Crystallography

Pecharsky 2nd ed. - Chapter 1, 2, 3

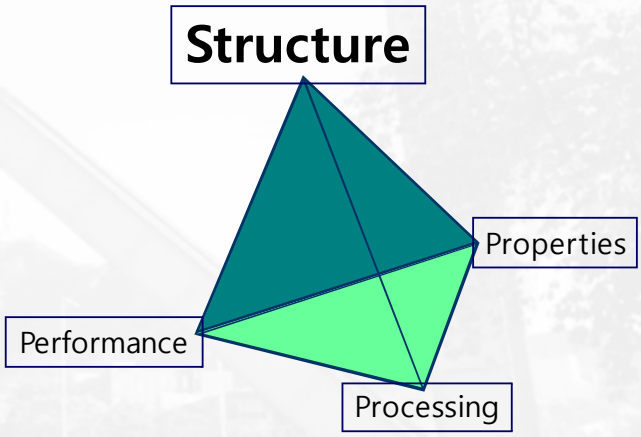
Cullity - Chapter 2

Krawitz - Chapter 1, 2

Hammond - Chapter 1, 2, 3, 4, 5, 6

Sherwood & Cooper - Chapter 1, 3

Jenkins & Snyder – Chapter 2



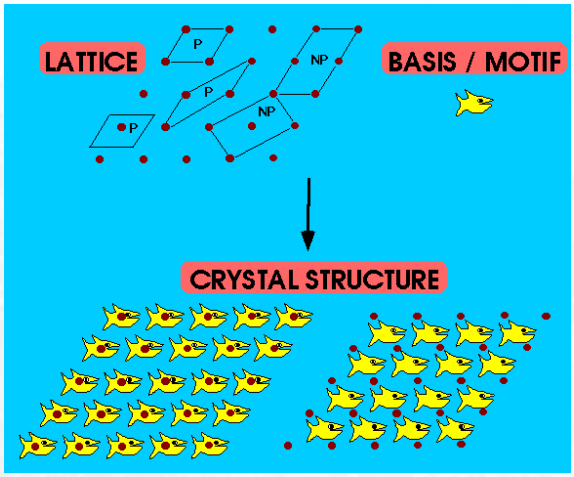
- Lattice
- Reciprocal lattice
- Miller indices
- Interplanar spacing
- 14 Bravais lattices, 7 crystal systems
- 32 Point groups, 230 Space groups
- PDF card
- International tables for crystallography

- Crystal - an anisotropic, homogeneous body consisting of a three-dimensional periodic ordering of atoms, ions, or molecules
- Crystal – solid chemical substances with a 3-dimensional periodic array of atoms, ions, or molecules
- This array → Crystal Structure
- Crystallography – concerned with the laws governing the crystalline state of solid materials with the arrangement of atoms (molecules, ions) in crystals and with their physical and chemical properties, their synthesis and their growth. (Ott)

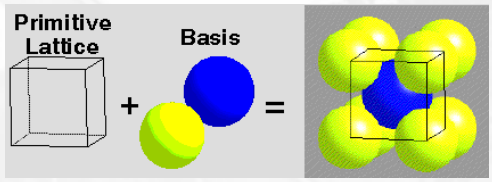
- Perfect crystal vs. crystals with defects
- Xtallography is a language.
- Nature does not allow any gap because it is a high energy configuration.
- Nature does not care about symmetry.
- Symmetry is in our head only, not in crystal.
- Nature has only one principle --- energy should be minimized.

Lattice

- Crystal Structure - the 3-dimensional periodic arrangement of atoms in the crystal
- Lattice (격자) - an infinite array of points in space, where each point has **identical surroundings** to all others



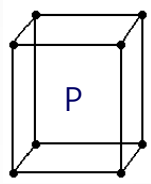
Lattice + Motif (Basis) = Crystal Structure

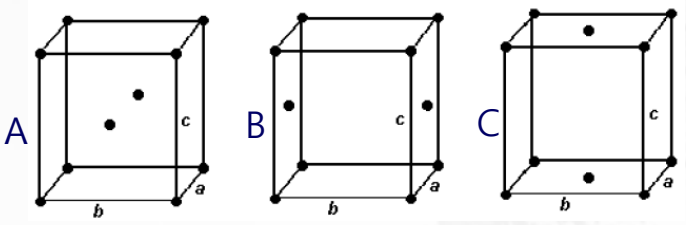


- What is the structure of the molecules within a crystal? → **motif**
- What is the nature of the geometrical array which defines the way the molecules are arranged in space? → **lattice**

