Crystallography

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

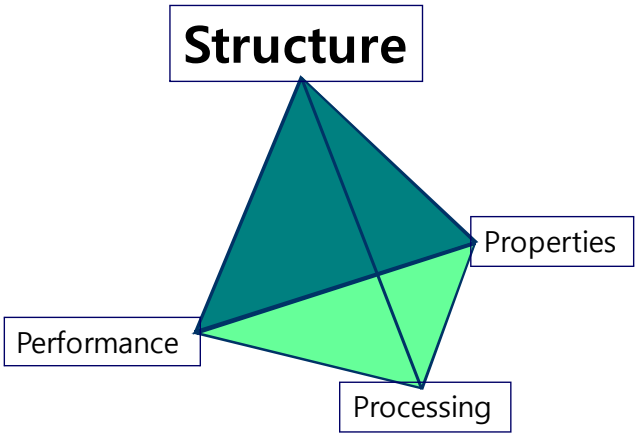
Cullity - Chapter 2

Krawitz - Chapter 1, 2

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

Sherwood & Cooper - Chapter 1, 3

Jenkins & Snyder – Chapter 2

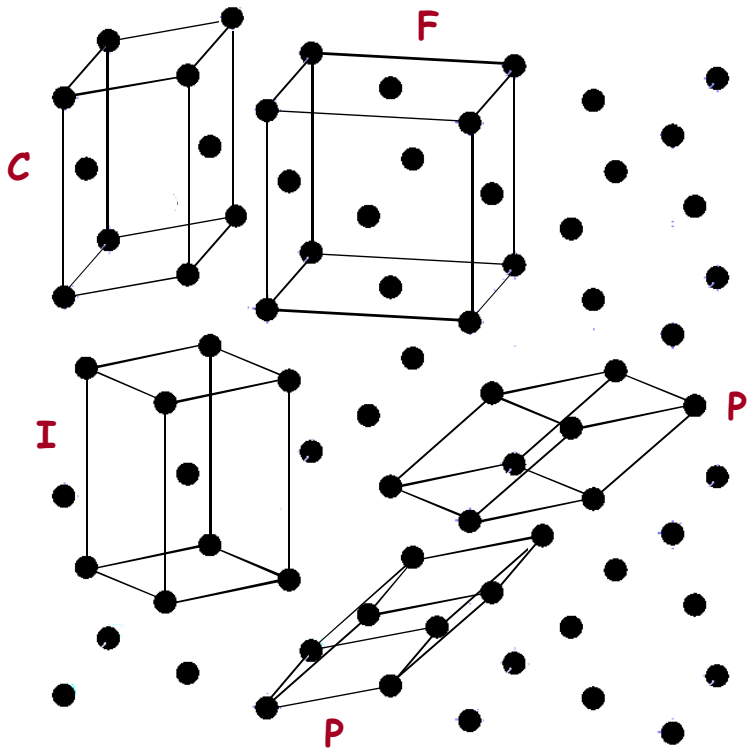


- Lattice
- Reciprocal lattice
- Miller indices
- Interplanar spacing
- 14 Bravais lattices, 7 crystal systems
- 32 Point groups, 230 Space groups
- PDF card
- International tables for crystallography

- 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)

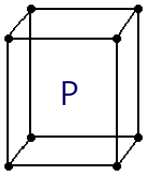
- Perfect crystal vs. crystals with defects
- Xtallography is a language
- Nature does not allow some gaps because it is a high energy configuration
- Nature does not care about symmetry
- Symmetry is in our head only, not in crystal.
- Nature has only one principle --- energy should be minimized

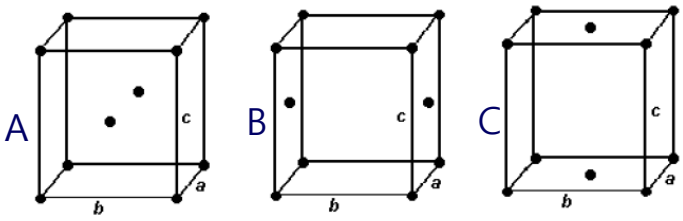
Lattice type P, I, F, C, R



Lattice type P, I, F, C, R

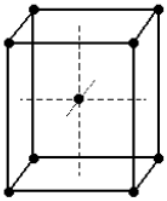
P; primitive



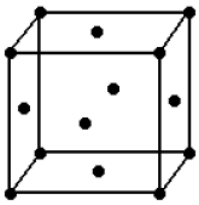


A, B, and C; end (base)-centered

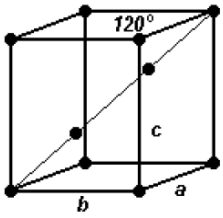
- I; body-centered
  - ✓ Point @ ½, ½, ½
  - ✓ Multiplicity = 2



- F; face-centered
  - ✓ ½, ½, 0
  - ✓ ½, 0, ½
  - ✓ 0, ½, ½
  - ✓ Multiplicity = 4

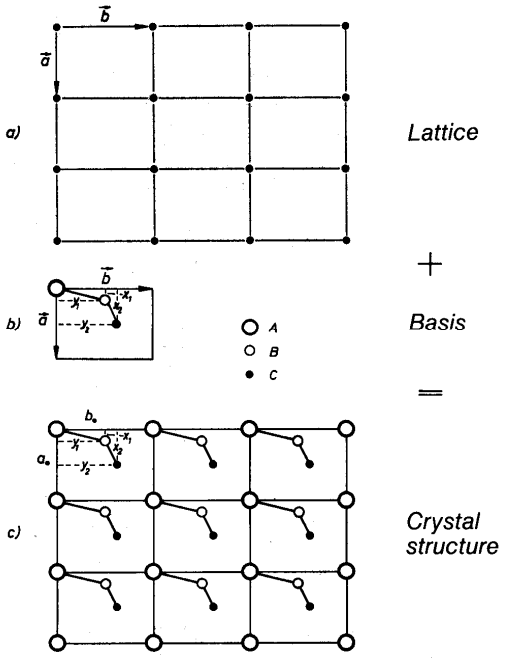


- R; rhombohedral
  - ✓ 2/3, 1/3, 1/3
  - ✓ 1/3, 2/3, 2/3
  - ✓ Multiplicity = 3
  - ✓ Trigonal system

