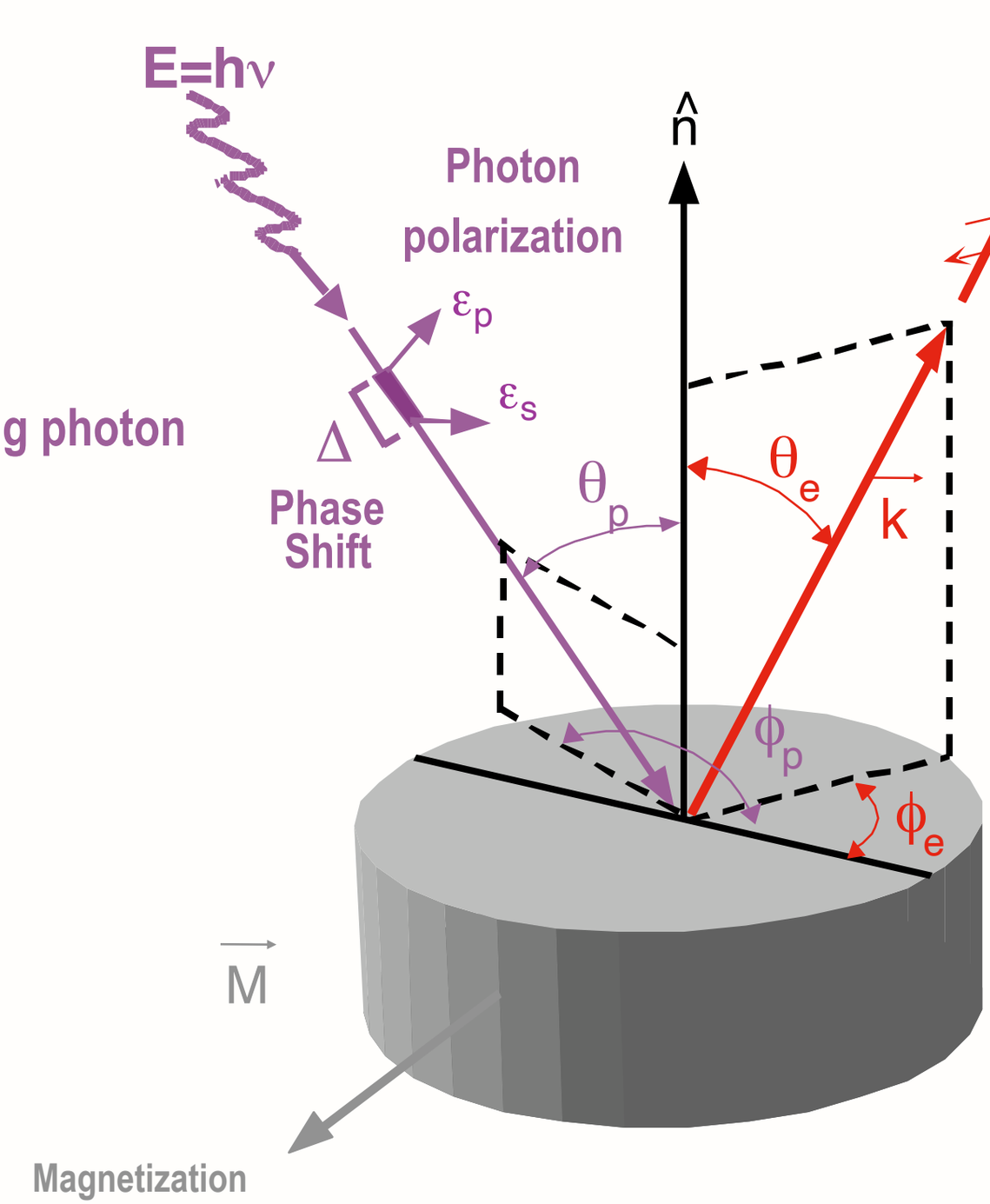
The photoemission experiment



$$E_k = \frac{h^2k^2}{2m}$$

Measure:

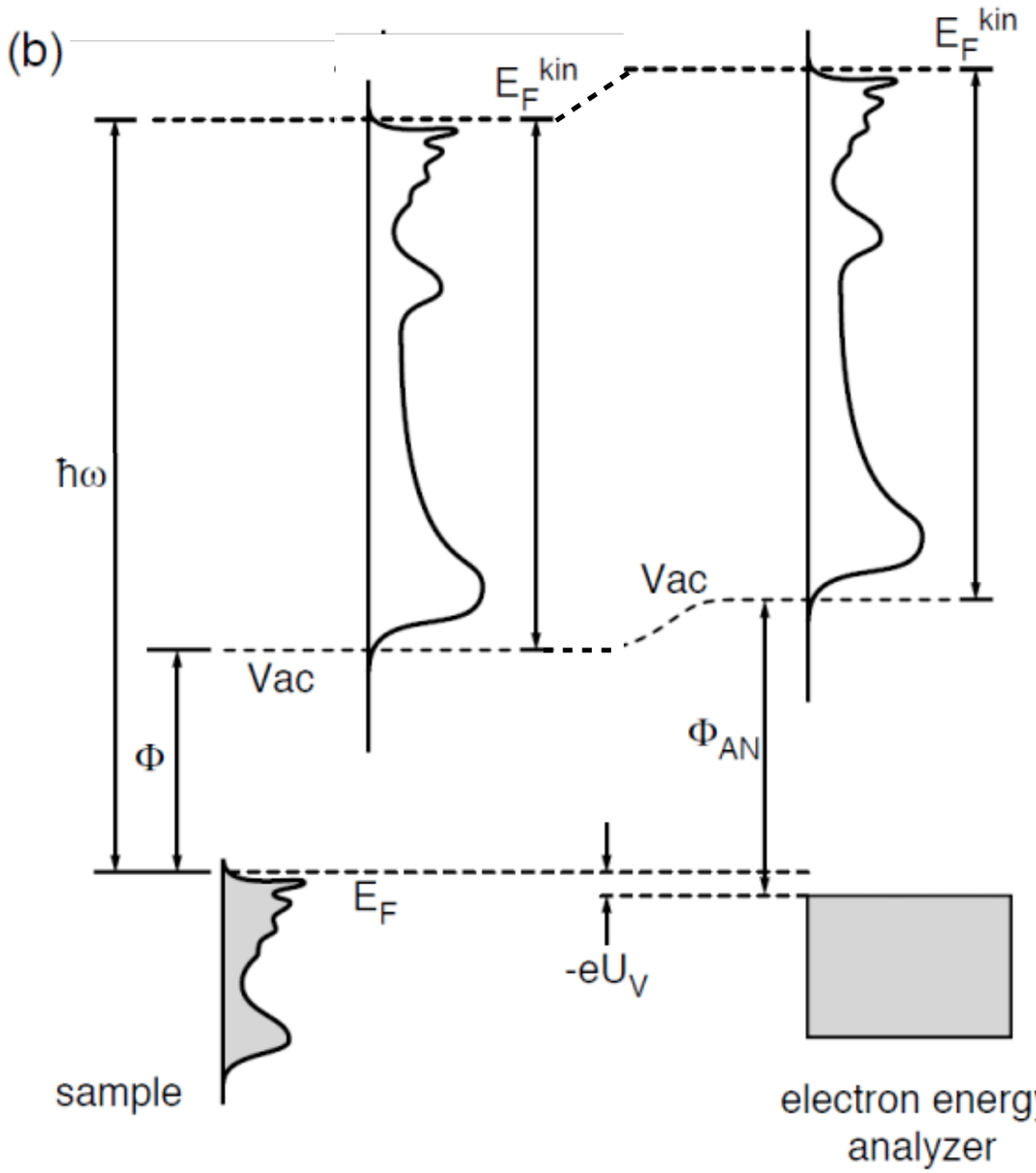
-Kinetic energy

-Emission angle

-Spin

Oriented single crystal

Energy conservation



$$E_b = h\nu - \Phi - E_k$$

Electron binding energy

Set photon energy

Work function

Measured kinetic energy

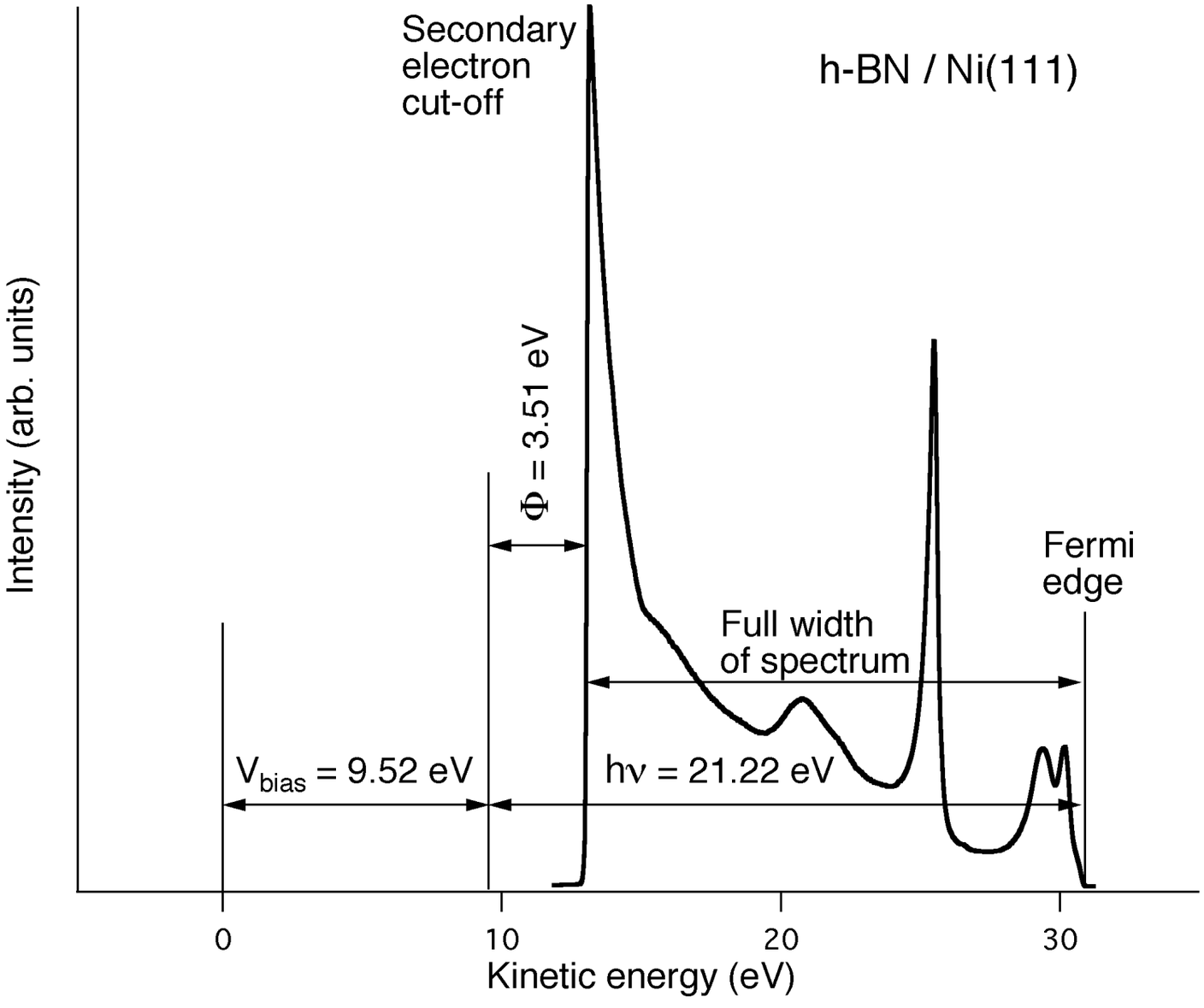
This is the analyser work function

Φ: Sample work function

Φ_{AN}: Analyser work function (typically 4.32 eV)

$-eU_V$: possible bias voltage between sample and analyser

Determining sample work function

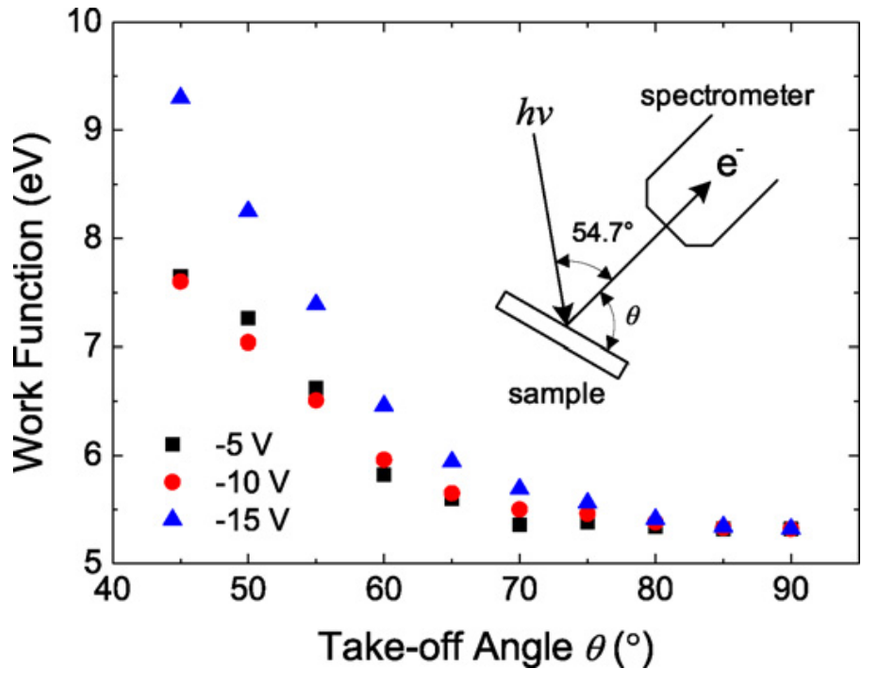


Fermi edge *secondary cut-off*

$$\Phi_S = h\nu - (E_k(\epsilon_F) - E_k^{min})$$

Bias sample to avoid low energy problems

Only valid at normal emission



M.G. Helander et al. Applied Surface Science 256, 2602 (2010)

Local work function (variations) from Photoemission of Adsorbed Xenon (PAX)

J. Küppers et al. PRL 43, 928 (1979)

H. Dil et al. Science 319, 1824 (2008)

Photoemission from a periodic potential

Momentum conservation demands a “vertical” or direct transition

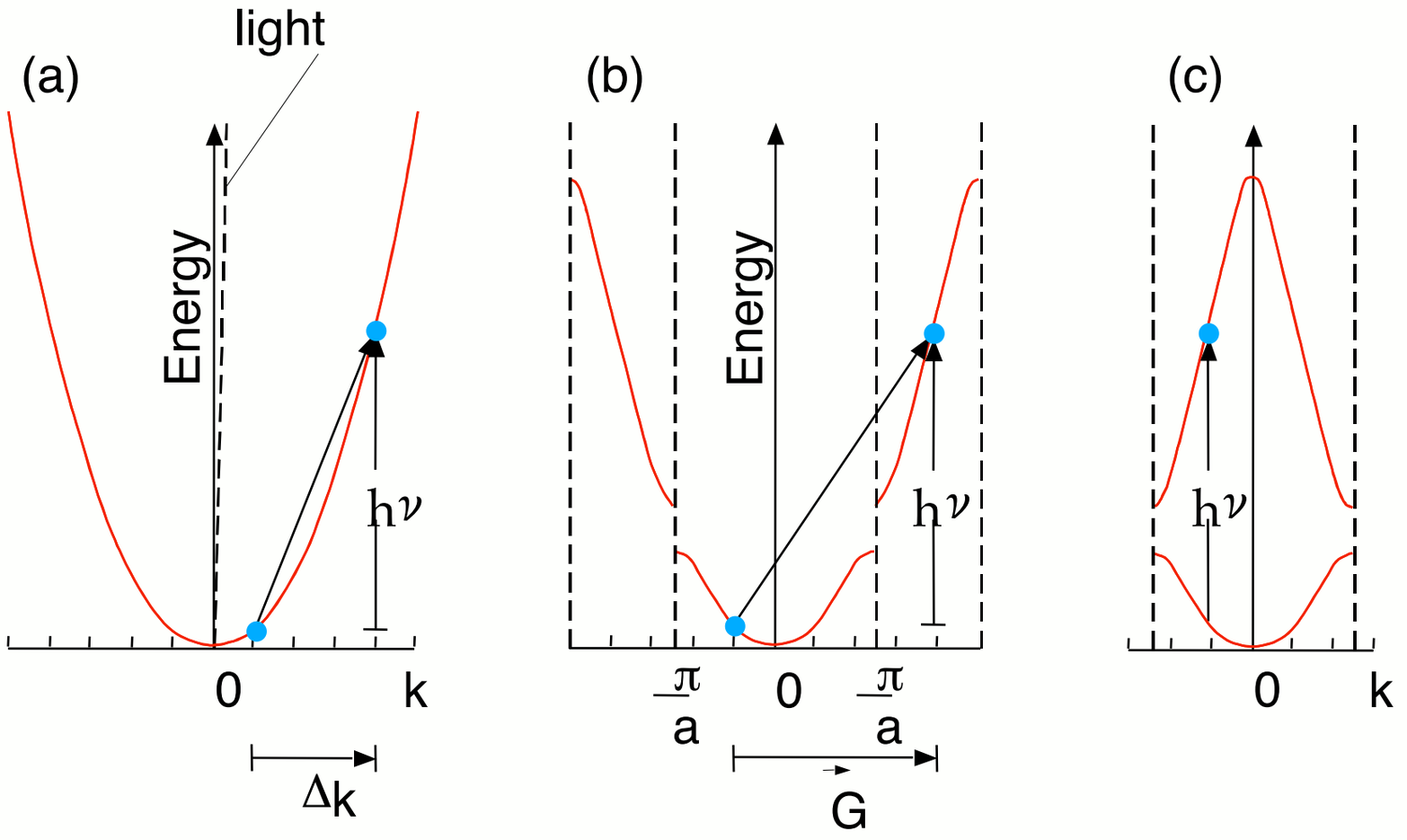
Conservation Laws:

$$\varepsilon_i(\vec{k}_i) + h\nu = \varepsilon_f(\vec{k}_f)$$

$$\vec{k}_i + \vec{k}_{h\nu} + \vec{G} + \vec{g} = \vec{k}_f$$

≈ 0 (for UV energies)

