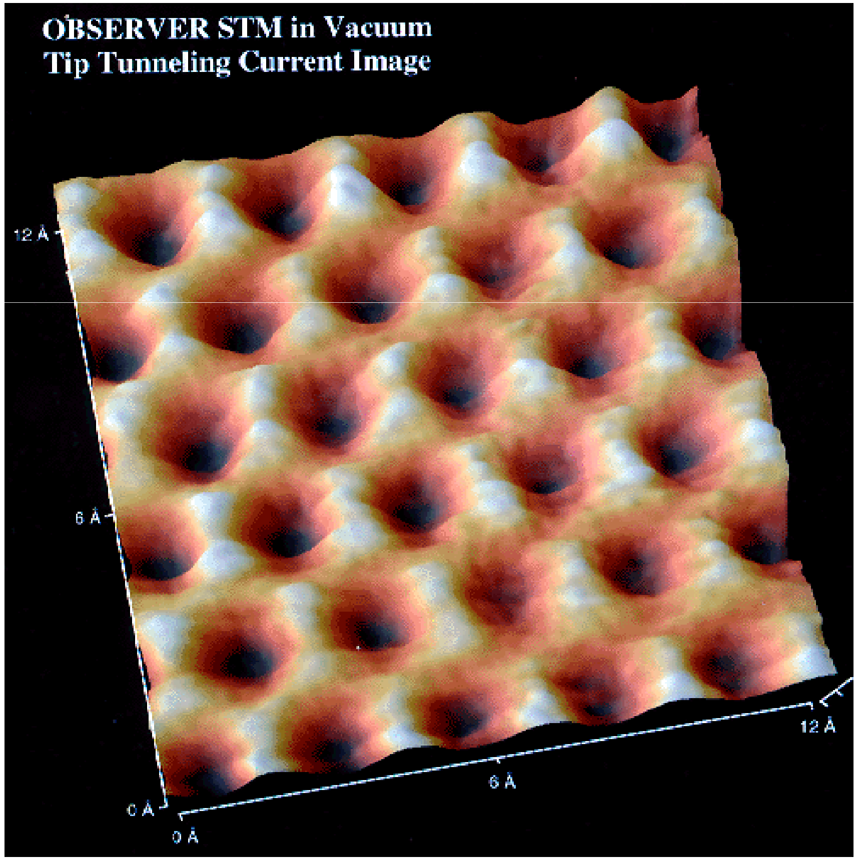
Chapter 3

The Structure of Crystalline Solids

Dr. Mubarak


OBSERVER STM in Vacuum
Tip Tunneling Current Image
12 Å
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Outline

How do atoms arrange themselves to form solids?

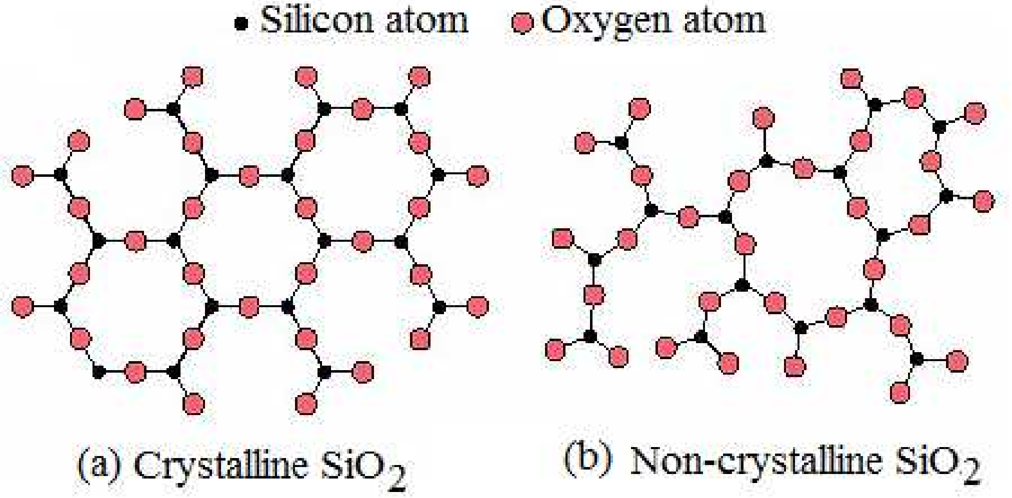
- Types of solids
    1. Single crystal
    2. Polycrystalline
    3. Amorphous
- Fundamental concepts
- Unit cells
- Crystal structures
    1. Simple cubic
    2. Face-centered cubic
    3. Body-centered cubic
    4. Hexagonal close-packed
- Close packed crystal structures
- Density computations•

Types of solids

Crystalline material: atoms self-organize in a periodic Array:

- Single crystal: atoms are in a repeating or periodic array over the entire extent of the material
- Polycrystalline material: comprised of many small crystals or grains

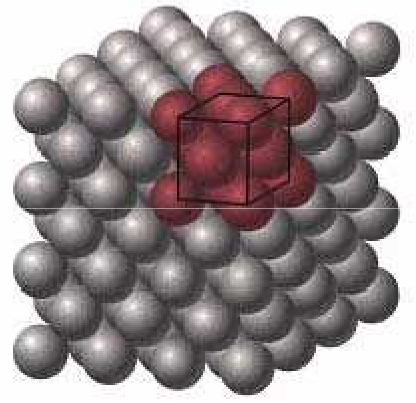
Amorphous: lacks a systematic atomic arrangement

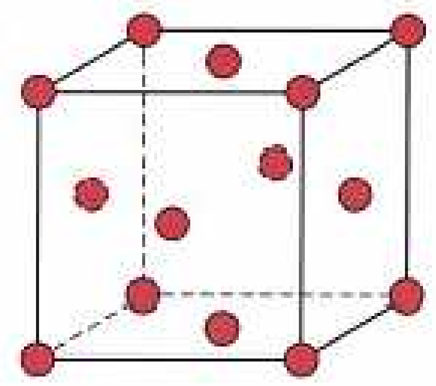


Silicon dioxide

Crystal Structure

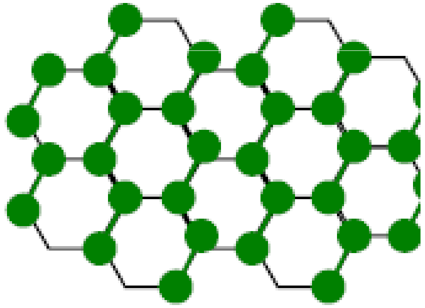
- To discuss crystalline structures it is useful to consider atoms as being hard spheres with well-defined radii.
- In this hard-sphere model, the shortest distance between two like atoms is one diameter.
- We can also consider crystalline structure as a lattice of points at atom/sphere centers.