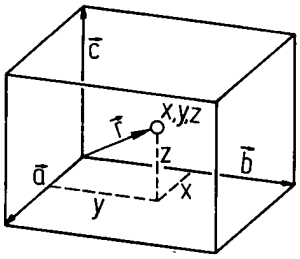


Crystal Structure

- 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

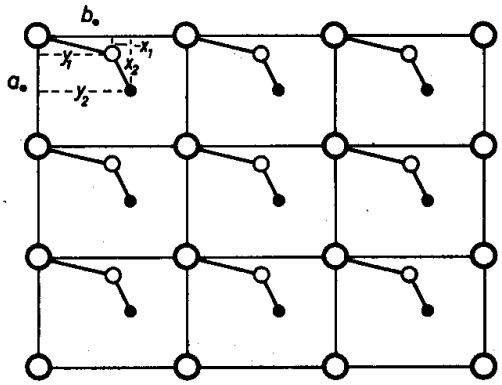


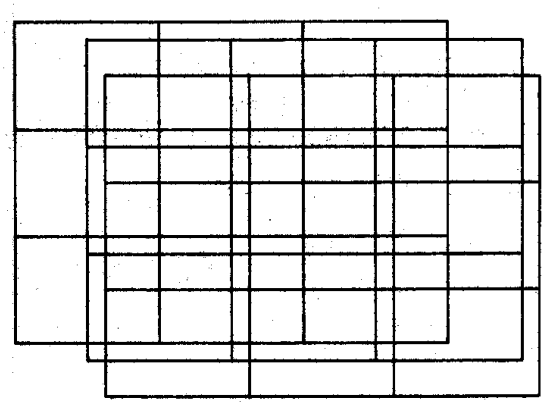
$$r = xa + yb + zc$$

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

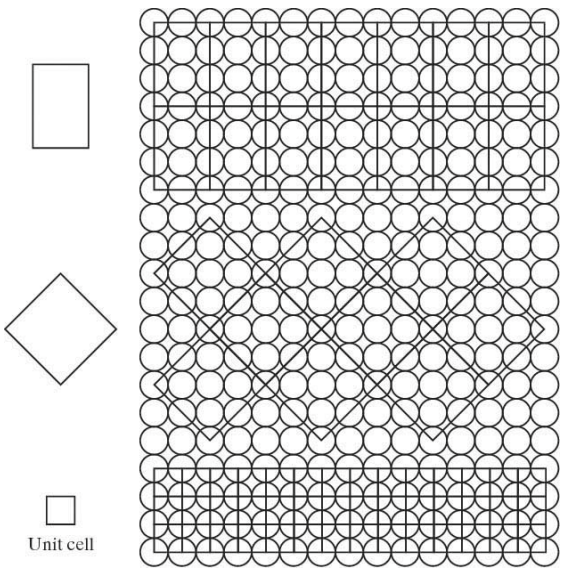
- Crystals; solid chemical substance with a long-range three-dimensional periodic array of atoms, ions, or molecules

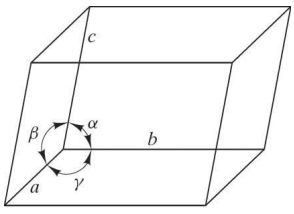
  → This array is called a **crystal structure**

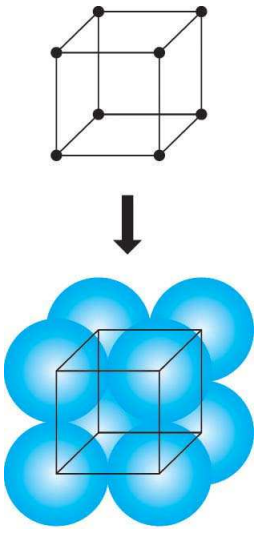




Unit cell





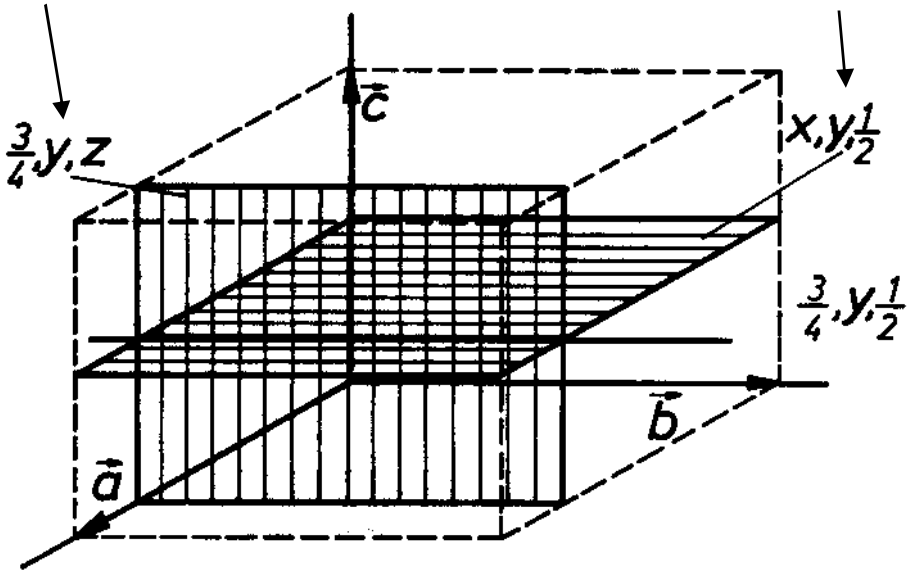


- Various structural units that describe the schematic crystalline structure
- The simplest structural unit is the unit cell
- The simple cubic lattice becomes the simple cubic crystal structure when an atom is placed on each lattice point

