Uniqueness of Surface Crystallographic Structure Solutions

I. K. Robinson
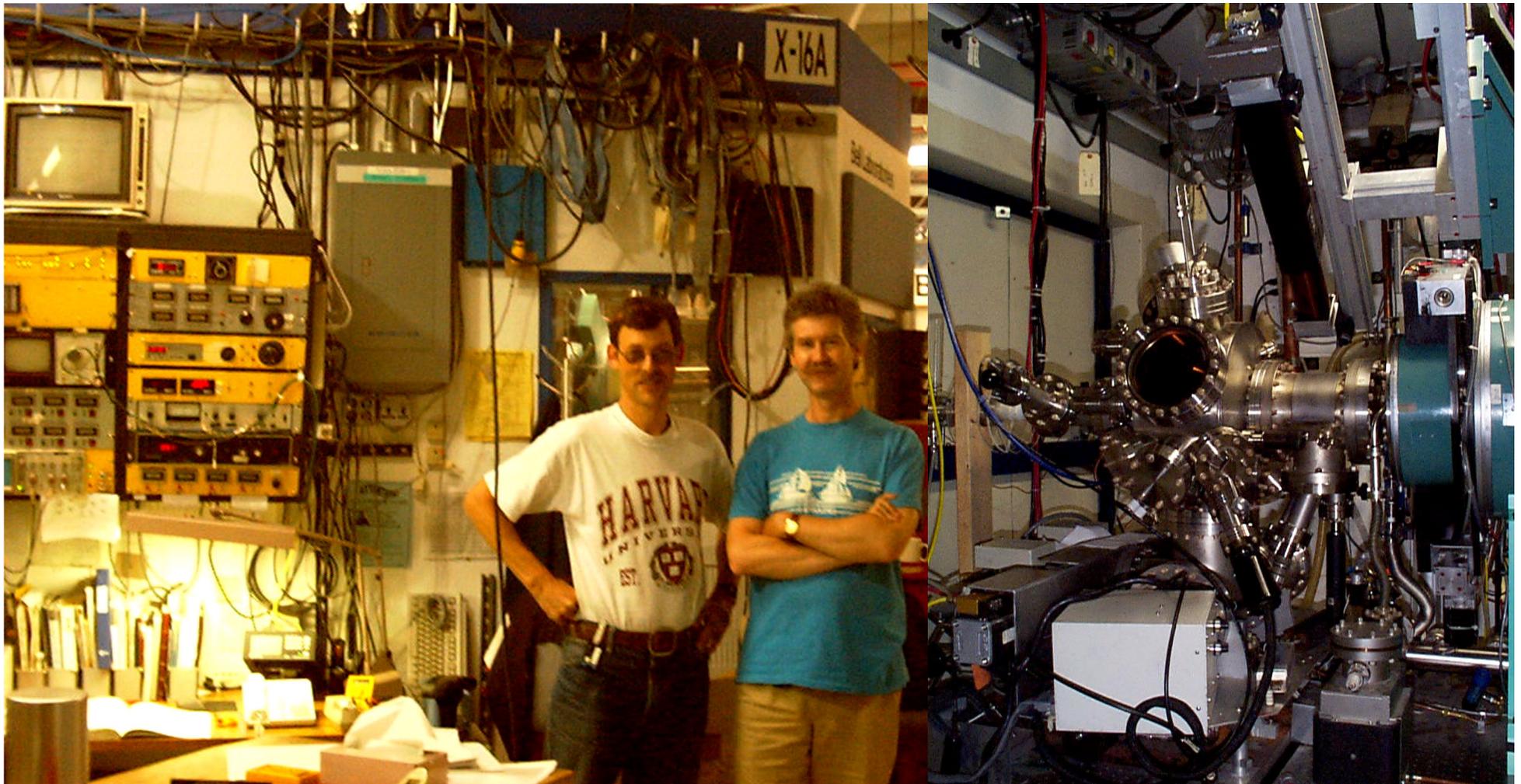
University of Illinois

APS Workshop on In-Situ Characterization of Surface and Interface Structures and Processes

September 2005

X16A Surface X-ray Diffraction
operating since 1987 …

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Homometric structures

$$F(Q) = F_1(Q)F_2(Q)$$

$$I(Q) = |F_1(Q)|^2|F_2(Q)|^2$$

$$F_j(Q) = \int \rho_j(x)e^{iqx}\,dx$$
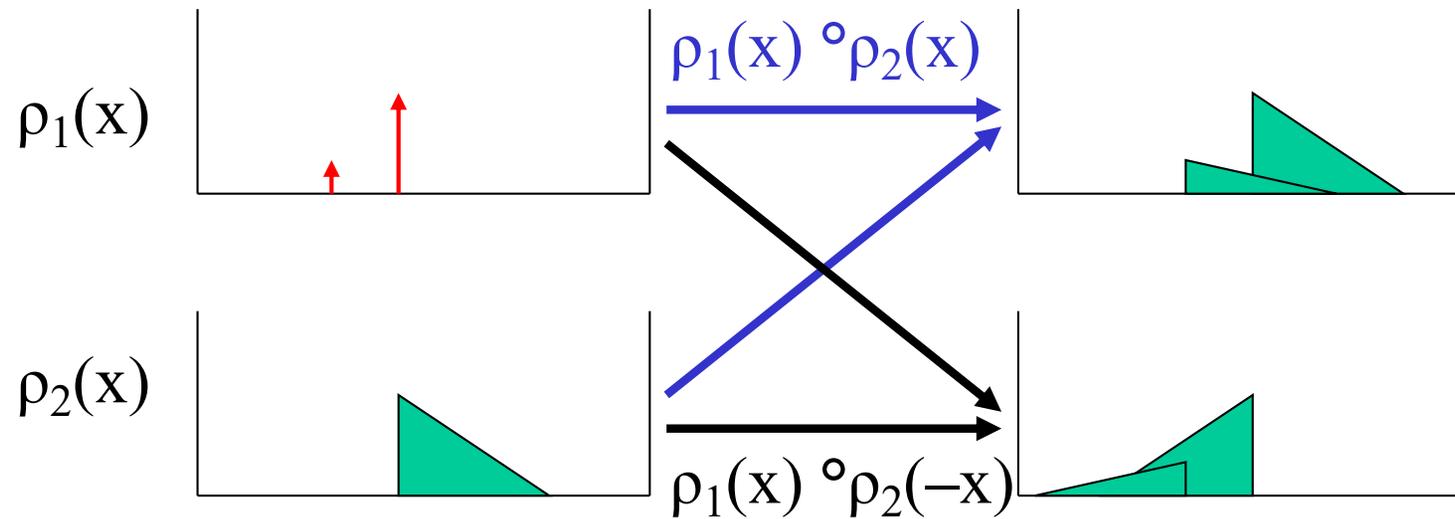
$$F_j^*(Q) = \int \rho_j(-x)e^{iqx}\,dx$$

