Surface and Interface Science
Physics 627; Chemistry 541

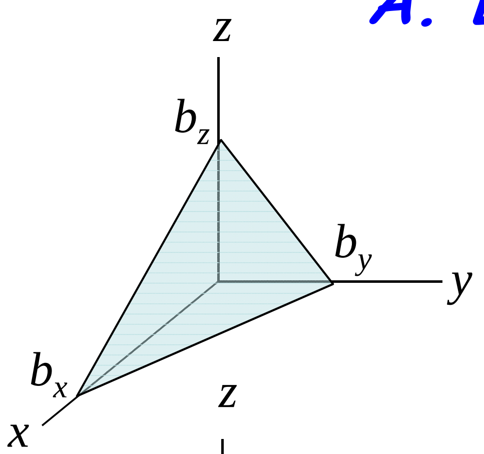
Lectures 3
Sept 9 2010

Surface Structure

References:

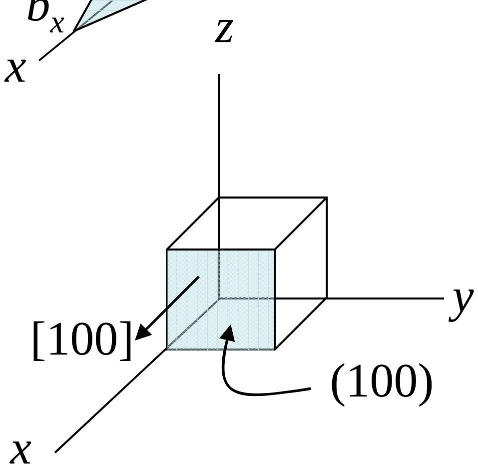
1) Zangwill, Pp. 28 - 32
2) Woodruff & Delchar, Chapter 2
3) Masel, Chapter 2
4) Ertl & Kuppers, 201-207
5) Luth, 78 – 94
6) Attard and Barnes, 17 - 22

A. Bulk truncation structures



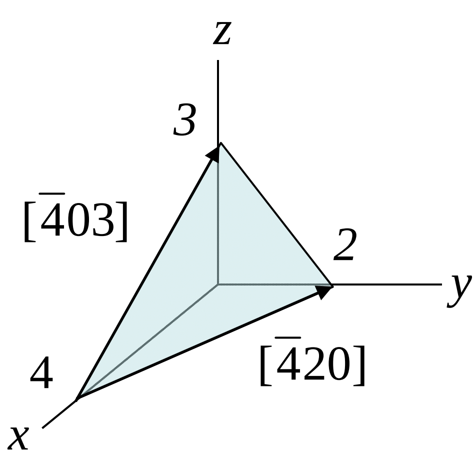
Miller Indices (again)

- For plane with intersections b_x, b_y, b_z write: $\left(\frac{1}{b_x}, \frac{1}{b_y}, \frac{1}{b_z}\right)$
- If all quotients rational or 0, this is Miller Index.
  - e.g., 1, 1, 0.5 → (112)
  - For cubic 1 ∞ ∞ → (100)



In general: (i j k) = $\left(\frac{cd}{b_x}, \frac{cd}{b_y}, \frac{cd}{b_z}\right)$

where cd = common denominator

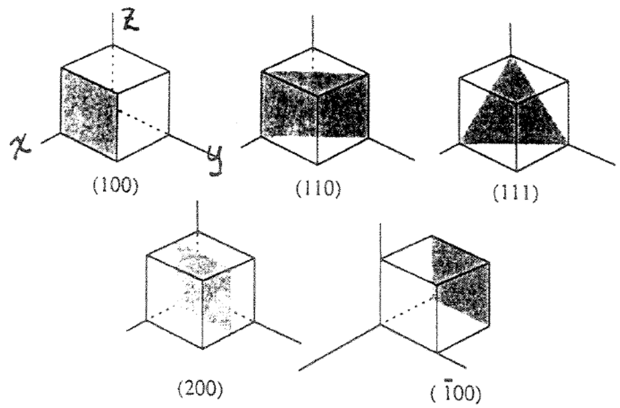


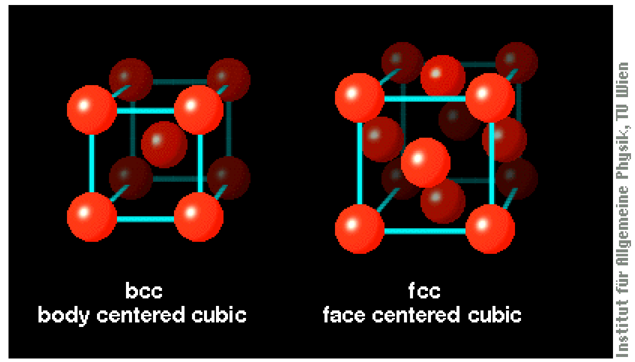
Here (i j k) = $\left(\frac{12}{4}, \frac{12}{2}, \frac{12}{3}\right) = (364)$

In fcc and bcc
x, y, z, -x, -y, -z all equivalent → (100), (010), $(\bar{1}00)$, etc. all equivalent.

NOTE: (i j k) identifies plane; [i,jk] identifies vector ⊥ plane defines direction.

A. Bulk truncation structures





Very different surfaces:
Close packed: fcc(111) bcc(110)
Very rough: fcc(210) bcc(111)

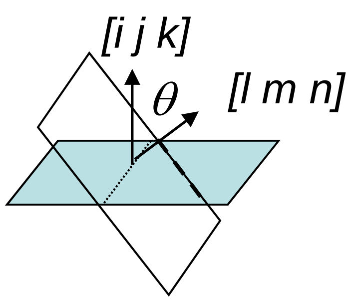
bcc: 8 n.n. fcc: 12 n.n.

