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Department of Chemistry

**ONLINE STUDY
RESOURCE
GE-T2: SEC-A**

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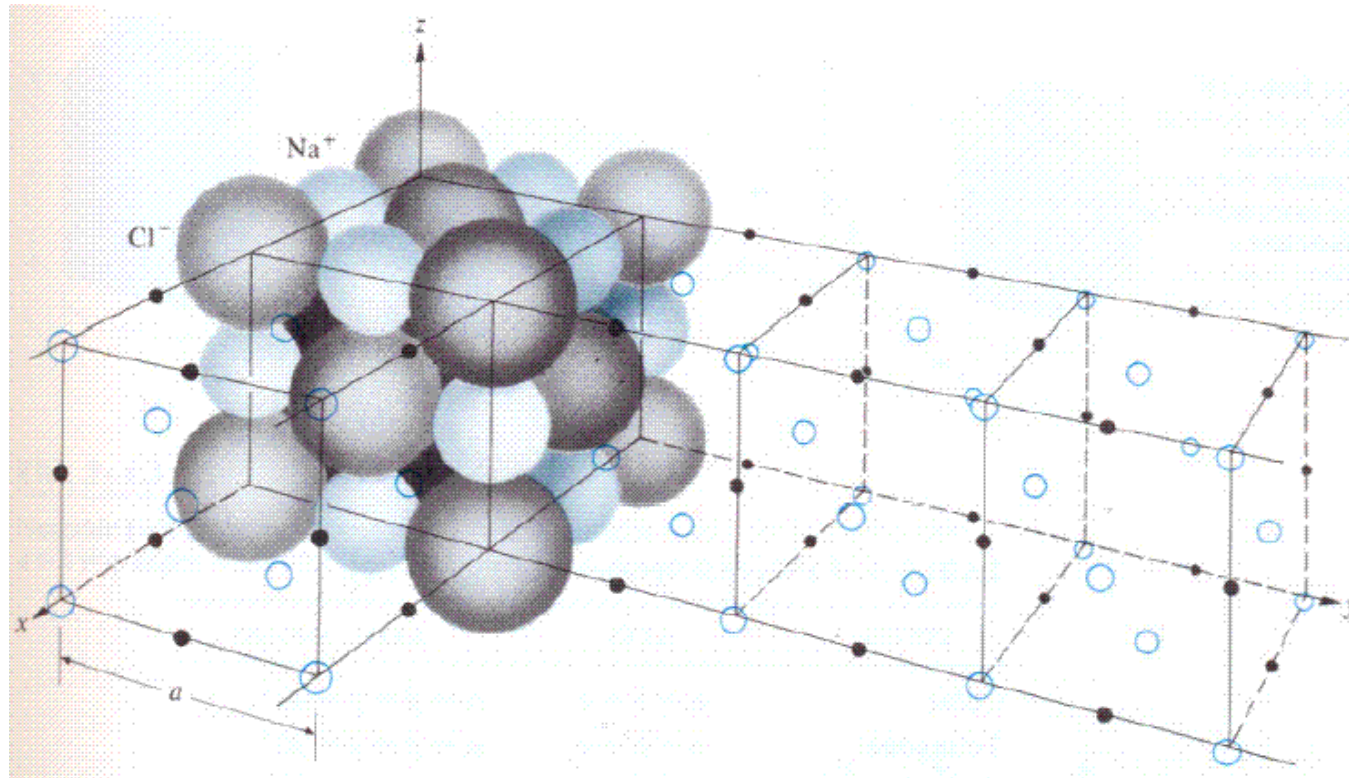
Crystalline Phases

- **Phase:** is that part of a material that is distinct from other parts in **structure and composition**, e.g. ice-water
 - The same composition but different in state
- **Phase boundary:** between the two states locates the discontinuity in **structure**
- Salt and saltwater brine, both contain NaCl but form different phases
- Alcohol-water (miscible) different composition but form **one phase**
- Oil-water (immiscible): **two phases**

Crystals

- Metals, ceramics and certain polymers crystallize by solidification
- **Crystalline phases:**
 - Posses a periodicity of long range order
 - i.e. the local atomic arrangement is repeated at regular intervals millions of times in 3-D of space.

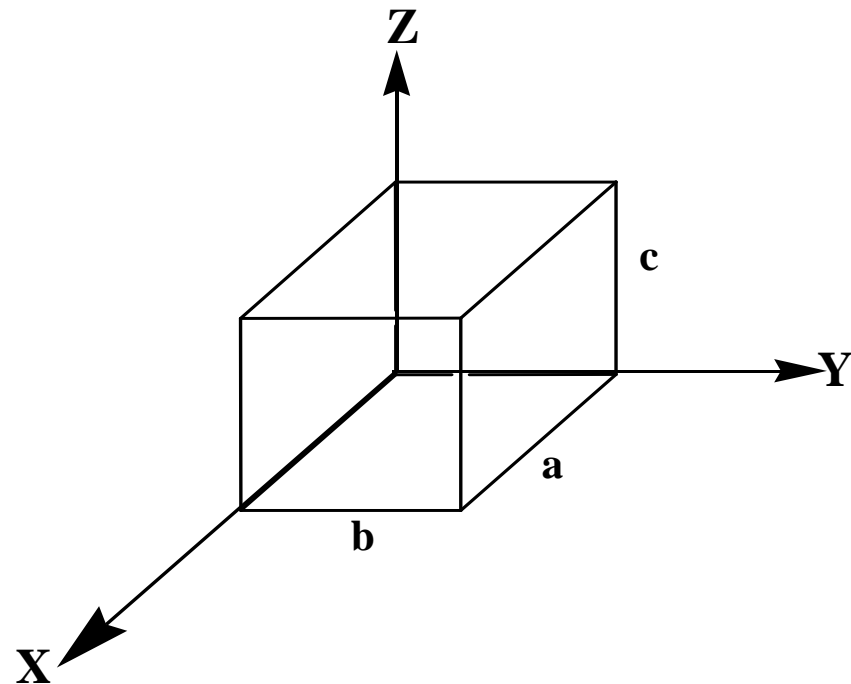
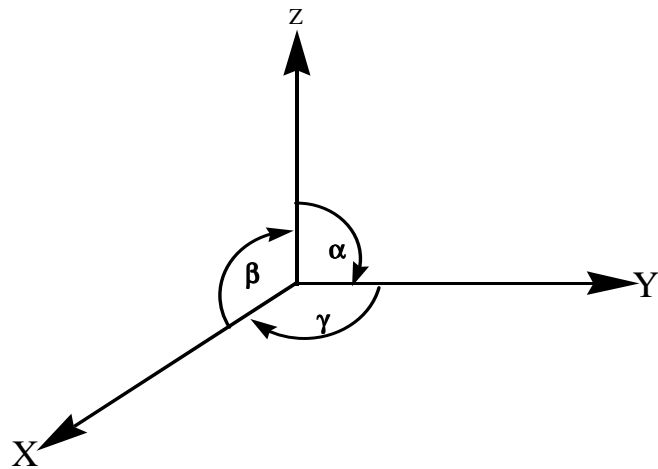
Crystalline structure (NaCl)



The atomic (or ionic) coordination is repeated to give a long range periodicity. The centers of all the cube faces duplicate the pattern at the cube corners. At the center of each cell there is a Na⁺

