Reconstruction-induced multiple gaps in surface bands of Au(111) vicinal surfaces and nanostructures : from weak to strong coupling limit

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CORPES 2007, April 23-27, MPI-Dresden (Germany)

Surface and Spectroscopies group in Nancy (SUSPECT)

Elaboration, characterization and study of electronic properties of ultra-thin films and nano-structures

$\Rightarrow$ **control and study simple or more complex model systems at surface**

<u>surface sensitive probe(s) :</u>

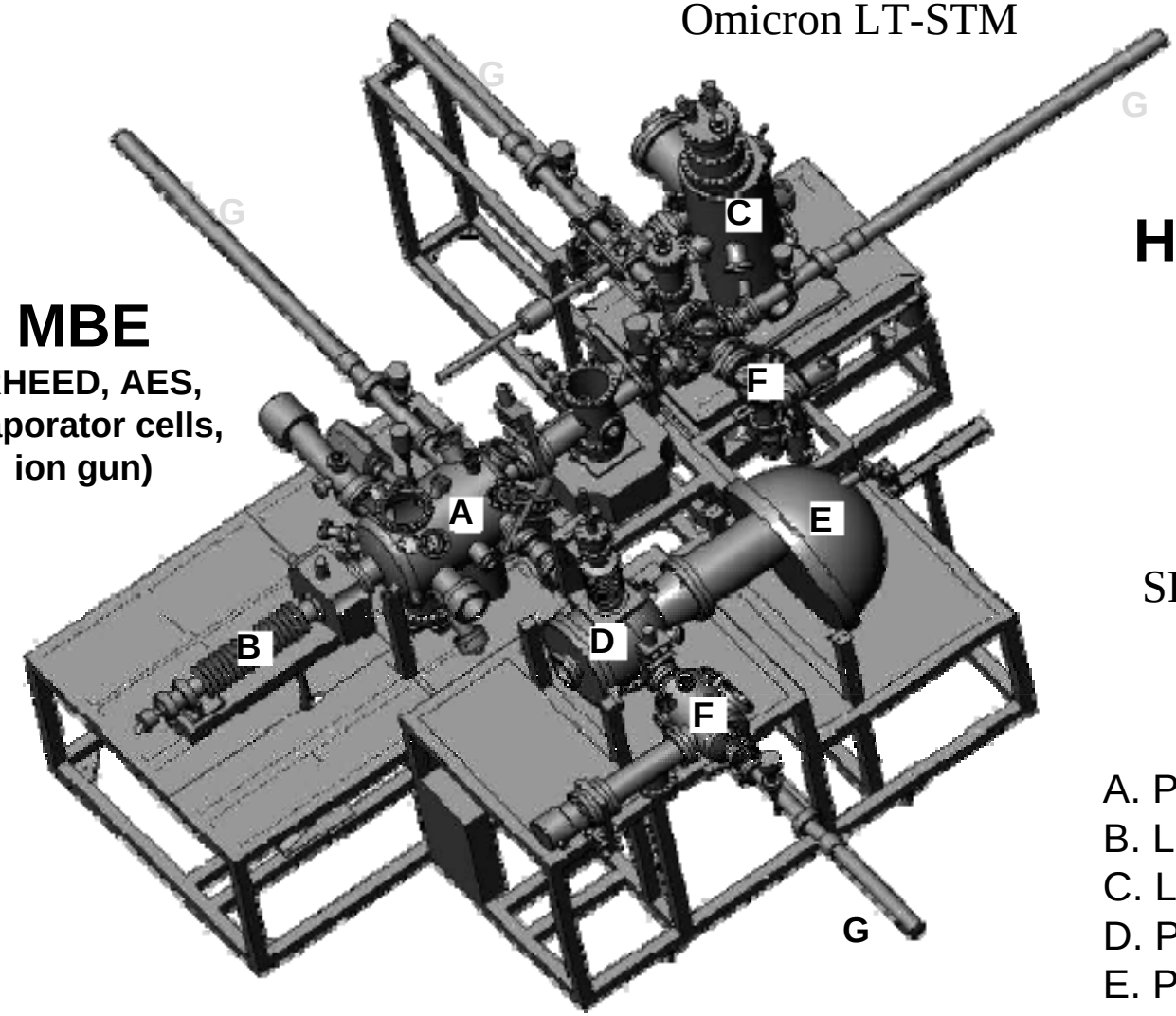
$\rightarrow$ ARPES : band structure E(k)

$\rightarrow$ STM/STS : local density of states (LDOS cartography)

Experimental set-up

5K STM/STS

Omicron LT-STM



MBE

(RHEED, AES, evaporator cells, ion gun)

High resolution ARPES

$\Delta\theta$<0.2° - ΔE<5 meV
T=14 K

SCIENTA SES-200

SPECS UVS 300 source

A. Preparation chamber
B. Linear translator
C. LT-STM chamber
D. Photoemission chamber
E. Photoelectrons Analyzer
F. Load lock
G. Sample transfert

→ Introduction : surface state spin-orbit splitting in Ag/Au(111)

PHD : H. Cercellier

→ Quasi-1D (nearly) free electrons in artificial periodic potential on Au(111) vicinal surfaces

PHD : C. Didiot

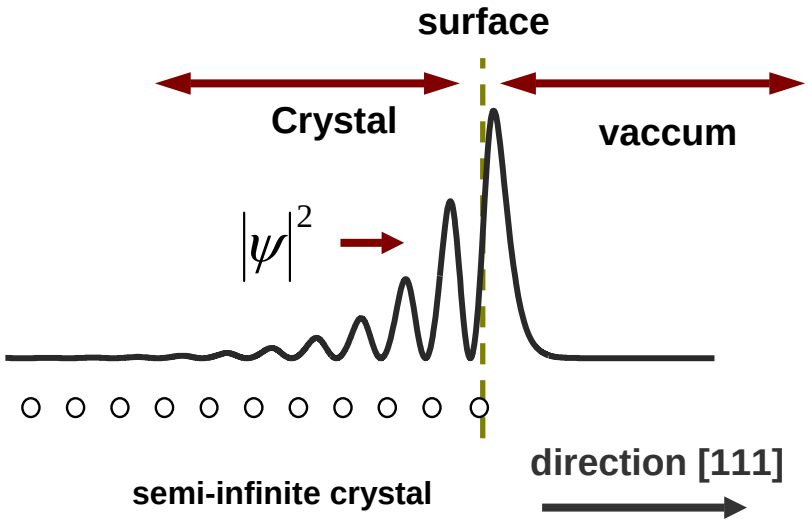
- Au(23 23 21)
- Au(788)

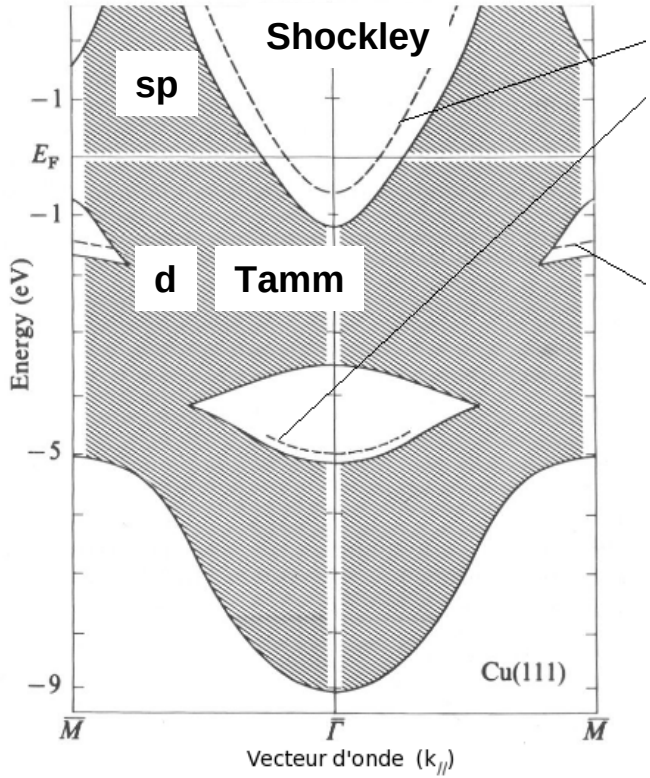
→ From nearly free electron behavior to strong confinement in self-organized nanostructures

PHD : C. Didiot

- Co on Au(788)
- Ag on Au(788) and Au(232321)

Shockley states in noble metals : Au(111), Ag(111) et Cu(111)





- Model system for 2D electron gas
- Strongly surface-type dependent

⇒ **Sensitive to adsorption, reconstruction, growth and catalysis etc…**

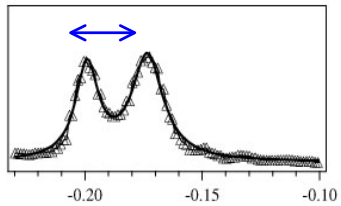
…But weakly interacting electrons !!!

Shockley state in Au(111)

$$\Delta k_{SO} = \frac{2\alpha_R m^*}{\hbar}$$

$\Delta k_{//}$ =0.023 Å^{-1}

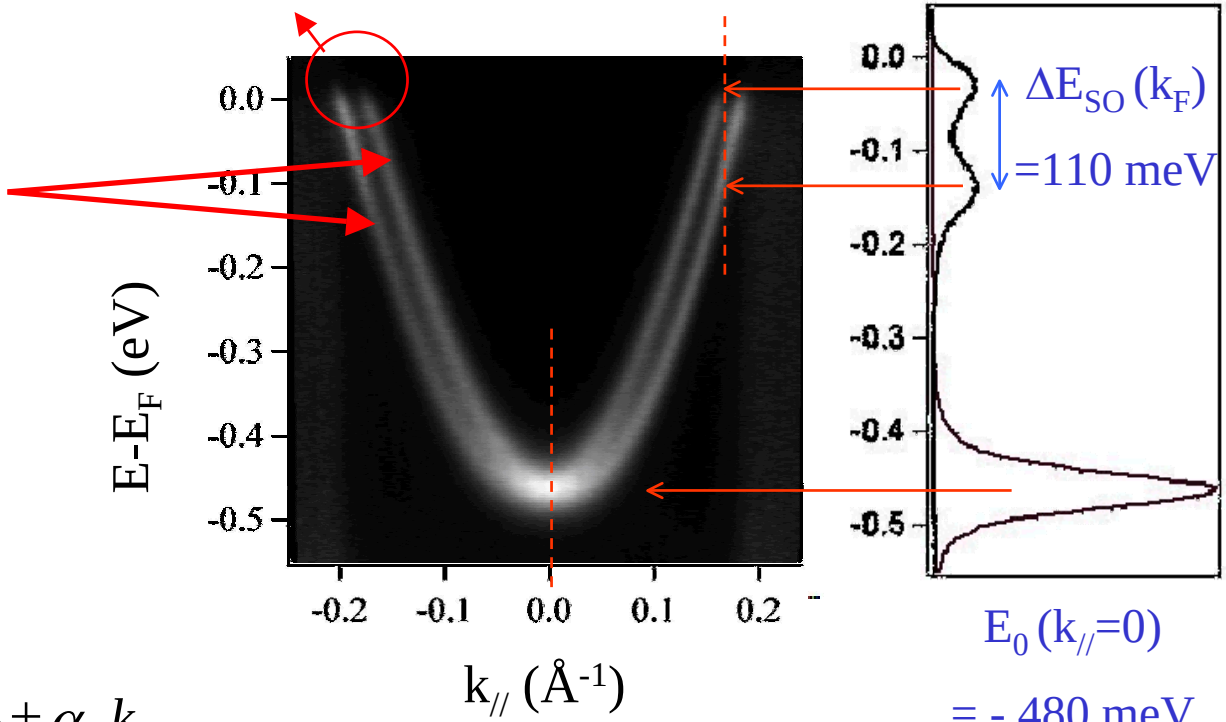
MDC (E=E$_F$)



EDC (k=0 et k=k$_F$[1])

Spin-orbit splitted surface state

Lashell et al., PRL 77, 3419 (96)



$$E(k_{//}) = E_0 + \frac{\hbar^2 k_{//}^2}{2m^*} \pm \alpha_R k_{//}$$

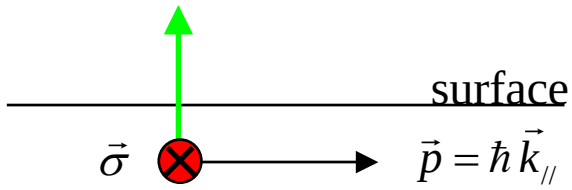
2 k-splitted parabolic bands

Rashba effect (spin-orbit coupling at surface)

E.I. Rashba et al., Sov. Phys. Solid State 2, 1109 (1960)

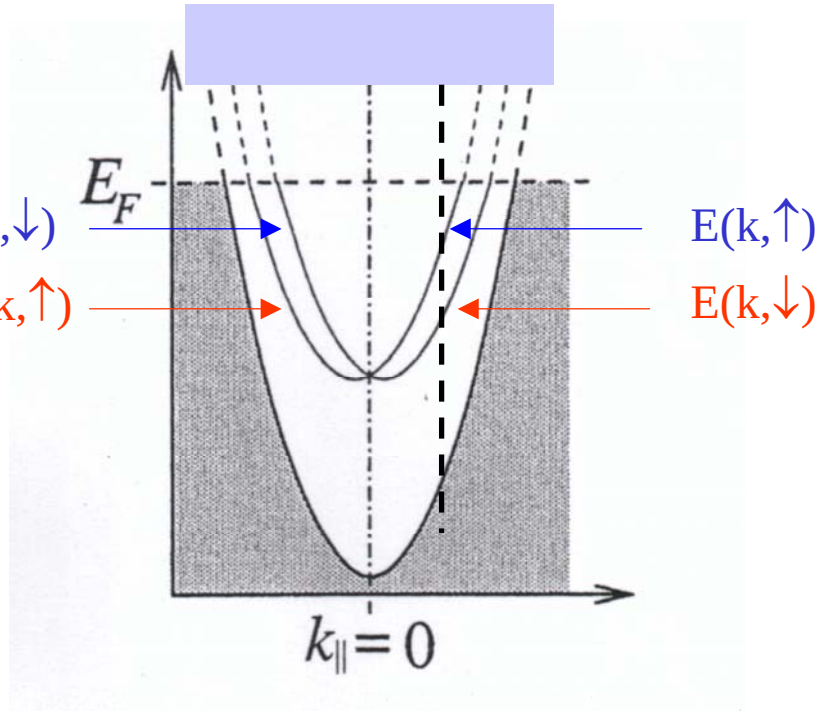
$$H_{so} = \frac{\hbar}{4m^2c^2}(\vec{\nabla} V \wedge \vec{p}).\vec{\sigma}$$

$$\vec{\nabla} V = \frac{dV}{dz}\vec{e}_z$$



-Inversion symetry is broken

-Time reversal symetry is conserved



⇒ 100% spin-polarized sub-bands

Munstwiller *et al., JESRP, 137, 119 (04)*

$$\alpha_R \propto \gamma_{at} \frac{dV}{dz}$$

Atomic SOC

Electric field gradient through the surface

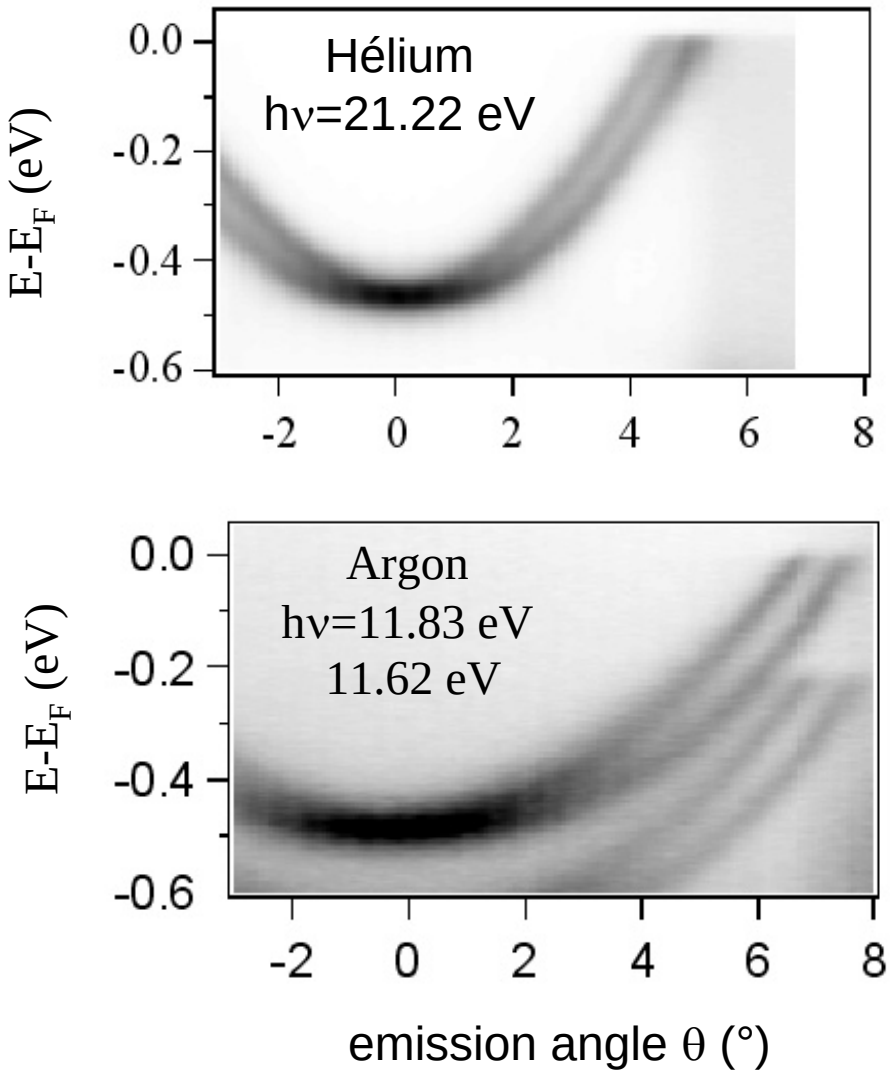
Pedersen and Hedegaard (2000)

