Determinação Estrutural de Superfícies via Difração de Fotoelétrons

Abner de Siervo
Instituto de Física - Unicamp

http://www.ifi.unicamp.br/gfs

Tópicos

- Introdução e Motivação
- Aspectos Experimentais e teóricos de Difração de Fotoelétrons (PED)
- Exemplos para Determinação Estrutural usando PED
- Perspectivas para PED e PH no LNLS

1 - Introdução

Porque Estudar Superfícies ?

A superfície é uma interface entre dois meios, muito comum na natureza:

• Solido-gás ; sólido-líqüido; sólido-sólido; **sólido-vácuo**; líqüido-gás.

• Grande relevância na Indústria: catálise, armazenamento de dados, microeletrônica, fotônica, tribologia, adesão, embalagens, proteção (corrosão/oxidação), biônica, ligas-2D, etc.

1.1 - Quais são as informações importantes ?

Conhecer a estrutura eletrônica e arranjo geométrico dos átomos presentes na superfície pode ser a chave para se compreender melhor as propriedades físico-químicas de um material

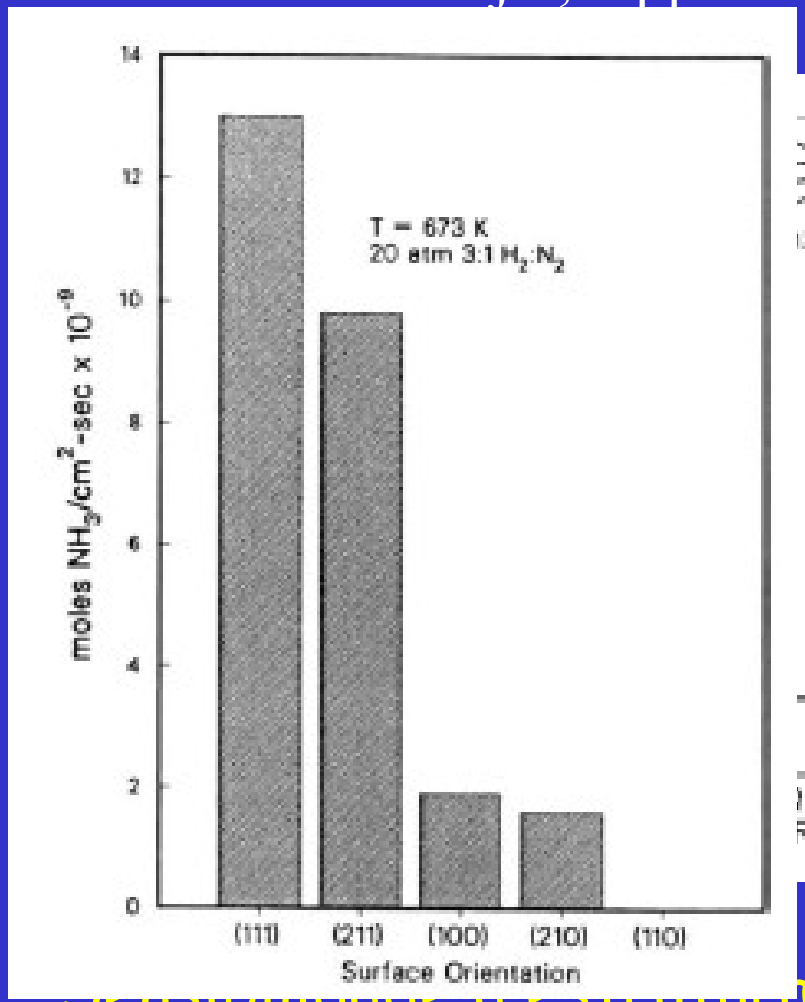
Sempre estamos interessados em saber:

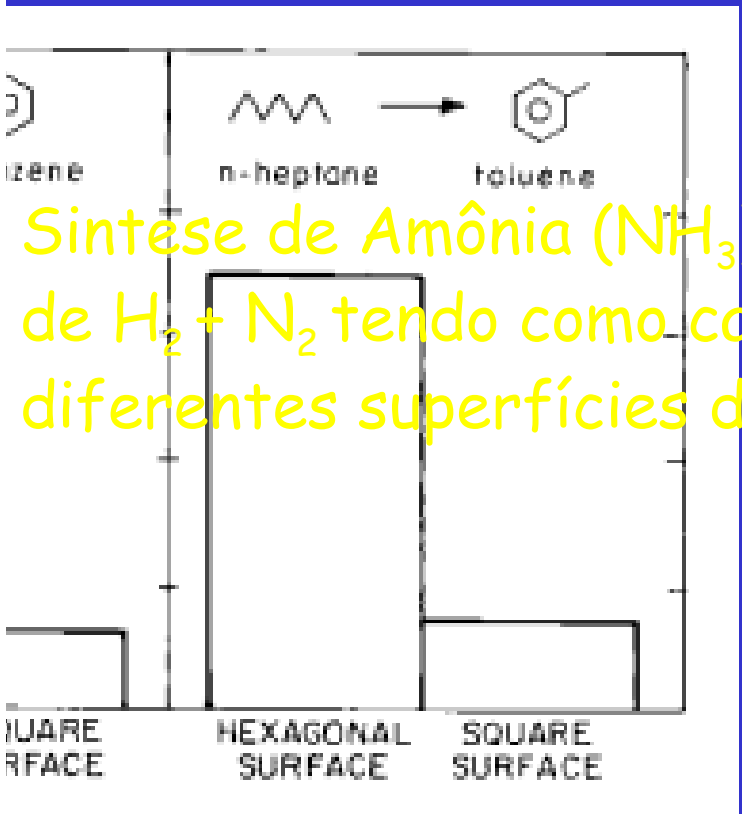
- identidade química, concentração, posições dos átomos, tipo de ligação, densidade de estados, energia total do sistema, etc.

Geometria da superfície aplicada à catálise

D.R. Strongin et al. J. Catal. 103, 213 (1987)

G.A. Samorjai, Appl. Catal. A 222, 3 (2001)

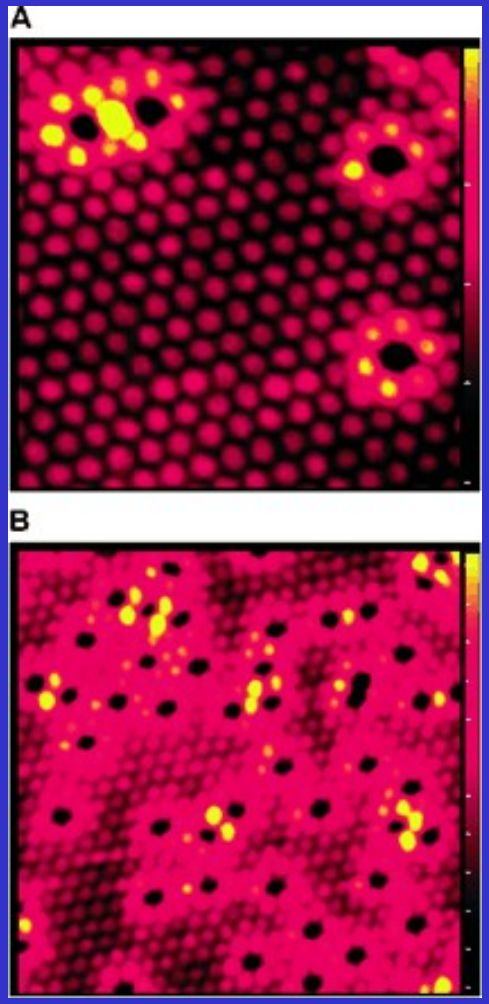




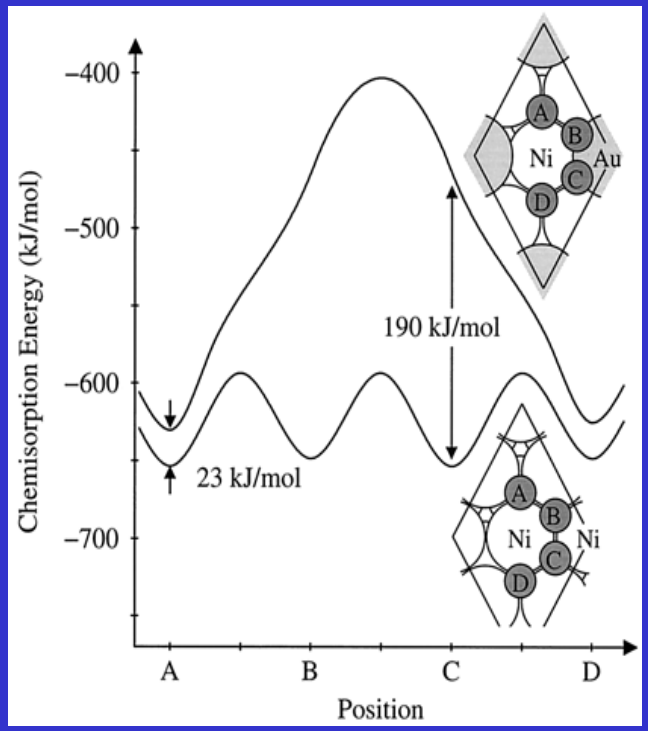
Síntese de Amônia (NH_3) a partir de H_2 + N_2 tendo como catalisador diferentes superfícies de Fe

Sensibilidade à estrutura na hidrogenação e desidrogenação de alquenos para hidrocarbonetos aromáticos

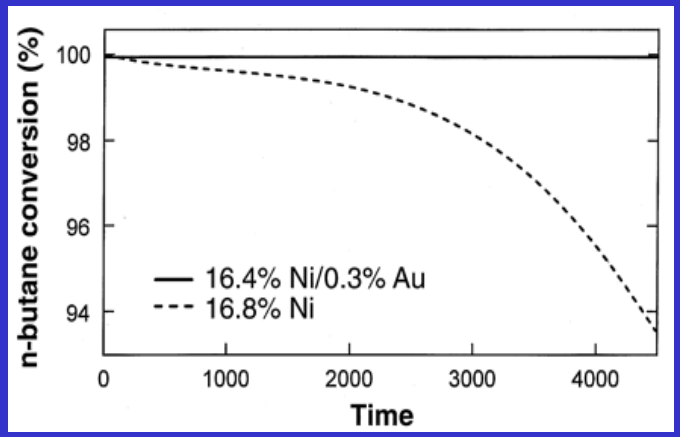
2D Alloy : Au on Ni(111) for n-butane conversion



