Chapter 3
CRYSTAL STRUCTURE & PROPERTIES

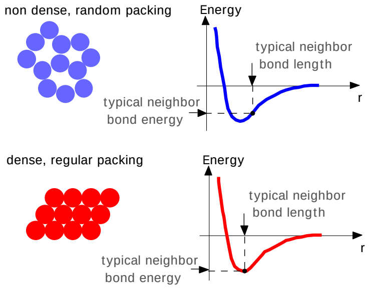
ISSUES TO ADDRESS...

1. How do atoms assemble into solid structures?
(For now, focus on metals)

2. How does density depend on the structure?

3. When do material properties vary with
sample (i.e., part) orientation?

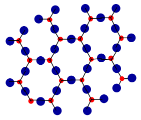
ENERGY AND PACKING



Dense, regular packed structures tend to have lower energy

MATERIALS AND PACKING

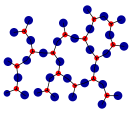
Crystalline
- **atoms pack in periodic, 3D arrays**
- **typical of: -metals**
  - **-many ceramics**
  - **-some polymers**



crystalline SiO_2

• Si ● Oxygen

Noncrystalline (amorphous)
- **atoms have no periodic packing**
- **occurs for:**
  - **-complex structures**
  - **-rapid cooling**



Noncrystalline SiO_2

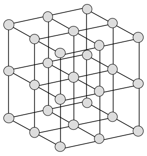
METALLIC CRYSTALS

- **Tend to be densely packed**
  Reasons:
  - **-Typically, only one element**
    (i.e., all atomic radii are the same)
  - **-Bonding is not directional**
  - **-Small nearest neighbor distances ⇨ lower energy**
- **Have simplest crystal structures.**
  We will look at three such structures...

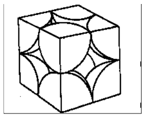
Simple Cubic Structure (SC)

- Rare due to poor packing (only Po has this structure):

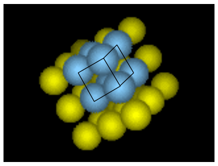
8 unit cells



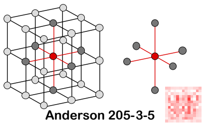
1 unit cell



(contains 8 x 1/8 = 1 atom)



- Coordination Number = 6
  (number of nearest neighbors)

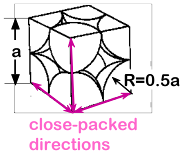


Atomic Packing Factor (APF)

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

*assume hard spheres

For simple cubic structure. . .



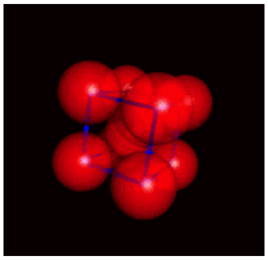
close-packed directions

contains 8 x 1/8 =
1atom/unit cell

APF = 0.52 for simple cubic

$$APF = \frac{\overset{\frac{\text{atom}}{\text{unit cell}}}{\boxed{1}}\ \overset{\frac{\text{volume}}{\text{atom}}}{\boxed{\frac{4}{3}\pi(0.5a)^3}}}{\underset{\frac{\text{volume}}{\text{unit cell}}}{\boxed{a^3}}}$$

Body-Centered Cubic Structure (BCC)



Courtesy of Materials Science: A Multimedia Approach , by John C. Russ

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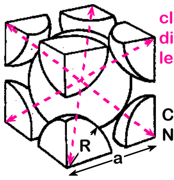
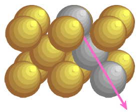
Body-Centered Cubic Structure (BCC)

1 unit cell



close-packed directions:
length = 4R
=√3 a

Coordination Number = 8



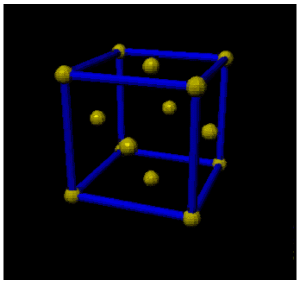
One of 4 close-packed directions

contains 1 + 8 x 1/8 = 2atoms/unit cell

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

APF =0.68 for BCC

Face-Centered Cubic Structure (FCC)



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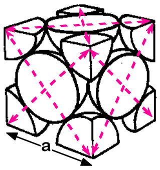
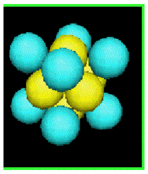
Face-Centered Cubic Structure (FCC)



close-packed directions:
length = 4R
= $\sqrt{2}$ a

Coordination Number = 12



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

$$\text{APF} = \frac{\boxed{4}\ \boxed{\frac{4}{3}\pi(\sqrt{2}a/4)^3}}{\boxed{a^3}}$$

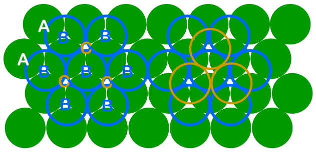
$\frac{\text{atoms}}{\text{unit cell}}$

$\frac{\text{volume}}{\text{atom}}$

$\frac{\text{volume}}{\text{unit cell}}$

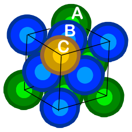
APF =0.74 for FCC

FCC Structure:
ABCABC Stacking Sequence...



