Photoelectron Spectroscopy

Friday, 19. November 2021 11:02

- Solids have a band structure $E_n(\vec{k})$ ← band index; ← crystal momentum
- How to measure the entire dispersion and not only the state near E_F?

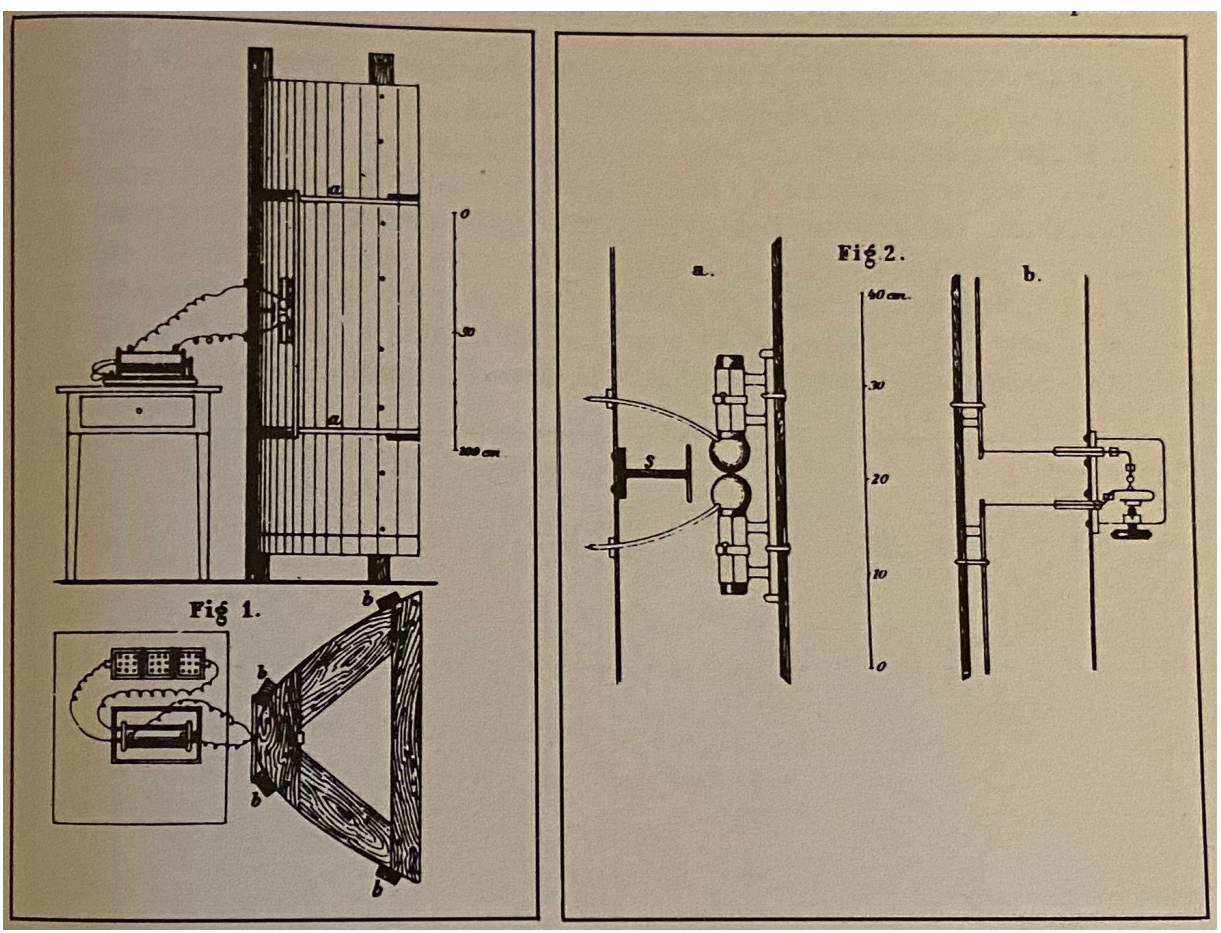
⇒ Angle - Resolved - PhotoEmission - Spectroscopy ARPES

Angle-Resolved: momentum resolution; PhotoEmission: "photon-in electron-out"; Spectroscopy: energy analysis

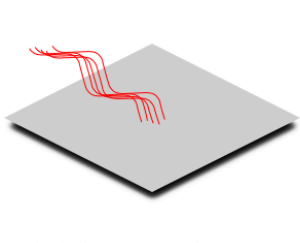
$E(\vec{k})$ of the occupied states

I) Photoemission history and Principles:

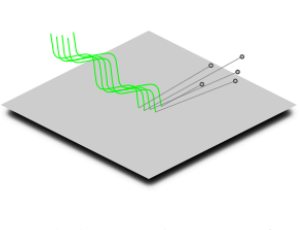
Based photoelectric effect discovered by Hertz in 1887 in Karlsruhe.



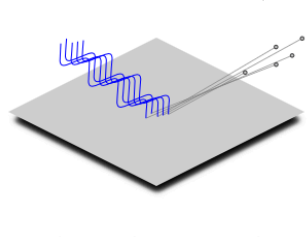
Experiment refined by Millikan: there is a threshold frequency



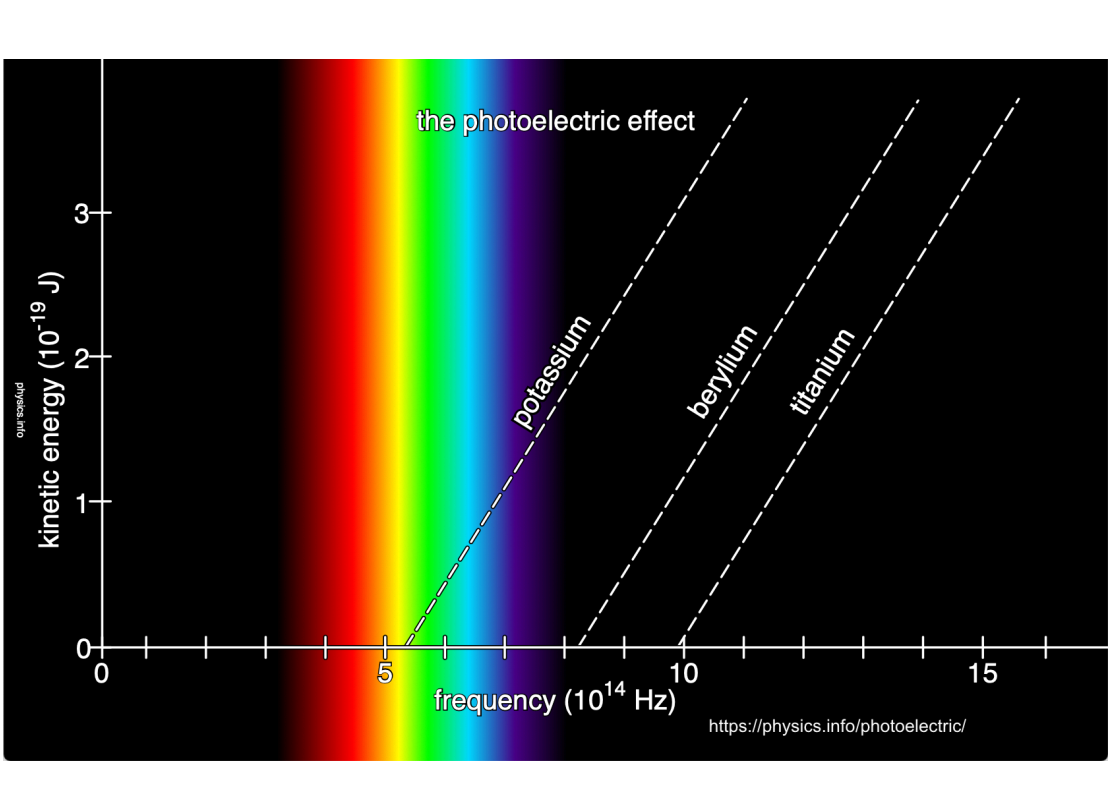
Red light does not eject photoelectrons (even if it is very bright).



