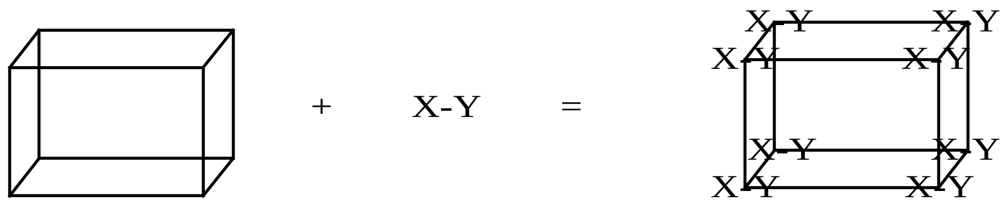
2.1. The Structure of Solids and Surfaces

2.1.1. Bulk Crystallography

A crystal structure is made up of two basic elements:



Lattice + Basis = Crystal Structure

A. Basis

simplest chemical unit present at *every* lattice point

1 atom - Na, noble gas

2 atoms - Si, NaCl

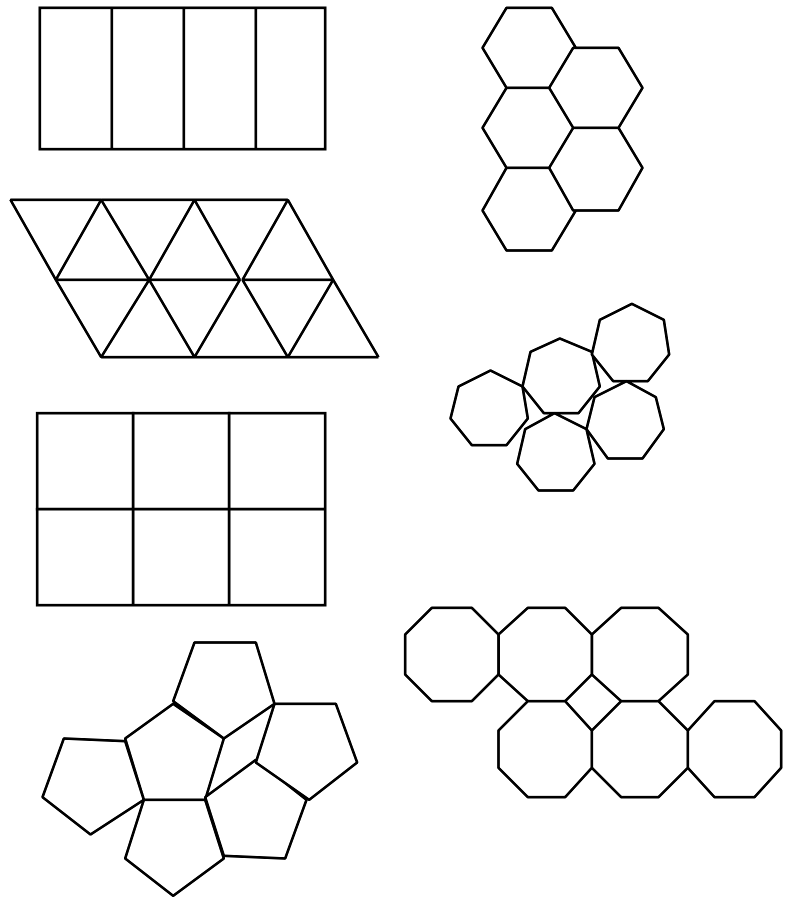
4 atoms - Ga

29 atoms - α-Mn

B. Lattice

Translatable, repeating 2-D shape that completely fills space

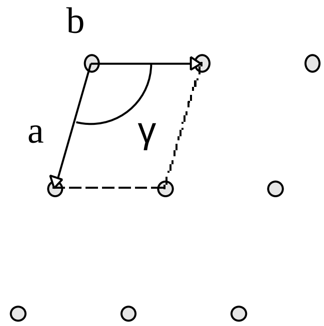
2.1.2. Two-dimensional Lattices (Plane Lattices)



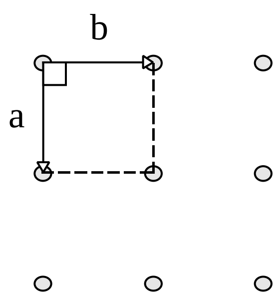
Note: In 2-D only lattices with 2, 3, 4 and 6-fold rotational symmetry possible

In fact, there are an infinite number of plane lattices based on one general shape (oblique lattice)

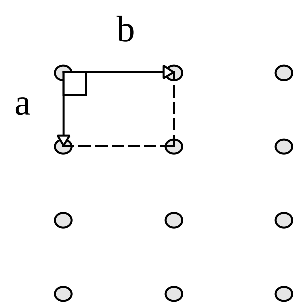
We recogonize four special lattices for total 5 2-D lattices



