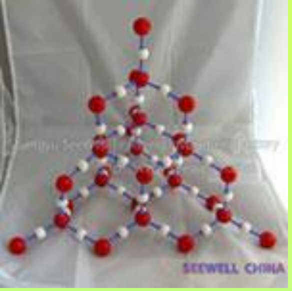
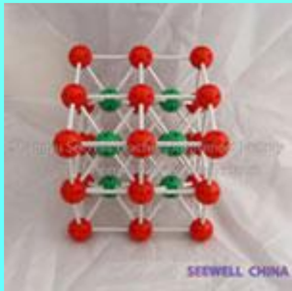


CHAPTER 3: CRYSTAL STRUCTURES & PROPERTIES

ISSUES TO ADDRESS...

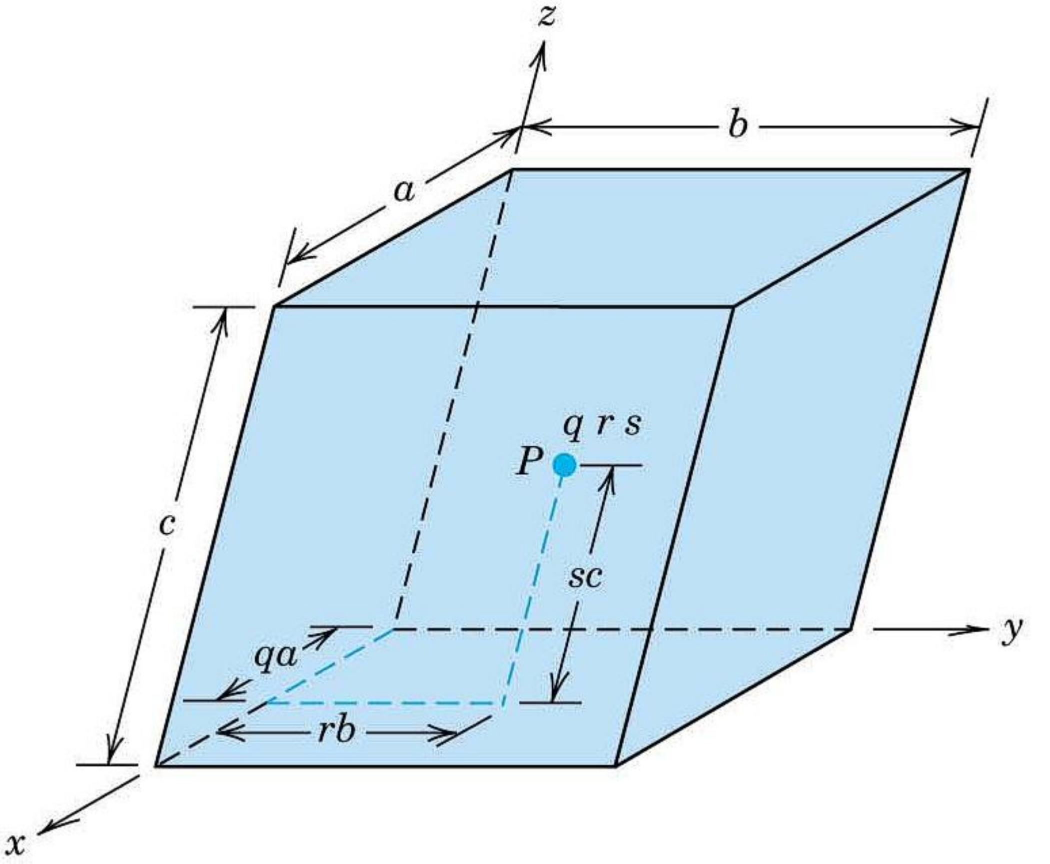
- How do atoms assemble into solid structures?
- How does the density of a material depend on its structure?
- When do material properties vary with the sample orientation?



Crystallographic Points, Directions and Planes

- As it will be shown in next Chapters (e.g. Chapter 4 and 6) the materials properties can vary in different sample directions. Thus it is important to specify a particular point within a unit cell, a crystallographic directions and crystallographic planes of atoms.

