Angle-resolved photoemission spectroscopy (ARPES)

Experimental study of the electronic structure of strongly-correlated electron systems

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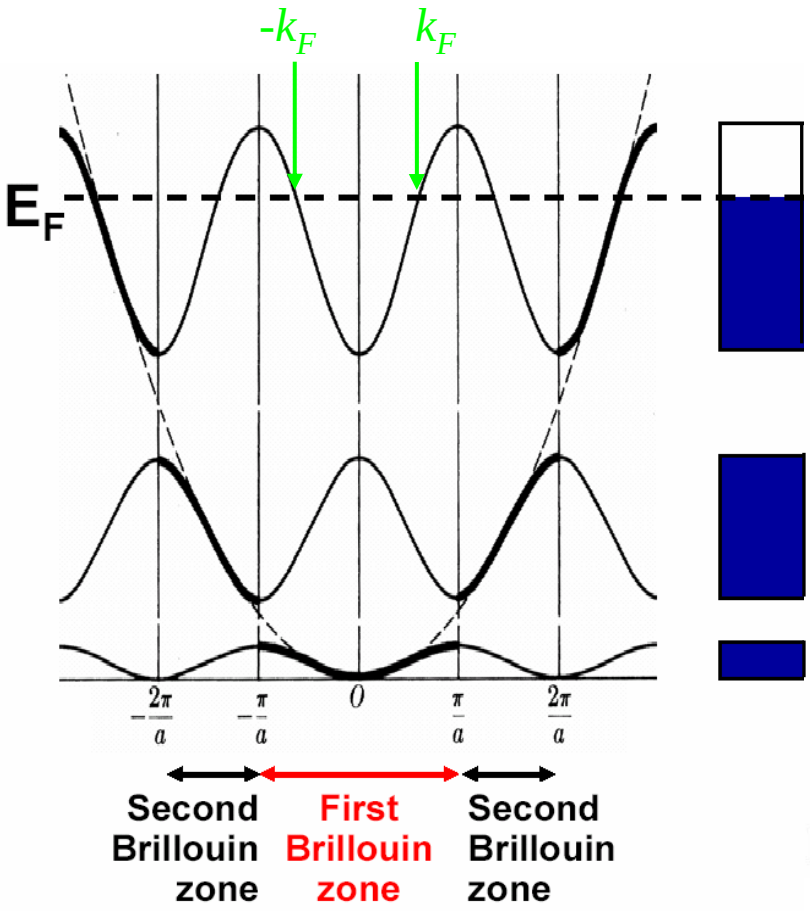
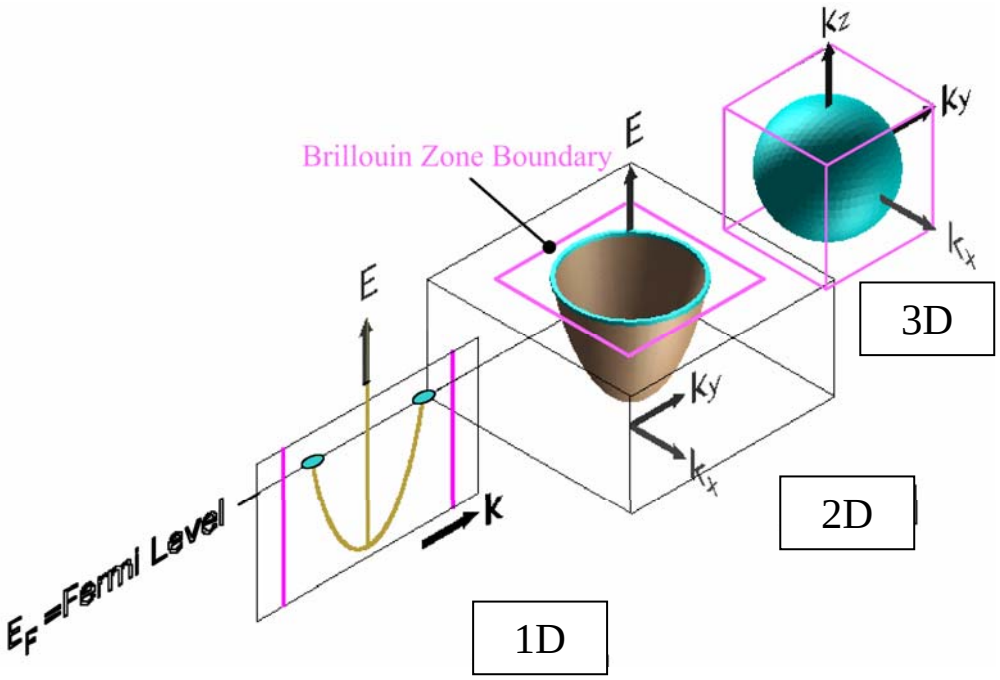
Condensed (crystalline) matter in a nutshell

Allowed electronic states
Repeated-zone scheme



Many **properties of solids** are determined by electrons within a **narrow energy slice (~k_BT) around E_F** (dc conductivity, magnetism, superconductivity…)

