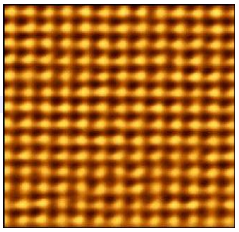
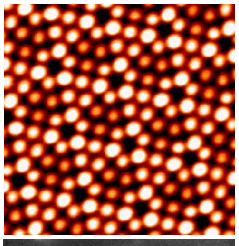
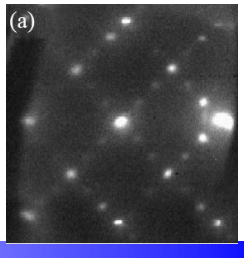
Lecture 2

Surface Structure







Quantitative Description of Surface Structure

- clean metal surfaces
- adsorbated covered and reconstructed surfaces
- electronic and geometrical structure

References:

1) Zangwill, p.28-32
2) Woodruff & Delchar, Chapter 2
3) Kolasinski, Chapter 1
4) Luth, 78-94
5) Attard & Barnes, 17-22

Basics: Clean Surfaces and Adsorption

1. The atom density in a solid surface is ~ 10^{15} cm^{-2} (10^{19} m^{-2})
2. Hertz-Knudsen equation

$$Z_W = \frac{p}{(2\pi m k_B T)^{1/2}}$$

$\Rightarrow$ If the probability that a molecule stays on the surface after it strikes it =1 (sticking coefficient = 1),

at p = 10^{-6} Torr it takes ~ 1 s to one molecule thick layer (1 ML)

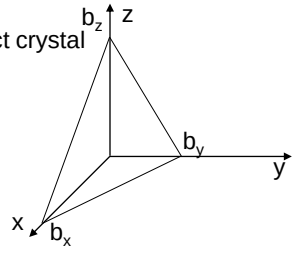
at p = 10^{-10} Torr it takes ~ 10^4 s = 2.75 hrs for 1 ML

When molecule adsorb via chemical interaction, they stick to well-defined sites

$\Rightarrow$ Need to understand the structure of clean and adsobate-covered surfaces as a foundation for understanding surface chemical problems

2.1 Bulk Truncation Structure

Ideal flat surface: truncating the bulk structure of a perfect crystal

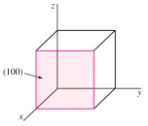


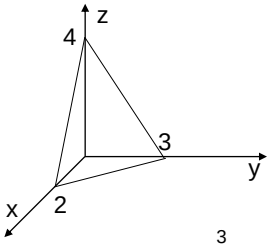
Miller Indices, revisited

- For plane with intersections at b_x, b_y b_z
write reciprocals: $\left(\frac{1}{b_x}\frac{1}{b_y}\frac{1}{b_z}\right)$

- If all quotients are rational integers or 0, this is Miller index

e.g., $b_x, b_y, b_z = 1, 1, 0.5 \Rightarrow (112)$

$b_x, b_y, b_z = 1, \infty, \infty \Rightarrow (100)$ 



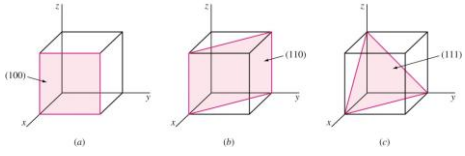
- In general

Miller index $(i,j,k) = \left(\frac{cd}{b_x}\frac{cd}{b_y}\frac{cd}{b_z}\right)$, where cd - common denom. of b_x, b_y, b_z

e.g., $cd = 12$; $(i,j,k) = \left(\frac{12}{2}\frac{12}{3}\frac{12}{4}\right) = (643)$

Crystallographic planes

- Single plane $(h\ k\ l)$



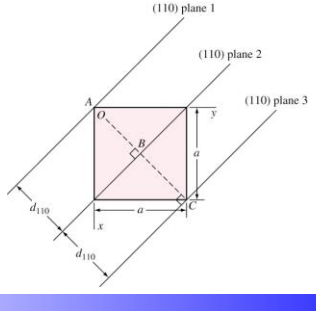
- Notation: planes of a family $\{h\ k\ l\}$

  $(100); (010); (001); \ldots \Rightarrow \{100\}$ are all equivalent

- *Only for cubic systems*: the direction indices of a direction perpendicular to a crystal plane have the same Miller indices as a plane