$$I(Q) = |\int \underline{\rho_1(x) \circ \rho_2(x)}e^{iqx}\,dx|^2$$

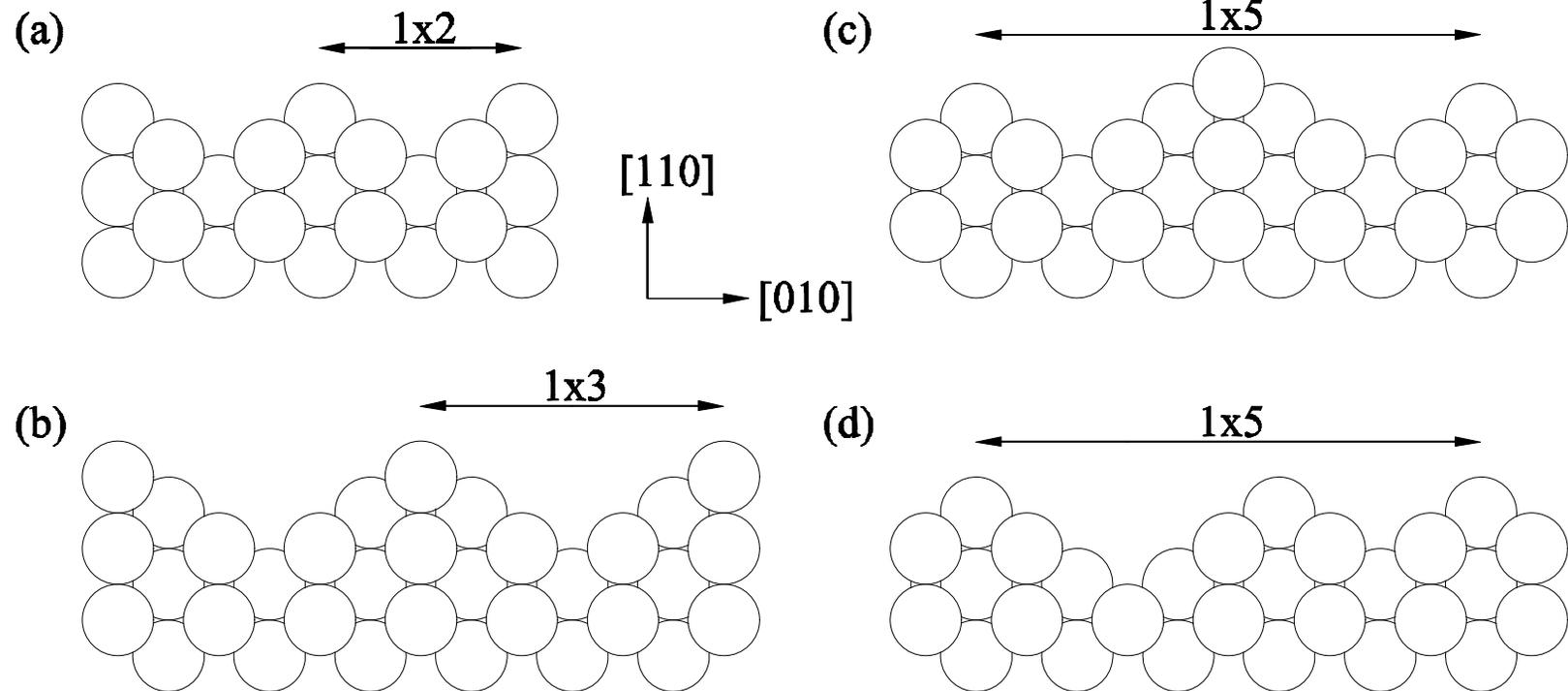$$I(Q) = |\int \underline{\rho_1(-x) \circ \rho_2(x)}e^{iqx}\,dx|^2$$

Identical diffraction from two structures whenever the structure factor is factorizable

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Homometric structures II

Convolution of two structures without mirror symmetry

$\rho_1(x)$

$\rho_2(x)$

$\rho_1(x) \,{}^{\circ}\rho_2(x)$

$\rho_1(x) \,{}^{\circ}\rho_2(-x)$

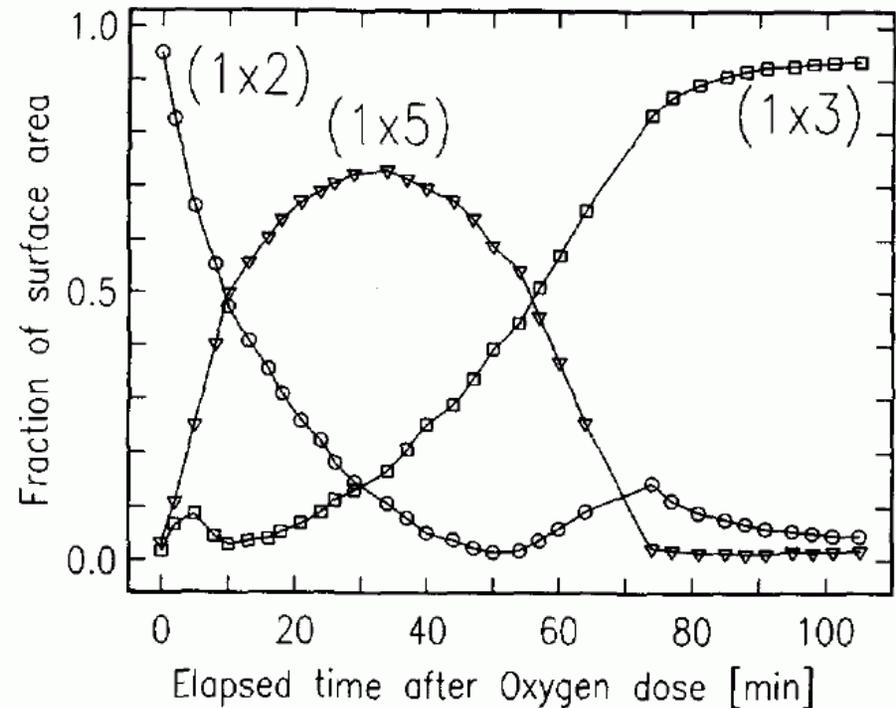# Missing Row structure of FCC(110)

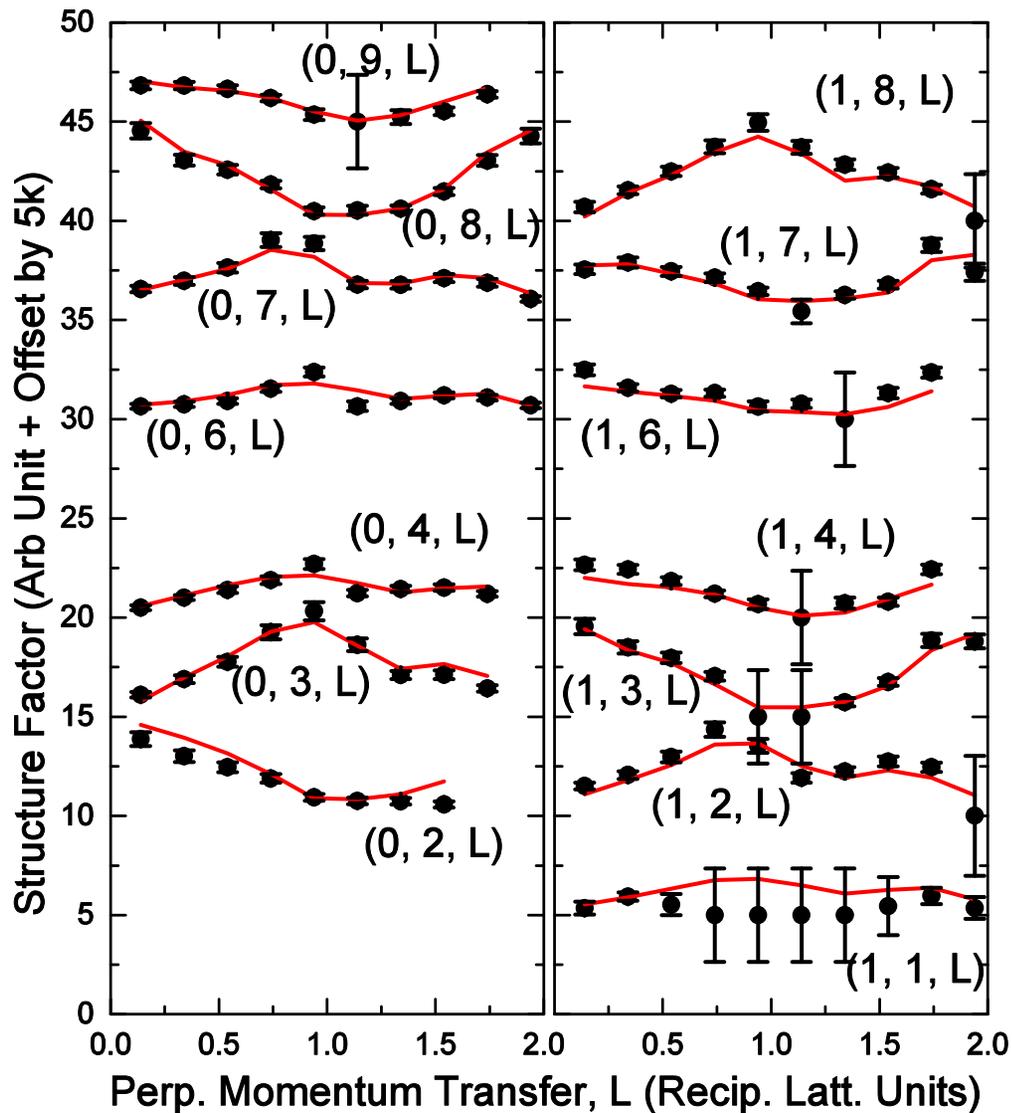(a)

