Chapter 3: Structure of Metals and Ceramics

Goals

– Define basic terms and give examples of each:
- Lattice
- Basis Atoms (Decorations or Motifs)
- Crystal Structure
- Unit Cell
- Coordination Numbers

– Describe hard-sphere packing and identify cell symmetry.
- **Crystals density**: the mass per volume (e.g. g/cm^3).
- **Linear Density**: the number of atoms per unit length (e.g. cm^{-1}).
- **Planar Densities**: the number of atoms per unit area (e.g. cm^{-2}).

Chapter 3: Structure of Metals and Ceramics

Learning Objective

– Know and utilize definitions to describe structure and defects in various solid phases (crystal structures).

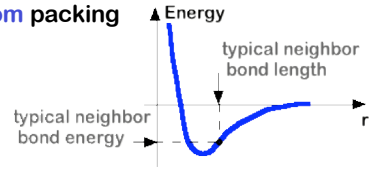
– Compute densities for close-packed structures.

– Identify Symmetry of Cells.

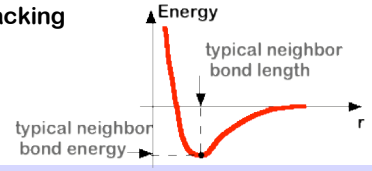
– Specify directions and planes for crystals and be able to relate to characterization experiments .

ENERGY AND PACKING

- Non dense, random packing



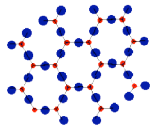
- Dense, regular packing



Dense, regular-packed structures tend to have lower energy.

Atomic PACKING

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

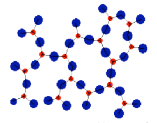


crystalline SiO_2
Adapted from Fig. 3.18(a), *Callister 6e.*

• Si • Oxygen

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

"Amorphous" = Noncrystalline



noncrystalline SiO_2
Adapted from Fig. 3.18(b), *Callister 6e.*

From Callister 6e resource CD.

Crystalline Solids: Unit Cells

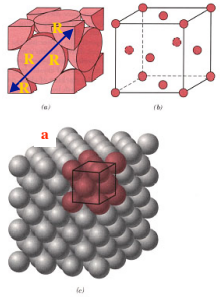
It's geometry!

Unit Cell: **The basic structural unit of a crystal structure. Its geometry and atomic positions define the crystal structure.**

A **unit cell** is the smallest component of the crystal that reproduces the whole crystal when stacked together with purely translational repetition.

Note:
More than one unit cell can be chosen for a given crystal structure but by convention/convenience **the one with the highest symmetry is chosen.**

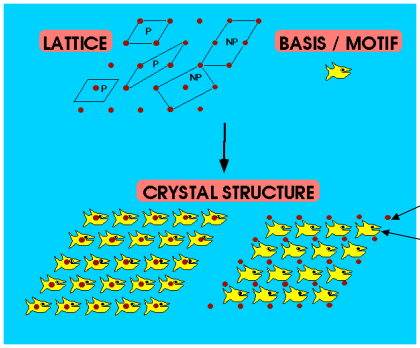
Fig. 3.1 Atomic configuration in **Face-Centered-Cubic** Arrangement



Several GIFS that follow were taken from Dr. Heyes (Oxford) excellent webpage.
http://www.chem.ox.ac.uk/icl/heyes/structure_of_solids/Strucsol.html

Crystalline Solids: Unit Cells

A **Space LATTICE** is an infinite, periodic array of mathematical points, in which each point has identical surroundings to all others.

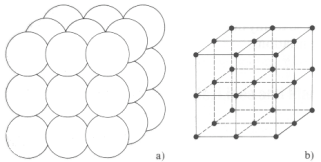


A **CRYSTAL STRUCTURE** is a periodic arrangement of atoms in the crystal that can be described by a LATTICE + ATOM DECORATION (called a BASIS).

