Some New Surface Structural Themes

I. K. Robinson
University of Illinois
MPI-Stuttgart, September 2004

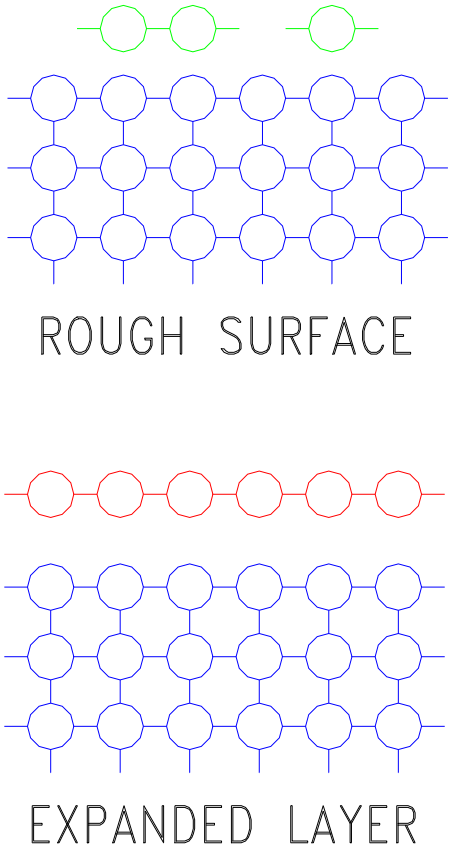
Important Contributions from

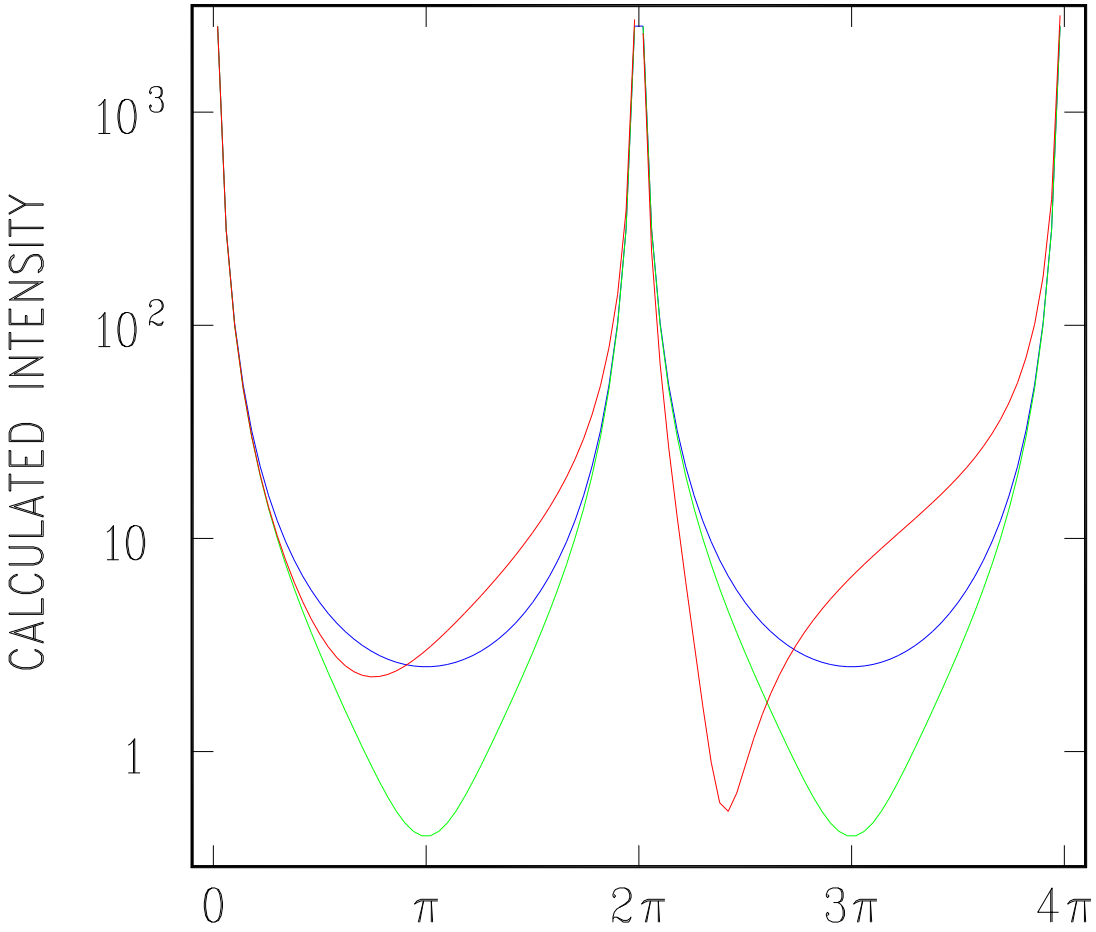
Sanjit Ghose	Urbana
Peter Bennett	Arizona
Franz Himpsel	Wisconsin
Jia Wang	Brookhaven
Ratko Adzic	Brookhaven
Ben Ocko	Brookhaven
Sebastien Boutet	Urbana
Marie-Claire St Lager	CNRS
Pierre Dolle	CNRS
Maurizio deSantis	CNRS
Robert Baudouing-Savois	CNRS
X16A, X22A	NSLS
BM32	ESRF

Theme Menu

- Au quantum nanowires on Stepped Si
- Au ‘physisorption’ on Si(111)7x7
- Deep subsurface strain in Pt(111)/CO
- ‘Homometric’ structures of Pt(110)1x5

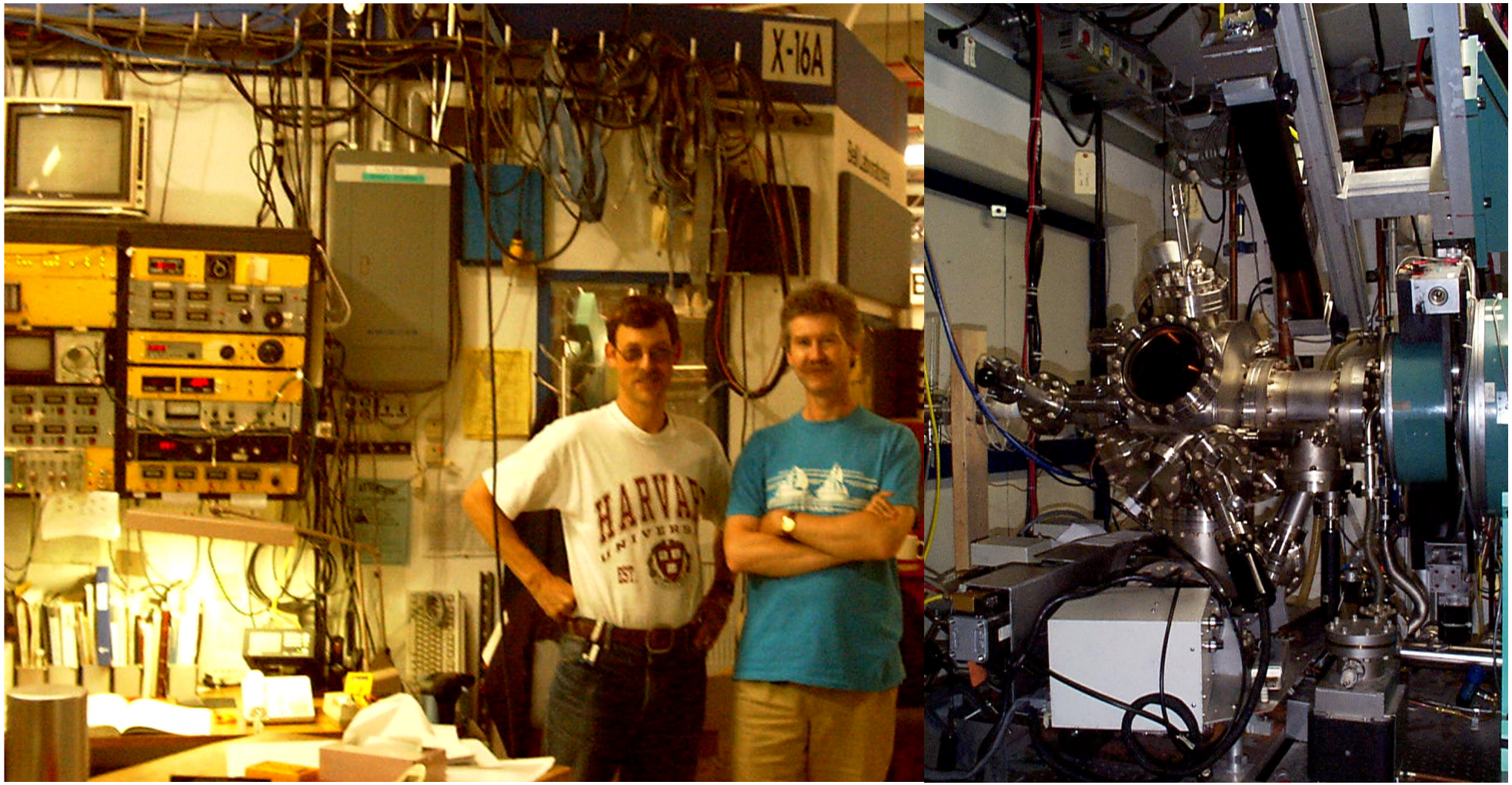
CTR is Sensitive to Surface Structure





X16A Surface X-ray Diffraction

operating since 1987 ...



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Theme Menu

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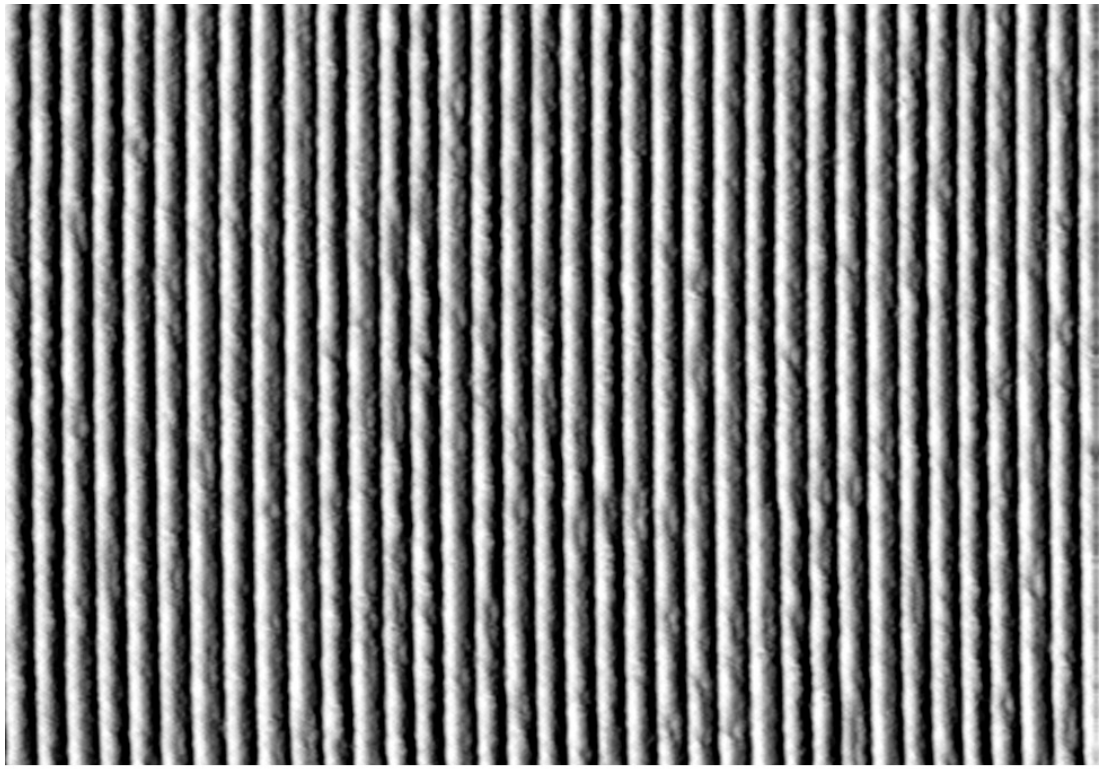

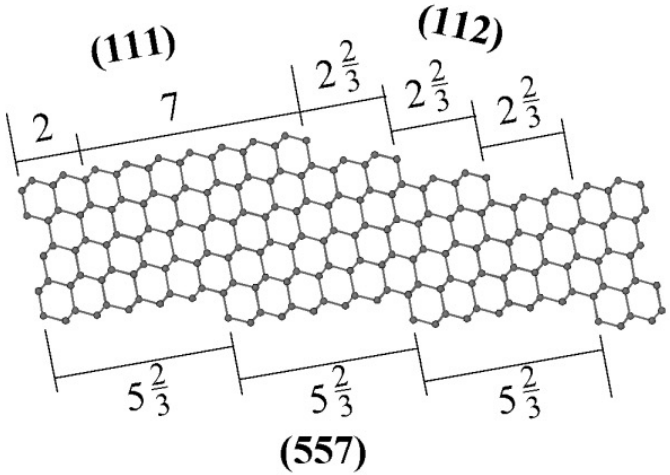

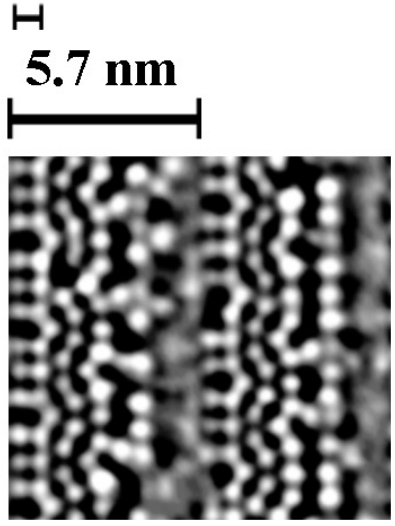

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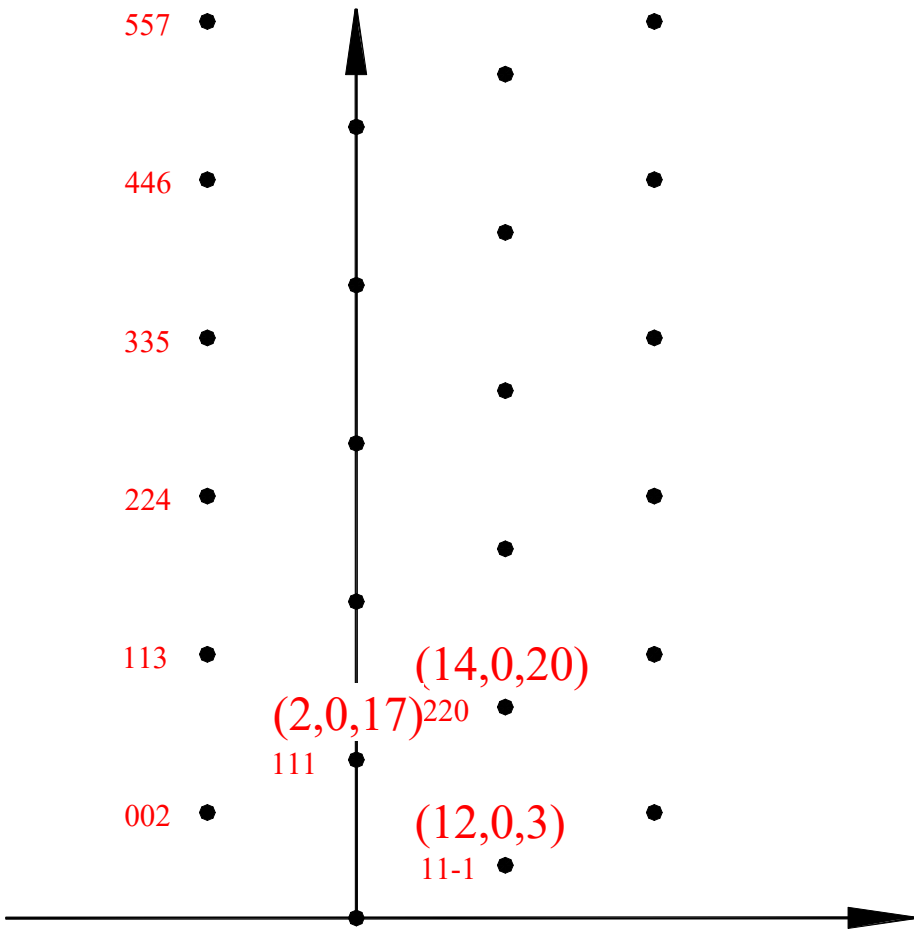
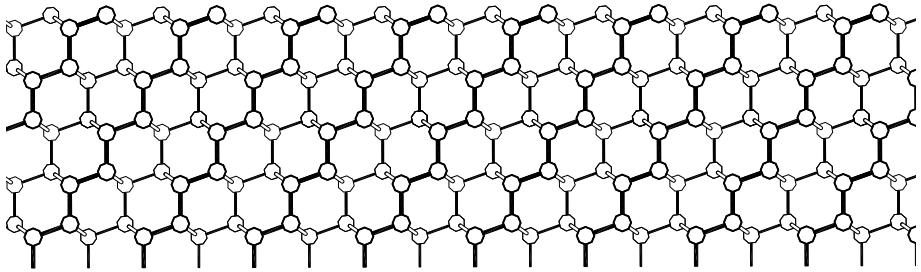
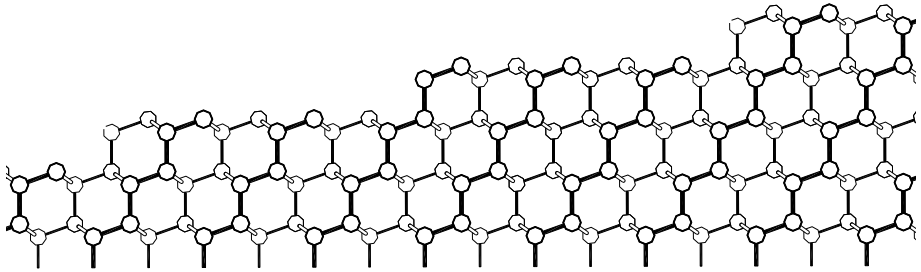
Crystallography of Stepped Surfaces



Silicon (111)



