Visualizing Electronic Structures of Quantum Materials

– By Angle Resolved Photoemission Spectroscopy (ARPES)

PART A: ARPES & Application

Yulin Chen

Oxford University / Tsinghua University

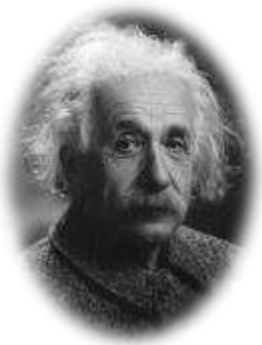
www.arpes.org.uk

Yulin.Chen@physics.ox.ac.uk ; yulinchen@mail.tsinghua.edu.cn

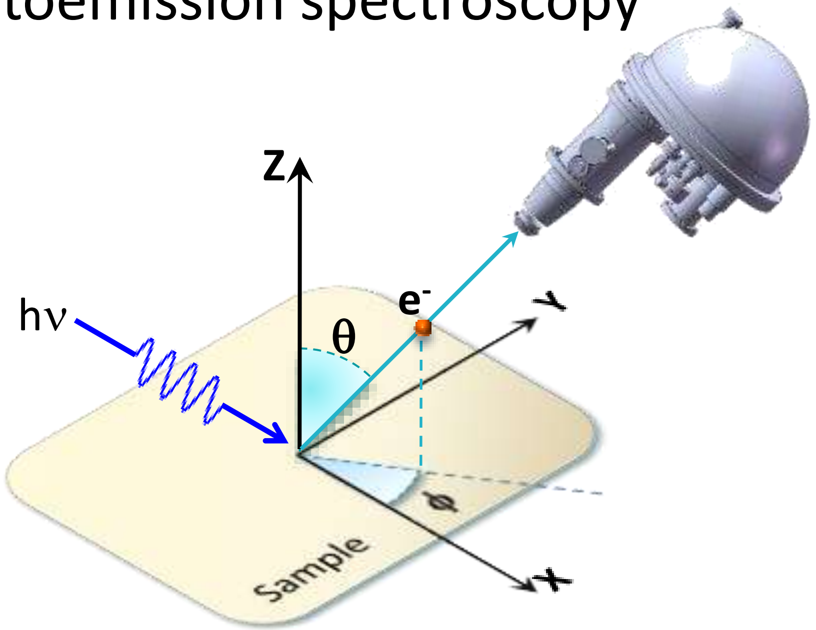
How to “see” band structures

Basic principle of angle resolved photoemission spectroscopy

Heinrich Hertz



Albert Einstein



ARPES:
k-space Microscope

Energy Conservation

$$E_B = h\nu - E_{kin} - \Phi$$

Momentum Conservation

$$K_{\|} = k_{\|} + G_{\|}$$

Synchrotron Radiation

Synchrotrons around the world

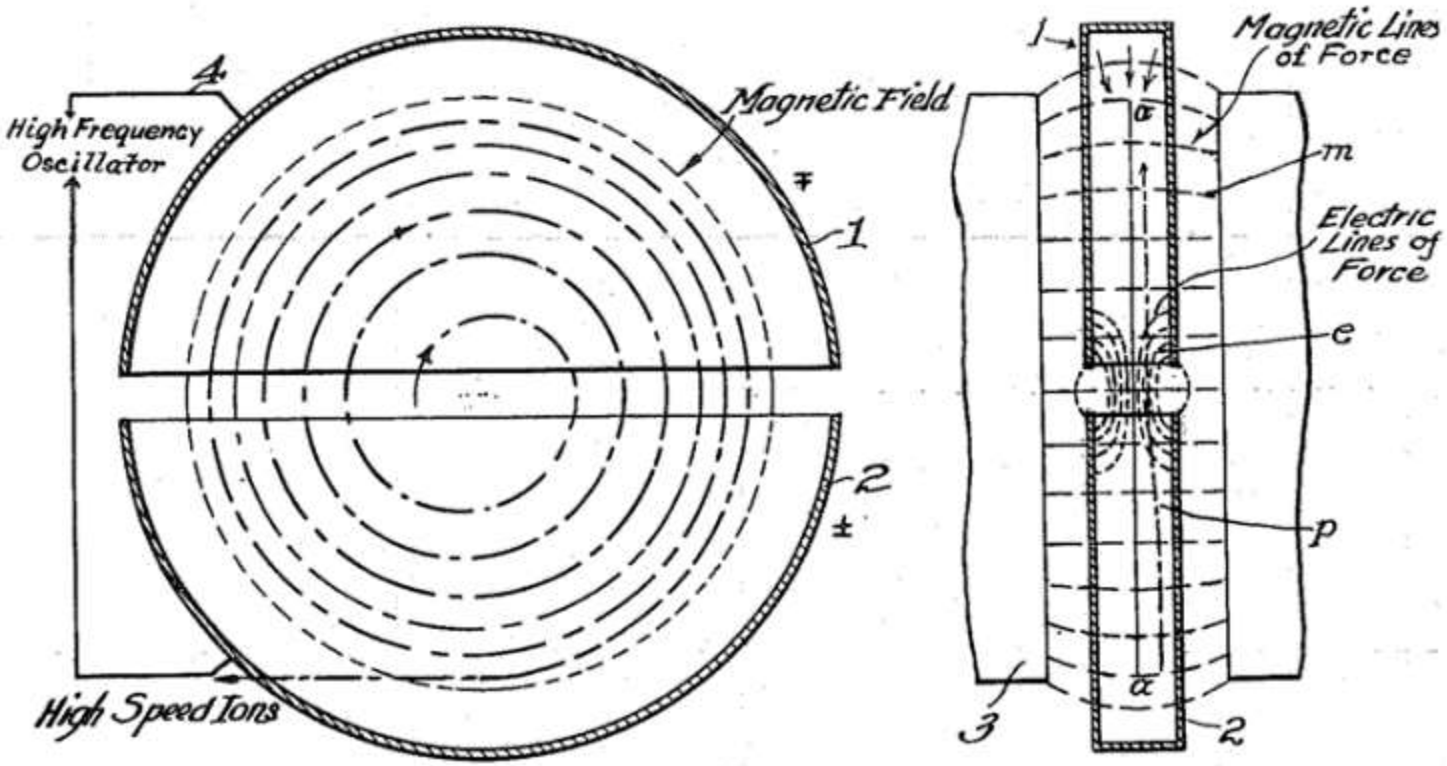
Synchrotron Radiation

Advantages

- ✓ **Broad Spectrum** (from microwaves to hard X-rays): the users can select the wavelength required for their experiment.
- ✓ **High Flux**: high intensity photon beam allows rapid experiments or use of weakly scattering crystals.
- ✓ **High Brilliance**: highly collimated photon beam generated by a small divergence and small size source (spatial coherence)
- ✓ **High Stability**: submicron source stability
- ✓ **Polarization**: both linear and circular
- ✓ **Pulsed Time Structure**: pulsed length down to tens of picoseconds allows the resolution of process on the same time scale.

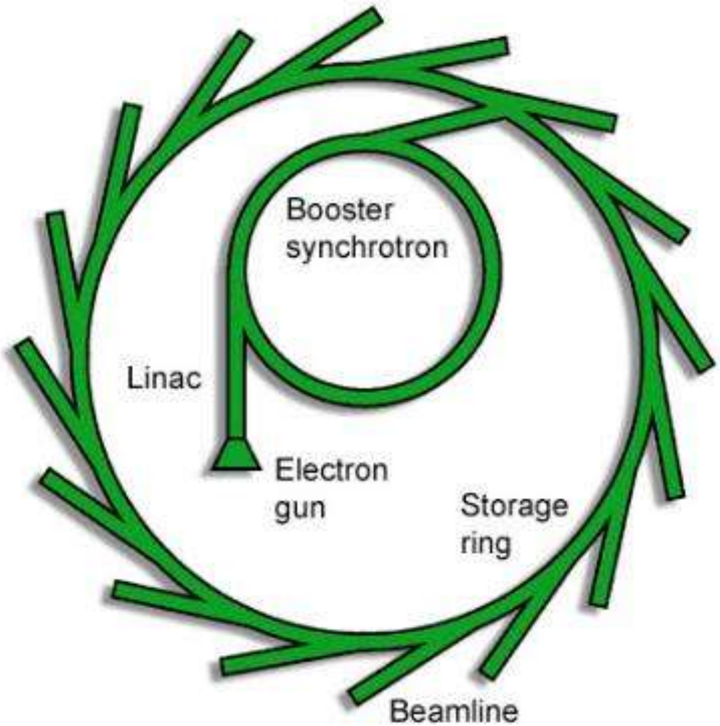
Synchrotron Radiation

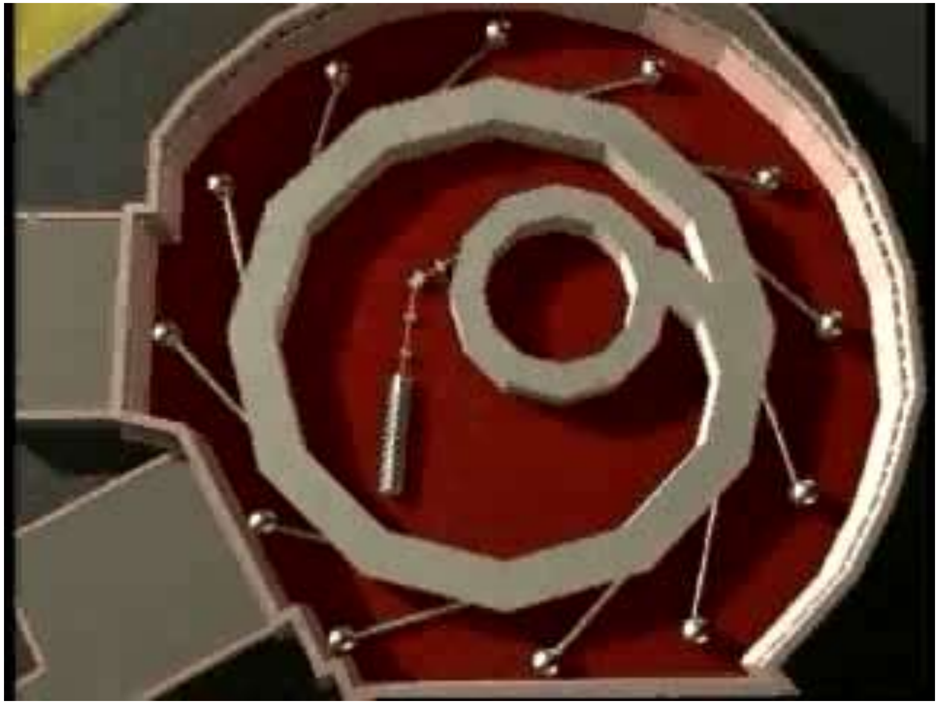
Developments of the Cyclotron



Synchrotron Radiation

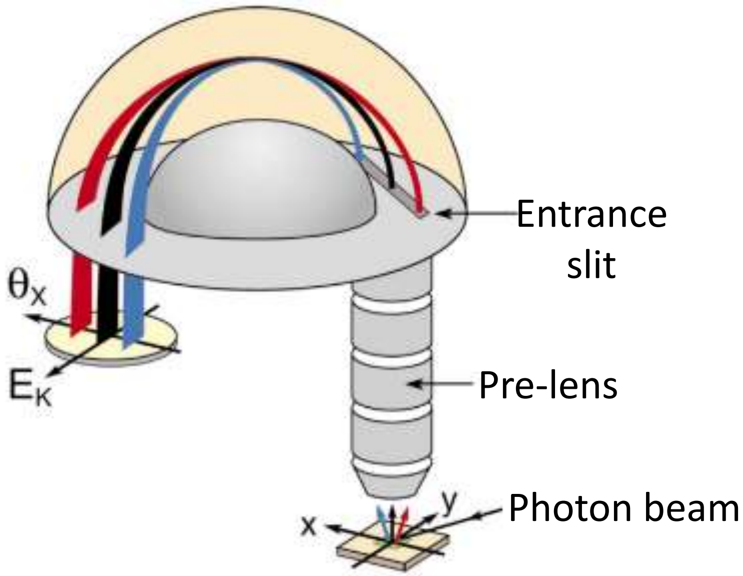
Cartoon

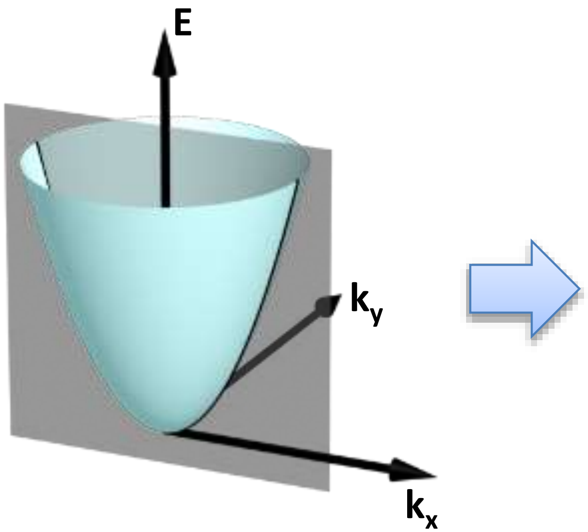


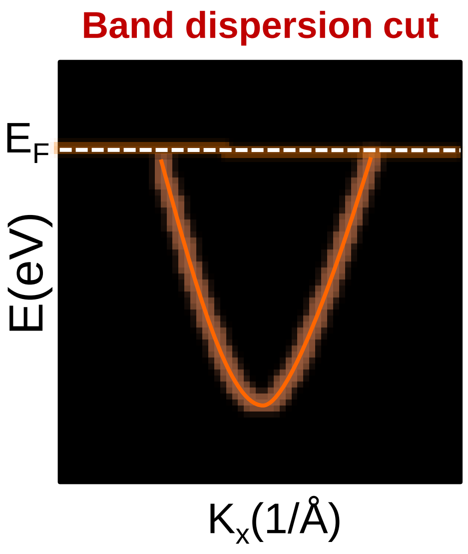


ARPES system

SDA Electron Analyzers

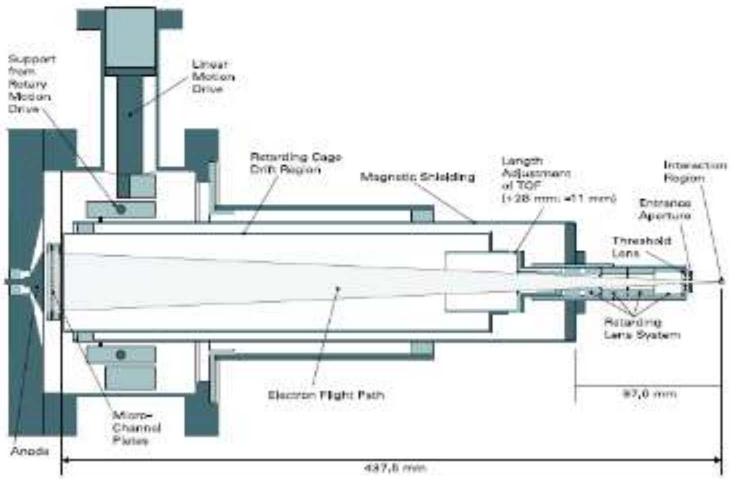


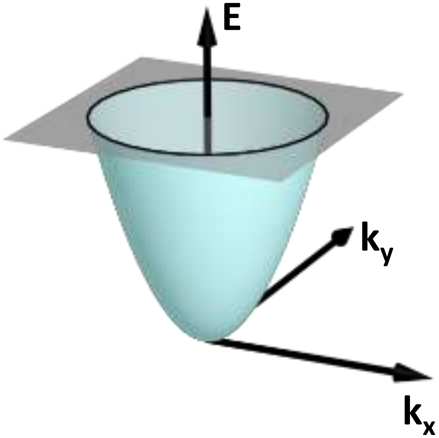


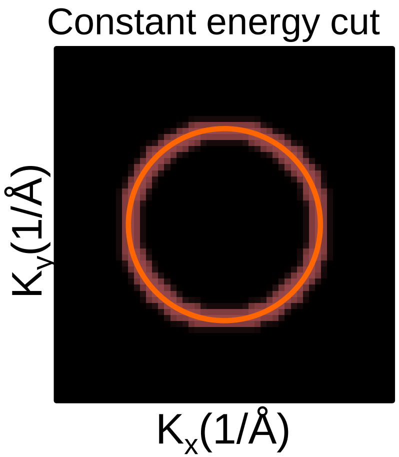


ARPES system

TOF electron Analyzers

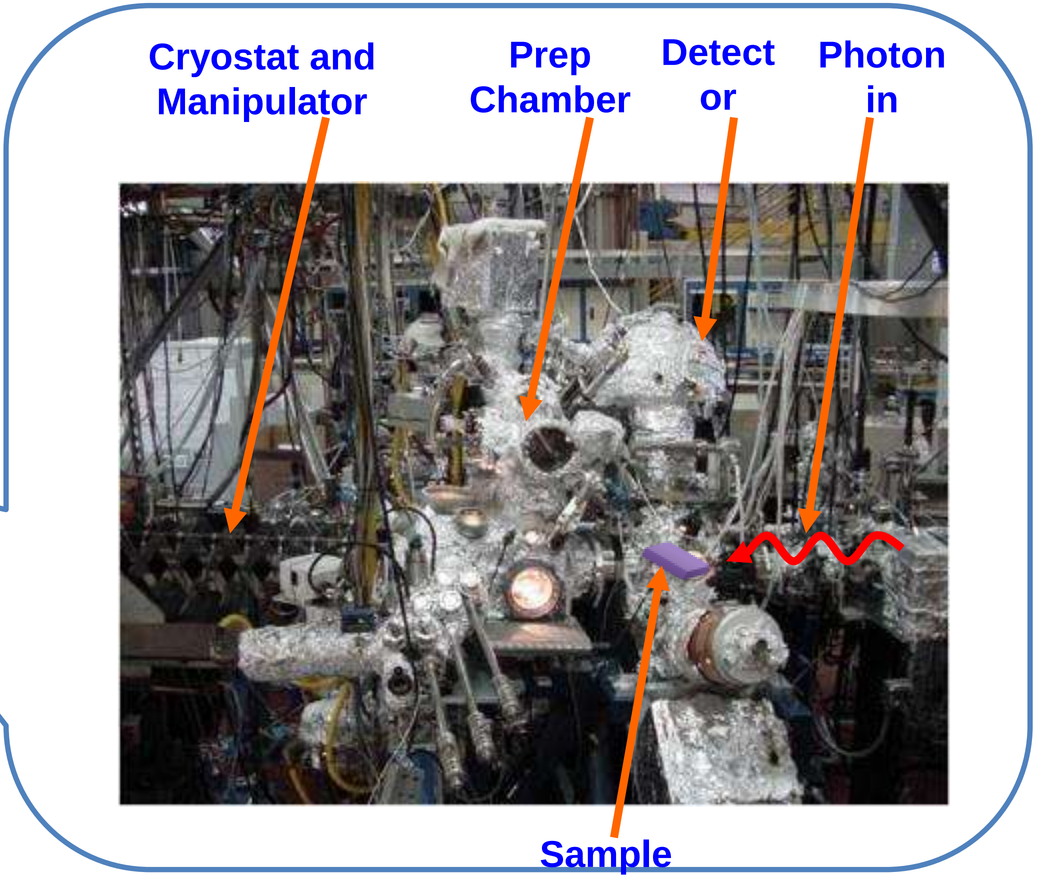






ARPES system

HERS endstation at ALS



Modern ARPES data taking

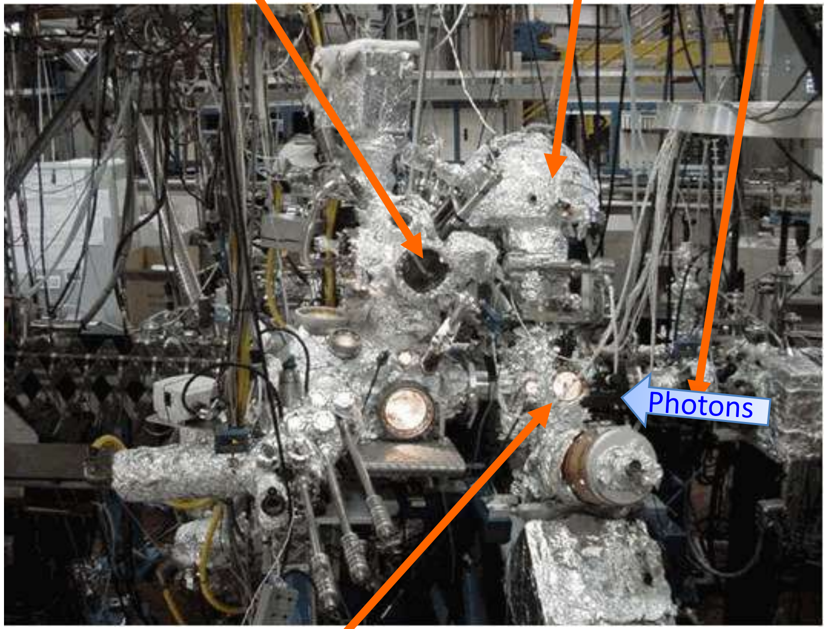
Experimental setup

Data acquired

Experiment Chamber

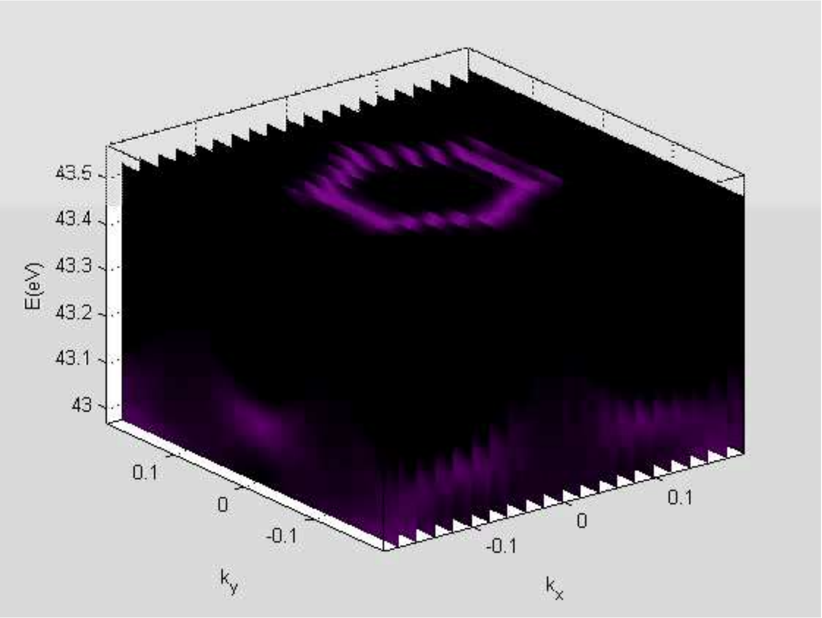
2D Electron analyzer

Photon in



ALS Bemline 10

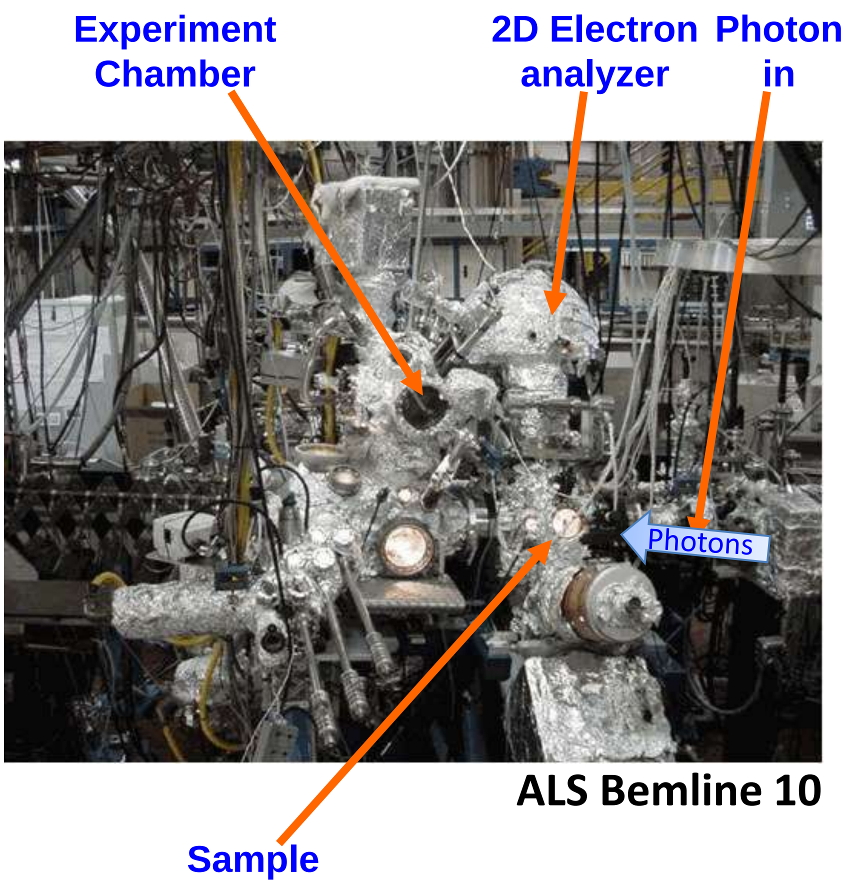
Sample



Modern ARPES data taking

Experimental setup

Data acquired



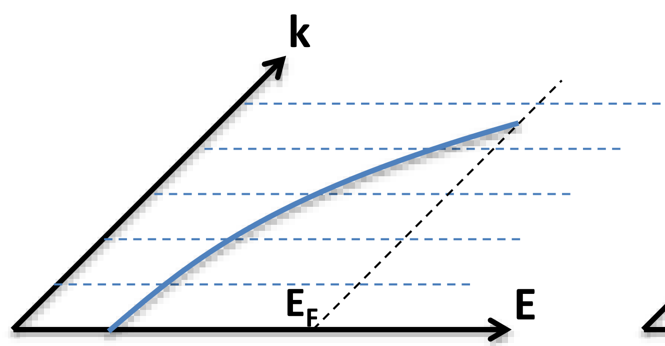
ALS Bemline 10

Some of our works on TQMs

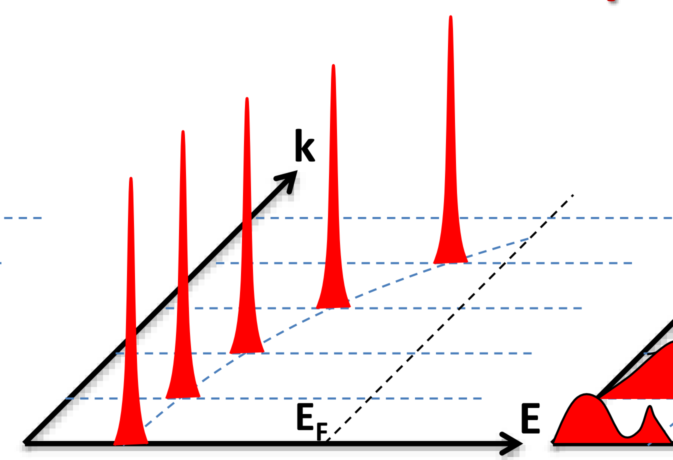
General principle

Electron band

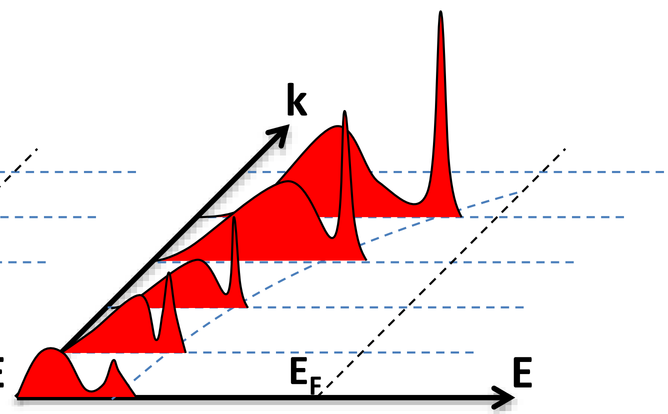
ARPES Spectra



Band dispersion



Non-interacting system



Interacting system

$$I_{PES} \propto F_{(T)} \cdot \delta_{(Ef-Ei-\hbar\omega)} \cdot |\langle \boldsymbol{\psi}_{f,N} | \boldsymbol{H}_{int} | \boldsymbol{\psi}_{i,N} \rangle|^2 \;+$$

$$|\psi_{i,N}\rangle = |\phi_{i,k}\rangle \, |\psi_i{}^k{}_{(N-1)}\rangle$$

$$|\psi_{f,N}\rangle = |\phi_{f,Ek}\rangle |\psi_f{}^k{}_{(N-1)}\rangle$$

Remaining N-1 Electron state

One electron state

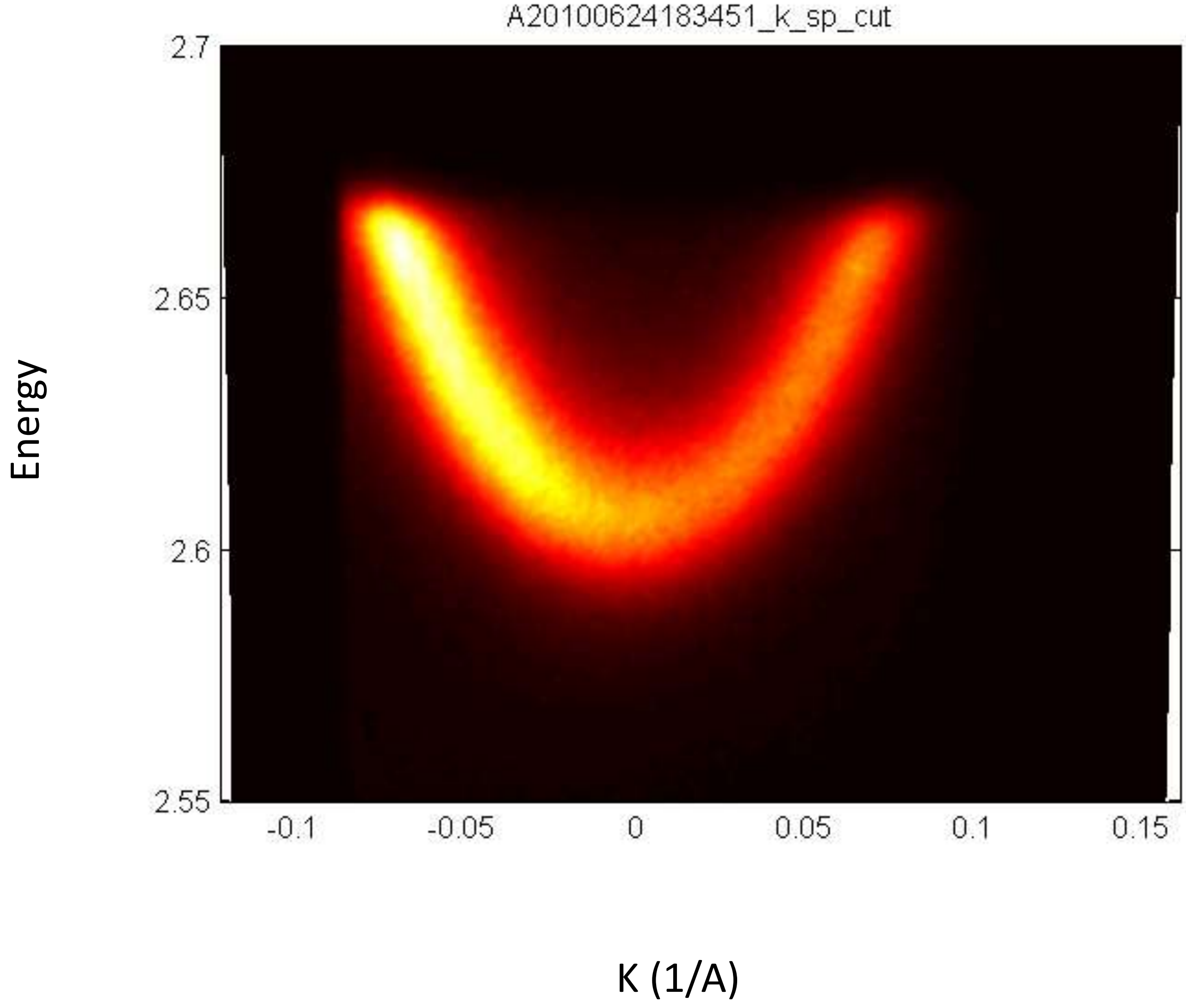
$$= F_{(T)} \cdot \delta_{(Ef-Ei-\hbar\omega)} \cdot |\langle \boldsymbol{\phi}_{f,E_k} | \boldsymbol{H}_{int} | \boldsymbol{\phi}_{i,k} \rangle \langle \boldsymbol{\psi}_f{}^k{}_{(N-1)} | \boldsymbol{\psi}_i{}^k{}_{(N-1)} \rangle|^2 \;+$$