High resolution ARPES on Au(111) surface state - T ≈ 90 K

$k_{//}$ conservation through the surface

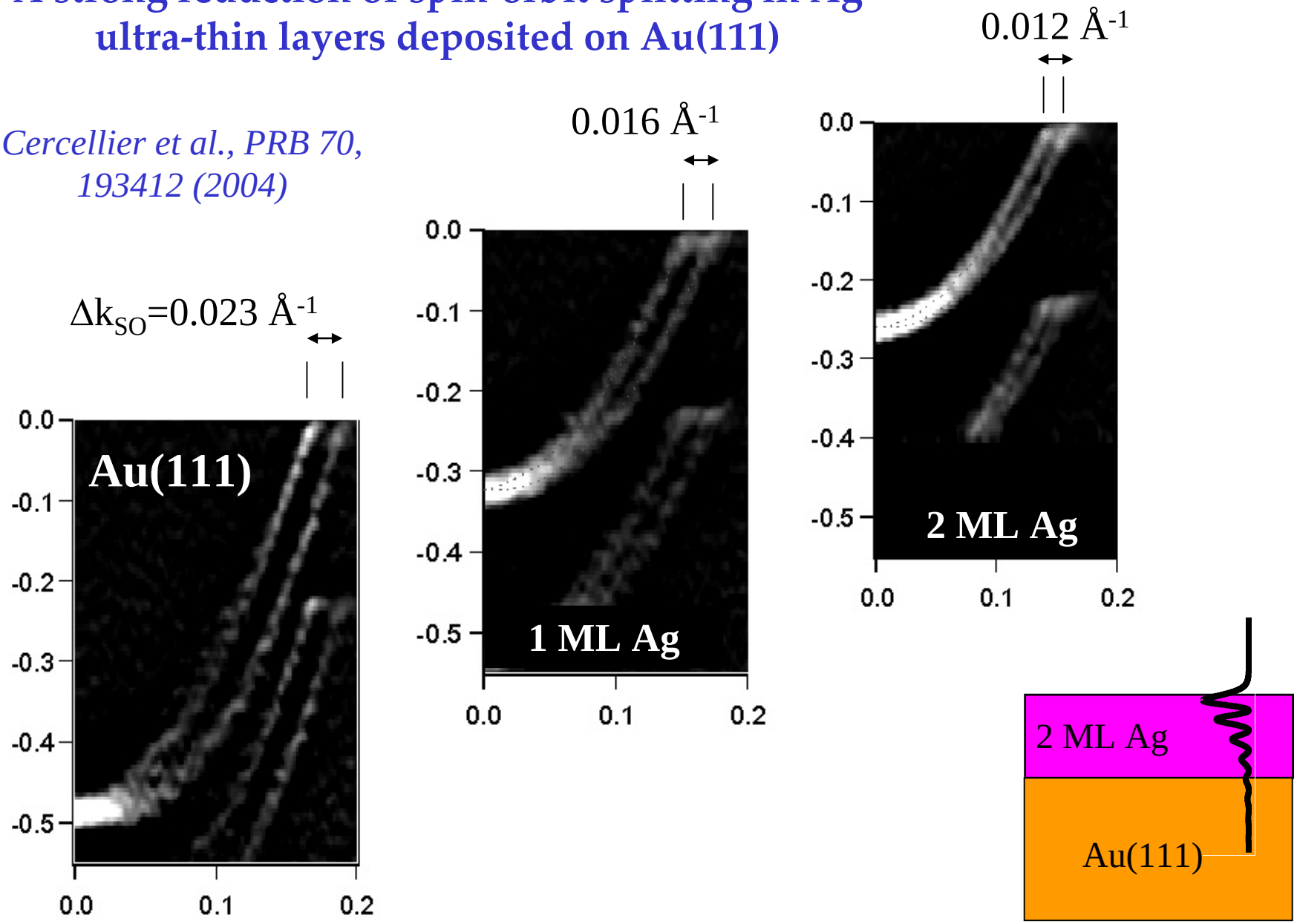
$$k_{//} = \sin(\theta)\sqrt{\frac{2m}{\hbar^2}E_c}$$

$\Rightarrow$ increase of $k_{//}$ resolution at low energy for a fixed angular resolution !

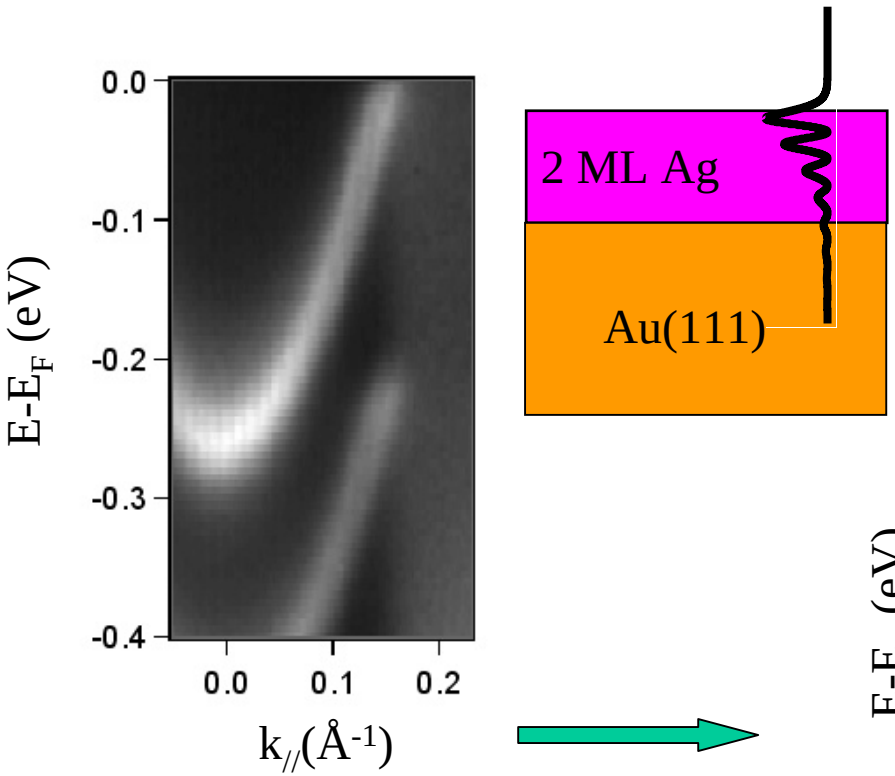


A strong reduction of spin-orbit splitting in Ag ultra-thin layers deposited on Au(111)

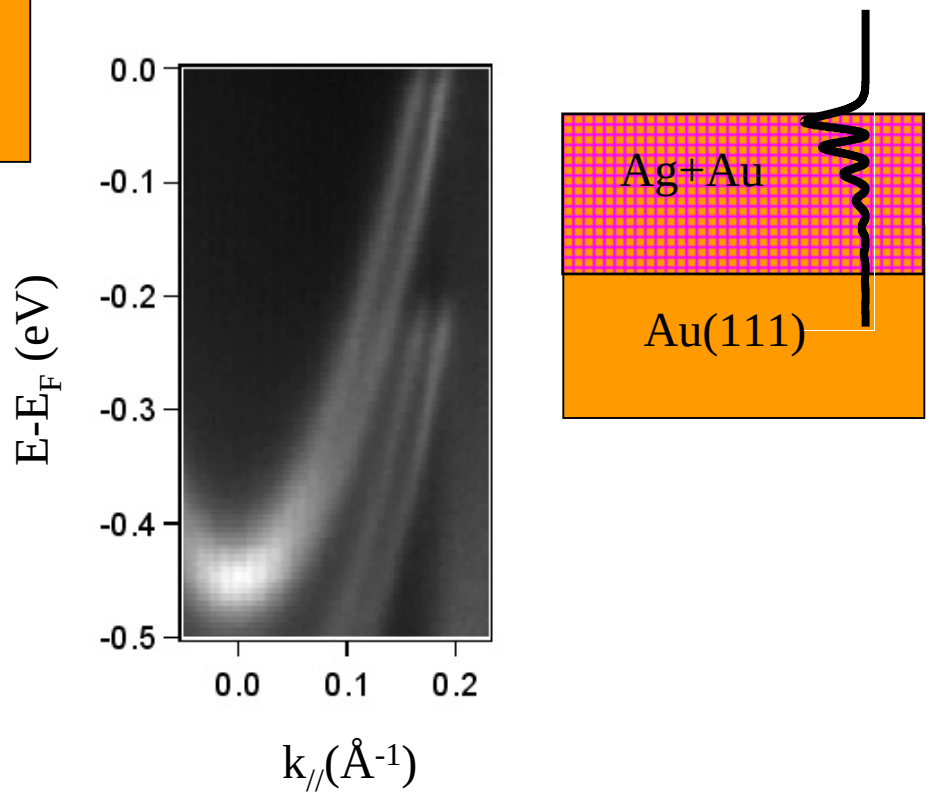
Cercellier et al., PRB 70, 193412 (2004)



Increase of spin-orbit splitting in $Ag_{1-x}Au_x$ alloys



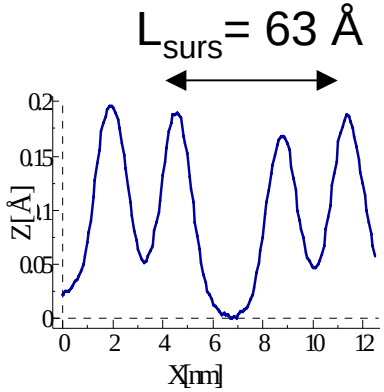
2 ML Ag/Au(111) annealing at T=230°C during 1 mn



Cercellier et al., PRB 73, 195413 (2006)

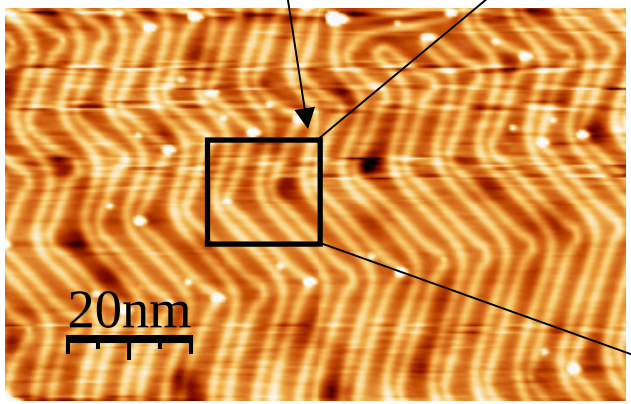
Cf. Giant spin-splitting in Pb,Bi/Ag(111) - talk M. Grioni - C. Ast et al., PRB (2006)

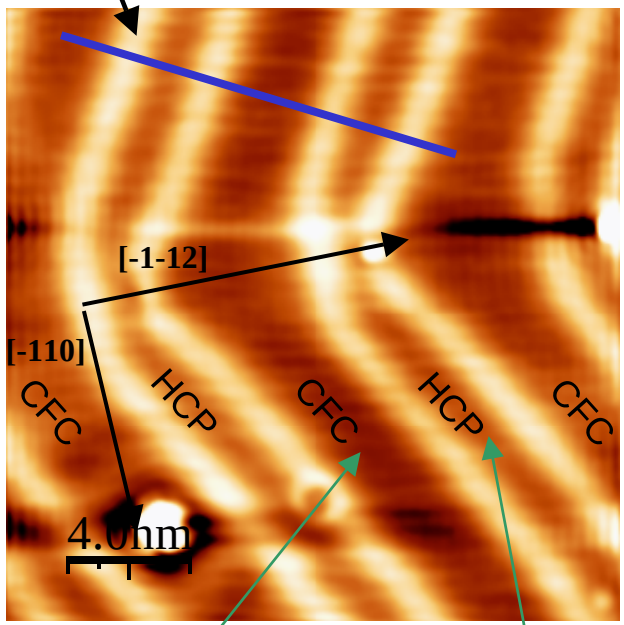
STM on Au(111) surface



Stacking faults

Herringbone surface
Reconstruction 22x√3





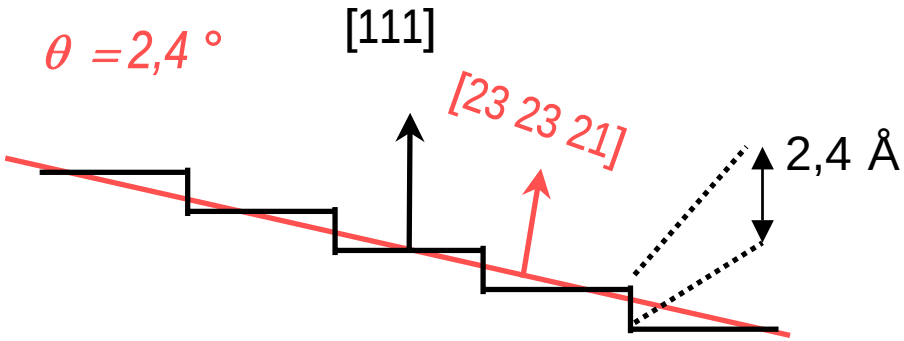
fcc
(ABCABC…)

hcp
(ABABAB…)

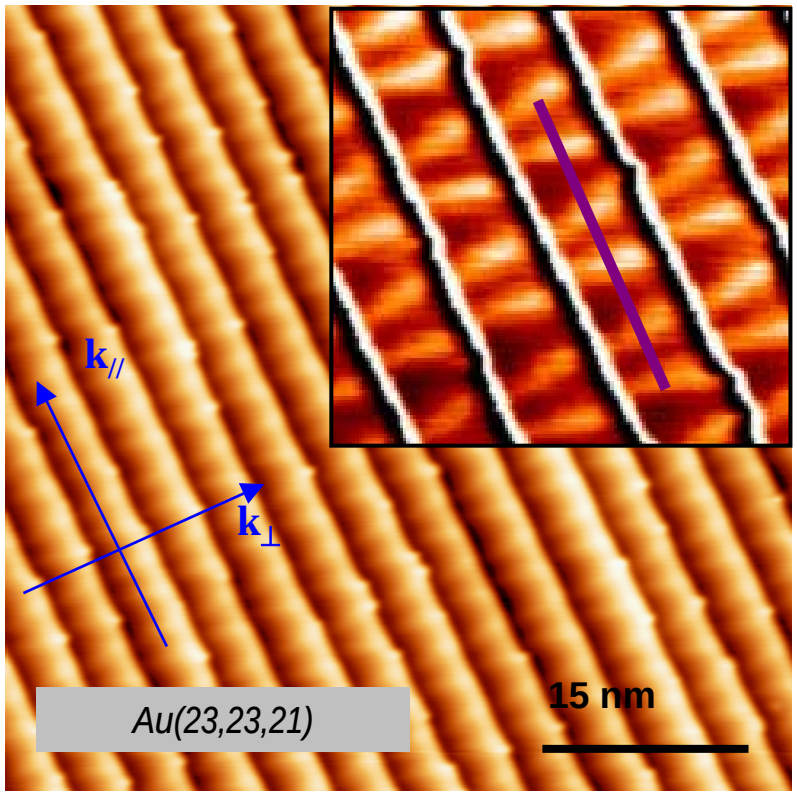
Harten et al., PRL 54 , 2619 (1985)

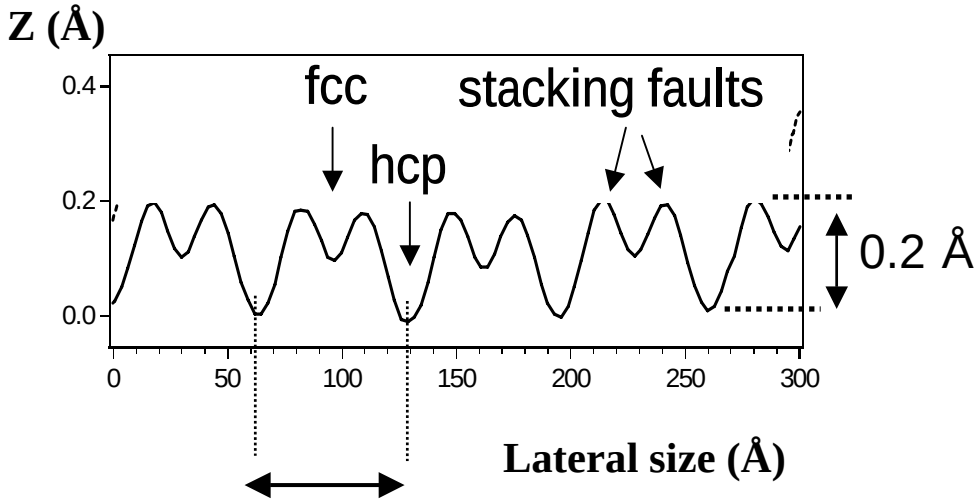
Barth et al., PRB 42 , 9307 (1990)

Au(111) vicinal surfaces



⇒ anisotropic nano-textured surface(s)