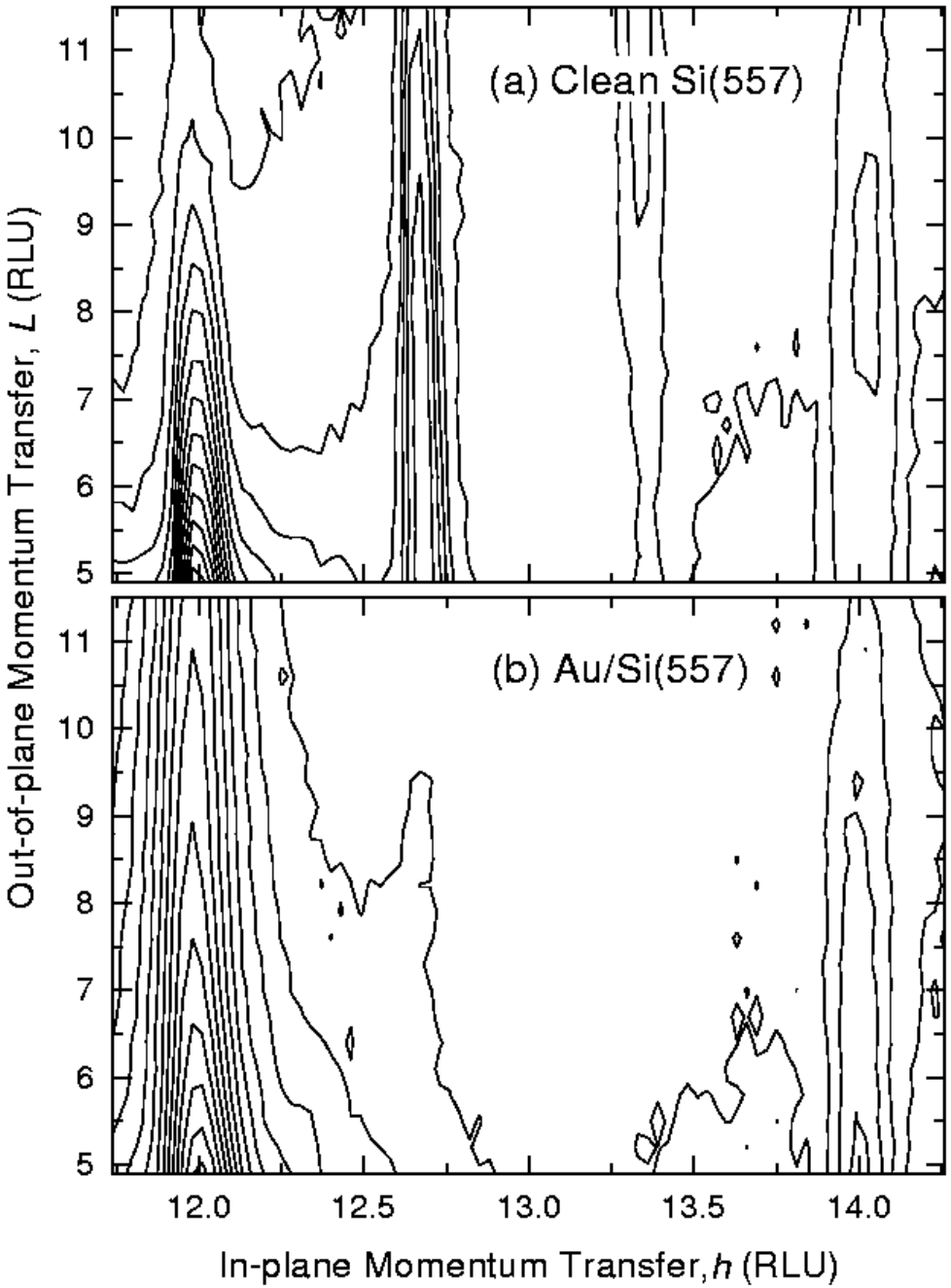


Si(557) surface

Alignment is Straightforward

```
CALCULATED PARAMETERS:
          A           B           C       ALFA    BETA    GAMMA
REC:  0.164431    1.63392    0.116412   90.06   90.03   89.93
DIR:   38.2118    3.84548     53.9736   89.94   89.97   90.07
          H    K     L     TTH      TH      PHI      CHI      ALP      CTS    ERROR
OR 1 = 12.0  0.0   3.0  21.938 112.920   50.308   -1.137    3.841    22456  0.0027
OR 2 = -5.0  1.0   7.0  20.284  97.018  307.482   -2.259    9.179    20719  0.0018
OR 3 = 14.0  0.0  20.0  26.411 113.142   40.844   -1.290   26.483    13639  0.0009
OR 4 = 12.0  2.0   3.0  43.135 110.470    4.520   -2.092    4.313    12772  0.0009
Lambda = 1.20913 A, wv = 5.19647, Energy = 10.2542 keV (FIXED)
Five-Circle Mode using alm = 2 and bem = 2:
```

Centered Orthorhombic unit cell contains two steps.

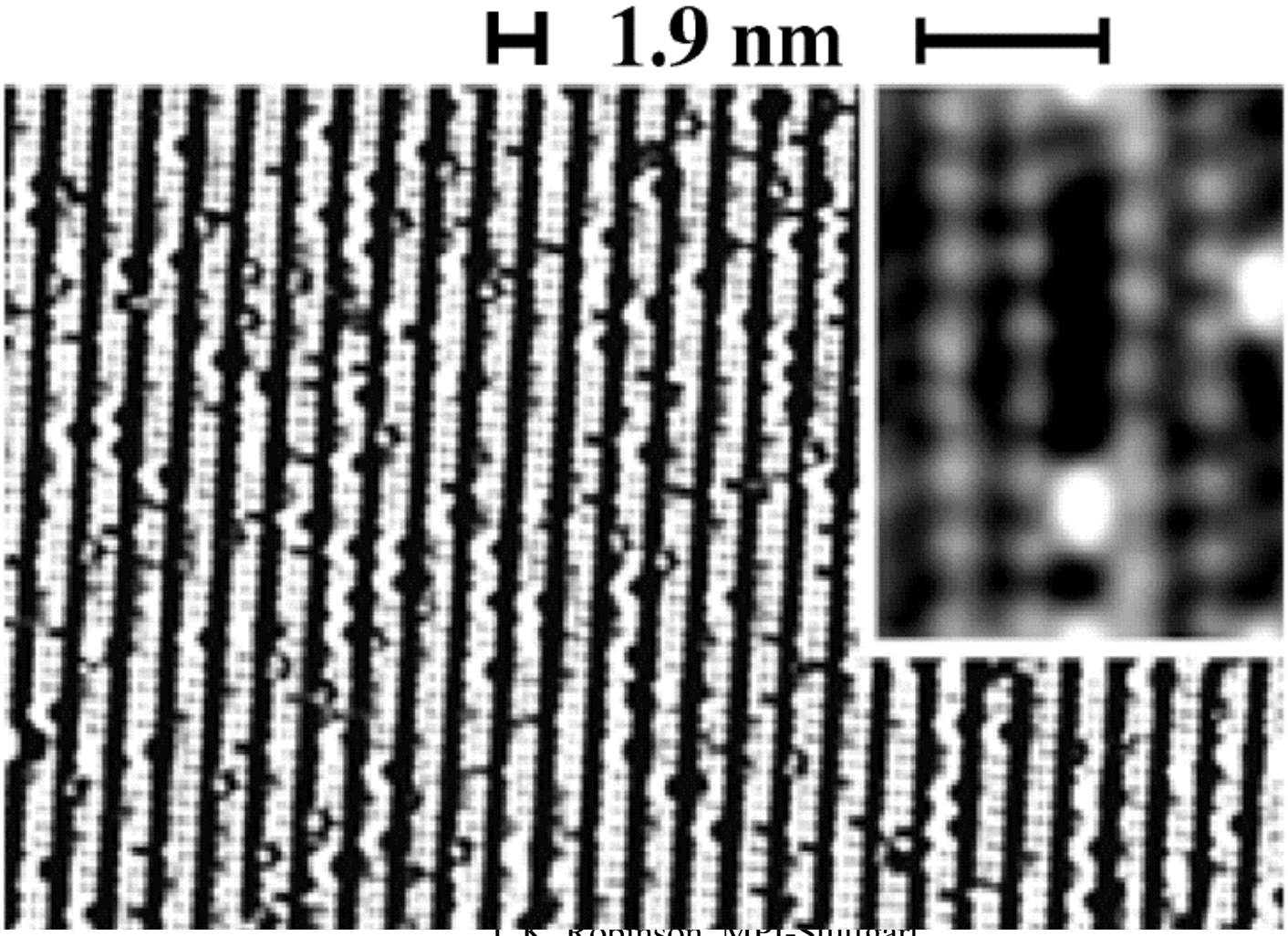


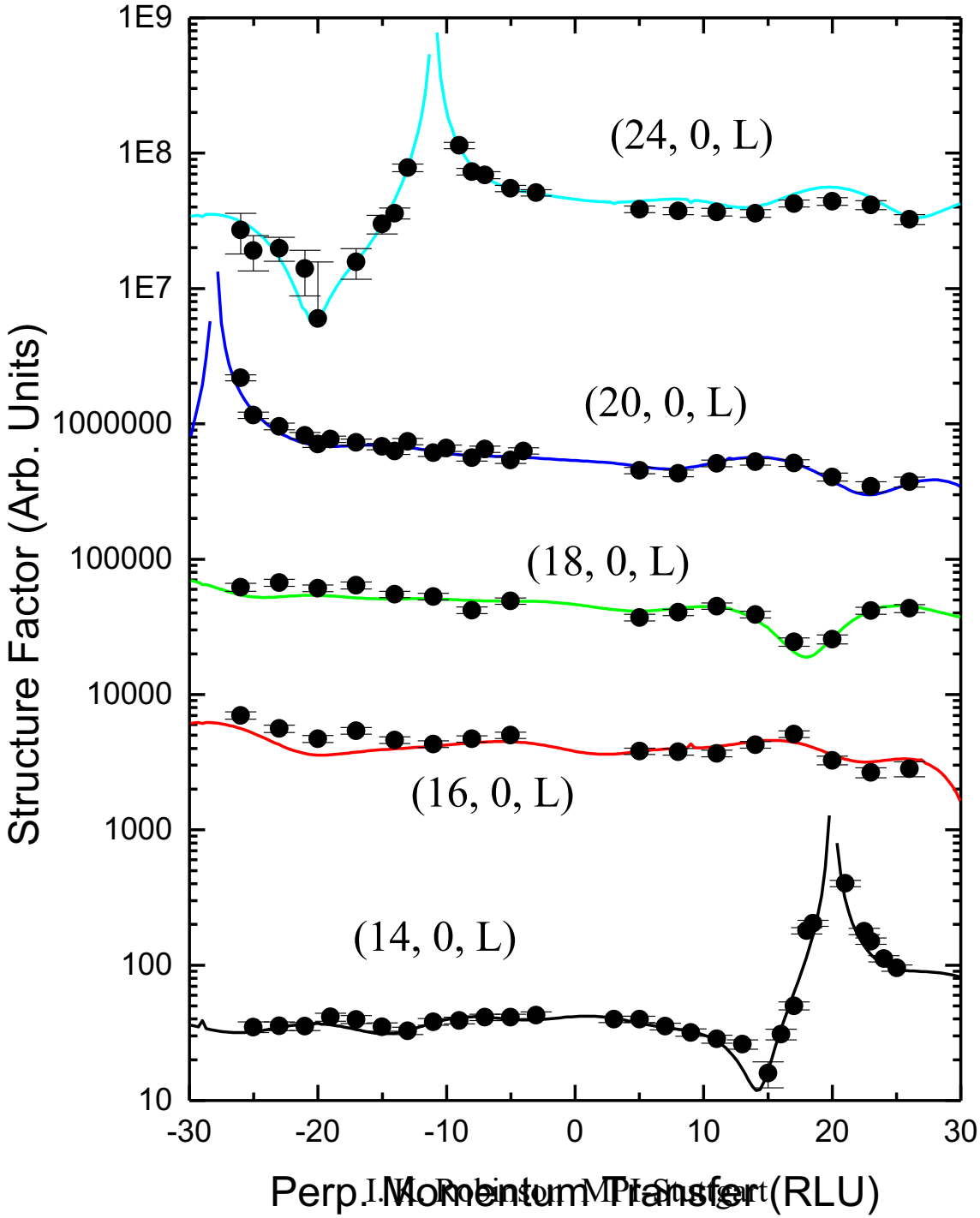
3×1 clean surface

1×1 surface with 0.2ML Au at 600C

STM of Si(557)/Au

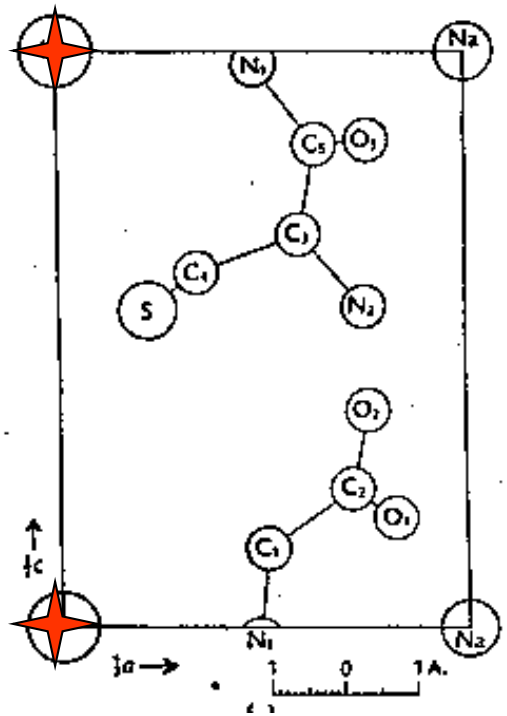
R. Losio, et. al., Phys. Rev. Lett. 86 4632 (2001)



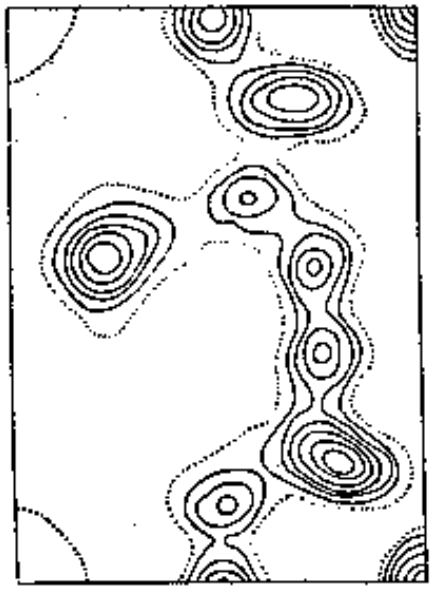

1E9
1E8
1E7
1000000
100000
10000
1000
100
10
(24, 0, L)
(20, 0, L)
(18, 0, L)
(16, 0, L)
(14, 0, L)
Structure Factor (Arb. Units)
-30
-20
-10
0
10
20
30
Perp. Momentum Transfer (RLU)

Phasing by a Single Heavy Atom

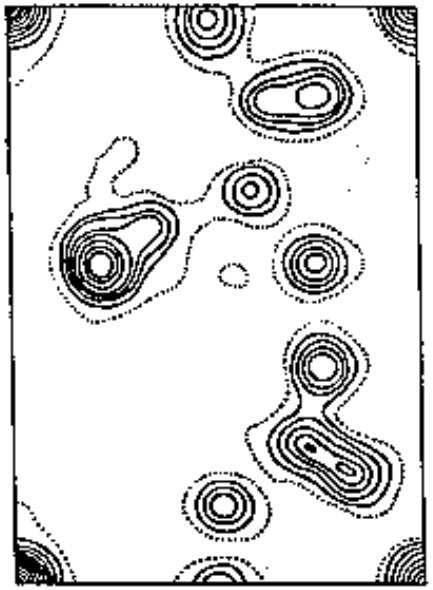
H. B. Dyer, Acta Cryst. 4 42 (1951)



Cysteinylglycine sodium iodide

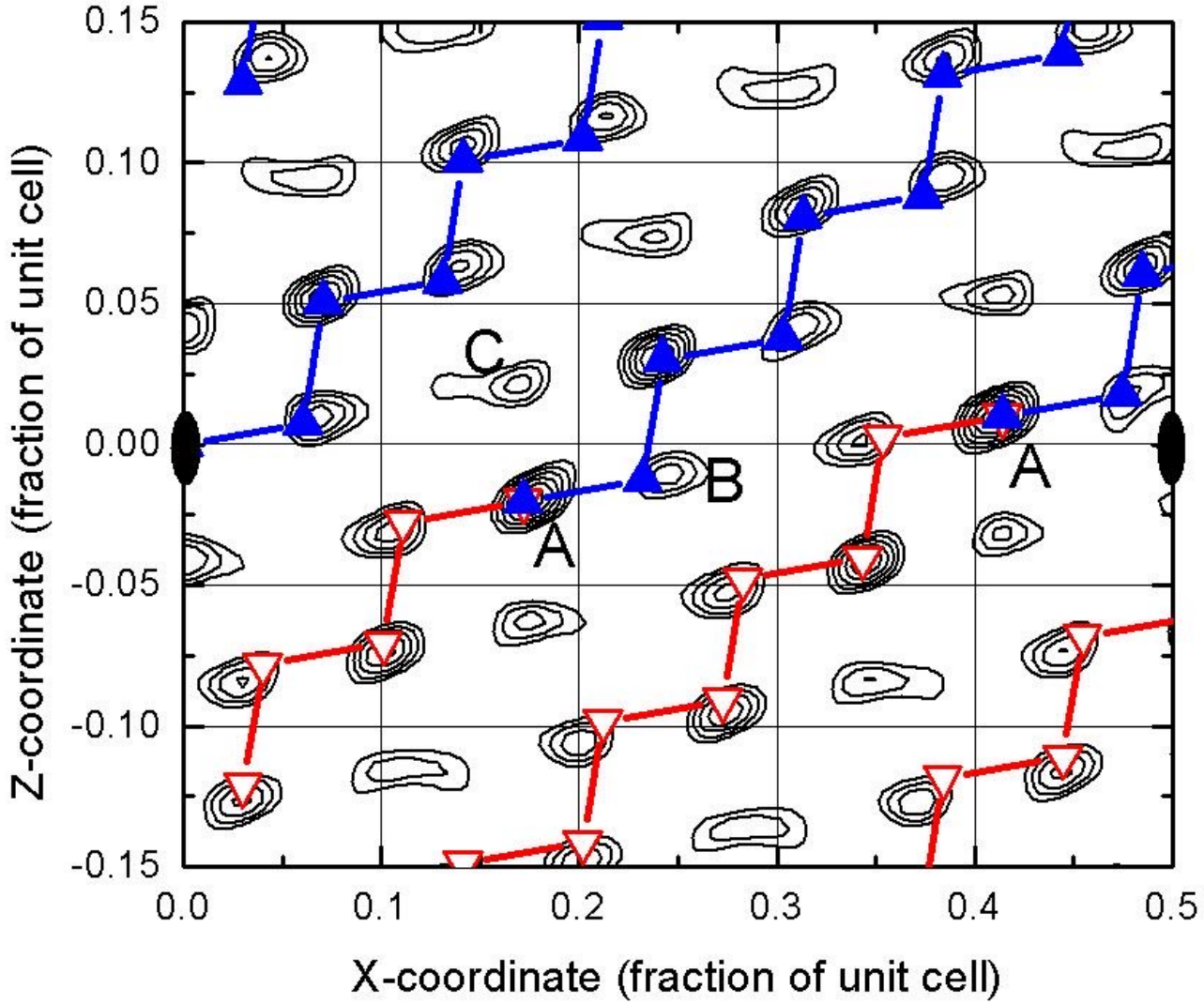


Patterson



Electron density

X-Z Patterson of Au/Si(557)