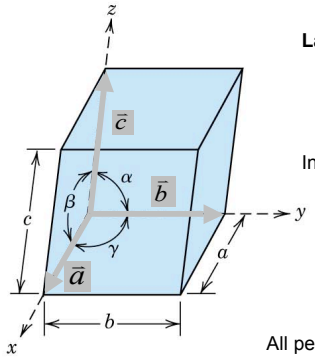
Crystalline Solids: Unit Cells

Important Note:
- Lattice points are a purely mathematical concept, whereas atoms are physical objects.
- So, don't mix up atoms with lattice points.
- Lattice Points do not necessarily lie at the center of atoms.

For example, the only element exhibiting Simple Cubic structure is Po.
In Figure (a) is the *3-D periodic arrangement of Po atoms*, and
Figure (b) is the corresponding *space lattice*.
In this case, atoms lie at the same point as the space lattice.



Unit Cells and Unit Cell Vectors



Lattice parameters
axial lengths: a, b, c
interaxial angles: α, β, γ
unit vectors: $\vec{a}$ $\vec{b}$ $\vec{c}$

In general: $a \neq b \neq c$
$\alpha \neq \beta \neq \gamma$

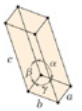
All period unit cells may be described via these vectors and angles.

Possible Crystal Classes

Table 3.6 Lattice Parameter Relationships and Figures Showing Unit Cell Geometries for the Seven Crystal Systems

Crystal System	Axial Relationships	Interaxial Angles	Unit Cell Geometry
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	

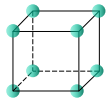
Possible Crystal Classes

Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	

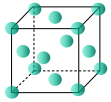
Unit Cells Types

A **unit cell** is the smallest component of the crystal that reproduces the whole crystal when stacked together with purely translational repetition.

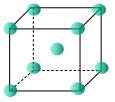
- **Primitive (P)** unit cells contain only a ***single lattice point***.
- **Internal (I)** unit cell contains an atom in the ***body center***.
- **Face (F)** unit cell contains atoms in the ***all faces of the planes*** composing the cell.
- **Centered (C)** unit cell contains atoms ***centered on the sides*** of the unit cell.



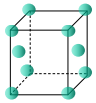
Primitive



Face-Centered



Body-Centered



End-Centered

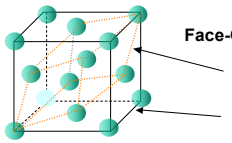
- Sometimes it is convenient to define a non-primitive unit cell to reveal overtly the higher ***symmetry***.
- Then, one has to count carefully "how many atoms are in unit cell" (see next).

Combining **7 Crystal Classes** (cubic, tetragonal, orthorhombic, hexagonal, monclinic, triclinic, trigonal) **with 4 unit cell types (P, I, F, C) symmetry** allows for only **14 types of 3-D lattice.**

KNOW THIS!

Unit Cells Types

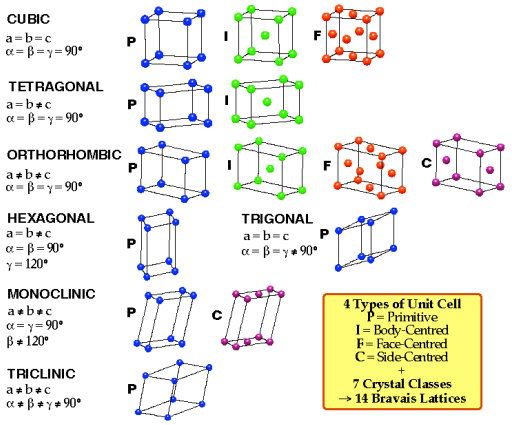
- Often it's convenient to define a non-primitive unit cell to reveal overtly the higher ***symmetry***.
- Then, one has to count carefully "how many atoms are in unit cell" (see next).



Combining 7 Crystal Classes
(cubic, tetragonal, orthorhombic, hexagonal, monclinic, triclinic, trigonal)
with 4 unit cell types (P, I, F, C) symmetry
allows for only **14 types of 3-D lattice.**

Combining these **14 Bravais lattices** with all possible symmetry elements (such as rotations, translations, mirrors, glides, etc.) yields
230 different Space Groups!