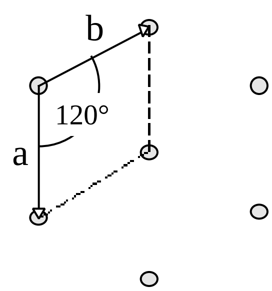
Oblique



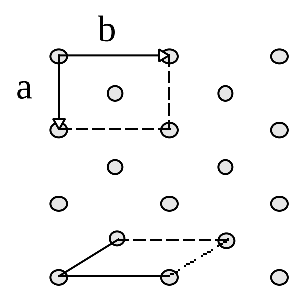
Square



Rectangular



Hexagonal



Centered Rectangular

Note: a and b are called translation or unit cell vectors

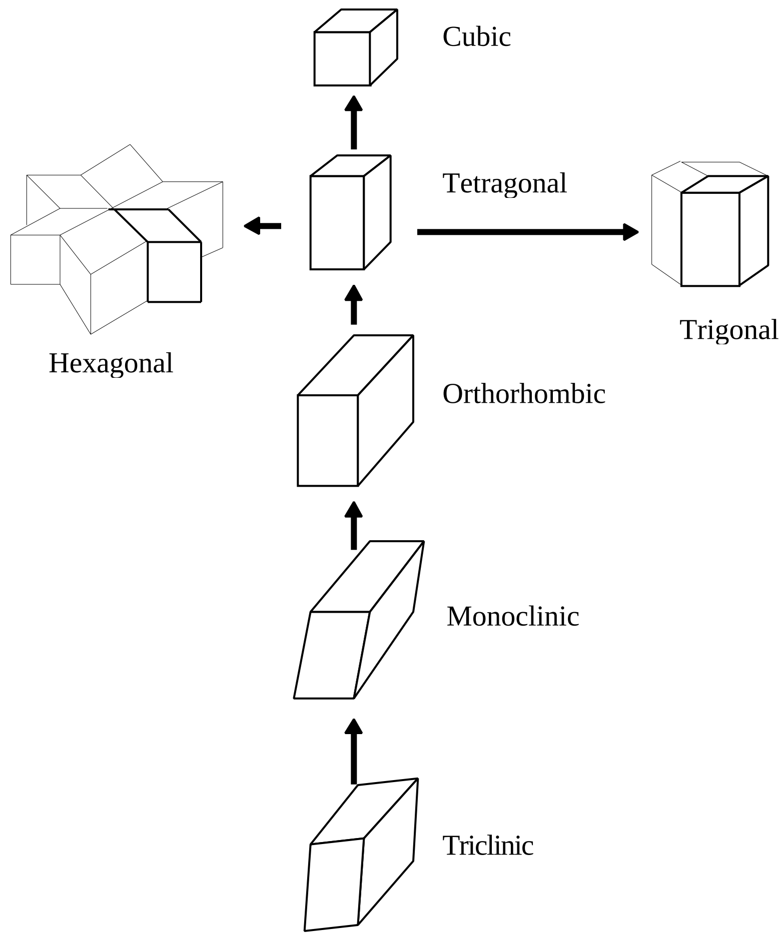
Lattice	Conventional Unit Cell	Axes of conventional unit cell	Point group symmetry of lattice about lattice point
Oblique	Parallelogram	$a \neq b \quad \alpha \neq 90°$	2
Square	Square	$a = b \quad \alpha = 90°$	4mm
Hexagonal	60° rhombus	$a = b \quad \alpha = 120°$	6mm
Primitive rectangular	Rectangle	$a \neq b \quad \alpha = 90°$	2mm
Centered rectangular	Rectangle	$a \neq b \quad \alpha = 90°$	2mm

2.1.3. Three-dimensional Lattices (Unit Cells)

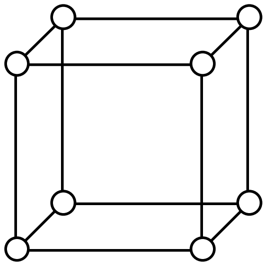
As before:

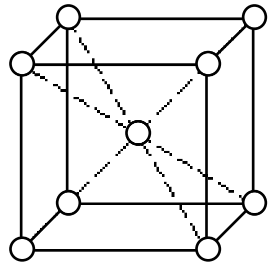
- infinite number of cells based on one general shape (triclinic)
- six special cells

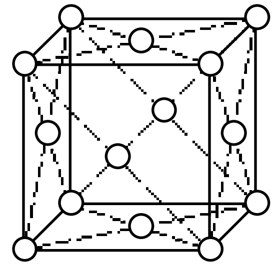
7 Crystal Systems

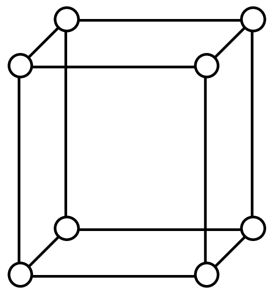


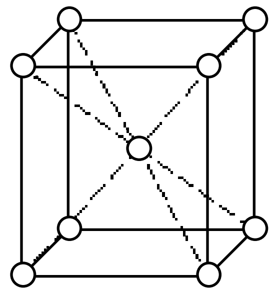
For convenience, these are further divided into 14 Bravais lattices

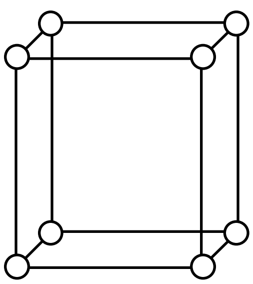

Cubic P (SC)

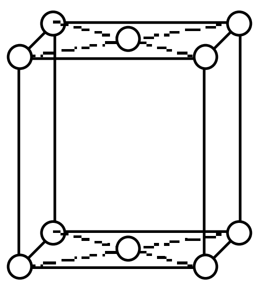

Cubic I (BCC)

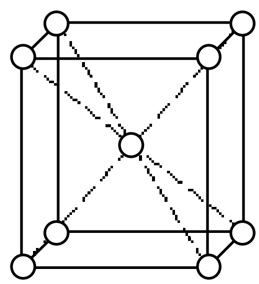

Cubic F (FCC)