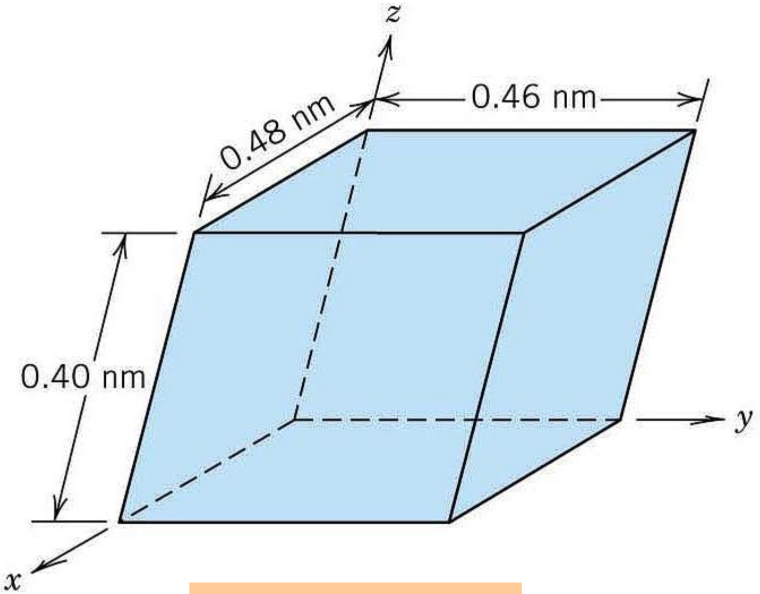
Point Coordinates

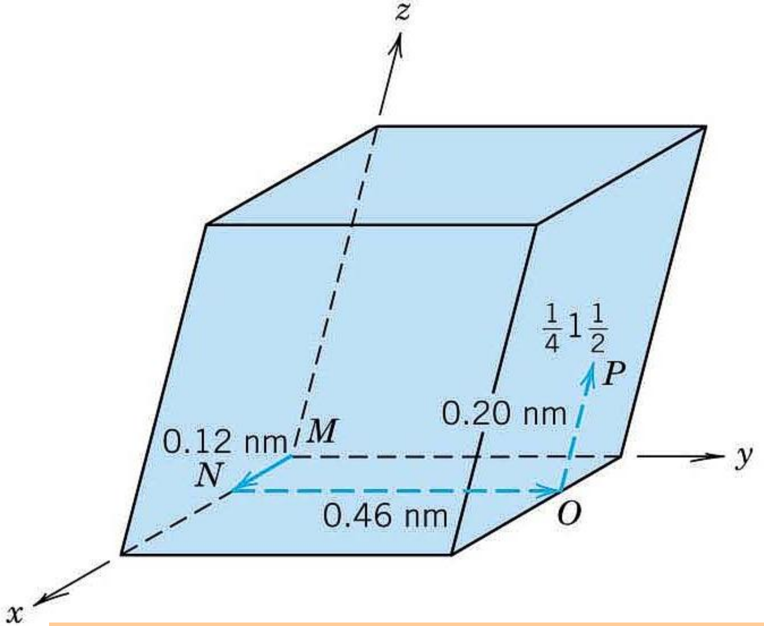


The position of any point (e.g. P) within the unit cell can be defined in terms of **generalized coordinates** (e.g. q, r, s) which are ***fractional multiples*** of the unit cell **edge length** (a, b, c respectively): **q r s**

Point Coordinates

Problem: Locate the point with coordinates ¼,1, ½



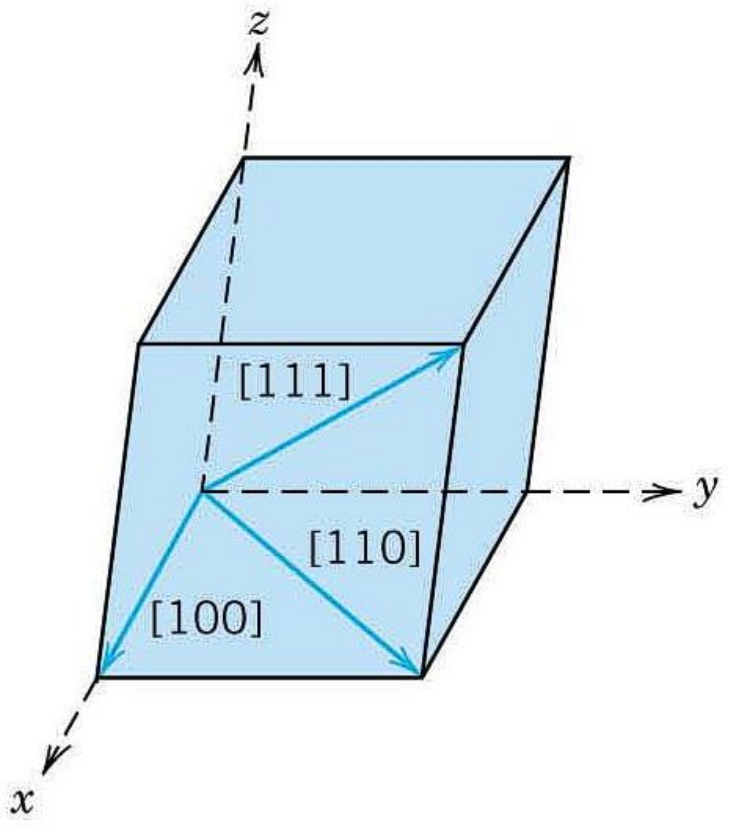


a =0.48 nm
b =0.46 nm
c =0.40nm

P: q r s = P: ¼ 1 ½
q_a = ¼ 0.48 nm = 0.12 nm
r_b =0.46 nm
s_c = ½ 0.40nm = 0.20 nm

Crystallographic Directions

is a **vector** connecting the coordinate origin and a specific point of a unit cell. In crystallography such vector is defined by **three directional indices** [**u ν w**]



Rules for indexes determination:

1. A vector of desired length is positioned that it pass through the origin of the coordinate system. ***Translate it through a crystal lattice if needed!!***

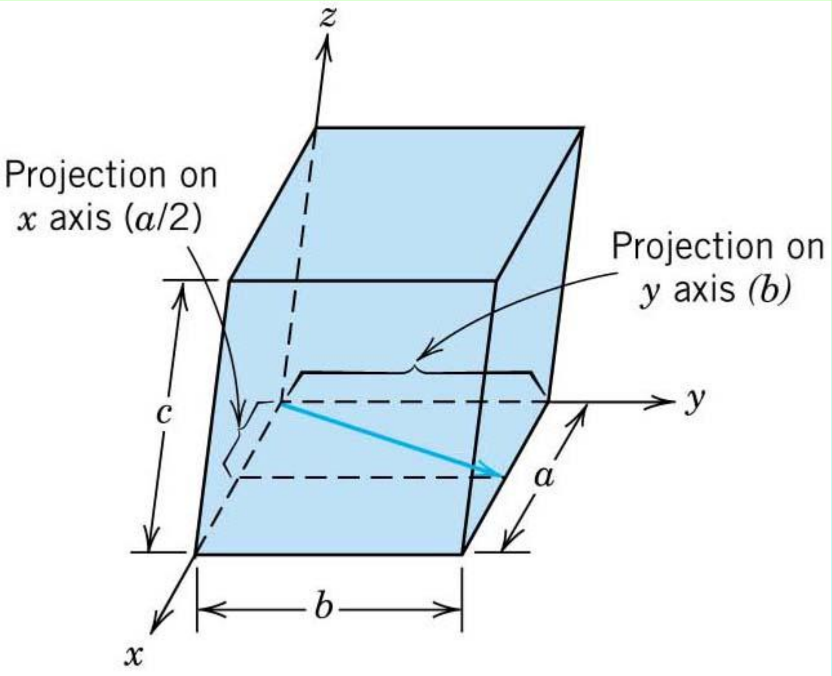
2. The length of the vector projection on each axis are determined again ***in terms of unit cell dimensions*** (a, b, c)

3. Obtained three numbers are multiplied or divided by a common factor to reduce them to **integer values (e.g. u ν** and **w**)

4. Notation **[u ν w]** defines the desired crystallographic direction

Crystallographic Directions

Problem: Determine the indices for the shown direction



Solution:

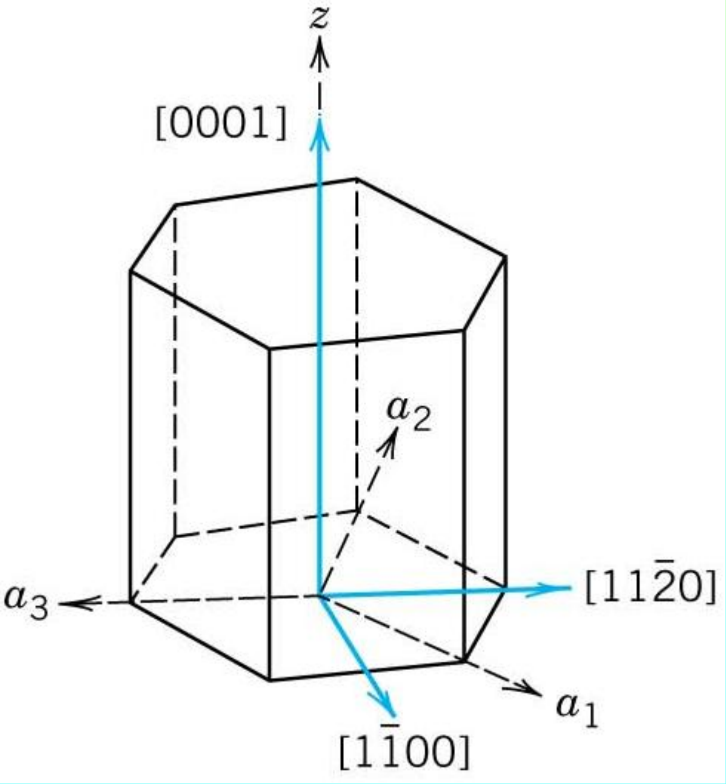
- The vector passes the coordinate origin thus no translation is required
- The length of the vector projection on the axis x, y and z respectable: a/2, b, 0c
- Common factor which reduces these indices to integer number is 2.

The multiplication yields 1,2 and 0.

- Thus the crystallographic directions indices are: **[120]**

Crystallographic Directions: *Hexagonal Crystals*

It is convenient to use a **four- axis** (Miller-Bravais) coordinate system: **a_1,a_2,a_3** axes lay in one **basal** plain and located at 120° to each other, while the **z** axis is perpendicular to the basal plane.



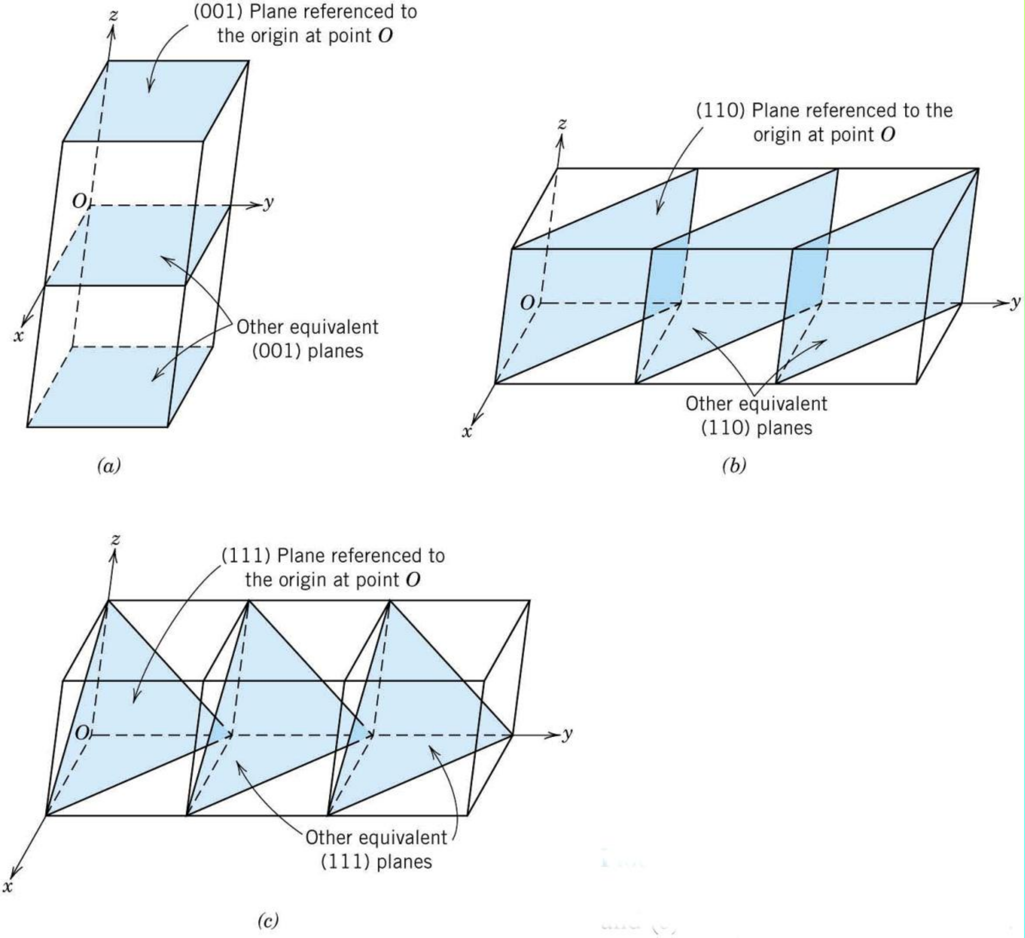
Same rules determine in this case four indices **[u ν t w]**:
by convention the first three pertain to projections in **a1, a2, a3** axes

