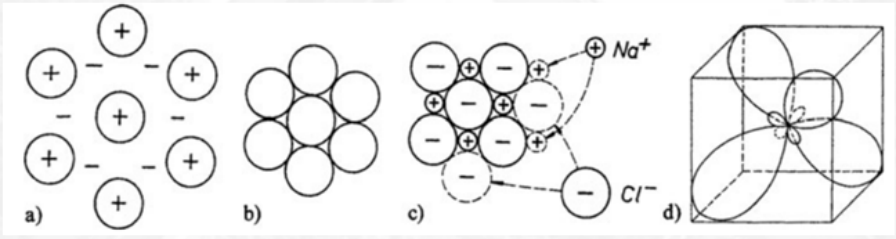
Crystal Chemistry

Read

- Ott Chapter 12 (top of page 258, structure of NiAs, Al2O3 & forsterite 제외)
- Hammond Chapter 1.1~1.6, 1.11.6 , 1.11.1
- Hammond Chapter 1.7~1.9

- Crystal structures of the elements & chemical compounds
- Hard sphere packing (metallic bonding, ionic bonding)
  - ✓ Closest packing – atoms in a structure attempt to arrange themselves in a manner which fills space most efficiently.
  - ✓ Symmetry - atoms in a structure attempt to achieve an environment of the highest possible symmetry.
  - ✓ Interaction - atoms in a structure attempt to achieve the highest coordination.
- Chemical bonding
  - ✓ metallic, ionic, covalent (directional), van der Waals



  - ✓ covalent bonding is directional → principles of closest packing and of highest coordination are rarely fulfilled.

Coordination

- Coordination number; # of nearest neighbors of a central atom or ion
- Coordination polyhedron; polyhedron formed when the nearest neighbors are connected by lines

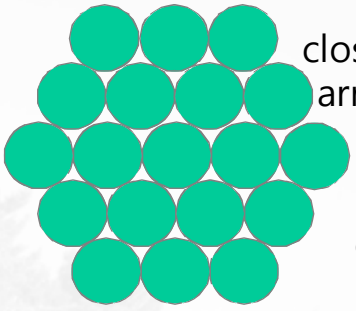
Ott Chap 12

Table 11.1. Important coordination polyhedra

	Coordination	Configuration	Polyhedron or polygon	R_A/R_X [a]	Examples
a)	[12]		Cuboctahedron	1	Cubic closest packing of spheres (Cu, Ne, etc.)
b)	[12]		Disheptahedron	1	Hexagonal closest packing of spheres (Mg, He, etc.)
c)	[8]		Cube	0,73	$Cs^{[8]}Cl$ $Ca^{[8]}F_2$
d)	[6]		Trigonal prism	0,53	$AlB_2^{[6]}$ [b]
e)	[6]		Octahedron	0,41	$Na^{[6]}Cl$ $Ti^{[6]}O_2$ $Pt^{[6]}Cl_6^{2-}$
f)	[4]		Square	0,41	$Pt^{[4]}Cl_4^{2-}$
g)	[4]		Tetrahedron	0,23	$Zn^{[4]}S$ $Si^{[4]}O_2$ $S^{[4]}O_4^{2-}$
h)	[3]		Equilateral triangle	0,15	$C^{[3]}O_3^{2-}$ $N^{[3]}O_3^{-}$

Metallic crystal system

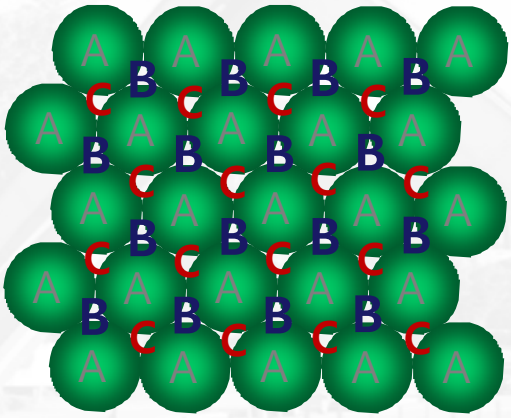
- Close packing crystal structure
  - How can we stack metal atoms to minimize empty space?



closed packed atomic arrangement in 2-D

can make 3-D structures by stacking the 2-D layers

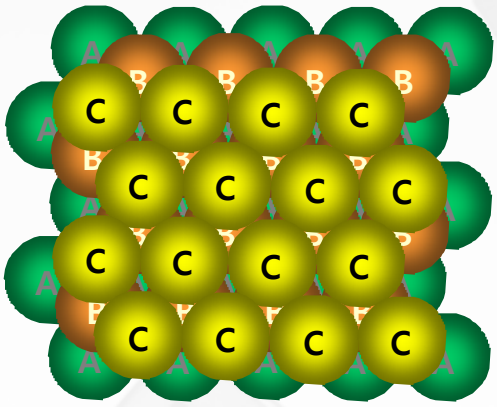
- Stacking sequence

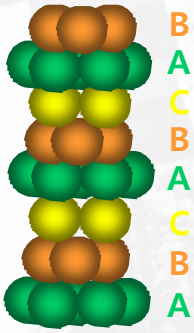


Metallic crystal system

- A – B – C – A stacking

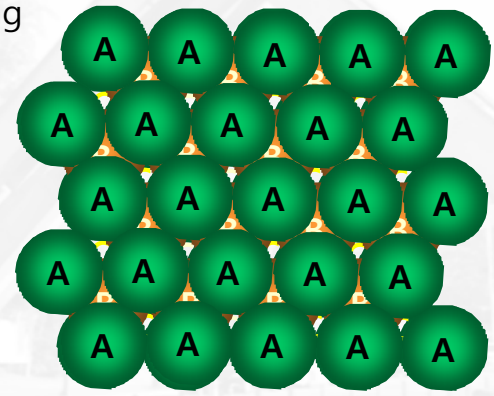
→ CCP (Cu-type)

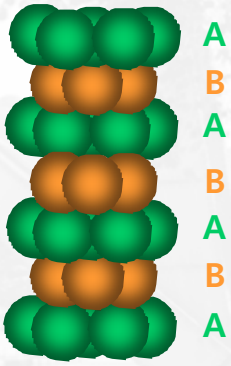




- A – B – A – B stacking

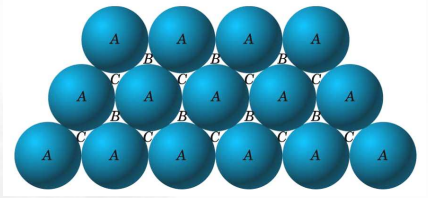
→ HCP (Mg-type)

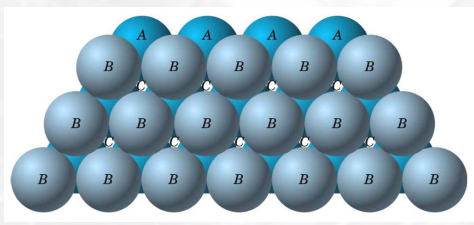




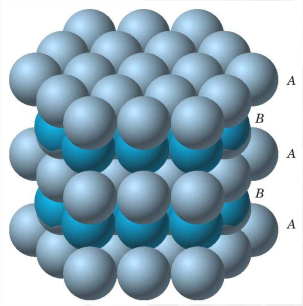
Structures of Metal

- Bonding forces are not directional
- Two ways to get max # of coordination (12)