- Interplanar spacing d_{hkl}:

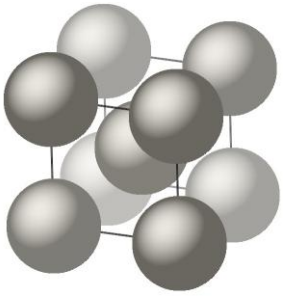
$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$



Metallic crystal structures (will talk about metal oxides later)

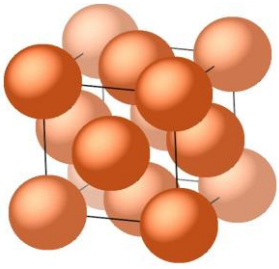
- >90% of elemental metals crystallize upon solidification into **3** densely packed crystal structures:

Body-centered cubic (bcc)



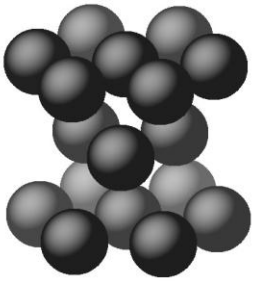
ex.: Fe, W, Cr

Face-centered cubic (fcc)



ex.: Cu, Ag, Au

Hexagonal close-packed (hcp)

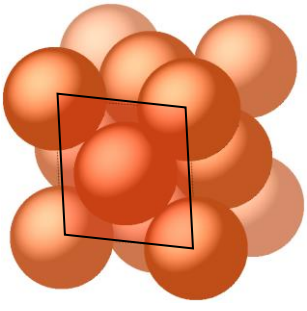


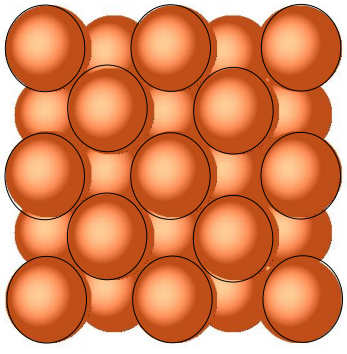
ex.: Zr, Ti, Zn

Very different surfaces!!!

fcc crystallographic planes

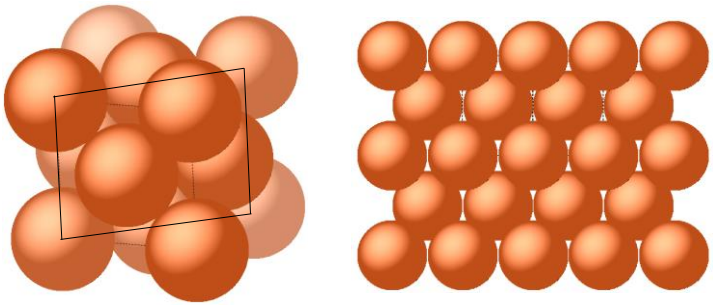
Cu (100)





fcc crystallographic planes

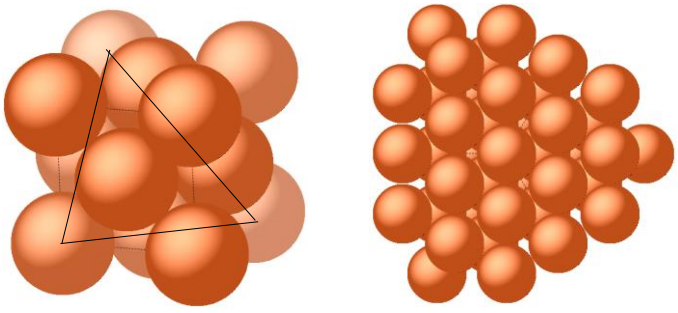
Cu (110)



Anisotropy of properties in two directions

fcc crystallographic planes

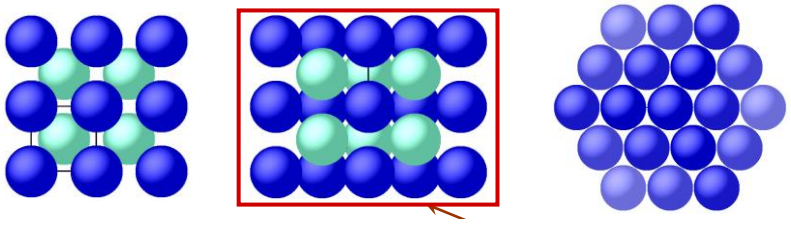
Cu (111)



