Low Energy Electron Diffraction - LEED

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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

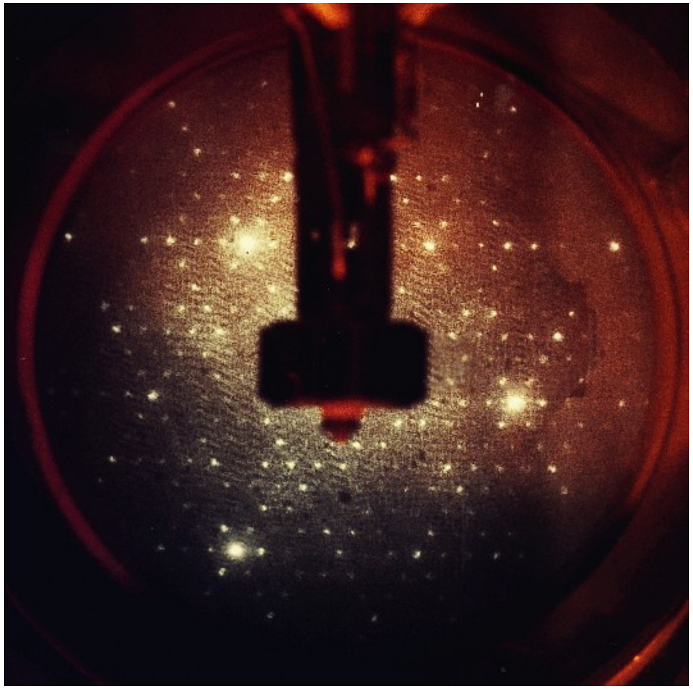
Surface science, UHV, p~10^{-10} mbar

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

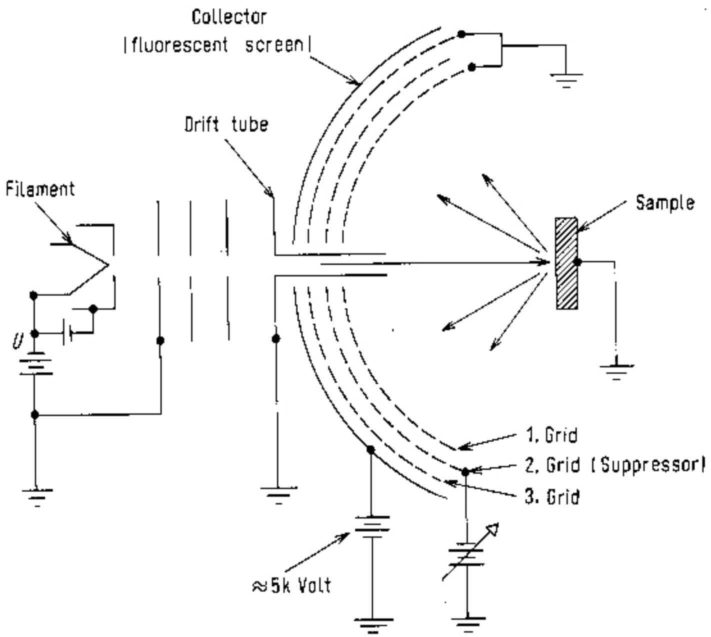
For electrons: $\lambda = \sqrt{150 / E_0}$ E_0 in eV, λ in Å.

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

corresponds to atomic dimensions, similar to XRD



Si(111)-(7x7)

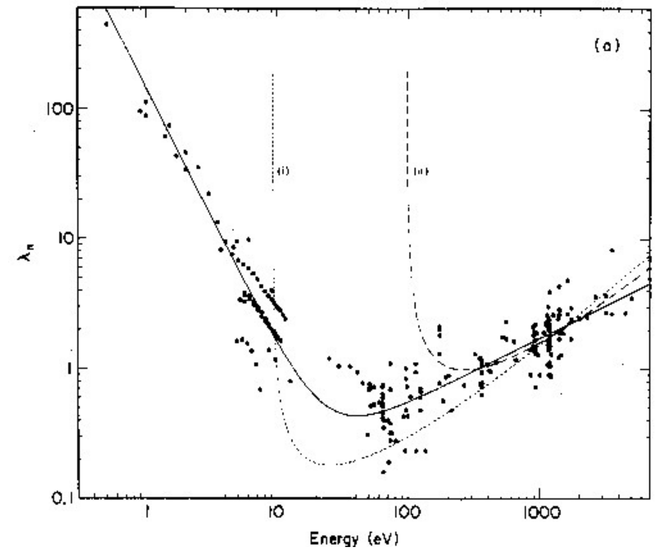


LEED display system

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.

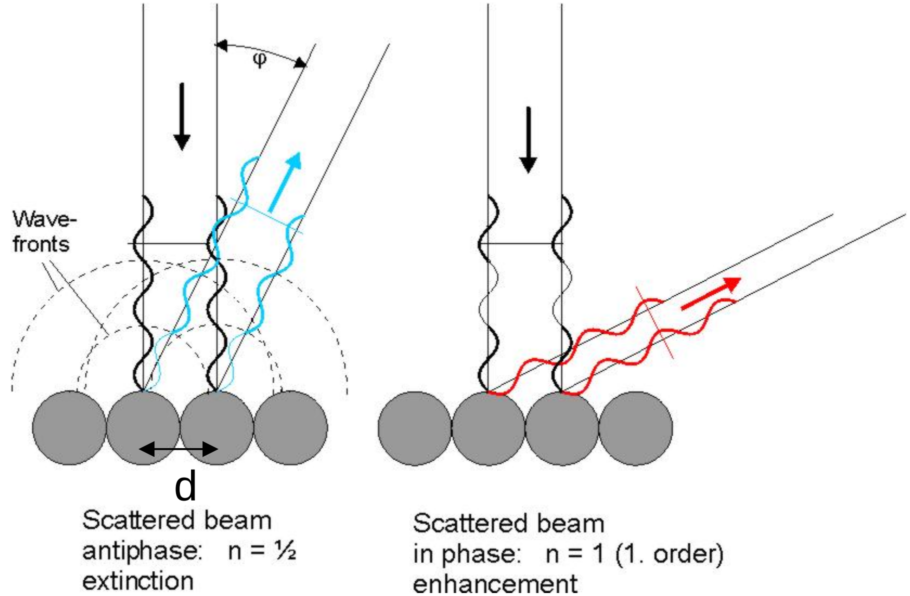
Analogy to optical grating.

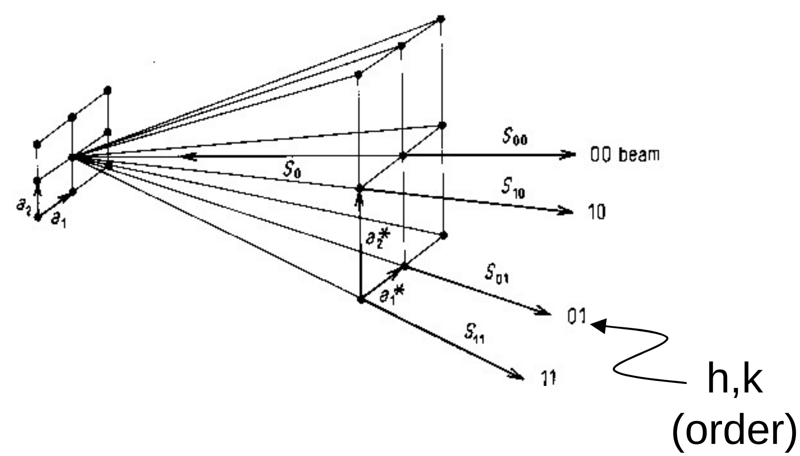
Constructive interference:
Enhancement of intensity only
in certain directions:

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

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

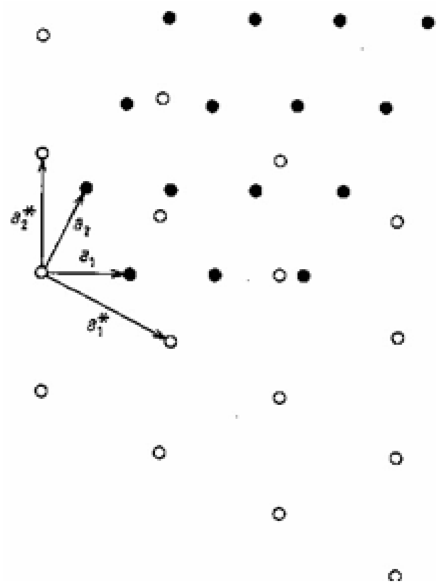
Constructive interference for:

$$\mathbf{a_1}\,(\mathbf{s} - \mathbf{s_0}) = h\,\lambda$$

$$\mathbf{a_2}\,(\mathbf{s} - \mathbf{s_0}) = k\,\lambda$$

(Laue conditions for 2 dimensions)

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



Example

Ertl/Küppers fig. 9.11, p 216

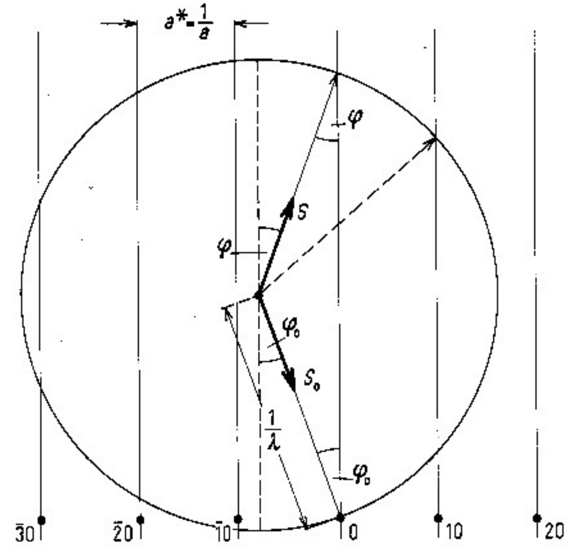
It follows for the direction of beams:

$$1/\lambda\,(\mathbf{s} - \mathbf{s_0}) = 1/\lambda\,\Delta\mathbf{s} = h\,\mathbf{a_1^*} + k\,\mathbf{a_2^*} = \mathbf{g}$$

