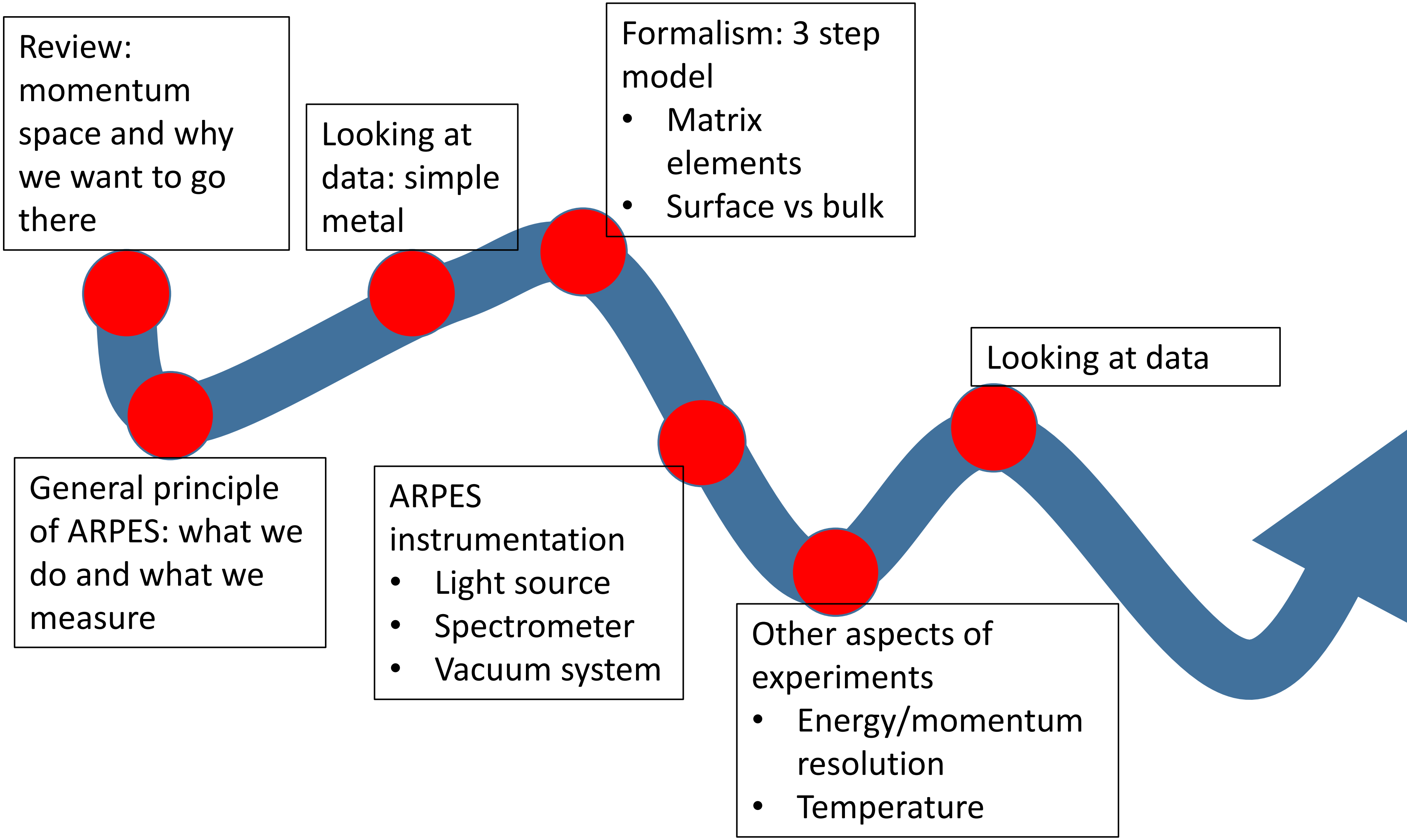
Angle-resolved photoemission spectroscopy (ARPES)

Overview

Outline



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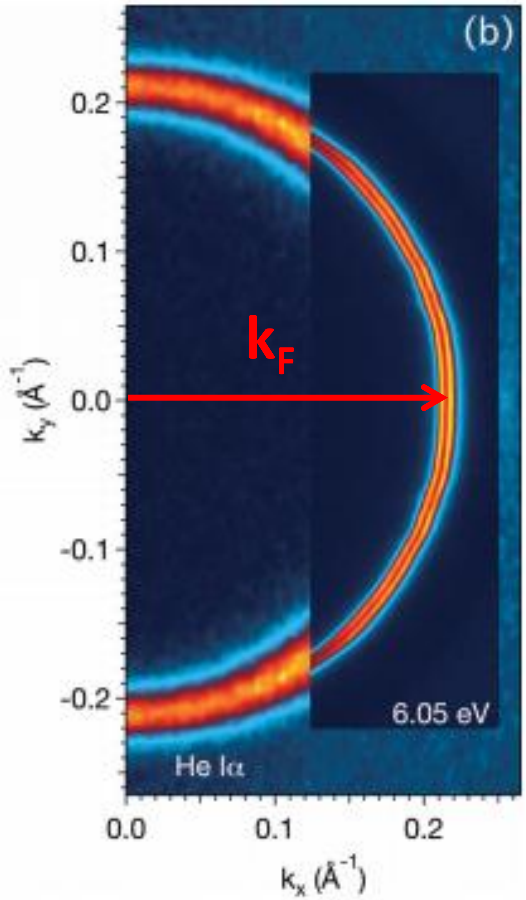
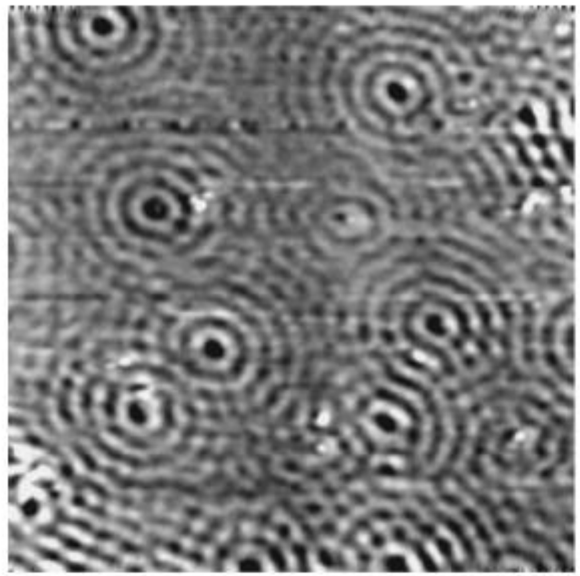
k (crystal momentum) vs **q** (momentum transfer)

Cu-111 Fermi surface



PRB **87**, 075113 (2013)

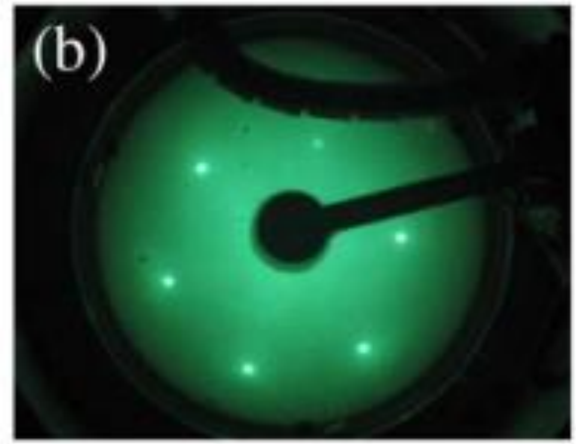
Cu-111 Friedel Oscillations



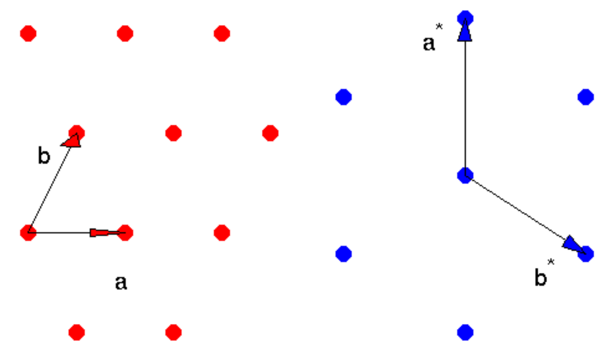
$\lambda=\pi/k_F$
$q=2k_F$

PRB **58** 7361 (1998)

Cu-111 Bragg peaks



Direct lattice Reciprocal lattice



Thin Solid Films **515** 8285 (2007)

Structures in momentum space

All materials

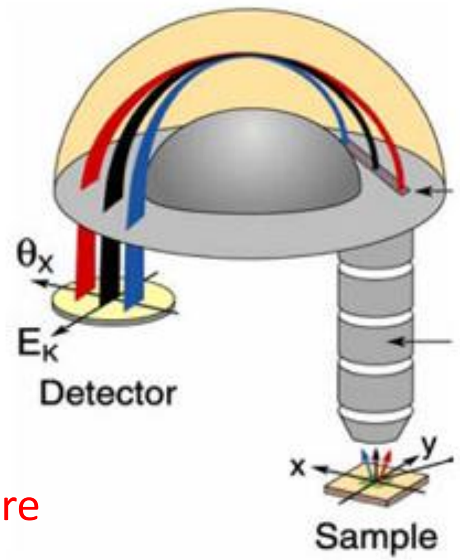
- Brillouin zones
- Fermi surfaces
- Band dispersion

Some materials

- Charge density wave gaps (most important for systems without perfect nesting)
- Superconducting gaps
- Spin density wave gaps
- Electron-boson coupling
- Heavy fermion hybridization gaps
- Spin momentum locking
- Surface states
- …

Angle-Resolved Photoemission spectroscopy overview

- Purpose: measure electronic band dispersion E vs k
- 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

$\phi = work\ function$ know/measure

$E_B = electron\ binding\ energy\ inside\ material, relative\ to\ Fermi\ level$ want