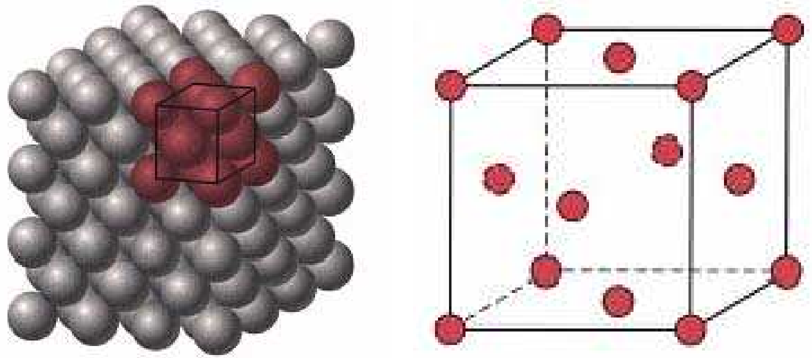


Unit Cell

- The unit cell is the smallest structural unit or building block that can describe the crystal structure.
- Repetition of the unit cell generates the entire crystal.
- Example: 2D honeycomb net can be represented by translation of two adjacent atoms that form a unit cell for this 2D crystalline structure

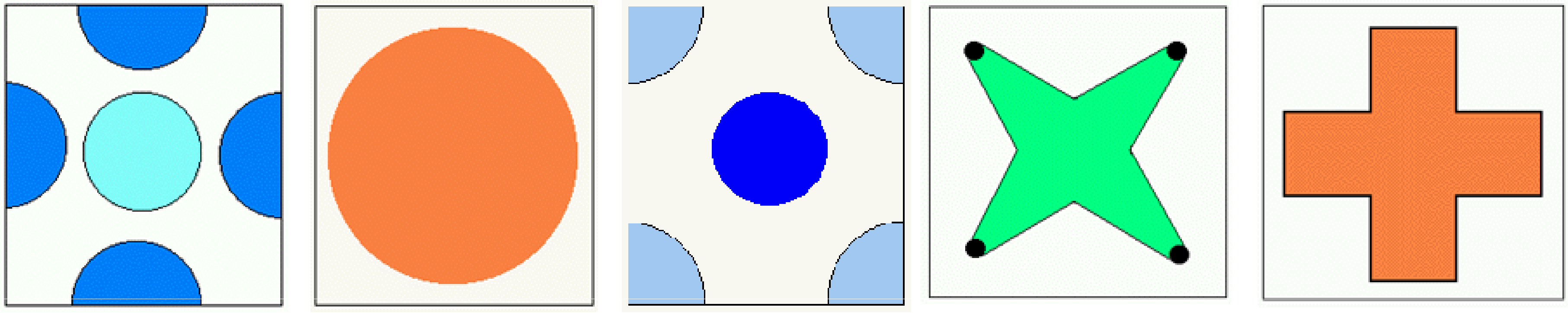


Example of 3D crystalline structure:

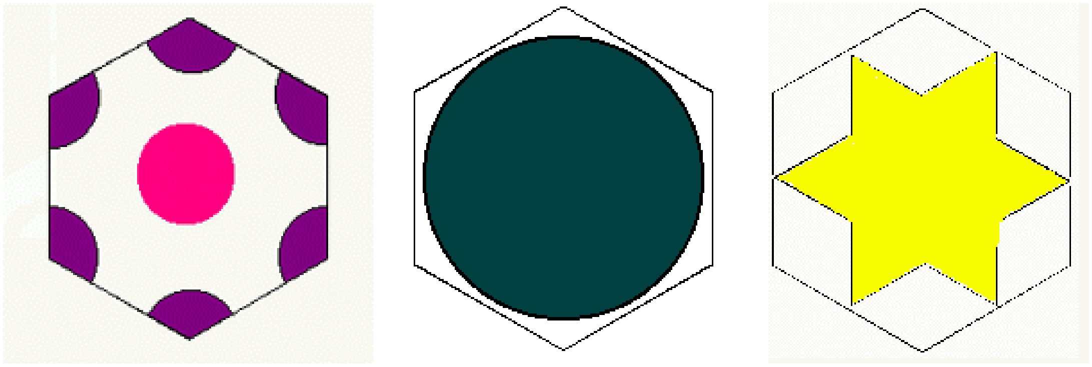


Different choices of unit cells are possible, for example:

- A square unit cell may contain any of the following object patterns.



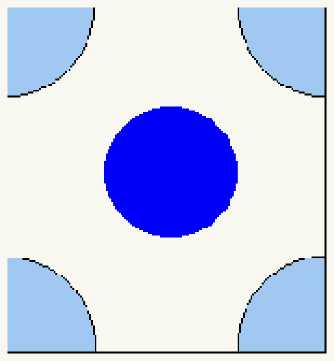
- One hexagonal unit cell might look like any of the following.



