

HW#2 due February 20th

- **Unit cell volume and density of tungsten**
- **Atoms / volume in gold**
- **Crystallographic directions**
- **Crystallographic planes**
- **Atomic radius of palladium**
- **BCC-FCC transition in iron**



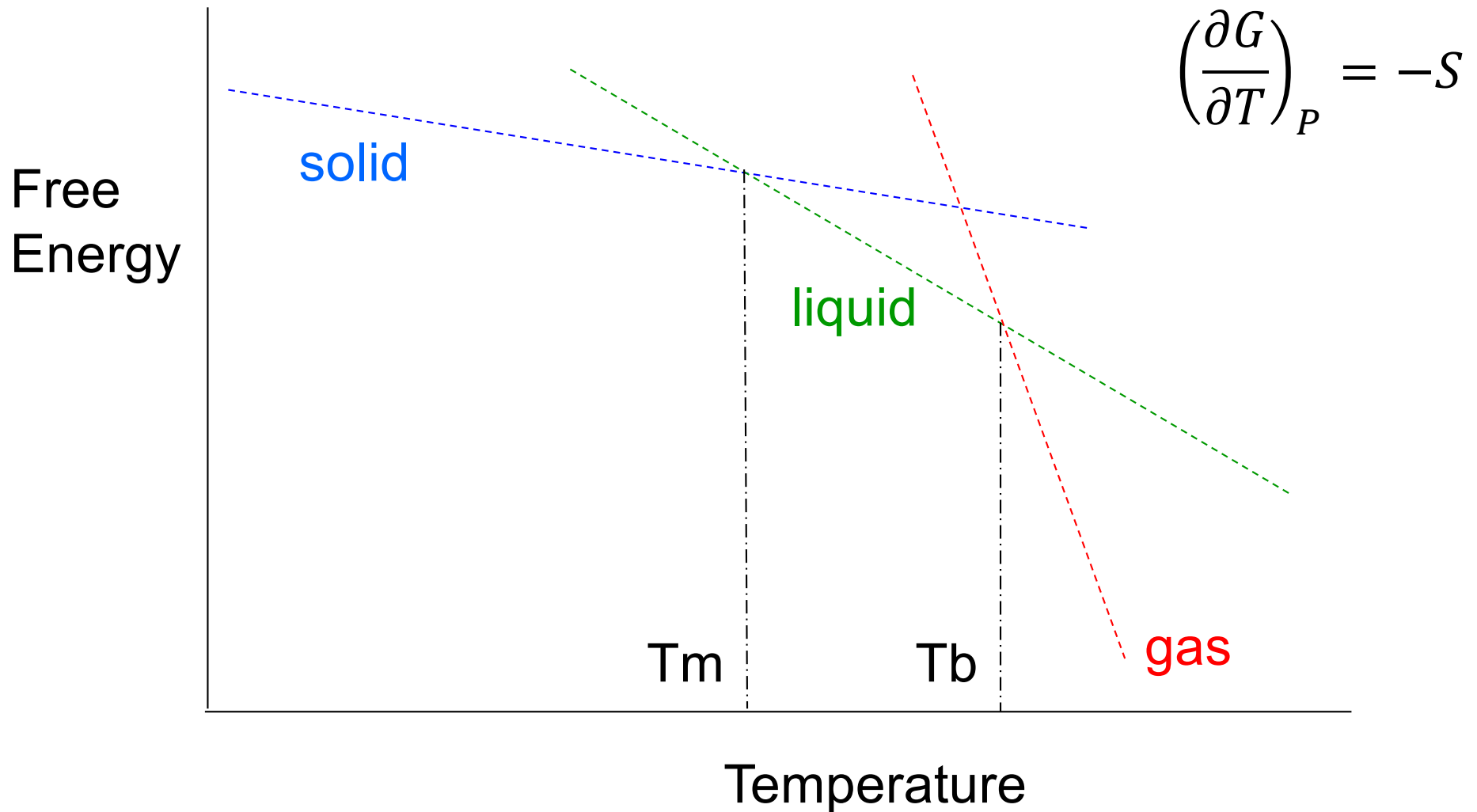
The Structure of Crystalline Solids

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 (i.e., part) orientation?



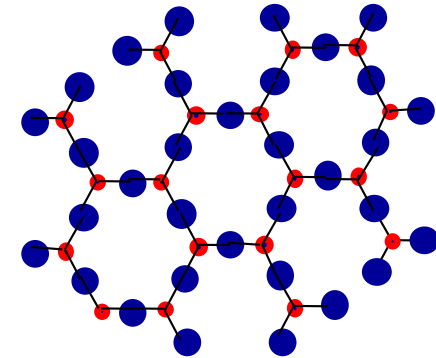
Energy vs. Temperature



Materials and Packing

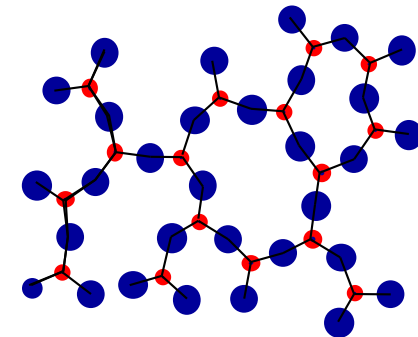
Crystalline materials...

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



crystalline SiO₂

• **Si** • **Oxygen**



noncrystalline SiO₂

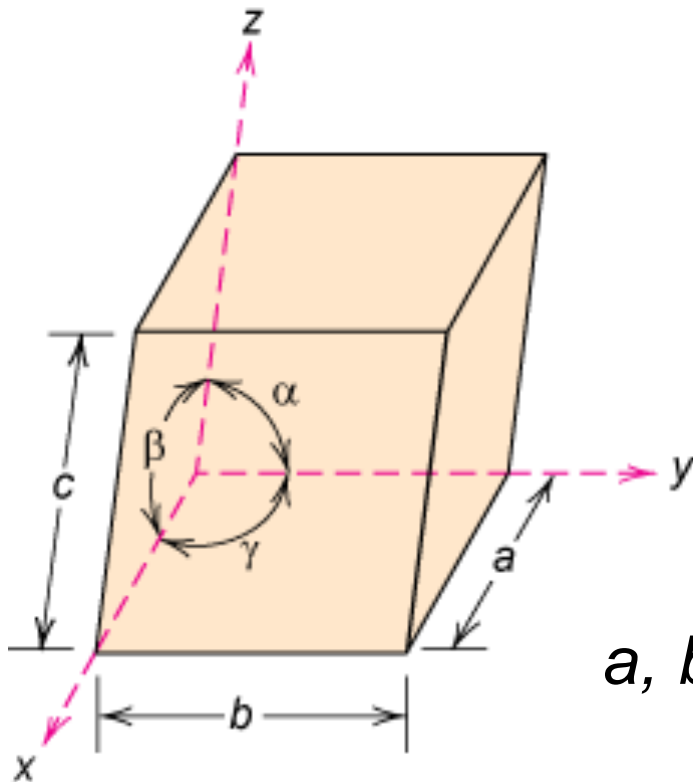
Noncrystalline materials...

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

"Amorphous" = Noncrystalline

Crystal Systems

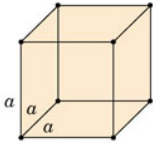
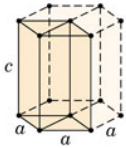
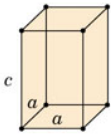
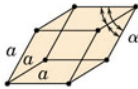
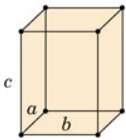
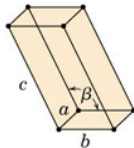
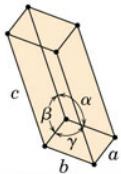
Unit cell: smallest repetitive volume which contains the complete lattice pattern of a crystal



7 crystal systems

14 crystal lattices

a , b , and c are the lattice constants

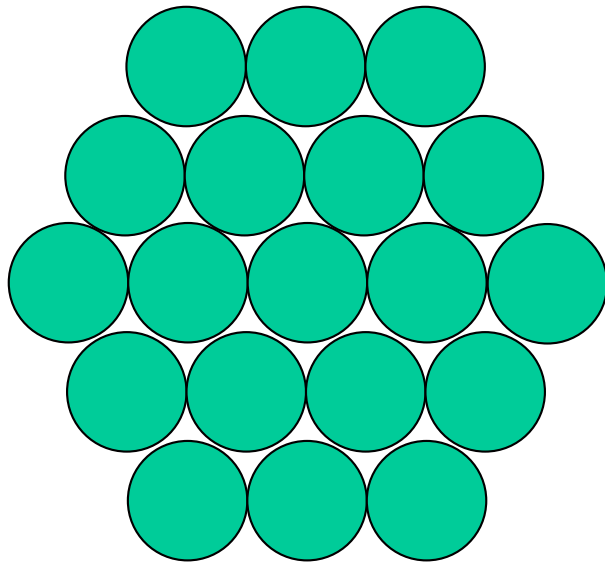
<i>Crystal System</i>	<i>Axial Relationships</i>	<i>Interaxial Angles</i>	<i>Unit Cell Geometry</i>
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	

230 possible combinations of symmetry:
space groups

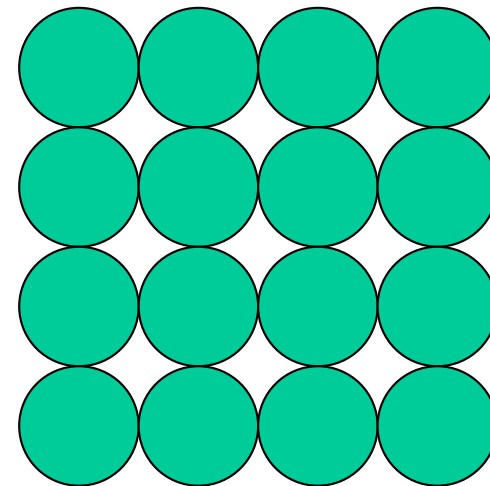
Metallic Crystal Structures

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

2-dimensions



vs.