3 fold symmetry

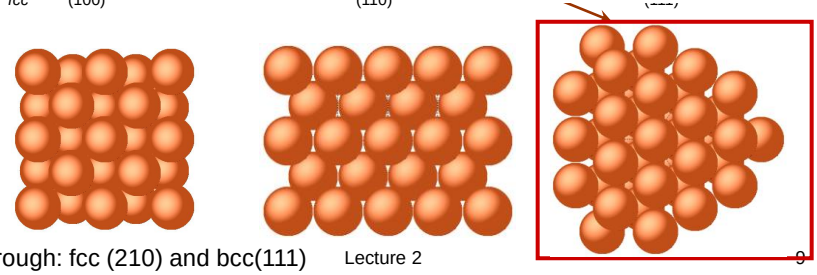
Atomic Packing in Different Planes

- *bcc* (100) (110) (111)



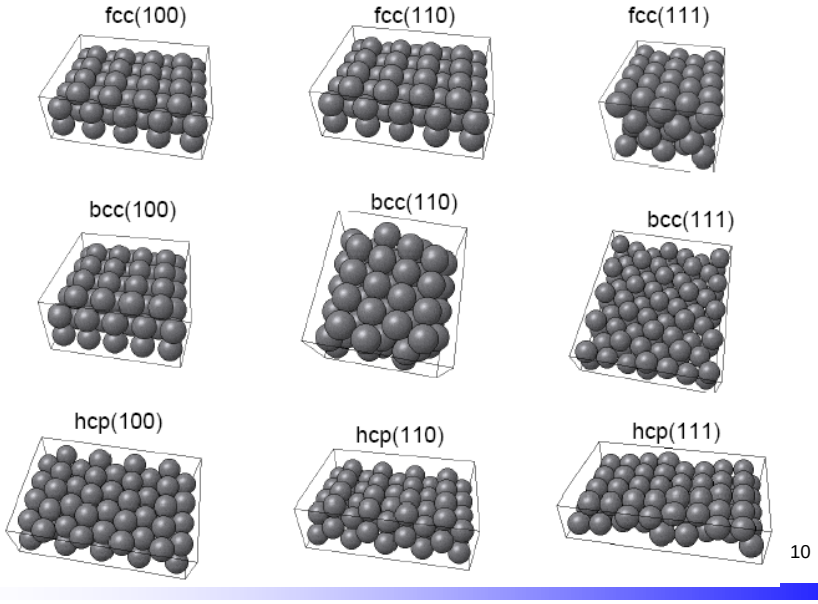
close-packed

- *fcc* (100) (110)



Very rough: fcc (210) and bcc(111)

Bulk Truncated Structures



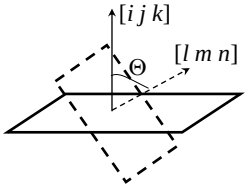
Cubic System

(i j k) defines plane

[i j k] is a vector ⊥ to plane, defining direction

Cross product of two vectors in a plane defines direction perpendicular to plane

$$[i\ j\ k] = [l\ m\ n] \times [\ o\ p\ q]$$



Angle between two planes (directions):

$$\cos\Theta = \frac{[ijk]\bullet[lmn]}{\sqrt{i^2+j^2+k^2}\sqrt{l^2+m^2+n^2}}$$

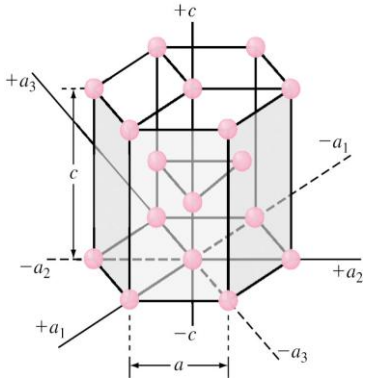
e.g., for [111], [211]

$$\cos\Theta = \frac{2+1+1}{\sqrt{1^2+1^2+1^2}\sqrt{2^2+1^2+1^2}} = \frac{4}{3\sqrt{2}} \Rightarrow \Theta = 19.47^o$$

Planes in hexagonal close-packed (hcp)

4 coordinate axes (a_1, a_2, a_3, and c) of the hcp structure (instead of 3)

