Angle-resolved photoemission spectroscopy (ARPES): applications to quantum materials

QS3 Summer School

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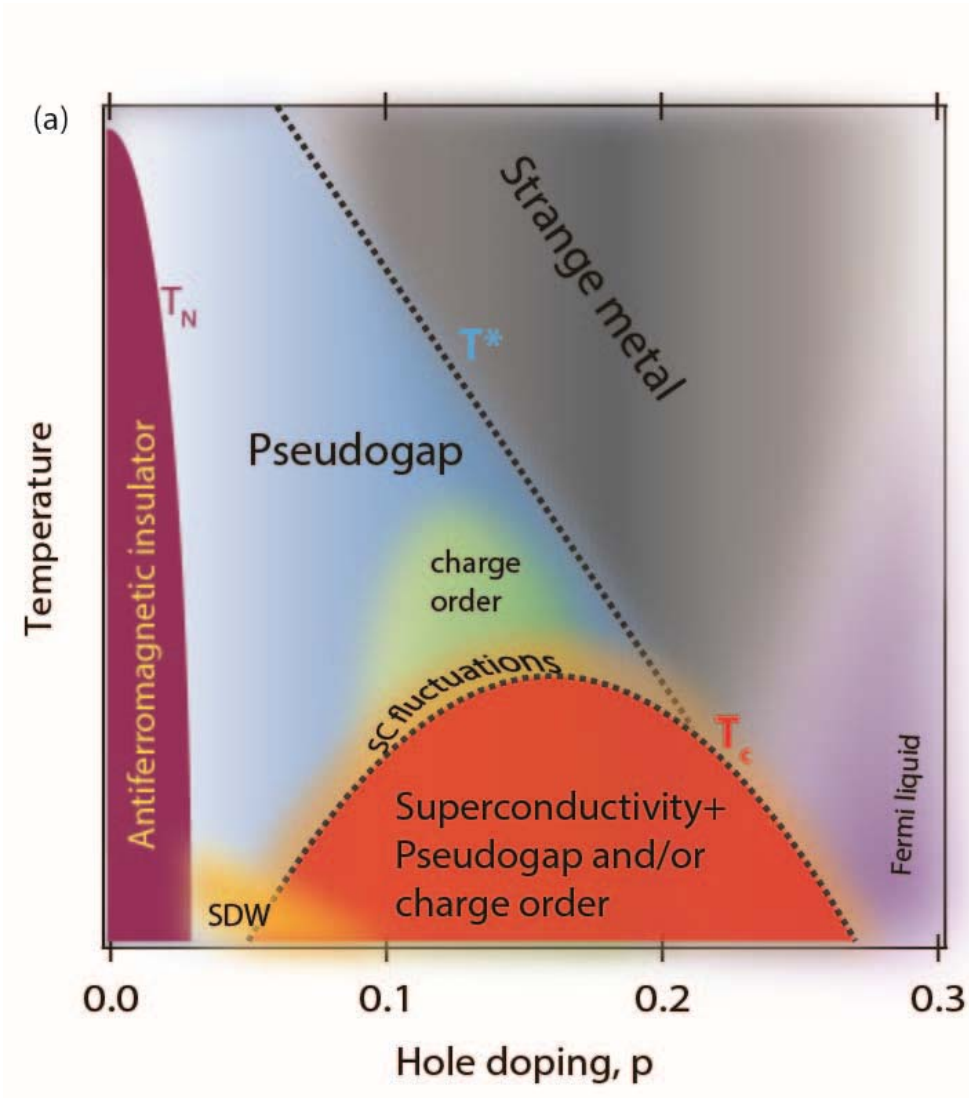
QS3

Theme

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

- Cuprates
- Iron-based superconductors
- Topological insulators
- Dirac materials
- 2D materials

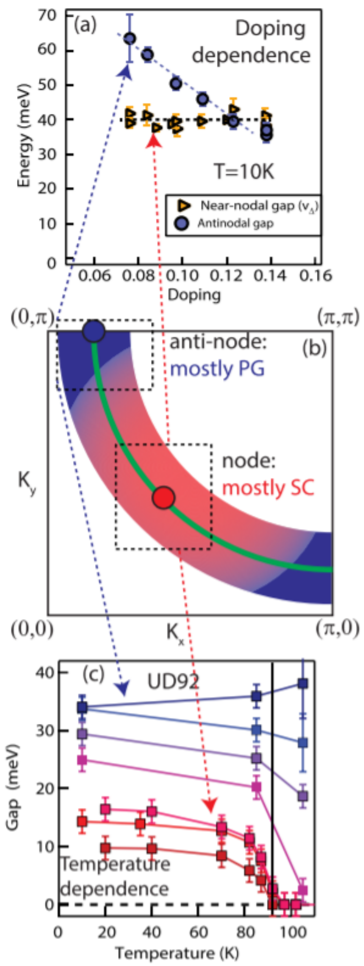
Complex phase diagram in cuprates



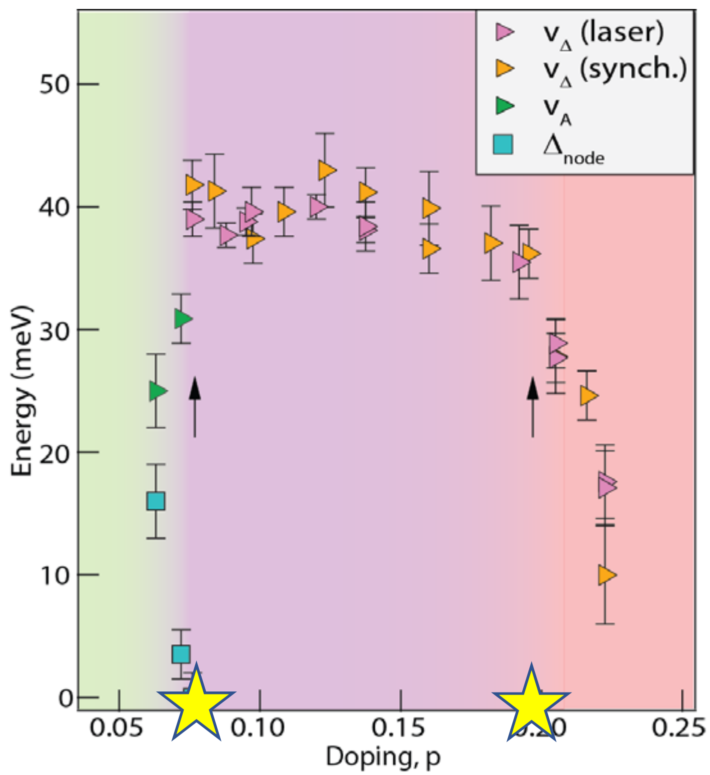
Vishik, ROPP 81, 062501 (2018)

Progress towards understanding phase diagram via gap measurements

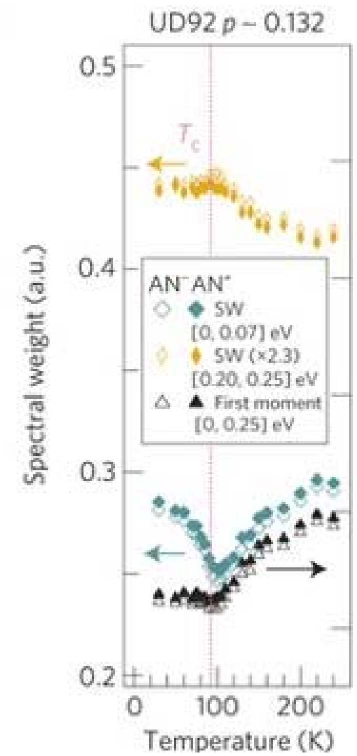
Pseudogap and superconductivity are distinct phases



Phase boundaries of pseudogap and SDW phase inside superconducting dome

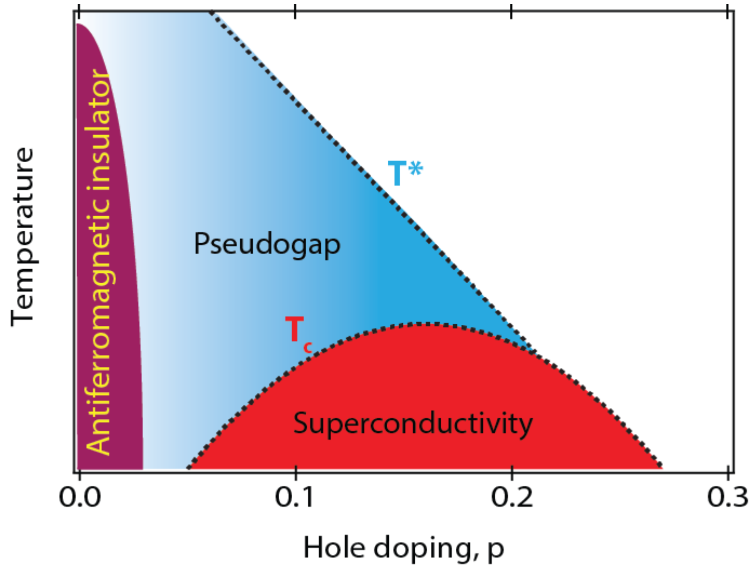


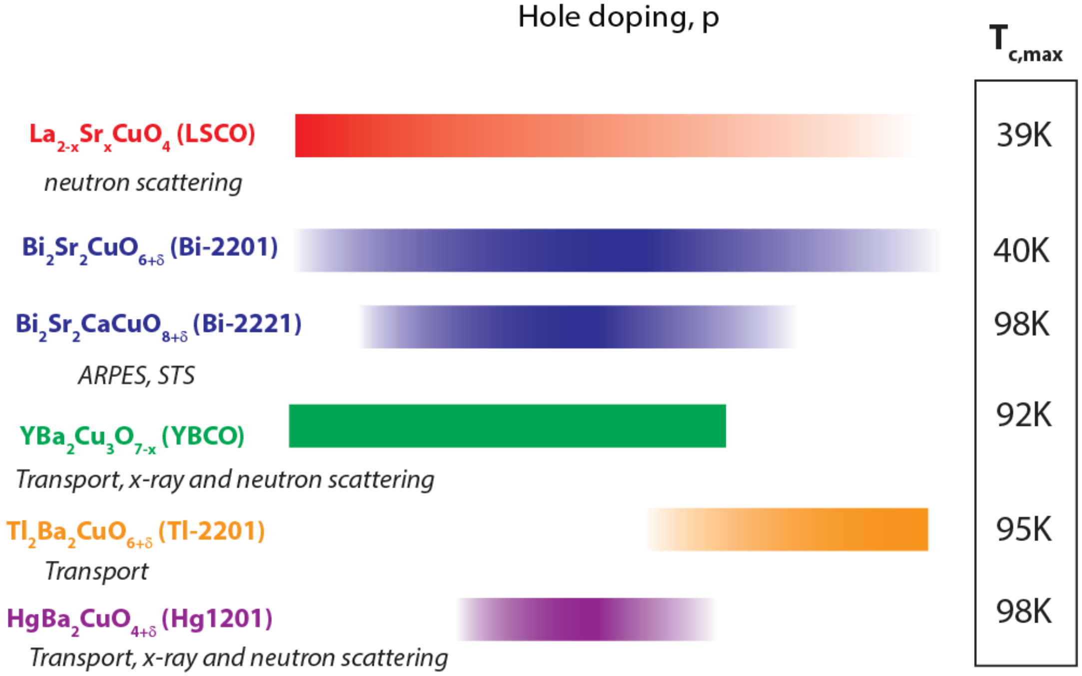
Competition between superconductivity and pseudogap



- W. S. Lee, I. Vishik, *et al* Nature **450** (2007)
- I. Vishik *et al* PNAS **109** (2012)
- M. Hashimoto *et al* Nat. Phys. **14** (2015)

Remaining questions





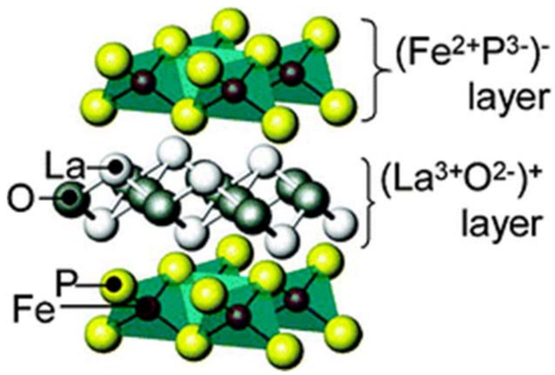
- Mechanism of SC and PG
- Universal vs materials dependent properties
- Is the overdoped side really conventional?
- Many obvious experiments that were never repeated
  - Isotope effect
  - Heat capacity through T*

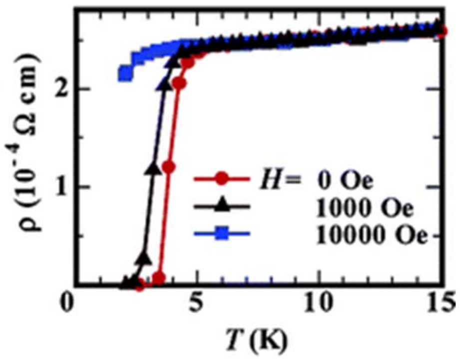
Iron-based high temperature superconductors

A multiband system for a momentum-resolved probe

Discovery of Fe-based SCs

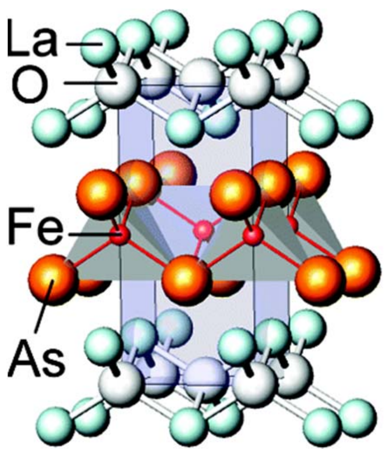
2006: LaFePO, Tc=**5K**

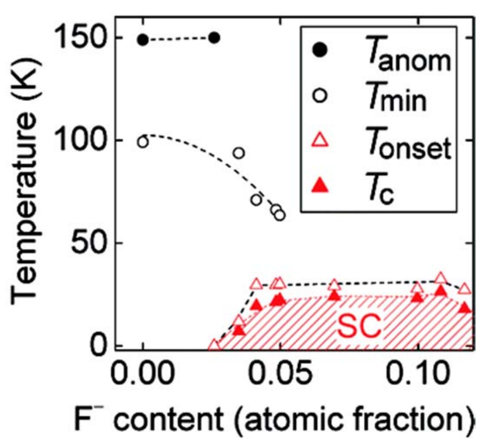




Kamihara et al, *J. Am. Chem. Soc.*, ***128***, pp 10012–10013 (2006)

2008: LaFeP[$O_{1-x}F_x$], Tc=**26K**

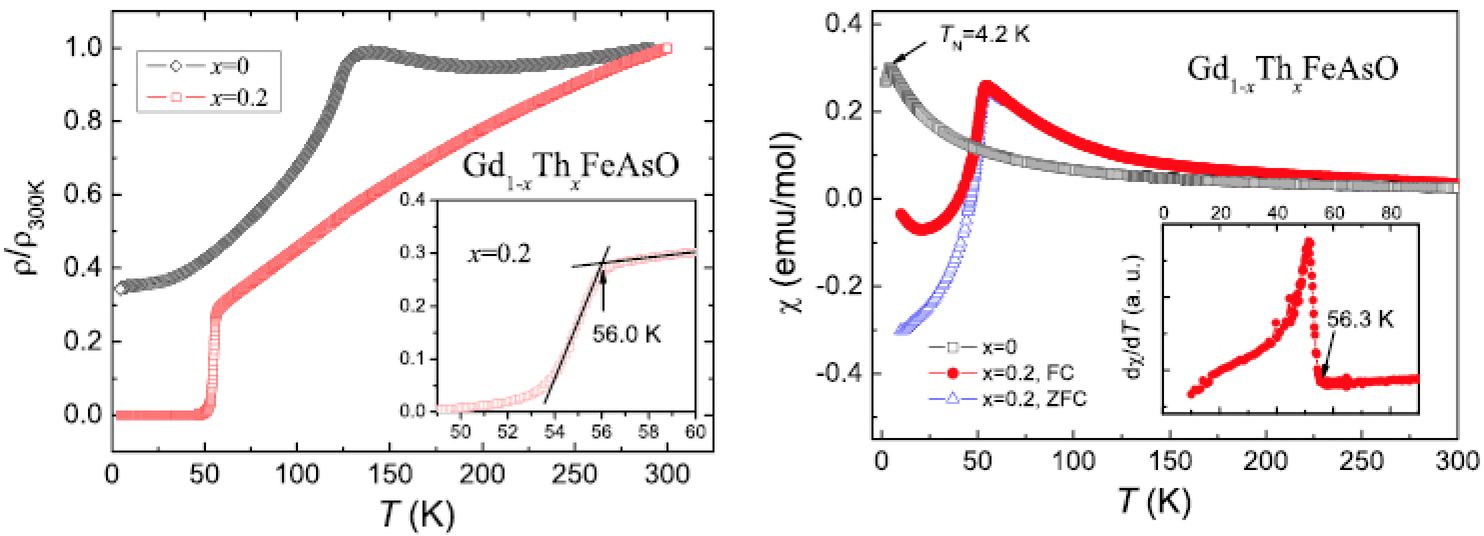




Kamihara *et al. . Am. Chem. Soc.*, ***130***, pp 3296–3297 (2008)

Discovery of Fe-based SCs

2008: $Gd_{1-x}Th_xFeAsO$, Tc=**56K**



Wang *et al.* Europhys. Lett. **83** 67006 (2008)

What is high T_c?