A) 0.02 ML of Au
B) 0.07 ML of Au

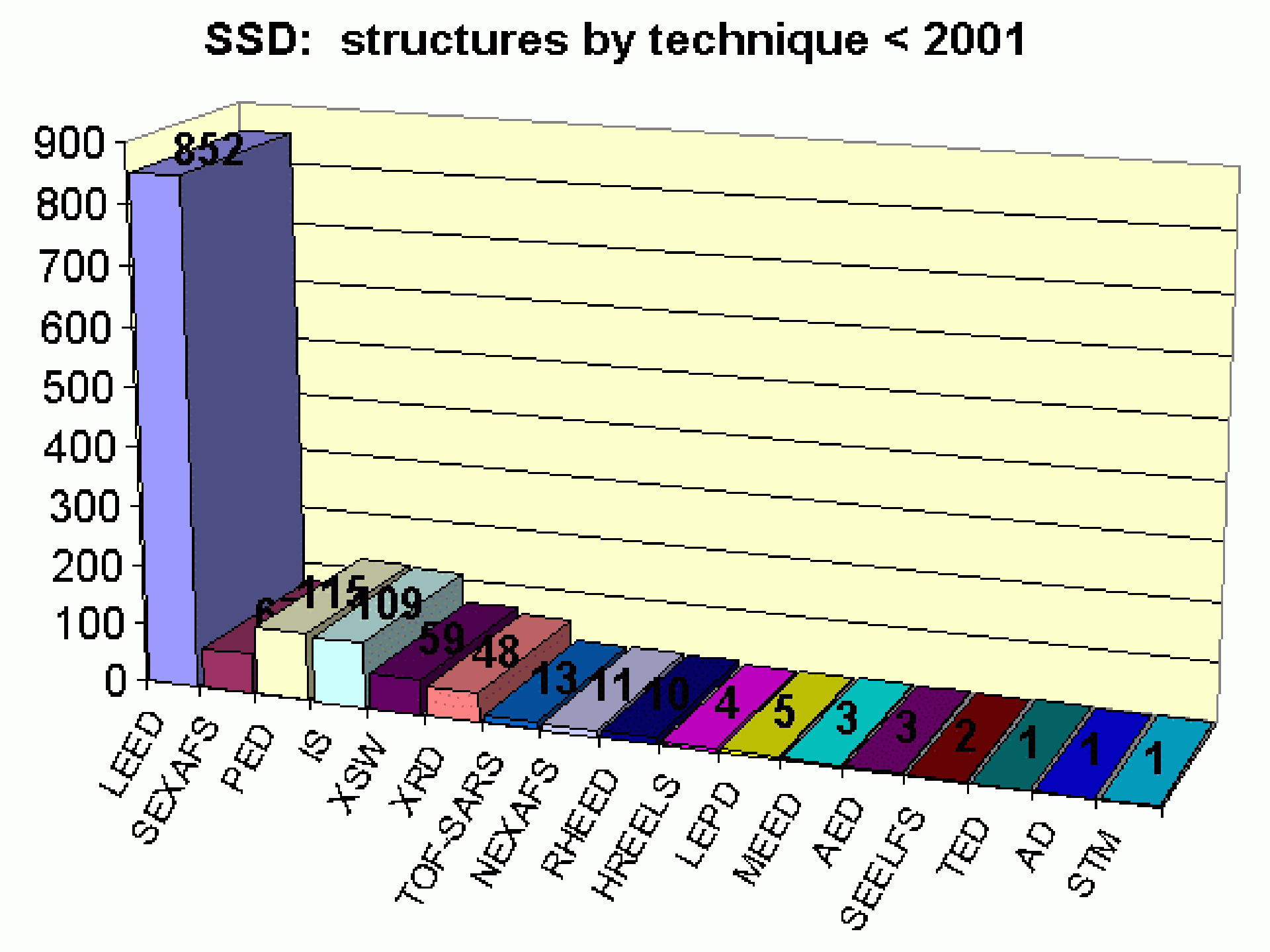


DFT calculated adsorption energy for C atoms on Ni(111) in two cases : clean Ni(111) and substitute some Ni for Au.



n-butane conversion by Ni and Au/Ni-supported catalyst

Besenbacher et al. Science, 279 (1998)


SSD: structures by technique < 2001
900
800
700
600
500
400
300
200
100
0
852
6
115
109
59
48
13
11
10
4
5
3
3
2
1
1
1
LEED
SEXAFS
PED
IS
XSW
XRD
TOF-SARS
NEXAFS
RHEED
HREELS
LEPD
MEED
AED
SEELFS
TED
AD
STM

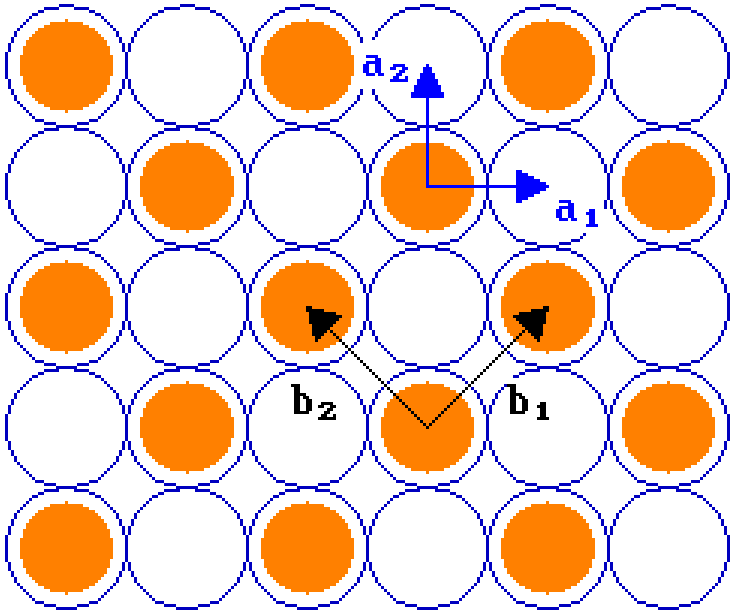
Técnicas Experimentais e Teóricas

	PED e PED Holography	STM	LEED
Tipo de ordem	Curto (< 10Å)	curto, longo e desordenado	Longo (>100Å)
Elemento/ Química	Sim	Comulmente Não	Não diretamente
Profundidade	5-40 Å	Majorit. DOS 1 camada	5-20 Å
Resolução Lateral	(300Å) - 1mm^2	Único átomo	1μm^2 - 1mm^2

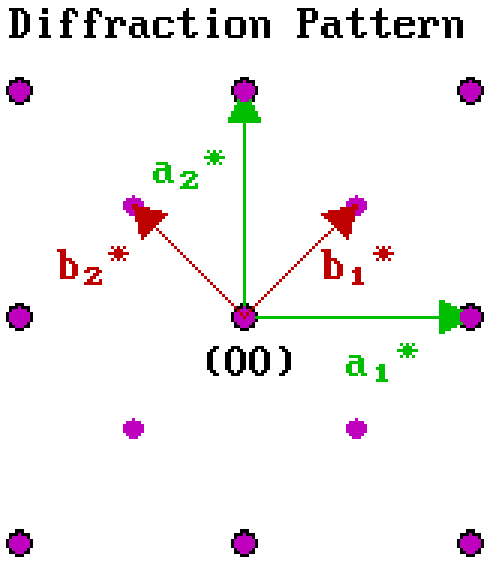
- RHEED → dinâmica de crescimento
- DFT, Monte Carlo, Dinâmica Molecular ...

Definições e Nomenclatura para superfícies ordenadas

Espaço Real



Espaço Recíproco



$$\begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

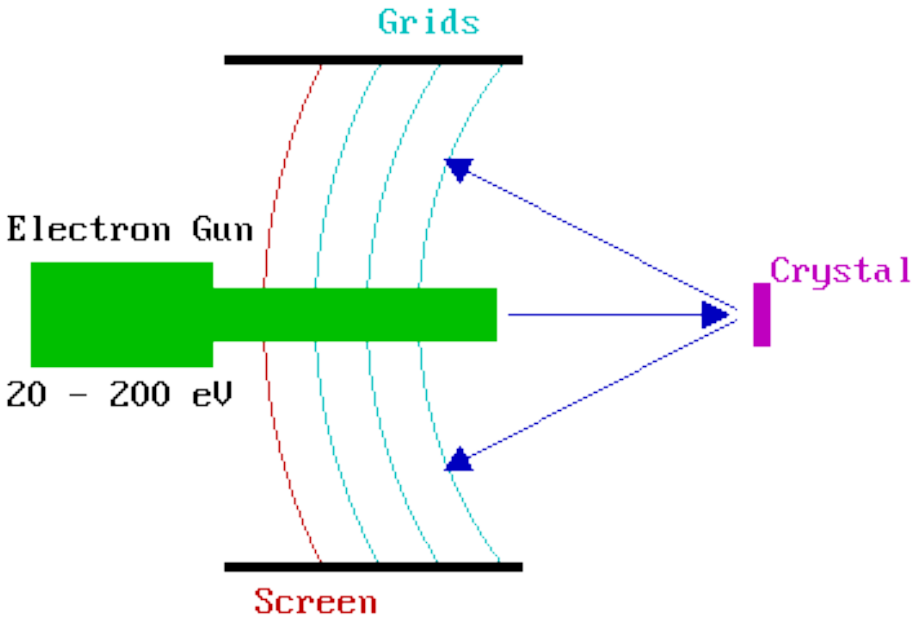
$$\vec{R} = n\vec{a}_1 + m\vec{a}_2$$

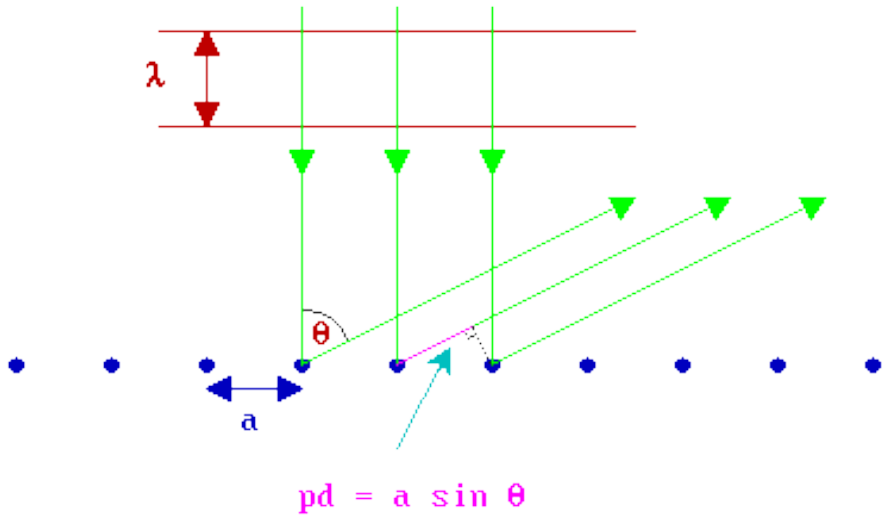
$$R' = n'b_1 + m'b_2$$

$$\vec{a}_1^{\,*} = 2\pi \frac{\vec{a}_2 \times \hat{n}}{\vec{a}_1 \cdot (\vec{a}_2 \times \hat{n})};$$

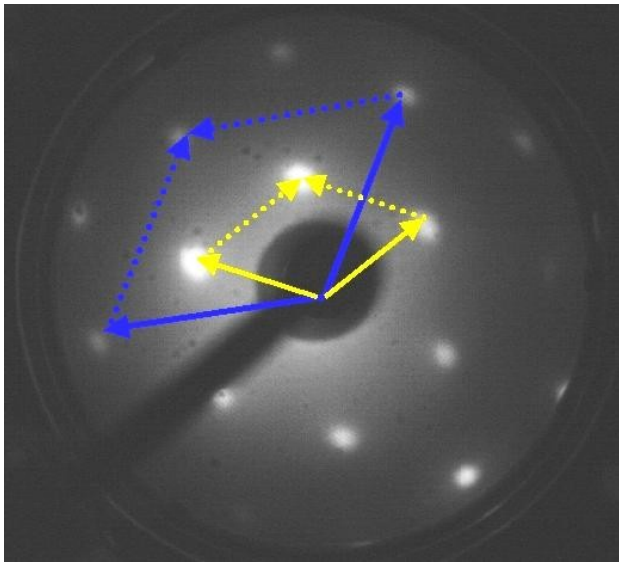
$$\vec{a}_2^{\,*} = 2\pi \frac{\vec{a}_1 \times \hat{n}}{\vec{a}_2 \cdot (\vec{a}_1 \times \hat{n})}$$

