Angle-resolved photoemission spectroscopy (ARPES) overview

Overview

QS3 Summer School

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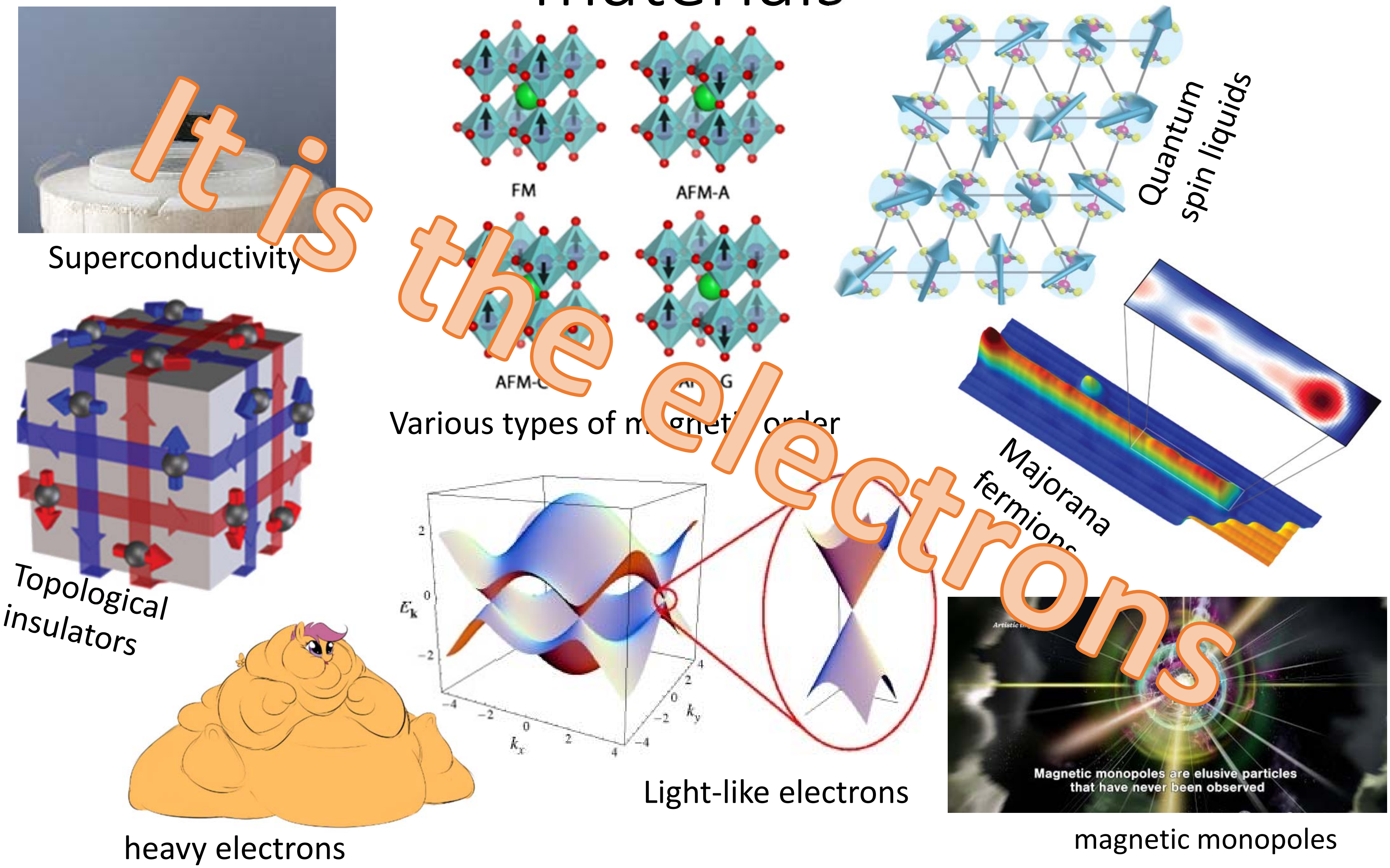
QS3

Many phenomena in quantum materials



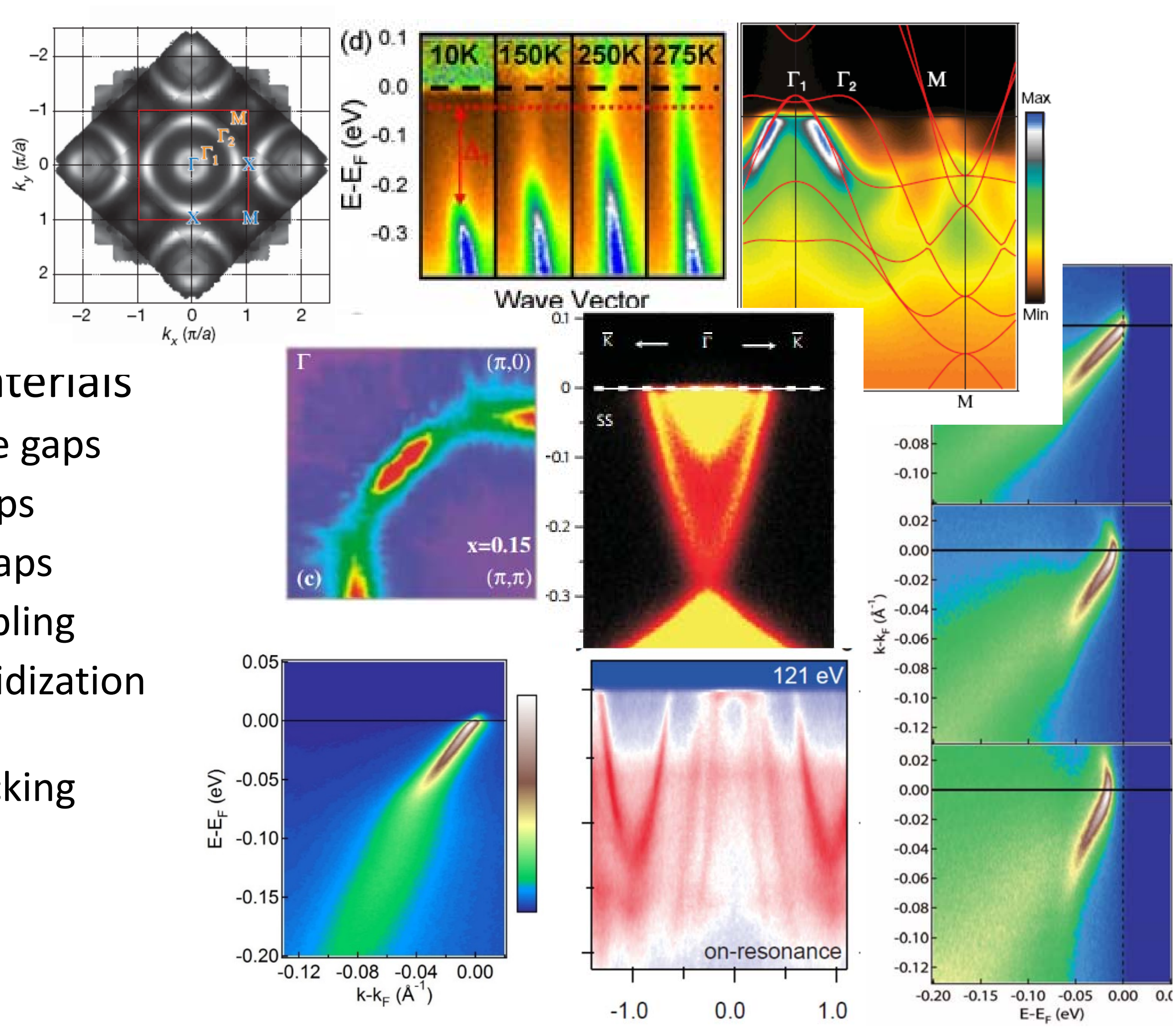
Structures in momentum space

All materials

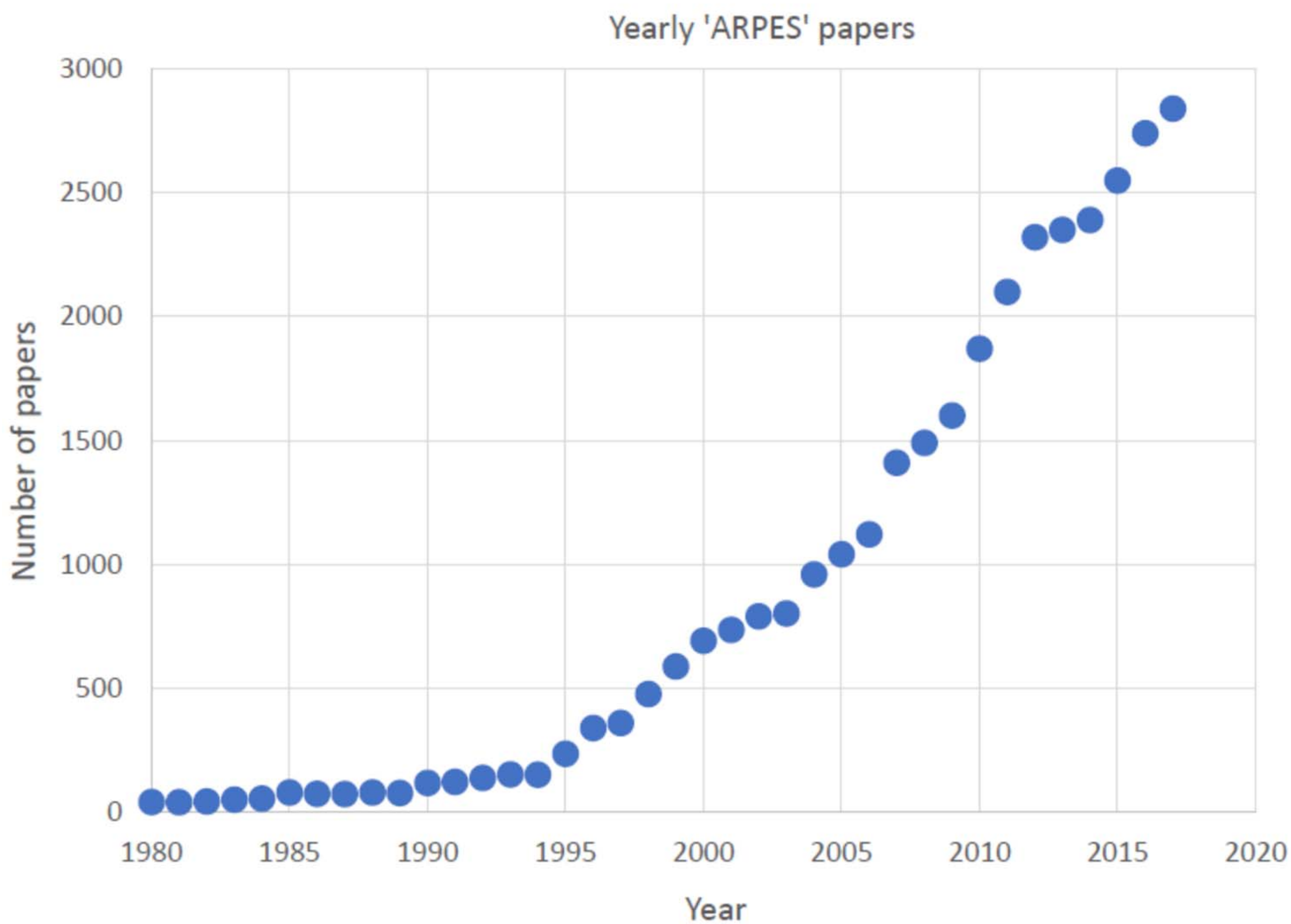
- Brillouin zones
- Fermi surfaces
- Band dispersion

