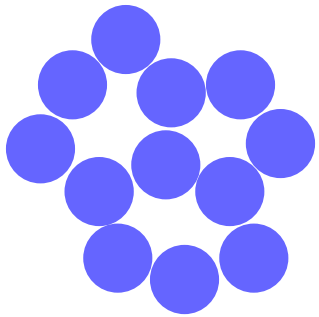
Chapter 3
Structure of Crystalline Solids

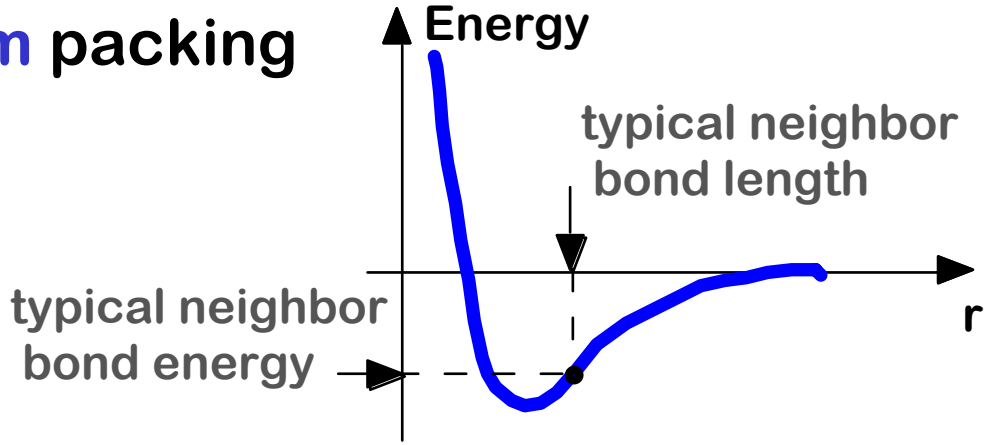
- Crystal Structures
- Points, Directions, and Planes
- Linear and Planar Densities
- X-ray Diffraction

  - **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?**

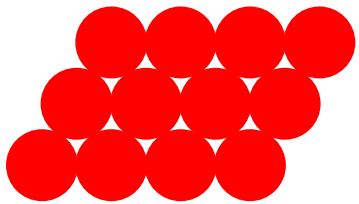
Energy and Packing

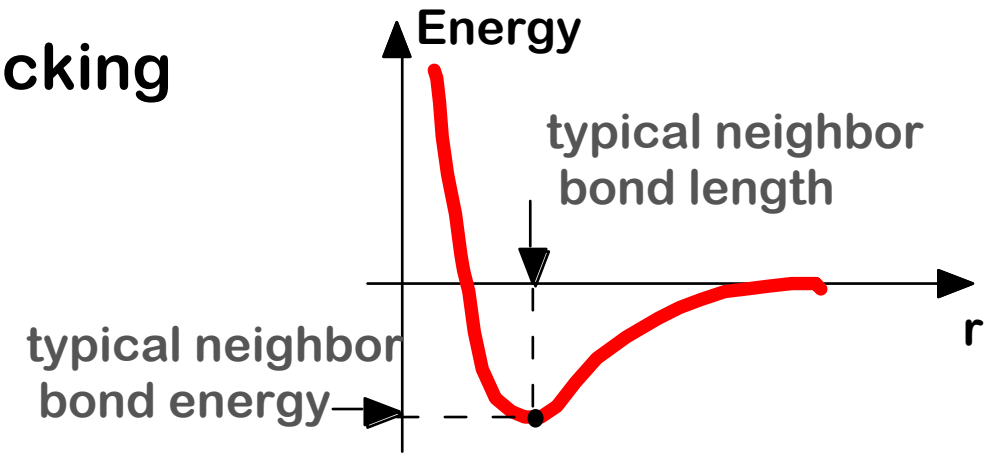
- Non dense, random packing





- Dense, regular packing



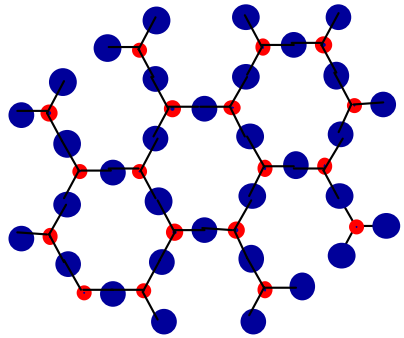


Dense, regular-packed structures tend to have lower energy.

Materials and Packing

Crystalline materials...