$[\mathbf{u^{`}}\ \mathbf{\nu^{`}}\ \mathbf{w^{`}}] \rightarrow \mathbf{[u\ \nu\ t\ w]}$ conversion:

$$u = n/3 \cdot (2u^{`} - \nu^{`})$$
$$\nu = n/3 \cdot (2\nu^{`} - u^{`})$$
$$t = -(u + \nu)$$
$$w = n\, w^{`}$$

where **n** is a factor required to reduce indices to integer numbers

Crystallographic Planes



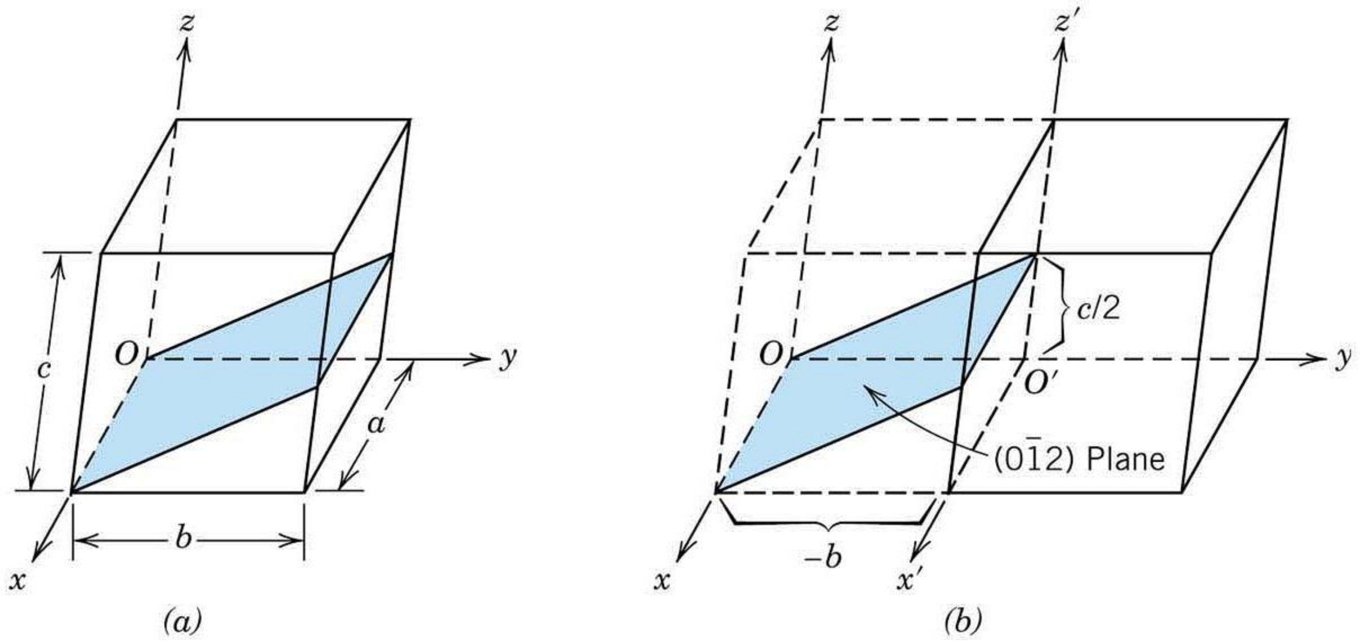
Crystallographic planes are typically specified by **three Miller** indices **(hkl)**

<u>**Rules** for indexes determination:</u>

1. If the plane passes through the origin, or another plane must be constructed by appropriate parallel translation or new origin must be selected at the corner of the another unit cell.
2. After such operation, the plane either intersects or // to the axes and the length of The planar intercept each axes is determined in *term of lattice parameters* **a, b** and **c**.
3. The **reciprocal** of these number are taken
4. If necessary these numbers are reduced to the set of **smallest integers (e.g. h,k,l)**
5. These integers in parentheses **(hkl)** represent the crystallographic plane

Crystallographic Planes

Problem: Determine the Miller indices for the plane



Solution:

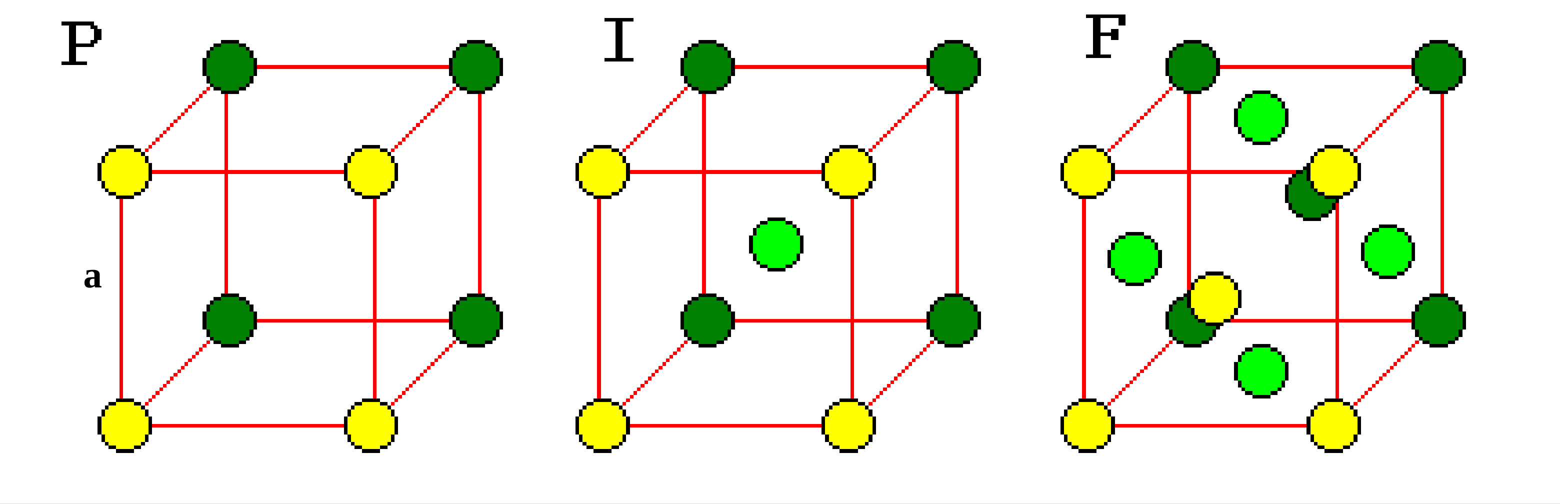
1. Since the plane passes through the existing origin the **new origin must be selected** at the corner of adjust unit cell.
2. As related to new origin the following **intercepts** (in *terms of lattice parameters a, b, and c*) with x, y, z axes can be referred: ∞ (plane is // to x-axis), -1, 1/2
3. The r**eciprocal** of these numbers are: 0, -1 and 2 and they **are already integer**!
4. Thus the Miller indices of the consider plane are: (0-12)

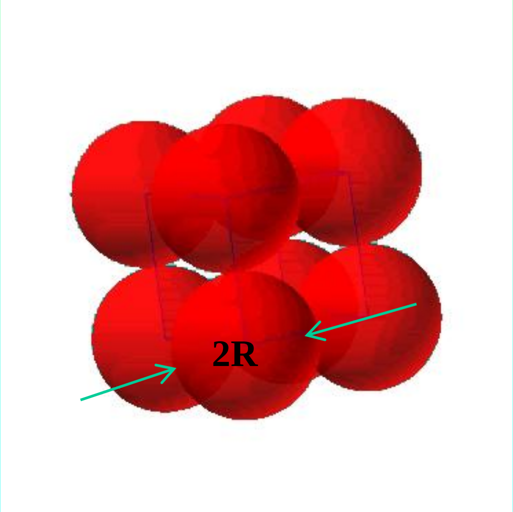
Metallic Crystals

- 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.