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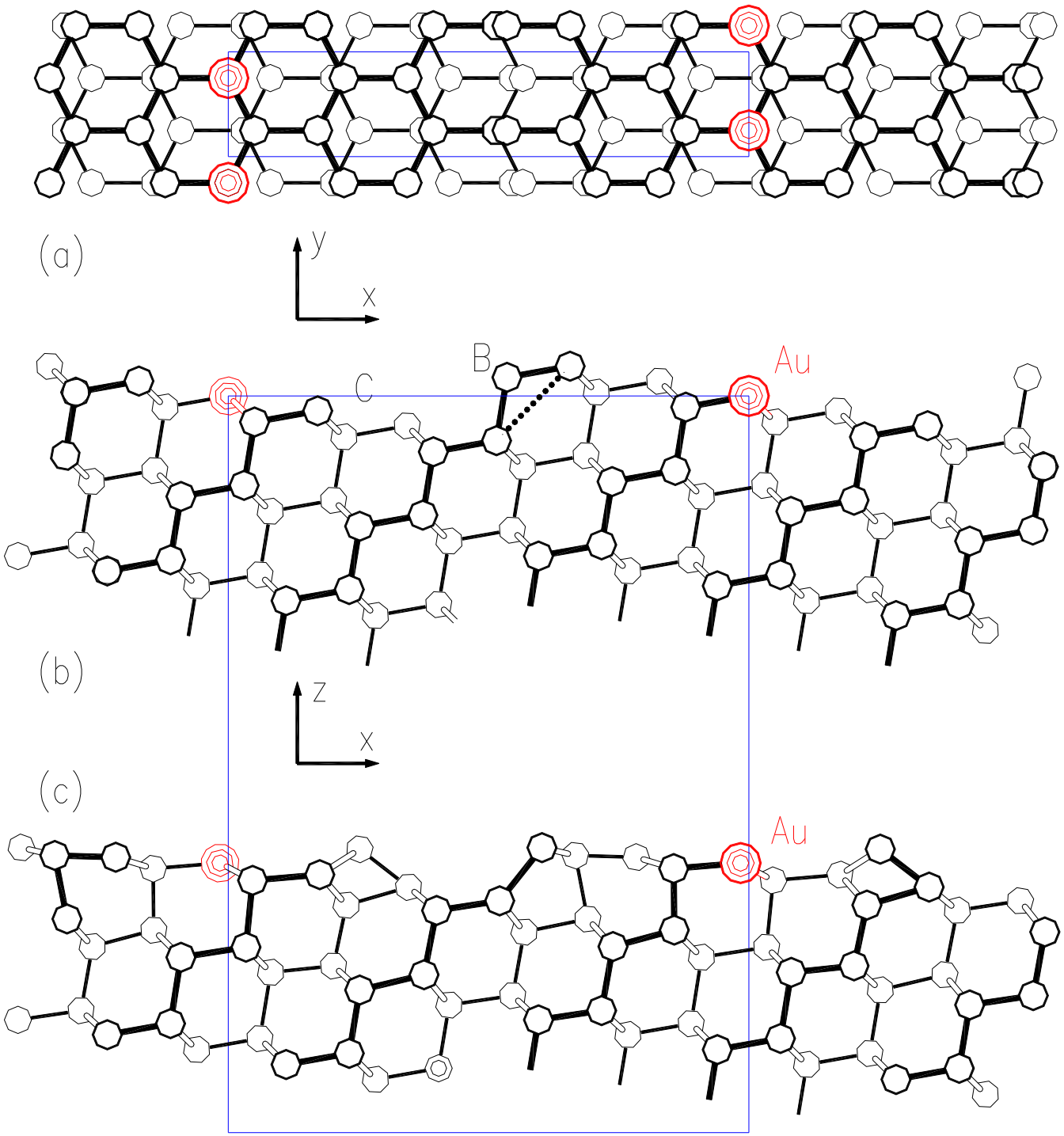
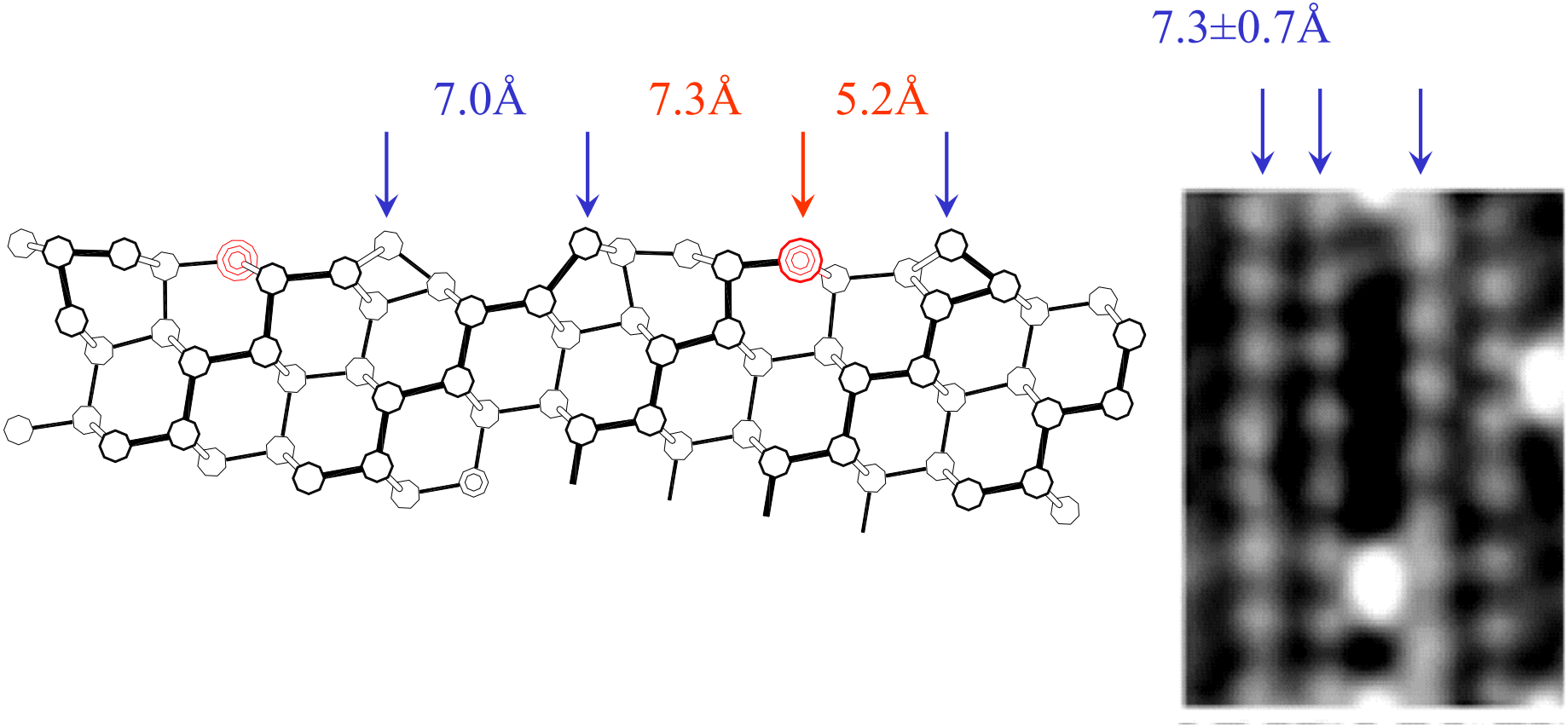
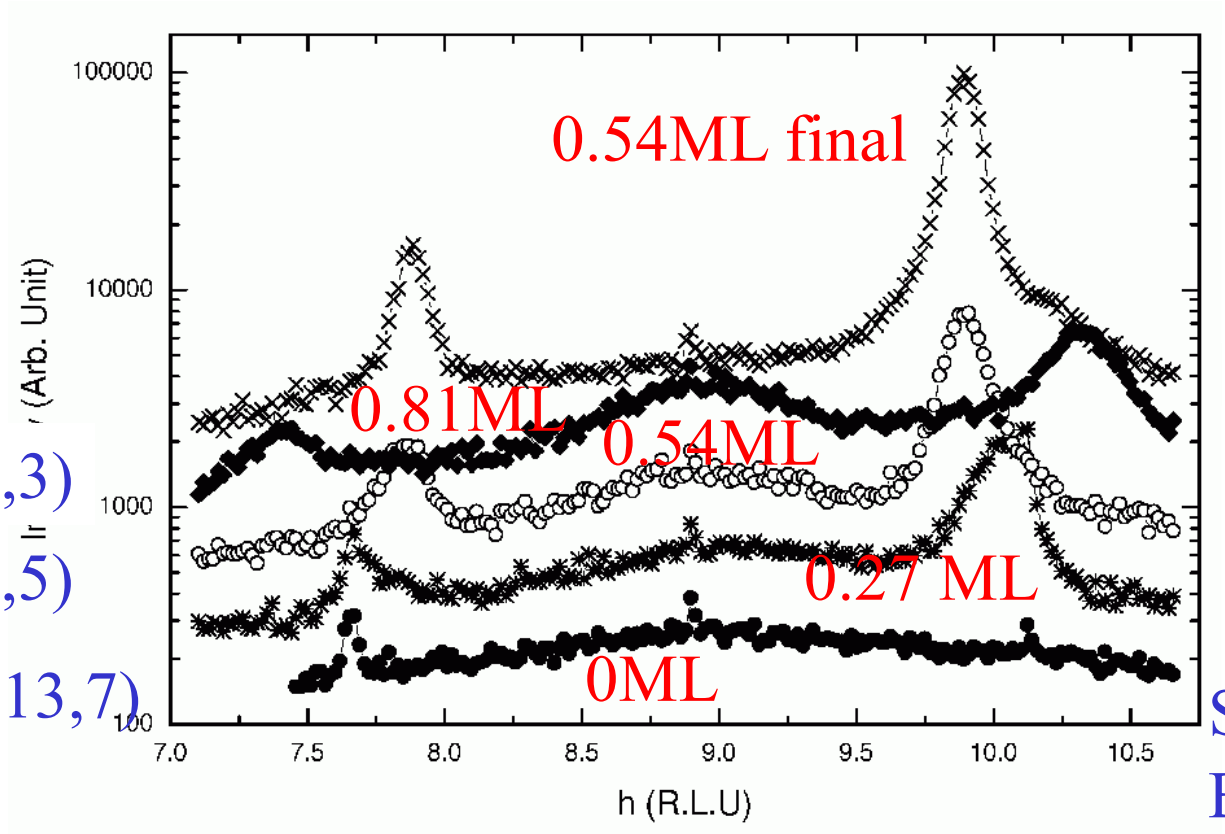
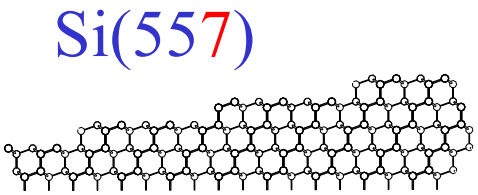

(a)
y
x
B
C
Au
(b)
z
x
(c)
Au

Comparison with STM

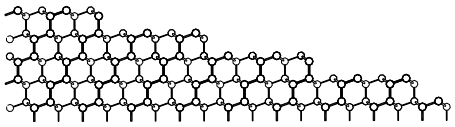


Au deposition on Si(13,13,7) at 650C





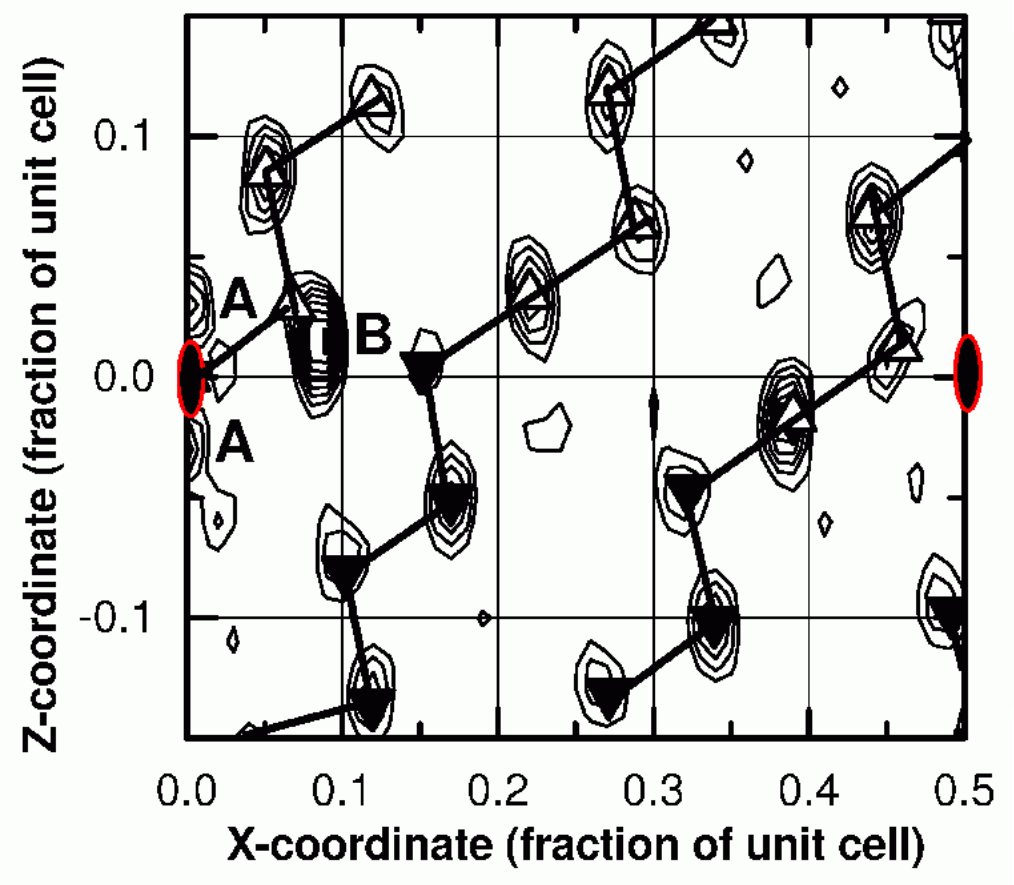
Si(557)

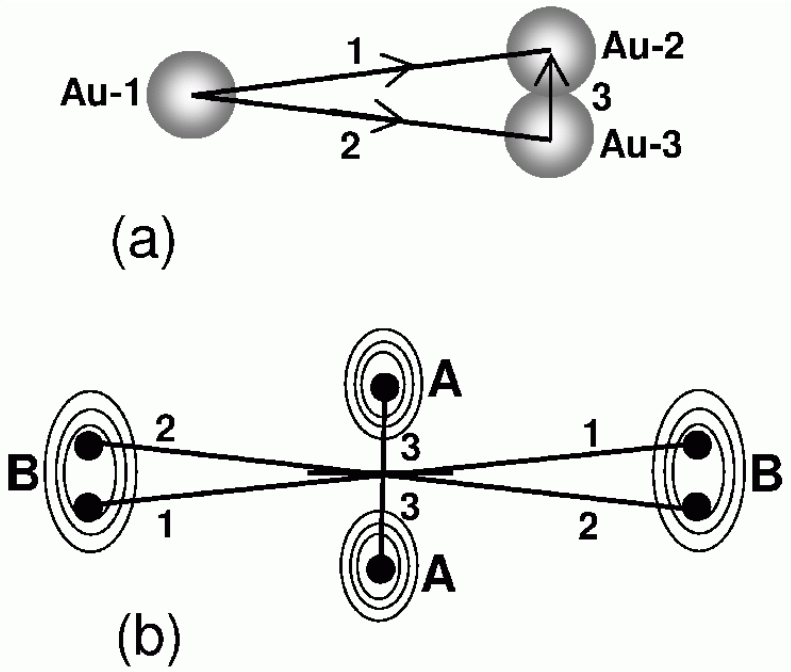


Si(553)

Scan along (h,0,11)
Bragg at (8,0,7)