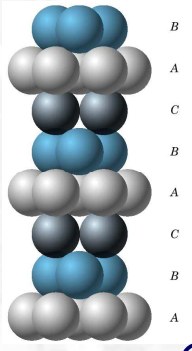


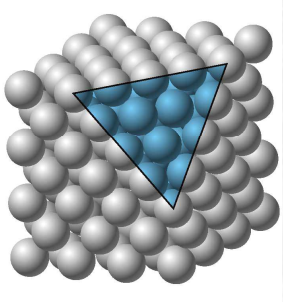


ABAB…
ABCABC…

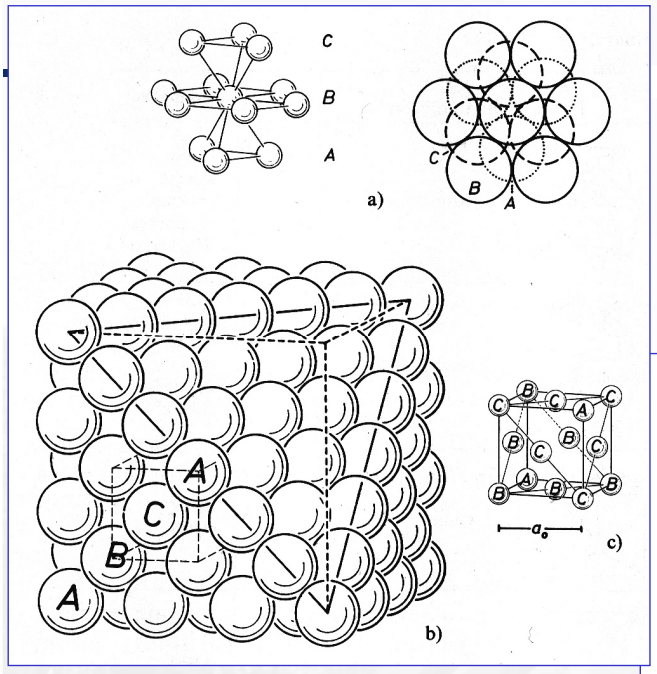


HCP

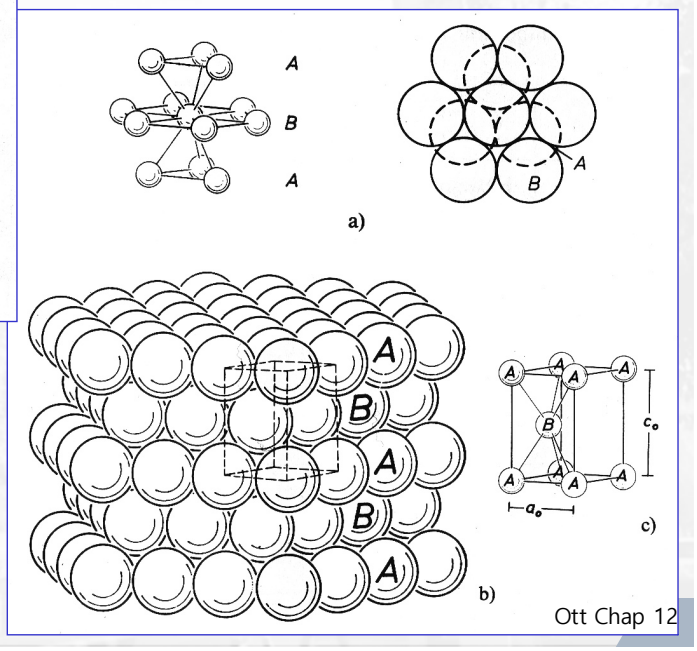




CCP



Cubic Close Packing (CCP)
Cubic F-lattice
Cu-type
F 4/m $\bar{3}$ 2/m (225)

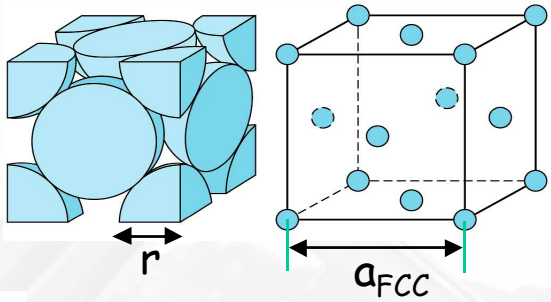


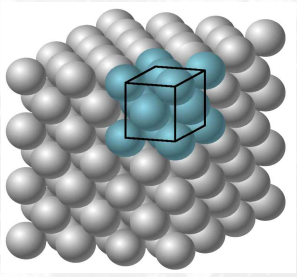
Hexagonal Close Packing (HCP)
Hexagonal P-lattice
Mg-type
P 6_3/m 2/m 2/c (194)

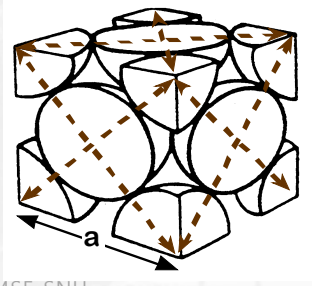
Ott Chap 12

CCP - cubic F lattice

- Close packed directions are edge diagonals <110>
- 4 atoms / unit cell (1 + 6 x 1/2) $a_{FCC} = 4r/2^{1/2}$
- Highest density plane {111} Coordination # = 12
- Cu, Al, Ag, Au, etc.
- Close-packed direction; length = $4r = 2^{1/2}a$
- Atomic Packing Factor (FCC) = 0.74



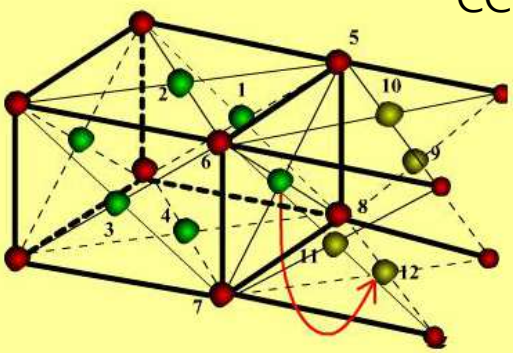




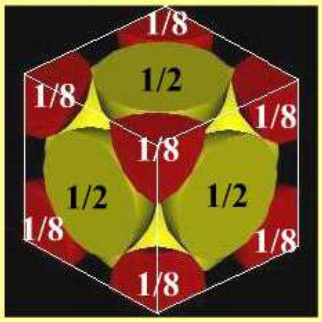
$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{4 \cdot \frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3}{a^3}$$

Its neighbors are shown as follows:

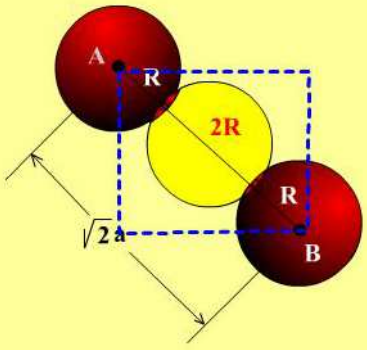
CCP



Therefore, the total number of atoms inside a FCC unit cell is (8 x 1/8) + (6 x 1/2) = 4.



We can therefore equate the right sides of the equalities.



$AB = \sqrt{2}\,a$

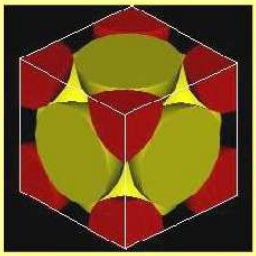
$AB = 4R$

$4R = \sqrt{2}\,a$

or

$a = \frac{4R}{\sqrt{2}}$

Question: Determine the APF for a FCC unit cell.



Hint

A	B	C	D
50%	68%	74%	82%

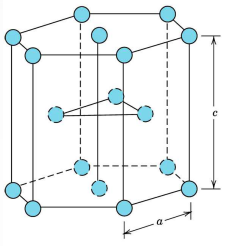
Continue

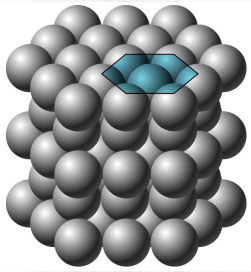
1-Find the volume of four atoms inside the cell.2- Find the volume of the unit cell (you need the relationship between a and R for this.3- Find APF.