(Suddent approximation)

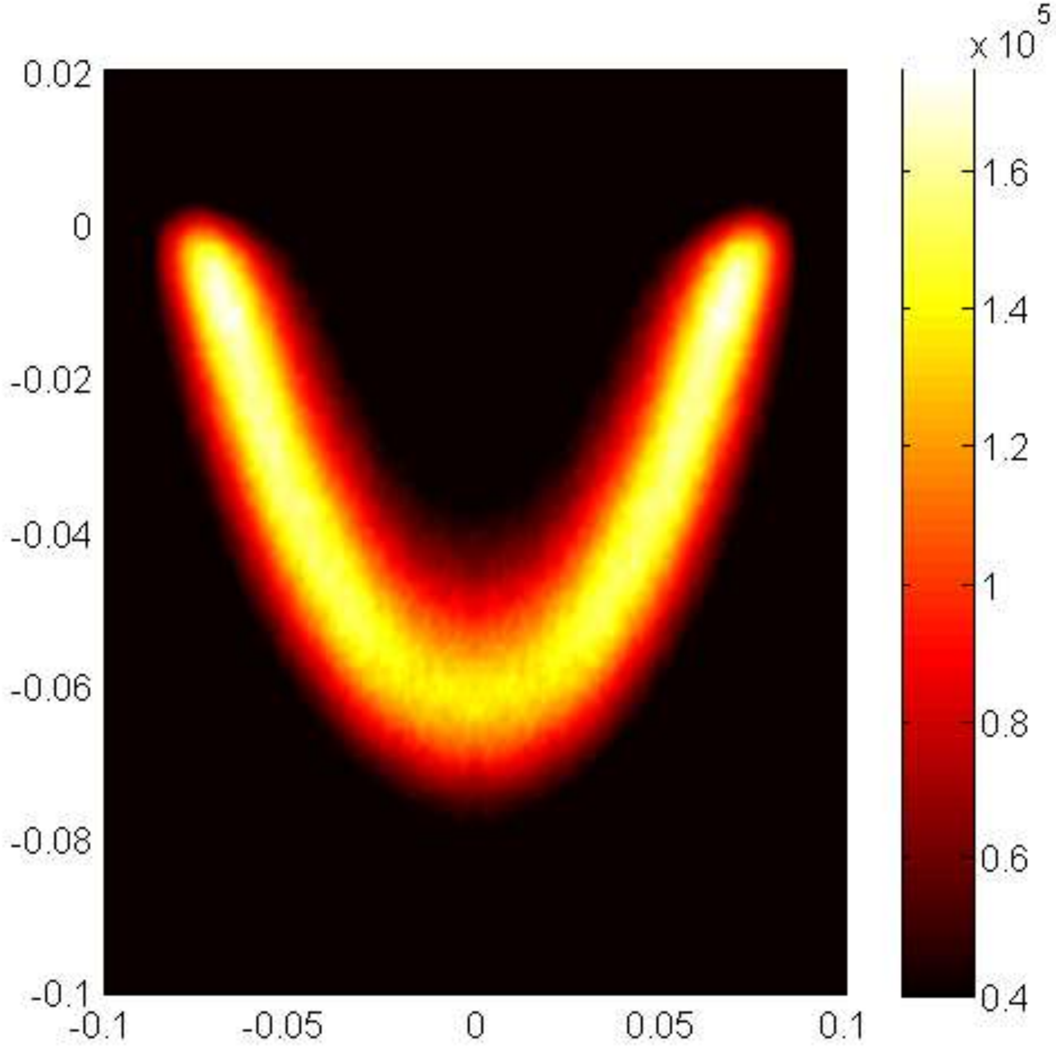
$$= \begin{cases} F_{(T)} \cdot \delta_{(Ef-Ei-\hbar\omega)} \cdot |\langle \boldsymbol{\phi}_{f,E_k} | \boldsymbol{H}_{int} | \boldsymbol{\phi}_{i,k} \rangle|^2 \\ F_{(T)} \cdot |\langle \boldsymbol{\phi}_{f,Ek} | \boldsymbol{H}_{int} | \boldsymbol{\phi}_{i,k} \rangle|^2 \sum_S \langle \boldsymbol{\psi}_f{}^k{}_{S(N-1)} | \boldsymbol{\psi}_i{}^k{}_{(N-1)} \rangle|^2 \, \delta_{(E_{f,Ek}+E_{S(N-1)}-Ei-\hbar\omega)} \end{cases}$$

(Non-interacting system)

ARPES observation

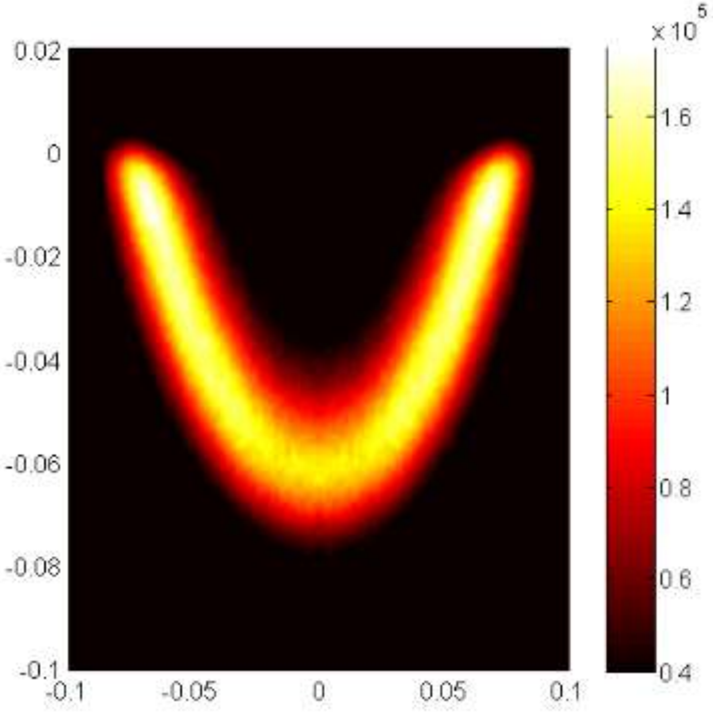


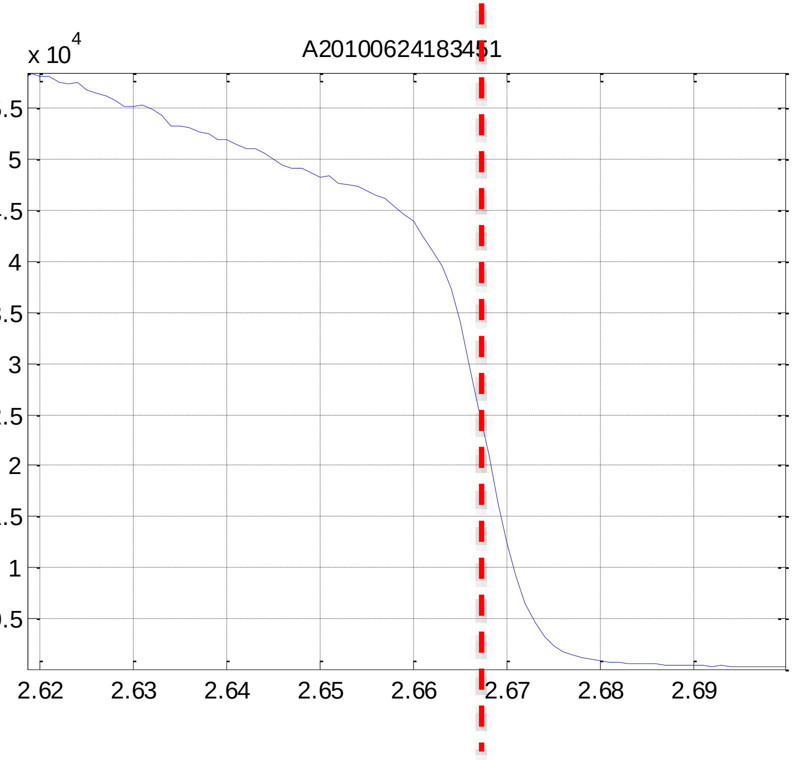
ARPES observation



ARPES observation

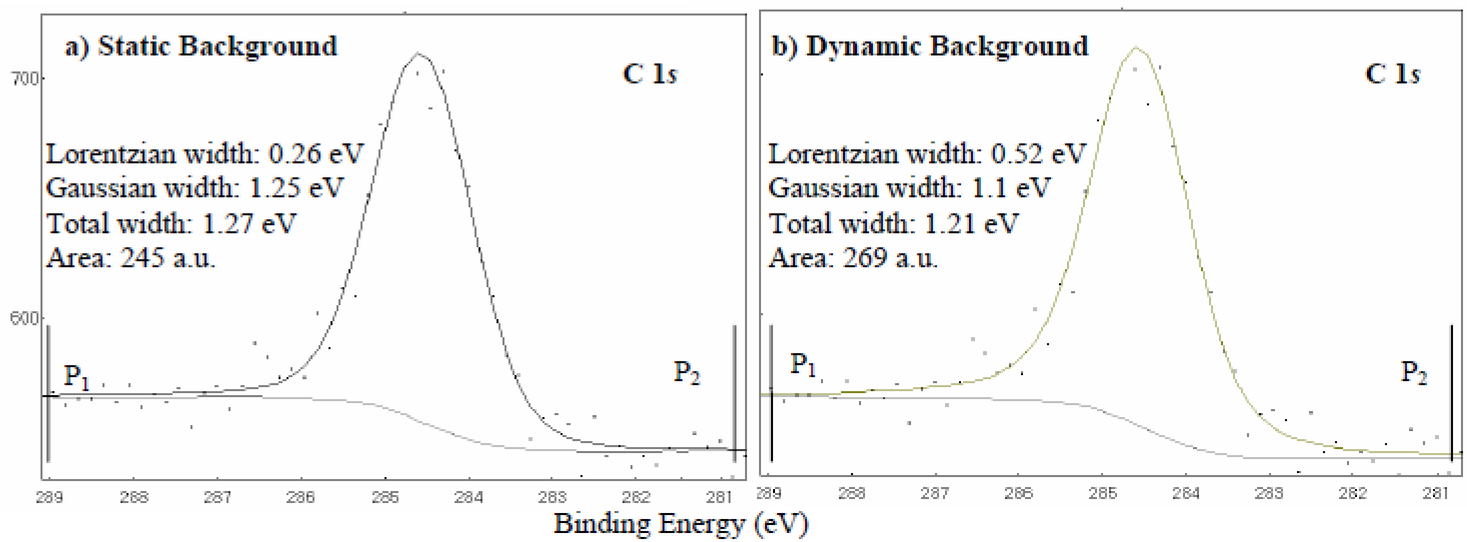
E_F location





ARPES observation

Background subtraction



$$B_1(E) = k_1 \int_E^{E_{\text{right}}} dE' \left[I(E') - I_{\text{right}} \right],$$

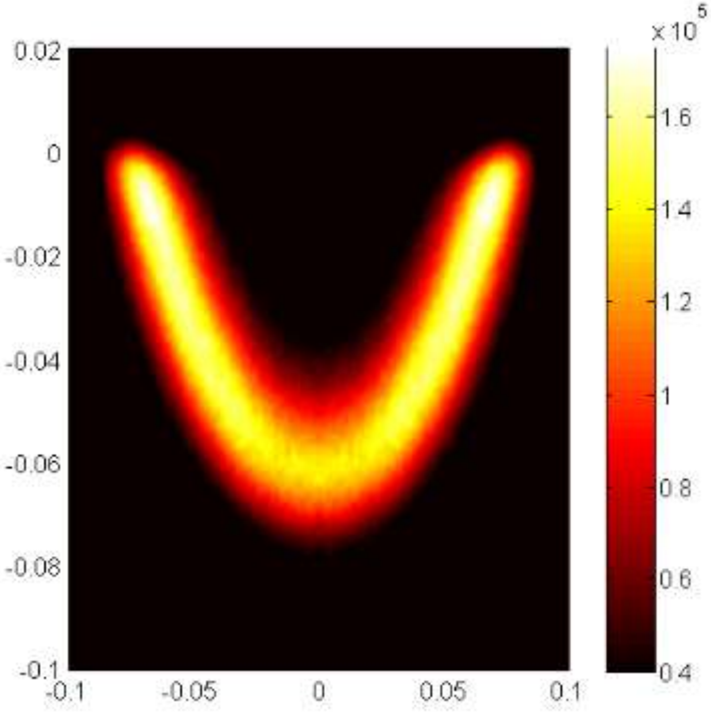
$$B_2(E) = k_2 \int_E^{E_{\text{right}}} dE' \left[I(E') - I_{\text{right}} - B_1(E') \right],$$

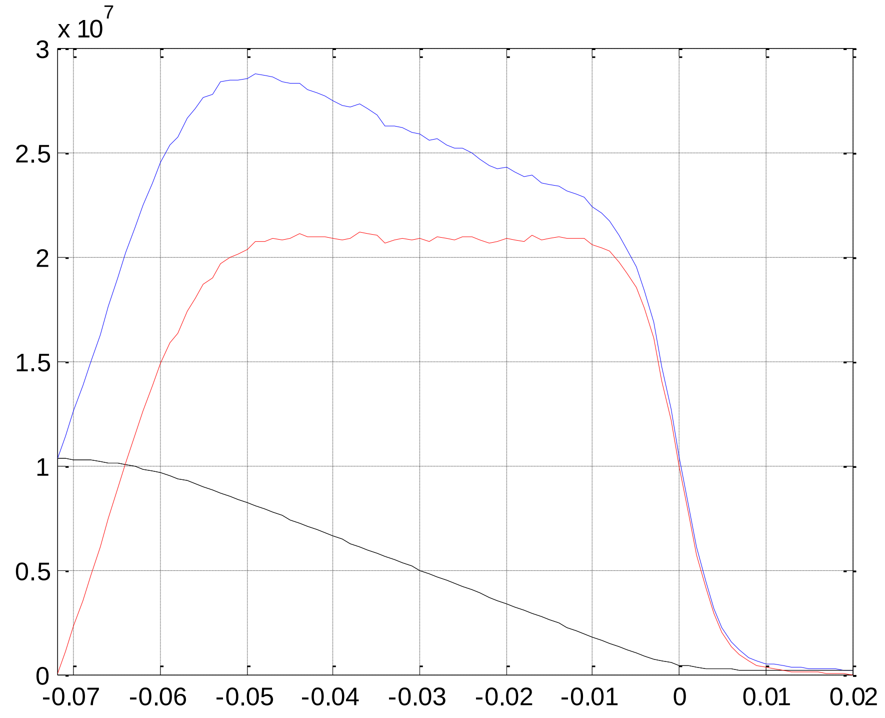
$$\ldots$$

$$B_n(E) = k_n \int_E^{E_{\text{right}}} dE' \left[I(E') - I_{\text{right}} - B_{n-1}(E') \right],$$