Determinação qualitativa da geometria da superfície por LEED





Espaço Recíproco

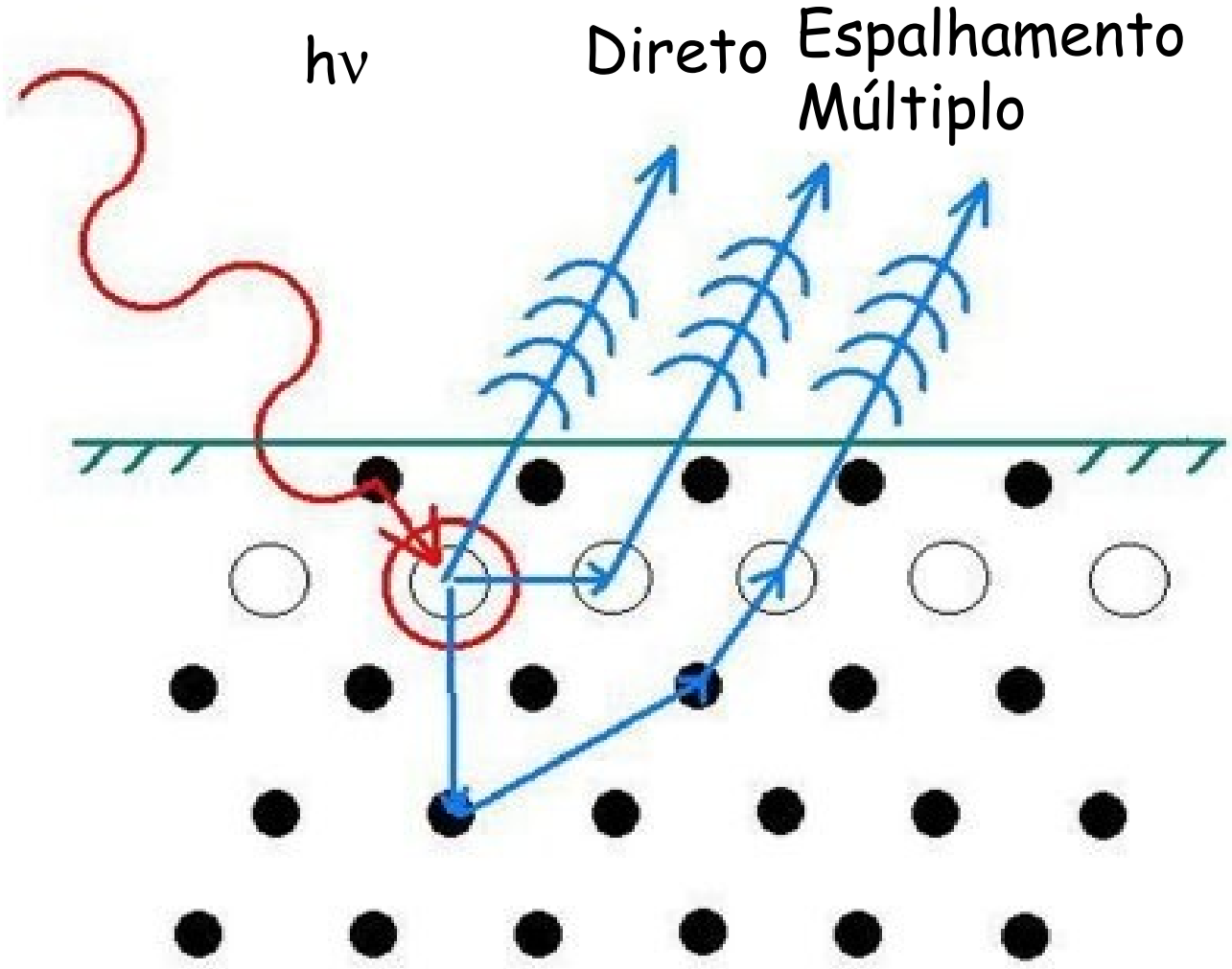


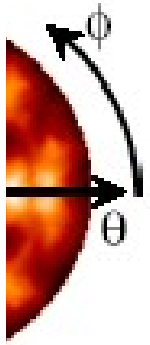
$$Pd(111)+\left(\sqrt{3}\times\sqrt{3}\right)R30^{o}$$

?

Espaço Real

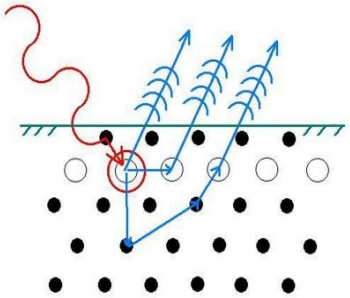
Photoelectron Diffraction (PED)





Espaço Real

Teoria Difração de Fotoelétrons



$$I(\vec{k},\theta,\phi) = \left|\phi_0 + \sum_j \phi_j\right|^2$$

Espalhamento de um pacote de onda:

$$H = \frac{p^2}{2m} + V = H_0 + V \rightarrow \Psi_k^{\rightarrow}(r) \sim \frac{1}{(2\pi)^{3/2}}\left(\frac{e^{ik.\vec{r}}}{r} + f_k(\hat{r})\frac{e^{ikr}}{r}\right)$$

Método das Funções de Green:

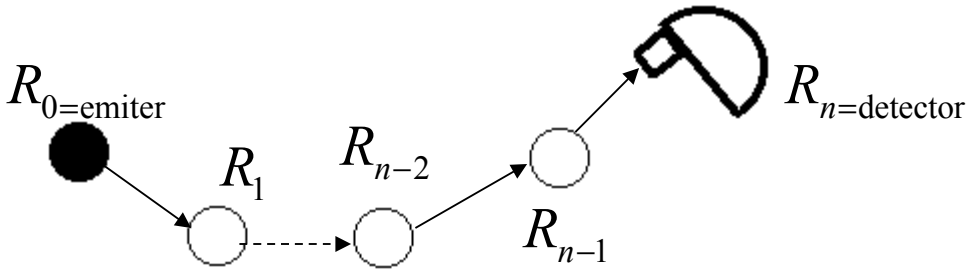
$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\Psi = E\Psi \rightarrow \left(\nabla^2 + k^2\right)\Psi = U\Psi$$

solução :

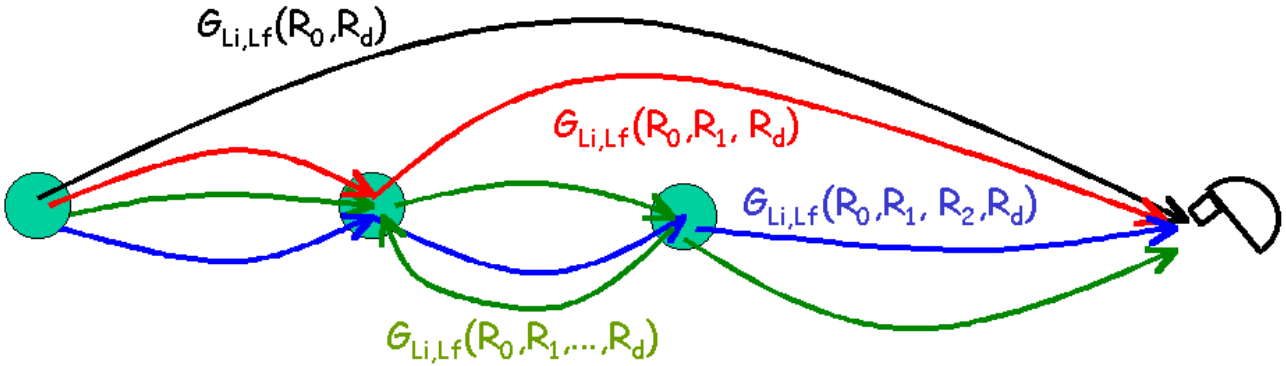
$$\Psi_k(\vec{r}) = \frac{1}{(2\pi)^{3/2}} e^{i\vec{k}.\vec{r}} - \frac{1}{4\pi}\int G(\vec{r},\vec{r}')U(r')\Psi(\vec{r}')d^3\vec{r}'$$

E.Marzbacher,"Quantum Mechanics", Cap.11

Espalhamento Múltiplo



- Diagonal PW scattering t- matrix : $t_l = \sin(\delta_l)\exp(i\delta_l)$
- **Matrizes radiais** : $m_{l_f,l_i} = \left\langle \Psi_{E_{Kin}}, l_f \middle| \varepsilon.r \middle| \Psi_{n_i}, l_i \right\rangle$
- Propagador de partícula livre: $G_{L,L'}(\rho) = \left\langle L,R \middle| G \middle| L,R' \right\rangle; \quad L=(l,m); \quad \rho = k(R-R')$



$$I_{n_i l_i}(k,\theta,\phi) = \sum_{\substack{\text{emissor}, \\ m_i}} \left| \sum_{l_f = l_i \pm 1} m_{l_f,l_i} \sum_n t_l G_{L,L_f}(\vec{\rho}_{ca\,\min ho}) \right|^2$$

Characteristics of Photoelectron Diffraction

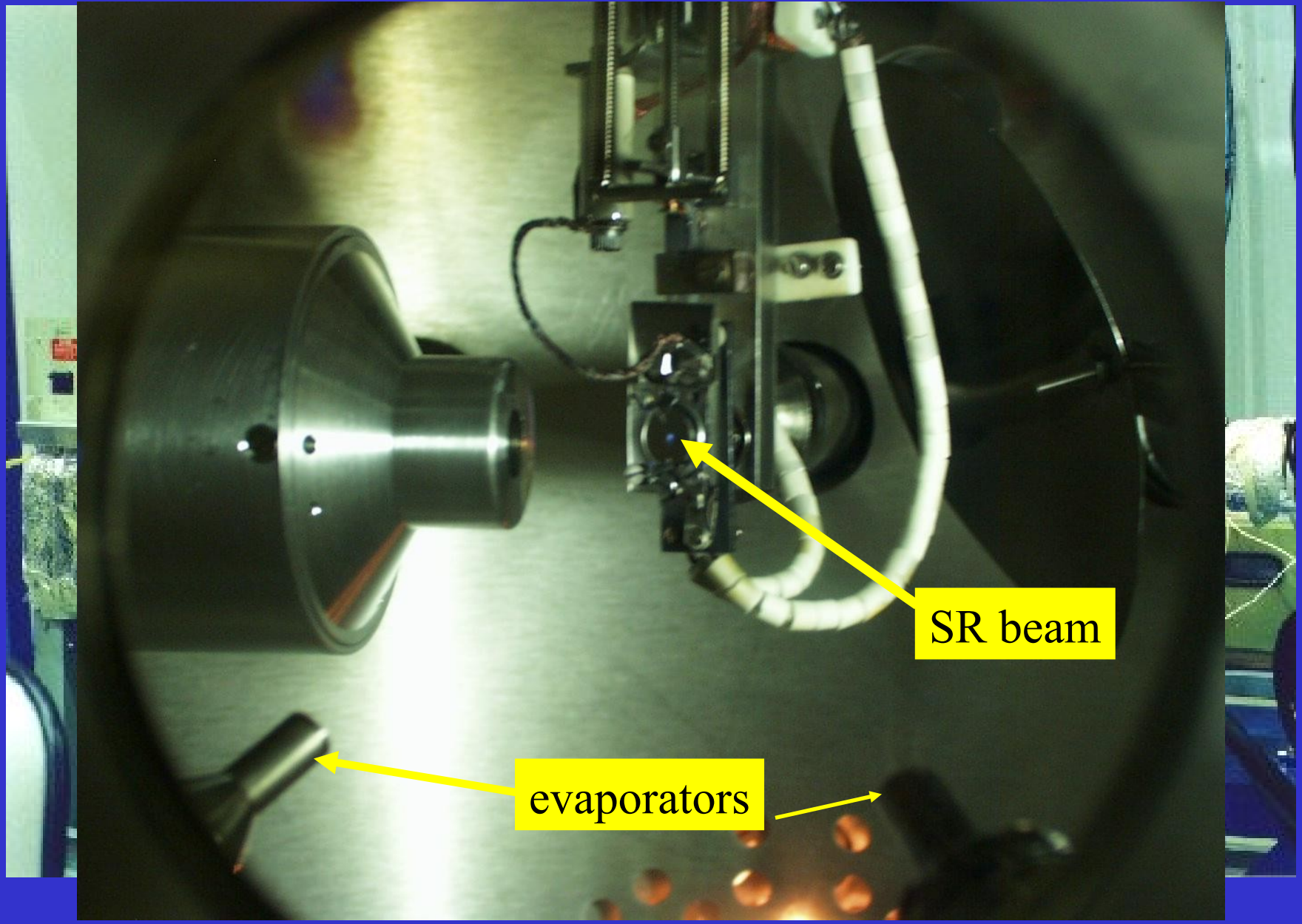
Advantages:

- Element Specific, Chemistry Specific
- Short range order probe (< 20 Å)
- Sub-surface Sensitivity
- Angular Momentum and Spin Dependence
- Selective excitation controlling photon energy and polarized light (Linear , Circular Dichroism)
- Direct Structure $\rightarrow$ 3 D atomic images from holographic analysis

Disadvantages:

- Expensive
- Most powerful with Synchrotron
- Slow : hours to days (conventional); minutes to hours (powerful SR)
- May be very depending of theoretical models (multiple scattering calculation)

Experimental Setup

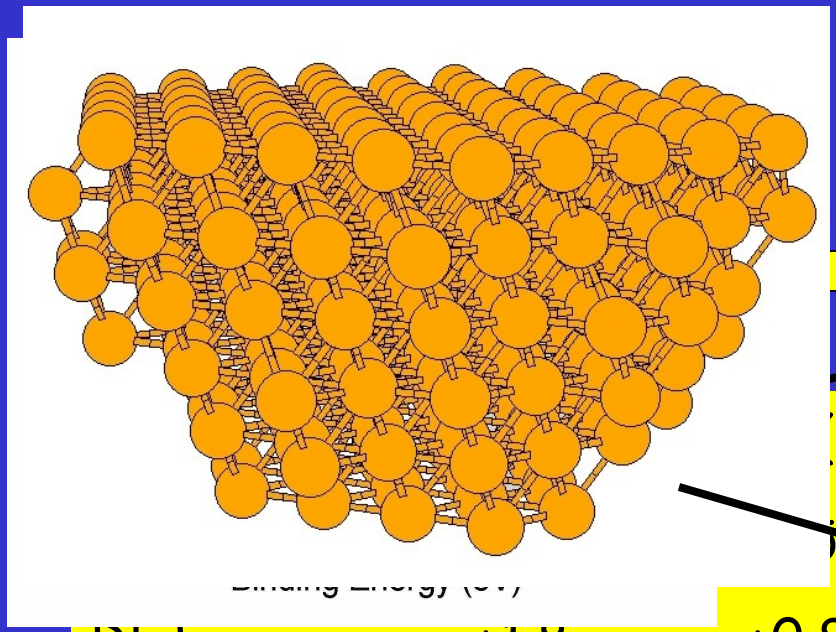


Some Examples of Surface Structure Determined by PD at LNLS

- Clean Metal Surface : Pd (111)
- Random Surface Alloys : Pd on Cu (111)
  and Cu on Pd(111)
- Ordered 2D Alloy : Pd(111) - Sb $\left(\sqrt{3}\times\sqrt{3}\right)R30^{\circ}$

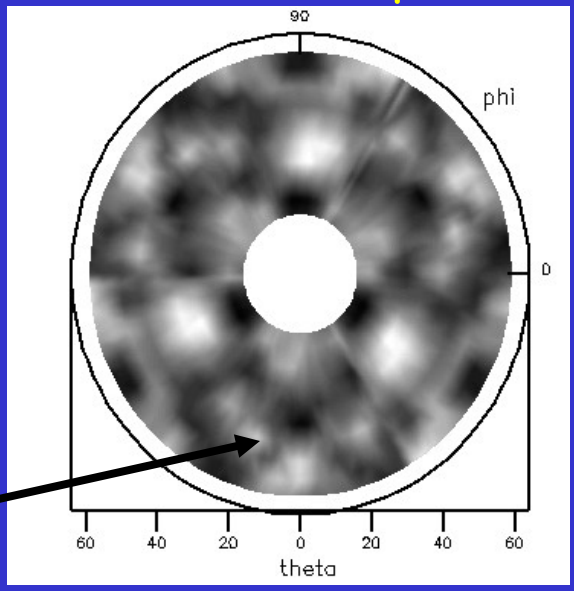
Clean Pd(111)

MSCD code (Y. Chen and M. Van Hove)
http://electron.lbl.gov/



~400 XPS

Pd 3d: PD experiment



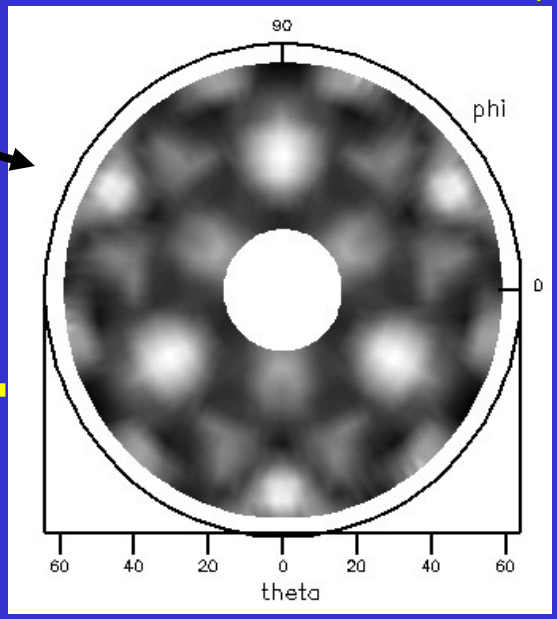
DFT	+1.8	+0.8
LEED[1]	+1.3	-1.3

[1] H. Ohtani *et al.*, Surf. Sci. **187**, 372 (1987)

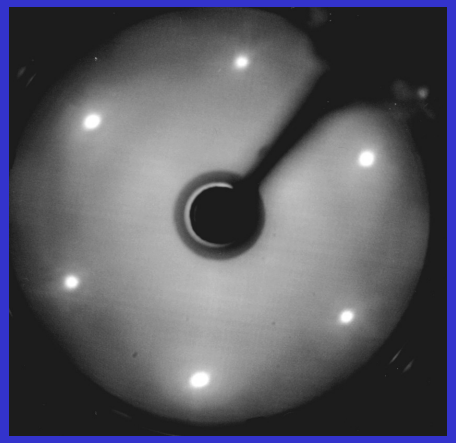
$$R_a = \sum_i \frac{\left(\chi_c^i - \chi_{ec}^i\right)^2}{\left(\chi_c^i\right)^2 + \left(\chi_{ec}^i\right)^2}$$

R_a=0.23

Pd 3d: MSCD Theory

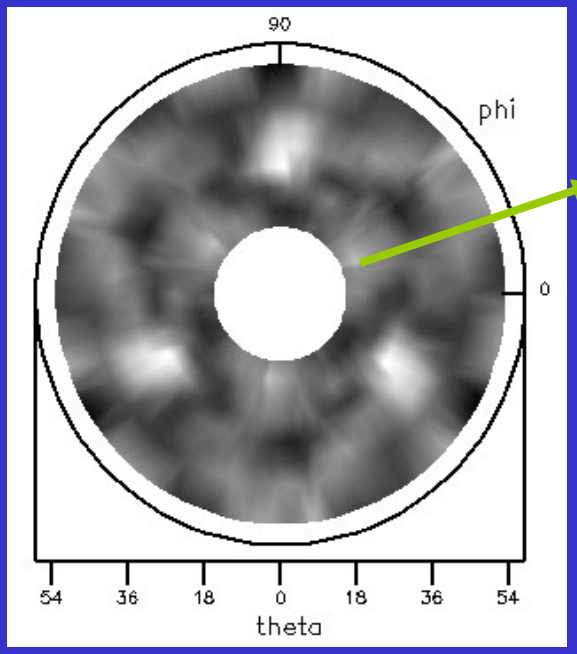


Random surface Alloy of Pd on Cu(111) after anneal.

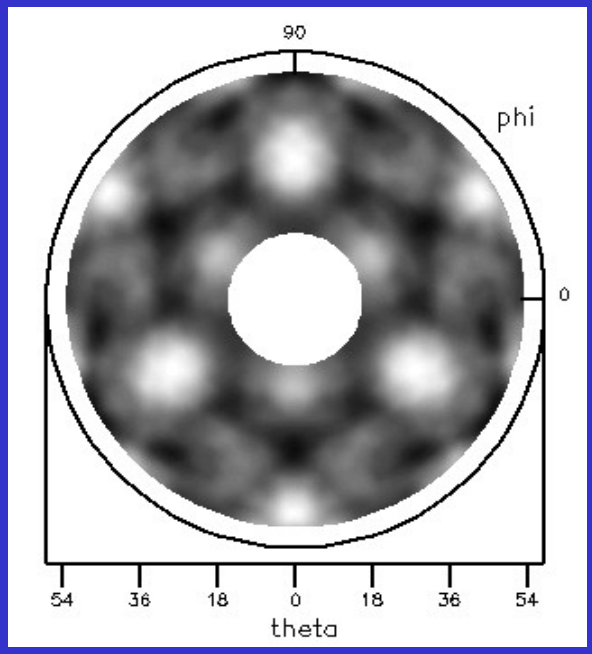


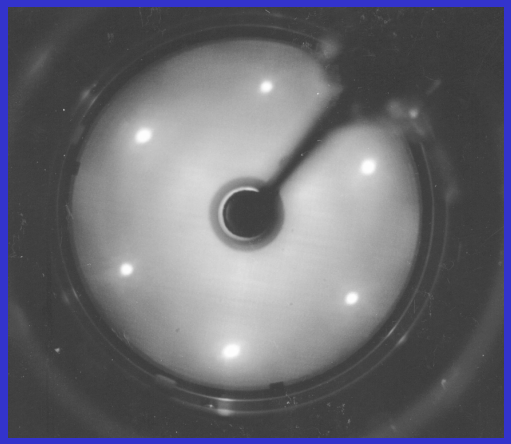
E_0=90 eV

(clean Cu(111))



θ 20°





E_0=90 eV

(PdCu alloy)

Pd 3d experimental PD Pd 3d MSCD Theory

- structure at θ 20° indicate Pd diffusion up to 3rd layer
- Best fit to : 20:70:20 % of Pd in the 1st, 2nd and 3rd layers respectively.
- 5% expansion of the first interlayer distance
- 2% contraction of second interlayer distance