$\mathbf{g}$ = reciprocal lattice vector

Ewald sphere construction

- plot reciprocal lattice (rods)
- plot direction of incident beam (**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)

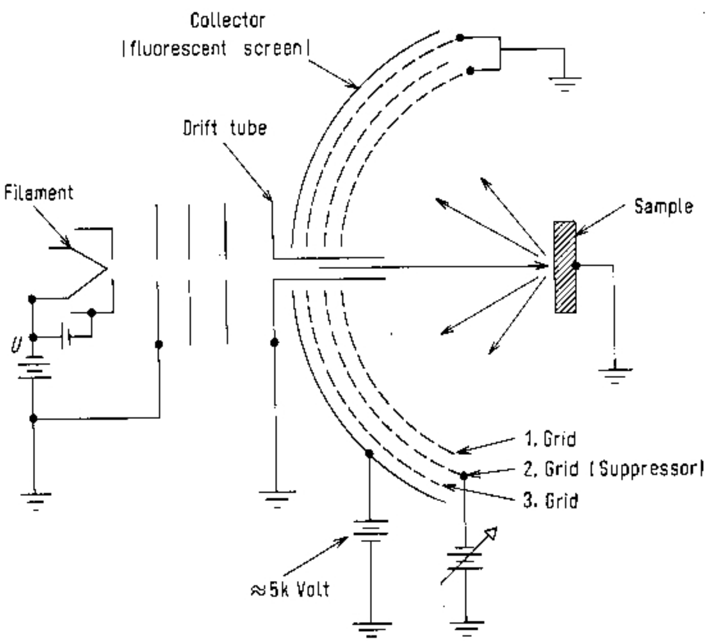


Ertl/Küppers fig. 9.13, p. 218

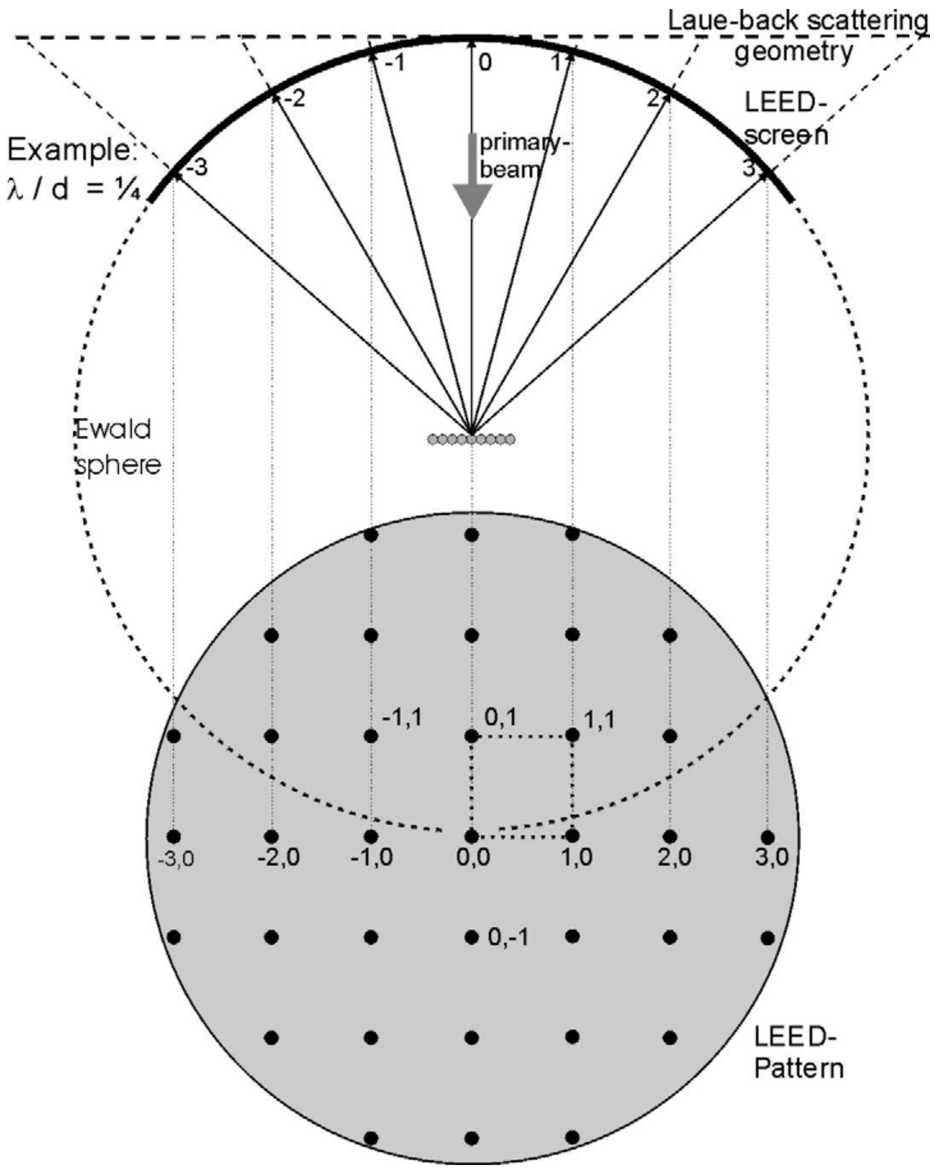
Usual arrangement:

Normal incidence,

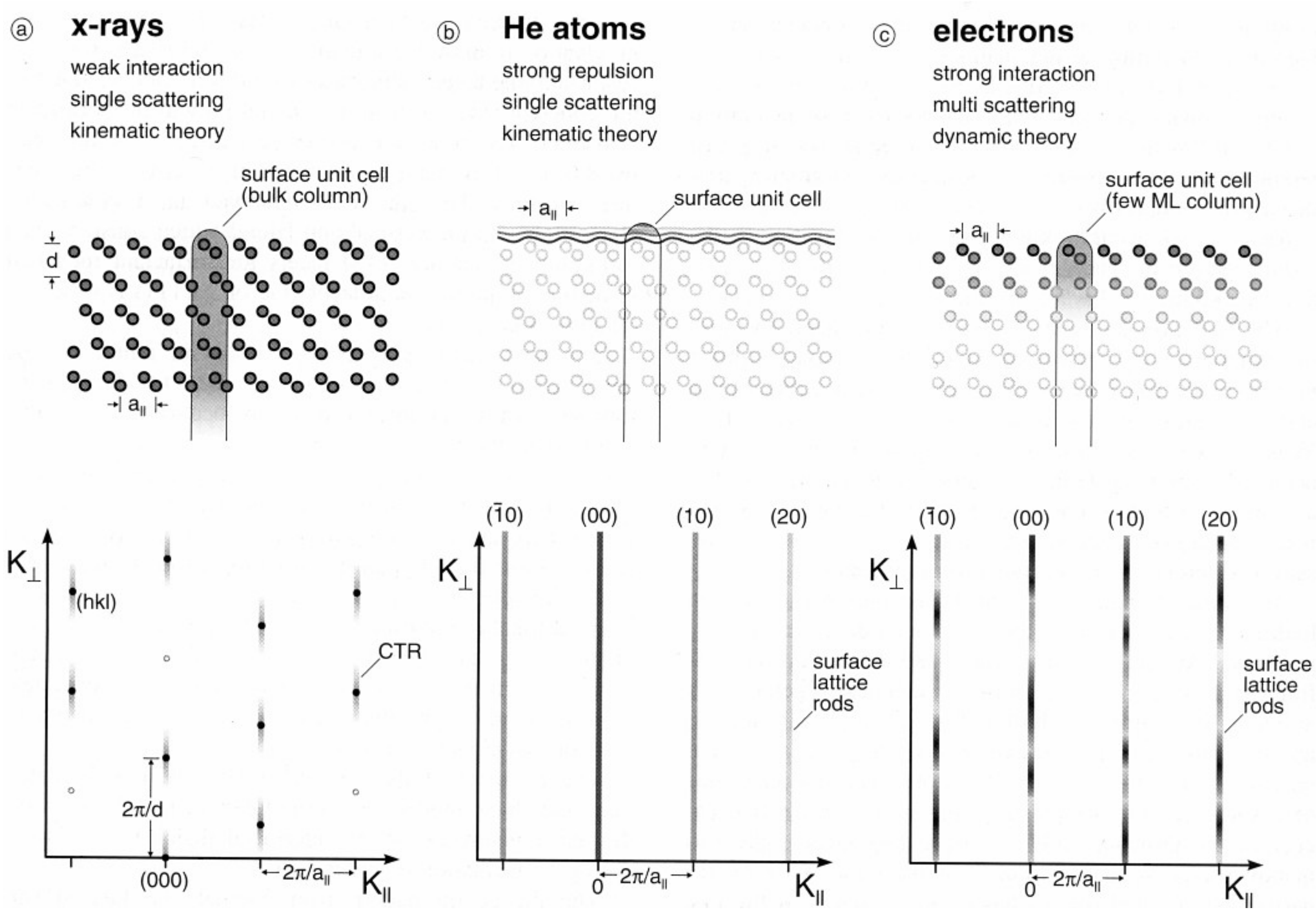
symmetrical diffraction pattern



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

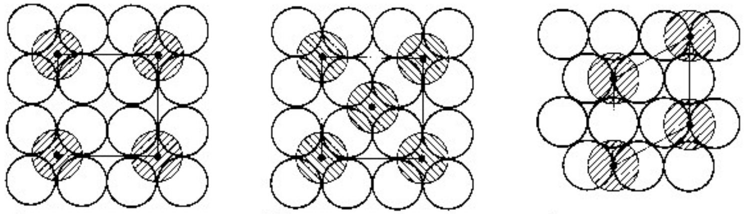
Superstructures result from:

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) c) (√3x√x)R30°

on square lattice on hex. lattice

Superstructure nomenclature

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

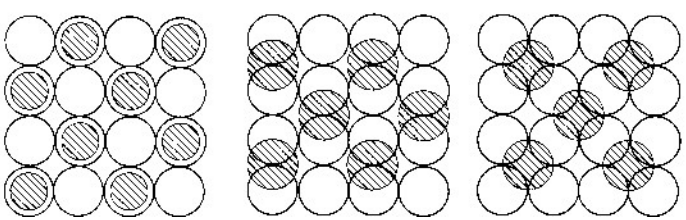
Matrix notation (Park and Madden)
more general

$$\begin{matrix} m_{11} & m_{12} \\ m_{12} & m_{22} \end{matrix} \qquad \mathbf{b_1} = m_{11}\, \mathbf{a_1} + m_{12}\, \mathbf{a_2}$$
$$\mathbf{b_2} = m_{12}\, \mathbf{a_1} + m_{22}\, \mathbf{a_2}$$

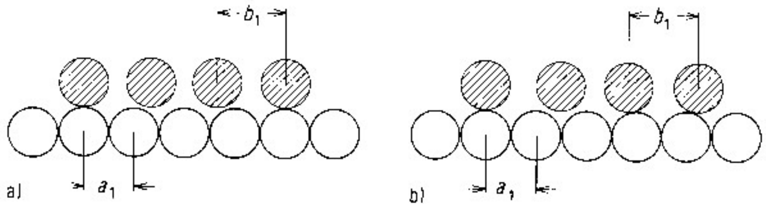
Wood	(2×2) [ϑ=0 is omitted]	(√3×√3)R30°
Matrix	$\begin{matrix} 2 & 0 \\ 0 & 2 \end{matrix}$	$\begin{matrix} 1 & 1 \\ 2 & -1 \end{matrix}$

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

Ertl/Küppers fig. 9.6, p.208



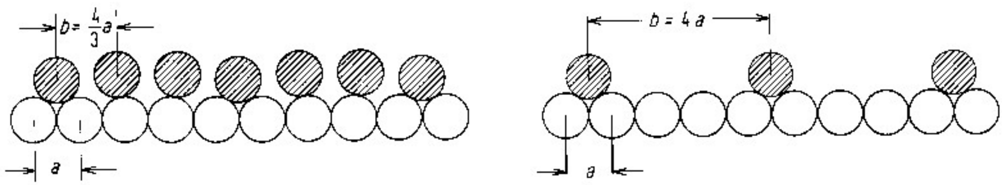
on top bridge 4-fold hollow



coincidence latt.
commensurate

incoherent,
incommensurate

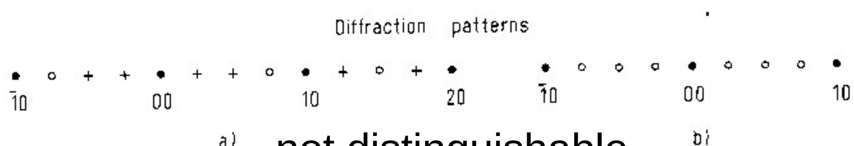
Ertl/Küppers fig. 9.3, p.205



coincidence latt.

simple overlayer struct.

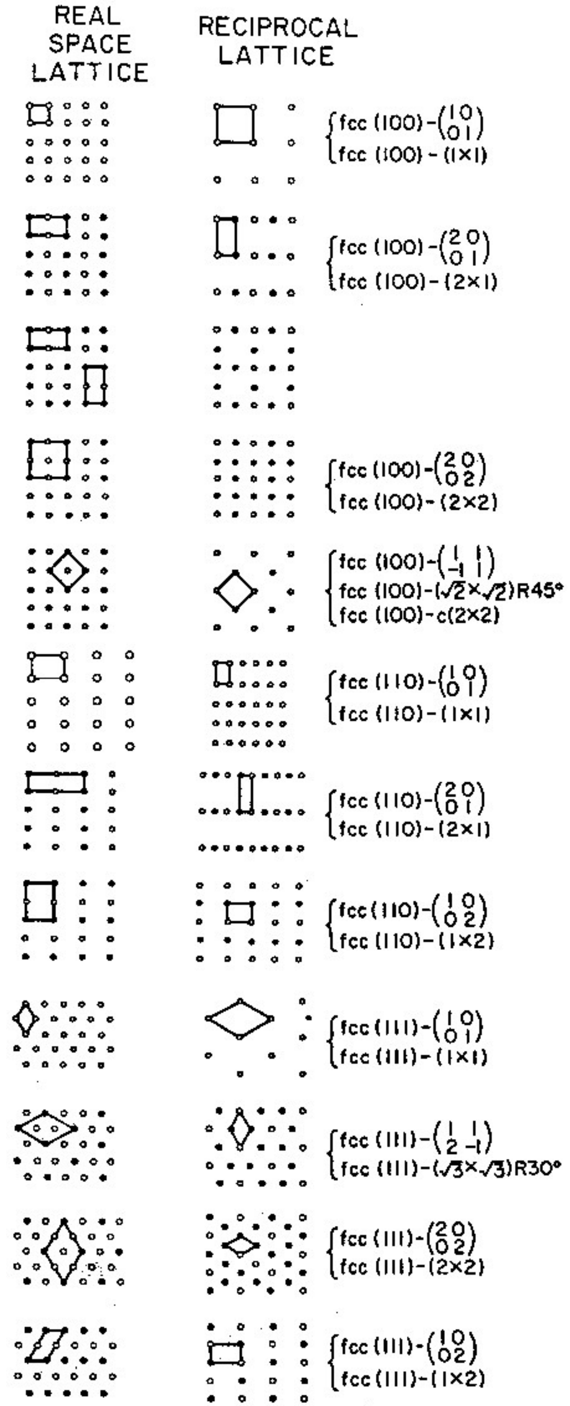
Ertl/Küppers fig. 9.19, p.224



not distinguishable

Real and reciprocal space lattices

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



Superstructures, example 1

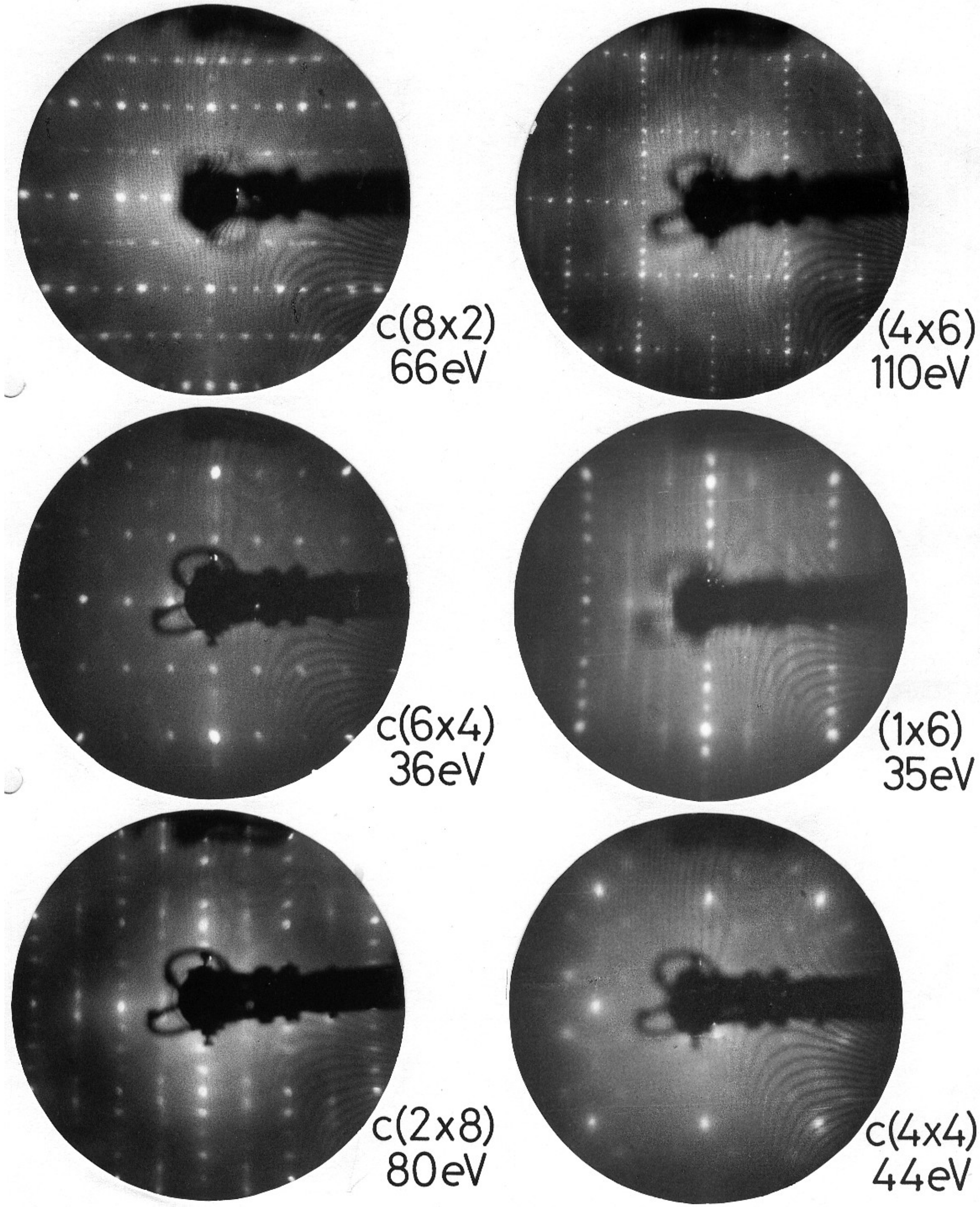
GaAs(001)
clean,
different preparations

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

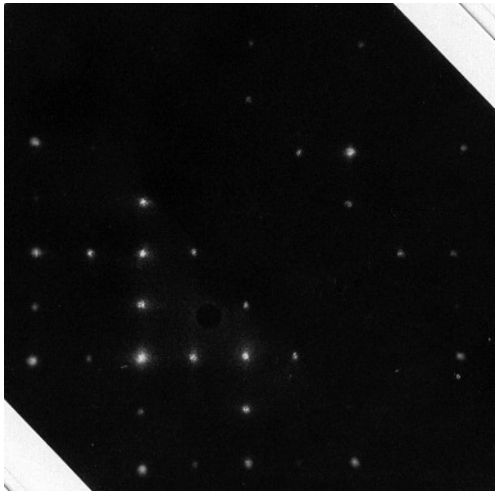
Information from patterns:
- symmetry of unit cell
- size and shape of surface unit cell
- sharpness of spots
  $\rightarrow$ domain size
- background intensity
  $\rightarrow$ concentration of point defects

