

THE STRUCTURE OF CRYSTALLINE SOLIDS

Subject: Material Science - Lecture #5

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WHY STUDY *The Structure of Crystalline Solids*?

- The properties of some materials are directly related to their crystal structures.

For example, pure and undeformed magnesium and beryllium, having one crystal structure, are much more brittle (i.e., fracture at lower degrees of deformation) than are pure and undeformed metals such as gold and silver that have yet another crystal structure

- Furthermore, significant property differences exist between crystalline and noncrystalline materials having the same composition.

For example, noncrystalline ceramics and polymers normally are optically transparent; the same materials in crystalline (or semicrystalline) form tend to be opaque or, at best, translucent.

Learning Objectives

After studying this chapter, you should be able to do the following:

1. Describe the difference in atomic/molecular structure between crystalline and noncrystalline materials.
2. Draw unit cells for face-centered cubic, body-centered cubic, and hexagonal close-packed crystal structures.
3. Derive the relationships between unit cell edge length and atomic radius for face-centered cubic and body-centered cubic crystal structures.
4. Compute the densities for metals having face-centered cubic and body-centered cubic crystal structures given their unit cell dimensions.

5. Given three direction index integers, sketch the direction corresponding to these indices within a unit cell.
6. Specify the Miller indices for a plane that has been drawn within a unit cell.
7. Describe how face-centered cubic and hexagonal close-packed crystal structures may be generated by the stacking of close-packed planes of atoms.
8. Distinguish between single crystals and polycrystalline materials.
9. Define *isotropy* and *anisotropy* with respect to material properties.

INTRODUCTION

- Previous lecture was concerned primarily with the various types of atomic bonding, which are determined by the electron structures of the individual atoms.
- The present discussion is devoted to the next level of the structure of materials, specifically, to some of the arrangements that may be assumed by atoms in the solid state.
- Within this framework, concepts of crystallinity and noncrystallinity are introduced.

- For crystalline solids, the notion of crystal structure is presented, specified in terms of a unit cell.
- The three common crystal structures found in metals are then detailed, along with the scheme by which crystallographic points, directions, and planes are expressed.
- Single crystals, polycrystalline materials, and noncrystalline materials are considered.
- Another section of this chapter briefly describes how crystal structures are determined experimentally using x-ray diffraction techniques.

Crystal Structures

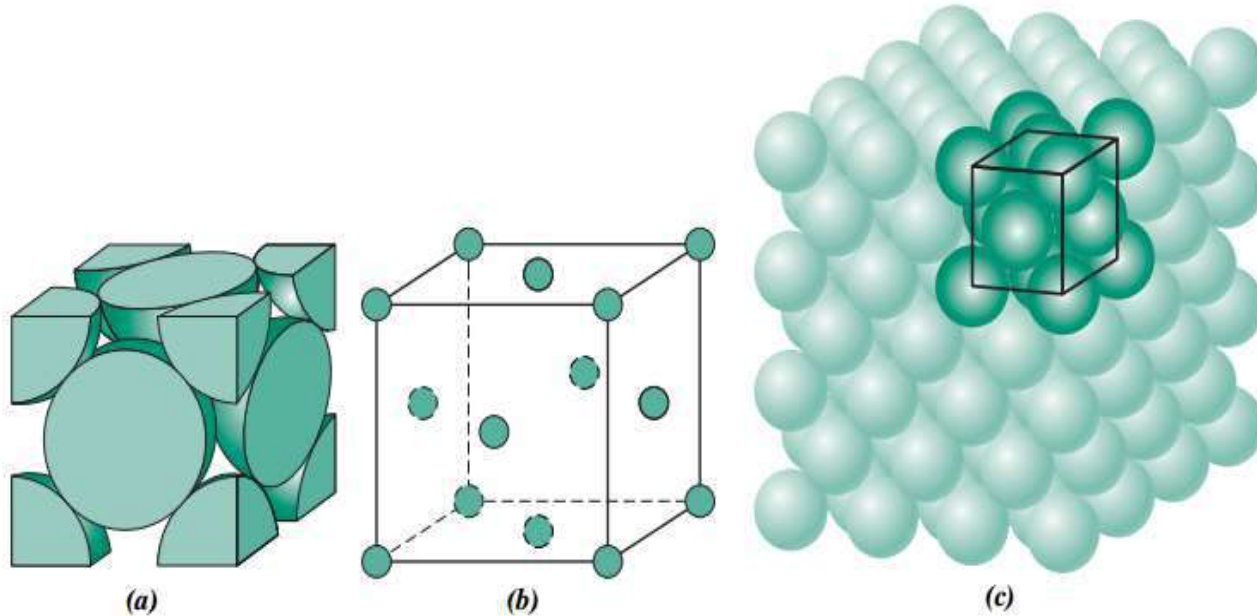
FUNDAMENTAL CONCEPTS

- Solid materials may be classified according to the regularity with which atoms or ions are arranged with respect to one another.
- A **crystalline** material is one in which the atoms are situated in a repeating or periodic array over large atomic distances—that is, long-range order exists, such that upon solidification, the atoms will position themselves in a repetitive three-dimensional pattern, in which each atom is bonded to its nearest-neighbor atoms.

- All metals, many ceramic materials, and certain polymers form crystalline structures under normal solidification conditions.
- For those that do not crystallize, this long-range atomic order is absent; these *noncrystalline* or *amorphous* materials are discussed briefly at the end of this chapter.
- Some of the properties of crystalline solids depend on the **crystal structure** of the material, the manner in which atoms, ions, or molecules are spatially arranged.
- There is an extremely large number of different crystal structures all having long-range atomic order; these vary from relatively simple structures for metals to exceedingly complex ones, as displayed by some of the ceramic and polymeric materials.

- The present discussion deals with several common metallic crystal structures.
- When crystalline structures are described, atoms (or ions) are thought of as being solid spheres having well-defined diameters. This is termed the atomic hard-sphere model in which spheres representing nearest-neighbor atoms touch one another.





For the face-centered cubic crystal structure, (a) a hard-sphere unit cell representation, (b) a reduced-sphere unit cell, and (c) an aggregate of many atoms.

- the term **lattice** is used in the context of crystal structures; in this sense *lattice* means a three-dimensional array of points set of mathematical points coinciding with atom positions (or sphere centers)



atom

+



lattice

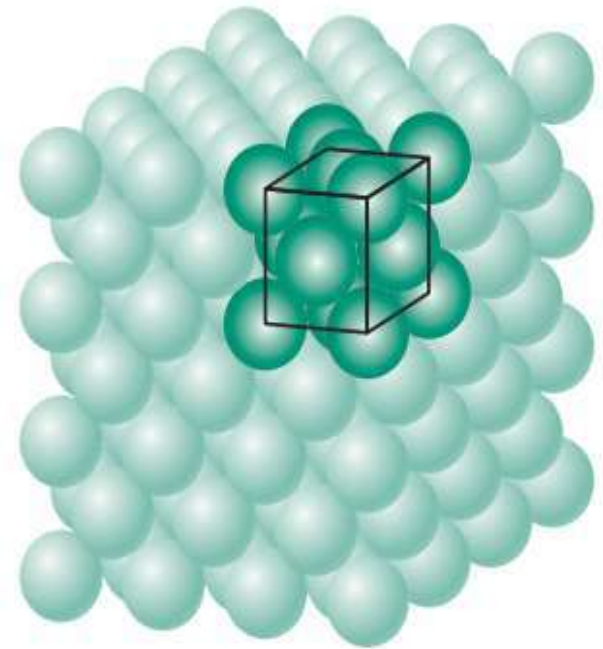
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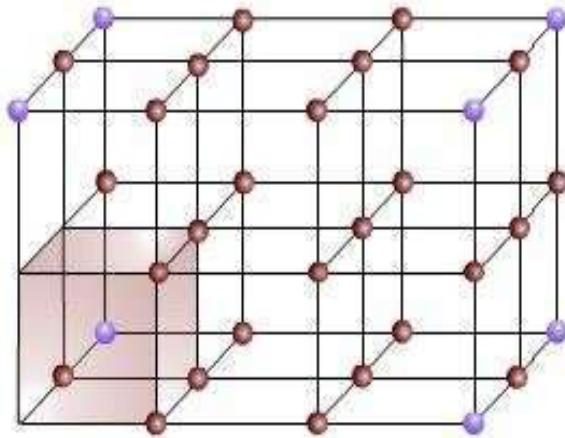
Crystal structure

UNIT CELLS

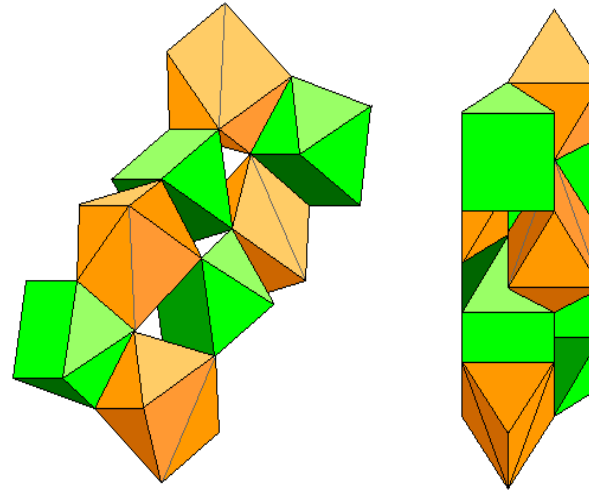
- The atomic order in crystalline solids indicates that small groups of atoms form a repetitive pattern. Thus, in describing crystal structures, it is often convenient to subdivide the structure into small repeat entities called **unit cells**.



