Low Energy Electron Diffraction - LEED

Wolfgang Ranke
Dep. Inorganic Chemistry
Group Model Surface Analysis
Fritz-Haber-Institut der MPG

For script:
see homepage
or
mail to: ranke@fhi-berlin.mpg.de

Literature:

G. Ertl, J. Küppers, Low Energy Electrons and Surface Chemistry, VCH, Weinheim (1985).
M. Henzler, W. Göpel, Oberflächenphysik des Festkörpers, Teubner, Stuttgart (1991).
M.A. Van Hove, W.H. Weinberg, C.-M. Chan, Low-Energy Electron Diffraction, Experiment, Theory and Surface Structure Determination, Springer Series in Surface Sciences 6, G. Ertl, R. Gomer eds., Springer, Berlin (1986).
M. Horn-von Hoegen, Zeitschrift für Kristallographie 214 (1999) 1-75.

FHI-Berlin, 16.01.2004

1. Introduction, General

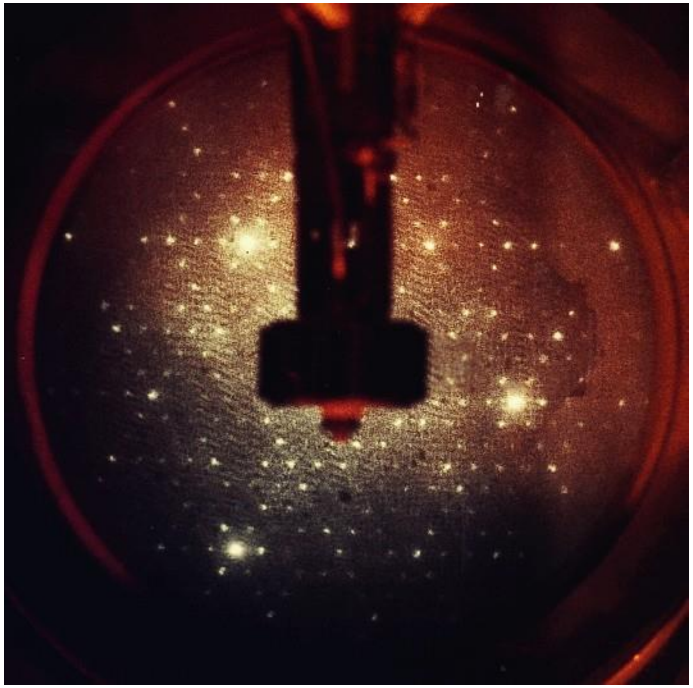
Surface science, UHV, p~10^{-10} mbar

De Broglie wavelength: $\lambda = h/(mv)$

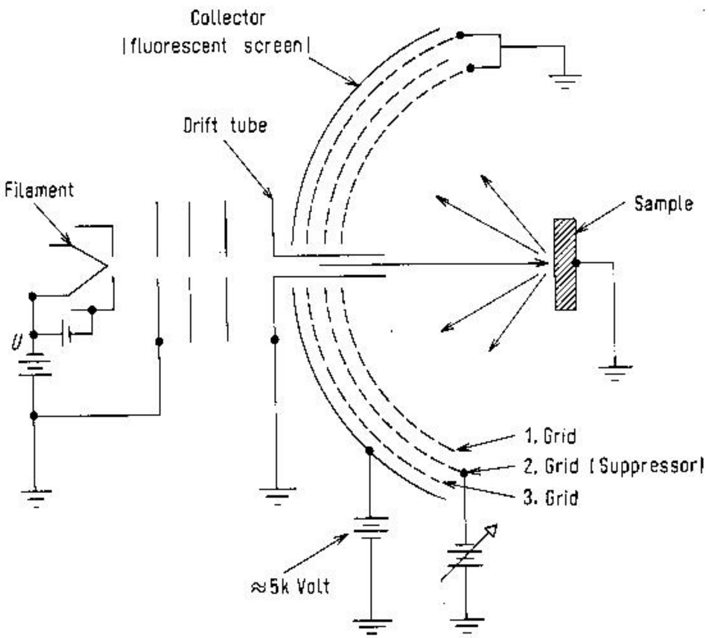
For electrons: $\lambda = \sqrt{150 / E_0}$ E_0 in eV, λ in Å.

For 100 eV-electrons: $\lambda(100) = 1.22$ Å (low energy)

corresponds to atomic dimensions, similar to XRD



Si(111)-(7x7)

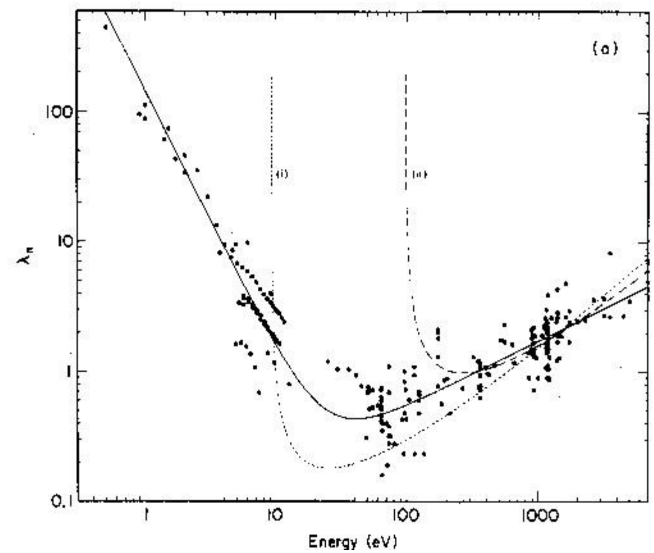


LEED display system

Ertl/Küppers fig. 9.7, p. 210

LEED is surface sensitive

Low energy electrons
interact strongly with matter:
electron mean free path λ_e
is small.
Only e^- scattered from near surface
can leave the surface,
surface sensitive



M.P. Seah, W.A. Dench, Surf. Interf. Anal. 1 (1979) 2

The observation of a LEED pattern
does not guarantee that the whole surface is ordered!

Coherence of e^- -beam limited by ΔE and beam divergence.
Coherence length = diameter of coherently scattering area.

The coherence length
of a standard LEED optics
is only 10 – 20 nm!

1st approximation:
Scattering from 2-D lattice.

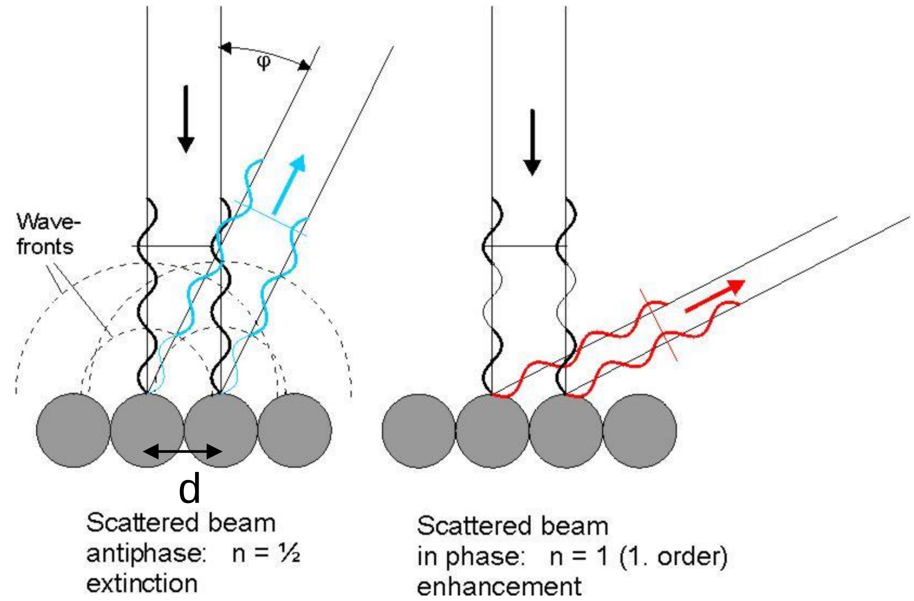
Analogy to optical grating.

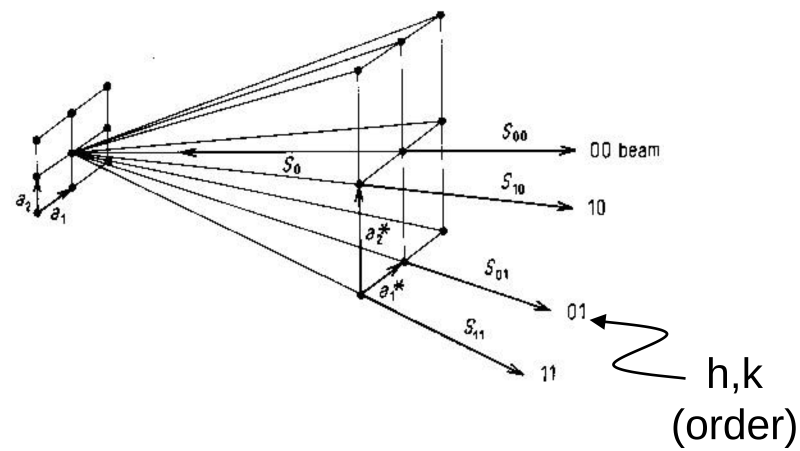
Constructive interference:
Enhancement of intensity only in certain directions:

$$n \lambda = d \sin \varphi$$

For 2D arrangement (plane lattice): scattering conditions have to be fulfilled in both directions

Note:
If the lattice constant(s) a_1 (a_2) <u>in</u>crease, the scattering angle for the beam h (k) <u>de</u>creases.
This is the reason for the reciprocity of the real and the s.c. reciprocal lattice.





Formation of diffraction pattern

Ertl/Küppers fig. 9.12, p. 217

Useful: Introduction of reciprocal lattice

Real lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$

Reciprocal lattice vectors $\mathbf{a}_1^*$, $\mathbf{a}_2^*$

Definitions:

$\mathbf{a}_1^*$ perpendicular to $\mathbf{a}_2$

$\mathbf{a}_2^*$ perpendicular to $\mathbf{a}_1$

$a_1^* = 1/(a_1 \sin \gamma)$

$a_2^* = 1/(a_2 \sin \gamma)$

γ angle between a_1 and a_1

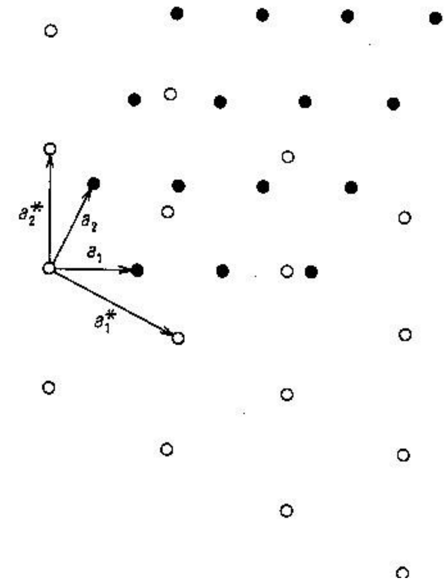
Constructive interference for:

$$\mathbf{a}_1 (\mathbf{s} - \mathbf{s}_0) = h \lambda$$

$$\mathbf{a}_2 (\mathbf{s} - \mathbf{s}_0) = k \lambda$$

(Laue conditions for 2 dimensions)

Real 2D system: 3rd Laue condition always fulfilled.