Crystal Systems

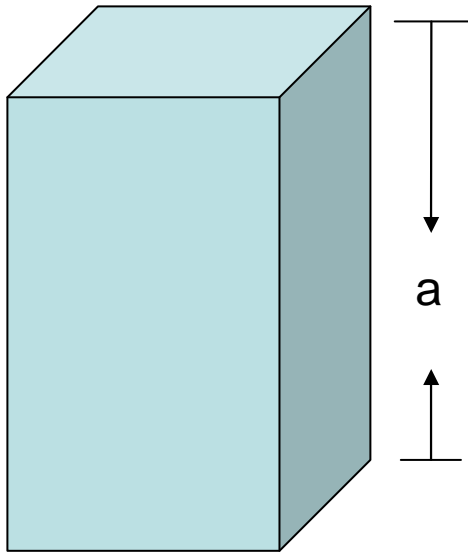
- Three dimensional system: x, y, z axes and α , β , and γ are the axial angles
- A, b, and c are the unit cell dimensions
- Crystal systems vary in the axial angles and the unit cell dimensions



Crystal Systems

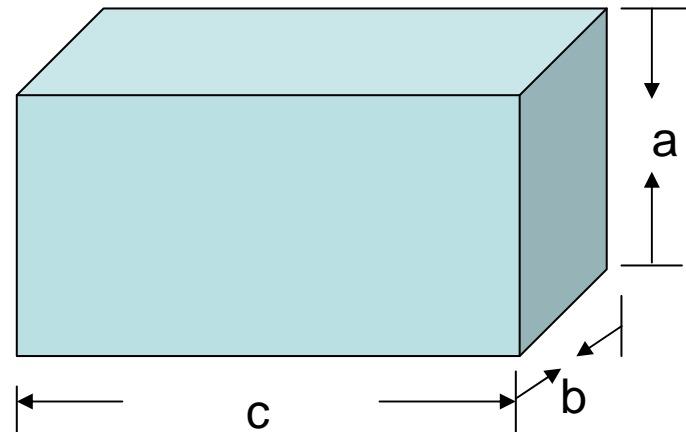
System	Axes	Axial Angle
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Triclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$
orthorhombic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$
Hexagonal	$a = a \neq c$	$\alpha = \beta = 90^\circ; \gamma = 120^\circ$
rhombhedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$

Noncubic unit cell



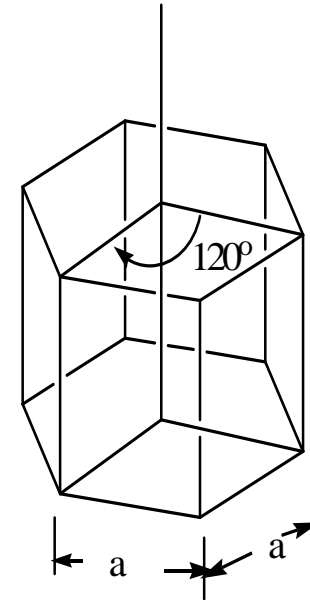
$a=b \neq c$, angles $=90^\circ$

Tetragonal system



$a \neq b \neq c$, angles $=90^\circ$

orthorhombic system



$a = a \neq c$, angles $=90^\circ$,
 120°

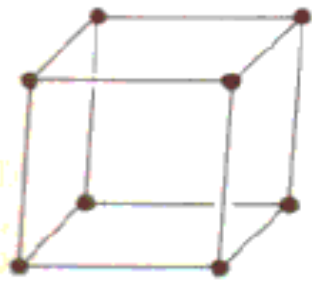
hexagonal system

Lattices

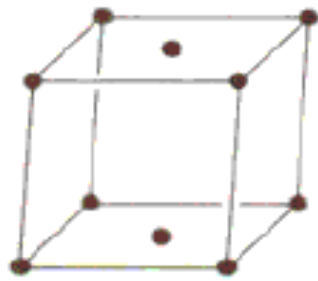
The above 7 systems can be divided into 14 patterns of points, called **Bravais lattices**.

e.g **Cubic systems:**

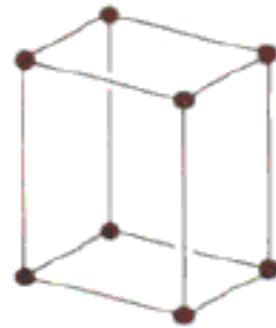
- i) Body centered cubic (BCC)
- ii) Face centered cubic (FCC)
- iii) Simple cubic



