Physik der Festkörperoberflächen und Grenzflächen

-

Oberflächenphysik I

Termin: dienstags, LS 19 514, 10:15- 11:45

Alexander Weismann

weismann@physik.uni-kiel.de

www.ieap.uni-kiel.de/surface/ag-berndt

PDFs auf Physikseiten Oberflächenphysik I
ID, PWD: werden noch bekannt gegeben

Contents

- Geometry
- Methods (diffraction, real space, spectroscopies)
- Electronic structure (surface states, adsorbates)
- Vacuum technology
- Dynamics (surface phonons, diffusion)
- Nucleation and growth
- Molecules at surfaces
- Nanoscience (molecular electronics, spintronics)

Literature: General

- H. Ibach, *Physics of Surfaces and Interfaces* (Springer, 2006)
- A. Zangwill, *Physics at surfaces* (Cambridge University Press, 1998)
- H. Lüth, *Surfaces and interfaces of sold materials* (Springer, 1995)
- M. Henzler, W. Göpel, *Oberflächenphysik des Festkörpers* (Teubner, 1994)
- G. Ertl, J. Küppers, *Low energy electrons and surface chemistry* (VCH 1974)
- Jörg Kröger, *Physics of surfaces and interfaces,* Lecture notes, CAU Kiel (now: TU Ilmenau)

- G. A. Somorjai, Y. Li, *Surface Chemistry and Catalysis* (Wiley, 2010)
- K. Christmann, Introduction to Surface Physical Chemistry (Steinkopff, Springer)
- A. Adamson, A. Gast, Physical Chemistry of Surfaces (Wiley 1997)
- R. Hoffmann, Solids and Surfaces: A Chemist's View of Bonding in Extended Structures (VCH)

- J. A. Venables, Introduction to Surface and Thin Film Processes (Cambridge, 2000)
- M.C. Desjonquères, D. Spanjaard, *Concepts in surface physics* (Springer, 1996)
- F. Bechstedt, *Principles of Surface Physics* (Springer, 2003)
- A. Gross, *Basic Theoretical Surface Science* (Springer, 2003)
- S.G. Davison, M. Stęślicka, *Basic Theory of Surface States* (Clarendon, Oxford, 1996)

Books you already read ...

- H. Ibach and H. Lüth, *Solid-State Physics* (Springer, Berlin, 2003)
- N.W. Ashcroft and N.D. Mermin, *Solid State Physics* (Saunders, New York, 1976)
- C. Kittel, *Introduction to Solid State Physics* (Wiley, 2005)
- Bergmann, Schaefer, *Lehrbuch der Experimentalphysik Band 6: Festkörper* (Walter de Gruyter, Berlin, 2005)

Techniques

- H. Kuzmany, *Solid-State Spectroscopy* (Springer, Berlin, 1998)
- K. Oura et al., *Surface science* (Springer, 2003)
- D.P. Woodruff, T.A. Delchar, *Modern techniques of surface science* (Cambridge University Press, 1994)
- D.J. O'Connor et al., *Surface analysis methods in materials science* (Springer, 2003)
- L. G. Feldman et al., "Fundamentals of Surface and Thin Film Analysis"
- J. T. Yates Jr., *Experimental innovations in surface science* (AIP Press, 1998)
- W. Umrath, *Grundlagen der Vakuumtechnik* (Leybold, 1997)

- J.H. Moore et al., *Building scientific apparatus* (Perseus, 1991)

Why Surface Physics ?

- Objects are contacted via their surface.
- Chemical reactions: Catalysis, electrodes of batteries
- Friction and Lubrication
- Nanotechnology is Surface Physics

"Gott schuf das Volumen,

der Teufel die Oberfläche."

(verm. Wolfgang Pauli)

Surface Physics – Since When?

1805, 1806: Discussion of surface tension by T. Young and P.S. de Laplace

1830: C.F. Gauss introduces concept of surface energy

1833: Döbereiner's Feuerzeug

1874: K. F. Brauns Gleichrichter

1877: Thermodynamics by W. Gibbs, including surfaces

1906/32: I. Langmuir, PhD / Nobel prize (surface chemistry)

1927: Electron diffraction by C.J. Davisson & L. Germer
Nobel laureates 1937

1932: Electronic surface states predicted by I. Tamm

Johann Wolfgang Döbereiner 1780–1849

Seit 1780: Fürstenberger Feuerzeug: H_2SO_4 + Zn > H_2 + Funken

1810 A*ußerordentlicher* Professor für Chemie, U Jena

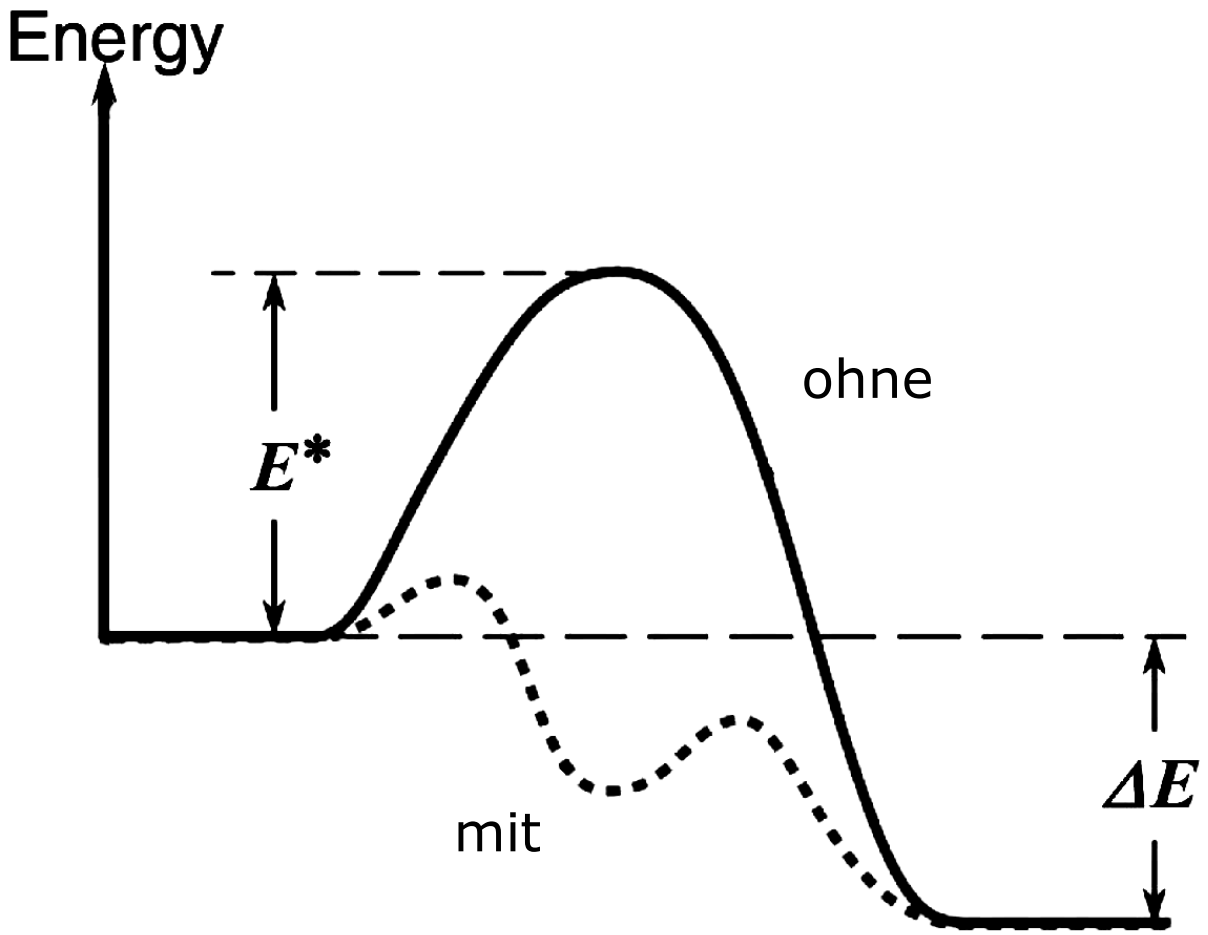
1823 H_2 entzündet sich selbst bei Durchströmen von Pt-Pulver, Pt weißglühend

Später Katalyse benannt (durch Berzelius); Feuerzeug vertrieben in D & GB, 1827 - 1880

Jöns Jakob Berzelius

Döbereiners Feuerzeug

Wirkprinzip eines Katalysators



1874 Karl Ferdinand Braun

Stapel aus C uns FeS weicht von ohmschem Gesetz ab

Vermutung: dünne Oberflächenschichten relevant

Gleichrichtung

Irving Langmuir

* 31 January 1881, Brooklyn, NY, USA

+16 August 1957, Falmouth, MA, USA

From: www.nobelprize.org

Dissertation 1906 bei Nernst, Göttingen

Gasdissoziation an heißem Platindraht

3 Jahre später erfindeter N_2-Leuchtstoffröhre (bei GE)

Grundlagenarbeiten zu

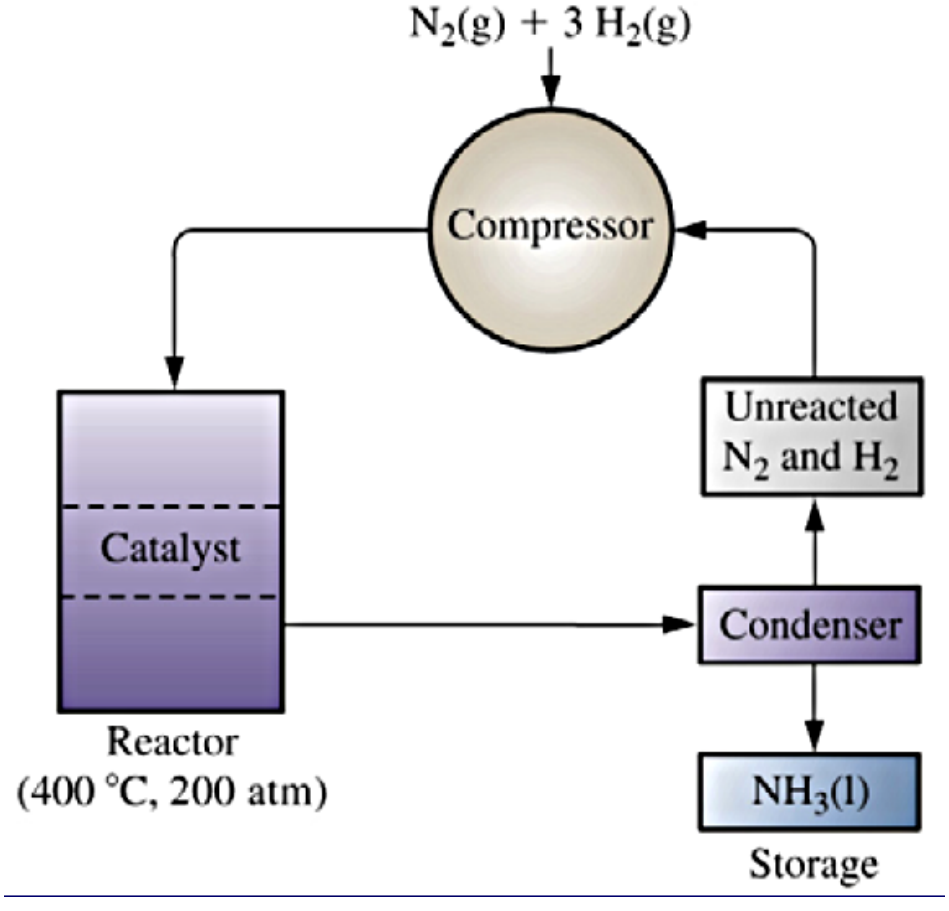
Adsorption, Katalyse, Austrittsarbeit

1932 Nobelpreis dafür

"Air to Food Food" - The greatest scientific discovery of last century

- At moderate T and high p, H_2 and N_2 (from thin air) will form NH_3.
- One century after invention, applied all over the world:

  $5x10^8$ t/a of fertilizer sustaining 40% of the worlds population Nature 427 (2004) 498
- 1% of the world's energy budget used for a single reaction Science 297 (1654) 2002
- TWO NOBEL PRIZES FOR ONE REACTION!



Beides wikipedia

Haber-Bosch-Verfahren

Phosgen

Clara

emigrierte 1933 nach Cambridge

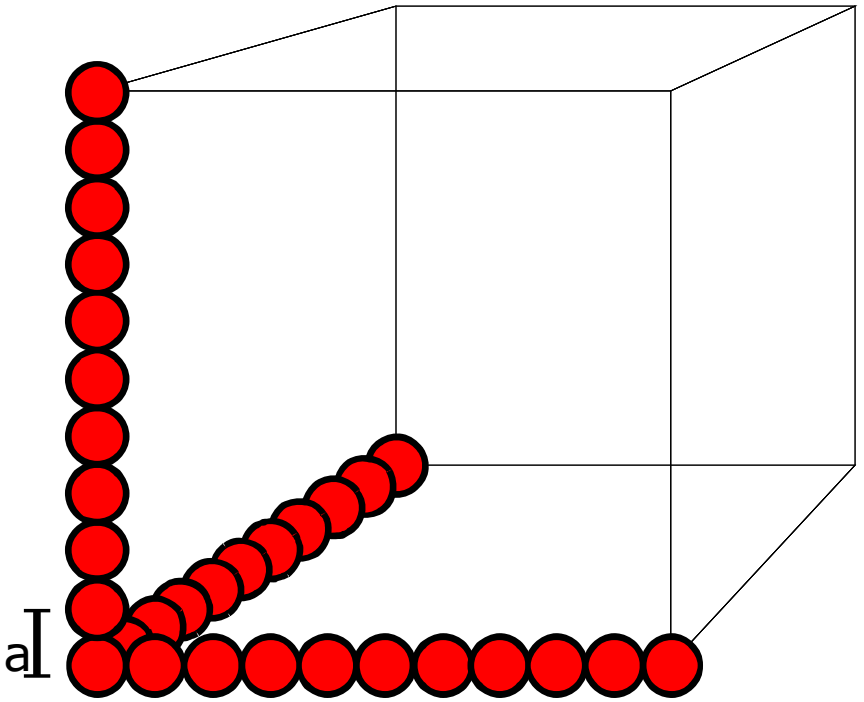
Haber-Bosch-Verfahren

Nobelpreise für Chemie

1918 Fritz Haber

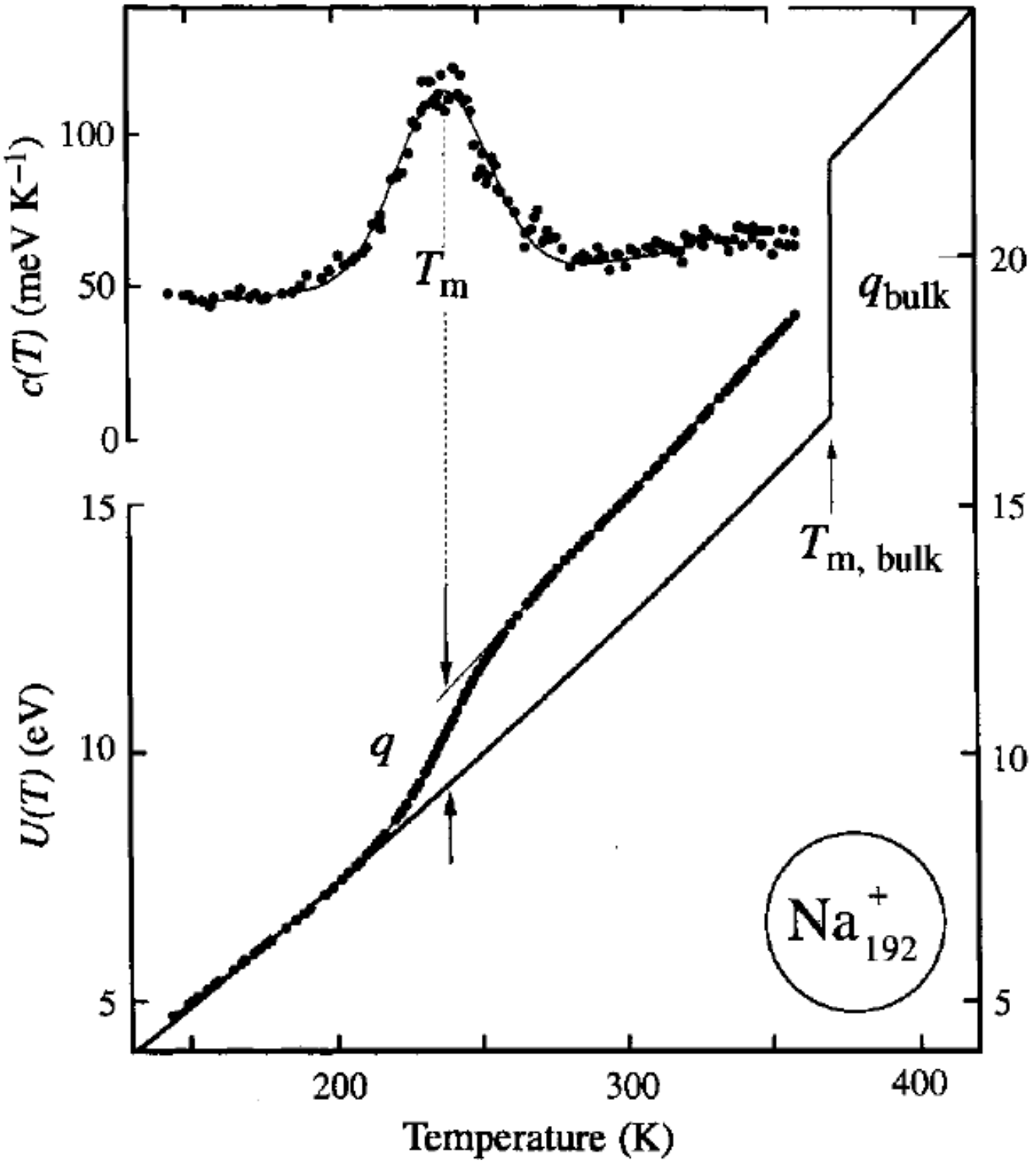
1931 Carl Bosch (mit Friedrich Bergius)

