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the
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international centre for theoretical physics

SMR/1270-29

# SCHOOL ON SYNCHROTRON RADIATION

**6 November - 8 December 2000**

***Miramare - Trieste, Italy***

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*Co-sponsors: Sincrotrone Trieste, Società Italiana di Luce di Sincrotrone (SILS) and the Arab Fund for Economic and Social Development*

# *Angle-Resolved Photoemission from One- and Two-Dimensional Systems - Surface States*

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Zurich, Switzerland

Lecture at the School on Synchrotron Radiation, ICTP Trieste, Nov. 29-Dec. 4 2000

# Photoemission from Valence Bands
# Fermi Surface Mapping

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**Lecture 1**
*Angle-Resolved Photoemission from One- and Two-Dimensional Systems – Surface states*

1) Electronic Bandstructure in 1-3 Dimensions
2) Photoemission from a Periodic Potential
3) The Three-Step Model
4) A 1D Example: p(2x1) O – Cu(110) -> Band Mapping
5) A 2D Example: The Shockley Surface State on Cu(111)
6) A Few Words about Surface States in General
7) Surface States and Nanostructures

**Lecture 2**
*Angle-Resolved Photoemission from Three-Dimensional Systems – Including Magnetism*

1) A Few Words about the Fermi Surface in General
2) Fermi Surface Mapping
3) Free Electron Final States
4) Mapping Final States in GaAs
5) Examples: Cu, Al
6) Itinerant Ferromagnetism: The Fermi Surface of Nickel

**Lecture 3**
*Spin- and Angle-Resolved Photoemission / Manybody Effects*

1) Spin-Resolved Photoemission
2) A Complete Photoemission Experiment in the Construction Phase
3) Fermi Surfaces in Multilayers
4) Thickness-Dependent Fermi Surface in Co Films on Cu(111)
5) Manybody Effects in Solids: Theoretical Concepts – Spectral Functions
6) Example: Valence Photoemission in Nickel

**Lecture 4**
*Photoemission Intensities and Line Widths*

1) Exploiting Photon Polarization Effects
2) Ultraviolet Photoelectron Diffraction: Cu as an Example
3) Diffraction versus Dispersion in Fermi Surface Mapping: K/Si(001)
4) Interpretation of Line Widths in Valence Photoemission
5) Momentum Distribution Curves
6) Example: Dispersion Curves from Ni(001)

**Lecture 5**
*X-Ray Excited Valence Photoemission – Highest Resolution Photoemission*

1) Determination of Partial Densities of States
2) Examples for Elemental Metals: Pt, Al
3) Application to a Binary System: $AuCu_3$
4) Highest Resolution Photoemission
5) Application to Superconductivity
6) Quantum Well States

**Lecture 6**
*Exploring the Limits of X-Ray Photoelectron Diffraction*

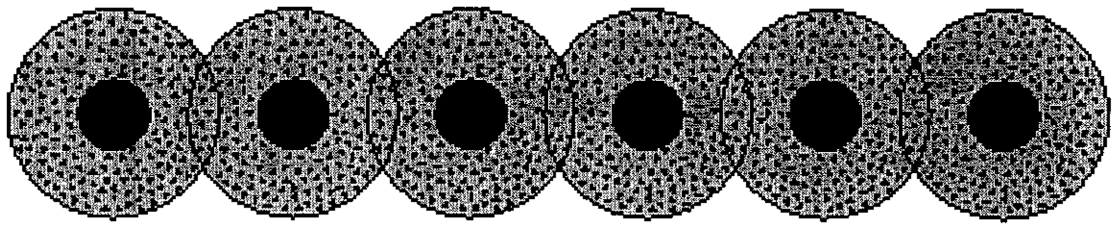
1) Surface Structure Problems Solved by XPD
2) Simple Structure Identification by Fingerprinting
3) Orientation of Large Molecules: $C_{60}$
4) Orientation and Conformation of Large Molecules: Chiral 7-Helicene
5) Monolayer Film Structure: Hexagonal Boron Nitride (h-BN)
6) Monolayer Film to Substrate Registry: again h-BN
7) Application to Catalysis: Determining Bonding Sites of Single Atoms
8) Application to Catalysis: Finding Subsurface Species (O/Rh(111))

**Further Reading (Photoemission from Valence Bands):**

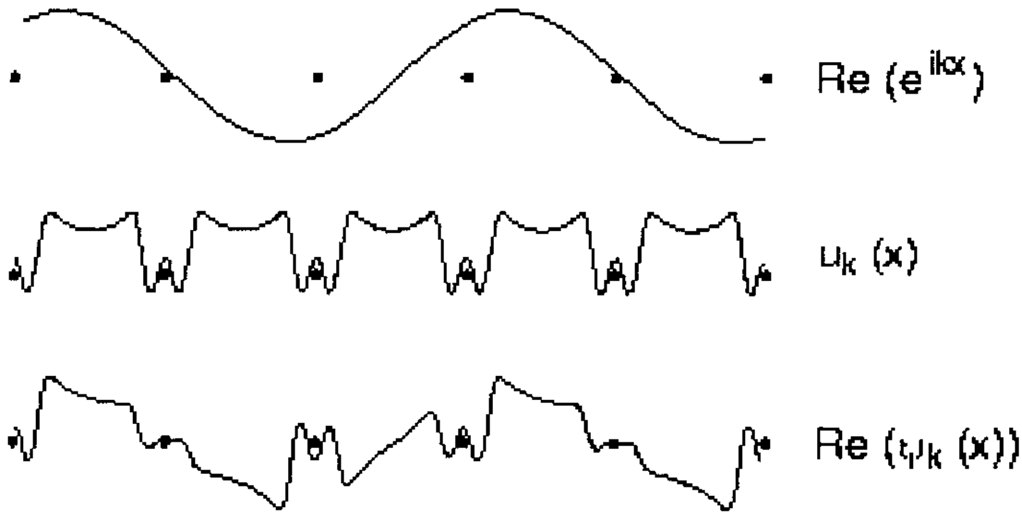

1) S. Hüfner, *Photoelectron Spectroscopy* (Springer, Berlin 1995)
2) E. W. Plummer and W. Eberhardt, Adv. Chem. Phys. 49 (1982) 533
3) S. D. Kevan (ed.), *Angle-Resolved Photoemission – Theory and Current Applications* (Elsevier, Amsterdam 1992)

# Electronic Bandstructure in 1 Dimension

chain of atoms:



wave functions:

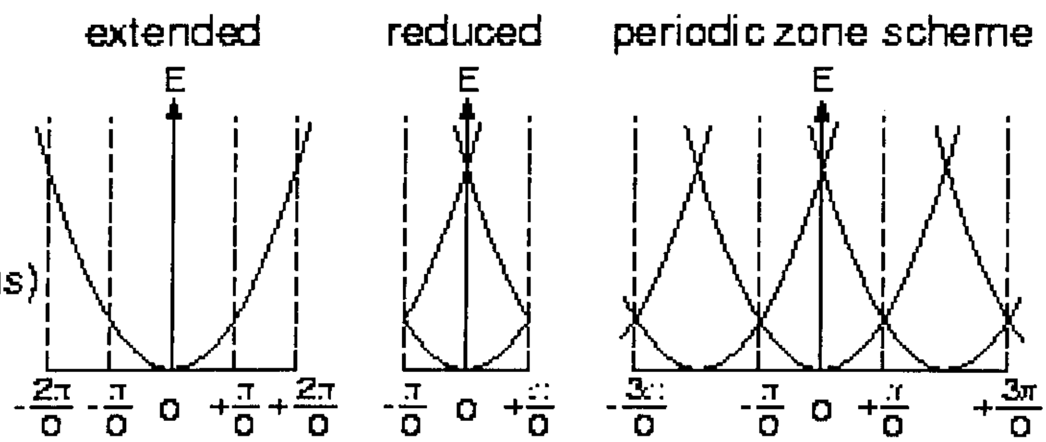



Bloch functions $\psi_k(x) = u_k(x)\, e^{ikx}$

dispersion relation (reciprocal space):

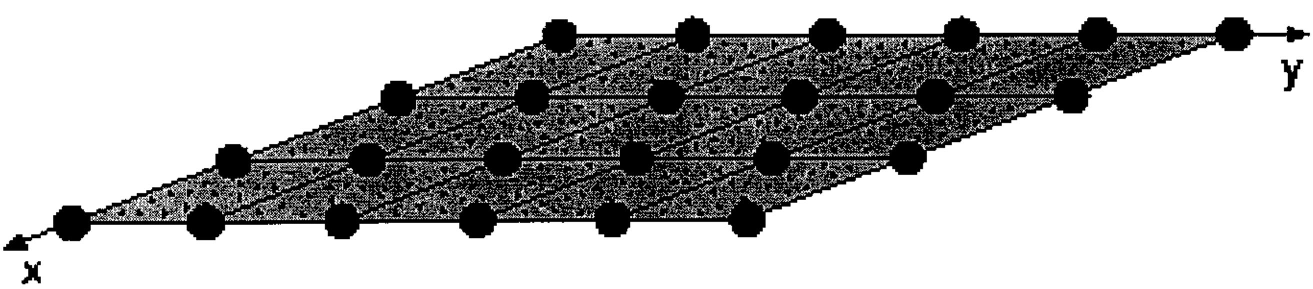
$$\varepsilon(k) = \frac{\hbar^2 k^2}{2m}$$

(free electrons)

