INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONE: 2240-1
CABLE: CENTRATOM - TELEX 460392 - I

SMR/291 - 45

SPRING COLLEGE IN CONDENSED MATTER
ON
"THE INTERACTION OF ATOMS & MOLECULES WITH SOLID SURFACES"
(25 April - 17 June 1988)

PHOTOEMISSION FROM ADSORBATES
(Parts III and IV)

Alexander M. BRADSHAW
Max-Planck Gesellschaft
Fritz Haber Institut
Faradayweg 4-6
D-1000 Berlin
Fedearl Republic of Germany

These are preliminary lecture notes, intended only for distribution to participants.

Part III : Adsorbate band structures; photoemission band mapping in two dimensions

At high coverages there is an additional interaction between the adparticles. If the layer is ordered two-dimensional Bloch states $|n, \vec{k}_{\parallel}\rangle$ are formed, where n is the band index and $\vec{k}_{\parallel}$ a two-dimensional wave vector in the surface Brillouin zone (SBZ)

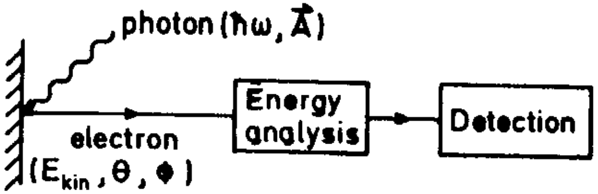
In the photoemission experiment this parallel component of momentum is conserved as the electron crosses the surface*. It is given (experimentally) by

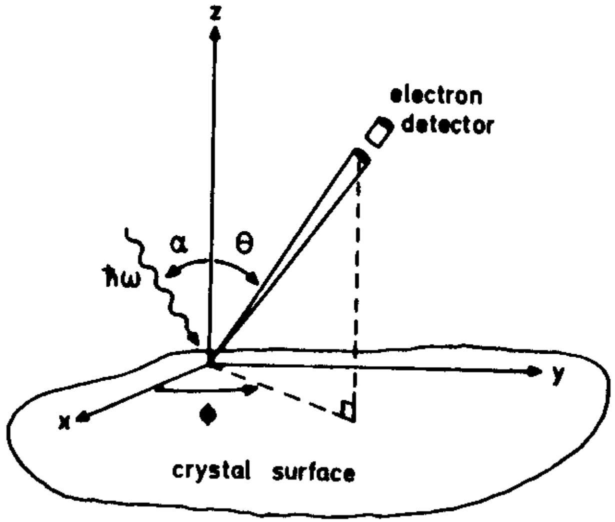
$$k_{\parallel}^{outs} = \left(\frac{2mE_{kin}}{\hbar^2}\right)^{1/2} \sin\,\theta$$

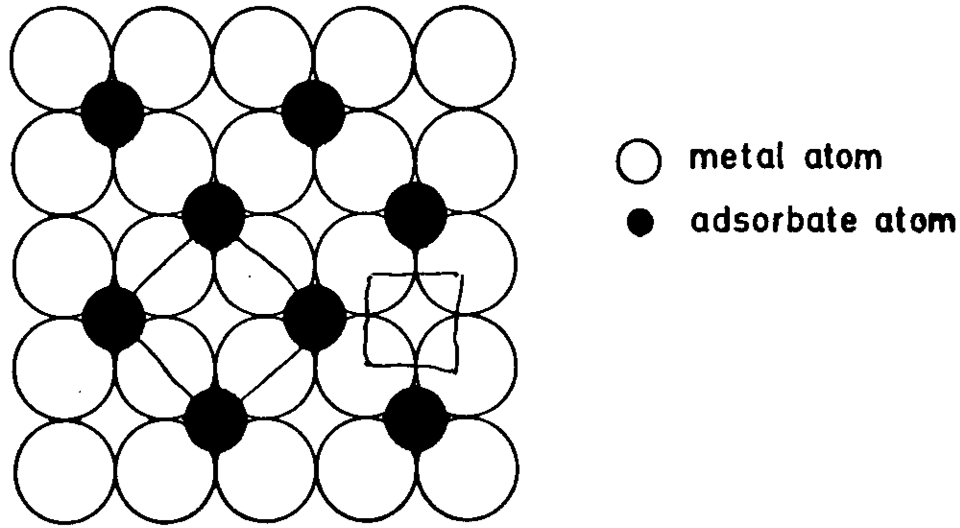
TWO-DIMENSIONAL BAND STRUCTURES CAN THEREFORE BE MAPPED OUT EXPERIMENTALLY

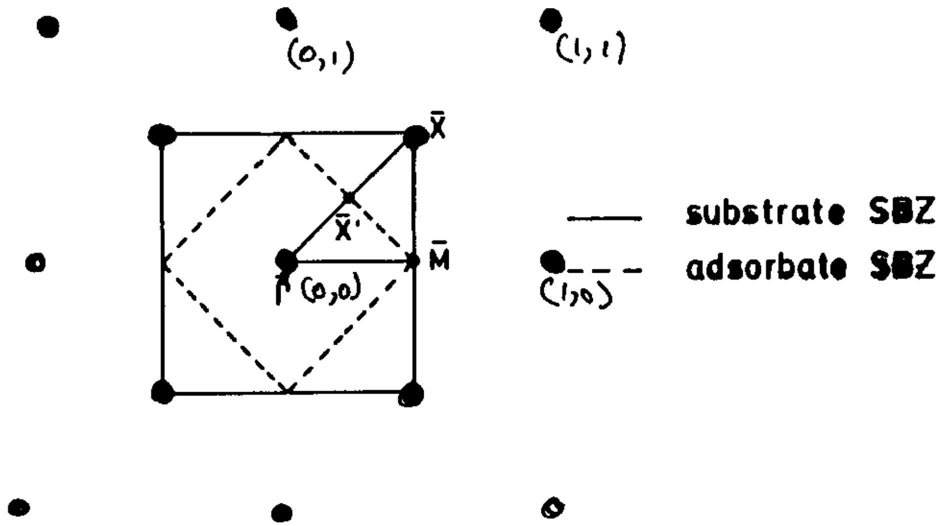
* $\vec{k}_{\parallel}^{outside} = \vec{k}_{\parallel}^{inside} \pm n\vec{g}_{sub.} \pm m\vec{g}_{ads.}$

The photoemission experiment

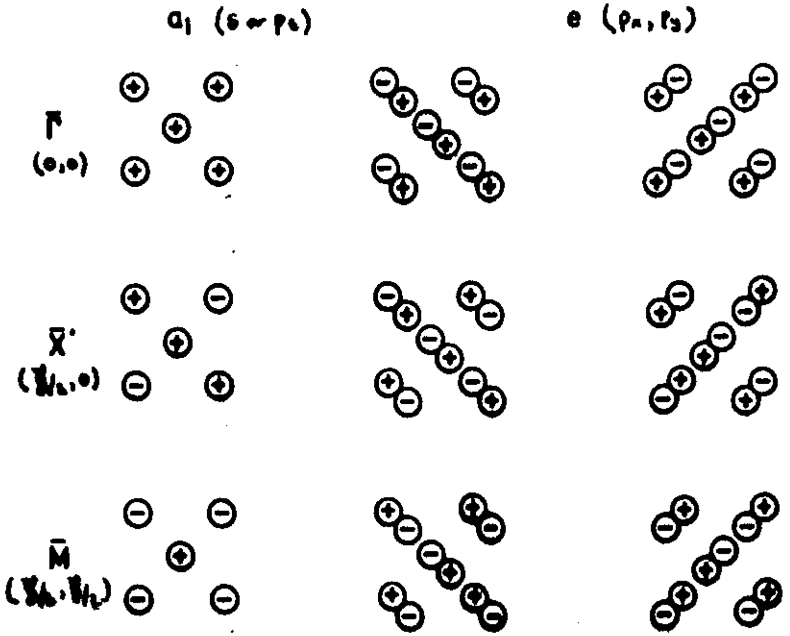


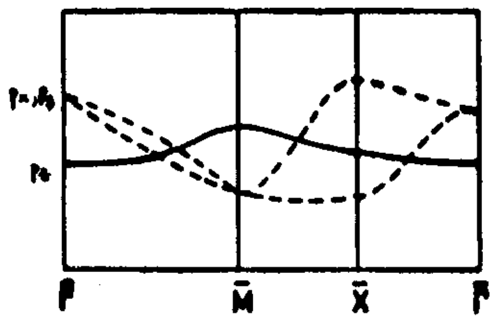


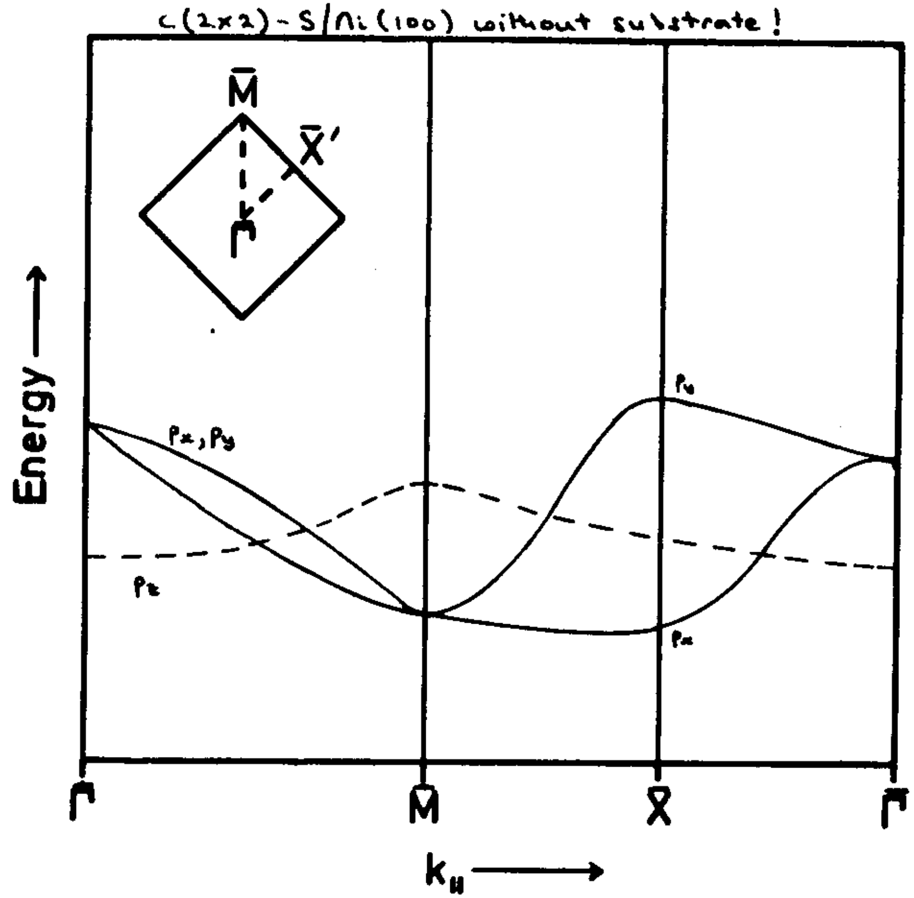




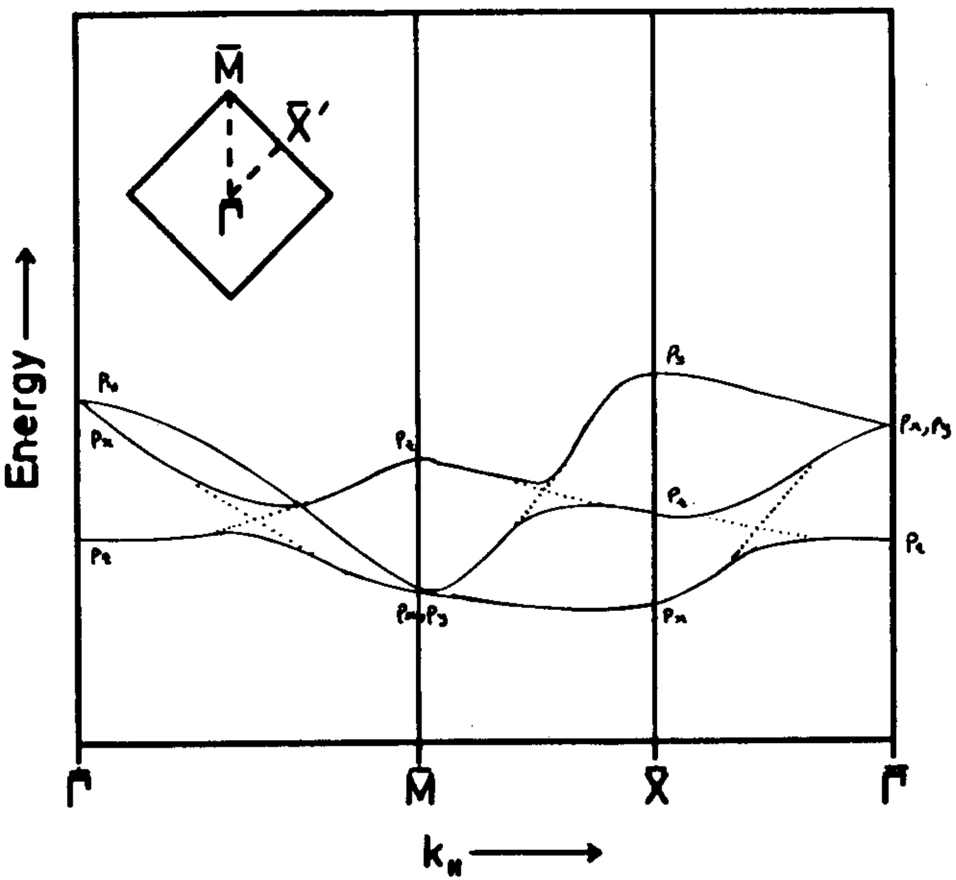
$$|n, \vec{k}_{\parallel}\rangle = \sum_{\vec{r}_j} e^{i\vec{k}_{\parallel}\cdot\vec{r}_j}\, \phi_n(\vec{r}-\vec{r}_j)$$