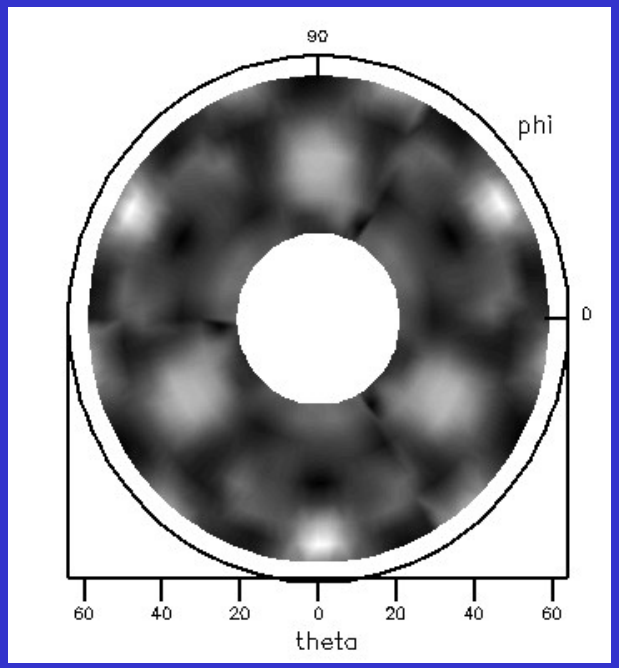
- E.A. Soares et. al Surface Science 497 (2002)205
- A. de Siervo et. al Surface Science 504C(2002) 215

~ 1ML Cu on Pd(111) after anneal. 600K

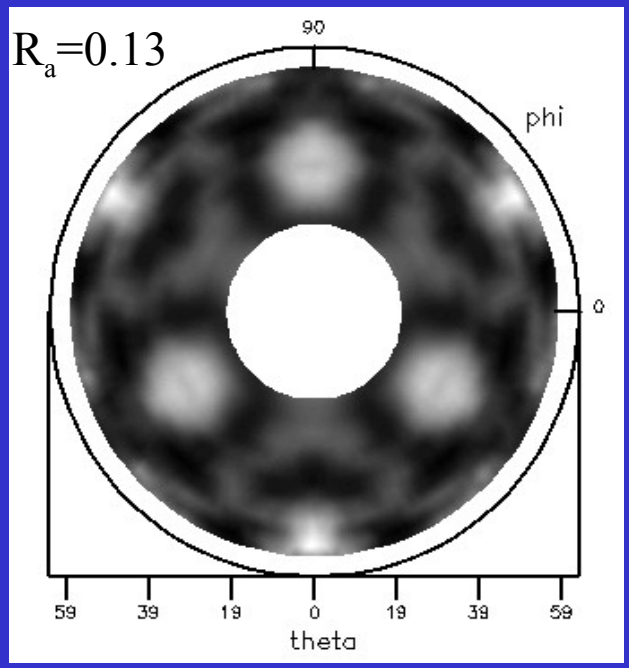
- Random Alloy
- Very good (1x1)LEED pattern
- ~ 100% Cu 1st layer
- ~ very little Cu in the 2nd layer and none in the 3rd layer.

Small Diffusion !!!

Cu 3p: Exp.



Cu 3p: theory



A.de Siervo et al. (unpublished)

~ 3ML Cu on Pd(111) Annealed to ~ 1000 K

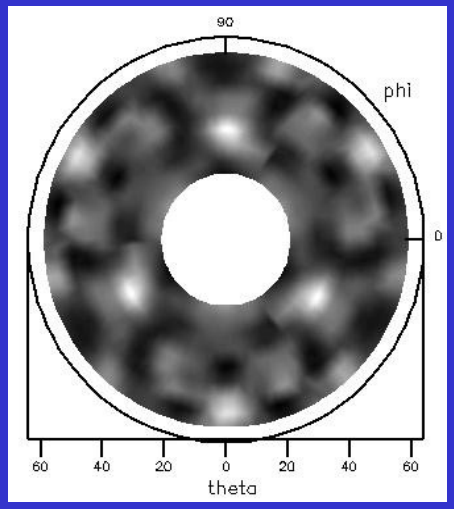
- Random Alloy
- > 90 % Cu 1st layer
- ~ 75 % Cu 2nd layer (Cu_3Pd)
- No diffusion to 3rd layer.

Agree with total energy theory
A.V.Ruban, PRB,59(1999)15990

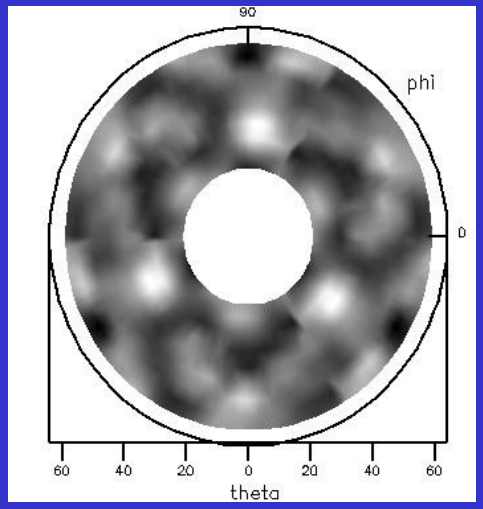
Relaxation with respect d_{bulk}

d_{12}=+10.9±1% d_{23}=-6.4±1%

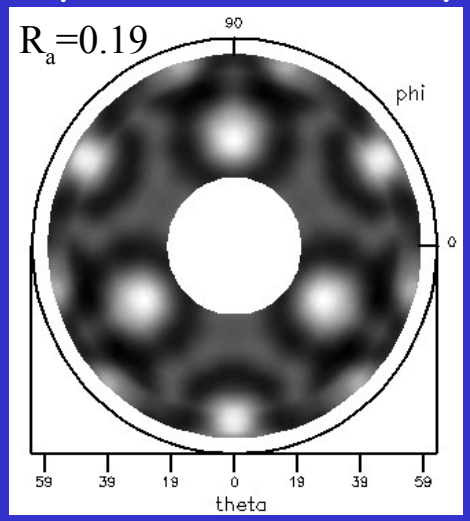
Cu 3p: Experimental



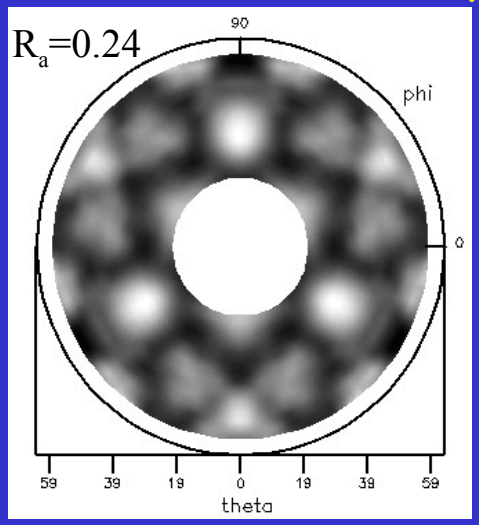
Pd 3d: Experimental



Cu 3p: MSCD Theory

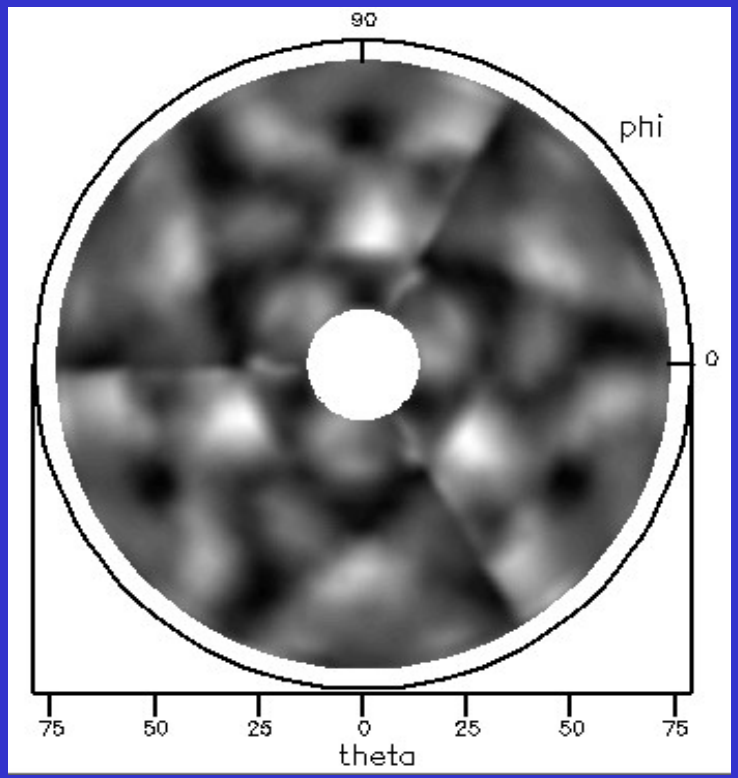


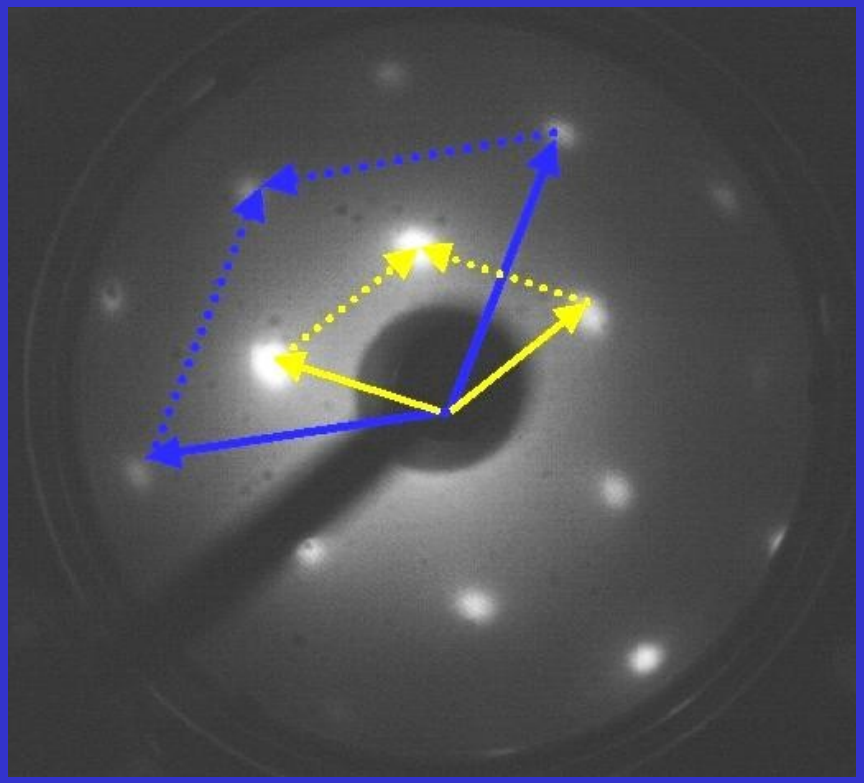
Pd 3d: MSCD Theory



Ordered 2D alloy: Sb over Pd(111)