1x2

(c)

1x5

[110]

[010]

1x3

(b)

(d)

1x5

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Pt(110) during heating at 600C

Accompanied by segregation of Carbon
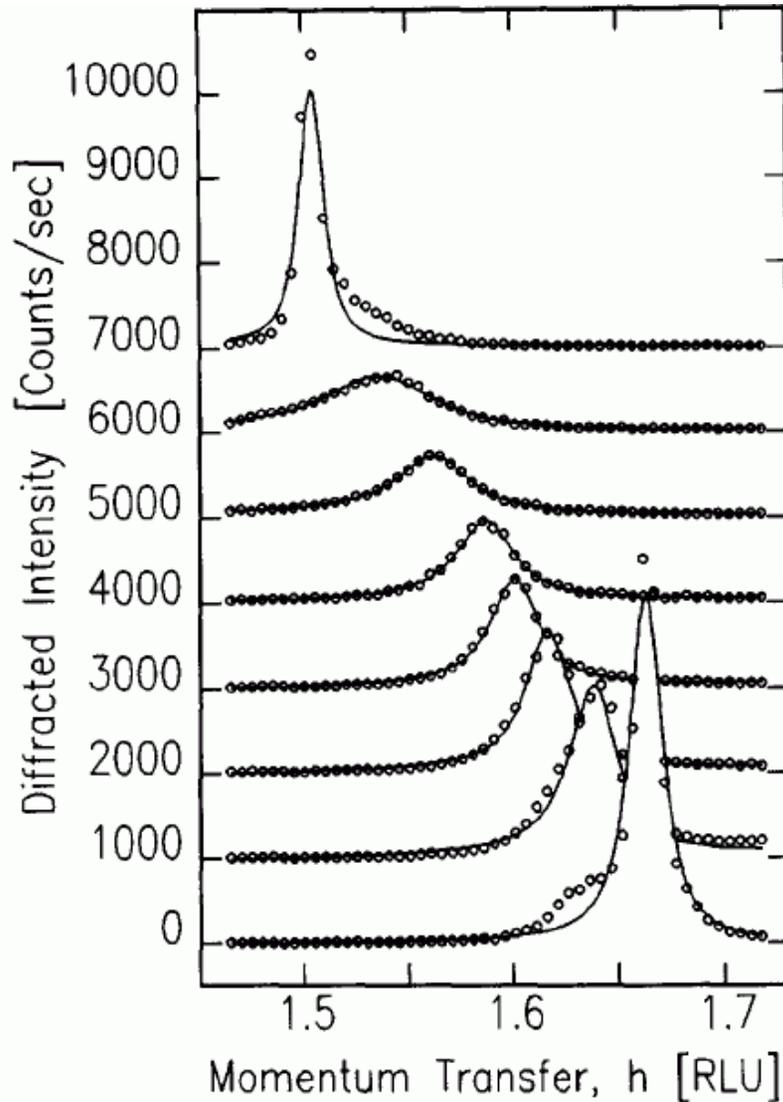
son APS-SI workshop

BM32 measurements of Pt(110)1x5
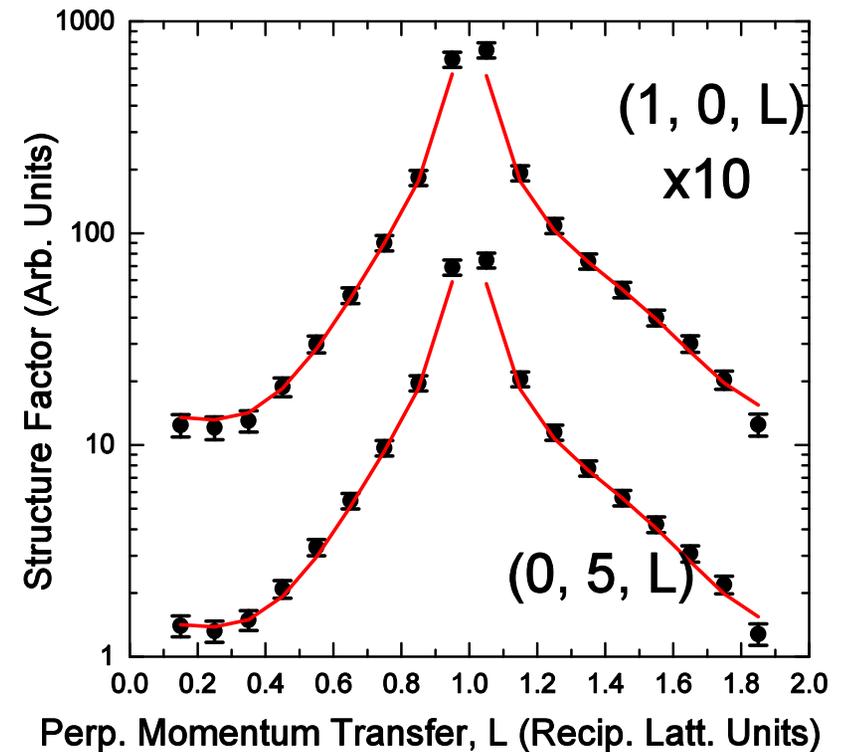
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Missing Row structure of FCC(110)

(a)

1x2

(c)

1x5

[110]

[010]

(b)

1x3

(d)

1x5

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Displacements in final model
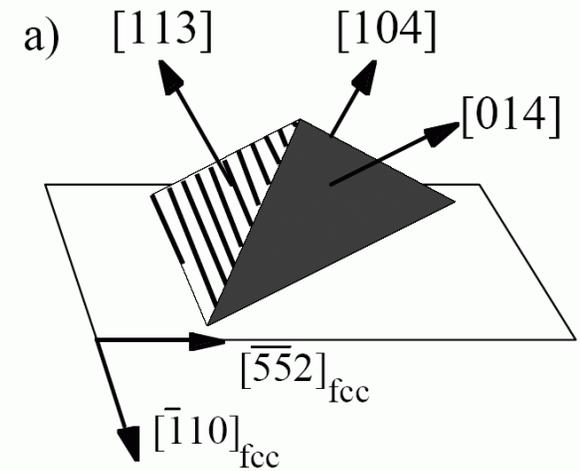

Pt(110)1x5 "hill" model

(a)

(b)

