Advanced Surface Science

2) Surface symmetry

For MChem, Spring, 2009

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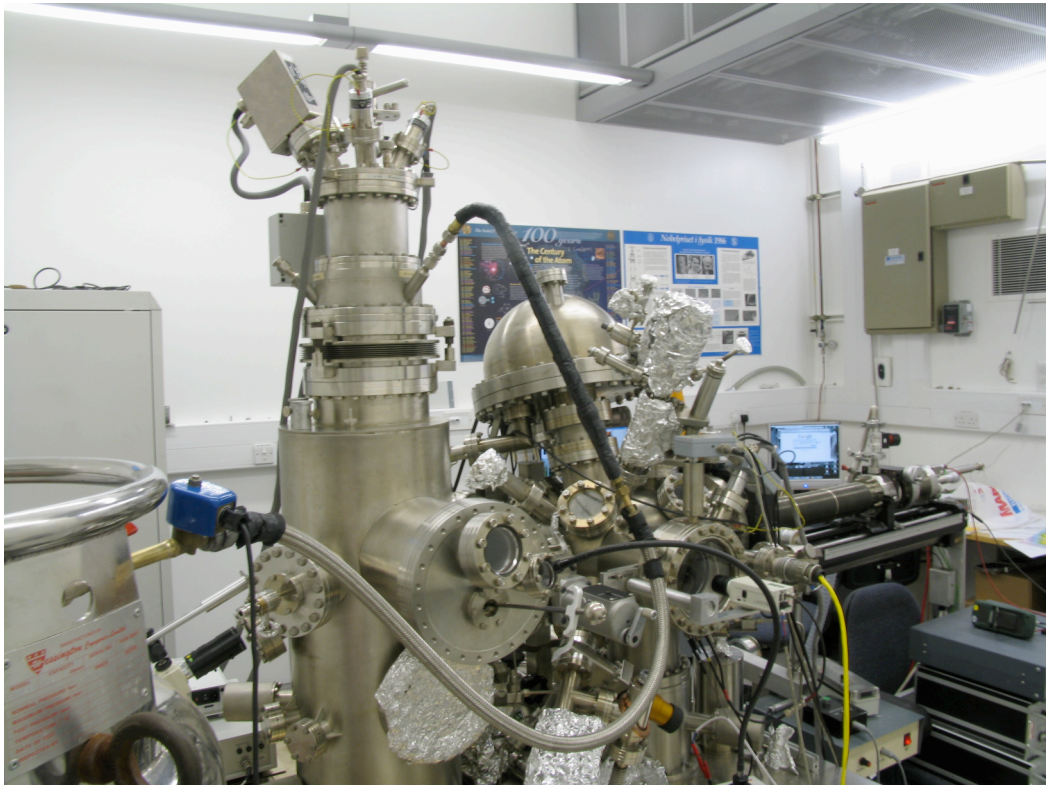
http://www.sussex.ac.uk/Users/qc25/

University of Sussex



Last lecture: Fundamental aspects of surface science

Challenges in surface science

Why UHV?

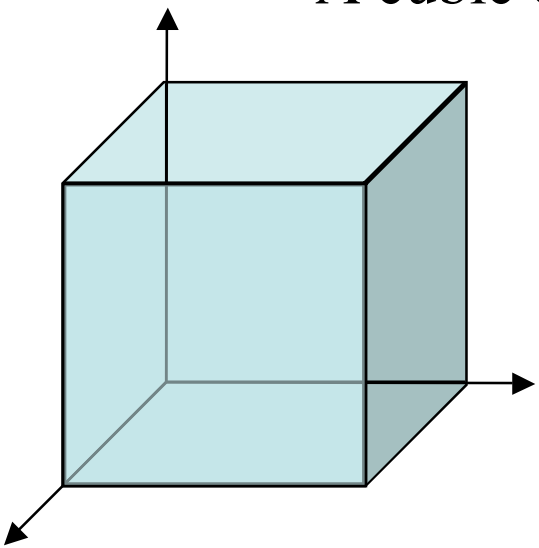
Pumps (rotary pump, diffusion pump, ion pump, TSP pump)

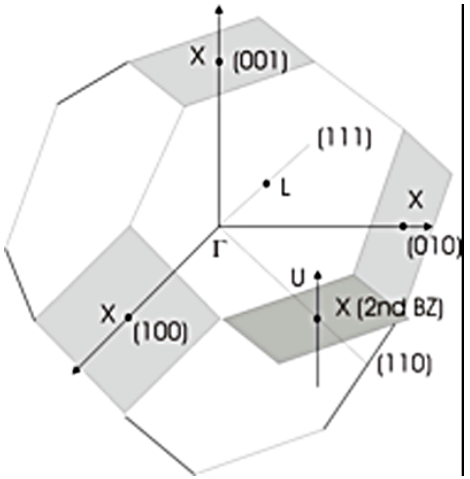
Vacuum gauges (Pirani gauge, Penning Gauge and ion gauge)

Single crystal surfaces vs amorphous

Simple structure
High purity
Well defined
Measurable crystal dimension
Clear bonding geometry

A cubic crystal





2. Fundamental aspects of surface science

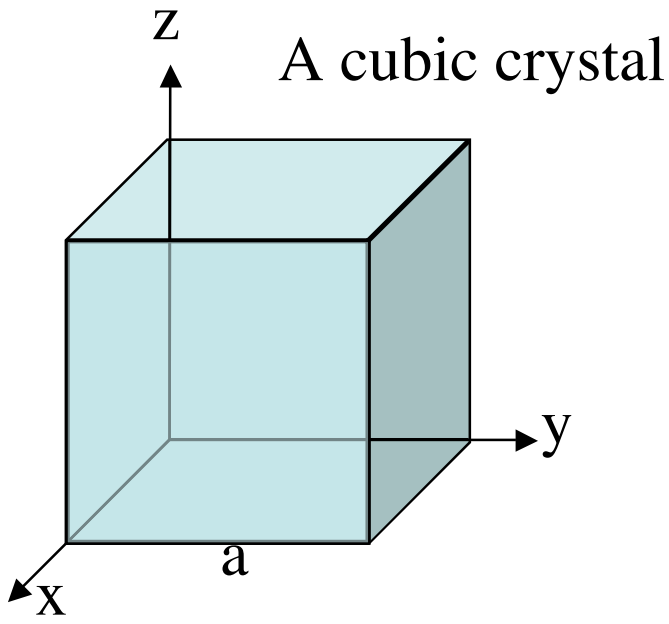
Surface Miller index and surface symmetry

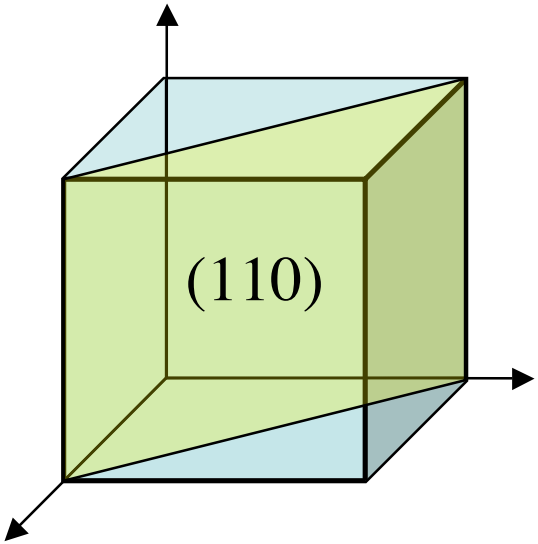
Miller index of a surface is the reciprocals of the fractional intercepts

