國家同步輻射研究中心
National Synchrotron Radiation Research Center

Angle-resolved photoemission spectroscopy of quantum materials

Cheng-Maw Cheng

National Synchrotron Radiation Research Center
Department of Physics, NSYSU
Graduate Institute of Applied Science and Technology, NTUST

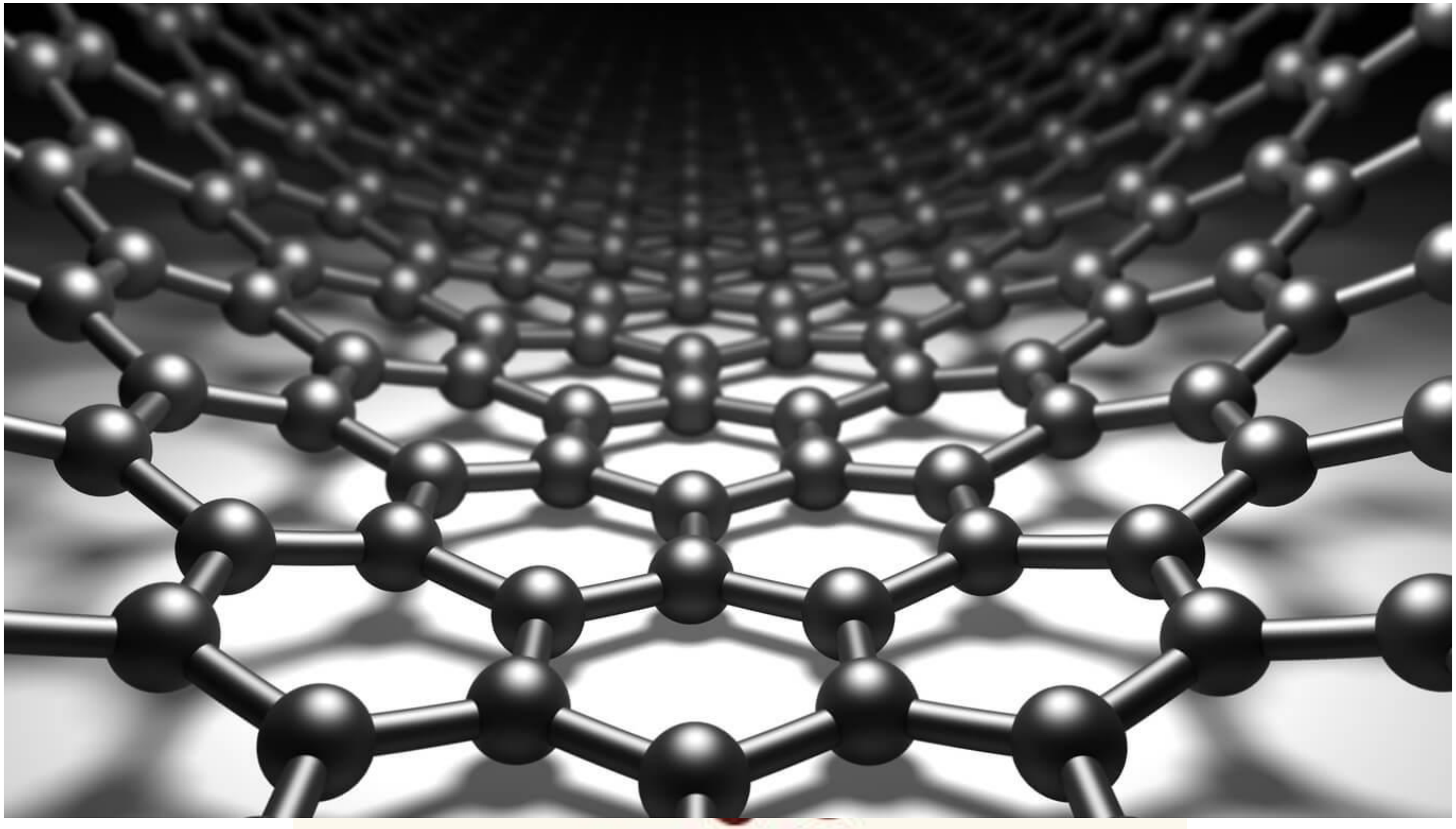
Outline

- Introduction to angle-resolved photoemission spectroscopy (ARPES)
  - *The concept of energy band.*
  - *The principle of ARPES.*
  - *Scientific case : cuprates, graphene, TMDs and topological insulators.*

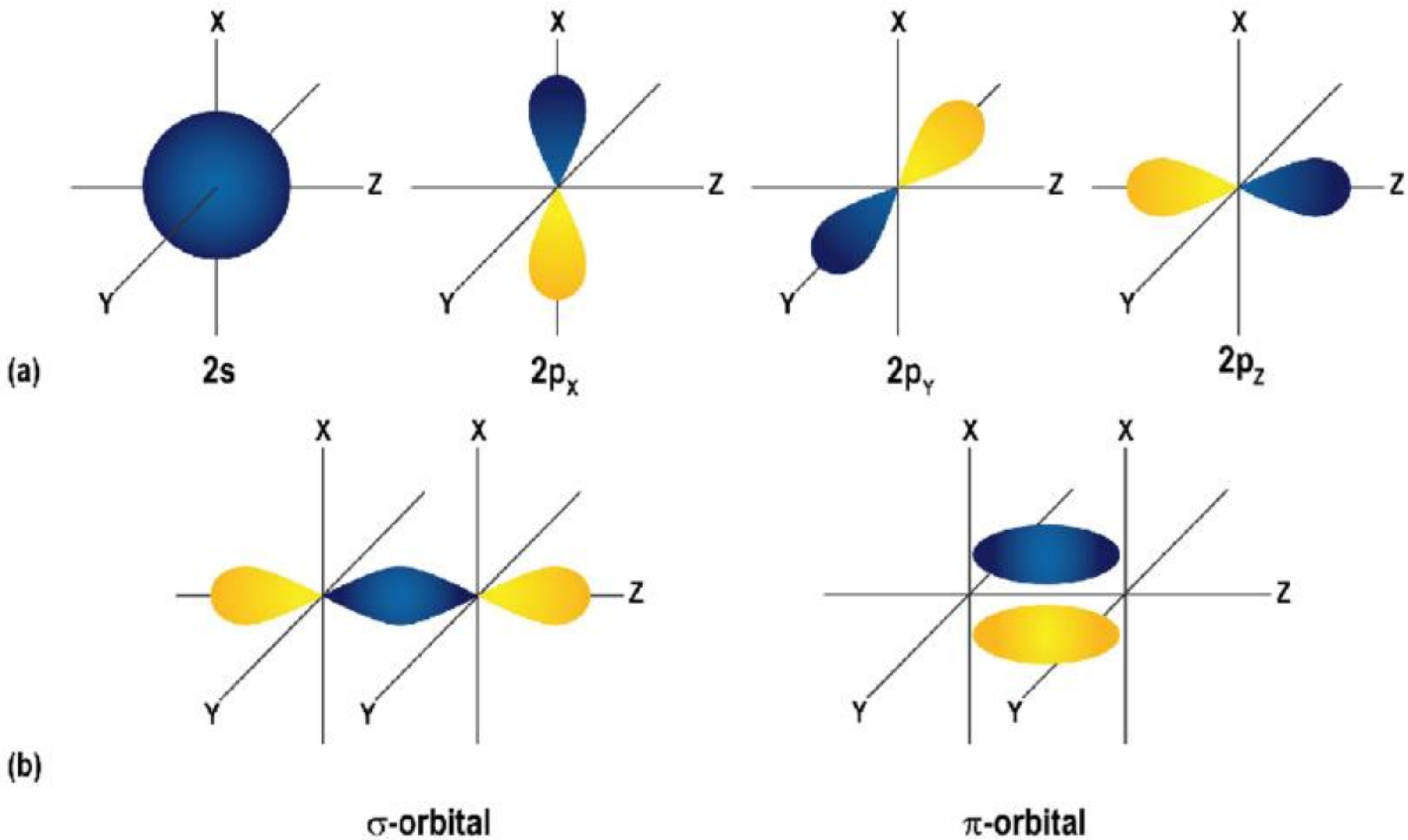
- Probe the electronic structure of emergent materials
  - *Scientific opportunities in nanoARPES.*
  - *The challenge and design concept of nanoARPES.*
  - *Beamline and end station design.*

- Summary

What we are interested in ....

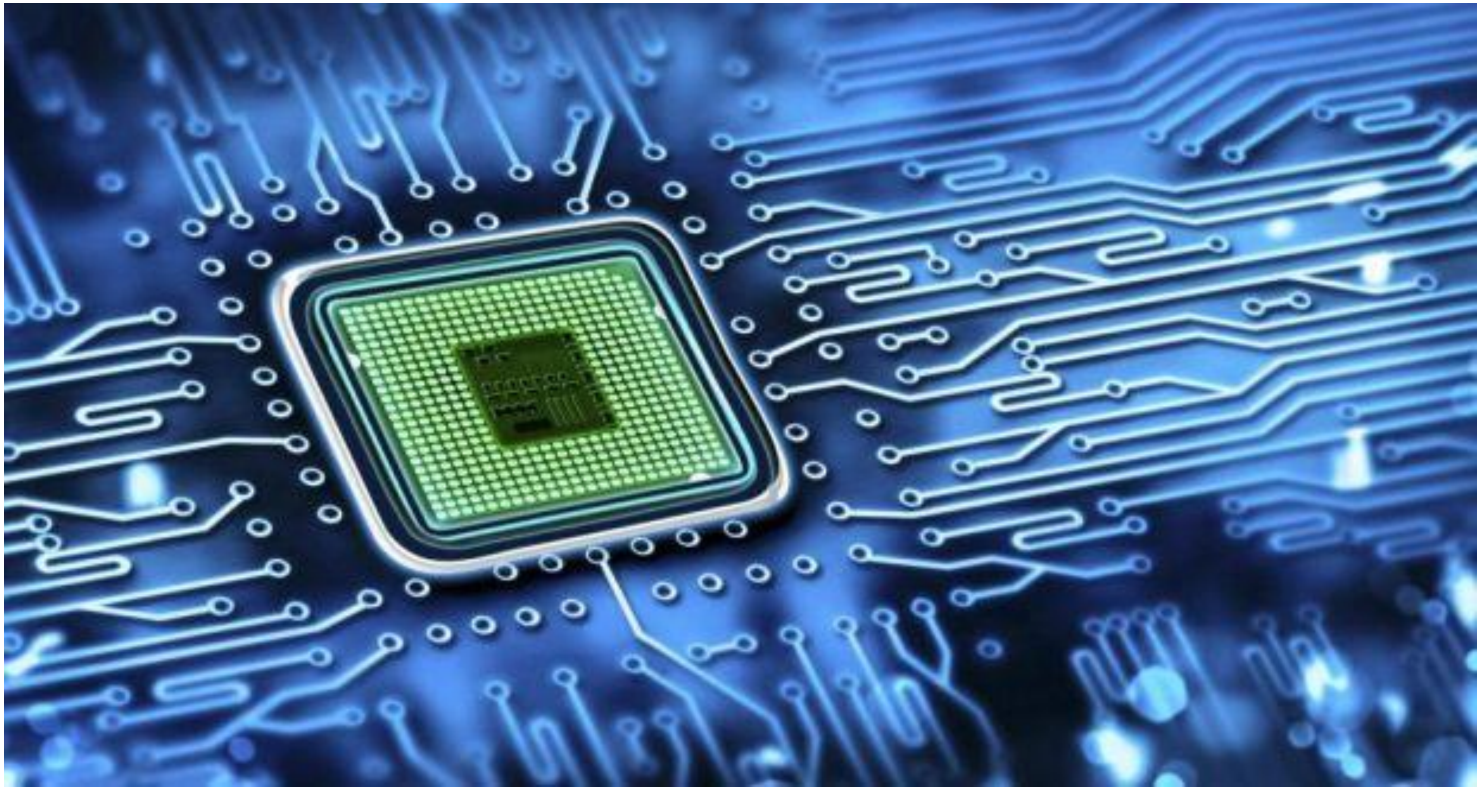


What we are interested in ....



Wijeratne, Kosala, Conducting Polymer Electrodes for Thermogalvanic Cells (2018)

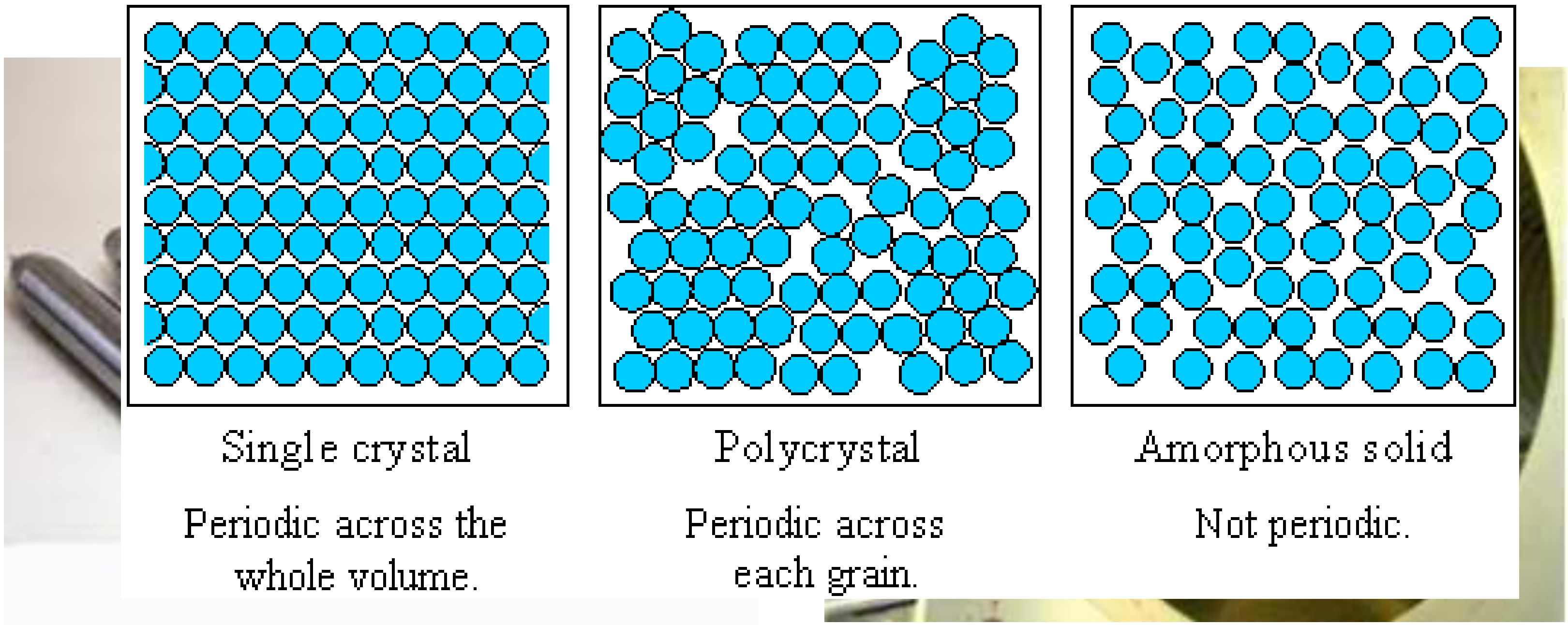
Silicon technology



https://theweek.com/articles/634470/next-great-race-between-china-over-computer-chips

What is single crystal

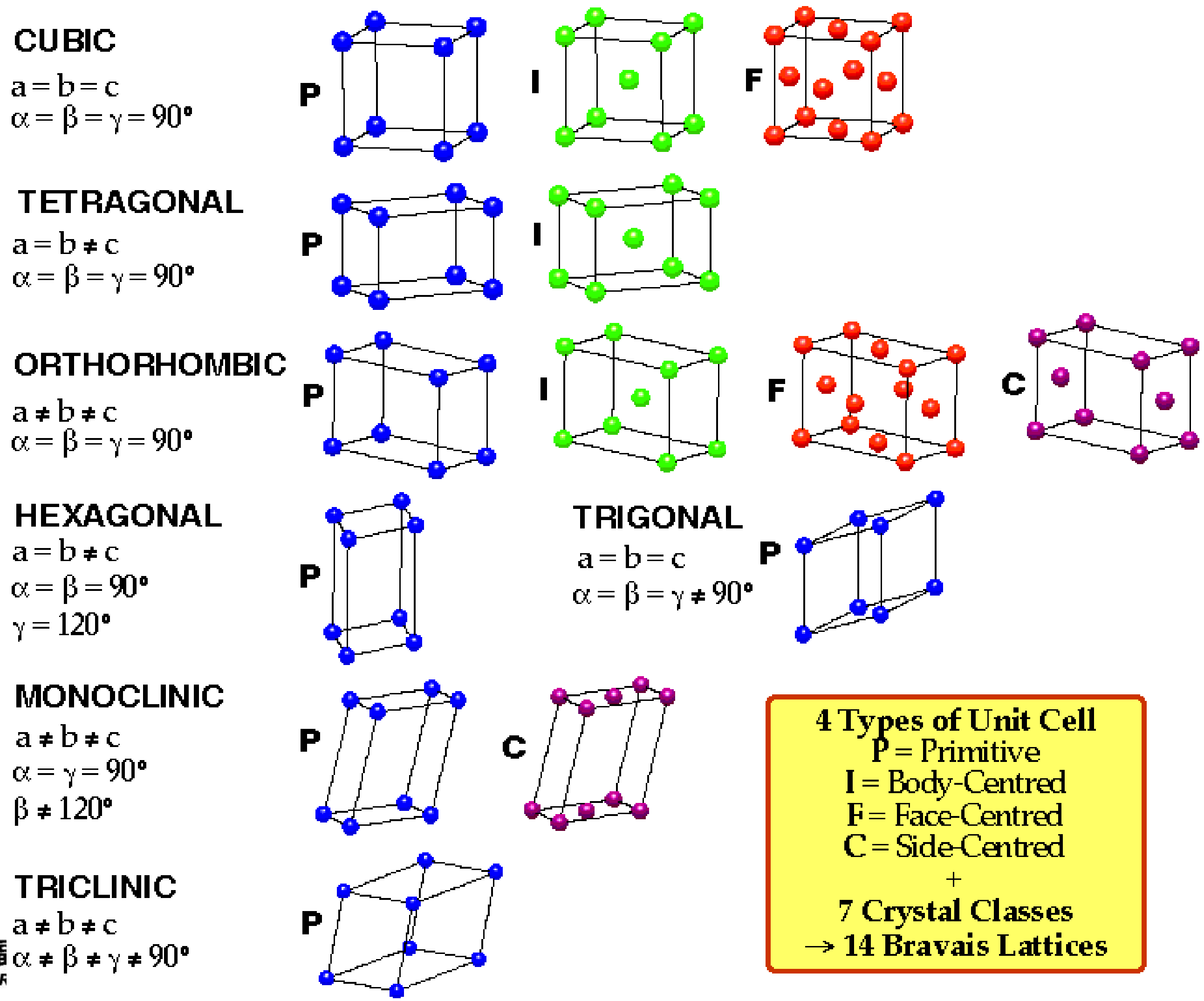
High quality single crystal



國家同步輻射研究中心
National Synchrotron Radiation Research Center

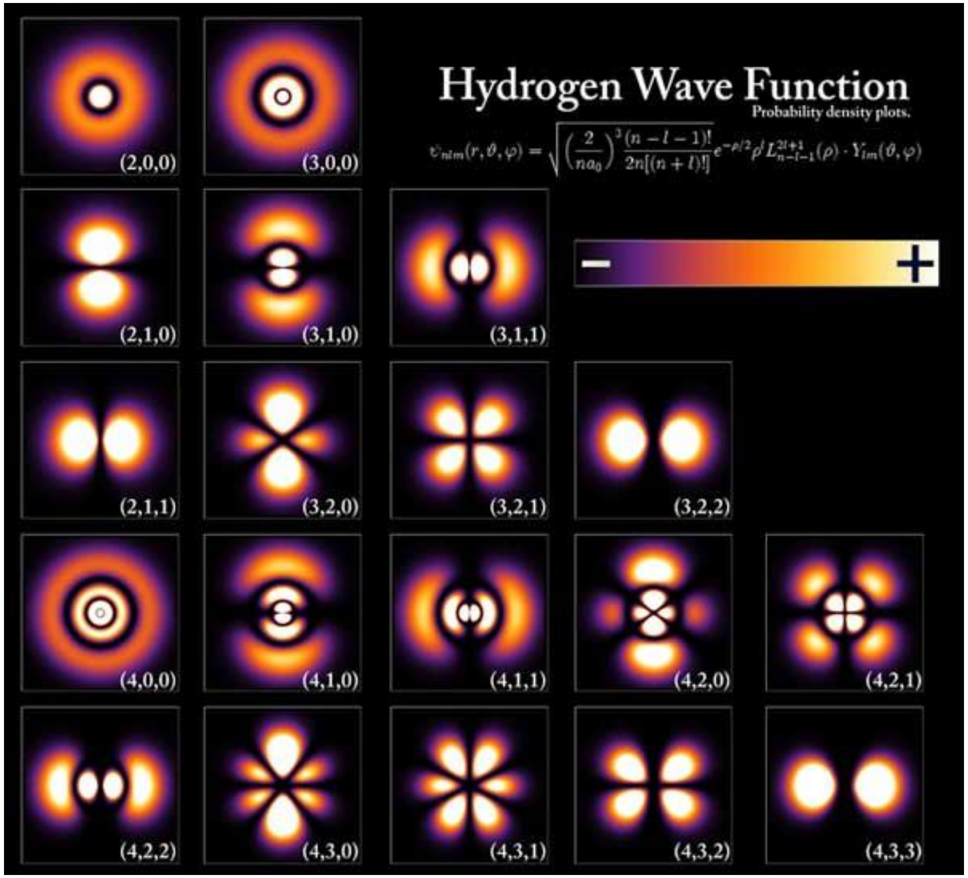
https://www.doitpoms.ac.uk/tlplib/atomic-scale-structure/intro.php

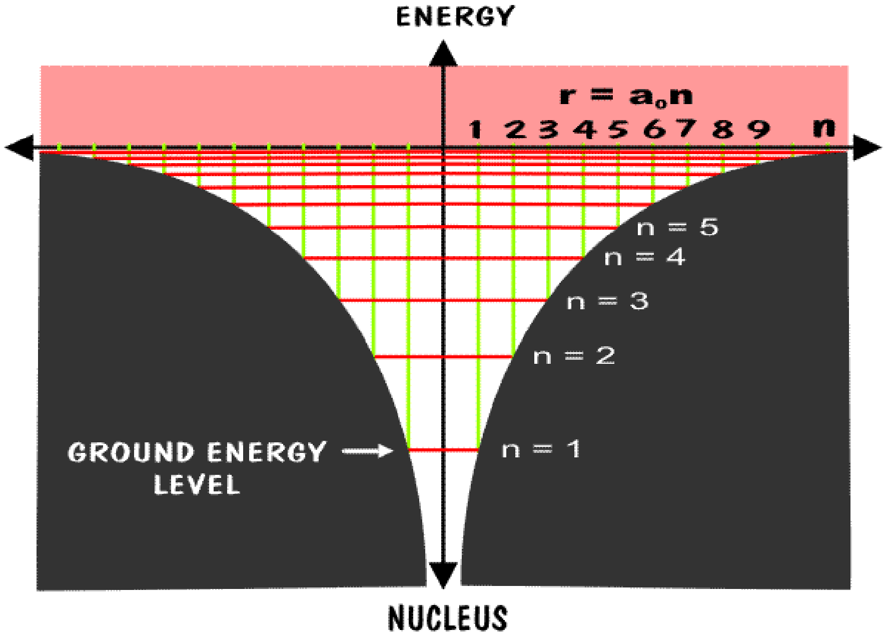
Crystal structures



國家同步輻
National Synchrotron R

The energy level of hydrogen atom

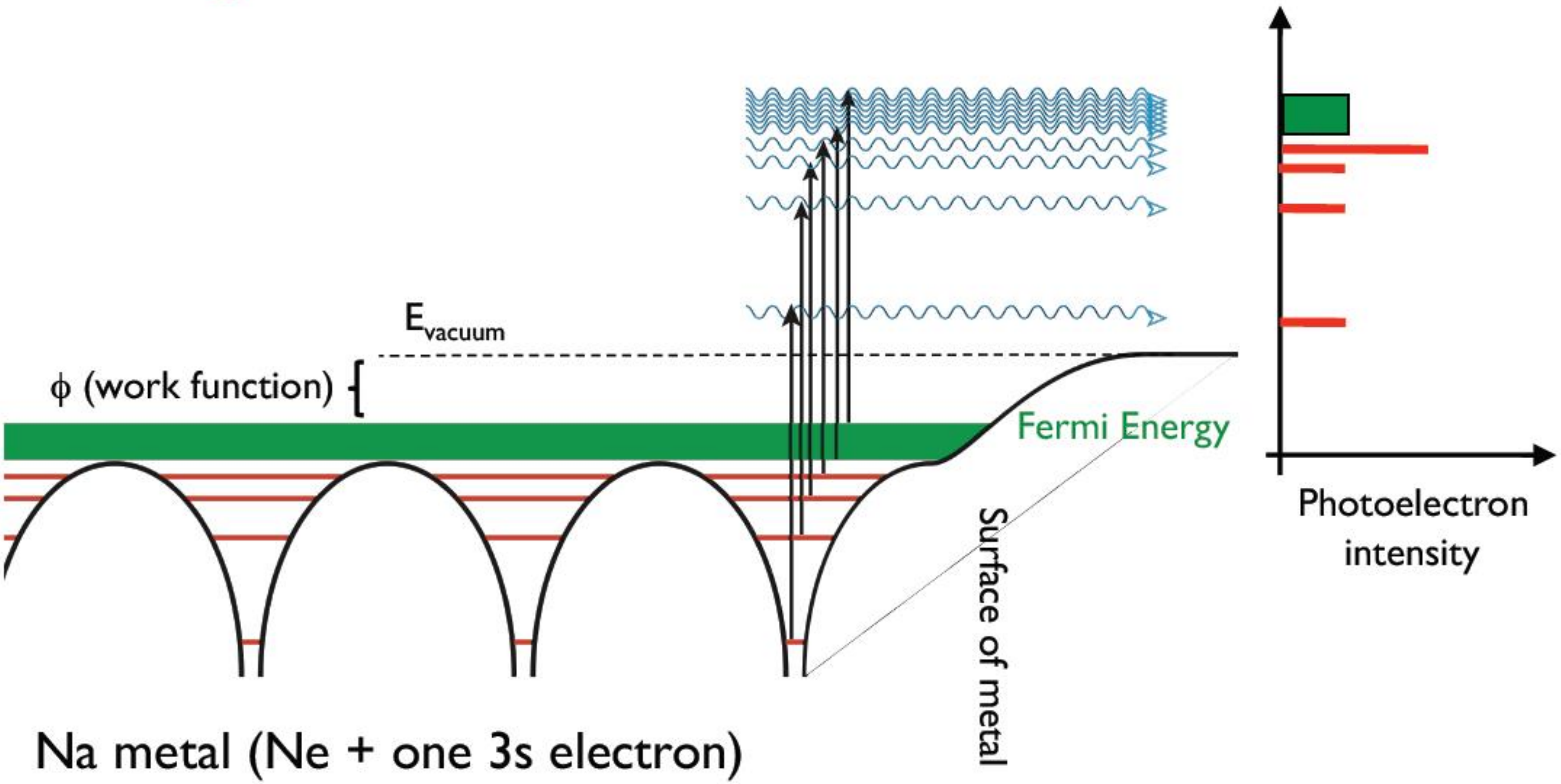




國家同步輻射研究中心
National Synchrotron Radiation Research Center

https://en.wikipedia.org/wiki/Quantum_mechanics

- Deeply bound "*core*" electrons remain basically unchanged
- Outermost "*valence*" electrons hybridize forming continuous "*energy bands*"



Band Theory

Two approximations

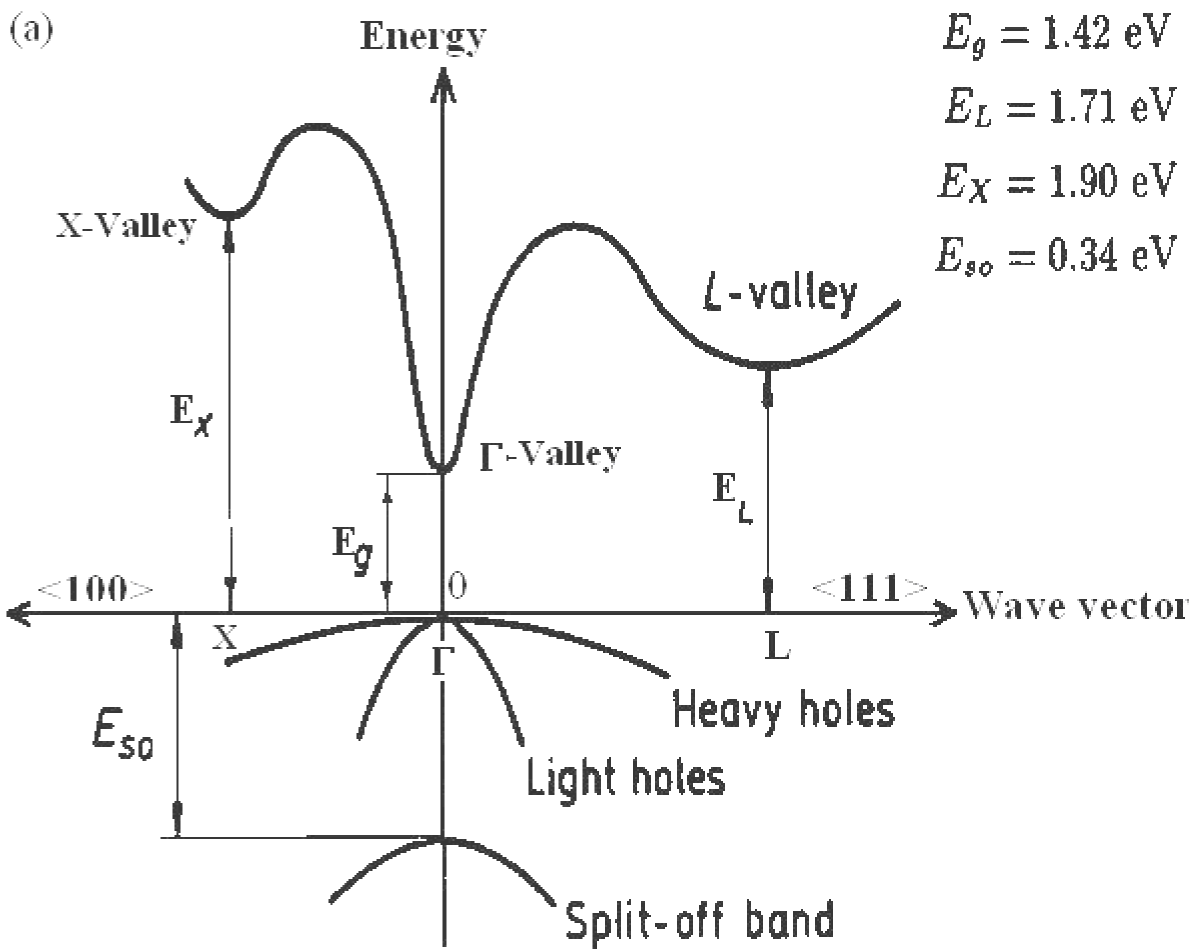
Nearly free electrons. Electrons are non-interacting in a periodic crystal potential which is relatively weak and can be treated as a perturbation. As in the free-electron-gas model, they are still subject to the Pauli exclusion principle.

Free electron gas :
The interactions between electrons and between electrons and nuclei are turned off, subject only to the Pauli exclusion principle.

Tightly-bonding approximation

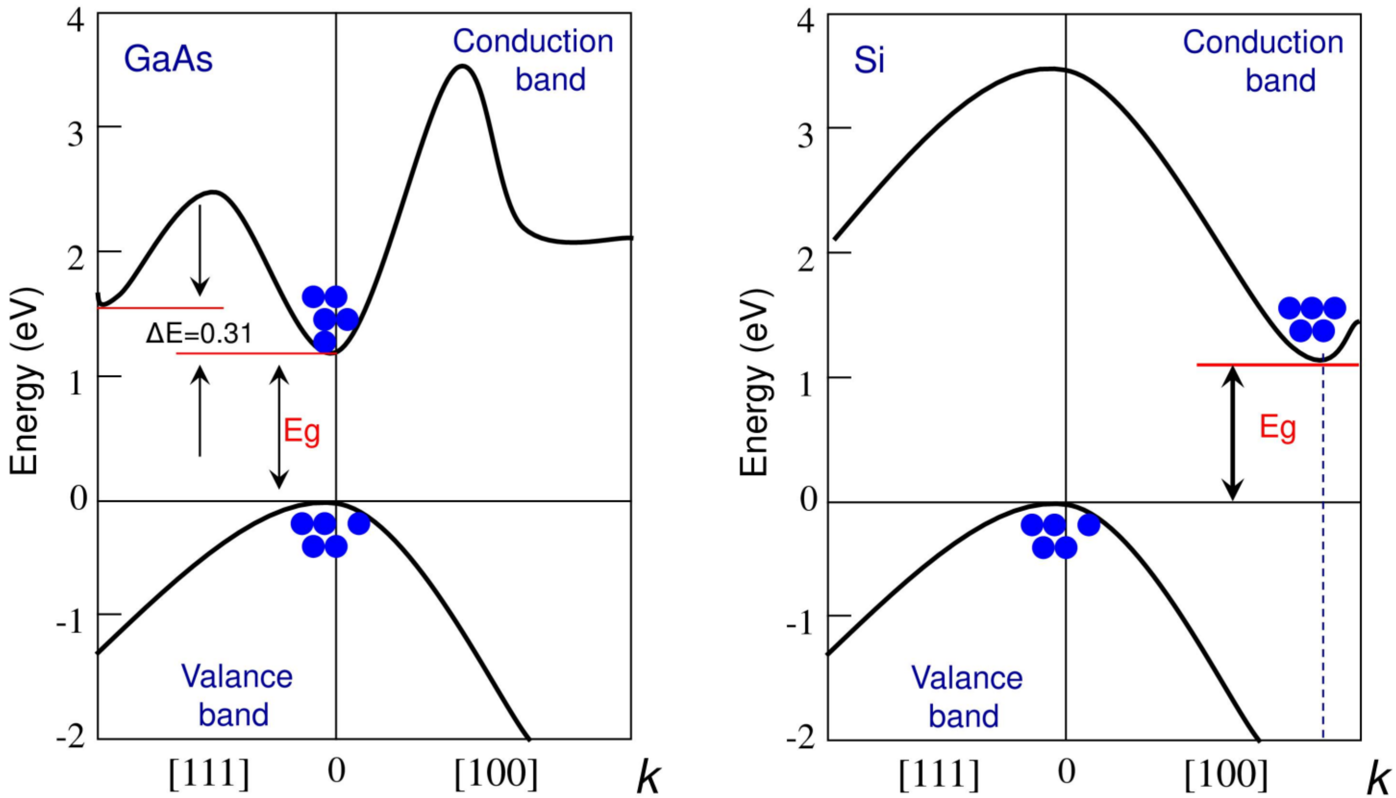
Electrons are tightly bound to particular atoms, overlapping only weakly with neighbors.

The main features of the E-k relation of GaAs



$E_g = 1.42$ eV
$E_L = 1.71$ eV
$E_X = 1.90$ eV
$E_{so} = 0.34$ eV

Direct and Indirect Band Gap



Energy band structures of *GaAs* and *Si*

Fermi-Dirac Distribution

Almost every electronic transport property of solids is proportional to $D(\mathcal{E}_F)$.

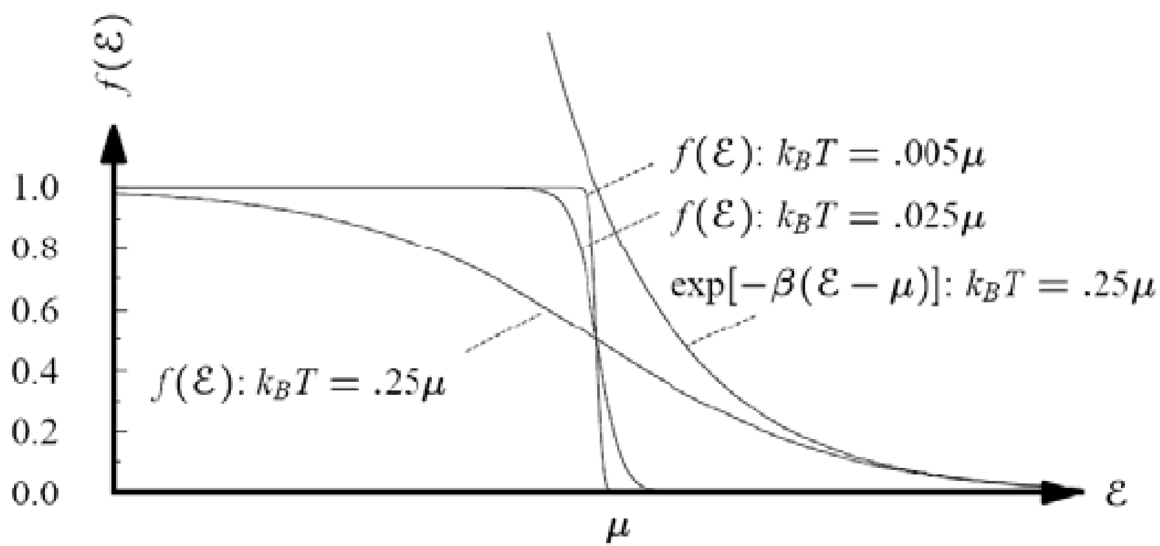
Thermal Properties of Free Electron Gas:

Fermi function (Fermi-Dirac distribution)

$$f(\mathcal{E}) = \frac{1}{e^{(\mathcal{E}-\mu)/k_BT}+1}$$

RT ~ 25 meV

4KT broadening ~ 100 meV



國家同步輻射研究中心
National Synchrotron Radiation Research Center

Measurement of the Fermi level

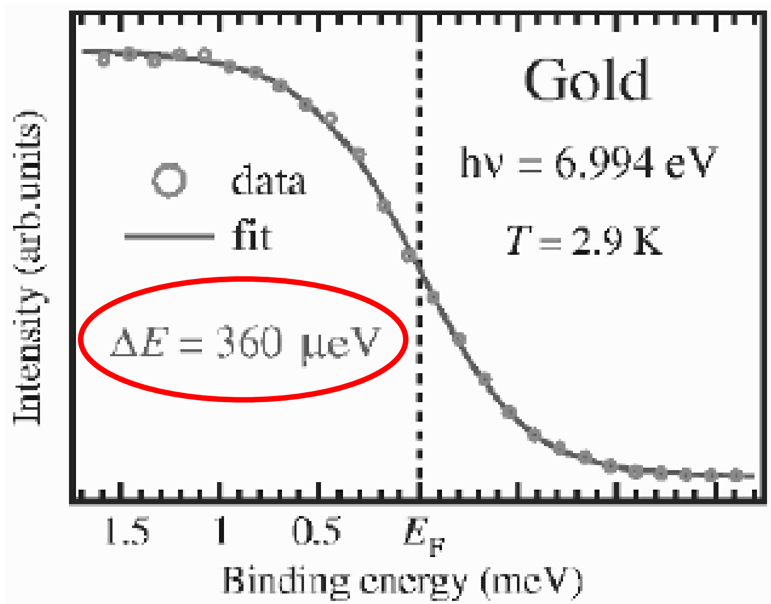
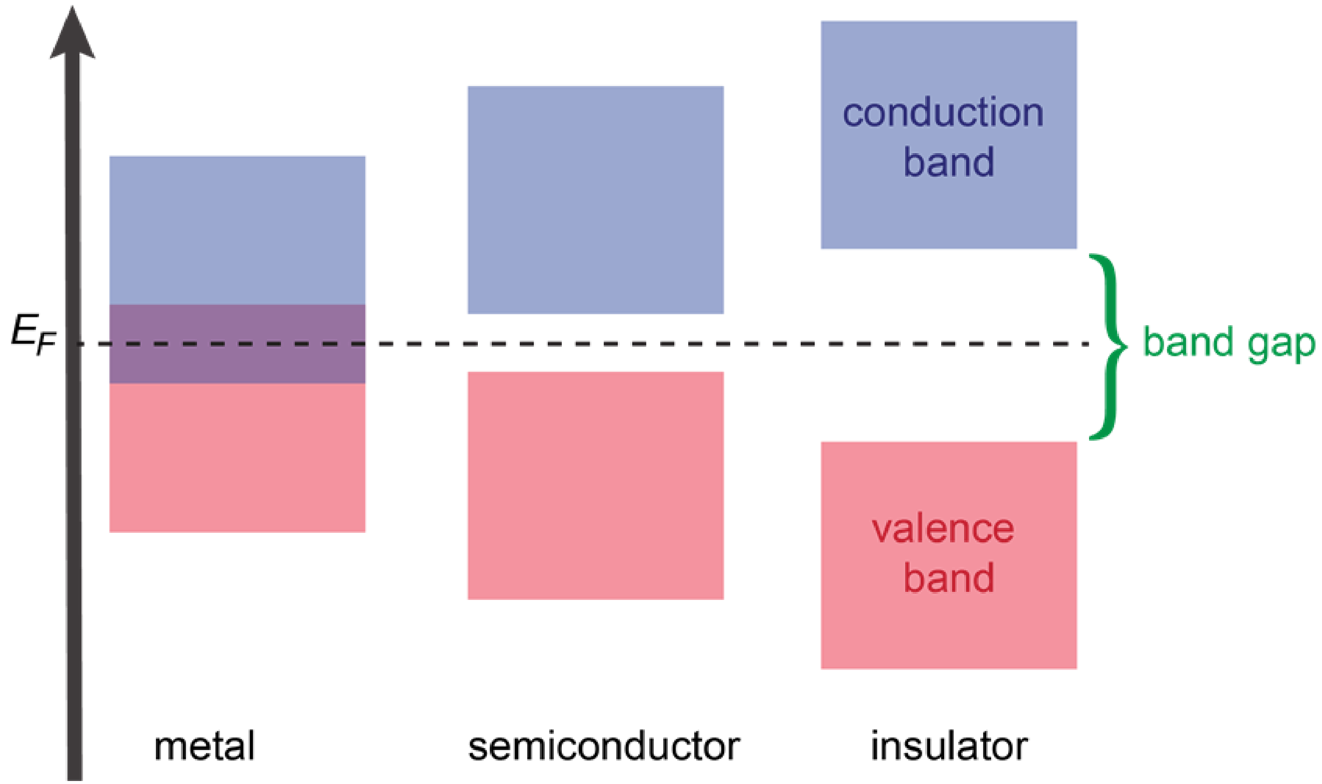


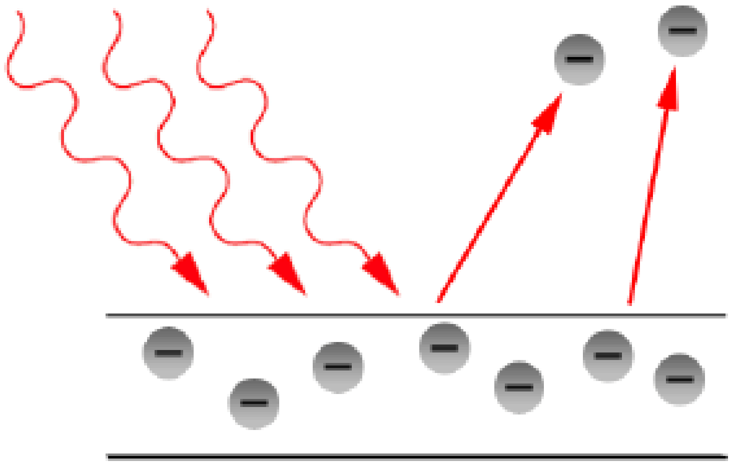
Fig. 2.3. Ultra-high resolution photoemission spectrum on a polycrystalline gold sample (evaporated Au film) for the determination of the energy resolution. The Fermi edge was measured at $T = 2.9\,K$ using a frequency tripled ($KBe_2BO_3F_2$ crystal, KBBF) YVO_3 laser for the photoexcitation ($h\nu = 6.994\,eV$) [15]

Hufner, Very high resolution photoelectron spectroscopy

Energy Band Diagram

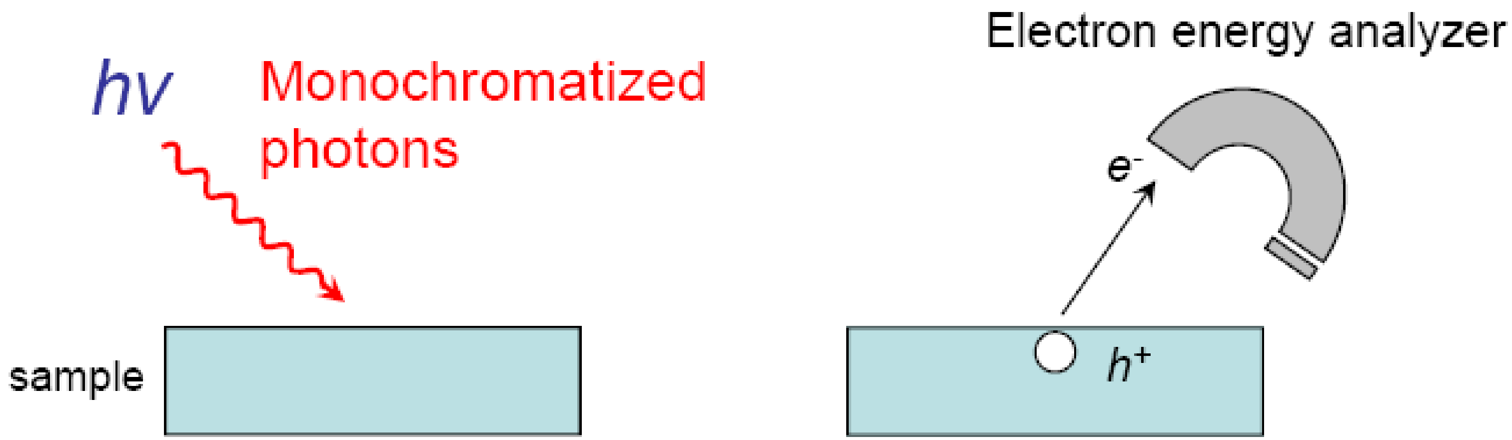


What is photoemission?