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

Metallic Crystal Structures

- Tend to be relatively densely packed
- 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.
 - Electron cloud shields cores from each other
- Have the simplest crystal structures

We will examine four such structures...

SC (simple cubic), BCC (body-centered cubic)

FCC (face-centered cubic), HCP (hexagonal-close packed)



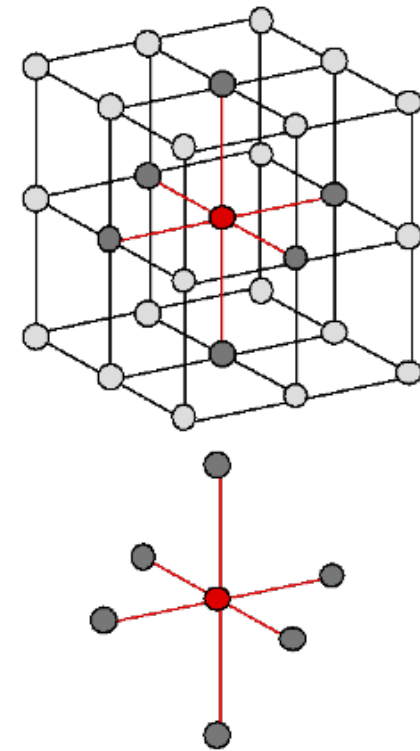
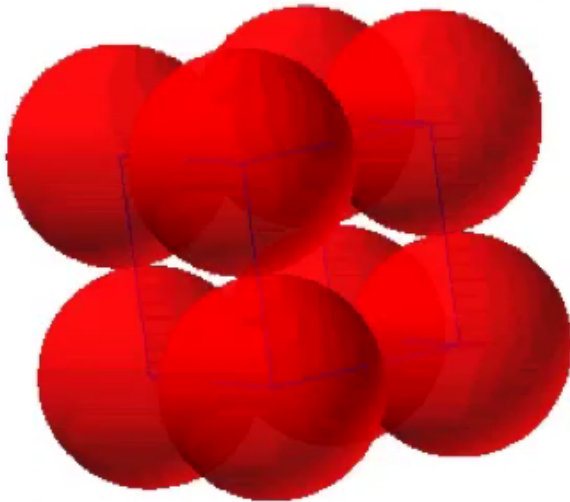
Computer models of crystal structures

- www.wileyplus.com



Simple Cubic Structure (SC)

- Rare due to low packing density
(for pure elements, only Po has this structure)
- Close-packed directions are cube edges
- Coordination # = 6
(# nearest neighbors)

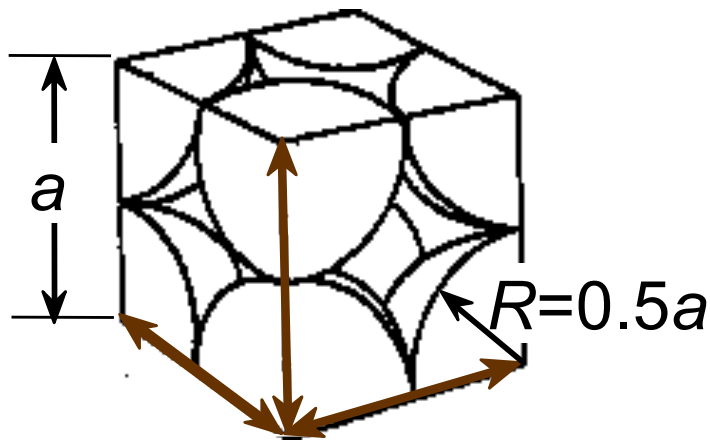


Atomic Packing Factor (APF)

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

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions
contains $8 \times 1/8 =$
1 atom/unit cell

$$\text{APF} = \frac{\begin{array}{c} \text{atoms} \\ \text{unit cell} \end{array} \quad \begin{array}{|c|c|} \hline 1 & \frac{4}{3} \pi (0.5a)^3 \\ \hline \end{array}}{\begin{array}{|c|} \hline a^3 \\ \hline \end{array}}$$

volume
atom

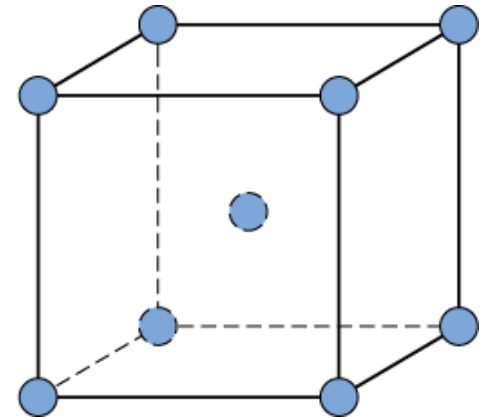
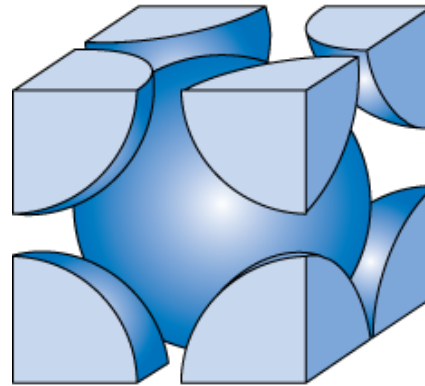
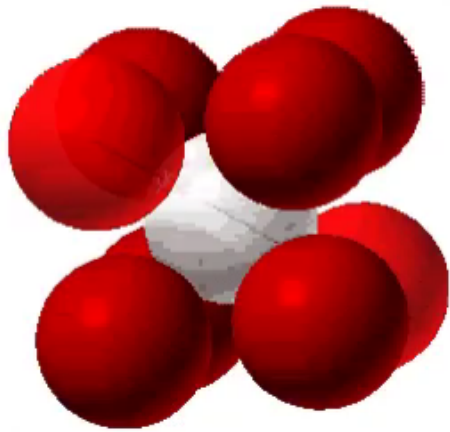
volume
unit cell

Body Centered Cubic Structure (BCC)

- Atoms touch each other along cube diagonals
 - Note: All atoms are identical; the center atom is shaded differently only for ease of viewing

ex: Cr, W, Fe (α), Tantalum, Molybdenum

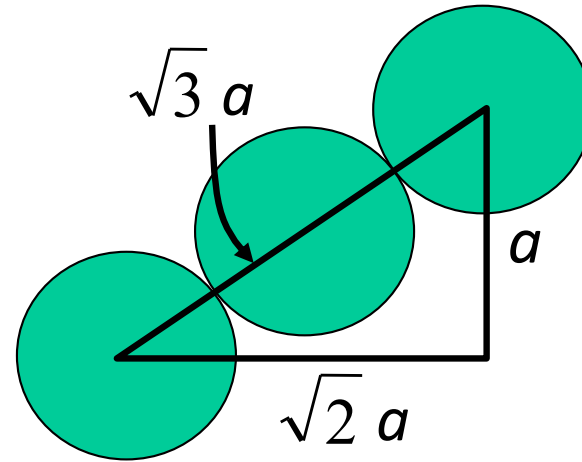
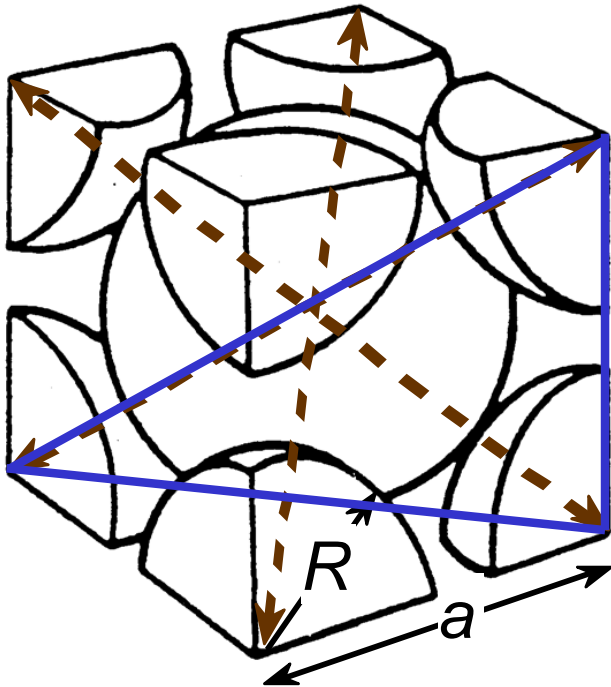
- Coordination # = 8