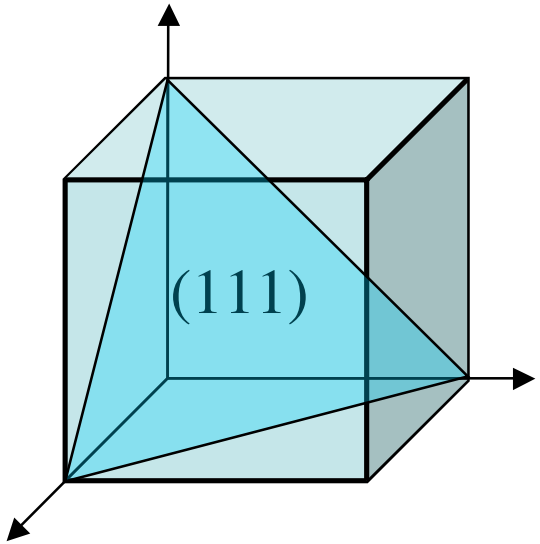
Fractional intercepts: h*, k*, l*

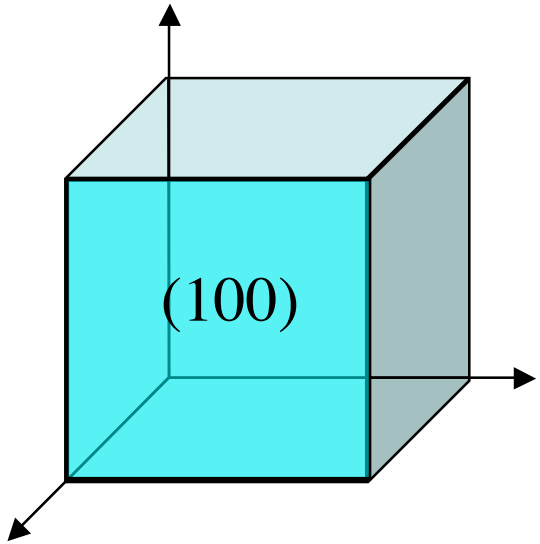
h=1/h* k=1/k* l=1/l*

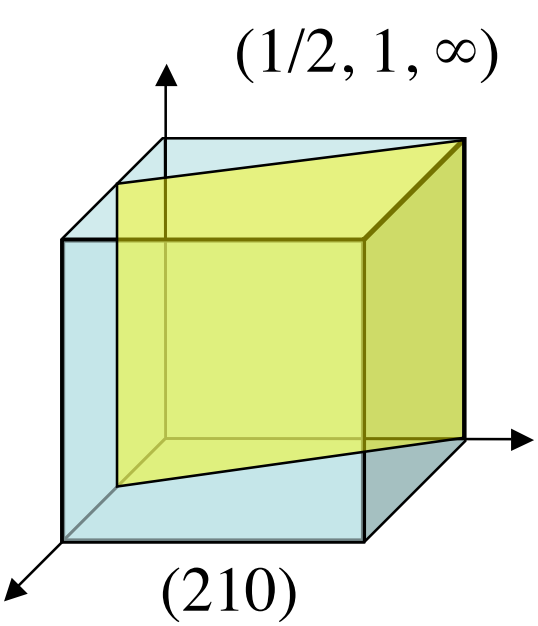
So, no ∞ or fractions, but all integers

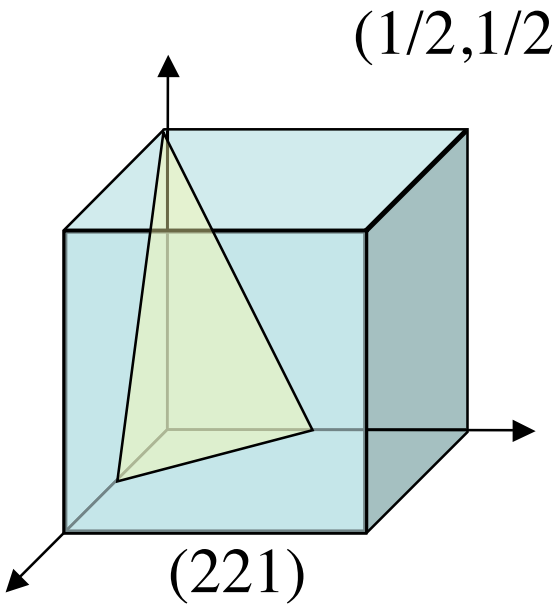









(1/2, 1, ∞)
(210)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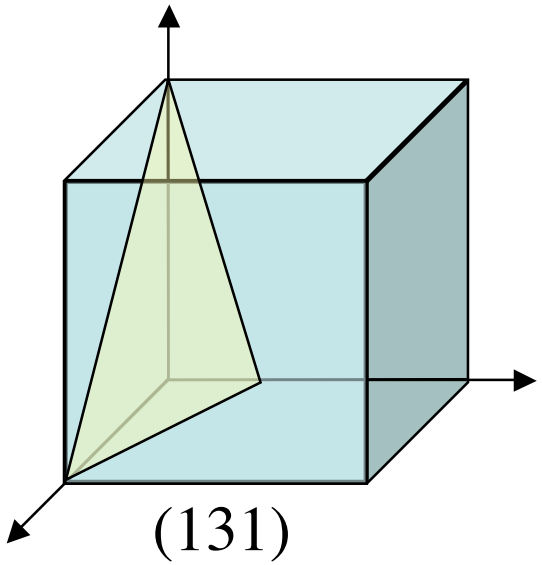
(221)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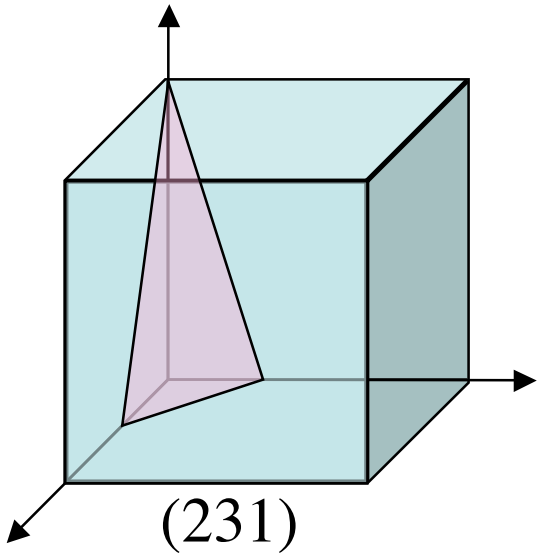
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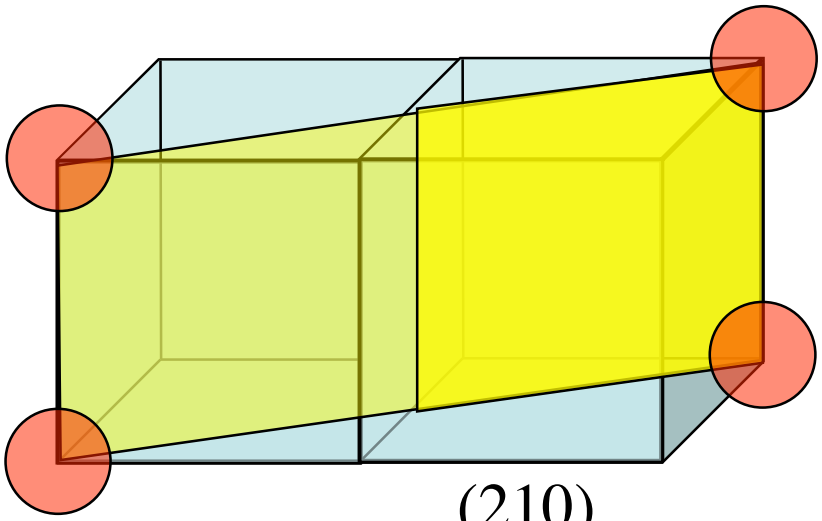
Unit cell of low index crystal surfaces



