Oct. 8, 2021

Bio-integrated Materials Science
(Online Lectures)

Metals and Ceramics
Lecture 2

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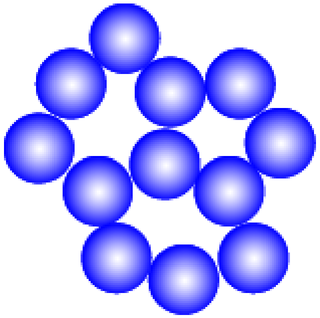
Structures of Metals & Ceramics

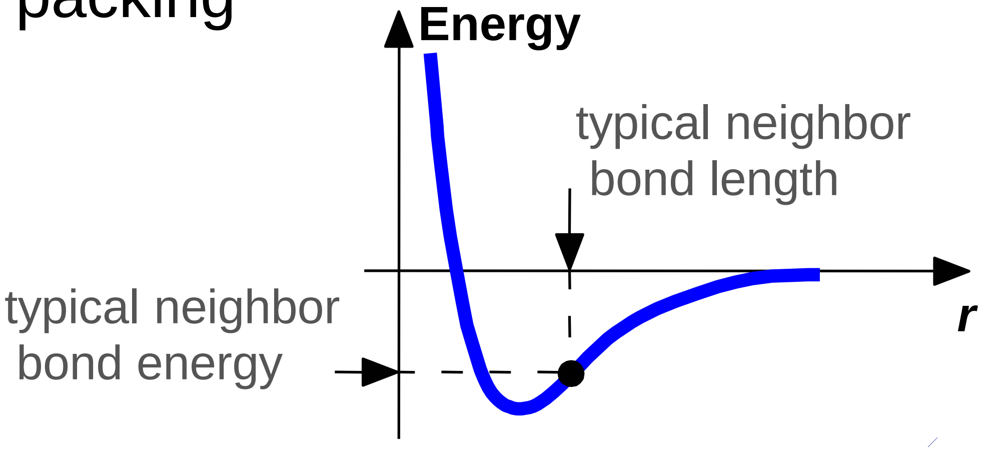
ISSUES TO ADDRESS...

- What is the difference in atomic arrangement between crystalline and noncrystalline solids?
- What features of a metal's/ceramic's atomic structure determine its density?
- How do the crystal structures of ceramic materials differ from those for metals?
- Under what circumstances does a material property vary with the measurement direction?

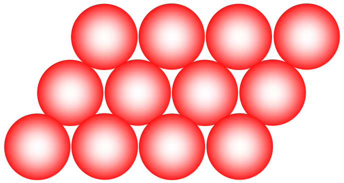
Energy and Packing

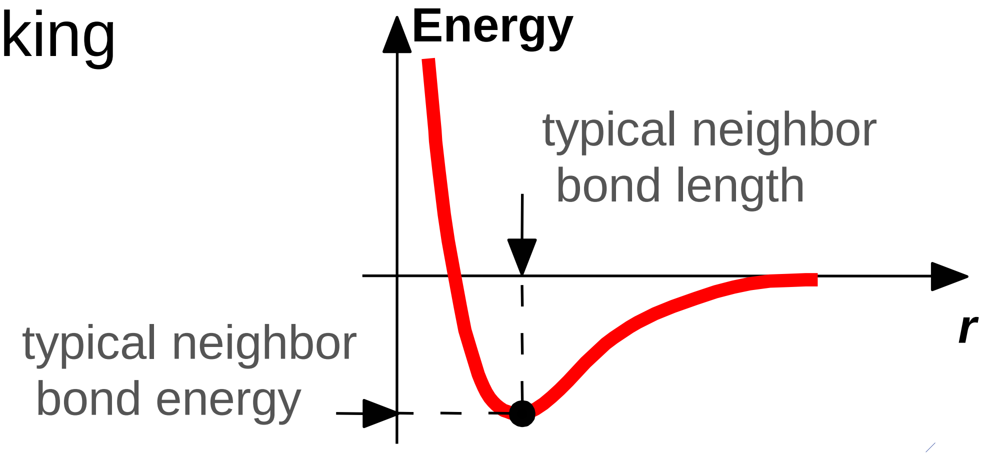
- Non dense, random packing





- Dense, ordered packing



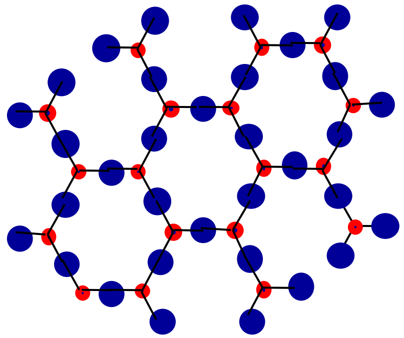


Dense, ordered packed structures tend to have ______ energies.

Materials and Packing

materials...

- atoms pack in periodic, 3D arrays
- typical of:
  - -metals
  - -many ceramics
  - -some polymers



crystalline SiO_2

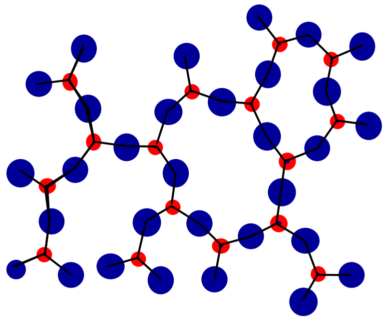
Adapted from Fig. 3.41(a), *Callister & Rethwisch 4e.*

• **Si** ● **Oxygen**

Noncrystalline materials...

- atoms have no periodic packing
- occurs for:
  - -complex structures
  - -rapid cooling

'' = Noncrystalline



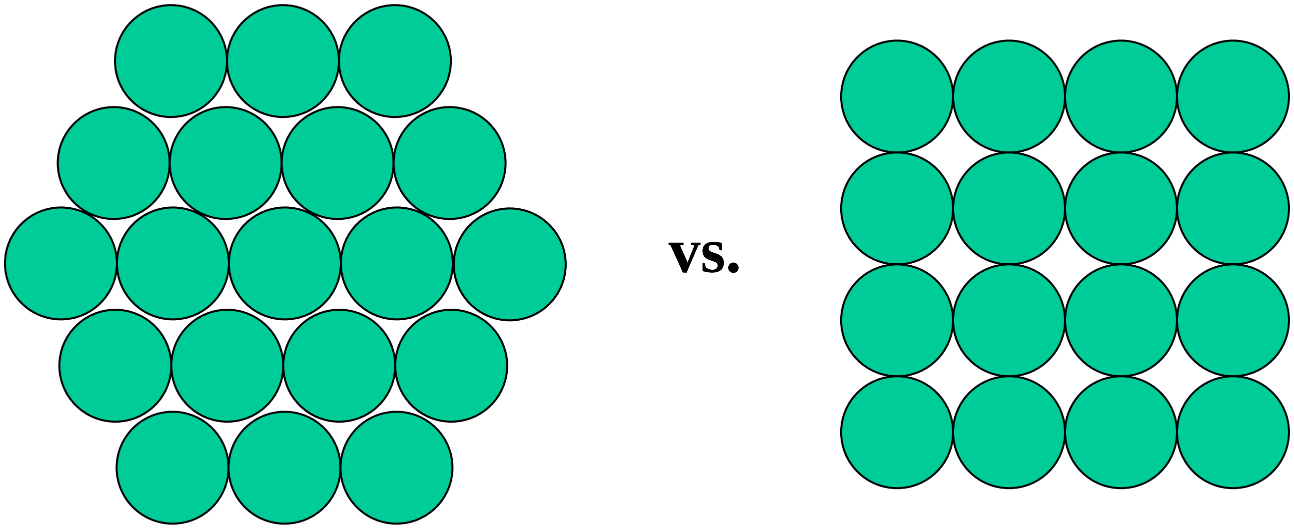
noncrystalline SiO_2

Adapted from Fig. 3.41(b), *Callister & Rethwisch 4e.*

Metallic Crystal Structures

- How can we stack metal atoms to minimize empty space?

2-dimensions



Now stack these 2-D layers to make 3-D structures

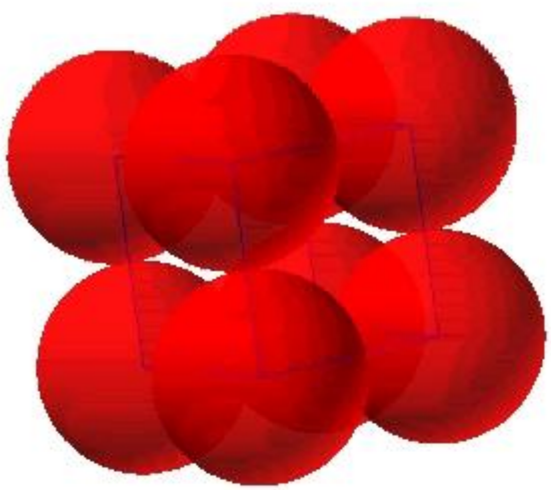
Metallic Crystal Structures

- Tend to be densely packed.
- Reasons for dense packing:
  - Typically, only one element is present, so all atomic radii are the
  - Metallic bonding is not directional.
  - Nearest neighbor distances tend to be in order to lower bond energy.
  - Electron cloud shields cores from each other
- Metals have the simplest crystal structures.

We will examine three such structures...

Simple Cubic Structure (SC)

- Rare due to low packing density (only Po has this structure)
- Close-packed directions are cube $\boxed{}$.