Example

Ertl/Küppers fig. 9.11, p 216

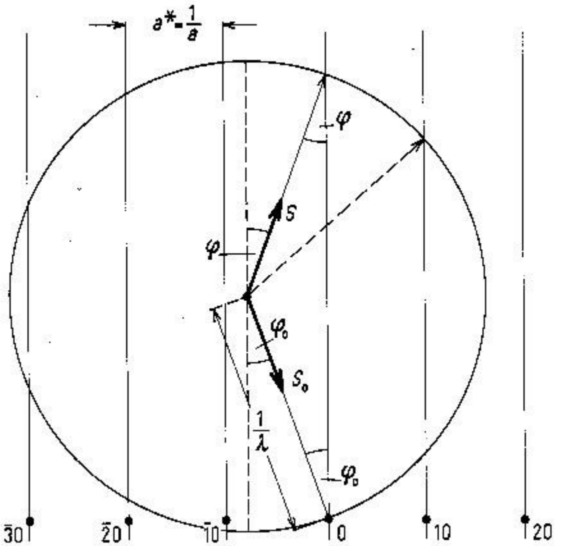
It follows for the direction of beams:

$$1/\lambda\ (\mathbf{s} - \mathbf{s}_0) = 1/\lambda\ \Delta\mathbf{s} = h\ \mathbf{a}_1^* + k\ \mathbf{a}_2^* = \mathbf{g}$$

$\mathbf{g}$ = reciprocal lattice vector

Ewald sphere construction

- plot reciprocal lattice (rods)
- plot direction of incident beam ($\mathbf{s_0}$) towards (00) spot
- go 1/λ along this direction
- make circle (sphere) with radius 1/λ
- direction from circle (sphere) center towards cut with reciprocal lattice rods gives direction of all possible diffraction spots (hk)

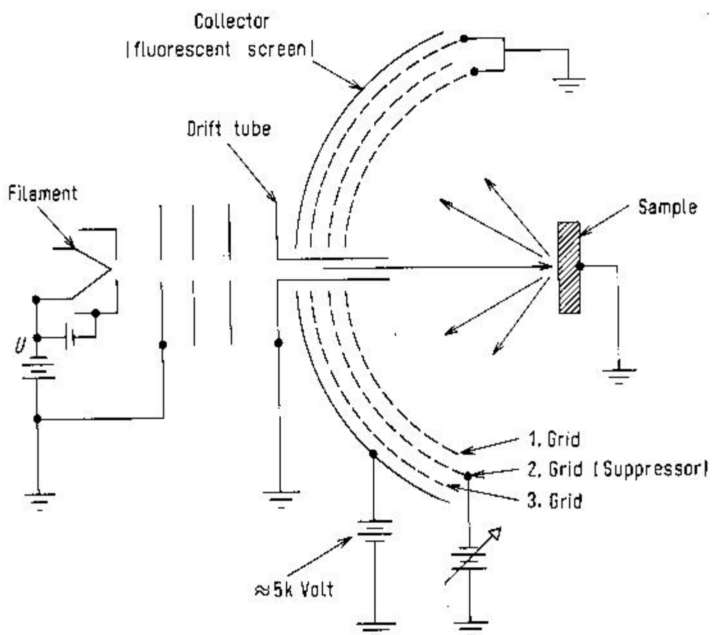


Ertl/Küppers fig. 9.13, p. 218

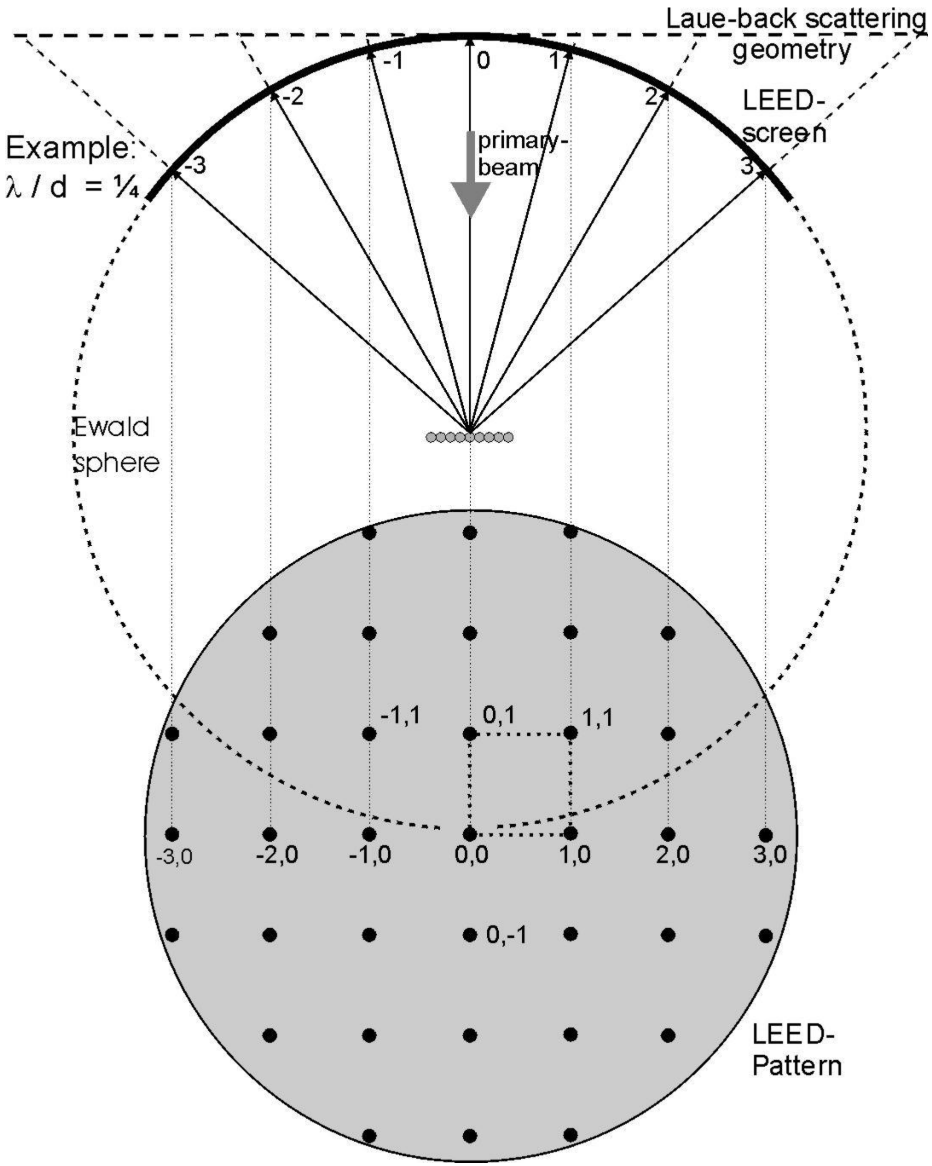
Usual arrangement:

Normal incidence,

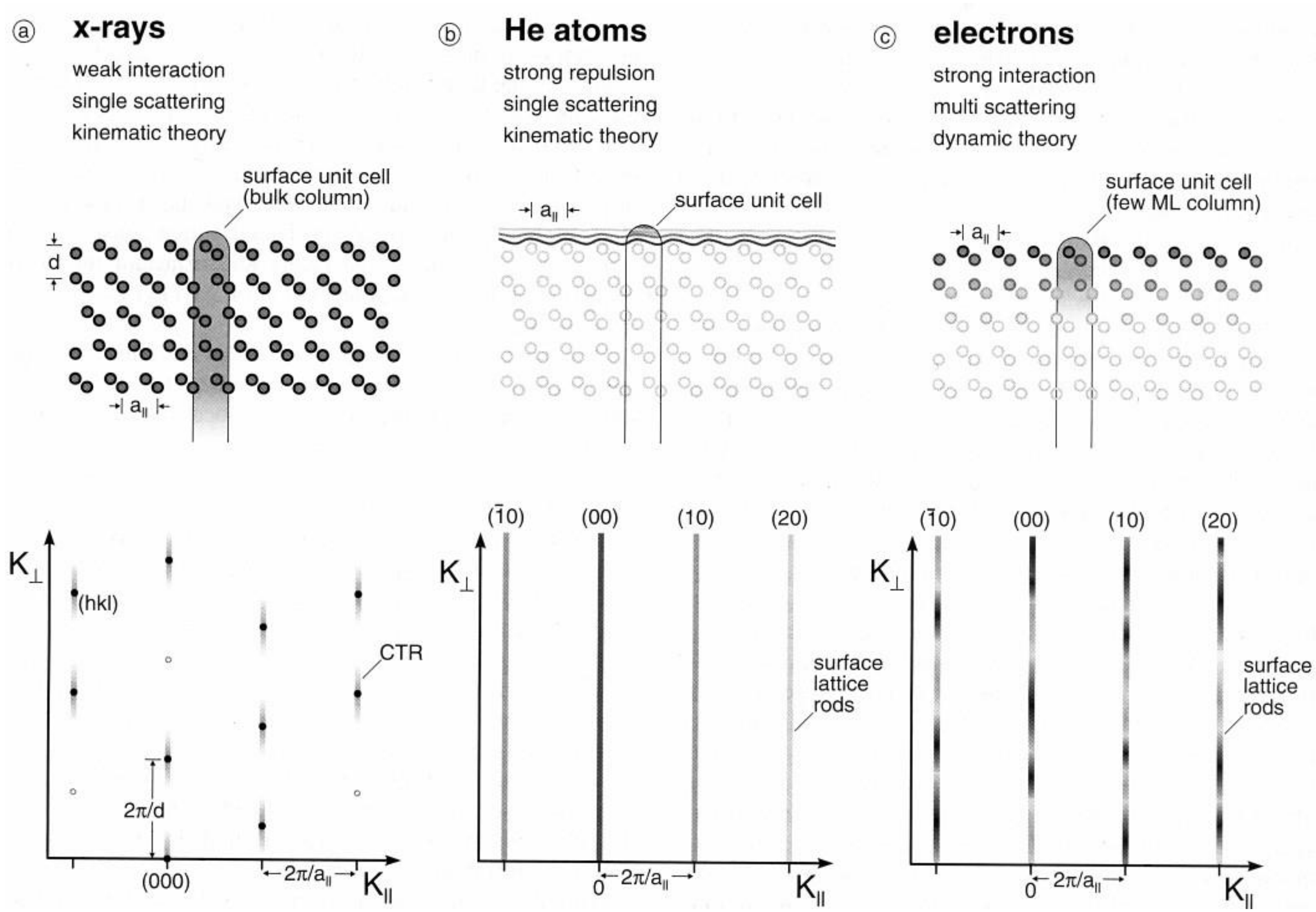
symmetrical diffraction pattern



Ertl/Küppers fig. 9.7, p. 210



Expected diffraction pattern for (001) surface,
e.g. Pt(001) (unreconstructed), E_0=313 eV