Pt(110)1x3

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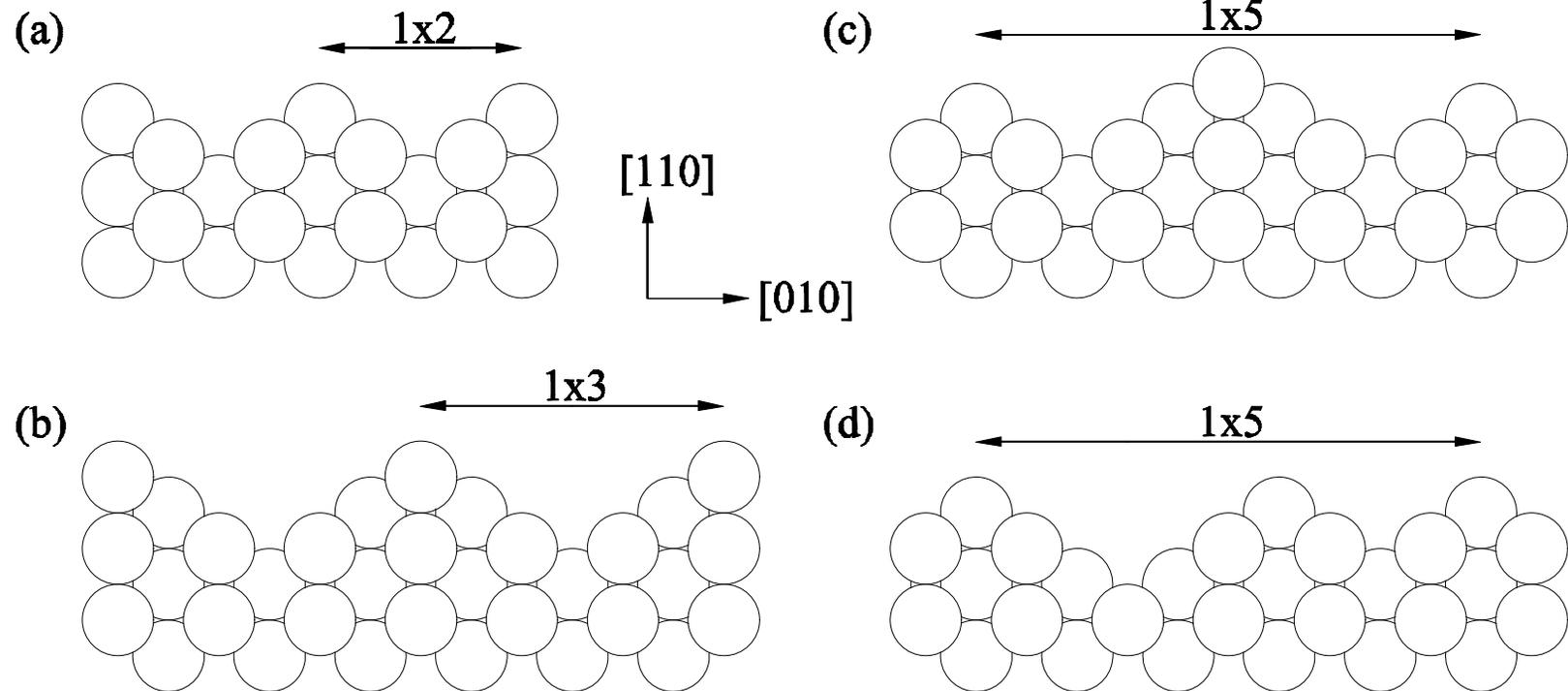
CTR is Sensitive to Surface Structure

ROUGH SURFACE

EXPANDED LAYER

CALCULATED INTENSITY
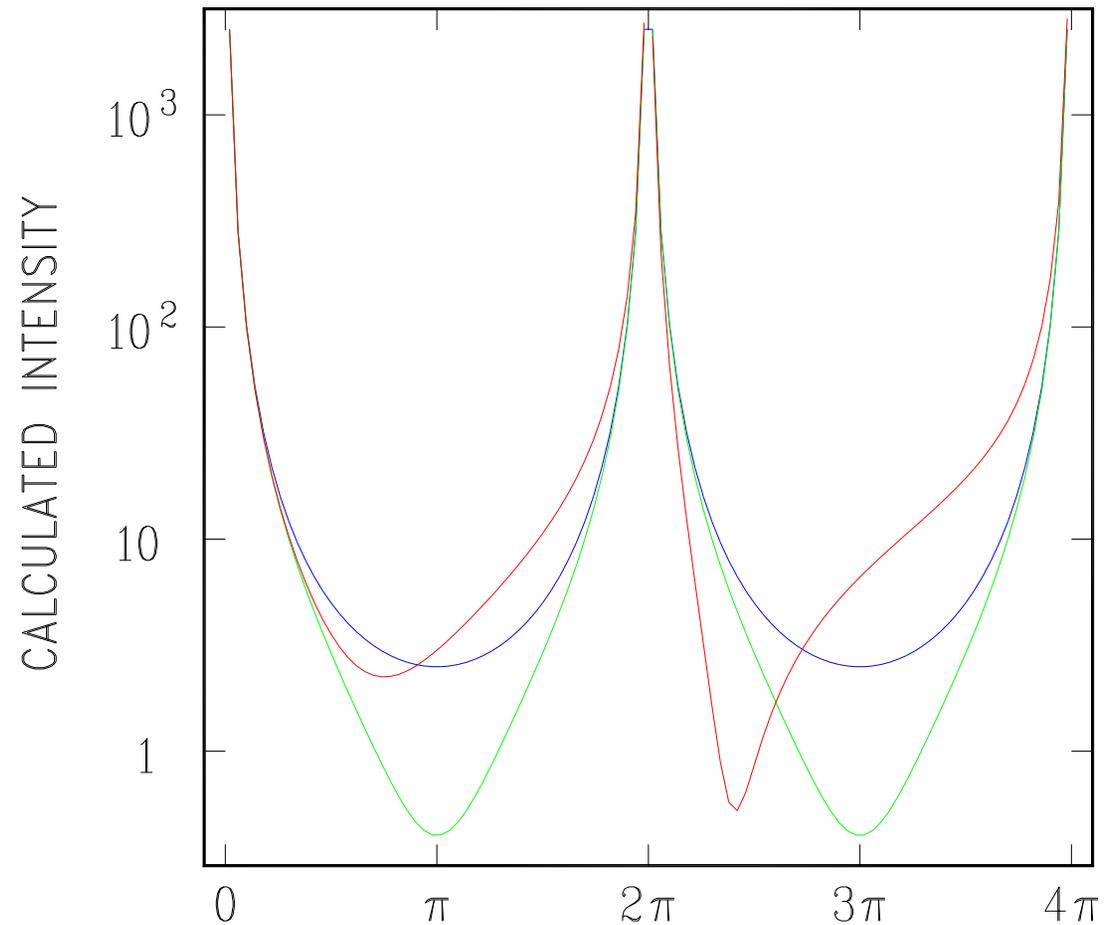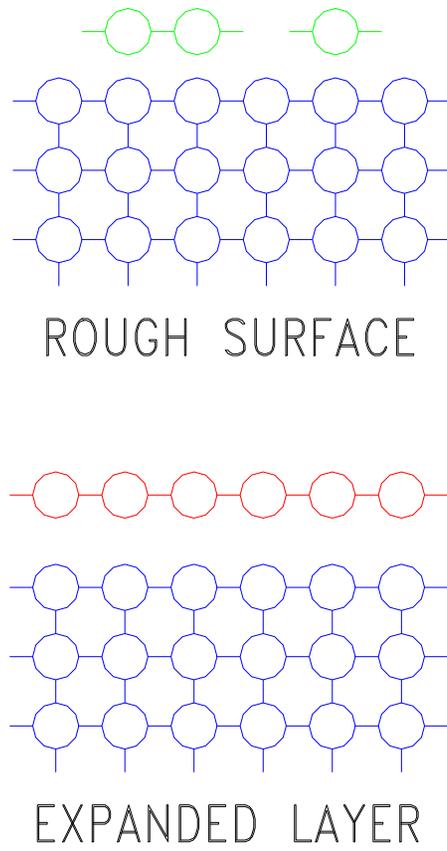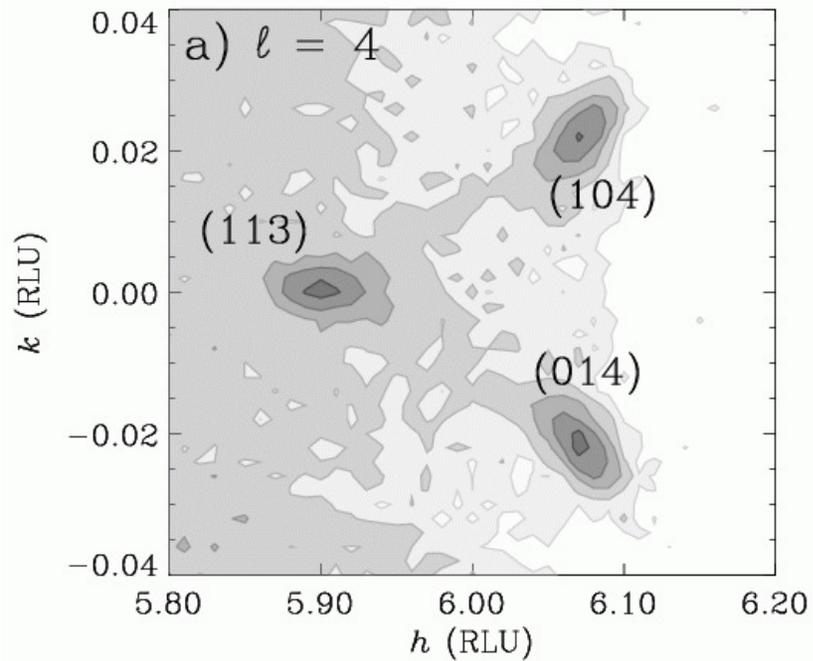
Cu(115) after Oxidation: STM

