Chapter Outline

How do atoms arrange themselves to form solids?

- **Fundamental concepts and language**
- **Unit cells**
- **Crystal structures**
  - **Face-centered cubic**
  - **Body-centered cubic**
  - **Hexagonal close-packed**
- **Close packed crystal structures**
- **Density computations**
- **Types of solids**
  - **Single crystal**
  - **Polycrystalline**
  - **Amorphous**

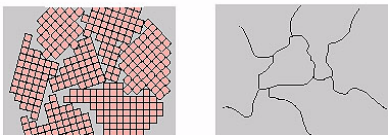
3.8–3.10 Crystallography – Not Covered / Not Tested
3.15 Anisotropy – Not Covered / Not Tested
3.16 Diffraction – Not Covered / Not Tested

Types of Solids

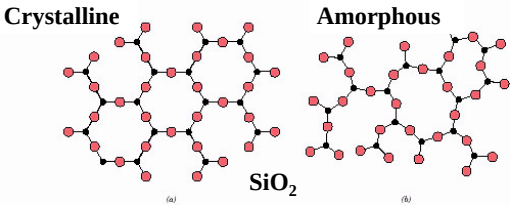
Crystalline material: atoms self-organize in a periodic array

Single crystal: atoms are in a repeating or periodic array over the entire extent of the material

Polycrystalline material: comprised of many small crystals or **grains**

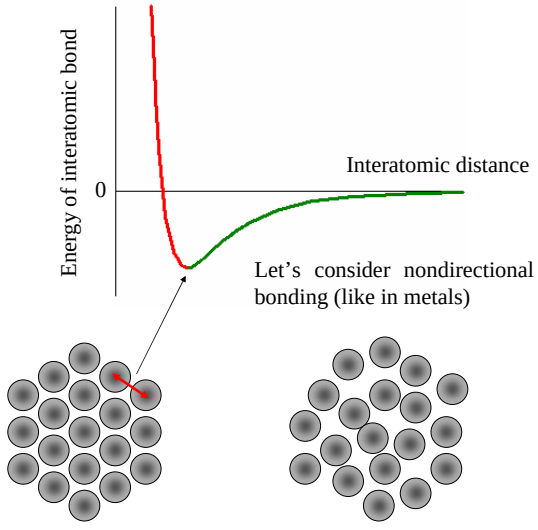


Amorphous: disordered – lack of a systematic atomic arrangement



Crystal structures

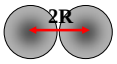
Why do atoms assemble into ordered structures (crystals)?



Energy of the crystal < Energy of the amorphous solid

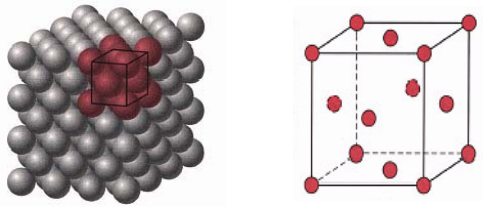
Crystal structure

To discuss crystalline structures it is useful to consider atoms as being hard spheres with well-defined radii. In this hard-sphere model, the shortest distance between two like atoms is one diameter of the hard sphere.



- hard-sphere model

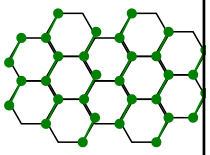
We can also consider crystalline structure as a lattice of points at atom/sphere centers.



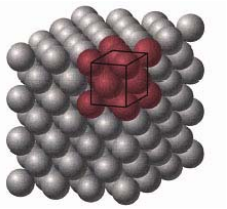
Unit Cell

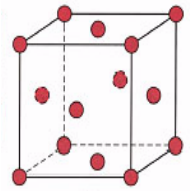
The unit cell is a structural unit or building block that can describe the crystal structure. Repetition of the unit cell generates the entire crystal.

