Chapter 3: 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 orientation?

1

•The properties of some materials are directly related to their crystal structures:

Pure and undeformed magnesium, having one crystal structure, is much more brittle (i.e., fracture at lower degrees of deformation) than are pure and undeformed metals such as gold and silver that have yet another crystal structure.

•Significant property differences exist between crystalline and noncrystalline materials having the same composition, as well:

Noncrystalline ceramics and polymers normally are optically transparent; the same materials in crystalline (or semicrystalline) form tend to be opaque or, at best, translucent.

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Defination:
Crystalline and **Noncrystalline (Amorphous)**

•Solid materials may be classified according to the regularity with which atoms are arranged with respect to one another.

•A **crystalline material** is one in which the atoms are situated in a repeating or periodic array over large atomic distances;

•Upon solidification, the atoms will position themselves in a repetitive three-dimensional pattern, in which each atom is bonded to its nearest-neighbor atoms.

• All metals, many ceramic materials, and certain polymers form crystalline structures under normal solidification conditions.

•For those that do not crystallize, this long-range atomic order is absent: these are called as ***noncrystalline*** or ***amorphous*** *materials.*

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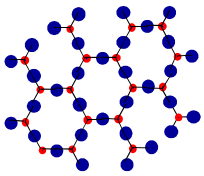
Materials and Packing

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

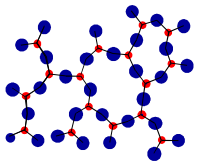


crystalline SiO_2
Adapted from Fig. 3.23(a), *Callister & Rethwisch 8e.*

• **Si** • **Oxygen**

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

"Amorphous" = Noncrystalline



noncrystalline SiO_2
Adapted from Fig. 3.23(b), *Callister & Rethwisch 8e.*

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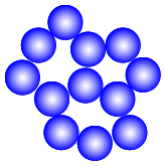
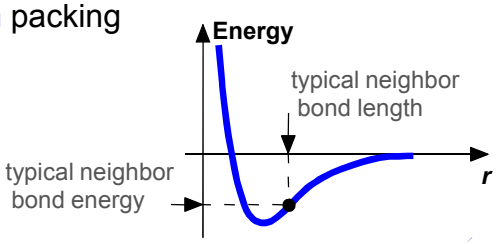
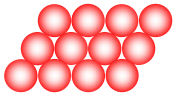
Energy and Packing

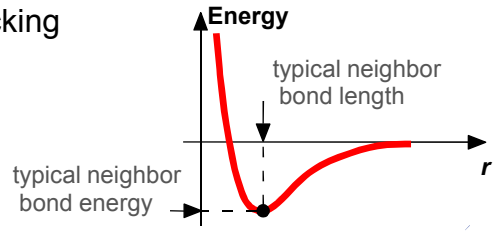
- Non dense, random packing





- Dense, ordered packing





Dense, ordered packed structures tend to have lower energies.

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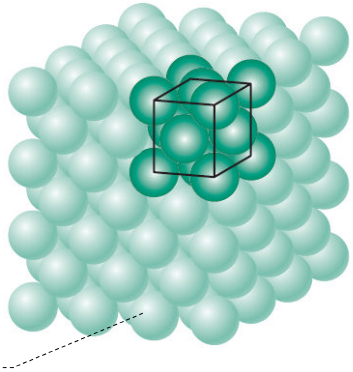
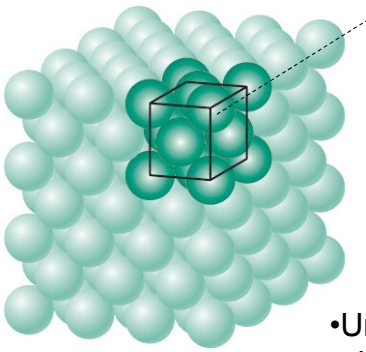
There is an extremely large number of different crystal structures all having long range atomic order; these vary from relatively simple structures for metals to exceedingly complex ones, as displayed by some of the ceramic and polymeric materials.

When describing crystalline structures, atoms (or ions) are thought of as being solid spheres having well-defined diameters. This is termed as "*atomic hard sphere model*" *in which spheres representing atoms touch one another.*



All the atoms are identical

6



Lattice: A three dimentional array of points coinciding with atom positions

•In describing crystal structures, it is often convenient to subdivide the structure into small repeat entities called **unit cells.**

•Unit cells for most crystal structures are prisms having three sets of parallel faces.

-The unit cell is the basic structural unit or building block of the crystal structure
-Defines the crystal structure by virtue of its geometry and the atom positions within.

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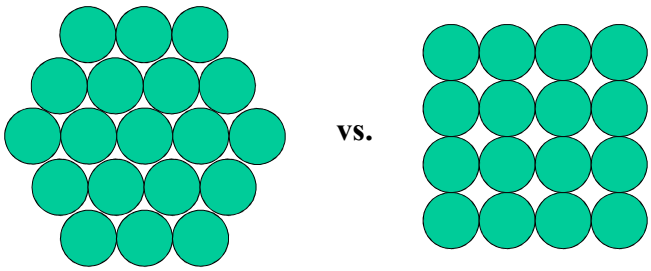
Metallic Crystal Structures

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

2-dimensions



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

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Metallic Crystal Structures

- Tend to be 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 three such structures...