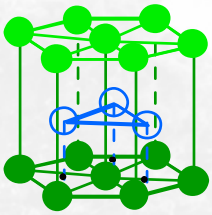
Hexagonal Close-Packed (HCP)
hexagonal P lattice

- ABAB… Stacking Sequence
- Close packed directions <100>
- 2 atoms / unit cell (1 + 4 x 1/6 + 4 x 1/12) (or 6 atoms/unit cell)
- $a_{HCP} = 2r$, $c_{HCP} = 2\,(2/3)^{1/2}a = 1.633a$
- Highest density plane {0001}
- Mg, Cd, Mn, Ti, Zn, etc.
- APF (HCP) = 0.74

CN = 1



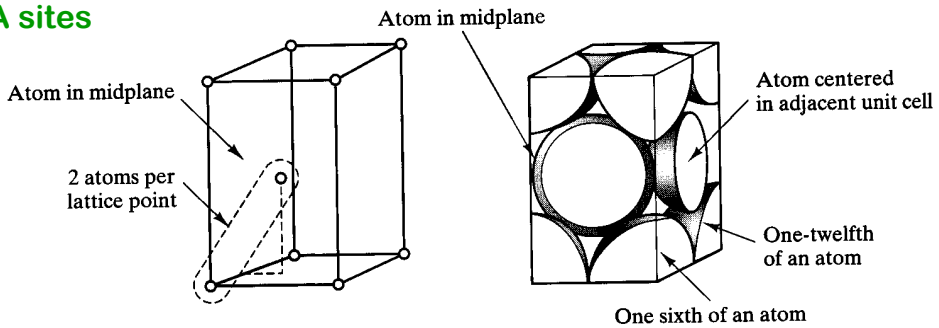


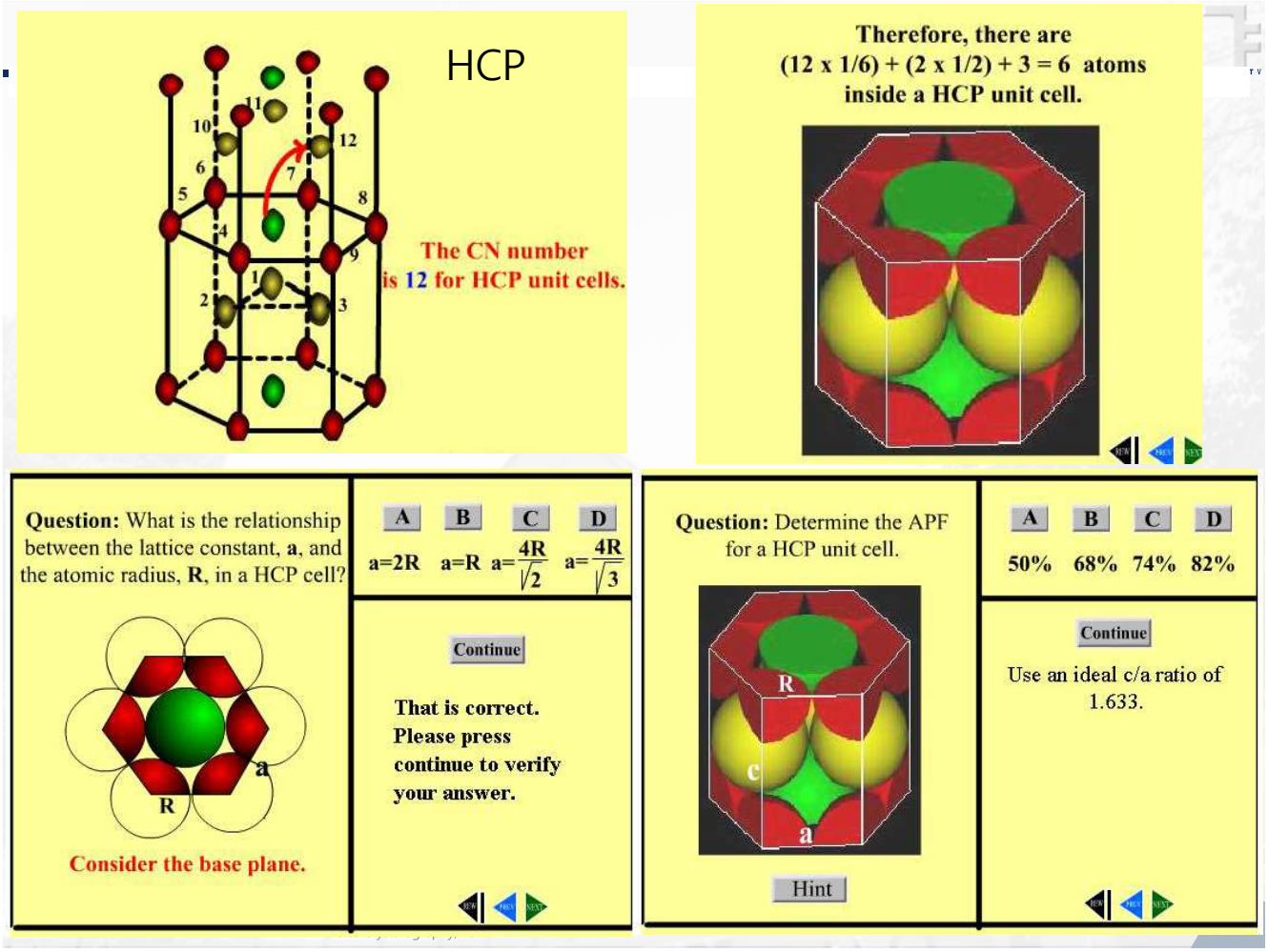


A sites

B sites

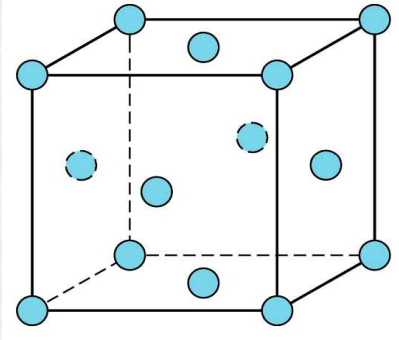
A sites

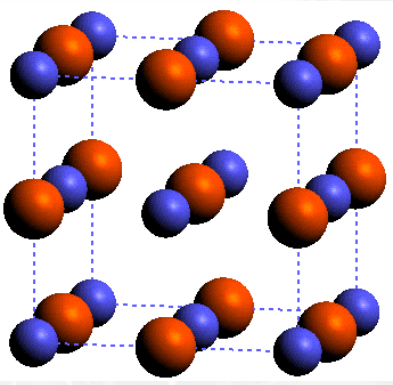




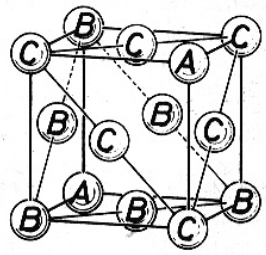
ccp ≡ fcc ?

- Not exactly
- ccp is a special case of fcc in which the atoms are all in contact along the face diagonals



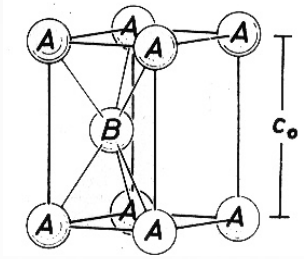


CCP



- All atoms are identical

HCP



- All atoms in A layer are identical
- All atoms in B layer are identical
- A & B atoms are equivalent but not identical

	Cu ccp	Mg hcp
Lattice + basis	Cubic F 0,0,0	Hexagonal P 0,0,0; $\frac{2}{3},\frac{1}{3},\frac{1}{2}$
Space group + Positions occupied	F 4/m $\bar{3}$ 2/m (a) 0,0,0	P 6_3/m 2/m 2/c (c) 0,0,0; $\frac{2}{3},\frac{1}{3},\frac{1}{2}$

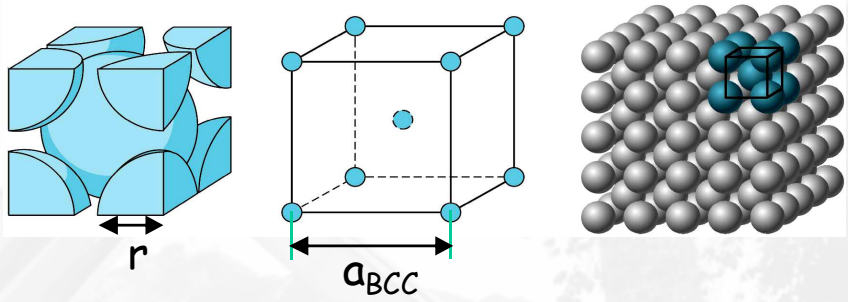
- Objects are equivalent to one another if they can be brought into coincidence by the application of a symmetry operation.
- If no symmetry operation except lattice translation is involved, the objects are said to be "equivalent by translation" or "identical" (Ott page 64)