Note: Cross product of two vectors iin a plane defines direction perp. To plane:

[i j k] = [l m n] x [p q r] where latter vectors lie in (i j k).

Angle between two planes:

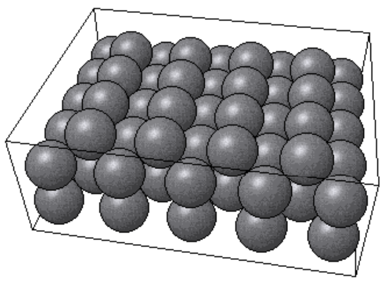
$$\cos\theta = \frac{[ijk]\cdot[lmn]}{\sqrt{i^2+j^2+k^2}\sqrt{l^2+m^2+n^2}}$$



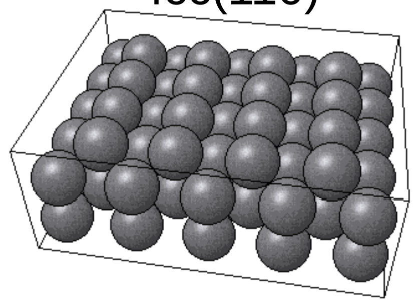
e.g., for [1 1 1] and [2 1 1] : $\cos\theta = \frac{2+1+1}{\sqrt{3}\sqrt{6}} \Rightarrow \theta = 19.47^\circ$

A. Bulk truncation structures

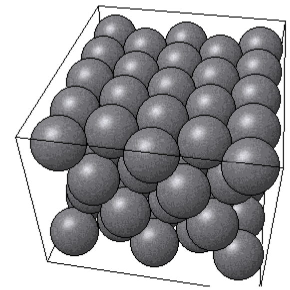
fcc(100)



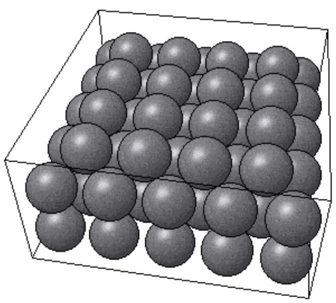
fcc(110)



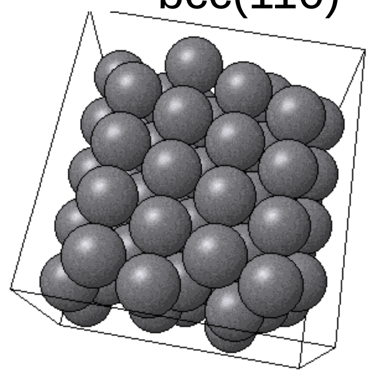
fcc(111)



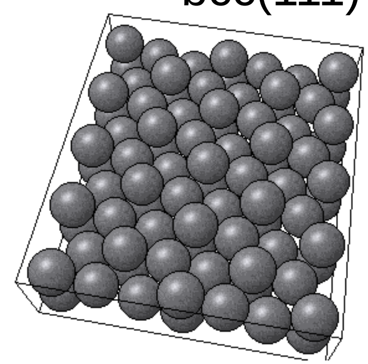
bcc(100)



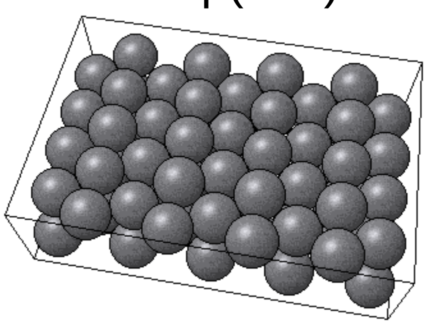
bcc(110)



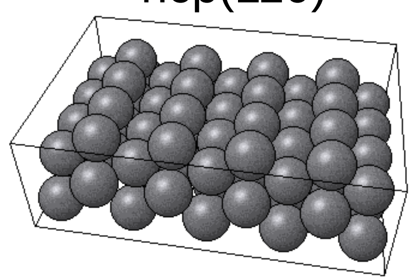
bcc(111)



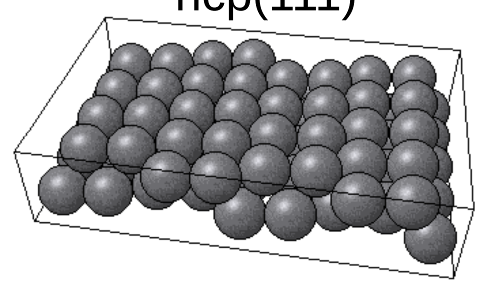
hcp(100)



hcp(110)



hcp(111)