→ **Fermi Surface**

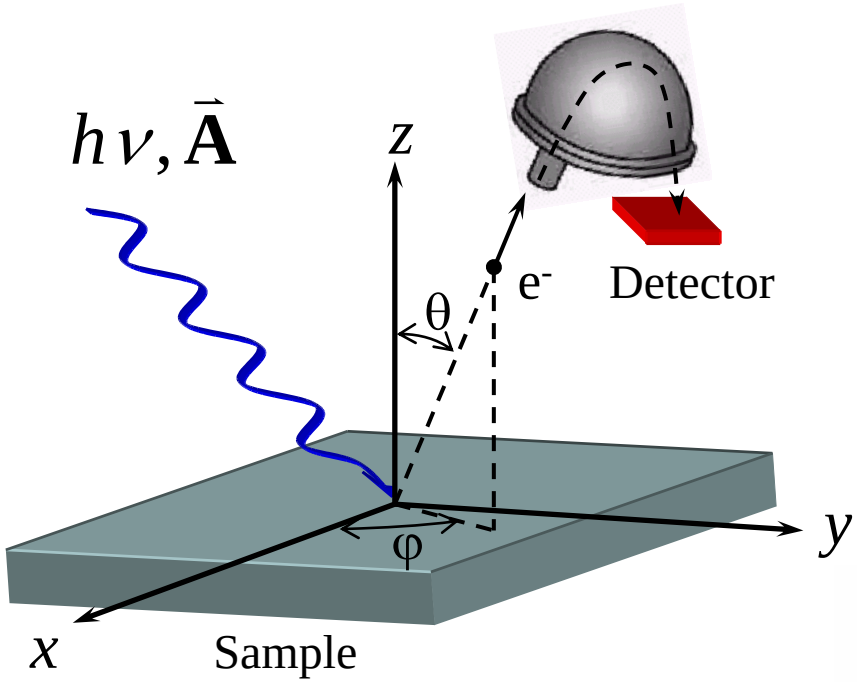


Adapted from A. Damascelli's *Exciting-2003* lecture and E. Rotenberg's lecture

Room temperature: $k_BT = 25$ meV

ARPES principle

Kinetic energy analyzer

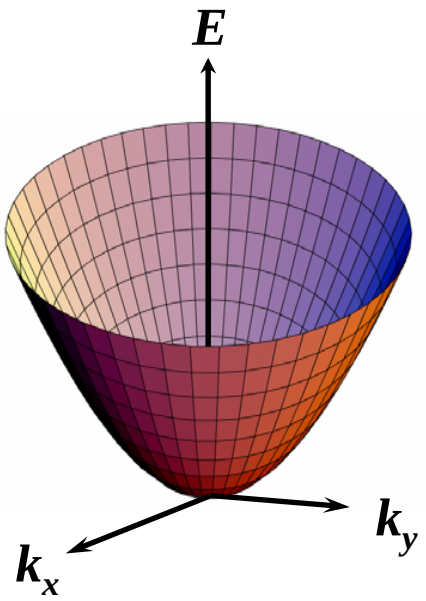


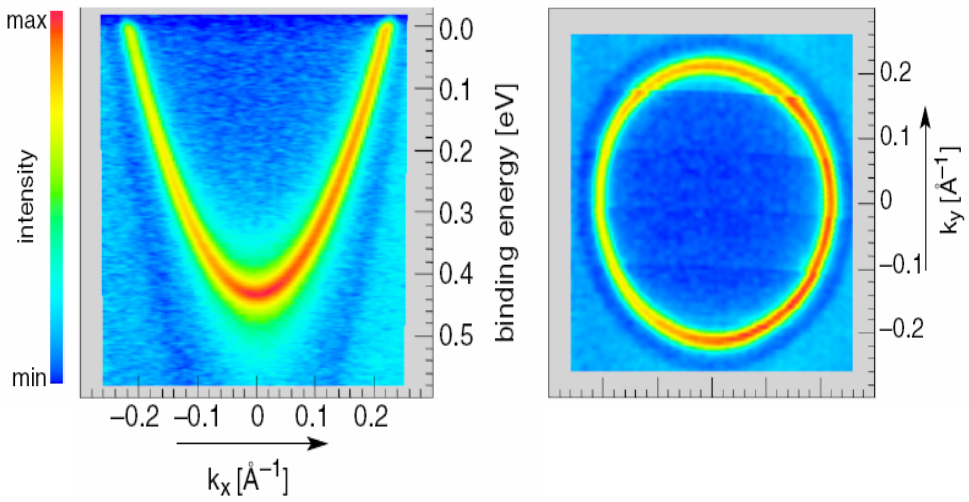
$$E_{kin} = h\nu - W - |E_B|$$

$$\hbar \mathbf{k}_{||} = \sqrt{2mE_{kin}} \sin\theta$$

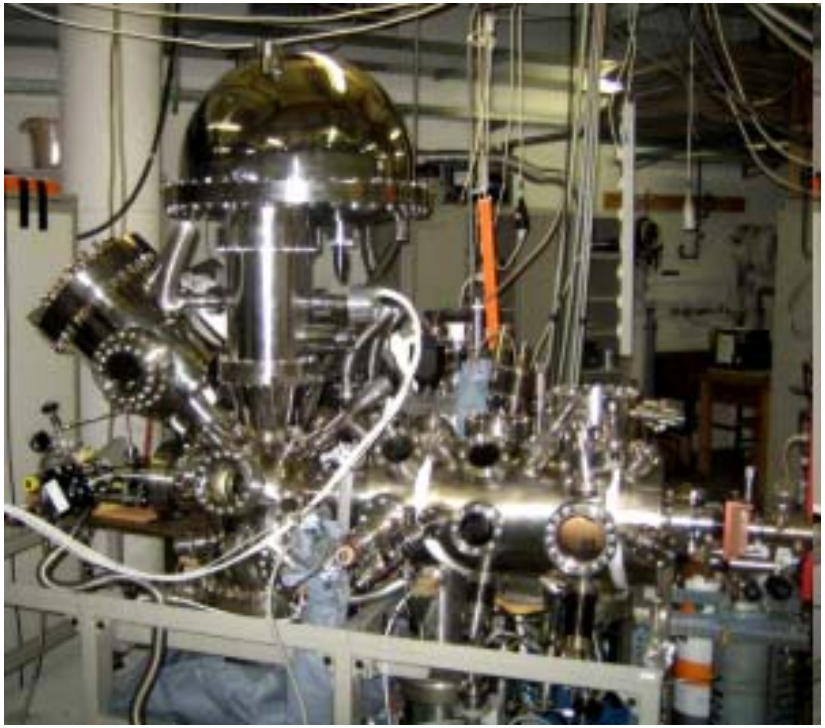
→ **Best for 2D or 1D systems**

Simple example:
Cu(111) surface-state



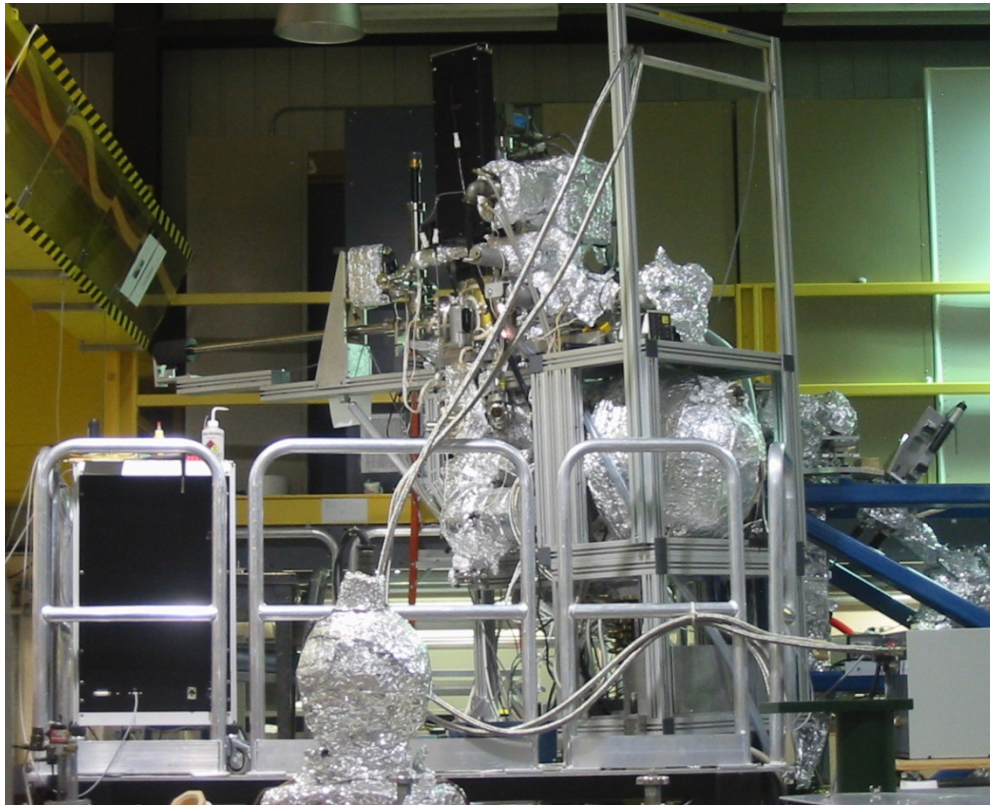


F. Reinert and S. Hüfner, *New Journal of Physics* **7**, 97 (2005)

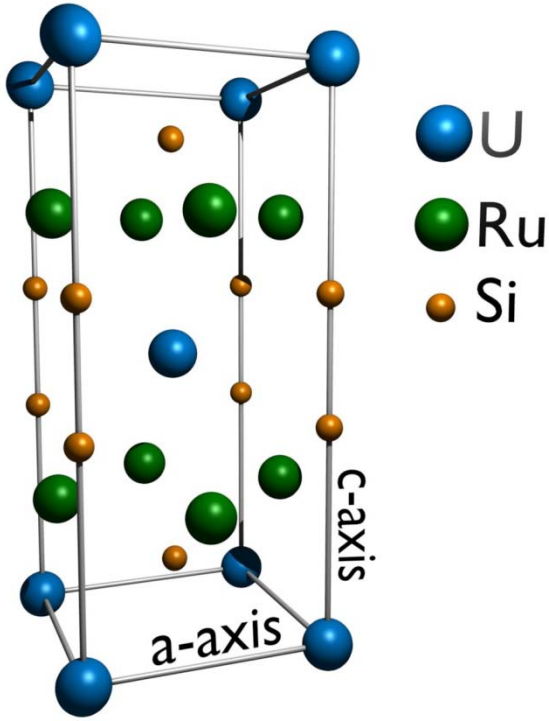


ARPES with He-lamp
Würzburg University (DE)
(F. Reinert's team)

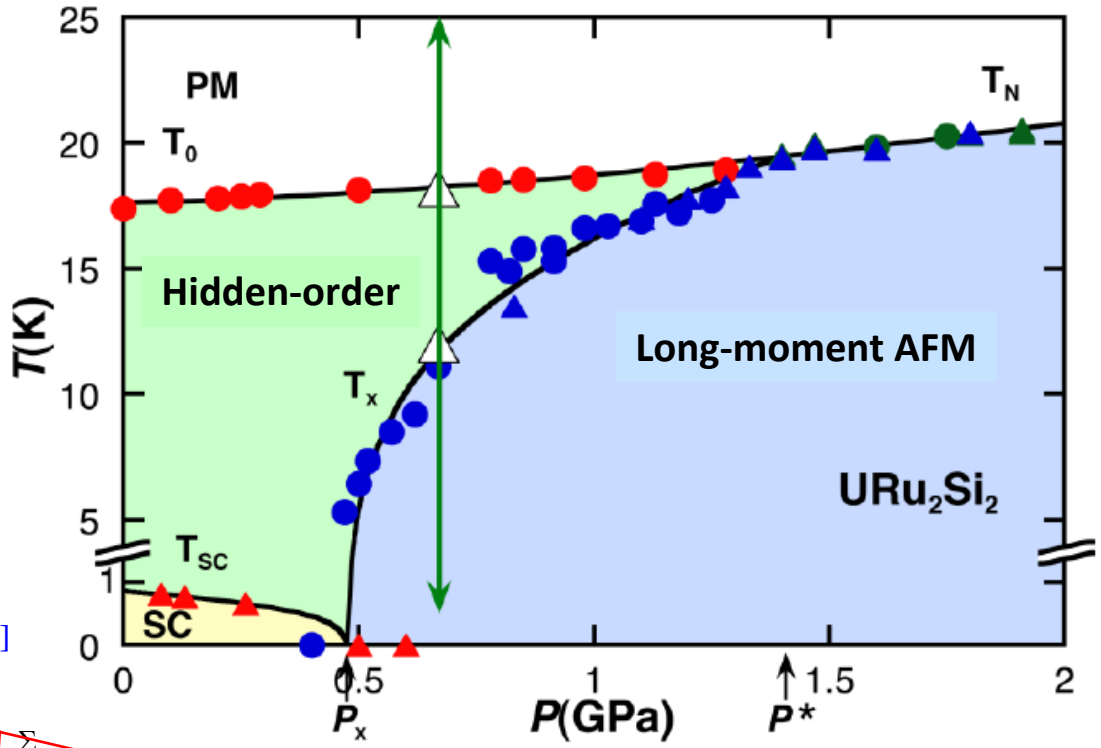
ARPES with synchrotron radiation
Synchrotron Radiation Center
University of Wisconsin – Madison (USA)

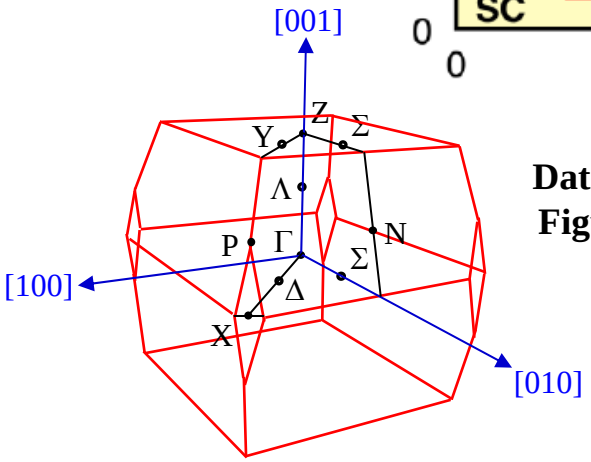


Example of state-of-the art ARPES: The hidden-order transition in URu_2i_2



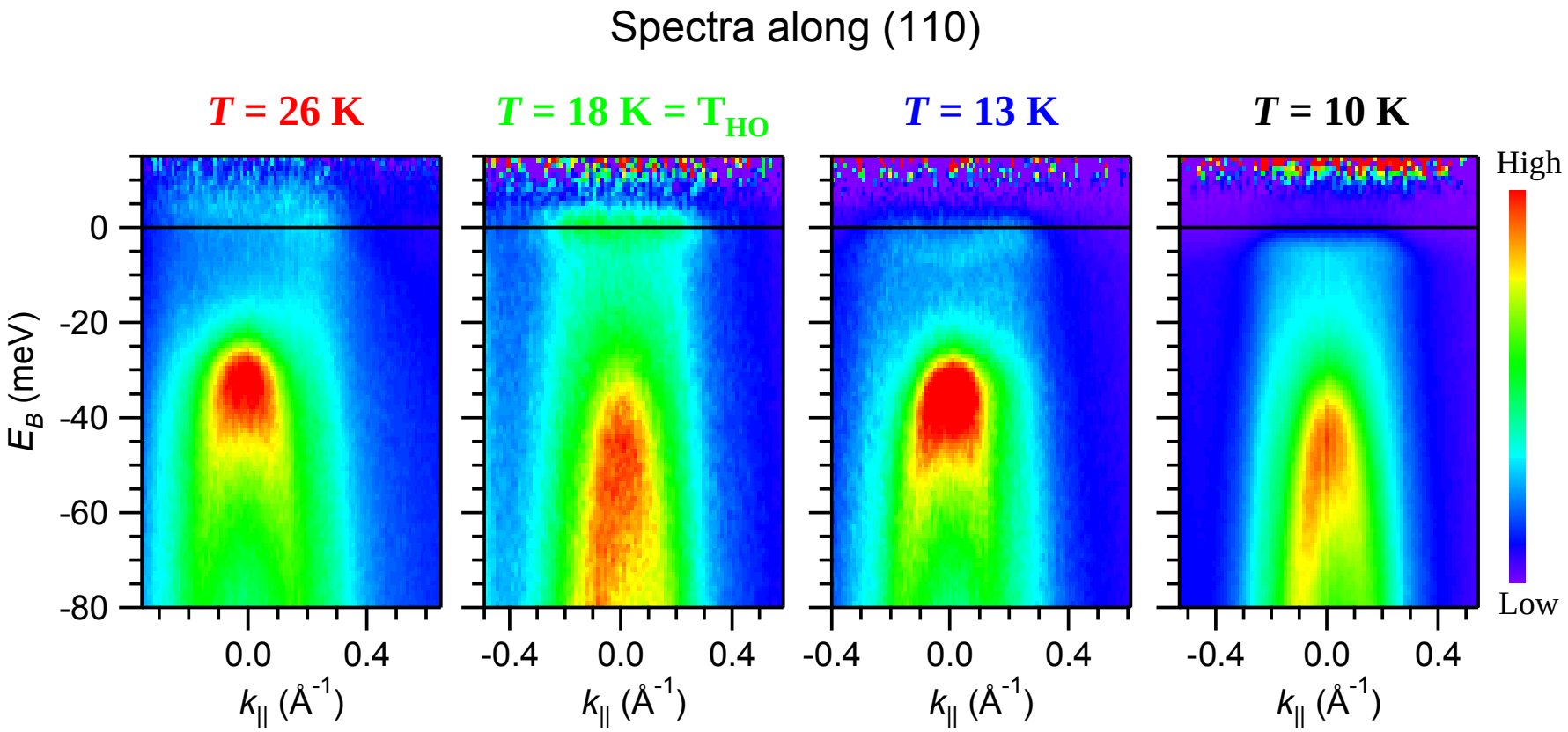
a = 4.129 Å
c = 9.58 Å





Data: E. Hassinger *et al.*, PRB B **77**, 115117 (2008).
Figure: A. Villaume *et al.*, PRB **78**, 012504 (2008).

ARPES view across the transition



→ **Change of Fermi-surface topology across the transition**

AFSS, M. Klein, F. L. Boariu, *et al.*, Nature Physics **5**, 637 - 641 (2009)

Photoemission in the N-electron system: theoretical snapshot

Photoemission intensity given by Fermi's golden rule:

$$I(\mathbf{k},\varepsilon) \propto \frac{2\pi}{\hbar}\left|\left\langle \Psi_f^N \middle| H_{int}^{(N)} \middle| \Psi_i^N \right\rangle\right|^2 \delta\left(E_f^N - E_i^N - h\nu\right)$$

Matrix element:
- k-conservation
- Symmetries

Energy conservation

$\left\|\Psi_i^N\right\rangle$	N-electron ground state (energy E_i^N) of unperturbed Hamiltonian

$\left\|\Psi_f^N\right\rangle$	Excited state (energy E_f^N) of unperturbed Hamiltonian: N-1 electrons in the solid + 1 free electron of energy ε and momentum $\mathbf{k}$

Light-matter interaction: perturbation theory + dipole approximation

$$H_{int}^{1-e} \approx \frac{e}{2mc}\left[\mathbf{A(r)}\cdot\mathbf{p}+\mathbf{p}\cdot\mathbf{A(r)}\right] \approx \frac{e}{mc}\mathbf{A}\cdot\mathbf{p}$$

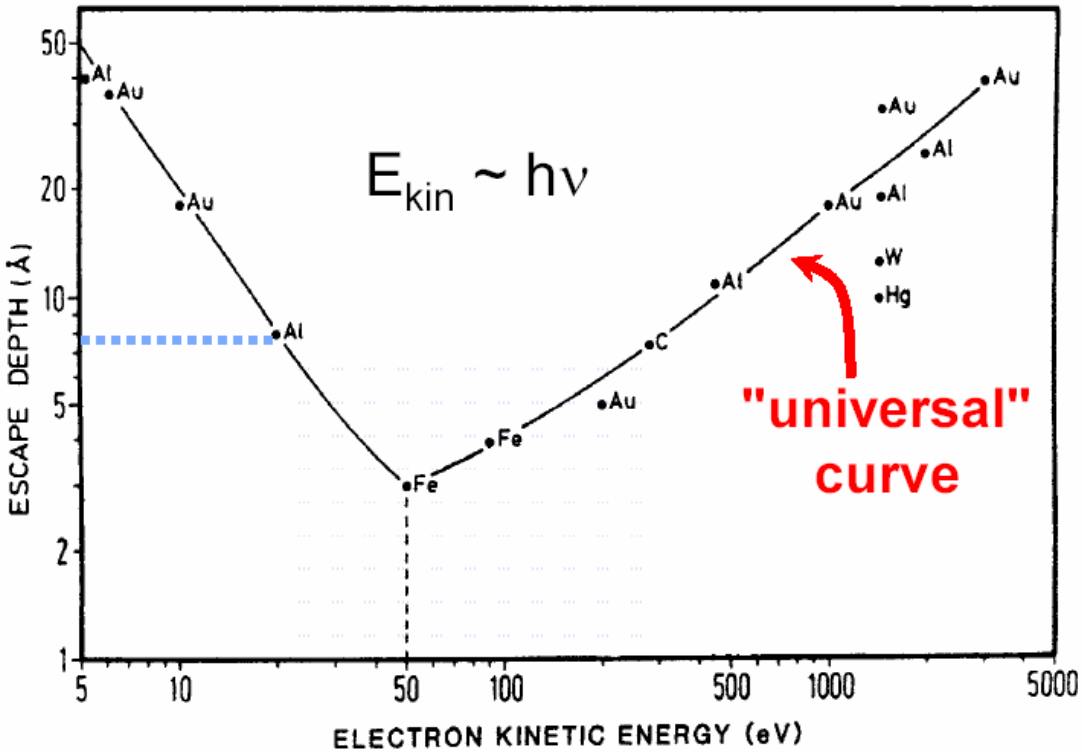
Dipole approximation: **A** constant over atomic dimensions

$$\left[\mathbf{p},\mathbf{A}\right] = i\hbar\nabla\cdot\mathbf{A} \approx 0$$

- true in the UV for electrons in the bulk
- not necessarily true at the surface
  - → indirect transitions interfering with bulk transitions
  - → asymmetric line-shapes

Electron escape to the surface

λ_{esc} (E_{kin})= Electron escape depth
(average distance traveled by electron without inelastic scattering)



→ ARPES is a surface technique: one needs clean surfaces + work under ultra-high vacuum (better than 10^{-9} Torr).