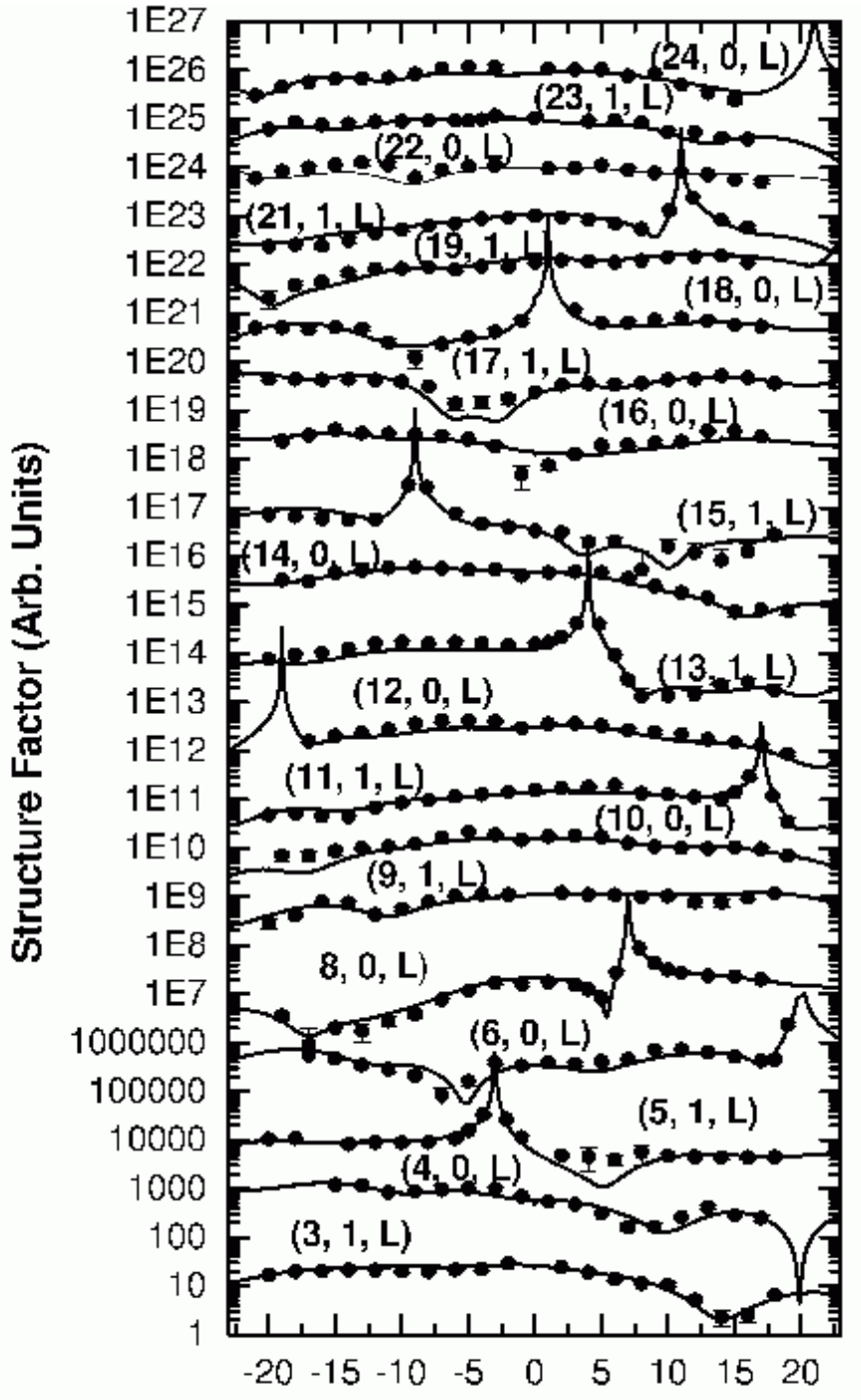
Patterson has extra peaks near origin



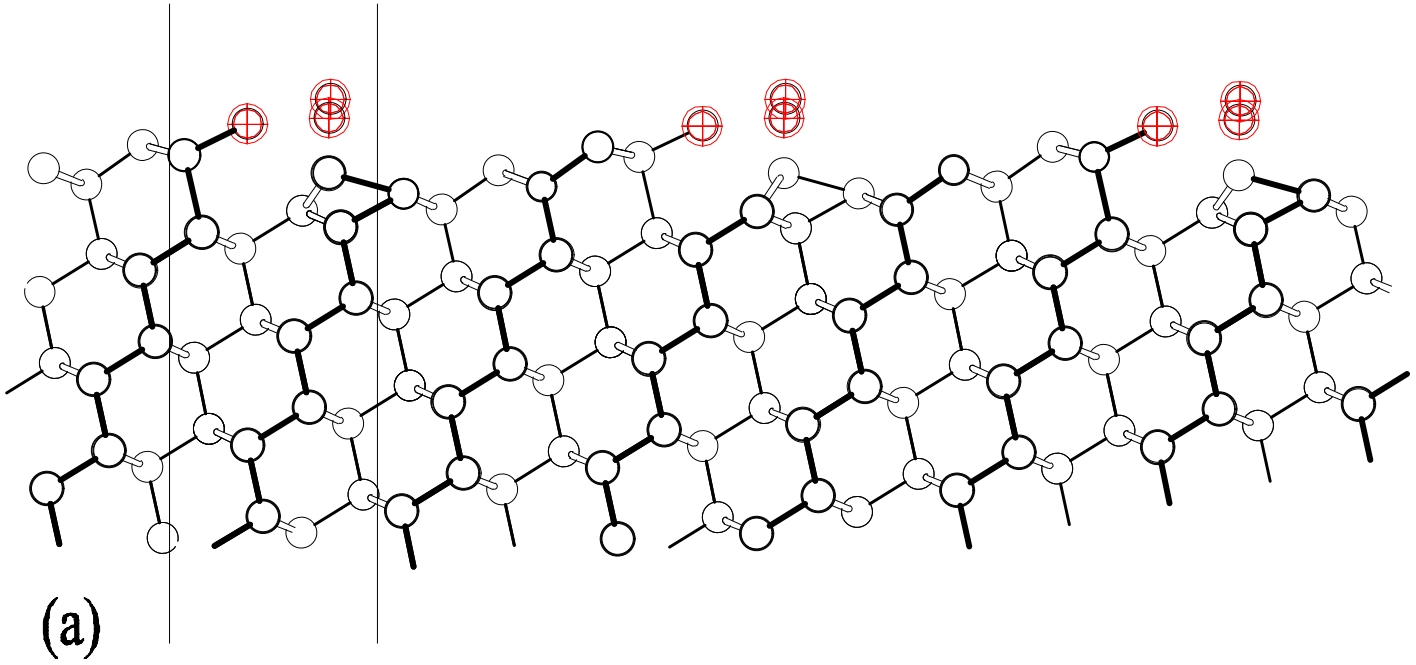


Fit to Data

- Chisq = 6.5
- Au-1 at 70%
- Au-2,3 at 38% ea
- Extra Si at 50%
- Relaxations



Final model of Au/Si(553)



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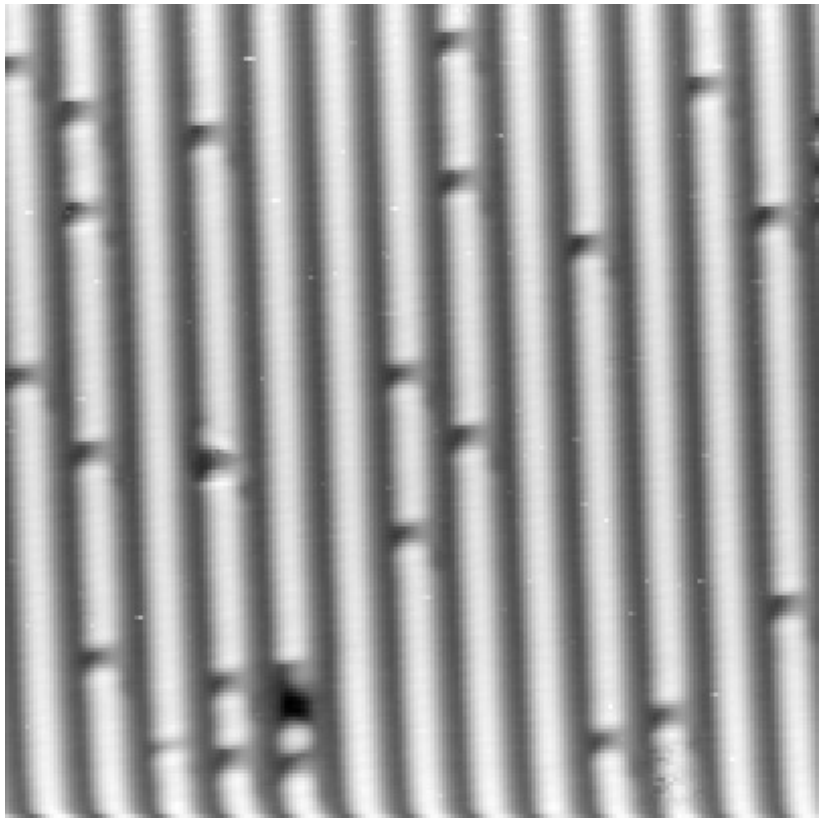
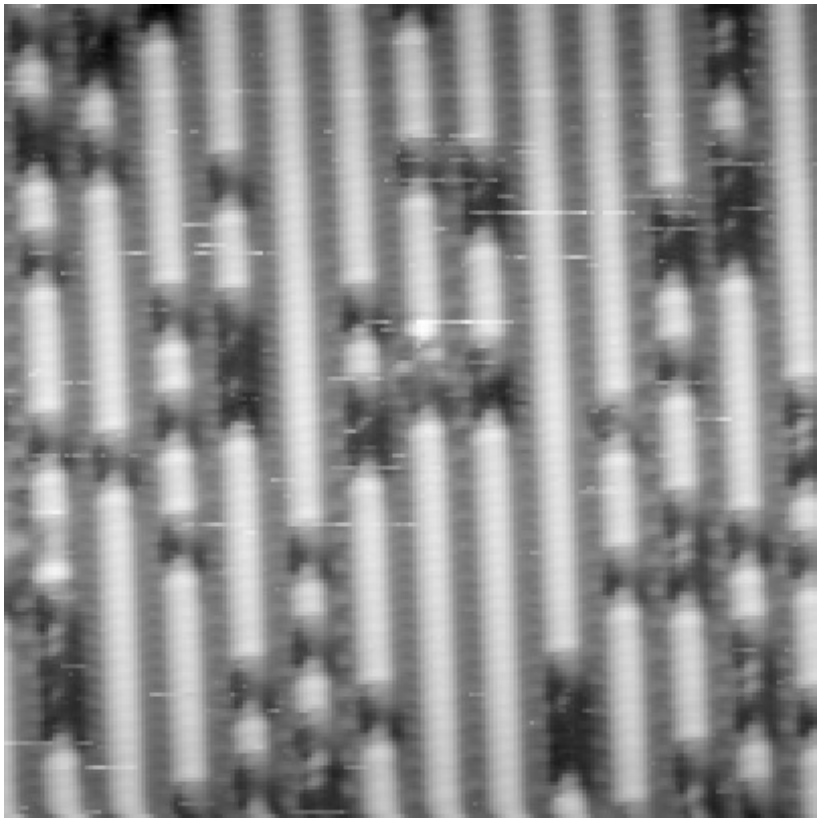
Defect Density Increases with Time After Preparation, [STM: J. Crain and F. Himpsel]

2 Hours After Preparation



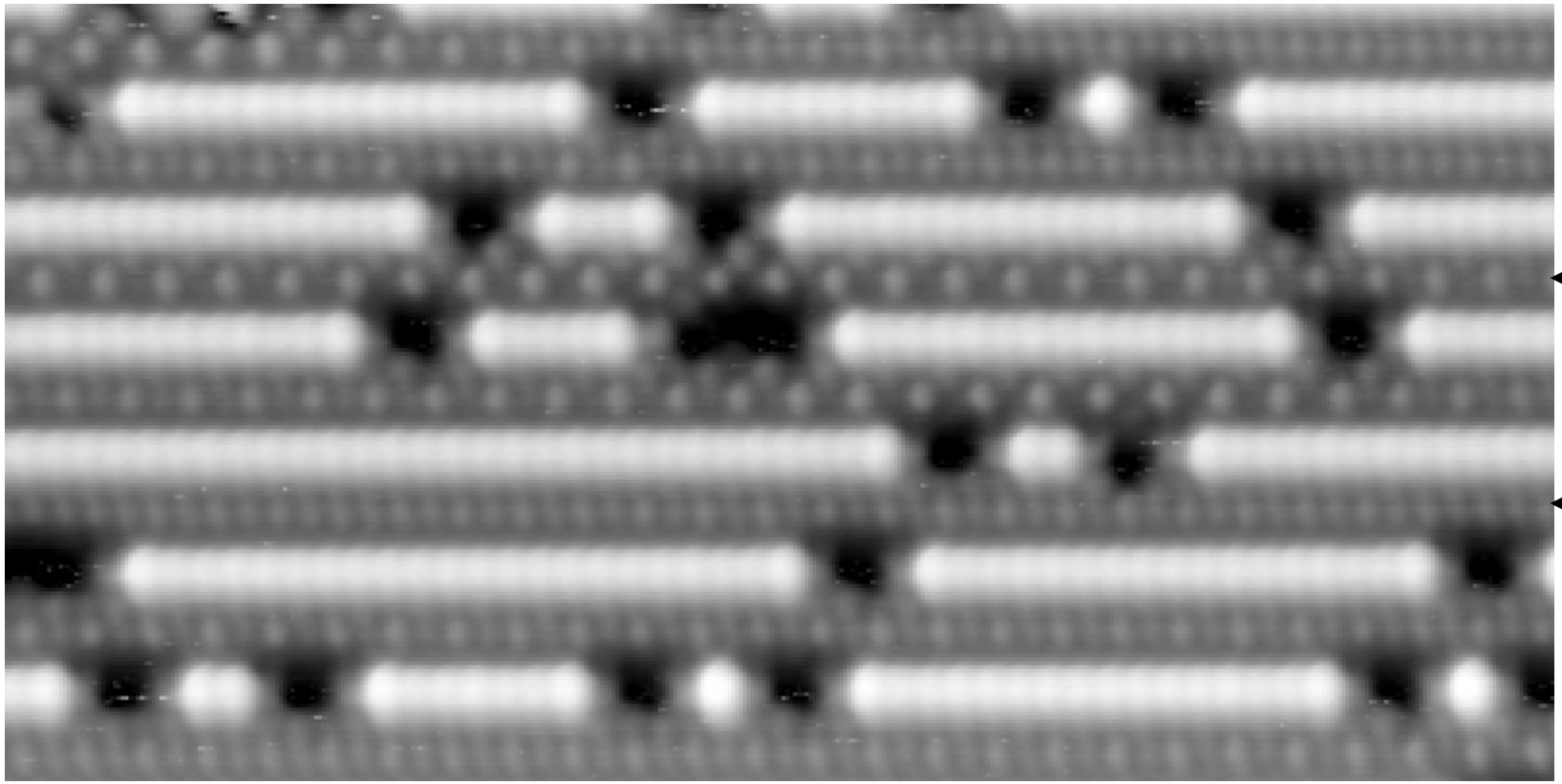
V = -1V, 20x20nm^2
26 defects

After sitting overnight



V = +0.5V, 20x20nm^2
~65 defects

Period Doubling Pinned at Defects



V = +0.5

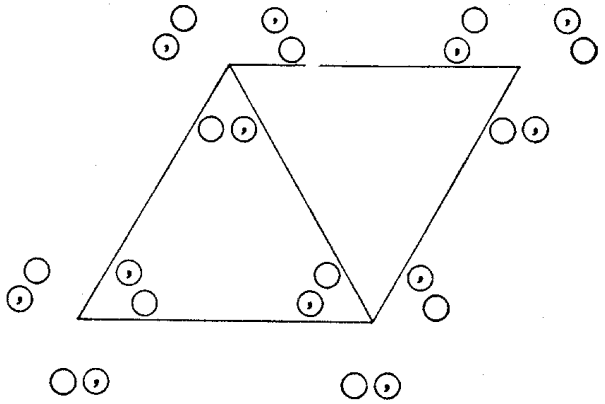
20x10nm^2

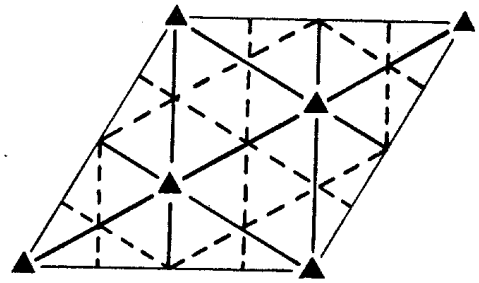
Period doubling visible near defects. No evidence for regular rows of x2 adatoms as was seen for Si(557)-Au.

Theme Menu

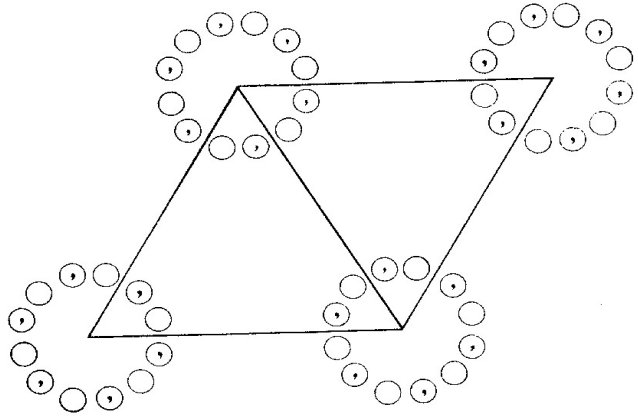
- Au quantum nanowires on Stepped Si
- Au ‘physisorption’ on Si(111)7x7
- Deep subsurface strain in Pt(111)/CO
- ‘Homometric’ structures of Pt(110)1x5

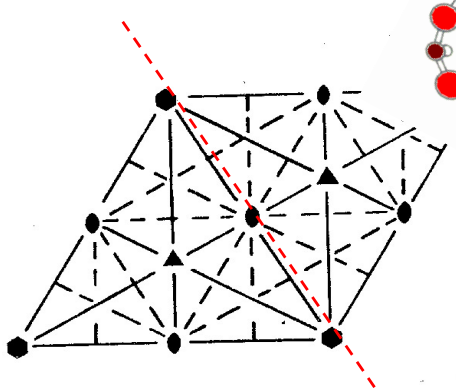
Importance of Symmetry in Si(111)7x7



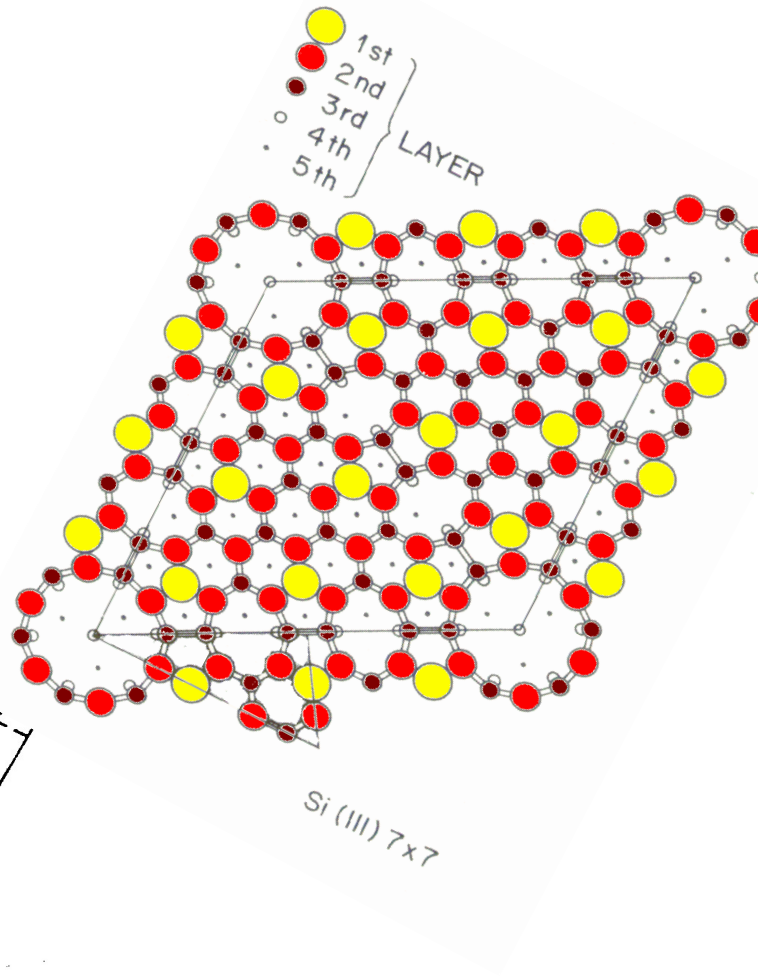


p3m1 → Bulk Symmetry





p6mm → Surface Symmetry



Au physisorption on Si(111)7x7?