2 atoms/unit cell: 1 center + 8 corners \times 1/8

Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68



Close-packed directions:
length = $4R = \sqrt{3} a$

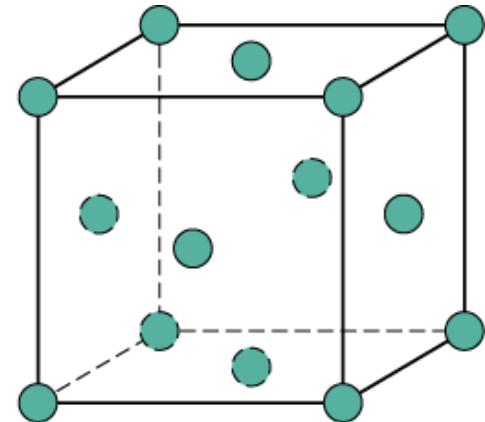
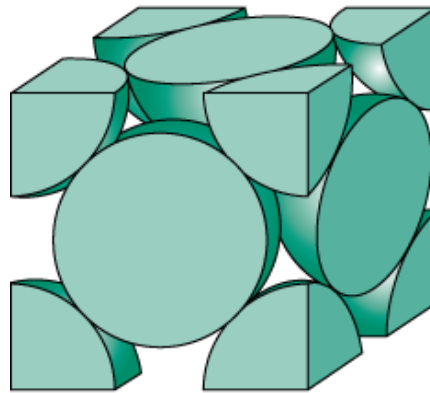
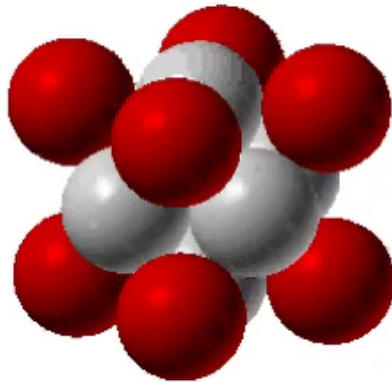
$$\text{APF} = \frac{\begin{array}{c} \text{atoms} \\ \text{unit cell} \end{array} \rightarrow 2 \cdot \begin{array}{c} \text{volume} \\ \text{atom} \end{array} \frac{4}{3} \pi (\sqrt{3}a/4)^3}{\begin{array}{c} \text{volume} \\ \text{unit cell} \end{array} a^3}$$

Face Centered Cubic Structure (FCC)

- Atoms touch each other along 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

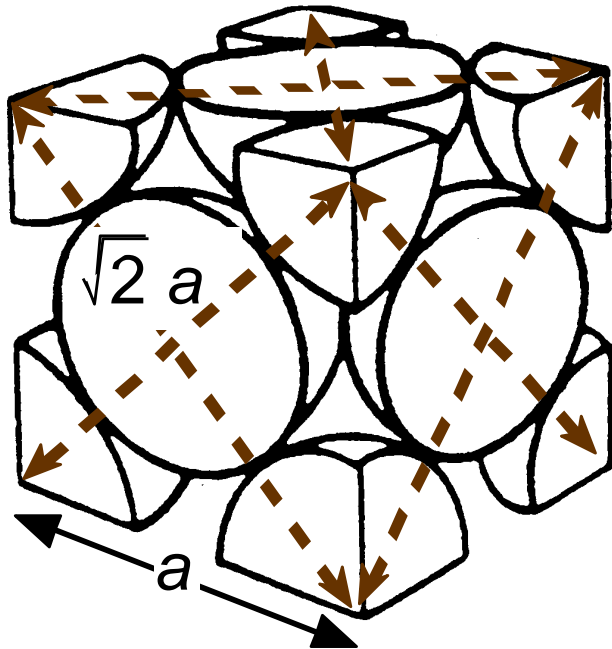
- Coordination # = 12



4 atoms/unit cell: $6 \text{ face} \times \frac{1}{2} + 8 \text{ corners} \times \frac{1}{8}$

Atomic Packing Factor: FCC

- APF for a face-centered cubic structure = 0.74
maximum achievable APF



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

Unit cell contains:
 $6 \times 1/2 + 8 \times 1/8$
= **4 atoms/unit cell**

$$\text{APF} = \frac{\text{atoms/unit cell} \times \text{volume/atom}}{\text{volume/unit cell}}$$

The diagram shows the calculation of the Atomic Packing Factor (APF) for an FCC unit cell. The numerator consists of two parts: the number of atoms per unit cell (4, highlighted in green) and the volume of a single atom ($\frac{4}{3} \pi (\sqrt{2}a/4)^3$, highlighted in orange). The denominator is the volume of the unit cell (a^3 , highlighted in blue). Arrows indicate the contribution of each term to the overall fraction.

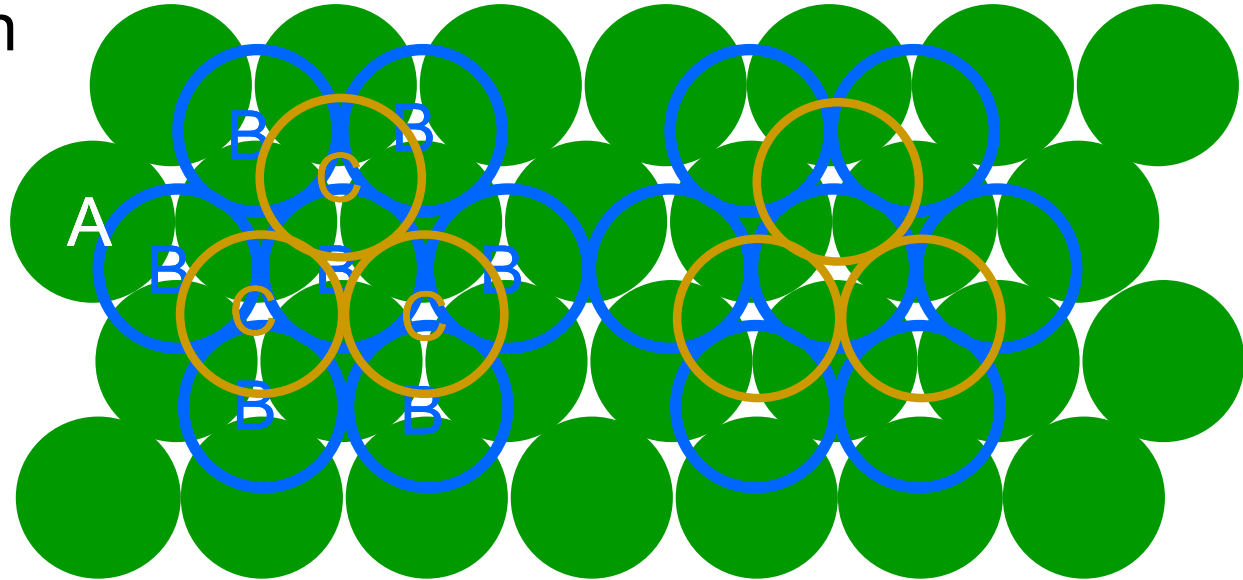
FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

