Electron confinement in metallic nanostructures

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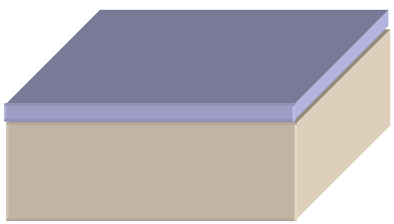
Introduction

Properties of solids : mainly related to their electronic structure

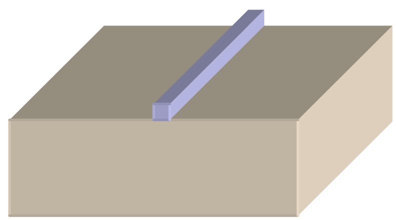
At surfaces, electronic properties are altered !

Surface states, confined in the direction perpendicular to the surface. Such surface states exist also for metals !

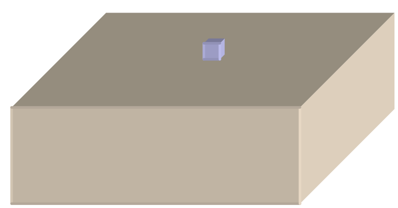
Theoretical predictions (1932-)
Experimental observation : UHV + electron spectroscopy



2D surface state



1D quantum wire



0D quantum dot

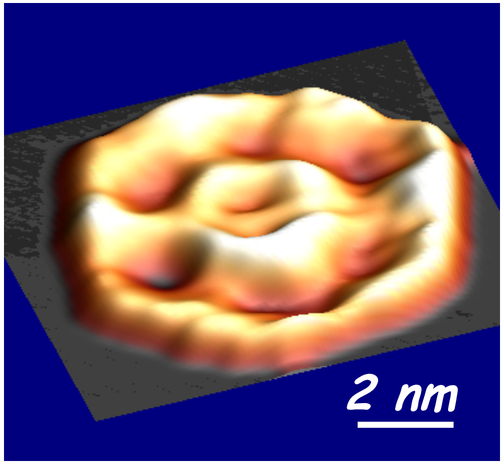
1981 : Scanning Tunneling Microscope (STM) is born !!!
Binnig & Rohrer → Nobel Price in 1986

subnanometric lateral resolution :

Topographic informations (morphology, growth, size distribution …)

Spatially resolved electron spectroscopy inside a single nanostructure !!!!

Ni island grown on Cu(111) →



Empty electronic states (+0.25 eV above the Fermi level)
UHV - STM conductance image at 40K

Topics

1. Shockley Surface states
2. Low Temperature STM/STS
3. Quantum interferences of Shockley surface state electrons
4. Quantum resonators
5. Interaction between an adsorbate and a 2D electron gas

1. Shockley Surface State

H. Lüth, Surfaces & interfaces of solid materials, Springer (1995)

N. Memmel, Surface Science Reports ***32****, 91 (1998)*

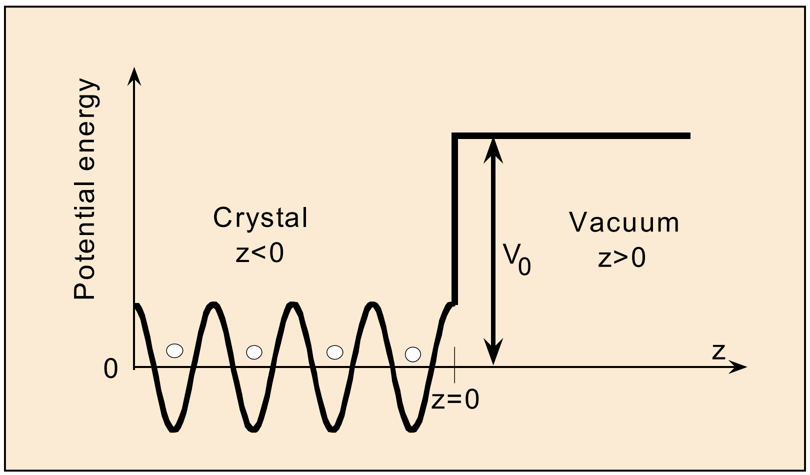
Theoretical description:

Semi-infinite Chain in the Nearly-Free Electron model

. Electron-electron interaction is neglected

. **1D model**

. V(z) (Effective potential induced by the cristal) has the following shape:



z<0 $\quad V(z) = 2\,V_g \cos gz \quad$ (with $g = 2\pi/a$)

z>0 $\quad V(z) = V_0$

We have to solve the single-electron Schrödinger equation:

$$\left[-\frac{{}^2}{2m}\frac{\partial^2}{\partial z^2}+V\right]\psi(z)=E\psi(z)$$

Bulk states solutions (z<0)

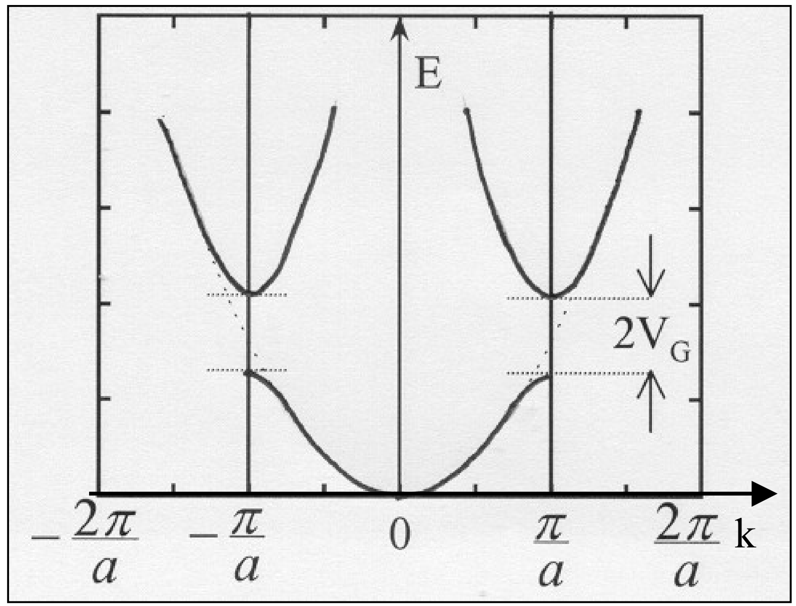
Near the center of Brillouin zone: plane wave and parabolic dispersion

Near the Brillouin zone boundary (k=g/2), solutions are well known :

$$\psi_B^{\pm}(z) = C\, e^{i\kappa z}\ [e^{i\pi z/a} + \left(\frac{-\,{}^{2}\pi\kappa}{ma|V_G|} \pm \sqrt{\left(\frac{{}^{2}\pi\kappa}{ma|V_G|}\right)^2 + 1}\ \right) e^{-i\pi z/a}\ ]$$

$$E^{\pm} = \frac{{}^{2}((g/2)^2+\kappa^2)}{2m} \pm \sqrt{V_g^2 + \frac{{}^{4}}{4\ m^2}\, g^2\kappa^2}$$ with κ = k – g/2

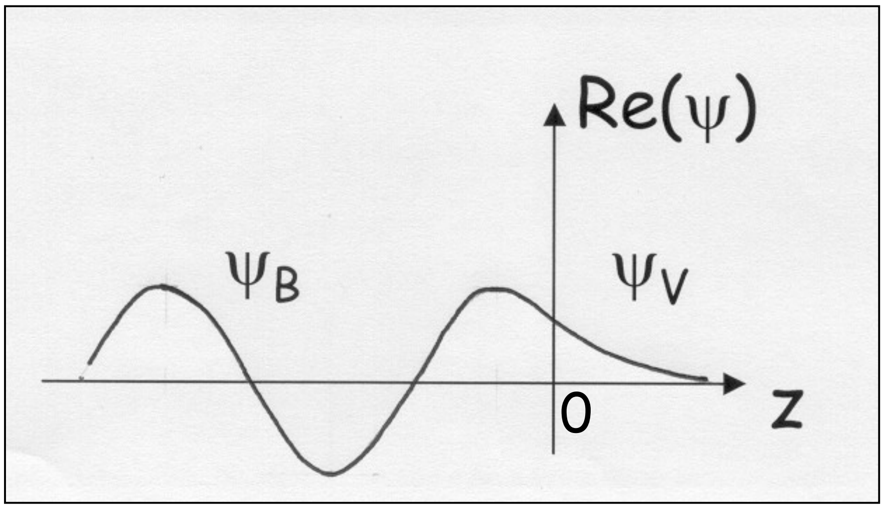
In this 1d model, a gap 2Vg is found at κ = 0, which separates the allowed bulk states.