reconstructed surface

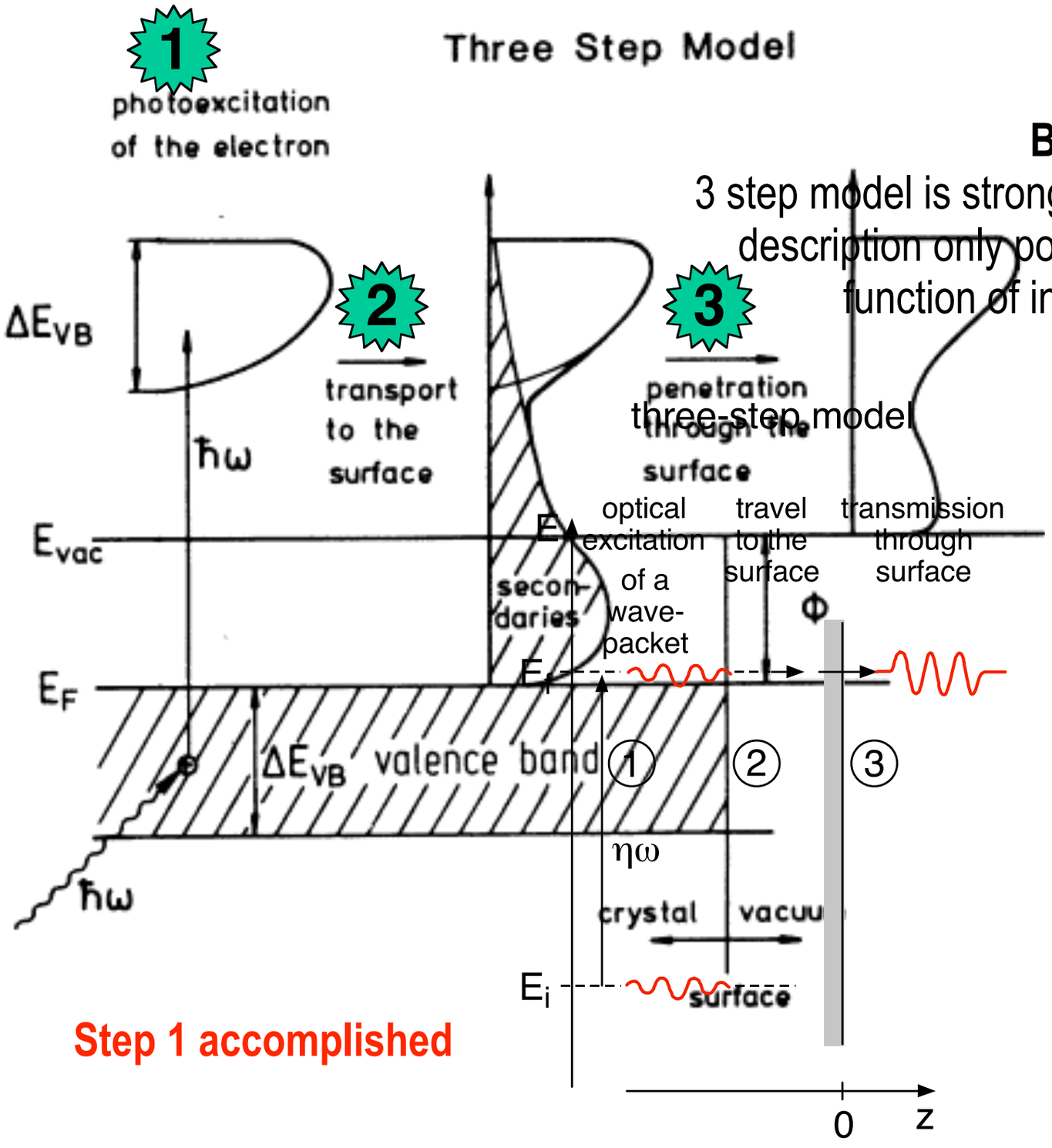


free electron

extend zone periodic potential

reduced zone periodic potential

The three step model

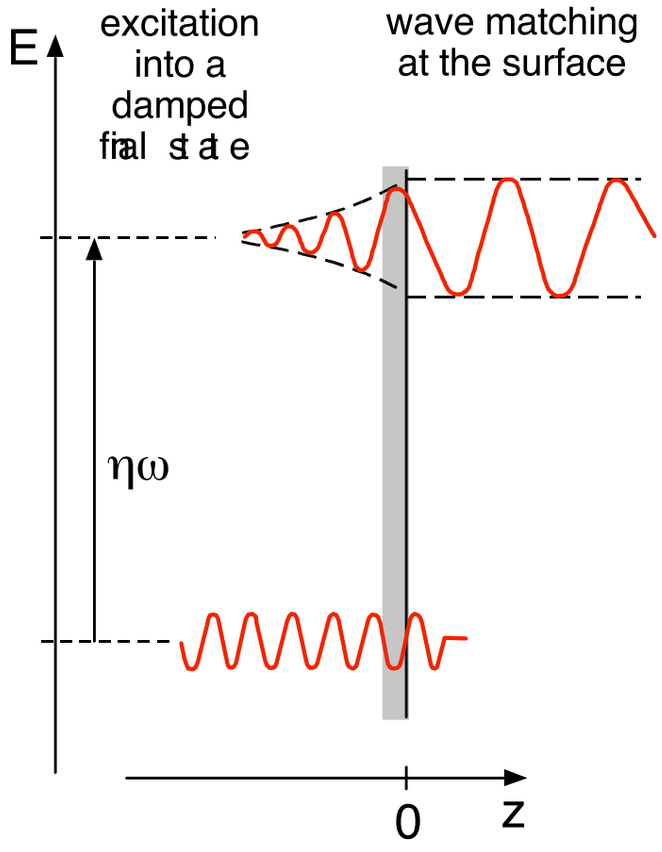


Step 1 accomplished

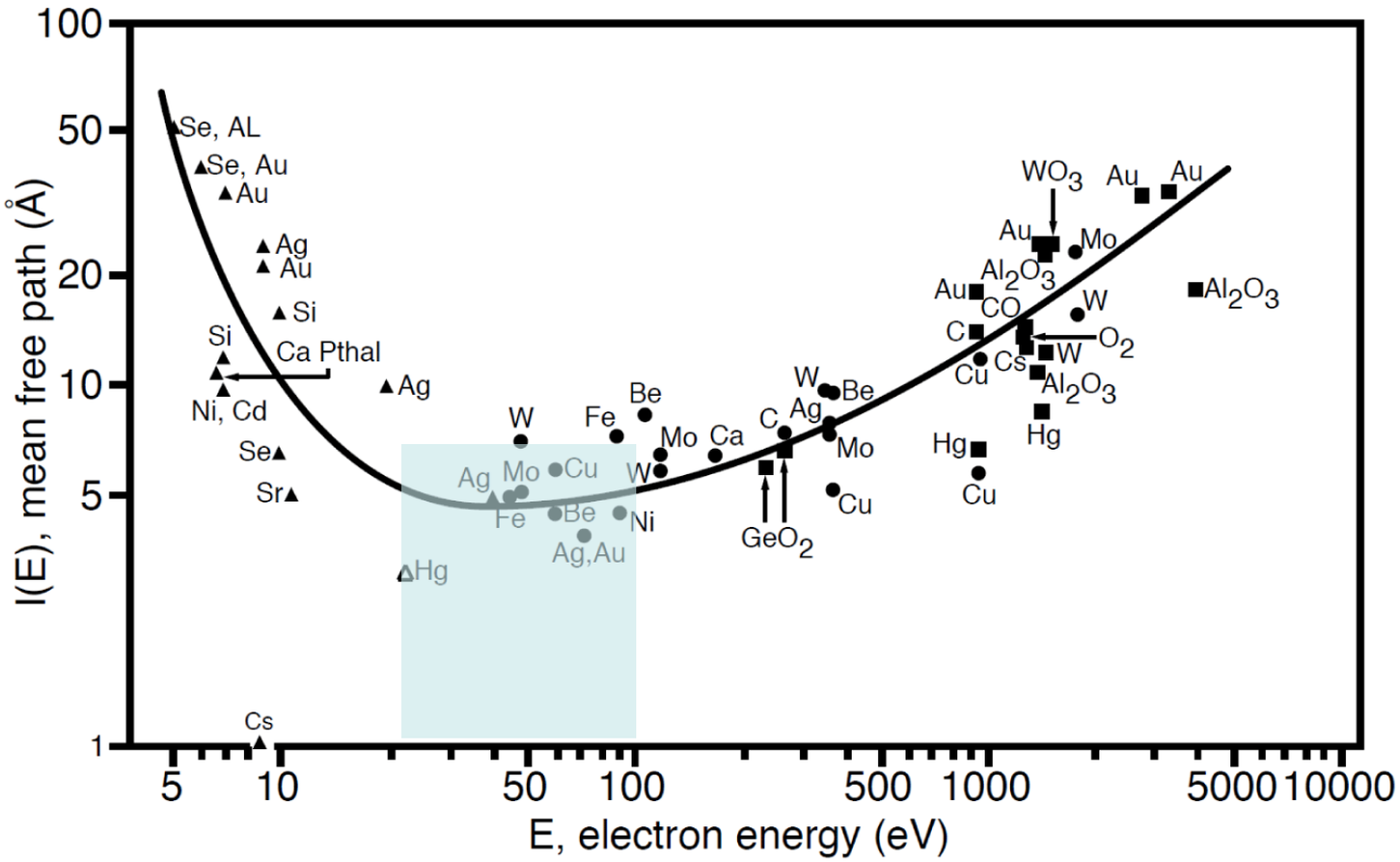
Beware!

3 step model is strong simplification; quantitative description only possible by matching wave function of initial and final state

three-step model — one-step model



Step 2: Transport to surface



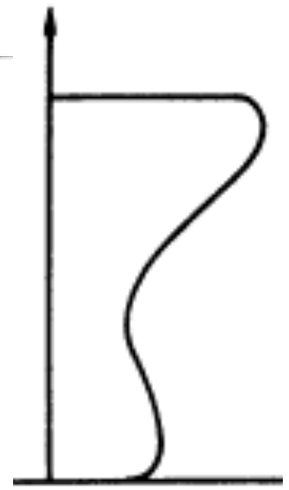
"Universal" curve

Strong simplification!

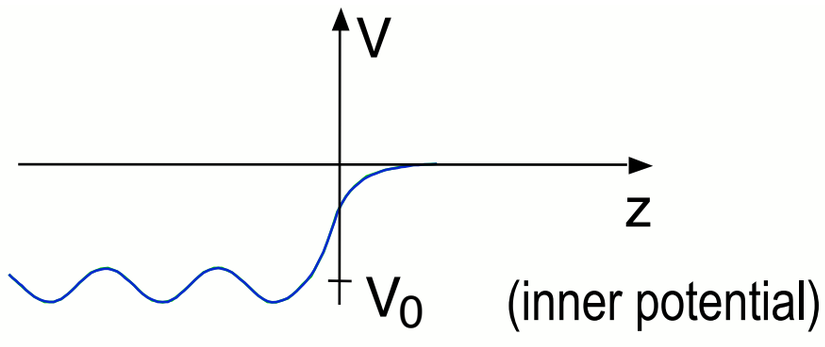
Only valid for localised states

- 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)

Step 3: Transmission through the surface



The potential barrier at the surface slows the electron in the direction normal to the surface → $k_{in\perp} > k_{out\perp}$

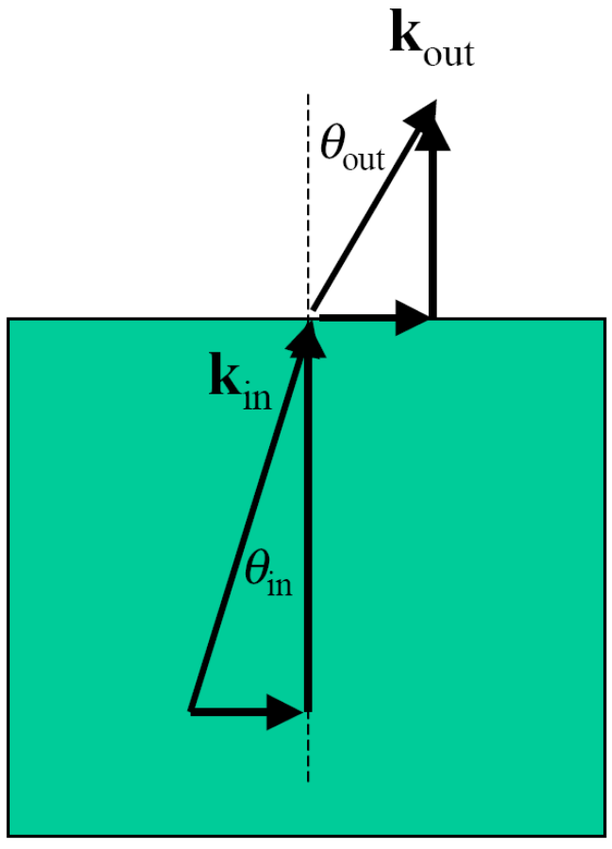


Kinematic relations:

$$k_{out} = \sqrt{\frac{2m}{\hbar^2} E_{kin}}$$

$$k_{in} = \sqrt{\frac{2m}{\hbar^2} (E_{kin} - V_0)}$$

$$k_{||out} = k_{||in} \equiv k_{||}$$

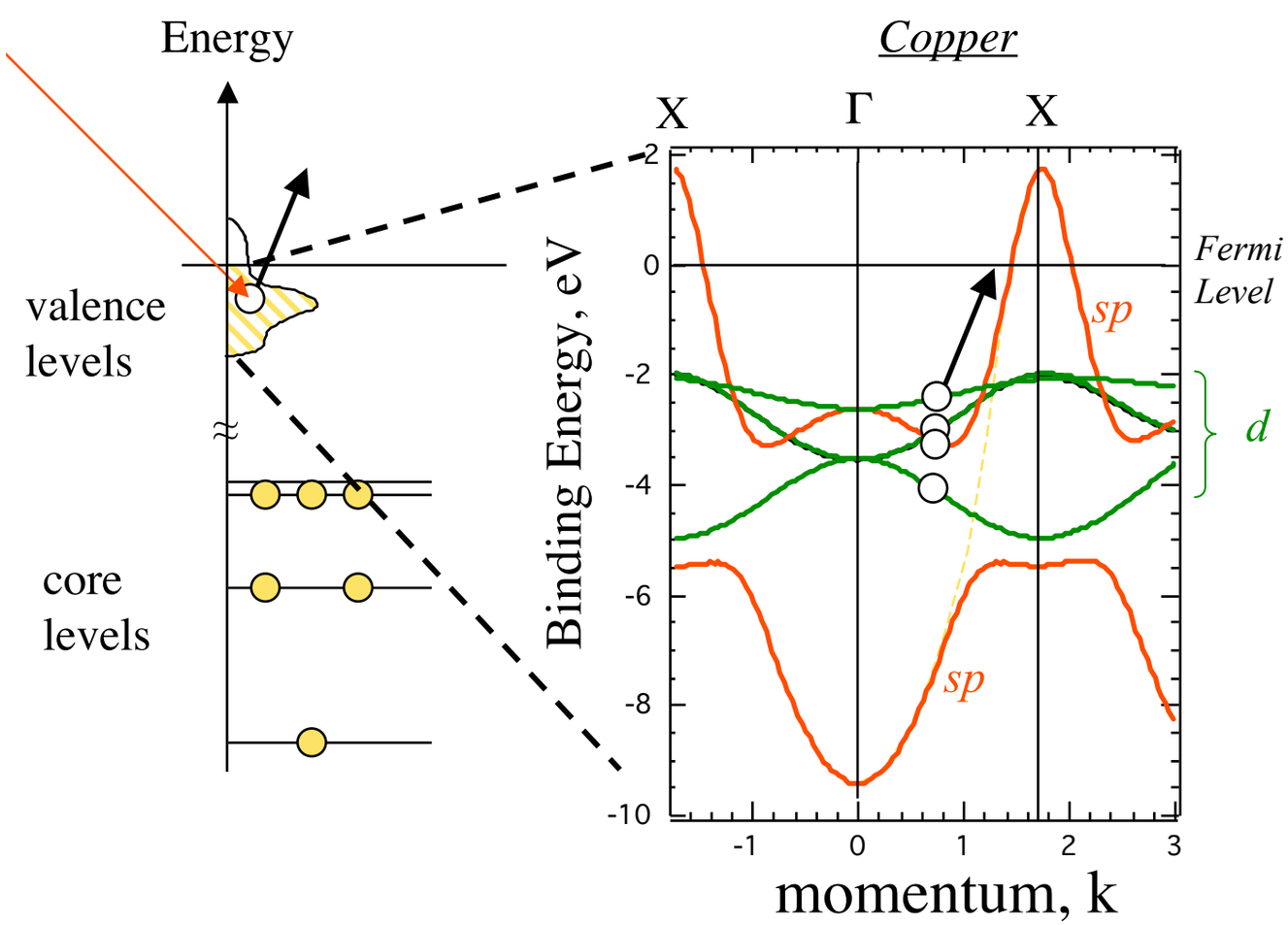


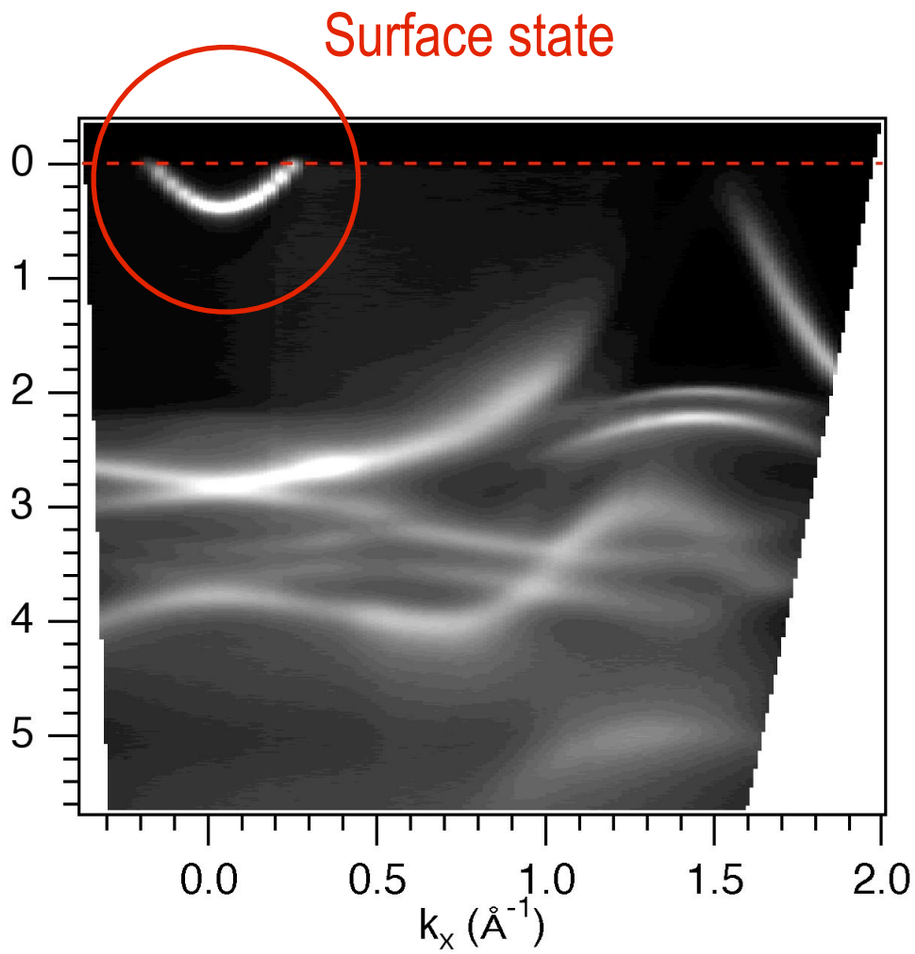
Snell's law:

$$k_{||} = \sin\theta_{out} \sqrt{\frac{2m}{\hbar^2} E_{kin}} = \sin\theta_{in} \sqrt{\frac{2m}{\hbar^2} (E_{kin} + V_0)}$$

$$k_{||} \approx 0.512 \sqrt{E_{kin}} \sin\theta_{out}$$

Angle-Resolved Photoemission from Cu(111)