Lattice type P, I, F, C, R

P; primitive

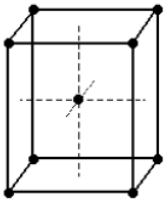




A, B, and C; end (base)-centered

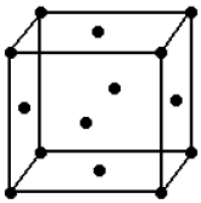
➢ I; body-centered

- ✓ Point @ ½, ½, ½
- ✓ Multiplicity = 2



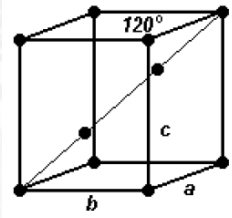
➢ F; face-centered

- ✓ ½, ½, 0
- ✓ ½, 0, ½
- ✓ 0, ½, ½
- ✓ Multiplicity = 4



➢ R; rhombohedral

- ✓ 2/3, 1/3, 1/3
- ✓ 1/3, 2/3, 2/3
- ✓ Multiplicity = 3
- ✓ Trigonal system

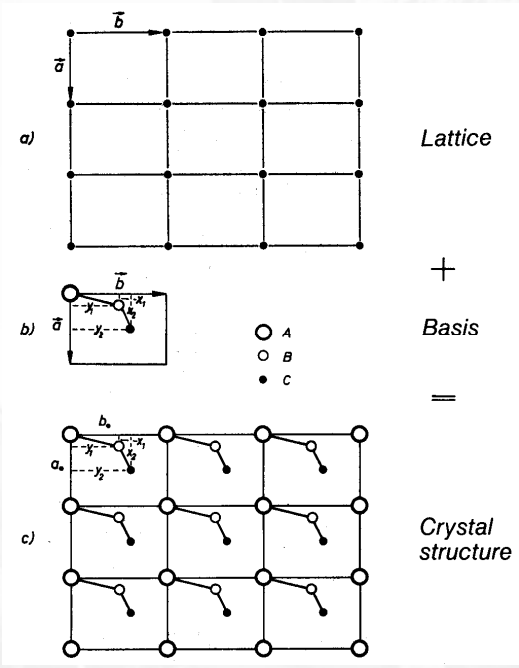


the number of lattice points in a unit cell

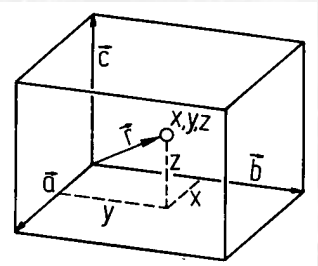
Crystal Structure

➢ Lattice → Crystal

- ✓ lattice points occupied by atoms, ions, or molecules
- ✓ lattice points- all identical, collection of objects - must be identical



- ➢ rectangular unit cell projected on a-b plane
- ➢ basis - molecule ABC
- ➢ A: 0,0,0 B: x_1, y_1, z_1 C: x_2, y_2, z_2

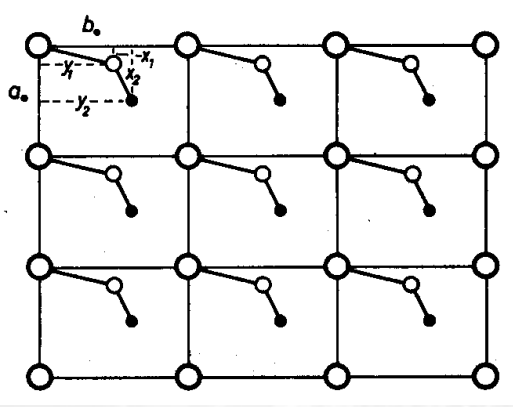


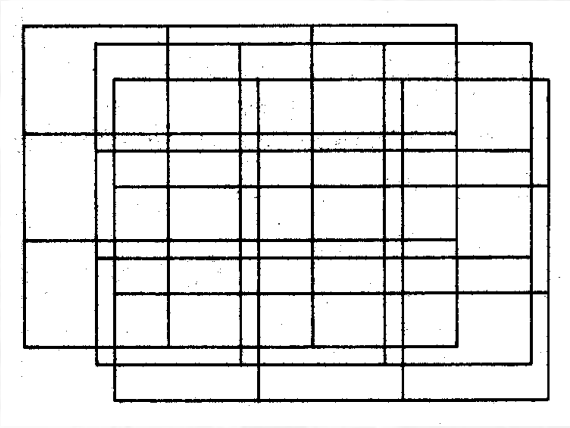
$$r = xa + yb + zc$$

$$0 \le x, y, z \le 1$$

- Crystals; solid chemical substance with a long-range three-dimensional periodic array of atoms, ions, or molecules

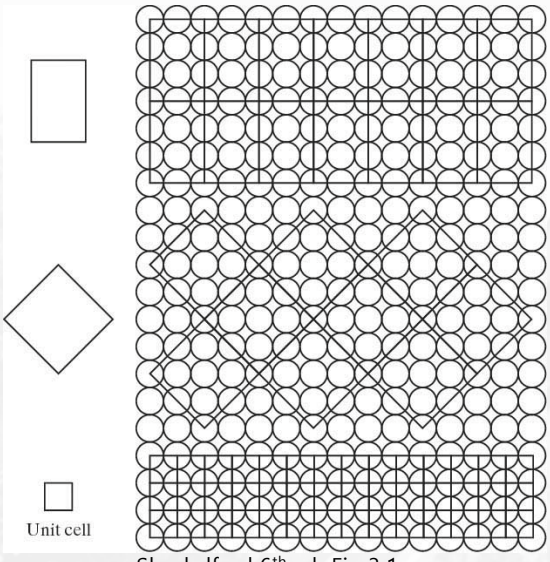
  → This array is called a **crystal structure.**





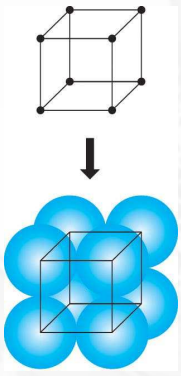
Unit cell

the smallest unit of volume that contains all of the structural and symmetry information and that can reproduce a pattern in all of space by translation.