Because the chain is semi-infinite, the wave function is evanescent in the vacuum:

$$\psi_V(z>0) = \mathrm{D}\, e^{-\frac{\sqrt{2m(Vo-E)}}{\hbar} z}$$

Matching of the wave functions and their derivative at z=0 (for each energy eigenvalue E within the allowed band).



Standing Block wave matched to an exponentially decaying wave function in vacuum.

Surface solutions

Since the crystal is not infinite, solutions with purely imaginary κ are also possible, with no divergence of $|\psi|^2$:

$\kappa = -iq$

$$E = \frac{{}^2((g/2)^2 - q^2)}{2m} \pm \sqrt{V_g^2 - \frac{4}{4\,m^2} g^2 q^2}$$

E has to be real : $0 < q < 2m|V_g|/g\hbar^2$

In that case, new states are found <u>inside the bulk gap:</u>

$$\psi_S(z<0) = D\, e^{qz} e^{-i\delta}\, 2i\sin(zg/2 + \delta)$$

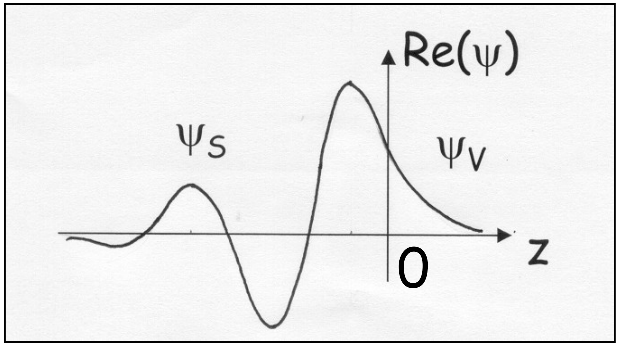
$$\psi_S(z<0) = D\, e^{qz} e^{+i\delta} \cos(zg/2 - \delta)$$

with $\sin(2\delta) = \frac{-\,{}^2\pi q}{ma|V_g|}$

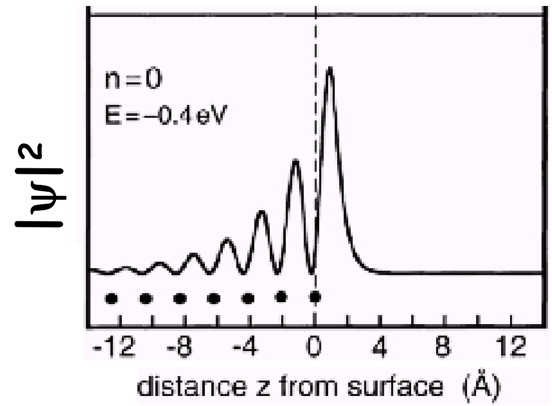
Matching of ψ_S and $\partial\, \psi_S / \partial z$ at z = 0 gives only 1 possible surface state (i.e. one value of E inside the gap)

The solution is a <u>standing wave</u> <u>with an exponentially decaying amplitude</u>.

Shockley surface state :



Example Cu(111) at Γ:



3D generalization

2D translational symmetry parallel to the surface:
→ the wave functions have 2DBloch waves component

Energy eigenvalues for the surface states become :

$$E_S(q\,,k_{//}) = \frac{{}^2((g/2)^2 + k_{//}^2 - q^2)}{2m} \pm \sqrt{V_g^2 - \frac{{}^4}{4\,m^2}\, g^2 q^2}$$

Matching conditions at the surface will give one energy value E_S for a given $k_{//}$