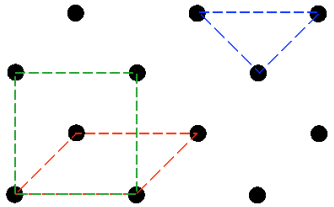
The 14 Bravais Lattices!



Counting Number of Atoms Per Unit Cell

Simple 2D Triangular Lattice

Lattice showing primitive unit cell (in red) and a square, non-primitive unit cell (in green).

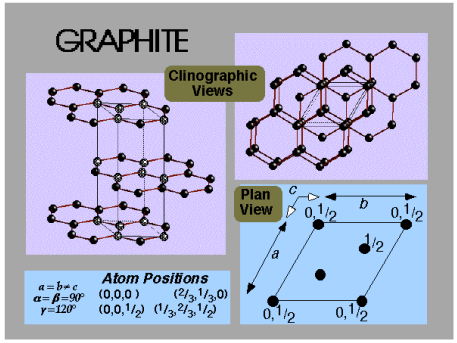


Self-Assessment: Why can't the blue triangle be a unit cell?

Counting Lattice Points/Atoms in 2D Lattices

- Unit cell is **Primitive (1 lattice point)** but contains **2 atoms** in the Basis.
- Atoms at the **corner** of the 2D unit cell contribute only **1/4** to unit cell count.
- Atoms at the **edge** of the 2D unit cell contribute only **1/2** to unit cell count.
- Atoms **within** the 2D unit cell contribute **1** as they are entirely contained inside.

UNIT CELL - 3D Lattices

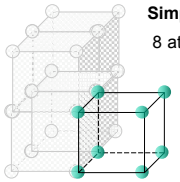


Counting Number of Atoms Per Unit Cell

Counting Atoms in 3D Cells

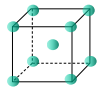
Atoms in different positions are shared by differing numbers of unit cells.

- Vertex atom shared by **8** cells => **1/8** atom per cell.
- Edge atom shared by **4** cells => **1/4** atom per cell.
- Face atom shared by **2** cells => **1/2** atom per cell.
- Body unique to **1** cell => **1** atom per cell.

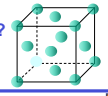


Simple Cubic

8 atoms **but** shared by 8 unit cells. So,
8 atoms/8 cells = **1 atom/unit cell**



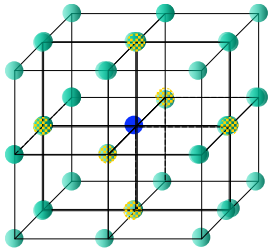
How many atoms/cell for *Body-Centered Cubic*?



And, *Face-Centered Cubic*?

Coordination Number of a Given Atom

Number of nearest-neighbor atoms



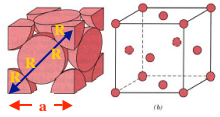
Simple cubic: coordination number, CN = 6

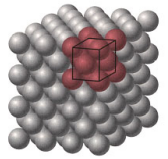
Unit Cells and Volume Packing

What are basic structural parameters, e.g. lattice constant or side of cube?
How many atoms per cell?
What is volume per cell?
What is the atomic packing factor (APF)?
What is the closed-packed direction?
What are (linear) densities of less close-packed directions?
What are planar densities of every plane?

It's all geometry.
- Need to relate cube dimension "a" to
- Packing of ideal spherical atoms of radius "R".

Atomic configuration in **Face-Centered-Cubic** Arrangement



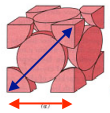


$\sqrt{2}a = 4R$

Atomic Packing Fraction for FCC

$$\text{APF} = \frac{\text{vol. of atomic spheres in unit cell}}{\text{total unit cell vol.}}$$

