Surface Electronic Properties of Selected Materials

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Atomic N adsorption on clean Cu(001) surface

collaboration with:

L.J. Cristina, R.A. Vidal and J. Ferrón (INTEC, Santa Fe)

Surface characterization of nitride structures on Cu(001)
Formed by implantation of N: ions: An AES, XPS and LEIS Study”

Surf. Sci. 602, 3454 (2008)

ARUPS characterization (Currently in progress)

N on Cu(001)

* N_2 molecules do not chemisorb on Cu(001)

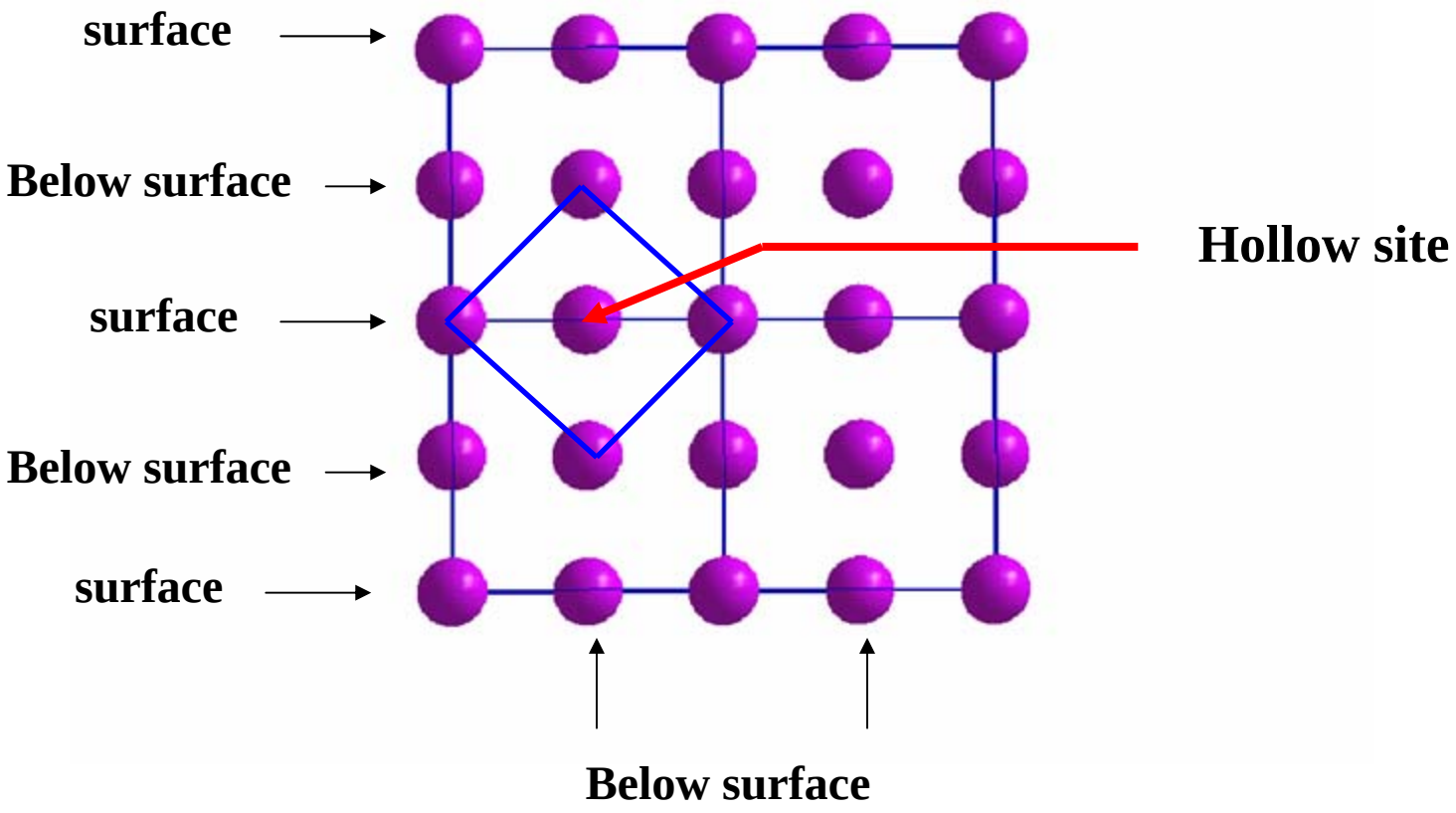
* Atomic N chemisorbed on Cu(001) at RT
  (Tibbetts et al. PRB 1977)

* N_2^+ implantation and annealing
  (Cristina et al. Surf. Sci. 2008)

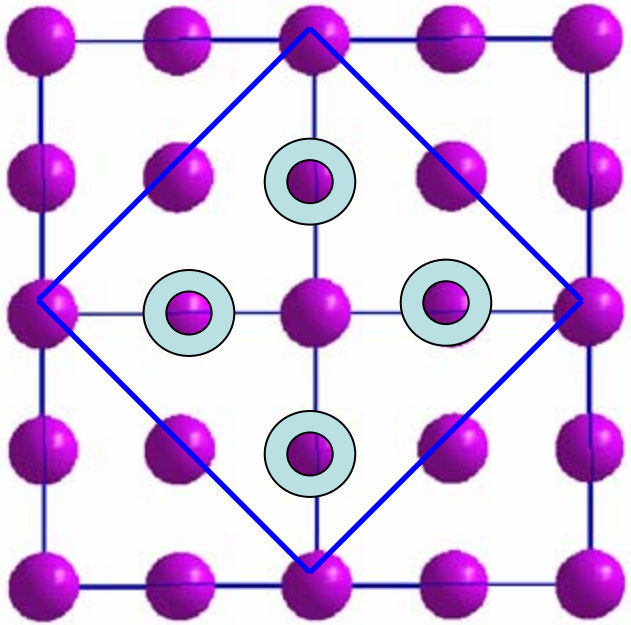
* N places on top of the hollow site (LEED, STM, LEIS)

* c(2x2) N surface structure (LEED, STM, LEIS)

fcc Cu (001)


surface
Below surface
surface
Below surface
surface
Hollow site
Below surface

C(2x2) N/Cu(001)



[010]

[001]

[001]: perpendicular

Distance (N-Cu surface)

(N on the hollow site, relaxing outward, and without any rumpling for Cu surface atoms)

* $d_{(N\text{-}Cu\ surface)} = 1.45$ Å (LEED, 1976)

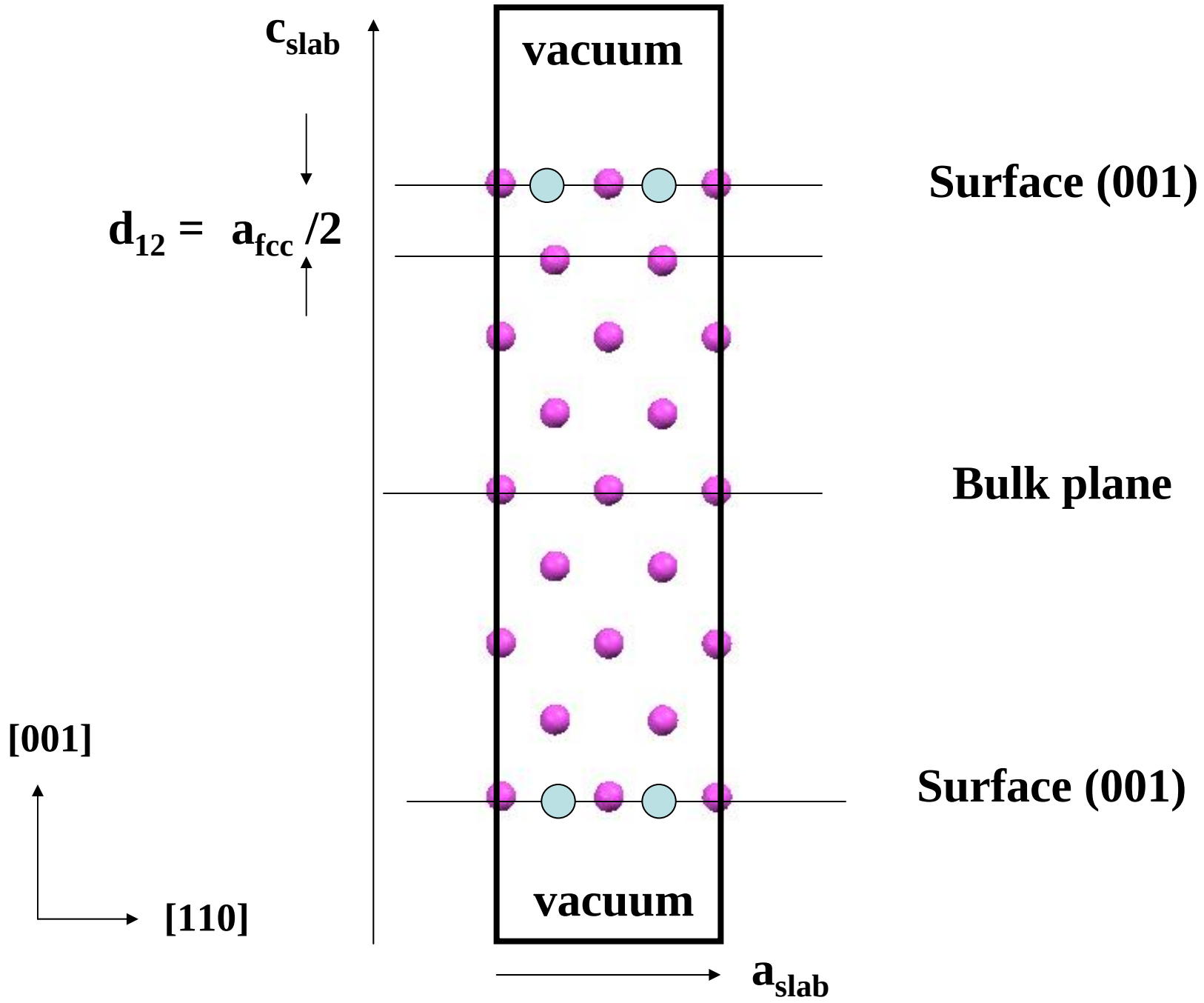
* $d_{(N\text{-}Cu\ surface)} = 0.0$ Å, but $d_{12} \geq 8\%$ (LEED, 1988)

* $d_{12} = 16\%$ (Ion-channeling, 2001)

* $d_{(N\text{-}Cu\ surface)} = 0.31$ Å with $d_{12} = 14\%$ and $d_{23} = 1.5\%$

  (Grazing incidence x-ray diffraction, GIXD, 2006)

* $d_{(N\text{-}Cu\ surface)} \leq 0.3$ Å (LEIS, 2008)


c_{slab}
vacuum
$d_{12} = a_{fcc}/2$
Surface (001)
Bulk plane
Surface (001)
[001]
[110]
vacuum
a_{slab}

All calculations made with

Wien2k package

P.Blaha, K.Schwarz, G.K.H.Madsen, D. Kvasnicka and J. Luitz

all electron - DFT code
GGA (Perdew,Burke and Ernzerhof, PRL, 77, 3865 (1977))

Basis set: (L)APW+lo
(Madsen et al. PRB, 64, 195134 (2001))

Total Energy Calculations
(N on hollow site; Relaxation: N and Cu surface)

d(N-Cu surface):
= 0.3 Å (GIXD, 2006)
and
$\leq$ 0.3 Å (LEIS, 2008)

= 0.23 Å (this calculation)

d_{12} expansion:
14% (GIXD, 2006)
16% (Ion-channeling, 2001)

8.6% (this calculation)

Work function

Cu(001): (4.77 ± 0.05) eV (Tibbetts et al.)

