united nations
educational, scientific
and cultural
organization

international atomic
energy agency

the
abdus salam
international centre for theoretical physics

ICTP 40th Anniversary

SCHOOL ON SYNCHROTRON RADIATION AND APPLICATIONS
In memory of J.C. Fuggle & L. Fonda

19 April - 21 May 2004

Miramare - Trieste, Italy

1561/19

Photoelectron Diffraction: Applications and Developments

Juerg Osterwalder

School on Synchrotron Radiation and Applications, ICTP Trieste, May 3-6, 2004

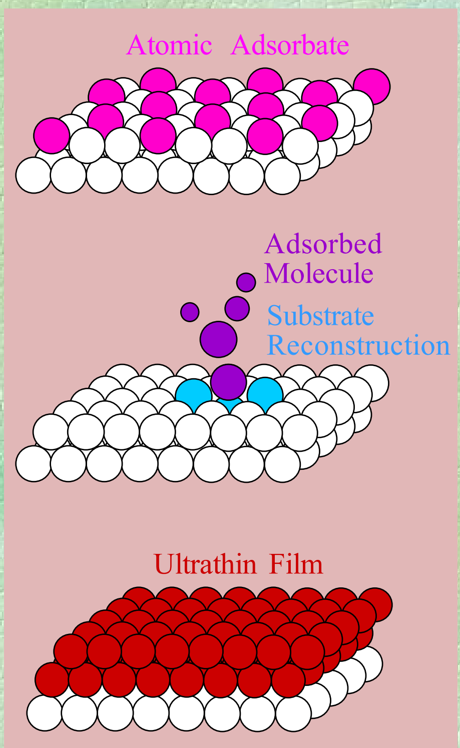
Photoelectron Diffraction: Applications and Developments

Jürg Osterwalder
Physik-Institut, Unversität Zürich, Winterthurerstr. 190,
CH-8057 Zürich, Switzerland - osterwal@physik.unizh.ch
http://www.physik.unizh.ch/groups/grouposterwalder/

Lecture 6

- Typical Surface Structure Problems
- Photoelectron Diffraction Patterns as Fingerprints
  - High-Temperature Superconductors
  - Tartaric Acid on Cu(110): Chiral Molecules
  - Na/Al(111): Atomic Adsorbates
- Application to Large Adsorbed Molecules: C_{60}
- Application to Heterogeneous Catalysis: O/Rh(111)
- Applications to Materials Science: *h*-BN/Ni(111)

Surface Structure Problems
… and their Solution by X-Ray Photoelectron Diffraction



Fingerprinting:

- Characteristic XPD pattern
- Forward Scattering Maxima
- Backscattering Cones
- 1st-Order Interference Fringes

Holography:

- Atomic-Resolution Image

Chemical Intuition:

- Reasonable Bond Lengths
- Coordination Number

Structural Refinement:

- Model Calculations (SSC, MSC)
- R-Factor Analysis

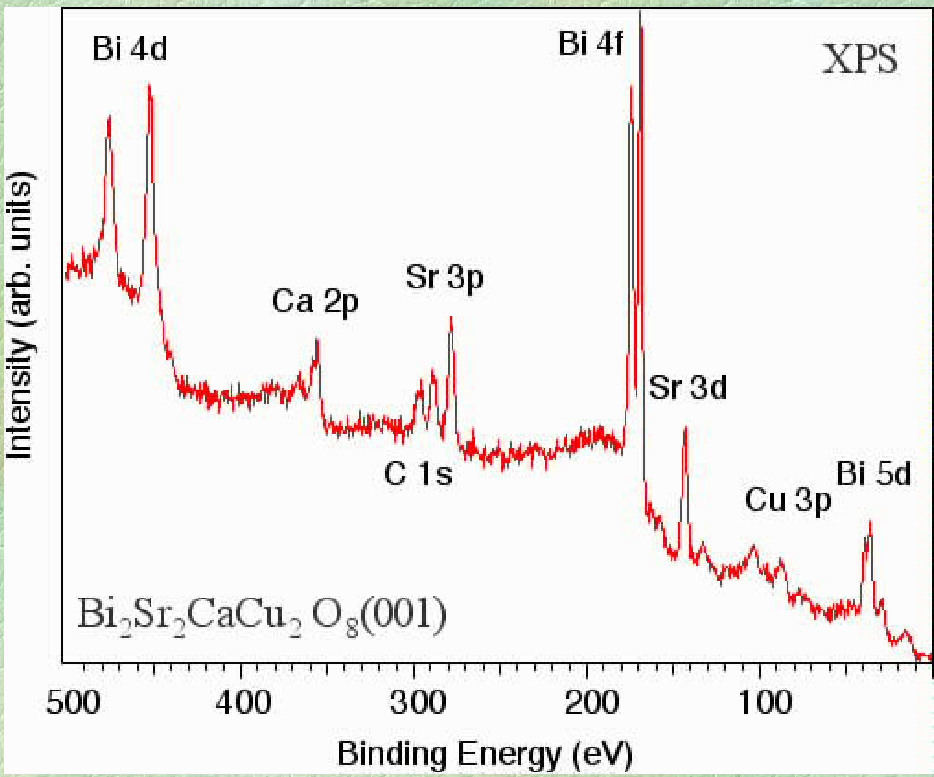
Resolution:

1.0 - 0.5Å

…

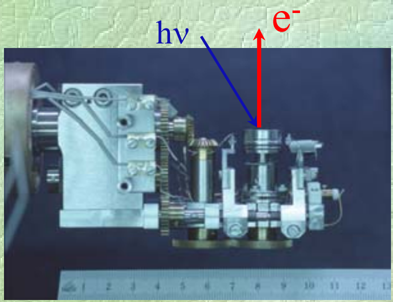
0.05Å

Exploiting the Elemental Sensitivity of XPS …

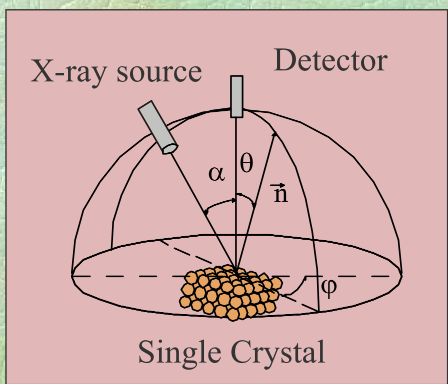


… for structural analysis

Full-hemispherical (2π) XPD patterns

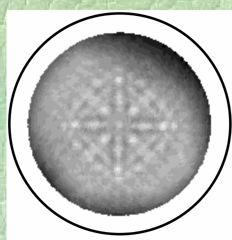


Fully automated two-axis sample goniometer (Fadley type)



Sequential measurement of core level intensities at ca. 4000 angular settings

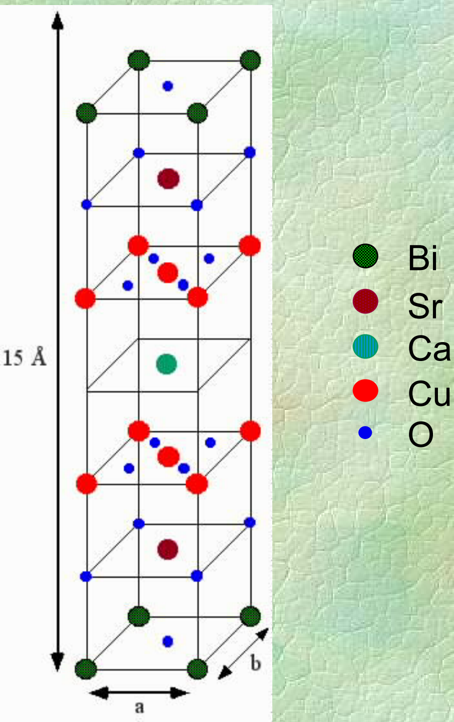
e.g. Bi 4f

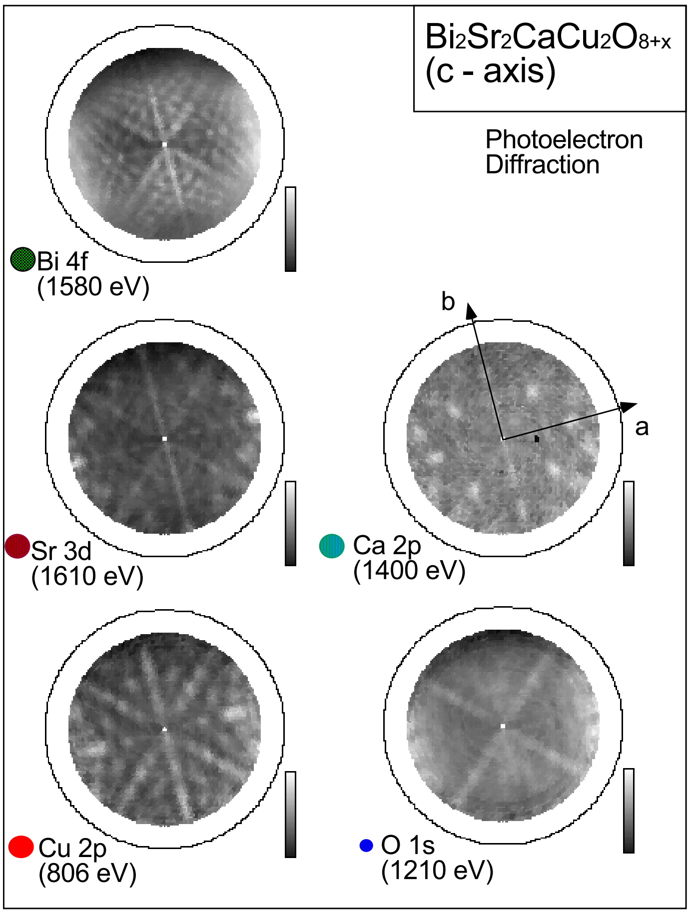


Intensities in grey scale, stereographic projection

Measuring times for full 2π XPD pattern: 1 hour to 24 hours (depending on count rates **and** on anisotropies)