→ 2D band structure for the surface state : $E_S(k_{//})$

1. 6 Shockley Surface State

Photoemission on Cu

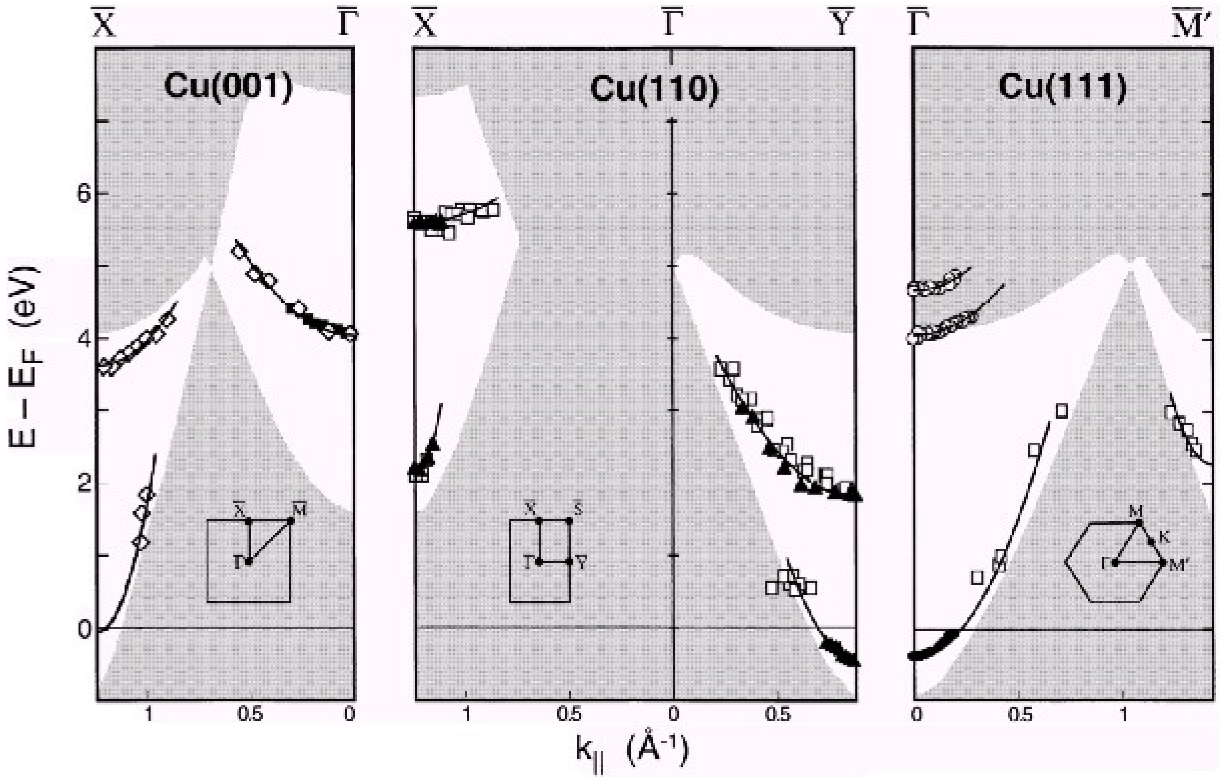
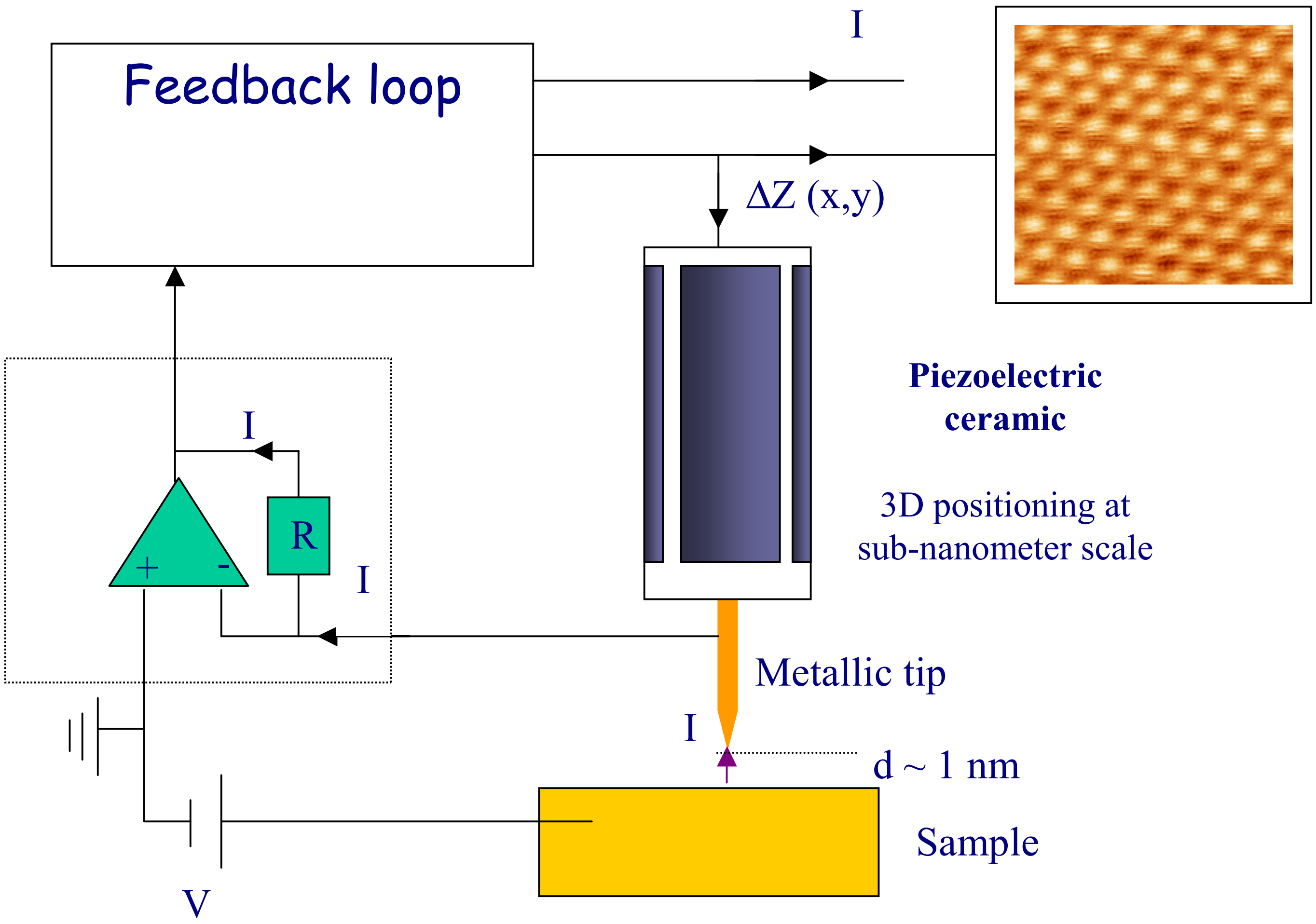


Fig. 1. Projected bulk band structures of Cu(0 0 1), Cu(1 1 0) and Cu(1 1 1) along high-symmetry lines of the SBZ. Gaps in the projected bulk band structures are indicated by white areas. Symbols denote experimentally determined surface-state dispersions. Open squares: Ref. [1], diamonds: Ref. [2], filled circles: Ref. [3], filled squares: Ref. [4], open circles: Ref. [5], triangles: Ref. [6]. Data from [5] are measured along $\overline{\Gamma}\,\overline{K}$, for the data of [4] the path in the surface Brillouin zone is not specified. Data points which are closer to the Fermi edge than the experimental resolution are omitted. Solid parabolas are guides to the eye. In the insets the 2D surface Brillouin zones (SBZ) are depicted.