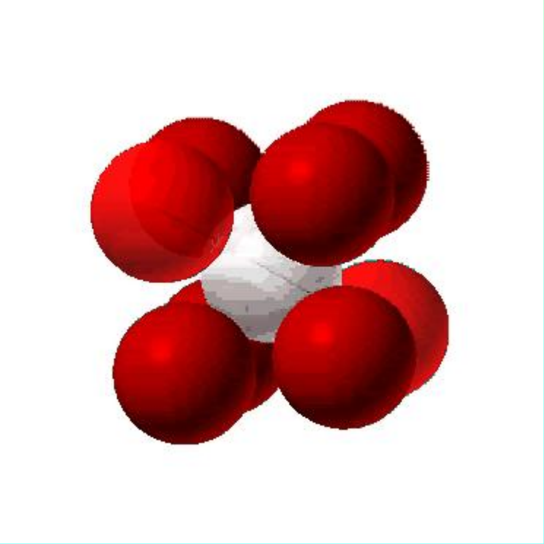
We will look at three such structures...

Cubic Unit Cells

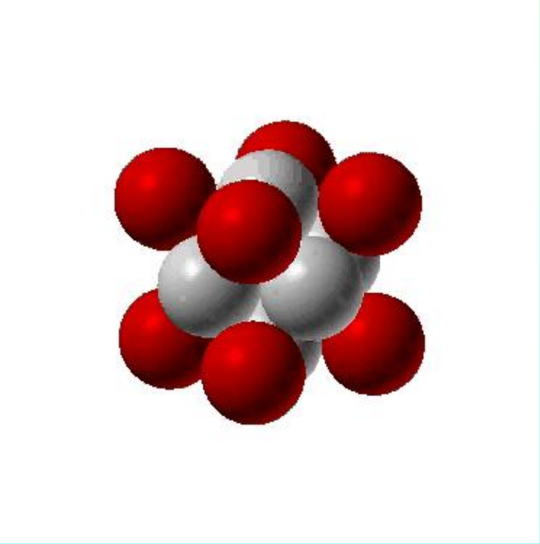




SIMPLE CUBIC STRUCTURE (SC)



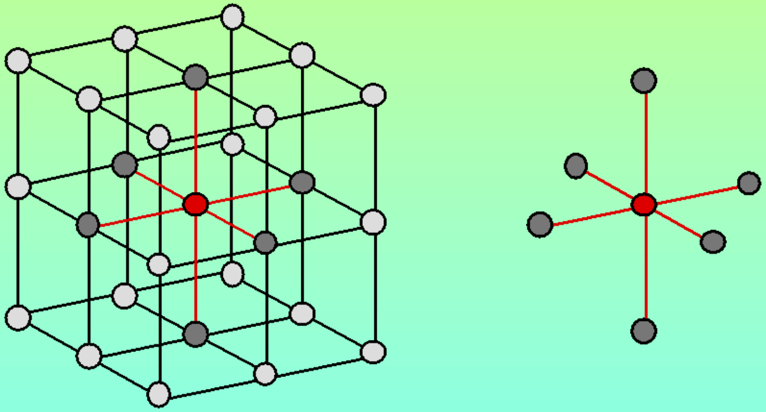
BODY CENTERED CUBIC STRUCTURE (BCC)

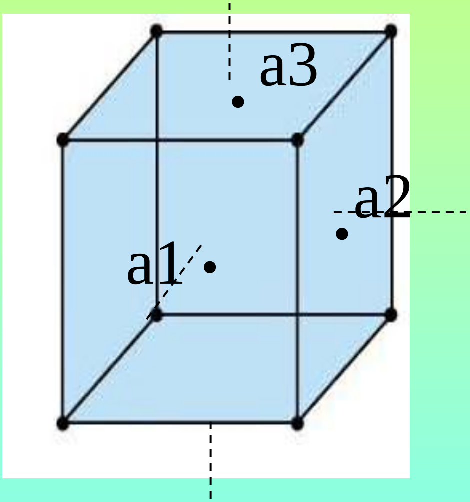


FACE CENTERED CUBIC STRUCTURE (FCC)

Simple Cubic (SC) Structure

- **Coordination number** is the number of nearest neighbors
- **Linear density** (LD) is the number of atoms per unit length along a specific crystallographic direction





Coordination number = 6

$LD_{110} = 1 \text{ atoms}/2\sqrt{2}\,R$

$\mathbf{LD_{100} = 1 \text{ atoms}/2R}$

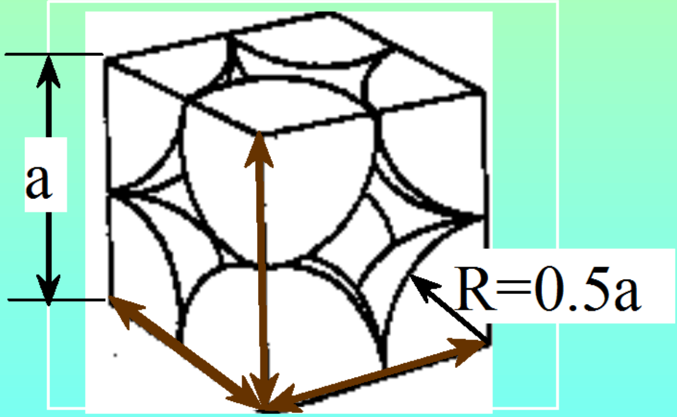
- Rare due to poor packing (only Po [84] has this structure)
- Close-packed directions are cube edges.