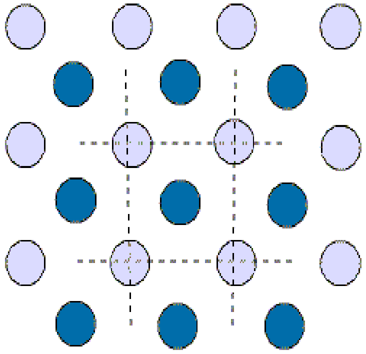
CRYSTAL LATTICES

- A crystal is a repeating array. In describing this structure we must distinguish between the pattern of repetition (the lattice type) and what is repeated (the unit cell).
- The most fundamental property of a crystal lattice is its symmetry. If we initially limit ourselves to 2 dimensions for simplicity, three types are present:

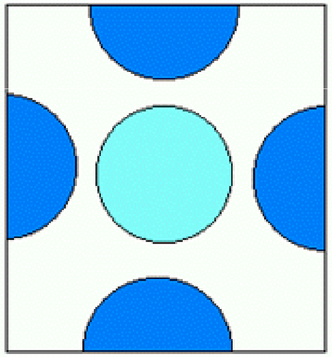
1. **Squares**
2. **Rectangles**
3. **Hexagons**



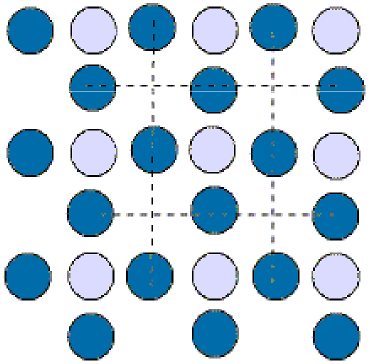
unit cell



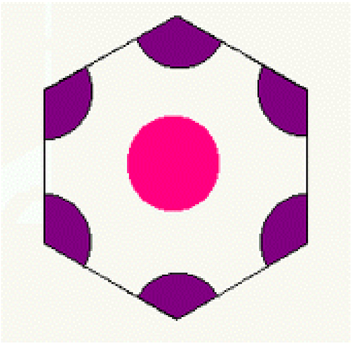
lattice



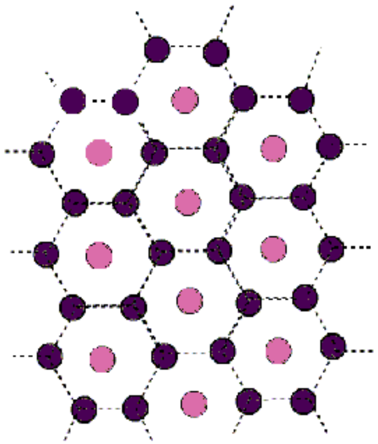
unit cell



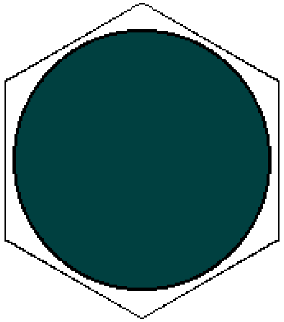
lattice



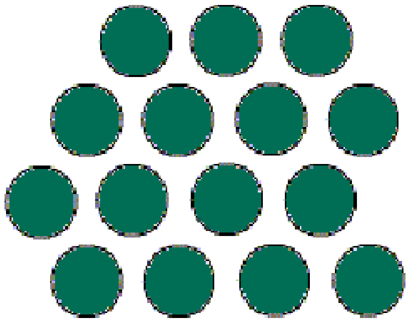
unit cell



lattice



unit cell



lattice

Metallic Crystal Structures

- Metals tend to be densely packed.
- Reasons for dense packing:

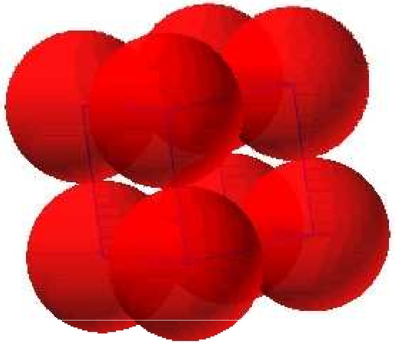
  - Typically, only one element is present, so all atomic radii are the same.
  - Metallic bonding is not directional.
  - Nearest neighbor distances tend to be small in order to lower bond energy.

- Have the simplest crystal structures.

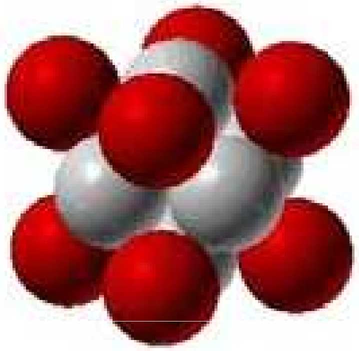
- Metals are usually (poly)crystalline.
- Although formation of amorphous metals is possible by rapid cooling.
- The atomic bonding in metals is non-directional ⇒ no restriction on numbers or positions of nearest-neighbor atoms ⇒ large number of nearest neighbors and dense atomic packing.
- Atom (hard sphere) radius, R, defined by ion core radius - typically 0.1 - 0.2 nm

The most common types of unit cells are:

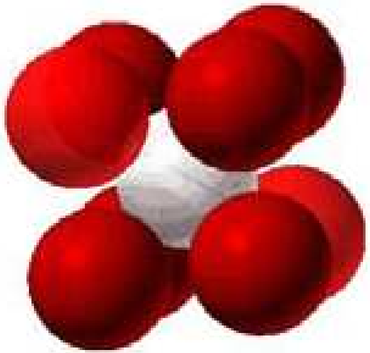
1- The simple cubic (SC)



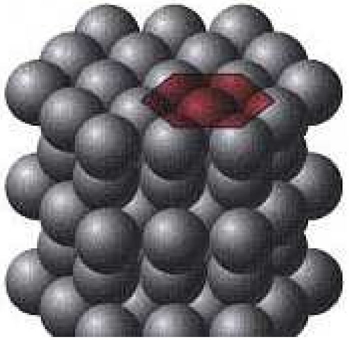
2- The faced centered cubic (FCC).