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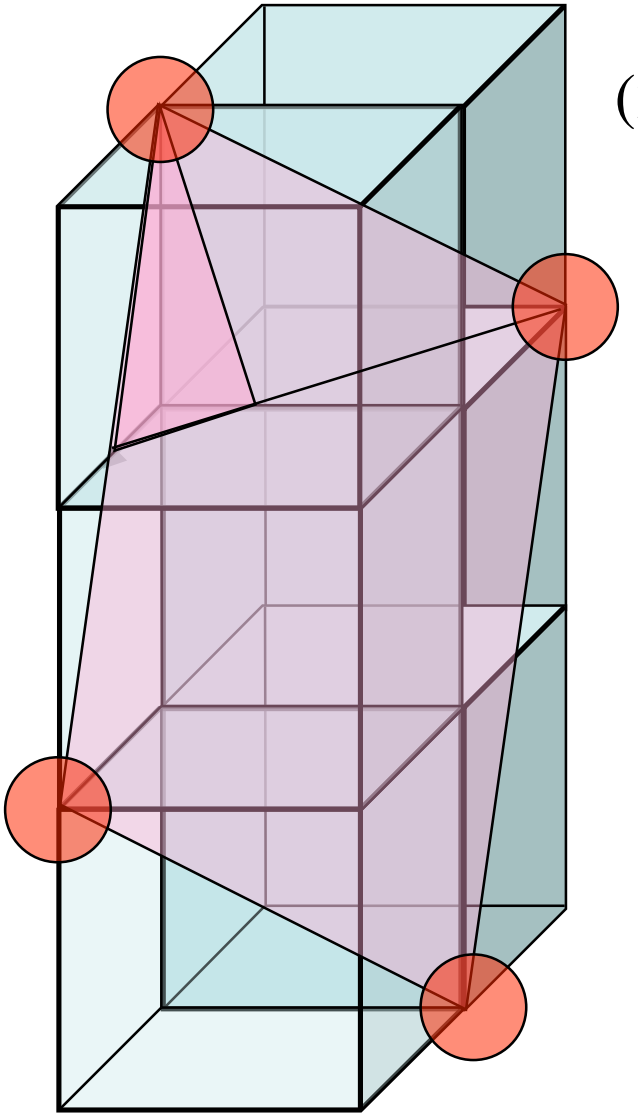
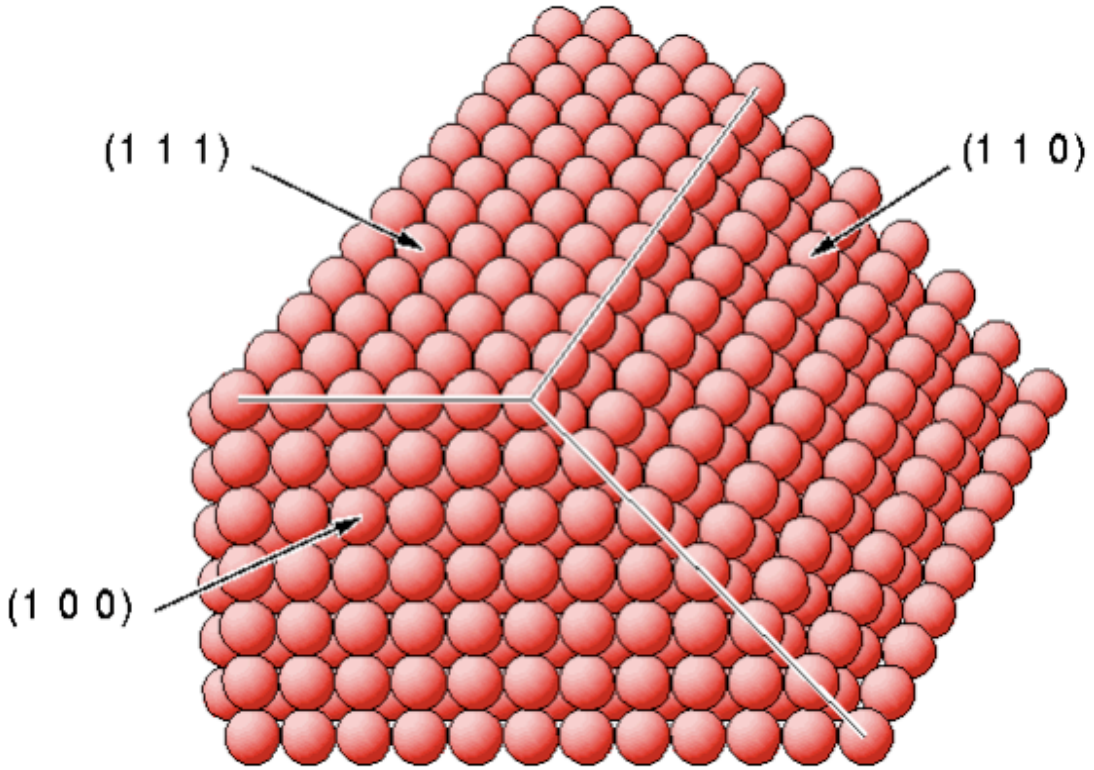
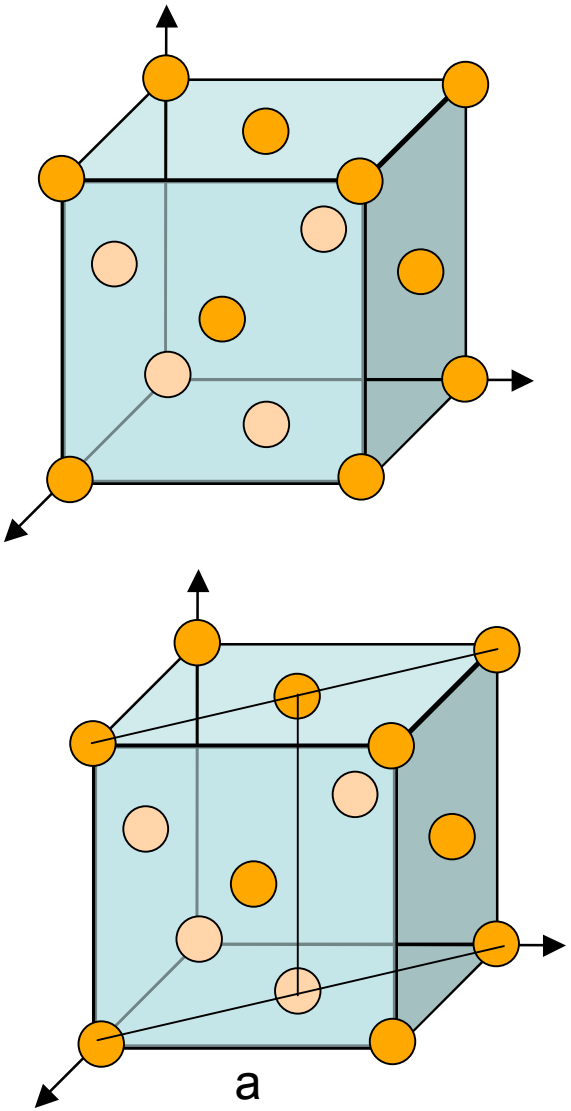
A unit cell has to contain at least one atom.