- Unit cells for most crystal structures are parallelepipeds or prisms

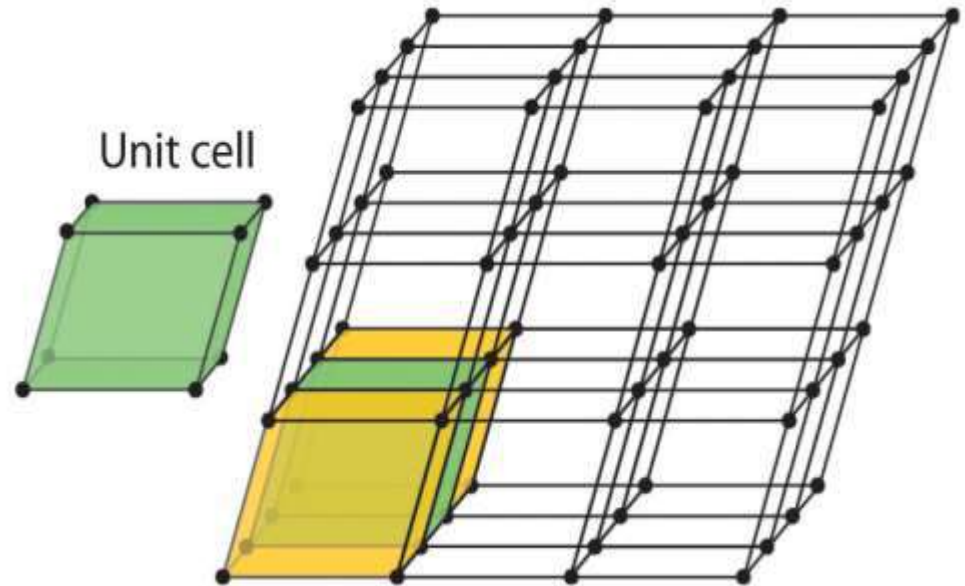


Representation of space
lattice and unit cell

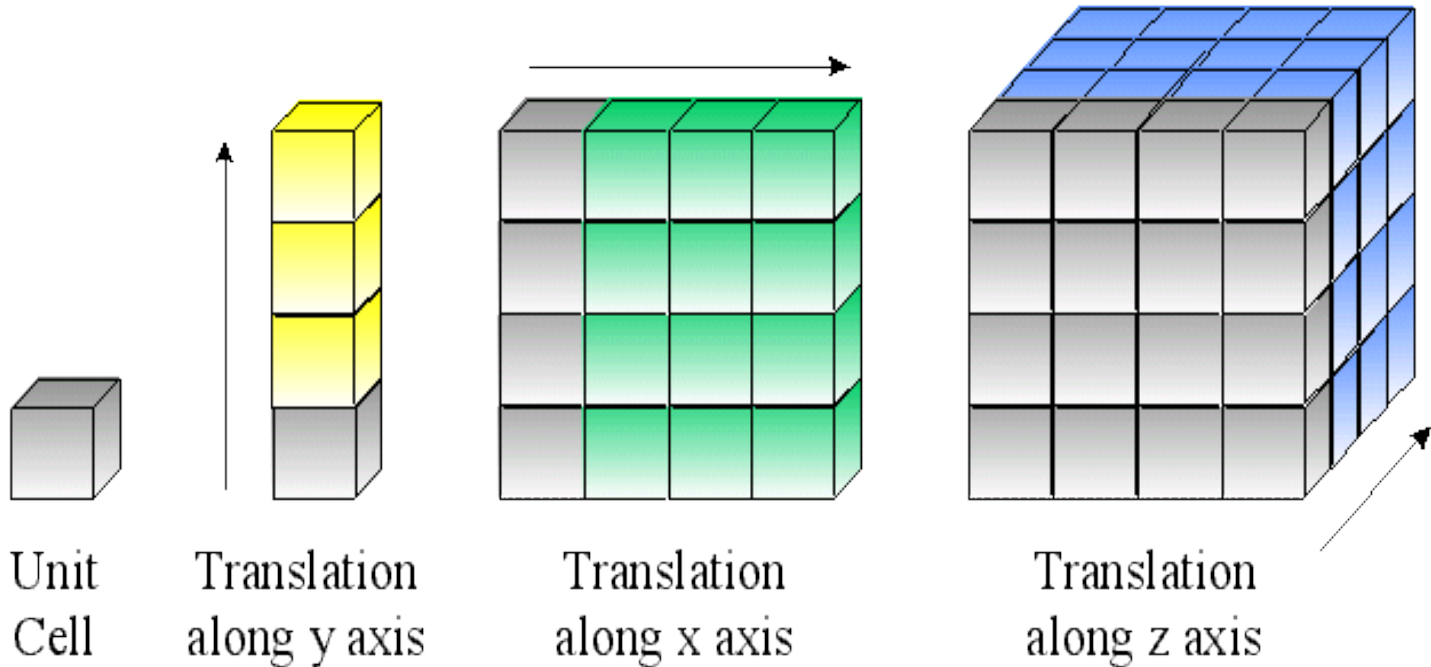


Stibnite crystal is a sulfide mineral with the formula Sb_2S_3

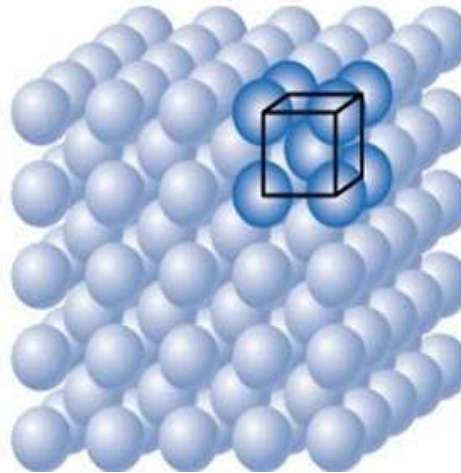
- A unit cell is chosen to represent the symmetry of the crystal structure, wherein all the atom positions in the crystal may be generated by translations of the unit cell integral distances along each of its edges.



A Crystalline Solid Can Be Constructed From
A “Unit Cell” Plus Translational Operators

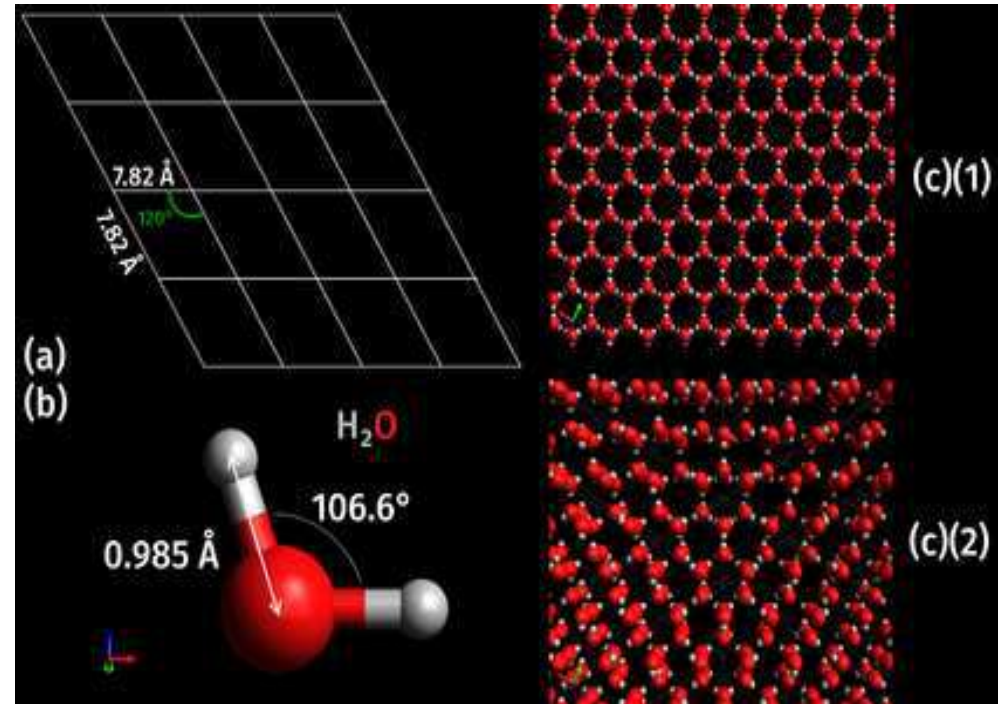


- The unit cell is the basic structural unit or building block of the crystal structure and defines the crystal structure by virtue of its geometry and the atom positions within.
- The unit cell usually dictates that parallelepiped corners coincide with centers of the hard-sphere atoms.