Face-Centered-Cubic Arrangement

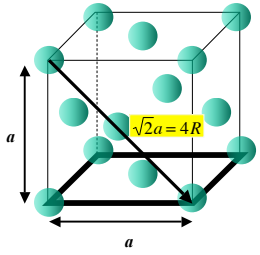


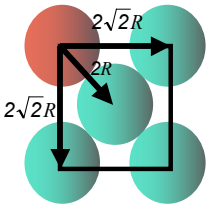
Unit cell contains:
6 x 1/2 + 8 x 1/8
= 4 atoms/unit cell

Depends on:
- Crystal structure.
- How "close" packed the atoms are.
- In simple close-packed structures with hard sphere atoms, independent of atomic radius

Basic Geometry for FCC

Geometry along close-packed direction give relation between a and R.





$$V_{unit\_cell} = a^3 = (2\sqrt{2}R)^3 = 16\sqrt{2}R^3$$

$$V_{atoms} = 4\left(\frac{4}{3}\pi R^3\right)$$

Geometry: $a = 2\sqrt{2}R$

4 atoms/unit cell

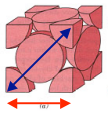
Coordination number = 12

Atomic Packing Fraction for FCC

APF = vol. of atomic spheres in unit cell / total unit cell vol.

How many spheres (i.e. atoms)? **4/cell**
What is volume/atom? **$4\pi R^3/3$**
What is cube volume/cell? **a^3**
How is "R" related to "a"? $\sqrt{2}a = 4R$

Face-Centered-Cubic Arrangement



Unit cell contains:
6 x 1/2 + 8 x 1/8
= 4 atoms/unit cell

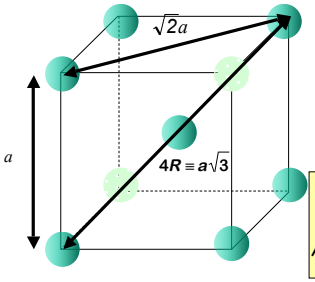
$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{4 \cdot \frac{4}{3}\pi(\sqrt{2}a/4)^3}{a^3}$$

= 0.74

Independent of R!

Summary APF for BCC

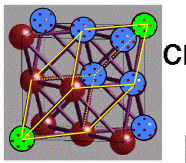
Again, geometry along close-packed direction give relation between a and R.

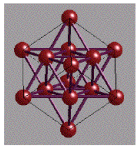


Geometry: $4R \equiv a\sqrt{3}$
2 atoms/unit cell
Coordination number = 8

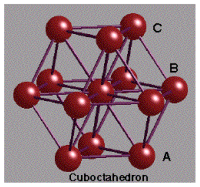
$$APF = \frac{V_{atoms}}{V_{cell}} = \frac{2\left(\frac{4}{3}\pi\left[\frac{a\sqrt{3}}{4}\right]^3\right)}{a^3} = \frac{\sqrt{3}\pi}{8} = 0.68$$

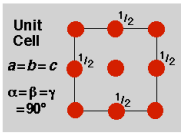
CUBIC CLOSE-PACKING

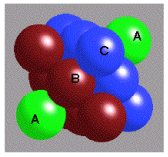




Face-Centred Cubic (FCC) Unit Cell





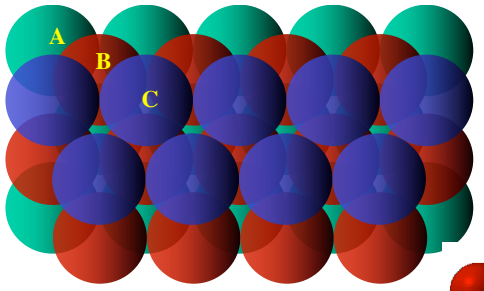


ABCABC.... repeat along <111> direction gives Cubic Close-Packing (**CCP**)

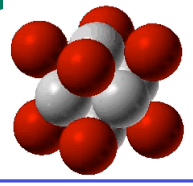
- Face-Centered-Cubic (FCC) is the most efficient packing of hard-spheres of any lattice.
- Unit cell showing the full symmetry of the FCC arrangement : $a = b = c$, angles all 90°
- 4 atoms in the unit cell: (0, 0, 0) (0, 1/2, 1/2) (1/2, 0, 1/2) (1/2, 1/2, 0)

Self-Assessment: Write FCC crystal as BCT unit cell.