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

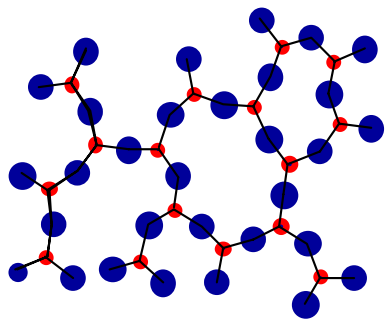


crystalline SiO_2

• Si • Oxygen

Noncrystalline materials...

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



noncrystalline SiO_2

"Amorphous" = Noncrystalline

Metallic Crystals

- **tend to be densely packed.**
- **have several reasons for dense packing:**

  -Typically, only one element is present, so all atomic radii are the same.

  -Metallic bonding is not directional.

  -Nearest neighbor distances tend to be small in order to lower bond energy.

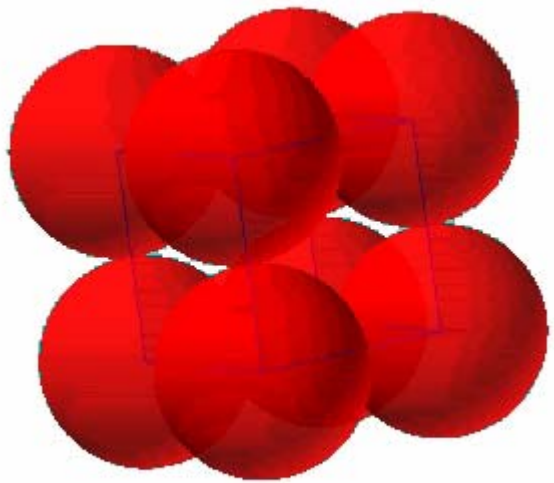
- **have the simplest crystal structures.**

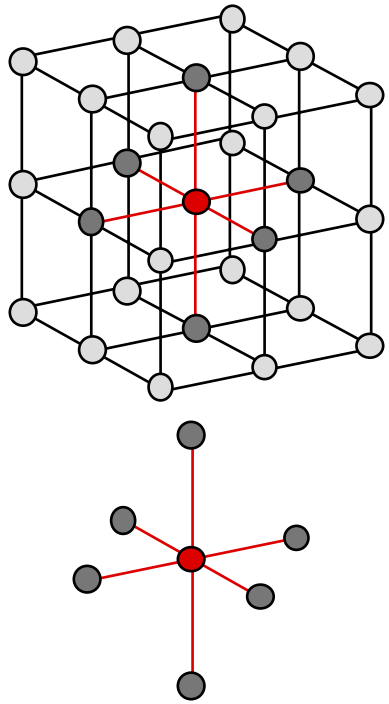
We will look at four such structures…

Simple Cubic Structure (SC)

- **Unit Cell (small repeat entity)**
- **Rare due to poor packing (only Po has this structure)**
- **Close-packed directions are cube edges.**

Coordination # = 6
(# nearest neighbors)



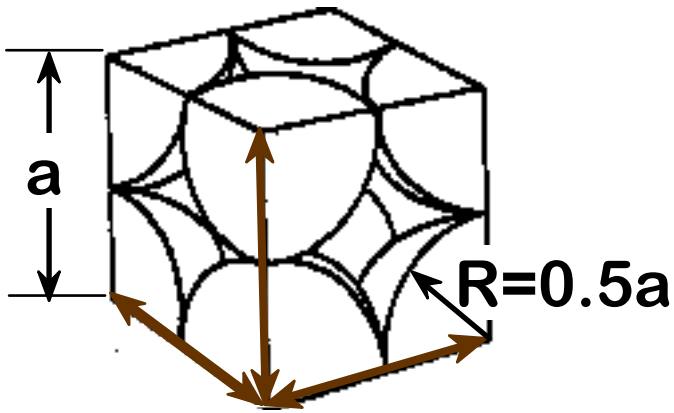


Atomic Packing Factor (APF)