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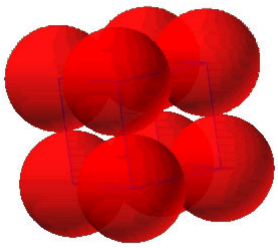
Lattice parameter relationships and figures showing unit cell geometries for the seven crystal system:

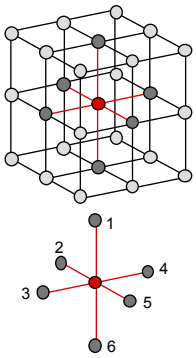
Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta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

- Simple Cubic Structure (SC)
- Body Centered Cubic Structure (BCC)
- Face Centered Cubic Structure (FCC)
- Hexagonal Close-Packed Structure (HCP)

Simple Cubic Structure (SC)

- Rare due to low packing density
- Only **Po** (Polonium) has this structure.
- Close-packed directions are cube edges.
  - Coordination # = 6
    (Number of nearest neighbors)





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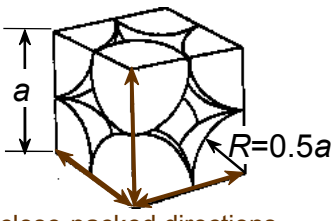
Atomic Packing Factor (APF)

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

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

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

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

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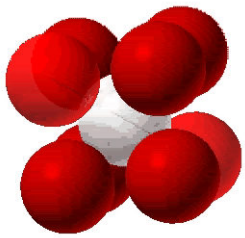
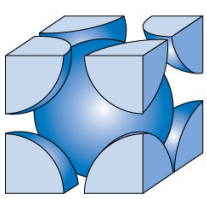
Body Centered Cubic Structure (BCC)

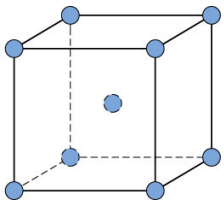
- Atoms touch each other along cube diagonals.
  --Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

ex: Cr, W, Fe (α)

- Coordination # = 8







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

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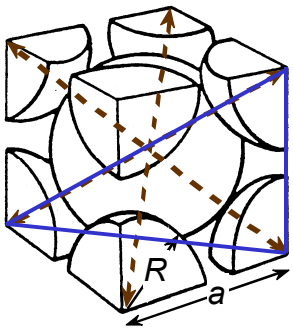
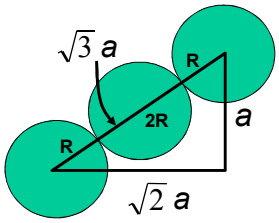
Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68





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

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

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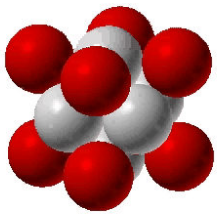
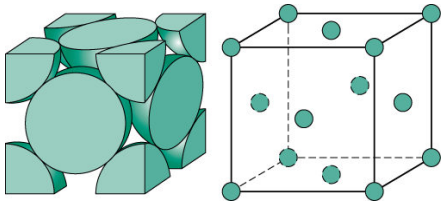
Face Centered Cubic Structure (FCC)

- 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, Ni, Ag

- Coordination # = 12





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

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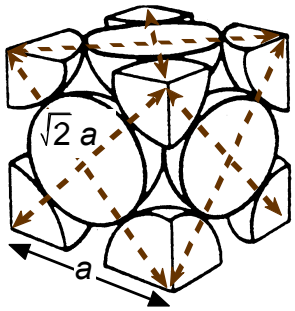
Atomic Packing Factor: FCC

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

maximum achievable APF



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

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

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

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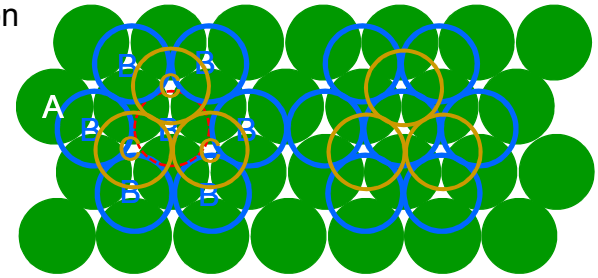
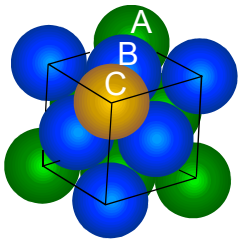
FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection



- FCC Unit Cell



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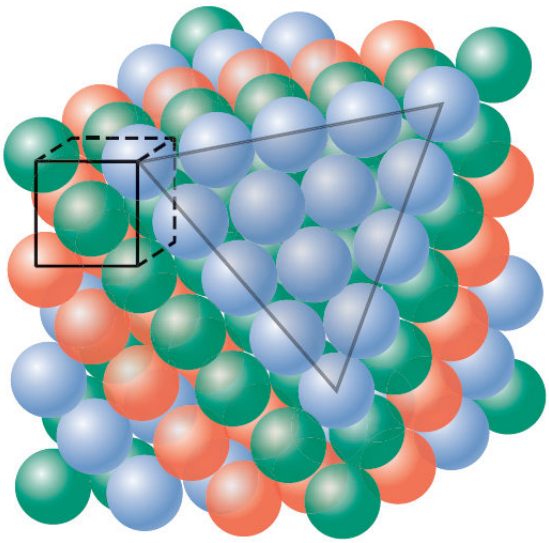
• 3D Projection of FCC Unit Cell: Close-packed (111) planes:



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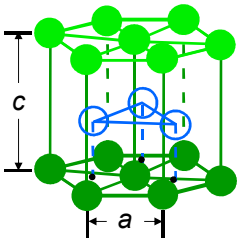
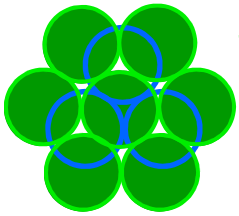
Hexagonal Close-Packed Structure (HCP)

- 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

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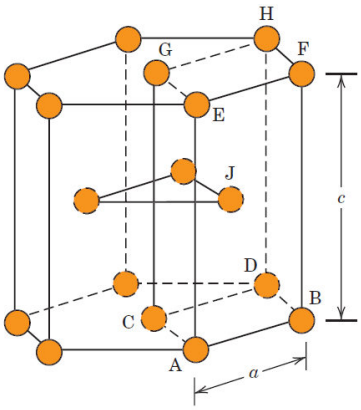
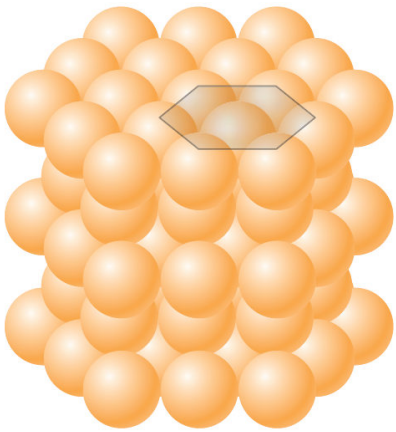
Hexagonal Close-Packed Structure (HCP)





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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
= 6.022×10^{23} atoms/mol

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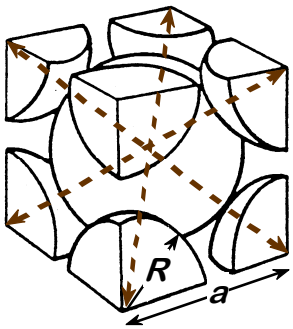
Theoretical Density, ρ



- Ex: Cr (Chromium) (BCC)
  - A = 52.00 g/mol
  - R = 0.125 nm
  - n = 2 atoms/unit cell

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

$$\rho = \frac{\frac{\text{atoms}}{\text{unit cell}} \cdot 2 \cdot 52.00 \cdot \frac{\text{g}}{\text{mol}}}{a^3 \cdot 6.022 \times 10^{23} \cdot \frac{\text{volume}}{\text{unit cell}} \cdot \frac{\text{atoms}}{\text{mol}}}$$

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

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Densities of Material Classes

In general

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

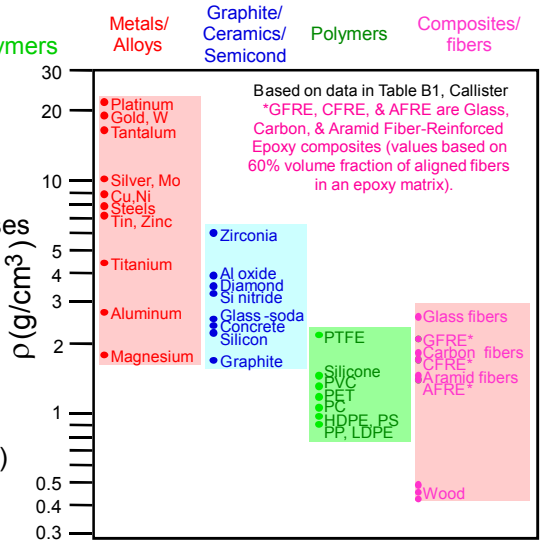
Why?

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



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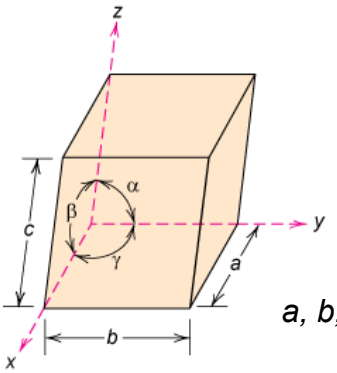
Crystal Systems

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

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Crystal Systems

•When dealing with crystalline materials, it often becomes necessary to specify a particular point within a unit cell, a crystallographic direction, or some crystallographic plane of atoms.

•Labeling conventions have been established in which **three numbers or indices** are used to designate point locations, directions, and planes.

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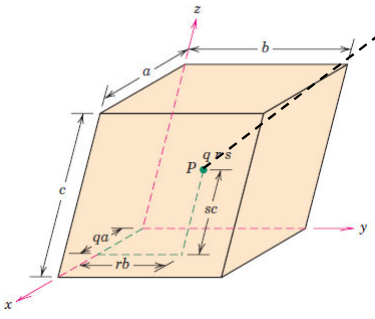
Point Coordinates

•The position of any point located within a unit cell may be specified in terms of its coordinates as fractional multiples of the unit cell edge lengths.
•We have chosen not to separate these coordinates by commas or any other punctuation marks.



Point Coordinates: **qrs**

The "***q"*** *coordinate* (which is a fraction) corresponds to the distance "*q**a**" along the x axis, where "a" is the* unit cell edge length. The respective ***r*** *and* ***s*** *coordinates for the y and z axes are* determined similarly.