XPD Patterns of All Elements



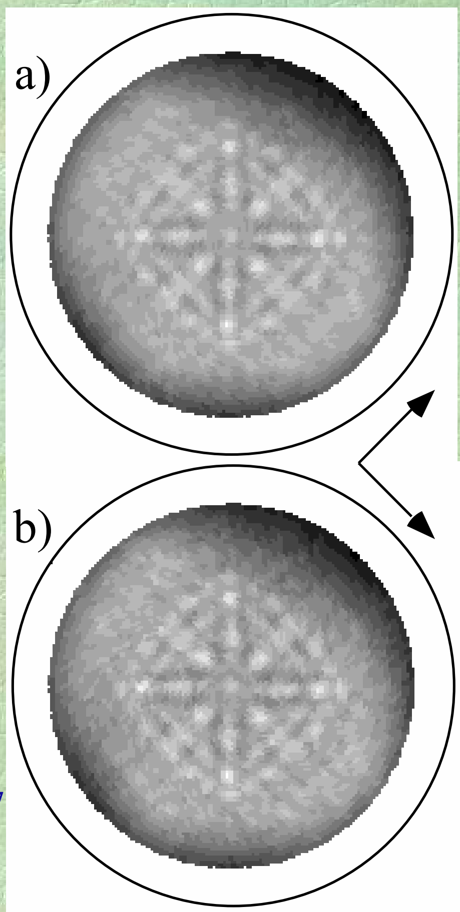


=> Surface Termination

M. Shimoda et al., Physica C 196 (1992) 236

Determination of Dopant Sites

$Pb_{0.4}Bi_{1.6}Sr_2CaCu_2\ O_8(001)$

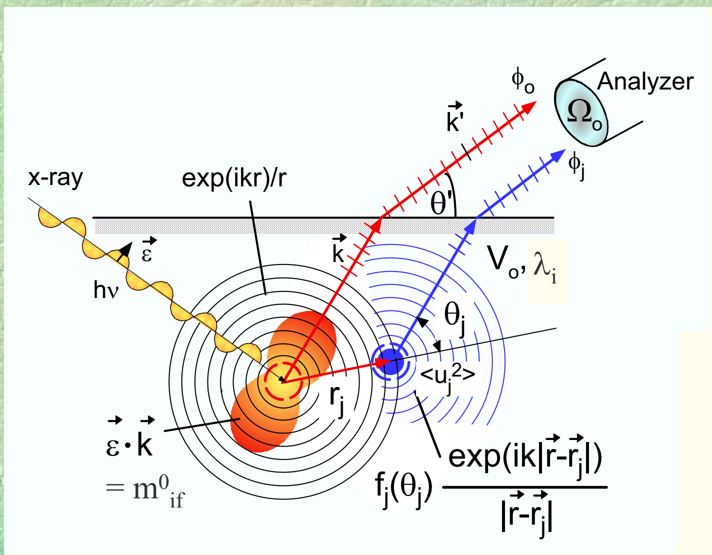


Bi 4f $_{5/2}$
E_{kin}=1095 eV

Pb 4f $_{7/2}$
E_{kin}=1110 eV

P. Schwaller et al., JES 76 (1995) 127

X-Ray Photoelectron Diffraction

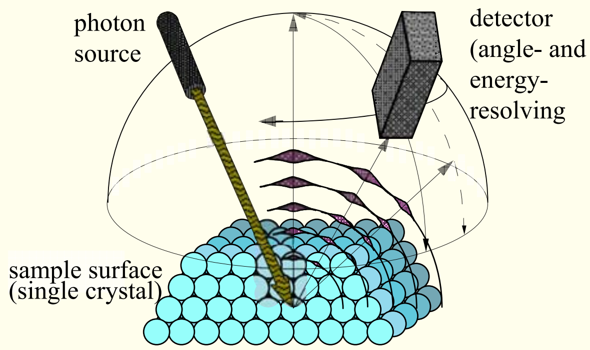


Photoemission matrix element

$P_{if} \propto |\langle\psi_f(\boldsymbol{r},\boldsymbol{k_f})|\boldsymbol{\varepsilon}\bullet\boldsymbol{r}|\psi_{nlm}(\boldsymbol{r})\rangle|^2$

Scattering final state wave function

$\psi_f(\boldsymbol{r},\boldsymbol{k_f}) = \phi_0(\boldsymbol{r},\boldsymbol{k_f}) + \Sigma_j\ \phi_j(\boldsymbol{r},\boldsymbol{l_j}\text{->}\boldsymbol{k_f})$



Single-scattering expression

$I(\boldsymbol{k_f}) \propto |\ m^0_{if}(\boldsymbol{k_f})\ \exp(-L_0/2\ \lambda_i\ (E_f)) +$

$\Sigma_j\ m^0_{if}(\boldsymbol{r_j})/r_j\ \exp(-L_j/2\ \lambda_i\ (E_f))\ W_j\ f_j(\theta_j)\ \exp(ik_f r_j(1-\cos\theta_j))\ |^2 + \text{TDS}$

atomic scattering factor

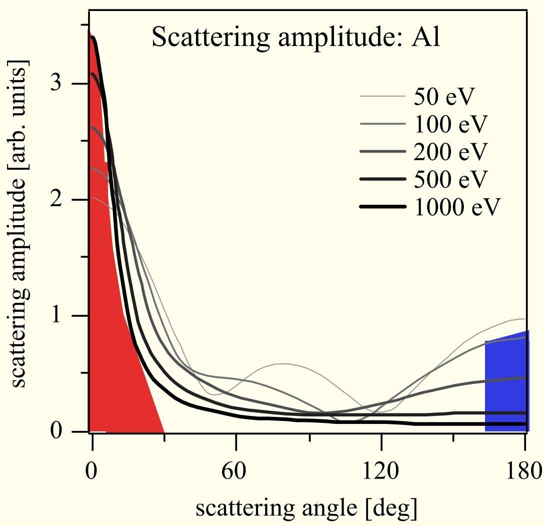
inelastic attenuation

geometrical and scattering phase shifts

temperature effects

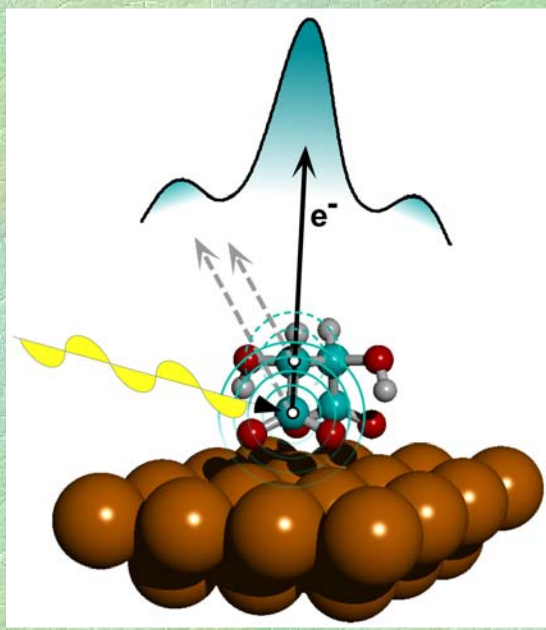
Forward Scattering in XPD

The atomic scattering factors have a characteristic dependence on the scattering angle θ_j.