Related to quantum materials

- Charge density wave gaps
- Superconducting gaps
- Spin density wave gaps
- Electron-boson coupling
- Heavy fermion hybridization gaps
- Spin momentum locking
- Dirac dispersions
- Surface states
- …



A growing experimental technique

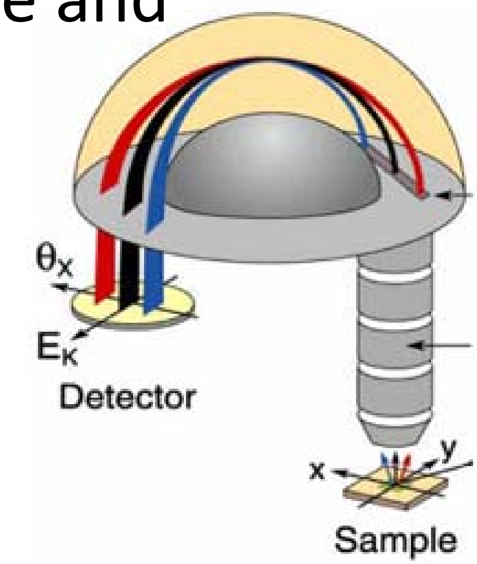


Outline

- General principles of ARPES and looking at simple data
- Formalism: three step model and single particle spectral function
- ARPES instrumentation and other experimental aspects
- Applications to quantum materials: unconventional superconductors, topological insulators, dirac materials

Angle-Resolved Photoemission spectroscopy overview

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



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

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

Definitions:

$E_{kin} = kinetic\ energy\ of\ photoelectron$ measure

$h\nu = photon\ energy$ Know (6-200 eV this lecture)

$\phi = work\ function$ know/measure (~ 4 eV)

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

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

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

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

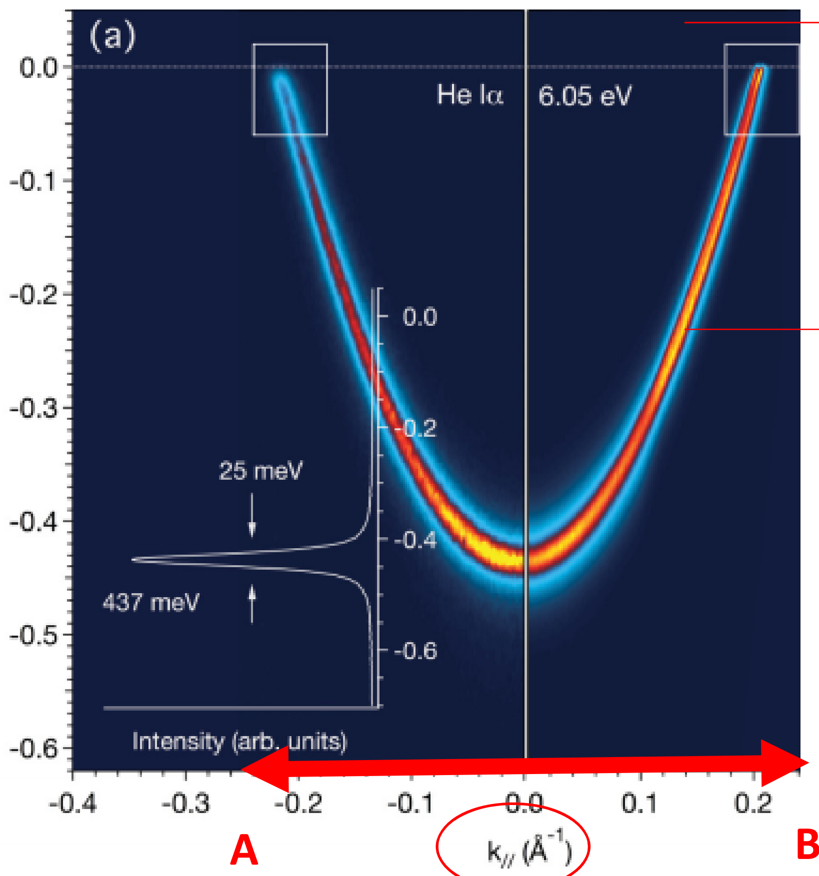
Linewidth or lifetime

Band structure
+
Interactions

Band structure: simple metal (Cu 111 surface)

Electron binding energy

$|E_B| = E - E_F$



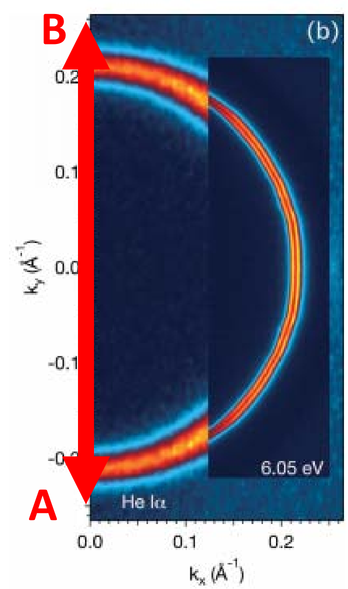
In-plane momentum

PRB **87**, 075113 (2013)

Fermi-Dirac cutoff

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

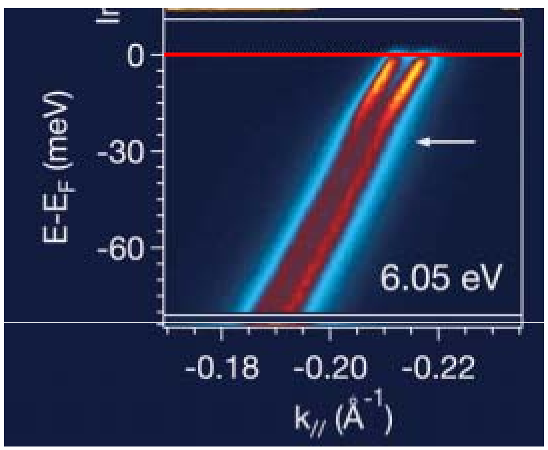
$$\epsilon_k = E(k) = \frac{\hbar^2 k^2}{2m^*}$$

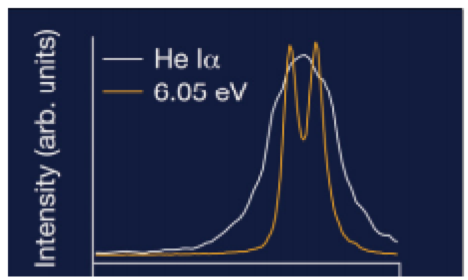


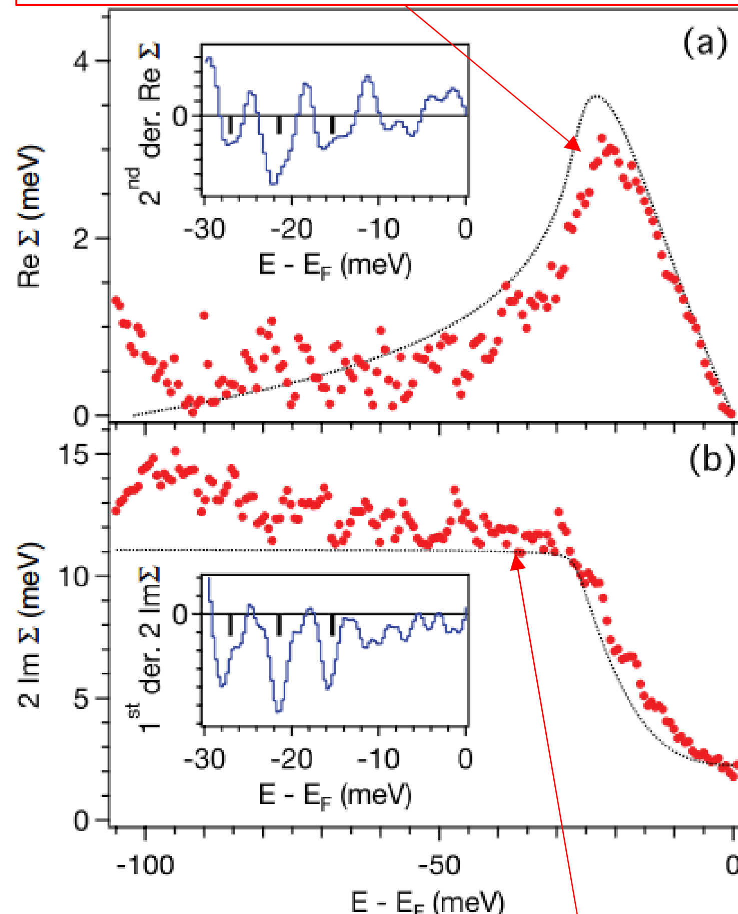
Fermi surface map is (usually) produced by pasting adjacent slices together

Self energy: simple metal (Cu 111 surface)

Measured dispersion minus calculated/assumed bare dispersion







Width of peaks

PRB **87**, 075113 (2013)

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

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

Photoemission basics: 3 step model

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

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

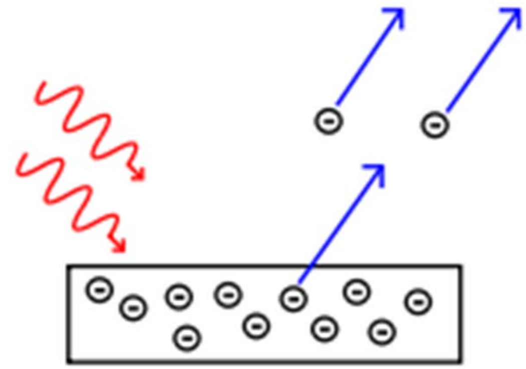
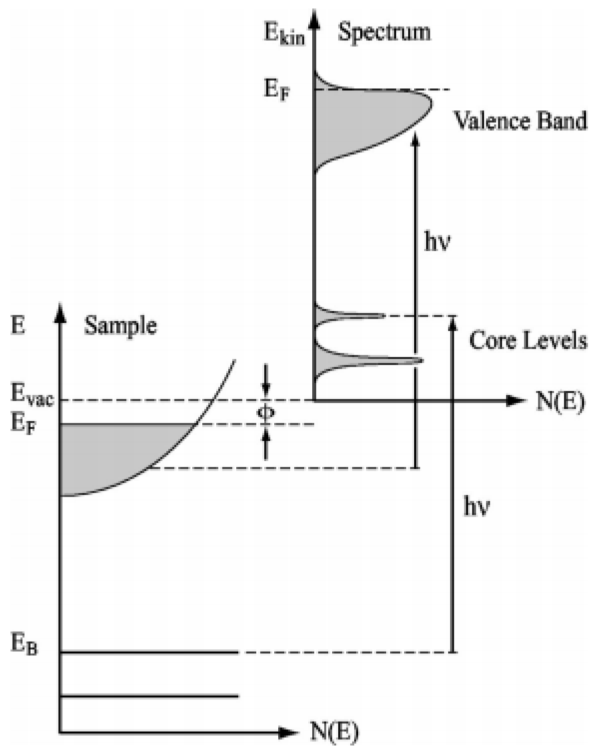