Photon in –> electron out (emission)

What is photoemission spectroscopy? (photoelectron spectroscopy) (PES)



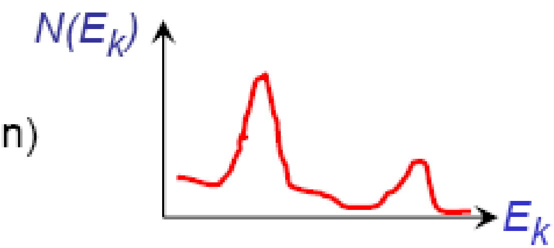
Initial state: ground (neutral) state

Final state: hole (excited) state

Conservation of energy

$$E_k = h\nu + E_i - E_f$$ (most general expression)

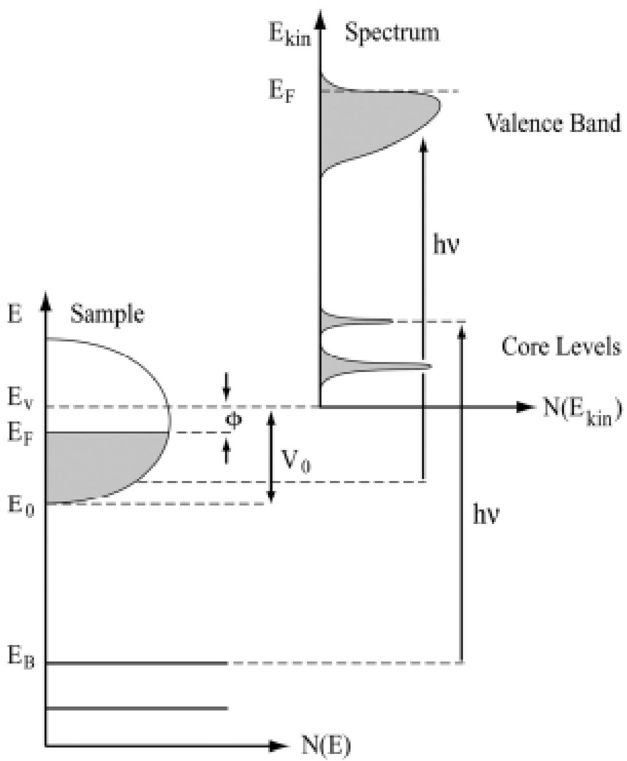
E_k : photoelectron kinetic energy
$E_i(N)$: total initial state system energy
$E_f(N\text{-}1)$: total final state system energy



Energy Distribution Curve (EDC) (Spectrum)

Conservation of energy in PES

Energetics in PES



Hufner, Damascelli

$E_k = h\nu - E_B - \phi$

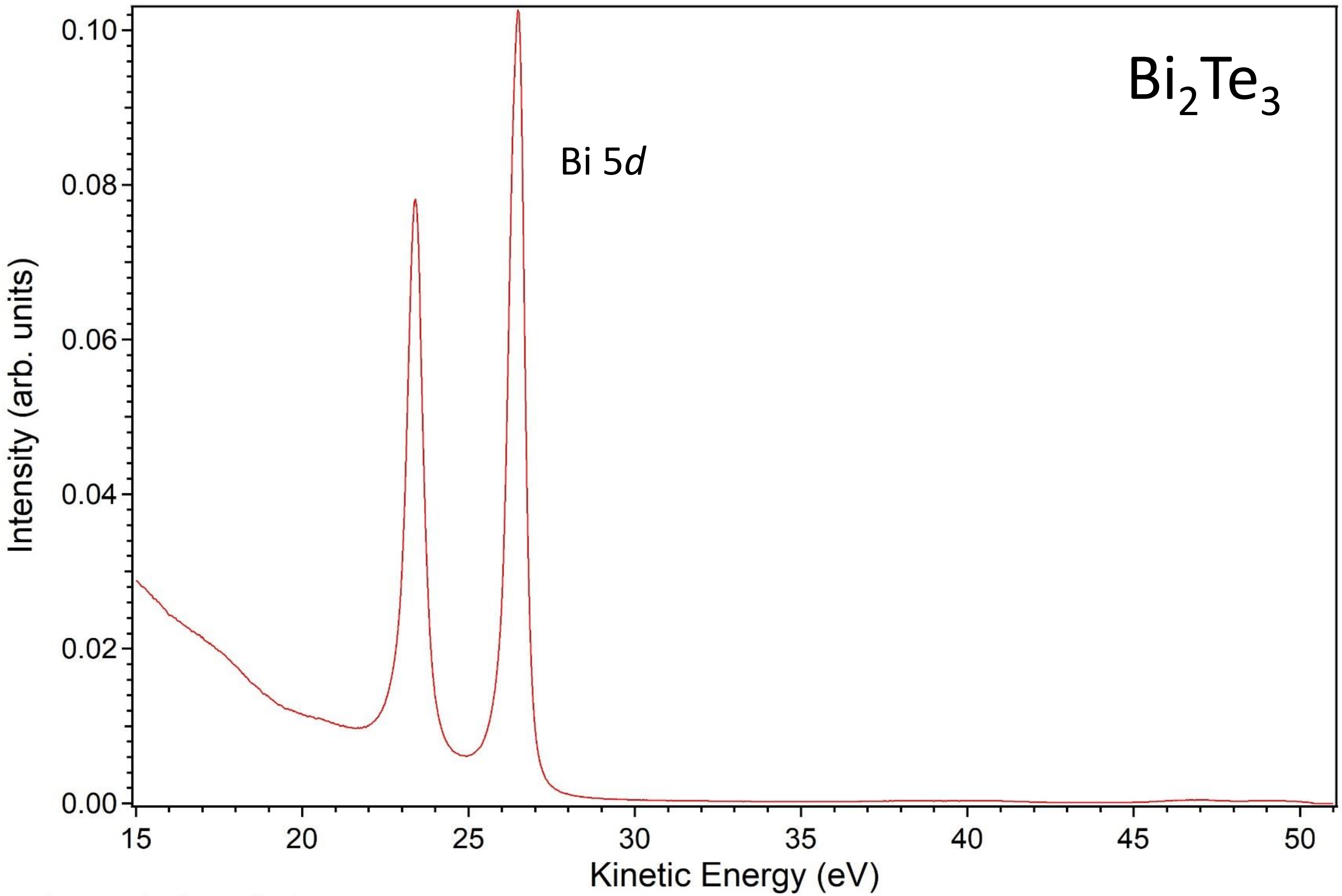
Conservation of energy

E_v : vacuum (energy) level
E_F : Fermi (energy) level
$\phi = E_v - E_F$: work function
E_0 : bottom of valence band
$V_0 = E_v - E_0$: inner potential

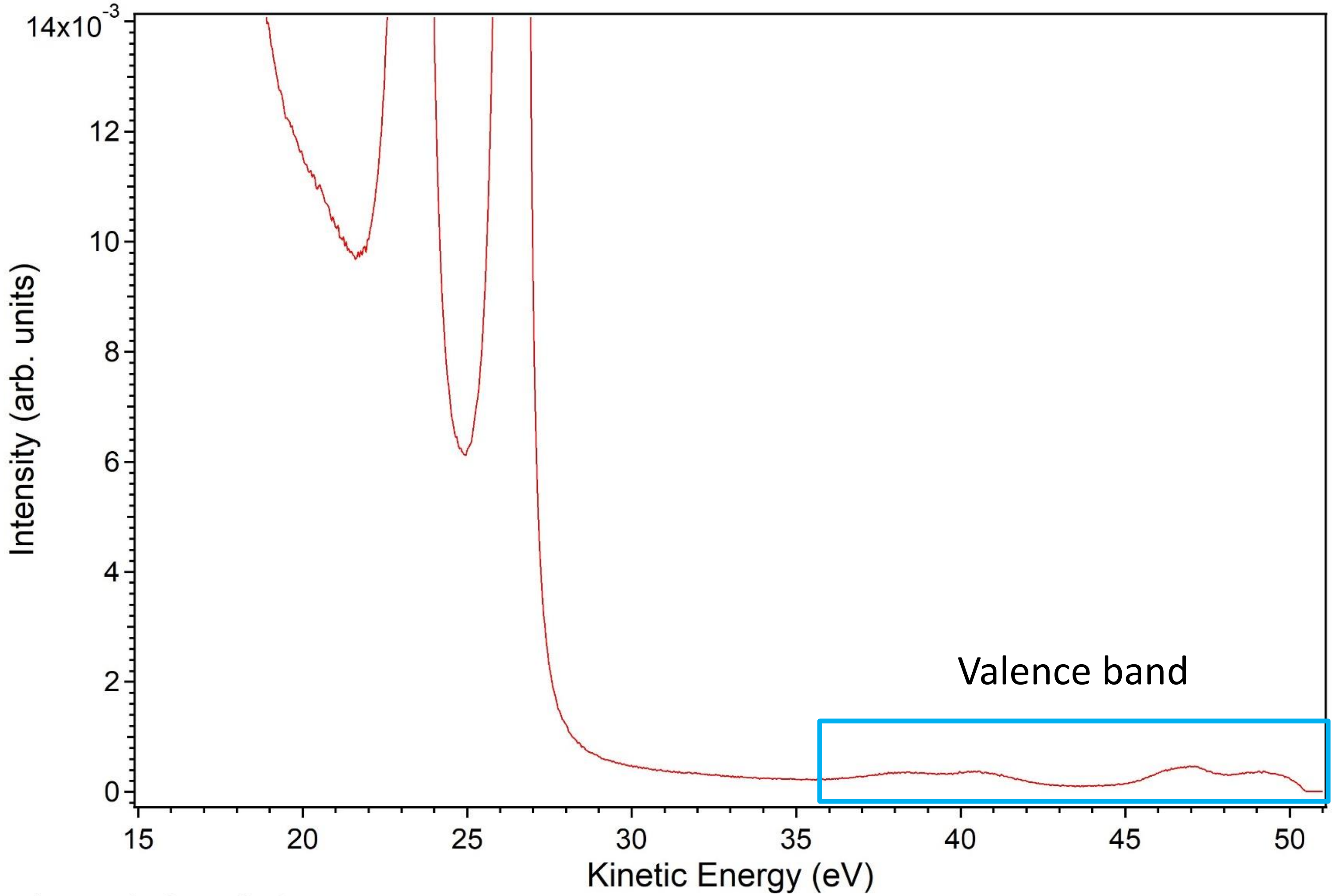
E_k^{max} marks E_F in spectra
E_B measured relative to $E_F = 0$

Usually fixed photon energy
scanning not needed

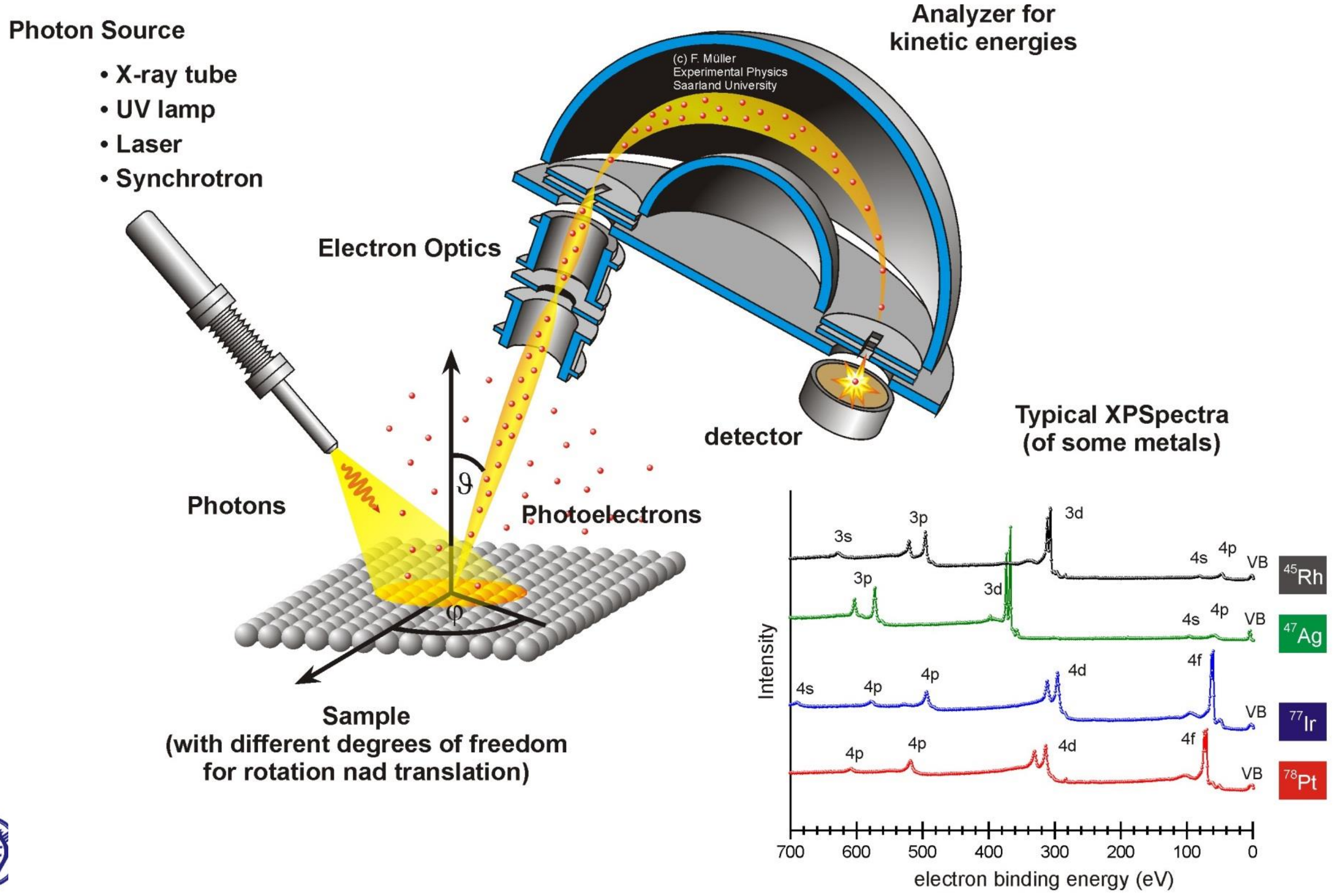
Energy Distribution Curve (EDC)



Energy distribution curve (EDC)



The Principle of Photoemission Spectroscopy



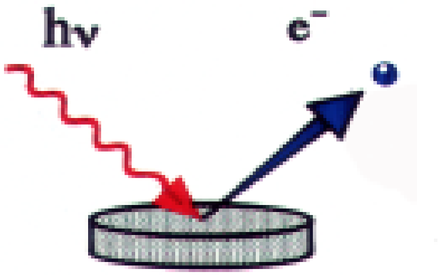
What are the Samples and Probed States

• Atoms	atomic orbitals (states)
• Molecules	molecular orbitals
	core level states (atomic like)
• Nanoparticles	valence bands/states
	core level states (atomic like)
• Solids	valence bands
	core level states (atomic like)

What are the samples and probed states

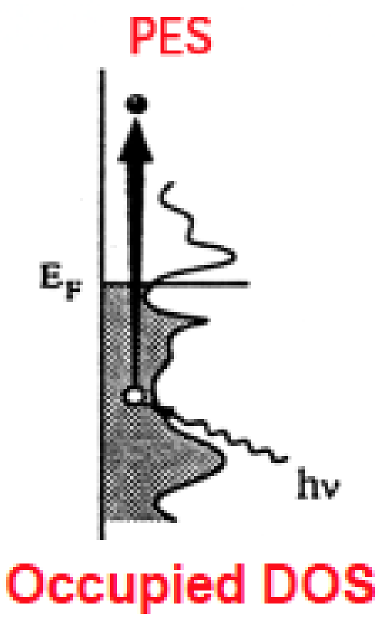
• Atoms	atomic orbitals (states)
• Molecules	molecular orbitals
	core level states (atomic like)
• Nanoparticles	valence bands/states
	core level states (atomic like)
• Solids	valence bands
	core level states (atomic like)

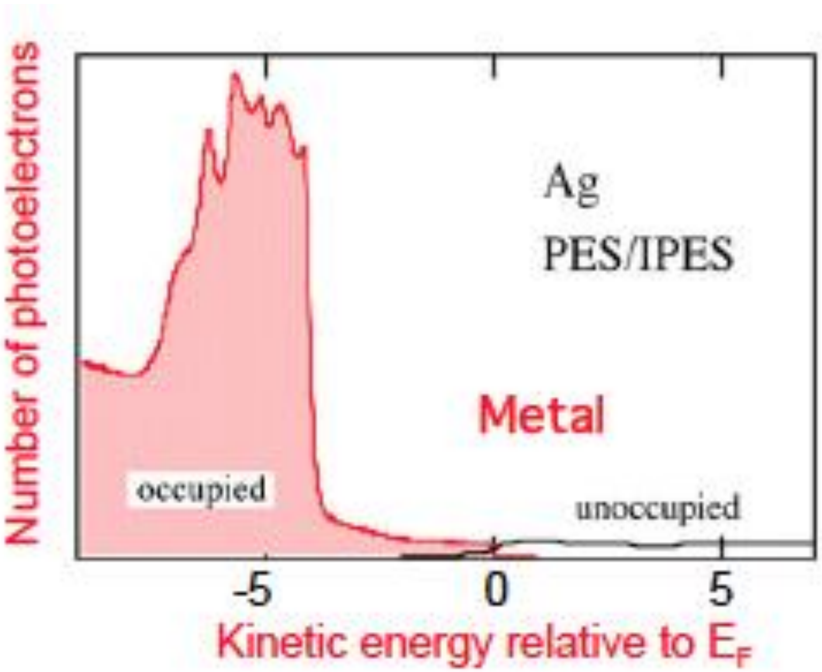
Angle-Iesolved Photoemission Spectroscopy



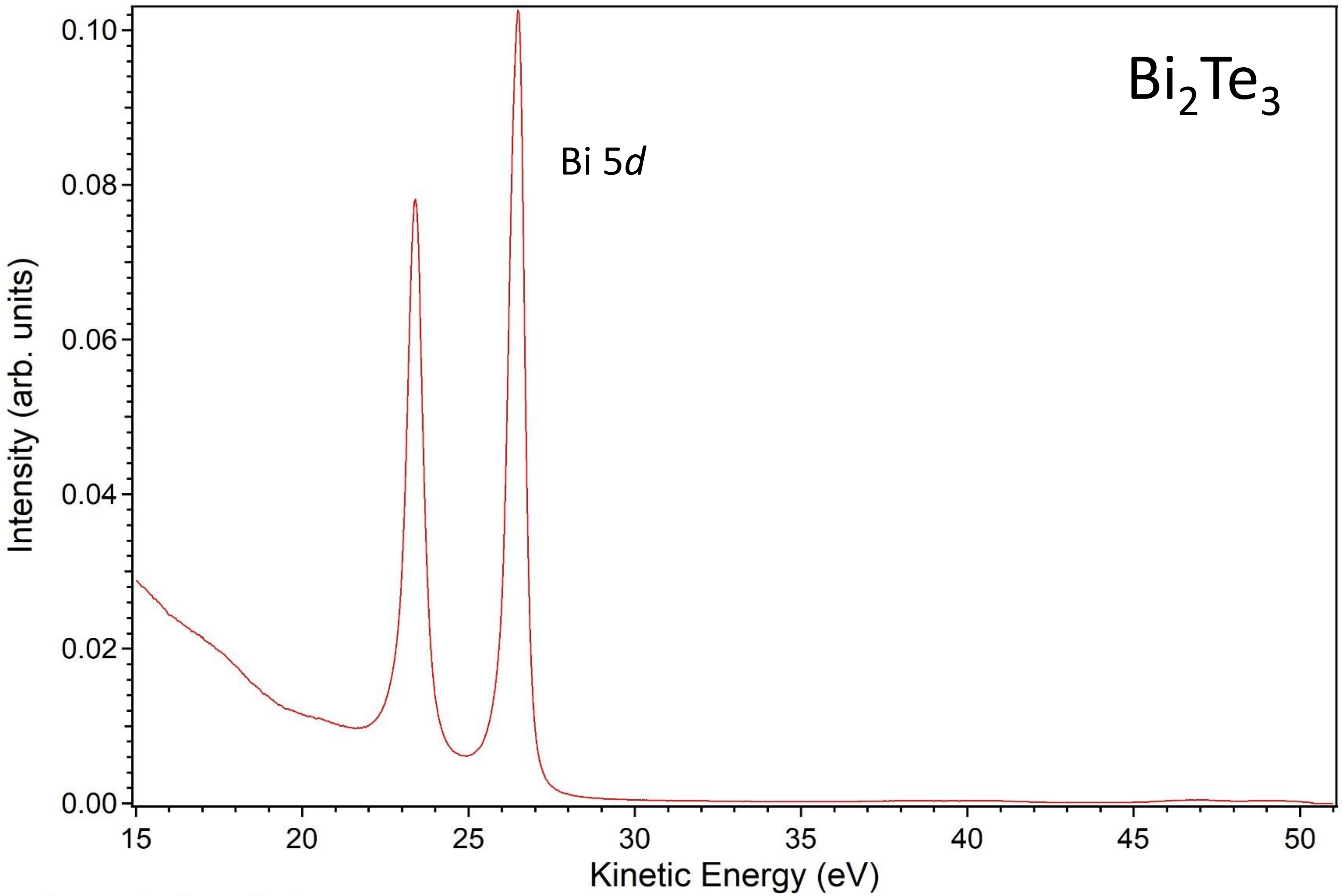
Conservation of Energy

$$\boxed{E_{ph} = E_b + \Phi + E_k}$$





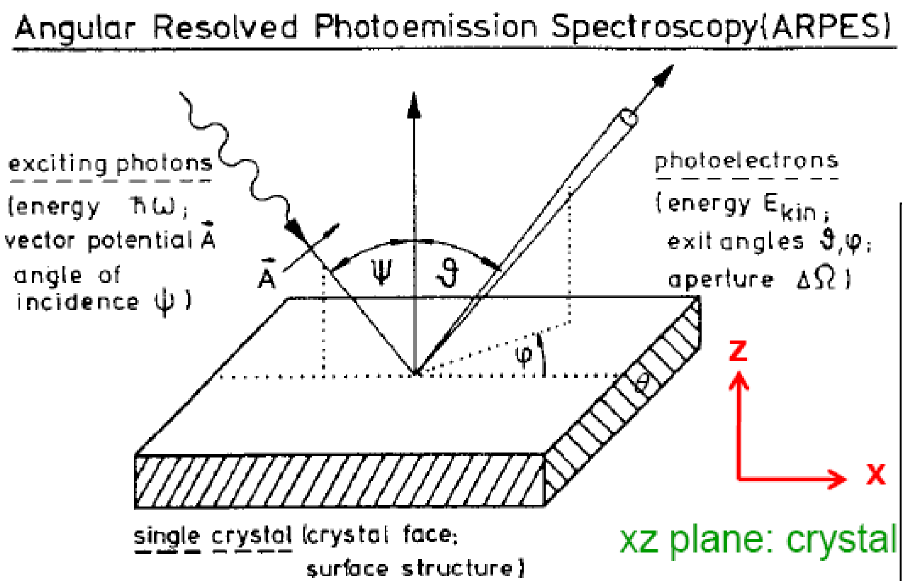
Energy Distribution Curve (EDC)



國家同步輻射研究中心
National Synchrotron Radiation Research Center

what is ARPES?

Angle-Resolved Photoemission Spectroscopy



xz plane: crystal

Electron emission angle: θ

Photon incident angle: ψ, *s*- and *p*-polarization

$$k_{//} = \sqrt{\frac{2m}{\hbar^2}E_k} \cdot \sin\theta$$

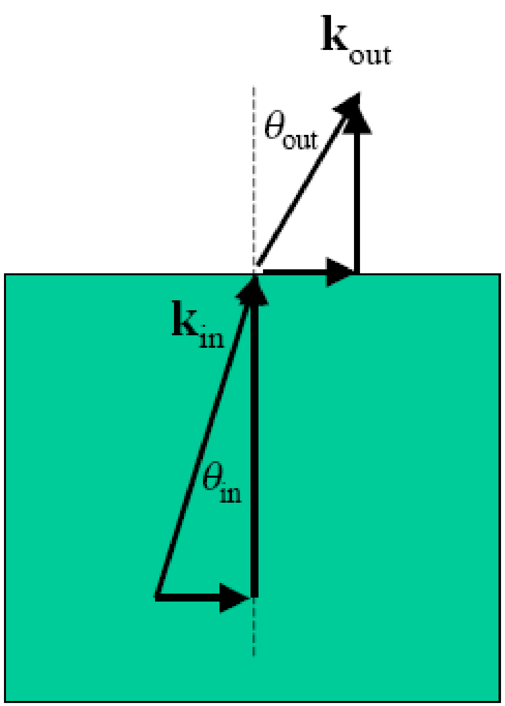
$$k_{//}(\text{Å}^{-1}) = 0.5123\sqrt{E_k(eV)} \cdot \sin\theta$$

$k_{||}$(inside) = $k_{||}$(outside)

Conservation of liner momentum

Important for 3D and 2D band mapping

Conservation of linear momentum parallel to surface



Kinematic relations

$$k_{out} = \sqrt{\frac{2m}{\hbar^2} E_{kin}}$$

$$k_{in} = \sqrt{\frac{2m}{\hbar^2} (E_{kin} + V_0)}$$

$$k_{out,\|} = k_{in,\|} \equiv k_{\|}$$

"Snell's Law"

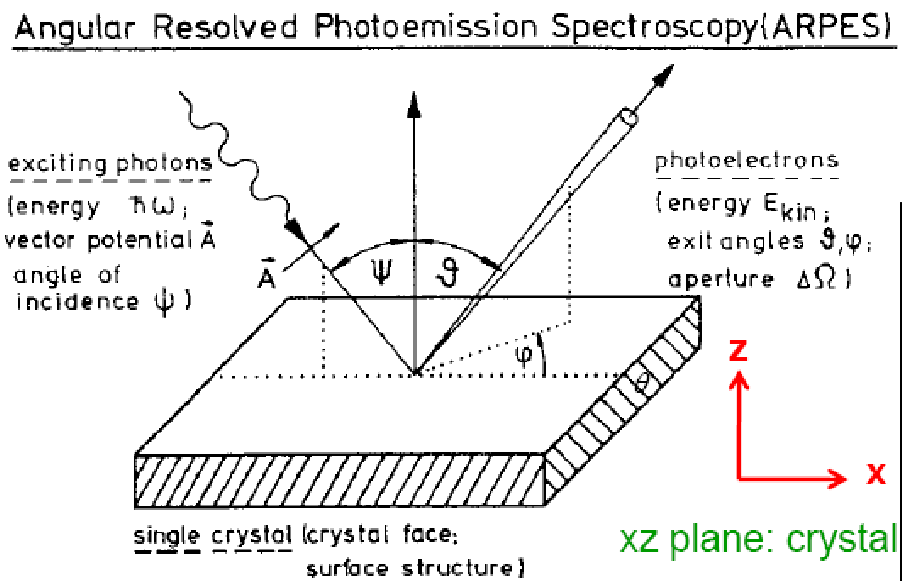
$$k_{\|} = \sin\theta_{out} \sqrt{\frac{2m}{\hbar^2} E_{kin}} = \sin\theta_{in} \sqrt{\frac{2m}{\hbar^2} (E_{kin} + V_0)}$$

Critical angle for emission

$$(\sin\theta_{out})_{\max} = \sqrt{\frac{E_{kin}}{E_{kin} + V_0}}$$

what is ARPES?

Angle-Resolved Photoemission Spectroscopy



xz plane: crystal

Electron emission angle: θ

Photon incident angle: ψ, *s*- and *p*-polarization

$$k_{//} = \sqrt{\frac{2m}{\hbar^2}E_k} \cdot \sin\theta$$

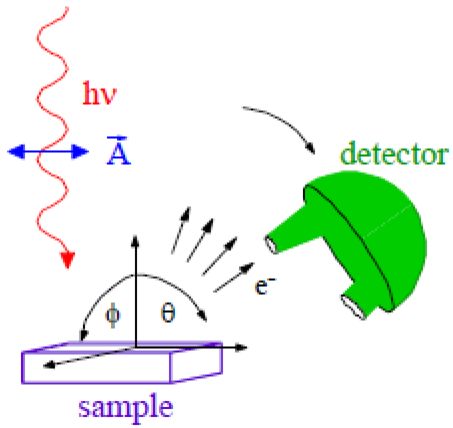
$$k_{//}(\text{Å}^{-1}) = 0.5123\sqrt{E_k(eV)} \cdot \sin\theta$$

$k_{||}$(inside) = $k_{||}$(outside)

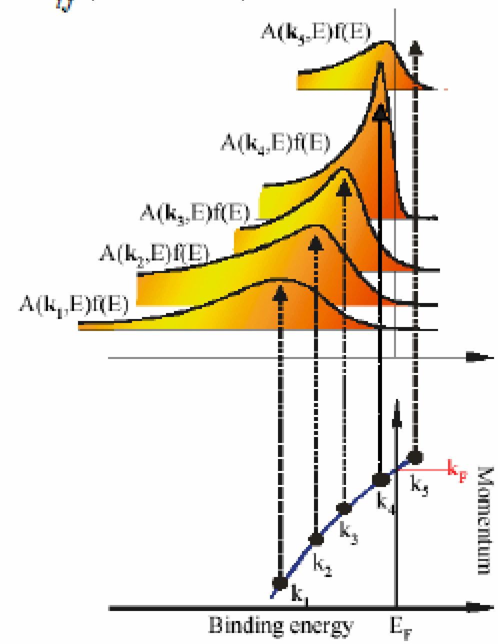
Conservation of liner momentum

Important for 3D and 2D band mapping

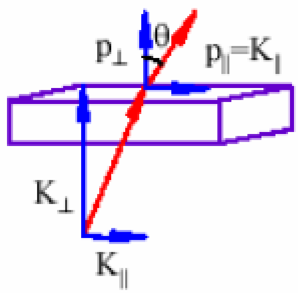
What is ARPES?



$$\text{Intensity} \propto \sum_{i,f} \left| \langle f | \vec{p} \bullet \vec{A} | i \rangle \right|^2 A(\vec{k}, E) f(E)$$



Electron momentum
Parallel to the surface is
conserved



- **Low photon energy provides better momentum resolution, but the covering range of BZ is also small.**

- **We expect to study the electronic structure of solids at VUV region (10 eV~ 100 eV).**

$$k_\perp = 0.5123\sqrt{(E_{kin}\cos^2\theta + V_0)}$$

$$k_{//} = 0.5123\sqrt{E_{kin}}\sin\theta$$

Light sources and terminology

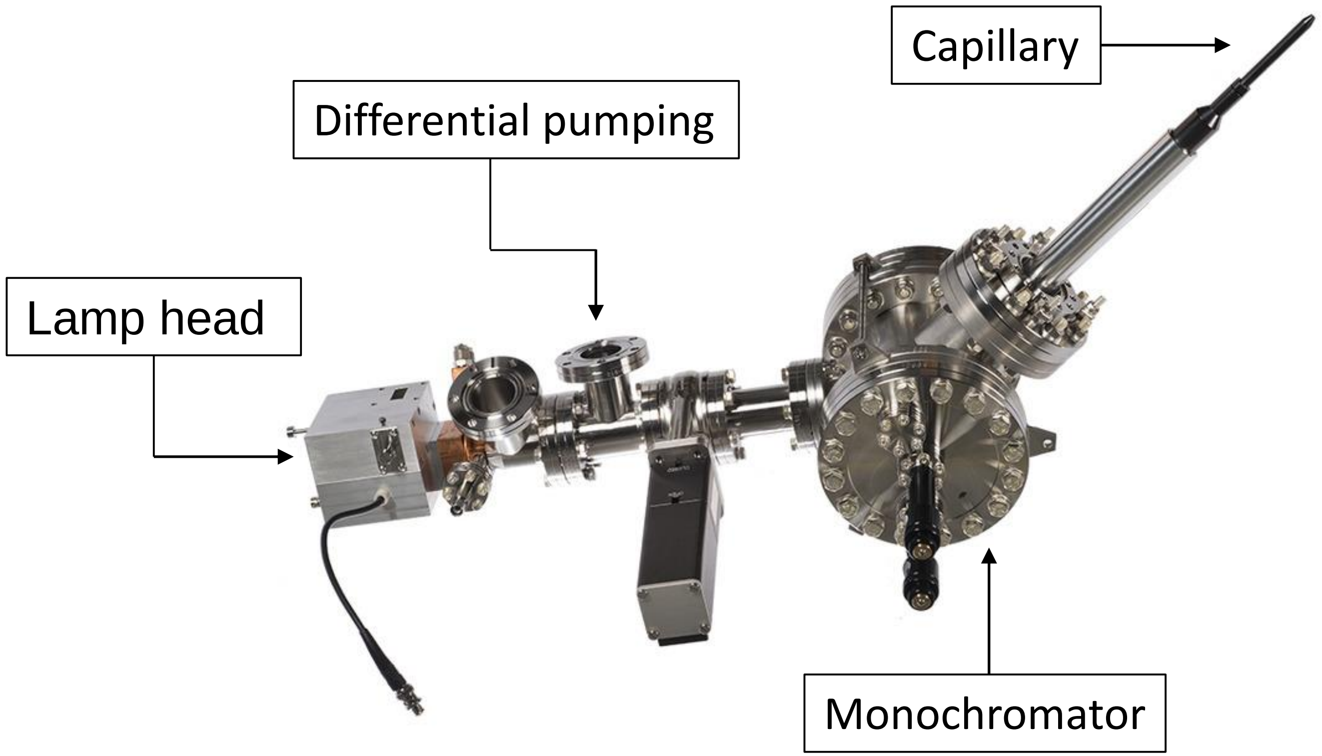
- **Ultraviolet Photoemission Spectroscopy (UPS)**
  - UV He lamp (21.2 eV, 40.8 eV)
  - Laser : 6 eV (BBO), 8 eV (KBBF), 11 eV (gas cell) or HHG (High harmonic generation)
  - Valence band PES, direct electronic state info.

- **X-ray Photoemission Spectroscopy (XPS)**
  (Electron Spectroscopy for Chemical Analysis) (ESCA)
  - X-ray gun (Al: 1486.6 eV, Mg: 1253.6 eV)
  - core level PE, indirect electronic state info
  - chemical analysis

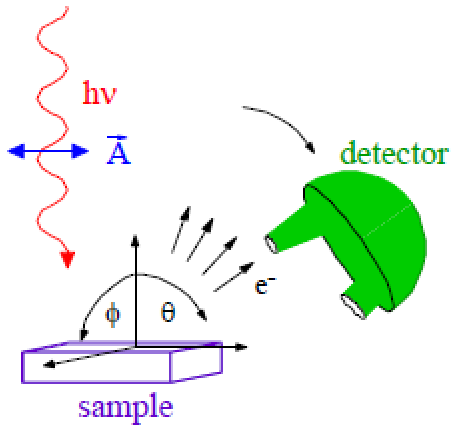
- **Synchrotron radiation**
  - continuous tunable wavelength
  - valance band and core level

Light sources and terminology

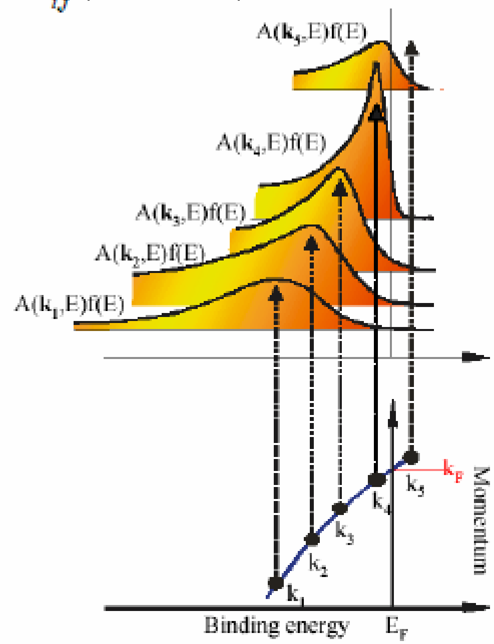
UV lamp (He I$_\alpha$ 21.2 eV, He II$_\alpha$ 40.8 eV)



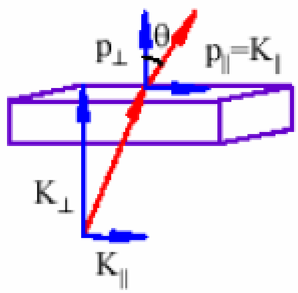
What is ARPES?



$$\text{Intensity} \propto \sum_{i,f} \left| \langle f | \vec{\mathbf{p}} \bullet \vec{\mathbf{A}} | i \rangle \right|^2 A(\vec{\mathbf{k}}, E) f(E)$$



Electron momentum
Parallel to the surface is
conserved



- **Low photon energy provides better momentum resolution, but the covering range of BZ is also small.**
- **We expect to study the electronic structure of solids at VUV region (10 eV~ 100 eV).**

$$k_{\perp} = 0.5123\sqrt{(E_{kin}\cos^2\theta + V_0)}$$

$$k_{//} = 0.5123\sqrt{E_{kin}}\sin\theta$$

Light sources and terminology

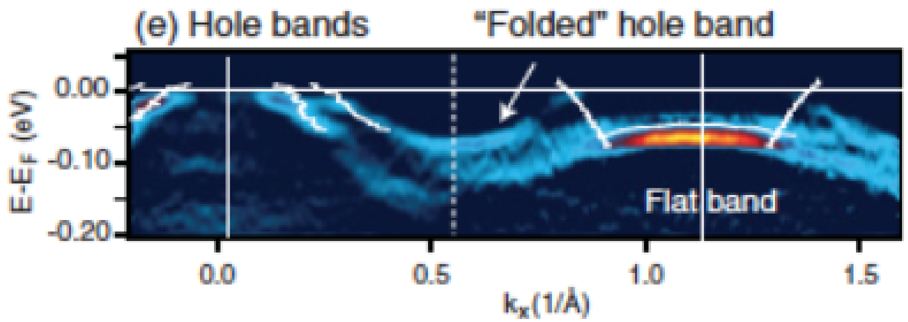
Photon energy

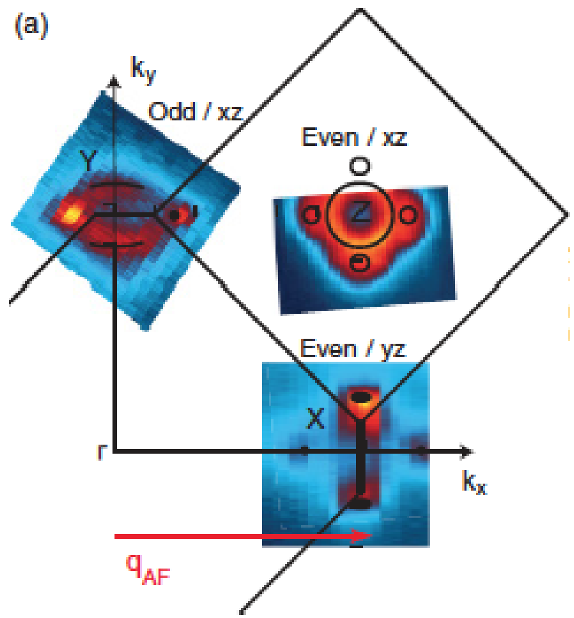
- defines the detectable area of Energy

$$E_{kin} = \hbar\nu - \phi$$

- defines the accessible area of BZ

$$k_{//} = \frac{1}{\hbar}\sqrt{2mE_{kin}}\sin\theta$$

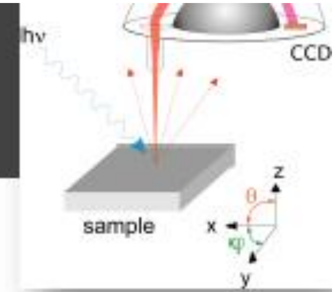




Phys. Rev. B 84, 014509 (2011)

Light sources and terminology

Photon energy

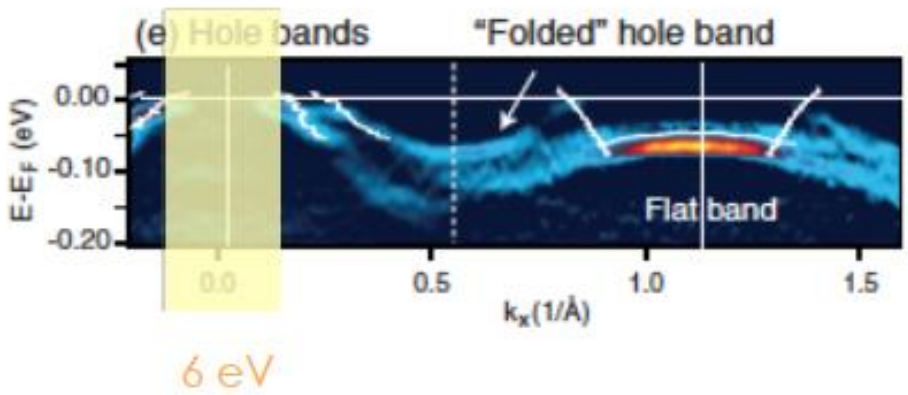


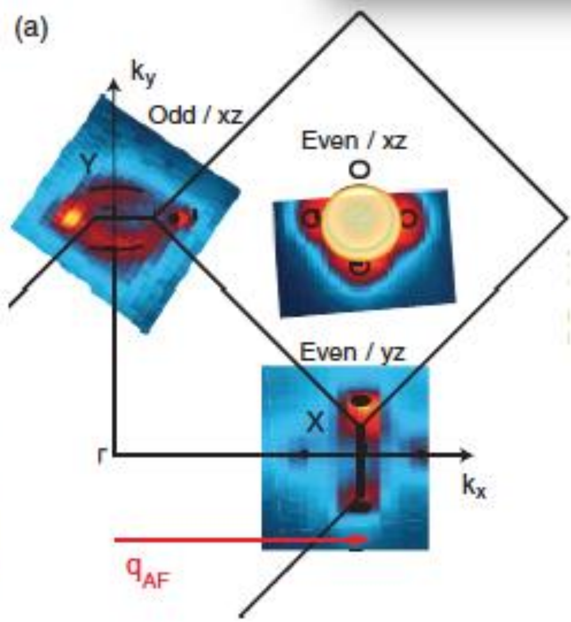
- defines the detectable area of Energy

$$E_{kin} = \hbar\nu - \phi$$

- defines the accessible area of BZ

$$k_{//} = \frac{1}{\hbar}\sqrt{2mE_{kin}}\sin\theta$$

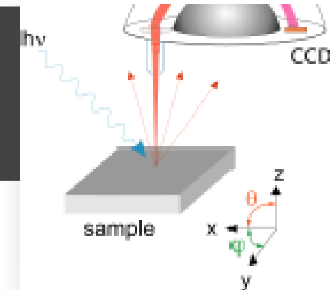




Phys. Rev. B 84, 014509 (2011)

Light sources and terminology

Photon energy

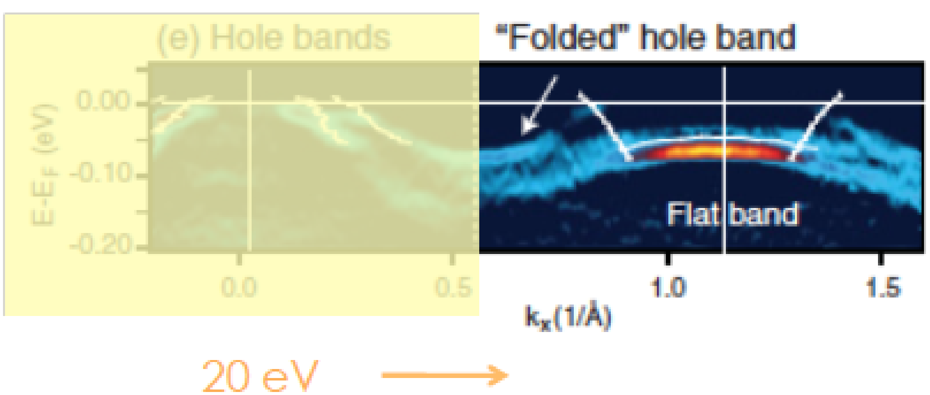


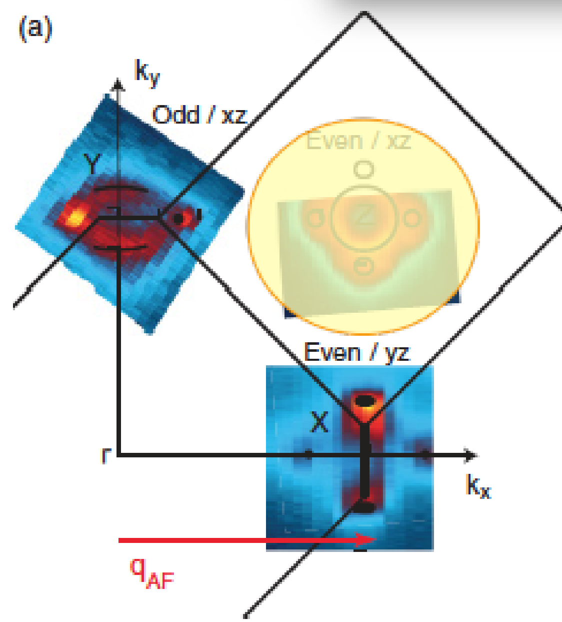
- defines the detectable area of Energy

$$E_{kin} = \hbar\nu - \phi$$

- defines the accessible area of BZ

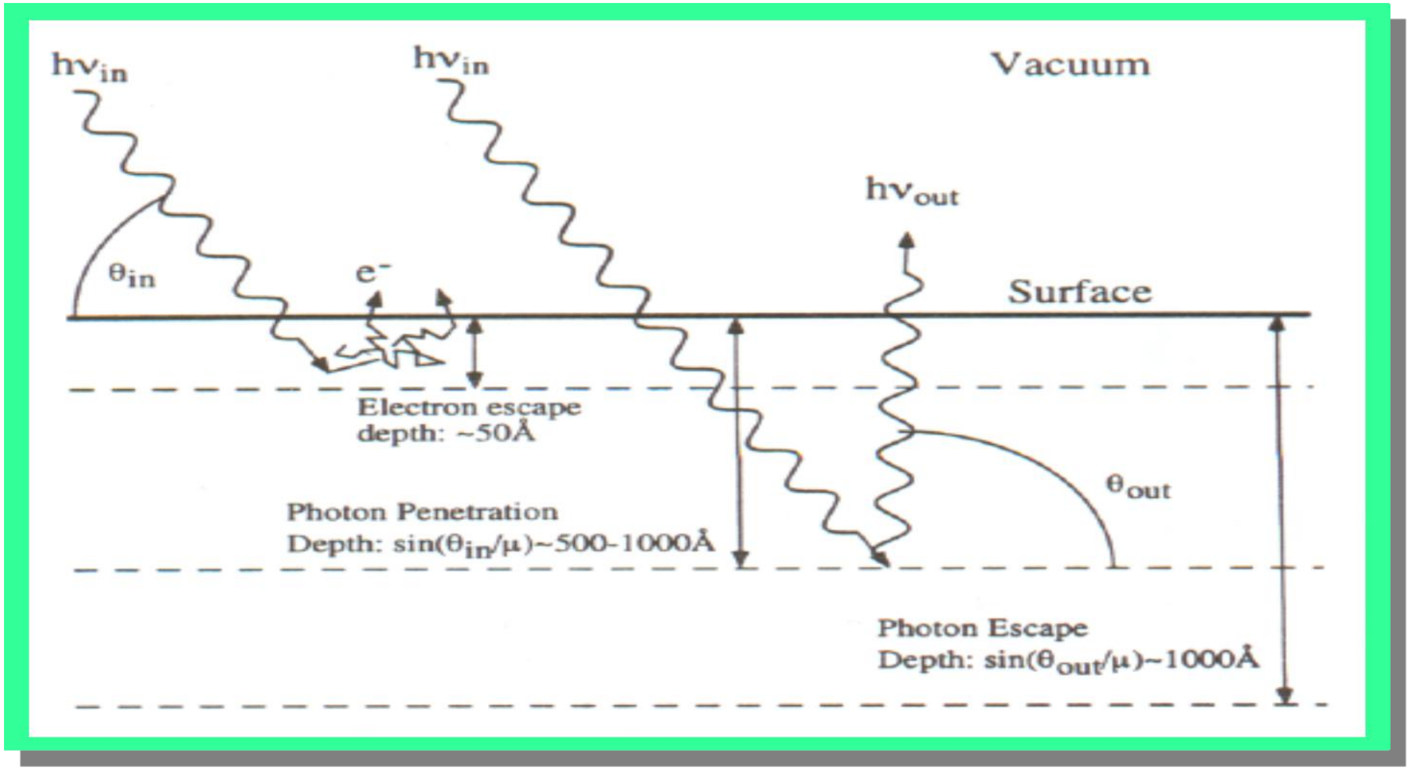
$$k_{//} = \frac{1}{\hbar}\sqrt{2mE_{kin}}\sin\theta$$





Phys. Rev. B 84, 014509 (2011)

Light sources and terminology



The powerful spectroscopic tools such as XPS and UPS might be limited in in-situ chemical analysis because of the short penetration depth of electrons.

Light sources and terminology

Why are electrons so useful as probes of surfaces?

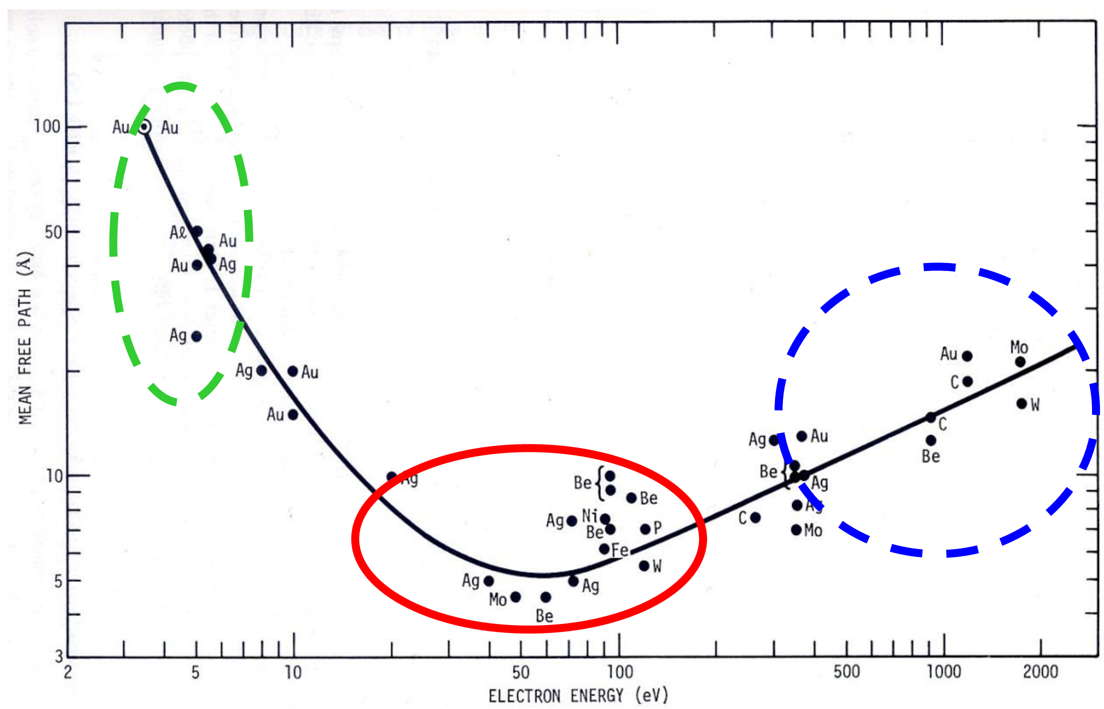
Or

Not so useful for studying bulk properties !!

Minimum due to electron-electron scattering, mainly plasmons

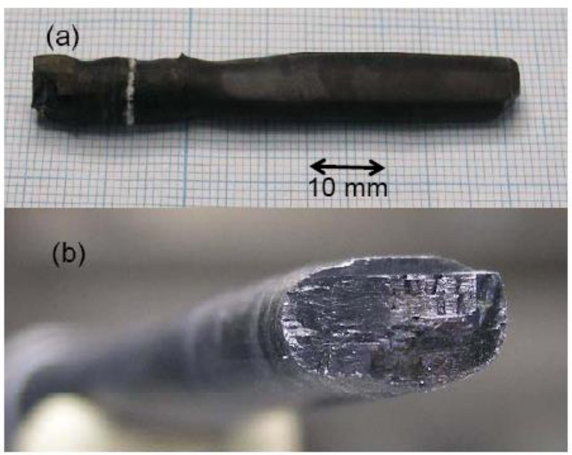
PES is a surface sensitive technique! (requires UHV)

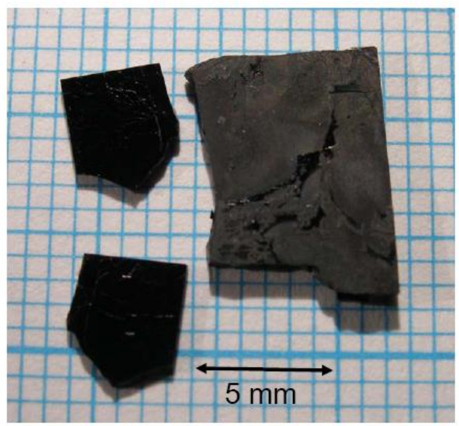
High energy photoemission: several keV to increase bulk sensitivity



Light sources and terminology

- UHV environment : better than 1×10^{-10} Torr
- Single crystals or *in-situ* growth thin films
- Conductors or semiconductors
- Tunable photon energies





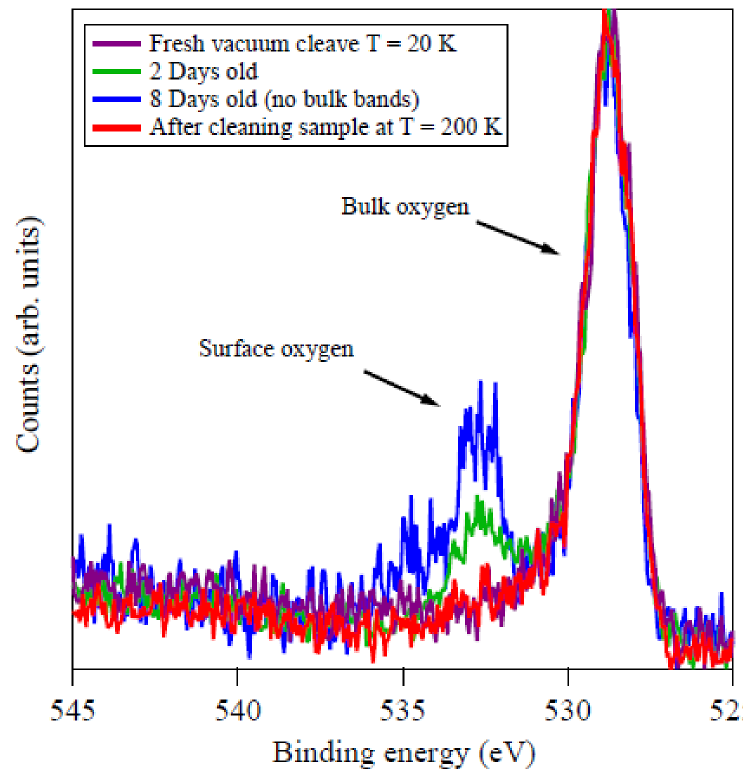
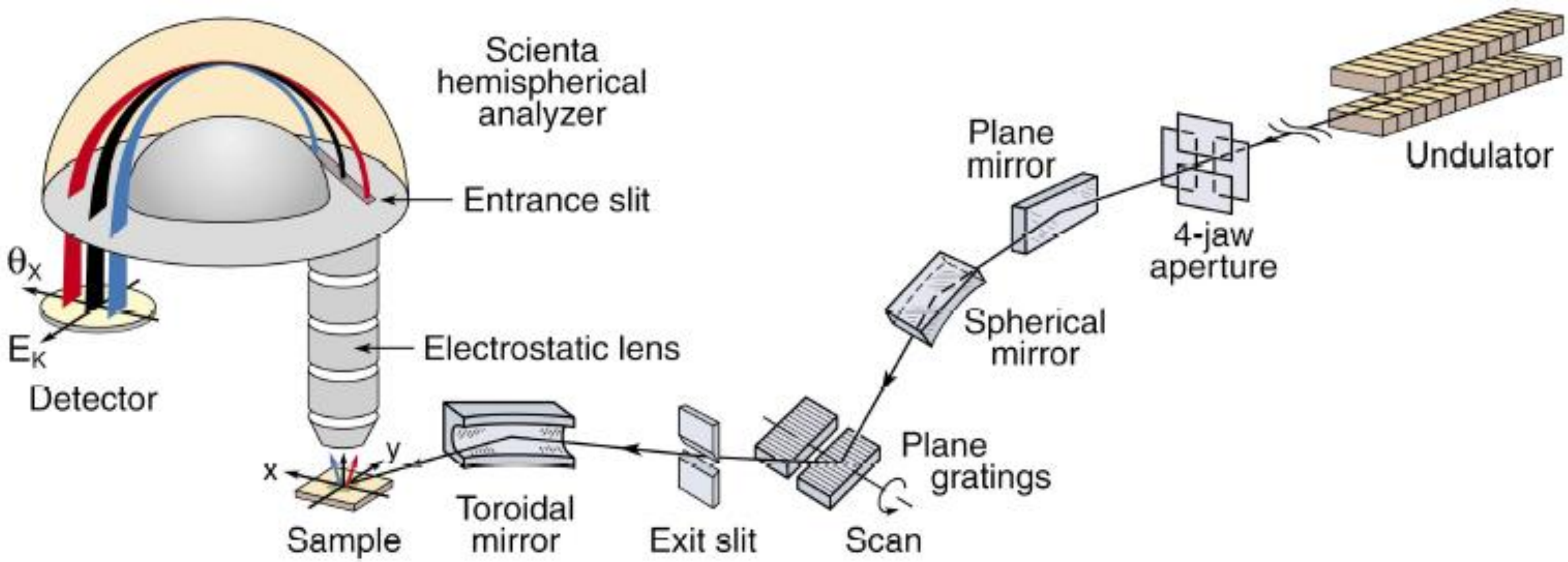


Figure 5.2: (color) The oxygen 1s peaks from Bi2212 at different times after the cleave. A constant background was subtracted from each spectrum to allow direct comparison. The peak derived from bulk oxygen is stable over time, while the surface oxygen peak grows as more oxygen sticks to the cold surface.