S. Reiter and E. Taglauer, Surf. Sci. **367** 33 (1996)

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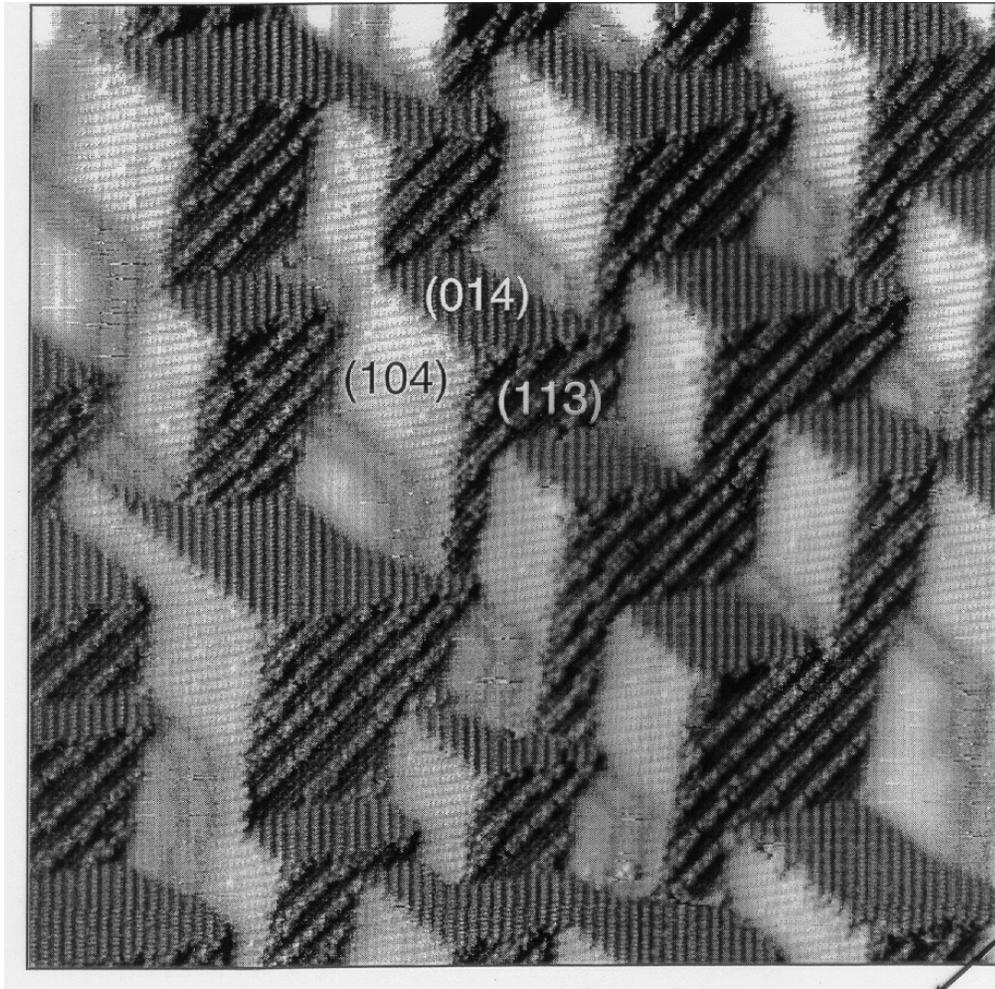
Cu(115) after Oxidation: X16A

Don Walko, UIUC PhD
Dissertation (2000)

a) $\ell = 4$

(104)

(113)

(014)

b) $\ell = 2$

(014)

(113)