ARPES observation

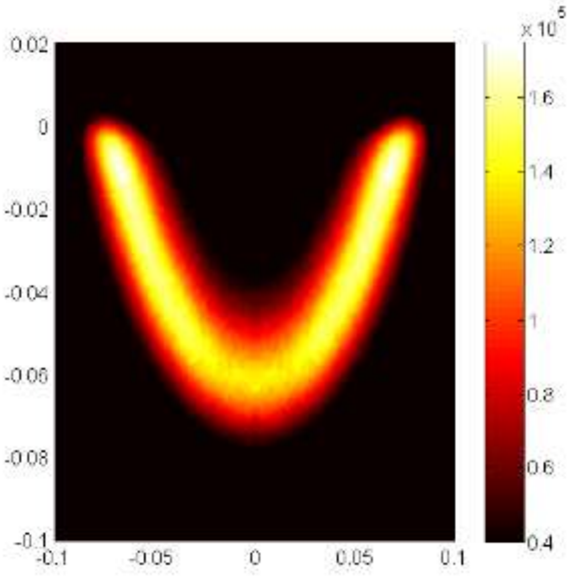
Background subtraction

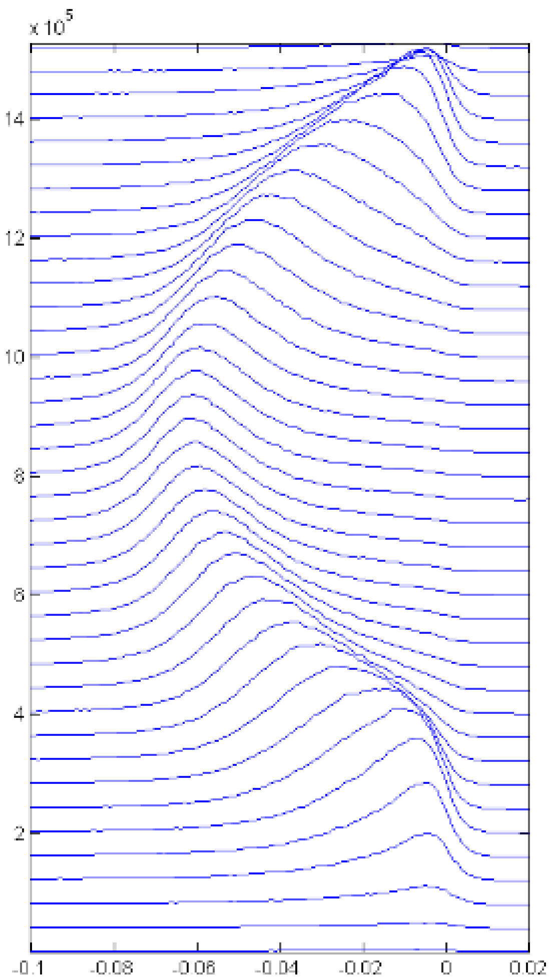




ARPES observation

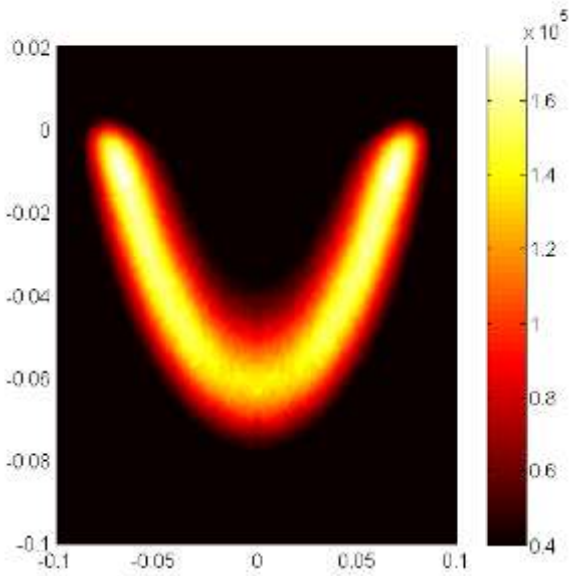
Energy distribution curves

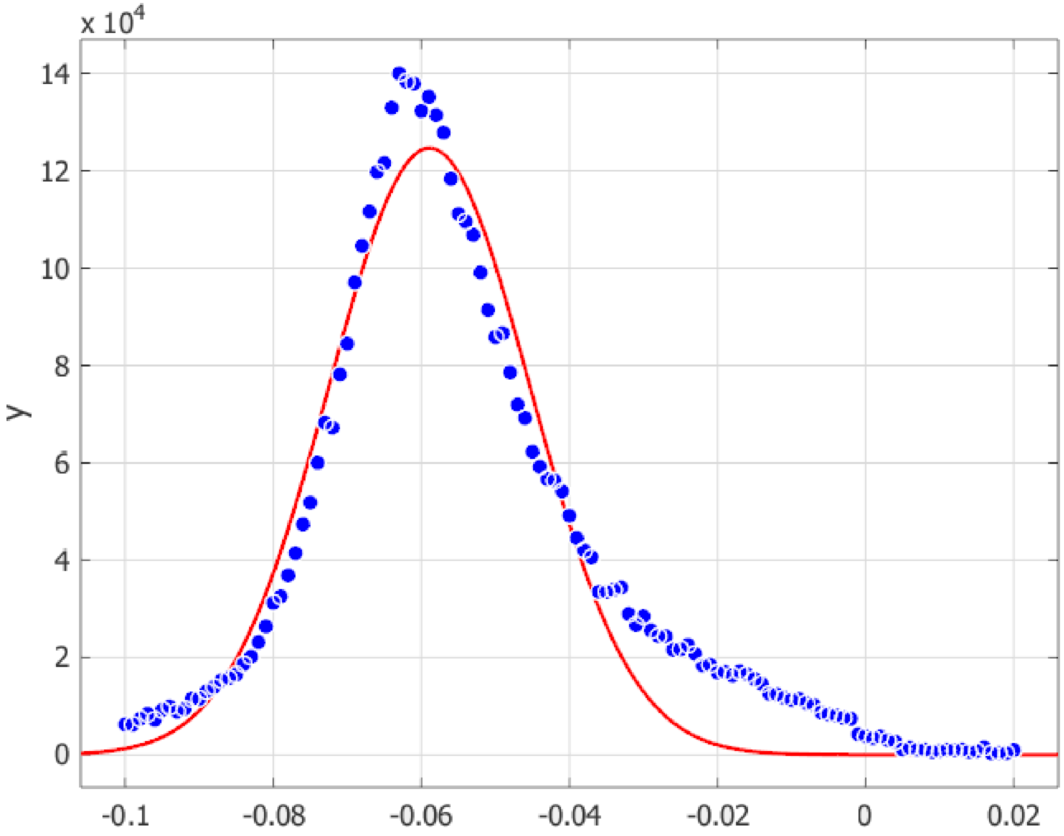




ARPES observation

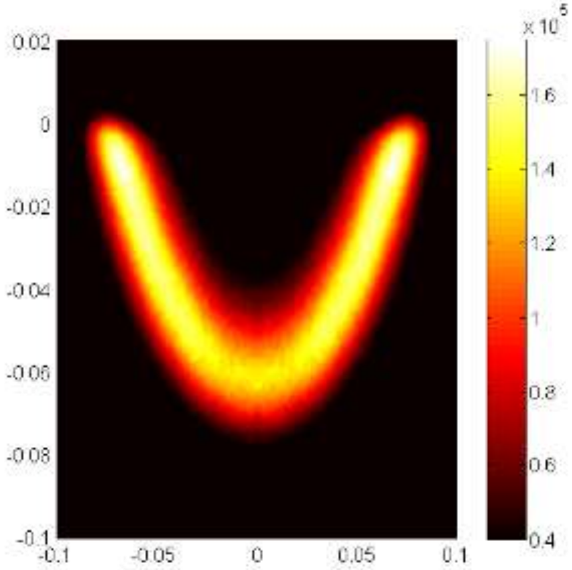
Energy distribution curves

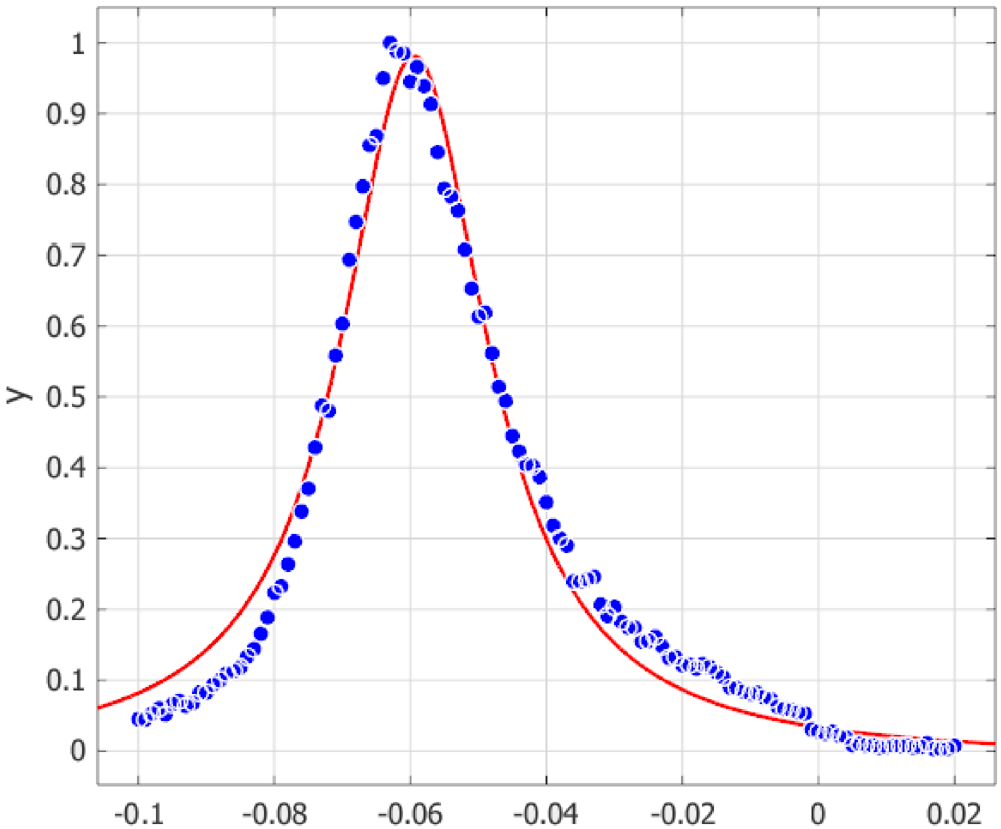




ARPES observation

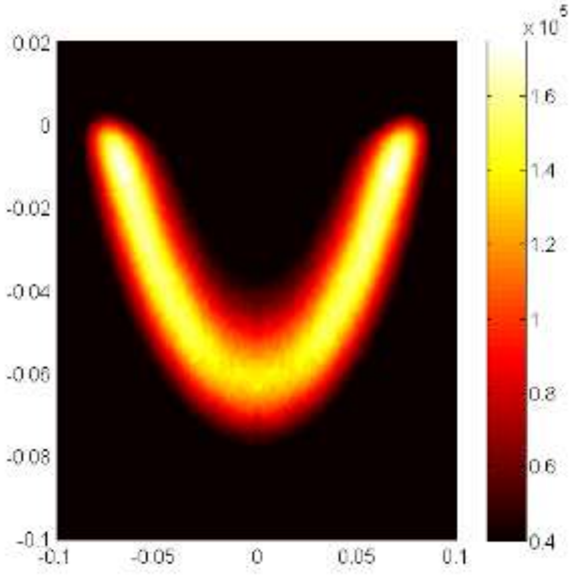
Energy distribution curves

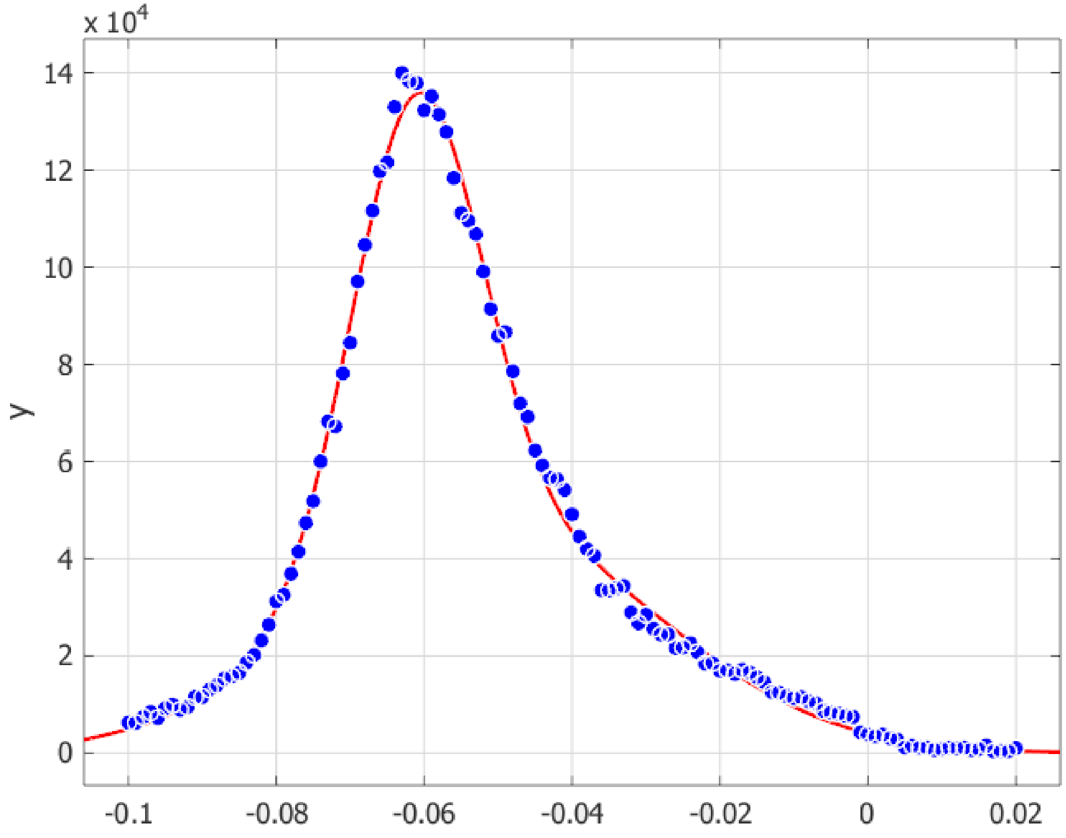




ARPES observation

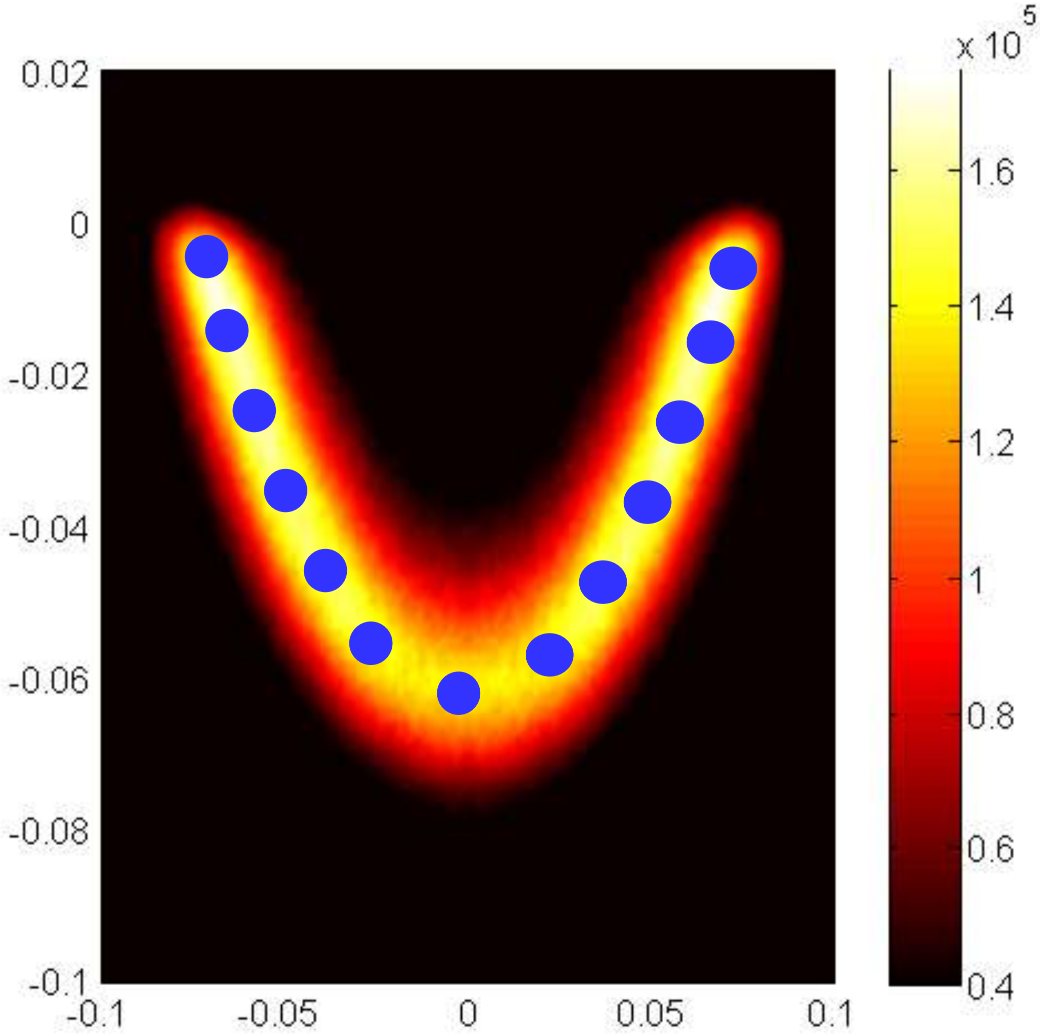
Energy distribution curves





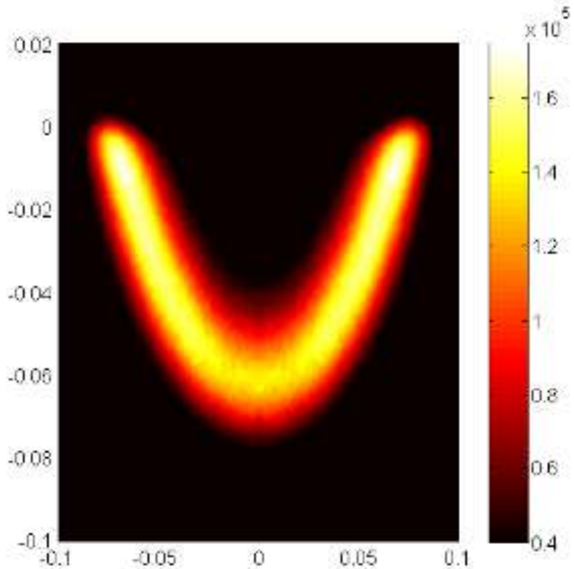
Line shape analysis

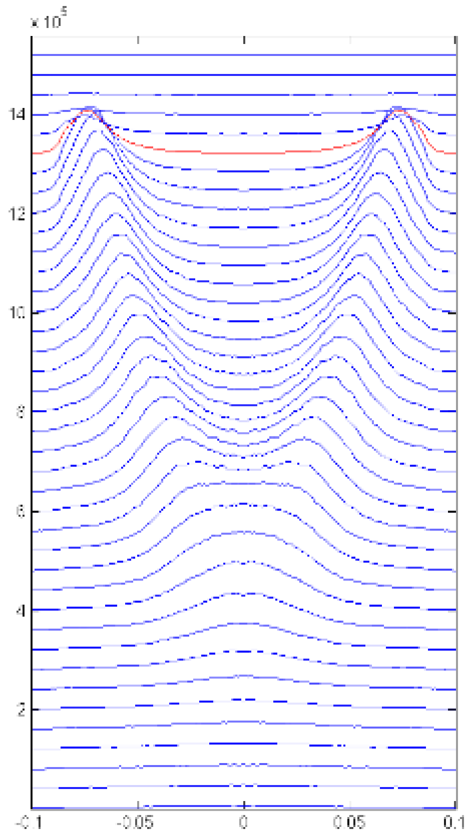
EDC

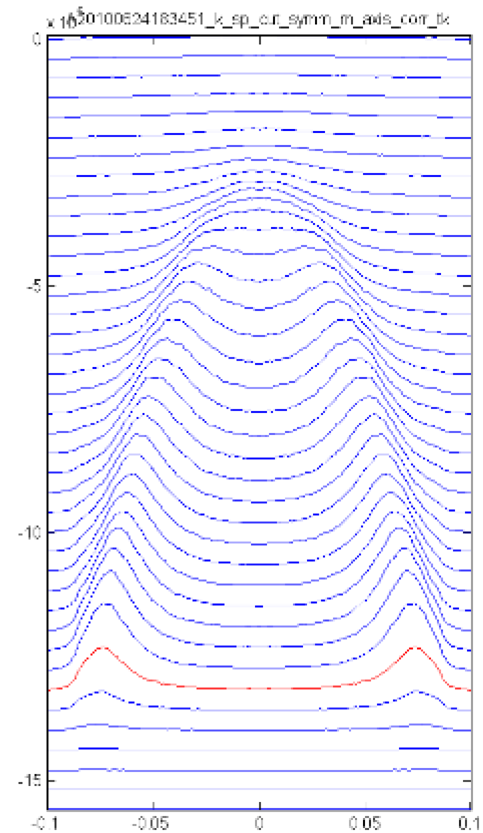


ARPES observation

Momentum distribution curves

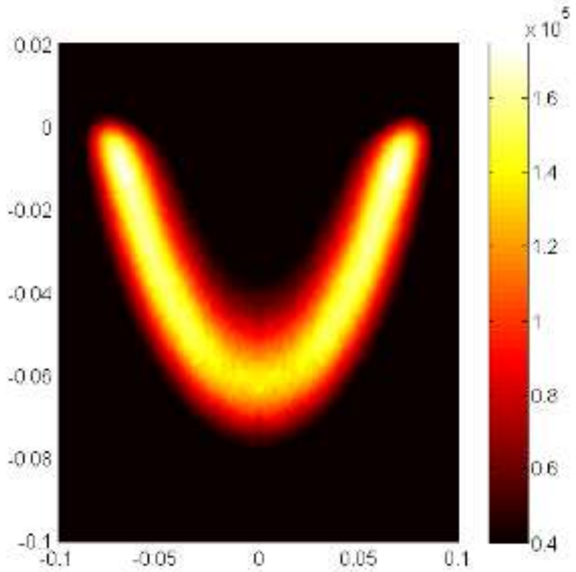


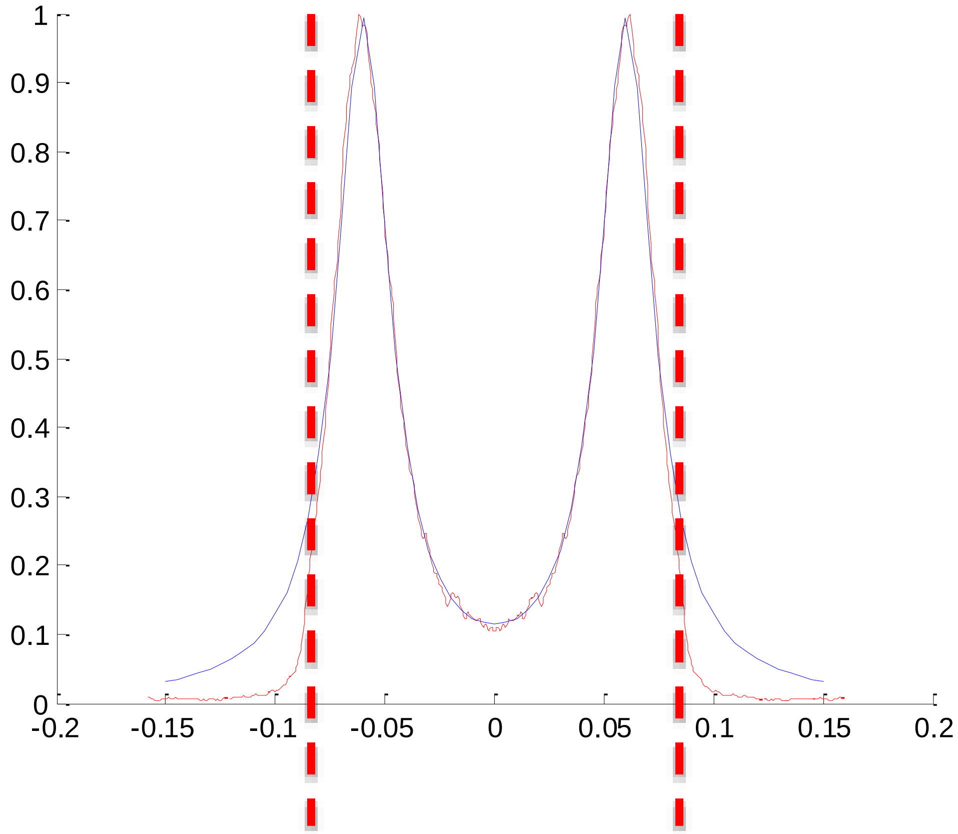




ARPES observation

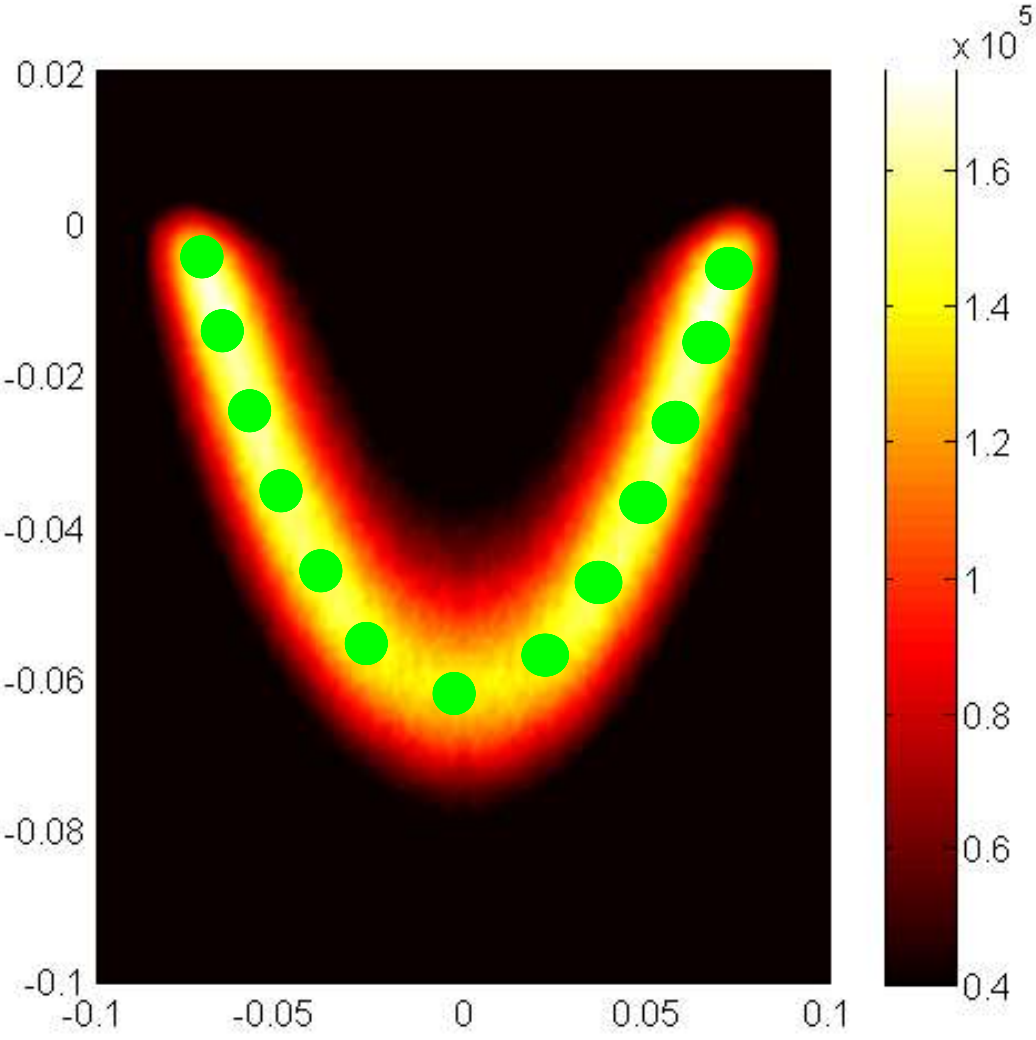
Momentum distribution curves





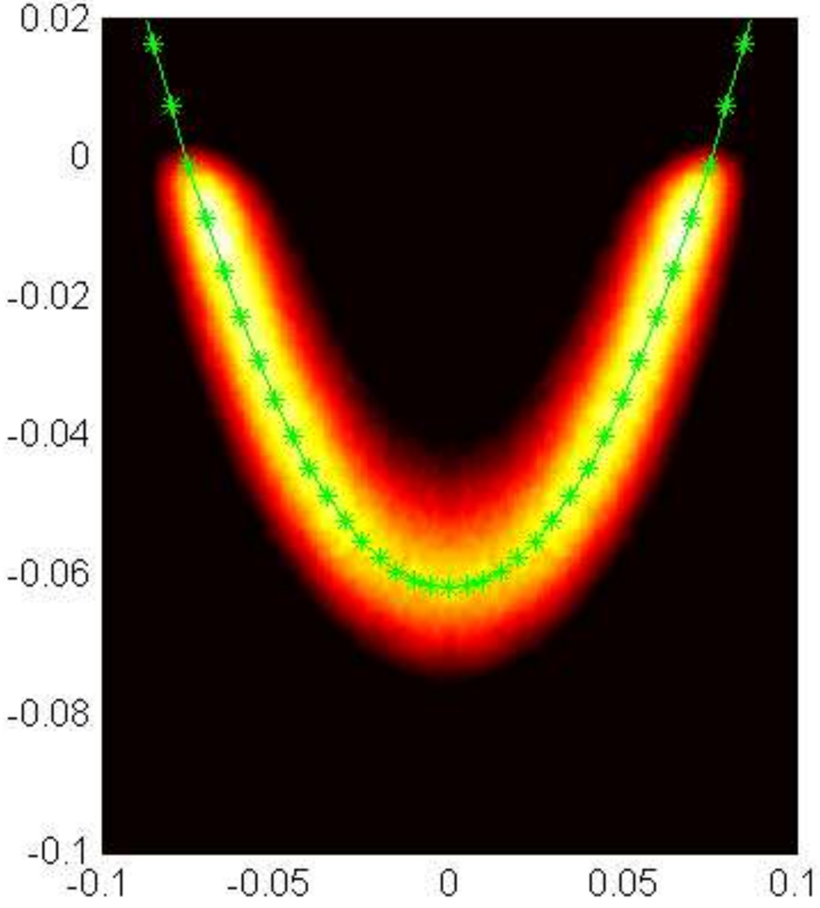
Line shape analysis

EDC



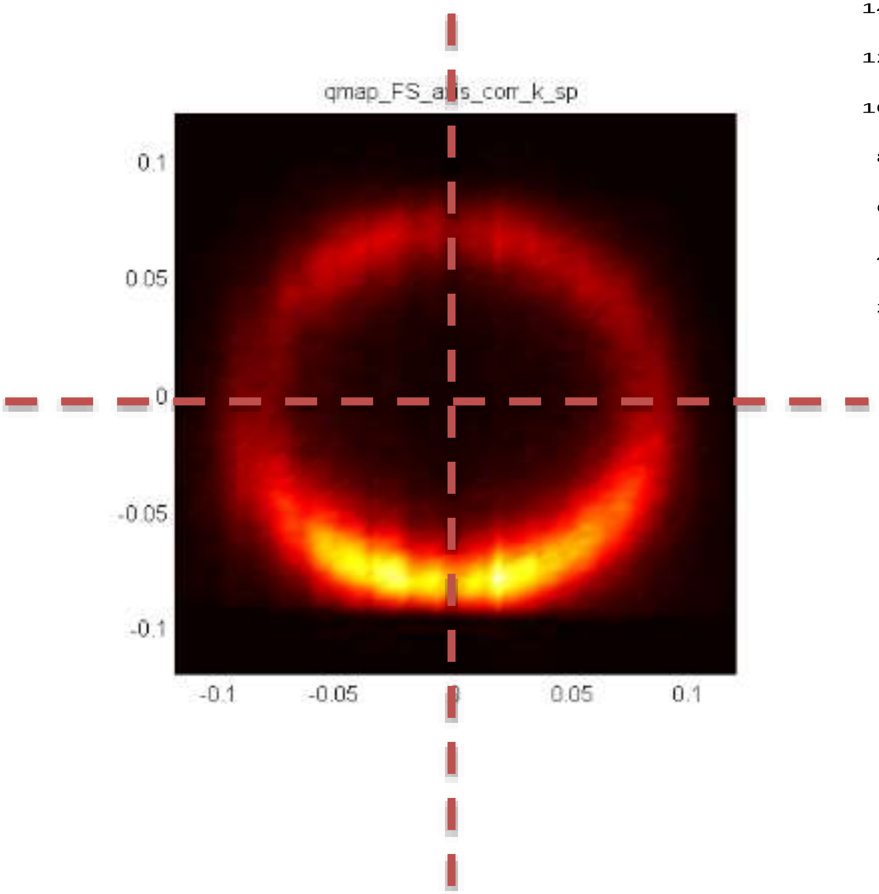
Line shape analysis

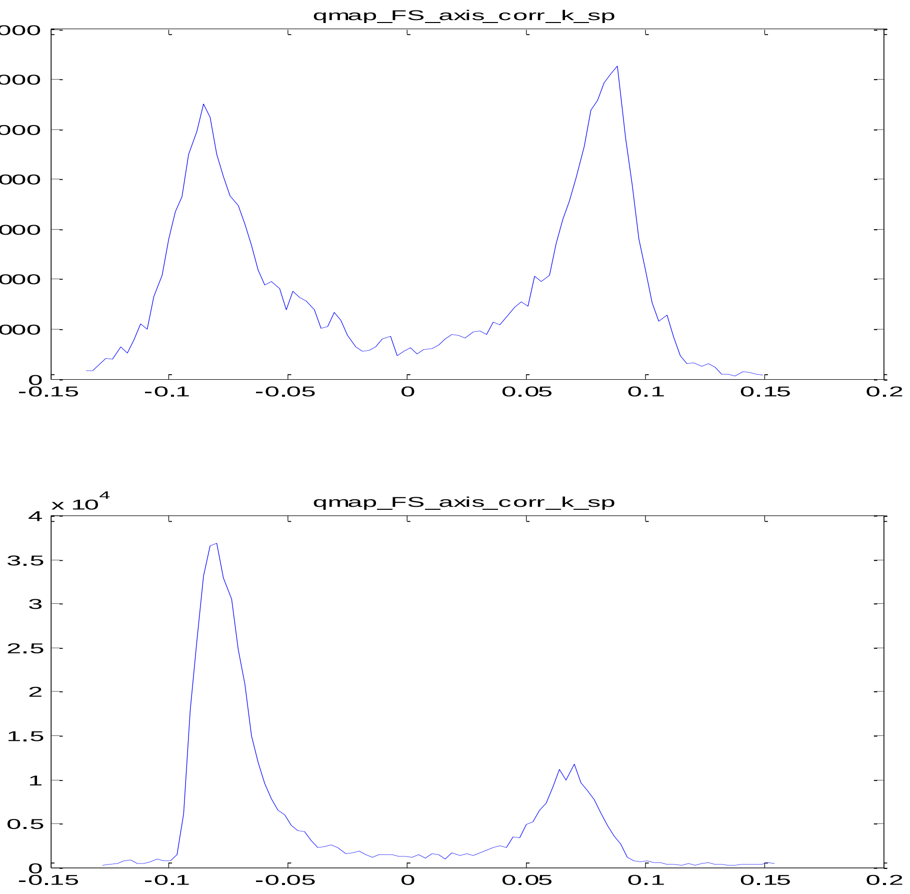
Difference EDC & MDC ?



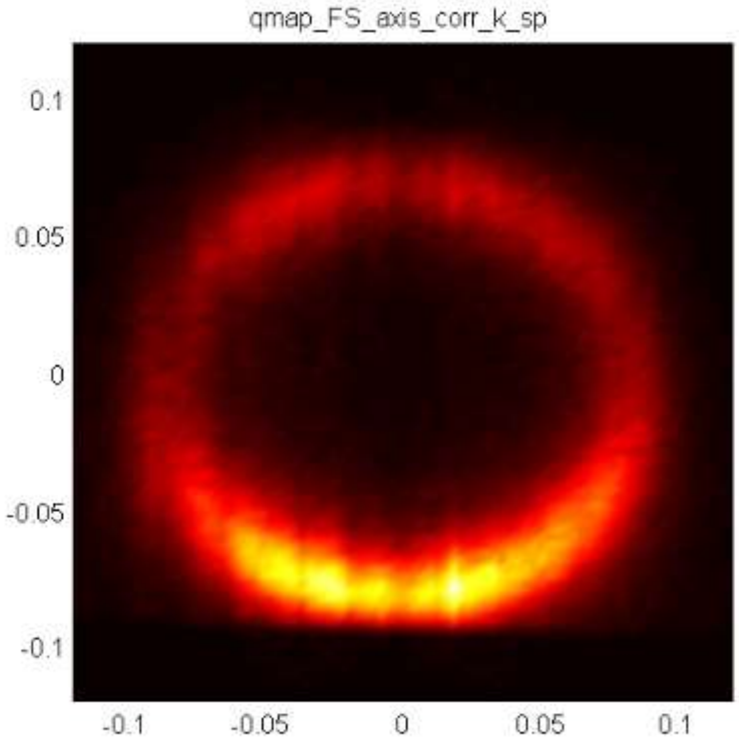
m_e=0.35m_0

Line shape analysis





Line shape analysis



Carrier density
~$4X10^{12}/cm^2$

Application of ARPES to Topological quantum materials

Classification of matter

Time

Topological insulators
Topological order

2005

Quantum Hall system
Topological order

1980

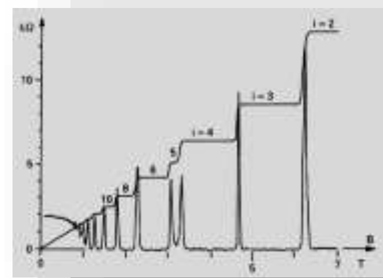
Regular matter:
Spontaneously
Broken symmetry

Topological insulator

Topological invariant:
"**Z_2 number**"

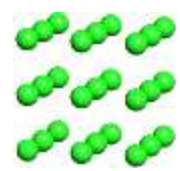
Klaus Von Klitzing

Integer quantum Hall effect



Topological invariant:
"**Chern number**"

Lev Landau



Translational symmetry

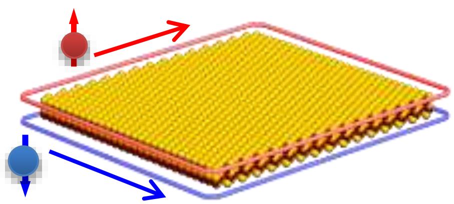
Rotational symmetry

Gauge symmetry

What is a topological insulator (TI)

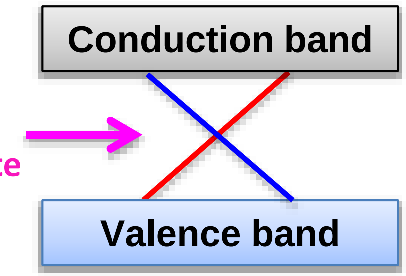
An Insulator that conducts

2D real space



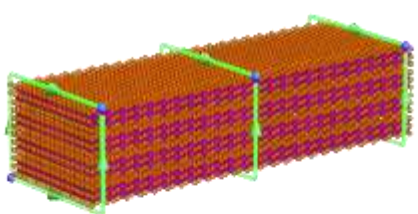
In gap 1D surface state

Band structure



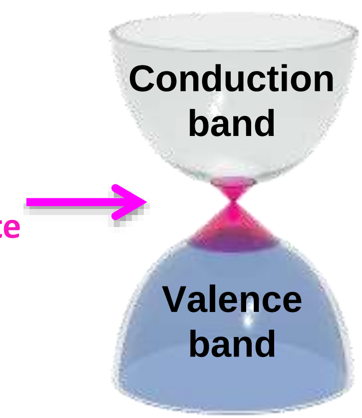
We also live on the surface…

3D real space



In gap 2D surface state

Band structure



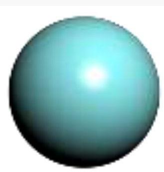
Why "topological"

Topologically distinct objects

Regular insulator

Topological insulator

Sphere

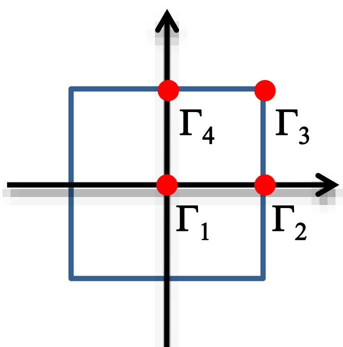


Torus

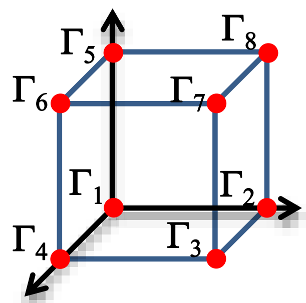
Characterization of TIs

Z_2 topological invariant

Band theory [Fu, Kane & Mele (2007) Moore & Balents (2007), Roy (2007)]



2D Brillouin Zone



3D Brillouin Zone

$$\delta_i = \frac{\sqrt{\det[B(\Gamma_i)]}}{Pf[B(\Gamma_i)]} \qquad B_{mn}(k) = \langle -k, m|T|k, n\rangle$$

$$(-1)^{\nu} = \prod_i \delta_i = \pm 1$$

$\nu =$
- **1: Topological insulators**
- **0: Regular insulators**

With inversion symmetry: ν **represents the *Parity of occupied Bloch states***

Field theory [Qi, Zhang, et. al., (2008, 2009), Wilczek, (1987,2009)]

$$S_\theta = \frac{\theta\alpha}{4\pi^2}\int d^3x dt E \cdot B$$

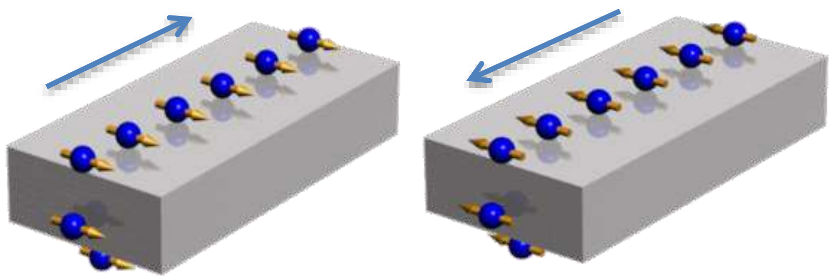
+

Time reversal symmetry

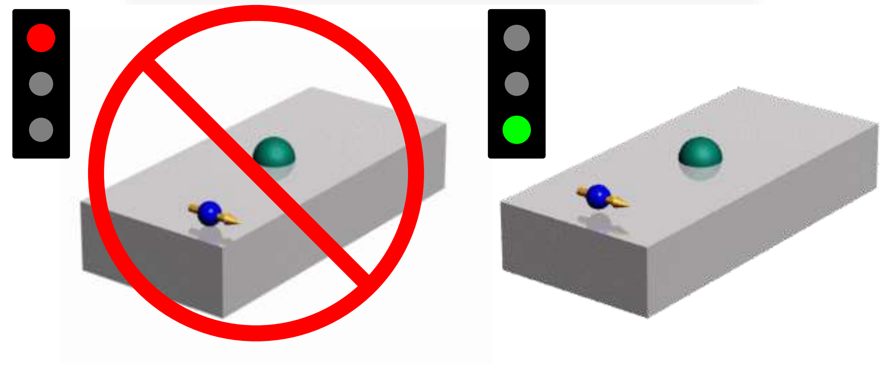
$\theta =$
- **π: Topological insulators**
- **0: Regular insulators**

Unique surface state properties of TIs

“Locking” between current & spin

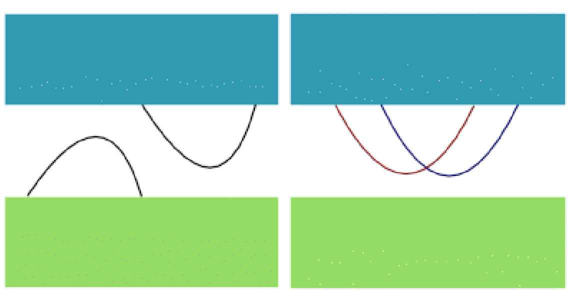


No back-scattering rule
(by non-magnetic impurities)