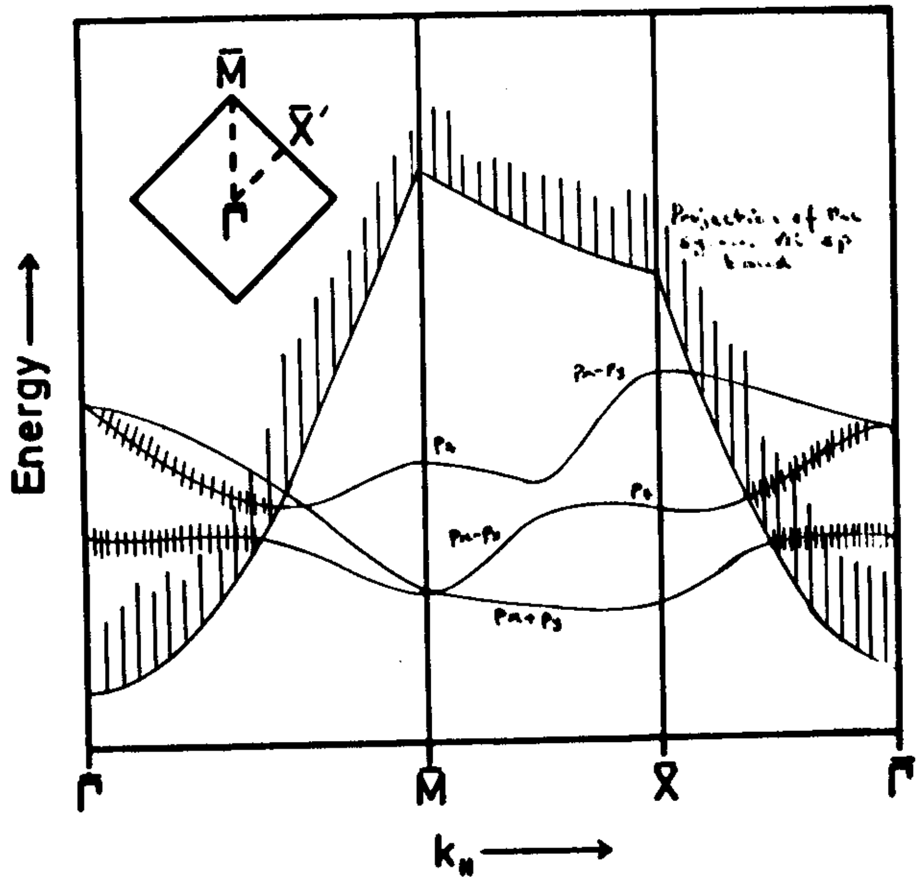




c(2×2)-S/Ni(100) incl. substrate but no chemistry!



c(2×2)-S/Ni(100)

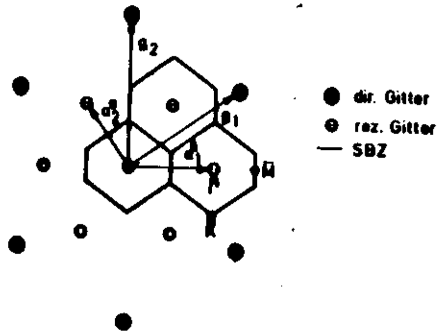


Best way to illustrate these effects is to consider rare gas overlayers where the influence of the substrate is very weak.

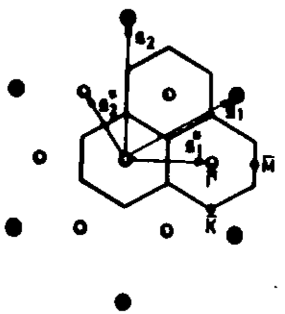
Mariani et al (1981)

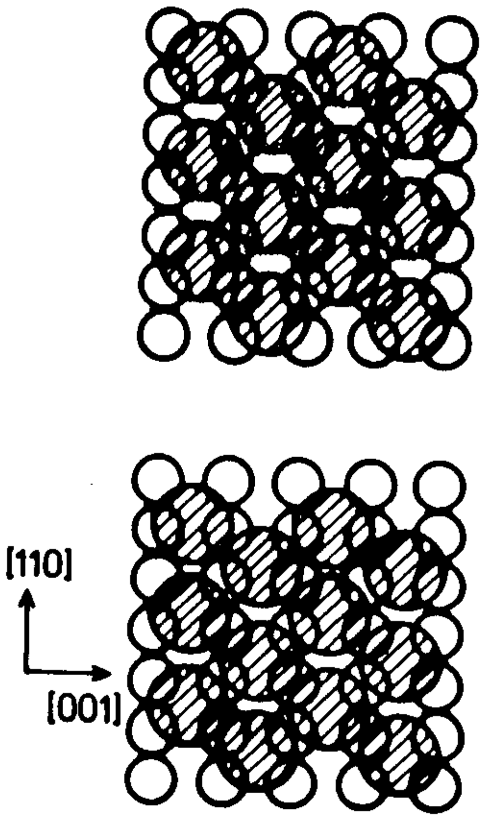
Xenon / Cu (110)

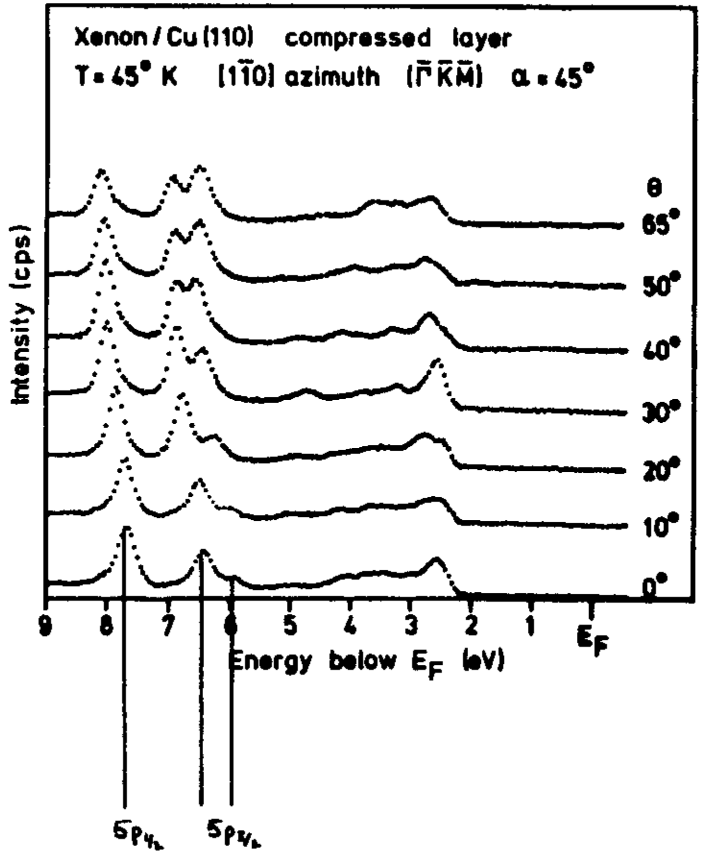
c(2x2) structure

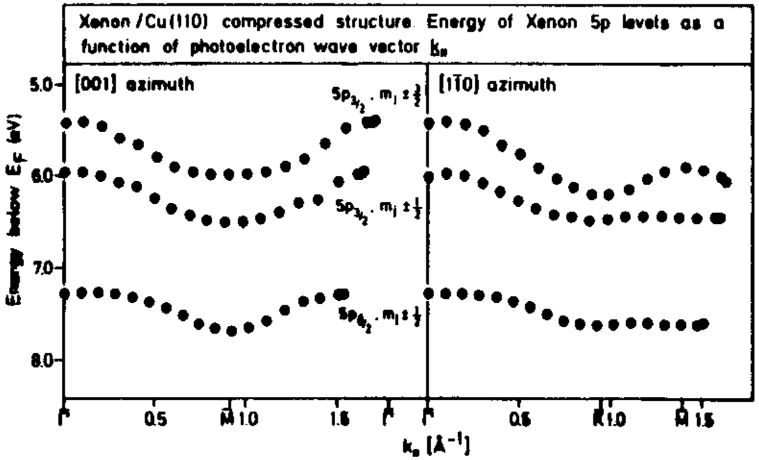


compressed structure



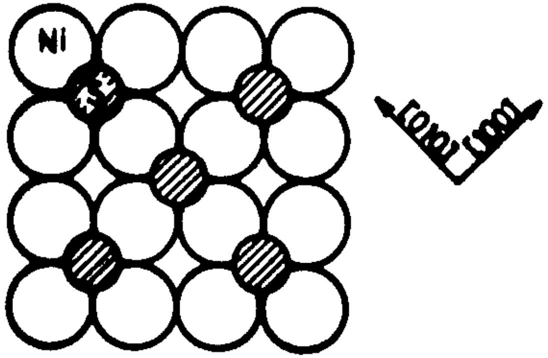


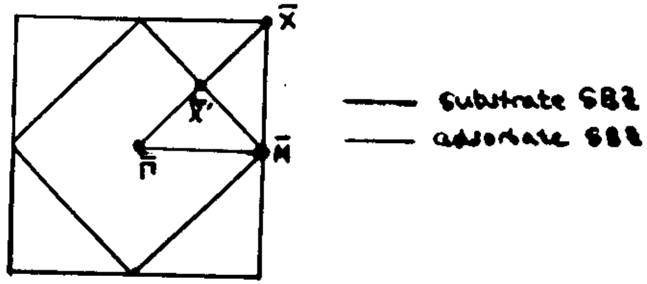




We return to:

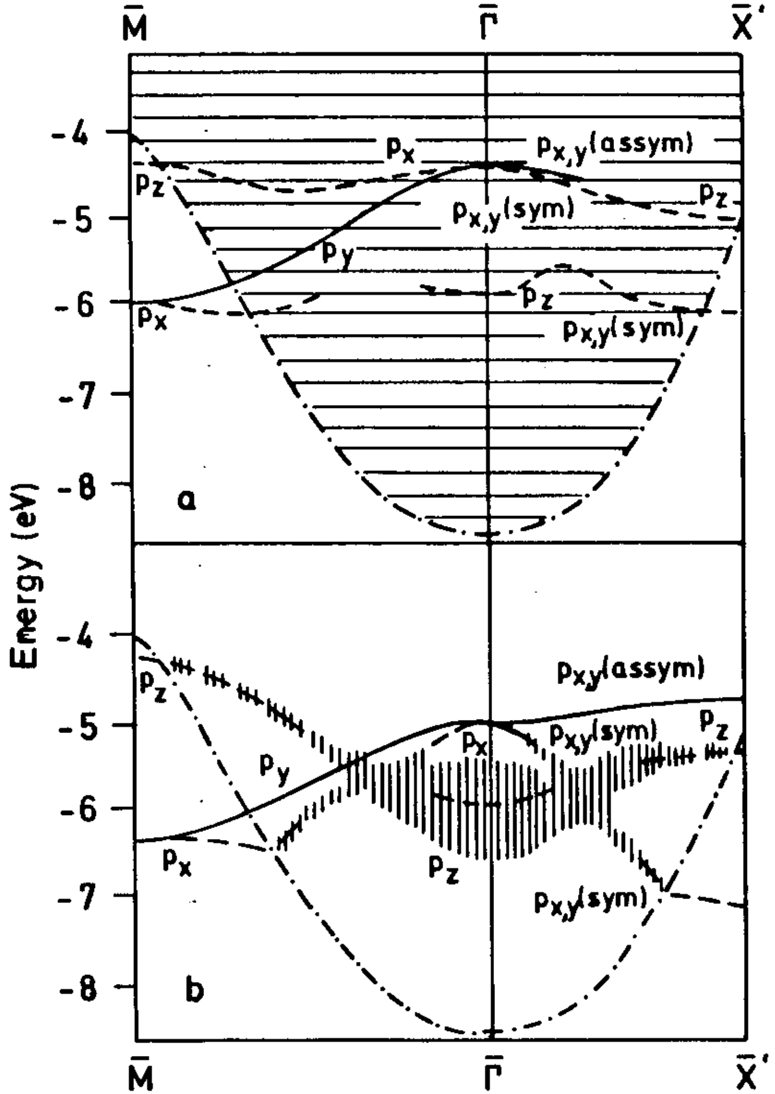
c(2 x 2)-S / Ni (001)