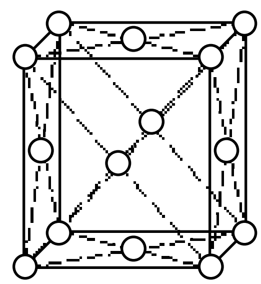

Tetragonal P

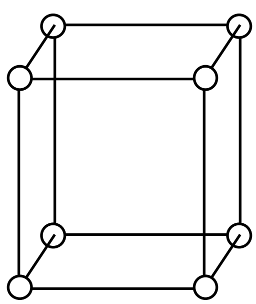

Tetragonal I

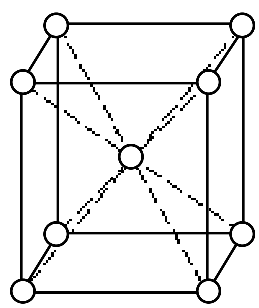

Orthorhombic P

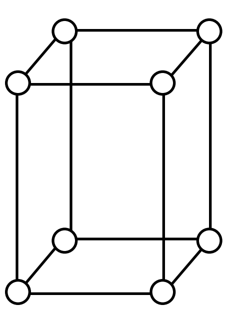

Orthorhombic C

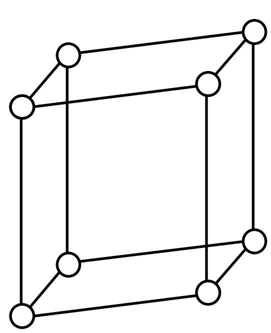

Orthorhombic I

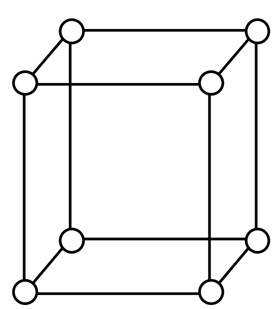

Orthorhombic F


Monoclinic P


Monoclinic I


Triclinic


Trigonal R

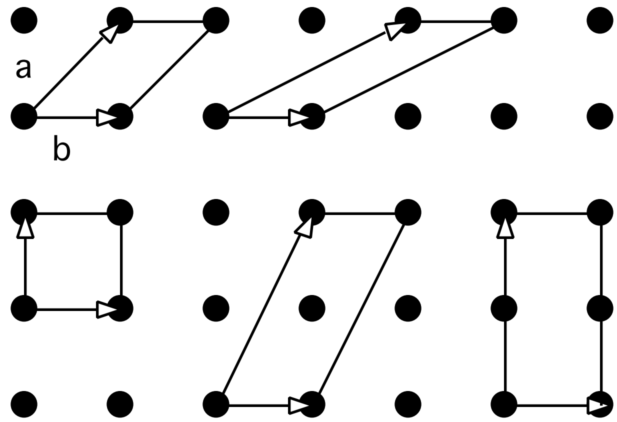

Trigonal and Hexagonal P (HCP

System	Angles and Dimensions	Lattices in System
Triclinic	a≠b≠c, α≠β≠γ	P (primitive)
Monoclinic	a≠b≠c, α=γ=90°≠β	P (primitive) I (body centered)
Orthorhombic	a≠b≠c, α=β=γ=90°	P (primitive) C (base centered) I (body centered) F (face centered)
Tetragonal	a=b≠c, α=β=γ=90°	P (primitive) I (body centered)
Cubic	a=b=c, α=β=γ=90°	P (primitive) I (body centered) F (face centered)
Trigonal	a=b=c, 120°>α=β=γ≠90°	R (rhombohedral primitive)
Hexagonal	a=b≠c, α=β=90°, γ=120°	R (rhombohedral primitive)

2.1.4. Primitive Lattices

A primitive lattice contains minimum number of lattice points (usually one) to satisfy translation operator

- often several choices
- *conventional* versus *primitive* lattice

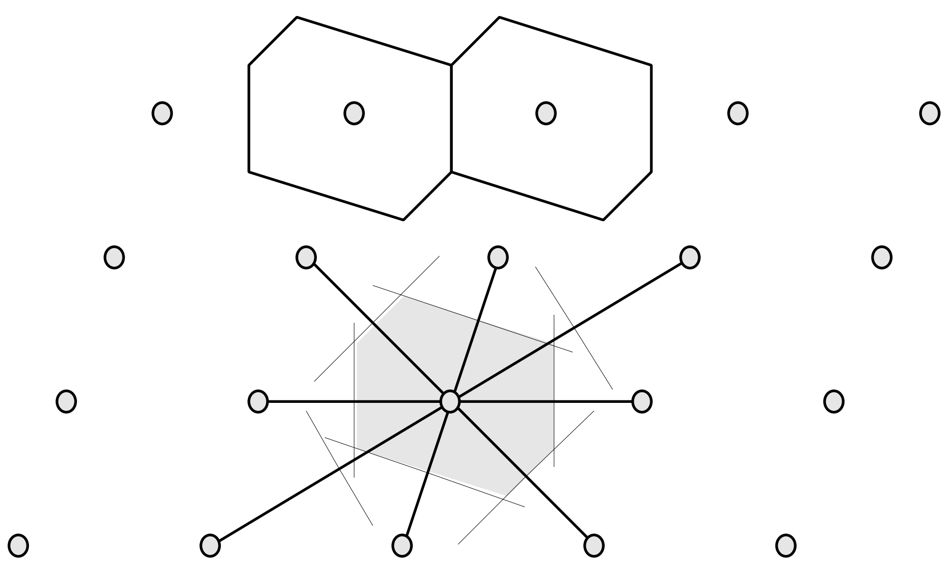


2.1.5. Wigner-Seitz Method for Finding Primitive Cell

Connect one lattice point to nearest neighbors

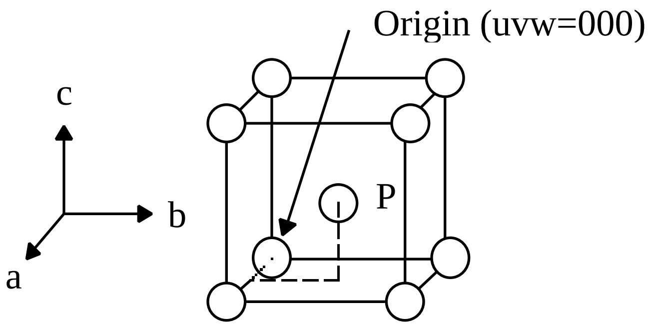
Bisect connecting lines and draw a line perpendicular to connecting line

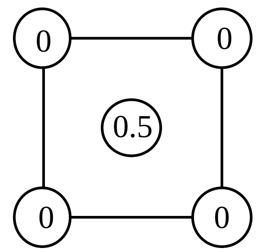
Area enclosed by all perpendicular lines will be a primitive unit cell