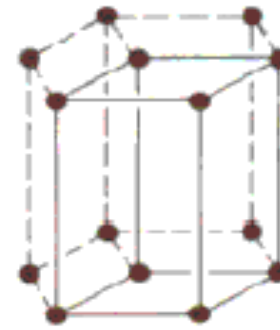
Simple
monoclinic



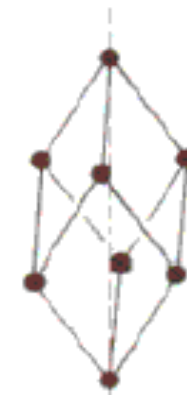
End-centered
monoclinic



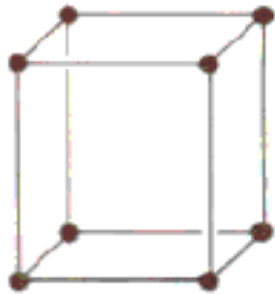
Triclinic



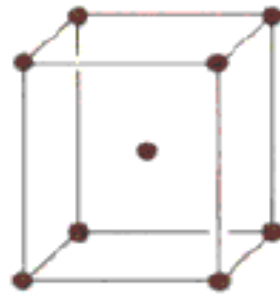
Hexagonal



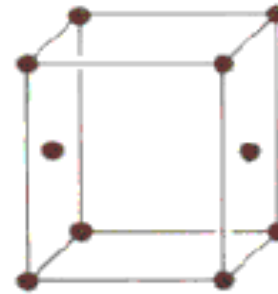
Rhomboidal



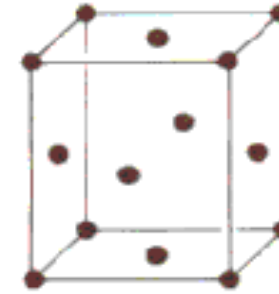
Simple
orthorhombic



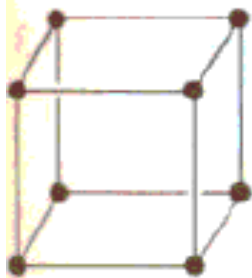
Body-centered
orthorhombic



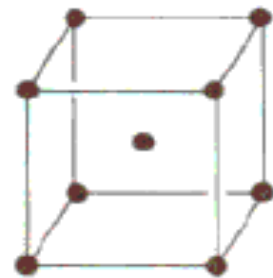
End-centered
orthorhombic



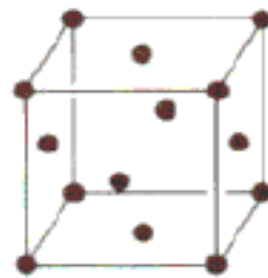
Face-centered
orthorhombic



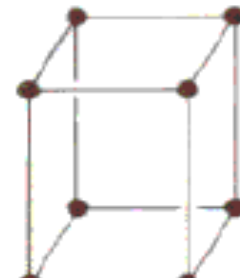
Simple
cubic



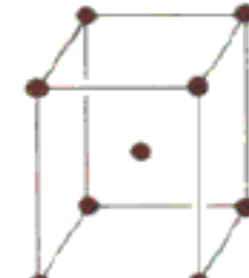
Body-centered
cubic



Face-centered
cubic



Simple
tetragonal



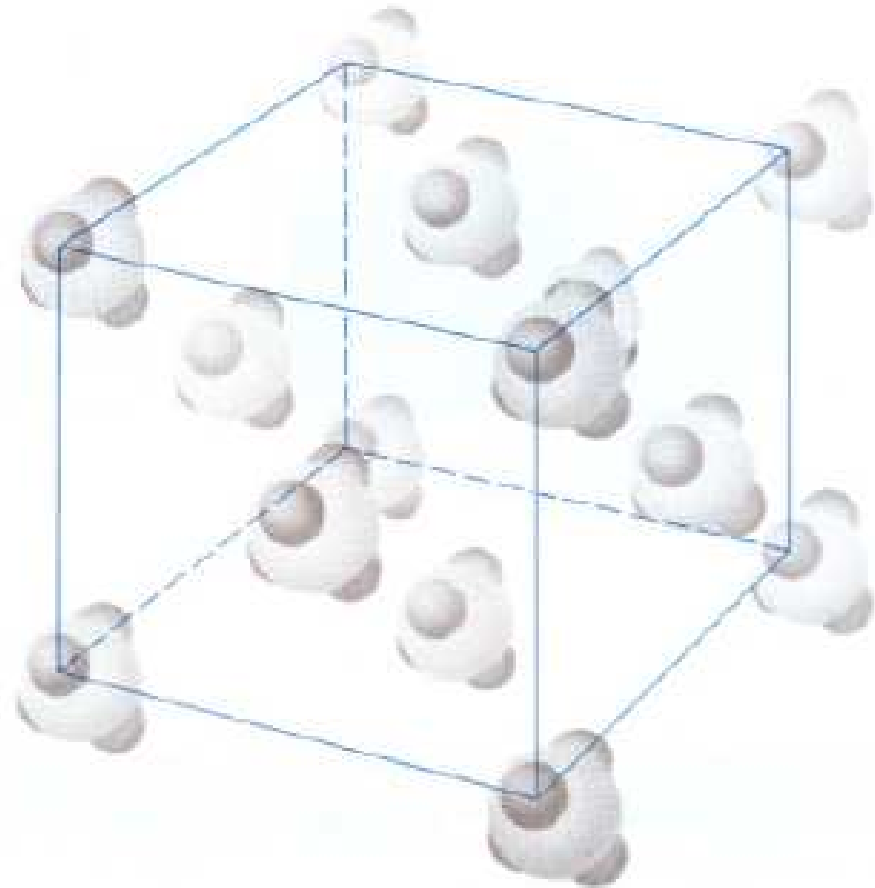
Body-centered
tetragonal

FCC lattice, e.g. solid methane.

CH_4 solidifies @ -183°C

between 20-90 K molecules rotate in their lattice sites.

Below 20 K, the molecules have identical alignments, as shown here.



Example 3-1.1:

the unit cell of Cr metal is cubic and contains 2 atoms, if the density of Cr = 7.19 Mg/m³, determine the dimension of Cr unit cell

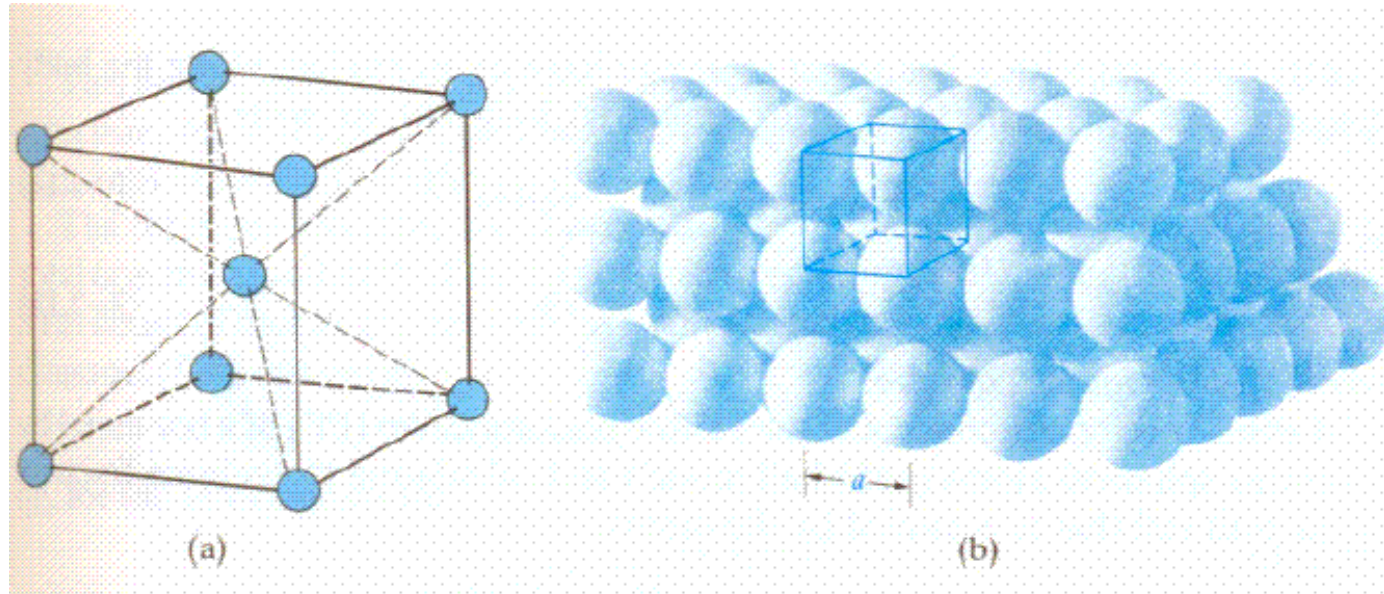
- Mass of a unit cell = $2 \text{ Cr}(52.0 \text{ g}) / (6.02 \times 10^{23} \text{ Cr})$
 $= 172.76 \times 10^{-24} \text{ g}$

$$\text{volume} = a^3 = (172.76 \times 10^{-24} \text{ g}) / (7.19 \times 10^6 \text{ g/m}^3)$$

$$= 24 \times 10^{-30} \text{ m}^3$$

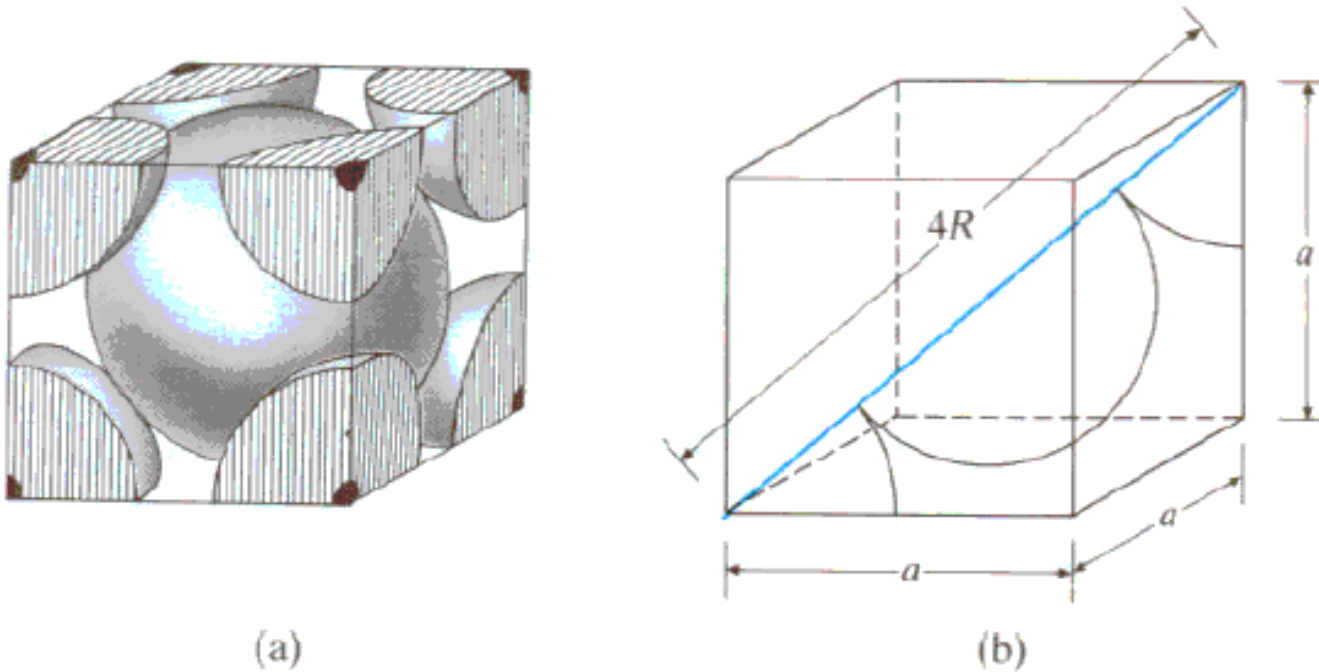
$$a = 0.2884 \times 10^{-9} \text{ m}$$

Cubic System (Body-centered cubic metals)