Furthermore, one has to make sure that the photoemission process itself does not modify the electronic structure of the material…

SUDDEN APPROXIMATION

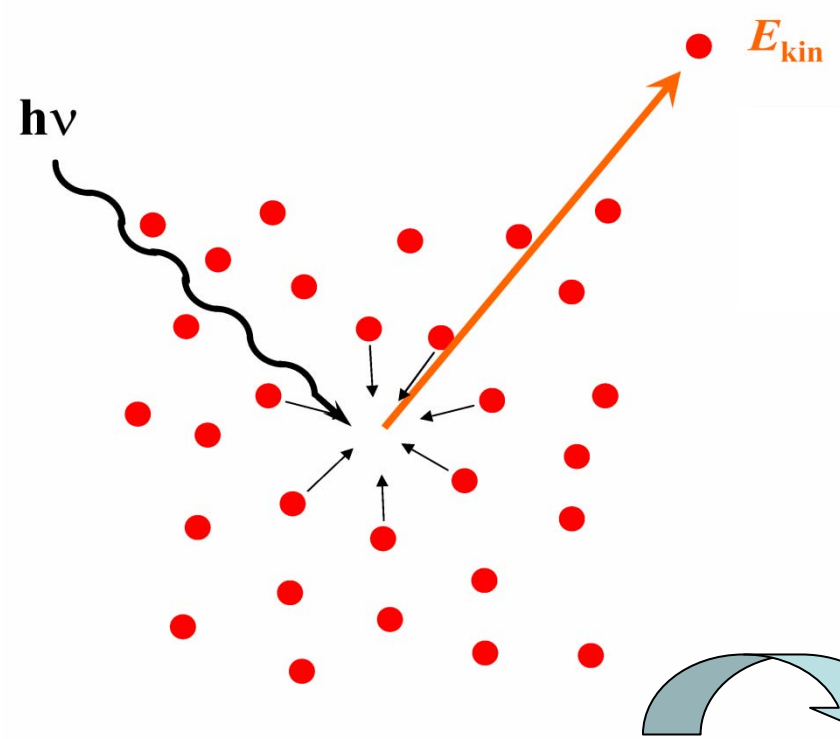
The ejected electron should be "fast enough" to neglect its interaction with the hole left behind

→E_{kin} must be large → hν must be large

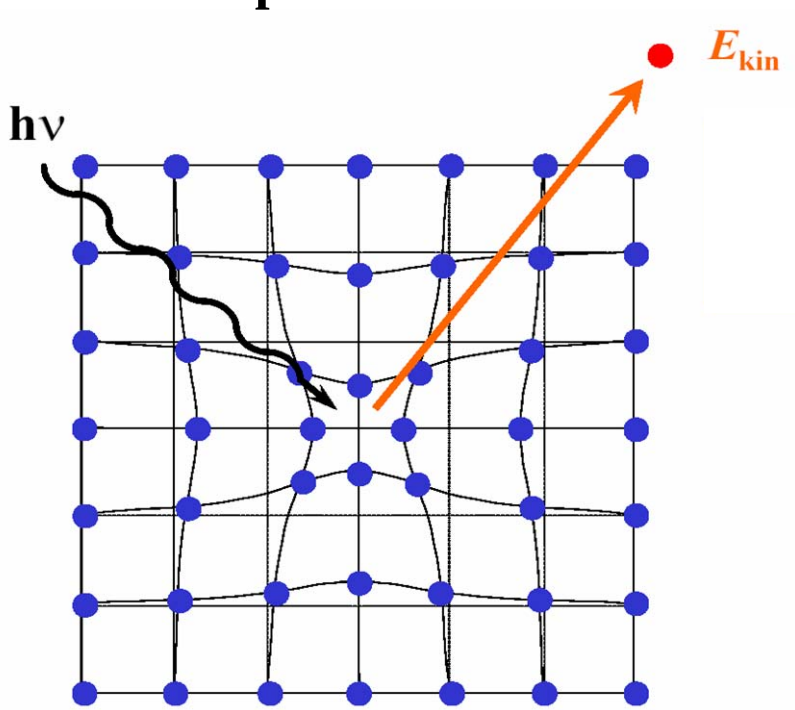
→ Final state = Plane wave in the vacuum

Photoemission: many-body effects

electron-electron interaction



electron-phonon interaction



"loss" of kinetic photoelectron energy due to excitation energy stored in the remaining interacting system

- **Shift in energy** of the main photoemission line
- **Broadening** of main line (life-time of excited interacting system)
- **Transfer of spectral-weight** to higher binding energies (excitations of the remaining interacting system)

Adapted from R. Claessen's *Cargese-2005* lectures

Spectra analysis

$$\left|E_B\right| \equiv \hbar\omega, \hbar = 1$$

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

$A(\mathbf{k},\omega)$ = Probability of adding or removing one electron at $(\mathbf{k},\omega)$

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

$\Sigma' \rightarrow$ Energy renormalization

$\Sigma'' \rightarrow$ Lifetime of dressed e^-

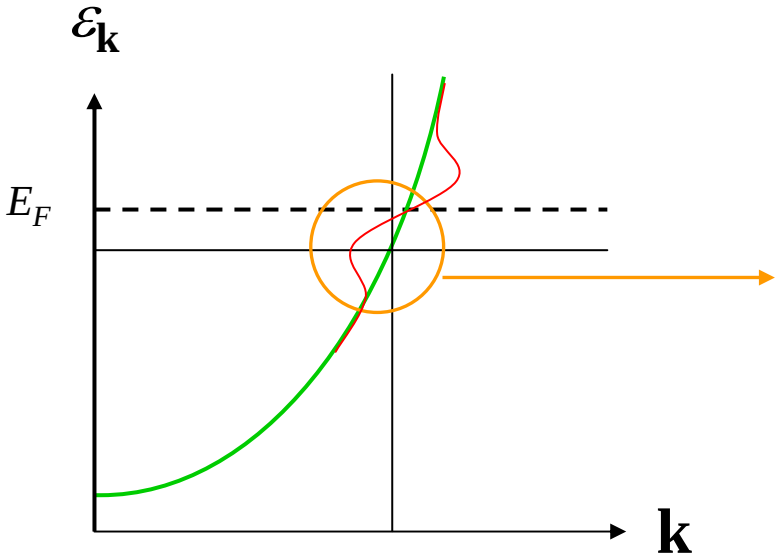
} Many-body physics

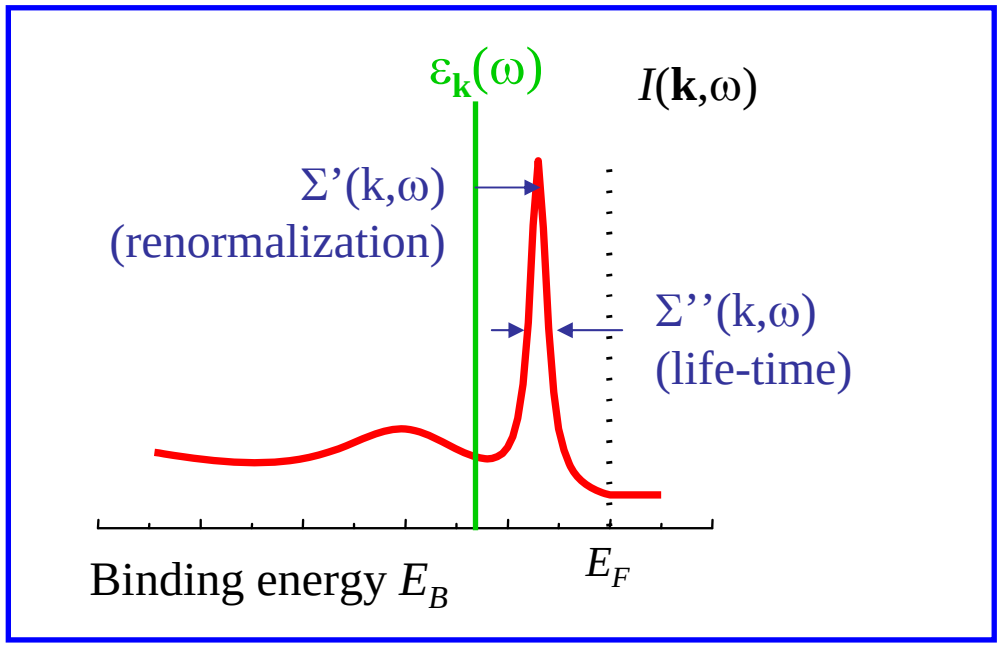
Interaction effects on ARPES spectra

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

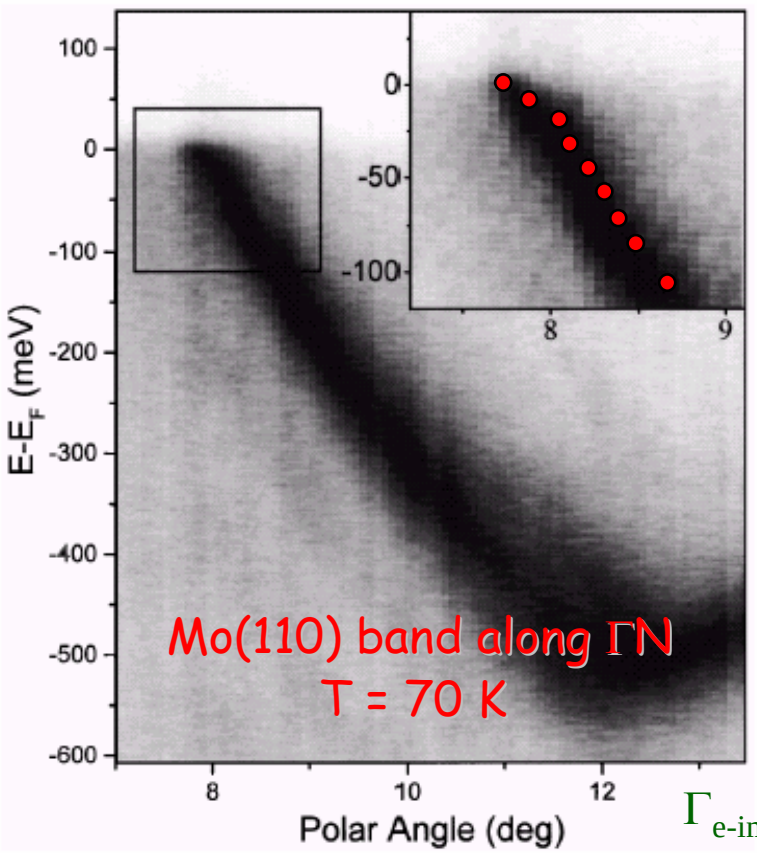
$A(\mathbf{k},\omega)$ = Probability of adding or removing one electron at $(\mathbf{k},\omega)$

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

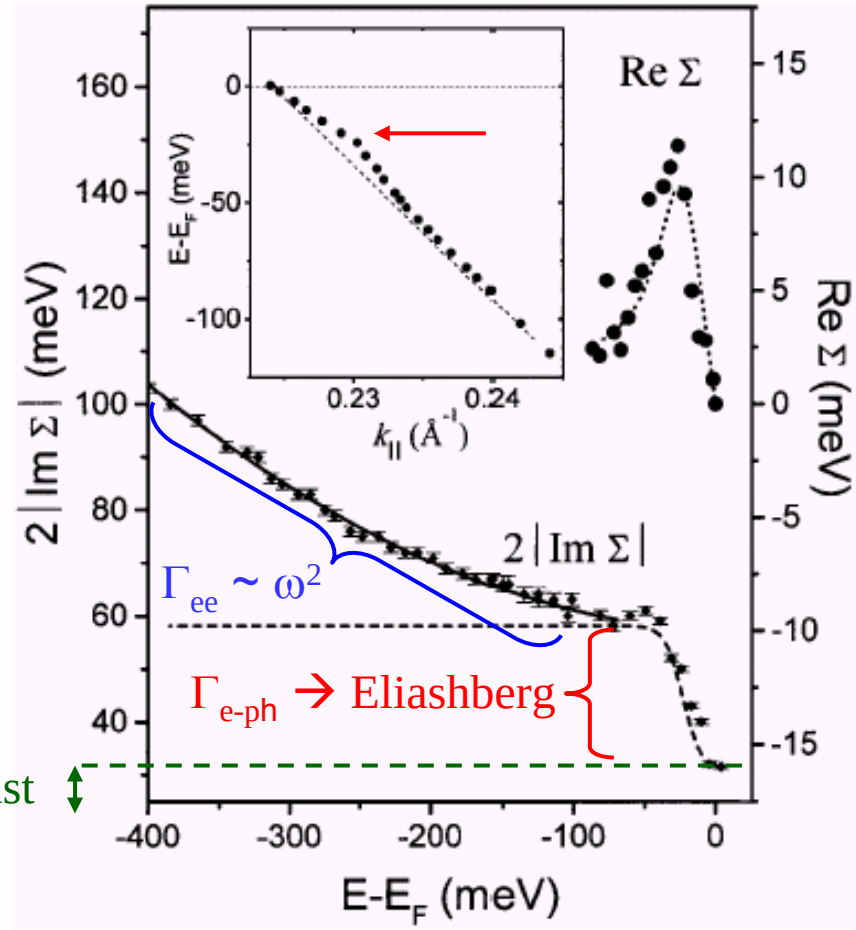




Many-body physics – Effects of the interactions on the band structure: Example of surface states of Mo(110)