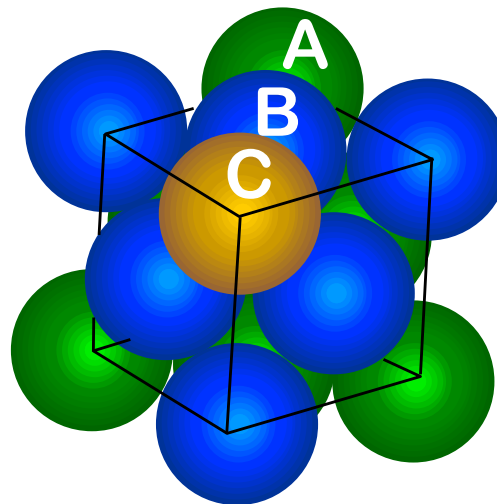
A sites

B sites

C sites

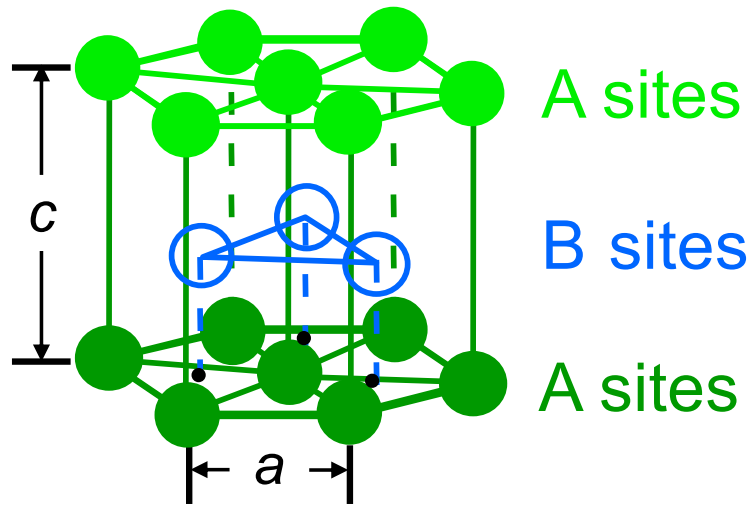


- FCC Unit Cell

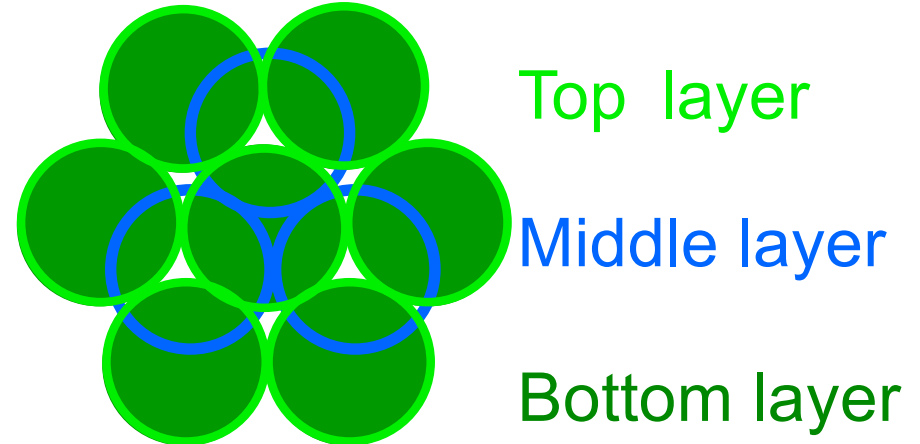


Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection



- 2D Projection



- Coordination # = 12
- APF = 0.74
- $c/a = 1.633$

6 atoms/unit cell

ex: Cd, Mg, Ti, Zn

Theoretical Density, ρ

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

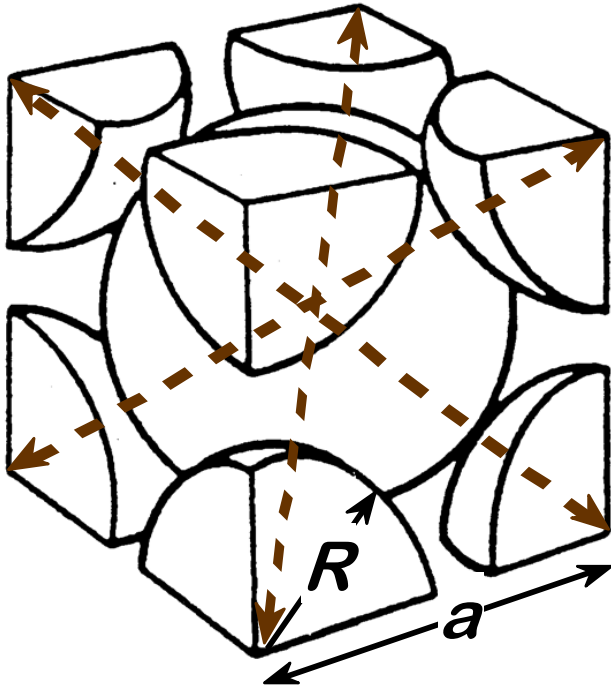
$$\rho = \frac{n A}{V_C N_A} \qquad \rho = \frac{\sum n_i A_i}{V_C N_A}$$

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
= 6.023×10^{23} atoms/mol



Theoretical Density, ρ



- Ex: Cr (BCC)

$$A = 52.00 \text{ g/mol}$$

$$R = 0.125 \text{ nm}$$

$$n = 2$$

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

$$\rho = \frac{\frac{\text{atoms}}{\text{unit cell}} \cdot A}{\frac{\text{volume}}{\text{unit cell}} \cdot N_A}$$

Diagram illustrating the calculation of theoretical density ρ for Cr (BCC):

- Numerator (Mass per unit cell): $2 \cdot 52.00$ (atoms/unit cell \times atomic weight)
- Denominator (Volume per unit cell): $a^3 \cdot 6.023 \times 10^{23}$ (volume/unit cell \times Avogadro's number)

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

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



Densities of Material Classes

In general

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

Why?

Metals have...

- close-packing (metallic bonding)
- often large atomic masses

Ceramics have...

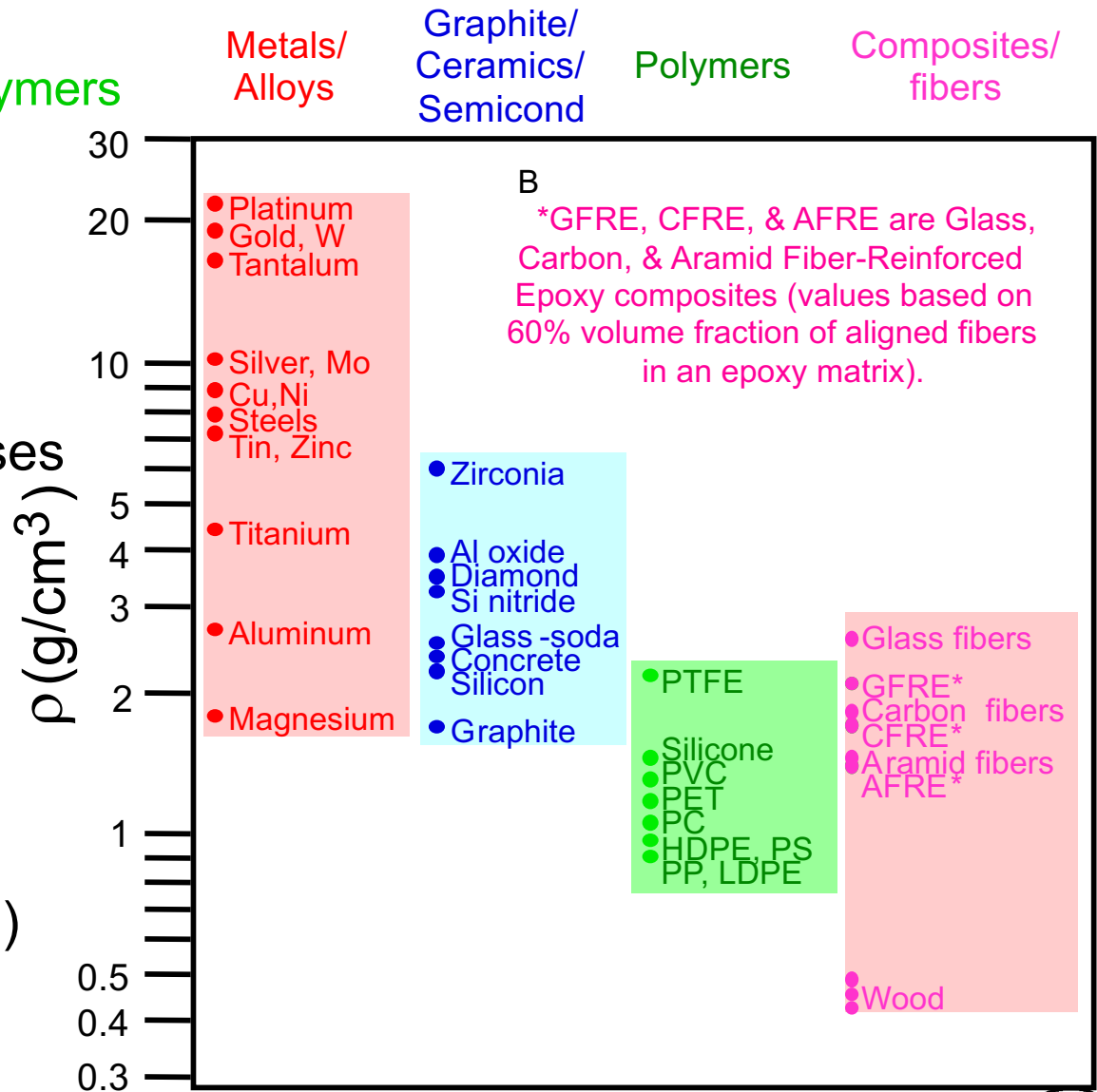
- less dense packing
- often lighter elements

Polymers have...

- low packing density (often amorphous)
- lighter elements (C,H,O)

Composites have...

- intermediate values



Crystals as Building Blocks

- *Some* engineering applications require single crystals:

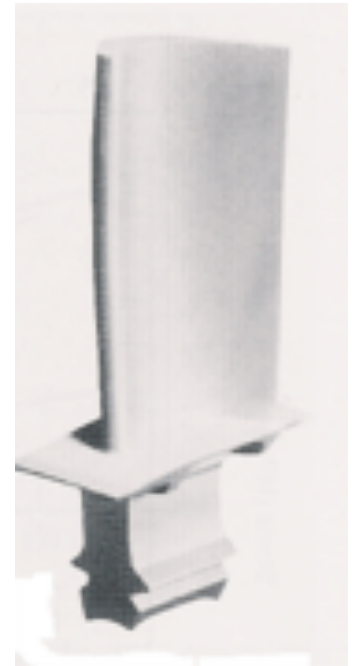
--diamond abrasives



--silicon electronics



--jet engine turbine blades:
Ni-based superalloys



- Properties of crystalline materials related to crystal structure
 - Ex: Quartz fractures more easily along some crystal planes than others



(Courtesy P.M. Anderson)



Polycrystals

- Most engineering materials are polycrystals.