(104)
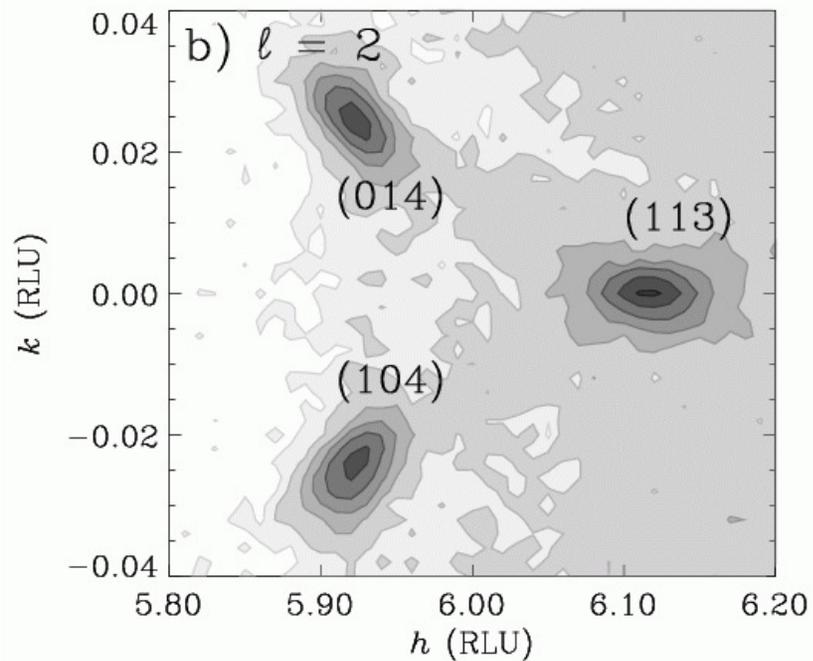
inson APS-SI workshop

Re-index CTRs for Cu(104) facets

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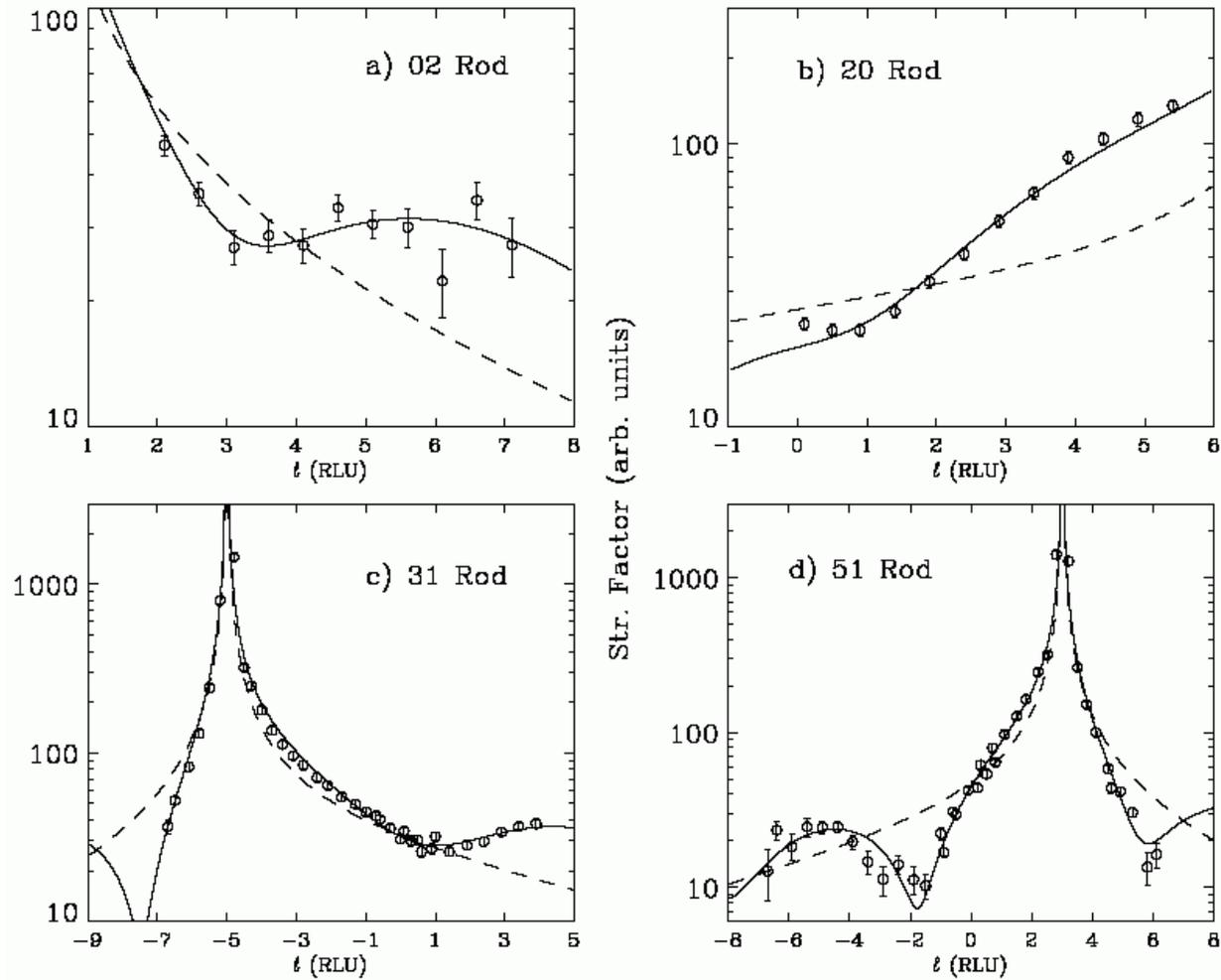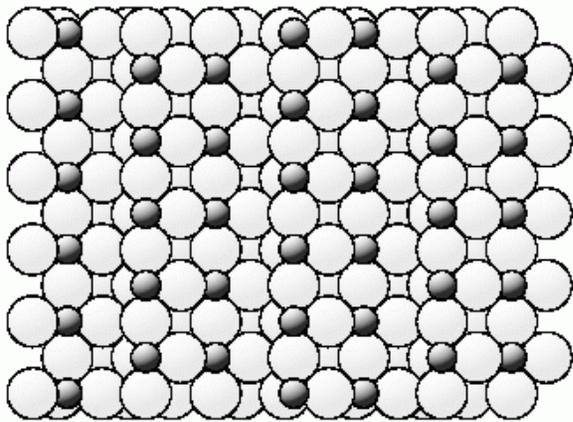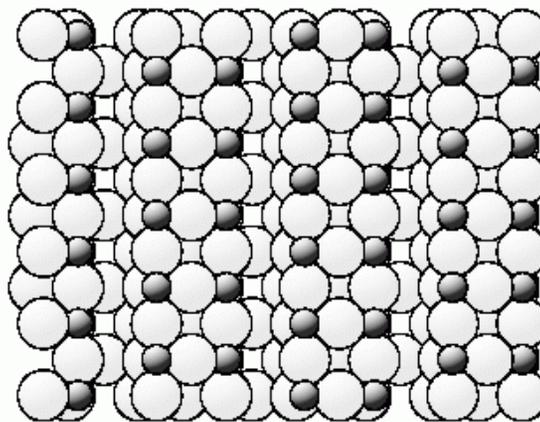
Surface Structures of Cu(104)-O

E. Vlieg, S. M. Driver, P. Goedtkindt, P. J. Knight, W. Liu, J. Luedecke, K. A. Mitchell, V. Murashov, I. K. Robinson, S. A. de Vries and D. P. Woodruff, Surface Science **516** 16-32 (2002)
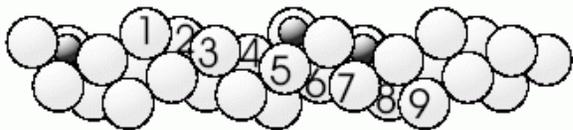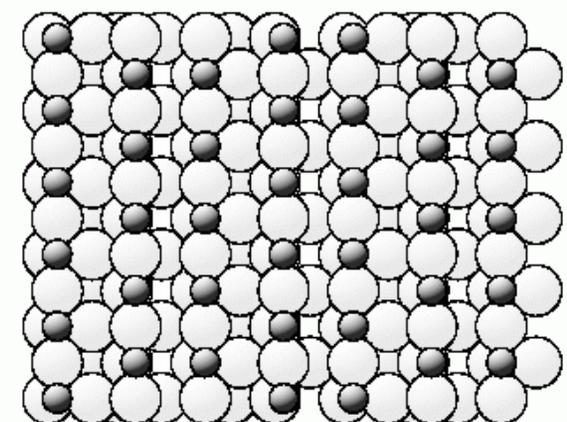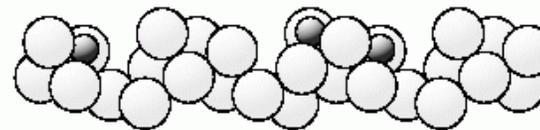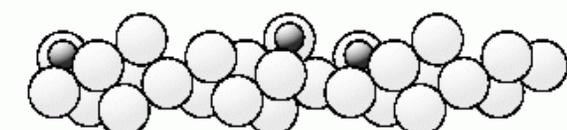