Miller-Bravais indices - (*h k i l*) – based on 4 axes coordinate system



a_1, a_2, and a_3 are 120° apart: *h k i*

c axis is 90°: *l*

3 indices (rarely used):

h + *k* = - *l*

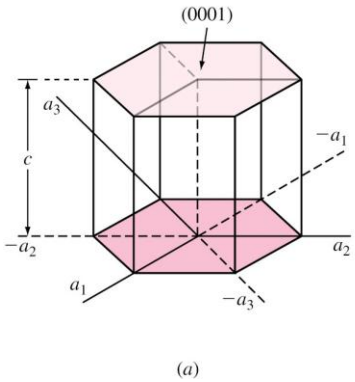
(h k i l) ⇒ *(h k l)*

Basal and Prizm Planes

Basal planes;

$a_1 = \infty$; $a_2 = \infty$; $a_3 = \infty$; $c = 1$

$\Rightarrow$ (0 0 0 1)

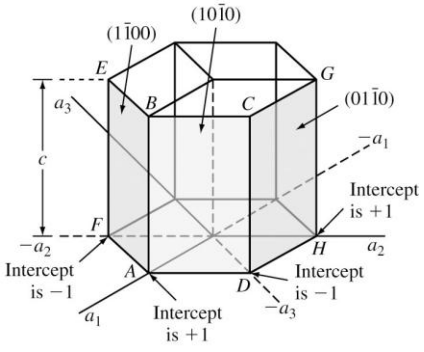


(a)

Prizm planes: ABCD

$a_1 = +1$; $a_2 = \infty$; $a_3 = -1$; $c = \infty$

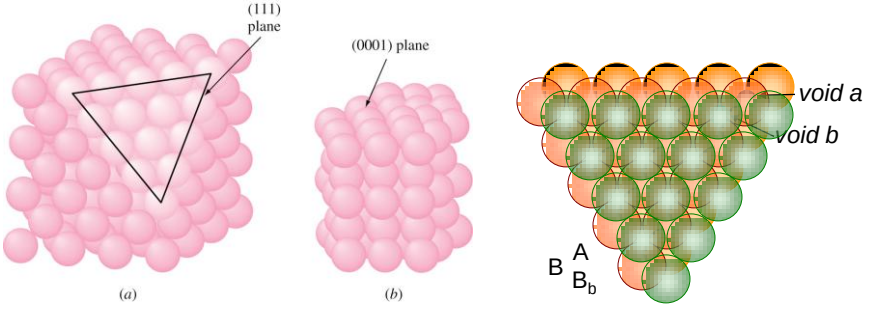
$\Rightarrow$ (1 0 -1 0)



(b)

Comparison of Crystal Structures

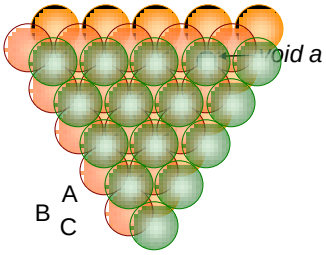
FCC and HCP metal crystal structures

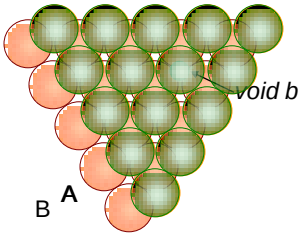


(a) (b)

- (111) planes of fcc have the same arrangement as (0001) plane of hcp crystal
- 3D structures are not identical: stacking has to be considered

FCC and HCP crystal structures





fcc

B plane placed in *a* voids of plane A

Next plane placed in *a* voids of plane B, making a new C plane

Stacking: ABCABC…

hcp

B plane placed in a voids of plane A

Next plane placed in *a* voids of plane B, making a new A plane

Stacking: ABAB…

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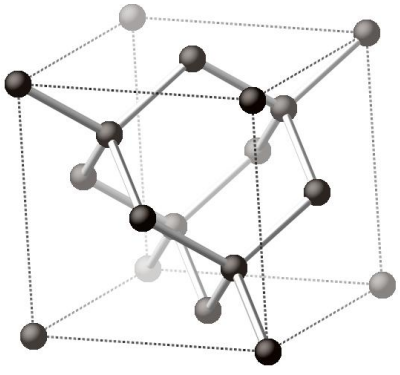
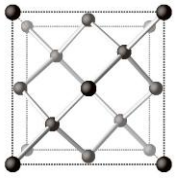
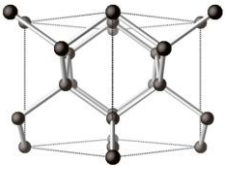
Diamond, Si and Ge surfaces