(231)

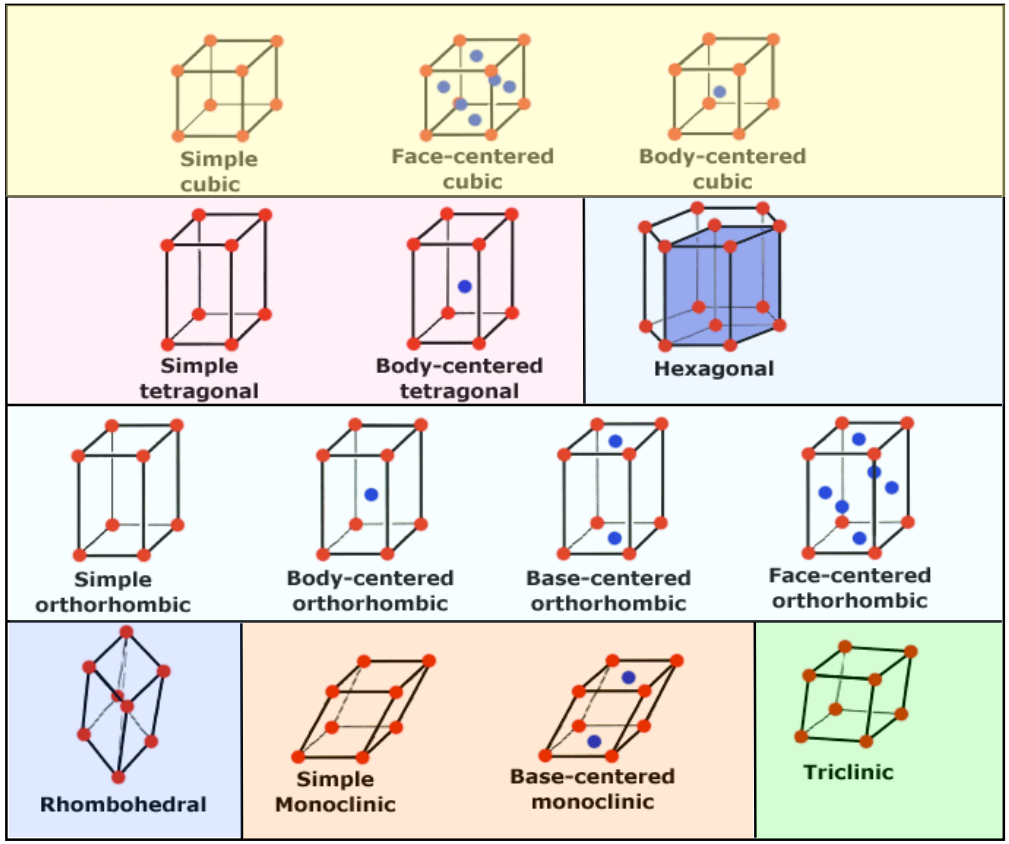
A fcc crystal



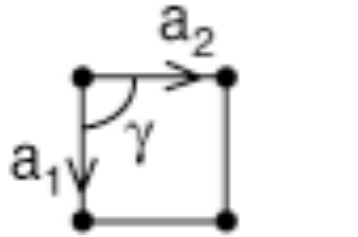


Type of bulk crystals: 14 bulk Bravais lattices

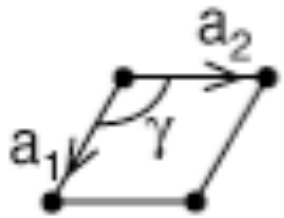
3D bulk possible crystal structures



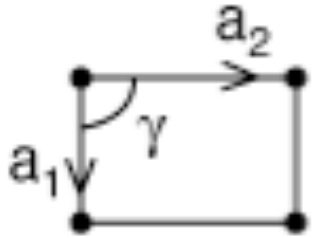
Five Surface Bravais Lattice



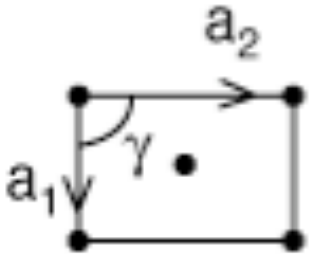
square $a_1 = a_2$ $\gamma = 90°$



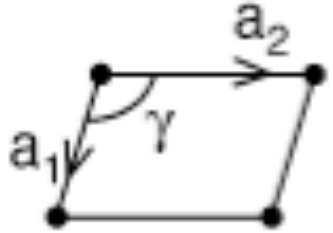
hexagonal $a_1 = a_2$ $\gamma = 120°$



rectangular $a_1 = a_2$ $\gamma = 90°$



centered rectangular $a_1 = a_2$ $\gamma = 90°$



oblique $a_1 = a_2$ $\gamma = 90°, 120°$

Symmetry operation

The symmetry elements and related operations that we will find in molecules are:

Element	Operation
Rotation axis, C_n	n-fold rotation
Improper rotation axis, S_n	n-fold improper rotation
Plane of symmetry, σ	Reflection
Center of symmetry, i	Inversion
	Identity, E

Common point groups

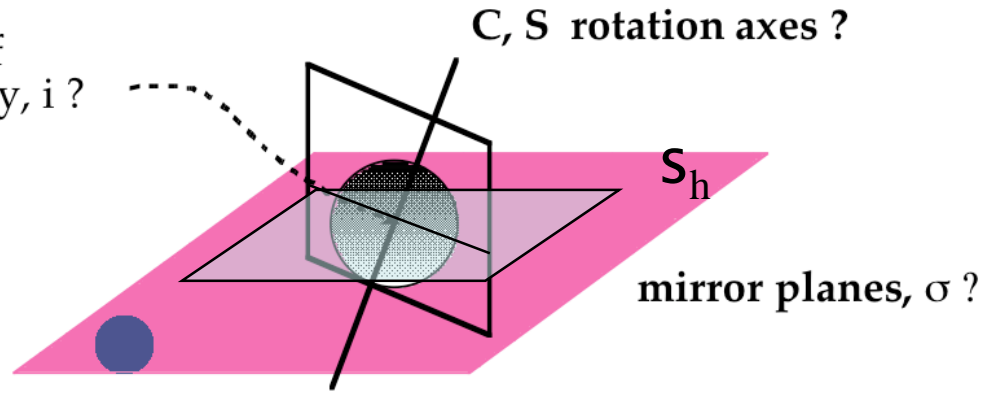
The following table contains a list of point groups with representative molecules. The description of structure includes common shapes of molecules based on VSEPR theory.