Green light does eject photoelectrons (even if it is very dim).



Blue light ejects photoelectrons with more energy than green light (even if it is very dim).



- Threshold completely unexpected at beginning of XX^th century
- linear dependence of the kinetic energy of the electron also unexpected

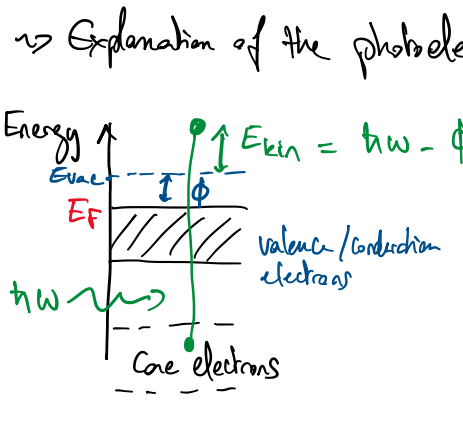
Classically the energy density of light in a beam:

$$W = \frac{1}{2}(\vec{E}\cdot\vec{D} + \vec{B}\cdot\vec{H}) = \underbrace{\frac{1}{2}(\varepsilon\varepsilon_0 E^2 + \mu\mu_0 H^2)}_{\text{none of this depends on the frequency}}$$

Empirically it was found that the energy of the emitted electrons depends on:

- the nature of the material
- the frequency of the light $E_{kin} = \hbar\omega - \phi$

⇝ Explanation of the photoelectric effect: Einstein 1905 ⇝ introducing photons



$$\phi = \phi_{vac} + E_B$$

ϕ_{vac}: energy required to extract the electron from the solid; E_B: binding energy of the electron in the solid

II. Photoemission Spectroscopy:

Basic idea: analyze the energy of the electrons emitted under light illumination in order to retrieve the energy distribution of the electrons in the material.

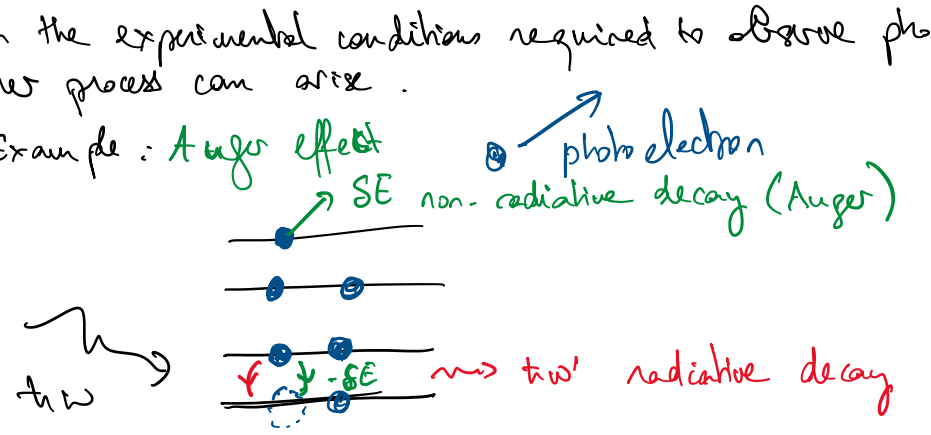
Development: Kai Siegbahn (Nobel Prize 1981)

Electron Spectroscopy for Chemical Analysis (ESCA)

⇒ Need to figure out the number of electrons "photo emitted" with a given kinetic energy under illumination by a monochromatic beam of energy $\hbar\omega$.

Disclaimer: in the experimental conditions required to observe photoemission other process can arise.

Example: Auger effect



- The number of photo-emitted electrons depends on the number of electrons that can potential be emitted, that is of the occupied density of states.

Core electrons and valence electrons will give qualitatively different spectra.

Core level photoemission (XPS)	Valence e⁻ photoemission (UPS)
X-ray photoelectron spectroscopy	UV photoelectron spectro.
- high energy photons (x-rays) - sharp lines = localized states	- UV / soft x-rays (3 - 100 eV) - Broad structures that reflect the dispersion of electrons

Damascelli et al. Review of Modern Physics 75, 473 (2003).

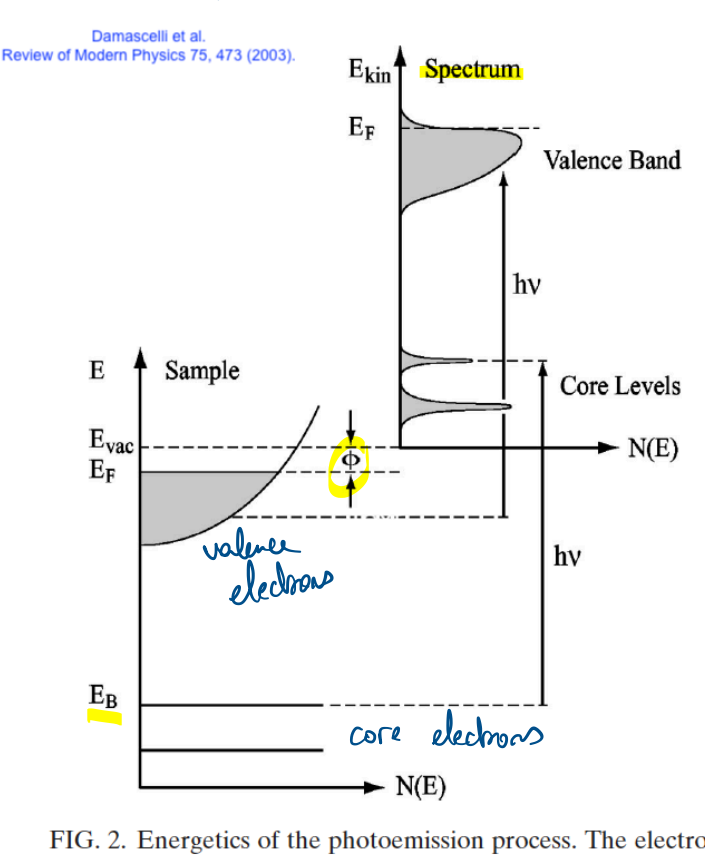


FIG. 2. Energetics of the photoemission process. The electron energy distribution produced by incoming photons and measured as a function of the kinetic energy E_{kin} of the photoelectrons (right) is more conveniently expressed in terms of the binding energy E_B (left) when one refers to the density of states inside the solid (E_B=0 at E_F). From Hüfner, 1995.

- Experimentally

Core levels have a finite energy width which has two origins:

1) Finite energy resolution of the experiment

$\frac{\Delta E}{E}$ = resolving power (detector, photon monochromatization) etc...