Anisotropic

Adapted from Fig. K, color inset pages of *Callister 5e*.
(Fig. K is courtesy of Paul E. Danielson, Teledyne Wah Chang Albany)

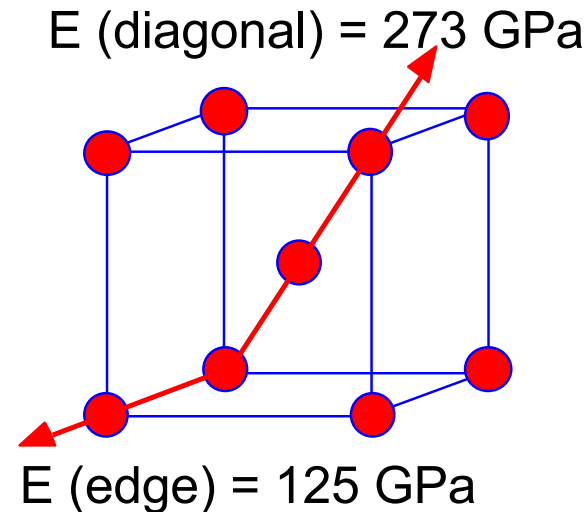
Isotropic

- Nb-Hf-W plate with an electron beam weld
- Each "grain" is a single crystal
- If grains are randomly oriented, overall component properties are not directional
- Grain sizes typically range from 1 nm to 2 cm (i.e., from a few to millions of atomic layers)

Single vs Polycrystals

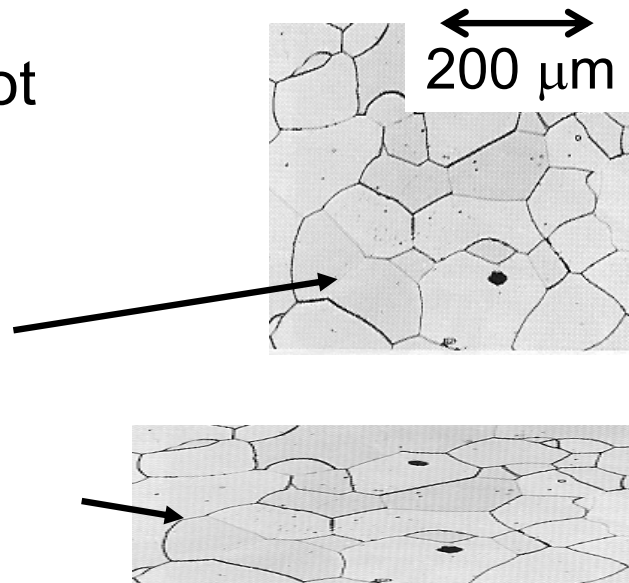
- Single Crystals

- 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**
($E_{\text{poly iron}} = 210 \text{ GPa}$)
- If grains are **textured**, anisotropic



Polymorphism

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

titanium

α , β -Ti

carbon

diamond, graphite

FCC iron (austenite) is more dense than BCC iron (ferrite), but has a bigger void in the structure, so it dissolves more carbon

iron system

liquid

1538°C

BCC

δ -Fe

1394°C

FCC

γ -Fe

Ductile
Up to 2 wt% C

912°C

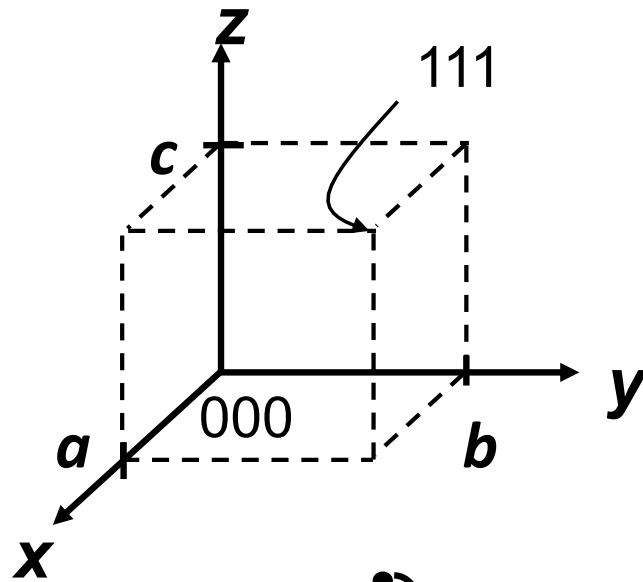
BCC

α -Fe

Not so ductile
Up to 0.02 wt% C



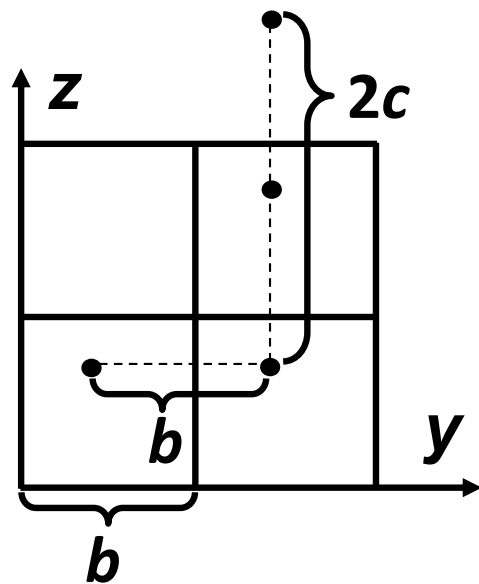
Point Coordinates



Point coordinates for unit cell center are

$$a/2, b/2, c/2 \quad \frac{1}{2} \frac{1}{2} \frac{1}{2}$$

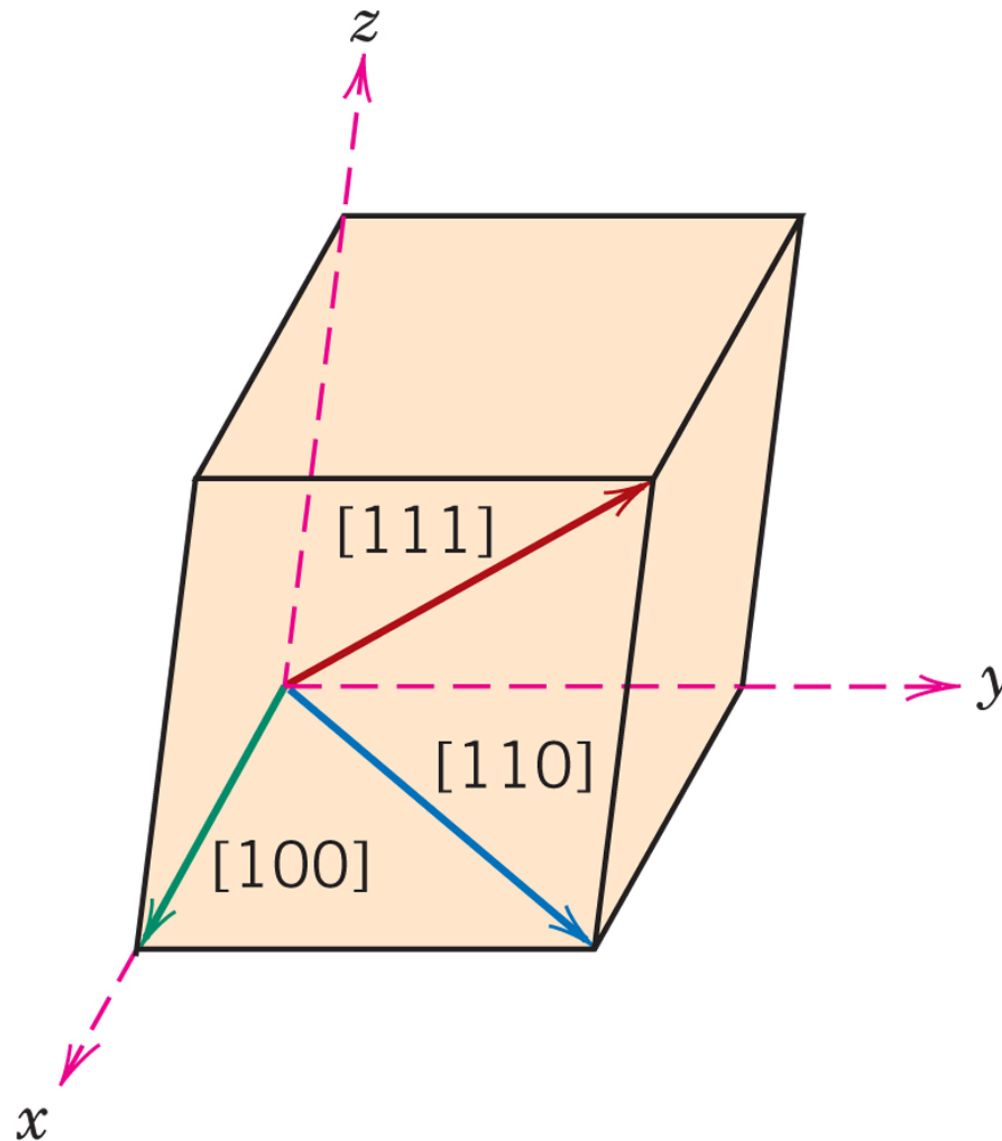
Point coordinates for unit cell corner are 111



