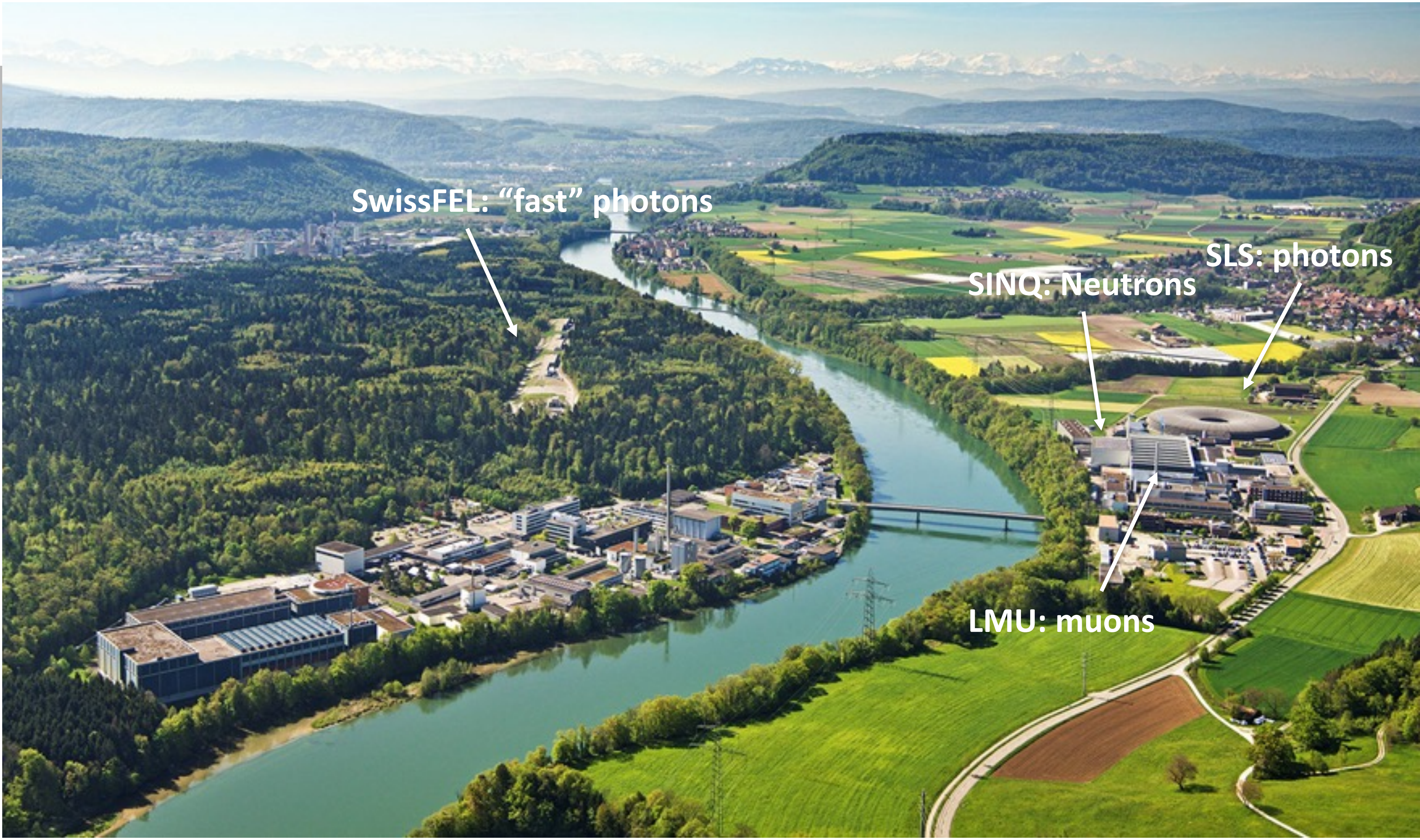
PAUL SCHERRER INSTITUT

Wir schaffen Wissen – heute für morgen

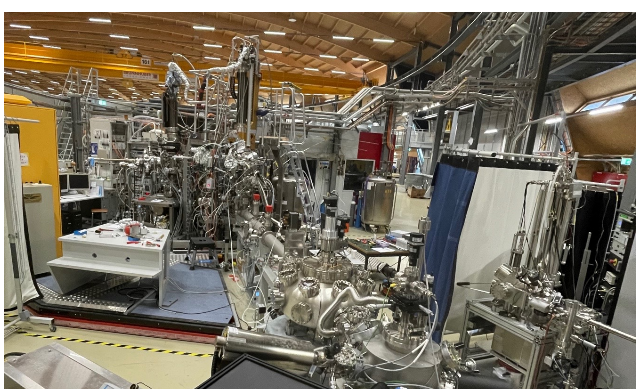
Angle-resolved photoemission spectroscopy, the microscope for the electronic structure

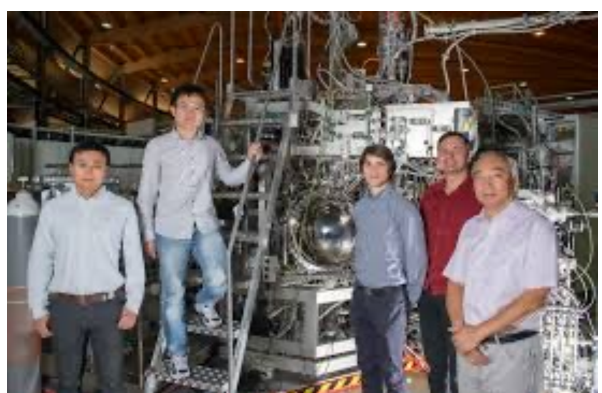
Milan Radovic

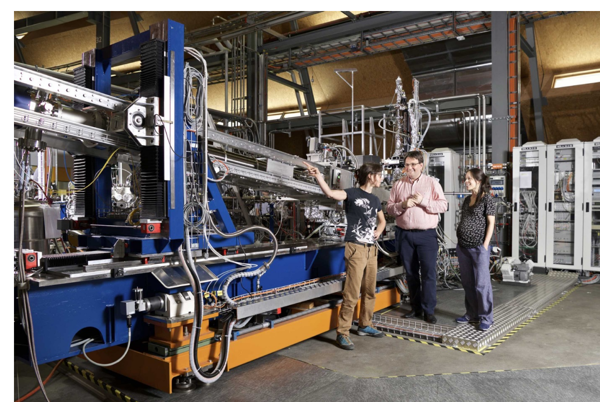
Large scale facilities at PSI: the unique toolset!



Swiss Light Source







Outline

- The general introduction of Transition Metal Oxides (TMOs)

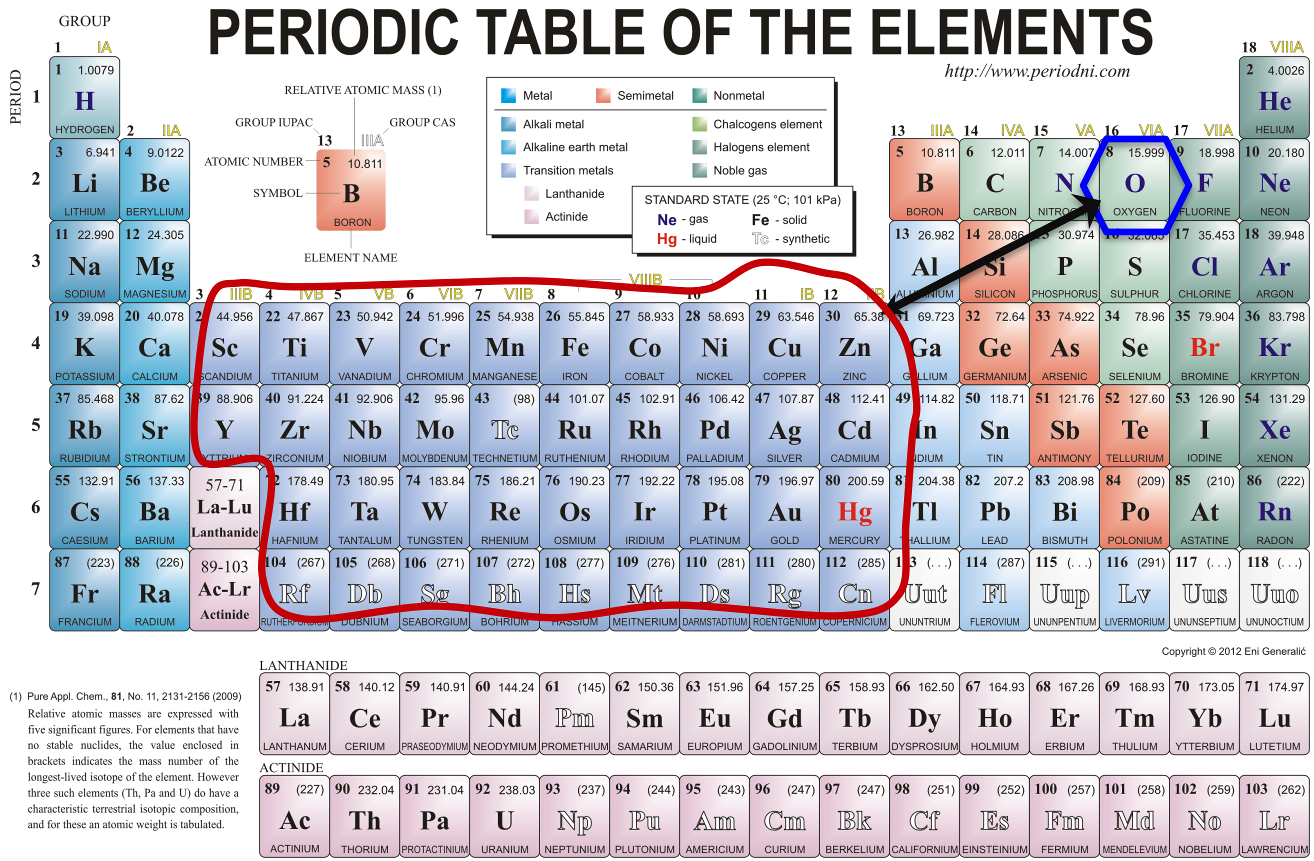
- Band structure: basic concept

- Angle-resolved photoemission spectroscopy –ARPES: overview

- Example: Depicting the electronic structure of Low Dimensional Electronic Structure at $ATiO_3$

PAUL SCHERRER INSTITUT

Creating novel PHASES and Tuning of ELECTRONIC states of artificial and hybrid materials based on TMOs

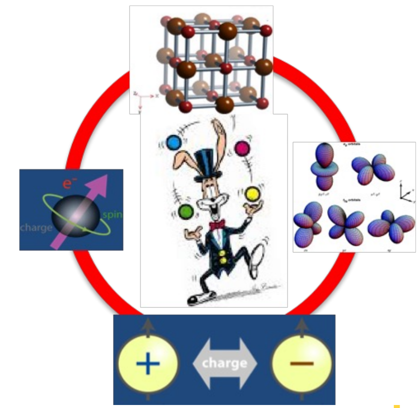


TMO show extraordinary electronic and magnetic properties: CMR, HTc, MIT, etc.

Transition Metal Oxides: Surface Chemistry and Catalysis H.H. Kung, Elsevier Science, NY, 1989.

What are Transition metal Oxides (TMO)?

- **Partly filled d-shell: electron-electron interactions, thus spin and orbital degrees of freedom play role.**
- **Multiple valence states: many electronic configurations.**
- **Easy charge exchange with Oxygen.**



Many structures possible, very different properties.

- **BO Rocksalt structure: NiO, ZnO, TiO, CoO...**
- **ABO$_3$ Perovskite: cubic SrTiO$_3$, Orthorombic: ReNiO$_3$, SrIrO$_3$, Tetragonal:TiO$_2$, BaTiO$_3$**
- **A$_2$BO$_4$ Perovskite (e.g La$_2$CuO$_4$): Layered structure (weak interplane coupling),**
- **Ruddlesden-Popper series A$_{n+1}$B$_n$O$_{3n+1}$ (Interpolates between 2 and 3 dimensional coordination: LaSr$_3$FeO$_{10}$, La$_3$Ni$_2$O$_7$ ...**
- **Double perovskite AA'BB'O$_6$ (Sr$_2$FeMoO$_6$)**
- ...