Drathen, Ranke, Jacobi, 1978



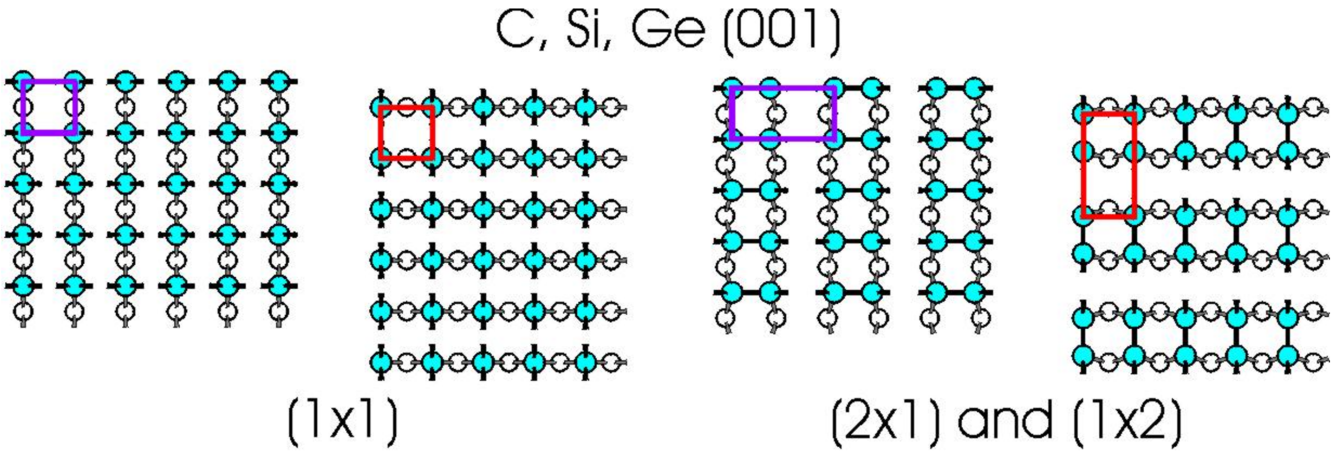
Superstructures, example 2

Si(001) clean

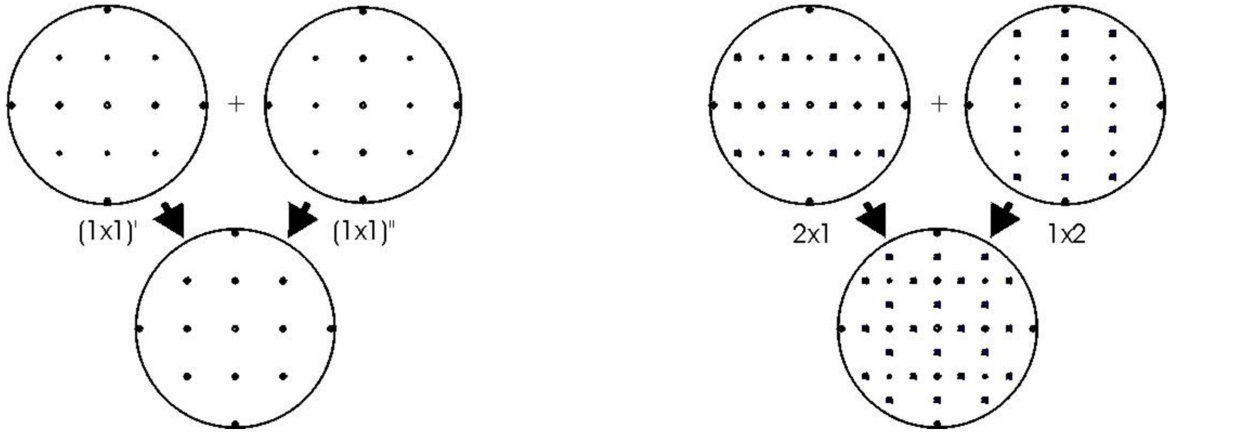


no 2x2 structure!
central spots missing
⟶ two-domain 2x1

Wasserfall, Ranke, 1994



no 4-fold rotation symmetry!



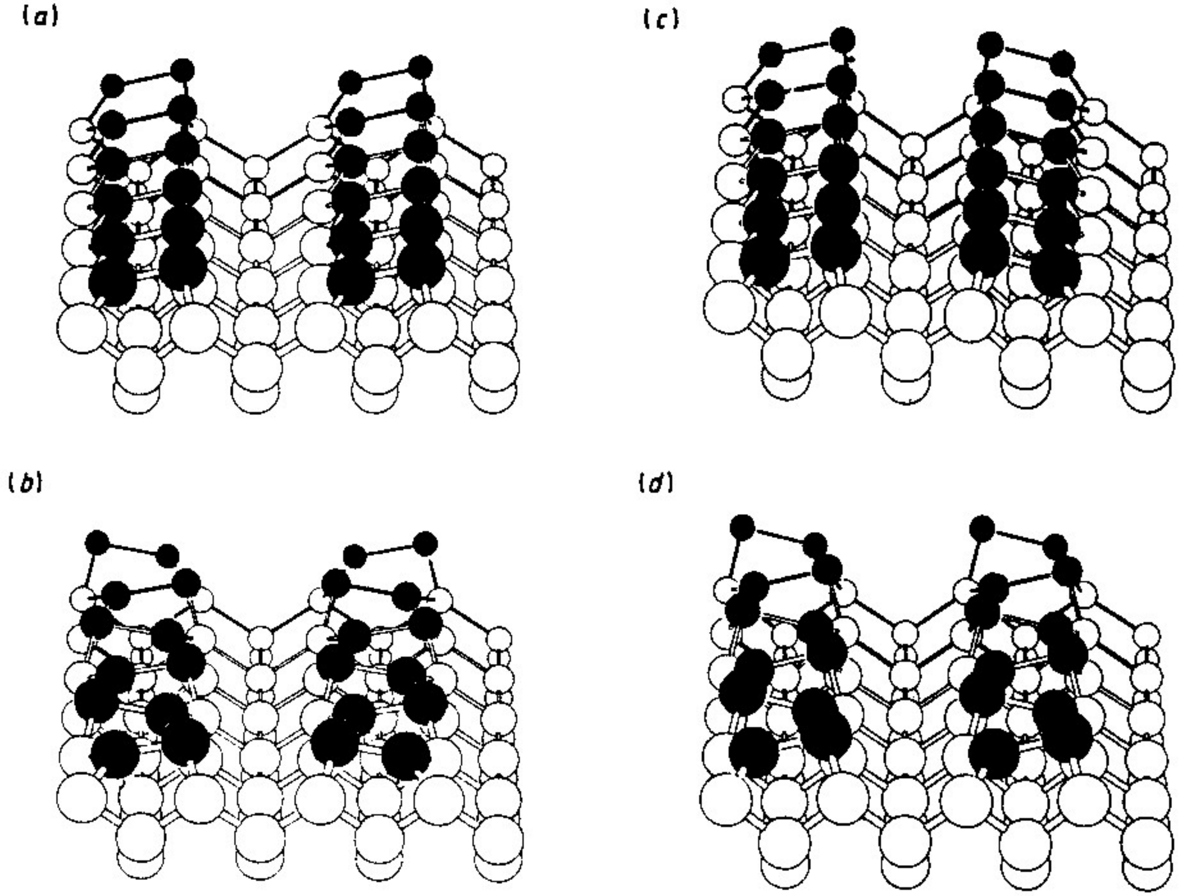
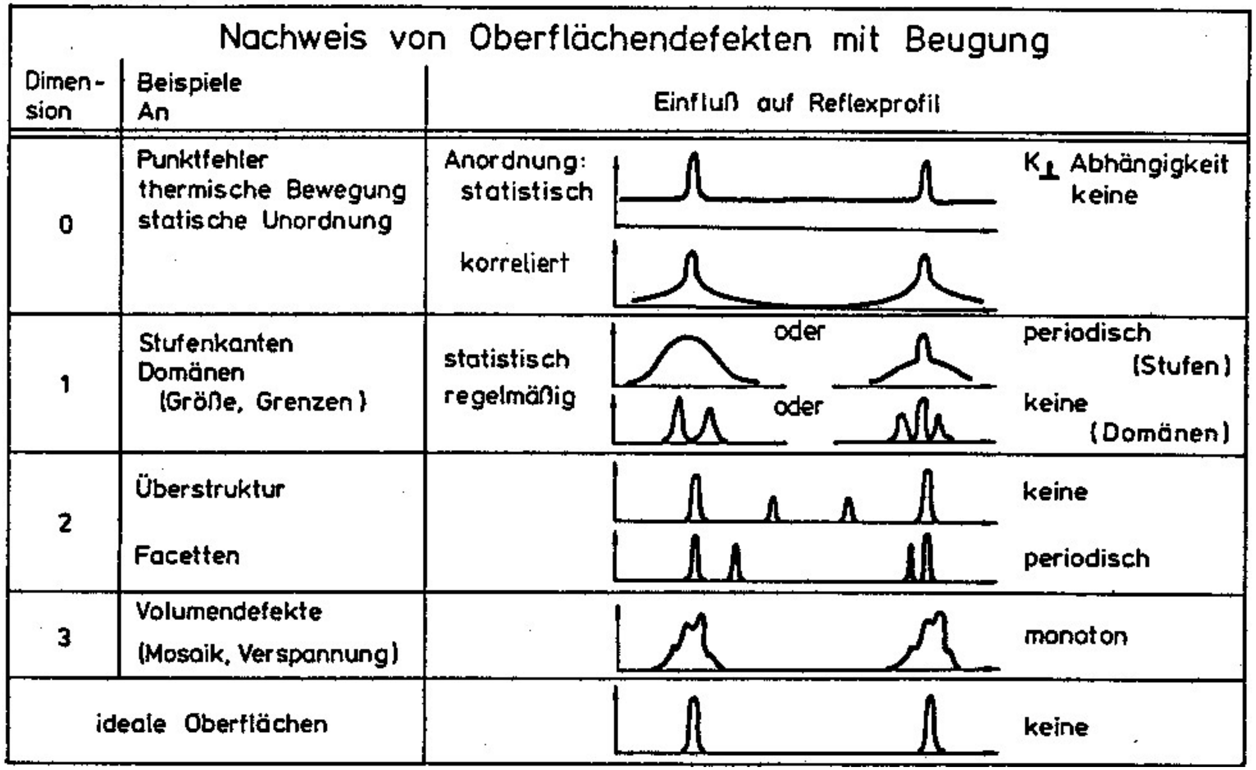


Figure 3. Buckled dimer reconstructions on the (001) surface of germanium: (*a*) b(2 × 1); (*b*) c(4 × 2); (*c*) p(4 × 1); (*d*) p(2 × 2).