Surface diffraction with X-rays, He-atoms and electrons.
Example: diamond-type (111) surface like C, Si, Ge.
The darkness of rec. latt. spots and rods symbolizes diffraction intensity

Horn-von Hoegen, fig. 2.1

LEED:

2. Simple

Kinematic theory (single scattering)
Size, shape and symmetry of surface unit cell,
Superstructures
Domains
only if long-range ordered

No information about atomic arrangement within the unit cell

3. Less simple

Kinematic theory
Deviations from long-range order:
Spot width $\rightarrow$ domain size
Background intensity $\rightarrow$ point defect concentration
Spot splitting $\rightarrow$ atomic steps

4. Difficult

Dynamic theory (multiple scattering)
Spot intensities $I(E_0)$ or I-V curces $\rightarrow$ structure within unit cell

2. LEED – simple

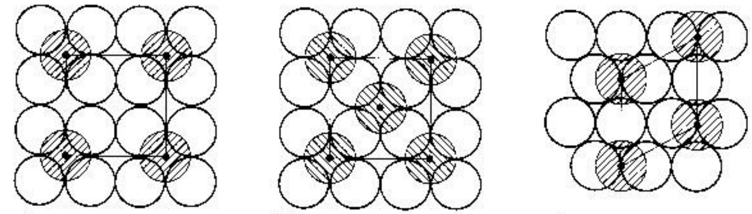
Superstructures result from:

Reconstruction = rearrangement of surface atoms on clean surfaces
Ordered adsorption

Structure examples

Overlayer structures

Ertl/Küppers fig. 9.2, p.204



a) p(2x2) b) c(2x2) on square lattice

c) (√3x√x)R30° on hex. lattice

Superstructure nomenclature

Wood: Simplest in most cases
p or c(n×m)Rϑ°
unit cell vector lengths
$b_1 = n\ a_1$ $b_2 = m\ a_2$
rotation ϑ p=primitive, c=centered

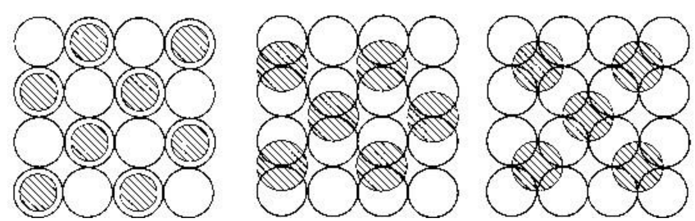
Matrix notation (Park and Madden)
more general

m_{11} m_{12} $\mathbf{b_1} = m_{11}\ \mathbf{a_1} + m_{12}\ \mathbf{a_2}$
m_{12} m_{22} $\mathbf{b_2} = m_{12}\ \mathbf{a_1} + m_{22}\ \mathbf{a_2}$

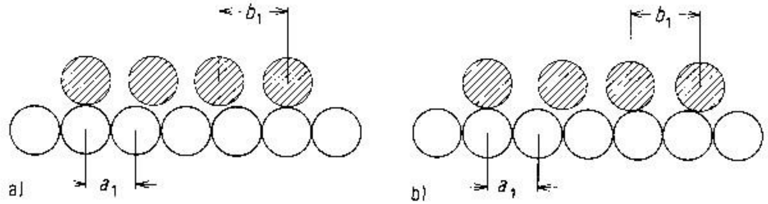
Wood	(2×2) [ϑ=0 is omitted]	(√3×√3)R30°
Matrix	2 0 0 2	1 1 2 -1

Three possible arrangements yielding c(2x2) structures.
Note: different symmetry!

Ertl/Küppers fig. 9.6, p.208



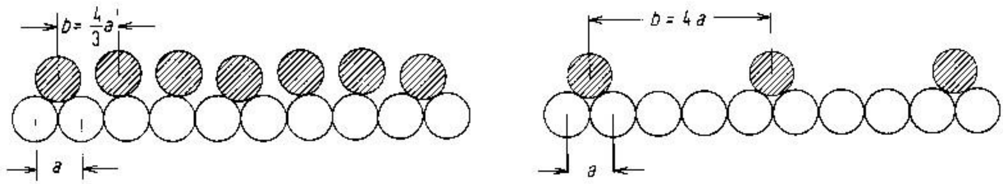
on top bridge 4-fold hollow



coincidence latt.
commensurate

incoherent,
incommensurate

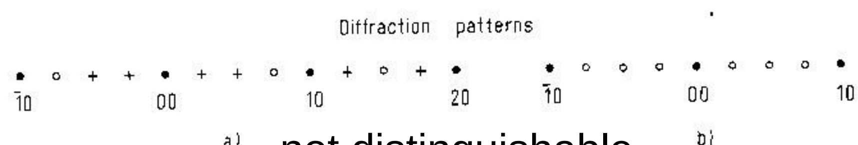
Ertl/Küppers fig. 9.3, p.205



coincidence latt.

simple overlayer struct.

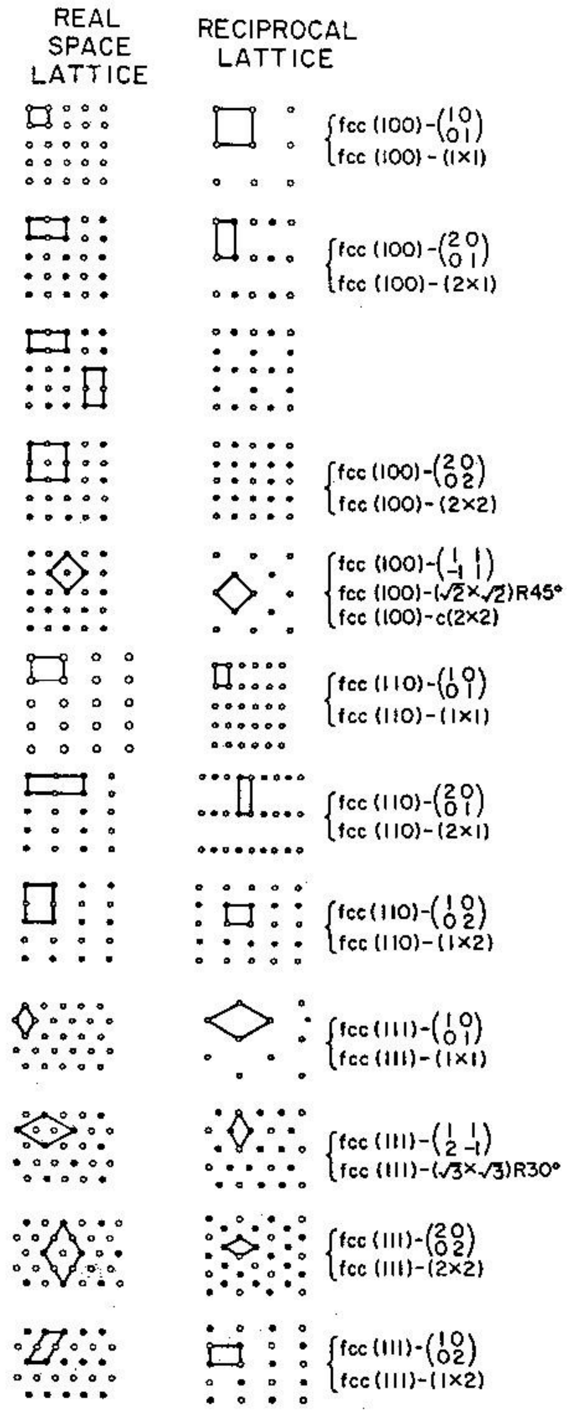
Ertl/Küppers fig. 9.19, p.224



not distinguishable

Real and reciprocal space lattices

Van Hove et al. fig. 3.5, p.55



Superstructures, example 1

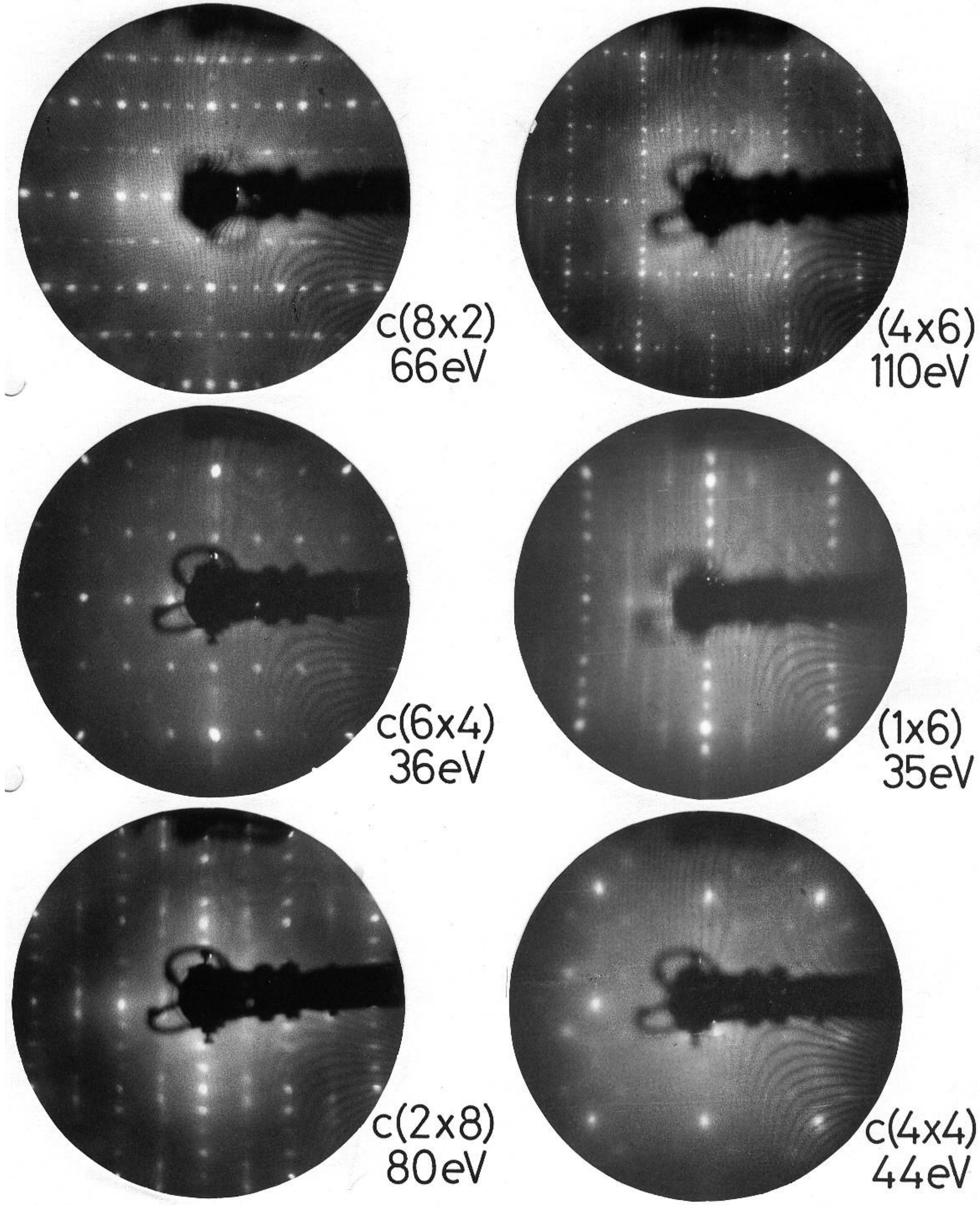
GaAs(001)
clean,
different preparations

As(31)/Ga(55)
Auger peak height ratios:

c(8x2)	1.74
(4x6)	1.77
c(6x4)	1.92
(1x6)	2.12
c(2x8)	2.25
c(4x4)	2.7

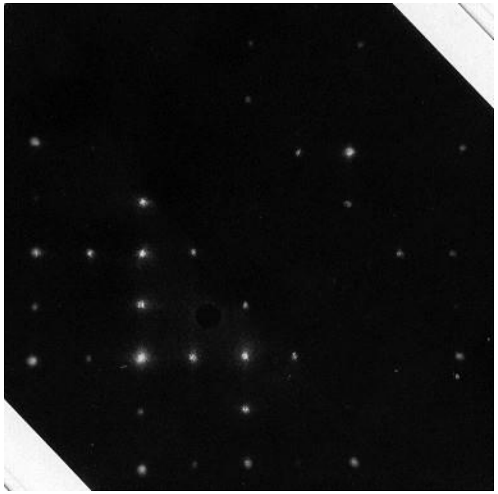
Information from patterns:
- symmetry of unit cell
- size and shape of surface unit cell
- sharpness of spots → domain size
- background intensity → concentration of point defects

Drathen, Ranke, Jacobi, 1978



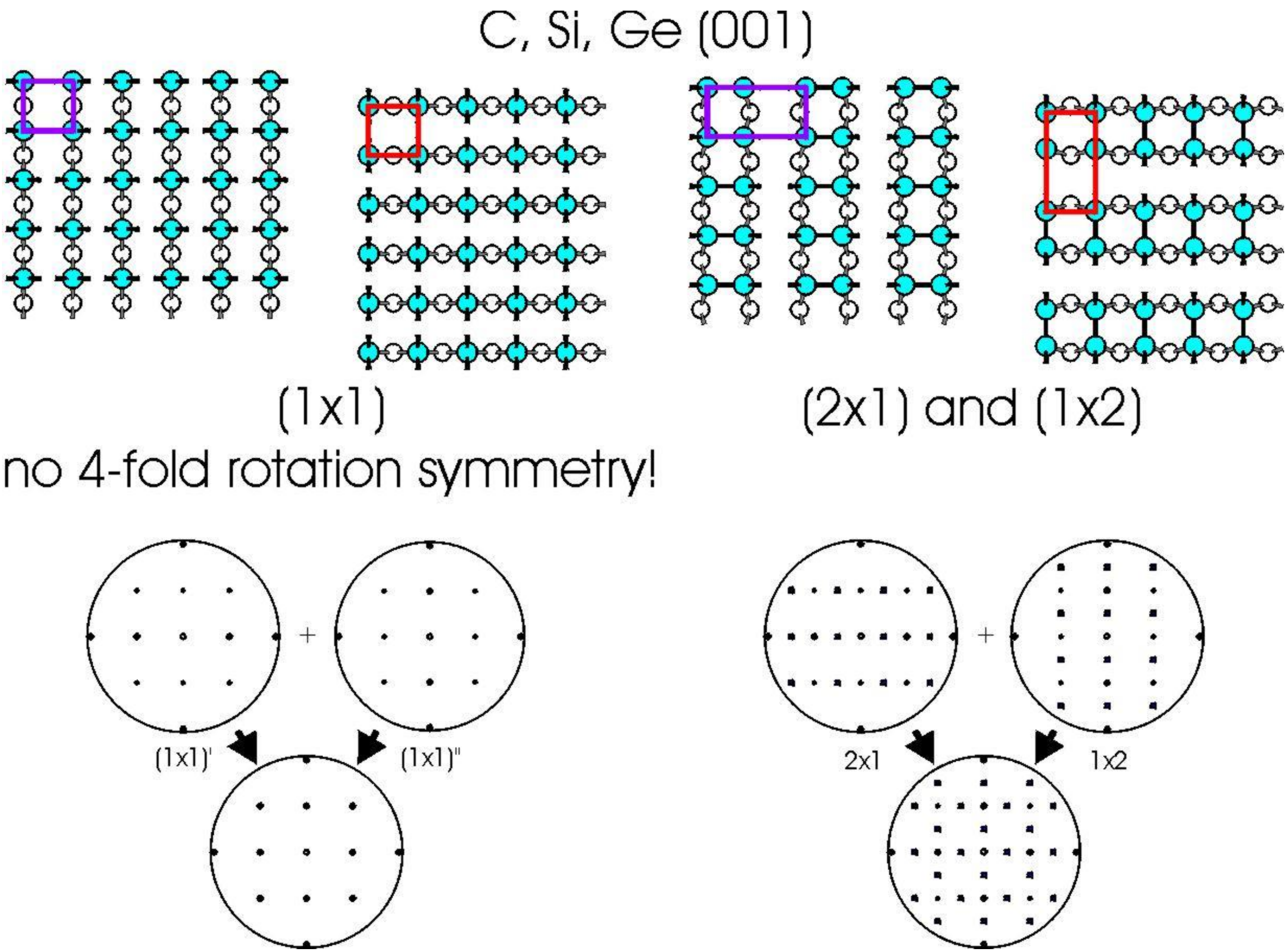
Superstructures, example 2

Si(001) clean



no 2x2 structure!
central spots missing
⟶ two-domain 2x1

Wasserfall, Ranke, 1994



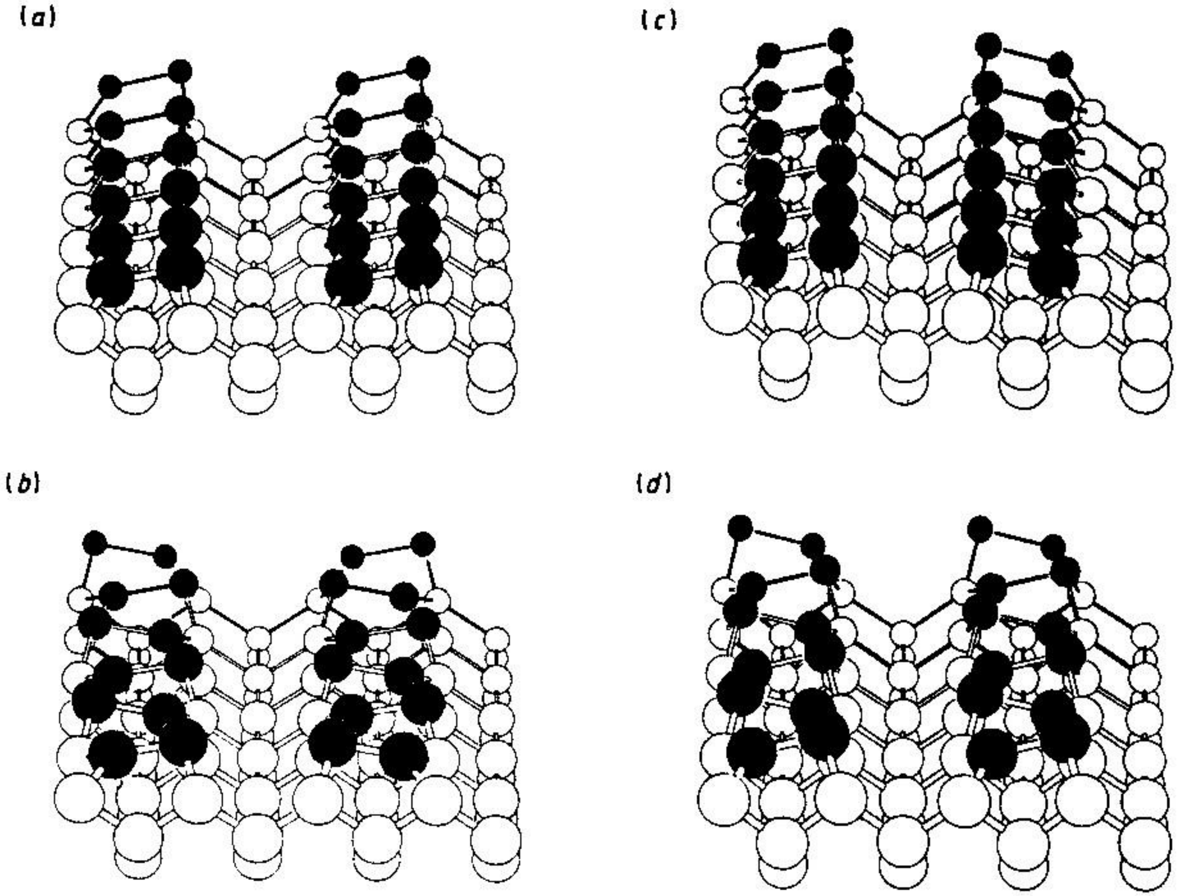
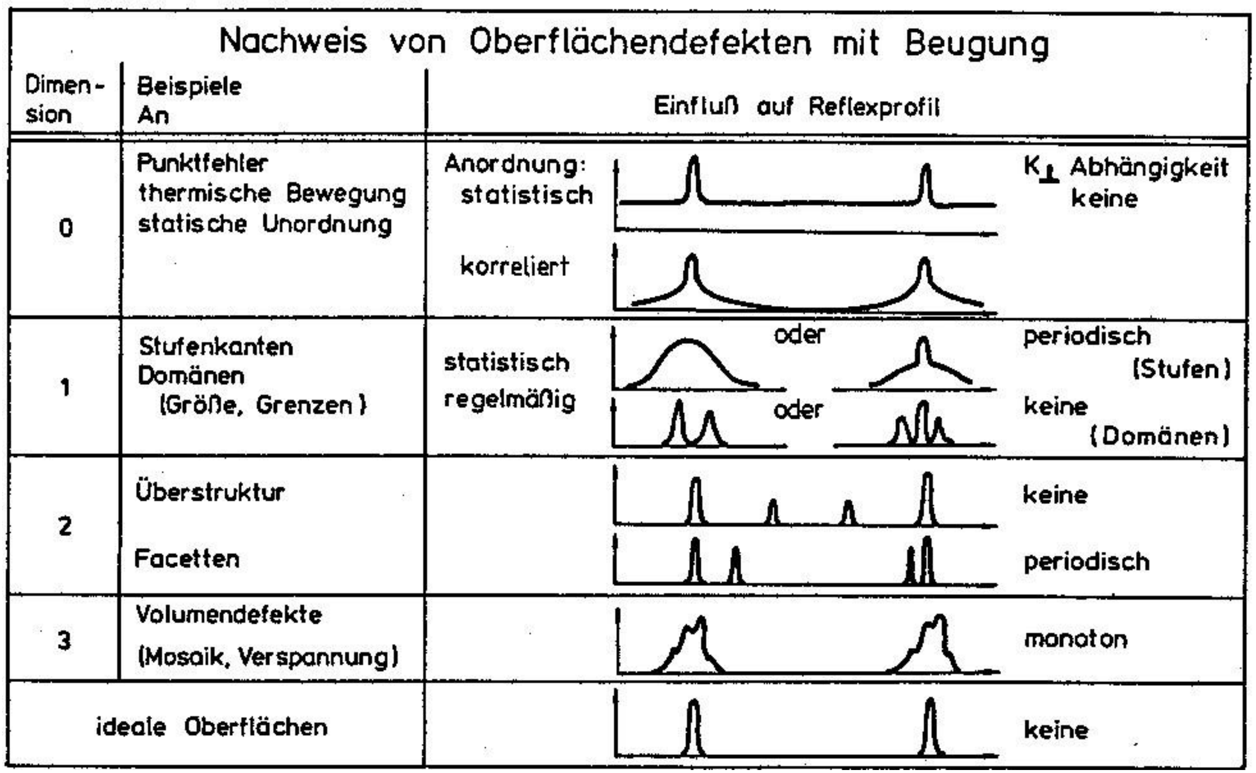


Figure 3. Buckled dimer reconstructions on the (001) surface of germanium: (*a*) b(2 × 1); (*b*) c(4 × 2); (*c*) p(4 × 1); (*d*) p(2 × 2).