Nanoscale: Surfaces increasingly important



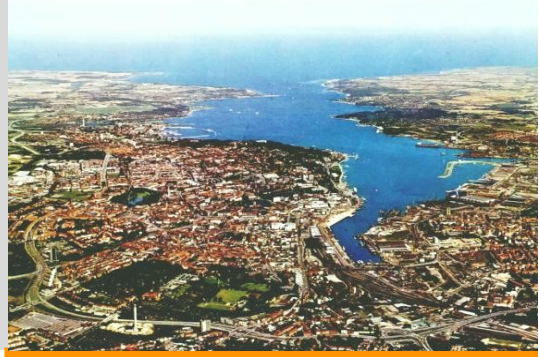
Simple cubic lattice
with lattice constant a

a (nm)	atome/kante	Atome insg.	Atome an OF	OF/gesamt
1.000	3.333	37.037.037.037	66.626.675	0,18%
500	1.667	4.629.629.630	16.646.675	0,36%
100	333	37.037.037	662.675	1,79%
50	167	4.629.630	164.675	3,56%
10	33	37.037	6.275	16,94%
5	17	4.630	1.475	31,85%
1	3	37	35	93,60%
	d_atom	0,3		


c(T) (meV K⁻¹)
100
50
0
T_m
q_bulk
20
15
T_m, bulk
U(T) (eV)
10
q
10
Na⁺192
5
5
200
300
400
Temperature (K)

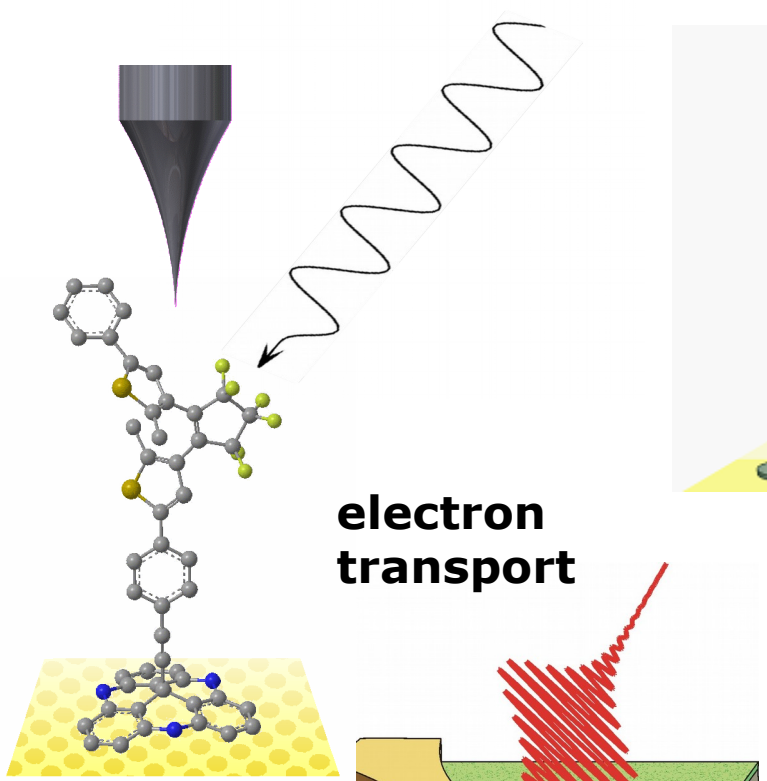
Institut für Experimentelle und Angewandte Physik