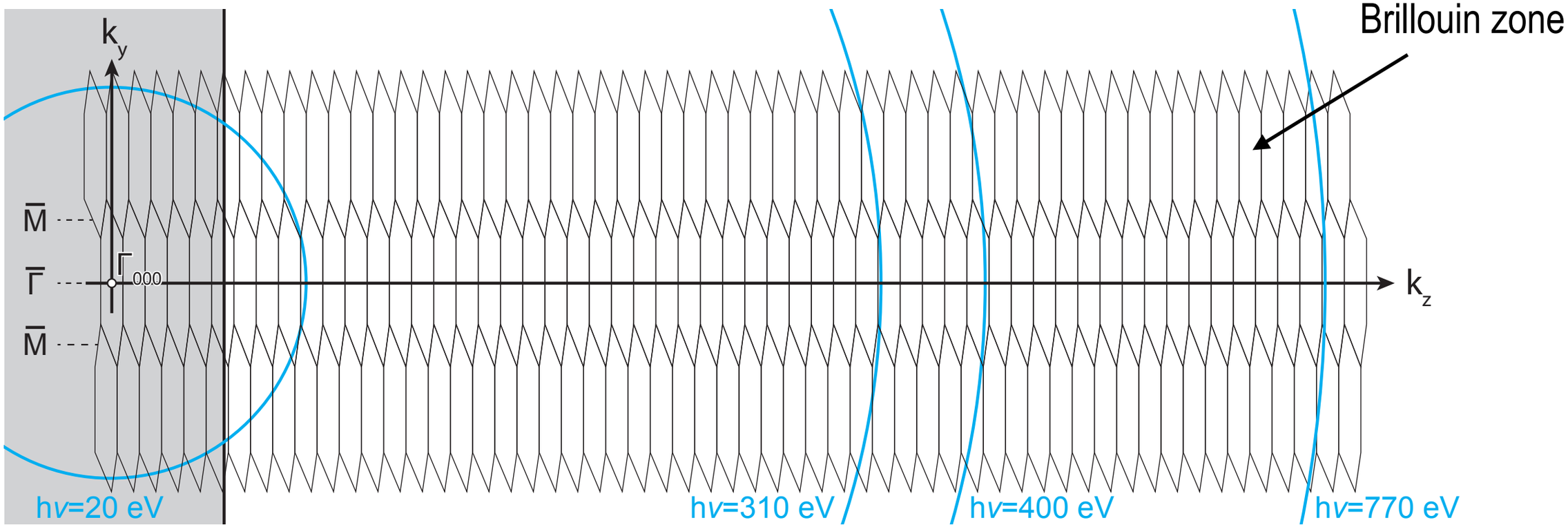




scanning of E_i *and* θ:

Band structure along curved line in 3D k - space

Determining the out-of-plane momentum



$$k_\perp = \sqrt{\frac{2m_e\left(E_{kin}+V_0\right)\cos\theta}{\hbar^2}}$$

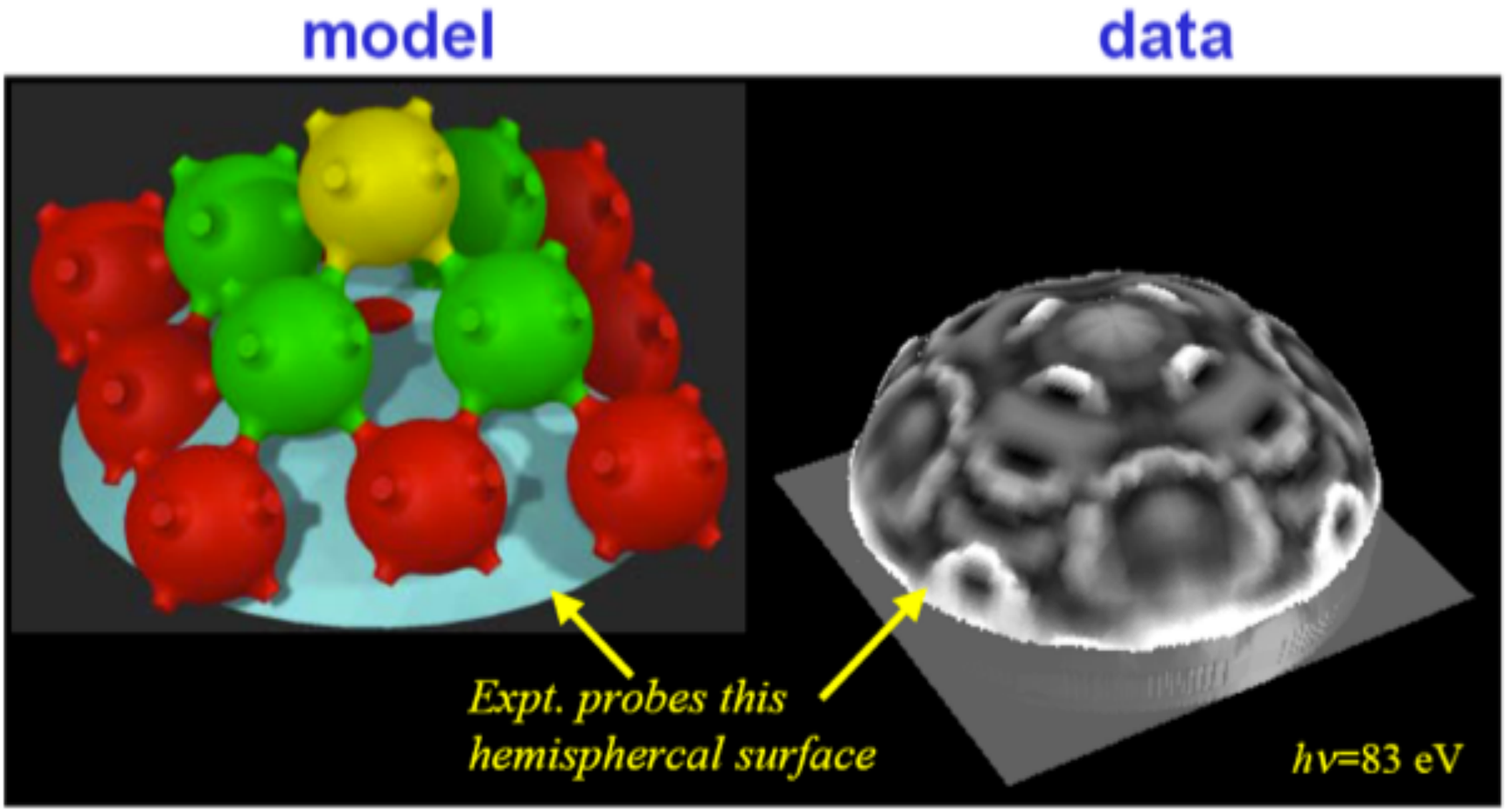
Only unknown parameter is inner potential: typically -20eV < V_0 < 20eV

Obtain from fitting to known lattice parameter *c*

In practice: around normal emission and to know where in the Brillouin zone

$$k_\perp^{\mathrm{BZ}} = 0.512\sqrt{E_{kin}+V_0}\,\frac{c}{2\pi}$$

Example Cu(100) (3D)



Courtesy E. Rotenberg and S. D. Kevan

Photon energy dependence

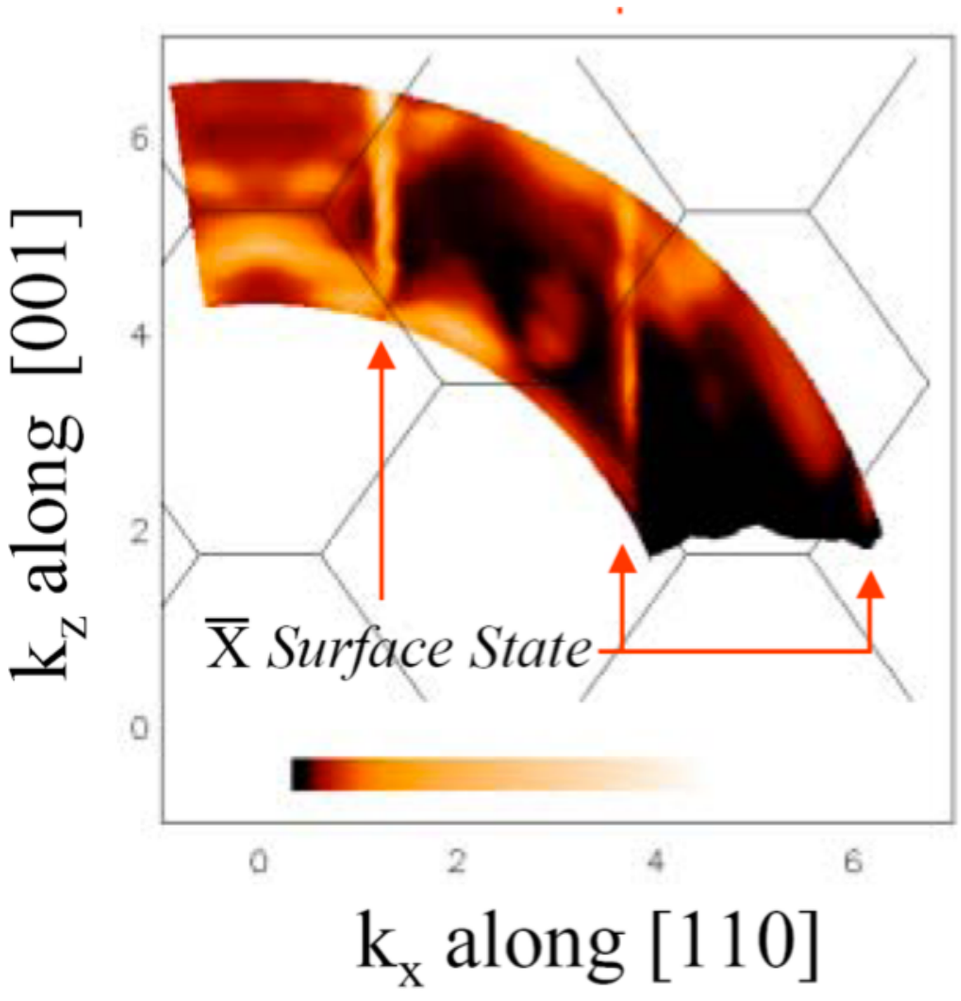
Cu(100) with varying photon energy

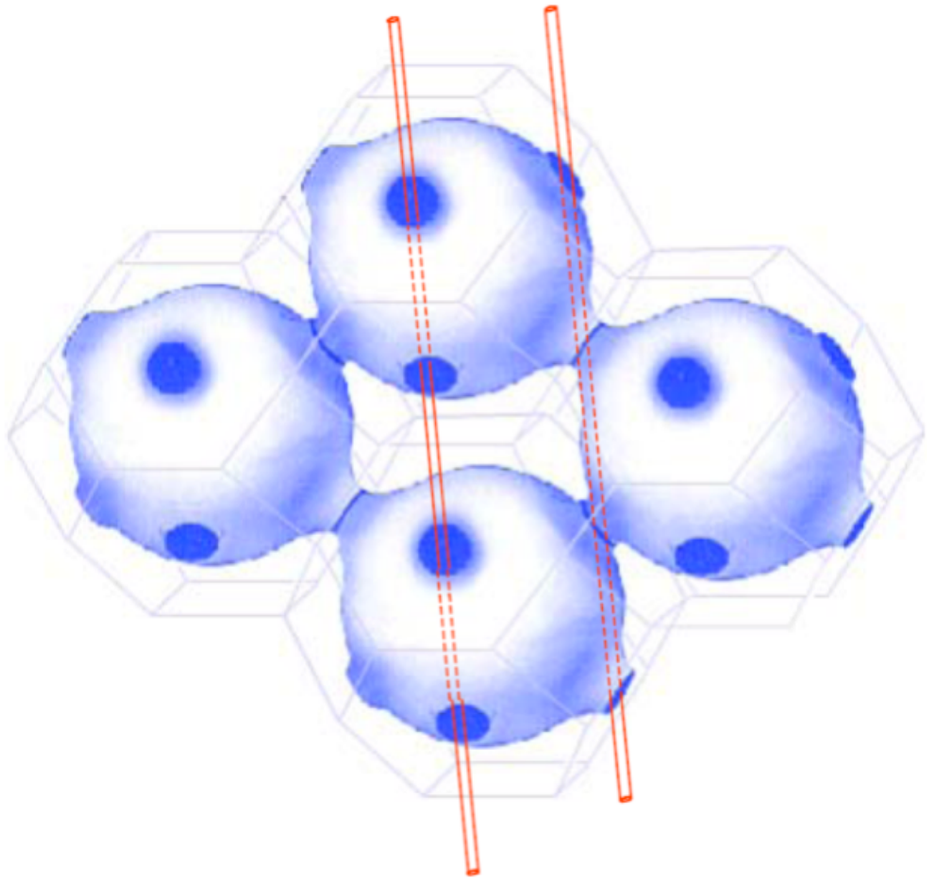
Surface states do not disperse with k_z and appear as lines

Bulk states show dispersion as expected

Easiest way to distinguish surface states from bulk states

Beware of k_z broadening due to finite probing depth



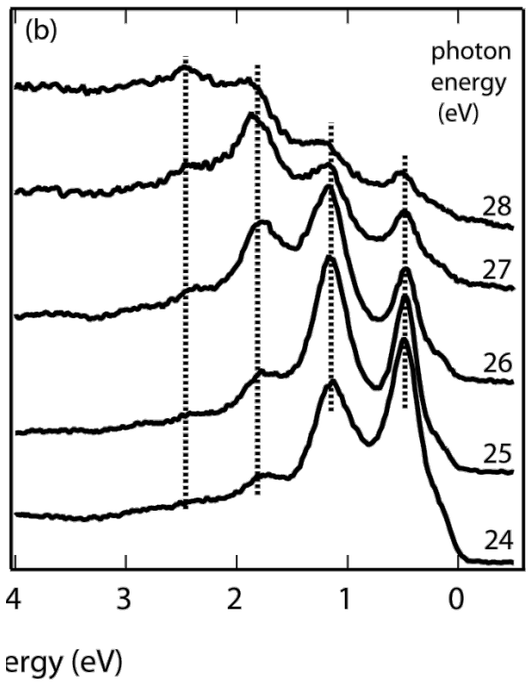


Courtesy E. Rotenberg

Quantitative aspects of ARPES

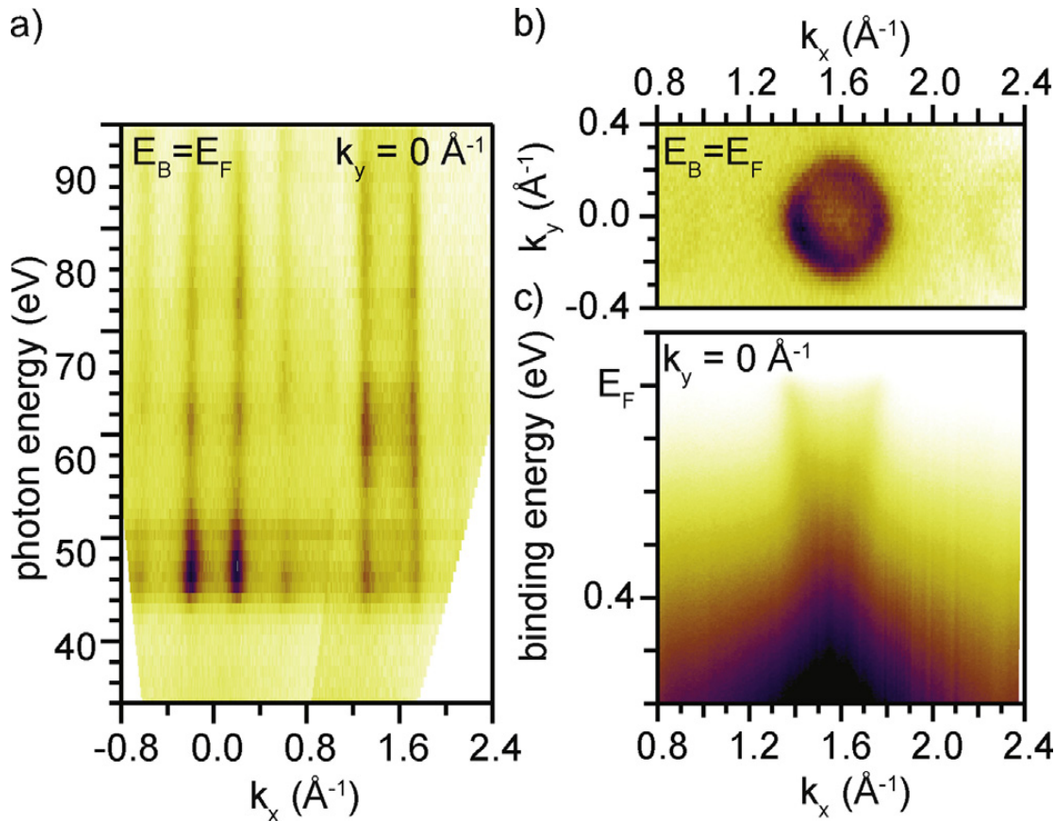
Intensity of photoemission lines measured with ARPES can vary strongly

Pb quantum well states on Cu(111)



J.H. Dil et al, Phys. Rev. B, 70, 45405, (2004)

Surface states of $CaTiO_3$(001)



S. Muff et al. Applied Surface Science 5, 229 (2017)

How meaningful is the intensity for the properties of the state?

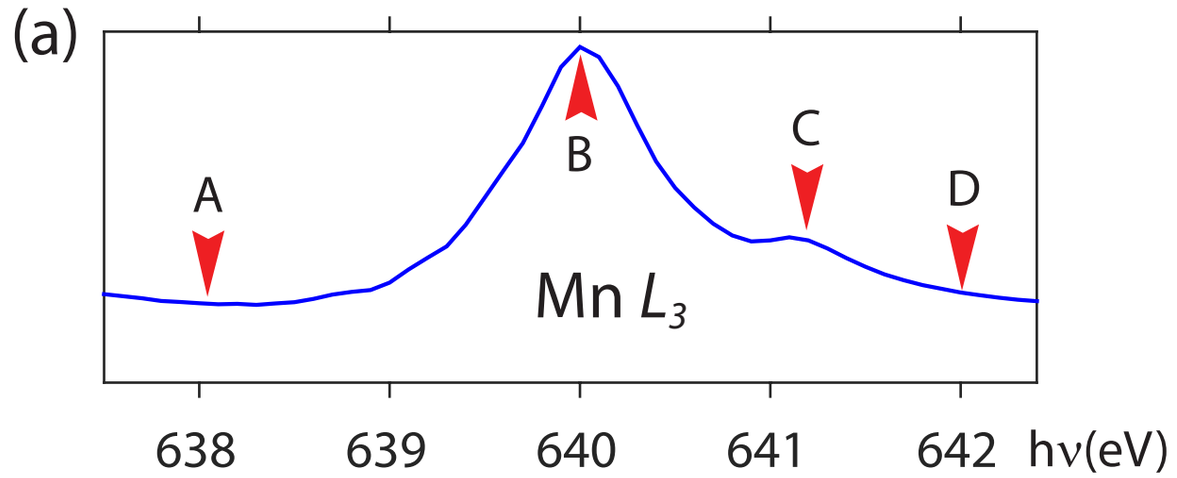
What determines these intensity variations and what can we learn from them?

Intensity is **not** measurement of density of states!