BCC of a metal

- a) Show the location of the atom centers.
- b) Model made from hard balls



Body centered (bcc) Metal structure: two metal atoms/unit cell and the atomic packing factor of 0.68. Since atoms are in contact along the body diagonals (b.d.) of the unit cell:

$$(b.d)_{\text{bcc metal}} = 4R = a_{\text{bcc metal}} \sqrt{3}$$

$$a_{\text{bcc metal}} = 4R/\sqrt{3}$$

a is the **lattice constant**, R = the **radius of the ion**

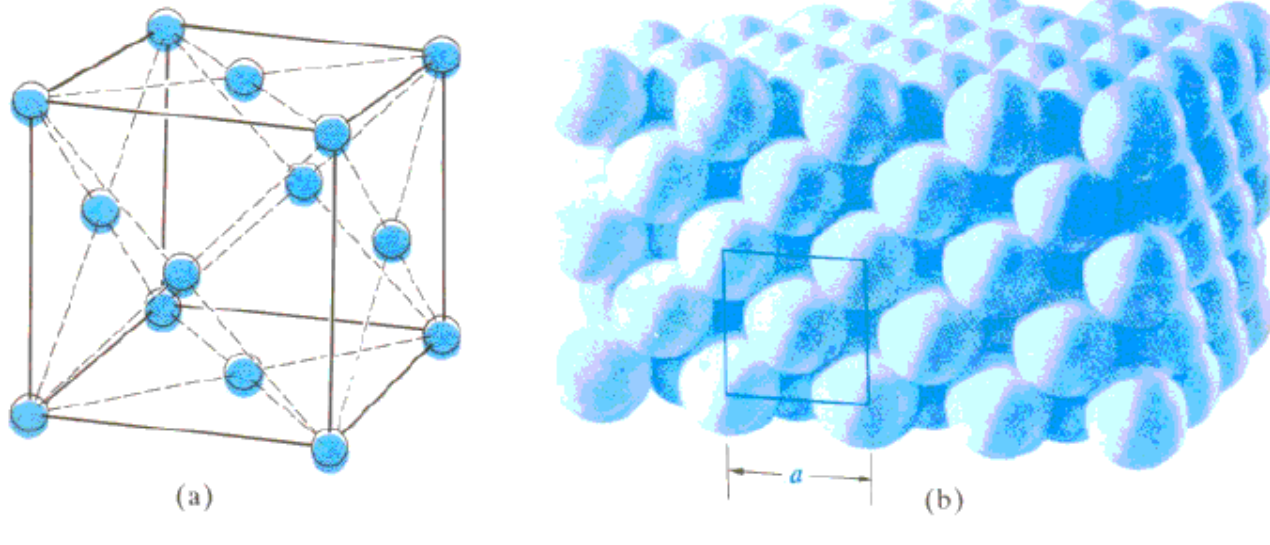
The atomic *packing factor (PF)* of a bcc metal assuming spherical atoms (hard ball model) and calculating the volume fraction of the unit cell that is occupied by the atoms

$$\text{PF (Packing factor)} = \frac{\text{volume of atoms}}{\text{volume of unit cell}}$$

There are 2 atoms per unit cell in a bcc metal, and we assuming spherical atoms

$$\text{PF} = \frac{2[4\pi R^3 / 3]}{a^3} = \frac{2[4\pi R^3 / 3]}{\left[4R / \sqrt{3}\right]^3} = 0.68$$

Face-centered cubic metals

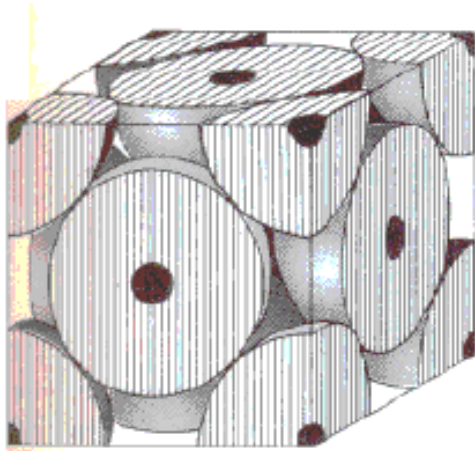


Fcc metal structure, a) Schematic view showing location of atom centers,
b) hard ball model. Each unit cell contains 4 atoms

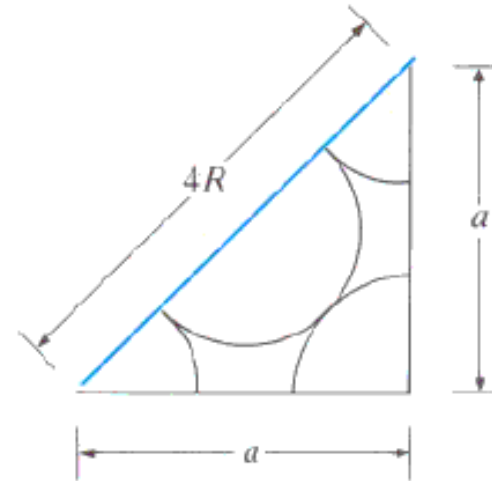
$$(f.d.)_{\text{fcc metal}} = 4R = a_{\text{fcc metal}} \sqrt{2}$$

$$a_{\text{fcc metal}} = 4R/\sqrt{2} \text{ and the PF} = 0.74$$

This is because each atom has 12 neighbours



(a)



(b)

FCC metal structure: 4 metal atoms/unit cell

atomic packing = 0.74

atoms are in contact along the face diagonals

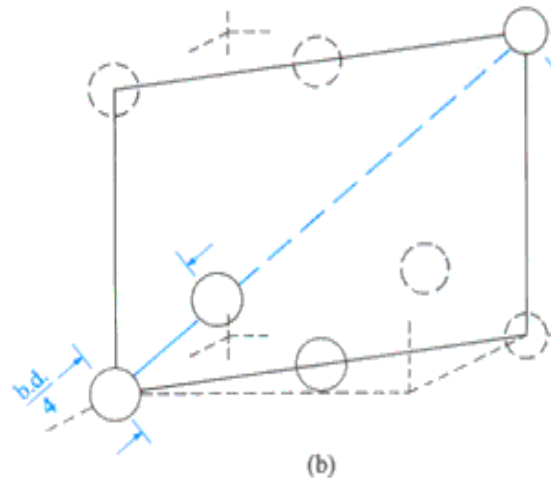
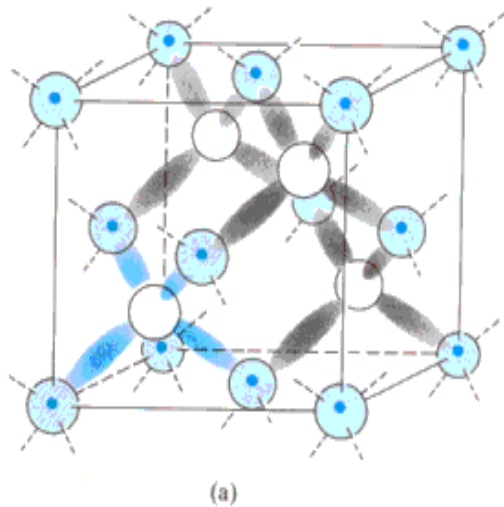
i.e. $a_{\text{fcc}} = 4R/\sqrt{2}$,