2.2. Specifying Points, Directions and Planes

2.2.1. Defining a Point in a Unit Cell





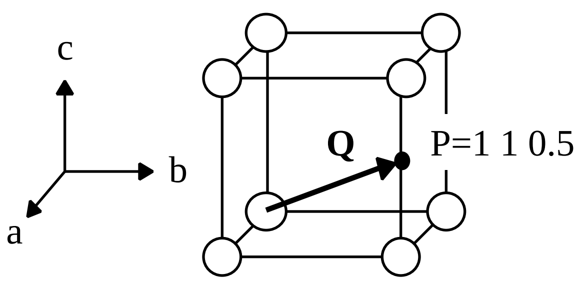
P=u·**a**+v·**b**+w·**c**
P=0.5 0.5 0.5

Note: Right hand axes!

P(uvw) = 0.5 0.5 0.5 or 1/2 1/2 1/2

A BCC lattice can be described as a single atom basis at 0 0 0 or a simple cubic lattice with a two atom basis at 0 0 0 and 0.5 0.5 0.5

2.2.2. Defining a Direction in a Unit Cell



P=u'·**a**+v'·**b**+w'·**c**

Q=$\overrightarrow{OP}$=[u':v':w']
Q=[1:1:0.5]=[221]

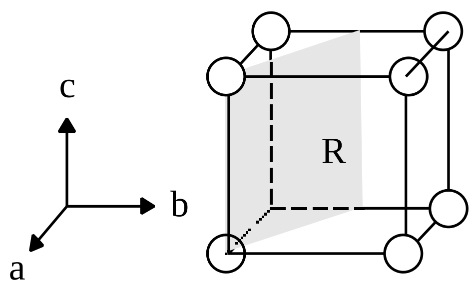
Parallel directions <221>

Q = [221]

[square brackets] denote single direction

<pointed bracket> denote a set of parallel directions

2.2.3. Defining a Plane in a Unit Cell - Miller Indices



R=u"·**a**+v"·**b**+w"·**c**

u"=1 v"=0.5 w"=0

Miller Indices (h:k:l)=(1/u" 1/v" 1/w")
h=1/1=1
k=1/0.5=2
l=1/∞=0

R=(hkl)=(120)

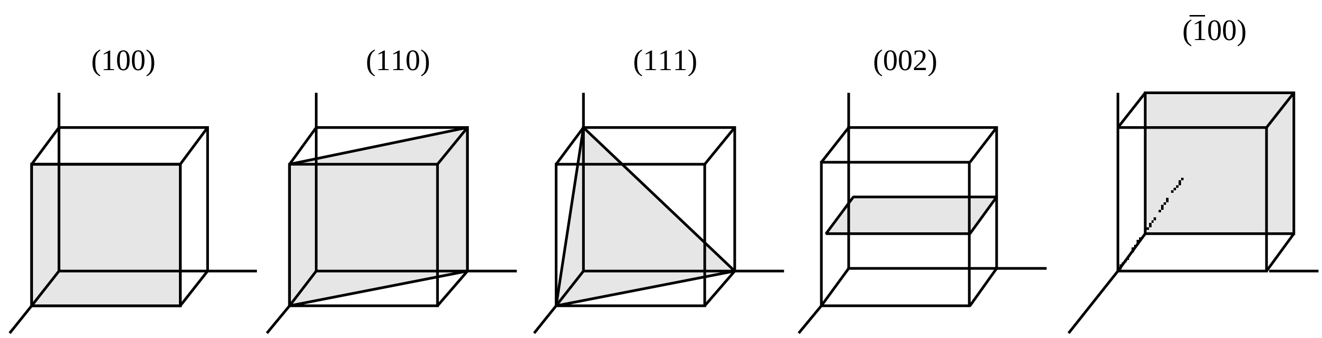
Parallel directions {120}

R=(120)

(regular brakets) one plane

{curly brackets} set of parallel planes

2.2.4. Common Planes (Cubic System)

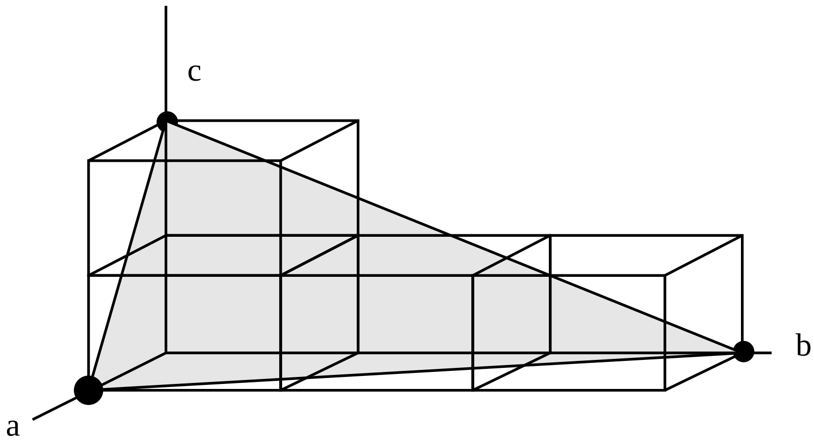


Note: (100), ($\bar{1}$00) , (200), (300) are parallel

(111), (222), (333) are parallel

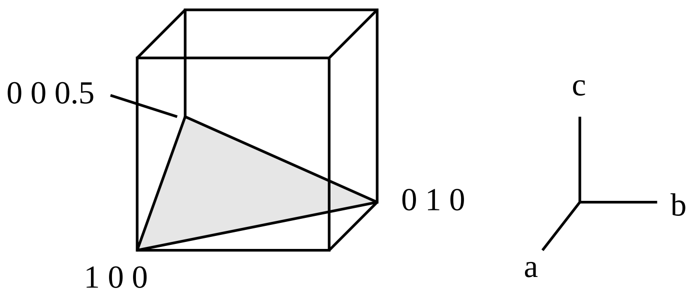
(100), (010), (001) are orthogonal and in some crystal systems *may* be identical

Note: h, k and l are always integers

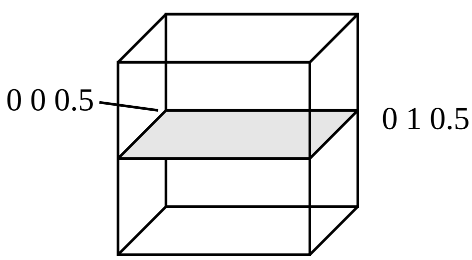


u'' = 1, v'' = 3, w'' = 2
h = 1/1 = 1
k = 1/3
l = 1/2
(1 1/3 1/2) ?