Resonant photoemission (impurities)

Atomic cross section also plays role for valence band

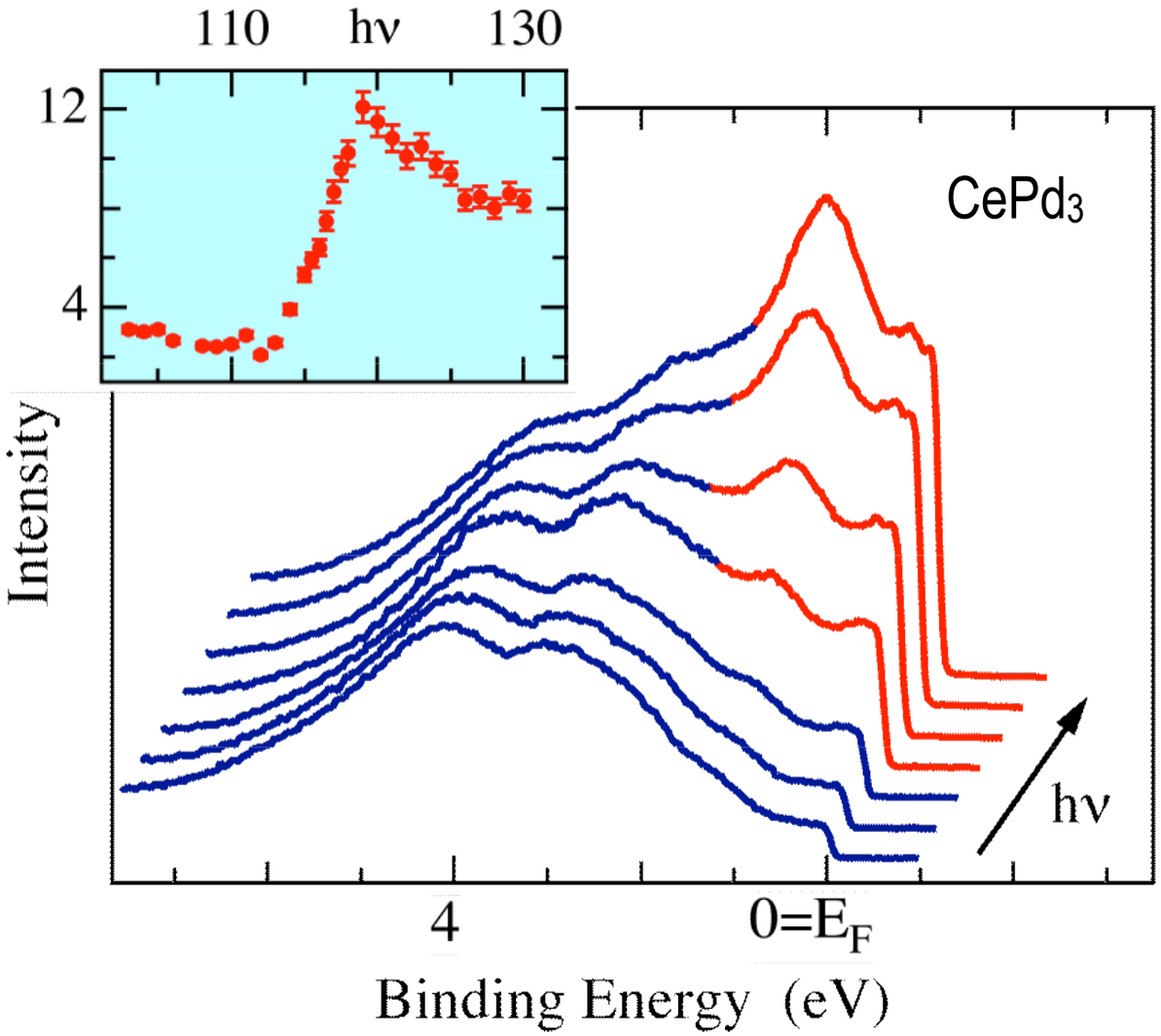
Mn doped GeTe



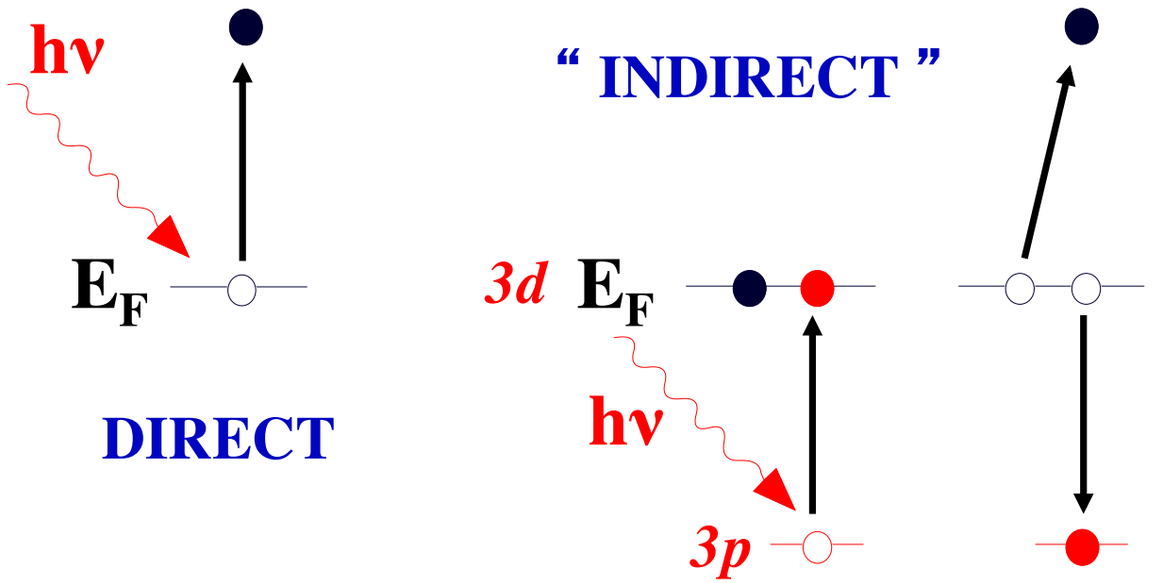
J. Krempasky et al. Nature Comm. 7, 13071 (2016)

Resonant photoemission (alloys)

Fano line shape



TWO INTERFERING PROCESSES



Requires a synchrotron to tune hv exactly

Matrix element effects

Relies on **sudden approximation**: photoelectron emitted from N particle system does not interact with N-1 system *after* photo-excitation

Fermi's Golden Rule for transition probability:

$$w = \frac{2\pi}{\hbar}|\langle\Psi_f|H_{int}|\Psi_i\rangle|^2\delta(E_f - E_i - \hbar\omega)$$

Deep thought:

What happens if ψ_i or ψ_f is degenerate and several transitions are allowed?

For dipole allowed transitions:

$$H_{int} = \frac{e}{mc}A \bullet p$$

Dipole Selection Rules:

$$\Delta l = \pm 1;$$
$$\Delta m = 0, \pm 1.$$

$$I \propto |\langle\Psi_f|A \bullet p|\Psi_i\rangle|^2$$

Final state

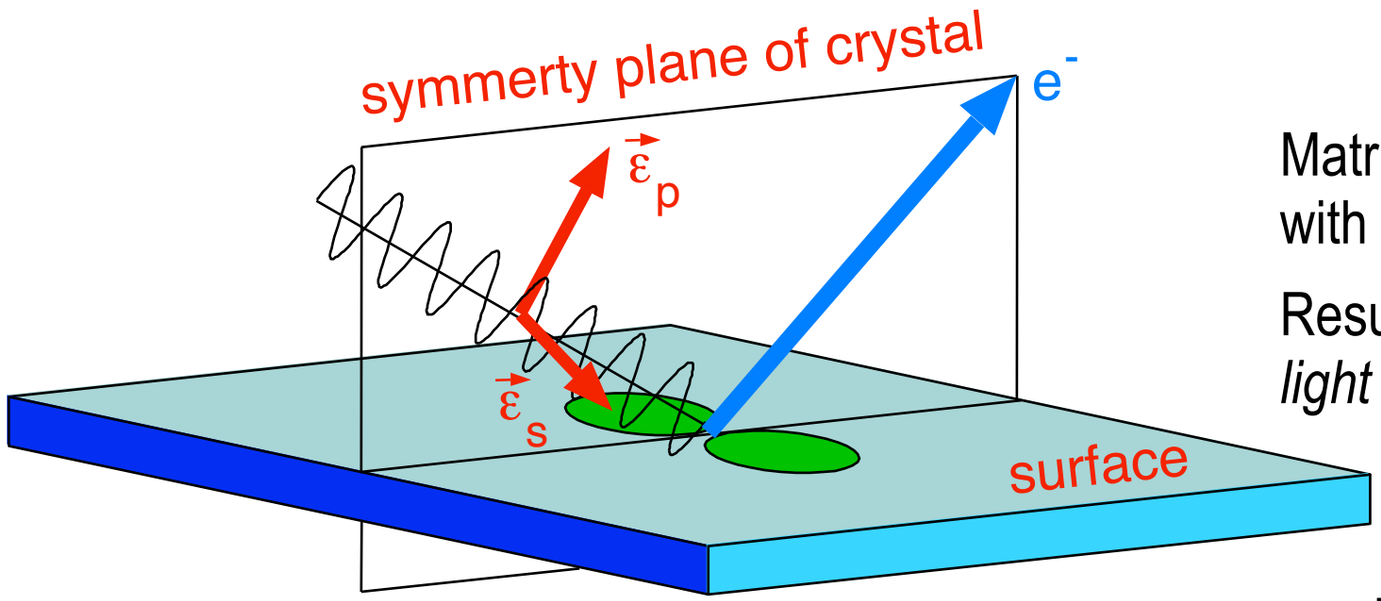
Initial state

Measured intensity

Photon E field

Electron momentum

Symmetry selection rules (simplified)



Matrix elements have individual symmetries with respect to sample

Result: *orbitals are excited if orbital lobe along light polarisation direction (projection)*

For accessible extensive description:
S. Moser J. Electron Spectroscopy and Related Phenomena 214, 29 (2017)

$\vec{\varepsilon}_p$ photon polarization in...

$\vec{\varepsilon}_s$ ...perpendicular ("senkrecht") to...scattering plane

$$I \propto \left|\langle \Psi_f | A \bullet p | \Psi_i \rangle\right|^2$$

Even for p-pol
odd for s-pol

$|\psi_f\rangle$ Plane wave always even

$A \bullet p$

$|\psi_i\rangle$ Depends on band symmetry (s, $p_{x,y,z}$)

p - pol.	+1	+1	-1	0
	+1	+1	+1	max.
s - pol.	+1	-1	-1	max.
	+1	-1	+1	0

Group theory and selection rules

Selection rules are formally derived from direct product of groups $G_A \otimes G_B$

When the symmetry operations of the group are applied, this matrix element must transform as a constant. Conversely, if the matrix element is not invariant under the symmetry operations which form the group of Schrödinger's equation, then the matrix element must vanish. "Applications of Group Theory to the Physics of Solids" M. S. Dresselhaus (2002)

TABLE VIII. Allowed dipole transitions (+) at P; $\vec{A}\cdot\vec{p}$ is represented by P_4.

T_d	P_1	P_2	P_3	P_4	P_5
P_1	...	...	...	+	...
P_2	...	...	...	...	+
P_3	...	...	...	+	+
P_4	+	...	+	+	+
P_5	...	+	+	+	+

TABLE II. Allowed dipole transitions (+) at Γ and H. $\vec{A}\cdot\vec{p}$ is represented by Γ_{15}.

O_h	Γ_1	Γ_2	Γ_{12}	$\Gamma_{15'}$	$\Gamma_{25'}$	$\Gamma_{1'}$	$\Gamma_{2'}$	$\Gamma_{12'}$	Γ_{15}	Γ_{25}
Γ_1	...	...	...	...	...	...	...	...	+	...
Γ_2	...	...	...	...	...	...	...	...	...	+
Γ_{12}	...	...	...	...	...	...	...	...	+	+
$\Gamma_{15'}$	...	...	...	...	...	+	...	+	+	+
$\Gamma_{25'}$	...	...	...	...	...	...	+	+	+	+
$\Gamma_{1'}$	...	...	...	+	...	...	...	...	...	...
$\Gamma_{2'}$	...	...	...	...	+	...	...	...	...	...
$\Gamma_{12'}$	...	...	...	+	+	...	...	...	...	...
Γ_{15}	+	...	+	+	+	...	...	...	...	...
Γ_{25}	...	+	+	+	+	...	...	...	...	...

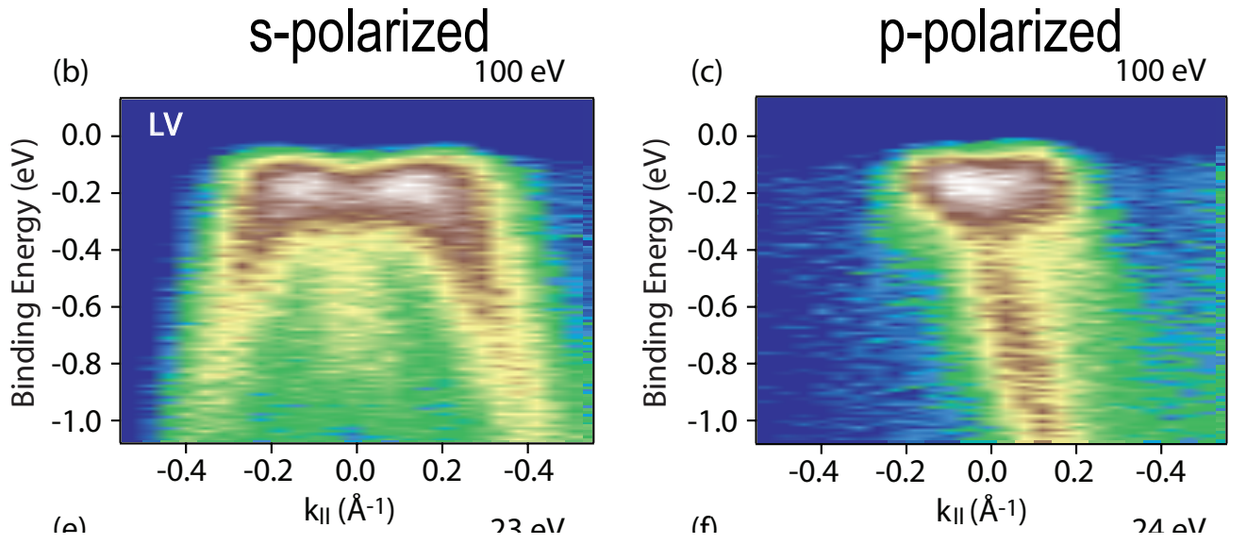
"Dipole selection rules for optical transitions in the fcc and bcc lattices" W. Eberhardt and F. J. Himpsel, Phys. Rev. B 21, 5572 (1980)

If spin-orbit interaction plays role, double group theory should be used

"Properties of the 32 Point Groups" by Koster, Dimmock, Wheeler and Statz

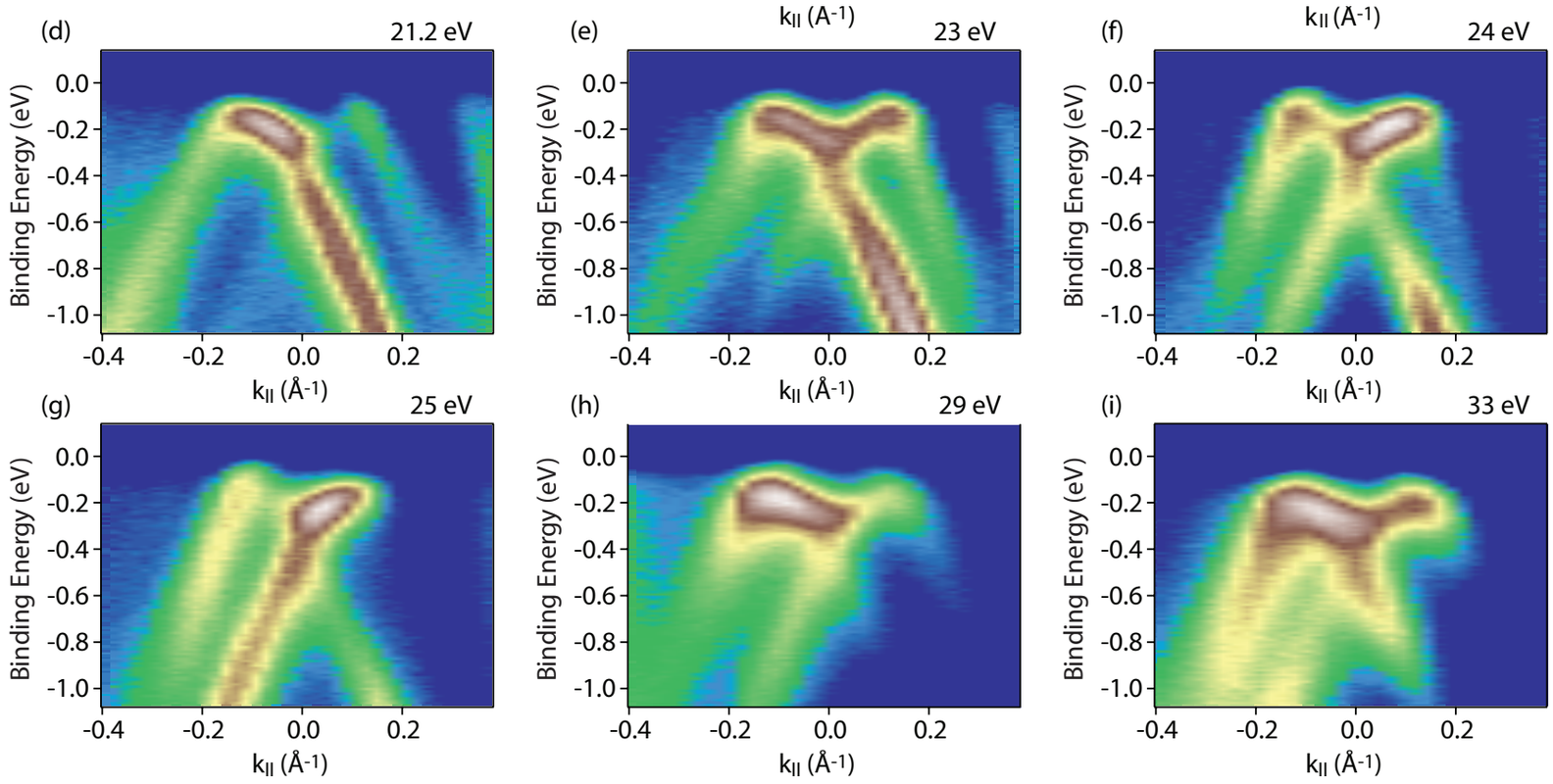
Three types of “matrix element effects”

1) Dipole transition matrix



2) Availability of (correct) final state: dependent on excitation energy

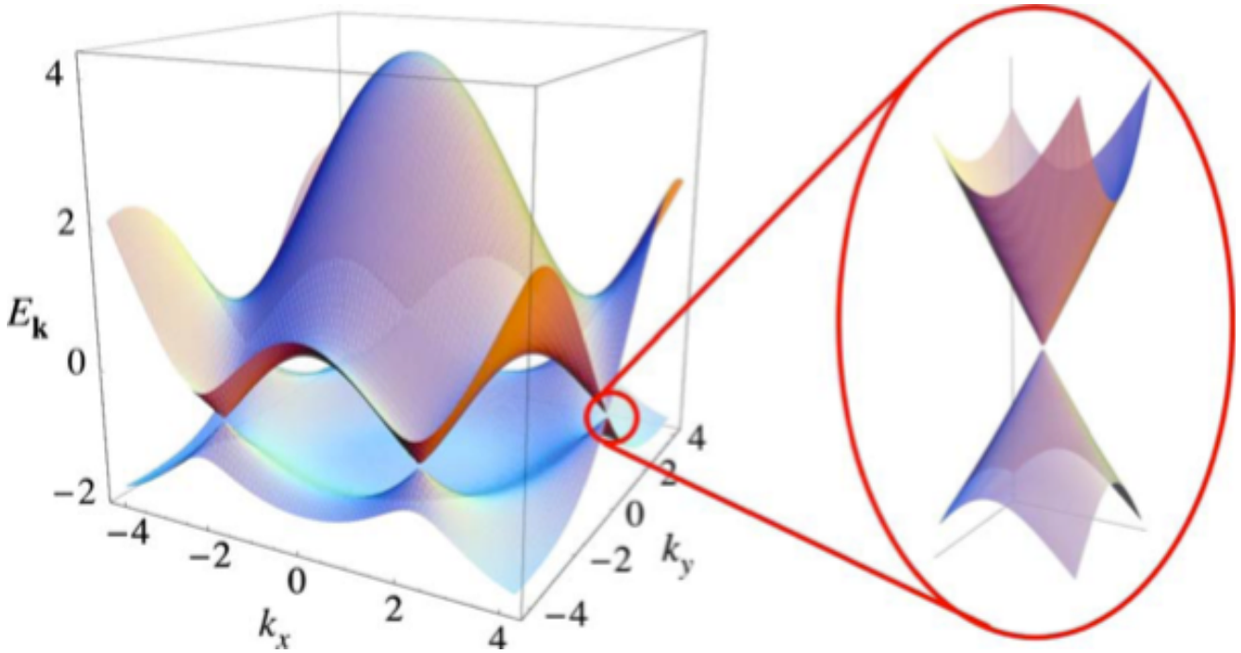
Here enhanced due to spin-orbit interaction