2) lifetime of the core-hole Δt

$\Delta t \cdot \Delta E \sim \hbar$

Generally core-hole spectra have complex lineshapes due to the fact that the photoelectron interacts with valence electrons on the way out "Doniach - Sunjic" lineshape + plasmons excitations

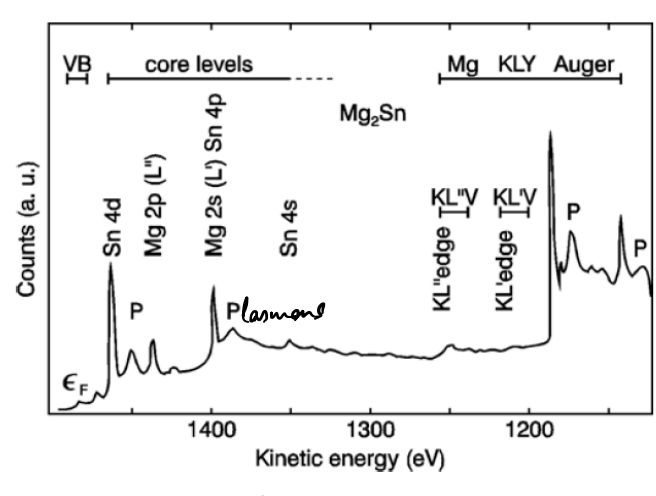
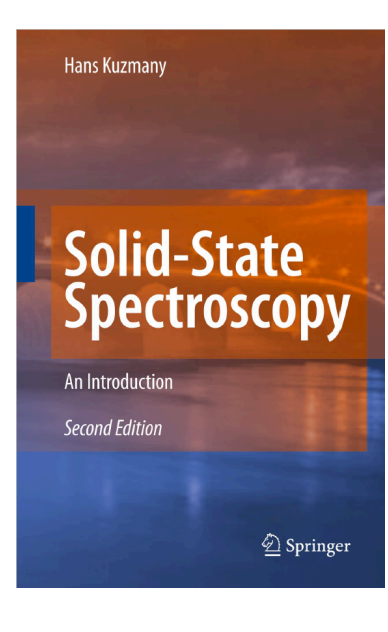


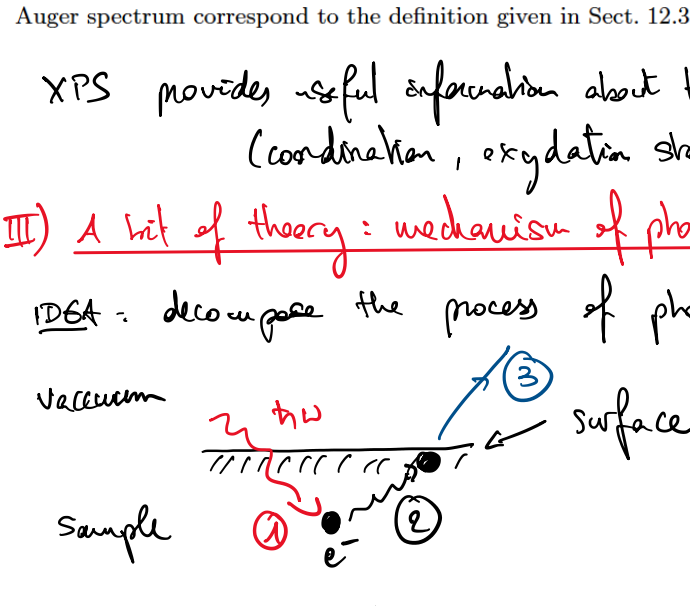
Fig. 12.13. XPS and Auger spectrum for Mg_2Sn after excitation with 1.486 KeV x rays. Left part: XPS spectrum, right part Auger spectrum. The symbols in the Auger spectrum correspond to the definition given in Sect. 12.3.1; after [12.7]



XPS provides useful information about the local electronic electronic structure (coordination, oxydation states, valence etc...)

III) A bit of theory: mechanism of photoemission "three steps model"

IDEA: decompose the process of photoemission



① Absorption of the photon and photo excitation of an electron inside the sample.

② Travel of photoelectron to the surface

③ Emission of the photoelectron in the vacuum

Each step is described by a probability:

① $\mathcal{P}(E_{kin}, \hbar\omega)$ = contains all the relevant information about the electronic structure.

② $T(E_{kin})$ = inelastic photoelectron scattering term

③ $D(E_{kin})$ = transmission probability of the photoelectron across the surface (has to overcome ϕ_{vac} ⇒ tunneling process)

Total photocurrent intensity:

$$I(E_{kin}, \hbar\omega) \propto \underbrace{\mathcal{P}(E_{kin}, \hbar\omega)}_{\text{we are mostly interested in this one!}} \times T \times D$$

a) Inelastic photoelectron scattering term.

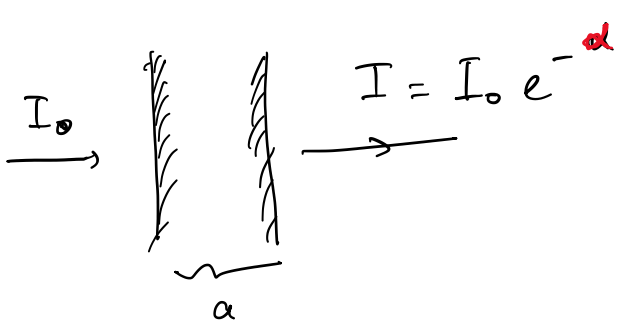
$T(E_{kin})$ represents the probability of a photoelectron to reach the surface without being scattered out.

≡ with the momentum and the energy at which it was emitted.

➡ Strongly depends on the distance the photoelectron has to cover - that distance is given by the absorption length of the photon:

$$\lambda = \frac{1}{\alpha(\hbar\omega)}$$

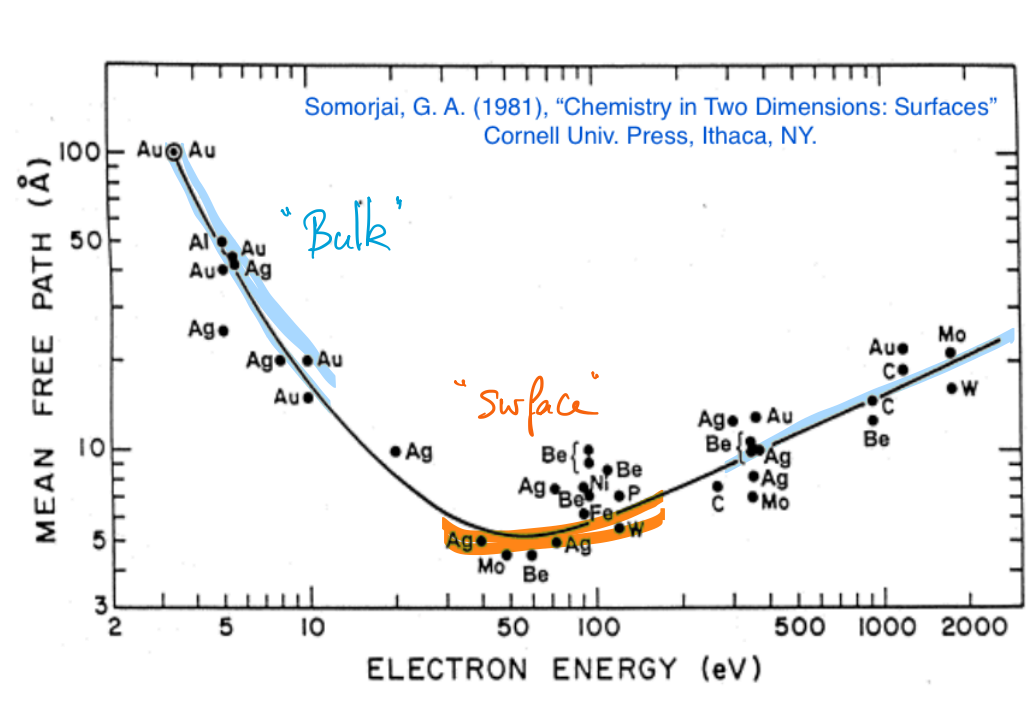
α = photon absorption coefficient



in the energy range 6eV - 10keV $\frac{1}{\alpha} \sim 100 - 1000$ Å

➡ T strongly depends on the electron mean free path ℓ

$\ell(E_{kin}) \ll \lambda$



$$T(E_{kin}) \approx \frac{\ell}{\lambda_{absorption}}$$ is generally small and strongly energy dependent!

b) Transmission probability across the surface.