A. Bulk truncation structures

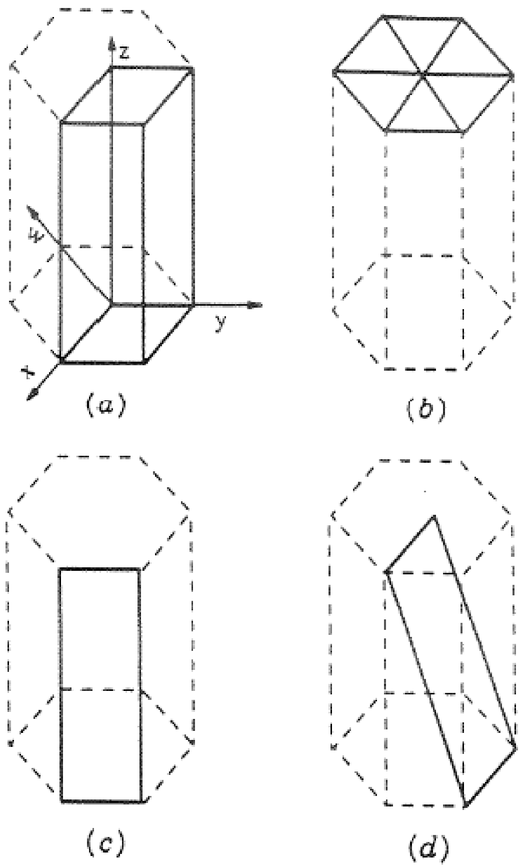
$$\left(ijkl\right)=\left(\frac{cd}{b_x}\frac{cd}{b_y}\frac{cd}{b_w}\frac{cd}{b_z}\right)$$

But $i + j = -l$
So often use 3-digit notation

Basal plane (b): (0 0 0 1) = (0 0 1)

Side (c)

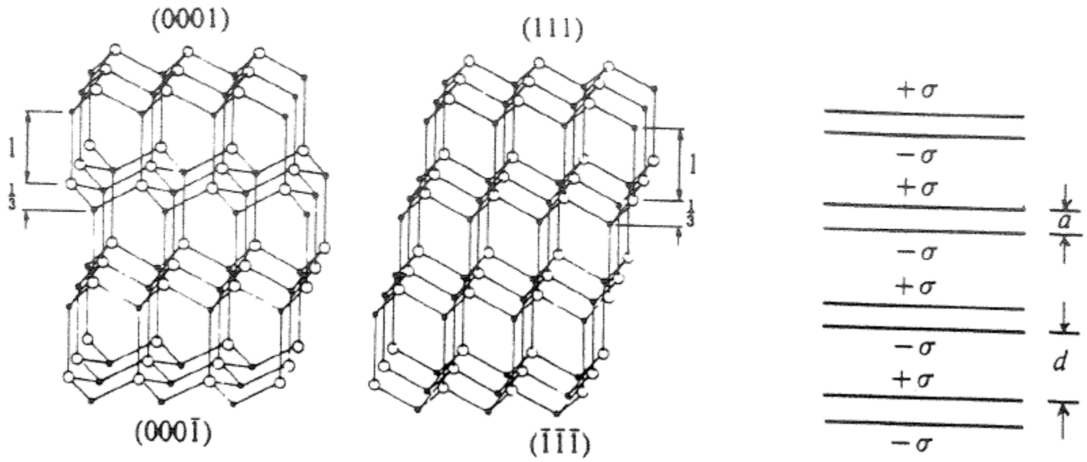
$$\left(\frac{1}{1}\frac{1}{\infty}\frac{1}{-1}\frac{1}{\infty}\right)=\left(10\bar{1}0\right)$$



In hcp, (1 0 0) ≠ (0 0 1)
NOTE: fcc(111) and hcp (0001) have same top layer structure, but stacking is different: hcp: *ABAB*…; fcc: *ABCABC*…

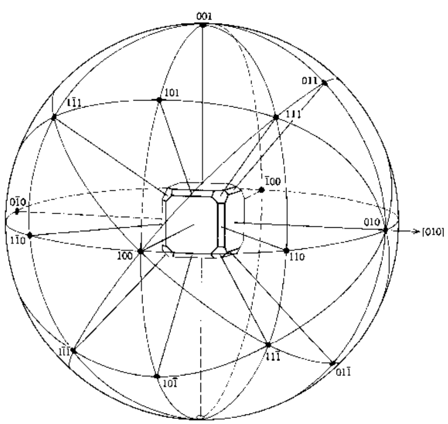
A. Bulk truncation structures

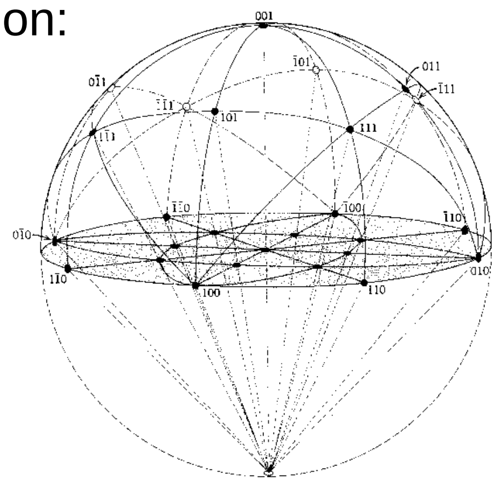
Other structures:

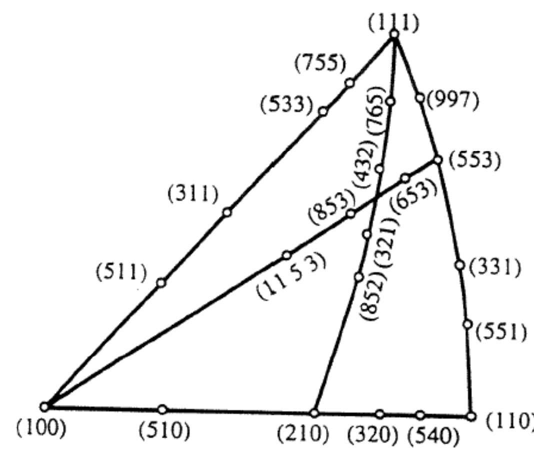


Wurtzite (interpenetrating fcc lattice), Zincblend (hex w/tetrahedral bonds)
NOTE: polar terminations not equivalent
Diamond (or Si): Like zincblend, but all atoms the same