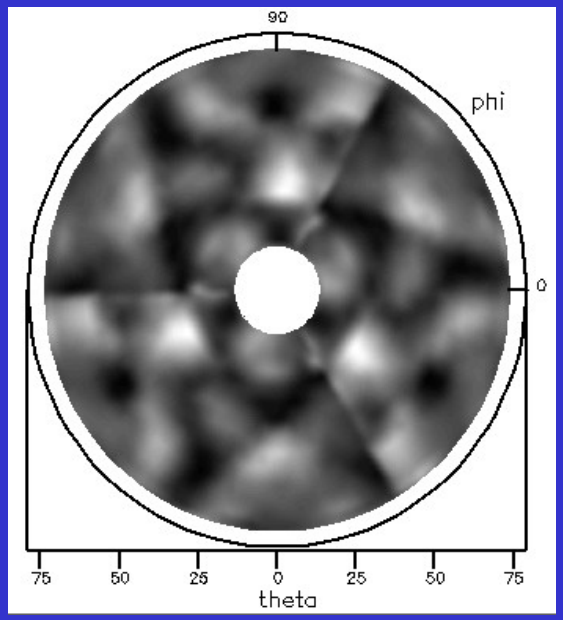
$$\mathrm{Sb}\left(\sqrt{3}\times\sqrt{3}\right)R30^{\circ}\ /\ \mathrm{Pd}(111)$$



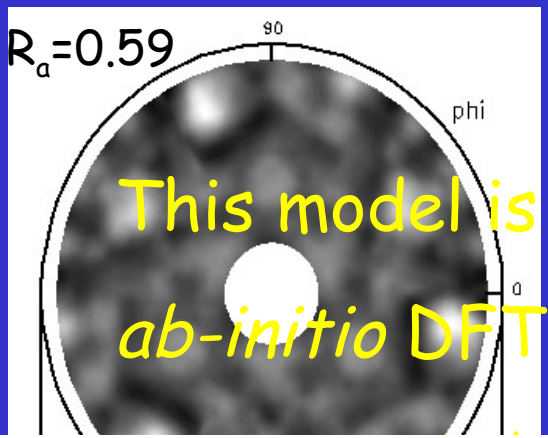


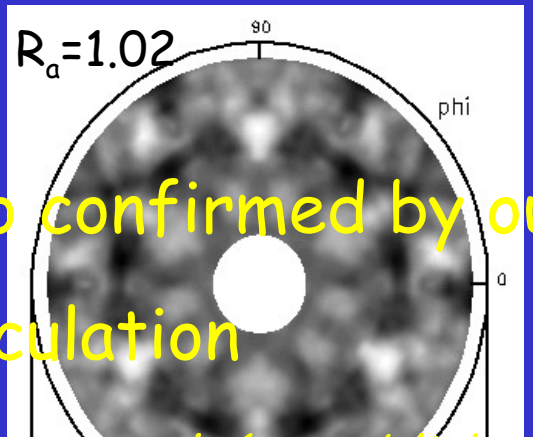
Emitter: Pd 3d

LEED: E_0=50 eV

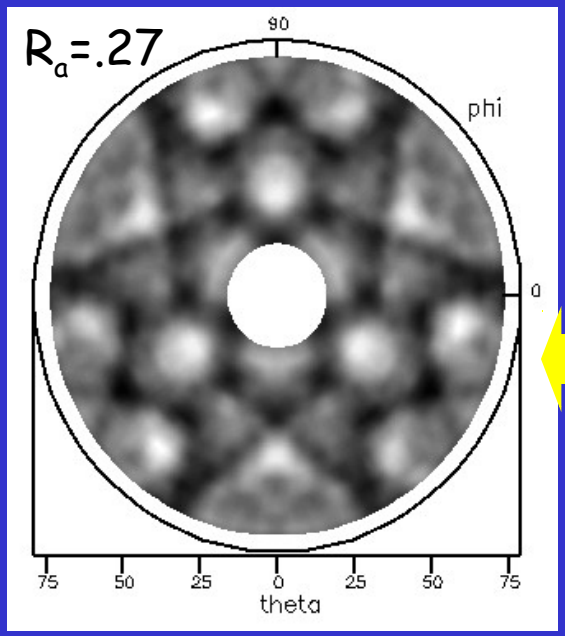


Exp. Pd 3d

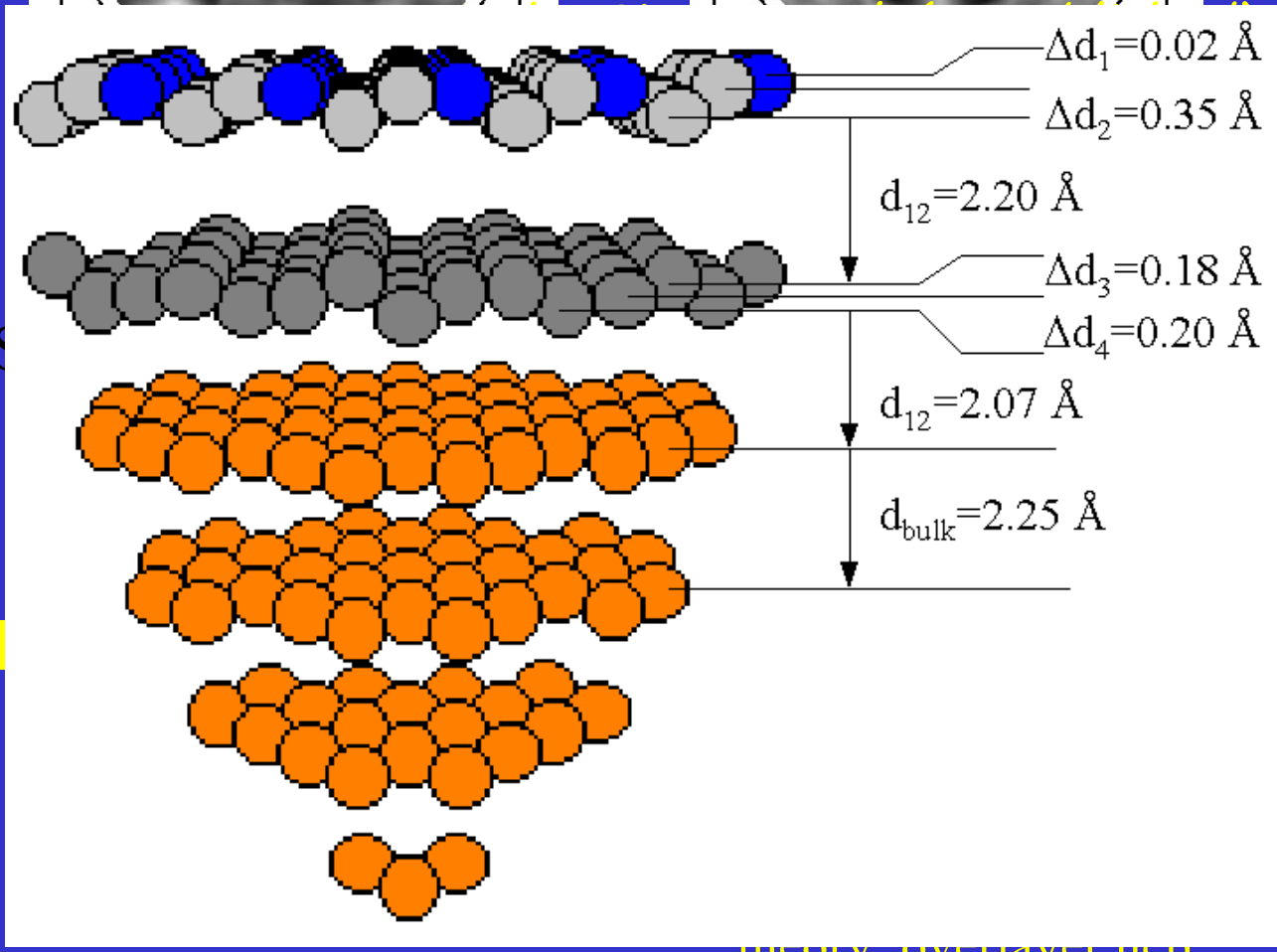




This model is also confirmed by our *ab-initio* DFT calculation



theory: Subst. fcc

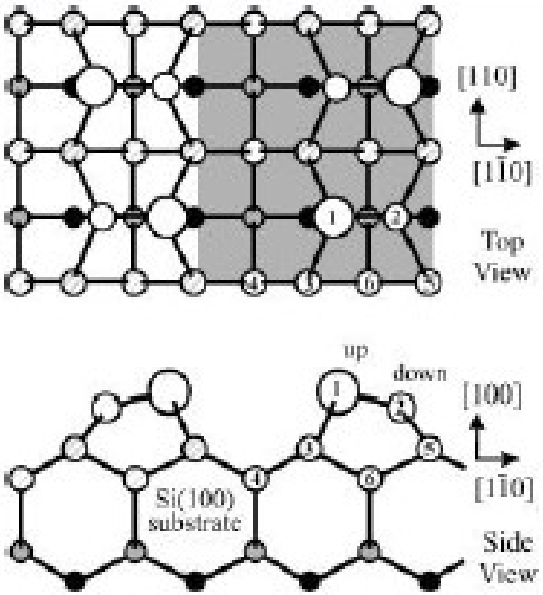


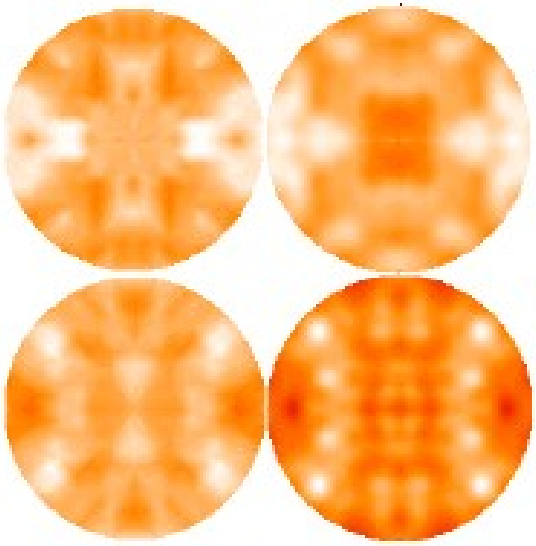
theory: overlayer hcp

Some Perspectives ... May be with an Undulator Beam Line at LNLS

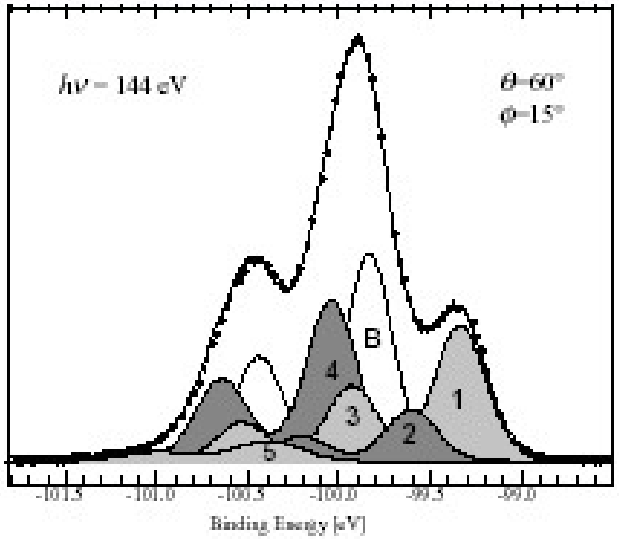
- PD Holography
- Near Node and In Node Photoelectron Diffraction for Holography Inversion
- Exploring Chemical Shift
- Time Resolve Photoelectron Spectroscopy