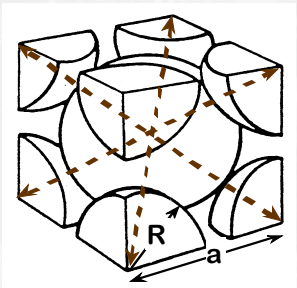
Table 11.2. Data for the three most important metal structure types, Cu, Mg and W, and for α-Po

	Cu ccp	Mg hcp	W bcc	α-Po sc
Lattice + basis	Cubic F 0,0,0	Hexagonal P 0,0,0; $\frac{2}{3},\frac{1}{3},\frac{1}{2}$	Cubic I 0,0,0	Cubic P 0,0,0
Space group + Positions occupied	F 4/m $\bar{3}$ 2/m (a) 0,0,0	P 6_3/m 2/m 2/c (c) 0,0,0; $\frac{2}{3},\frac{1}{3},\frac{1}{2}$	I 4/m $\bar{3}$ 2/m (a) 0,0,0	P 4/m $\bar{3}$ 2/m (a) 0,0,0
Coordination number	[12]		[8]	[6]
Atomic radii	$\frac{1}{4}a_0\sqrt{2}$	$\frac{1}{2}a_0$	$\frac{1}{4}a_0\sqrt{3}$	$\frac{1}{2}a_0$
Packing efficiency	0.74		0.68	0.52
Further examples	Ag, Au Ni, Al Pt, Ir Pb, Rh	Mg (1.62) Ni (1.63) Ti (1.59) Zr (1.59) Be (1.56) Zn (1.86)	Mo, V Ba, Na Zr, Fe	–
	225, Fm $\bar{3}$ m	194, $P6_3/mmc$		

Body centered cubic (BCC), W-type, cubic I-lattice

- Close packed directions are cube diagonals <111>
- 2 atoms / unit cell (1 + 8 x 1/8) $a_{BCC} = 4r/3^{1/2}$
- Highest density plane {110} Coordination # = 8
- Close-packed direction; length = 4r = $3^{1/2}a$
- APF (BCC) = 0.68

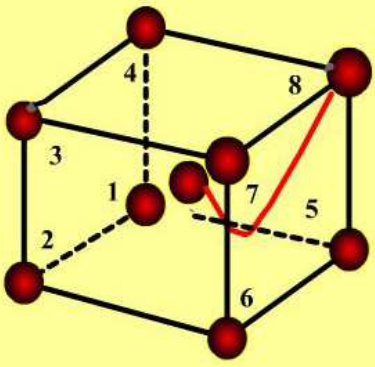




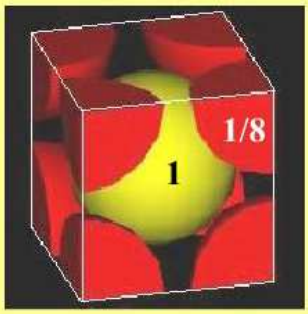
$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{2 \cdot \frac{4}{3}\pi(\sqrt{3}a/4)^3}{a^3}$$

BCC

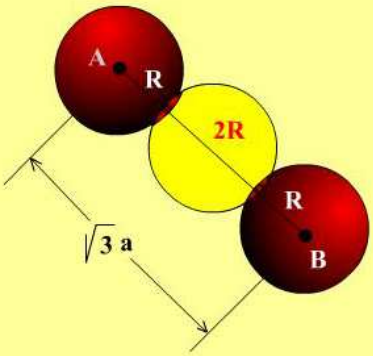
Each atom has eight neighbors.



Therefore, the total number of atoms inside a BCC unit cell is (8 x 1/8) + 1 = 2.



We can therefore equate the right sides of the equalities.



$AB = \sqrt{3}\,a$

$AB = 4R$

$4R = \sqrt{3}\,a$

or

$a = \frac{4R}{\sqrt{3}}$

Note that R^3 terms cancel out and APF will reduce to a constant.

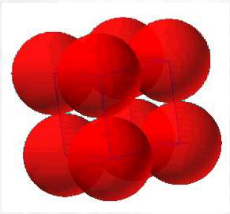
$$APF = \frac{2\,(4/3\,\pi R^3)}{4^3 R^3 / \sqrt{3}^3}$$

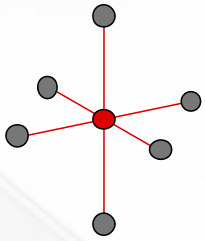
APF = 0.68

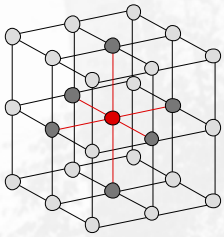
This means that 68% of the unit cell is filled with matter and 32% is empty space.

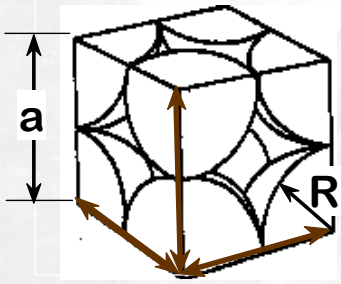
Simple cubic structure (SC), cubic P-lattice

- Rare due to poor packing (only Po has this structure)
- Close-packed directions are cube edges
- Coordination # = 6
- APF (simple cubic structure) = 0.52









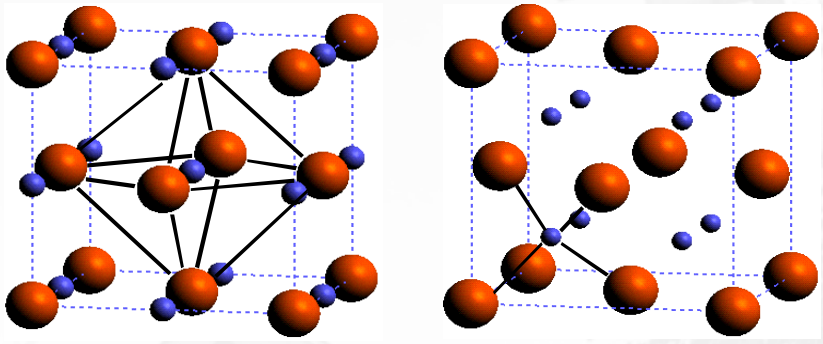
close-packed directions

contains 8 x 1/8 =
1 atom/unit cell

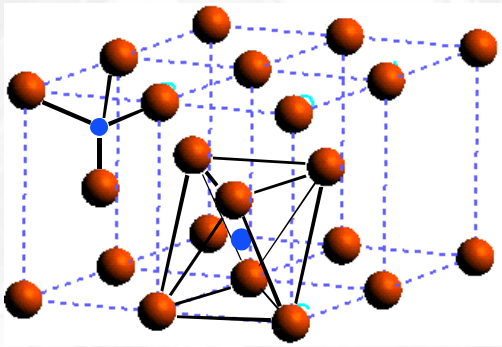
$$\text{APF} = \frac{\frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}}}{\frac{\text{volume}}{\text{unit cell}}} = \frac{1 \cdot \frac{4}{3}\pi (0.5a)^3}{a^3}$$

Octahedral & tetrahedral interstices

CCP



HCP



Interstitial positions in FCC & HCP structure

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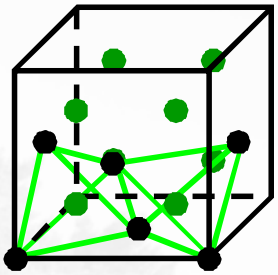
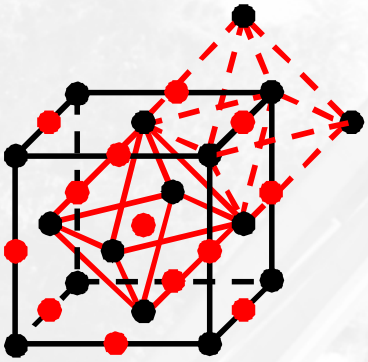
FCC