Stereographic projection:

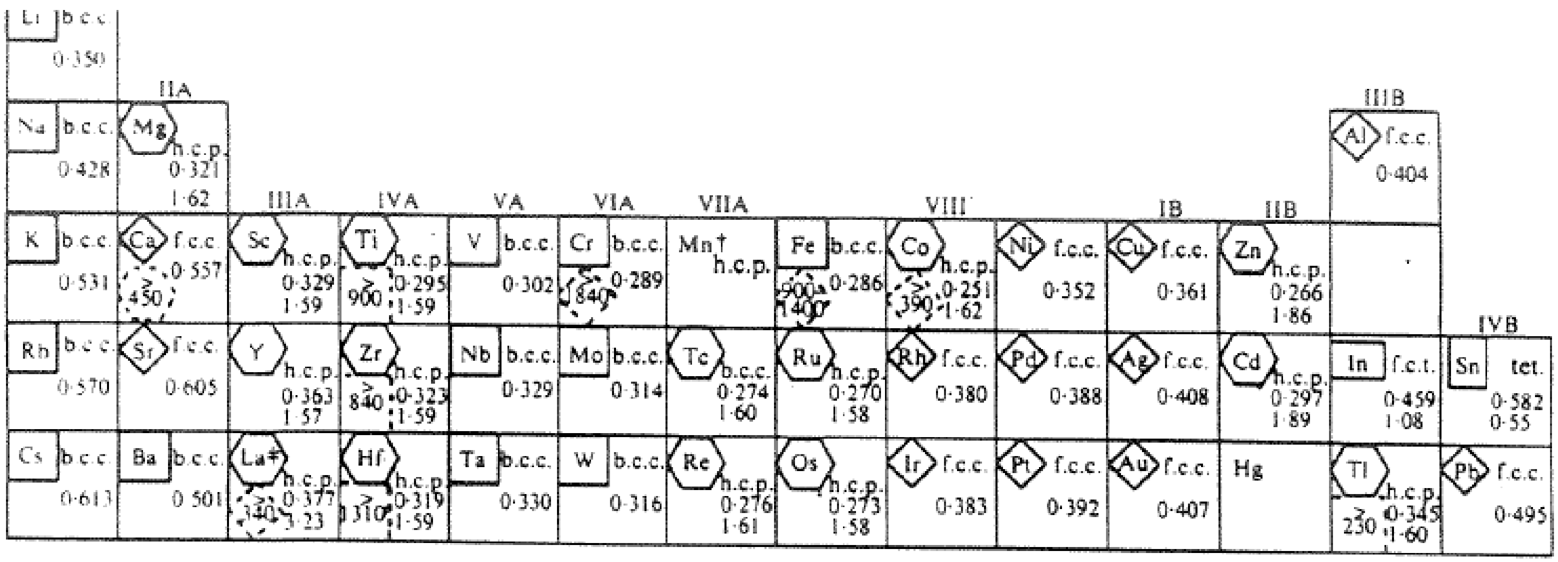






Surface atom density: ~ 10^{15}

A. Bulk truncation structures



□ body-centred cubic (b.c.c.); ◇ face-centred cubic (f.c.c.); ⬡ hexagonal close-packed (h.c.p.); ▯ tetragonal (tet); ▭ face-centred tetragonal (f.c.t.). Solid-line symbols represent the forms stable at room temperature. Other forms are indicated by broken-line symbols, with the temperature range of their stability shown in degrees Celsius.

Values of the unit cell parameter a (nm) and of the axial ratio c/a (where appropriate) are given in each case.

† Two complicated structures, α and β, with 58 and 20 atoms per unit cell respectively, both cubic.

‡ Structure possesses a doubled axial ratio; stacking sequence ABACABAC....

(Data taken from Smithells 1976 and Hume-Rothery 1966).