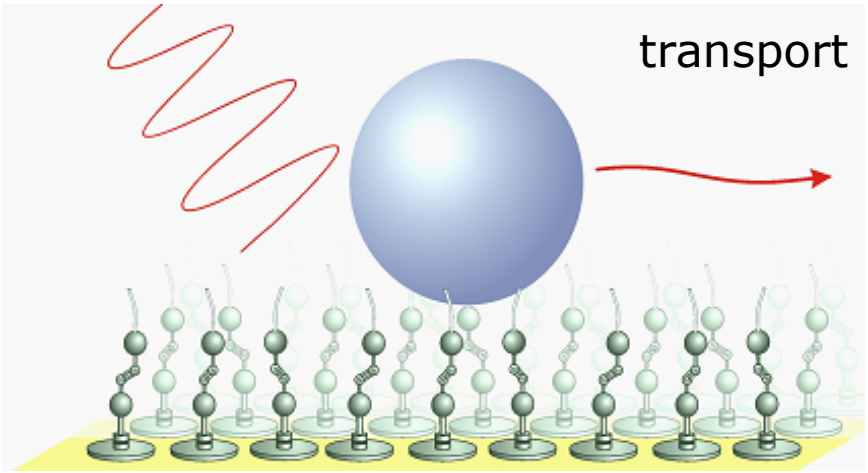
Christian-Albrechts-Universität zu Kiel



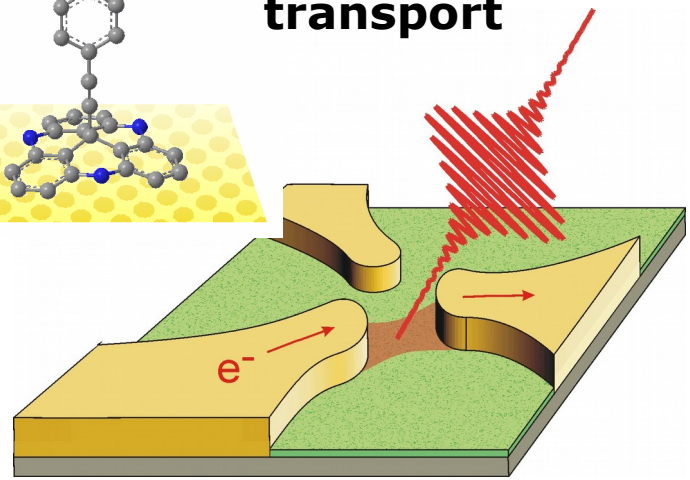
Richard Berndt

Molecular conductors and switches at surfaces

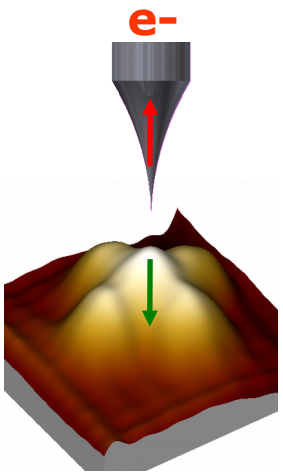


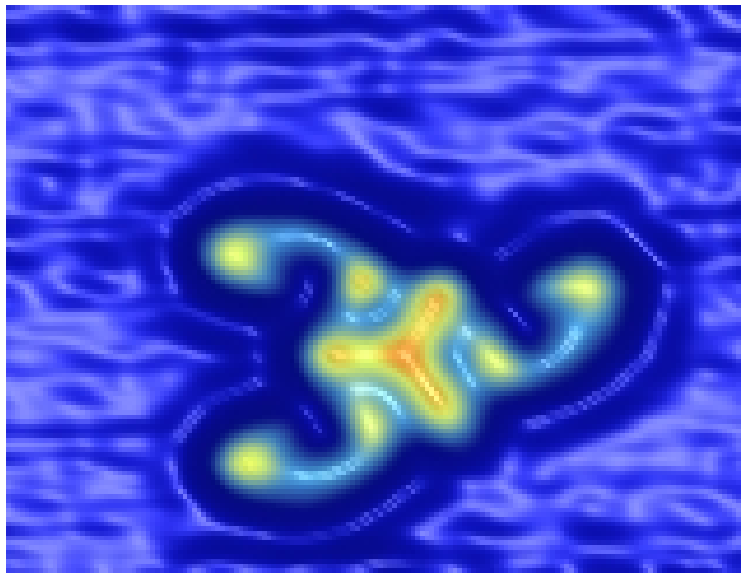


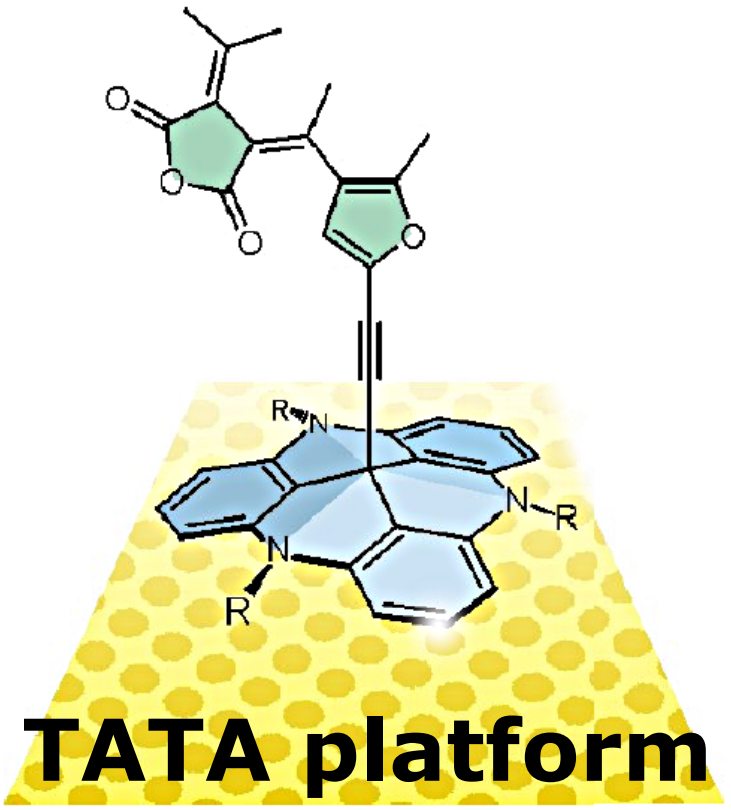
electron transport



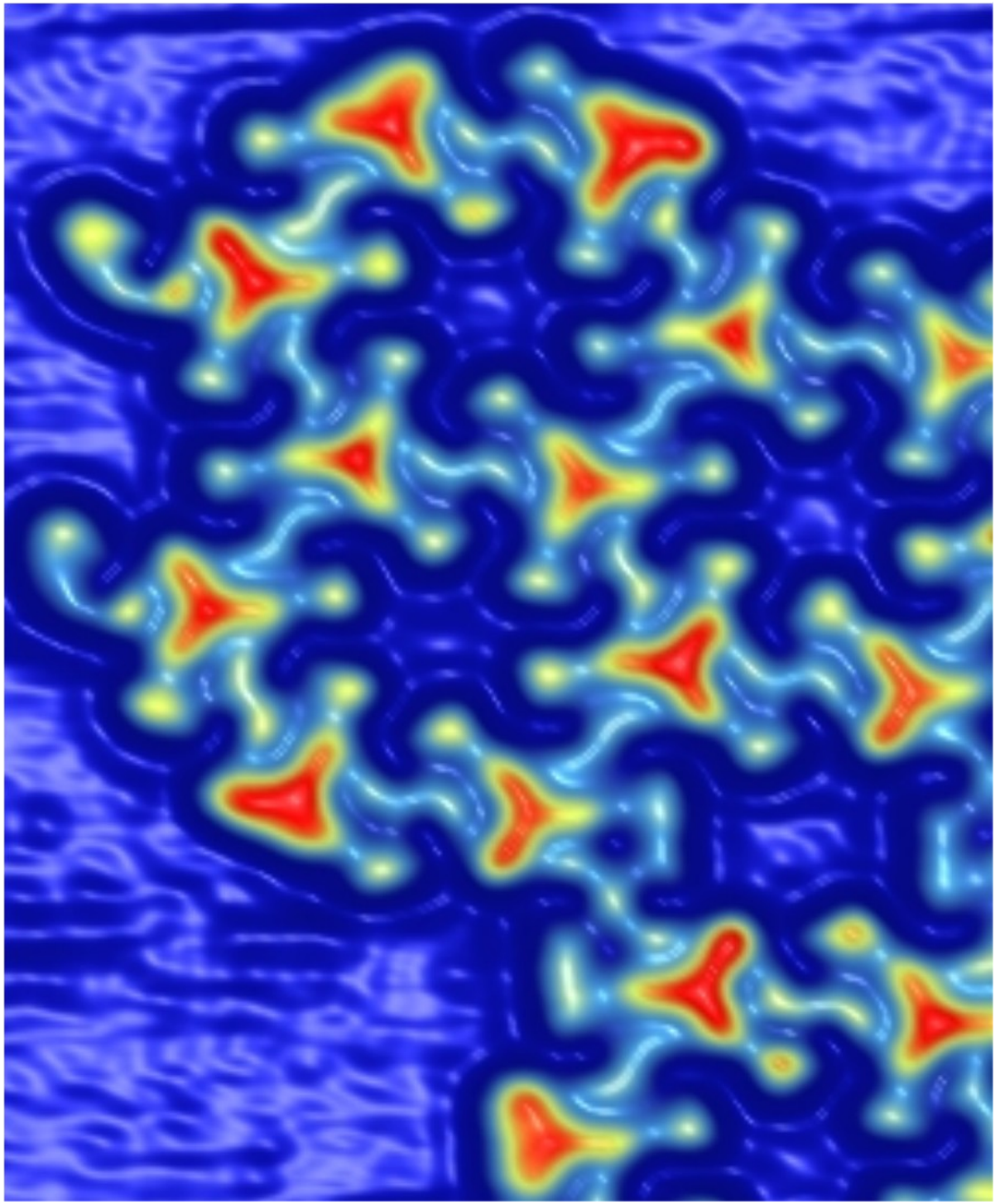
magnetic moment



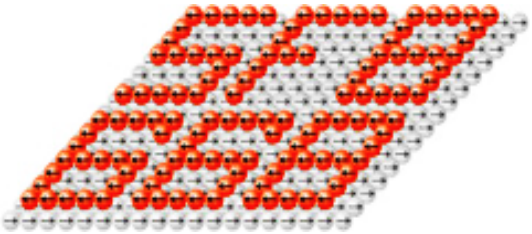




TATA platform

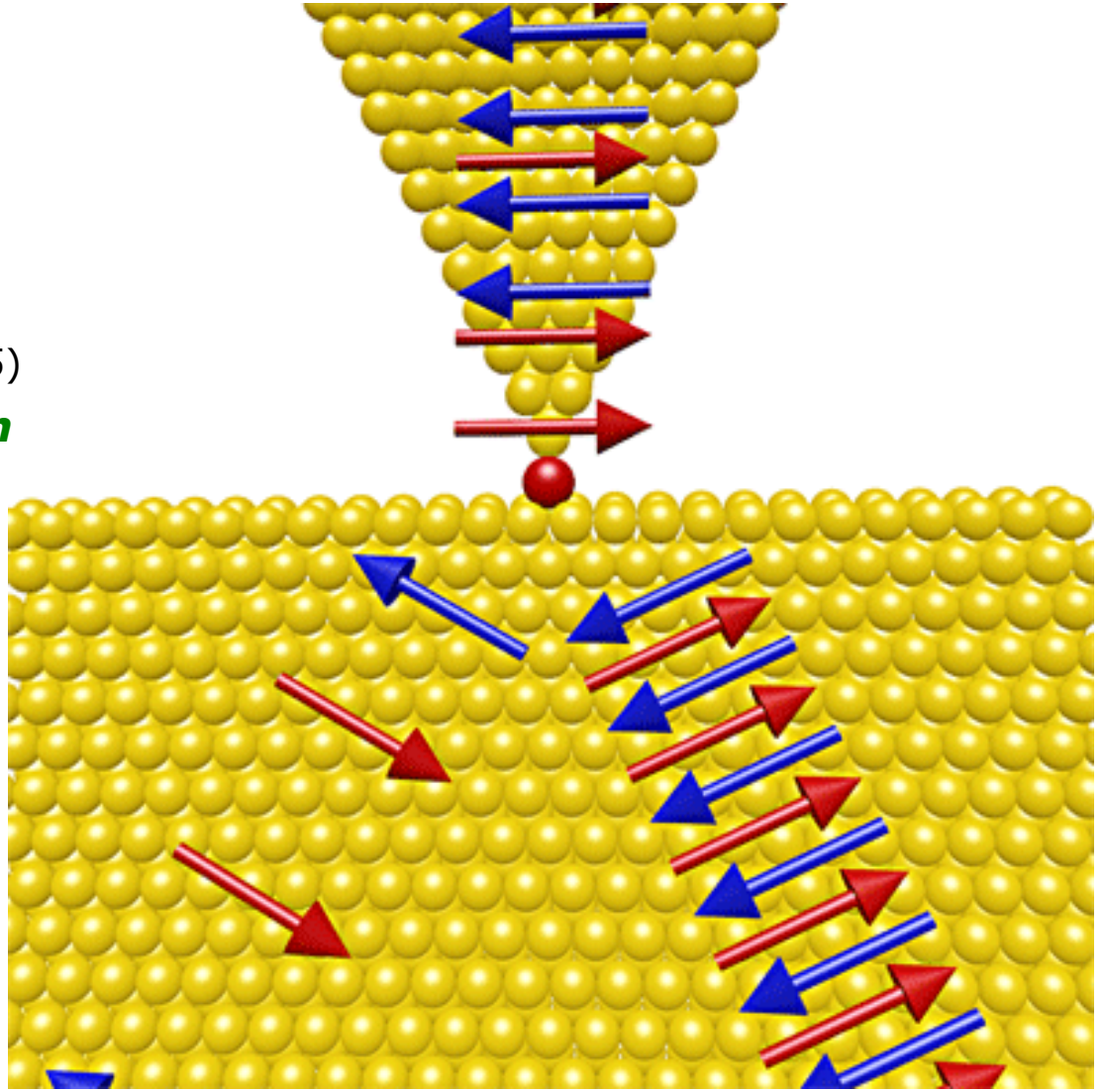


Gopakumar, unpublished

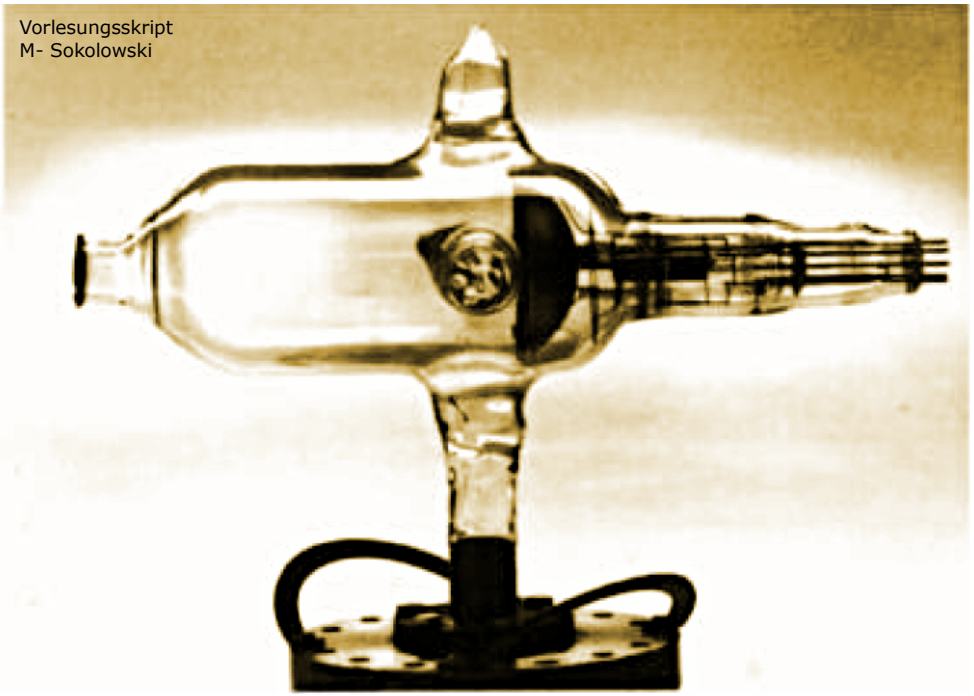


Burtzlaff, Weismann,
Brandbyge, Berndt,
PRL **114**, 016602 (2015)

Editors' Suggestion

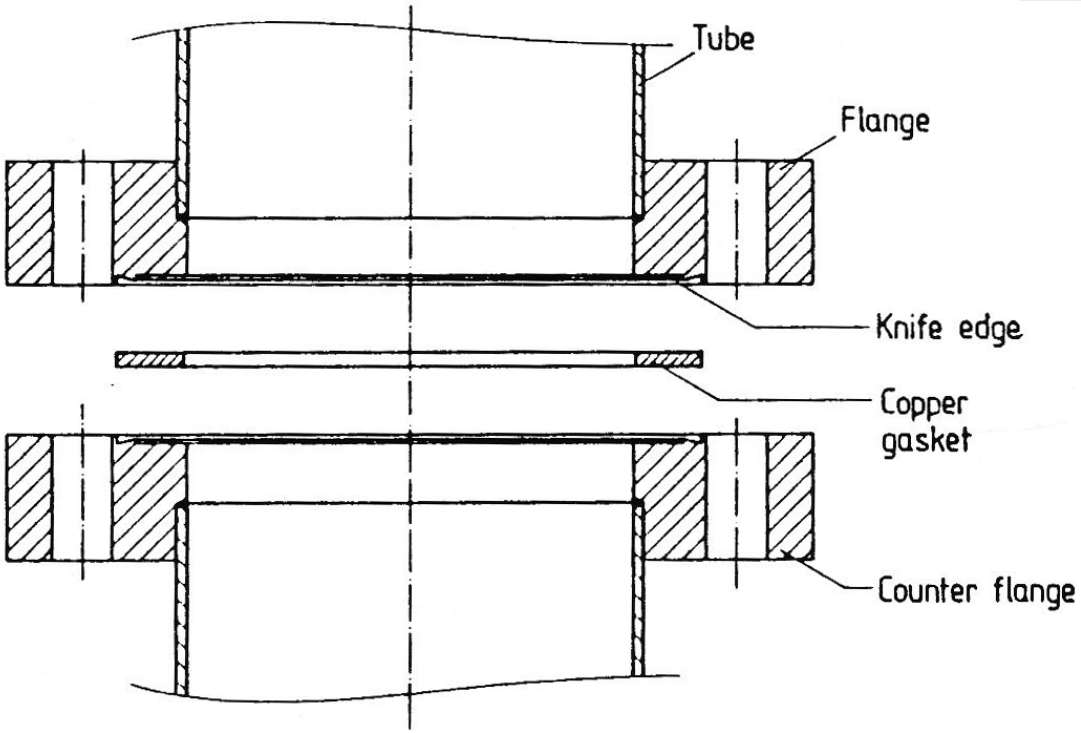


Vorlesungsskript
M- Sokolowski



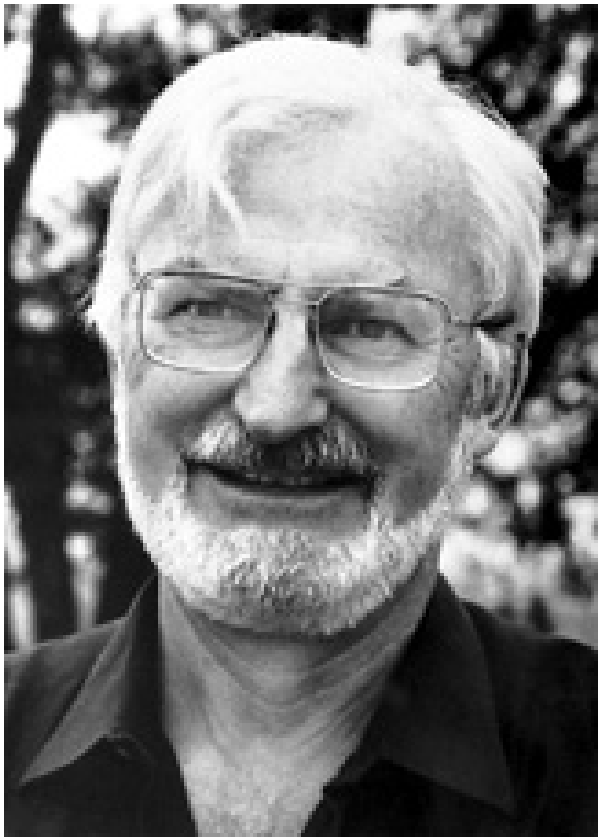
LEED-optics 1960, Prof. Dr. K. Müller, Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg.

A Breakthrough for Surface Science: Ultra-High Vacuum (≥1960)



Nobel Prizes: Physics

Kai M. Siegbahn
Nobel Prize 1981
Development of ESCA



G. Binnig, H. Rohrer
Nobel Prize 1986
Development STM

Albert Fert & Peter Grünberg
Nobel Prize 2007 – Physics
Interfaces

Gerhard Ertl
Nobel Prize 2007 – Chemistry
Surface Chemistry

Kristallstruktur = Gitter + Basis

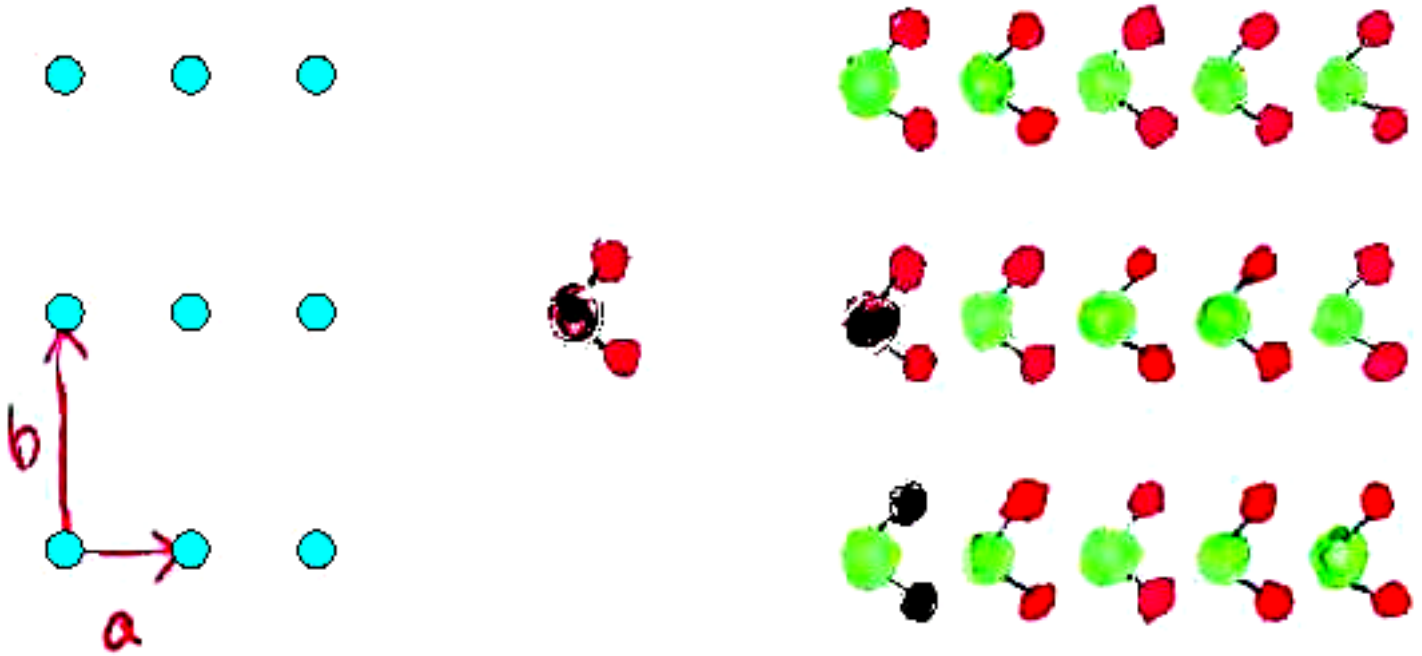
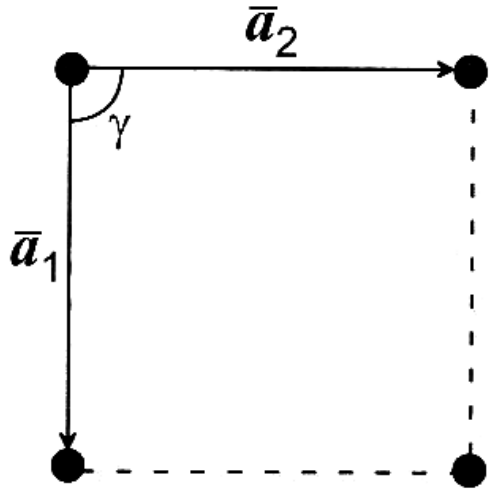
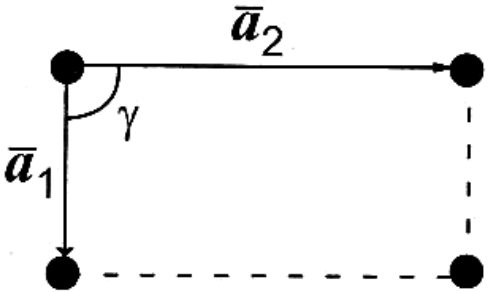


Fig. 1.4. The five two-dimensional Bravais lattices. Besides primitive unit cells (dashed lines) also a non-primitive cell (dotted lines) is shown.