High energies: forward scattering

Low energies: forward and backscattering

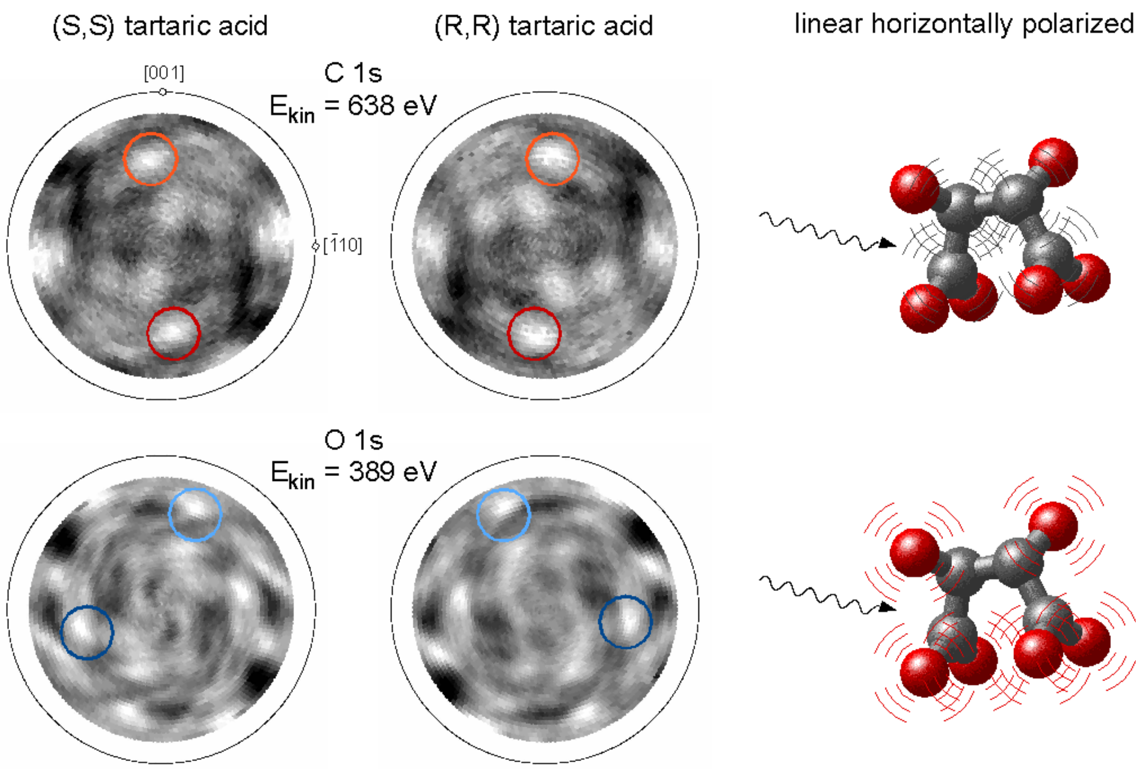


© R.Fasel
EMPA Dübendorf

Example: Adsorption geometry of tartaric acid (chiral molecule) on Cu(110)

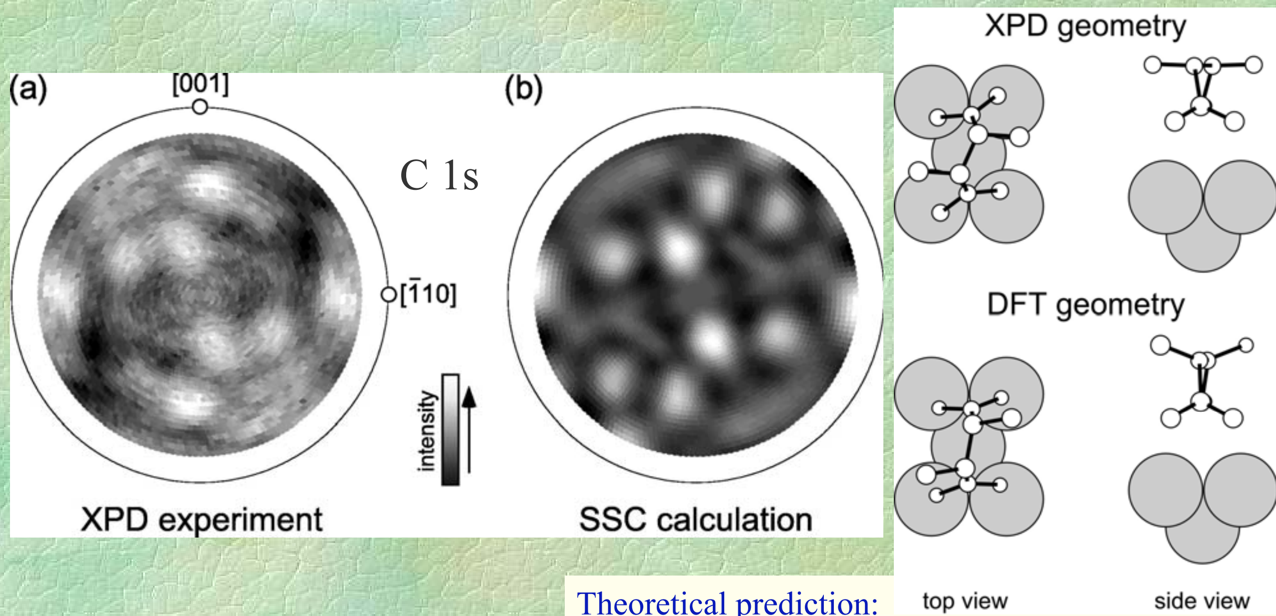
XPD Patterns for Two Enanthiomers

x-rays:
$\hbar\omega$ = 920 eV SIM / SLS
linear horizontally polarized



R. Fasel, K.-H. Ernst, J. Wider, Ch. Quitmann, T. Greber, Angew. Chem. (2004)

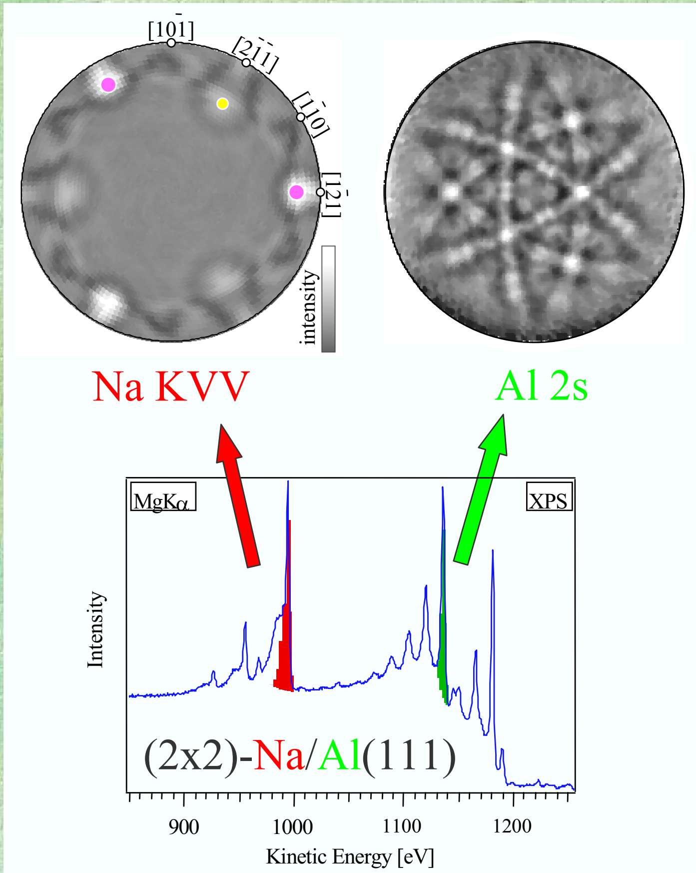
Refinement of Adsorption Geometry by Comparison with Single-Scattering Cluster Calculations



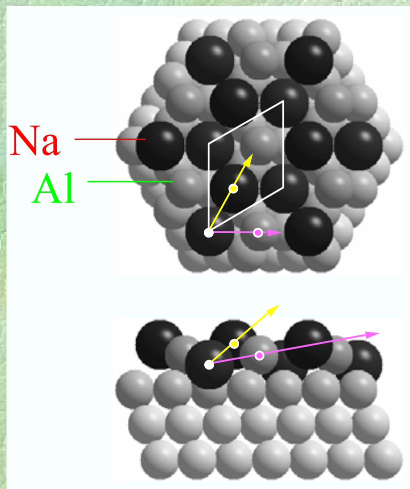
Theoretical prediction:
L.A.M.M. Barbosa, P. Sautet
J. Am. Chem. Soc. 123 (2001) 6639