Cu (polycrystalline): 4.65 eV (Eastman, 1970)

Clean Cu(001): 4.27 eV (this work, without relax.)

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c(2x2) N/Cu(001): **4.59 eV** (Tibbetts et al.)

c(2x2) N/Cu(001): 4.09 eV (this work, unrelaxed)

c(2x2) N/Cu(001): 4.64 eV (this work, only N relaxed)

c(2x2) N/Cu(001): **4.55 eV** (this work, N and Cu relaxed)

UPS valence band spectra

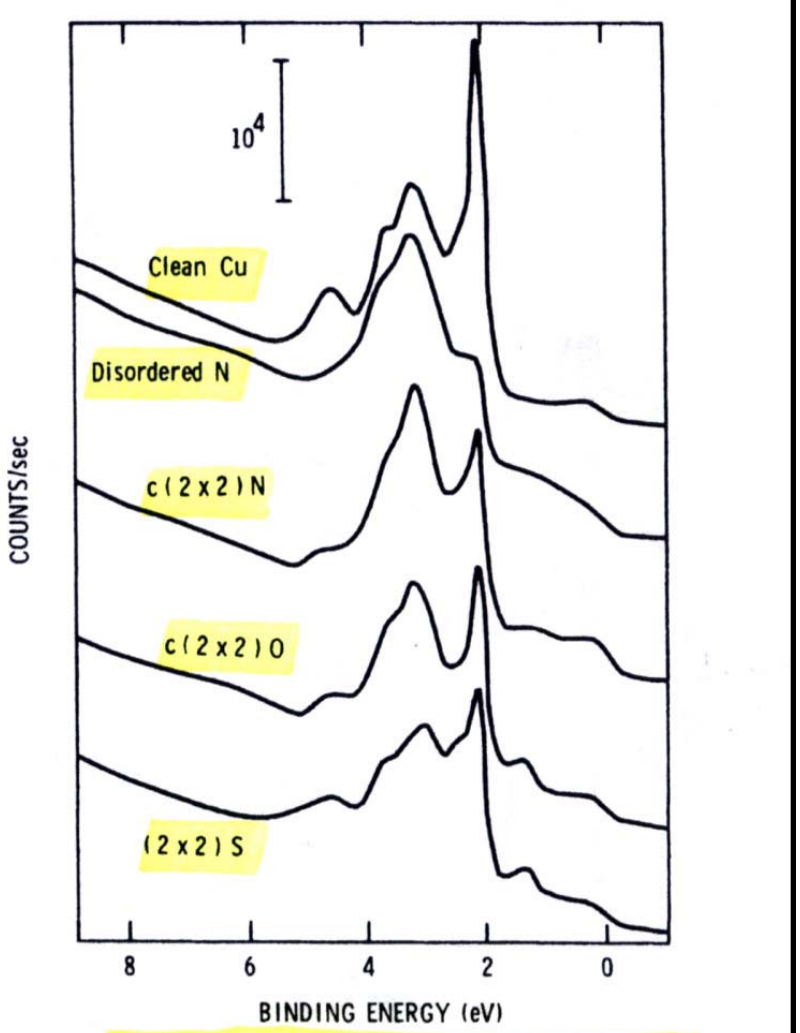


FIG. 1. He I photoemission spectra ($h\nu = 21.2$ eV) for various Cu(100) surfaces. Binding energies are referred to the Fermi level.

Tibbetts et al.
PRB 1977

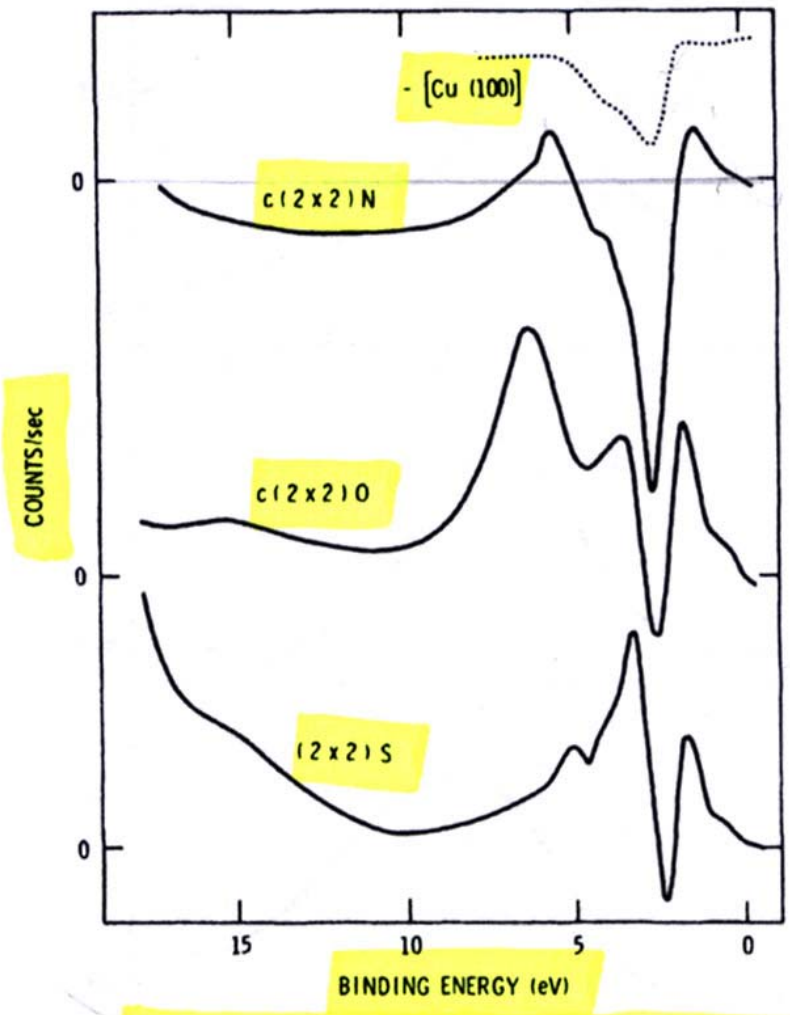
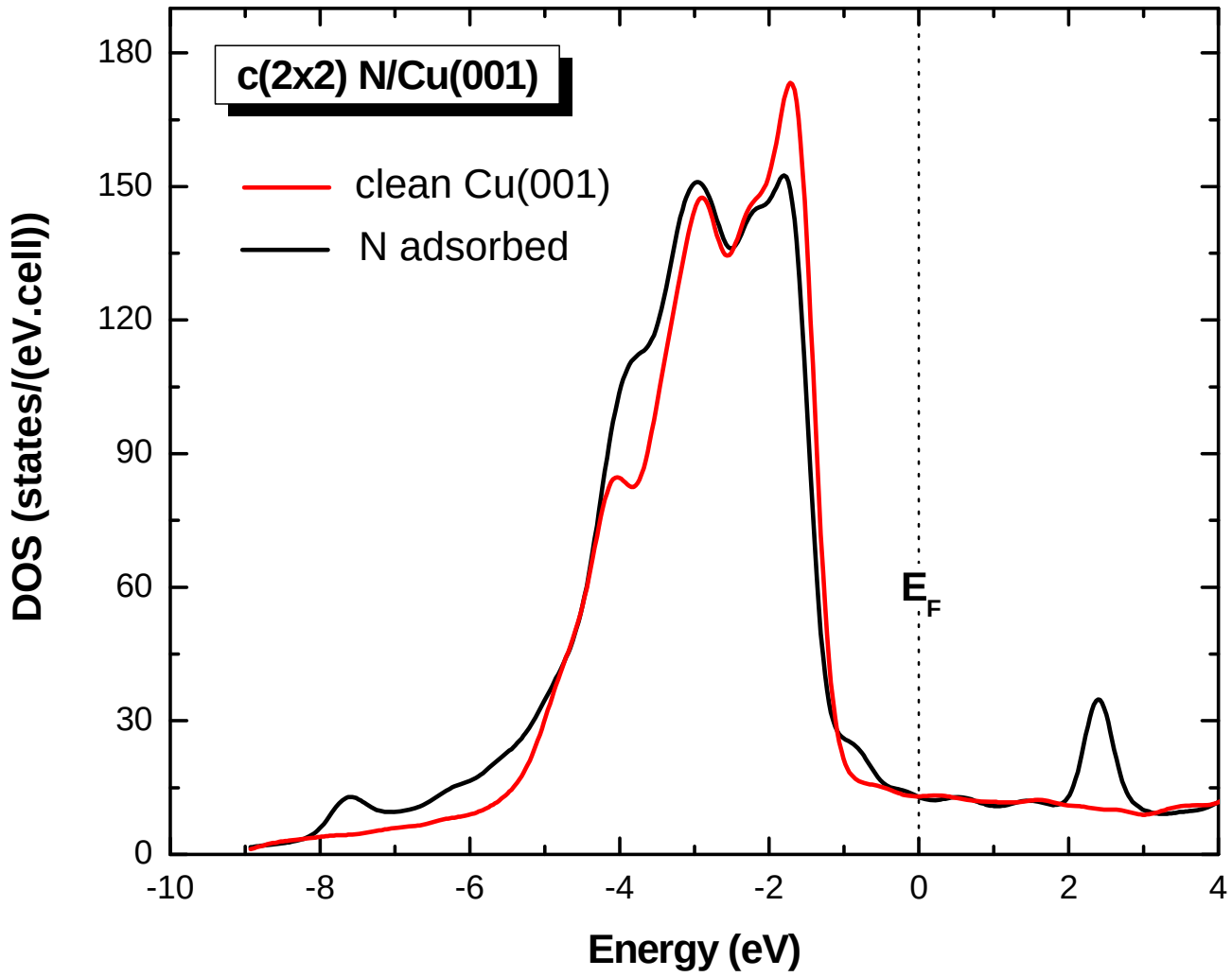


FIG. 3. He II difference curves for adsorbate covered Cu(100). Dashed line is $-\frac{1}{5}$ times the UPS of clean Cu(100).