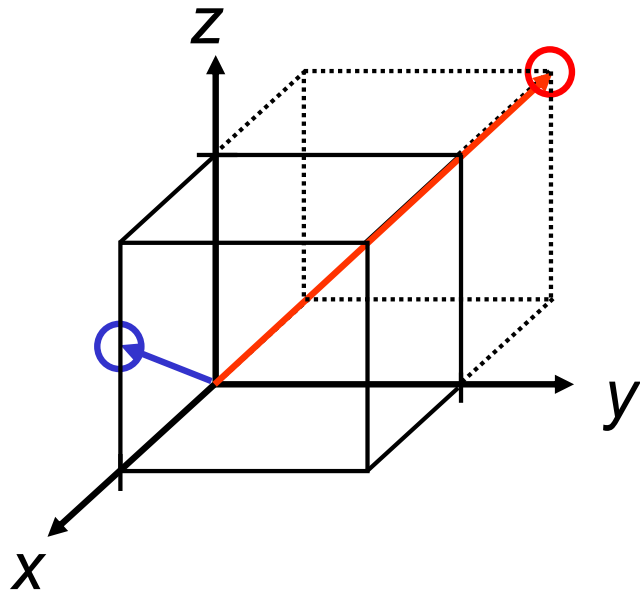
Translation: integer multiple of lattice constants \rightarrow identical position in another unit cell



Crystallographic Directions



Crystallographic Directions



Algorithm

1. Vector repositioned (if necessary) to pass through origin
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: $1, 0, \frac{1}{2} \Rightarrow 2, 0, 1 \Rightarrow [201]$

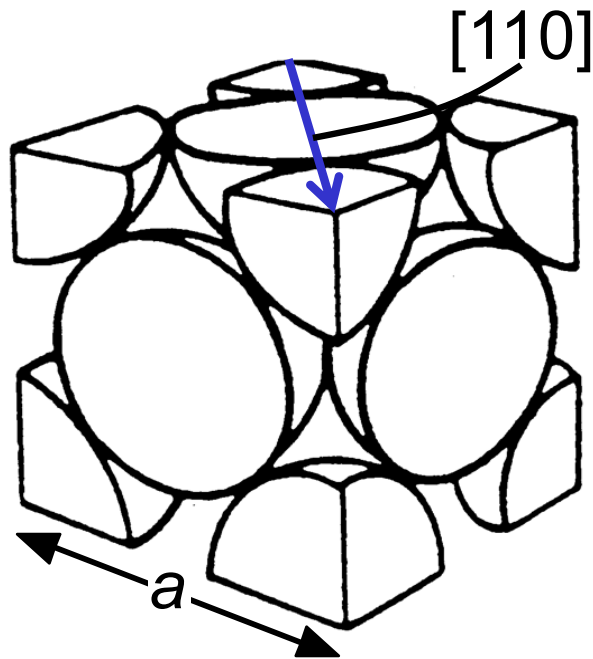
$-1, 1, 1 \Rightarrow [\bar{1}11]$ where overbar represents a negative index

families of directions $\langle uvw \rangle$



Linear Density

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

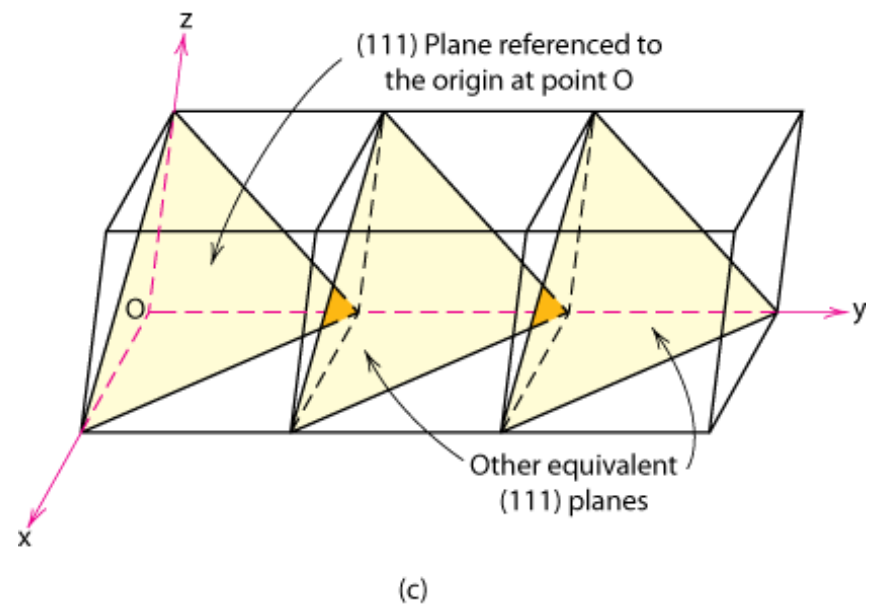
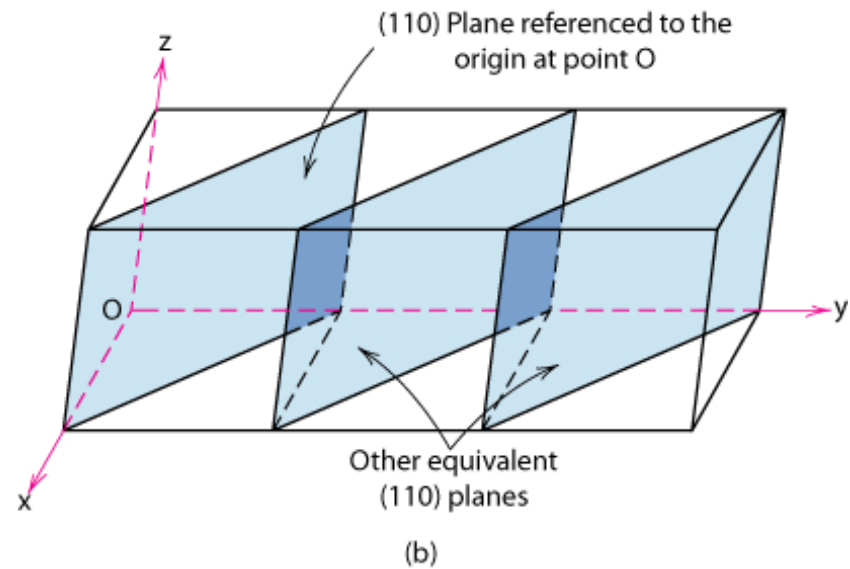
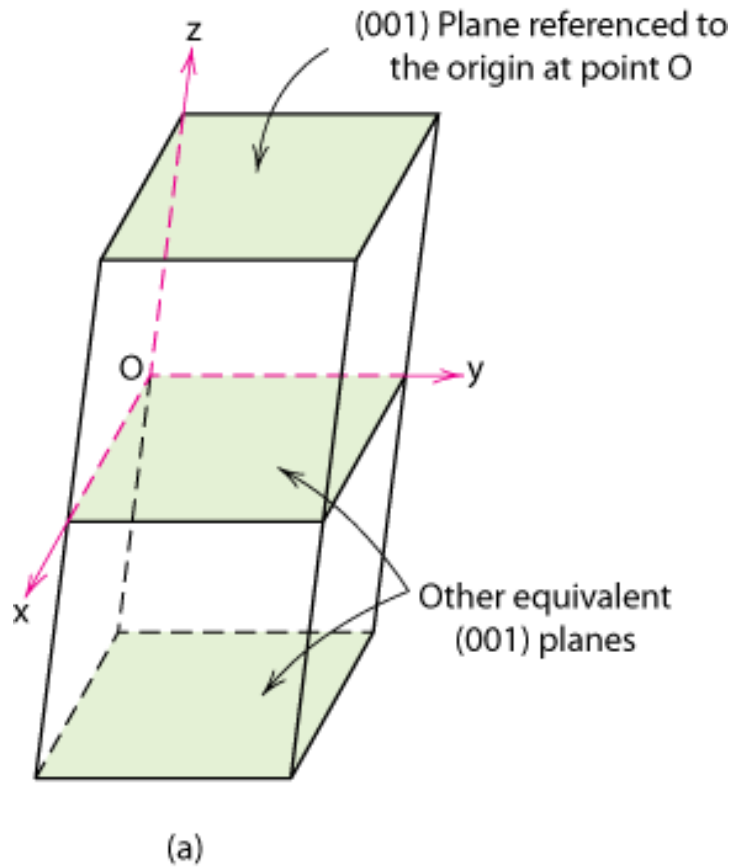