R. Fasel, K.-H. Ernst, J. Wider, Ch. Quitmann, T. Greber, Angew. Chem. (2004)

Characteristic Substrate and Adsorbate Patterns



⇒ Structure determination by forward scattering peaks



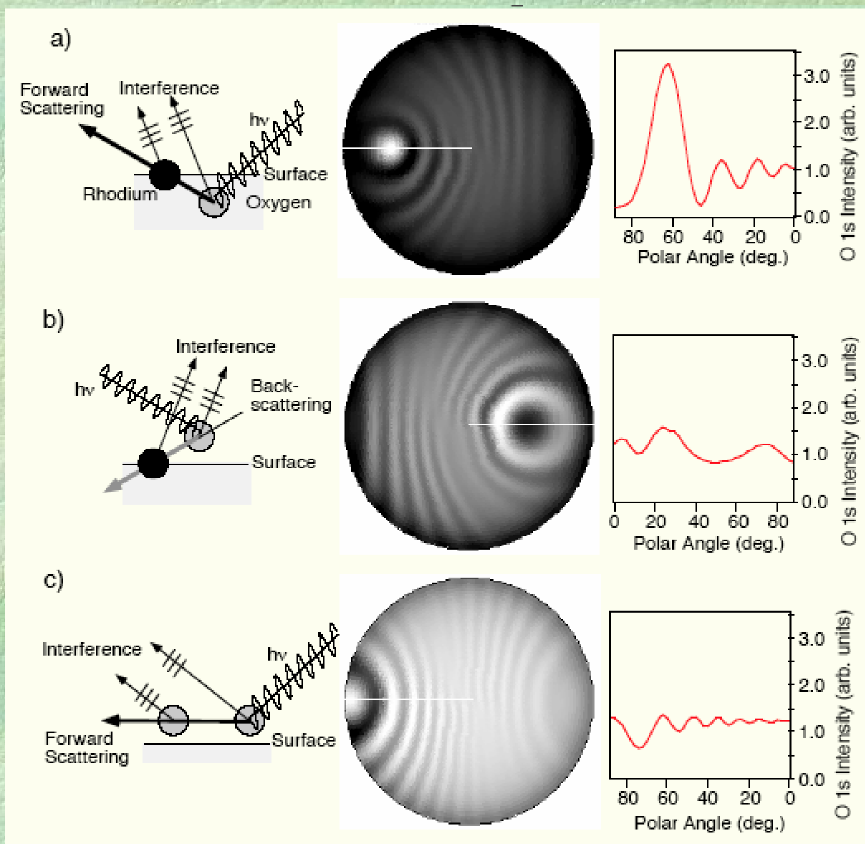
Courtesy R. Fasel

Interpretation of XPD 2π diffraction patterns

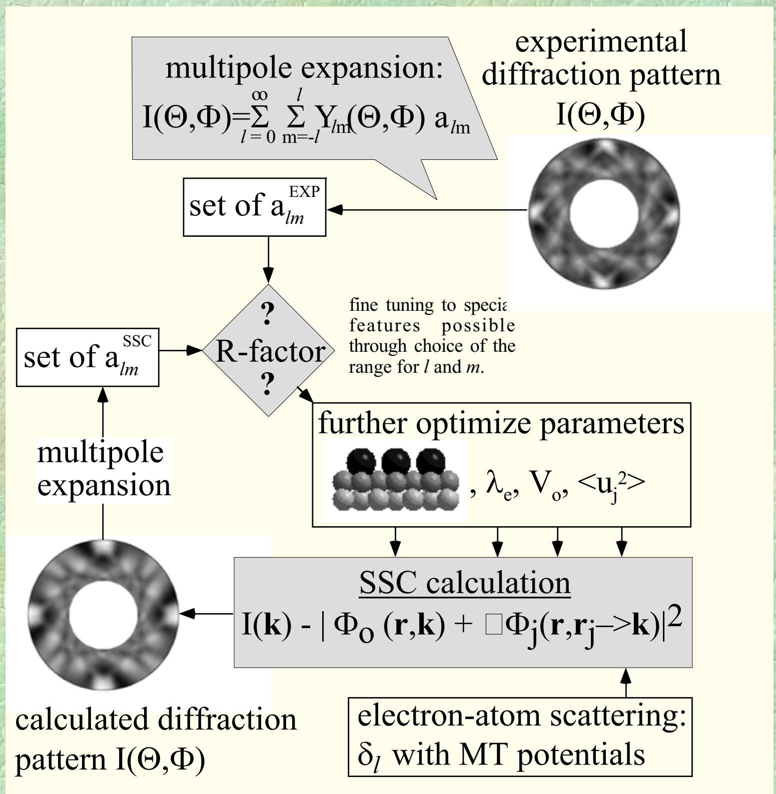
Adsorbate below top layer

Adsorbate in top layer

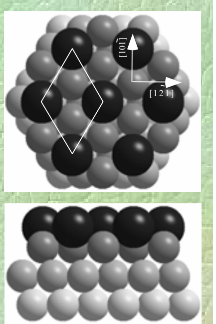
Adsorbate-adsorbate in-plane scattering

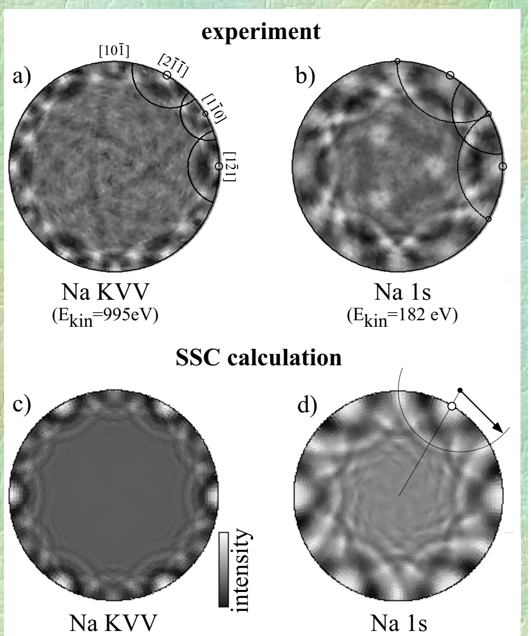


SSC calculations and *R*-factor analysis



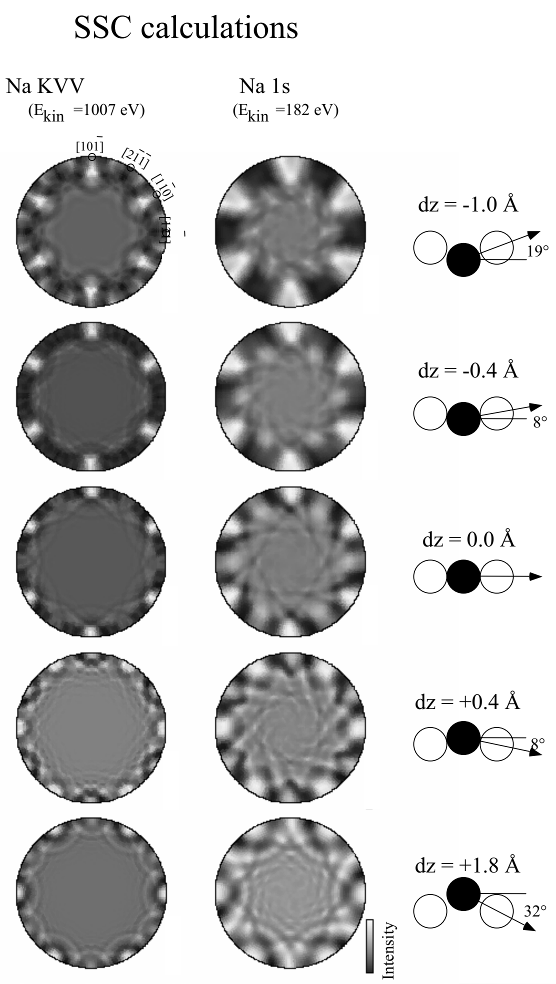
Example:
$(\sqrt{3}x\sqrt{3})R30°$-Na/Al(111)



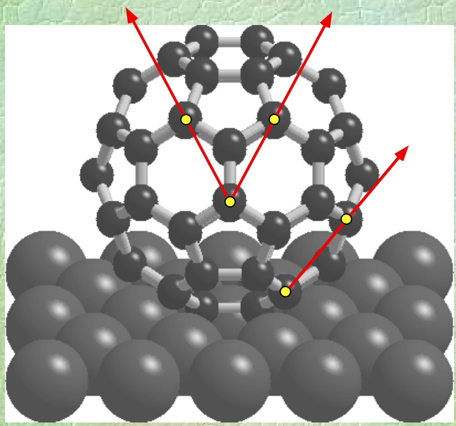


high energy low energy

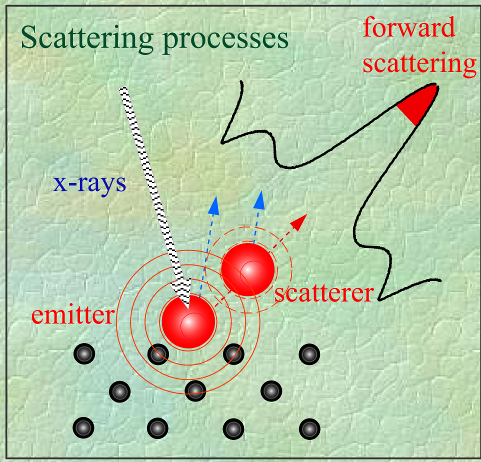
R. Fasel et al.,
Surf. Sci. 331-333 (1995) 80



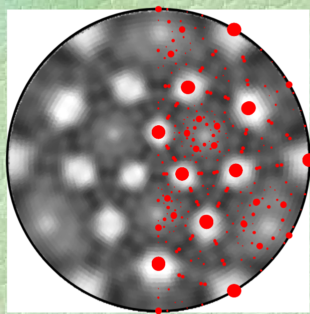
XPD pattern: Fingerprint of molecular orientation