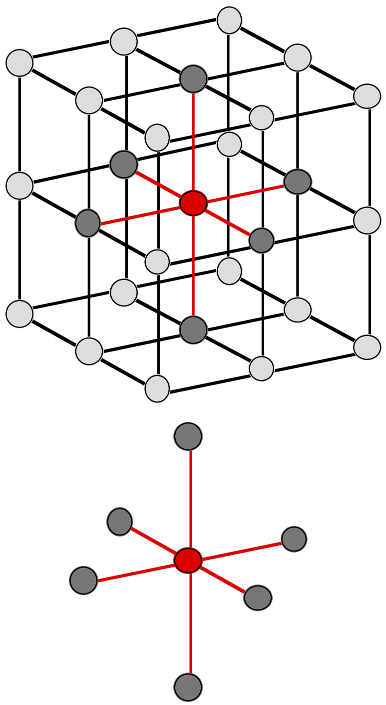


Click once on image to start animation

(Courtesy P.M. Anderson)

- Coordination # = $\boxed{}$

  (# nearest neighbors)

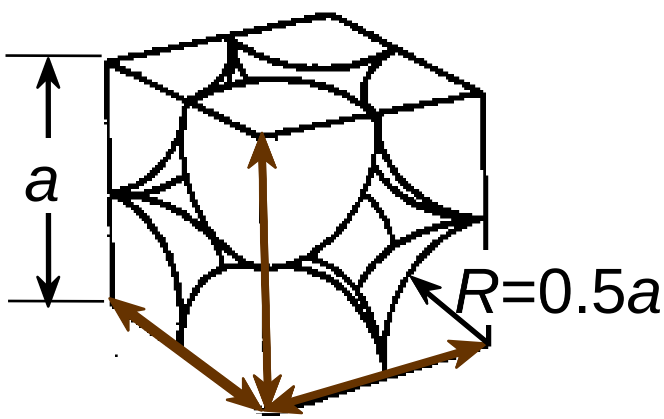


Atomic Packing Factor (APF)

$$\text{APF} = \frac{\text{Volume of atoms in unit cell*}}{\text{Volume of unit cell}}$$

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

contains 8 x 1/8 =

1 atom/unit cell

Adapted from Fig. 3.43,
Callister & Rethwisch 4e.

$$\text{APF} = \frac{\dfrac{\text{atoms}}{\text{unit cell}} \quad \dfrac{\text{volume}}{\text{atom}}}{a^3 \quad \dfrac{\text{volume}}{\text{unit cell}}}$$

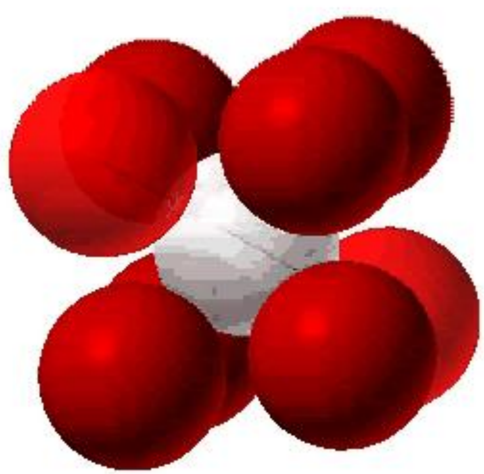
Body Centered Cubic Structure (BCC)

- Atoms touch each other along cube $\boxed{}$.

  --Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

ex: Cr, W, Fe (α), Tantalum, Molybdenum

- Coordination # = $\boxed{}$



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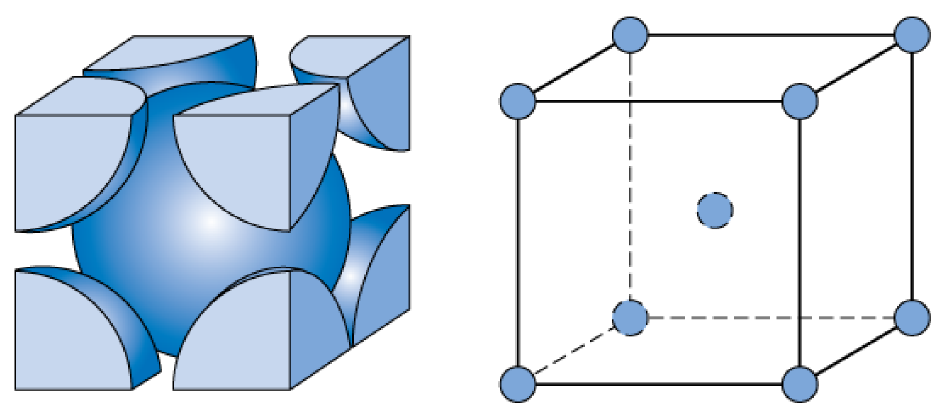


Adapted from Fig. 3.2, *Callister & Rethwisch 4e.*

2 atoms/unit cell: $\boxed{}$ center + $\boxed{}$ corners x $\boxed{}$

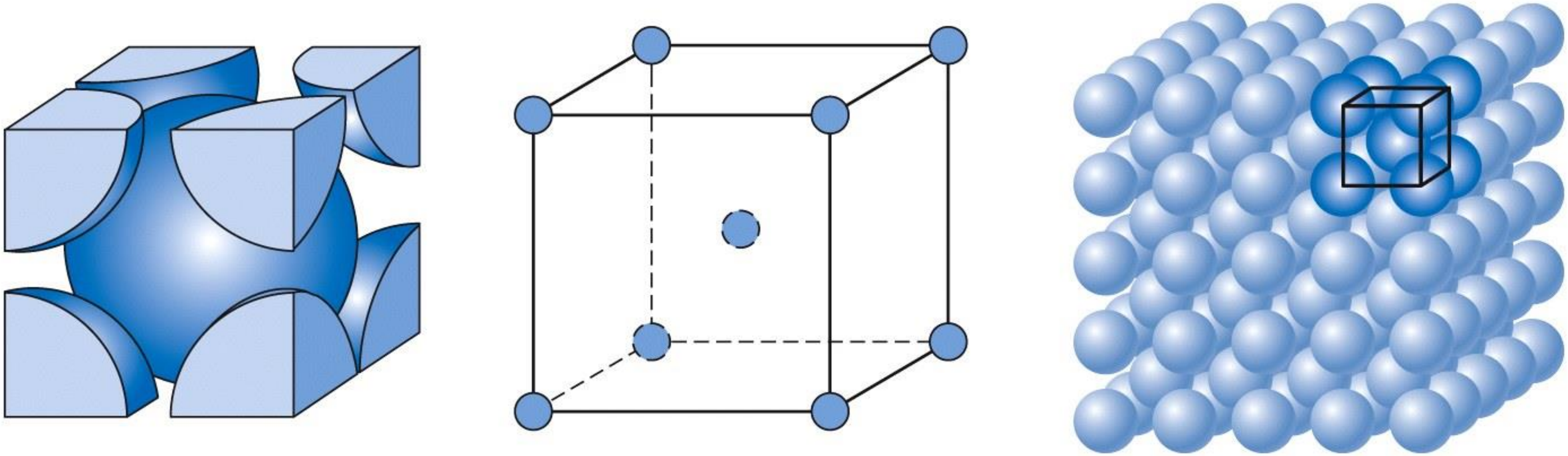
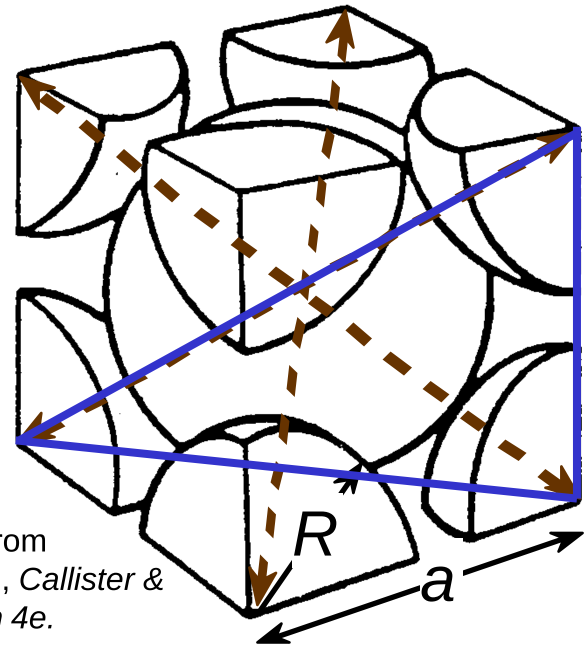


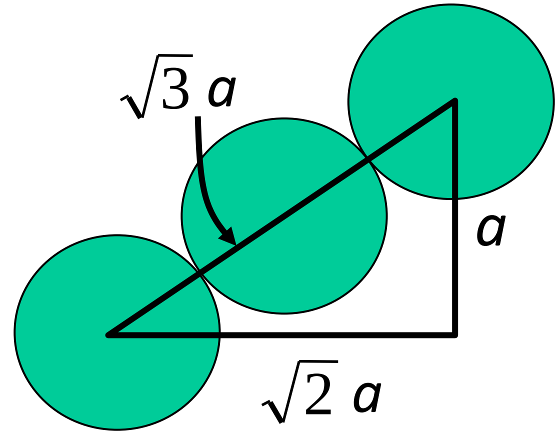
Figure 3.2

Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68



Adapted from Fig. 3.2(a), *Callister & Rethwisch 4e.*



Close-packed directions:
length =

$$APF = \frac{\frac{\text{atoms}}{\text{unit cell}} \quad \frac{\text{volume}}{\text{atom}}}{\frac{\text{volume}}{\text{unit cell}}}$$