國家同步輻射研究中心
National Synchrotron Radiation Research Center

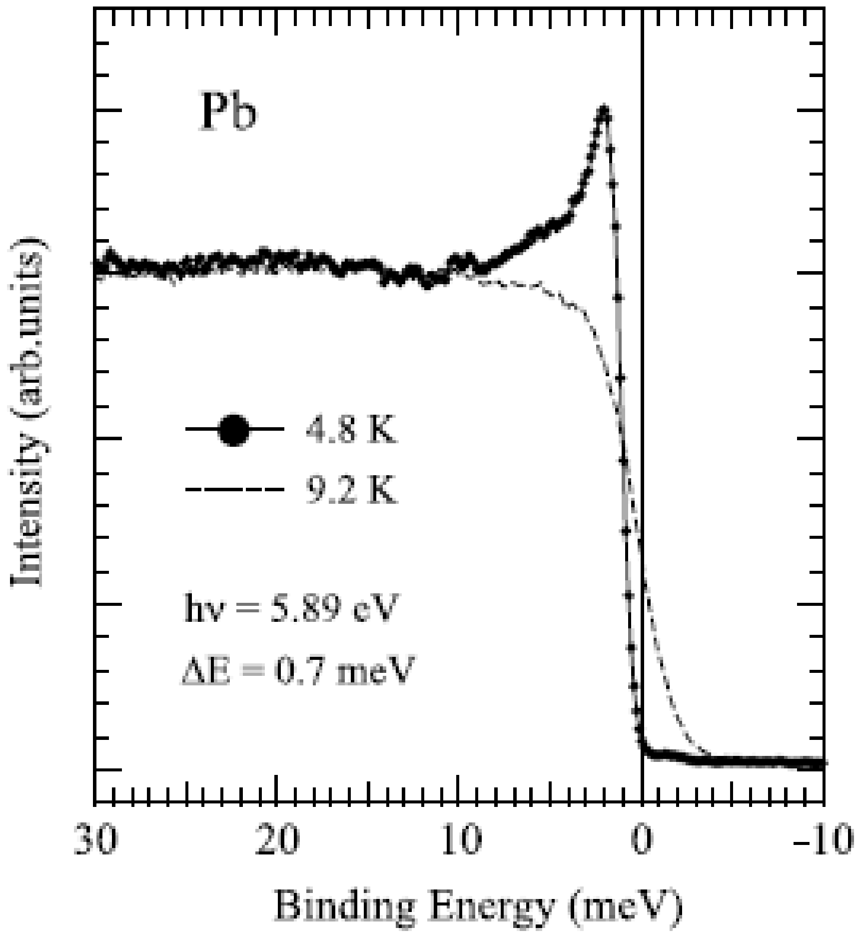
HC Hsu, Ph.D. Thesis NTNU(2010)
Koralek, U. Colorado Ph.D. Thesis (2007)

Light sources and terminology



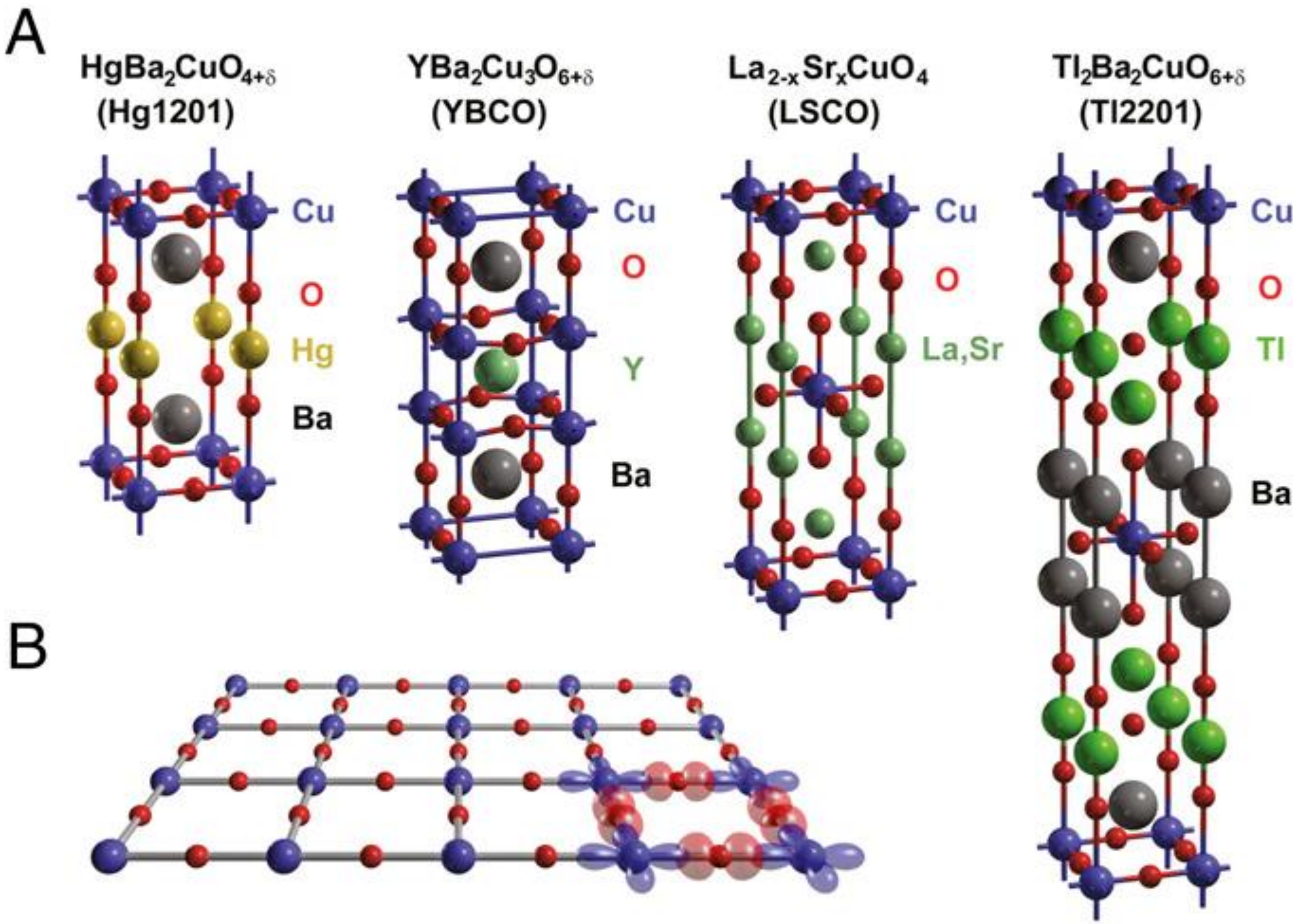
Scientific Case : High- Tc Superconductor

Superconducting gap

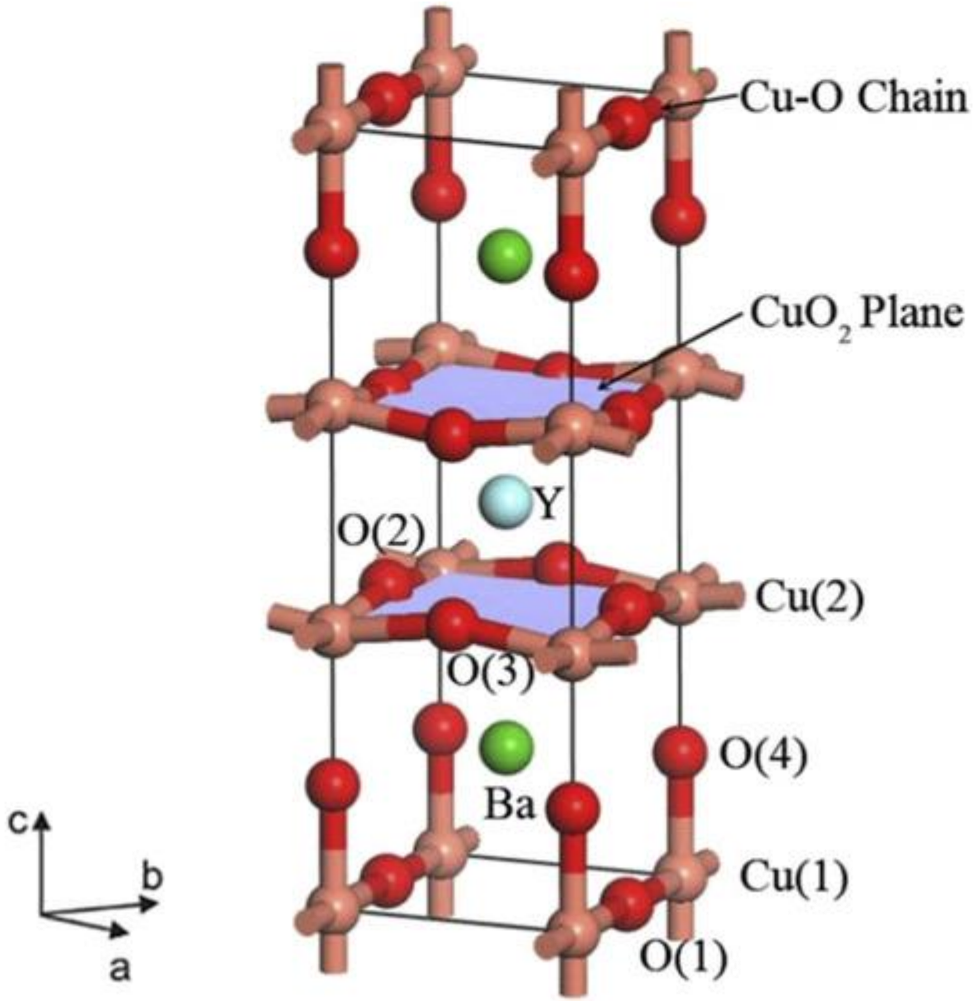


Hufner, Very high resolution photoelectron spectroscopy

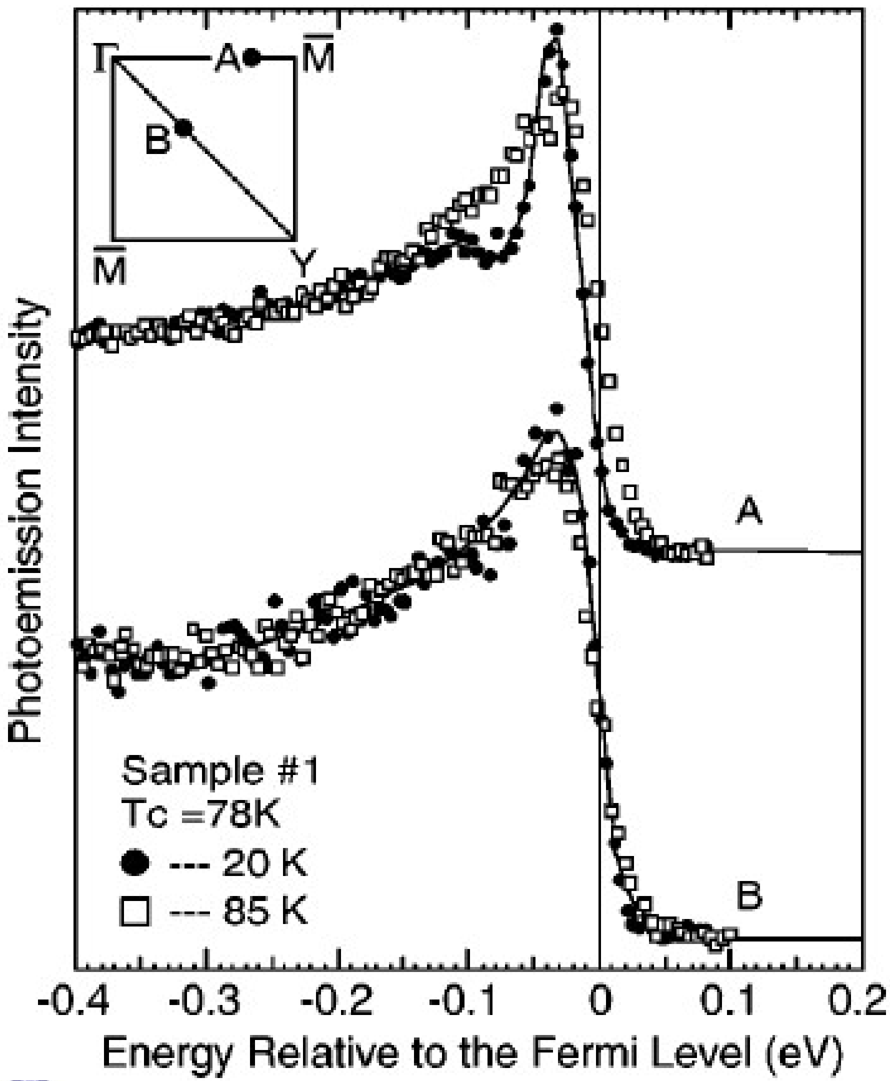
Scientific Case : High- Tc Superconductor



Scientific Case : High- Tc Superconductor



Scientific Case : High- Tc Superconductor

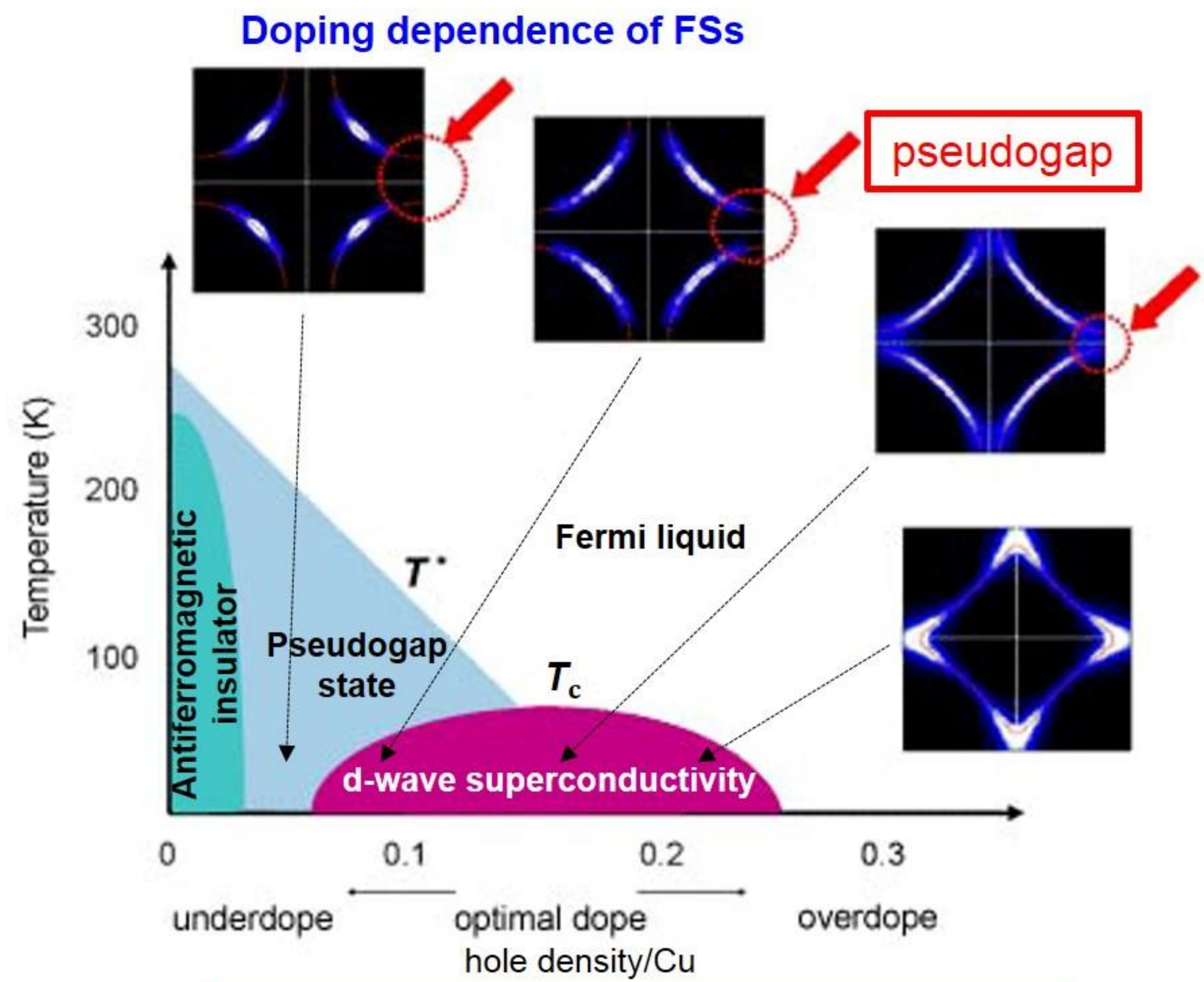


Overdoped Bi-2212 sample at two different momenta in the Brillouin zone.

These results strongly suggest that the superconducting gap is anisotropic and, in particular, consistent with a d-wave order parameter (*Scalapino, 1995*). Together with the microwave penetration depth results (*Hardy et al., 1993*), this direct evidence for gap anisotropy played a major role in the early debate on the pairing symmetry (*Levi, 1993*).

ZX Shen, PRL (1993)

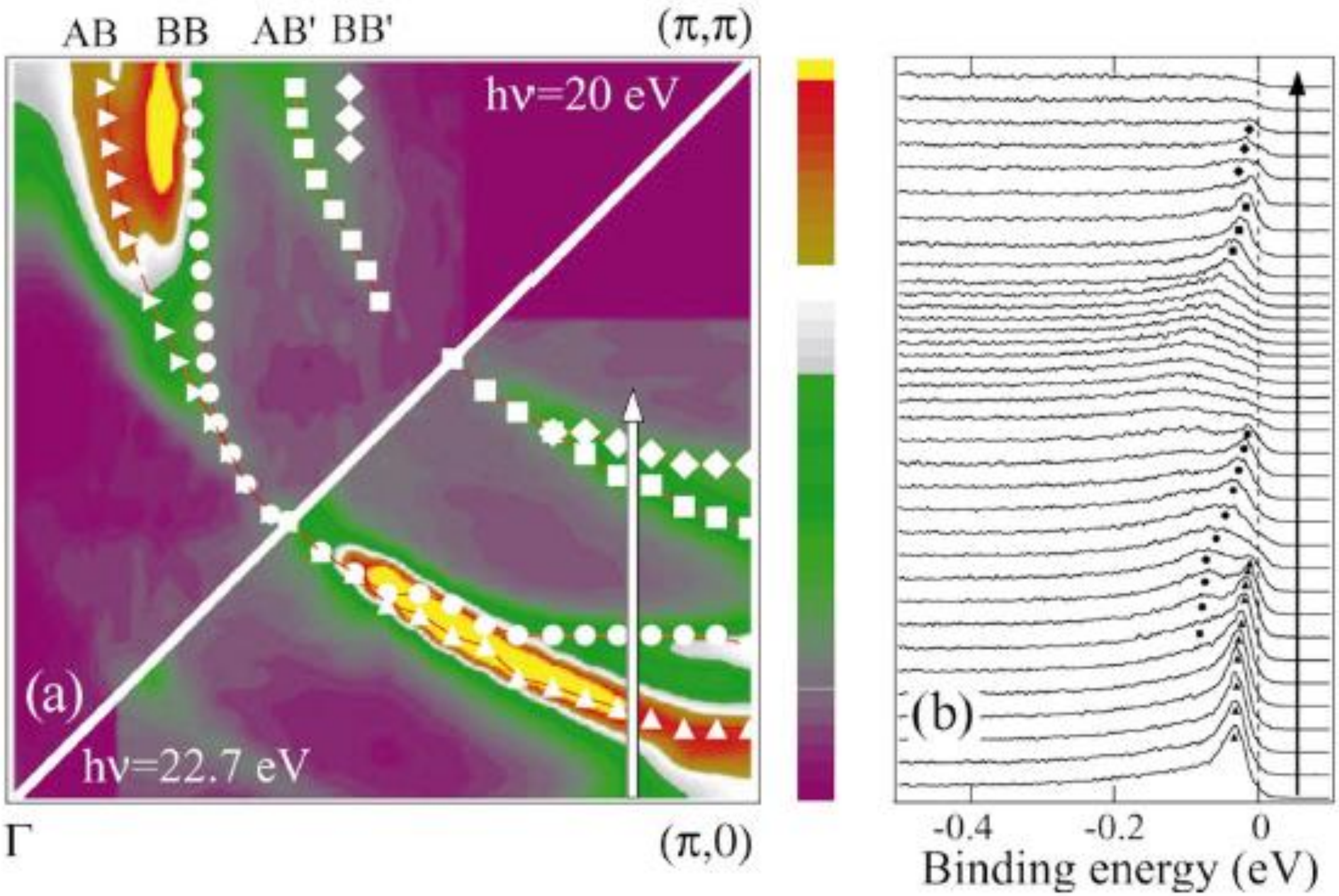
Scientific Case : High- Tc Superconductor



Phase diagram of hole-doped high-Tc superconductors

Scientific Case : High- Tc Superconductor

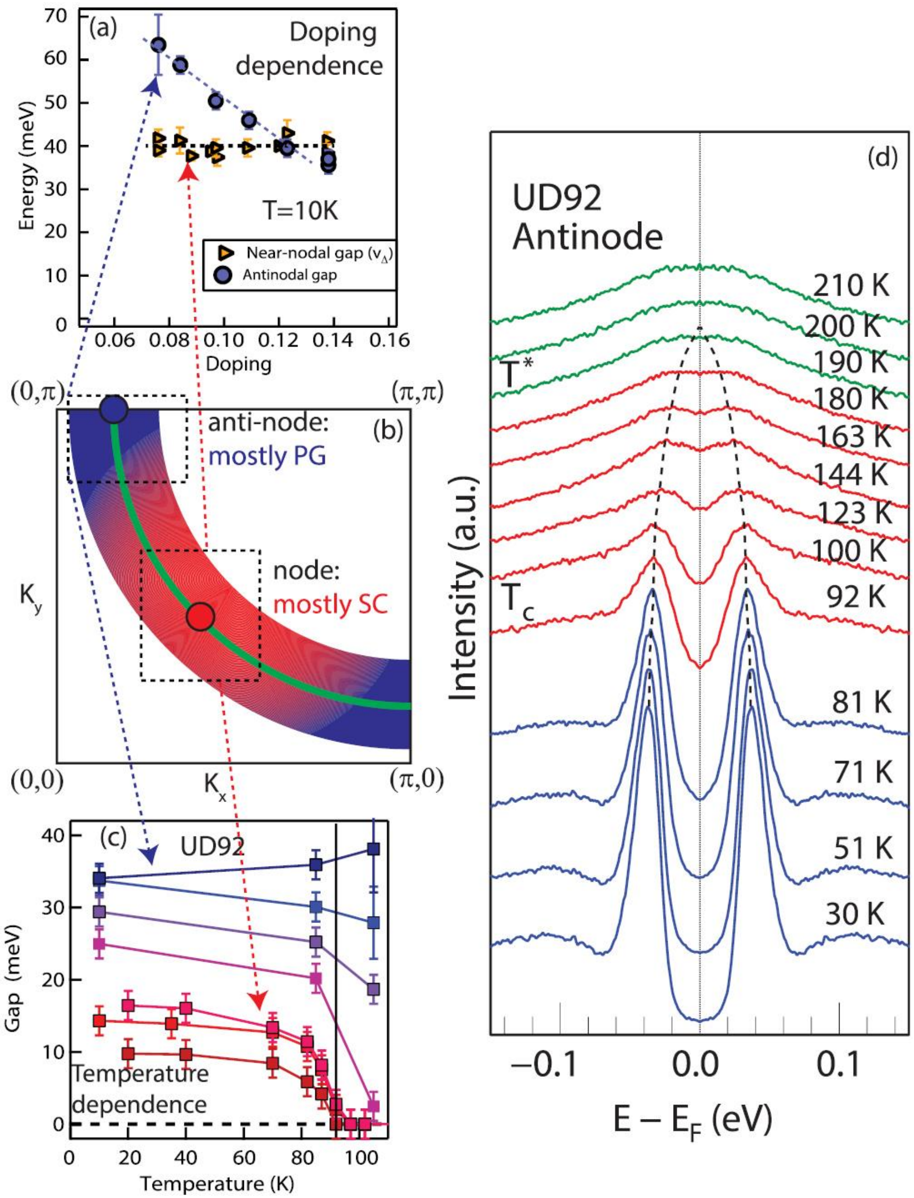
Bilayer band splitting in overdoped Bi-2212 (Tc = 65 K)



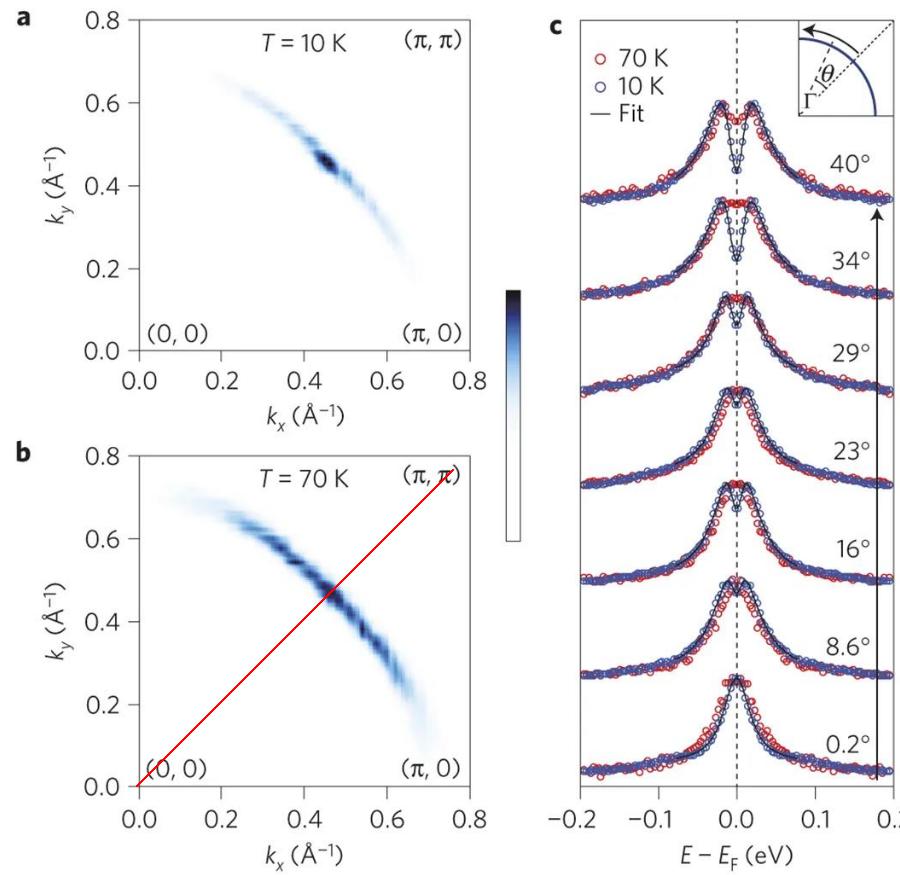
國家同步輻射研究中心
National Synchrotron Radiation Research Center

DL Feng, PRL (2001)

Scientific Case : High- Tc Superconductor



Sr_2IrO_4



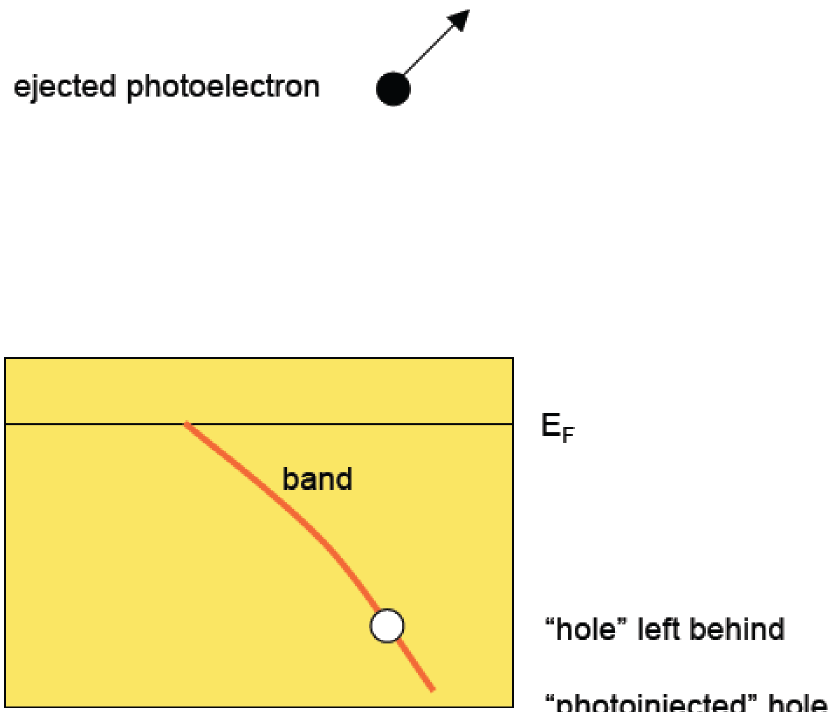
Kim et al., Nat. Phys. (2015)

Scientific Case : High- Tc Superconductor

$$I \propto \sum_{f,i,\mathbf{k}} \left| \langle \phi_f | H_{\text{int}} | \phi_i \rangle \right|^2 A(\mathbf{k}, E)$$

Matrix element

Spectra function



we believe the properties of the photoelectron reflect the properties of the injected hole

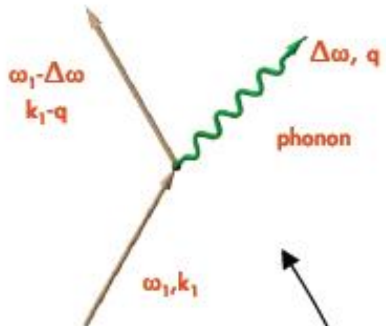
namely,

we can learn about the scattering and lifetime of the injected hole

Eli Rotenberg, ALS summer school

Scientific Case : High- Tc Superconductor

The carriers have a finite lifetime due to absorption and emission of phonons and other excitations

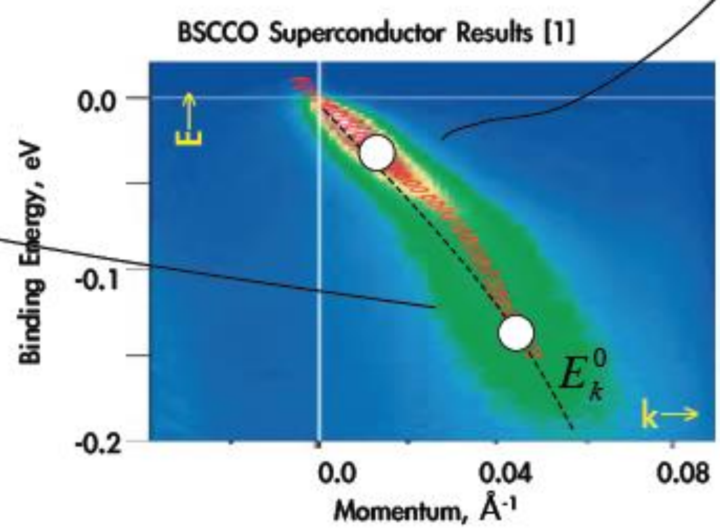


electron emits a phonon : change of energy **ω** and momentum *k*

The measured state is broader in momentum and energy

electron emits and reabsorbs a phonon :Change of mass and slope

The mass of carrier is increased



there is no direct way to probe these processes except through ARPES measurments

Eli Rotenberg, ALS summer school

Scientific Case : High- Tc Superconductor

The quantity determined in ARPES experiments is the single-particle spectral function

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

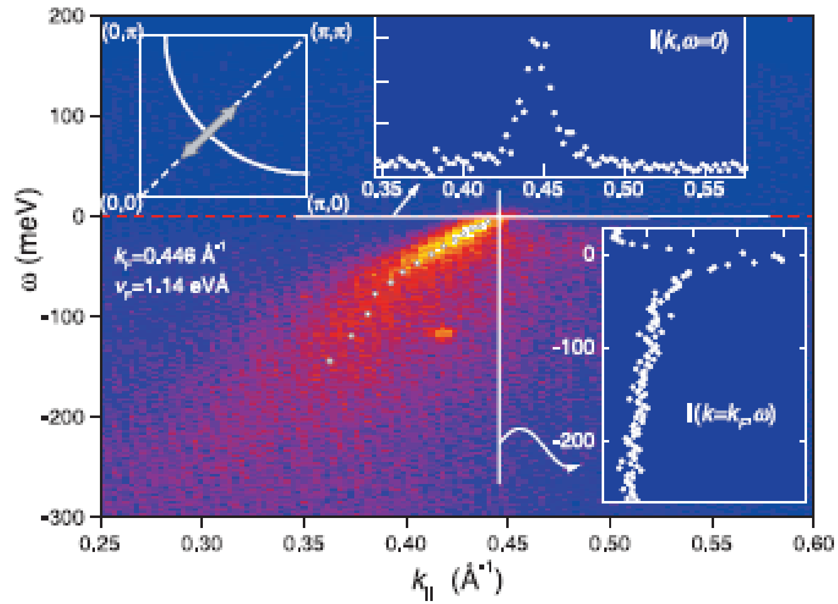
$$A(k,\omega) = \frac{\mathrm{Im}\,\Sigma(k,\omega)}{[\omega - \varepsilon_k - \mathrm{Re}\,\Sigma(k,\omega)]^2 + [\mathrm{Im}\,\Sigma(k,\omega)]^2}$$

$$\Sigma = \mathrm{Re}\,\Sigma + i\,\mathrm{Im}\,\Sigma$$

Dispersion:
***E-k* Relation (Velocity; Effective mass etc.)**

Scattering rate (Lifetime)

Optimally doped Bi-2212 cuprate



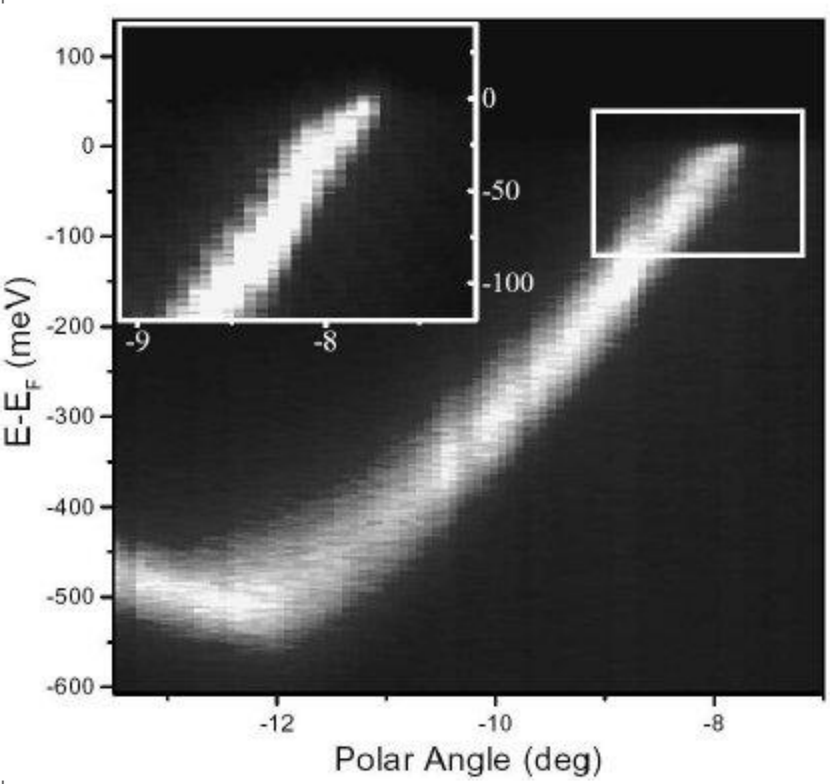
$$\hbar v_k \Delta k = \frac{\hbar v_k}{l} = \left| 2\,\mathrm{Im}\,\Sigma(k,\omega) \right|$$

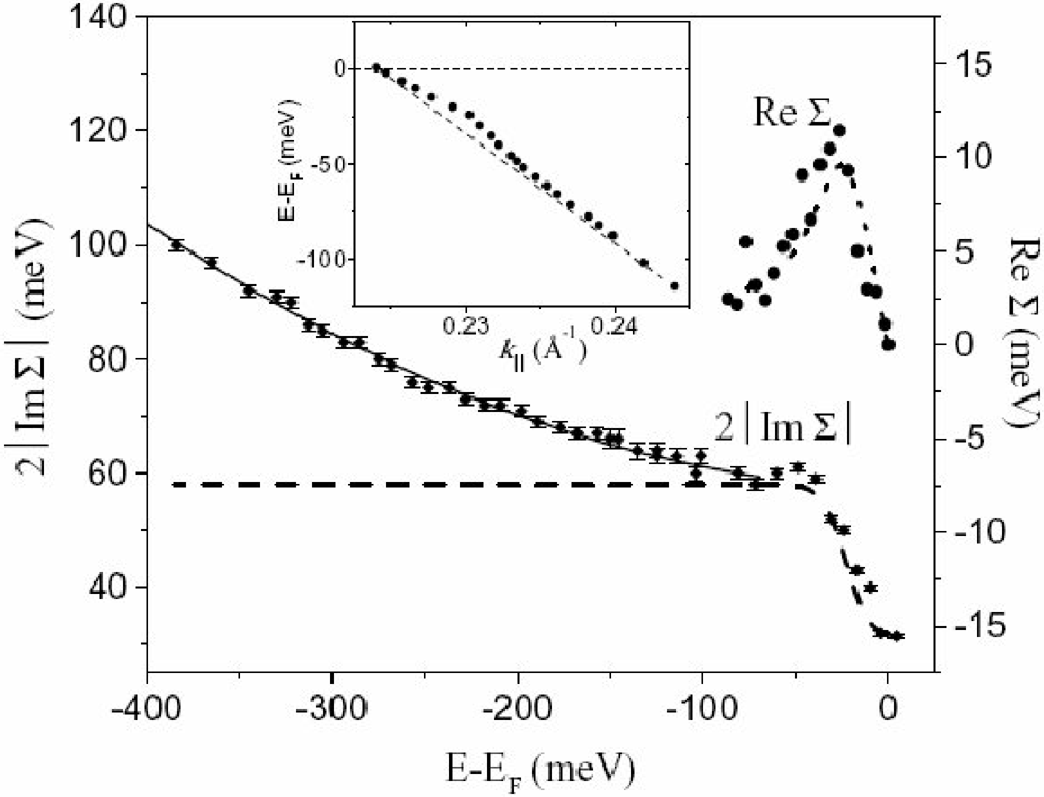
國家同步輻射研究中心
National Synchrotron Radiation Research Center

T. Valla et al., Science (2000)

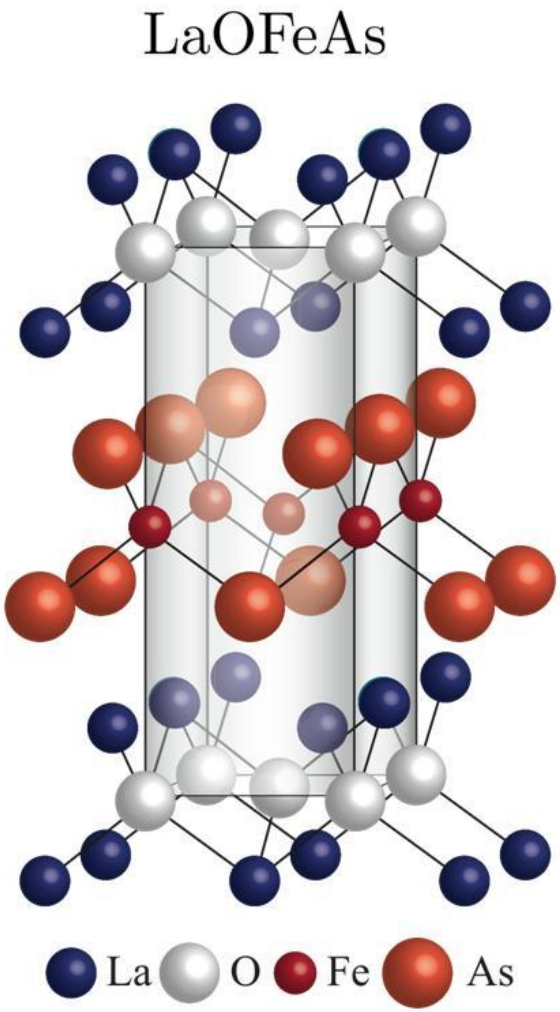
Scientific Case : High- Tc Superconductor

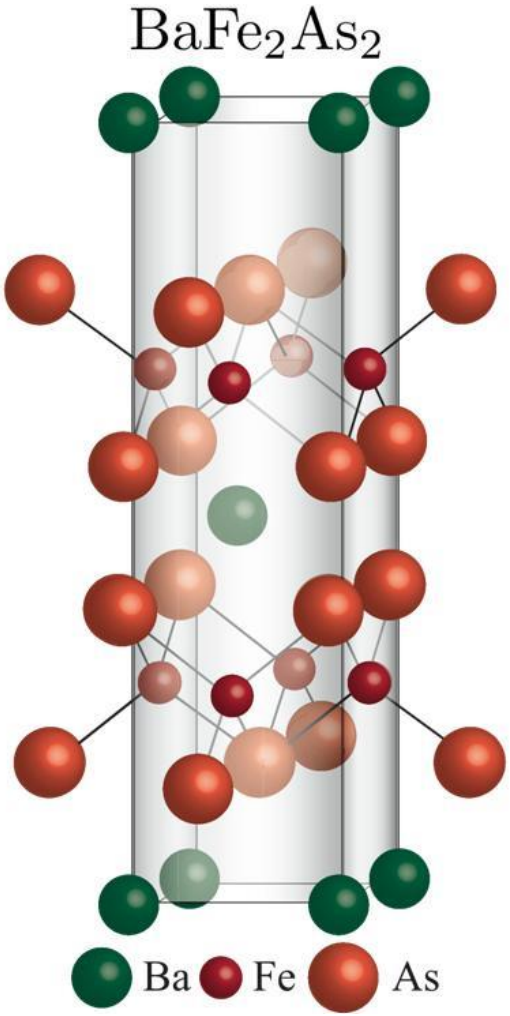
Line shape analysis





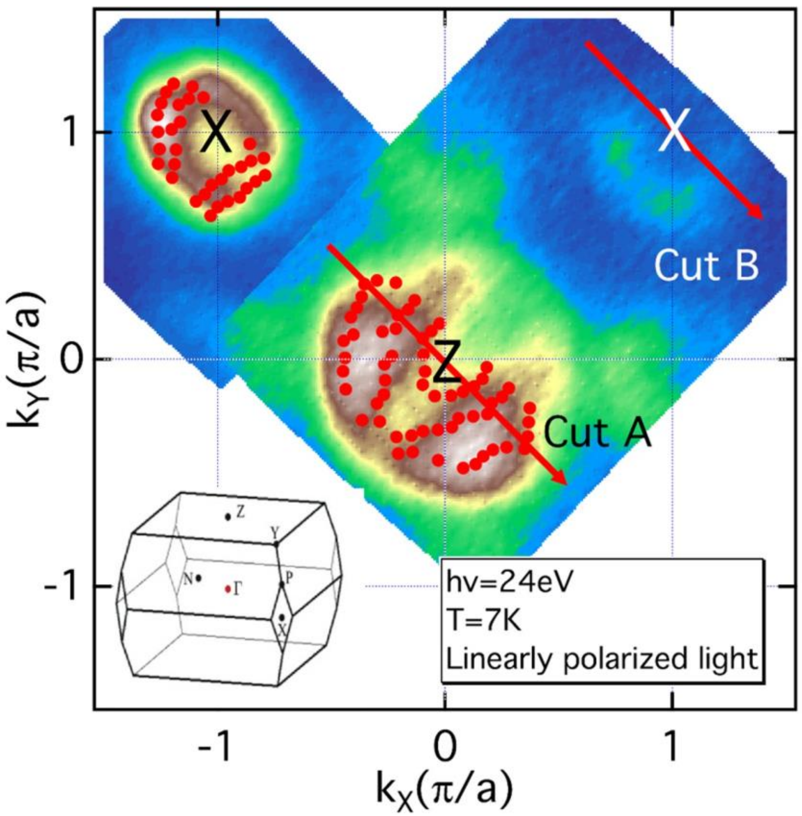
Scientific Case : High- Tc Superconductor

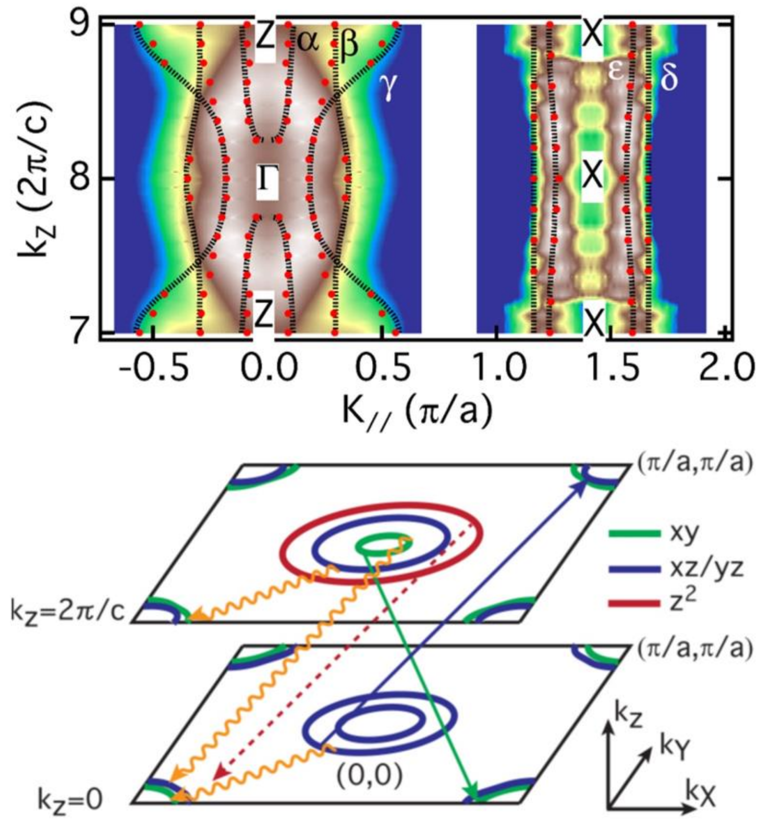




Scientific Case : High- Tc Superconductor

FS shapes of $SrFe_2(As_{0.65}P_{0.35})_2$ and
k_z dependence of the FSs



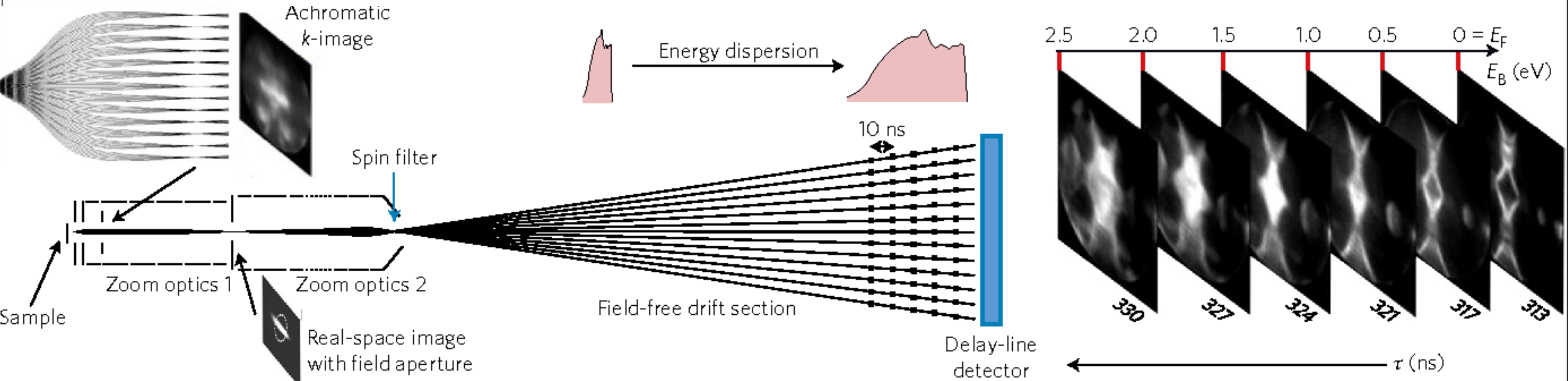


$$k_{\perp} = 0.5123\sqrt{(E_{kin}\cos^2\theta + V_0)}$$

$$k_{//} = 0.5123\sqrt{E_{kin}}\sin\theta$$

Suzuki et al., PRB (2017)

Scientific Case : Direct 3D Fermi surface mapping

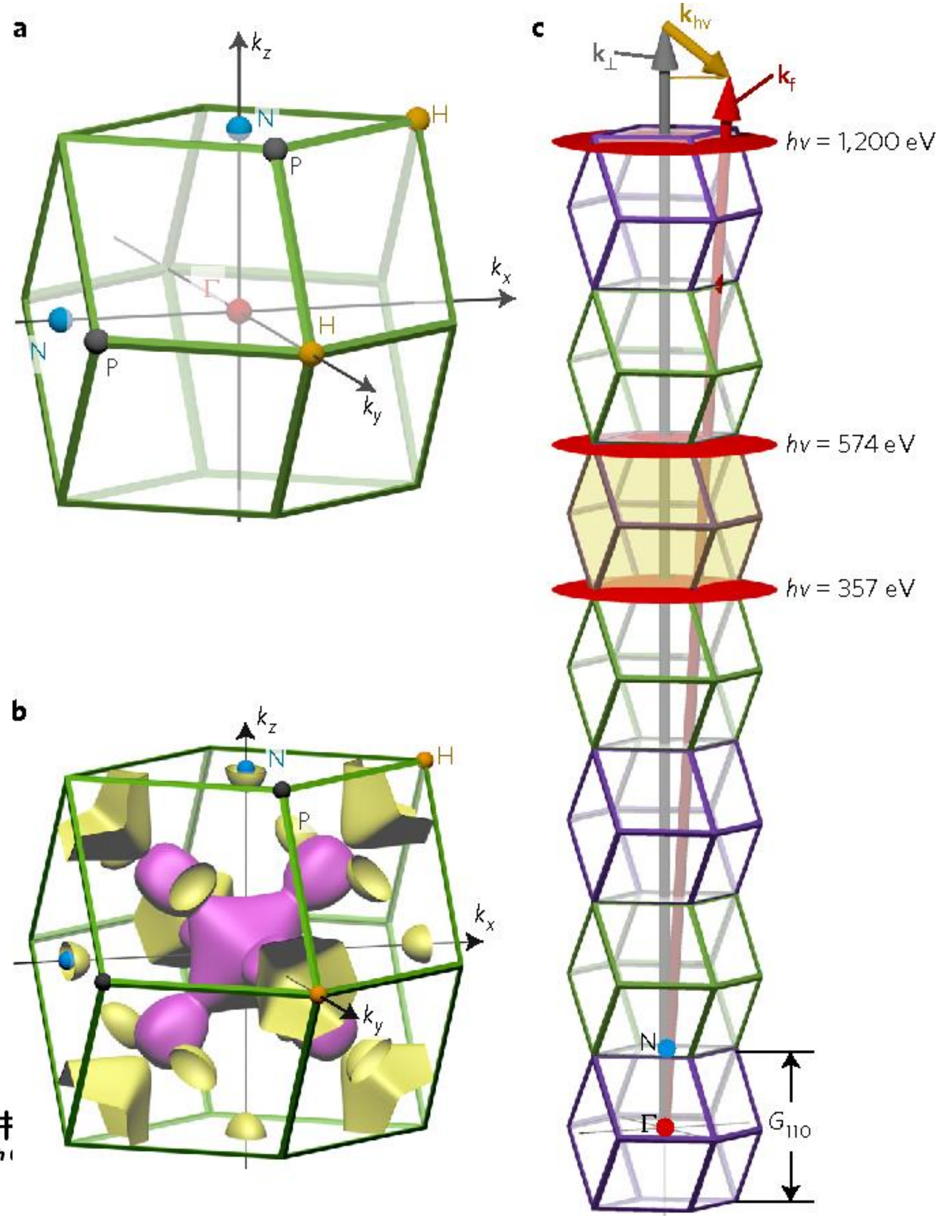


国家同步輻射研究中心
National Synchrotron Radiation Research Center

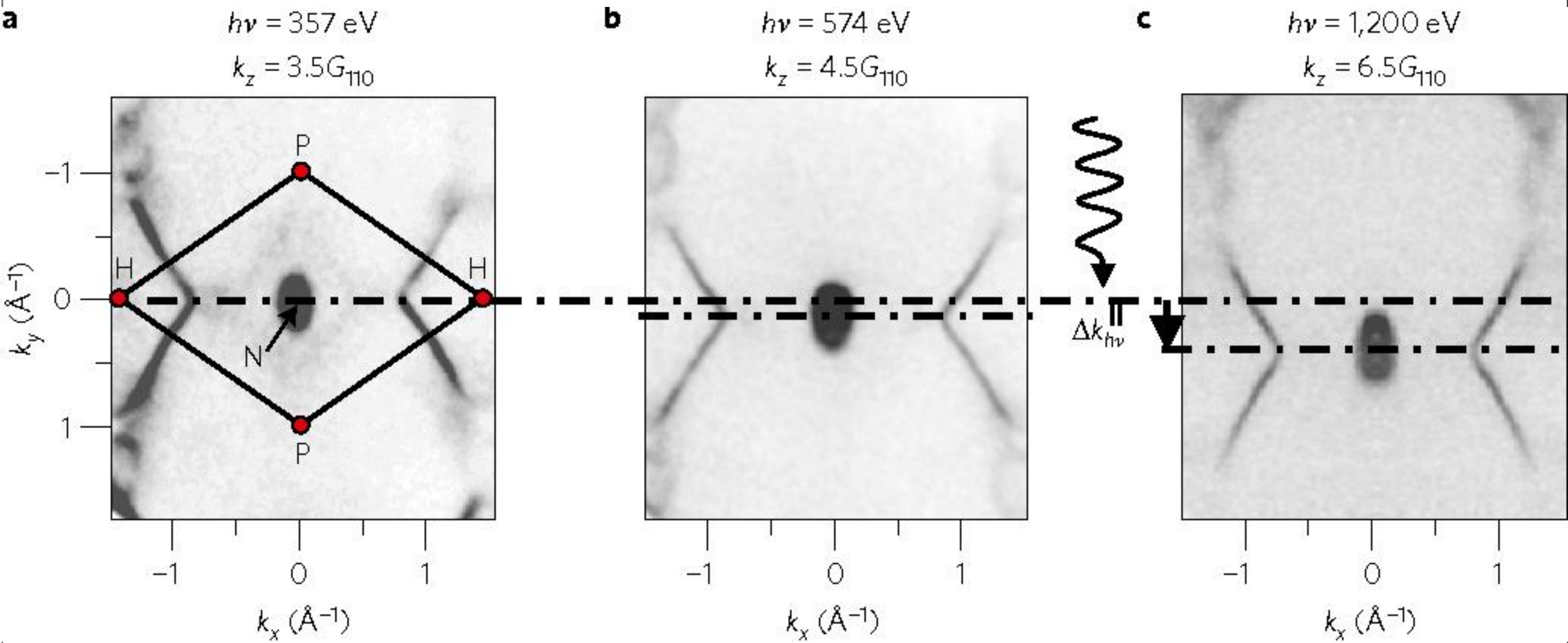
Medjanil et al., Nat. Mater. (2017)