Image: https://en.wikipedia.org/wiki/Photoelectric_effect

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 (points in direction of polarization)

Express as antisymmetric 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'

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

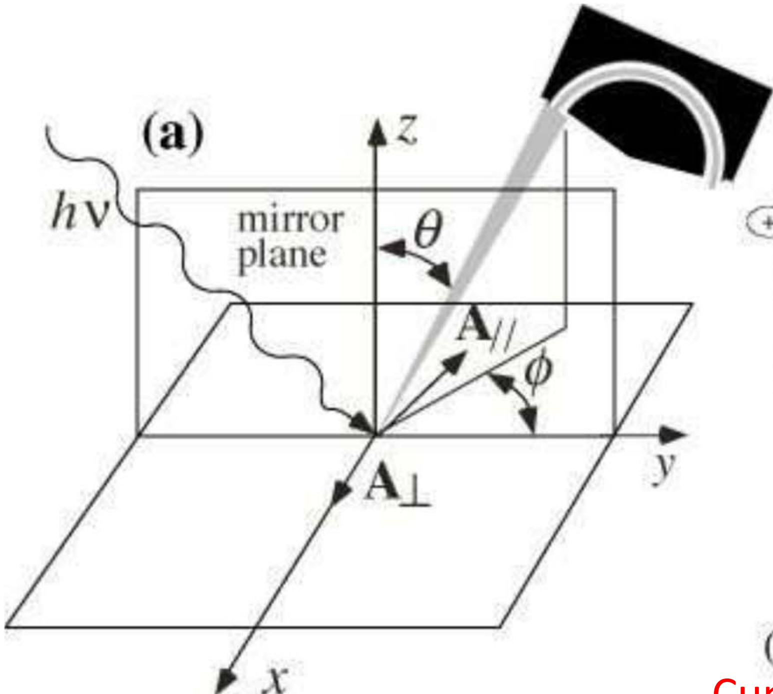
Total photoemission intensity originating from this step:

$$I(\boldsymbol{k}, E_{kin}) = \Sigma_{f,i} w_{f,i}$$

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

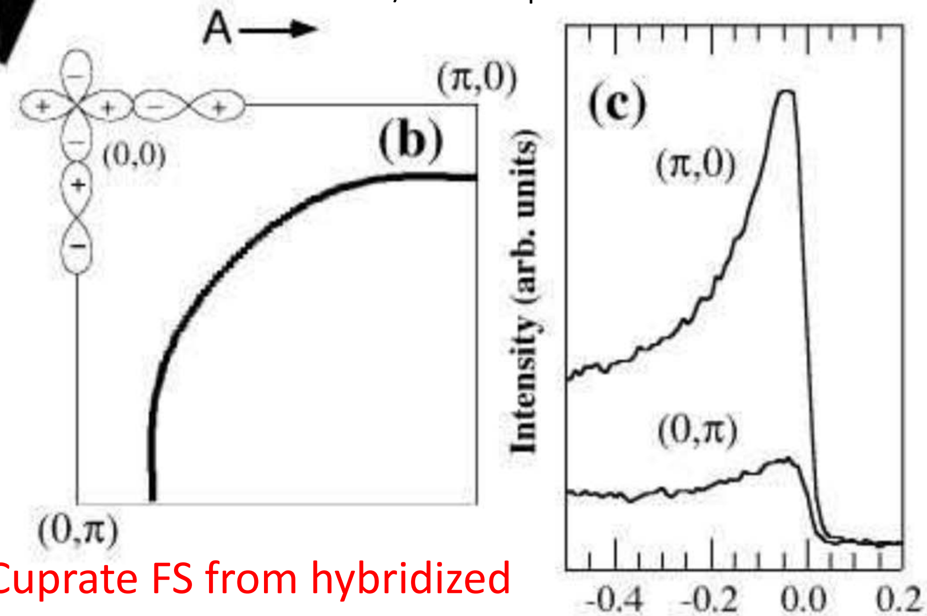
Consequences of step 1: Observed band intensity is a function of experimental geometry, photon energy, photon polarization
"Matrix element effects"

Matrix elements example 1: cuprates



Expt geometry: beam and detector in mirror plane of sample

Campuzano *et al,* https://arxiv.org/pdf/cond-mat/0209476.pdf



Cuprate FS from hybridized $Cu - d_{x^2-y^2}$ and $O - p_{x,y}$ orbitals

Measurement along $(0{,}0) \rightarrow (\pi, 0)$ is dipole-allowed (forbidden) if **A** is parallel (perpendicular) to mirror plane along $(0{,}0) \rightarrow (\pi, 0)$

- Ψ_f must be even wrt mirror plane (otherwise it would vanish at detector)
- Dipole transition allowed if matrix element even overall
- 2 options for Ψ_i and **A**

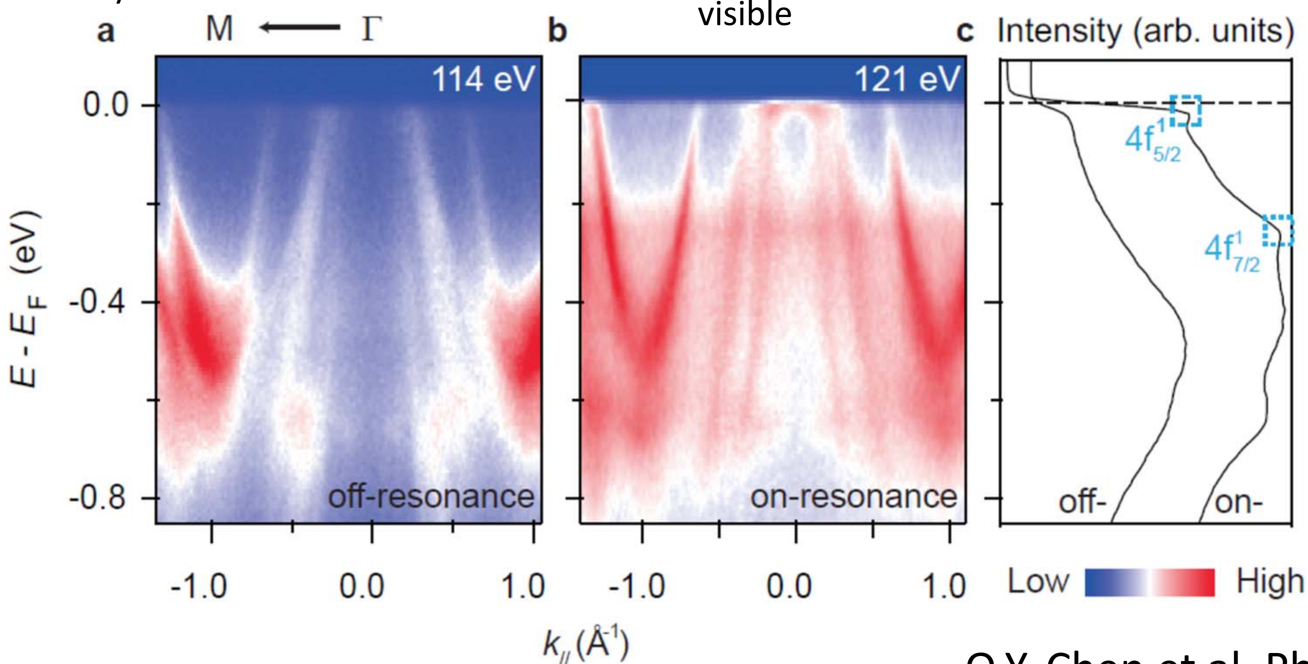
$$\langle \Psi_f | \boldsymbol{A} \cdot \boldsymbol{p} | \Psi_i \rangle = \begin{cases} \Psi_i \; even \;\; \langle + | + | + \rangle \rightarrow \boldsymbol{A} \; even \; (||) \\ \Psi_i \; odd \;\; \langle + | - | - \rangle \rightarrow \boldsymbol{A} \; odd \; (\perp) \end{cases}$$

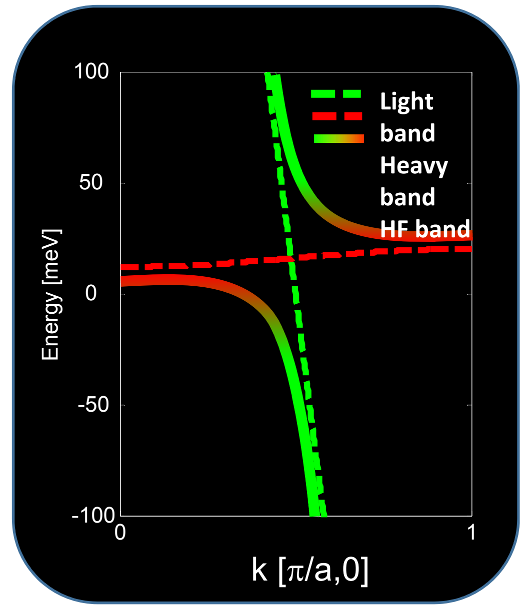
Matrix elements example 2: heavy fermions

- Different parts of hybridized band structure originate from different orbitals
- Ce^{3+} corresponds to a $4f^1$ electronic configuration.
- At 121 eV photon energy, there is resonance between a “core” 4d state and the 4f state.

114 eV: Photoemission dominated by Co 3d and Ce 5d states.

