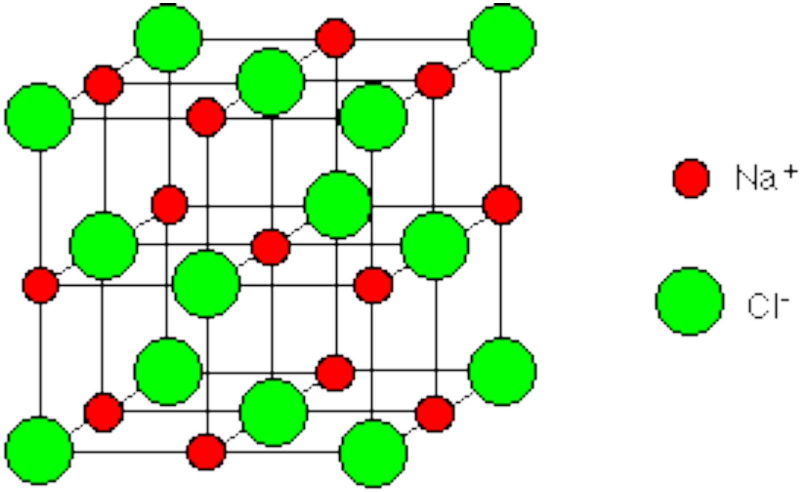
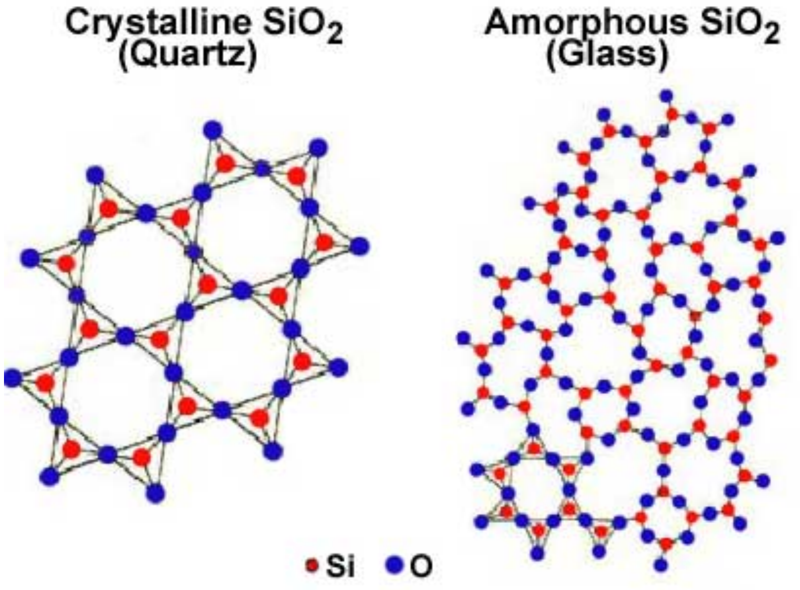


# Chapter 3: Crystal Structure of Solids



# Why do we care about crystal structures, directions, planes ?

Physical properties of materials depend on the geometry of crystals

## ISSUES TO ADDRESS...

- How do atoms assemble into solid structures? (for now, focus on metals)
- How does the density of a material depend on its structure?
- When do material properties vary with the sample (i.e., part) orientation?

# Structure of Solids

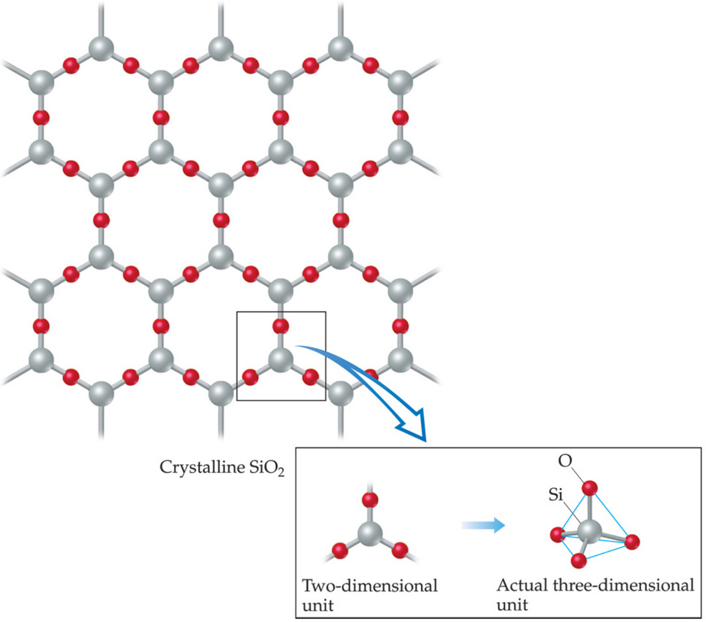
**SOLID:** Smth. which is dimensionally stable, i.e., has a volume of its own

## Crystalline

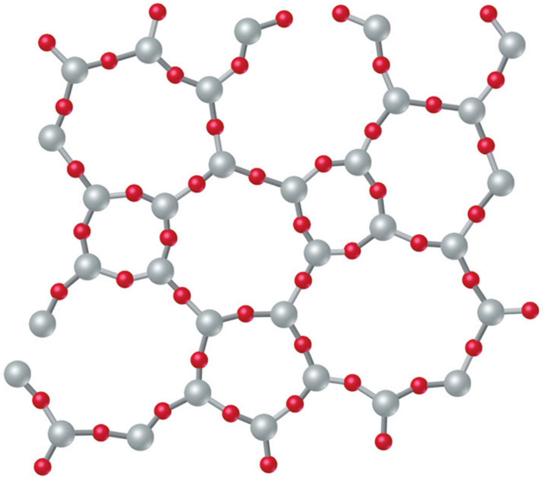
Particles are in highly ordered arrangement.

## Amorphous (non crystalline)

No particular order in the arrangement of particles.



Crystalline $SiO_2$



Amorphous $SiO_2$

# Atomic Arrangement

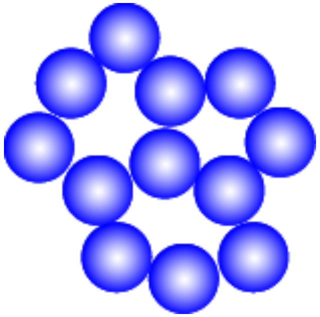
**SOLID**: Smth. which is dimensionally stable, i.e., has a volume of its own

**classifications of solids by atomic arrangement**

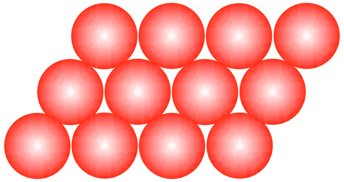
| | **ordered** | **disordered** |
|---|---|---|
| **atomic arrangement** | regular | random* |
| **order** | long-range | short-range |
| **name** | **crystalline**<br>“crystal” | **amorphous**<br>“glass” |

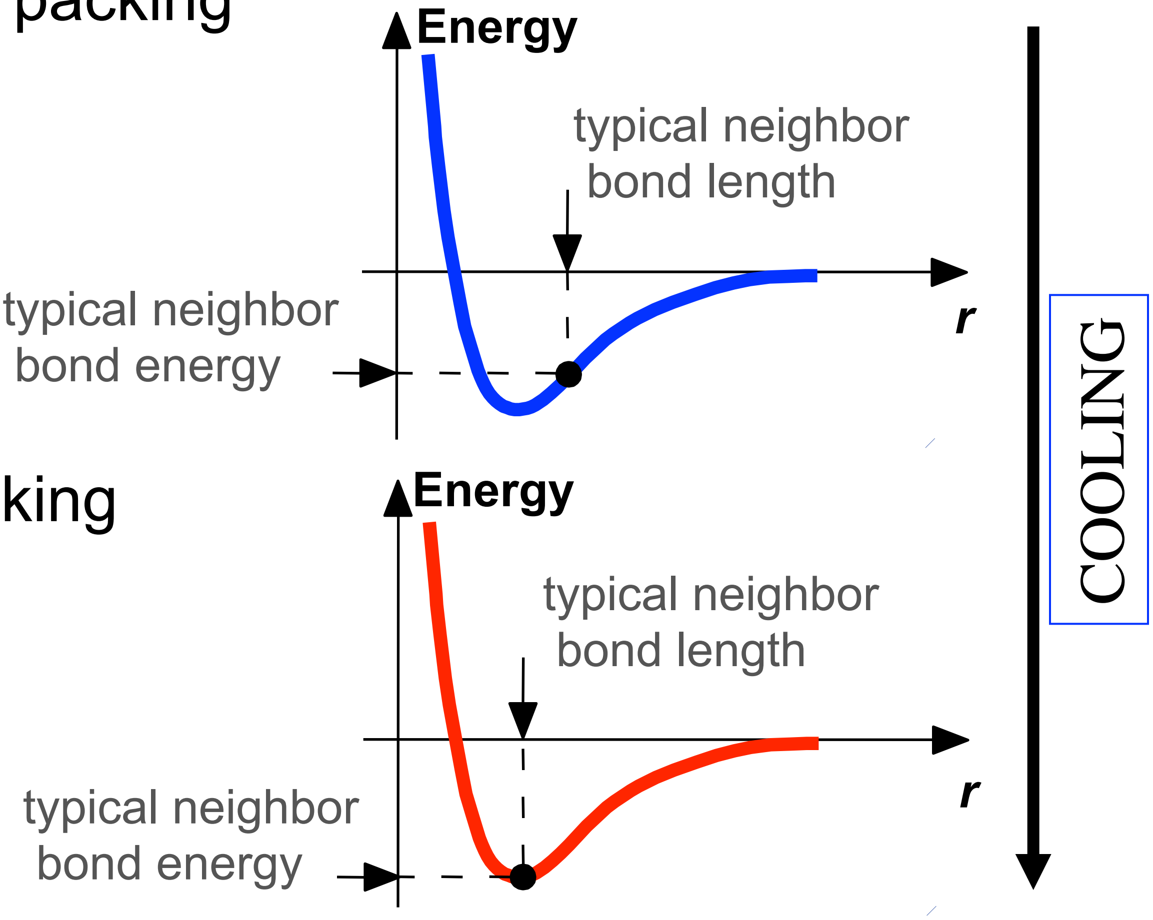
# Energy and Packing

- Non dense, random packing



- Dense, ordered packing





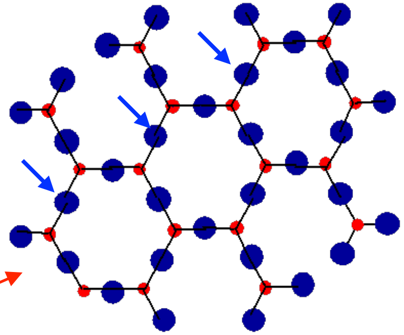
Dense, ordered packed structures tend to have lower energies.