$\Gamma_{e\text{-}imp}$ = const

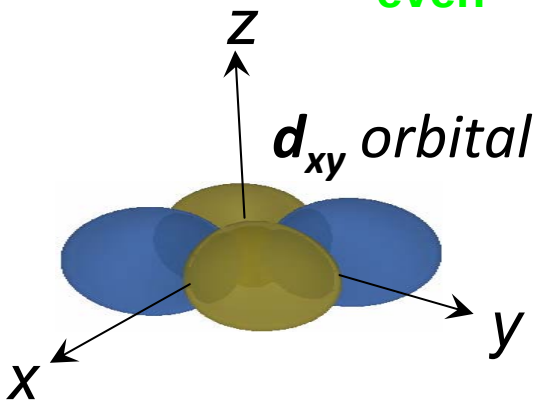


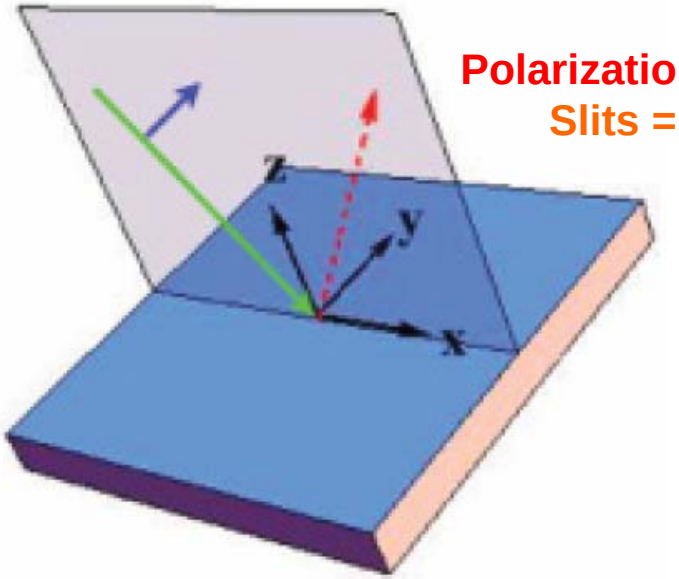
T. Valla *et al.*, PRL **83**, 2085 (1999)

ARPES: Effects of orbital symmetries

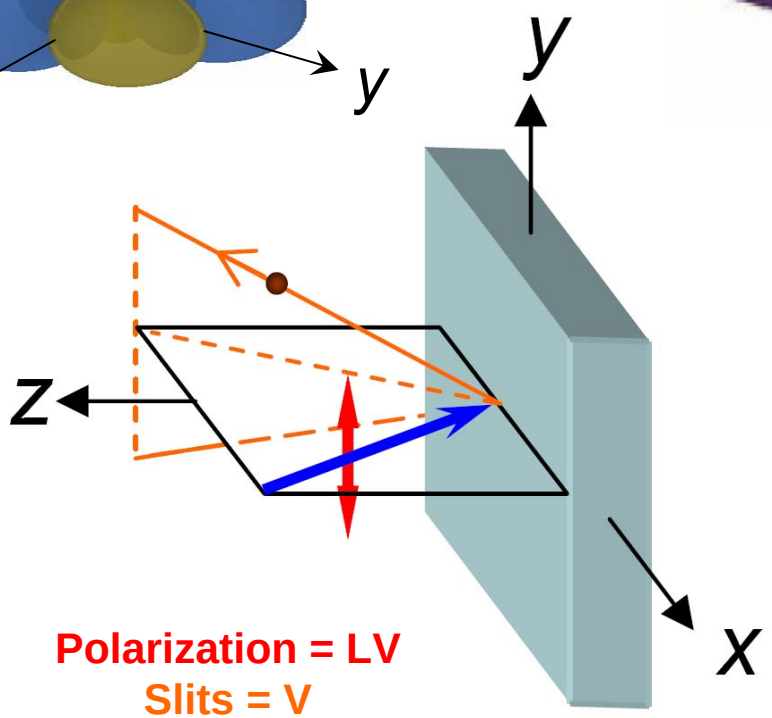
$$\left|M_{i,f}(\mathbf{k})\right|^2 \propto \left|\left\langle \Psi_f^N \left| \mathbf{A}\cdot\mathbf{p} \right| \Psi_i^N \right\rangle\right|^2$$

even

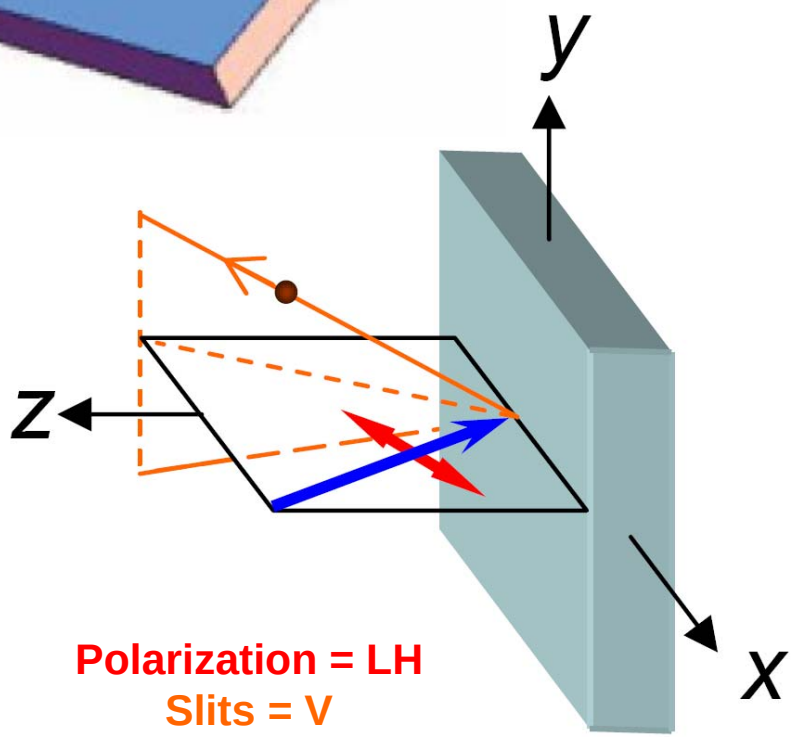




Polarization = LH
Slits = H

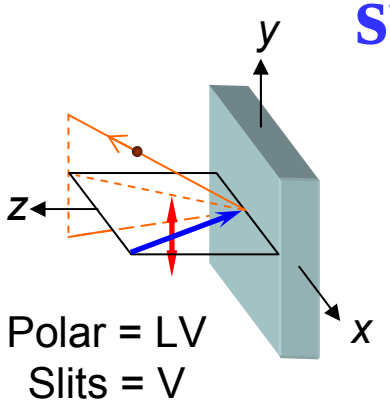


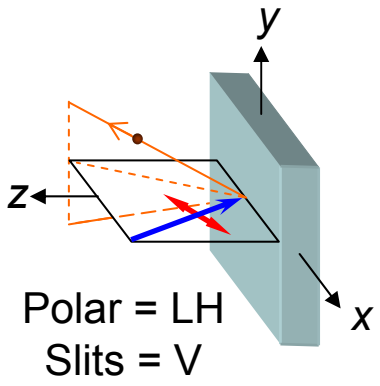
Polarization = LV
Slits = V

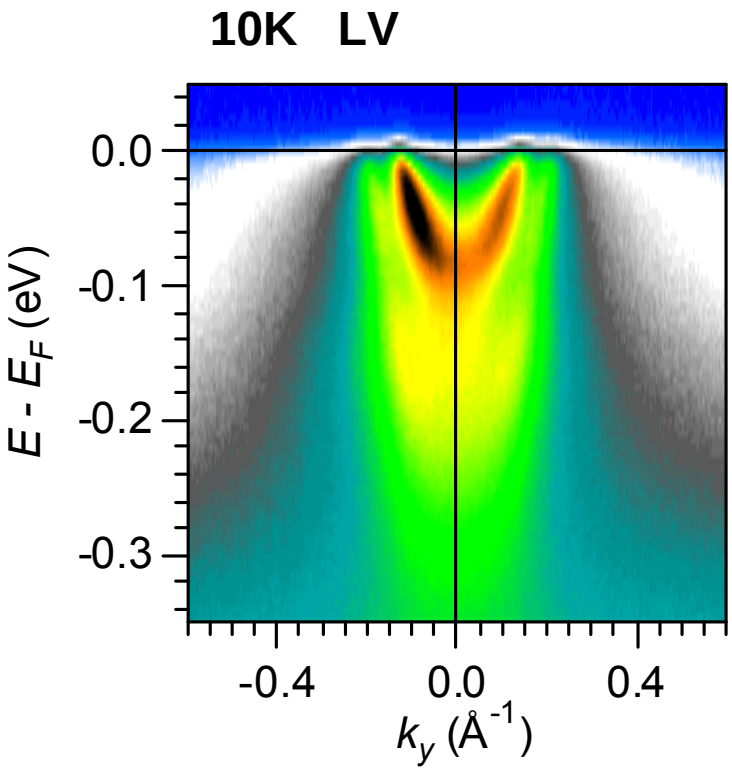


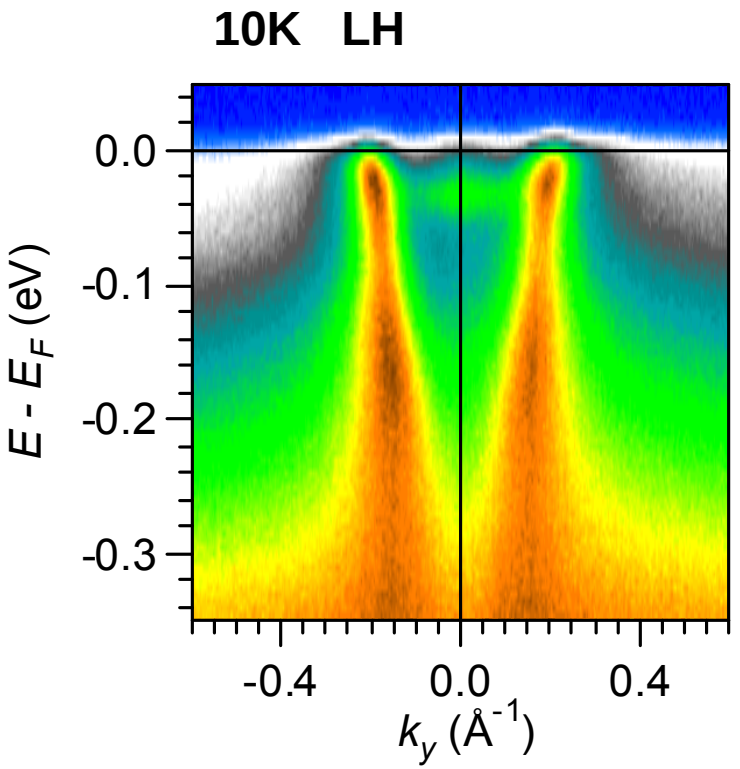
Polarization = LH
Slits = V

Example: subbands with orbital order at the surface of $SrTiO_3$









Summary of ARPES technique

When it works…

ARPES is a powerful technique for the study of the electronic structure of complex systems