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

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

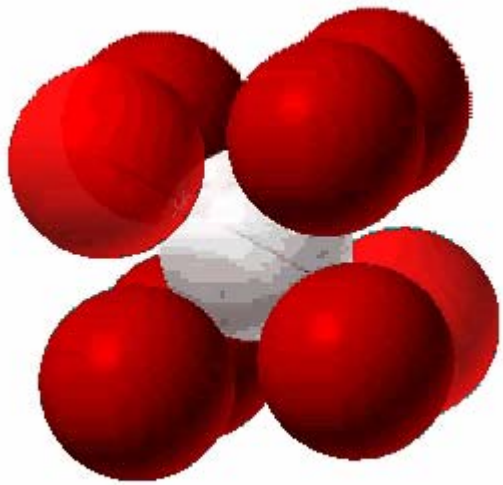
contains 8 x 1/8 =

1 atom/unit cell

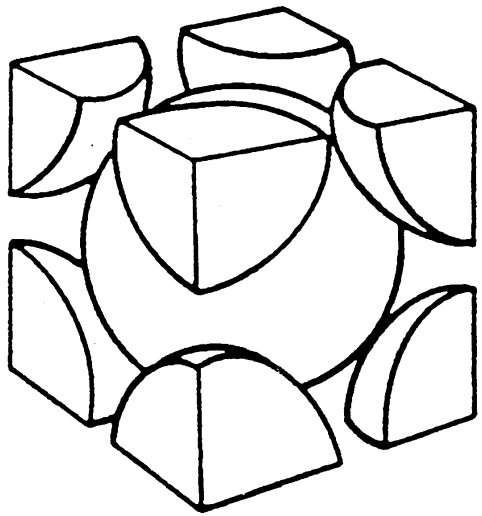
$$APF = \frac{\frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}}}{\frac{\text{volume}}{\text{unit cell}}} = \frac{1 \cdot \frac{4}{3}\pi (0.5a)^3}{a^3}$$

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.

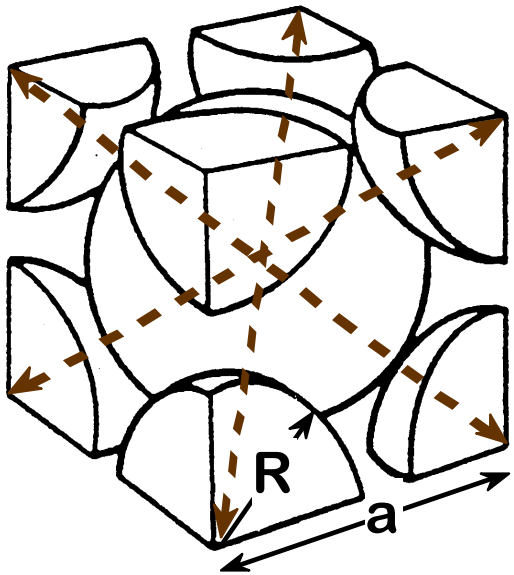


- **Coordination # = 8**



APF of BCC

- **APF for a body-centered cubic structure = 0.68**



Close-packed directions:

length = 4R

$= \sqrt{3}\, a$

Unit cell contains:

1 + 8 x 1/8

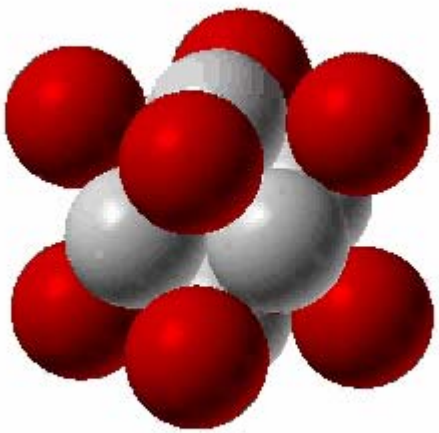
= 2 atoms/unit cell

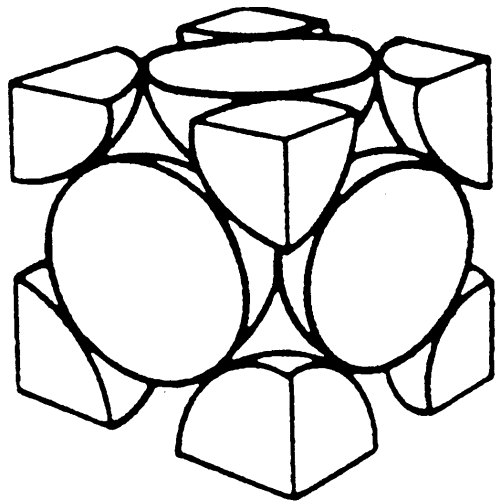
$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{2 \cdot \frac{4}{3}\pi (\sqrt{3}a/4)^3}{a^3}$$

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.