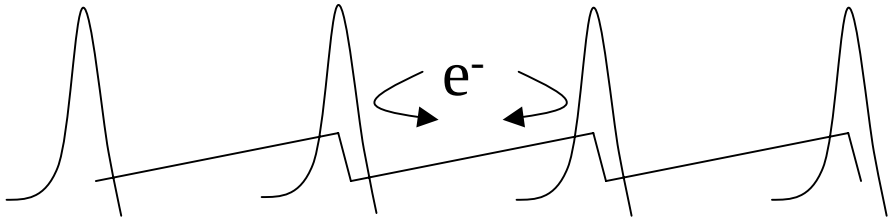


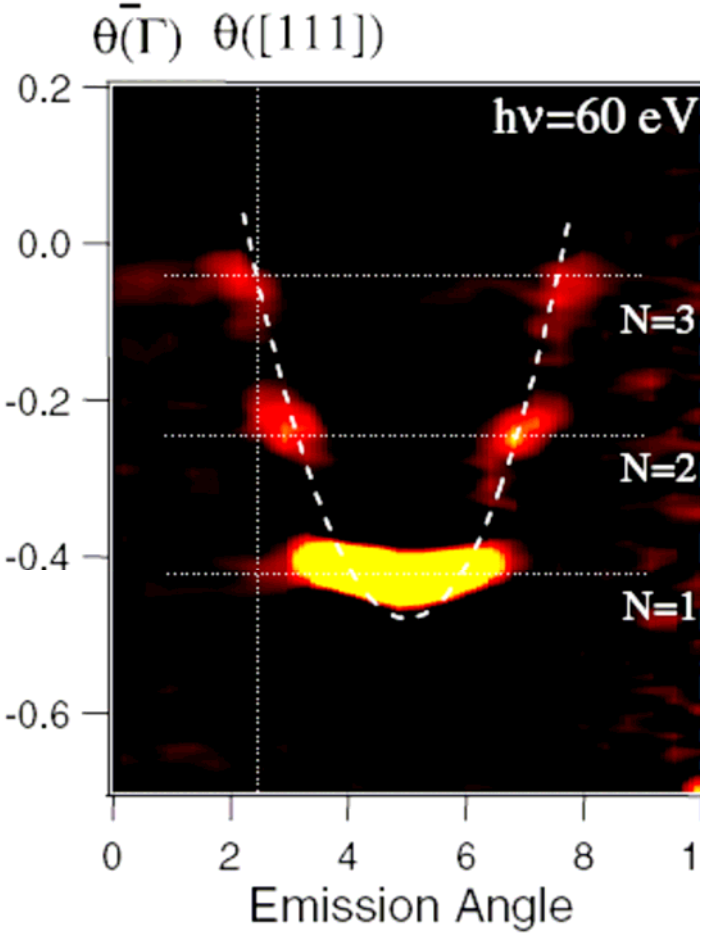
$L_{terrace} = (56 \pm 9)$ Å

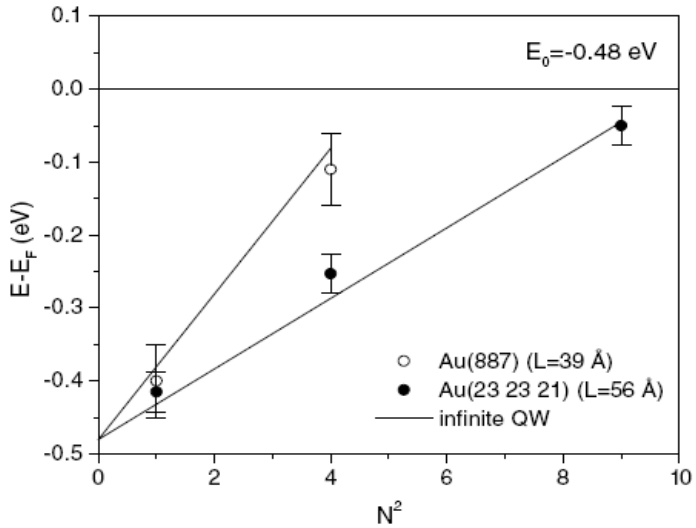
$L_{232321} = (65 \pm 5)$ Å

Au(232321) : the prototype for step-induced nearly infinite quantum well states

Steps = (nearly) infinite potential barrier







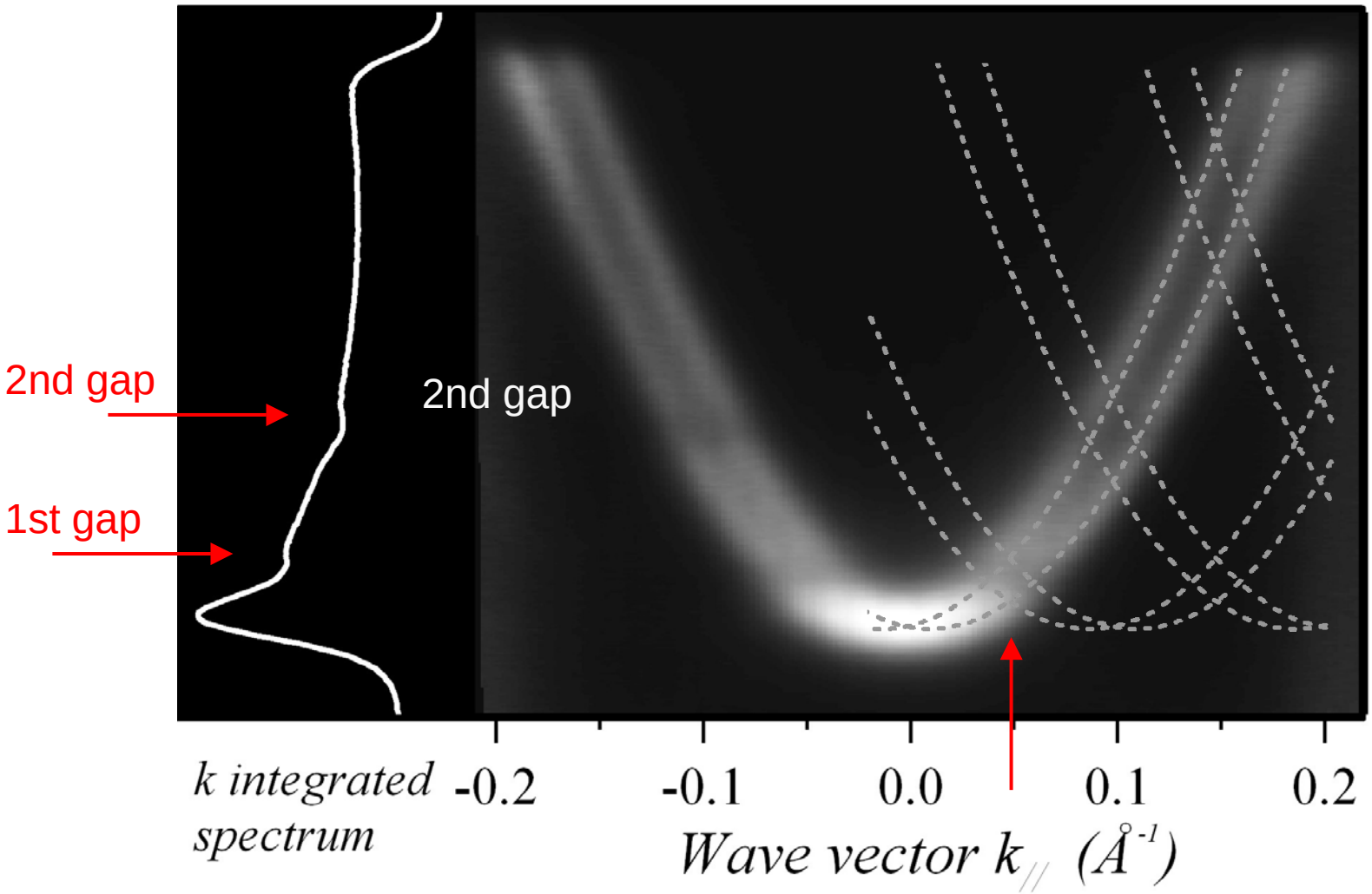
$$E - E_F = E_0 + \frac{\hbar^2}{2m^*}\left[k_{//}^2 + \left(\frac{N\pi}{L}\right)^2\right]$$

$k_\perp = N\pi/L_{terrace}$

Mugarza et al., PRL 87, 107601 (2001)

Surface state dispersion $E(k_{//})$ along terraces on Au(23 23 21)

ARPES intensity map – T=90 K



C. Didiot et al., PRB 74, 081404, Rap. Comm. (2006)

$k_{crossing} = 0.048\ Å^{-1} = \pi / L_{232321}$

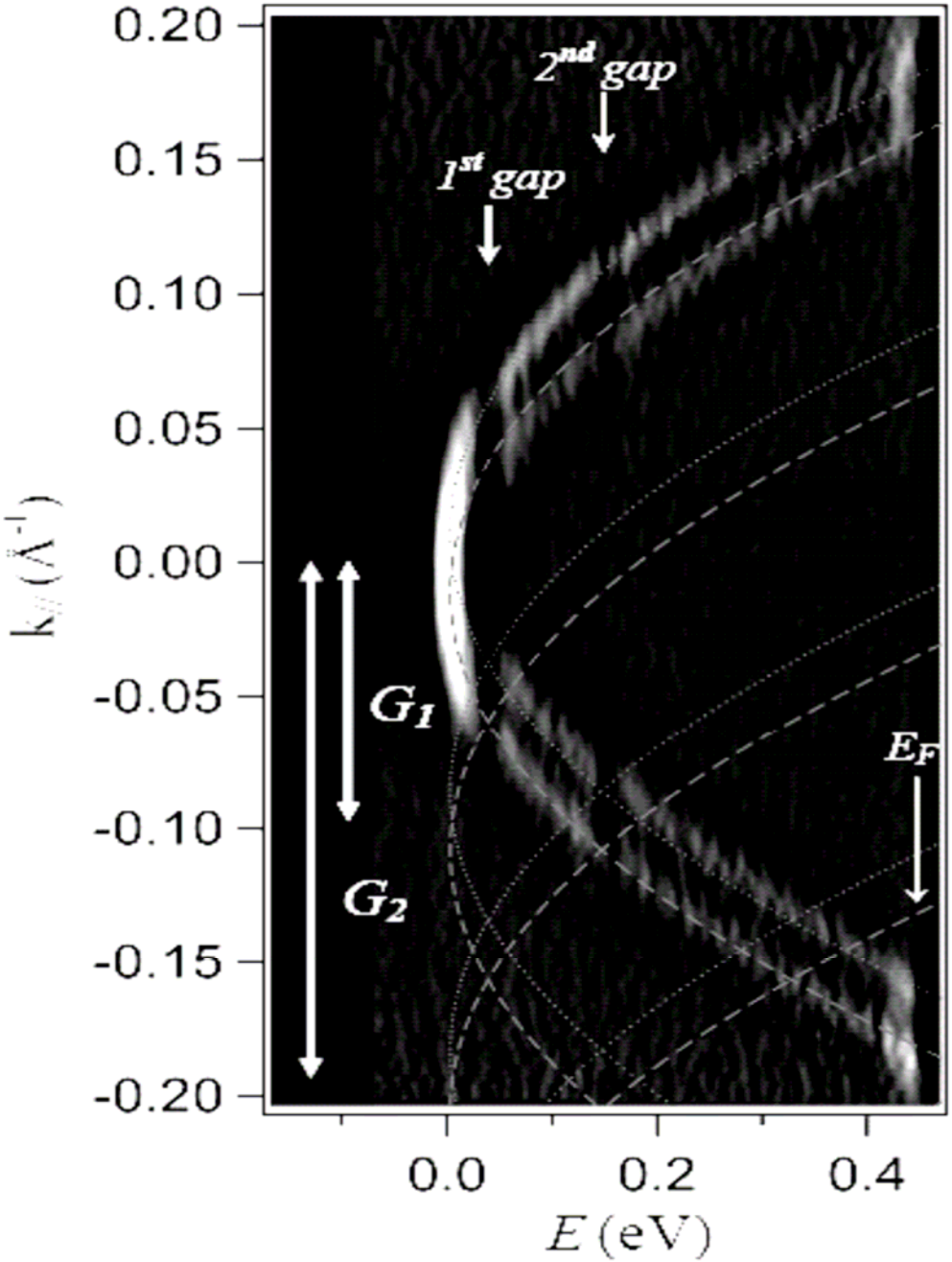
ARPES

- evidence of 2 gaps in the spin-orbit bands at 45 meV and 145 meV.

- k values correspond to $\frac{2\pi}{L_{232321}} \times n$

-Very weak intensity in the folded bands

- only two gaps are clearly seen



The nearly free electrons in the two bands model

Solid state physics book : Kittel, Ashcroft&Mermin…

- Fourier decomposition of the periodic potential

$$V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}}\ e^{i\vec{G}\cdot\vec{r}}$$

- Bloch wave function

$$|\Psi_{\vec{k}}\rangle = \sum_{\vec{G}}\ C_{\vec{k}+\vec{G}}\ |\vec{k}+\vec{G}\rangle$$

- Energy is periodic in k-space

$$E_{\vec{k}} = E_{\vec{k}+\vec{G}}$$

$\Rightarrow$ solve the Schrödinger equation in k-space

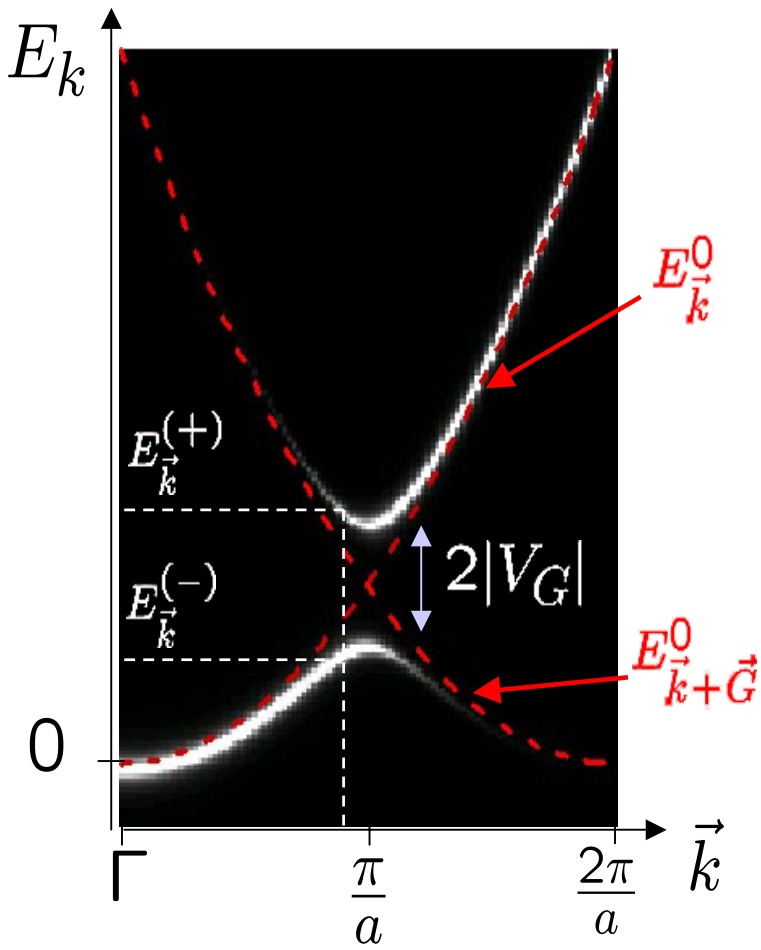
(1st order perturbation theory)

Bragg diffraction of electronic waves at k =N π/a ⇒ band folding

Two bands model

$$E_{\vec{k}}^{(\pm)} = \frac{1}{2}(E_{\vec{k}}^{0} + E_{\vec{k}+\vec{G}}^{0}) \pm \frac{1}{2}\sqrt{(E_{\vec{k}}^{0} - E_{\vec{k}+\vec{G}}^{0})^2 + 4|V_{\vec{G}}|^2}$$

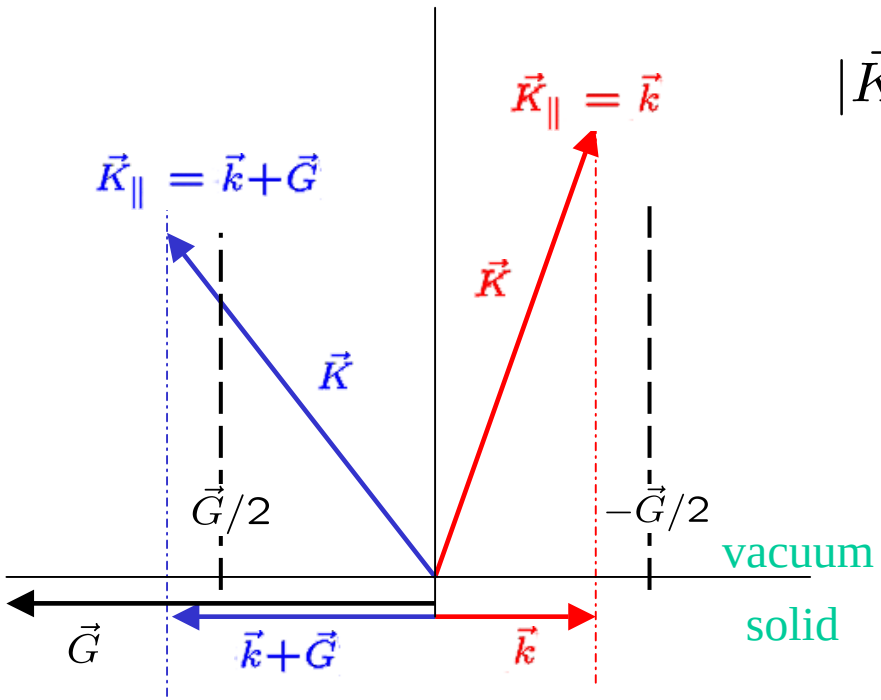
$$|\Psi_{\vec{k}}^{(\pm)}\rangle = C_{\vec{k}}^{(\pm)}|\vec{k}\rangle + C_{\vec{k}+\vec{G}}^{(\pm)}|\vec{k}+\vec{G}\rangle$$



⇒ Energy gap at k=Nπ/a prop. To the N_{th} Fourier component of the perturbative potential :

$$E_g \propto 2V_g$$

…but the ARPES spectral weight is not periodic !