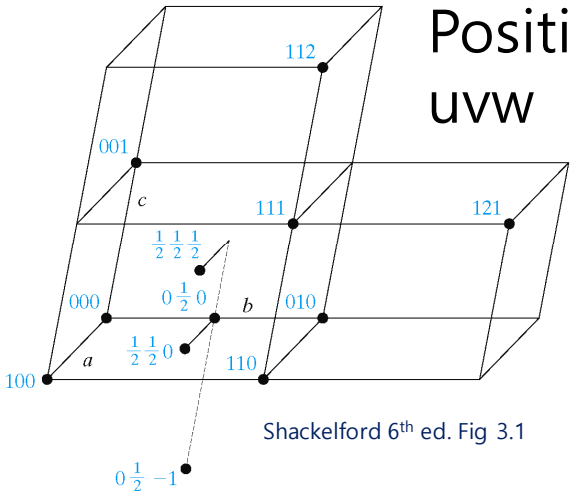
planes and lines in the cell

- 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



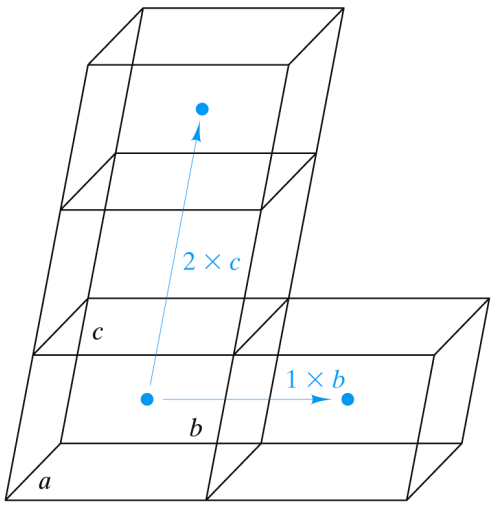
Lattice positions, lattice translation



Shackelford 6th ed. Fig 3.1

Position uvw

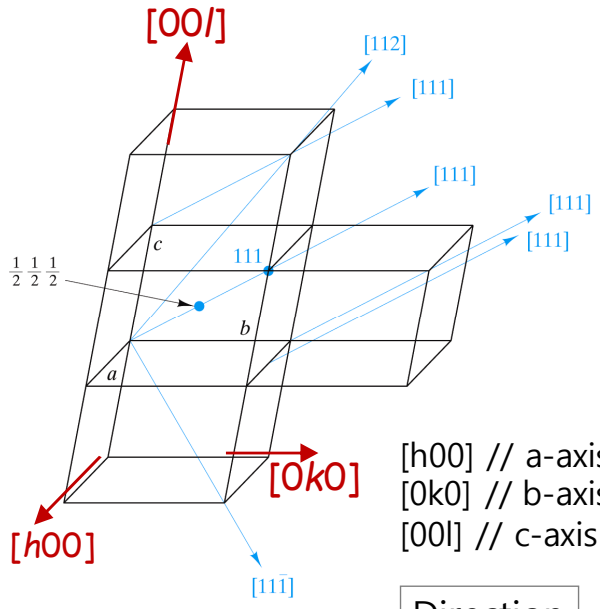
Lattice translations connect structurally equivalent positions (e.g. the body center) in various unit cells



Shackelford 6th ed. Fig 3.27

Directions

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

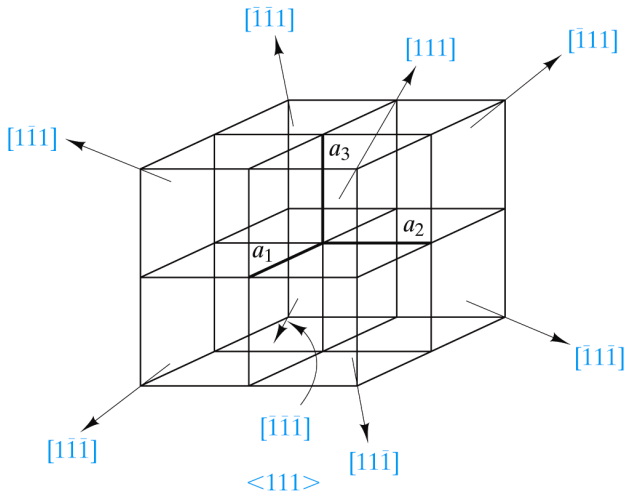


[h00] // a-axis
[0k0] // b-axis
[00l] // c-axis

Direction [uvw]

Family of directions

<111> represents all body diagonals



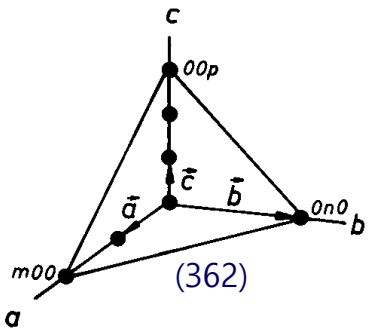
Family of direction <uvw>

Shackelford 6th ed.