Shackelford 6th ed. Fig 3.1

- The simple cubic lattice becomes the simple cubic crystal structure when an atom is placed on each lattice point



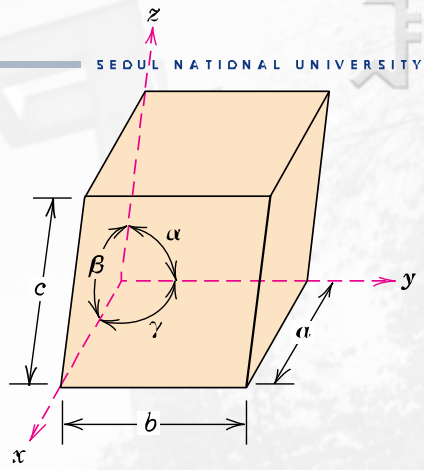
- Various structural units that describe the schematic crystalline structure
- The simplest structural unit → unit cell

An ASYMMETRIC UNIT
the smallest unit of volume that contains all of the structural information and that can reproduce the UNIT CELL by application of the symmetry operations.

Parameters to define a unit cell

Basis vectors : $\vec{a}$ $\vec{b}$ $\vec{c}$

Lattice parameters : a b c α β γ



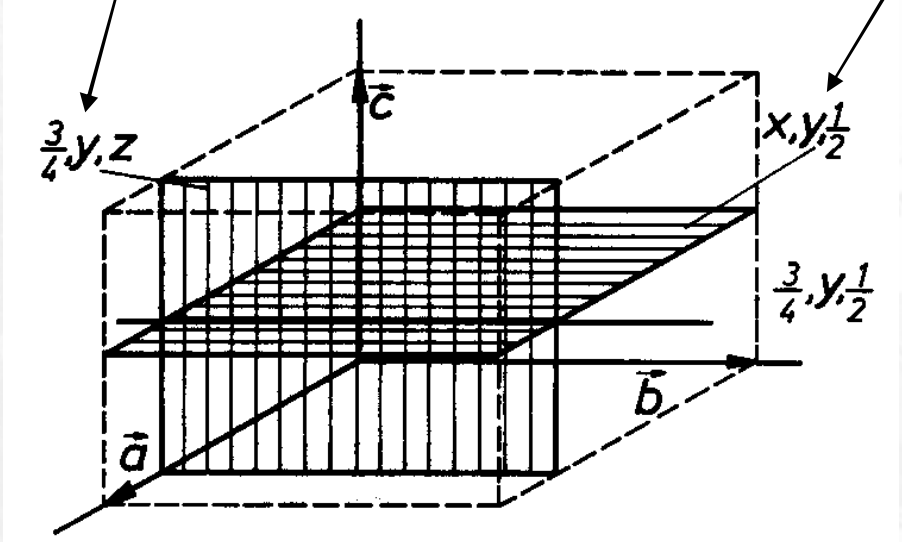
7 crystal systems

System	Conventional unit cell	
Triclinic	$\mathbf{a}_1 \neq \mathbf{a}_2 \neq \mathbf{a}_3$	$\alpha \neq \beta \neq \gamma$
Monoclinic	$\mathbf{a}_1 \neq \mathbf{a}_2 \neq \mathbf{a}_3$	$\alpha = \gamma, \quad \beta \geq 90°$
Orthorhombic	$\mathbf{a}_1 \neq \mathbf{a}_2 \neq \mathbf{a}_3$	$\alpha = \beta = \gamma = 90°$
Tetragonal	$\mathbf{a}_1 = \mathbf{a}_2 \neq \mathbf{a}_3$	$\alpha = \beta = \gamma = 90°$
Trigonal	$\mathbf{a}_1 = \mathbf{a}_2 = \mathbf{a}_3$	$\alpha = \beta = \gamma \neq 90°$
Hexagonal	$\mathbf{a}_1 = \mathbf{a}_2 \neq \mathbf{a}_3$	$\alpha = \beta = 90°, \gamma = 120°$
Cubic	$\mathbf{a}_1 = \mathbf{a}_2 = \mathbf{a}_3$	$\alpha = \beta = \gamma = 90°$

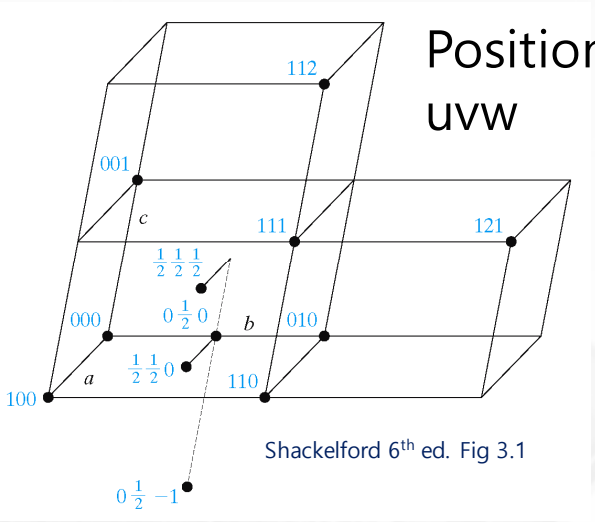
Planes and Lines in the cell

- all points in the plane // to **b** and **c** axes which cuts **a** axis @ ¾
- not a Miller index

- all points in the plane // to **a** and **b** axes which cuts **c** axis @ ½
- not a Miller index