# MATERIALS AND PACKING

**Crystalline materials...**

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

LONG RANGE ORDER



crystalline $SiO_2$

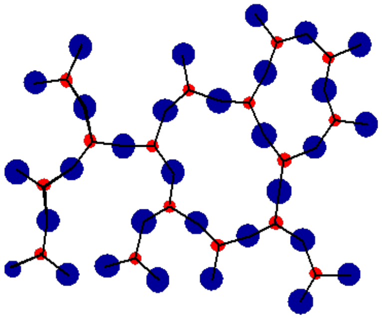
Adapted from Fig. 3.18(a), *Callister 6e.*

• Si ● Oxygen

**Noncrystalline materials...**

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

"**Amorphous**" = Noncrystalline



noncrystalline $SiO_2$

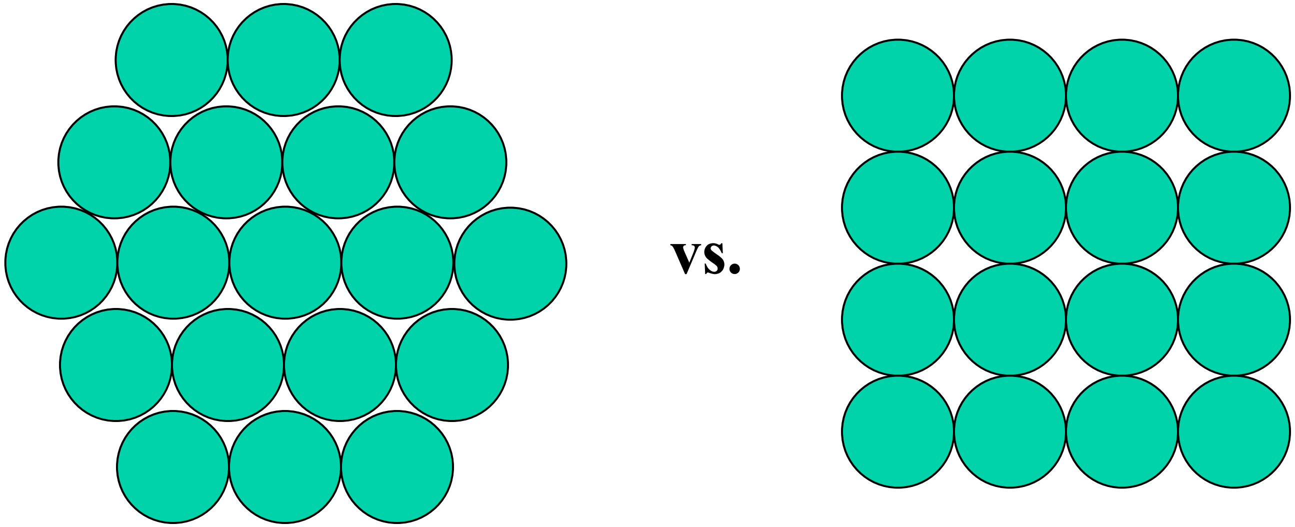
Adapted from Fig. 3.18(b), *Callister 6e.*

SHORT RANGE ORDER

# Metallic Crystal Structures

- How can we stack metal atoms to minimize empty space?

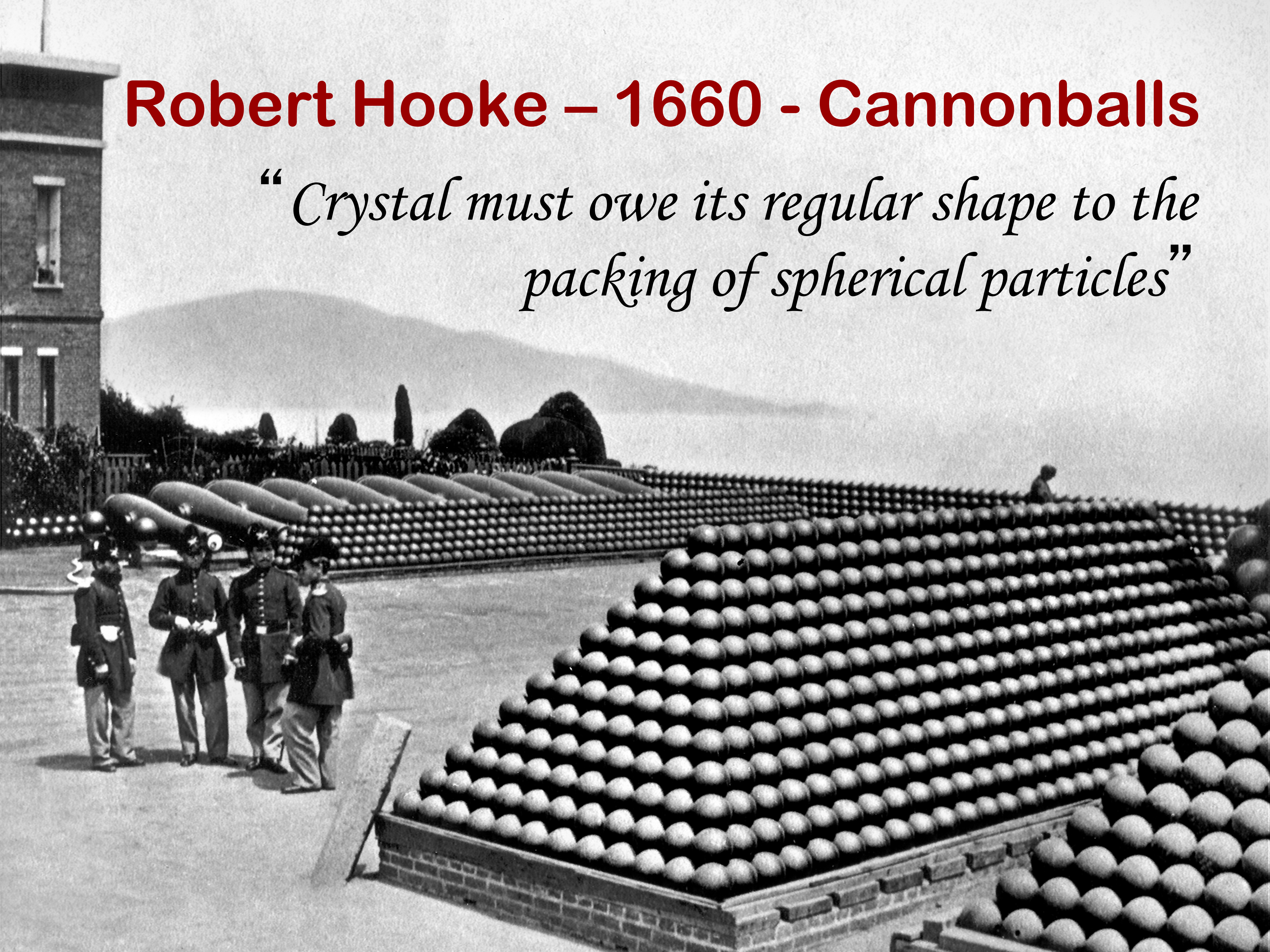
2-dimensions



Now stack these 2-D layers to make 3-D structures

# Robert Hooke – 1660 - Cannonballs

*"Crystal must owe its regular shape to the packing of spherical particles"*



# Niels Steensen ~ 1670

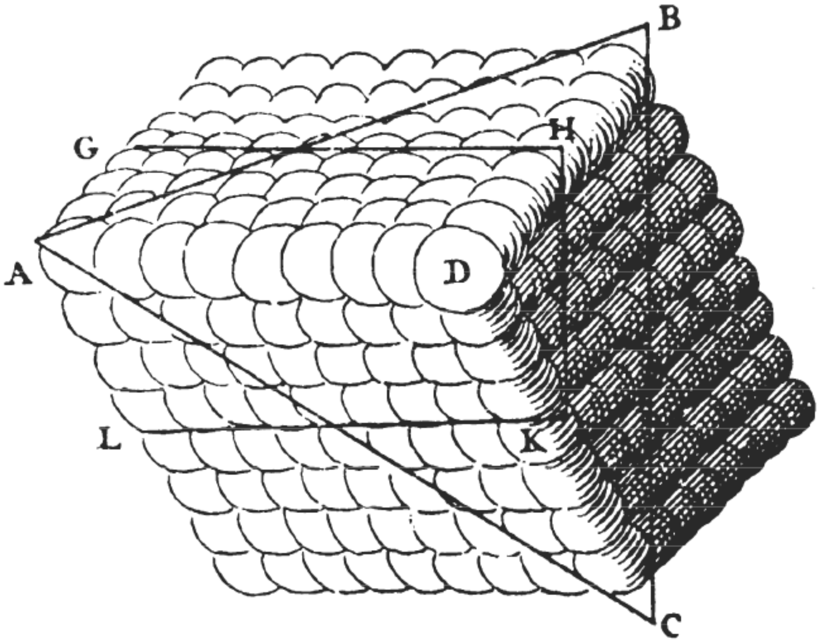
observed that quartz crystals had the same angles between corresponding faces regardless of their size.

# SIMPLE QUESTION:

If I see something has a macroscopic shape very regular and cubic, can I infer from that if I divide, divide, divide, divide, divide....
if I get down to atomic dimensions,
**will there be some cubic repeat unit?**

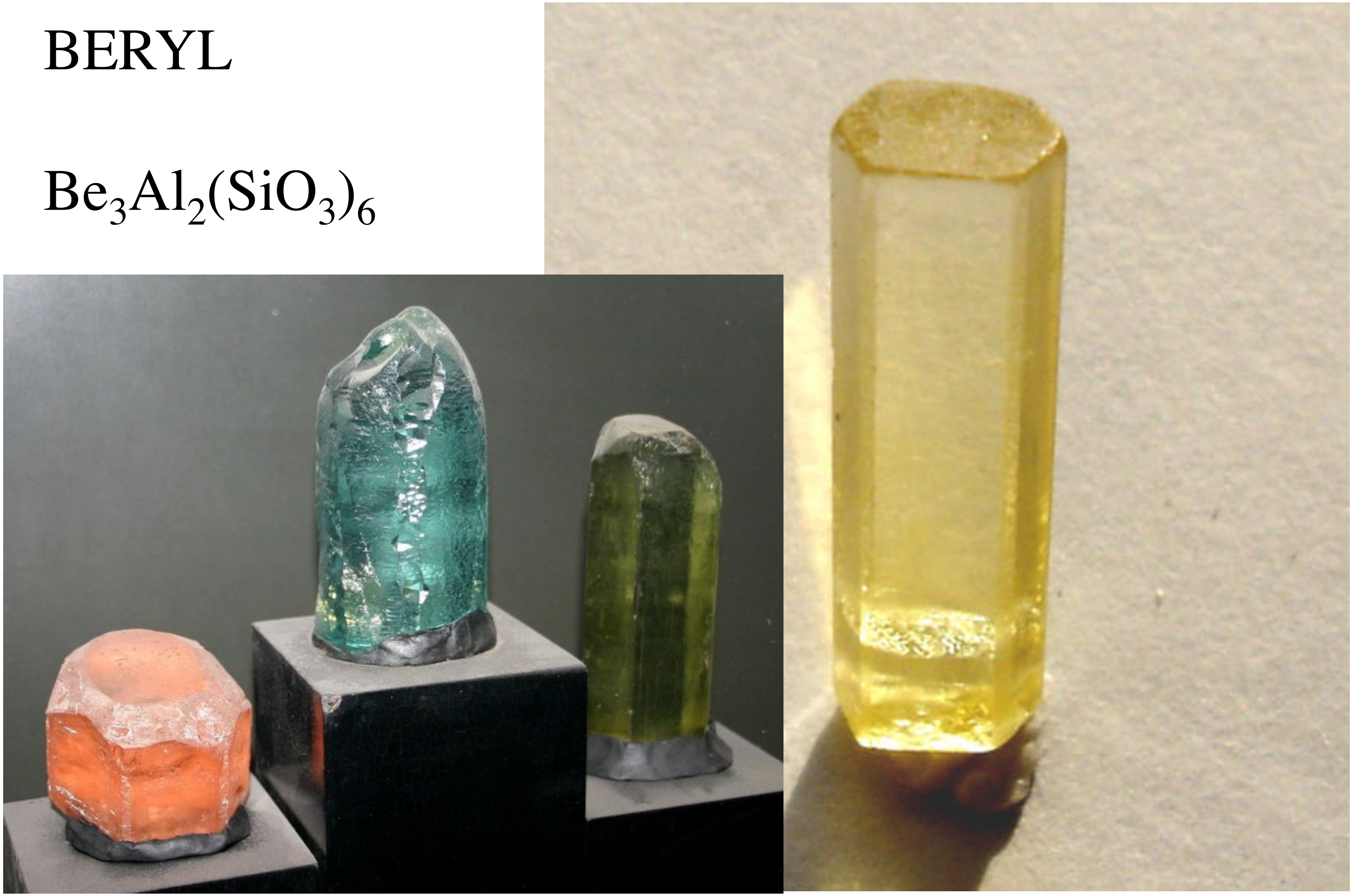
# Christian Huygens - 1690

Studying calcite crystals made drawings of atomic packing and bulk shape.