C_{60} scattering situation

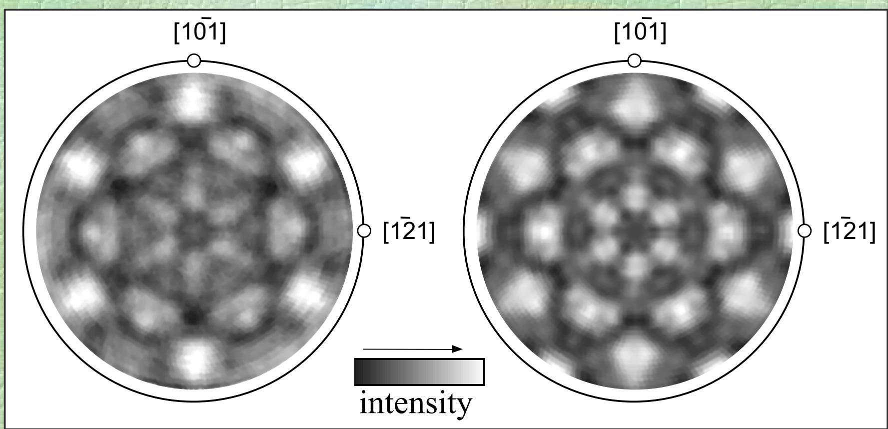


Single scattering cluster
(SSC) calculation
for C_{60} on 6-ring



Projections of
interatomic
(C-C)
directions

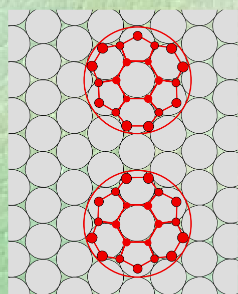
XPD from C_{60} / Cu(111)



XPD Experiment

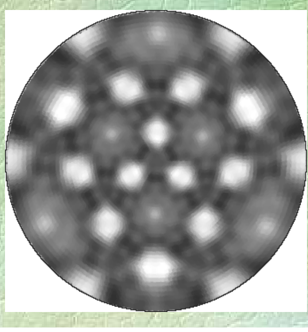
SSC Calc. 6-ring

LEED: (4x4)



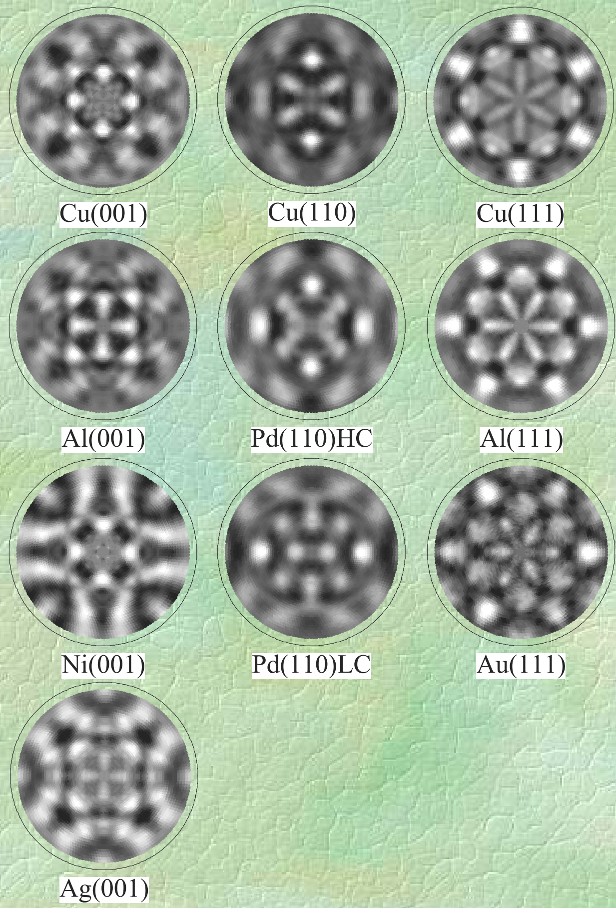
6-ring (2 domains)

Single
orientation:



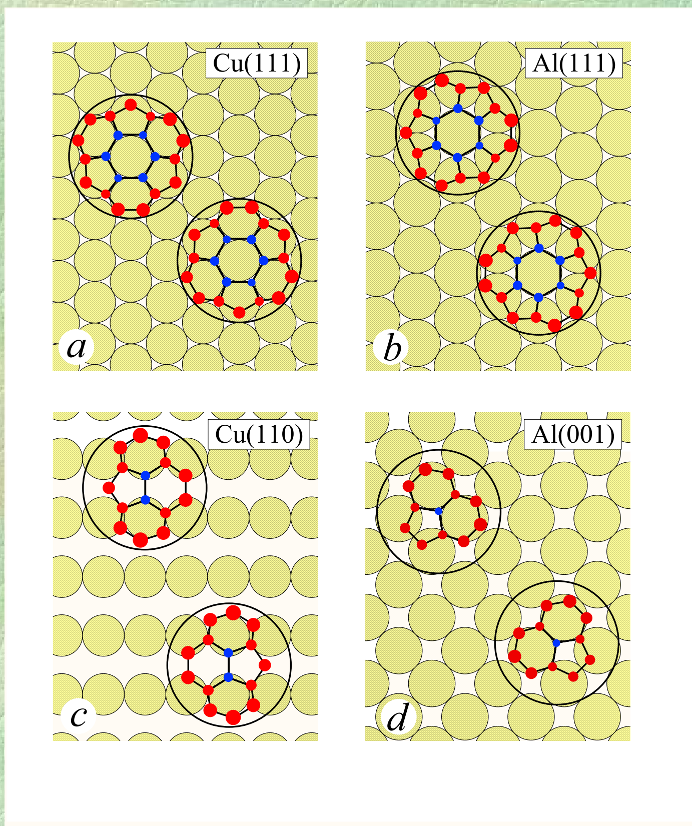
R. Fasel et al., PRL **76**, 4733 (1996)

… one finds a variety of patterns for C_{60} monolayers adsorbed on different substrates !



⇒one can determine the orientation(s) of the molecules by cumbersome trial and error methods

… Here Are Some Examples

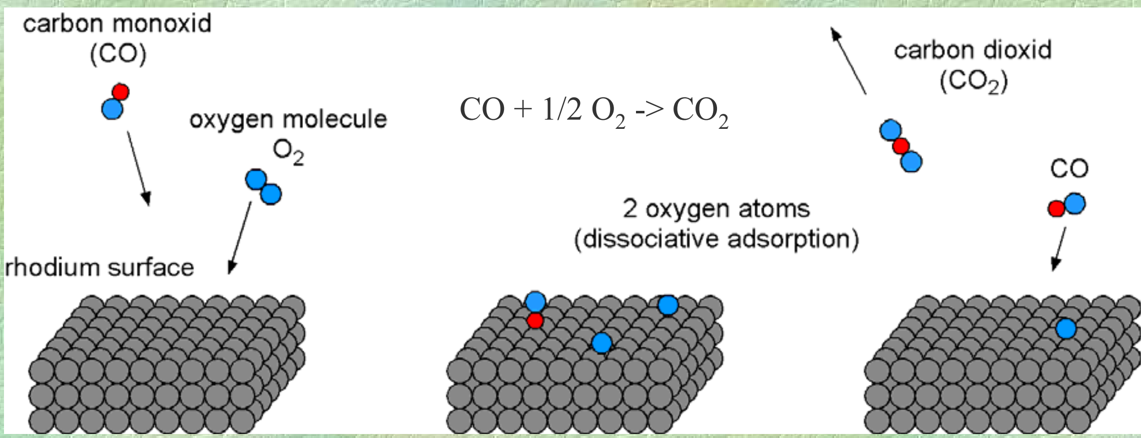


Usually there are several symmetry-equivalent orientation (depending on the symmetry of the substrate

In some cases, there are 2 or more non-equivalent orientation which makes the analysis very hard !

Application of XPD to Catalysis Research

Example for heterogeneous catalysis:
Catalytic combustion of CO

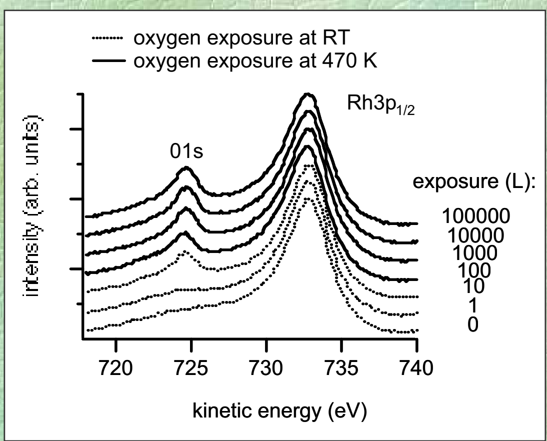


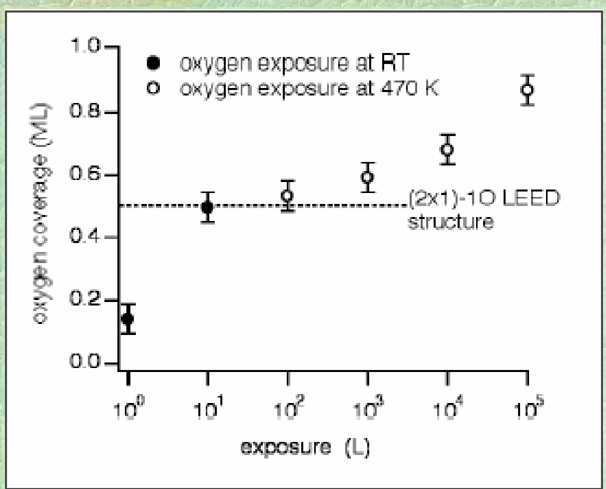
Reaction does not take place in the gas phase:
dissociation of O_2 costs too much energy (a few eV!).

… it is important where the adsorbed O sits !