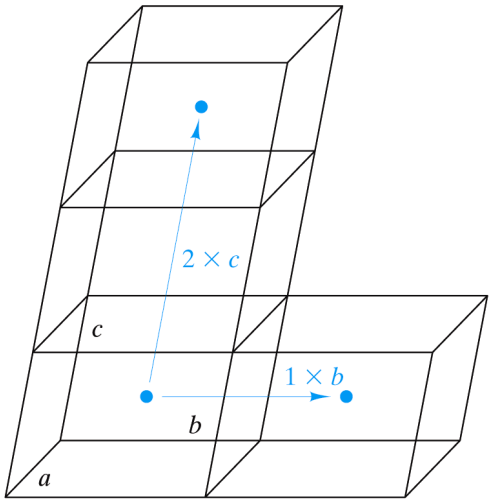
Lattice positions, lattice translation



Position
uvw

Shackelford 6th ed. Fig 3.1

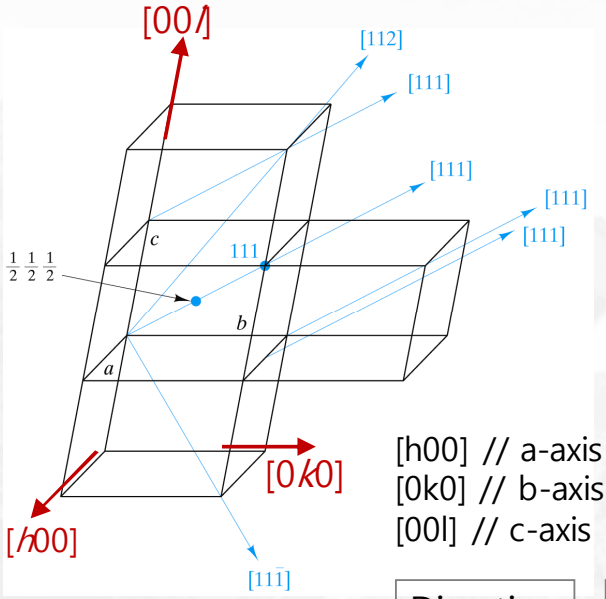
Lattice translations connect structurally equivalent positions (e.g. the body center) in various unit cells.



Shackelford 6th ed. Fig 3.27

Directions

Parallel [uvw] directions share the same notation because only the origin is shifted.

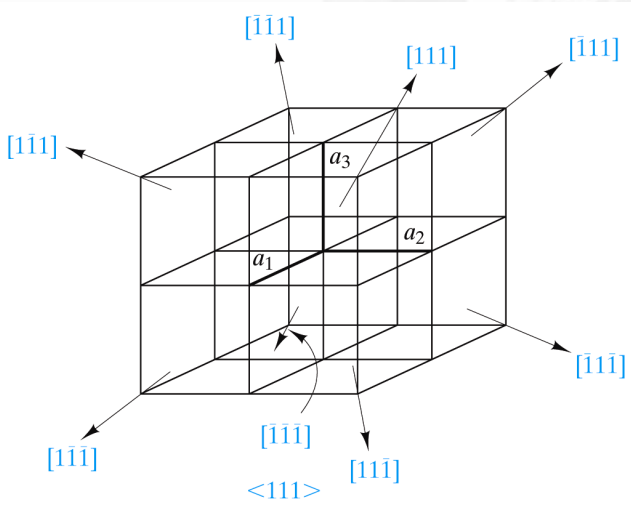


[h00] // a-axis
[0k0] // b-axis
[00l] // c-axis

Direction
[uvw]

Family of directions

<111> represents all body diagonals.

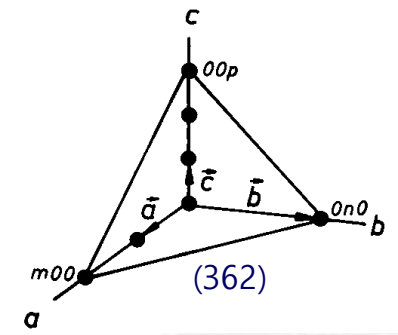


Family of directions
<uvw>

Lattice plane (Miller index)

m, n, ∞ : ∞ when no intercepts with axes.

Intercepts @ (mnp)	2	1	3
Reciprocals	½	1	1/3
Miller indicies	3	6	2
(362) plane			



- (hkl) is // to (n*h n*k n*l) → (110) // (220) // (330) // (440)
- Planes are orthogonal if (hkl) • (h'k'l') = 0.

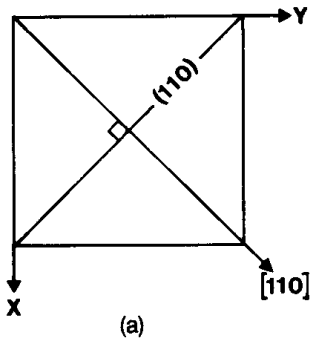
- Some planes may be equivalent because of symmetry. → In a cubic crystal, (100) (010) and (001) are equivalent. → family of planes {100}
- [h00] is // to a-axis, [0k0] // b-axis, [00l] // c-axis

Miller index ; the smallest integral multiples of the reciprocals of the plane intercepts on the axes

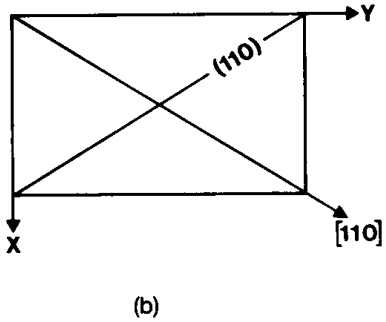
Plane (hkl)
Family of planes {hkl}

Direction vs. Planes of Same Indices

cubic



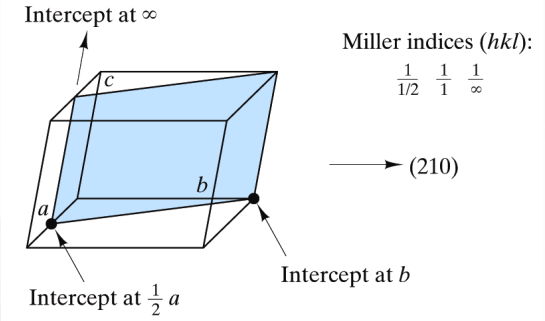
orthorhombic

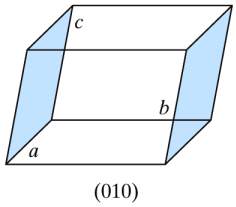


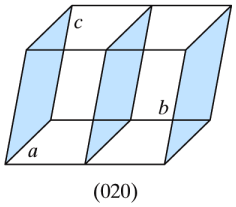
Plans of (a) cubic and (b) orthorhombic unit cells perpendicular to the *z*-axis, showing the relationships between planes and zone axes of the same numerical indices.