Payne et al. J. Phys.: Cond. Matter 1 (1989) SB63

3. LEED – less simple

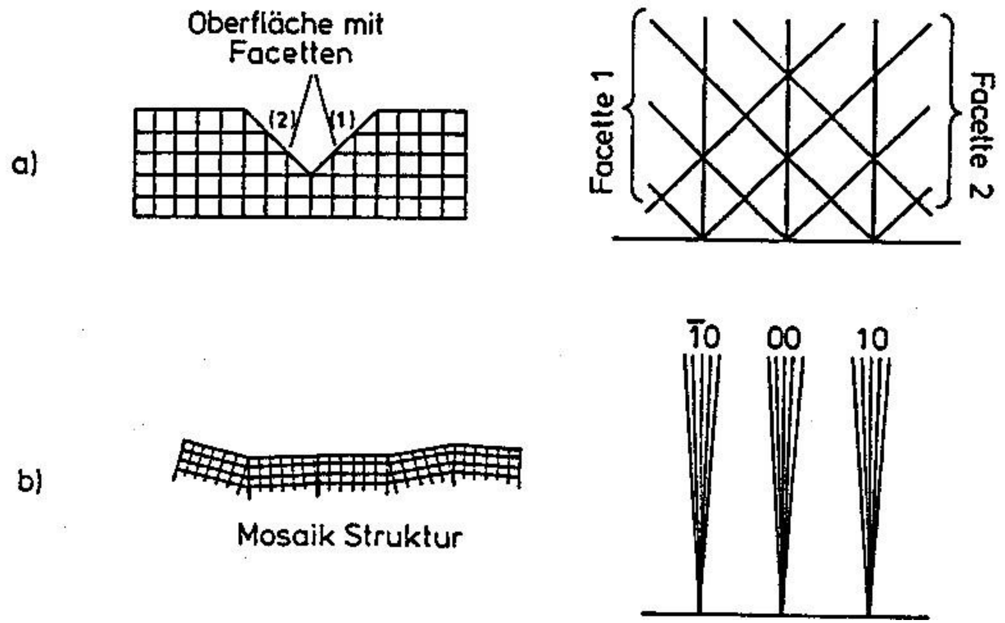
Information from spot shape (profile), background, E_0-dependence ($k_\perp$-dependence)