121 eV: 4f states visible

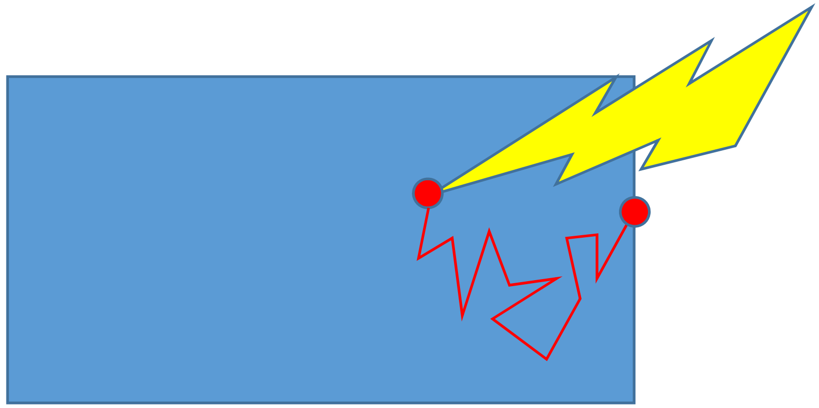




Q.Y. Chen et al. Phys. Rev. B **96**, 045107 (2017)

Slide courtesy of E. H. da Silva Neto

2. Travel of excited electron to the surface

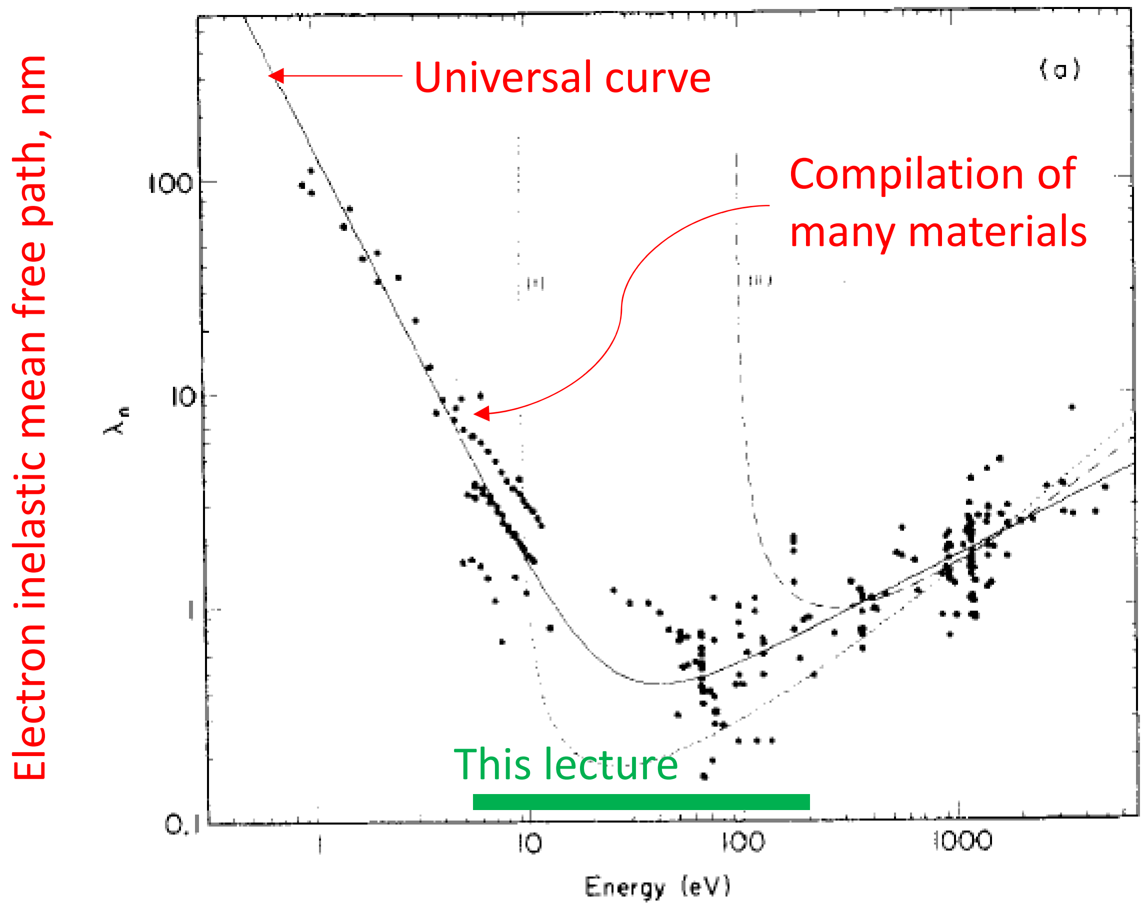


- Excited electrons can scatter traveling to surface
- Typical distance between scattering events = electron mean free path

Select the correct combination of parameters:

	Penetration depth of 20 eV light into Cu	Inelastic mean free path of electrons with 20 eV kinetic energy	Unit cell of Cu
A	6 nm	0.1 nm	3.6 nm
B	11 nm	0.6 nm	0.36 nm
C	0.6 nm	11 nm	0.36 nm
D	11 nm	6 nm	3.6 nm
E	110 nm	6 nm	.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

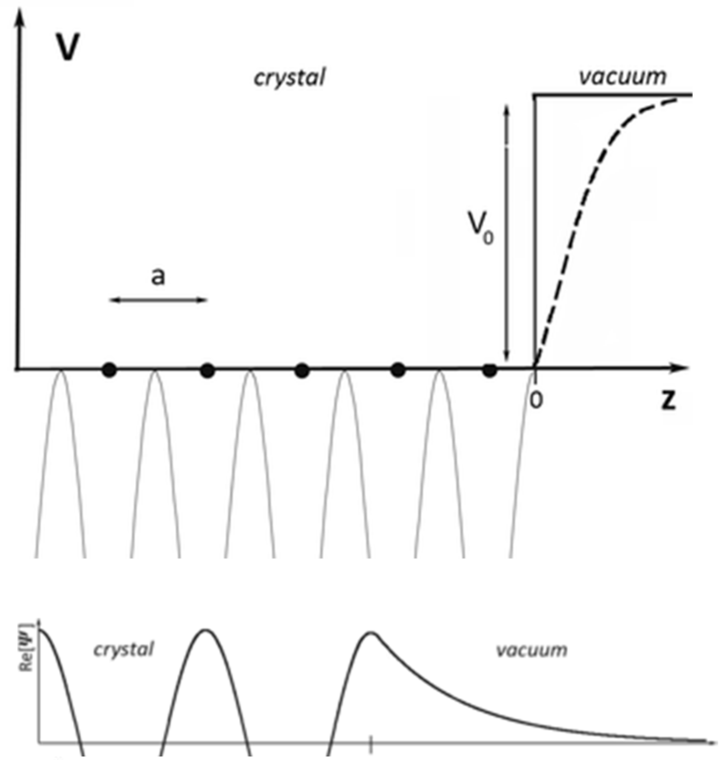
Surface vs bulk

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

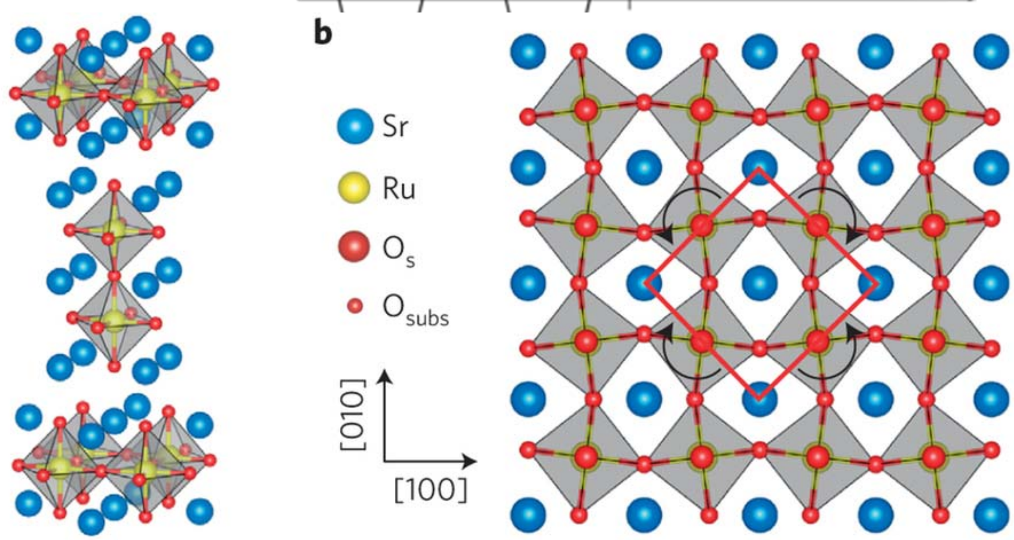
At surface: deviation from periodicity

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

Relationship between ARPES and single particle spectral function

- Photoemission removes an electron and inverse photoemission adds an electron
- Electron removal/addition described by one-electron addition and removal Green's function:

$$G^{\pm}(\boldsymbol{k},\omega)=\sum_{m}\frac{\left|\left\langle\Psi_m^{N\pm1}\middle|c_{\boldsymbol{k}}^{\pm}\middle|\Psi_i^N\right\rangle\right|^2}{\omega-E_m^{N\pm1}+E_i^N\pm i\eta}$$

$c_{\boldsymbol{k}}^{\pm}$ creates/annihilates electron with energy ω and momentum **k**

η is positive infinitesimal

- Retarded Green's function is related to one-electron spectral function via:

$$G(\boldsymbol{k},\omega)=\int_{-\infty}^{\infty}d\omega'\,\frac{A(\boldsymbol{k},\omega')}{\omega-\omega'\pm i\eta}$$

- $(x\pm i\eta)^{-1}=\mathcal{P}\left(\frac{1}{x}\right)\mp i\pi\delta(x),\eta\to0^{+}$
- $-\left(\frac{1}{\pi}\right)Im\ G(\boldsymbol{k},\omega)=A^{+}(\boldsymbol{k},\omega)+A^{-}(\boldsymbol{k},\omega)$ where $\mathrm{G}(\boldsymbol{k},\omega)$ is the retarded Green's function given by $G(\boldsymbol{k},\omega)=G^{+}(k,\omega)+[G^{-}(k,\omega)]^{*}$

Single particle spectral function (continued)

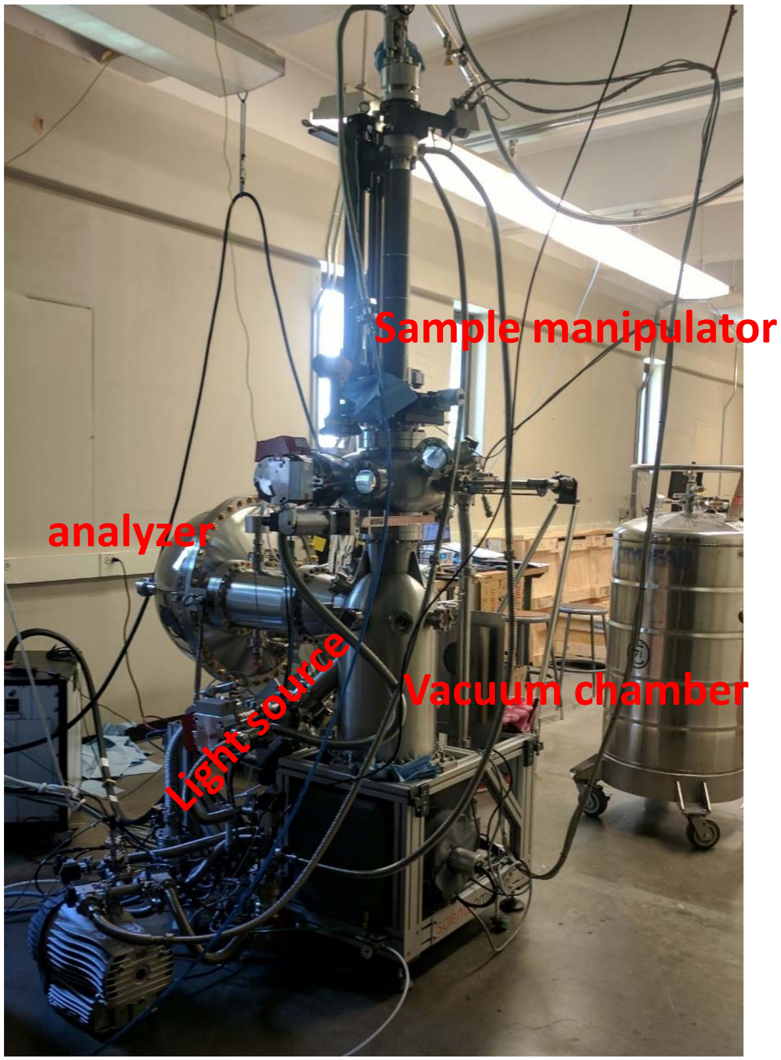
- $A^{\pm}(\boldsymbol{k},\omega) = \sum_m |\langle \Psi_m^{N\pm1} | c_{\boldsymbol{k}}^{\pm} | \Psi_i^N \rangle|^2 \delta(\omega - E_m^{N\pm1} + E_i^N)$
- Corrections to Green's function originating from interactions:

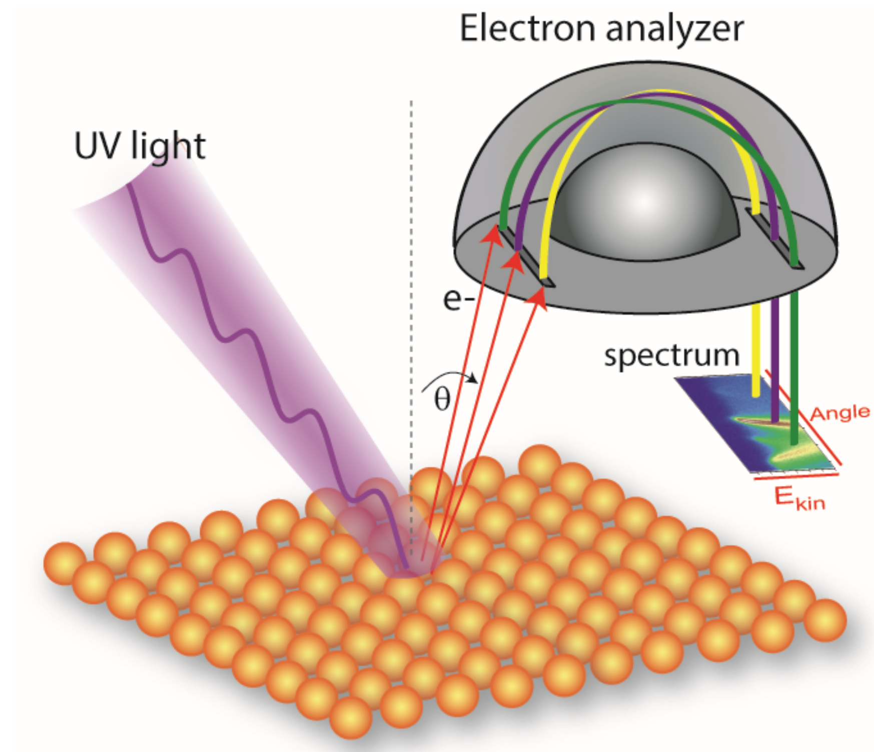
$$G(\boldsymbol{k},\omega) = \frac{1}{\omega - \epsilon_{\boldsymbol{k}} - \Sigma(\boldsymbol{k},\omega)}$$

  where $\epsilon_{\boldsymbol{k}}$ is bare band dispersion, and $\Sigma(\boldsymbol{k},\omega) = \Sigma'(\boldsymbol{k},\omega) + i\,\Sigma''(\boldsymbol{k},\omega)$ is the self-energy
- This allows to write the single-particle spectral function in terms of self energies as well:

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

General setup of ARPES experiment





ARPES light sources (6-200 eV)

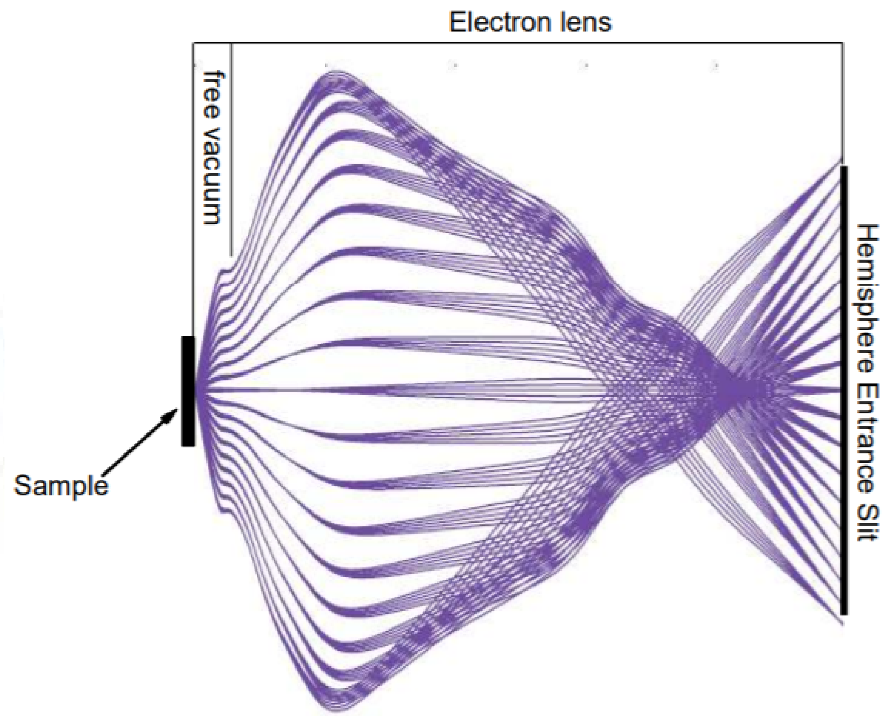
Type	Available photon energies	Bandwidth/monochromaticity	Intensity	Polarization
Laser	6-11 eV; not much variation for a given laser	Can be <<1 meV	Potentially high	Variable polarization
Gas (He, Xe, Ne, Ar…) discharge lamp	21.2, 40.8, 8.4, 9.6, 11.6 eV (and more)	Can be small (<1 meV) with monochromator	Sometimes low	unpolarized
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	Several fixed polarizations

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

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

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

ARPES spectrometer/analyzer



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
- Discriminate photoelectron energies based on different flight times from sample to detector
- 3D detection of electrons, E vs (k_x,k_y)

(Ultra high) vacuum chambers

Q: How long does it take to deposit one monolayer of adsorbants at a pressure of 10^{-9} Torr?

A. 1 second
B. 1.5 minutes
C. 95 minutes
D. 16 hours
E. 6 days

Ultrahigh vacuum chambers

	High vacuum (HV)	Ultrahigh vacuum (UHV)
Pressure	1e-3 to 1e-9 torr	1e-9 to 1e-12 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	95 minutes to 65 days

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

p=pressure in torr

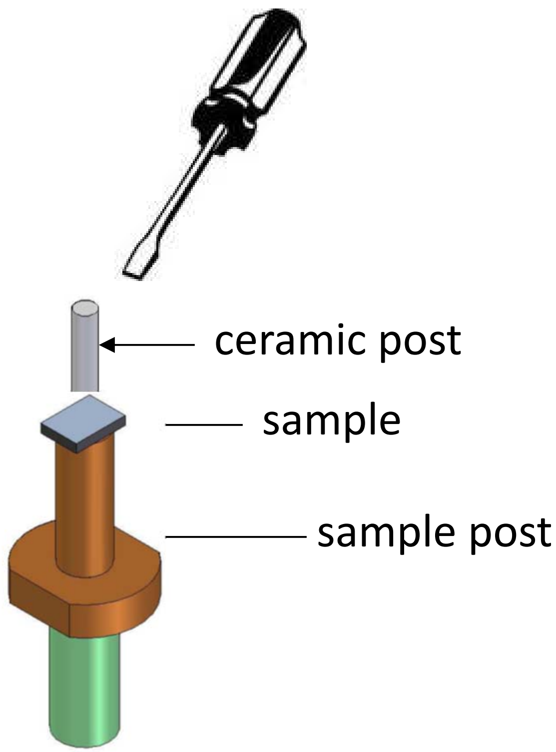
S=sticking coefficient (between 0 and 1)

Ref: Hufner, *Photoelectron Spectroscopy*

Sample preparation

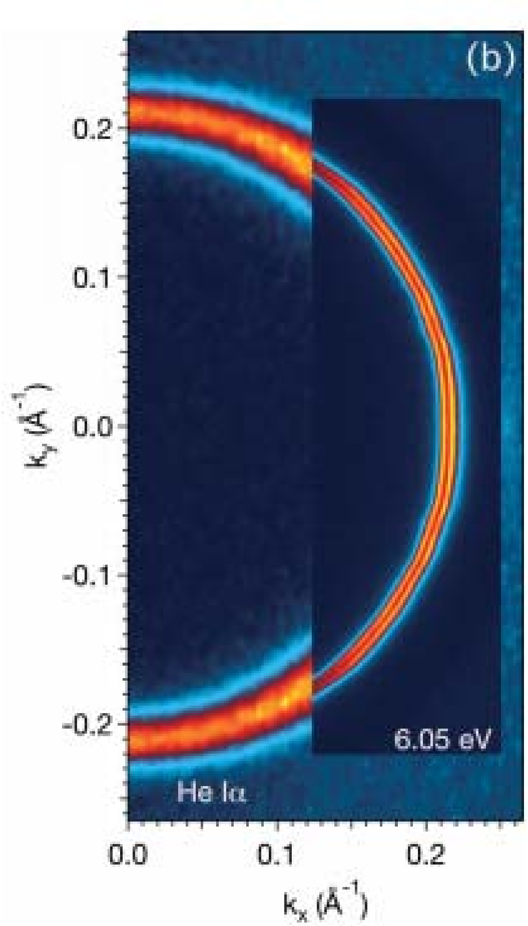
Achieve atomically clean surface by…

- Cleaving in-situ
- Growing material in-situ
- Sputter-and-anneal (e.g. Cu 111 surface)
- Exfoliation, if there is glove box attached to UHV



Sample cleaving

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
- Analyzer (ΔE_a)