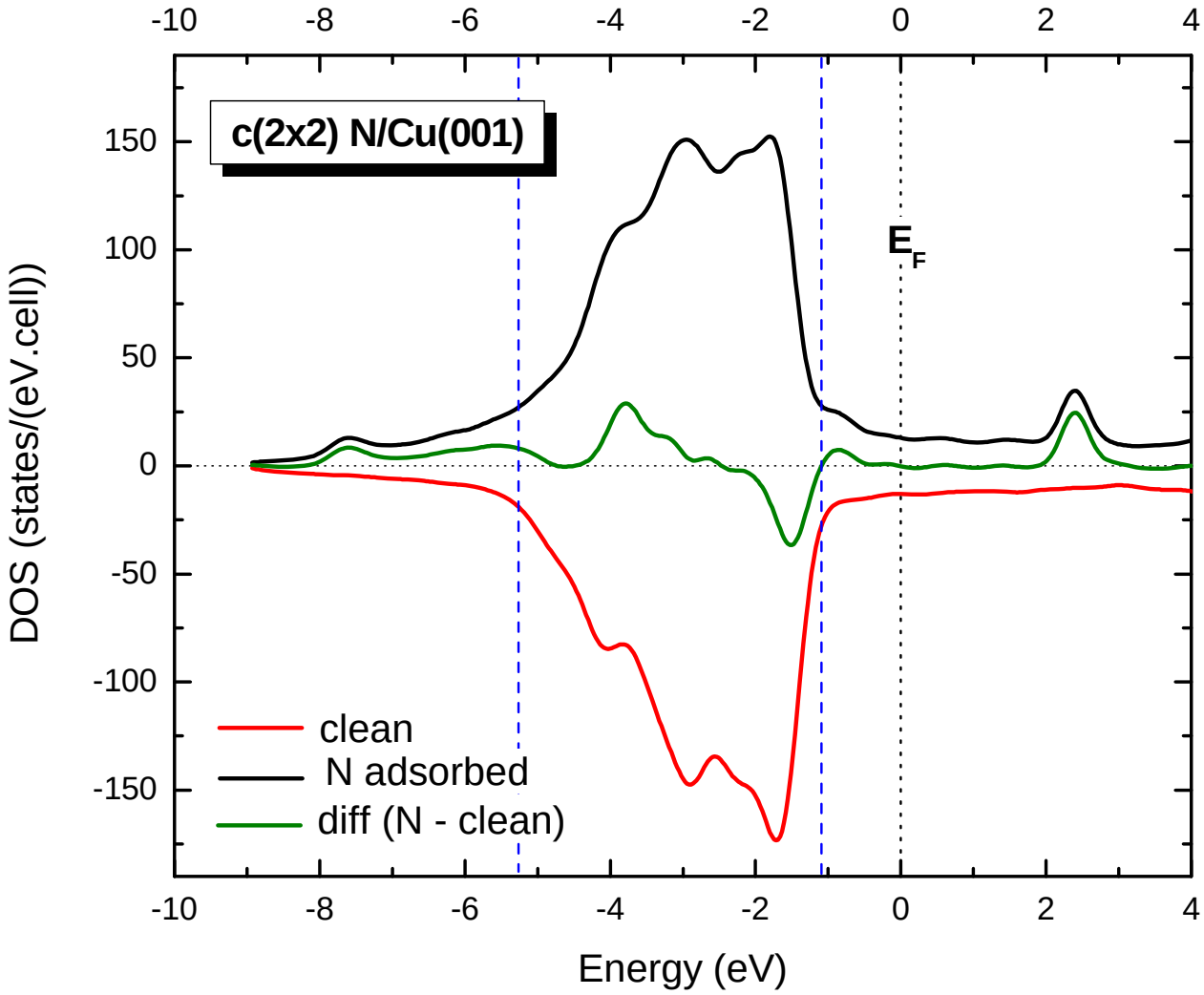
UPS difference
N - clean

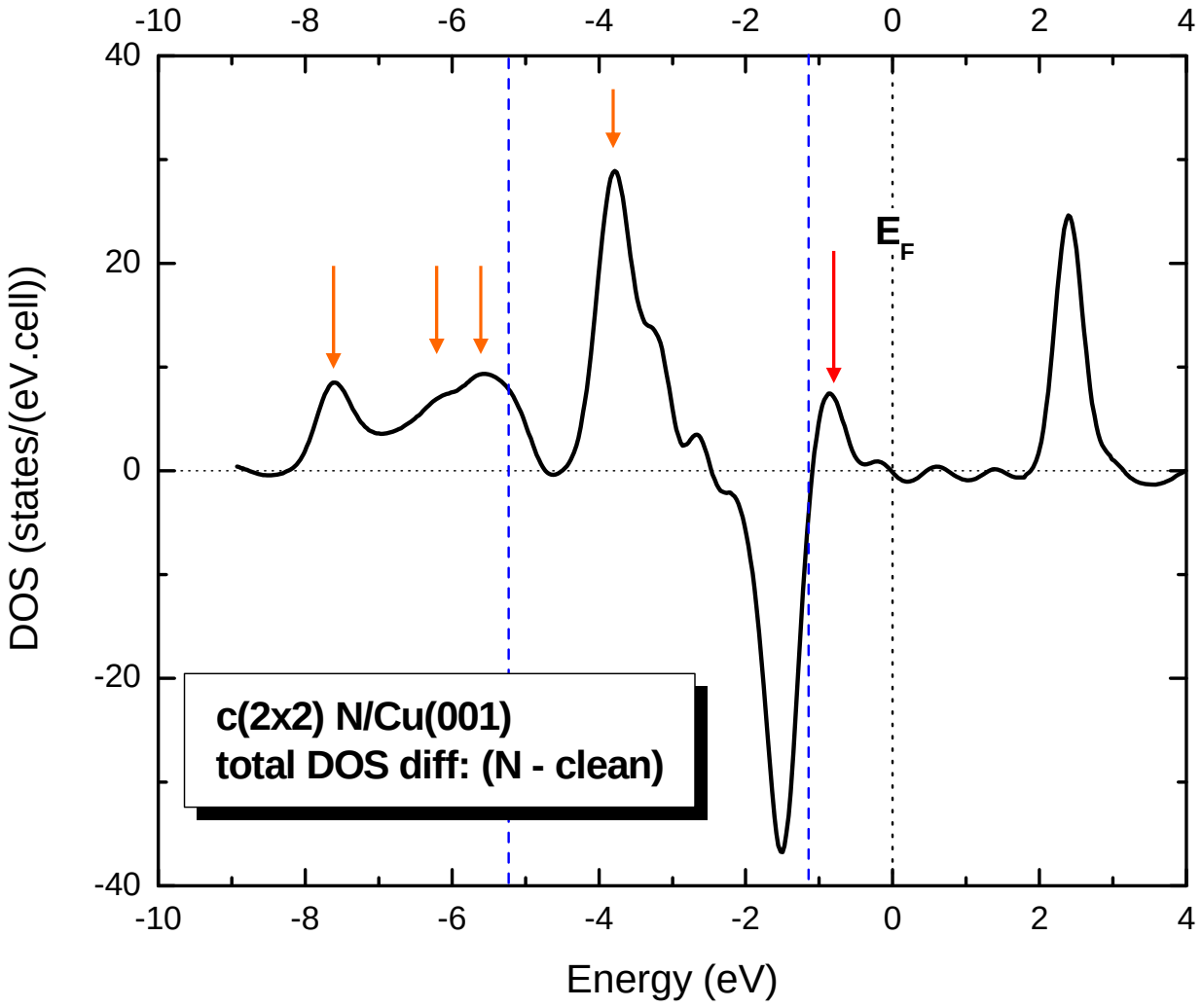
Tibbetts et al.
PRB 1977

Total DOS for clean and N/Cu(001) slabs



Total DOS for clean and N/Cu(001) slabs




-10
-8
-6
-4
-2
0
2
4
40
20
0
-20
-40
DOS (states/(eV.cell))
Energy (eV)
E_F
c(2x2) N/Cu(001)
total DOS diff: (N - clean)