snowflakes



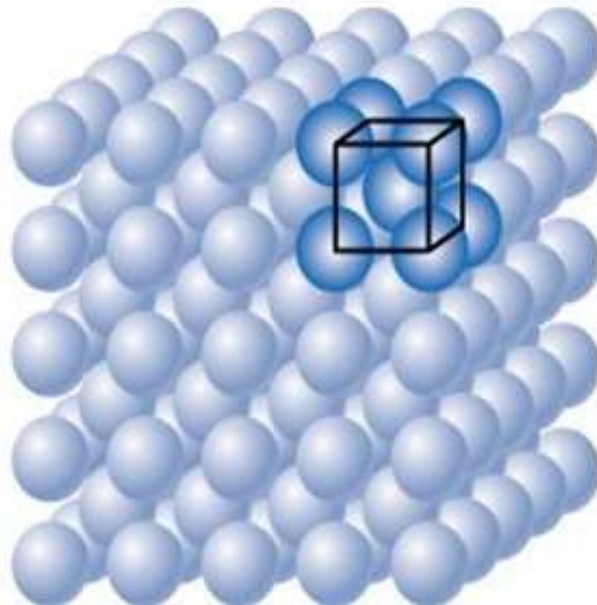
The (3-D) crystal structure of H_2O ice Ih (c) consists of bases of H_2O ice molecules (b) located on lattice points within the (2-D) hexagonal space lattice (a).

METALLIC CRYSTAL STRUCTURES

- The atomic bonding in this group of materials is metallic and thus nondirectional in nature.
- Consequently, there are minimal restrictions as to the number and position of nearest-neighbor atoms; this leads to relatively large numbers of nearest neighbors and dense atomic packings for most metallic crystal structures.

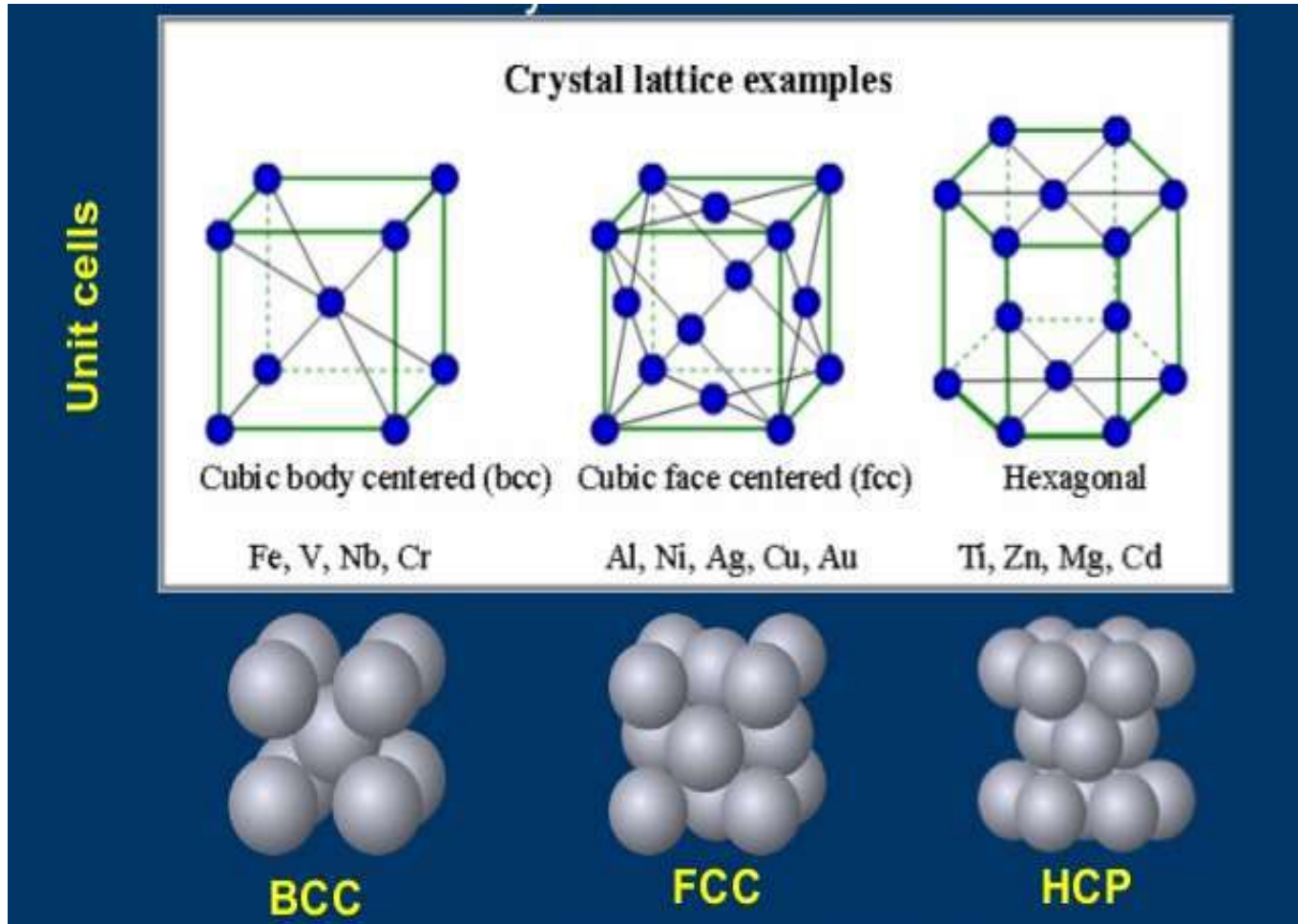


- For metals, when we use the hard-sphere model for the crystal structure, each sphere represents an ion core.



- Table below presents the atomic radii for a number of metals.
- Three relatively simple crystal structures are found for most of the common metals: face-centered cubic (FCC), body-centered cubic (BCC), and hexagonal close-packed (HCP).

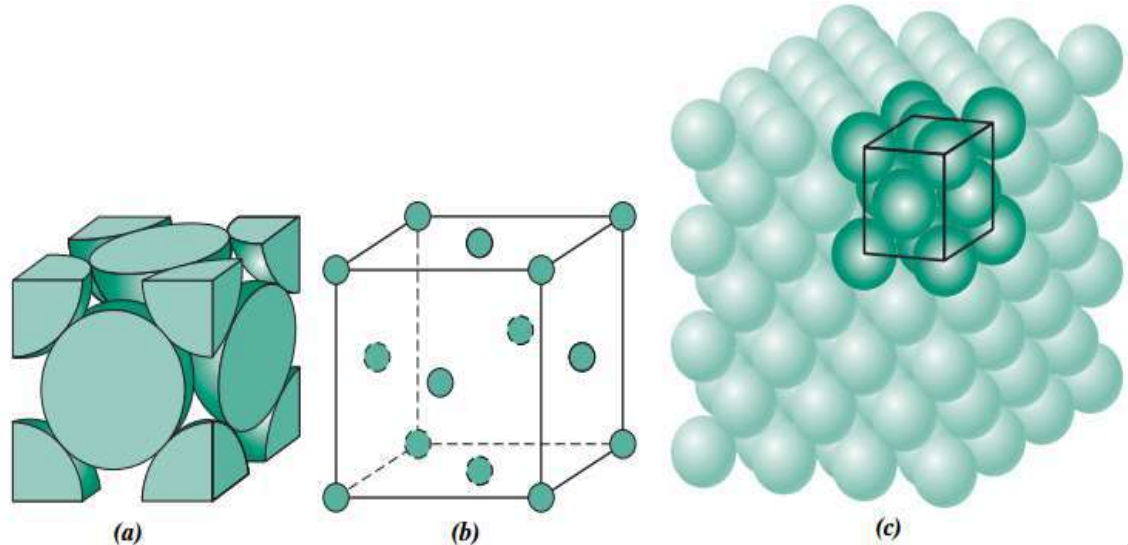
<i>Metal</i>	<i>Crystal Structure^a</i>	<i>Atomic Radius^b (nm)</i>	<i>Metal</i>	<i>Crystal Structure</i>	<i>Atomic Radius (nm)</i>
Aluminum	FCC	0.1431	Molybdenum	BCC	0.1363
Cadmium	HCP	0.1490	Nickel	FCC	0.1246
Chromium	BCC	0.1249	Platinum	FCC	0.1387
Cobalt	HCP	0.1253	Silver	FCC	0.1445
Copper	FCC	0.1278	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



The Face-Centered Cubic Crystal Structure (FCC)

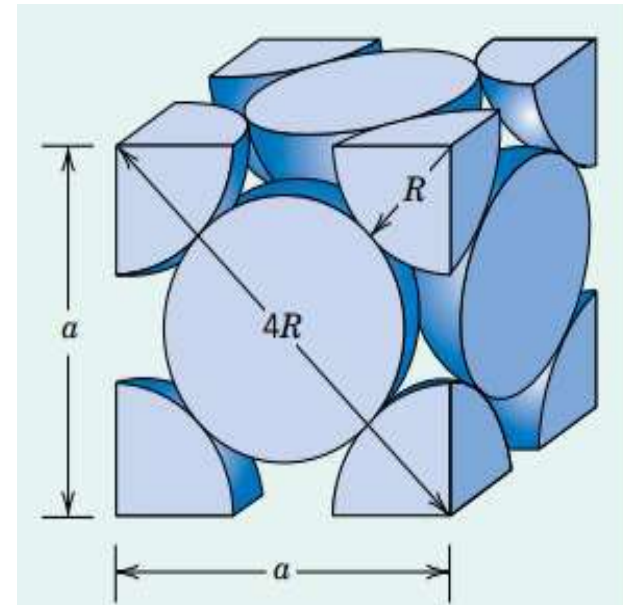
- The crystal structure found for many metals has a unit cell of cubic geometry, with atoms located at each of the corners and the centers of all the cube faces. It is called the **face-centered cubic (FCC)** crystal structure.