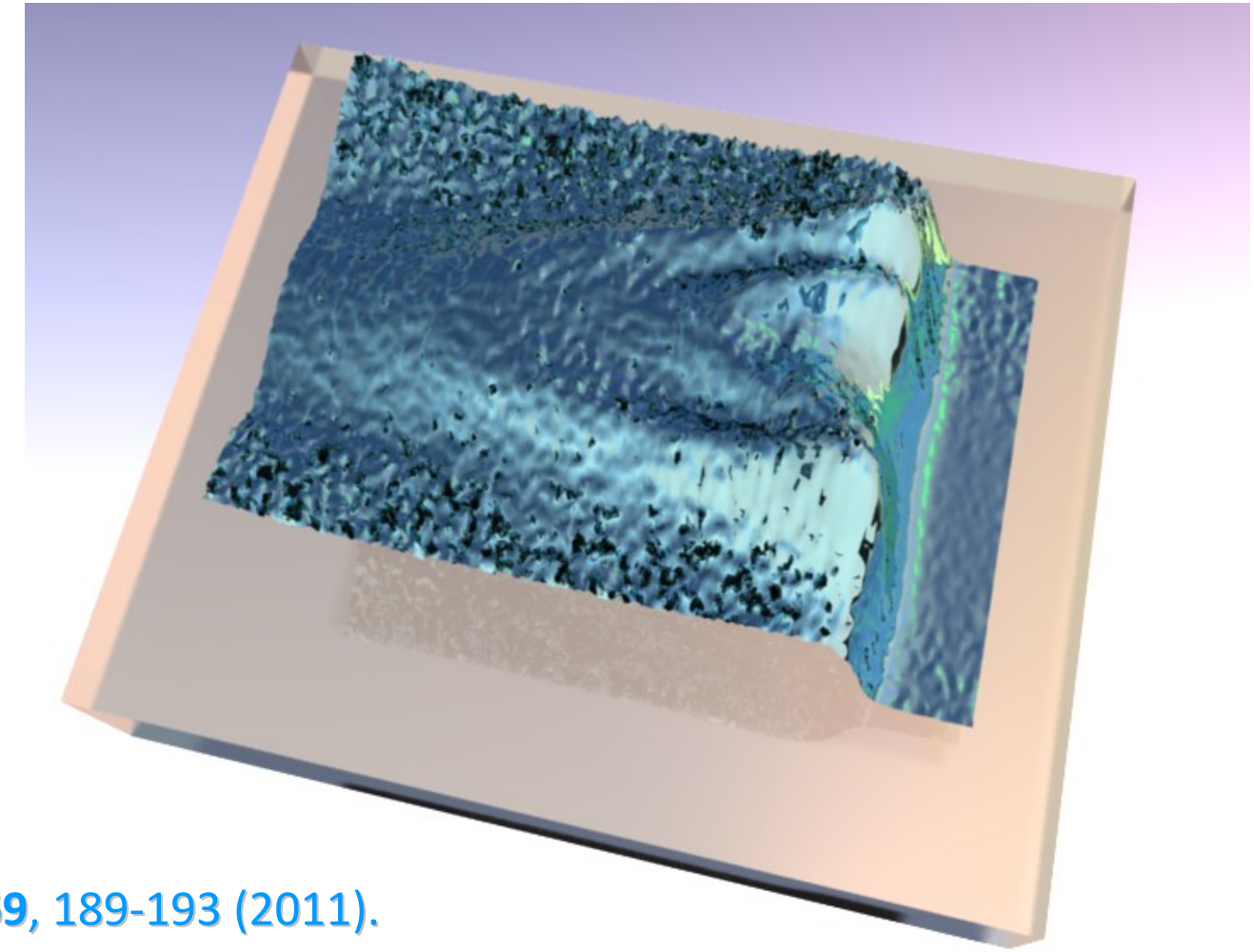
- → Detailed band structures and Fermi surfaces
- → Fermi velocity and effective mass
- → Gaps
- → Many-body effects

Rapidly developing…

- → Spin-resolved ARPES
- → Time-resolved ARPES
- → Micro-ARPES
- → Laser-ARPES using UV/X-ray lasers (HHG in noble gases)
- → Ultra-high resolution ARPES using TOF detector

Superficially metallic

A 2D electron gas with universal subbands at the surface of $SrTiO_3$

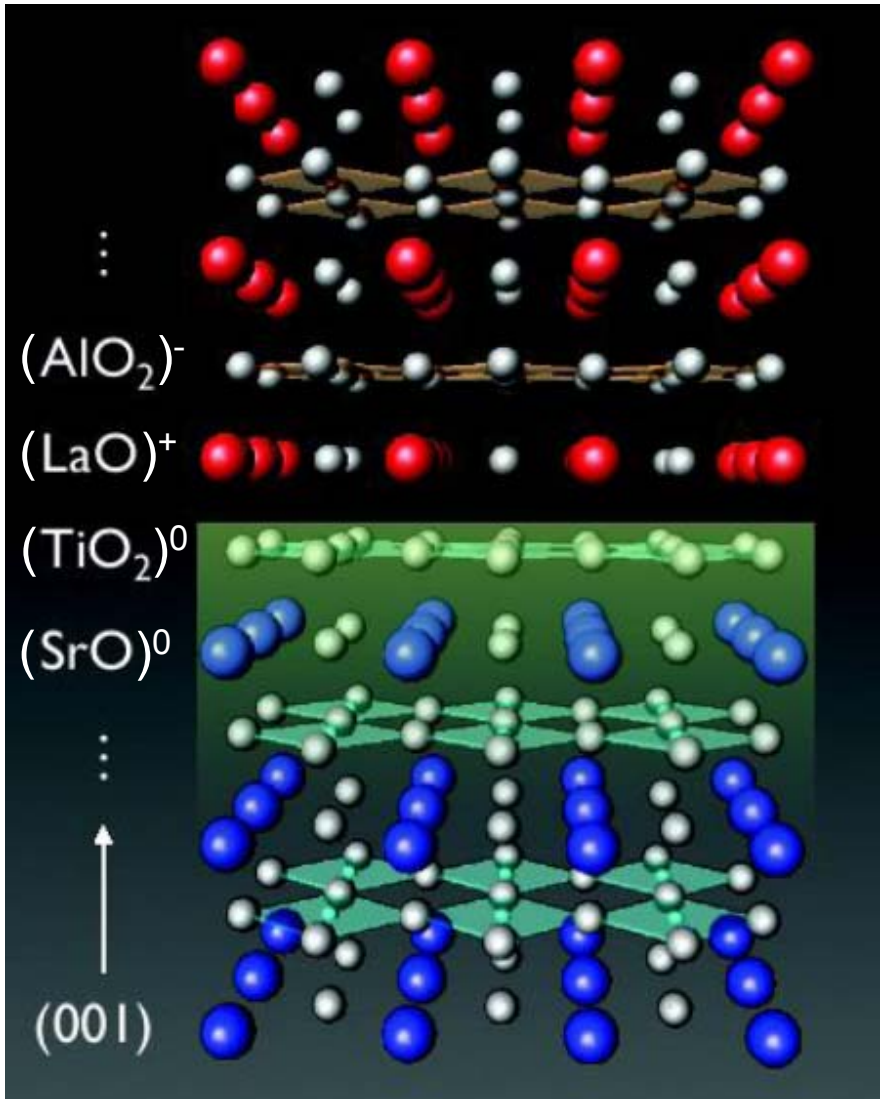


Nature **469**, 189-193 (2011).

Preliminaries:

A 2D metal that spontaneously forms at the interface between two insulators

High-mobility 2DEG at the $LaAlO_3/SrTiO_3$ interface



$LaAlO_3$:

Band insulator

Δ = 5.6 eV

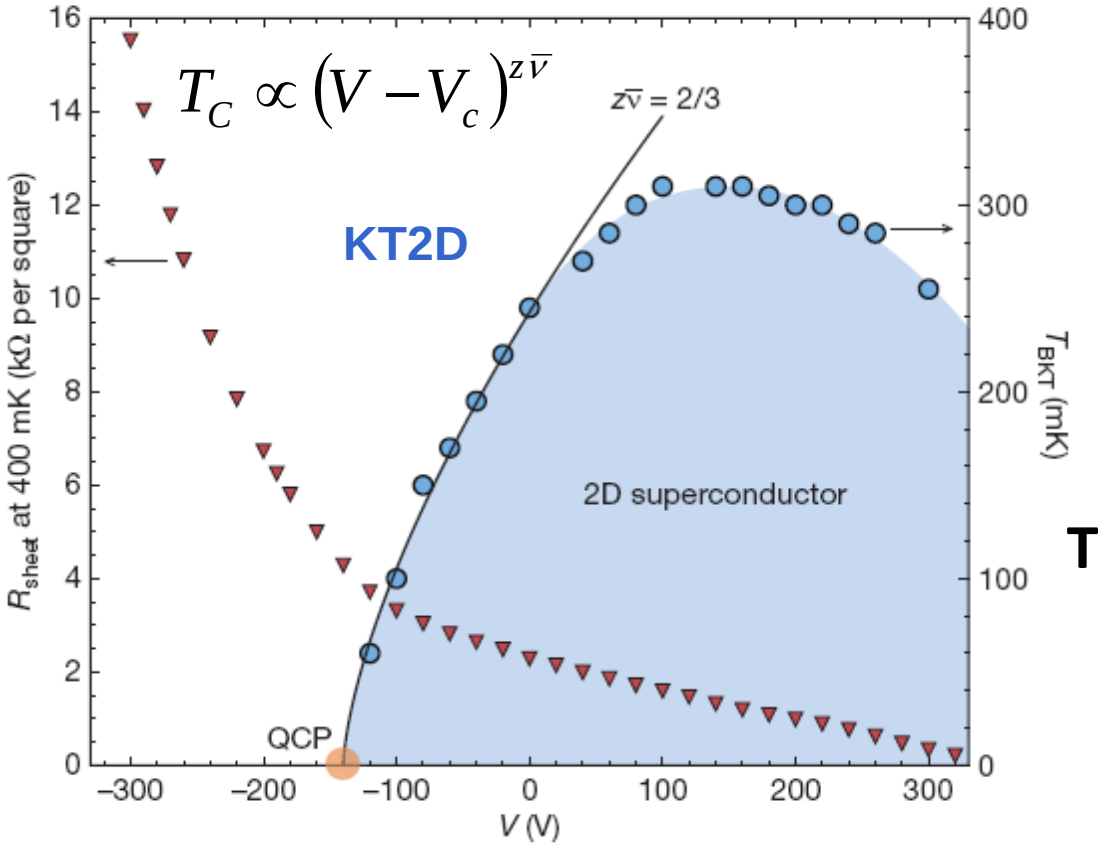
$SrTiO_3$:

Band insulator
(quantum paraelectric)

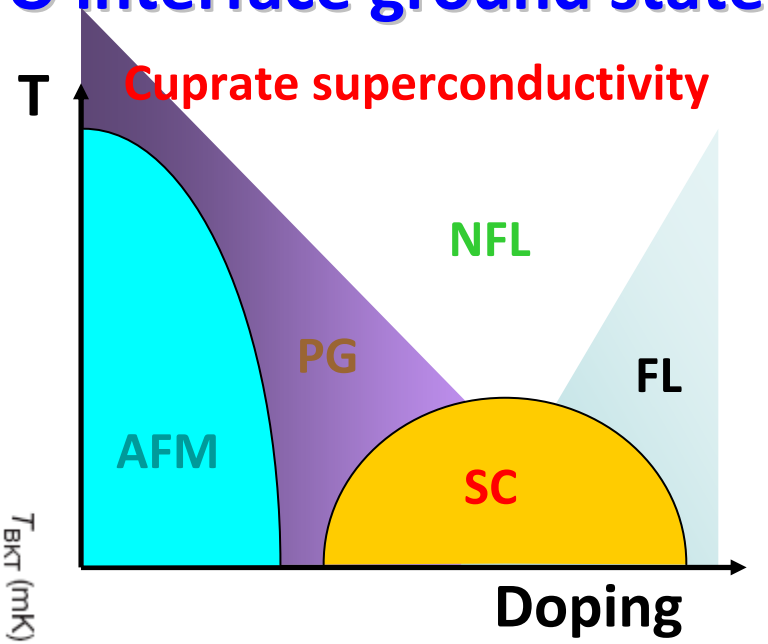
Δ = 3.2 eV

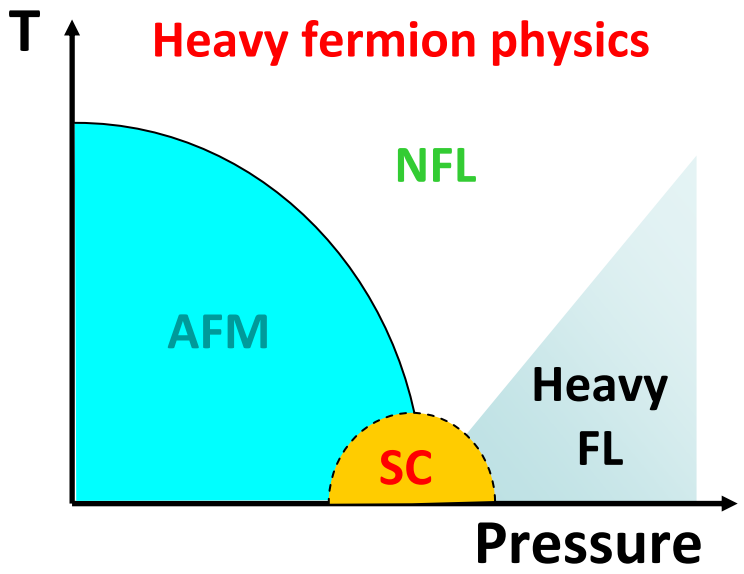
A. Ohtomo and H. Y. Hwang, Nature **427**, 423 (2004).

Electric field control of the LAO/STO interface ground state



A. D. Caviglia *et al.*, Nature **456**, 624 (2008).





Why so important?

→ 2DEGs (*e.g.* at semiconductor interfaces) are the first step in the design of useful micro-electronic devices, like FETs.

→ $SrTiO_3$ is the preferred substrate to grow thin films of transition-metal oxides.

→Transition-metal oxides have properties that surpass those of semiconductors: high-temperature superconductivity, colossal magnetoresistance, high thermoelectric power *with* good conductivity, multiferroic behavior, …

→ Possibility of combining two or more of these functionalities in a single device through (multi)-thin films of transition metal oxides. A 2DEG at the interface provides a conduction channel.

→ Controllable systems to study fundamental aspects of the physics of transition-metal oxides, which are often "strongly-correlated electron systems".