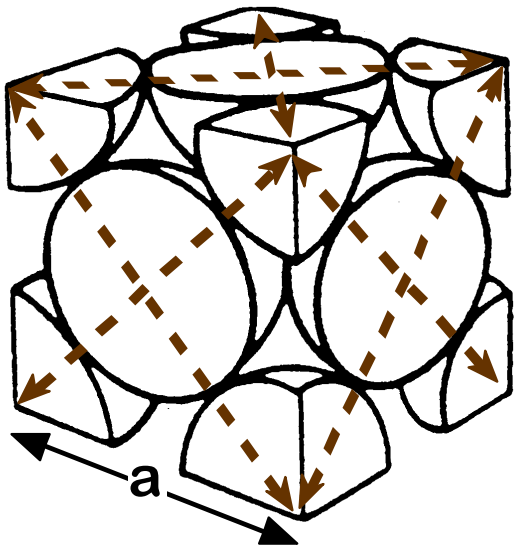
- **Coordination # = 12**





APF of FCC

- **APF for a body-centered cubic structure = 0.74**



Close-packed directions:

length = 4R

$= \sqrt{2}\, a$

Unit cell contains:

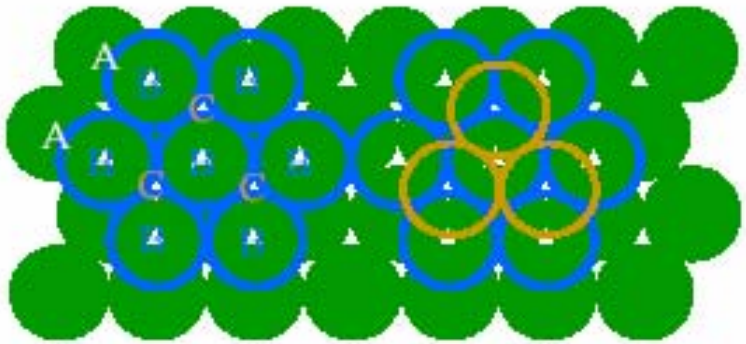
6 x 1/2 + 8 x 1/8

= 4 atoms/unit cell

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

FCC Stacking Sequence

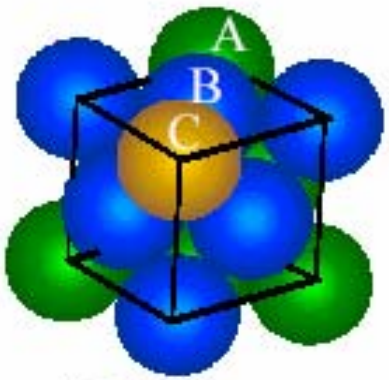
- ABCABC... Stacking Sequence
- 2D Projection