$D(E_{kin})$ can be estimated assuming that the photoelectron is "free"

It can be shown that $D(E_{kin}) = \frac{1}{2}\left(1 - \sqrt{\frac{E_F + \phi}{E_{kin}}}\right)$ for $E_{kin} > E_F + \phi$ (minimal energy required to escape the sample)

$D(E_{kin}) \sim$ constant over the typical ranges of investigated energies (~100 meV for valence electrons)

Conclusion: Both T and D will modulate the overall photocurrent but not "deform" it (at least on given ranges of energy)

$$I(E_{kin}, \hbar\omega) \propto P(E_{kin}, \hbar\omega)$$

c) Photoexcitation probability.

⇒ Fermi Golden rule.

$$\mathcal{P}(E_{kin}, \hbar\omega) \propto \sum_{F,I} \omega_{F,I}$$

$\omega_{F,I}$: transition rate between the initial state of the system $|I\rangle$ and its final state $|F\rangle$

$$= \frac{2\pi}{\hbar} \left|\langle F | \mathcal{H}_{int} | I \rangle\right|^2 \delta(E_F(N) - E_I(N) - \hbar\omega)$$

What system are we talking about?

N electrons + $n_{\hbar\omega}$ photons

$|I\rangle$ = total initial state (N electrons + $n_{\hbar\omega}$ photons of energy $\hbar\omega$)

$|F\rangle$ = N-1 electrons, 1 photo electron, $n_{\hbar\omega} - 1$ photons

$$|F\rangle = \underbrace{|n_{\hbar\omega} - 1\rangle}_{\text{photon field}} \underbrace{|E_{kin}\rangle}_{\text{photoelectron}} \underbrace{|E_f(N-1)\rangle}_{\text{N-1 electrons left behind}}$$

$$|I\rangle = |n_{\hbar\omega}\rangle \underbrace{|\phi\rangle}_{\text{vacuum}} |E_i(N)\rangle$$

Perturbation: $\mathcal{H}_{int} = ?$

recall electrons in the EM field:

$$\mathcal{H} = \frac{\hbar^2}{2m}(\vec{p} - q\vec{A})^2$$

$\vec{p}$: momentum of the electron; $\vec{A}$: vector potential (describes the photon field)

$$\mathcal{H}_{int} \propto \sum_{j=1}^{N} (\vec{A}\cdot\vec{p}_j + \vec{p}_j\cdot\vec{A})$$

sum over the N electrons

$$\begin{cases} \vec{A}(\vec{r}_j) = \text{vector potential at the position } \vec{r}_j \text{ of the electron } j \\ \vec{p}_j = -i\hbar\vec{\nabla}_j \end{cases}$$

$$\vec{p}_j\cdot\vec{A} = -i\hbar \underbrace{\vec{\nabla}_j\cdot\vec{A}}_{\text{composition operator}} = \underbrace{(\vec{\nabla}\cdot\vec{A})}_{\text{divergence of } \vec{A}} - \vec{A}\cdot\vec{\nabla}$$

Coulomb Gauge: $\vec{\nabla}\cdot\vec{A} = 0$

$$\mathcal{H}_{int} \propto \sum_j \vec{A}\cdot\vec{p}_j$$

$$\vec{A}(\vec{r},t) = \sum_{\vec{q},\epsilon} A_0 \left[\hat{\epsilon}\, a_{\epsilon,q}\, e^{i(\vec{q}\cdot\vec{r} - \omega t)} + \hat{\epsilon}^* a^+_{\epsilon,q}\, e^{-i(\vec{q}\cdot\vec{r} - \omega t)}\right]$$

$\hat{\epsilon}$: photon polarization; $a^+_{\epsilon,q}$: creation operator; $\vec{q}$: photon momentum; $\omega = cq$: photon energy

- Dipole approximation: $e^{i(\vec{q}\cdot\vec{r})} \sim 1$ when $\lambda \gg$ interatomic distance ✓
- Sudden approximation: the photo electron does not interact with the (N-1) electrons left behind

OK when E_{kin} is "not too low" ≳ 10 eV

when the time scale of the photoemission is ≪ time scale of e⁻/e⁻ interaction.

$$E_f(N) = E_{kin} + E_f(N-1)$$

⇒ result:

$$\boxed{\mathcal{P}(E_{kin}, \hbar\omega) = n_{\hbar\omega} \sum_f |M_{k_{in},f}|^2\, \delta(\hbar\omega - \phi - E_B - E_{kin})}$$

Density of occupied electron state modulated by a matrix element (dipole selection rules ⇒ polarization dependence of the signal)

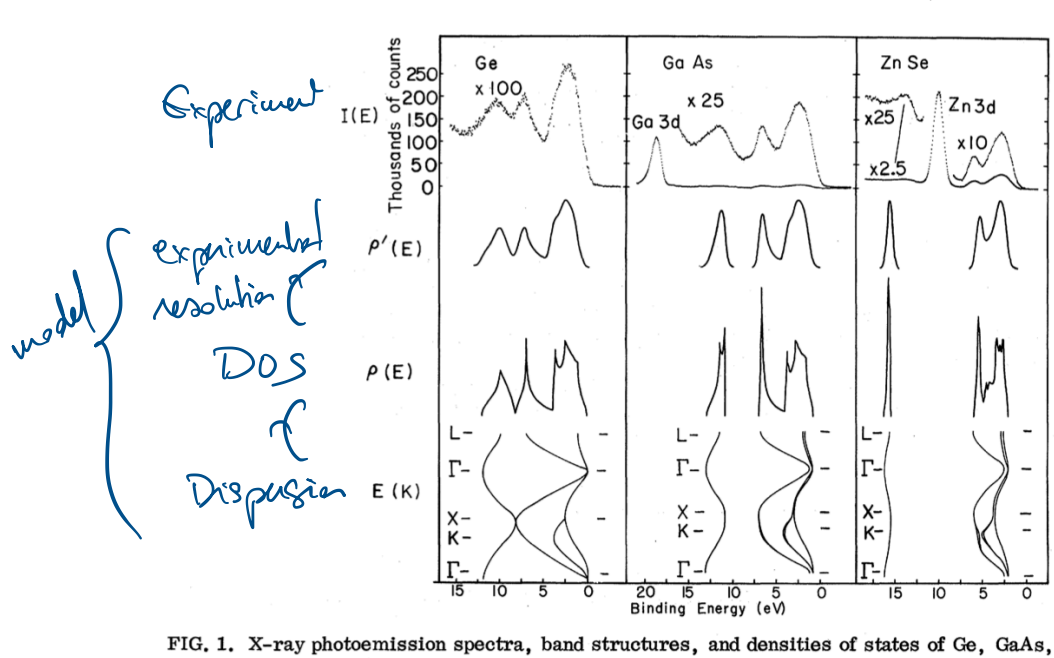
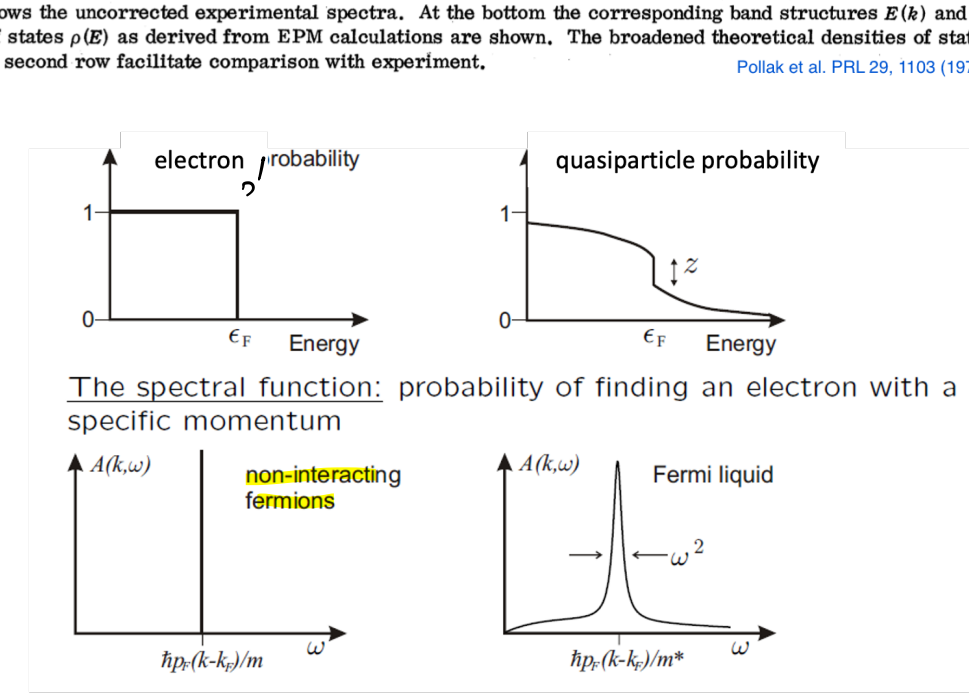