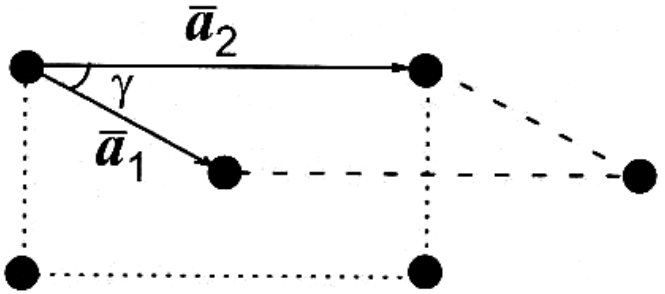
Square $|\bar{a}_1| = |\bar{a}_2|$

$\gamma = 90°$



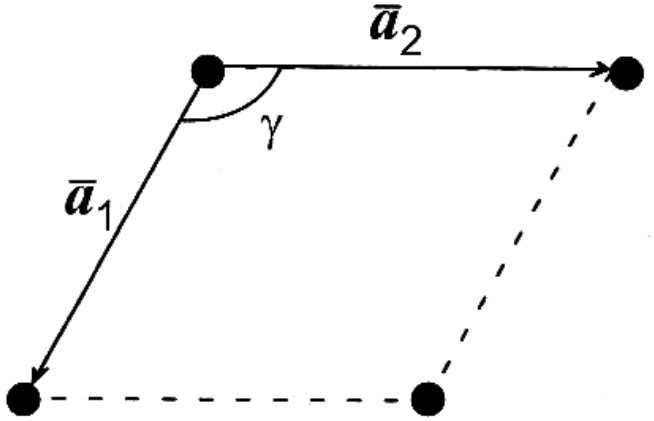
Rectangular

$|\bar{a}_1| \neq |\bar{a}_2|$, $\gamma = 90°$



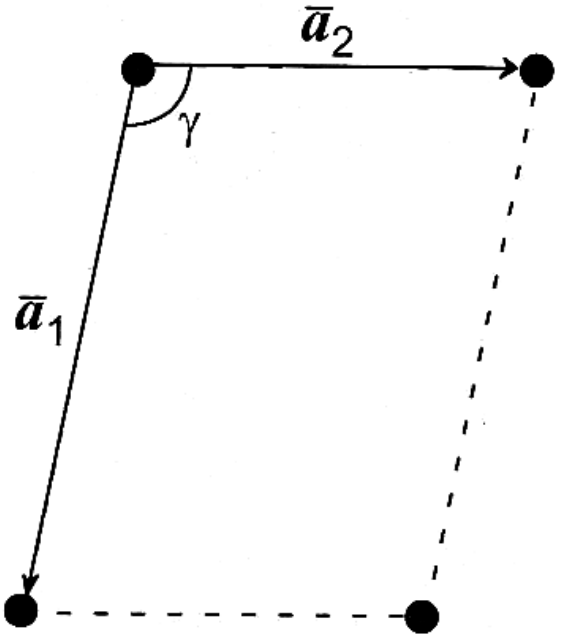
Centered rectangular

$|\bar{a}_1| \neq |\bar{a}_2|$, $\cos\gamma = |\bar{a}_2|/(2|\bar{a}_1|)$



Hexagonal $|\bar{a}_1| = |\bar{a}_2|$

$\gamma = 120°$



Oblique $|\bar{a}_1| \neq |\bar{a}_2|$

$\gamma \neq 90°$

Bechstedt

FCC

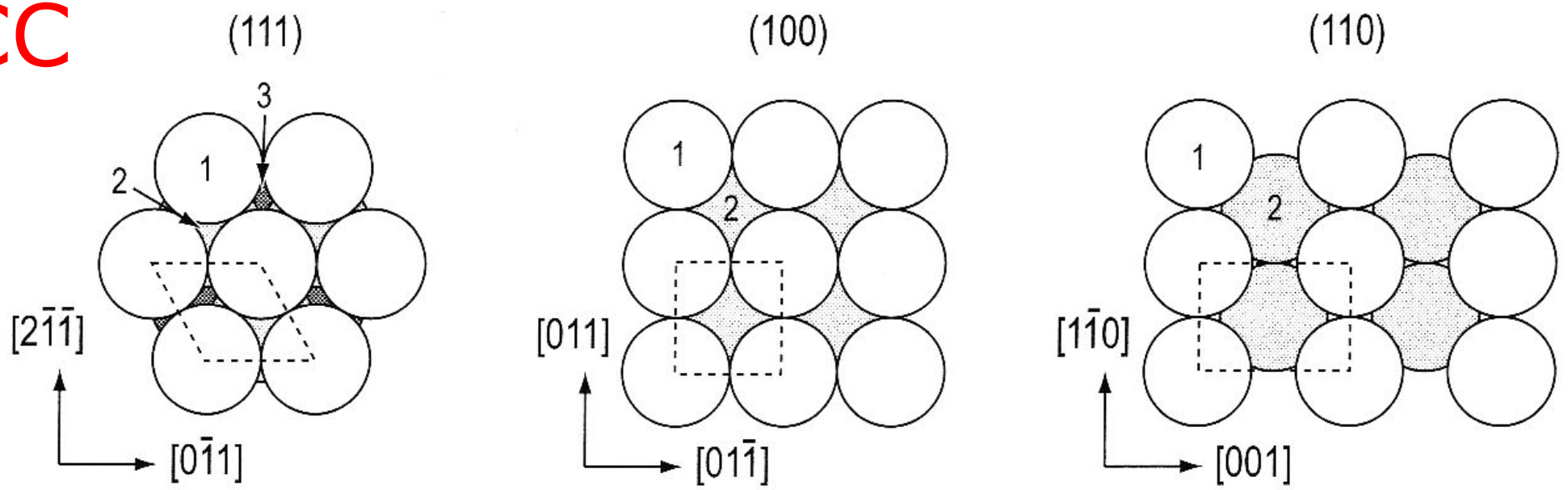


Fig. 2.6. Main low-index planes of a fcc (face-centered cubic) crystal

BCC

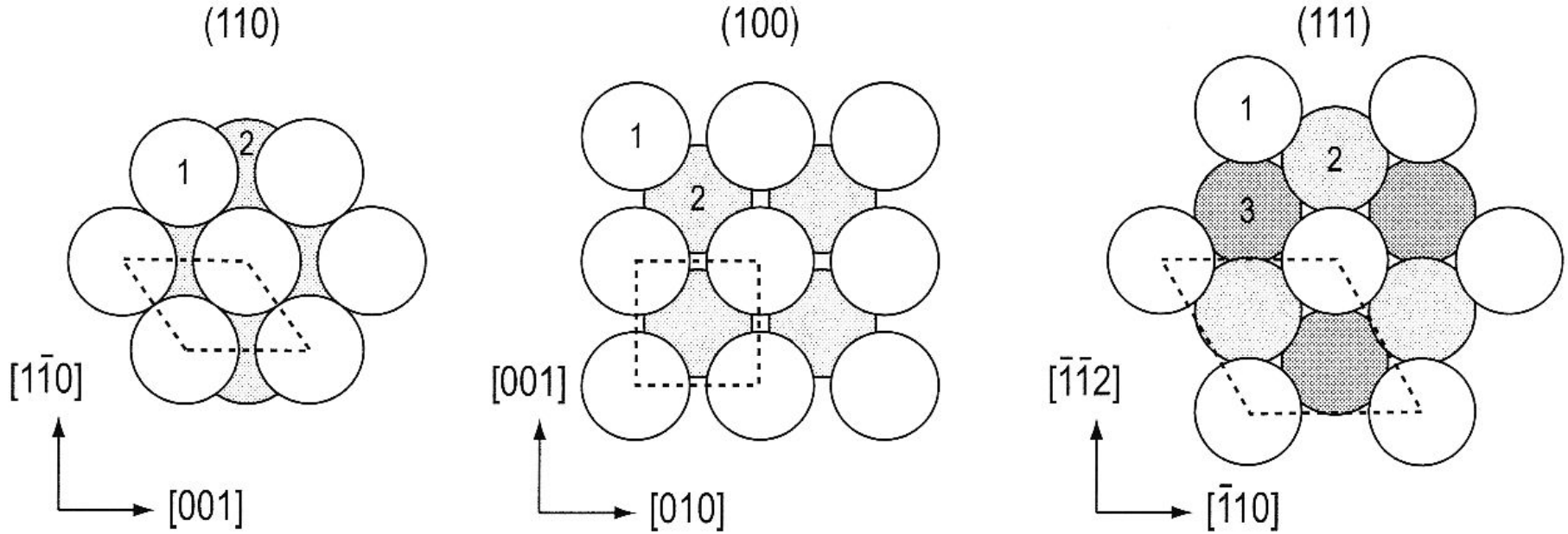
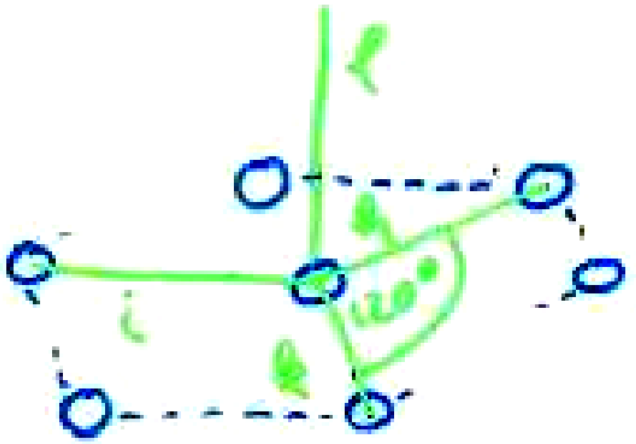


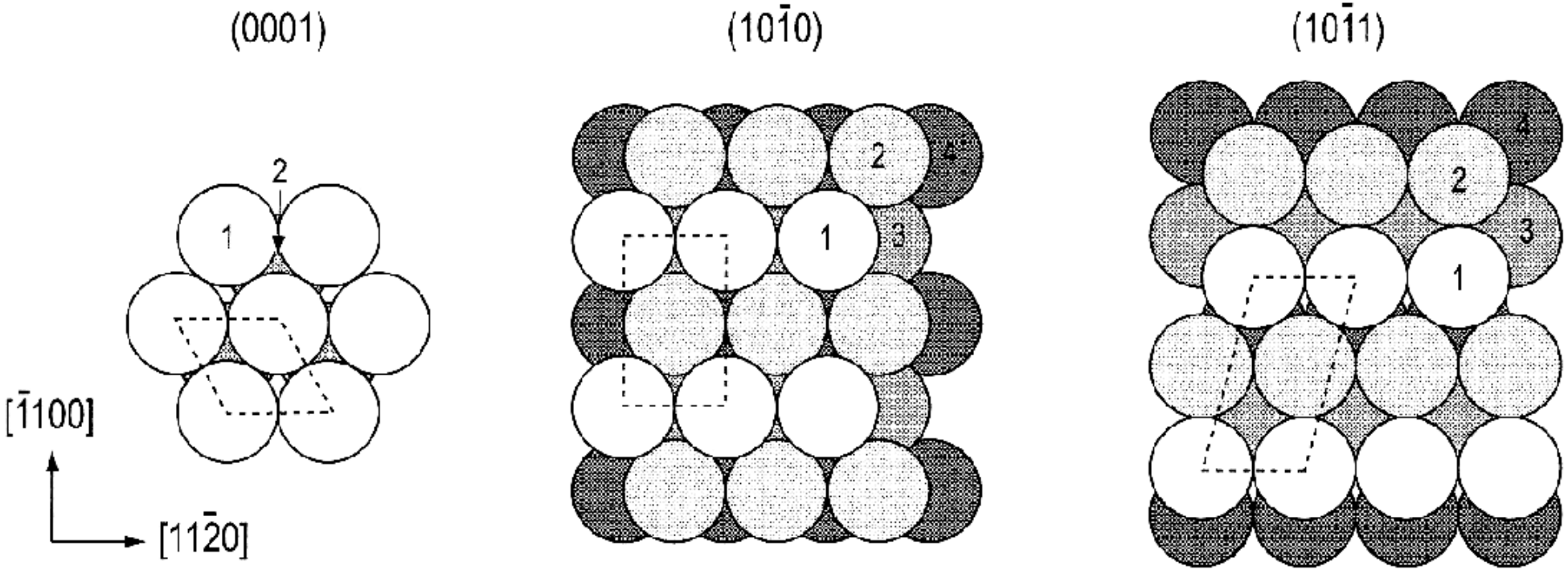
Fig. 2.7. Main low-index planes of a bcc (body-centered cubic) crystal

HCP: Usually 4 Miller indices



$$i = - h - k$$

HCP



Diamond

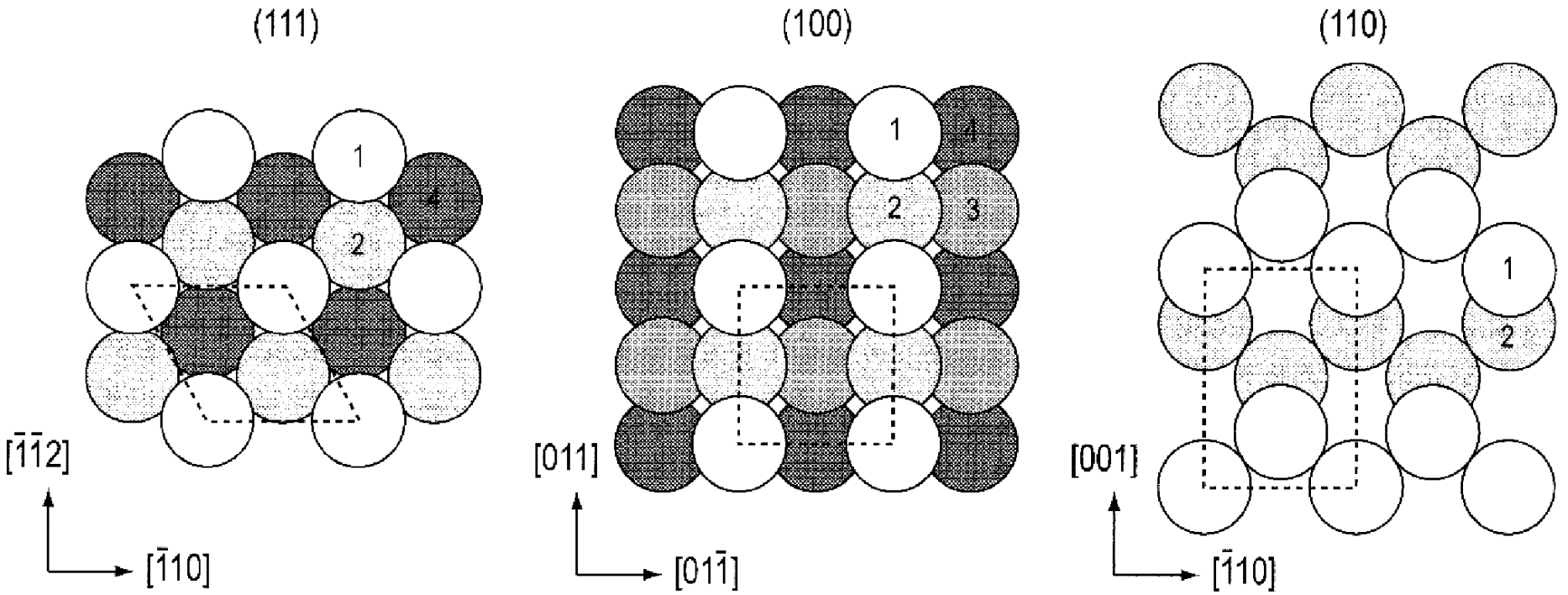


Fig. 2.9. Main low-index planes of a diamond crystal

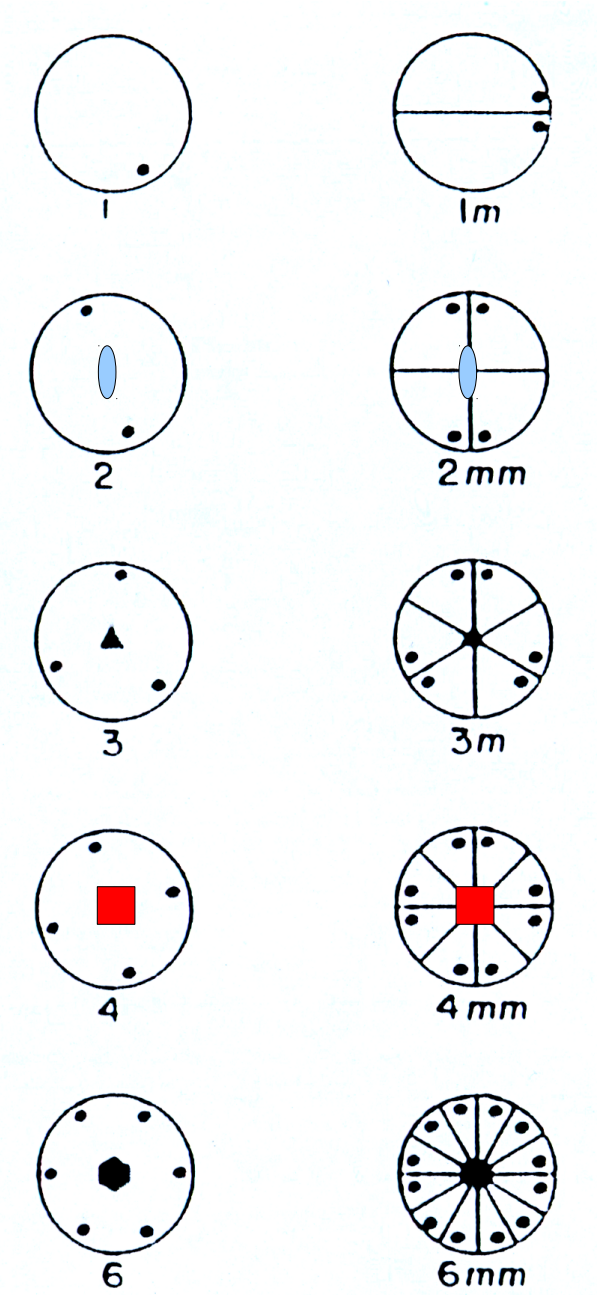
'1' ≈ 6 Atome / 10^{-14} cm^2

TABLE 2.4
Surface-atom densities

f.c.c. structure									
Plane	(100)	(110)	(111)	(210)	(211)	(221)	(310)	(311)	(320)
Density relative to (111)	0·866	0·612	1·000	0·387	0·354	0·289	0·274	0.522	0·240
Metal	Al	Rh	Ir	Ni	Pd	Pt	Cu	Ag	Au
Density of (111) (atom $cm^{-2} \times 10^{-15}$)	1·415	1·599	1·574	1·864	1·534	1·503	1·772	1·387	1·394
b.c.c. structure									
Plane	(100)	(110)	(111)	(210)	(211)	(221)	(310)	(311)	(320)
Density relative to (110)	0·707	1·000	0·409	0·316	0·578	0·236	0·447	0·213	0·196
Metal	V	Nb	Ta	Cr	Mo	W	Fe		
Density of (110) (atom $cm^{-2} \times 10^{-15}$)	1·547	1·303	1·299	1·693	1·434	1·416	1·729		
h.c.p. structure									
Plane	(0001)	$(10\bar{1}0)$	$(10\bar{1}1)$	$(10\bar{1}2)$	$(11\bar{2}0)$	$(11\bar{2}2)$			
Density relative to (0001)	1·000	$\frac{3}{2r}$	$\frac{\sqrt{3}}{(4r^2+3)^{\frac{1}{2}}}$	$\frac{\sqrt{3}}{(4r^2+12)^{\frac{1}{2}}}$	$\frac{1}{r}$	$\frac{1}{2(r^2+1)^{\frac{1}{2}}}$			
Metal	Zr	Hf	Re	Ru	Os	Co	Zn	Cd	
Density of (0001) (atom $cm^{-2} \times 10^{-15}$)	1·110	1·130	1·514	1·582	1·546	1·830	1·630	1·308	
axial ratio $r = c/a$	1·59	1·59	1·61	1·58	1·58	1·62	1·86	1·89	