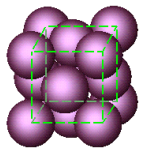
FCC Stacking



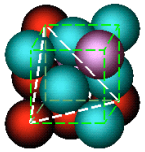
Highlighting the stacking



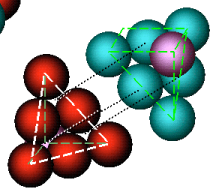
Highlighting the faces



FCC Unit Cell



Highlighting the ABC planes and the cube.



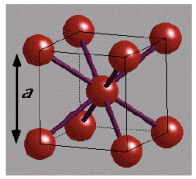
A Planes

B Planes

C Planes

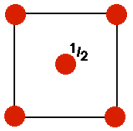
Highlighting the hexagonal planes in each ABC layer.

A less close-packed structure is Body-Centered-Cubic (BCC).
Besides FCC and HCP, BCC structures are widely adopted by metals.



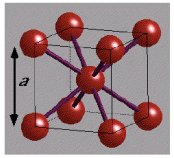
Body-Centred Cubic

BCC



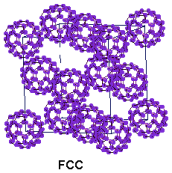
- Unit cell showing the full cubic symmetry of the BCC arrangement.
- BCC: $a = b = c = a$ and angles $\alpha = \beta = \gamma = 90°$.
- 2 atoms in the cubic cell: (0, 0, 0) and (1/2, 1/2, 1/2).

Body-Centered-Cubic (BCC) can be template for more Complex Structures: Lattice with Basis Atoms



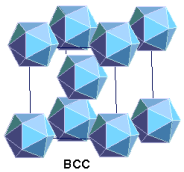
Lattice points in space decorated with "buckeyballs" or viruses.

BUCKMINSTERFULLERENE

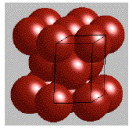


FCC

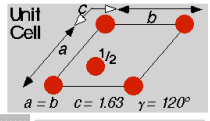
FOOT & MOUTH VIRUS

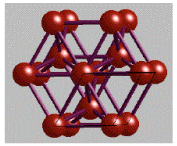


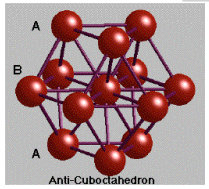
BCC

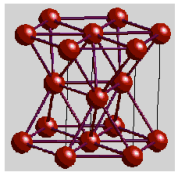


HEXAGONAL CLOSE-PACKING





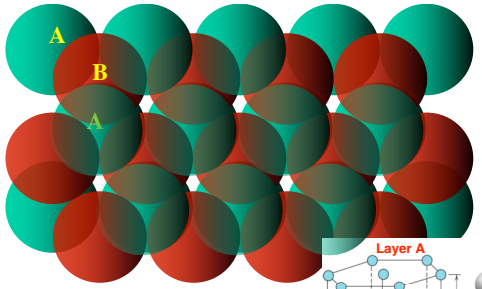




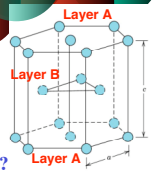
ABABAB.... repeat along <111> direction gives Hexagonal Close-Packing (**HCP**)

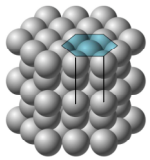
- Unit cell showing the full symmetry of the HCP arrangement is hexagonal
- Hexagonal: $a = b$, $c = \mathbf{1.633}a$ and angles $\alpha = \beta = 90°$, $\gamma = 120°$
- 2 atoms in the smallest cell: (0, 0, 0) and (2/3, 1/3, 1/2).

HCP Stacking



Highlighting the stacking

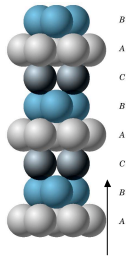




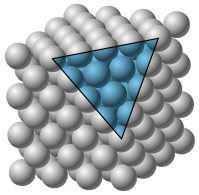
Highlighting the cell
Figure 3.3

Self-Assessment: How many atoms/cell?

