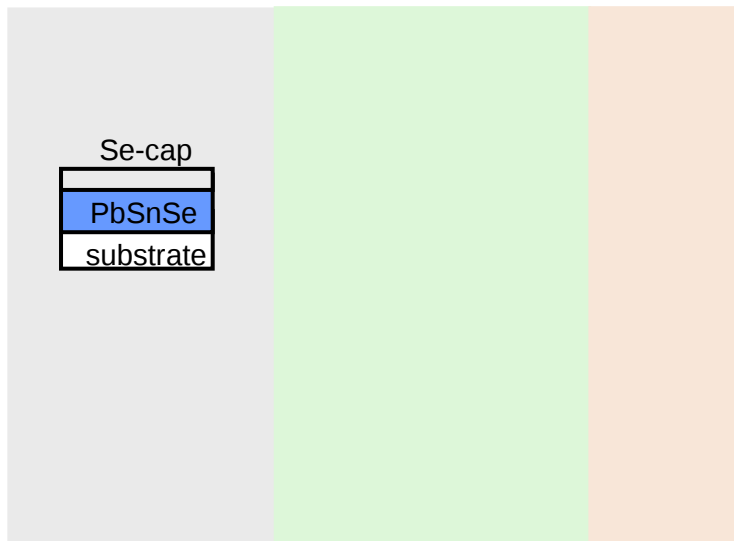
Rozlišení 50nm

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:

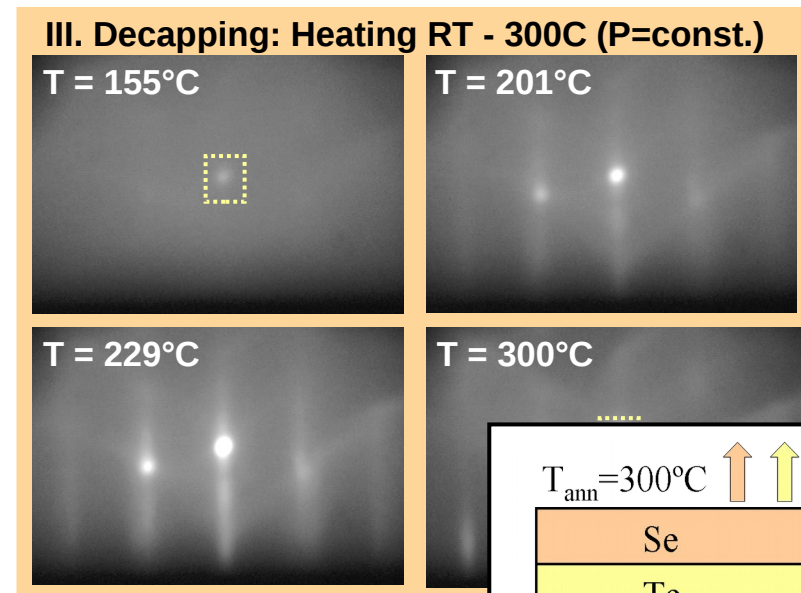
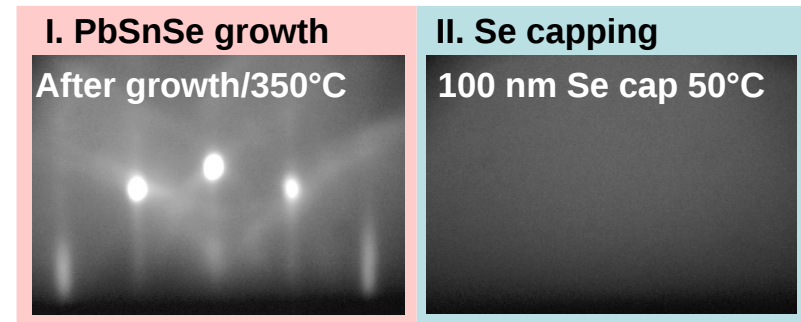
Amorphous Se cap layer (~ 100 nm) deposited at RT: Volatile surface oxide



⇒ 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.