FIG. 1. X-ray photoemission spectra, band structures, and densities of states of Ge, GaAs, and ZnSe. The top row $I(E)$ shows the uncorrected experimental spectra. At the bottom the corresponding band structures $E(k)$ and densities of states $\rho(E)$ as derived from EPM calculations are shown. The broadened theoretical densities of states $\rho'(E)$ in the second row facilitate comparison with experiment.

Pollak et al. PRL 29, 1103 (1972)



Photoemission experiment: $I(E_{kin}, \hbar\omega) \propto \sum_f |M_f|^2 \underbrace{A(\vec{k},\omega)}_{\text{spectral function}} \times \underbrace{f(\omega)}_{\text{Fermi Dirac distribution}}$

$A(\vec{k},\omega)$ = probability of finding an electron of momentum $\vec{k}$ with energy $\hbar\omega$

$$= \frac{1}{\pi} \frac{\Sigma''(\vec{k},\omega)}{[\hbar\omega - E_0(\vec{k}) - \Sigma'(\vec{k},\omega)]^2 + |\Sigma''(\vec{k},\omega)|^2}$$

$$\Sigma(\vec{k},\omega) = \Sigma'(\vec{k},\omega) + i\,\Sigma''(\vec{k},\omega)$$

= self energy.

$\Sigma'' \sim 1/\tau$ scattering rate

IV) Angle-resolved Photoemission Spectroscopy:

What can we learn from the momentum of the photoelectron??

- Initial momentum of an electron "to be photoemitted" $\vec{k}_i$
- photon with $\hbar\omega$ has a momentum $\vec{q}$

$\|q\| = \frac{2\pi}{\lambda}$

- Final momentum of the electron in the crystal but after absorption of the photon $\vec{k}_f$

Momentum conservation: $\vec{k}_f = \vec{k}_i + \vec{q}$

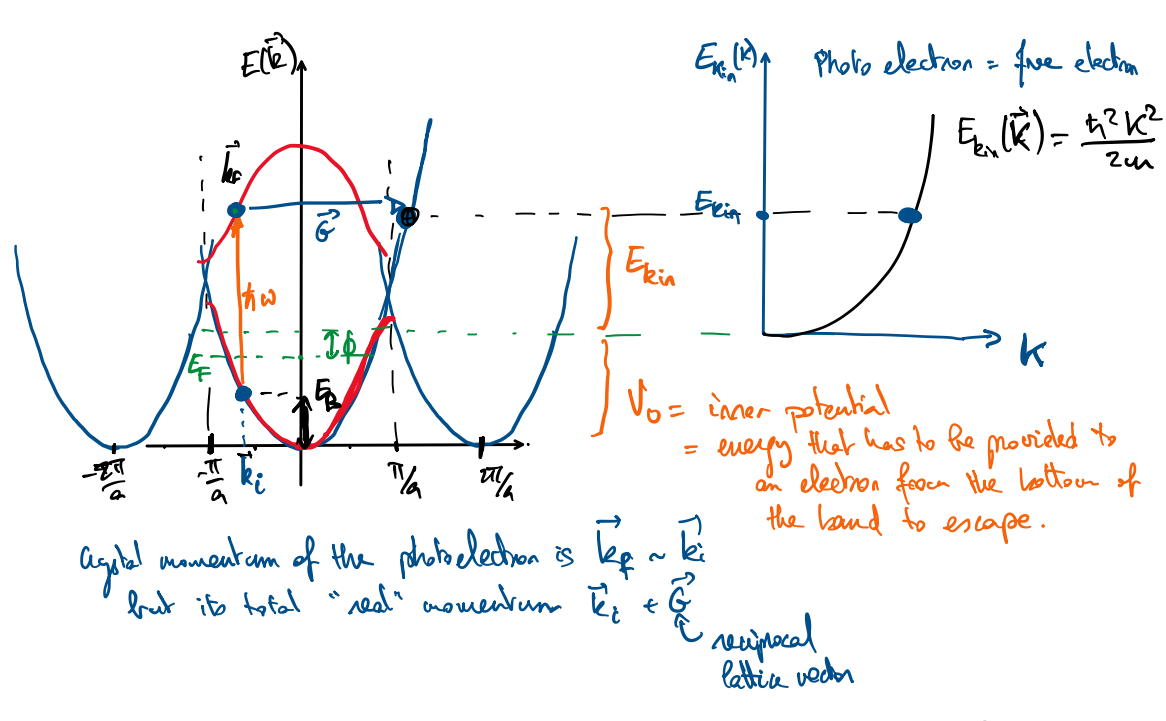
Typical photon energy ~ 3 - 100 eV

λ ~ 10 - 100 nm ≫ lattice spacing a ~ 3 Å

$q \ll \frac{2\pi}{a}$ ⇒ $q \sim 0$

$\vec{k}_f \sim \vec{k}_i$

⇒ the photoelectron is emitted in the direction of the original momentum of the electron.

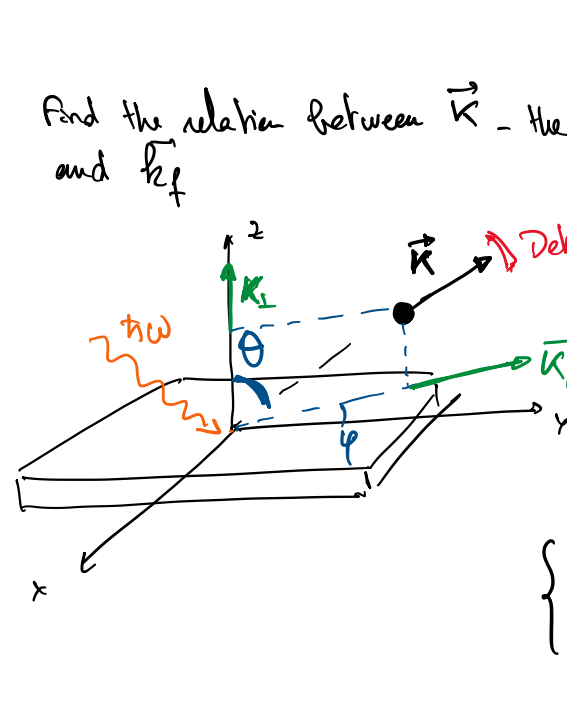

$E(\vec{k})$
$\vec{k}_f$
$\vec{G}$
$\hbar\omega$
E_F
E_B
$\vec{k}_i$
$-\frac{2\pi}{a}$
$-\frac{\pi}{a}$
π/a
$2\pi/a$
E_{kin}
$E_{kin}(\vec{K})$
Photo electron = free electron
$E_{kin}(\vec{K}) = \frac{\hbar^2 K^2}{2m}$
E_{kin}
K
V_0 = inner potential = energy that has to be provided to an electron from the bottom of the band to escape.