This is not applied to all fcc systems

Other face-centered cubic structure

- e.g. molecular structure of solid methane with 5 atoms occupying the fcc positions as a molecular unit.
- NaCl structure, since the atoms are unlike.
- $a_{\text{fcc NaCl}} = 2(r_{\text{Na}^+} + R_{\text{Cl}^-})$
- Note that there is a gap between the Cl⁻ ions, we can not apply the eqn used for lattice constant.

Diamond (fcc)



Diamond-Cubic Structure.

(a) Face-centered cubic (fcc).
The centers of all six faces are identical to the cube corners.

(b) Body diagonal = 4(bond length)
 $= a\sqrt{3}$.

$$(\text{b.d.})_{\text{diamond}} = 4(\text{C}-\text{C}) = (a_{\text{diamond}})\sqrt{3}$$

OR

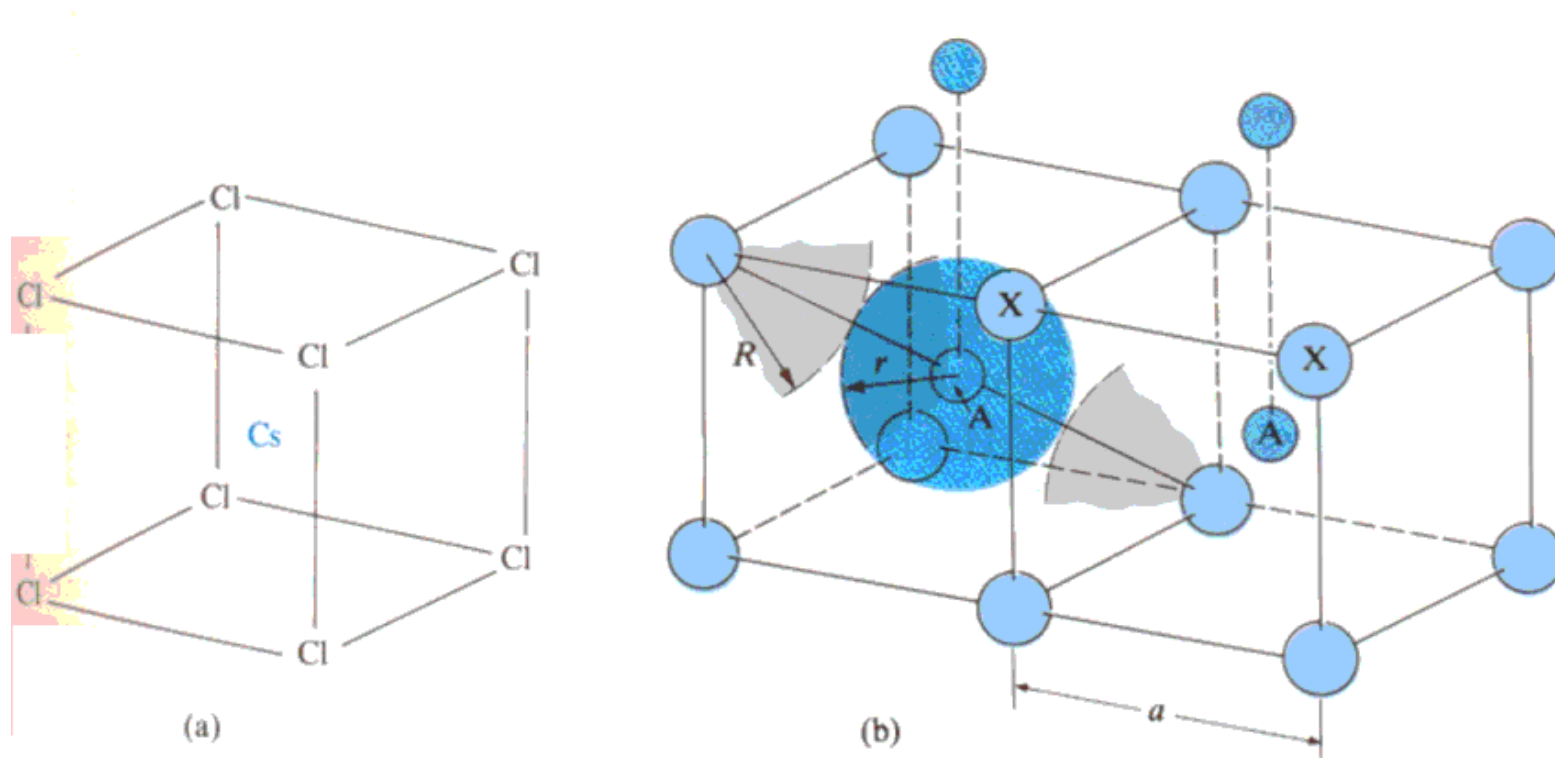
$$a_{\text{diamond}} = 4(0.154 \text{ nm})/\sqrt{3}$$

to give a value of 0.356 nm for a lattice constant, a .

Simple cubic structures

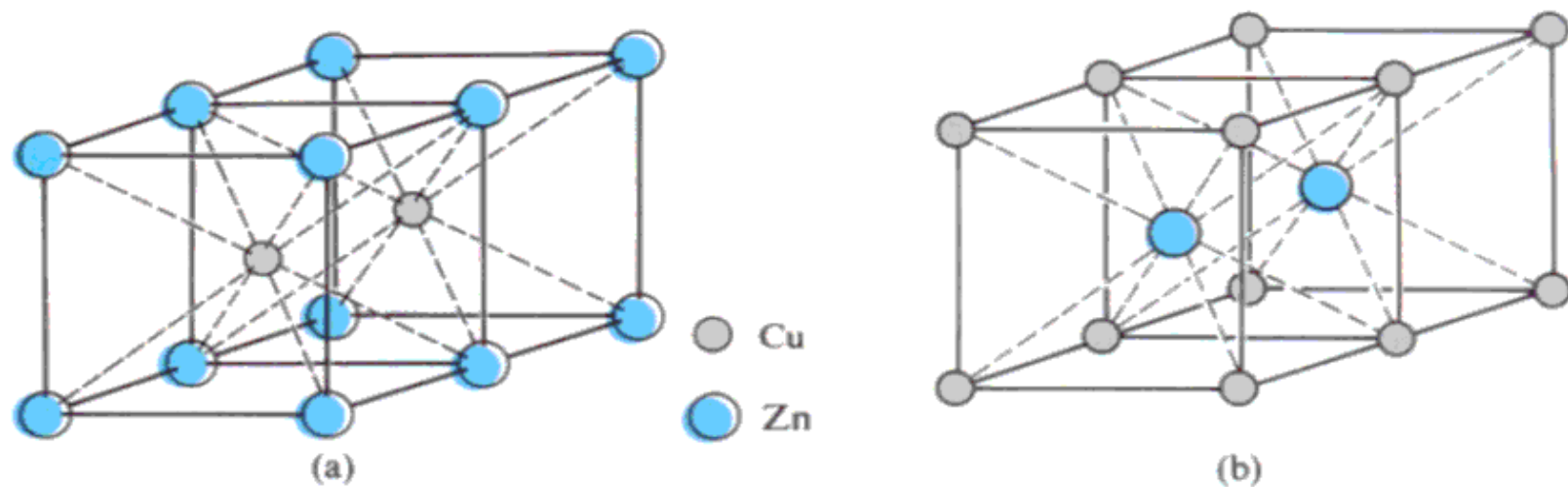
- It can be more complex than fcc or bcc
- Simple means a crystal structure with repetition at only full unit cell increments.
- bcc structure is replicated at the centre of the unit cell as well as the corners.
- fcc is replicated at the face centers as well as the corners.
- A simple cubic (sc) cell lacks at both these centered locations.
- In CsCl, (sc), Cl⁻ at the cell corners; Cs⁺ at the cell centre. But this **is not bcc** , because the cell centre possesses an ion different from that at the cell corner.