Spect. weight

$$|\vec{K}_{\parallel}\rangle = \begin{cases} |\vec{k}\rangle \rightarrow |C^{(\pm)}_{\vec{k}}|^2 \\ |\vec{k}+\vec{G}\rangle \rightarrow |C^{(\pm)}_{\vec{k}+\vec{G}}|^2 \end{cases}$$

$\Rightarrow$ the ratio between the two component k and k+G of the wave function can be calculated :

- as function of the k-location in the 1st or 2nd Brillouin zone

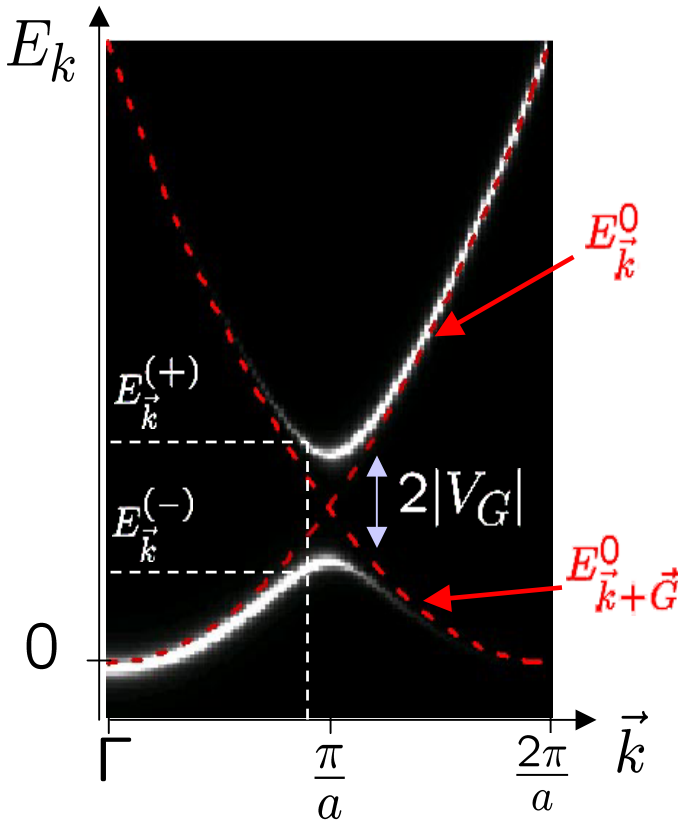
- as function of V_G

$$\frac{C^{(\pm)}_{\vec{k}}}{C^{(\pm)}_{\vec{k}+\vec{G}}} = \frac{-2V_{\vec{G}}}{(E^0_{\vec{k}} - E^0_{\vec{k}+\vec{G}}) \mp \sqrt{(E^0_{\vec{k}} - E^0_{\vec{k}+\vec{G}})^2 + 4|V_{\vec{G}}|^2}}$$

$$E_{\vec{k}}^{(-)} \approx E_{\vec{k}}^{0}$$

$$|C_{\vec{k}}^{(-)}| >> |C_{\vec{k}+\vec{G}}^{(-)}|$$

Spectral weight
in the first ZB



$$E_{\vec{k}}^{(+)} \approx E_{\vec{k}+\vec{G}}^{0}$$

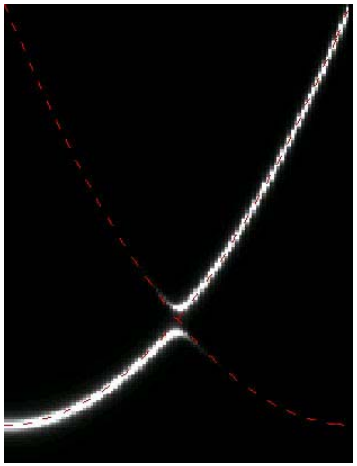
$$|C_{\vec{k}}^{(+)}| << |C_{\vec{k}+\vec{G}}^{(+)}|$$

Spectral weight
In the second ZB

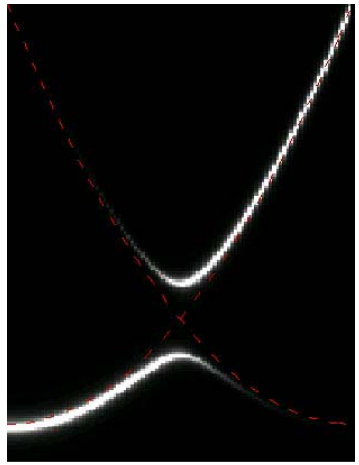
Increasing V_G :

- increase in the gap amplitude
- **more spectral weight in the folded bands**
- slight change in the bottom of the band

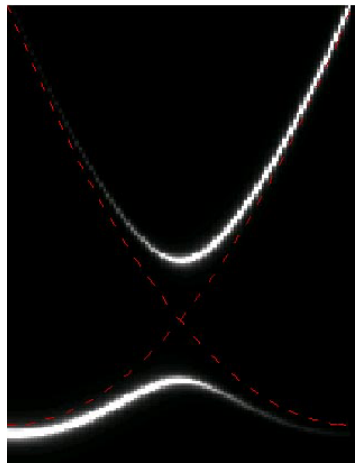
V_G=0.1



V_G=0.3



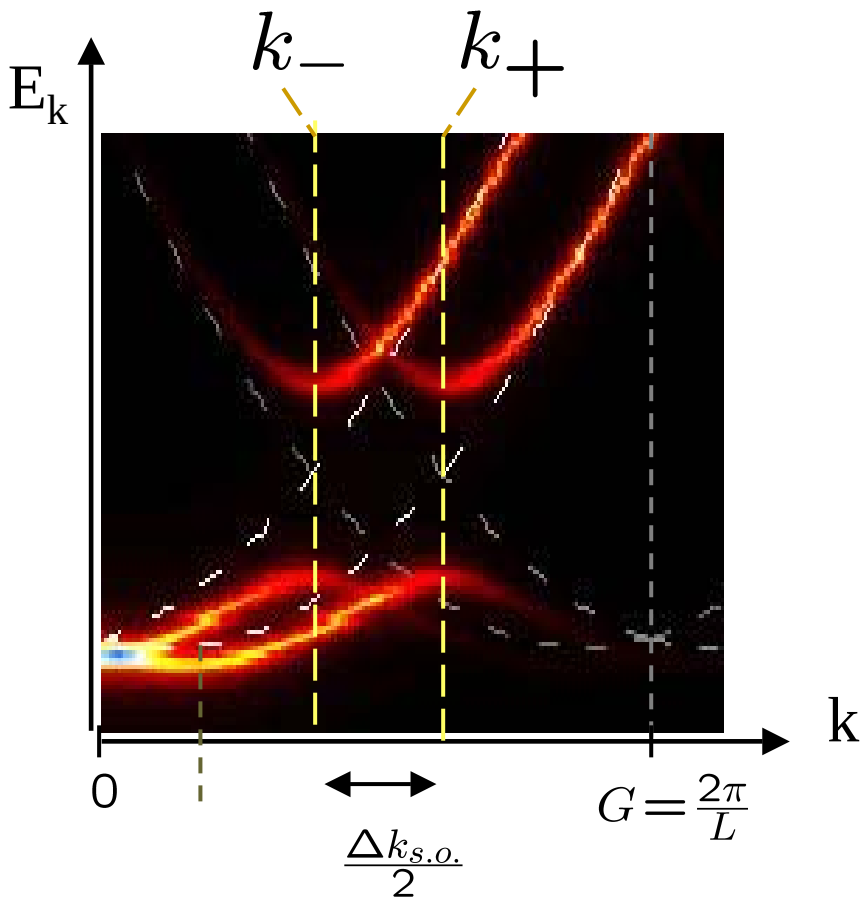
V_G=0.5



V_G=0.9

$\Rightarrow$ from weak to strong coupling Limit

2 identical gaps opened at 2 different k-values (because of SOC)



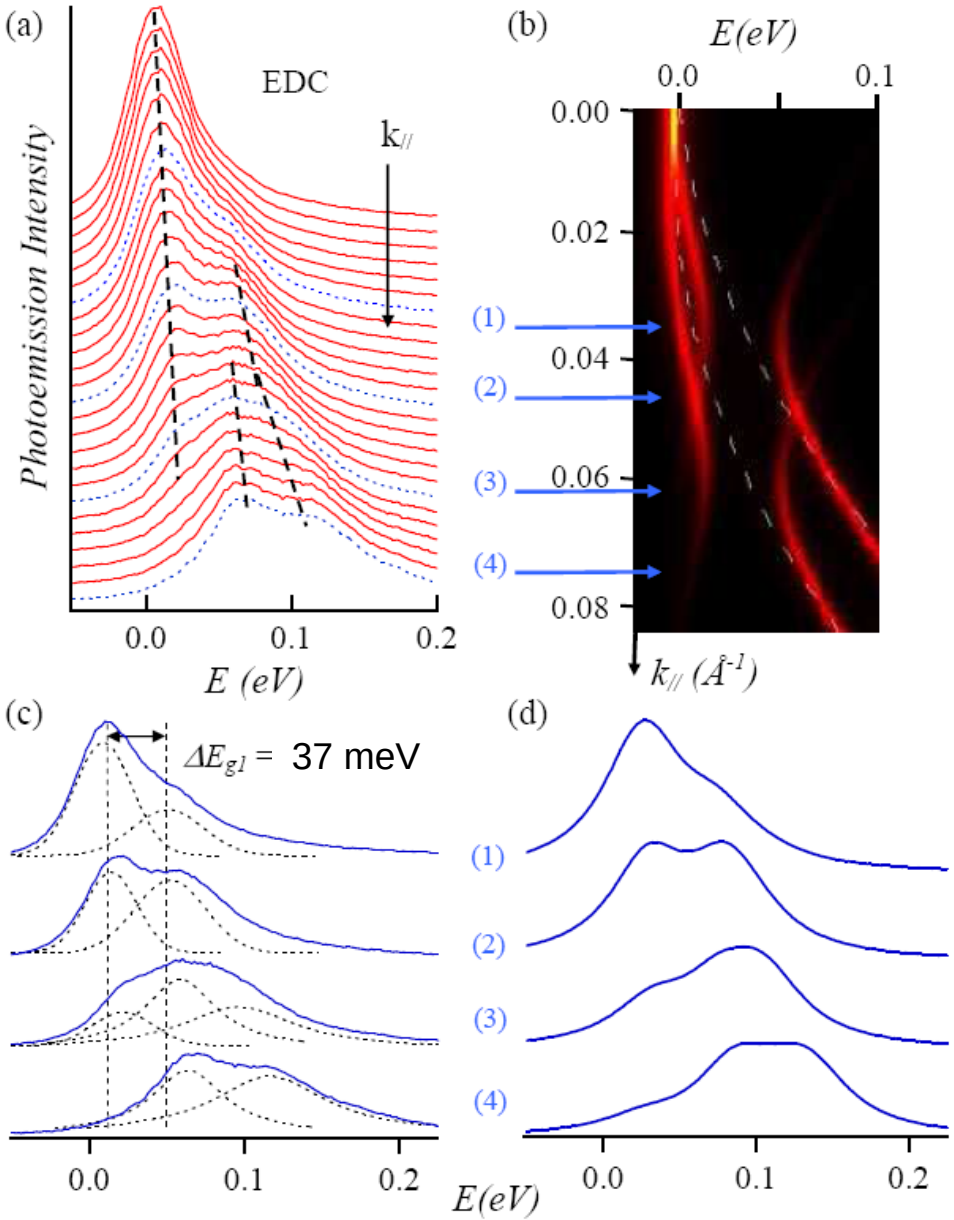
The superpperiodic potential is not spin-dependent !

$\Rightarrow$ Here, the crossings of the spin-orbit bands occur at the same energy for the two spin-splitted bands

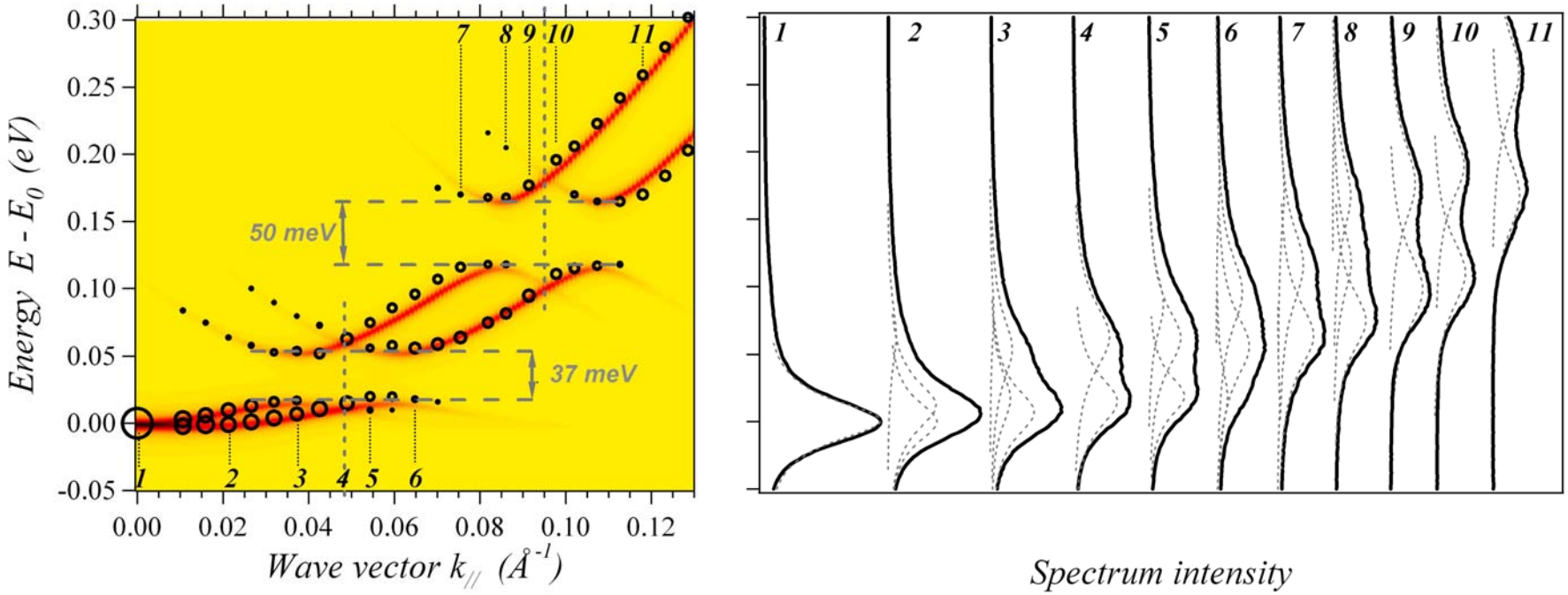
$$k_{\pm} = \frac{\pi}{L} \pm \frac{\Delta k_{s.o.}}{2}$$

1st ARPES gap determination :

E_1= 37 ±5 meV



full determination of E(k) by adjusting experimental EDC's



E_2=50 meV > E_1= 37 $\pm$5 meV

Scanning tunnelling spectroscopy (STS)

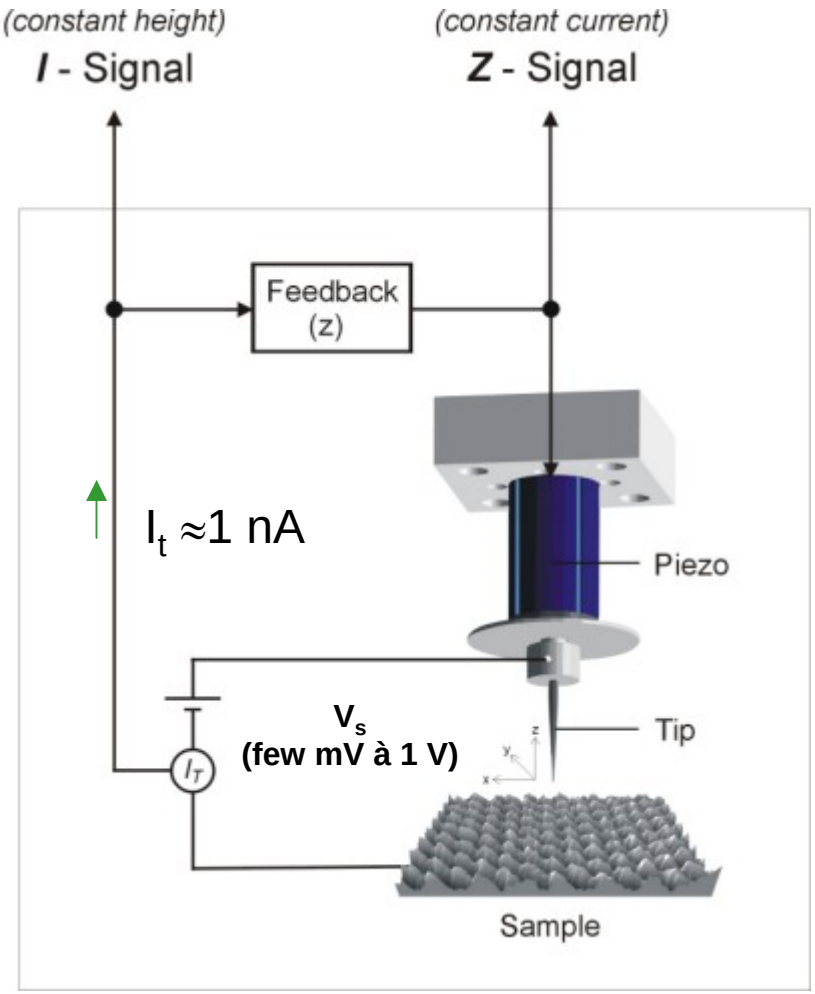
$$I_t \propto \int_{E_F}^{E_F + e \cdot V_{sample}} \rho_{sample}(E) \cdot \rho_{tip}(E - e.V_{sample}) \cdot dE$$

Tunnel conductance

$$\frac{dI_t}{dV}(V_{sample}) \propto \rho_{sample}(E)$$

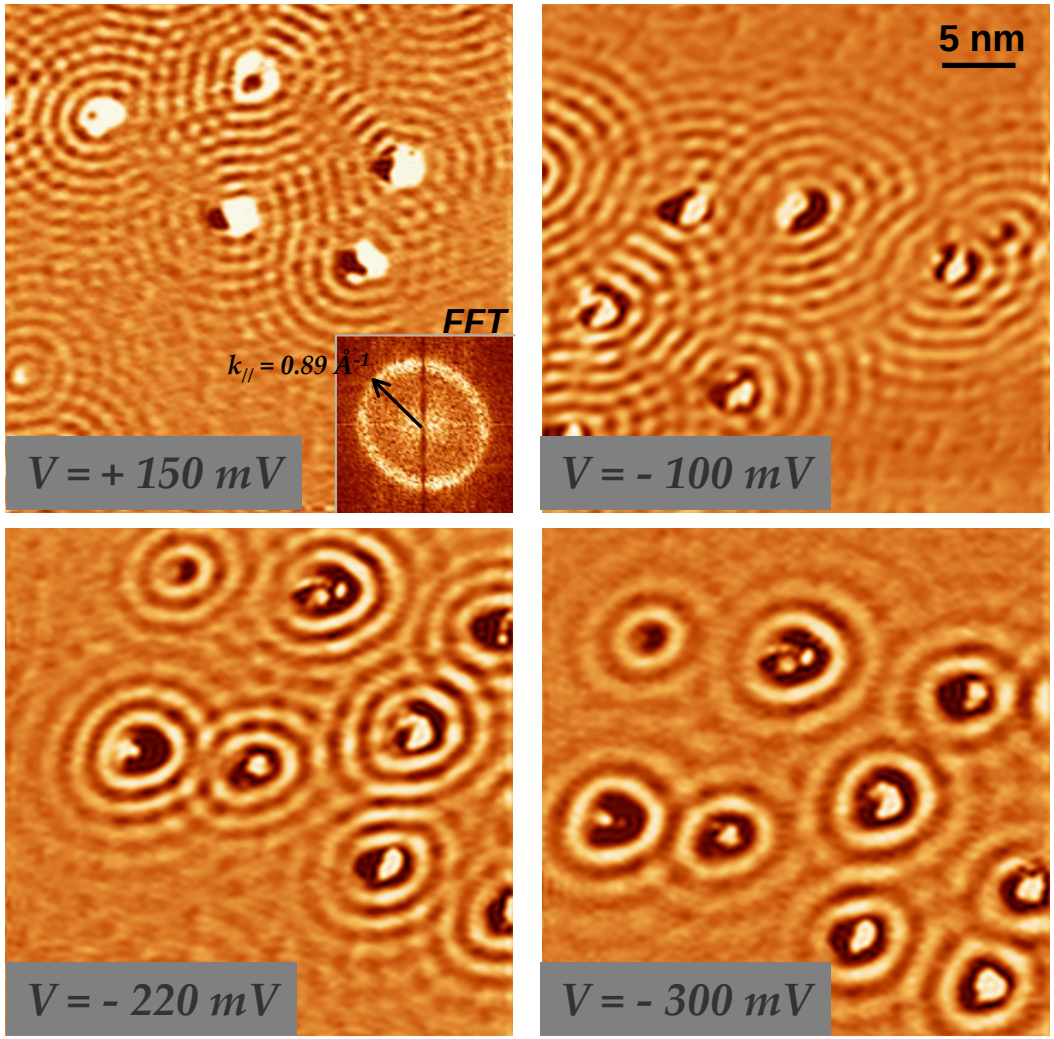
- Spectra : $dI_t/dV_s = f(V_s)$
- Local density of states cartography