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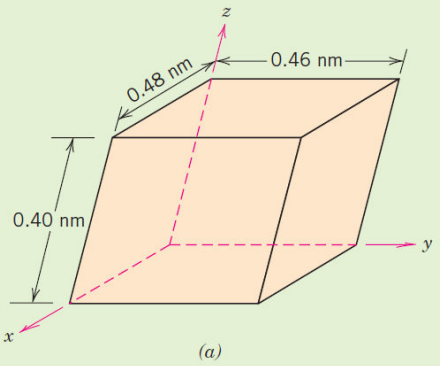
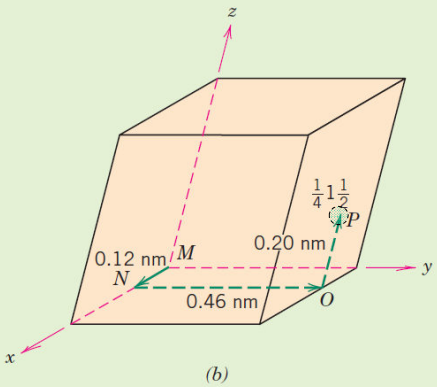
EXAMPLE 1: Fractional multiples of the unit cell edge lengths

For the unit cell shown in the accompanying sketch (*a*), locate the point having coordinates $\frac{1}{4}\ 1\ \frac{1}{2}$.



(*a*)



(*b*)

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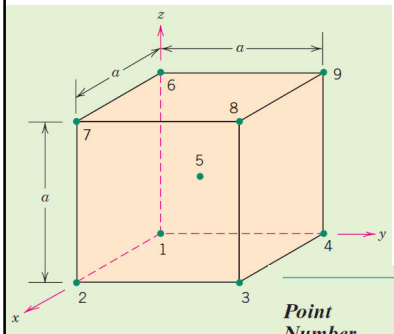
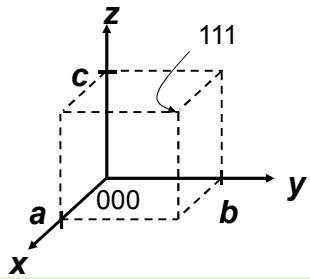
EXAMPLE 2: Specify point coordinates for all atom positions for a **BCC** unit cell.



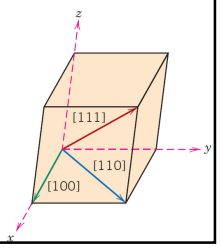


Point Number	Fractional Lengths x axis	y axis	z axis	Point Coordinates
1	0	0	0	0 0 0
2	1	0	0	1 0 0
3	1	1	0	1 1 0
4	0	1	0	0 1 0
5	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$
6	0	0	1	0 0 1
7	1	0	1	1 0 1
8	1	1	1	1 1 1
9	0	1	1	0 1 1

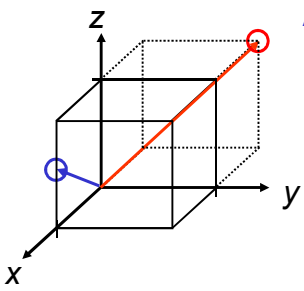
Crystallographic Directions

•A crystallographic direction is defined as a line between two points, or a vector.

1. A vector of convenient length is positioned such that it passes through the origin of the coordinate system.
2. The length of the vector projection on each of the three axes is determined; *these are measured in terms of the unit cell dimensions a, b, and c.*
3. These three numbers are multiplied or divided by a common factor to reduce them to the smallest integer values.
4. The three indices, not separated by commas, are enclosed in square brackets, thus: [*uvw]. The u, v, and w integers correspond to the reduced projections* along the *x, y, and z axes, respectively.*



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

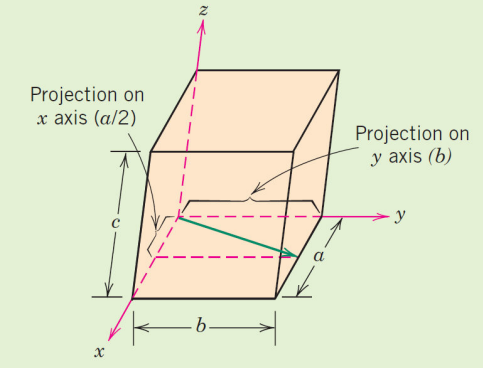
[*uvw*]

ex: 1, 0, ½ => 2, 0, 1 => [201]

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

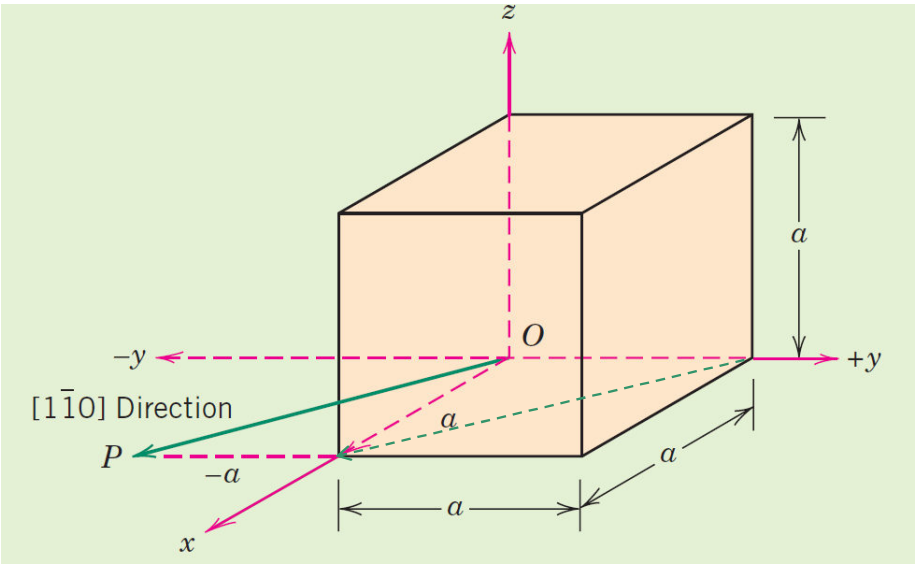
30

EXAMPLE: Determine the indices for the direction shown in the accompanying figure:



	x	y	z
Projections	$a/2$	b	$0c$
Projections (in terms of a, b, and c)	$\frac{1}{2}$	1	0
Reduction	1	2	0
Enclosure		[120]	

EXAMPLE: Draw a [$1\bar{1}0$] direction within a cubic unit cell:



32

Families of directions:

•For some crystal structures, several nonparallel directions with different indices are actually **equivalent**: The spacing of atoms along each direction is the same.
•For example, in cubic crystals, all the directions represented by the following indices are equivalent:

[100], [$\bar{1}$00], [010], [0$\bar{1}$0], [001], and [00$\bar{1}$]

•As a convenience, equivalent directions are grouped together into a ***family***, *which are enclosed* in "**angle** brackets":

•Families of directions <100>

•Directions in cubic crystals having the same indices without regard to order or sign, for example, [123] and [$\bar{2}$1$\bar{3}$], are equivalent. However, this is not true for other crystal systems.

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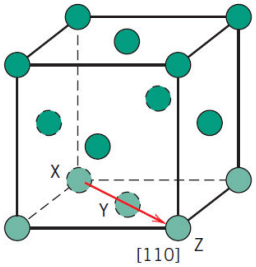
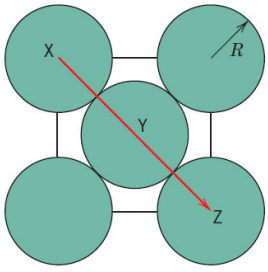
Linear Density

•Linear density (**LD**) is defined as the number of atoms per unit length whose **centers** lie on the direction vector for a specific crystallographic direction;

•Equivalent directions have identical linear densities.





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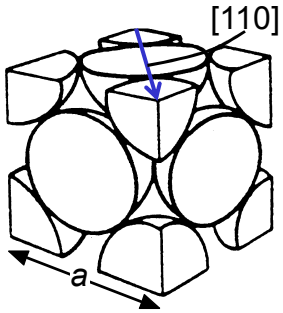
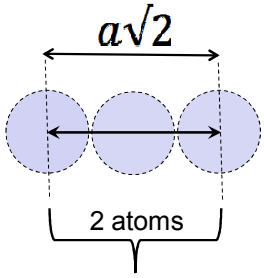
Linear Density:

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



Ex: linear density of Al in [110] direction

a = 0.405 nm



atoms → 2

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

length → $\sqrt{2}a$

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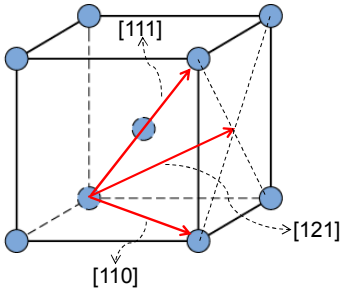
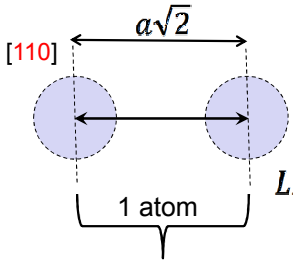
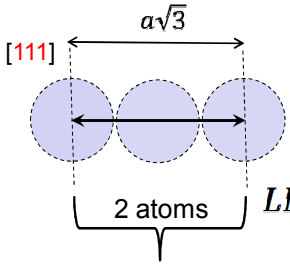
EXAMPLE: Determine the **LD** on the directions shown in below BCC unit cell.

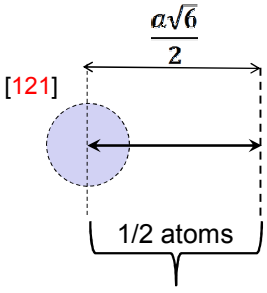




$$LD = \frac{1}{a\sqrt{2}}$$



$$LD = \frac{2}{a\sqrt{3}}$$



$$LD = \frac{1/2}{a\sqrt{6}/2}$$

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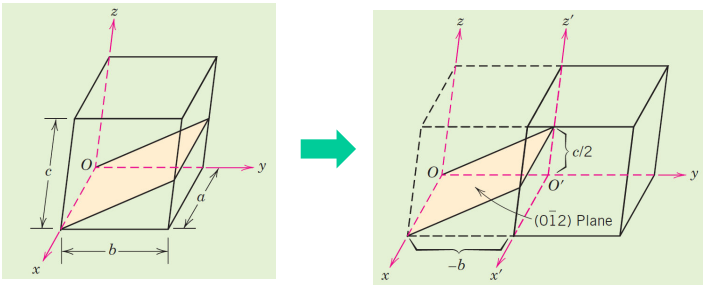
Crystallographic Planes

•In all but the hexagonal crystal system, crystallographic planes are specified by three **Miller indices** as (***hkl***).