Overlayer — Missing Row 4 — Missing Row 2

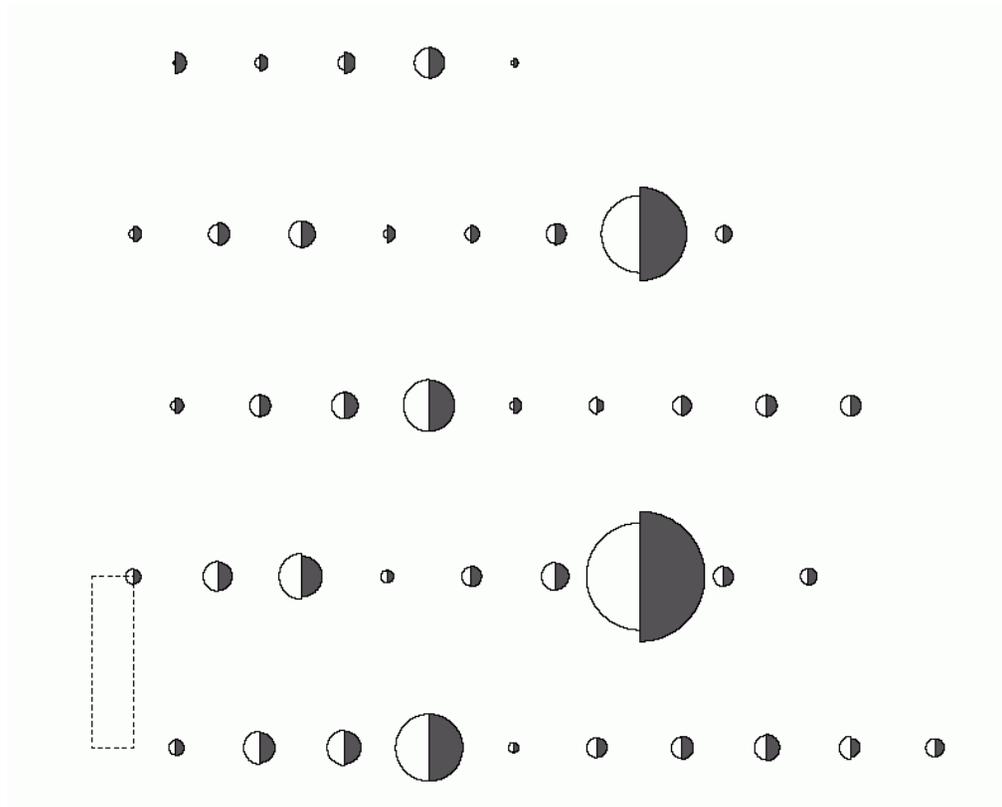Perderau and Rhead — Robinson et al — Woodruff et al

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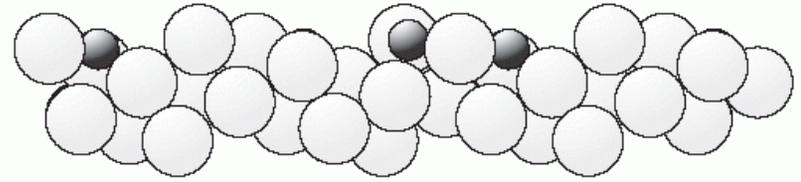
In-plane and CTR data at Daresbury

(5,1) rod

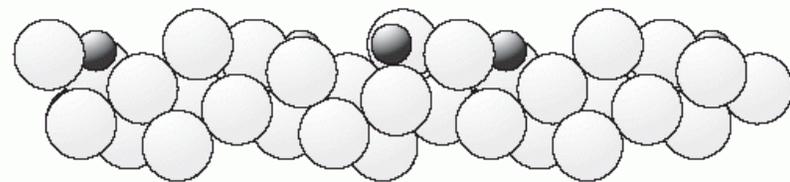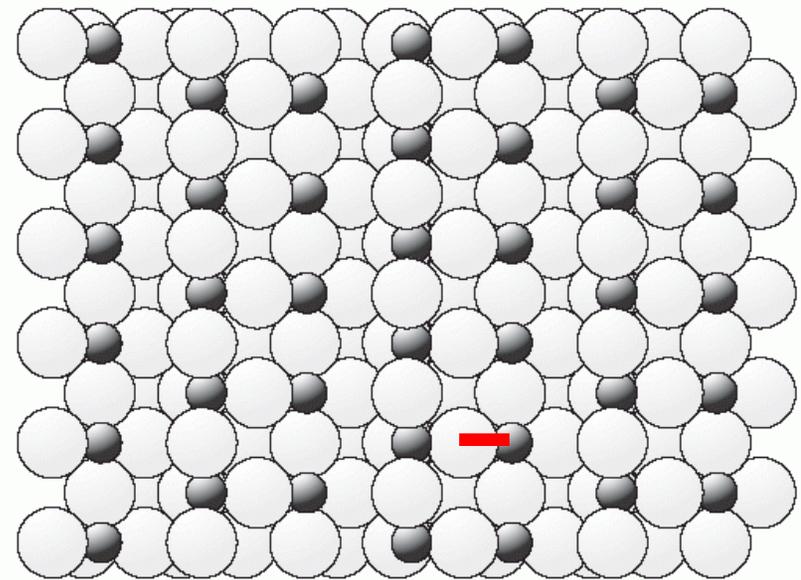(0,2) rod

I. K. Robinson APS-SI wor
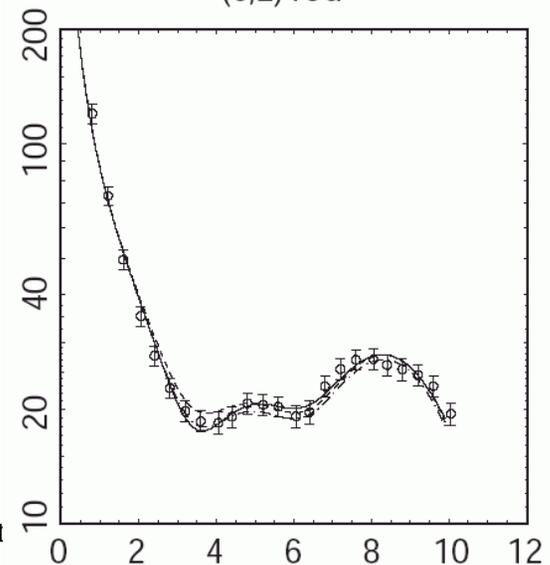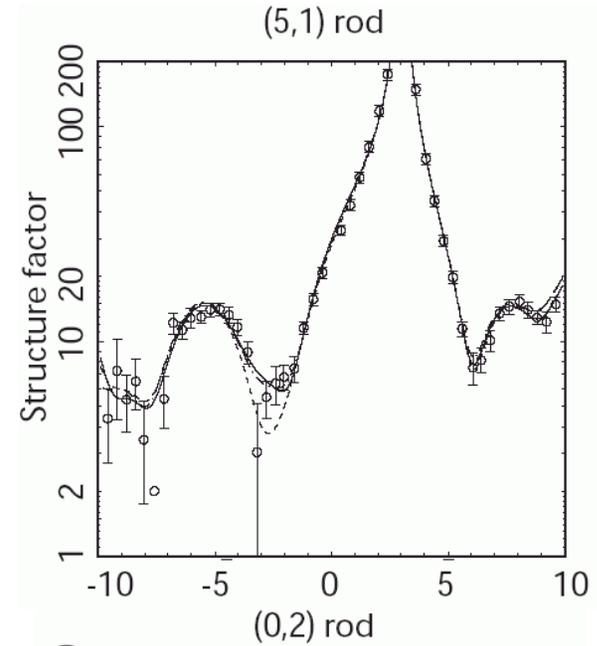
Problems with refinement of structure

O row number	Cu row number	Unconstrained fit	Constrained fit LJ1	Constrained fit LJ2	Walko & Robinson	DFT calculation
1	1	1.86	1.86	1.82	1.86	1.85
1	2	2.55	2.49	1.88	2.41	1.90
1	5	2.08	1.94	1.99	2.55	2.21
3	2	1.53	1.71	1.79	1.85	1.90
3	3	1.96	1.93	1.88	1.84	1.98
3	4	2.25	2.11	1.93	1.85	2.03
3	7	2.69	2.61	2.52	2.43	2.72

$$\chi^2 = 2.66 \qquad \chi^2 = 2.83$$

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Two Structures that fit the Data

LJ1

LJ2

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If we had measured ...