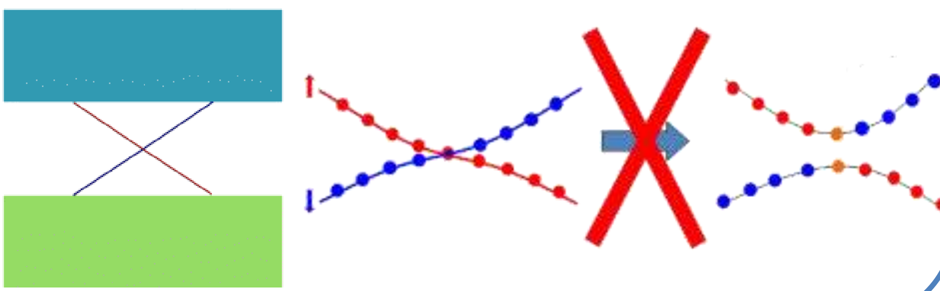


Robustness of the topological surface state

Surface state in regular insulator
vulnerable

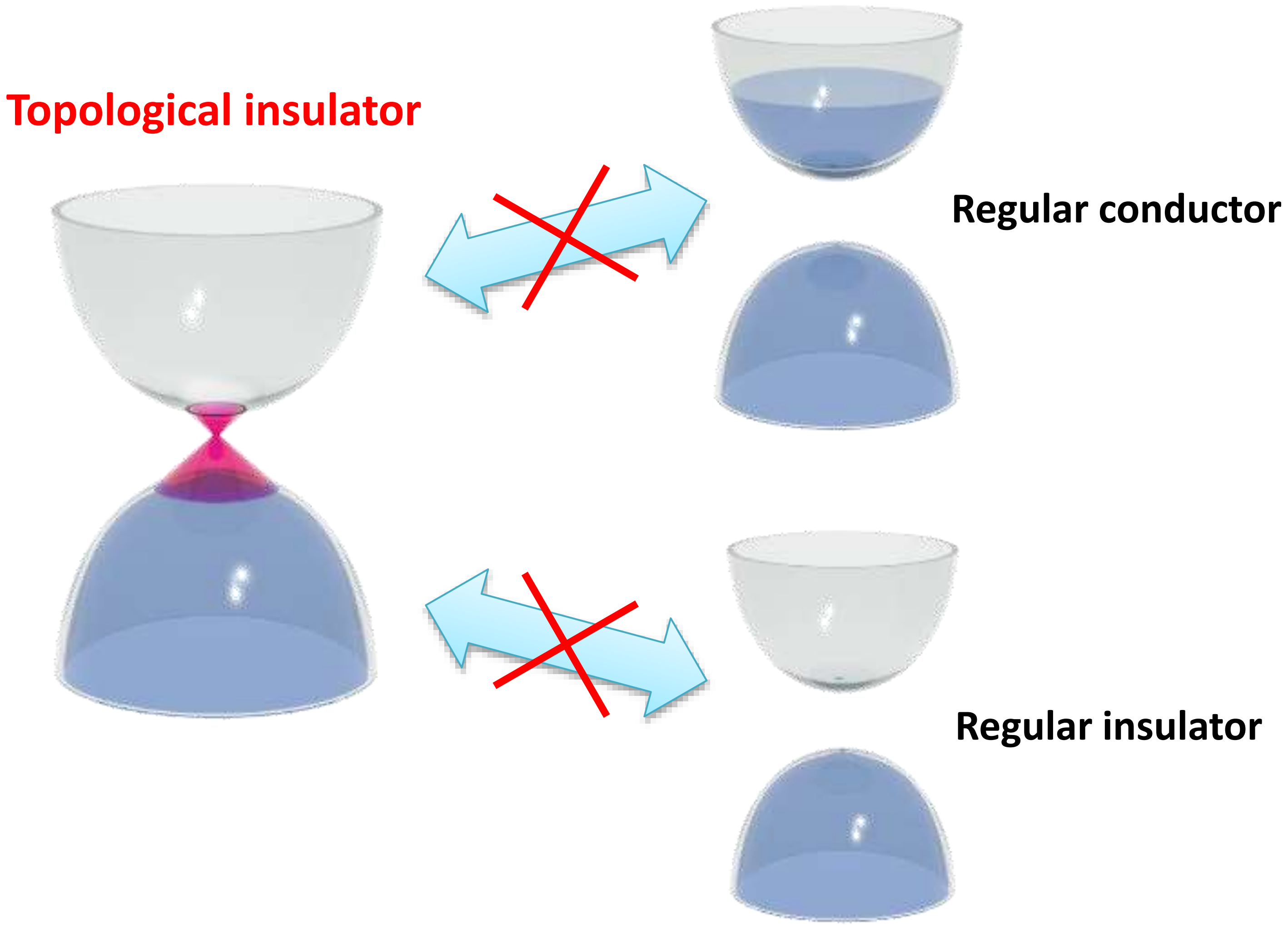


Surface state in topological insulator
robust



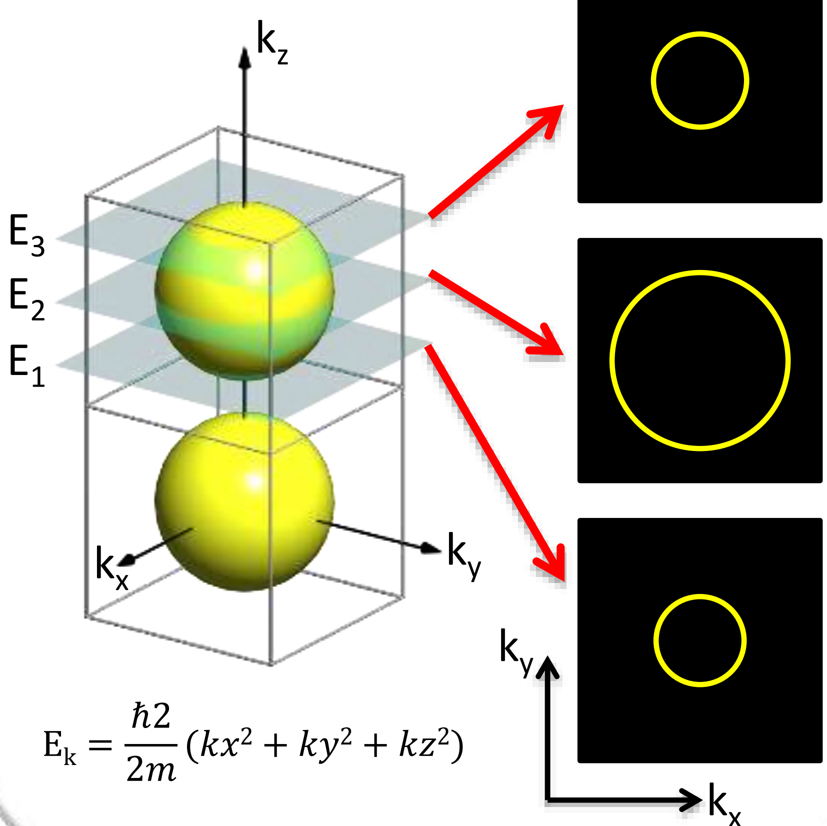
How to find TIs

Search for the unique band structure



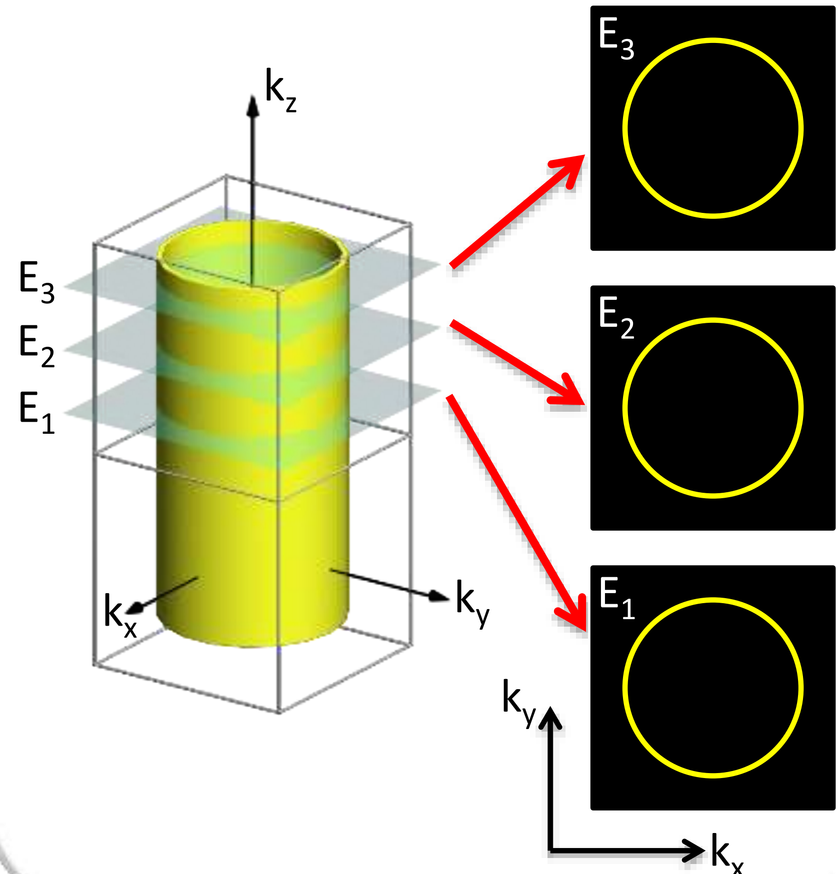
How to discriminate bulk & surface?

3D FS
(e.g. FS from bulk state)



$$E_k = \frac{\hbar 2}{2m}(kx^2 + ky^2 + kz^2)$$

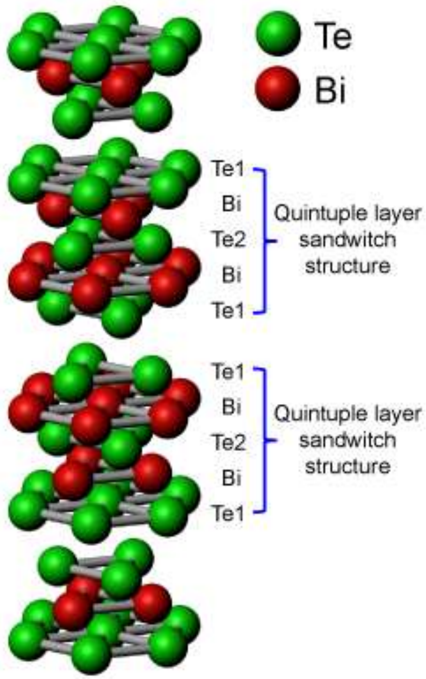
2D FS
(e.g. FS from surface state)



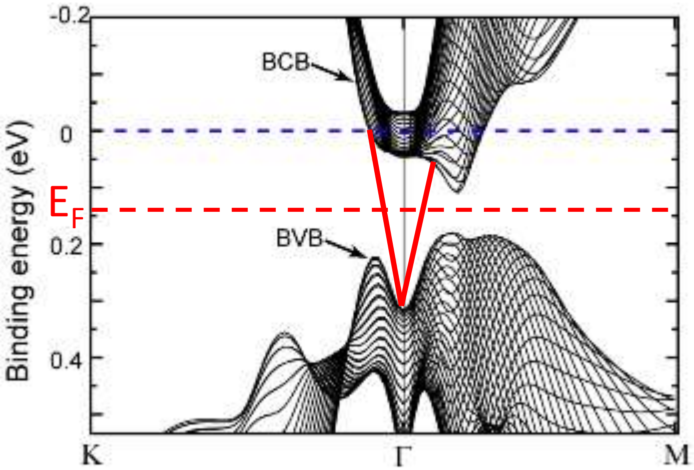
Realization of TI state in Bi_2Te_3

Y. L. Chen, *et. al., Science* 325, 178 (2009)

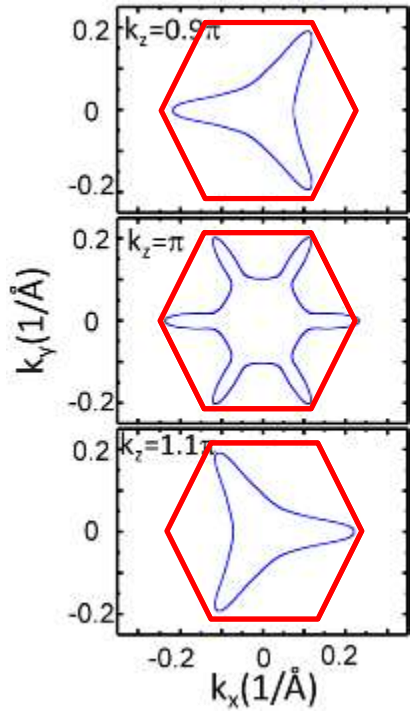
Crystal Structure



Bulk band structure



Bulk Fermi surface (n-type)



TI Checklist:

1. **There exist Dirac surface states**
2. **There are odd number of Dirac fermions in a Brillouin Zone**
3. **The E_F is in the gap**

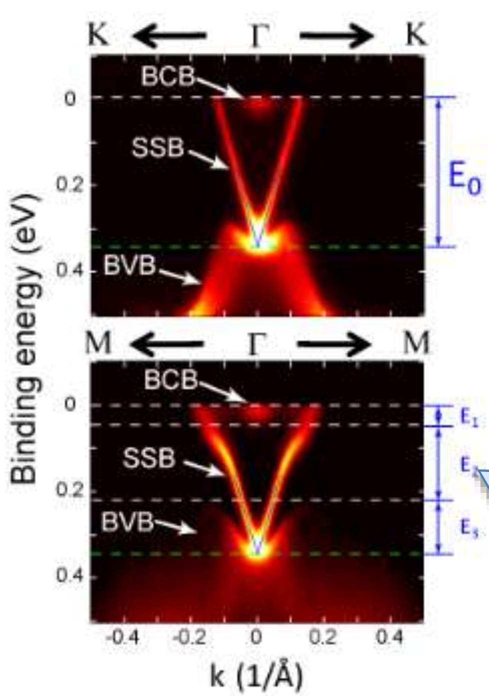
Realization of TI state in Bi_2Te_3

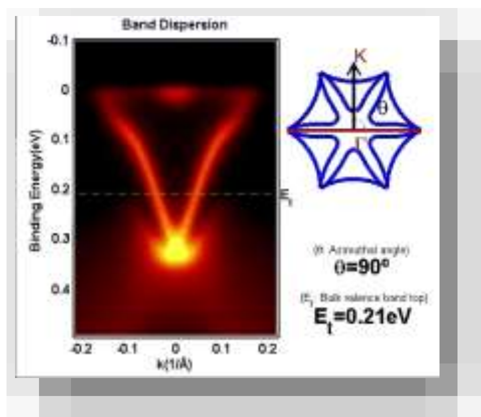
Y. L. Chen, *et. al.*, *Science* 325, 178 (2009)

TI Checklist:

✓ 1. **There exist Dirac surface states**
2. **There are odd number of Dirac fermions in a Brillouin Zone**
3. **The E_F is in the gap**

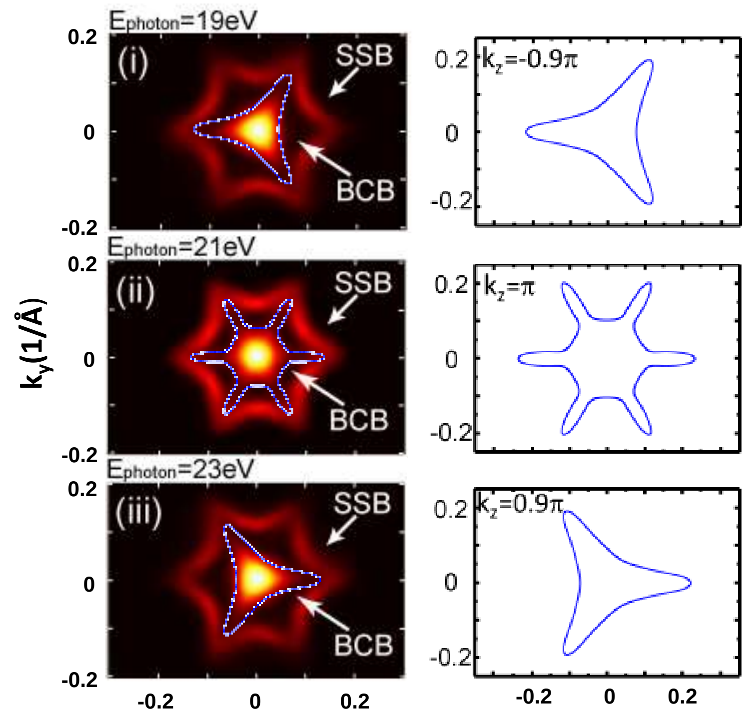
Dirac fermion





Bulk band gap
E_2=165meV

Dirac Fermion's Surface nature



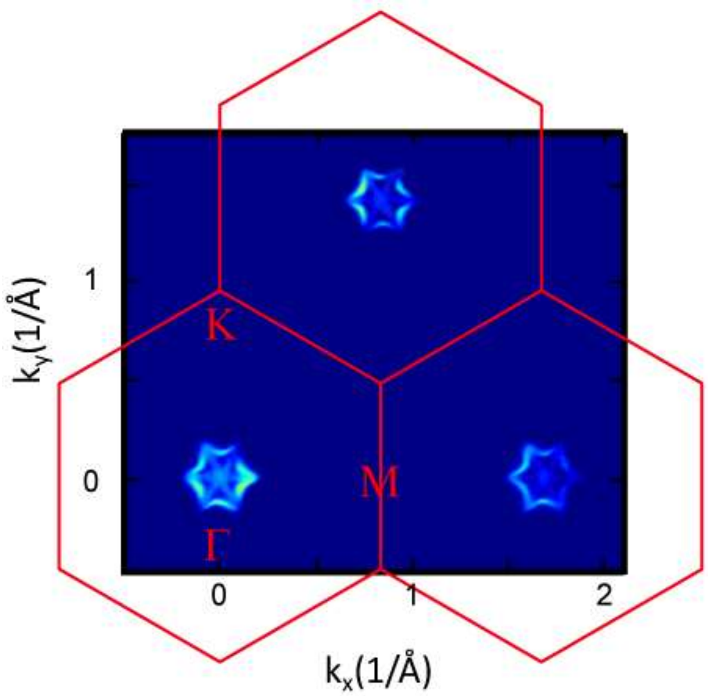
Realization of TI state in Bi_2Te_3

Y. L. Chen, *et. al.*, *Science* 325, 178 (2009)

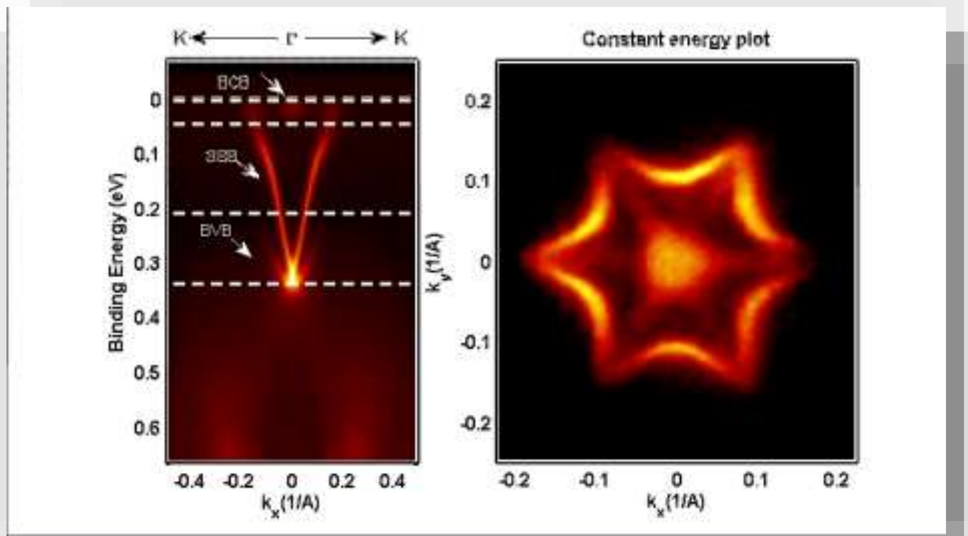
TI Checklist:

1. ✓ **There exist Dirac surface states**
2. ✓ **There are odd number of Dirac fermions in a Brillouin Zone**
3. **The E_F is in the gap**

Single Dirac fermion in each BZ



Evolution of the Band



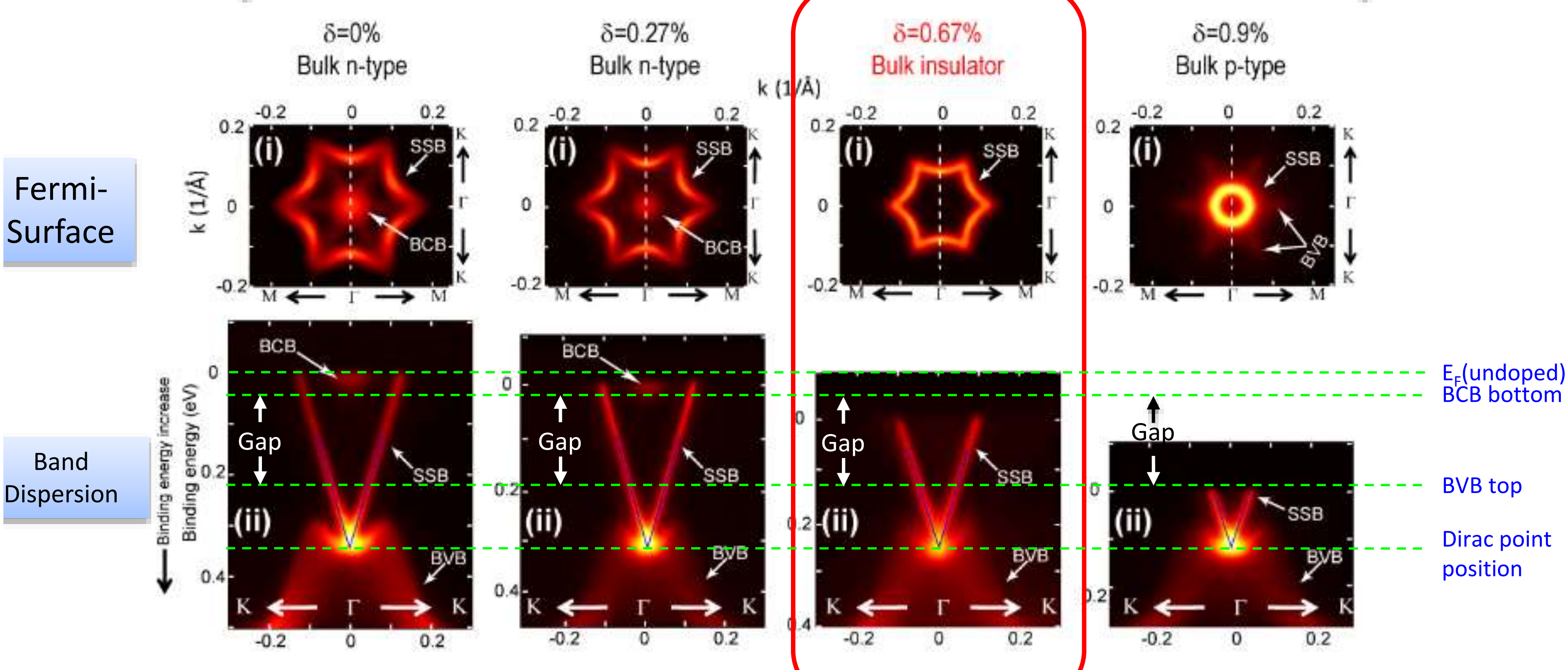
Realization of TI state in Bi_2Te_3

Y. L. Chen, *et. al.*, *Science* 325, 178 (2009)

TI Checklist:

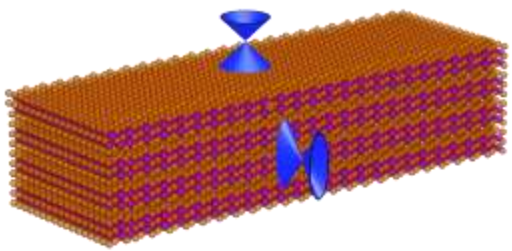
1. **There exist Dirac surface states**
2. **There are odd number of Dirac fermions in a Brillouin Zone**
3. **The E_F is in the gap**

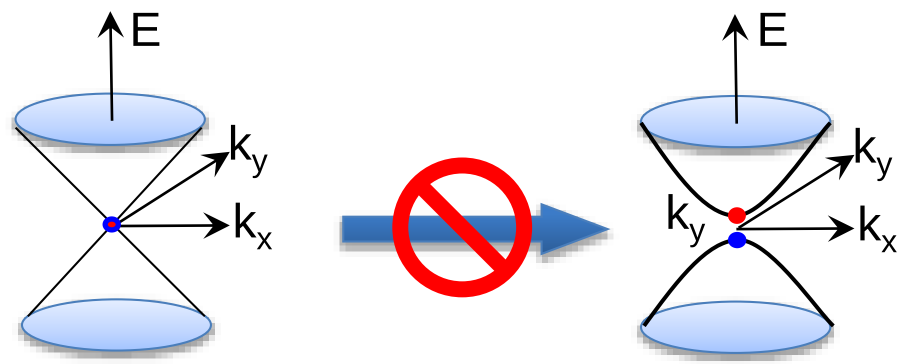
Different charge doping



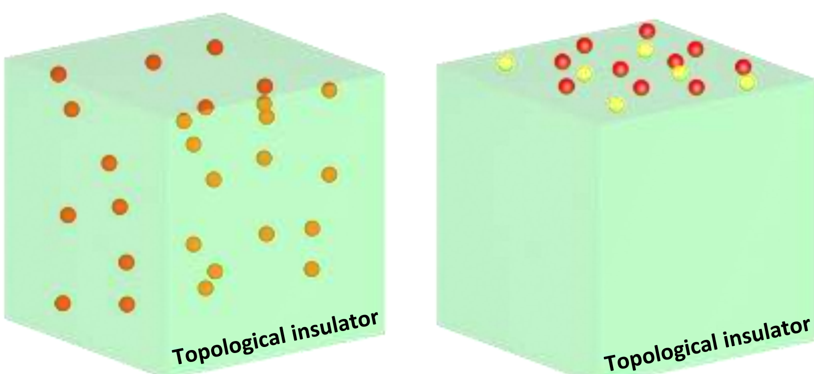
Protection of the time reversal symmetry

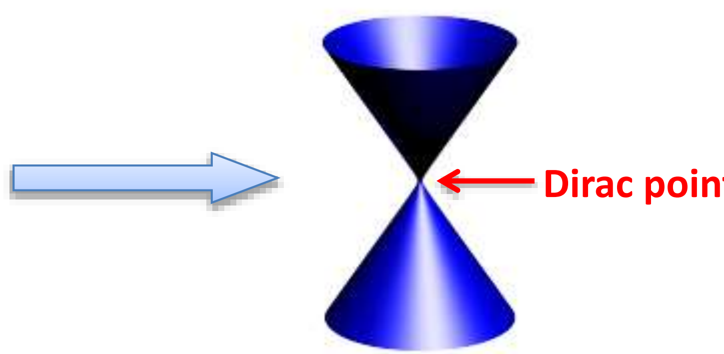
Massless Dirac fermion is protected by time reversal symmetry (Kramers' theorem)





Non-magnetic bulk & surface doing

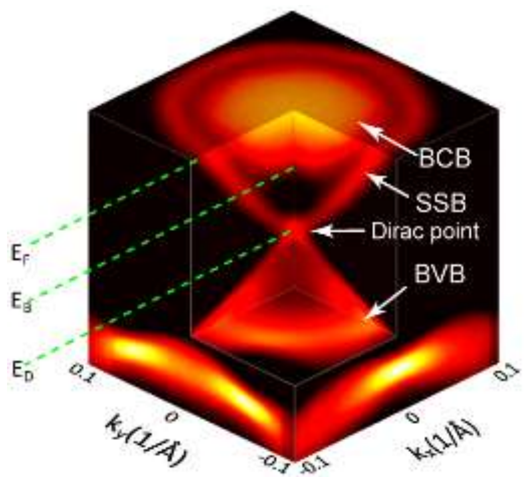




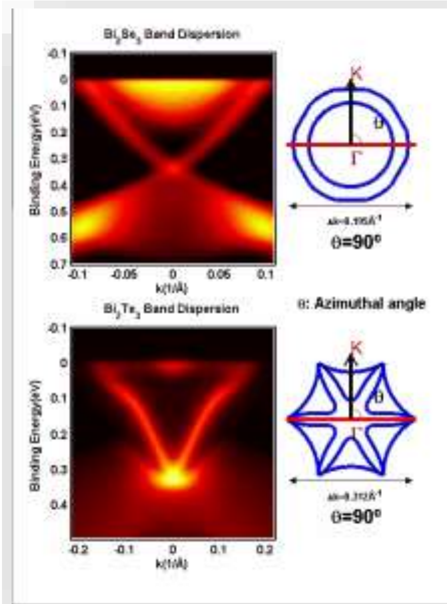
TRS protection – bulk doping

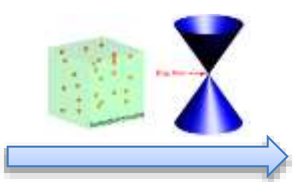
Y. L. Chen, *et. al., Science* 329, 659 (2010)

In gap Dirac point of Bi_2Se_3

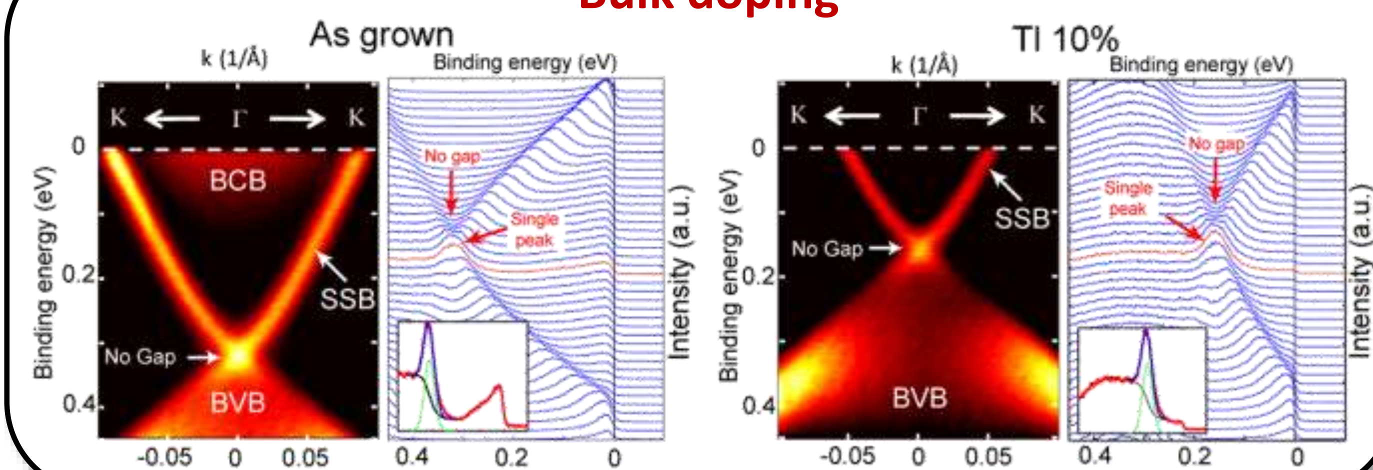


Compare to Bi_2Te_3





Bulk doping



TRS protection – surface doping

Y. L. Chen, *et. al.*, *Science* 329, 659 (2010)

Surface doping

Oxygen Hydrogen Carbon monoxide Carbon dioxide Potassium

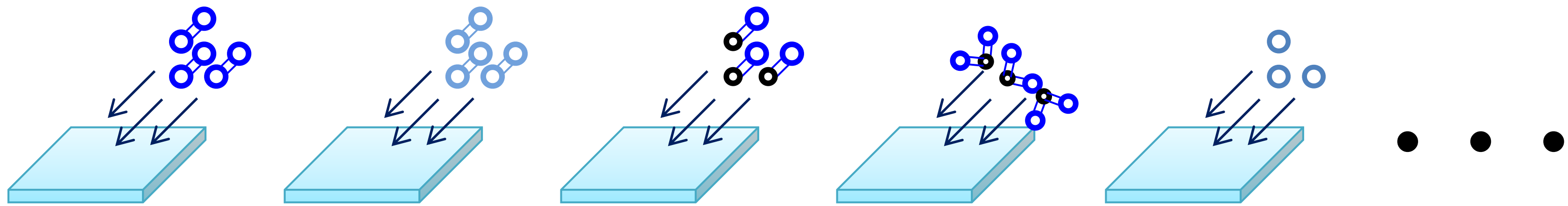
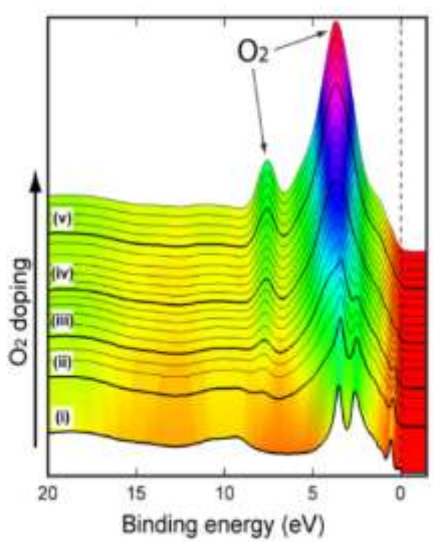
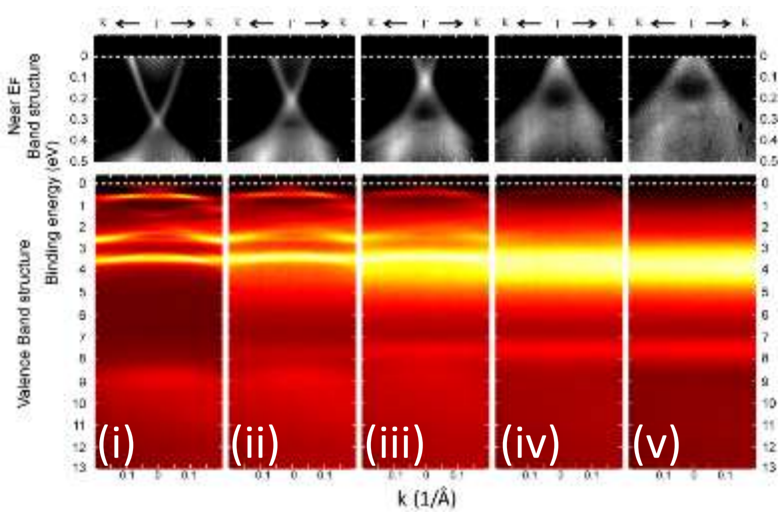
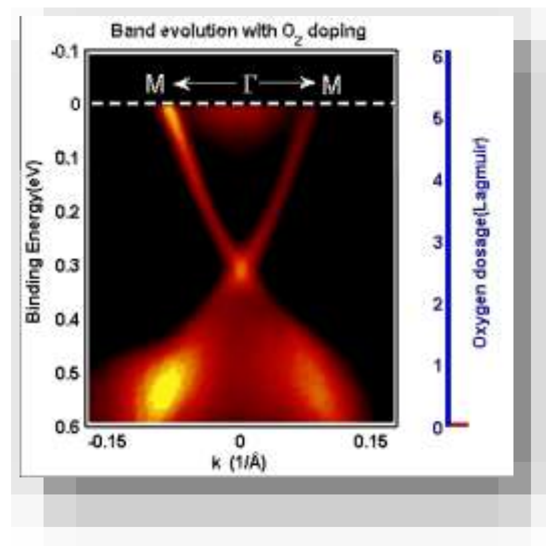