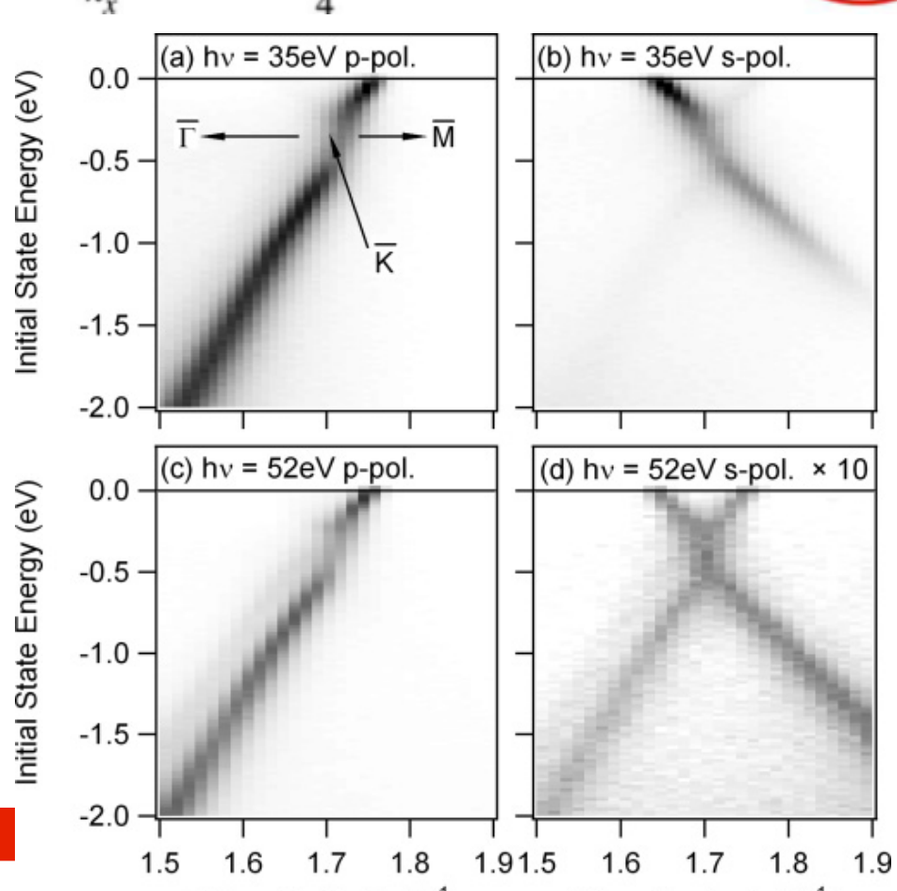


3) Electron diffraction/interference: dependent on photon energy and Brillouin zone

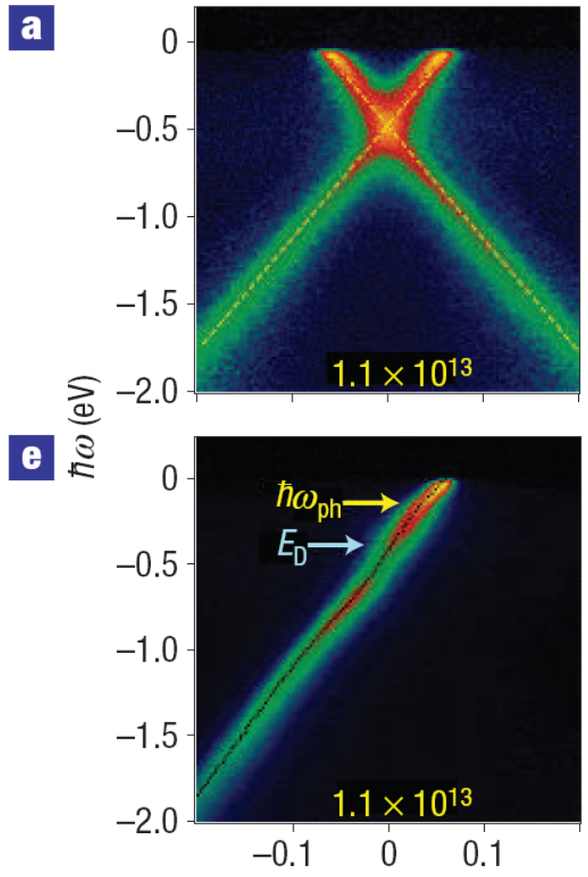
Intensity interference effects for graphene

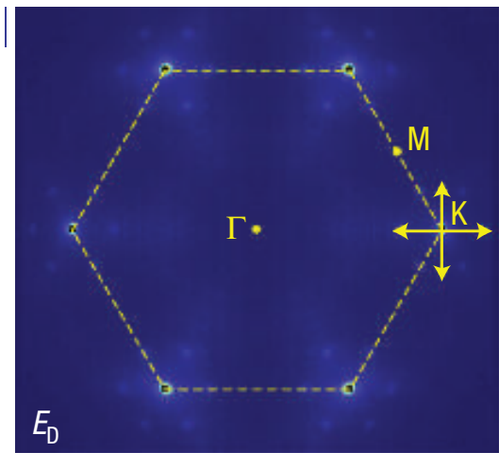
Graphene band structure





Dirac cone suppressed along one direction





A. Bostwick et al. Nature Physics **3**, 36 (2007)

Full cone can be made visible by different light polarization and energy

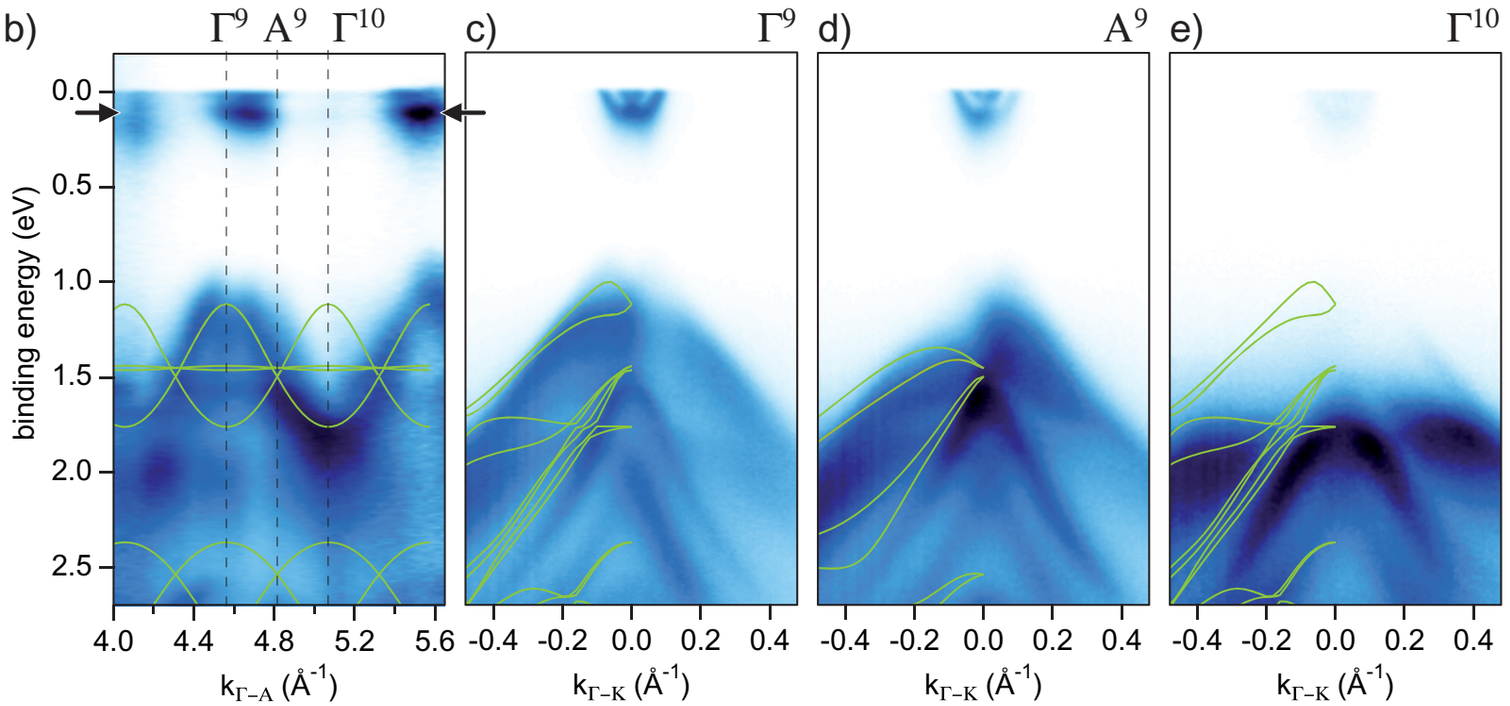
Same (even/odd) symmetry, but originating from different Brillouin zone

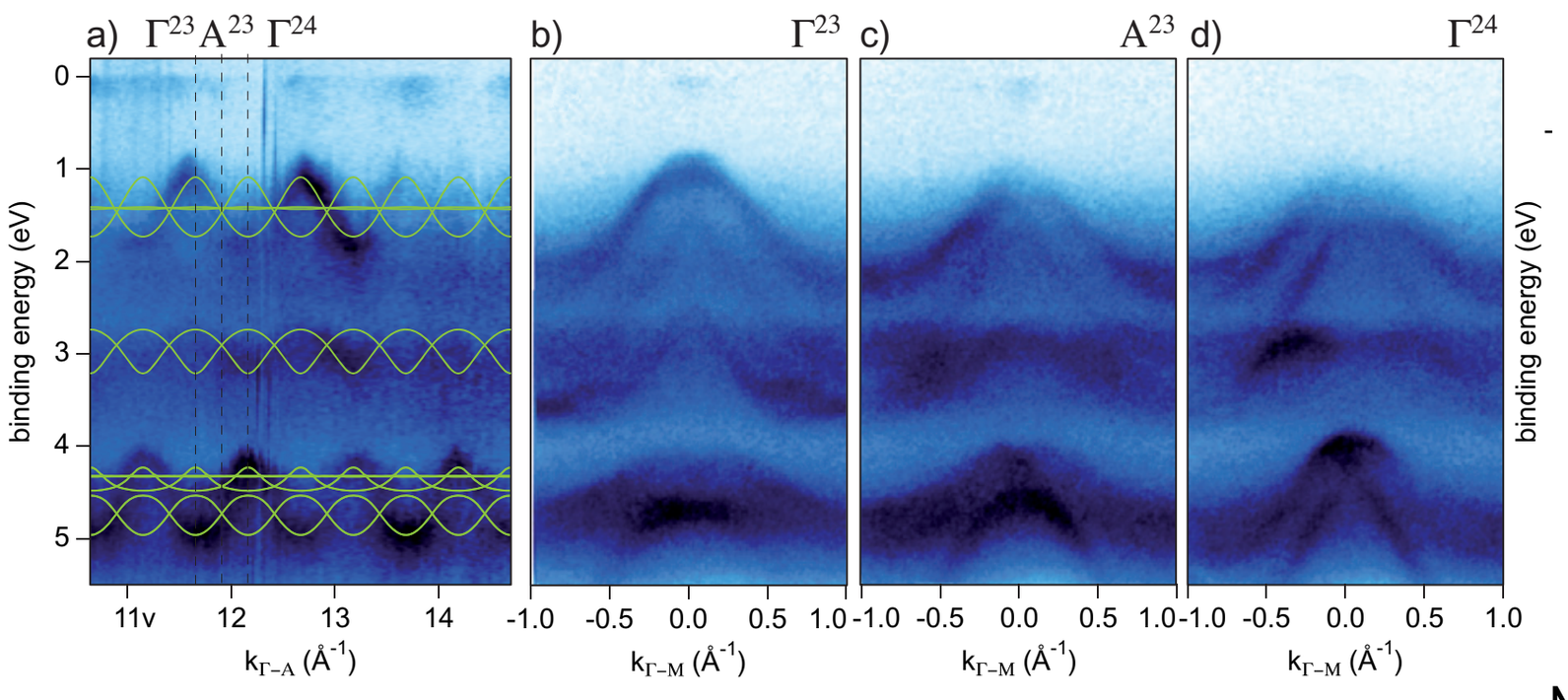
I. Gierz et al. PRB 83, 121408(R) (2011)

EPFL

PSI

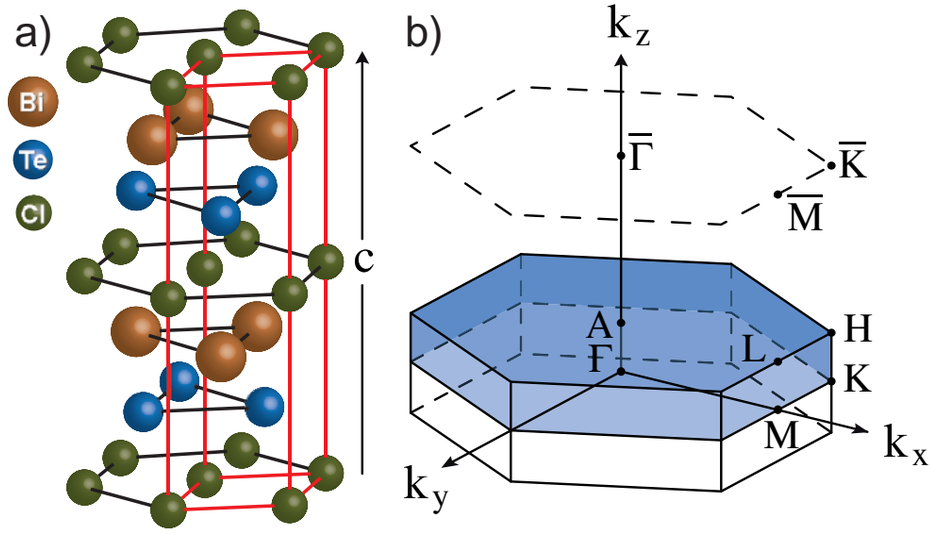
Non-symmorphic space group of BiTeCl





G. Landolt et al. New Journal of Physics 15, 085022 (2013)

Non-symmorphic space group:
Screw axis or glide plane in unit cell



Band visible only in every 2nd BZ due to interference

D. Pescia et al. Solid State Commun. 56 809 (1985)

Not every Brillouin zone looks the same!