B. Relaxations and reconstructions

Crystal termination often not bulk-like

Shifts in atomic positions may be perp and/or parallel to surface

Selvedge region extends several atomic layers deep

Rationale for metals: Smoluchowski smoothing of surface electronic charge

dipole formation

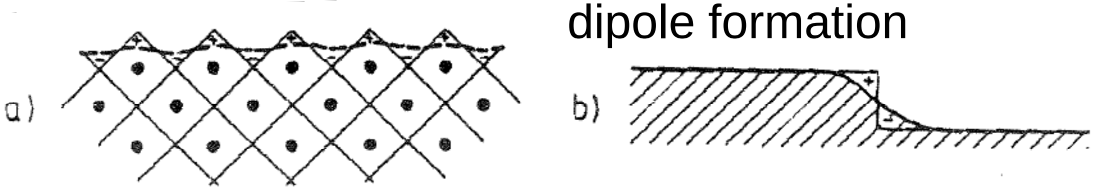
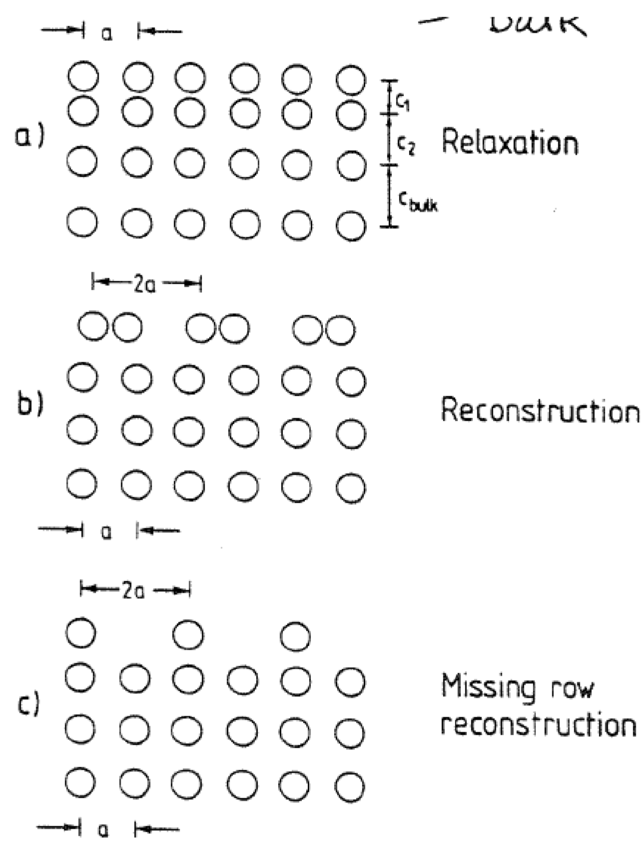
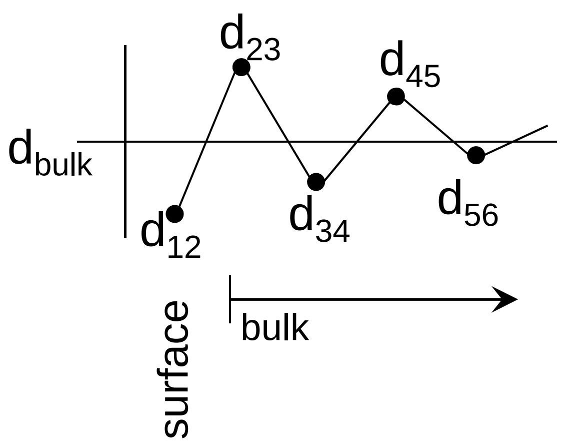


Fig.3.7. Schematic representation of the formation of electronic surface dipoles at metal surfaces (a) by smearing out of the electronic charge distribution of the Wigner Seitz cells at the surface (*rectangles*), and (b) by smearing out of the electronic charge distribution at a step

Inward relaxation;
little or no lateral motion



For semiconductors: heal “dangling bonds;
often lateral motion. Relax. Often oscillatory



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

C. Classification of 2-D periodic structures

Periodic Lattice: repeat unit is unit cell

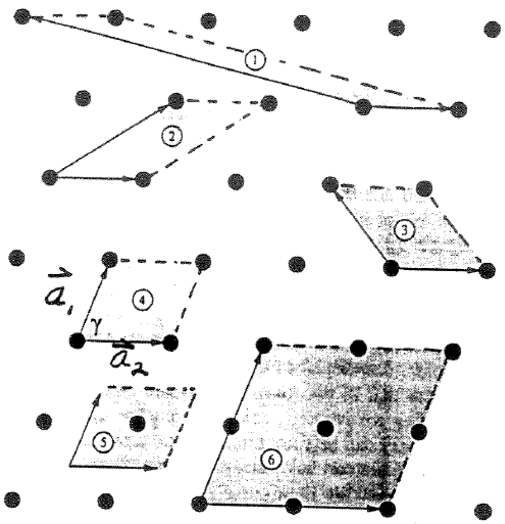


Figure 2.8 A picture of several different possible choices of unit cells (shaded) and lattice vectors (arrows) for a two-dimensional lattice.

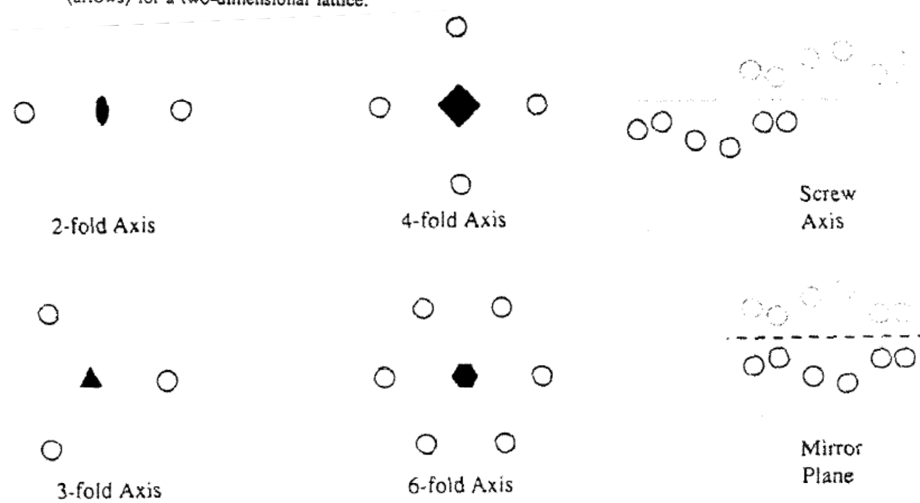


Figure 2.10 An illustration of structures containing a twofold axis (oval), a threefold axis (triangle), a fourfold axis (diamond), and a sixfold axis (hexagon), a mirror plane (dashed lines), and a screw axis (dotted line).

Unit cell is not unique.