Point group	symmetry elements	Description of structure	Examples
C_1	E	No symmetry	CFClBrH, lysergic acid
C_s	E σ_h	Planar, no other symmetry	thionyl chloride, hypochlorous acid
C_i	E i	Inversion center, no other symmetry	*anti*-1,2-dichloro-1,2-dibromoethane
$C_{\infty v}$	E $2C_\infty$ σ_v	linear, no other symmetry	hydrochloric acid, dicarbon monoxide
$D_{\infty h}$	E $2C_\infty$ $\infty\sigma_i$ i $2S_\infty$ ∞C_2	linear with inversion center	dihydrogen, azide anion, carbon dioxide
C_2	E C_2	"open book geometry"	hydrogen peroxide
C_{2h}	E C_2 i σ_h	Planar with inversion center	trans-1,2-dichloroethylene
C_{2v}	E C_2 $\sigma_v(xz)$ $\sigma_v'(yz)$	angular (H_2O) or see-saw (SF_4)	water, sulfur tetrafluoride, sulfuryl fluoride
C_{3v}	E $2C_3$ $3\sigma_v$	trigonal pyramidal	ammonia, phosphorus oxychloride
C_{4v}	E $2C_4$ C_2 $2\sigma_v$ $2\sigma_d$	square pyramidal	xenon oxytetrafluoride
D_{2h}	E $C_2(z)$ $C_2(y)$ $C_2(x)$ i $\sigma(xy)$ $\sigma(xz)$ $\sigma(yz)$	planar with inversion center	ethylene, dinitrogen tetroxide, diborane
D_{3h}	E $2C_3$ $3C_2$ σ_h $2S_3$ $3\sigma_v$	trigonal planar or trigonal bipyramidal	boron trifluoride, phosphorus pentachloride, sulfur trioxide
D_{4h}	E $2C_4$ C_2 $2C_2'$ $2C_2$ i $2S_4$ σ_h $2\sigma_v$ $2\sigma_d$	square planar	xenon tetrafluoride
D_{5h}	E $2C_5$ $2C_5^2$ $5C_2$ σ_h $2S_5$ $2S_5^3$ $5\sigma_v$	pentagonal planar	eclipsed ferrocene,[7] C_{70} fullerene
D_{6h}	E $2C_6$ $2C_3$ C_2 $3C_2'$ $3C_2$ i $3S_3$ $2S_6^3$ σ_h $3\sigma_d$ $3\sigma_v$	hexagonal planar	benzene, bis(benzene)chromium
D_{2d}	E $2S_4$ C_2 $2C_h$ $2C_2'$ $2\sigma_d$	90° twist	allene, tetrasulfur tetranitride
D_{3d}	E $2C_3$ $3C_2$ i $2S_6$ $3\sigma_d$	60° twist	ethane or disilane (staggered rotamer)
D_{4d}	E $2S_8$ $2C_4$ $2S_8^3$ C_2 $4C_2'$ $4\sigma_d$	45° twist	dimanganese decacarbonyl (staggered rotamer)
D_{5d}	E $2C_5$ $2C_5^2$ $5C_2$ i $3S_{10}^3$ $2S_{10}$ $5\sigma_d$	36° twist	ferrocene (staggered rotamer)
T_d	E $8C_3$ $3C_2$ $6S_4$ $6\sigma_d$	tetrahedral	methane, germanium tetrachloride, phosphorus pentoxide, adamantane
O_h	E $8C_3$ $6C_2$ $6C_4$ $3C_2$ i $6S_4$ $8S_6$ $3\sigma_h$ $6\sigma_d$	octahedral	cubane, sulfur hexafluoride
I_h	E $12C_5$ $12C_5^2$ $20C_3$ $15C_2$ i $12S_{10}$ $12S_{10}^3$ $20S_6$ 15σ	icosahedral	fullerene