Backscattering XPD from (2x1)-1 Oxygen on Rh(111)

Coverage (XPS) vs. Exposure:

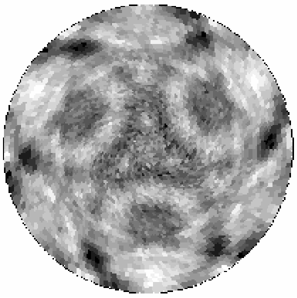




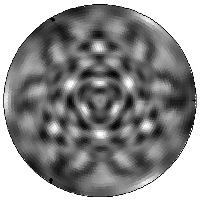
- (2x1)-1 adsorption site
- subsurface oxygen

The (2x1)-1 Oxygen Adsorption Site

Experiment

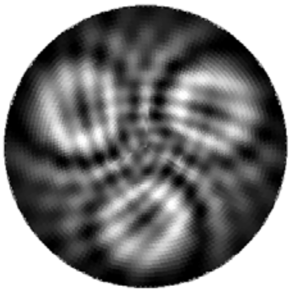


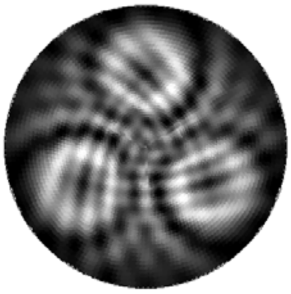
O 1s (723 eV)



Rh 3d emission
(E_{kin} = 947 eV)

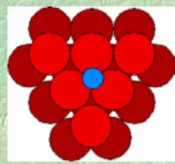
SSC calculations





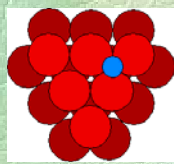
Cluster
(top view)

fcc site



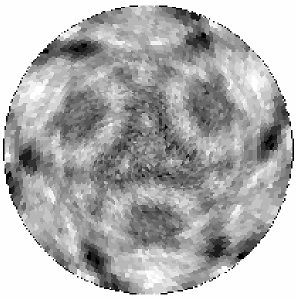
Oxygen
Rhodium

hcp site

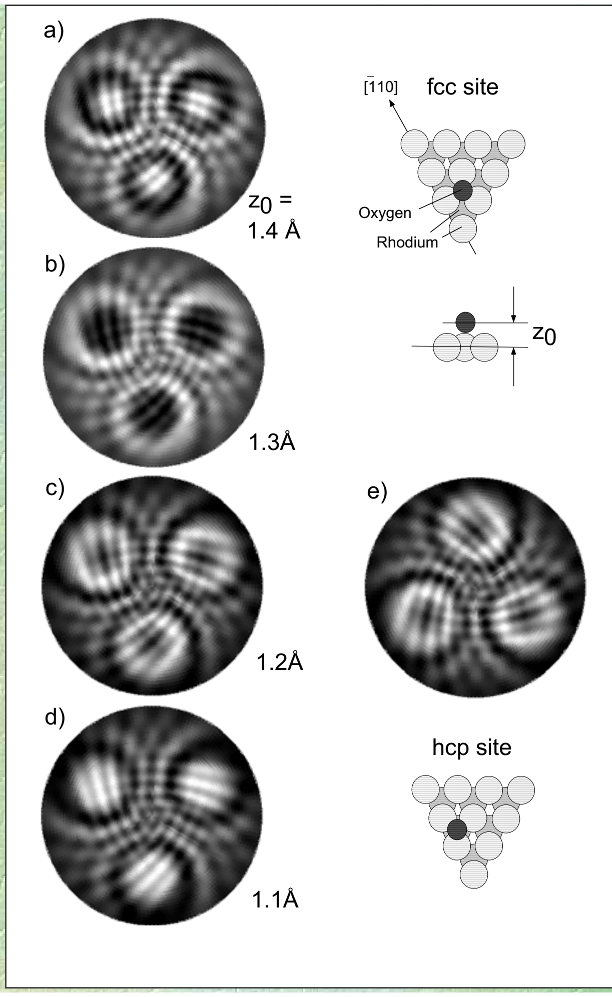


… and the Bond Length

Experiment



O 1s (723 eV)

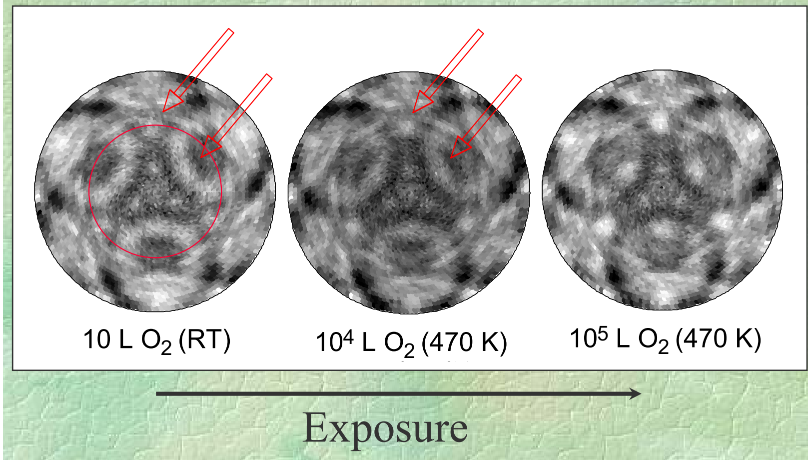


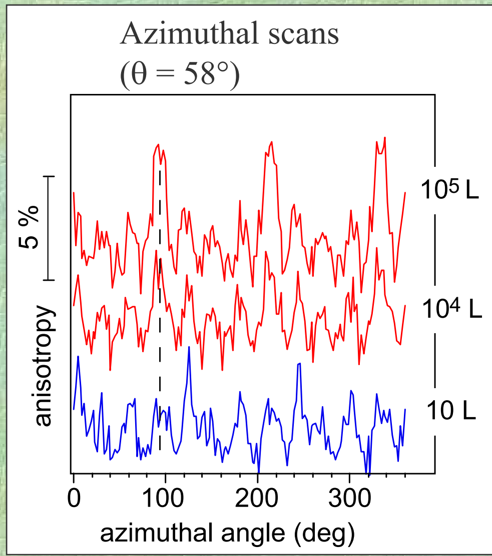
=> A Sensitive
Electron Interferometer !

T. Greber et al., PRL 81 (1998) 1654

Uncovering the Subsurface Oxygen in Rh(111)

O 1s emission
(E_{kin} = 723 eV)

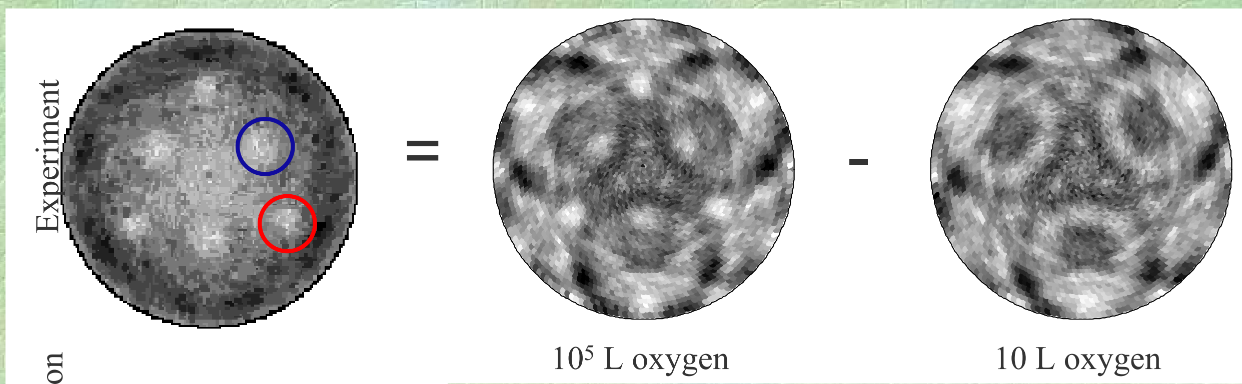


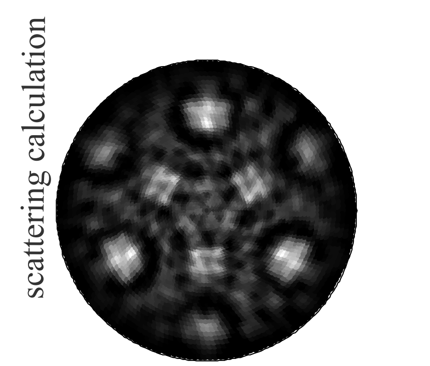


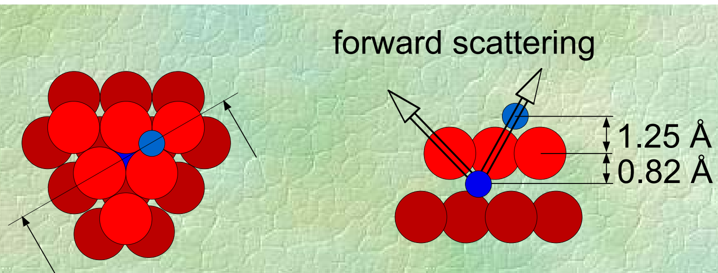
⇒ Forward scattering peaks appear

⇒ Subsurface oxygen (ca 5% ML) !