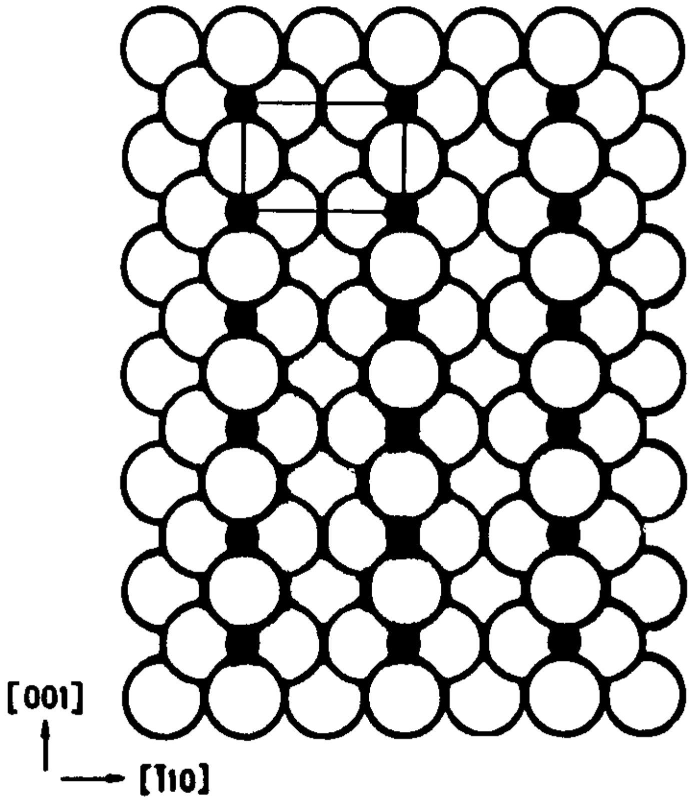
Since the Bloch states along the main directions of the SBZ possess a defined symmetry (i.e. belong to irreducible representations of the appropriate point group), photoemission selection rules can be applied.

c(2×2) S – Ni(100)   Plummer & Lübeck



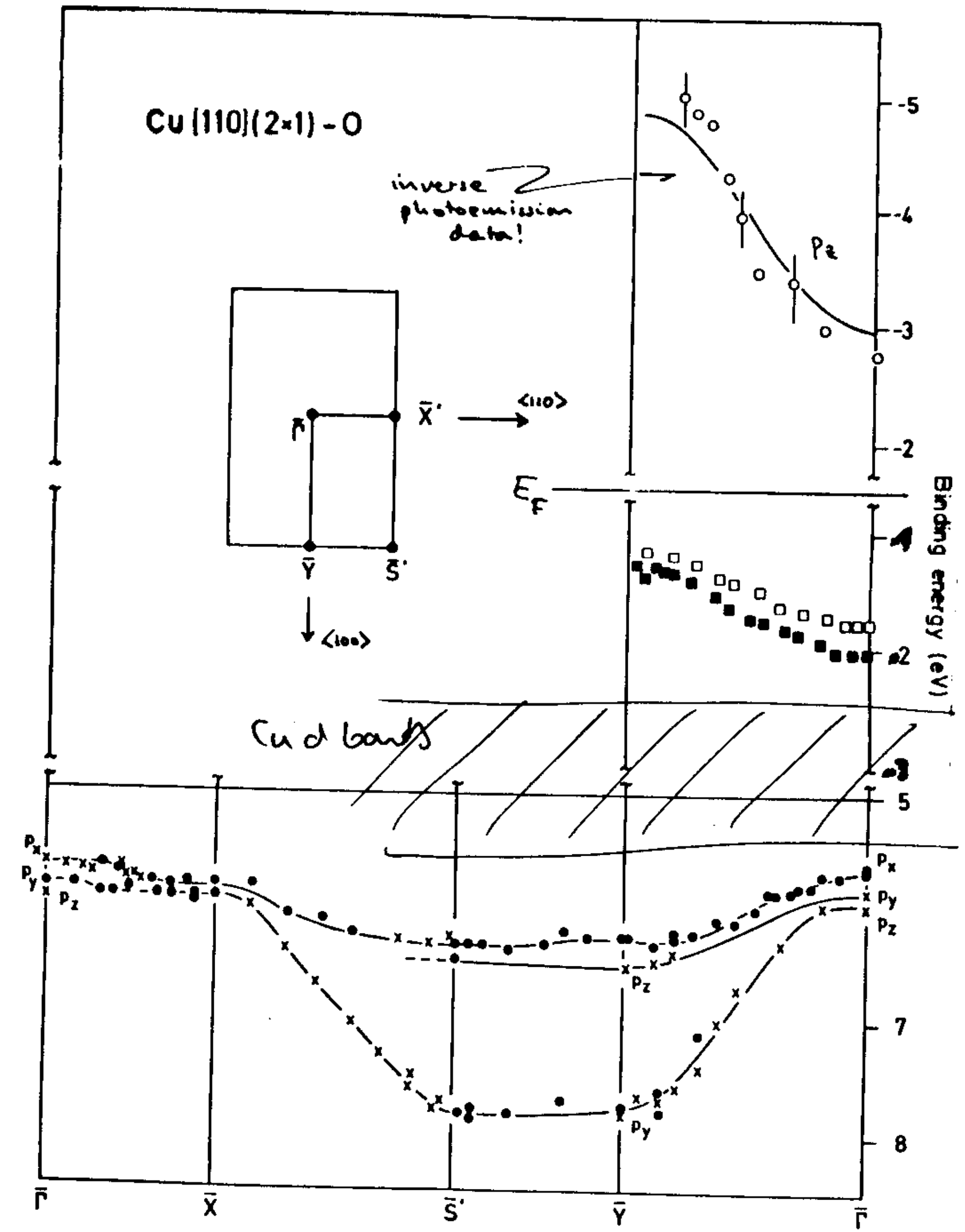
13

Cu(110) – O(2x1)



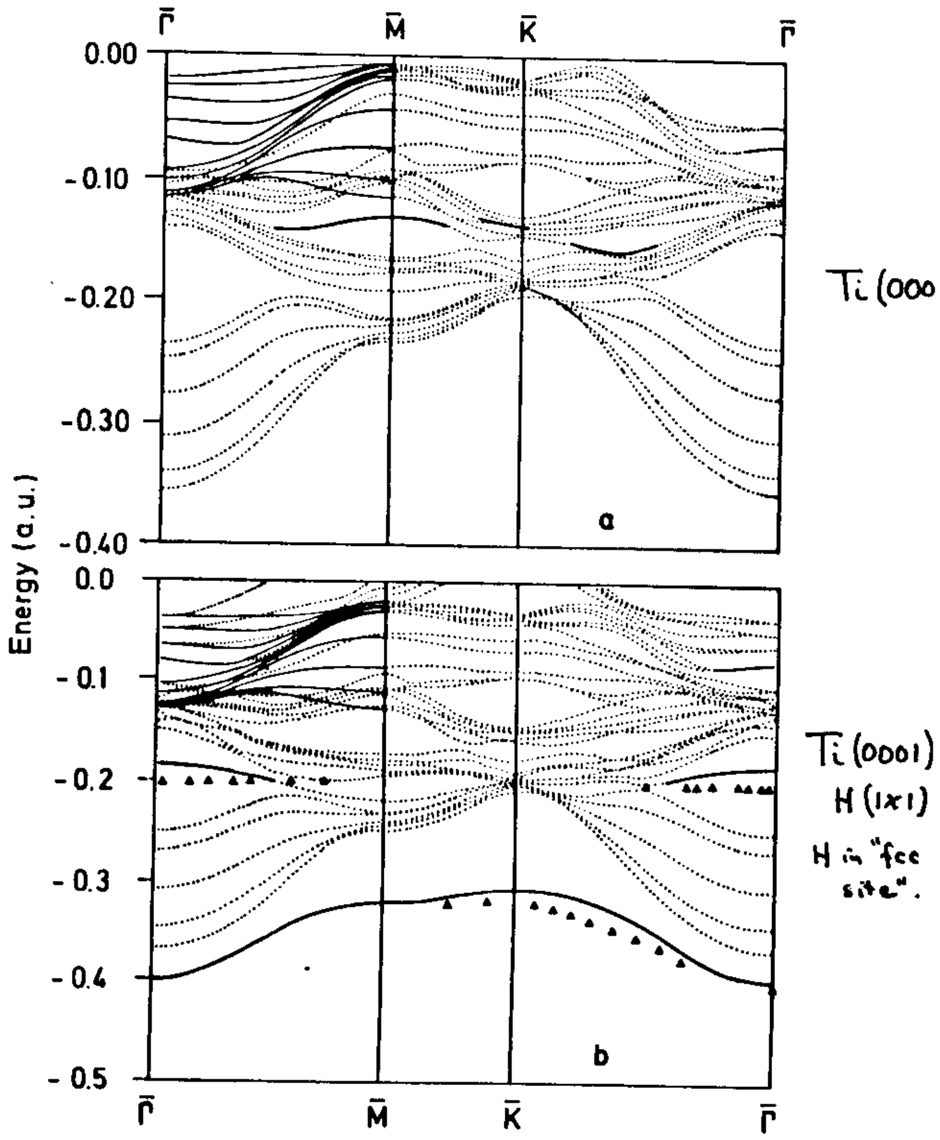
R.P.N. Bronckers and A.G.J. de Wit
Surf. Sci. 112 (1983) 133

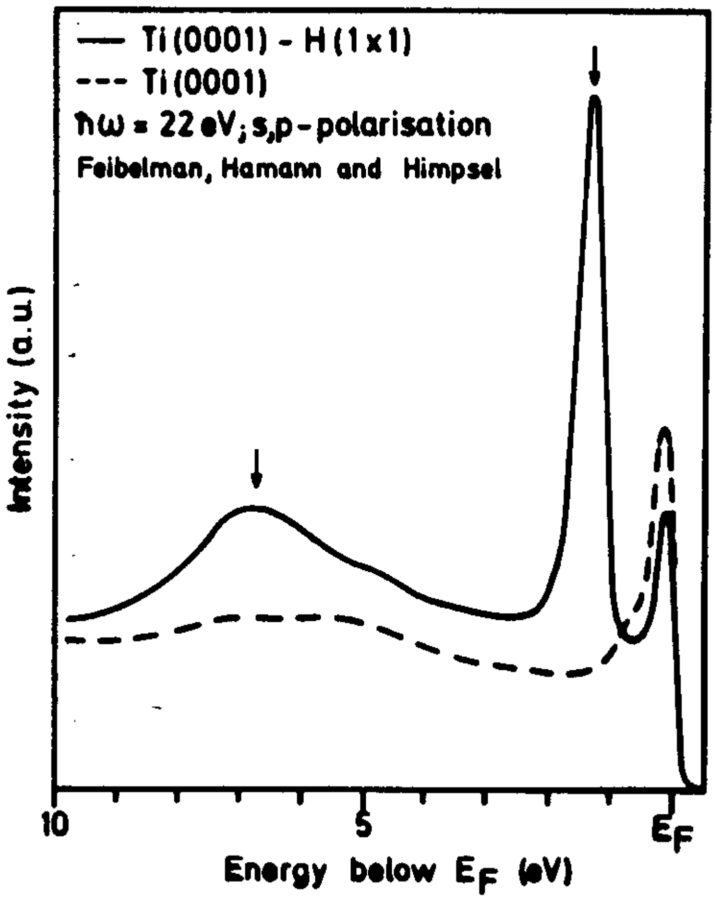
11



Data from Plummer, Lowths and Doso (three arrows !)