Propagate lattice: n, m constants

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

Primitive cell: unit cell w/smallest area, shortest lattice vectors, smallest number of atoms

(if possible: $|a_1| = |a_2|$; γ = 60, 90, 120; 1 atom)

Symmetry:

translational symmetry // surface;

rotational symmetry: 1, 2, 3, 4, 6

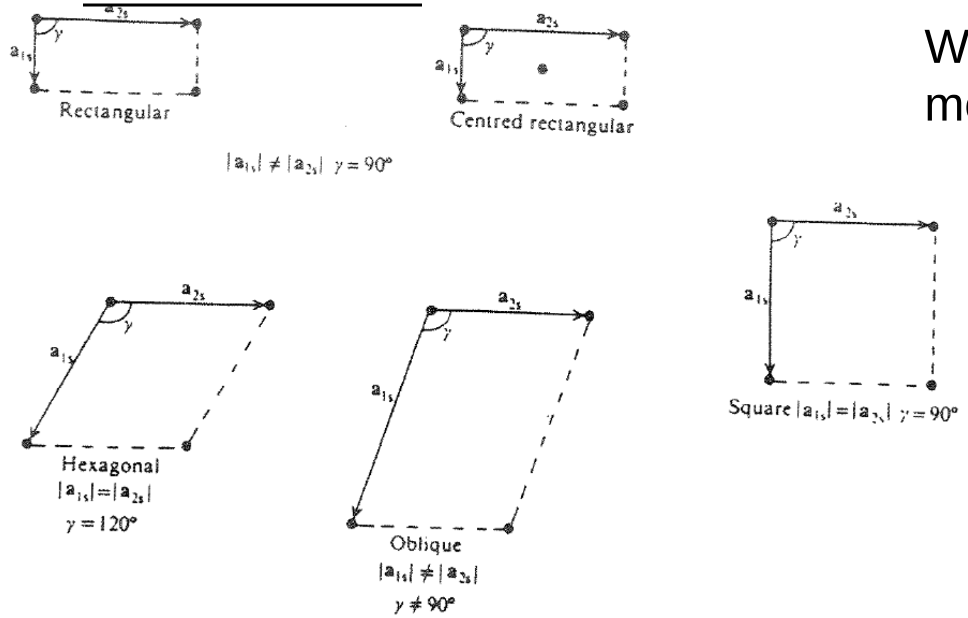
mirror planes; glide planes.

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

C. Classification of 2-D periodic structures

For 1 atom/cell and 2-D periodic structure, only 5 symmetrically different lattices

<u>*Bravais Lattices*</u>



When more than 1 atom/cell, more complicated

5 Bravais lattices
10 2-D point symmetry groups
17 types of surface structure

D. Substrate and Surface Structures

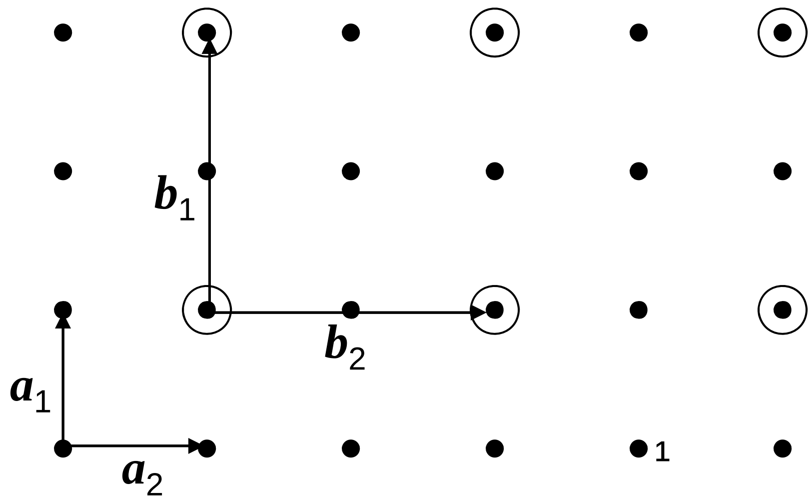
Suppose overlayer of substrate surface layer has lattice different from bulk:

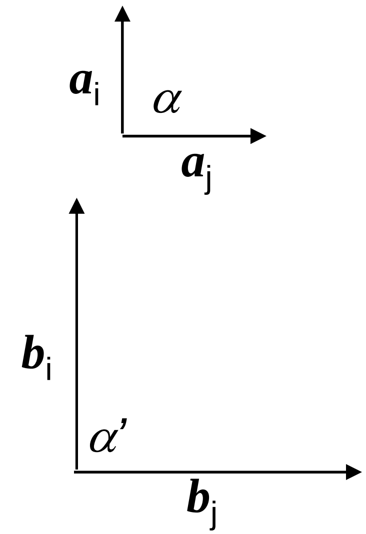
Substrate: $\vec{T}_a = n\vec{a}_1 + m\vec{a}_2$

Overlayer: $\vec{T}_b = n\vec{b}_1 + m\vec{b}_2$

D. Substrate and Surface Structures

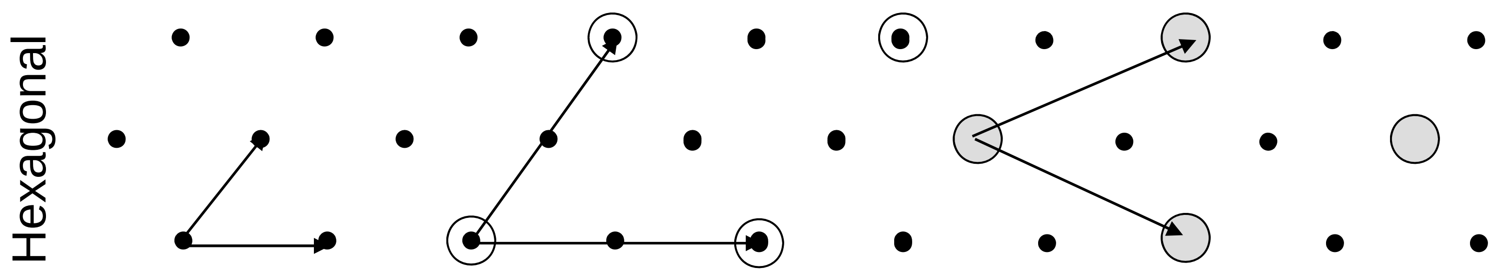
Wood's Notation: Simplest, most descriptive notation method
(NOTE: fails if $\alpha \neq \alpha'$ or b_i/a_i irrational)