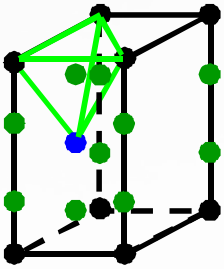
Tetrahedral sites ; 8

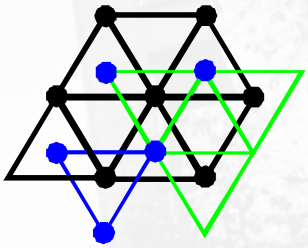




Octahedra sites ; 4

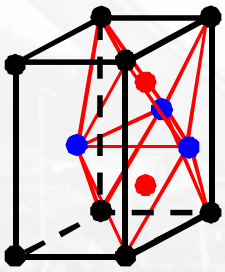
HCP

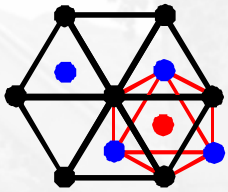




Tetrahedral sites ; 4

$(0, 0, \frac{3}{8})\ (0, 0, \frac{5}{8})\ (\frac{1}{3}, \frac{2}{3}, \frac{1}{8})\ (\frac{1}{3}, \frac{2}{3}, \frac{7}{8})$





Octahedral sites ; 2 $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})\ (\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$

Interstitial sites

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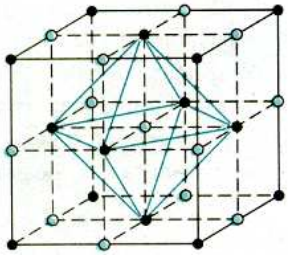
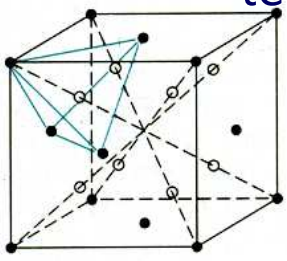
octahedral

tetrahedral

4

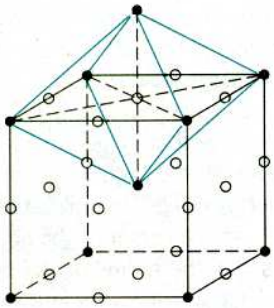


FCC

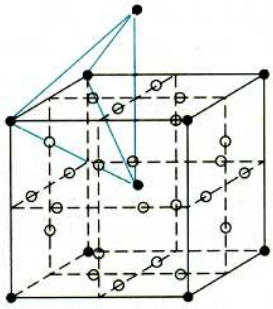


8

6



BCC



12

Structure – Property in metals

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- High electrical & thermal conductivity ← electron clouds between atom (ion) cores can move freely.

- Plastic deformation – related to # slip system

  → ductile vs. brittle

Structure of metal

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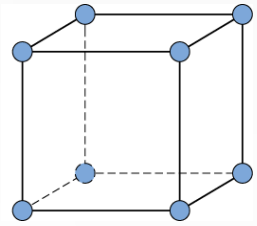
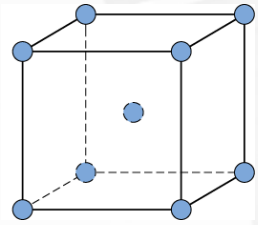
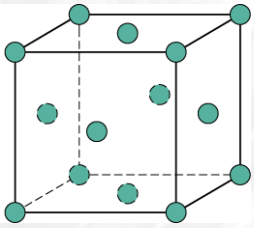


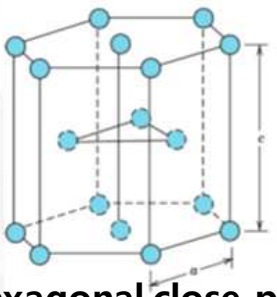
Simple cubic
Po



Body centered cubic
Cr, W, Fe (α), Ta, Mo



Face centered cubic
Al, Cu, Au, Pb, Ni, Pt, Ag

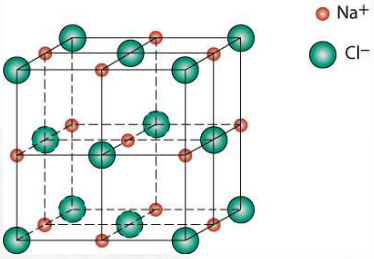


Hexagonal close packing
Cd, Mg, Ti, Zn

Structure of ceramics

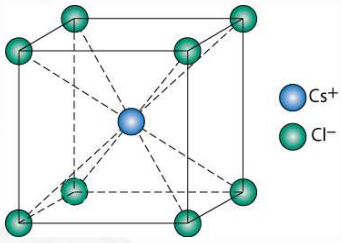
Rock Salt structure

NaCl, CaO, MgO, KCl, PbS



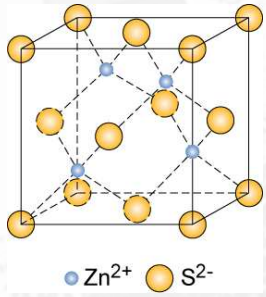
CsCl structure

CsCl, CsI



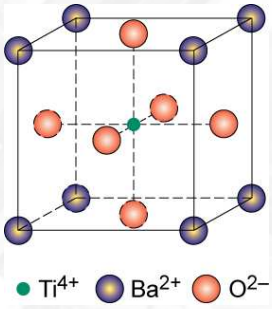
Zinc Blende structure

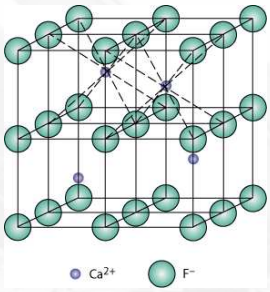
ZnO, ZnS, SiC



Perovskite structure

$CaTiO_3$, $BaTiO_3$, $SrTiO_3$, $PbTiO_3$, $LaMnO_3$



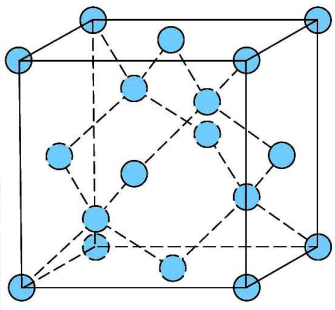


Fluorite structure

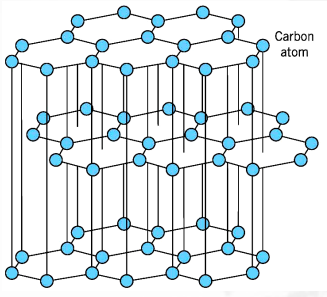
UO_2, ThO_2, ZrO_2, CeO_2

Structure of carbon

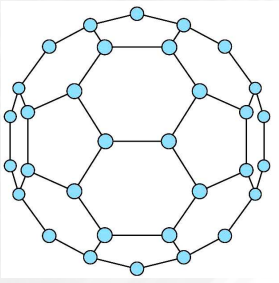
- Diamond (Si, Ge)



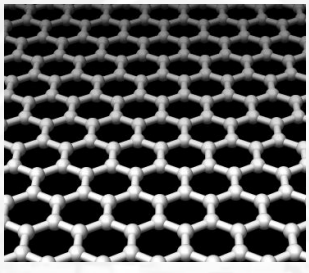
- Graphite (BN)



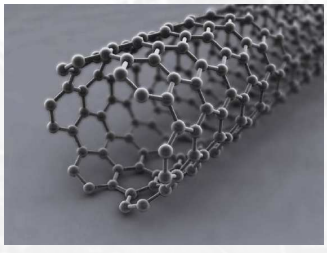
- Fullerene



- Graphene



- Carbon Nanotube

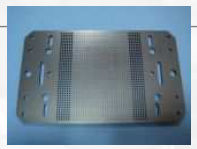


Carbon-diamond

- Extremely hard
- Very low electrical conductivity
- Unusually high thermal conductivity
- Optically transparent and high index of refraction
- Metastable carbon polymorph
- Synthetic diamonds, from 1950's
  - ✓ Thin film of diamond (thickness<1um)
  - ✓ Polycrystalline
  - ✓ Applications: surface of drills, dies, bearings, knifes, saws,---

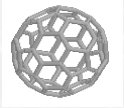
Carbon - graphite

- More stable than diamond
- Strong bonding inside layer
- Weak bonding between layers
  - → Planes slide easily, good lubricant
- High electrical conductivity
- High strength and good chemical stability at high temp
- High resistance to thermal shock
- Applications; heating elements for electric furnace, electrodes, high temperature refractories and insulations



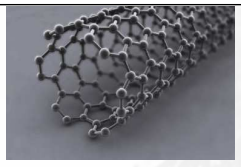
Carbon – fullerene

- Discovered in 1985
- Nobel prize (chemistry) in 1996
- Buckminster fullerenes (buckyball)
- A single molecule of 60 carbon atoms
  - ✓ Like a soccer ball C_{60}
- A hollow spherical cluster of 60 atoms (20 hexagons and 12 pentagons)