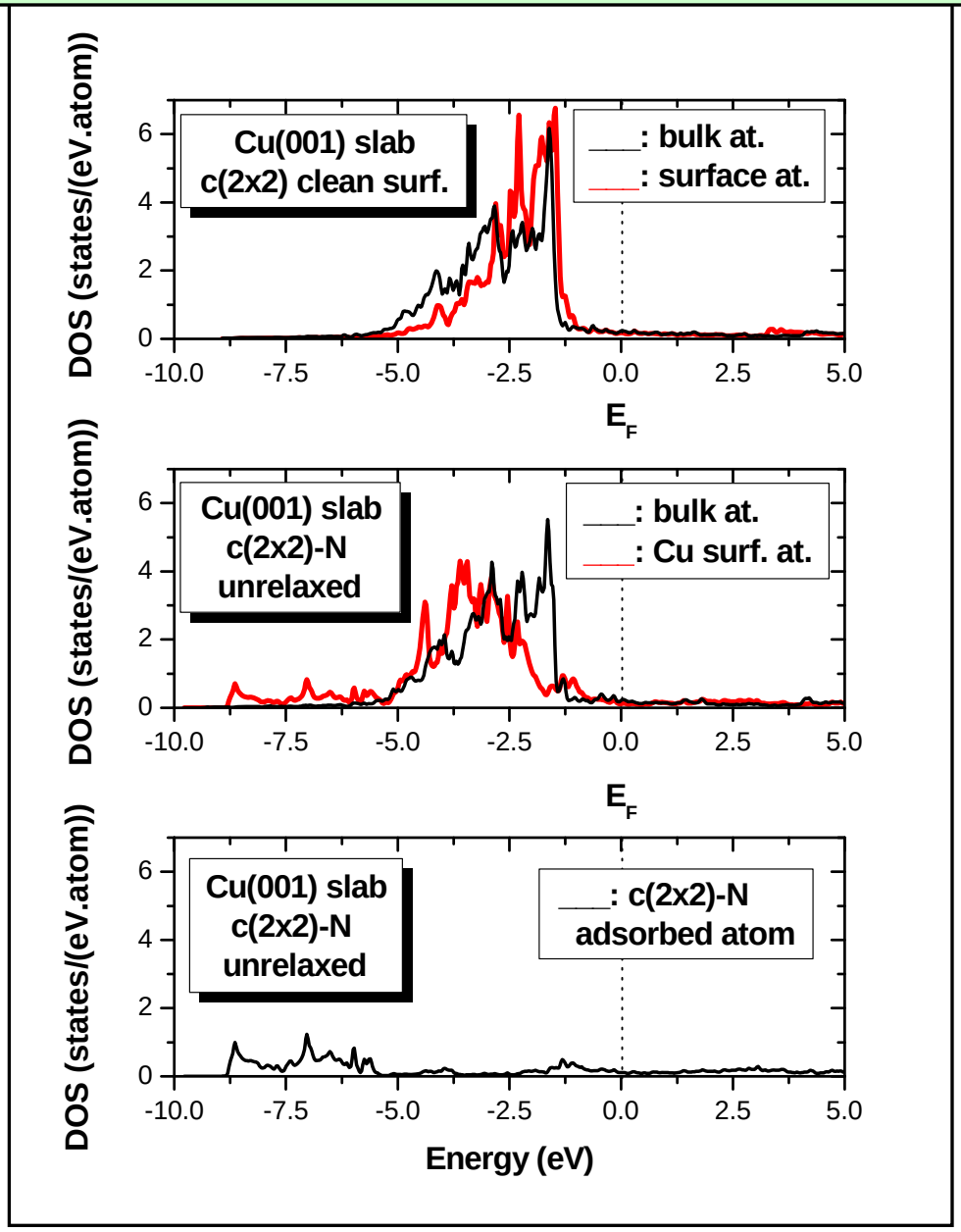
Total DOS changes due to N adsorbed on Cu(001) on the UPS (He I and II, normal emission) spectra of Tibbetts et al (1977)

A resonance above the d bands of Cu, at 1.3 eV (this work: ~ 1 eV)

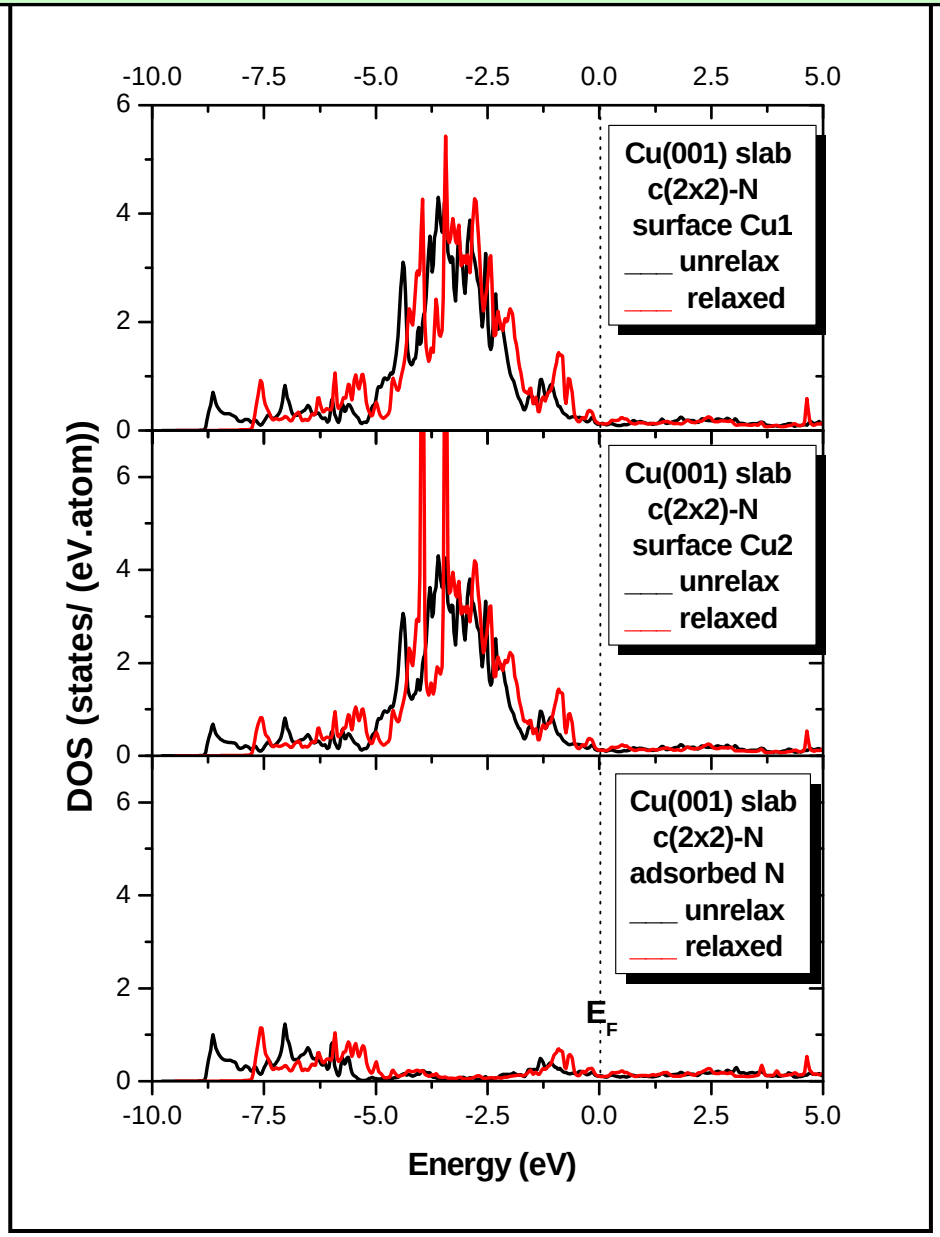
A resonance below the d bands of Cu, at 6 eV (this work: ~ 6 to 7.8 eV)

Exp. “d band” width of clean Cu(001): ~ 3.5 eV (2 to 5.5 eV)
Theoretical “d band” width: ~ 4 eV (1.5 to 5.5 eV)

PDOS of Cu bulk, Cu surface, and N atoms in slabs



relaxed and unrelaxed Cu surface and N atoms

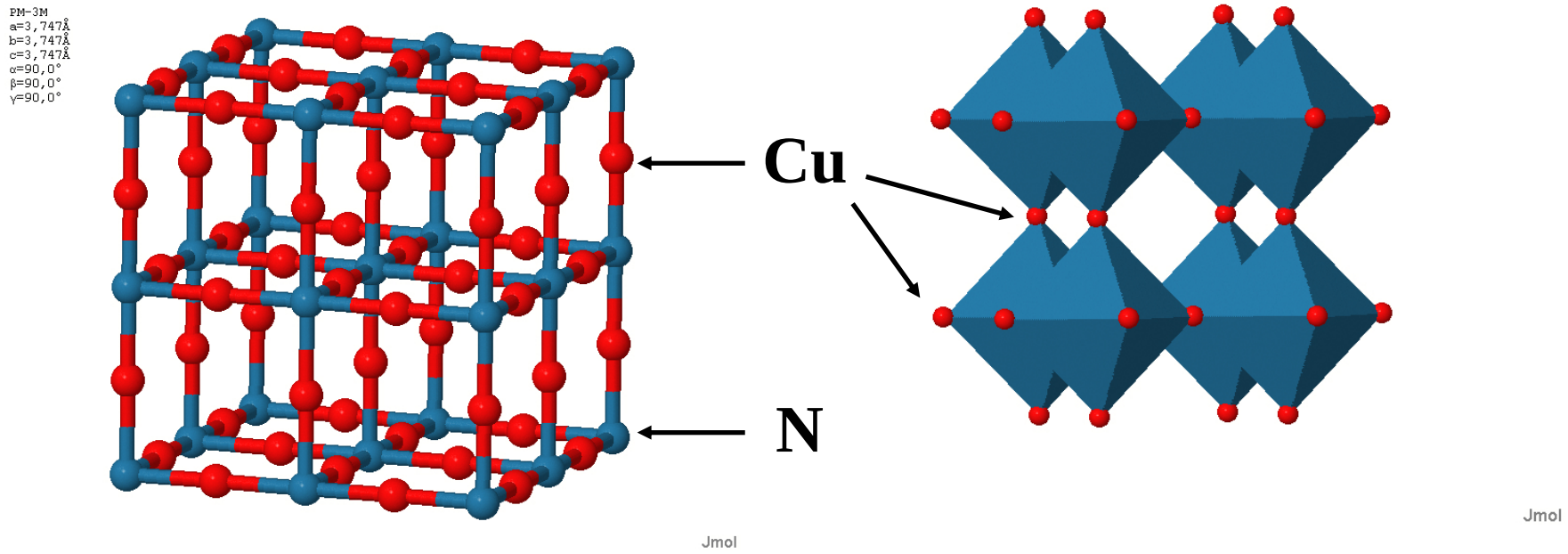


crystalline Copper Nitride (Cu_3N)