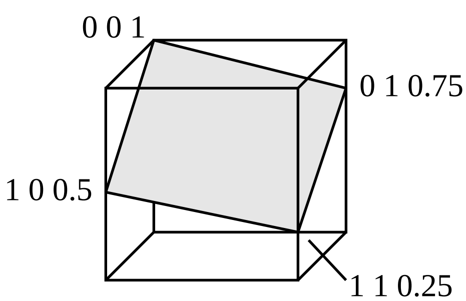
Multiply by 6
(623)



h=1/1
k=1/1
l=1/0.5=2
(hkl)=(112)
A parallel plane would be (224)

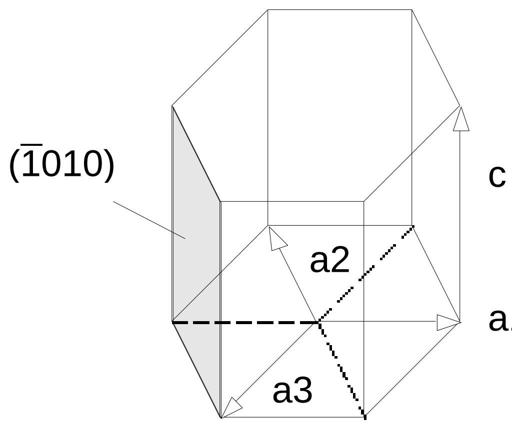


h=1/inf=0
k=1/inf=0
l=1/0.5=2
(hkl)=(002)
A parallel plane would be (001)



h=1/2=0.5
k=1/4=0.25
l=1/1=1
(hkl)=(0.5 0.25 1)=(214)
A parallel plane would be (428)

Note: Hexagonal and trigonal lattices use four Miller indices by convention (really only need three)



The angle between any two planes or two directions can be calculated (by geometry) as

$$\cos\varphi = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\left(h_1^2 + k_1^2 + l_1^2\right)^{0.5}\left(h_2^2 + k_2^2 + l_2^2\right)^{0.5}}$$

Note: In cubic systems *only*, the [hkl] direction is perpendicular to the (hkl) plane.

2.3. Perfect Surfaces

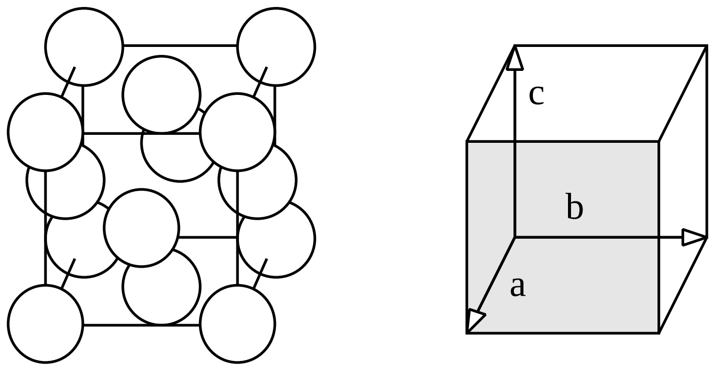
2.3.1. Bulk Termination

Question: What is the theoretical atomic arrangement of the resulting surface when a known crystal structure is sliced along a low index plane?

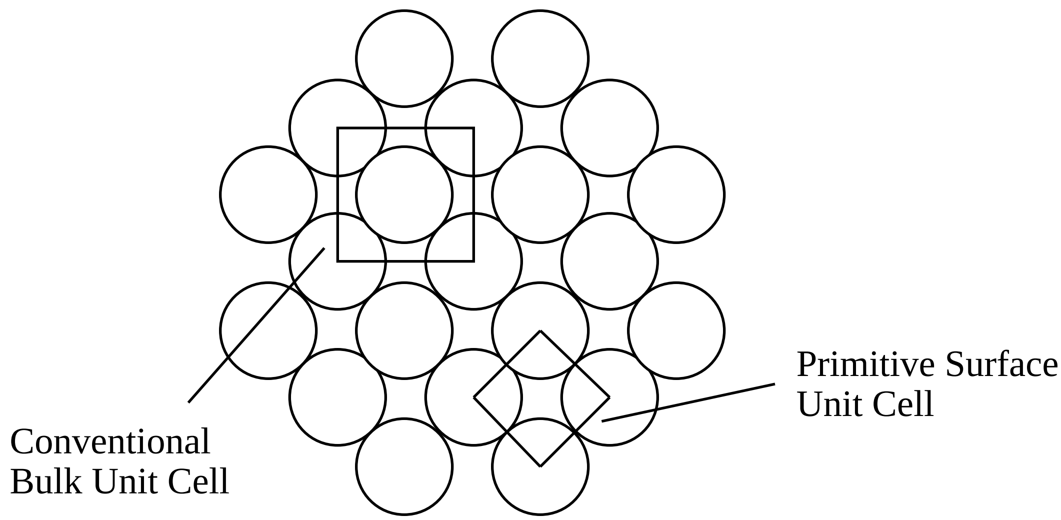
Need (i) crystal structure (ii) index of plane.