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)



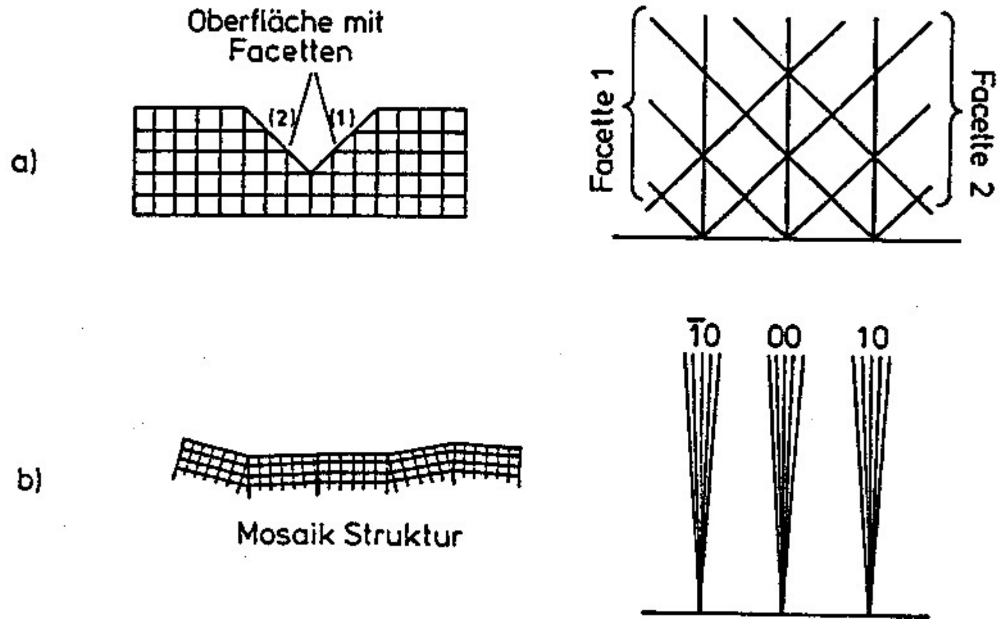
Nachweis von Oberflächendefekten mit Beugung

Dimension	Beispiele An	Einfluß auf Reflexprofil		$K_\perp$ Abhängigkeit
0	Punktfehler thermische Bewegung statische Unordnung	Anordnung: statistisch		keine
		korreliert		
1	Stufenkanten Domänen (Größe, Grenzen)	statistisch	oder	periodisch (Stufen)
		regelmäßig	oder	keine (Domänen)
2	Überstruktur			keine
	Facetten			periodisch
3	Volumendefekte (Mosaik, Verspannung)			monoton
ideale Oberflächen				keine