Determination of the Subsurface Site



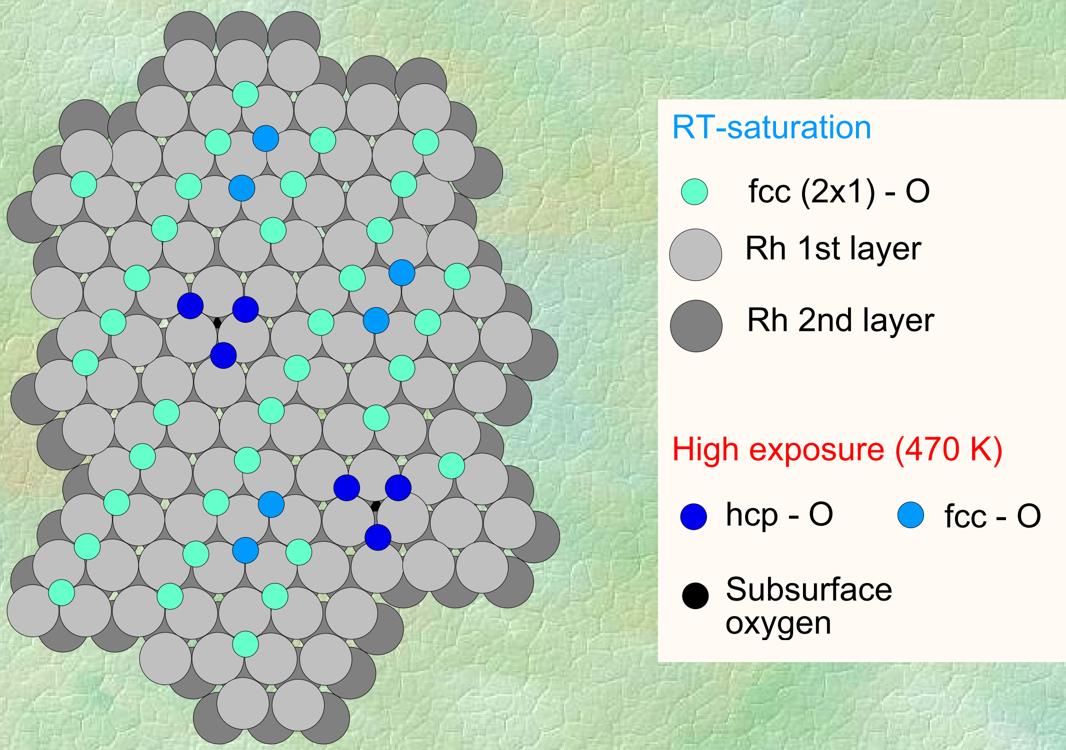




=> Adsorption site switches to hcp !

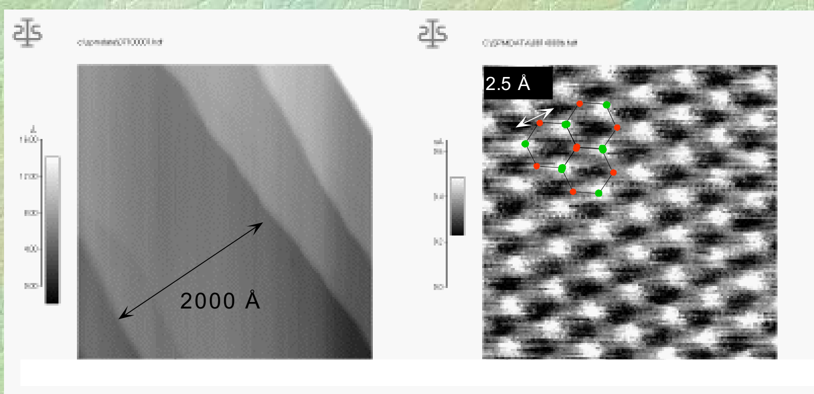
J. Wider et al., Surf. Sci. 417 (1998) 301

The Oxygen - Rh(111) System - Summary



The Powerful Combiniation of XPD and STM: Hexagonal Boron-Nitride Monolayers on Ni(111)

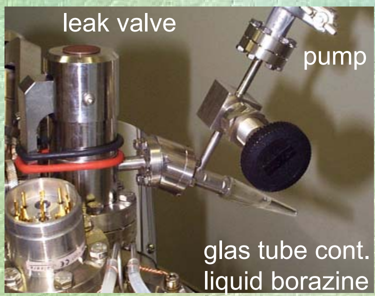
… forms large and perfectly flat terraces !

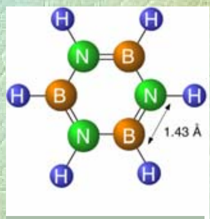


(1x1) translational symmetry
(from LEED and STM)

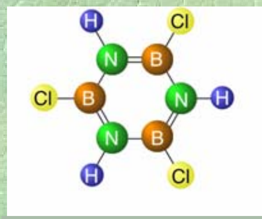
W. Auwärter et al., Surf. Sci. 429, 229 (1999)

Growth of a *h*-BN monolayer on Ni(111)

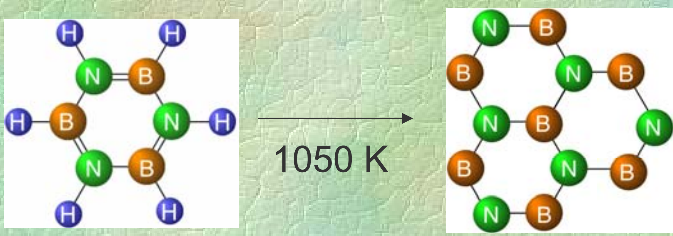




borazine
$(BN)_3H_6$

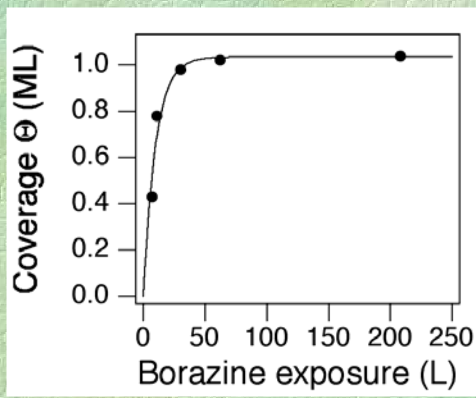


trichloroborazine
$(BCl)_3(NH)_3$

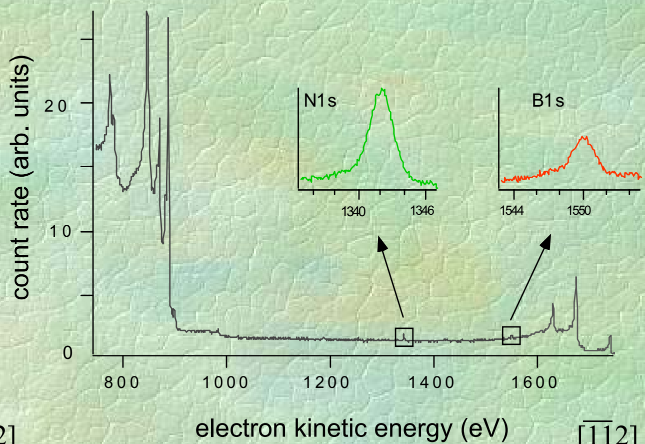


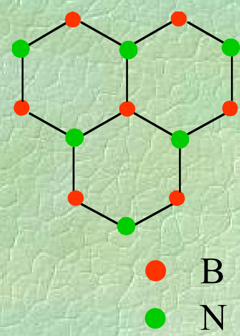
Borazine+Ni(111) *h*-BN on Ni(111)+$3H_2$

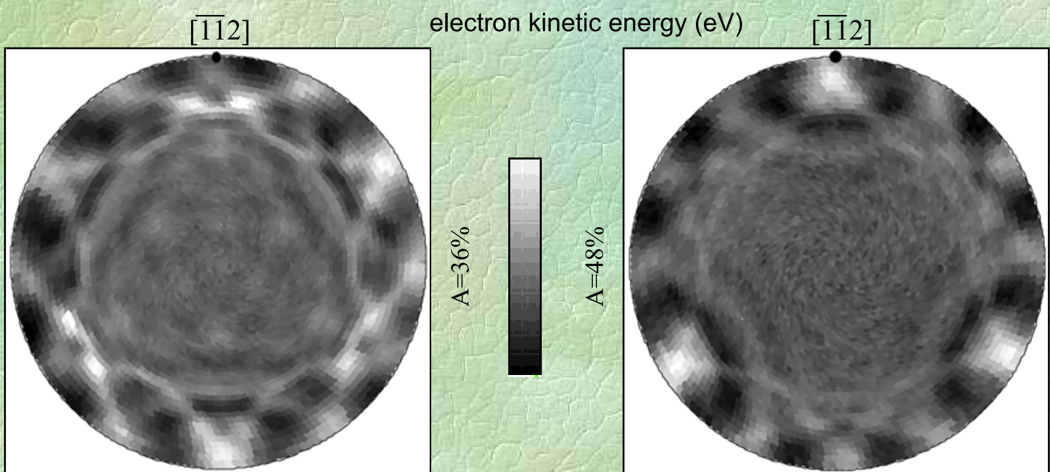
Nagashima et al., PRB 51, 4606 (1995)