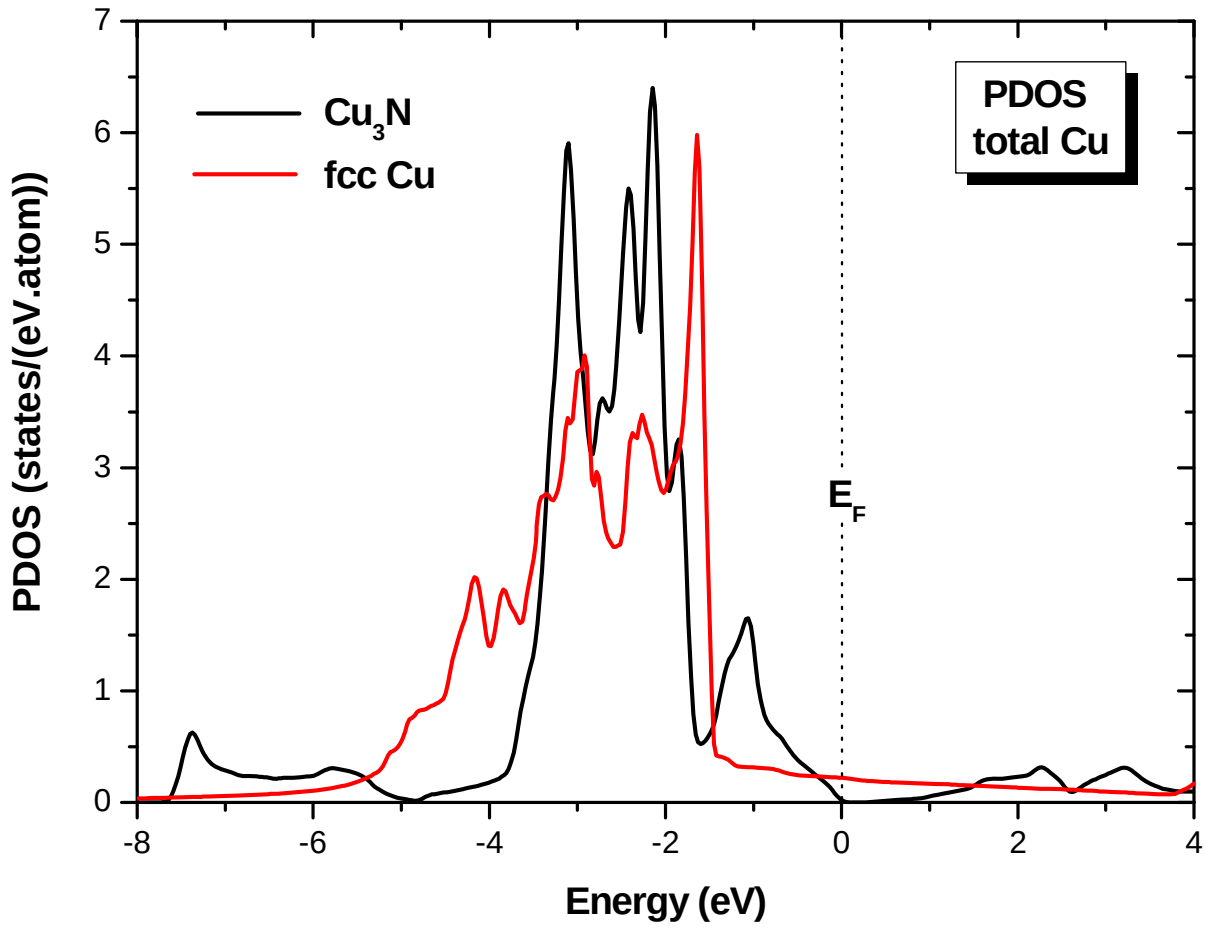
Cu: two N nearest neighbors

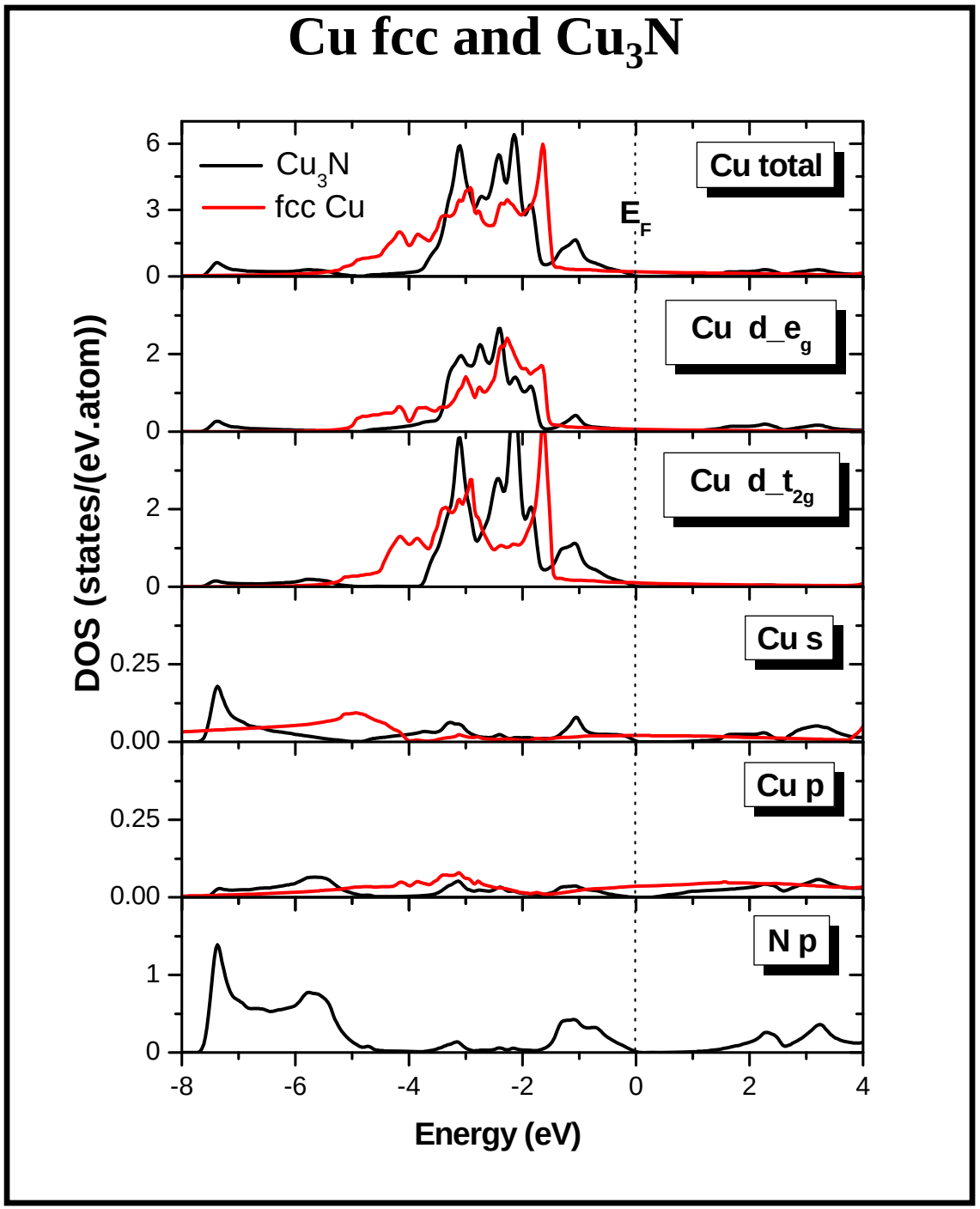
N: six Cu " "

Cu with the same coordination as in Cu_2O: Cu(I)

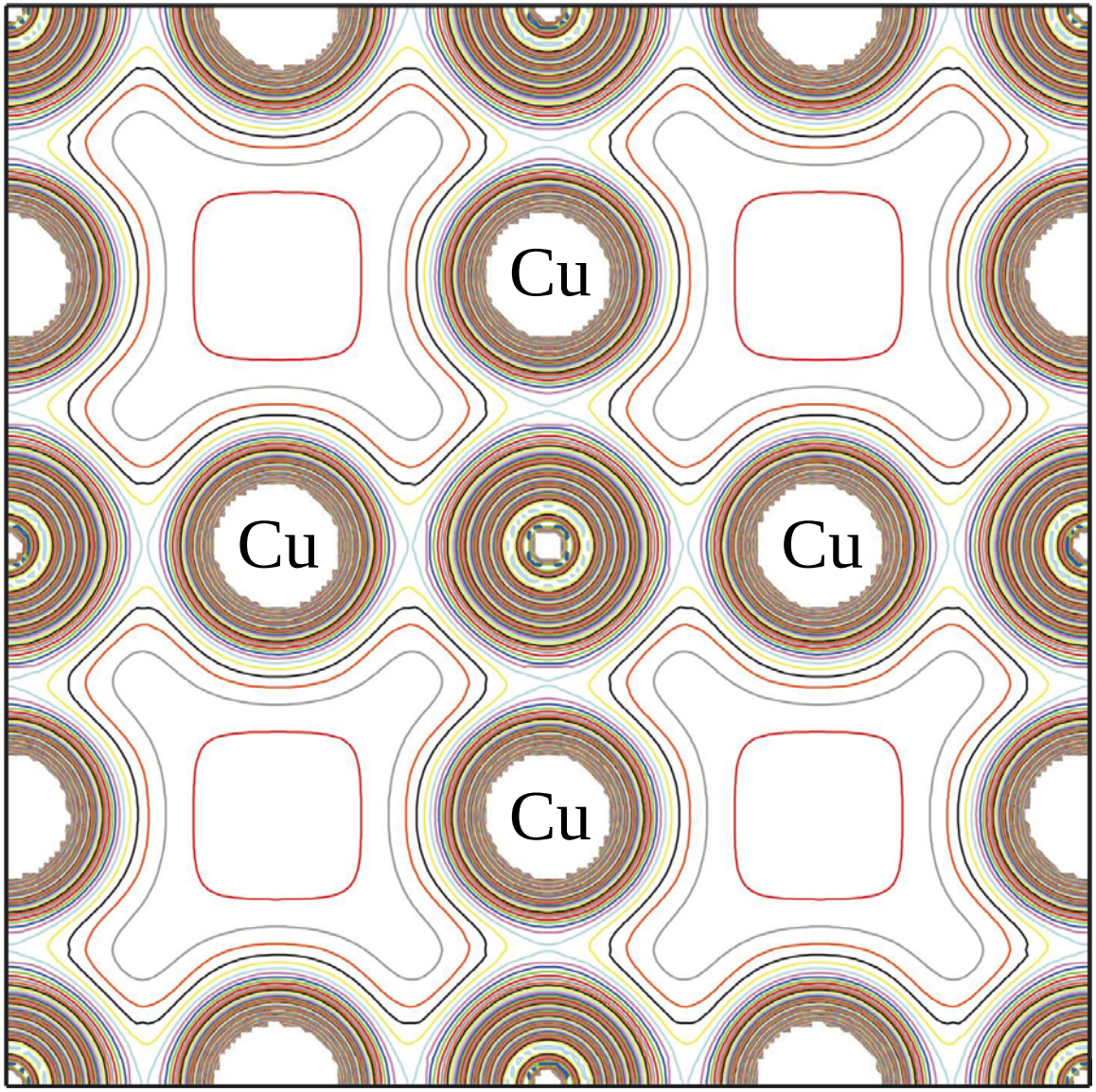


Cu fcc and Cu_3N
PDOS of Cu atom in both systems




Cu fcc and Cu3N
Cu3N
fcc Cu
Cu total
E_F
Cu d_e_g
Cu d_t_2g
Cu s
Cu p
N p
DOS (states/(eV.atom))
Energy (eV)
6
3
0
2
0
2
0
0.25
0.00
0.25
0.00
1
0
-8
-6
-4
-2
0
2
4

Cu_3N



Chemical bonding

Cu_3N:

Ionic (Cu^{+1}, N^{3-})? Not in that limit, but may be in some extent

Covalent? May also be in some extent, because…

there are s,p, and d hybridization on Cu in Cu_3N

The hybridization does not seem to contribute charge in the nn directions.