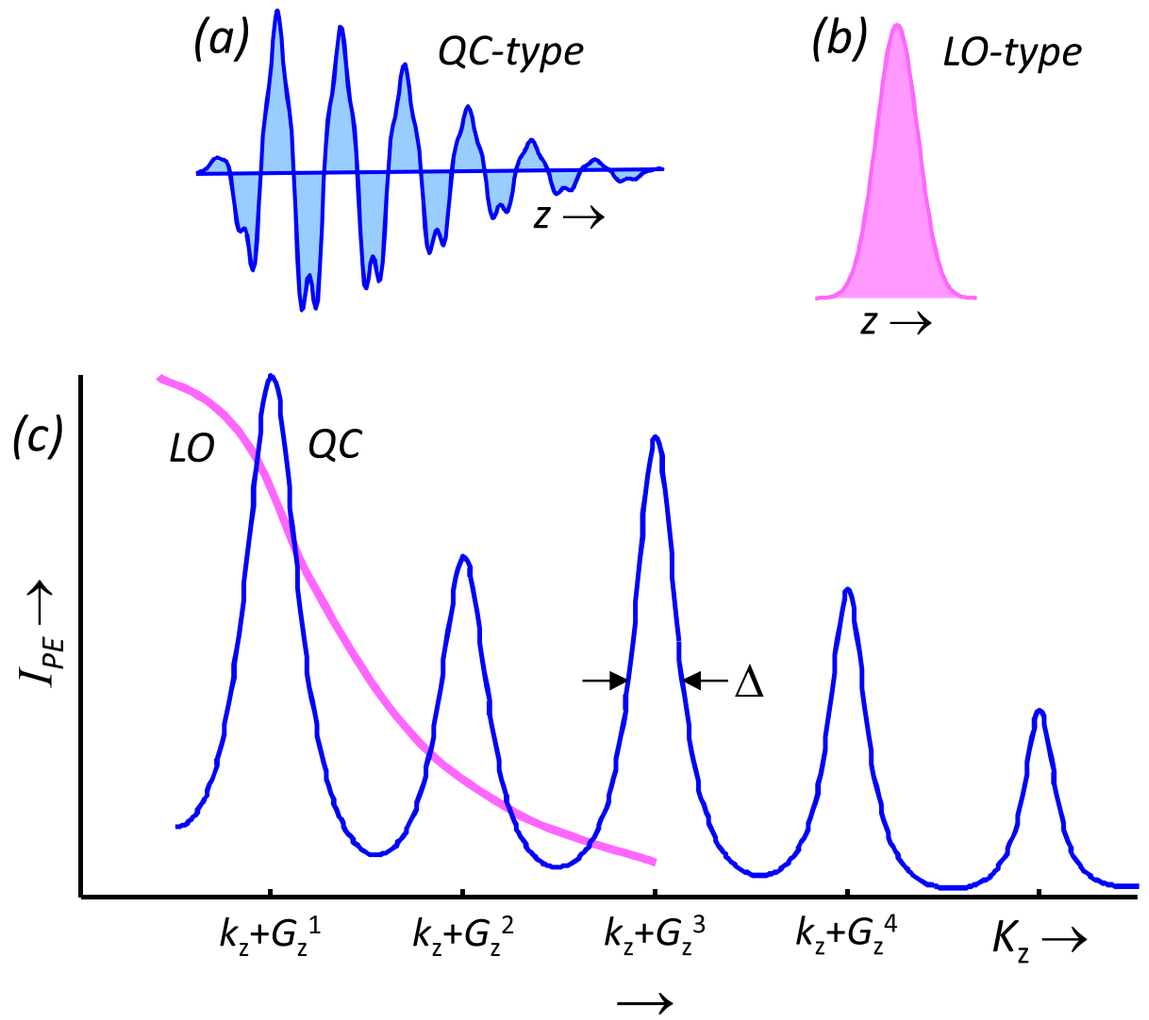
Initial state wave function extension

QC: quantum confinement

Shockley surface states

Quantum well states

…



LO: local orbital

Absorbed molecules

Dangling bond states

Surface reconstructions

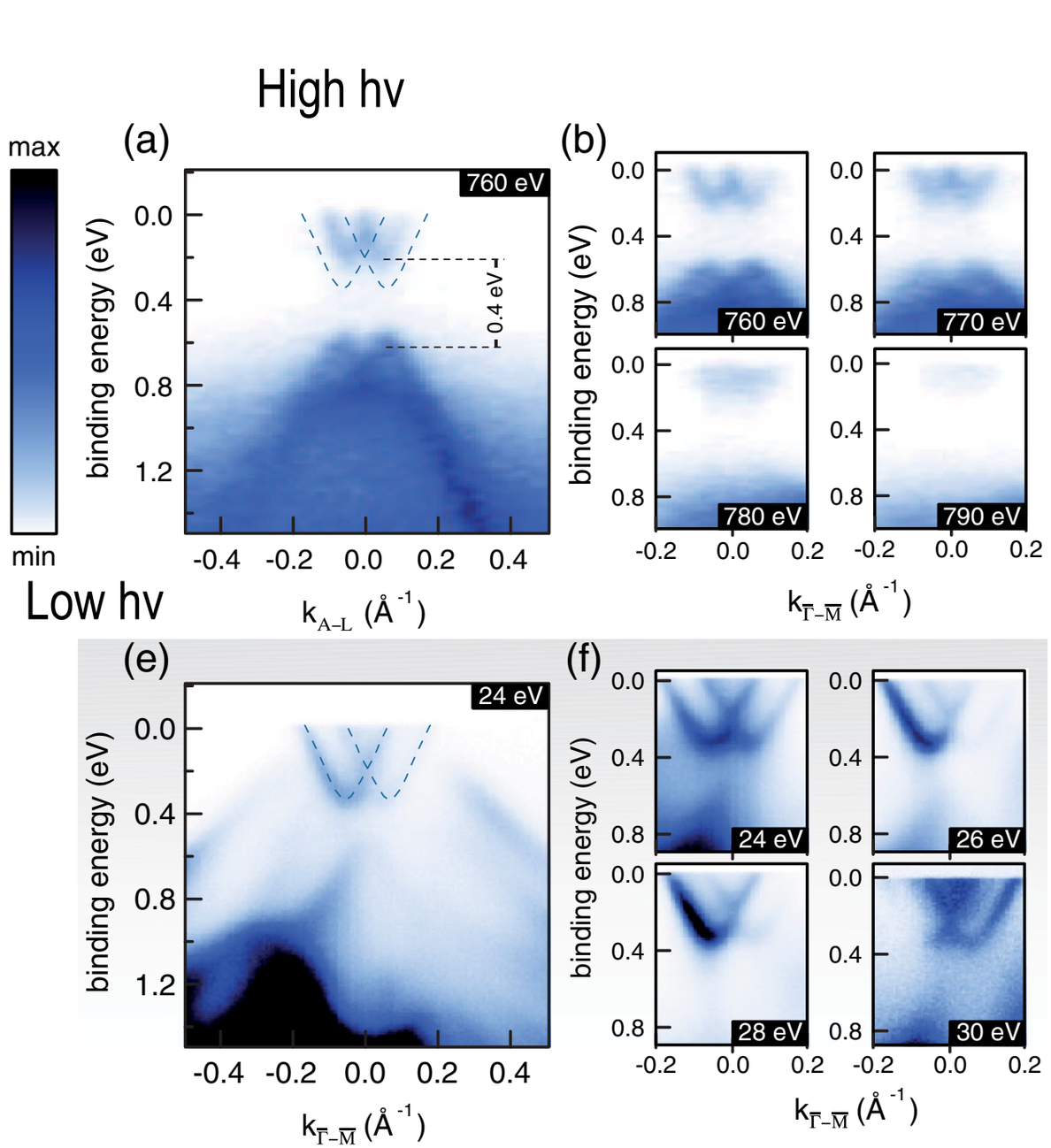
…

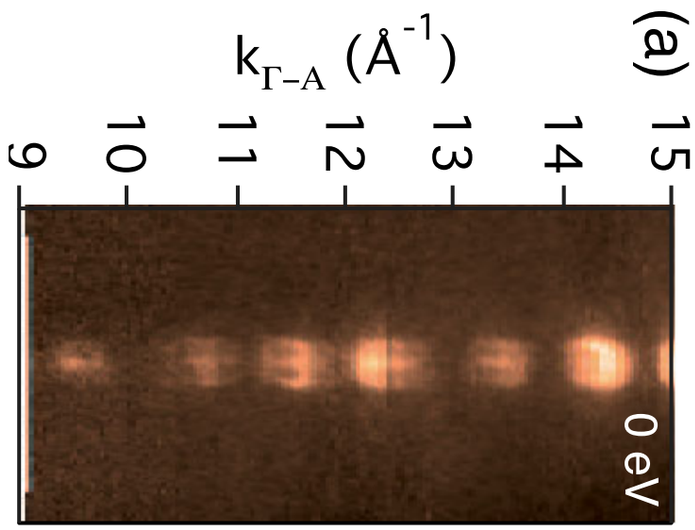
Fourier transform of single peak is single decaying feature along k_z (or hv)

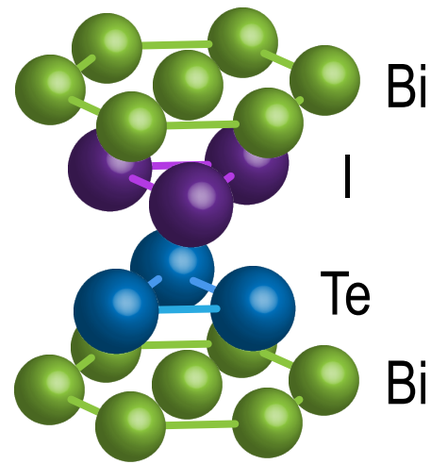
Localised surface states disappear at high hv, Shockley-like surface states remain visible

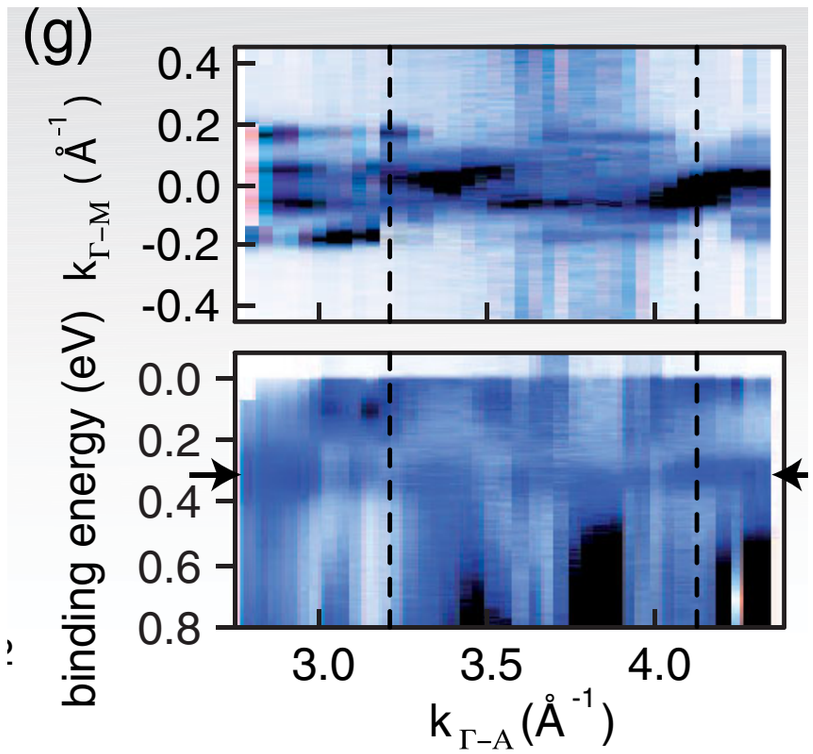
V.N. Strocov, JESRP 229, 100 (2018)

Local orbital type wave function (BiTeI)







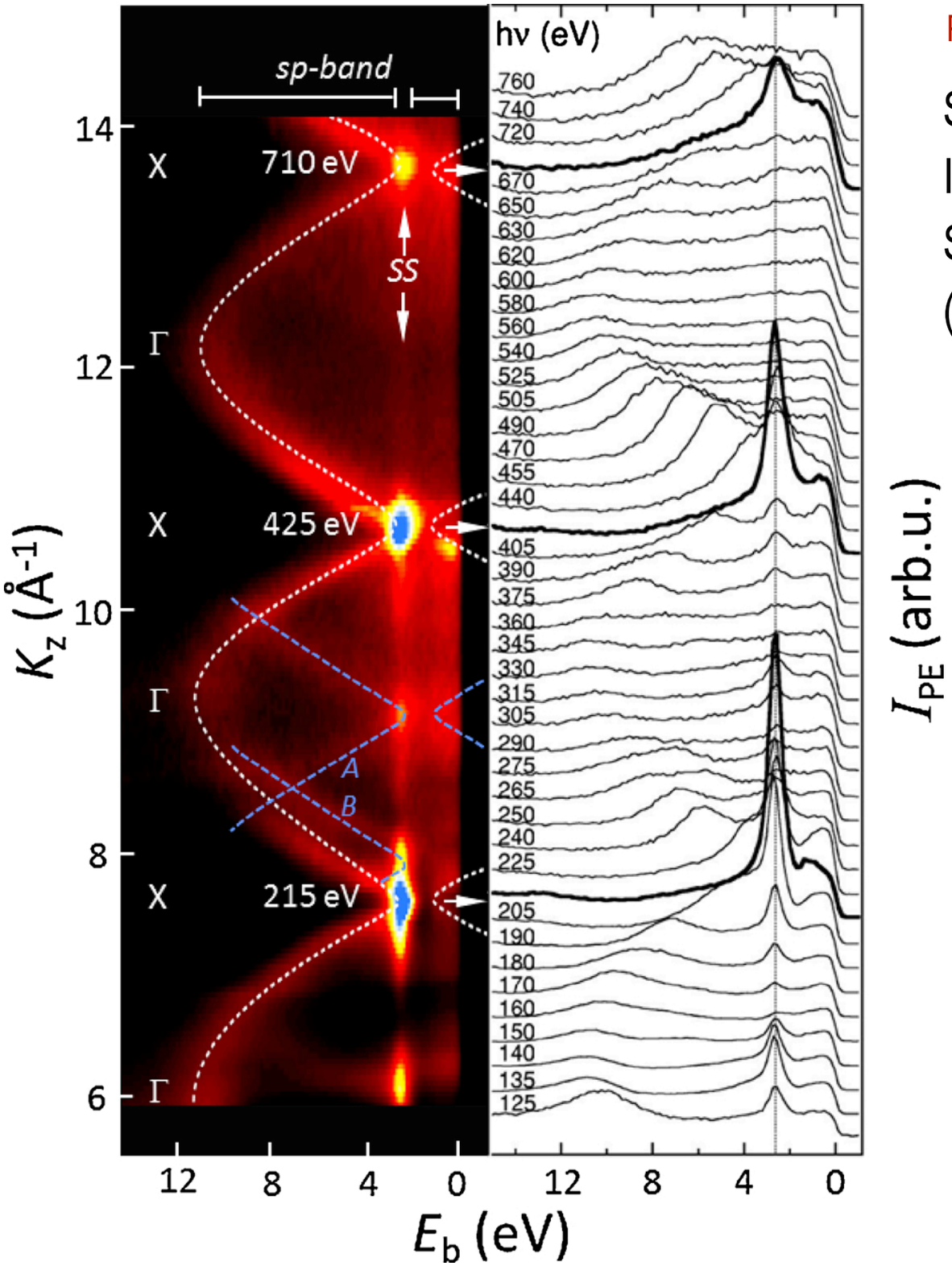


Sample cleaving leaves uncompensated (localised) states at surface

No surface states at high hv, clear surface states at low hv

Landolt et al., PRL 109, 116403 (2012)

Quantum confined wave function



P. Hofmann et al, Phys. Rev. B 66 245422. (2002)

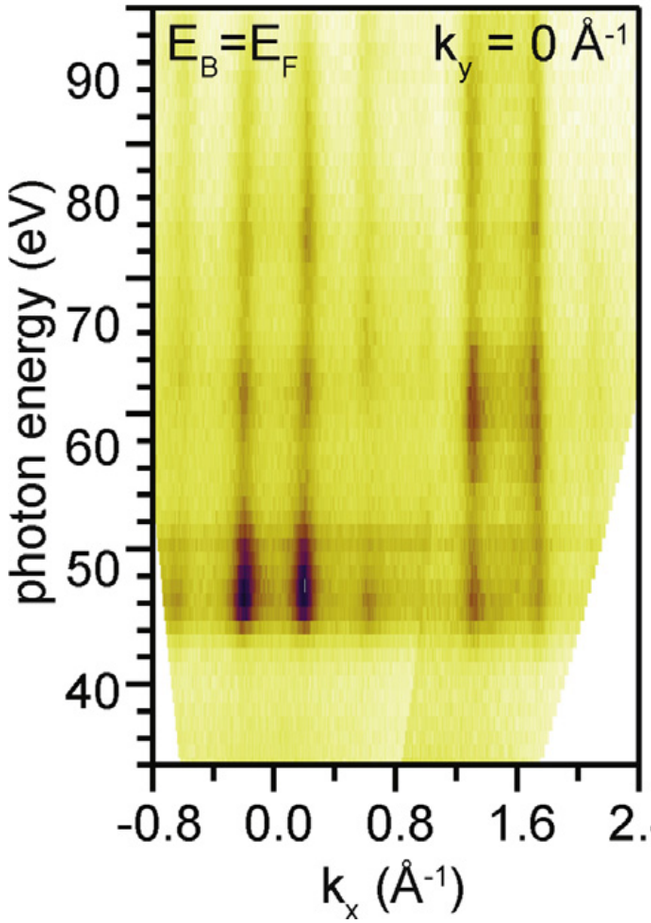
Shockley surface state of Al(100)

Intensity oscillates with photon energy

Still visible at high hv

(Topological SS is also Shockley type)

Similar effect for surface states of $CaTiO_3$(001)

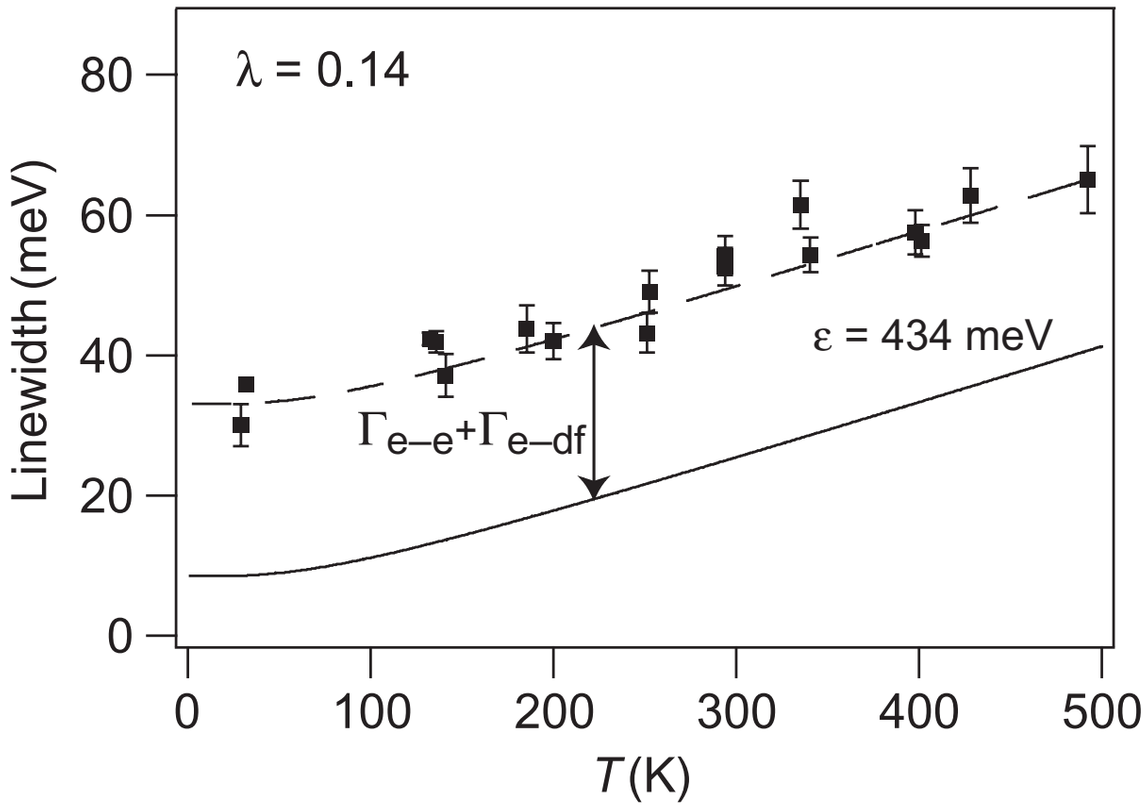


S. Muff et al. Applied Surface Science 5, 229 (2017)

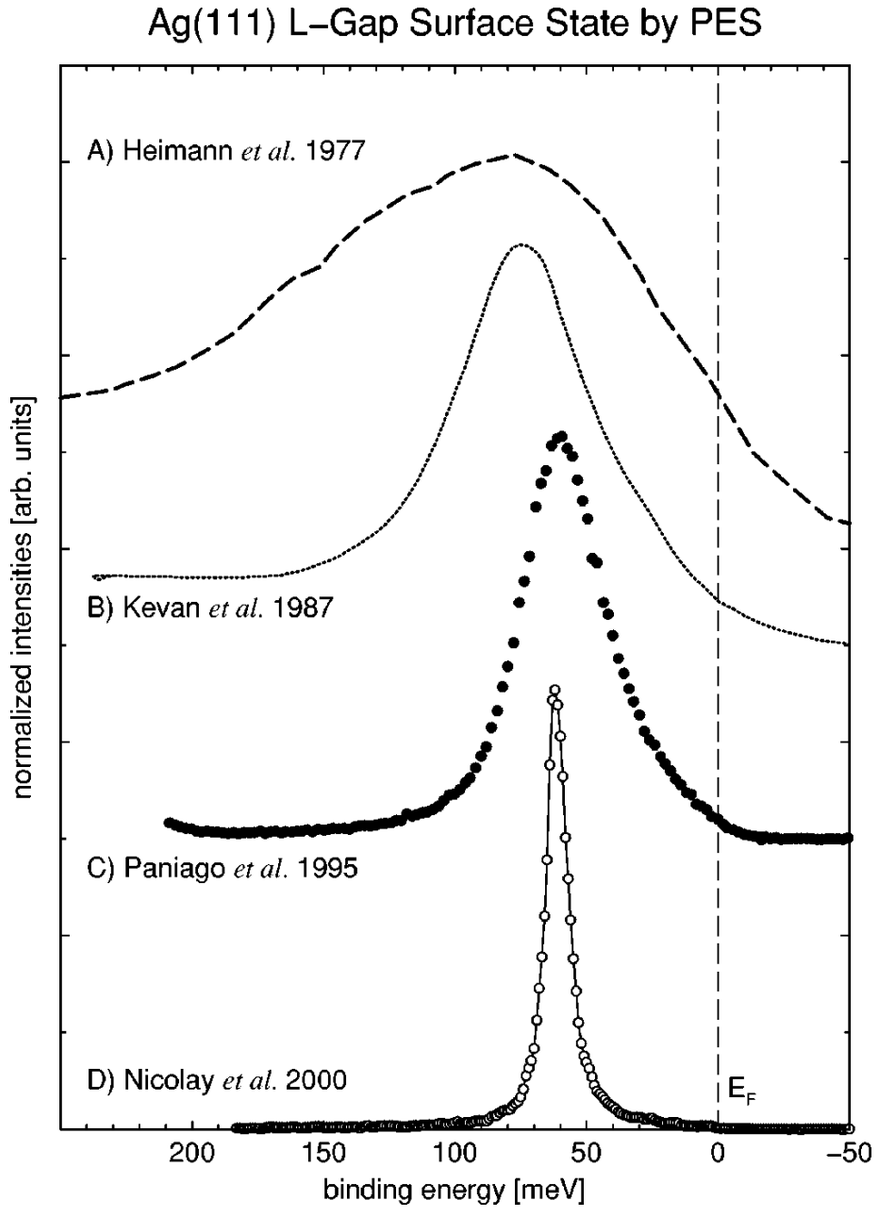
Linewidth in ARPES data

Contributions to measured linewidth:

- Instrumental resolution (photon, electron analyzer)
- Temperature (Fermi Dirac, phonons)
- Initial state lifetime
- Final state lifetime $\Gamma = \hbar/\tau$
- Interactions (electron-electron, electron-defect, …)

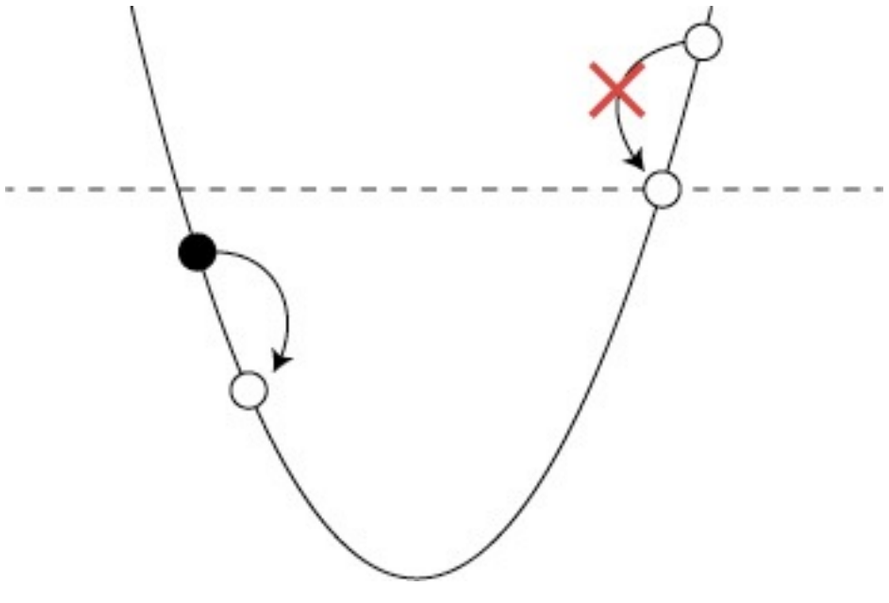


P. Hofmann et al. NJP **11** 125005 (2009)



F. Reinert et al. PRB 63, 115415 (2001)

What do we measure in ARPES?