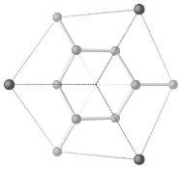
(100)



(110)



(111)



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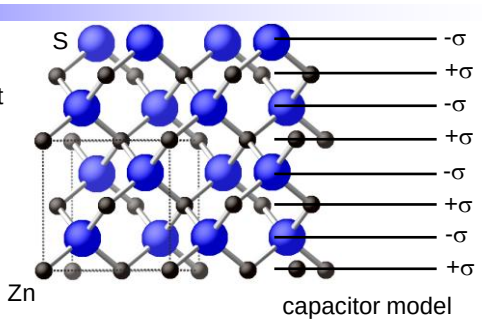
Beyond Metals: polar termination

Zincblend structure

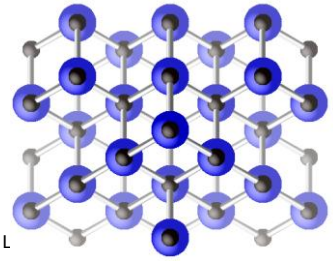
Note that polar terminations are not equivalent for (100) and (111)

ZnS (100)



capacitor model

ZnS (111)



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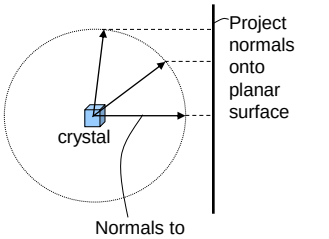
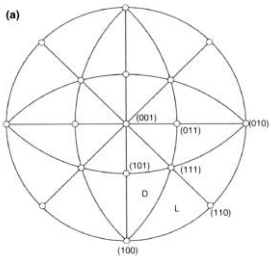
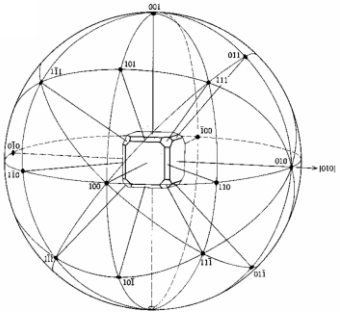
Stereographic Projections







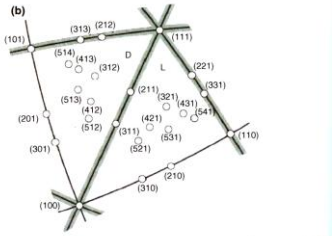


Figure 1.12 Stereogram projected on (001) showing the mirror zones relevant to primitive fcc, bcc and simple cubic crystal surfaces. Note that right-handed axes are used. The chiralities of two triangles are labelled D and L according to the symmetry-based convention of Pratt et al.[51] Reproduced from S.J. Pratt et al., Surf. Sci., 585, 1159. Copyright (2005), with permission from Elsevier.

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from K.Kolasinski

2.2 Relaxations and Reconstructions

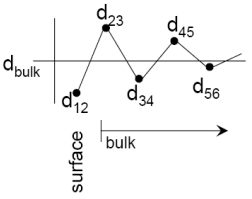
Often surface termination is <u>not</u> bulk-like

There are atom shifts ⊥ or ∥ to surface

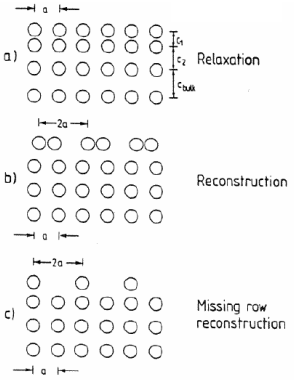
These surface region extends several atom layer deep

Rationale for metals: Smoluchowski smoothing of surface electron charge; dipole formation

Fig.3.7. Schematic representation of the formation of electronic surface dipoles at metal surfaces (a) by smearing out of the electronic charge distribution of the Wigner Seitz cells at the surface (*rectangles*), and (b) by smearing out of the electronic charge distribution at a step



Surface	d_{12}(%)
Ag(110)	-8
Al(110)	-10
Au(100)	0
Cu(110)	-10
Cu(310)	-5
Mo(100)	-12.5



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Reconstructions

Rationale for semiconductors: heal "dangling bonds

often lateral motion

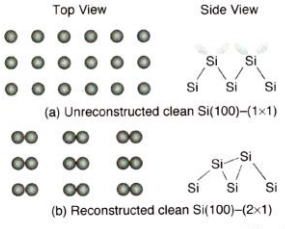

Figure 1.9 The Si(100)–(2×1) reconstruction: (a) unreconstructed clean Si(100)–(1×1); (b reconstructed clean Si(100)–(2×1).