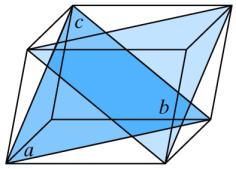
Hammond page 109
Sherwood & Cooper page 72

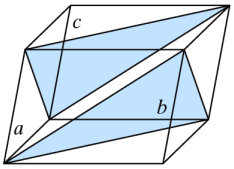
Lattice plane (Miller indices)



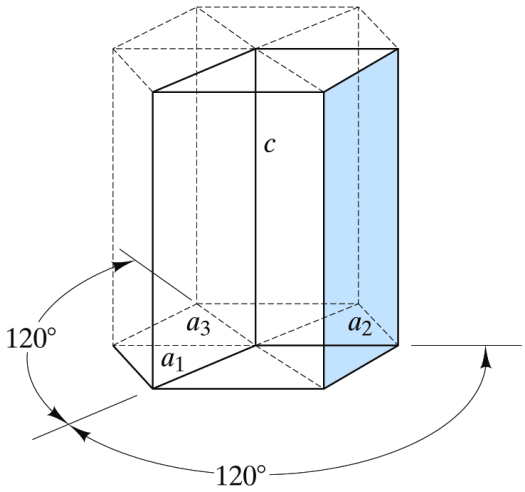








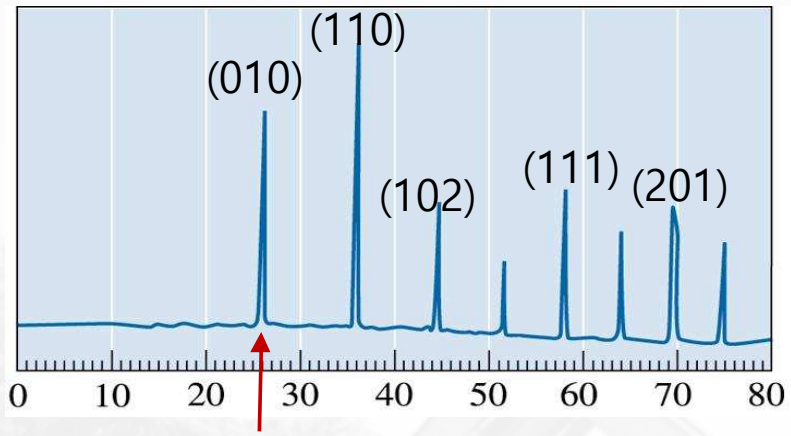
Miller Bravais indices (hkil) for hexagonal system



Miller–Bravais indices (*hkil*): $\frac{1}{\infty}, \frac{1}{1}, \frac{1}{-1}, \frac{1}{\infty} \rightarrow (01\bar{1}0)$

Note: $h + k = -i$

XRD pattern vs Miller index

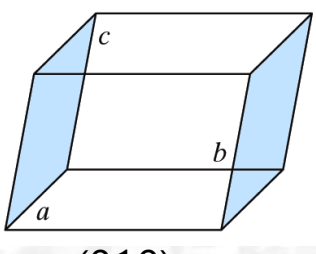


➢indexing

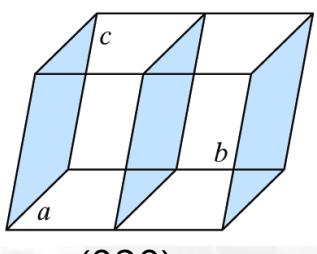
Peak position

d_{010}

d_{020}



(010)

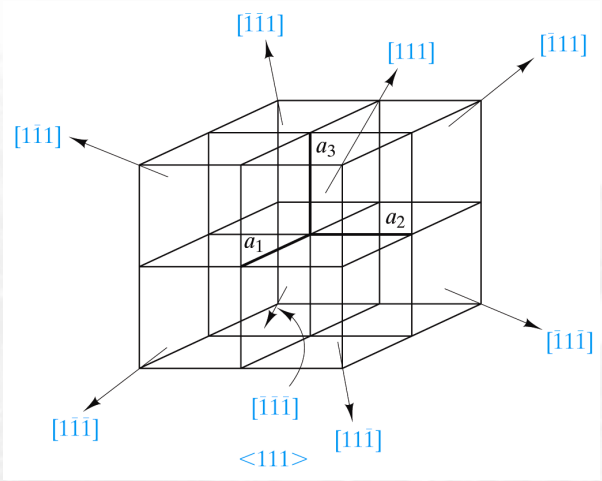


(020)

d_{hkl}
Interplanar spacing
(면간 거리)