*N. Memmel, Surface Science Reports **32**, 91 (1998)*

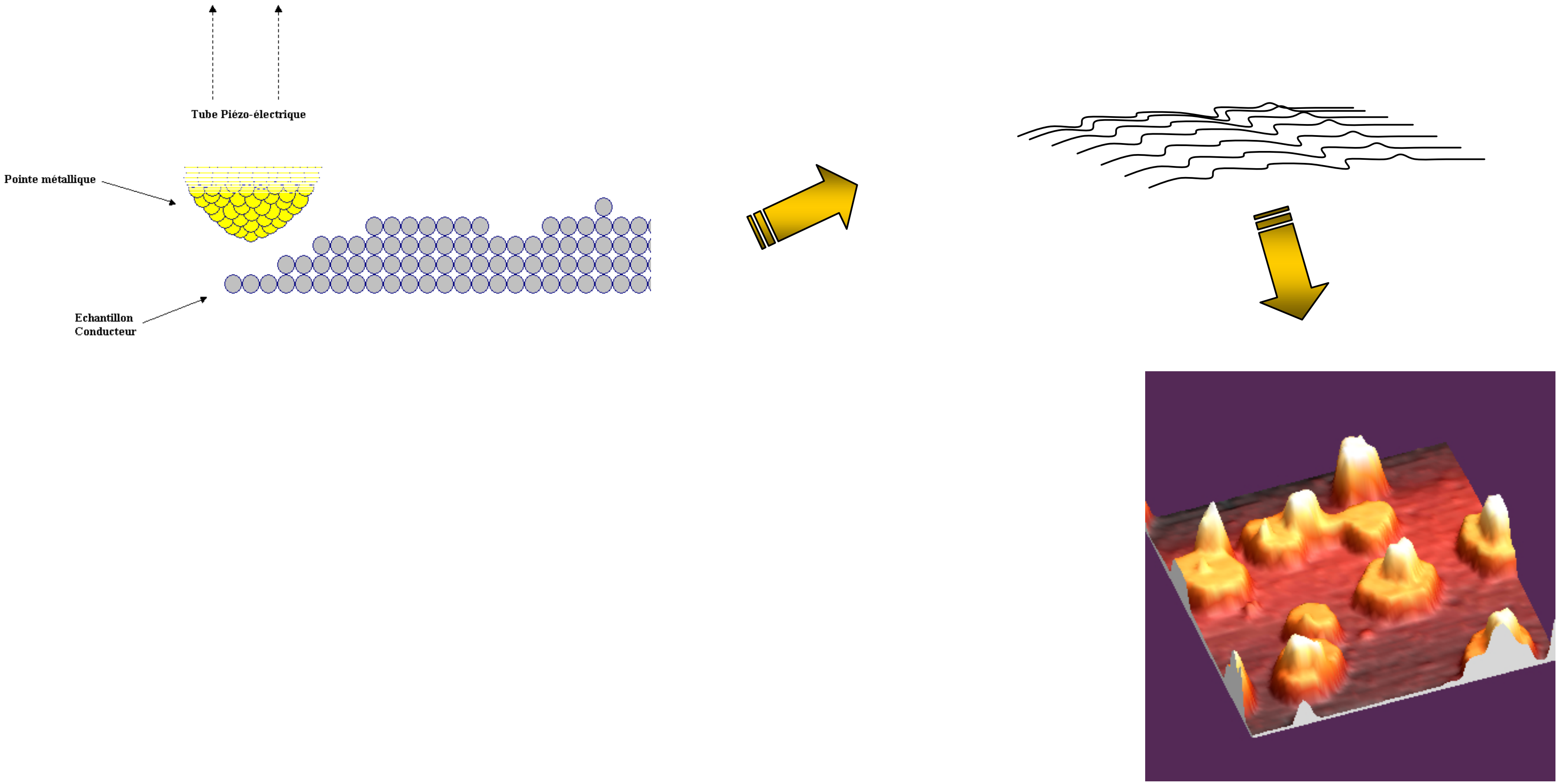
2. STM/STS

Basic principle of STM



2.2 Low temperature STM/STS – Constant current image

Constant current mode, feedback on : topography



Beyond topography

Tersoff & Hamann + Lang extension

$$I(V,T,r) = \int_{-\infty}^{+\infty} TR(E,V,z)\, \rho_s(E,r)\, \rho_t(E-eV) \times [\mathrm{f(E\text{-}eV,T) - f(E,T)}]\, dE$$

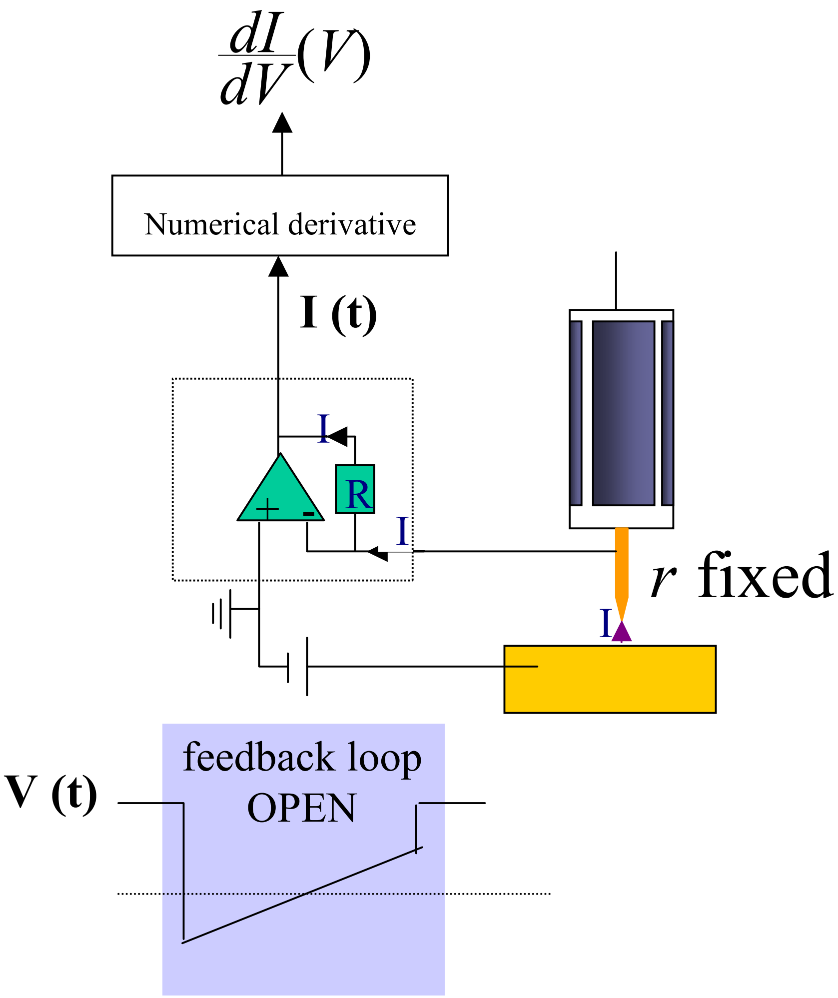
At low temperature
at low bias V (lower than work functions)
with the assumption $\rho_t(E) \approx \rho(E_F)$

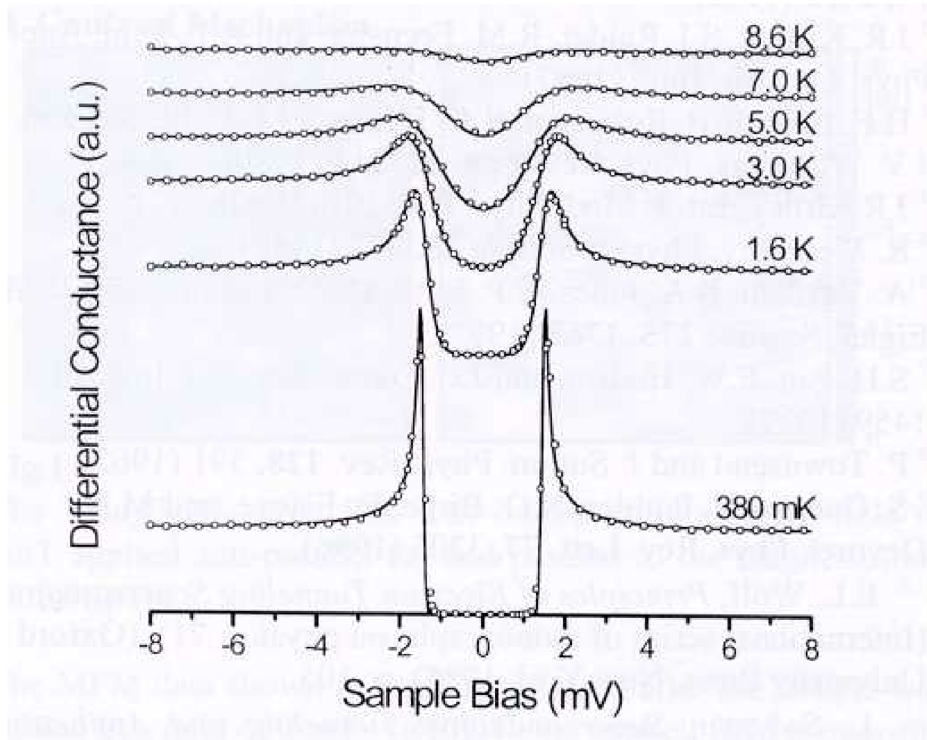
$$\frac{dI}{dV}(V,r) \propto \rho_s(E_F + eV, r)$$