$k_{||} = crystal\ momentum, parallel\ to\ sample\ surface\ plane$ want

$m = mass\ of\ free\ electron$ know

$\vartheta = emission\ angle\ of\ photoelectron$ measure

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

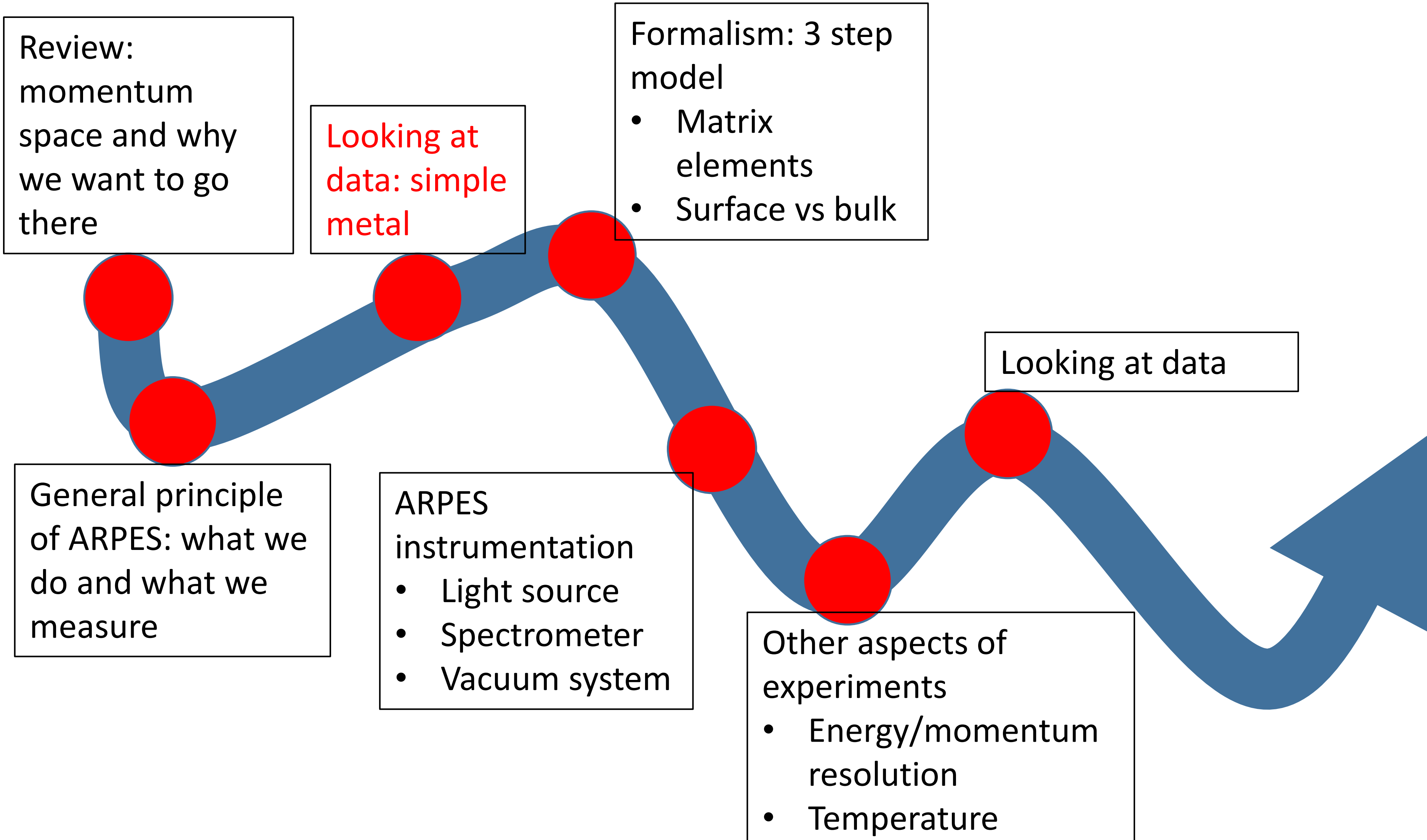
Self Energy: $$\Sigma(\mathbf{k},\omega) = \Sigma'(\mathbf{k},\omega) + i\Sigma''(\mathbf{k},\omega)$$

Band position ← $\Sigma'(\mathbf{k},\omega)$

$\Sigma''(\mathbf{k},\omega)$ → Linewidth or lifetime

Band structure
+
Interactions

Outline



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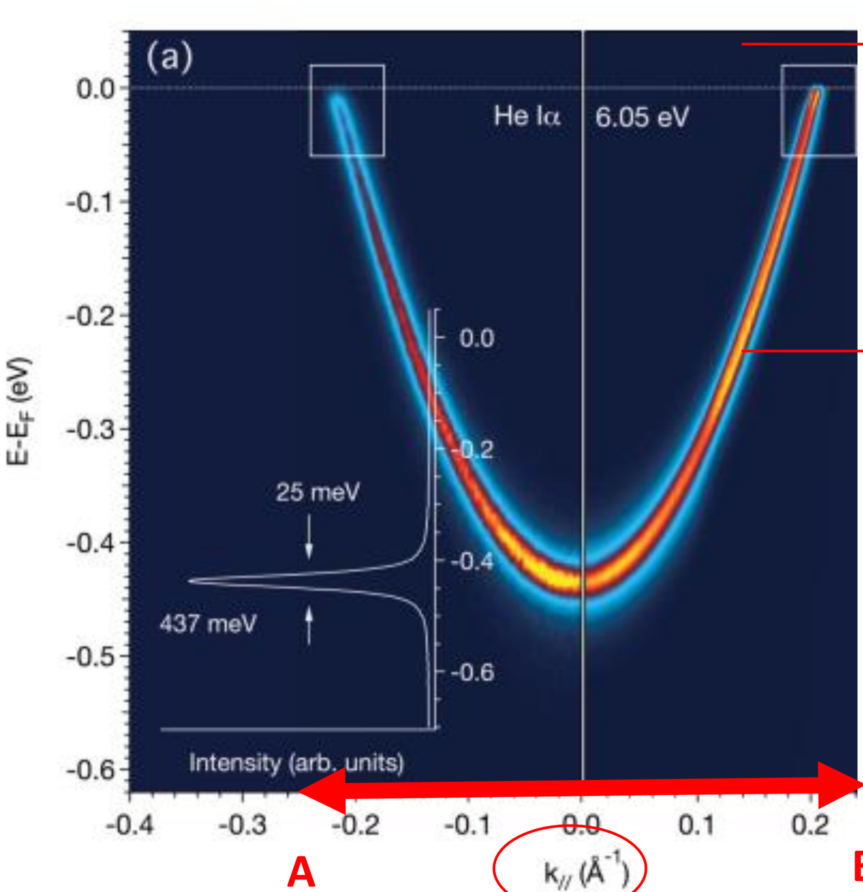
Band structure: simple metal (Cu 111 surface)

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

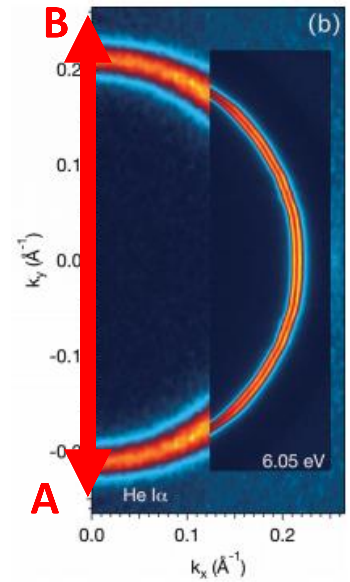


In-plane momentum

Fermi-Dirac cutoff

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

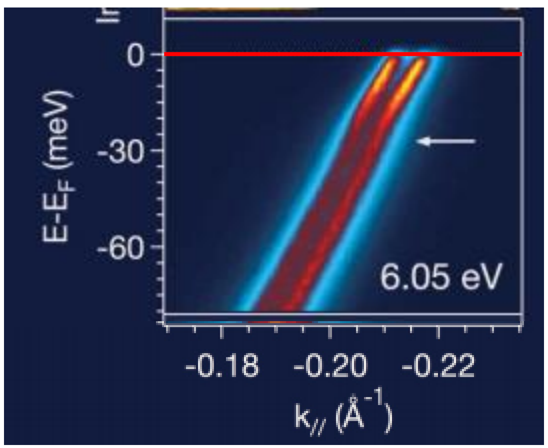
$$\epsilon_k = E(k) = \frac{\hbar^2 k^2}{2m^*}$$

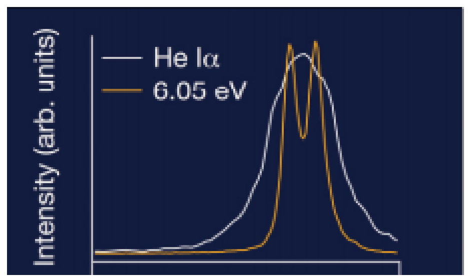


Fermi surface map is (usually) produced by pasting adjacent slices together

PRB **87**, 075113 (2013)

Self energy: simple metal (Cu 111 surface)



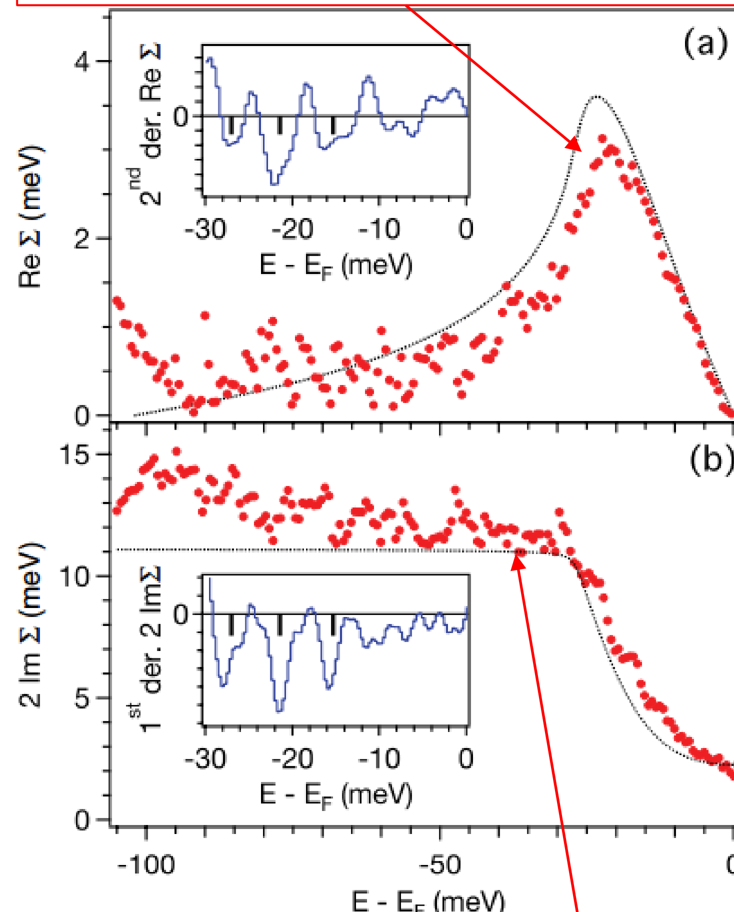


PRB **87**, 075113 (2013)