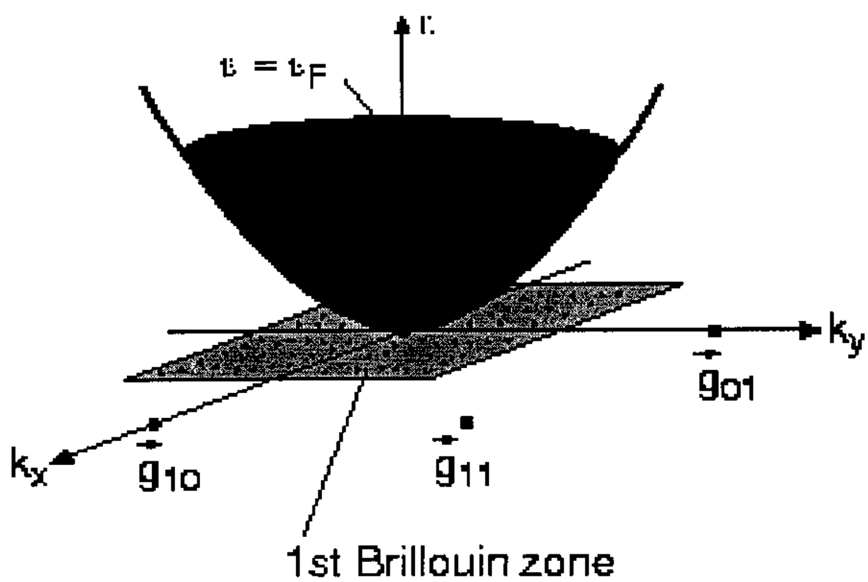


## Electronic Structure in 2 Dimensions

(Plane of atoms)

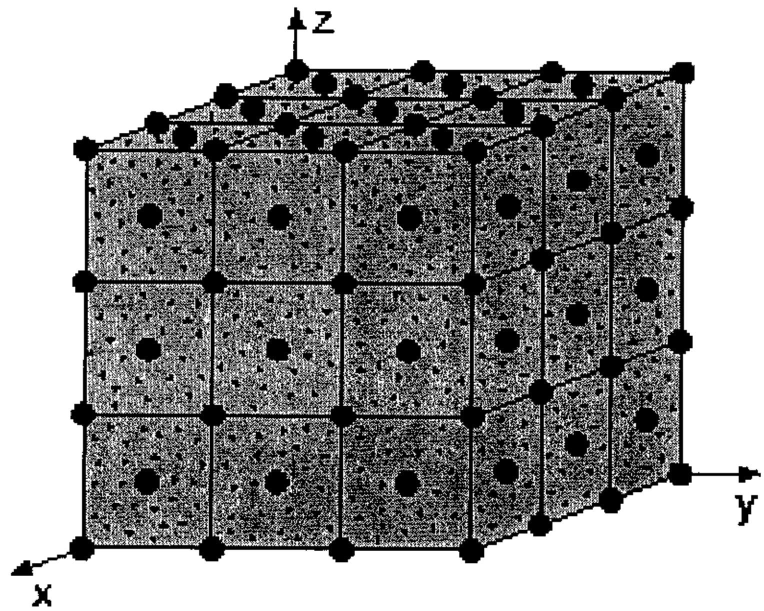



dispersion relation

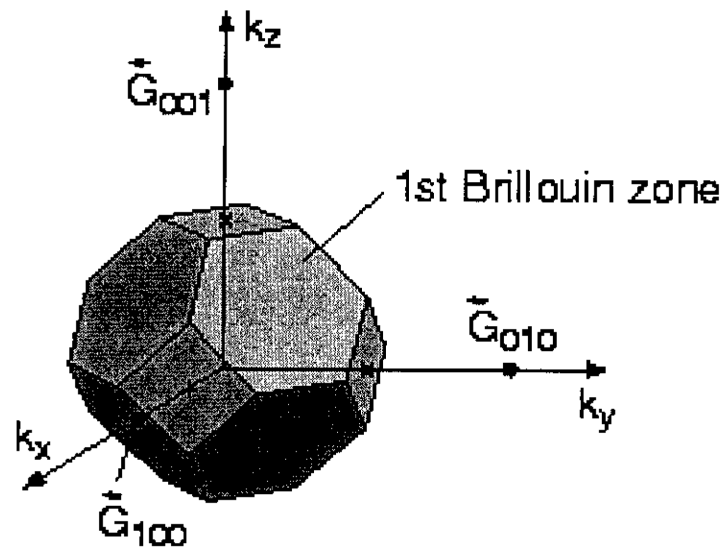


# Electronic Structure in 3 Dimensions

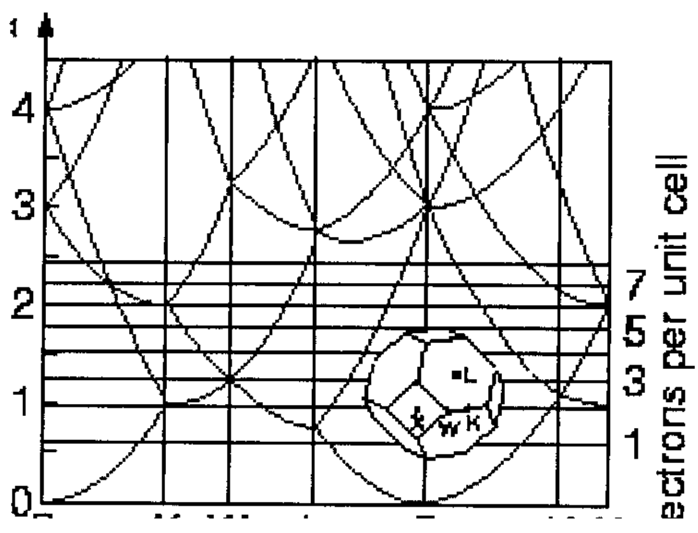
real space:
(face-centered cubic lattice)

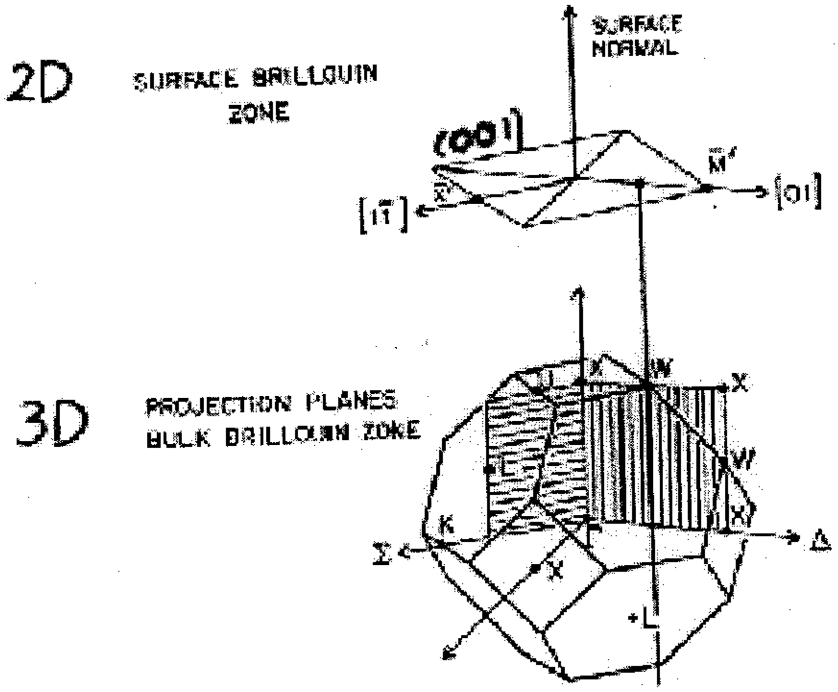



reciprocal space:




dispersion relation:

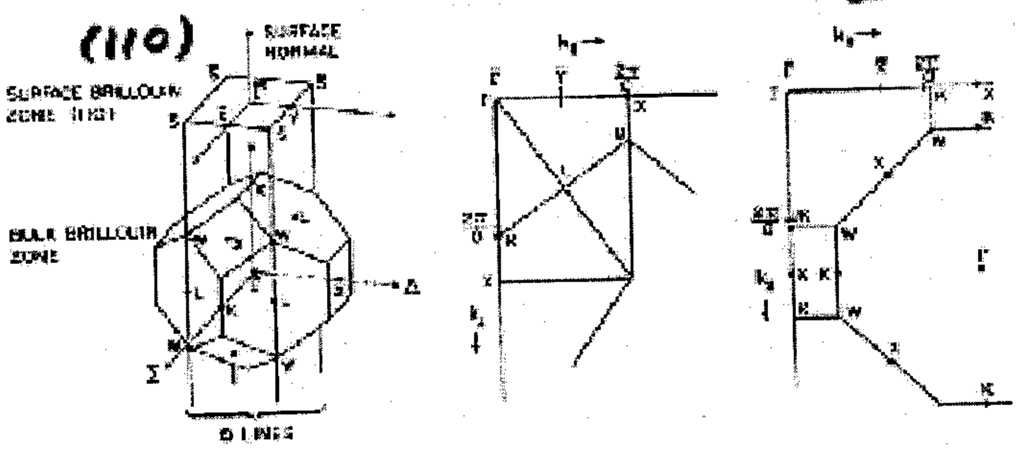


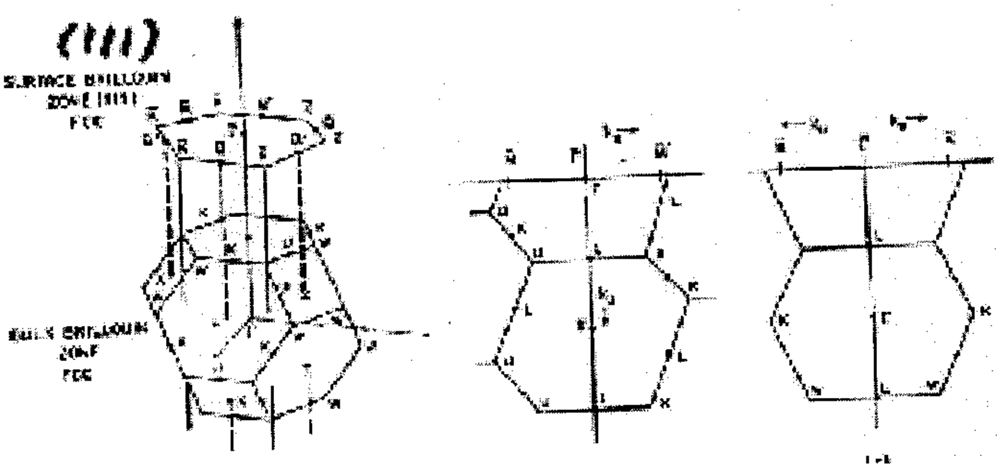



fcc

E. W. PLUMMER AND W. EBERHARDT

*Adv. Chem. Phys.* #?, 533 (1982)



# Photoemission of a free electron

| | Energy | Momentum |
|---|---|---|
| free electron | $\varepsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}$ | $\hbar\vec{k}$ |
| photon ($h\nu$) | $\varepsilon(\vec{k}) = \lvert\hbar\vec{k}\rvert c$ | $\hbar\vec{k}$ |

## wave numbers k

$e^-$ : $k = 0.51\sqrt{E[eV]}\ \text{Å}^{-1}$

$h\nu$ : $k = 0.51 \cdot \varepsilon[eV] \cdot 10^{-3}\ \text{Å}^{-1}$

## Photoemission:


## Conservation Laws:

$$\varepsilon_1 + h\nu = \varepsilon_2$$

$$\vec{k}_1 + \vec{k}_{h\nu} = \vec{k}_2$$

... cannot be simultaneously fullfilled !
→ process forbidden

Atoms, Molecules : Recoil

Solids : Recoil (= reciprocal lattice vector)

## Photoemission from a Periodic Potential

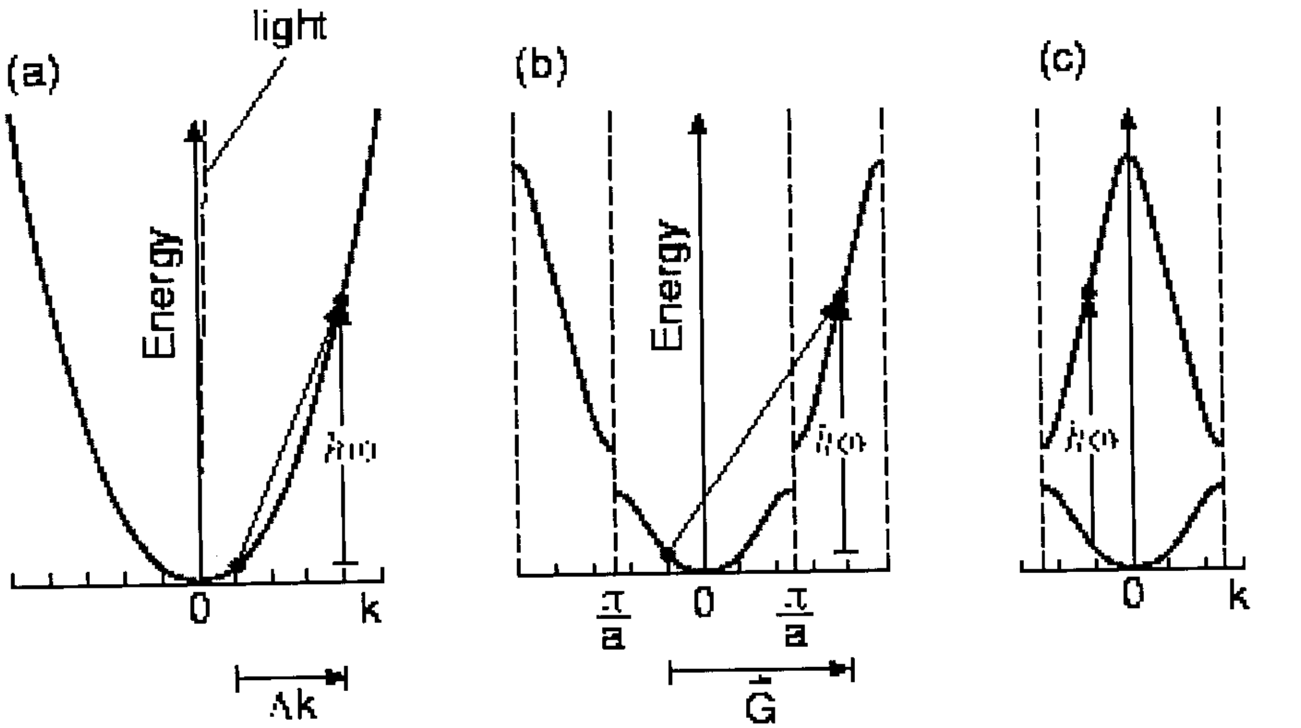
Conservation Laws:

$$\varepsilon_i(\vec{k}_i) + h\nu = \varepsilon_f(\vec{k}_f)$$

$$\vec{k}_i + \vec{k}_{h\nu} + \vec{G} + \vec{g} = \vec{k}_f$$

$\vec{k}_{h\nu} \approx 0$

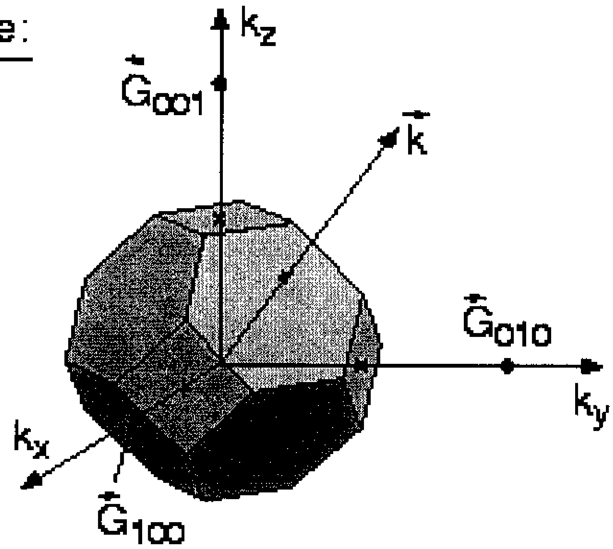
$\vec{g}$: reconstructed surface



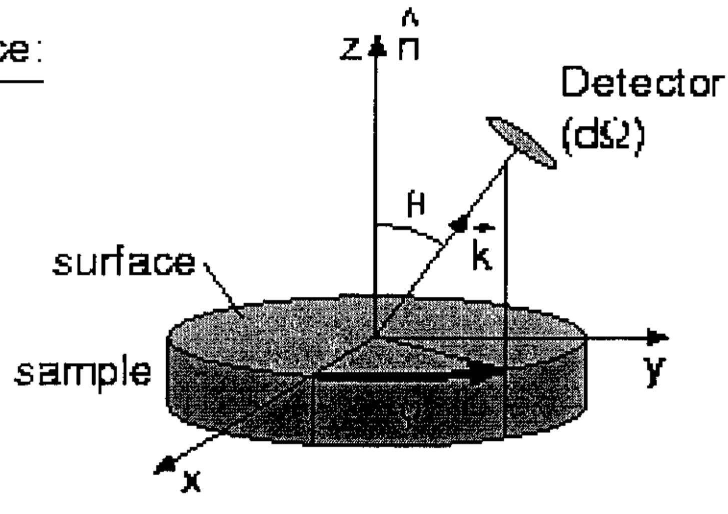

free electron — extend zone periodic potential — reduced zone periodic potential

## Measurement of the Photoelectron Momentum

reciprocal space:



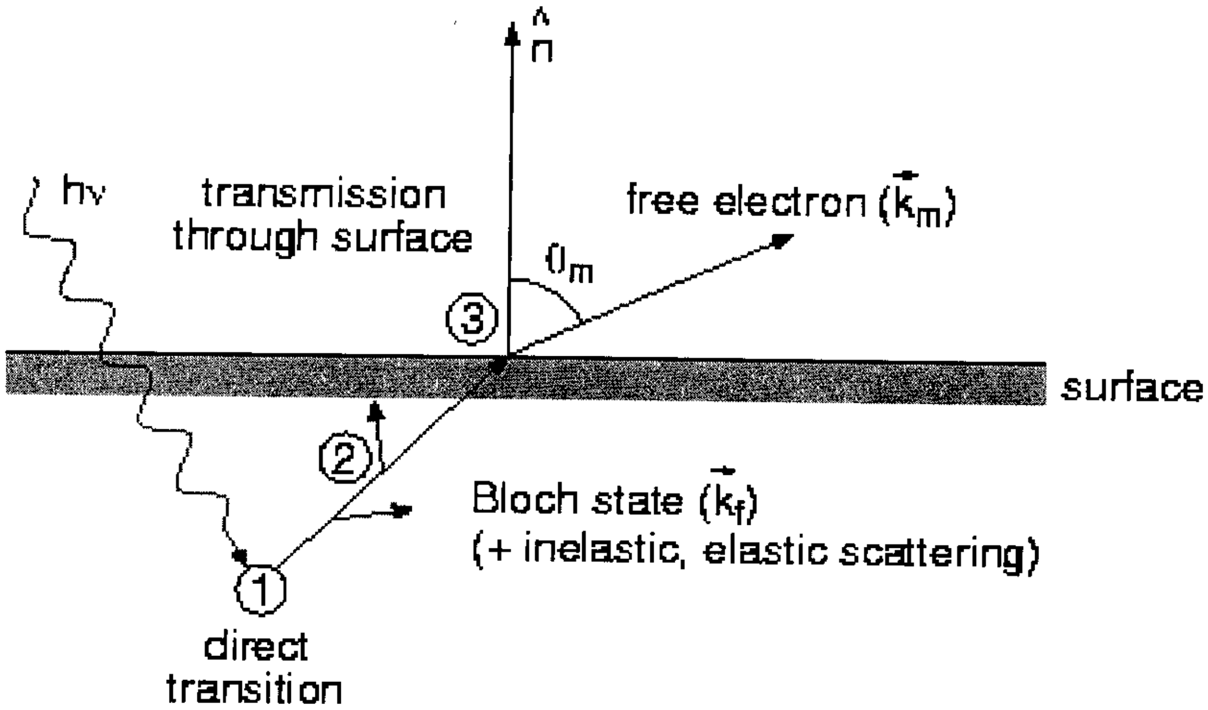

real space:




| | |
|---|---|
| direction: | $\hat{k} = \theta, \phi$ (watch for refraction) |
| magnitude: | from $\varepsilon_f(\vec{k})$ ($\varepsilon_f$ is measured) |
| Problem: | $\varepsilon_f(\vec{k})$ usually not known |
| Solution: | free electron final state |

$$\varepsilon_f(k) = \frac{\hbar^2 k^2}{2m}$$

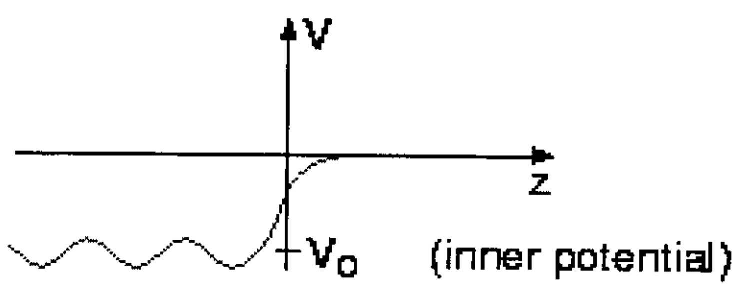
# The 3-Step Model




① Photoexcitation

② Propagation to surface

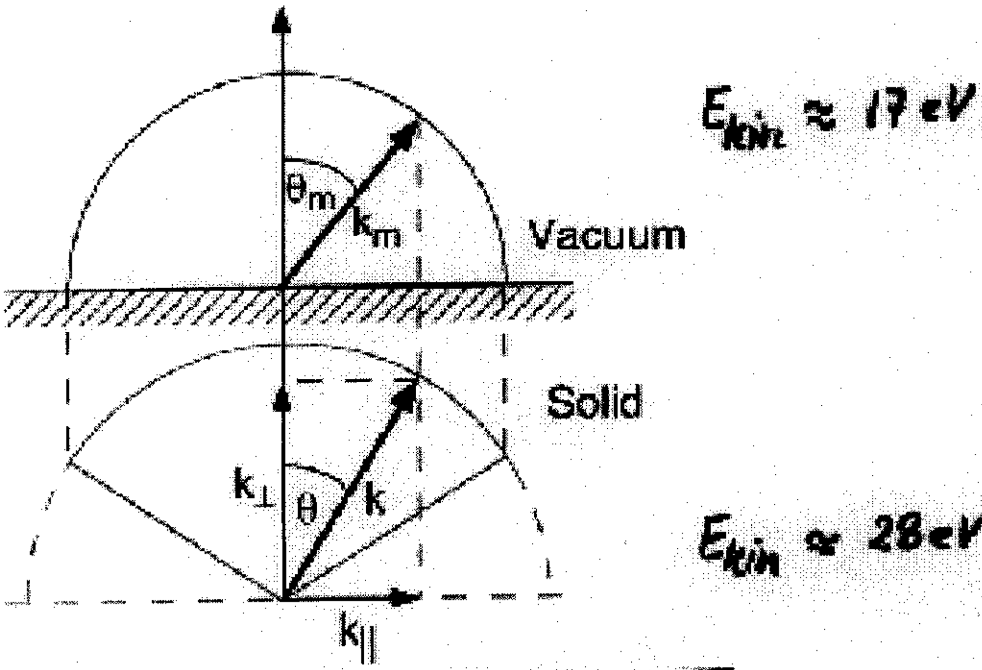
③ surface potential step → Refraction




periodicity within surface → $\vec{k}_{f\parallel} = \vec{k}_{m\parallel}$

surface potential step → $\vec{k}_{f\perp} > \vec{k}_{m\perp}$

Refraction at the Surface Potential Step

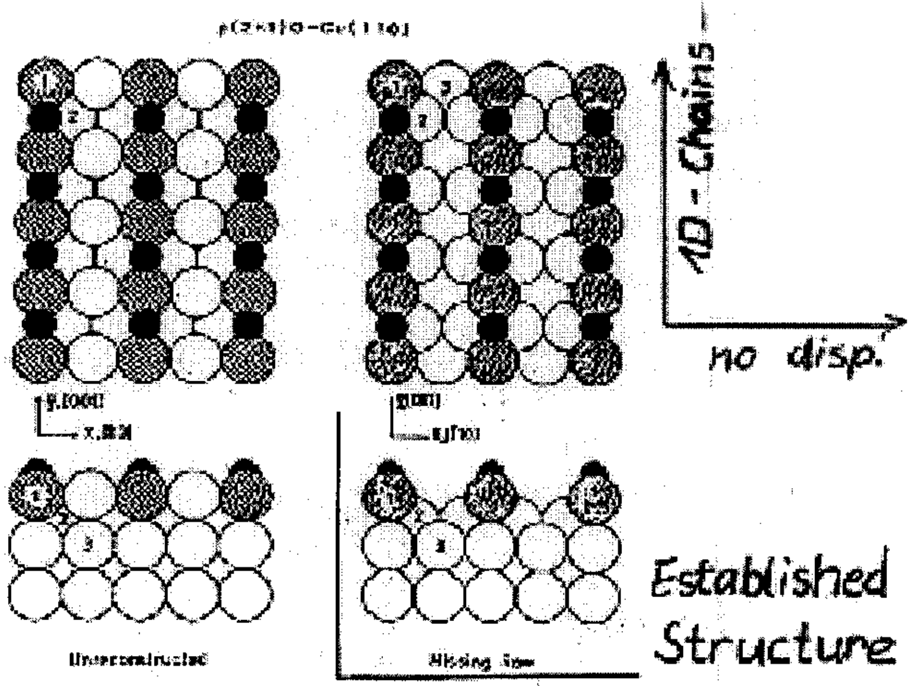


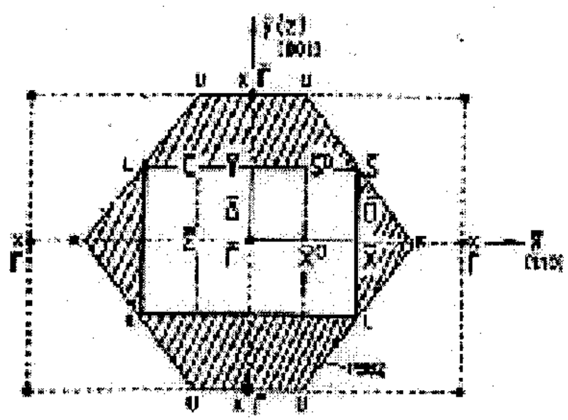

$$\sin\theta = \sin\theta_m \sqrt{\frac{h\nu - \Phi}{h\nu - \Phi + V_o}}$$

$\Phi$ : work function

$V_o$ : inner potential

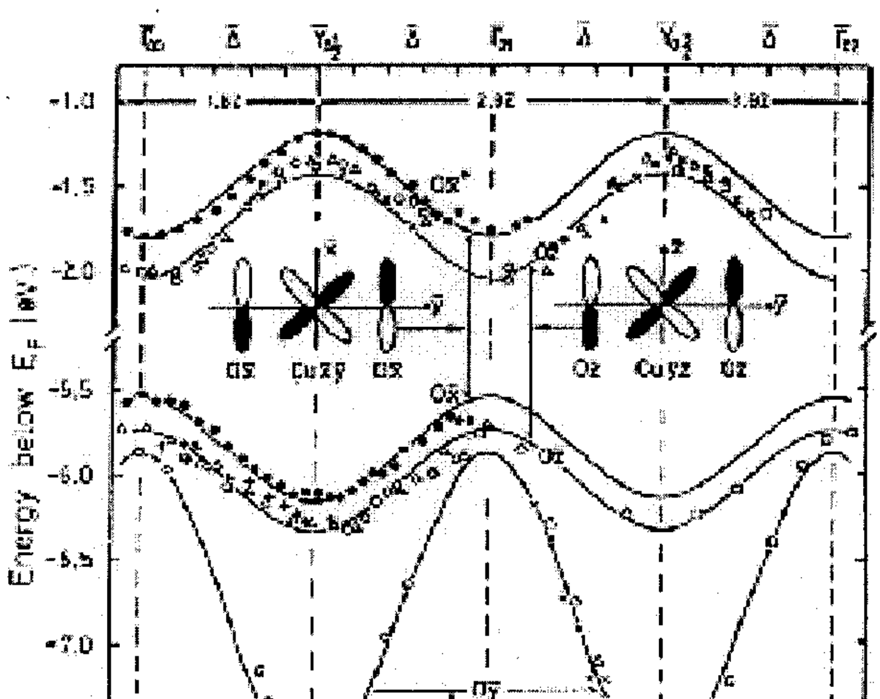
# A One-Dimensional Example:
## p(2×1) O - Cu(110)