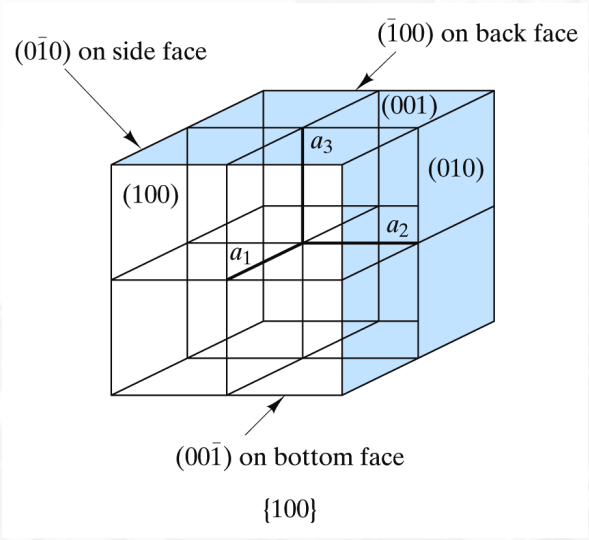
Family of directions <uvw> & Family of planes {hkl}

<111> angular bracket represents all body diagonals.



[111] square bracket; line, direction

{100} braces represents all faces of unit cells in the cubic system.

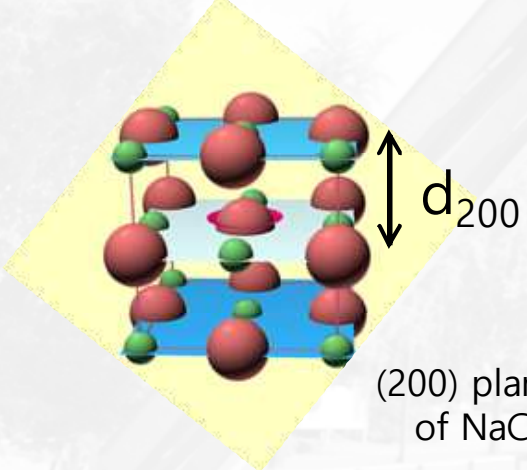


(100) round bracket; planes (Parentheses)

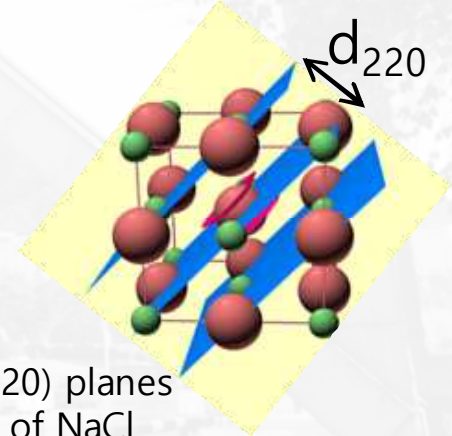
Shackelford 6th ed. Fig 3.29
Shackelford 6th ed. Fig 3.32

[uvw] & (hkl)

[uvw] direction line	a lattice line through the origin and point uvw
	the infinite set of lattice lines which are parallel to it and have the same lattice parameter
(hkl) plane	the infinite set of parallel planes which are apart from each other by the same distance (d)



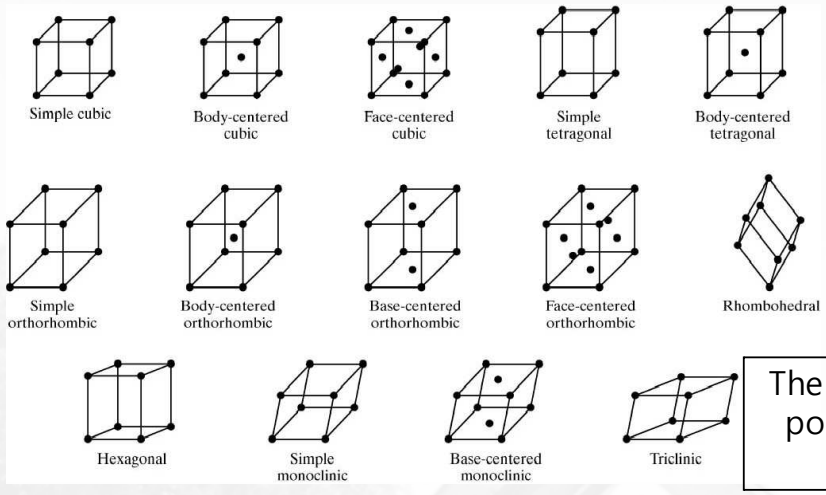
(200) planes of NaCl



(220) planes of NaCl

Scott Speakman

14 Bravais Lattice



The 14 and only way in which it is possible to fill space by a 3-dim periodic array of points

Lattice	No. of lattice points in unit cell	Coordinates of lattice points in unit cell
P	1	$0,0,0$
A	2	$0,0,0;\ 0,\frac{1}{2},\frac{1}{2}$
B	2	$0,0,0;\ \frac{1}{2},0,\frac{1}{2}$
C	2	$0,0,0;\ \frac{1}{2},\frac{1}{2},0$
I	2	$0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}$
R	3	$0,0,0;\ \frac{2}{3},\frac{1}{3},\frac{1}{3};\ \frac{1}{3},\frac{2}{3},\frac{2}{3}$
F	4	$0,0,0;\ \frac{1}{2},\frac{1}{2},0;\ \frac{1}{2},0,\frac{1}{2};\ 0,\frac{1}{2},\frac{1}{2}$