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

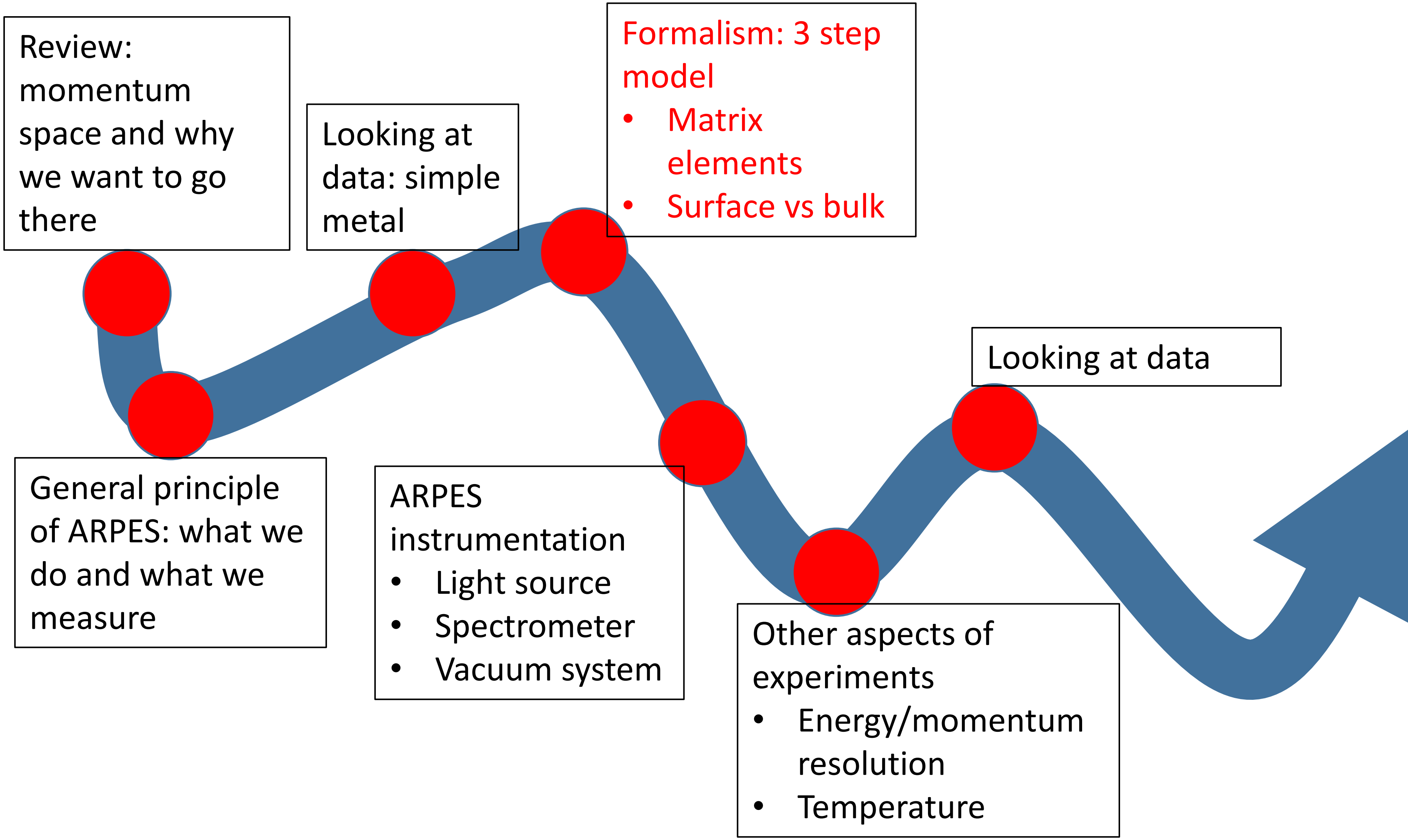
$$\Sigma(\mathbf{k},\omega)\rightarrow\Sigma(\omega)=\Sigma'(\omega)+i\,\Sigma''(\omega)$$

Measured dispersion minus calculated/assumed bare dispersion



Width of peaks

Outline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Back to the beginning: 3 step model

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

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

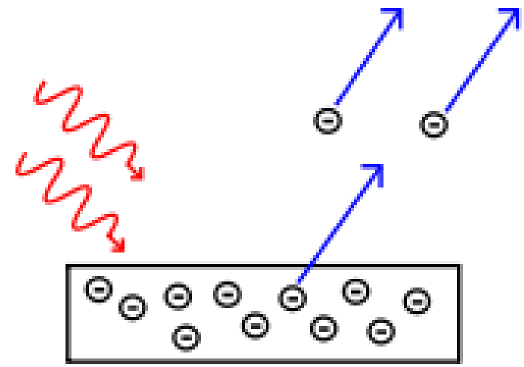
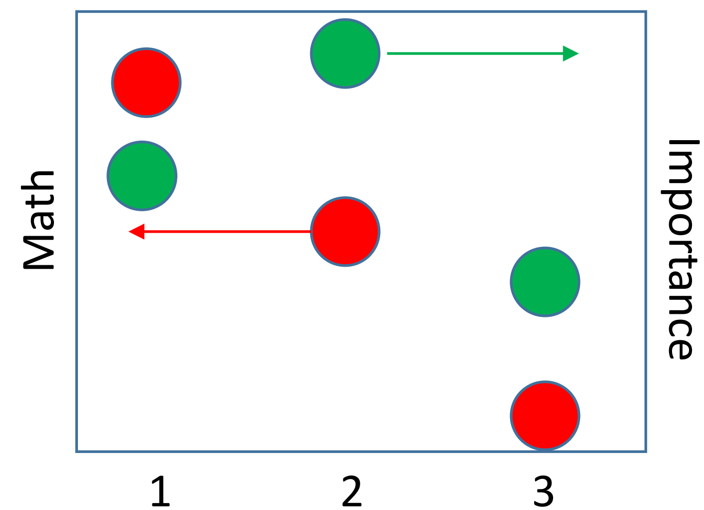


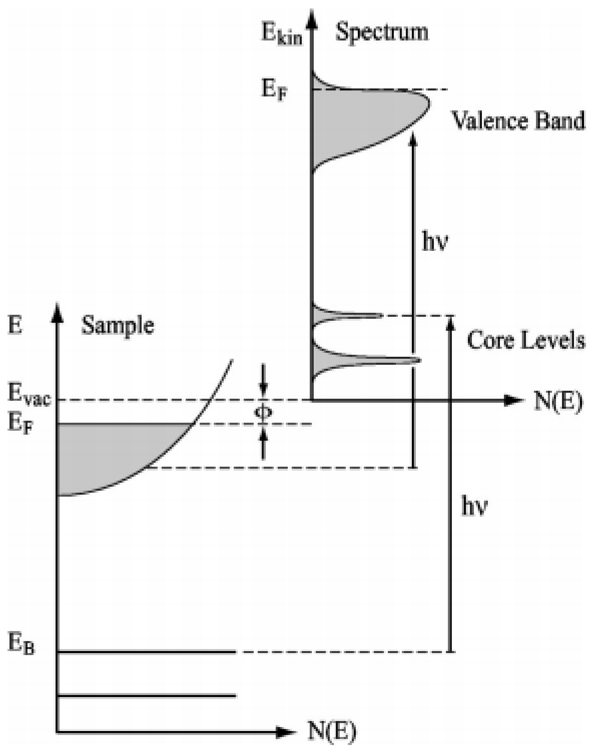
Image: https://en.wikipedia.org/wiki/Photoelectric_effect

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:

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

p=electron momentum

A=vector potential of photon

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

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

1. Optical excitation of electron in bulk (continued)

$$<\Psi_f^N \left| -\frac{e}{mc}\boldsymbol{A}\cdot\boldsymbol{p} \right| \Psi_i^N> = <\phi_f^{\boldsymbol{k}}| -\frac{e}{mc}\boldsymbol{A}\cdot\boldsymbol{p}|\phi_i^{\boldsymbol{k}}><\Psi_m^{N-1}|\Psi_i^{N-1}>$$

$$\equiv M_{f,i}^{\boldsymbol{k}} <\Psi_m^{N-1}|\Psi_i^{N-1}>$$

$M_{f,i}^{\boldsymbol{k}}$= 'ARPES matrix elements'=experimental details which affect measured intensity

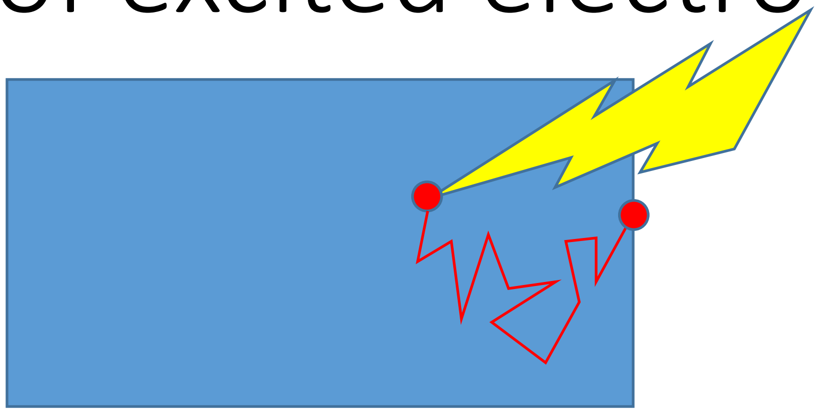
m=index given to N-1-electron excited state with eigenfunction Ψ_m^{N-1} and energy E_m^{N-1}

Total photoemission intensity originating from this step:

$$I(\boldsymbol{k}, E_{kin}) = \Sigma_{f,i} w_{f,i} = \sum_{f,i} |M_{f,i}^{\boldsymbol{k}}|^2 \sum_m |<\Psi_m^{N-1}|\Psi_i^{N-1}>|^2 \delta(E_{kin} + E_m^{N-1} - E_i^N - h\nu)$$

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

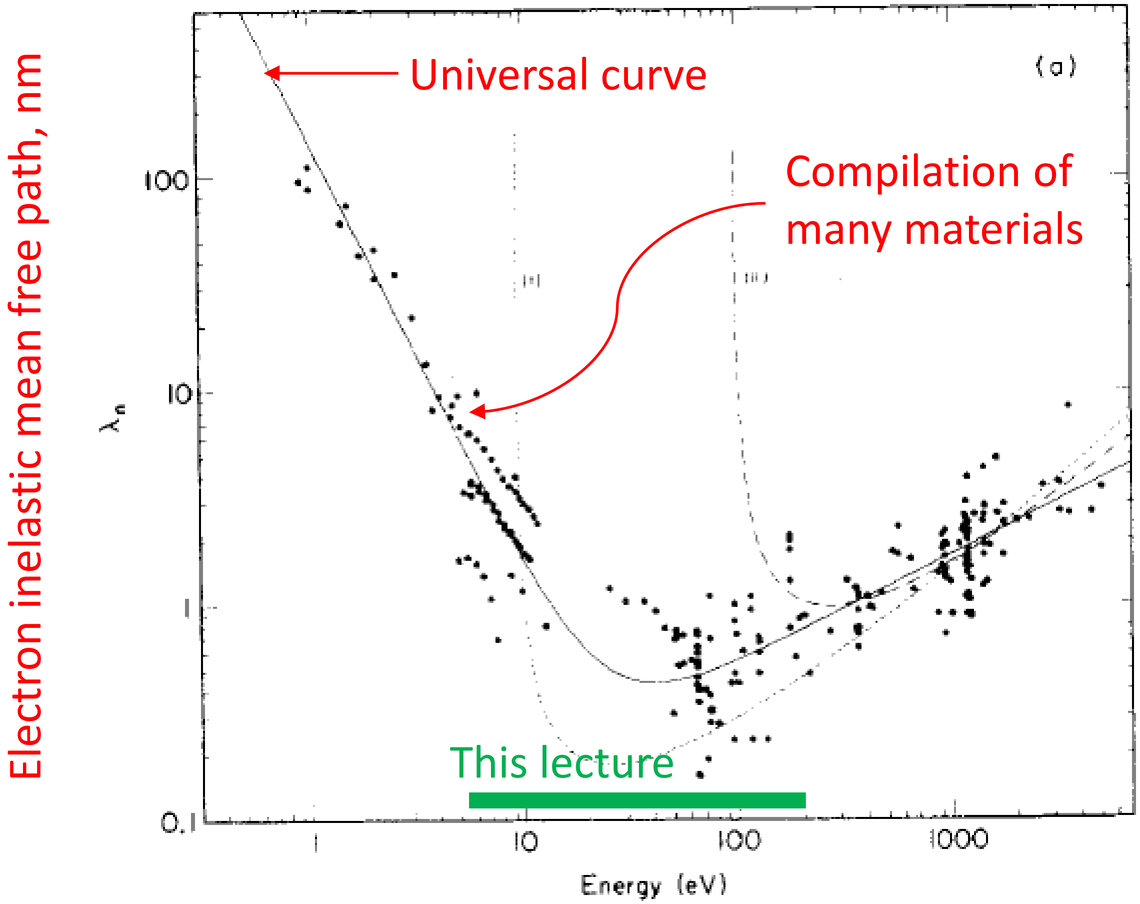
2. Travel of excited electron to the surface