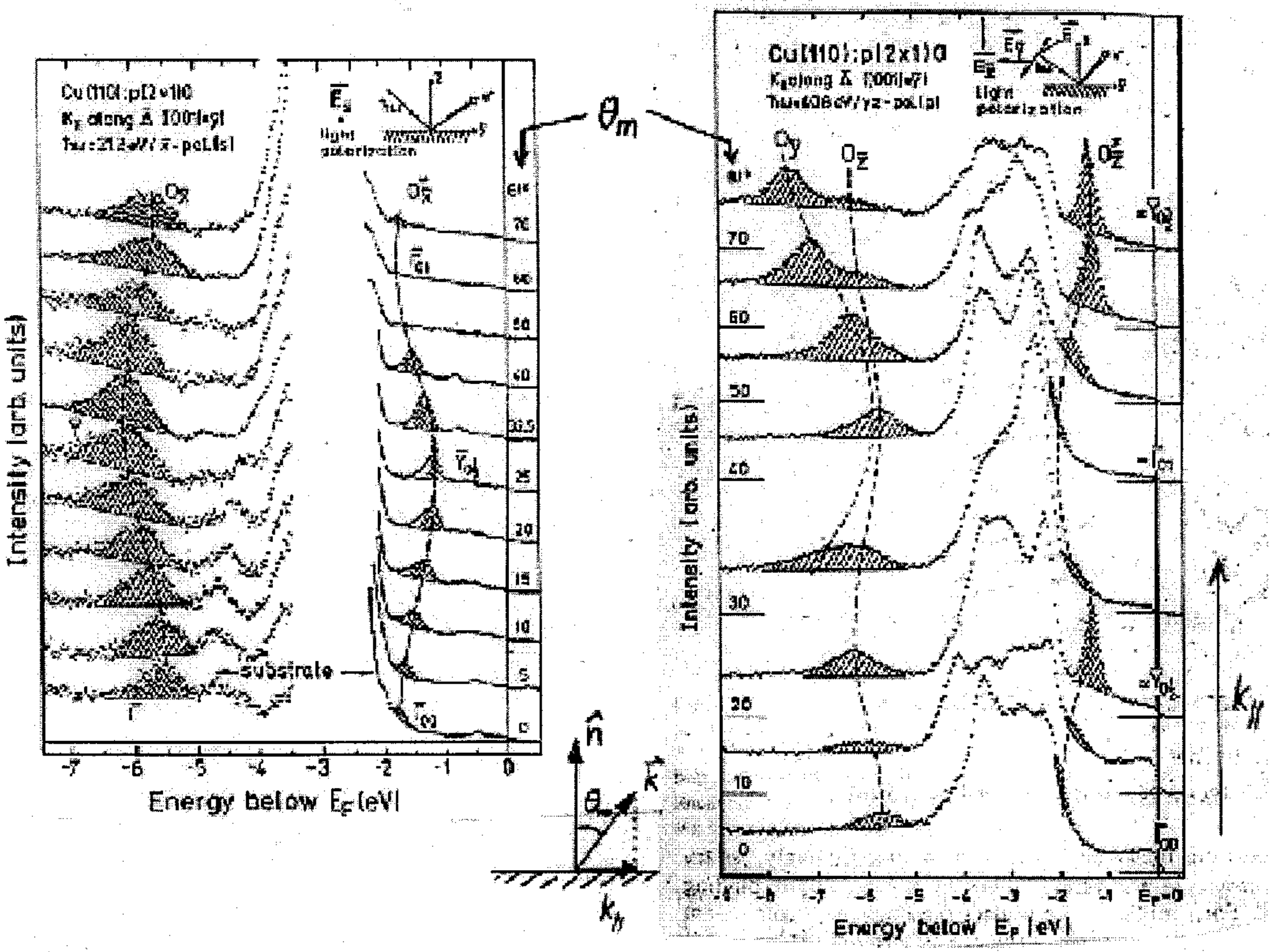


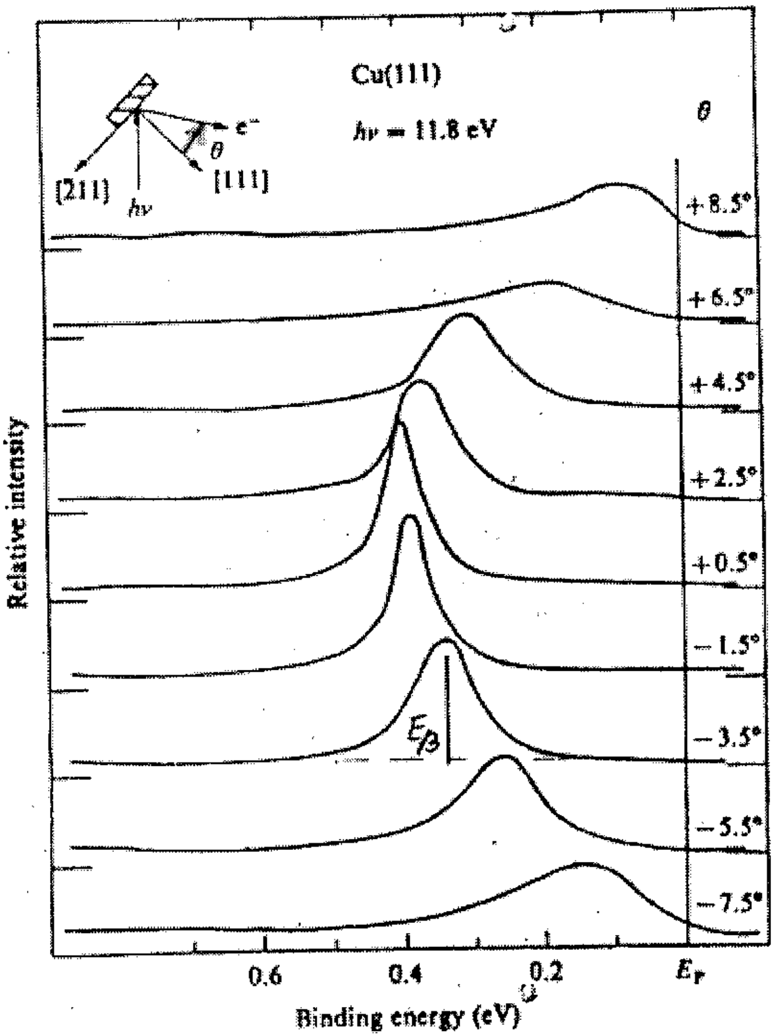
fcc (110) surface Brillouin zone (SBZ)

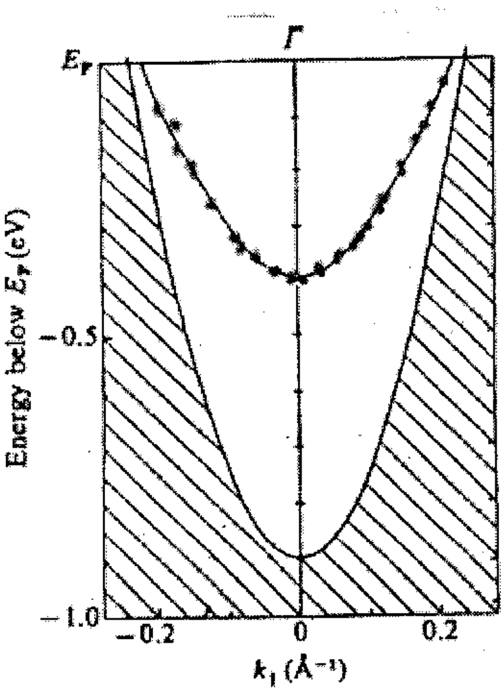
From S. Hüfner "Photoelectron Spectrosc."