  $dI_t/dV_s = f(X,Y)_{Vs}$=LDOS(X,Y)

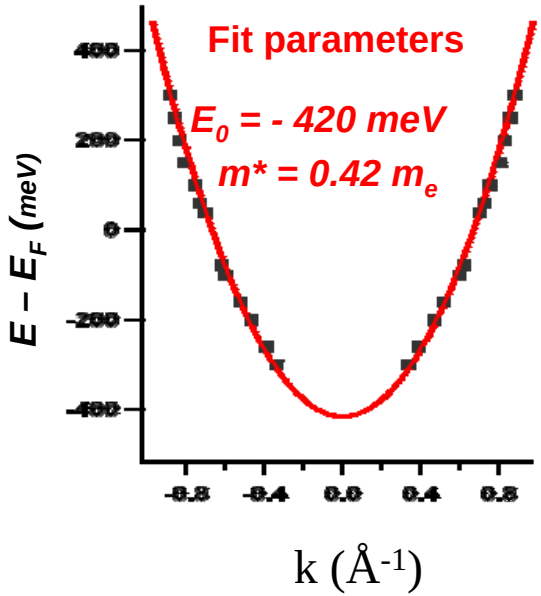


dI/dV(x,y) = LDOS(x,y) at different bias voltages ⇒ standing waves pattern near impurities

Conductance map
(mapping of the surface DOS)



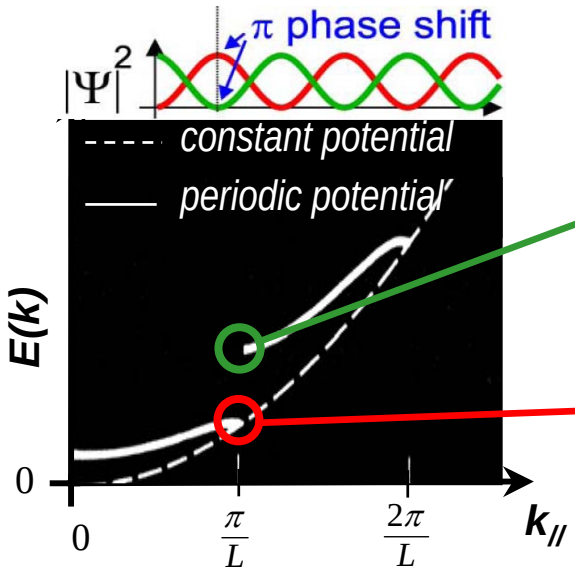
Surface state dispersion
Cu(111) - LT-STM (5K)



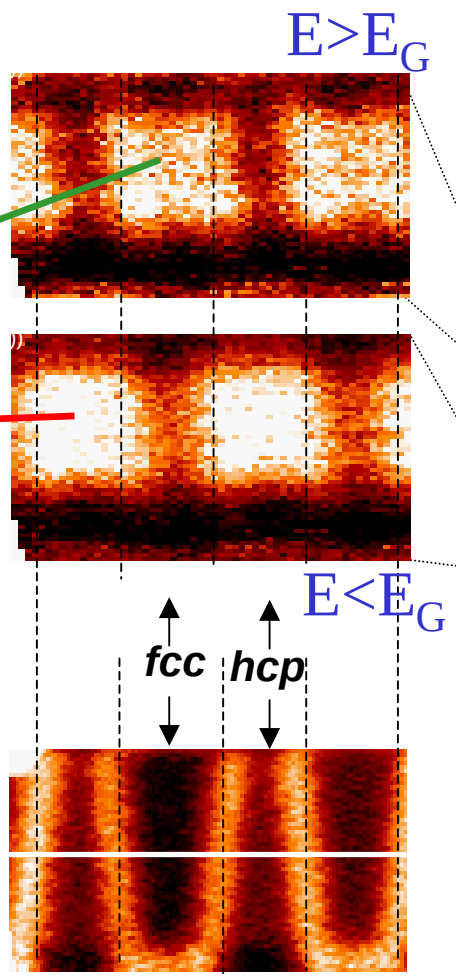
LDOS cartography

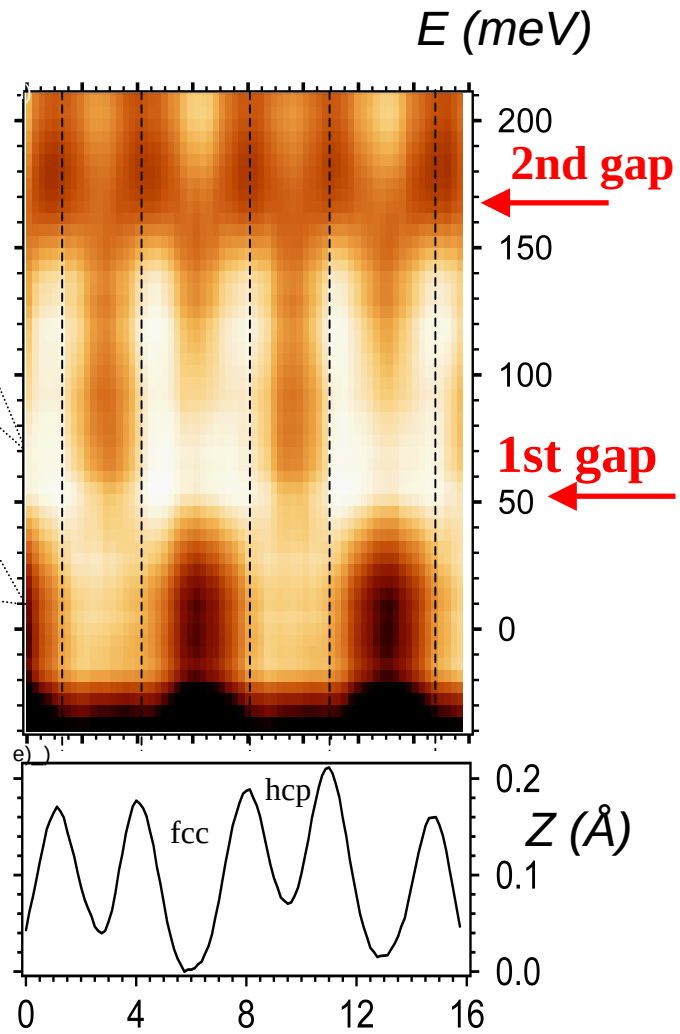
dI/dV (x, y, V)

dI/dV (x, V)

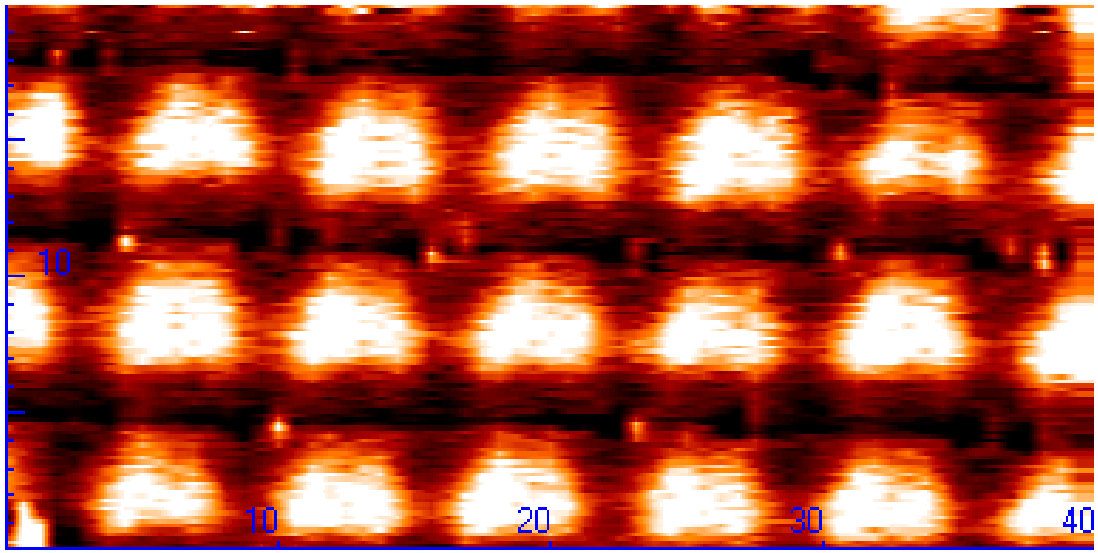


$\Rightarrow$ Phase shift of the wave function localization in the vicinity of the gap(s) !





LDOS(x,y, E = - 440 meV) – 40 nm x 20 nm



A coherent state over a large scale !

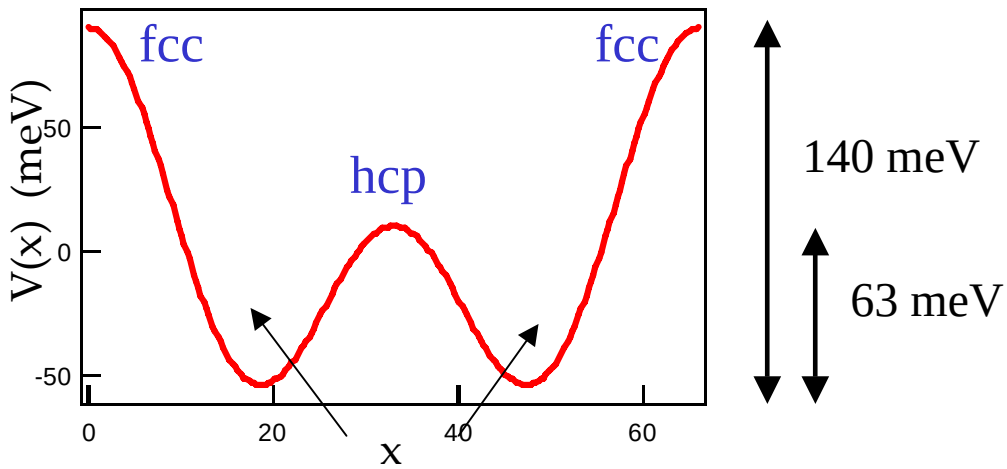
An original method to extract the potential (amplitude + shape)

1- Gap(s) are determined by ARPES $\Rightarrow 2V_{Gi} = E_i$

2- 1D potential is deduced from these gaps, the phase (sign of V_{Gi}) being given by dI/dV maps !

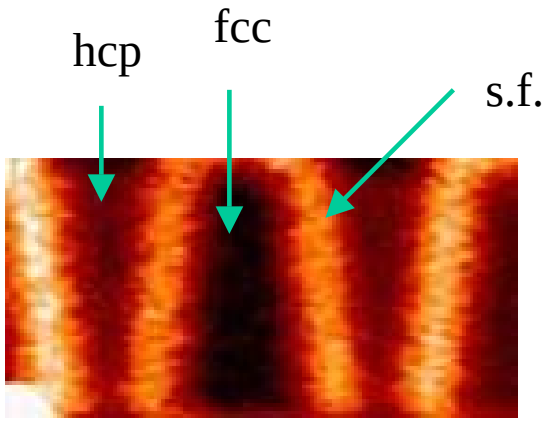
Two Fourier component for V(x) !

$$V(x) = 2V_{G_1}\cos(G_1 x) + 2V_{G_2}\cos(G_2 x)$$



stacking faults

Taking into account the real 2D-potential



$V(x,y)$

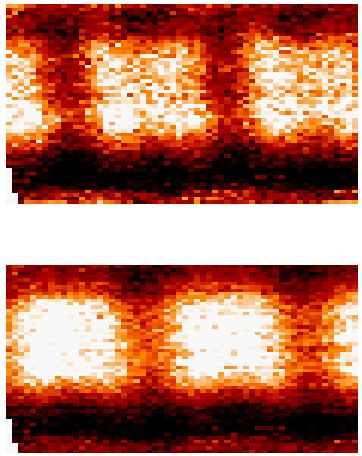
⇒ solving the Schrödinger equation with a more realistic V(x,y) potential :

- periodic boundary conditions along x

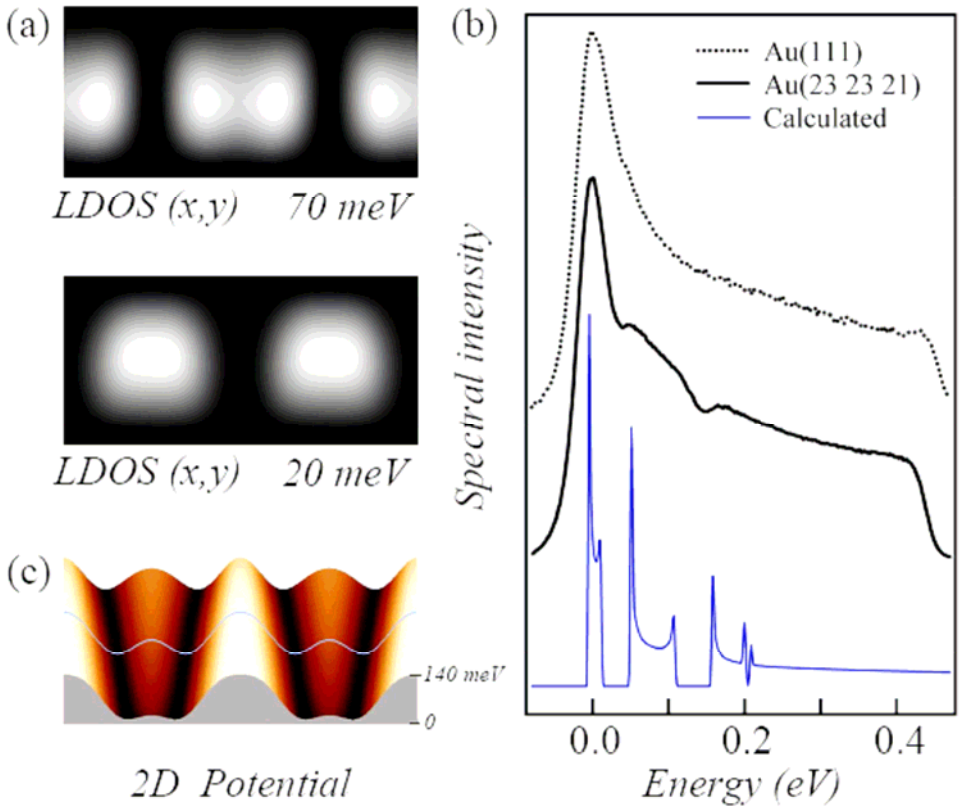
- wave function should be zero on steps (infinite quantum well)

-C. Chatelain – LPM (Nancy)

simulations of STS and ARPES results



Exp. LDOS (x,y)



ARPES gaps : E_g^1= 37±5 meV, E_g^2= 50±5 meV, E_g^3 =0 meV

Calculated gaps : E_g^1= 38 meV, E_g^2= 50 meV, E_g^3 = 5 meV

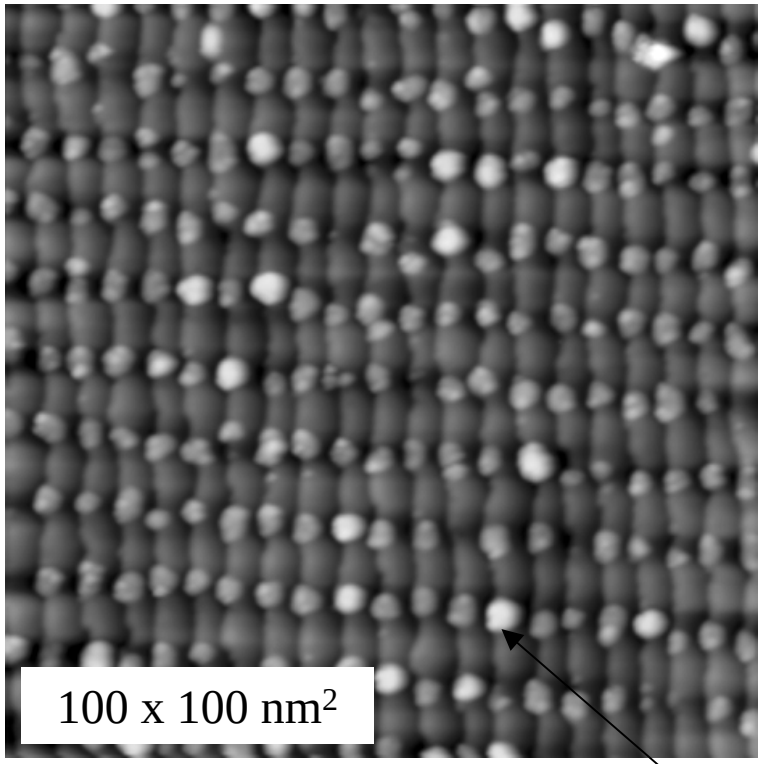
→ From nearly free electron behavior
to strong confinement in self-organized nanostructures

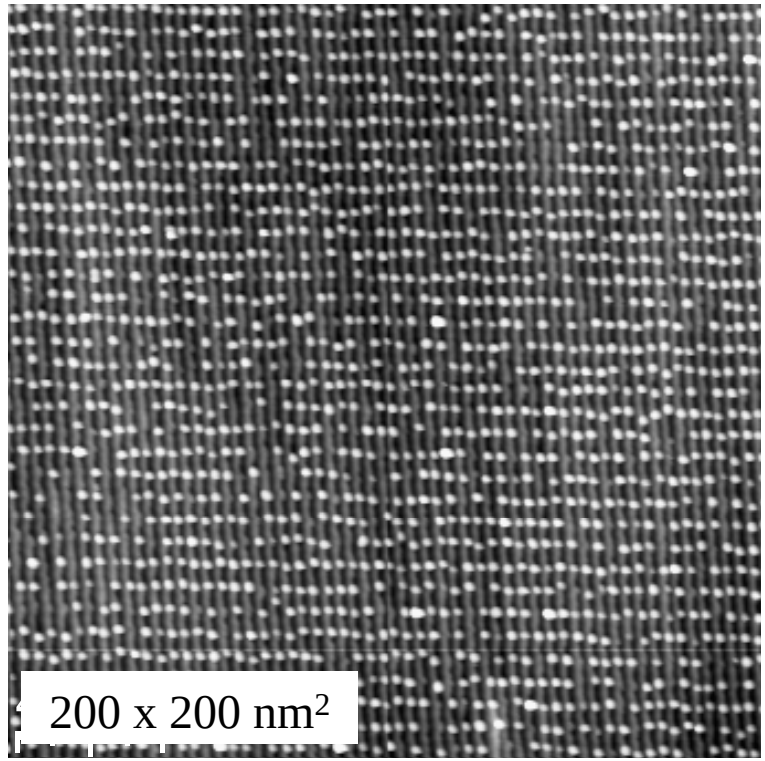
• Ag on v-Au(111) :
weak potential → Nearly free electron behavior