3- The body-centered cubic (BCC)

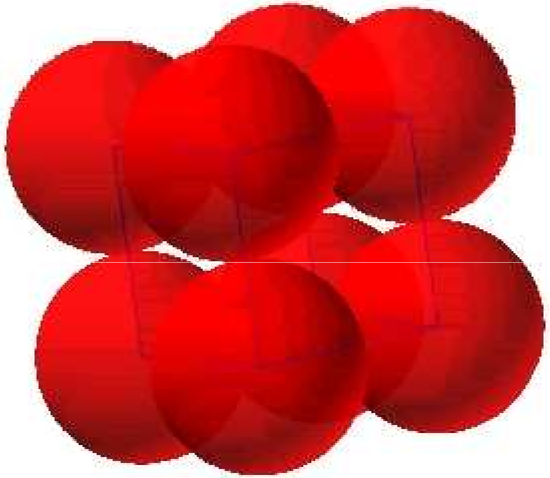


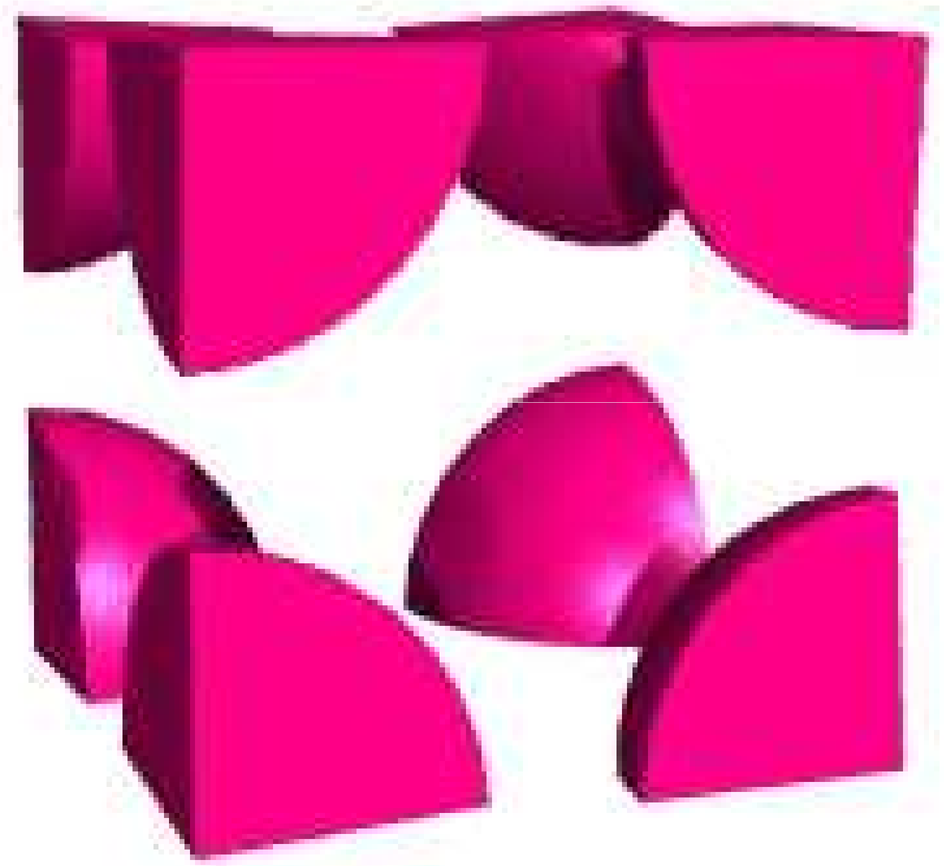
4- The hexagonal close-packed (HCP).



SIMPLE CUBIC METAL

- Rare due to low packing density.
- Only Po has this structure.
- Close-packed directions are cube edges.
- In a metal the atoms are all identical, and most are spherical (the bonding does not depend on direction).
- Metals thus tend to adopt relatively simple structures. The simplest is simple cubic.





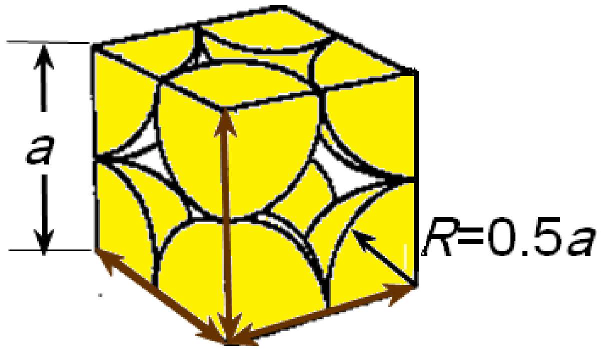
Animation

Coordination number = 6 atoms

Number of atoms per unit cell:

= 8 corners x 1/8

= 1 atoms



close-packed directions

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

In 3-D the packing efficiency is given by :

P.E. = (Volume of spheres) / (volume of cell)

For a simple cubic lattice, this is:

$$\text{Volume of sphere} = \frac{1}{8} \times 8 \times \frac{4}{3} \times \frac{22}{7} \times (0.5a)^3$$

$$Volume of cell = (a)^3$$

$$\therefore P.E. = \frac{88}{168} = 0.523$$

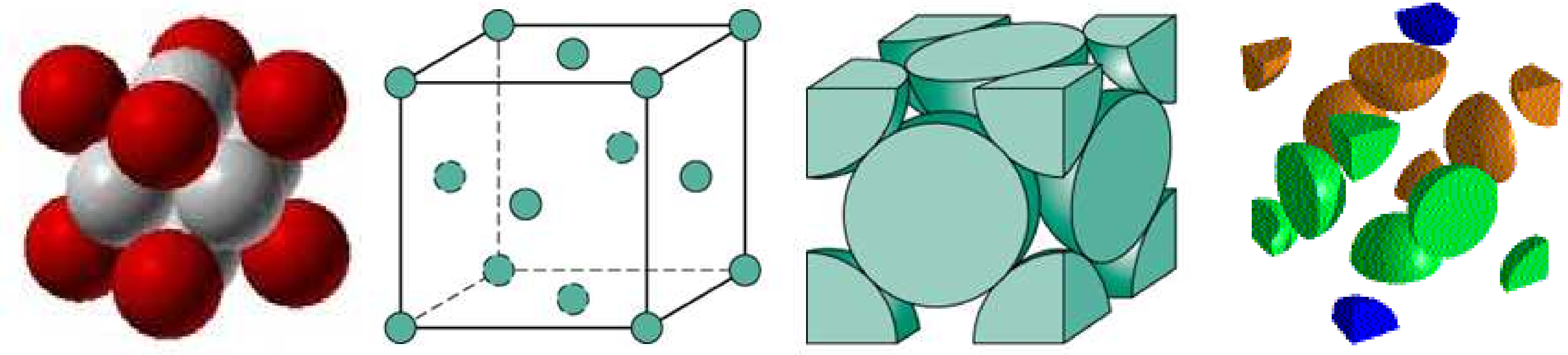
Face Centered Cubic (FCC)