Photo assisted surface Oxygen doping



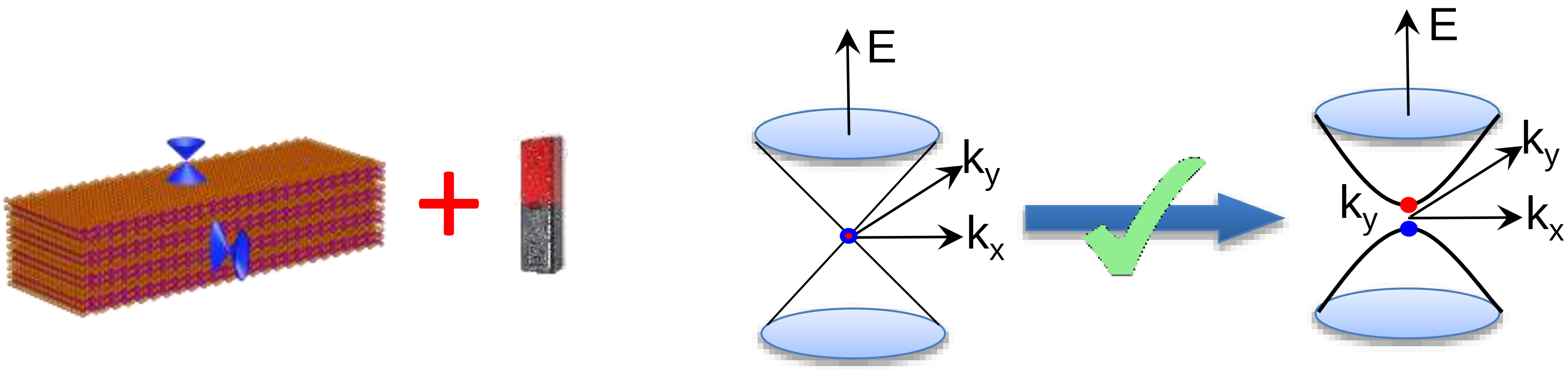




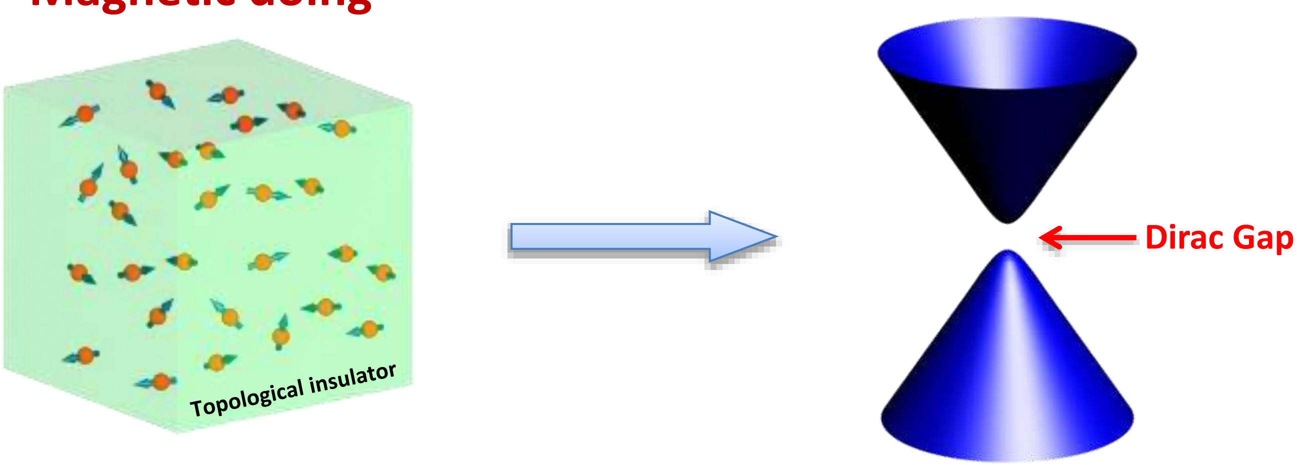
What if TRS is broken?

Y. L. Chen, *et. al.*, *Science* 329, 659 (2010)

Formation of massive Dirac fermion if TRS is broken

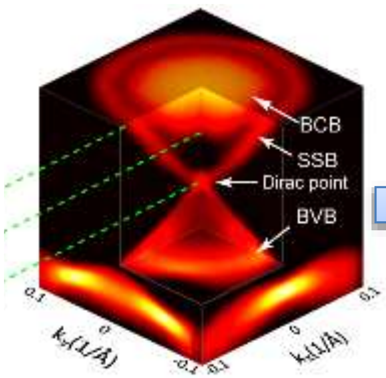


Magnetic doing



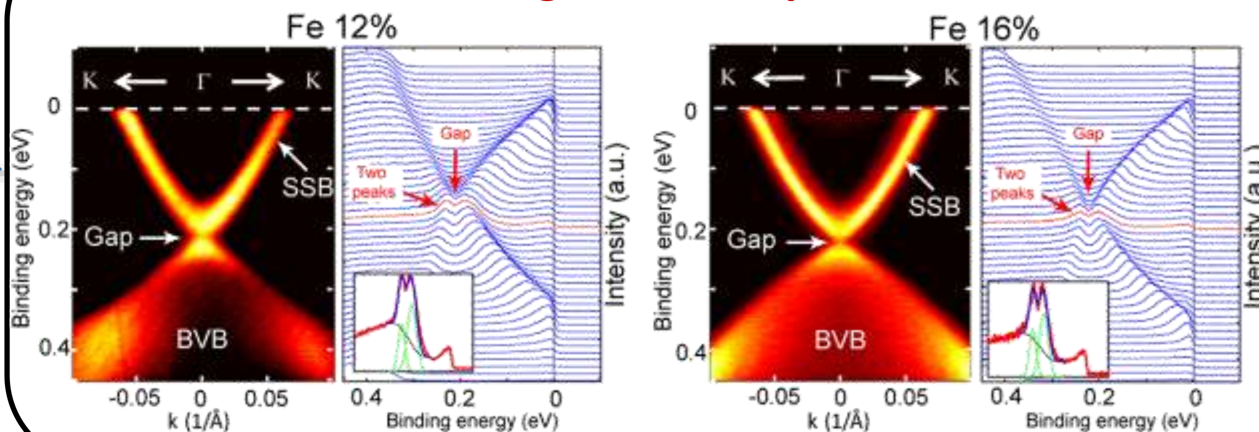
Dirac fermion becomes massive

Y. L. Chen, *et. al.*, *Science* 329, 659 (2010)

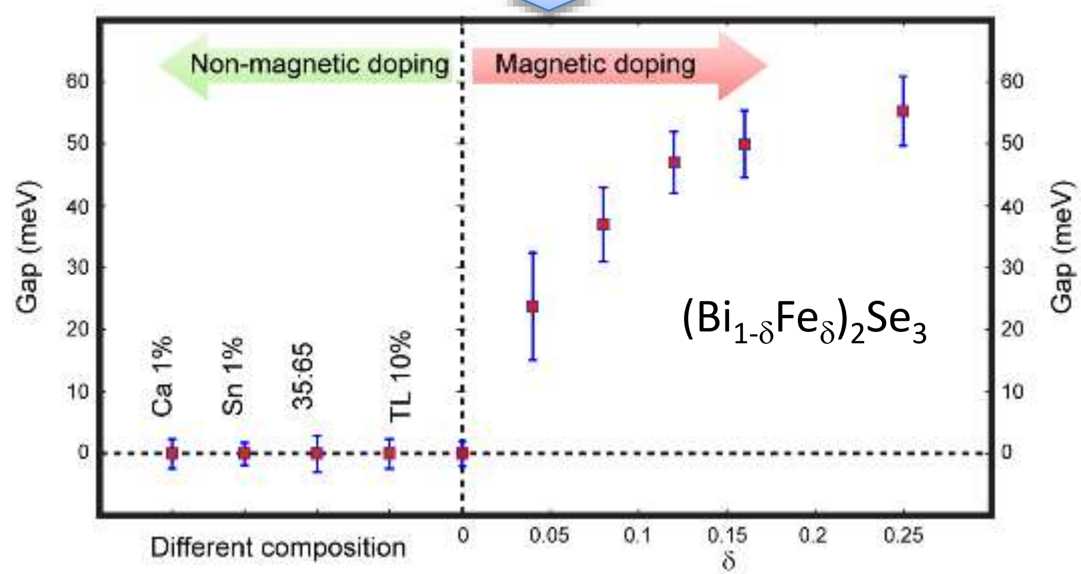


Magnetic impurities

Braking the Dirac point

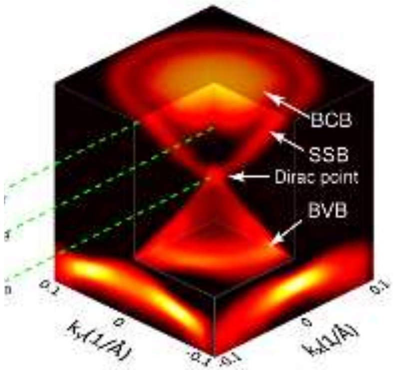


Summary of different doping effects



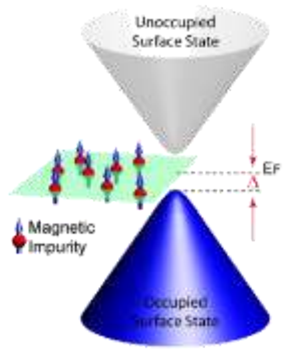
Realize insulating massive Dirac fermion state

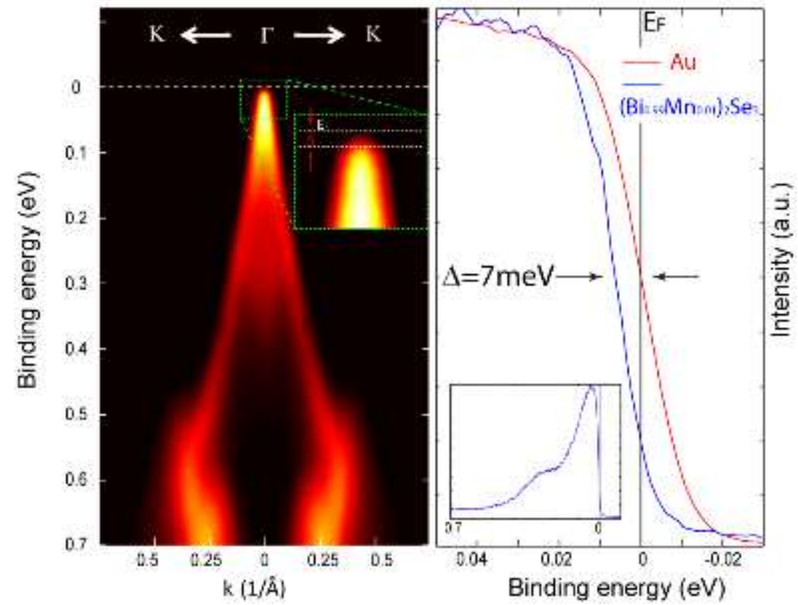
Y. L. Chen, *et. al.*, *Science* 329, 659 (2010)



Magnetic impurity

+ E_F Tuning





Why insulating massive Dirac fermion state?

Realize new phenomena

Provide control for applications

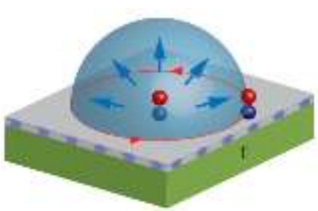
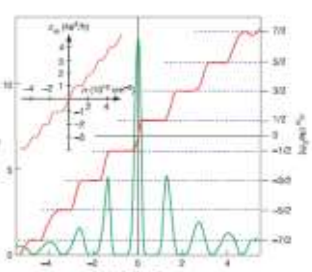
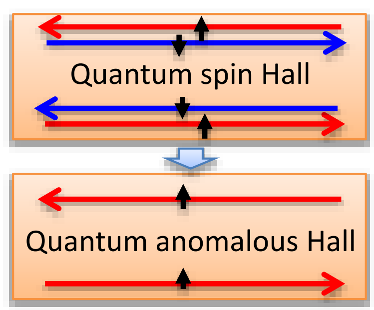


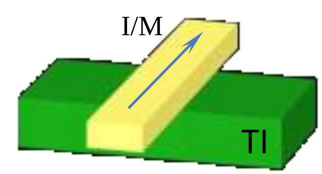
Image Surface Monopole



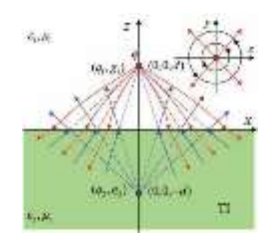
Half Hall conductance $\sigma_H = e^2/2h$



2D quantum anomalous Hall state



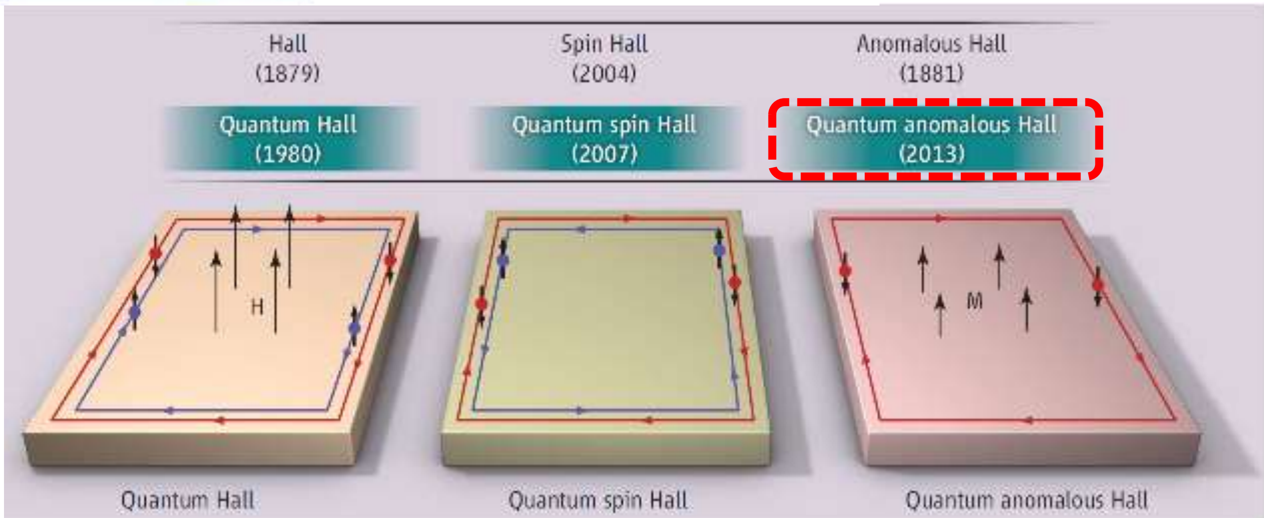
Turn off surface conduction



All electric magnetic writing

Completing the table of Hall effects

The Complete Quantum Hall Trio
Seongshik Oh
Science **340**, 153 (2013);
DOI: 10.1126/science.1237215



Realize new phenomena

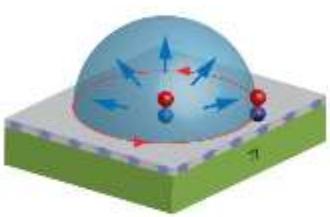
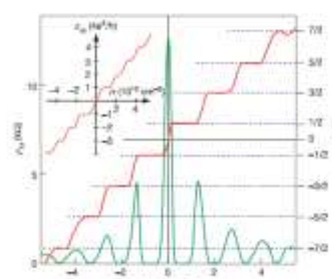
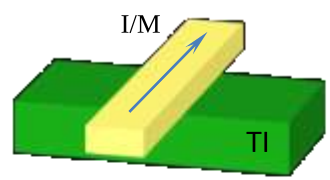


Image
Surface Monopole

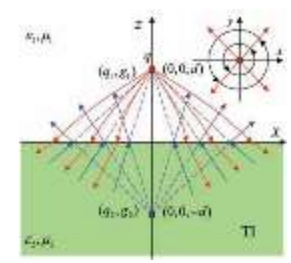


Half Hall
conductance $\sigma_H = e^2/2h$

Provide control for applications



Turn off
surface conduction

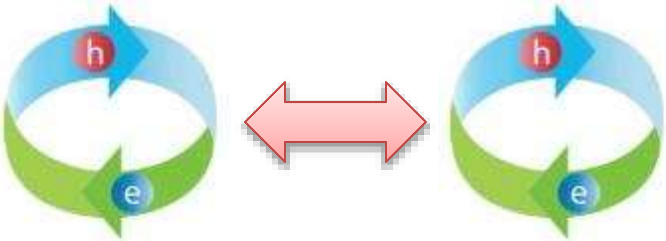


All electric
magnetic writing

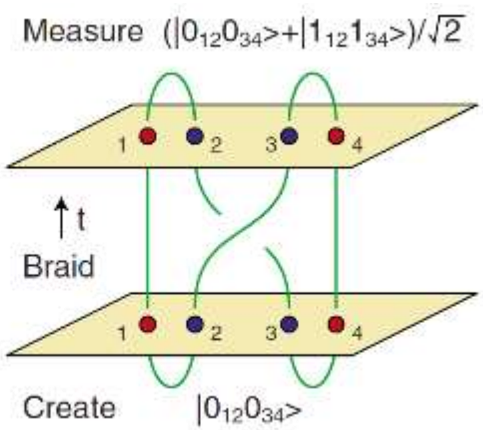
New topological states

Search for topological superconductors

Majorana fermion



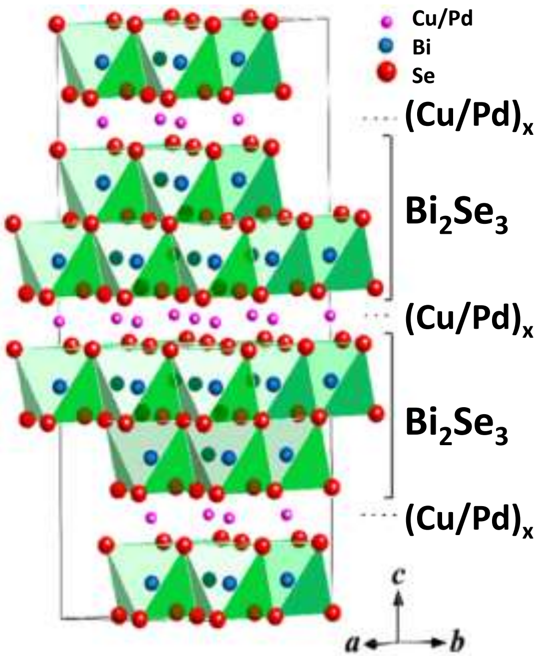
Quantum computation



Fu, Kane (2008)
Hasan, Kane (2010)
Qi, Zhang (2010)

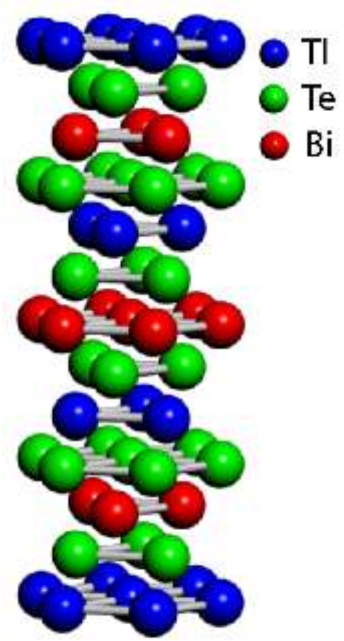
Some candidates

$Cu_xBi_2Se_3$, $Pd_xBi_2Te_3$



Hor, et. al., (2010)
Fu, Berg, (2010)
Wray, et.al., (2010)

$TlBiTe_2$

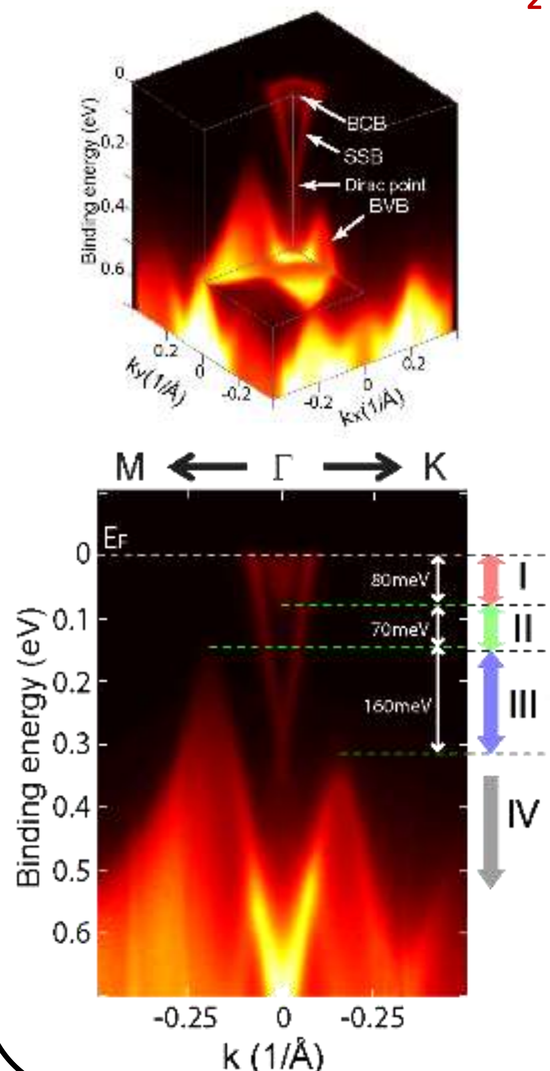


Hein/Swiggard, (1970)
Yan, et. al., (2010)
Chen, et. al., (2010)

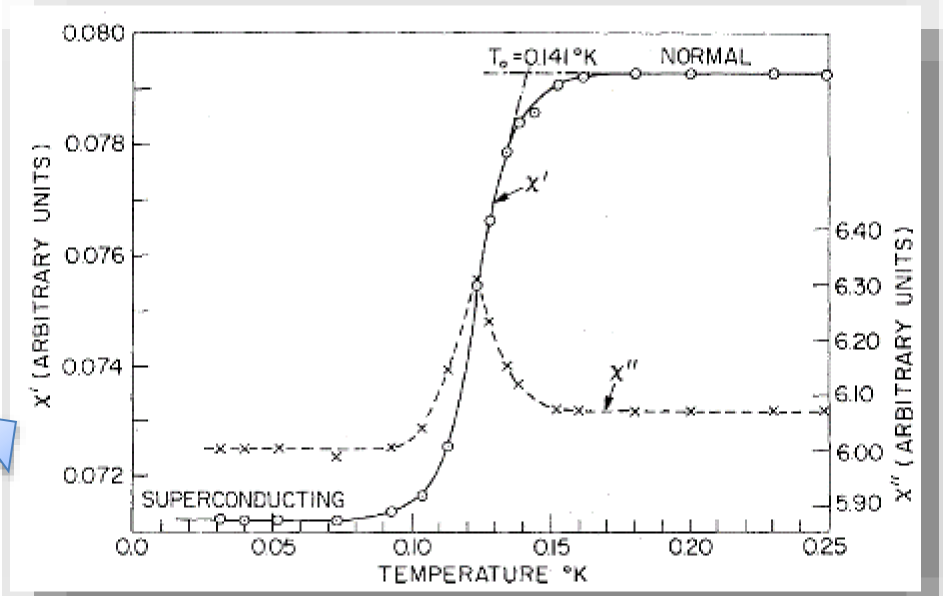
A candidate for topological superconductors

Y. L. Chen *et. al., Phys. Rev. Lett.* 105, 266401 (2010)

Band structure of $TlBiTe_2$



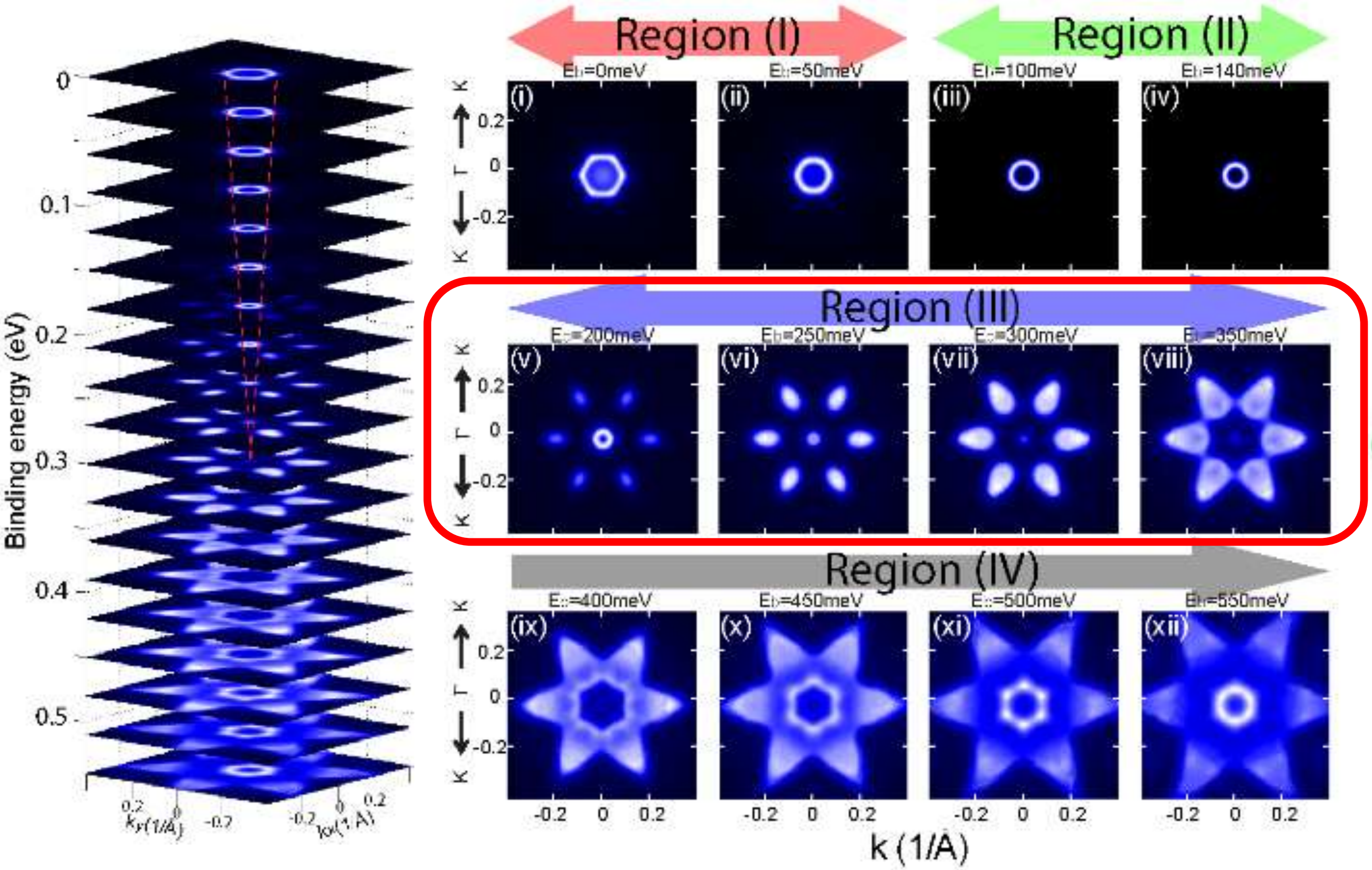
Superconducting transition

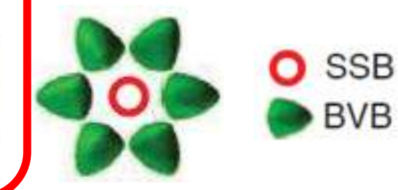


Hein & Swiggard *Phys. Rev. Lett.* 24, 53 (1970)

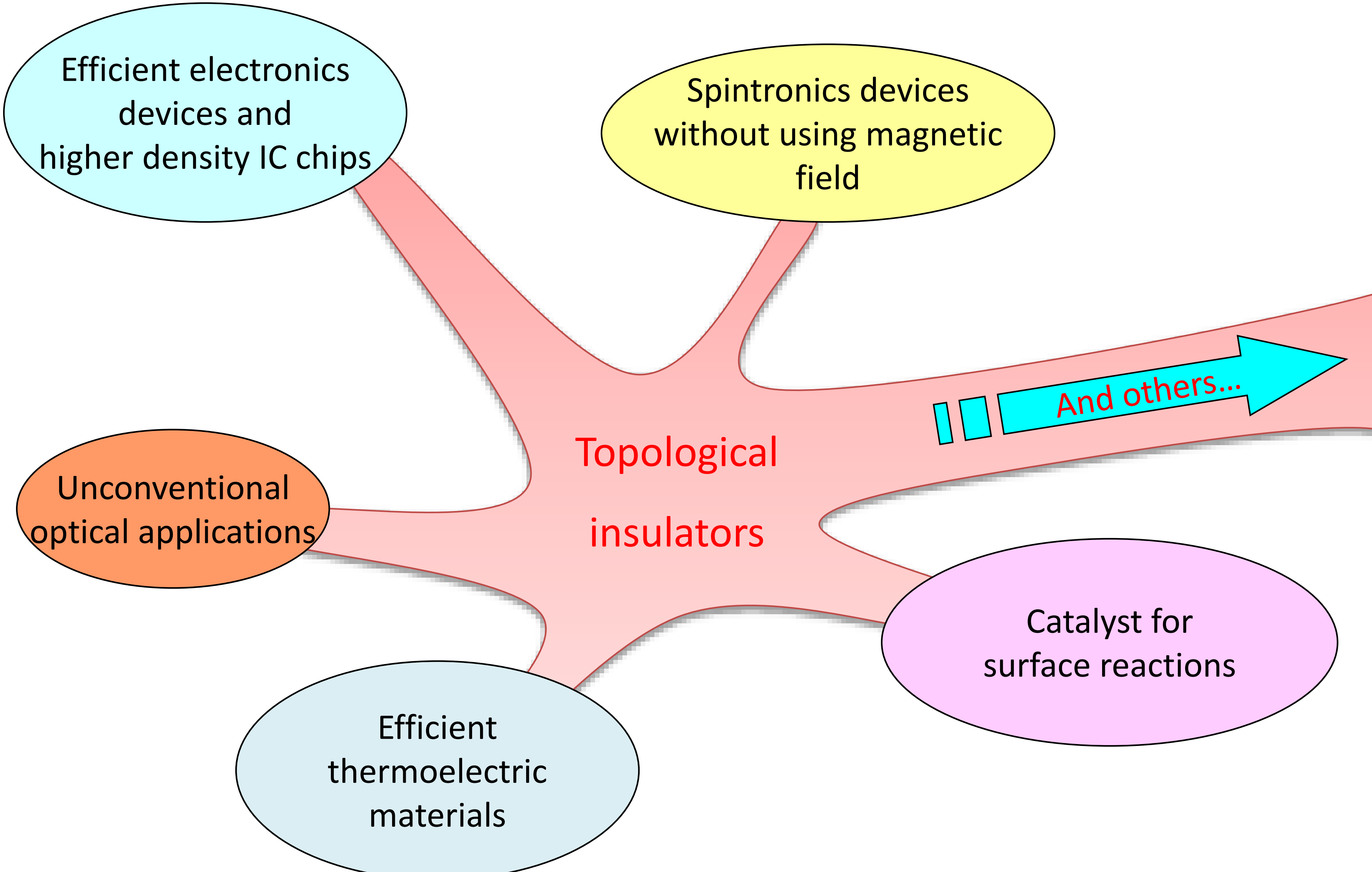
A candidate for topological superconductors