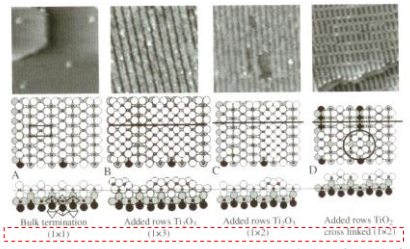

Figure 1.8 The surface structures observed on TiO_2(110) as a function of increasing bulk reduction of the crystal. Upper panels are scanning tunnelling microscope images with 20 nm scan size. The lower two panels display the proposed surface structures. Reproduced from M. Bowker, Curr. Opin. Solid State Mater. Sci. **10**, 153. Copyright (2006), with permission from Elsevier Science.

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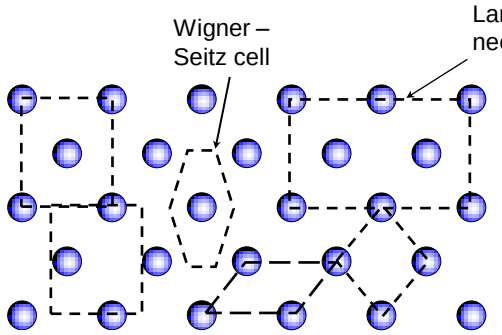
2.3 Classification of 2D periodic Structures

Unit cell: a convenient repeating unit of a crystal lattice; the axial lengths and axial angles are the lattice constants of the unit cell



Unit cell is not unique!

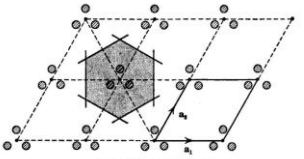


Fig. 3. Wigner–Seitz cell.

Wigner – Seitz Cell : place the symmetry centre in the centre of the cell; draw the perpendicular bisector planes of the translation vectors from the chosen centre to the nearest equivalent lattice site

2D Periodic Structures

Propagate lattice: n, m – integers $\vec{T} = n\vec{a}_1 + m\vec{a}_2$

Primitive unit cell: generally, smallest area, shortest lattice vectors, small number of atoms (if possible $|a_1|=|a_2|$, α=60º, 90º, 120º, 1 atom/per cell)

Symmetry:
- translational symmetry || to surface
- rotational symmetry 1(trivial), 2, 3, 4, 6
- mirror planes
- glide planes

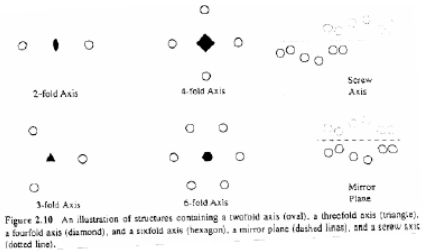
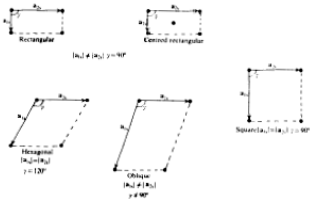


Figure 2.10 An illustration of structures containing a twofold axis (oval), a threefold axis (triangle), a fourfold axis (diamond), and a sixfold axis (hexagon), a mirror plane (dashed line), and a screw axis (dotted line).