• Co on v-Au(111) :
strong potential → Confinement

Co growth on Au(788)

0.18 ML Co deposited on Au(788) at 120 K and annealed at 300 K



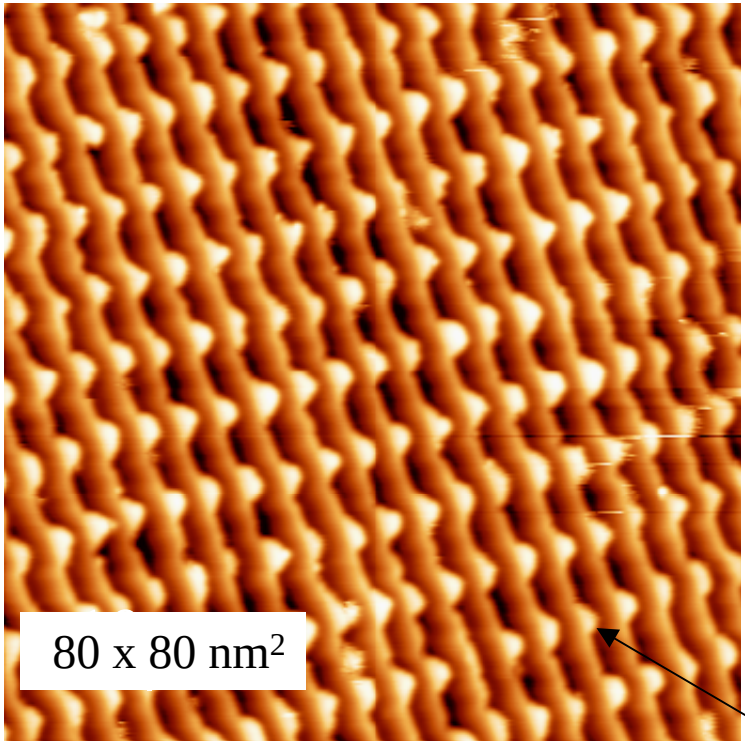


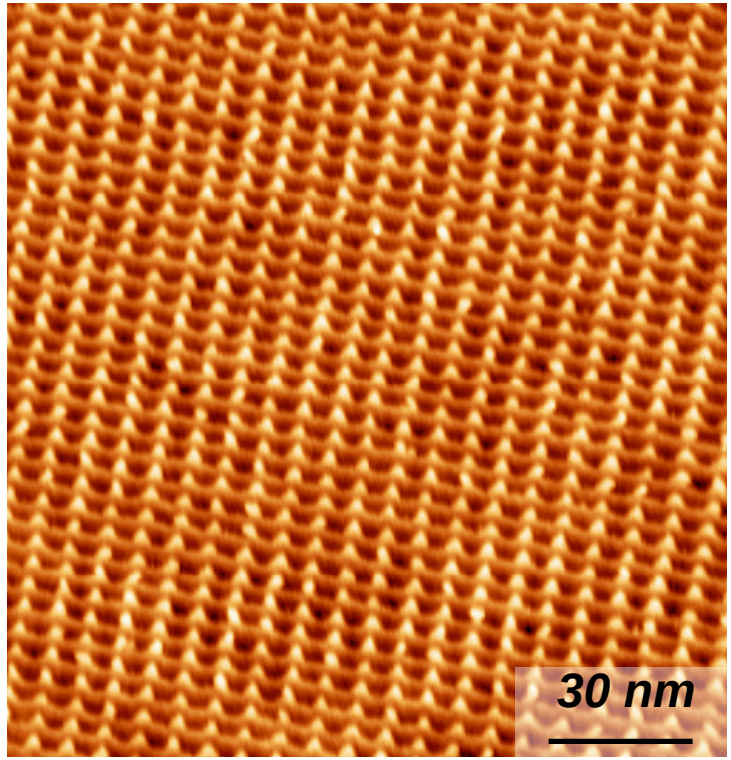
bilayer isotropic Co islands

V. Repain et al. Mater. Sci. Eng. B 96 178 (2002)

Ag growth on Au(788)

0.21 ML Ag on Au(788) deposited at 130 K



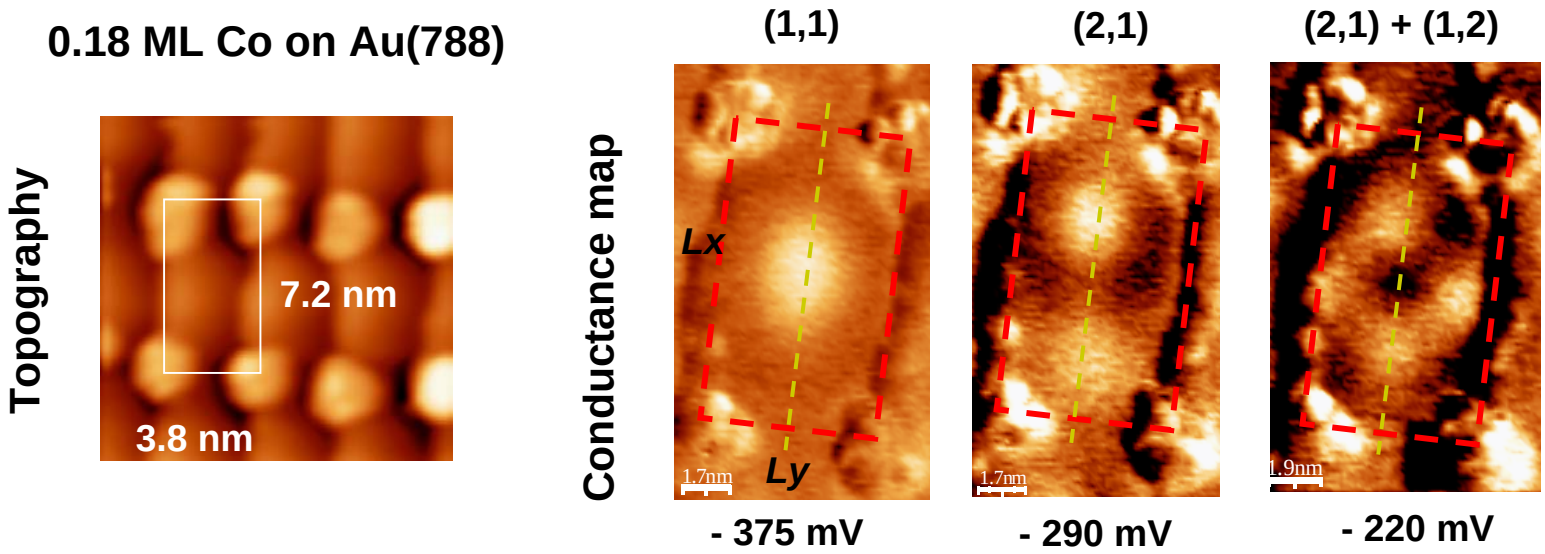


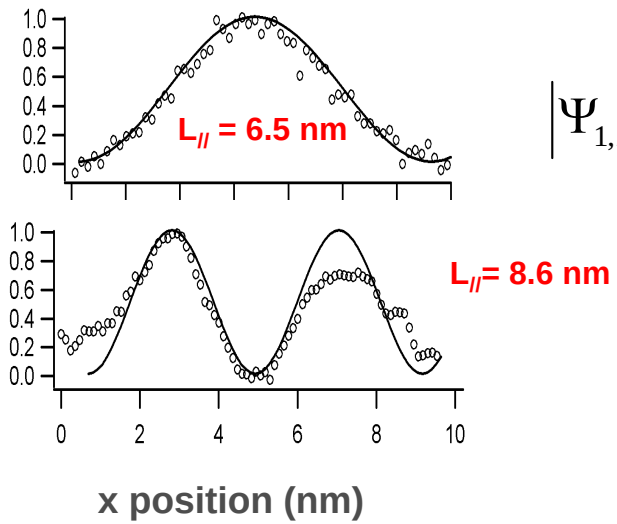
Didiot et al., ECOSS-23&24, Surf. Sci. (2006)
Didiot et al., submitted to Nanolett. (2006)

Monolayer triangular islands

(stress, step attraction/repulsion…)

Surface state properties of the Co/Au(788) interface

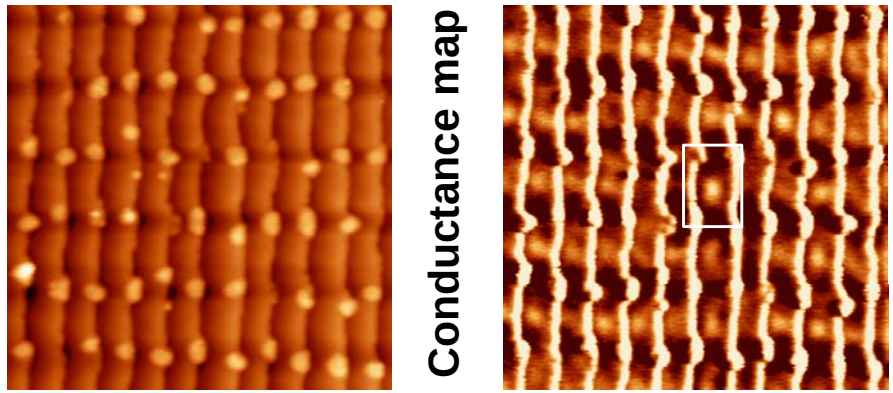




$$\left|\Psi_{1,n//}\right|^2 \propto \sin(n_{//}\frac{\pi}{L_{//}}x)$$

$\Rightarrow$ Localized electrons trapped inside 4-Co islands quantum boxes but…<u>non-infinite quantum well</u> !

Long-range ordered (nearly)-quantum well in Co/Au(788)



0.18 ML Co on Au(788)

=

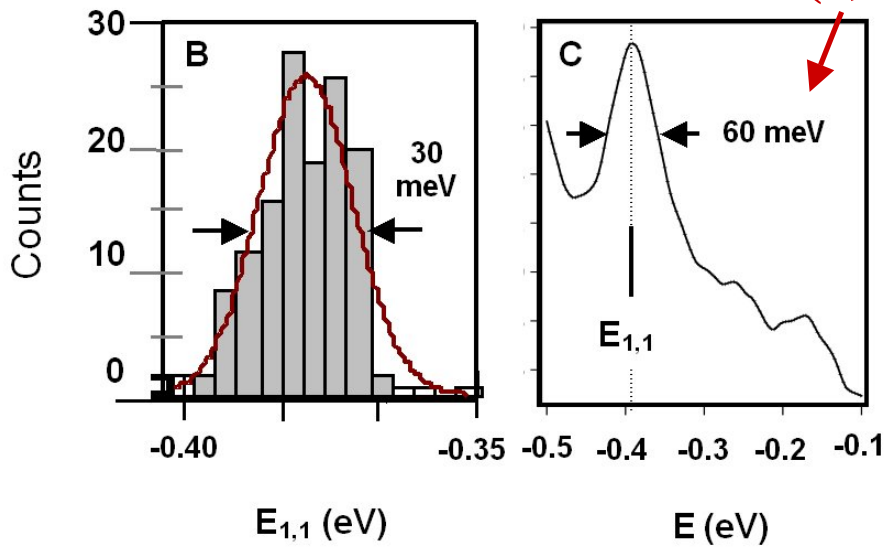
Self-organized quantum well

FWHM of a (1,1) mode

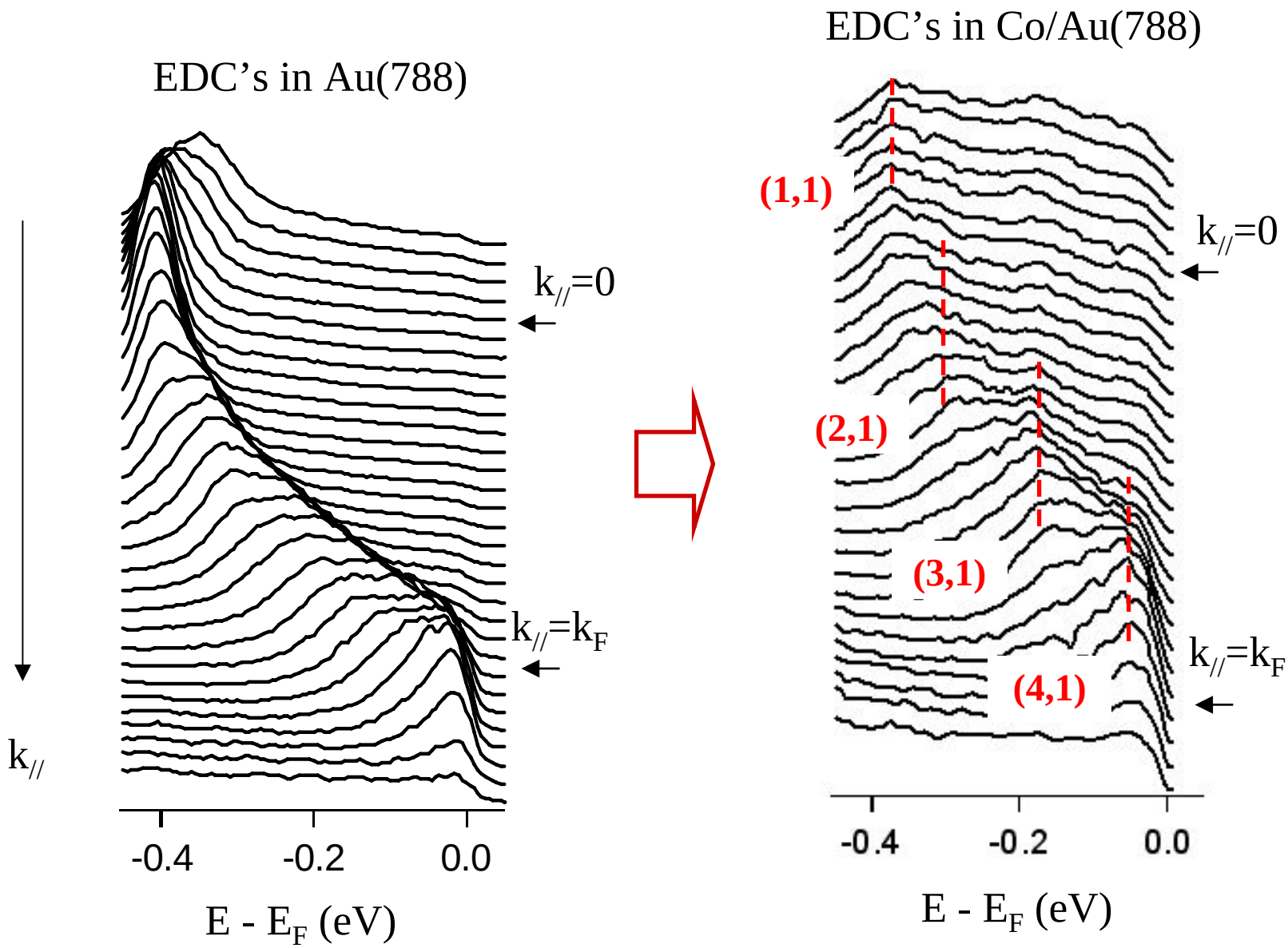
Statistics on the fundamental (1,1) quantum modes

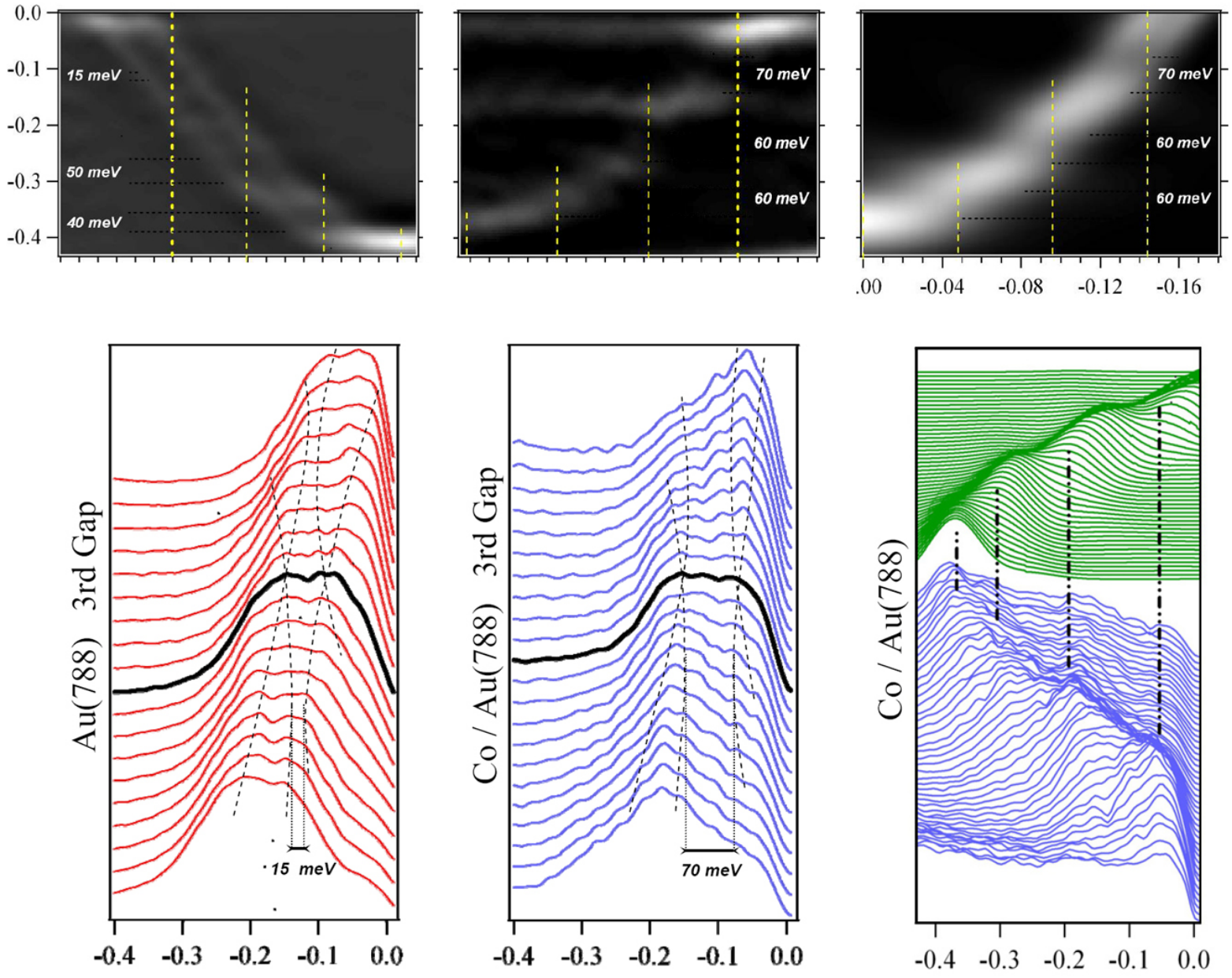
=

Narrow distribution !