Y. L. Chen *et. al.*, *Phys. Rev. Lett.* 105, 266401 (2010)





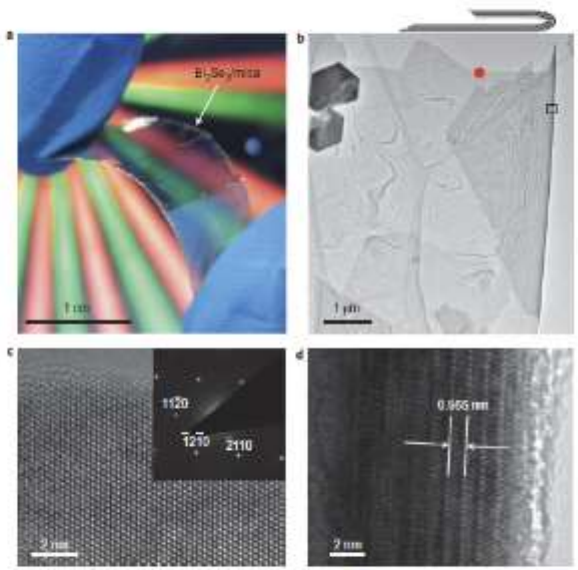
What can TI be used in real life

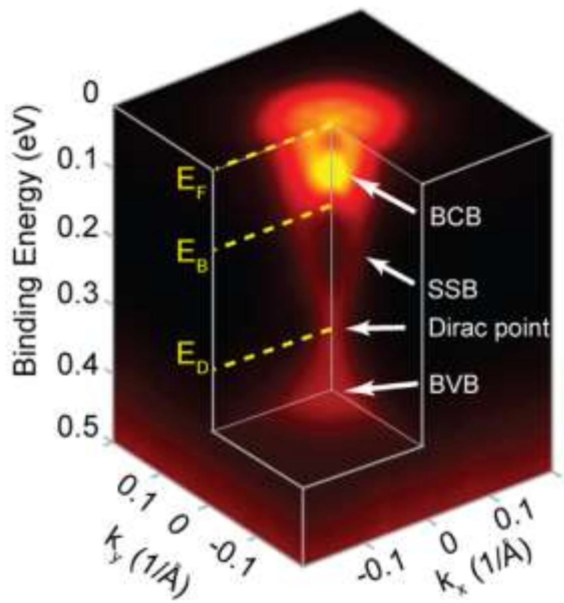


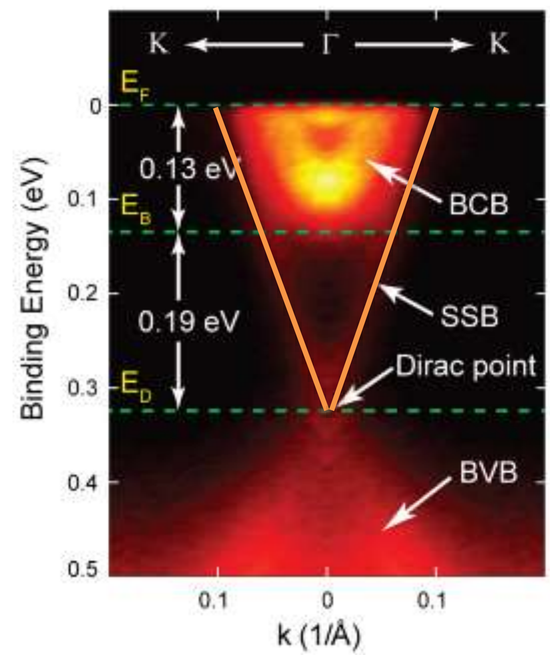
Flexible transparent electrodes – band structure

H. L. Peng, *et. al., Nature Chemistry, 4, 281 (2012)*

Electronic structure of a 10nm Bi_2Se_3 film







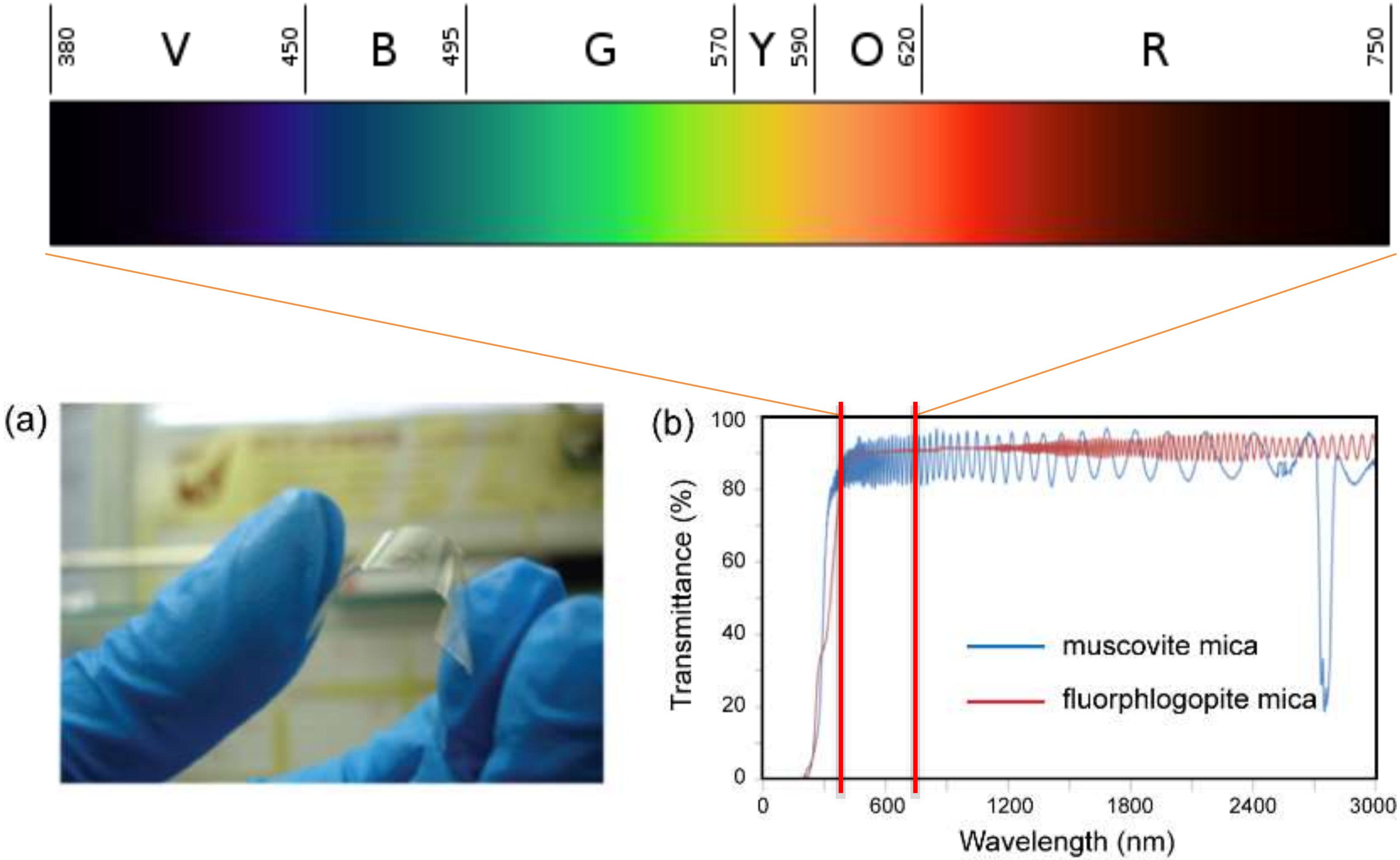
Estimate surface states Carrier density (up and down surfaces):

$2\times\pi\times k_f^2/(2\times\pi)^2 = 0.0016$ Å^{-2}=<u>1.6×10^{13} cm^{-2}</u>

Effective 2D density of bulk carrier for a 10nm film is roughly:

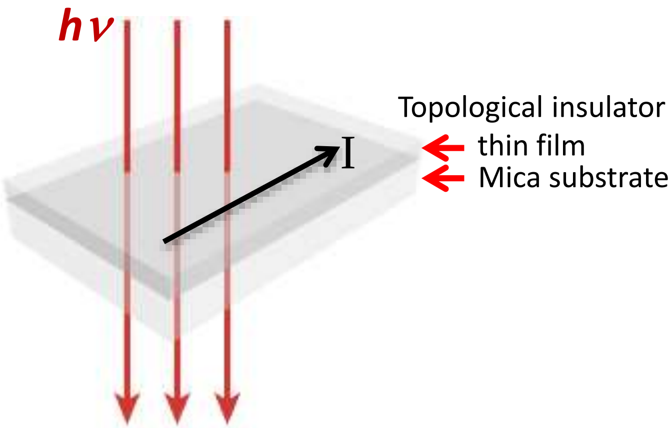
$(4/3\times\pi\times k_f^3\times$ (10nm))/$(2\times\pi)^3$ = 0.0017 Å^{-2} =<u>1.7×10^{13} cm^{-2}</u>

Transparent electrode for IR application

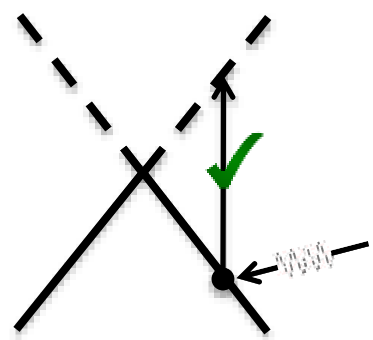


Flexible transparent electrodes - Transmittance

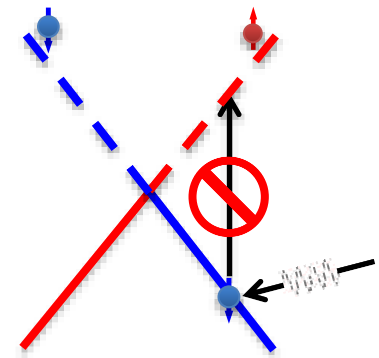
H. L. Peng, *et. al.*, *Nature Chemistry, 4, 281 (2012)*

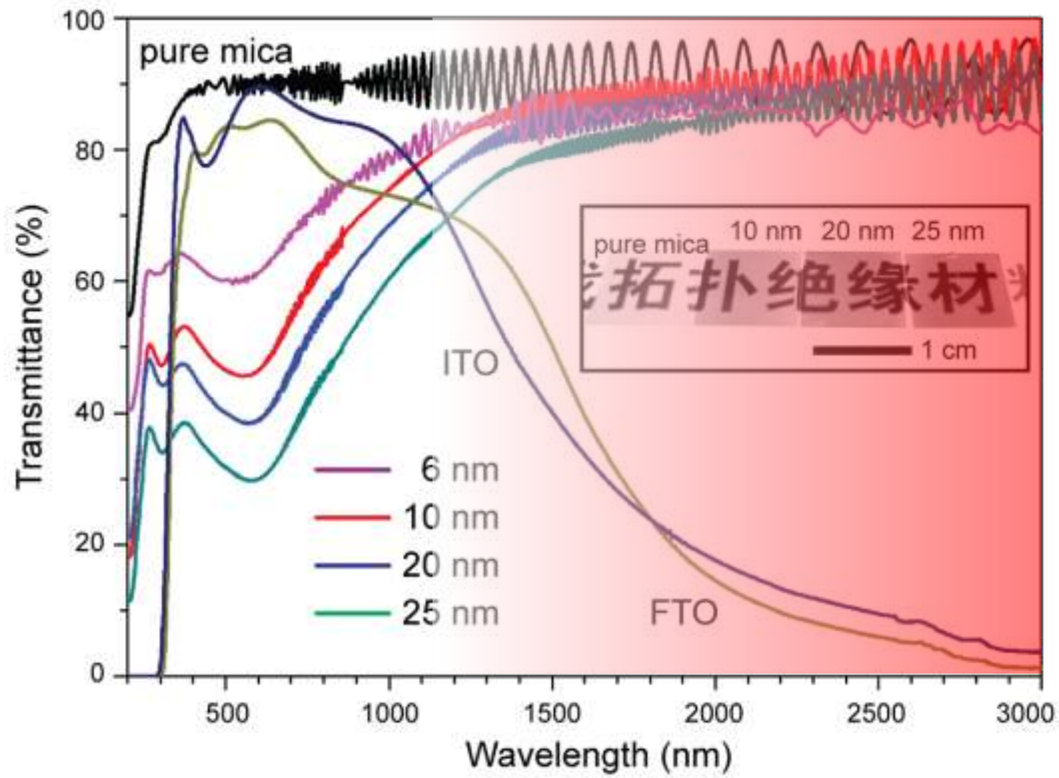


Regular Dirac fermion



Helical Dirac fermion in TI

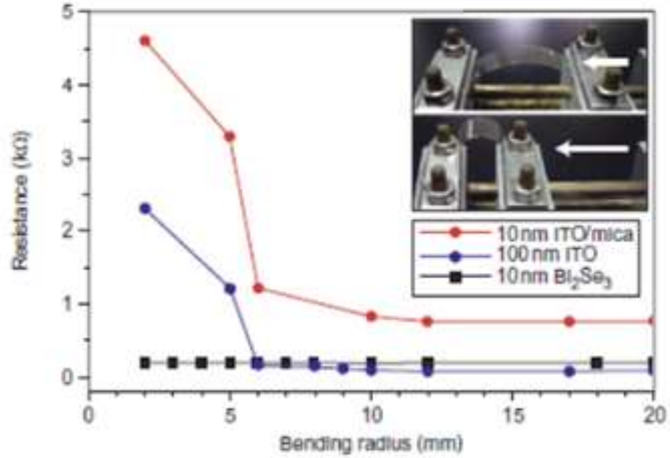


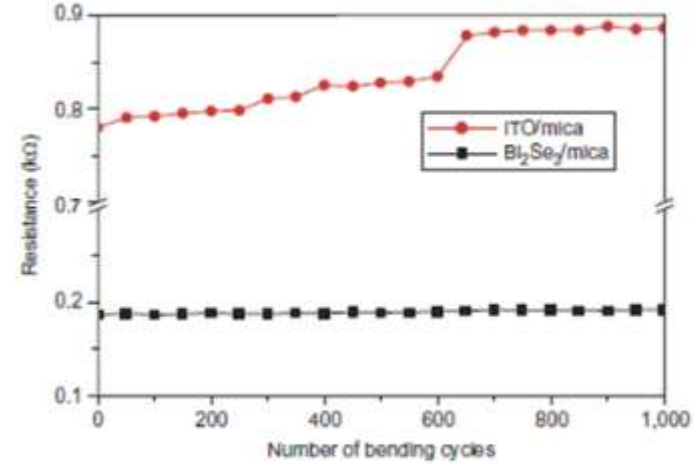


Flexible transparent electrodes - Durability

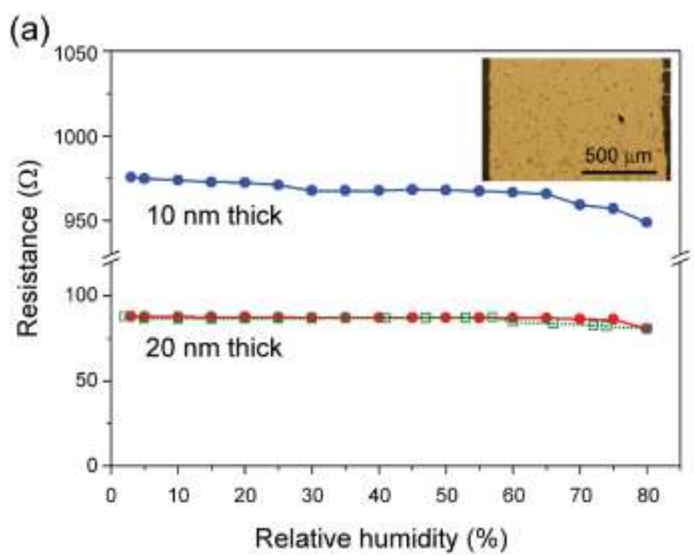
H. L. Peng, *et. al., Nature Chemistry, 4, 281 (2012)*

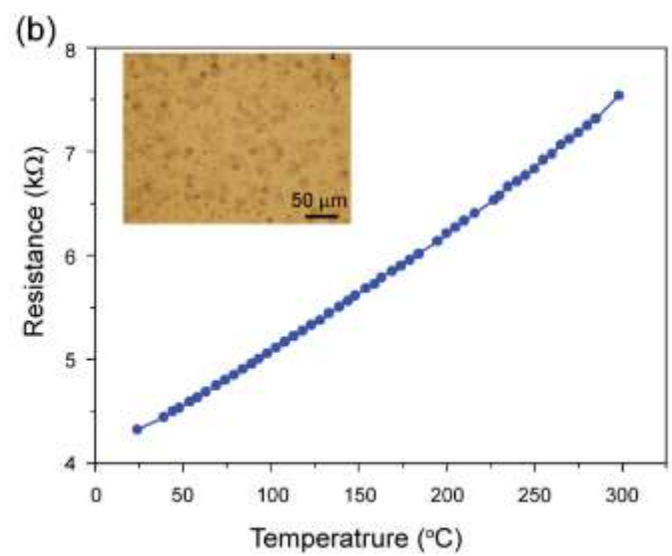
Bending test





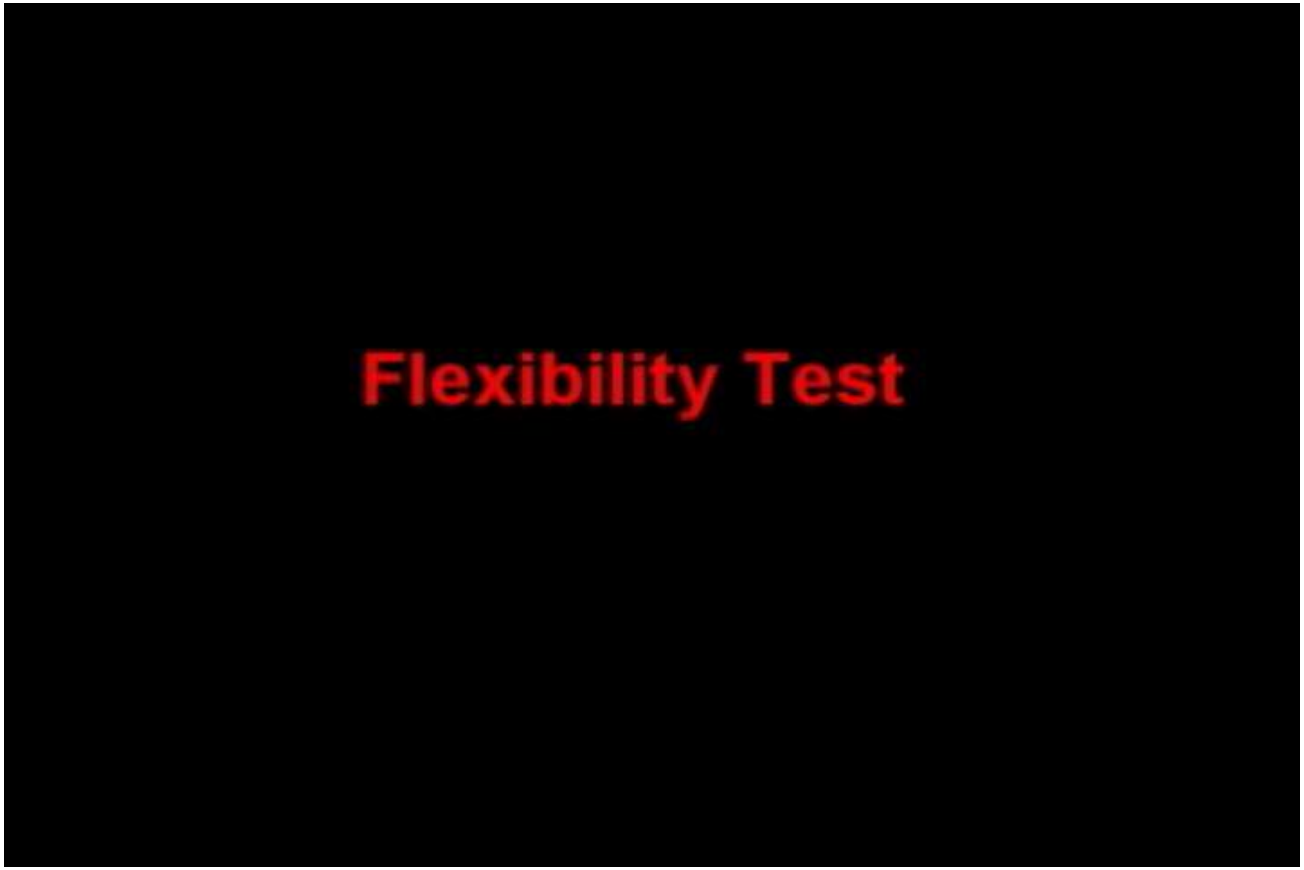
Humidity and Heating test





Flexible transparent electrodes

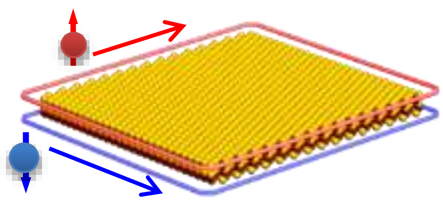
Flexibility and durability test

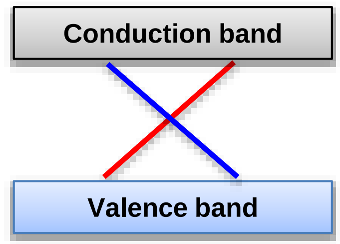


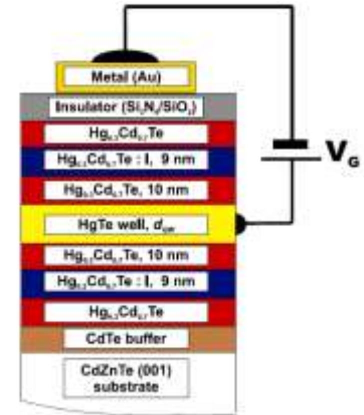
Dirac electron systems

1D Dirac fermions

Quantum spin Hall edge state

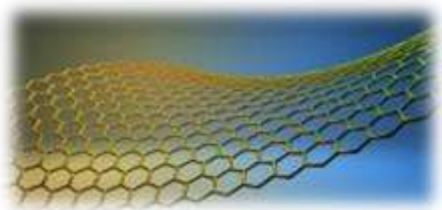


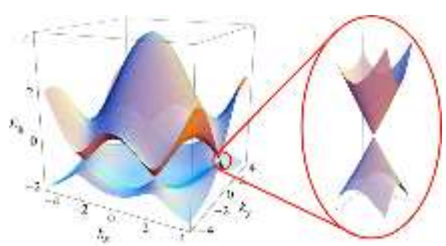




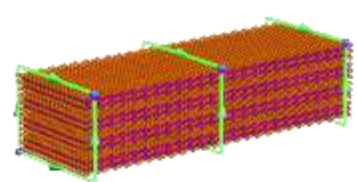
2D Dirac fermions

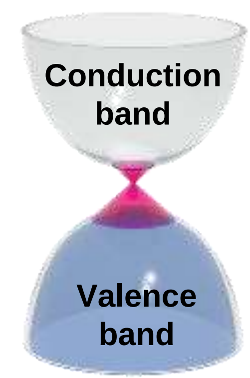
Graphene





3D TI surface state





Can we find other topological matter?

Insulator	→	Topological Insulator
Semimetal	→	Topological Semimetal
Superconductor	→	Topological Superconductor

……

3D Topological Dirac Semi-metal (TDS)

Z. K. Liu. *et. al.*, Science, 343, 864 (2014)

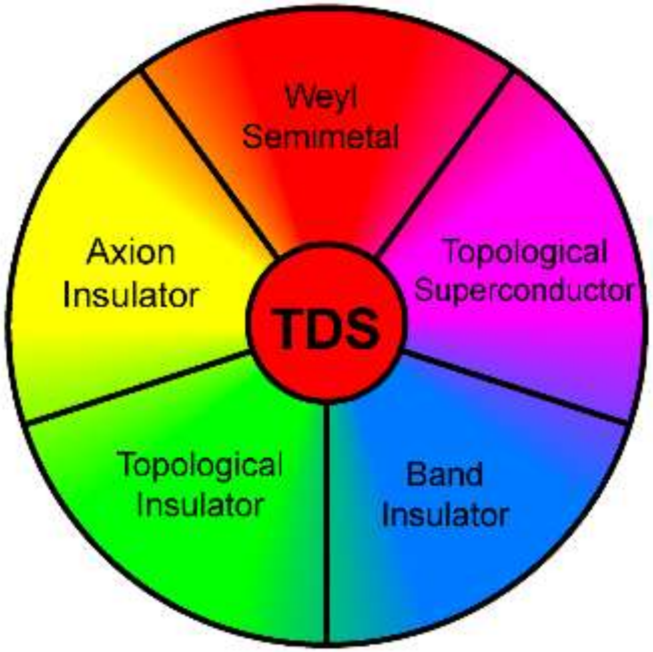
Interesting phenomena

A platform for rich novel states

- Giant diamagnetism
  E. Röber, et. al., *Phys. Status Solidi B,* **93**, K99 (1979)
  M. Koshino, et. al., *Phys. Rev. B,* **81**, 195431 (2010)

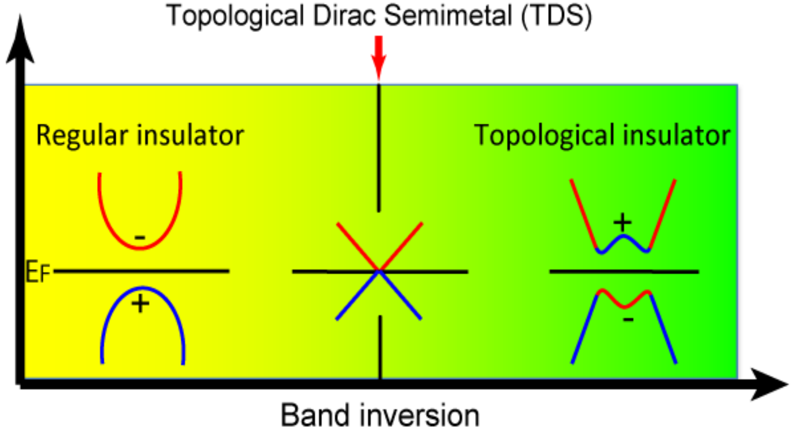
- Linear quantum magnetoresistance in bulk
  A. A. Abrikosov, *Phys. Rev. B,* **58**, 2788 (1998)
  W. Zhang *et al., Phys. Rev. Lett.,* **106**, 156808 (2011)

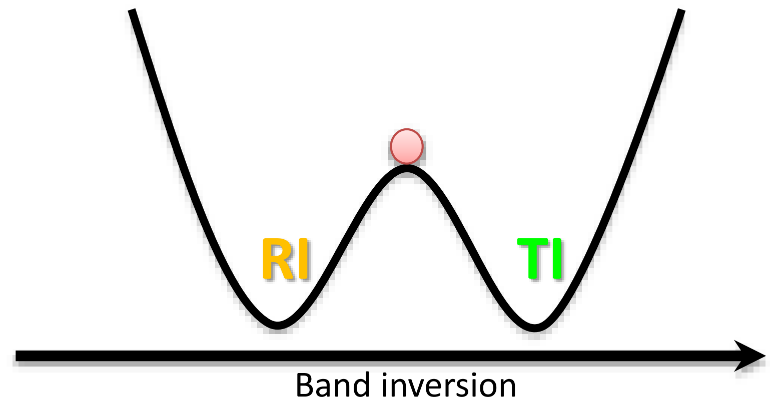
- Oscillating QSH effect in quantum well
  W. Zhang *et al., Phys. Rev. Lett.,* **106**, 156808 (2011).
  Z. Wang *et al., Phys. Rev. B* **85**, 195320 (2012)



3D Topological Dirac Semi-metal (TDS)

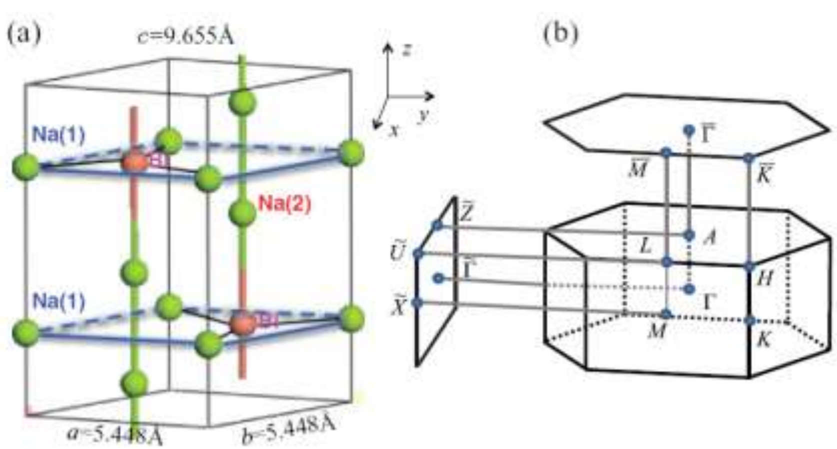
Realize 3D TDS state through topological phase transition

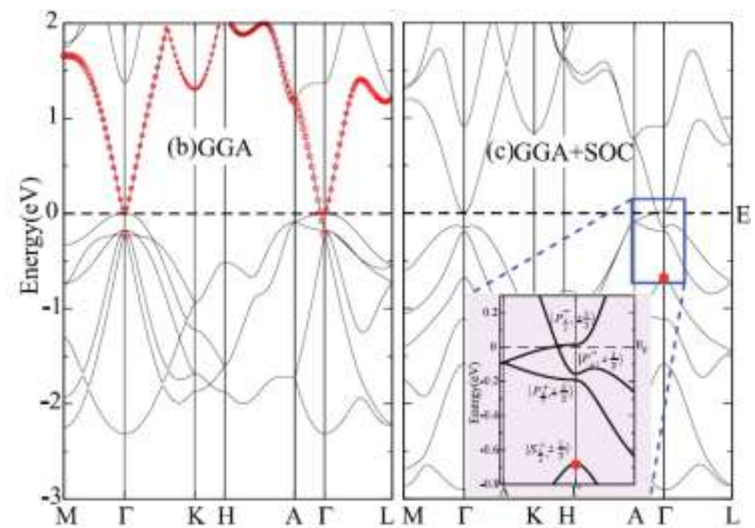




A better candidate: Na_3Bi

Phys. Rev. B **85**, 195320 (2012)