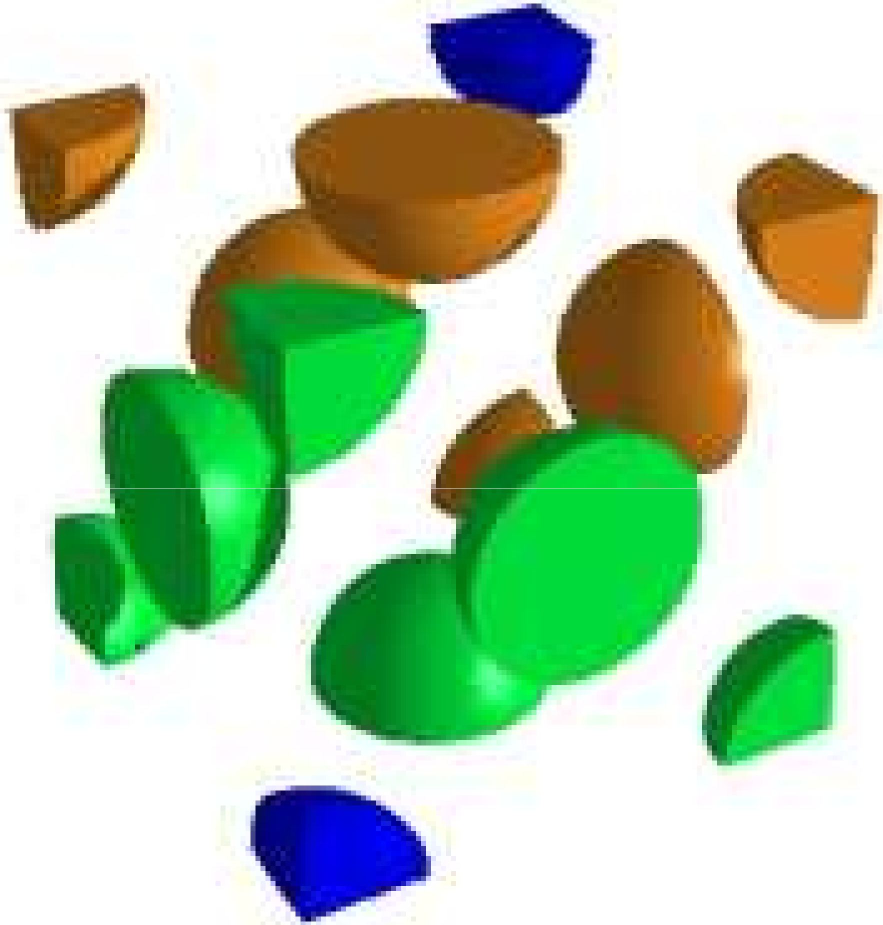
or

Cubic Close Packed (CCP)

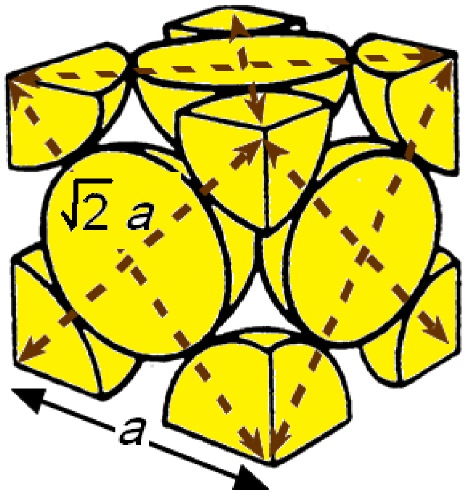
Think of this cell as being made by inserting another atom into each face of the simple cubic lattice - hence the "face centered cubic" name .

The reason for the various colors is to help point out how the cells stack in the solid .





- Atoms touch each other along face diagonals.
  Note: All atoms are identical.
- Example:
  Al, Cu, Au, Pb, Ni, Pt, Ag
- Coordination number = 12 atoms
- Number of atoms per unit cell:
  = 6 face x 1/2 + 8 corners x 1/8 = 4



In 3-D the packing efficiency is given by :
P.E. = (Volume of spheres) / (volume of cell)

For a face centered cubic lattice, this is:

$$\text{Volume of sphere} = 4 \times \frac{4}{3} \times \frac{22}{7} \times \left(\frac{\sqrt{2}a}{4} \right)^3$$