All 2D structures w/1atom/unit cell have at least one two-fold axis

2.4 2D Substrate and Surface Structures

Considering all possibilities and redundancies for 2D periodic structures (e.g., 3-fold symmetry for γ=60°, 120°, we get only 5 symmetrically different Bravais nets with 1 atom per unit cell



When more than 1 atom/unit cell
more complicated:
- 5 Bravais lattices
- 10 2D point symmetry group (cf. Woodruff)
- 17 types of surface structures

Substrate and Overlayer Structures

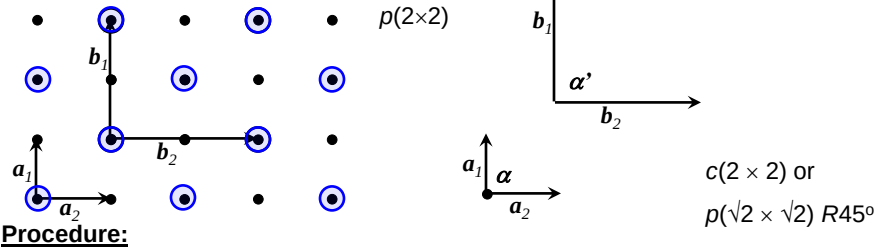
Suppose overlayer (or reconstructed surface layer) lattice different from substrate

$$\vec{T}_A = n\vec{a}_1 + m\vec{a}_2$$

$$\vec{T}_B = n\vec{b}_1 + m\vec{b}_2$$

2.5 Wood's notation

Simplest, most descriptive notation method (note: fails if $\alpha \neq \alpha'$ or b_i/a_i irrational)

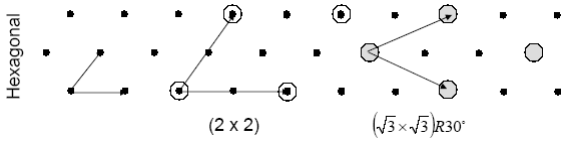


c(2 × 2) or
p(√2 × √2) *R*45°

Procedure:

- Determine relative magnitude of $\boldsymbol{a_1}$, $\boldsymbol{b_1}$, and $\boldsymbol{a_2}$, $\boldsymbol{b_2}$
- Identify angle of rotation (here ϕ = 0)

Notation: $\left(\frac{b_1}{a_1} \times \frac{b_2}{a_2}\right) R\phi$



2.6 Matrix Notation

Use matrix to transform substrate basis vectors, $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, into overlayer basis vectors, $\boldsymbol{b}_1$, $\boldsymbol{b}_2$

$$\vec{b}_1 = G_{11}\vec{a}_1 + G_{12}\vec{a}_2$$
$$\vec{b}_2 = G_{21}\vec{a}_1 + G_{22}\vec{a}_2$$

where: $\hat{G} = \begin{bmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{bmatrix}$ so that: $\begin{bmatrix} \vec{b}_1 \\ \vec{b}_2 \end{bmatrix} = \hat{G}\begin{bmatrix} \vec{a}_1 \\ \vec{a}_2 \end{bmatrix}$

For p(2 X 2) on cubic (100)

$$\vec{b}_1 = 2\vec{a}_1 + 0 \qquad \hat{G} = \begin{bmatrix} 2 & 0 \\ 0 & 2 \end{bmatrix}$$
$$\vec{b}_2 = 0 + 2\vec{a}_2$$

For p(2 X 2) on fcc(111)

$$\vec{b}_1 = 2\vec{a}_1 + 0 \qquad \hat{G} = \begin{bmatrix} 2 & 0 \\ 0 & 2 \end{bmatrix}$$
$$\vec{b}_2 = 0 + 2\vec{a}_2$$

For $\left(\sqrt{3}\times\sqrt{3}\right)R30^\circ$ on fcc(111)

$$\vec{b}_1 = \vec{a}_1 + \vec{a}_2 \qquad \hat{G} = \begin{bmatrix} 1 & 1 \\ -1 & 2 \end{bmatrix}$$
$$\vec{b}_2 = -\vec{a}_1 + 2\vec{a}_2$$

Areas: A = $|\boldsymbol{a}_1 \times \boldsymbol{a}_2|$; B = $|\boldsymbol{b}_1 \times \boldsymbol{b}_2|$; $\det \hat{G} = B/A$

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2.7 Comparison of Wood's and Matrix Notation