crystal momentum of the photoelectron is $\vec{k}_f \sim \vec{k}_i$ but its total "real" momentum $\vec{k}_i + \vec{G}$ ← reciprocal lattice vector

Energy conservation: $E_{kin} = \hbar\omega - \phi - E_B = \frac{\hbar^2 K^2}{2m}$

$$\|K\| = \frac{1}{\hbar}\sqrt{2m E_{kin}}$$

Find the relation between $\vec{K}$ - the momentum of the photoelectron and $\vec{k}_f$



$\vec{K} = \vec{K}_\parallel + \vec{K}_\perp$

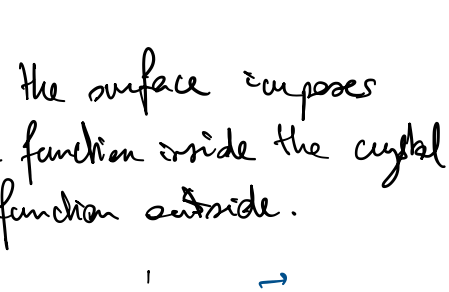
$\vec{K}_\parallel$: parallel to the surface of the sample; $\vec{K}_\perp$: normal to the surface

$$\begin{cases} K_\perp = K\cos\theta = \frac{1}{\hbar}\sqrt{2m E_{kin}}\cos\theta \\ K_\parallel = K\sin\theta = \frac{1}{\hbar}\sqrt{2m E_{kin}}\sin\theta \end{cases}$$

- Quantum mechanics requires a continuous transition of the wave function across the interface.
- translational symmetry conserved along the surface imposes matching between the Bloch wave function inside the crystal and the free electron plane wave function outside.

⇒ $\vec{K}_\parallel = \vec{k}_{f\parallel}$

$$\frac{1}{\hbar}\sqrt{2m E_{kin}}\sin\theta = \sin\theta_{in}\sqrt{\frac{2m}{\hbar^2}(E_{kin} + V_0)}$$



since $\vec{k}_f = \vec{k}_i$

$$\boxed{\vec{k}_{f\parallel} = \vec{k}_{i\parallel} = \frac{1}{\hbar}\sqrt{2m E_{kin}}\sin\theta}$$

On the other hand $k_{f\perp}$ is not conserved (broken translational symmetry across the surface) but is needed to reconstruct the dispersion for a 3D system.

$$E_f(k_f) = \frac{\hbar^2}{2m}(k_{f\parallel}^2 + k_{f\perp}^2) = E_{kin} + V_0$$

$$= E_{kin}\sin^2\theta + k_{f\perp}^2 \times \frac{\hbar^2}{2m}$$

$$\frac{\hbar^2 k_{f\perp}^2}{2m} = E_{kin}\cos^2\theta + V_0$$

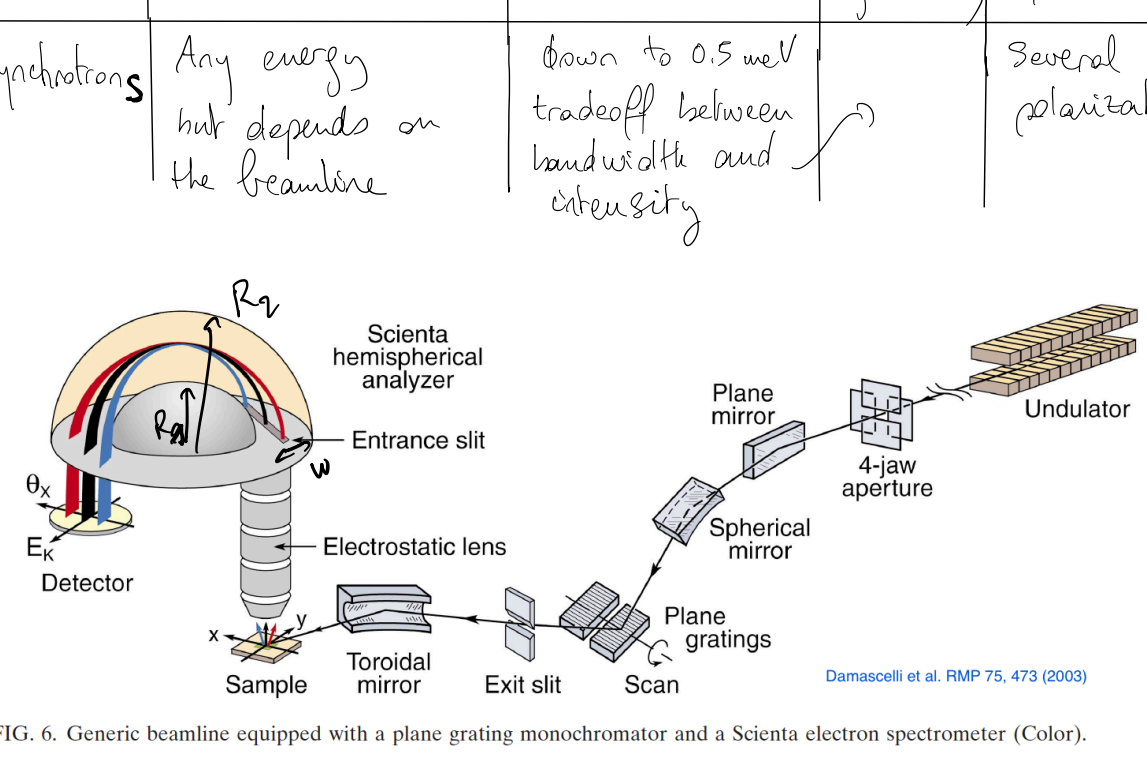
$$\boxed{k_{f\perp} = \frac{1}{\hbar}\sqrt{2m(E_{kin}\cos^2\theta + V_0)}}$$ ⇝ it is possible to retrieve $k_{f\perp}$ by changing $\hbar\omega$ (the photon energy)

⇒ By measuring the kinetic energy of photoelectrons and the direction in which they are emitted it is possible to reconstruct the full dispersion.

V) Experimental Set-up.

usual UV sources for ARPES (6 - 200 eV)

Type	Available photon energies	Bandwidth / monochromaticity	Intensity	Polarization
Gas discharge Lamp (He, Xe, Ne, Ar)	21,2 eV ; 40,8 eV 11,6 eV ; ... discrete set of lines	Rather small with a monochromator < 1 meV	fairly low	unpolarized Lab Available
LASER	6 - 11 eV	≪ 1 meV	very high intensity	Variable polarization
Synchrotrons	Any energy but depends on the beamline	Down to 0.5 meV tradeoff between bandwidth and intensity	↗	Several polarizations.



Damascelli et al. RMP 75, 473 (2003)

FIG. 6. Generic beamline equipped with a plane grating monochromator and a Scienta electron spectrometer (Color).