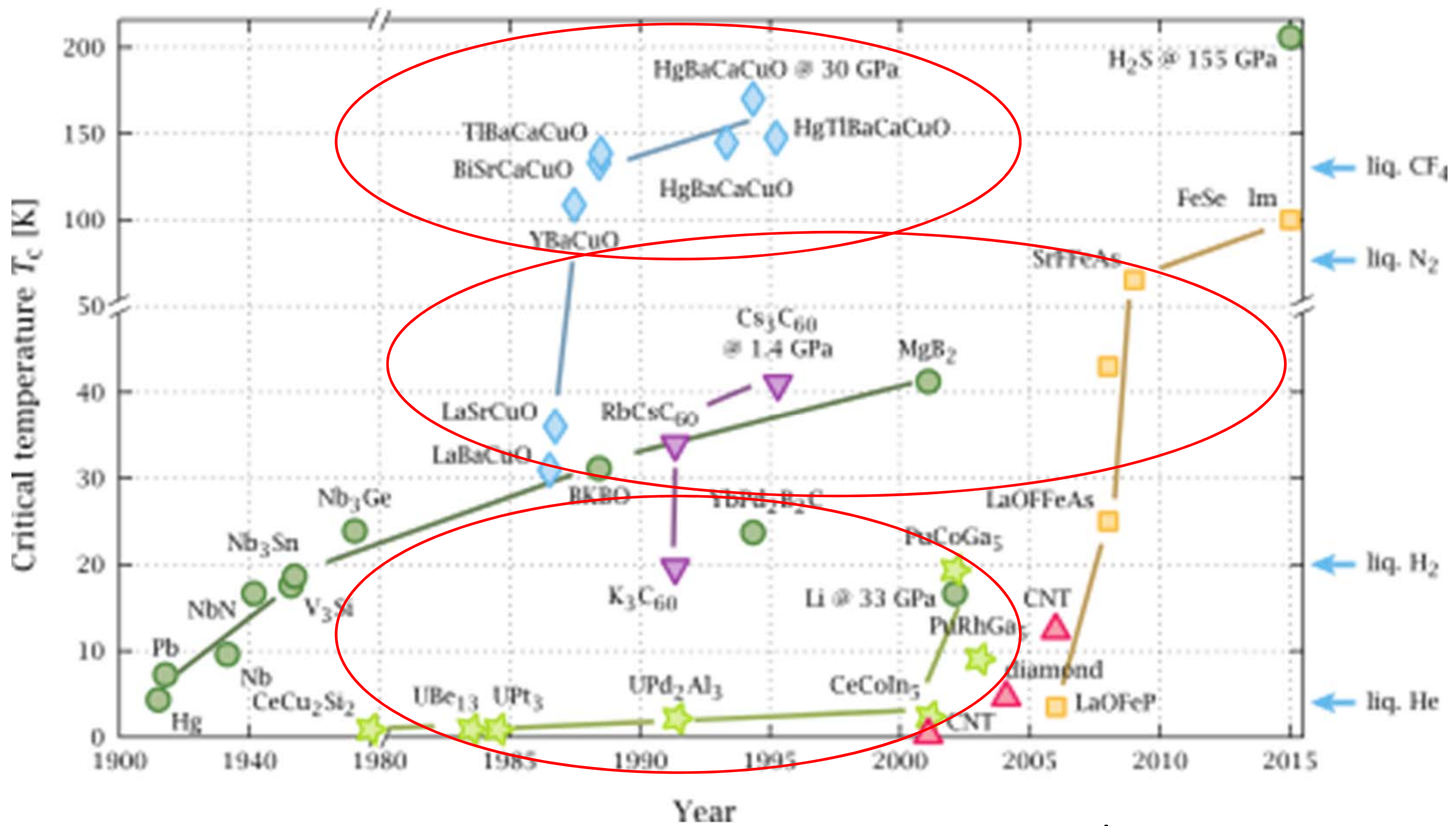
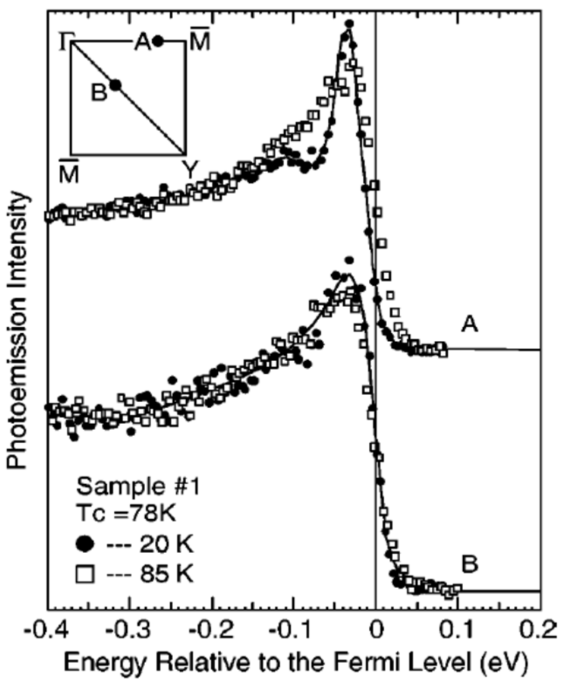


Image source: https://en.wikipedia.org/wiki/High-temperature_superconductivity

- T_c>77K (boiling point of liquid nitrogen)
- T_c>30K (former BCS “limit”)
- T_c large relative to Fermi energy
- Mechanism unknown (not BCS)

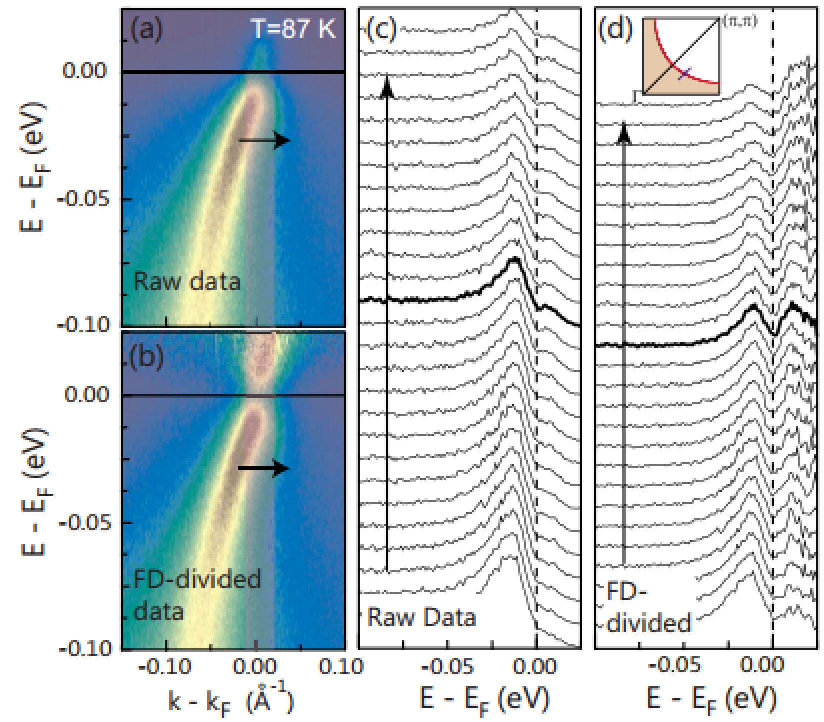
A second family of high-T_c materials!!

- High-T_c is not unique to one material class
- Benefit of hindsight
- Better tools



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

1993:
- 6hrs per trace
- One momentum at a time



Balatsky, Lee, Shen, PRB **79** (2009)

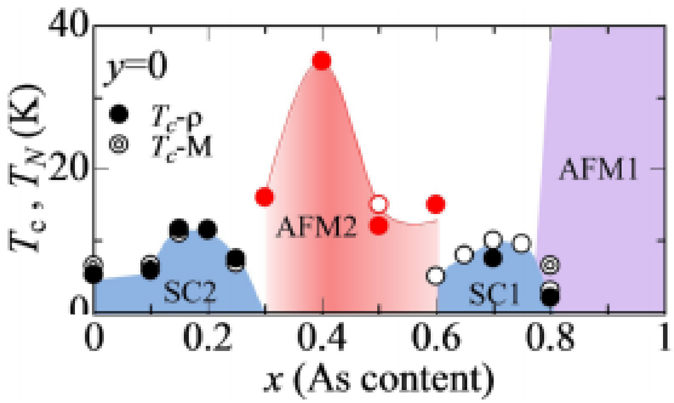
~2008
- ~10 mins per cut
- Many momenta at a time, along 1D trajectory in k-space

Questions when a new superconductor is discovered

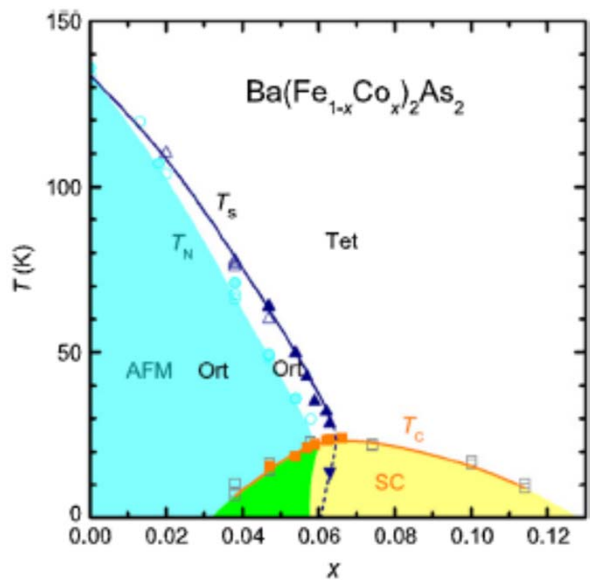
- What is its fermiology?
- What is its superconducting order pararameter?
- What are nearby electronic phases?
- What is its mechanism?

(A small selection of) Fe-SC phase diagrams

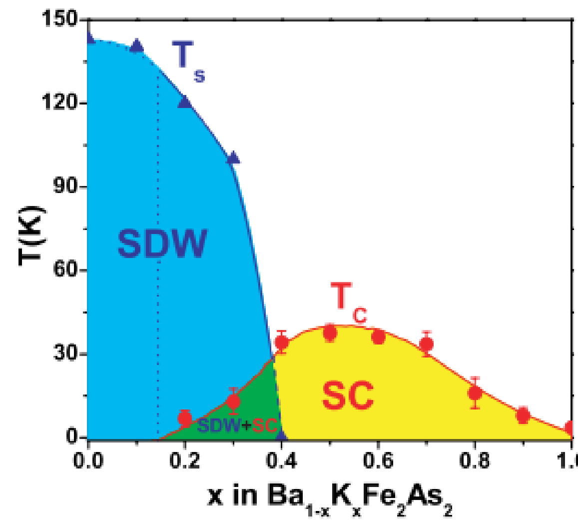
LaFe(P,As)O



Lai *et al*, PRB **90**, 064504 (2014)

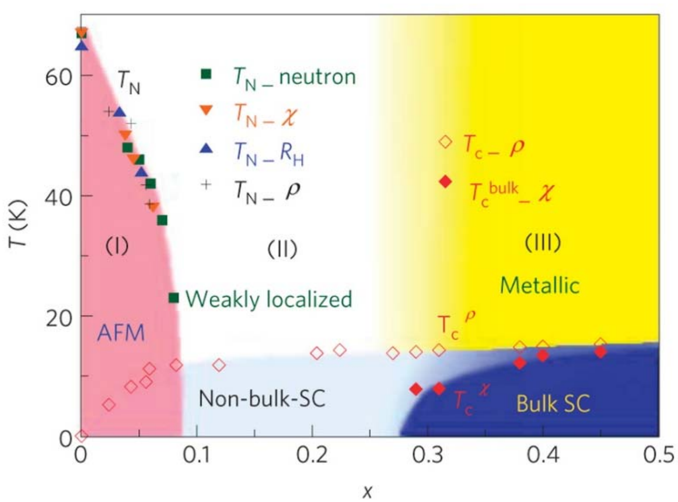


Nandi *et al*, PRL **104**, 057006 (2010)

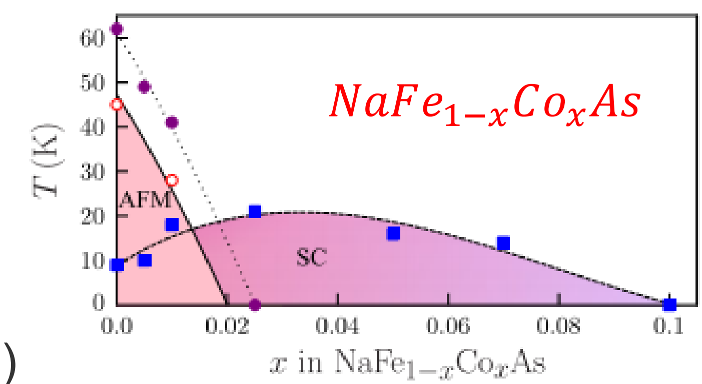


Chen *et al.*, EPL **85** 17006 (2009)

$Fe_{1.02}Te_{1-x}Se_x$

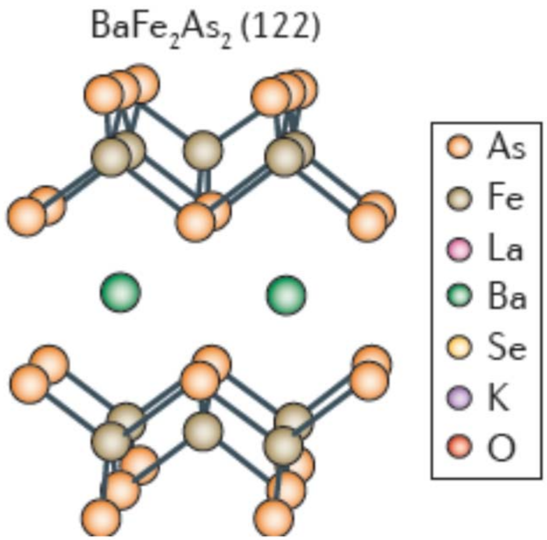


Liu *et al., Nat. Mater.* **9**, 718–720 (2010)

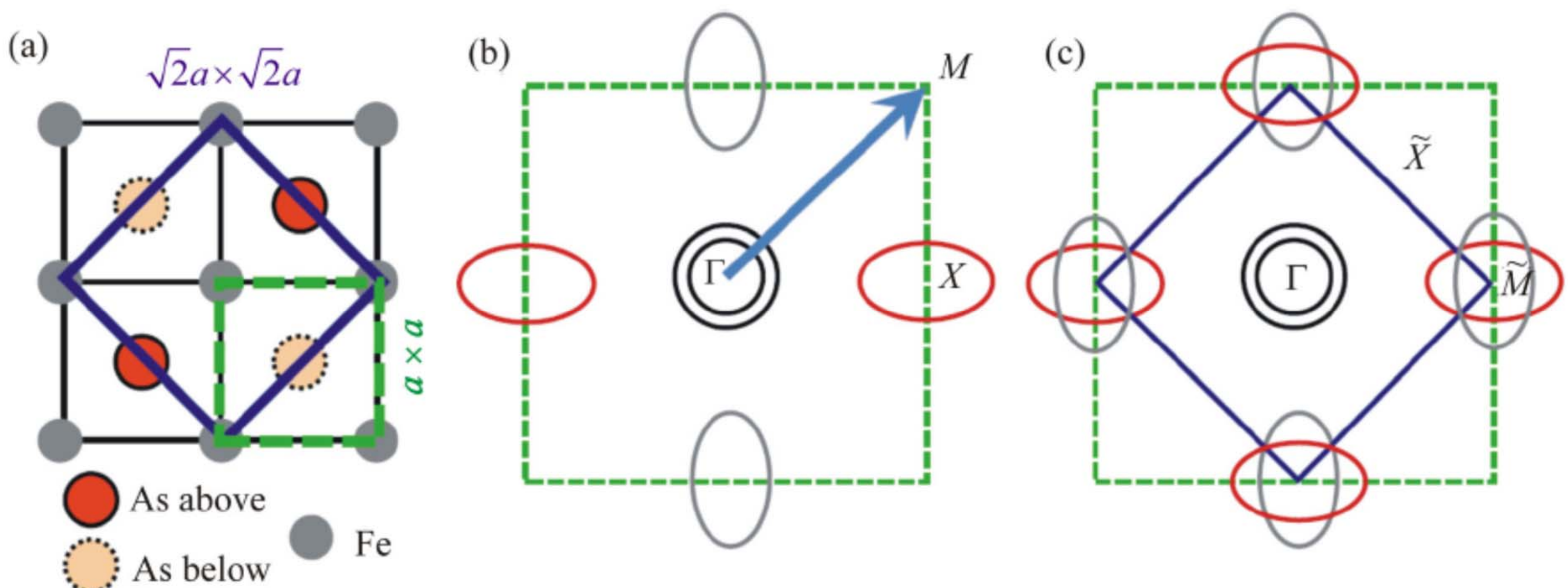


Parker *et al.* PRL **104**, 057007 (2010)

Fe-SC Brillouin zone



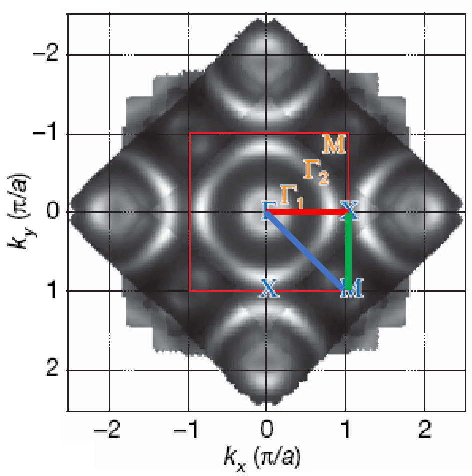
- 1-Fe unit cell (ignore As/Se)
- 2-Fe unit cell (consider larger unit cell due to Fe/Se)
- Multiple Fermi surfaces: momentum-resolved tool is very useful!



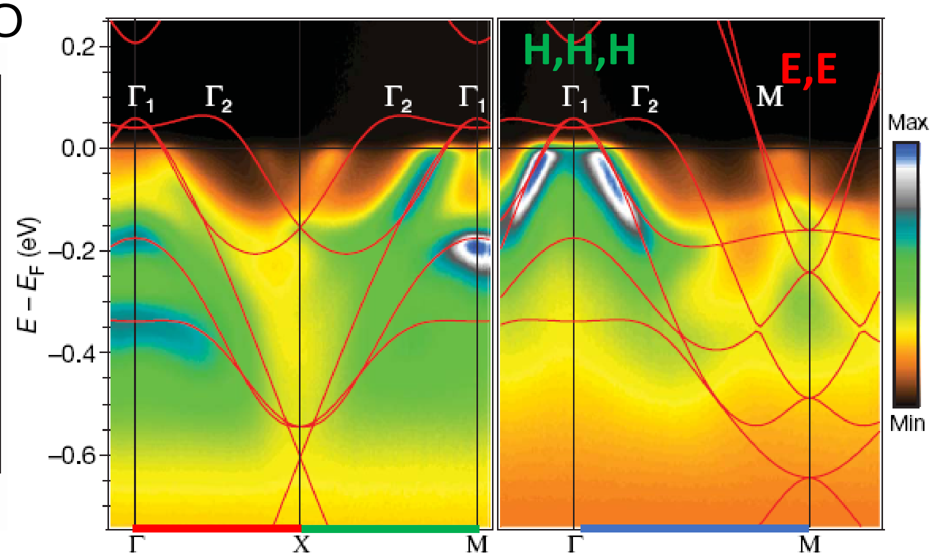
Kordyuk, *Low Temp Phys*, **38**, 888 (2012)