Energy below $E_F$ (eV)
Wavevector $K_\parallel$/(2π/a) along [001](y)
0.0
0.5
1.0
1.5
2.0
-1.0
-1.5
-2.0
-5.5
-6.0
-6.5
-7.0
-7.5
-8.0
Ox
Cu zy
Oz
Cu yz
Oy
Cu $\bar{y}^2$


Intensity (arb. units)
Energy below E_F (eV)
substrate
light polarization
Cu(110):p(2x1)O
θm
Intensity (arb. units)
Energy below E_F (eV)
light polarization
k∥

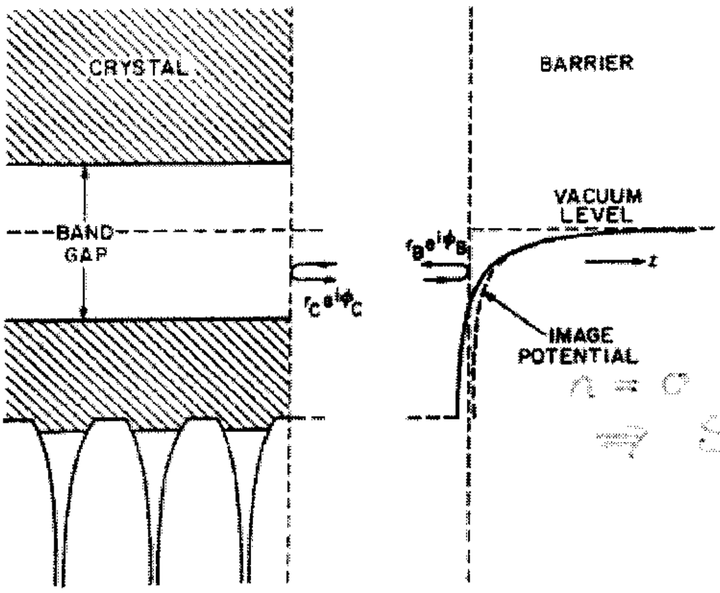
# A 2D Example: Shockley Surface State on Cu(111)




S.D. Kevan et al.
PRB 12 ('87) 5809

# Surface States

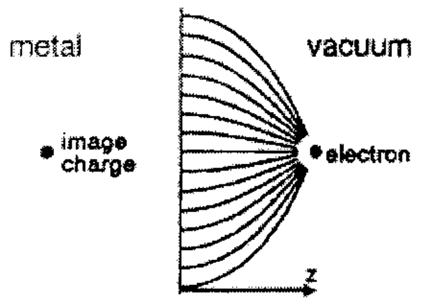



n = 0

⇒ Surface State

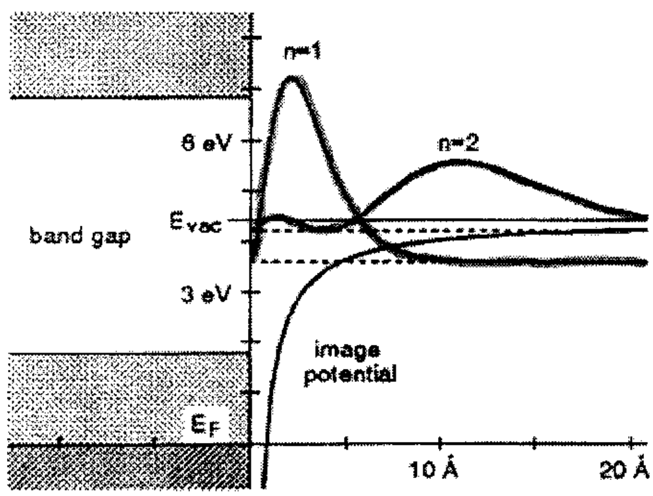
from N. V. Smith, PRB 32, 3549 (1985)

n = 1, 2, ⋯



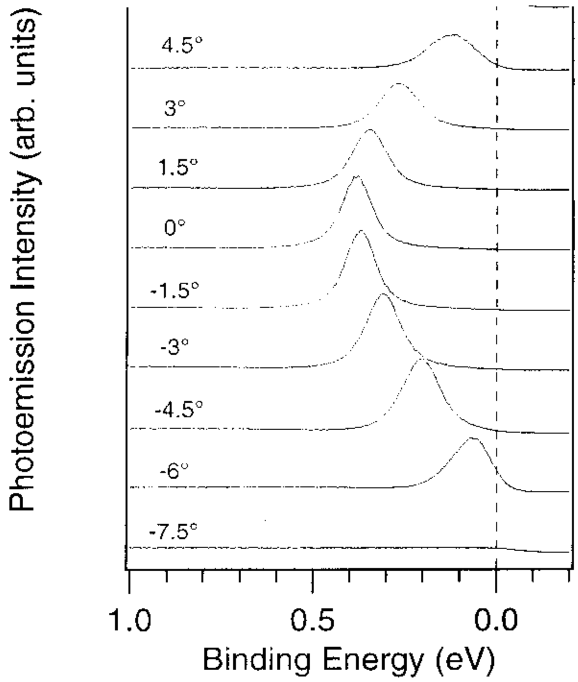

⇒ Image Potential States

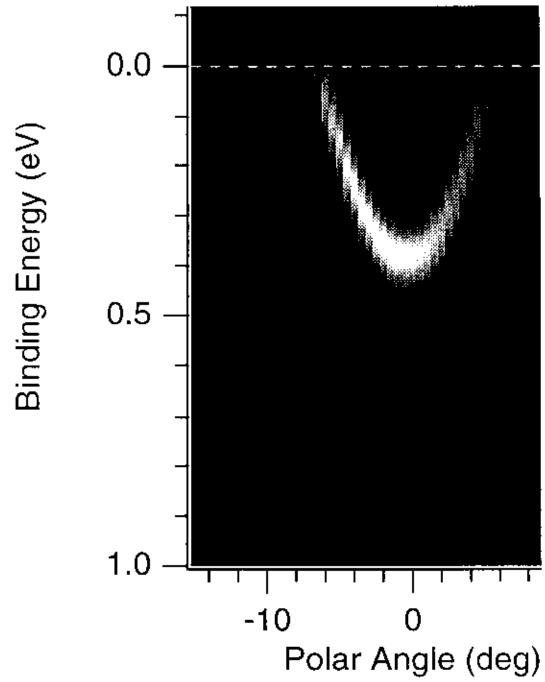
(Rydberg Series)




T. Fauster, Appl. Phys. A 59 (1994) 639

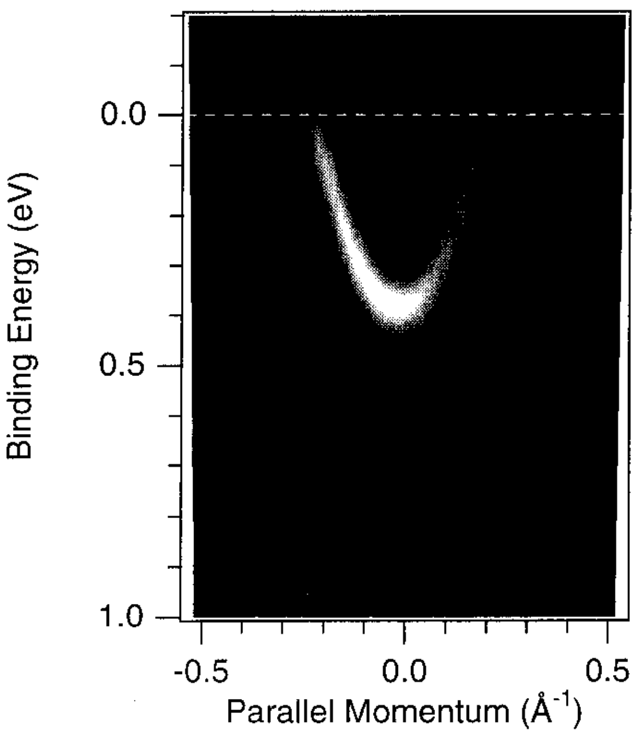
**Fig. 1.** Top: The electric field of an electron in front of a metal surface can be described by the concept of an image charge. Bottom: The corresponding attractive image potential leads to a series of bound states if the electron cannot penetrate into the metal along certain directions due to a band gap. For the lowest two states the square of the wave function is shown.




... in $k_{//}$

occupation numbers re



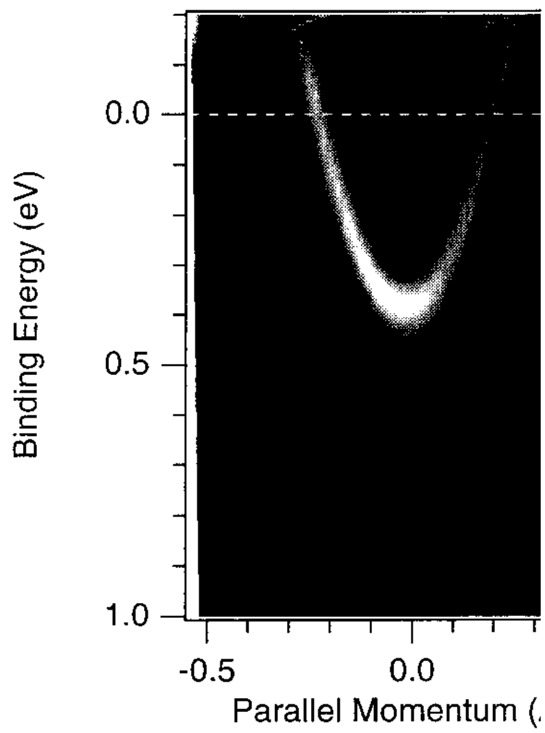
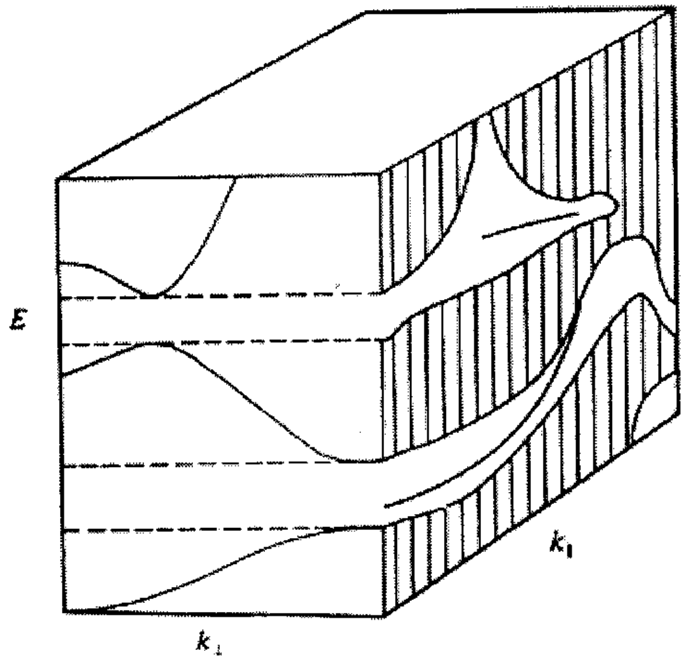



Fig. 4.15. Projected bulk band structure at the surface of a metal. The dispersion of two possible surface state bands is indicated.