Scientific Case : Direct 3D Fermi surface mapping

W(110)



Scientific Case : Direct 3D Fermi surface mapping

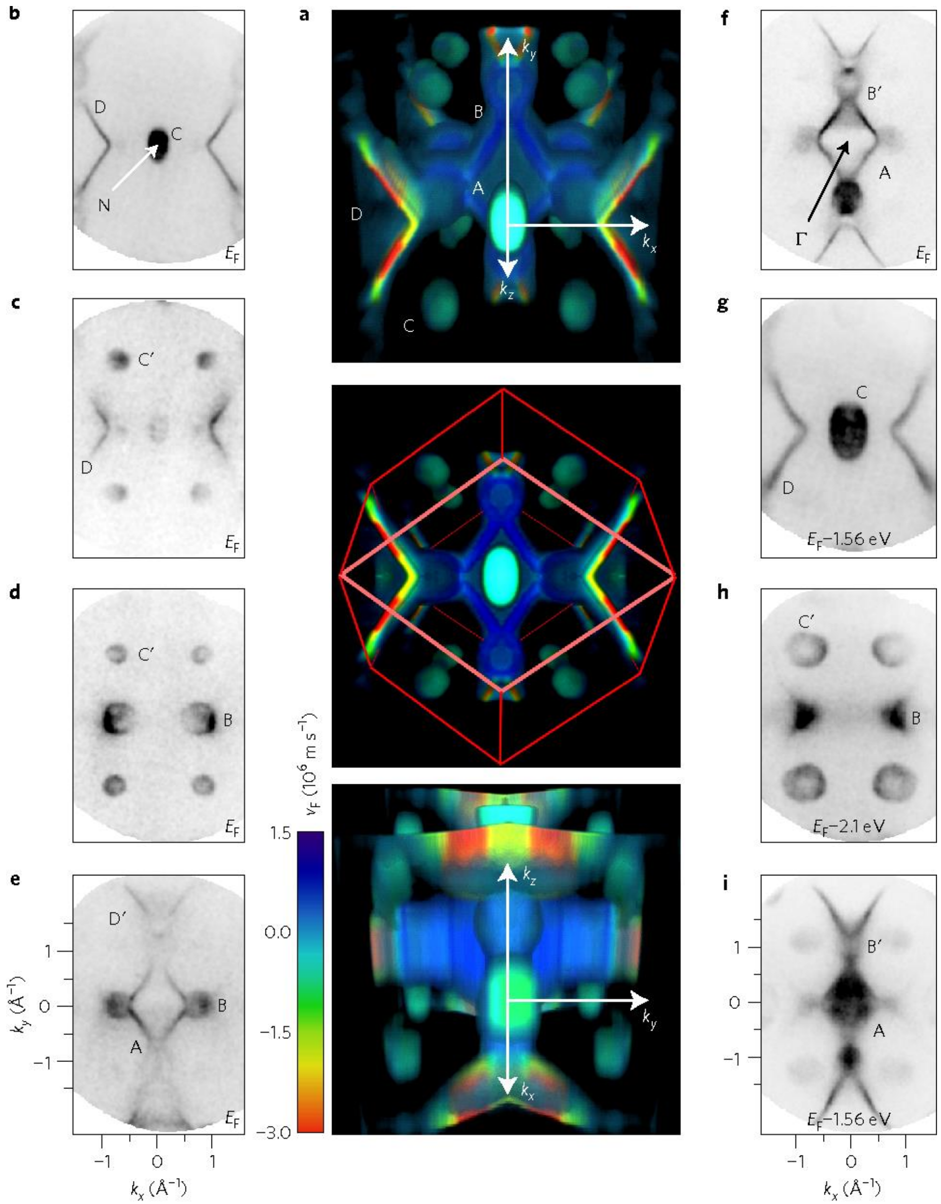


国家同步輻射研究中心
National Synchrotron Radiation Research Center

Scientific Case : Direct 3D Fermi surface mapping

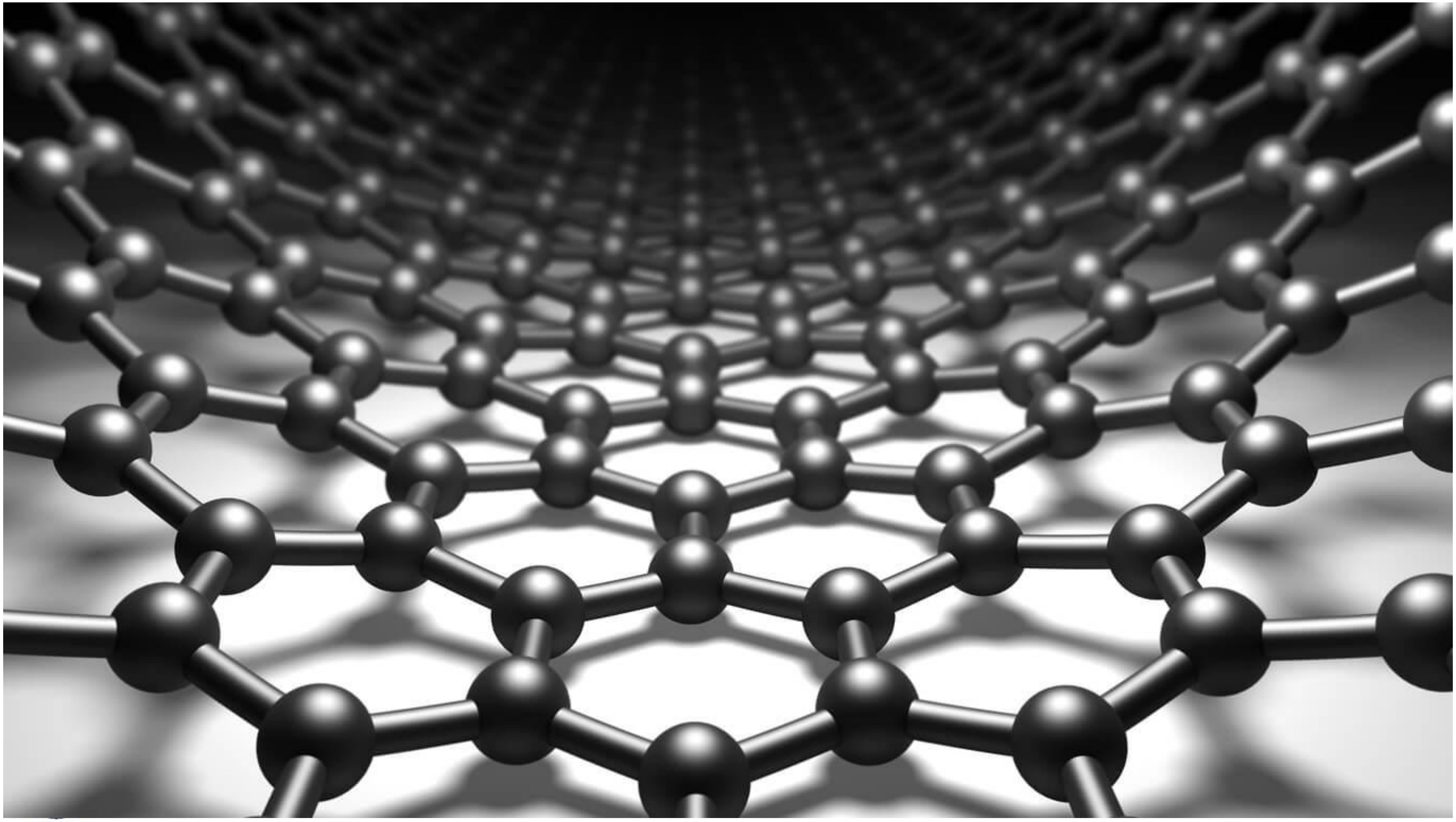
$$k_{\perp} = 0.5123\sqrt{(E_{kin}\cos^2\theta + V_0)}$$

$$k_{//} = 0.5123\sqrt{E_{kin}}\sin\theta$$

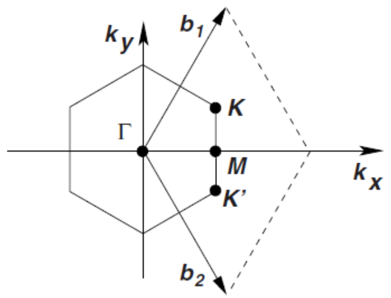


國家同步輻射研究中心
National Synchrotron Radiation Research Center

Scientific Case : Graphene

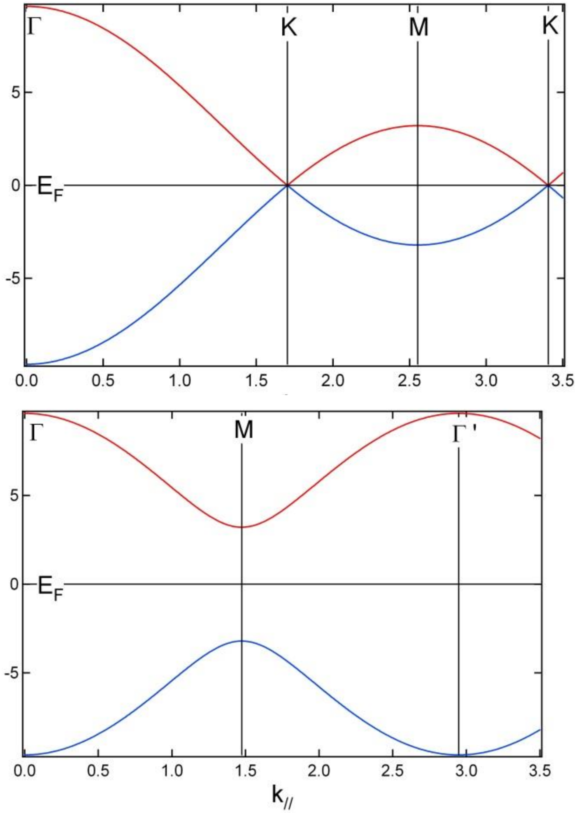


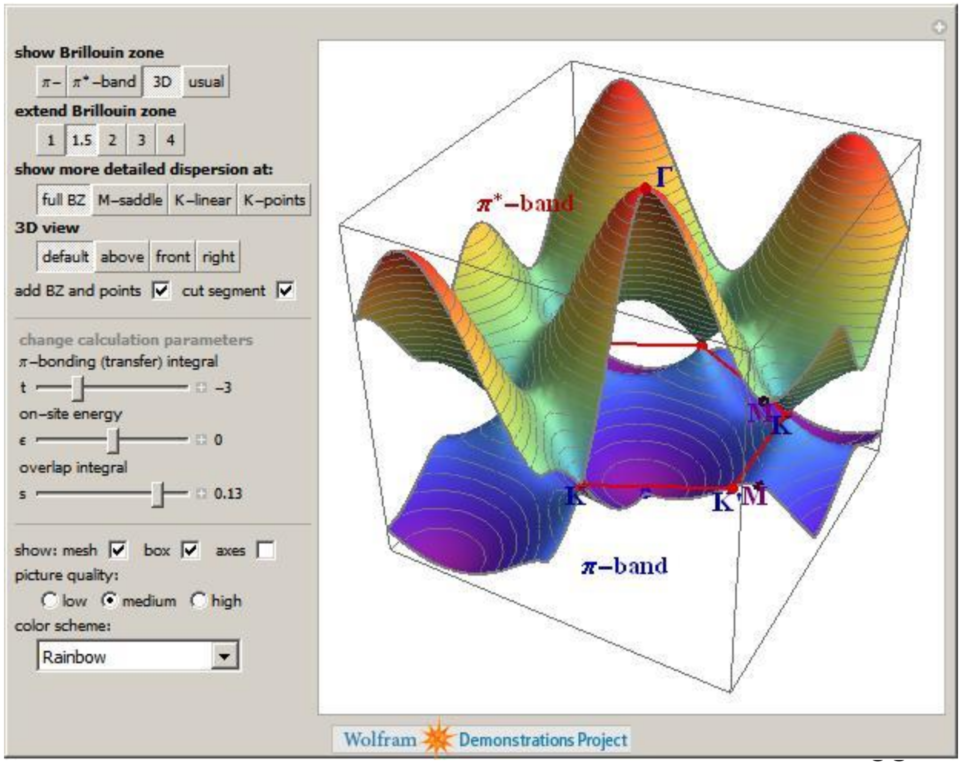
Scientific Case : Graphene



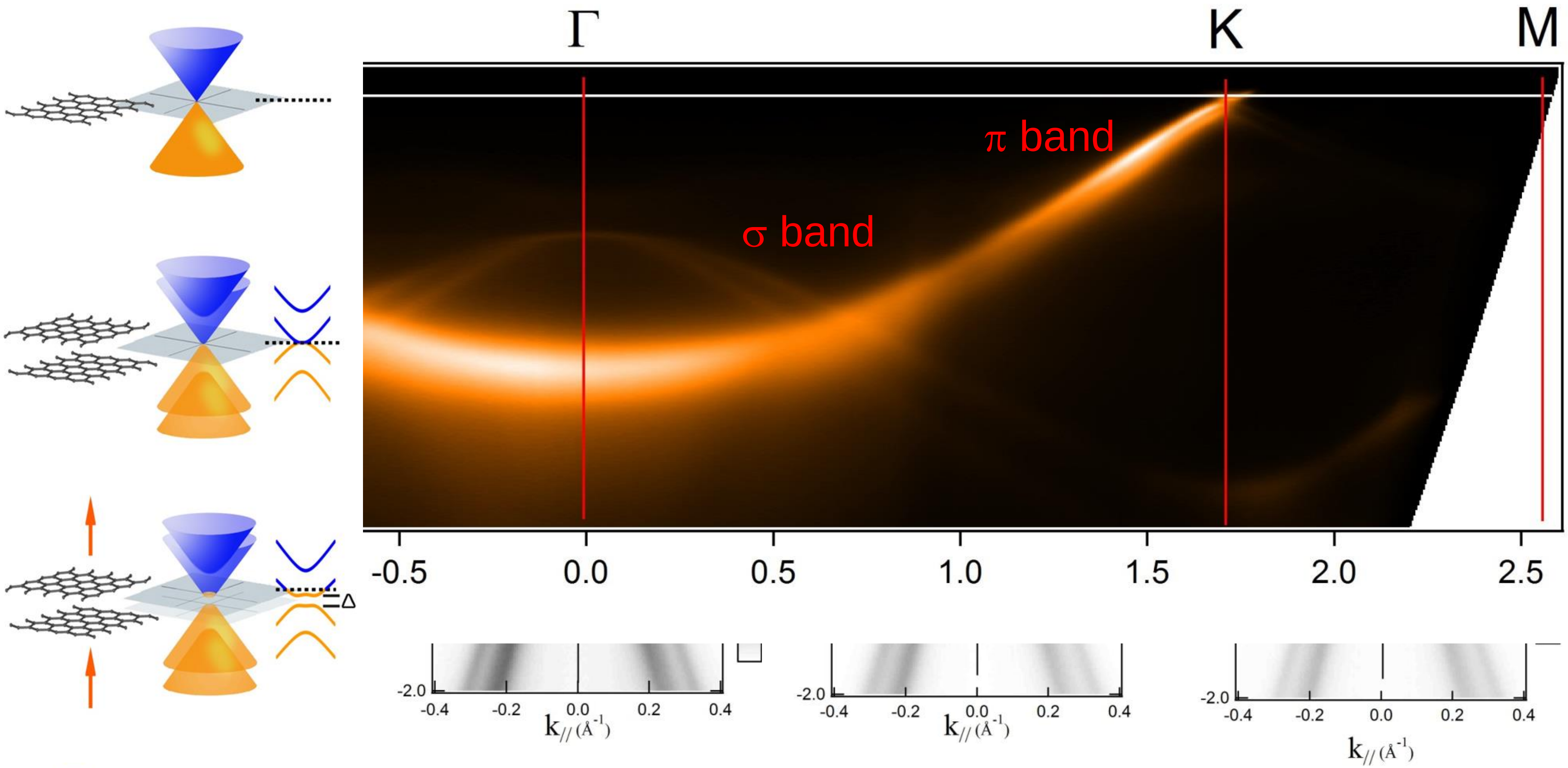
$$\boldsymbol{b}_1 = \frac{2\pi}{3a}(1, \sqrt{3}), \quad \boldsymbol{b}_2 = \frac{2\pi}{3a}(1, -\sqrt{3})$$

$$\boldsymbol{K} = \left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a}\right), \quad \boldsymbol{K}' = \left(\frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a}\right)$$

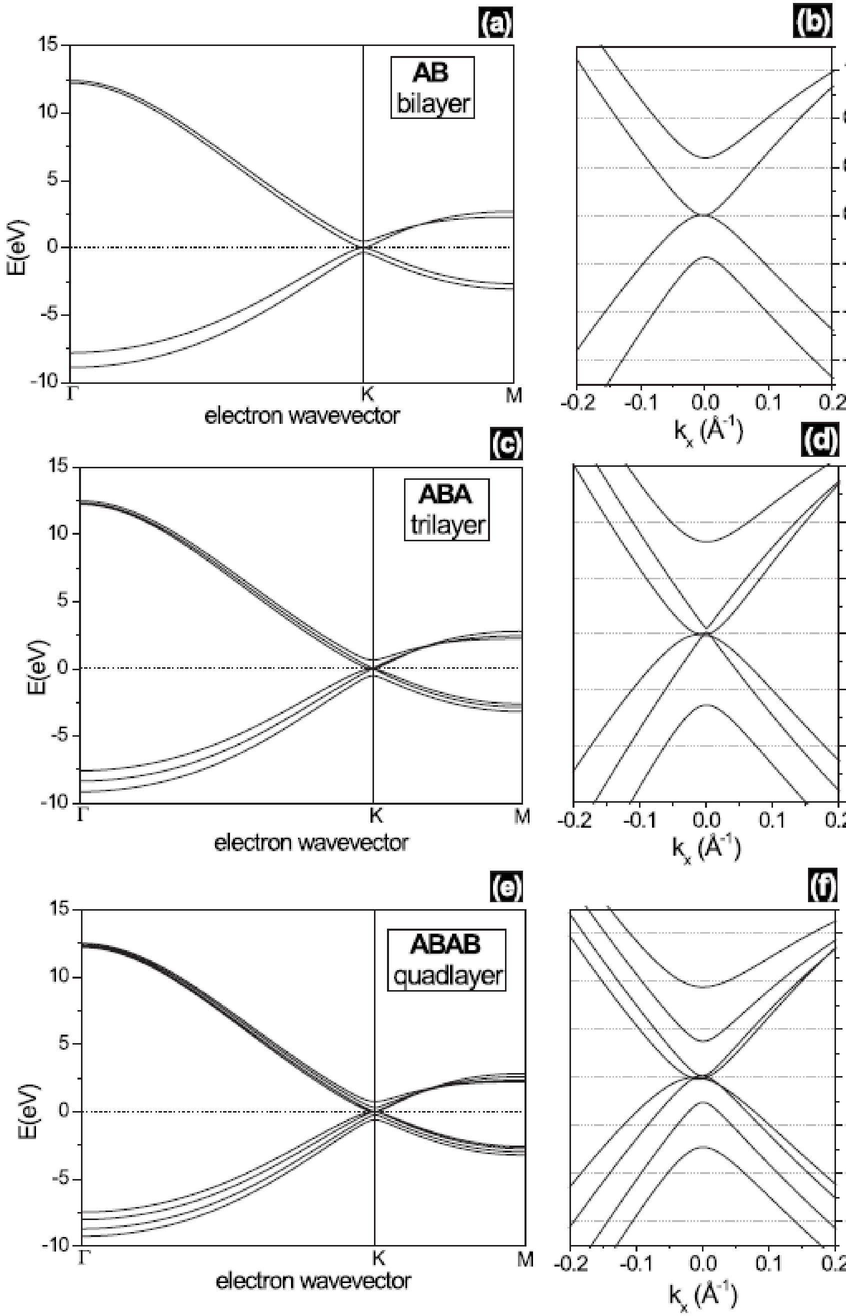


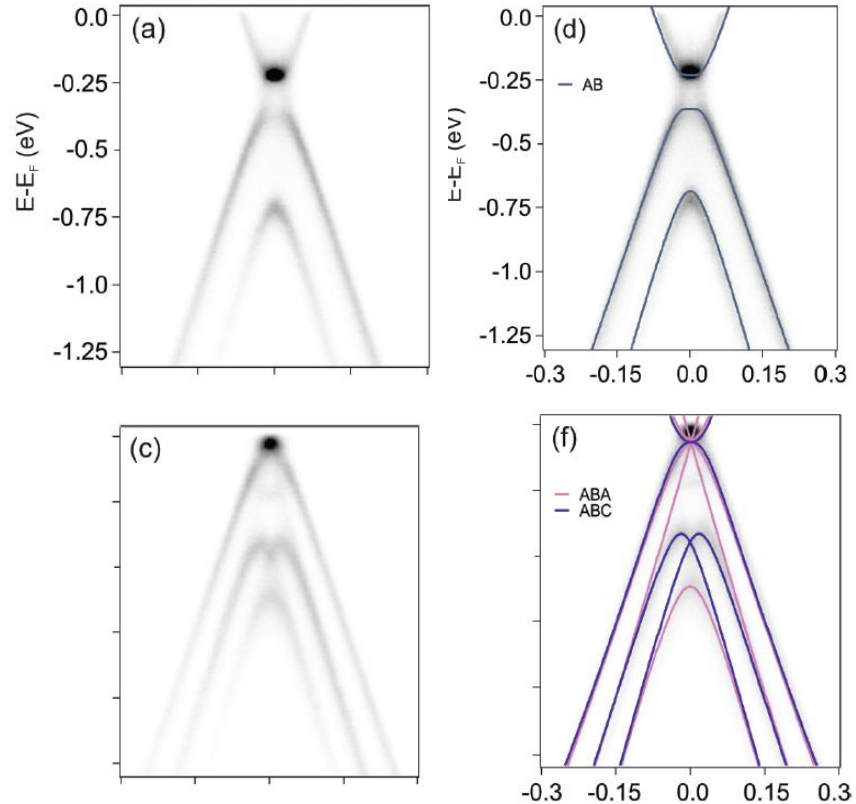


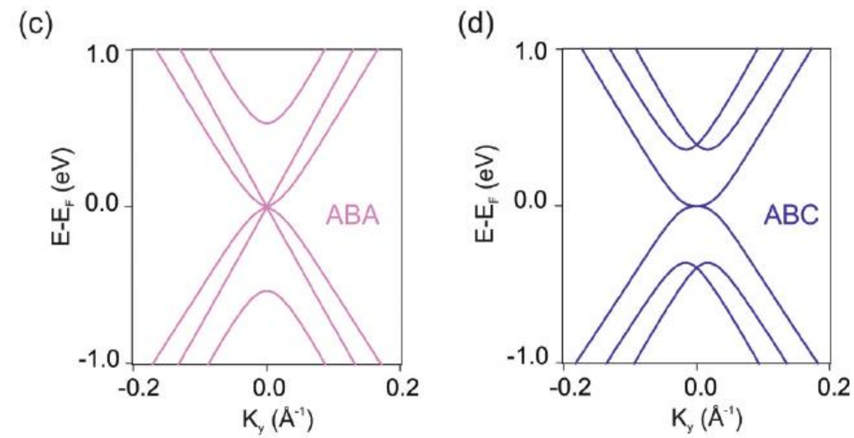
What we expect to observe in ARPES



國家同步輻射研究中心
National Synchrotron Radiation Research Center



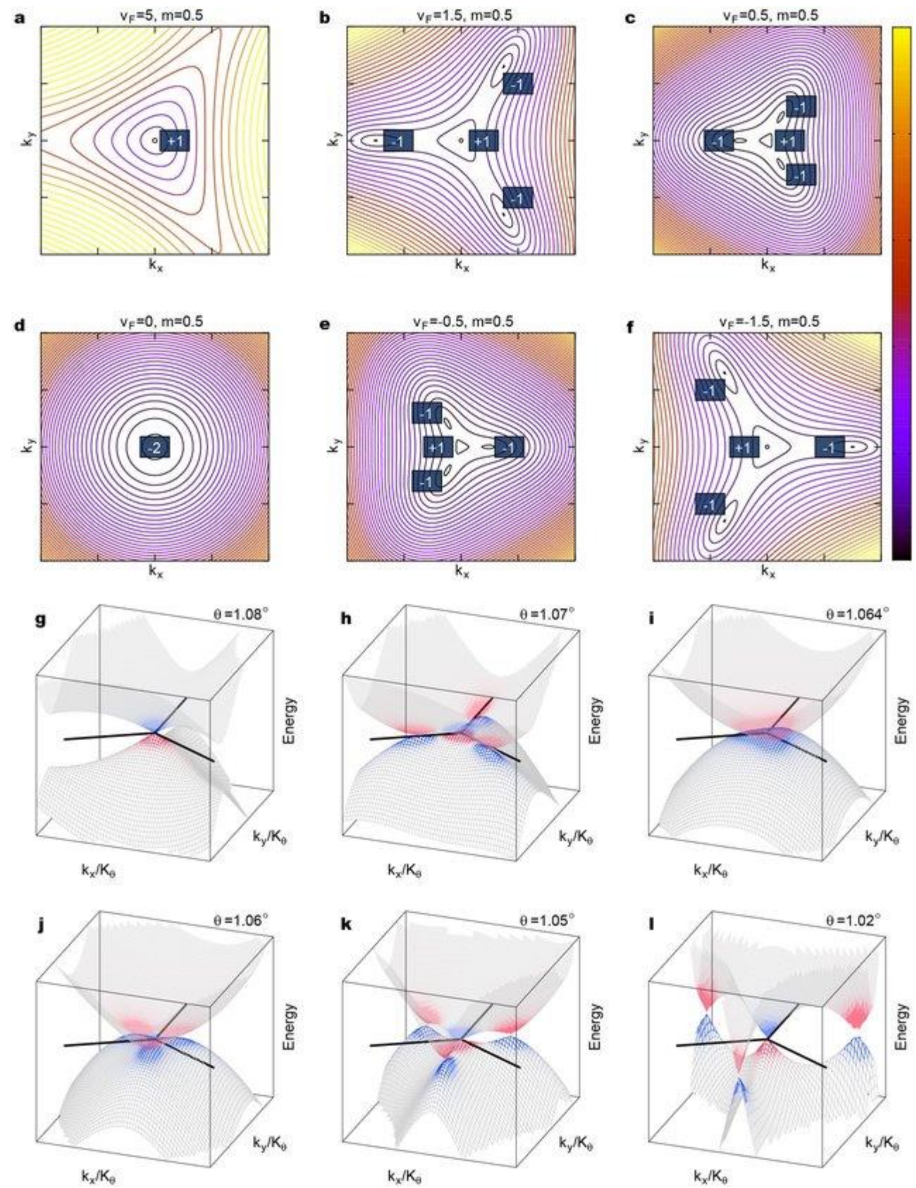




Coletti et al., PRB (2013)

Scientific Case : Twisted Bilayer Graphene

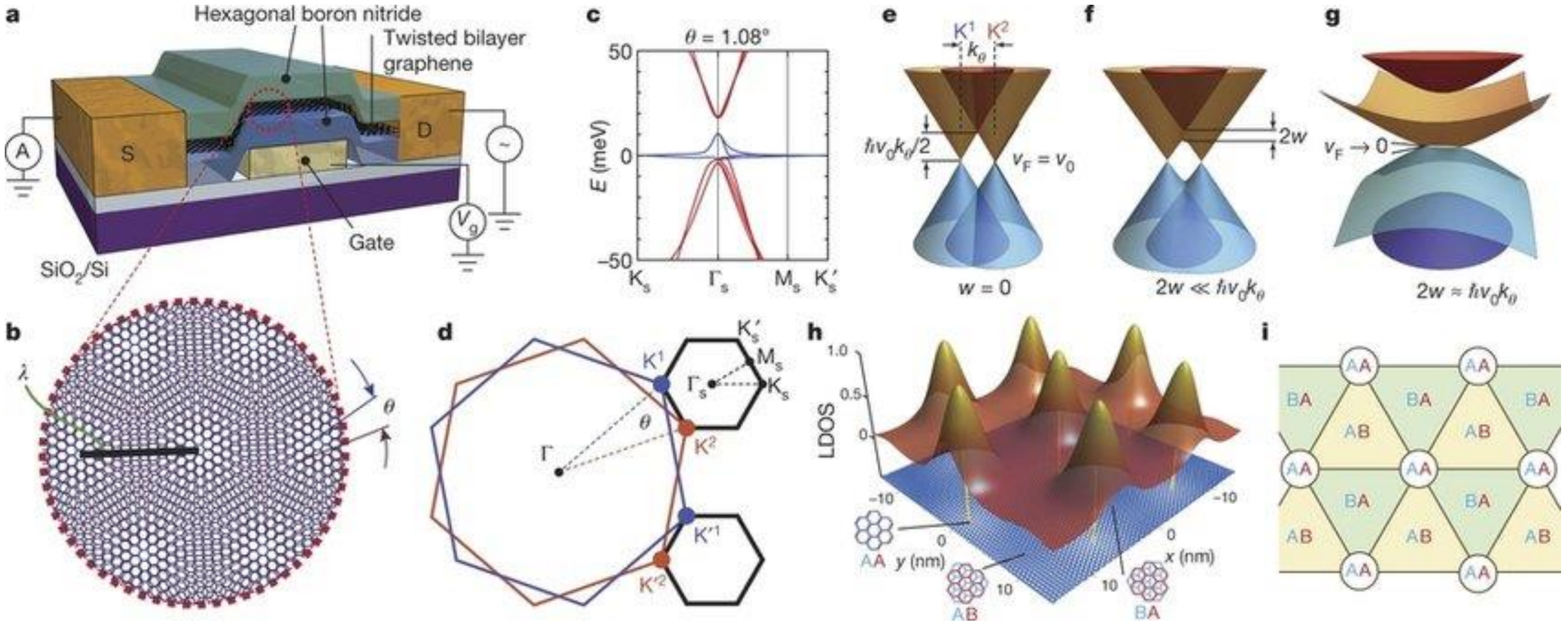
The simulated band structure of twisted bilayer graphene



國家同步輻射研究中心
National Synchrotron Radiation Research Center

Scientific Case : Twisted Bilayer Graphene

The simulated band structure of twisted bilayer graphene



Cao et al., Nature (2018)

ARPES – Characterization of emergent quantum materials

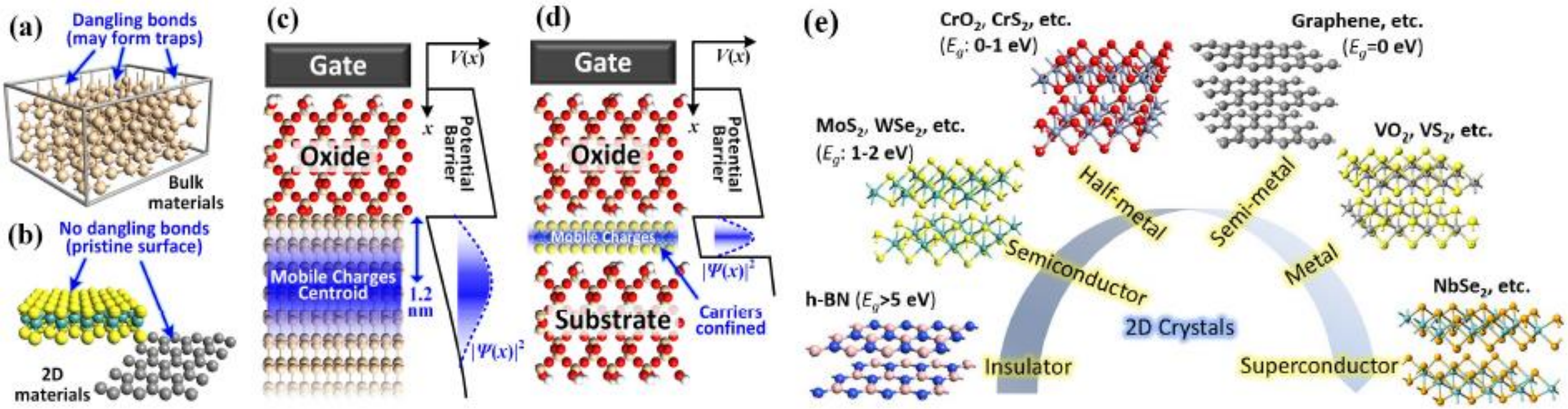
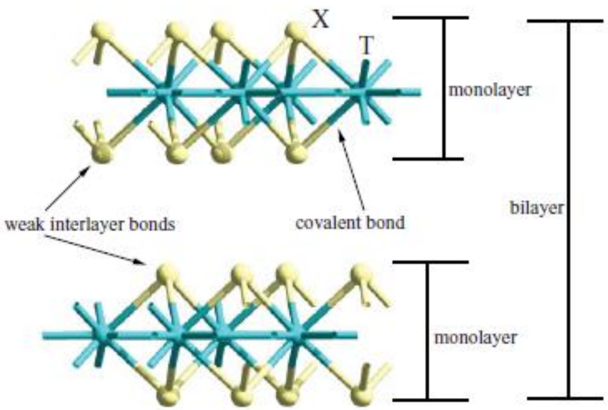
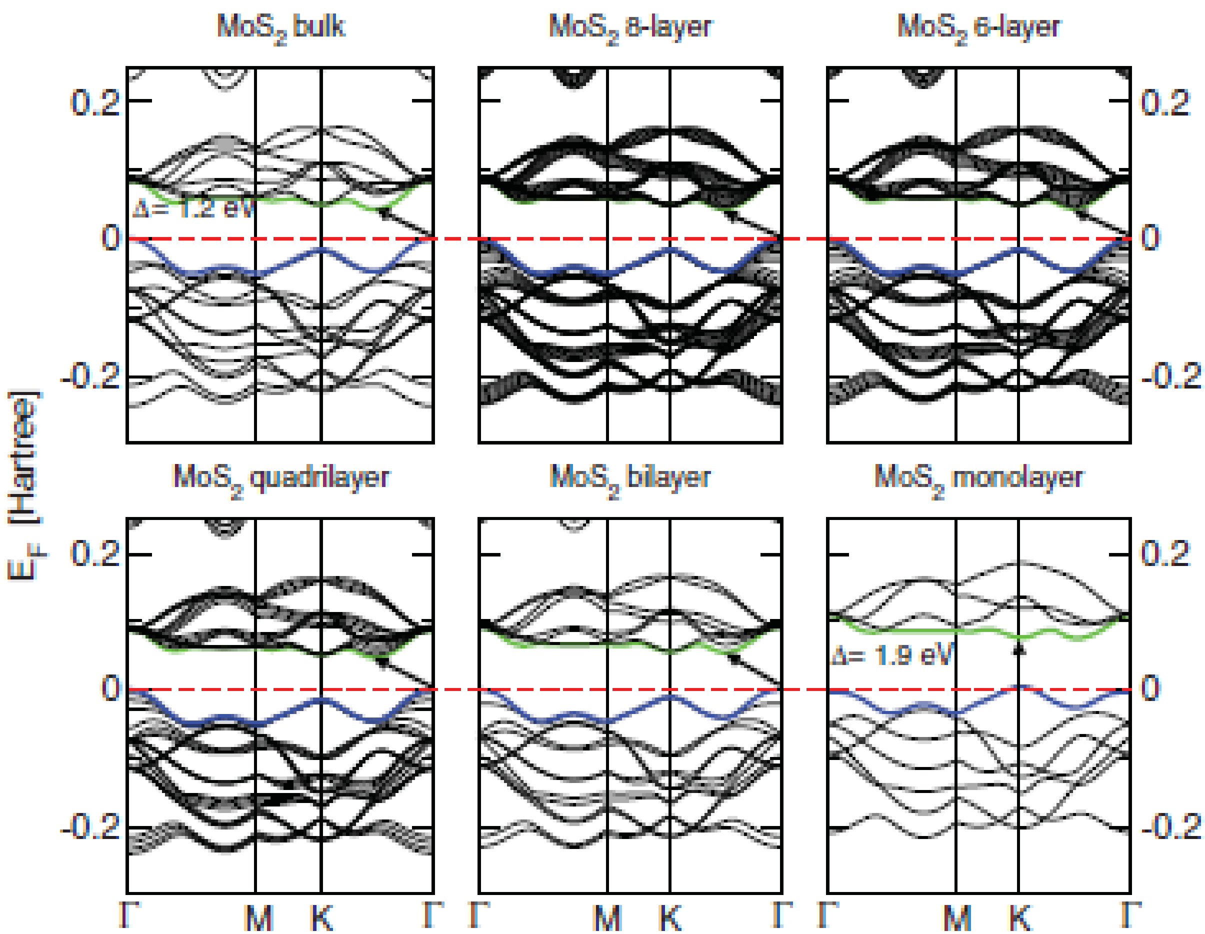


Figure 1. Schematic illustrating advantages of 2D materials: surfaces of **(a)** 3D and **(b)** 2D materials. The pristine interfaces (without out-of-plane dangling bonds) of 2D materials help reduce the interface traps. Mobile charge distribution in **(c)** 3D and **(d)** 2D crystals used as channel materials. The carrier confinement effect in 2D materials leads to excellent gate electrostatics. **(e)** Various types of 2D materials from insulator to superconductor. E_g denotes the band gap.

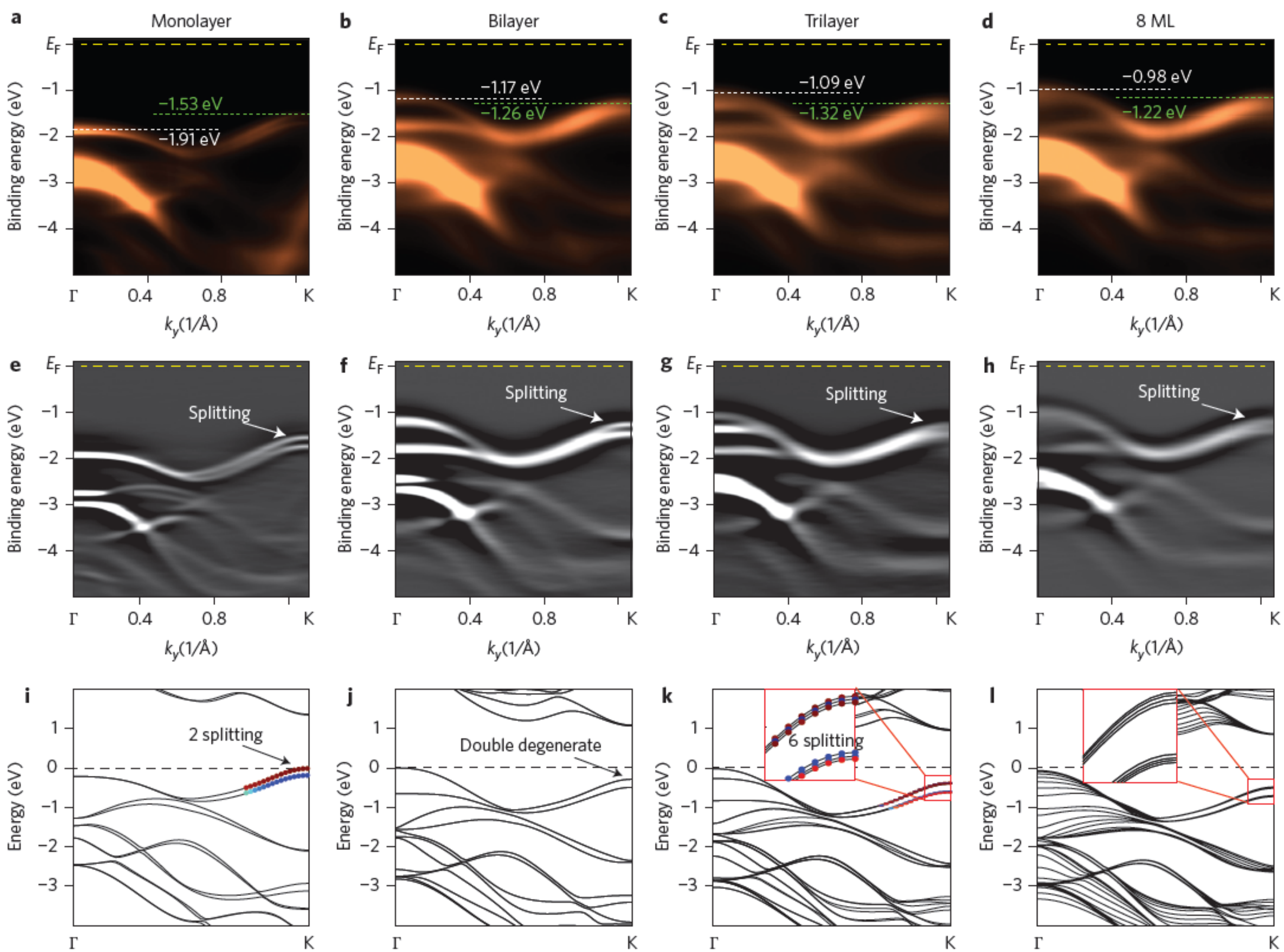
Transition Metal Dichalcogenides : MoS_2





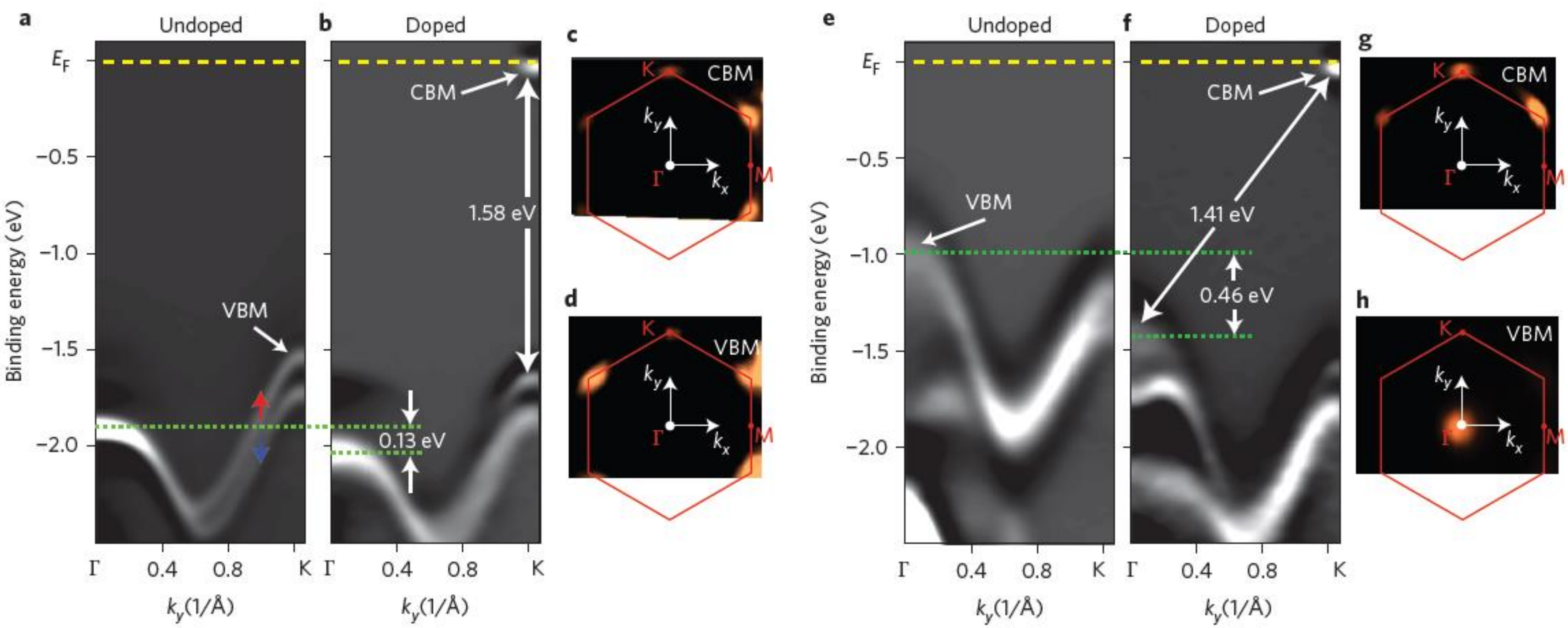
Kuc et. al., PRB (2011)

Transition Metal Dichalcogenides : $MoSe_2$



Zhang et al., Nat. Nano. (2013)

Transition Metal Dichalcogenides :$MoSe_2$



Scientific Cases: Topological protected surface state

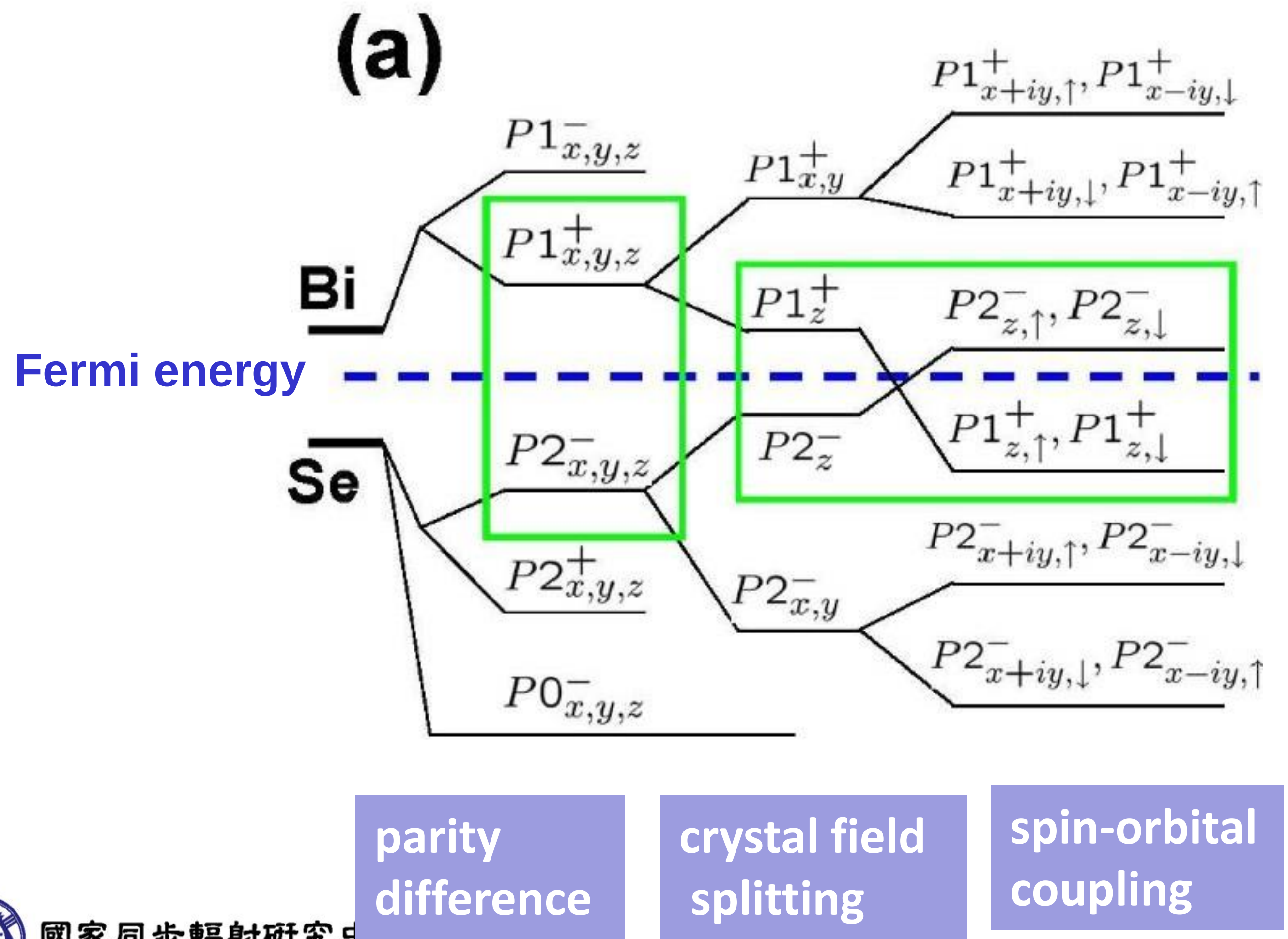
Shou-Cheng Zhang (1963-2018)

Strong spin-orbital interaction

Heavy elements

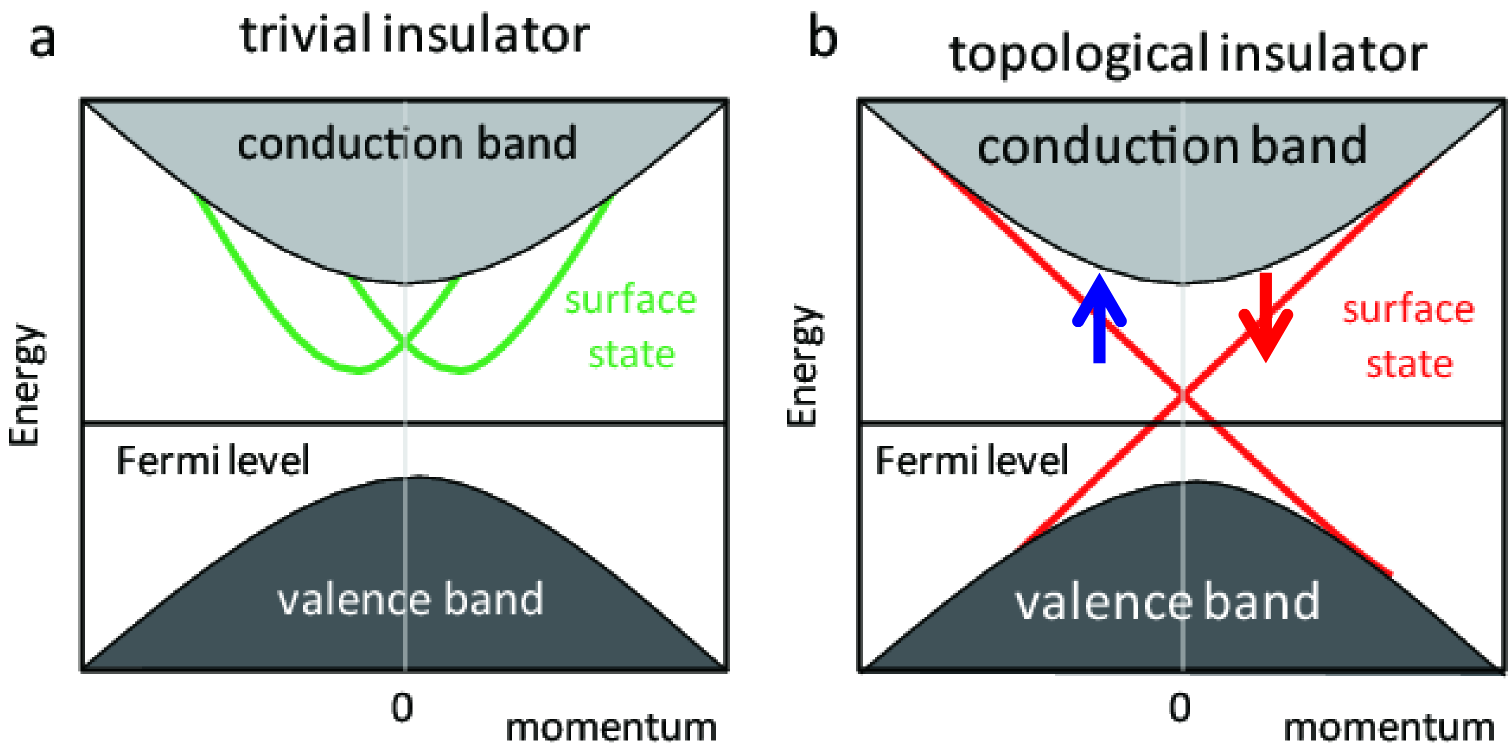
10	11	12	13	14	15	16	17	18
			5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
			13 Al Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessine	118 Og Oganesson