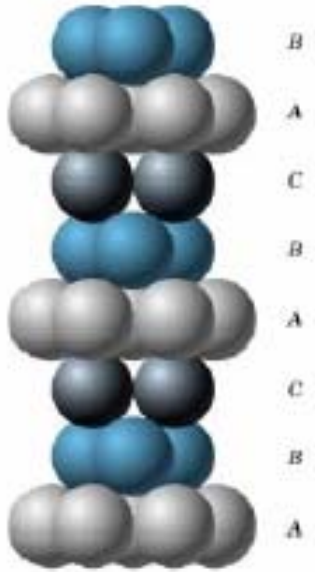
A sites

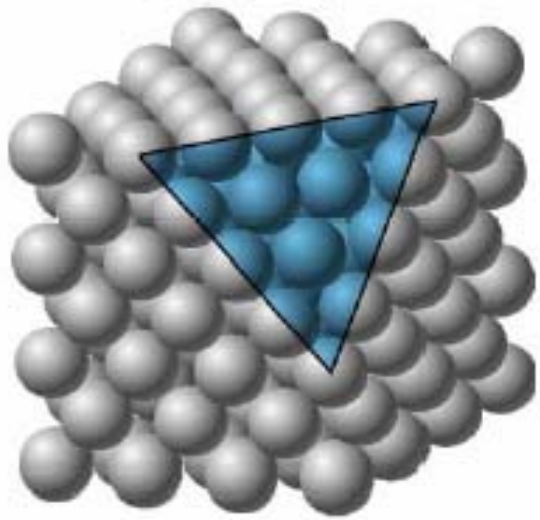
B sites

C sites



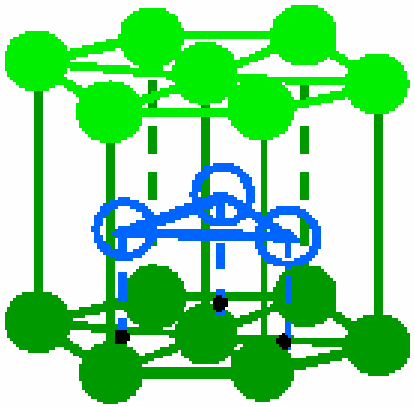
- FCC Unit Cell



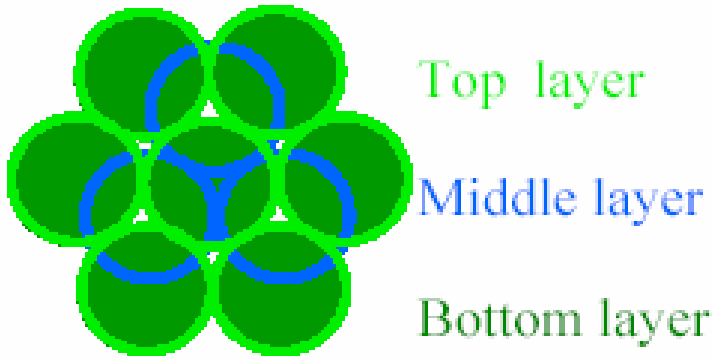


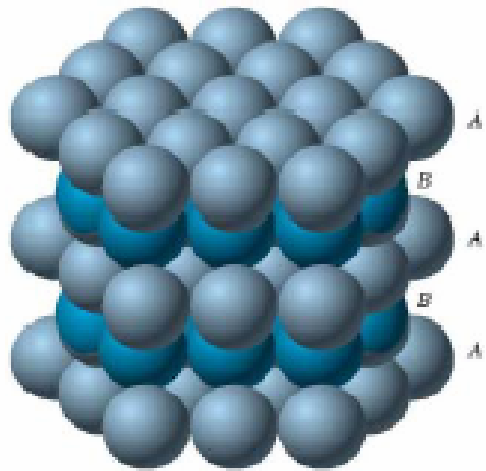
Hexagonal Closed-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection



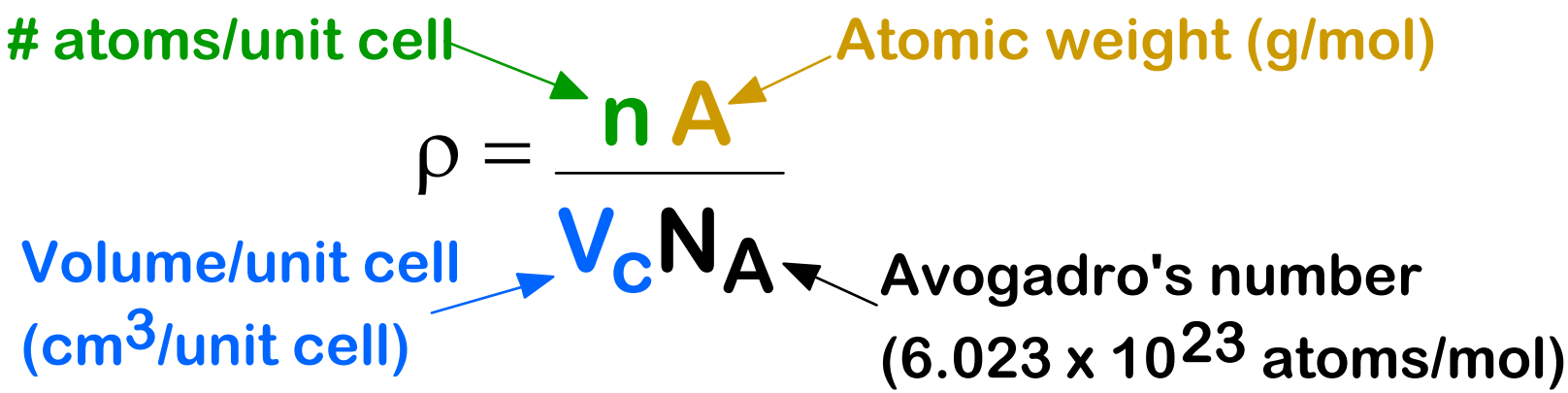
- 2D Projection





- Coordination # = 12
- APF = 0.74

Theoretical Density



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^{-7} cm)

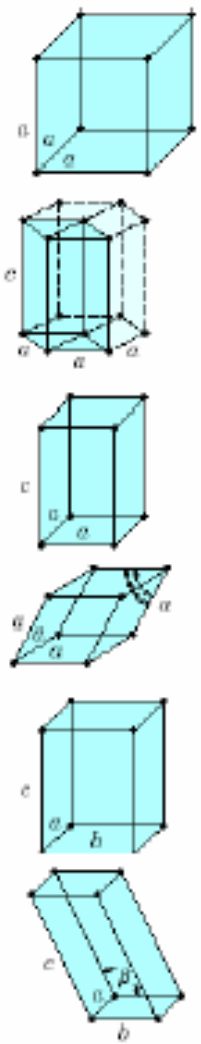
$V_C = a^3$; For FCC, $a = 4R\sqrt{2}$; $V_C = 4.75 \times 10^{-23} cm^3$