Induces a quite strong deformation of the d states, like polarization, inside the atomic MT radius.

c(2x2) N/Cu(001): more like Cu3N

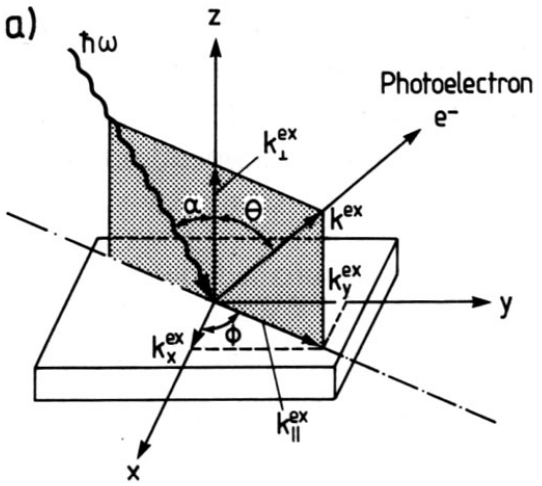
Band structure measurements

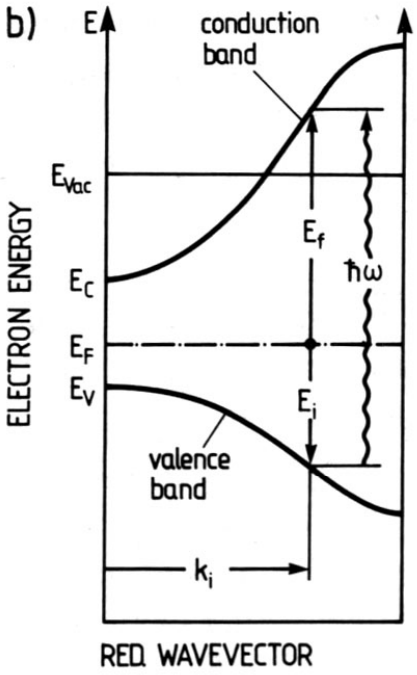
ARUPS: Angle Resolved Ultraviolet Photoemission Spectroscopy

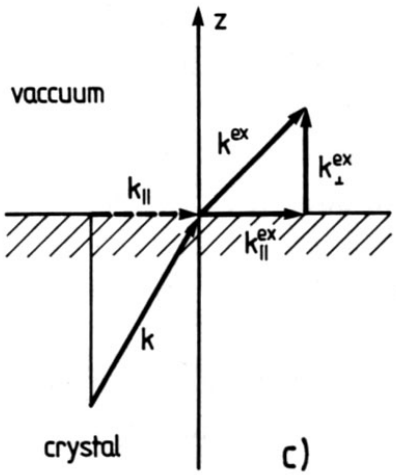
“… the band structure of a solid is not just an abstract concept with no real existence outside the minds of solid-state theorists; band structures can be mapped directly from experiment”

N.V. Smith in
Photoemission in Solids I
M.Cardona and L.Ley (editors)
Springer, 1978