$$Volume\ of\ cell = (a)^3$$

$$\therefore P.E. = \frac{995.6}{1344} = 0.7405$$

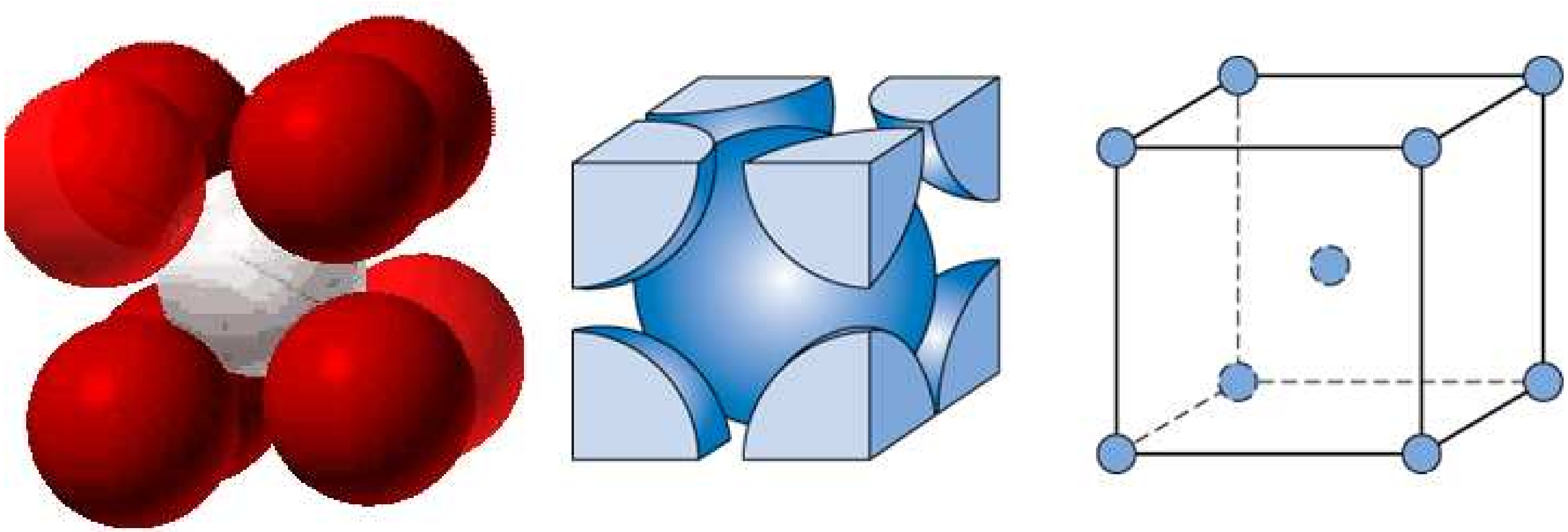
Animation

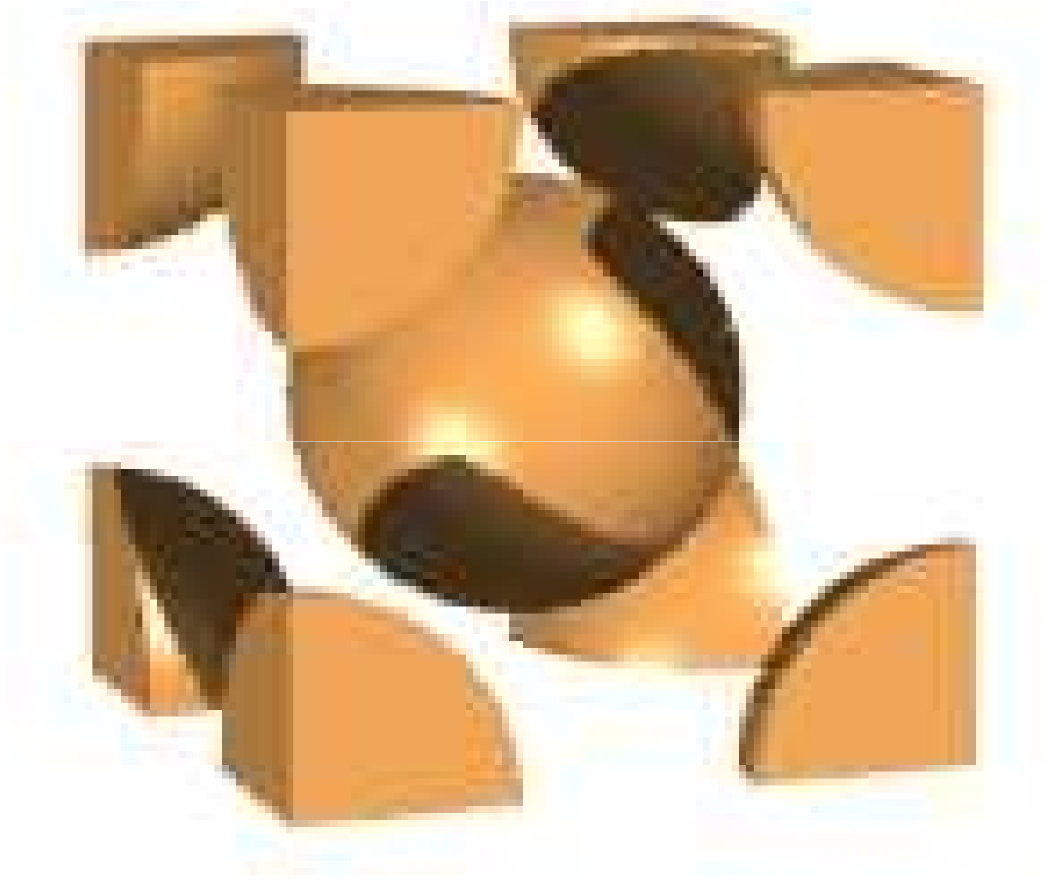
Body Centered Cubic Structure (BCC)

Think of this unit cell as made by stuffing another atom into the center of the simple cubic lattice, slightly spreading the corners.

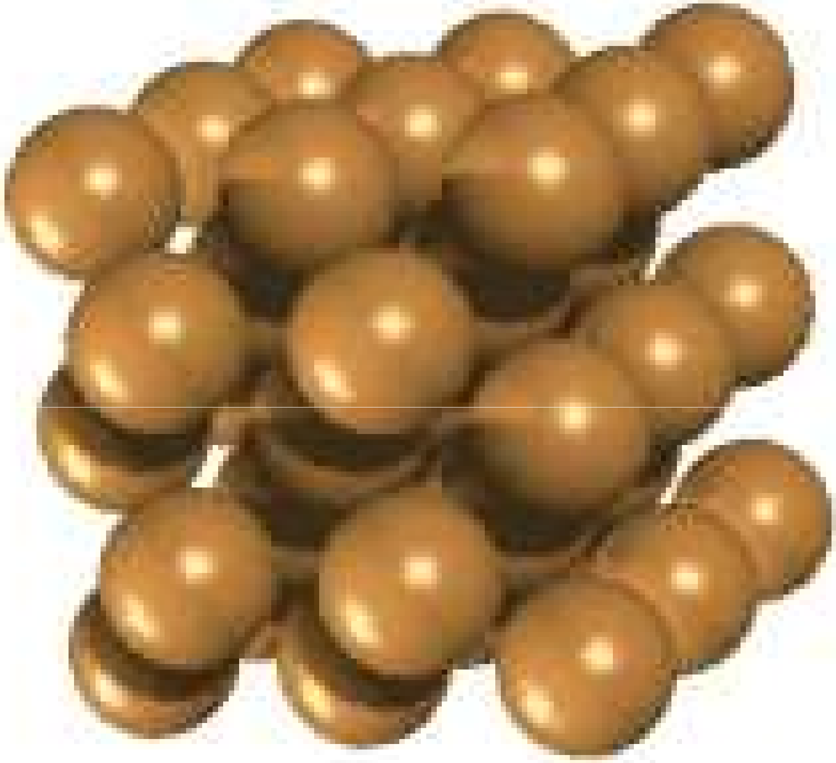
The corner spheres no longer quite touch one another, but do touch the center.