Surface group theory

Unit cell symmetry

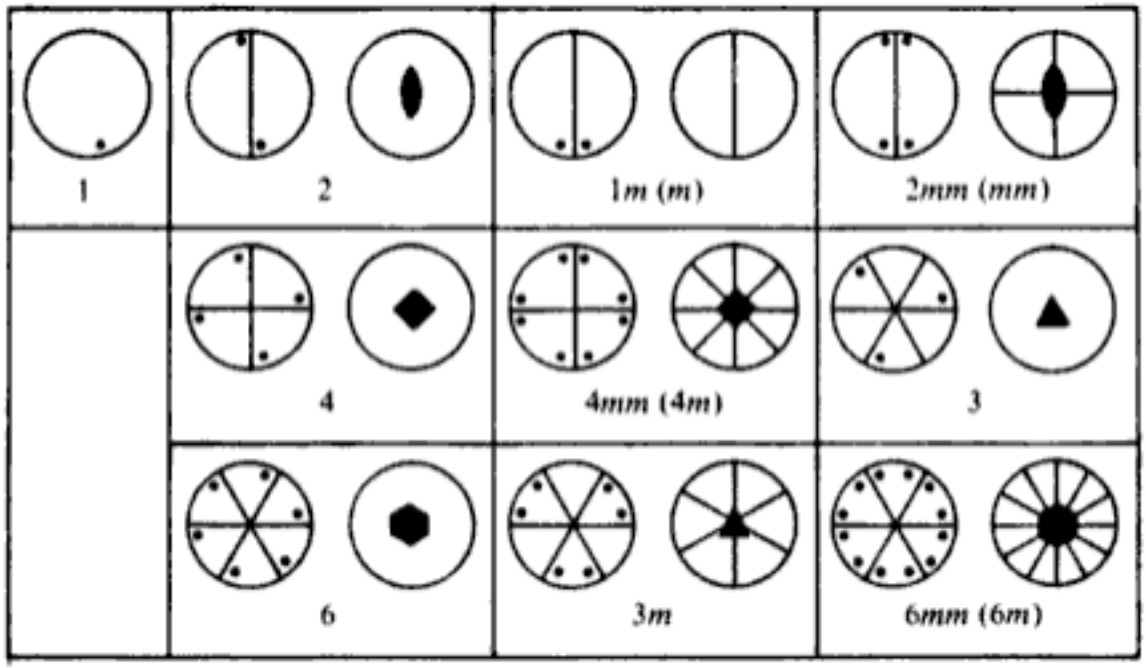
Limited symmetry survived



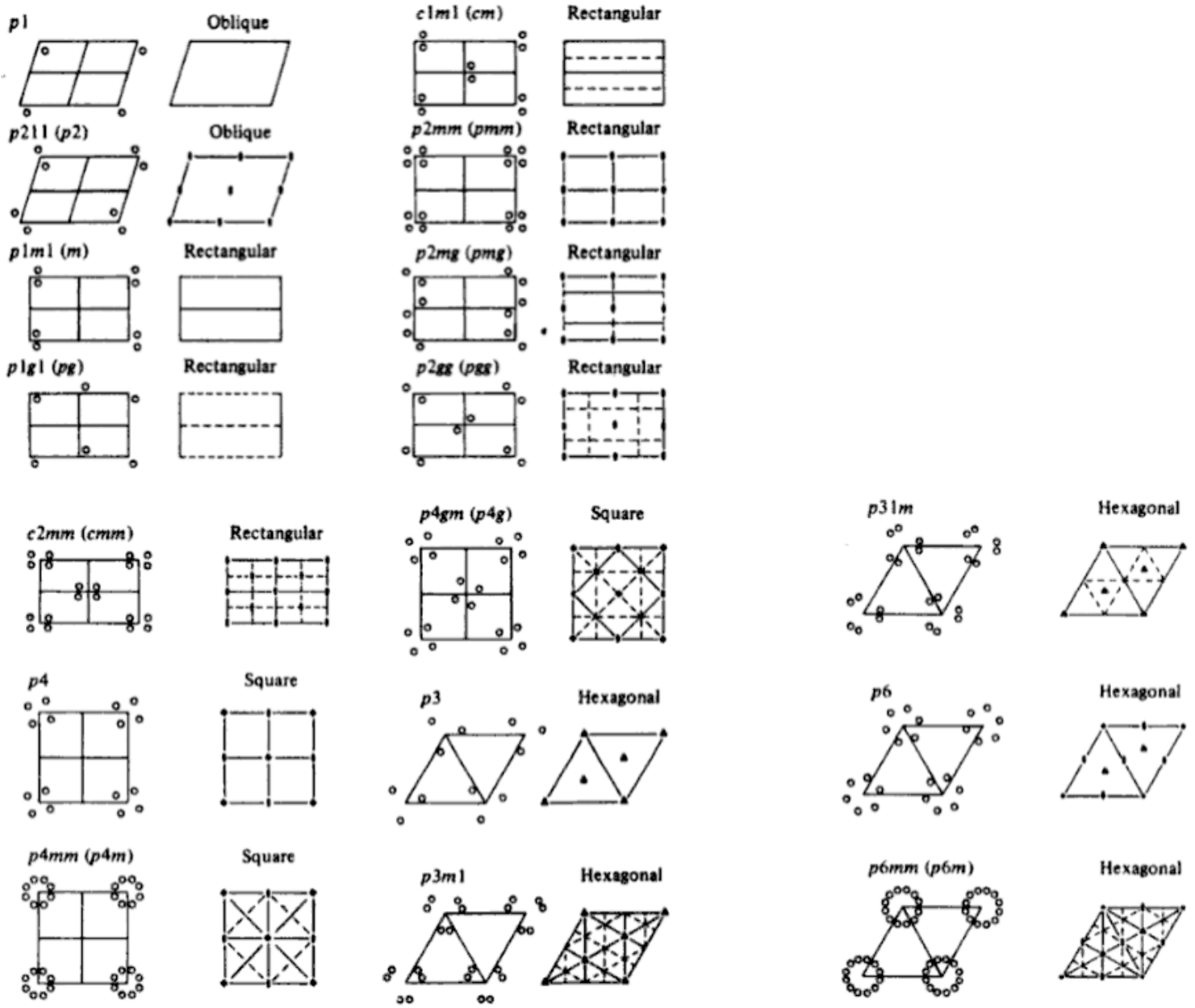
Ten point goups

C_{6v} C_{4v} C_{3v} C_{2v} C_s

C_6 C_4 C_3 C_2 C_1



2D 17 space group



In 3 dimensions

32 crystallographic point groups

230 space groups

14 Bravais lattices

7 crystal structures

In 2 dimensions

10 crystallographic point groups

no centre of symmetry, i

no improper rotations, Sn

rotations ⊥ to surface

mirror planes ⊥ to surface

17 space groups

no screw axes

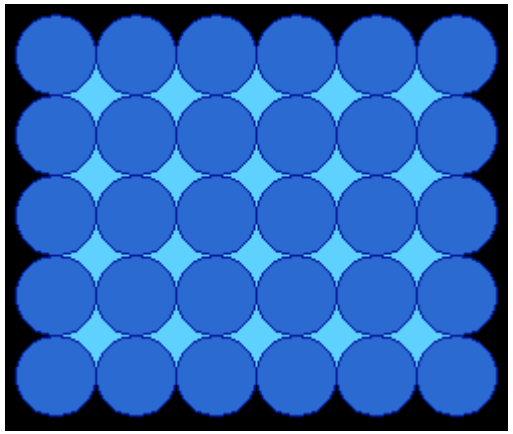
glide planes ⊥ to surface

5 Bravais lattices

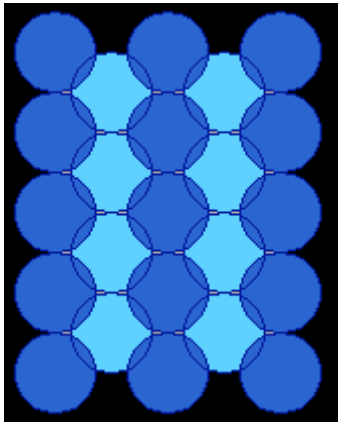
4 (5) crystal structures

Examples of Bravais lattices in 2D