Henzler, Göpel Abb. 3.8.10, p.176

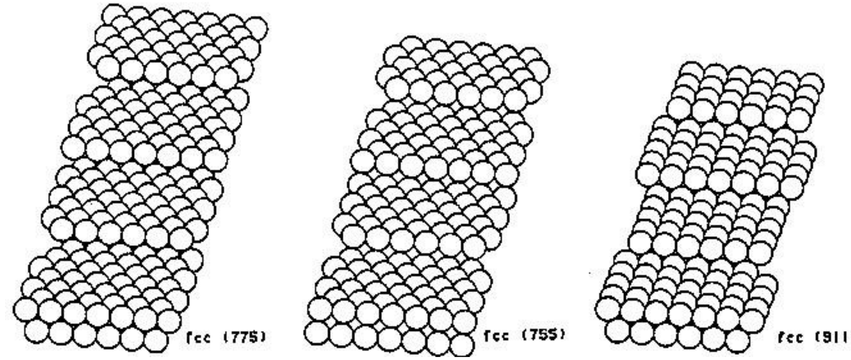
Facets and mosaic

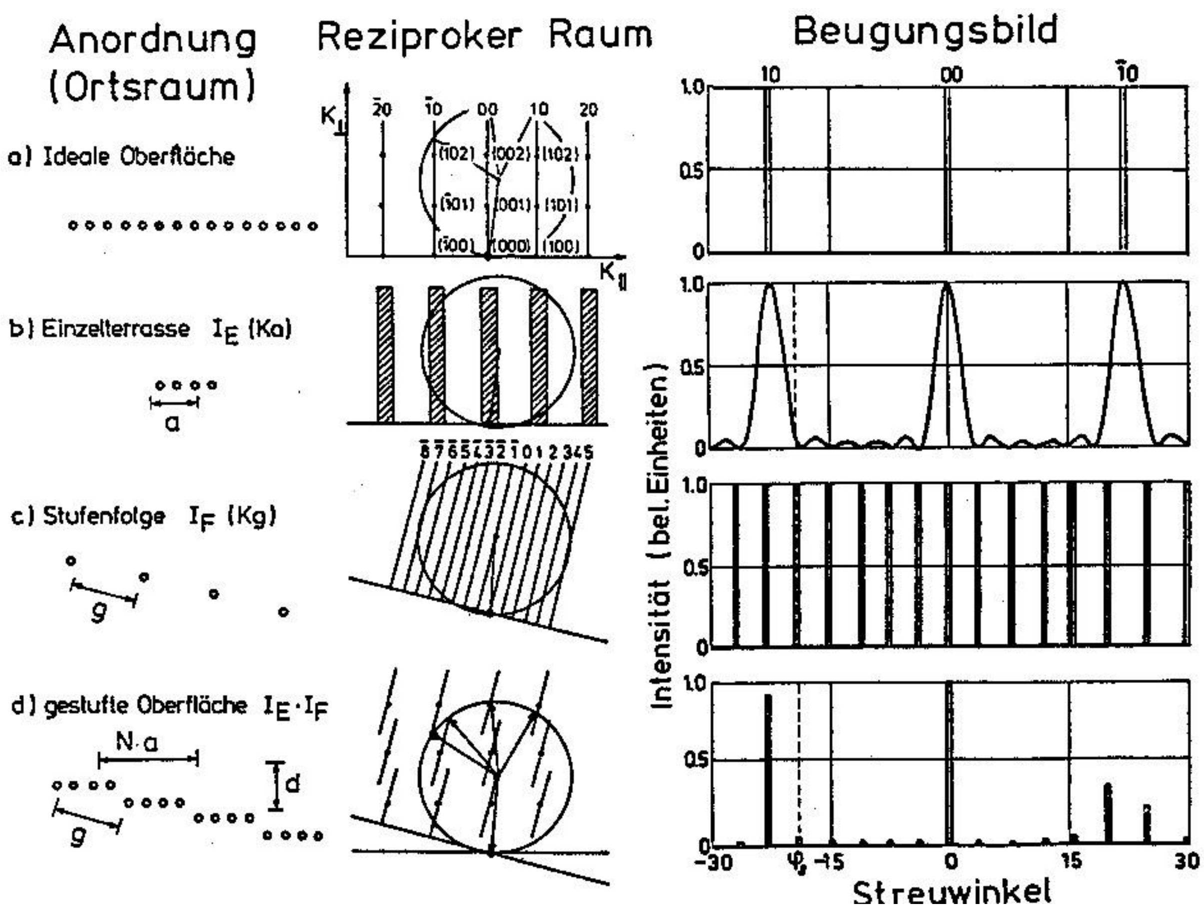
Henzler, Göpel
Abb. 3.8.4, p.167



Regular atomic steps

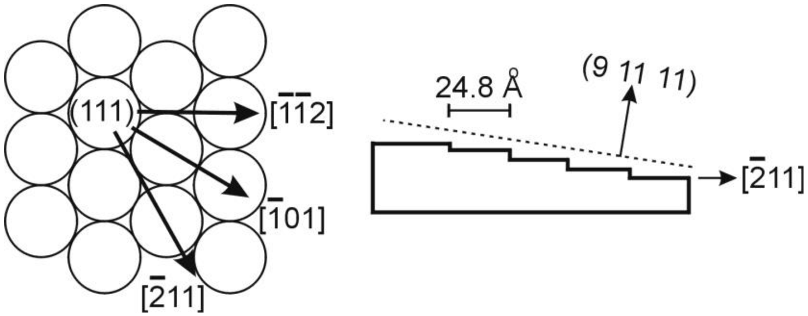
Van Hove et al., fig. 3.6, p.58

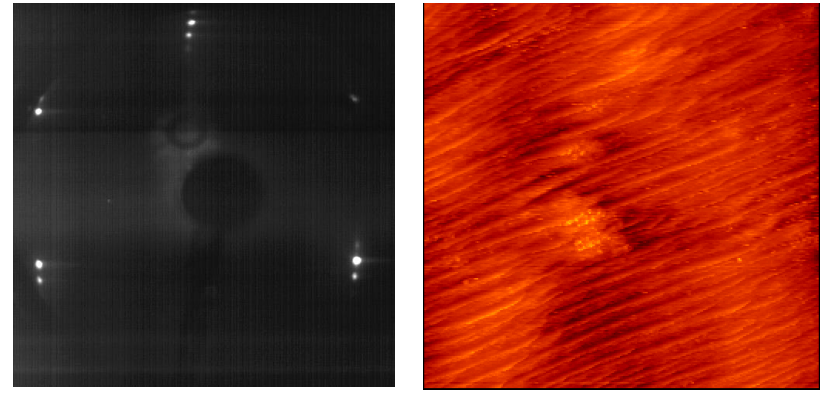




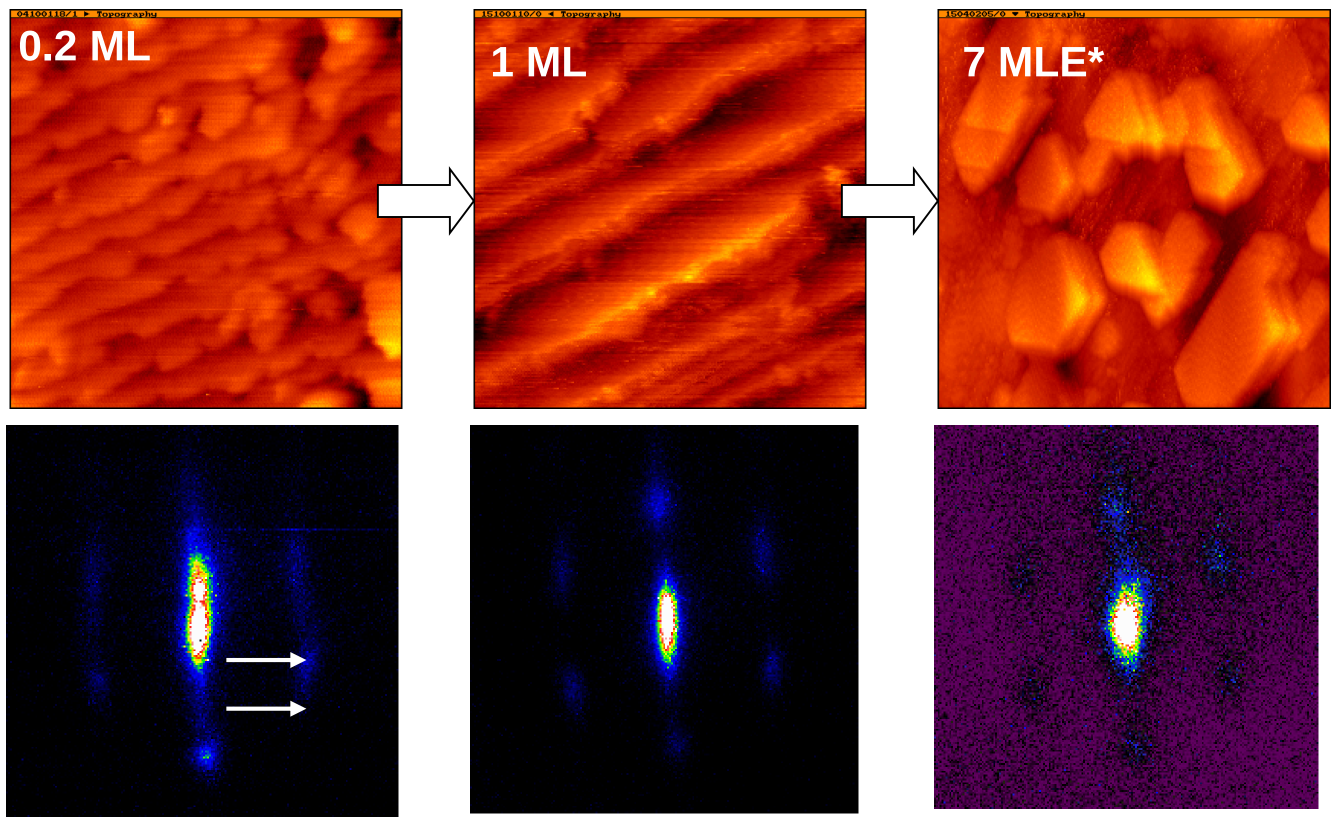
Henzler, Göpel, fig. 3.8.3, p.165

Pt(9,11,11)

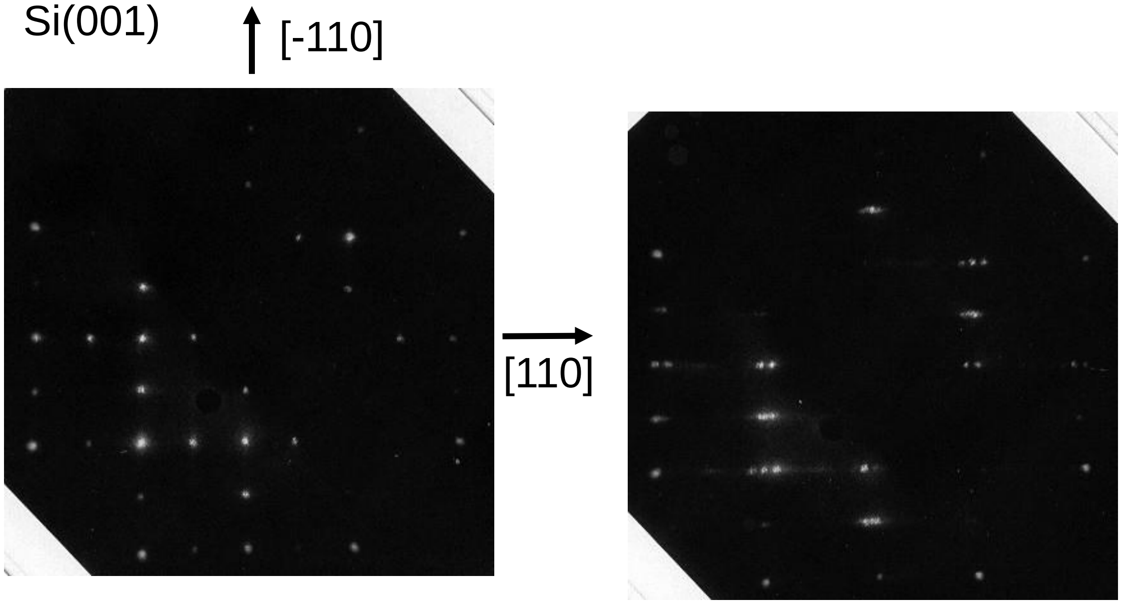




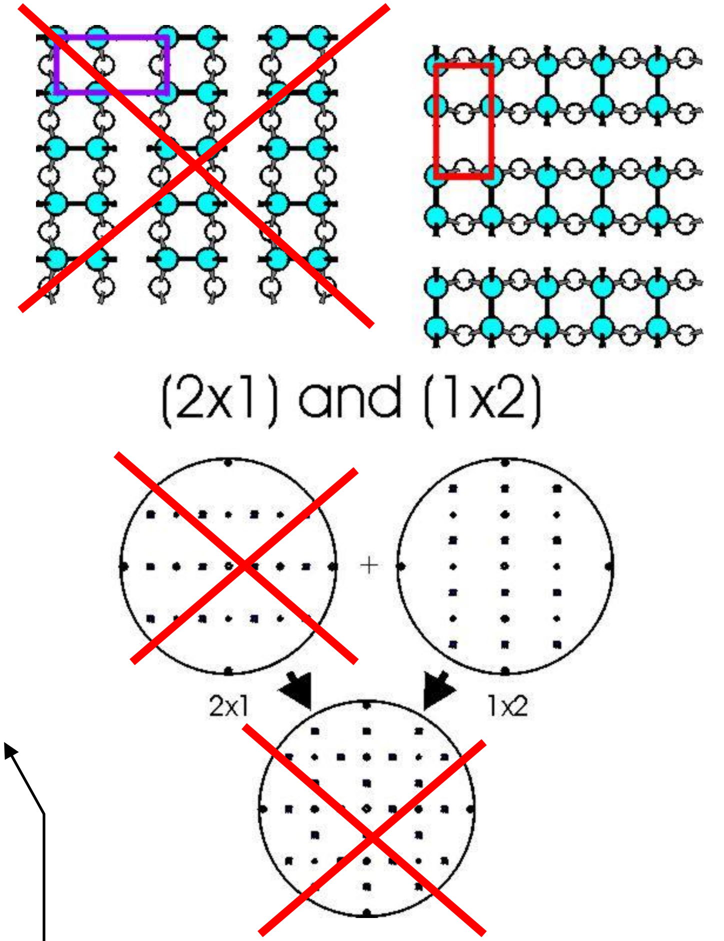
T=1000K

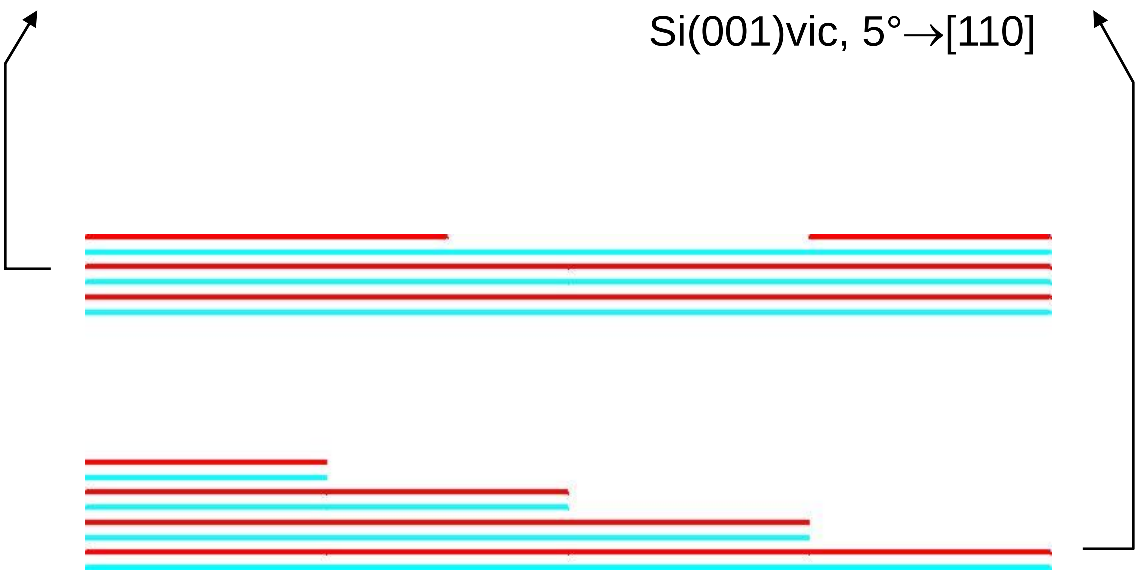


Example: Si(001)vic



Si(001)vic, 5°→[110]





Wasserfall, Ranke, 1994

4. LEED – difficult

Spot intensities contain information on structure within the unit cell

$$I \sim |F|^2 \cdot |G|^2$$

$|G|^2$ = structure factor or lattice factor

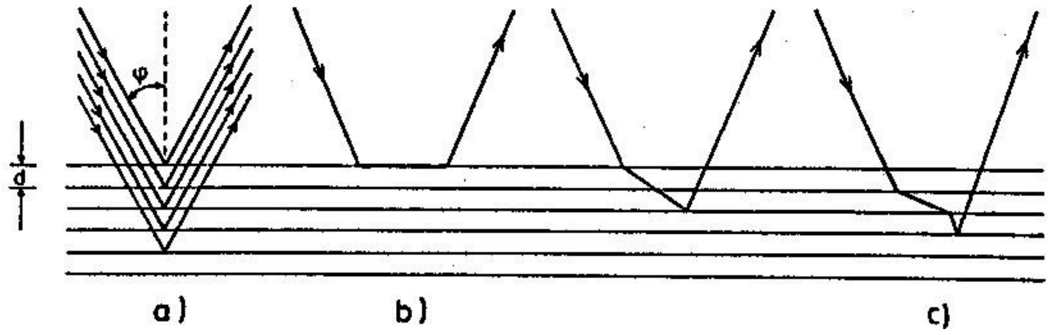
contains shape and arrangement of repeat units (unit cells)
yields reciprocal lattice
determines location and shape of spots,
kinematic theory