Photoemission experiments



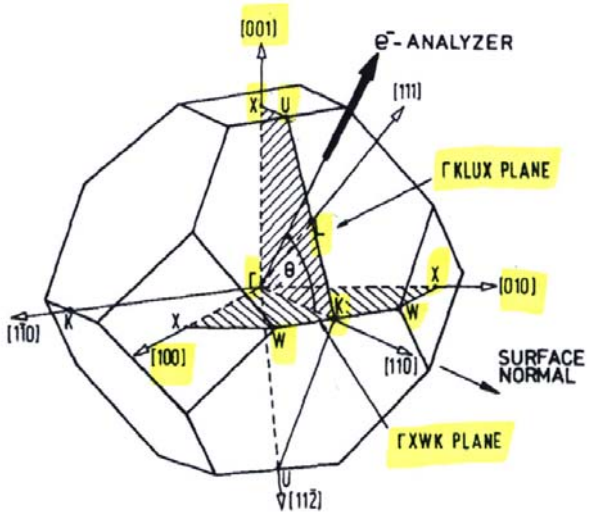




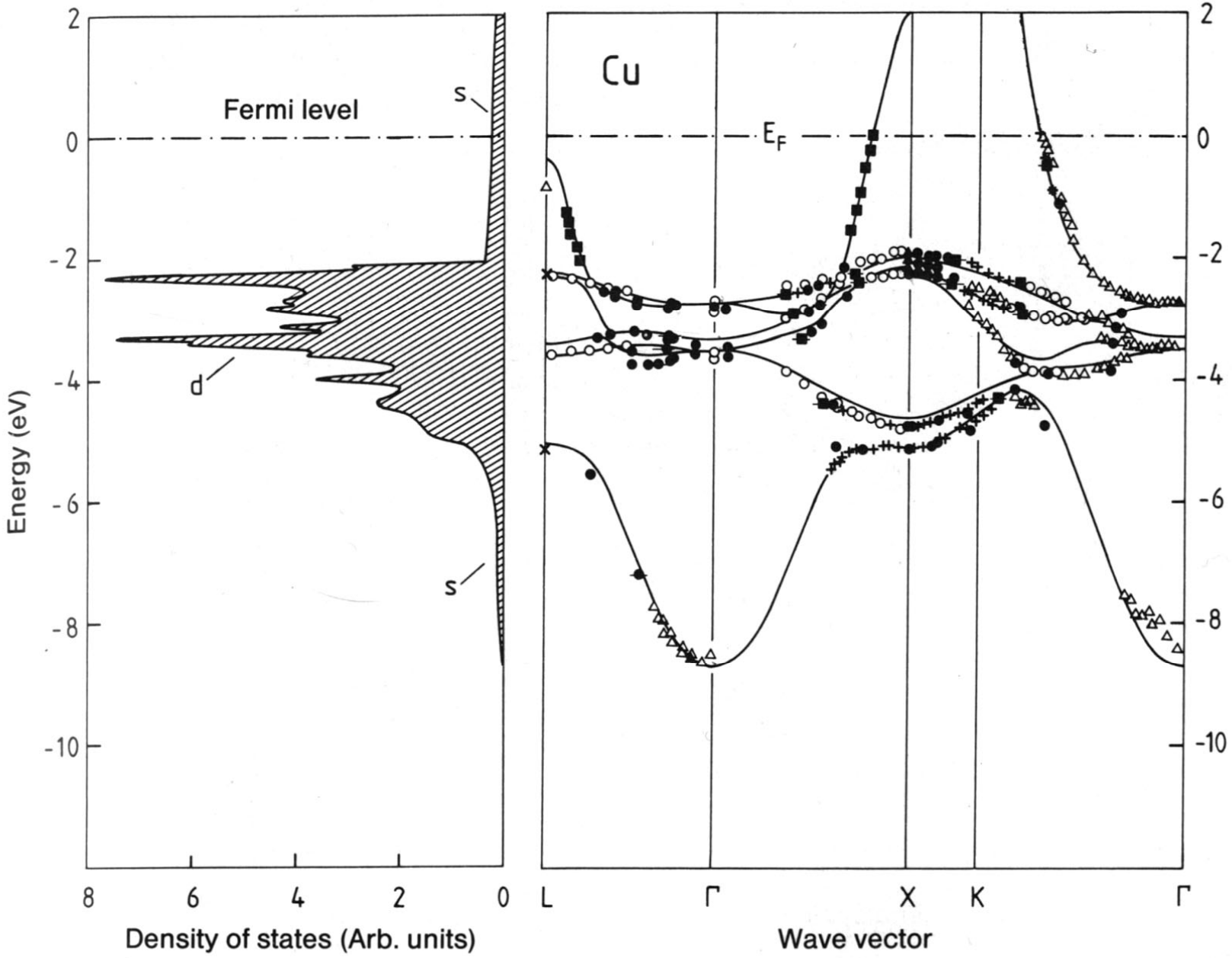
$k_{//}$ conservation
$k_\perp$ unknown

H.Lüth, Surfaces and Interfaces
Of solid materials, 3rd ed., 1997

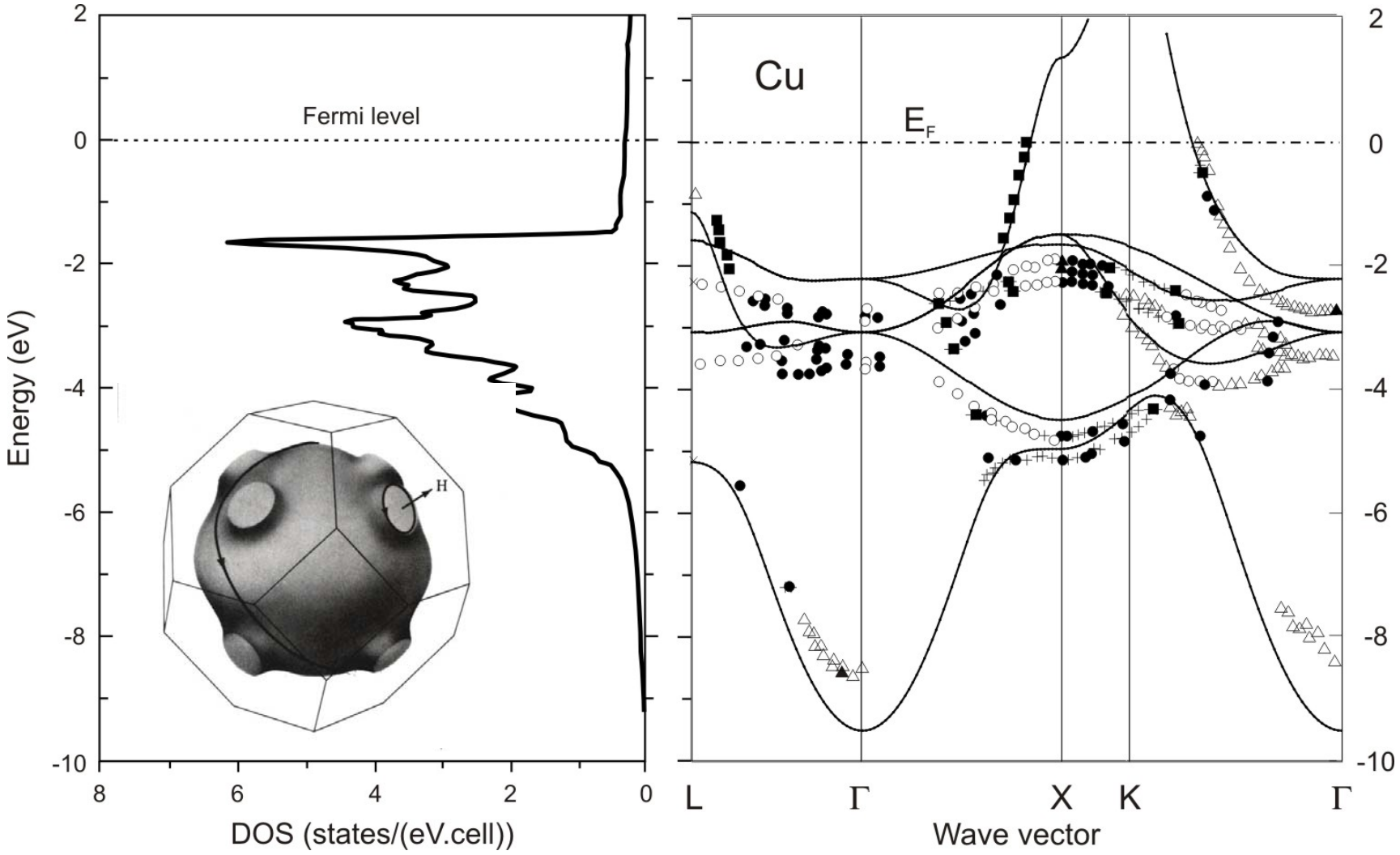
ARUPS



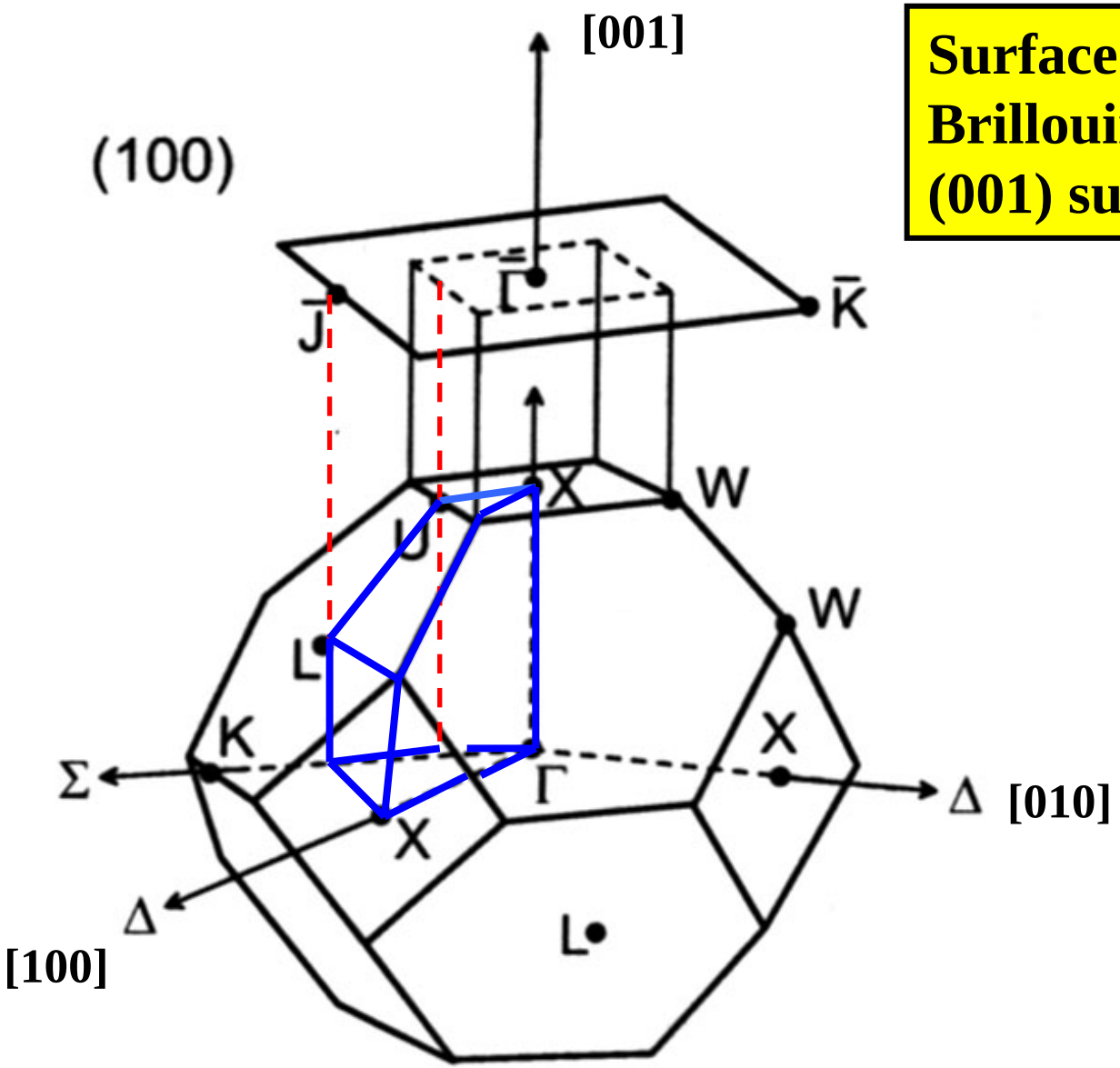
R. Courths and S.Hüfner
Phys. Rep., 1984



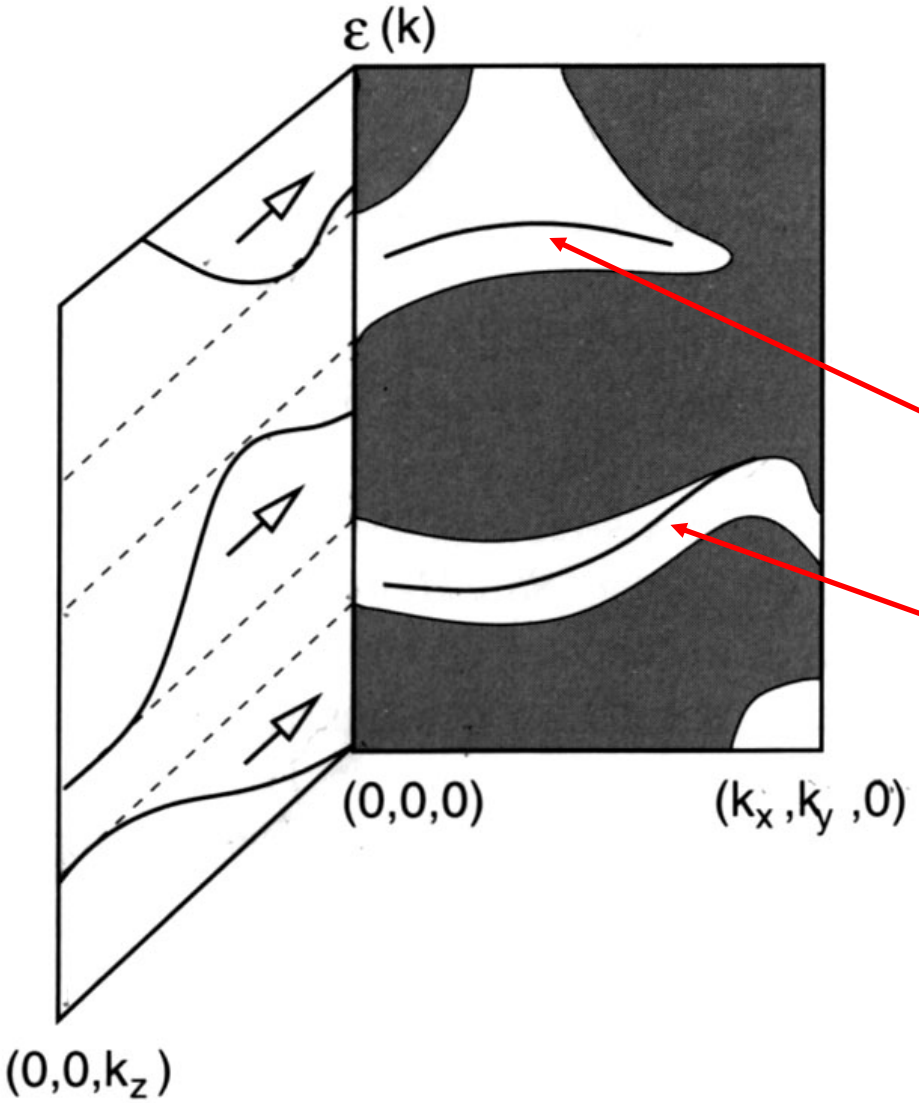
Ibach-Lüth: Solid-State Physics, 1993


Fermi level
Energy (eV)
2
0
-2
-4
-6
-8
-10
8
6
4
2
0
DOS (states/(eV.cell))
H
Cu
E_F
L
Γ
X
K
Γ
Wave vector

Surface and bulk Brillouin Zones for (001) surface of fcc



F.Bechstedt, Principles of Surface Physics, 2003



$k_\perp$ bulk bands projection on the $k_\parallel$ plane

True surface state

Surface resonance

A.Groß, Theoretical Surface Science, 2003

Bulk band states projection on a surface BZ case of bulk fcc on the (001) surface