Creation and Control of the electronic properties of ABO_3 Perovskite

Distortion of the BO_6 octahedron

Energy splitting of the d_{xy} & d_{xz} & d_{yz} bands

Doping (trough A or O vacansies)

Filling of the bands

Octahrdral rotations, Binding angles

Hopping probability,
Effective mass
Band width

Proximity effects

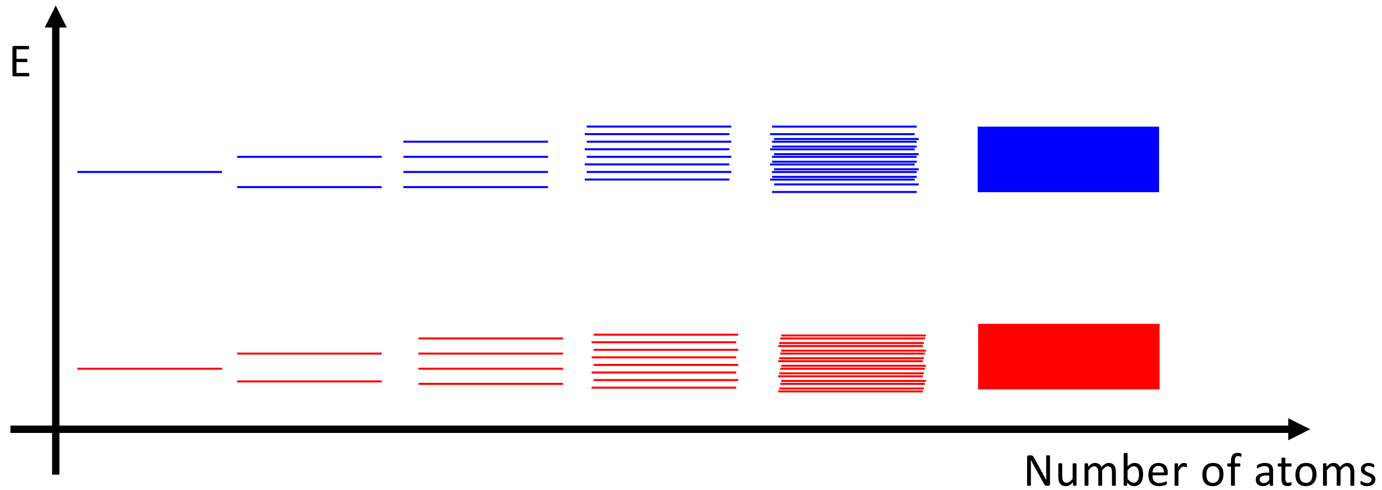
Doping via charge transfer,
Inducing orders
(magnetism superconductivity…)

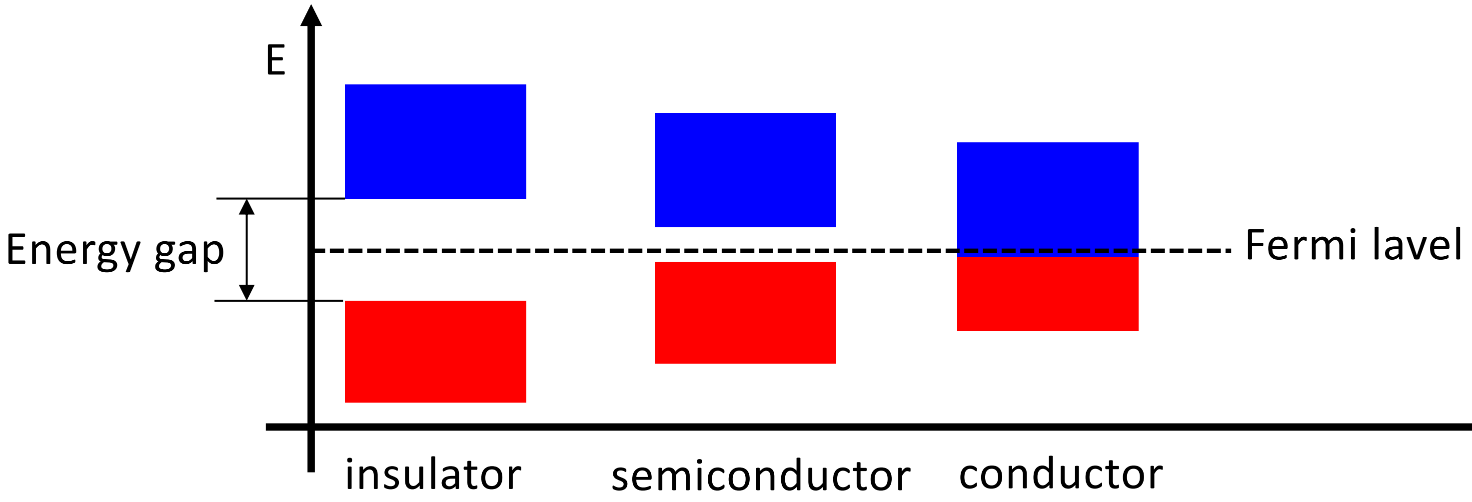
How to turn the knobs?

- ✓ Temperature (phase transition);
- ✓ **Defects;**
- ✓ **Cristal structure;**
- ✓ ***lattice strain, proximty…***
- ✓ **Stacking (artificial VdW materials)**

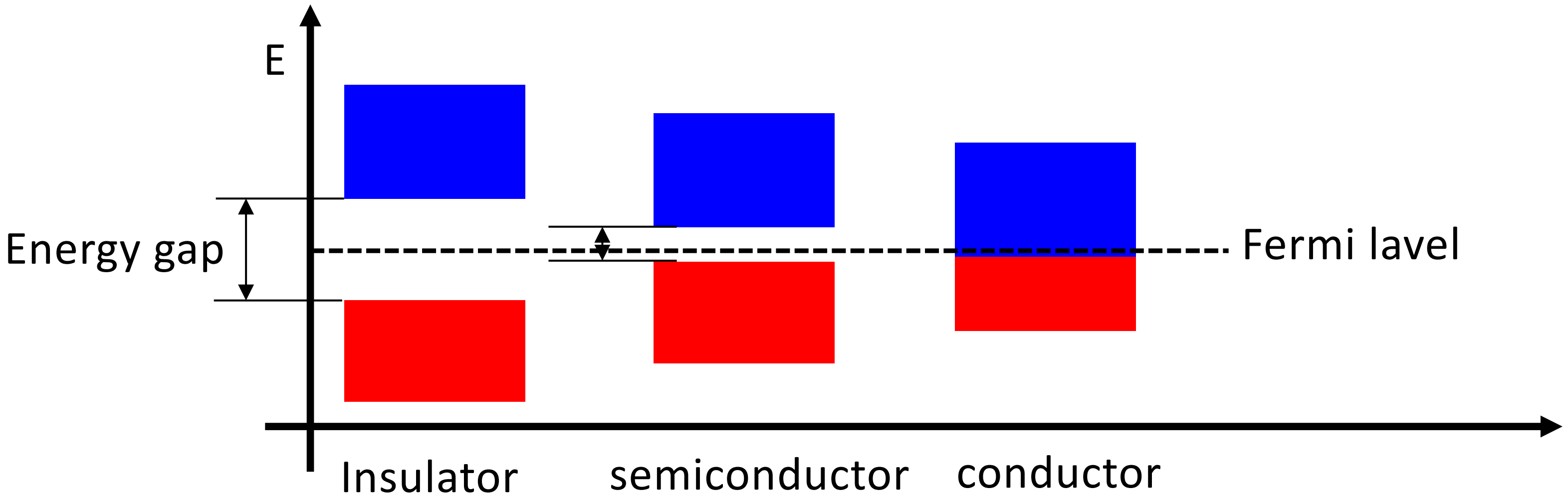
https://news.vanderbilt.edu

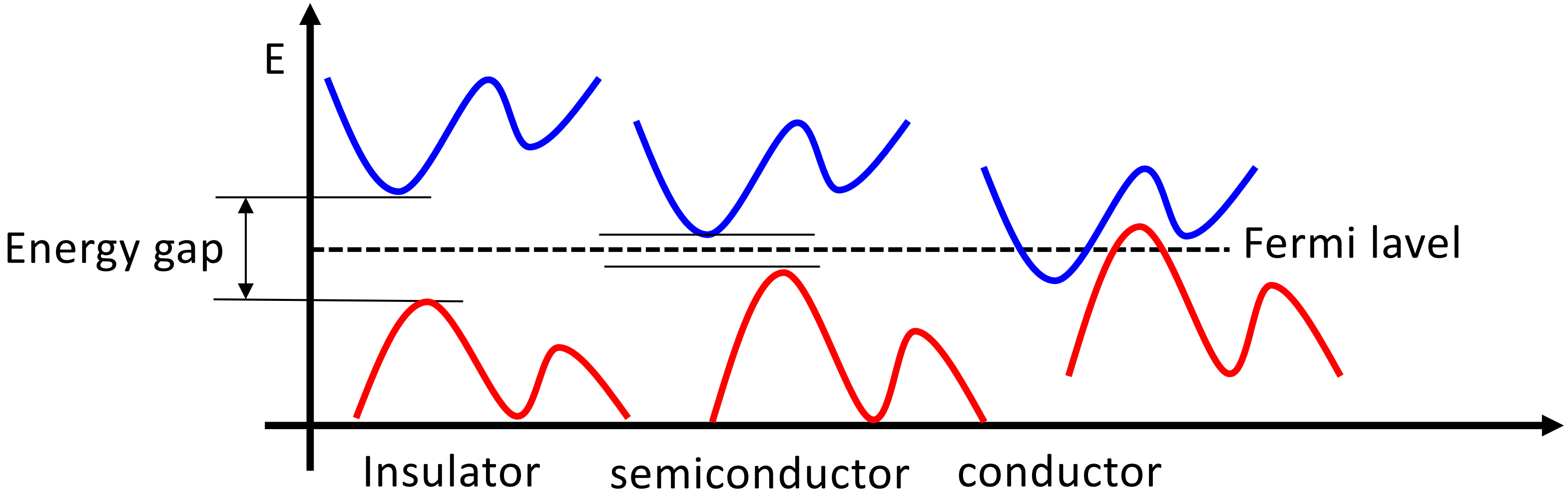
Band structure



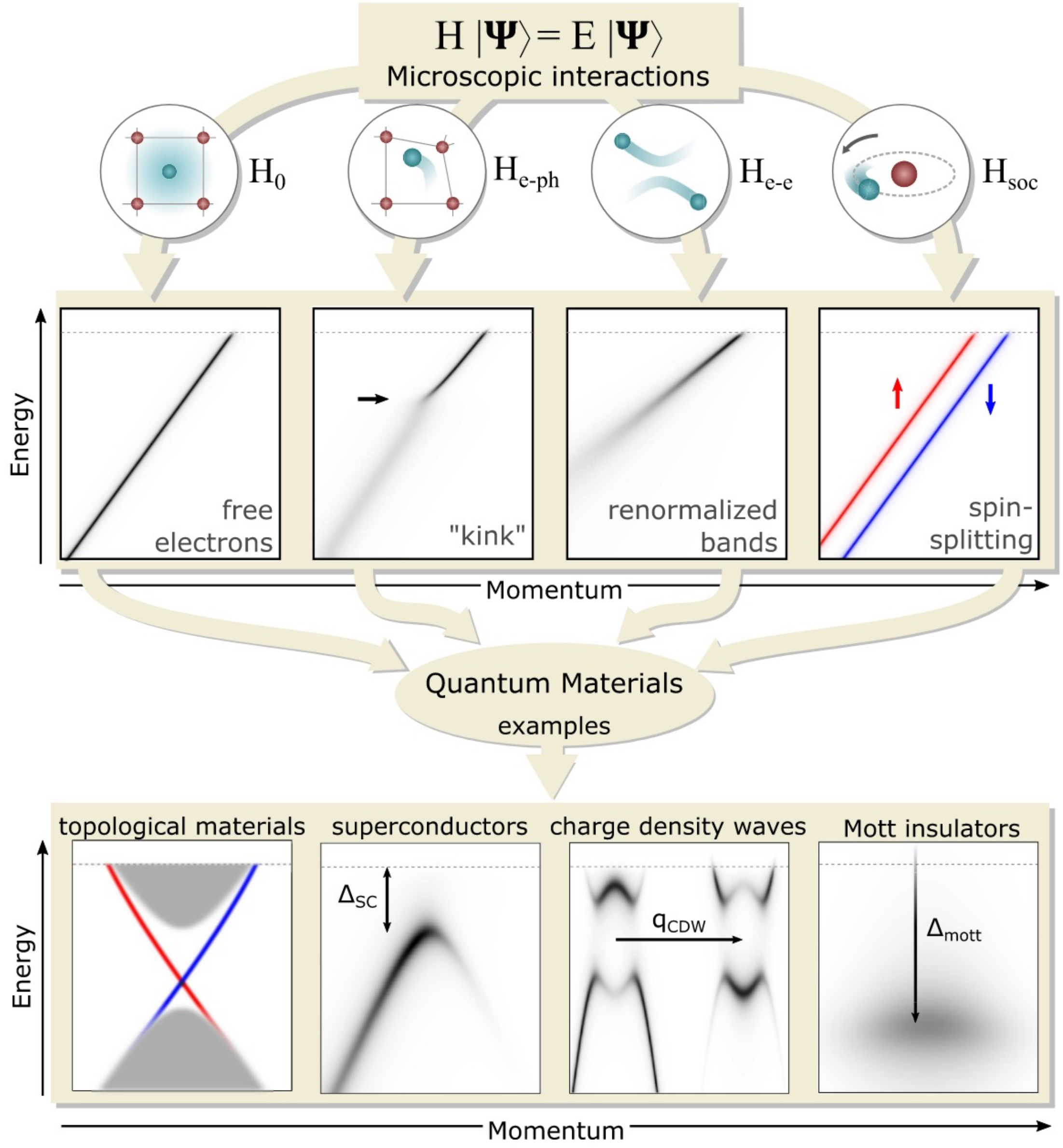


Band structure





Band structure of quantum materials



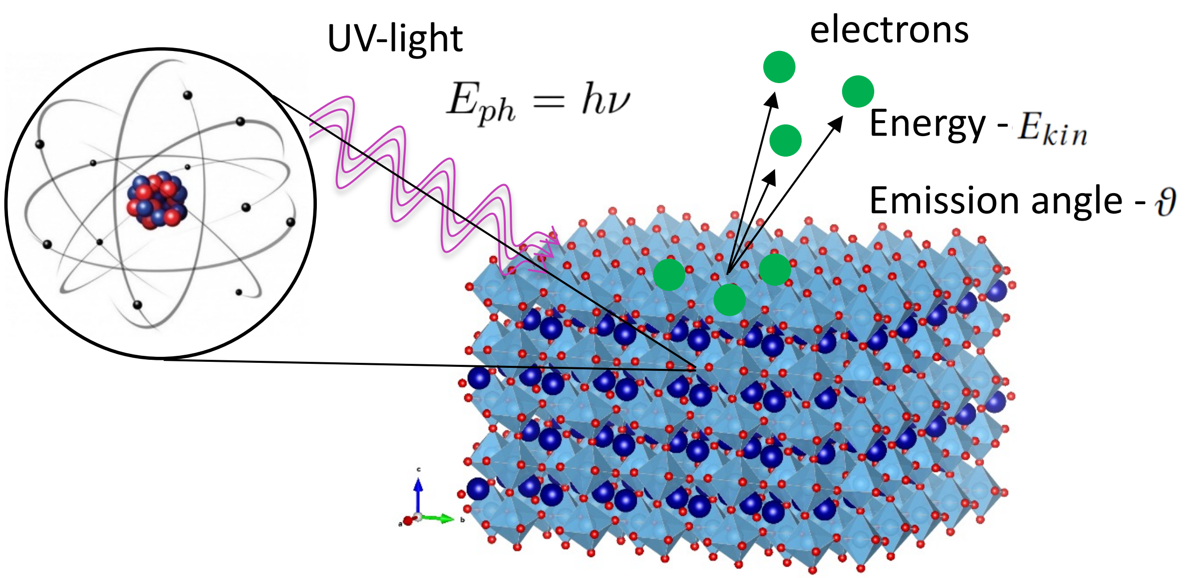
Jonathan A. Sobota, Yu He, and Zhi-Xun Shen, Rev. Mod. Phys. 93, 025006 (2021)