Scientific Cases: Topological protected surface state



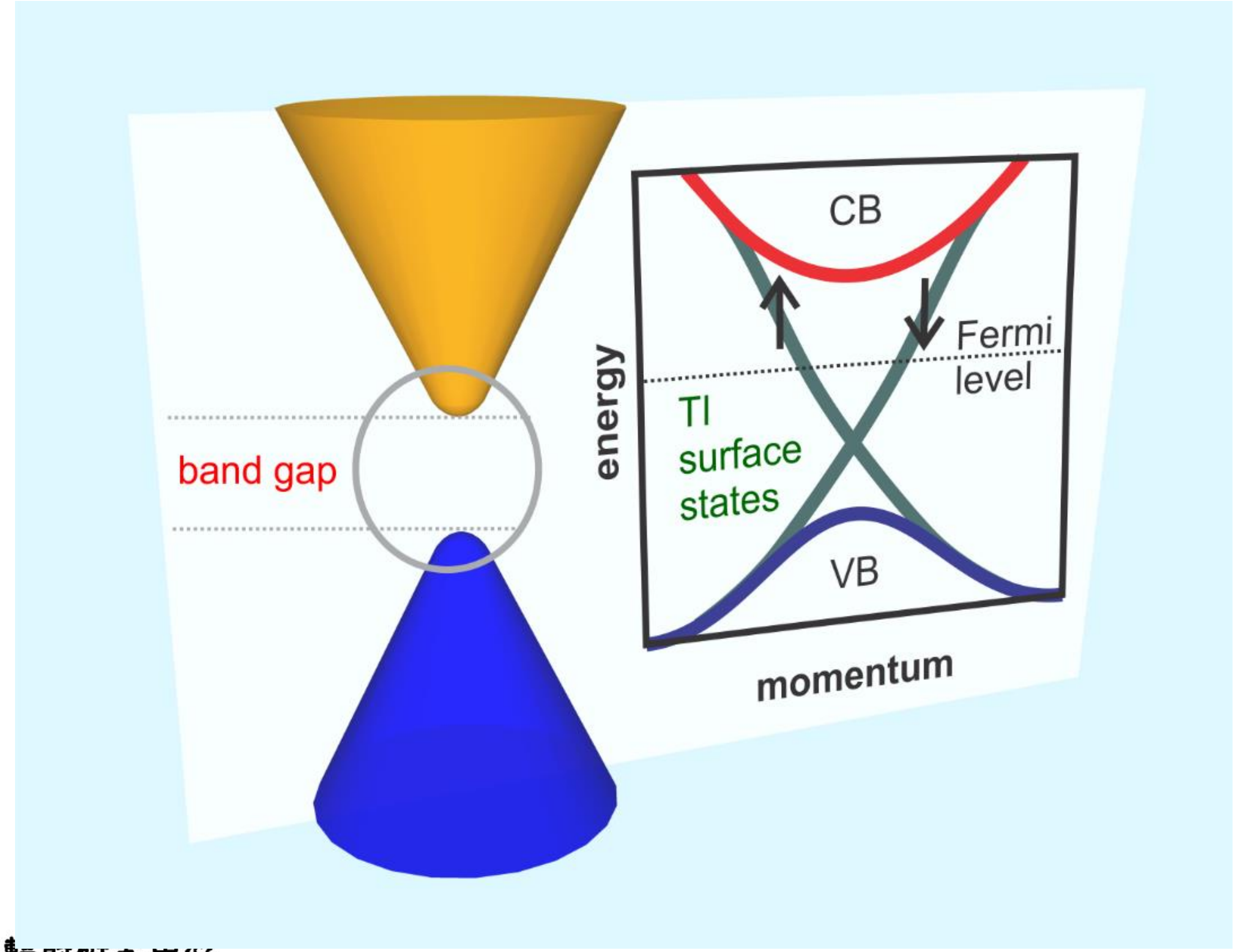
Xiao-Liang Qi and Shou-Cheng Zhang, RMP (2011)

Scientific Cases: Topological protected surface state

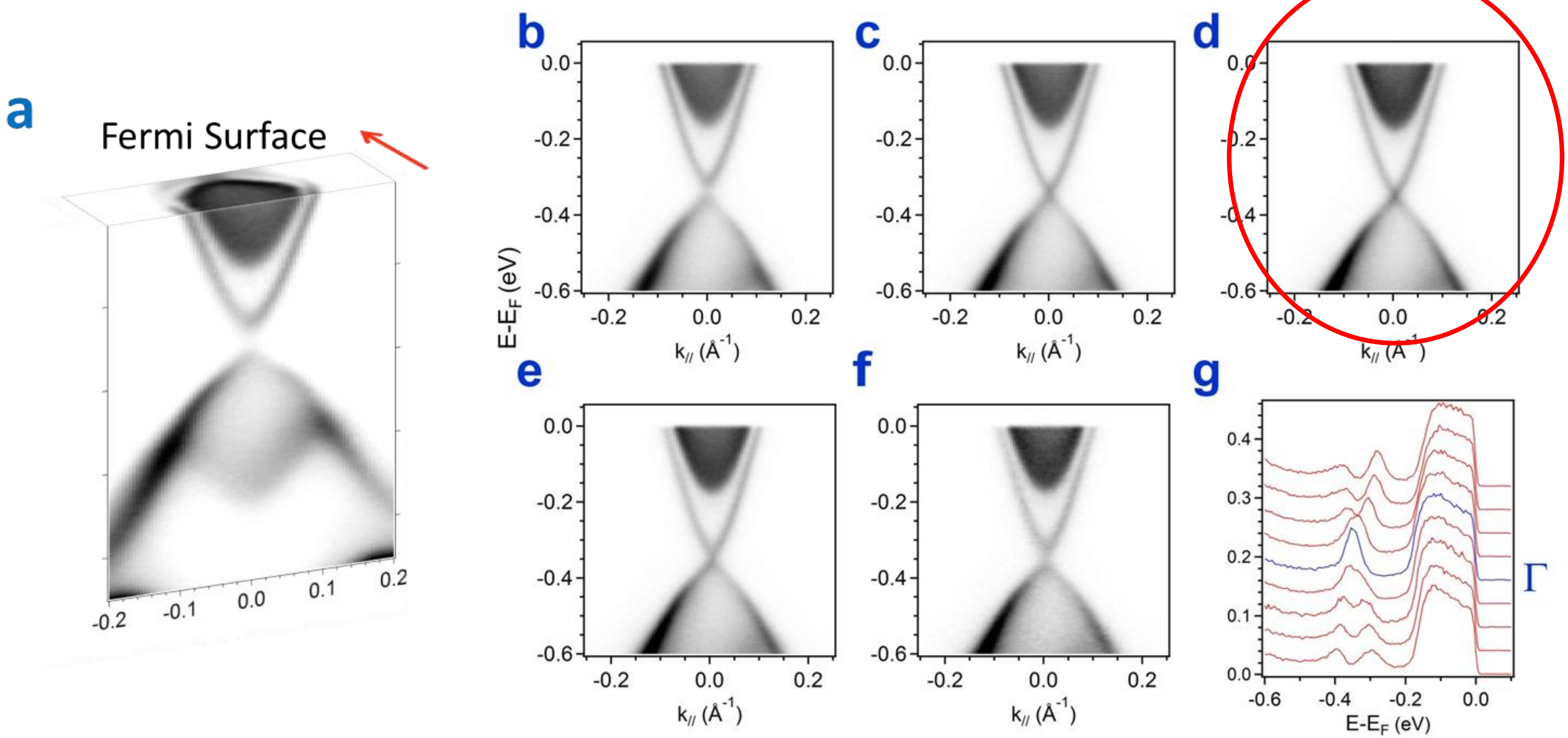


time-reversal symmetry protected

Scientific Cases: Topological protected surface state

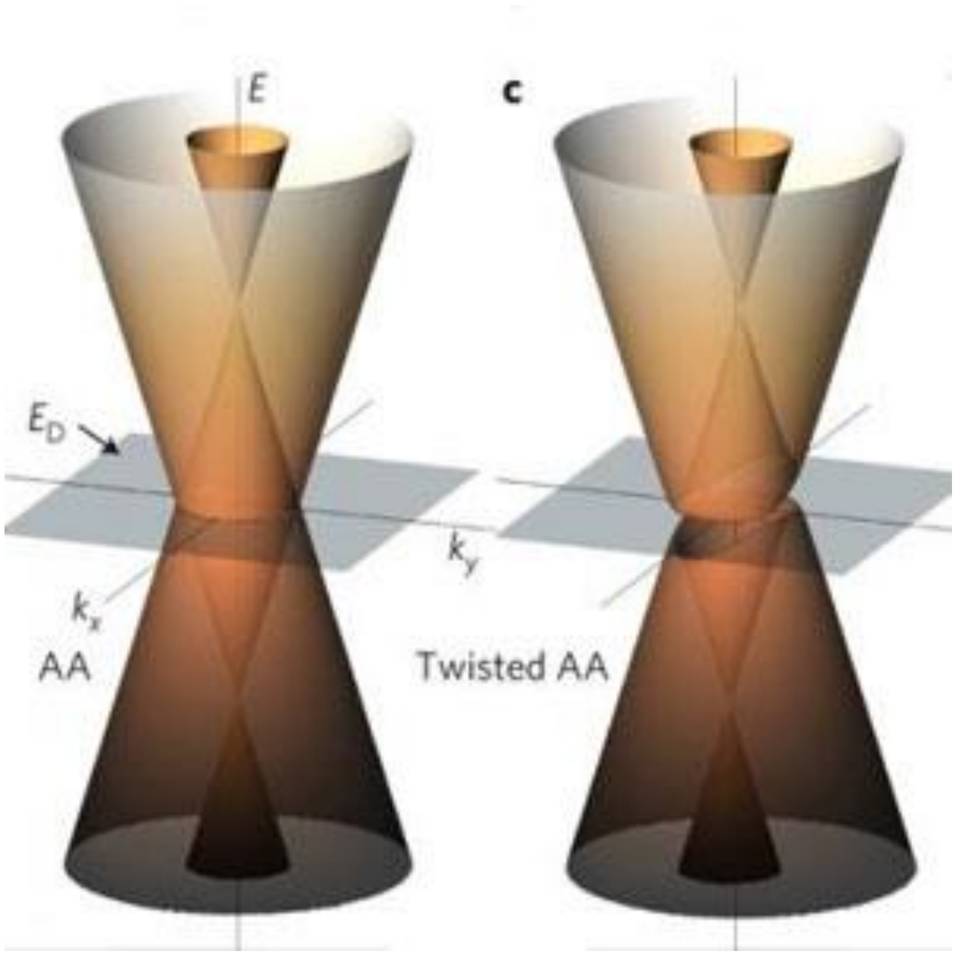


Topological Insulators probed by ARPES

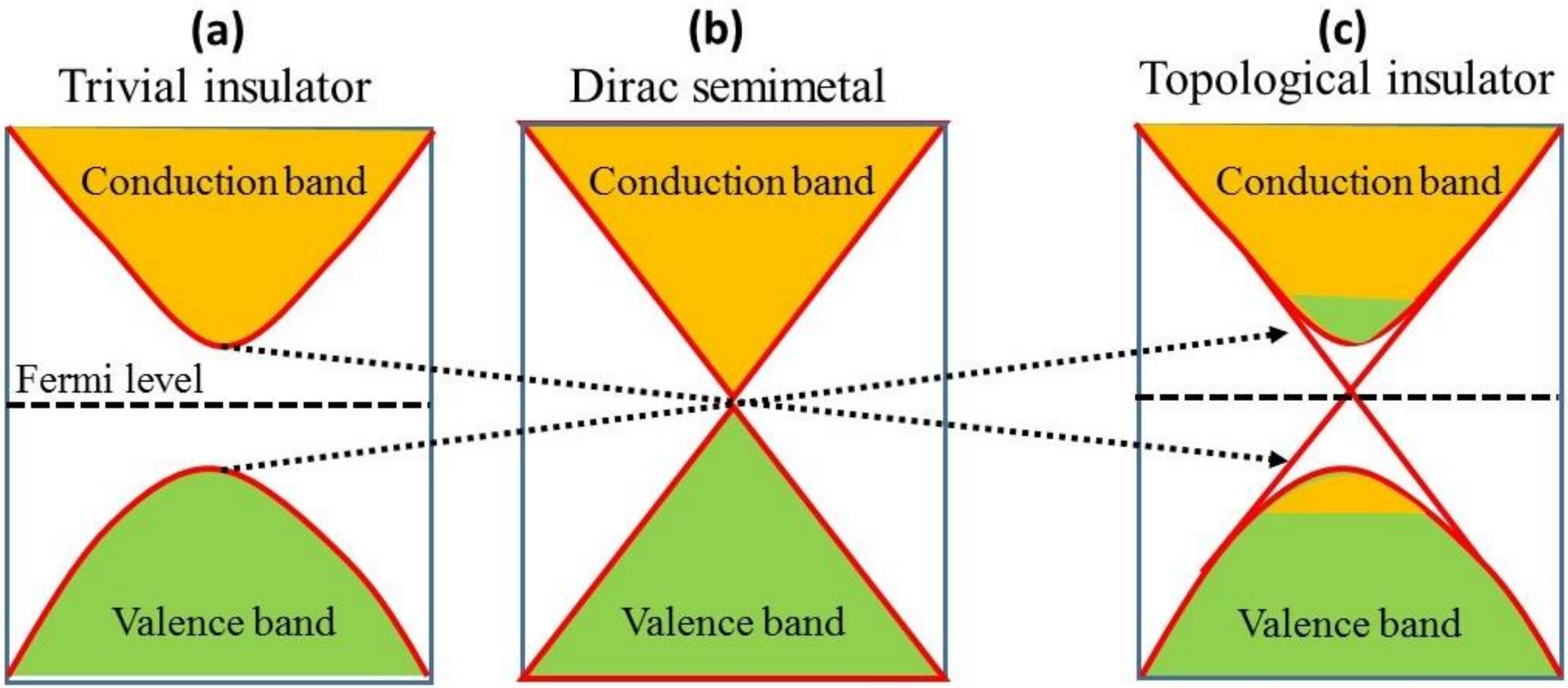


國家同步輻射研究中心
National Synchrotron Radiation Research Center

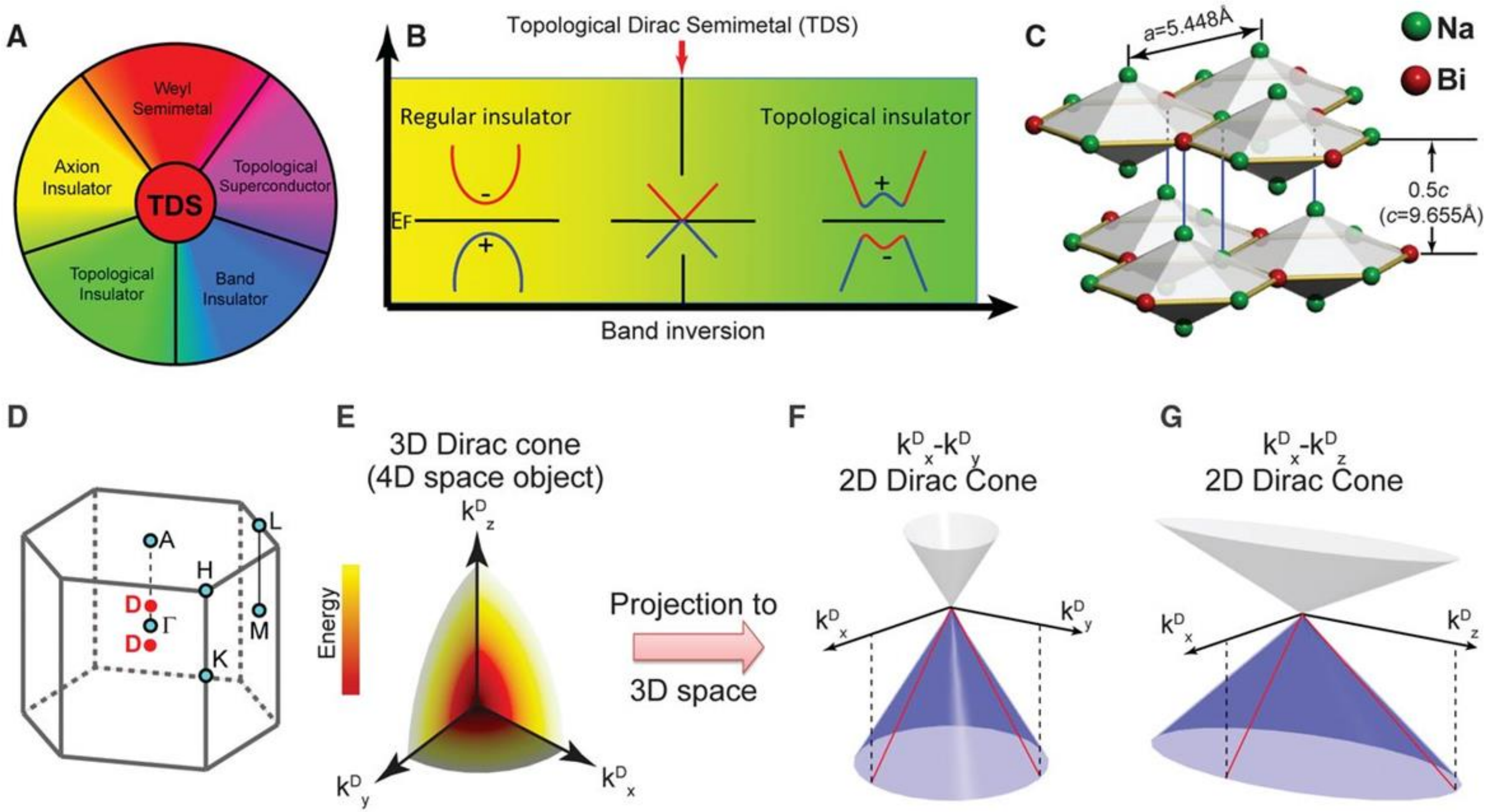
Scientific Cases: Dirac semimetal and Weyl semimetal



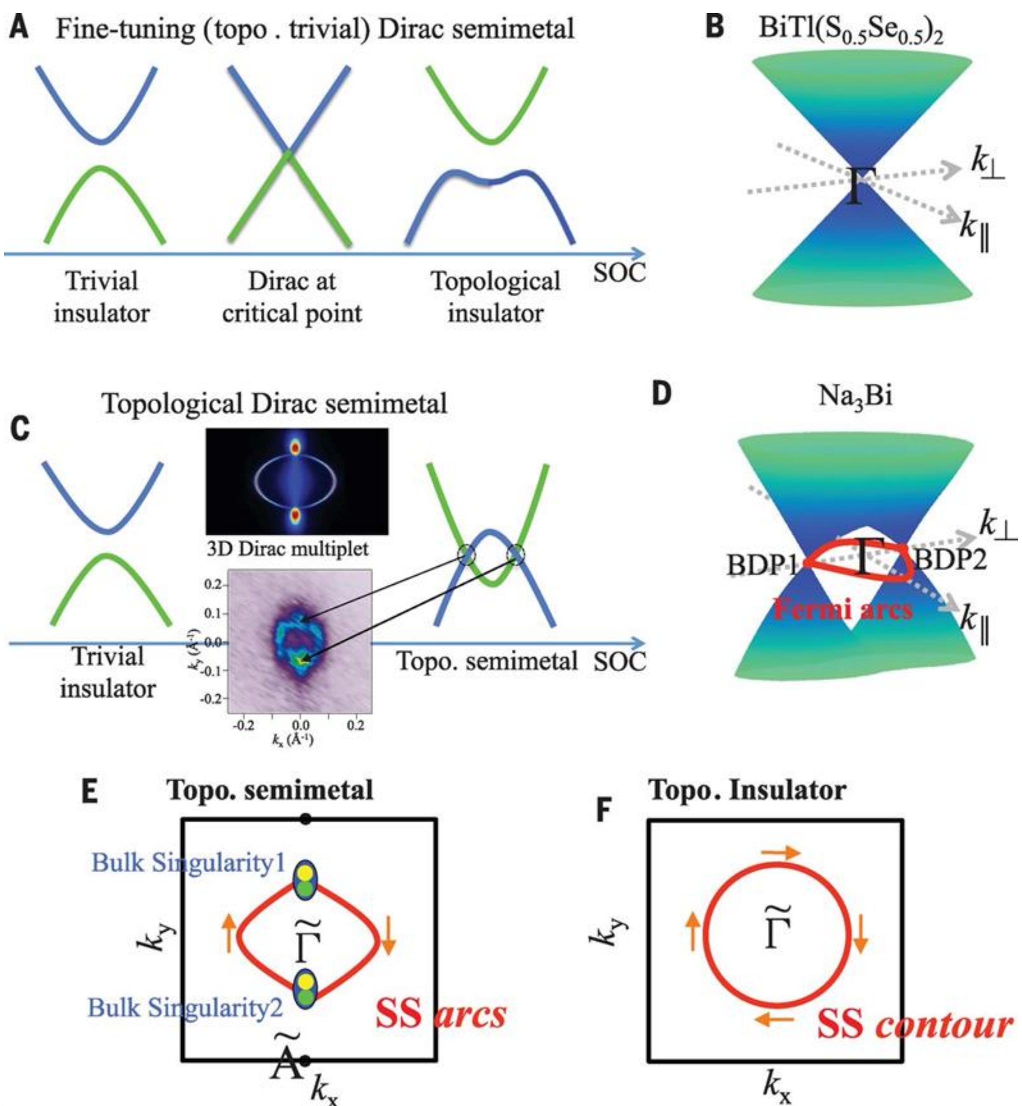
Scientific Cases: Dirac semimetal and Weyl semimetal



Scientific Cases: Dirac semimetal and Weyl semimetal

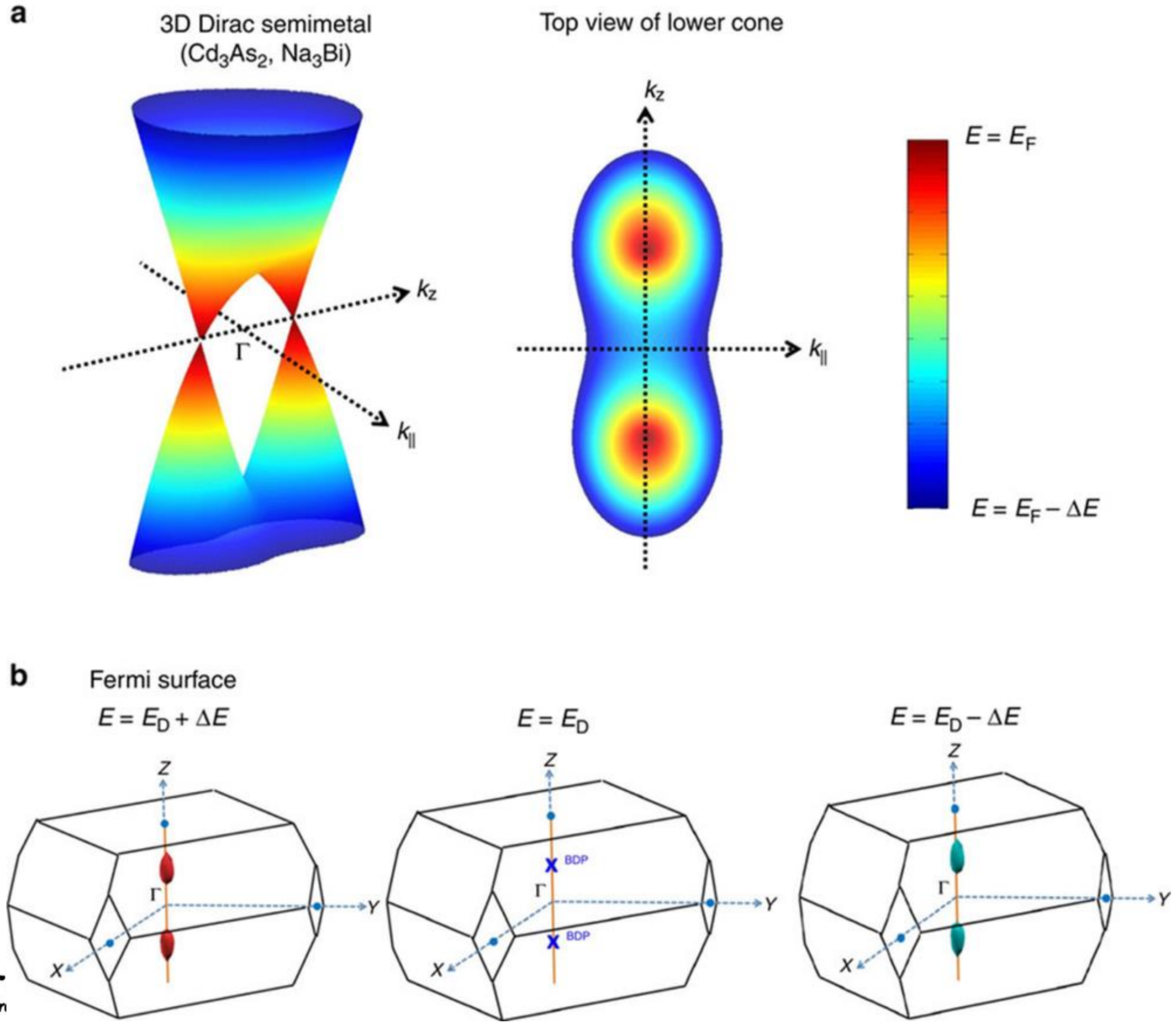


Scientific Cases: Dirac semimetal and Weyl semimetal



國家同步輻射研究中心
National Synchrotron Radiation Research Center

Scientific Cases: Dirac semimetal and Weyl semimetal

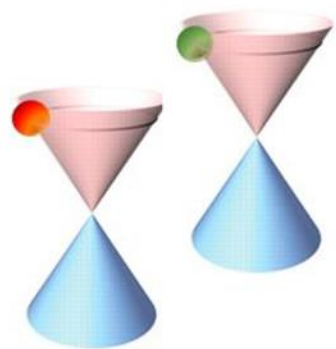


國家同步
National Synchrotr

Scientific Cases: Dirac semimetal and Weyl semimetal

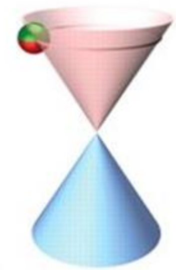
3D semimetals with linear dispersion

Weyl semimetal
(non-degenerated bands)



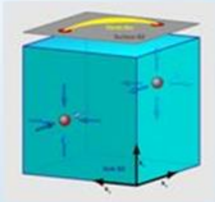
TaAs
NbAs
NbP
TaP

Dirac semimetal
(doubly degenerated bands)



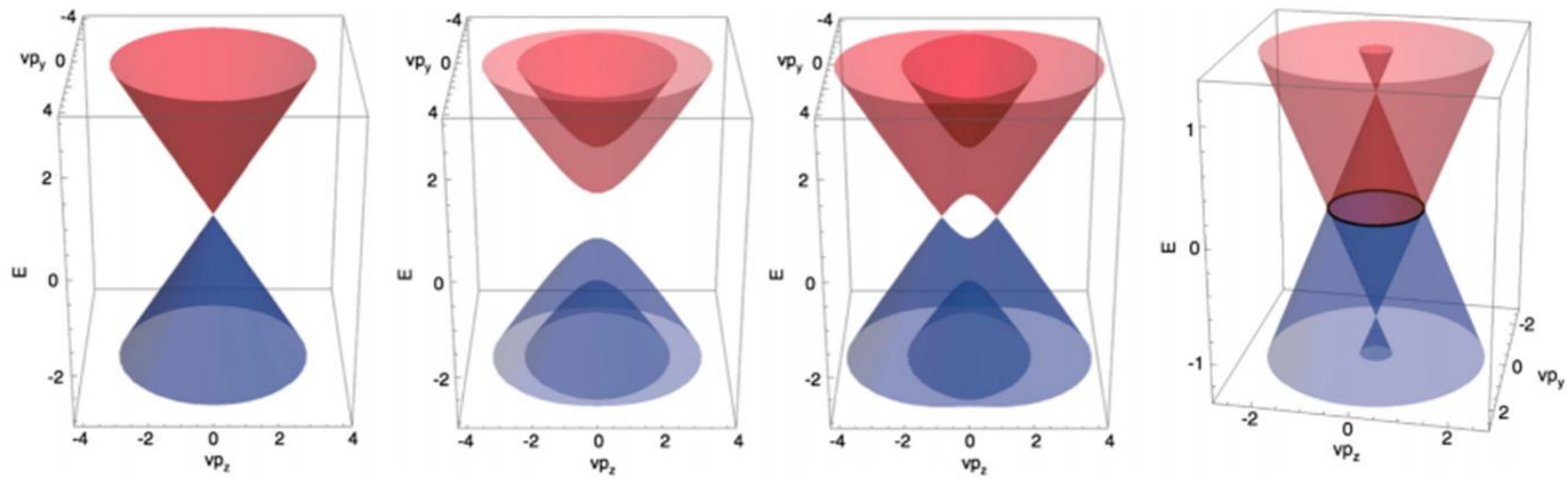
$ZrTe_5$
Na_3Bi,
Cd_3As_2

- The Dirac point can split into two Weyl points either by breaking the crystal inversion symmetry or time-reversal symmetry.
- In condensed matter physics, each Weyl point act like a singularity of the Berry curvature in the Brillion Zone – magnetic monopole in *k*-space

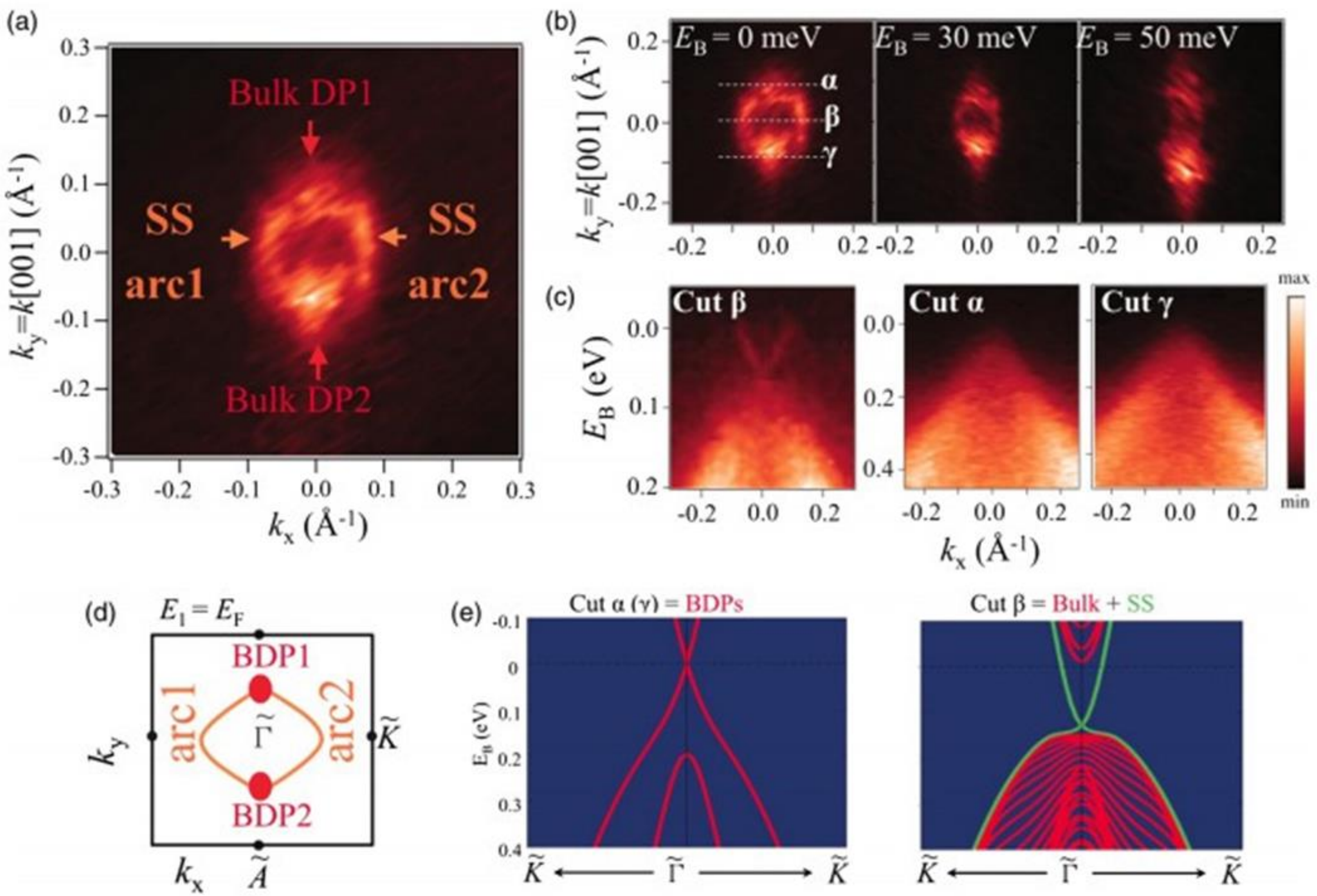


Scientific Cases: Dirac semimetal and Weyl semimetal

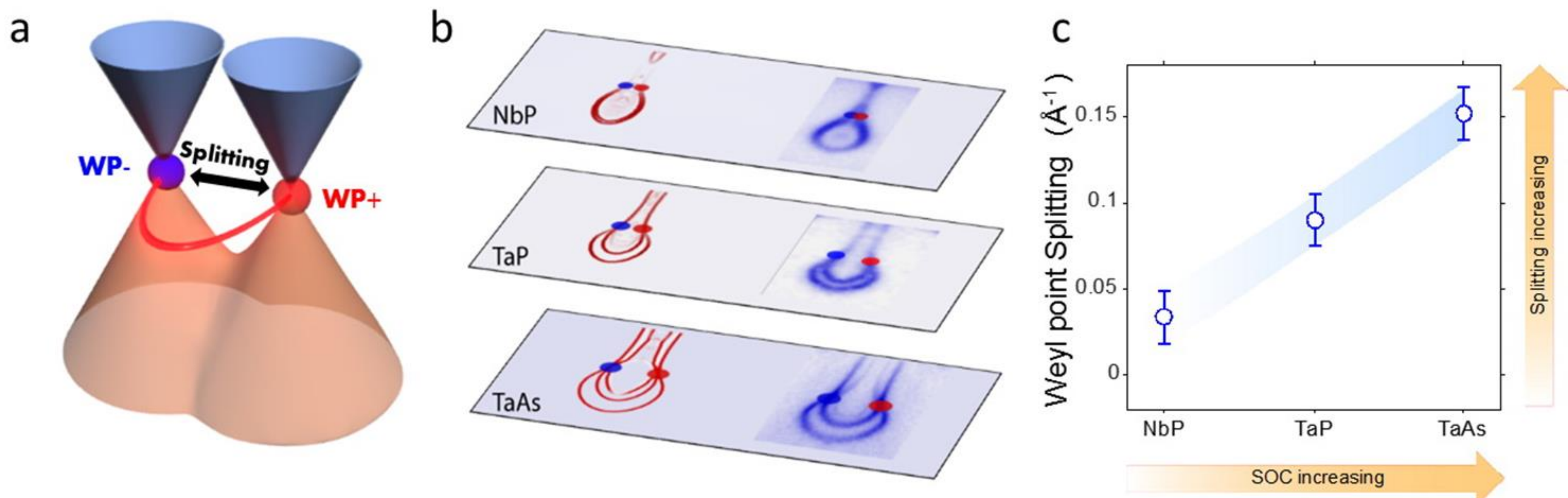
Dirac semimetal | Magnetic semicond. | Weyl semimetal | Line node semimetal



Scientific Cases: Dirac semimetal Na_3Bi



Scientific Cases: Dirac semimetal and Weyl semimetal



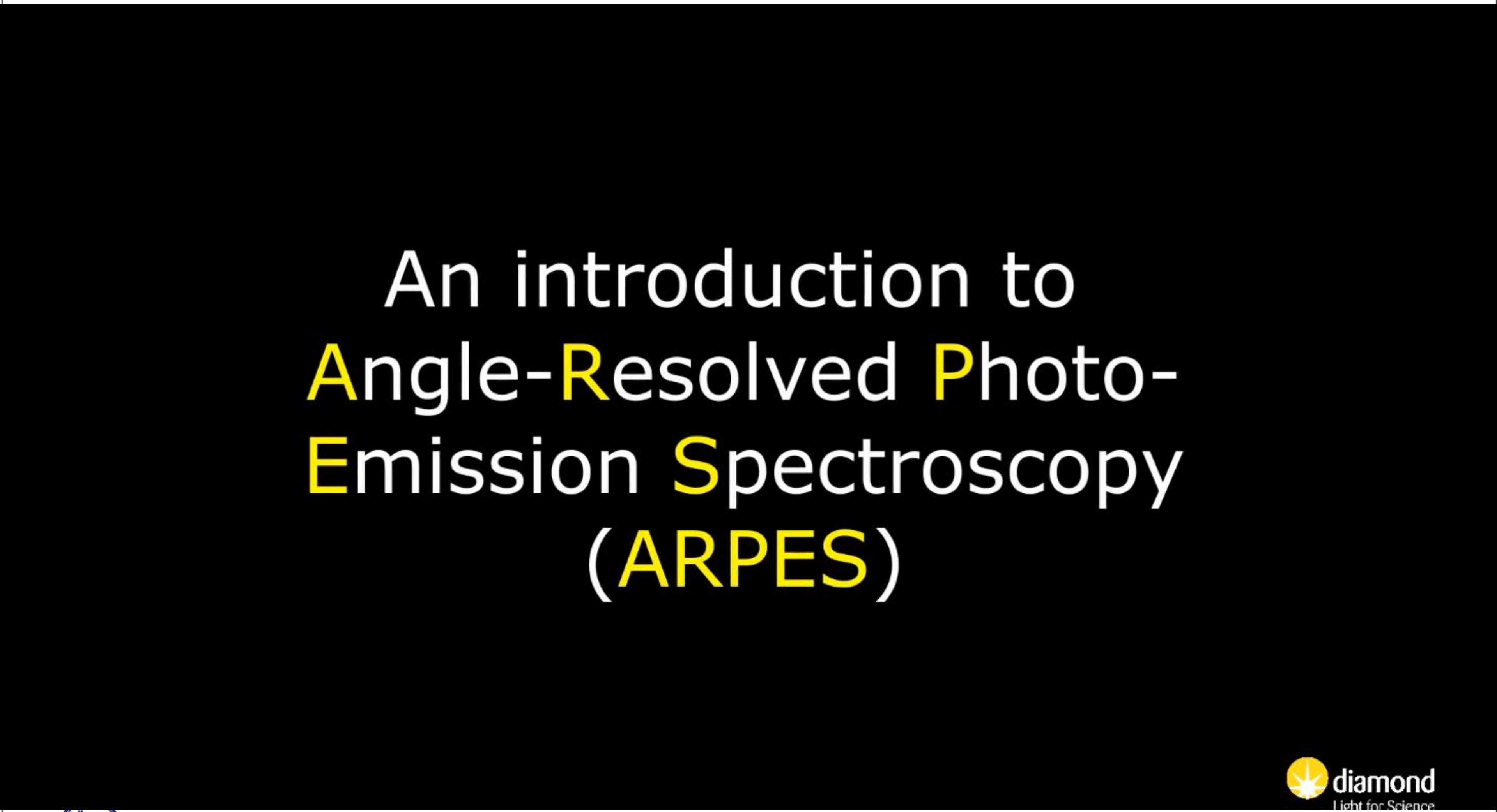
国家同步輻射研究中心
National Synchrotron Radiation Research Center

ARPES - key technique for the electronic structure mapping

- Angle-resolved photoemission spectroscopy (ARPES) is the most general tool to probe band structure, electronic interactions or spectral function mapping.

- Broad applications: surfaces, thin films, bulk materials, superconductors, magnetic/spin systems, complex materials, topological insulators, graphene based materials, charge density wave materials, low-dimensional systems, artificial stacks, device configurations, etc.

How to Conduct ARPES Experiment



Future and outlook

- *Spin and dynamic behavior*
  - *Topological insulator, 2D materials, superconductors, complex oxides, graphene-based materials….*
  - *Time-resolved ARPES*
  - *Spin-resolved ARPES*

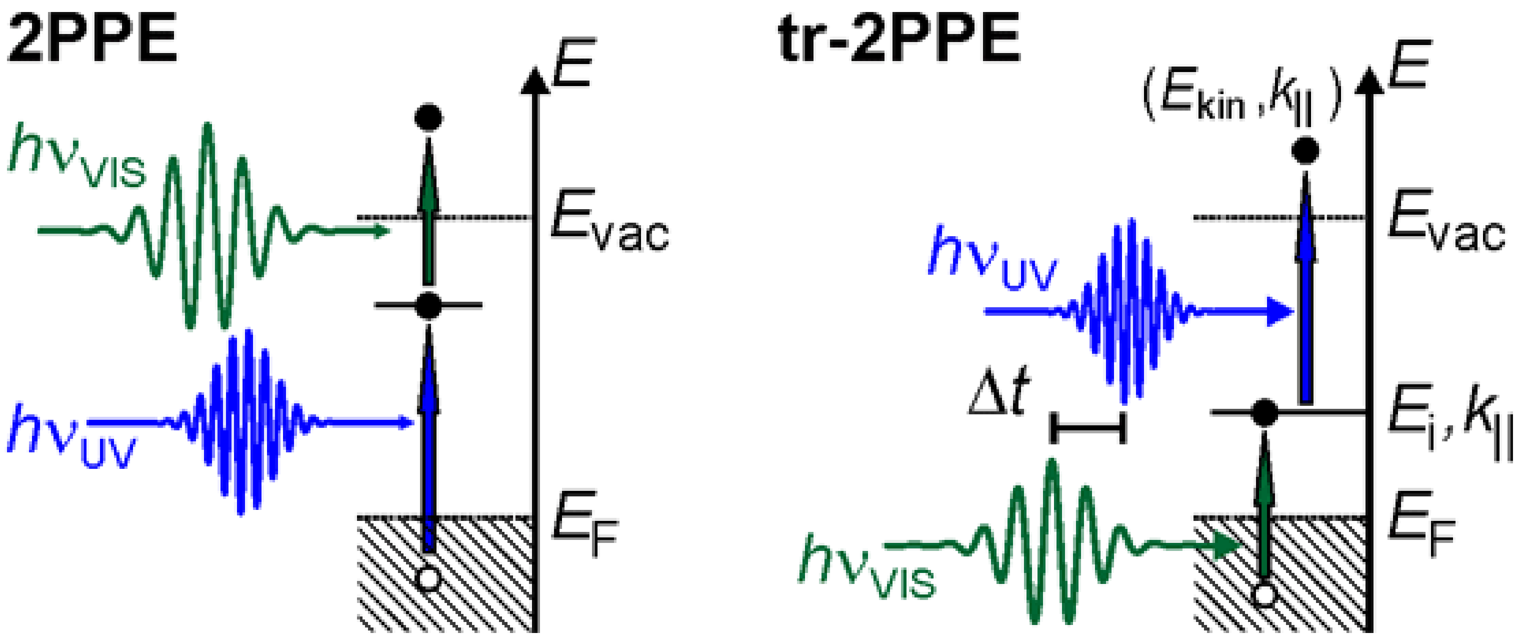
- Discovery and characterization of advanced materials
  - *Novel materials fabricated with the CVD method, micro-mechanic exfoliation… usually have smaller domain size in the early stage of material discovery. (van der Waals heterostructure, twisted bilayer graphene, 2D materials)*
  - *Single crystals with broken surface after in-situ cleaving.*
  - *Gating Effects in 2D Materials*

Time-resolved ARPES

Table 1. Some typical laser light sources used in ARPES.