Example: 2D honeycomb net can be represented by translation of two adjacent atoms that form a unit cell for this 2D crystalline structure



Example of 3D crystalline structure:





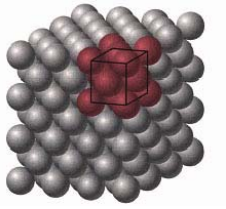
Different choices of unit cells possible, we will consider parallelepiped unit cell with highest level of symmetry

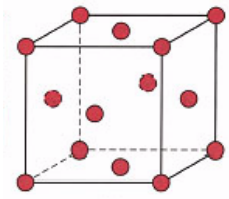
Metallic Crystal Structures

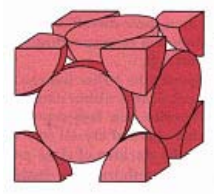
- Metals are usually (poly)crystalline; although formation of amorphous metals is possible by rapid cooling
- As we learned in Chapter 2, the atomic bonding in metals is non-directional ⇒ no restriction on numbers or positions of nearest-neighbor atoms ⇒ large number of nearest neighbors and dense atomic packing
- **Atomic (hard sphere) radius, R,** defined by ion core radius - typically 0.1 - 0.2 nm
- The most common types of unit cells are
  - faced-centered cubic (FCC)
  - body-centered cubic (BCC)
  - hexagonal close-packed (HCP).

Face-Centered Cubic (FCC) Crystal Structure (I)

- Atoms are located at each of the corners and on the centers of all the faces of cubic unit cell
- Cu, Al, Ag, Au have this crystal structure

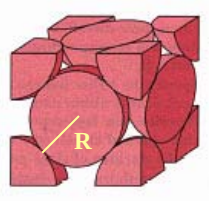


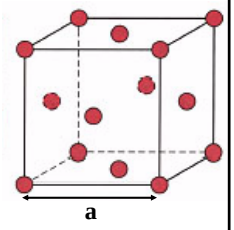




Two representations of the FCC unit cell

Face-Centered Cubic Crystal Structure (II)





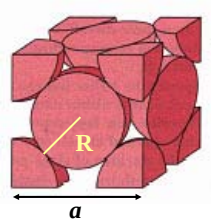
- The hard spheres touch one another across a face diagonal ⇒ the cube edge length, **a= 2R√2**
- **The coordination number, CN** = the number of closest neighbors to which an atom is bonded = number of touching atoms, **CN = 12**
- **Number of atoms per unit cell, n = 4**. (For an atom that is shared with m adjacent unit cells, we only count a fraction of the atom, 1/m). In FCC unit cell we have:

  6 face atoms shared by two cells: 6×1/2 = 3

  8 corner atoms shared by eight cells: 8×1/8 = 1
- **Atomic packing factor, APF** = fraction of volume occupied by hard spheres = (Sum of atomic volumes)/(Volume of cell) **= 0.74** (maximum possible)

Face-Centered Cubic Crystal Structure (III)

Let's calculate the **atomic packing factor** for FCC crystal



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

APF = (Sum of atomic volumes)/(Volume of unit cell)

Volume of 4 hard spheres in the unit cell: $4 \times \frac{4}{3}\pi R^3$

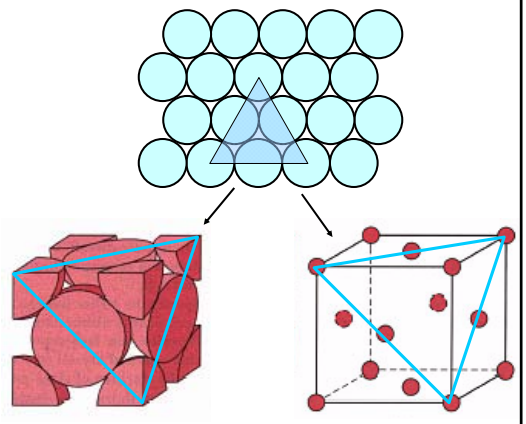
Volume of the unit cell: $a^3 = 16R^3\sqrt{2}$

$$APF = \frac{16}{3}\pi R^3 \Big/ 16R^3\sqrt{2} = \pi / 3\sqrt{2} = 0.74$$

maximum possible packing of hard spheres

Face-Centered Cubic Crystal Structure (IV)

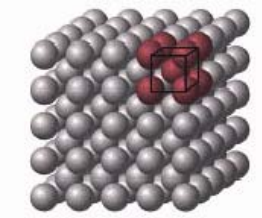
- Corner and face atoms in the unit cell are equivalent
- FCC crystal has APF of 0.74, the maximum packing for a system equal-sized spheres ⇒ FCC is a **close-packed structure**
- FCC can be represented by a stack of **close-packed planes** (planes with highest density of atoms)