Where do surface states exist ?

Shockley St.

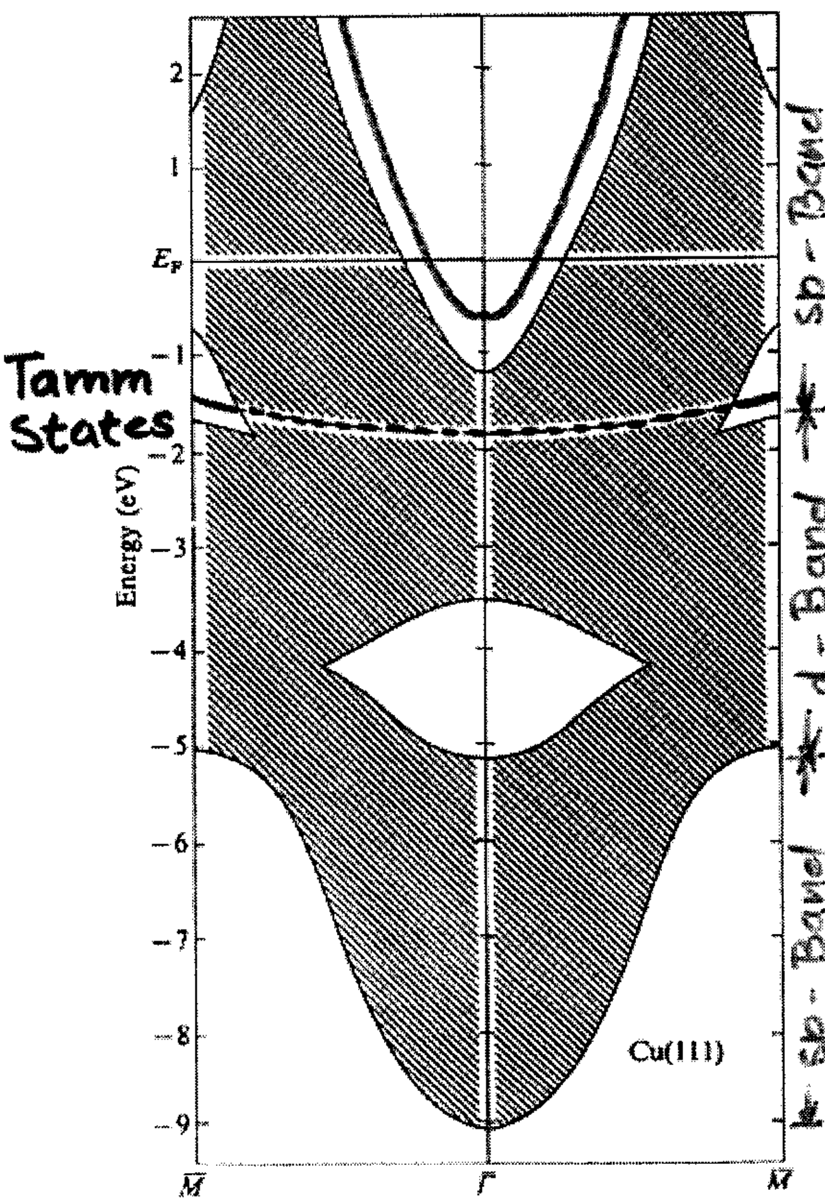



Fig. 4.17. Surface states (dashed curves) and bulk projected bands at a Cu(111) surface according to a six-layer surface band structure calculation (Euceda, Bylander & Kleinman, 1983).

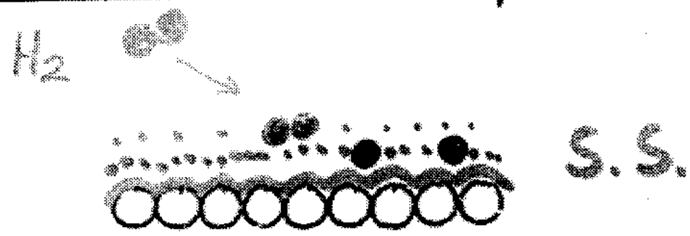
Experimental identification:

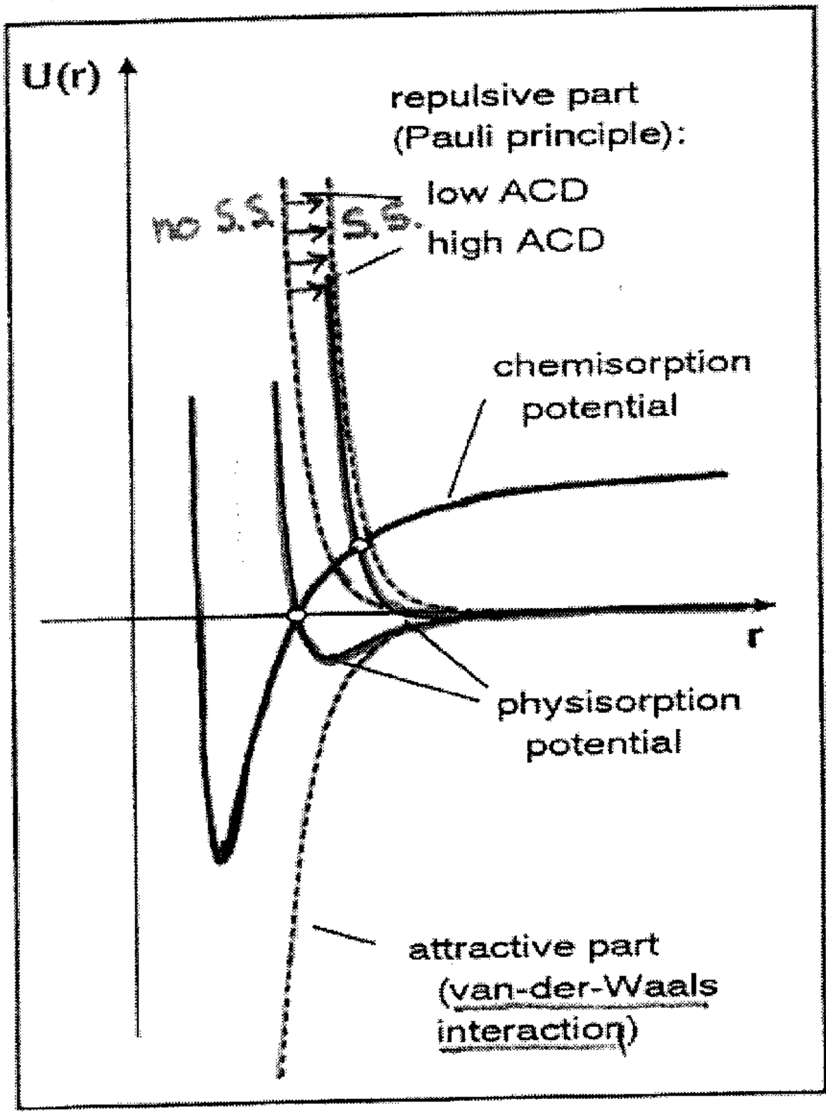
- "crud" test
- no dispersion in $k_\perp$ (→ S.R.)

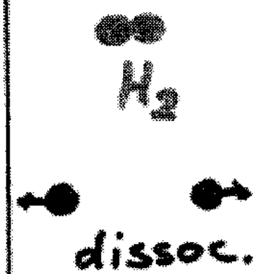
aus Zangwill

# Importance of Surface States

→ dissociative chemisorption




→ surface diffusion

E. Bertel et al. Appl. Phys. A 63 (1996) 523

Schwöbl barrier

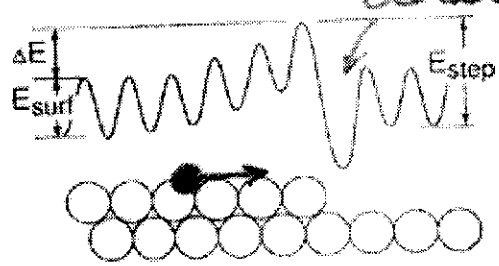



FIG. 1. Schematic representation of the diffusion potential at a step.