$|F|^2$ = structure factor or form factor

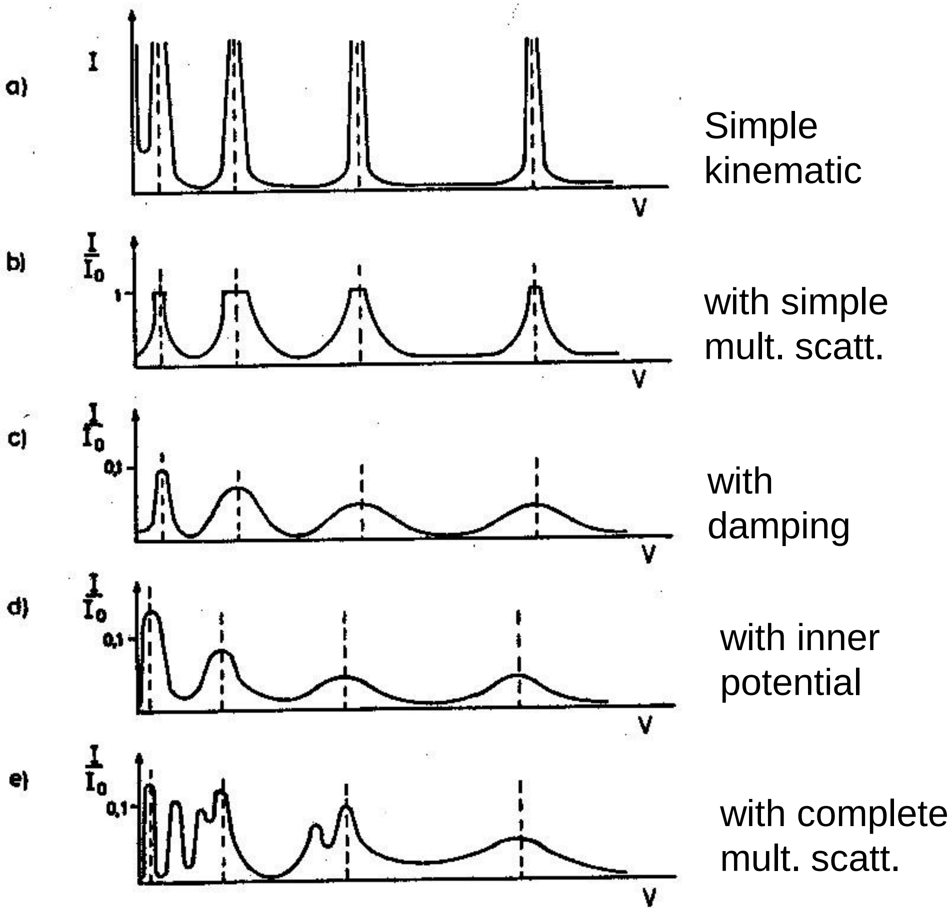
contains contribution from all atoms within the repeat unit,
includes multiple scattering, in-depth attenuation,
dynamic theory

Multiple scattering

Henzler/Göpel fig. 3.7.3, p.151



I-V-curve (schem.)



Henzler/Göpel, fig. 3.7.4, p.152

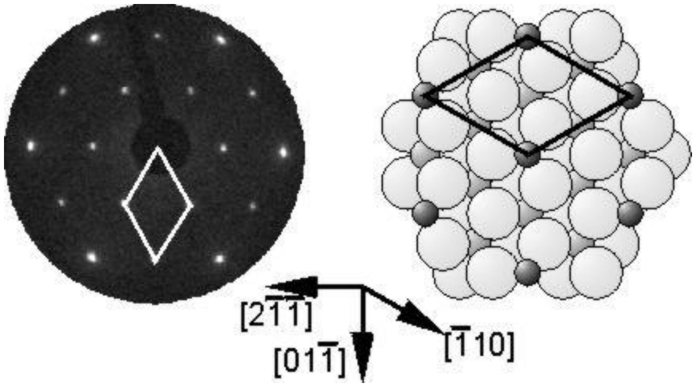
Dynamic LEED analysis:
No direct deduction of structure from I-V-curves:

Guess structure model
calculate I-V-curves
compare with measured curves
modify model
check if improval
if yes: proceed modifying in this direction
if no: modify in another direction
or guess new model

Disadvantage:
Only for ordered structures
Much computer time

But:
One of very few methods for structure analysis of first few atomic layers (~1 nm)

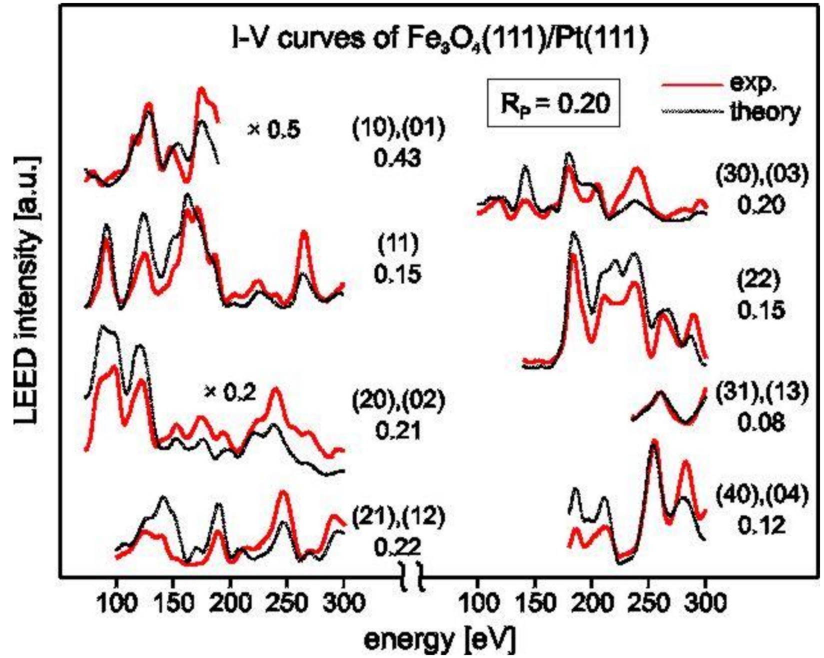
Pt(111)



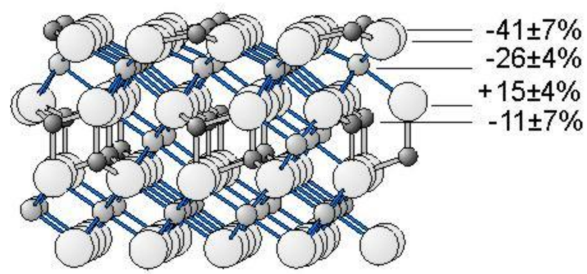
Fe_3O_4(111),
(inverse spinel)
10 nm thick
on Pt(111)

LEED-I-V analysis is one of very few reliable surface structure analysis methods!

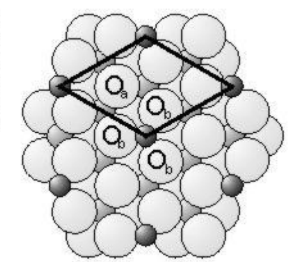
Michael Ritter,
Werner Weiss
Guido Ketteler



a)



b)



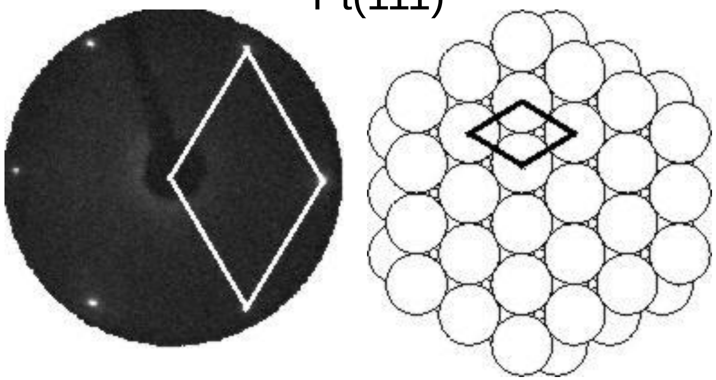
c)

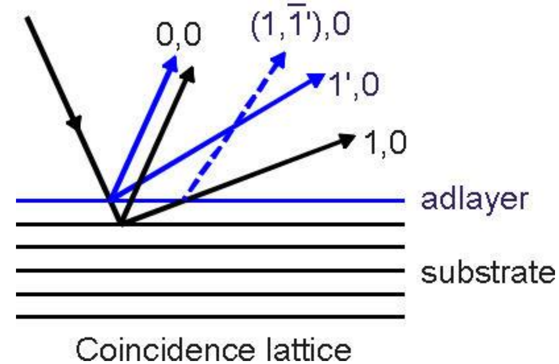
bulk repeat unit

Fe_3O_4(111) surface		layer distances [Å] bulk	surface	relaxations [%]
Fe_{tet1}	d_1	0.64	0.38±0.05	-41±7
O_1 (O_b, O_a)	b_1	0.04	0.08±0.09	
	d_2	1.18	0.87±0.05	-26±4
Fe_{oct1}	d_3	1.18	1.36±0.05	+15±4
O_2 (O_b, O_a)	b_2	0.04	0.12±0.09	
	d_4	0.64	0.57±0.05	-11±7
Fe_{tet2}	d_5	0.60	0.60	0
Fe_{oct2}				

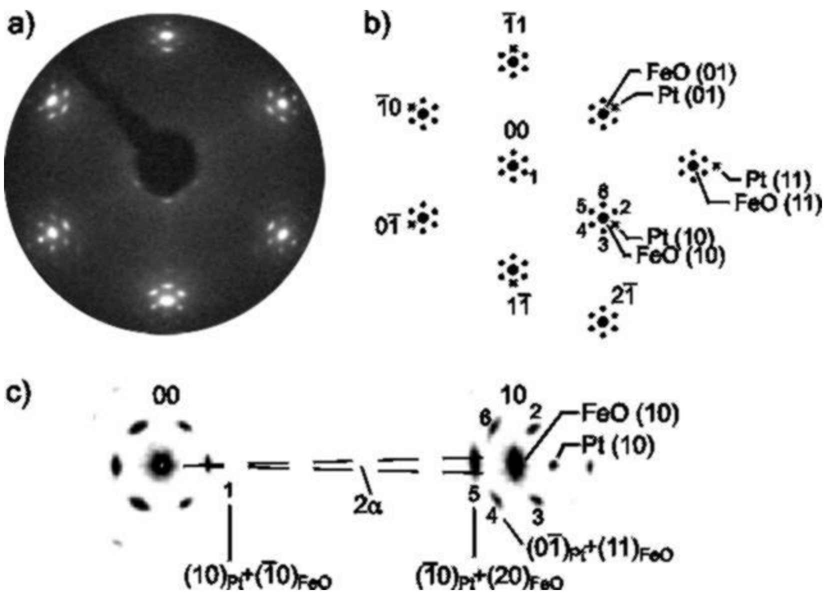
FeO/Pt(111), satellite pattern: multiple scattering, kinematic