Some physics philosophy

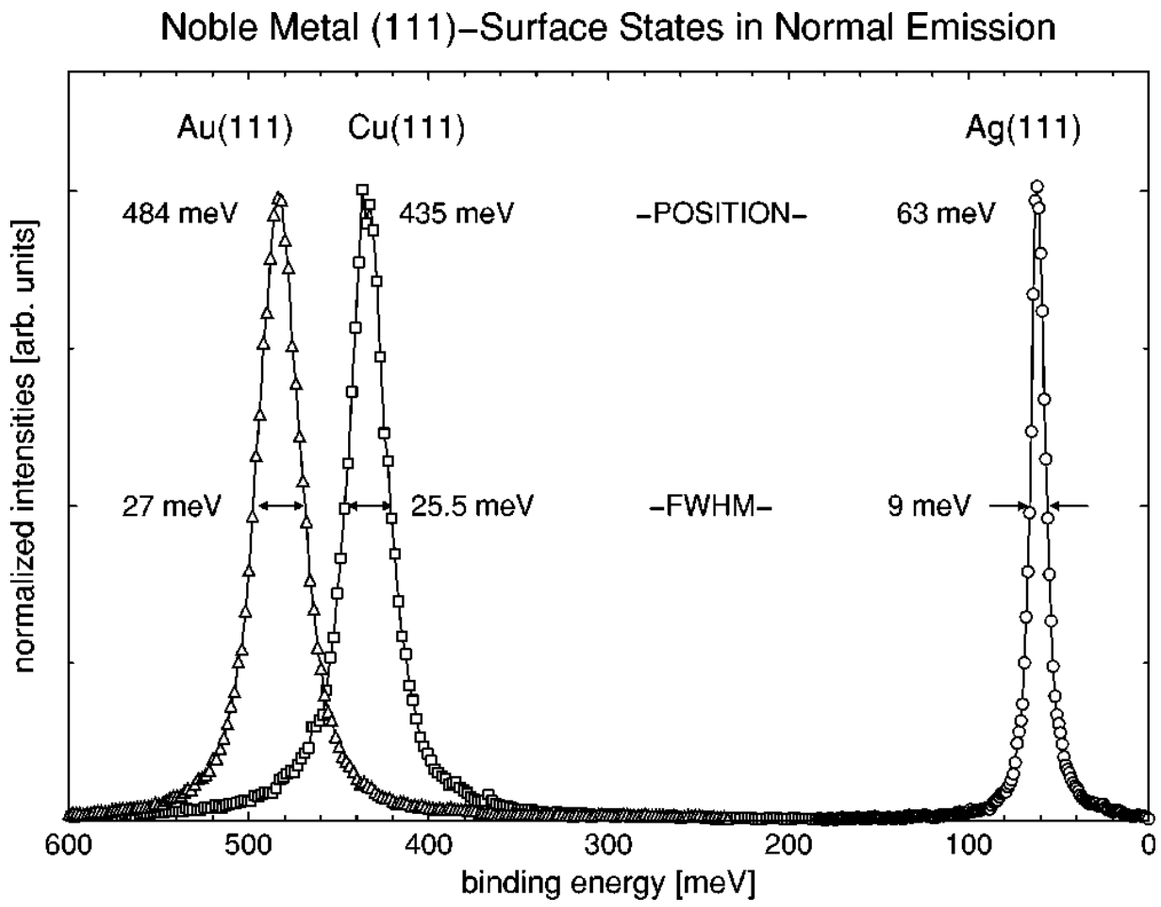
We **detect** the photoelectron, but **measure** properties of photohole

For states at Fermi level

$$\tau = \infty \Rightarrow \Gamma_i = 0$$

Lifetime (linewidth) decreases (increases) with increasing E_B

Referred to as electron-electron interaction



F. Reinert et al. PRB 63, 115415 (2001)

Effective mass and Fermi velocity

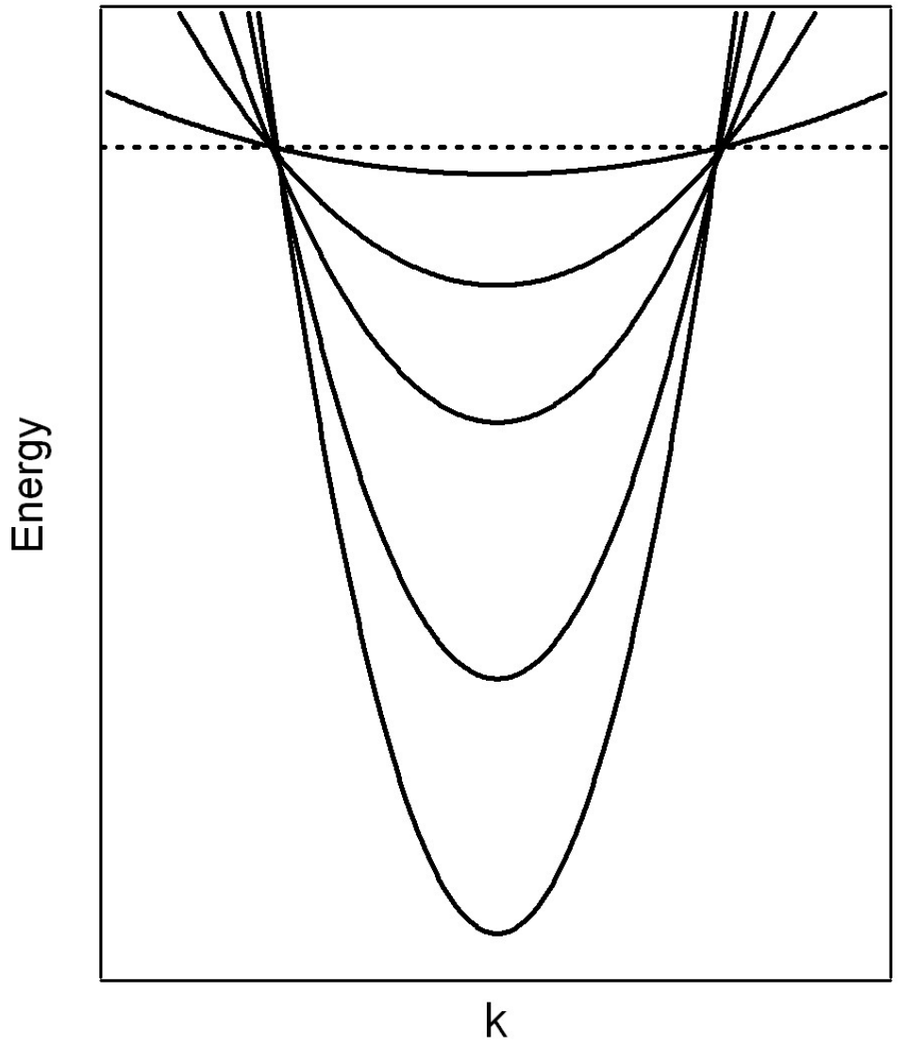
$$E(k) = \frac{h^2 k^2}{2m^*}$$

effective mass m* from the curvature of the bands

Indicates the degree of localization of the electrons

Fermi velocity from slope at E_F

The group velocity of the conduction electrons



Momentum conservation (again)

$$\vec{k}_i + \vec{k}_{h\nu} + \vec{G} + \vec{g} = \vec{k}_f$$

	Energy	Momentum
free electron	$\varepsilon(\vec{k}) = \frac{h^2k^2}{2m}$	$h\vec{k}$
photon ($h\nu$)	$\varepsilon(\vec{k}) = \lvert h\vec{k}\rvert c$	$h\vec{k}$

Can be corrected
(angles depend on geometry)

$$k_{\parallel}^{x} = +\sqrt{\frac{2m}{\hbar}E_{kin}}\ \sin(\vartheta_M + \vartheta_A) - \frac{h\nu}{\hbar c}\ \sin(\alpha - \vartheta_M)$$

$$k_{\parallel}^{y} = -\sqrt{\frac{2m}{\hbar}E_{kin}}\ \sin(\varphi_M + \varphi_A) - \frac{h\nu}{\hbar c}\ \cos(\alpha - \vartheta_M)\ \sin(\varphi_M)$$

$$k_z = \sqrt{\frac{2m}{\hbar}(E_{kin} + V_0 + \Phi_A) - \boldsymbol{k}_{\parallel}^2} + \frac{h\nu}{\hbar c}\cos(\alpha - \vartheta_M),$$

wave numbers k

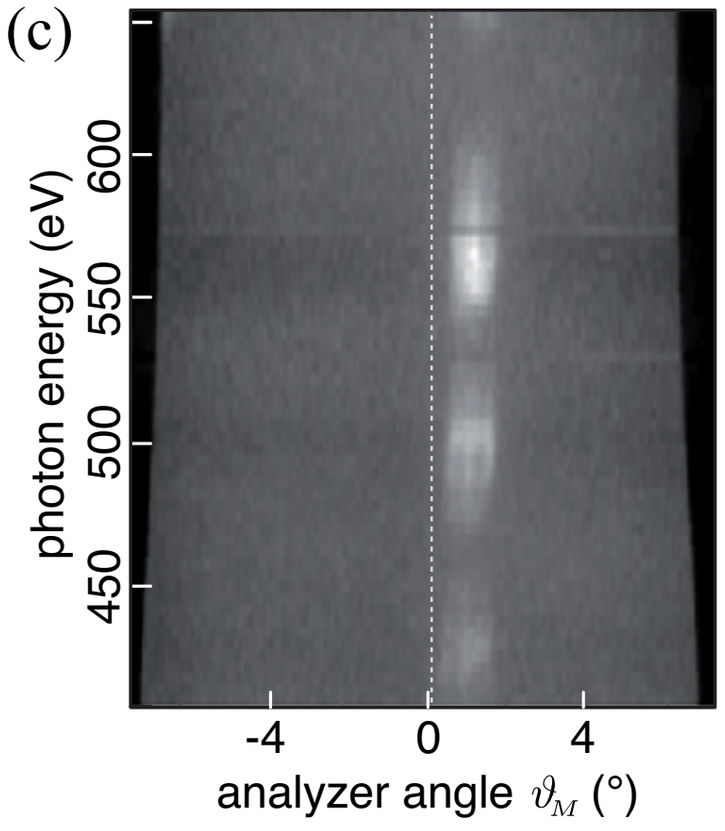
e^- : $k = 0.51\sqrt{\varepsilon\ [eV]}\ \text{Å}^{-1}$

$h\nu$: $k = 0.51 \cdot \varepsilon\ [eV] \cdot 10^{-3}\text{Å}^{-1}$

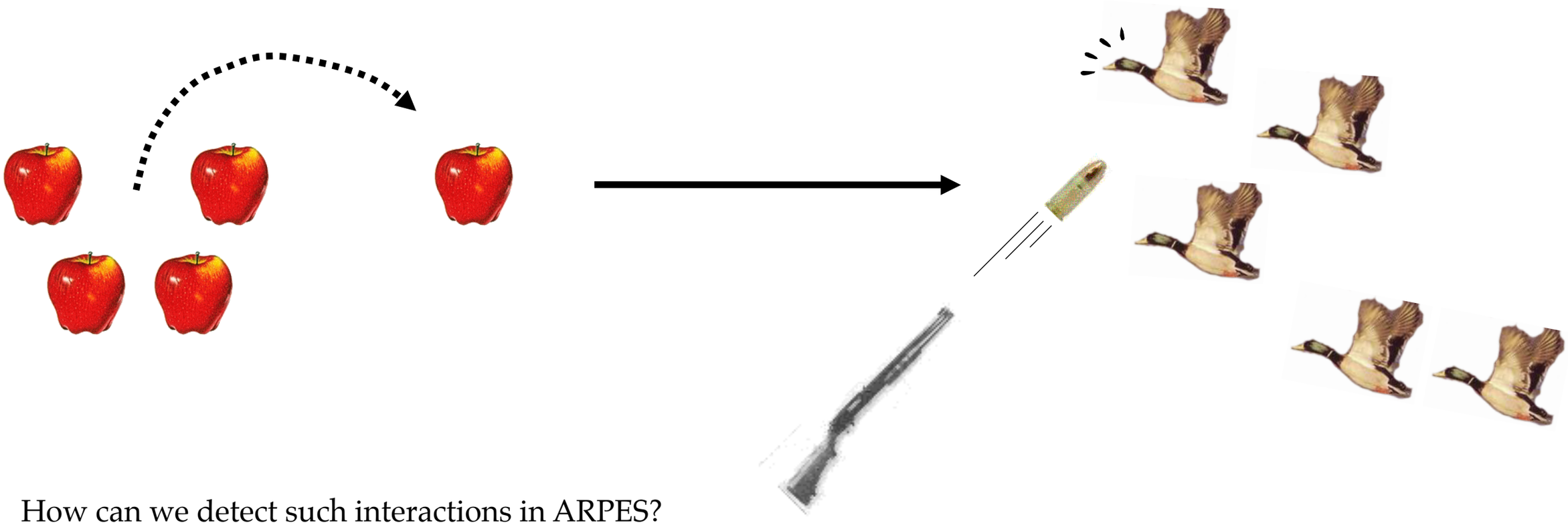
For 20-100 eV: $k_{photon} \approx 0.01$ to 0.05 Å^{-1}

For 300-1000 eV: $k_{photon} \approx 0.1$ to 0.5 Å^{-1}

At high energy photon momentum
does play a role



Beyond the single particle model



How can we detect such interactions in ARPES?

Green's function: $G(\mathbf{k},E) = \dfrac{1}{E - E_{\mathbf{k}} - \Sigma(\mathbf{k},E)}$ indicates how the binding energies are modified

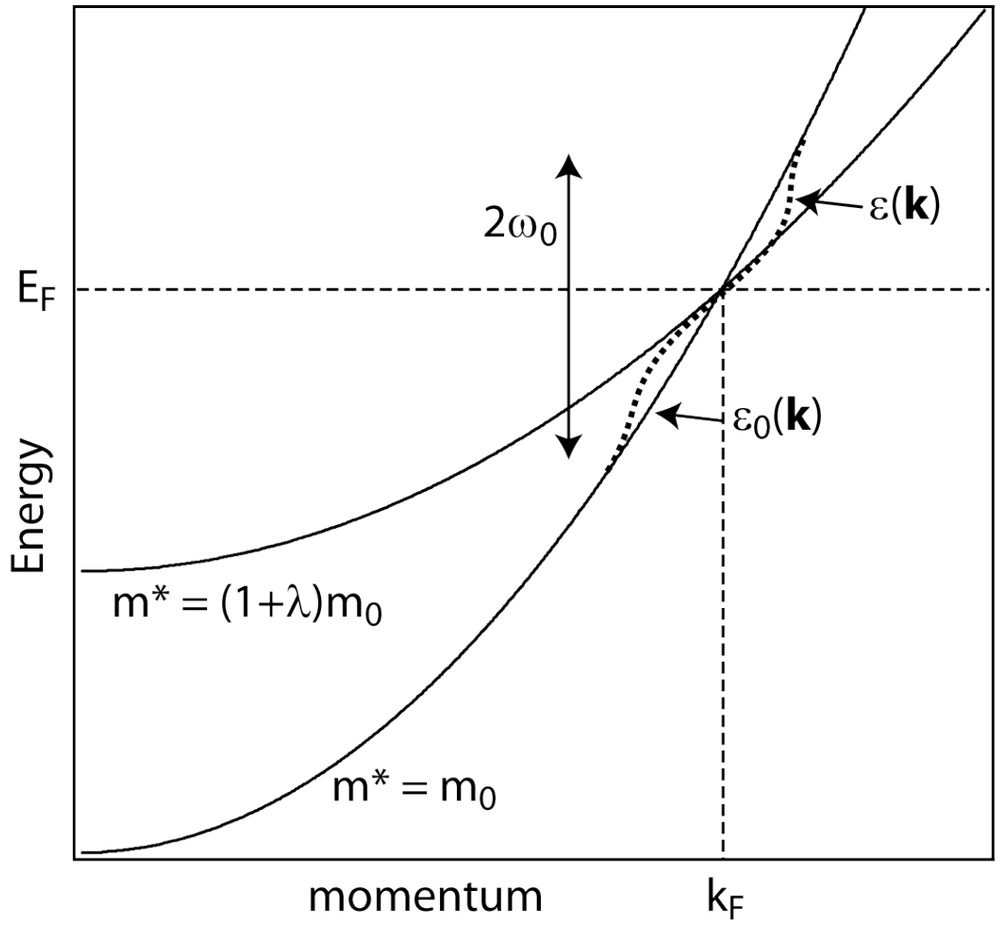
Spectral function: $A(\mathbf{k},E) = \dfrac{1}{\pi}\dfrac{Im\Sigma(\mathbf{k},E)}{\left[E - E_{\mathbf{k}} - Re\Sigma(\mathbf{k},E)\right]^2 + \left[Im\Sigma(\mathbf{k},E)\right]^2}$ indicates how the lines look

Self energy: $\Sigma(\mathbf{k},E) = \mathrm{Re}\Sigma(\mathbf{k},E) + \mathrm{Im}\Sigma(\mathbf{k},E)$ (zero for non interacting situation)