Heteropolar interfaces based on STO: OPEN QUESTIONS

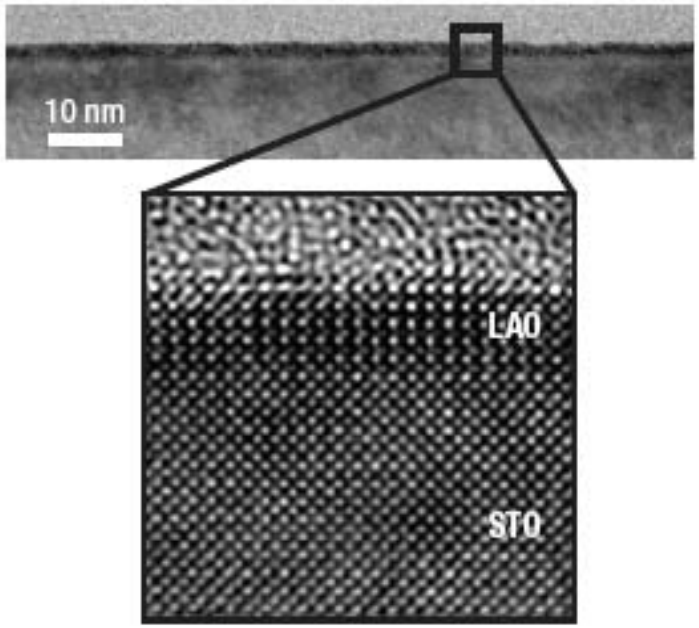
→ What is the origin of the metallic electron gas?

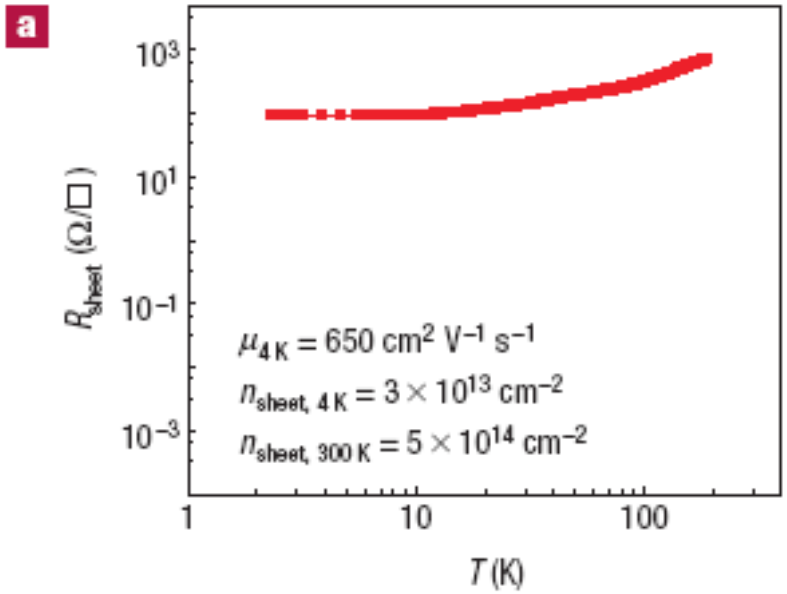
→ What is its thickness?

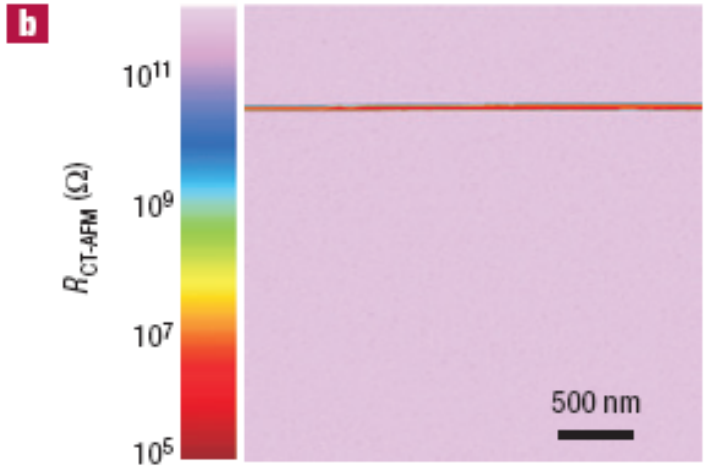
→ What is its dimensionality? (2D, 3D; *i.e.*, can $d_{gas} < \lambda_F$)

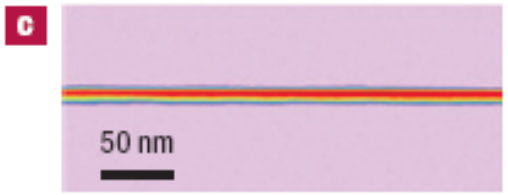
→ What is (are) the mechanisms responsible for (super)conductivity and high mobility?

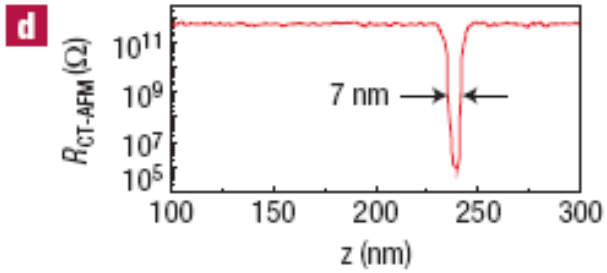
Extension of 2DEG at LAO/STO interface





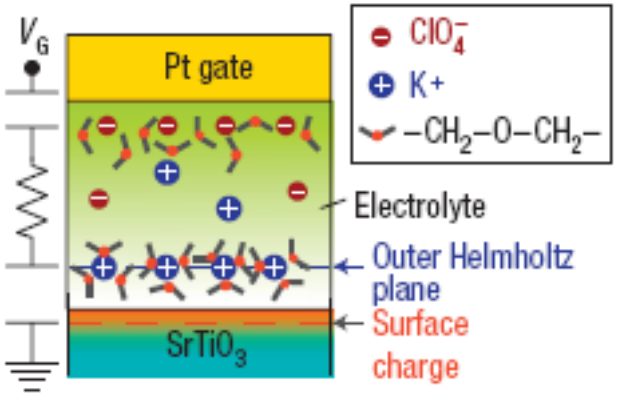


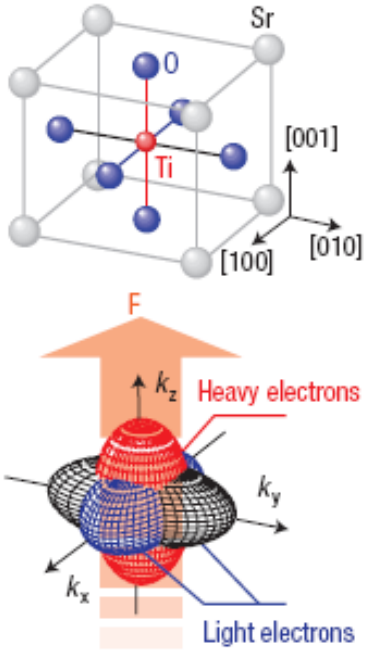


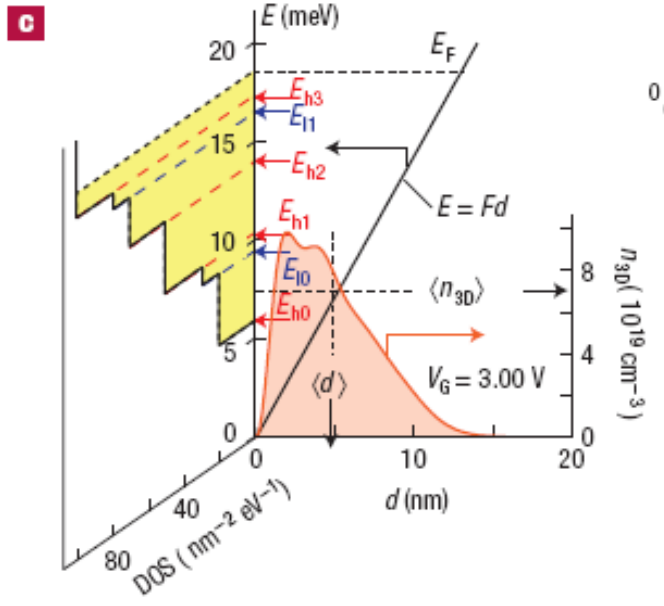


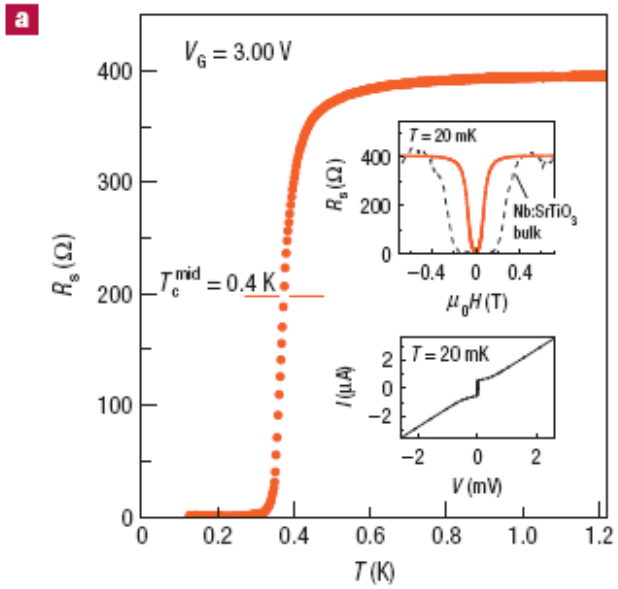
M. Baslestic *et al*., Nature Materials 2008, doi: 10.1038/nmat2223

Metallic 2DEG can also be induced by electrostatic doping of the pure STO surface









K. Ueno *et al*., Nature Materials **7**, 855 (2008)

Scenarios invoked

- Oxygen vacancies
- Polar catastrophe (build-up of electric field due to the polar LaO layer)
- Electronic reconstruction (charge leakage between $LaTiO_3$ and $SrTiO_3$)
- Atomic diffusion
- Surface reconstruction to avoid polar catastrophe

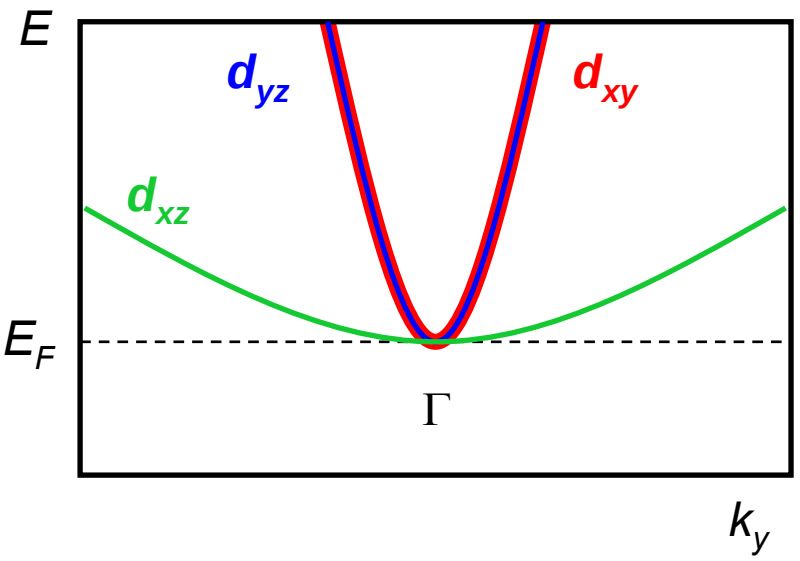
Surprise … surprise!

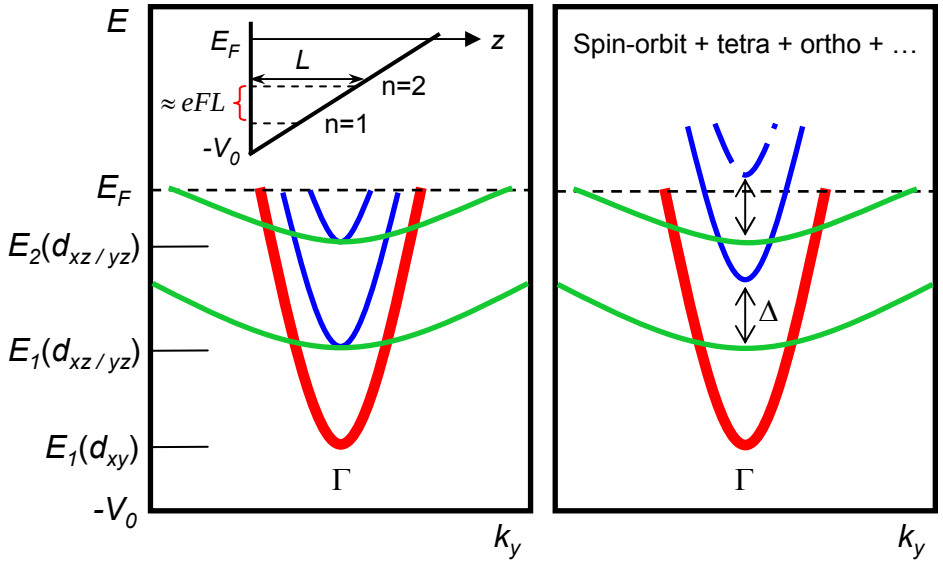
→ A 2DEG spontaneously forms at the vacuum-cleaved surface of $SrTiO_3$