(5,1) rod

Structure factor

LJ1

LJ2

(1,3) rod

Structure factor

LJ2

LJ1

Diffraction index *l*

d) 51 Rod

l (RLU)

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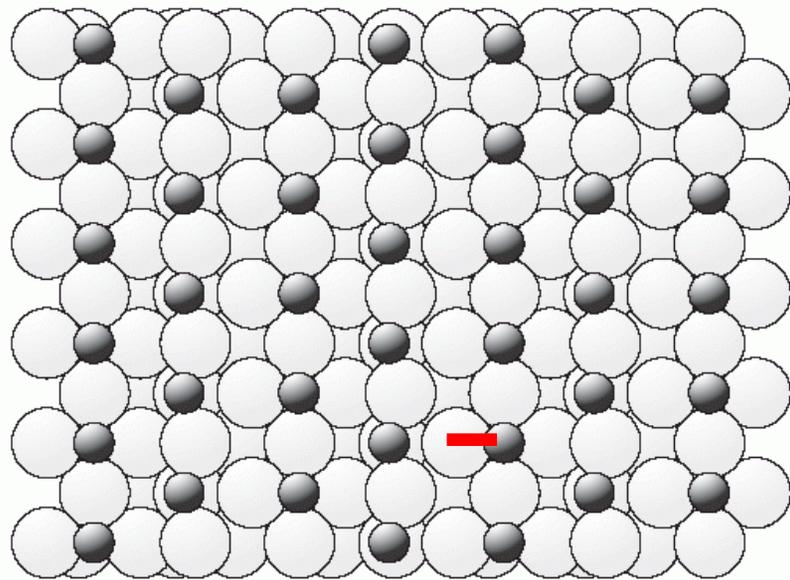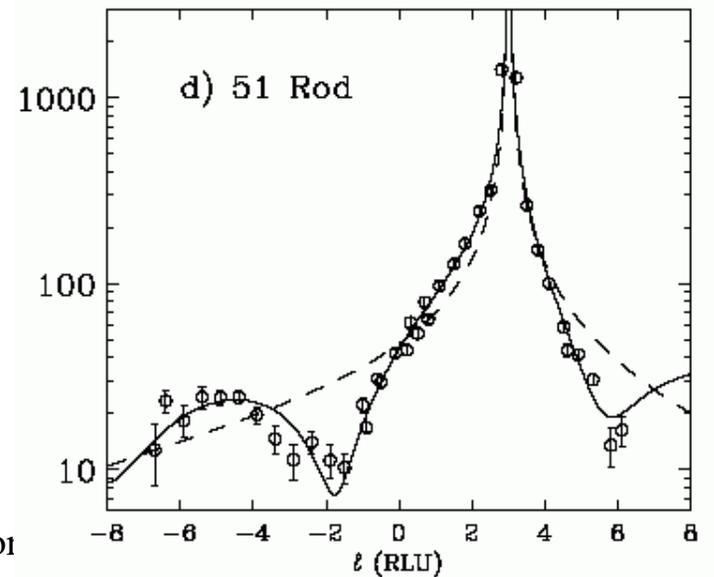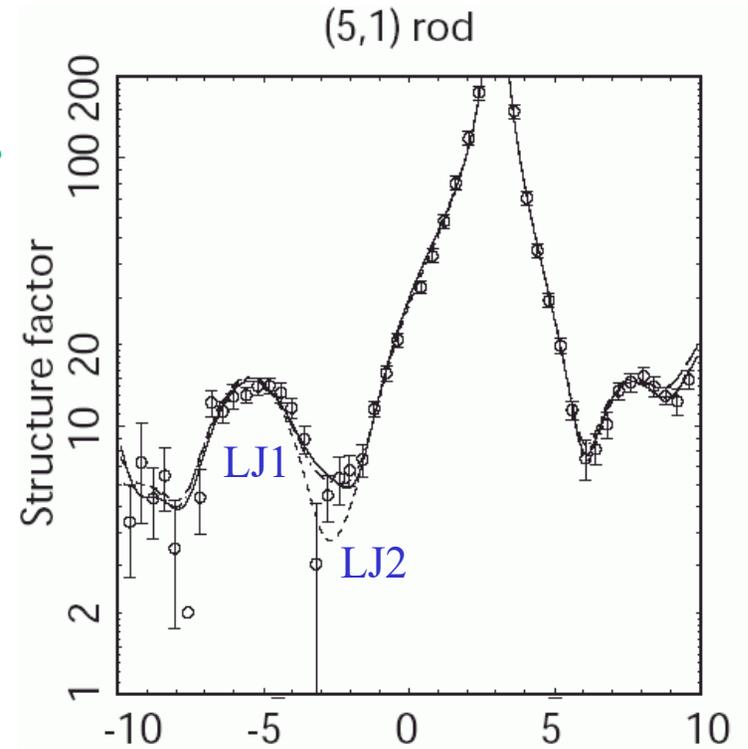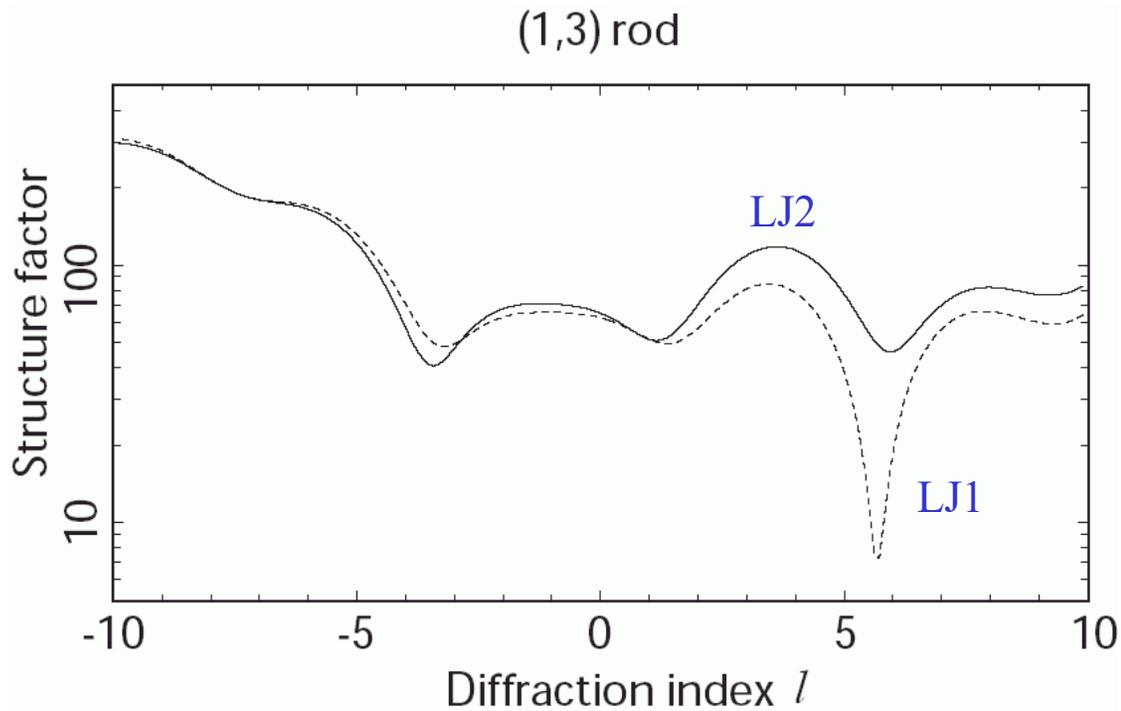
Future Directions

- Surfaces of light elements

- Buried interfaces, such as solid-liquid

- Quantum dots and wires CXD

- Fluctuating surfaces, capillary waves XPCS

- Nanostructured rough surfaces GISAXS, XPCS

- Continuum models of strain

- Improved parallel techniques for large datasets

CCD

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Conclusions

- Uniqueness not guaranteed

- 'Homometric' structures of Pt(110)1x5

- Pick out facet stuctures of Cu(104)-O

- Large data sets still needed

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