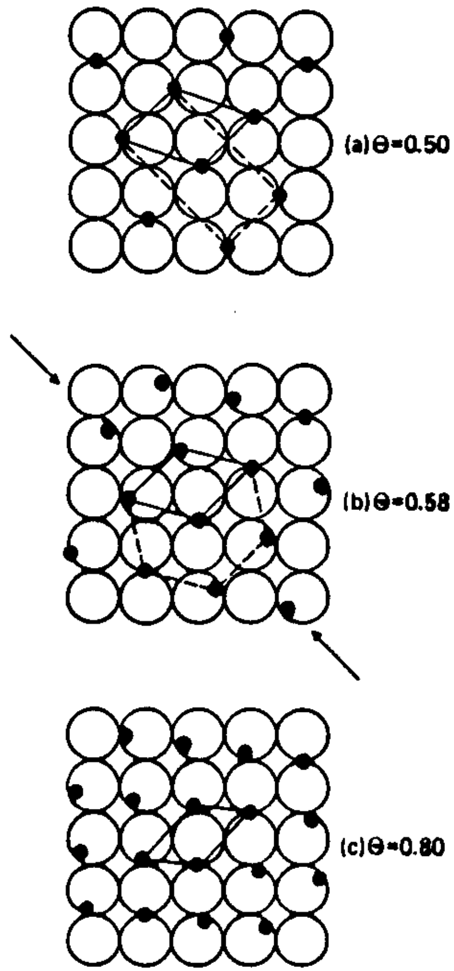
SC-LCAO 11 atom Ti slab.

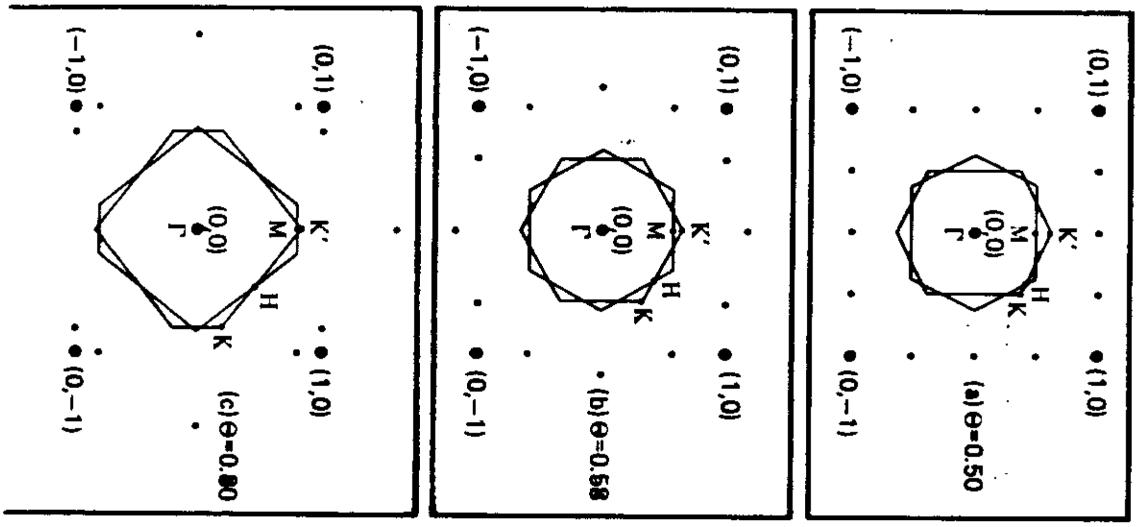




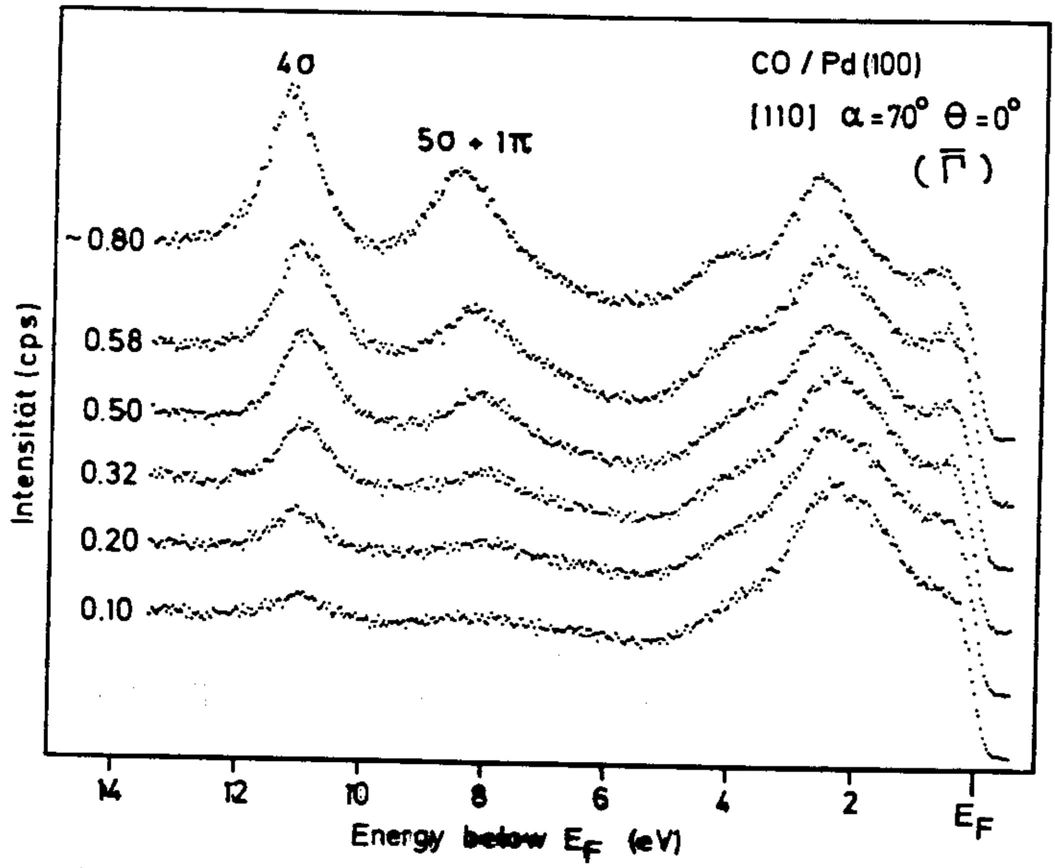
CO | Pd(100)

Horn et al (1979)



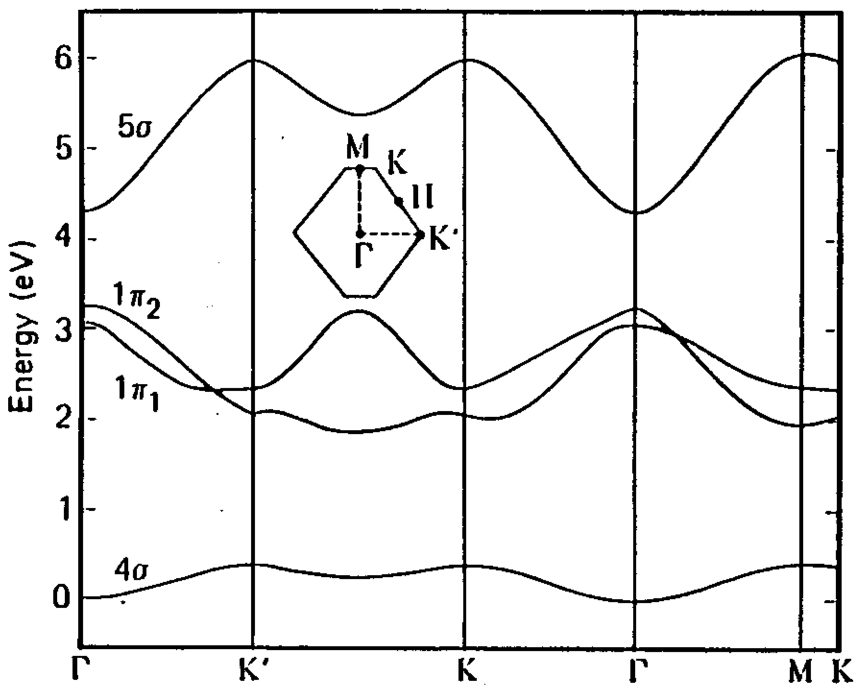


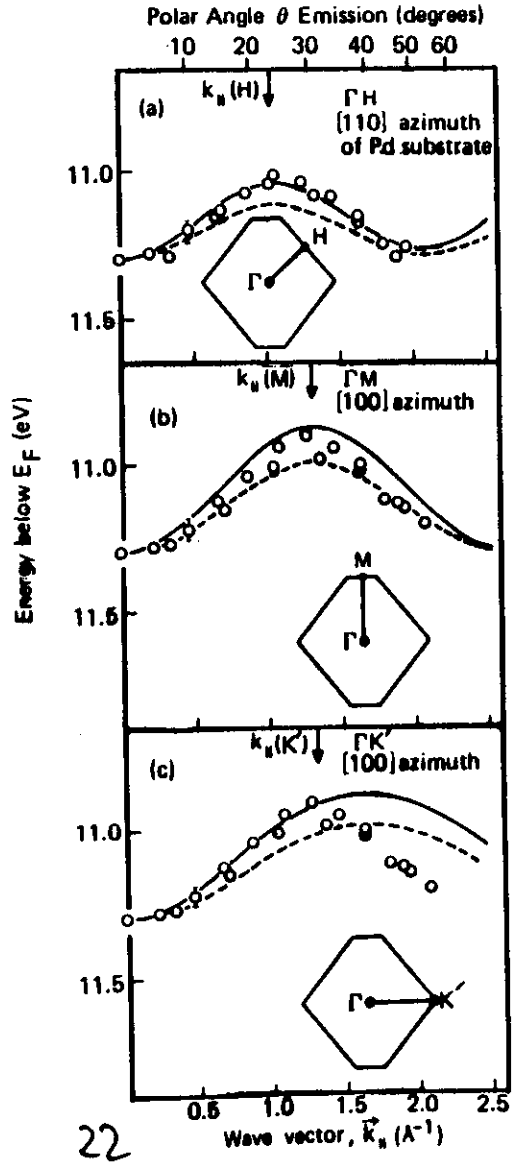
coverage dependence: note the shift in 4σ between
θ = 0.58 & θ = 0.80 due to dispersion



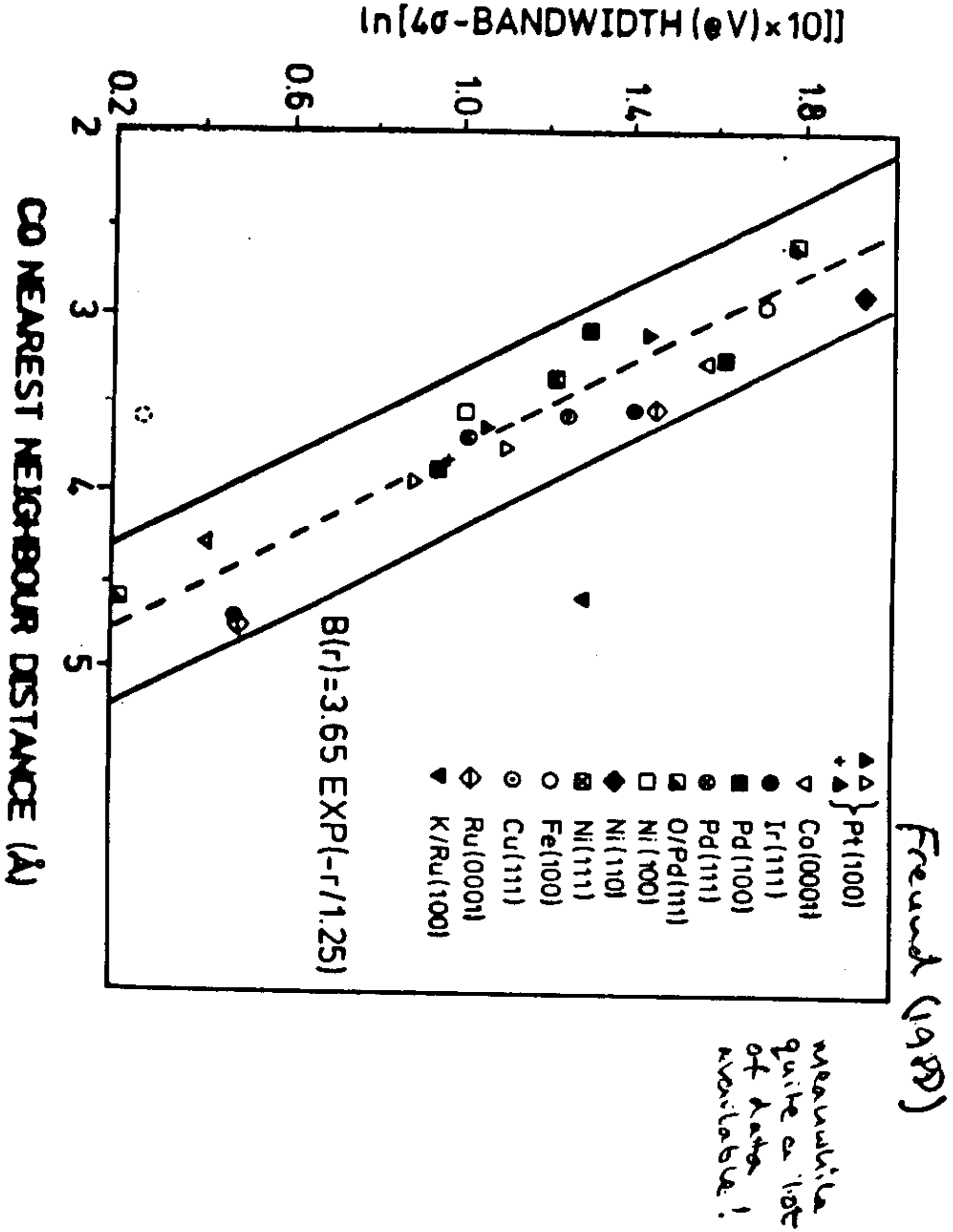
Comparison theory/experiment
4σ dispersion CO/Pd(100) Θ ~ 0.8

Calculated CO band structure
for CO/Pd(100) Θ = 0.8





22



Part IV: Core level photoelectron spectroscopy at surfaces; surface core level shift; "fingerprinting" of adsorbates; satellites; photoelectron diffraction.