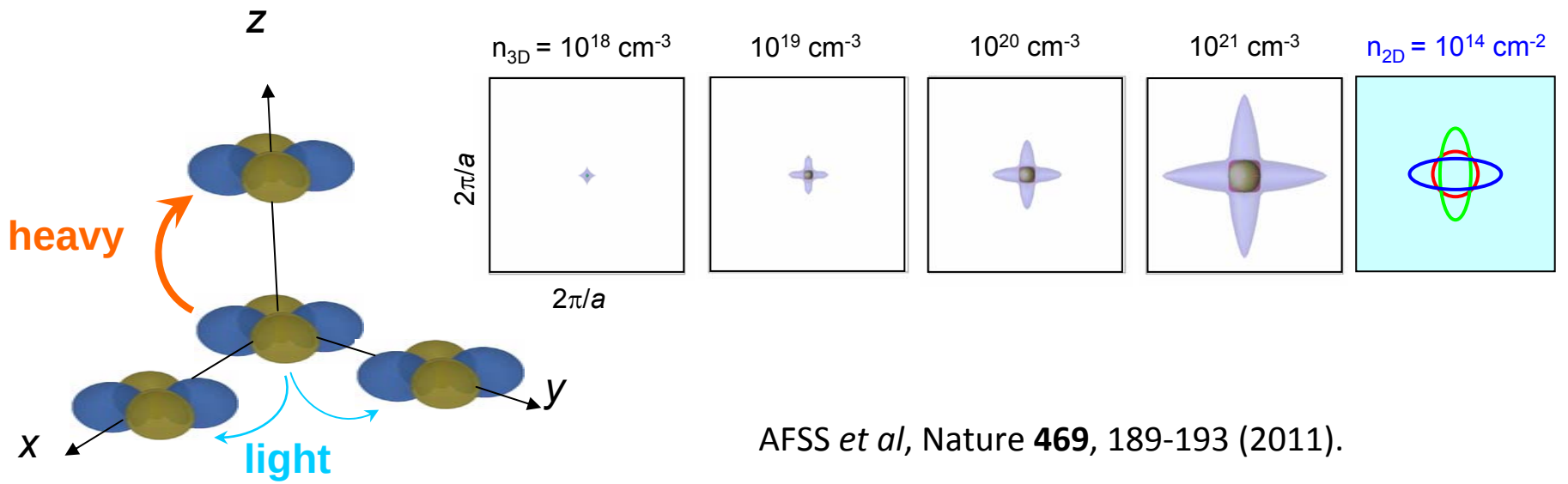
→ Subband structure, carrier density, confinement size similar to those found in other STO-related interfaces

→ For this 2DEG, the mechanism is well understood → door wide open to generate novel 2DEGs in other oxides!

$SrTiO_3$: bulk *vs* 2D-confined electronic structure

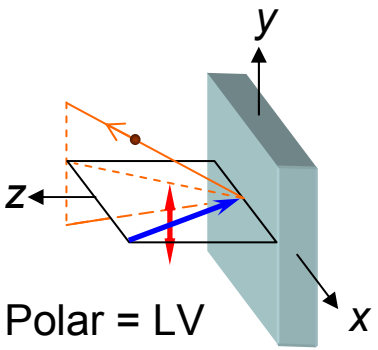




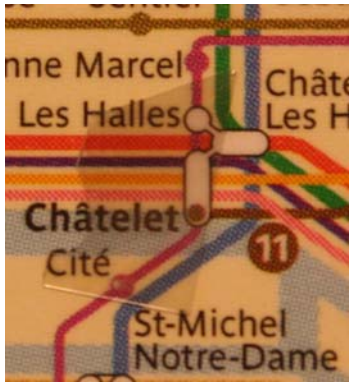


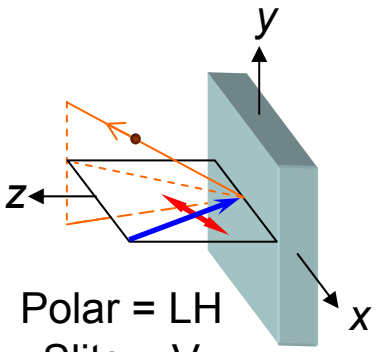
AFSS *et al*, Nature **469**, 189-193 (2011).

Metallic 2DEG at the surface of insulating $SrTiO_3$

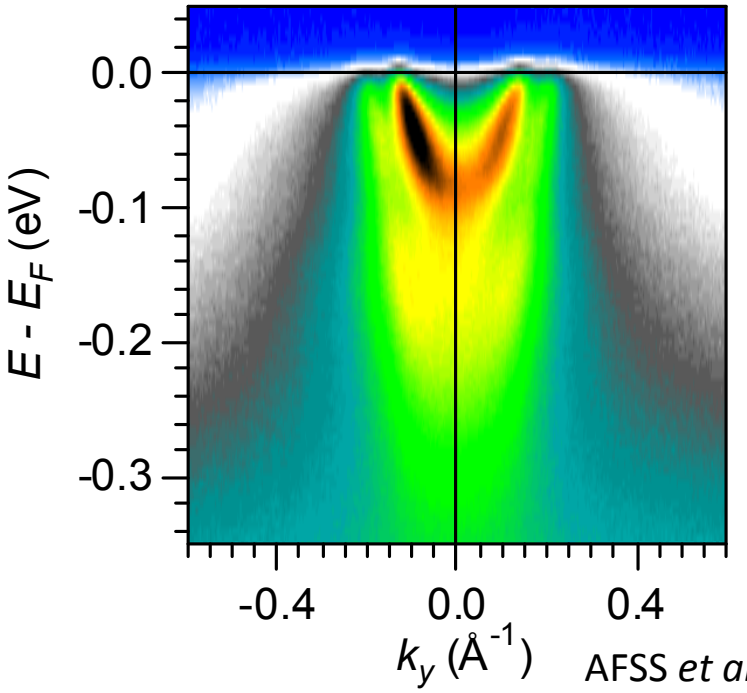


$n_{3D} < 10^{13}$ cm^{-3}

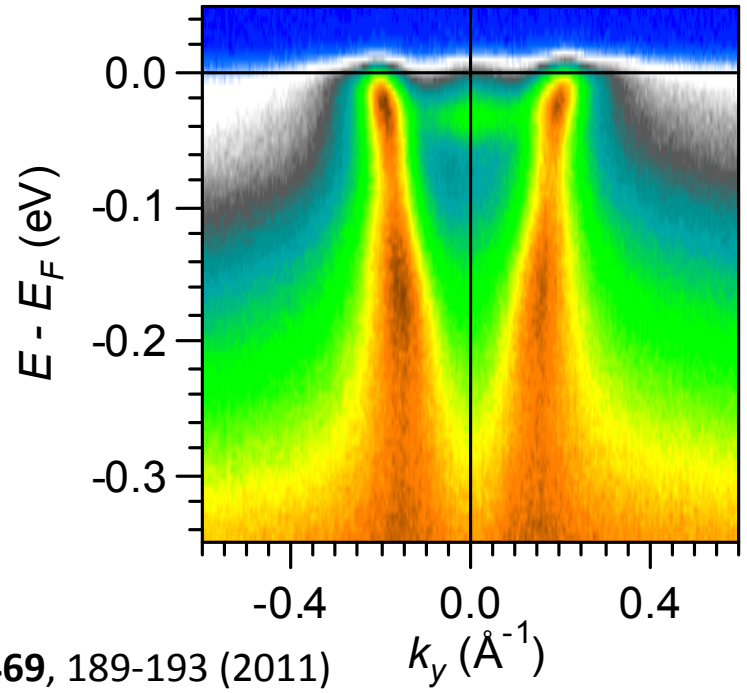




10K LV



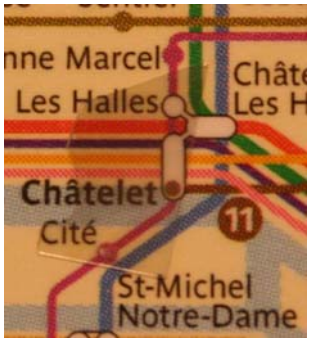
10K LH



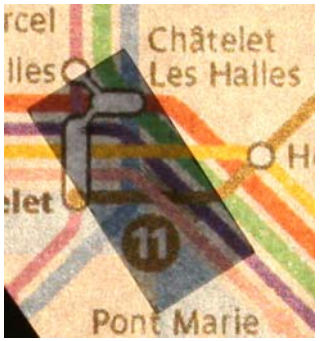
AFSS *et al*, Nature **469**, 189-193 (2011)

$SrTiO_3$: universal electronic structure at the surface

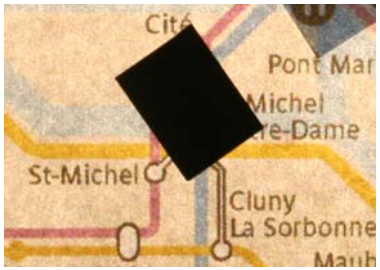
$n_{3D} < 10^{13}$ cm^{-3}

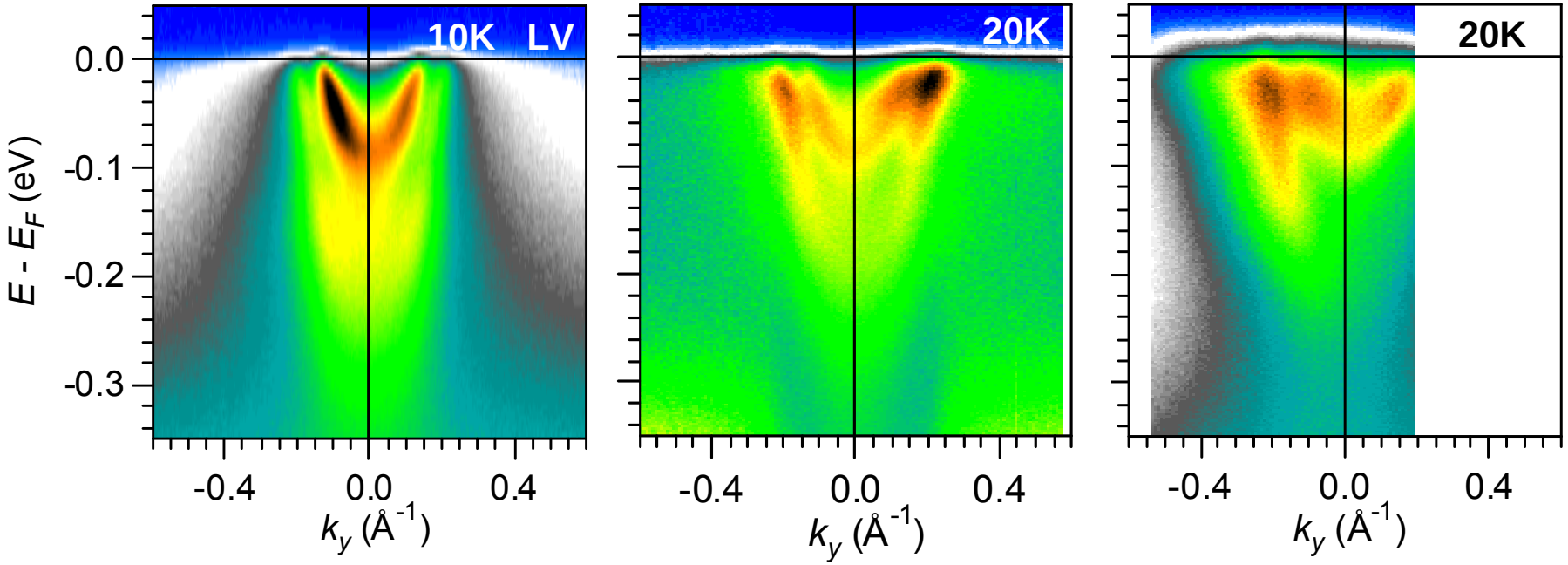


$n_{3D} \sim 10^{18}$ cm^{-3}



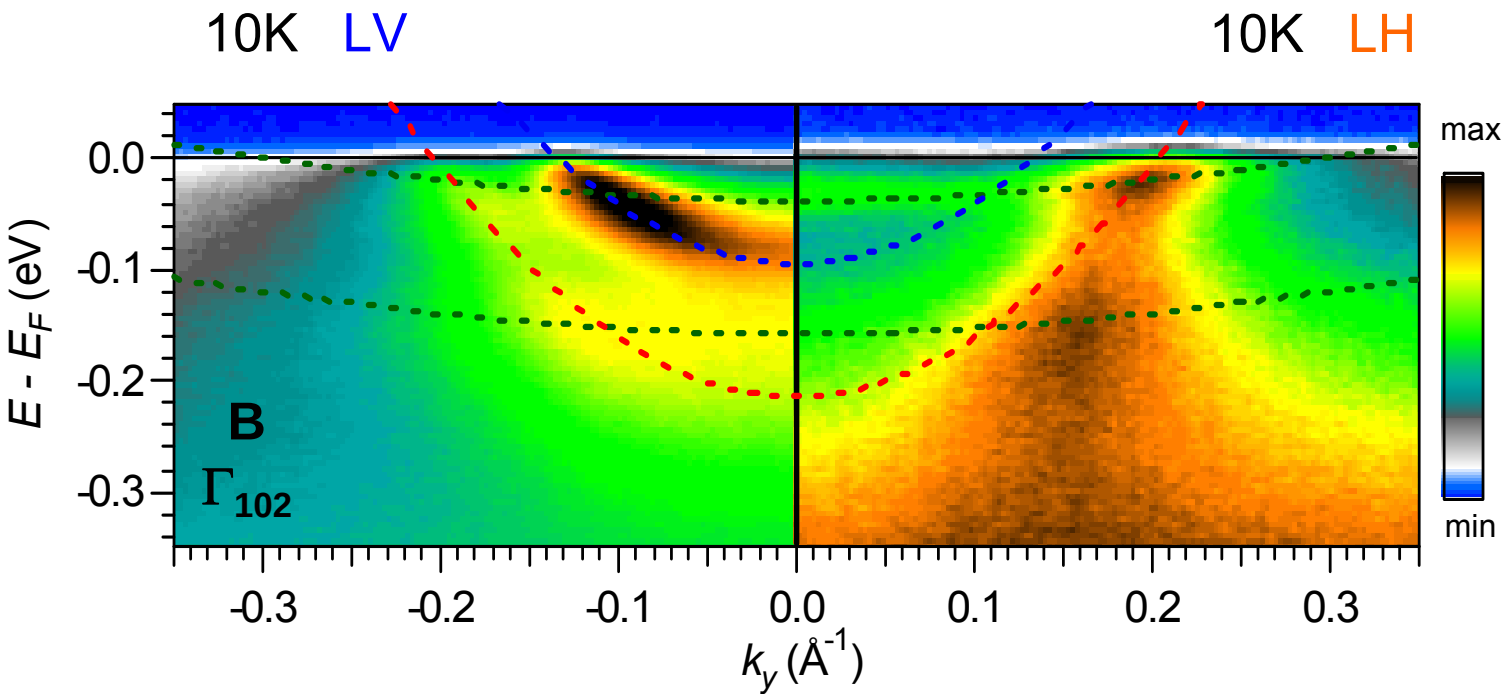
$n_{3D} \sim 10^{20}$ cm^{-3}





AFSS *et al*, Nature **469**, 189-193 (2011)