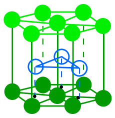
A sites
B sites
C sites

2D projection

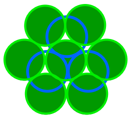


FCC Unit Cell

Hexagonal Close Packed Structure (HCP)
ABABAB...Stacking Sequence



A sites
B sites
A sites



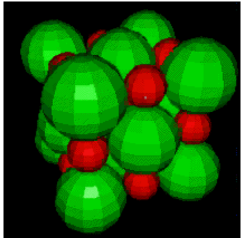
Top layer
Middle layer
Bottom layer

Coordination Number = 12

APF =0.74 for HCP

Compounds have Similar Structures
(sometimes more complicated)

example: NaCl



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THEORETICAL DENSITY, ρ

atoms/unit cell

Atomic weight (g/mol)

$$\rho = \frac{n\,A}{V_c N_A}$$

(units = mass/volume)

Volume/unit cell
(cm^3/unit cell)

Avogadro's number
(6.023×10^{23} atoms/mol)

Example: Copper

from Table inside from 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 (1nm = 10^{-7} cm)
  $V_c = a^3$; For FCC ⇨ $a = 4R/\sqrt{2}$; ⇨ $V_c = 4.75 \times 10^{-23} cm^3$

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

$\boxed{\text{actual: } 8.94\ g/cm^3}$

Characteristics of Selected Elements (inside cover-Callister)

Element	Symbol	At. Weight (amu)	Density @20C g/cm^3	Crystal Structure @20C	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	------	------	------

DENSITIES OF MATERIAL CLASSES

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

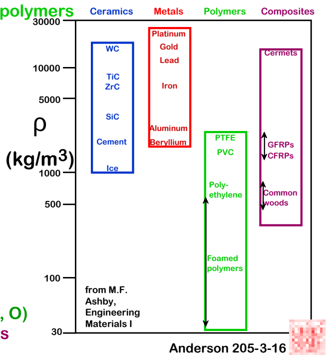
Why?

Metals have...
- close-packing
  (metallic bonding)
- large atomic masses

Ceramics have...
- less dense packing
  (covalent bonding)
- often lighter elements
  (oxygen, carbon)

Polymers have...
- poor packing
  (often amorphous)
- lighter elements (C, H, O)

Composites-average values



from M.F. Ashby, Engineering Materials I

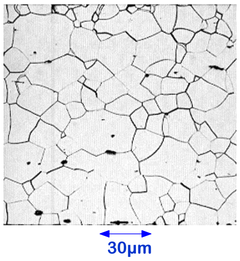
Crystals are the Building Blocks of Many Engineering Materials

diamonds
(single
crystals)

Diamond facets:
Certain crystal planes pull apart (fracture) more easily.

Some engineering applications require single crystals
- gems
- semi-conductors
- turbine blades

Most Engineering Materials are Polycrystals



Low carbon steel.

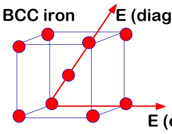
Each 'grain' is itself a single crystal.

As each is randomly oriented, overall component is not directional.

Crystals typically range from 1 nm to 2 cm
(from a few to 10^8 atomic layers)

Single vs. Poly Crystals

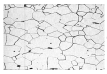
- Single crystals
  - Properties vary with direction ⇨"**Anisotropic**" material
  - Example of anisotropy: BCC iron



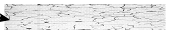
E (diagonal) = 272 GPa

E (edge) = 125 GPa

- Polycrystals
  - Properties may/may not vary with direction
  - Example: Common steel is polycrystalline.
    - If grains are random ⇨ **isotropic** (E ~ 210 GPa)
    - If grains are "textured" ⇨ anisotropic.

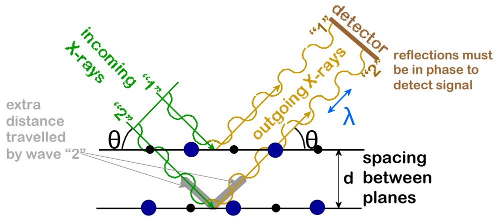


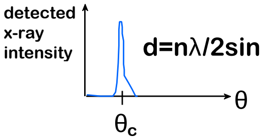
random grain
orientation



"textured"
(from rolling)

X-Rays can confirm we have crystals





$$d=n\lambda/2\sin\theta_c$$

Scanning Tunneling Microscopy confirms crystals

Images of atoms in a $MoSi_2$ coating!

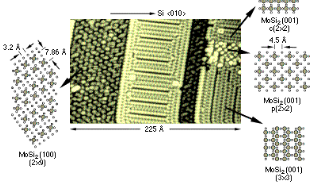


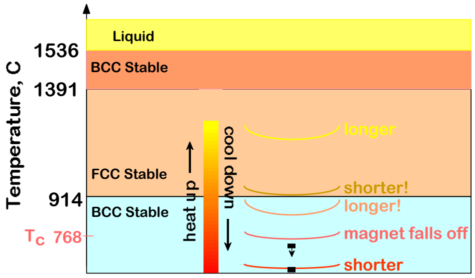
Figure 6. A 225-Å STM image of the surface resulting from the deposition of four monolayers of molybdenum on Si(100) at 770°C. The spacings between the atoms are indicated in the diagram.

figs from:
www.llnl.gov/str/scan.html

DEMO 1: HEATING AND COOLING AN IRON WIRE

- This demonstrates " polymorphism"

the same atoms can have more than one crystal structure.



Summary-Crystal Structure & Properties

- Atoms may pack in
  - -periodic arrays (crystals)
  - -nonperiodic (amorphous) structures
- Theoretical density can be calculated based on:
  - -crystal structure
  - -atomic radius
- The ranking of density generally follows...
  - -metals: largest
  - -ceramics: intermediate
  - -polymers: smallest
  - -composites: intermediate
- Single crystals: generally anisotropic.
- Polycrystals w/randomly oriented crystals: isotropic