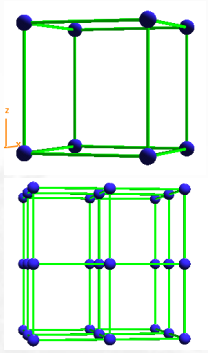
7 crystal systems, 14 Bravais lattices

Xtal systems	a1, a2, a3, α, β, γ	Bravais lattice	Lattice symbol
Cubic	a1 = a2 = a3 α = β = γ = 90°	Simple	P
		Body-centered	I
		Face-centered	F
Tetragonal	a1 = a2 ≠ a3 α = β = γ = 90°	Simple	P
		Body-centered	I
Orthorhombic	a1 ≠ a2 ≠ a3 α = β = γ = 90°	Simple	P
		Body-centered	I
		Base-centered	C
		Face-centered	F
Rhombohedral	a1 = a2 = a3, α = β = γ < 120° , ≠ 90°	Simple	R
Hexagonal	a1 = a2 ≠ a3, α = β = 90° , γ = 120°	Simple	P
Monoclinic	a1 ≠ a2 ≠ a3, α = γ = 90° ≠ β	Simple	P
		Base-centered	C
Triclinic	a1 ≠ a2 ≠ a3, α ≠ β ≠ γ ≠ 90°	Simple	P

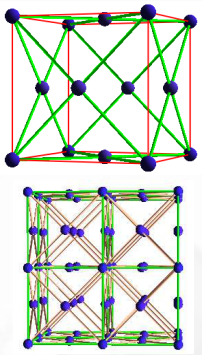
Simple cubic lattices

$a_1 = a_2 = a_3$
$\alpha = \beta = \gamma = 90^o$

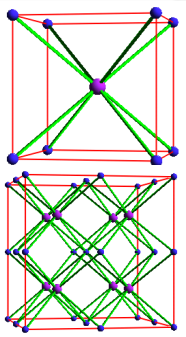
P simple cubic



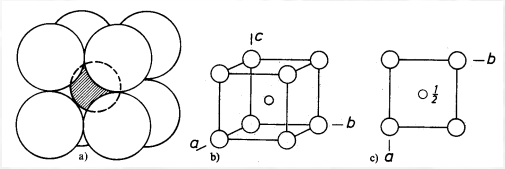
F face centered cubic



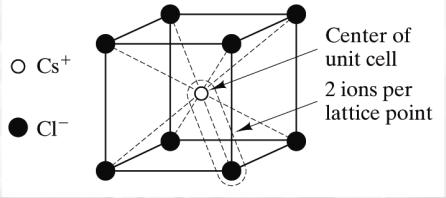
I body centered cubic



- cesium iodide (CsI)
  - ✓ $a_o = b_o = c_o = 4.57$Å, $a = b = g = 90^o$
  - ✓ basis I^-: 0,0,0 Cs^+:½,½,½



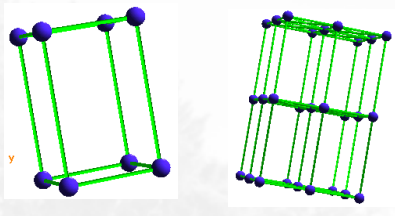
Structure: CsCl type
Bravais lattice: simple cubic
Ions/unit cell: $1Cs^+ + 1Cl^-$



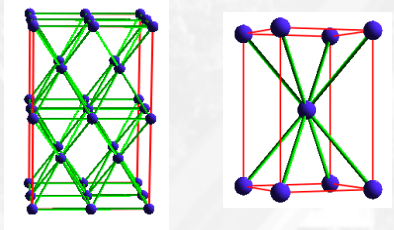
Tetragonal lattices

$a1 = a2 \neq a3$
$\alpha = \beta = \gamma = 90^o$

P simple tetragonal



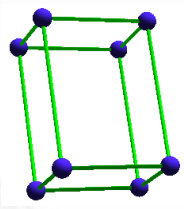
I body centered tetragonal



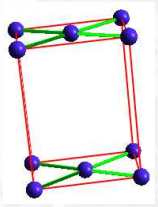
Orthorhombic lattices

$a1 \neq a2 \neq a3$
$\alpha = \beta = \gamma = 90^o$

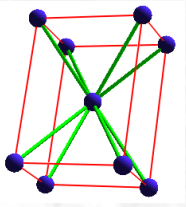
P



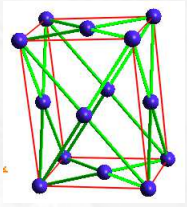
C



I



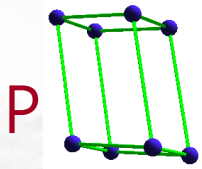
F



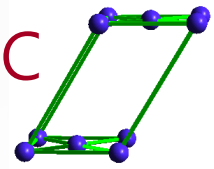
Monoclinic lattices

$a1 \neq a2 \neq a3$
$\alpha = \gamma = 90^o \neq \beta$

Simple monoclinic

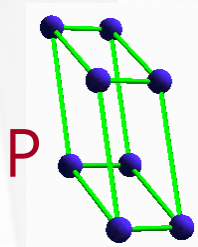


Base centered monoclinic



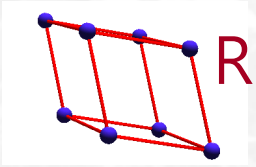
Triclinic lattice

$a1 \neq a2 \neq a3$
$\alpha \neq \beta \neq \gamma \neq 90^o$



Trigonal (Rhombohedral) lattice

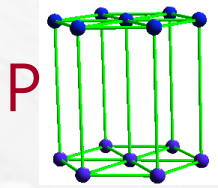
$a1 = a2 = a3$
$\alpha = \beta = \gamma < 120^o , \neq 90^o$