# BERYL

$Be_3Al_2(SiO_3)_6$



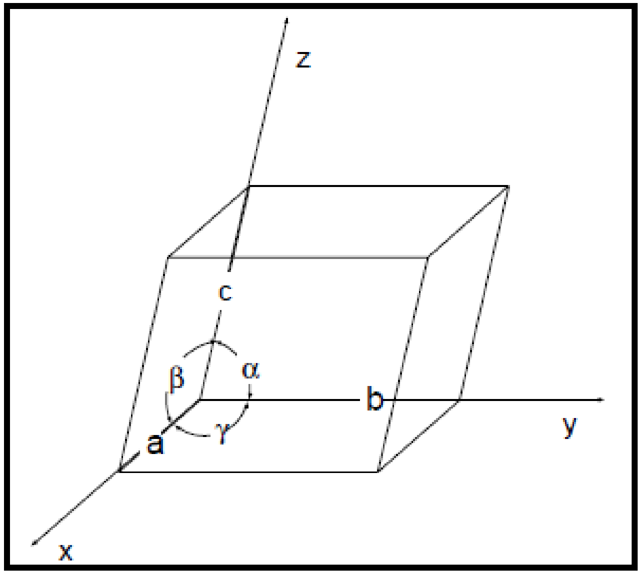
# Early Crystallography

***René-Just Haüy*** (1781): cleavage of calcite

- Common shape to all shards: rhombohedral
- How to model this mathematically?
- What is the maximum number of distinguishable shapes that will fill three space?
- Mathematically proved that there are only 7 distinct space-filling volume elements

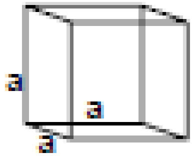
# The Seven Crystal Systems

BASIC UNIT

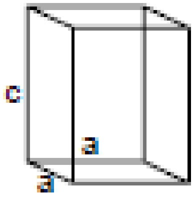


Specification of unit cell parameters

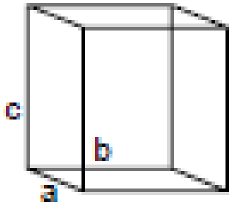
cubic
$a=b=c$
$\alpha=\beta=\gamma=90^o$



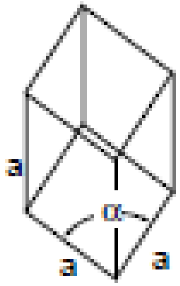
tetragonal
$a=b\neq c$
$\alpha=\beta=\gamma=90^o$



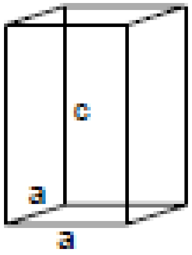
orthorhombic
$a\neq b\neq c$
$\alpha=\beta=\gamma=90^o$



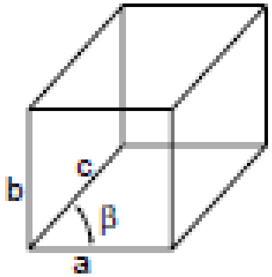
rhombohedral
$a=b=c$
$\alpha=\beta=\gamma\neq 90^o$



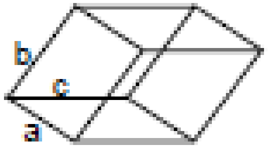
hexagonal
$a=b\neq c$
$\alpha=\beta=90^o$
$\gamma=120^o$



monoclinic
$a\neq b\neq c$
$\alpha=\gamma=90^o\neq\beta$



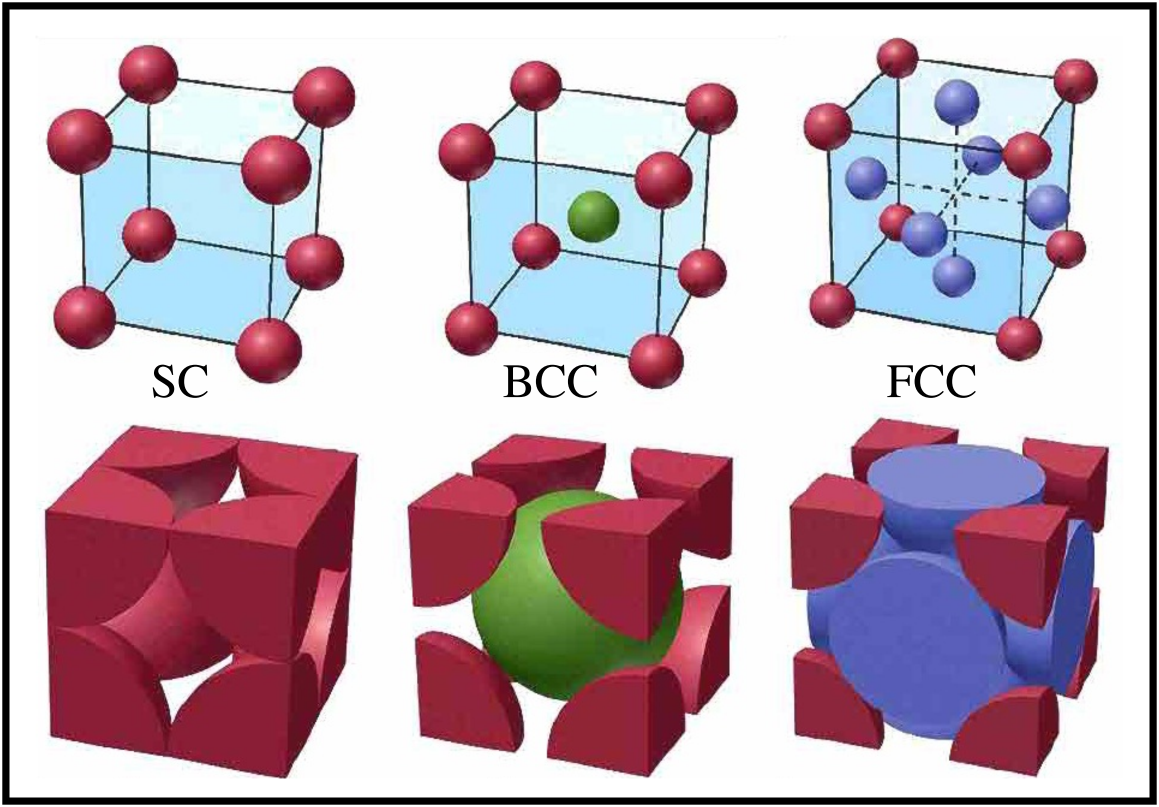
triclinic
$a\neq b\neq c$
$\alpha\neq\beta\neq\gamma\neq 90^o$



# August Bravais

- How many different ways can I put atoms into these seven crystal systems, and get distinguishable point environments?

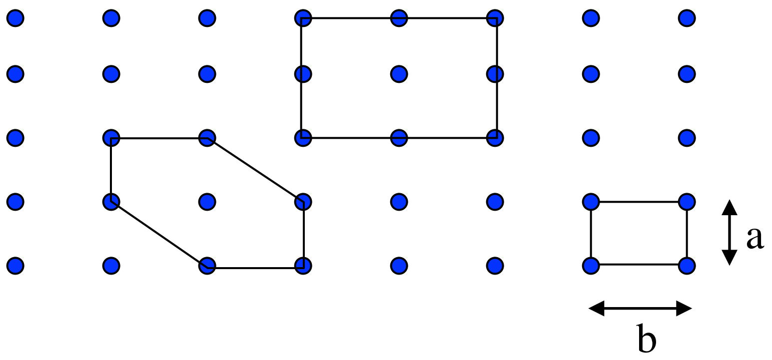
When I start putting atoms in the cube, I have three distinguishable arrangements.



And, he proved mathematically that there are 14 distinct ways to arrange points in space.

# Unit Cell Concept

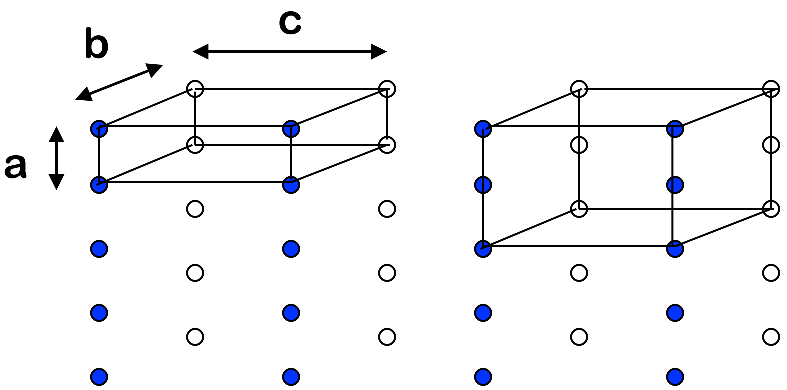
- The unit cell is the *smallest structural unit* or building block that uniquely can describe the crystal structure. Repetition of the unit cell generates the entire crystal. By simple translation, it defines a *lattice* .
- Lattice: The periodic arrangement of atoms in a Xtal.



Lattice Parameter : Repeat distance in the unit cell, one for in each dimension

# Crystal Systems

- Units cells and lattices in 3-D:
  - When translated in each lattice parameter direction, MUST fill 3-D space such that no gaps, empty spaces left.

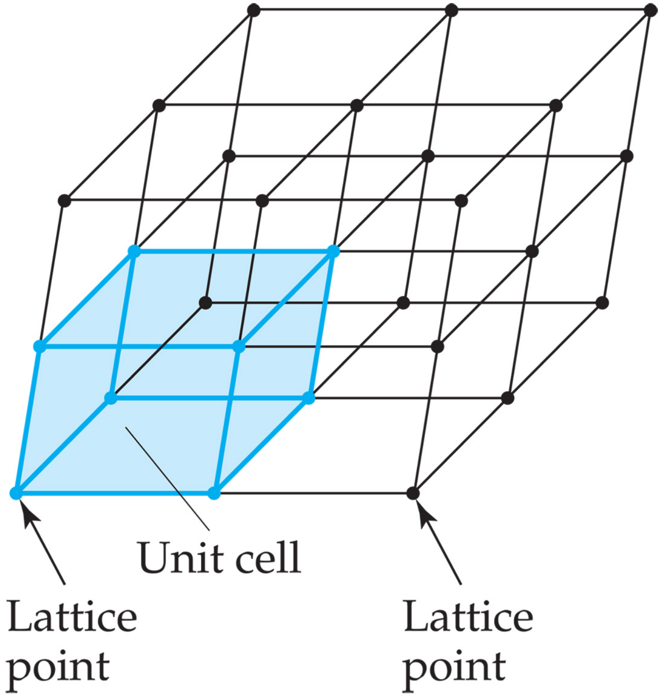


Lattice Parameter : Repeat distance in the unit cell, one for in each dimension

# Structure of Solids

Because of the order in a crystal, we can focus on the repeating pattern of arrangement called the **unit cell.**

A crystalline solid can be represented by a three dimensional array of points that is called **crystal lattice.**



**Simple crystal lattice and its associated unit cell.**

# Crystal Systems

Unit cell:  smallest repetitive volume which contains the complete lattice pattern of a crystal.