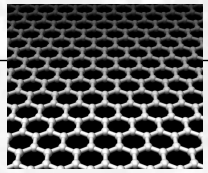


Carbon - nanotube

- A single sheet of graphite rolled into a tube
- Tube diameter < 100 nm
- Each nanotube is a single molecule
- Multiple-walled or single-walled nanotubes
- Strong and stiff, and relatively ductile



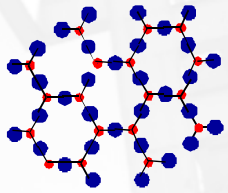
Carbon - Graphene



- Nobel prize (physics) in 2010
- one-atom-thick planar sheet of sp2-bonded carbon atoms
- basic structural element of graphite, carbon nanotube and fullerene
- 200 times stronger than steel → one of the strongest materials in the world

Structure of SiO_2

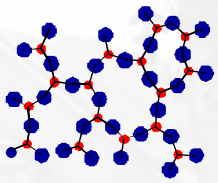
1. **Crystalline** materials
   - ✓ atoms pack in periodic, 3D arrays
   - ✓ Metals, many ceramics, some polymers



crystalline SiO_2 = **quartz**

2. **Noncrystalline** materials
   - ✓ atoms have no periodic packing
   - ✓ complex structures
   - ✓ rapid cooling

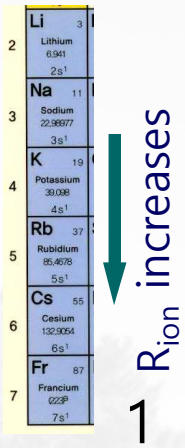
Si Oxygen



noncrystalline SiO_2 = **fused silica**

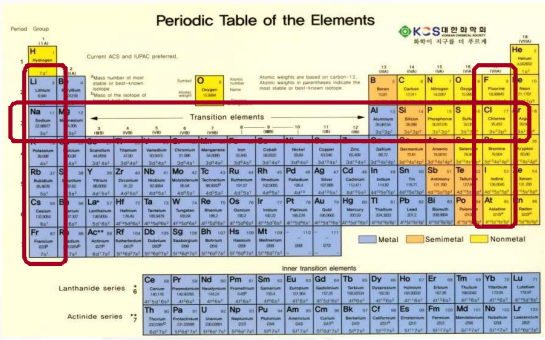
➢ "**Amorphous**" = Noncrystalline

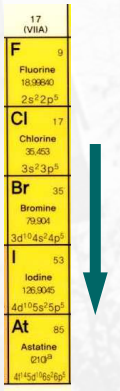
Ionic Radius (R_{ion})



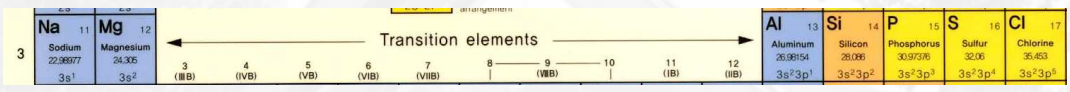
R_{ion} increases

1





R_{ion} increases

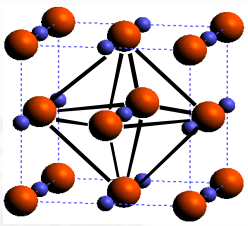


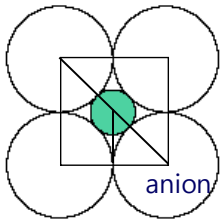
2 R_{ion} ↓ as nuclear charge ↑, when the # of e' is same.

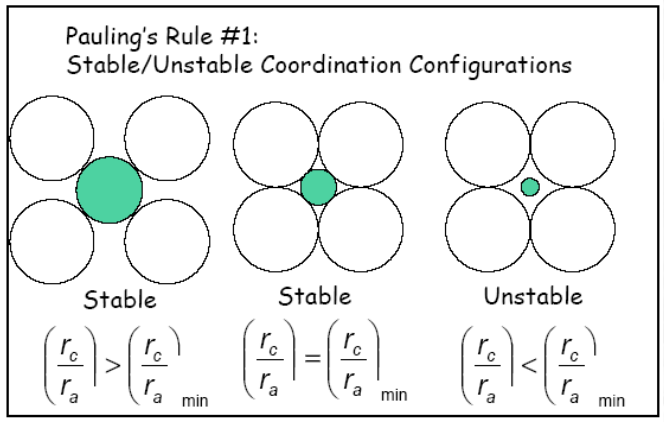
3 $R_{ion}\ (Mn^{+2}) > R_{ion}\ (Mn^{+3}) > R_{ion}\ (Mn^{+4})$

Octahedral coordination

- r(cation) + r(anion) = √2 r(anion) → r(cation)/r(anion) = √2-1 = 0.41
- Octahedron coordination is stable if r(cation)/r(anion) ≥ 0.41



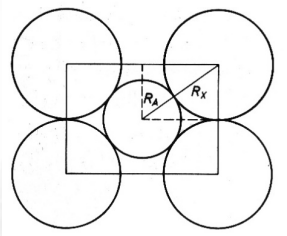




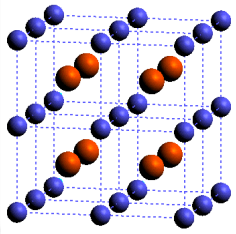
- NaCl (Rock Salt)
  - ✓ r(cation)/r(anion) = 0.54
  - ✓ anions - ccp
  - ✓ cations - octahedral sites
  - ✓ Cubic F lattice
  - ✓ Basis Na^+ 0,0,0; Cl^- ½,0,0
- $MgAl_2O_4$ ($MgO \cdot Al_2O_3$) (spinel)
  - ✓ anions - ccp
  - ✓ Mg^{2+} ⅛ of tetrahedral sites
  - ✓ Al^{+3} ½ of octahedral sites

Cubic coordination

- r(cation) + r(anion) = √3 r(anion) → r(cation)/r(anion) = √3-1 = 0.73
- 0.41 < r(cation)/r(anion) < 0.73 → octahedral coordination stable
- r(cation)/r(anion) > 0.73 → cubic coordination stable

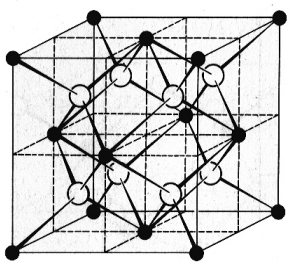


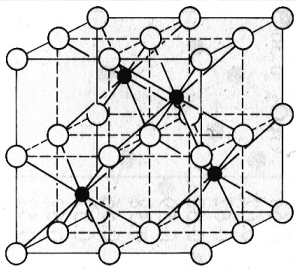
Section thru a cube parallel to (110)



Cesium Chloride (CsCl)

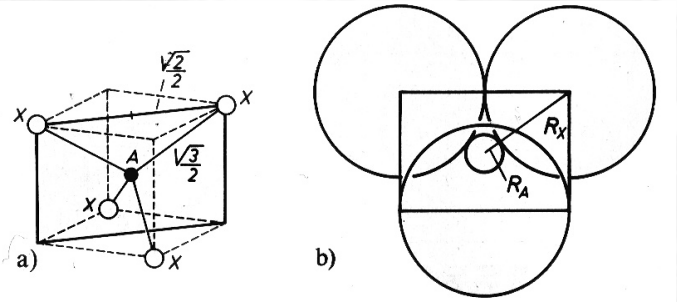
Ca - ccp F - tetrahedral sites	Fluorite CaF_2
S - ccp Li - tetrahedral sites	Antifluorite Li_2S



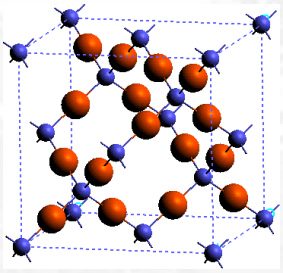


Tetrahedral coordination

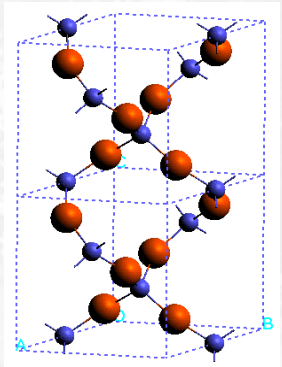
- r(cation) + r(anion) = √3a/2 (half the body diagonal)
- r(anion) = √2a/2 (half the face diagonal)
- [r(cation) + r(anion)]/r(anion) = √3/√2 → r(cation)/r(anion) = 0.225
- 0.225 < r(cation)/r(anion) < 0.41 → tetrahedral coordination stable