Simple cubic structures



AX Structure (CsCl-Type). The A atom, or ion, sits in the interstitial site among eight X atoms (8-f sites). These $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ locations are occupied on all unit cells.

Also note that X atoms sit among eight A atoms. the lattice constant a equals $2(r + R)/\sqrt{3}$.



Simple Cubic (sc) Structure (β' Brass). Each copper atom is coordinated with eight zinc atoms; and each zinc atom is coordinated with eight copper atoms. The choice between (a) and (b) is arbitrary. The structure is simple cubic, because the center site does not duplicate the corner sites. The prototype for this structure is CsCl

Properties of simple cubic structures

- Binary (Two component system)
- The unit cell has two radii.
- $a_{\text{CsCl-type}} = 2(r_{\text{Cs}^+} + R_{\text{Cl}^-})/\sqrt{3}$
- CN = 8, $r/R = 0.73$,
- not in case of MgO $r_{\text{Mg}^{2+}}/R_{\text{O}^{2-}} = 0.47$

Calcium titanate, CaTiO₃ is also SC

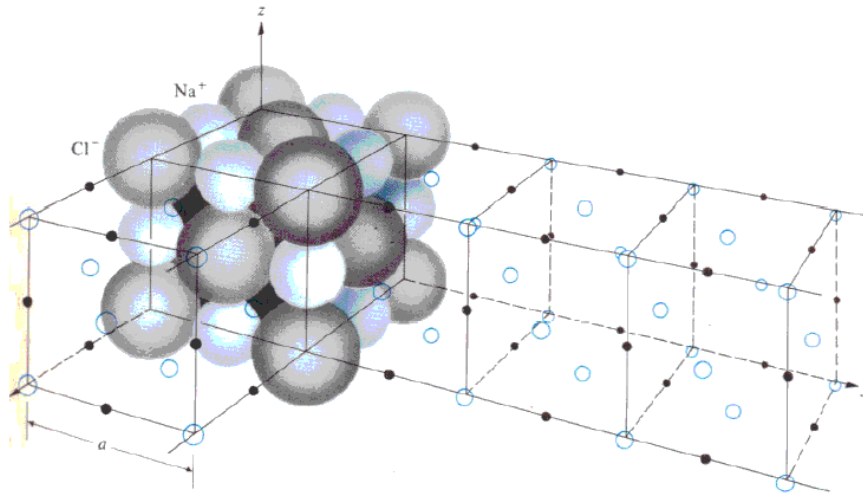
- Ca²⁺ are located at the corners of the unit cell
- Ti⁴⁺ are located at the center
- O²⁻ at the center of each face
- **Therefore, it is neither bcc nor fcc**

Example 3-21

Calculate (a) the atomic packing factor of an fcc metal

(b) the ionic packing factor of fcc NaCl

There are 4 atoms/unit cell in an fcc metal structure



- But there are 4 Na⁺ and 4 Cl⁻ per unit cell.

- Note: The lattice constants is related differently from fcc

$$\text{a) Packing factor} = \frac{\text{volume of atoms}}{\text{volume of unit cell}} = \frac{4(4\pi R^3 / 3)}{a^3} = \frac{16\pi R^3 2\sqrt{2}}{(3)(64R^3)}$$

b) for fcc NaCl

$$\text{Packing factor} = \frac{4(4\pi r^3 / 3) + 4(4\pi R^3 / 3)}{(2r + 2R)^3} = \frac{16\pi[(0.097)^3 + (0.181)^3]}{(3)(8)(0.097 + 0.181)^3} = 0.67$$

Example 3-2.2

p71

Copper has an fcc metal structure with an atom radius of 0.1278 nm. Calculate its density and check this value with the density listed in Appendix B.

Procedure: Since $\rho = m/V$, we must obtain the mass per unit cell and the volume of each unit cell. The former is calculated from the mass of four atoms; the latter requires the calculation of the lattice constant, a , for an fcc metal structure.

$$a = \frac{4}{\sqrt{2}} (0.1278 \text{ nm}) = 0.3615 \text{ nm}$$

$$\begin{aligned} \text{density} &= \frac{\text{mass/unit cell}}{\text{volume / unit cell}} \\ &= \frac{(\text{atoms/unit cell})(\text{g/atom})}{(\text{lattice constant})^3} \\ &= \frac{4[63.5 / (0.602 \times 10^{24})]}{(0.3615 \times 10^{-9})^3} = 8.93 \text{ Mg/m}^3 \end{aligned}$$

Example 3-2.2 p71

$$a = \frac{4}{\sqrt{2}} (0.1278 \text{ nm}) = 0.3615 \text{ nm}$$

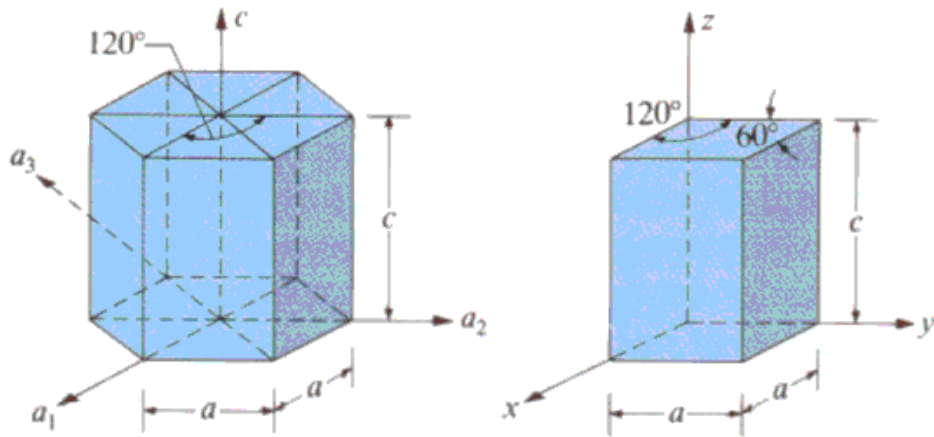
$$\text{density} = \frac{\text{mass/unit cell}}{\text{volume / unit cell}}$$

$$\text{density} = \frac{(\text{atoms/unit cell})(\text{g/atom})}{(\text{lattice constant})^3}$$