Lattice plane (Miller index)

m, n, ∞ : 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

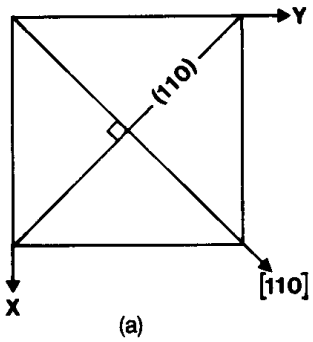
- Some planes may be equivalent because of symmetry → in a cubic crystal, (100) (010) and (001) are equivalent → family of planes {100}
- [h00] is // to a-axis, [0k0] // b-axis, [00l] // c-axis

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

Plane (hkl)
Family of planes {hkl}

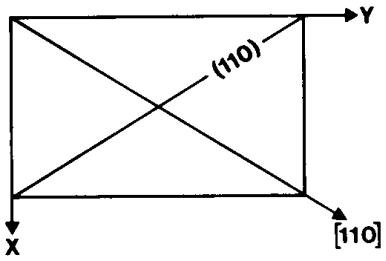
Direction vs. Planes of Same Indices

cubic



(a)

orthorhombic



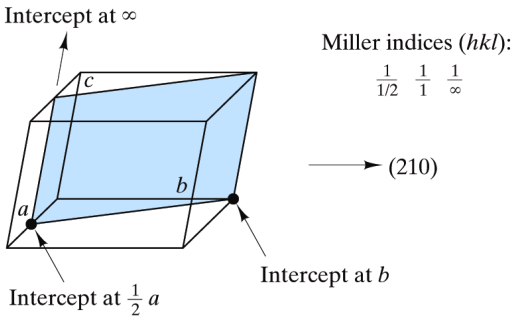
(b)

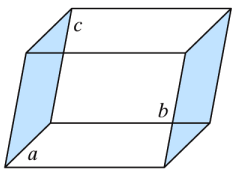
Plans of (a) cubic and (b) orthorhombic unit cells perpendicular to the z-axis, showing the relationships between planes and zone axes of the same numerical indices.

Hammond page 109

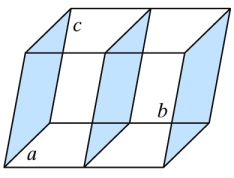
Sherwood & Cooper page 72

Lattice plane (Miller indices)

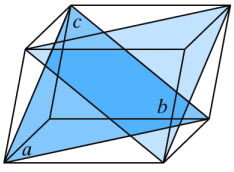




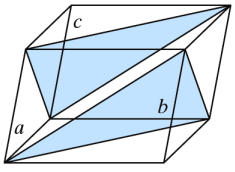
(010)



(020)

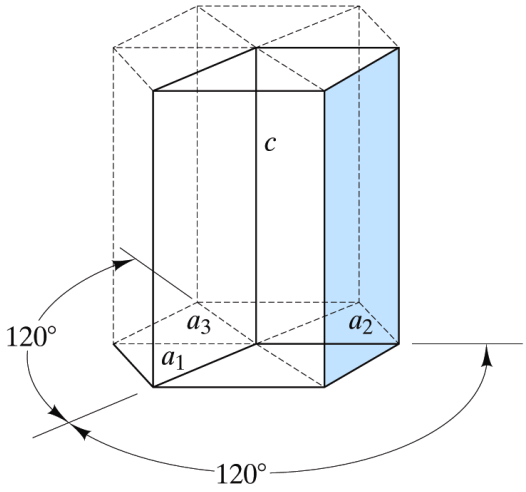


(111)



(11$\bar{1}$)

Miller Bravais indices (hkil) for hexagonal system

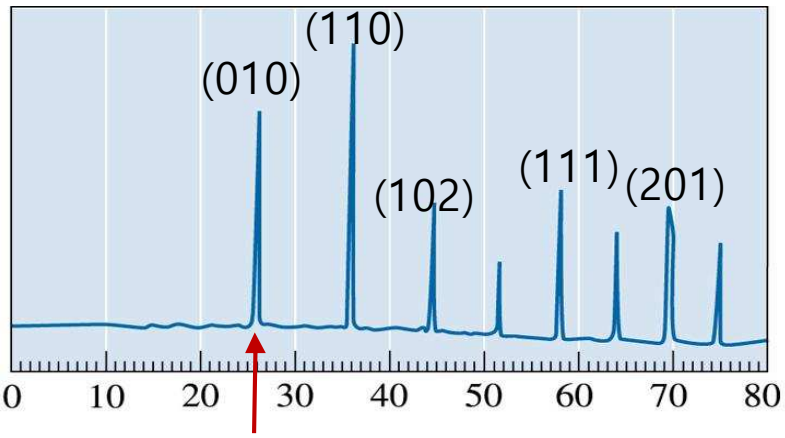


Miller–Bravais indices ($hkil$): $\frac{1}{\infty}, \frac{1}{1}, \frac{1}{-1}, \frac{1}{\infty} \rightarrow (01\bar{1}0)$

Note: $h + k = -i$

Shackelford 6th ed.