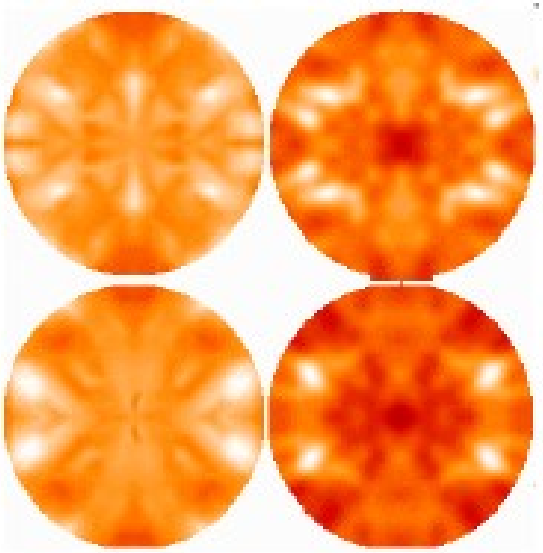
XPD for surface structure determination: The case of Si(100)c4x2





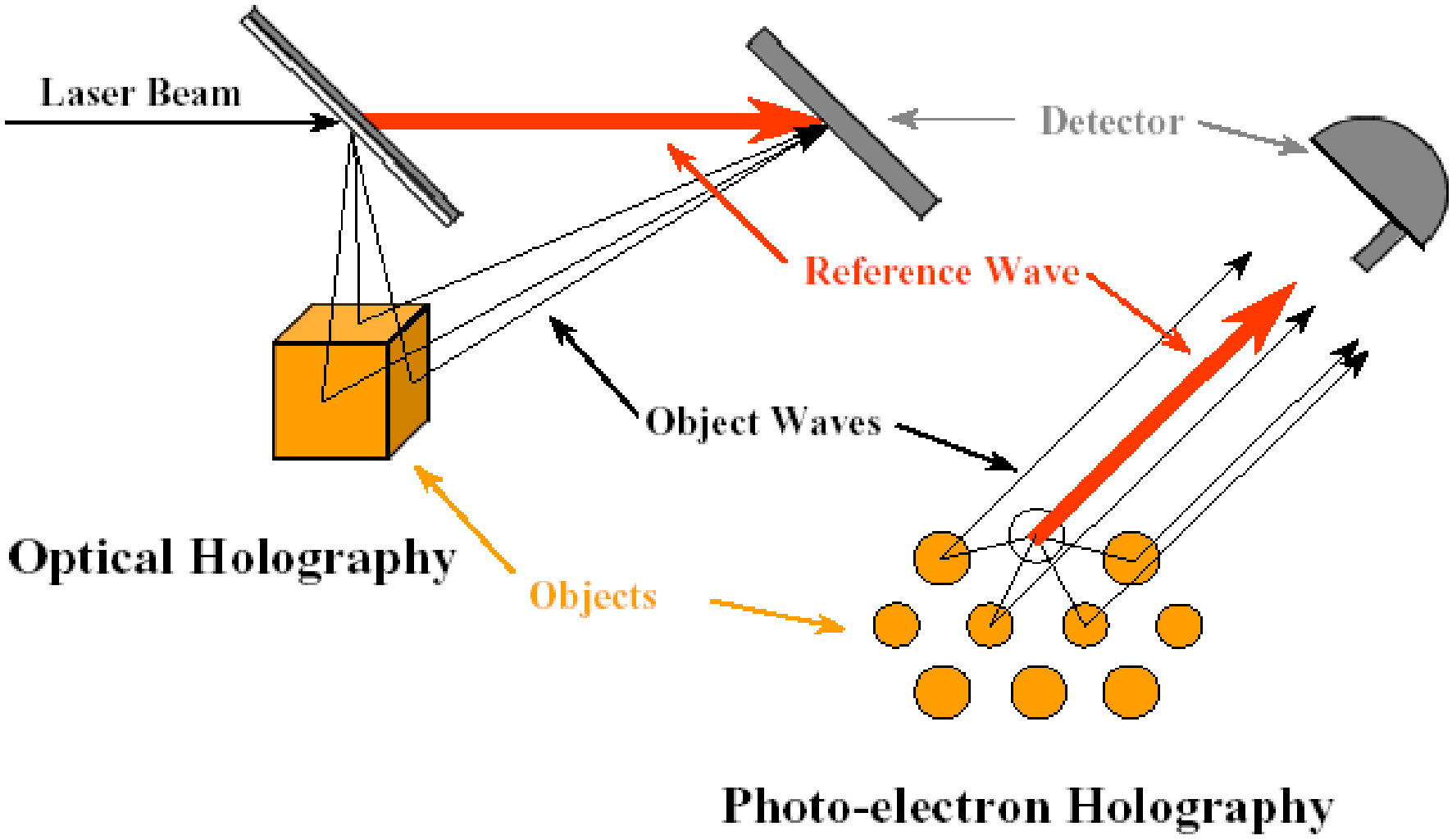
S1-XPD (left) and MS simulations (right) at hv=140 and 160 eV. Dimer atoms only (Atom 1)



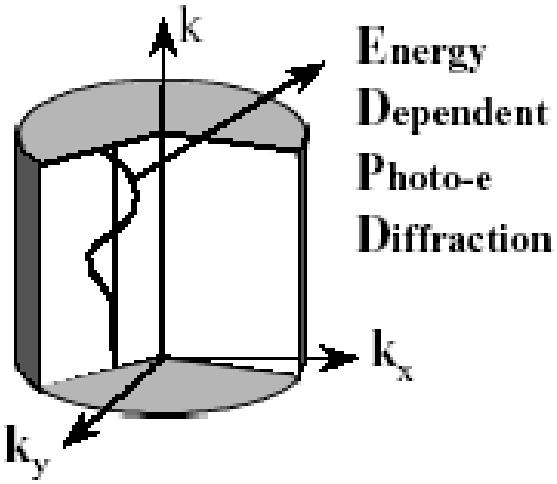


S_4-XPD (left) and MS simulations (right) at hv=145 and 160 eV. Emitters are those silicon atoms in the second layer substrate labeled as ATOM 4.

Photoelectron Holography: Analogy to Optical Holography



Method of Photoelectron Holography Inversions



•Barton Algorithm

$$A(\mathbf{r}) = \iiint_{k_x,k_y,k} \chi(k_x,k_y,k)\exp(i\mathbf{k}.\mathbf{r} - ikr)dk_x dk_y dk$$

•Synchrotron Data

$$A(\mathbf{r}) = \sum_{\theta,\varphi,k} \chi(\theta,\varphi,k)\exp(i\mathbf{k}.\mathbf{r} - ik.r)E_{out}\sin(\theta)\frac{1}{\theta_{out}}\frac{\cos(\theta_{out})}{\cos(\theta)}$$

•Geometric corrections
(Data, angular integration)

•Refraction effects
(Low energy)

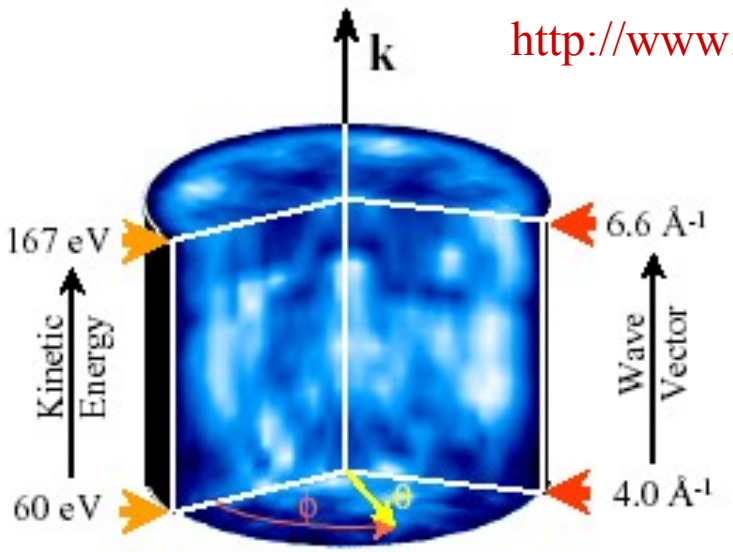
•Improvements

$$\chi(\theta,\varphi,k) \rightarrow \frac{\chi(\theta,\varphi,k)}{f(\theta,\varphi,k)\exp(i\alpha(\theta,\varphi,k))S(\theta,\varphi,k)}$$

- s/d ratio (shift)
- Polarization (asymmetry)

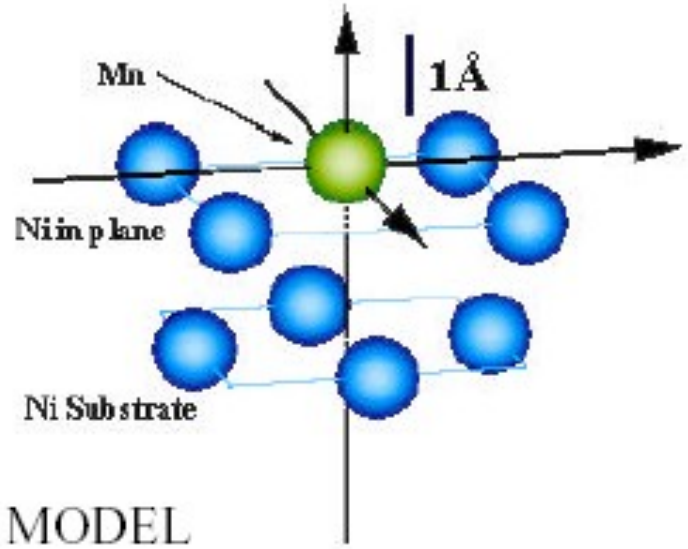
•Scattering factor, phase (SWIFT)

XPH example: Mn on Ni(100)

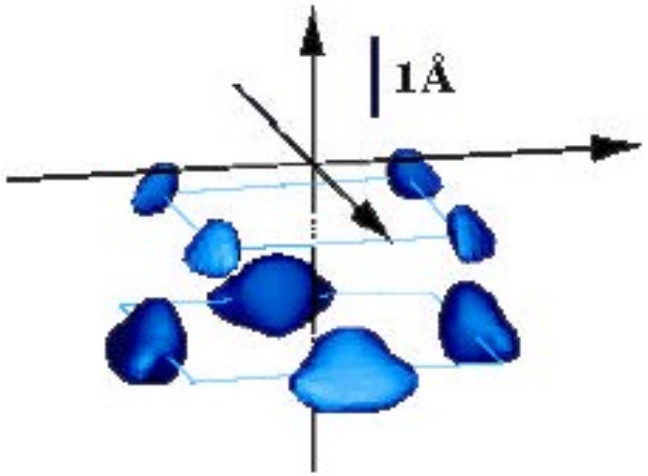


http://www.als.lbl.gov/als/science/sci_archive/surfalloy.html

Direct inversion of XPD volumes, using a model called "photelectron holography." The case of Mn atoms on a Ni(100) substrate is shown.



MODEL



EXPERIMENTAL HOLOGRAM

Colaboradores em PED

- Prof. Richard Lander (UNICAMP -SP)
- Prof. George G. Kleiman (UNICAMP-SP)
- Prof. Jonder Morais (UFRGS -RS)
- Prof. Vagner E. De Carvalho (UFMG-MG)
- Prof. Roberto Paniago (UFMG -MG)
- Dr. Edmar A. Soares (UFMG -MG)
- Dr. Carla Bittencourt (UNICAMP -SP)
- PhD. Student Abner de Siervo (UNICAMP-SP)
- Terezinha Ap. Fazan (UNICAMP -SP)
- IUV stuff (LNLS -SP)

www.ifi.unicamp.br/gfs

asiervo@ifi.unicamp.br

Oportunidades em Física de Superfícies (IC, MS, DT, PosDoc)

- Experimental: XPS, UPS,XAES, LEED, PED
- Teoria: PED, Auger e Teoria do Funcional-Densidade (DFT)
- Tópicos: Ligas 2D (ligas de superfície), ligas metálicas suportadas em óxidos

PD Holography for direct 3D atomic images

- Measure I(k) for several $\hat{k}$ direction and several energies |k|. A volume in k-space can be produce suppression of twin images

~4000 XPS . (only for high performance beam line !!!)