Motivation

To study the structure of self assembled metal nanostructures on Si(111)7x7 surface

Adsorption processes of Au on Si(111)7x7 surface

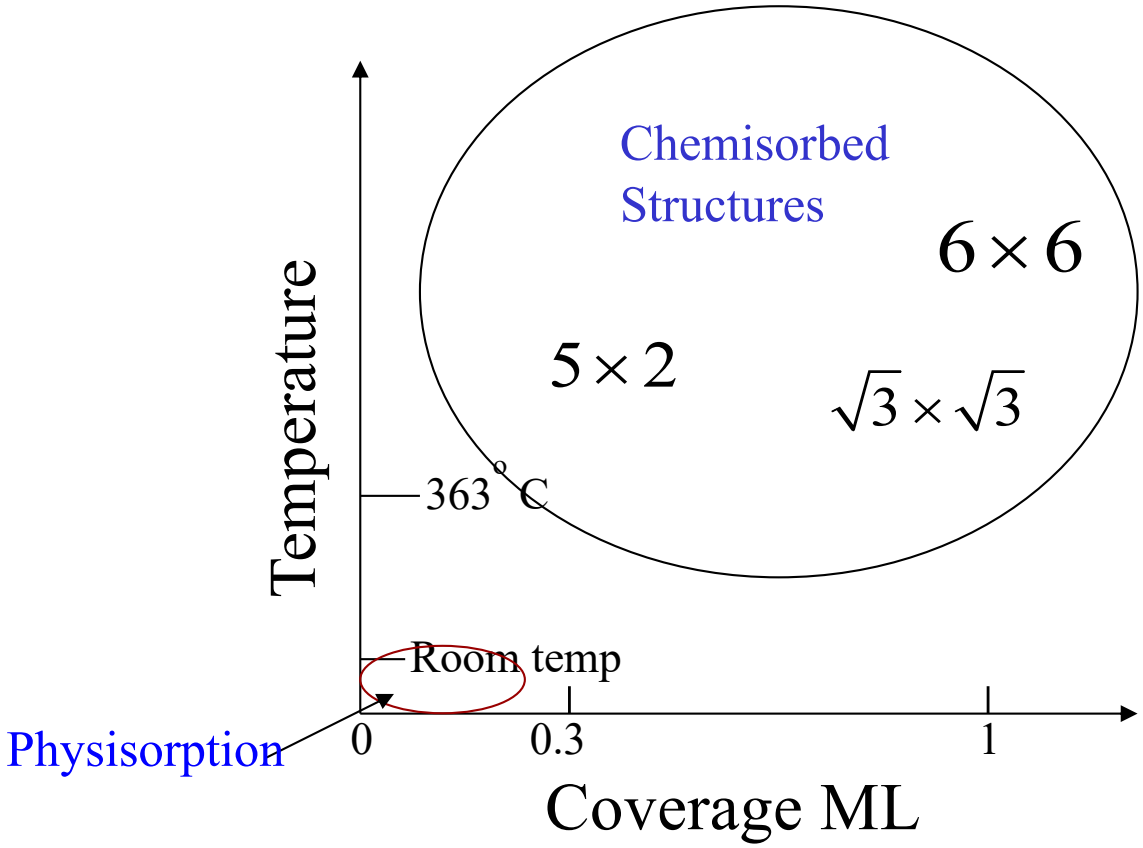
Physisorption (Physical absorption)

Adsorption in which the forces involved are inter-molecular (van der Waals forces), which do not involve a significant change in electronic orbital patterns of the species involved

Chemisorption (Chemical absorption)

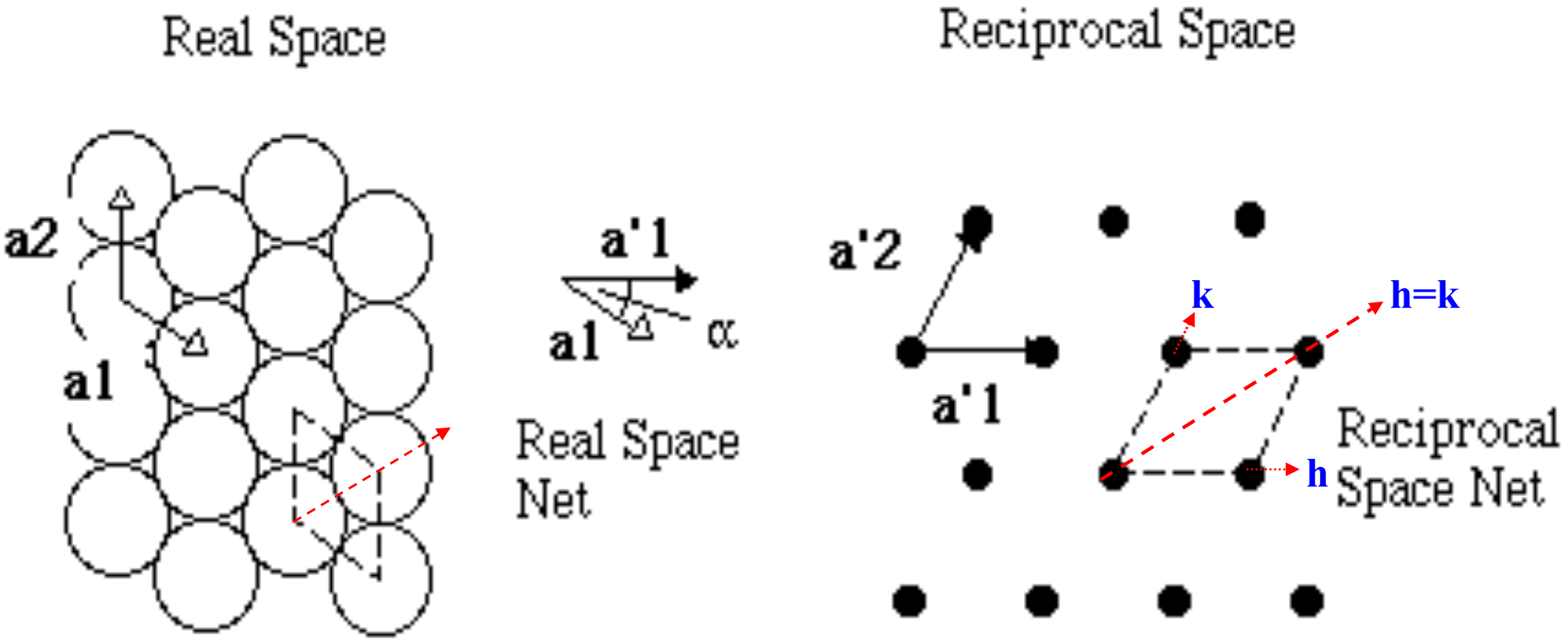
Adsorption in which the forces involved are electronic valence forces of the same kind as those operating in the formation of chemical compounds, i.e., ionic and covalent bonds

Au on Si(111) Phase Diagram



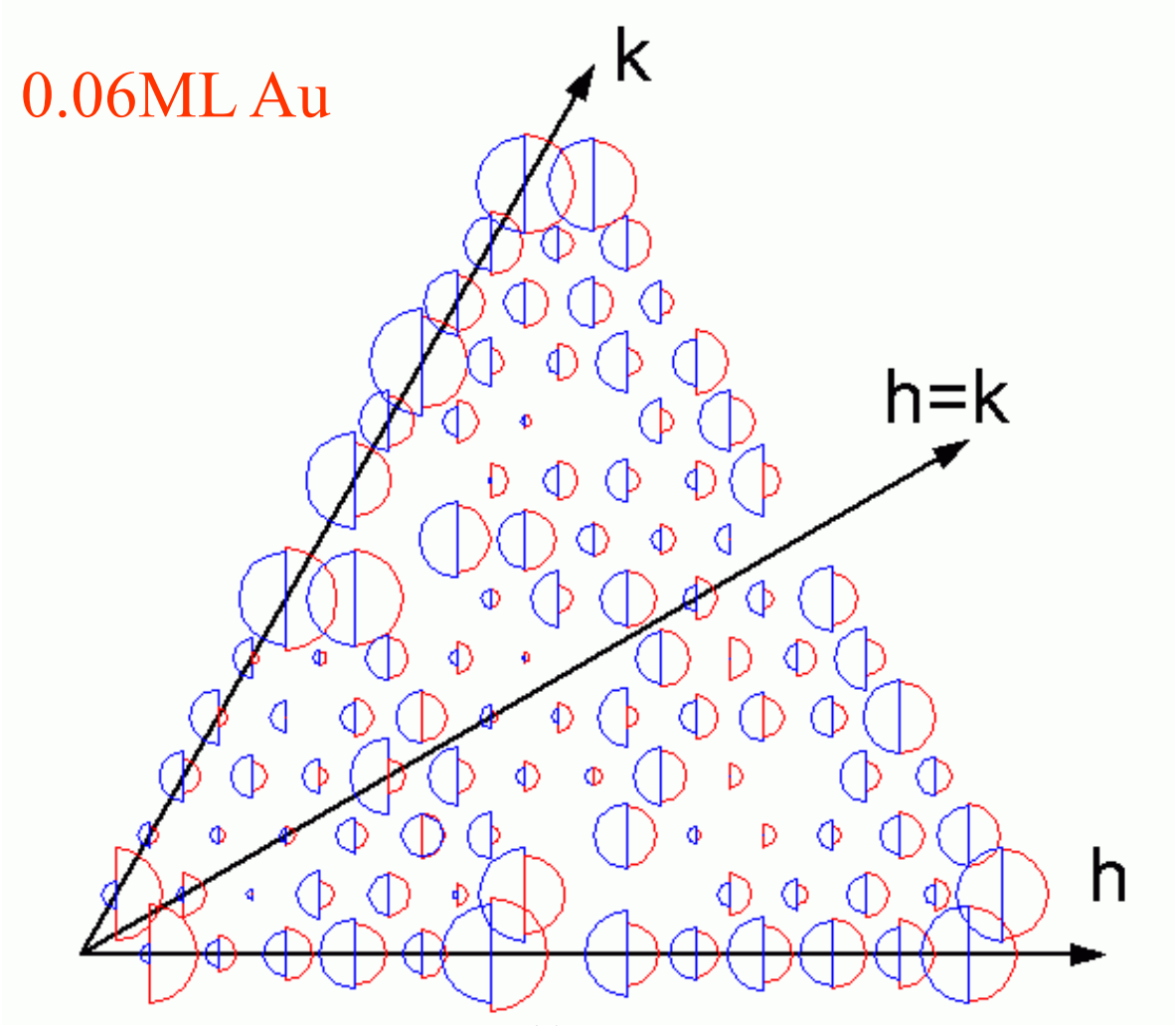
D. Grozea, E. Bengu and L. D. Marks, Surf.Sci. 461, 23(2000)

Surface Symmetry



L=1.5 symmetry breaking

Clean | 0.06ML Au



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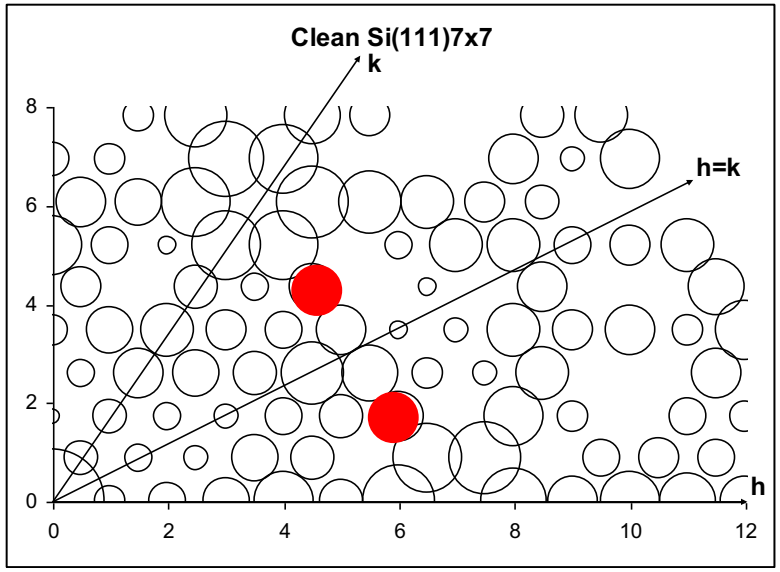
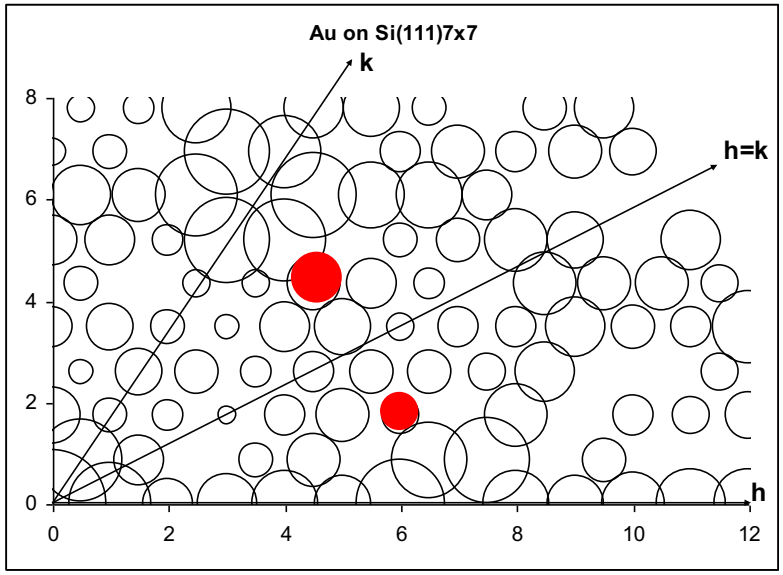
Structure factor data shows p6mm symmetry breaking

Clean Si(111)7x7



0.06 ML Au on -Si(111)7x7

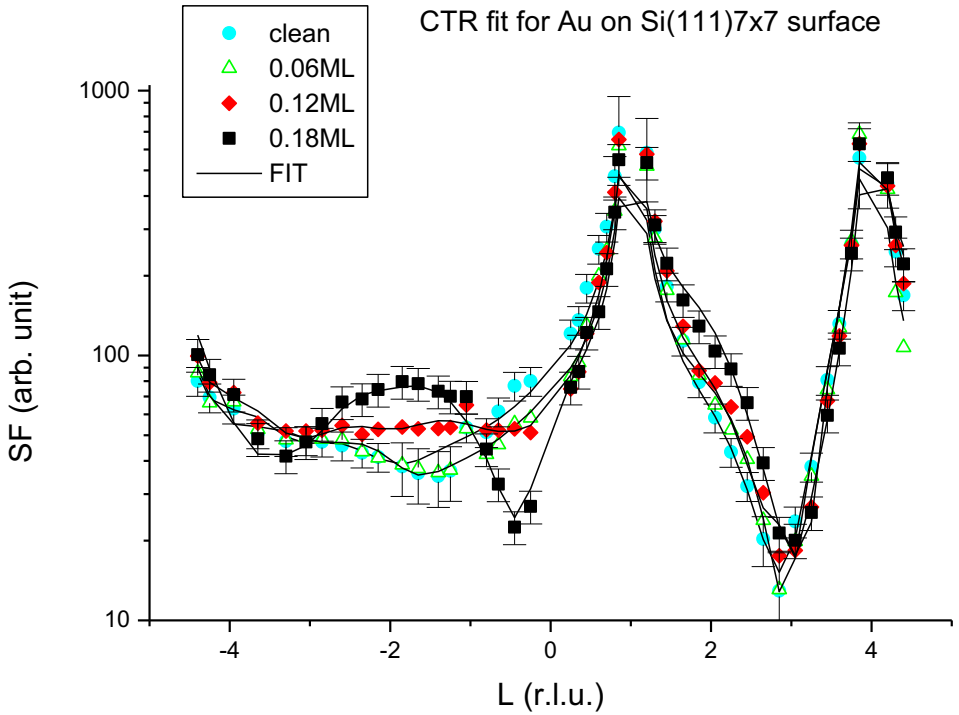


Agreement factor (□) between equivalent reflections (L = 1.5) averaged assuming P3m1 and P6mm symmetry

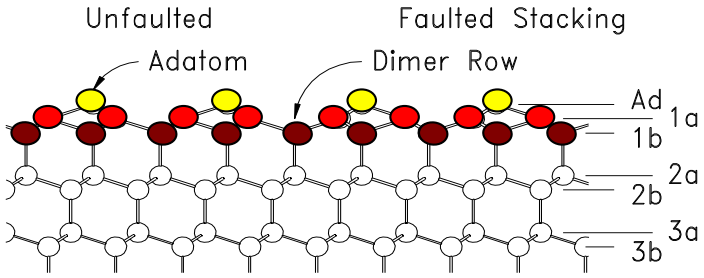
Sample Type	Agreement factor (□) P3m1	P6mm
clean	0.061	0.076
Au-0.06 ML	0.079	0.156
Au-0.12 ML	0.059	0.110
Au-0.18 ML	0.056	0.079

CTR's vs Au coverage

(10L) CTR for different coverage of Au

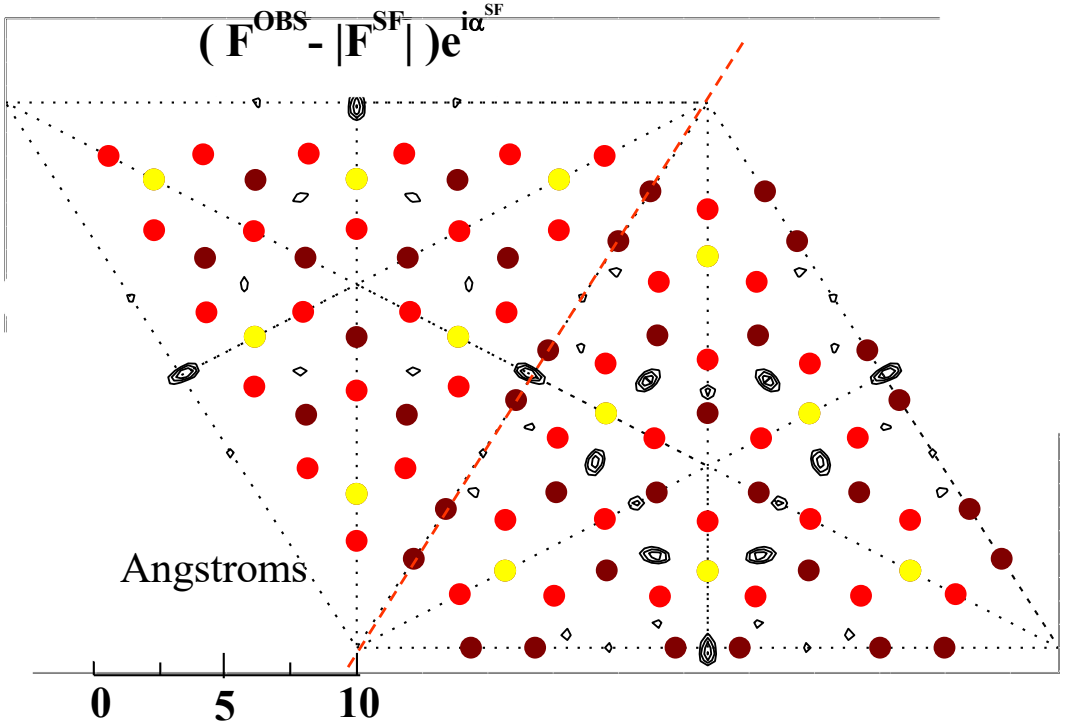


Model "1x1"



- Best fit obtained with two Au atoms positions
- Occupancy of Au atom increases for higher coverage Au
- CTR fit gives the z-positions of Au atoms

Real Space 3D-Density Difference Map



$$\rho_{xyz}^{obs} = \sum_{hkl} (|F_{hkl}^{obs}| - |F_{hkl}^{c}|) e^{i\alpha_{hkl}^{c}} \exp(-2\pi(hx + ky + lz))$$

z~ adatom height

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Cho & Kaxiras Surf. Sci. 396 L261 (1988)

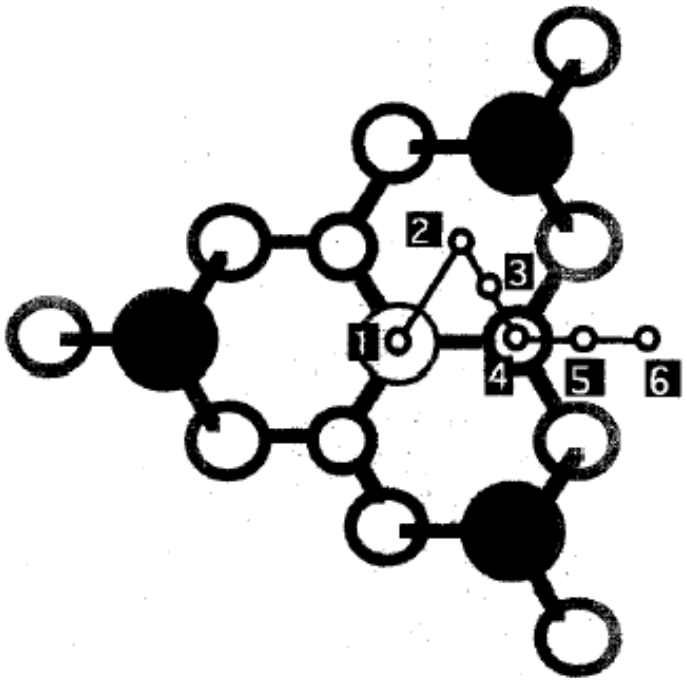

Fig. 1. Schematic top-view representation of a portion of the Si(111) reconstruction containing three Si adatoms (large black circles) and one rest-atom (grey circle) as well as the substrate atoms directly bonded to those (smaller open circles). The sites where the adsorbate atoms are placed are indicated by the numbers 1–6. These sites are used for the energy plots in Fig. 2.