1. If the plane passes through the selected origin, either another parallel plane must be constructed within the unit cell by an appropriate translation, or a new origin must be established at the corner of another unit cell.



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Crystallographic Planes

2. At this point the crystallographic plane either intersects or parallels each of the three axes; the length of the planar intercept for each axis is determined in terms of the lattice parameters *a, b, and c.*

3. The reciprocals of these numbers are taken. A plane that parallels an axis may be considered to have an infinite intercept, and, therefore, a zero index.

4. If necessary, these three numbers are changed to the set of smallest integers by multiplication or division by a common factor.

5. Finally, the integer indices, not separated by commas, are enclosed within parentheses, thus: (*hkl*).

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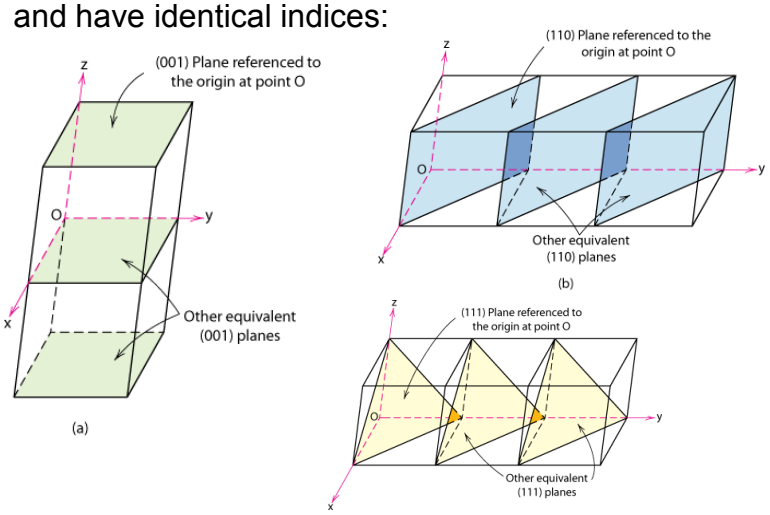
Crystallographic Planes

•Any two planes parallel to each other are equivalent and have identical indices:



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Crystallographic Planes

- **Miller Indices**: Reciprocals of the (three) axial intercepts for a plane, cleared of fractions & common multiples.

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

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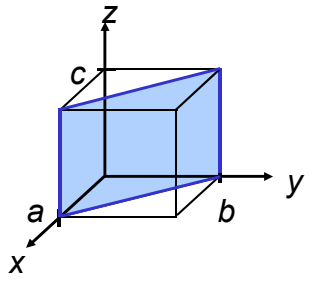
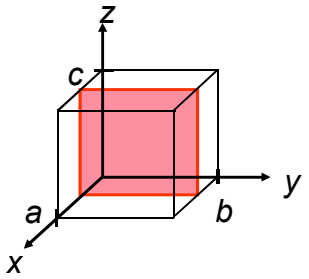
Crystallographic Planes

Example		*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)		



Example		*a*	*b*	*c*
1.	Intercepts	1/2	∞	∞
2.	Reciprocals	1/½	1/∞	1/∞
		2	0	0
3.	Reduction	2	0	0
4.	Miller Indices	(200)		



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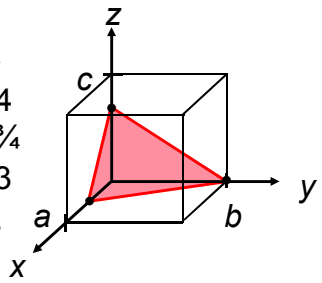
Crystallographic Planes

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}$)

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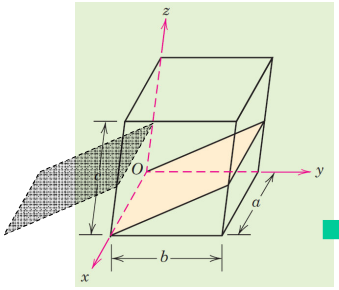
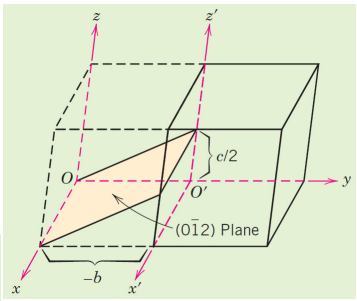
Crystallographic Planes

Example: Determine the Miller indices for the plane shown in below figure.



Since the plane passes through the selected origin ***O***, a new origin must be chosen at the corner of an adjacent unit cell, taken as ***O'***



	x	*y*	*z*
Intercepts	∞a	$-b$	$c/2$
Intercepts (in terms of lattice parameters)	∞	-1	$\frac{1}{2}$
Reciprocals	0	-1	2
Reductions (unnecessary)			
Enclosure		$(0\bar{1}2)$	

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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.