Photoelectron binding energy of the ith level (an experimental quantity) is given by

$$E_B(i) = E^i(N-1) - E(N)$$

Since there is usually (but not always) a one-to-one correspondence between orbitals and photoelectron peaks, it is useful to work in terms of a one-electron picture:

$$[illegible] \; E_R + \Delta E_c$$

[illegible]

E_R = relaxation energy

ΔE_c = change in correlation energy

For valence levels,

$$E_R \approx \Delta E_c$$

so that

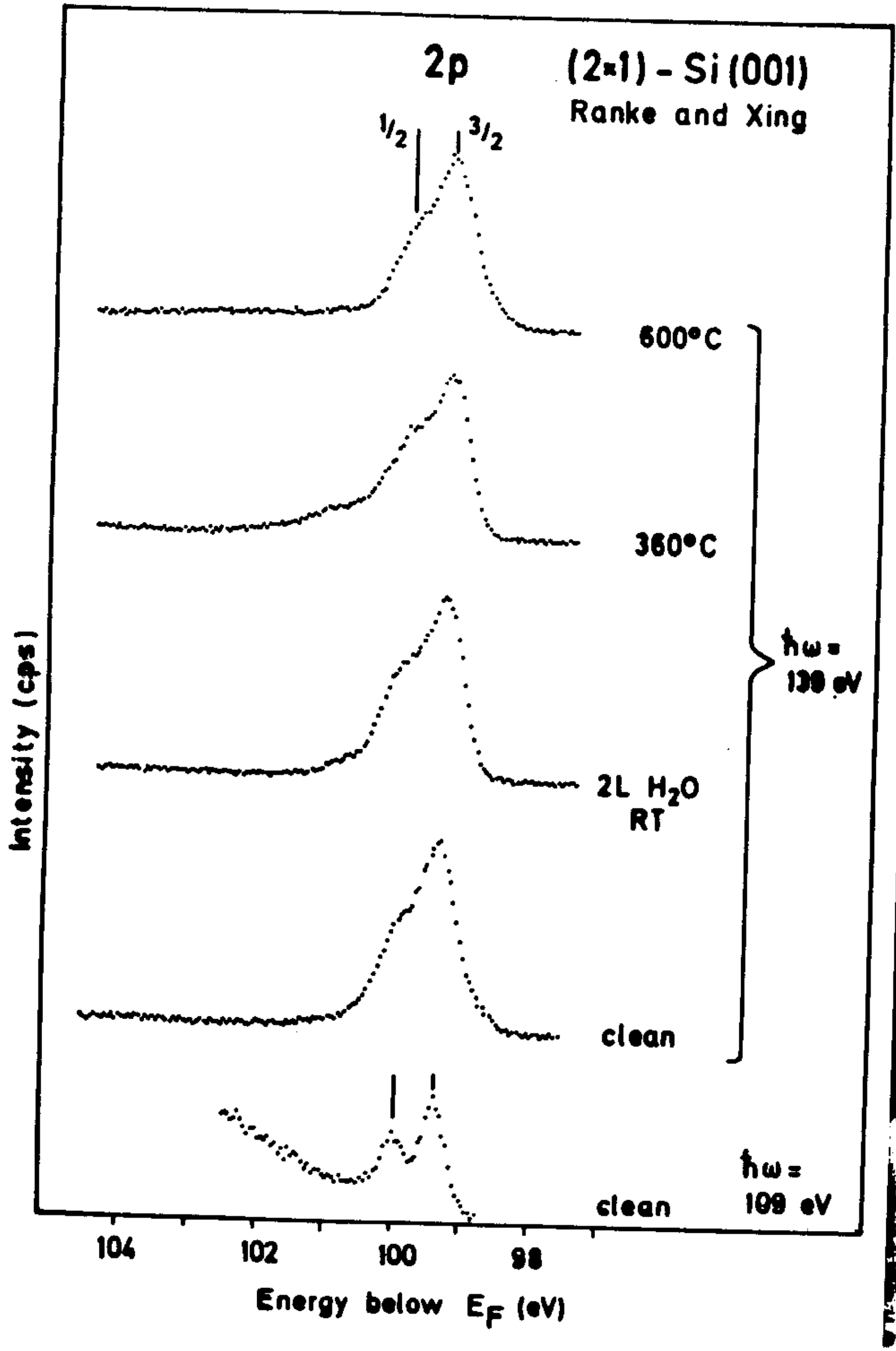
$$E_B(i) \approx \varepsilon_i \quad \text{(Koopmans' theorem)}$$

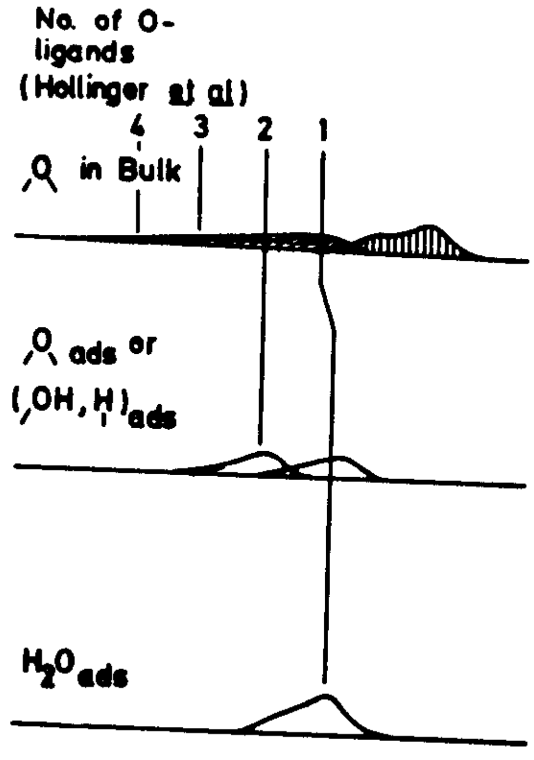
Since this is not necessarily true for core levels, we must describe the <u>chemical shift</u> explicitly as

$$\Delta E_B = \underbrace{\Delta \varepsilon_i}_{\text{initial state contribution}} + \underbrace{\Delta E_R + \Delta(\Delta E_c)}_{\text{final state contribution}}$$

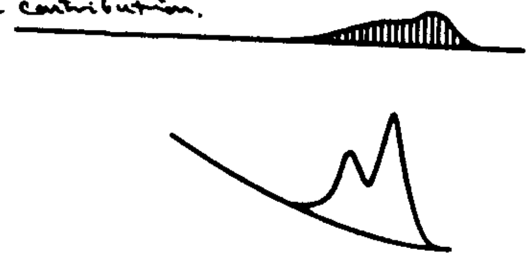
Core level photoelectron spectroscopy in surface science

- surface analysis, in future with higher spatial resolution
- gas-solid reactions (eg. oxidation, nitridation) and interface formation (eg. Schottky barrier).
- surface segregation
- "fingerprinting" of chemisorbed species; interesting satellite effects
- surface structure via photoelectron diffraction (= angle resolved XPS).

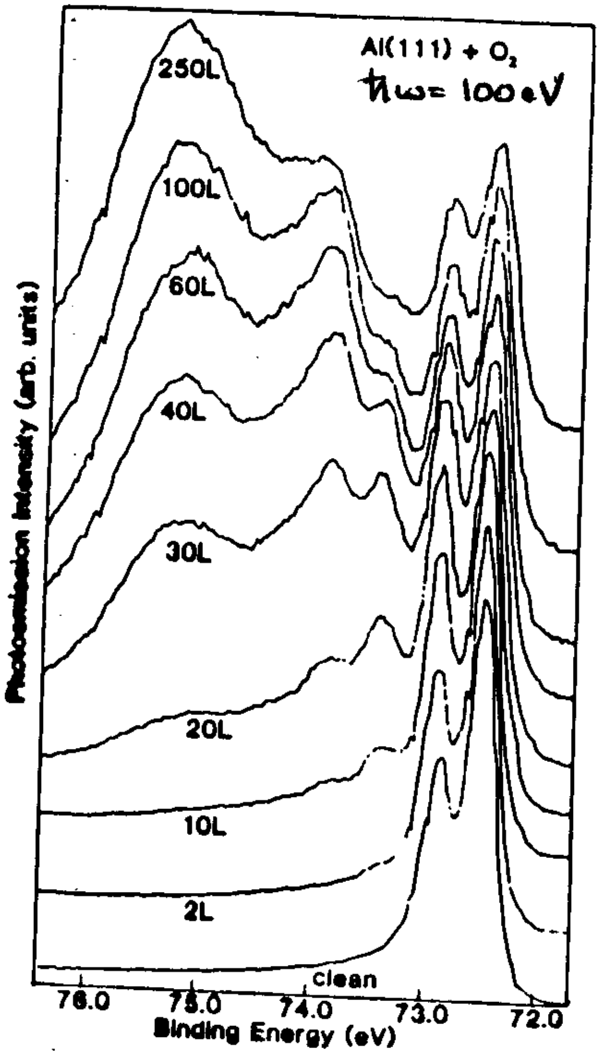


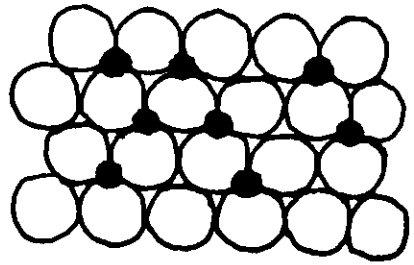


At 139eV photon energy the photoelectron kinetic energy is ~40eV, giving rise to an appreciable surface contribution.

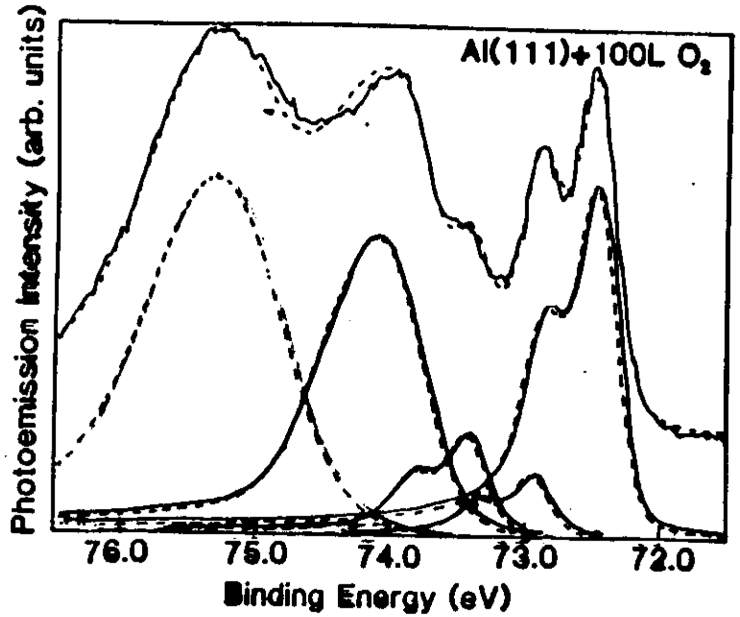


McConville et al (1988)

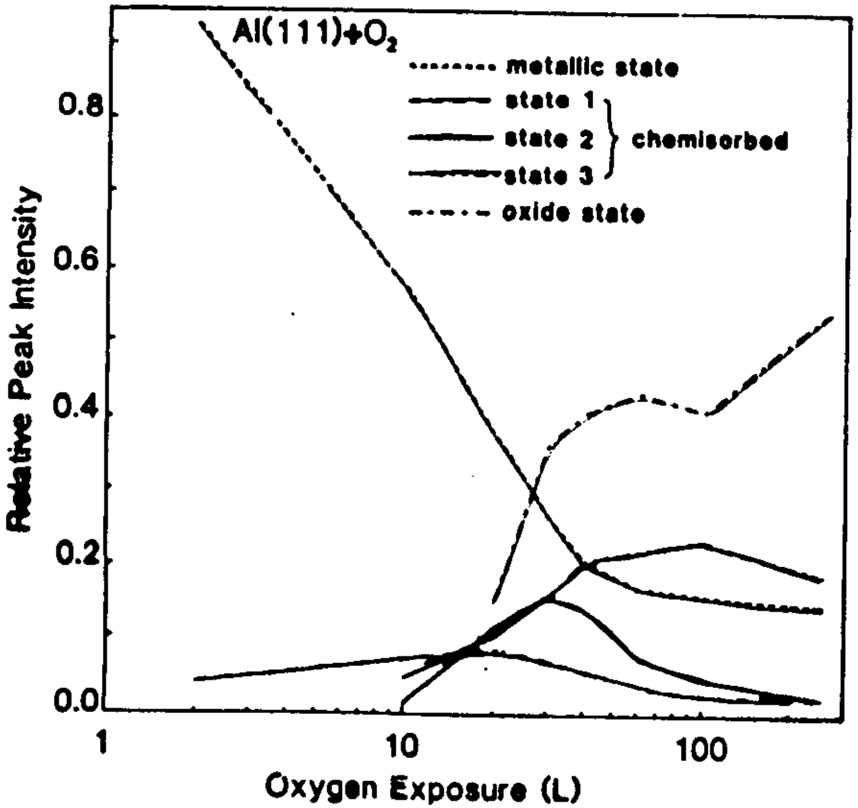




incomplete c(1x1) overlayer on Al(111)



Three distinct Al surface core level shifts for the chemisorbed phase due to the incomplete (1x1) overlayer.