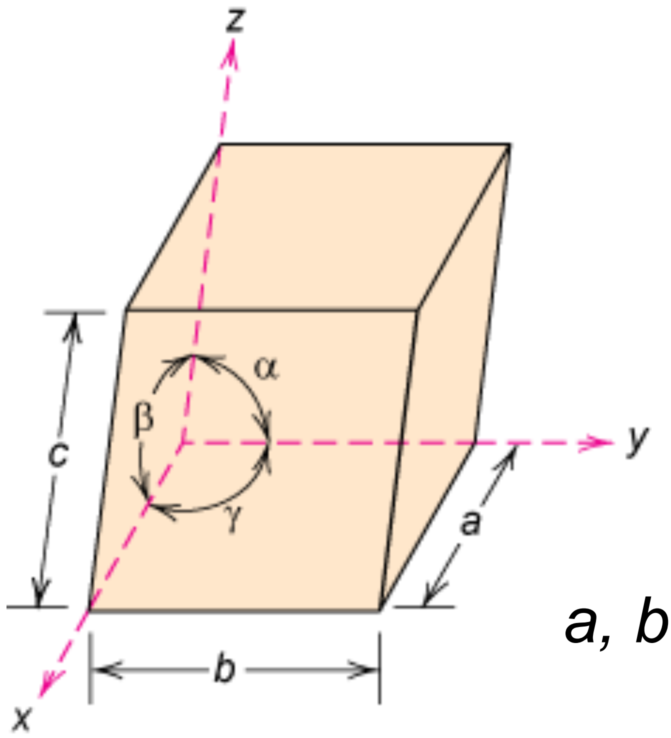


Fig. 3.4, *Callister 7e.*

7  crystal systems

14  crystal lattices

*a*, *b*, and *c* are the lattice constants

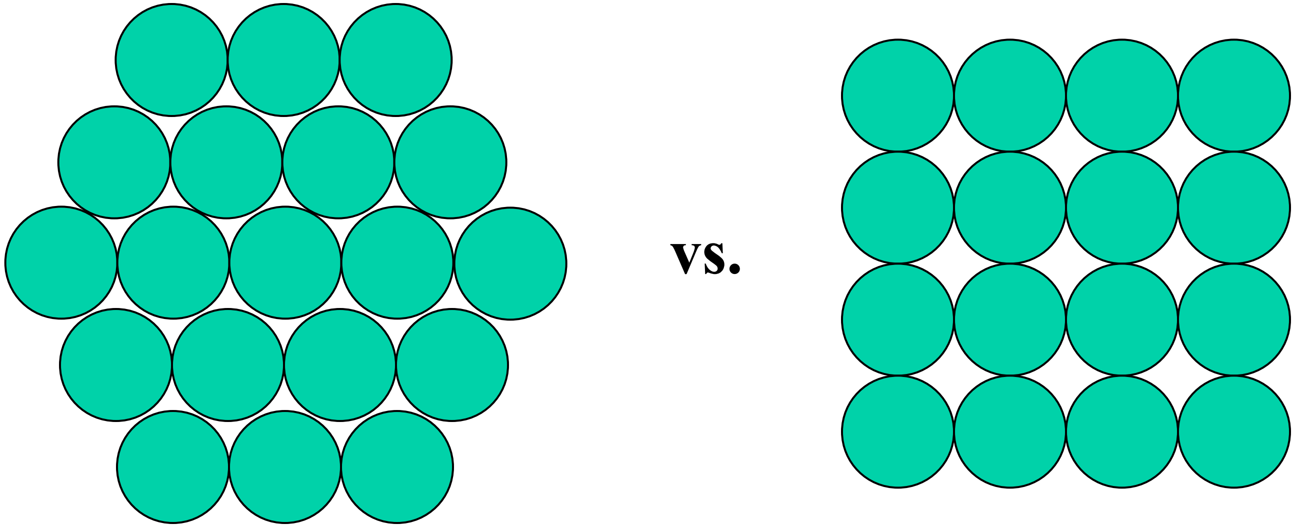
# The Importance of the Unit Cell

- One can analyze the Xtal as a whole by investigating a representative volume.
- Ex: from unit cell we can
  - **Find the distances between nearest atoms** for calculations of the forces holding the lattice together
  - Look at the **fraction of the unit cell volume filled by atoms** and **relate the density of solid to the atomic arrangement**
  - The properties of the periodic Xtal lattice determine the allowed **energies of electrons that participate in the conduction process**.

# Metallic Crystal Structures

- How can we stack metal atoms to minimize empty space?

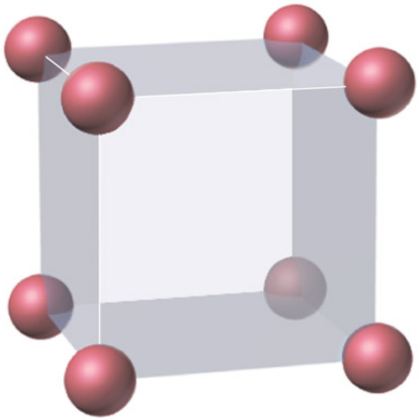
2-dimensions



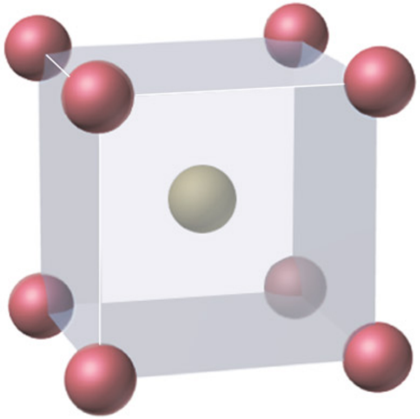
Now stack these 2-D layers to make 3-D structures

# Structure of Solids

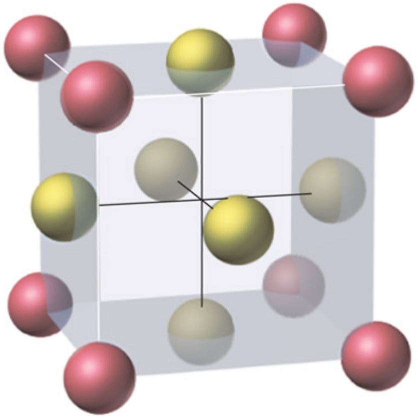
There are seven basic types of **unit cells.** The simplest of these is the cubic unit cell which has three kinds.



Primitive cubic



Body-centered cubic



Face-centered cubic

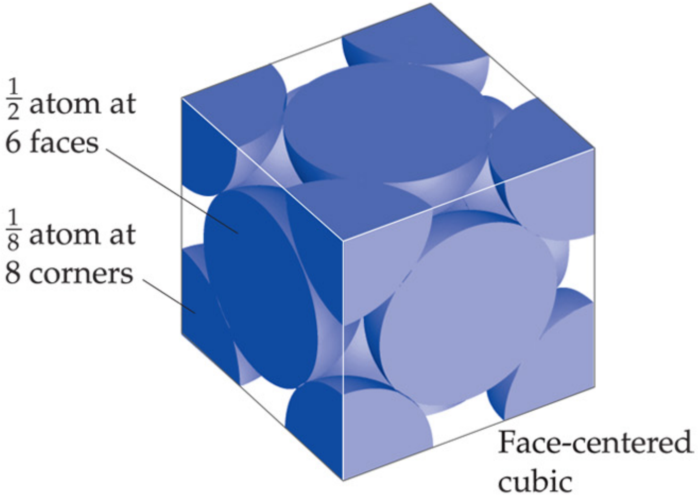
*Lattice points are at corners*

*Lattice points are at corners and at the center of the unit cell*

*Lattice points are at corners and at the center of each face*

# Structure of Solids

The atoms on the corners and faces are shared between unit cells.

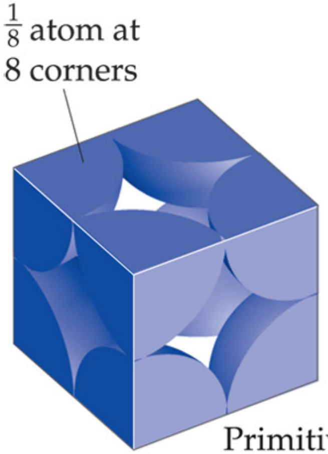


| Position in Unit Cell | Fraction in Unit Cell |
|---|---|
| Center | 1 |
| Face | $\frac{1}{2}$ |
| Edge | $\frac{1}{4}$ |
| Corner | $\frac{1}{8}$ |

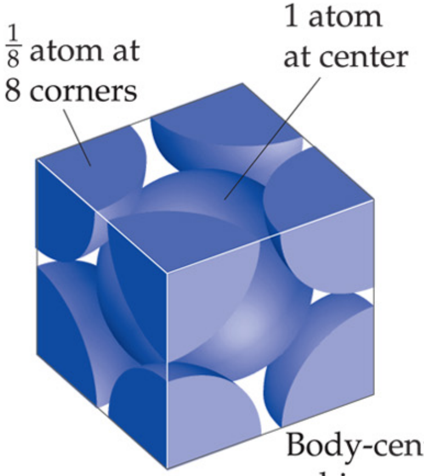
The empirical formula of an ionic solid can be also determined by determining how many ions of each element fall within the unit cell.

# Structure of Solids

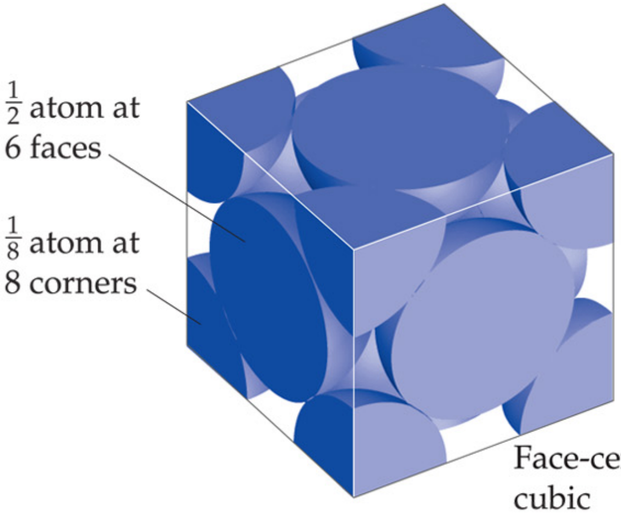
There are several types of basic arrangements in crystals. For example, Ni has a FCC, sodium has a BCC unit cell.



Primitive cubic



Body-centered cubic



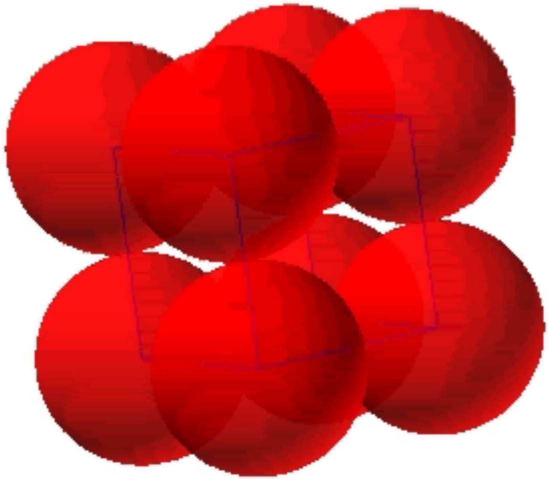
Face-centered cubic

# SIMPLE CUBIC STRUCTURE (SC)

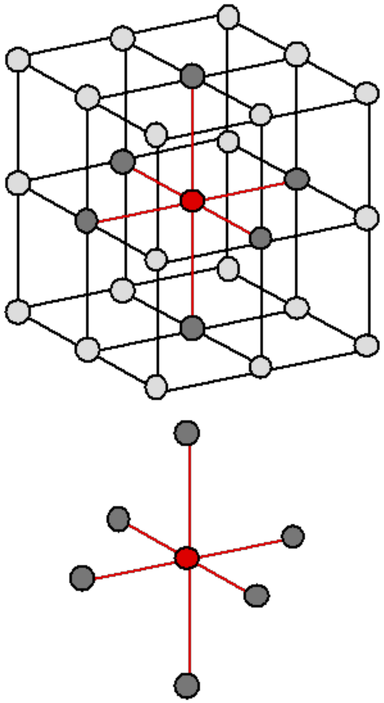
- **Rare due to poor packing**
- **Close-packed directions are cube edges.**

Closed packed direction is where the atoms touch each other

- **Coordination # = 6**
  **(# nearest neighbors)**



(Courtesy P.M. Anderson)

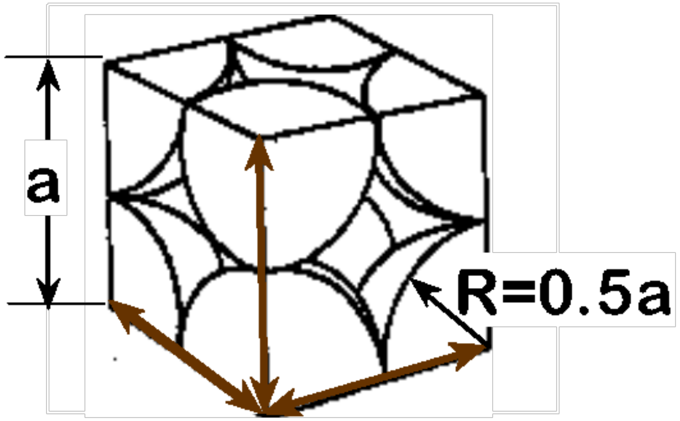


# ATOMIC PACKING FACTOR

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

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

contains 8 x 1/8 =

1 atom/unit cell

Adapted from Fig. 3.19, *Callister 6e.*

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

atoms / unit cell

volume / atom

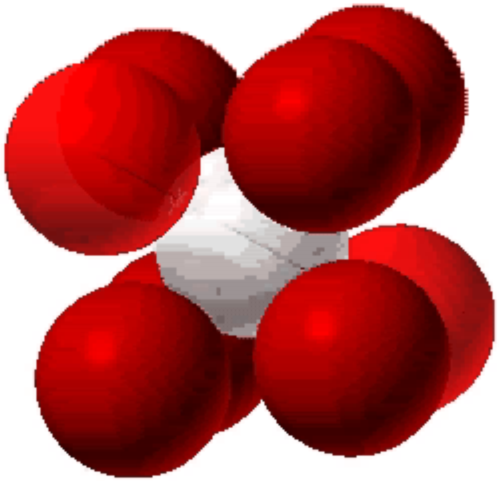
volume / unit cell

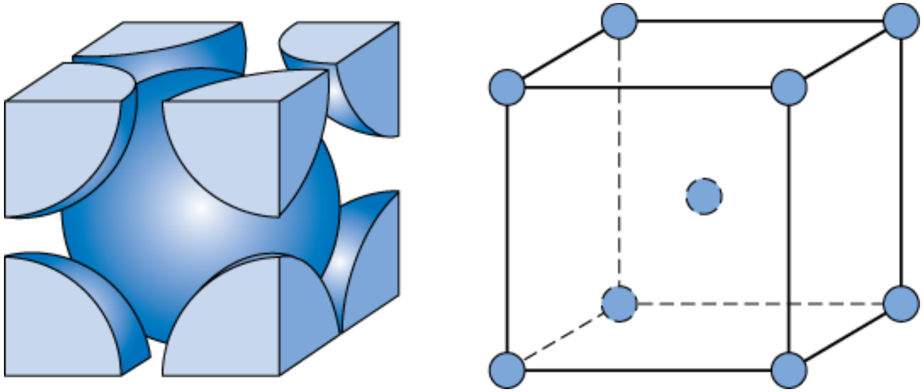
# BODY CENTERED CUBIC STRUCTURE (BCC)