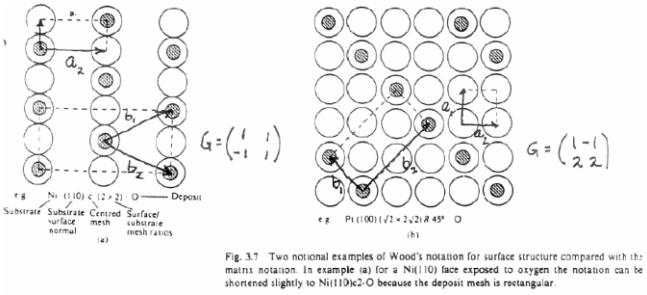
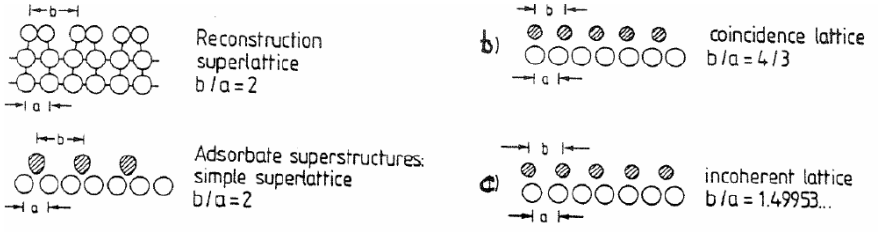


Fig. 3.7 Two notional examples of Wood's notation for surface structure compared with the matrix notation. In example (a) for a Ni(110) face exposed to oxygen the notation can be shortened slightly to Ni(110)c2-O because the deposit mesh is rectangular.

Classification of lattices:



Examples of Coincidence Lattice

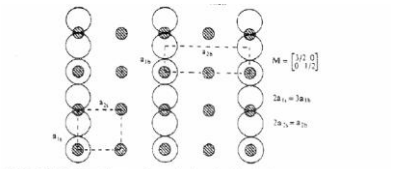
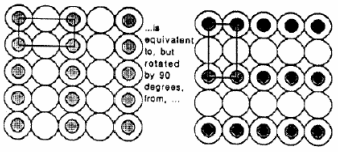


Fig. 3.6 Relationships between surface and bulk meshes. The simple and coincidence meshes are illustrated by the cases of deposit atoms (hatched circles) on the bulk exposed (110) plane of an f.c.c. material (open circles).

Note that symmetry does not identify adsorption sites, only how many there are

all (2 X 2)
θ = 1/4

Domain structures:
(1 X 2) = (2 X 1)



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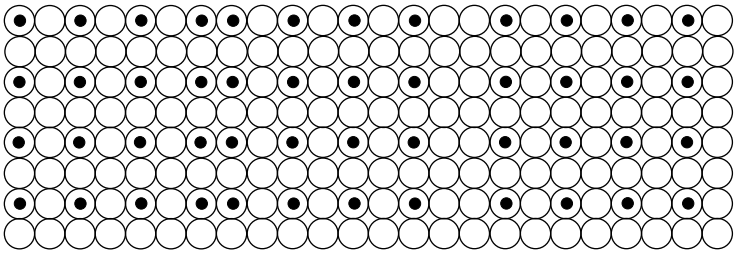
Domains and domain walls



heavy wall

light wall

Lecture 2

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Consider that in the pictures you are looking down at a surface. The larger circles represent the substrate atom positions and dark dots represent the overlayer atom positions. Overlayer unit cells are shown. For each structure:

(1) Draw the substrate unit cell and vectors, and the primitive overlayer unit cell and unit cell vectors.

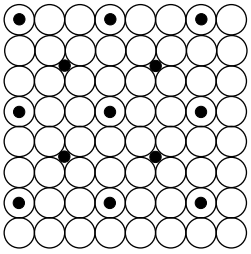
(2) Calculate the ideal coverage (in monolayers) of the overlayer.

(3) If the primitive overlayer surface unit cell can be named with Wood's notation, do so. If it cannot, try to identify a nonprimitive cell which can be so named.

(4) Give the matrix notation for the primitive overlayer unit cell.

(5) Classify the surface overlayer as simple, coincident or incoherent.

(a)



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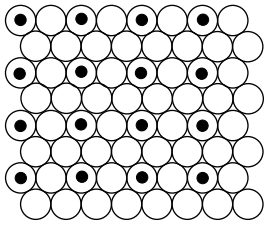
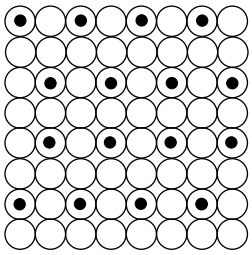
(b)



Lecture 2 30

Try (c) and (d) at home

(c)



(d)