- Excited electrons can scatter traveling to surface
- Typical distance between scattering events = electron mean free path

- What photon energies of light are used in photoemission experiments?
  6-6000 eV (this course: 6-150 eV)
- What is the penetration of 20 eV light into copper?
  ~11nm (source: http://xdb.lbl.gov/Section1/Sec_1-6.pdf)
- What is the electron inelastic mean free path of electrons with kinetic energy 20eV? ~0.6 nm (Seah and Dench)
- What is the size of the Cu unit cell? 0.36 nm

Electron mean free path universal curve



Seah and Dench, SURFACE AND INTERFACE ANALYSIS, VOL. 1, NO. 1, 1979

Conclusion of Step 2: electron mean free path determines how deep into a sample ARPES studies

Question: which photon energy ranges give more bulk sensitivity?

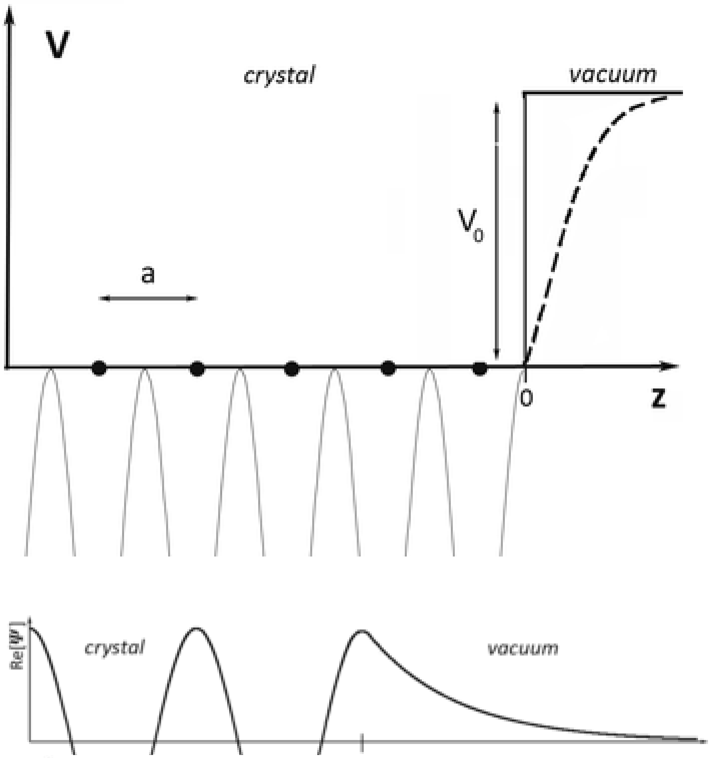
Surface vs bulk

Inside bulk: $\Psi_{n,\boldsymbol{k}} = e^{\imath \boldsymbol{k}\cdot\boldsymbol{r}} u_{n,k}(r)$

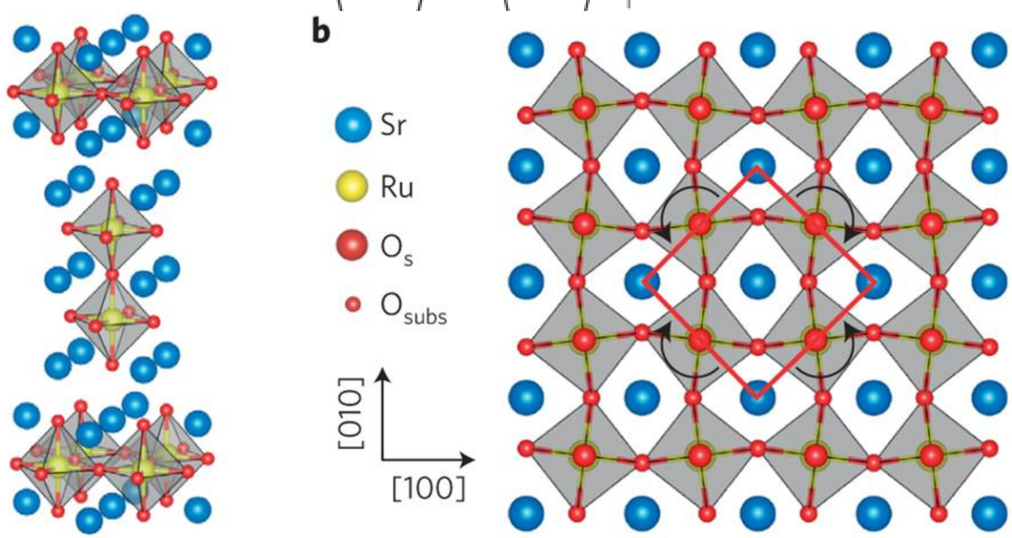
At surface: deviation from periodicity

Various scenarios:

- Electronically distinct state at surface (e.g. Shockley state on Cu 111)
- In quasi-2D materials with weak coupling between layers, surface termination may not matter much
- Sometimes surface states are interesting (e.g. topological insulators)
- Sometimes atoms on surface will relax/move, changing unit cell



Solution inside bulk

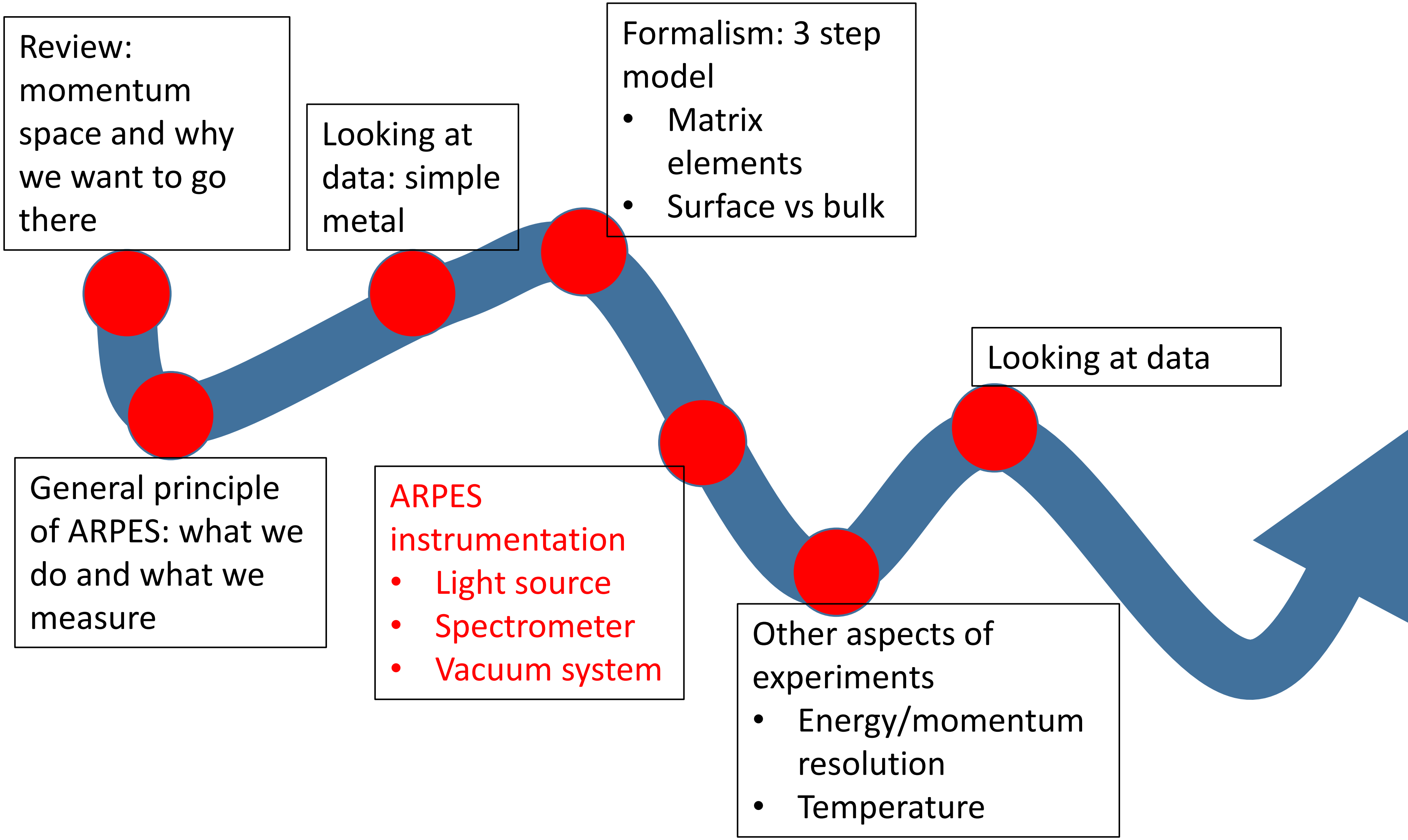


Halwidi *et al.* *Nature Materials* **15**, 450–455 (2016)

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

Outline



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General setup of ARPES experiment