(110 section

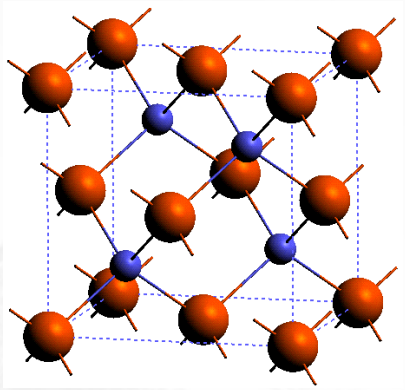


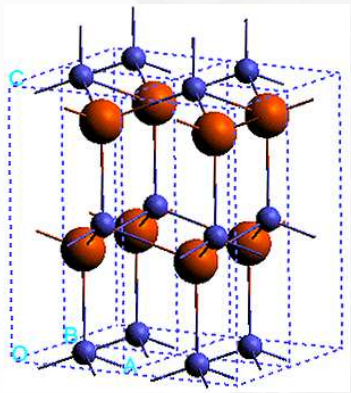
SiO_2
Crystobalite



SiO_2
Quartz

Tetrahedral coordination





Zinc Blende

(ZnS; CdS; GaAs)

F $\bar{4}$ 3m

Cubic F lattice

Basis S @ 0,0,0; Zn @ ¼,¼,¼

S ccp & Zn @ half tetrahedral sites

Wurtzite

(ZnS; CdS)

$P6_3mc$

Hexagonal P lattice

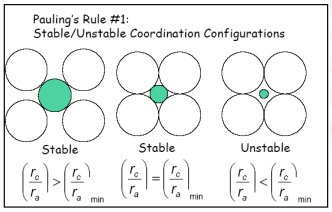
Basis S @ 0,0,0; ⅔,⅓,½

Zn @ 0,0,½+z; ⅔,⅓,z (z ≈ ⅛)

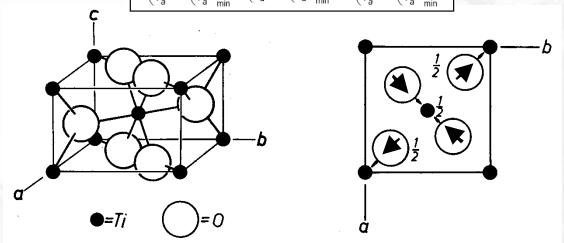
S hcp & Zn @ half tetrahedral sites

Pauling's rules

- Empirical relationships between ion properties (size and valence) and crystal packing/structures



- **Rule 1**: Predict anion coordination polyhedron from the radius ratio: r_{cation}/r_{anion}
  - ✓ Based on geometries of hard spheres
  - ✓ Calculate the *minimum* ratio possible for each coordination polyhedron

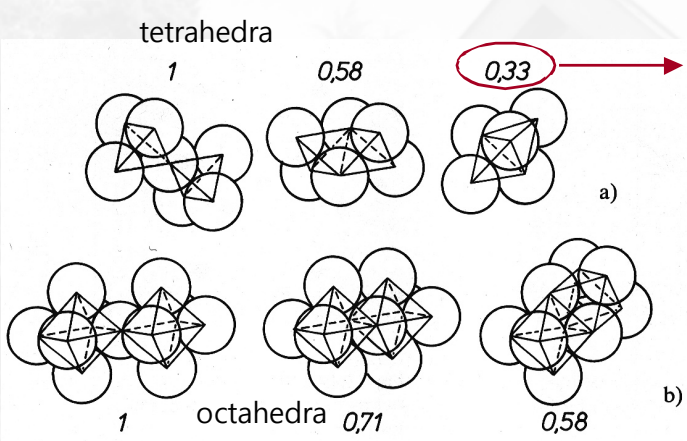


- **Rule 2**: Predict anion CN from valences and cation CN
  - ✓ Electrostatic bond strength ≈ valence/CN
  - ✓ e.g., TiO_2: from Pauling's 1st law: $rTi^{4+}/rO^{2-} \approx 0.61/1.40 = 0.44$
  - ✓ $CN(Ti^{4+})=6$

$$\frac{Ti^{4+}\ Charge}{Ti^{4+}\ CN} = \frac{4}{6} = \frac{O^{2-}\ charge}{O^{2-}CN} = \frac{2}{O^{2-}CN},\ O^{2-}\ CN = 3$$

Pauling's rules (continued)

- **Rule 3**: Stable structures prefer that cations are kept far apart (avoid cation - cation repulsion). (see page 261 of Ott)
  - ✓ Neighboring polyhedra will share corners before edges and faces.
- **Rule 4**: Stable crystals have minimum number of structural sub-units.
  - ✓ simpler structures have lower energies
  - ✓ difficult to pack coordination polyhedra of different sizes



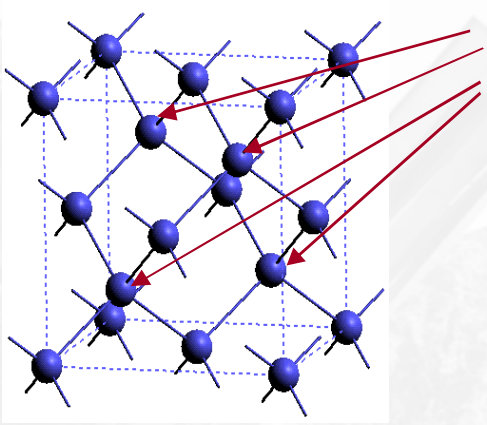
#'s ; relative distances between the two coordinated cations

The closer the cations, the ↑ is the Coulombic repulsion, the ↓ the stability of the structure.

The effect is greater when the cations have higher charge.

Covalent structures

- Directional bonding → hard sphere packing model is not suitable
- APF of diamond is not high
- Bonding in diamond is very strong → great hardness



4 sp^3 orbitals

Diamond

$Fd\bar{3}m$

Cubic F lattice

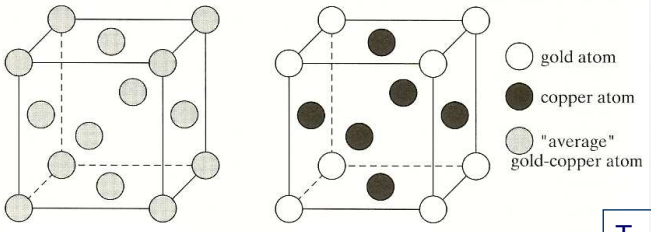
Basis; C @ 0,0,0 and ¼,¼,¼

Isotypes, solid solutions & isomorphism

- **Isotypes** – crystals which have the same crystal structure
  - ✓ NaCl (ionic) & PbS (metallic), Cu (metallic) & Ar (van der Waals)
- **Solid solution**
  - ✓ A solid that consists of two or more elements atomically dispersed in a single-phase structure
  - ✓ Crystals in which one or more positions are occupied by a statistical distribution of two or more different atom types (Ott)
  - ✓ (Ag, Au), K(Cl, Br), $(Mg, Fe)_2SiO_4$
- Conditions needed for extensive solid solubility of one element in another (**Hume-Rothery rules**)
  - ✓ < 15% difference in atomic radii
  - ✓ Same crystal structure & same valence
  - ✓ Similar electronegativities
- **Isomorphous** – when crystals of the same structure (isotypic crystals) form solid solutions with one another, the structure is said to be ISOMORPHOUS