(a) a hard-sphere unit cell representation, (b) a reduced sphere unit cell, and (c) an aggregate of many atoms.



- These spheres or ion cores touch one another across a face diagonal; the cube edge length a and the atomic radius R are related through:

$$a = 2R\sqrt{2} \quad \dots \dots \dots (3.1)$$



EXAMPLE

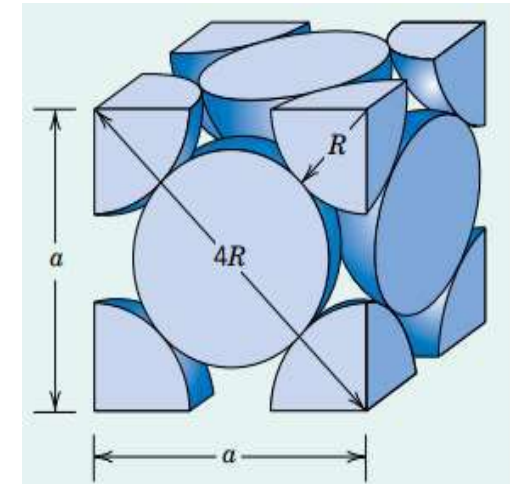
Determination of FCC Unit Cell Volume

Calculate the volume of an FCC unit cell in terms of the atomic radius R .

Solution

In the FCC unit cell illustrated, the atoms touch one another across a face-diagonal, the length of which is $4R$. Because the unit cell is a cube, its volume is a^3 , where a is the cell edge length. From the right triangle on the face,

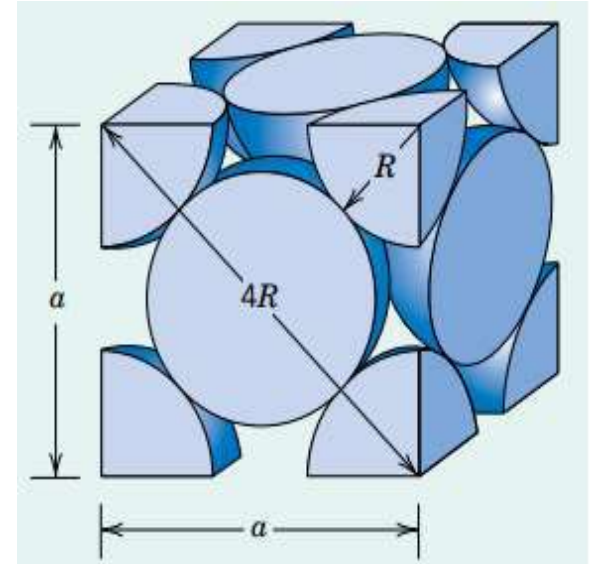
$$a^2 + a^2 = 4R^2$$



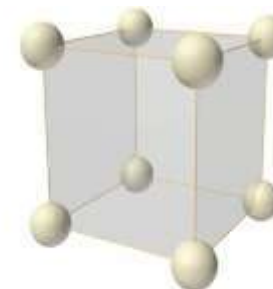
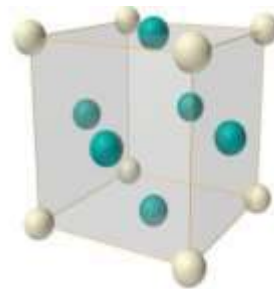
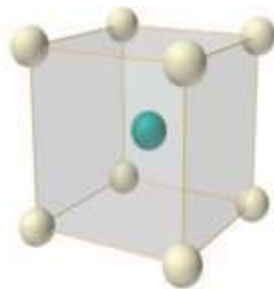
$$\begin{aligned}a^2 + a^2 &= (4R)^2 \\2a^2 &= (4R)^2 \\a &= 2R\sqrt{2}\end{aligned}$$

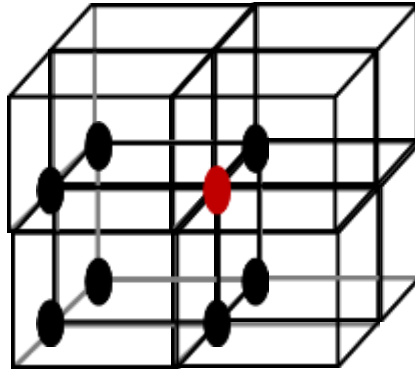
The FCC unit cell volume V_C may be computed from

$$V_C = a^3 = (2R\sqrt{2})^3 = 16R^3\sqrt{2} \quad \dots \dots \dots (3.6)$$



- To determine the number of atoms associated with each unit cell. Depending on an atom's location, it may be considered to be shared with adjacent unit cells—that is, only some fraction of the atom is assigned to a specific cell.
- For example, for cubic unit cells,
 - 1- an atom completely within the interior “belongs” to that unit cell,
 - 2- an atom at a cell face is shared with one other cell
 - 3- an atom residing at a corner is shared among eight.





- The number of atoms per unit cell, N , can be computed using the following formula:

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8} \quad \dots \dots \dots (3.2)$$

where

N_i = the number of interior atoms

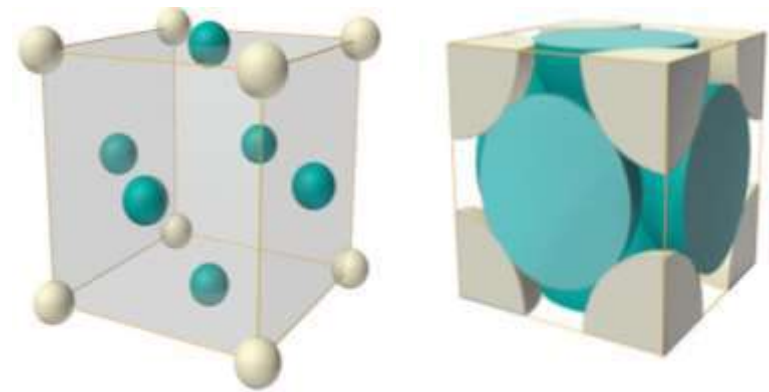
N_f = the number of face atoms

N_c = the number of corner atoms

- For the FCC crystal structure, there are eight corner atoms ($N_c = 8$), six face atoms ($N_f = 6$), and no interior atoms ($N_i = 0$). Thus, from Equation 3.2,

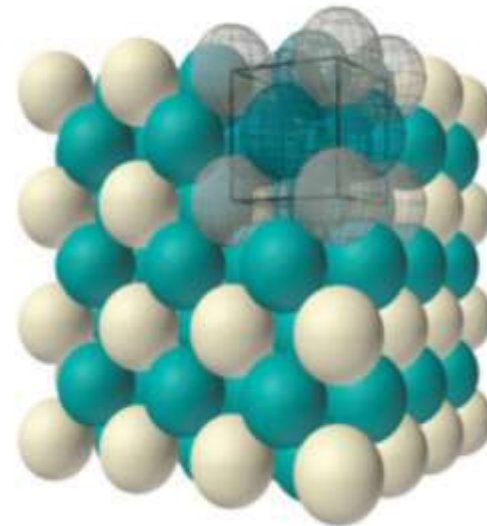
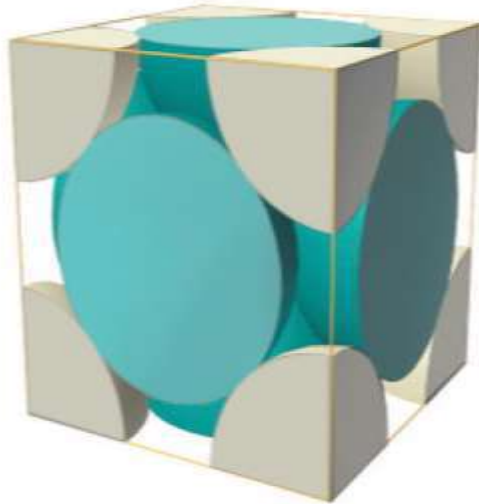
$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8} \quad \dots \dots \dots (3.2)$$