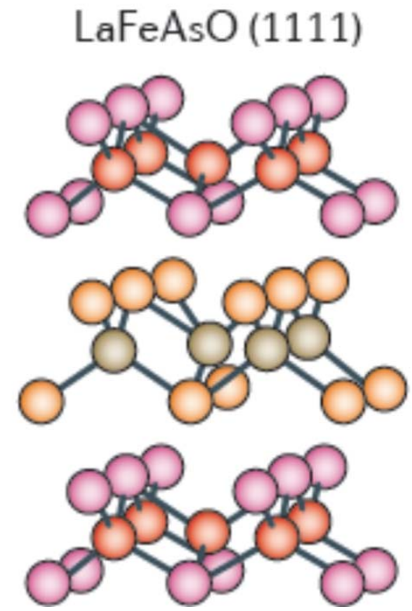
1111-Fermi surface

LaOFeP
Now called: LaFePO



T=20K

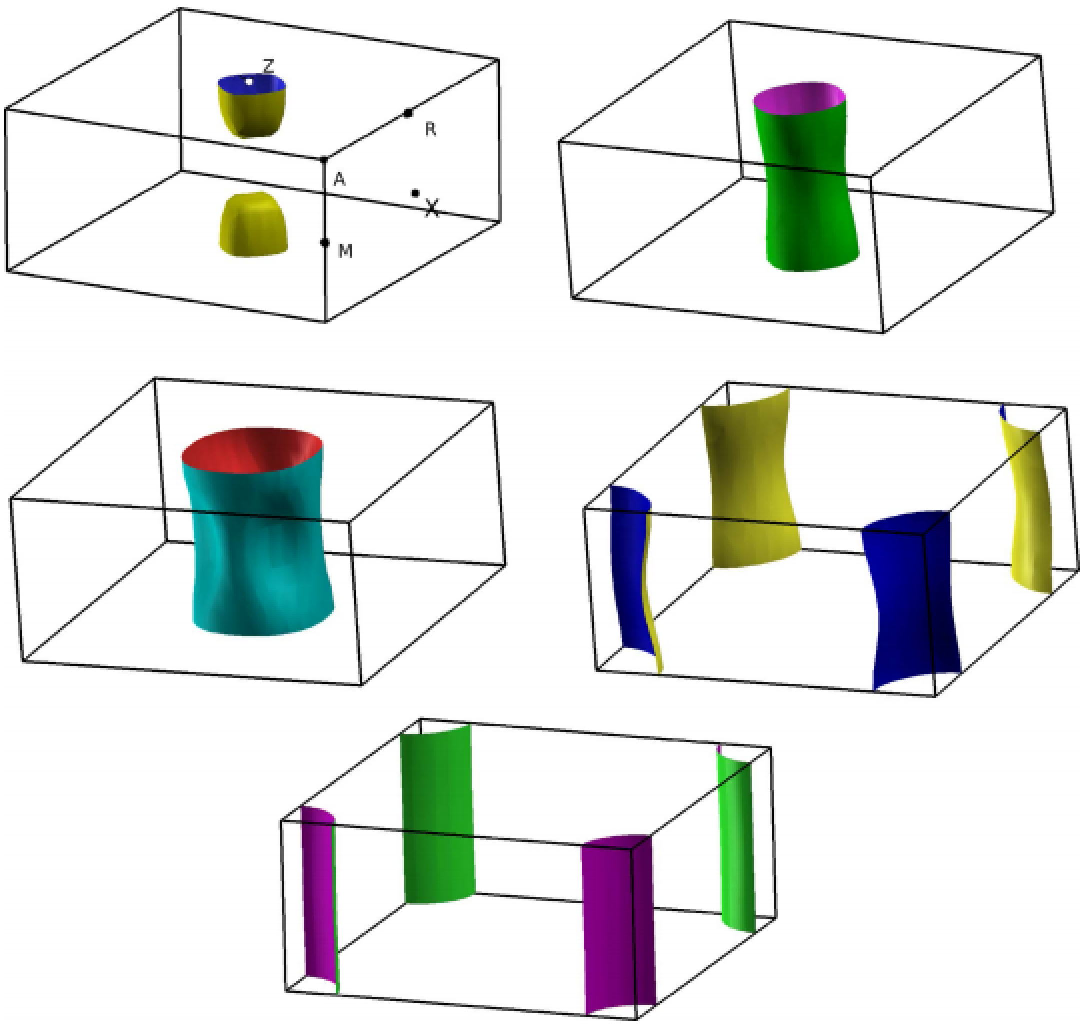


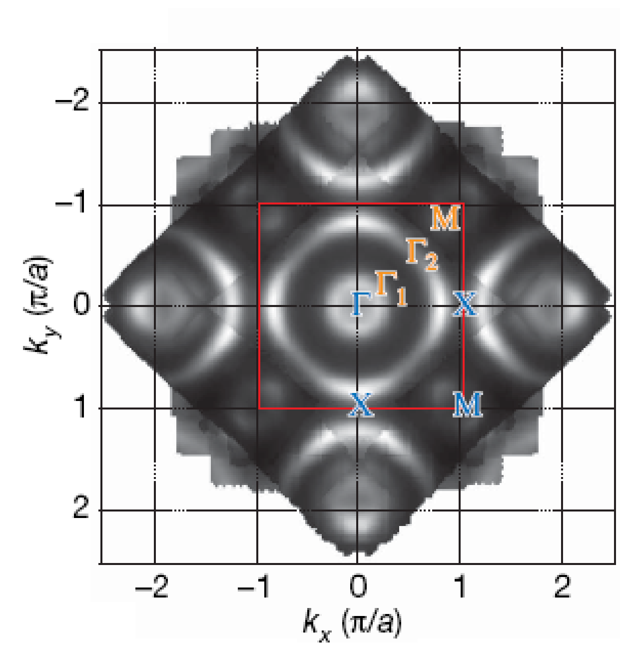


D. H. Lu, *et al.* Nature **455** 81 (2008)

"A quantitative agreement can be found between the angle-resolved photoemission spectra and the calculated band dispersions after shifting the calculated bands up by 0.11 eV and then renormalizing by a factor of 2.2."

Comparison to Fermi surface calculations

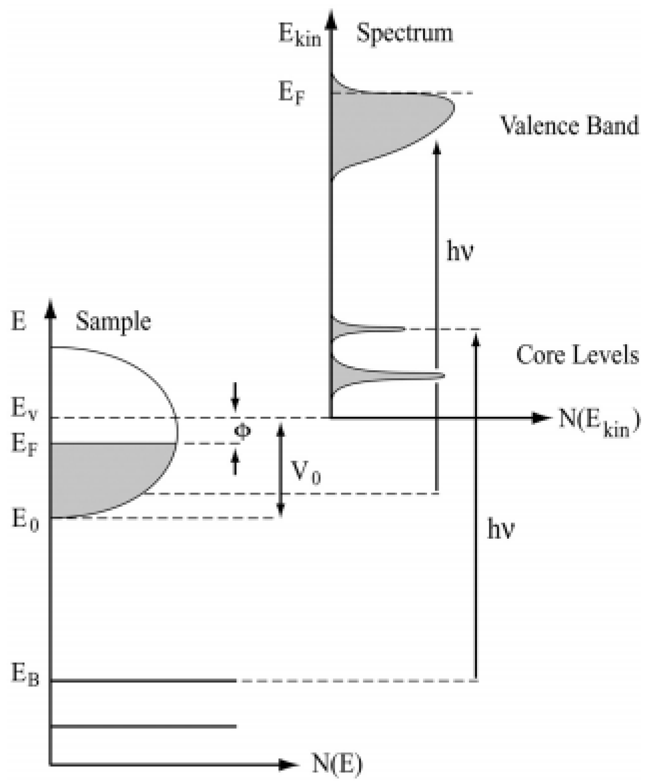




S. Lebègue, PRB **75**, 035110 (2007)

k_z ($k_\perp$) in ARPES

Final state dispersion assumed to be free-electron-like: $E_f(\boldsymbol{k}) = \frac{\hbar^2 k^2}{2m} - |E_0| = \frac{\hbar^2(k_\parallel^2 + k_\perp^2)}{2m} - |E_0|$



$E_{kin} = E_f - \Phi$

$\hbar k_\parallel = \sqrt{2mE_{kin}} sin\vartheta$

$$k_\perp = \frac{1}{\hbar}\sqrt{2m(E_{kin}\cos^2\vartheta + V_0)}$$

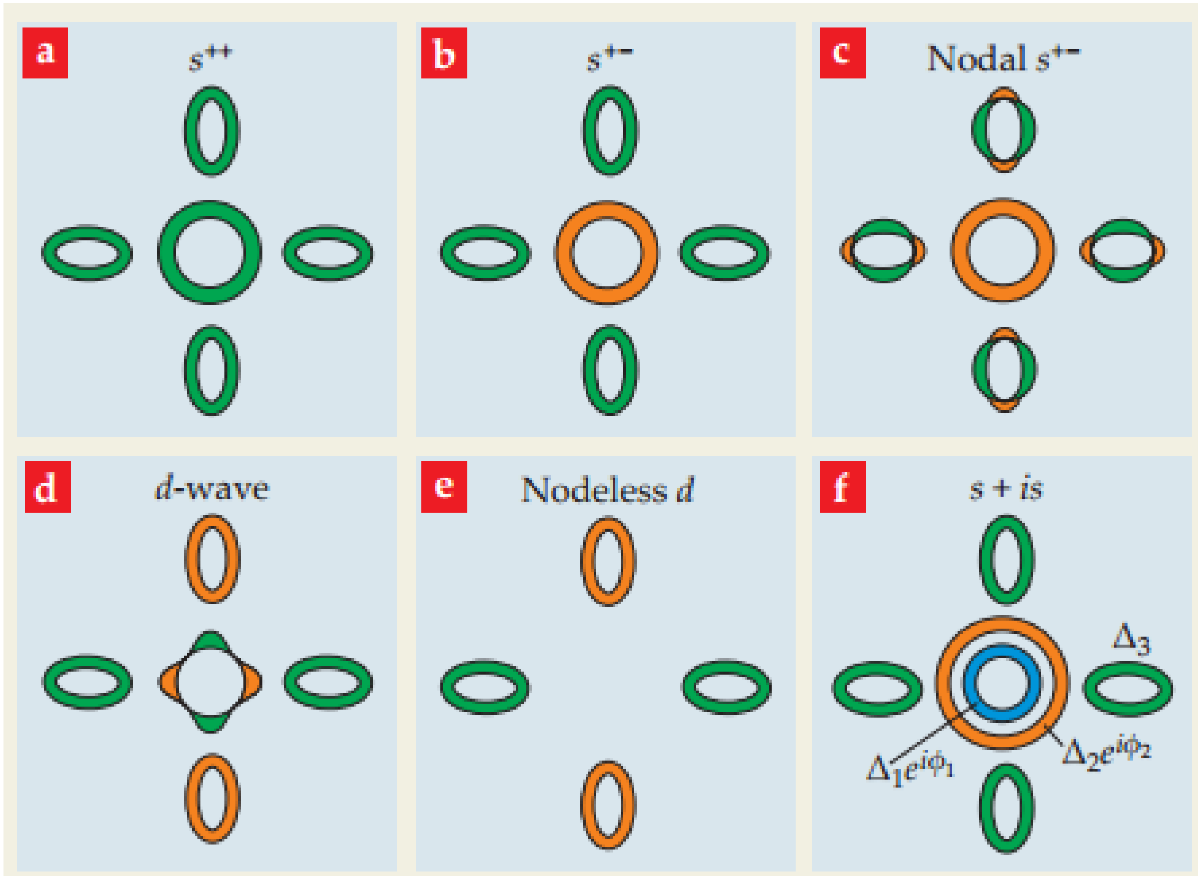
V_0=inner potential

Determined by:

- Comparison to band structure calculations
- Experimentally observed periodicity of $E_f(\boldsymbol{k})$, measured by varying photon energy
- Guess

A. Damascelli, https://www.cuso.ch/fileadmin/physique/document/Damascelli_ARPES_CUSO_2011_Lecture_Notes.pdf

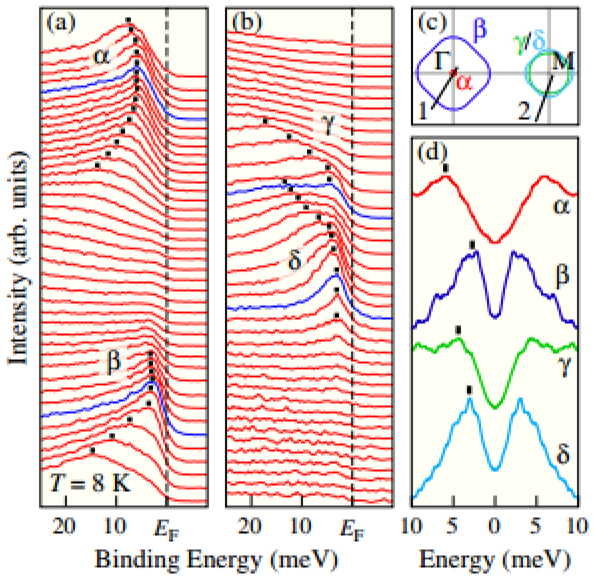
Potential gap symmetries



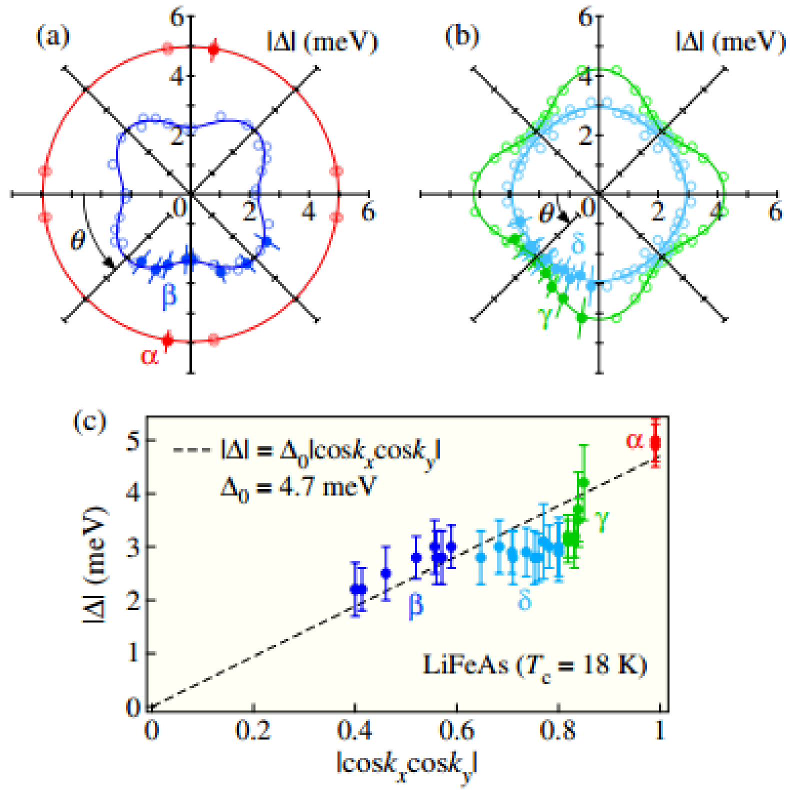
Chubukov and Hirschfeld, Phys. Today **68**, 46 (2015)

Results from ARPES: inconclusive

Superconducting gap in LiFeAs (T_c=18K)

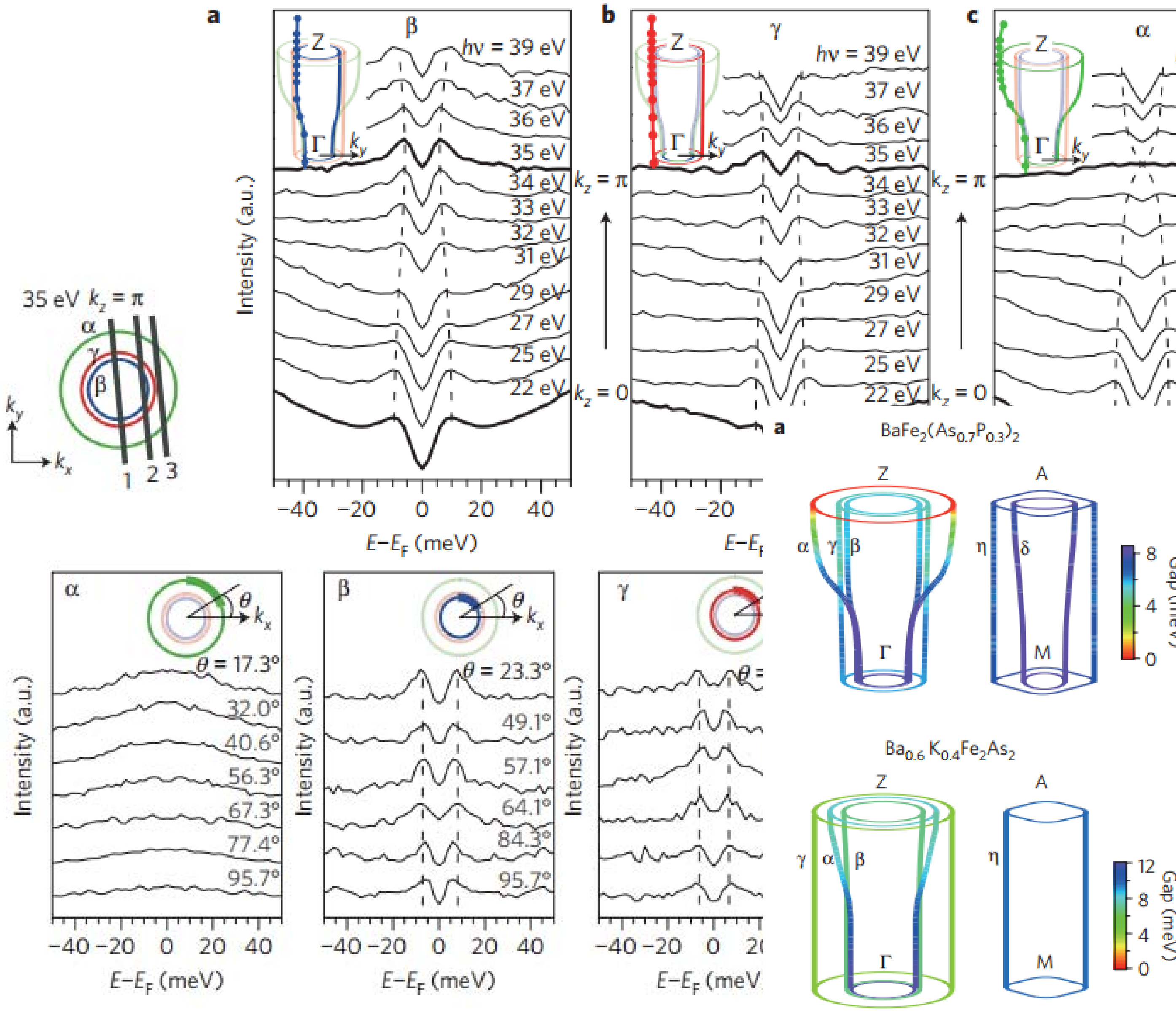


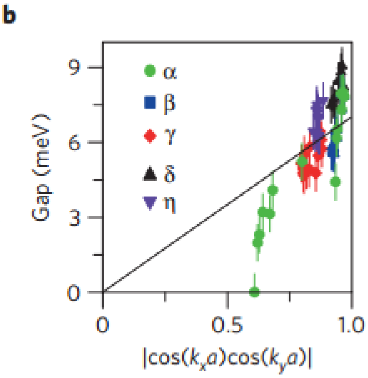
K. Umezawa *et al,* PRL **108**, 037002 (2012)



- Gaps are anisotropic but there are no nodes
- Consistent with $s_{\pm}$ pairing

SC gap in $BaFe_2(As_{0.7}P_{0.3})_2$ (T_c=30K)

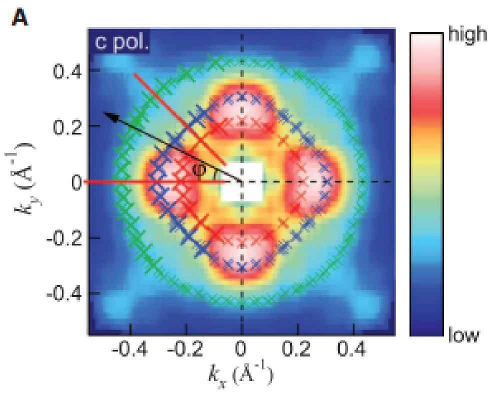


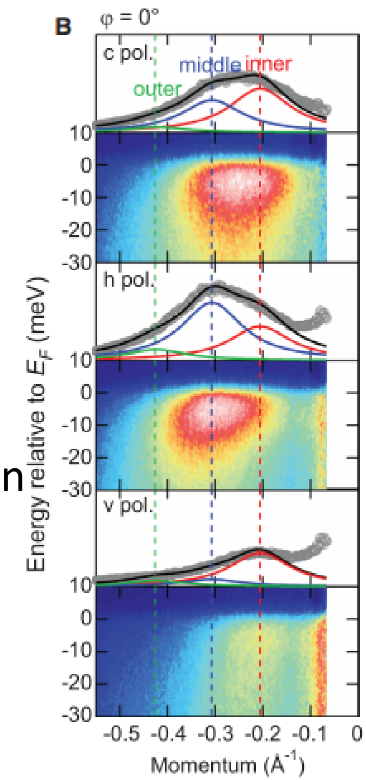


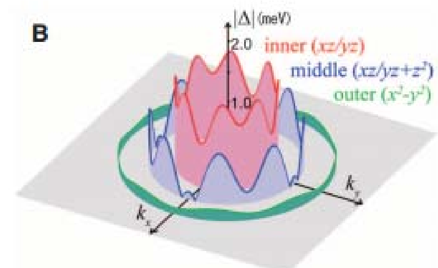
Compared to $s^{\pm}$

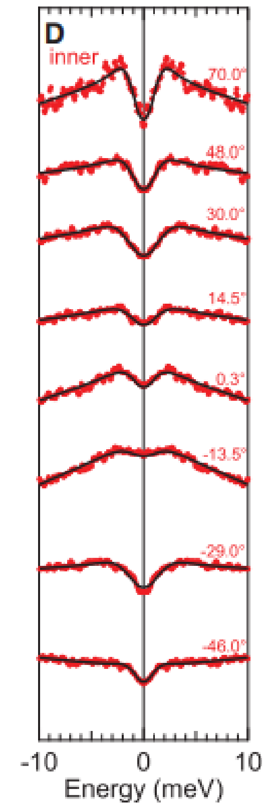
Zhang *et al*,
Nat. Phys. **8**
371 (2012)