r= c/a

Zweidimensionale kristallographische Punktgruppen



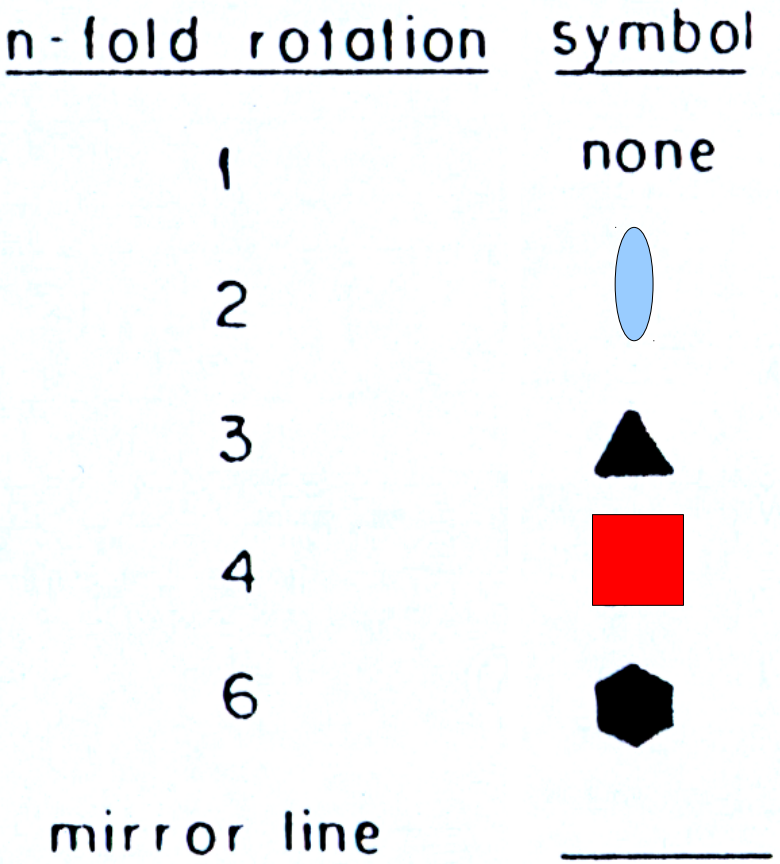


Fig. 3. (a) Graphical representation of the ten two-dimensional crystallographic point groups. Equivalent points are shown as dots. (b) Symbols for the various symmetry operations.

2d lattices: point groups and space groups

International Tables for X-Ray Crystallography (1965)

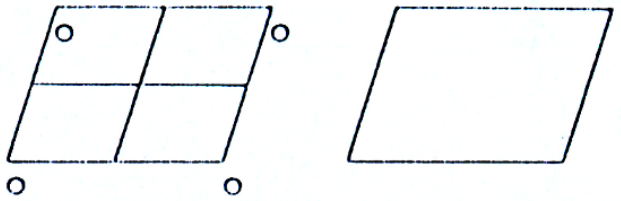
Crystal system *lattice symbol*	Point group	Space group symbols full	 short	Space group number
Oblique *p (primitive)*	1 2	p1 p211	p1 p2	1 2
Rectangular *p & c (centered)*	m	p1m1 p1g1 c1m1	pm pg cm	3 4 5
	2mm	p2mm p2mg p2gg c2mm	pmm pmg pgg cmm	6 7 8 9
Square *p*	4	p4	p4	10
	4mm	p4mm p4gm	p4m p4g	11 12
Hexagonal *p*	3	p3	p3	13
	3m	p3m1 p31m	p3m1 p31m	14 15
	6 6mm	p6 p6mm	p6 p6mm	16 17

The two distinct space groups p3m1 and p31m correspond to different orientations of the point group relative to the lattice. This does not lead to distinct groups in any other case.

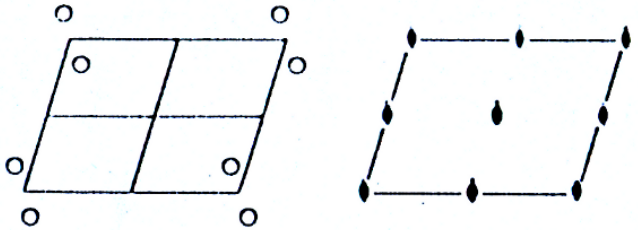
Zweidimensionale kristallographische Raumgruppen

Struktur Gruppe

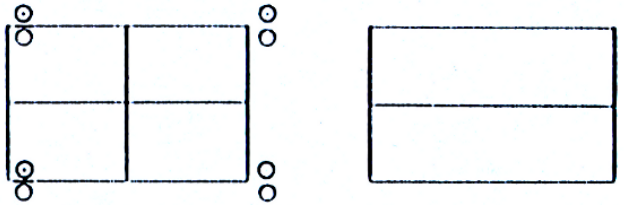
p 1 No. 1 p 1 1 Oblique



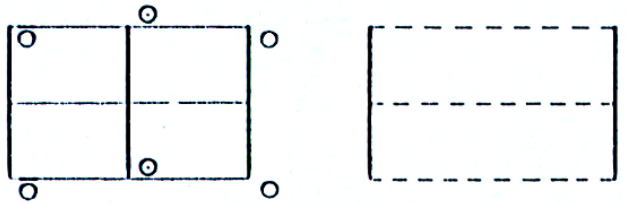
p 2 No. 2 p 211 2 Oblique



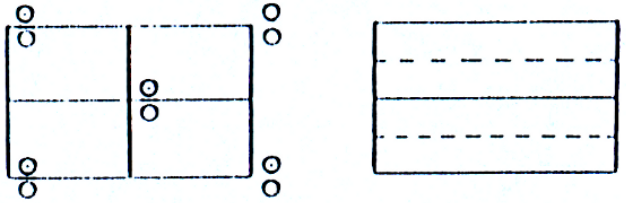
Rectangular *m* p 1 m 1 No. 3 p m



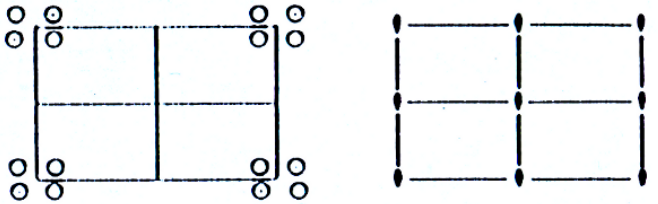
Rectangular *m* p 1 g 1 No. 4 pg



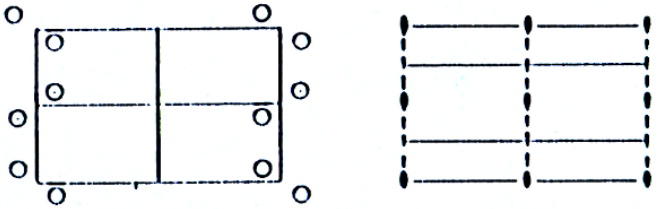
c m No. 5 c 1 m 1 m Rectangular



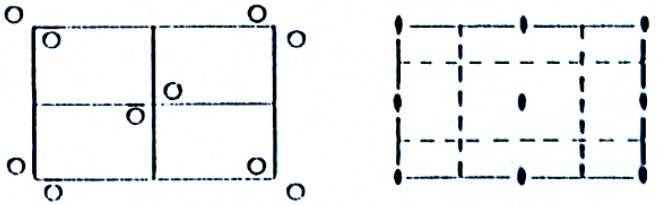
Rectangular *mm* p 2 mm No. 6 pmm



pmg No. 7 p2mg mm Rectangular

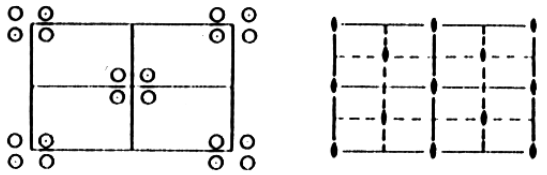


Rectangular *mm* p 2 gg No. 8 pgg

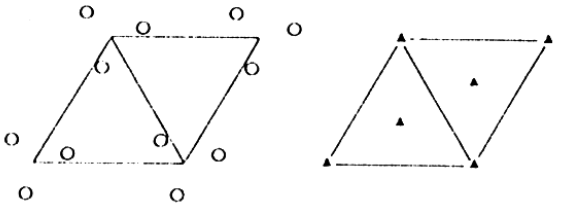


Zweidimensionale kristallographische Raumgruppen

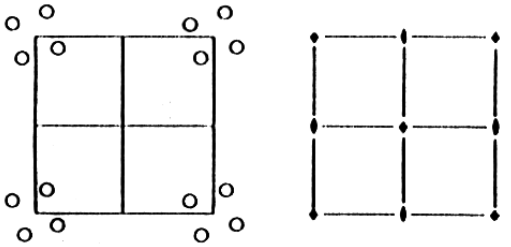
cmm No. 9 c2mm mm Rectangular



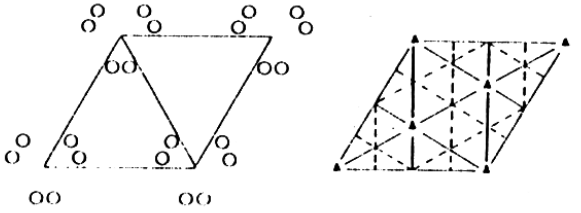
p 3 No 13 p 3 3 Hexagonal



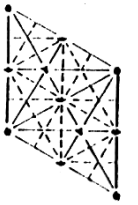
Square 4 p4 No 10 p4



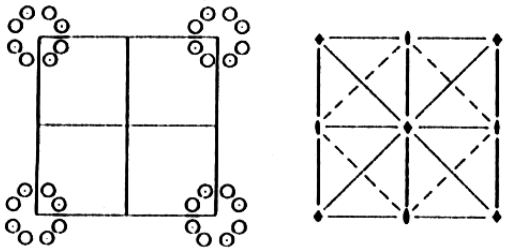
Hexagonal 3m p3m1 No. 14 p3m1



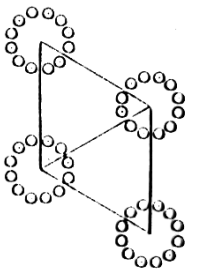
6 mm Hexagonal



p4m No. 11 p4mm 4 mm Square

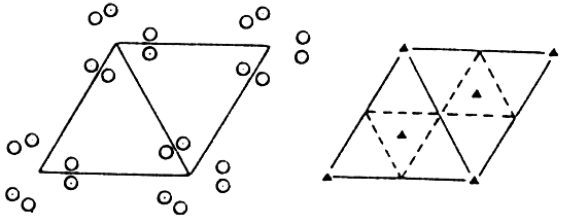


p6mm



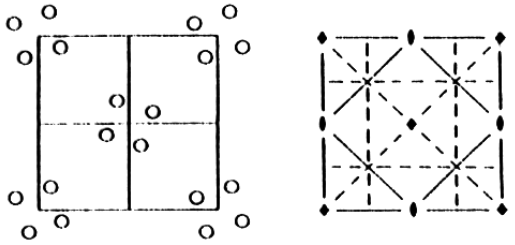
No. 17

p 31 m No. 15 p 31 m 3m Hexagonal

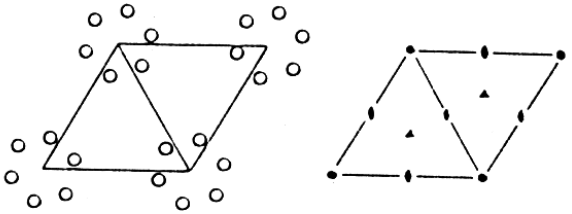


p6 m

Square 4mm p4gm No 12 p4g

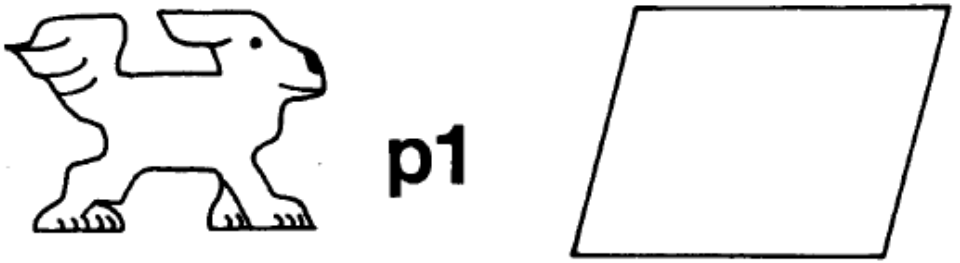


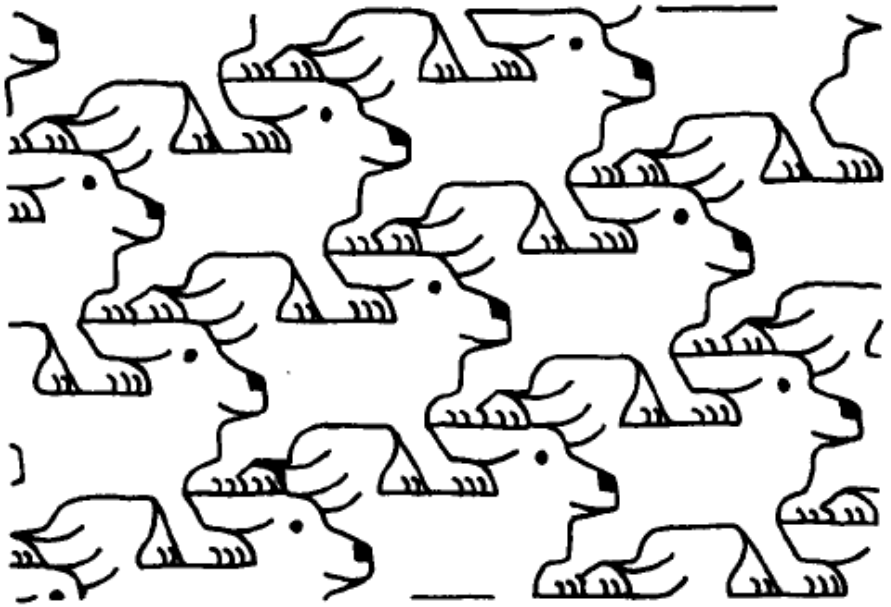
Hexagonal 6 p6 No. 16 p6



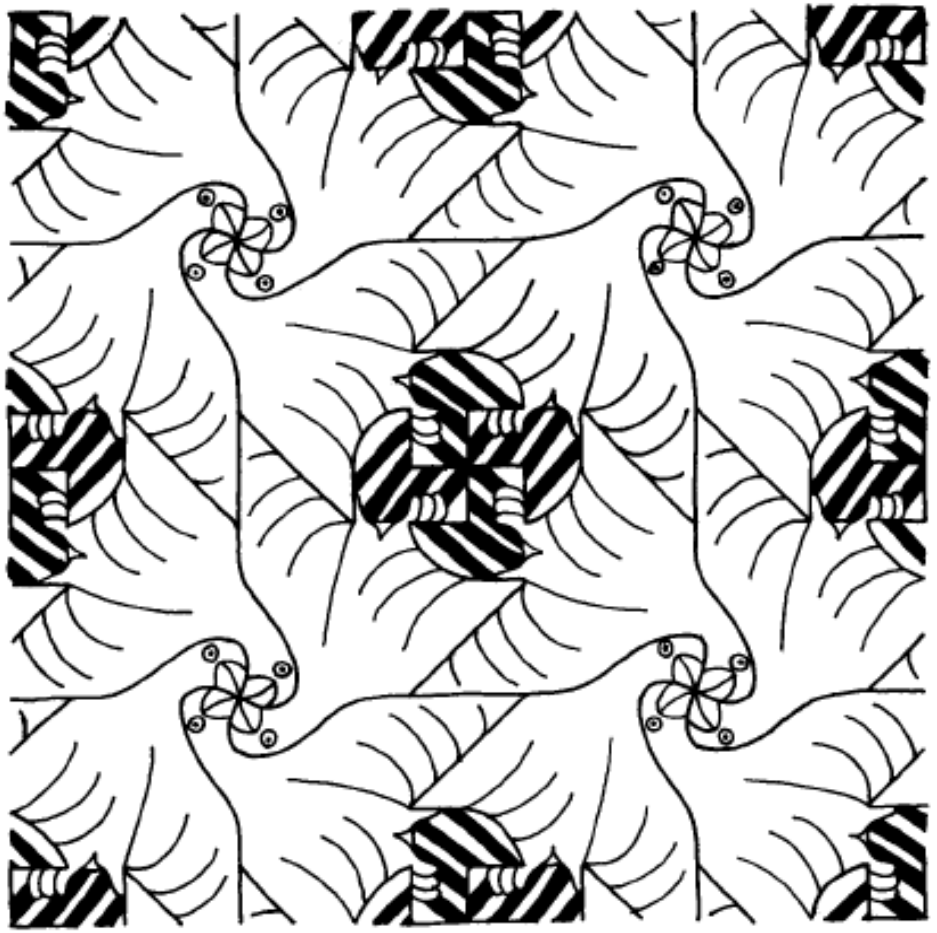
A. Gavezzotti: Illustrations of the Two-Dimensional Space Groups