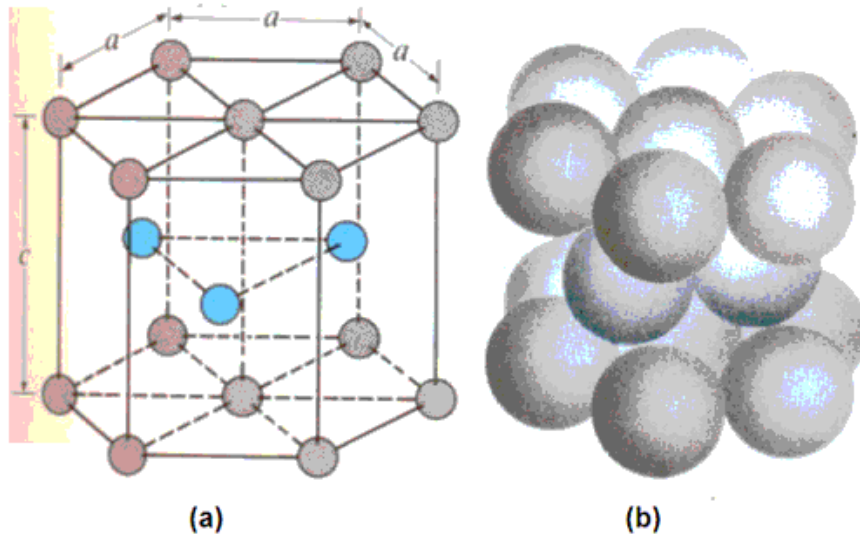
$$\text{density} = \frac{4[63.5/(6.02 \times 10^{24})]}{(0.3615 \times 10^{-9} \text{ m})^3} = 8.93 \text{ Mg / m}^3$$

Noncubic structures

Hexagonal Close-Packed Metals



Hexagonal Cells. (a) Hexagonal representation (four axes). (b) Rhombic representation (three axes). The two representations are equivalent geometrically, with $a \neq c$, $\gamma = 120^\circ$, and $\alpha = \beta = 90^\circ$; however, $V_a = 3 V_b$.



Hexagonal Close-Packed (hcp) Metal Structure. (a) Schematic view showing the location of atom centers. (b) Model made from hard balls.

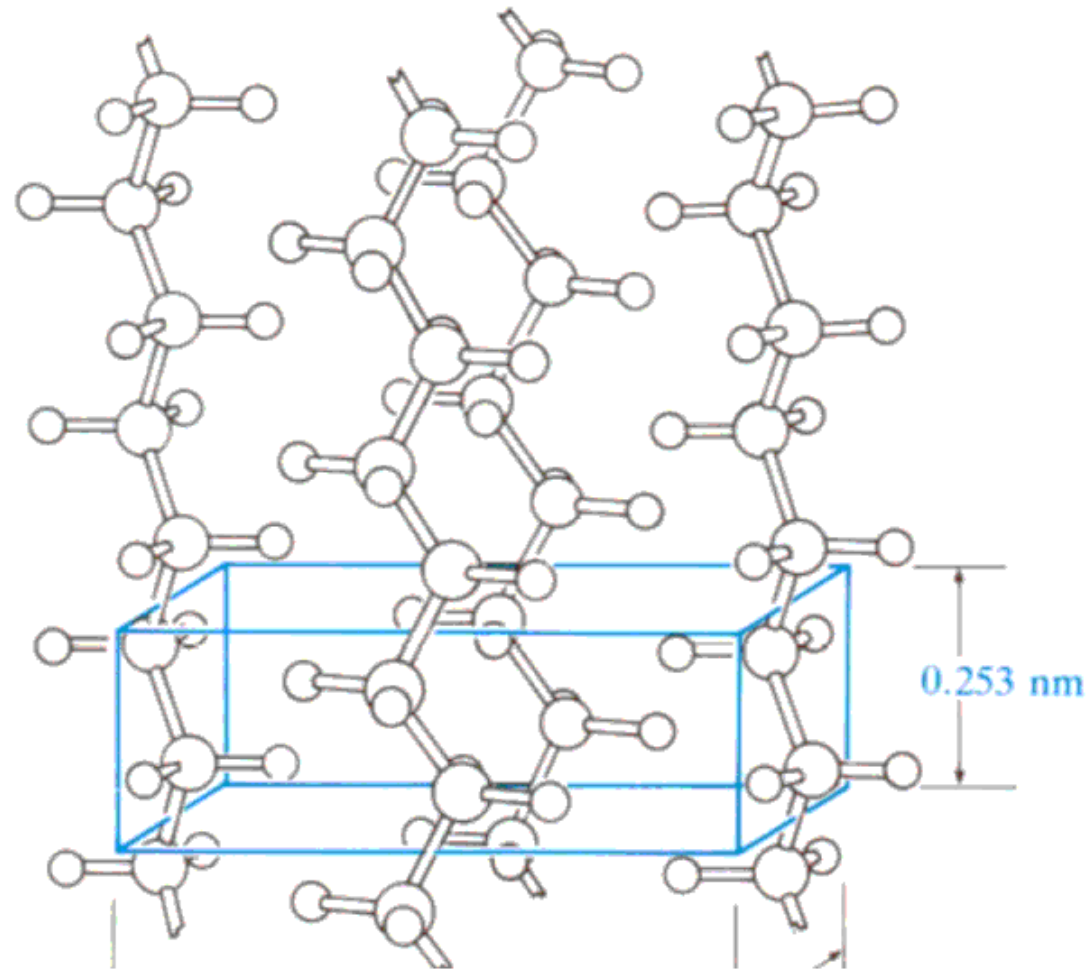
Noncubic structures

Hexagonal Close-Packed Metals

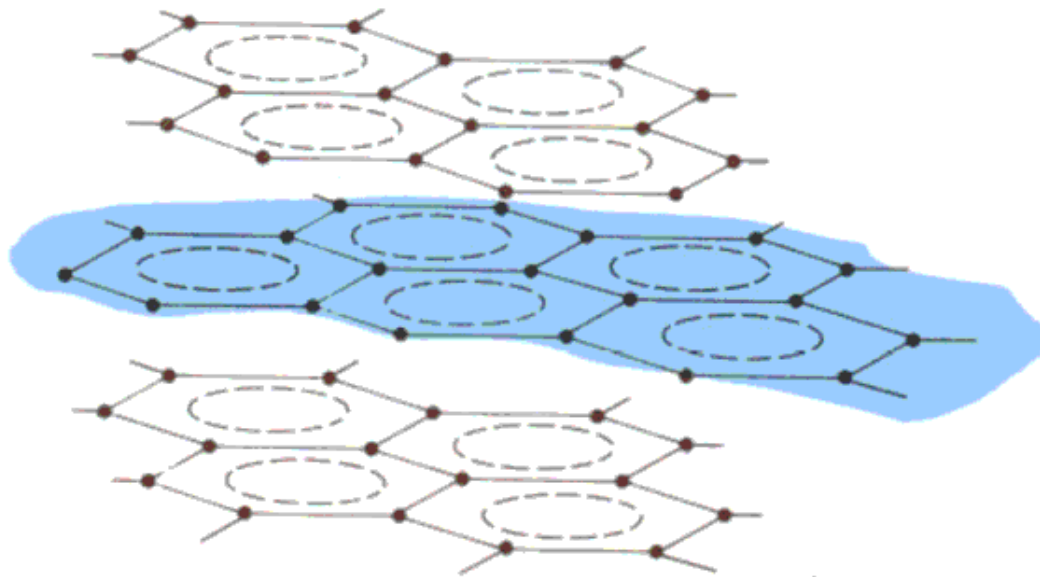
- Examples are Mg, Ti and Zn
- Called the hexagonal closed-packed structure (hcp)
- Each atom is located directly above or below interstices among three atoms in the adjacent layer below its plane
- Each atom touches 3 atoms below and 6 atoms in the same plane.
- Average of 6 atoms/ unit cell.
- Such as the fcc CN =12
- Therefore, the packing factor = 0.74

Other non cubic structure

- Iodine → orthorhombic, because I_2 is not spherically sym.
- Polyethylene → orthorhombic, complex, due to the large and linear molecules.
- Graphite → hexagonal structure



Molecular Crystal (Polyethylene). The chains are aligned longitudinally. The unit cell is orthorhombic with 90° angles.