Atomic Packing Factor (APF)

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

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

contains 8 x 1/8 =

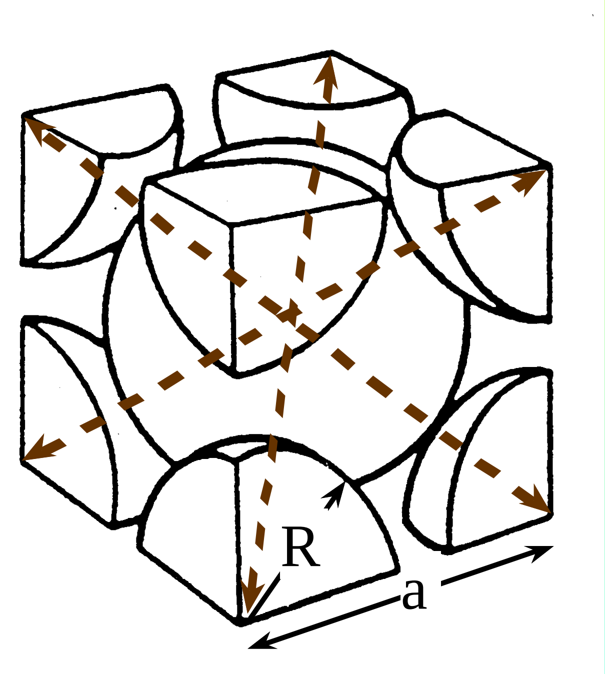
1 atom/unit cell

$$\frac{\text{atoms}}{\text{unit cell}} \qquad \frac{\text{volume}}{\text{atom}}$$

$$\mathrm{APF} = \frac{1 \quad \frac{4}{3}\pi\,(0.5a)^3}{a^3}$$

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

Body Centered Cubic (BCC) Structure



- **Coordination number** = 8
- **Close packed directions** are cube diagonals:

LD_{110}= 1 atom/(4R√(2/3))=1/(2R√8/3)

LD_{001} = 1 atom/(4R/√3))= 1/(2R √4/3)

LD_{111} = 2 atoms/4R = 1/(2R)

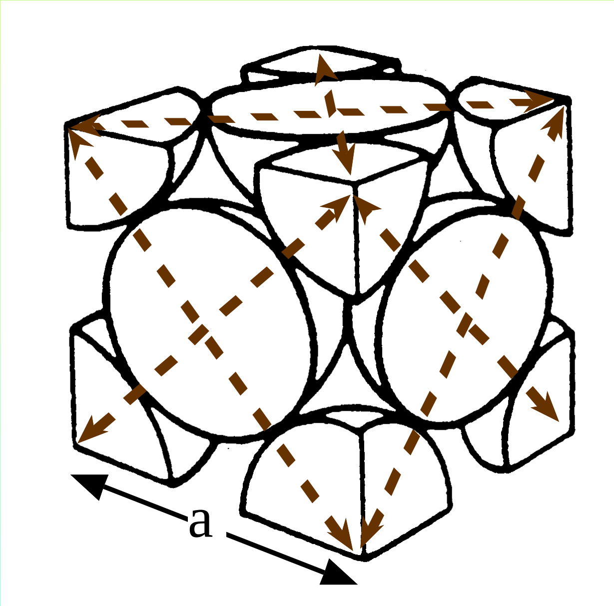
- **Unit cell contains:**

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

- **APF** = 0.68:

$$\mathrm{APF} = \frac{\underset{\uparrow\ \frac{\text{atoms}}{\text{unit cell}}}{2}\ \ \underset{\uparrow\ \frac{\text{volume}}{\text{atom}}}{\frac{4}{3}\pi\left(\sqrt{3}\,a/4\right)^3}}{\underset{\uparrow\ \frac{\text{volume}}{\text{unit cell}}}{a^3}}$$

Face-Centered Cubic (FCC) Structure



- **Coordination number** = 12
- **Close packed directions** are face diagonals:

LD_{110}= 2 atom/(4R)= 1/2R

LD_{001} = 1 atom/(2R√2))= 1/(2R √2)

LD_{111} = 1 atoms/4R = 1/(2R √6)

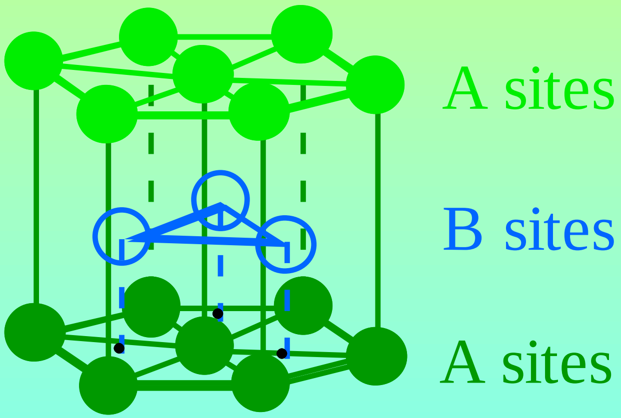
- **Unit cell contains**:
  6 x 1/2 + 8 x 1/8 = **4** atoms/unit cell