⇨ ARPES on Co/Au(788) along terraces




0.0
-0.1
-0.2
-0.3
-0.4
15 meV
50 meV
40 meV
70 meV
60 meV
60 meV
70 meV
60 meV
60 meV
.00
-0.04
-0.08
-0.12
-0.16
Au(788) 3rd Gap
15 meV
-0.4
-0.3
-0.2
-0.1
0.0
Co / Au(788) 3rd Gap
70 meV
-0.4
-0.3
-0.2
-0.1
0.0
Co / Au(788)
-0.4
-0.3
-0.2
-0.1
0.0

Concluding remarks

Au(232321)

- the super-periodic potential induced by the surface reconstruction in Au vicinal surfaces leads to the opening of (at least) two gaps (37 meV/50 meV) on each spin-polarized subband at $k=\pi/L\pm\Delta k_{SO}$

- standing wave patterns are clearly identified by LDOS mapping (STS) with a π-phase shift of the wave function both through the 1st and 2nd gap

- an original method is proposed to extract the full 1D-perturbative potential V(x) based on its Fourier analysis

Co/Au(788)

- A strong increase of the perturbative surface potential is clearly induced by bilayer Co islands leading to quantum modes and increase of spectral weight in folded bands observed in ARPES pushing it in the strong coupling limit

Co-authors on these results

Surface and spectroscopies

(LPM - Nancy)

H. Cercellier (PHD)

C. Didiot (PHD)

B. Kierren

S. Pons

D. Malterre

L. Moreau (technical help)

C. Chatelain (LPM, Nancy)

(2D-simulations)

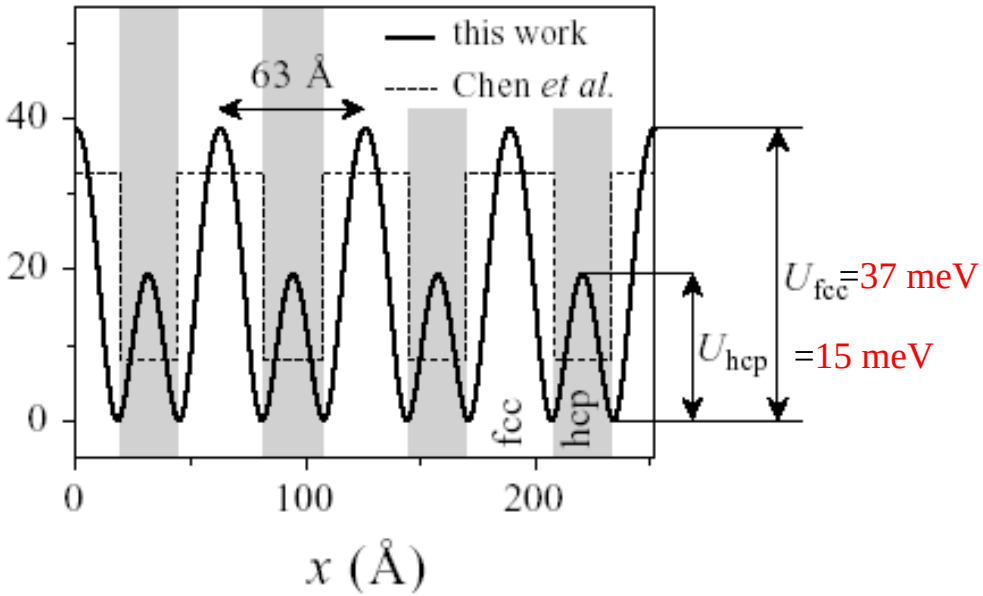
A. Tejeda, S. Rousset

(MPQ, Paris)

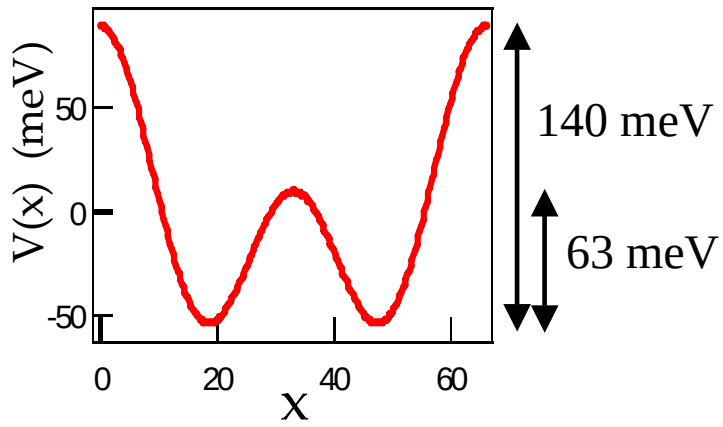
(coll. Co/Au(788))

Comparison to previous works…

Burgi et al. PRL 89, 176801 (2002)



Didiot et al. PRB 74, 081404 ® (2006)



Very similar to the shape of the reconstruction potential of Au(111) determined by Bürgi et al. from STS

But, the magnitude of V is significantly larger (by a factor 3.5) than in Au(111)

⇨ 15 meV gap in Au(111) ?

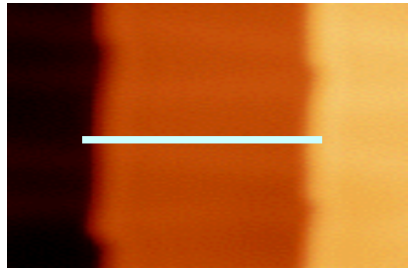
Reinert et al. Appl. Phys. A 78, 817 (2004)

Au(232321) : STS in Nancy (2006)

PHD : C. Didiot

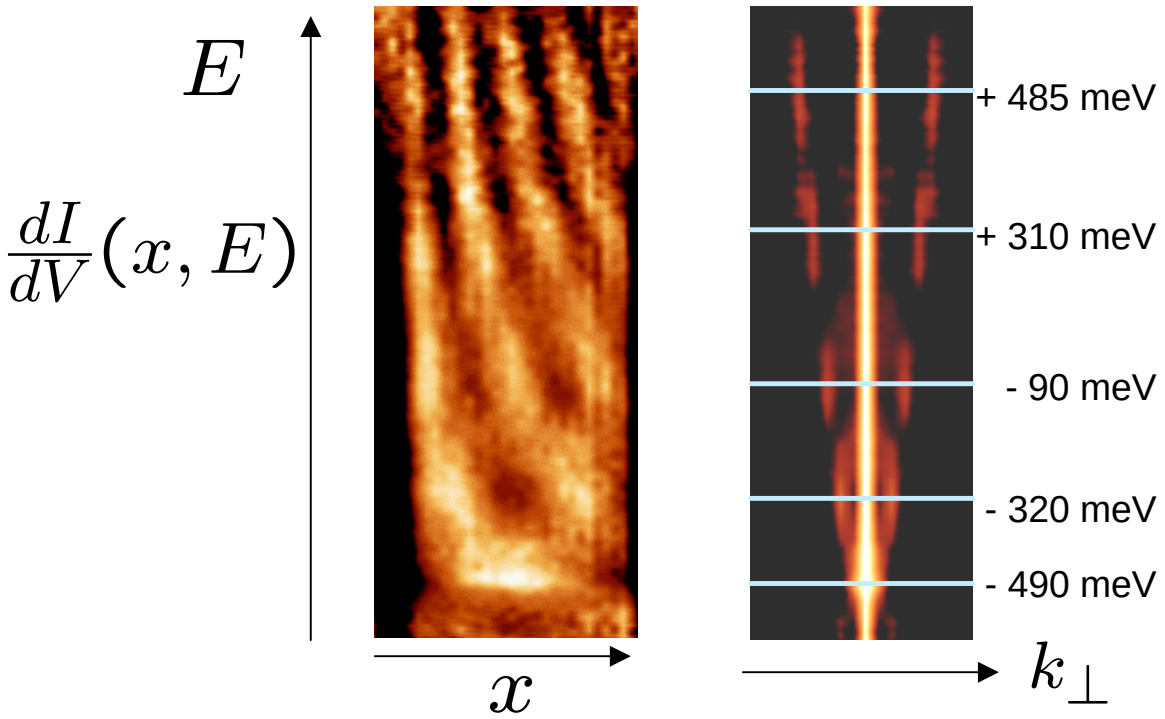
STM topography

Scan line
in a terrace



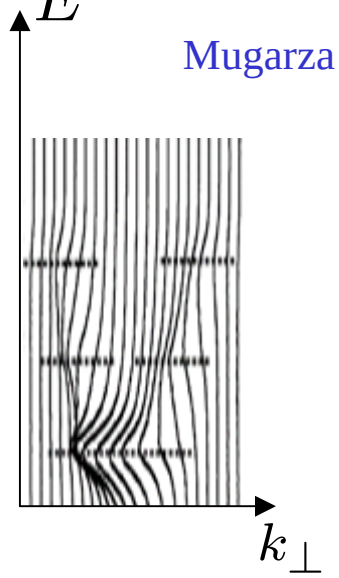
dispersion curve $E(k_\perp)$
can be obtained by 1D FFT

1D conductance map



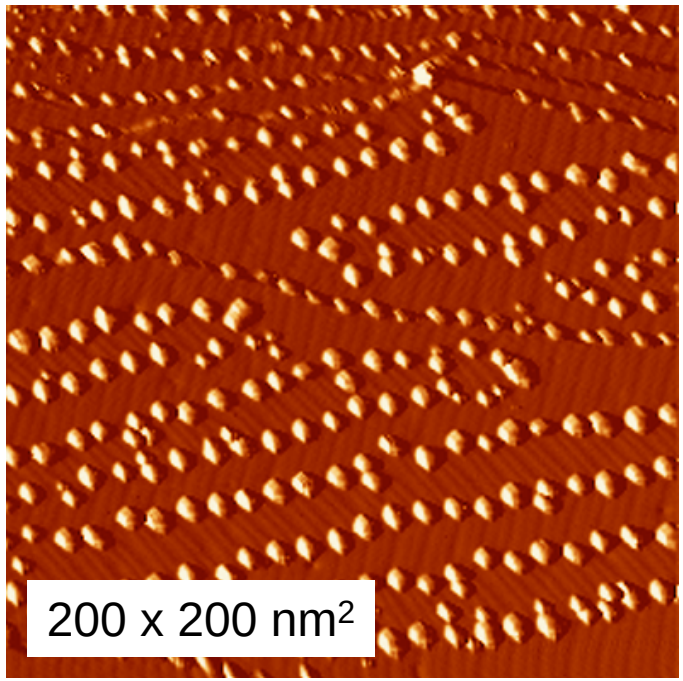
agreement
with previous
ARPES

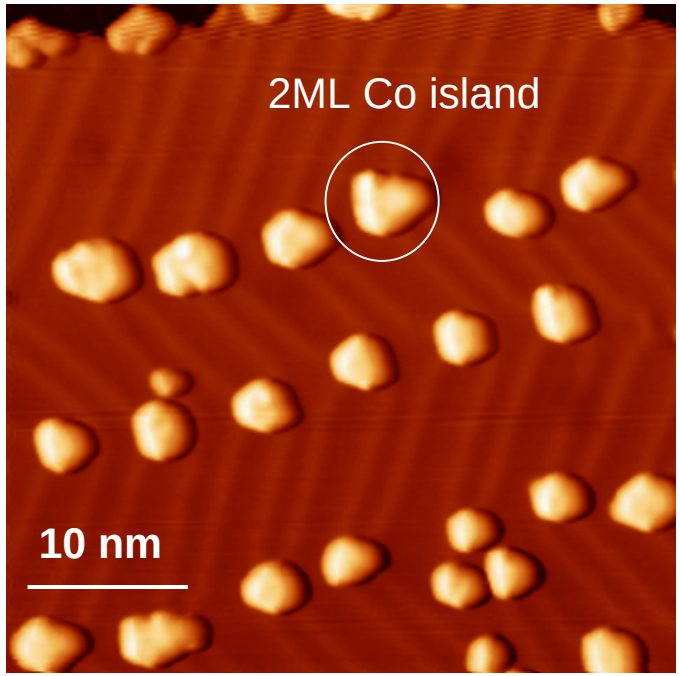
Mugarza (2001)



⇨ Co growth on reconstructed Au(111)

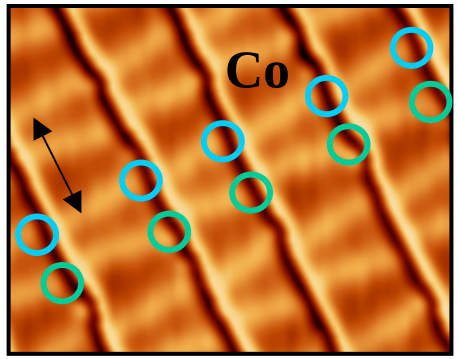
Growth of isotropic bi-layer Co islands at the elbow of the 22x√3 reconstruction (Co-Au exchange process at the dislocation loops)





Voigtlander et al.
PRB 44, 10354 (91)

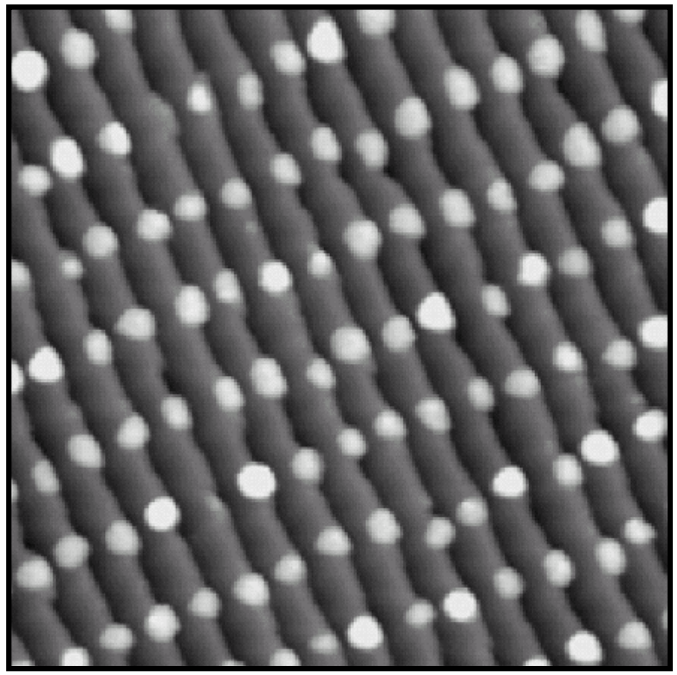
⇨ Co growth on Au(788) vicinal surfaces



2 nucleation centers on stacking faults-step crossing

V. Repain et al. Mater. Sci. Eng. B 96 178 (2002)

0.36 ML Co on Au(788)



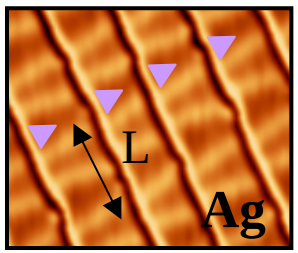
⇒ self-organized co islands growth

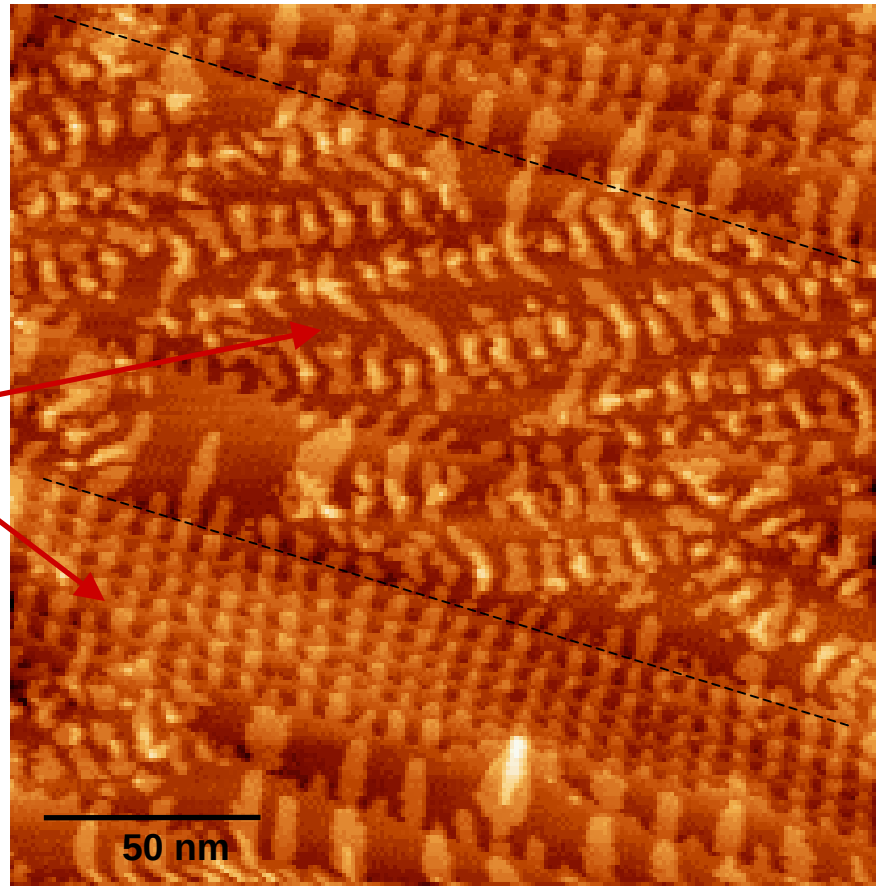
⇨ Ag growth on Au(111)

Cercellier et al. PRB 73, 195413 (06)