Angle-resolved photoelectron spectroscopy: the microscope for the electronic structure

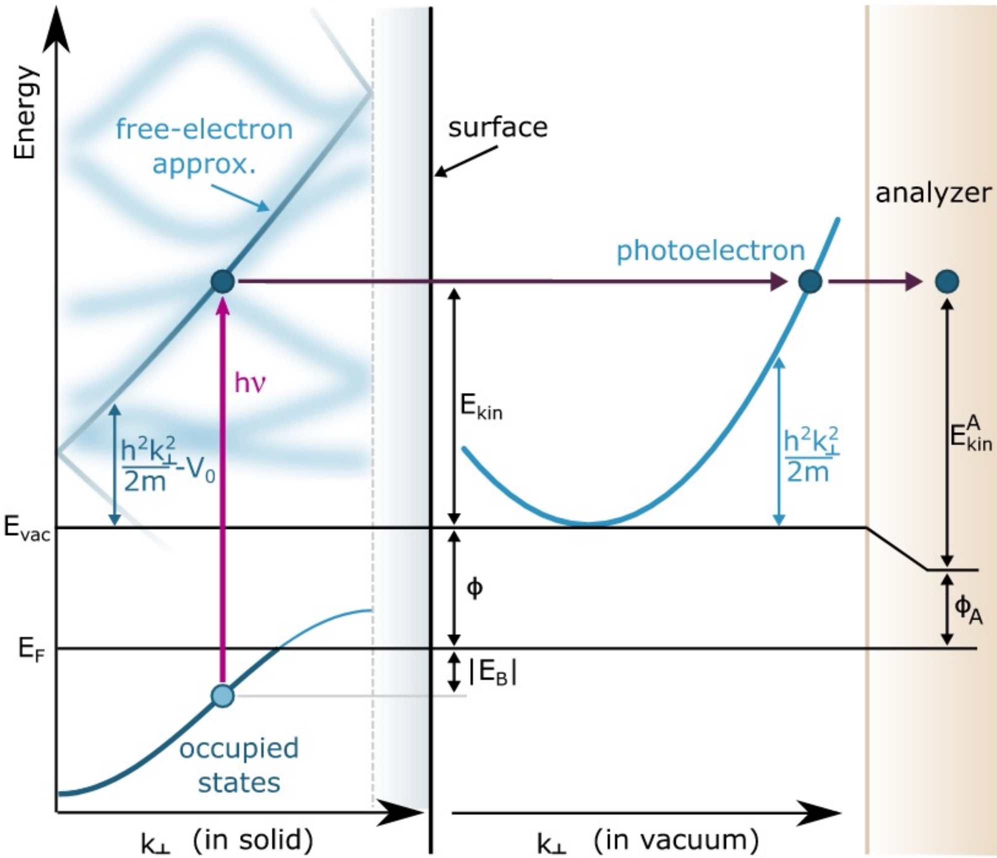
<u>**Two important papameters of electrons in a solid**</u>

Bound to the lattice
→ binding energy
$$E_{bin}$$

Movement with velocity $\vec{v}$
→ momentum
$$\vec{k} = m\vec{v}/\hbar$$



Angle-resolved photoelectron spectroscopy: the microscope for the electronic structure



Electron energy → binding energy in the crystal:

$$E_{bin} = h\nu - E_{kin} - \Phi_A$$

Emission angle → in-plane momentum:

$$k_{\parallel} = \sqrt{\frac{2m_e}{\hbar^2} E_{kin}} \sin\vartheta$$

Changing photon energy → out-of-plane momentum:

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

Emission angle - ϑ

Jonathan A. Sobota, Yu He, and Zhi-Xun Shen, Rev. Mod. Phys. 93, 025006 (2021)

A bit more

ARPES intensity:

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

$$I_0 \sim M_{f,i}^{k} = \langle \phi_f^k | \mathbf{A}\cdot\mathbf{p} | \phi_i^k \rangle.$$

proportional to the square of the dipole matrix element

$$A(\mathbf{k},\omega) = -\frac{1}{\pi}\frac{\Sigma''(\mathbf{k},\omega)}{\left[\omega - \varepsilon_0(\mathbf{k}) - \Sigma'(\mathbf{k},\omega)\right]^2 + \left[\Sigma''(\mathbf{k},\omega)\right]^2}$$

the single-particle spectral function: electronic band structures and lifetimes

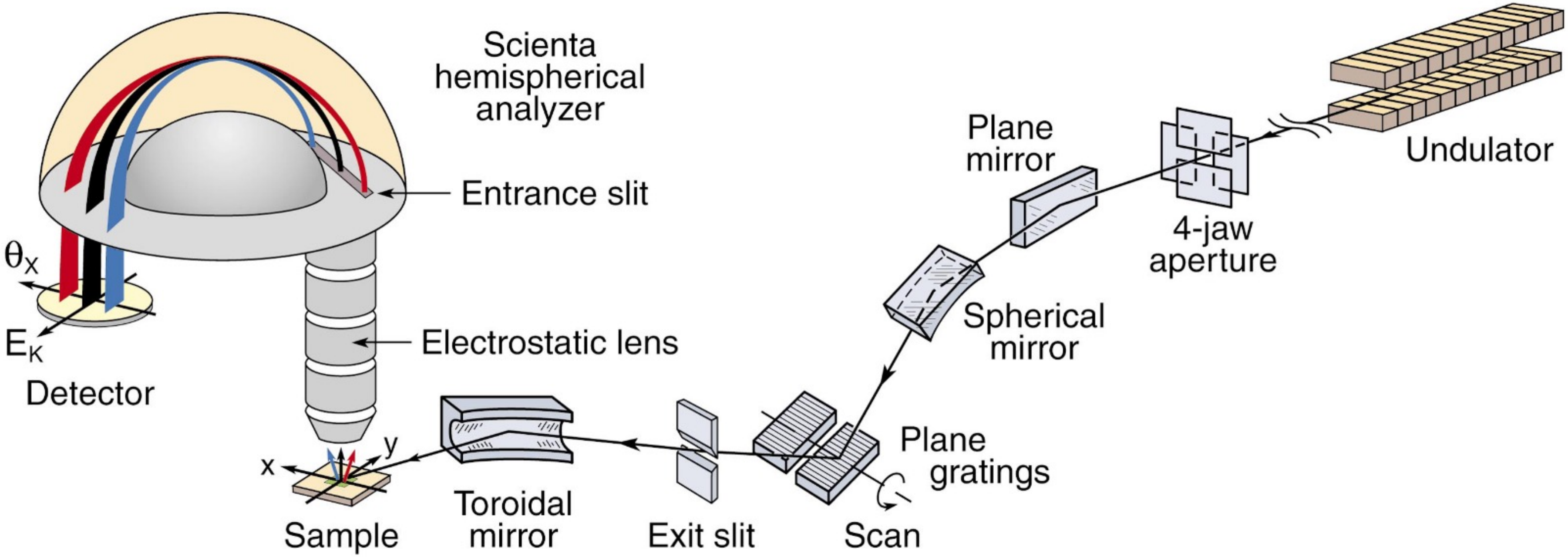
$\varepsilon_0(\mathbf{k})$: the non-interacting (bare) energy-band dispersion

$$f(\mathbf{k},\omega) = 1/\left(e^{\omega/k_B T} + 1\right),$$

Fermi–Dirac function

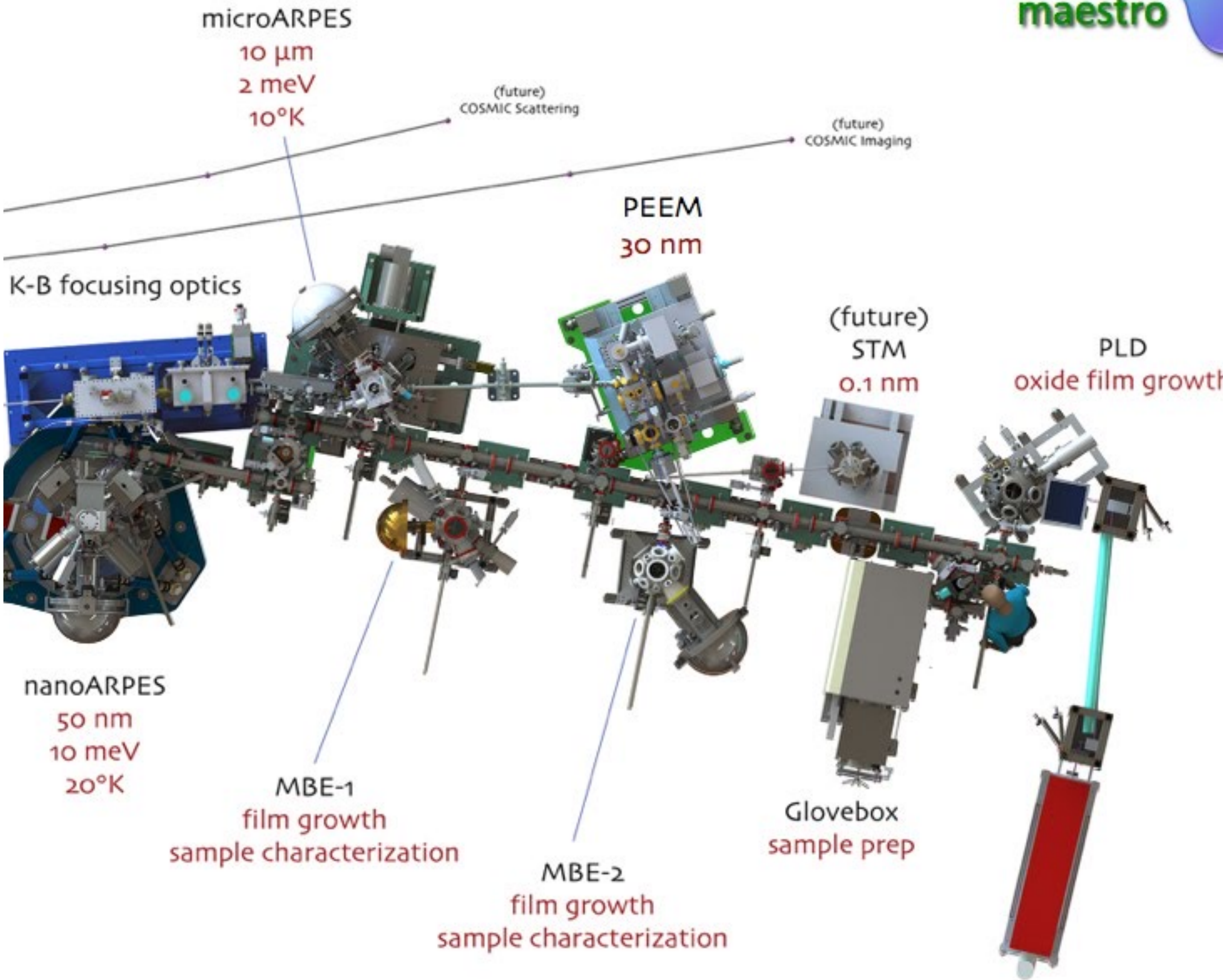
Hideaki Iwasawa, Electron. Struct. 2) 043001 (2020)

Angle-resolved photoelectron spectroscopy: the microscope for the electronic structure.