Energy resolution: $\Delta E \simeq E\underbrace{\left(\frac{w}{R_0} + \frac{\Delta\theta^2}{4}\right)}_{\text{parameters of the detector}}$

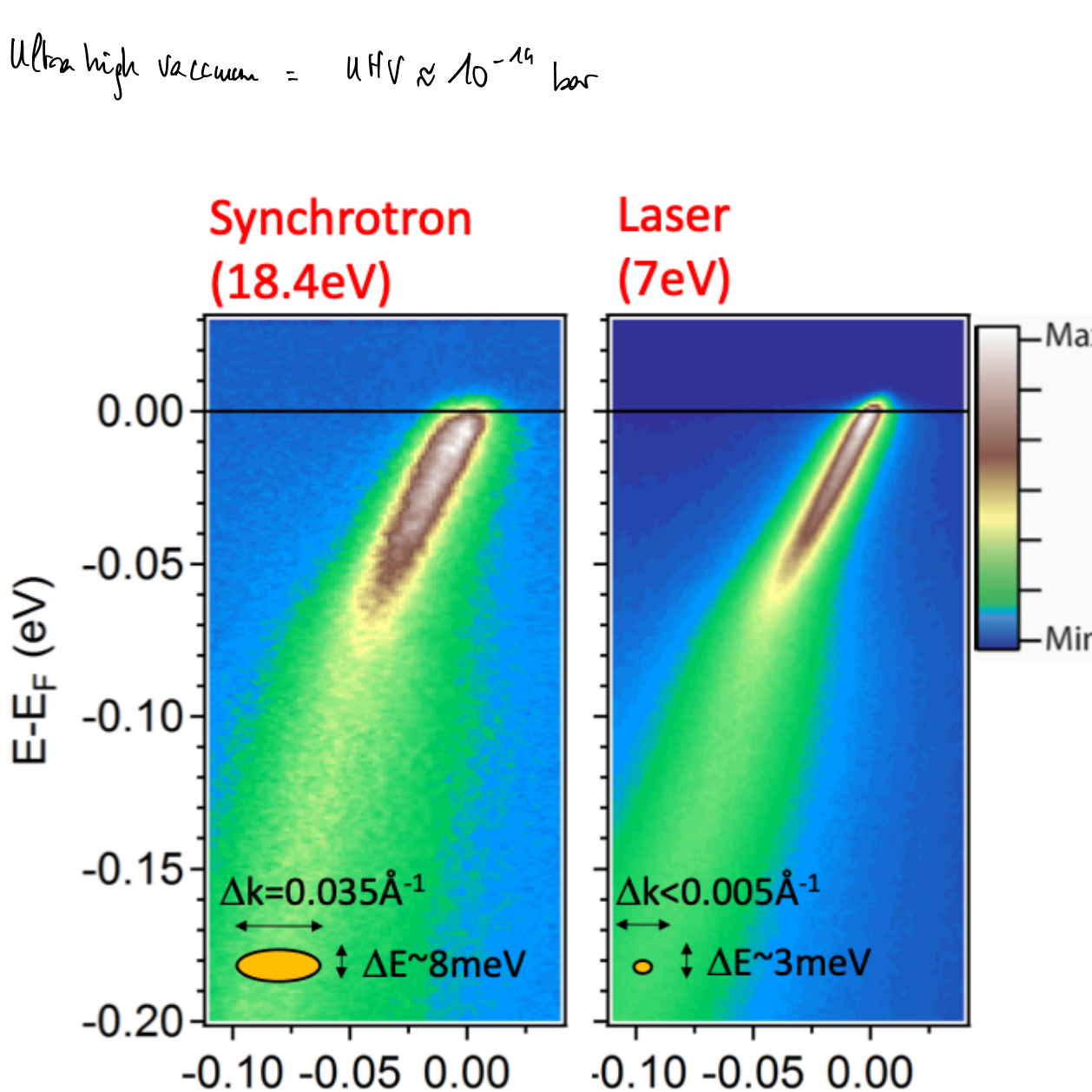
$R_0 = \frac{R_1 + R_2}{2}$

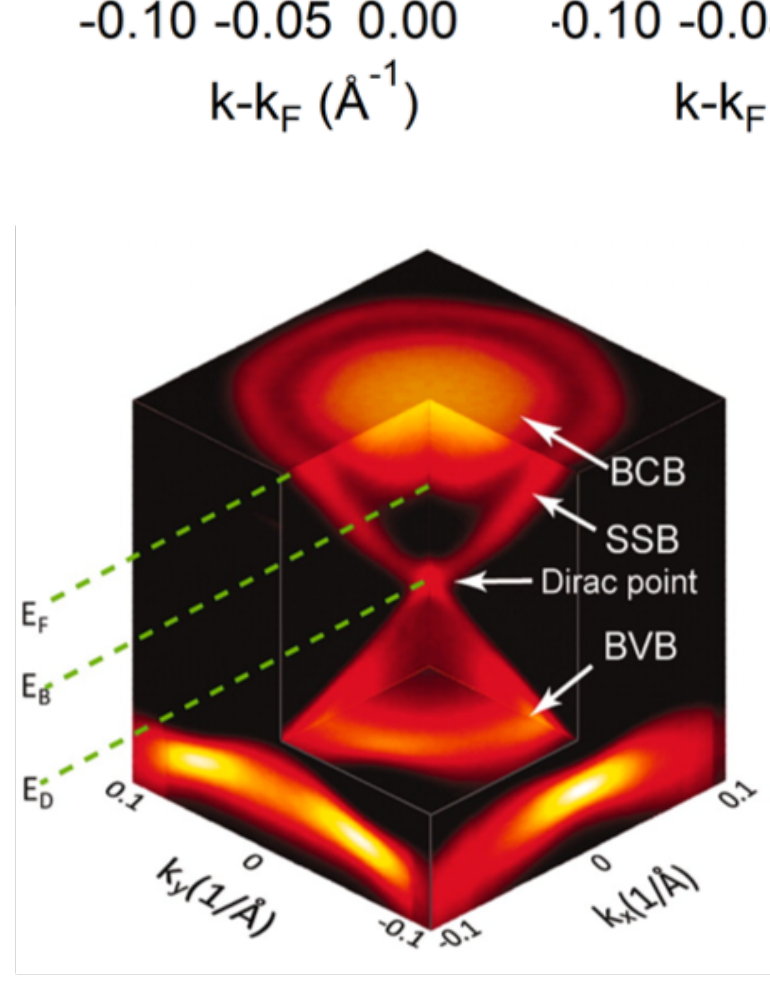
w = width of the entrance slit

Δθ = acceptance angle of the detector.

Momentum resolution $\Delta k_\parallel = \sqrt{\frac{2m}{\hbar} E_{kin}}\cos\theta\,\Delta\theta$

Ultra high vacuum = UHV ≈ 10^{-14} bar





Electronic band structure of undoped Bi_2Se_3 measured by ARPES. (**A**) The bulk conduction band (BCB), bulk valence band (BVB), and surface-state band (SSB) are indicated, along with the Fermi energy (E_F), the bottom of the BCB (E_B), and the Dirac point (E_D).