SC gap in KFe_2As_2 (T_c=3.4K)



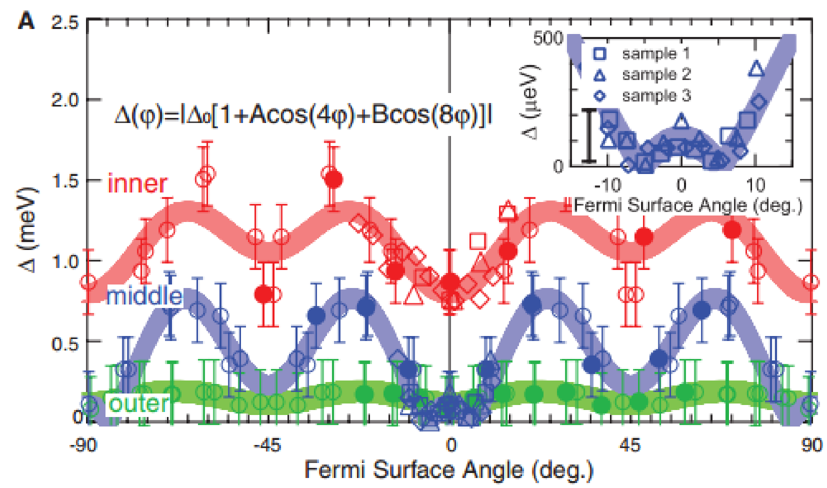






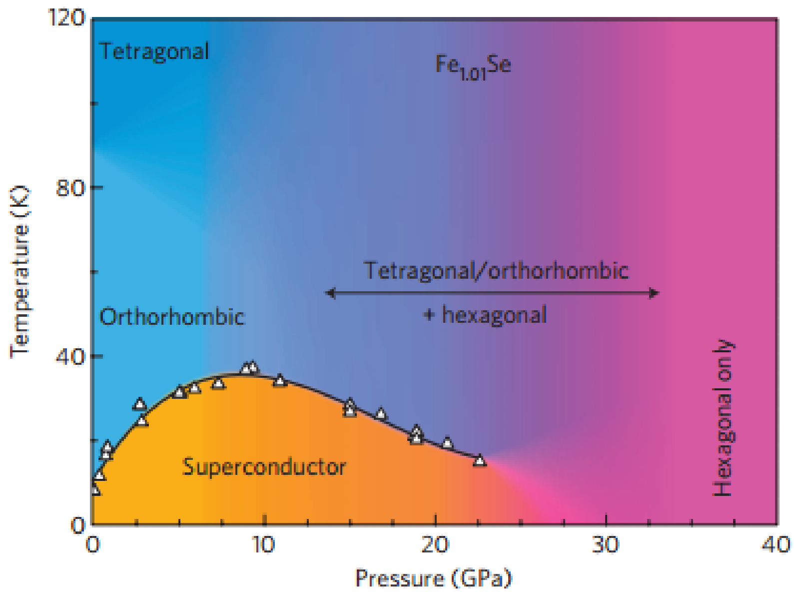
- Different fermiology than most FeSCs
- Measurement temperature=2K
- Total energy resolution: $70\mu eV$

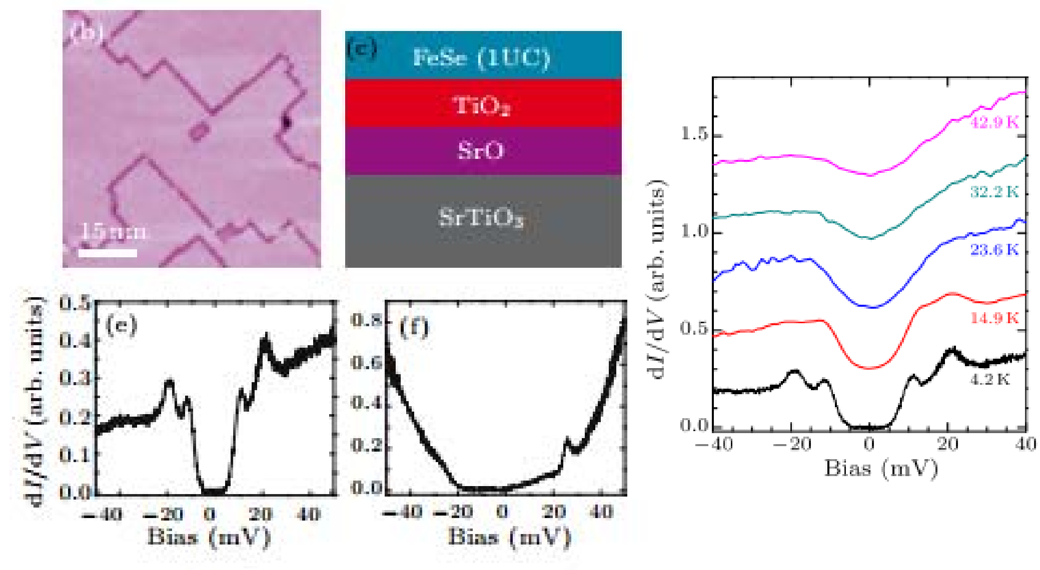
"An eight noded monster"



Okazaki *et al*, Science **337** p1314 (2012)

Monolayer FeSe





Bulk FeSe

- T_c=9K at ambient pressure
- T_c can be increased to 37K with pressure

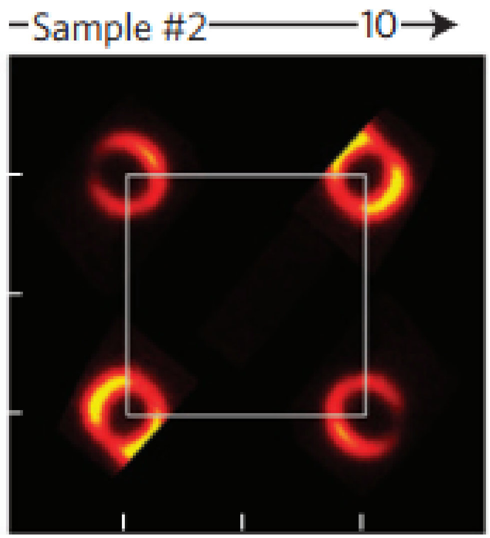
Monolayer (1 unit cell) FeSe on $SrTiO_3$ (TiO_2 terminated)

- Gap ~20 meV→suggests high Tc
- Gap persists to >50K
- Highest reported Tc=109K, highest accepted Tc=65K

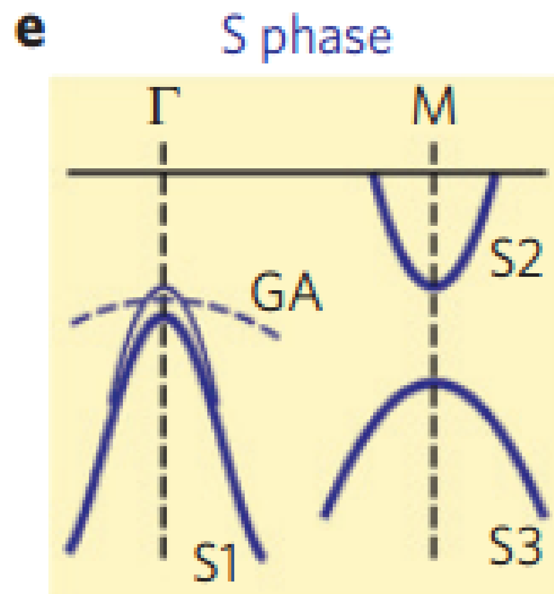
Medvedev *et al,* Nat. Mater **8** 630 (2009)

Wang *et al,* Chin. Phys. Lett. **29** 037402 (2012)

Monolayer FeSe: Fermiology

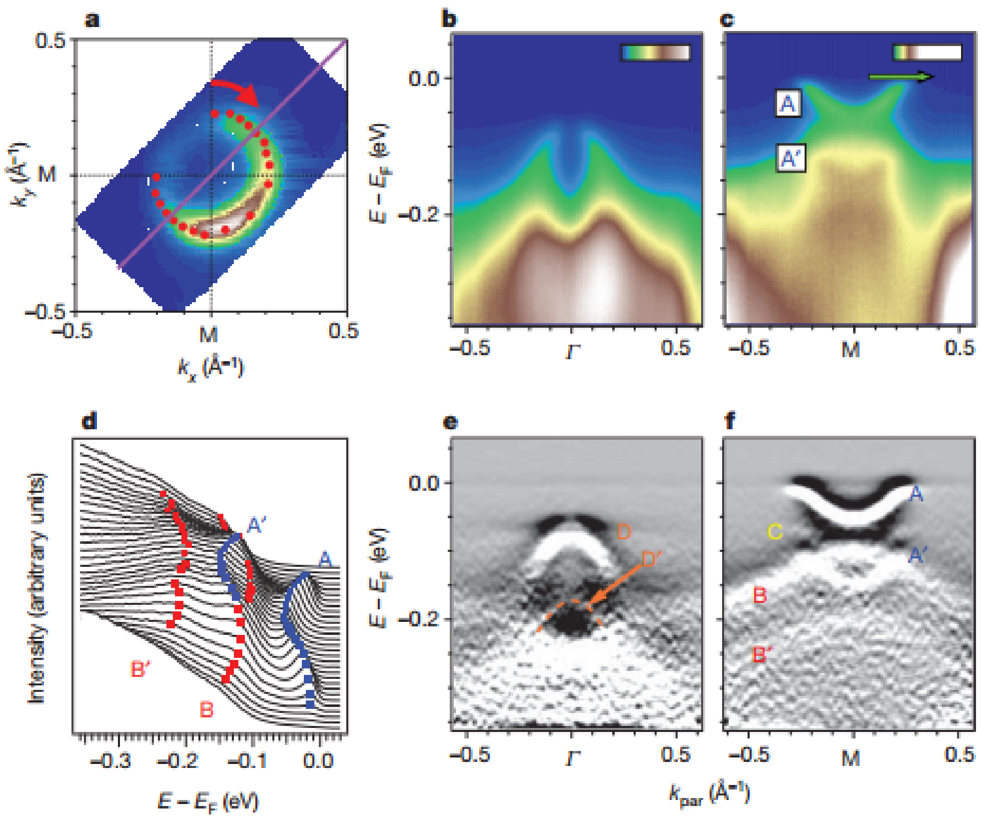


High-Tc FeSe monolayer does not have FS at Γ, unlike bulk FeSe and most other Fe-SCs



He *et al.* Nat. Mater. **12** 605 (2013)

Monolayer FeSe: possible mechanism of T_c enhancement



- Observation: 'copies' of band structure in a way which is not consistent with quantum well state
- Interpretation: strong coupling to phonon mode in STO at q=0
- Consequence: interface e-ph coupling is responsible for T_c enhancement

Lee *et al.* Nature **515** 245 (2014)

Topological insulators

A standard candle for technique development

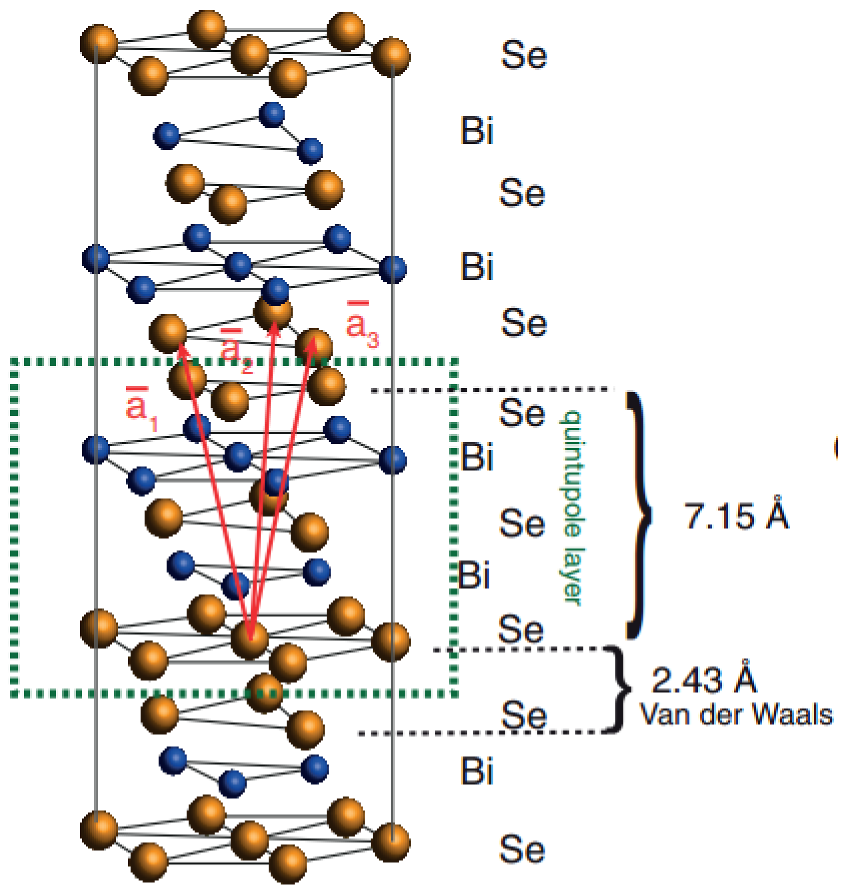
Expectations for ARPES spectra of 3D topological insulators

- Correlated electron systems and unconventional superconductors ➔ Experiments drive theory
- Topological materials➔Theory drives experiment

- Insulator in bulk
- Surface state
  - Odd number of them
  - Dirac-like dispersion
  - Spin-momentum locking
  - Difficult to destroy except by breaking time reversal symmetry

Topological insulator materials

- Bi_2Te_3
- Bi_2Se_3
- Sb_2Te_3
- $Bi_{2-x}Sb_xTe_{3-y}Se_y$



Bianchi *et al.* Semicond. Sci. Technol. **27** 124001 (2012)

Materials history

PHYSICAL REVIEW VOLUME 108, NUMBER 5 DECEMBER 1, 1957

Electrical and Thermal Properties of Bi_2Te_3

C. B. SATTERTHWAITE AND R. W. URE, JR.
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

(Received August 15, 1957)

Samples of both n-type and p-type Bi_2Te_3 containing from 3×10^{17} to 5×10^{19} extrinsic carriers were prepared and the phase diagram in the region about Bi_2Te_3 has been clarified. The Hall mobility parallel to the cleavage planes varies as $T^{-1.5}$ for holes and $T^{-2.7}$ for electrons. Room temperature values are $\mu_p=420$ cm^2 v^{-1} sec^{-1} and $\mu_n=270$ cm^2 v^{-1} sec^{-1}. The energy gap is $E_g=0.20$ electron volts. From thermal conductivity measurements over the temperature range from 77°K to 380°K the lattice conductivity was found to be $\kappa_L=5.10\times10^{-2}/T$ watt-deg^{-1} cm^{-1}. The sharp rise in the thermal conductivity in the vicinity of room temperature was attributed to transport of energy by ambipolar diffusion of electrons and holes.

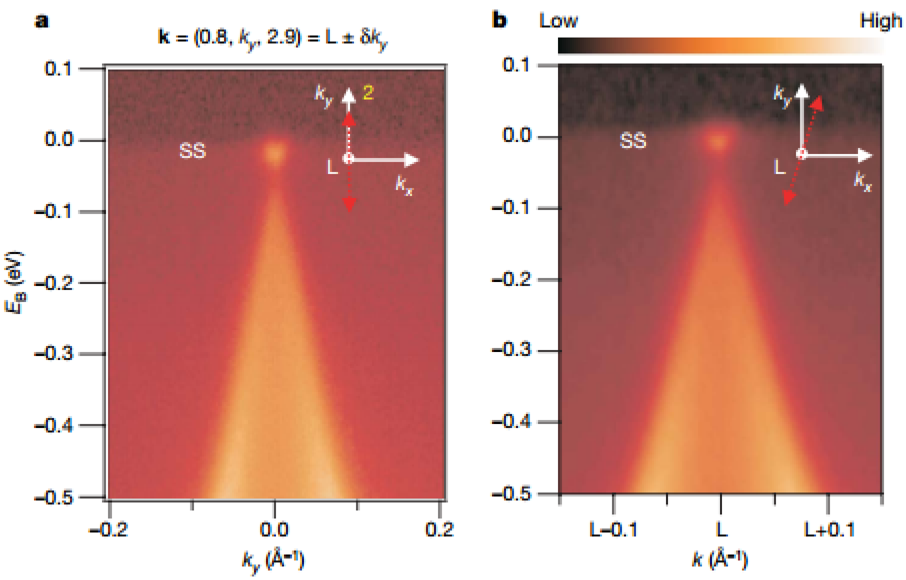
I. INTRODUCTION

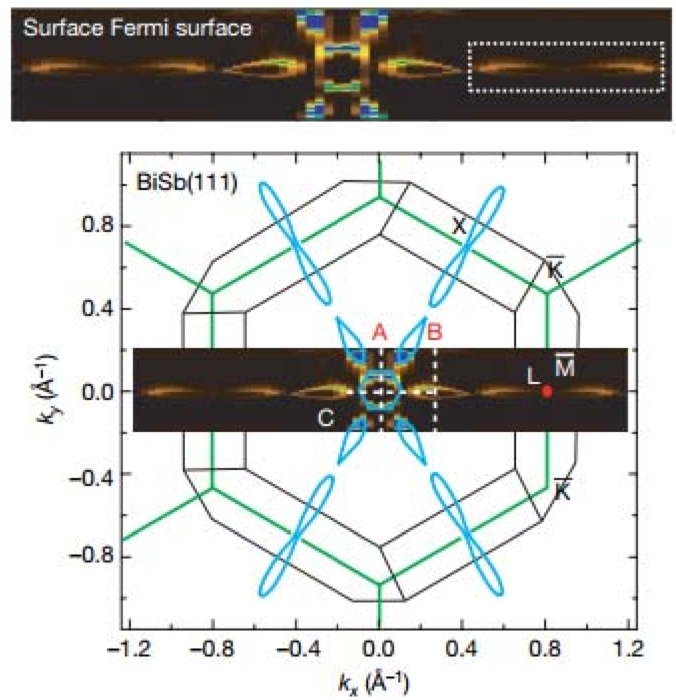
BISMUTH telluride recently has been of considerable interest, particularly as a thermoelectric material; however, the electrical and thermal properties of this material have not been established. The present paper describes the preparation of bismuth telluride of known composition and a study of the thermal conductivity and the electrical properties of both n- and p-type material.

This was found not to be the case. Whether the starting material contained an excess of Bi or an excess of Te the zone refined Bi_2Te_3 contained approximately 2×10^{19} excess holes.

By the technique described below the details of the phase diagram in the region of Bi_2Te_3 were clarified and also a series of single crystal samples of varying carrier concentration were produced for studies of the electrical and thermal properties.