XRD pattern vs Miller index

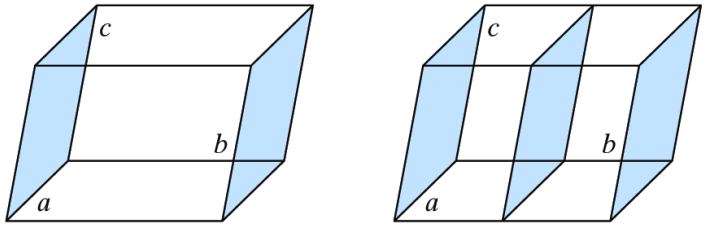


➢indexing

Peak position

d_{010}

d_{020}

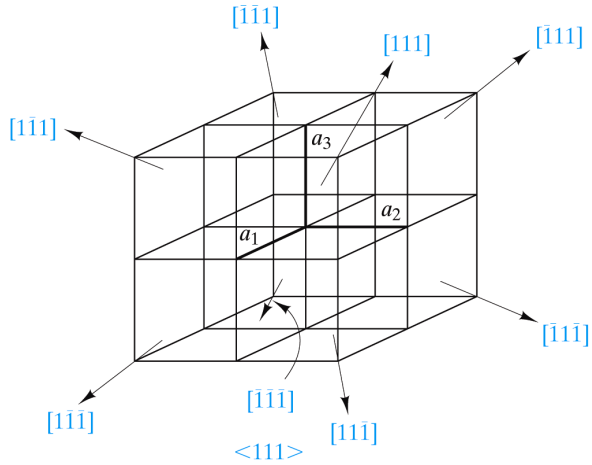


(010) (020)

d_{hkl}
Interplanar spacing
(면간 거리)

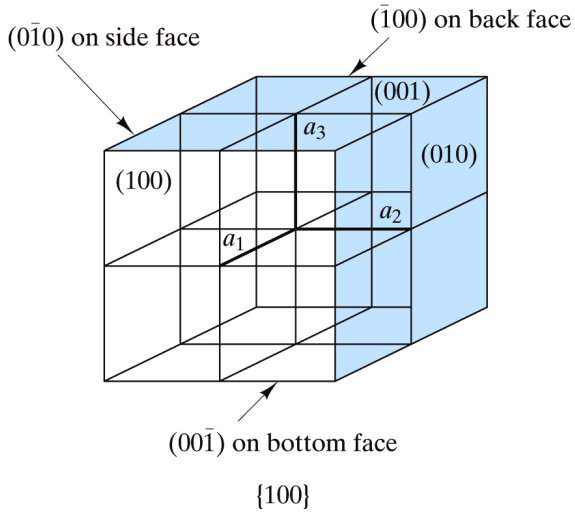
Family of directions & Family of planes

<111> angular bracket represents all body diagonals



[111] square bracket; line, direction

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

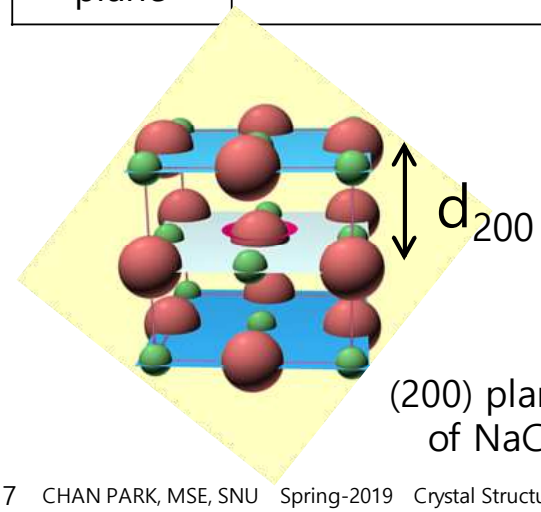


(100) round bracket; planes (Parentheses)

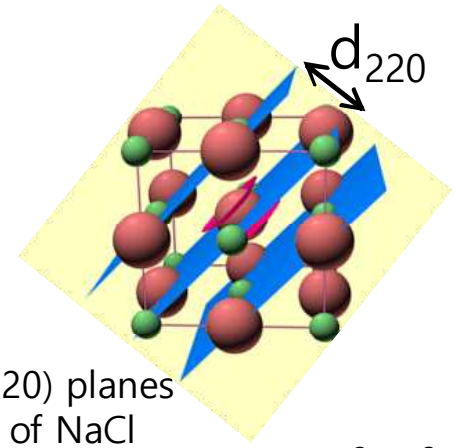
Shackelford 6th ed. Fig 3.29
Shackelford 6th ed. Fig 3.32

[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)



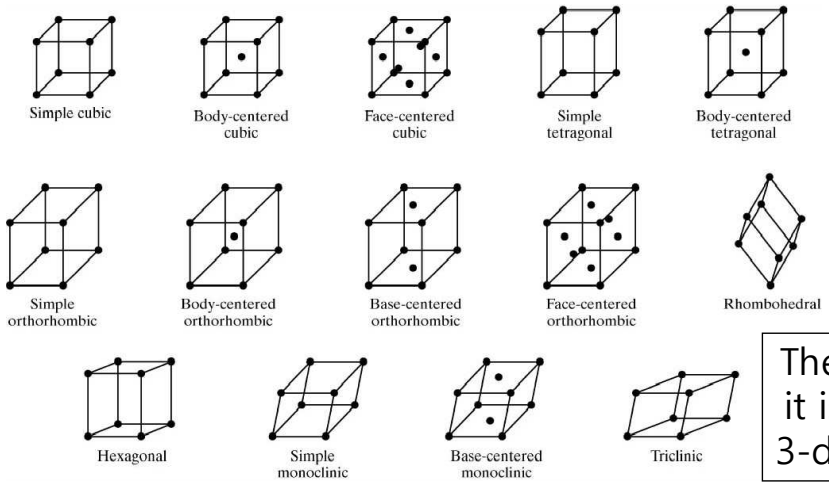
(200) planes of NaCl



(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	$0,0,0;\ \frac{1}{2},\frac{1}{2},0;\ \frac{1}{2},0,\frac{1}{2};\ 0,\frac{1}{2},\frac{1}{2}$