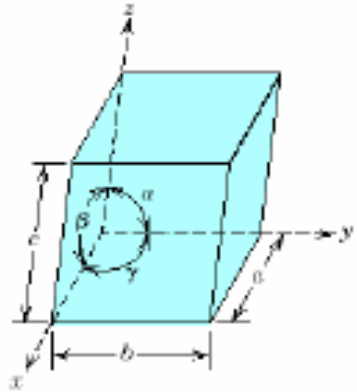
Result: theoretical $\rho_{Cu} = 8.89$ g/cm^3

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

Seven Crystal Systems

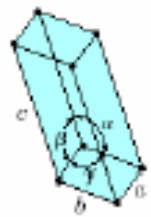
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$





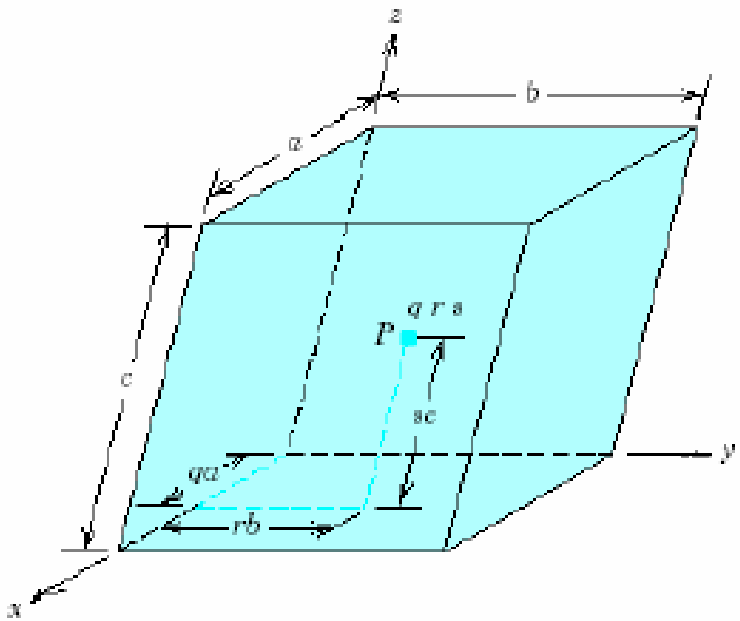
Triclinic

$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$



Crystallographic Points

- Be specified in terms of its coordinates
- Fractional multiples of the unit cell edge length



Crystallographic Directions

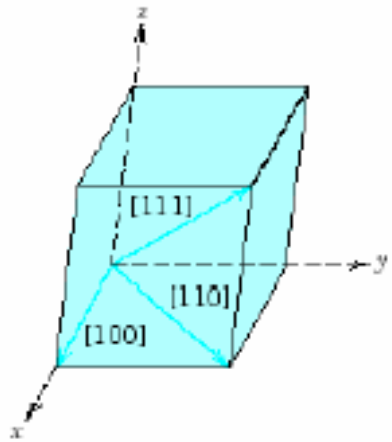
Steps to determine the direction

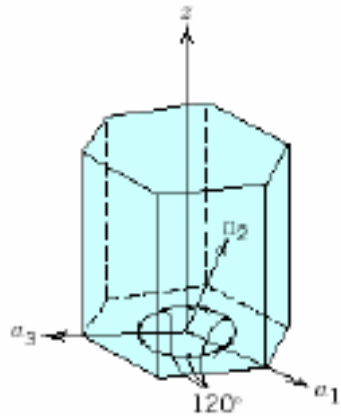
- Let the vector pass origin
- Project to the axes
- Reduce the number to the smallest integer values
- Enclose in Square Brackets
- Use upper bar for negative value

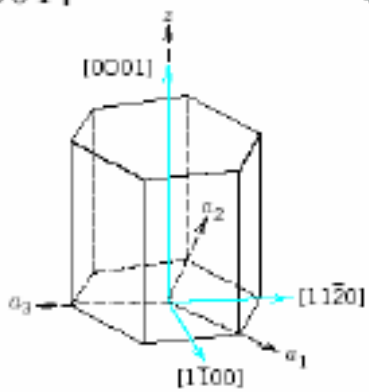
Direction family: use Angle Brackets

<100>: [100], [$\bar{1}$00], [010], [0$\bar{1}$0], [001], [00$\bar{1}$]