Chen et al. Science 329, 659 (2010)

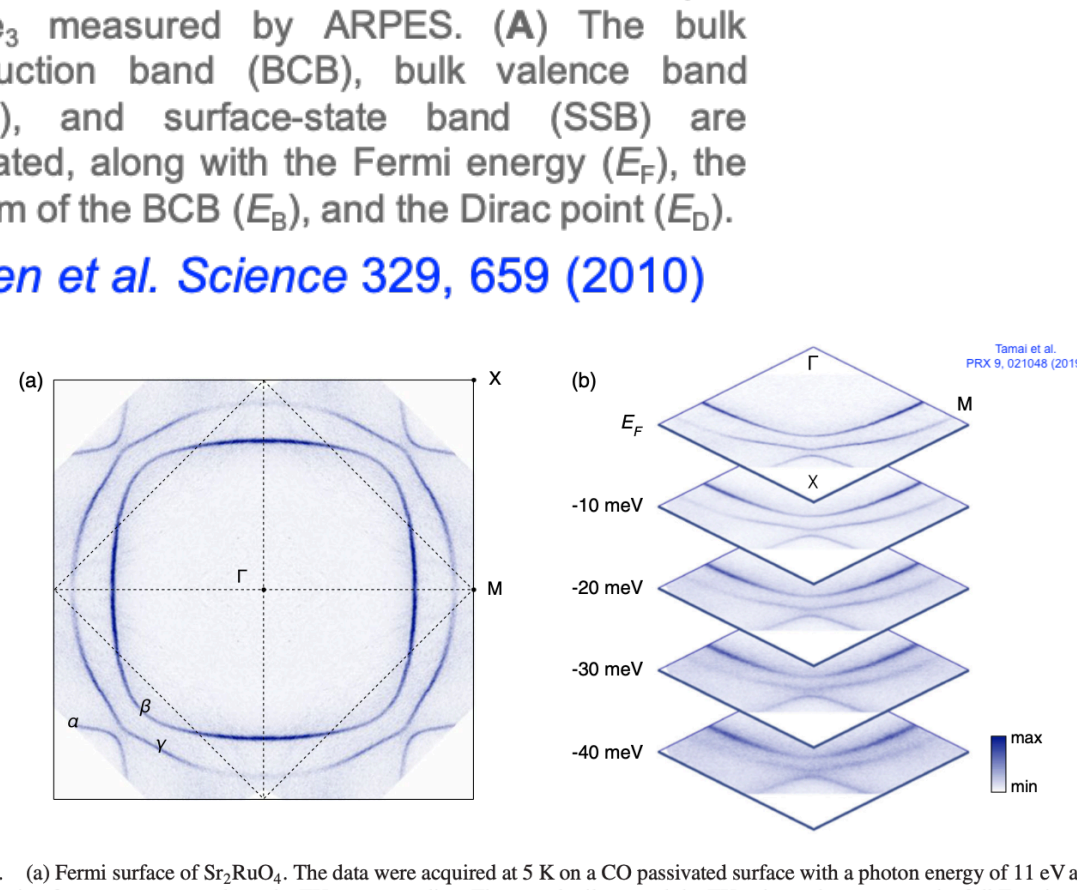


FIG. 1. (a) Fermi surface of Sr_2RuO_4. The data were acquired at 5 K on a CO passivated surface with a photon energy of 11 eV and *p* polarization for measurements along the ΓX symmetry line. The sample tilt around the ΓX axis used to measure the full Fermi surface results in a mixed polarization for data away from this symmetry axis. The Brillouin zone of the reconstructed surface layer is indicated by diagonal dashed lines. Surface states and final-state umklapp processes are suppressed to near the detection limit. A comparison with ARPES data from a pristine cleave is shown in the Appendix A. The data in panel (a) have been mirror symmetrized for clarity. Original measured data span slightly more than a quadrant of the Brillouin zone. (b) Constant energy surfaces illustrating the progressive broadening of the quasiparticle states away from the Fermi level E_F.

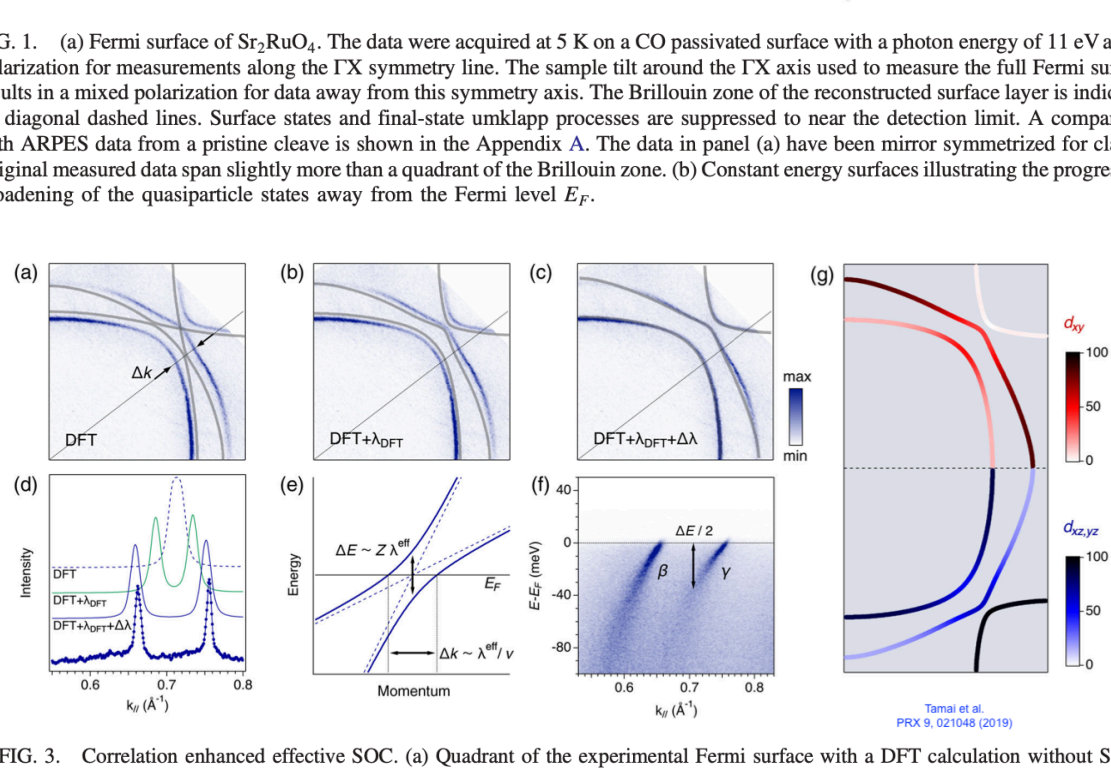


FIG. 3. Correlation enhanced effective SOC. (a) Quadrant of the experimental Fermi surface with a DFT calculation without SOC ($\hat{H}^{DFT}$) at the experimental $k_z \approx 0.4\pi/c$ (grey lines). (b,c) Same as panel (a), with calculations including SOC (DFT + λ_{DFT}) and enhanced SOC ($\lambda_{DFT} + \Delta\lambda$), respectively. For details, see the main text. (d) Comparison of the experimental MDC along the *k*-space cut indicated in panel (a) with different calculations shown in panels (a)–(c). (e) Schematic illustration of the renormalization of a SOC-induced degeneracy lifting. Here, $Z = \sqrt{Z_\nu Z_{\nu'}}$, where ν, ν' label the two bands, and $v = \sqrt{v_\nu v_{\nu'}}$, where v_ν, $v_{\nu'}$ are bare velocities in the absence of SOC [23] (see text). (f) Experimental quasiparticle dispersion along the *k*-space cut indicated in panel (a). (g) Orbital character of the DFT + λ_{DFT} + Δλ eigenstates along the Fermi surface.

VI) Conclusions

Advantages:

- ⇝ Direct information about the electronic states
- ⇝ Straightforward comparison to theory
- ⇝ Both energy and momentum resolution
- ⇝ Many-body effects (self energy etc...)
- ⇝ Small samples (100 μm) - high temperatures

Limitations

- ⇝ Not so much bulk sensitive: strongly surface sensitive
- ⇝ Ultra clean surfaces = sample has to cleave in UHV
- ⇝ No measurements under magnetic field or pressure!