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

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

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

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

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

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

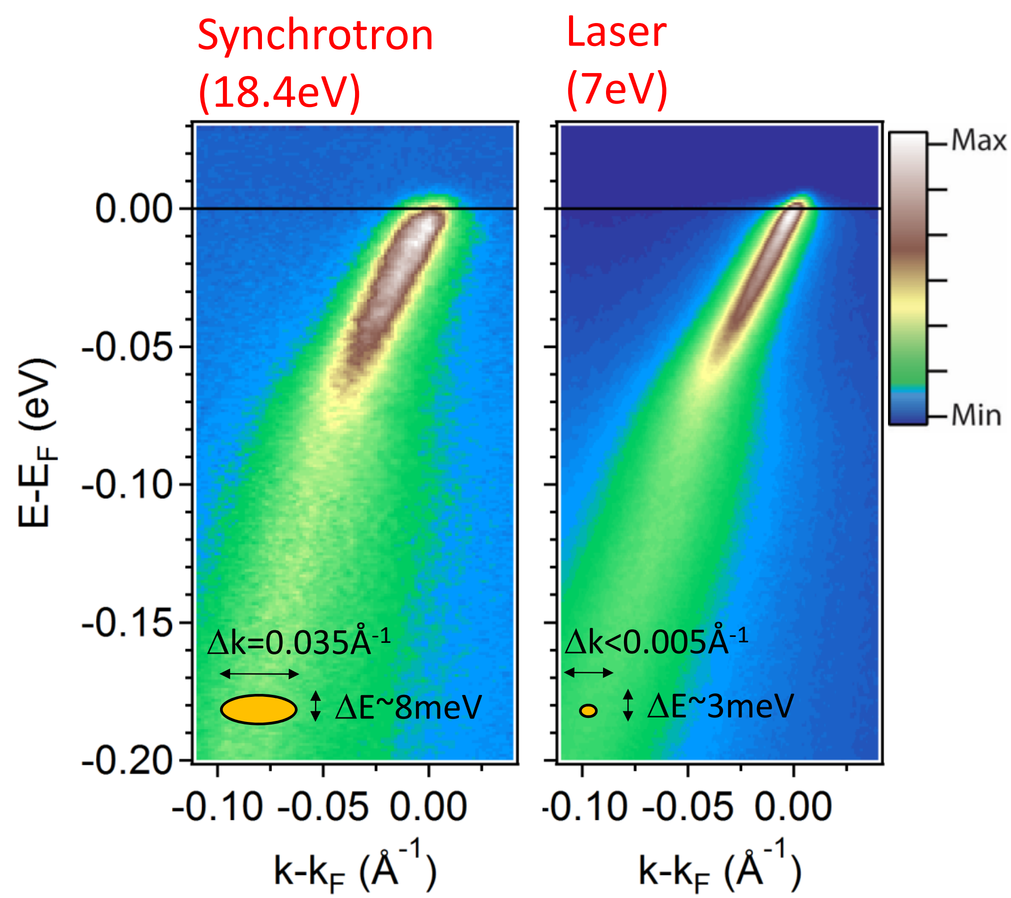
Related to angular resolution of spectrometer and beam spot size

Other sources of momentum broadening:

- Sample curvature
- Finite width of entrance slit

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
- 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



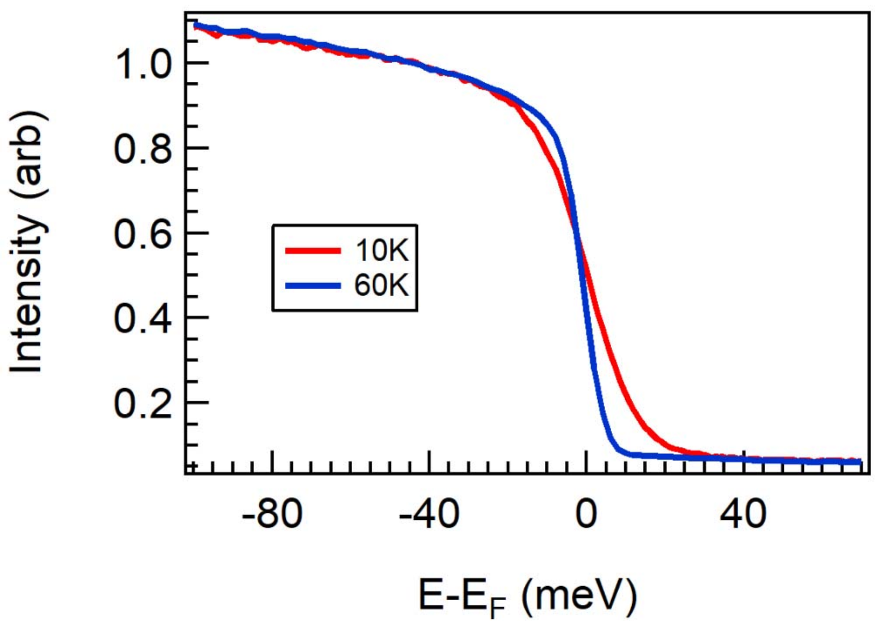
What about temperature?

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

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

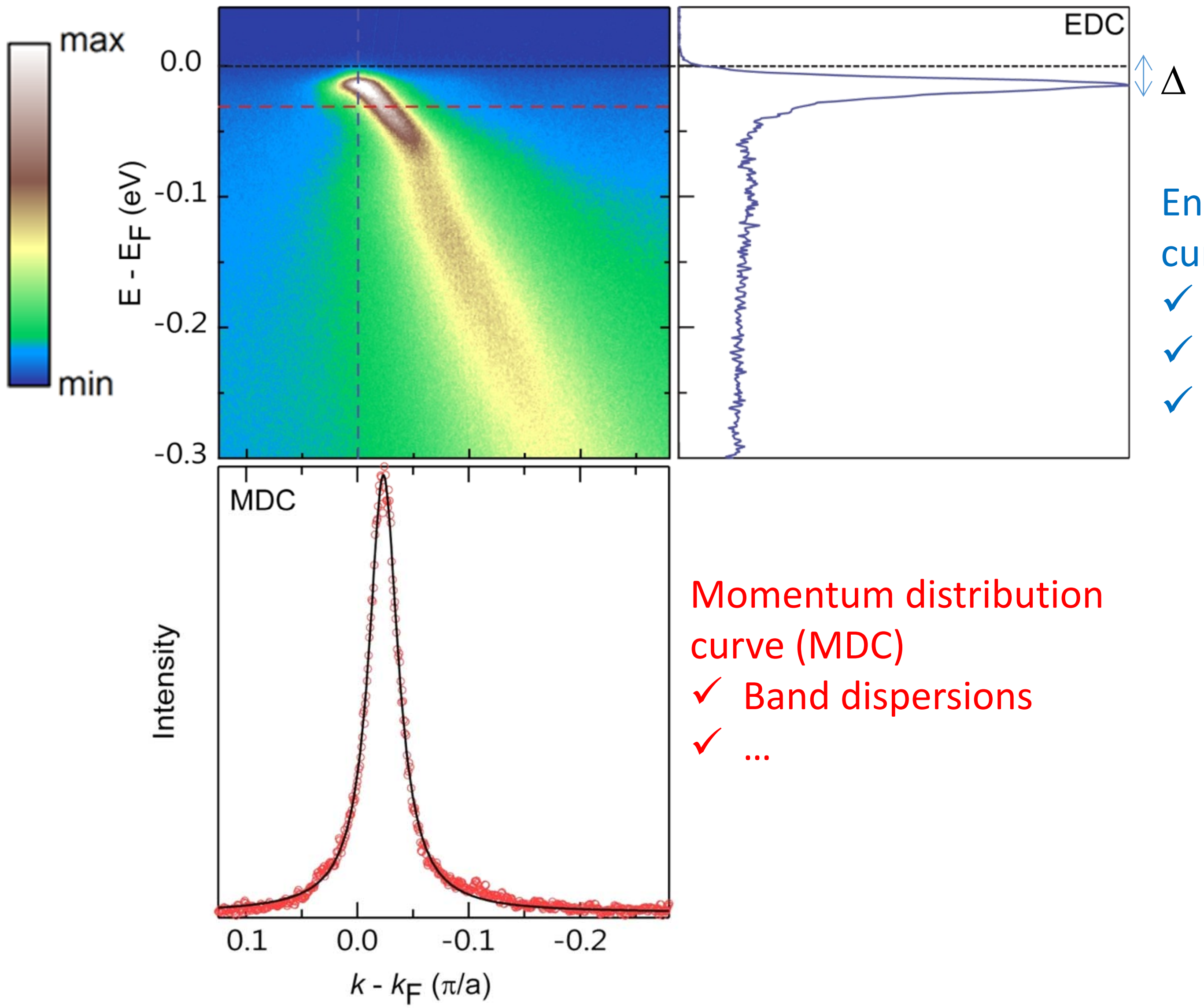
Temperature control during experiment:

- Flow cryostat
- Typical minimum temperature: 5-20K
- He-3 systems capable of reaching 1K exist but are rare



Fermi-Dirac cutoff
Polycrystalline Au

Slicing up ARPES data



Energy distribution curve (EDC)

- ✓ Spectral gaps
- ✓ Lineshapes
- ✓ …

Momentum distribution curve (MDC)

- ✓ Band dispersions
- ✓ …

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)*

Outline

- General principles of ARPES and looking at simple data
- Formalism: three step model and single particle spectral function
- ARPES instrumentation and other experimental aspects
- Applications to quantum materials: unconventional superconductors, topological insulators, Dirac materials

Theme

Emergent phenomena in quantum materials are readily characterized by photoemission, and problems in quantum materials drive development of experimental technology

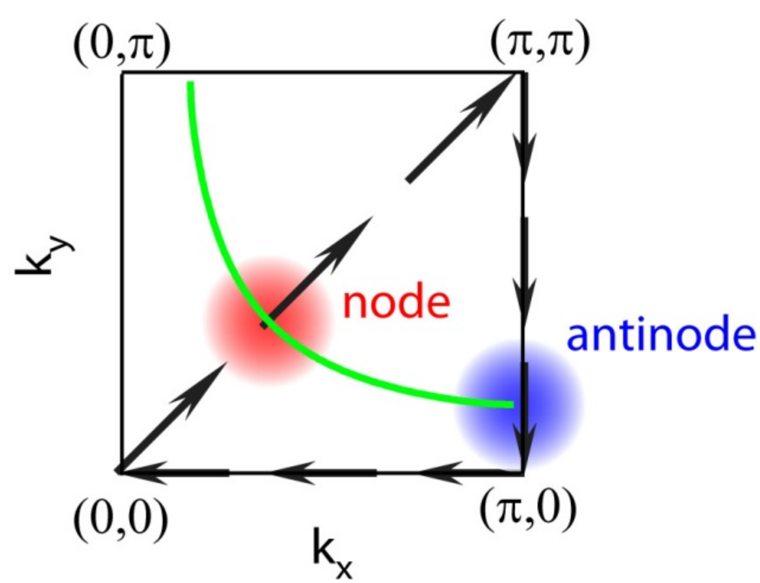
Cuprate high temperature superconductors