Schnell et al (1985)

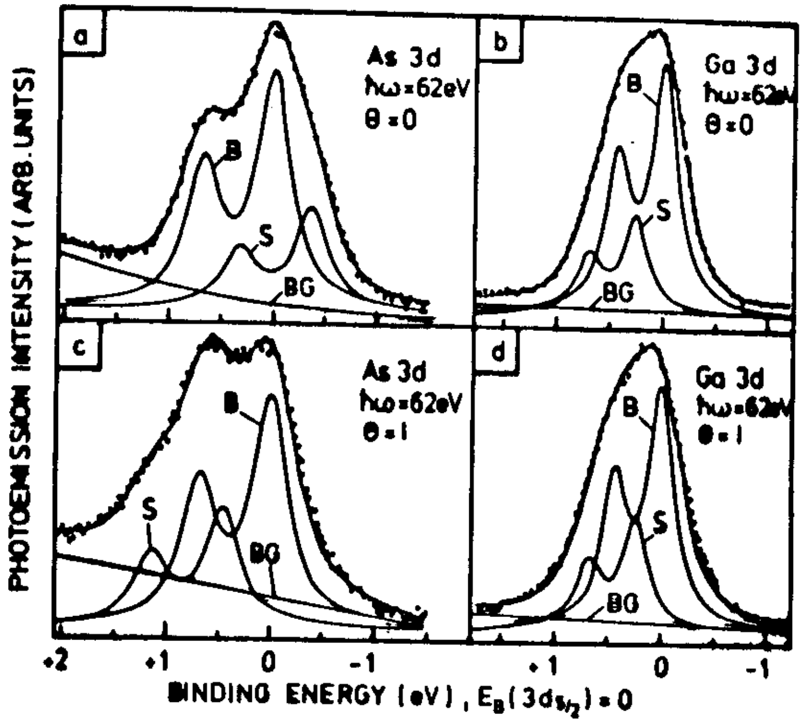


Fig. 1. Photoemission core-level spectra for clean and chlorine saturated GaAs (1 1 0). The experimental and fitting results are plotted together with the surface (*S*), bulk (*B*) and photoelectron background (*BG*) contributions that are shown without instrumental broadening.

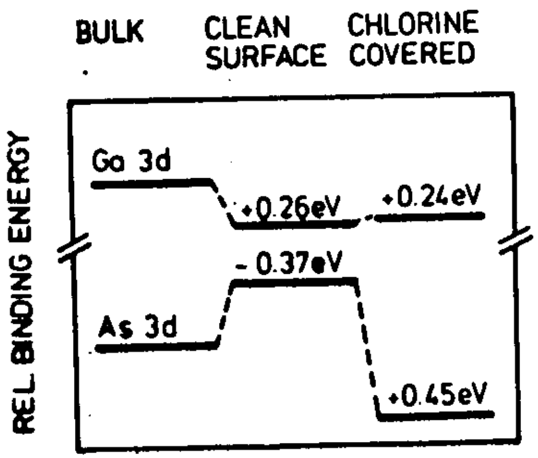
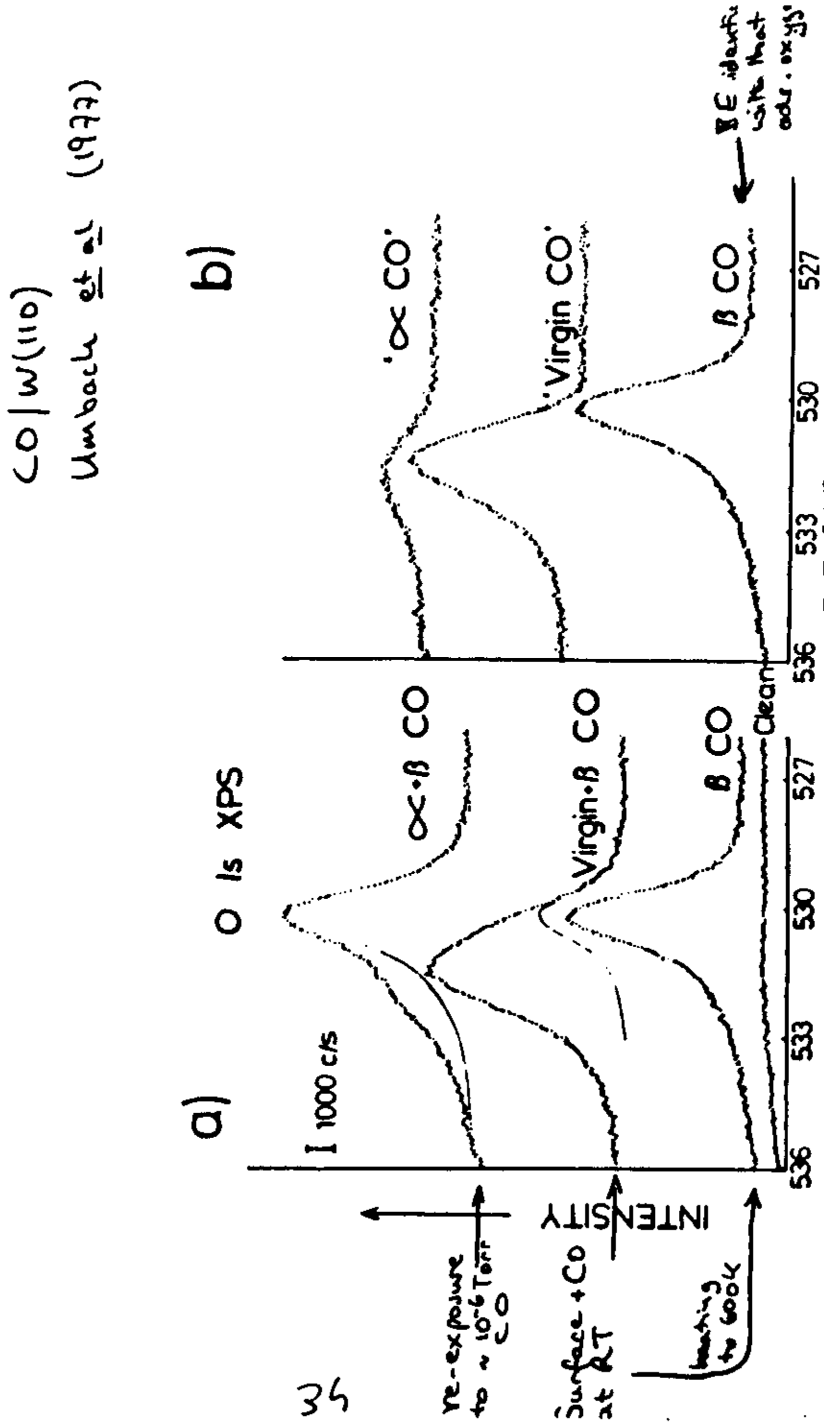


Fig. 2. Summary of the relative surface-to-bulk core-level binding energy shifts for clean and chlorine saturated GaAs (1 1 0).

Intrinsic surface core level shifts in III-V semi-conductors cannot be simply interpreted in terms of increased charge transfer (in this case Ga→As) at the surface. The Madelung energy and final state effects play a role.

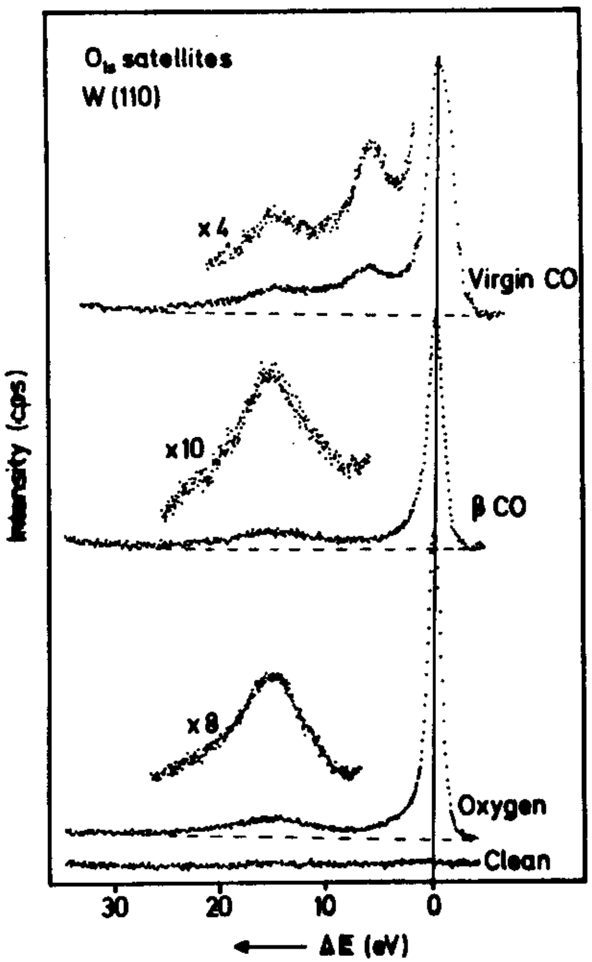
However, on chlorine adsorption it is clear that charge transfer is very important for the measured shifts: the Cl appears to adsorb on the outer-lying As atoms.