Delocalized Electrons in Graphite Layers. Each layer contains “multiple benzene rings” The conductivity is more than 100 times greater in the parallel direction than it is in the perpendicular direction.

Graphite is ***anisotropic***: it has directional variation in structure and properties

It retain its hexagonal arrangement up to 2200°C.

The weak bonds between the planes permit graphite layers to slide over each other

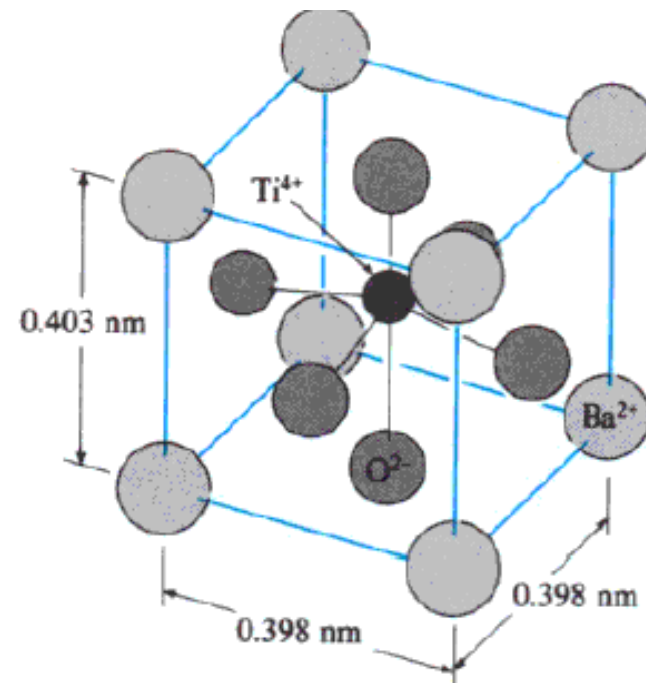
Iron carbide:

- Called cementite., Fe_3C
- The crystal lattice contains 2 elements in a fixed 3:1 ratio
- Orthorhombic, 12 Fe and 4 C atoms in each unit cell.
- Carbon in the interstices among the larger Fe atoms.
- it greatly affects the properties of steel due to its superior hardness.

Barium Titanate:

- BaTiO_3 , Tetragonal system

Tetragonal BaTiO_3 : The base of the unit cell is square; but unlike in CaTiO_3 , $c \neq a$. Also, the Ti^{4+} and O^{2-} ions are not symmetrically located with respect to the corner Ba^{2+} ions. Above 120°C , BaTiO_3 changes from this structure to that of CaTiO_3 .



Example 3–3.1

The atomic packing factor of magnesium, like that of all hcp metals, is 0.74. What is the volume of magnesium's unit cell, which is shown in Fig. 3–3.2(a)?

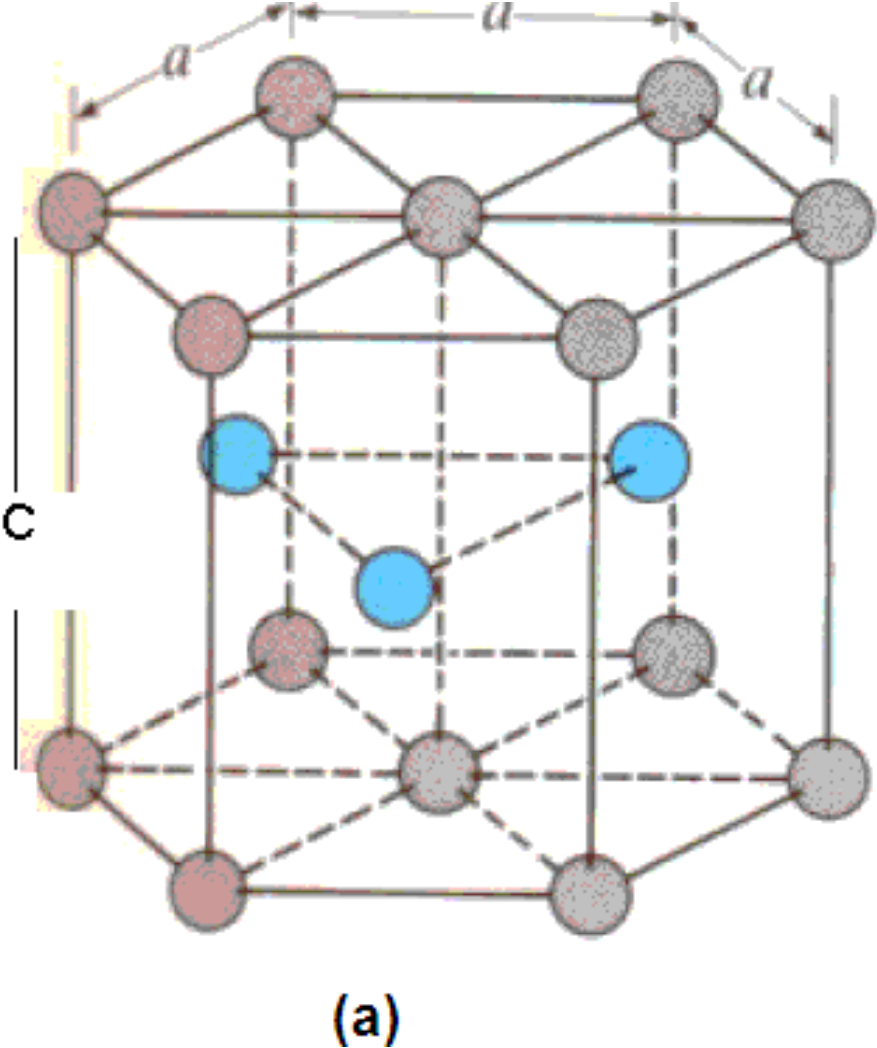
Procedures From Appendix B, magnesium has $\rho = 1.74 \text{ Mg/m}^3$ (or 1.74 g/cm^3); its atomic mass = 24.31 amu, and $R_{\text{Mg}} = 0.161 \text{ nm}$. From Fig. 3–3.2(a), $12/6 + 2/2 + 3 = 6$ atoms/unit cell.

Two approaches are possible. (a) Since the packing factor is given as 0.74, calculate the volume of six atoms per unit cell. (b) Since $\rho = m/V$, calculate the mass of six atoms per unit cell, then the volume per unit cell.

Calculation

$$\begin{aligned} \text{(a) } V_{\text{u.c.}} &= 6 \text{ atoms } (4\pi/3)(0.161 \text{ nm})^3/0.74 \\ &= 0.14 \text{ nm}^3 \qquad \qquad \qquad \text{(or } 1.4 \times 10^{-28} \text{ m}^3) \end{aligned}$$

Fig. 3-3.2



$$(b) m_{\text{u.c.}} = 6 \text{ atoms } (24.31 \text{ g}) / (0.602 \times 10^{24}) = 2.42 \times 10^{-22} \text{ g}$$

$$V_{\text{u.c.}} = \frac{m}{\rho} = (2.42 \times 10^{-22} \text{ g}) / (1.74 \times 10^6 \text{ g/m}^3)$$

$$= 1.4 \times 10^{-28} \text{ m}^3$$

(or 0.14 nm^3)

Comments The average radius, \bar{R} , of the magnesium atom is 0.161 nm. However, X-ray diffraction data show that the Mg atoms are compressed almost 1 percent to become oblate spheroids. (See the Comments in Example 3-3.2 and the footnote to Appendix B.)