Taking ARPES into its modern implementation

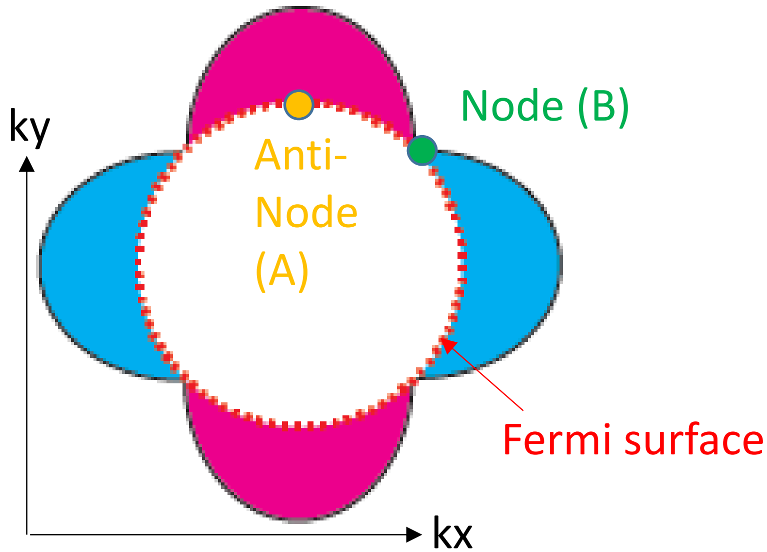
Questions when a new superconductor is discovered

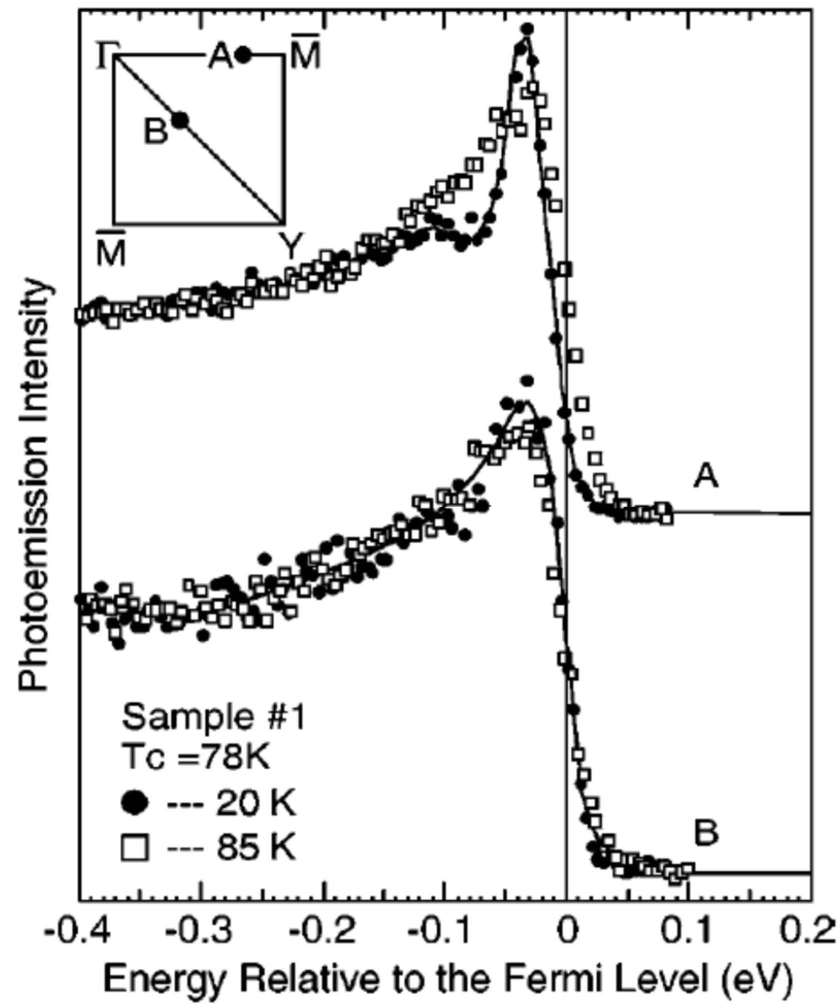
- What is its fermiology?
- What is its superconducting order pararameter?
- What is its mechanism?

¼ Brillouin zone and Fermi surface



Cuprates have $d_{x^2-y^2}$ pairing symmetry



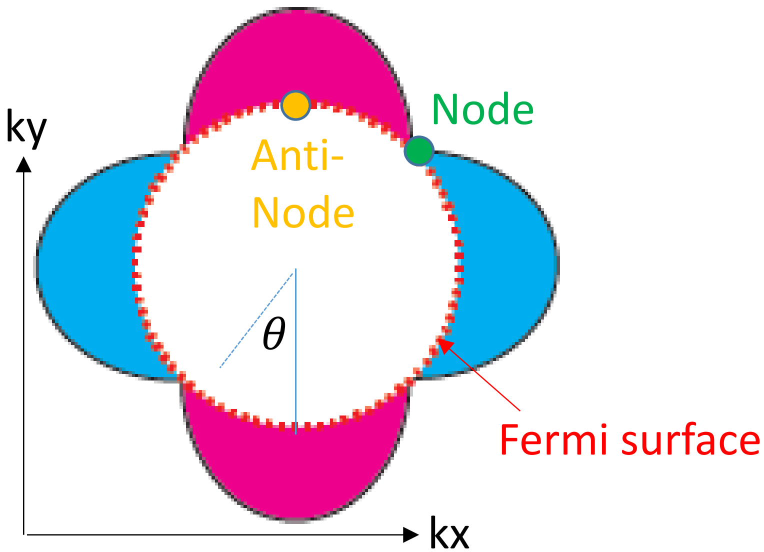


Shen *et al.* PRL **70** (1993)

Other evidence for a $d_{x^2-y^2}$ gap?

- Phase sensitive experiments:
    - *Wollman* et al, *Phys. Rev. Lett.* **71**, 2134–2137 (1993)
    - Kirtley *et al,* Nature **373**, 225–228 (1995)
- Other evidence for line nodes:
    - Hardy et al, Phys. Rev Lett. 70, 3999–4002 (1993)

Momentum dependence of superconducting gap

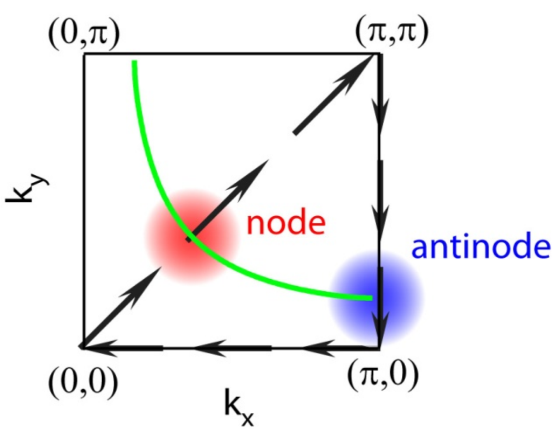


$d_{x^2-y^2}$ superconducting gap on tetragonal lattice (to leading order):

$$\Delta(k_x, k_y) = \frac{\Delta_0}{2}[cosk_x - cosk_y]$$

$$|\Delta(k_x, k_y)| = \frac{\Delta_0}{2}|cosk_x - cosk_y|$$

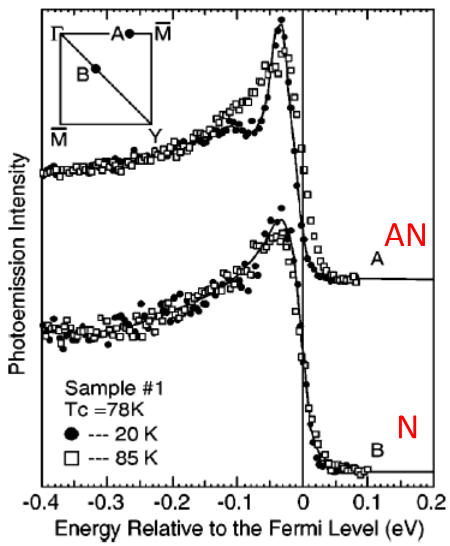
$$\Delta(\theta) = \Delta_0 cos2\theta$$



Momentum-space anisotropy
➔Good for ARPES

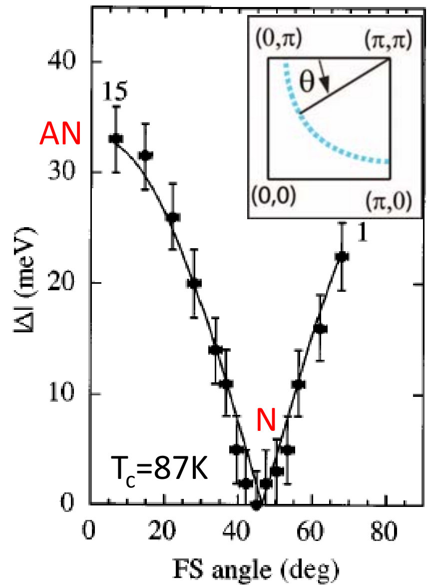
Evolution of experimental technology

ΔE=30meV



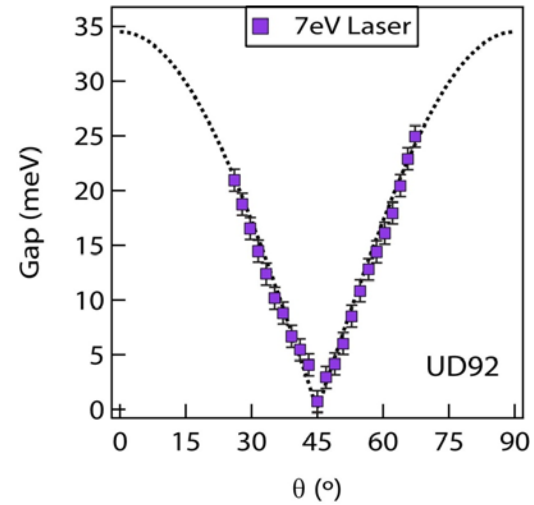
Shen *et al.* PRL **70** (1993)

ΔE=17meV

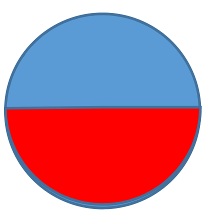


Ding *et al.* PRB **54** (1996)

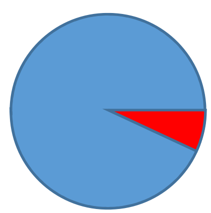
Laser ARPES
ΔE=1-3meV



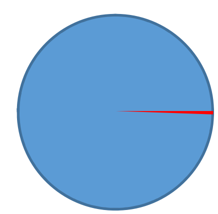
Vishik *et al.* PNAS **109** (2012)