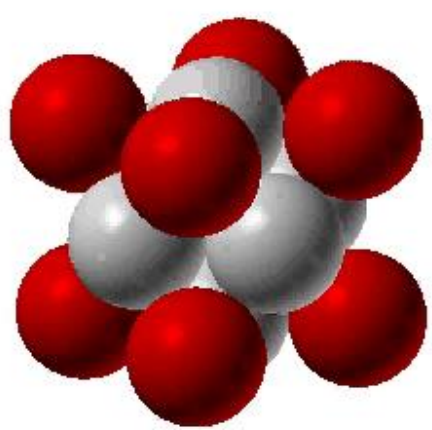
Face Centered Cubic Structure (FCC)

- Atoms touch each other along

--Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

ex: Al, Cu, Au, Pb, Ni, Pt, Ag

- Coordination # =



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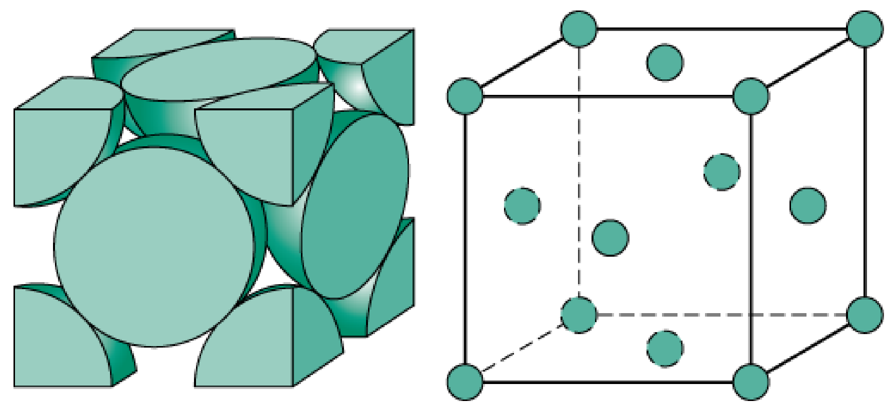
(Courtesy P.M. Anderson)



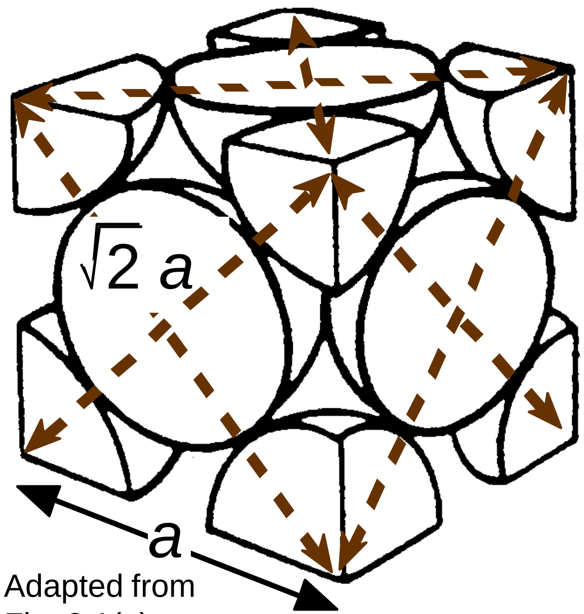
Adapted from Fig. 3.1, *Callister & Rethwisch 4e.*

atoms/unit cell: face x + corners x

Atomic Packing Factor: FCC

- APF for a face-centered cubic structure = 0.74

maximum achievable APF



Adapted from Fig. 3.1(a), *Callister & Rethwisch 4e.*

Close-packed directions:

length =

Unit cell contains:

6 x 1/2 + 8 x 1/8

= 4 atoms/unit cell

$$\text{APF} = \frac{\frac{\text{atoms}}{\text{unit cell}} \quad \frac{\text{volume}}{\text{atom}}}{a^3 \quad \frac{\text{volume}}{\text{unit cell}}}$$

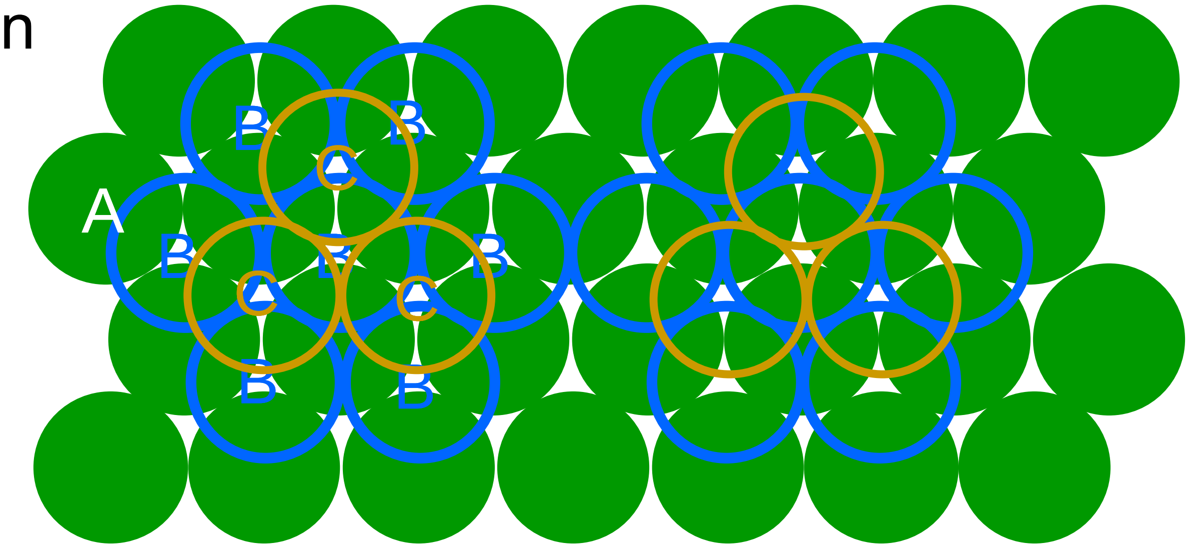
FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

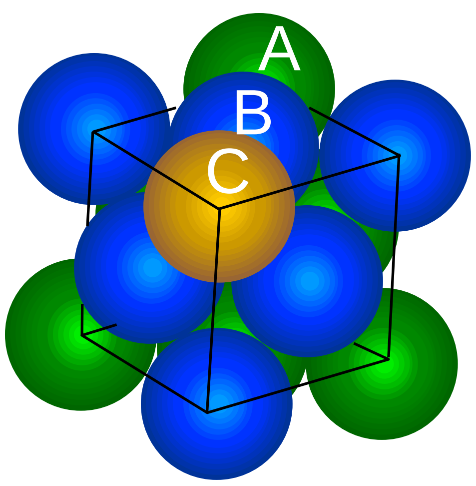
A sites

B sites

C sites

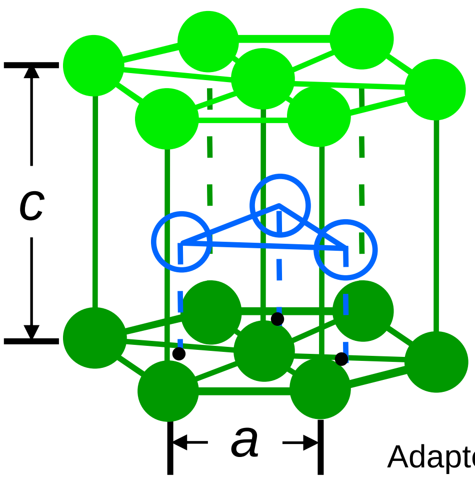


- FCC Unit Cell



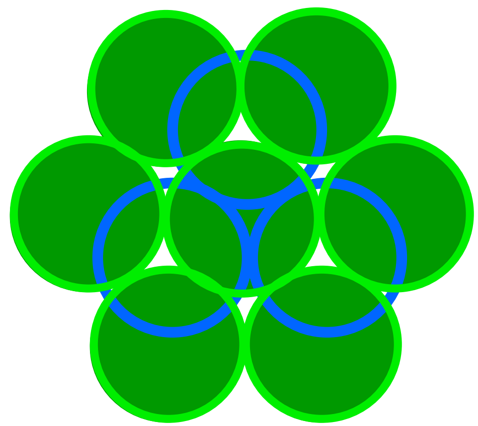
Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection



Adapted from Fig. 3.3(a), *Callister & Rethwisch 4e.*

- 2D Projection



- Coordination # = 12
- APF = 0.74
- *c*/*a* = 1.633

6 atoms/unit cell

ex: Cd, Mg, Ti, Zn

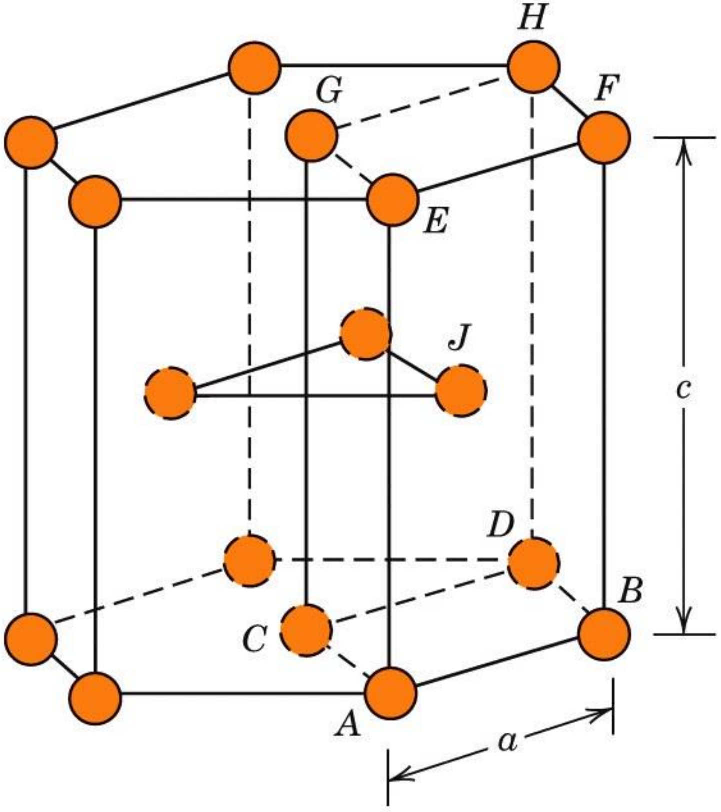
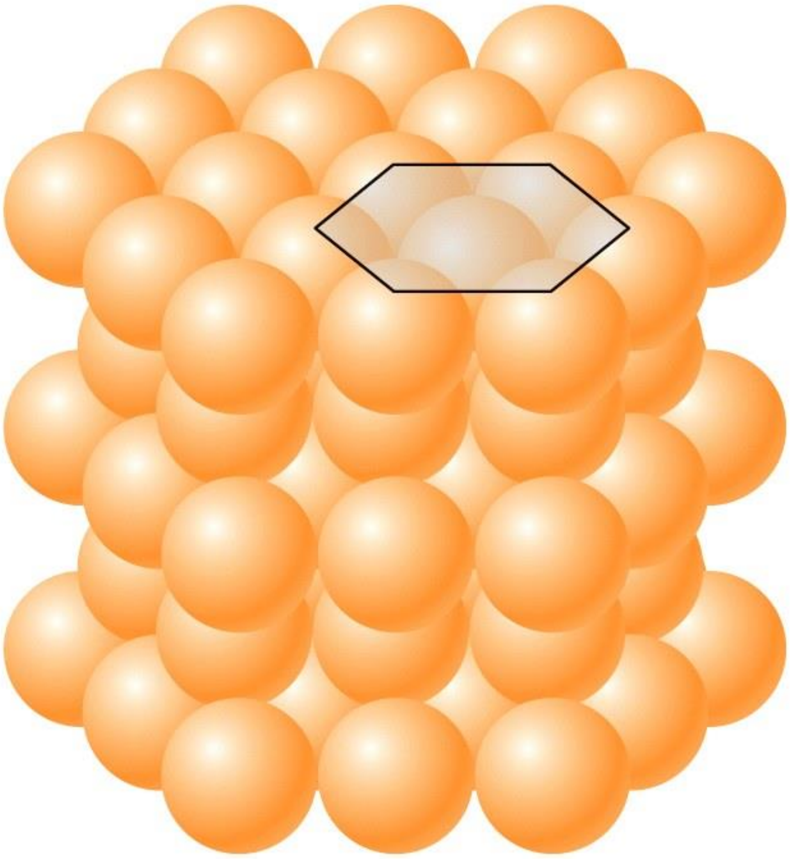


Figure 3.3



Theoretical Density, ρ

$$\text{Density} = \rho = \frac{\text{Mass of Atoms in Unit Cell}}{\text{Total Volume of Unit Cell}}$$

$$\rho = \frac{\boxed{}}{\boxed{}}$$

where n = number of atoms/unit cell

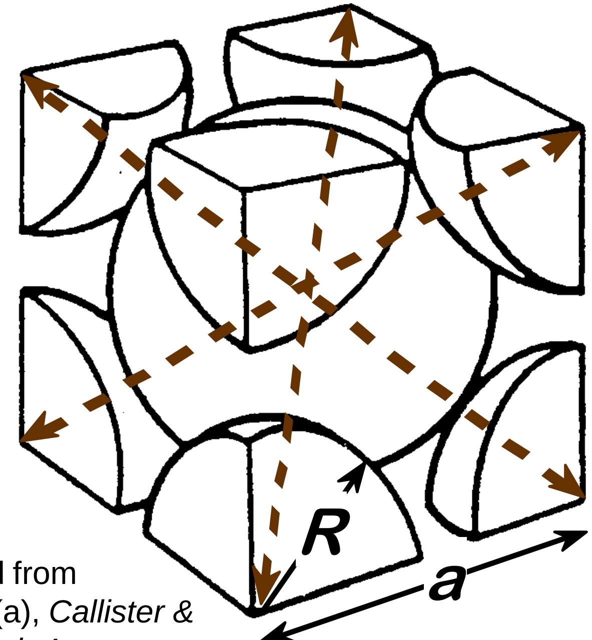
A = atomic weight

V_C = Volume of unit cell = a^3 for cubic

N_A = Avogadro's number

= 6.022×10^{23} atoms/mol

Theoretical Density, ρ



Adapted from Fig. 3.2(a), *Callister & Rethwisch 4e.*

- Ex: Cr (BCC)

  $A = 52.00$ g/mol

  $R = 0.125$ nm

  $n = 2$ atoms/unit cell

  $a = 4R/\sqrt{3} = 0.2887$ nm

$$\rho = \frac{\overset{\frac{\text{atoms}}{\text{unit cell}}}{2}\ \overset{\frac{\text{g}}{\text{mol}}}{52.00}}{\underset{\frac{\text{volume}}{\text{unit cell}}}{a^3}\ \underset{\frac{\text{atoms}}{\text{mol}}}{6.022 \times 10^{23}}}$$

$\rho_{theoretical} = 7.18$ g/cm^3

$\rho_{actual} = 7.19$ g/cm^3

Table 3.1
Atomic Radii and Crystal Structures for 16 Metals

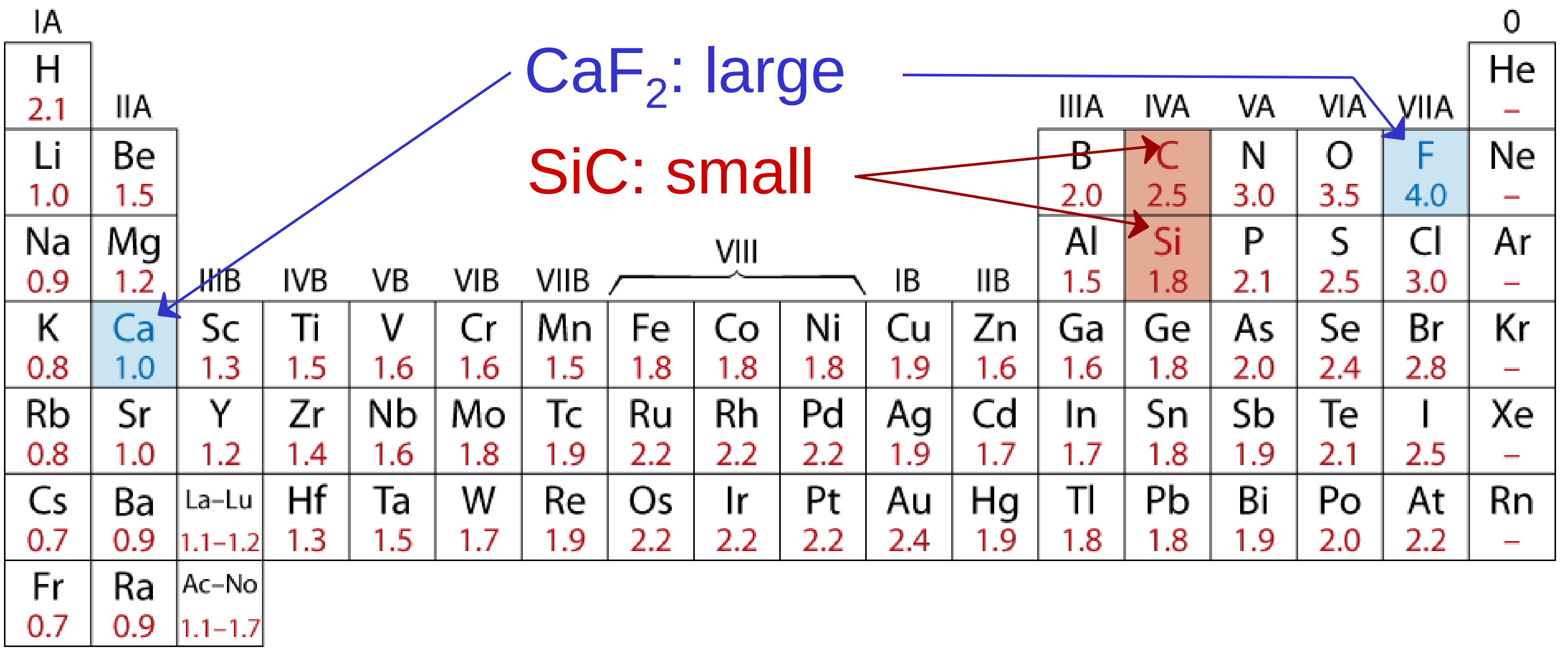
Metal	*Crystal Structure*[a]	*Atomic Radius*[b] *(nm)*	*Metal*	*Crystal Structure*	*Atomic Radius (nm)*
Aluminum	FCC	0.1431	Molybdenum	BCC	0.1363
Cadmium	HCP	0.1490	Nickel	FCC	0.1246
Chromium	BCC	0.1249	Platinum	FCC	0.1387
Cobalt	HCP	0.1253	Silver	FCC	0.1445
Copper	FCC	0.1278	Tantalum	BCC	0.1430
Gold	FCC	0.1442	Titanium (α)	HCP	0.1445
Iron (α)	BCC	0.1241	Tungsten	BCC	0.1371
Lead	FCC	0.1750	Zinc	HCP	0.1332

[a] FCC = face-centered cubic; HCP = hexagonal close-packed; BCC = body-centered cubic.
[b] A nanometer (nm) equals 10^{-9} m; to convert from nanometers to angstrom units (Å), multiply the nanometer value by 10.