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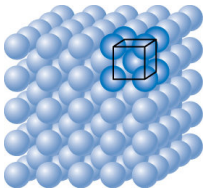
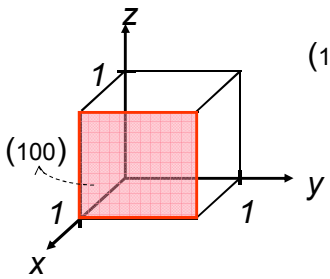
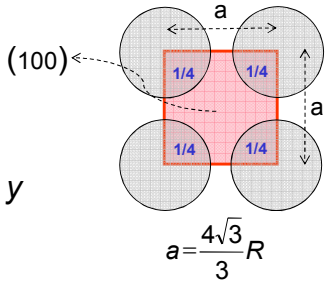
Planar Density of (100) Iron

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







Radius of iron R = 0.1241 nm

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

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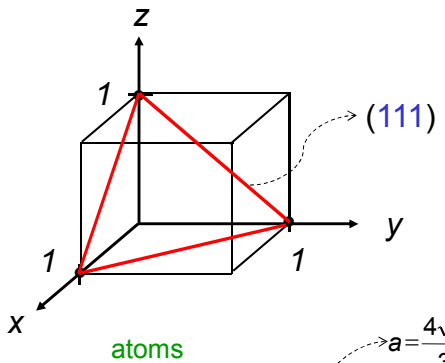
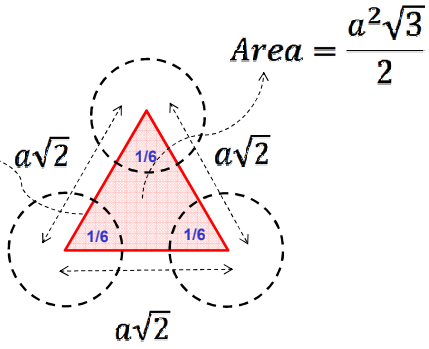
Planar Density of (111) Iron

Solution (cont): (**111**) plane:





$$\text{Planar Density} = \frac{\text{atoms}}{\text{area}} = \frac{\text{2D repeat unit}}{\text{2D repeat unit}} = \frac{3\text{x}1/6}{\frac{a^2\sqrt{3}}{2}} \quad a = \frac{4\sqrt{3}}{3}R$$

$$= 7.0\ \frac{\text{atoms}}{\text{nm}^2} = 0.70 \times 10^{19}\ \frac{\text{atoms}}{\text{m}^2}$$

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Polymorphism

- **Two or more distinct crystal structures for the same material**: Some metals, as well as nonmetals, may have more than one crystal structure: **Polymorphism** (allotropy/polymorphism)

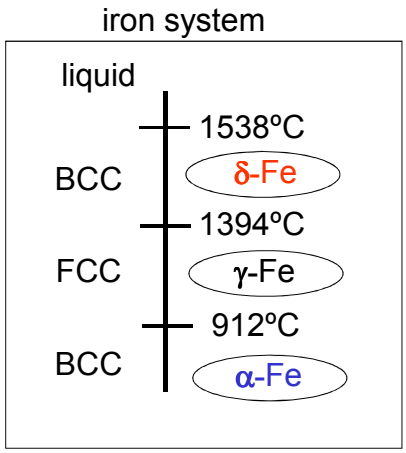
titanium

α, β-Ti

carbon

diamond, graphite

(Graphite is the stable polymorph at ambient conditions, whereas diamond is formed at extremely high pressures)



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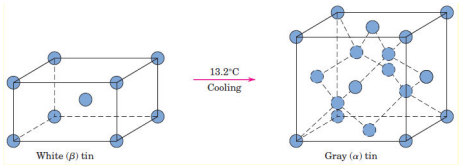
Tin (Its Allotropic Transformation) (**Sn**)



•White tin, having a body-centered tetragonal crystal structure at room temperature, transforms, at 13.2 Cº, to gray tin, which has a crystal structure similar to diamond.

The rate at which this change takes place is extremely slow; however, the lower the temperature the faster the rate. Accompanying this white tin-to-gray tin transformation is an increase in volume (27 percent), and, accordingly, a decrease in density (from 7.30 g/cm^3 to 5.77 g/cm^3). Consequently, this volume expansion results in the disintegration of the white tin metal into a coarse powder of the gray allotrope. For normal subambient temperatures, there is no need to worry about this disintegration process for tin products, due to the very slow rate at which the transformation occurs.

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Crystalline and Noncrystalline Materials

•Single Crystals:

- For a crystalline solid, when the periodic and repeated arrangement of atoms is perfect or extends throughout the entirety of the specimen without interruption, the result is a single crystal.
- All unit cells interlock in the same way and have the same orientation.
- Within the past few years, single crystals have become extremely important in many of our modern technologies, in particular electronic microcircuits, which employ single crystals of silicon and other semiconductors.

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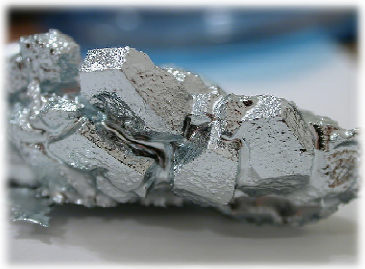
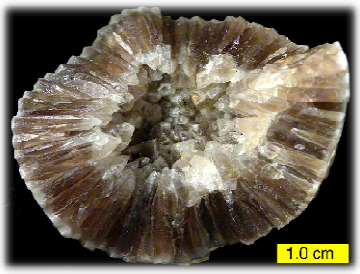


Gallium, a metal that easily forms single crystals.



Fossile shell with calsite crystals.

Garnet (*lal taşı*) single crystal.