0^{th} 3D Topological insulator: $Bi_{1-x}Sb_x$

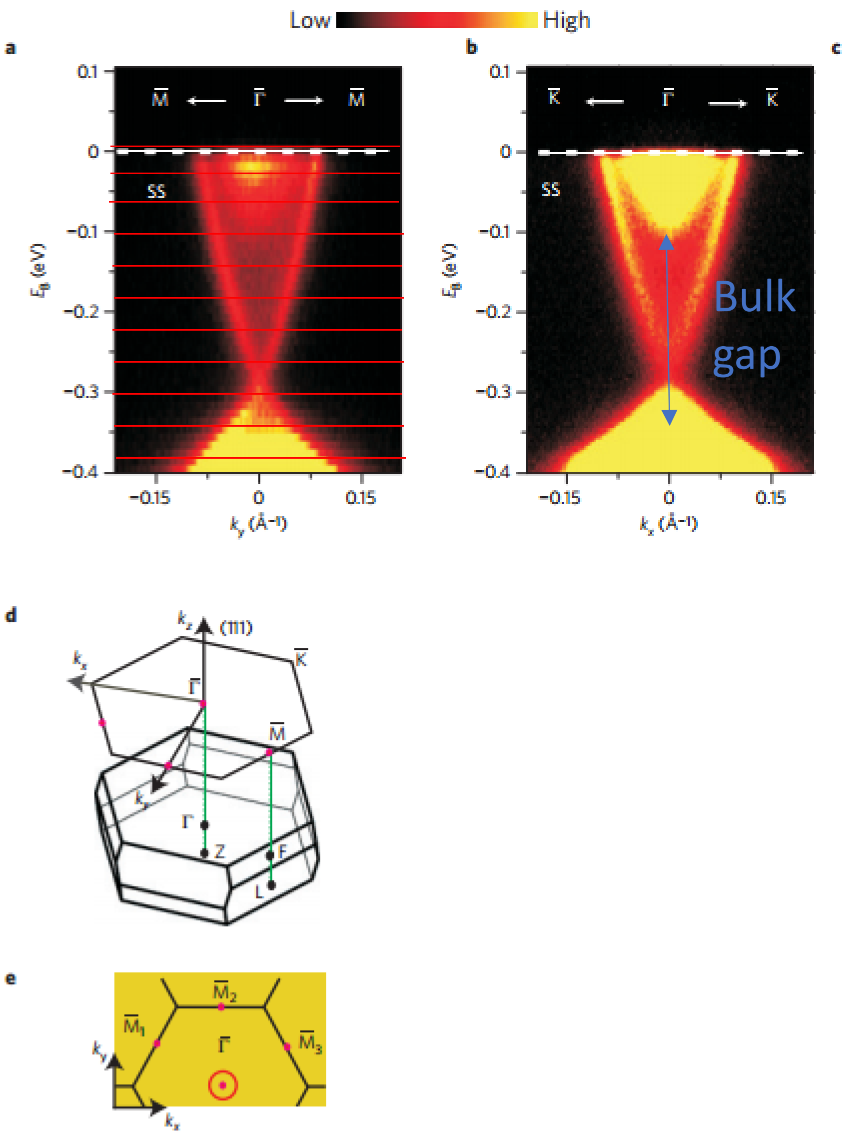




Problem: too many surface states

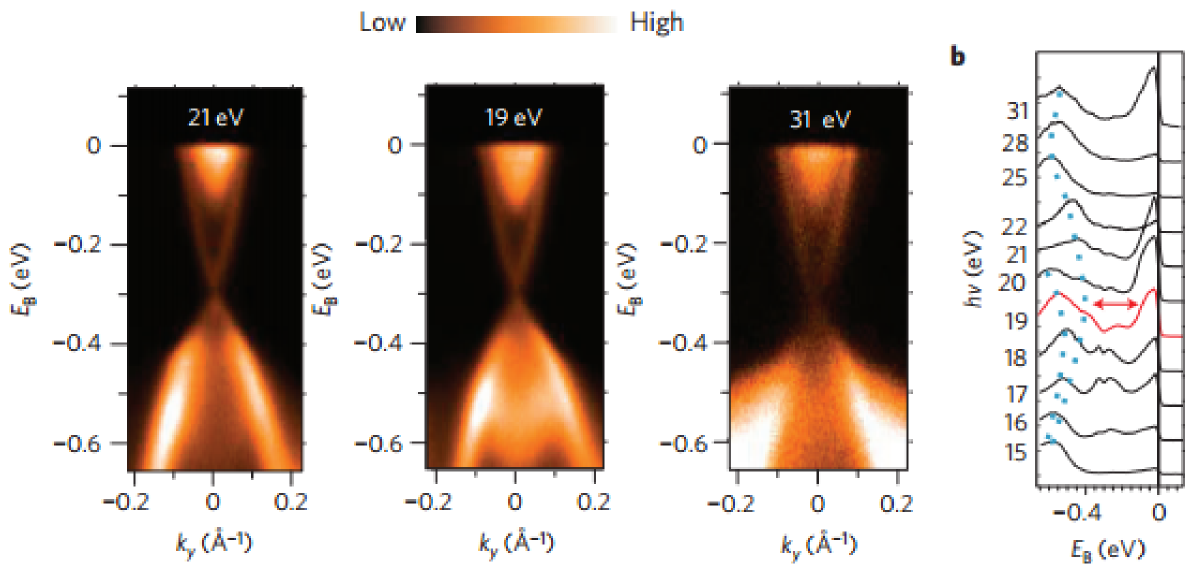
Hsieh *et al*. Nature **452** (2008)

1st 3D Topological insulator: Bi_2Se_3



Xia *et al.* Nat. Phys. **5** May 2009

Distinguishing surface from bulk states

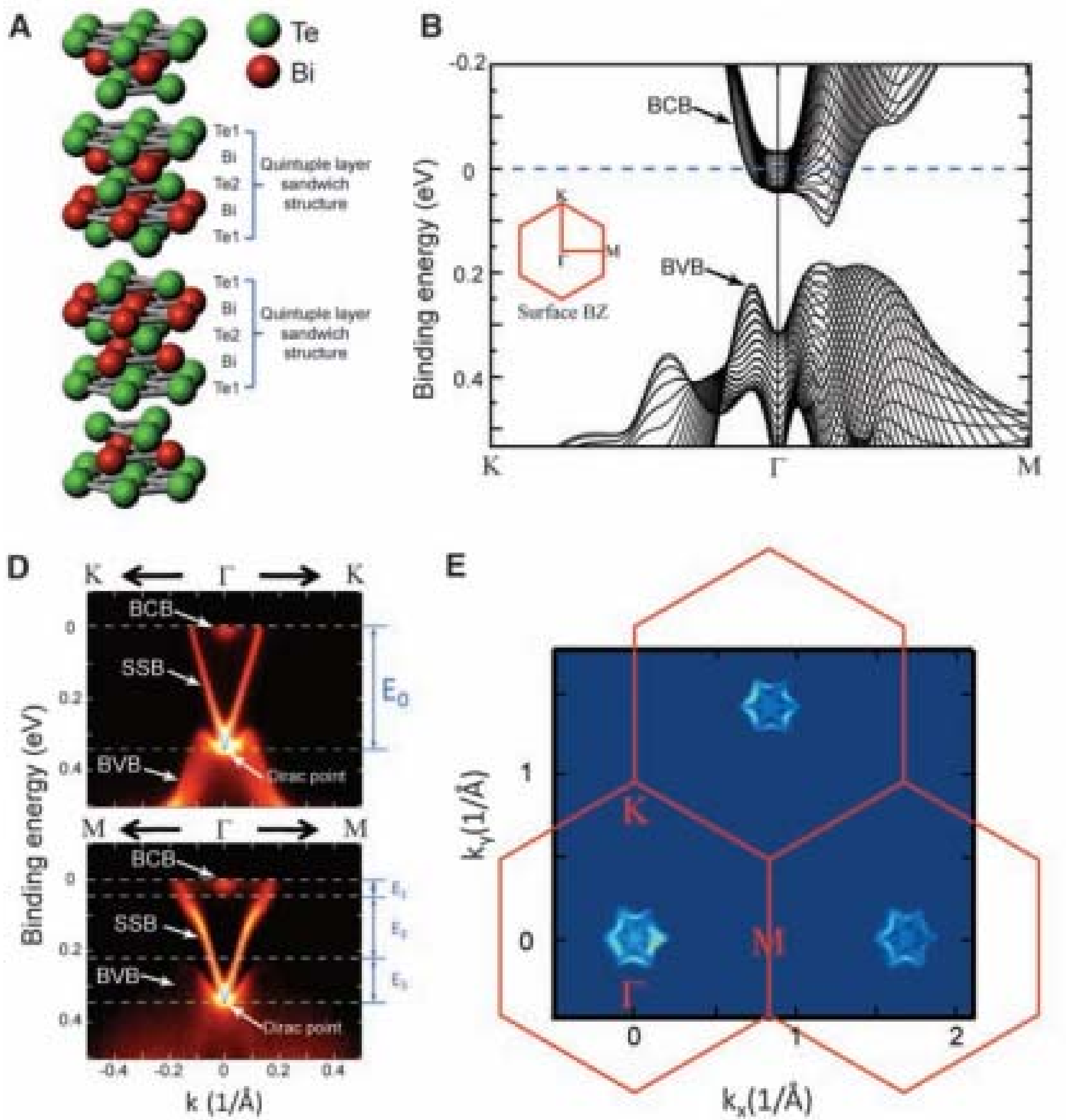


Vary photon energy

- Surface bands **do not** disperse because they are strictly 2D
- Bulk bands **do** disperse because they have some 3D character
- Complication: matrix element effects can make surface state look brighter or dimmer at different photon energies

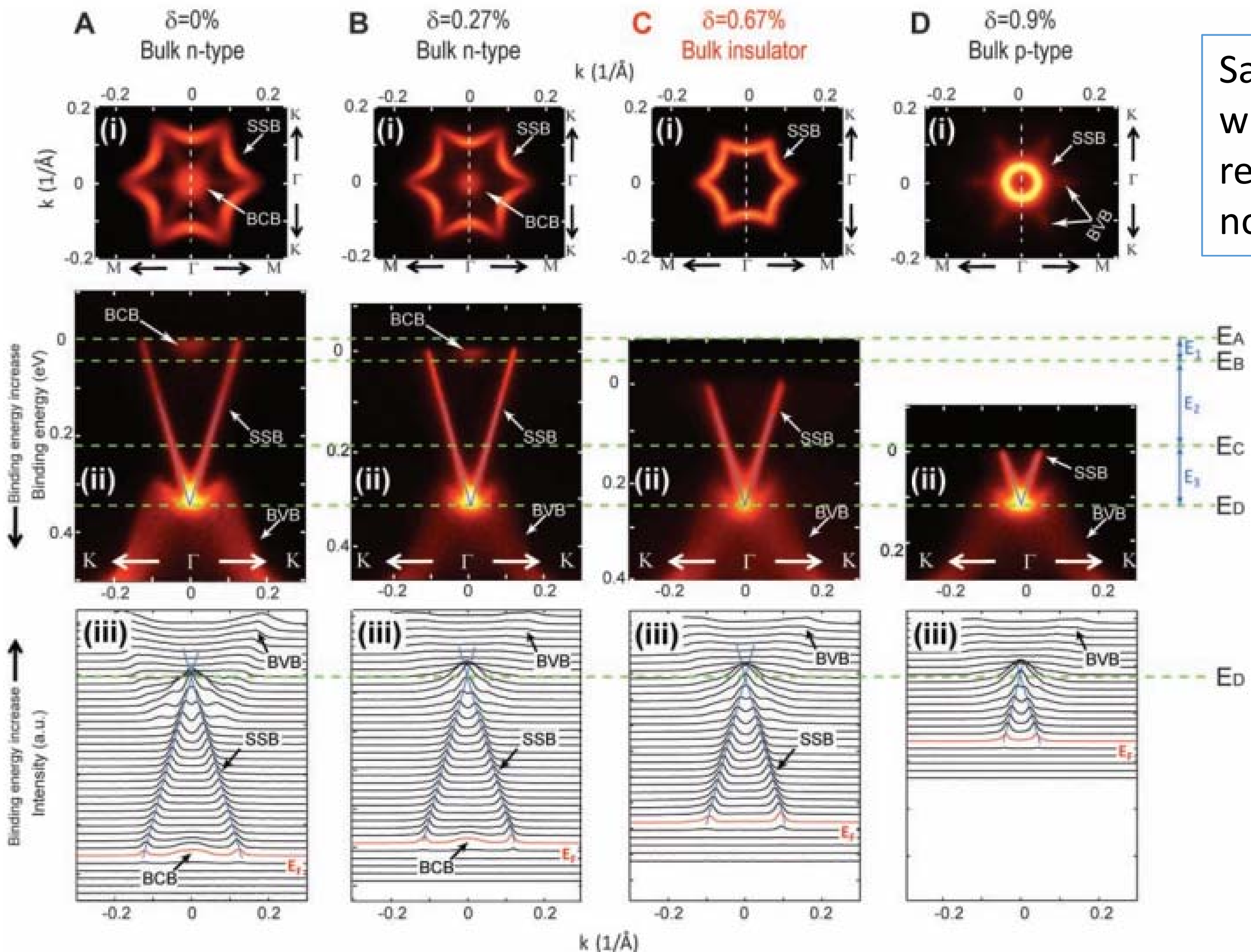
Xia *et al.* Nat. Phys. **5** May 2009

2^{nd} 3D topological insulator: Bi_2Te_3



Chen *et al.* Science **325** July 2009

Tuning doping: $(Bi_{1-\delta}Sn_{\delta})_2Te_3$



Same surface state, whether bulk is really insulating or not

Chen *et al.* Science **325** July 2009

Measuring spin texture via spin-resolved ARPES

Which of these is a really **bad** way of distinguishing different spin states via ARPES

A. Mott scattering
B. Stern Gerlach experiment
C. Exchange scattering
D. Circularly polarized light
E. Ask a theorist

Spin texture via spin ARPES

How can we measure electron spin in photoemission experiments?

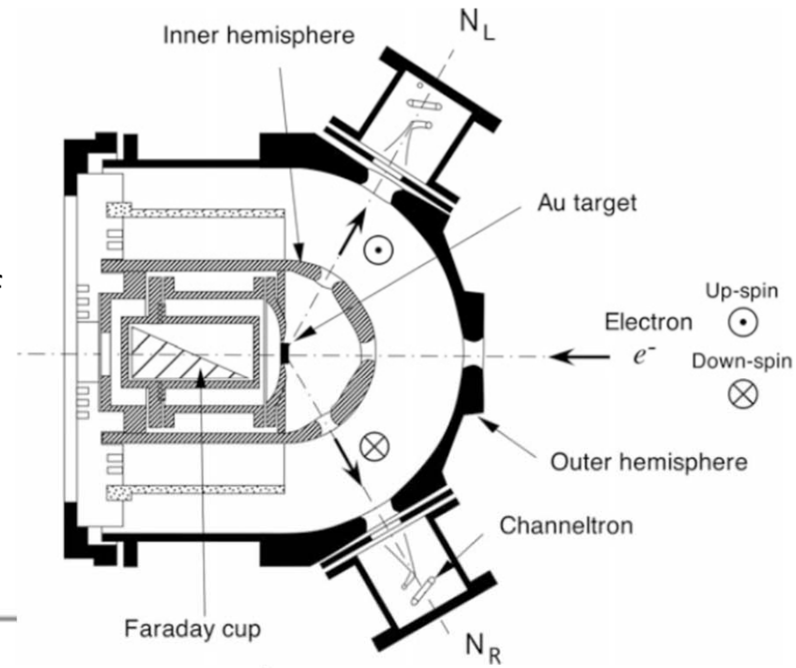
Method	Interaction	Operation voltage	S_{eff}	Figure of merit	Target
Mott	Spin-orbit	20–100 kV	0.1–0.2	$1–5 \times 10^{-4}$	Au thin film
SPLEED	Spin-orbit	150 V	0.2–0.3	$1–2 \times 10^{-4}$	W single crystal
Diffuse scattering	Spin-orbit	150 V	~0.2	$\sim 1 \times 10^{-4}$	Au thin film
VLEED	Spin-exchange	6–10 V	0.3–0.4	$\sim 10^{-2}$	Fe single crystal

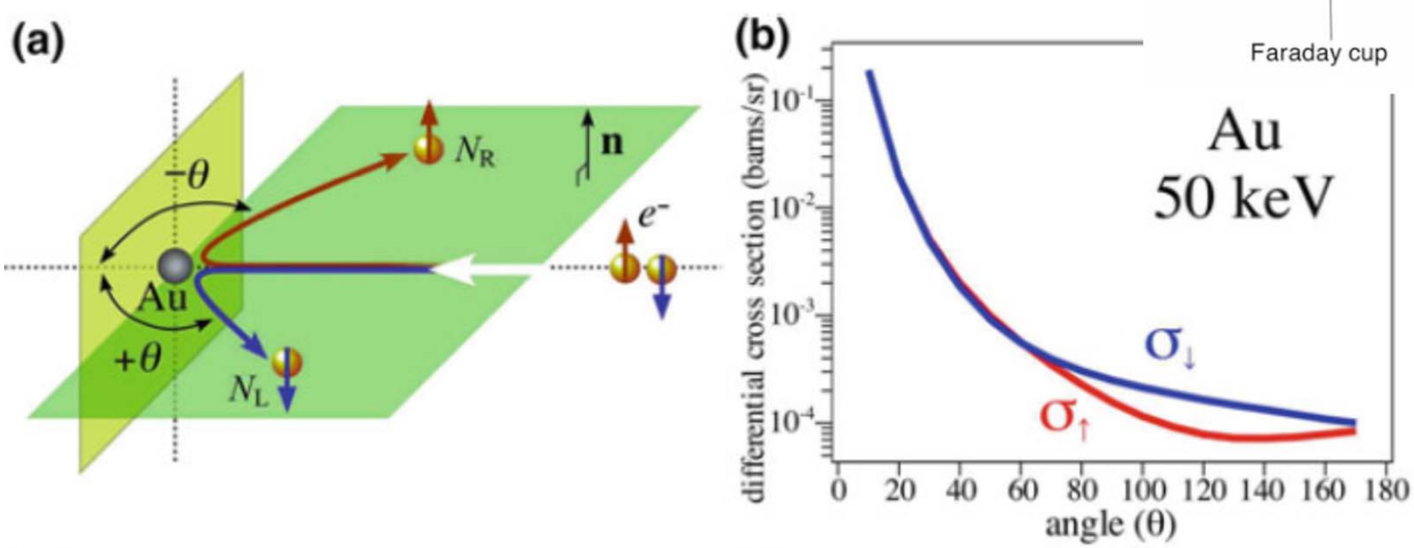
1. **Jozwiak *et al.* Rev. Sci. Instr. 81 (2010) 053904**
2. **Okuda *et al*, Journal of electron spectroscopy and related phenomena 201 23 (2015)**

Table source: A. Takayama, *High-resolution spin-resolved photoemission spectrometer and the Rashba effect in Bismuth thin films (2015)*