Table 3.1

Atomic Bonding in Ceramics

- Bonding:
  -- Can be ionic and/or covalent in character.
  -- % ionic character increases with difference in ______ of atoms.
- Degree of ionic character may be large or small:



IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
H 2.1																	He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr –
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe –
Cs 0.7	Ba 0.9	La–Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn –
Fr 0.7	Ra 0.9	Ac–No 1.1–1.7															

Adapted from Fig. 2.7, *Callister & Rethwisch 4e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition. Copyright 1939 and 1940, 3rd edition copyright © 1960 by Cornell University.

Ceramic Crystal Structures

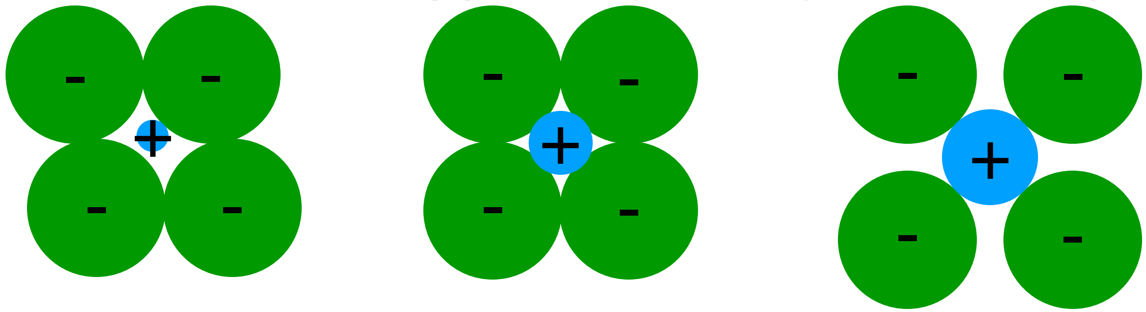
Oxide structures

- oxygen anions larger than metal cations
- close packed oxygen in a lattice (usually FCC)
- fit into interstitial sites among oxygen ions

Factors that Determine Crystal Structure

1. Relative of ions – Formation of stable structures:

--maximize the # of oppositely charged ion neighbors.



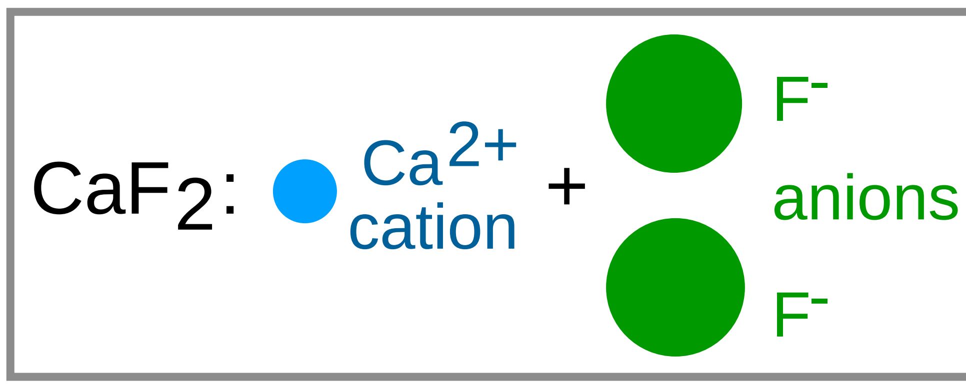
unstable stable stable

Adapted from Fig. 3.4, *Callister & Rethwisch 4e.*

2. Maintenance of Neutrality :

--Net charge in ceramic should be zero.

--Reflected in chemical formula:



$$A_m X_p$$

m, p values to achieve charge neutrality

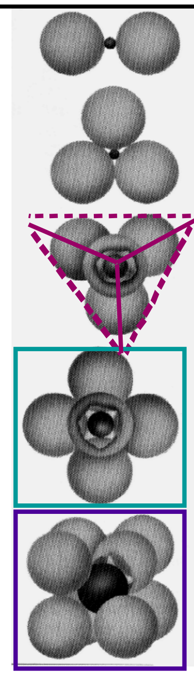
Coordination Number and Ionic Radii

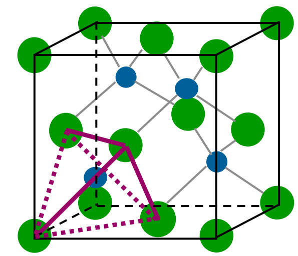
- Coordination Number increases with

To form a stable structure, how many anions can surround around a cation?

$\frac{r_{cation}}{r_{anion}}$	Coord. Number	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	tetrahedral
0.414 - 0.732	6	octahedral
0.732 - 1.0	8	cubic

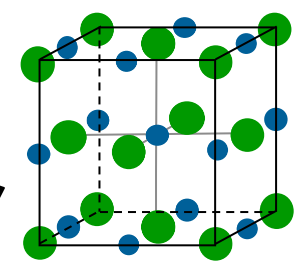
Adapted from Table 3.3, *Callister & Rethwisch 4e.*





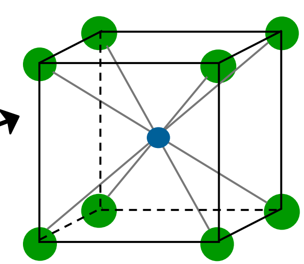
ZnS (zinc blende)

Adapted from Fig. 3.7, *Callister & Rethwisch 4e.*



NaCl (sodium chloride)

Adapted from Fig. 3.5, *Callister & Rethwisch 4e.*

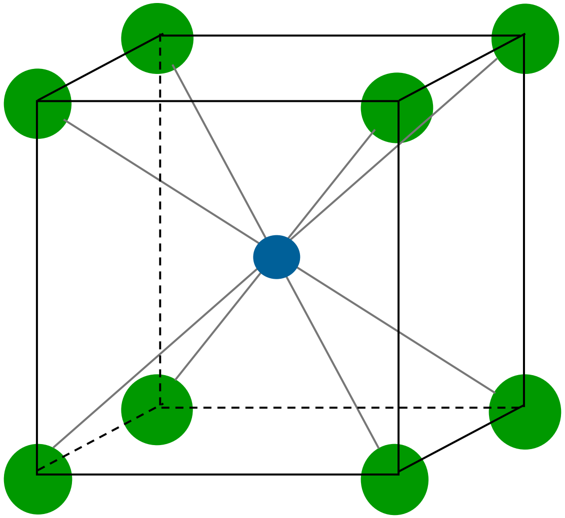


CsCl (cesium chloride)

Adapted from Fig. 3.6, *Callister & Rethwisch 4e.*

Computation of Minimum Cation-Anion Radius Ratio

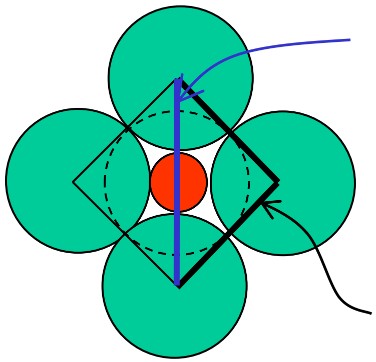
- Determine minimum r_{cation}/r_{anion} for a cubic site (C.N. = 8)

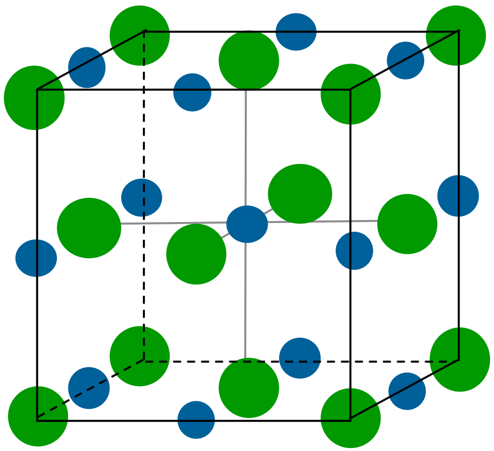


Adapted from Fig. 3.6, *Callister & Rethwisch 4e.*

Computation of Minimum Cation-Anion Radius Ratio

- Determine minimum r_{cation}/r_{anion} for an octahedral site (C.N. = 6)





$$2r_{anion} + 2r_{cation} = 2\sqrt{2}r_{anion}$$

$$r_{anion} + r_{cation} = \sqrt{2}r_{anion} \qquad r_{cation} = (\sqrt{2} - 1)r_{anion}$$

$$\frac{r_{cation}}{r_{anion}} = \boxed{} = \boxed{}$$

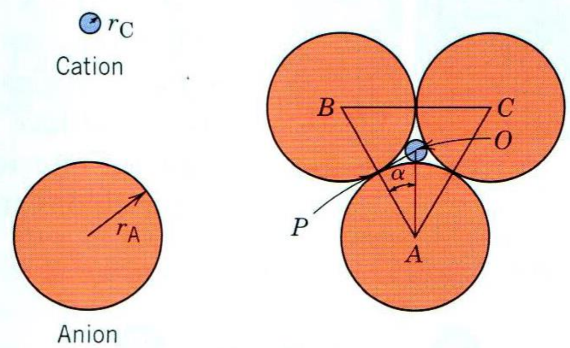
EXAMPLE PROBLEM 3.4

Computation of Minimum Cation-to-Anion Radius Ratio for a Coordination Number of 3

Show that the minimum cation-to-anion radius ratio for the coordination number 3 is 0.155.