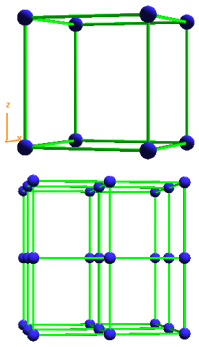
7 crystal systems, 14 Bravais lattices

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

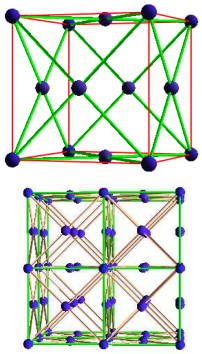
Simple cubic lattices

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

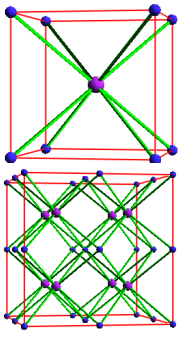
P simple cubic



F face centered cubic

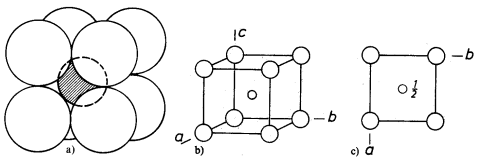


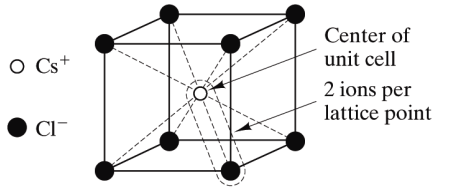
I body centered cubic



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

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

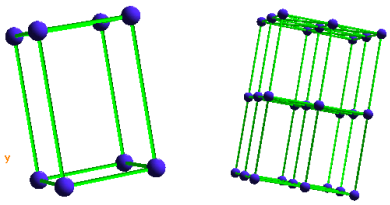




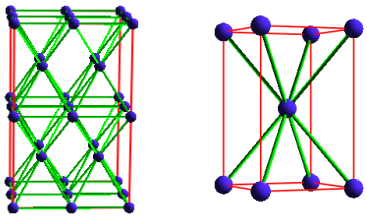
Tetragonal lattices

a1 = a2 ≠ a3
α = β = γ = 90°

P simple tetragonal



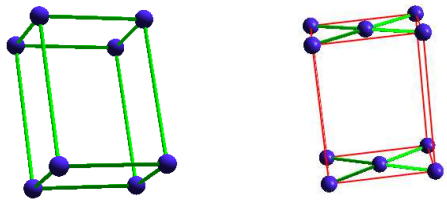
I body centered tetragonal



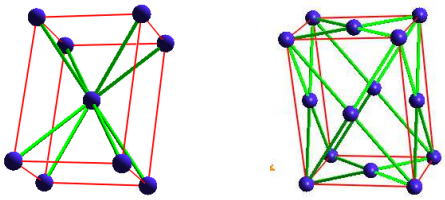
Orthorhombic lattices

a1 ≠ a2 ≠ a3
α = β = γ = 90°

P C



I F



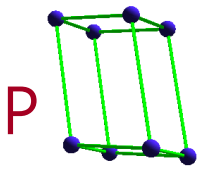
phycomp.technion.ac.il/~sshaharr/cubic.html

Monoclinic lattices

a1 ≠ a2 ≠ a3
α = γ = 90° ≠ β

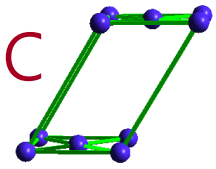
Simple monoclinic

P



Base centered monoclinic

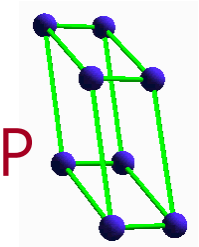
C



Triclinic lattice

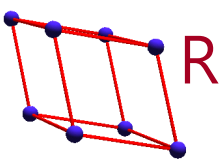
a1 ≠ a2 ≠ a3
α ≠ β ≠ γ ≠ 90°

P



Trigonal (Rhombohedral) lattice

a1 = a2 = a3
α = β = γ < 120° , ≠ 90°

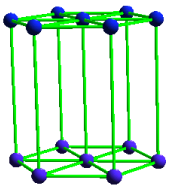


obtained by stretching a cube along one of its axes

Hexagonal lattice

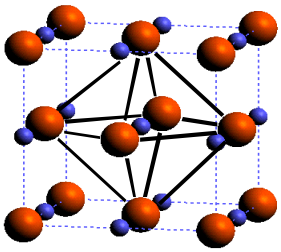
a1 = a2 ≠ a3
α = β = 90° , γ = 120°

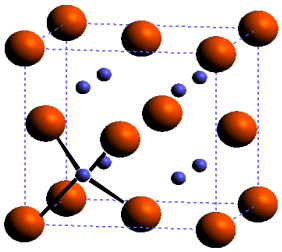
P



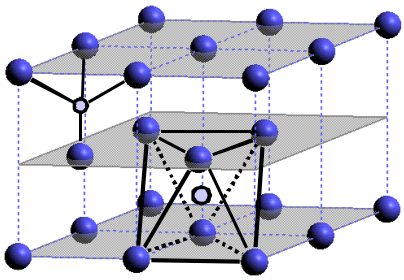
phycomp.technion.ac.il/~sshaharr/cubic.html

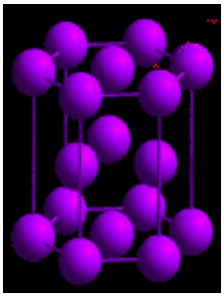
octahedral & tetrahedral interstices
in cubic closed-packed (CCP) lattice