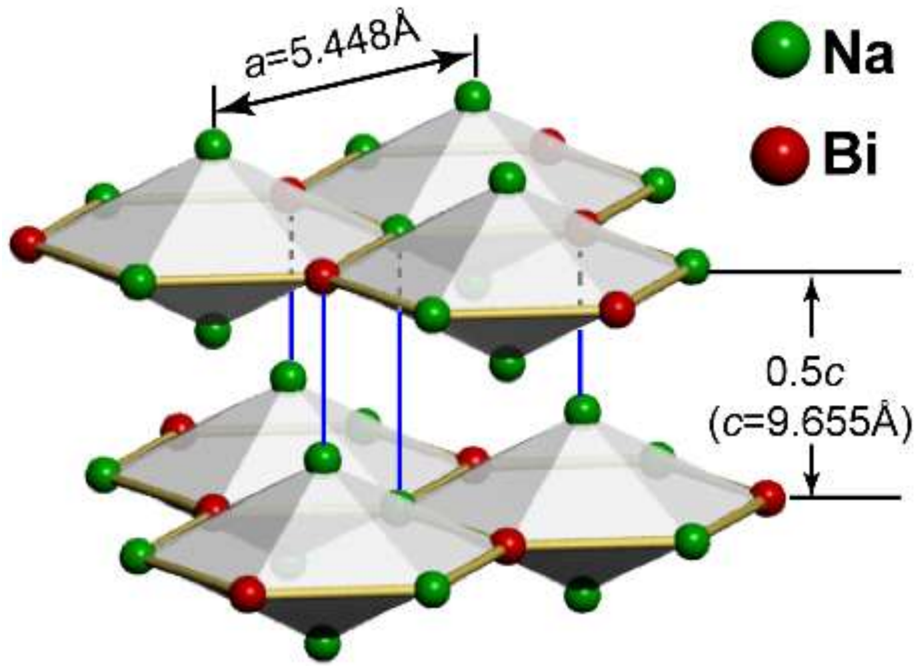




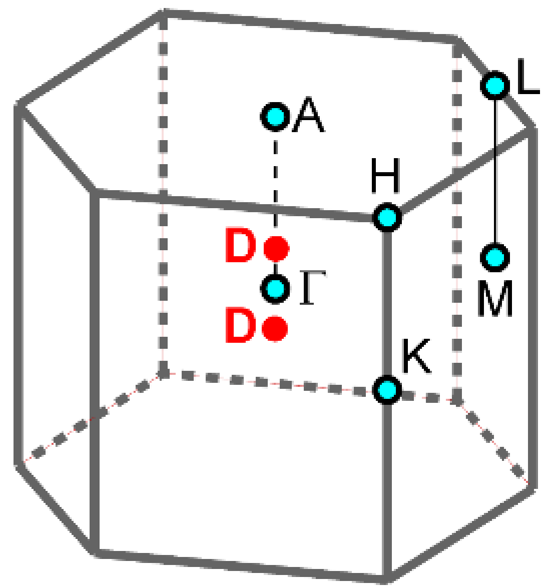
3D Topological Dirac Semi-metal (TDS)

Z. K. Liu. *et. al.*, Science, 343, 864 (2014)

Crystal structure



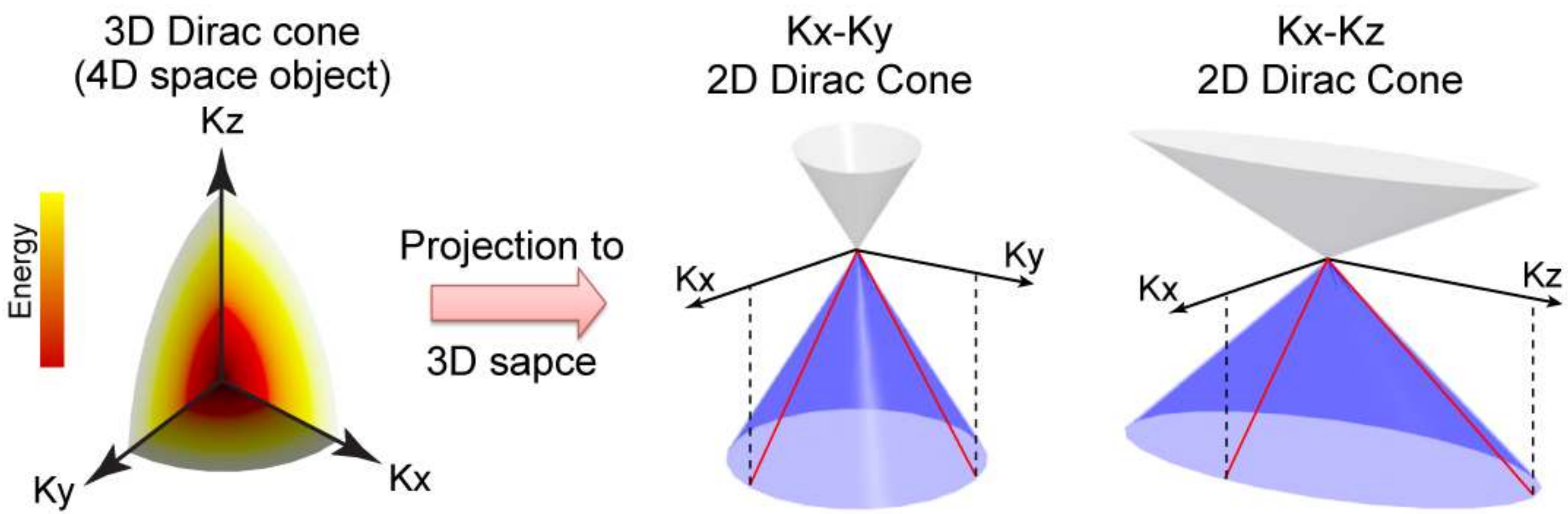
Brillouin Zone



How to identify a 3D TDS?

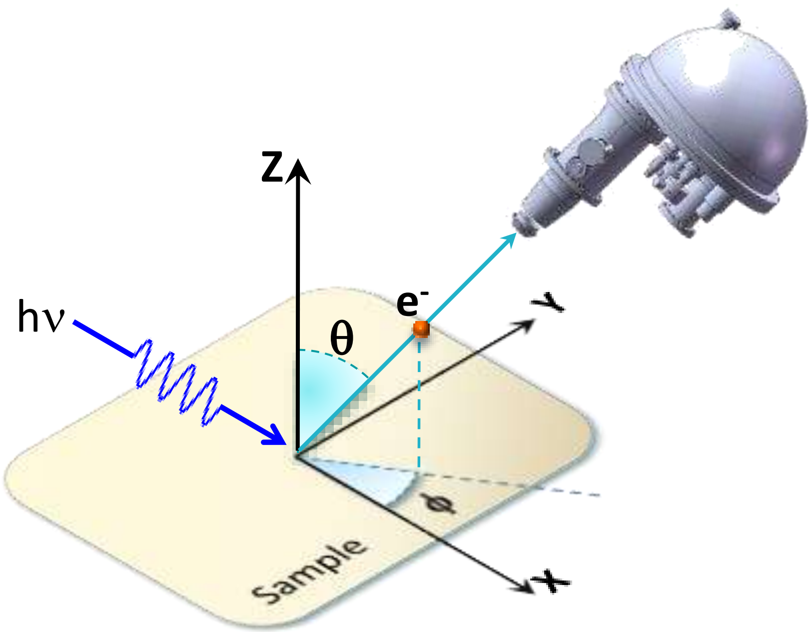
The 3D counterpart of graphene

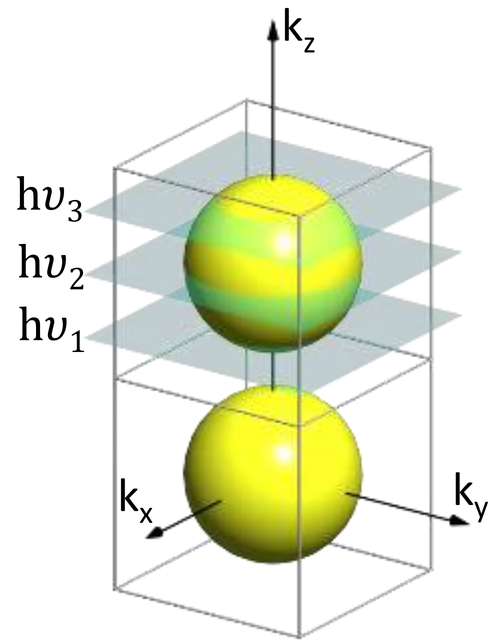
Identify the band structure



How to determine *kz*?

Photon energy dependent ARPES measurement





$$E_k = h\upsilon - w - E_B$$

In vacuum:

$$k^V{}_x = \frac{\sqrt{2m_e E_k}}{\hbar}\sin(\theta)\cos(\Phi)$$

$$k^V{}_y = \frac{\sqrt{2m_e E_k}}{\hbar}\sin(\theta)\sin(\Phi)$$

$$k^V{}_z = \frac{\sqrt{2m_e E_k}}{\hbar}\cos(\theta)$$

In crystal:

$$k_x = \frac{\sqrt{2m_e E_k}}{\hbar}\sin(\theta)\cos(\Phi) \quad = k^V{}_x$$

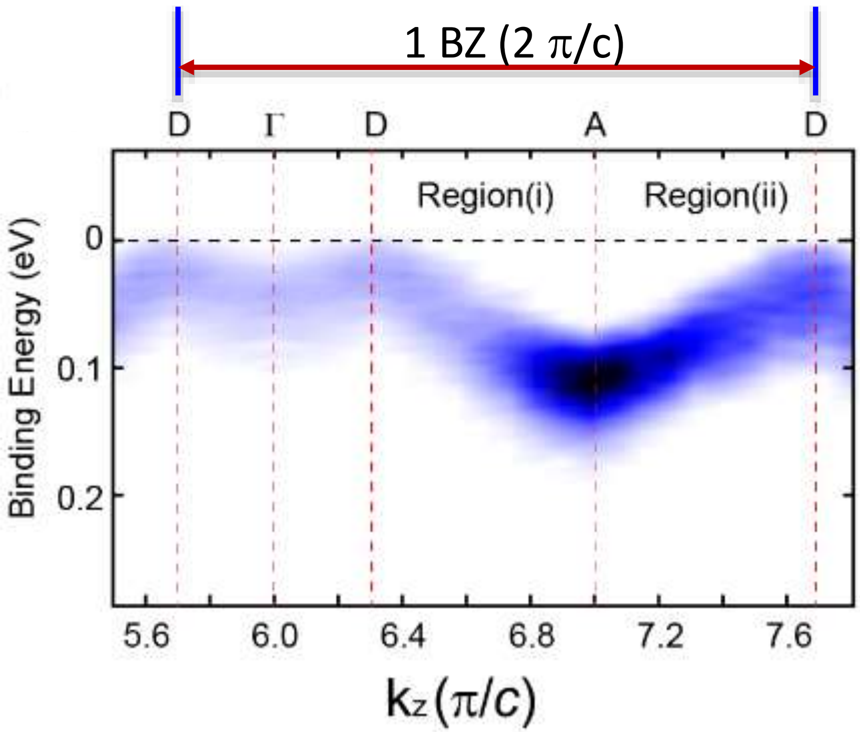
$$k_y = \frac{\sqrt{2m_e E_k}}{\hbar}\sin(\theta)\,sin(\Phi) \quad = k^V{}_y$$

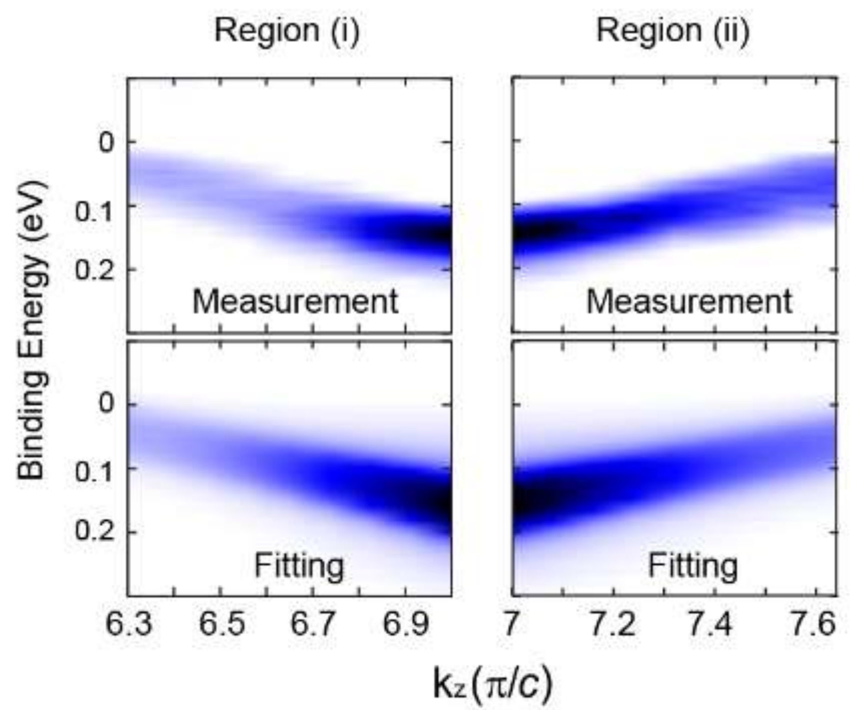
$$k_z = \sqrt{\frac{2m_e{}^*}{\hbar^2}(E_k + V_0) - \frac{2m_e E_k}{\hbar^2}\sin^2\theta} \neq k^V z$$

Extracting *kz* dispersions

$$I(k_z, E) \propto [|M^k_{f,i}|^2 \cdot A(k_z, E) \cdot f(E)] * R(\delta k_z, \delta E)$$

$$\delta k_z \approx 0.08 \text{ kBZ}$$





$|M^k_{f,i}|$: Photoemission matrix element

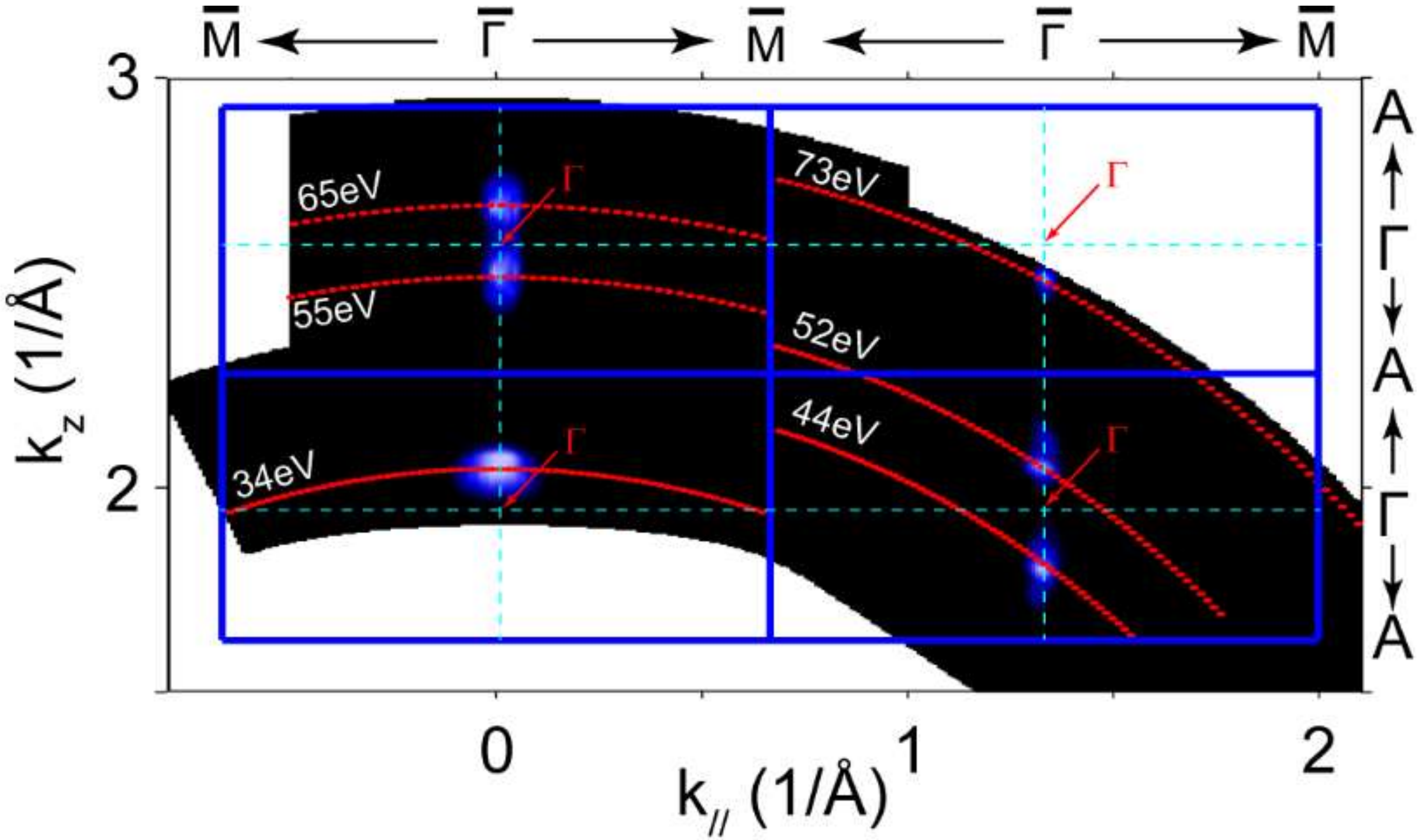
$A(k, E)$ Spectrum function

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

$$R(\delta k, \delta E) = e^{\left\{-\frac{1}{\sqrt{2}} \cdot \left(\left(\frac{K_Z}{\delta K_Z}\right)^2 + \left(\frac{E}{\delta E}\right)^2\right)\right\}}$$

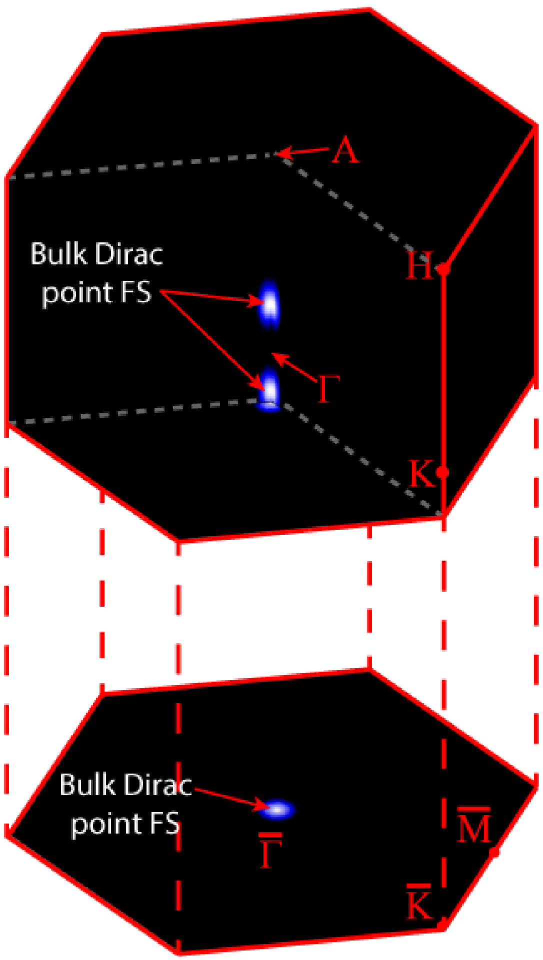
Extracting *kz* dispersions

Multiple BZ mapping along kz

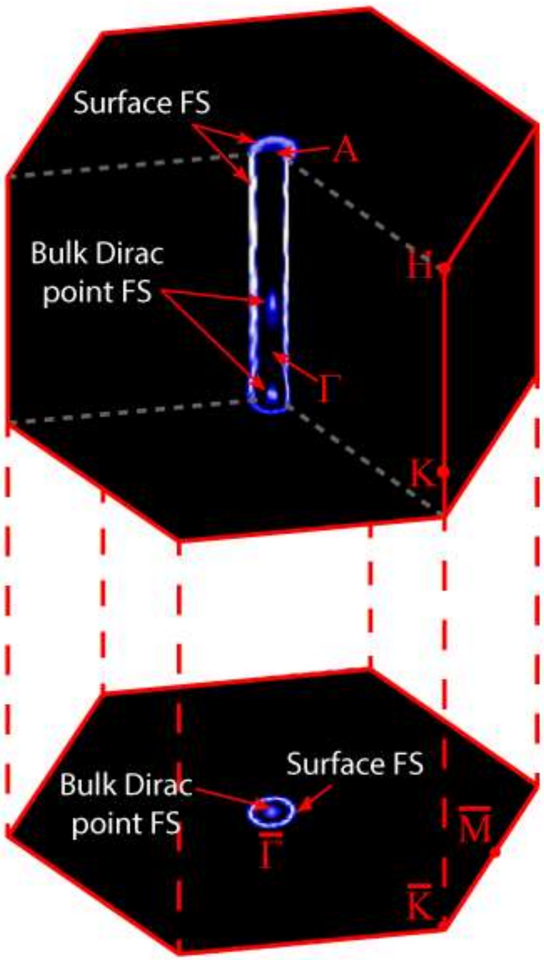


Complete 3D Fermi-surface mapping

Pristine surface

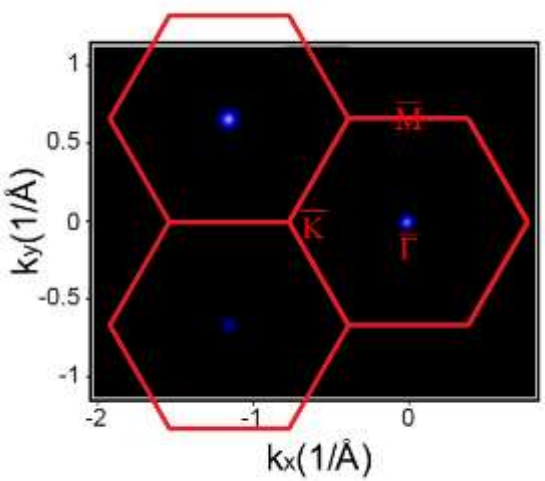


Surface with *Na*-vacancies

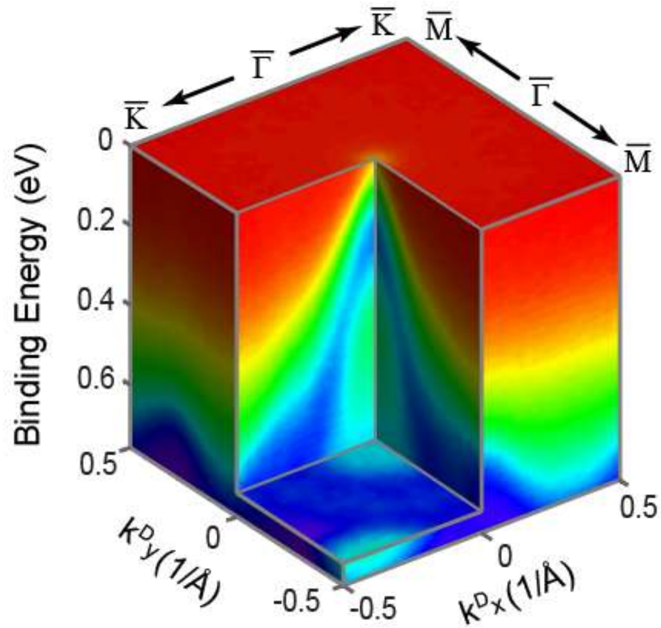


Projections to (*kx, ky, E*) space

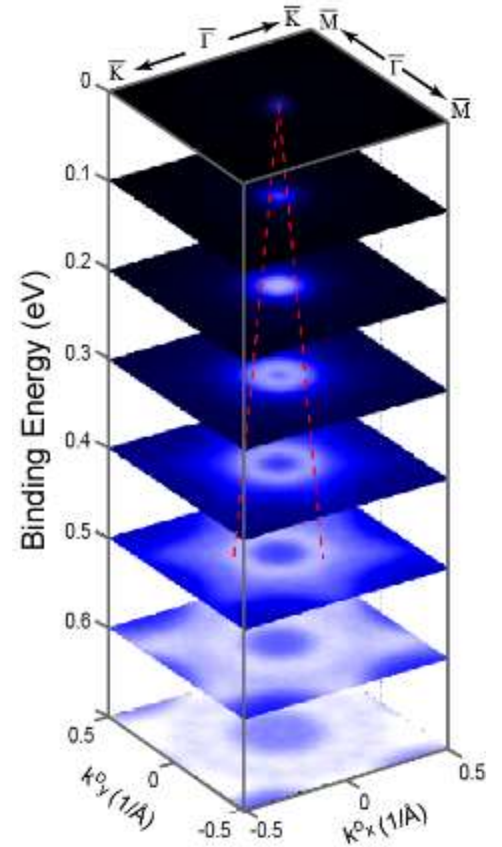
Fermi-surface



Band dispersion



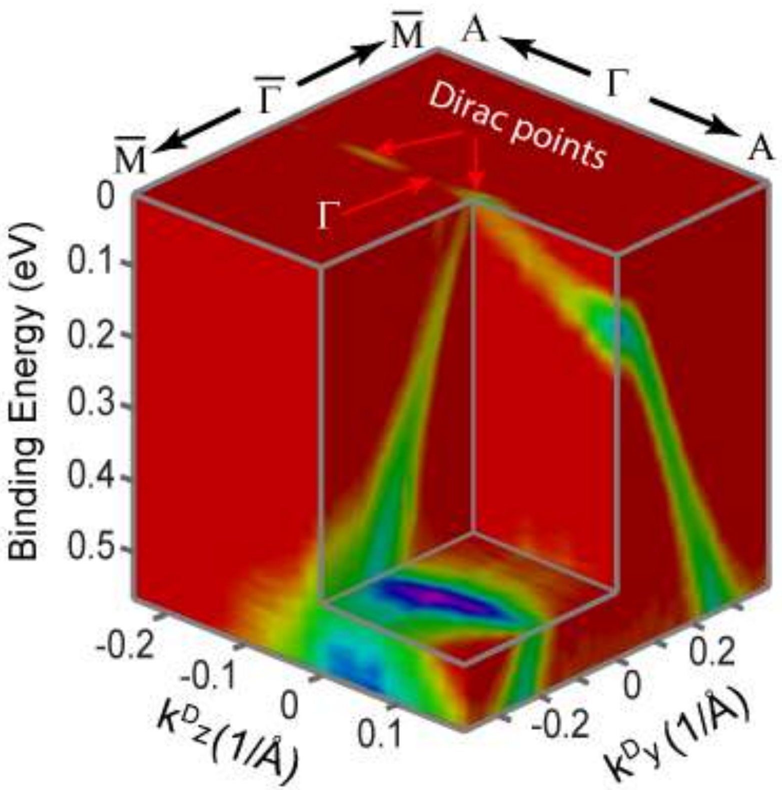
Constant energy contours



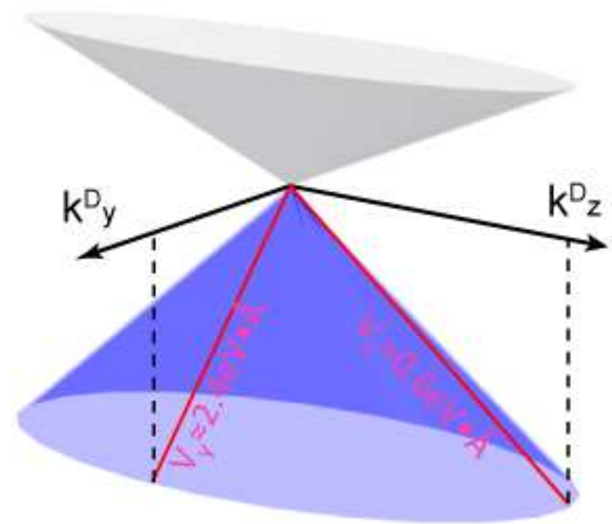
Vx = 2.75 eV•A or 4.17×10^5m/s
Vy = 2.39 eV•A or 3.63×10^5m/s