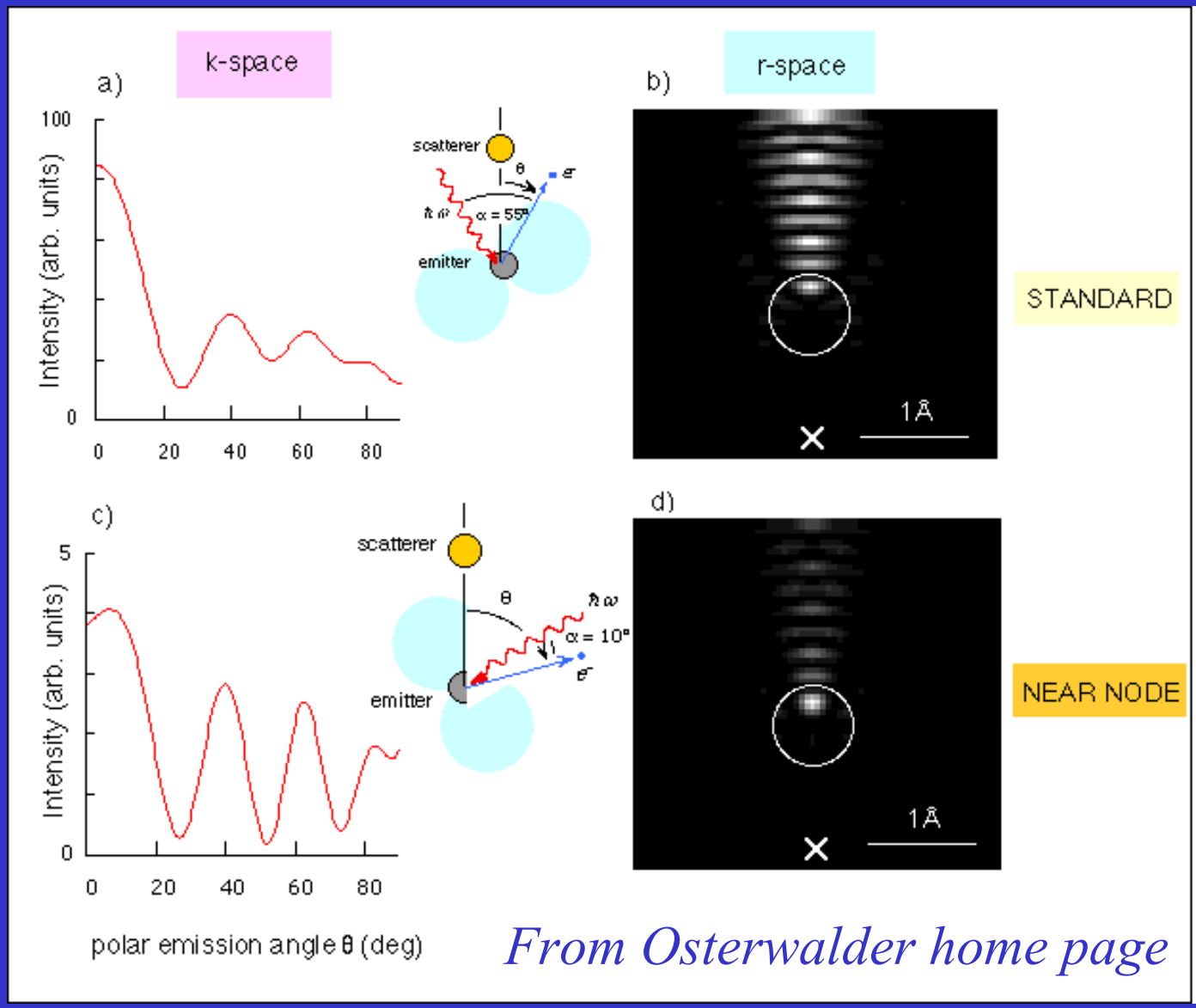
Szöke (1986), Barton (1988) and several papers Fadley group (199x)

- Exploring circular polarized light (CDAD)

•G.H.Fecher, et. al. J.Electron.Spectrosc.Rel. Phen. 76 (1995) 97

- Suppression of forward scattering by
" Near Node photoemission "

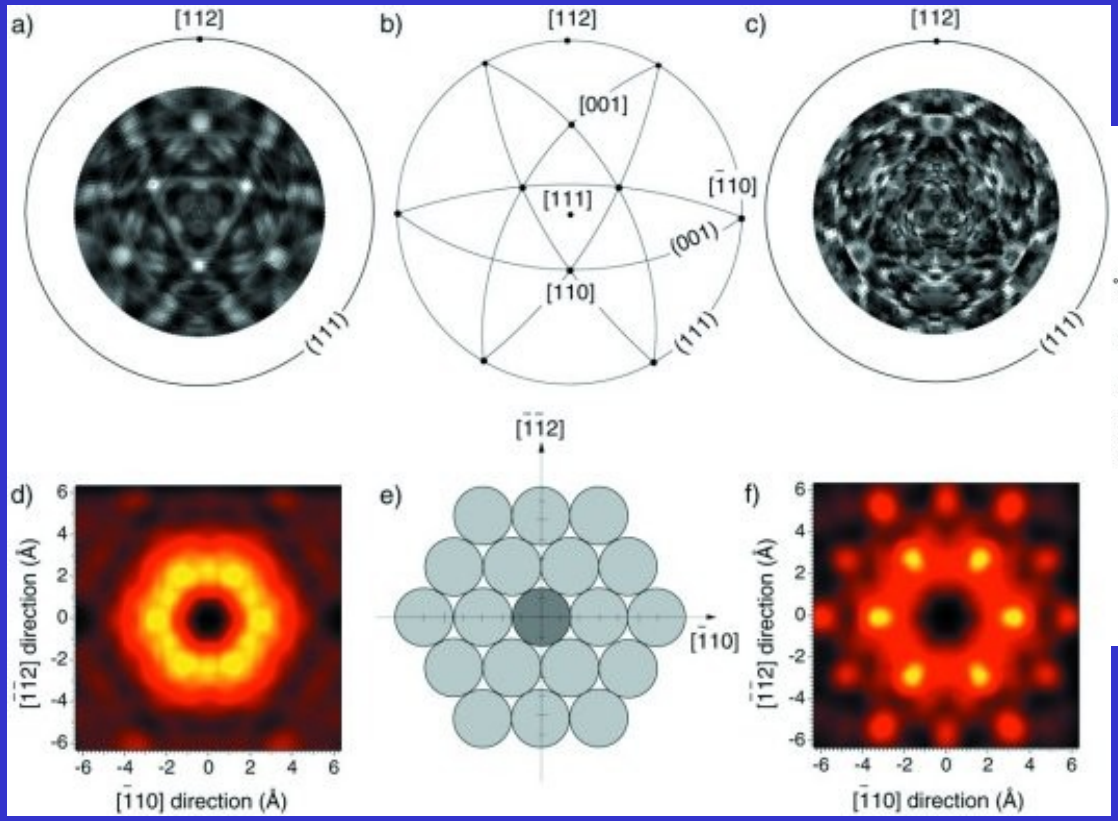
Advantages of Near Node Photoemission proposed by Osterwalder

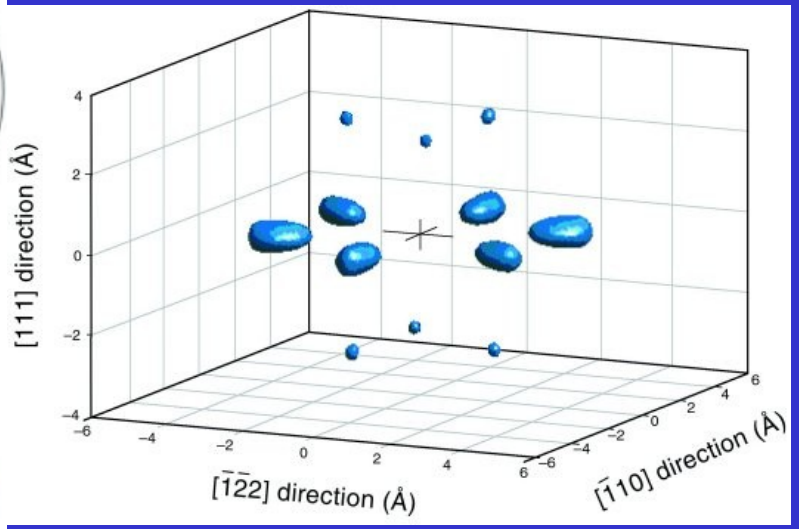


From Osterwalder home page

Imaging atom sites with near node photoelectron holography

Al(111) using 2s level *p-radiation* at the ALOISA beam line - ELETTRA by Osterwalder group.





Real space

far node

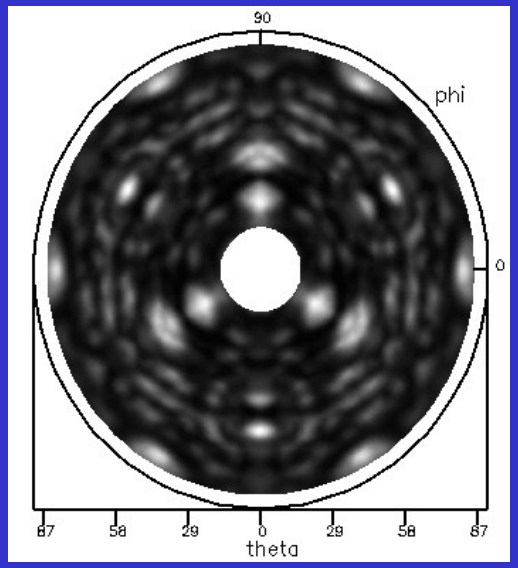
near node

J. Wider et al., Phys. Rev. Lett. **86**, 2337, (2001).

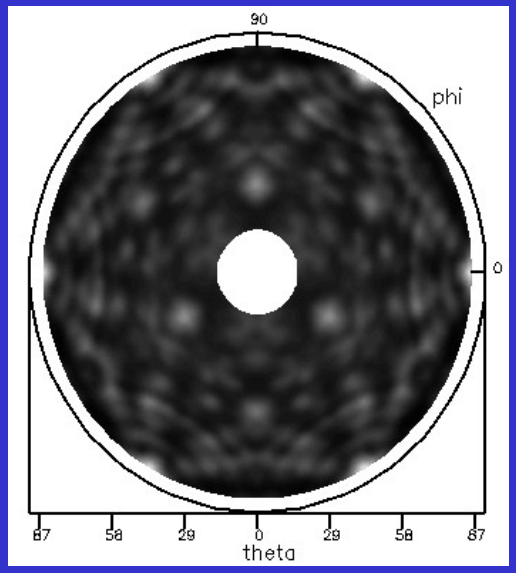
"Near Node" or "In Node" Photoelectron Diffraction at LNLS

* *In Node* - Align the backside of Omicron EA 125HR analyzer with SGM beam line . SR traveling through electrostatic lens

Al(111)
2s



In node simulation



Near node simulation

* Near Node - Using In-situ omicron AR-65 analyzer :
Need New Chamber and twin-plane goniometer