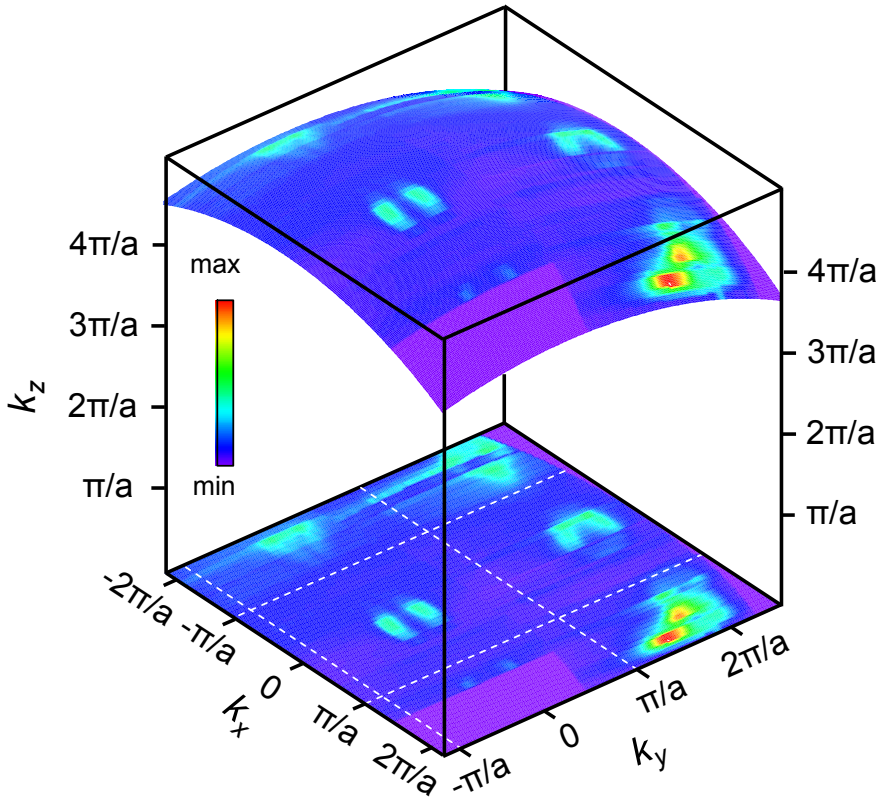
$SrTiO_3$: summary of subbands for the surface 2DEG

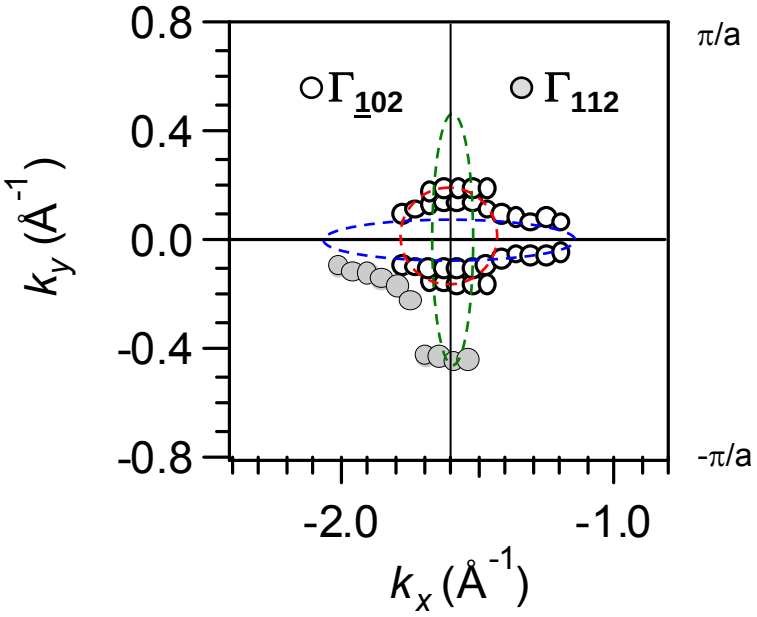


$$m_{light} = 0.7m_e \quad m_{heavy} \approx 20m_e$$

AFSS *et al*, Nature **469**, 189-193 (2011)

Fermi surface and density of carriers





$$n_{2D} = \frac{A_F}{2\pi^2}$$

A_F = Fermi surface area

→ $n_{2D\text{-Total}} = 1.9 - 2.4 \times 10^{14}$ cm^{-2} ≈ $0.29 - 0.35\ e/a^2$

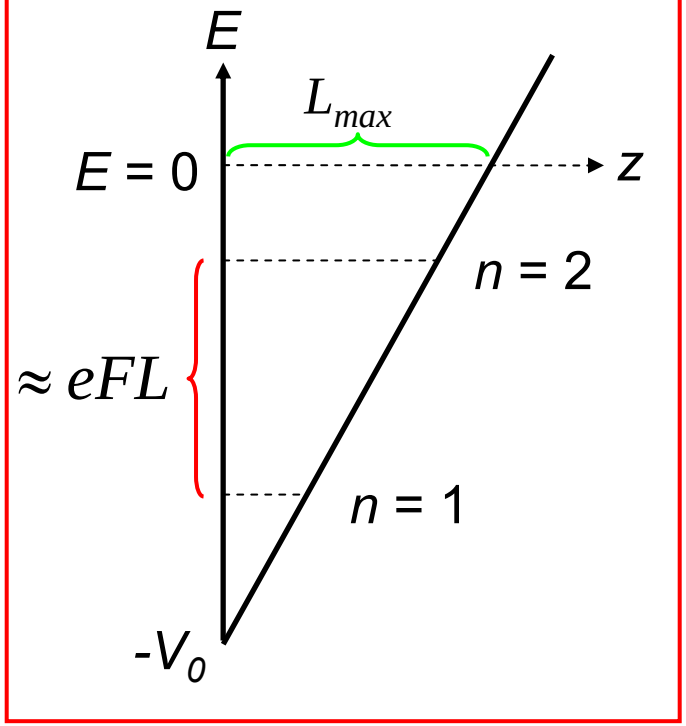
AFSS *et al*, Nature **469**, 189-193 (2011)

Confinement potential and size of 2DEG:

T. Ando, A. B. Fowler, and F. Stern, *Rev. Mod. Phys.* **54**, 437-672 (1982).

$$E_n = -V_0 + \left(\frac{\hbar^2}{2m_z^*}\right)^{1/3}\left[\left(\frac{3\pi}{2}\right)\left(n-\frac{1}{4}\right)eF\right]^{2/3}$$

$$V(z) = -V_0 + eFz$$



$\Delta E = E_2(d_{xz}) - E_1(d_{xz}) = 120$ meV

$m_L^* = 0.7m_e \quad m_H^* \approx 20m_e$

→ $F \approx 83$ MV/m

$E_1(d_{xy}) = -210$ meV → $V_0 \approx 260$ meV

$eFL \approx \Delta E \rightarrow L \approx 14.5$ Å ≈ 4 u.c.

$eFL_{max} = V_0 \rightarrow L_{max} \approx 31$ Å ≈ 8 u.c.

4 u.c. ≤ L ≤ 8 u.c.

Carrier density from confinement potential:

- K. Ueno *et al.*, *Nature Mater.* **7**, 855 (2008).
- R. C Neville, B. Hoeneisen, and C. A. Mead. *J. Appl. Phys.* **43**, 2124 (1972).

$$\frac{e}{2} n_{2D} = \int_0^F \varepsilon_0 \varepsilon(F') dF'$$

$$\varepsilon(F) = \frac{1}{A + BF}$$

F [V/m]

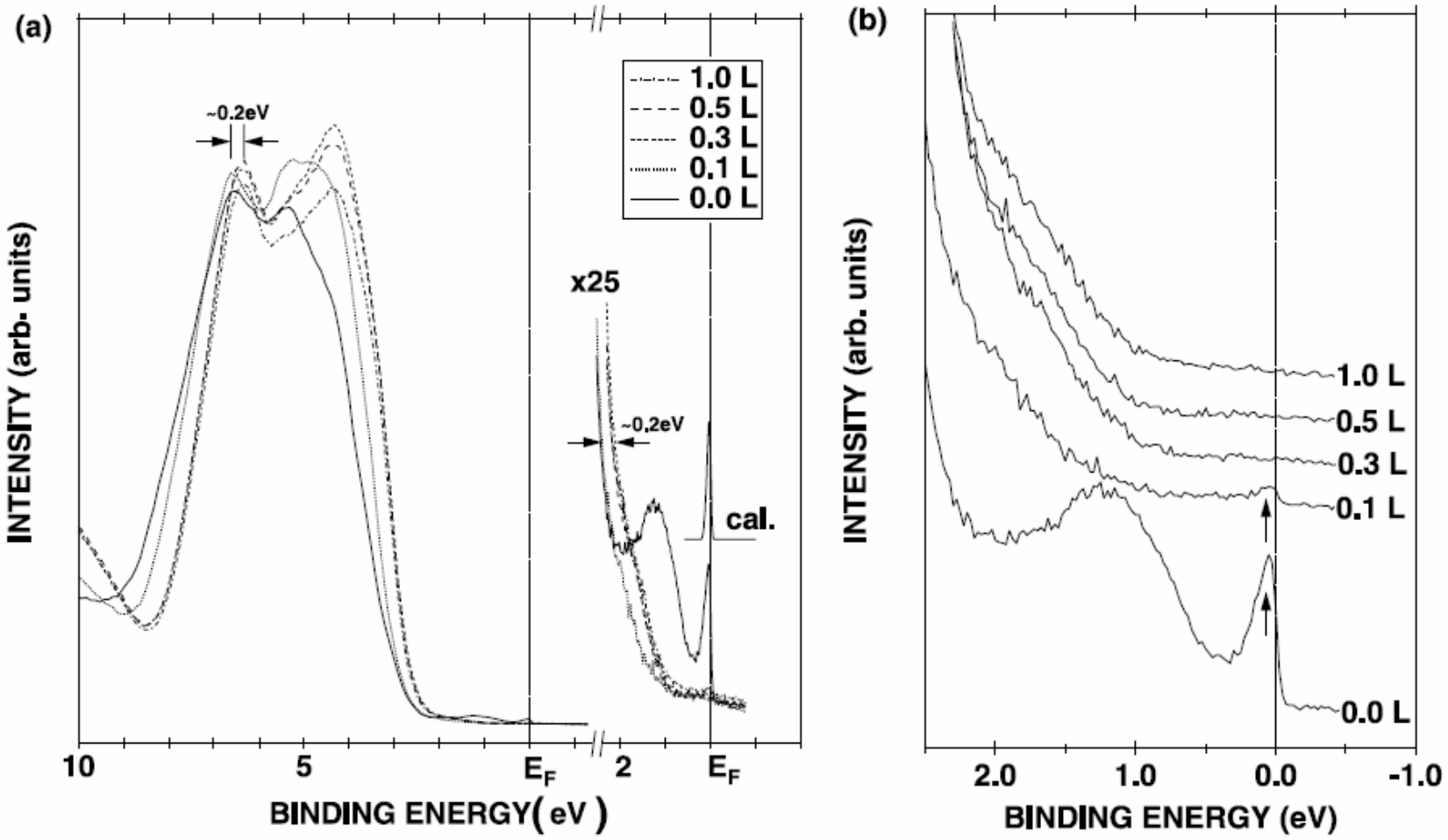
$A(4\text{K}) = 4.097 \times 10^{-5}$

$B(4\text{K}) = 4.907 \times 10^{-10}$ m/V

→ $n_{2D} \approx 0.25\ e/a^2$

Valence band bending due to O-vacancies at the vacuum-fractured surface of STO

Y. Aiura *et al.*, Surface Science **515**, 61-74 (2002)



Conclusions

→ Observation of subband structure with orbital ordering at the bare surface of STO.

→ Universal metallic 2DEG. Exists even at the surface of non-doped, bulk-insulating STO!

→ Characteristics of this 2DEG in quantitative agreement with 2DEGs in STO-based interfaces/heterostructures.

→ Origin of the observed 2DEG: oxygen vacancies.