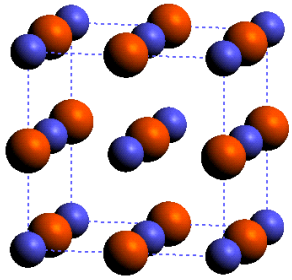


octahedral & tetrahedral interstices in
hexagonal closed-packed (HCP) lattice

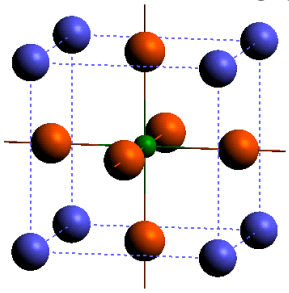


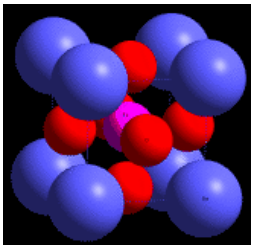


Rock-Salt (NaCl; MgO)



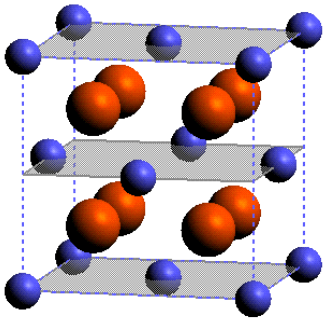
Perovskite

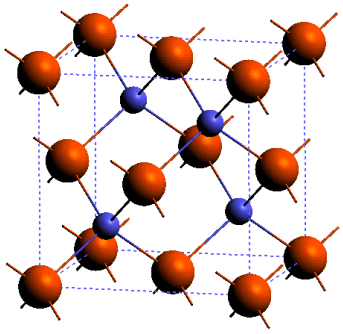




$CaTiO_3$; $BaTiO_3$; $SrTiO_3$; $PbTiO_3$; $PbZrO_3$; $LaAlO_3$

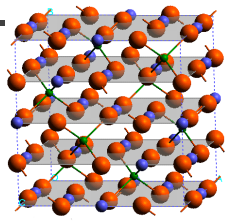
Fluorite
(CaF_2; ZrO_2; CeO_2)





Zinc Blende
(ZnS; CdS; GaAs)

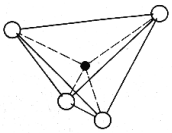
- Spinel (AB_2O_4)
- Oxygen cubic close packing



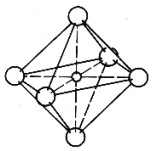
$MgAl_2O_4$

$ZnFe_2O_4$

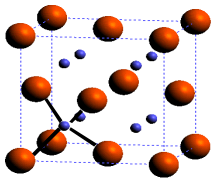
$MnFe_2O_4$



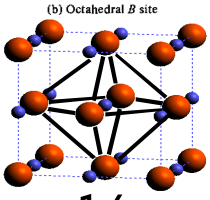
(a) Tetrahedral *A* site



(b) Octahedral *B* site

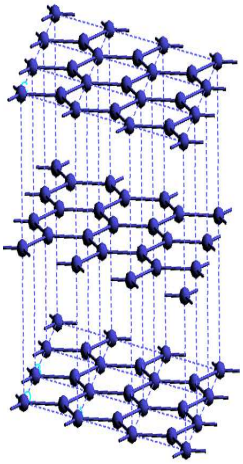


1/8

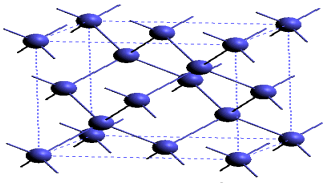


1/2

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+}



Graphite
(Carbon; BN)



Diamond

Symmetry

Point group

Space Group

Symmetry operation & 32 point groups

- Rotation, 1, 2, 3, 4, 6
- Mirror plane
- Center of symmetry (inversion)
- Rotation-inversion, 1bar, 2bar, 3bar, 4bar, 6bar
- Screw axis; rotation + translation
- Glide plane; reflection + translation

Table 8.2. The 32 point groups

Crystal system	Point groups	
Triclinic	$\bar{1}$	1
Monoclinic	2/m	m, 2
Orthorhombic	2/m 2/m 2/m (mmm)	mm2, 222
Tetragonal	4/m 2/m 2/m (4/mmm)	$\bar{4}$2m, 4mm, 422 4/m, $\bar{4}$, 4
Trigonal	$\bar{3}$ 2/m ($\bar{3}$m)	3m, 32, $\bar{3}$, 3
Hexagonal	6/m 2/m 2/m (6/mmm)	$\bar{6}$m2, 6mm, 622 6/m, $\bar{6}$, 6
Cubic	4/m $\bar{3}$ 2/m (m$\bar{3}$m)	$\bar{4}$3m, 432, 2/m$\bar{3}$, 23 ($\bar{m3}$)

neon.mems.cmu.edu/degraef/pg/pg.html#AGM

Table 8.9. Characteristic symmetry elements of the seven crystal systems

Crystal system	Point groups[a]	Characteristic symmetry elements
Cubic	4/m $\bar{3}$ 2/m $\bar{4}$3m, 432, 2/m$\bar{3}$, 23	4 ▲
Hexagonal	6/m 2/m 2/m $\bar{6}$m2, 6mm, 622, 6/m, $\bar{6}$, 6	⬢ or ⏃
Tetragonal	4/m 2/m 2/m $\bar{4}$2m, 4mm, 422, 4/m, $\bar{4}$, 4	1 ■ or 1 ◪ (3 ■ or 3 ◪ ⇒ cubic)
Trigonal	$\bar{3}$ 2/m 3m, 32, $\bar{3}$, 3	1 ▲ (remember that m normal to 3 gives $\bar{6}$ → hexagonal
Orthorhombic	2/m 2/m 2/m mm2, 222	2 and/or m in three orthogonal directions
Monoclinic	2/m m, 2	2 and/or m in one direction
Triclinic	$\bar{1}$ 1	$\bar{1}$ or 1 only

[a] Characteric symmetry elements are underlined.