Comparing the FCC and HCP Planes Stacking

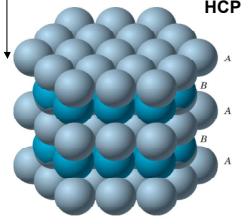


FCC



Looking down (0001) plane

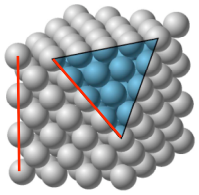
HCP



Looking down (111) plane!

Packing Densities in Crystals: Lines Planes and Volumes

FCC



Concepts

Linear Density:
No. of atoms along a direction vector per length of direction vector

Planar Density:
No. of atoms per area of plane per area of plane

Versus

Linear and Planar Packing Density
which are independent of atomic radius!

Also, **Theoretical Density**

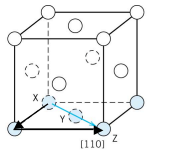
Linear Density in FCC

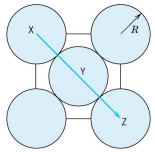
$$LD = \frac{\text{Number of atoms centered on a direction vector}}{\text{Length of the direction vector}}$$

Example: Calculate the linear density of an FCC crystal along [1 1 0].

ASK
a. How many spheres along blue line?
b. What is length of blue line?

ANSWER
a. 2 atoms along [1 1 0] in the cube.
b. Length = 4R





(b)

$$LD_{110} = \frac{2 atoms}{4R} = \frac{1}{2R}$$

XZ = 1*i* + 1*j* + 0*k* = [110]

Self-assessment: Show that $LD_{100} = \sqrt{2}/4R$.

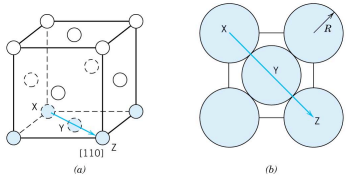
Linear Packing Density in FCC

$$\text{LDP} = \frac{\text{Number of radii along a direction vector}}{\text{Length of the direction vector}}$$

Example: Calculate the LPD of an FCC crystal along [1 1 0].

ASK
a. How many radii along blue line?
b. What is length of blue line?

ANSWER
a. 2 atoms * 2R.
b. Length = 4R



$$LPD_{110} = \frac{2 * 2R}{4R} = 1$$

Fully CLOSE-PACKED.

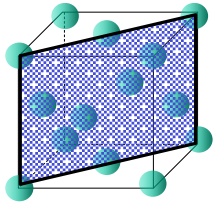
Always independent of R!

Self-assessment: Show that $LPD_{100} = \sqrt{2}/2$.

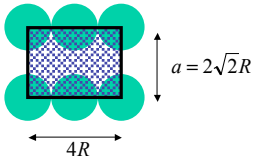
Planar Density in FCC

$$\text{PD} = \frac{\text{Number of atoms centered on a given plane}}{\text{Area of the plane}}$$

Example: Calculate the PD on (1 1 0) plane of an FCC crystal.



- Count atoms within the plane: **2 atoms**
- Find Area of Plane: **$8\sqrt{2}\,R^2$**

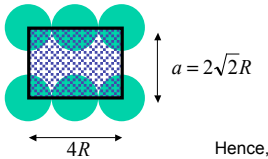


Hence, $$PD = \frac{2}{8\sqrt{2}R^2} = \frac{1}{4\sqrt{2}R^2}$$

Planar Packing Density in FCC

$$\text{PPD} = \frac{\text{Area of atoms centered on a given plane}}{\text{Area of the plane}}$$

Example: Calculate the PPD on (1 1 0) plane of an FCC crystal.



- Find area filled by atoms in plane: **$2\pi R^2$**
- Find Area of Plane: **$8\sqrt{2}\,R^2$**

Hence, $$PPD = \frac{2\pi R^2}{8\sqrt{2}R^2} = \frac{\pi}{4\sqrt{2}} = 0.555$$

Always independent of R!