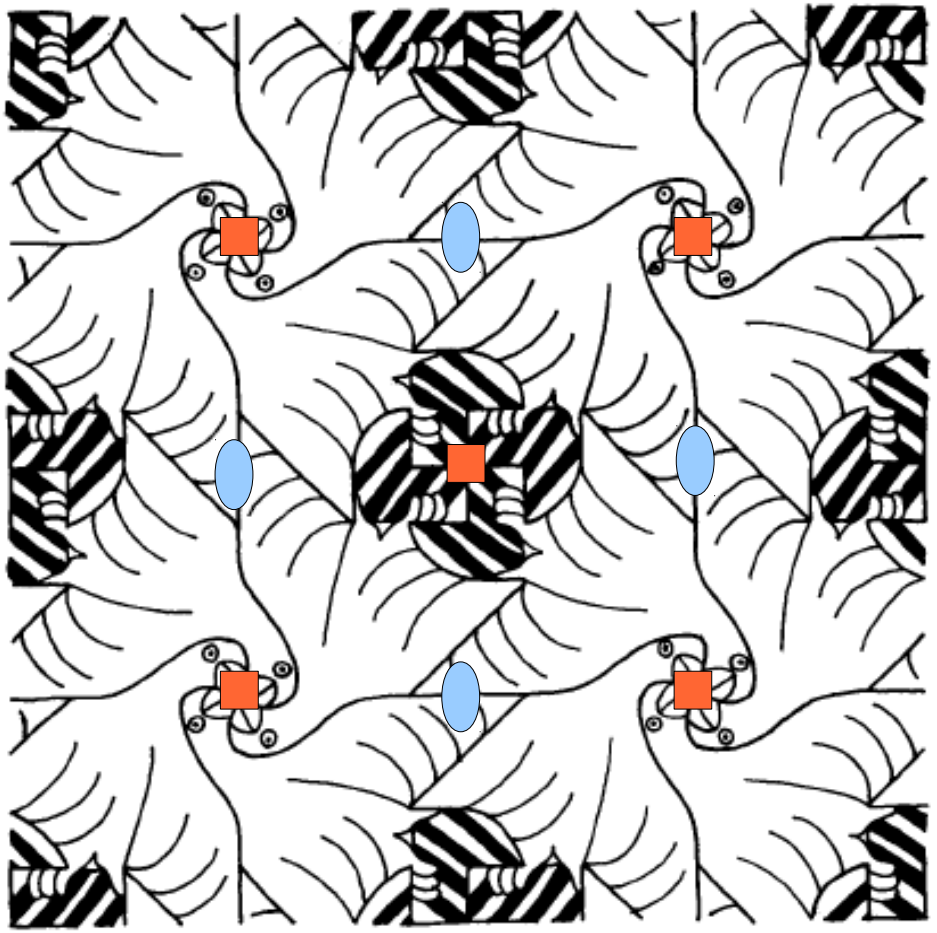
Basis Raumgruppe Gitter





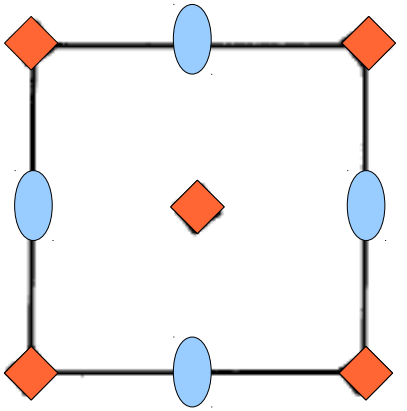
''Übung'':

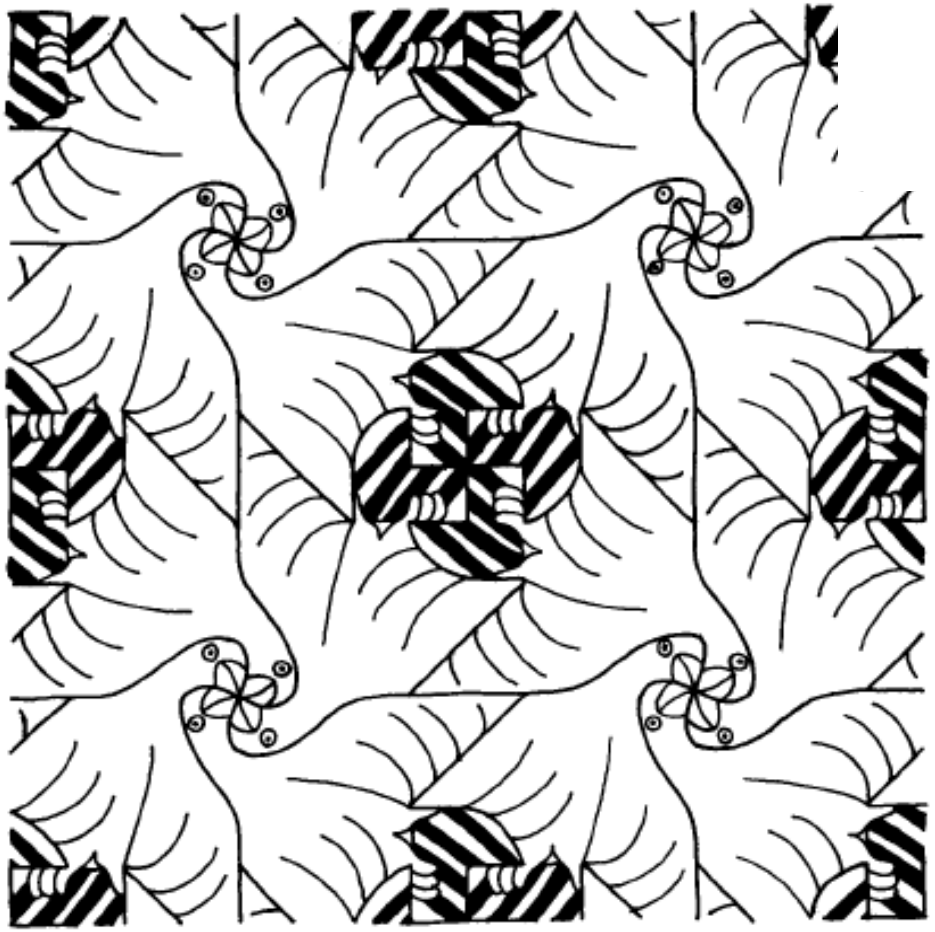




Basis Raumgruppe Gitter

p4





Surface symmetry not equal to slab symmetry

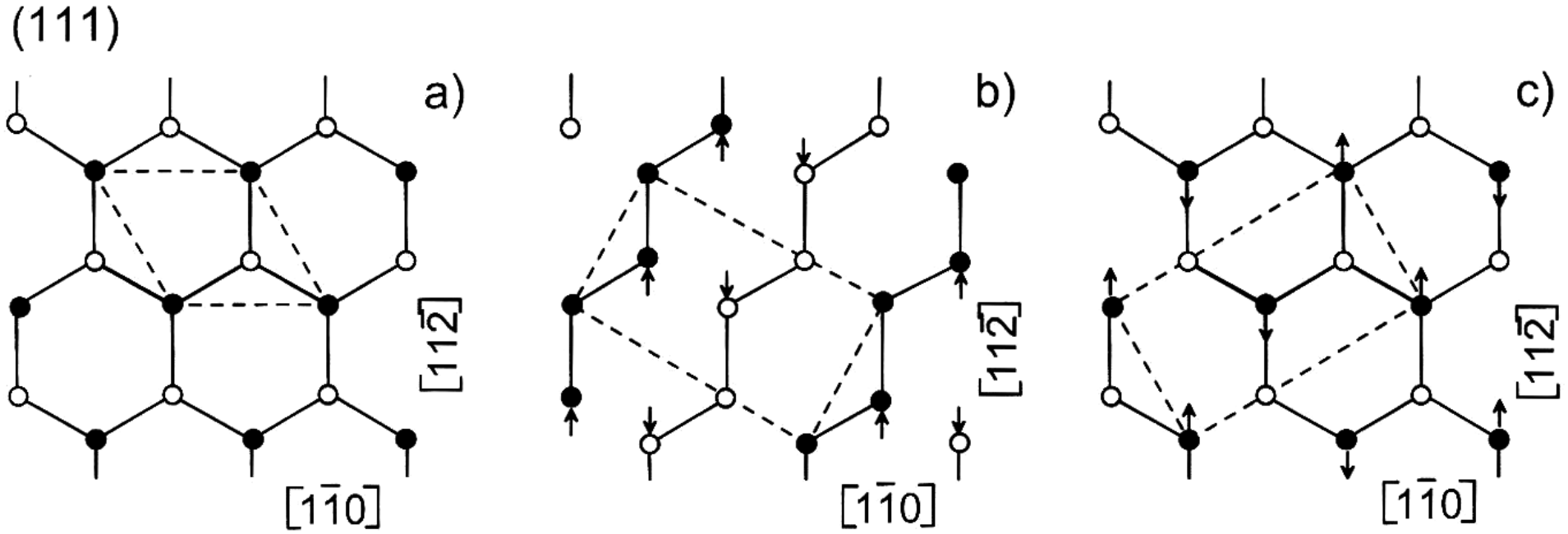


Fig. 1.15. Two different 2×1 reconstructions of the (111) surface of diamond-structure crystals. (a) ideal surface; (b) 2×1 reconstructed surface due to chain formation; and (c) 2×1 reconstructed surface due to an inequivalent buckling of surface atoms. Dots: nominal first-layer atoms; circles: nominal second-layer atoms.

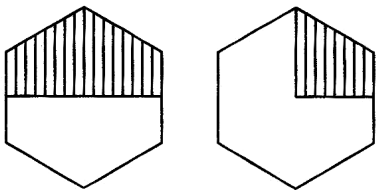
1st	p6mm
1st & 2nd	p3m1

Anwendung: z. B. Auswahlregeln

c-rectangular lattice

Symmetry point	Space group	
or line	$c1m1$	$c2mm$
$\bar{\Gamma}$	m	$2mm$
$\Delta'\Delta''$	m	m
$\bar{X}$	m	$2mm$
Z	–	m
$\bar{Y}'$	–	m
$\bar{Y}$	–	m
Δ	–	m

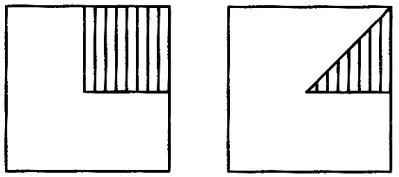
Irreducible part of BZ



Square lattice

Symmetry point	Space group		
or line	$p4$	$p4mm$	$p4mg$
$\bar{\Gamma}$	4	$4mm$	$4mm$
Δ	–	m	m
$\bar{J}$	2	$2mm$	$2mm$
Z	–	m	m
$\bar{K}$	4	$4mm$	$4mm$
Σ	–	m	m

Irreducible part of BZ



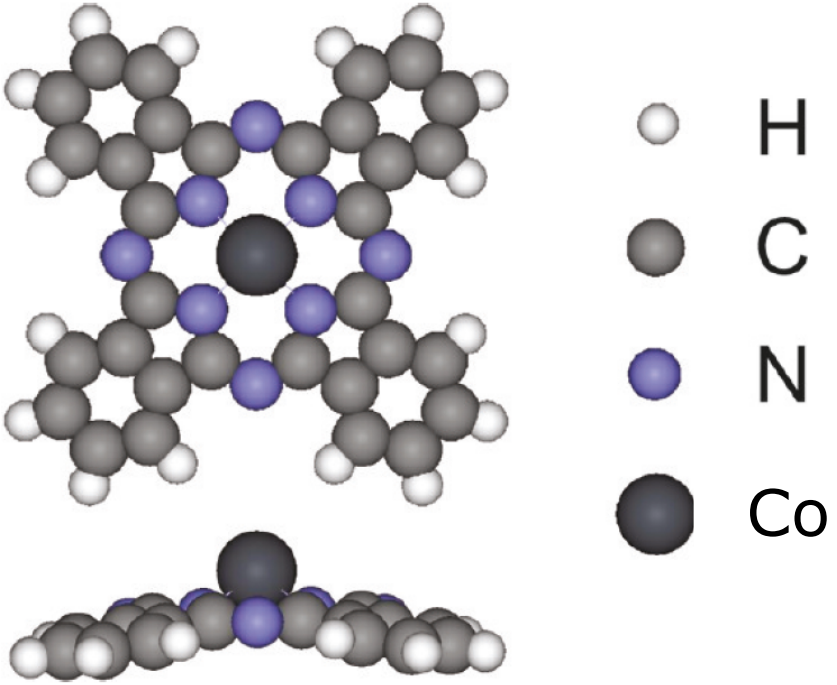
Kann man das gleich wieder vergessen?

Alle Nicht-Röntgenleute meist schon …

aber besser nicht ganz:

Supramolecular Patterns Controlled by Electron Interference and Direct Intermolecular Interactions

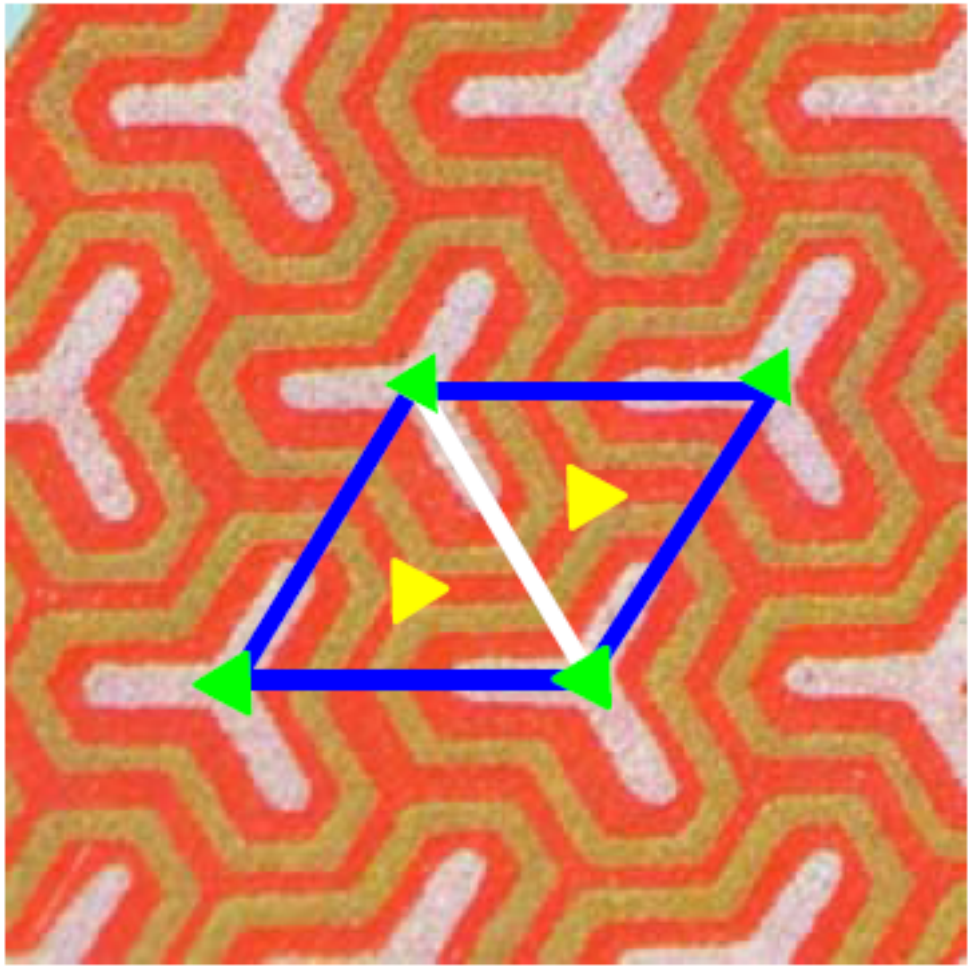
Yongfeng Wang et al., JACS 2009, 131, 10400