Ott page 145

Symmetry directions

Xtal systems	Symmetry directions			
Triclinic	a	b	c	$a1 \neq a2 \neq a3, \alpha \neq \beta \neq \gamma \neq 90^o$
Monoclionic	a	b	c	$a1 \neq a2 \neq a3, \alpha = \gamma = 90^o \neq \beta$
Orthorhombic	a	b	c	$a1 \neq a2 \neq a3, \alpha = \beta = \gamma = 90^o$
Tetragonal	c	<a>	<110>	$a1 = a2 \neq a3, \alpha = \beta = \gamma = 90^o$
Trigonal	c	<a>	-	$a1 = a2 = a3, \alpha = \beta = \gamma < 120^o \neq 90^o$
Hexagonal	c	<a>	<210>	$a1 = a2 \neq a3, \alpha = \beta = 90^o, \gamma = 120^o$
Cubic	<a>	<111>	<110>	$a1 = a2 = a3, \alpha = \beta = \gamma = 90^o$

Symmetry operations, Point groups Plane groups, Space groups

- Symmetry operations
  - ✓ Translation
  - ✓ Rotation, Reflection, Inversion
- Shape of the unit cell, symmetry within the unit cell, translation of the unit cell → define a repeating pattern
- Point groups (32) – set of symmetry operations about a point in space (except for translation)
- Plane groups (17) ← (ten 2-D point groups + five 2-D plane lattices)
- Space groups (230) ← (32 point groups + 7 crystal systems)
- Space (plane) lattice; 3(2)-dimensional arrays of points in space that have a basic repeating pattern, a unit cell, that can be translated to fill all space

Space Groups

- 32 point groups - symmetry groups of many molecules and of all crystals so long as morphology is considered
- space group - symmetry of crystal lattices and crystal structures
  - ✓ 14 Bravais lattice
  - ✓ centered lattices - new symmetry operations
  - ✓ reflection + translation
  - ✓ rotation + translation

- Bravais lattice + point group → 230 space groups
  + screw axis
  + glide plane

Space Group

- If translation operations are included with rotation, reflection and inversion → 230 three-dimensional space groups

- Translation operations
  - ✓ Unit cell translations
  - ✓ Centering operations (Lattices) (***A, B, C, I, F***)
  - ✓ Glide planes (reflection + translation) (*a, b, c, n, d*)
  - ✓ Screw axes (rotation + translation) (2_1, 3_1, 3_2)

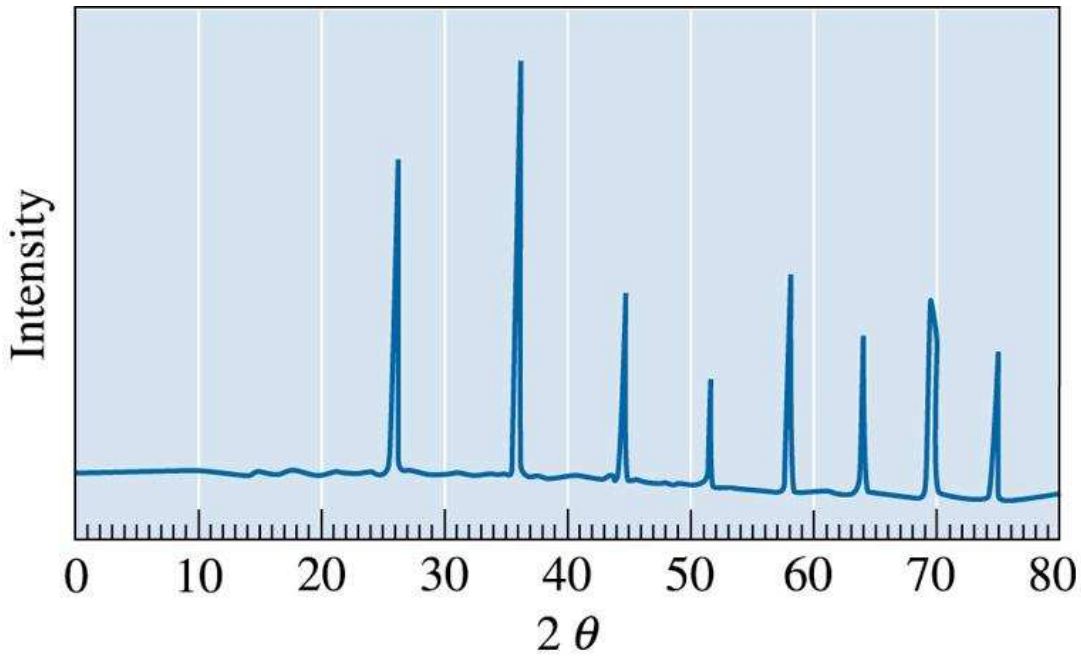
- Hermann-Mauguin symbols (4 positions)
  - ✓ First position is Lattice type (P, A, B, C, I, F or R)
  - ✓ Second, third and fourth positions as with point groups

- 3-D, 14 possible lattices, 7 different axis systems

- The application and permutation of all symmetry elements to patterns in space give rise to **230 space groups** (instead of 17 plane groups) distributed among **14 space lattices** (instead of 5 plane lattices) and **32 point group symmetries** (instead of 10 plane point group symmetries)

- Point group symmetry & space group symmetry has to be distinguished
- Space group symmetry – the way things are packed together and fill space
- Space group – translational component = point group

theta-2theta X-ray diffraction pattern



- Laue class → Pecharsy page 40
- Laue index → Hammond page 138