Henzler, Göpel Abb. 3.8.10, p.176

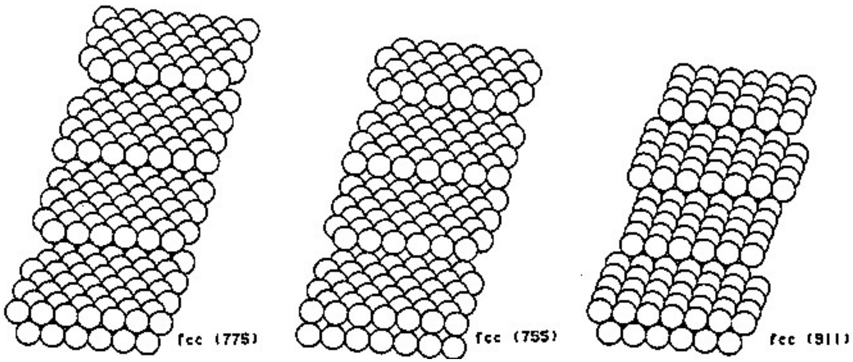
Facets and mosaic

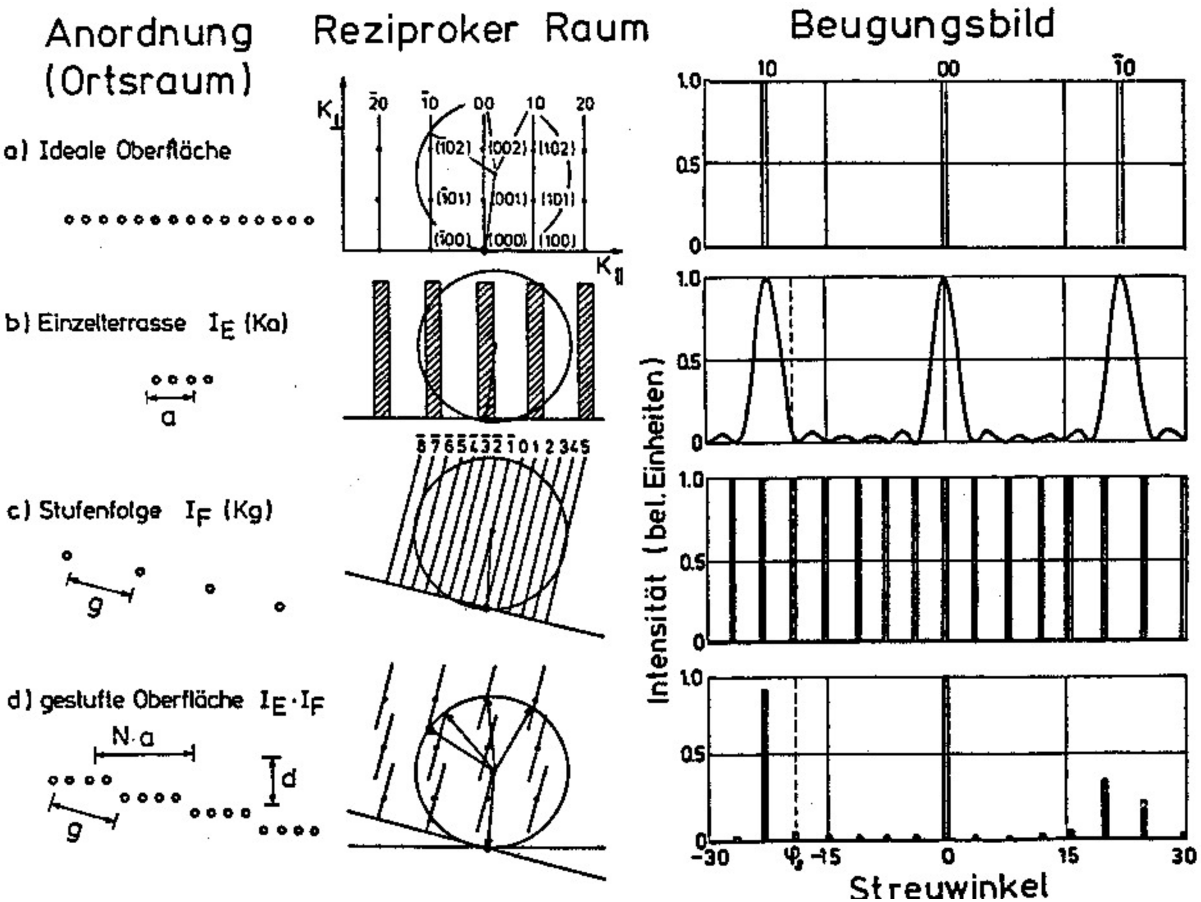
Henzler, Göpel
Abb. 3.8.4, p.167



Regular atomic steps

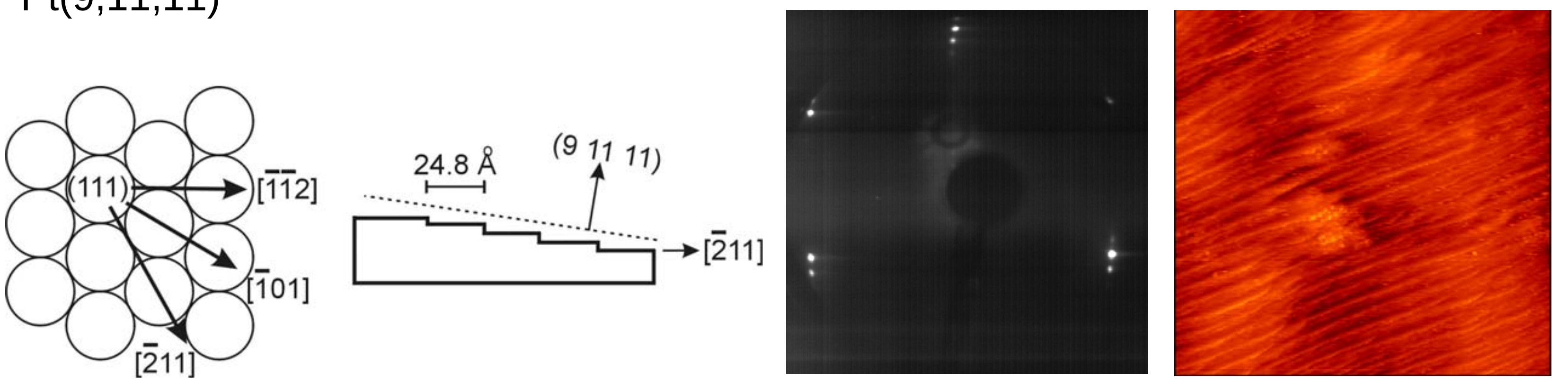
Van Hove et al., fig. 3.6, p.58



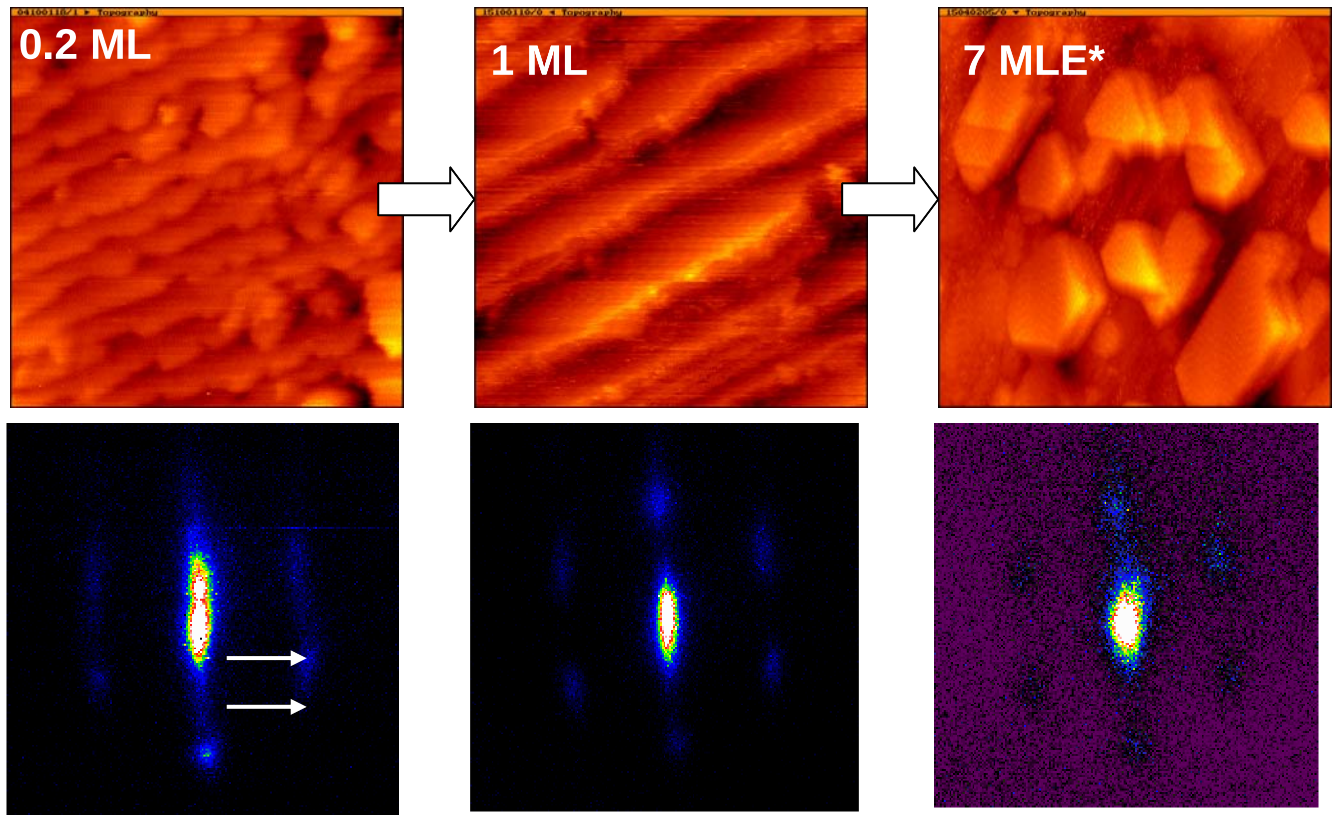


Henzler, Göpel, fig. 3.8.3, p.165

Pt(9,11,11)



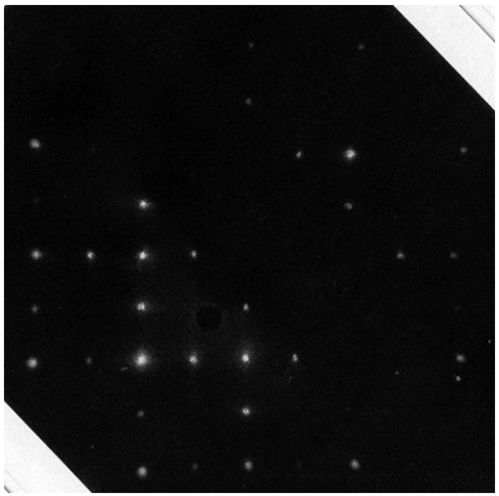
T=1000K



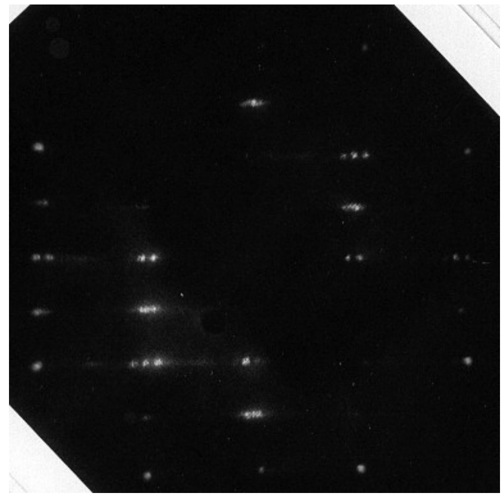
Example: Si(001)vic

Si(001)

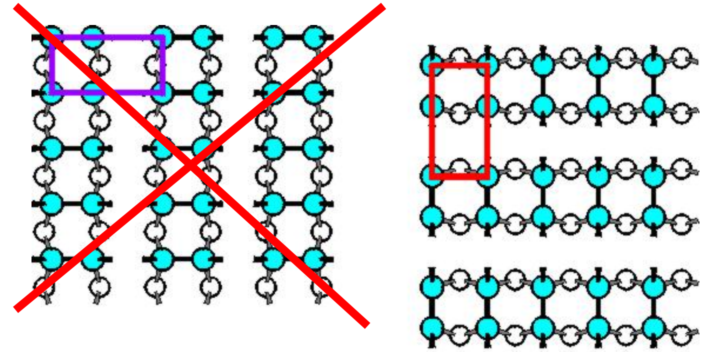
[-110]



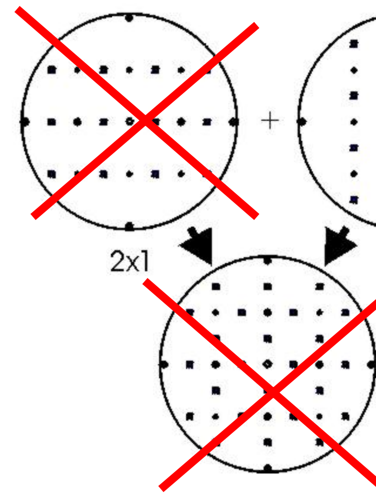
[110]

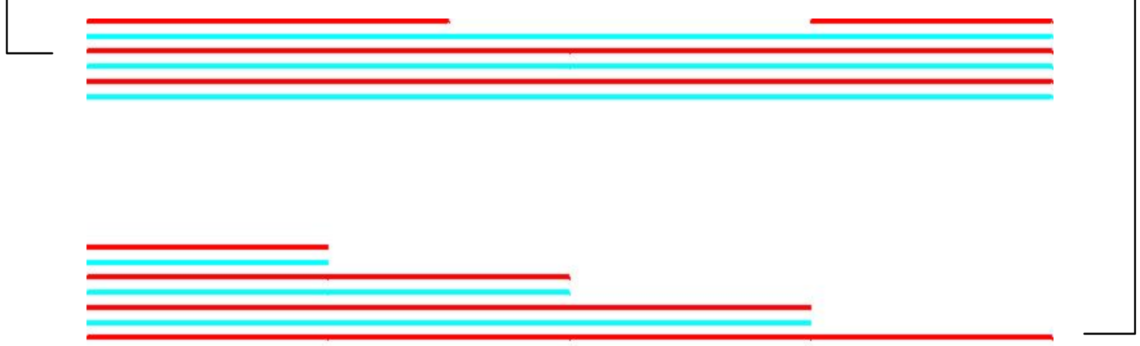


Si(001)vic, 5°→[110]



(2x1) and (1x2)





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

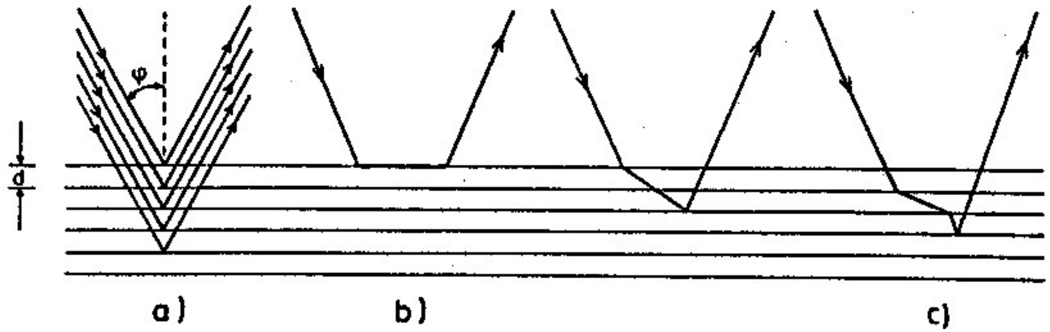
contains shape and arrangement of repeat units (unit cells)
yields reciprocal lattice
determines location and shape of spots,
kinematic theory