0.5 ML Ag/Au(111) deposited at T=80 K

Self-assembled Ag islands on small or large terraces





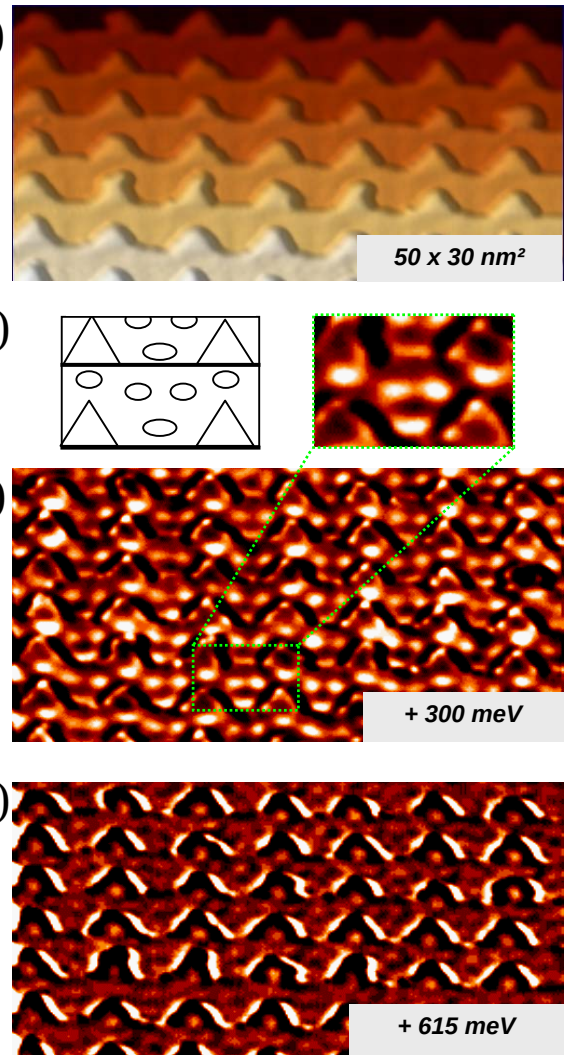
1 nucleation site,

the fcc domain

⇨ Long-range ordered delocalized states in Ag/Au(788)

topography

differential conductance image



0.21 ML Ag on Au(788)

Coherent state over a large scale

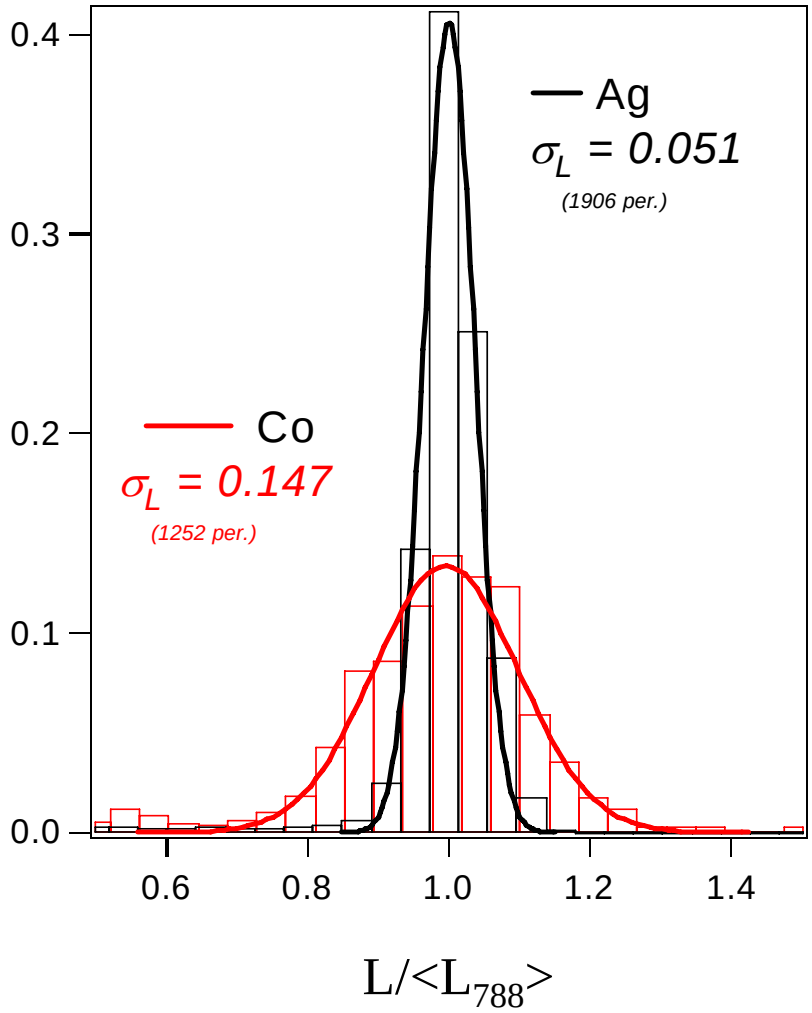
-at low energy (-190 meV)
in the Au terraces only

-at higher energy (+125 meV)
in Ag nano-islands

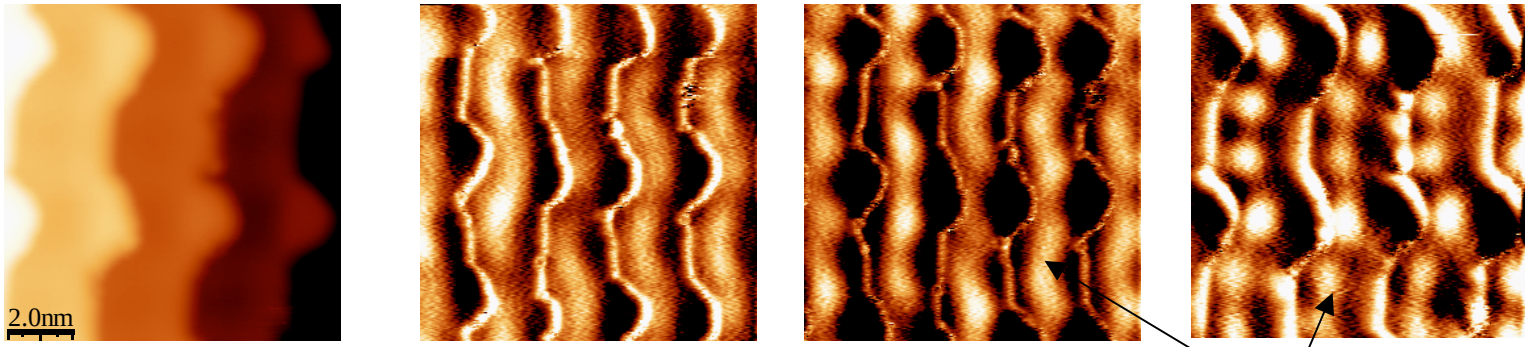
⇨ Co vs Ag ordering of islands

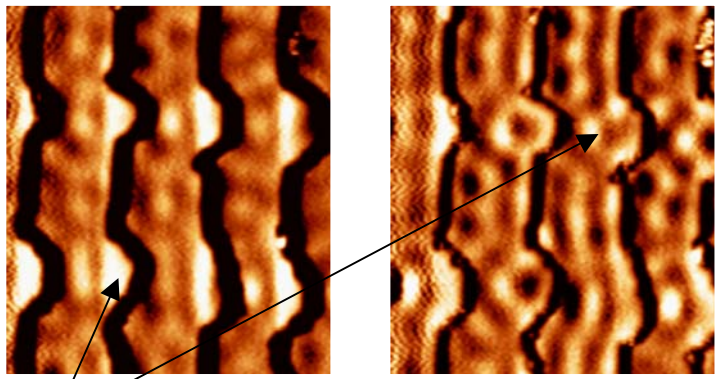
island-island distance in the // direction (along the reconstruction)

(Statistics > 1800 events)



⇨ Surface state properties of 0.21 ML Ag/Au(788)





inside Au terraces

⇒ delocalized states inside terraces but…

⇒ strong confinement inside Ag islands

inside Ag islands

+ Au terraces

unoccupied states !

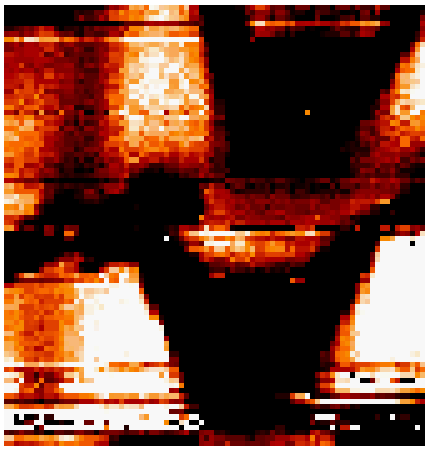
⇨ Steering the surface state energy from Ag/Au(788)→Au(232321)

- by increasing Ag coverage
- by changing the terrace width from Au(788) -> Au(232321)

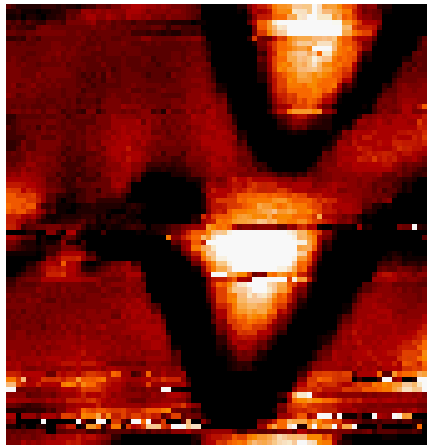
=> larger Ag islands

0.33 ML Ag on Au(23,23,21)

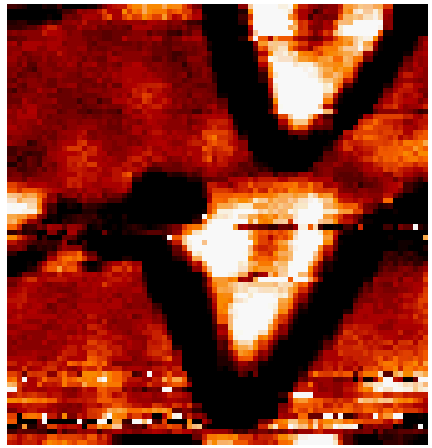
occupied states !



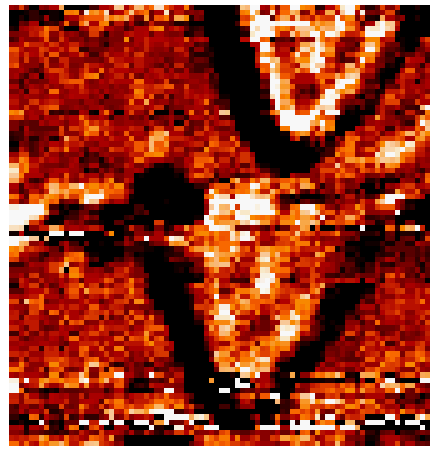
- 415 meV



- 205 meV



- 45 *meV*

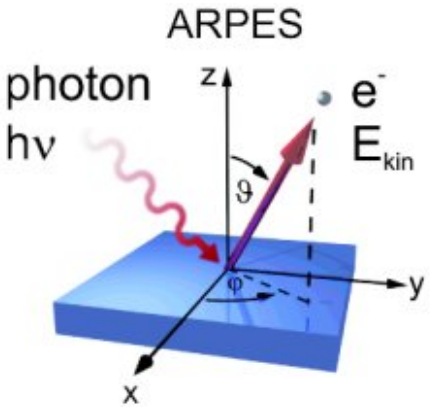


435 meV

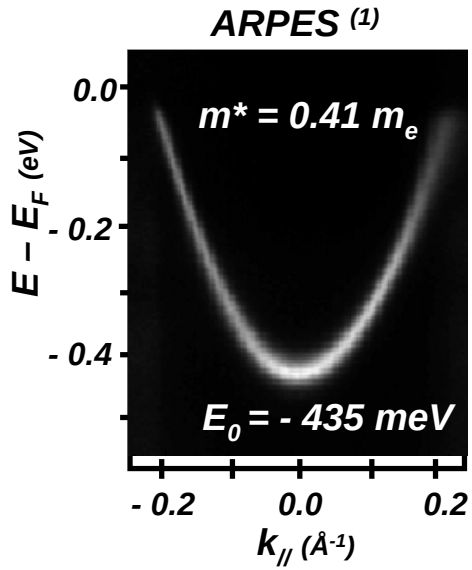
differential conductance map(s)

➔ quantum well in the triangular Ag nano-islands

⇨ Spectroscopic techniques : ARPES vs STS

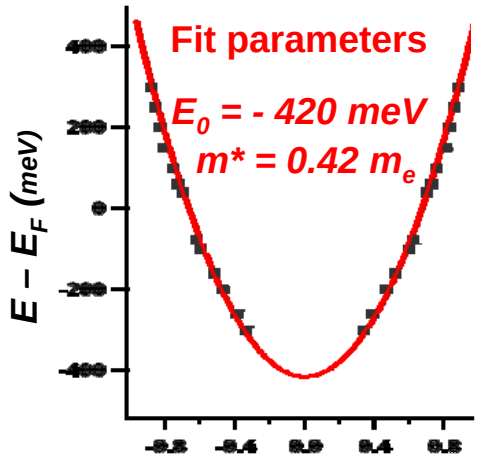


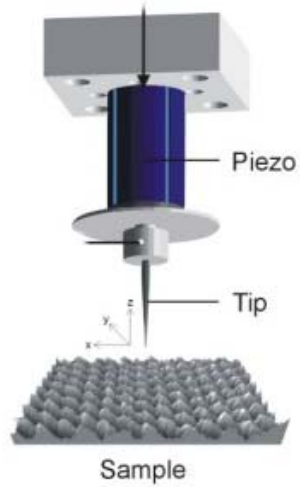
(E<E_F)
k-sensitive



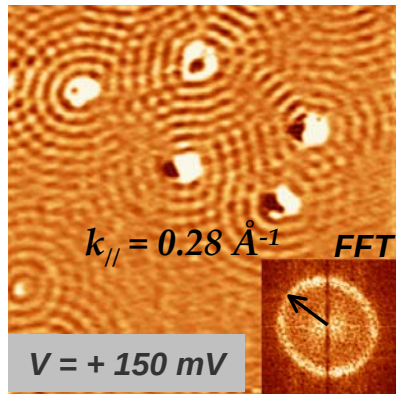
dI/dV map
=
LDOS cartography

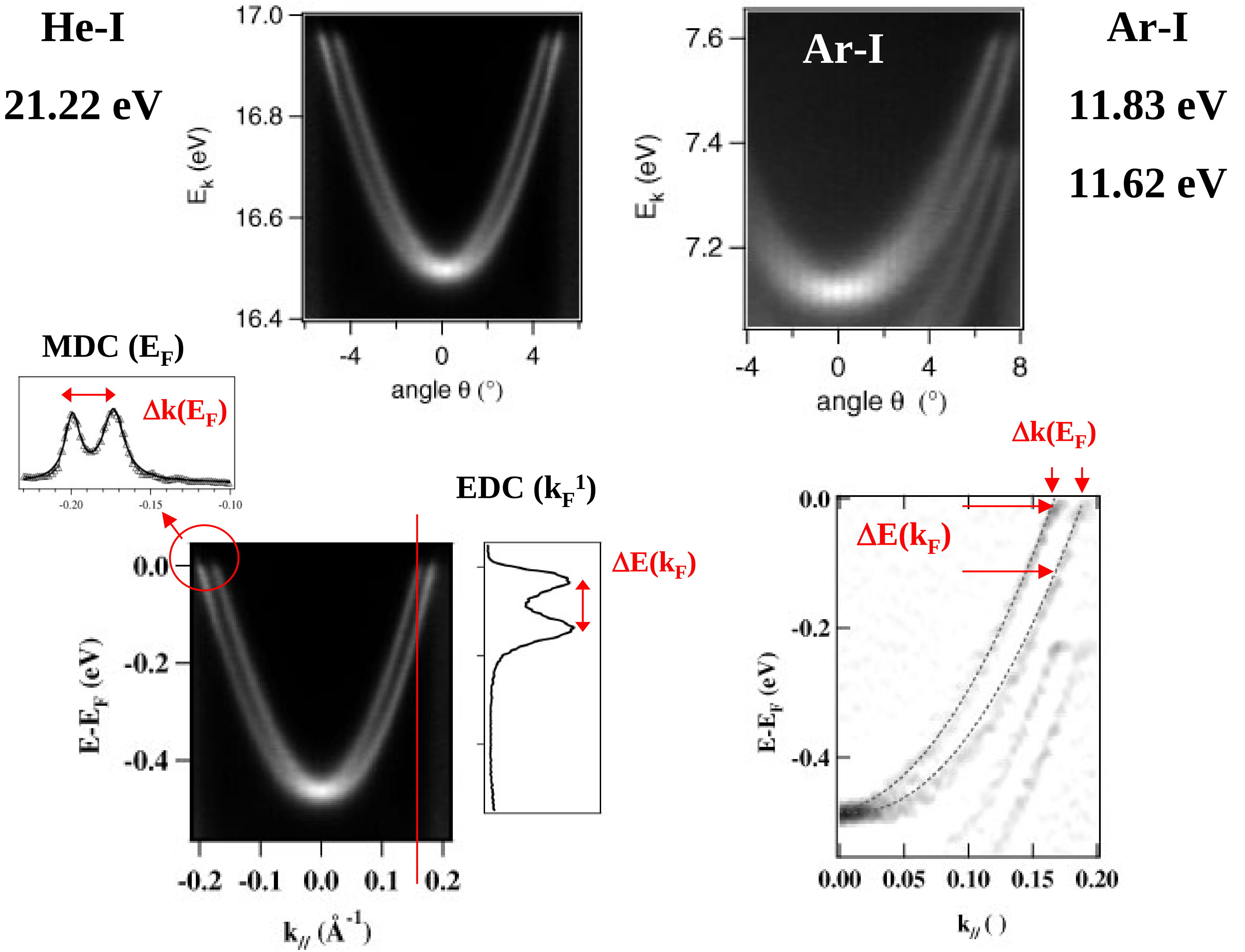
$$\frac{dI}{dV} \propto \rho(E, \vec{r})$$





LDOS probed by STS





He-I
21.22 eV
17.0
16.8
16.6
16.4
E_k (eV)
-4
0
4
angle θ (°)
Ar-I
Ar-I
11.83 eV
11.62 eV
7.6
7.4
7.2
E_k (eV)
-4
0
4
8
angle θ (°)
MDC (E_F)
Δk(E_F)
-0.20
-0.15
-0.10
EDC (k_F^1)
ΔE(k_F)
0.0
-0.2
-0.4
E-E_F (eV)
-0.2
-0.1
0.0
0.1
0.2
$k_{//}$ (Å^{-1})
Δk(E_F)
ΔE(k_F)
0.0
-0.2
-0.4
E-E_F (eV)
0.00
0.05
0.10
0.15
0.20
$k_{//}$ ( )

Concluding remark(s)

by combining local (STS) and macroscopic (ARPES) techniques :

This study : ***Long-range ordering of electronic properties obtained by self-organisation (bottom-up approach) is able to extract the physical properties of a single object of nanometric scale***

Future : ***modify these nanostructures to enhance optical, magnetic, catalytic or unknown properties !***