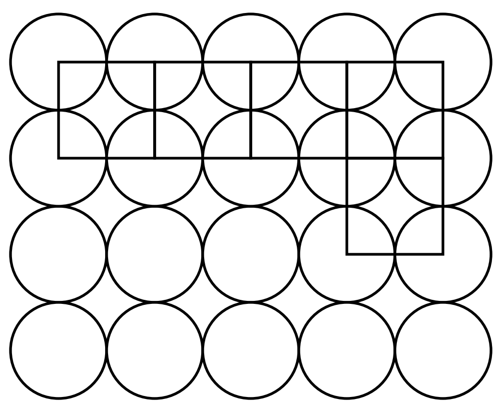
Example: Au(100) surface?

Au is FCC, (100) plane cuts the unit cell at position **a**=1 but is parallel to **b** and **c** axes.

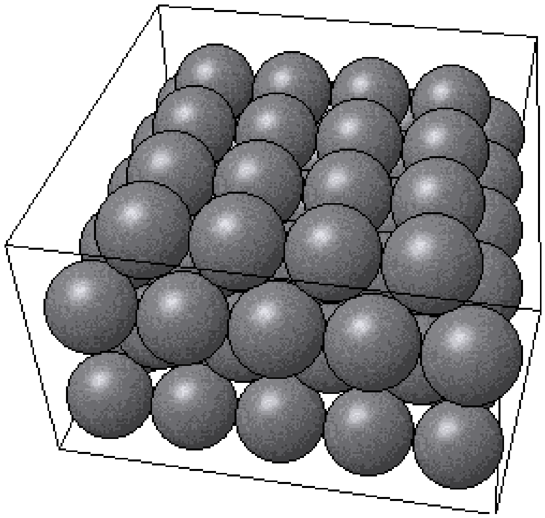


FCC(100)

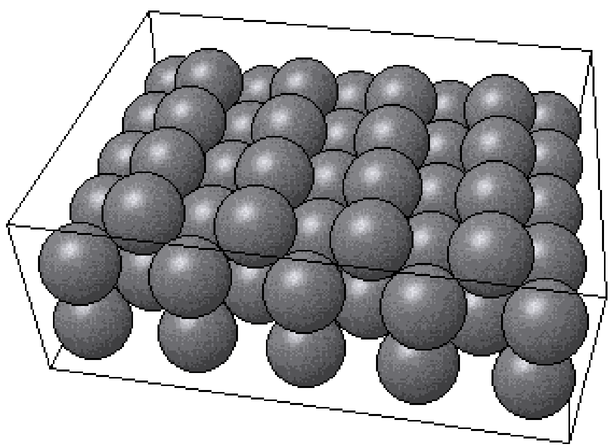




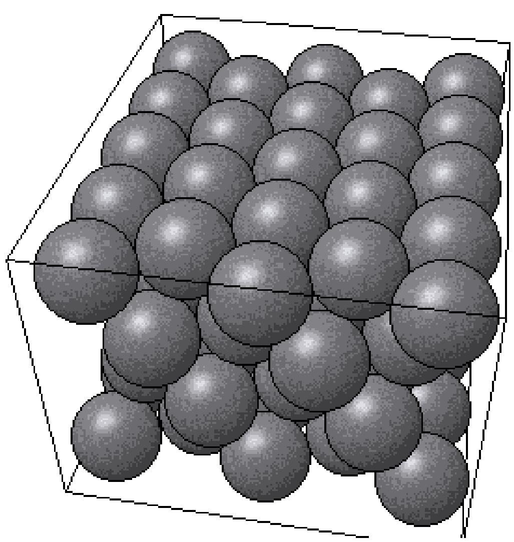
Primitive Cell Obeys Translation



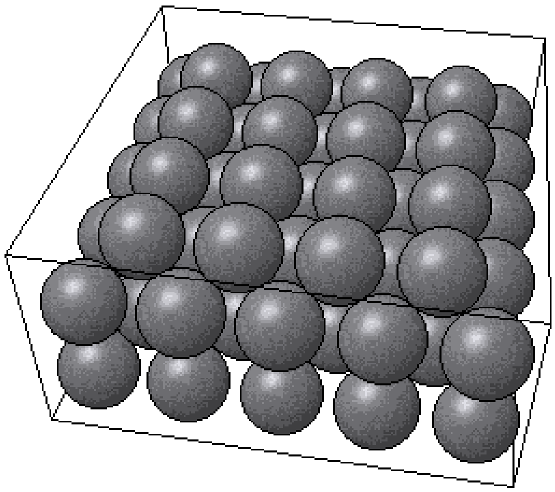
FCC(100)



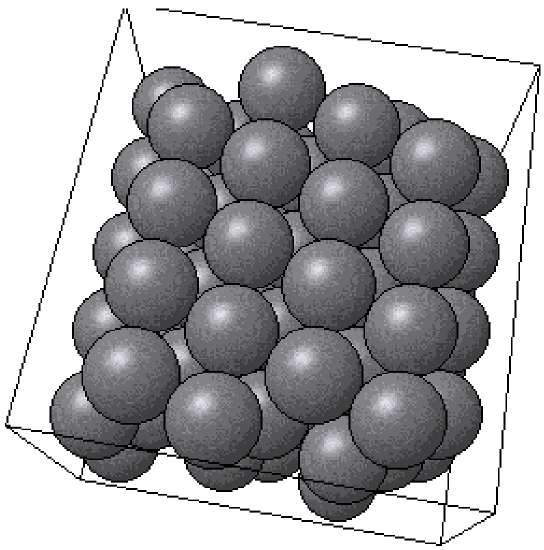
FCC(110)