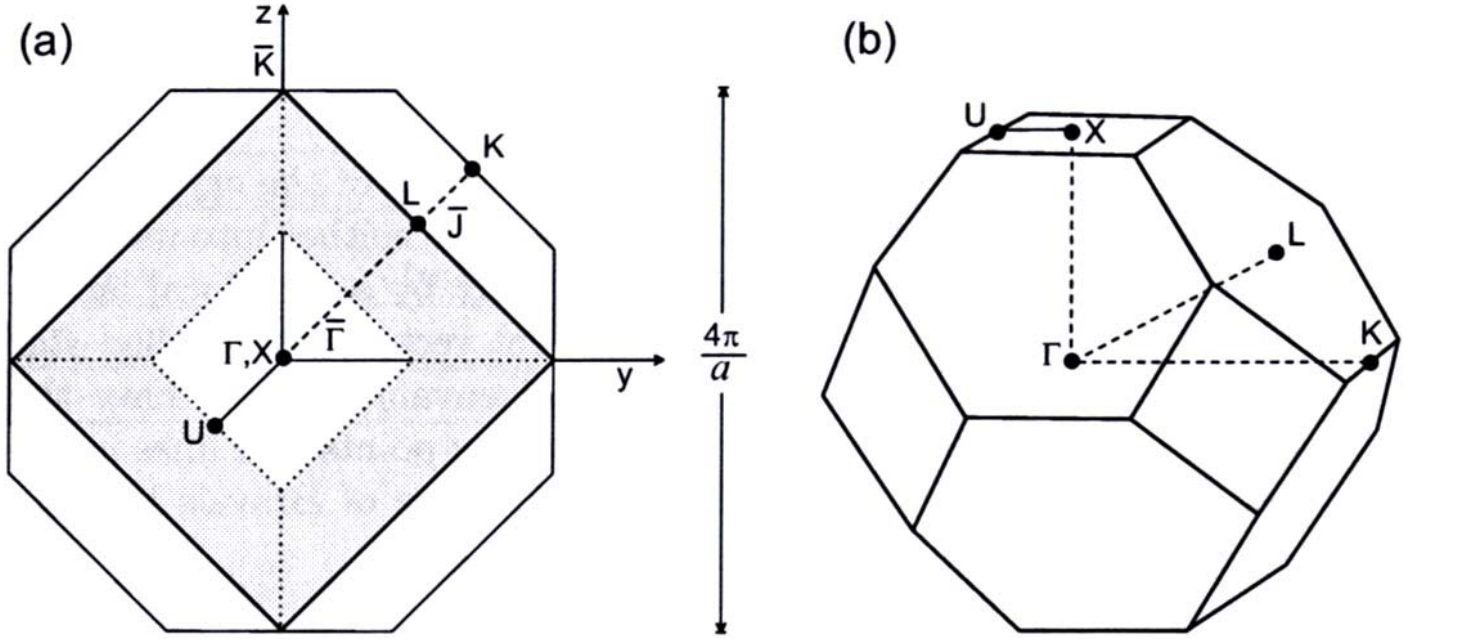
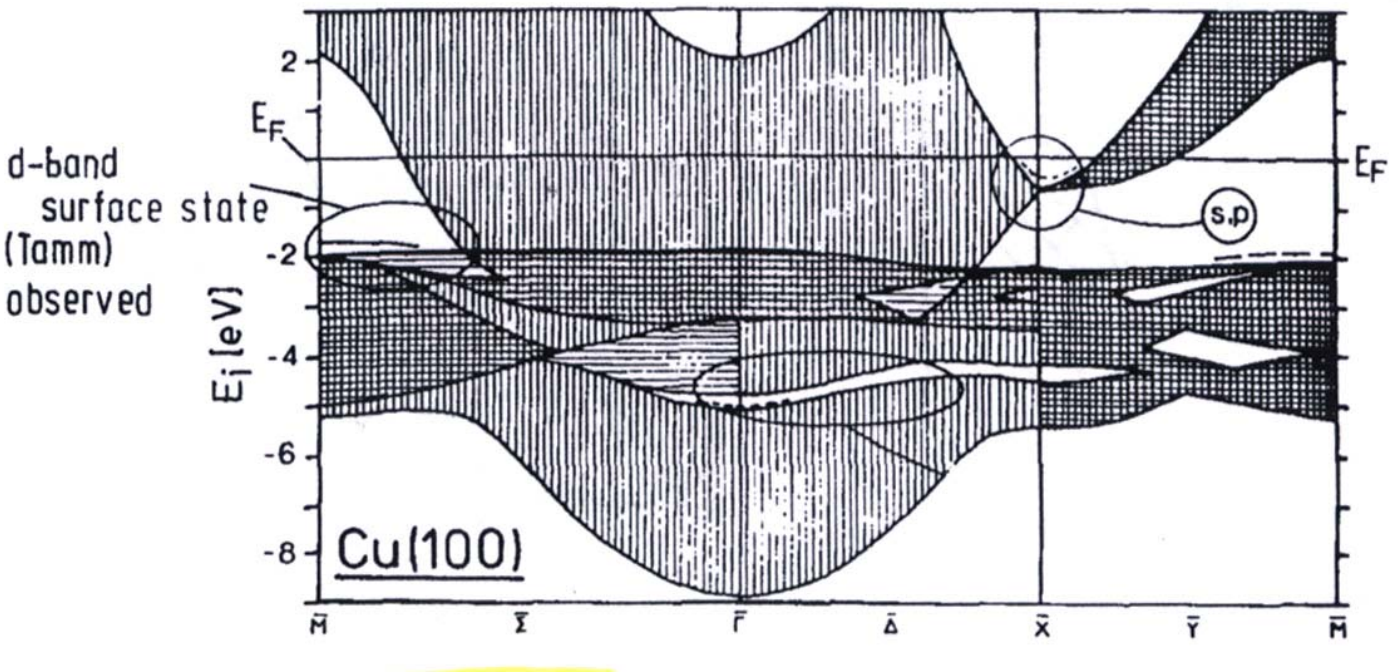


Fig. 1.26. (a) Brillouin zone of a (100) surface (shaded area) together with the projected bulk BZ of an fcc crystal. Projected critical points of the 3D BZ are indicated along a [011] direction. (b) Bulk BZ for comparison.

F.Bechstedt, Principles of Surface Physics, 2003

fcc Cu bulk states projected on the Cu(001)



R. Courths and S. Hüfner, Phys. Rep., 1984
(taken from P. Thiry, Thesis, 1979)

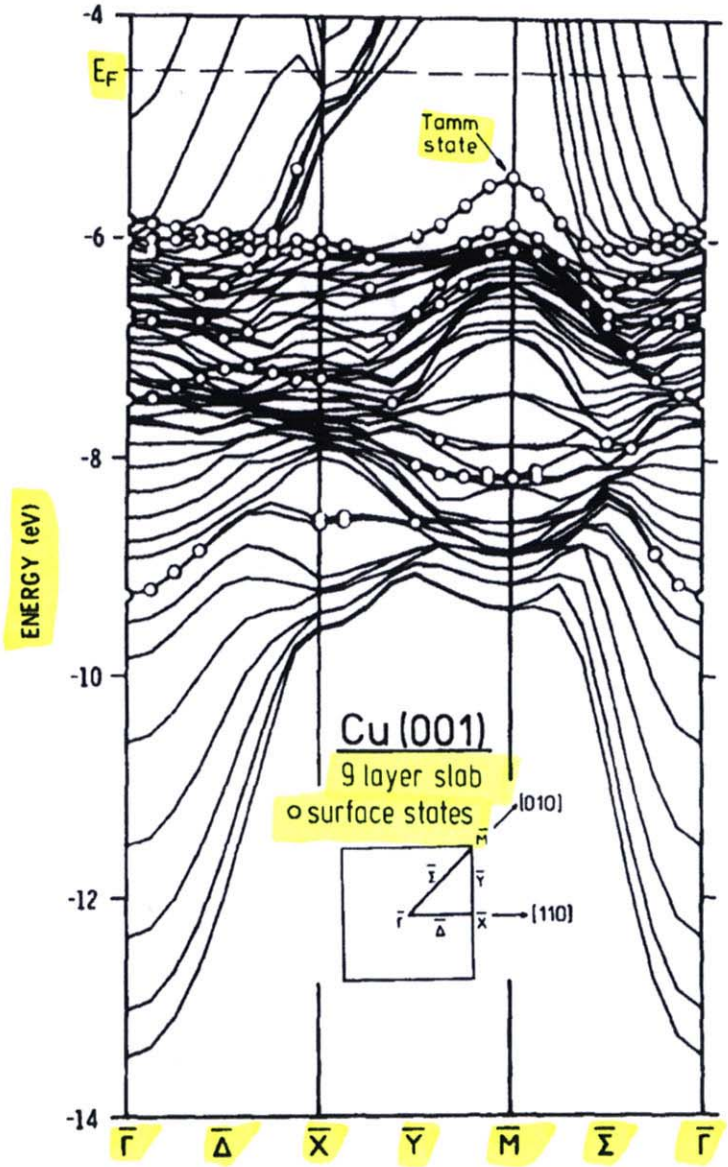


Fig. 77. Two-dimensional energy bands for a nine-plane Cu(100) slab. The open circles represent states which are highly localized in the surface. (Taken from ref. [205].)

R. Courths and S. Hüfner, Phys. Rep., 1984
(from Gay, Smith, Arlinghaus, PRL, 1979)

Scheme of calculation to identify surface or adsorbate features

We should carry out:

* Slab scf calculations for clean surfaces or with adsorbates
* Band structure slab calculations on the Surface BZ
* With character plotting we may identify which of these band states are localized on the surface layer
* Superpose the band structure calculation with the bulk band states projected on the surface of interest (both calculations are referred to the same surface BZ)

Surface states, surface resonance states, adsorbate related states

Conclusions

* Slab calculations allow us to identify a variety of surface properties
  * geometry of minimal total energy (relaxation, reconstruction, adsorbate sites)
  * work function, binding energies of core levels
  * surface states and surface resonances
  * adsorbate related states
  * XPS DOS spectra
  * UPS DOS spectra (for ex., at normal emission)
  * ARUPS spectra

  (complicated issues remain with the $k_{\parallel}$ and $k_{\perp}$)

Thank you very much
for your attention