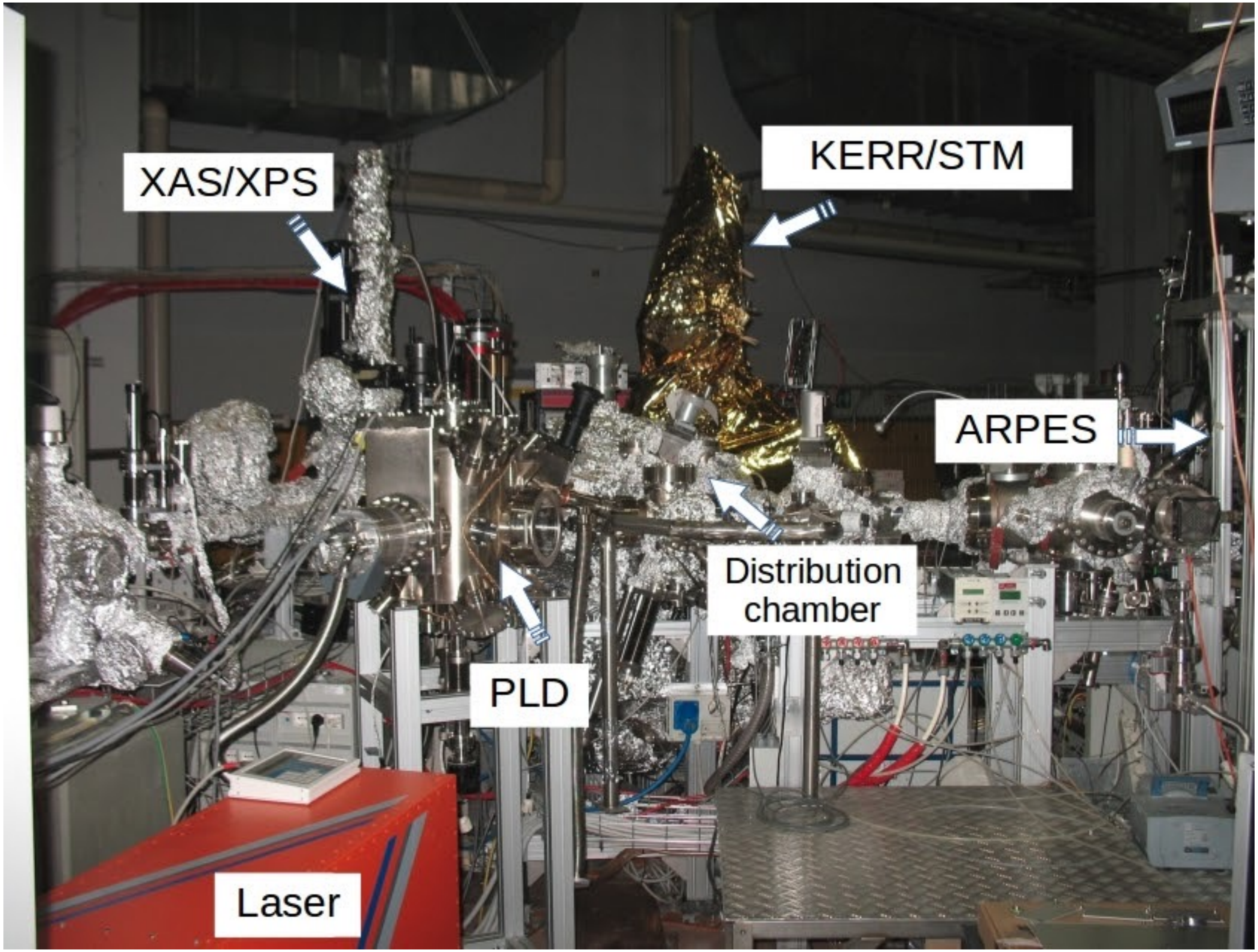


A. Damascelli,, Z. Hussain, and Z.-X. Shen, Rev. Mod. Phys. 75, .473, 2003

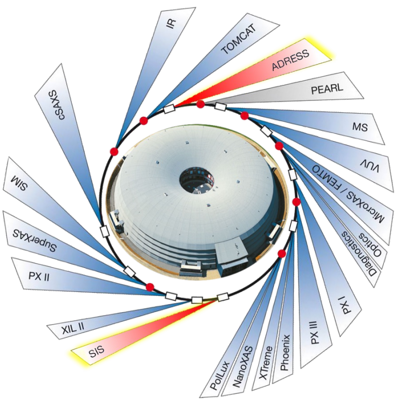
PLD + ARPES at MESTRO bemline, Advanced Ligh Sourece (USA)



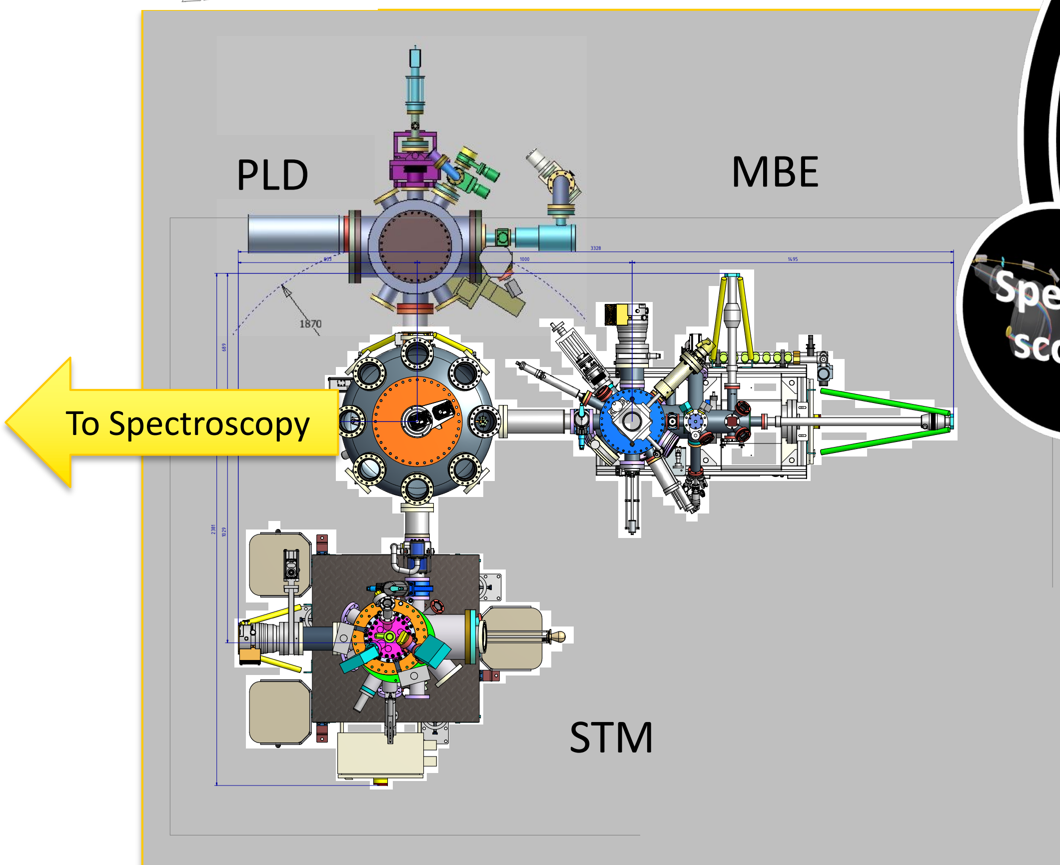
PLD + ARPES at APE bemline, Elettra (Italy)



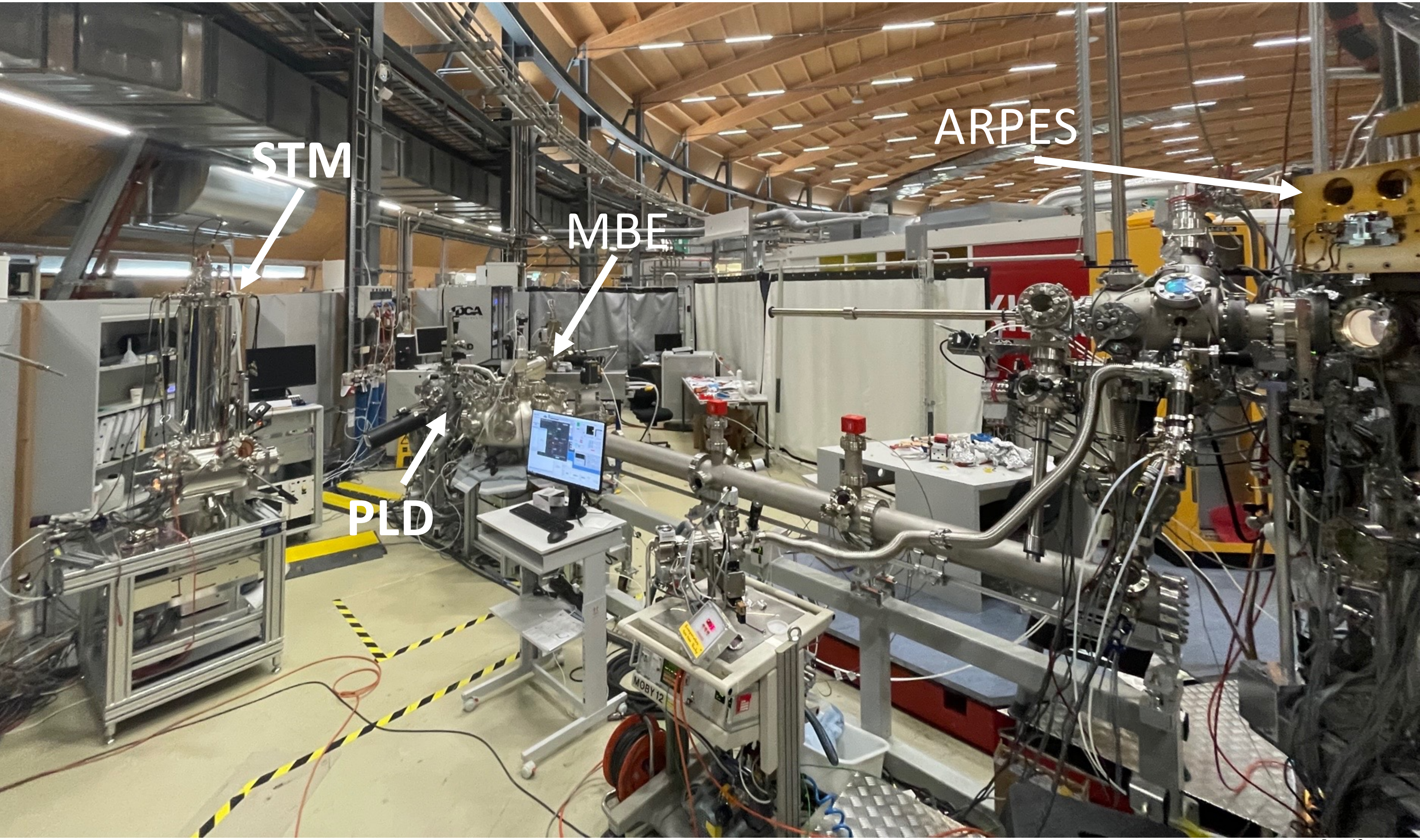
The modular system at the SIS beamline: PLD+STM+MBE



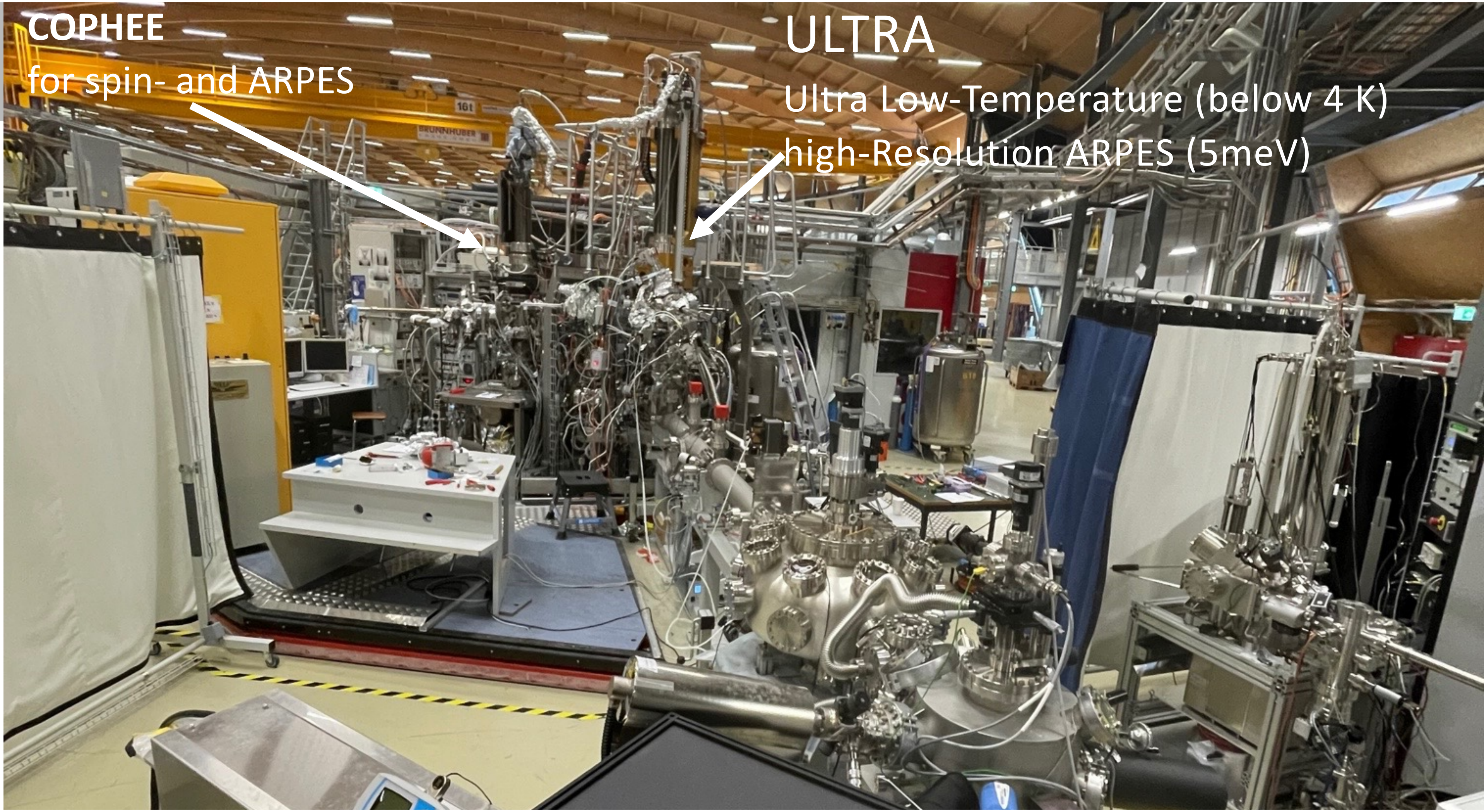
<u>Designing novel functional materials</u> with novel electrical, magnetic, thermal, chemical or electrochemical properties.