$V\nearrow$, r constant
Scanning Tunneling Spectroscopy

V constant, r $\nearrow$
Dynamic conductance imaging

Scanning Tunneling Spectroscopy



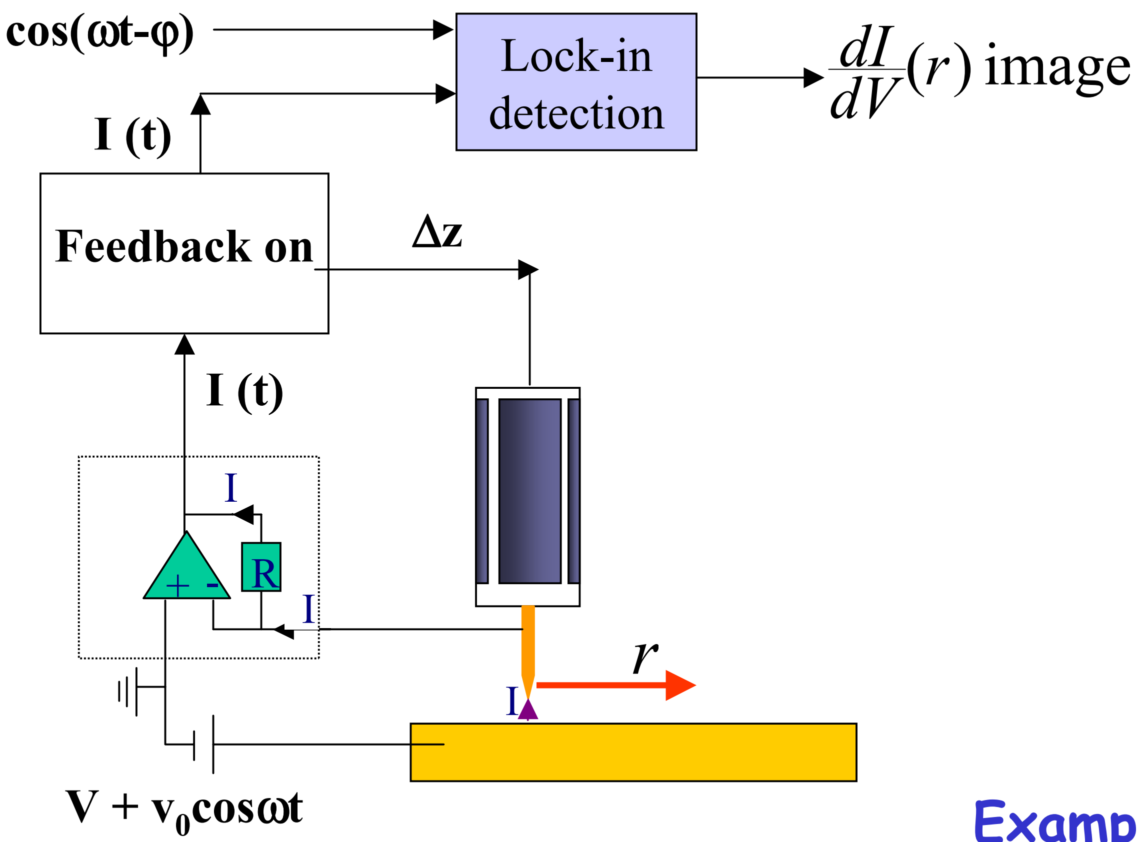


Example: STS on superconducting Nb

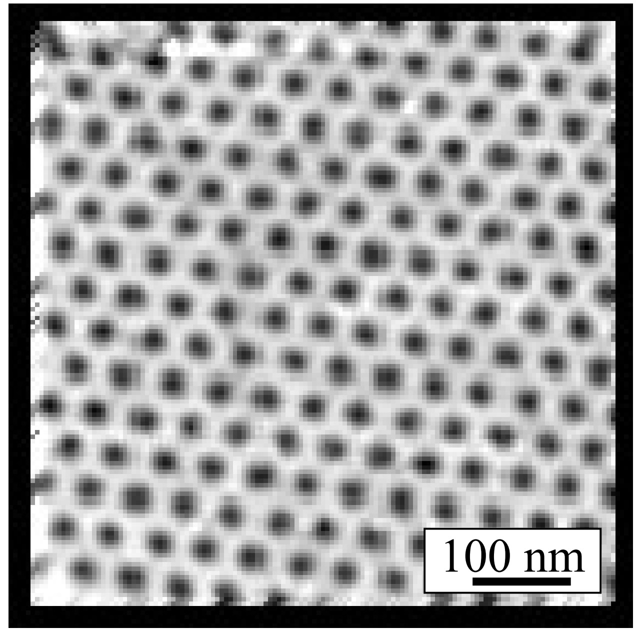
Direct probe of the gap in the quasiparticles LDOS

S.H. Pan et al., Appl. Phys. Lett. 73, 2992 (1998)

Conductance imaging : dI/dV (r) at fixed V



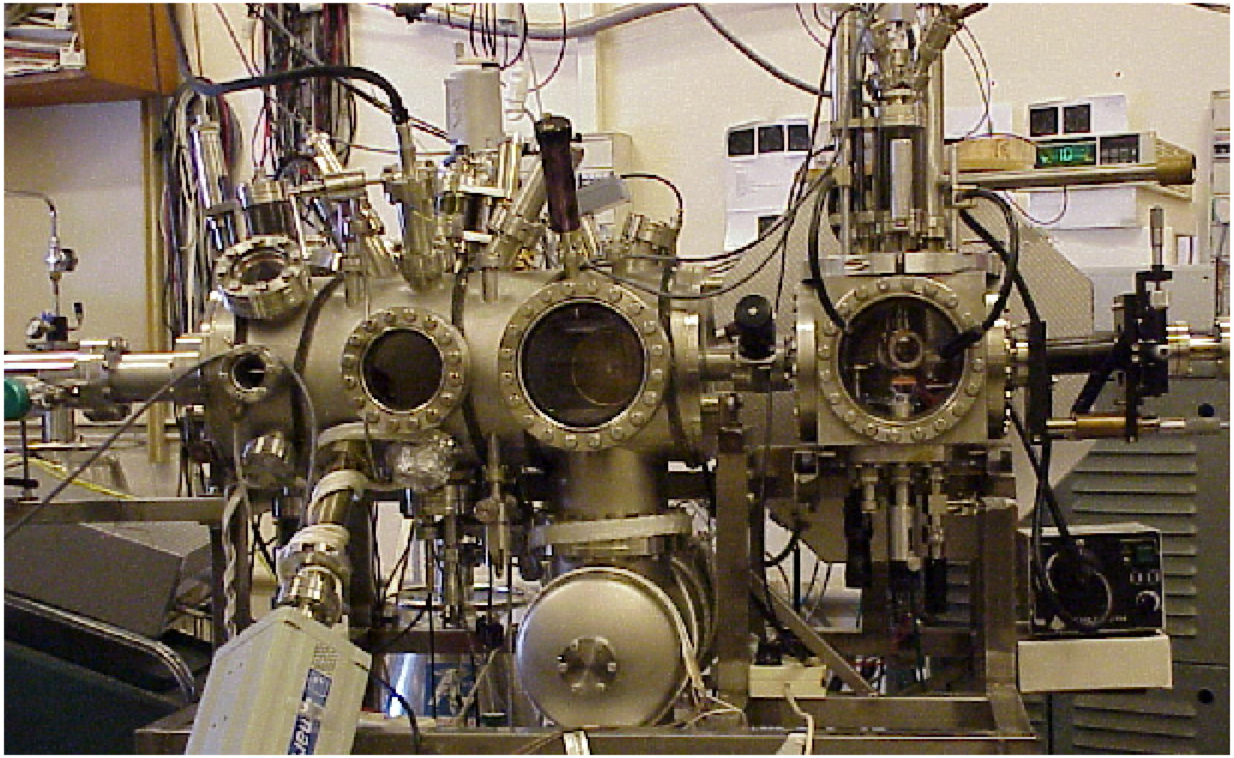
Frequency of the bias modulation higher than the band pass of the feedback loop !!!