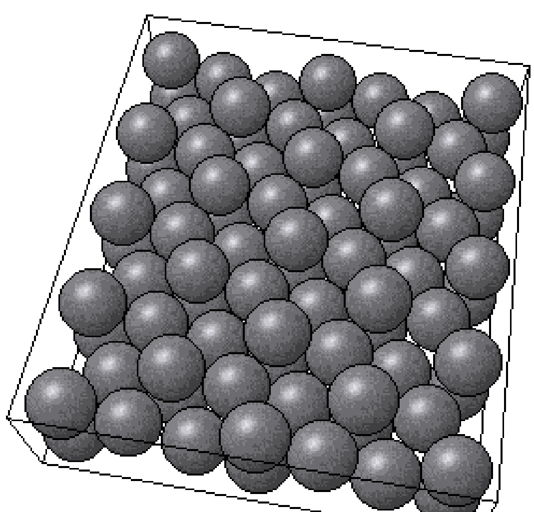
FCC(111)



BCC(100)



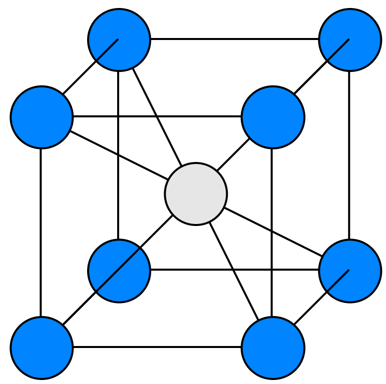
BCC(110)

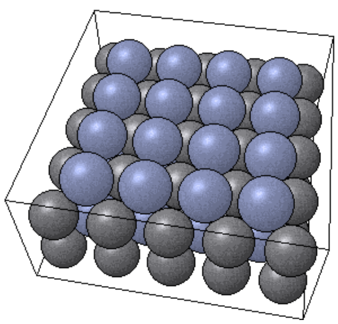


BCC(111)

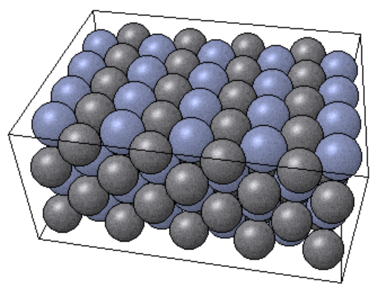
What about multiple atom basis?

CsCl has simple cubic lattice with two-atom basis Cs(0 0 0) and Cl(0.5 0.5 0.5) (looks similar to BCC)

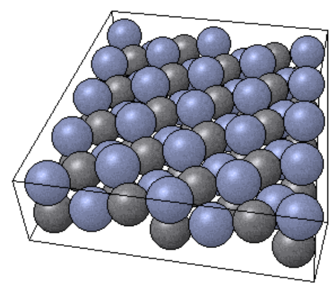




CsCl(100)



CsCl(110)



CsCl(111)

Note: If a plane cuts through an atom in a unit cell, how do you decide whether to include it in surface?

If ≥50 % atom is left on surface - include entire atom

If <50 % atom is left on surface - discard entire atom

2.3.2. Stepped Surfaces

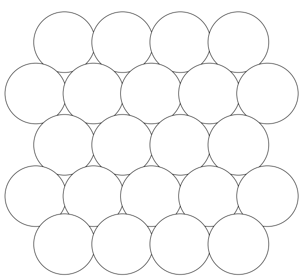
Characterized by high (hkl) values - (977), (755) or (533)

Terrace and step often resemble simple low index planes

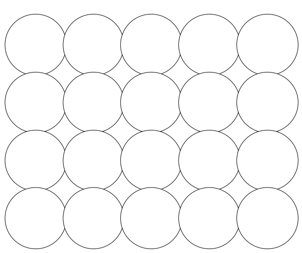
Alternate notation:

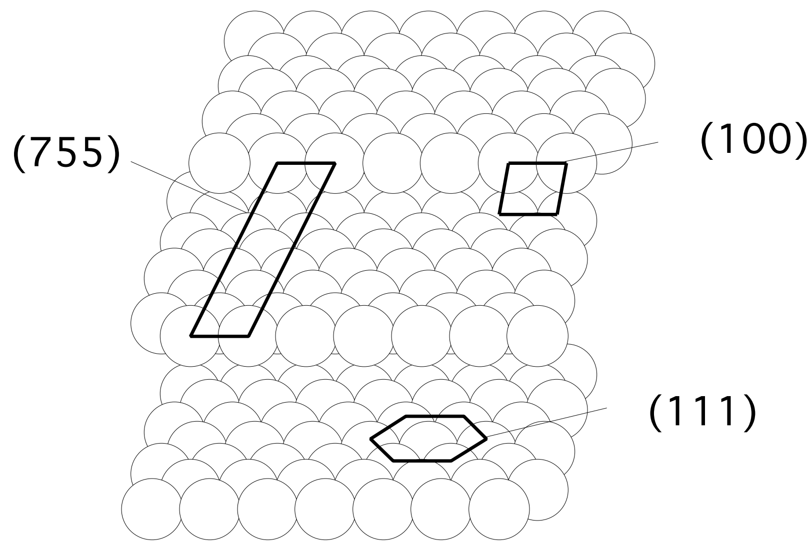
$$(544) \equiv \underbrace{(S)}_{\substack{\text{denotes}\\ \text{stepped}\\ \text{surface}}} -[9\underbrace{(111)}_{\substack{(111)\\ \text{terrace}\\ \text{9 atoms}\\ \text{wide}}} \times \underbrace{(100)}_{\substack{(100)\\ \text{step}\\ \text{1 atom}\\ \text{high}}}]$$

FCC(111)