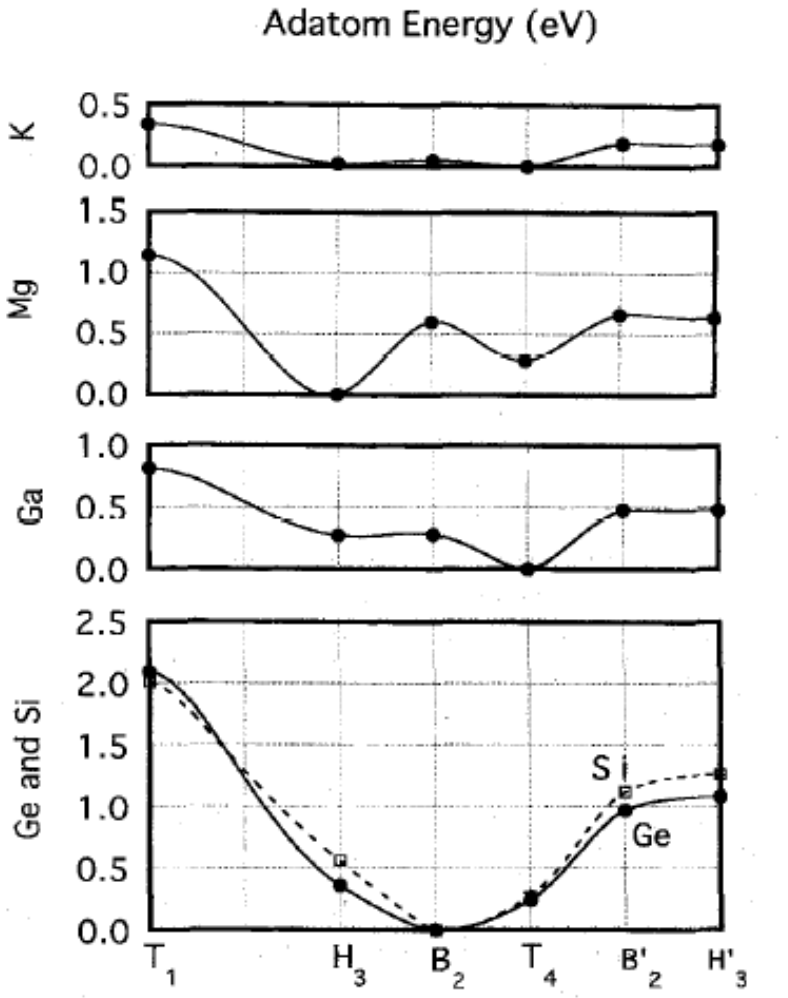

Fig. 2. Plots of the adsorbate atom energies along the six sites defined in Fig. 1 (from left to right the six sites are T_1, H_3-type, B_2-type, T_4-type, B_2'-type and H_3'-type). The energies are relative to the lowest energy sites for each adsorbate atom (see Table 1).

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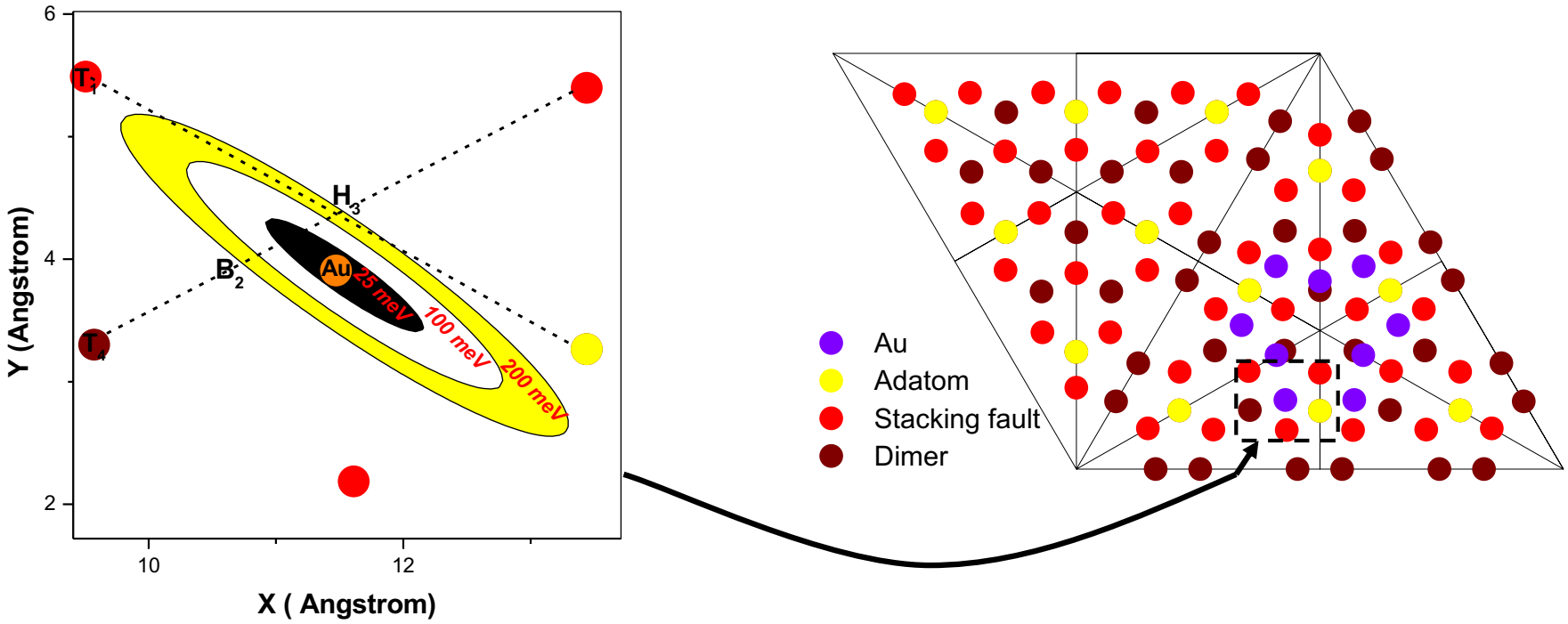
Potential from Anistropic DWF

One Particle Potential $V(x,y) = - k_B T [\text{Log} \{ \text{FT (DWF)} \}]$
$= -25.84 [\text{Log} \{ \text{FT (DWF)} \}]$ meV at 300 K

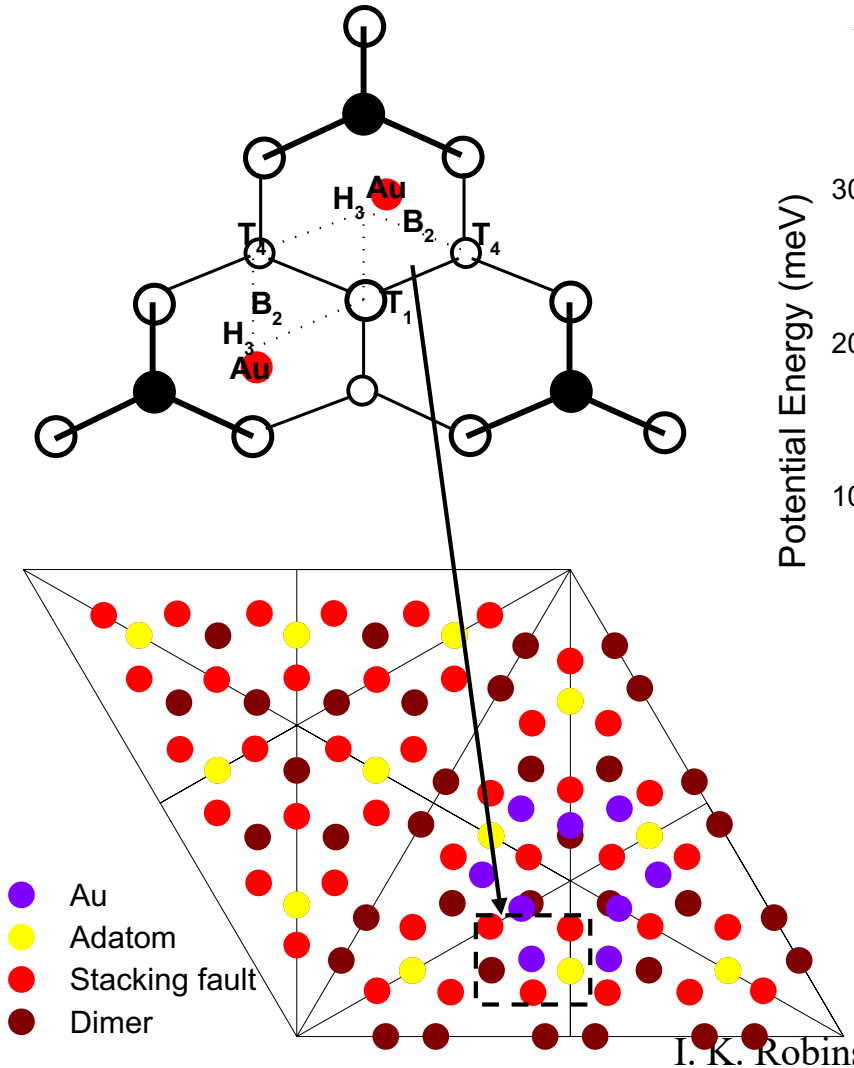
Potential Energy within Basin of Attraction



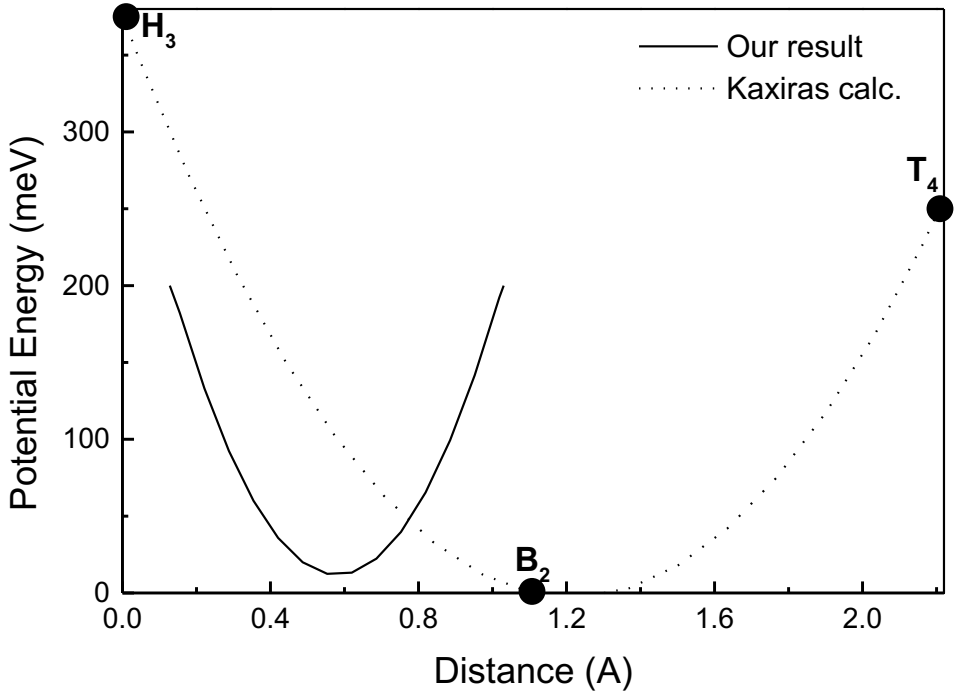
H. L. Meyerheim, I. K. Robinson and R. Schuster, Surf. Sci., 370,268(1997)

Comparison with Theory

Basin of Attraction



Potential Energy within Basin of Attraction

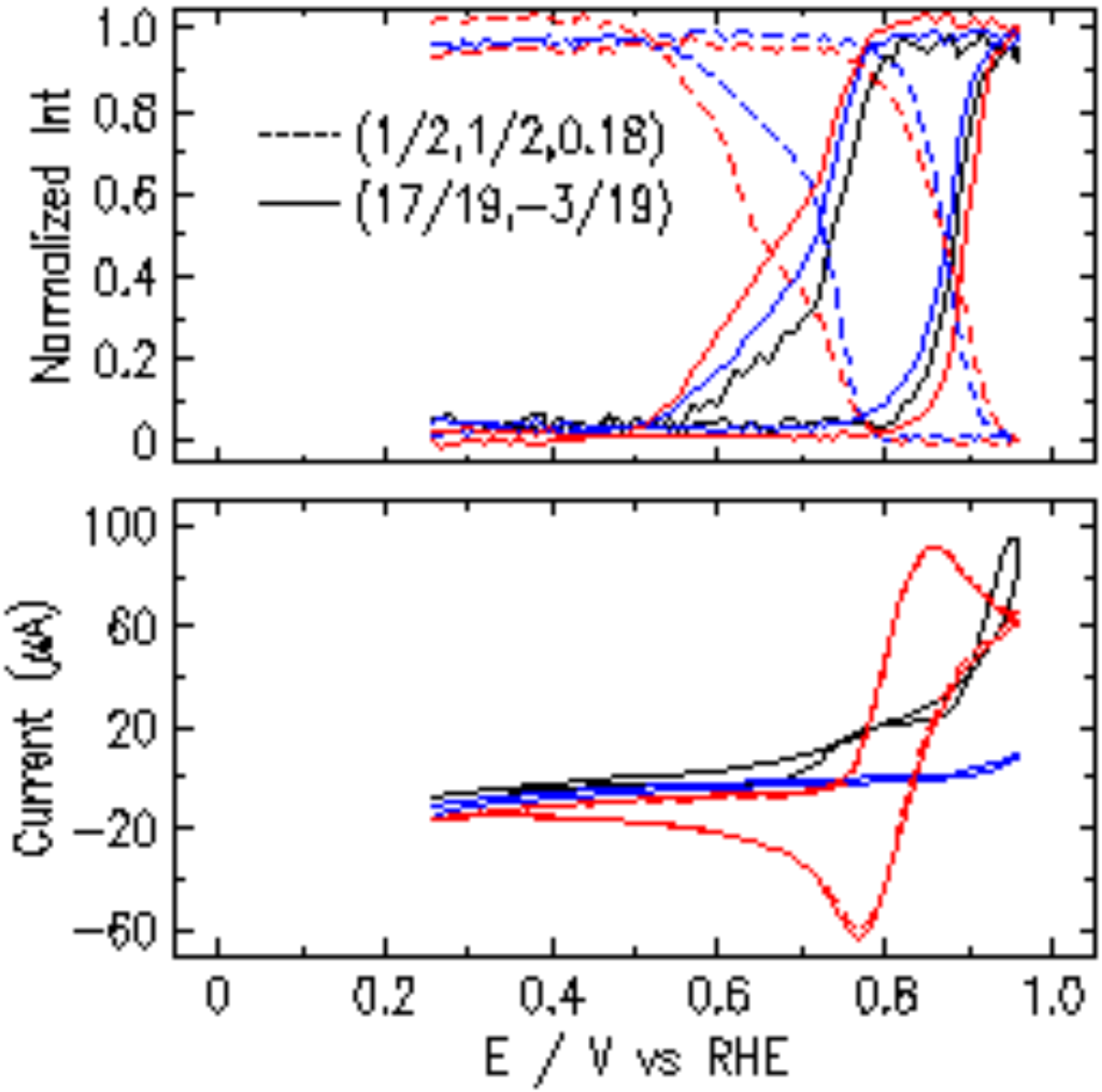


Kyeongjae Cho and Efthimios Kaxirax, Surf. Sci, 396, L261(1998)

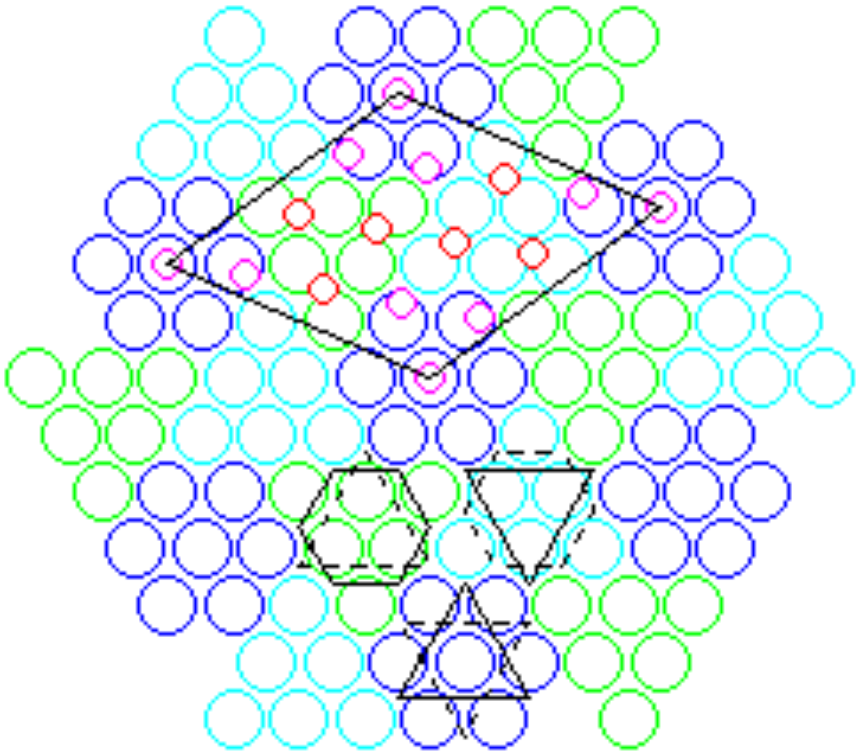
Theme Menu

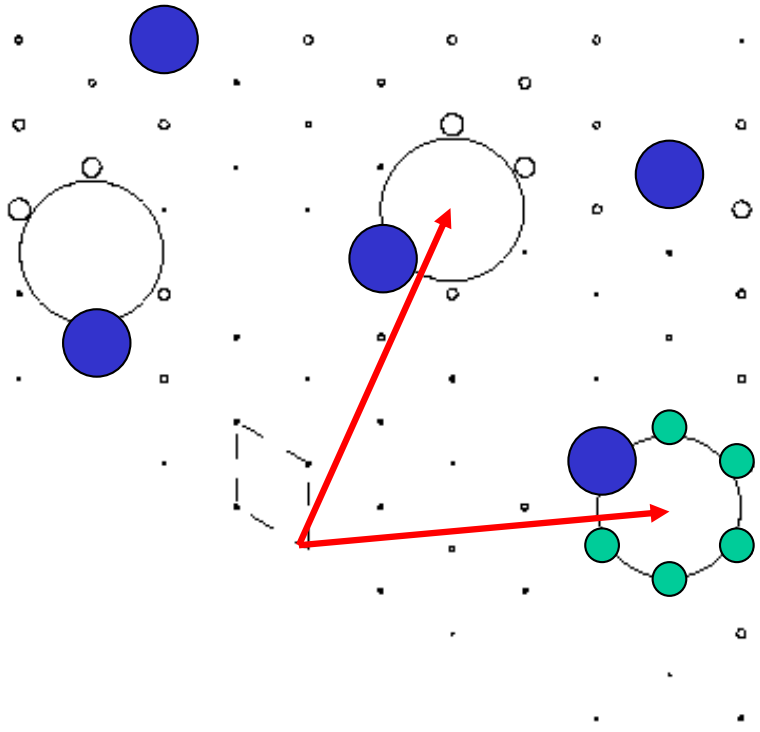
- Au quantum nanowires on Stepped Si
- Au ‘physisorption’ on Si(111)7x7
- Deep subsurface strain in Pt(111)/CO
- ‘Homometric’ structures of Pt(110)1x5