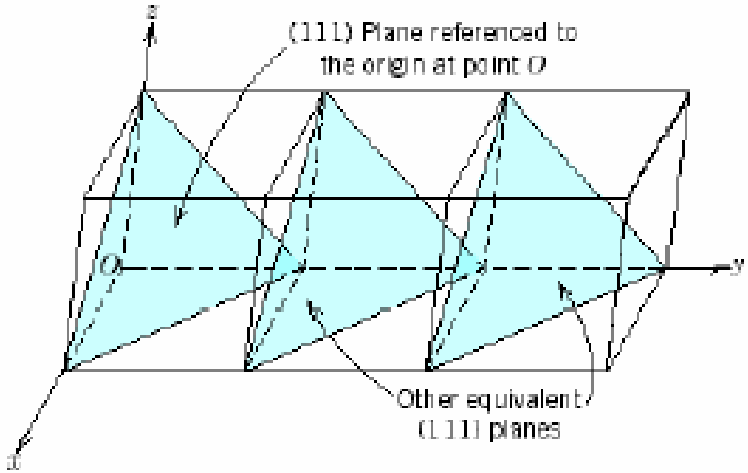
Four-axis system for hexagonal crystal







Crystallographic Planes



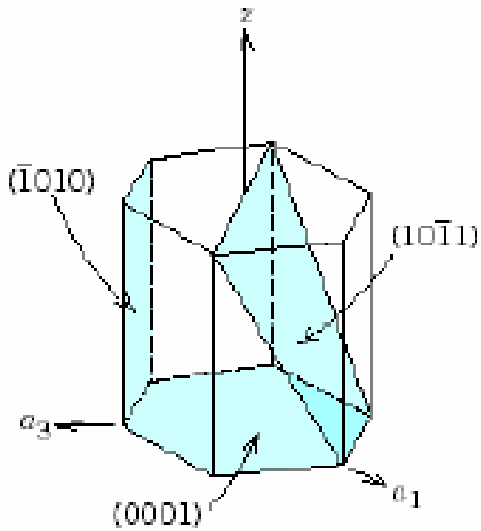
Steps to determine the plane

- Choose right origin
- Intercept to the axes
- Take reciprocals
- Reduce the number to the smallest integer values
- Enclose in Parentheses
- Use upper bar for negative value

Plane family: use Braces

$\{111\}$: $(\bar{1}11)$, $(1\bar{1}1)$, $(11\bar{1})$, (111)……

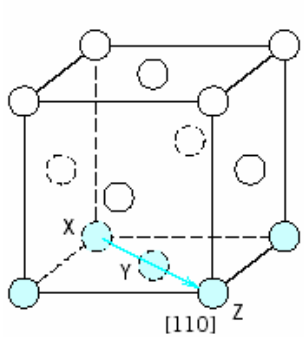
Four-axis system for hexagonal crystal

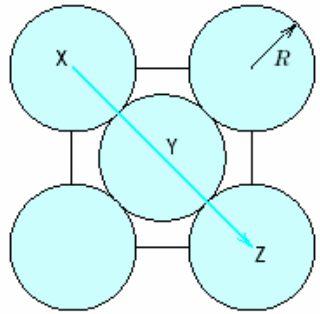


Linear and Planar Densities

- **Linear Density**

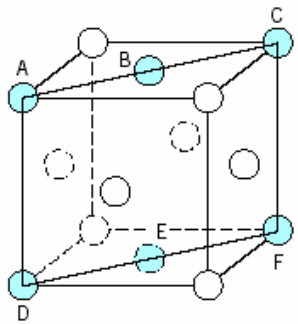
$$LD = \frac{\text{number of atoms centered on direction vector}}{\text{length of direction vector}}$$