- **Close packed directions are cube diagonals.**
  - **--Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.**

ex: Cr, W, Fe ($\alpha$), Tantalum, Molybdenum

- **Coordination # = 8**



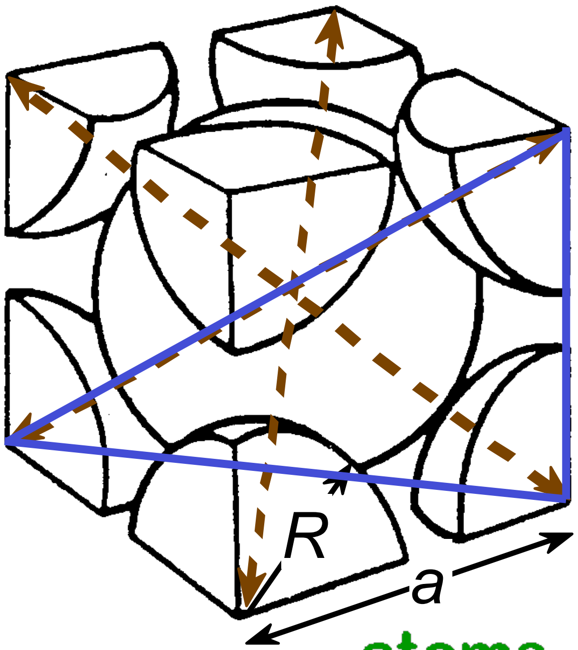


2 atoms/unit cell: 1 center + 8 corners x 1/8

(Courtesy P.M. Anderson)

# ATOMIC PACKING FACTOR: BCC

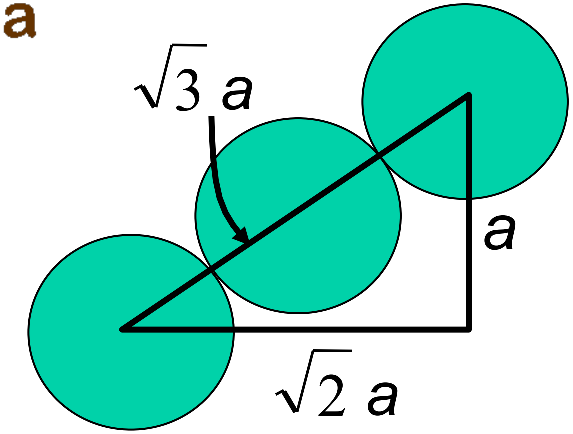
- APF for a body-centered cubic structure = 0.68



Close-packed directions:

length = 4R

$= \sqrt{3}\,a$



$$\text{APF} = \frac{\overbrace{2}^{\text{atoms/unit cell}}\ \overbrace{\frac{4}{3}\pi\left(\sqrt{3}a/4\right)^3}^{\text{volume/atom}}}{\underbrace{a^3}_{\text{volume/unit cell}}}$$

atoms / unit cell → 2

volume / atom → $\frac{4}{3}\pi\left(\sqrt{3}a/4\right)^3$

volume / unit cell → $a^3$

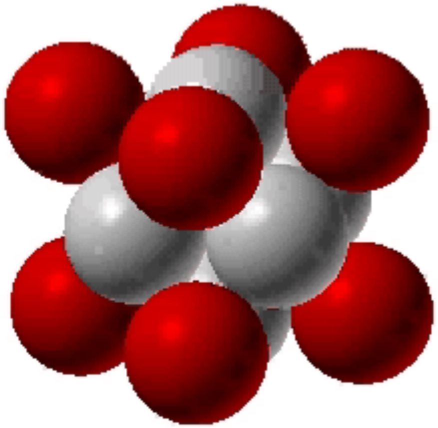
# FACE CENTERED CUBIC STRUCTURE (FCC)

- **Close packed directions are face diagonals.**

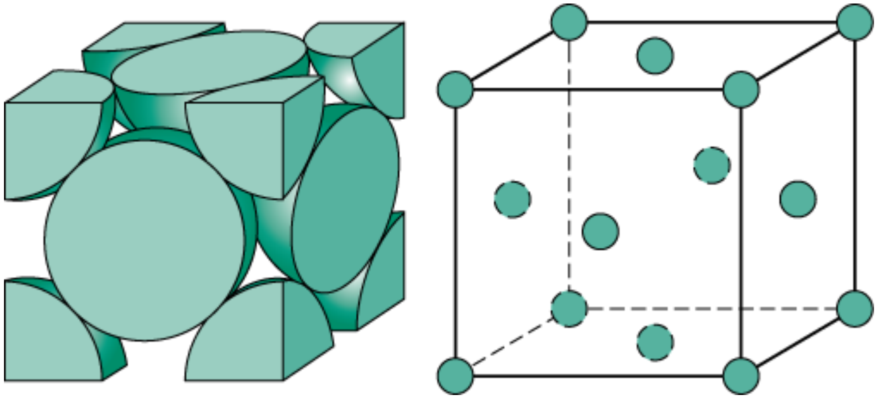
  **--Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.**

ex: Al, Cu, Au, Pb, Ni, Pt, Ag

- Coordination # = 12



**(Courtesy P.M. Anderson)**

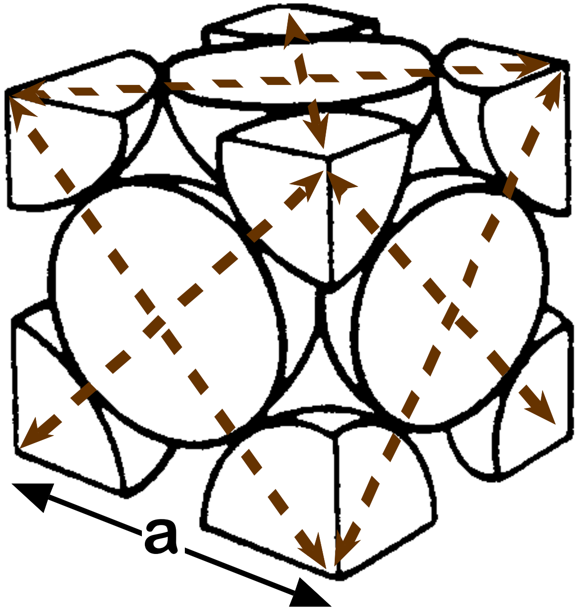


Adapted from Fig. 3.1, *Callister 7e.*

4 atoms/unit cell: 6 face x 1/2 + 8 corners x 1/8

# ATOMIC PACKING FACTOR: FCC

- APF for a body-centered cubic structure = 0.74



Close-packed directions:

length = 4R

$= \sqrt{2}\, a$

Unit cell contains:

$6 \times 1/2 + 8 \times 1/8$

= 4 atoms/unit cell

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

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

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

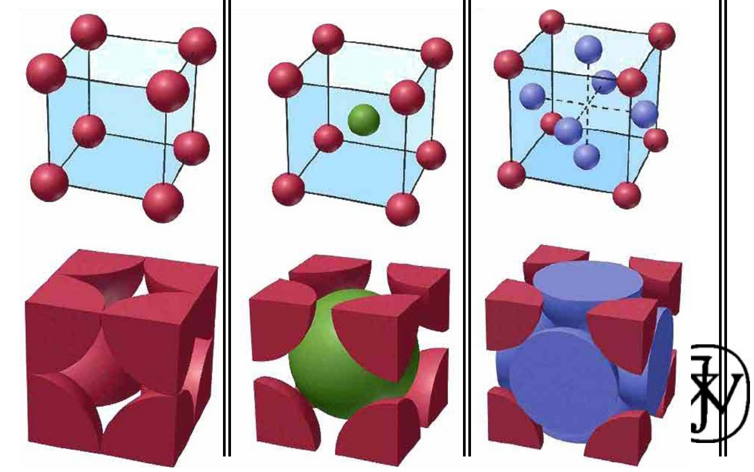
$\frac{\text{volume}}{\text{unit cell}}$

# Characteristics of Cubic Lattices

| | SC | BCC | FCC |
|---|---|---|---|
| Unit Cell Volume | $a^3$ | $a^3$ | $a^3$ |
| Lattice Points per cell | 1 | 2 | 4 |
| Nearest Neighbor Distance | $a$ | $a\sqrt{3}/2$ | $a\sqrt{2}/2$ |
| Number of Nearest Neighbors | 6 | 8 | 12 |
| Atomic Packing Factor | 0.52 | 0.68 | 0.74 |

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

*assume hard spheres



# Theoretical Density, ρ

$$\text{Density} = \rho = \frac{\text{Mass of Atoms in Unit Cell}}{\text{Total Volume of Unit Cell}}$$

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

where $n$ = number of atoms/unit cell

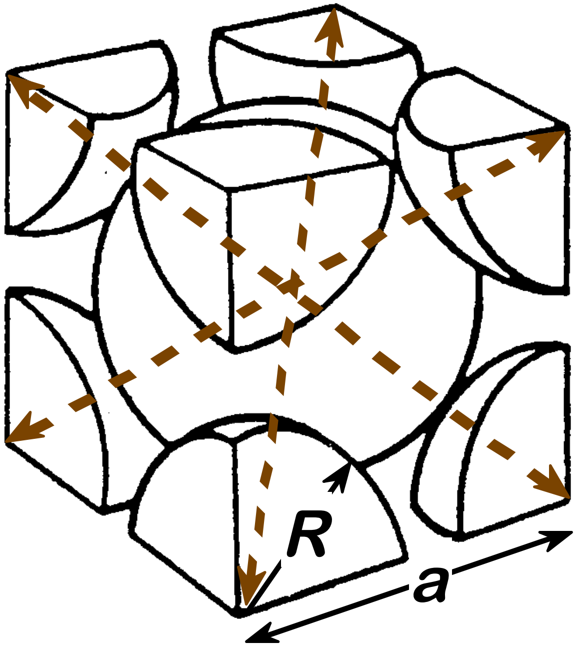
$A$ = atomic weight

$V_C$ = Volume of unit cell = $a^3$ for cubic

$N_A$ = Avogadro's number

= $6.023 \times 10^{23}$ atoms/mol

# Theoretical Density, ρ



- Ex: Cr (BCC)

  $A = 52.00$ g/mol

  $R = 0.125$ nm

  $n = 2$

  $a = 4R/\sqrt{3} = 0.2887$ nm

$$\rho = \frac{\overbrace{2}^{\frac{\text{atoms}}{\text{unit cell}}}\ \overbrace{52.00}^{\frac{\text{g}}{\text{mol}}}}{\underbrace{a^3}_{\frac{\text{volume}}{\text{unit cell}}}\ \underbrace{6.023 \times 10^{23}}_{\frac{\text{atoms}}{\text{mol}}}}$$

$\rho_{\text{theoretical}} = 7.18\ \text{g/cm}^3$

$\rho_{\text{actual}} = 7.19\ \text{g/cm}^3$

# Characteristics of Selected Elements at 20C

| 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 $\rho$ceramics $\rho$polymers