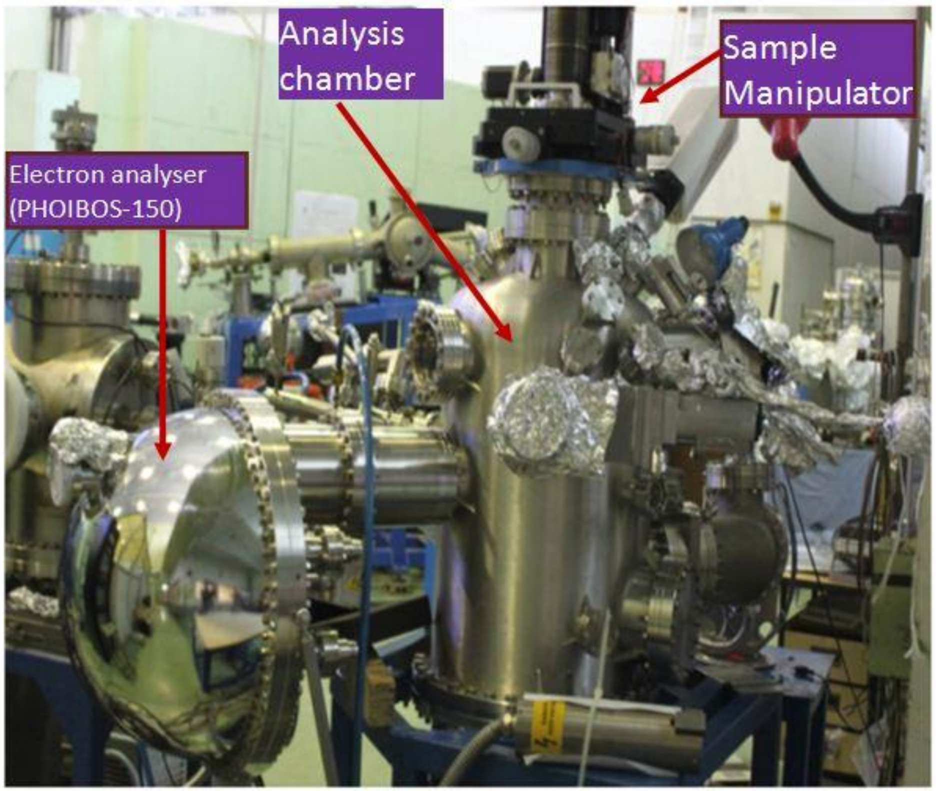


Image source:
http://www.cat.ernet.in/technology/accel/srul/indus1beamline/arpes.html

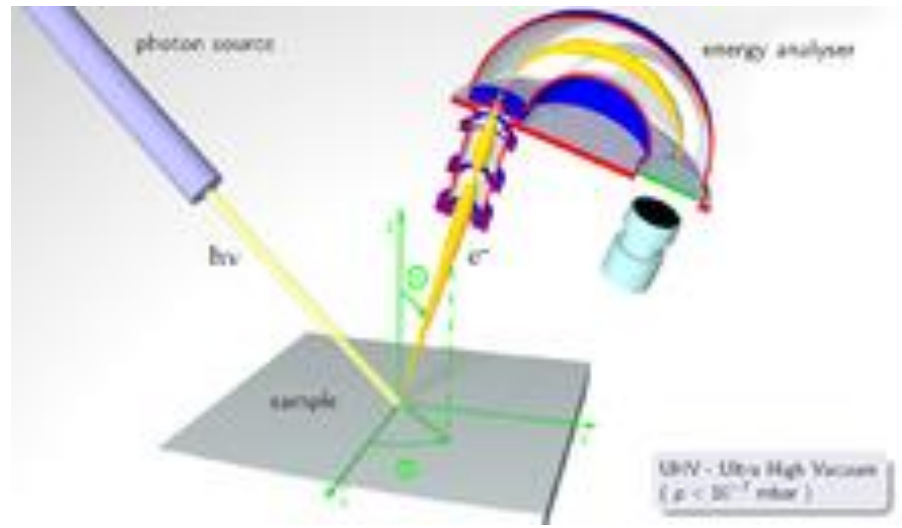


Image source:
https://en.wikipedia.org/wiki/Angle-resolved_photoemission_spectroscopy

ARPES light sources (6-150 eV)

Type	Available photon energies	Bandwidth/monochromaticity	Intensity	Polarization
Laser	6-11 eV; not much variation for a given laser	Can be <<1 meV	Potentially high	Variable polarization
Gas (He, Xe, Ne, Ar…) discharge lamp	21.2, 40.8, 8.4, 9.6, 11.6 eV (and more)	Can be small (<1 meV) with monochromator	Sometimes low	random polarization
Synchrotron	Variable; different synchrotrons and endstations specialize in different energy ranges	0.5 to several meV; tradeoff between bandwidth and intensity	tradeoff between bandwidth and intensity	Fixed polarization

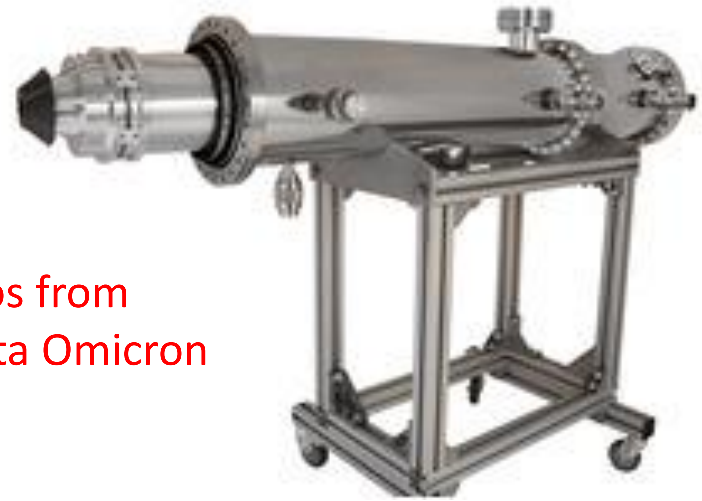
$$E_{kin} = h\nu - \phi - |E_B|$$

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

$$M_{f,i}^{\boldsymbol{k}} \equiv \langle \phi_f^{\boldsymbol{k}} | -\frac{e}{mc} \boldsymbol{A} \cdot \boldsymbol{p} | \phi_i^{\boldsymbol{k}} \rangle$$

ARPES spectrometer/analyzer

Photos from
Scienta Omicron

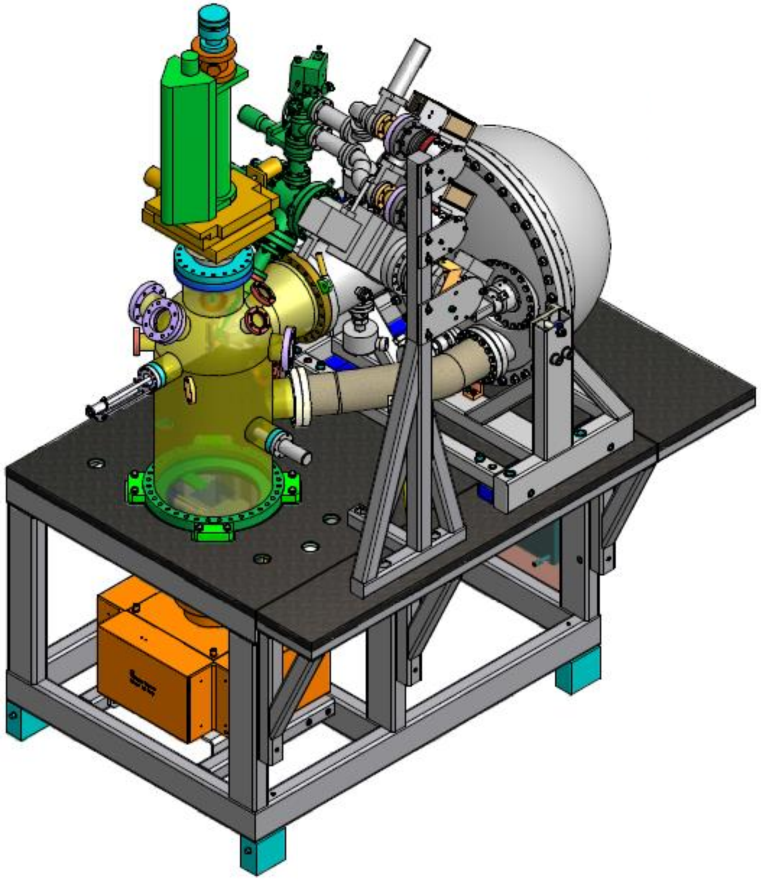


nit.edu/ge
rch.html

- Select 1D trajectory in momentum space by rotating sample relative to entrance slit
- Electrostatic lens decelerates and focuses electrons onto entrance slit
- Concentric hemispheres kept at potential difference so that electrons of different energy take different trajectory
- 2D detection of electrons, E vs k

- Electrostatic lens images photoemitted electrons onto position sensitive detector (PSD)
- Discriminate photoelectron energies based on different flight times from sample to detector
- 3D detection of electrons, E vs (kx,ky)

(Ultra high) vacuum chambers



	High vacuum (HV)	Ultrahigh vacuum (UHV)
Pressure	1e-3 to 1e-9 torr	1e-12 to 1e-9 torr
Molecular mfp	10 cm to 1000km	1000 to 100,000 km
Amount of time to deposit a monolayer on sample surface*	.006s to 95 minutes (typical estimate: 6s)	95 minutes to 65 days (typical estimate: 20 hours)

$*t = \frac{1.7\times10^{-6}}{0.6 * p * S}$

p=pressure in torr

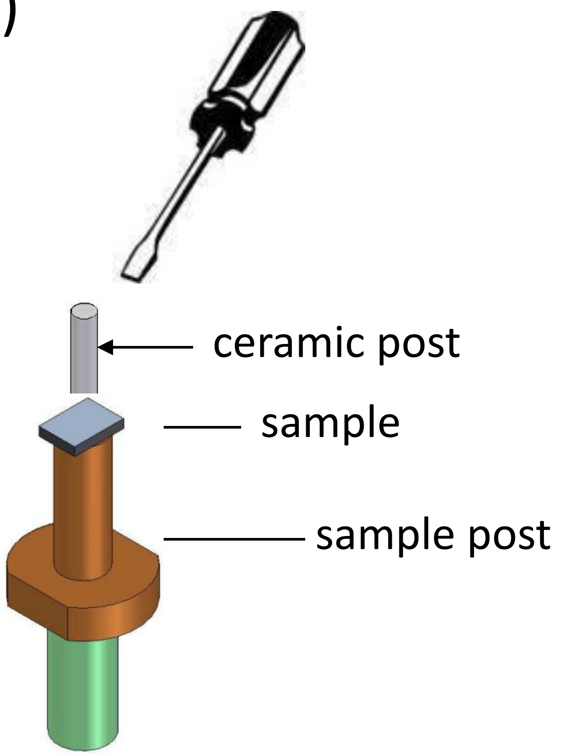
S=sticking coefficient (between 0 and 1)

Ref: Hufner, *Photoelectron Spectroscopy*

Sample preparation

Achieve atomically clean surface by…

- Cleaving in-situ
- Growing material in-situ
- Sputter-and-anneal (e.g. Cu 111 surface)