The modular system at the SIS beamline: ARPES+ PLD+STM+MBE



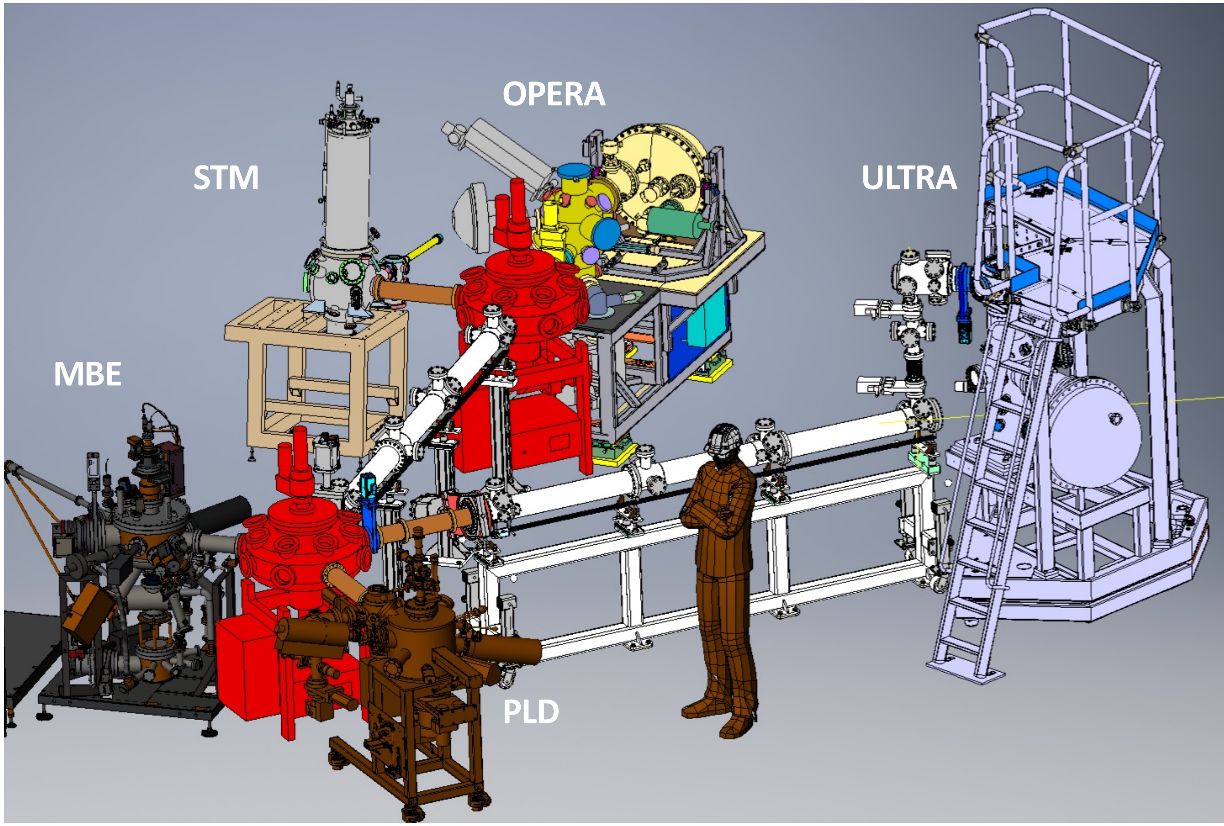
Two ARPES stations at SIS beamline:



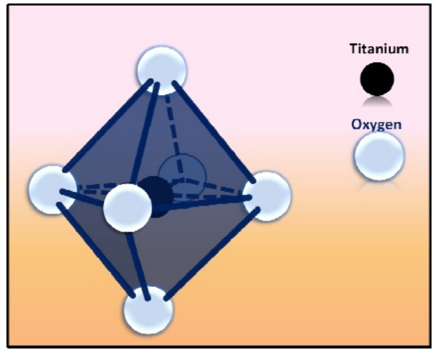
The FUTURE beamline

QUEST (QUantum matter Electron Spectroscopy Tool)

- **2 end stations** – each utilizing **both** sources
  - **ULTRA** end station: low temperature, high resolution + spin detection.
  - **OPERA** end station: complex systems, operando, micro-focus.
- **Advanced sample preparation.** methods: PLD, MBE.
- **Complementary instrumentation** STS, STM, AFM.



Control of the electronic properties of $ATiO_3$



Distortion of the TiO_6 octahedron

Energy splitting and, the ordering of the d_{xy} & d_{xz} & d_{yz} bands (from one to multiple bands conductivity)

Doping (trough A or O vacansies)

Filling of the bands (Career density, electron-phonon coupling..)

Octahrdral rotations, Binding angles

Hopping probability (effective mass, band width, transport)

PAUL SCHERRER INSTITUT PSI

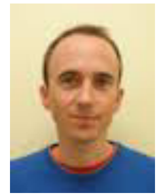
Collaborators

SIS beamline @ SLS:


Ming Shi


Nick.Plumb


Hugo Dil (EPFL)


F.Baumberger (PSI&U. Geneva)


E. Bonini Guedes


S. Muff


M. Naamneh


A. Chikina


Hang Li


J. Jandke


M. Caputo

ADRESS beamline @ SLS


Thorsten Schmitt


V.Strocov

PSI


M. Maedarde


Z. Salman


L. Patthey


J. Mesot

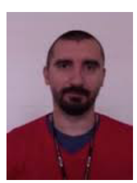
International

CNR-SPIN, Napoli, IT

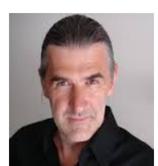

M.Salluzzo


F. Miletto

University of BG, SERBIA


Zoran Ristic

Oak Ridge Nat.Lab. USA


Gyula Eres

NIMBO Inst. CAS, China


Z. Wang

Universität München


Jan Minar

DTU

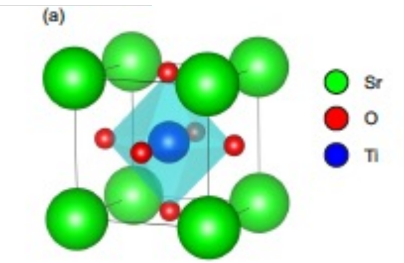

NIni Pryds

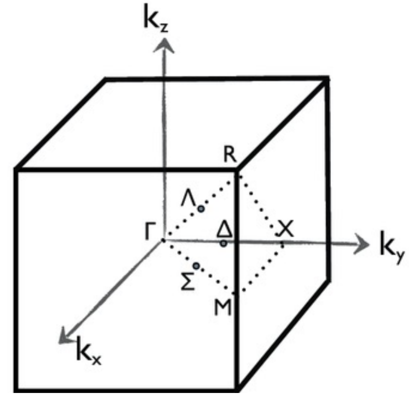
UFMG


Walber Hugo de Brito

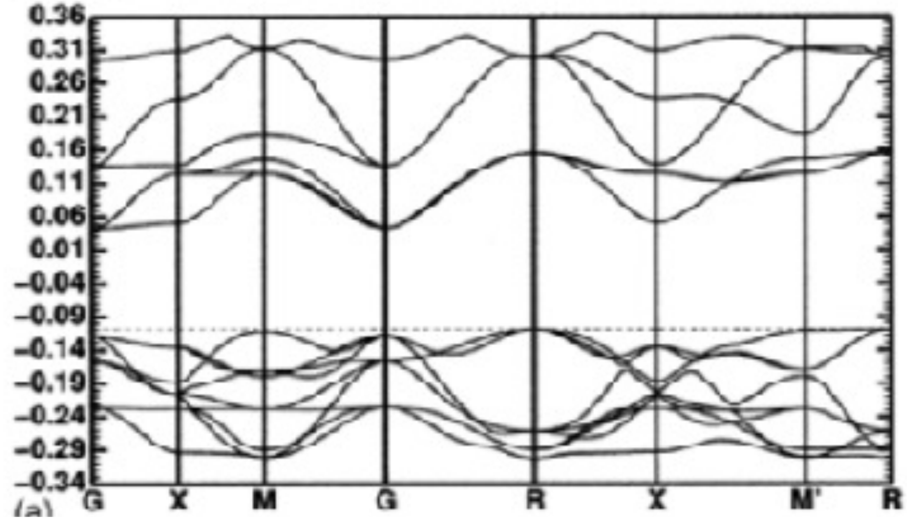
Band structure of $SrTiO_3$

- **cubic above105 K,**
- **slightly tetragonal below**

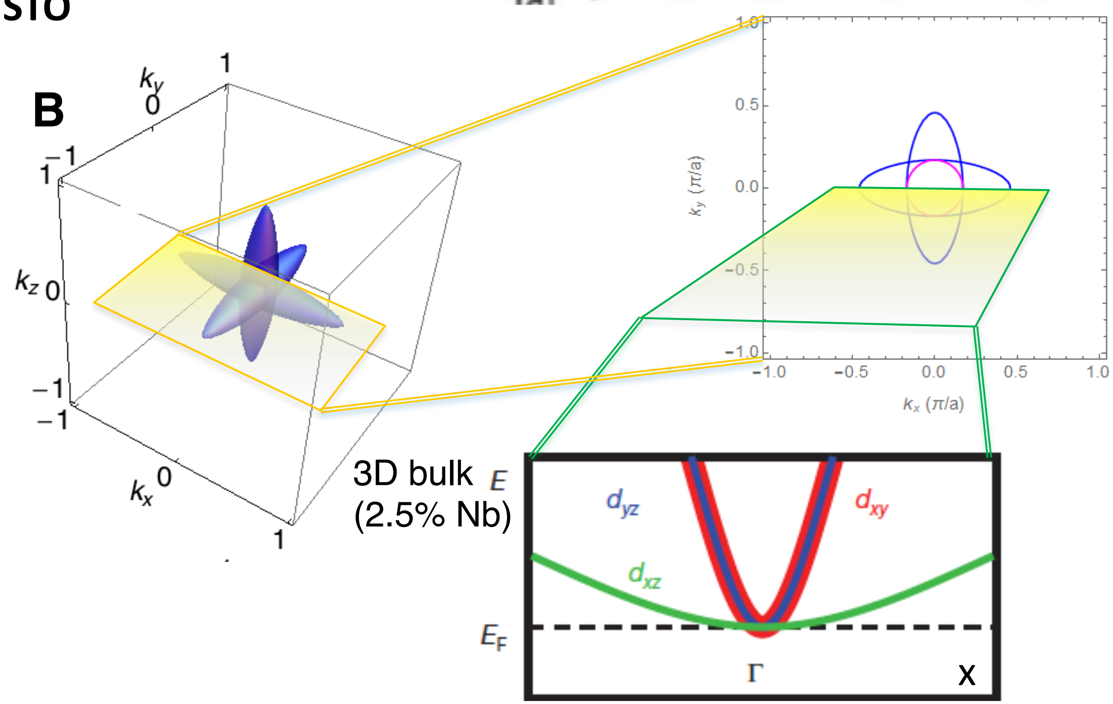




E Heifets, et al.,PRB (2001), E Heifets, et al., Surf. Sc. (2002).



Fermi surface of doped STO

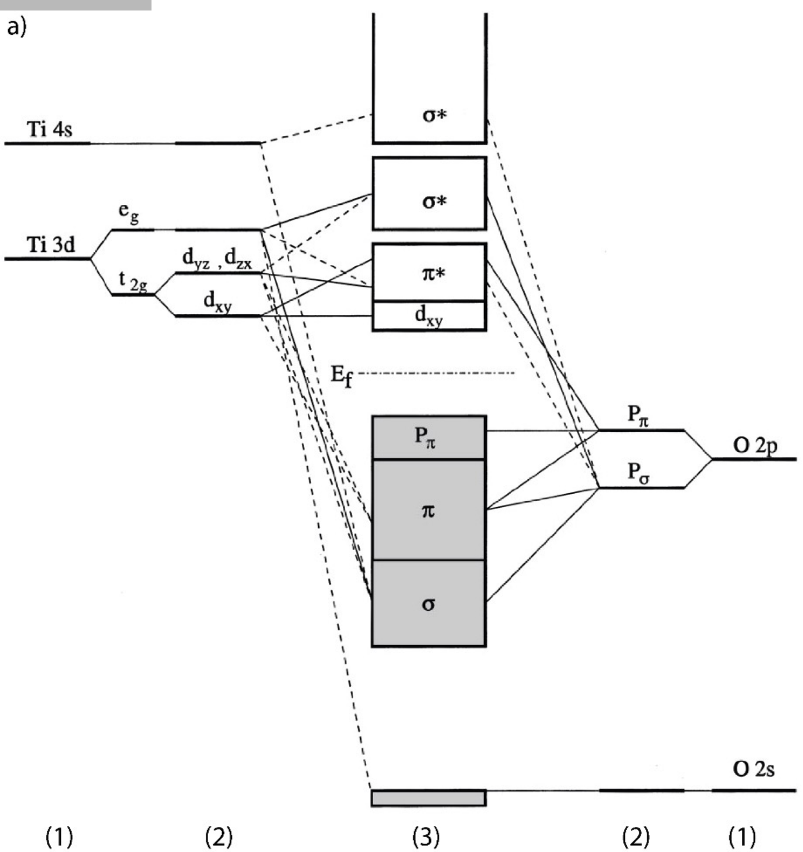


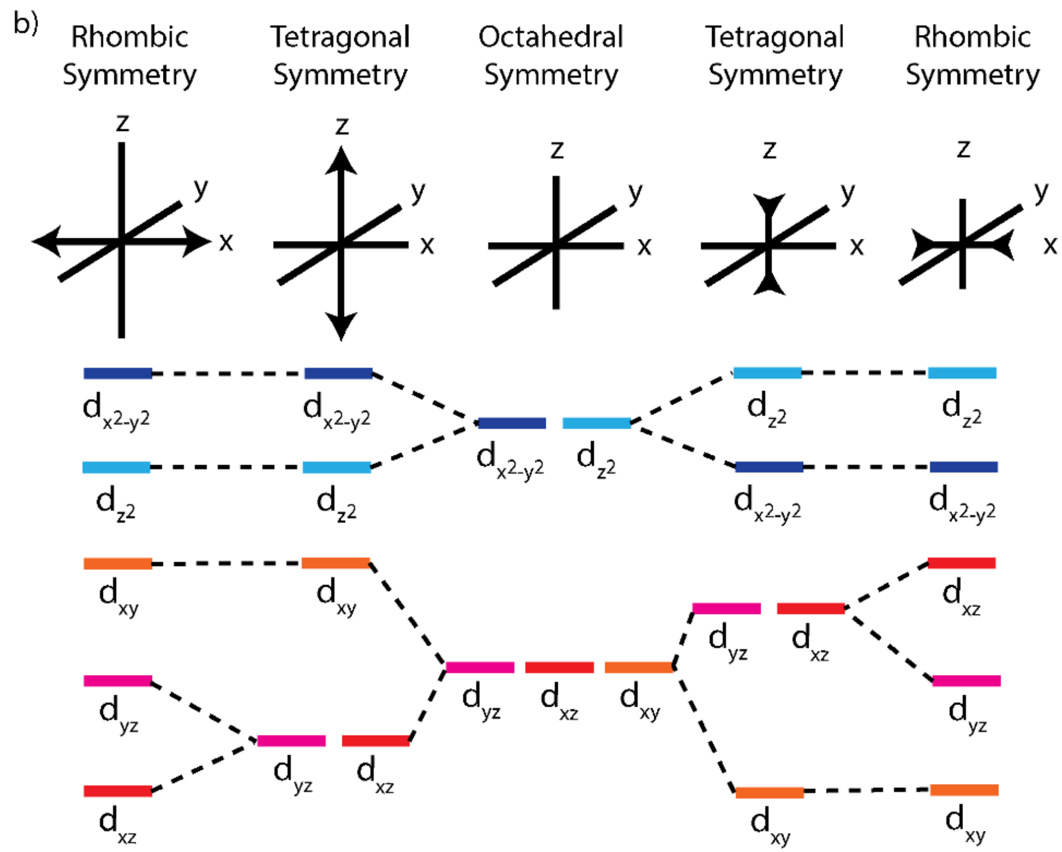
N. C. Plumb & M. Radovic, Review J. Phys.: Condensed Matter (2017).