CO dissolved in $HClO_4$ on Pt(111)

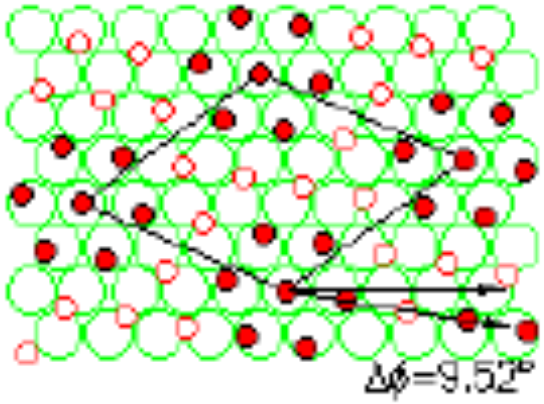


CO reciprocal lattice, rt19

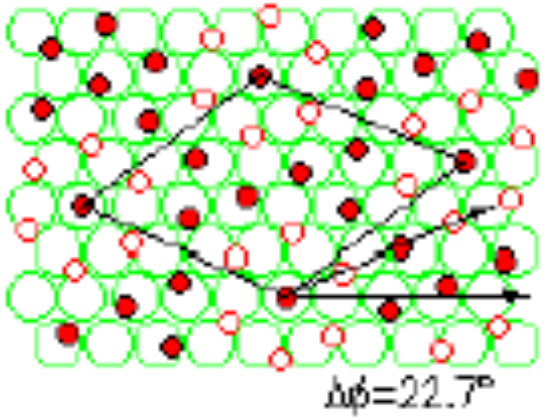




Two inequivalent packings of 13 CO's into rt(19) Pt(111) cell

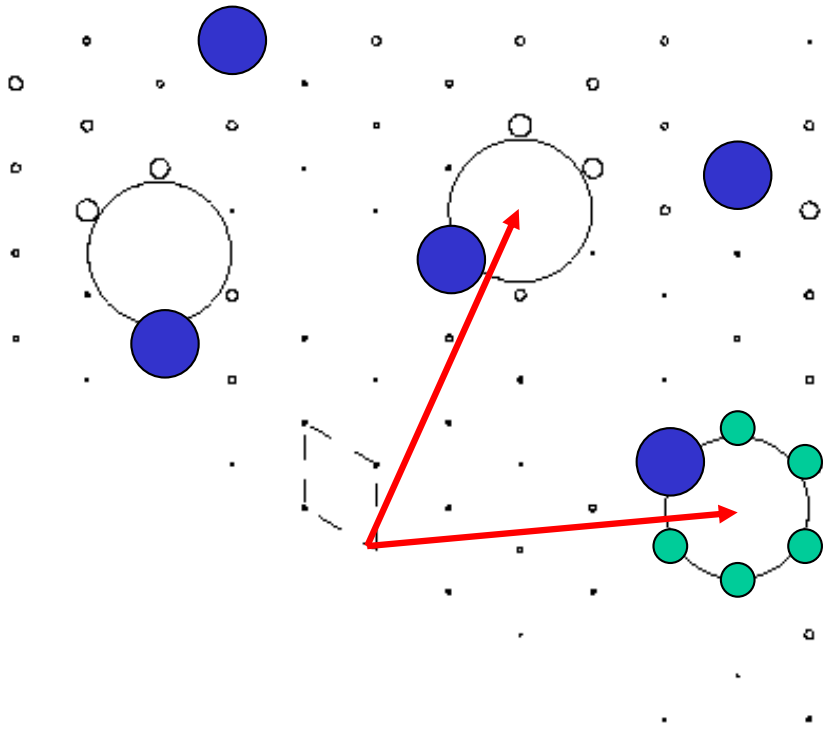


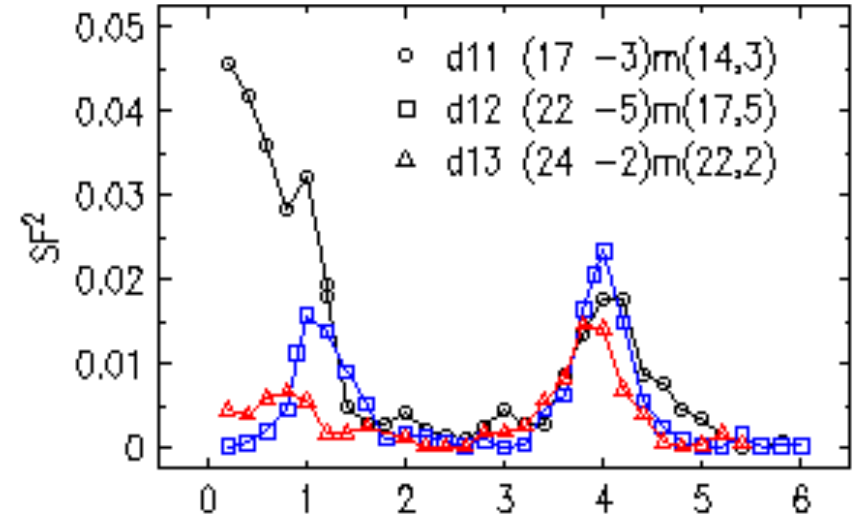
This 'patch' model is the only one observed, by the CO peak positions

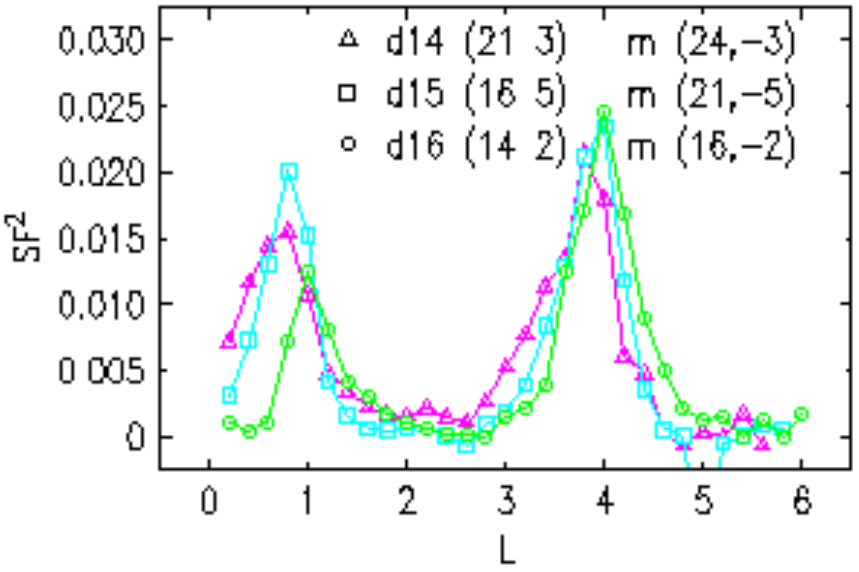


This 'ring' model is not seen.

rt19×rt19 CO/Pt(111)

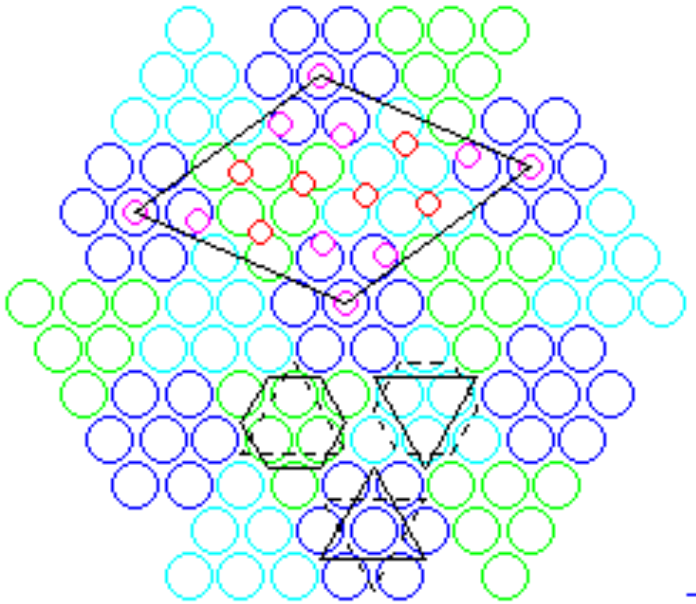


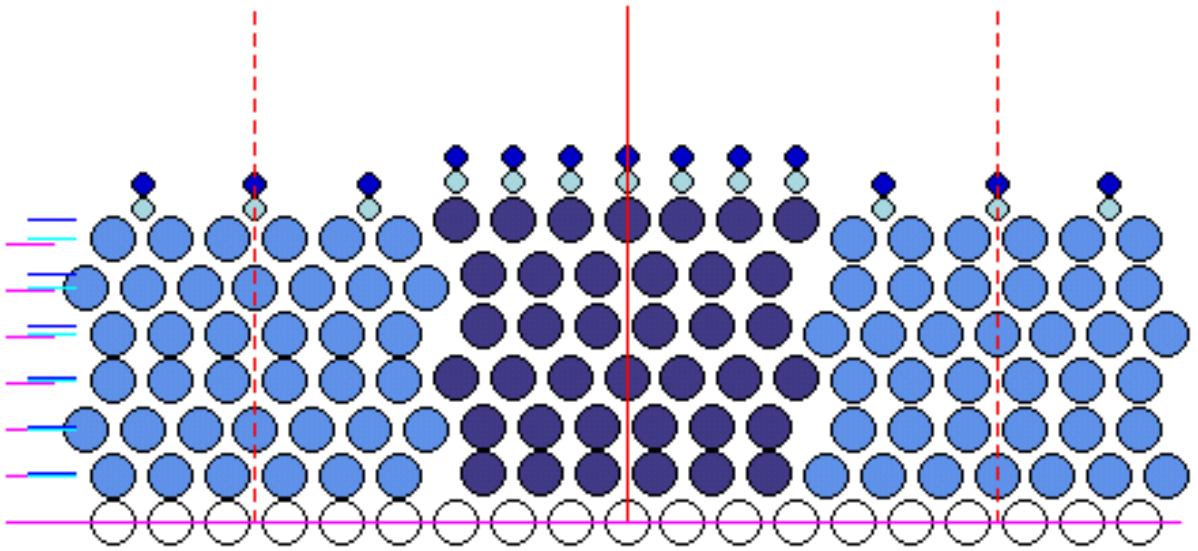




I. K. Robinso

Top and Side Views of Model





Depth=1.8 layers

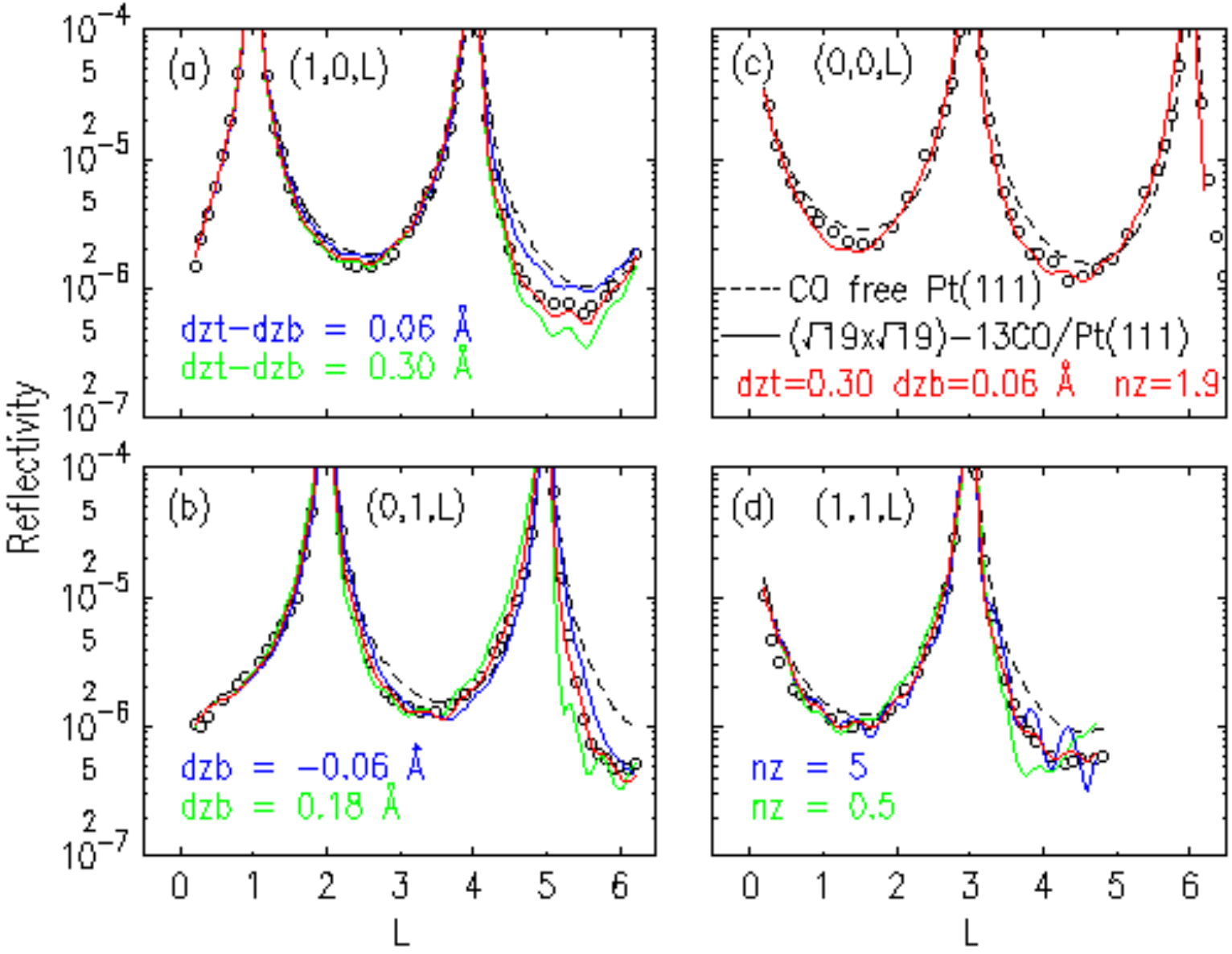
D_7=0.28 A

D_{6+6}=0.04 A

σ_{CO}=0.3 A

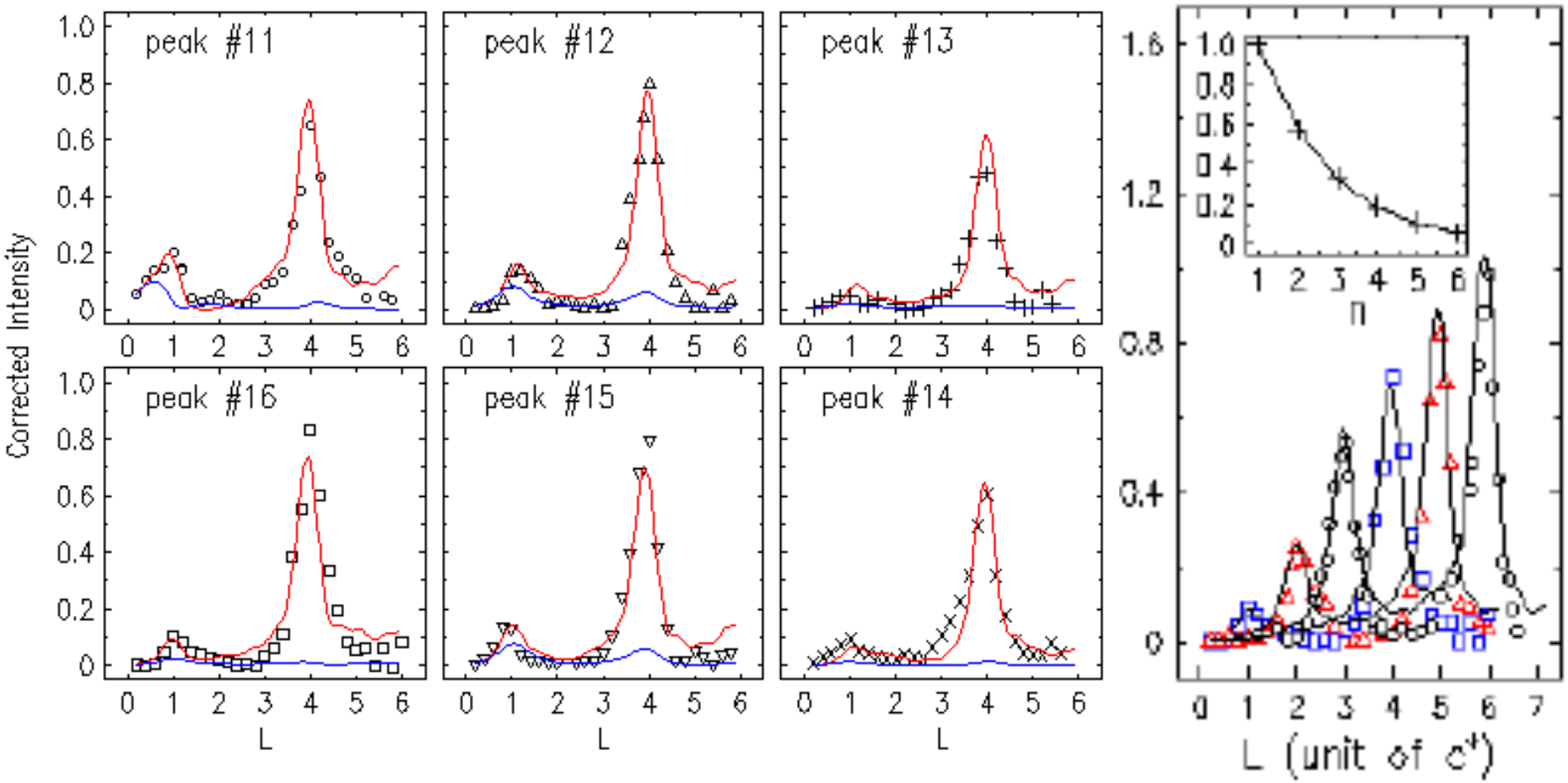
Fit of Model to CTR Data

Dashed curve is clean Pt(111)