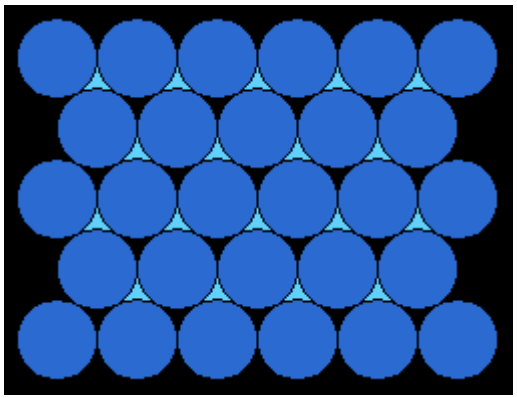
Square – fcc{100}



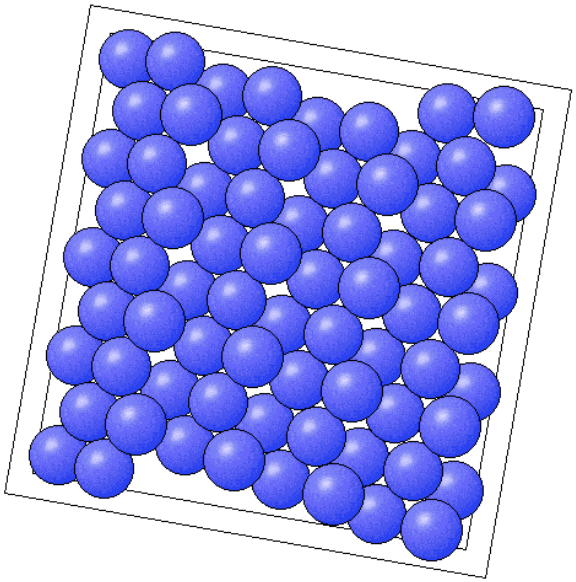
Rectangular primitive: fcc{110}



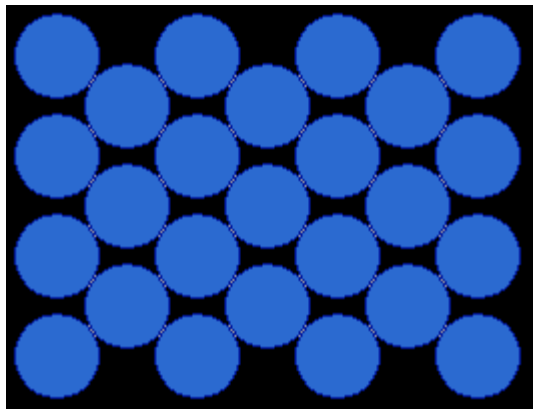
Hexagonal- hcp{0001}



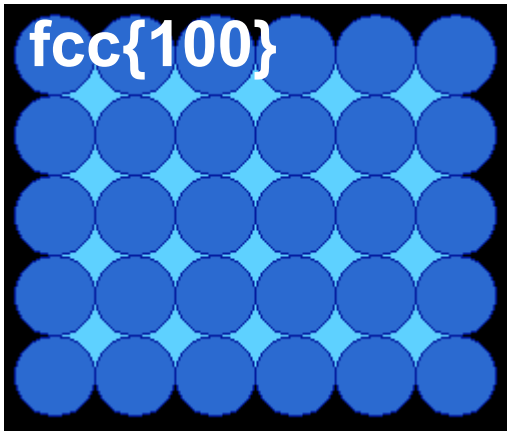
Oblique:fcc{531}

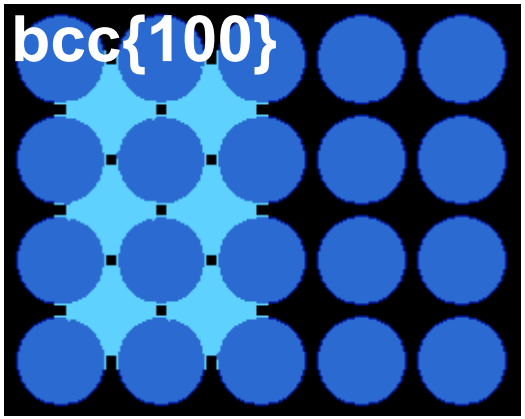


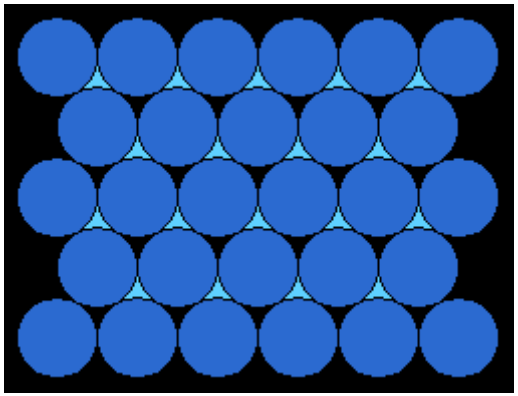
Rectangular centred:bcc{110}



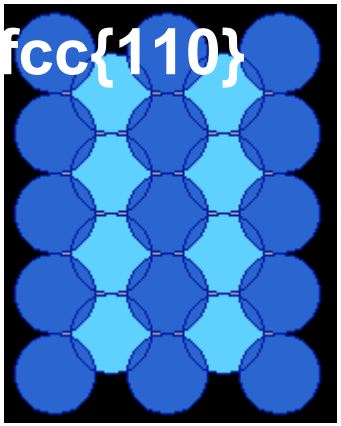
Surface geometry: truncated bulk

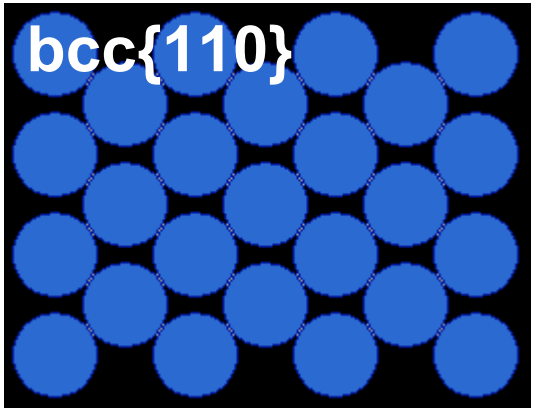


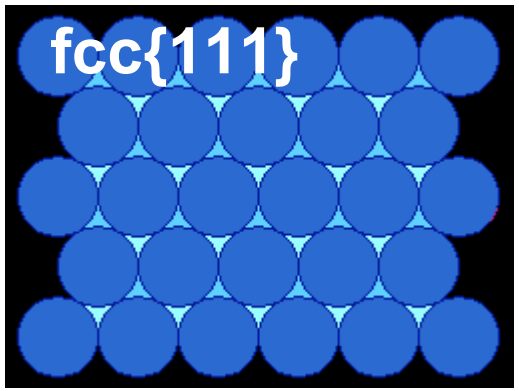


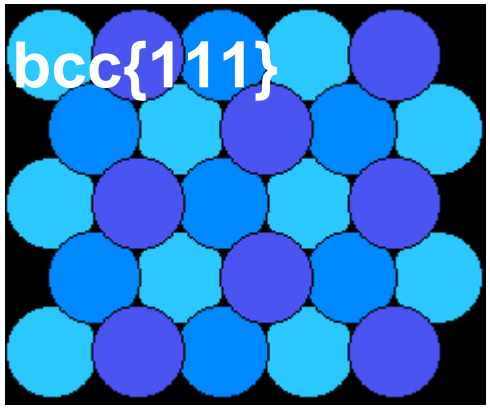


hcp{0001}



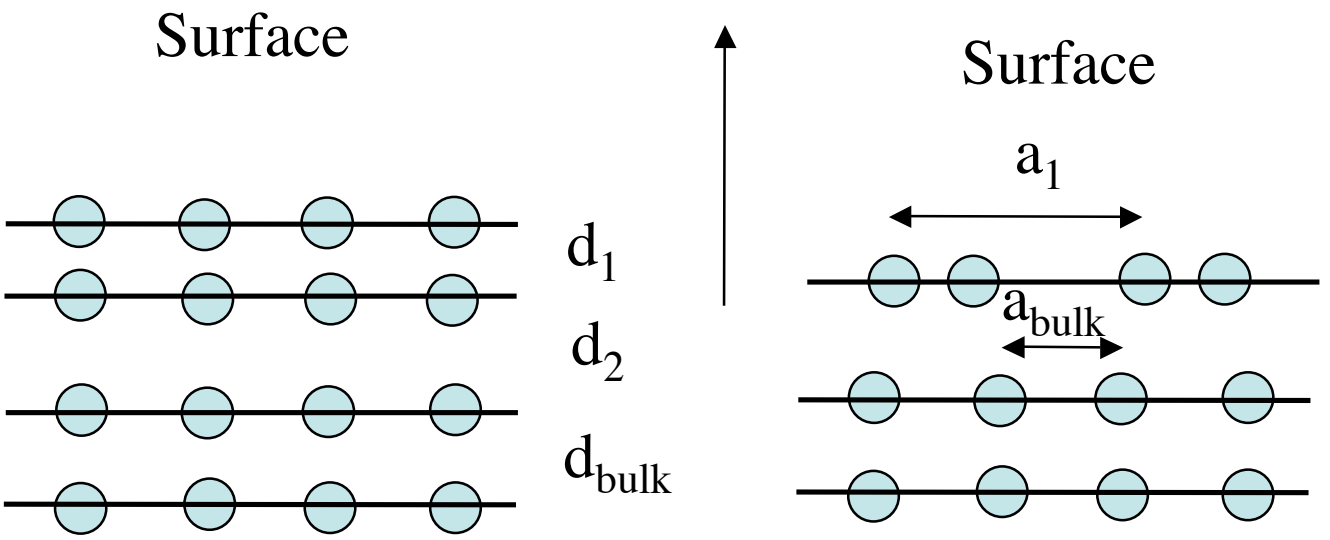






Surface geometry:
truncated bulk,
relaxation,
defects,
reconstruction,
super-structures