Photoelectron Diffraction Experiments:



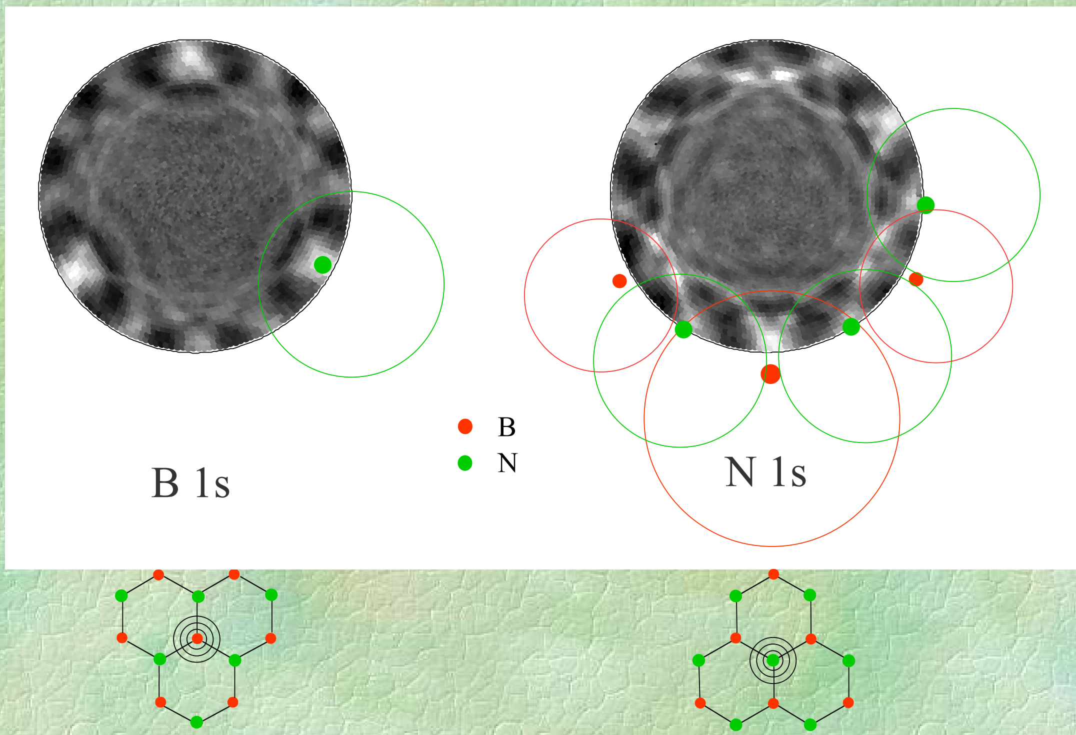




N 1s
(1342 eV)

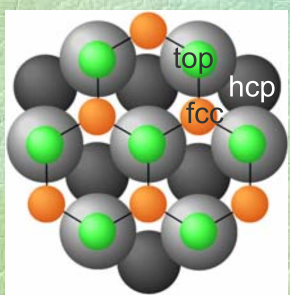
B 1s
(1550 eV)

Forward scattering and interference fringes in B1s and N 1s emission



=> Intuitive structural assignments !

Summary of structural parameters:

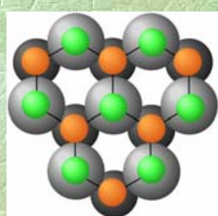


(N,B)=(top,fcc)

	Gamou (LEED)	this work (XPD)	Grad (DFT)
registry (N,B)	(top,fcc)	(top,fcc)	(top,fcc)
corrugat	0.18 Å	0.07 Å	0.11 Å
d N -Ni	2.22 Å	1.95 Å	2.19 Å
d Ni-Ni,1	1.98 Å	2.03 Å	2.03 Å

G. Grad *et al.*, submitted
Gamou *et al.*,Sci. Rep.RITU A 44, 221 (1997)

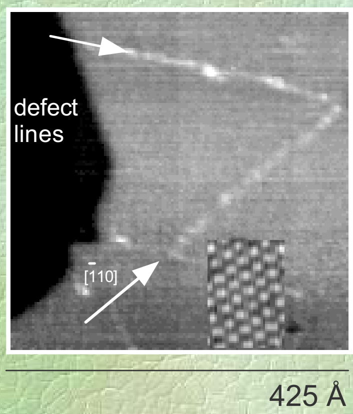
The structure is well understood ! … but:



2nd stable DFT structure
+ 18 meV

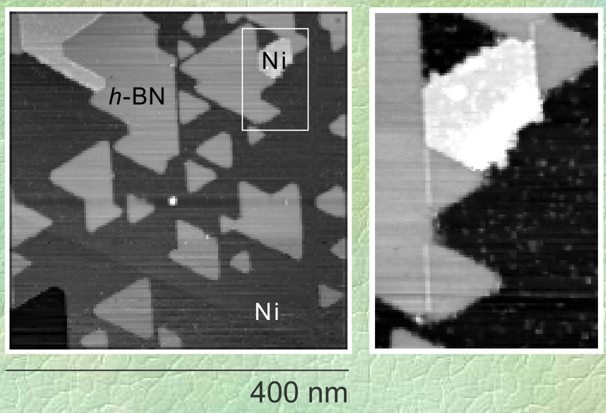
(N,B)=(top,hcp)

Defects and two-domain monolayers



Defect lines in 1 ML *h*-BN
(cf. Co deposits)

Where do they come from ?

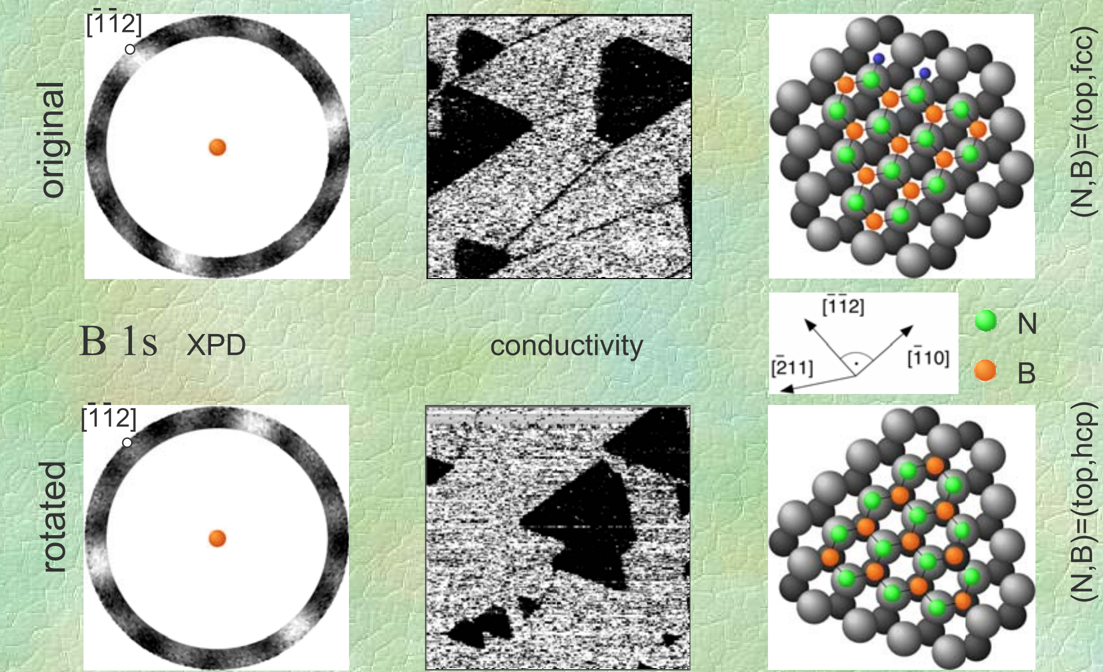


h-BN partial coverage:

⇒ Triangular islands of two orientations coexist on the surface.

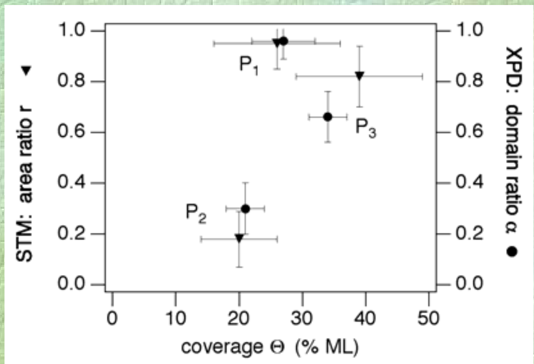
⇒ Defect lines appear where they touch

Different preparation can lead to predominantly one or the other domain!



⇒XPD reveals the occurrence of the secondmost stable geometry from the DFT study (ΔE=18meV)!

Quantitative comparison of XPD and STM Data



Compare areas of differently oriented islands

Determine domain ratios from B 1s forward scattering peaks

⇒ Island shape and bonding geometry correspond !

⇒ We know the atomic structure of the defect lines:

W. Auwärter et al.,
Surf. Sci. Lett. 545 (2003) L735