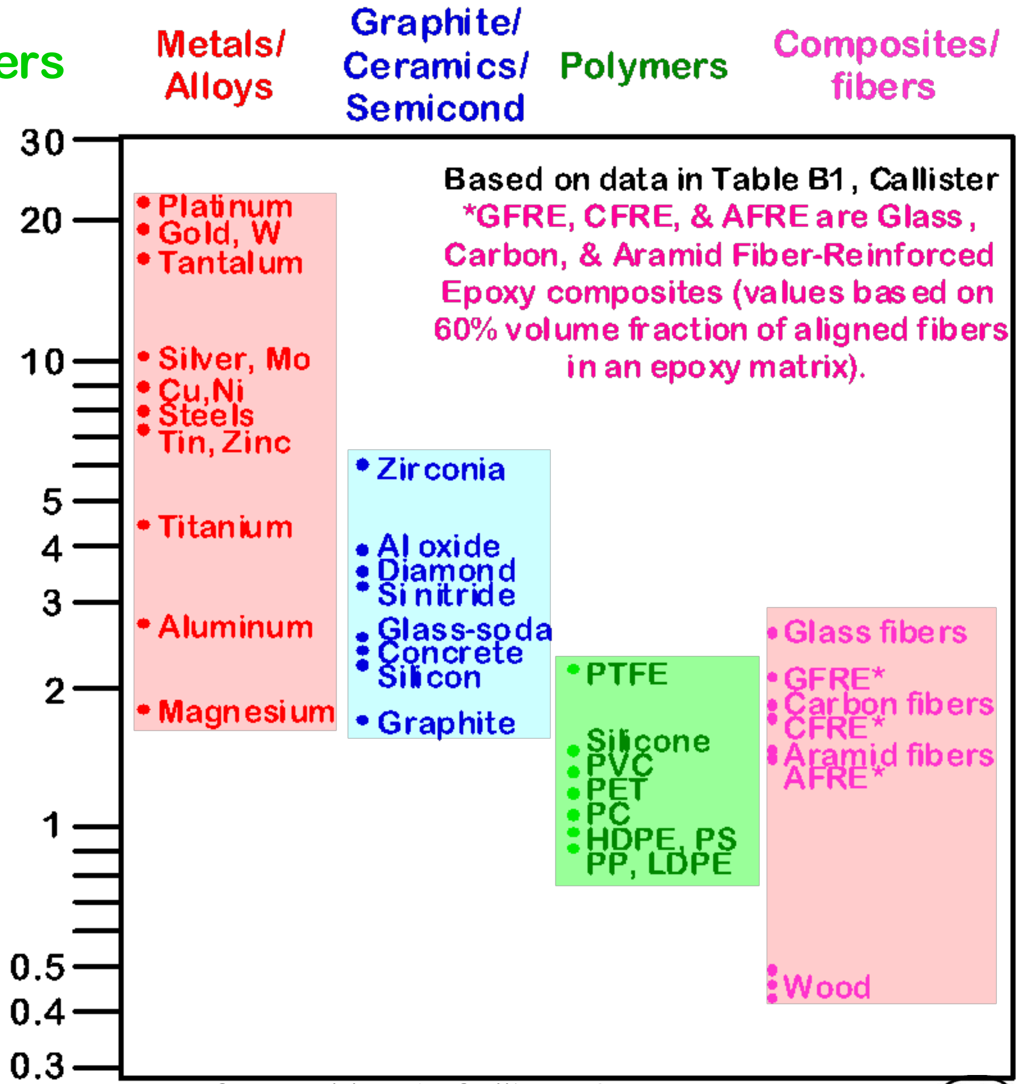
**Why?**

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

**Ceramics have...**
- less dense packing (covalent bonding)
- often lighter elements

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

**Composites have...**
- intermediate values



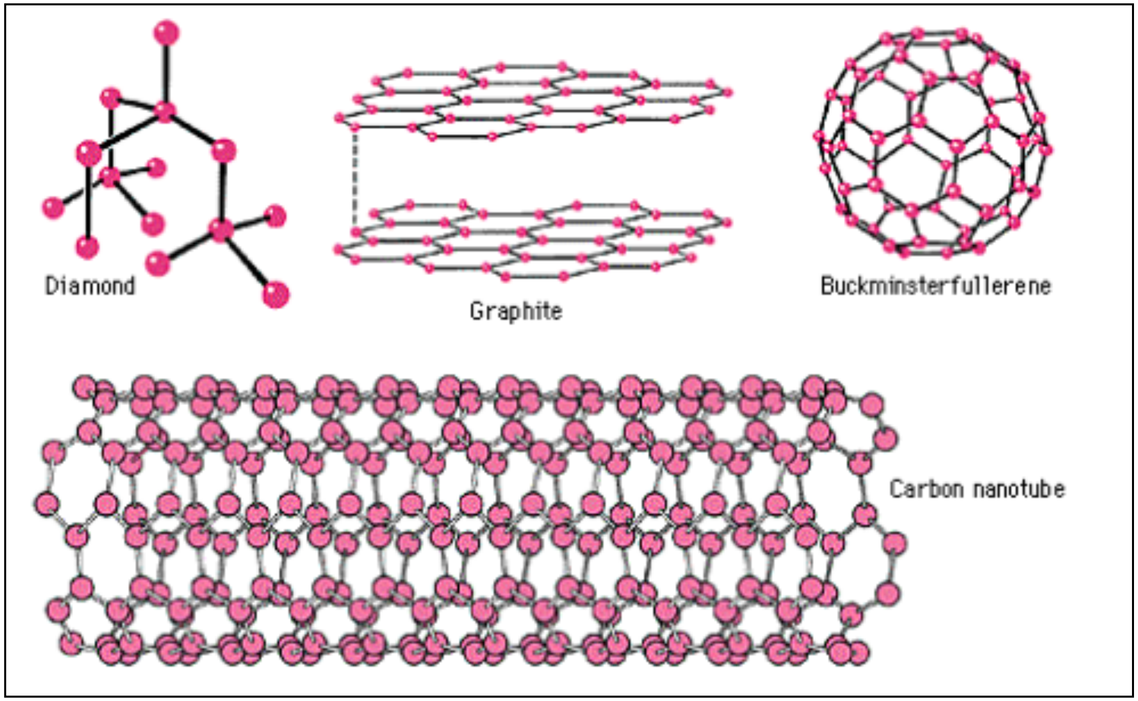
Based on data in Table B1, Callister

*GFRE, CFRE, & AFRE are Glass, Carbon, & Aramid Fiber-Reinforced Epoxy composites (values based on 60% volume fraction of aligned fibers in an epoxy matrix).

Data from Table B1, *Callister 6e.*

# POLYMORPHISM & 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.



# Polymorphism

- Two or more distinct crystal structures for the same material (allotropy/polymorphism)

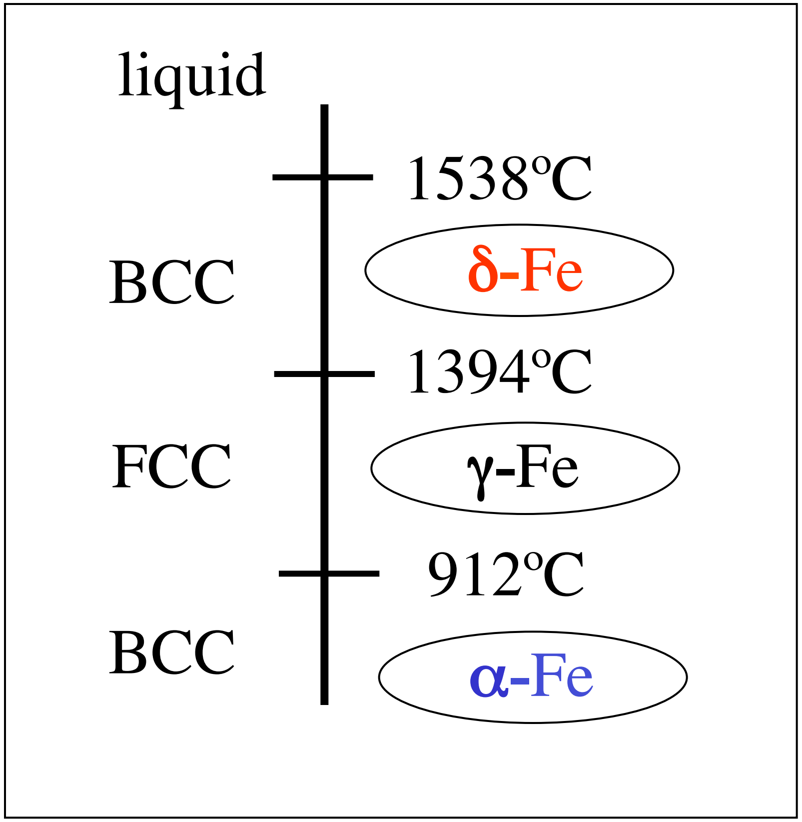
titanium

α, β-Ti

carbon

diamond, graphite

iron system



liquid

1538ºC

BCC δ-Fe

1394ºC

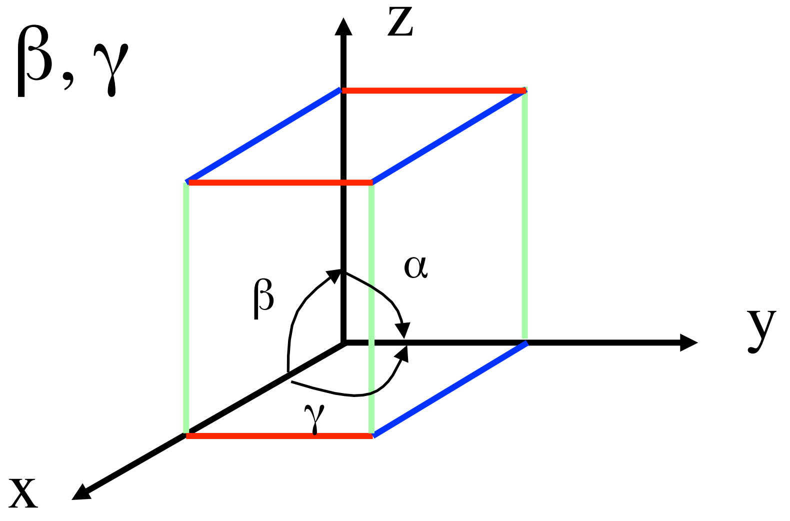
FCC γ-Fe

912ºC

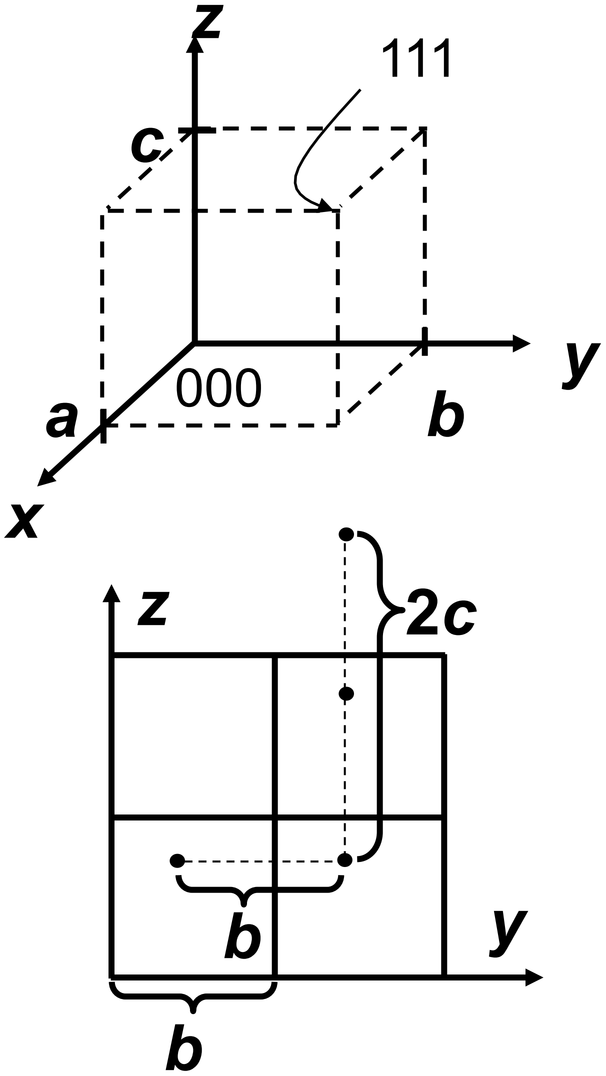
BCC α-Fe

# Crystallographic Points, Directions, and Planes

- It is necessary to specify a particular point/location/atom/ direction/plane in a unit cell
- We need some labeling convention. Simplest way is to use a 3-D system, where every location can be expressed using three numbers or *indices*.
  - **a**, **b**, **c** and α, β, γ