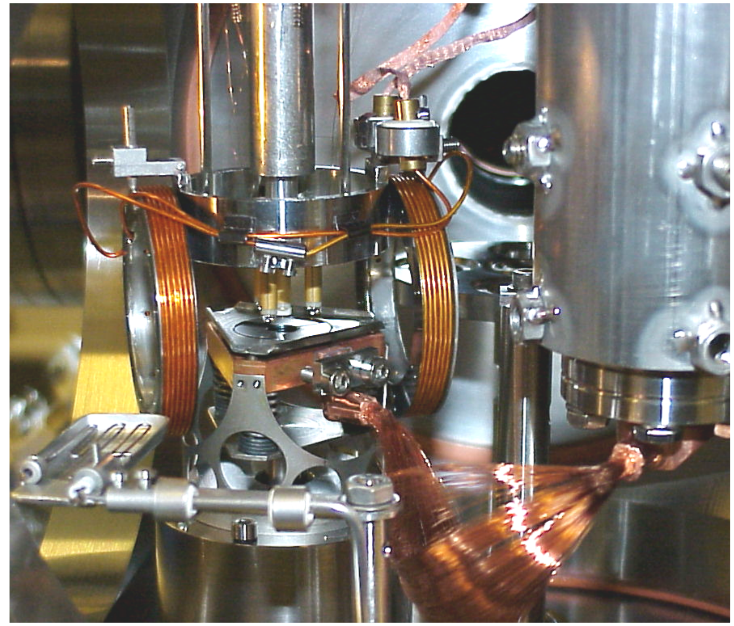
Example of dI/dV map of a type II superconductor ($NbSe_2$) at V = 1,3 mV, with an external magnetic field of 1T.

H.F. Hess et al., Physica B ***169****, 422 (1991)*

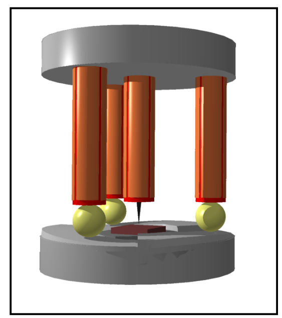
2.6 Low temperature STM/STS –experimental set-up at LEPES



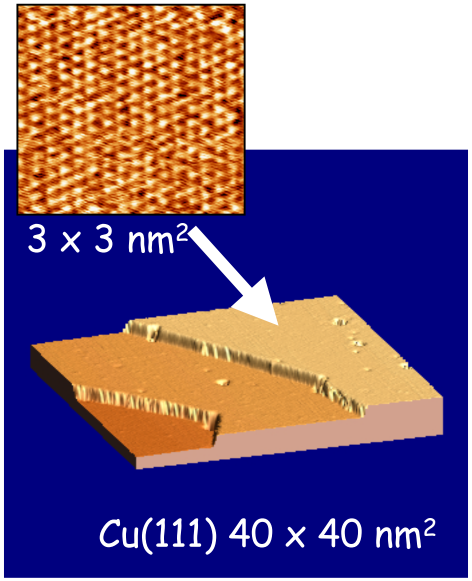
Ultra-High Vacuum Chambers



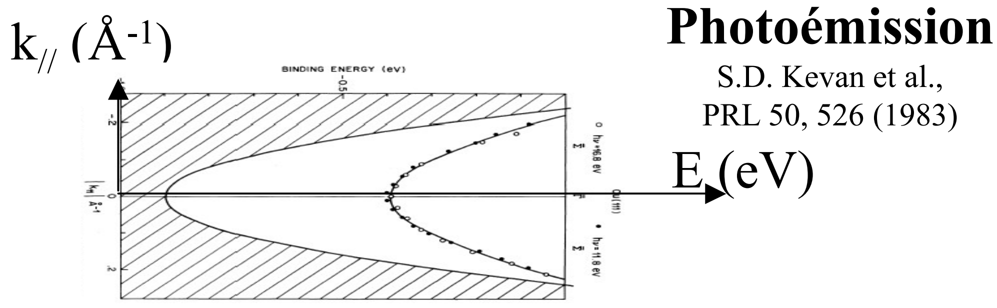
Home made
Low temperature STM
Beetle design