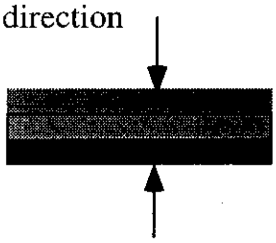
... reduced by S.S.

Memmel, Bertel PRL 75 ('95) 485.

# Surface States and Nanostructures

| 2D Electron Gas: | GaAs/AlGaAs | met. surf. state |
|---|---|---|
| electron concentrations | ~ $10^{11}cm^{-2}$ | ~ $10^{15}cm^{-2}$ Al(001)<br>~ $10^{14}cm^{-2}$ Cu(111) |
| Fermi wave length | ~40 nm | ~0.7nm Al(001)<br>~3 nm Cu(111) |
| phase coherence length | ~50μm (4K) | ~1000nm (4K)<br>~10nm (300K)<br>... can be lower |
| | mesoscopic physics | nanostructures ! |
| | Quantum Size Effects | |

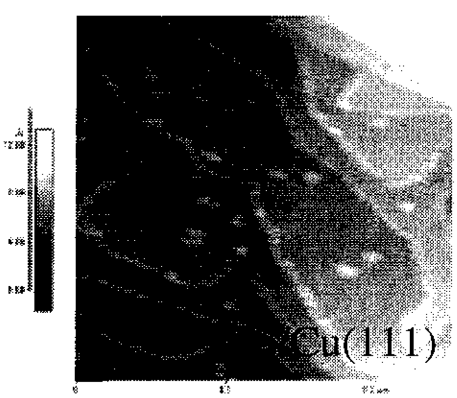
vertical direction



no problem
(e.g. surface states)

horizontal direction

challenge !




steps,
step decoration,
self assembly, ...

# Quantum Mirages

... hand-made
nanostructures !

... viewed by the
Kondo effect

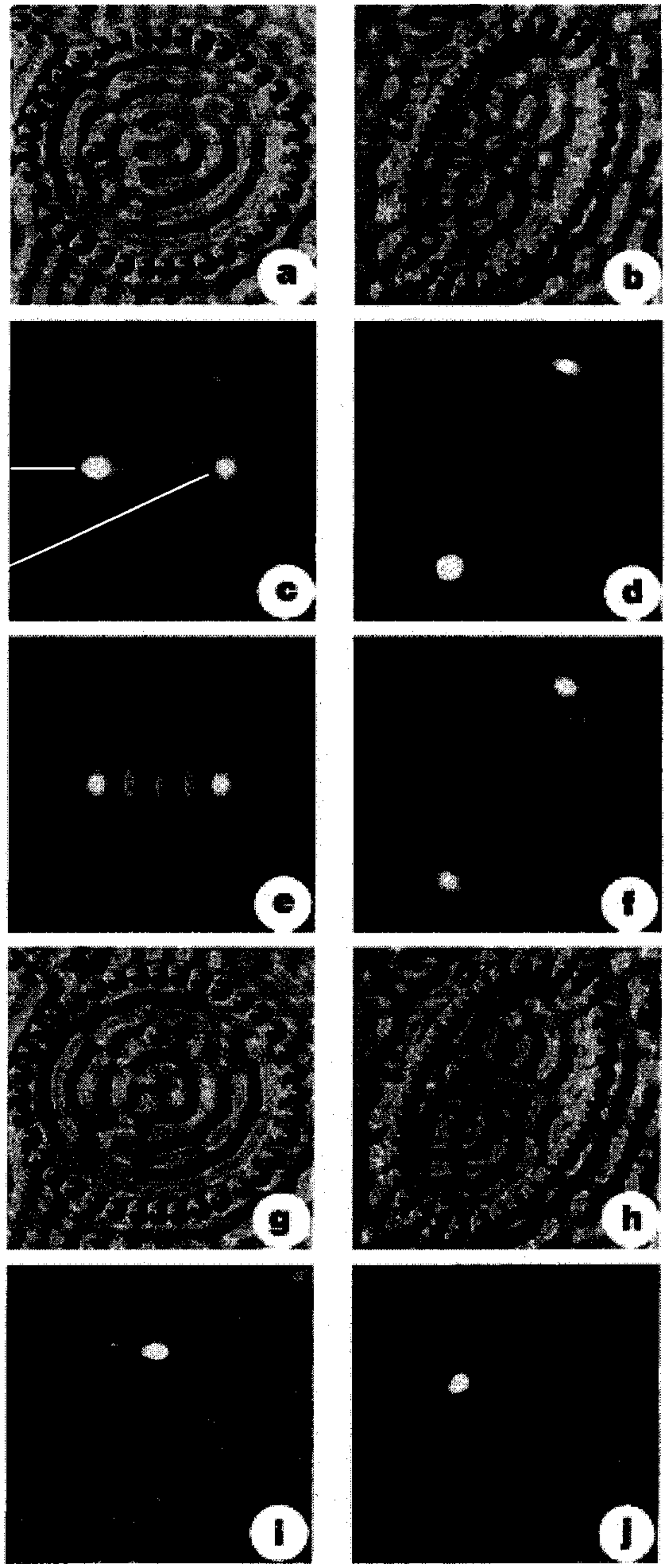
Atom

"Mirage"

Calculated
Eigenmodes

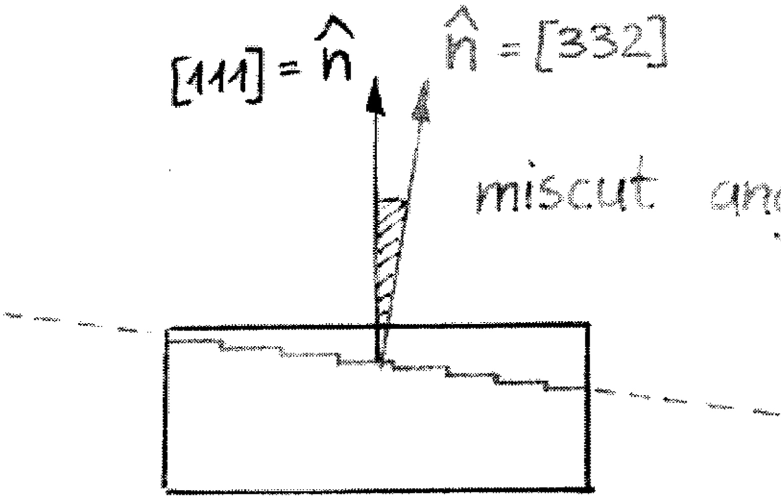
... put atom off the
focal point :

... no mirage !




H. C. Manoharan, C. P. Lutz,
D. M. Eigler,
Nature 403 (2000) 512

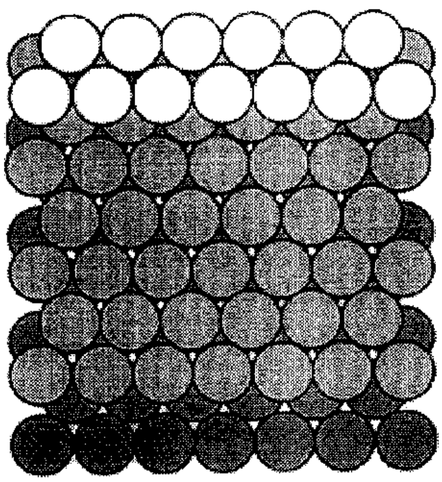
# Surface State on Stepped Cu Surfaces



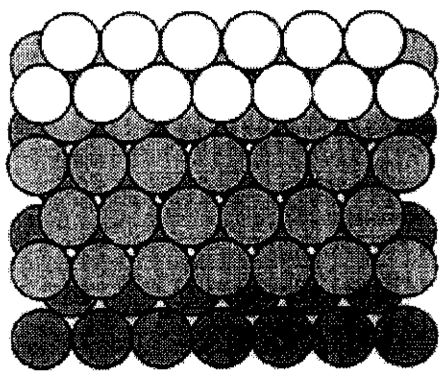

→ Interaction Steps ⇄ Surf. State

... → chem. Reactivity ?

**Cu(332)**
(10° miscut, 12Å terraces)

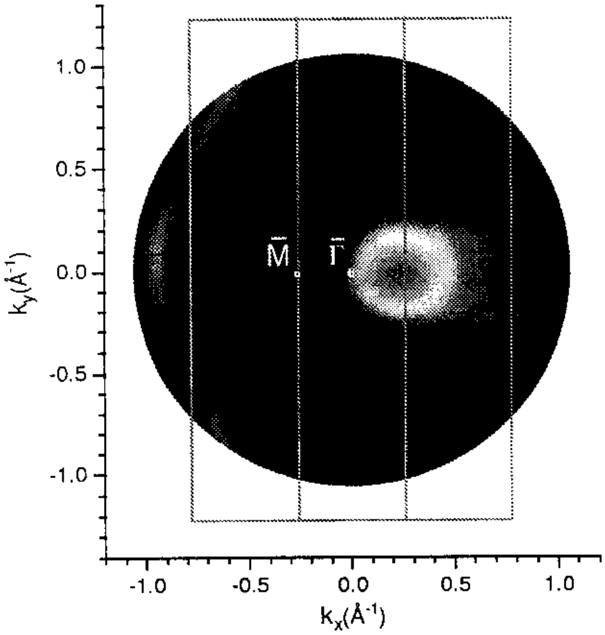


**Cu(221)**
(15.8° miscut, 7.7Å terraces)



# 1D Shockley Surface State Resonance on Cu(332)

Fermi
Surface
Map




Dispersion
Plots