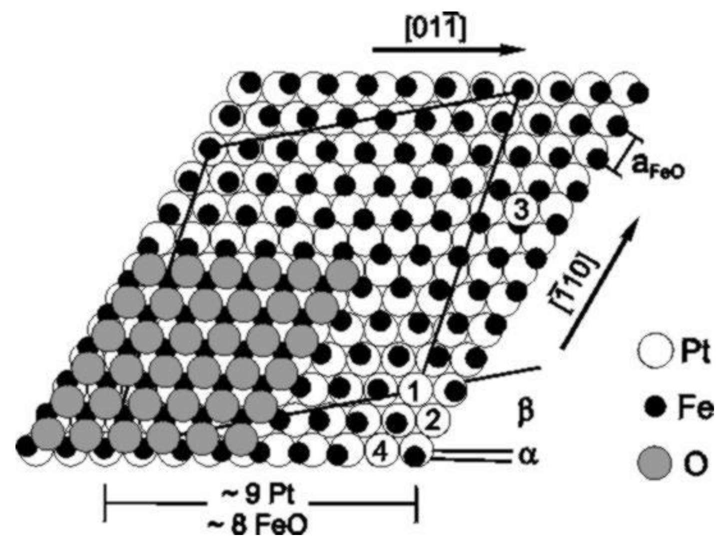
Pt(111)





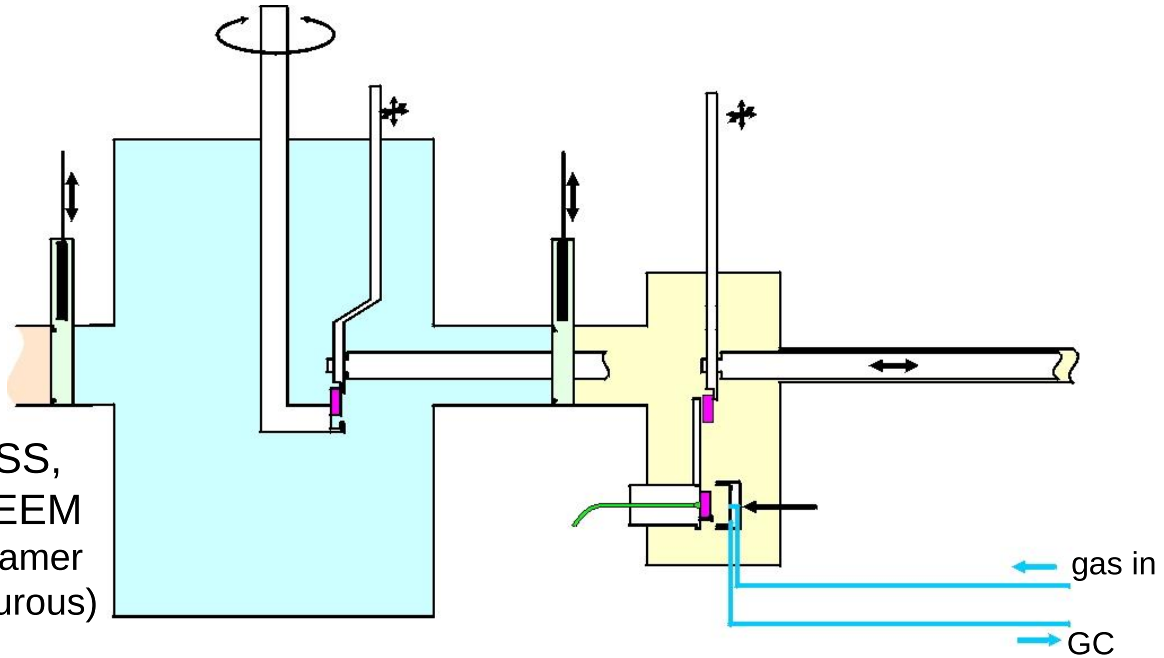
0.9 ML FeO(111) on Pt(111), „structure 1"





M. Ritter, W. Ranke, W. Weiss

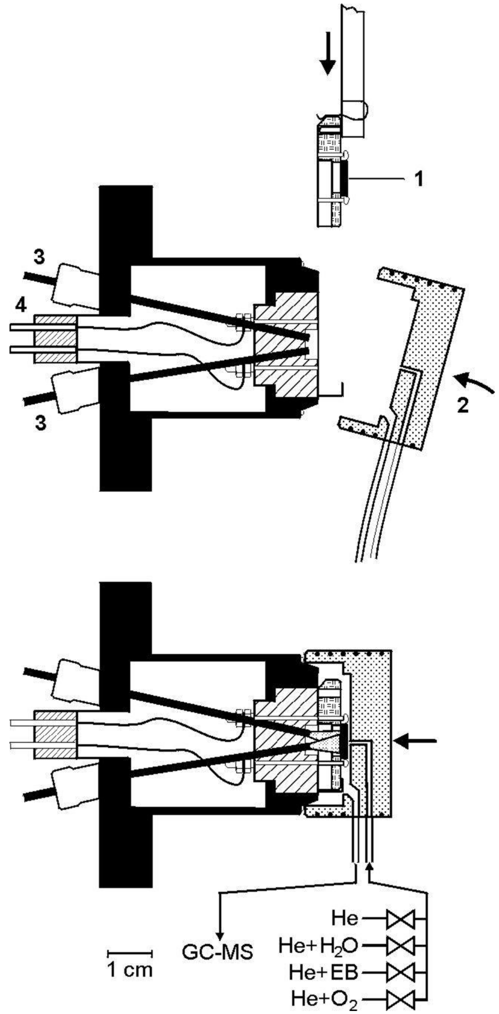
5. LEED in model catalysis - example

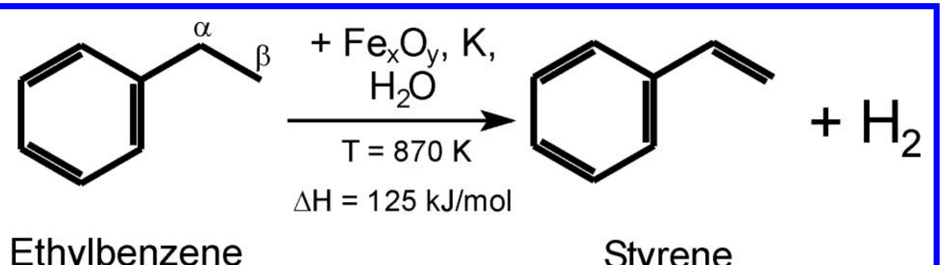


ISS,
PEEM
(Samer
Aburous)

UHV
LEED, AES, TDS
p= 10^{-6} to
10^{-10} mbar

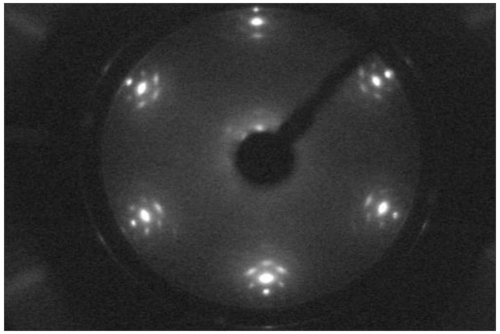
Preparation
reactor
p=1000 to
10^{-6} mbar



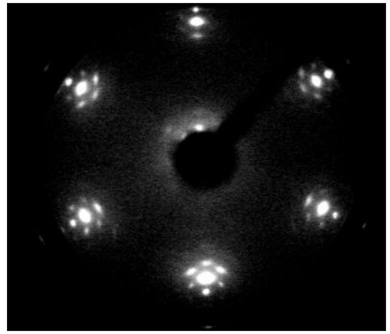


Manfred Swoboda
Christian Kuhrs
Werner Weiss

Distinguish different Fe-O-phases

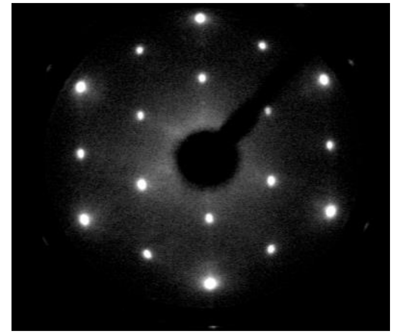


as measured

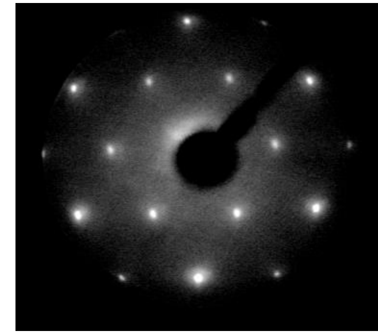


contrast enhanced

FeO(111)/Pt(111), 1 ML

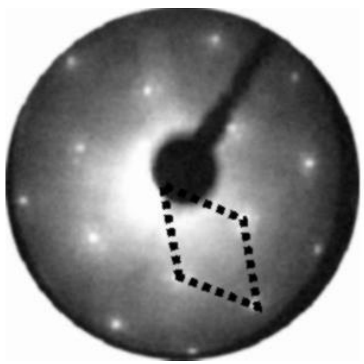


$Fe_3O_4(111)$

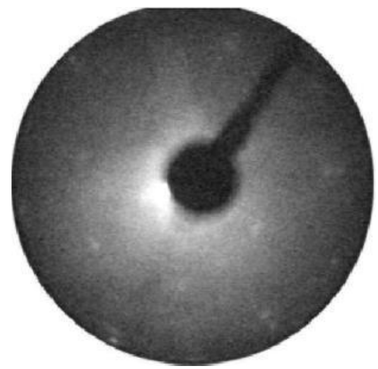


α-$Fe_2O_3(0001)$

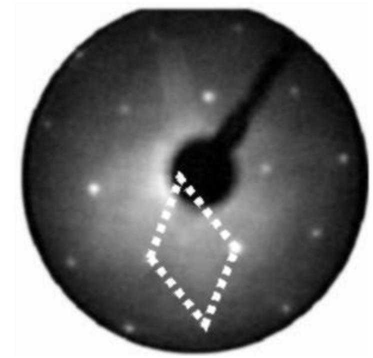
Change of order and phase during reaction



Starting surface: α-$Fe_2O_3(0001)$ (hematite), defective



After reaction
- no long-range order
- strong C peak in AES



After mild TPO (thermal programmed oxidation)
- reordered
- no longer hematite but $Fe_3O_4(111)$ (magnetite

Osama Shekhah

6. Conclusions

For qualitative information on surface structure very simple (display LEED)
- Order
- Periodicity
- Symmetry

For quantitative information on deviations from ideal order (SPA-LEED)
- Domain size
- Antiphase domains
- atomic steps

For quantitative analysis of surface structure (dynamic I-V-curve analysis)
- Precise atomic arrangements
- Relaxations
- Reconstructions