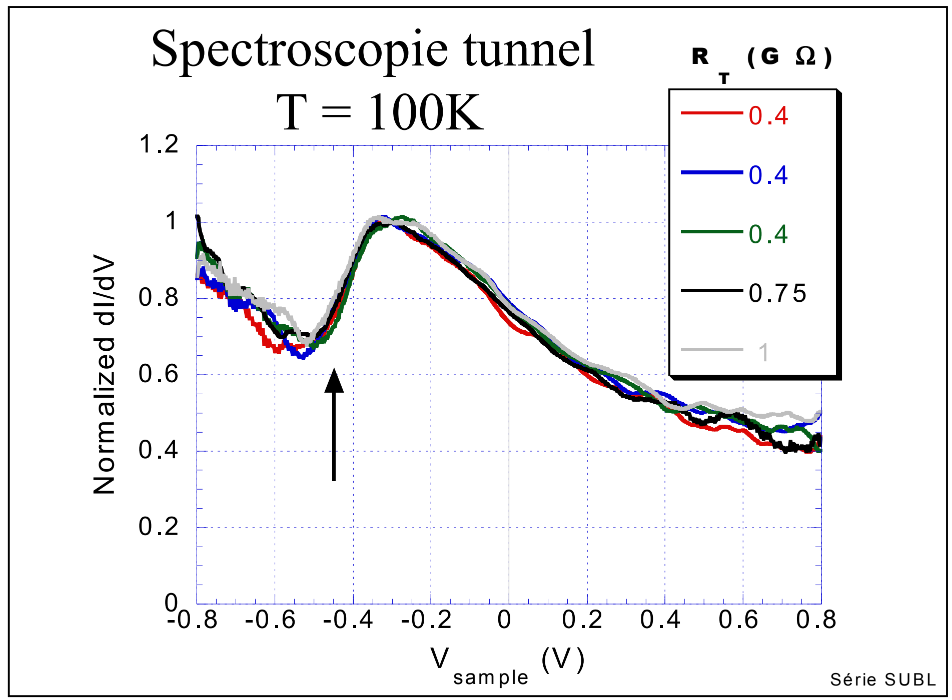


Tunneling spectroscopy of Cu(111) Shockley surface state



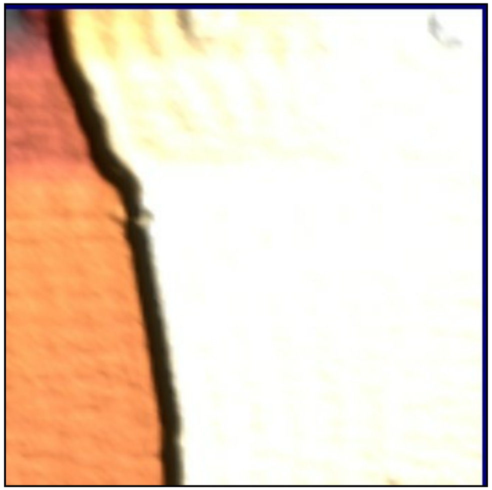
Constant current image



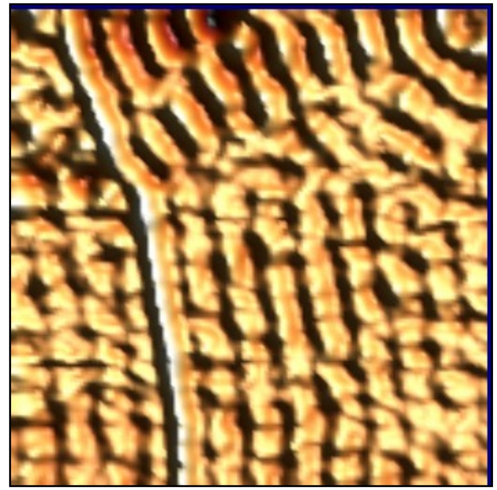


3. Scattering of surface state electrons

20 x 20 nm² STM images of Cu(111)   T = 100K



Topography :
2 terraces separated by
a monoatomic step



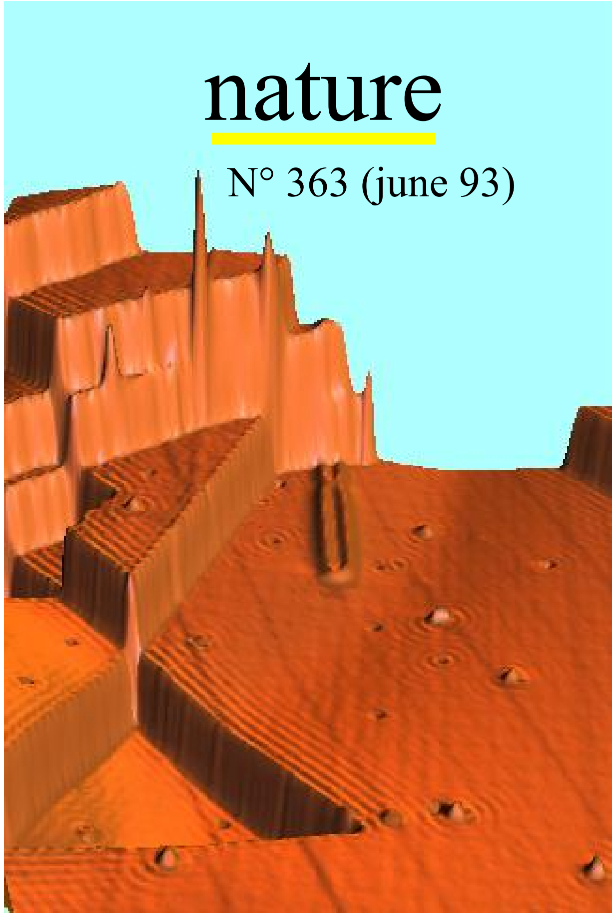
dI/dV map
V = +200mV

dI/dV map shows nice standing waves...

Standing waves on Cu(111)

First STM observation in june 1993 by Eigler's group (IBM San-José, California)

Same month, same phenomena observed on Au(111) by Hasegawa and Avouris (IBM, New York)



Origin of these waves?

Shockley-like surface state : a quasi 2D free-electron gas lies in the surface plane.

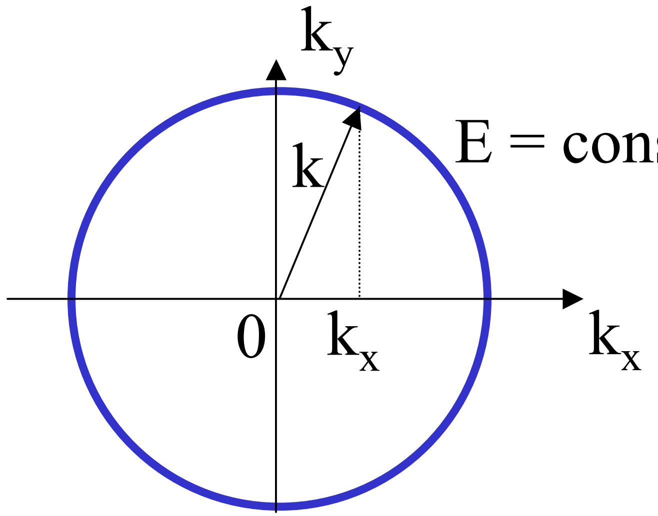
Part of the electrons are scattered coherently by the surface defects (step, adsorbate, vacancy), generating quantum interferences.

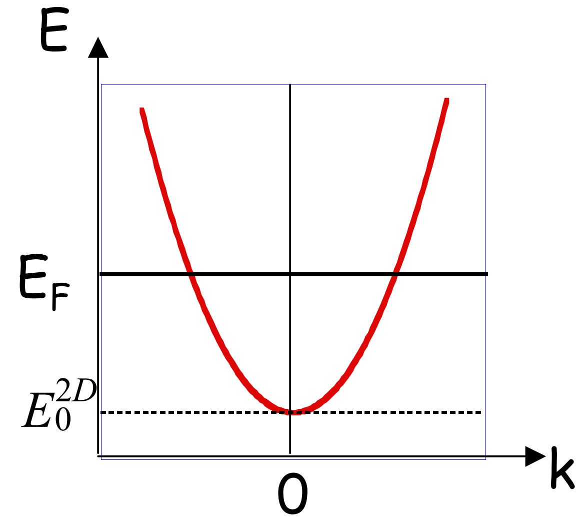
⇨ Spatial modulation of the LDOS is imaged by STM

Surface LDOS :

$$\rho\,(E,x,y) = \sum_{k_x\,,\,k_y} \left|\psi_k(x,y)\right|^2 \delta(\text{E-E}_k)$$

for a parabolic dispersive surface state:





$$E_k = E_0^{2D} + \frac{{}^2 k^2}{2m^*}$$

E_0^{2D} **: band edge energy**

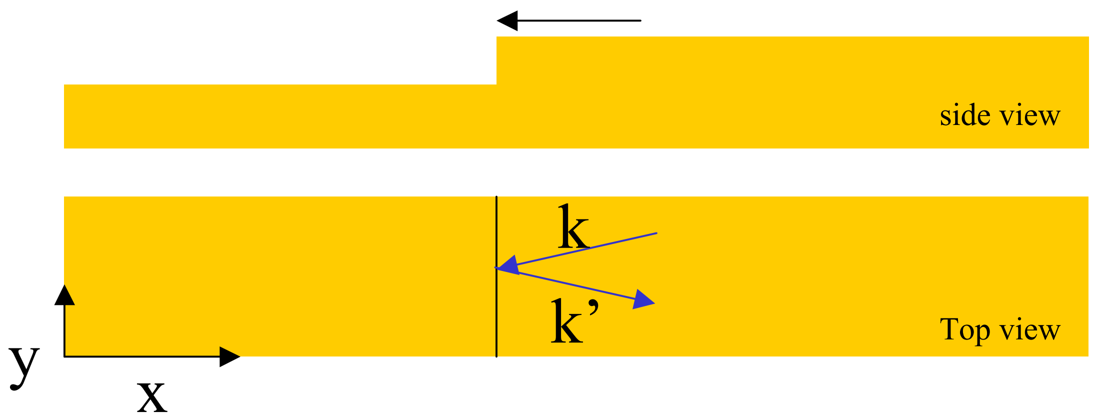
m^* **: effective mass**

$$\rho\,(E,x,y) = \frac{L_0}{\pi} {}_0^{k} \frac{1}{\sqrt{k^2 - k_x^2}} \cdot \left|\psi_k(x,y)\right|^2 \, dk_x$$

L_0 : LDOS of a 2D electron gas without any scattering

$$L_0 = \frac{m^*}{\pi\ {}^2}$$

In the vicinity of a step edge :



Coherent elastic processes
→ E is conserved |k|=|k'|

Problem invariant under translation along y
$k_y = k'_y$ and $k_x = -k'_x$

The step is modelled by a coherent reflection (amplitude : $r(k_x)$ and phase: $\varphi(k_x)$)

The incoming plane wave has to be superimposed **coherently** by the reflected plane wave :

$$\psi_k(x,y)=\left(e^{ik_x x}+r(k_x)e^{i\varphi(k_x)}e^{-ik_x x}\right)e^{ik_y y}$$

Electrons may also be :

transmitted in the surface state of the adjacent terrace : prob. $t(k_x)^2$

absorbed at the step (scattering into bulk states) :prob. $a(k_x)^2$

Incoherent processes <u>at the **step** !</u>

Particle conservation : $r^2 + t^2 + a^2 = 1$

3.5 Quantum interferences – coherent reflection model c

Surface LDOS is then obtained using the previous integral:

$$(*) \quad \rho(E,x,y) = \frac{L_0}{\pi}\int_0^k \frac{1}{\sqrt{k^2-k_x^2}} \cdot \underbrace{\left(|\psi_k(x,y)|^2 + t^2 + e^2\right)}_{\text{Incoherent summation}} dk_x$$

t^2: Electrons transmitted from the adjacent terrace

e^2: Electrons emitted from bulk to surface states ($a^2=e^2$)