ex: linear density of Al in [110] direction

$$a = 0.405 \text{ nm}$$

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

Crystallographic Planes



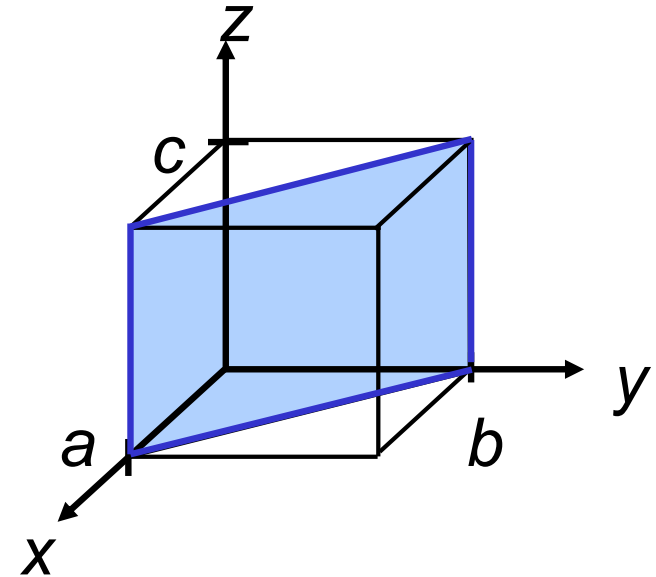
Crystallographic Planes

- Miller Indices: Reciprocals of the (three) axial intercepts for a plane, cleared of fractions.
- All planes with the same Miller indices are parallel. Planes with higher h,k,l indices are closer together.
- Algorithm
 1. Read off intercepts of plane with axes in terms of a, b, c
 2. Take reciprocals of intercepts
 3. Multiply to make integers if necessary
 4. Enclose in parentheses, no commas i.e., (hkl)

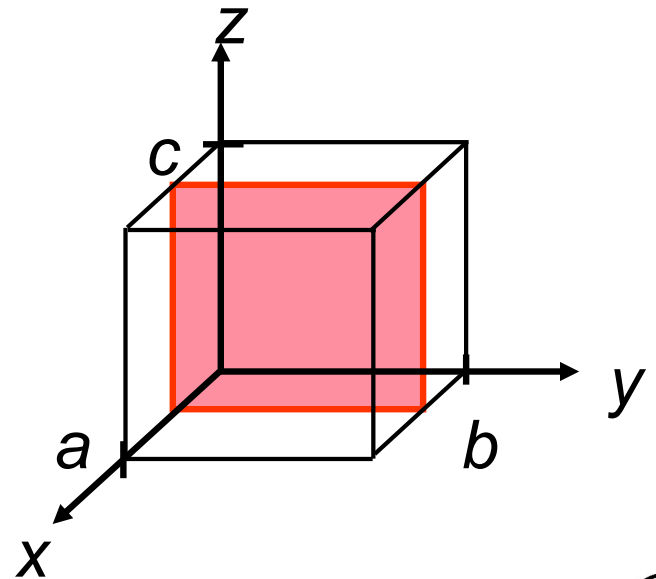


Crystallographic Planes

<u>example</u>	<i>a</i>	<i>b</i>	<i>c</i>
1. Intercepts	1	1	∞
2. Reciprocals	1/1	1/1	1/ ∞
	1	1	0
3. Miller Indices	(110)		



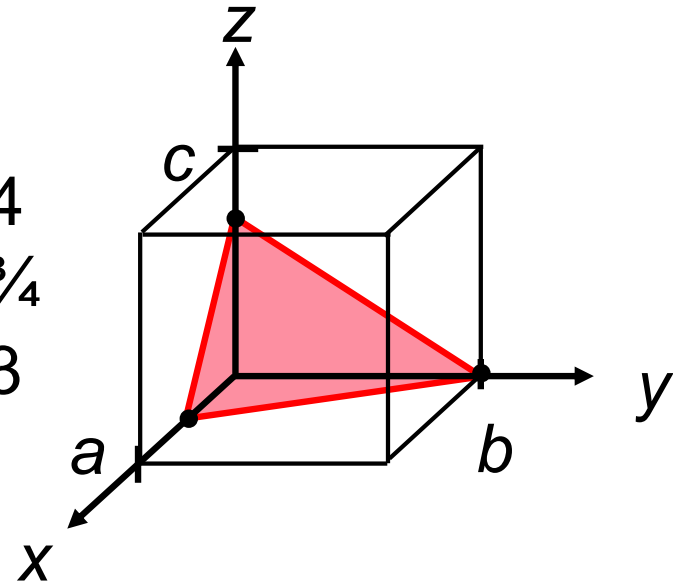
<u>example</u>	<i>a</i>	<i>b</i>	<i>c</i>
1. Intercepts	1/2	∞	∞
2. Reciprocals	1/1/2	1/ ∞	1/ ∞
	2	0	0
3. Miller Indices	(200)		



If plane passes through origin,
pick a different origin in a neighboring unit cell

Crystallographic Planes

<u>example</u>	<i>a</i>	<i>b</i>	<i>c</i>
1. Intercepts	$1/2$	1	$3/4$
2. Reciprocals	$1/1/2$	1/1	$1/3/4$
	2	1	$4/3$
3. Reduction	6	3	4
4. Miller Indices	(634)		



Family of Planes $\{hkl\}$

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



Linear and Planar Densities

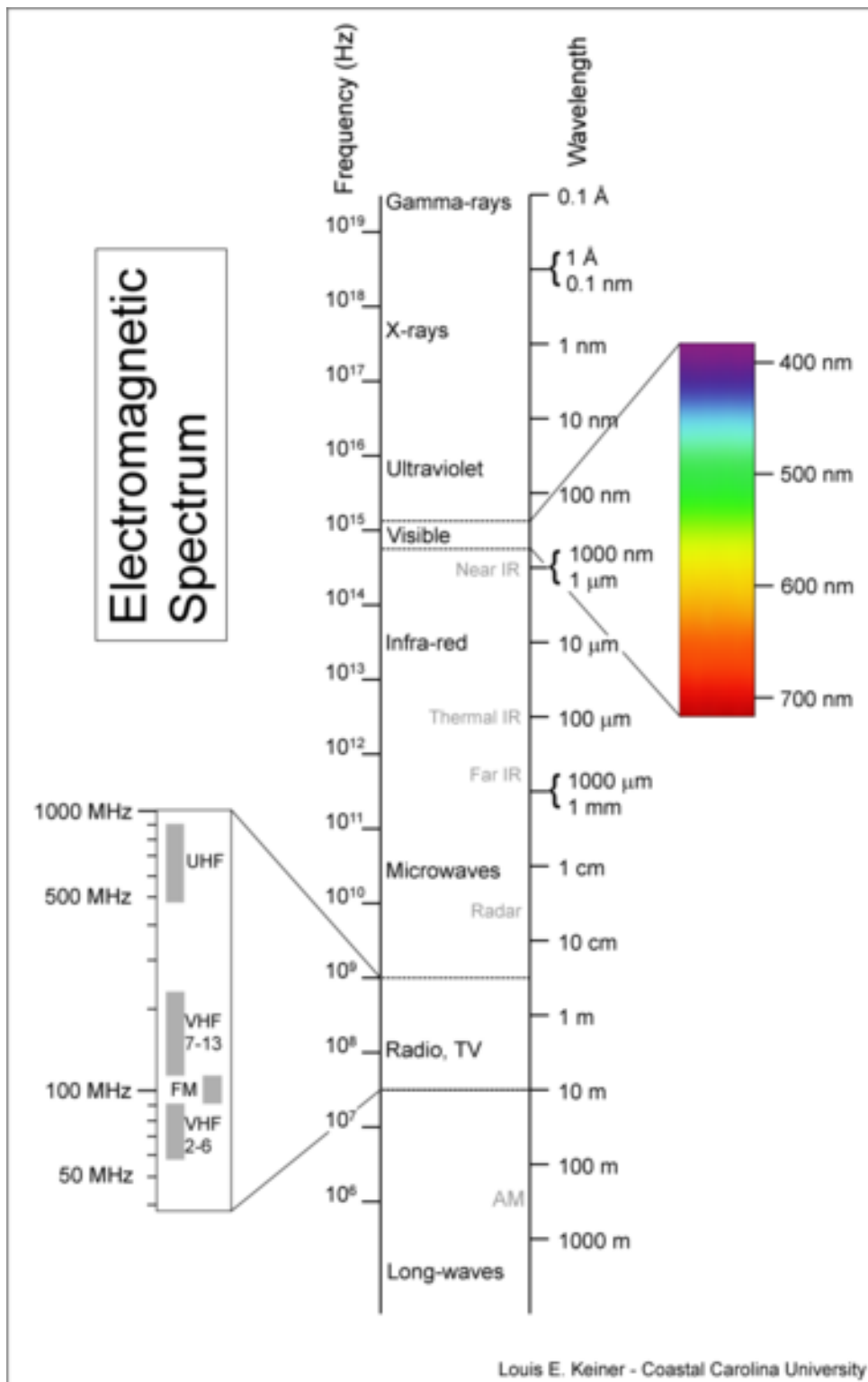
LD = atoms centered on a direction vector /
length of direction vector