Solution

For this coordination, the small cation is surrounded by three anions to form an equilateral triangle as shown here, triangle ABC; the centers of all four ions are coplanar.



This boils down to a relatively simple plane trigonometry problem. Consideration of the right triangle APO makes it clear that the side lengths are related to the anion and cation radii r_A and r_C as

$$\overline{AP} = r_A$$

and

$$\overline{AO} = r_A + r_C$$

Furthermore, the side length ratio $\overline{AP}/\overline{AO}$ is a function of the angle α as

$$\frac{\overline{AP}}{\overline{AO}} = \cos\alpha$$

The magnitude of α is 30° because line $\overline{AO}$ bisects the 60° angle BAC. Thus,

$$\frac{\overline{AP}}{\overline{AO}} = \frac{r_A}{r_A + r_C} = \cos 30° = \frac{\sqrt{3}}{2}$$

Solving for the cation–anion radius ratio, we have

$$\frac{r_C}{r_A} = \frac{1 - \sqrt{3}/2}{\sqrt{3}/2} = 0.155$$

Bond Hybridization

Bond Hybridization is possible when there is significant covalent bonding

- hybrid electron orbitals form
- For example for SiC
  - $X_{Si} = 1.8$ and $X_C = 2.5$

$$\%\text{ ionic character } = 100\{1 - \exp[-0.25(\boxed{\phantom{X_{Si}-X_C}})^2]\} = 11.5\%$$

- ~ 89% covalent bonding
- Both Si and C prefer sp^3 hybridization
- Therefore, for SiC, Si atoms occupy tetrahedral sites

Table 3.2

Percent Ionic Character of the Interatomic Bonds for Several Ceramic Materials

Material	*Percent Ionic Character*
CaF_2	89
MgO	73
NaCl	67
Al_2O_3	63
SiO_2	51
Si_3N_4	30
ZnS	18
SiC	12

Table 3.2

Example Problem: Predicting the Crystal Structure of FeO

- On the basis of ionic radii, what crystal structure would you predict for FeO?

Cation	Ionic radius (nm)
Al^{3+}	0.053
Fe^{2+}	0.077
Fe^{3+}	0.069
Ca^{2+}	0.100

Anion	
O^{2-}	0.140
Cl^{-}	0.181
F^{-}	0.133

- Answer:

$$\frac{r_{cation}}{r_{anion}} = \boxed{}$$

$$= 0.550$$

based on this ratio,
-- coord # = 6 because

$$0.414 < \boxed{} < 0.732$$

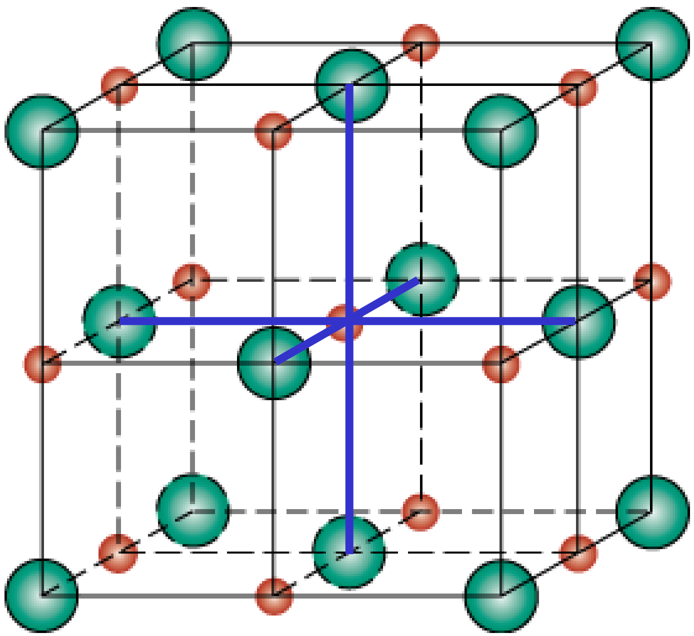
-- crystal structure is NaCl

Data from Table 3.4, *Callister & Rethwisch 4e.*

Rock Salt Structure

Same concepts can be applied to ionic solids in general.

Example: NaCl (rock salt) structure



Na^+ $r_{Na} = 0.102$ nm

Cl^- $r_{Cl} = 0.181$ nm

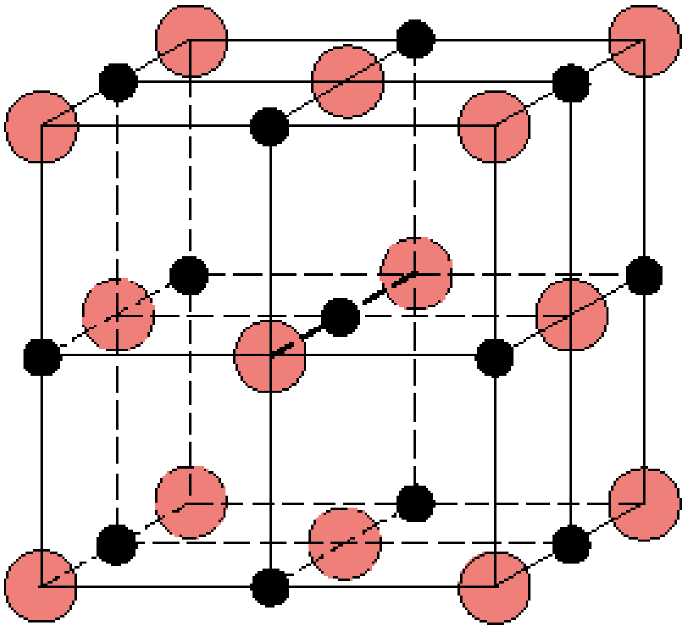
$r_{Na}/r_{Cl} = 0.564$

$\therefore$ cations (Na^+) prefer octahedral sites

Adapted from Fig. 3.5,
Callister & Rethwisch 4e.

MgO and FeO

MgO and FeO also have the NaCl structure



Adapted from Fig. 3.5,
Callister & Rethwisch 4e.

O^{2-} $r_O = 0.140$ nm

Mg^{2+} $r_{Mg} = 0.072$ nm

$r_{Mg}/r_O = 0.514$

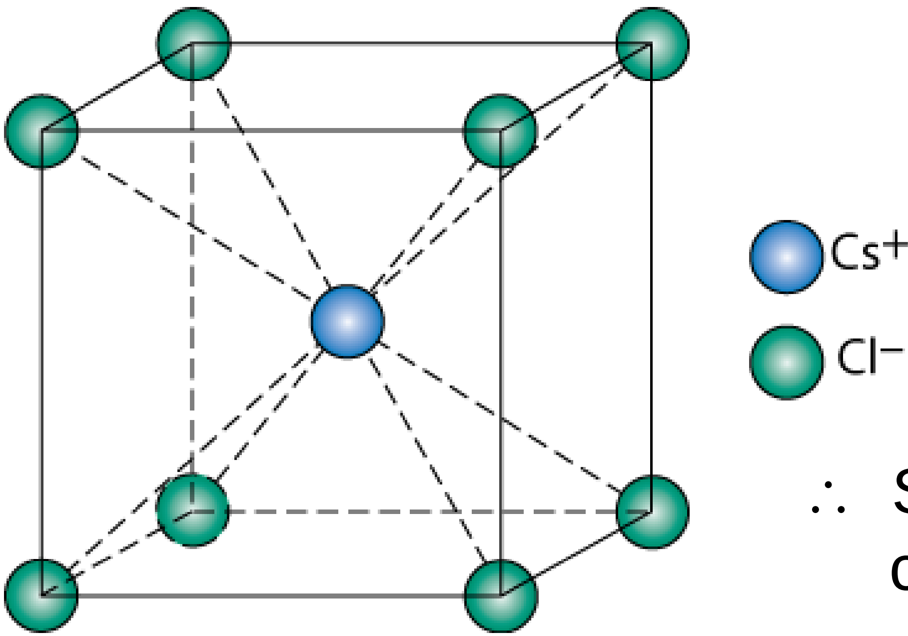
$\therefore$ cations prefer octahedral sites

So each Mg^{2+} (or Fe^{2+}) has 6 neighbor oxygen atoms

AX Crystal Structures

AX–Type Crystal Structures include NaCl, CsCl, and zinc blende

Cesium Chloride structure:



$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{0.170}{0.181} = 0.939$$

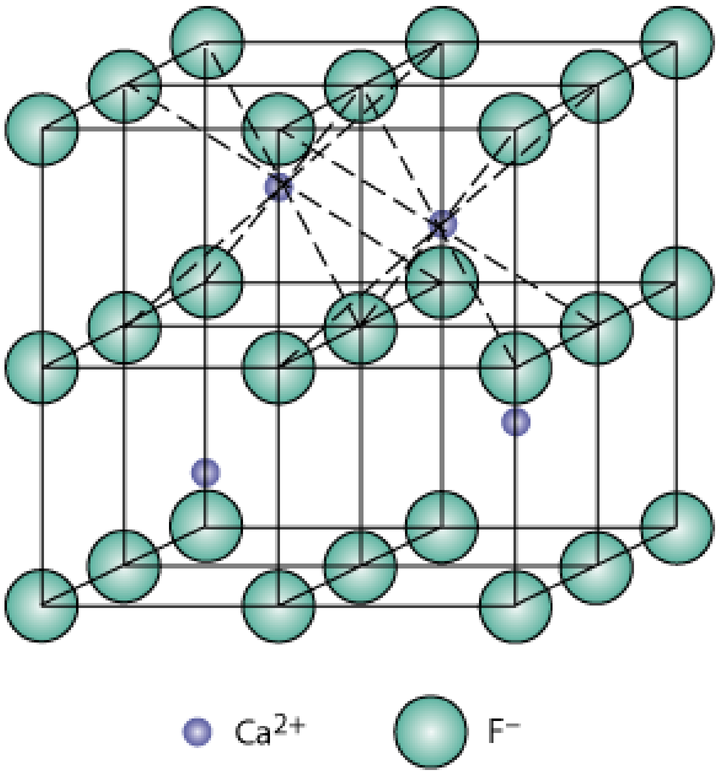
Adapted from Fig. 3.6, *Callister & Rethwisch 4e.*

∴ Since 0.732 < 0.939 < 1.0, cubic sites preferred

So each Cs^+ has 8 neighbor Cl^-

AX_2 Crystal Structures

Fluorite structure



Adapted from Fig. 3.8,
Callister & Rethwisch 4e.