# Point Coordinates – Atom Positions



Point coordinates for unit cell center are

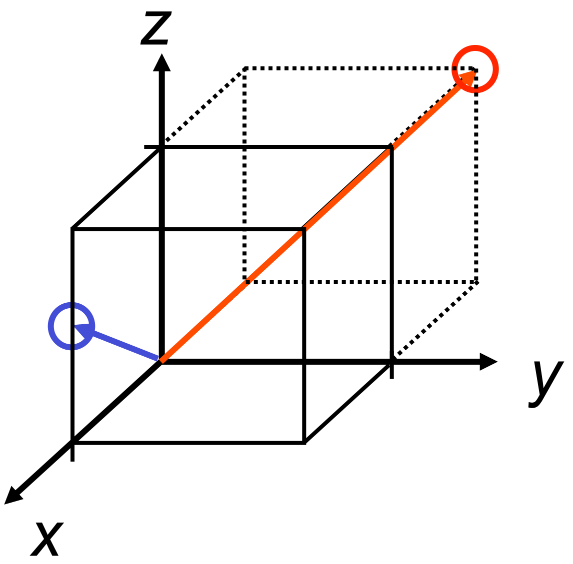
$a/2, b/2, c/2$ ½ ½ ½

Point coordinates for unit cell corner are 111

Translation: integer multiple of lattice constants → identical position in another unit cell

# Crystallographic Directions

Crystallographic direction is a vector [uvw]



## Algorithm

1. Vector repositioned (if necessary) to pass through origin. (Always passes thru origin 000)
2. Read off projections in terms of unit cell dimensions *a*, *b*, and *c*
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas

[*uvw*]

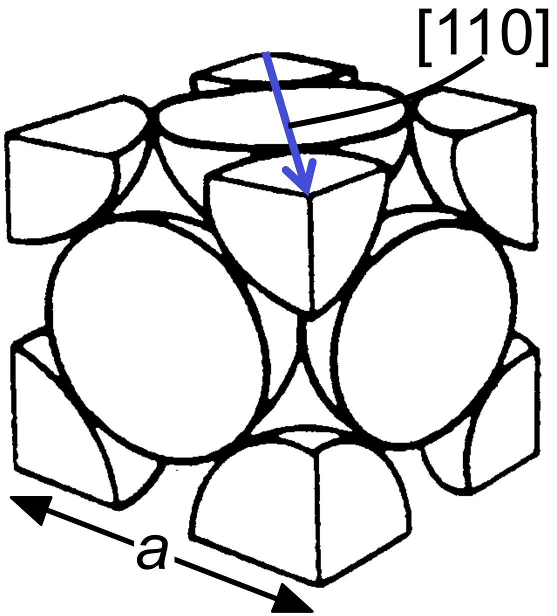
ex: 1, 0, ½ => 2, 0, 1 => [201]

-1, 1, 1 => $[\bar{1}11]$ where overbar represents a negative index

families of directions <*uvw*>

# Linear Density

- Linear Density of Atoms ≡ LD = $\dfrac{\text{Number of atoms}}{\text{Unit length of direction vector}}$



ex: linear density of Al in [110] direction

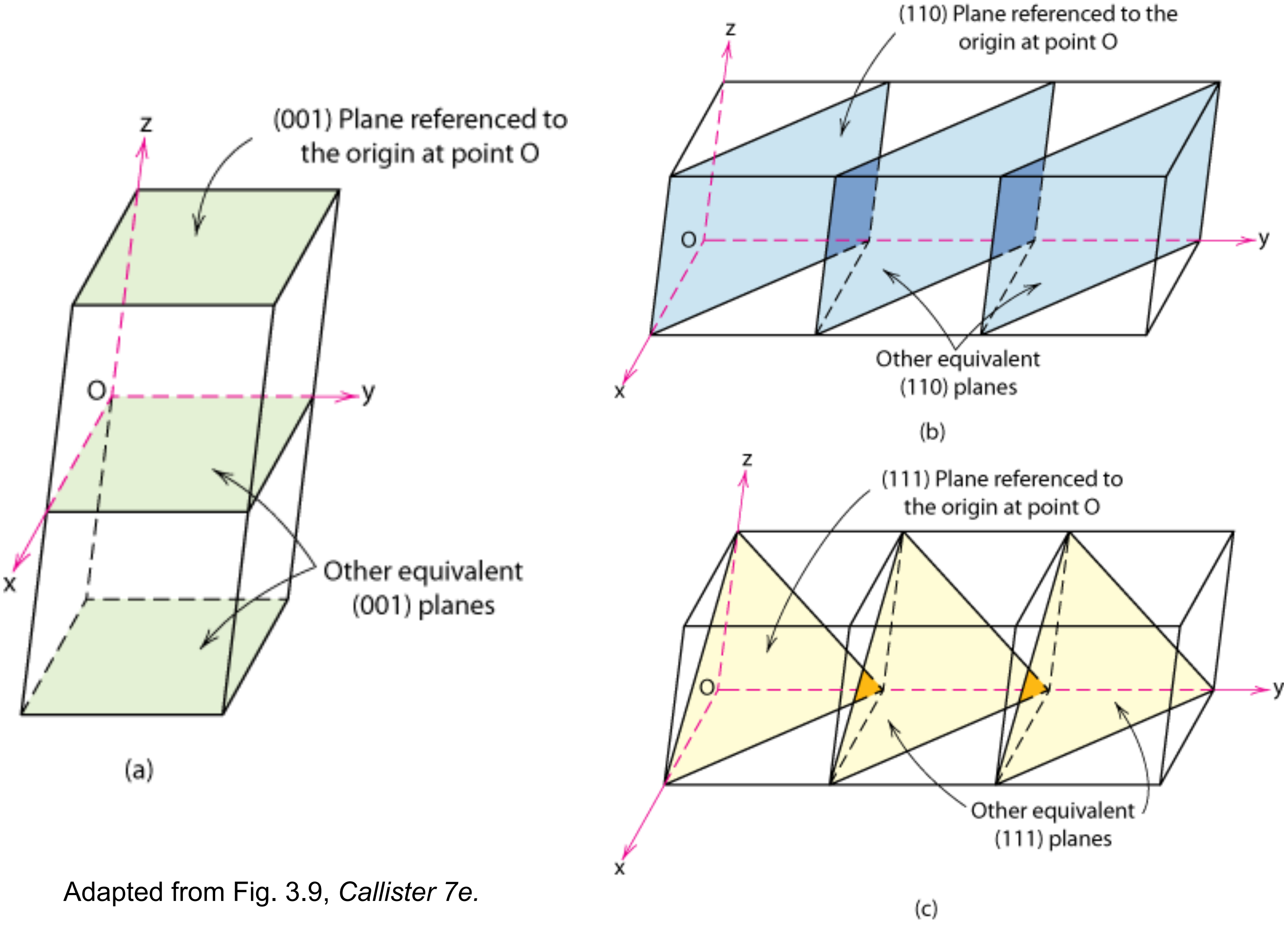
$a = 0.405$ nm

# atoms

$$\text{LD} = \frac{2}{\sqrt{2}a} = \boxed{3.5\ \text{nm}^{-1}}$$

length

# Crystallographic Planes



Adapted from Fig. 3.9, *Callister 7e.*

# Crystallographic Planes

- Miller Indices: Reciprocals of the (three) axial intercepts for a plane, cleared of fractions & common multiples. All parallel planes have same Miller indices.

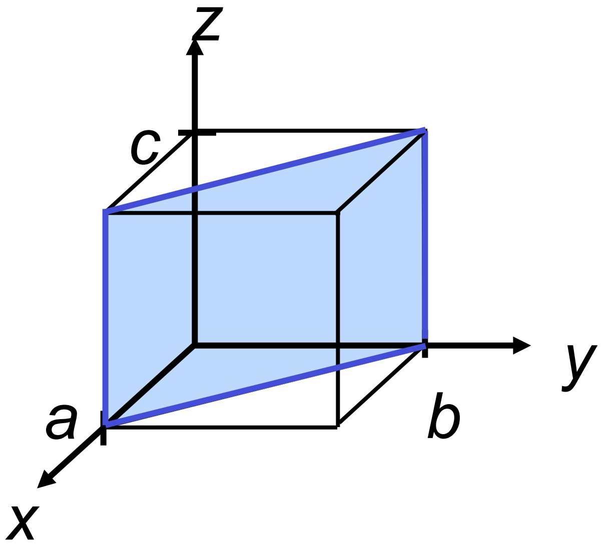
- Algorithm
  1. If plane passes thru origin, translate
  2. Read off intercepts of plane with axes in terms of *a*, *b*, *c*
  3. Take reciprocals of intercepts
  4. Reduce to smallest integer values
  5. Enclose in parentheses, no commas i.e., (*hkl*)

# Crystallographic Points, Directions, and Planes

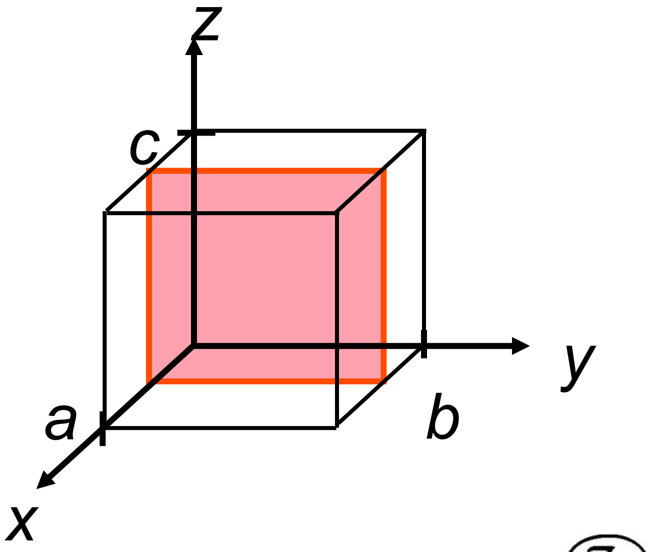
- Crystallographic direction is a vector [uvw]
  - Always passes thru origin 000
  - Measured in terms of unit cell dimensions *a, b, and c*
  - Smallest integer values
- Planes with Miller Indices (hkl)
  - If plane passes thru origin, translate
  - Length of each planar intercept in terms of the lattice parameters *a, b, and c*.
  - Reciprocals are taken
  - If needed multiply by a common factor for integer representation

# Crystallographic Planes

| <u>example</u> | *a* | *b* | *c* |
|---|---|---|---|
| 1. Intercepts | 1 | 1 | ∞ |
| 2. Reciprocals | 1/1 | 1/1 | 1/∞ |
| | 1 | 1 | 0 |
| 3. Reduction | 1 | 1 | 0 |
| 4. Miller Indices | (110) | | |

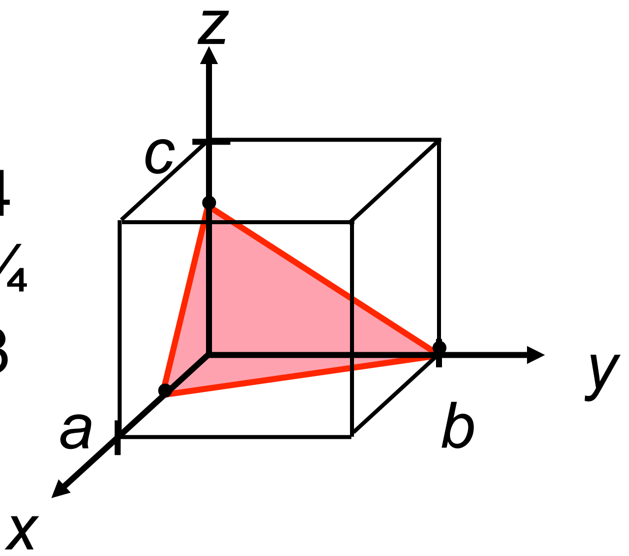


| <u>example</u> | *a* | *b* | *c* |
|---|---|---|---|
| 1. Intercepts | 1/2 | ∞ | ∞ |
| 2. Reciprocals | 1/½ | 1/∞ | 1/∞ |
| | 2 | 0 | 0 |
| 3. Reduction | 2 | 0 | 0 |
| 4. Miller Indices | (100) | | |