$$N = 0 + \frac{6}{2} + \frac{8}{8} = 4$$

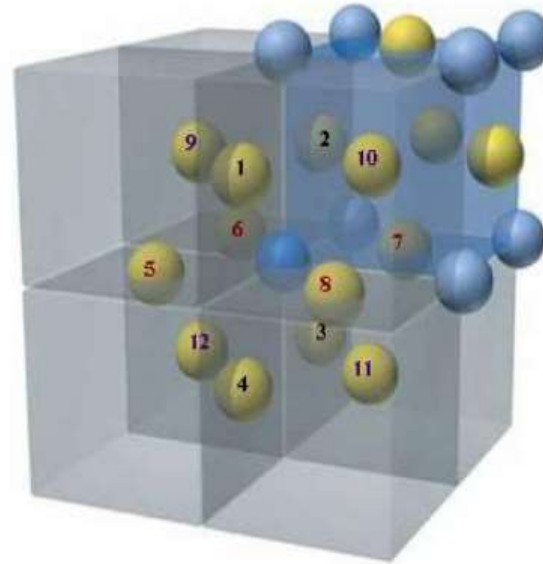


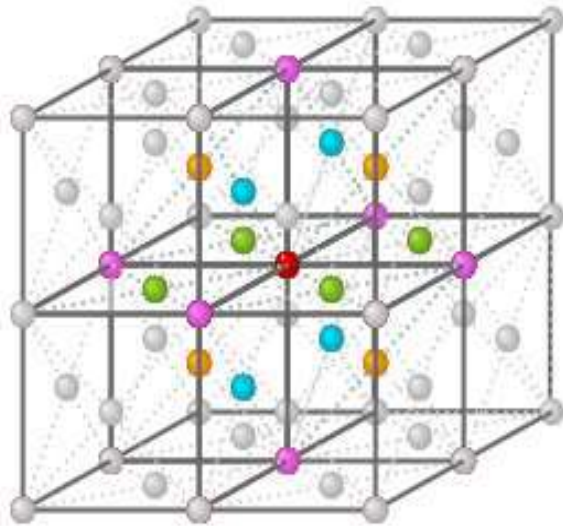
A total of four whole atoms may be assigned to a given unit cell.

- The cell is composed of the volume of the cube that is generated from the centers of the corner atoms.
- Corner and face positions are really equivalent—that is, translation of the cube corner from an original corner atom to the center of a face atom will not alter the cell structure.



- Two other important characteristics of a crystal structure are the **coordination number** and the **atomic packing factor (APF)**.
- For metals, each atom has the same number of nearest-neighbor or touching atoms, which is the coordination number.
- For face-centered cubic, the coordination number is 12.





● reference point

● ● ● 12 nearest neighbours

● 6 next-nearest neighbours

$$\frac{fd}{2} = \frac{1.4}{2} = 0.7a$$

a

Where : $(fd)^2 = a^2 + a^2 = 2a^2 \rightarrow fd = \sqrt{2}a = 1.4a$

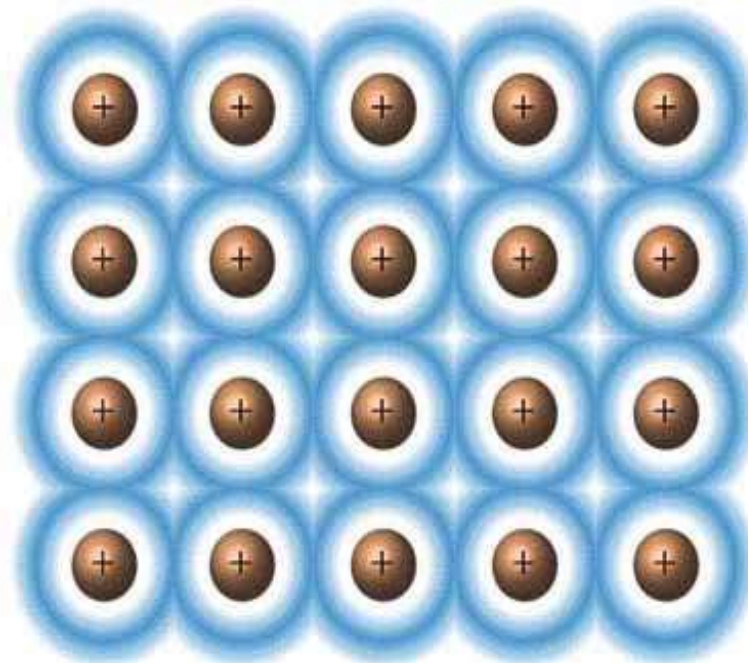
$$\frac{fd}{2} = \frac{1.4}{2} = 0.7a$$

- The APF is the sum of the sphere volumes of all atoms within a unit cell (assuming the atomic hard-sphere model) divided by the unit cell volume—that is,

$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}}$$

- For the FCC structure, the atomic packing factor is 0.74, which is the maximum packing possible for spheres all having the same diameter.

- Metals typically have relatively large atomic packing factors to maximize the shielding provided by the free electron cloud.



EXAMPLE**Computation of the Atomic Packing Factor for FCC**

Show that the atomic packing factor for the FCC crystal structure is 0.74.

Solution

The APF is defined as the fraction of solid sphere volume in a unit cell, or

$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} = \frac{V_s}{V_c}$$

Both the total atom and unit cell volumes may be calculated in terms of the atomic radius R .

The volume for a sphere is $\frac{4}{3}\pi R^3$, and because there are four atoms per FCC unit cell, the total FCC atom (or sphere) volume is

$$V_S = 4 \times \frac{4}{3}\pi R^3 = \frac{16}{3}\pi R^3$$

From Example Problem 3.1, the total unit cell volume is

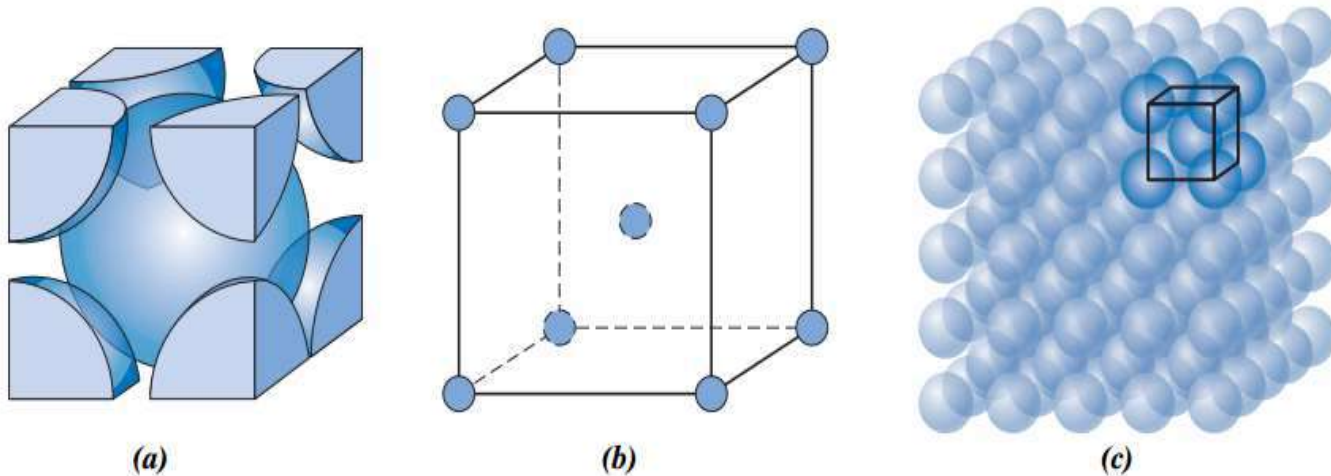
$$V_C = a^3 = (2R\sqrt{2})^3 = 16R^3\sqrt{2}$$

Therefore, the atomic packing factor is

$$\text{APF} = \frac{V_S}{V_C} = \frac{\frac{16}{3}\pi R^3}{16R^3\sqrt{2}} = 0.74 = 74\%$$

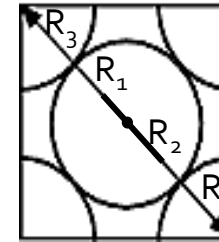
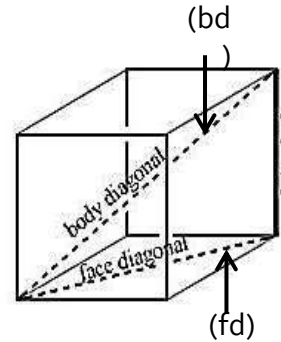
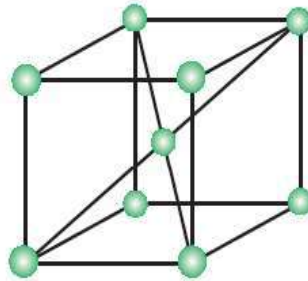
The Body-Centered Cubic Crystal Structure

- Another common metallic crystal structure also has a cubic unit cell with atoms located at all eight corners and a single atom at the cube center. This is called a **body-centered cubic (BCC)** crystal structure.