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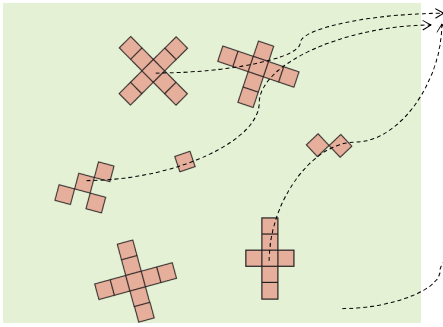
•Polycrystalline Materials:

•Most crystalline solids are composed of a collection of many small crystals or **grains;** such materials are termed **polycrystalline.**

•Initially, small crystals or nuclei form at various positions. These have random crystallographic orientations, as indicated by the square grids.



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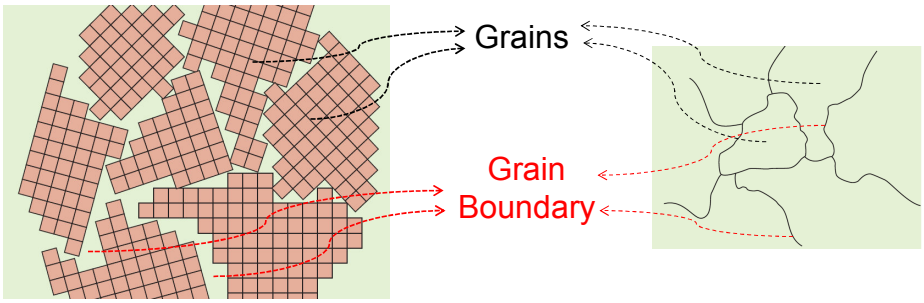
•The small grains grow by the successive addition from the surrounding liquid of atoms to the structure of each.
•Adjacent grains touch each other as the solidification process approaches completion.



•The crystallographic orientation varies from grain to grain.
• There exists some atomic mismatch within the region where two grains meet: **Grain Boundary**.

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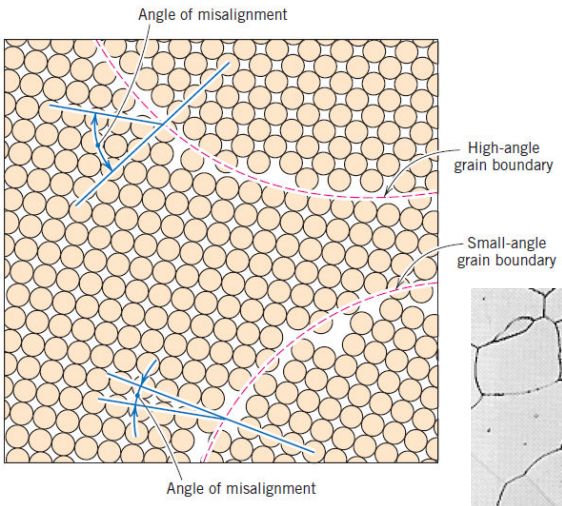
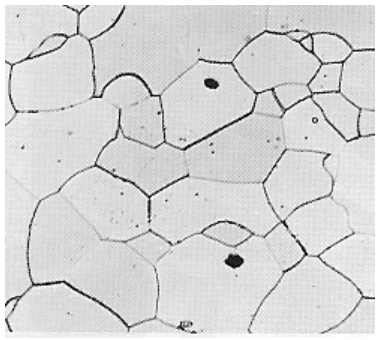
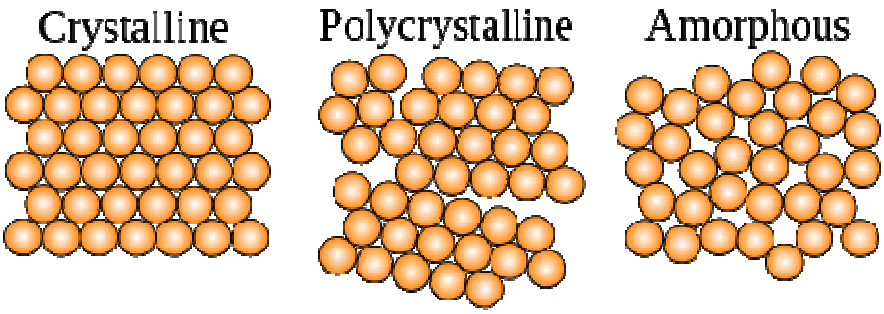

Angle of misalignment
High-angle grain boundary
Small-angle grain boundary
Angle of misalignment



53


Crystalline
Polycrystalline
Amorphous

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Crystals as Building Blocks:

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

-- The elastic modulus, the electrical conductivity, and the index of refraction may have different values in the [100] and [111] directions. This directionality of properties is termed **anisotropy**, and it is associated with the variance of atomic or ionic spacing with crystallographic direction.

-- Materials in which measured properties are independent of the direction of measurement are **isotropic.**

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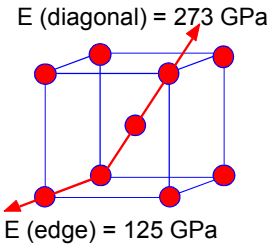
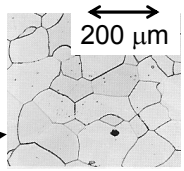
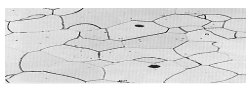
Single vs Polycrystals

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





Preferential crystallographic orientation

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Polycrystals

- *Most* engineering materials are polycrystals.

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

- 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).

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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.

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SUMMARY

- Materials can be single crystals or polycrystalline. Material properties generally 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).

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