Sample cleaving

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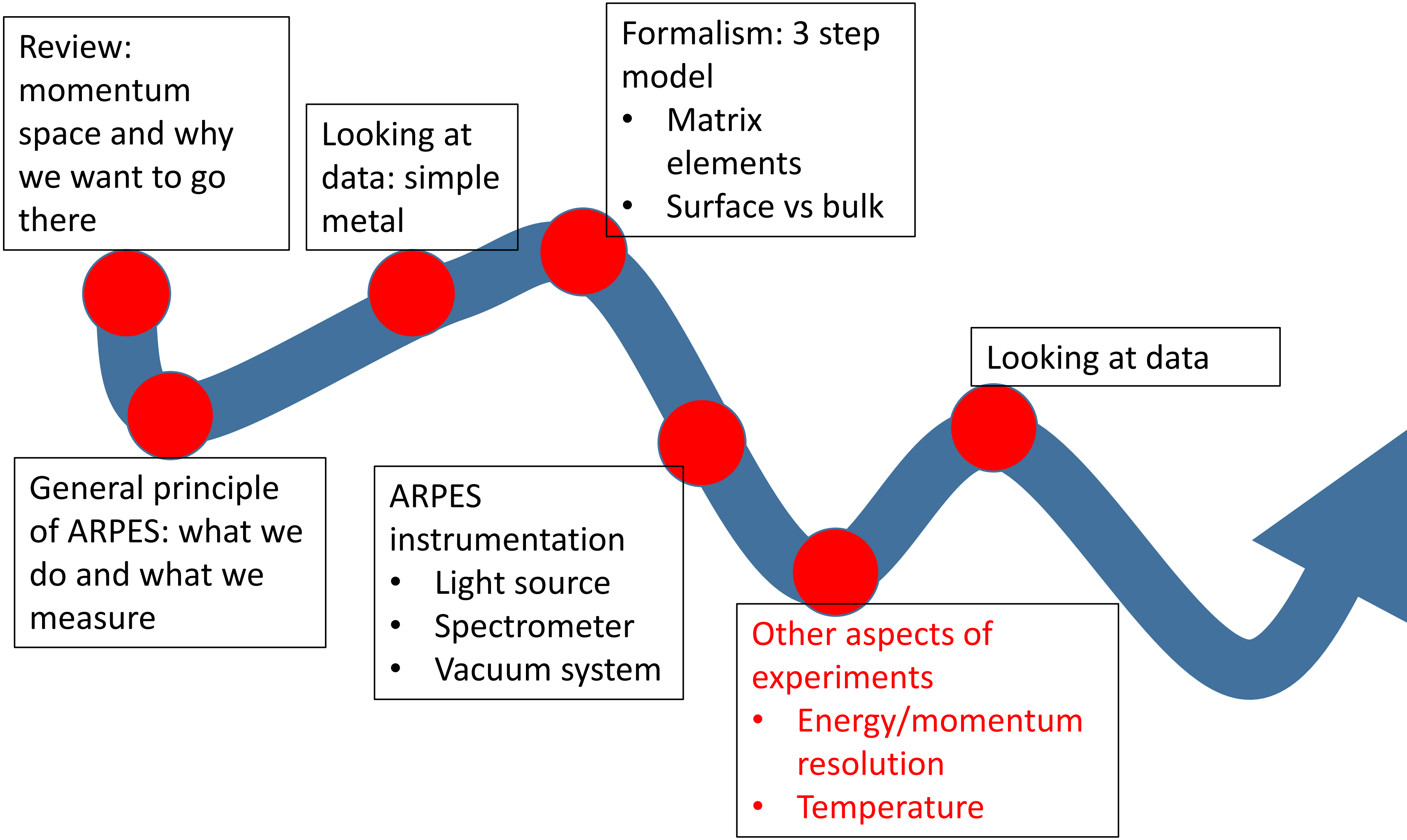
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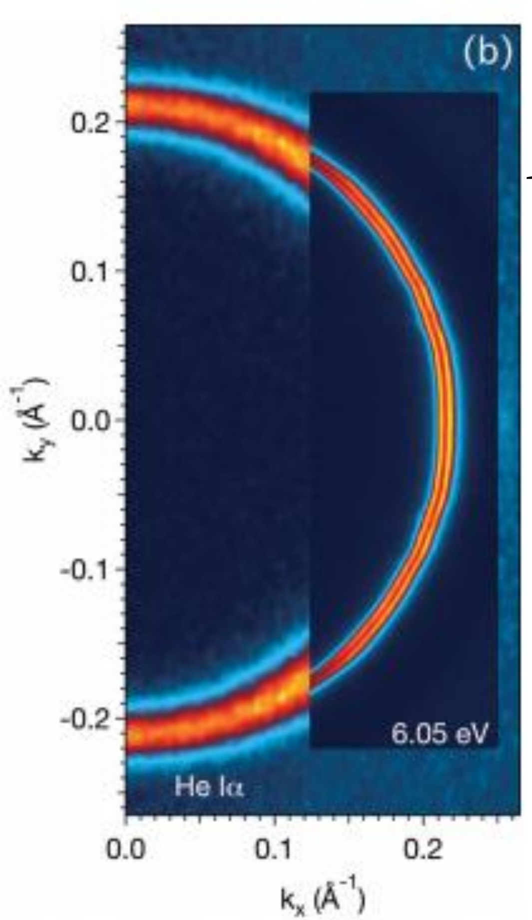
Resolution in ARPES experiment



PRB **87**, 075113 (2013)

Intensity in ARPES experiment:

$$I(\mathbf{k},\omega) = I_0(\mathbf{k},\nu,\mathbf{A})\, f(\omega) A(\mathbf{k},\omega) \otimes R(\Delta k, \Delta\omega)$$

"Matrix elements"

Fermi-Dirac Function

Convolution

Resolution Ellipsoid

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

"band structure + Interactions"

Energy resolution

Origins of energy broadening

- Light source bandwidth
- Electrical noise
- Spectrometer

$E_{pass} = \frac{e\Delta V}{\frac{R_1}{R_2} - \frac{R_2}{R_1}} = 0.5, 1, 2, 5, 10\text{eV}$, or more

$$\Delta E_a = E_{pass}\left(\frac{w}{R_0} + \frac{\alpha^2}{4}\right)$$

w =width of entrance slit (as small as .05 mm)
R_0=average radius of analyzer (~20 cm)
α =angular resolution (as small as .05°)

Momentum resolution

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

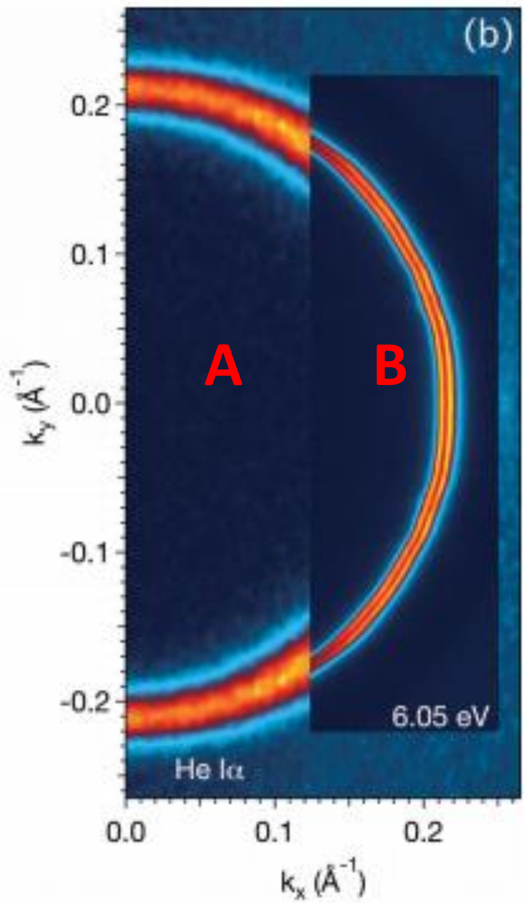
$$\mathbf{p}_{||} = \hbar \mathbf{k}_{||} = \sqrt{2mE_{kin}} \cdot \sin\vartheta$$

$$\Delta \mathbf{k}_{||} = \frac{\sqrt{2mE_{kin}} \cdot \cos\vartheta}{\hbar} \Delta\vartheta$$

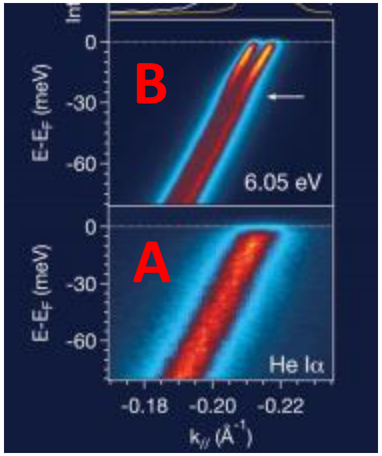
Related to angular resolution of spectrometer and beam spot size

For a given spectrometer, how can one improve momentum resolution?

Cu 111 ARPES: origin of superior resolution?



PRB **87**, 075113 (2013)



Why is B sharper than A?

Some notes on resolution…

- Instrument resolution represents a convolution of original spectrum with 2D resolution ellipsoid. It does not represent the smallest energy or momentum scale which can be resolved
- Resolution can move spectral features around a bit
- There are sometimes tradeoffs to achieving better resolution (e.g. sacrificing photon intensity or ability to access all of momentum space) which may be unacceptable for some experiments
- Resolution has improved a lot in the last 30 years

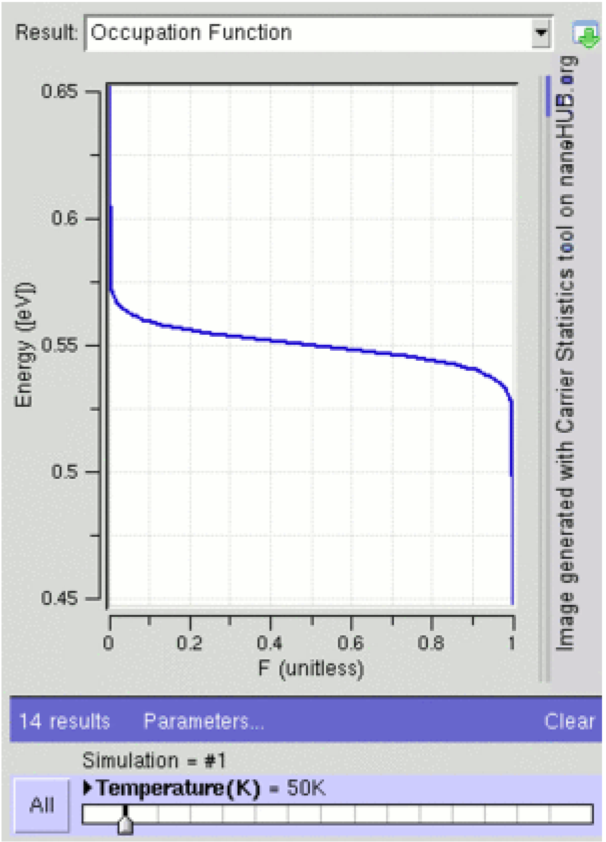
What about temperature?

$$I(\mathbf{k},\omega) = I_0(\mathbf{k},\nu,\mathbf{A}) f(\omega) A(\mathbf{k},\omega) \otimes R(\Delta k,\Delta\omega)$$

- Fermi-Dirac cutoff gets broader giving access to more unoccupied states
- Spectra get broader, generally following electron lifetime of material system

Temperature control during experiment:

- Flow cryostat
- Maximum temperature ~400K
- Minimum temperature
  - 20K standard
  - ~7K with radiation shielding
  - ~1K high end