(a) a hard-sphere unit cell representation, (b) a reduced sphere unit cell, and (c) an aggregate of many atoms.

- Center and corner atoms touch one another along cube diagonals
- unit cell length a and atomic radius R are related through



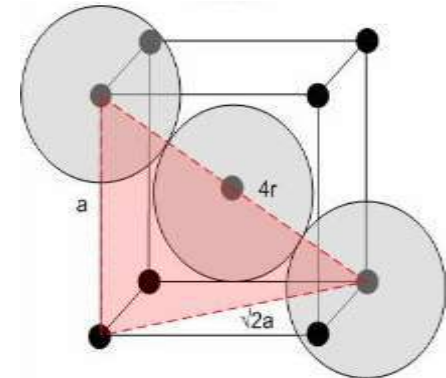
$$bd = 4R$$

Pythagorean theorem : $(bd)^2 = (fd)^2 + a^2$

Where : $(fd)^2 = a^2 + a^2 = 2a^2$

$$(bd)^2 = 2a^2 + a^2 = 3a^2 \quad \rightarrow \quad bd = \sqrt{3}a$$

$$a = \frac{4R}{\sqrt{3}} \quad \dots \dots \dots (3.4)$$



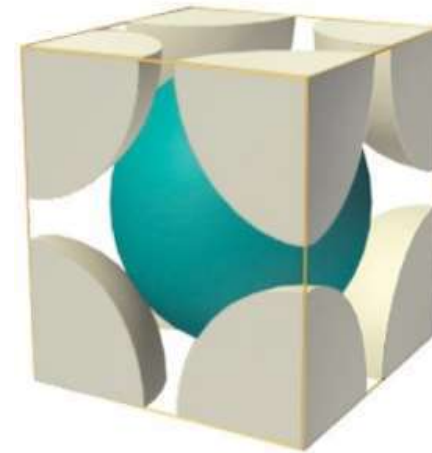
- Table below presents the atomic radii for a number of metals.
- Three relatively simple crystal structures are found for most of the common metals: face-centered cubic (FCC), body-centered cubic (BCC), and hexagonal close-packed (HCP).

<i>Metal</i>	<i>Crystal Structure^a</i>	<i>Atomic Radius^b (nm)</i>	<i>Metal</i>	<i>Crystal Structure</i>	<i>Atomic Radius (nm)</i>
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

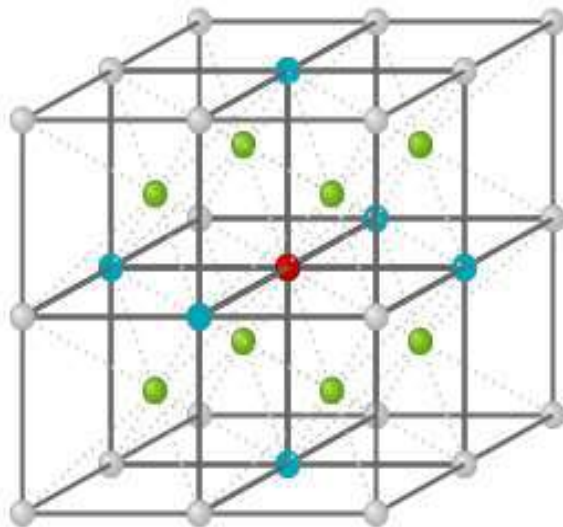
- Each BCC unit cell has eight corner atoms and a single center atom, which is wholly contained within its cell; therefore, from Equation 3.2, the number of atoms per BCC unit cell is

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8} \quad \dots \dots \dots (3.2)$$

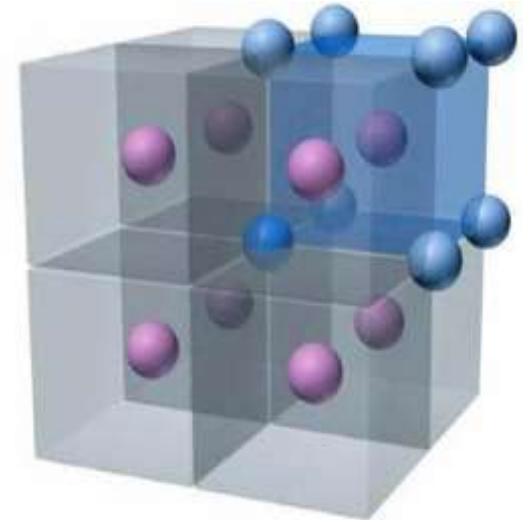
$$N = 1 + 0 + \frac{8}{8} = 2$$



- The coordination number for the BCC crystal structure is 8;
- each center atom has as nearest neighbors its eight corner atoms.
- Because the coordination number is less for BCC than for FCC, the atomic packing factor is also lower for BCC=0.68 versus

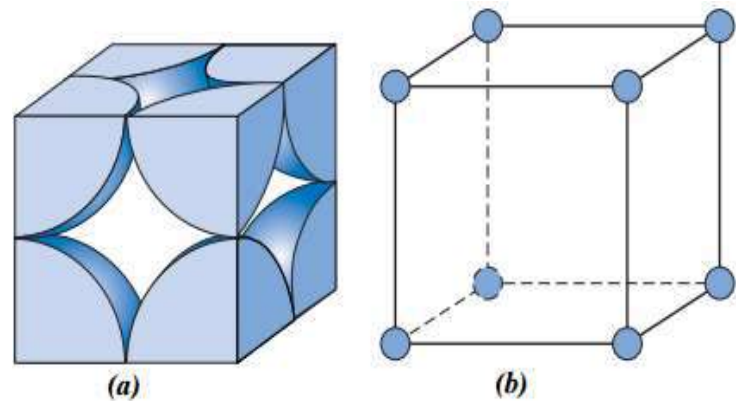


- reference point
- 8 nearest neighbours
- 6 next-nearest neighbours



The Simple Cubic Crystal Structure

- It is also possible to have a unit cell that consists of atoms situated only at the corners of a cube. This is called the **simple cubic (SC)** crystal structure.
- None of the metallic elements have this crystal structure because of its relatively low atomic packing factor 0.524. The only simple-cubic element is polonium, which is considered to be a metalloid (or semi-metal).



Periodic Table of the Elements

Element symbol represents state at room temperature:
Solid, Liquid or Gas

Atomic Number
Symbol
Name
Electron Shell
Electron Configuration

Lanthanide Series

Actinide Series

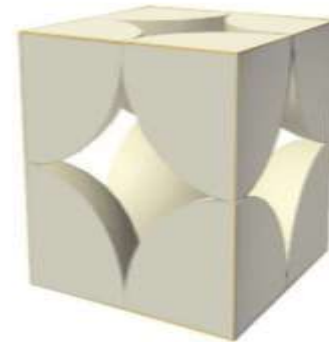
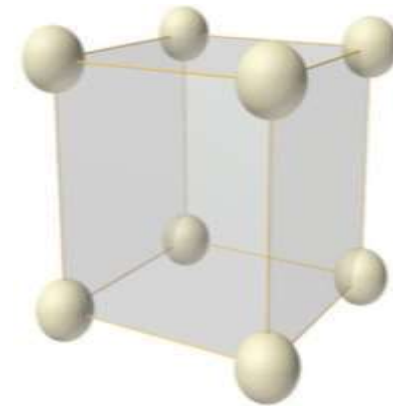
Legend:

- Alkali Metal
- Alkaline Earth
- Transition Metal
- Basic Metal
- Metalloid
- Nonmetal
- Halogen
- Noble Gas
- Lanthanide
- Actinide

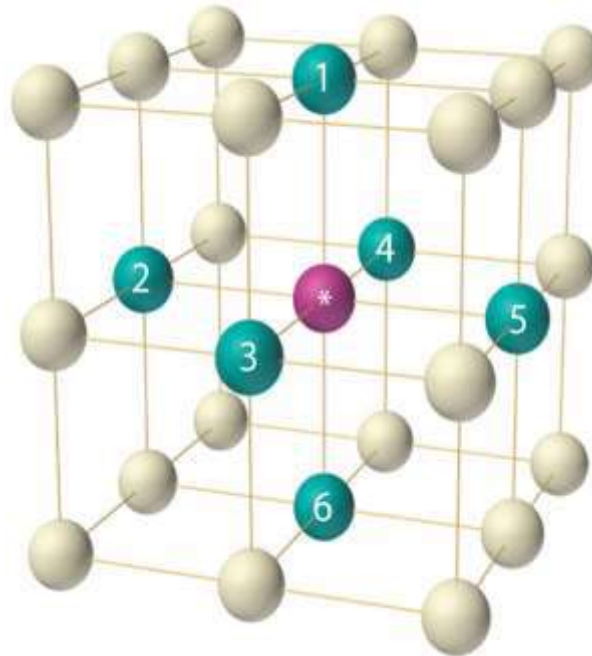
- Each SC unit cell has eight corner atoms therefore, from Equation 3.2, the number of atoms per SC unit cell is