Surface relaxation and reconstruction



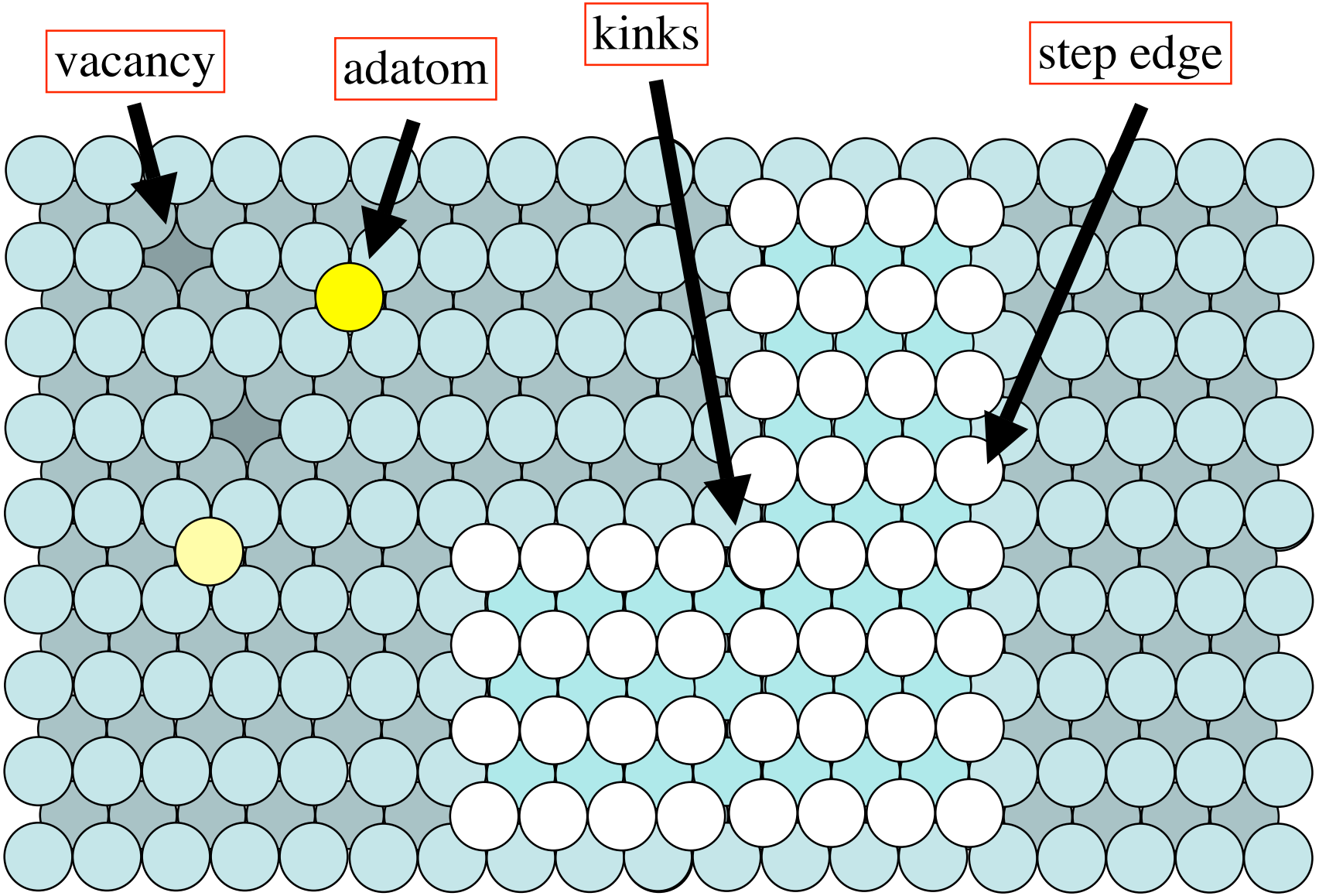
Side view

Side view

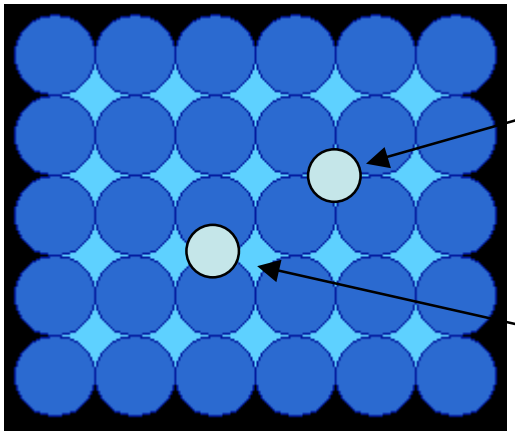
$d_1 < d_{bulk} < d_2$

$a_1 = 2a_{bulk}$

Surface defects:



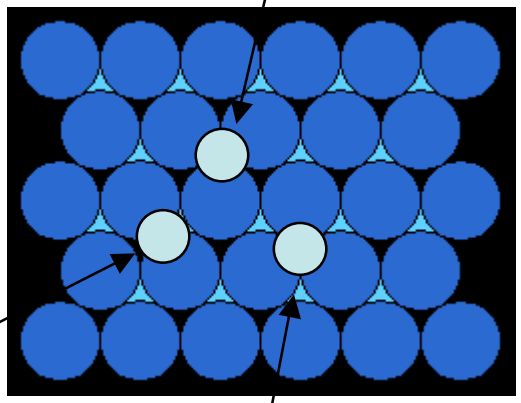
Surface adsorption sites:



4-fold hollow sites

2-fold bridge sites

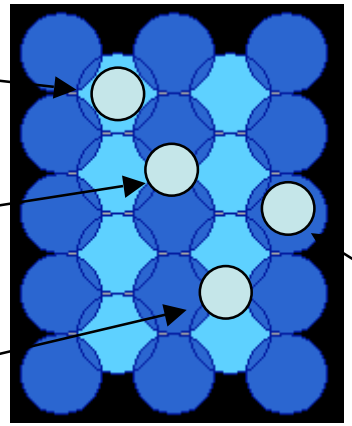
3-fold type B sites



bridge sites

3-fold type A sites

Hollow sites



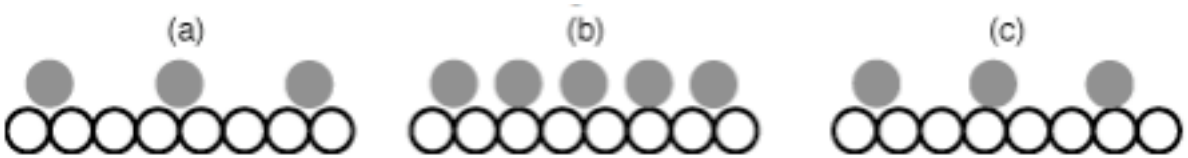
Short bridge sites

Atop site

Long bridge sites

Overlayer structures:

Commensurate vs incommensurate



Simply related **rational related** **incommensurate**

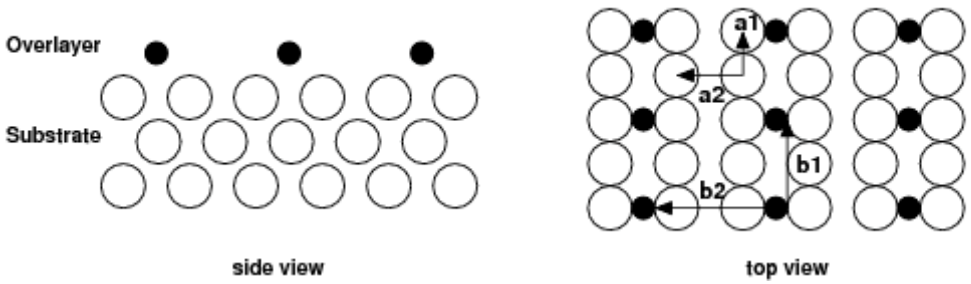
Growth modes:

Frank-van der Merwe
Stranski-Krastanov
Volmer-Weber

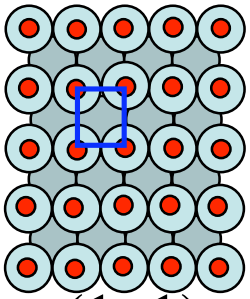
Superstructure:

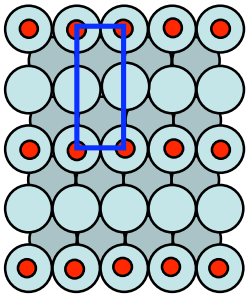
substrate: vectors $\mathbf{a}_1$ and $\mathbf{a}_2$
overlayer: vectors $\mathbf{b}_1$ and $\mathbf{b}_2$

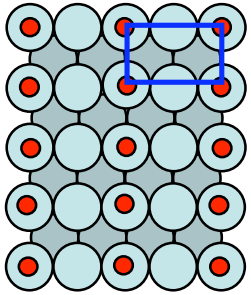
$b_1=2a_1$, $b_2=2a_2$ p(2x2)



Examples of adlayer super structures:


p(1x1)


p(1x2)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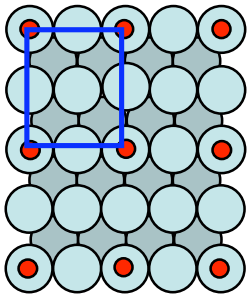
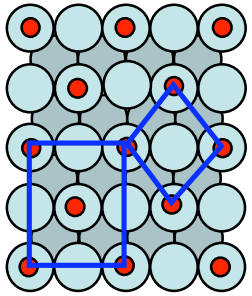
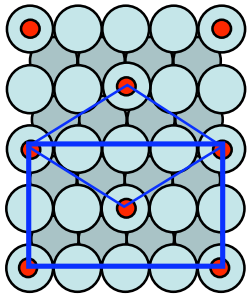
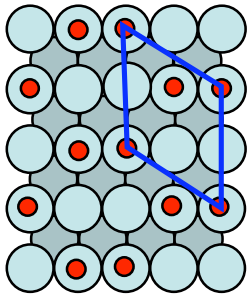

p(2x2)


c(2x2)


c(4x2)



$\begin{pmatrix} 0 & 2 \\ 2 & 1 \end{pmatrix}$

A more general description of the surface structure is the so-called matrix notation.

$b_1 = m_{11}a_1 + m_{12}a_2$

$b_2 = m_{21}a_1 + m_{22}a_2$

$\begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix}$

a_1 and a_2 are the substrate unit cell vectors, b_1 and b_2 are overlayer unit cell vectors.

In summary:

1. Surface crystal index, define crystal plane
2. Surface Bravais lattice
3. Surface symmetry, unit cell symmetry, 2D space group
4. Surface defects and sites
5. Surface relaxation
6. Superstuctures