Orbital ordering of titanates

Tuning Orbital energies:

Splitting of the Ti 3*d* in t_{2g} and e_g determined by octahedra crystal field



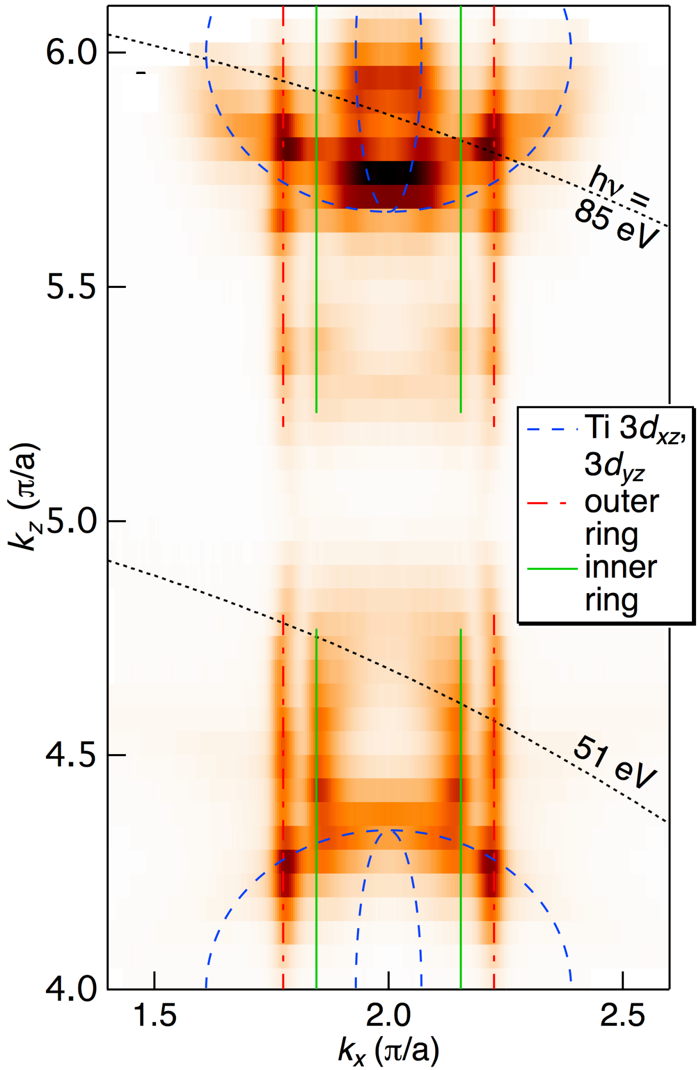


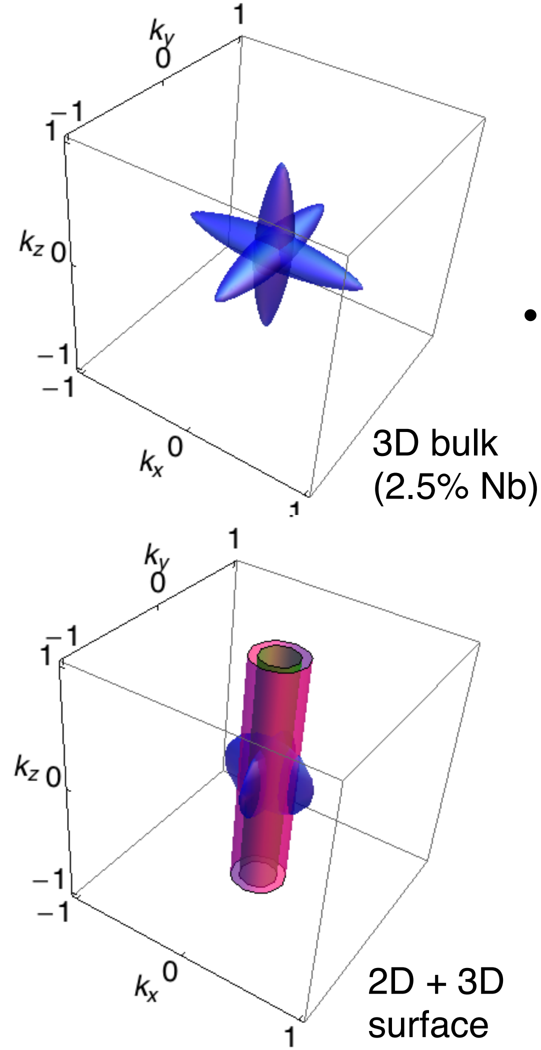
R. Asahi et al. PRB, 61, 7459 (2000),

S. Muff, Phd Thesis, EPFL, Lausanne (2017)

Study of Metallic surface on STO: Surface-driven state with 3D dispersion

N.C. Plumb et al. PRL, 2014.



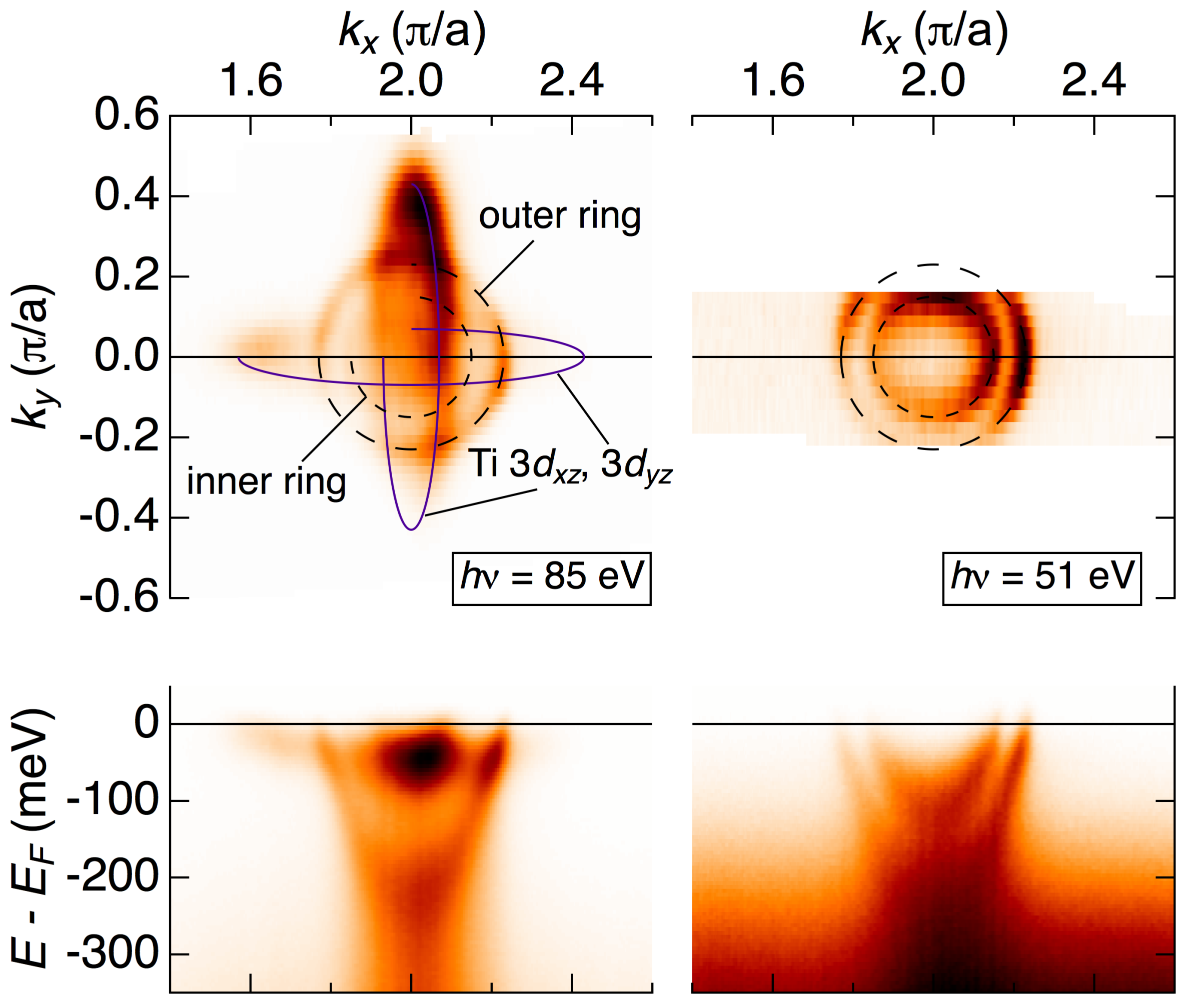


- All FS components differ drastically from bulk: From 3 prolate spheroids to:
  - d_{xy} → 2D cylinder(s)
  - d_{xz}, d_{yz} → 3D oblate ellipsoids

A. Santander-Syro et al., Nature 469 189–193, 2011; W. Meevasana et al., Nat. Mater. 10 114–118 , 2011.

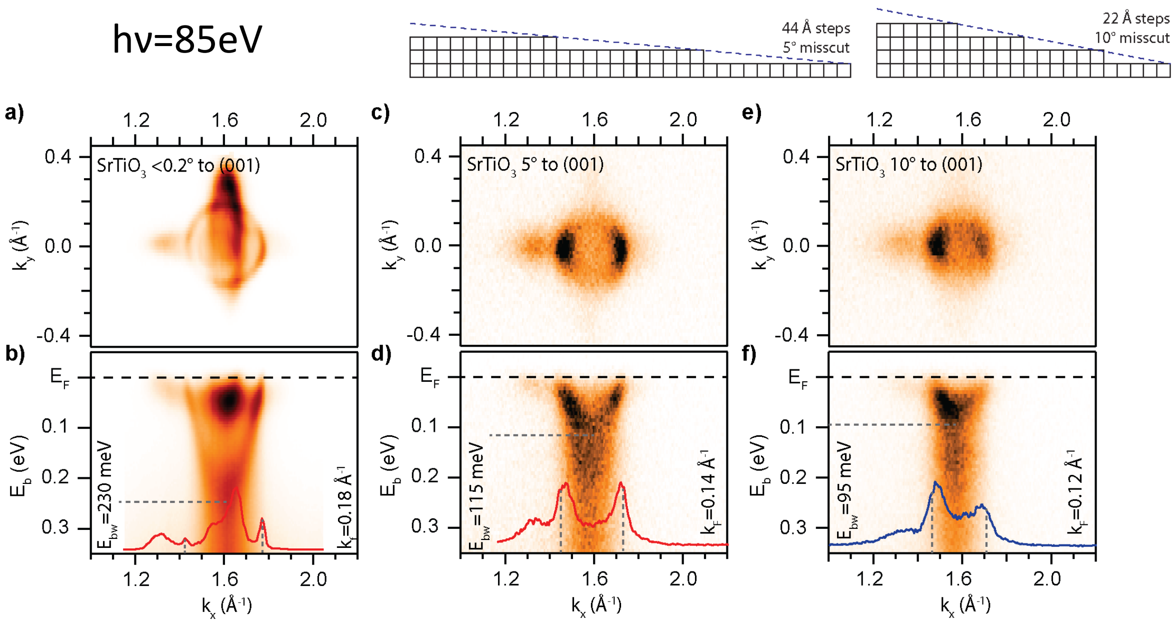
Study of Metallic surface on STO:
Surface-driven state with 3D dispersion

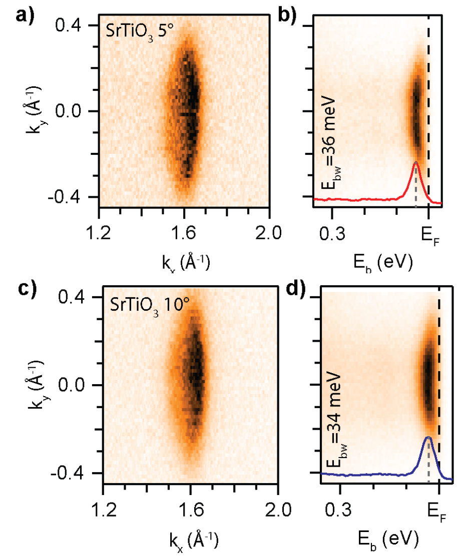
N.C. Plumb et al. PRL, 2014.