Mott Detectors

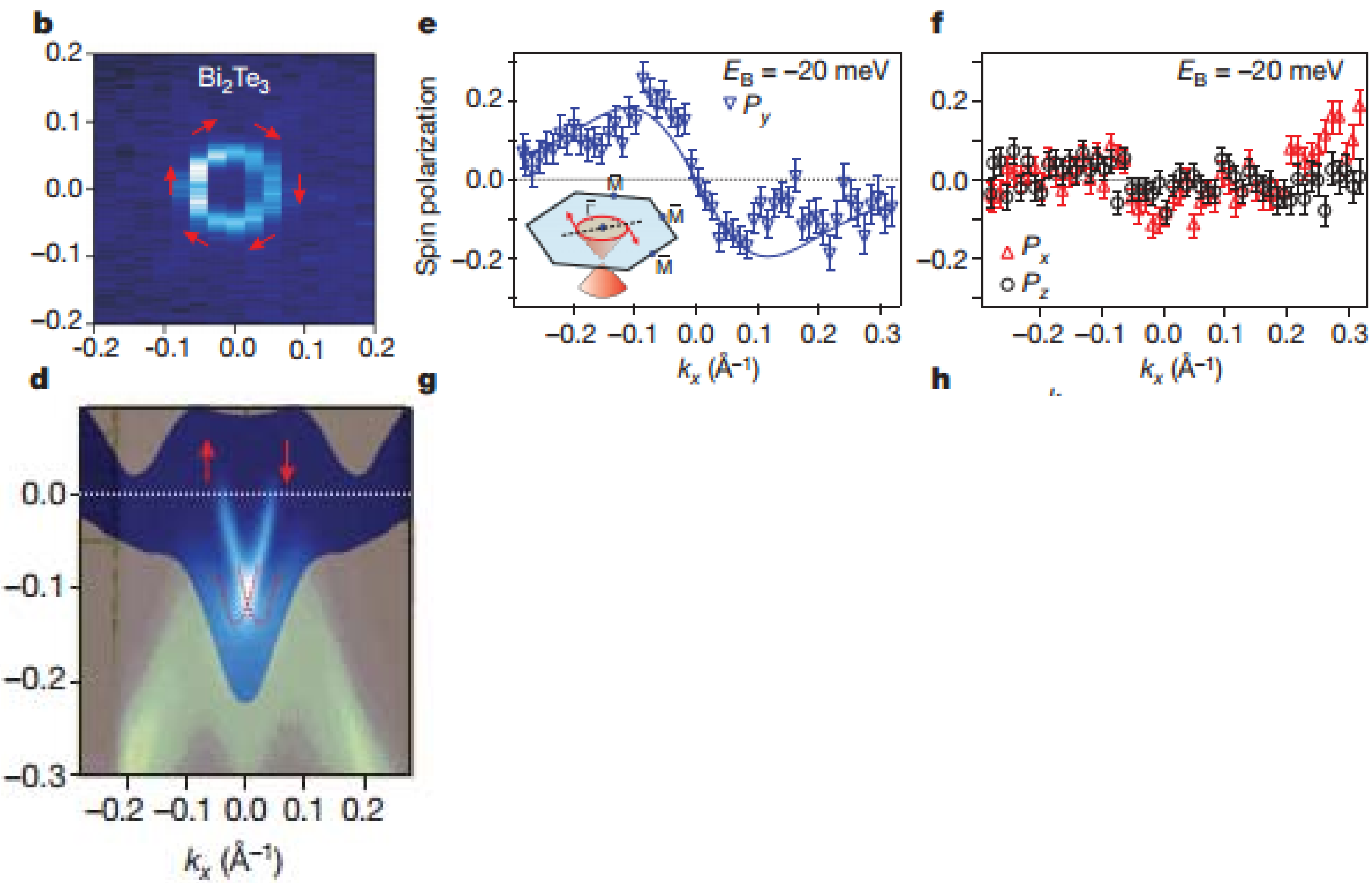
- Spin-orbit coupling (SOC): positively charged nucleus provides effective **B**-field in rest frame of electron:
$\boldsymbol{B} = -\frac{1}{c}\boldsymbol{v} \times \boldsymbol{E} = -\frac{1}{c}\frac{Ze}{r^3}\boldsymbol{v} \times \boldsymbol{r} = \frac{Ze}{mcr^3}\boldsymbol{L}$
- Magnetic moment of electron:
$$\mu_e = -\frac{g_s e}{2mc}\boldsymbol{S}$$
- Interaction between electron and effective B field of nucleus:
$$v_{LS} = -\mu_e \cdot \boldsymbol{B} = \frac{\mathrm{Ze}^2}{2\mathrm{m}^2\mathrm{c}^2\mathrm{r}^3}\mathbf{L} \cdot \boldsymbol{S}$$
- Scattering cross section has angular asymmetry





A. Takayama, *High-resolution spin-resolved photoemission spectrometer and the Rashba effect in Bismuth thin films (2015)*

Spin texture of Bi_2Te_3 via Mott scattering



Hsieh *et al.* Nature **460** (2009)

Major contribution of 3D topological insulators: playground for time-resolved ARPES

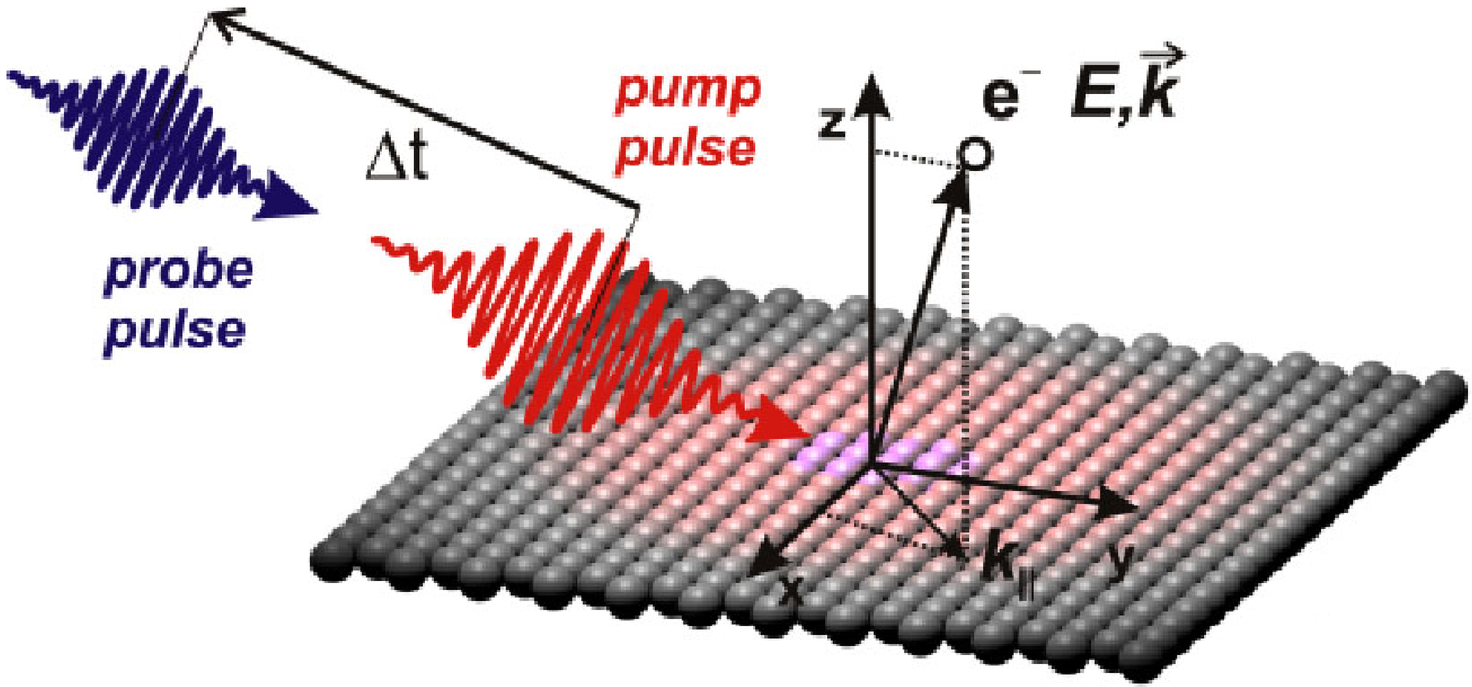
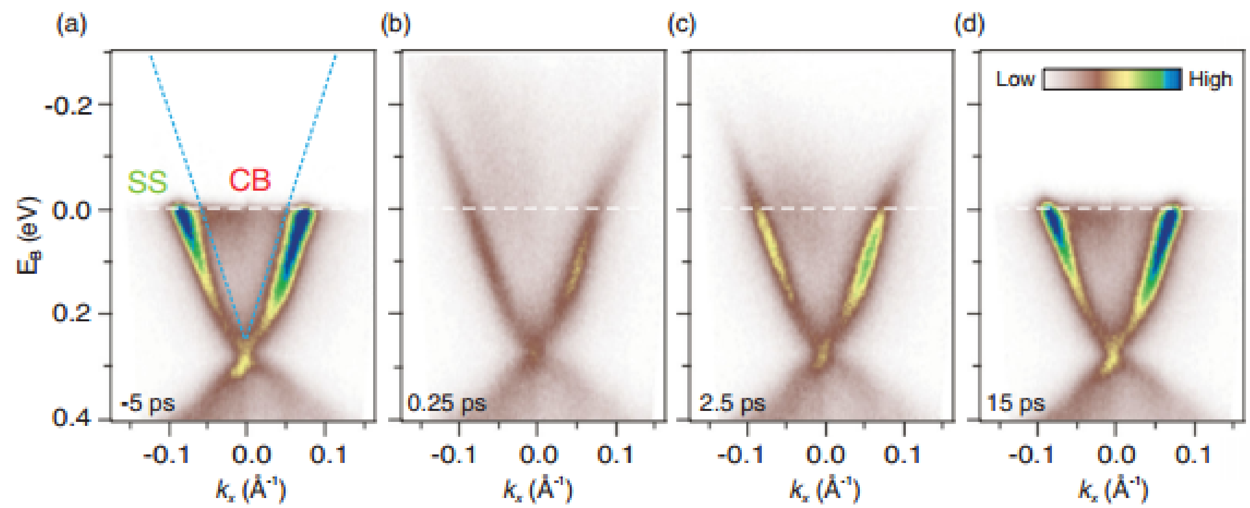
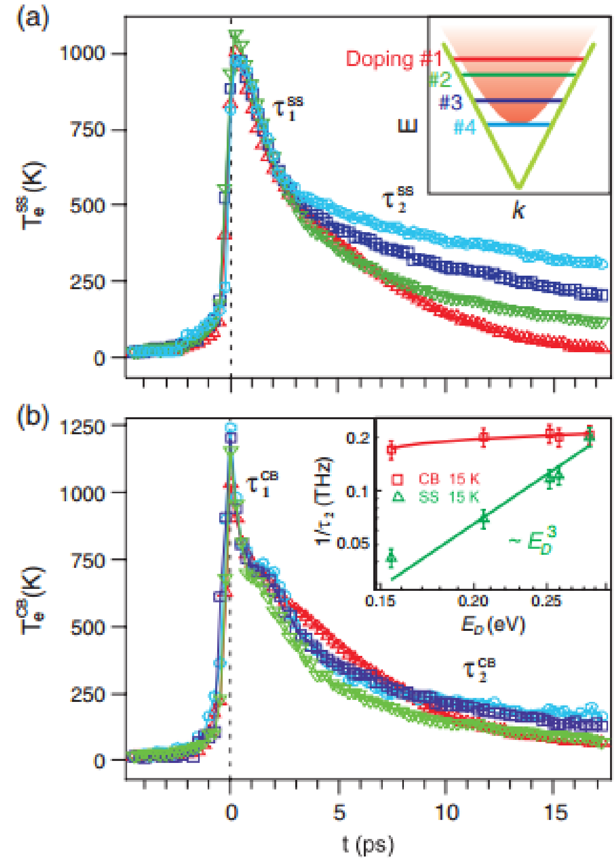


Image source: http://www.fhi-berlin.mpg.de/pc/PCres_methods.html

Surface-bulk coupling in Bi_2Se_3



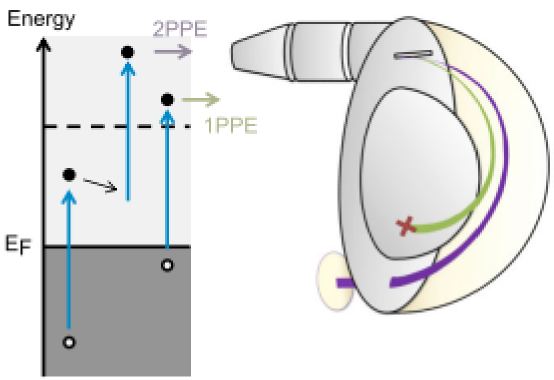


- 1.5 eV pump, 6 eV probe
- Pump deposits energy into **electrons**, effectively giving them higher temperature than surrounding lattice
- In ordinary metals: electron thermalization with lattice set by e-ph coupling
- In metallic surface state: hot electrons in surface state can cool down faster by thermalizing with bulk bands first

Wang *et al.* PRL **109**, 127401 (2012)

2 photon photoemission (2PPE) as a substitute for inverse photoemission

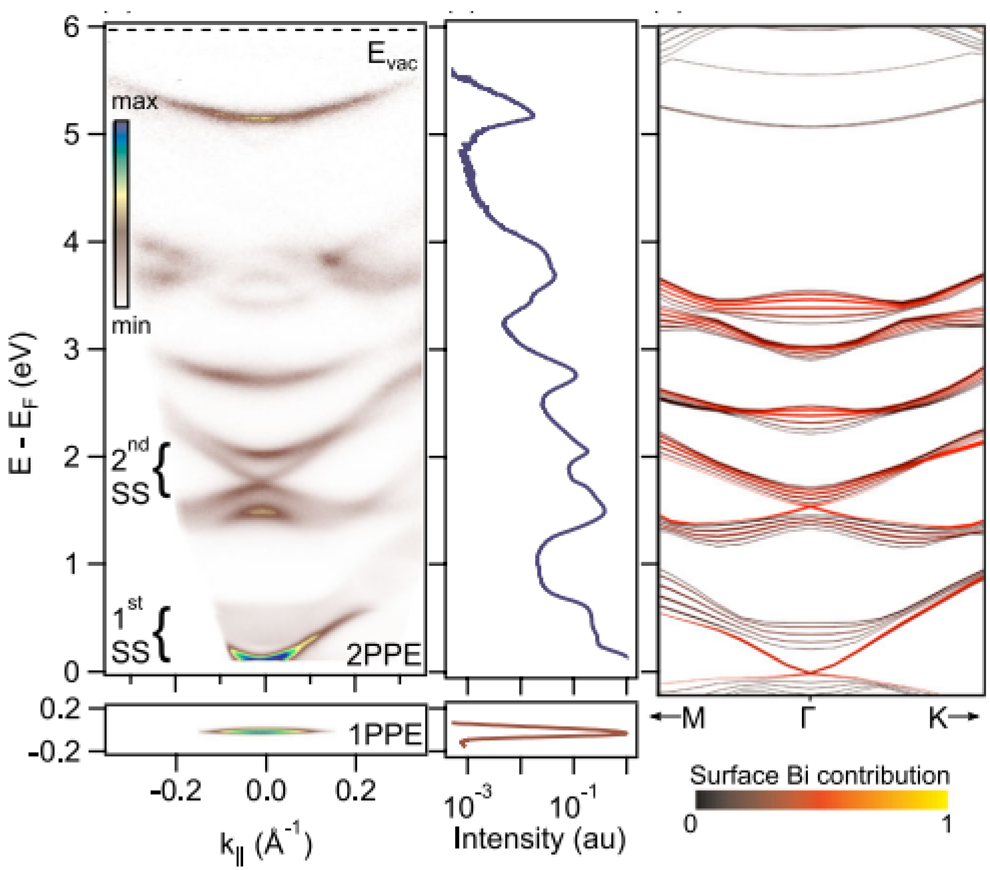
Photoemission	Photon in, electron out	Measure **occupied** electronic states	Sub-meV resolution common
Inverse photoemission	Electron in, photon out	Measure **unoccupied** electronic states	~500 meV resolution



Use time-resolved ARPES to measure unoccupied states

- Pulse 1 (pump): make excitation into unoccupied state
- Pulse 2 (probe): perform photoemission out of pump-populated unoccupied state
- Time resolution is not very important, but light **intensity** is because this is 2nd order process

2 PPE experiments in Bi_2Se_3



- 1.5 eV pump, 5.98 eV probe, $\Delta t \sim 100 fs$
- 2^{nd} surface state observed above E_F!
- Applicable to many different materials

Sobota *et al*. PRL **111**, 136802 (2013)

Floquet-Bloch states

- Spatially periodic:

$$H(r+R) = H(r)$$

$$\Psi_{nk}(r) = e^{ik\cdot r} u_{nk}(r)$$

$$u_{nk}(r+R) = u_{nk}(r)$$

$$k \text{ and } k+nG$$
$$(G = 2\pi/R)$$

- Temporally periodic

$$H(t+T) = H(t)$$

$$\Psi_\alpha(t) = e^{-\frac{i}{\hbar}\epsilon_\alpha(t-t_0)}\phi_\alpha(t)$$

$$\phi_\alpha(t) = \phi_\alpha(t+T)$$

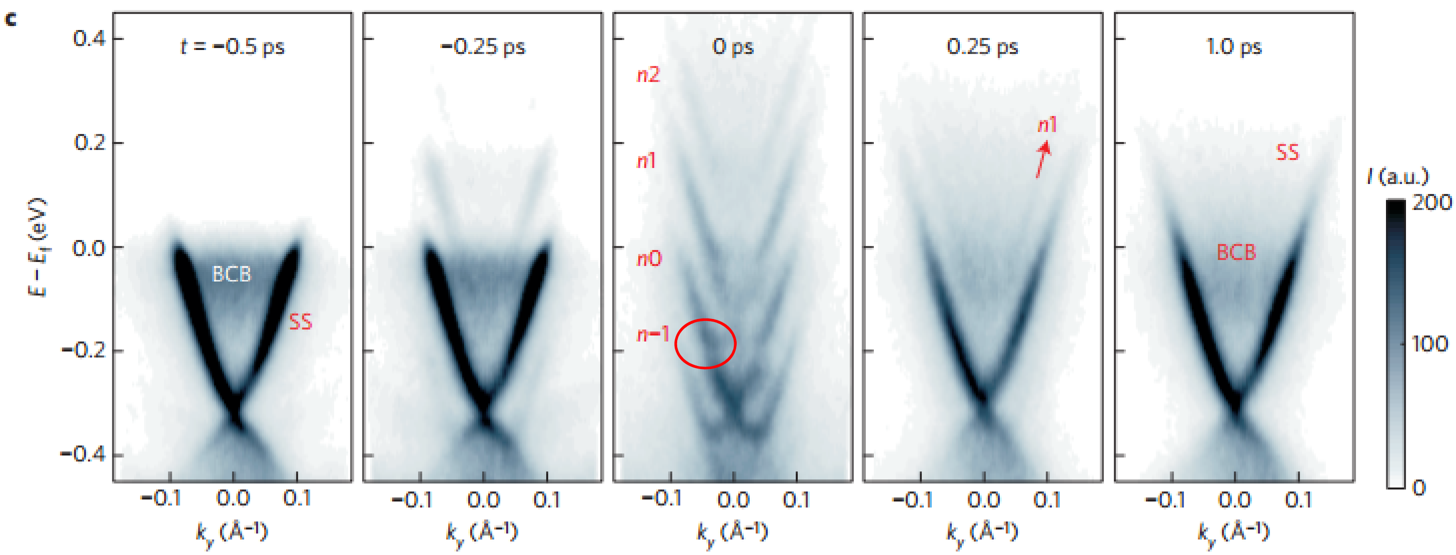
$$\epsilon_\alpha \text{ and } \epsilon_\alpha + n\hbar\omega$$
$$(\omega = 2\pi/T)$$

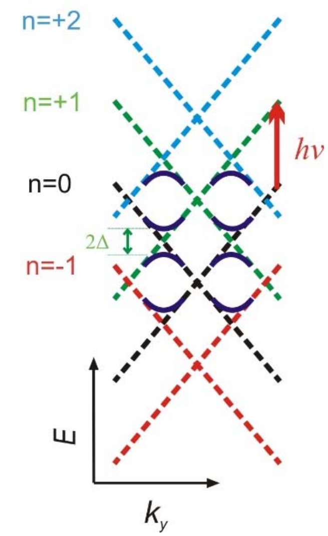
If you have both spatially and temporally periodic Hamiltonian,
Eigenvalues are periodic both in k and E! -> Floquet-Bloch states!