Determine relative magnitude of respective ***a***'s and ***b***'s.
Identify angle of rotation (= 0 here).

Notation: $\left(\frac{b_1}{a_1} \times \frac{b_2}{a_2}\right) R\phi^\circ$ for above overlayer, (2 x 2) [often called p(2 x 2)]



(2 x 2) $\left(\sqrt{3} \times \sqrt{3}\right) R30^\circ$

D. Substrate and Surface Structures

Matrix Notation: Use mtx 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)

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

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

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

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

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

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

D. Substrate and Surface Structures

Comparison of Wood's and Matrix Notation

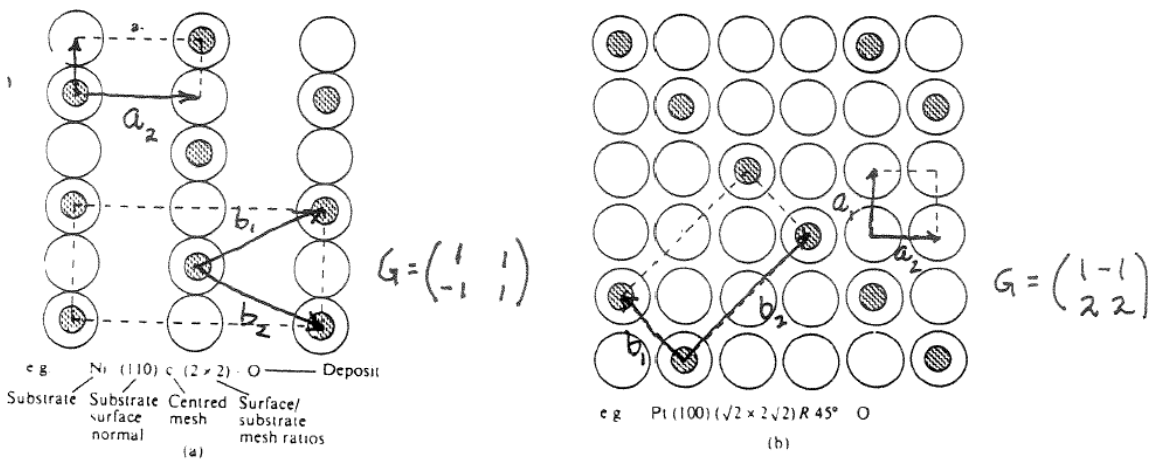
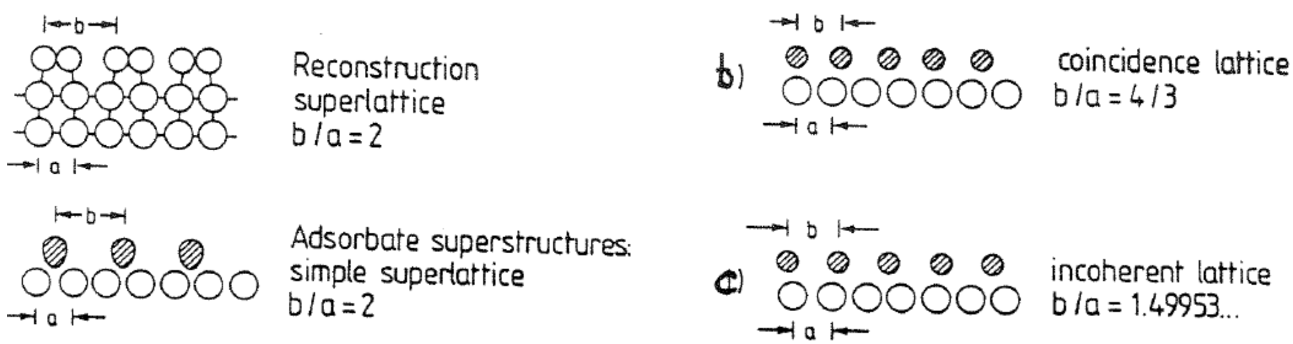


Fig. 3.7 Two notional examples of Wood's notation for surface structure compared with the matrix notation. In example (a) for a Ni(110) face exposed to oxygen the notation can be shortened slightly to Ni(110)c2-O because the deposit mesh is rectangular.

Classification of Lattices



(a) Simple: All G_{ij} are integers → all sites identical in overlayer (strong corrugation). Here b = 2a
(b) Coincidence: one or more of G_{ij} are rational numbers → different types of sites
(c) Incoherent: one or more of G_{ij} are irrational → inf. Number of ads sites, flat surface pot'l.