6 hrs/k



1 hr/k

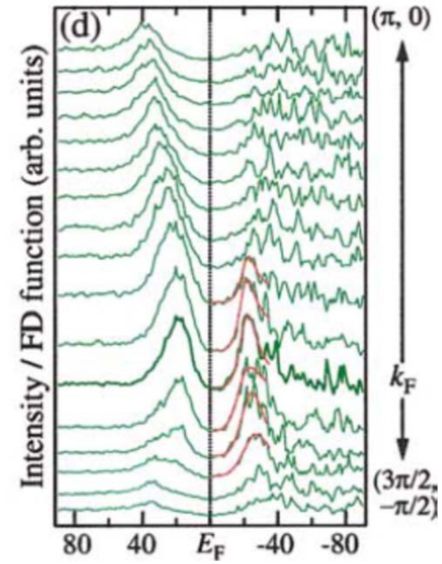


5 min/k

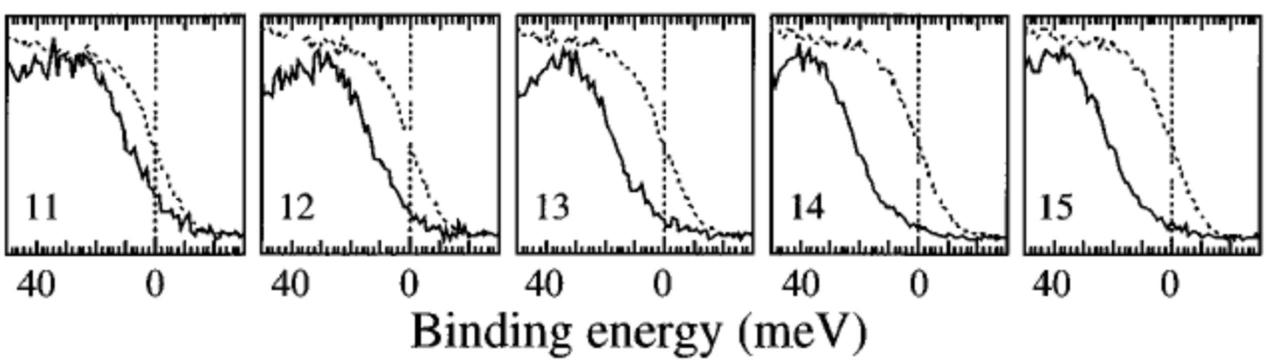
Every new generation of gap measurements was able to uncover new physics!

Quantifying gaps with ARPES

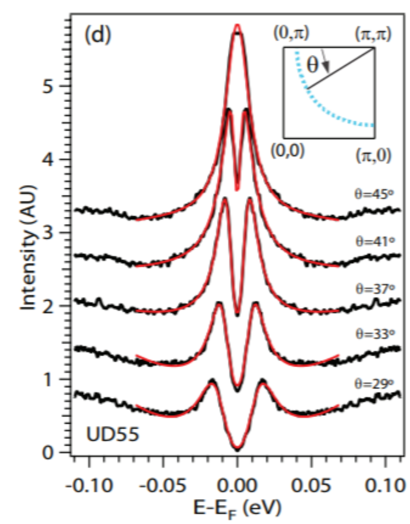
1. Account for Fermi-Dirac cutoff
   - Compare leading edge of data to polycrystalline metal
   - Divide spectrum by Fermi-Dirac function
   - Symmetrize
2. Quantify gap magnitude
   - Leading edge midpoint
   - Peak position
   - Fitting to a model



Matsui *et al.* PRL **90** (2003)

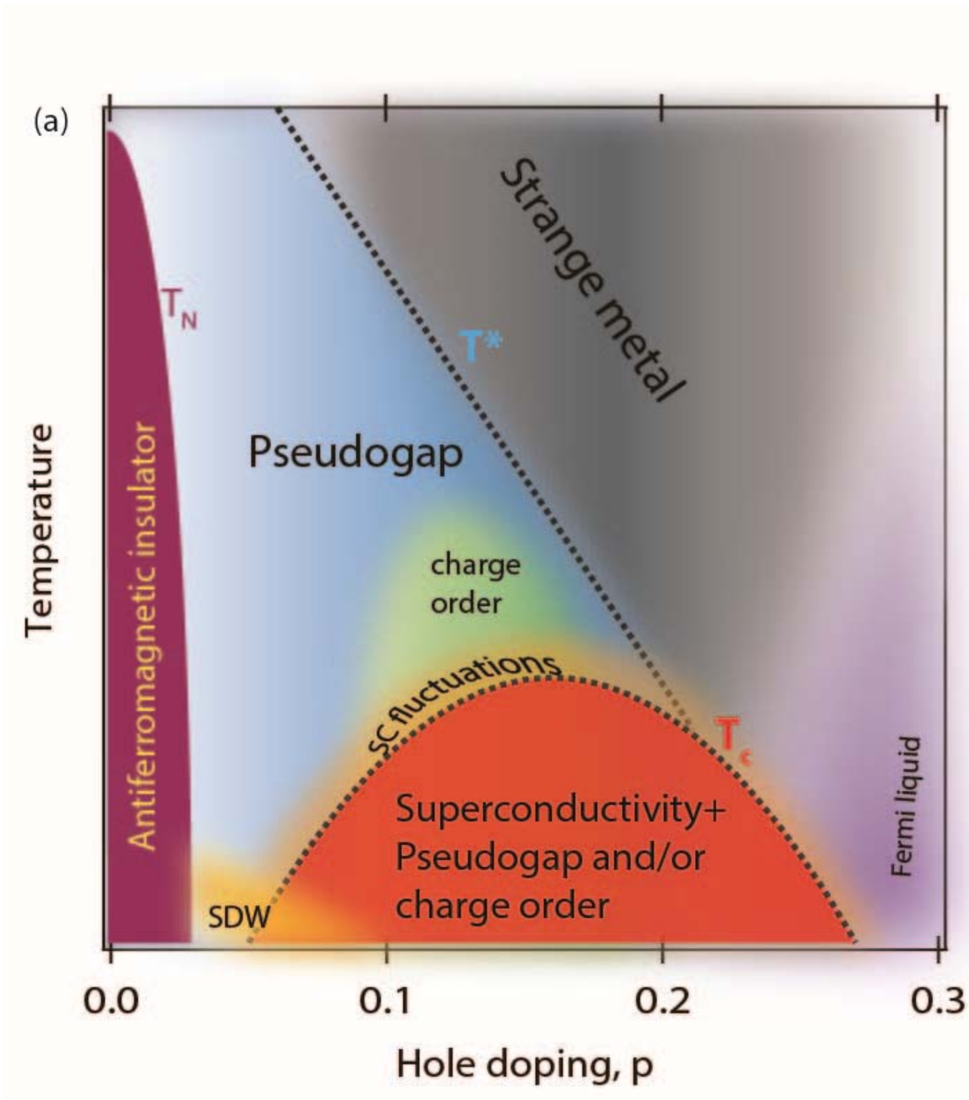


H. Ding *et al,* PRB **54** (1996)



Vishik *et al.* PNAS **109** (2012)

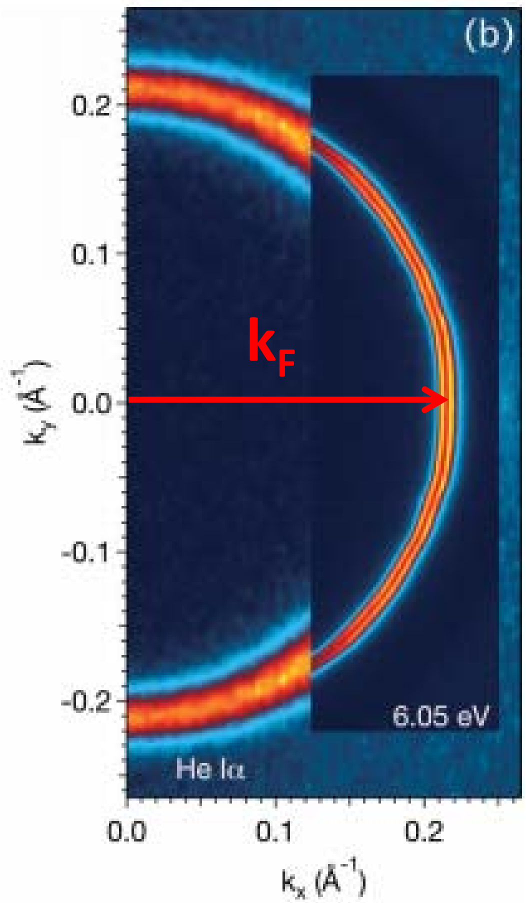
Complex phase diagram in cuprates



Vishik, ROPP 81, 062501 (2018)

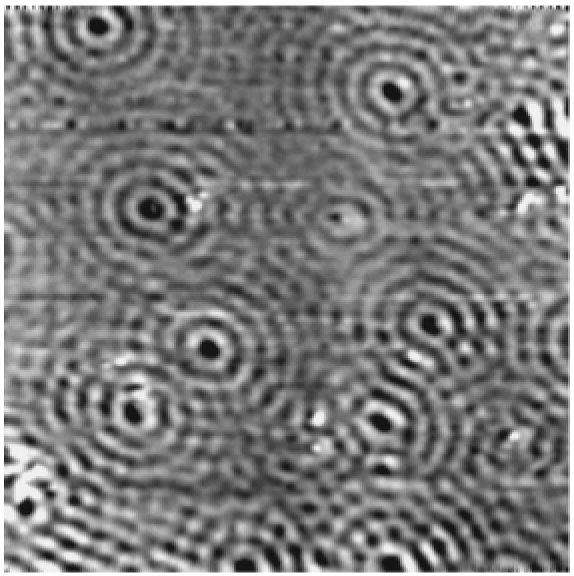
k (crystal momentum) vs **q** (momentum transfer); momentum space vs reciprocal space

Cu-111 Fermi surface



PRB **87**, 075113 (2013)

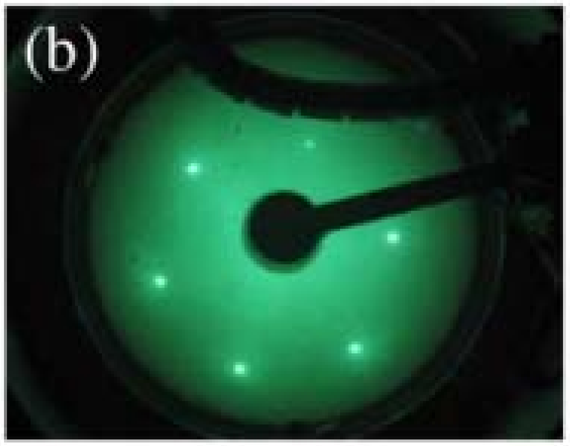
Cu-111 Friedel Oscillations

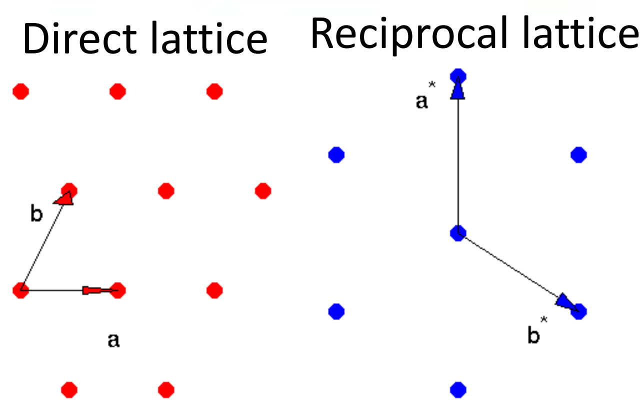


$\lambda=\pi/k_F$
$q=2k_F$

PRB **58** 7361 (1998)

Cu-111 Bragg peaks





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