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

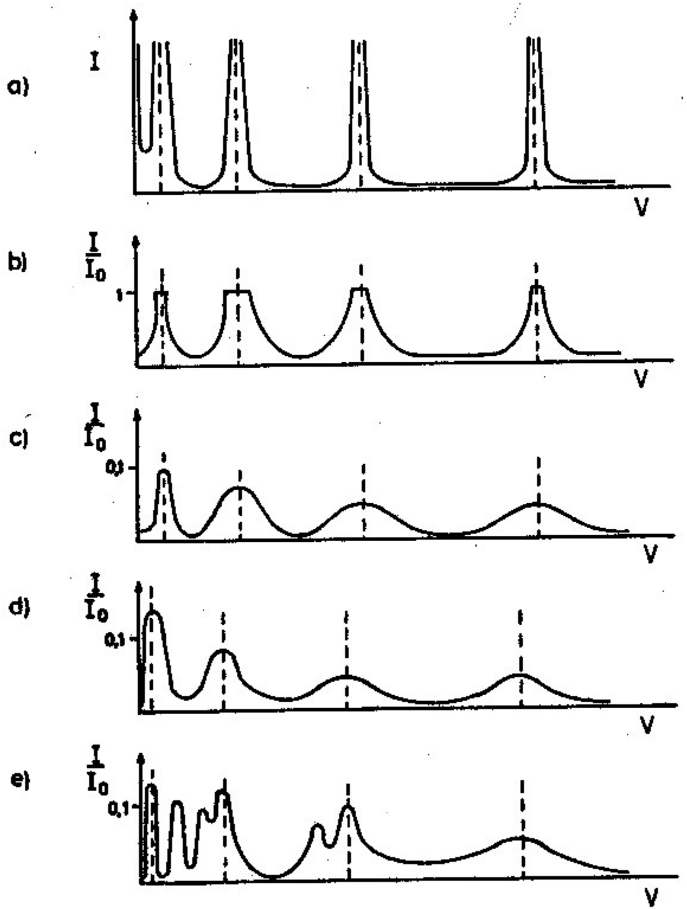
contains contribution from all atoms within the repeat unit,
includes multiple scattering, in-depth attenuation,
dynamic theory

Multiple scattering

Henzler/Göpel fig. 3.7.3, p.151



I-V-curve (schem.)



Simple kinematic

with simple mult. scatt.

with damping

with inner potential

with complete mult. scatt.

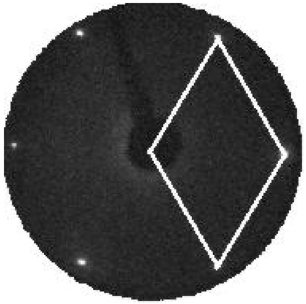
Henzler/Göpel, fig. 3.7.4, p.152

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

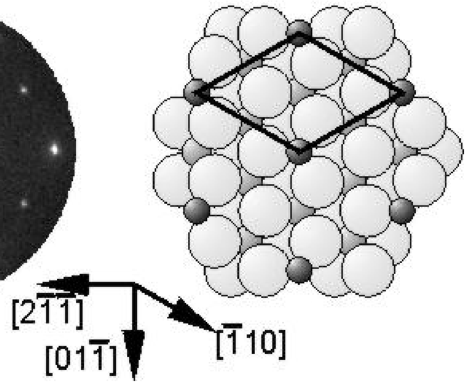
Guess structure model
calculate I-V-curves
compare with measured curves
modify model
check if improval
if yes: proceed modifying in this direction
if no: modify in another direction
or guess new model

Disadvantage:
Only for ordered structures
Much computer time

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



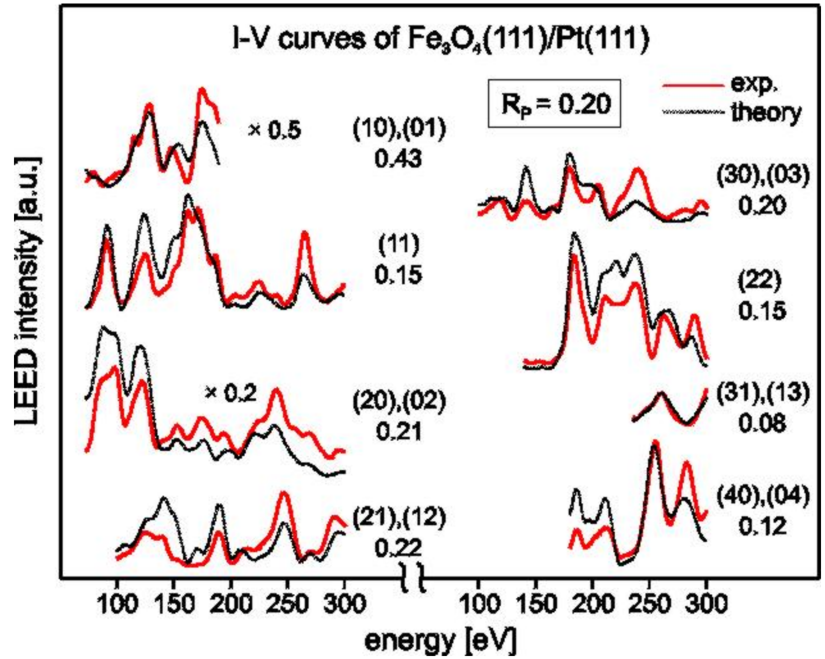
Pt(111)



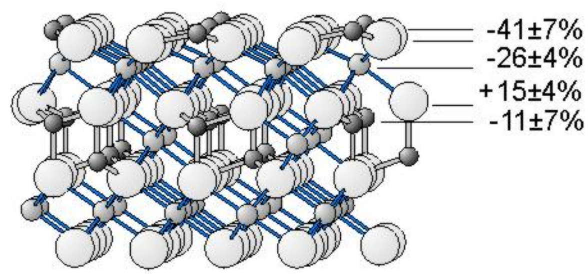
Fe_3O_4(111),
(inverse spinel)
10 nm thick
on Pt(111)

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

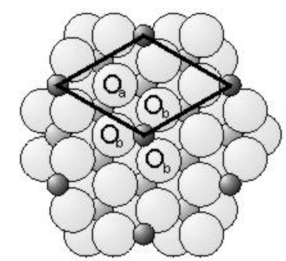
Michael Ritter,
Werner Weiss
Guido Ketteler



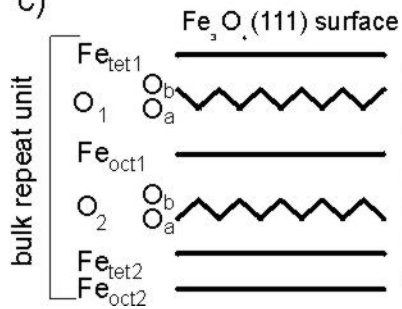
a)



b)



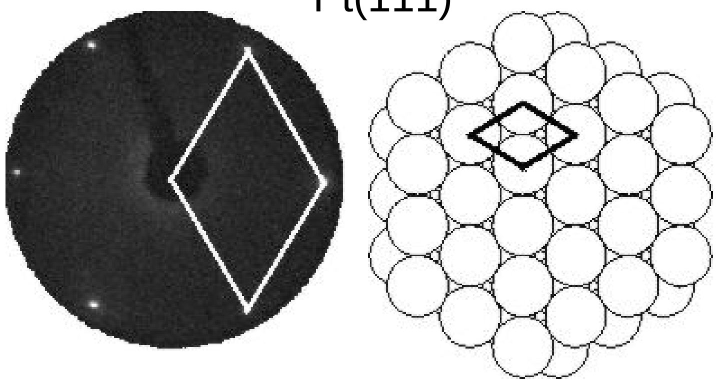
c)

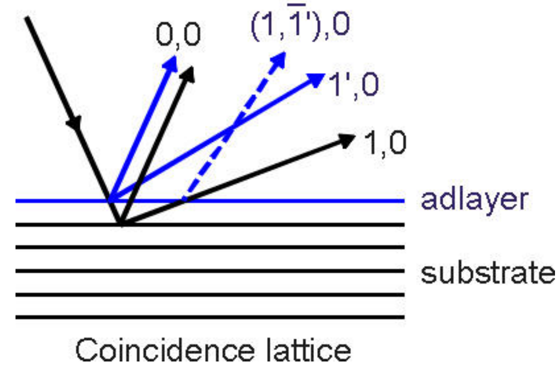


	layer distances [Å] bulk	surface	relaxations [%]
d_1	0.64	0.38±0.05	**-41±7**
b_1	0.04	0.08±0.09	
d_2	1.18	0.87±0.05	**-26±4**
d_3	1.18	1.36±0.05	**+15±4**
b_2	0.04	0.12±0.09	
d_4	0.64	0.57±0.05	**-11±7**
d_5	0.60	0.60	**0**

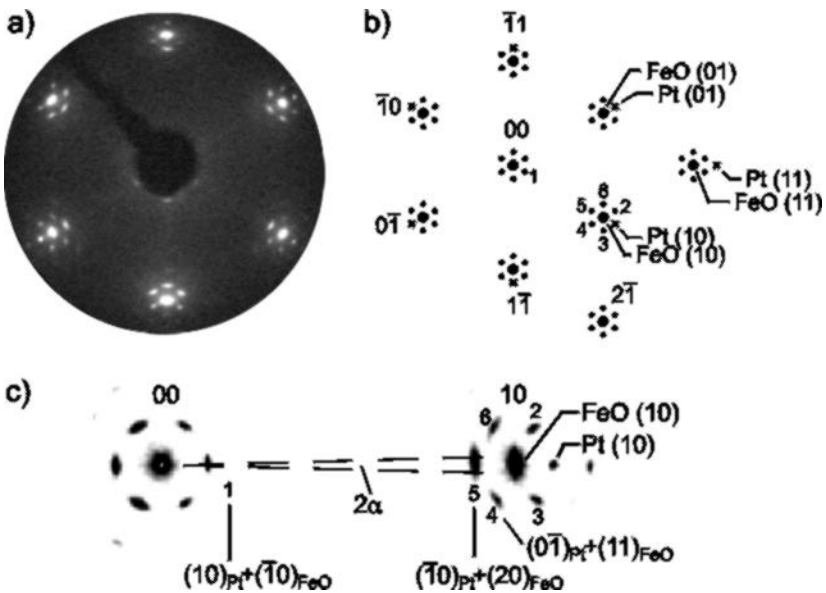
FeO/Pt(111), satellite pattern: multiple scattering, kinematic