Terrace width controls the band splitting!

hν=85eV



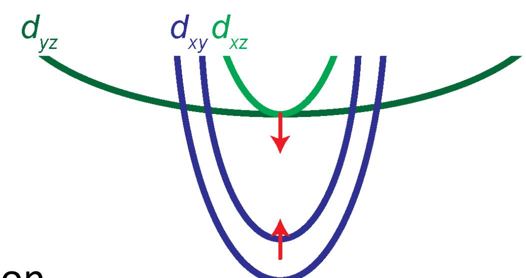


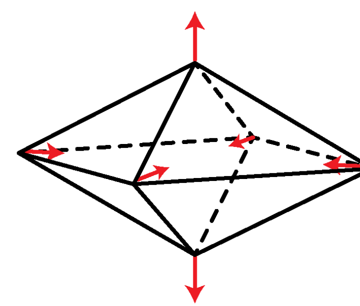
Terrace size directly controls the two dimensional states:

Flat $SrTiO_3$ $m^* \approx 0.65\ m_e$ $E_{bandbot.} \approx 235$ meV

5° misscut $m^* \approx 0.7\ m_e$ $E_{bandbot.} \approx 110$ meV

10° misscut $m^* \approx 0.7\ m_e$ $E_{bandbot.} \approx 90$ meV





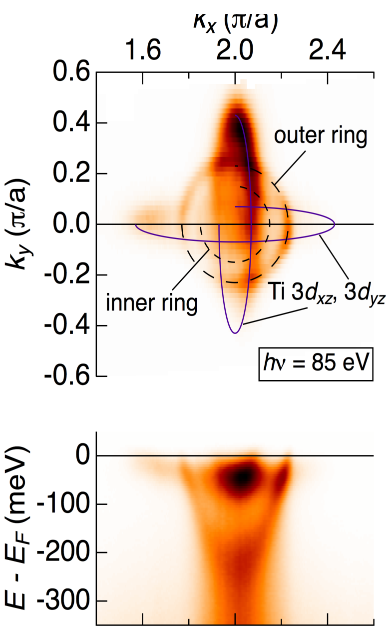
→ altered octahedral distortion due to surface relaxation

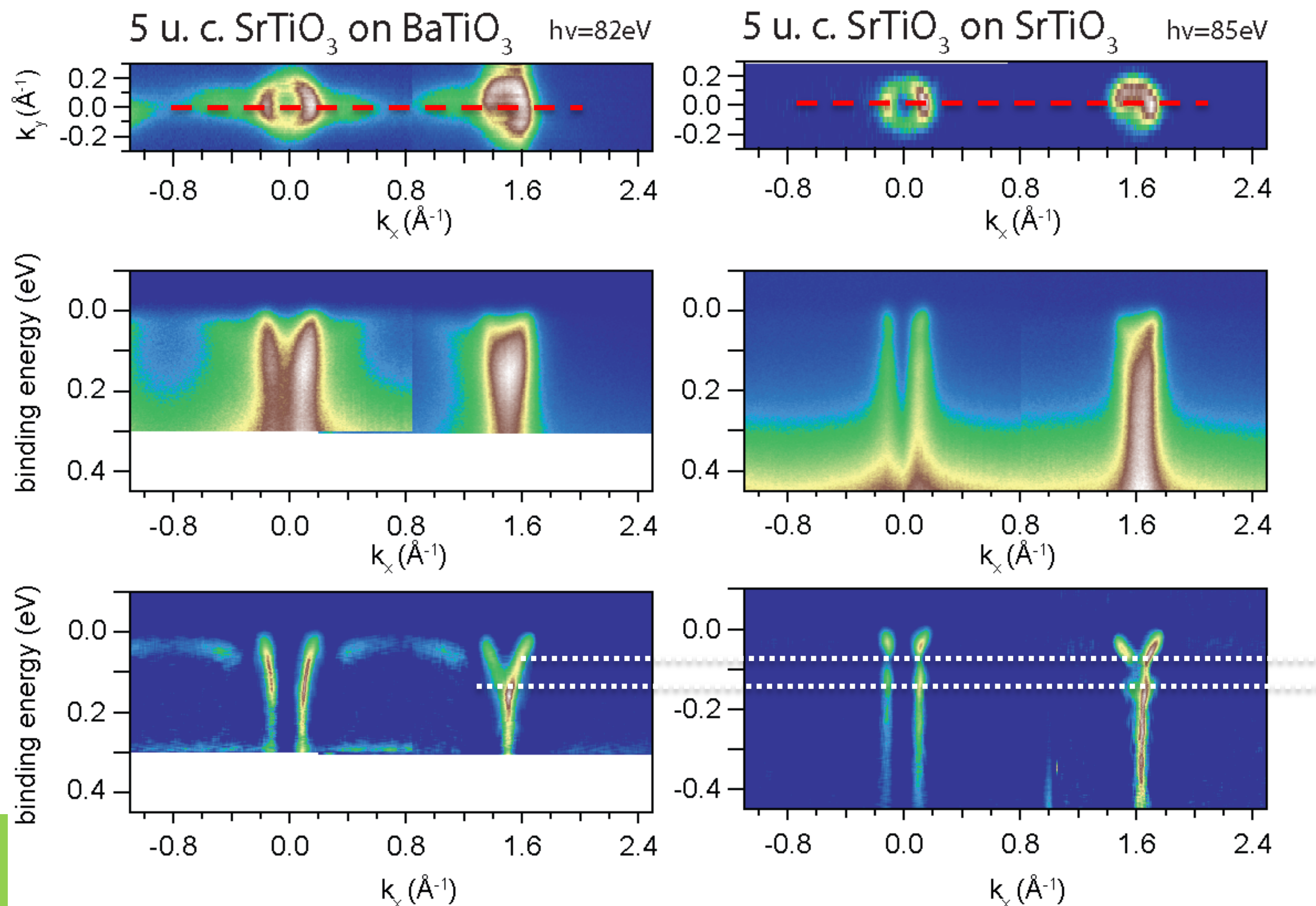
→ altered band filling due to changed electron affinity

S. Muff, Phd Thesis, EPFL, Lausanne (2017); E. Bonini, Advanced Science 8 (19), 2101516, (2021).

An under layer controls the doping!

$SrTiO_3$ Wafer





$SrTiO_3$
- d_{xy} and degenereted d_{xz}, d_{yz}
- $E_{bandbottom} \approx 240$ meV
- Band splitong ≈ 150 meV

N.C. Plumb et al. PRL, 2014.

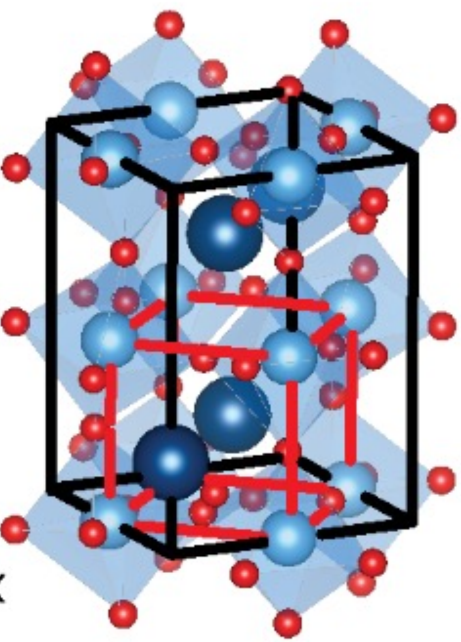
5 u.c. $SrTiO_3$ on $BaTiO_3$
- 3d/heavy states formed
- $E_{bandbottom} \approx 150$ meV

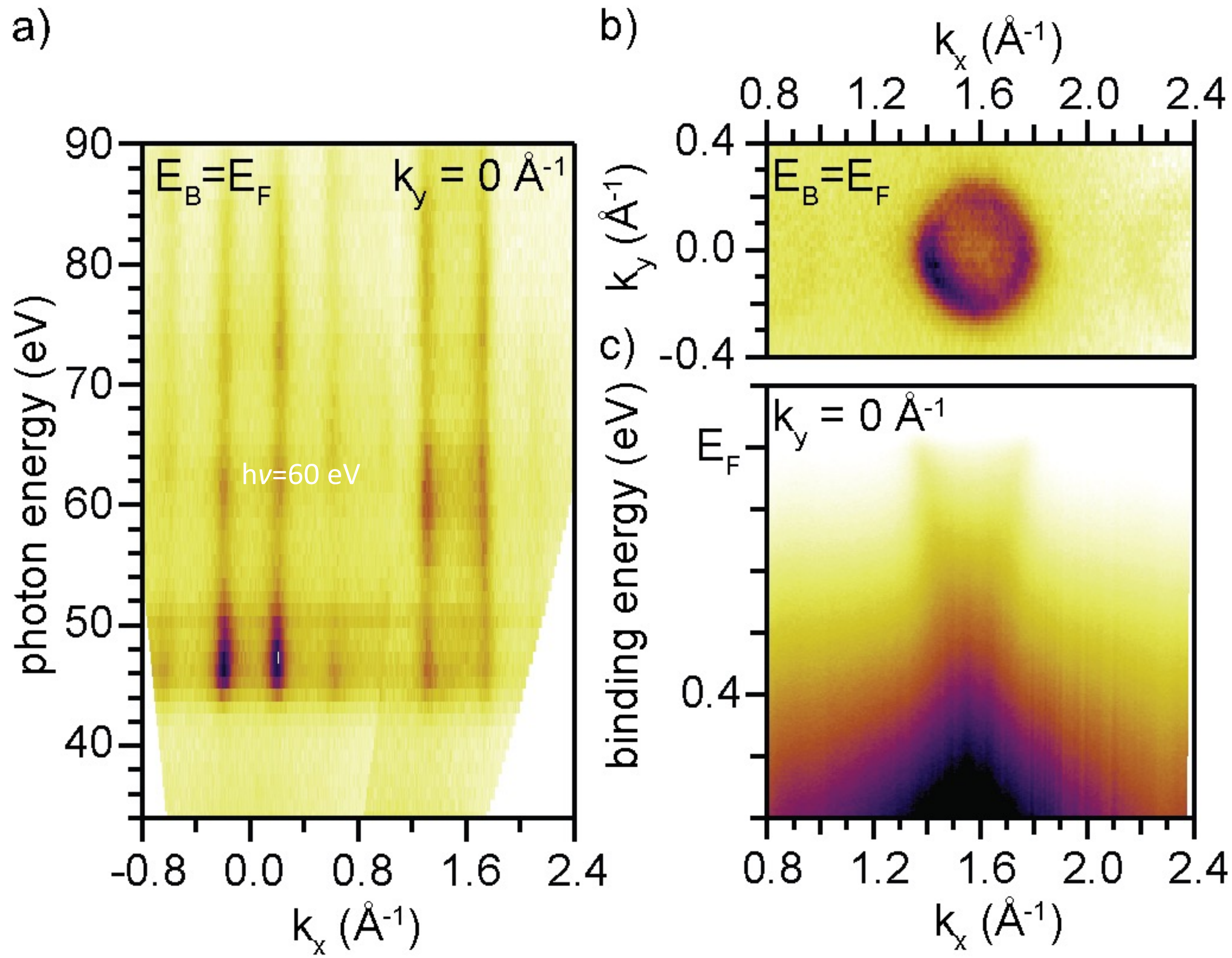
5 u.c. $SrTiO_3$ on Nb:$SrTiO_3$
- No 3d/heavy bands, only d_{xy}
- $E_{bandbottom} \approx 60$ meV

S. Muff, Phd Thesis, EPFL, Lausanne (2017); E. Bonini, Physical Review Research 2 (3) (2020).

Distortion and a rotation of the TiO6 octahedron control the band spliting and filing

20 u.c. $CaTiO_3$ on Nb:$SrTiO_3$





Purely 2D electronic state

Only d_{xy} character (no d_{xz}, d_{yz})

E_{bb}≈400 meV, m*=0.4 m_e

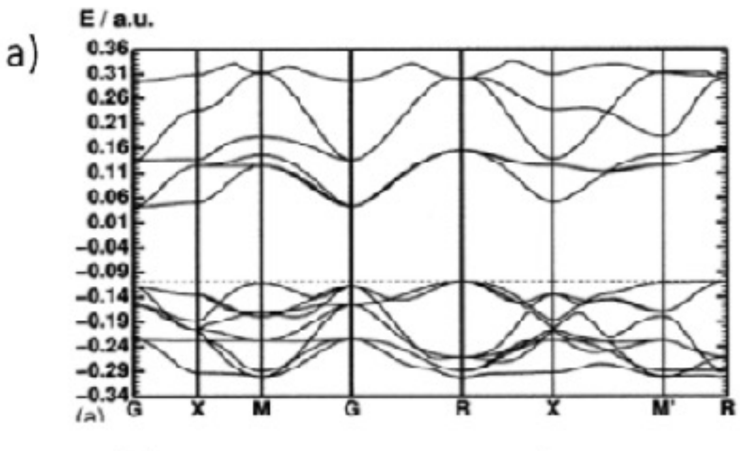
($SrTiO_3$: E_{bb}≈230 meV, m=0.7 m_e)*

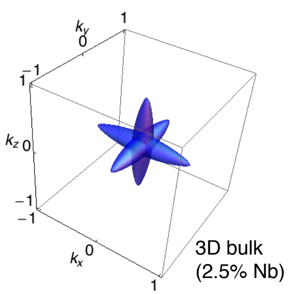
S. Muff, Applied Surface Science, 2018

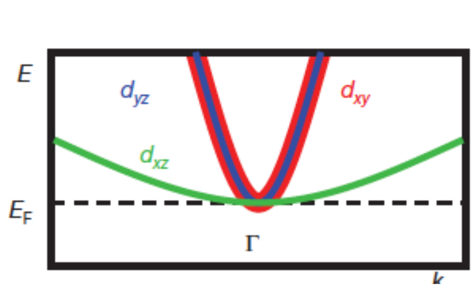
From cubic to tetragonal TiO_2 octaedron…

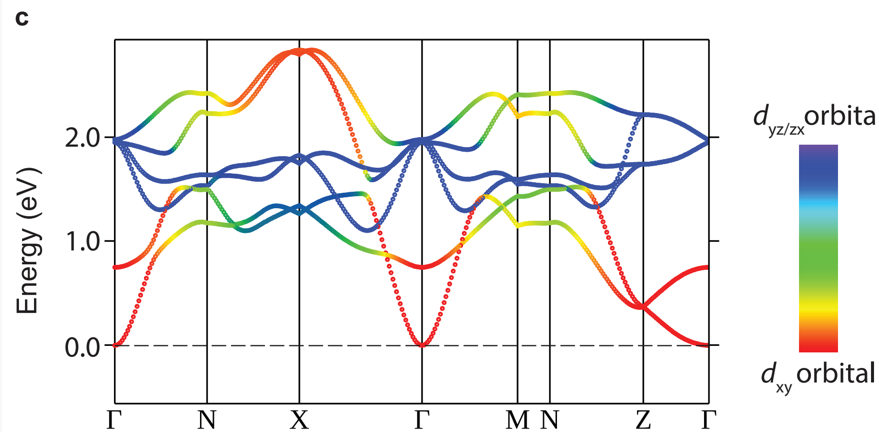
Cubic (e.g. STO)