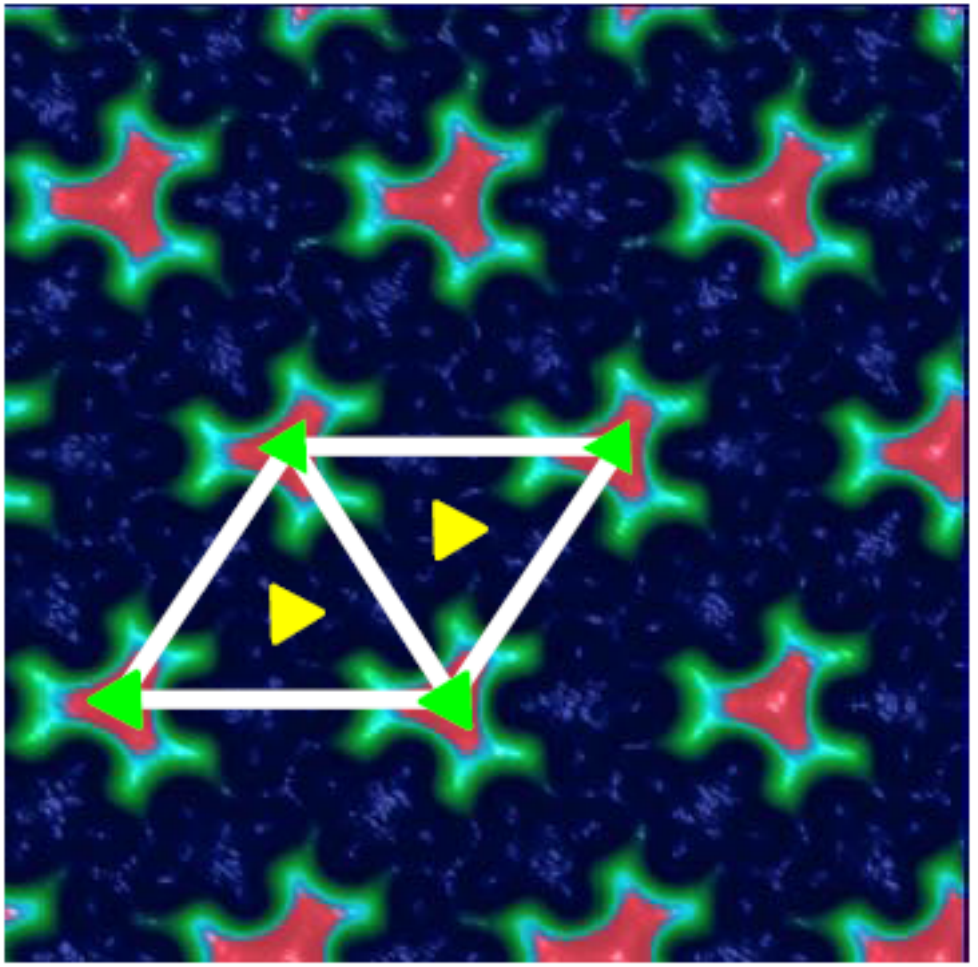
Supramolecular Patterns Controlled

by Electron Interference and Direct Intermolecular Interactions

First observation of molecules orderd according to p31m

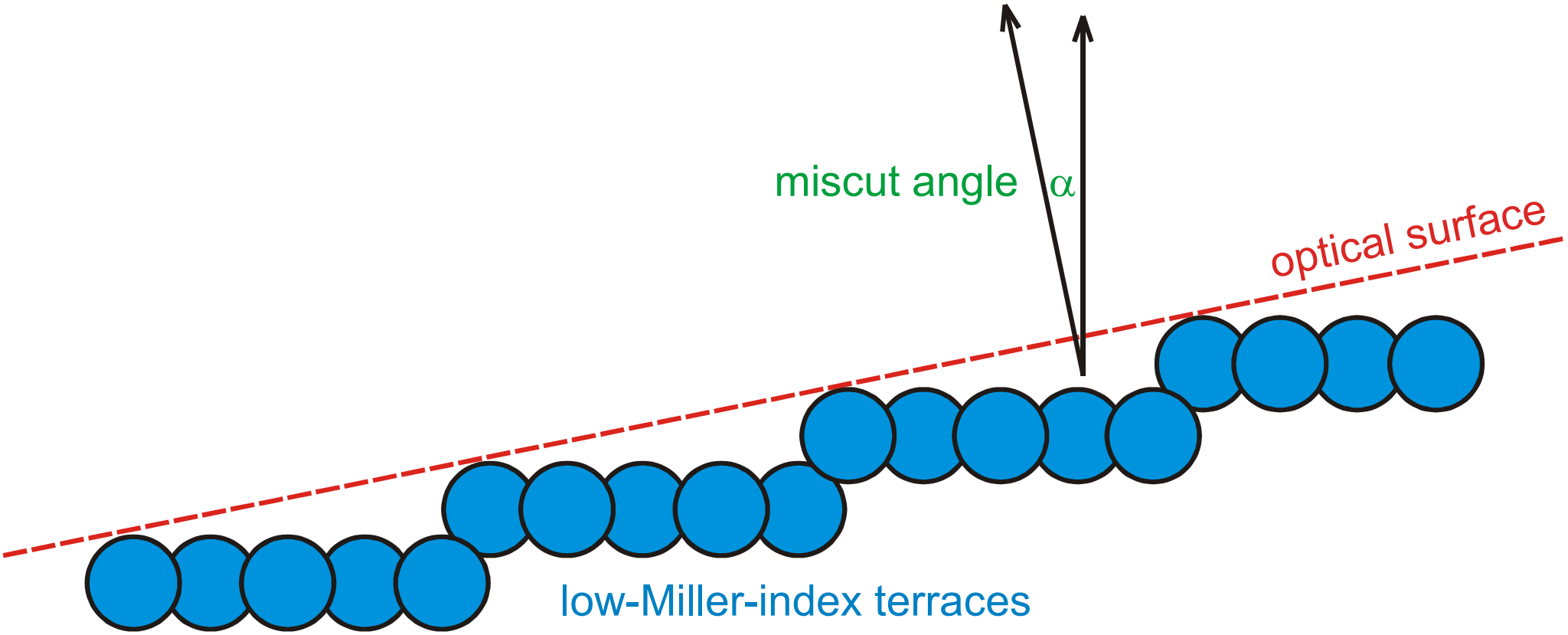


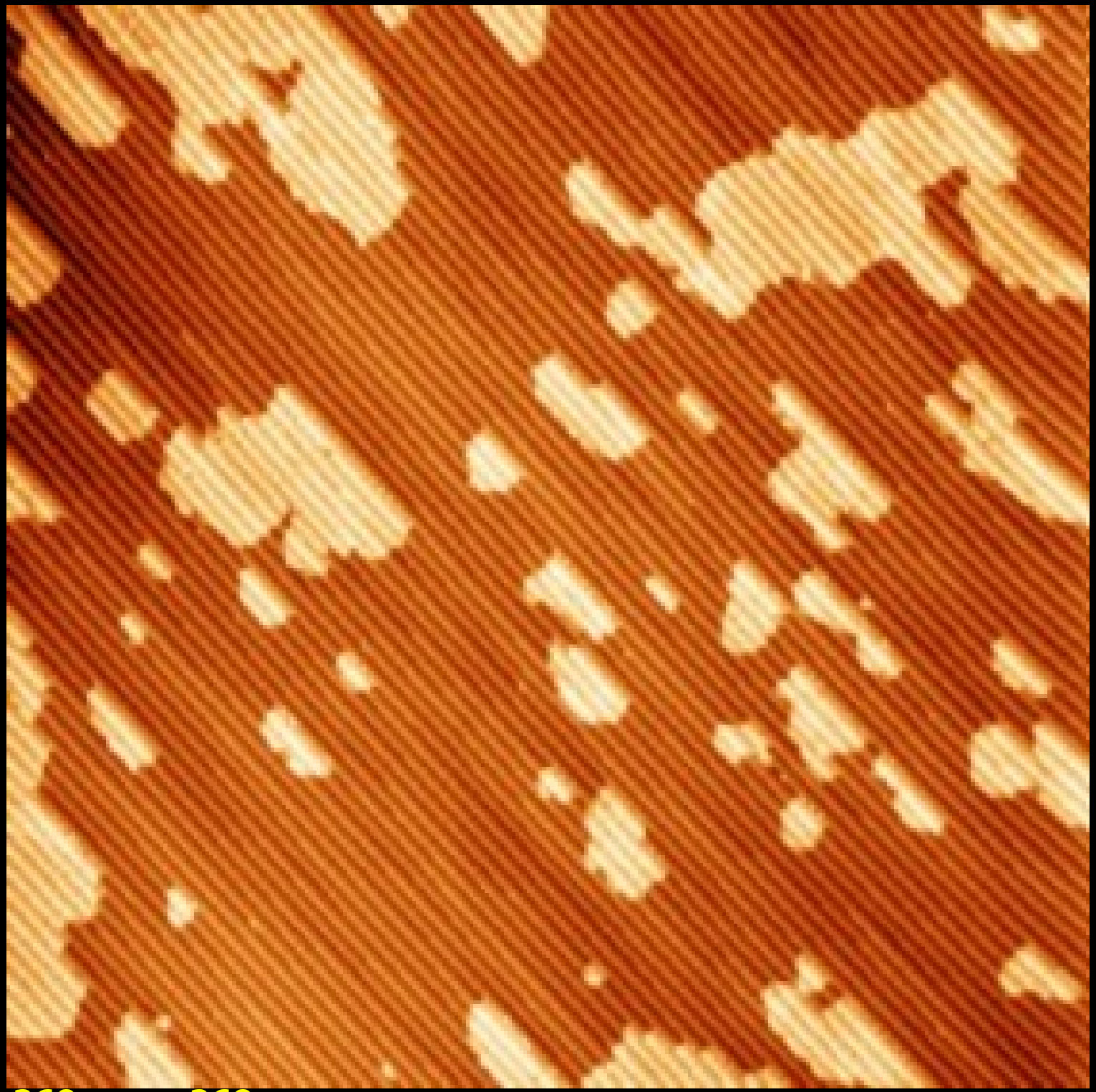
Painting, China, *p31m*



CoPc on Cu(111), *p31m*

Stepped or Vicinal Surfaces

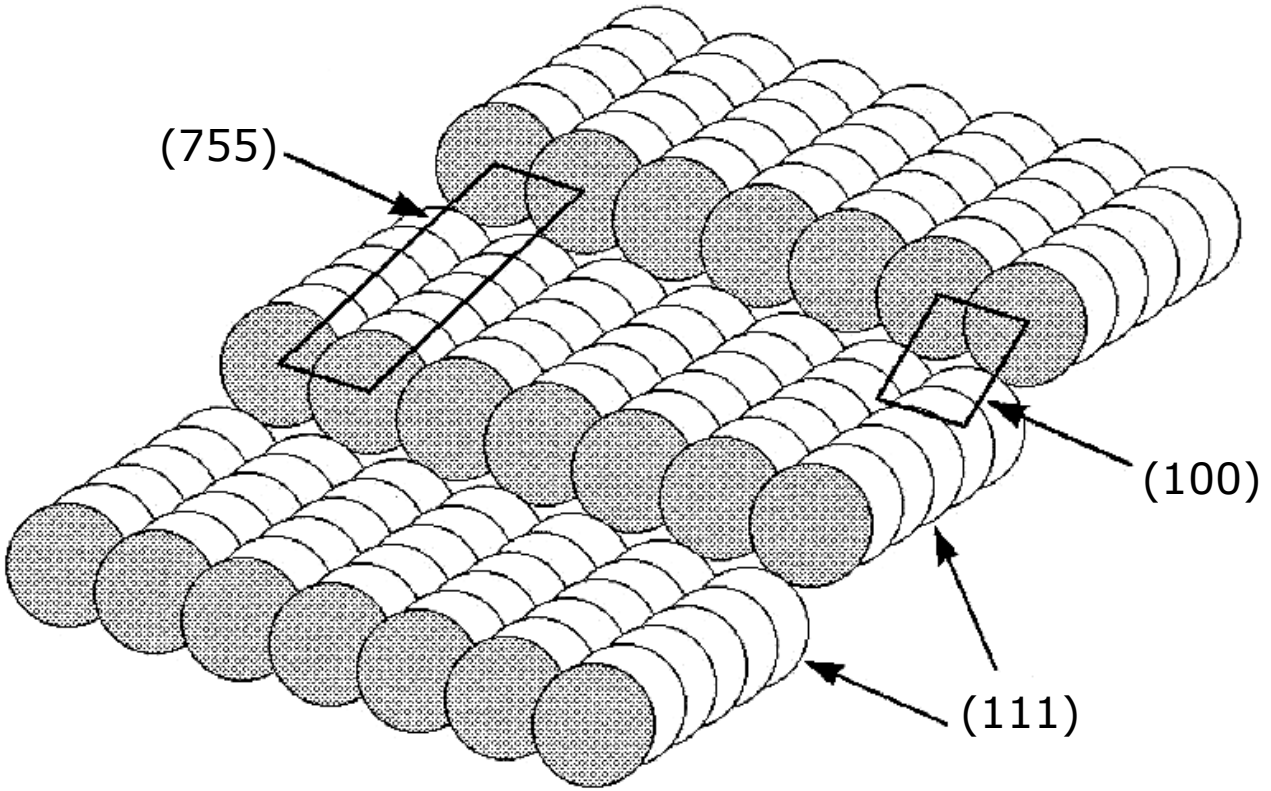




Au(788)

260 nm × 260 nm

Kröger, Jensen, Berndt,
Rurali, Lorente,
Chem. Phys. Lett. (2007).



fcc (755)

or

fcc [6(111)x(100)]

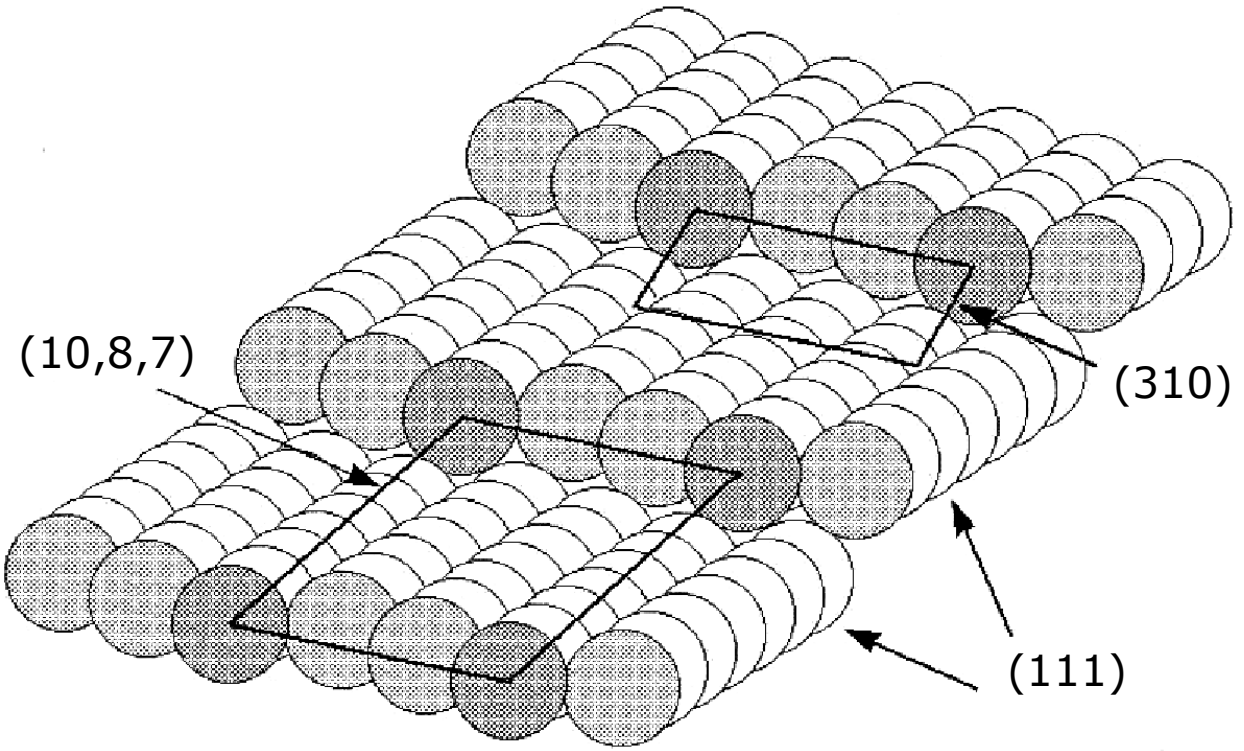
stepped

fcc (10 8 7)