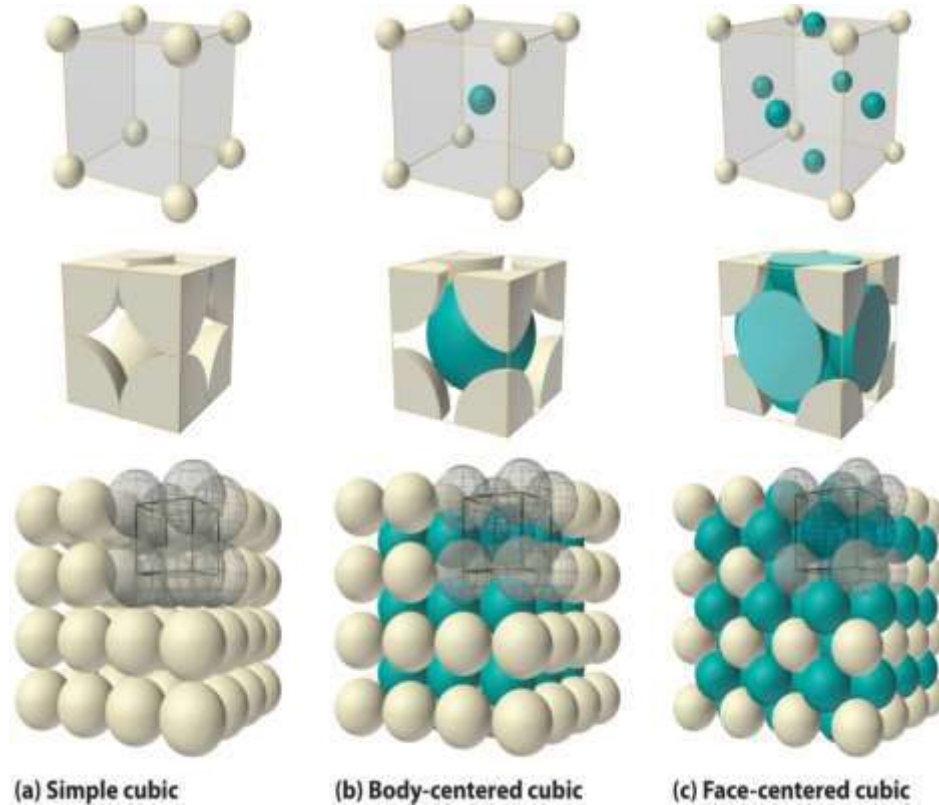
$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8} \quad \dots \dots \dots (3.2)$$

$$N = 0 + 0 + \frac{8}{8} = 1$$



- The coordination number for the SC crystal structure is 6;





Packing fraction is
52.4%

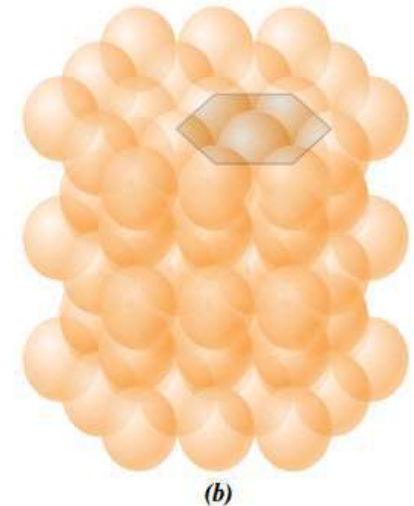
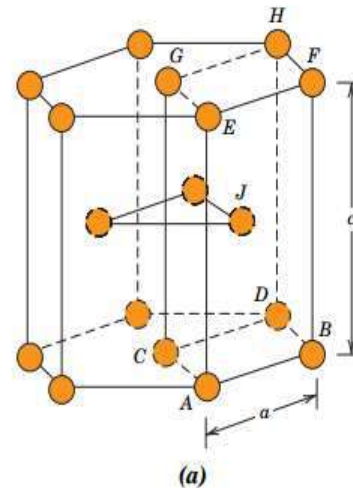
Packing fraction is
68%

Packing fraction is
74%

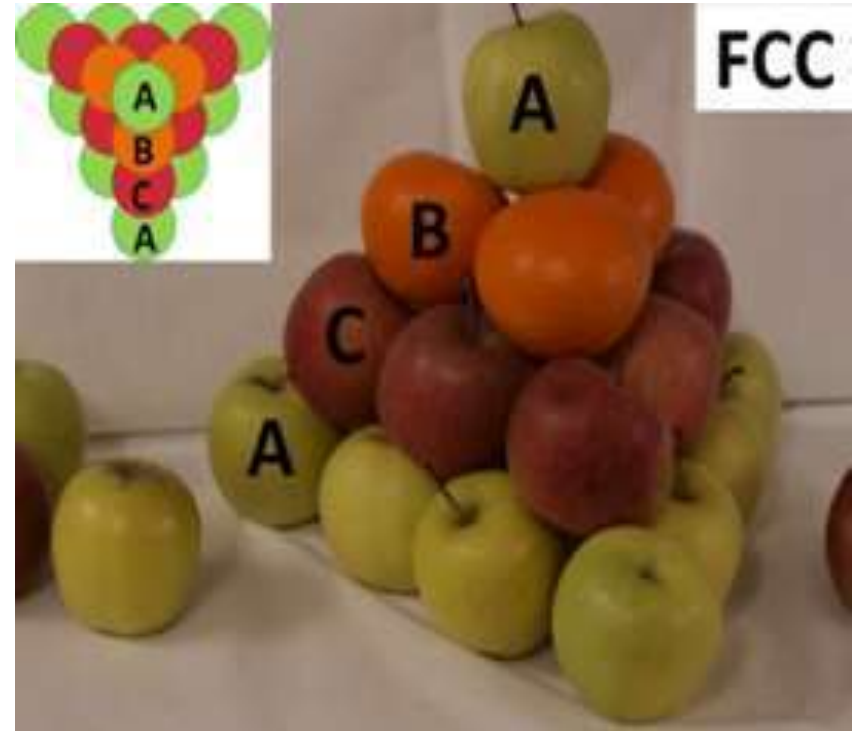
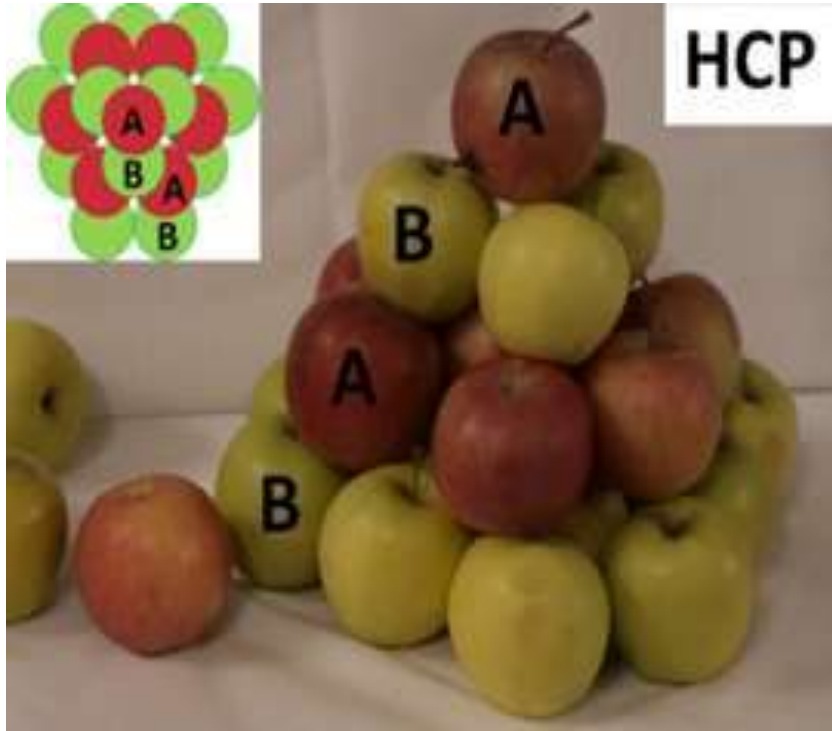
APF always less than unity

The Hexagonal Close-Packed Crystal Structure

hexagonal close-packed (HCP); The top and bottom faces of the unit cell consist of six atoms that form regular hexagons and surround a single atom in the center. Another plane that provides three additional atoms to the unit cell is situated between the top and bottom planes. The atoms in this midplane have as nearest neighbors atoms in both of the adjacent two planes.



(a) a reduced-sphere unit cell (a and c represent the short and long edge lengths, respectively), and (b) an aggregate of many atoms.