D. Substrate and Surface Structures

Examples of coincidence lattice

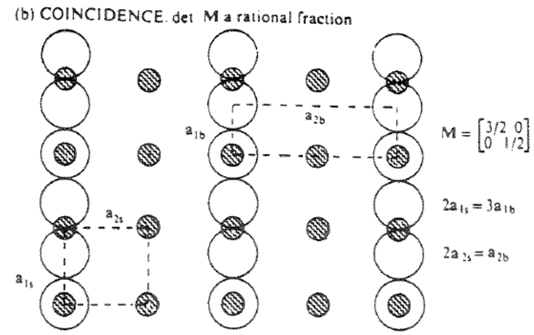
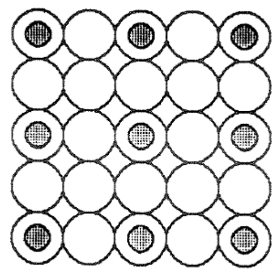
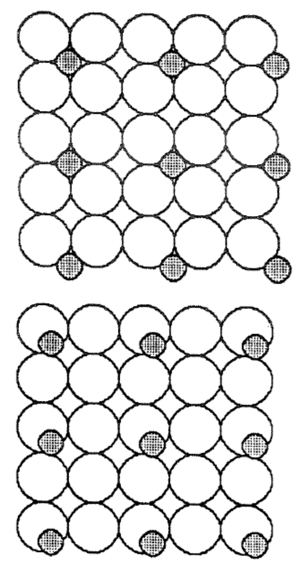


Fig. 3.6 Relationships between surface and bulk meshes. The simple and coincidence meshes are illustrated by the cases of deposit atoms (hatched circles) on the bulk exposed (110) plane of an f.c.c. material (open circles).

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

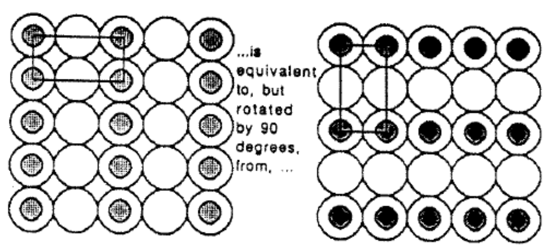


or



all (2 X 2)
θ = 1/4

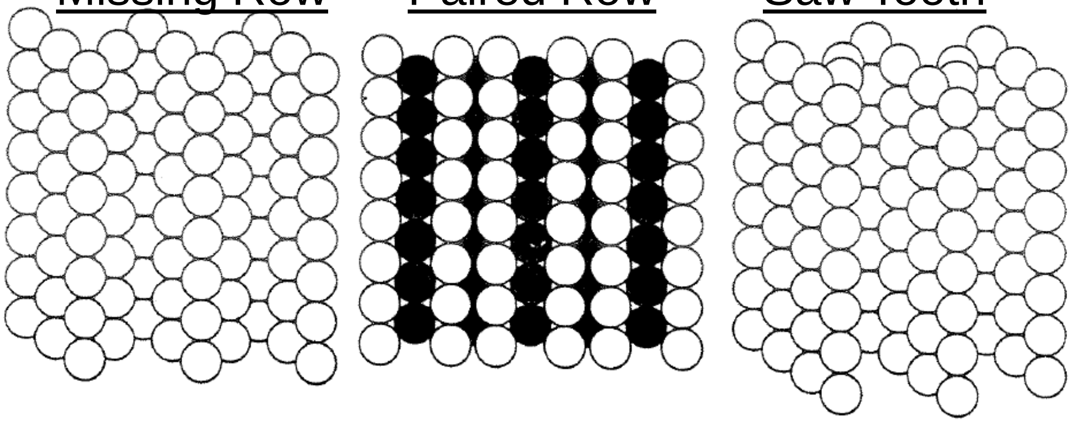
Domain structures:
(1 X 2) = (2 X 1)



D. Substrate and Surface Structures

Ambiguity: fcc(110) reconstruction models for (2 X 1) periodicity

Missing Row   Paired Row   Saw Tooth



Another complication:

indexing of stepped surfaces

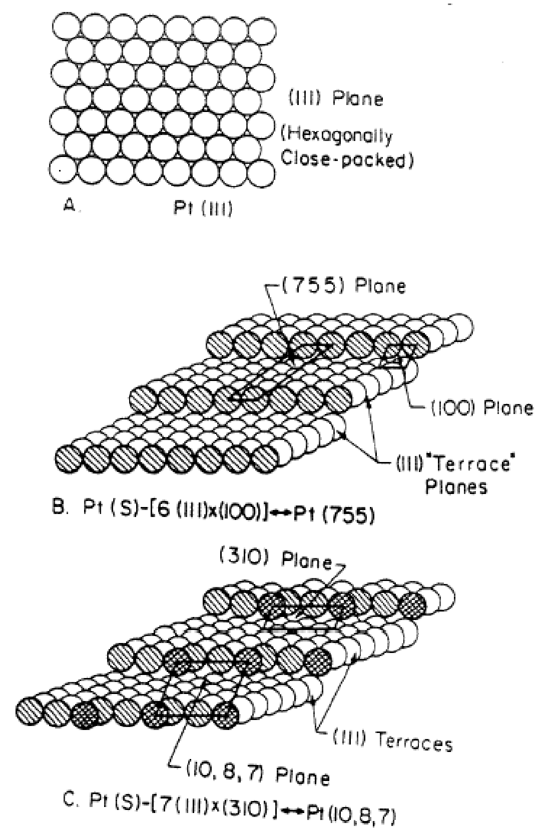


Figure 2.10. Surface structures in real space and LEED diffraction patterns of the flat Pt(111), stepped Pt(755), and kinked Pt(10,8,7) crystal faces.