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

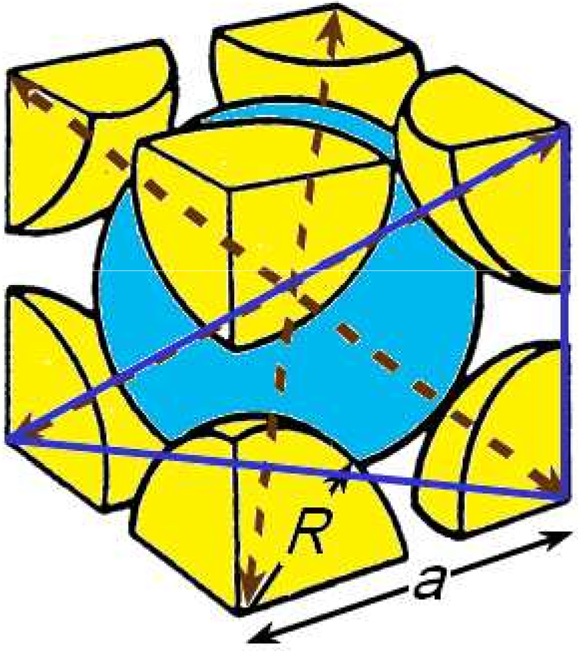




Animation



Body Centered Cubic Structure (BCC)



The hard spheres touch one another along cube diagonal

The coordination number, CN = 8

Number of atoms per unit cell, n = 2

- 1 center atom shared by no other cells: 1 x 1 = 1
- 8 corner atoms shared by eight cells: 8 x 1/8 = 1

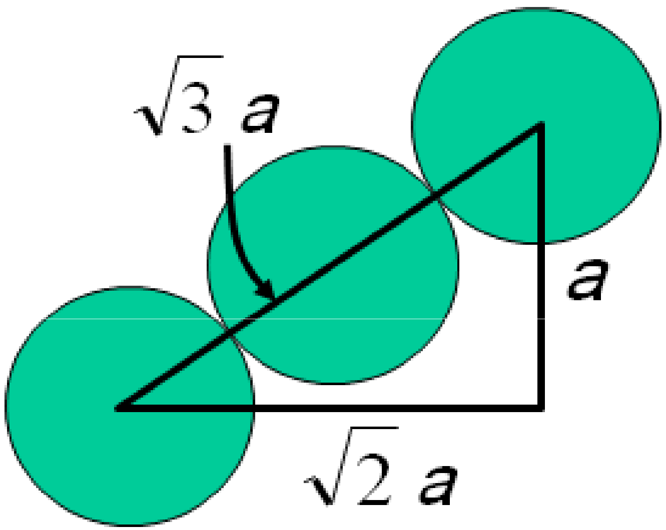
Corner and center atoms are equivalent

⇒ the cube edge length, a= 4R/√3

$$\text{Volume of sphere} = 2\times\frac{4}{3}\times\frac{22}{7}\times\left(\frac{\sqrt{3}a}{4}\right)^3$$

$$Volumeofcell = (a)^3$$

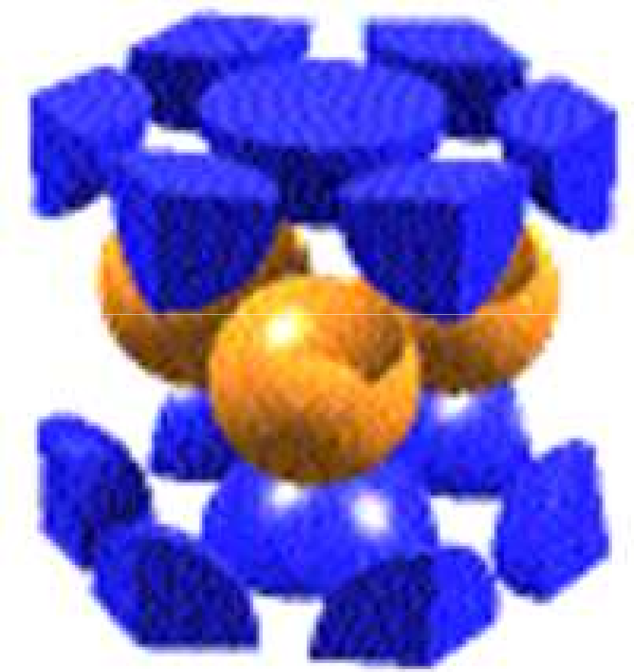
$$\therefore P.E. = \frac{914.5}{1344} = 0.6805$$



The higher coordination number and packing efficiency mean that this lattice uses space more efficiently than simple cubic.

Hexagonal Close-Packed Crystal Structure

- HCP is one more common structure of metallic crystals.
- Six atoms form regular hexagon, surrounding one atom in center.
- Another plane is situated halfway up unit cell (c-axis), with 3 additional atoms situated at interstices of hexagonal (close-packed) planes.
- Example: Cd, Mg, Zn, Ti have this crystal structure.



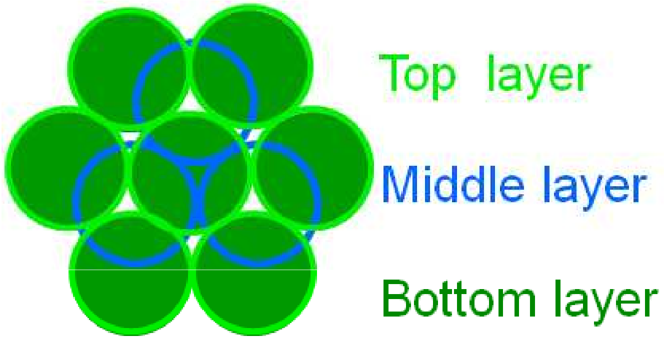
The hexagonal close packed structure can be made by piling layers in the A - B - A - B - A - B . . . . . . sequence.