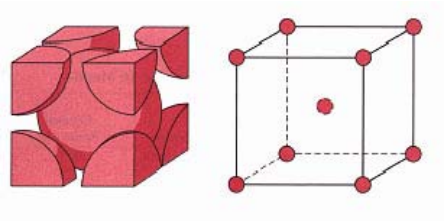


Body-Centered Cubic (BCC) Crystal Structure (I)

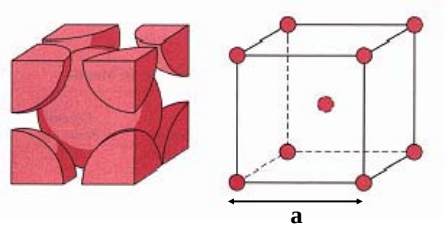
Atom at each corner and at center of cubic unit cell

Cr, α-Fe, Mo have this crystal structure





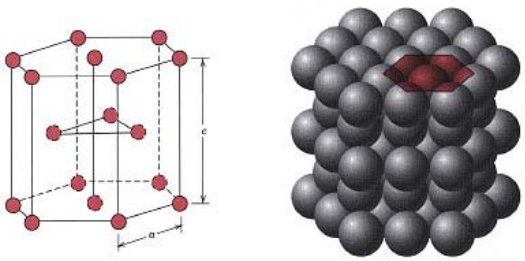
Body-Centered Cubic Crystal Structure (II)



- The hard spheres touch one another along cube diagonal ⇒ the cube edge length, **a= 4R/√3**
- **The coordination number, CN = 8**
- **Number of atoms per unit cell, n = 2**
  Center atom (1) shared by no other cells: 1 x 1 = 1
  8 corner atoms shared by eight cells: 8 x 1/8 = 1
- **Atomic packing factor, APF = 0.68**
- Corner and center atoms are equivalent

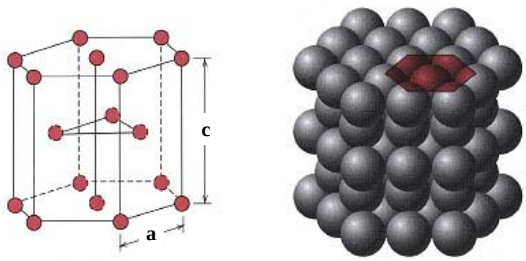
Hexagonal Close-Packed Crystal Structure (I)

- HCP is one more common structure of metallic crystals
- Six atoms form regular hexagon, surrounding one atom in center. Another plane is situated halfway up unit cell (c-axis), with 3 additional atoms situated at interstices of hexagonal (close-packed) planes
- Cd, Mg, Zn, Ti have this crystal structure



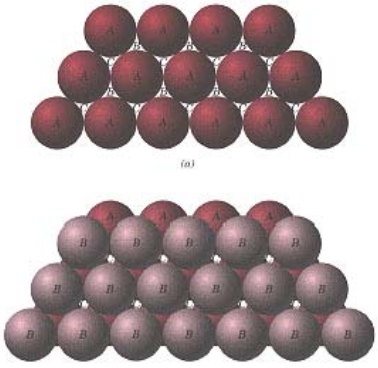
Hexagonal Close-Packed Crystal Structure (II)

- Unit cell has two lattice parameters a and c. Ideal ratio c/a = 1.633
- **The coordination number, CN = 12 (same as in FCC)**
- **Number of atoms per unit cell, n = 6.**
  3 mid-plane atoms shared by no other cells: 3 x 1 = 3
  12 hexagonal corner atoms shared by 6 cells: 12 x 1/6 = 2
  2 top/bottom plane center atoms shared by 2 cells: 2 x 1/2 = 1
- **Atomic packing factor, APF = 0.74 (same as in FCC)**
- All atoms are equivalent



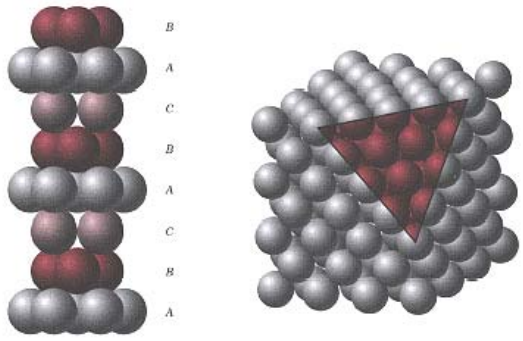
Close-packed Structures (FCC and HCP)