- **APF = 0.74**

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

Hexagonal Close-Packed (HCP) Structure

- ABAB... Stacking Sequence
- 3D Projection
- 2D Projection

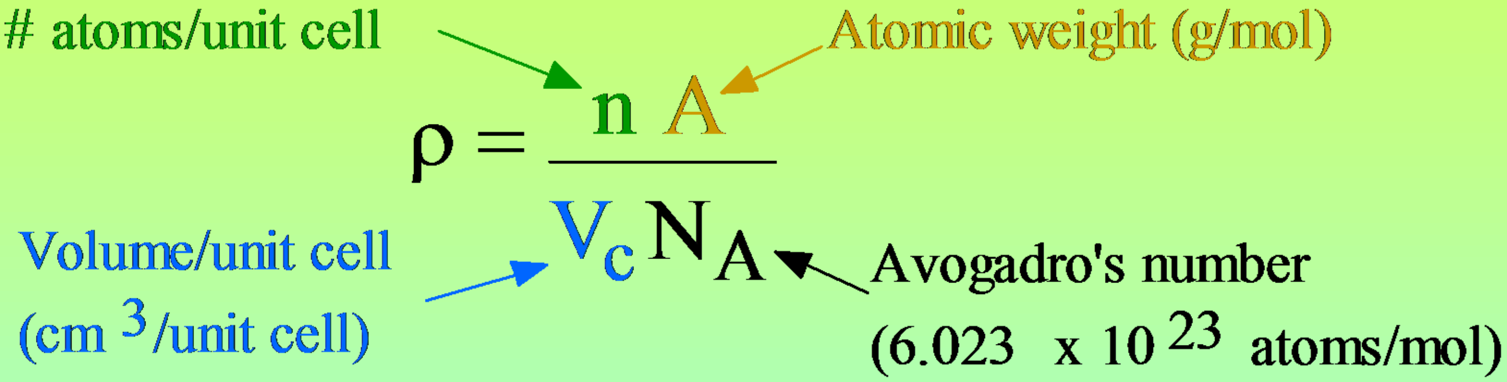


- Coordination number = ?
- APF = ?

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	------	**------**	------

Theoretical Density, ρ



atoms/unit cell

Atomic weight (g/mol)

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

Volume/unit cell

(cm ^{3}/unit cell)

Avogadro's number

(6.023 x 10^{23} atoms/mol)

Example: Copper

- crystal structure **FCC**
- # atoms/unit cell **= 4**
- atomic weight = **63.55 g/mol**
- atomic radius R = **0.128 nm**
- for FCC **a = 2R√2**; V_c=a^3; V_c=4.75 10^{-23} $^{-7}$ cm^3

Result: theoretical ρ_{Cu} = 8.89 g/cm ^{3}

Compare to actual: ρ_{Cu} = 8.94 g/cm ^{3}

Densities of Materials Classes

$\rho_{\text{metal}} > \rho_{\text{ceramics}} > \rho_{\text{polymers}}$

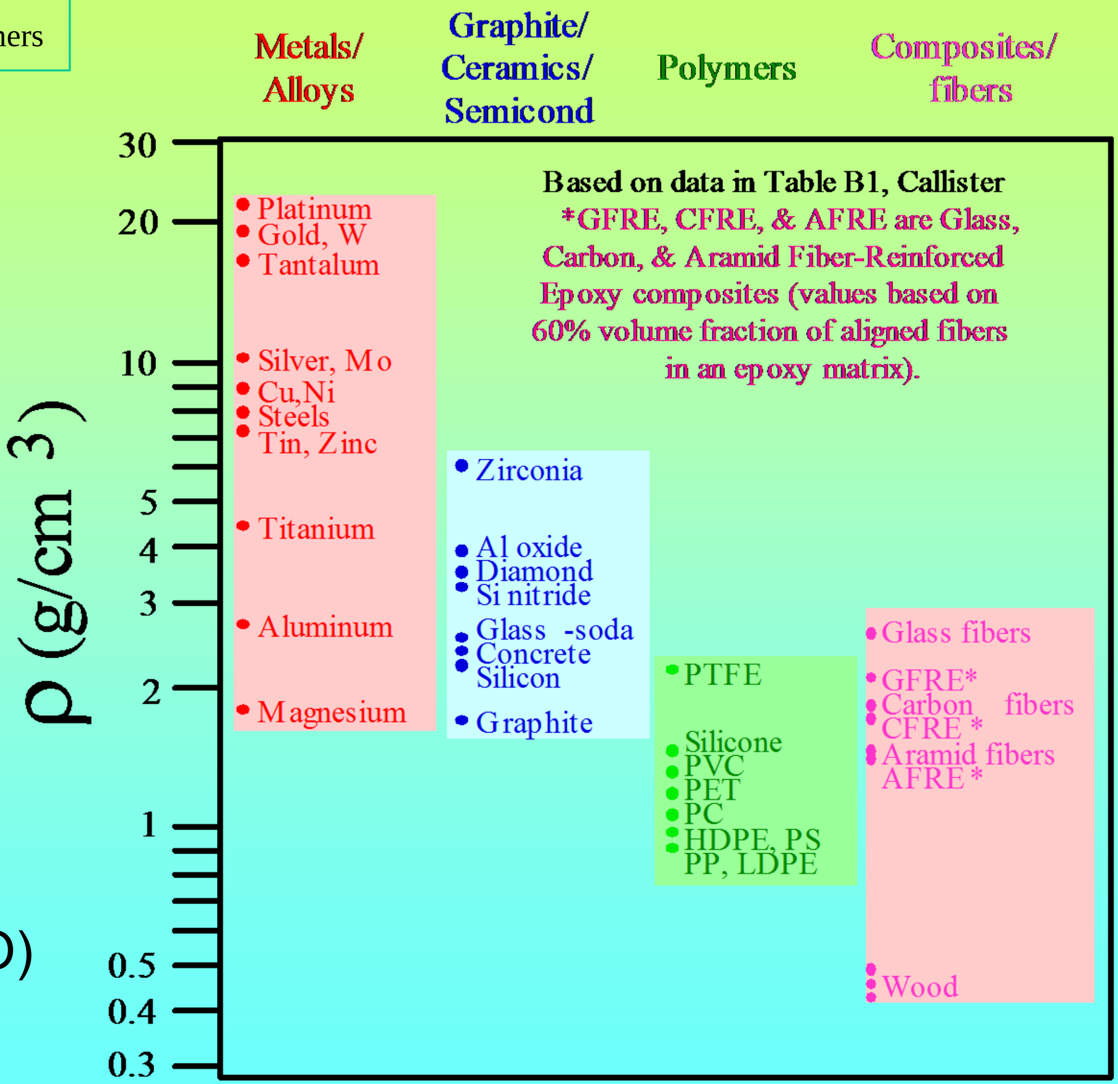
Why?

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)

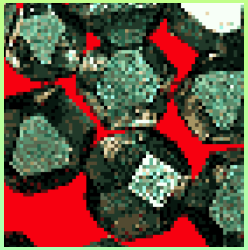
Composites have...
- intermediate values


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).

CRYSTALS AS BUILDING BLOCKS

- *Some* engineering applications require single crystals:



diamond single crystals for abrasives

turbine blades

- Crystal properties reveal features of atomic structure.