obtained by stretching a cube along one of its axes

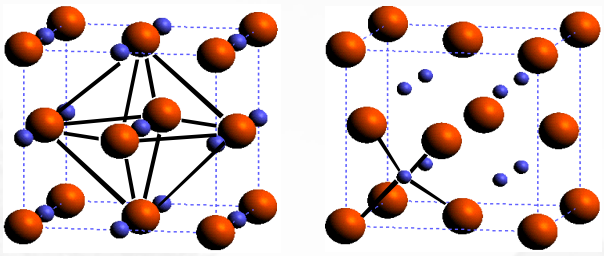
Hexagonal lattice

$a1 = a2 \neq a3$
$\alpha = \beta = 90^o , \gamma = 120^o$

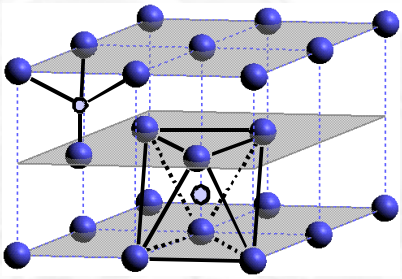


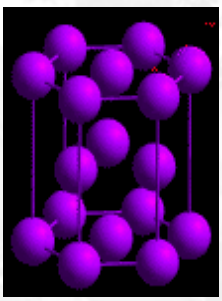
Interstitial sites of CCP & HCP

octahedral & tetrahedral interstices in cubic closed-packed (CCP) lattice

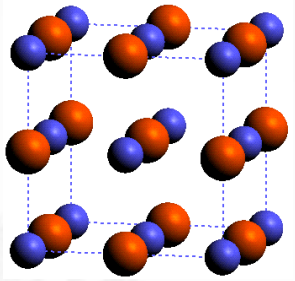


octahedral & tetrahedral interstices in hexagonal closed-packed (HCP) lattice

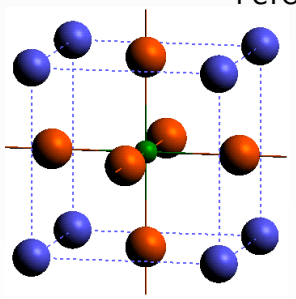


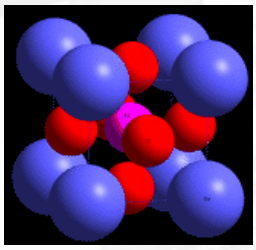


Rock-Salt (NaCl; MgO)



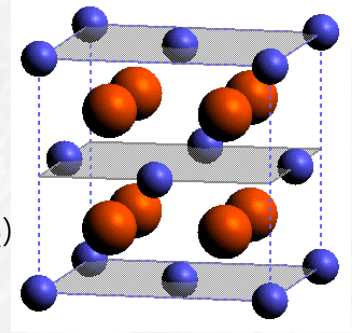
Perovskite

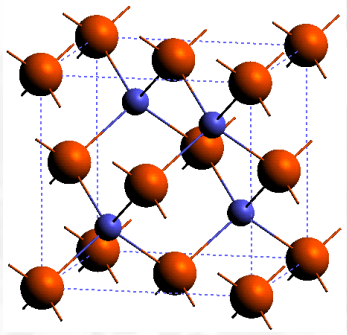




$CaTiO_3$; $BaTiO_3$; $SrTiO_3$; $PbTiO_3$; $PbZrO_3$; $LaAlO_3$

Fluorite
(CaF_2; ZrO_2; CeO_2)





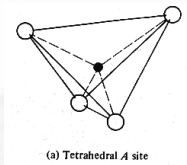
Zinc Blende
(ZnS; CdS; GaAs)

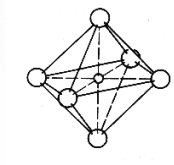
- Spinel (AB_2O_4)
- Oxygen cubic close packing

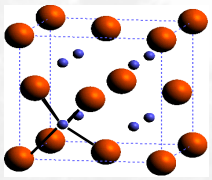
$MgAl_2O_4$

$ZnFe_2O_4$

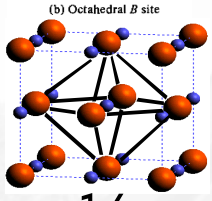
$MnFe_2O_4$



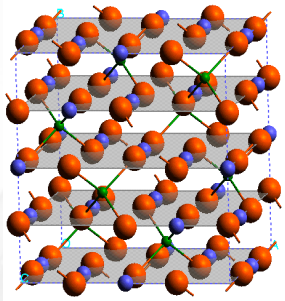


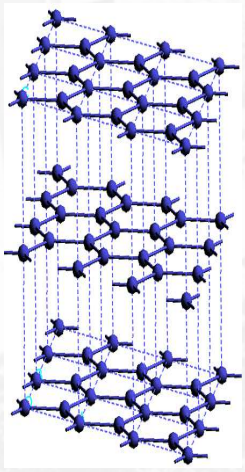


1/8



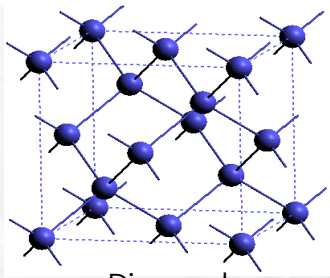
1/2





Graphite
(Carbon; BN)

Kind of site	Number available	Number occupied	Occupants: Normal spinel	Occupants: Inverse spinel
Tetrahedral (A)	64	8	8 M^{2+}	8 Fe^{3+}
Octahedral (B)	32	16	16 Fe^{3+}	8 Fe^{3+} 8 M^{2+}



Diamond