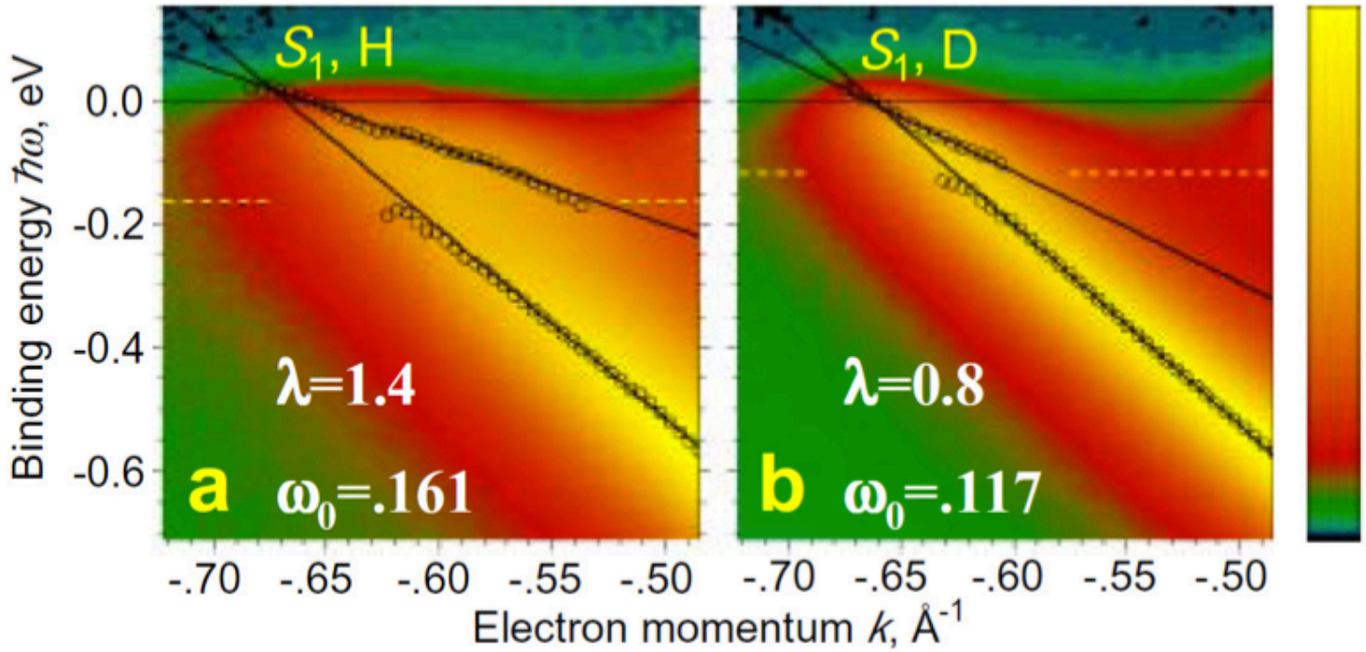
Change in energy

Change in lifetime (linewidth)

Electron-phonon coupling



Hydrogen and deuterium on W, influence on surface state



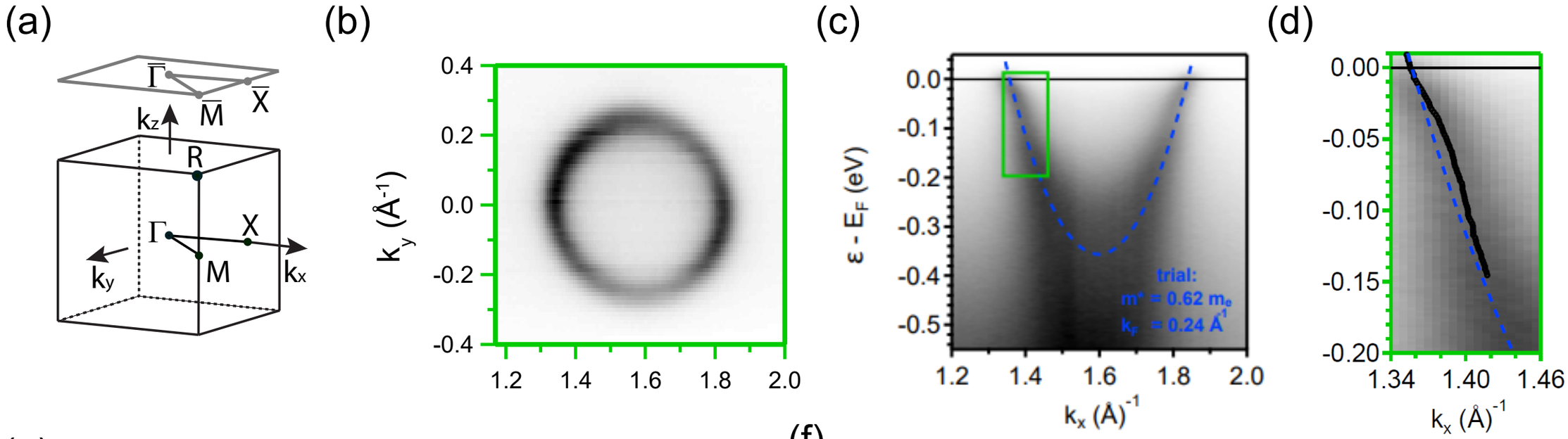
Coupling Between Adsorbate Vibrations and an Electronic Surface State, E. Rotenberg, J. Schaefer, S.D. Kevan, Phys. Rev. Lett. 84, 2925 (2000)

Two main parameters; λ and ω_0, coupling strength and energy region

Formation of second band with higher effective mass

Parameters can only be determined by comparison to non-interacting part of band

Real and imaginary part of self energy



Real and imaginary part of self energy are related via Kramers-Kronig or Hilbert transform

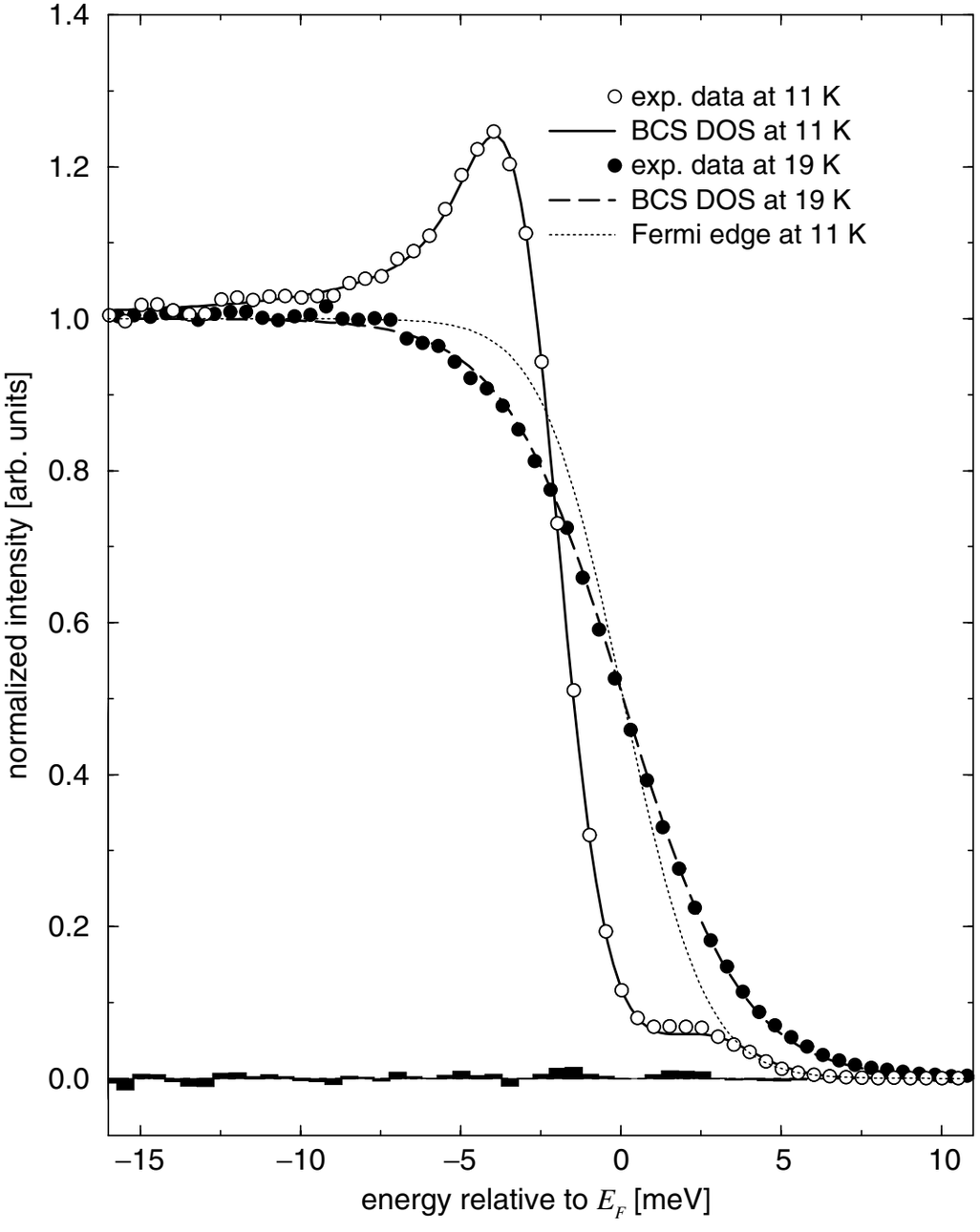
$$\Sigma_{\mathrm{ph}}(\varepsilon, \mathbf{k}) = \int_0^\infty \alpha^2 F(\omega, \mathbf{k}) K(\varepsilon, \omega) \mathrm{d}\omega$$

$\alpha^2 F(\omega, k)$ is Eliashberg function, containing all info on e-ph coupling

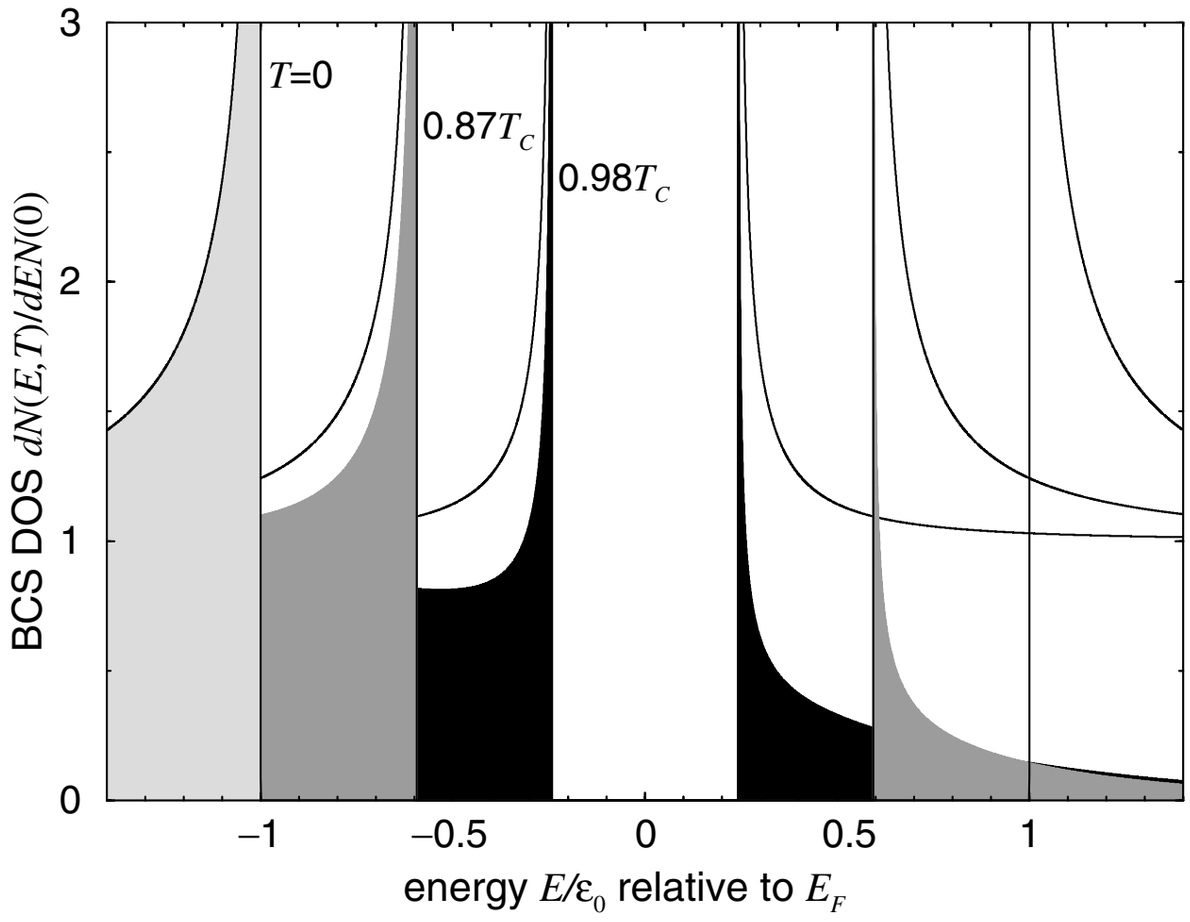
E.B. Guedes, T van Waas, et al. (in preparation)

BCS Superconductor

V_3Si $T_C = 17$ K
Resolution < 5 meV



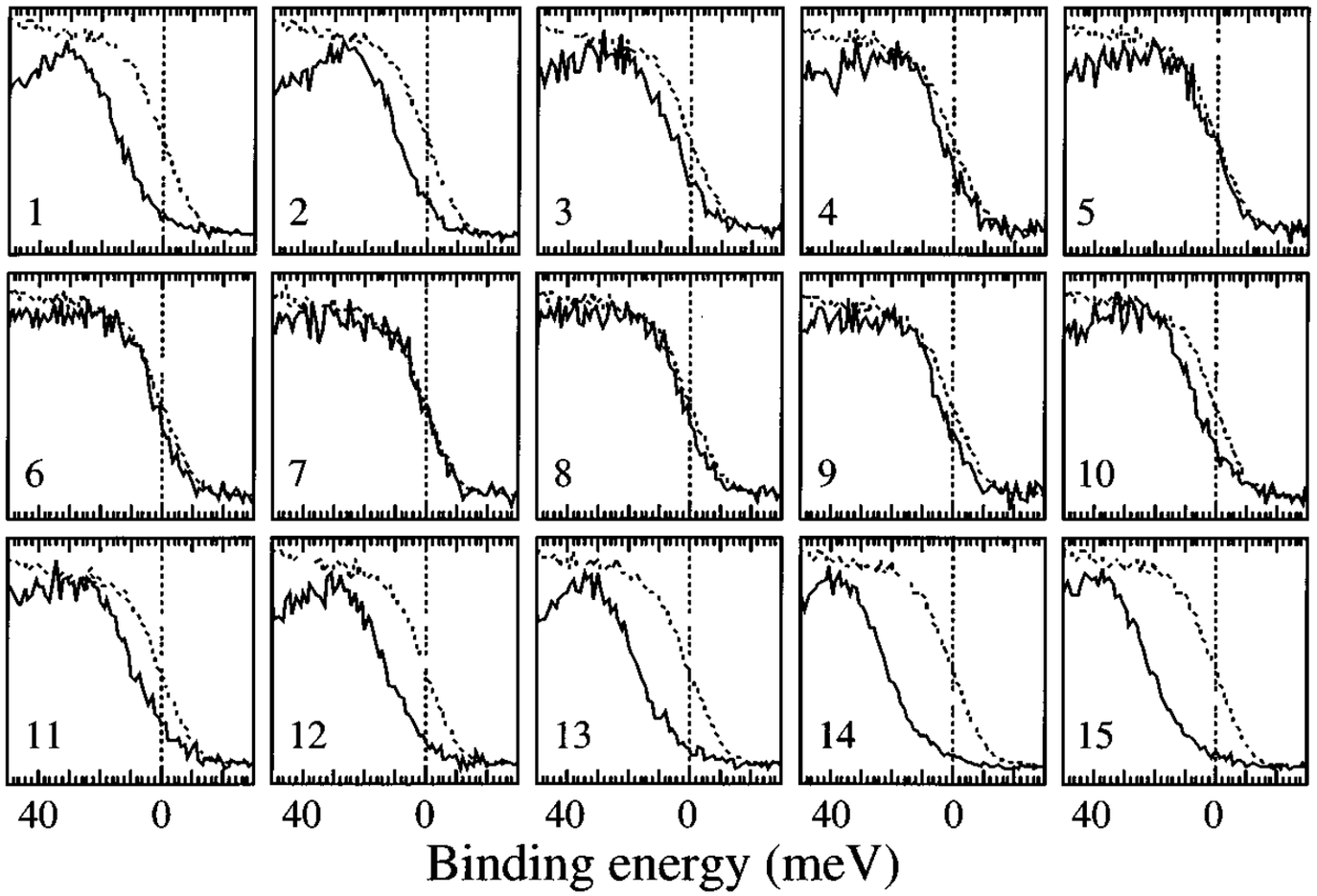
Phys. Rev. Lett. 85, 3930–3933 (2000)

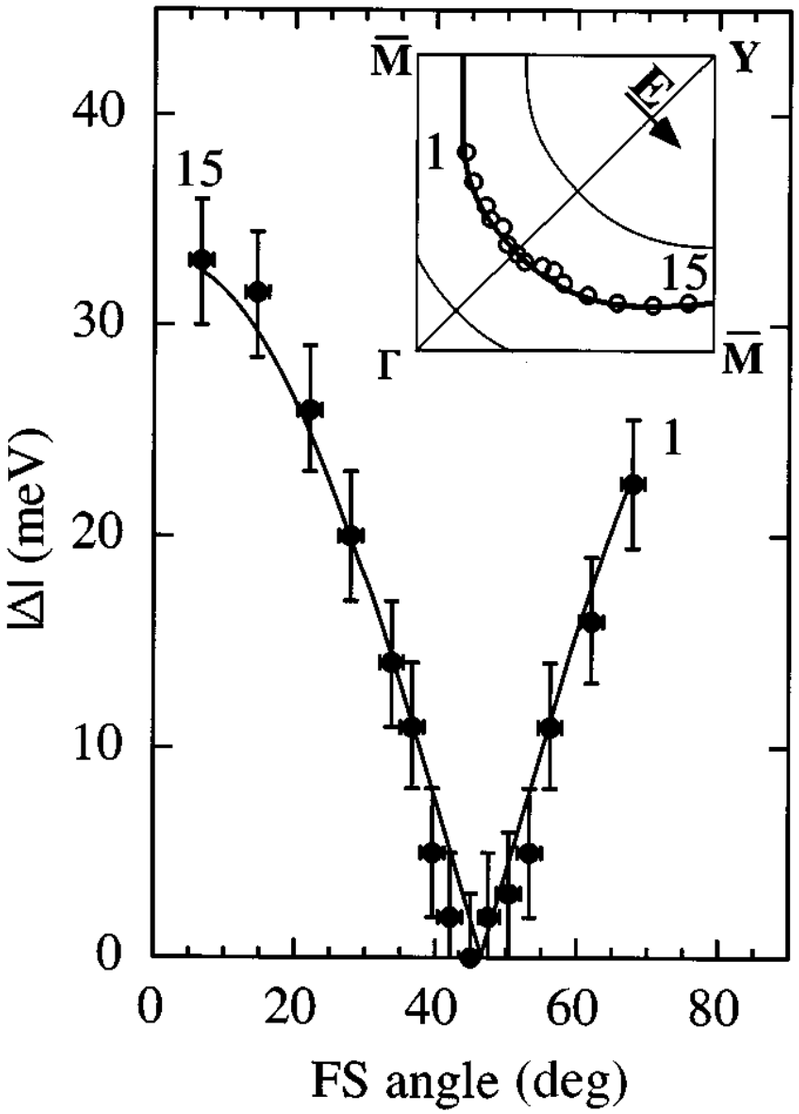


No electron DOS inside superconducting gap (only Cooper pairs)

D-wave superconductor

$Bi_2Sr_2CaCu_2O_{8+x}$ $T_C = 87$ K





Measured at 13 K

Determine gap from comparison to Pt

Phys. Rev. B 54, R9678 (1996)