Ex: Certain crystal planes in quartz fracture more easily than others.

POLYCRYSTALS

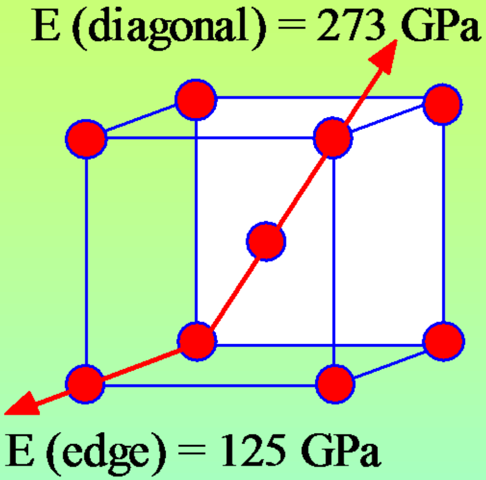
- *Most* engineering materials are polycrystals.

- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- If crystals are randomly oriented,

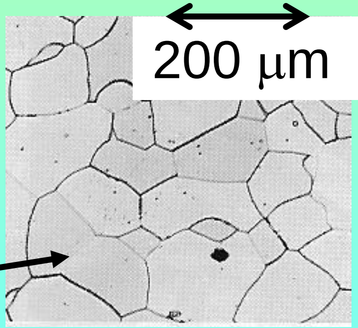
  overall component properties are not directional.
- Crystal sizes typ. range from 1 nm to 2 cm

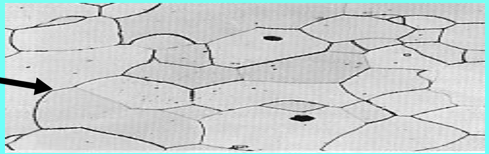
  (i.e., from a few to millions of atomic layers).

SINGLE VS POLYCRYSTALS



- Single Crystals
  - -Properties vary with direction: anisotropic.
  - -Example: the modulus of elasticity (E) in BCC iron:



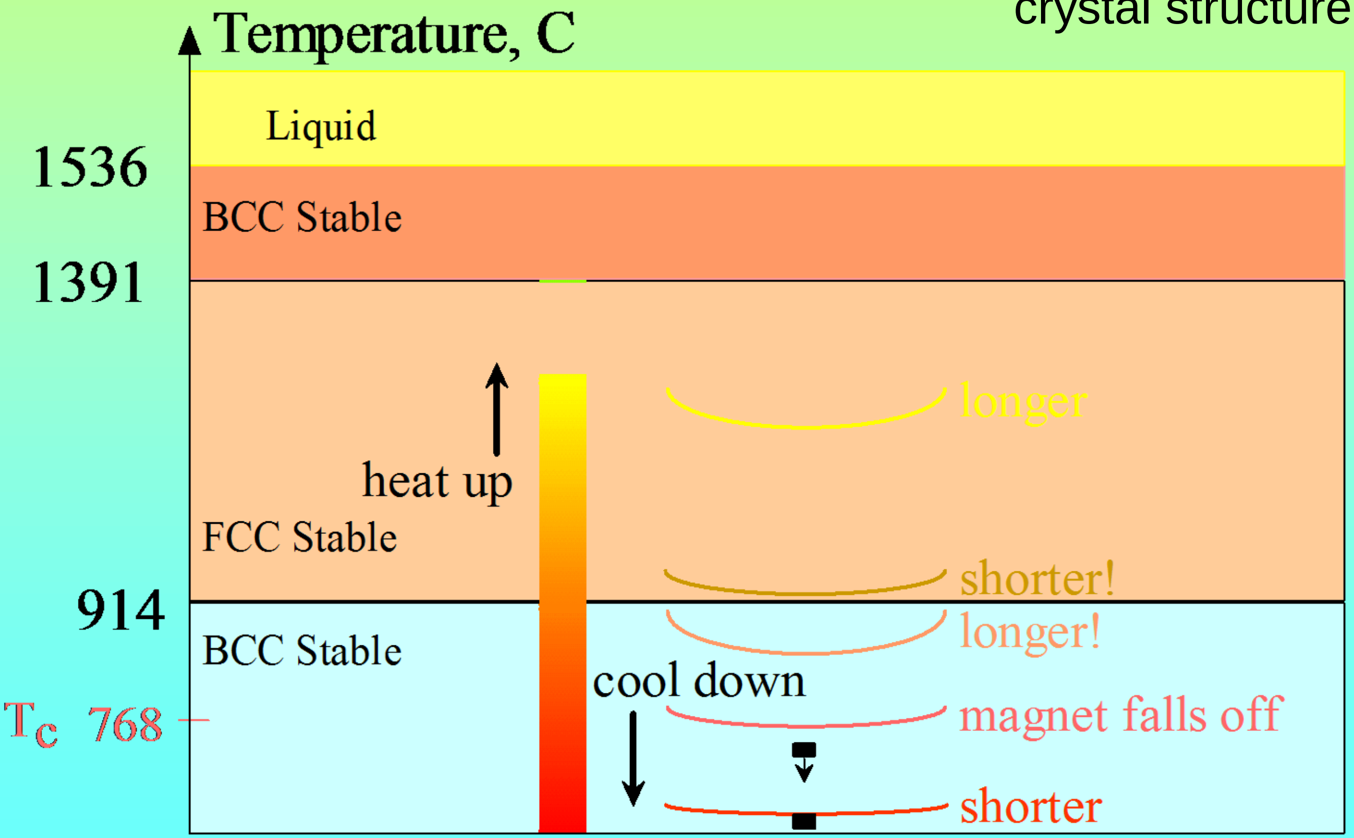


- Polycrystals
  - -Properties may/may not vary with direction.
  - -If grains are randomly oriented: isotropic. ($E_{\text{poly iron}}$ = 210 GPa)
  - -If grains are textured, anisotropic.

DEMO: HEATING AND COOLING OF AN IRON WIRE

- Demonstrates "polymorphism"

← The same atoms can have more than one crystal structure.



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).
- Material properties generally vary with single crystal orientation (i.e., they are anisotropic), but properties are generally non-directional (i.e., they are isotropic) in polycrystals with randomly oriented grains.