Source: https://en.wikipedia.org/wiki/Fermi%E2%80%93Dirac_statistics

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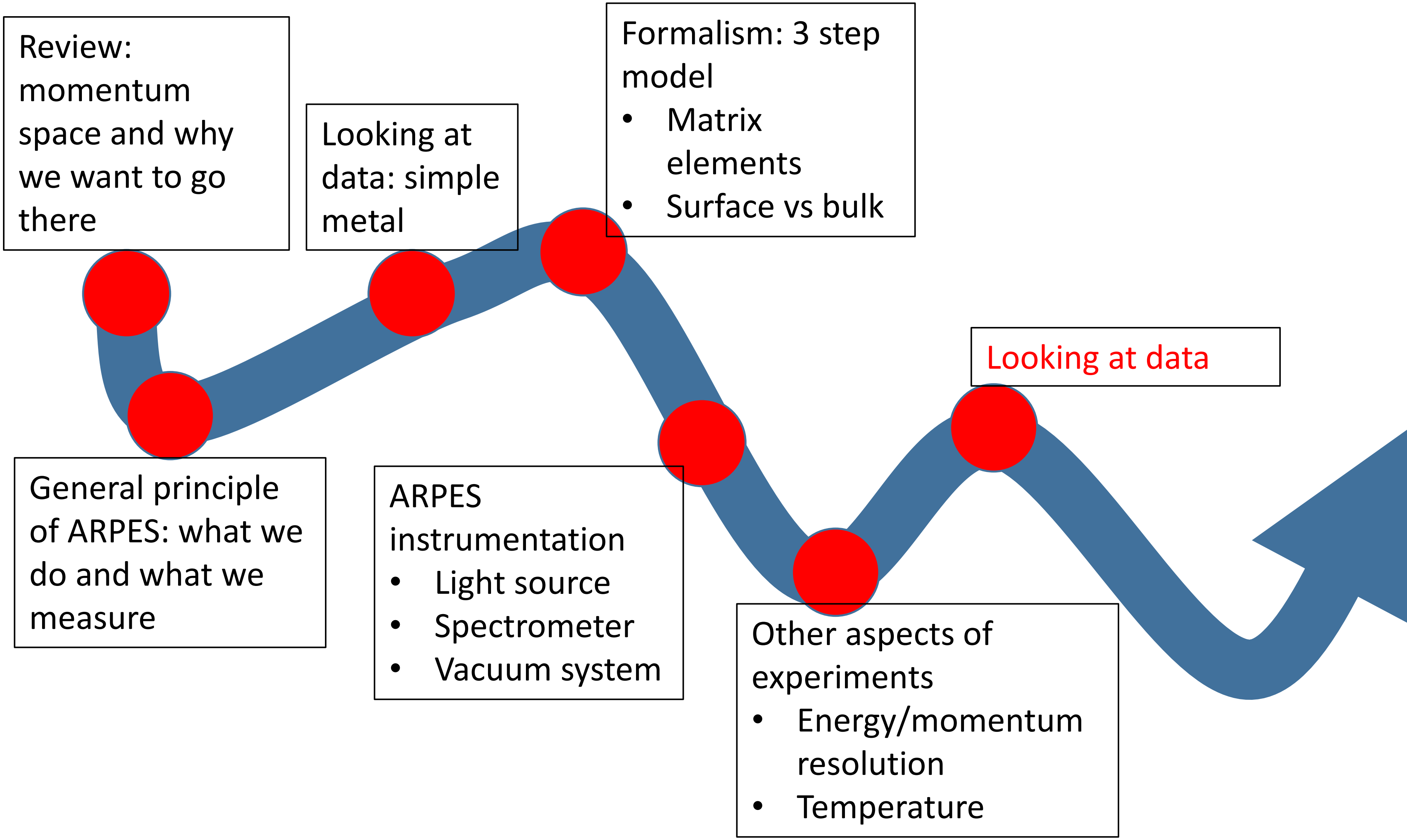

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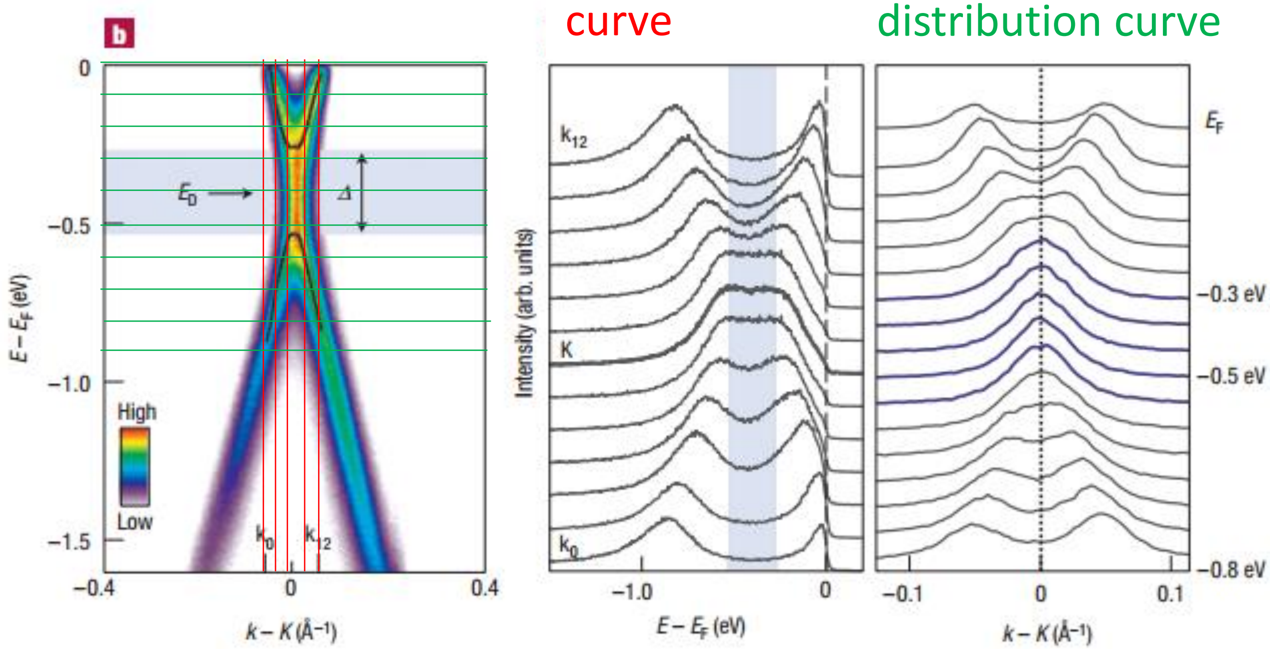
Looking at data…

EDC: Energy distribution curve

MDC: Momentum distribution curve



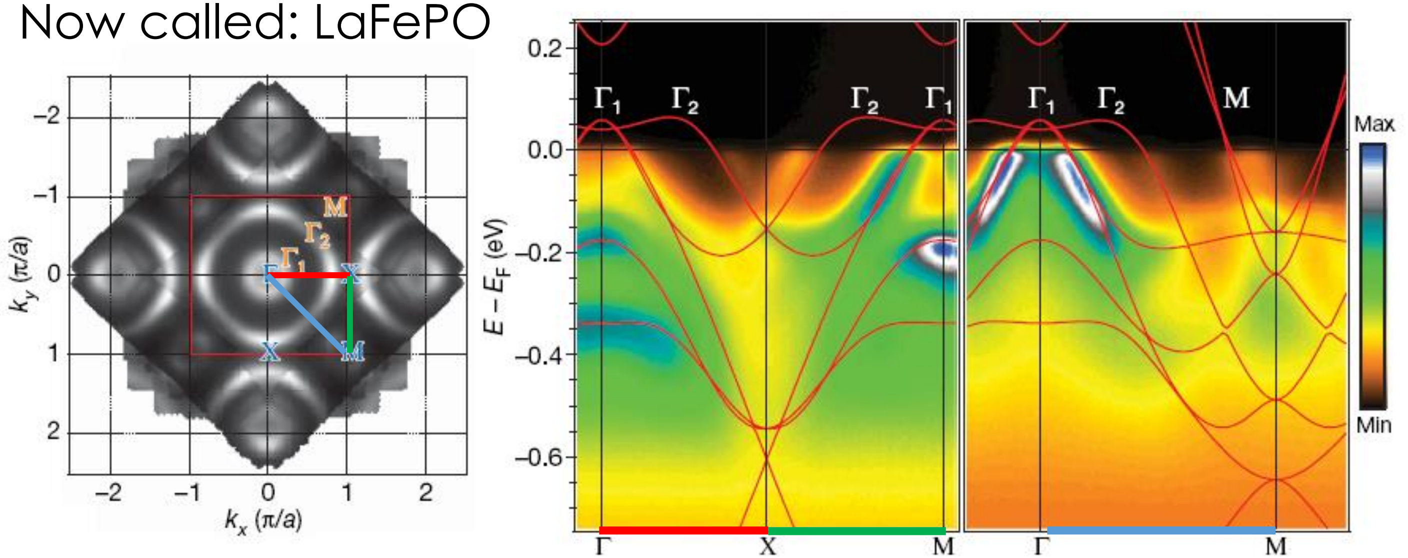
Zhou *et al* Nat. Mater **6** 770 (2007)

Main result: substrate (SiC) breaks sublattice symmetry of graphene, opening a gap at the Dirac point

Which analysis (EDC or MDC) illustrates this result better?