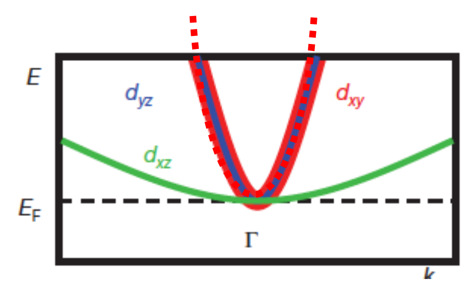
Tetragonal (e.g. anatase)









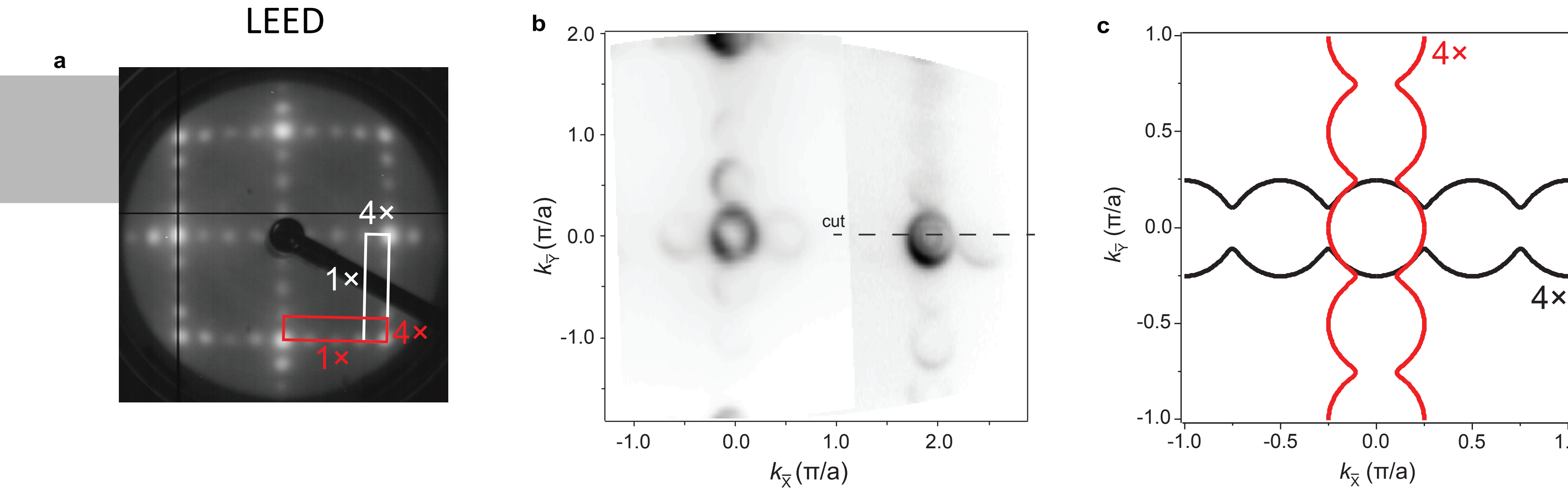


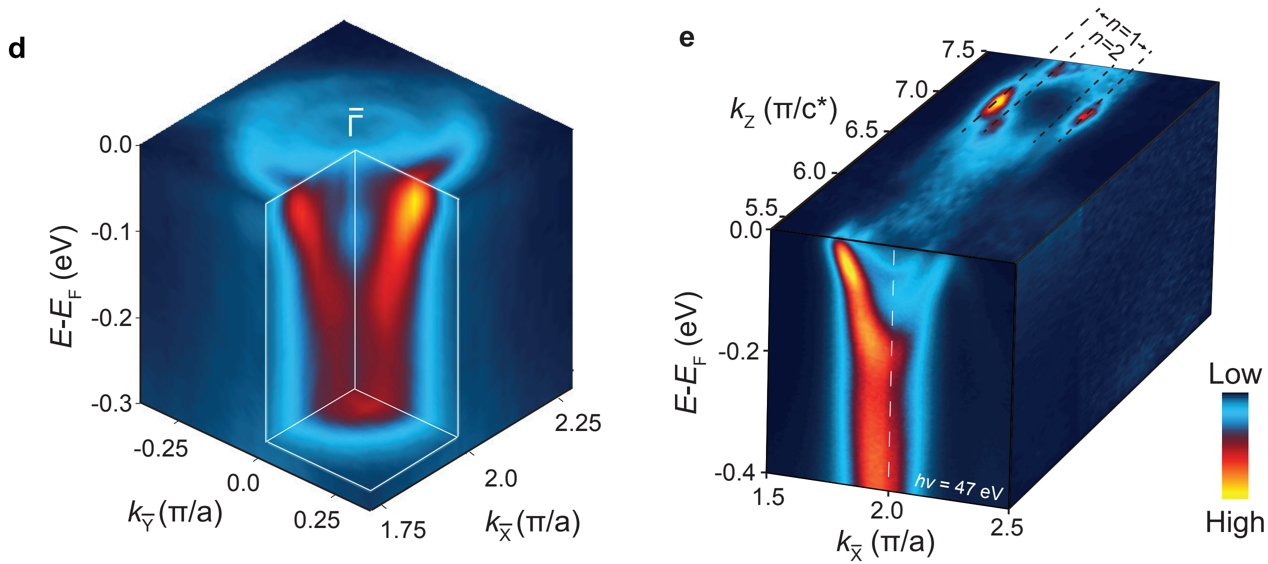
E Heifets, et al.,PRB (2001),
E Heifets, et al. Surf. Sc. (2002).

Z. Wang, et al., Nano Letters, (2017).

ARPES on TiO_2 anatase film (20 u.c.)

ARPES: 85 eV of the photon energy.

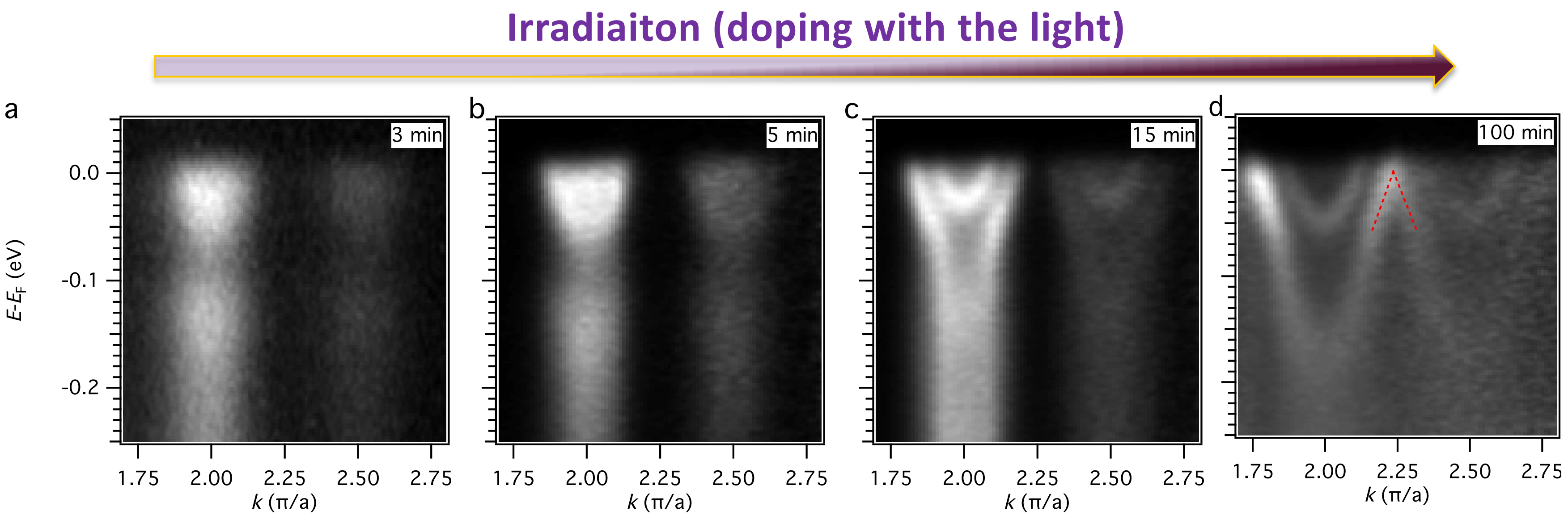


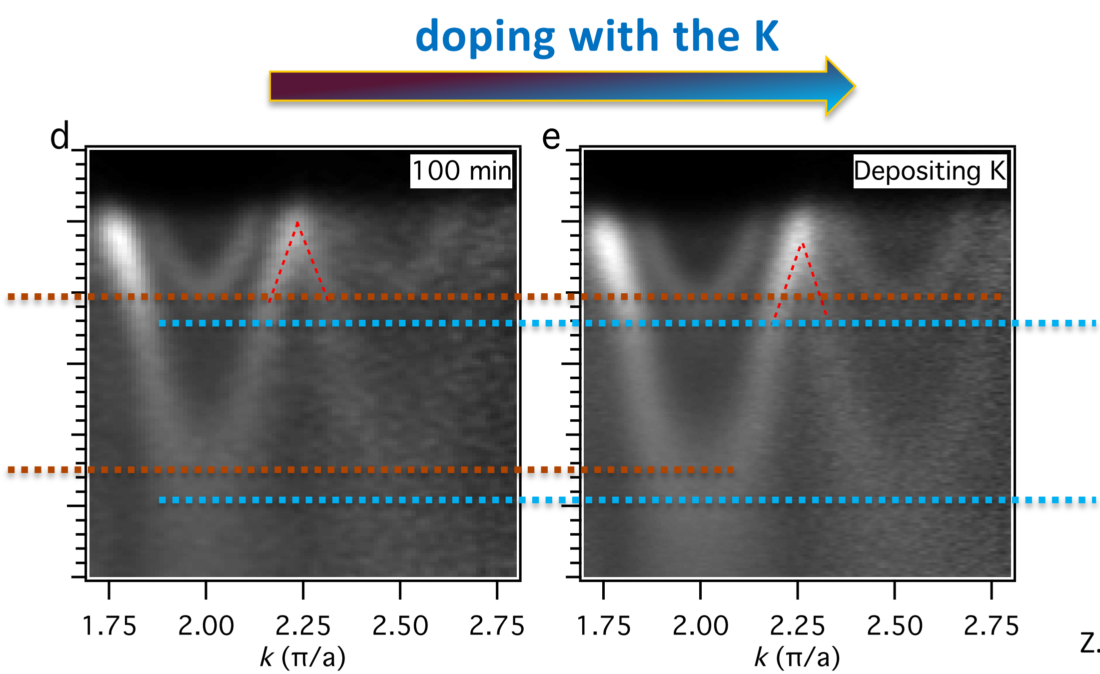


Z. Wang et al., Nano Letters, 2017

S. Moser et al., PRL 2013

Control over the doping of anatase - TiO_2 film



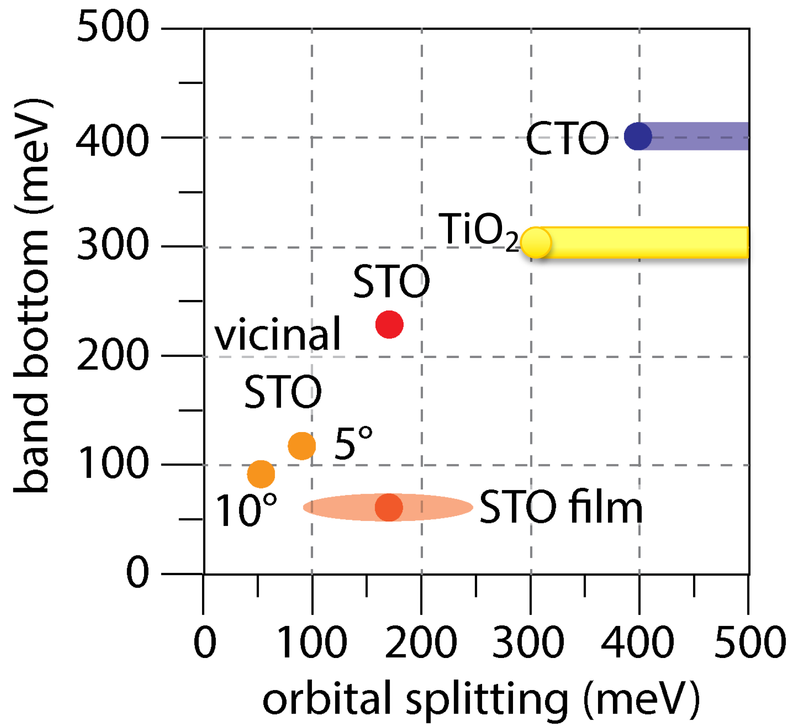


Z. Wang et al., Nano Letters, 2017

Take Home massage :

Growth +ARPES is the powerful method for Engineering the electronic structure!

$SrTiO_3$ with different vicinality:
→ Surface energy and distortion of octrahdrons
✓ reduced orbital splitting;
✓ reduced band filling;
✓ both also affected by temperature.



$CaTiO_3$ films:
→ Orthorhombic distortion of octrahdrons
✓ increased orbital splitting
✓ increased band filling

$SrTiO_3$ films:
→ **defects**
✓ reduced band filling
✓ altered band bending
Single spin polarized band?

TiO_2 films:
tetragonal distortion of octrahdrons
✓ large band filling
→ altered band bending
Spin polarized band?

- Phys. Rev. B. 86, 155425 (2012).
- Phys. Rev. Lett. 113, 086801 (2014).
- Nature Mat. 13, 1085–1090 (2014).
- Nature Mat. 15, 835–839 (2016).
- Nano Letters, 17 (4), pp 2561–2567 (2017).
- Applied Surface Science, 432A, (2018).
- Phys. Rev. B 98 (2018).
- Physical Review Research 2 (3) (2020).
- Advanced Science 8 (19), 2101516, (2021).