Slide courtesy of N. Gedik

Creating new states of matter with light

- Use mid-IR pump with energy **smaller** than band gap of Bi2Se3
- Use oscillating electric field of pump to create floquet-bloch state
- Photoinduced gaps at band crossings
- Circularly polarized light can open gap at Dirac point!

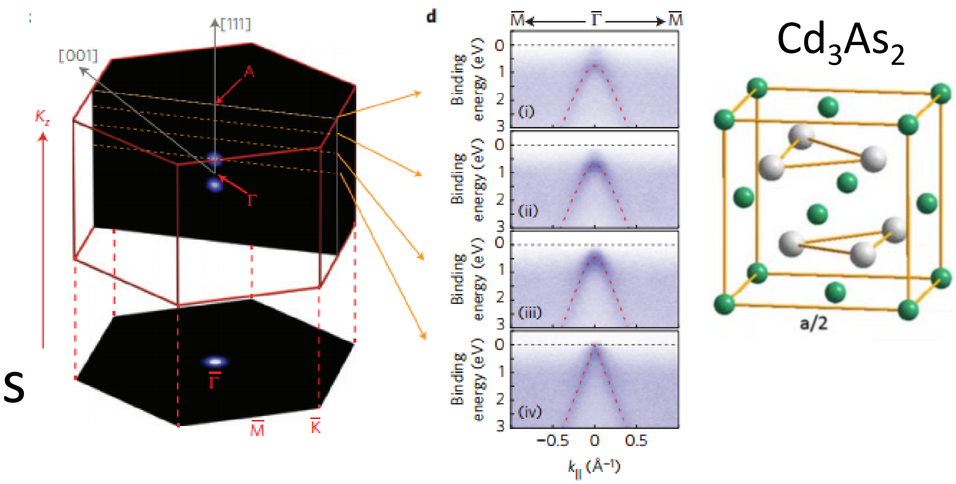




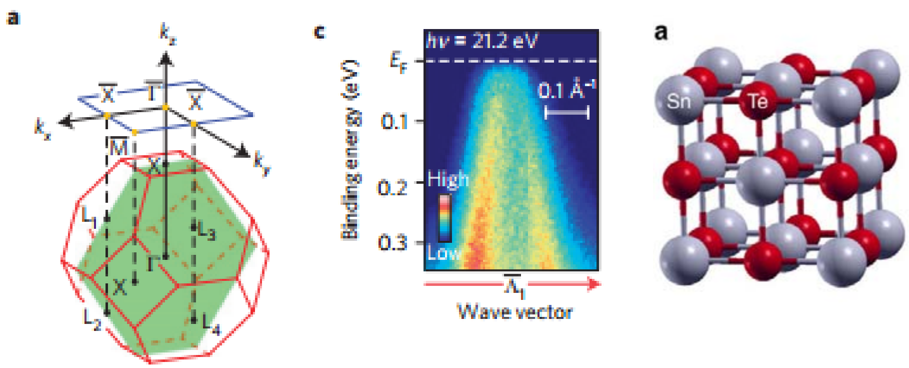
Wang *et al.* Science **342** 514 (2013)
Mahmood *et al.* Nat. Phys. **12** 453 (2016)

Intellectual descendants of topological insulators

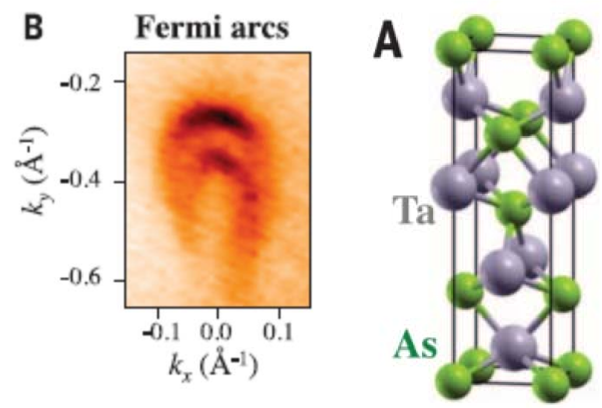
- Topological crystalline insulators (2012)
- Dirac Semimetals (2013)
- Weyl Semimetals (2015)
- Nodal line/chain/loop semimetals (2016)



DSM: Liu *et al,* Nat. Mater. **13** 677 (2014)



TCI: Tanaka *et al.* Nat. Phys. **8** 800 (2012)

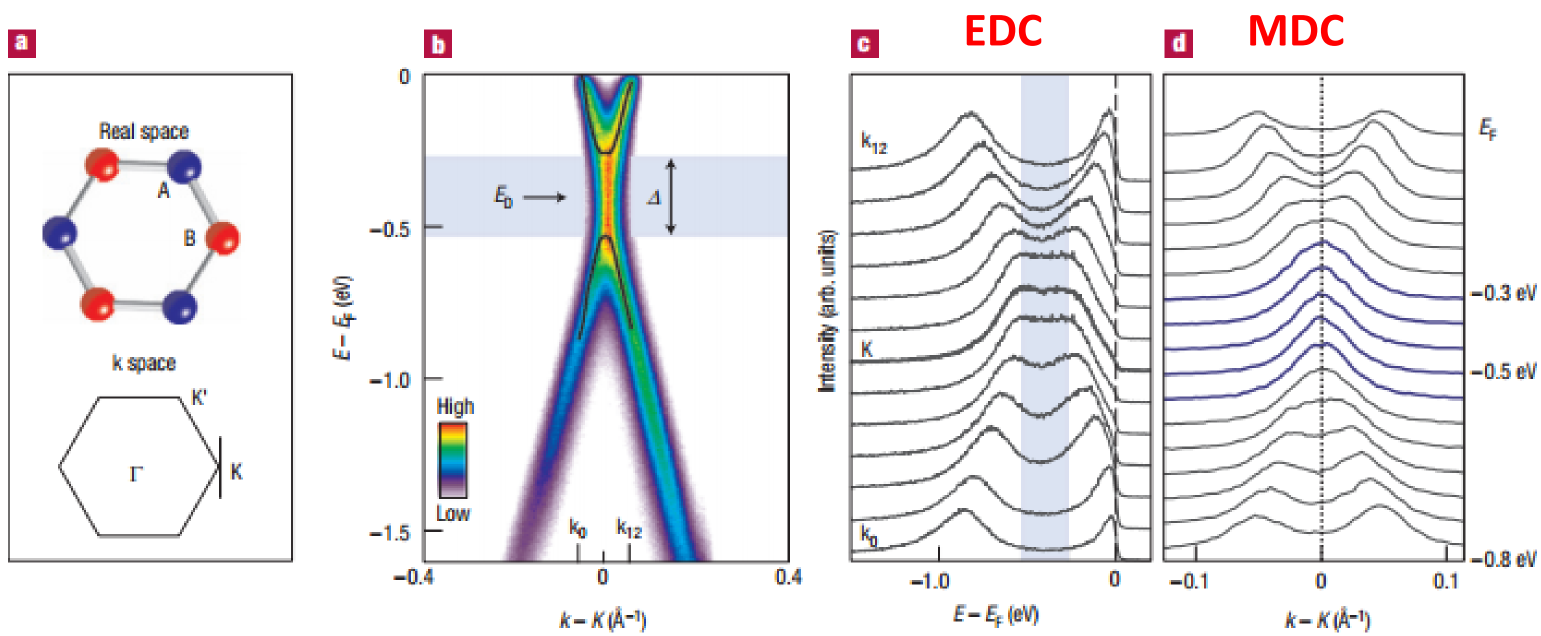


Xu *et al.* Science **349** 613 (2015)

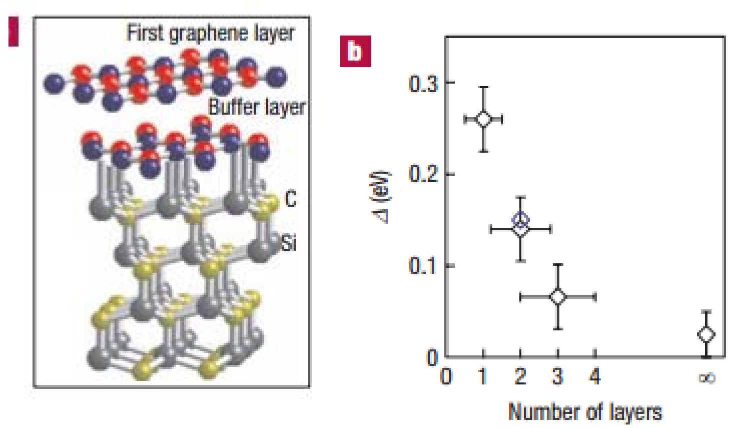
2D materials

A diverse platform for microARPES

ARPES on not-so-isolated graphene

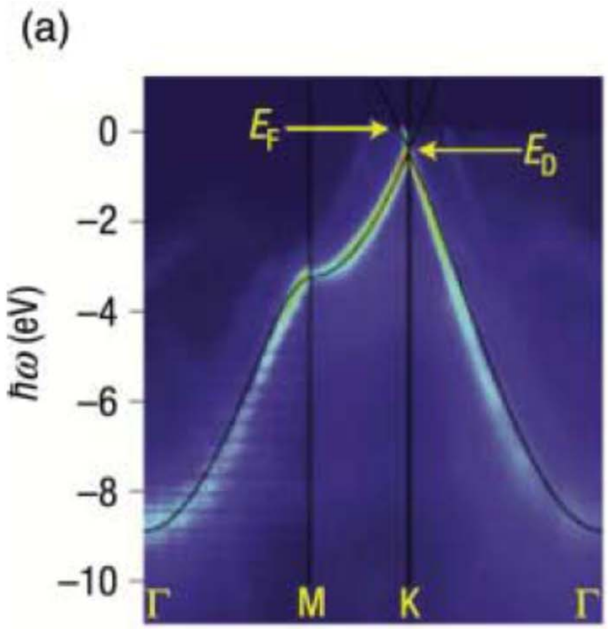


Zhou *et al.* Nat. Mater. **6** 770 (2007)

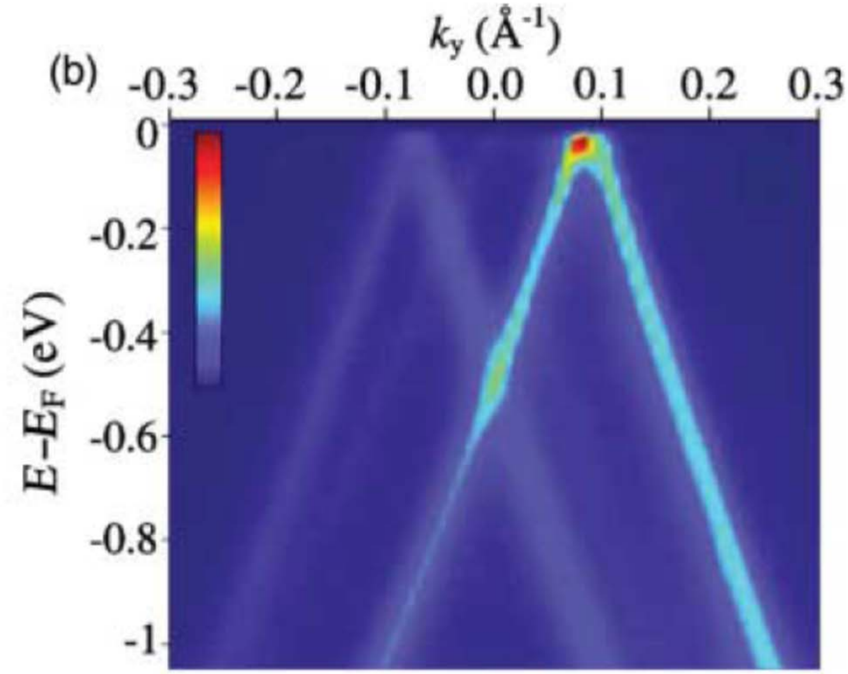


- Mass appears in dispersion because of sublattice symmetry breaking due to substrate
$$H_D = c\boldsymbol{\sigma}\cdot\boldsymbol{p} + mc^2\sigma_z$$
$$\boldsymbol{\sigma} = (\sigma_x, \sigma_y)$$
- Total of 36 ways to turn graphene massive (Ryu *et al,* PRB **80**, 205319 (2009))

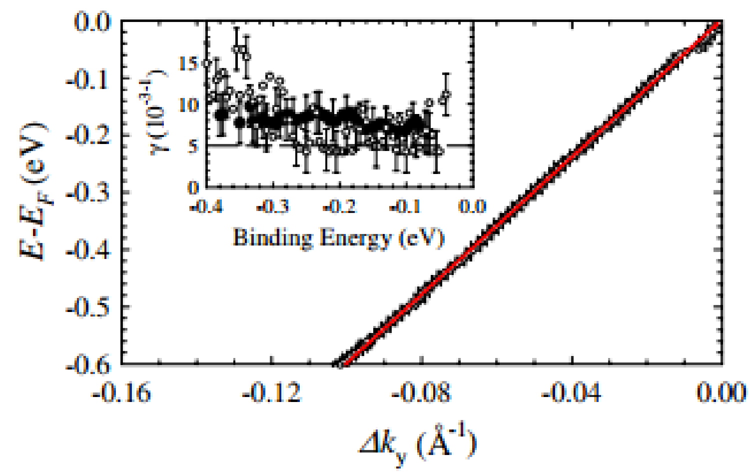
ARPES on isolated graphene



Bostwick *et al,* Nat. Phys. **3** 36 (2007)



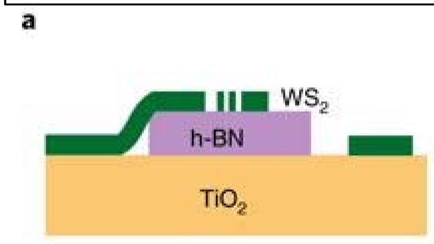
Sprinkle *et al,* PRL 103, 226803 (2009)

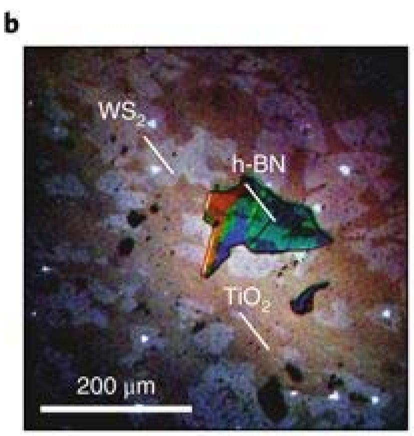


- Extra bands (right) from misoriented layers
- Band dispersion is linear over at least 600 meV

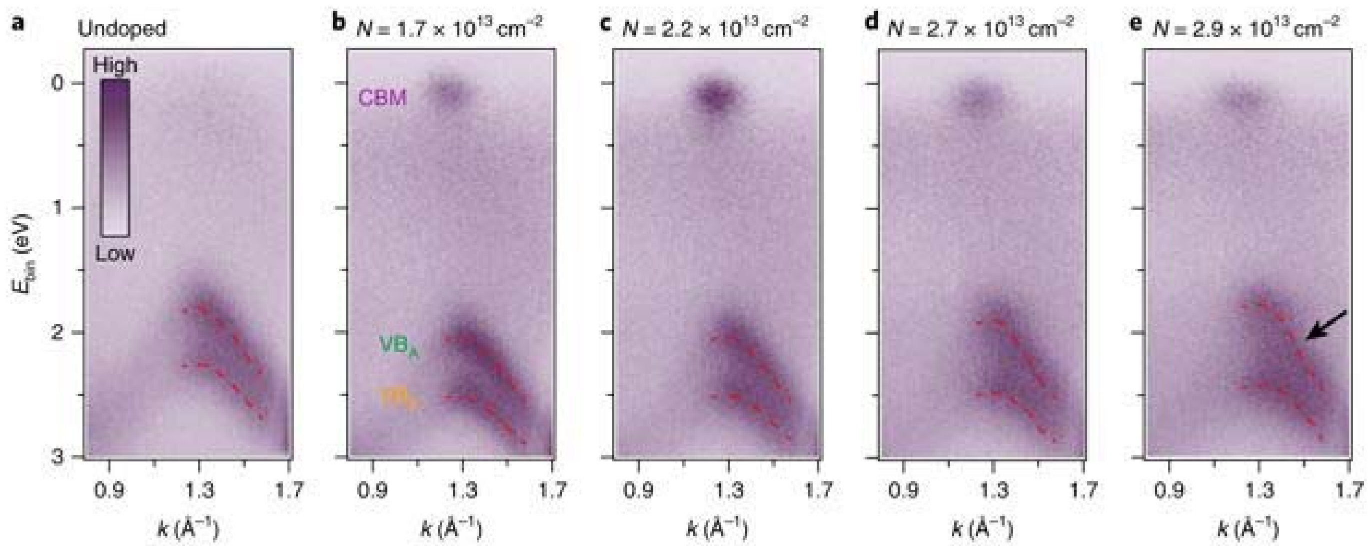
TDMC example: WS_2/h-BN microARPES

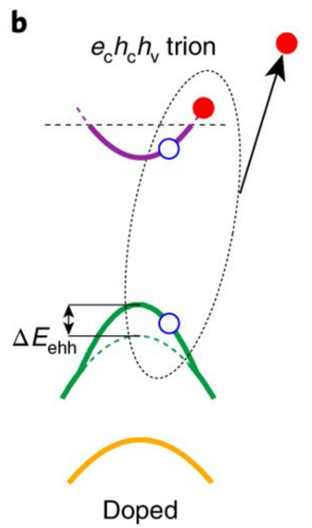
Regular ARPES: $100\ \mu m - 1mm$
Micro ARPES: $5 - 40\ \mu m$
Nano ARPES: $200\ nm - 1\mu m$





Potassium dosing



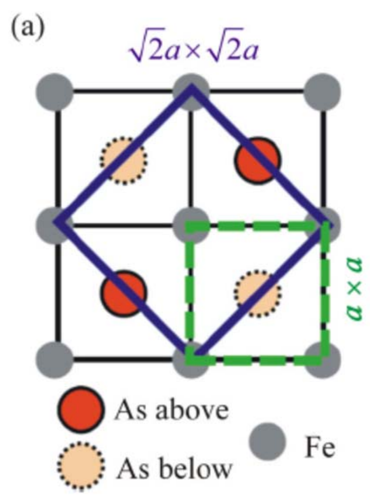


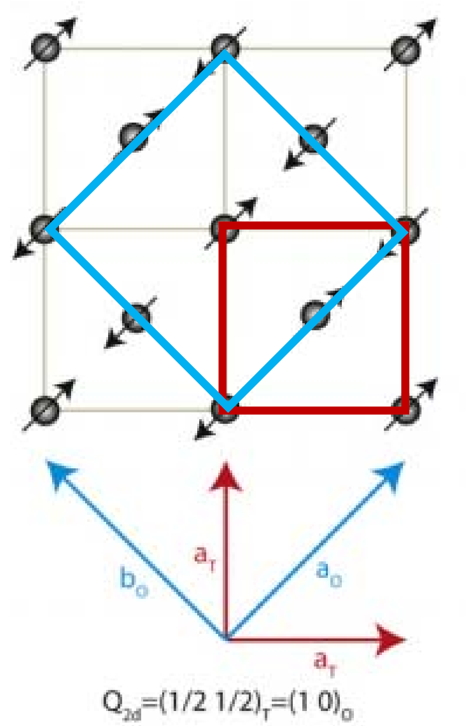
Katoch *et al. Nat. Phys.* **14**, 355 (2018)