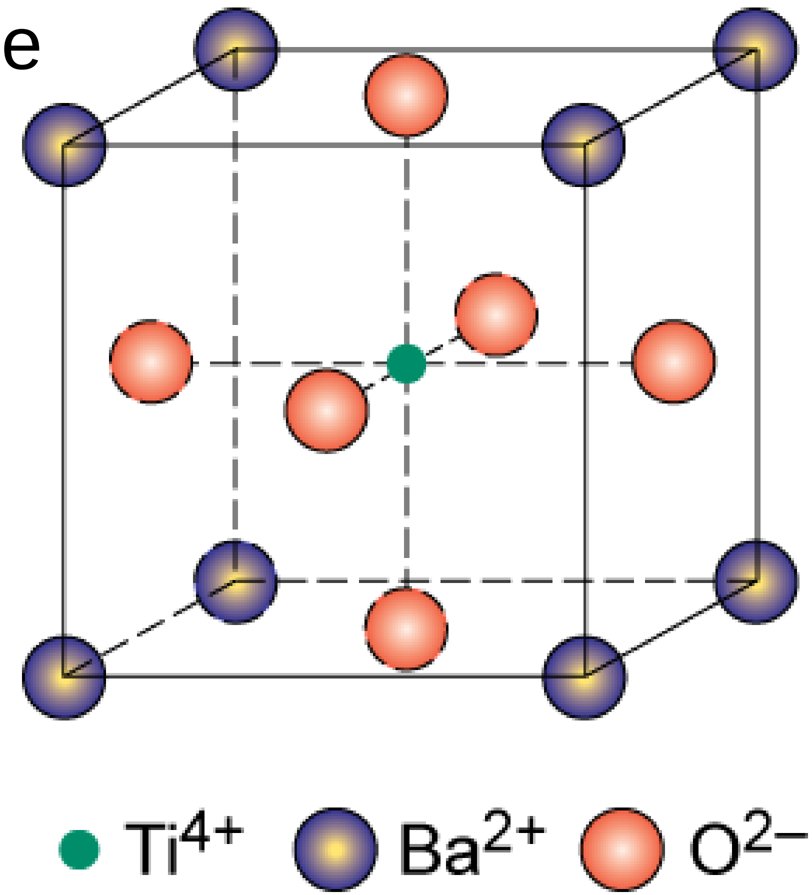
- Calcium Fluorite (CaF_2)
- Cations in cubic sites
- UO_2, ThO_2, ZrO_2, CeO_2
- Antifluorite structure – positions of cations and anions reversed

ABX_3 Crystal Structures

- Perovskite structure

Ex: complex oxide

$BaTiO_3$



Adapted from Fig. 3.9,
Callister & Rethwisch 4e.

Table 3.5 Summary of Some Common Ceramic Crystal Structures

Structure Name	*Structure Type*	*Anion Packing*	*Coordination Number* Cation	*Coordination Number* Anion	*Examples*
Rock salt (sodium chloride)	AX	FCC	6	6	NaCl, MgO, FeO
Cesium chloride	AX	Simple cubic	8	8	CsCl
Zinc blende (sphalerite)	AX	FCC	4	4	ZnS, SiC
Fluorite	AX_2	Simple cubic	8	4	CaF_2, UO_2, ThO_2
Perovskite	ABX_3	FCC	12 (A) 6 (B)	6	$BaTiO_3$, $SrZrO_3$, $SrSnO_3$
Spinel	AB_2X_4	FCC	4 (A) 6 (B)	4	$MgAl_2O_4$, $FeAl_2O_4$

Source: W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics,* 2nd edition. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

Table 3.5

Density Computations for Ceramics

Number of formula units/unit cell

$$\rho = \frac{n'(\Sigma A_C + \Sigma A_A)}{V_C N_A}$$

Avogadro's number

Volume of unit cell

ΣA_C = sum of atomic weights of all cations in formula unit

ΣA_A = sum of atomic weights of all anions in formula unit

Densities of Material Classes

In general

ρ [ ] > ρ [ ] > ρ [ ]

Why?

Metals have...

- close-packing (metallic bonding)
- often large atomic masses

Ceramics have...

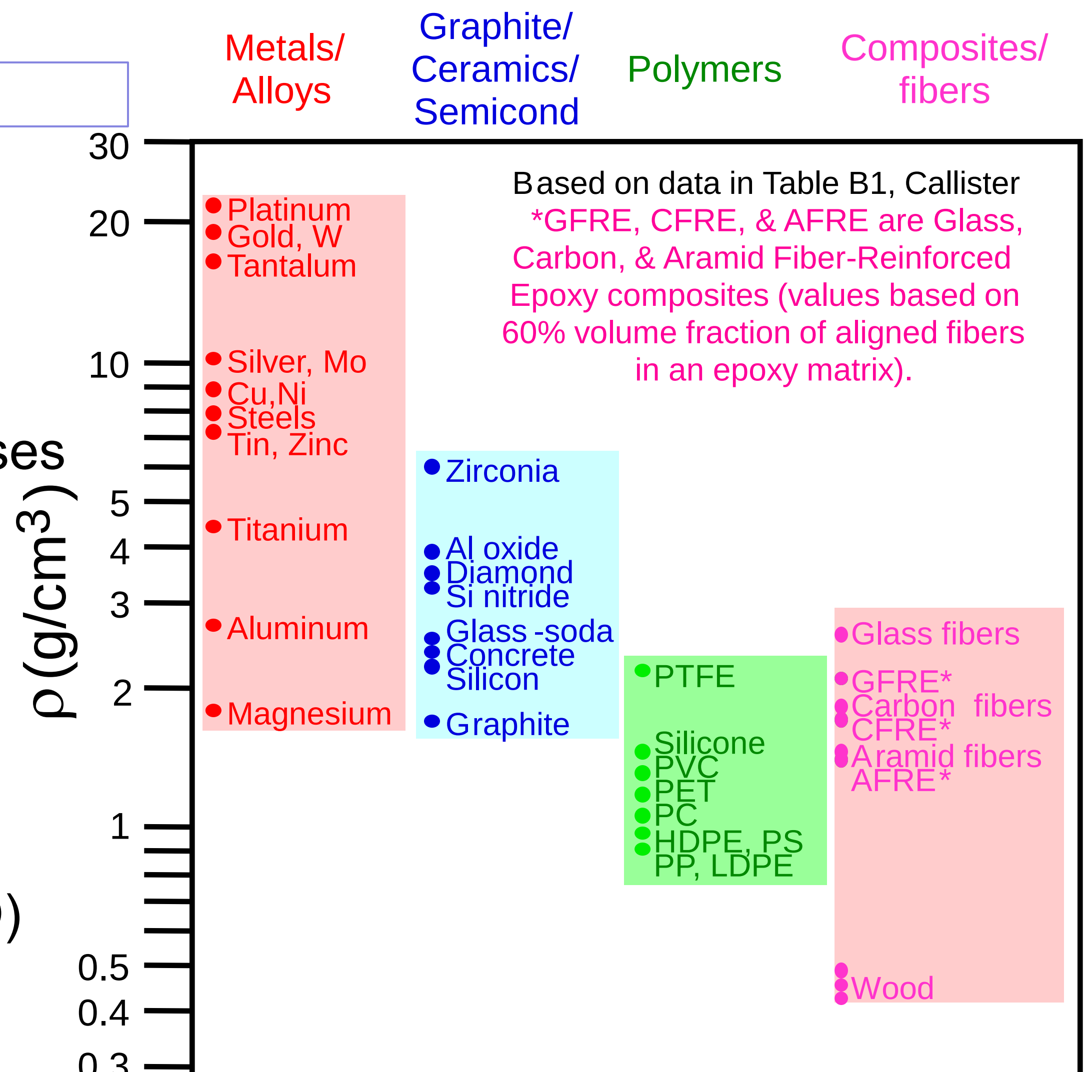
- less dense packing
- often lighter elements

Polymers have...

- low packing density (often amorphous)
- lighter elements (C,H,O)

Composites have...

- intermediate values

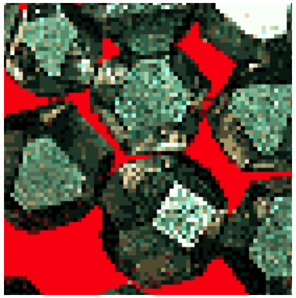


Data from Table B.1, *Callister & Rethwisch, 4e.*

Single Crystals

- When the periodic arrangement of atoms (crystal structure) extends without interruption throughout the entire specimen.