# Crystallographic Planes

| example | a | b | c |
|---|---|---|---|
| 1. Intercepts | 1/2 | 1 | 3/4 |
| 2. Reciprocals | 1/½ | 1/1 | 1/¾ |
| | 2 | 1 | 4/3 |
| 3. Reduction | 6 | 3 | 4 |
| 4. Miller Indices | (634) | | |



Family of Planes {*hkl*}

Ex: {100} = (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, $(00\bar{1})$

# Crystallographic Planes

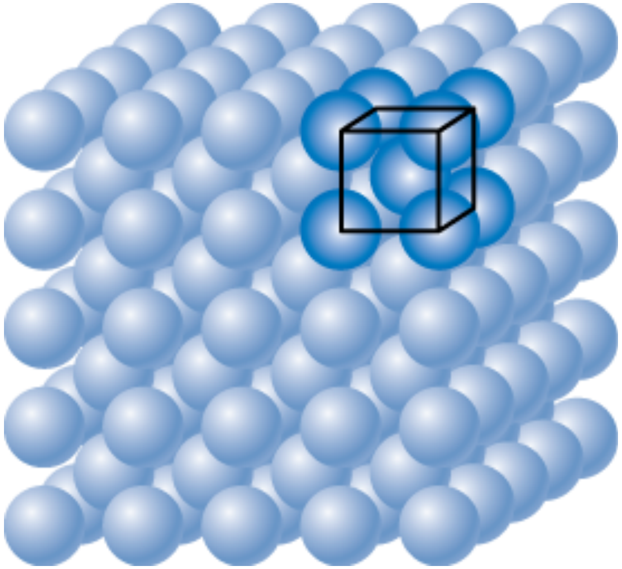
- We want to examine the atomic packing of crystallographic planes
- Iron foil can be used as a catalyst. The atomic packing of the exposed planes is important.

a) Draw (100) and (111) crystallographic planes for Fe.

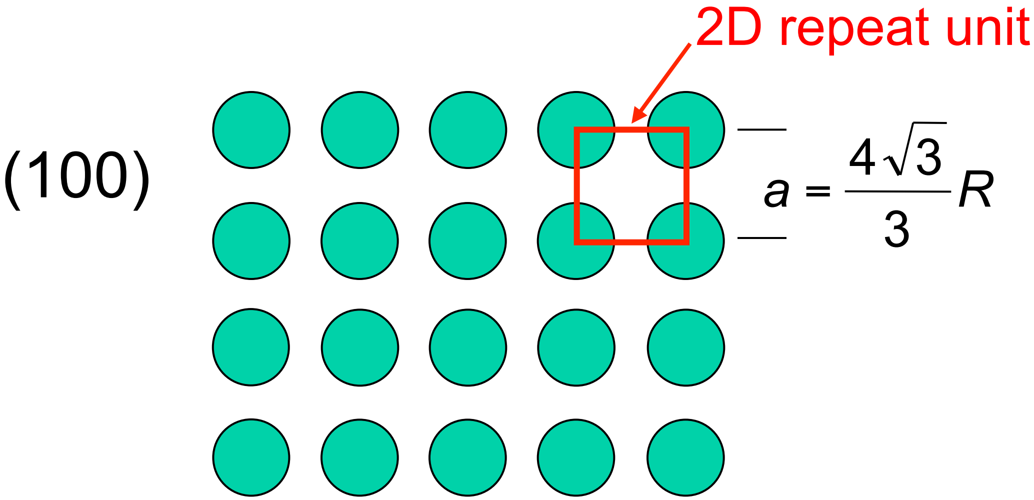
b) Calculate the planar density for each of these planes.

# Planar Density of (100) Iron

Solution: At T < 912°C iron has the BCC structure.



Adapted from Fig. 3.2(c), *Callister 7e.*

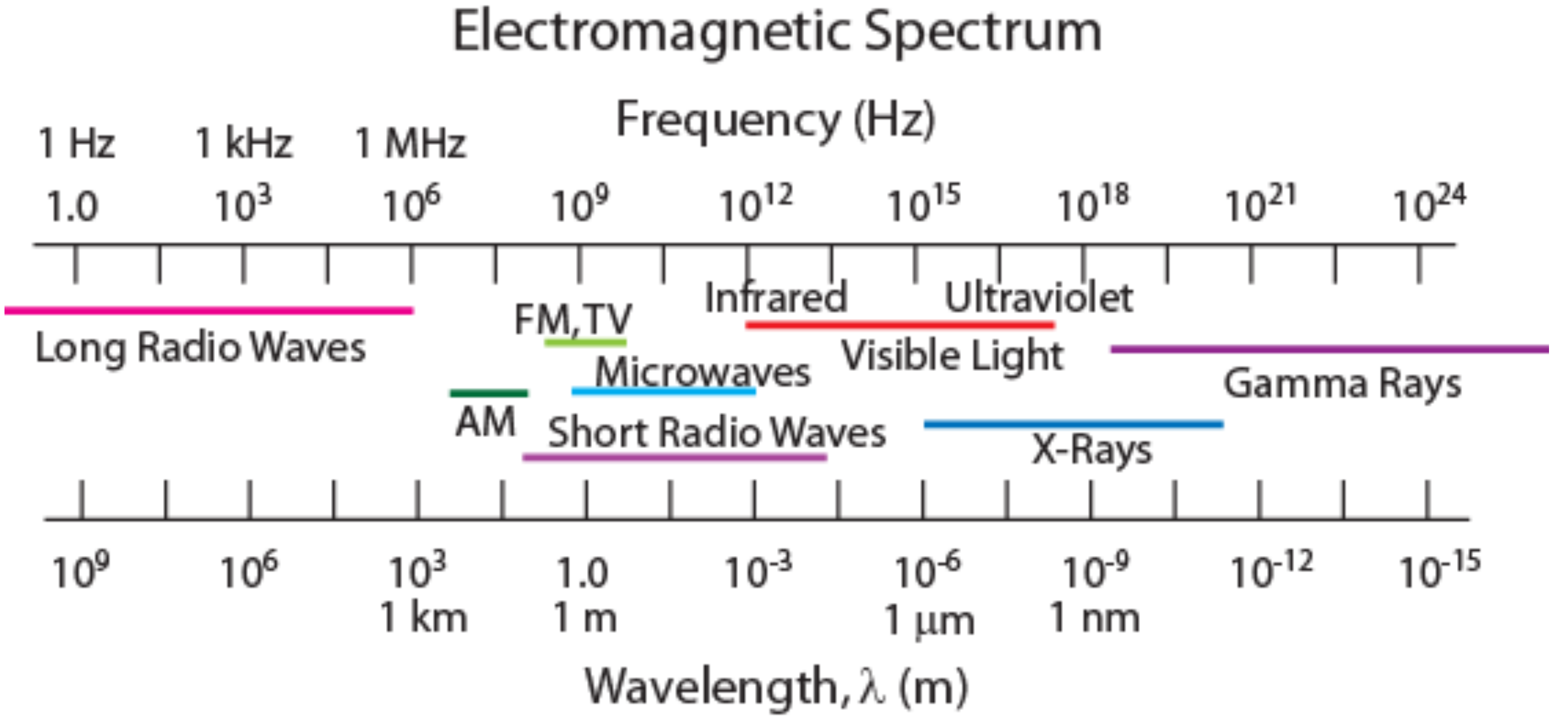


$$a = \frac{4\sqrt{3}}{3}R$$

Radius of iron $R = 0.1241$ nm

$$\text{Planar Density} = \frac{\dfrac{\text{atoms}}{\text{2D repeat unit}} \rightarrow 1}{\dfrac{\text{area}}{\text{2D repeat unit}} \rightarrow a^2} = \frac{1}{\left(\dfrac{4\sqrt{3}}{3}R\right)^2} = 12.1\,\frac{\text{atoms}}{\text{nm}^2} = \boxed{1.2 \times 10^{19}\,\frac{\text{atoms}}{\text{m}^2}}$$

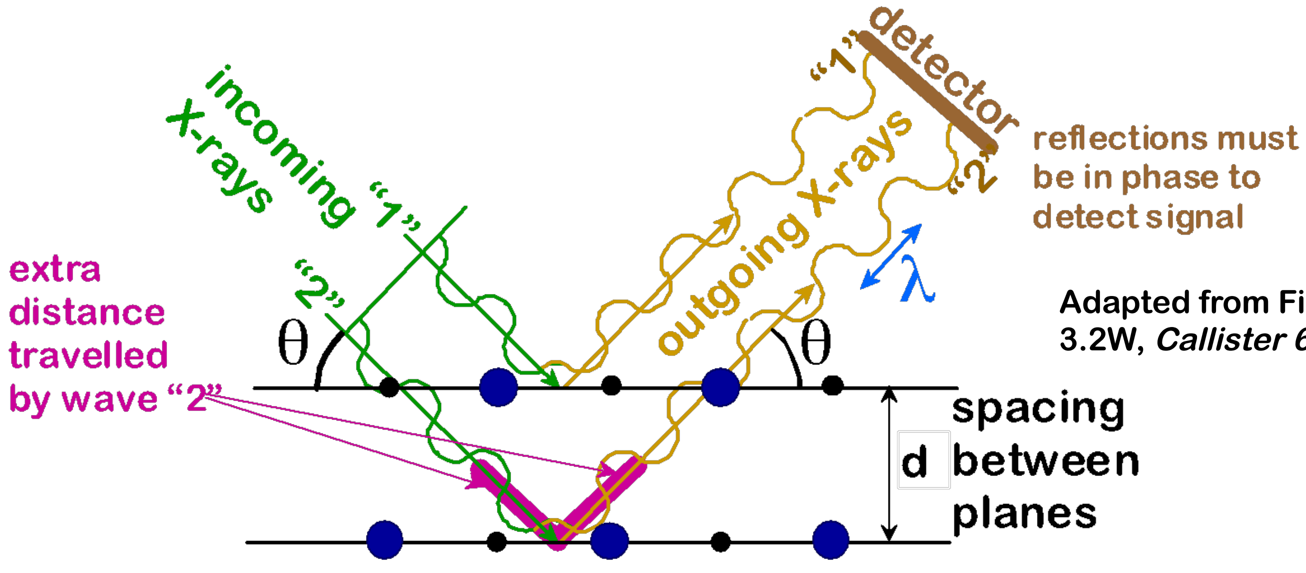
# Section 3.16 - X-Ray  Diffraction



- Diffraction gratings must have spacings comparable to the wavelength of diffracted radiation.
- Can't resolve spacings < λ
- Spacing is the distance between parallel planes of atoms.

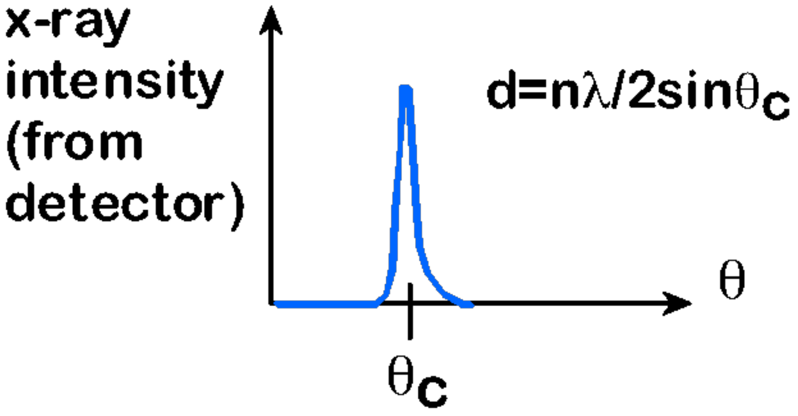
# X-RAYS TO CONFIRM CRYSTAL STRUCTURE

- **Incoming X-rays diffract from crystal planes.**



Adapted from Fig. 3.2W, *Callister 6e*.

- **Measurement of:**
  Critical angles, $\theta_c$, for X-rays provide atomic spacing, d.



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

# SUMMARY

- Atoms may assemble into crystalline or amorphous structures.
- We can predict the density of a material, provided we know the atomic weight, atomic radius, and crystal geometry (e.g., FCC, BCC, HCP).