Projection to (ky, kz, E) space

Band dispersions



Strong anisotropy

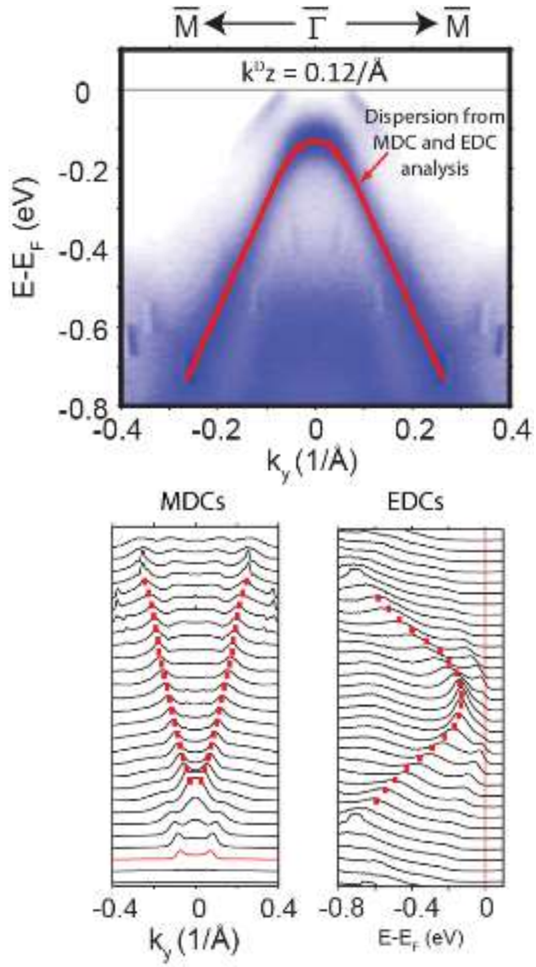


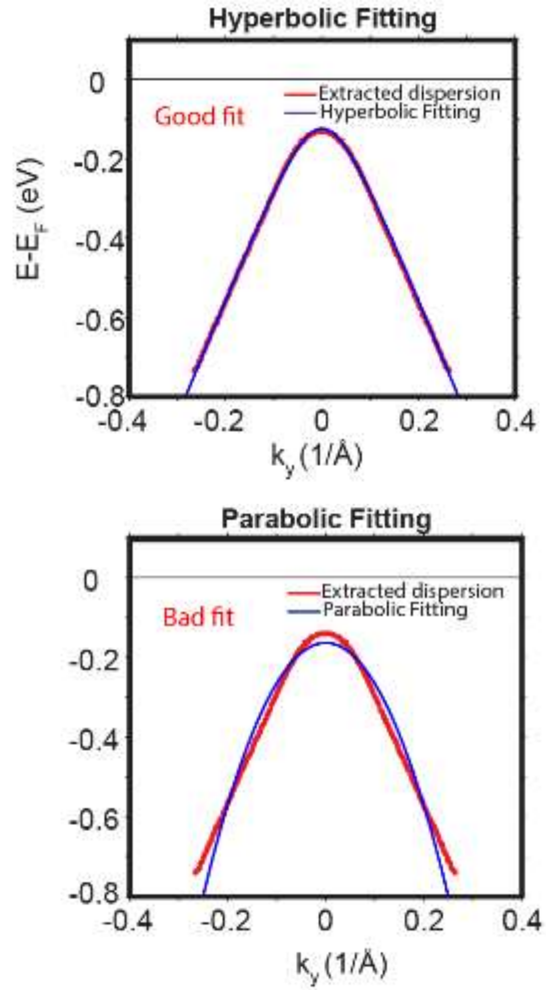
V_x = 2.75 eV•A or 4.17×10^5m/s

V_y = 2.39 eV•A or 3.63×10^5m/s

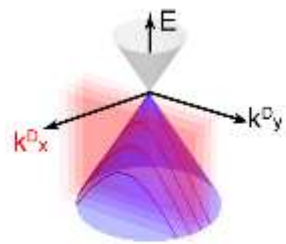
V_z = 0.6 eV•A or 0.95×10^5m/s

Unusual hyperbolic dispersion

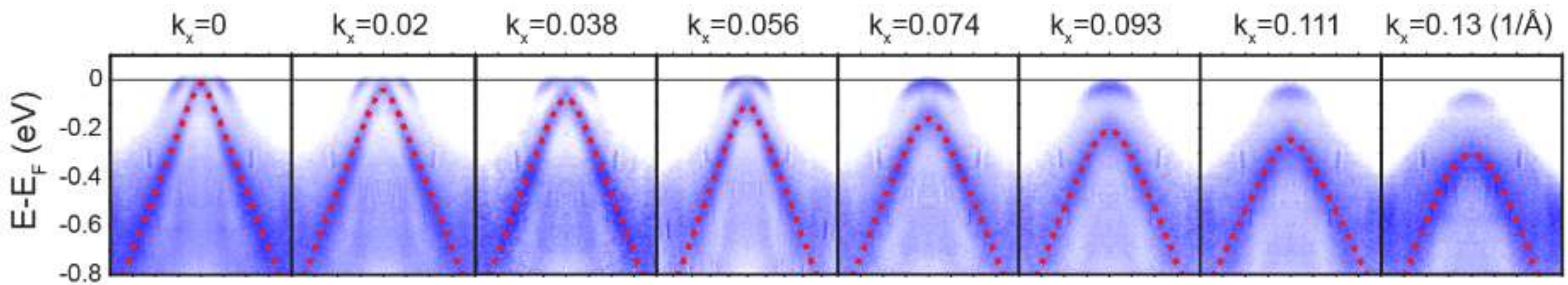


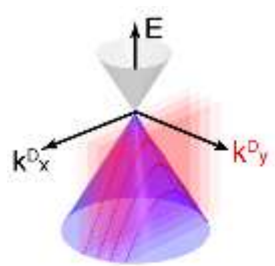


Dispersions at different *kx, ky* values

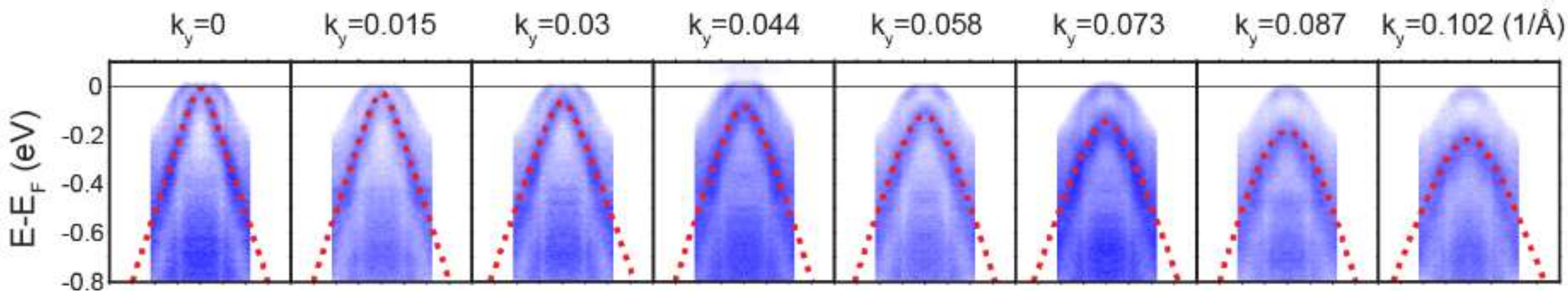


V_x = 2.75 eV•A or 4.17×10^5m/s

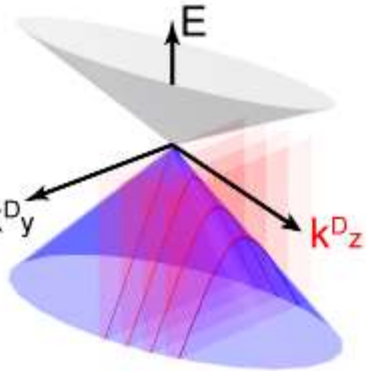




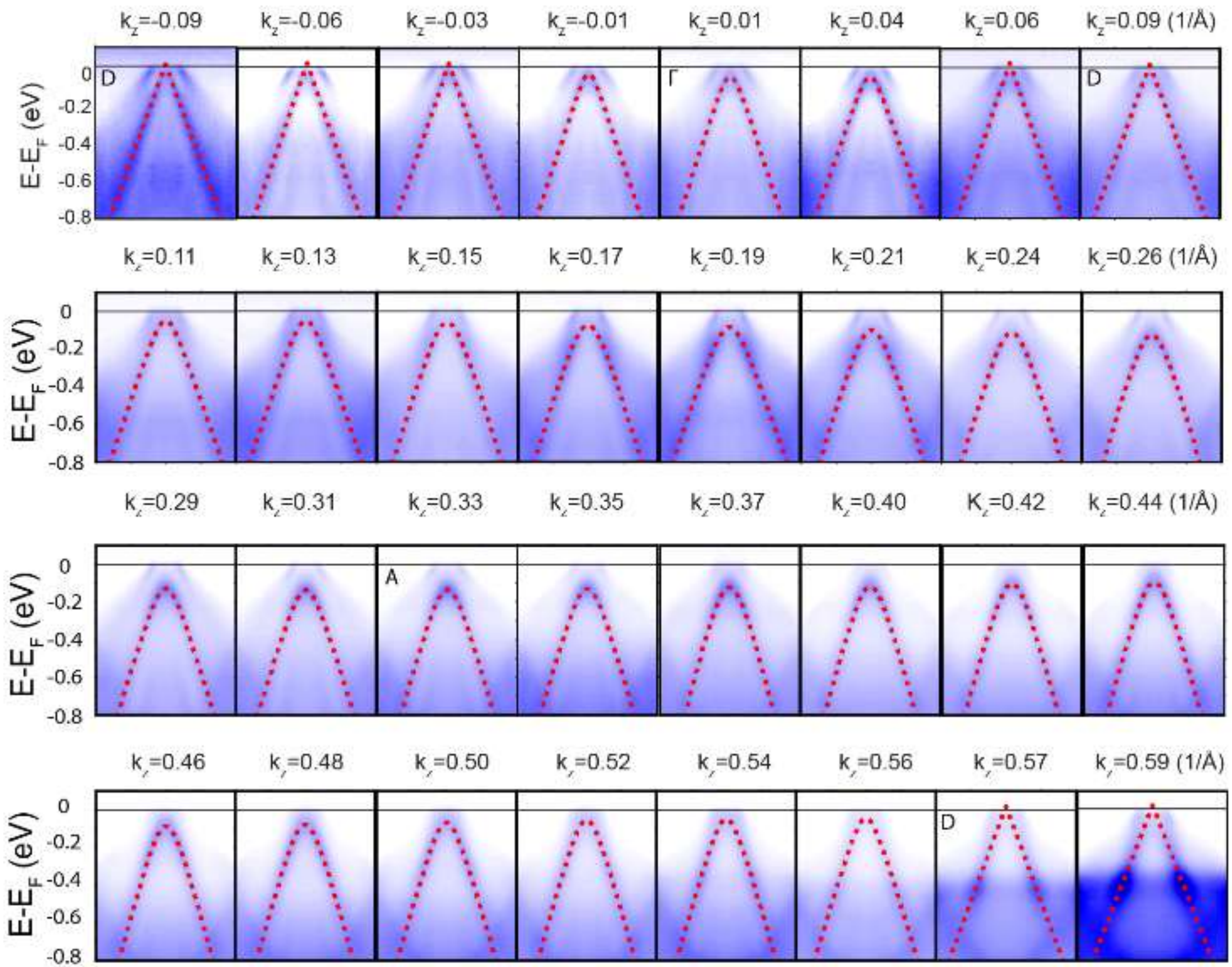
V_y = 2.39 eV•A or 3.63×10^5m/s



Dispersions at different *kz* values

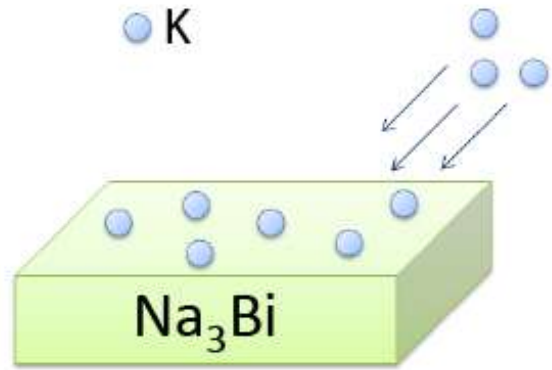


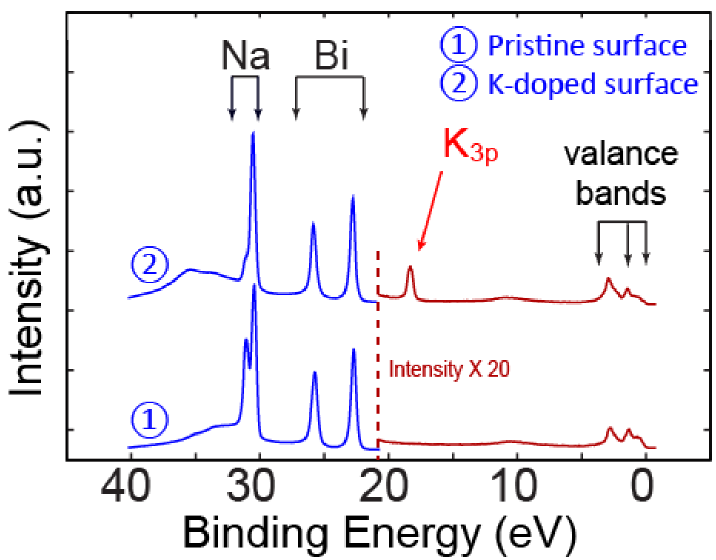
Vz = 0.6 eV•A
or 0.95×10^5m/s

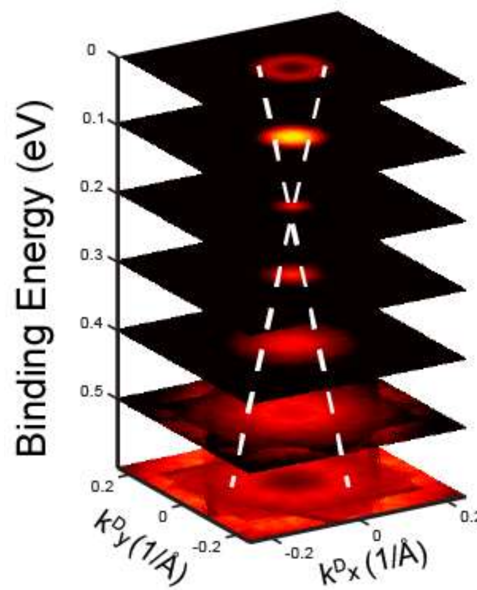


Observing the Dirac point and upper cone

***In-situ K*-doping**



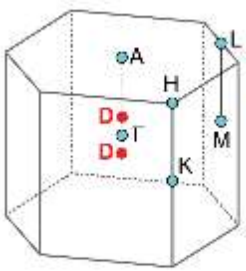




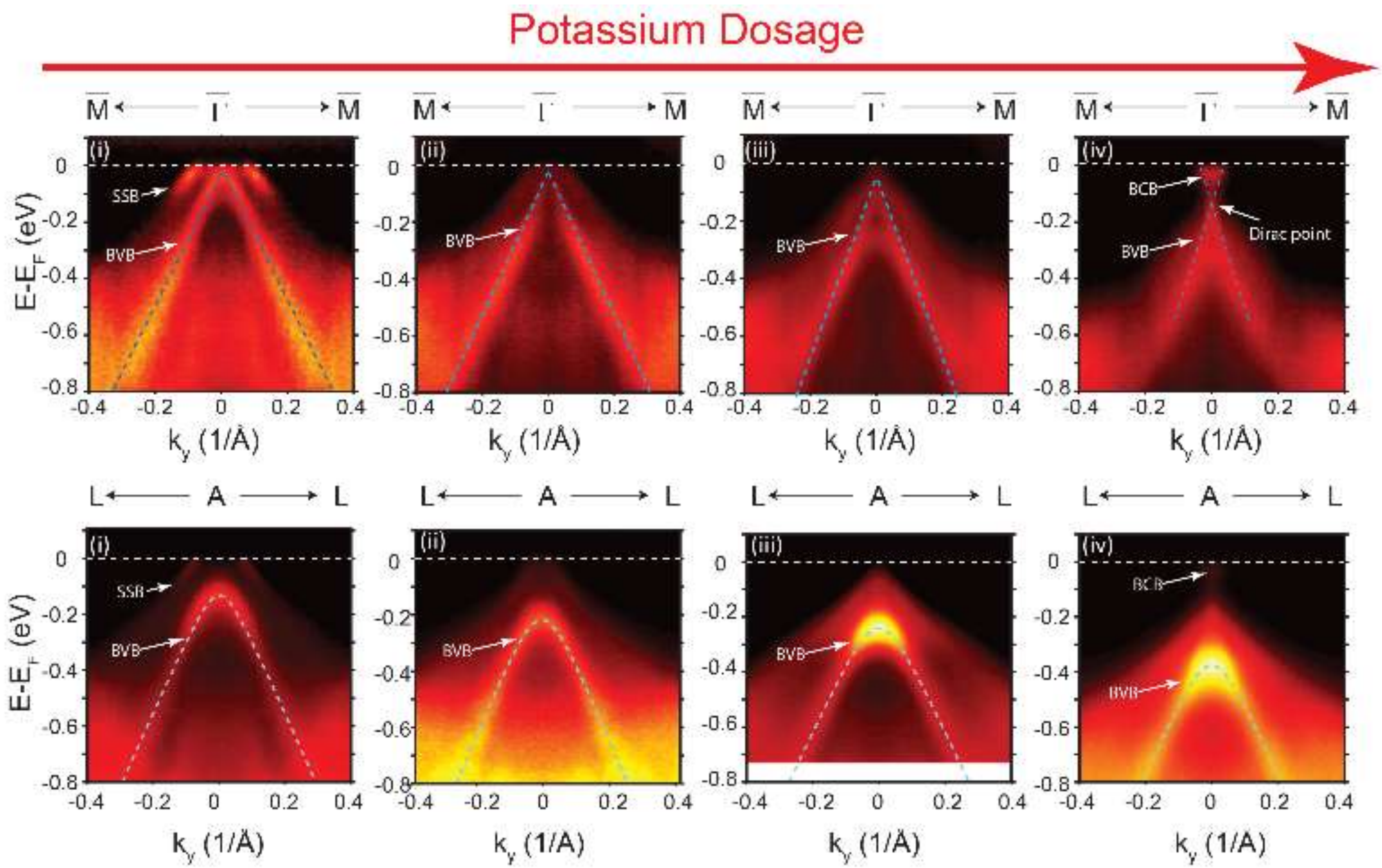
Protection of the crystalline symmetry

Disrupted surface state but intact bulk

kz=-0.09/Å
(Cut across the bulk Dirac point)

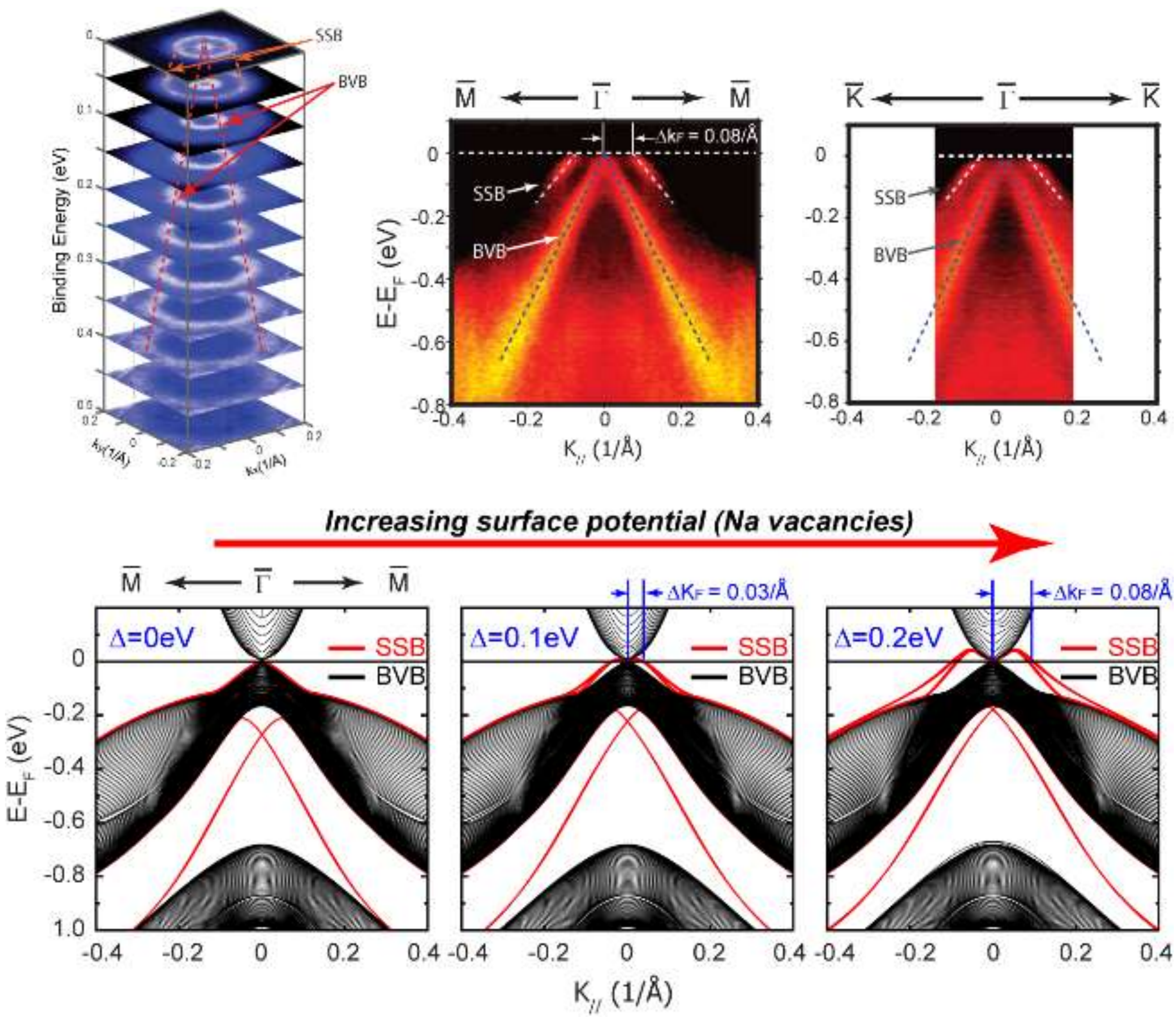


kz=0.327/Å
(Cut across the "A" point at the top of the BZ)



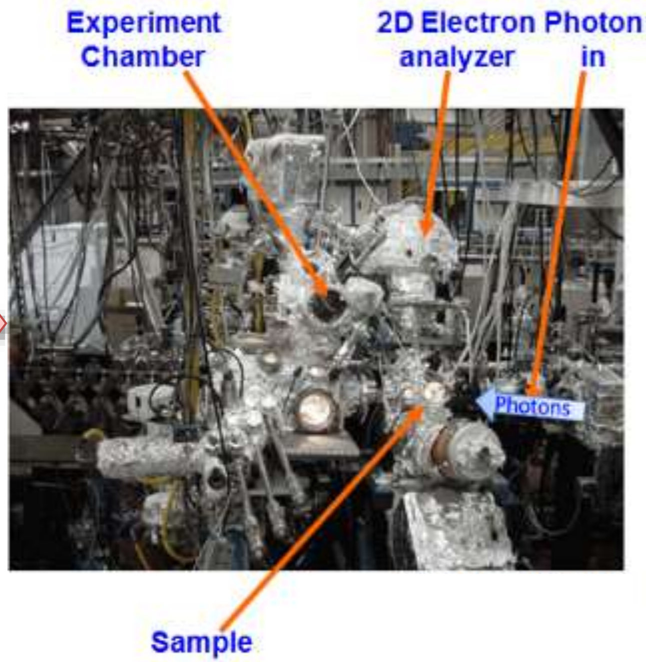
Emerge of the surface state

Results of the Na vacancies



The problem of Na_3Bi

Too reactive in ambient environment …

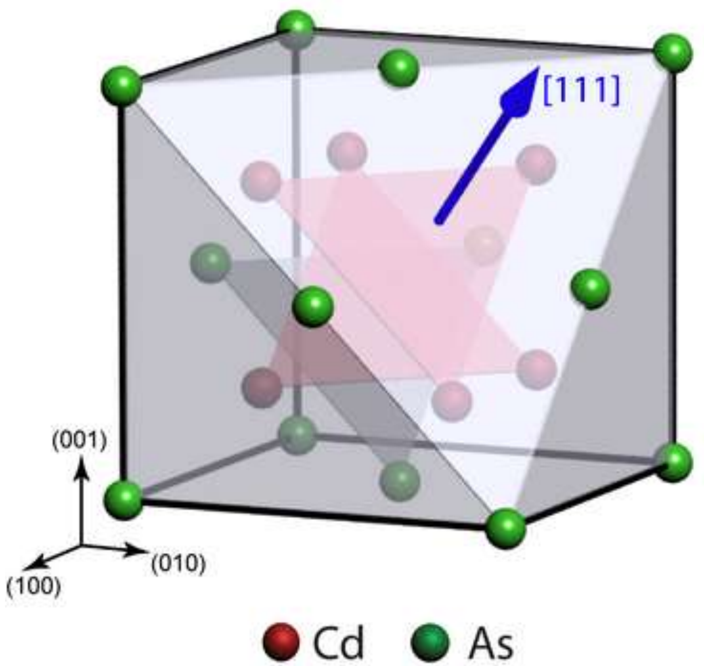


Hard to handle and used in functional devices

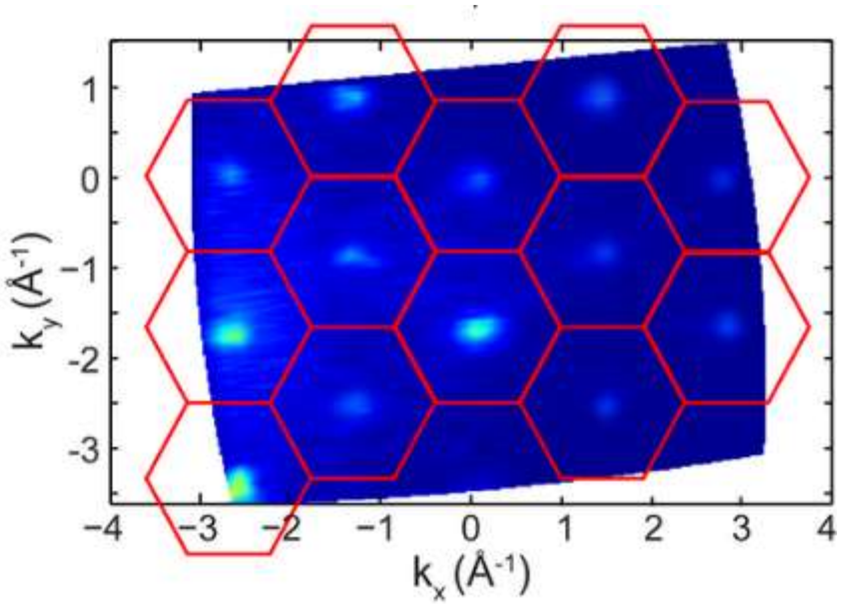
A stable 3D TDS, Cd_3As_2

Z. K. Liu. *et. al.*, Nature Materials, 13, 677 (2014)

Crystal structure



Brillouin Zone

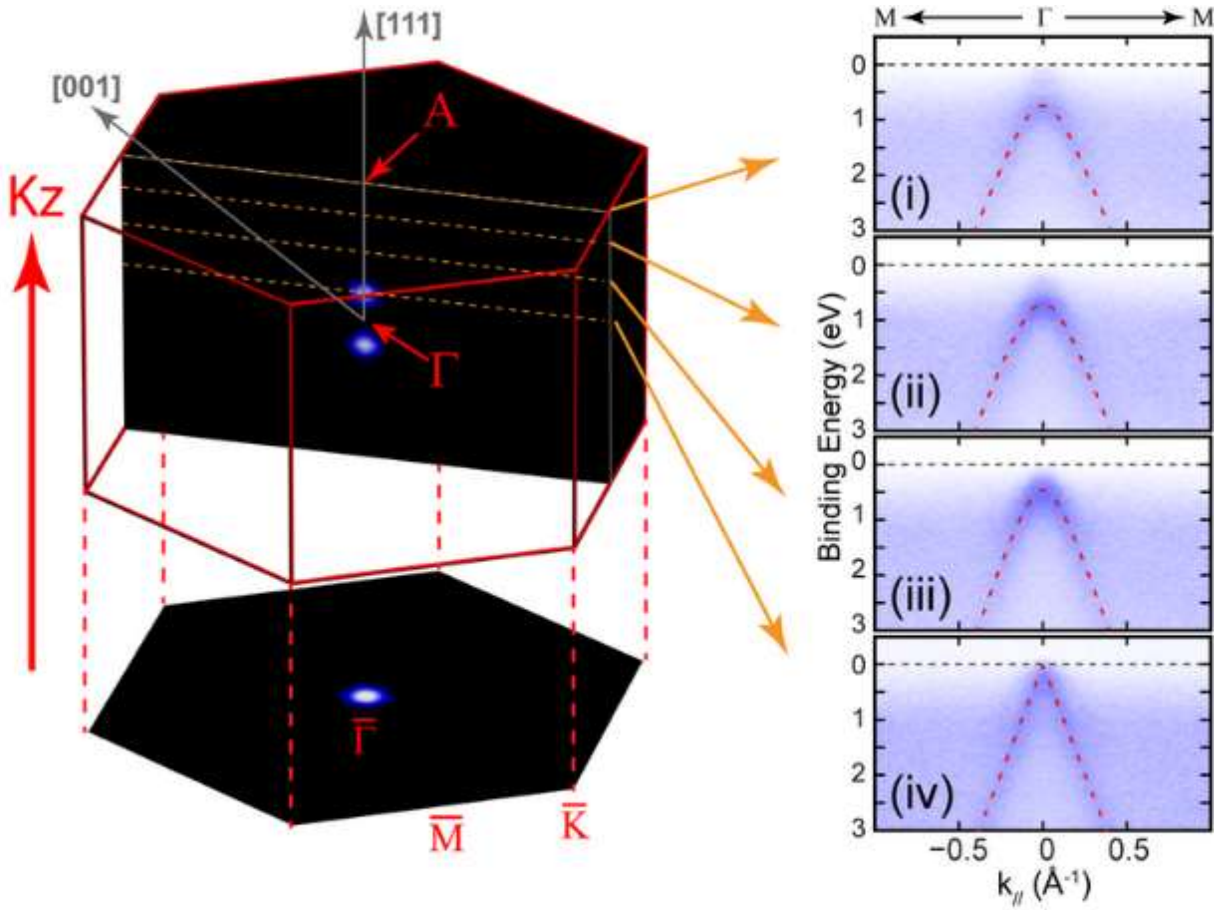


A stable 3D TDS, Cd_3As_2

Z. K. Liu. *et. al.*, Nature Materials, 13, 677 (2014)

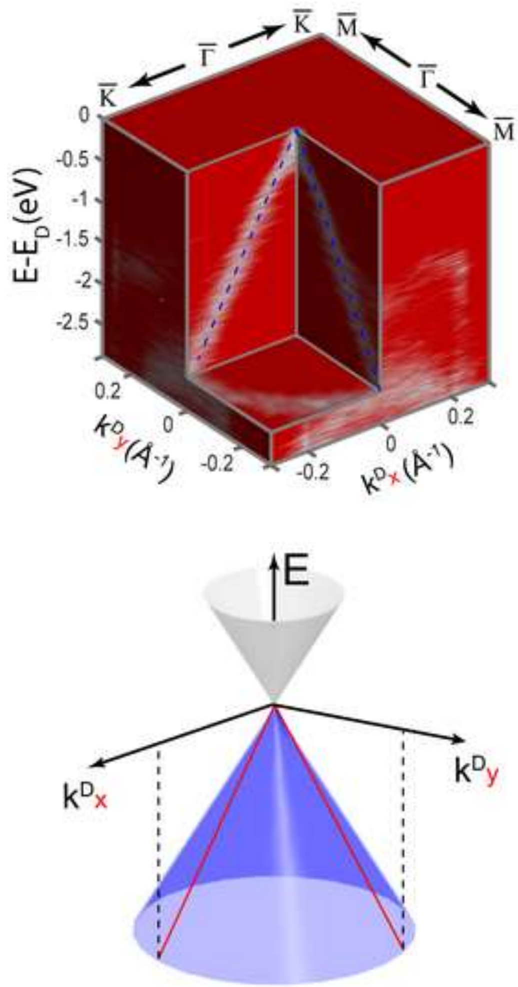
3D Brillouin Zone

Dispersion at different k_z

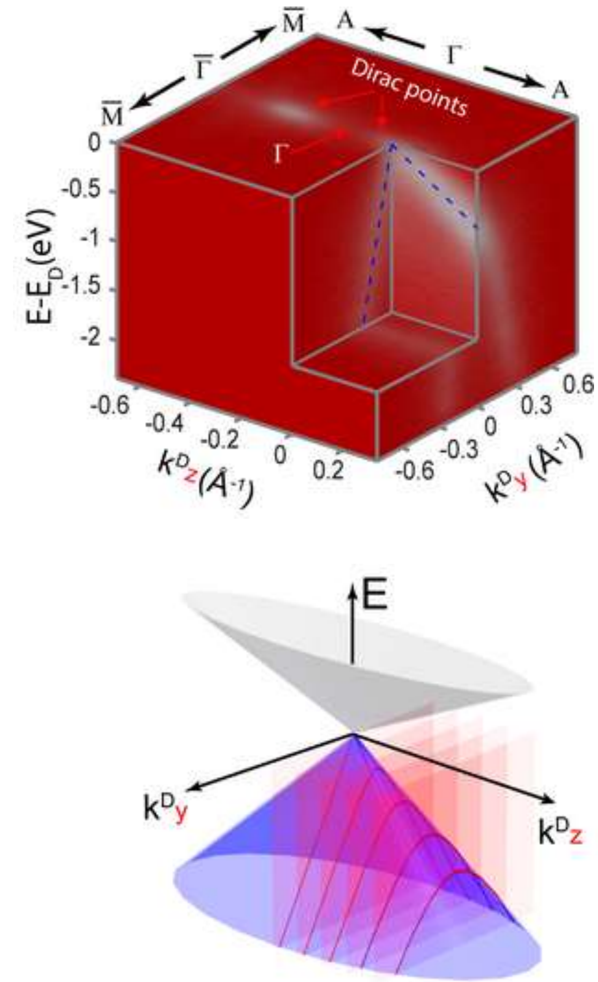


A stable 3D TDS, Cd_3As_2

Projection to (K_x,k_y,E)



Projection to (K_y,k_z,E)



Can we find other topological matter?

Topologically **trivial** world

Topologically **non-trivial** world

What’s next?