33

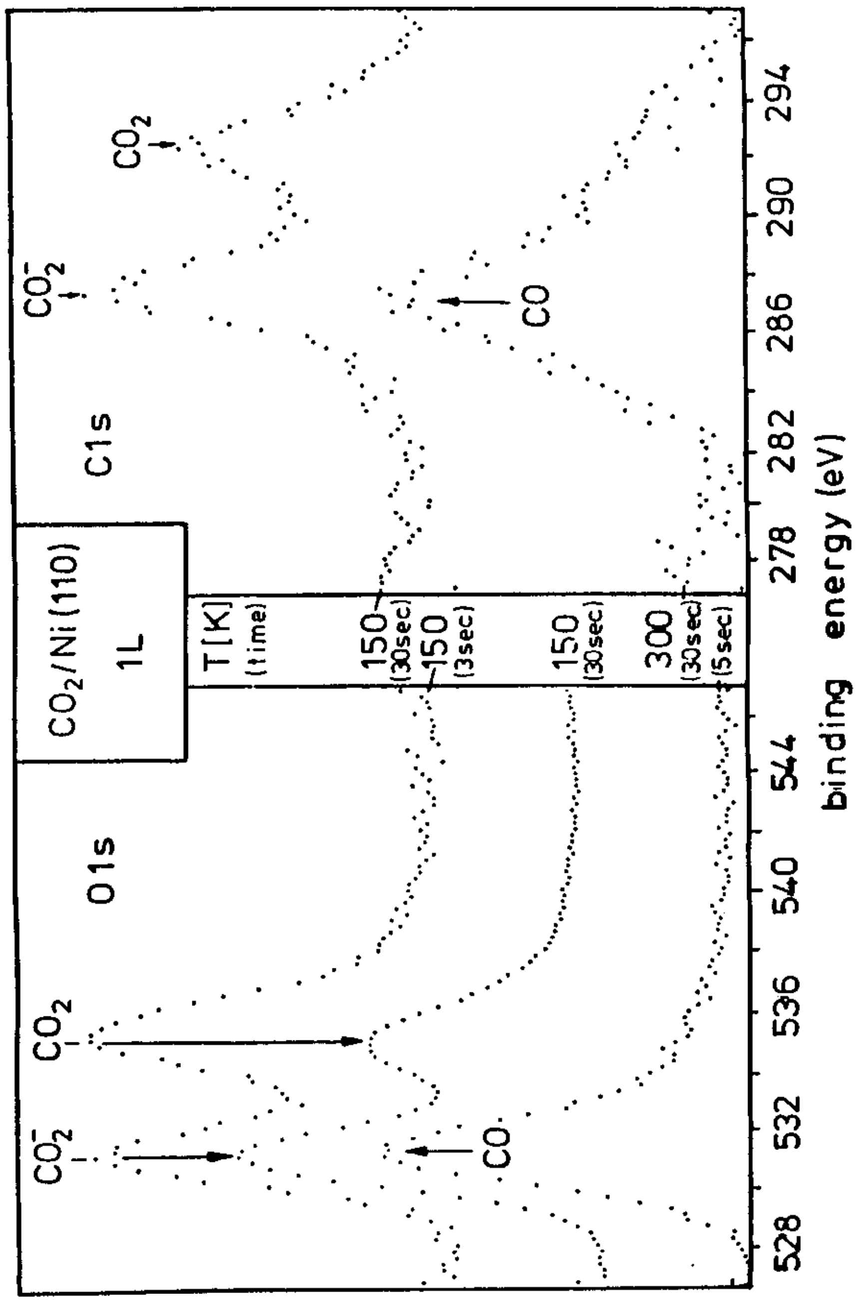


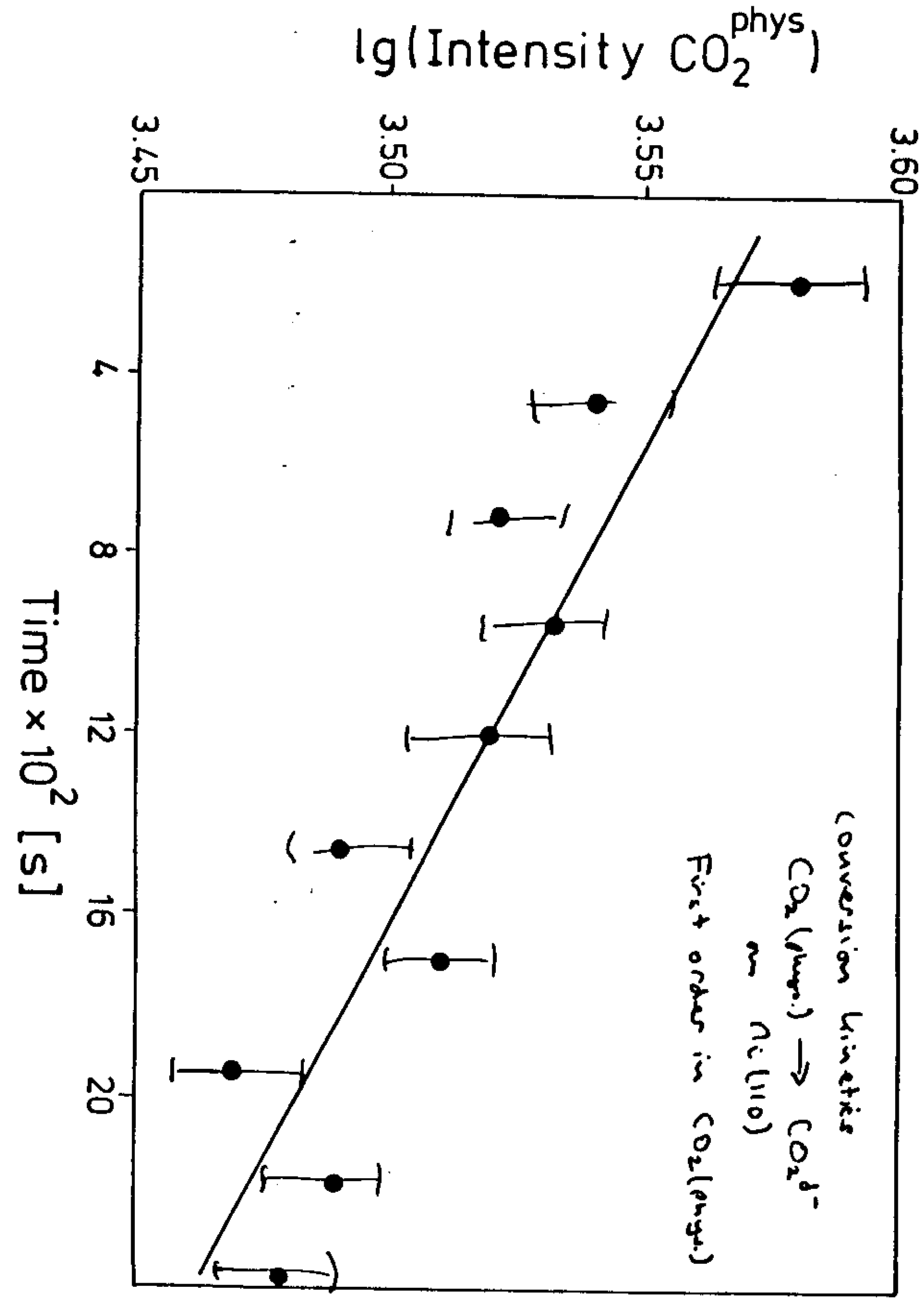
34

Umbach et al (1978)



Illing et al (1988): x-ray induced conversion from physisorbed into chemisorbed CO_2





We consider the additional processes which are likely to contribute to the relaxation energy, E_R, for a core level in an atom or a molecule adsorbed on a metal surface (assume $\Delta E_R \approx 0$).

The valence electrons will re-arrange in the new potential in response to the creation of the core hole i.e. they "screen" the hole. Two effects:

— image charge screening
— unfilled orbital mechanism (charge transfer)

Depending on the dynamics of the screening process satellites may appear in the spectrum.

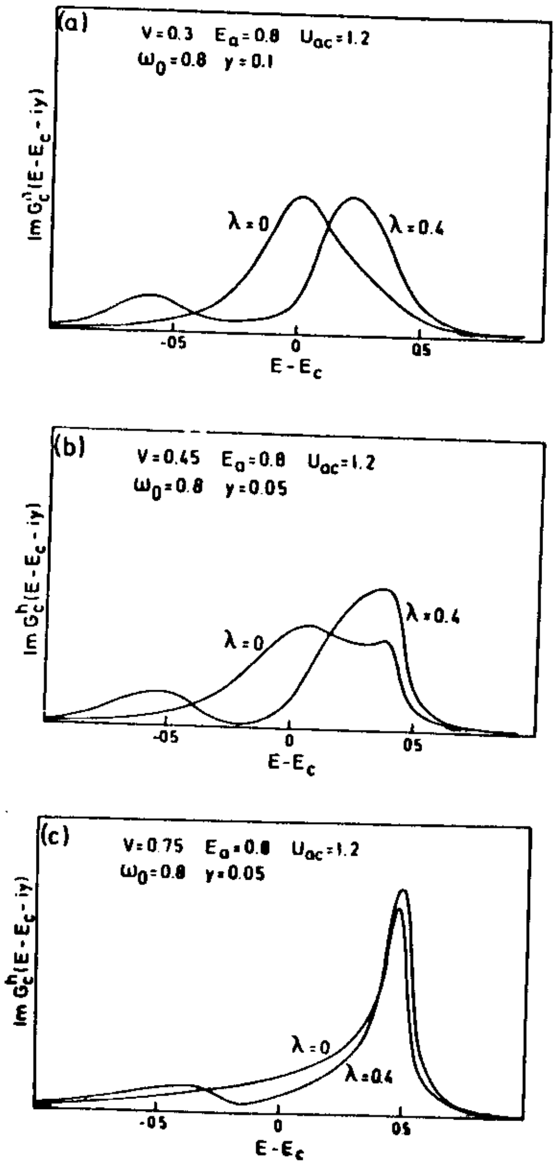
The screening processes cannot be turned on instantaneously so there is the possibility that the N-1 particle system is left in an excited (not fully relaxed) state. In the case of image charge screening, for example, surface plasmon satellites appear in the spectrum.

In the adiabatic limit (perhaps reached at very low photoelectron kinetic energies) the N-1 particle system is fully relaxed and there are no satellites. The other extreme is the sudden limit (photo-electron removed very quickly): for some screening mechanisms a sum rule will operate.

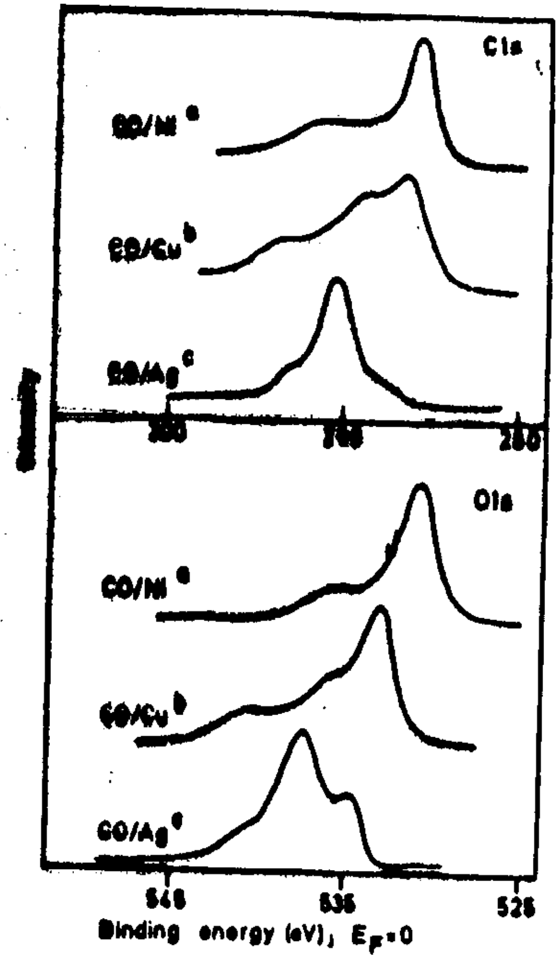
Model calculations:
Schönhammer & Gunnarsson

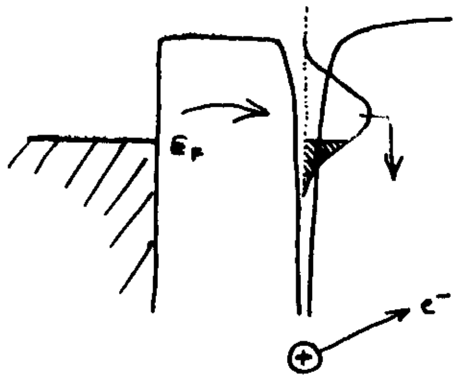
V - strength of metal - adsorbate coupling

λ - strength of coupling to surface plasmons



Krause et al





unfilled orbital mechanism

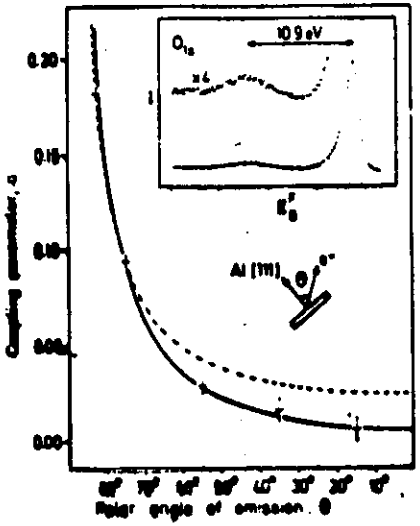
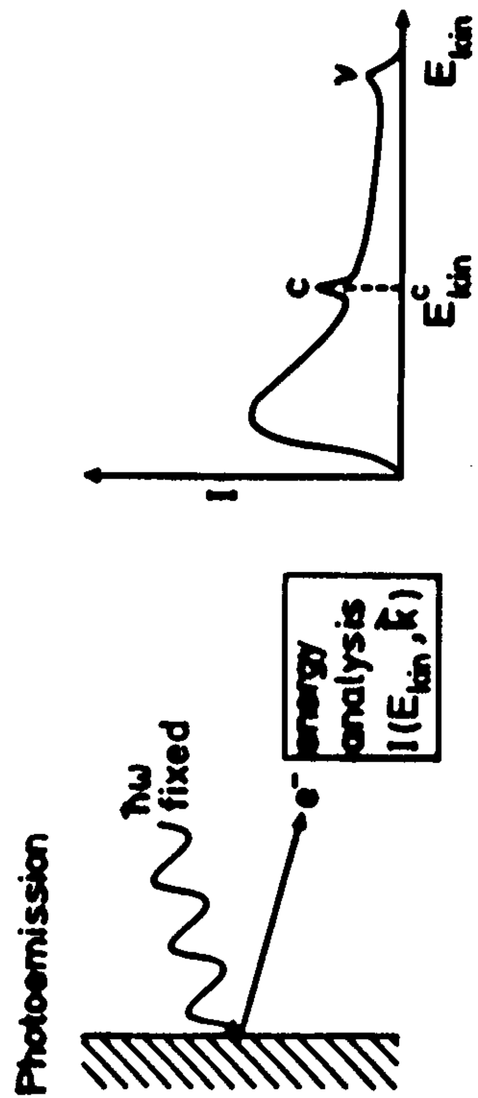


Fig. 45. Angular dependence of the surface plasmon coupling parameter for the O 1s level in the system oxygen/Al{111}. The solid line is a fitted curve using a two-parameter expression derived in ref. 108. The broken line represents the extrinsic effect (~ 1/cos θ) and is fitted at the two highest emission angles. The inset shows a typical O 1s core level spectrum with the surface plasmon satellite. After Bradshaw et al. [102].

extrinsic contribution must be separated!