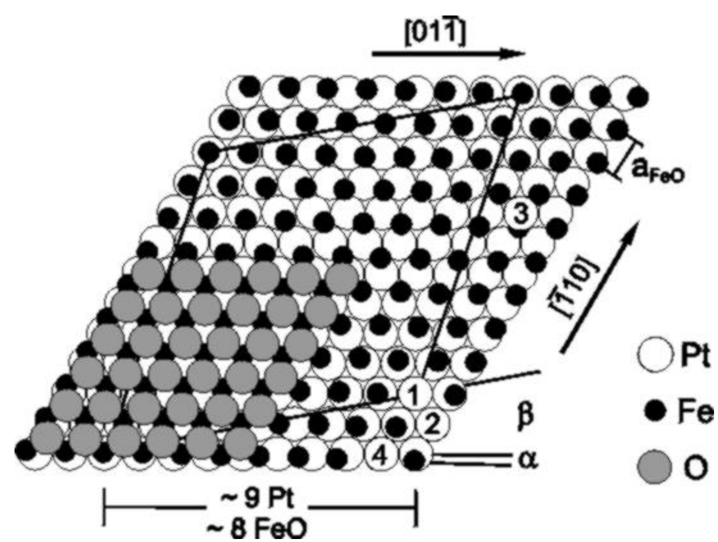
Pt(111)





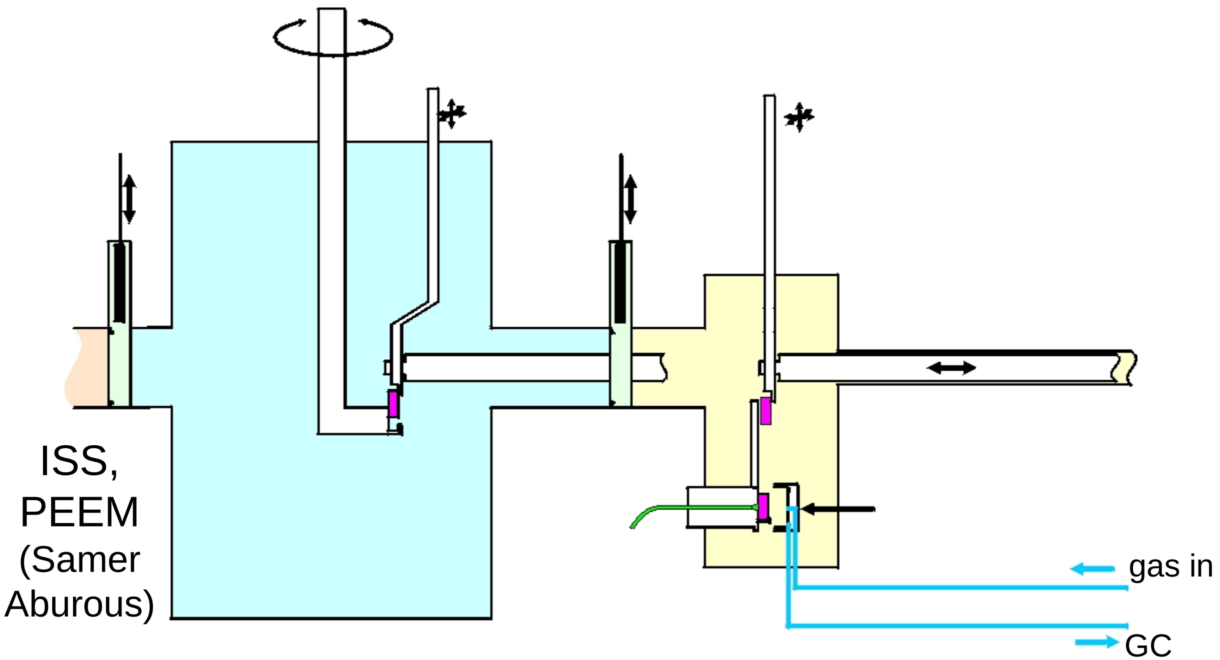
0.9 ML FeO(111) on Pt(111), „structure 1“





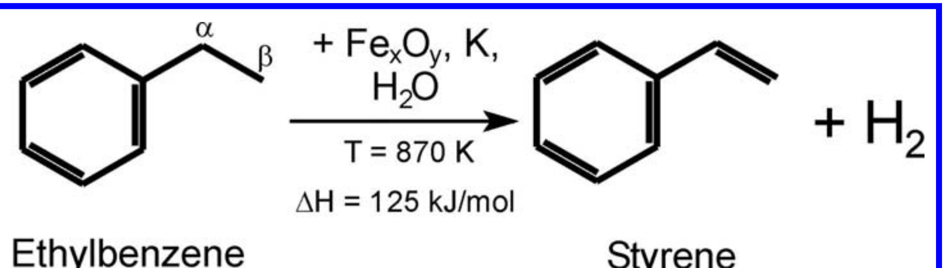
M. Ritter, W. Ranke, W. Weiss

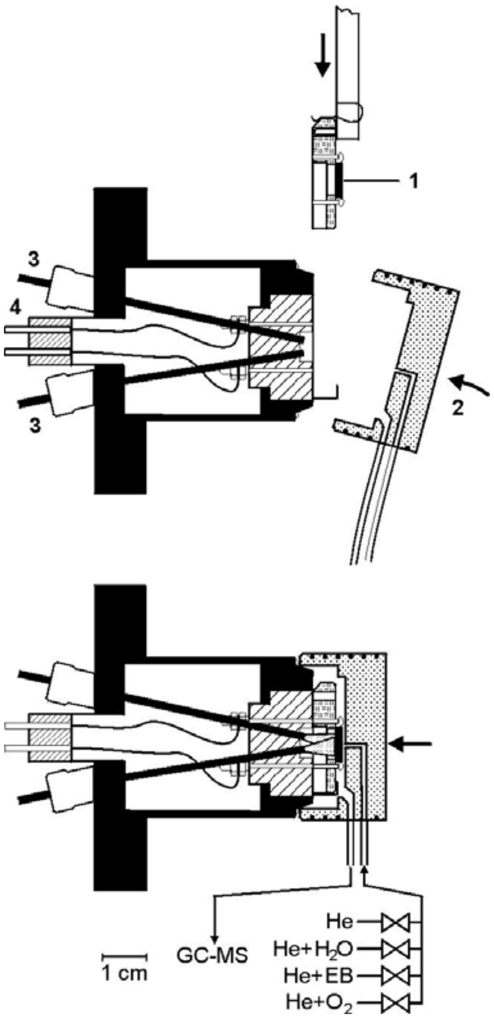
5. LEED in model catalysis - example



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

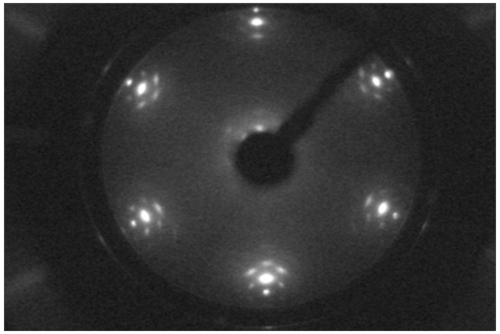
Preparation
reactor
p=1000 to
10^{-6} mbar



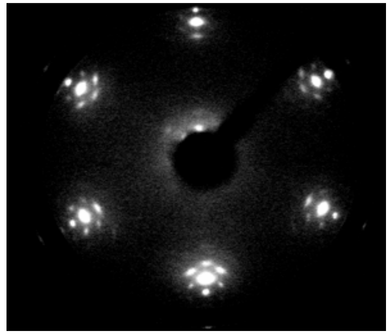


Manfred Swoboda
Christian Kuhrs
Werner Weiss

Distinguish different Fe-O-phases

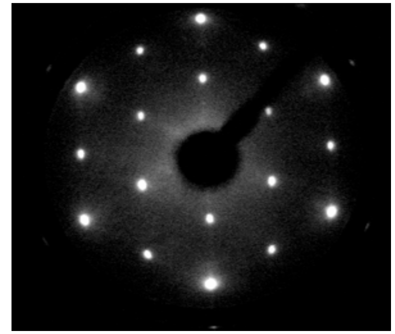


as measured

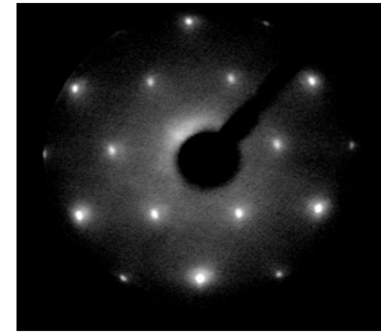


contrast enhanced

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

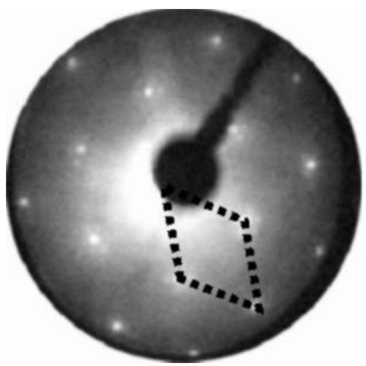


Fe_3O_4(111)

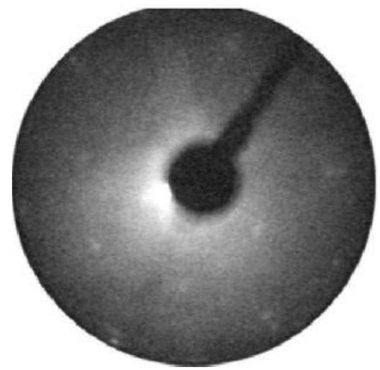


α-Fe_2O_3(0001)

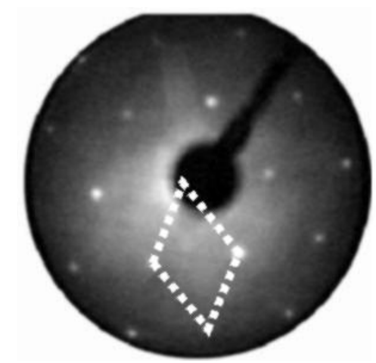
Change of order and phase during reaction



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