PD= atoms centered on a plane /
area of plane

High density planes tend to slip past one
another during plastic deformation

Planes tend to slip in the high density
directions



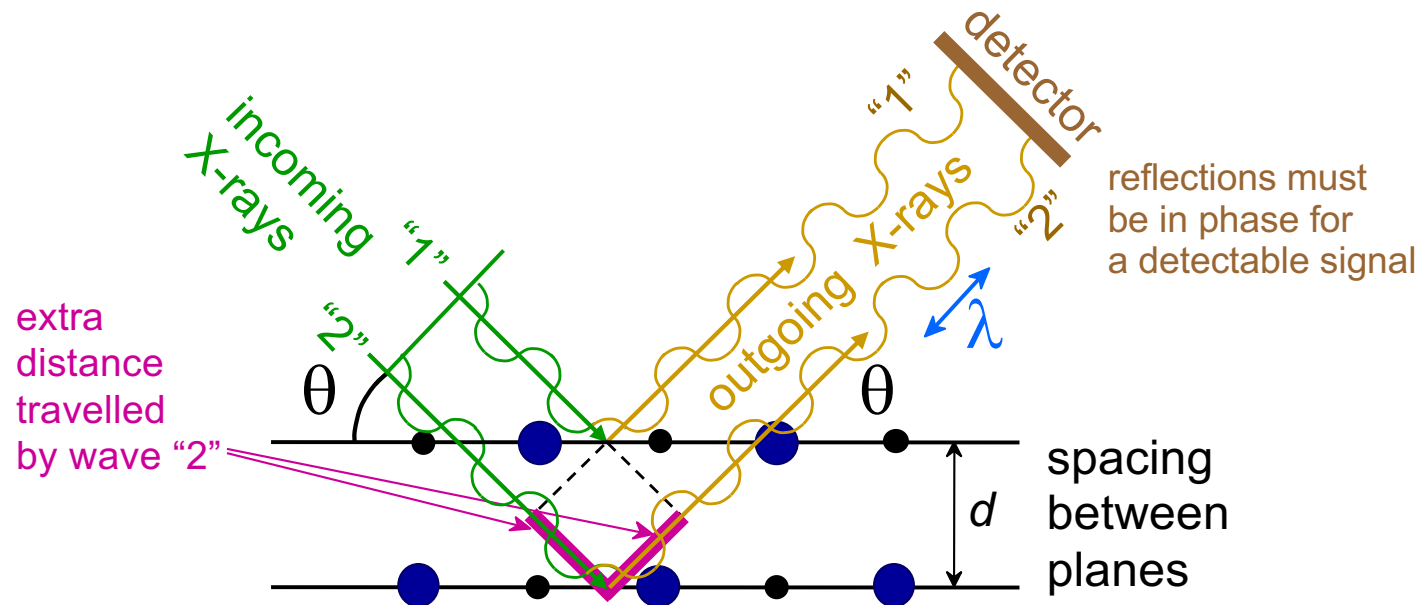


X-Ray Diffraction

- Diffraction gratings have spacings comparable to the wavelength of diffracted radiation.
- Spacing is the distance between parallel planes of atoms.
- For solid materials, often use Cu $K\alpha$ X-rays: $\lambda=0.154$ nm

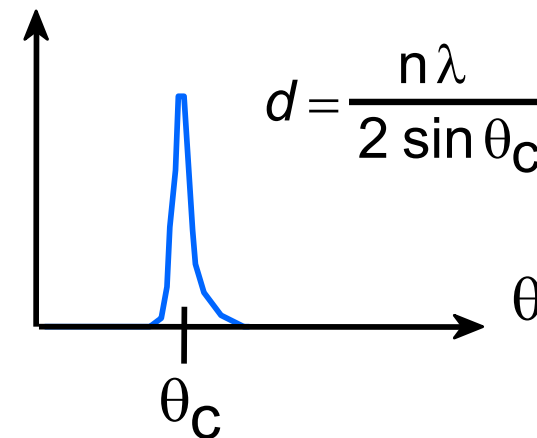
X-Rays to Determine Crystal Structure

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



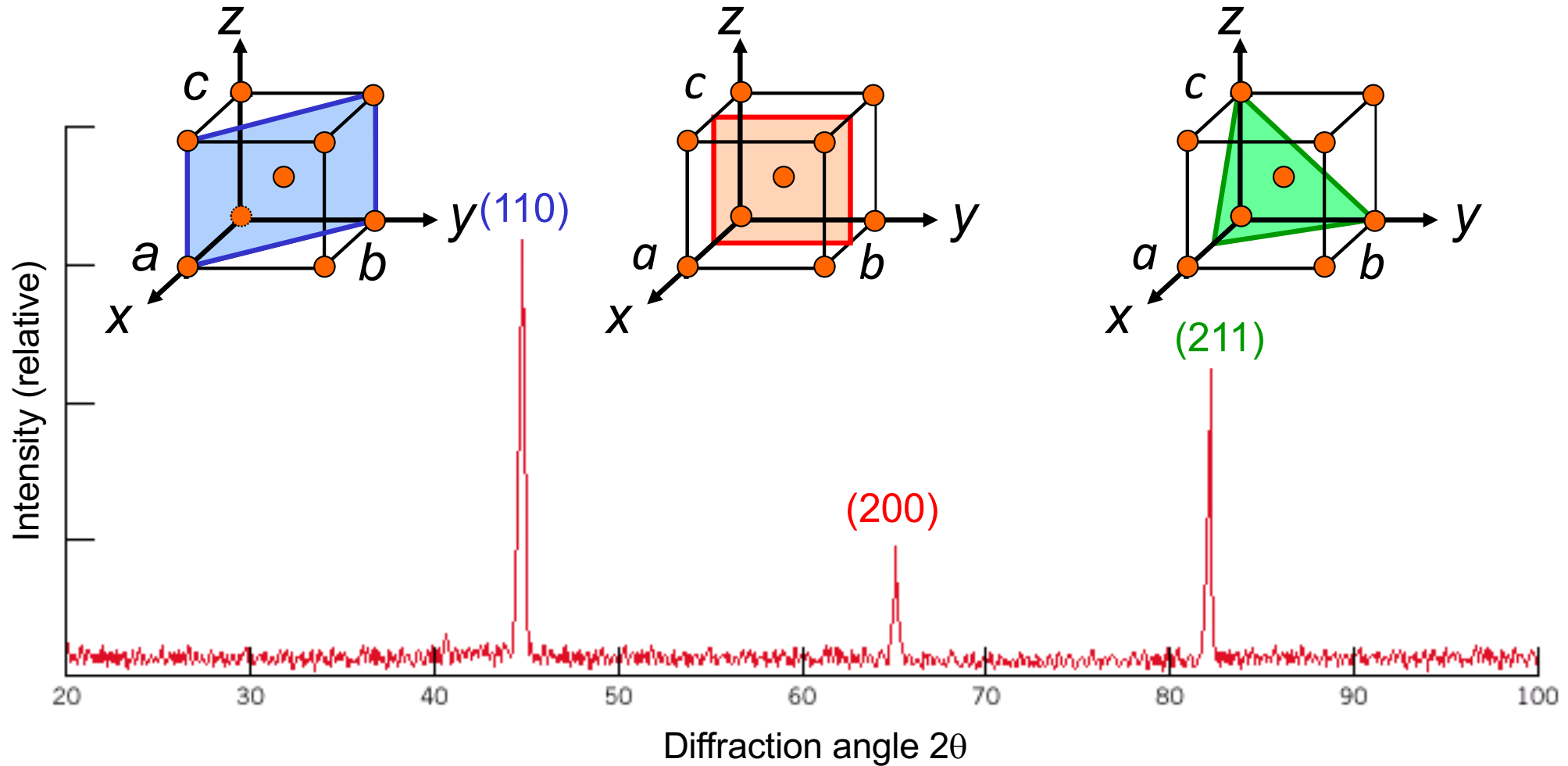
Measurement of critical angle, θ_c , allows computation of planar spacing, d

X-ray intensity (from detector)



Bragg's law: $n\lambda = 2d \sin(\theta)$

X-Ray Diffraction Pattern



Diffraction pattern for polycrystalline α -iron (BCC)

SUMMARY

- Atoms may assemble into **crystalline** or **amorphous** structures
- Common metallic crystal structures are **FCC**, **BCC**, and **HCP**. **Coordination number** and **atomic packing factor** are the same for both FCC and HCP crystal 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)
- **Crystallographic points**, **directions** and **planes** are specified in terms of indexing schemes
Crystallographic directions and planes are related to **atomic linear densities** and **planar densities**



SUMMARY

- Crystalline materials can be **single crystals** or **polycrystalline**.

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

- Some materials can have more than one crystal structure. This is referred to as **polymorphism** (or **allotropy**)
- **X-ray diffraction** is used for crystal structure and **interplanar spacing** determinations