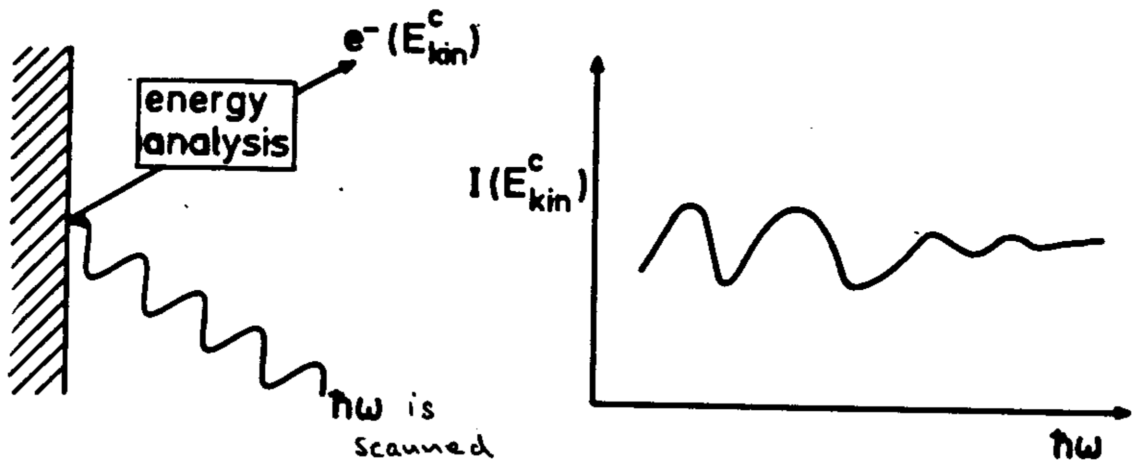


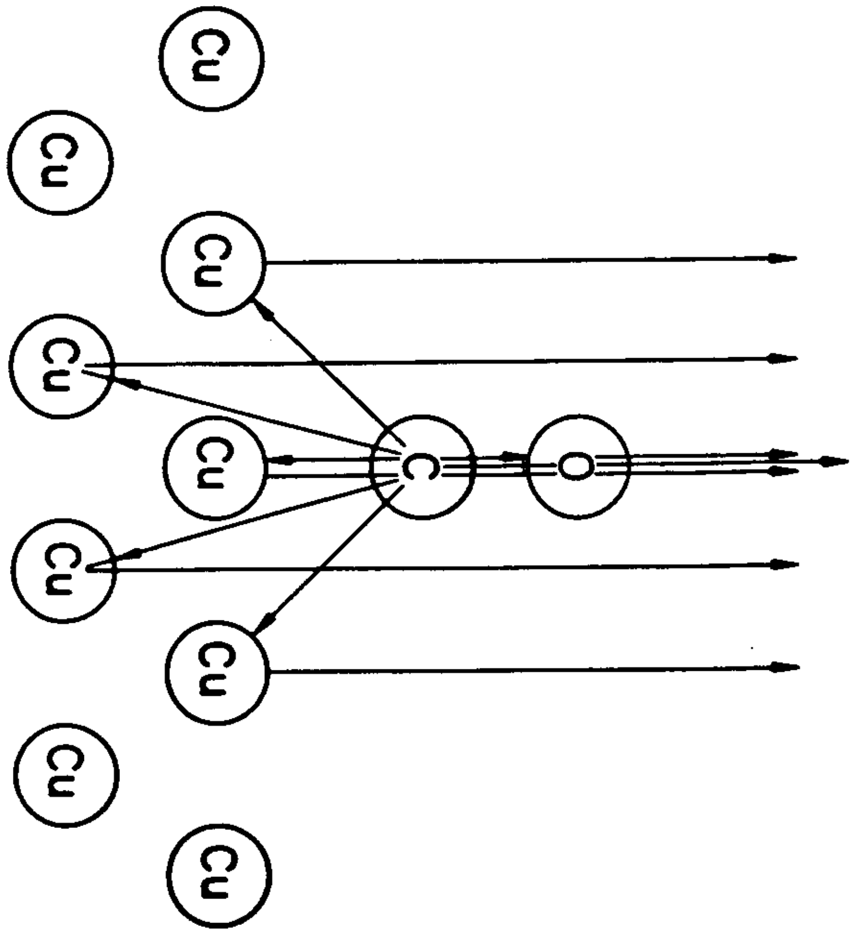
41

"Angular-scan" photoelectron diffraction at fixed $\hbar\omega$ is also possible.

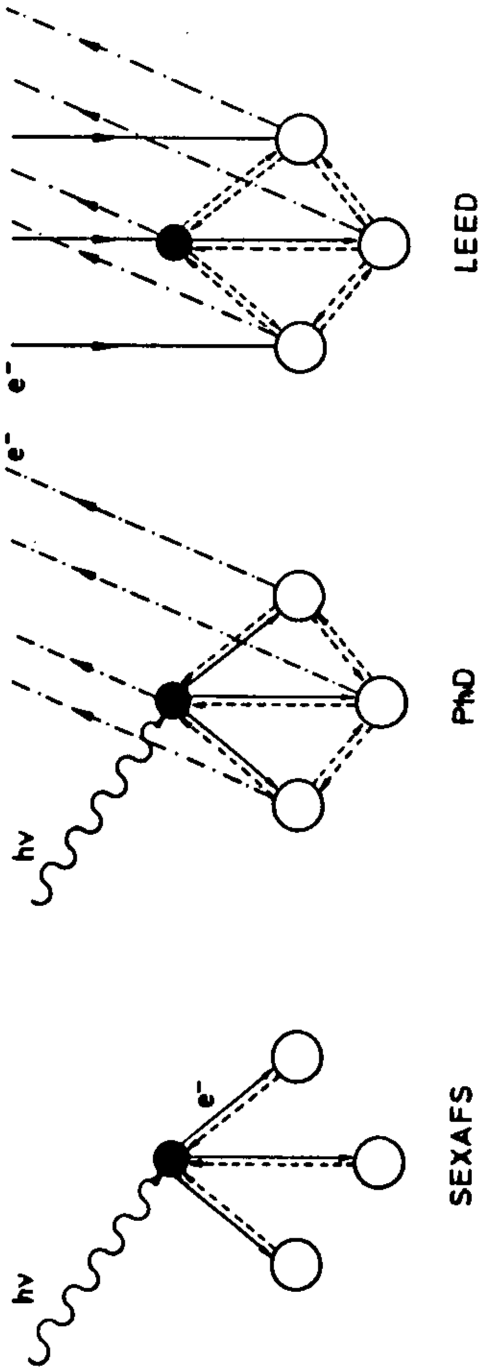
Both experiments require angle-resolved core level measurements.

Photoelectron diffraction (energy-scan mode)

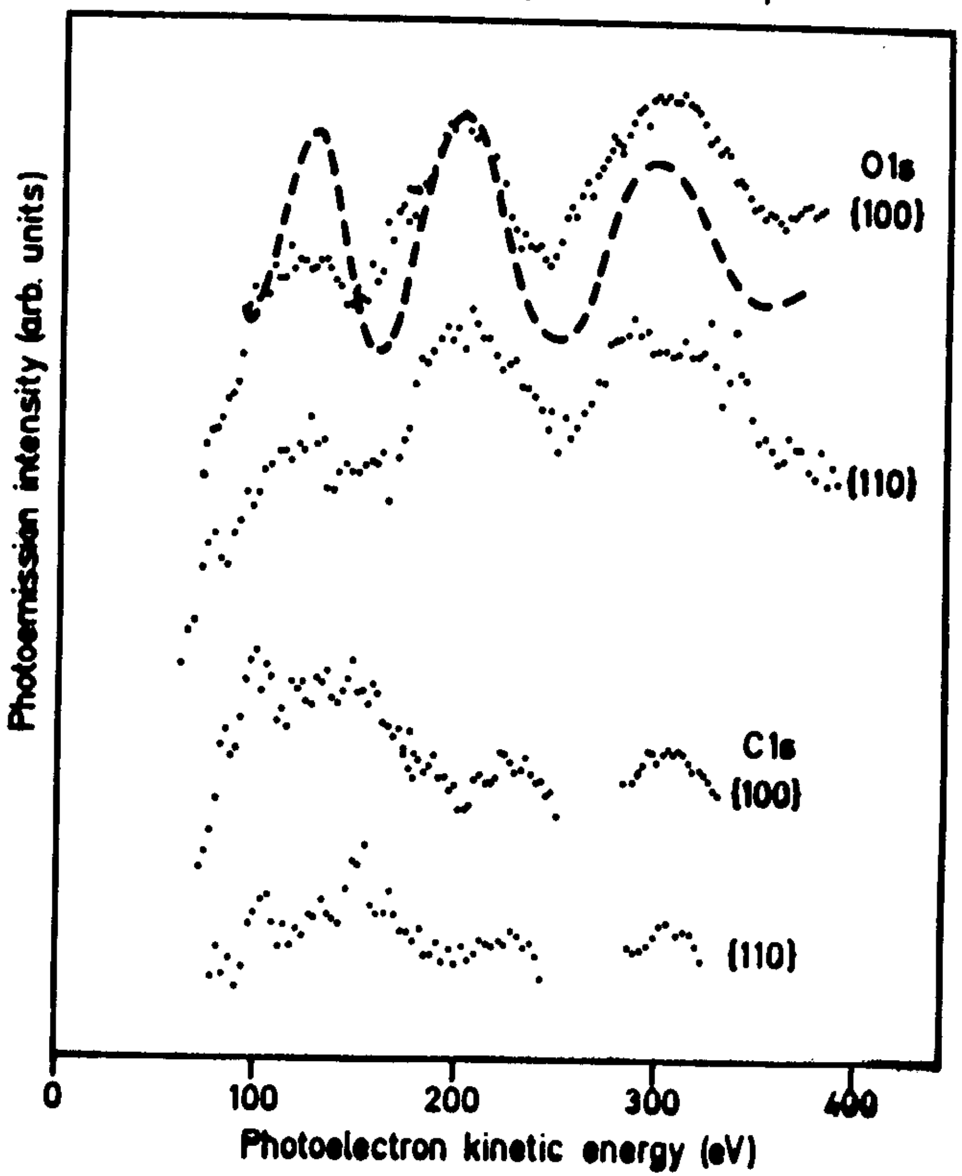




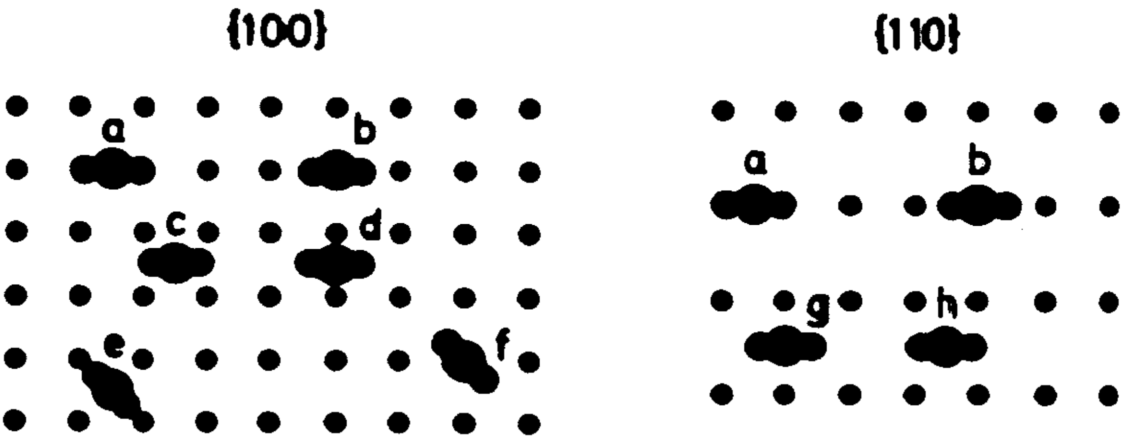
Photoelectron diffraction (PED)



PED of the formate species on Cu(100) and Cu(110)



47



a = the aligned bridge site
b = the aligned atop site