-- diamond single crystals for abrasives



(Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.)

-- Quartz single crystal

Courtesy P.M. Anderson

-- single crystal for turbine blade

Fig. 9.42(c), *Callister & Rethwisch 5e.*
(courtesy of Pratt and Whitney)

Polycrystalline Materials

- *Most* engineering materials are composed of many small, single crystals (i.e., are *polycrystalline*).

Courtesy of Paul E. Danielson, Teledyne Wah Chang Albany

- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- Grain sizes typically range from 1 nm to 2 cm

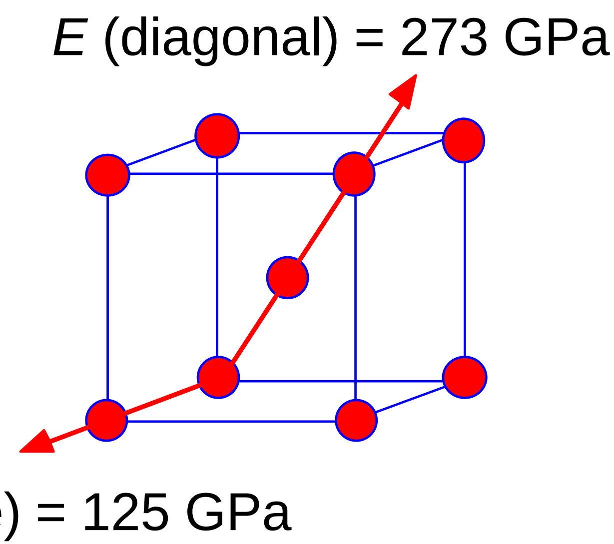
  (i.e., from a few to millions of atomic layers).

Anisotropy

- Anisotropy — Property value depends on crystallographic direction of measurement.

  - Observed in single crystals.
  - Example: modulus of elasticity (E) in BCC iron

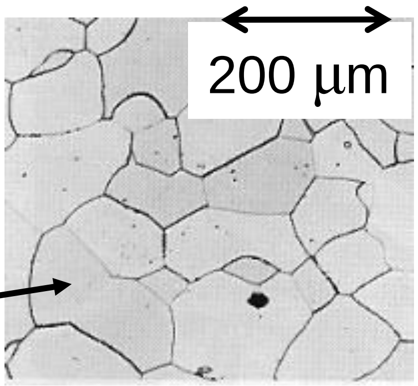
$$E(\text{edge}) \neq E(\text{diagonal})$$



Unit cell of BCC iron

Isotropy

- Polycrystals
  - Properties may/may not vary with direction.
  - If grains randomly oriented: properties $\boxed{}$ ($E_{\text{poly iron}} = 210$ GPa)
  - If grains **textured** (e.g., deformed grains have preferential crystallographic orientation): properties $\boxed{}$



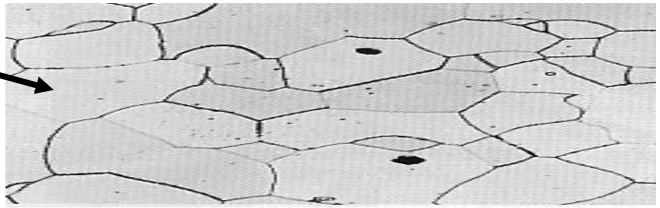


Fig. 5.20(b), *Callister & Rethwisch 5e*.
[Fig. 4.15(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC (now the National Institute of Standards and Technology, Gaithersburg, MD).]

Polymorphism/Allotropy

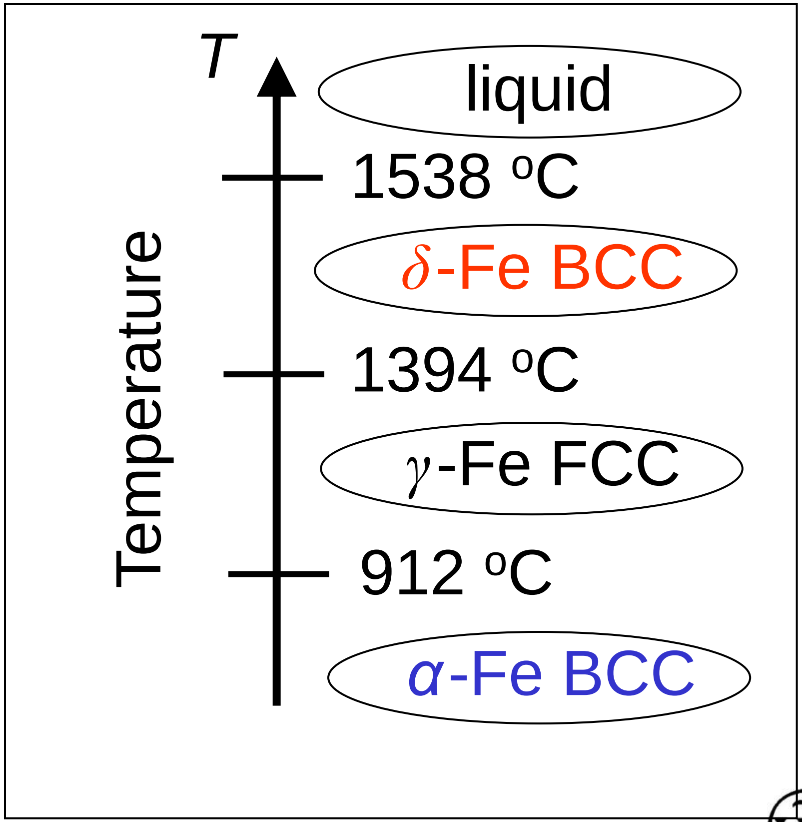
- Two or more distinct crystal structures for the same material (allotropy/polymorphism)

Titanium: α or β forms

Carbon:

diamond, graphite

Iron system



Polymorphic Forms of Carbon

Diamond

– tetrahedral bonding of carbon
  - hardest material known
  - very high thermal conductivity
– large single crystals – gem stones
– small crystals – used to grind/cut other materials
– diamond thin films
  - hard surface coatings – used for cutting tools, medical devices, etc.

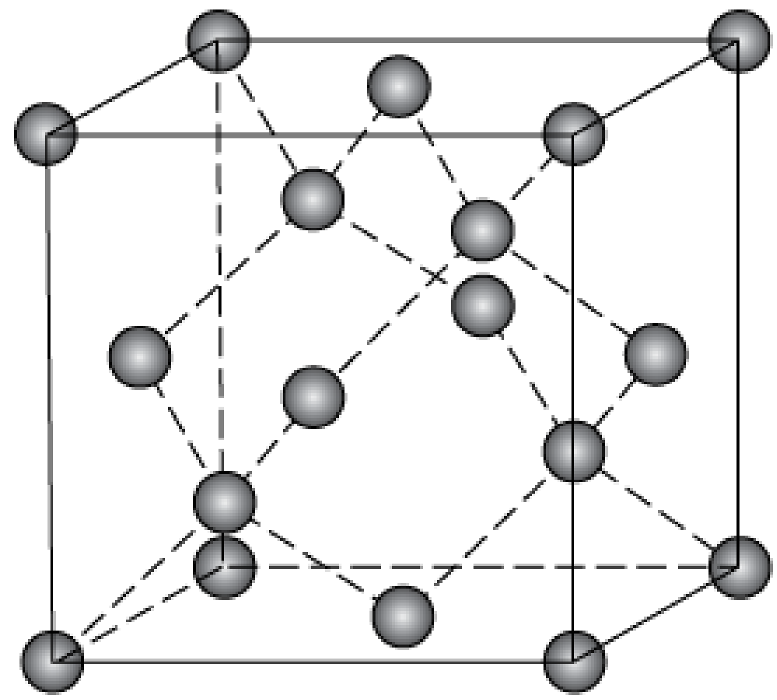


Fig. 3.17, *Callister & Rethwisch 5e.*

Polymorphic Forms of Carbon (cont)

Graphite

– layered structure – parallel hexagonal arrays of carbon atoms

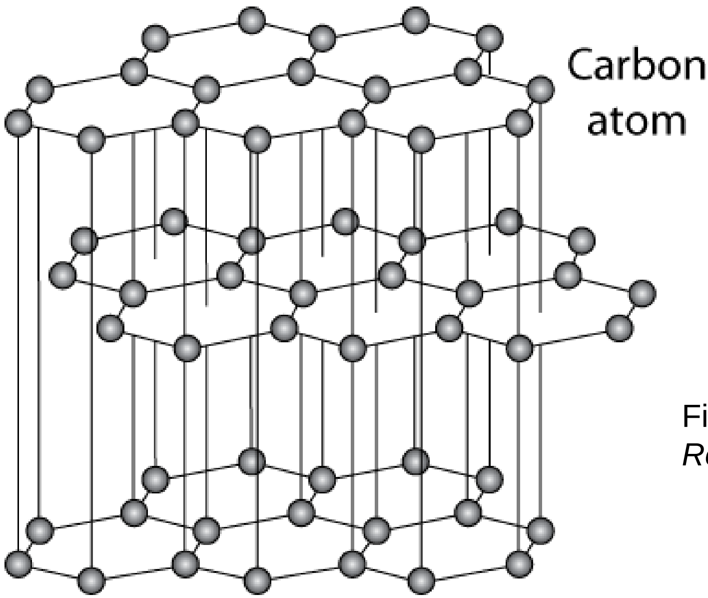


Fig. 3.18, *Callister & Rethwisch 5e.*

– weak van der Waal's forces between layers

– planes slide easily over one another -- good lubricant