Resources

- Lu, Vishik, *et al, Angle-resolved photoemission studies of quantum materials,* Ann. Rev. Cond. Matt. Phys., **3** 129 (2012)
- Hashimoto, Vishik, *et al, Energy gaps in high-transition-temperature cuprates superconductors,* Nat. Phys. **10** 483 (2014)
- Gedik and Vishik, *Photoemission of quantum materials,* Nat. Phys. **13** 1029 (2017)
- Contemporary Concepts of Condensed Matter Science, Volume 6, Pages 1-324 (2013) **Topological Insulators,** Chapters 1,2, 6 http://www.sciencedirect.com/science/bookseries/15720934/6/supp/C
- T.O. Wehling *et al.* "Dirac Materials" *Advances in Physics*, **63** p1-76 (2014) http://www.tandfonline.com/doi/abs/10.1080/00018732.2014.927109
- Cattelan and Fox, *A Perspective on the Application of Spatially Resolved ARPES for 2D Materials*, Nanomaterials, ***8***, 284 (2018)

Magnetism and structural phase transition in 122 materials





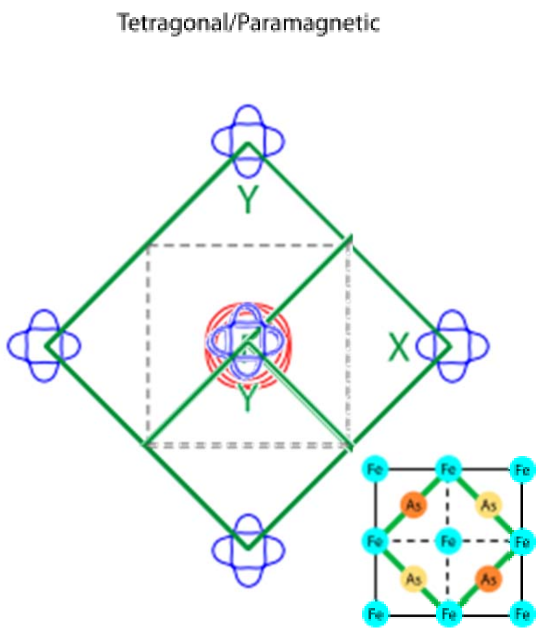
2 Fe tetragonal unit cell

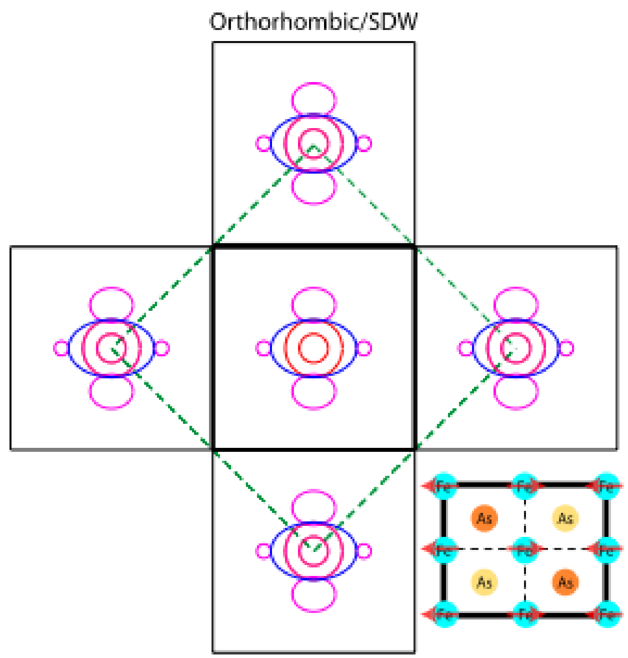
Magnetic order with orthorhombic unit cell

*Structural and magnetic ordering have same unit cell, but orthorhombic phase transition usually happens first

Lumsden *et al*, J. Phys.: Condens. Matter **22** 203203 (2010)

Expected FS reconstruction





Note broken 4-fold rotation symmetry!

Yi *et al.* PNAS **108** 6878 (2011)

Problem: twinning

$BaFe_2As_2$

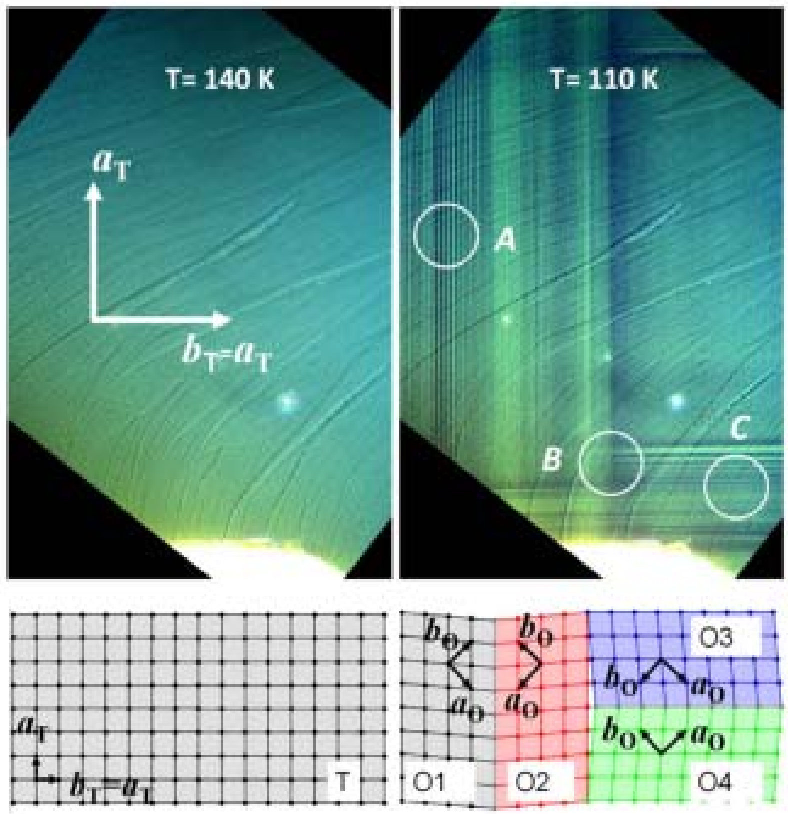
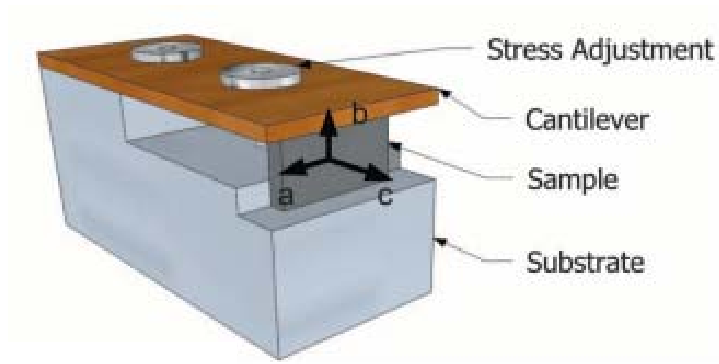


Image size is several hundred microns and characteristic domain size is 10-50 microns

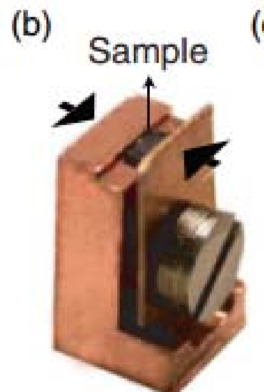
Tanatar *et al.* PRB **79**, 180508R (2009)

Mechanical de-twinning

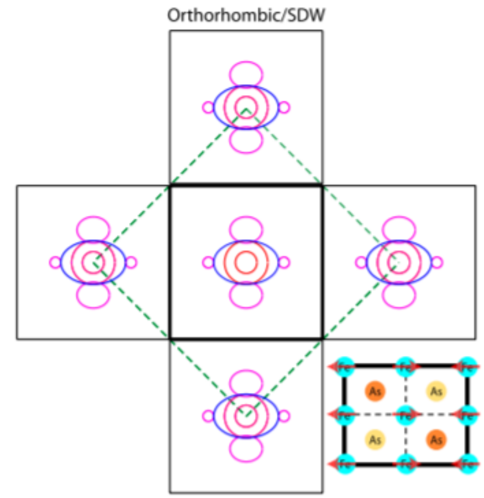
Material: $BaFe_2As_2$

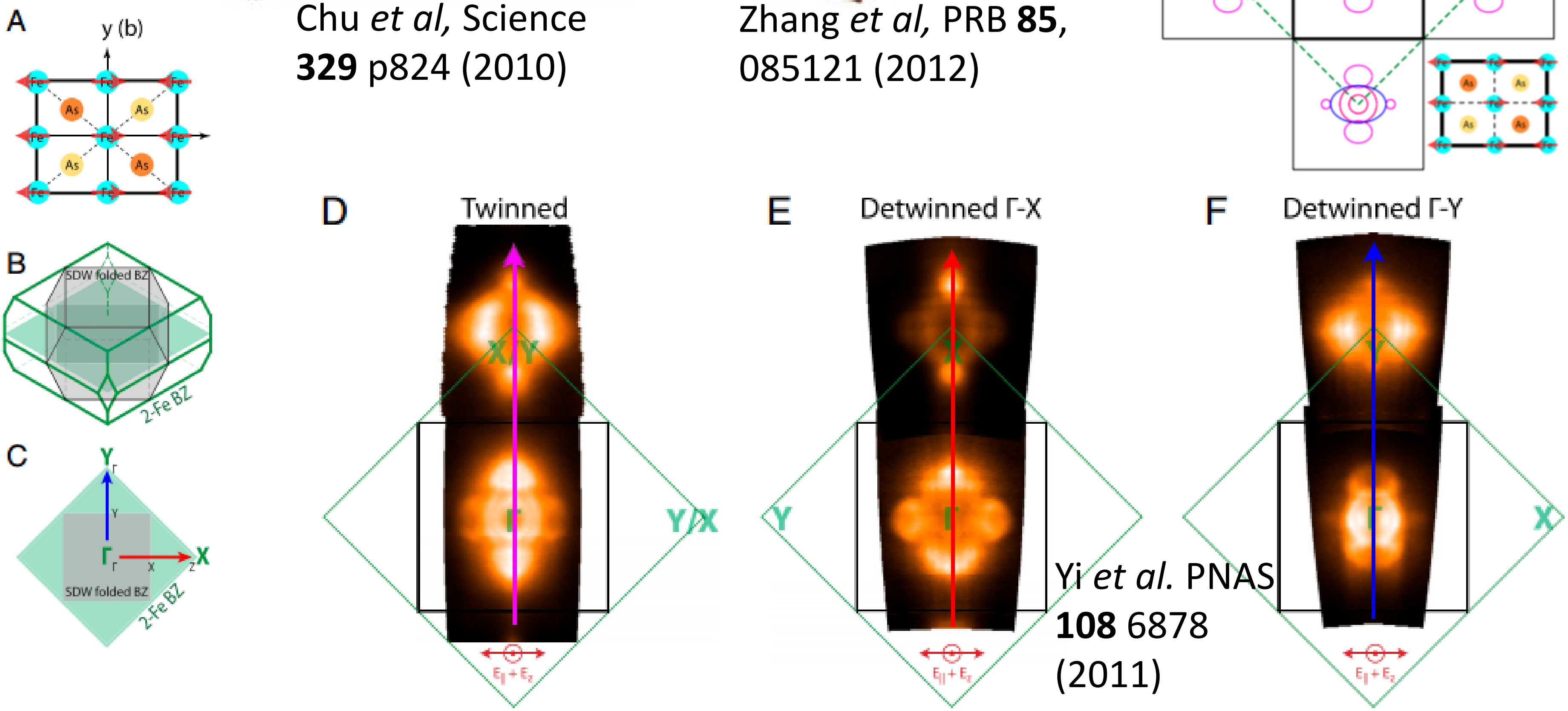


Chu *et al*, Science **329** p824 (2010)



Zhang *et al*, PRB **85**, 085121 (2012)



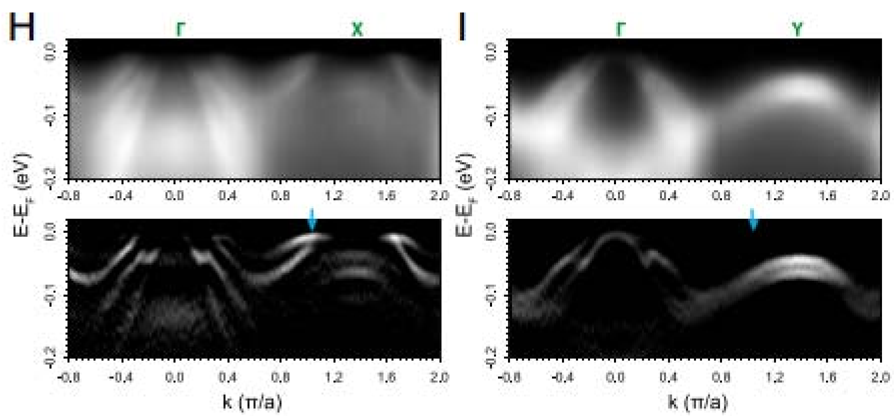


Yi *et al.* PNAS **108** 6878 (2011)

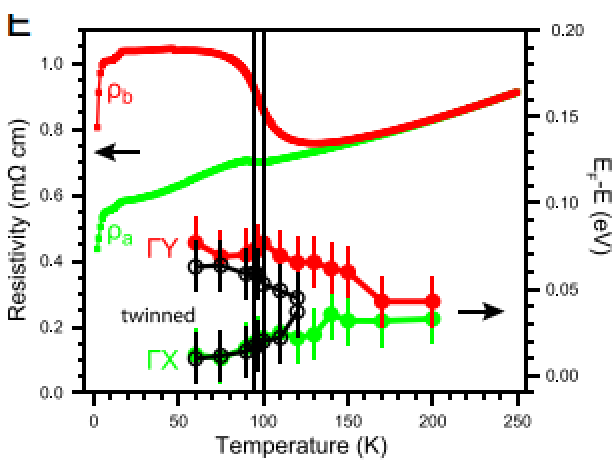
Signatures of band folding: extra bands

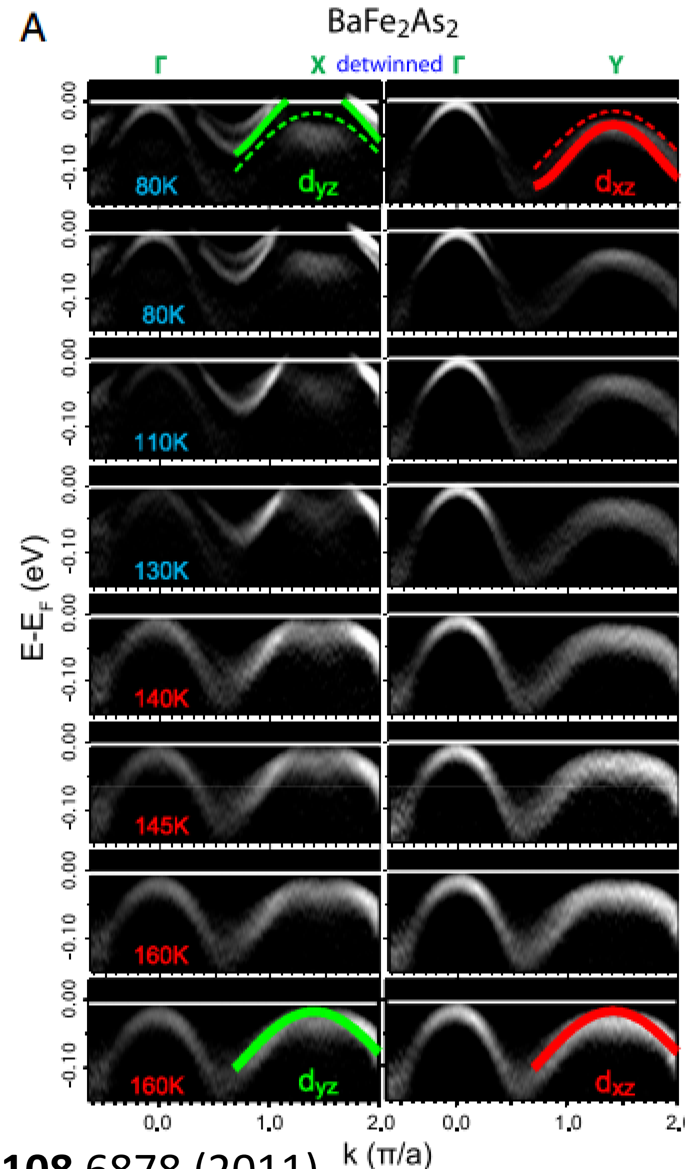
Material: $BaFe_2As_2$

Raw data



2nd derivative

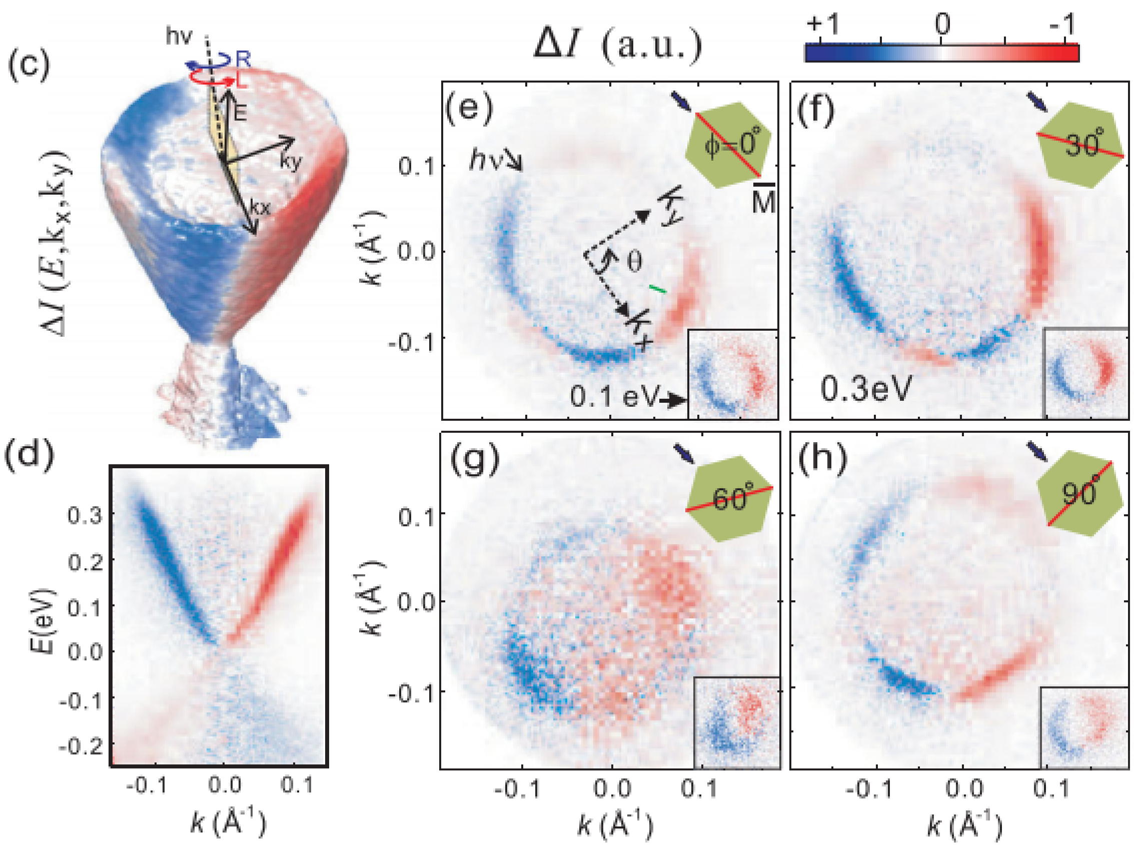




Yi *et al.* PNAS **108** 6878 (2011)

Spin texture via circular dichroism

1. Measure ARPES spectrum with left-circularly polarized (LCP) light
2. Measure ARPES spectrum with right-circularly polarized (RCP) light
3. $\Delta I(E, k_x, k_y) = I_{LCP} - I_{RCP}$



Wang *et al.* PRL **107**, 207602 (2011)