Self-assessment: Show that $PPD_{100} = \pi/4 = 0.785$.

Theoretical Density, ρ

$$\rho = \frac{n A}{V_C N_A}$$

n: # atoms/unit cell
A: Atomic weight (g/mol)
V_C: Volume/unit cell (cm^3/unit cell)
N_A: Avogadro's number (6.023×10^{23} atoms/mol)

Example: Copper

Data from Table inside front cover of Callister (see next slide):

- **crystal structure = FCC: 4 atoms/unit cell**
- **atomic weight = 63.55 g/mol (1 amu = 1 g/mol)**
- **atomic radius R = 0.128 nm (1 nm = 10 cm)**

$V_C = a^3$; For FCC, $a = 4R/\sqrt{2}$; $V_C = 4.75 \times 10^{-23} cm^3$

Result: theoretical $\rho_{Cu} = 8.89\ g/cm^3$

Compare to actual: $\rho_{Cu} = 8.94\ g/cm^3$

Characteristics of Selected Elements at 20 C

Element	Symbol	At. Weight (amu)	Density (g/cm^3)	Crystal Structure	Atomic radius (nm)
Aluminum	Al	26.98	2.71	FCC	0.143
Argon	Ar	39.95	------	------	------
Barium	Ba	137.33	3.5	BCC	0.217
Beryllium	Be	9.012	1.85	HCP	0.114
Boron	B	10.81	2.34	Rhomb	------
Bromine	Br	79.90	------	------	------
Cadmium	Cd	112.41	8.65	HCP	0.149
Calcium	Ca	40.08	1.55	FCC	0.197
Carbon	C	12.011	2.25	Hex	0.071
Cesium	Cs	132.91	1.87	BCC	0.265
Chlorine	Cl	35.45	------	------	------
Chromium	Cr	52.00	7.19	BCC	0.125
Cobalt	Co	58.93	8.9	HCP	0.125
Copper	Cu	63.55	8.94	FCC	0.128
Flourine	F	19.00	------	------	------
Gallium	Ga	69.72	5.90	Ortho.	0.122
Germanium	Ge	72.59	5.32	Dia. cubic	0.122
Gold	Au	196.97	19.32	FCC	0.144
Helium	He	4.003	------	------	------
Hydrogen	H	1.008	------	------	------

Adapted from Table, "Characteristics of Selected Elements", inside front cover, *Callister 6e.*

DENSITIES OF MATERIAL CLASSES

$\rho_{metals} \geq \rho_{ceramics} \geq \rho_{polymers}$

Metals have...
- close-packing

(metallic bonds)
- large atomic mass

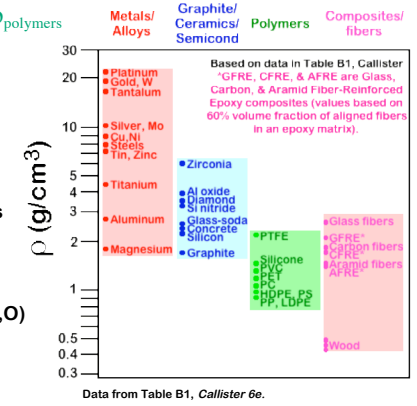
Ceramics have...
- less dense packing

(covalent bonds)
- often lighter elements

Polymers have...
- poor packing

(often amorphous)
- lighter elements (C,H,O)

Composites have...
- intermediate values



Data from Table B1, *Callister 6e.*

SUMMARY

• Materials come in **Crystalline** and **Non-crystalline** Solids, as well as **Liquids/Amoprhous**. Polycrystals are important.

•Crystal Structure can be defined by space lattice and basis atoms (lattice decorations or motifs).

• Only 14 Bravais Lattices are possible. We focus only on FCC, HCP, and BCC, I.e., the majority in the periodic table and help determine most CERAMIC structures.

• Crystal types themselves can be described by their atomic positions, planes and their atomic packing (linear, planar, and volumetric packing fraction).

• *We now know how to determine structure mathematically. So how to we do it experimentally? DIFFRACTION.*