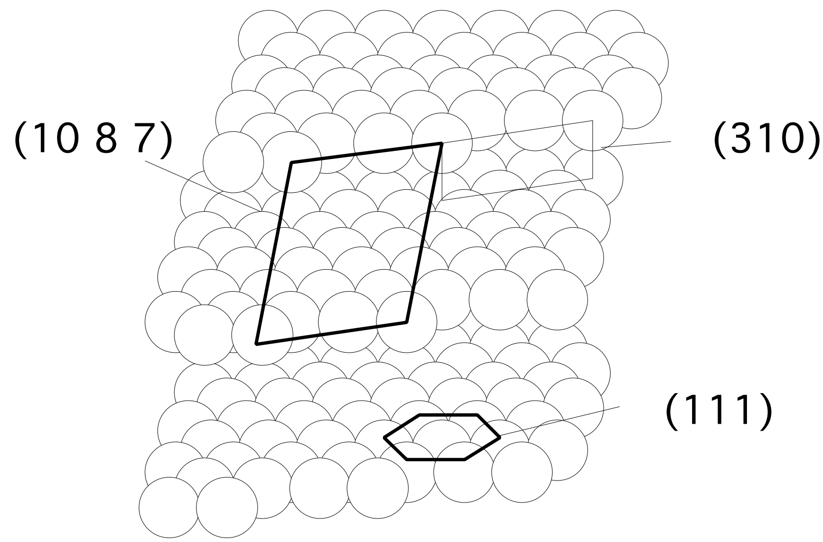
FCC(100)





Pt(755)
Pt S-[7(111)x(110)]

Some steps in a stepped surface have *kinks* in them



Pt(10 8 7)
Pt S-[7(111)x(310)]

Miller Index	Stepped Surface Designation
(544)	(S)-[9(111)x(100)]
(755)	(S)-[6(111)x(100)]
(533)	(S)-[4(111)x(100)]
(511)	(S)-[3(100)x(111)]
(332)	(S)-[6(111)x(111)]
(331)	(S)-[3(111)x(111)]
(310)	(S)-[3(100)x(110)]

Correspondence between Miller index and stepped-surface designation not obvious nor trivial to determine.

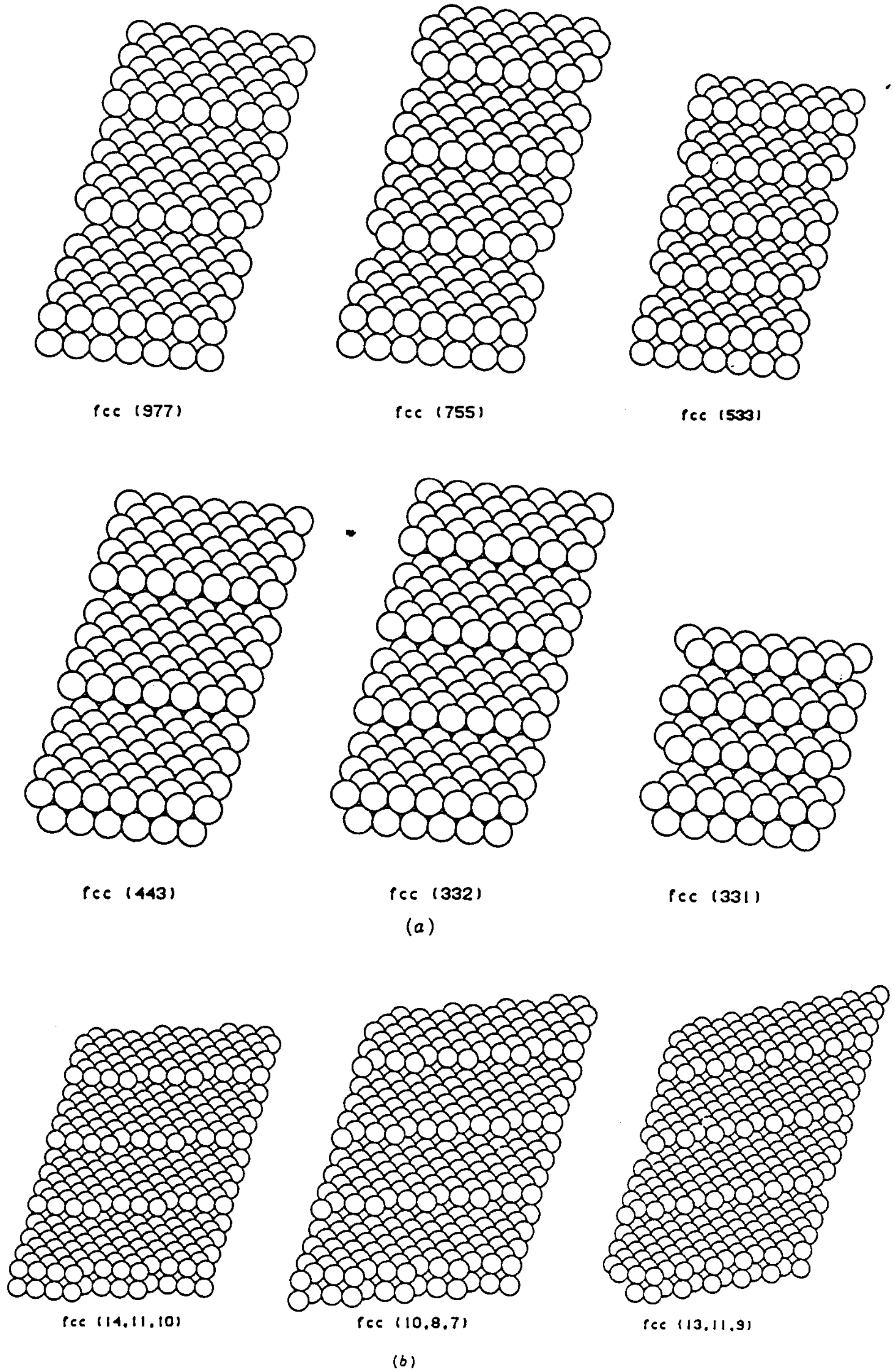


Figure 2.11. Schematic representation of the surface structures of several stepped (a) and kinked (b) crystal faces deduced from the bulk unit cell. Contraction of interlayer spacing and other modes of restructuring that are commonly observed are not shown.