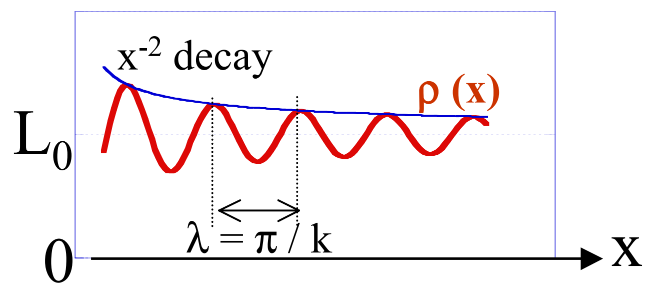
Which is rewritten as

$$\rho(E,x) = \frac{2L_0}{\pi}\int_0^k \frac{1+r(k_x)\cos(2k_x x+\varphi(k_x))}{\sqrt{k^2-k_x^2}} dk_x$$

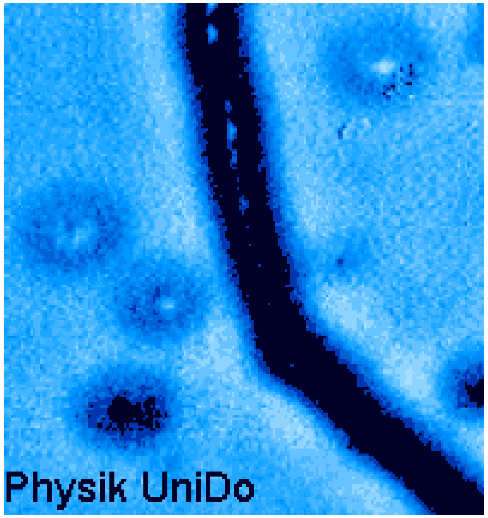
For $\varphi(k_x) \approx -\pi$ (see part 4), and $r(k_x)$ dominated by $r(k)$ in the integral, an analogic solution is found:

$$\rho(E,x) = L_0\left(1 - r(k)\, J_0(2kx)\right)$$

This model of coherent reflection on a step explains the LDOS oscillations but **shows also a decay** due to the summation in k space. $r \neq 1$ (inelastic processes at the step) reduces homogeneously the LDOS.



Wavelength of the standing waves versus energy…



Ag(111), T=5K
55 x 55 nm^2 dI/dV maps

http://omicron-instruments.com/products/lt_stm/r_ltstmm.html
Data courtesy : H. Hovel et al., Dortmund university, Germany

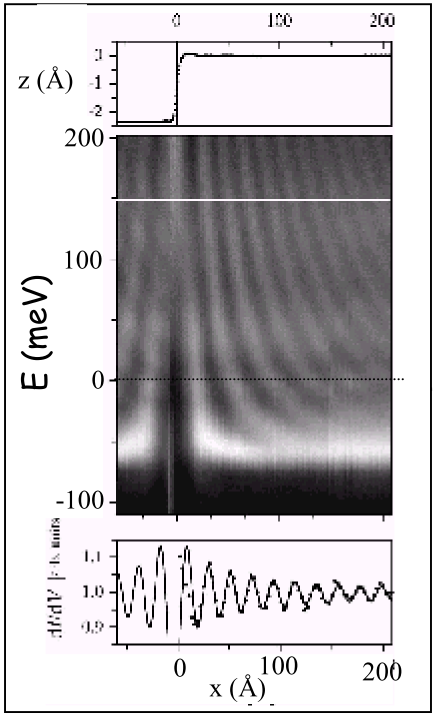
$$\rho(E,x) = L_0 (1 - r(k) J_0(2kx))$$

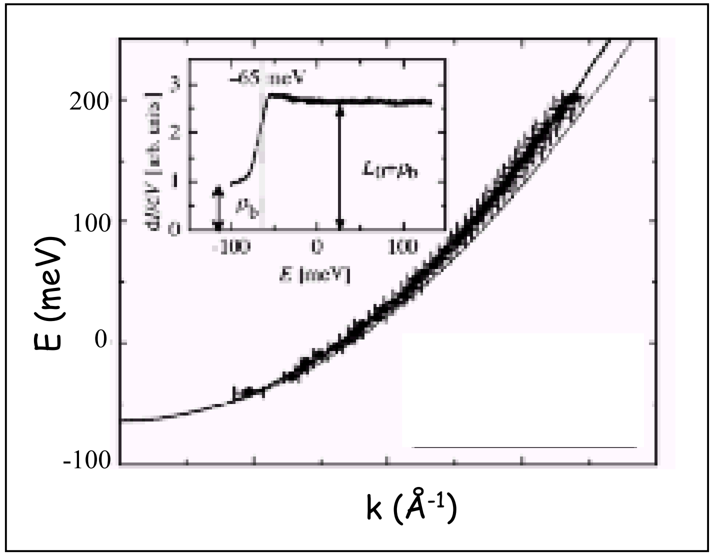
Parabolic dispersion of the surface state Ag(111), T=5K

TOPO →

dI/dV (V) →

dI/dV (+150 meV)→





Accurate determination of the surface state parameters:

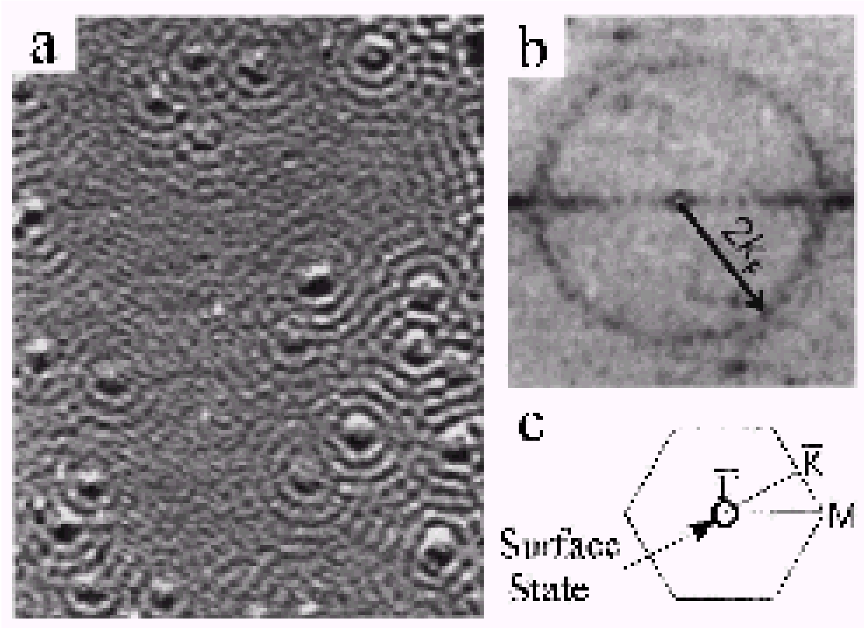
E_0^{2D} = (-65±3) meV

m^* = (0.40 ±0.01) m_e

O. Jeandupeux, L. Bürgi, A. Hirstein, H. Brune and K. Kern, Phys. Rev. B ***59****, 15926 (1999)*

Mapping of the Fermi Surface

Constant current image at +5mV
42,5 x 55 nm^2



FFT

Cu(111), T=150K

L. Petersen,… E.W. Plummer, Phys. Rev. B 57, R6858 (1998)