Fit of Model to Rt19 Data

Blue line has vertical relaxations turned off



I. K. Robinson MPI-Stuttgart

Theme Menu

- Au quantum nanowires on Stepped Si
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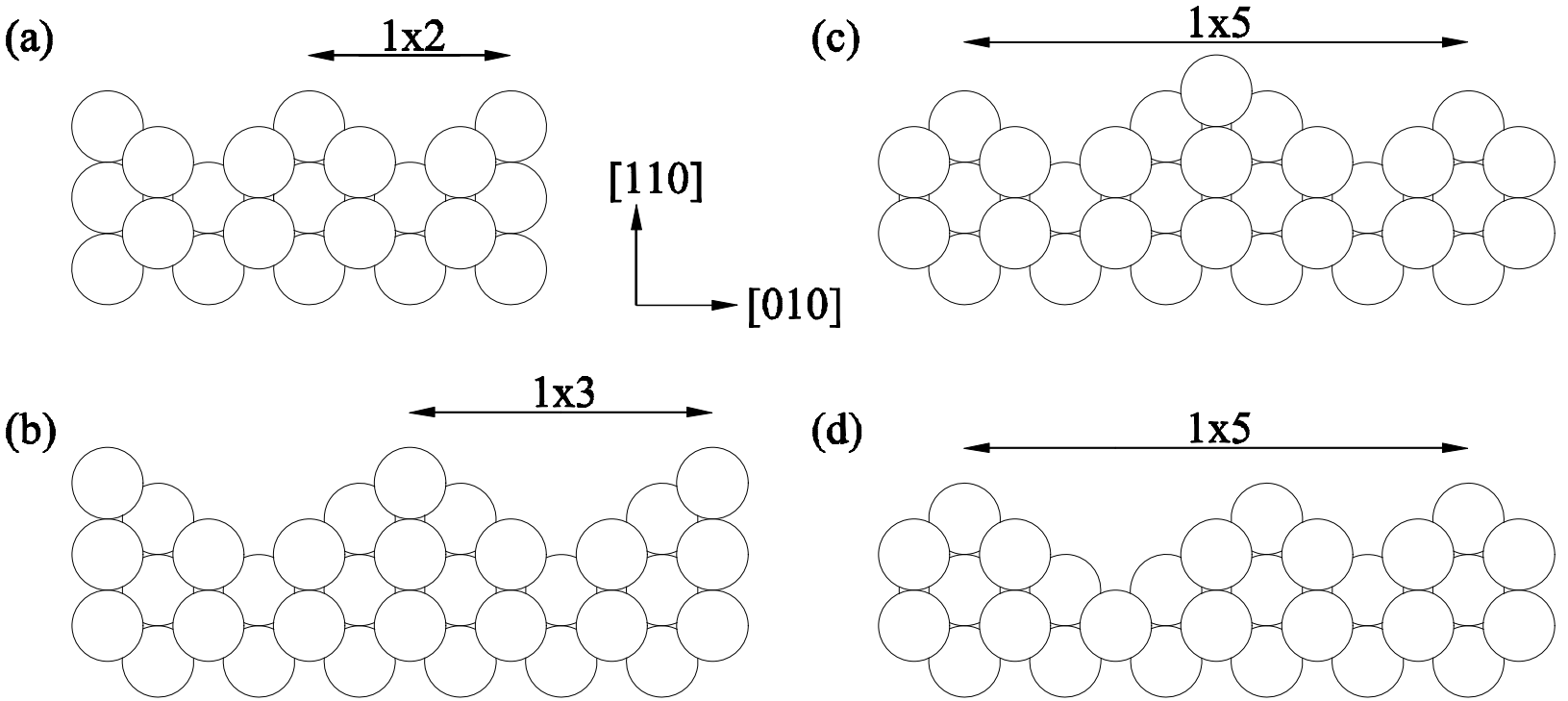
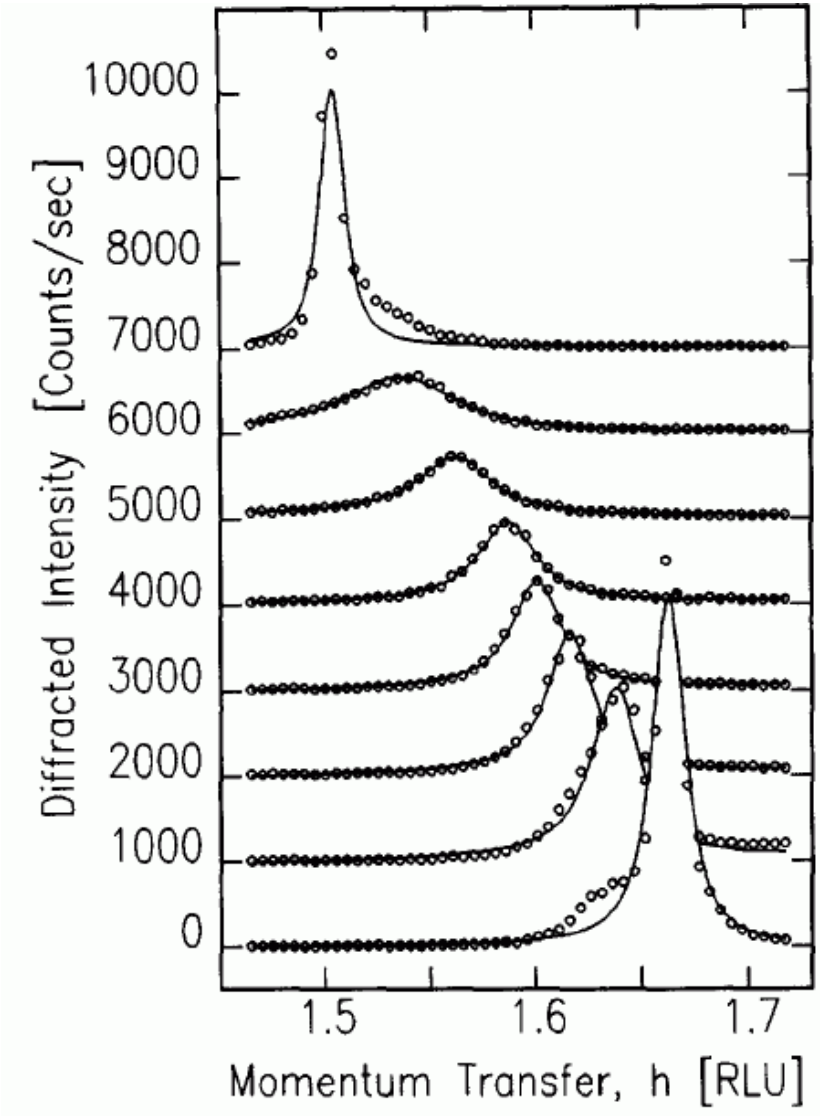
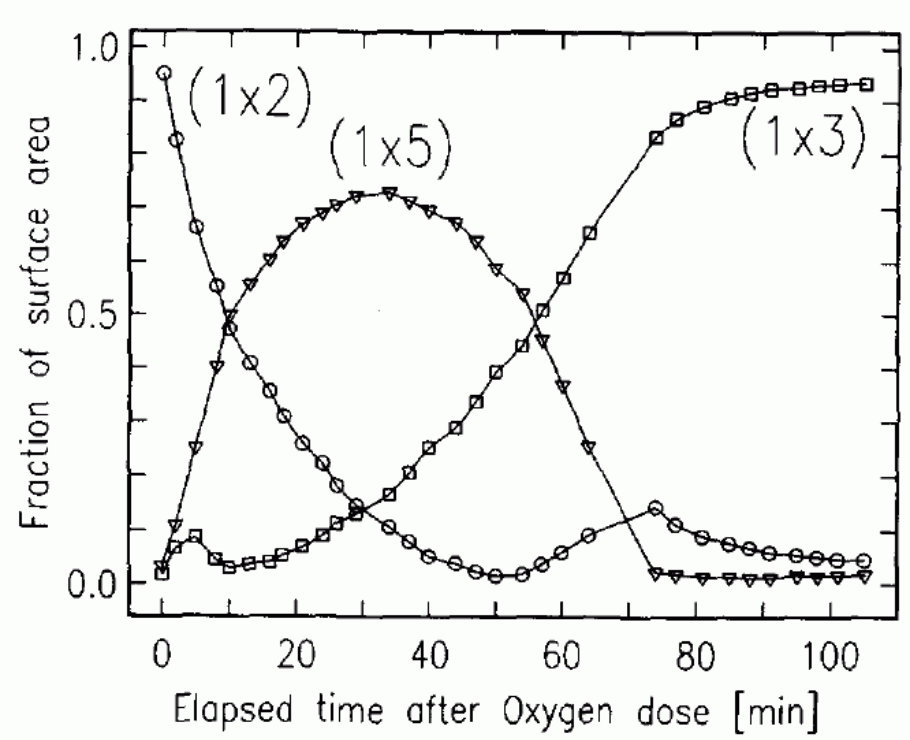
Missing Row structure of FCC(110)



Pt(110) during heating at 600C

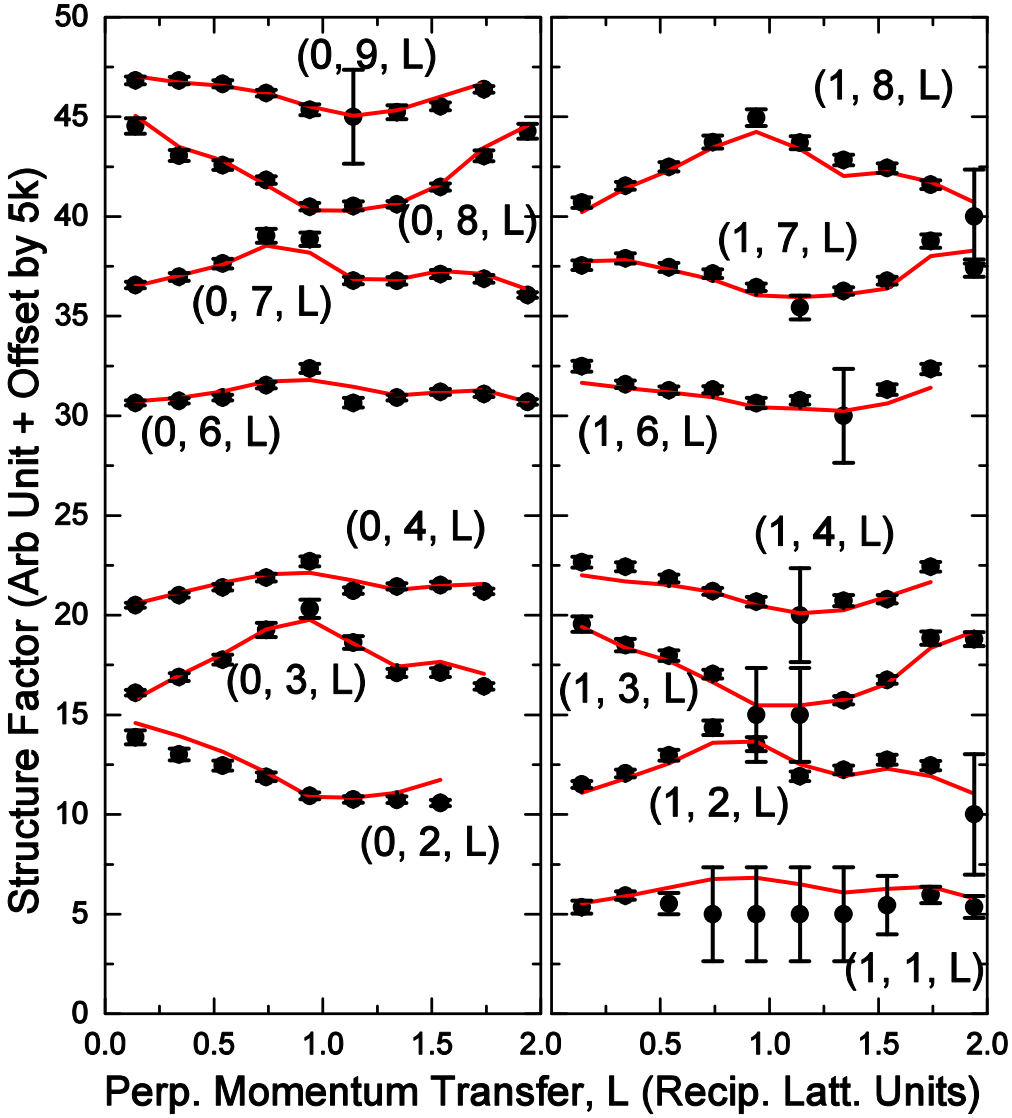
Accompanied by segregation of Carbon

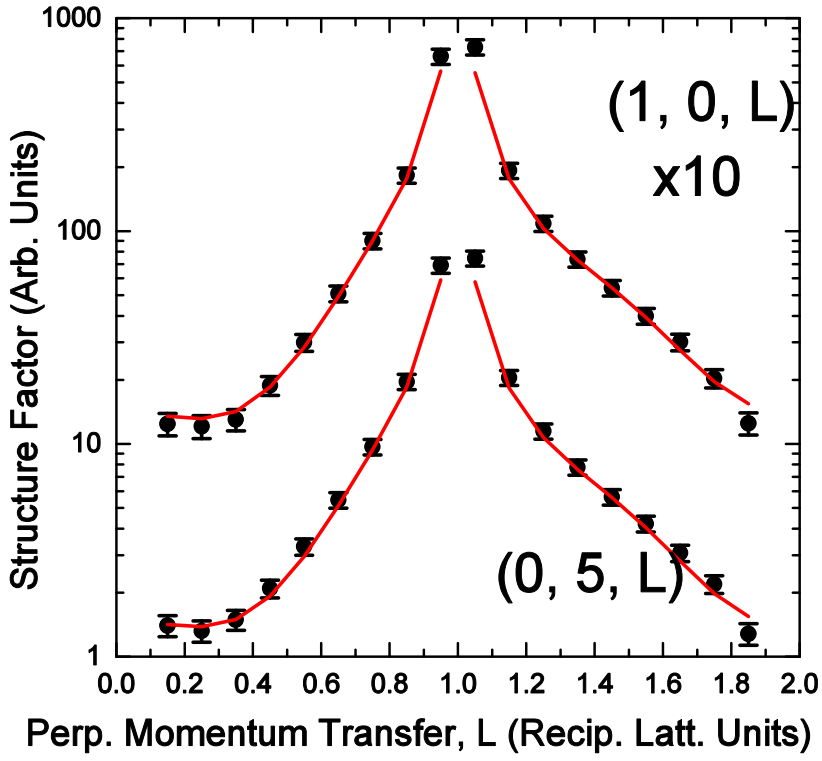




I. K. Robinson, P. J. Eng, C. Romainczyk and K. Kern, Surf. Sci. **367** 105-112 (1996)

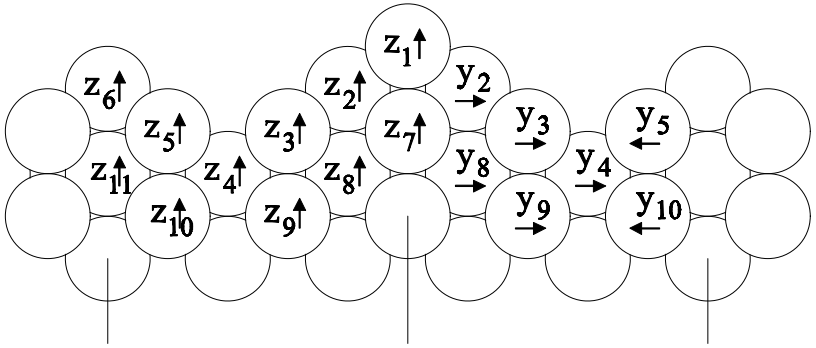
BM32 measurements of Pt(110)1x5



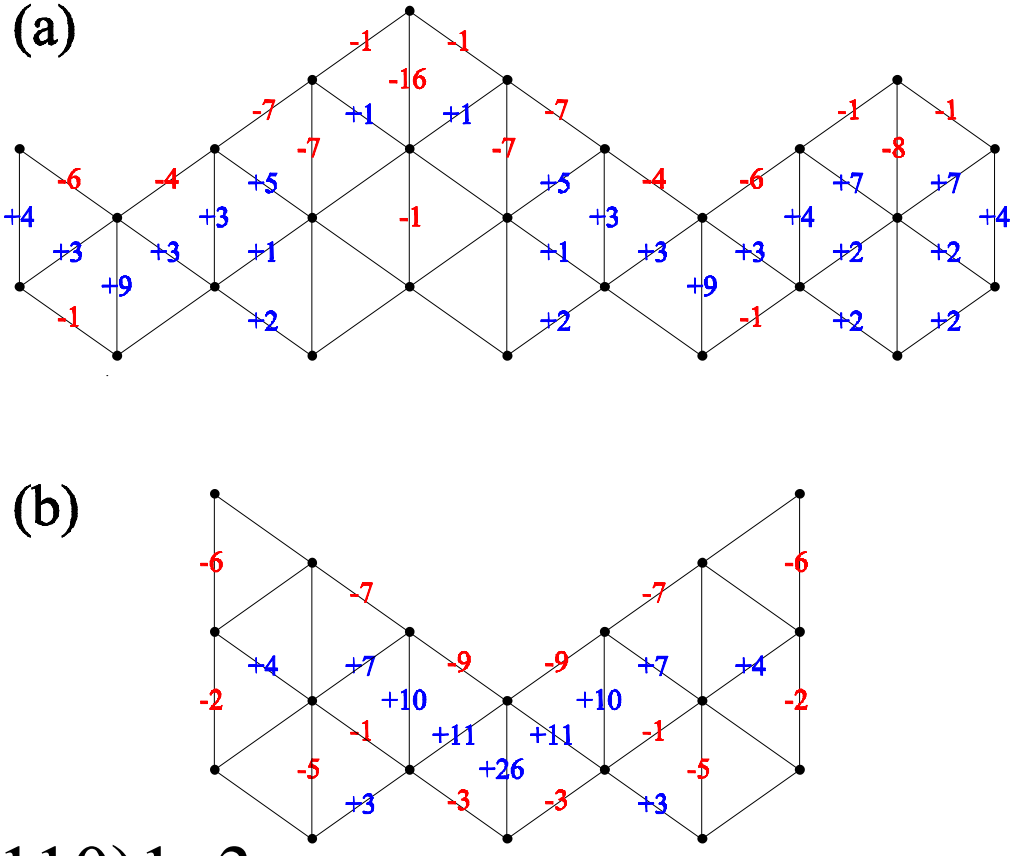


Displacements in final model

Pt(110)1x5 “hill” model



Chisq=2.7
90% hill, 10% valley
7% “1x1”



Pt(110)1x3

Conclusions

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- Au ‘physisorption’ on Si(111)7x7
- Deep subsurface strain in Pt(111)/CO
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