- Both FCC and HCP crystal structures have atomic packing factors of 0.74 (maximum possible value)
- Both FCC and HCP crystal structures may be generated by the stacking of close-packed planes
- **The difference between the two structures is in the stacking sequence**



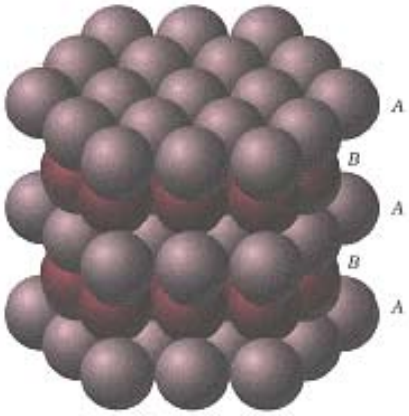
HCP: ABABAB... **FCC: ABCABCABC…**

FCC: Stacking Sequence ABCABCABC...



Third plane is placed above the “holes” of the first plane not covered by the second plane

HCP: Stacking Sequence ABABAB...



Third plane is placed directly above the first plane of atoms

Density Computations

Since the entire crystal can be generated by the repetition of the unit cell, the density of a crystalline material, ρ = the density of the unit cell = (atoms in the unit cell, n) × (mass of an atom, M) / (the volume of the cell, V_c)

Atoms in the unit cell, n = 2 (BCC); 4 (FCC); 6 (HCP)

Mass of an atom, M = Atomic weight, A, in amu (or g/mol) is given in the periodic table. To translate mass from amu to grams we have to divide the atomic weight in amu by the Avogadro number $N_A = 6.023 \times 10^{23}$ atoms/mol

The volume of the cell, $V_c = a^3$ (FCC and BCC)
$a = 2R\sqrt{2}$ (FCC); $a = 4R/\sqrt{3}$ (BCC)
where R is the atomic radius

Thus, the formula for the density is:

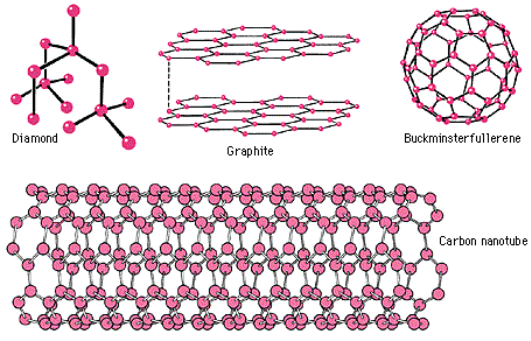
$$\rho = \frac{nA}{V_c N_A}$$

Atomic weight and atomic radius of many elements you can find in the table at the back of the textbook front cover.

Polymorphism and Allotropy

Some materials may exist in more than one crystal structure, this is called **polymorphism**. If the material is an elemental solid, it is called allotropy.

An example of allotropy is carbon, which can exist as diamond, graphite, and amorphous carbon.

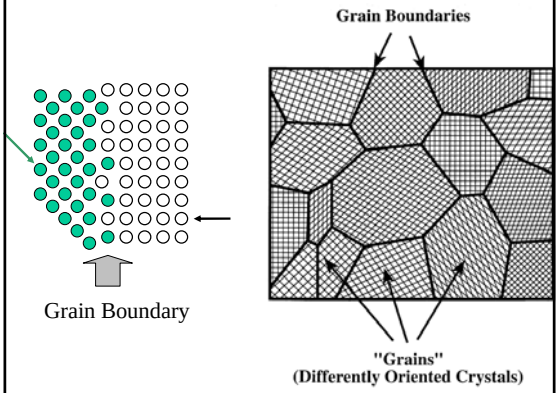


Pure, solid carbon occurs in three crystalline forms – diamond, graphite; and large, hollow fullerenes. Two kinds of fullerenes are shown here: buckminsterfullerene (buckyball) and carbon nanotube.