Looking at more data…

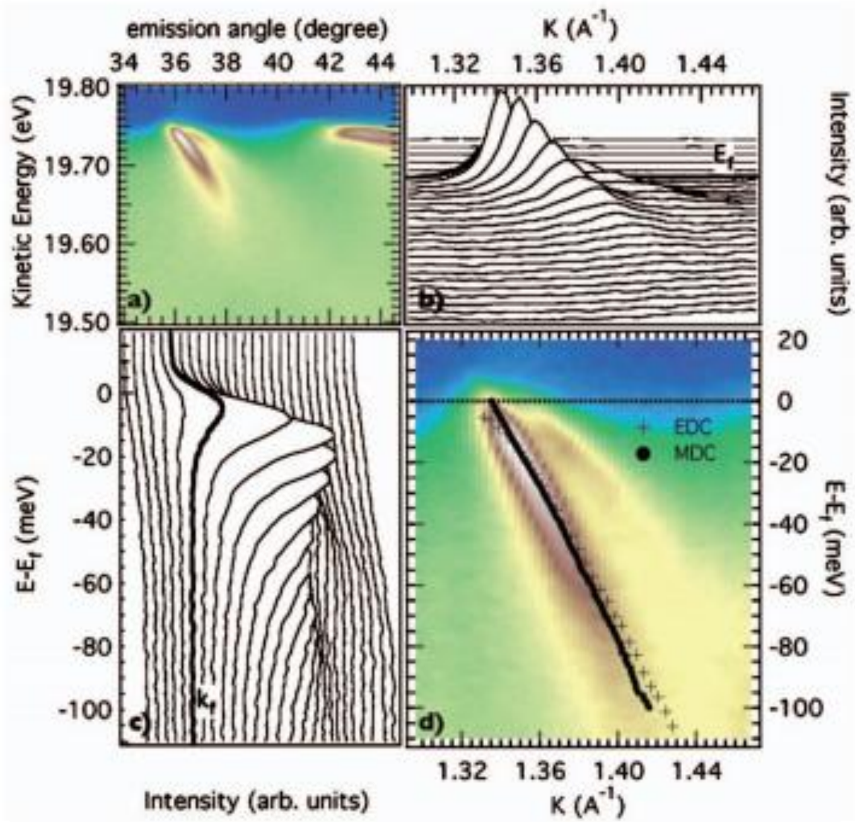
LaOFeP
Now called: LaFePO



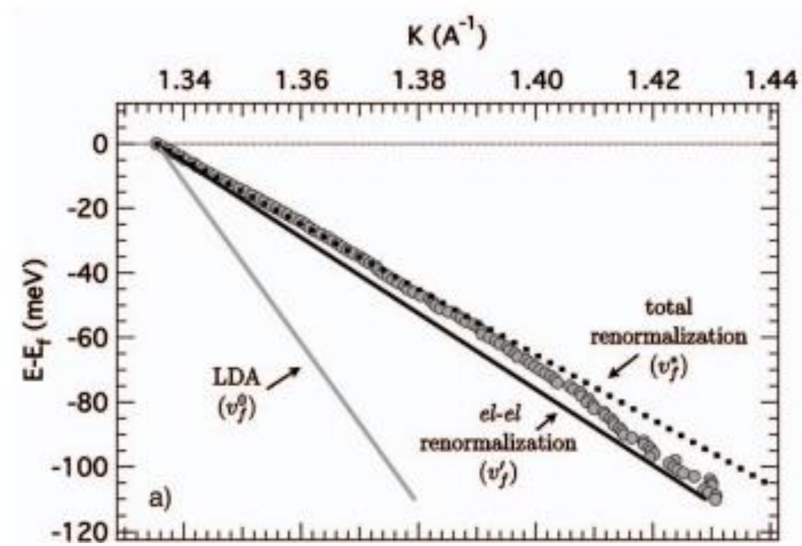
D. H. Lu, *et al.* Nature **455** 81 (2008)

- Data taken along 1D trajectories in k-space (cuts); high-symmetry cuts in these data, but not always
- Fermi surface map produced by pasting many 1D cuts together
- Matrix elements: same band has different brightness for different experiment geometries
- Interaction between experiment and theory

More data: quantitative analysis of Sr_2RuO_4 lineshape

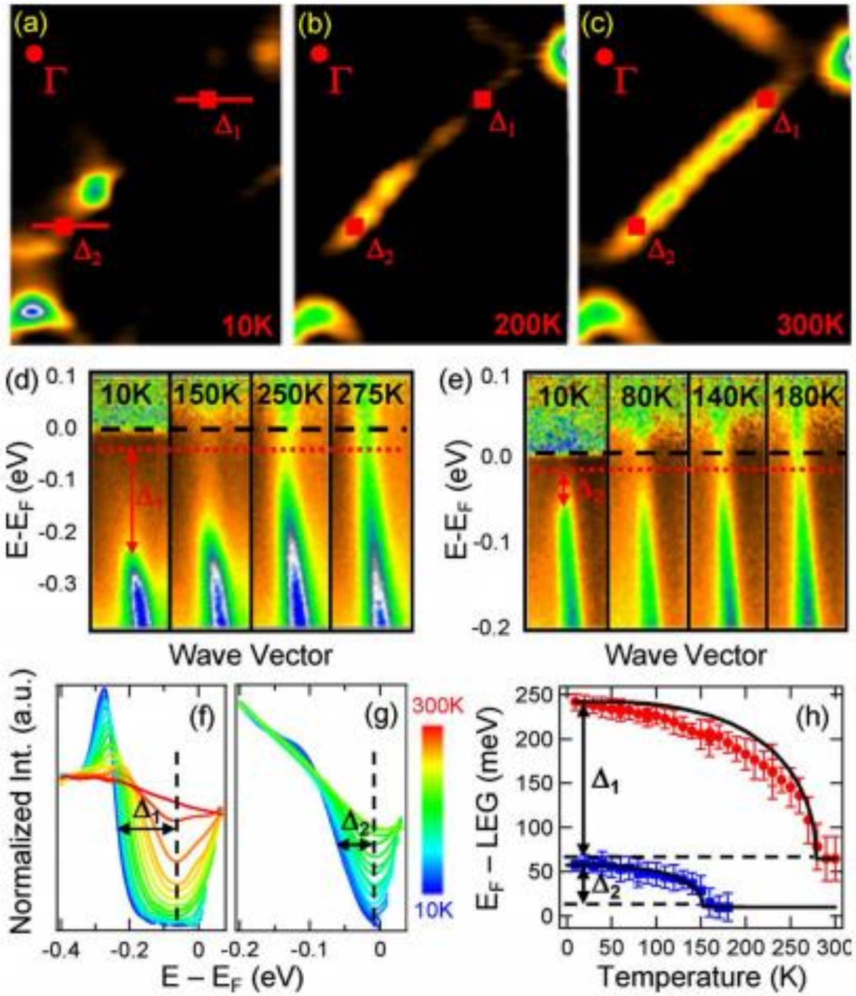


Why does EDC and MDC analysis give different band position?



N. Ingle *et al.* PRB 72, 205114 2005

Spectral gaps in ARPES: example ErTe3 (CDW system)



Moore *et al.* PRB **81**, 073102 (2010)

Method 1: Disappearance of intensity in fermi surface map (only works if gap opens at E_F)

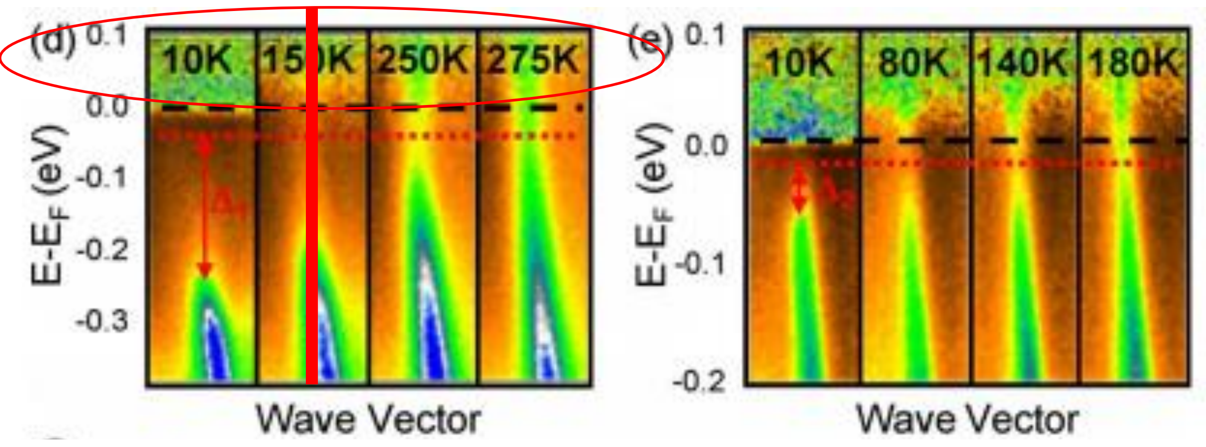
Method 2: Energy vs k dispersion

Method 2.5: Energy distribution curve (EDC) + reasonable definition of gap edge

Resources

- Campuzano, Norman, Randeria. *Photoemission in the high-Tc superconductors.* https://arxiv.org/pdf/cond-mat/0209476.pdf
- Damascelli, Hussain, Shen. *Angle-resolved photoemission studies of the cuprate superconductors.* Rev. Mod. Phys. **75** 473 (2003)
- Damascelli. *Probing the Electronic Structure of Complex Systems by ARPES.* Physica Scripta. Vol. T109, 61–74, 2004 (https://www.cuso.ch/fileadmin/physique/document/Damascelli_ARPES_CUSO_2011_Lecture_Notes.pdf)
- Hufner, *Photoelectron Spectroscopy, Springer (2003)*

Extracting spectral gaps



1. Get rid of Fermi-Dirac cutoff by dividing by Fermi-Dirac distribution or symmetrizing (only if there is e-h symmetry)

Extra: imaging of electrons onto entrance slit via electrostatic lens

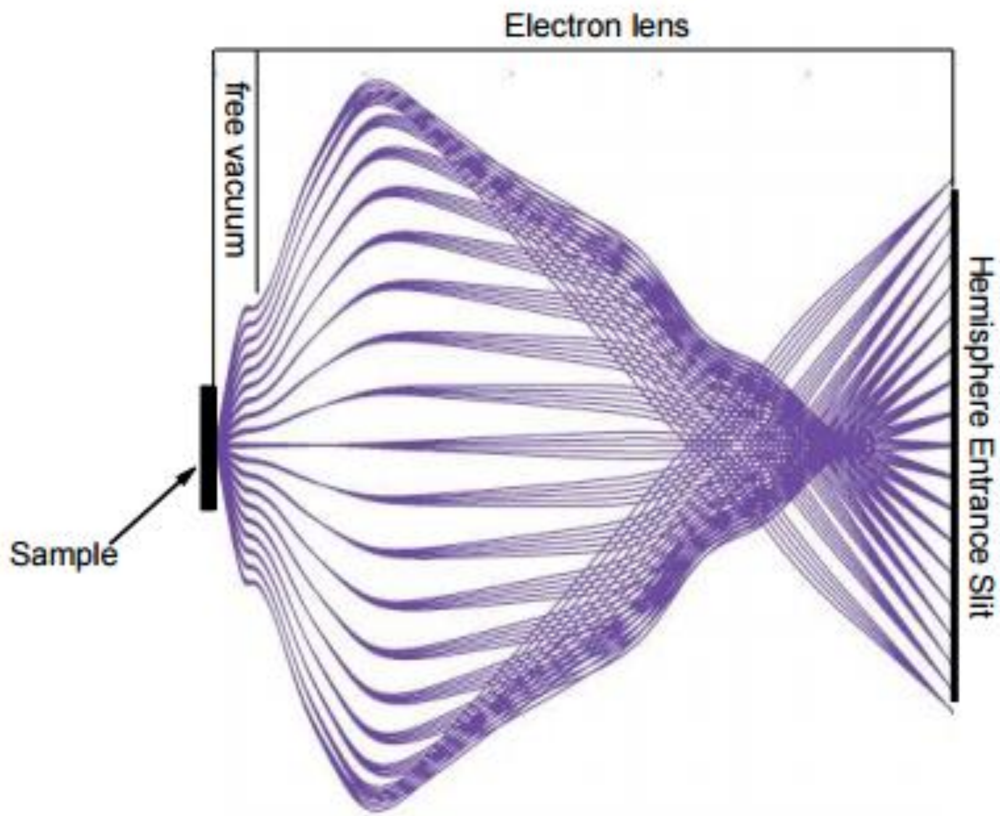


Image from VG Scienta and PhD Thesis of Dr. Ari Deibert Palczewski
(http://lib.dr.iastate.edu/cgi/viewcontent.cgi?article=2629&context=etd)