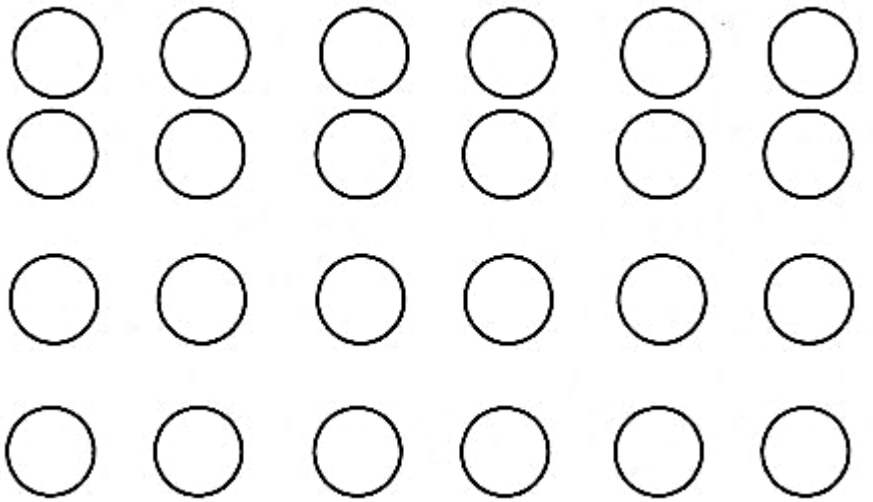
or

fcc [7(111)x(310)]

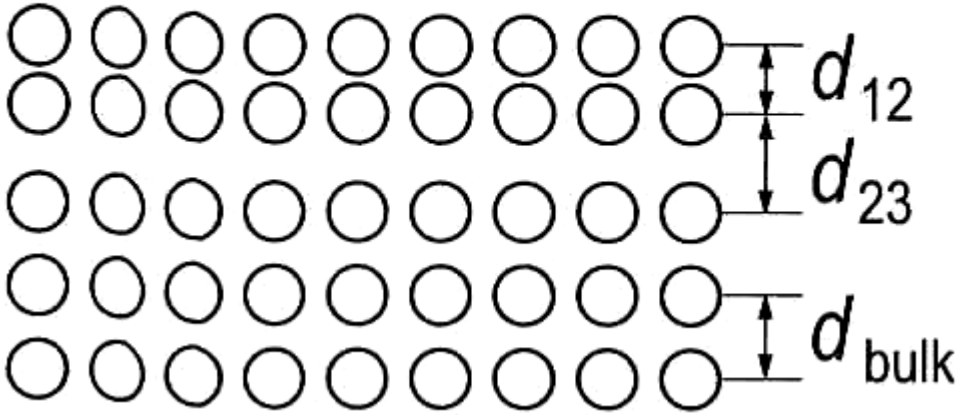
kinked



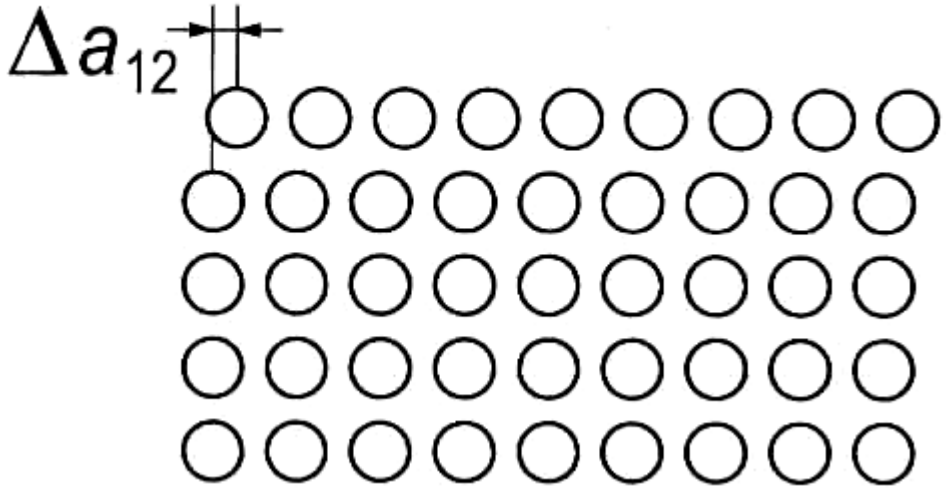
Relaxation



normal



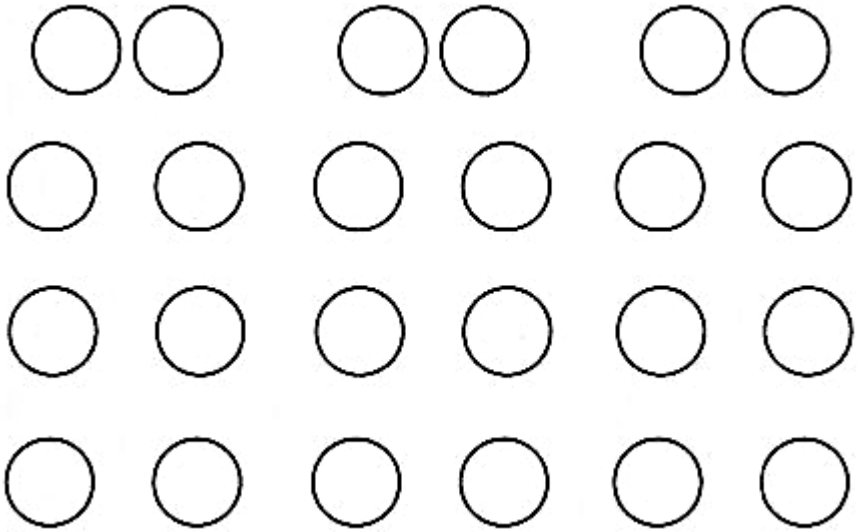
parallel



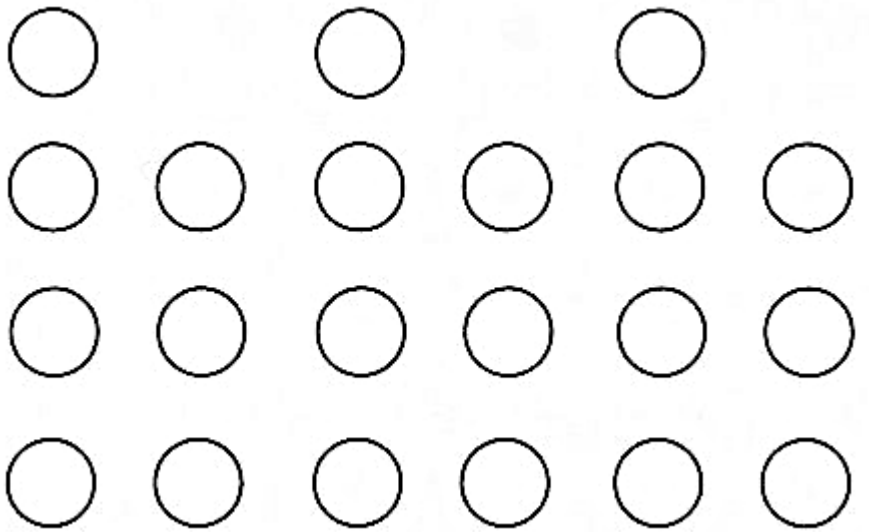
Metalle oft: d_{12} < d_{bulk} < d_{23} manchmal: $a_1 < a_{bulk}$

~10% ~1%

Rekonstruktion



pairing



Missing row

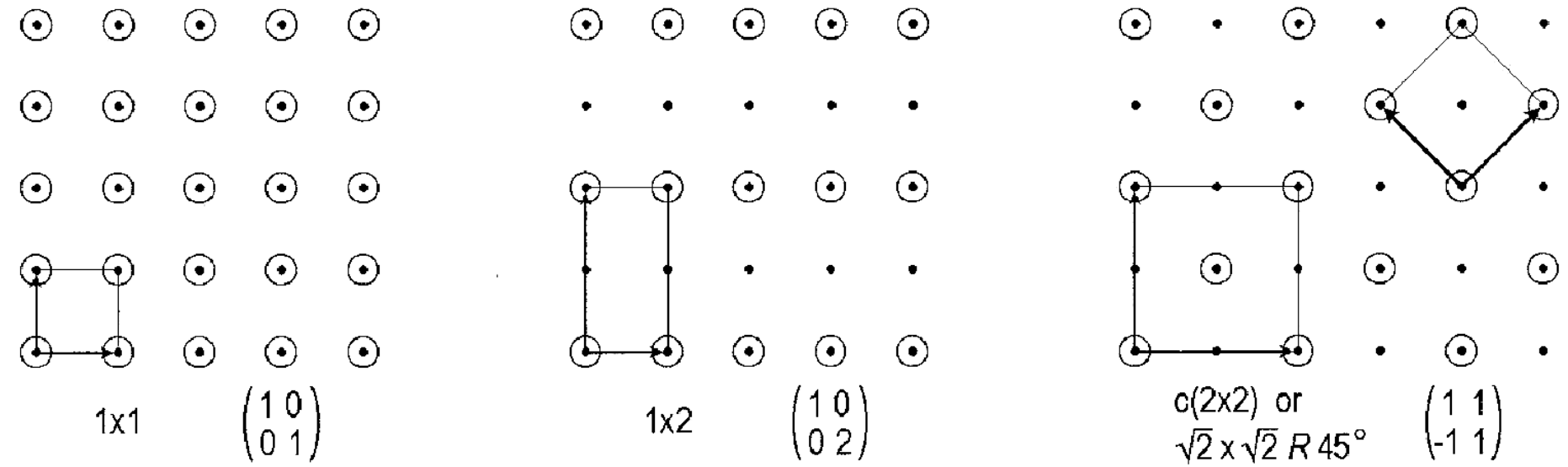


Fig. 2.13. Wood's and matrix notation for some superlattices on a square 2D lattice

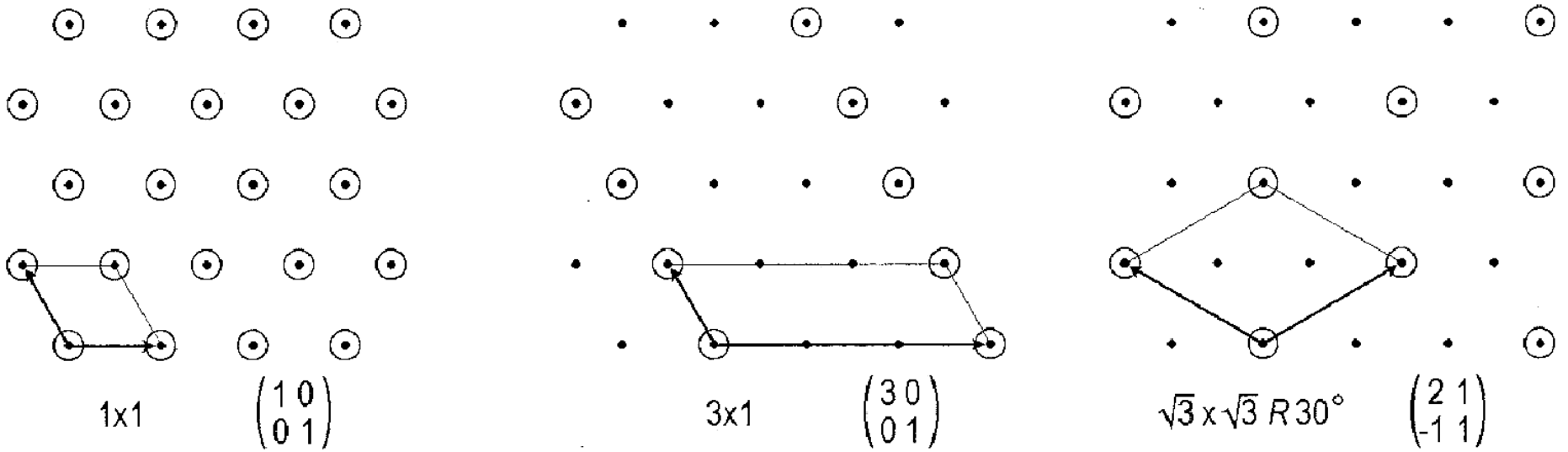
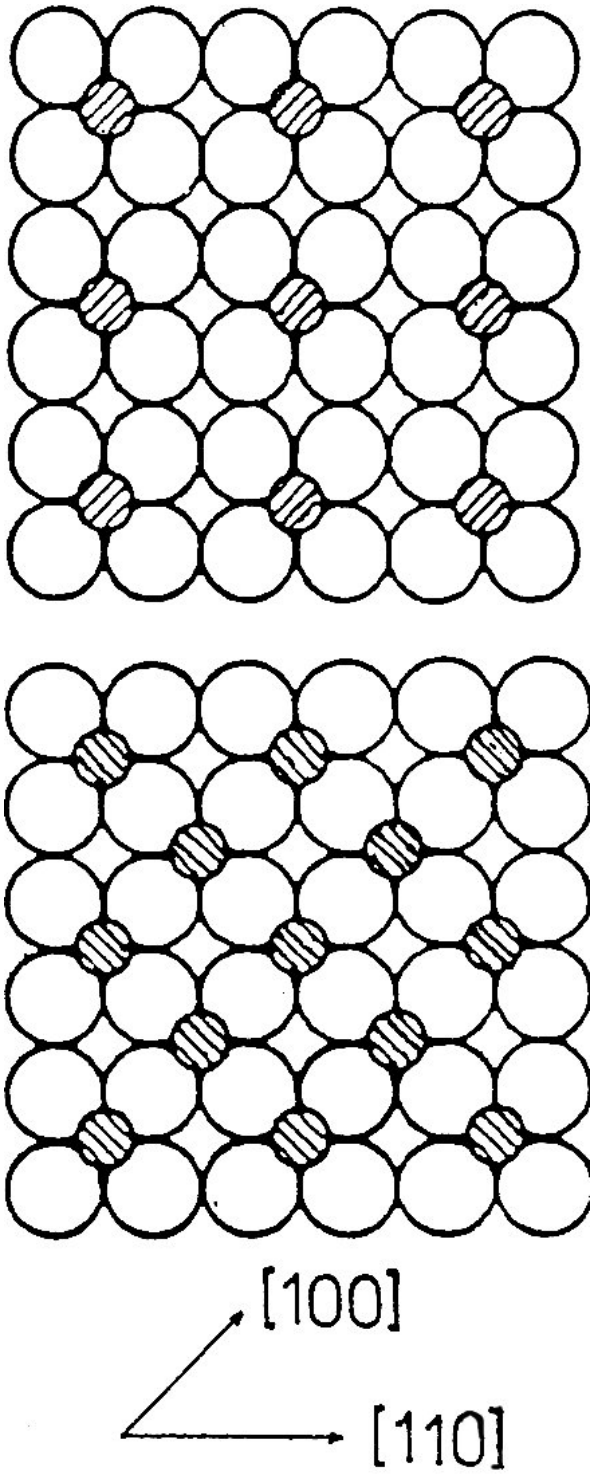
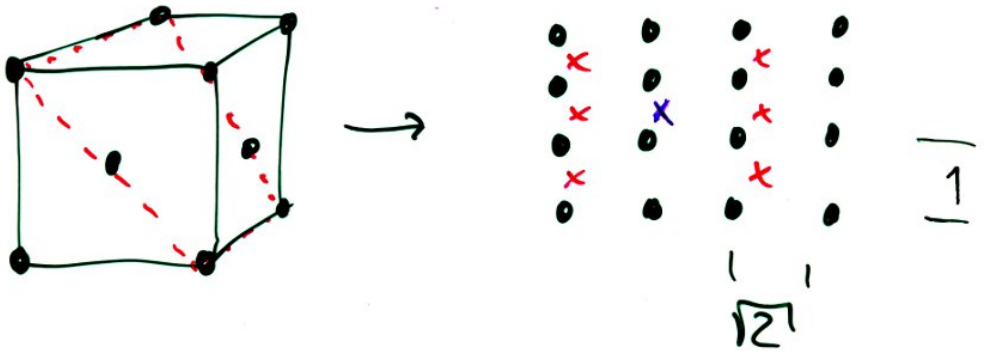


Fig. 2.12. Wood's and matrix notation for some superlattices on a hexagonal 2D lattice



Kristallographische Nomenklatur



Au (110) c (1×2)

Substratfläche — p/c — Maschenweite — Drehwinkel

Abb.4.1: Schematische Darstellungen von (2x1)-Überstrukturen auf der (001)-Oberfläche eines kubisch flächenzentrierten Kristalles in Orsaneau. Offene Symbole bezeichnen Substratatome, schraffierte Kreise bezeichnen die Adsorbatatome.
oben: die p(2x1)-Struktur
unten: die c(2x1)-Struktur