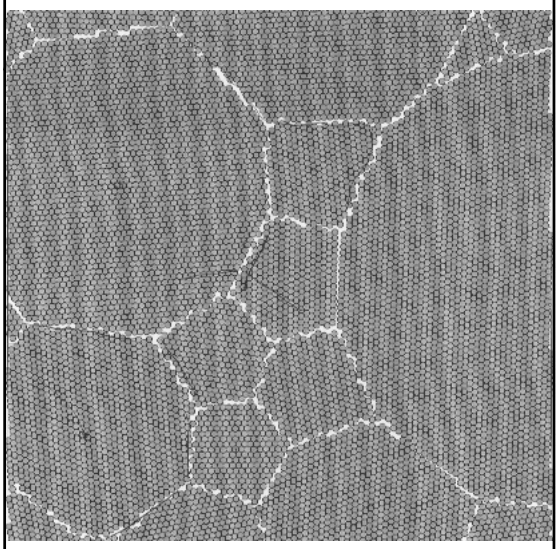
Single Crystals and Polycrystalline Materials

Single crystal: atoms are in a repeating or periodic array over the entire extent of the material

Polycrystalline material: comprised of many small crystals or **grains.** The grains have different crystallographic orientation. There exist atomic mismatch within the regions where grains meet. These regions are called **grain boundaries**.

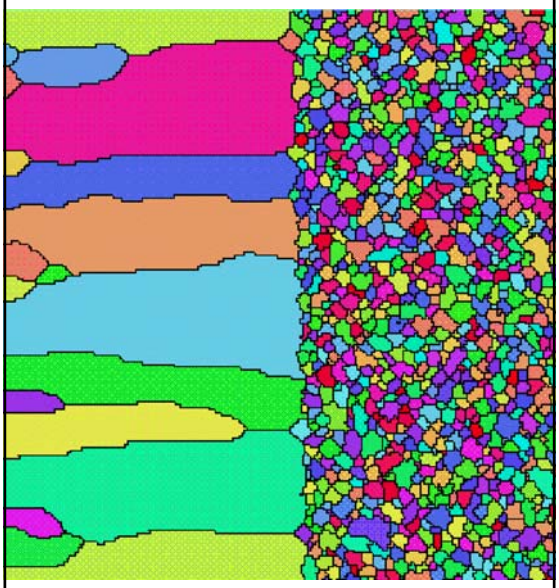


Polycrystalline Materials



Atomistic model of a nanocrystalline solid by Mo Li, JHU

Polycrystalline Materials



Simulation of annealing of a polycrystalline grain structure
from http://cmpweb.ameslab.gov/cmsn/microevolproj.html (link is dead)

Anisotropy

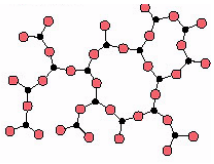
Different directions in a crystal have different packing. For instance, atoms along the edge of FCC unit cell are more separated than along the face diagonal. This causes **anisotropy** in the properties of crystals, for instance, the deformation depends on the direction in which a stress is applied.

In some polycrystalline materials, grain orientations are random, so bulk material properties are **isotropic**

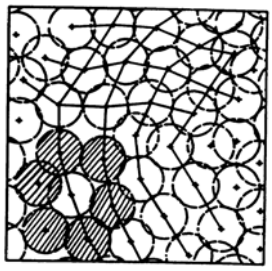
Some polycrystalline materials have grains with preferred orientations (**texture**), so properties are dominated by those relevant to the texture orientation and the material exhibits anisotropic properties

Non-Crystalline (Amorphous) Solids

In amorphous solids, there is no long-range order. But amorphous does not mean random, in many cases there is some form of short-range order.



Schematic picture of amorphous SiO_2 structure



Amorphous structure from simulations by E. H. Brandt

Summary

Make sure you understand language and concepts:

- Allotropy
- Amorphous
- Anisotropy
- Atomic packing factor (APF)
- Body-centered cubic (BCC)
- Coordination number
- Crystal structure
- Crystalline
- Face-centered cubic (FCC)
- Grain
- Grain boundary
- Hexagonal close-packed (HCP)
- Isotropic
- Lattice parameter
- Non-crystalline
- Polycrystalline
- Polymorphism
- Single crystal
- Unit cell

Homework #1: 2.14, 2.15, 2.20, 3.7, and 3.17
Due date: Monday, September 6.

Reading for next class:

Chapter 4: Imperfections in Solids

Point defects (vacancies, interstitials)
Dislocations (edge, screw)
Grain boundaries (tilt, twist)
Weight and atomic composition

Optional reading (Parts that are not covered / not tested):

4.9 – 4.10 Microscopy

4.11 Grain size determination