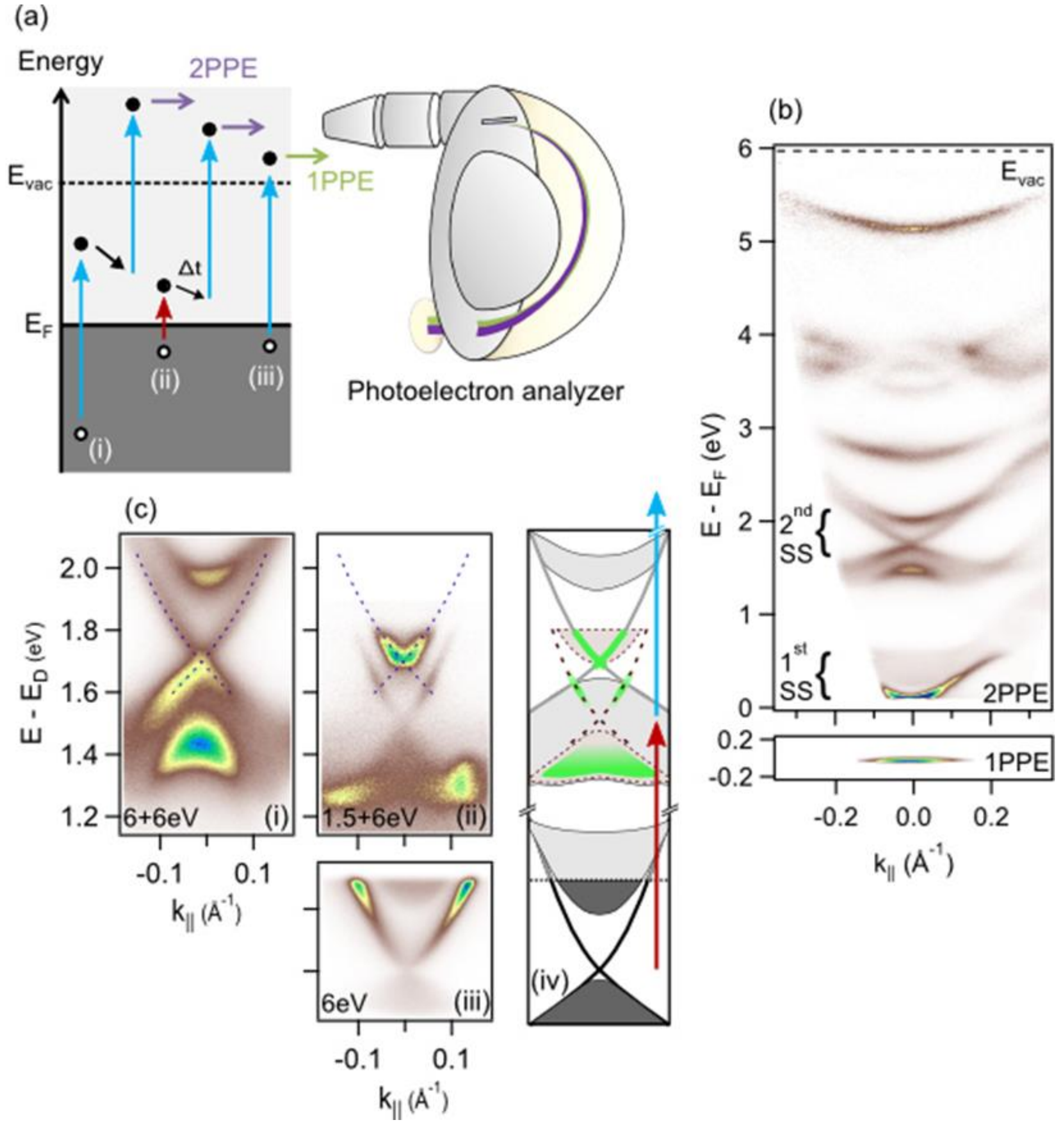
Laser catagory	Generation	Applica- tion	Pho. energy (eV)	Pulse width (ps, fs)	Rep. rate (kHz, MHz)	Max.Pho. flux (photons s^{-1})	Energy res. (meV)	Tem. Res. (fs)	References	Remarks
Quasi-CW	NLO crystal SFG+SHG	High-res ARPES	7	~10 ps	80 MHz	1.5×10^{15}	0.26 meV	/	Liu *et al* [21]	(a)
			6	~70 fs (seed)	100 MHz	$\sim 10^{15}$	4.7 meV	/	Koralek *et al* [20]	(b)
			7	~10 ps	120 MHz	Unknown	0.025 meV	/	Okazaki *et al* [186]	(c)
			5.3–7	5 ps	76 MHz	$\sim 10^{14}$	Unsecified	/	Jiang *et al* [87]	(d)
CW	NLO crystal SFG+SHG	High-res ARPES	6.05	Infinite	Infinite	1×10^{15}	0.01	/	Tamai *et al* [37]	(e)
			6.49	Infinite	Infinite	1.25×10^{15}	$\sim 10^{-7}$ meV	/	Scholz *et al* [54]	(f)
Pulsed laser	NLO crystal SFG+SHG	Tr-ARPES	1.5,6	50 fs, 160 fs	80 MHz	Unspecified	<22 meV	163 fs	Sobota *et al* [41]	(g)
			1.5,6.04	35 fs, 55 fs	250 kHz	$\sim 10^{13}$	40 meV	65 fs	Faure *et al* [40]	
			1.48, 5.92	170 fs,-	250 kHz	Unspecified	⩾10.5 meV	⩾240 fs	Ishida *et al* [149]	
HHG	Noble gas HHG	Tr-ARPES	1.58, 15–40	40 fs, 100 fs	10 kHz	3.6×10^{17}	90 meV@35.6 eV	125 fs	Frietsch *et al* [43]	(h)
			1.6, 22.1	30 fs, 11 fs	10 kHz	Unspecified	170 meV	13 fs	Rohde *et al* [42]	(i)
			1.57, 20.4	30 fs	1 kHz	Unspecified	Unspecified	30 fs	Petersen *et al* [31]	
Mod./ Reson. type HHG	Mixed rare gas	High-res ARPES	10.5	10 ps,	0.2–8 MHz	9×10^{12}	<1 meV	/	Berntsen *et al* [75]	(j)
			10.9	100 ps,	1–20 MHz	$\times 10^{13}$	<2 meV	/	Yu He *et al* [76]	(k)
FEL	Long undu- lator	Tr-ARPES	26–300	30–150 ps	<10 Hz	Very high	300 meV	700 fs	Hellmann *et al* [59]	

Time-resolved ARPES



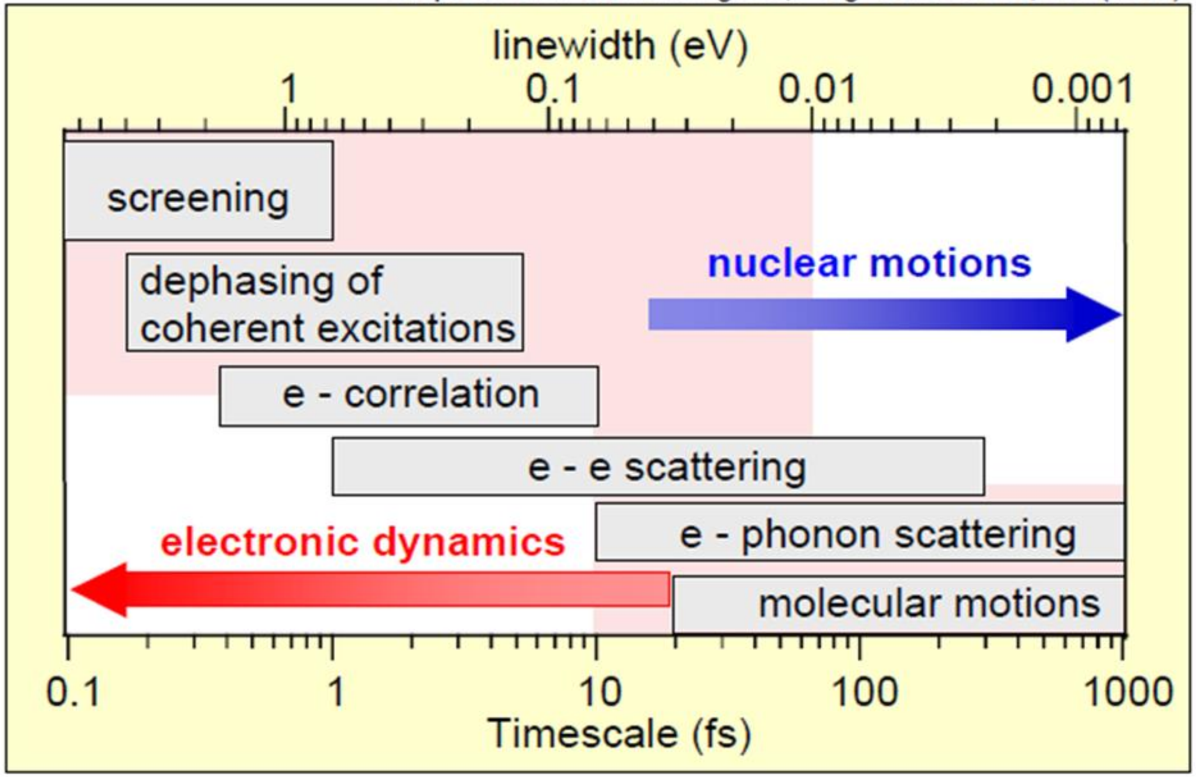
Time-resolved ARPES

Probing unoccupied states of Bi_2Se_3 with 2PPE



Time-resolved ARPES

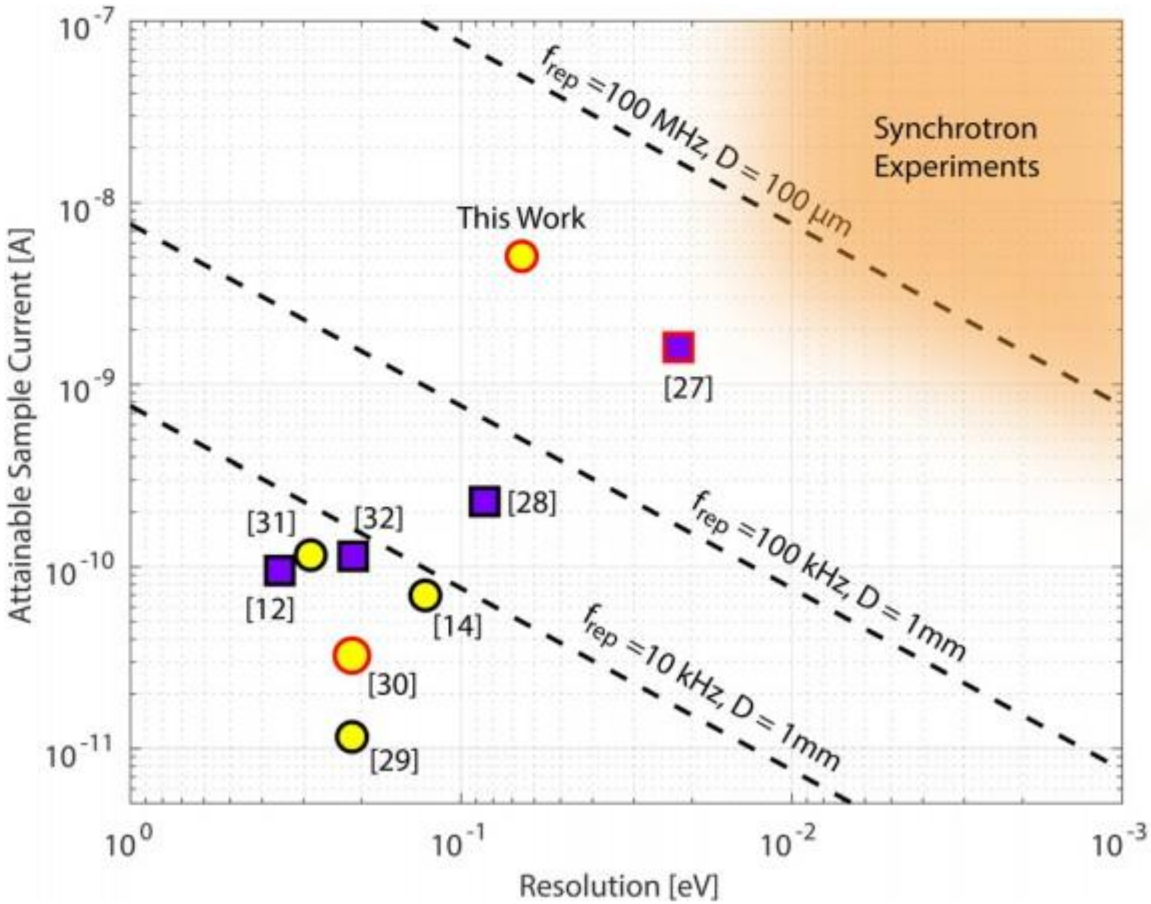
adapted from Petek and Ogawa, Prog. Surf. Sci. **56**, 239 (1997)



- Hierarchy of time scales: from as to ps
- Separation of electronic and nuclear dynamics

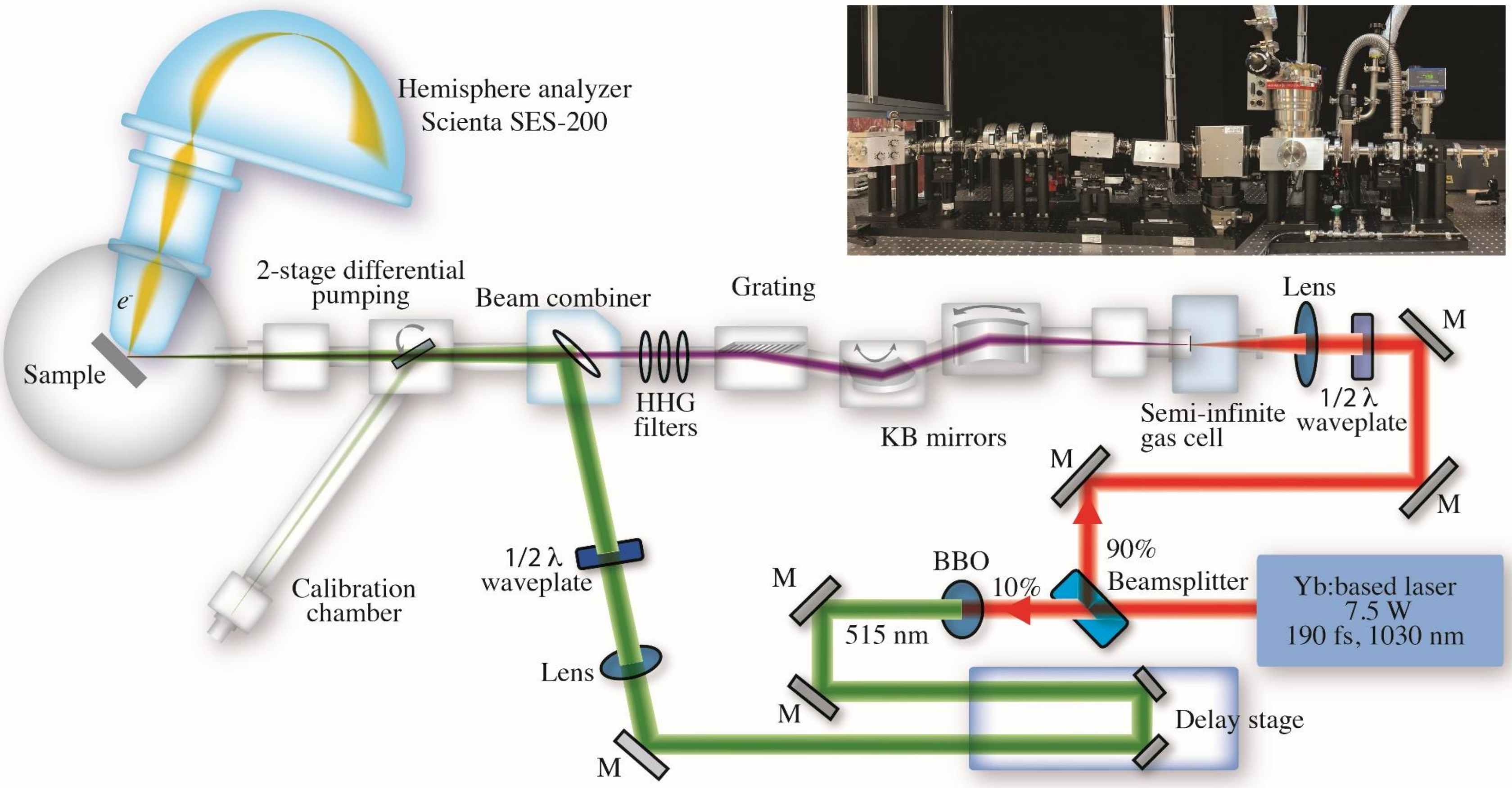
Time-resolved ARPES

High repetition rate/ lower photon flux in single pulse

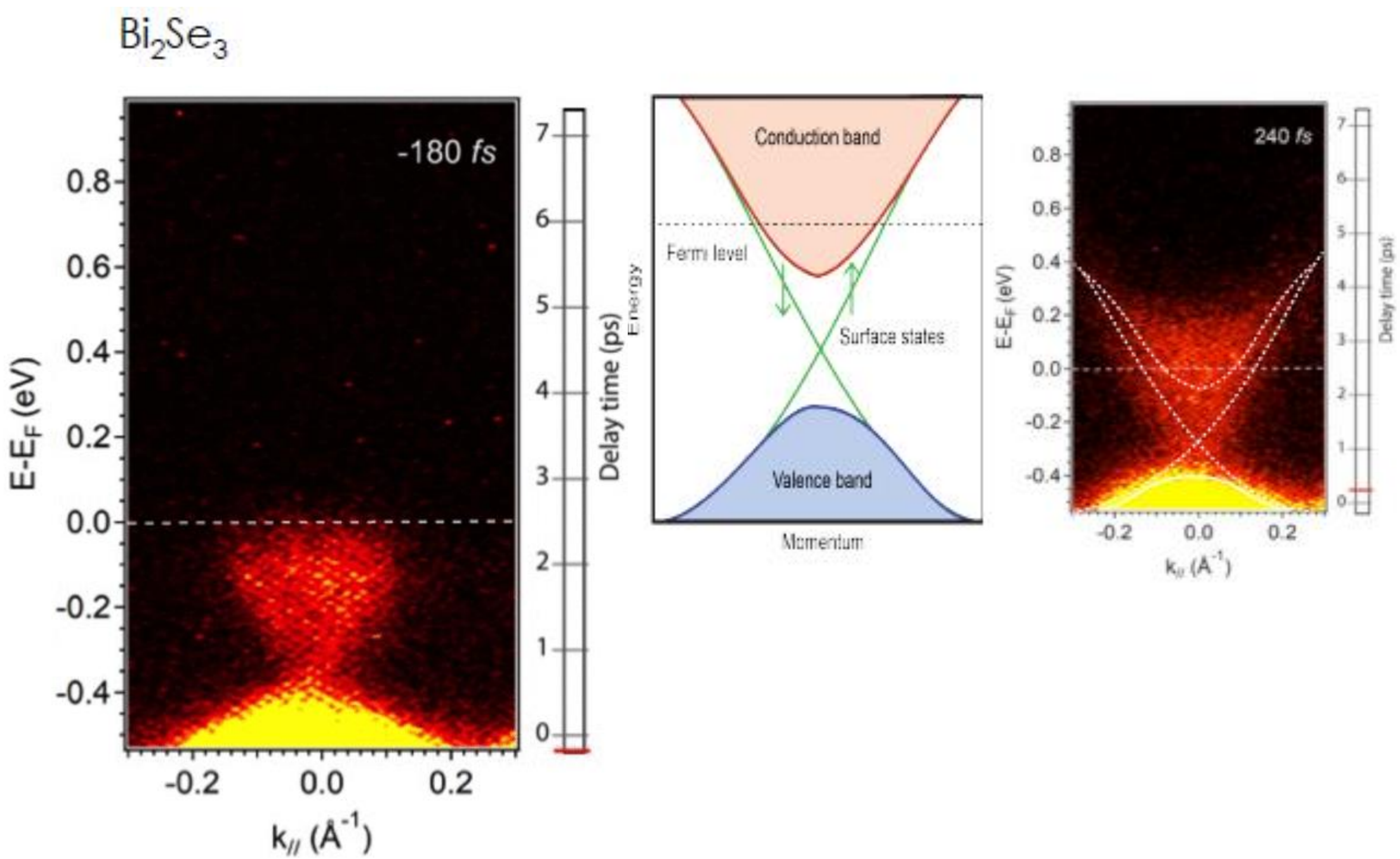


國家同步輻射研究中心
National Synchrotron Radiation Research Center

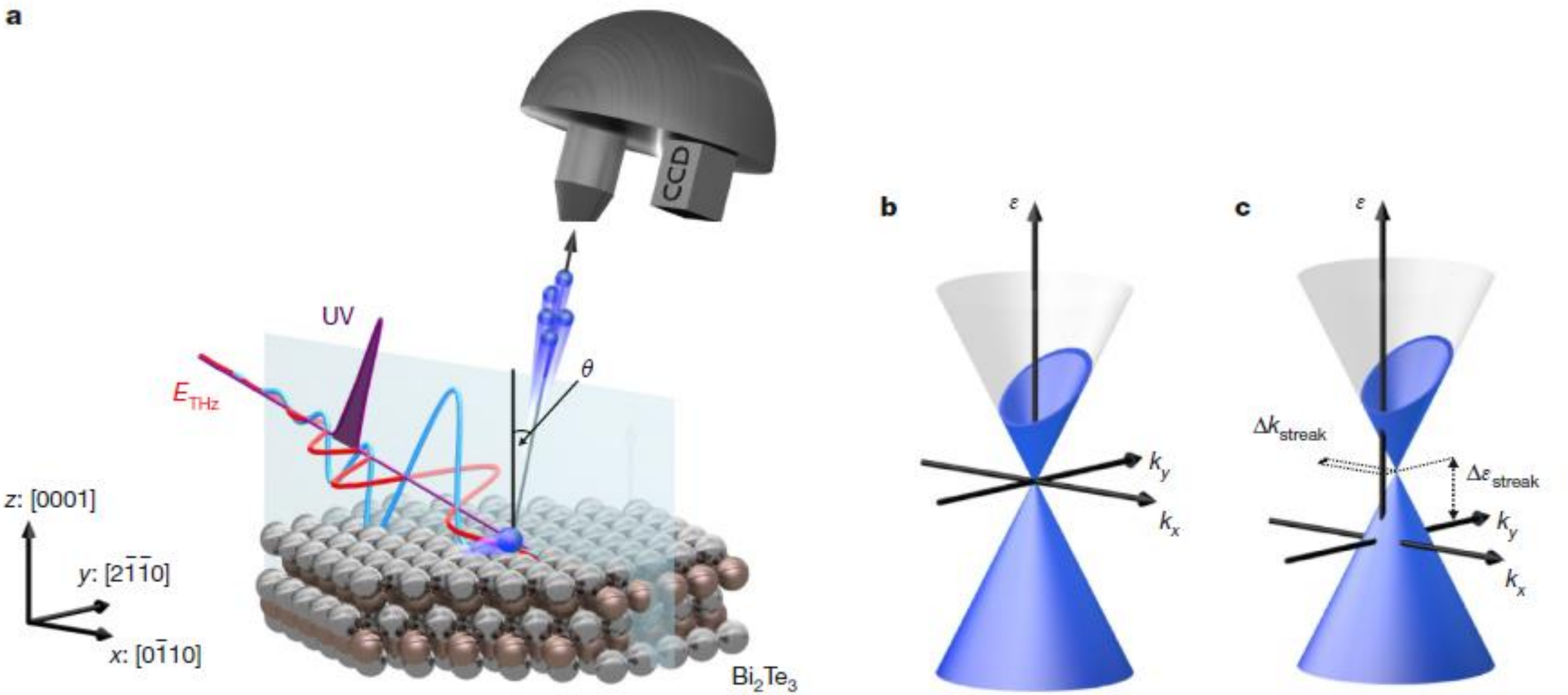
Time-resolved ARPES



Time-resolved ARPES



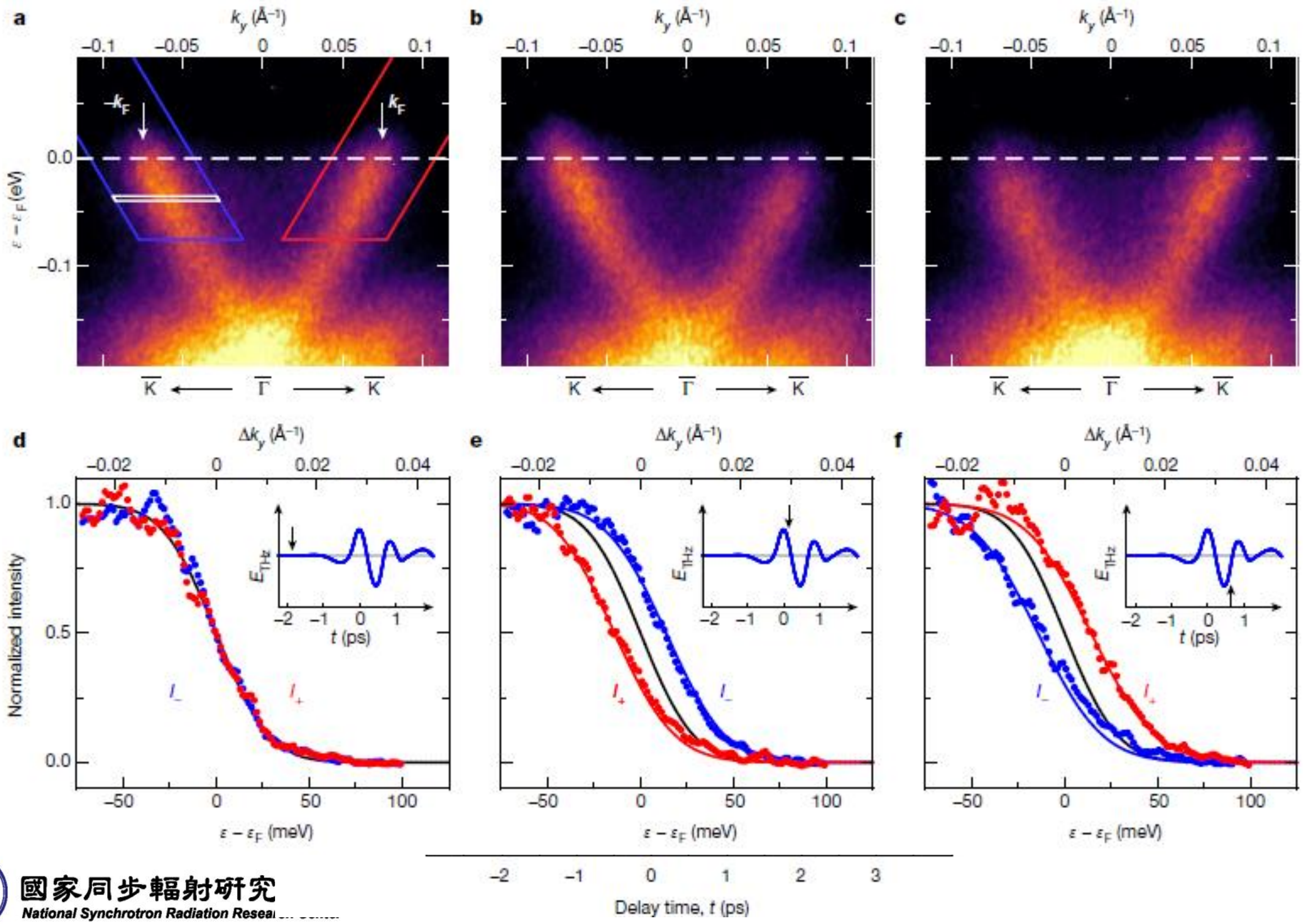
Time-resolved ARPES : THz exciting source



國家同步輻射研究中心
National Synchrotron Radiation Research Center

Reimann et al., Nature (2018)

Time-resolved ARPES :THz exciting source



國家同步輻射研究
National Synchrotron Radiation Resea... ...

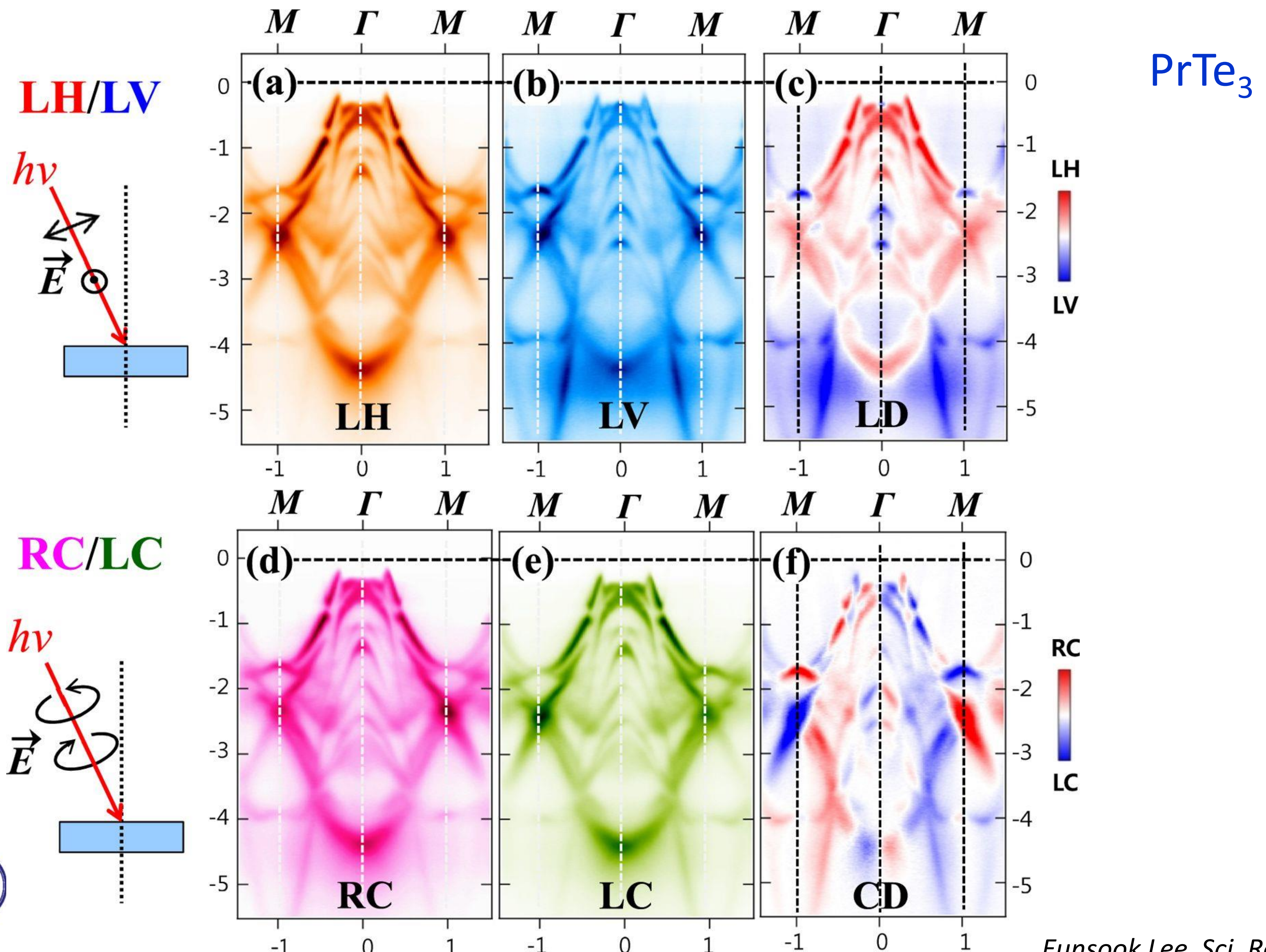
Reimann et al., Nature (2018)

Future and outlook

- *Spin and dynamic behavior*
  - *Topological insulator, 2D materials, superconductors, complex oxides, graphene-based materials….*
  - *Time-resolved ARPES.*
  - *Spin-resolved ARPES*

- Discovery and characterization of advanced materials
  - *Novel materials fabricated with the CVD method, micro-mechanic exfoliation… usually have smaller domain size in the early stage of material discovery. (van der Waals heterostructure, twisted bilayer graphene, 2D materials)*
  - *Single crystals with broken surface after in-situ cleaving.*
  - *Gating Effects in 2D Materials*

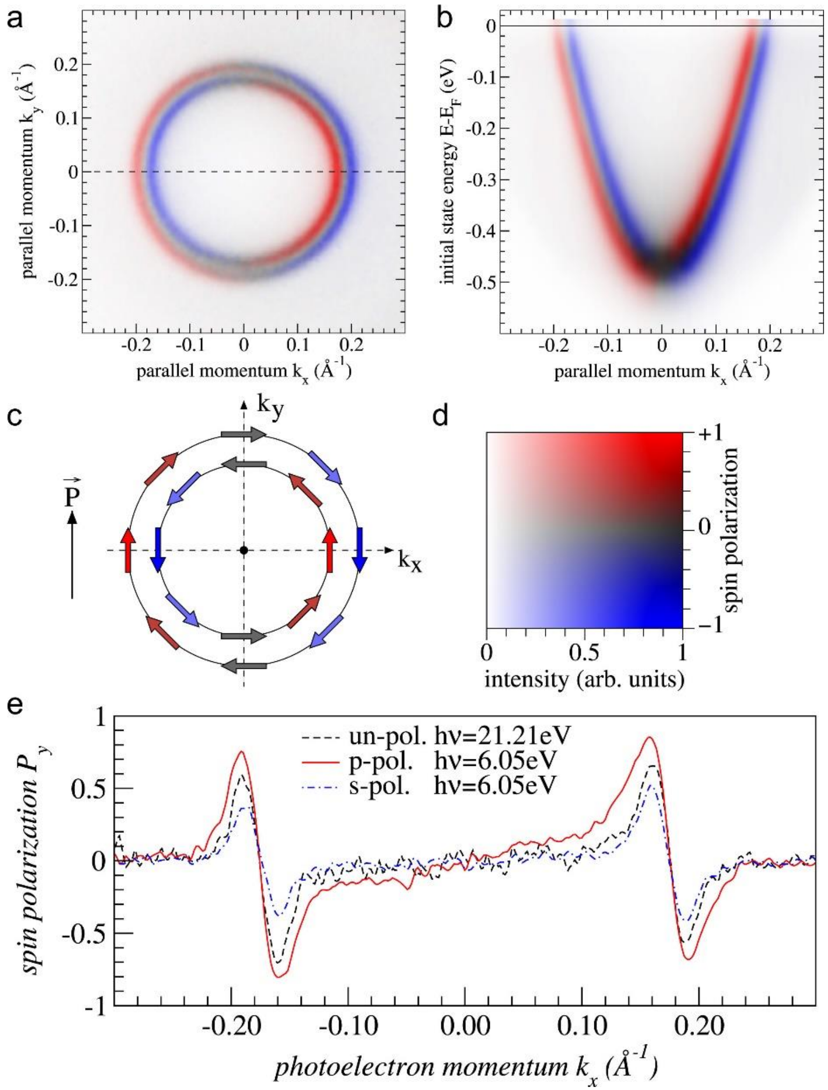
Future and outlook : Circular Dichroism (CD)-ARPES



Eunsook Lee, Sci. Rep. (2016)

Future and outlook : Spin-resolved ARPES

Rashba Splitting in Au(111)



國家同步輻射研究中心
National Synchrotron Radiation Research Center

Future and outlook

- *Spin and dynamic behavior*
  - *Topological insulator, 2D materials, superconductors, complex oxides, graphene-based materials….*
  - *Time-resolved ARPES.*
  - *Spin-resolved ARPES*

- Discovery and characterization of advanced materials
  - *Novel materials fabricated with the CVD method, micro-mechanic exfoliation… usually have smaller domain size in the early stage of material discovery. (van der Waals heterostructure, twisted bilayer graphene, 2D materials)*
  - *Single crystals with broken surface after in-situ cleaving.*
  - *Gating Effects in 2D Materials*

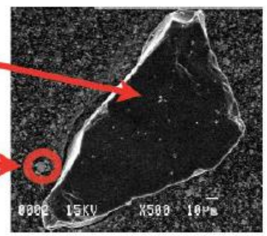
Nano Everywhere

Materials of interest often contain intrinsic, extrinsic, and designed nanoscale features.

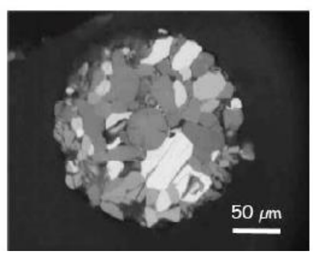
Need rapid electronic structure mapping at the nanoscale

Large MgB_2 single crystal ~200 μm- available two years after discovery

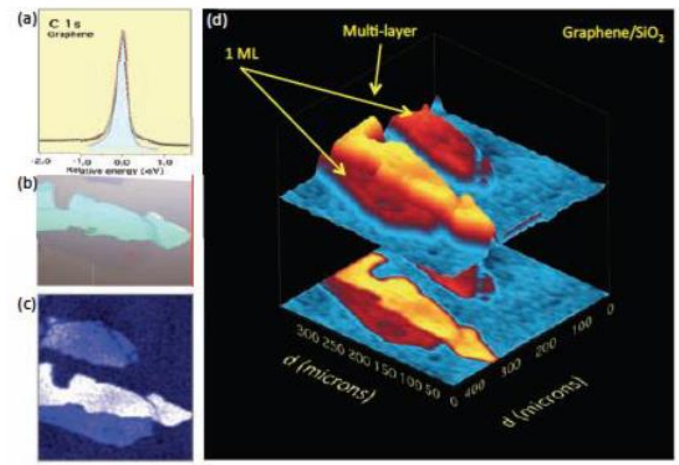
10 μm - available shortly after discovery



MgB_2 wire - available few months after discovery



Multi-thickness domains existed in an exfoliated graphene flake

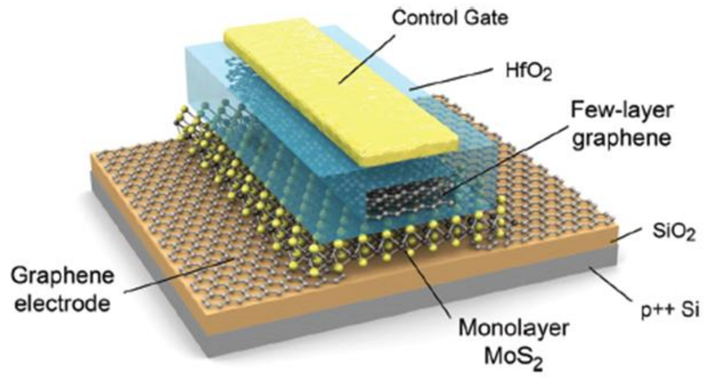


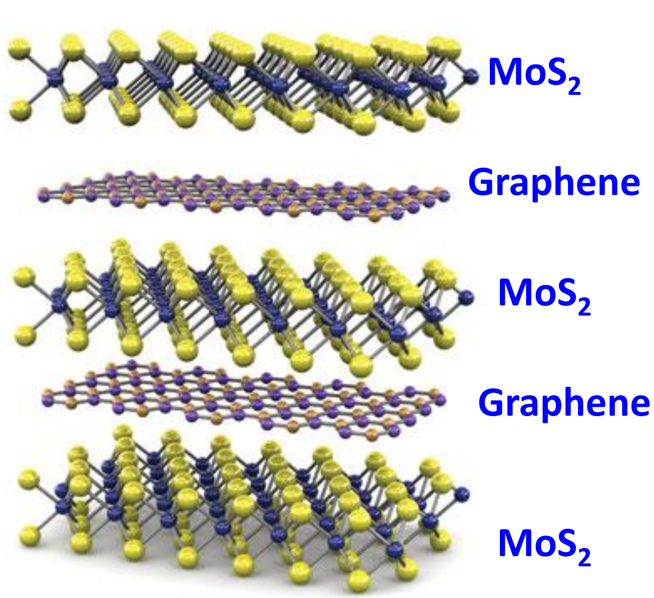
97

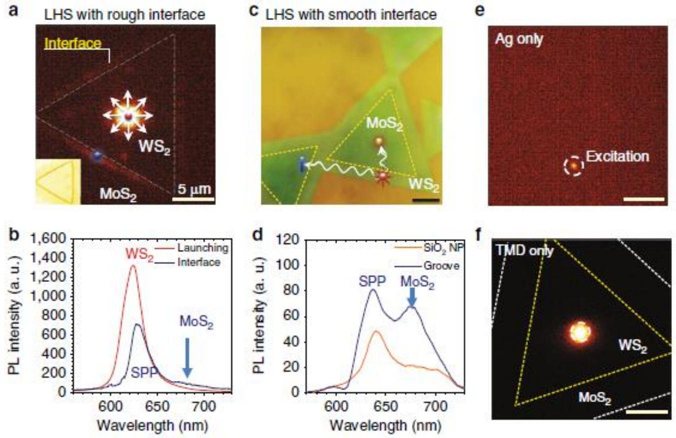
國家同步輻射研究中心
National Synchrotron Radiation Research Center

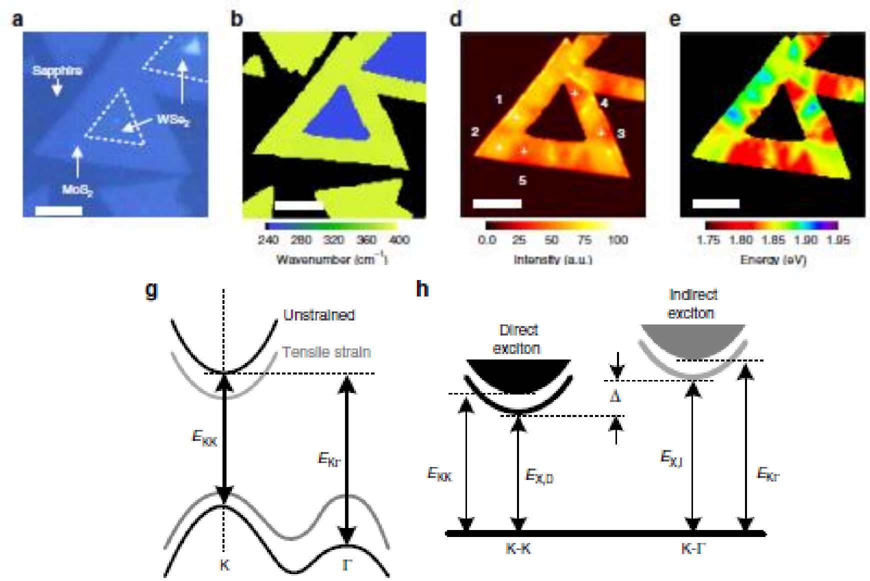
Ref : Avila, Synchrotron Radiation News (2014)

Van der Waals Heterostructures





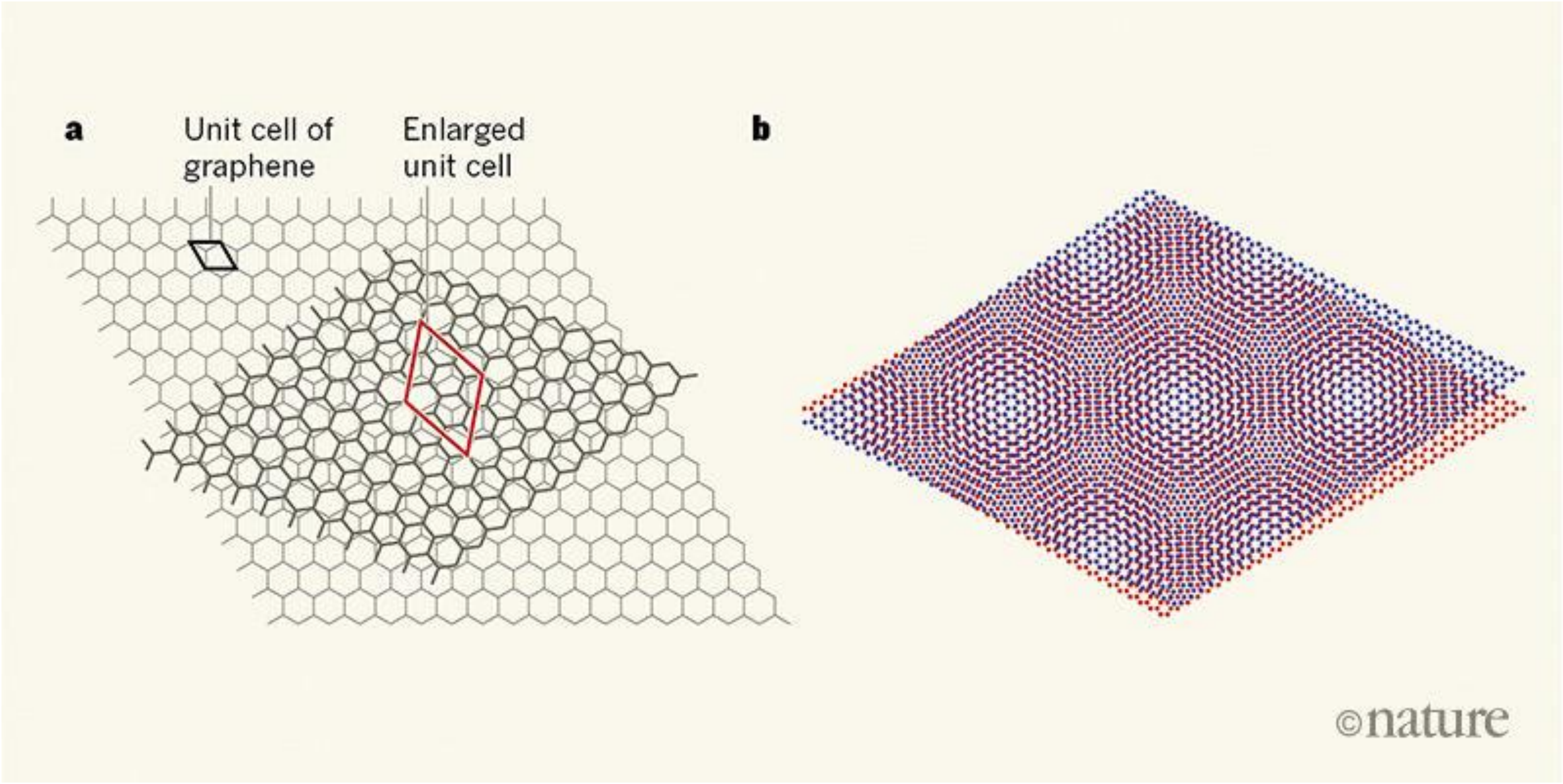




Ref : Shi et al., Nat. Comm. (2017)
Hsu et al., Nat Comm. (2017)

Magic Angle in Twisted Graphene

'Magic' Twist in Stacked Graphene Reveals Potentially Powerful Superconducting Behavior



Future and outlook

- Spin and dynamic behavior
  - *Topological insulator, 2D materials, superconductors, complex oxides, graphene-based materials….*
  - *Time-resolved ARPES.*
  - *Spin-resolved ARPES*

- Discovery and characterization of advanced materials
  - *Novel materials fabricated with the CVD method, micro-mechanic exfoliation… usually have smaller domain size in the early stage of material discovery. (van der Waals heterostructure, twisted bilayer graphene, 2D materials)*
  - *Single crystals with broken surface after in-situ cleaving.*
  - *Gating Effects in 2D Materials*

Single crystals with broken surface

Anomalously large gap anisotropy in the a-b plane of BSCCO

VOLUME 70, NUMBER 10 PHYSICAL REVIEW LETTERS 8 MARCH 1993

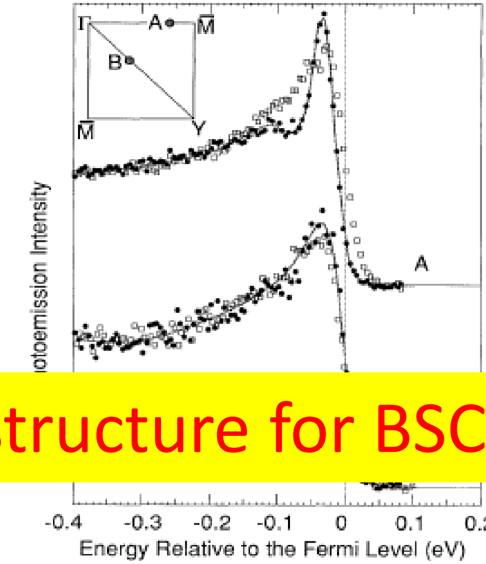


FIG. 1. High resolution photoemission spectra from sample 1 recorded at **k**-space locations *A* and *B*, as illustrated in the inset. The spectra at *B* were measured before those at *A*. The spectral changes above and below T_c are caused by the opening of the superconducting gap. The change at *A* is quite visible, yielding a larger gap. The change at *B* is hardly visible, suggesting a very small or null gap.

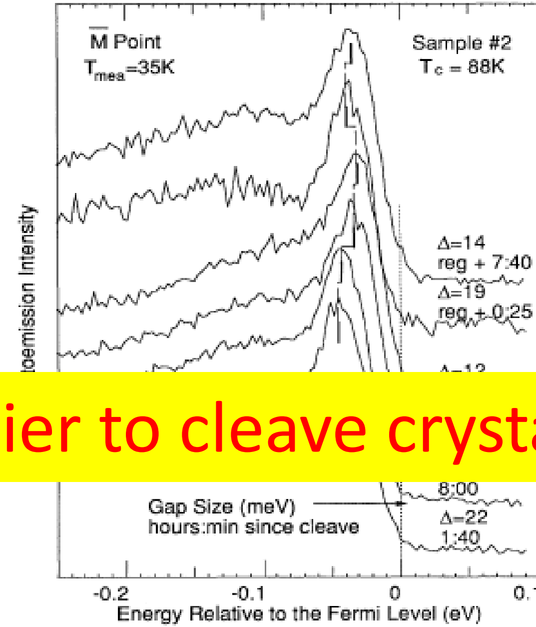


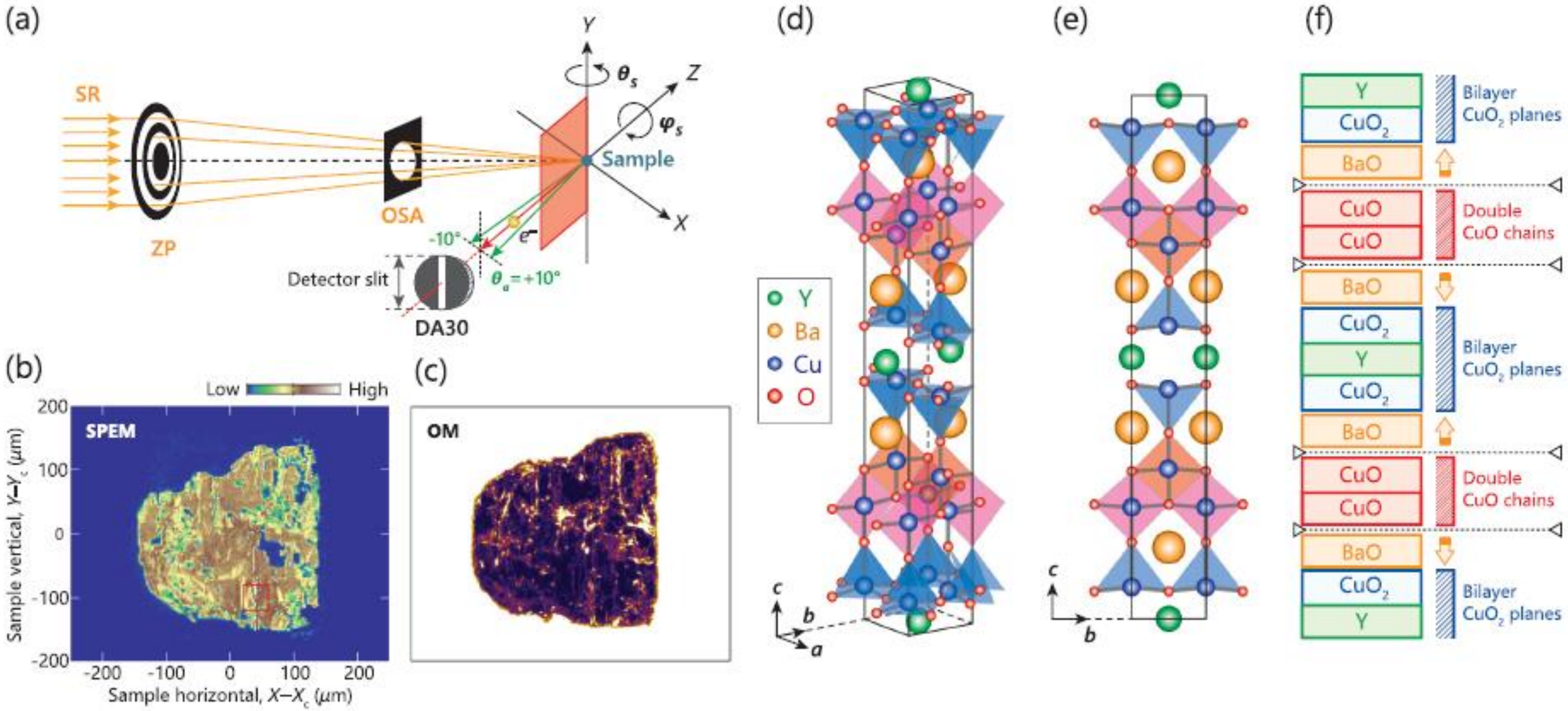
FIG. 2. Spectra from sample 2 recorded at $\bar{M}$ at different times after the sample was cleaved and kept at low temperature. As the sample ages, the superconducting gap becomes smaller. The numbers marked are the gap size and its aging time after the cleave. A decrease of the intensity of the −80 meV dip is clearly visible. The clean sample surface can be regenerated by warming up the sample to room temperature, and then cooling down again.