Order-Disorder

AuCu3



Ordered structure

T > ~390 °C

Cubic F

solid solution

disordered

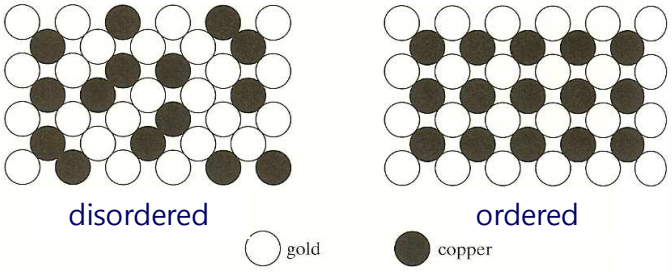
ordered

T < ~390 °C

Cubic P

superstructure

Basis 3Cu + Au

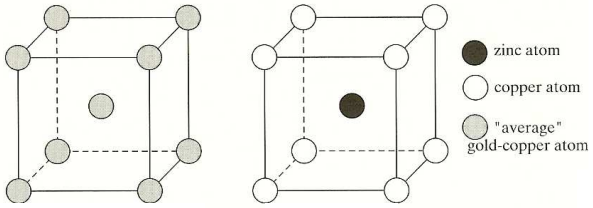


disordered ordered

CuZn

T > ~460 °C

Cubic I



disordered ordered

T < ~460 °C

Cubic P

superstructure

Basis Cu + Zn

Cullity page 316, Hammond p244

Polymorphism

- "polymorphism" - The same atoms can have more than one crystal structure
- different crystalline modifications of the same chemical substance
- Many solid substances can produce different crystal structures of the same chemical constitution → polymorphism

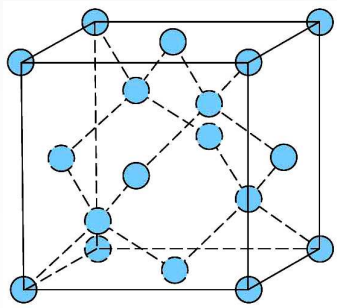
- C – diamond, graphite, nano tube, graphene
- Ni – ccp & hcp
- Zr – hcp & bcc
- ZnS – Zinc Blende & Wurtzite

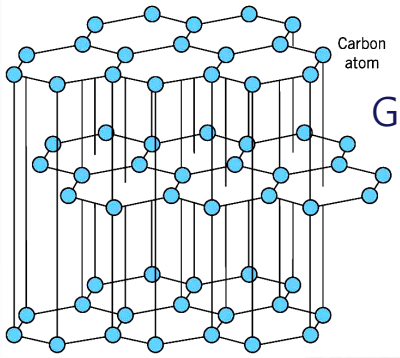
- Interconversion of polymorphs = structure transformation

Cullity

Polymorphism > carbon

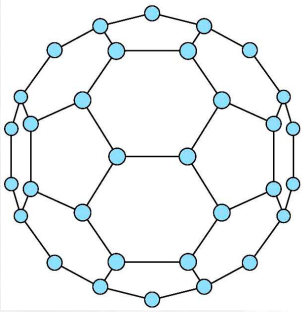
Diamond



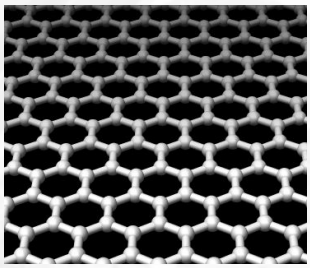


Graphite

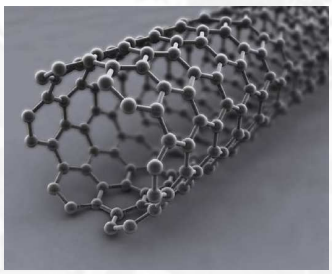
Fullerene



Graphene

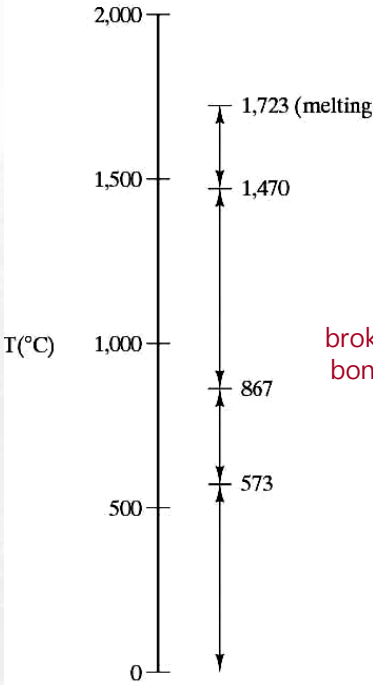


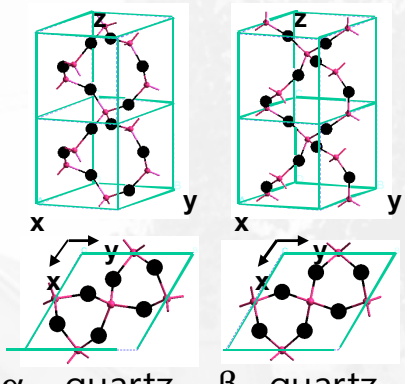
Carbon Nanotube



Polymorphism > SiO_2

	Xtallographic form	Bravais Lattice
	cristobalite	fcc
	reconstructive	
	tridymite	hexagonal
broken bonds	reconstructive	
	β– quartz	hexagonal
	displacive (Rotation only, no broken bonds)	
	α – quartz	hexagonal



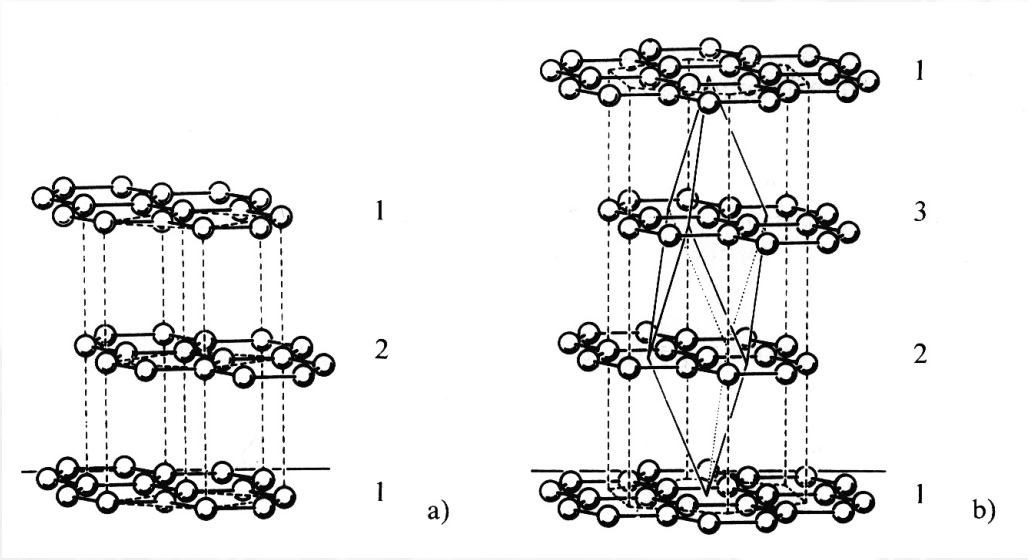


α – quartz β– quartz

Structure transformations; interconversion of polymorphs

- Transformations of 1st coordination – transformation which has change of coordination numbers
- Transformations in 2nd coordination – transformation in which there is no change in the arrangement of nearest neighbors, but which has change in the arrangement of next-nearest neighbors
  - ✓ Displacive – polyhedra undergoes rotation only, no bonds are broken (low-quartz to high-quartz transformation)
  - ✓ Reconstructive – bonds are broken (high quartz to tridymite)
- Order-disorder transformation
  - ✓ (Au, Cu)
- Transformations involving changes in type of bonding
  - ✓ Carbon – graphite, diamond, fullerenes

Polytypes of graphite structure



2H-polytype
Hexagonal unit cell

3R-polytype
Rhombohedral unit cell

See Hammond 1.11.6 (was excluded but included here)

todos

- Read
  - ✓ Ott Chapter 12 (top of page 258, structure of NiAs, Al_2O_3 & forsterite 제외)
  - ✓ Hammond Chapter 1.1~1.6, 1.11.6 , 1.11.1
  - ✓ Hammond Chapter 1.7~1.9

- Crystal Chemistry HW (due in 1 week)
  - ✓ Ott chapter 12 --- 1, 2, 3, 4, 5, 6, 7, 8, 10, 12
  - ✓ Hammond chapter 1 --- 1, 2, 4, 5