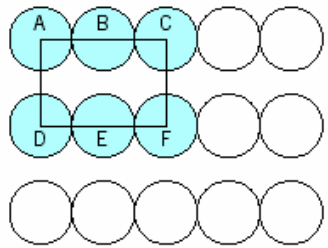


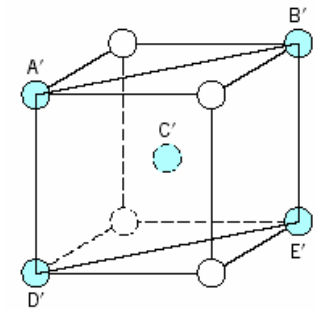


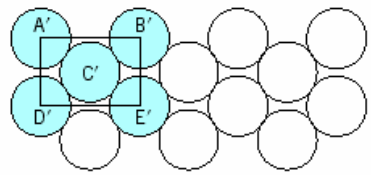
- **Planar Density**

$$PD = \frac{\text{number of atoms centered on a plane}}{\text{area of plane}}$$





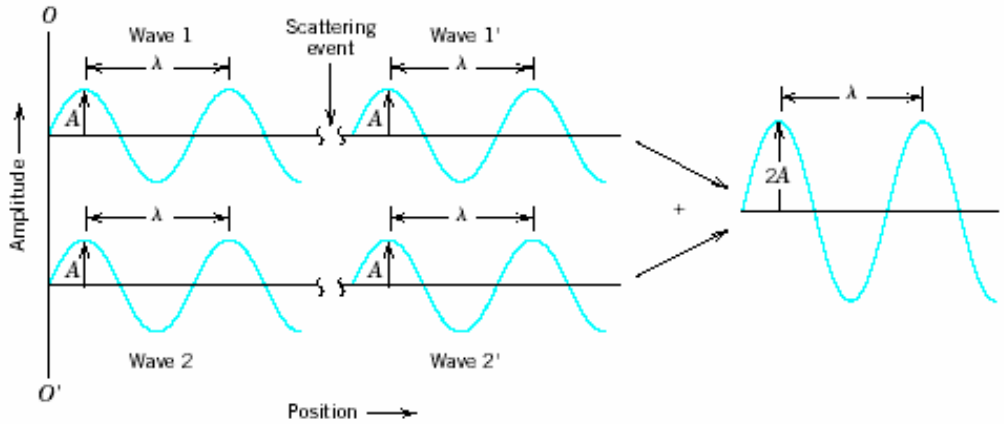




X-ray Diffraction

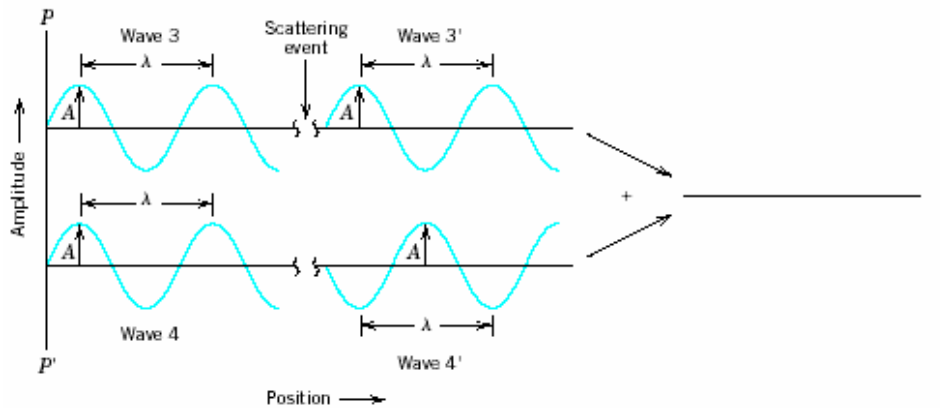
Diffraction Phenomenon

- A series regularly spaced obstacles
- Spacing ~ wavelength



- Constructive interference
  Path length difference ~ n λ

- Destructive interference
  Path length difference ~ n/2 λ



Bragg's Law

Constructive interference:

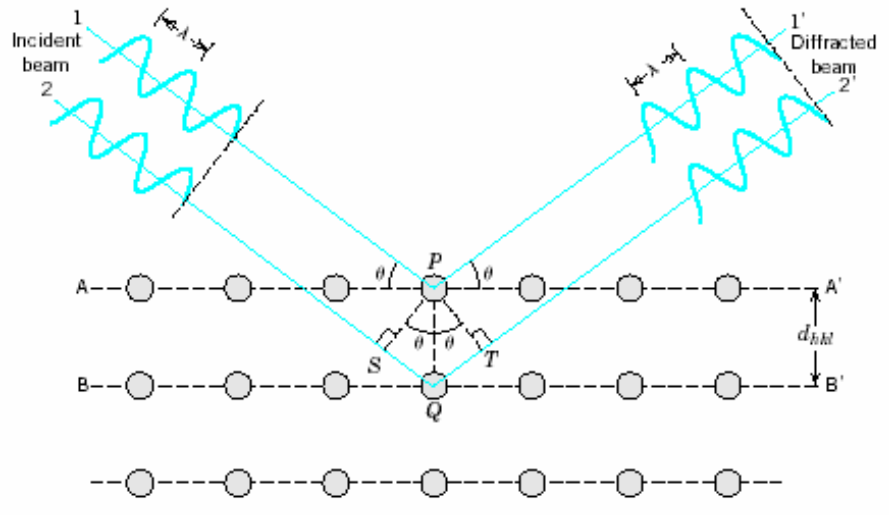
$$n\lambda = \overline{SQ} + \overline{QT}$$

$$n\lambda = d_{hkl}\sin\theta + d_{hkl}\sin\theta$$

$$= 2d_{hkl}\sin\theta$$

For cubic system:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$



Diffractometer

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