Layer structure for BSCCO, easier to cleave crystal in UHV

ing of the superconducting energy gap. At the same

Single crystals with broken surface

$YBa_2Cu_4O_8$ studied with nano-ARPES at I05 beamline, DLS
Beam size ~ 500 nm



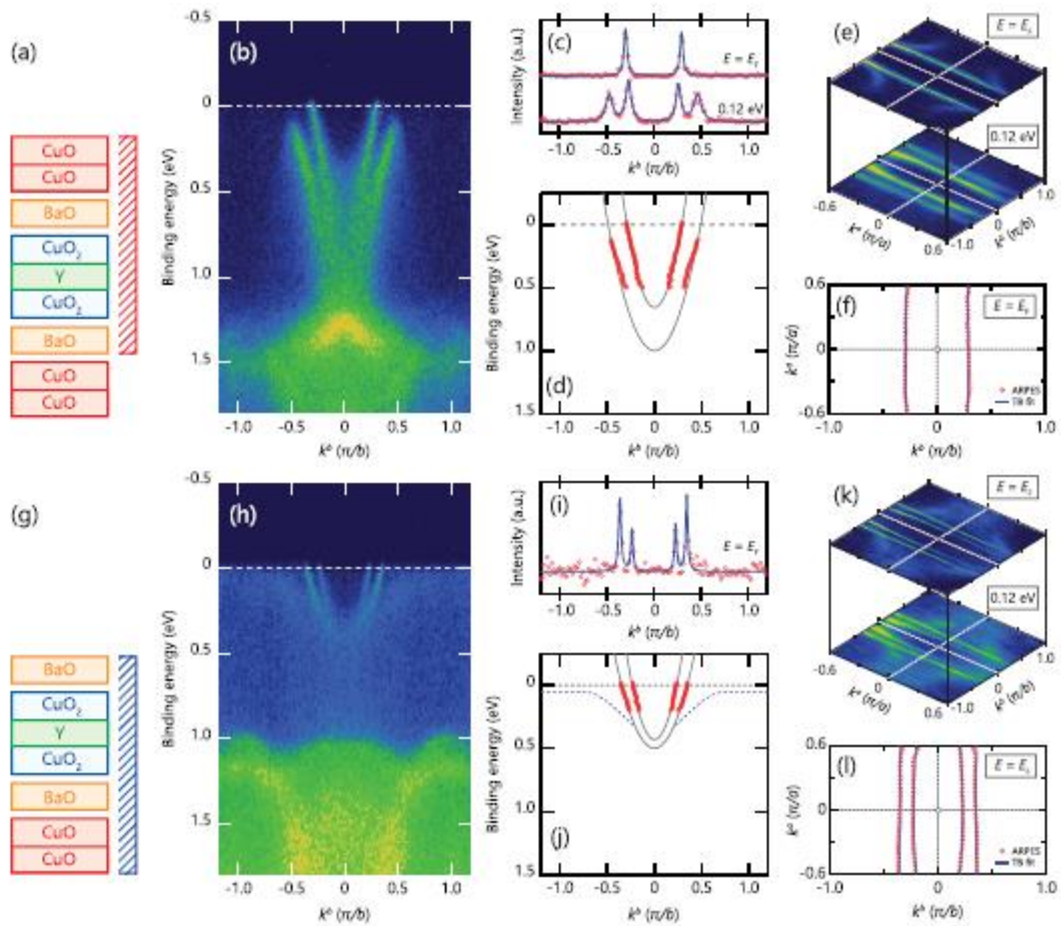
國家同步輻射研究中心
National Synchrotron Radiation Research Center

H.Iwasawa, PRB 99, 140510 (2019)

102

Single crystals with broken surface

$YBa_2Cu_4O_8$ studied with nano-ARPES at I05 beamline, DLS
Beam size ~ 500 nm



國家同步輻射研究中心
National Synchrotron Radiation Research Center

H. Iwasawa, PRB 99, 140510 (2019)

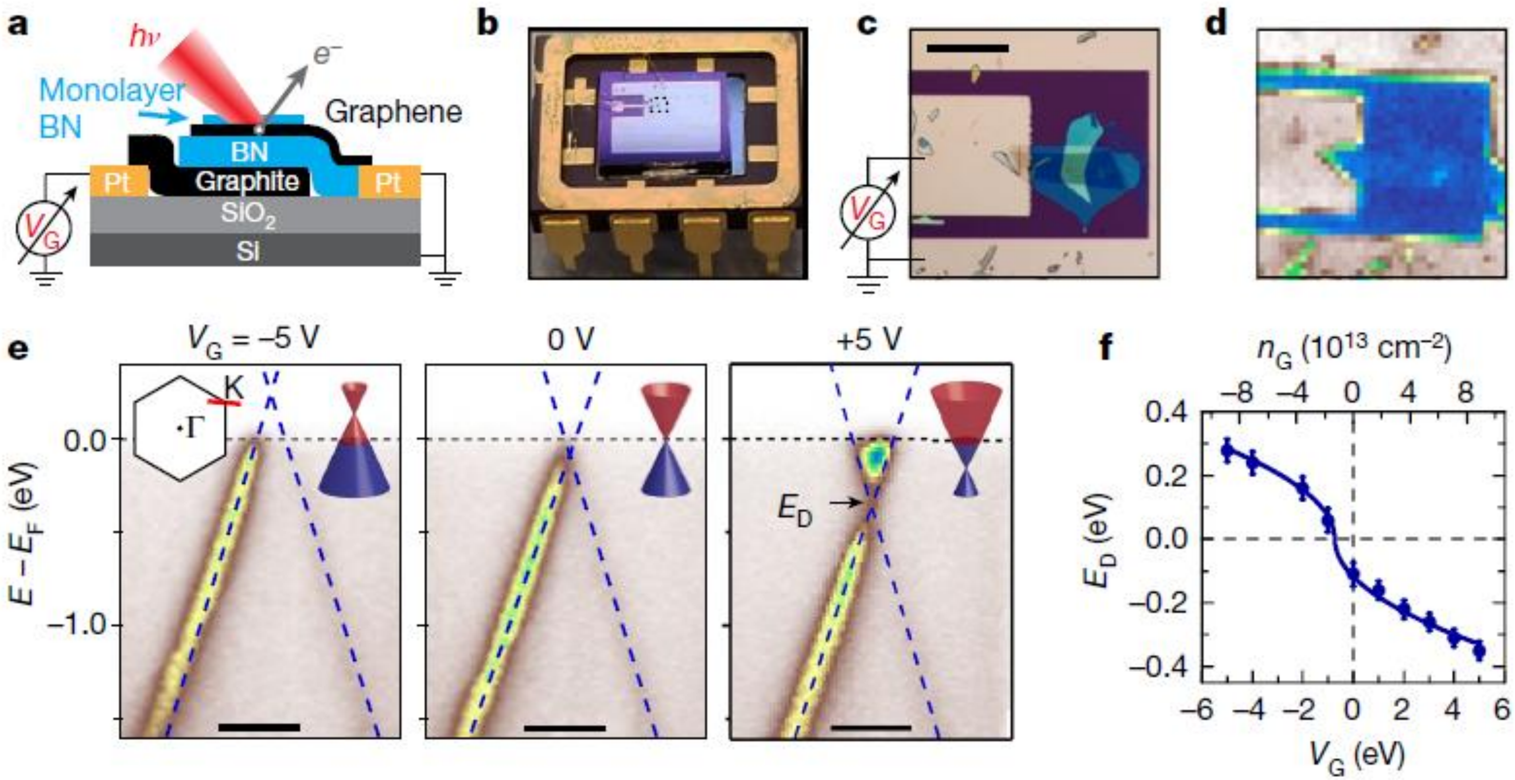
103

Future and outlook

- *Spin and dynamic behavior*
  - *Topological insulator, 2D materials, superconductors, complex oxides, graphene-based materials….*
  - *Time-resolved ARPES.*
  - *Spin-resolved ARPES*

- Discovery and characterization of advanced materials
  - *Novel materials fabricated with the CVD method, micro-mechanic exfoliation… usually have smaller domain size in the early stage of material discovery. (van der Waals heterostructure, twisted bilayer graphene, 2D materials)*
  - *Single crystals with broken surface after in-situ cleaving.*
  - *Gating Effects in 2D Materials*

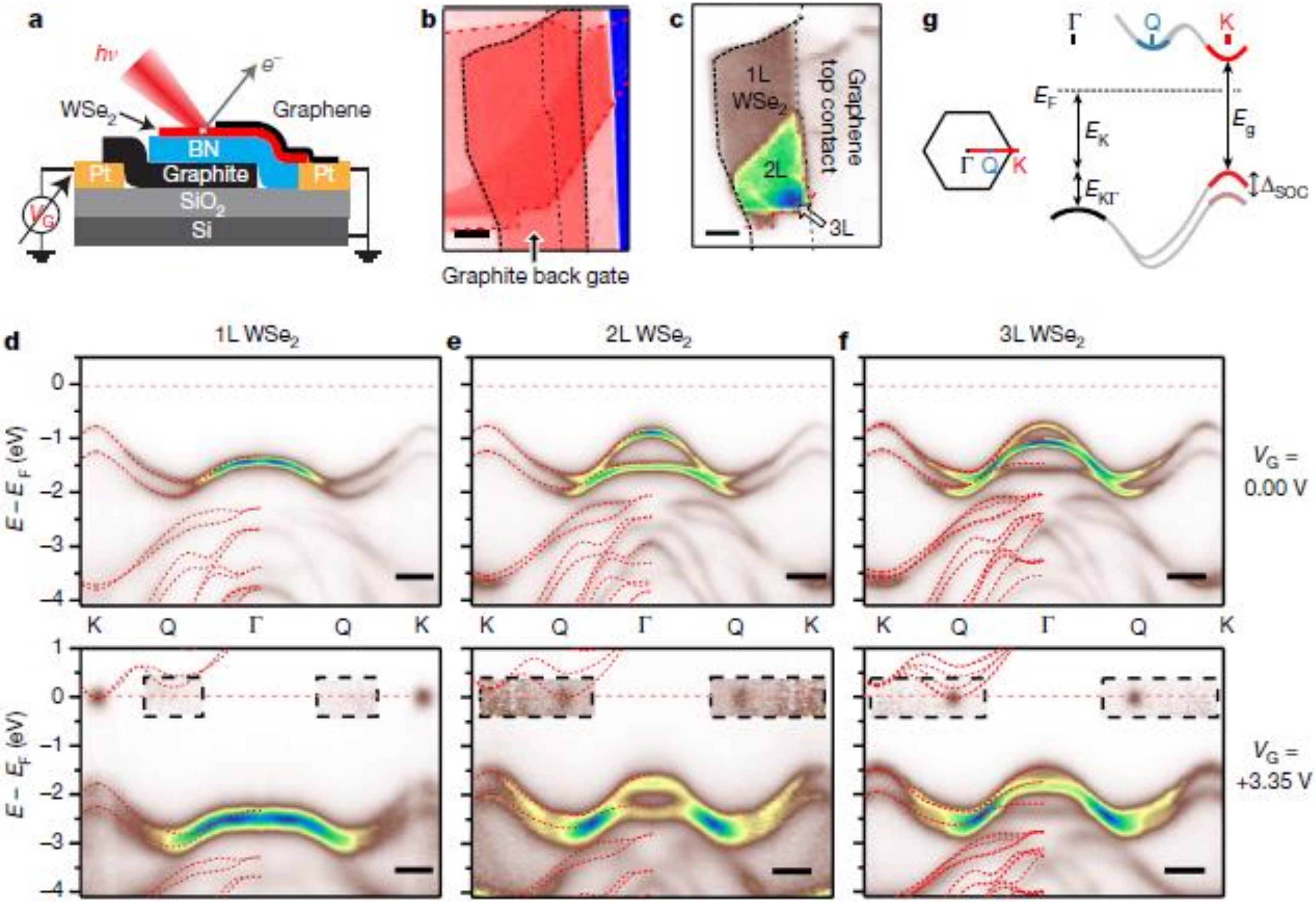
Gating Effects in 2D Materials



國家同步輻射研究中心
National Synchrotron Radiation Research Center

Paul V. Nguyen et al., Nature (2019)

Gating Effects in 2D Materials



Paul V. Nguyen et al., Nature (2019)

Future and outlook

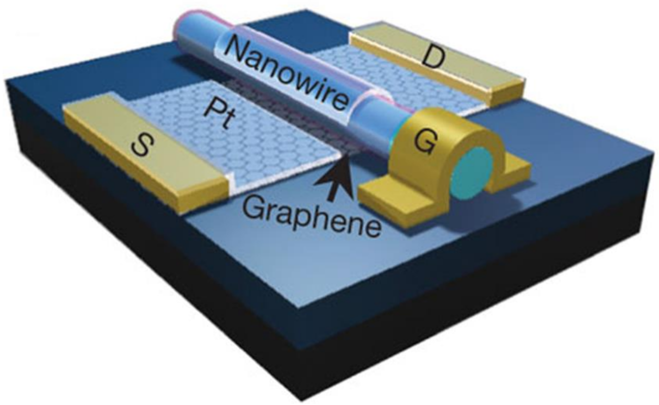
- Spin and dynamic behavior
  - Topological insulator, 2D materials, superconductors, complex oxides, graphene-based materials….
  - Time-resolved ARPES.
  - Spin-resolved ARPES

- Discovery and characterization of advanced materials
  - Novel materials fabricated with the CVD method, mi… mechanic exfoliation… usually have smaller domain… stage of material discovery. (van der Waals hete… …ed bilayer graphene, 2D materials)
  - Single cr… surface after in-situ cleaving.
  - Gat… in 2D Materials

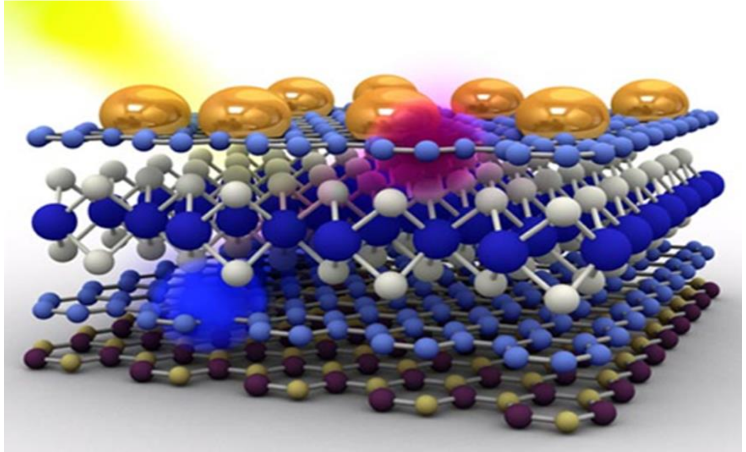
nanoARPES with beam size ~ 100 nm

With spatial and momentum k information

Electronic and Chemical imaging of Nanowires and patterned Samples



Band structure of transition metal dichalcogenides and their correlation effects

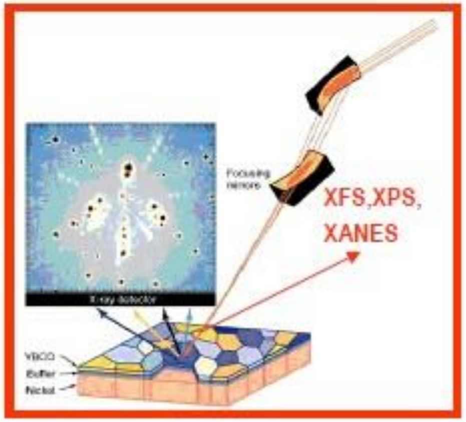


Conduct ARPES experiment for much smaller sample size

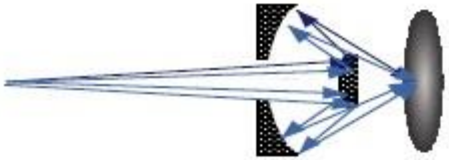
nanoARPES : X-ray focusing optics

X-ray focusing optics:
zone plates, mirrors, capillaries

Zone Plate optics – circular grating with decreasing width: from ~ 200 to ~ 10000 eV
Monochromatic:
Resolution achieved 15 nm in transmission

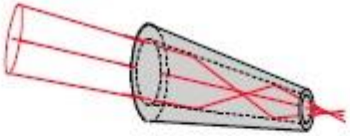


KP-B mirrors each focusing in one direction: soft & hard X-rays: ~ 100 nm
Soft & hard x-rays!
achromatic focal point, easy energy tunability, comfortable working distance
Resolution ≤ 100 nm



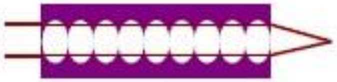
Normal incidence:
spherical mirrors with multilayer interference coating (Schwarzschild Objective)
Monochromatic, good for E < 100eV
Resolution: best ~ 100 nm

Capillary: multiple reflection concentrator



Hard x-rays ~ 8-18 keV
Resolution: > 3000 nm

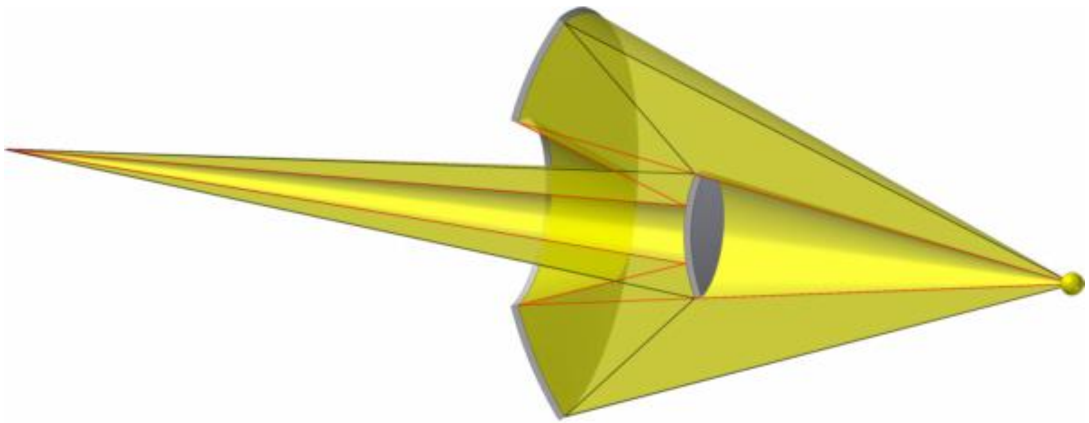
Refractive lenses



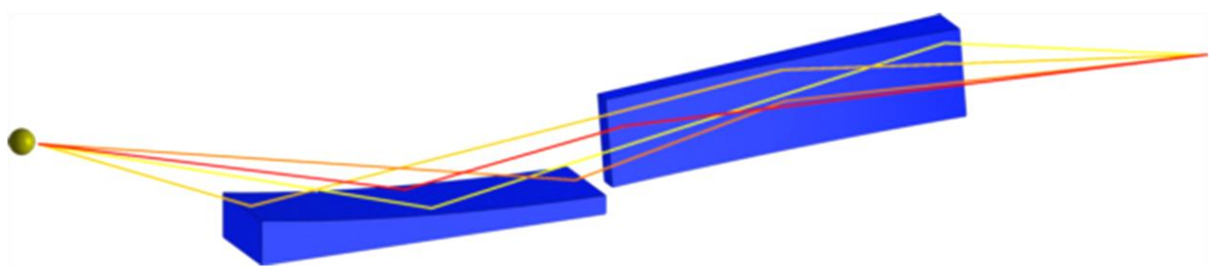
Hard x-rays ~ 4-70 keV
Resolution: > 1000 nm

nanoARPES : Curved Mirror Optics

Schwarzschild-optics

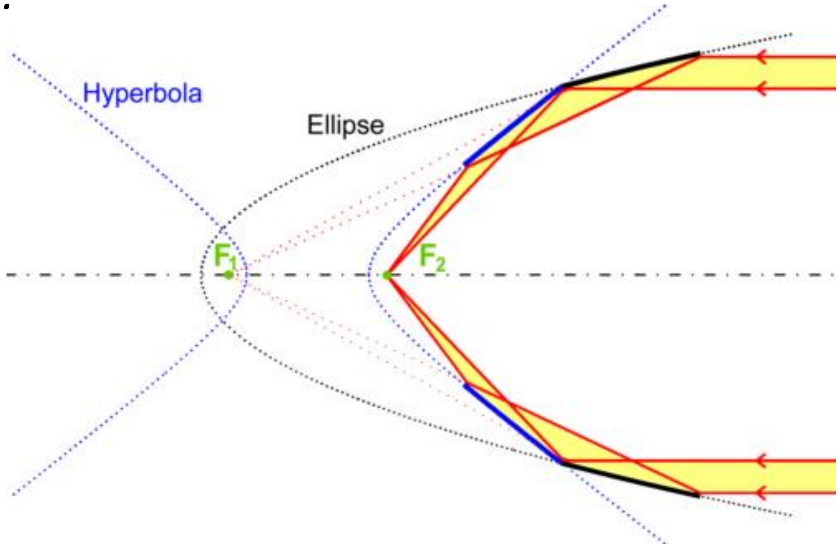


Kirkpatrick-Baez-optics

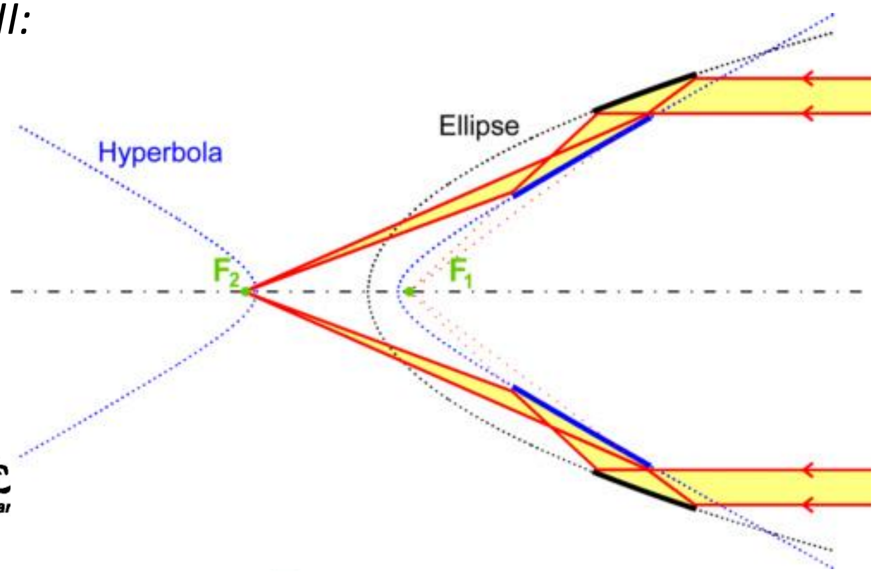


nanoARPES : Curved Mirror Optics

Wolter optics type I:

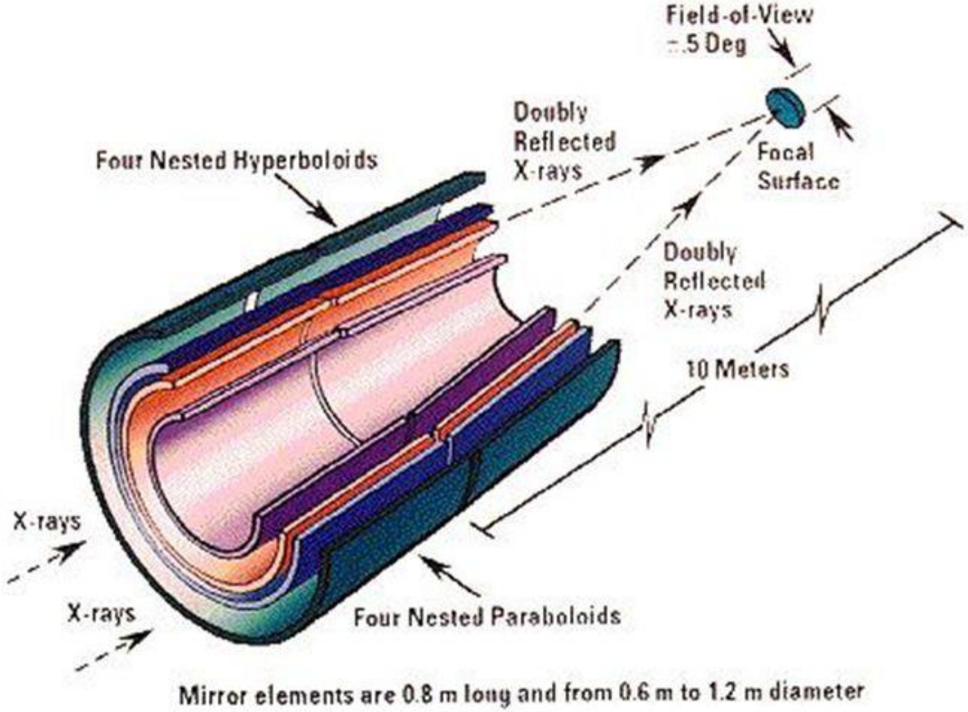


Wolter optics type II:



nanoARPES : Curved Mirror Optics

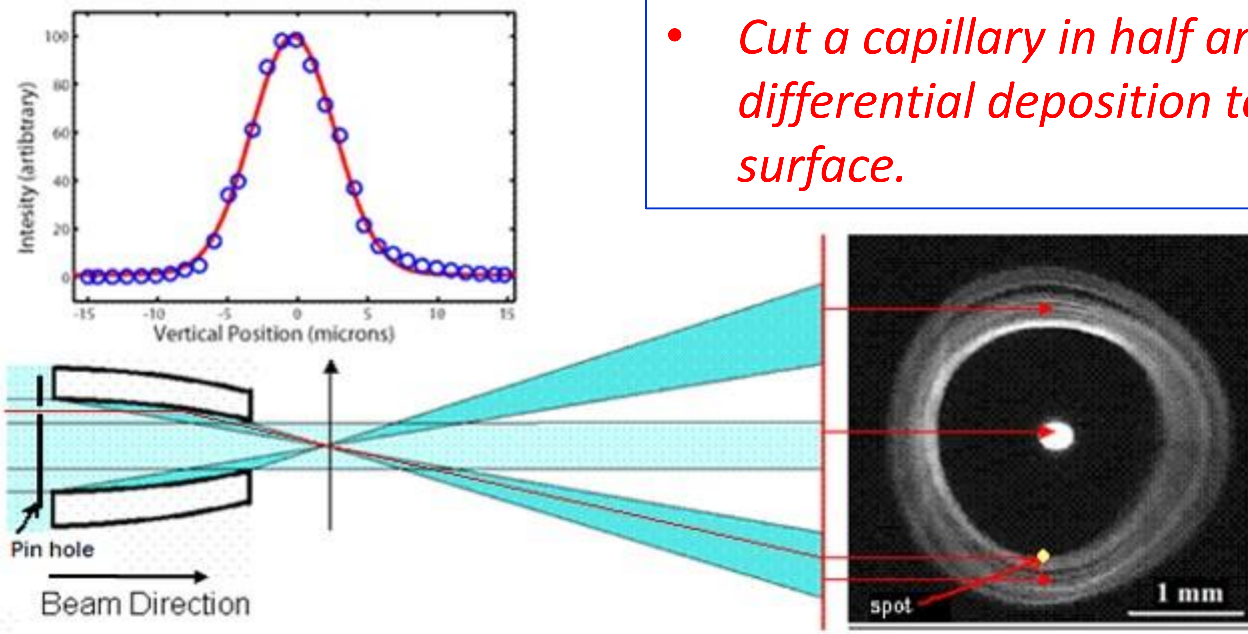
Nest of Grazing-Incidence Mirrors

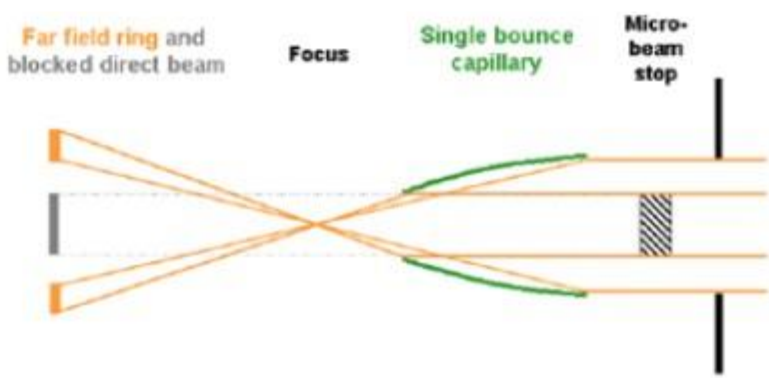


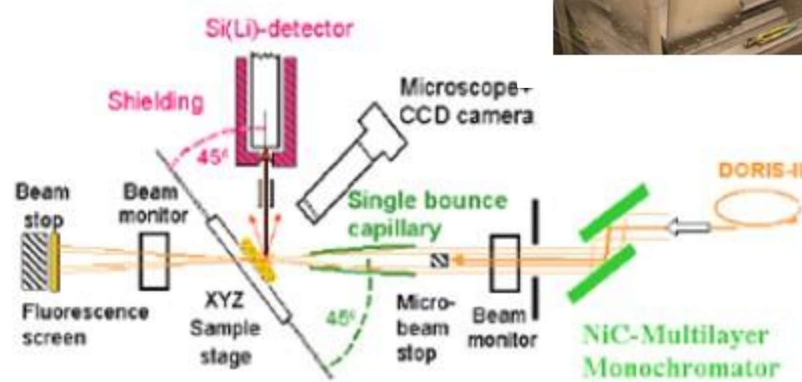
Mirror Design of Chandra X-Ray Telescope

Capillary focusing method

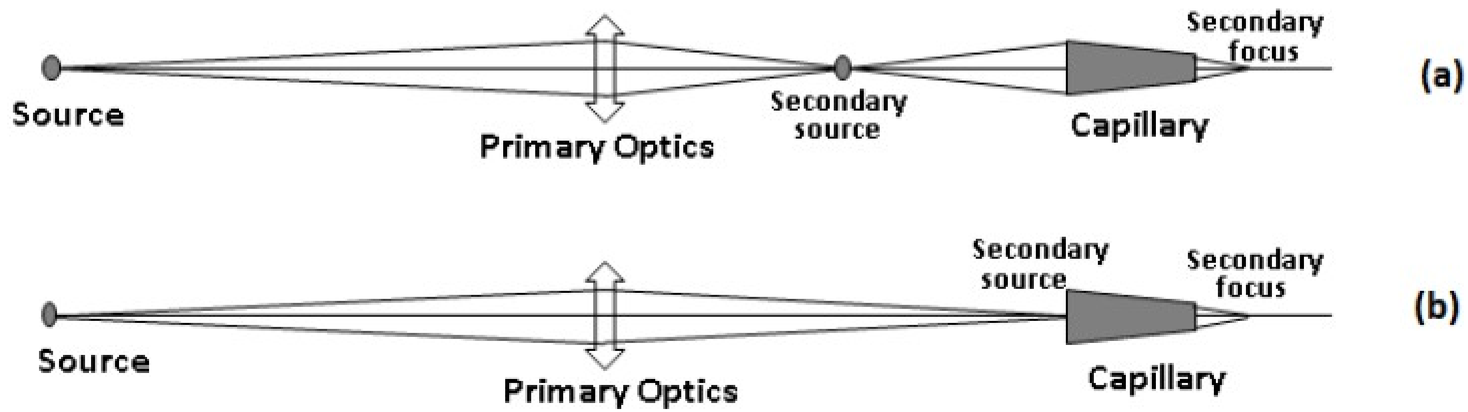
- *Many capillaries have a small mismatch between calculated and measured profiles near the tip.*
- *Cut a capillary in half and attempt to use differential deposition to smooth out inner surface.*







Evaluation of Capillary focusing method



The secondary focal size is $\sigma = F * \theta$, where F is the focal length of secondary optics and θ is the incident beam divergence

Huang et al., J. Phys. Conf. Series (2014)

Evaluation of Capillary focusing method

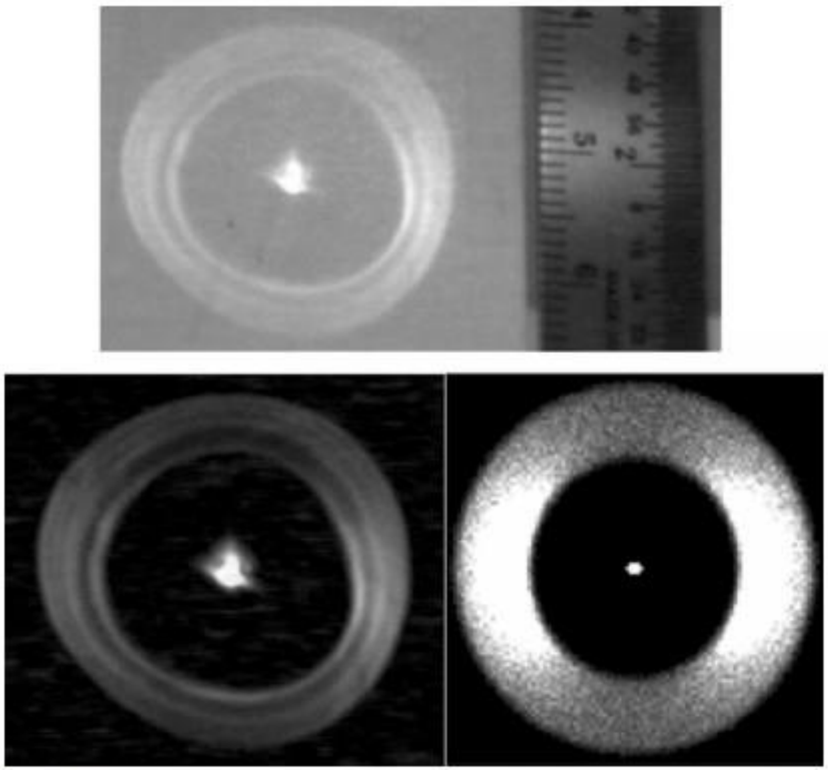
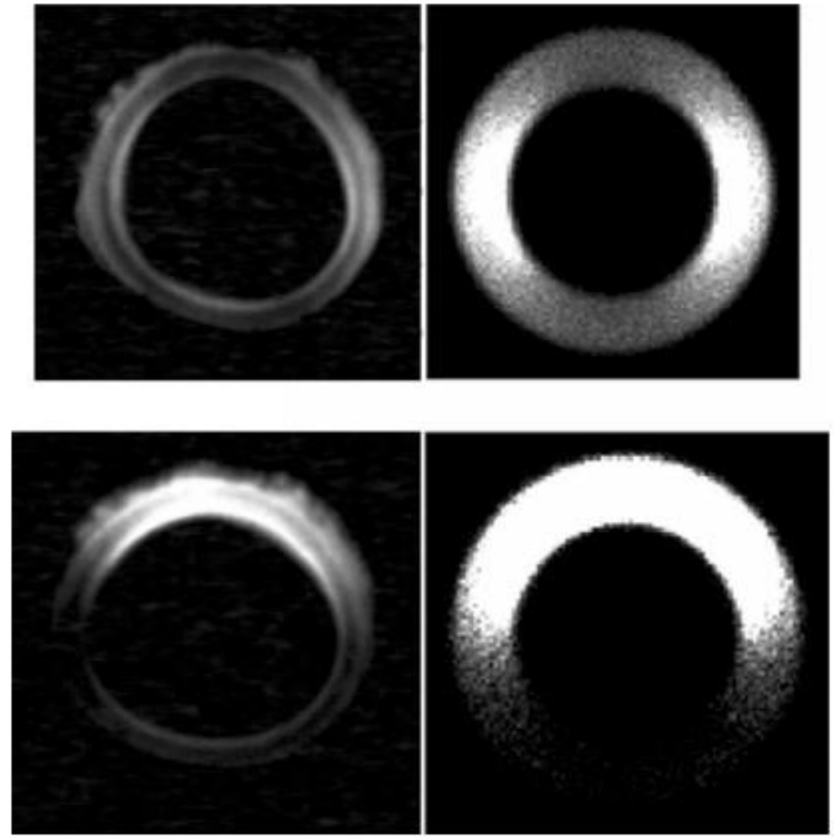
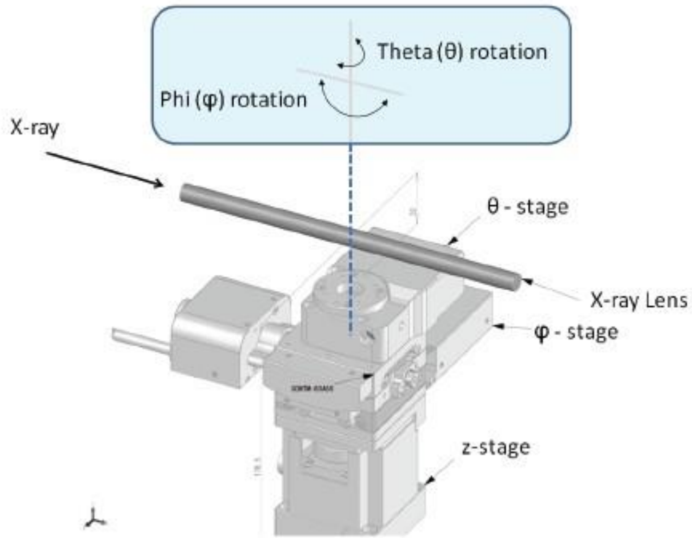
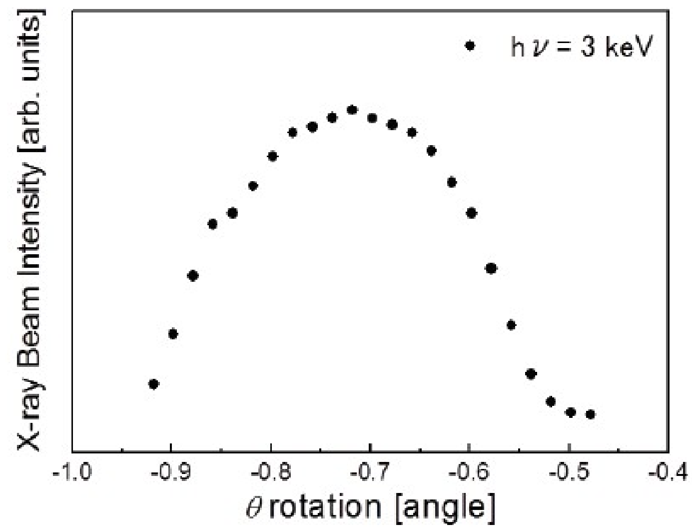


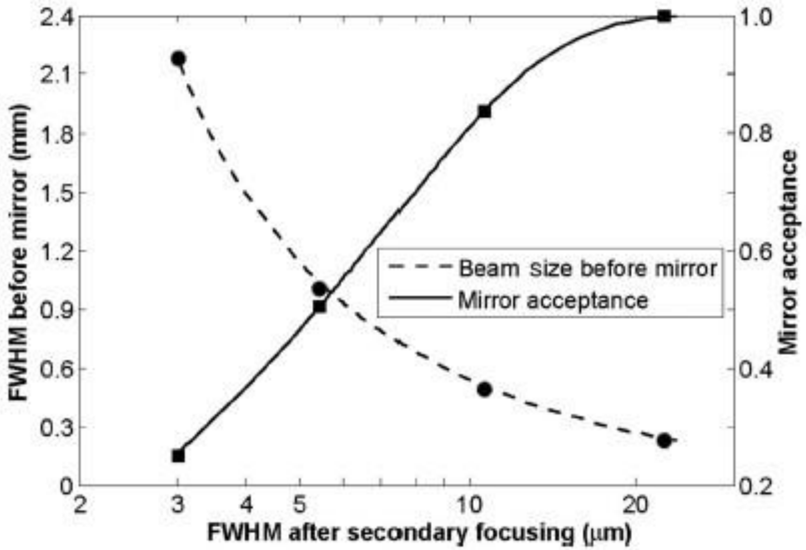
Figure 1
Top: far-field image without beam stop; the ruler shows the actual size of the image (approximately 25 mm outer diameter). Bottom: the same rings with external lights turned off for better contrast, and its ray-tracing simulation.

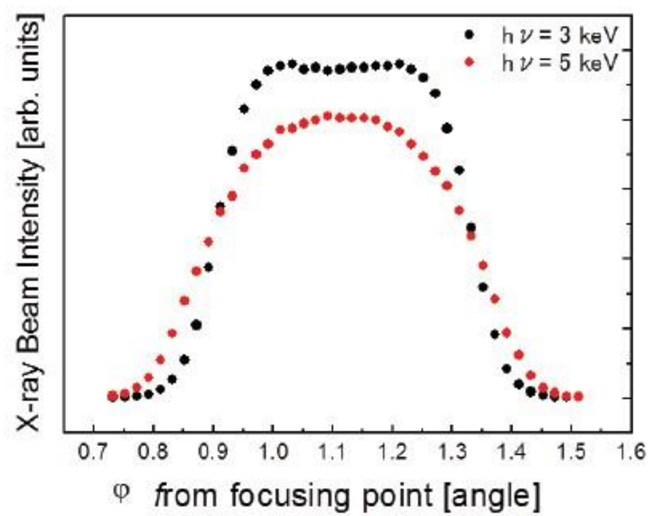


Barrea et al., J. Synchrotron Radiation (2008)



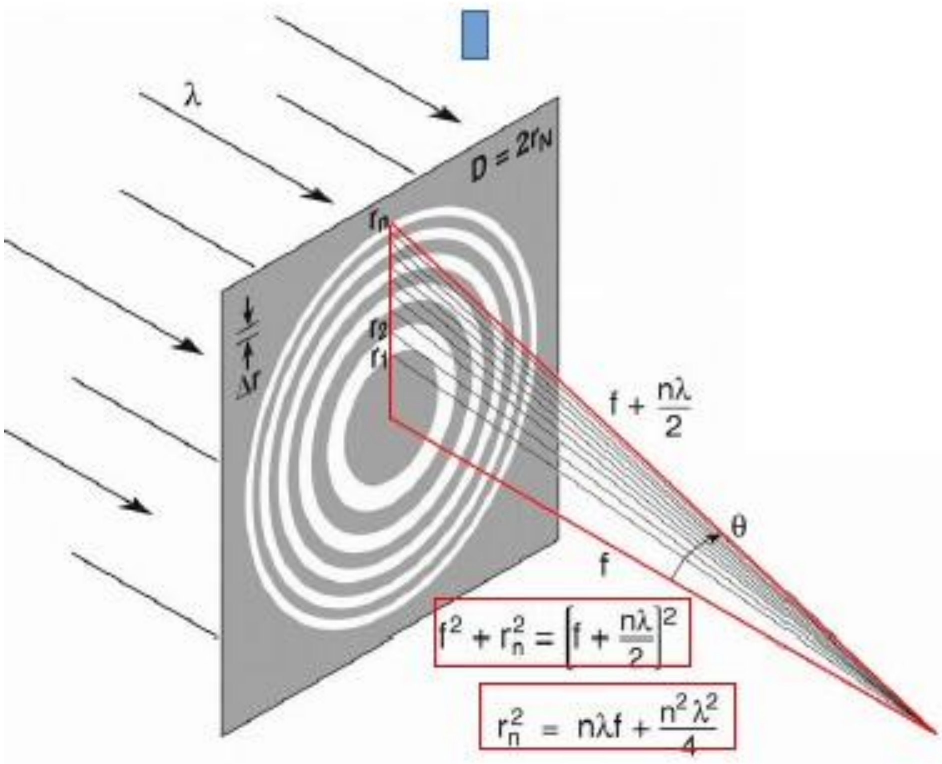






Barrea et al., J. Synchrotron Radiation (2010)

nanoARPES : Fresnel Zone Plate



For f >> nλ/2, which corresponds to a small NA lens

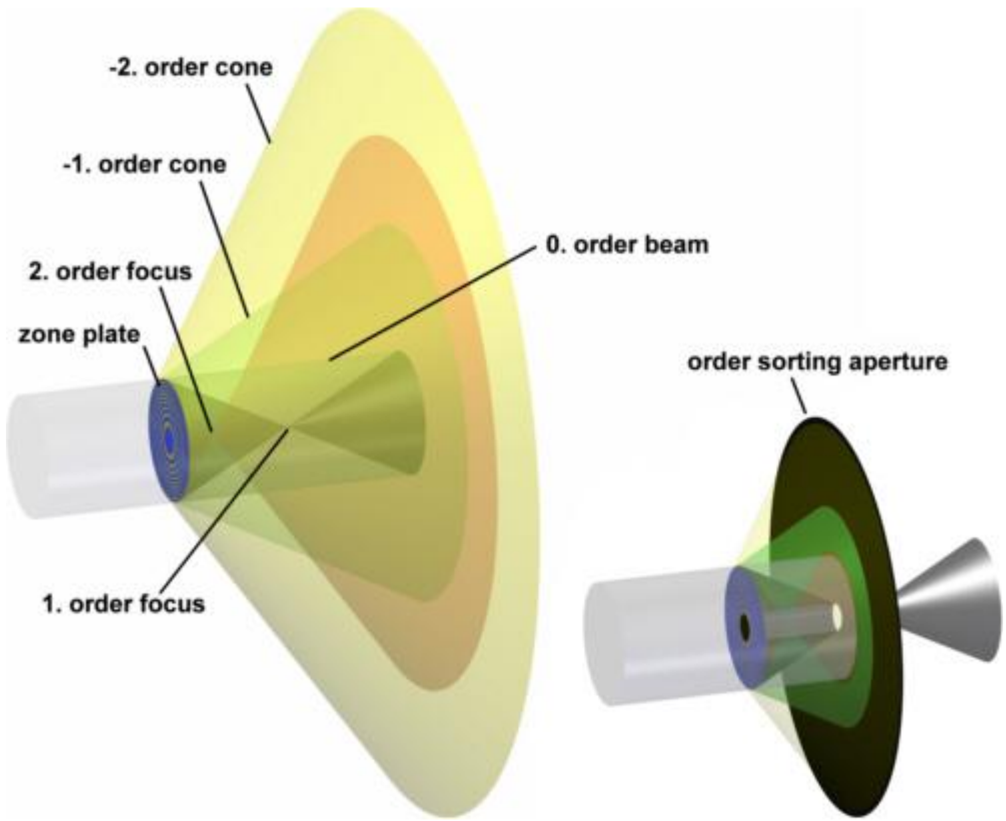
$$NA = \sin\theta = \lambda/_{2\Delta r} << 1$$

the radius of the nth zone is given by:

$$r_n \approx \sqrt{n\lambda f}$$

- A real first focus is achieved when successive zones increase in radius by $\sqrt{n}$
- FZP are highly chromatic

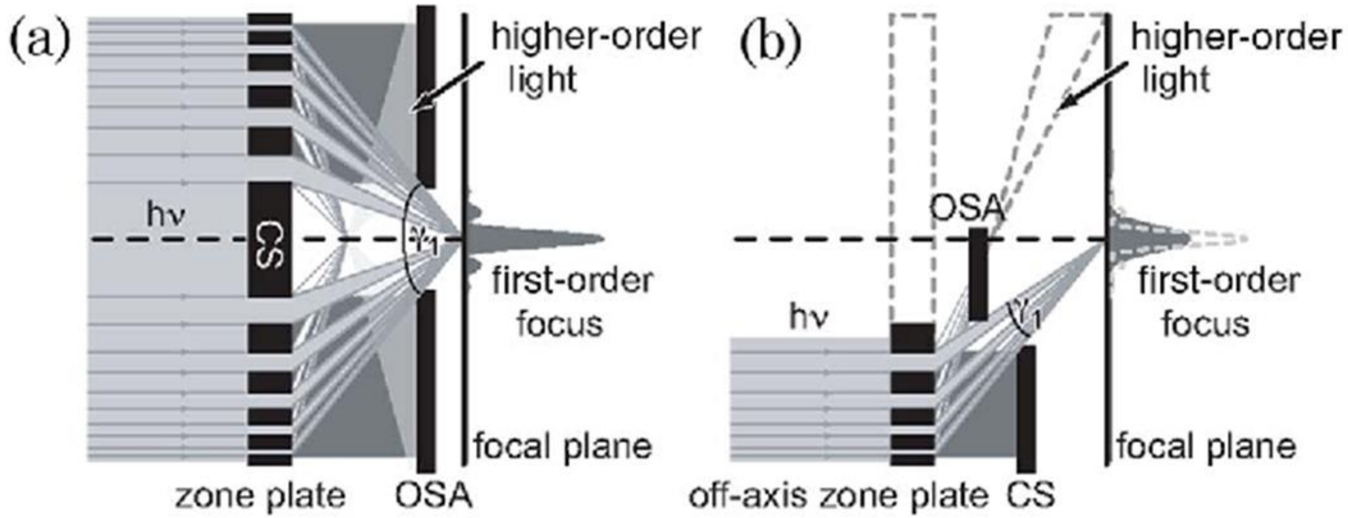
nanoARPES : Fresnel zone plate

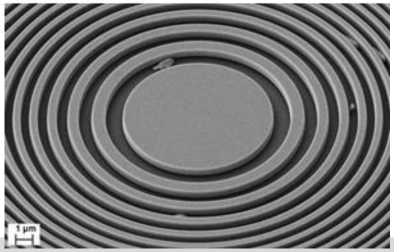


nanoARPES : Fresnel zone plate

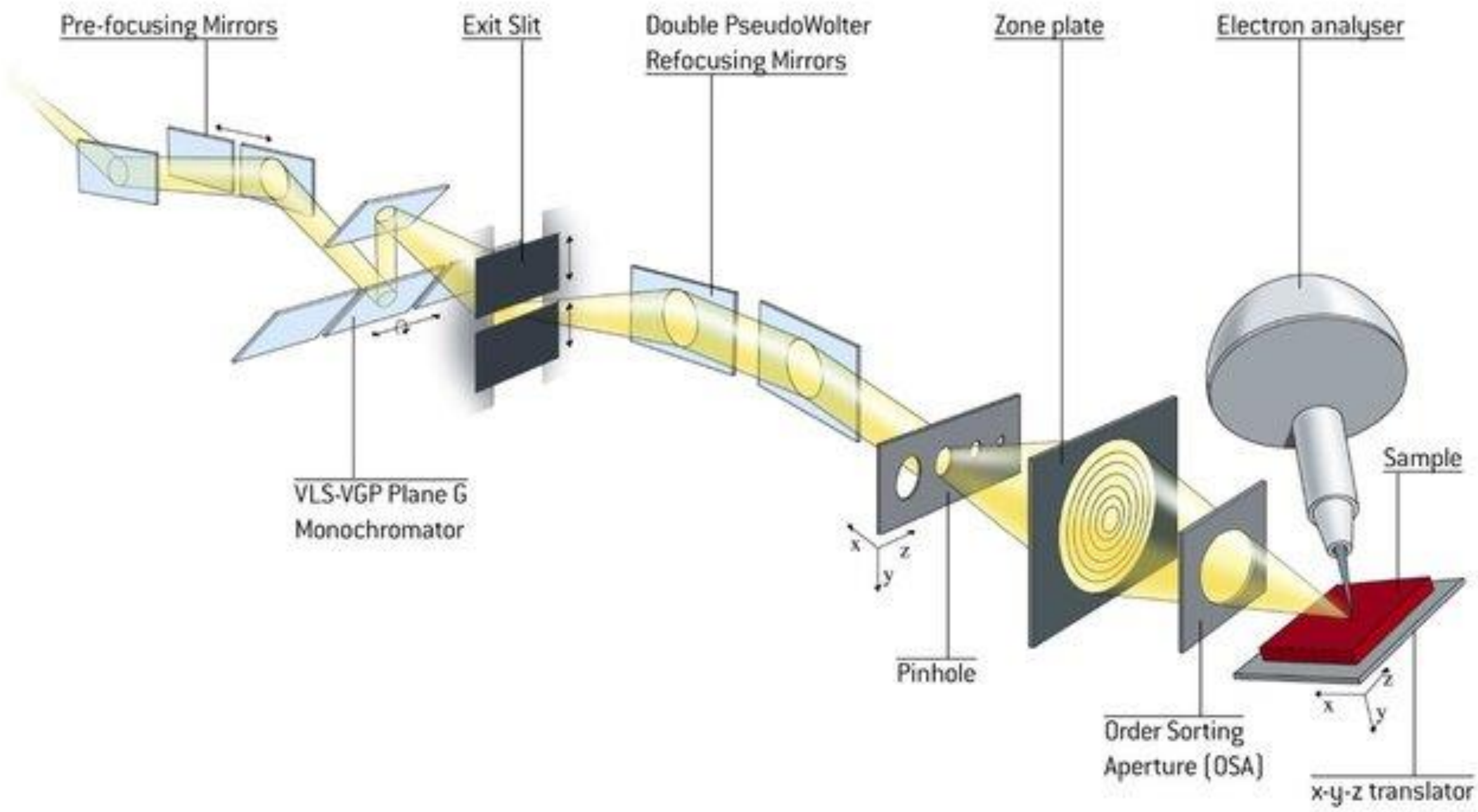
Working distance @ 100 eV ~ 4 mm

Focal length $f = \frac{2r_N \Delta r_N}{\lambda}$





nanoARPES : Beamline design



Beamlines in light sources worldwide for micro- or nano-ARPES

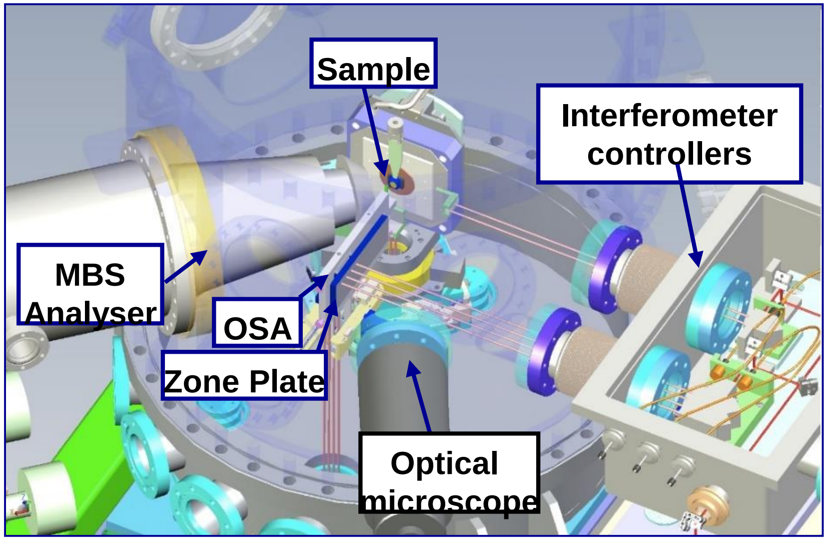
valence band nanoARPES

operating:
Elettra, Soleil, DLS

planning/commissioning:
TPS, NSLS-2

國家同步輻射研究中心
National Synchrotron Radiation Research Center

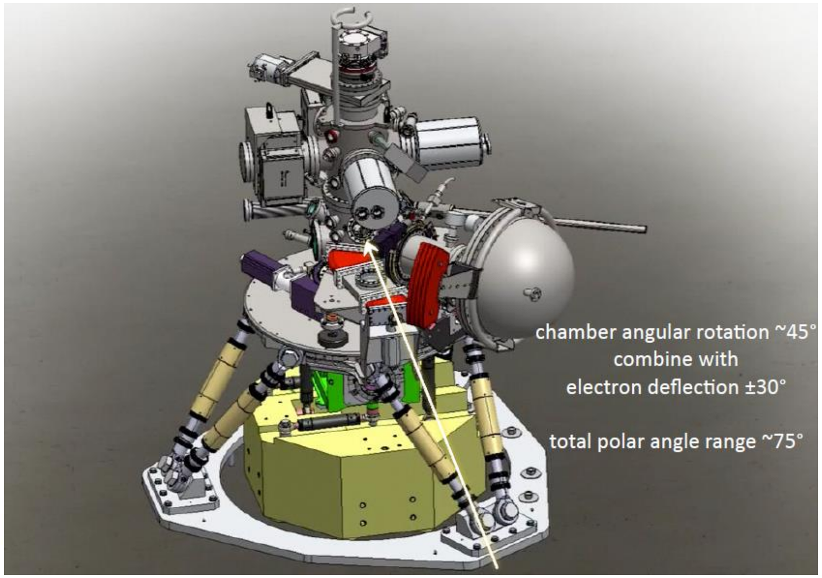
The challenge of nanoARPES end station

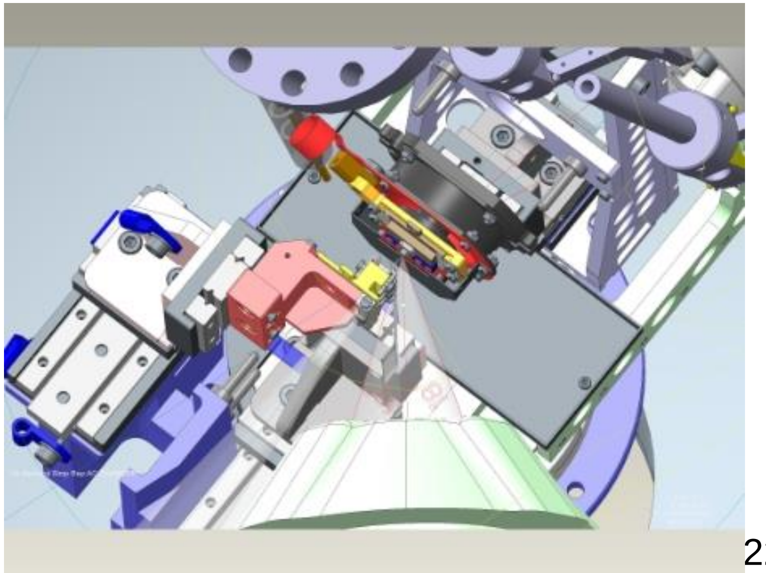


nanoARPES - *With spatial and momentum k information in the electronic structure*

Spatially-resolved ARPES

Zone-plate focusing: beam size ~ 100 nm





Optical Layout of TPS 39A nanoARPES Beamline

Core techniques:

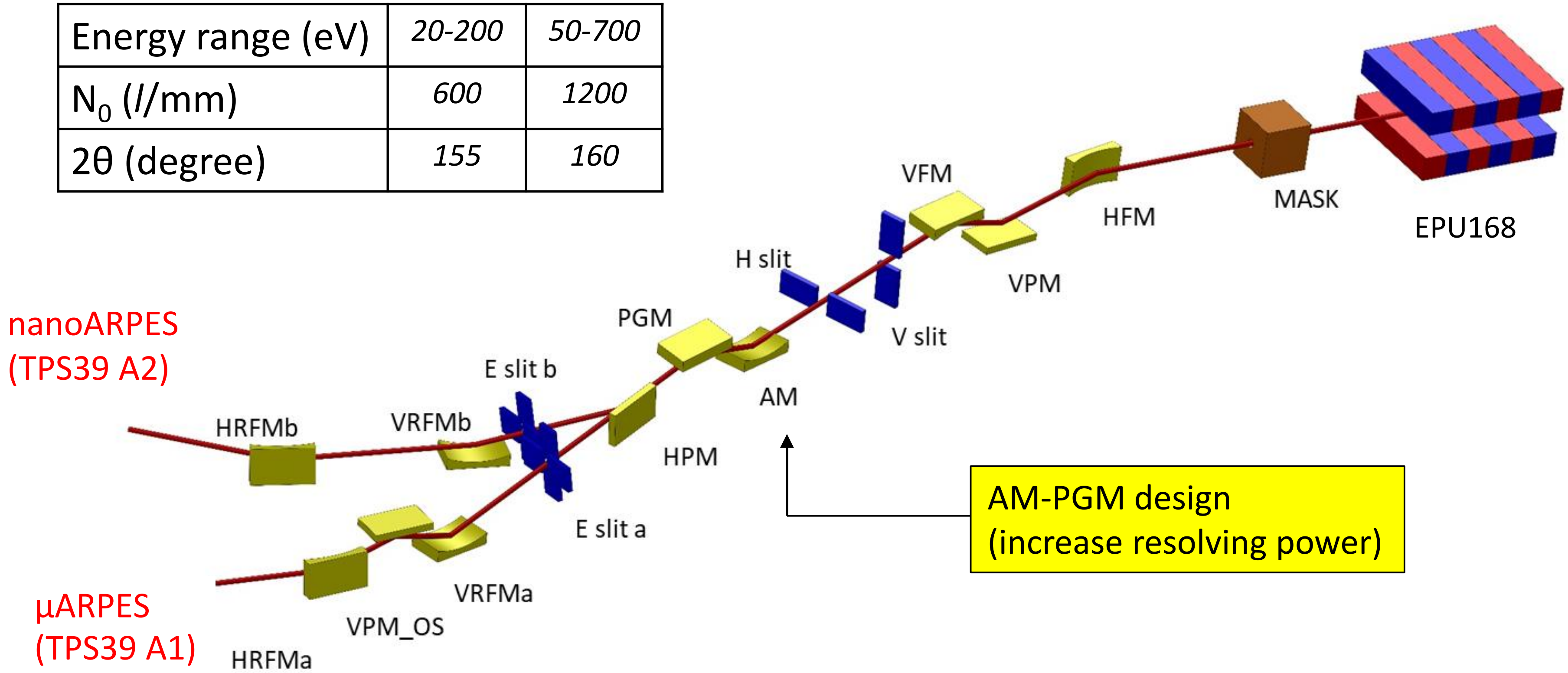
Probe the electronic structure of solids

- ✓ μARPES (TPS3 9A1)
  Beam size ~ 10 μm
- ✓ nanoARPES (TPS 39A2)
  Beam size ~ 100 nm

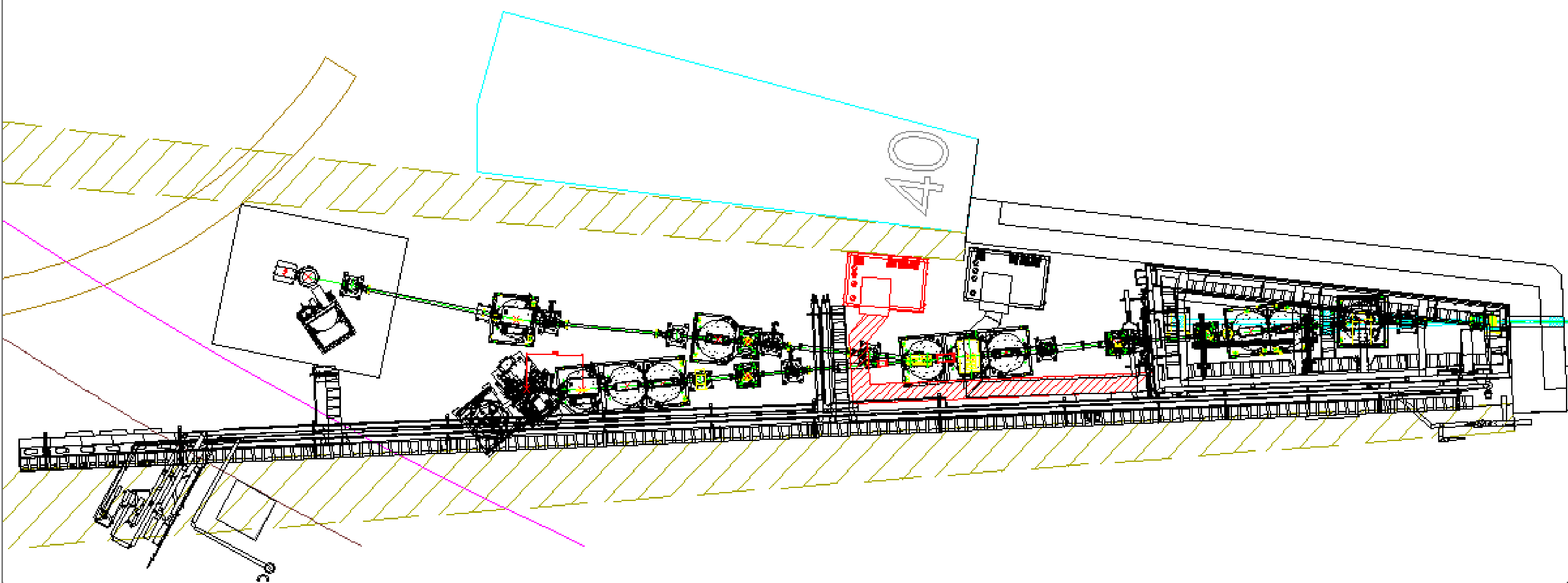
BL specification:

- Photon energy: **20 – 650 eV**
- Resolving power >$\mathbf{10^5}$
- Flux ~ 10^{12} ph/s with 10^4 resolving power

Energy range (eV)	*20-200*	*50-700*
N_0 (l/mm)	*600*	*1200*
2θ (degree)	*155*	*160*

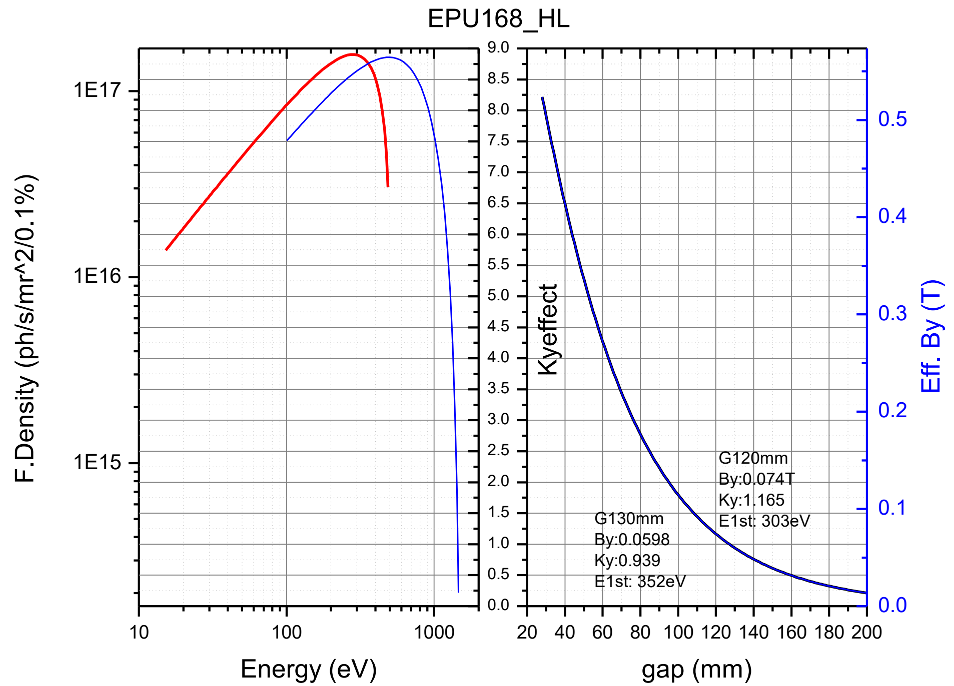


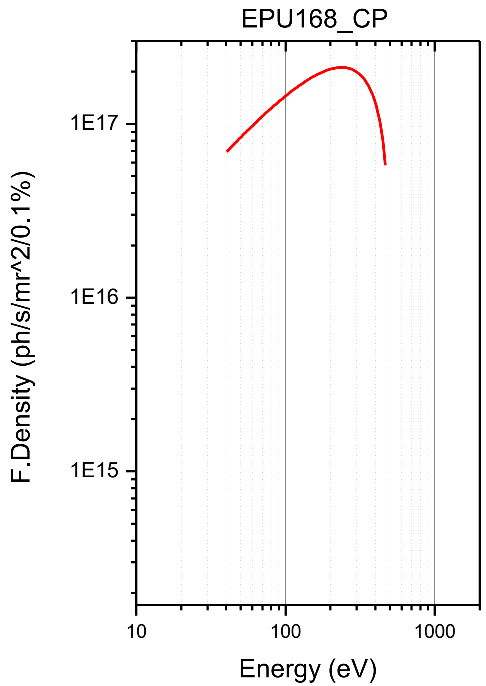
Optical Layout of TPS 39A nanoARPES Beamline



Insertion Device of TPS 39A nanoARPES Beamline

- *Gap operation : 28 ~ 120mm/ 4.3 m length with 23 periods*



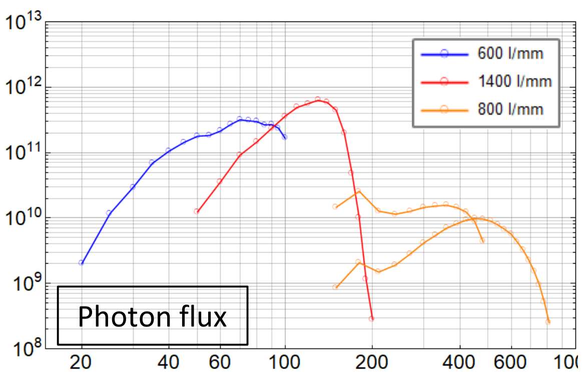


Mode	Magnetic field (T)	K	E1st (eV)	Partial power within 4.4 sigma (kW)	Partial power on B1 chamber Miss steering 2mm/0.2mrad (W)
Horizontal linear	By ≤ 0.516	Ky ≤ 8.1	≥ 15	0.568	~ 0
Circular	By=Bx ≤ 0.223	Ky=Kx ≤ 3.5	≥ 39	~ 0	40/16
Vertical linear	Bx ≤ 0.223	Kx ≤ 3.5	≥ 72	0.237	3.6/2

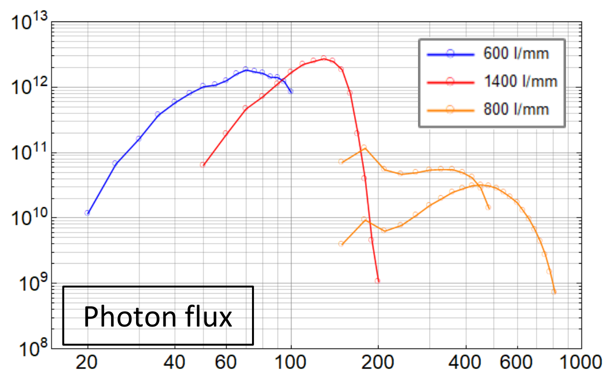
Beam Size and Resolving Power of TPS 39A nanoARPES

	Opening width of exit slit (*E slit*)	Beam size at 20 eV (*HxV*)	Beam size at 100 eV (*HxV*)	Photon flux at 20 eV (*photons/s*)	Photon flux at 100 eV	Resolving power $E/\Delta E$
High energy resolution	**2 μm**	**8 x 7 μm^2**	**5 x 4 μm^2**	2 x 10^9	4x10^{11}	100,000
Medium photon flux	**10 μm**	9 x 16 μm^2	6 x 16 μm^2	1.2 x 10^{10}	2x10^{12}	20,000
High photon flux	**20 μm**	10 x 32 μm^2	7 x 32 μm^2	3 x 10^{10}	4x10^{12}	8,000

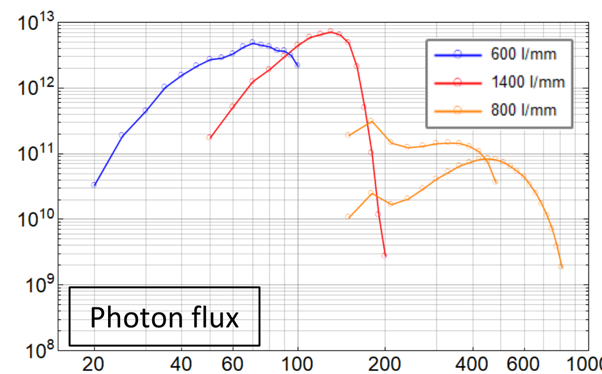
High energy resolution



Medium photon flux



High photon flux

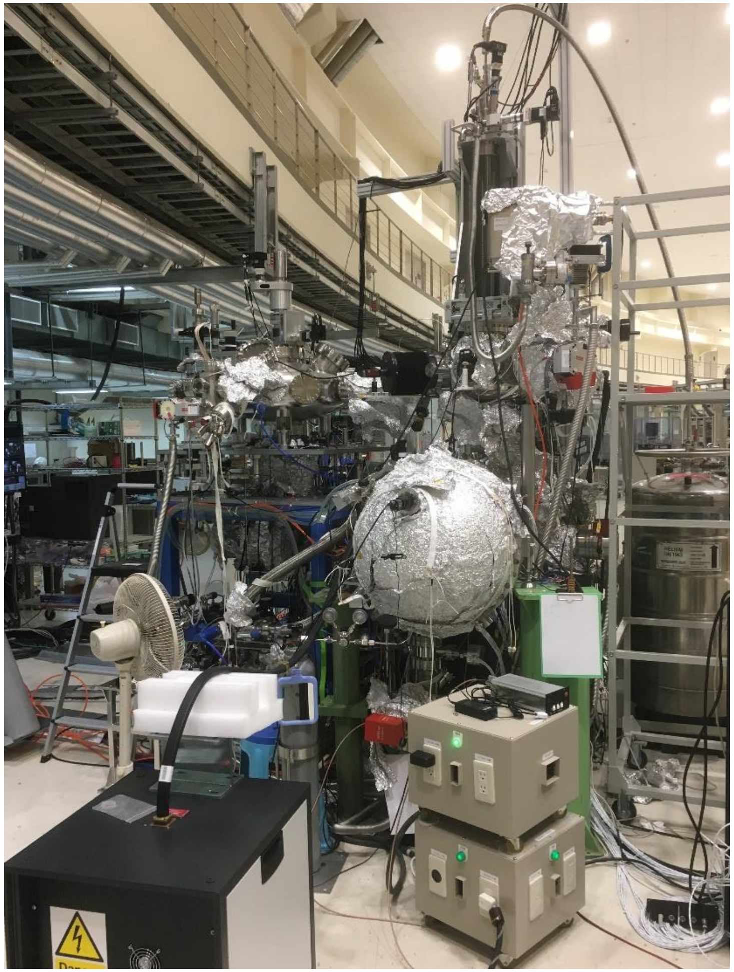


國家同步輻射研究中心
National Synchrotron Radiation Research Center

The end station of TPS 39A1

μARPES – led and constructed by Prof. Deng-Sung Lin (NTHU) from an user community

Spatially-resolved ARPES/Spin-resolved ARPES/Conventional ARPES
Temperature range 5 – 1500 K
In-situ thin film preparation
2D-VLEED spin-detector



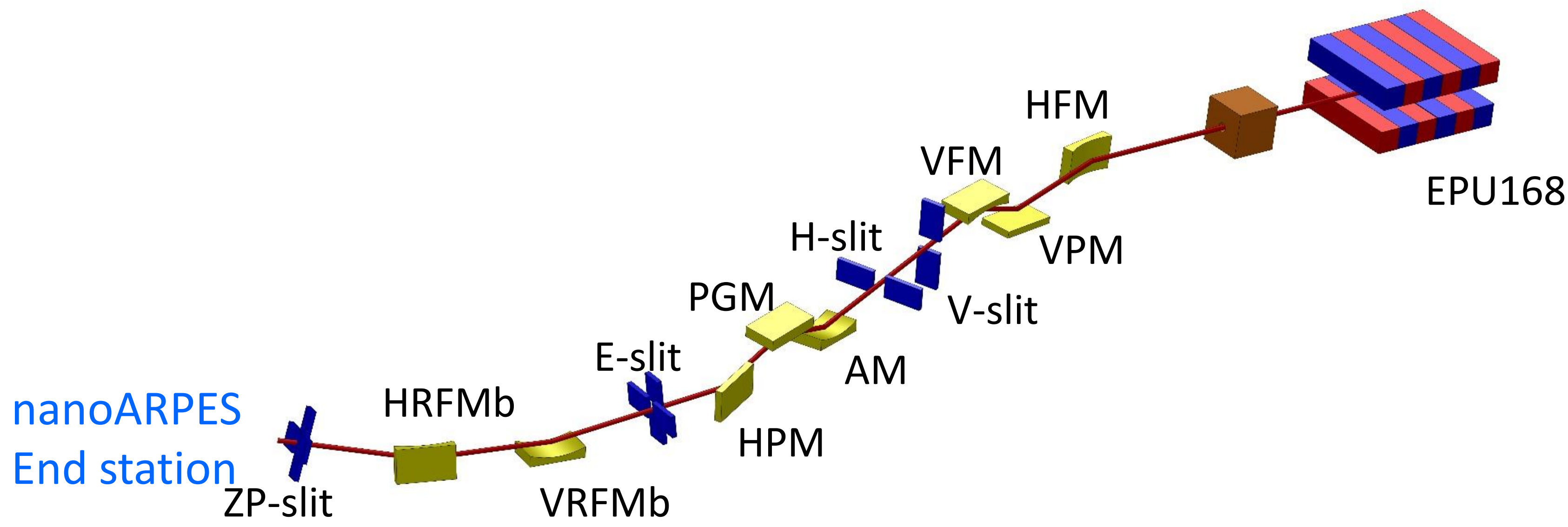
- ✓ Assembled in February 2018
- ✓ Located at TPS 39A1
- ✓ Conducted **Spin-resolved ARPES/Conventional ARPES** with **He-lamp** before the completion of beamline construction

The end station of TPS 39A2

Core techniques:
Probe the electronic structure of solids with much smaller domain size

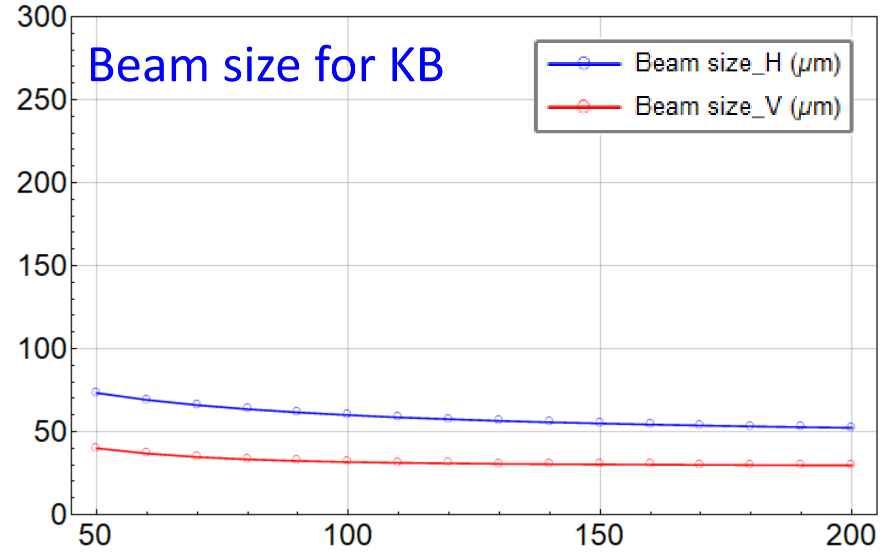
- ✓ nanoARPES (TPS39 A2)
  - ✓ **Beam size ~ 100 nm**
  - ✓ **Bendable mirrors for HRFMb & VRFMb**

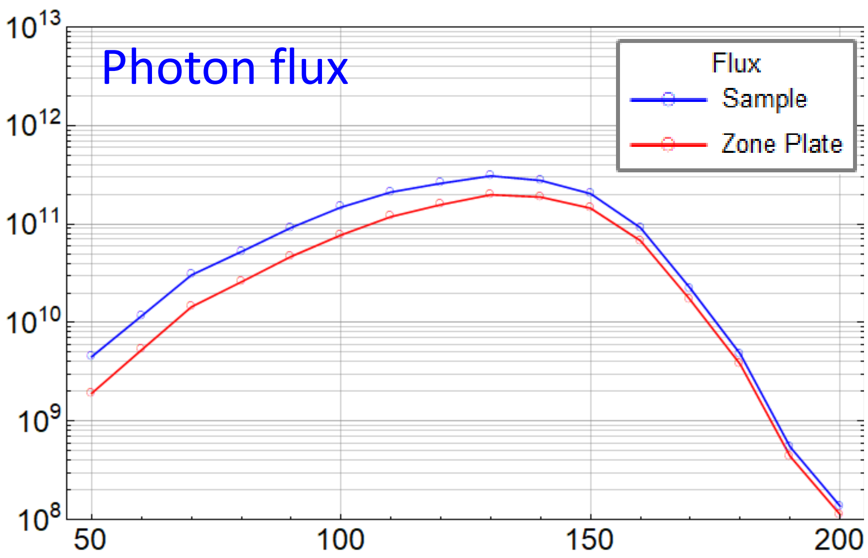
Two focal points of KB bendable mirrors
- At ZP-slit with ZP focusing
- Behind ZP-slit ~ 2.5 m without ZP focusing

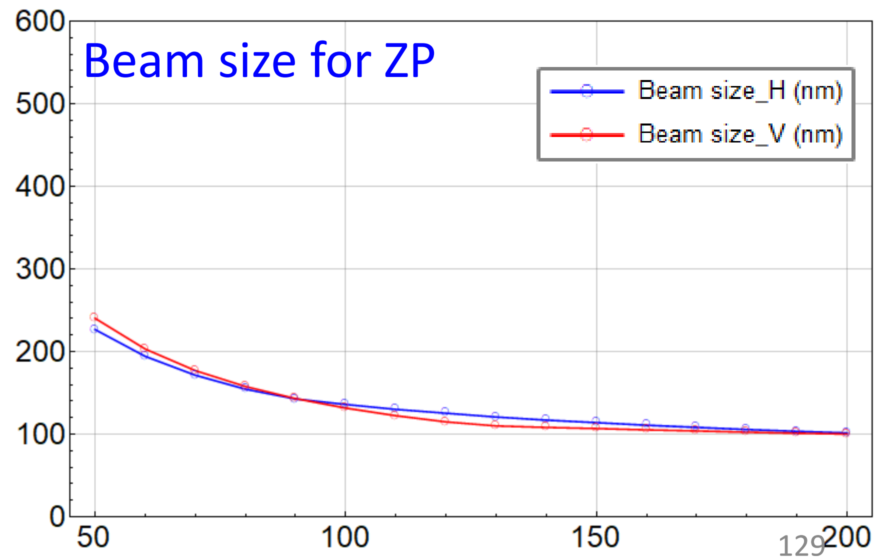


Simulation result of zone plate & KB focusing stage at TPS

Z.P. object distance	2250 mm
Z.P. image distance	**6 mm**
Z.P. diameter	0.9 mm
KB focus positin (after HRFMb)	2500 mm
Z.P. position (after HRFMb)	4750 mm
Foocus2 position (after HRFMb)	4756 mm







Experimental Sequence of nanoARPES

	Beam Size	Scanned range	Spitial resolution
With KB focusing	~ 50 μm	5 mm x 5 mm	100 nm
With ZP focusing	~100 nm	200 μmx200μm	20 nm

- ✓ With KB focusing, we can make a large area mapping of core level to find the position and bonding termination of sample.
- ✓ With ZP focusing, we can make a fine scan of band structure and Fermi surface mapping for sample area.

The end station design of NanoARPES branch

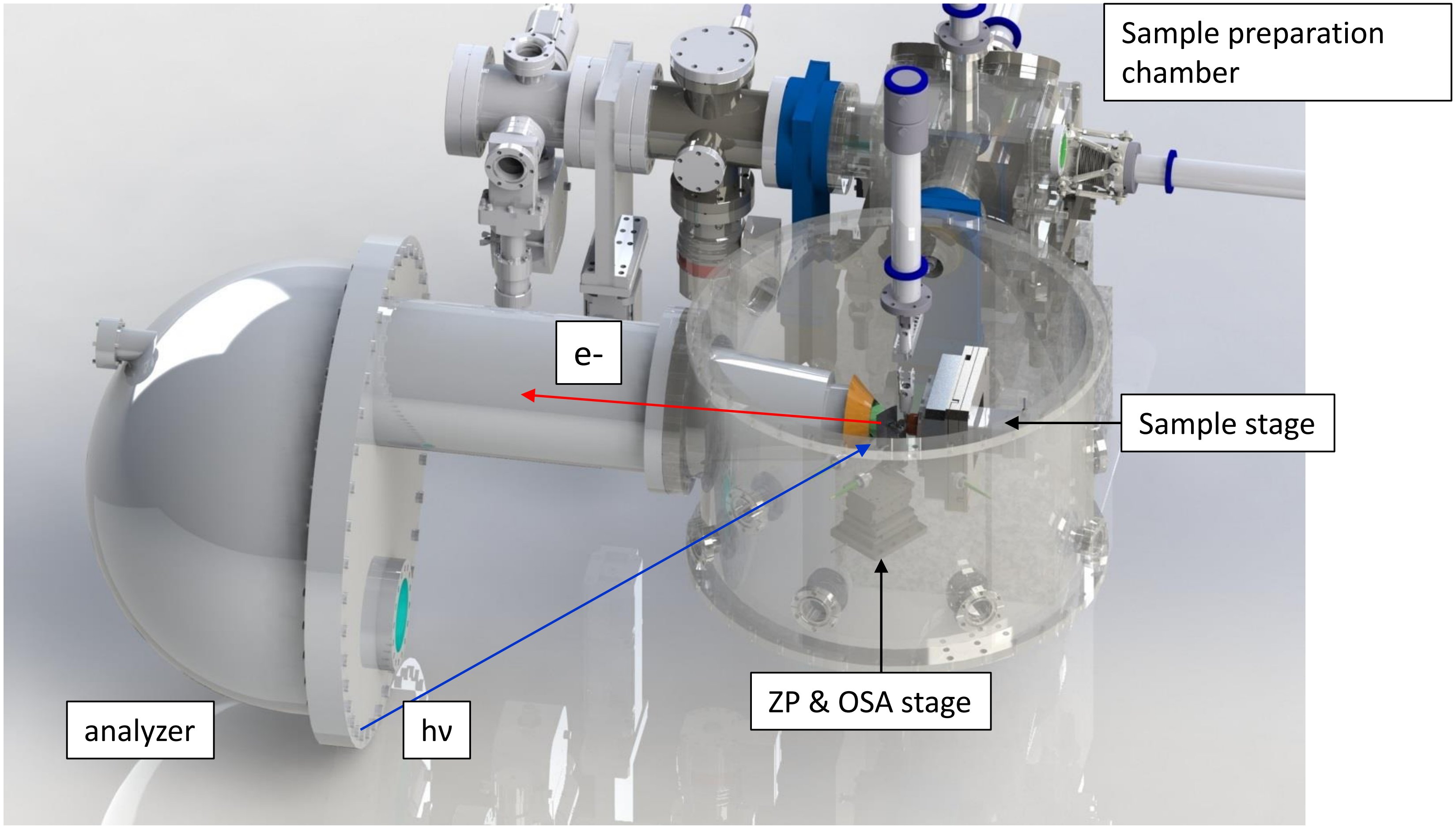
nanoARPES - *With spatial and momentum k information in the electronic structure*

Goal : Spatially-resolved ARPES
Zone-plate focusing: beam size ~ 100 nm

Sample stage :
- ✓ 6-axis degrees of freedom (*x,y,z,yaw,roll,pitch*)
- ✓ LHe & LN_2 cooling : 45K & 100 K
- ✓ Optical hutch required
- ✓ Monitor the position of sample, OSA and ZP stages with laser interferometer
- ✓ UHV compatible stages

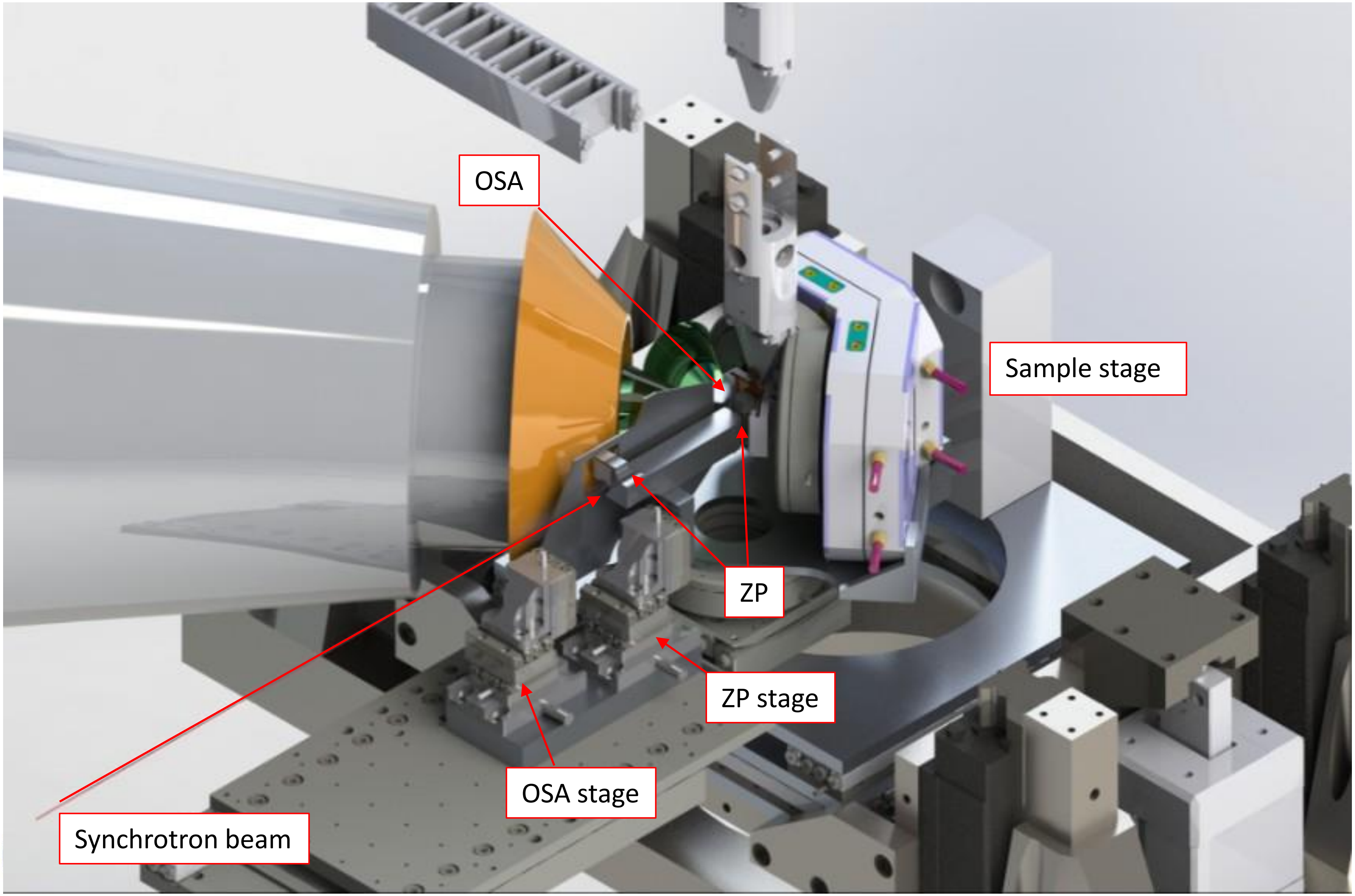
- ➢ UHV environment/UHV compatible stage
  - ✓ Baking temperature
- ➢ Magnetic field shielding
  - ✓ Motor with long traveling length
- ➢ 6-axis sample stage with high spatial resolution
  - ✓ Stability
- ➢ Very short working distance for ZP in VUV region
  - ✓ low photon energy (50-200 eV)
- ➢ Vibration control (< 30 nm)
  - ✓ Environment, pumps…
- ➢ Temperature drift
  - ✓ Optical hutch required
- ➢ Space charging issue

The end station design of NanoARPES branch

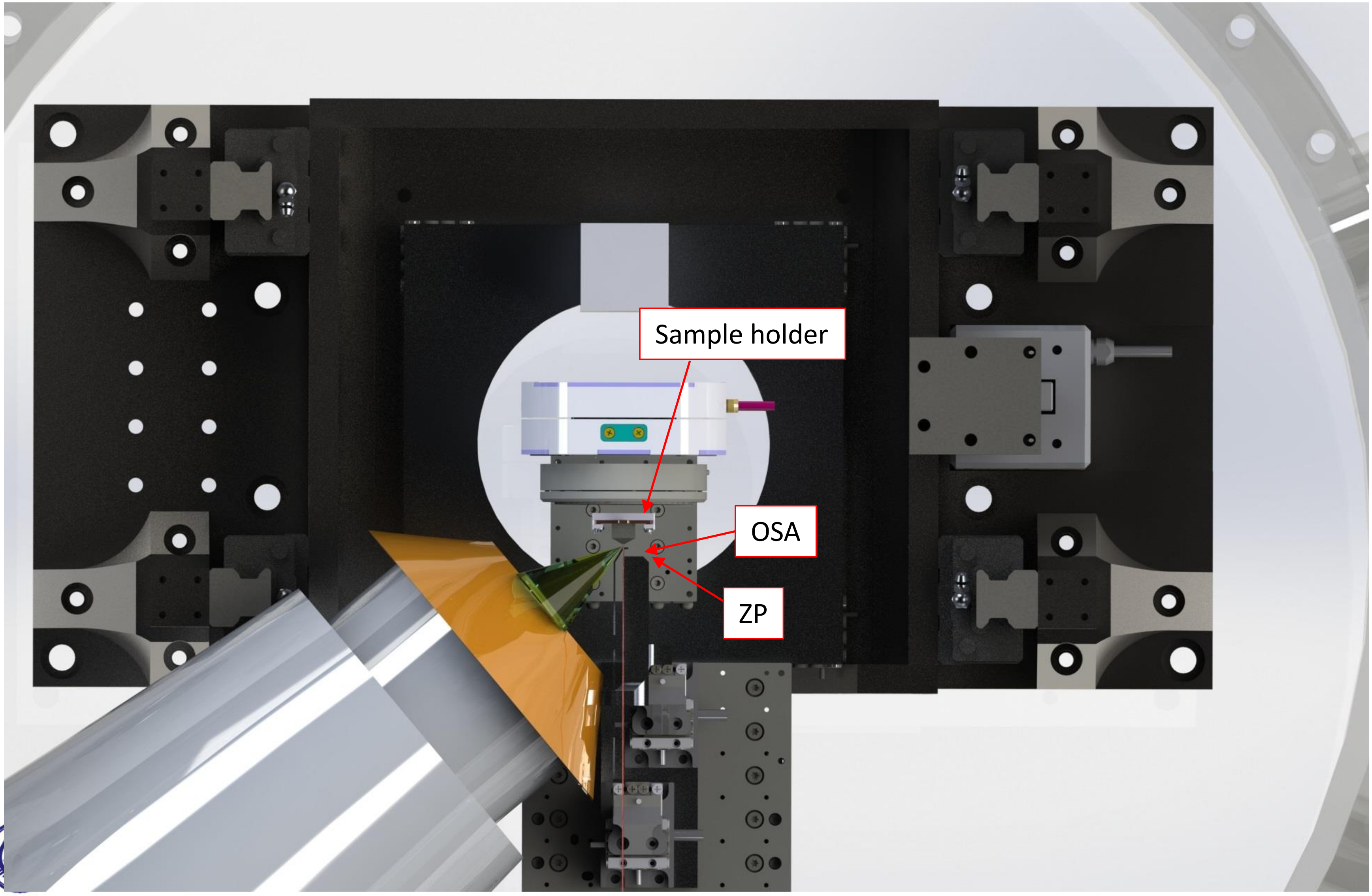


国家同步輻射研究中心
National Synchrotron Radiation Research Center

The end station design of NanoARPES Branch



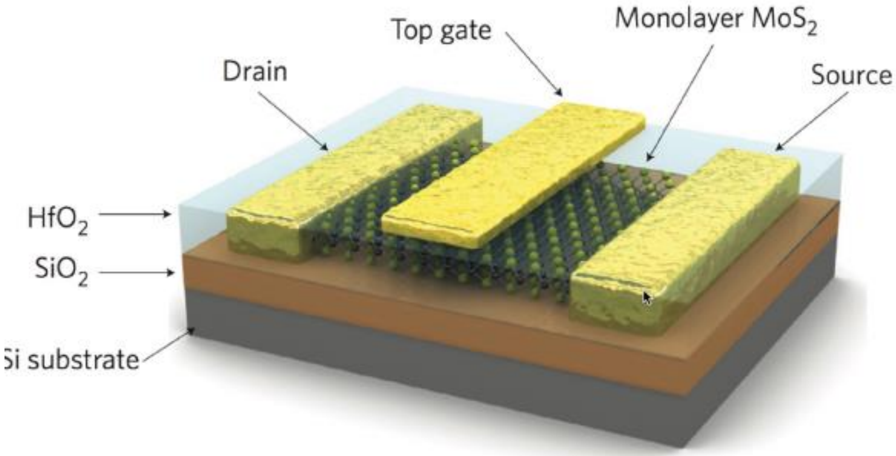
The end station design of NanoARPES branch

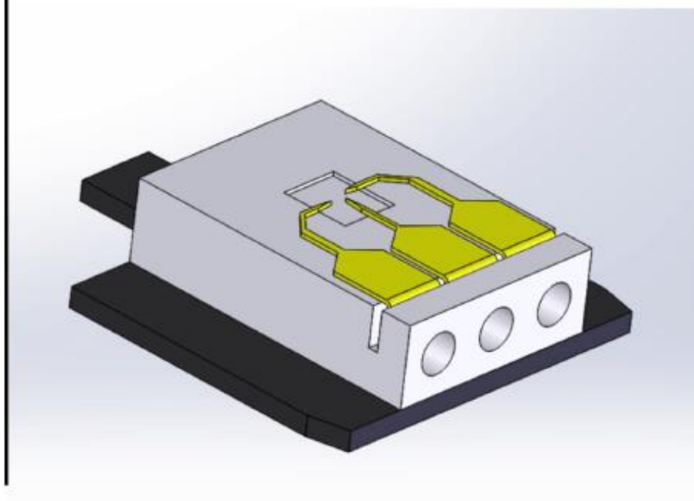


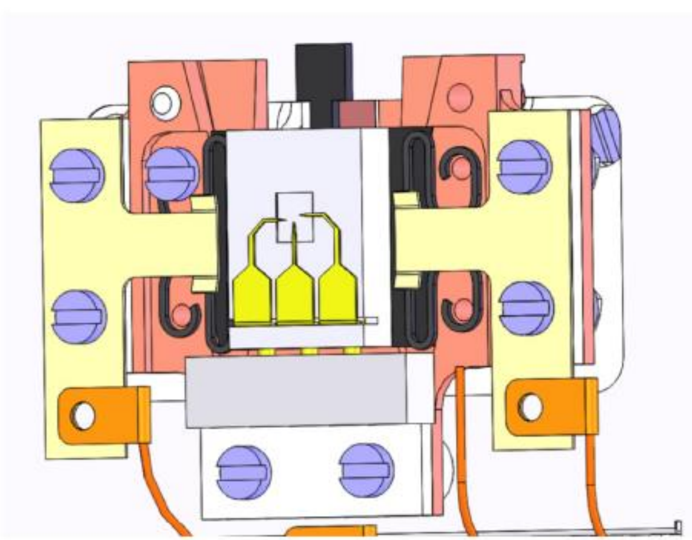
The end station design of NanoARPES branch

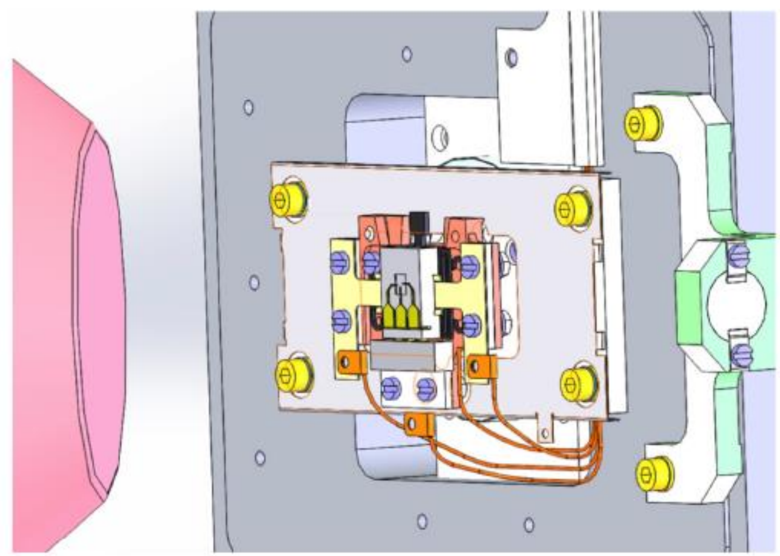
The end station design of NanoARPES branch

In-operando setup

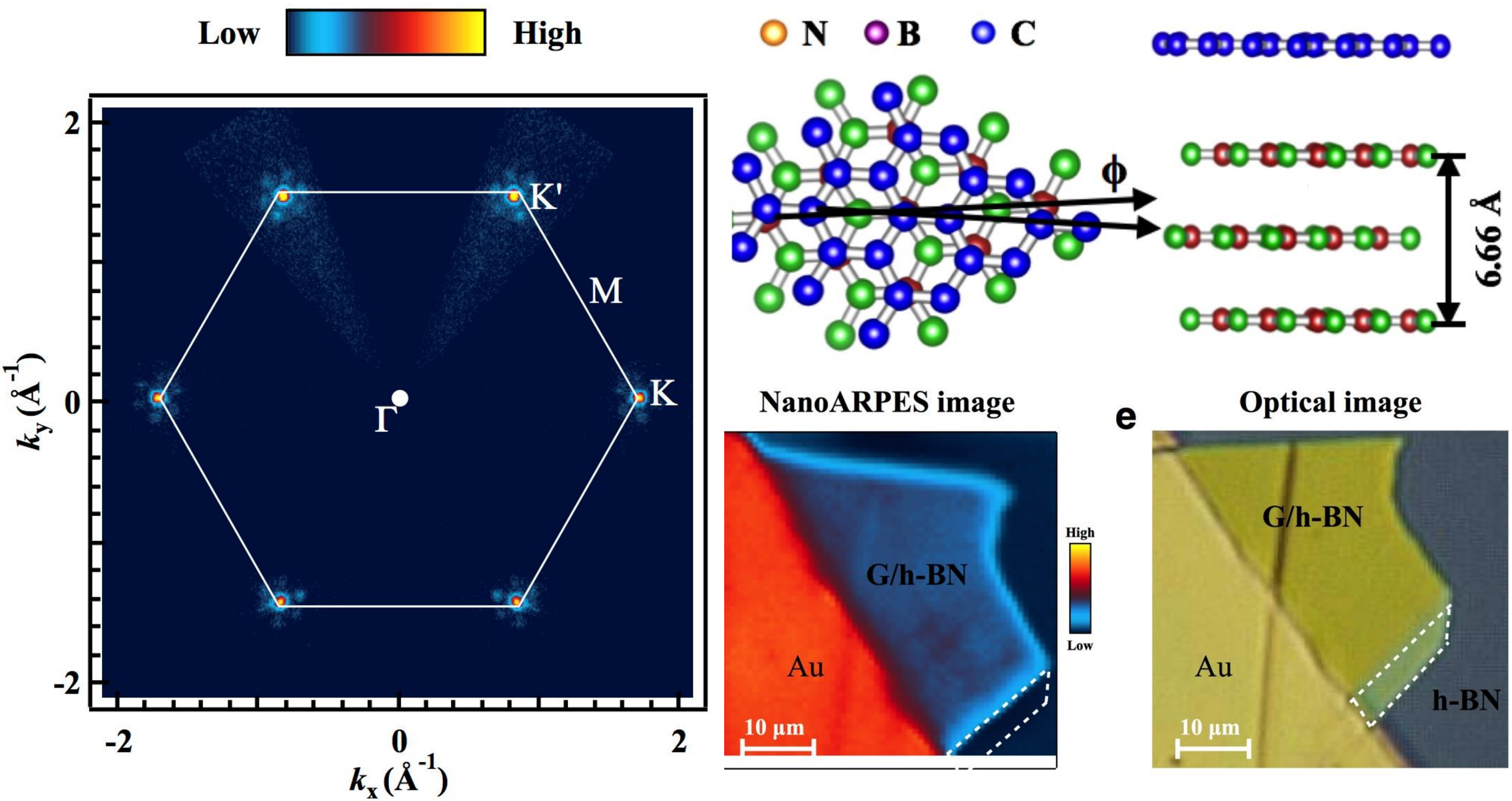




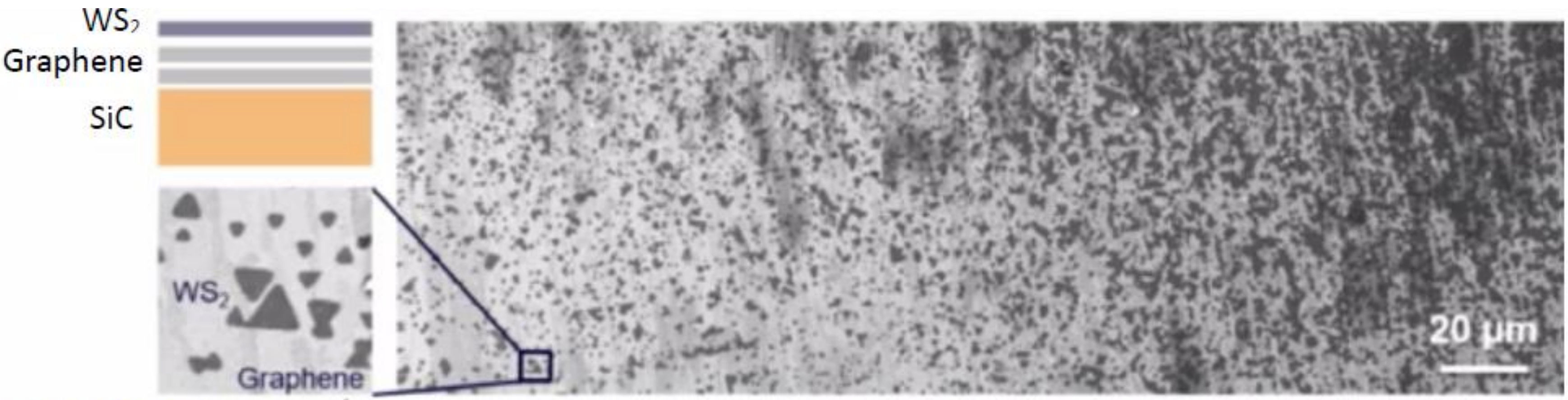


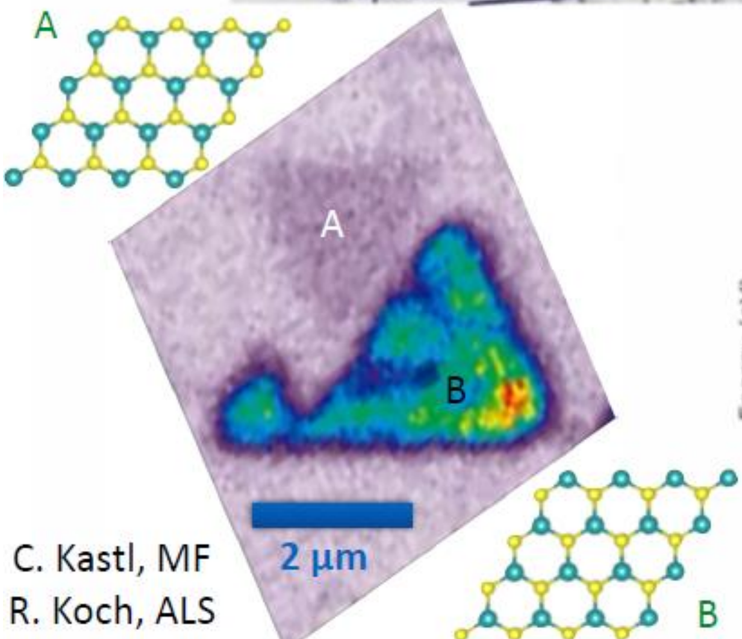


nanoARPES in Exfoliated Graphene on h-BN

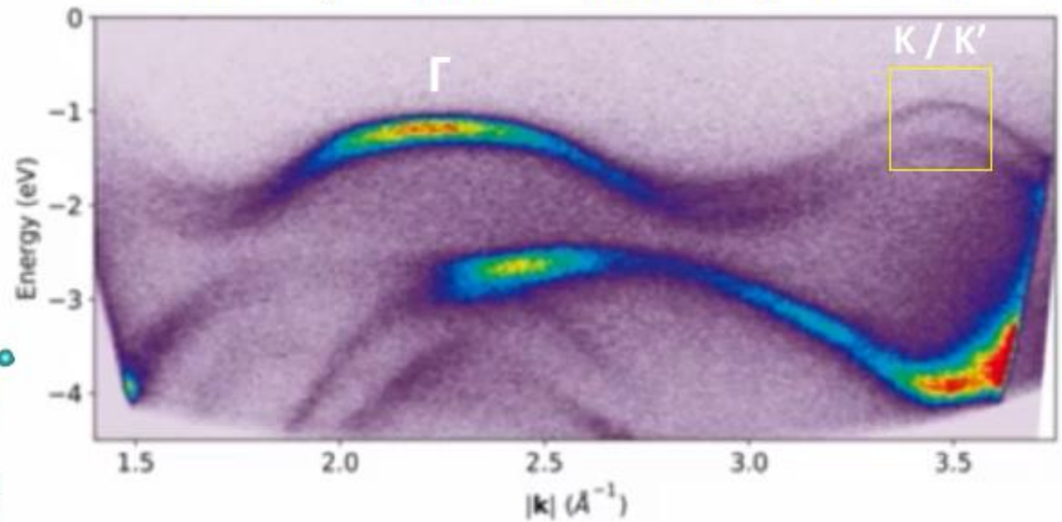


Typical result at MAESTRO beamline, ALS





ARPES spectrum, 300nm integrated region



C. Kastl, MF
R. Koch, ALS

Summary

- *With spatial and momentum-resolved information in electronic structure, nanoARPES is a powerful tool for probing the band structure of solids with small domain size.*

- *Combine with Time-resolved ARPES and Spin-resolved ARPES, extensive scientific topics can be studied.*

- *With an in-operando setup, a gate configuration of 2D materials is possible to conduct ARPES for probing the effect of gate voltage.*

- *In conventional ARPES, non-layer structure of crystals are difficult to measure its band structure, such as YBCO…. With nanoARPES, we can revisit these interest topics.*

Constrution Team

- *Insertion Device*
  Dr. Ting-Yi Chung, Dr. Ching-Hsiang Hwang

- *Beamline construction :*
  Huang-Wen Fu, Dr. Gung-Chian Yin, Ming-Ying Hsu, Dr. Bo-Yi Chen, Liang-Jen Huang, Chao-Yu Chang, Ming-Han Lee, Dr. Yi-Jr Su, Robert Lee, Dr. Chien-Te Chen

- *TPS 39A1 : μARPES*
  Prof. Deng-Sung Lin (NTHU)

- *TPS 39A2 : nanoARPES*
  Cheng-Maw Cheng, Ping-Hui Lin

Acknowledgement

- Dr. Jose Avila
- Dr. Maria Carmen Asensio

  ANTARES beamline, SOLEIL, France

- Dr. Moritz Hoesch

  P04 XUV beamline, PETRA III, DESY, Germany

- Dr. Eli Rotenberg
- Dr. Aaron Bostwick

  MAESTRO beamline, ALS, USA