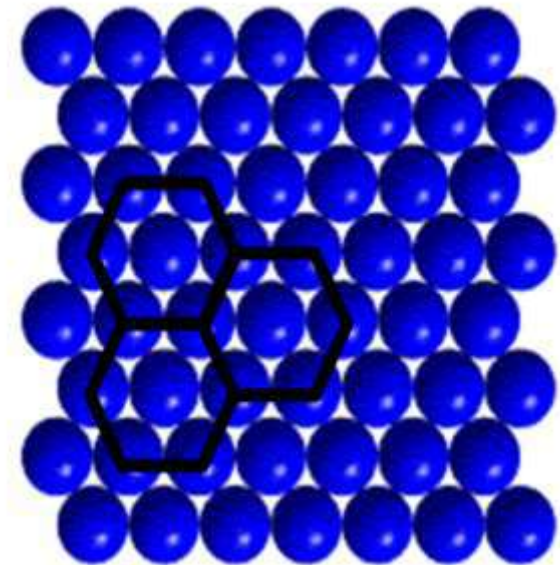
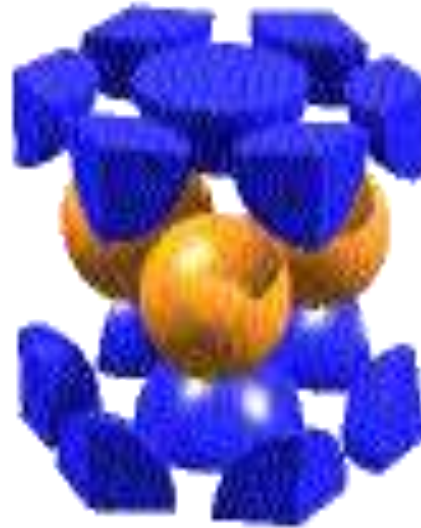


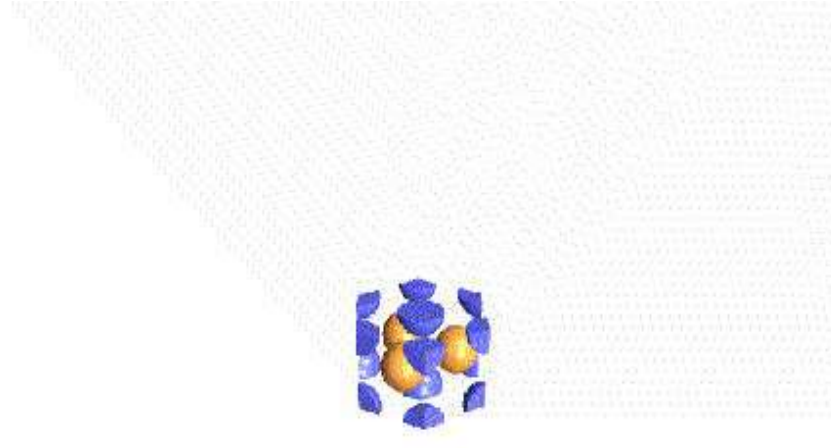
In order to compute the number of atoms per unit cell for the HCP crystal structure, Equation 3.2 is modified to read as follows:

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{6} \quad \dots \dots \dots (3.5)$$

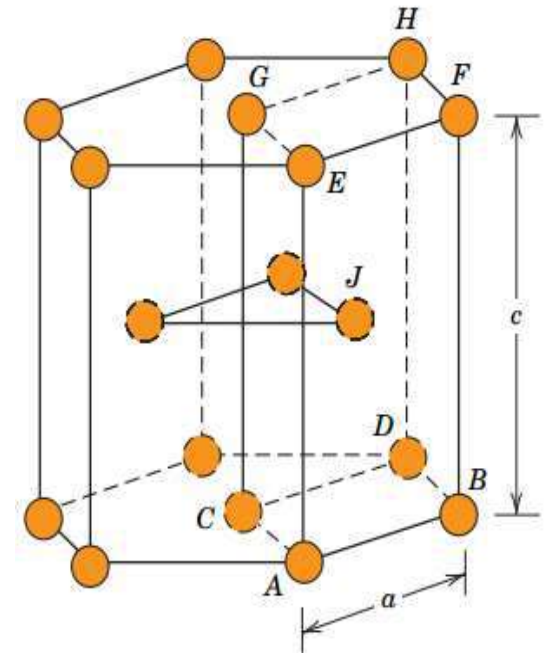
$$N = 3 + \frac{2}{2} + \frac{12}{6} = 6$$

Thus, 6 atoms are assigned to each unit cell.





- If a and c represent, respectively, the short and long unit cell dimensions, the $\frac{c}{a}$ ratio should be 1.633;
- however, for some HCP metals, this ratio deviates from the ideal value.
- The coordination number and the atomic packing factor for the HCP crystal structure are the same as for FCC: 12 and 0.74, respectively.



- Table below presents the atomic radii for a number of metals.
- Three relatively simple crystal structures are found for most of the common metals: face-centered cubic (FCC), body-centered cubic (BCC), and hexagonal close-packed (HCP).

<i>Metal</i>	<i>Crystal Structure^a</i>	<i>Atomic Radius^b (nm)</i>	<i>Metal</i>	<i>Crystal Structure</i>	<i>Atomic Radius (nm)</i>
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

DENSITY COMPUTATIONS

The theoretical density ρ of crystal structure of a metallic solid can be calculate through the relationship:

$$\rho = \frac{nA}{V_c N_A} \quad \dots \dots \dots (3.8)$$

where

n = number of atoms associated with each unit cell

A = atomic weight

V_c = volume of the unit cell

N_A = Avogadro's number ($6.022 \times 10^{23} \frac{\text{atoms}}{\text{mol}}$)

EXAMPLE

Theoretical Density Computation for Copper

Copper has an atomic radius of 0.128 nm, an FCC crystal structure, and an atomic weight of 63.5 g/mol. Compute its theoretical density, and compare the answer with its measured density.

Solution

Because the crystal structure is FCC, n , the number of atoms per unit cell, is 4. Furthermore, the atomic weight A_{Cu} is given as 63.5 g/mol. The unit cell volume V_c for FCC was determined in Example Problem 3.1 as $16R^3\sqrt{2}$, where R , the atomic radius, is 0.128 nm.

$$\rho = \frac{nA}{V_c N_A} \quad \dots \dots \dots (3.8)$$

$$\rho = \frac{nA}{V_c N_A}$$

$$\rho = \frac{(4 \frac{\text{atoms}}{\text{unit cell}})(63.5 \frac{\text{g}}{\text{mol}})}{[\frac{16\sqrt{2}(1.28 \times 10^{-8} \text{cm})^3}{\text{unit cell}}](6.022 \times 10^{23} \frac{\text{atoms}}{\text{mol}})}$$

$$\rho = 8.89 \frac{\text{g}}{\text{cm}^3}$$

The literature value for the density of copper is $8.94 \frac{\text{g}}{\text{cm}^3}$ which is in very close agreement with the theoretical result.

POLYMORPHISM AND ALLOTROP

Some metals, as well as nonmetals, may have more than one crystal structure, a phenomenon known as **polymorphism**. When found in elemental solids, the condition is often termed **allotropy**.

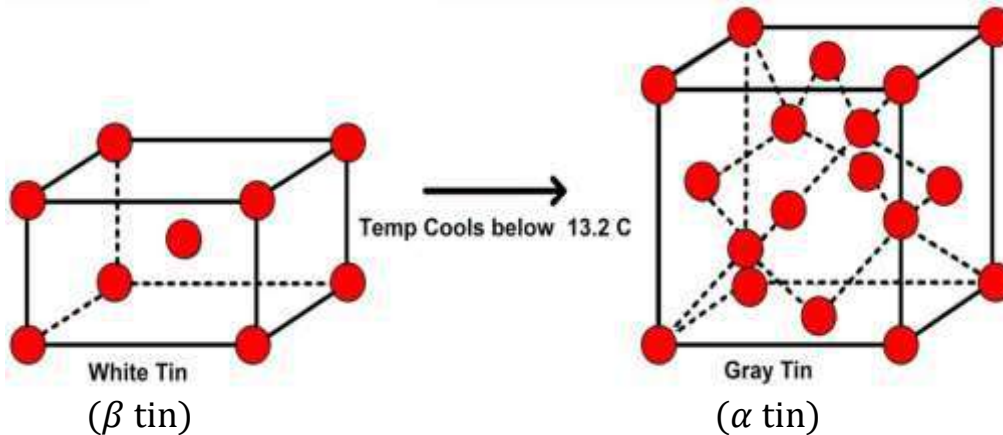
The prevailing crystal structure depends on both the temperature and the external pressure.

One familiar example is found in carbon: graphite is the stable polymorph at ambient conditions, whereas diamond is formed at extremely high pressures.

Pure iron has a BCC crystal structure at room temperature, which changes to FCC iron at 912°C (1674°F).

Most often a modification of the density and other physical properties accompanies a polymorphic transformation.

Another common metal that experiences an allotropic change is tin. White (or β) tin, having a body-centered tetragonal crystal structure at room temperature, transforms, at 13.2°C (55.8°F), to gray (or α) tin, which has a crystal structure similar to that of diamond (i.e., the diamond cubic crystal structure)



Thank you for your attention