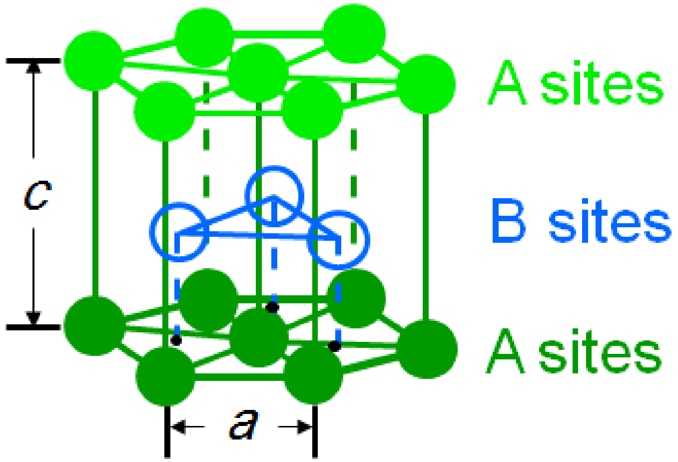
Unit cell has two lattice parameters a and c. ratio c/a = 1.633

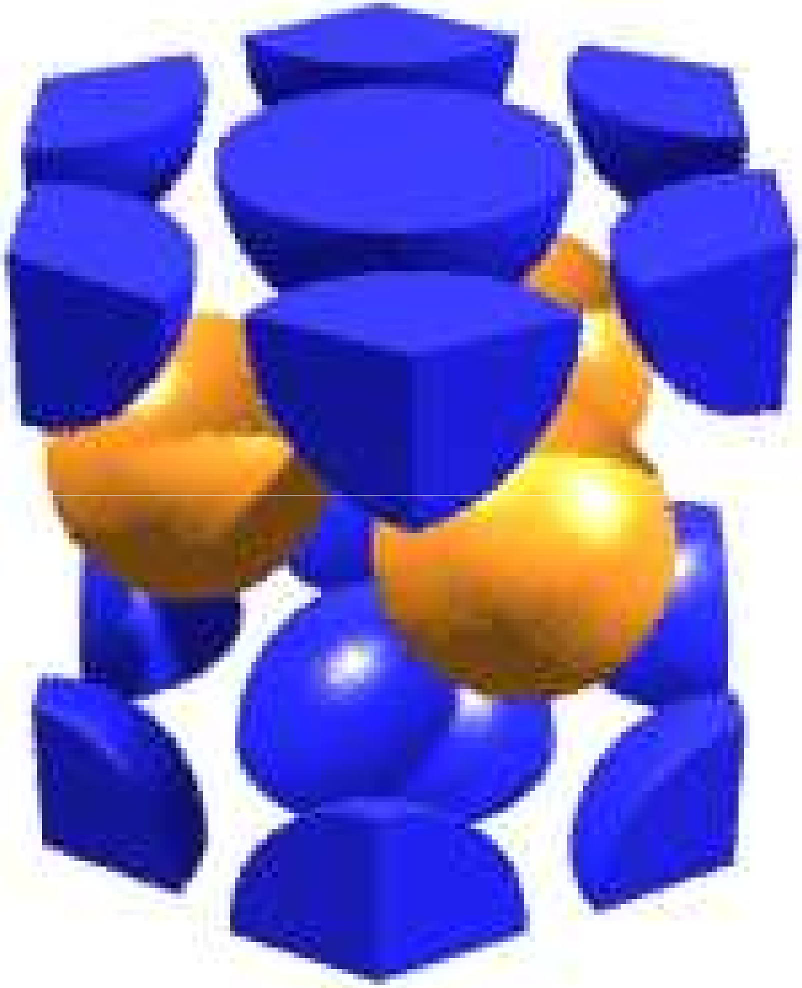
The coordination number, CN = 12

Number of atoms per unit cell, n= 6.

- 3 mid-plane atoms shared by no other cells: 3 x 1 = 3
- 12 hexagonal corner atoms shared by 6 cells: 12 x 1/6 = 2
- 2 top/bottom plane center atoms shared by 2 cells: 2 x 1/2 = 1







$$Volume\ of\ \ spheres = 6 \times \frac{4}{3} \times \frac{22}{7} r^3$$

$$= 25.14286 r^3$$

$$Volume\ of\ \ unit\ cell\ \ = 24\sqrt{2} r^3$$

$$Packing\ \ factor = 0.7405$$

Density Computations

Since the entire crystal can be generated by the repetition of the unit cell, the density of a crystalline material,

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

$$\rho = \frac{nA}{V_C N_A}$$

Where: n = number of atoms/unit cell

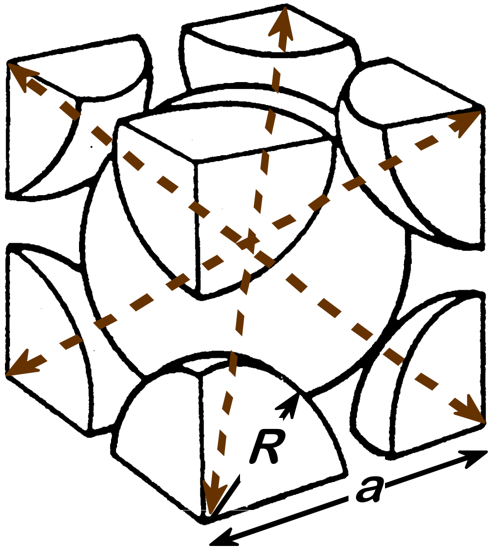
A = atomic weight

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

N_A = Avogadro's number

= 6.023 x 1023 atoms/mol

Theoretical Density, ρ



- Ex: Cr (BCC)

  $A = 52.00$ g/mol

  $R = 0.125$ nm

  $n = 2$

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

$$\rho = \frac{2 \quad 52.00}{a^3 \quad 6.023 \times 10^{23}}$$

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

$\frac{\text{g}}{\text{mol}}$

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

$\frac{\text{atoms}}{\text{mol}}$

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

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

Densities of Material Classes

In general

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

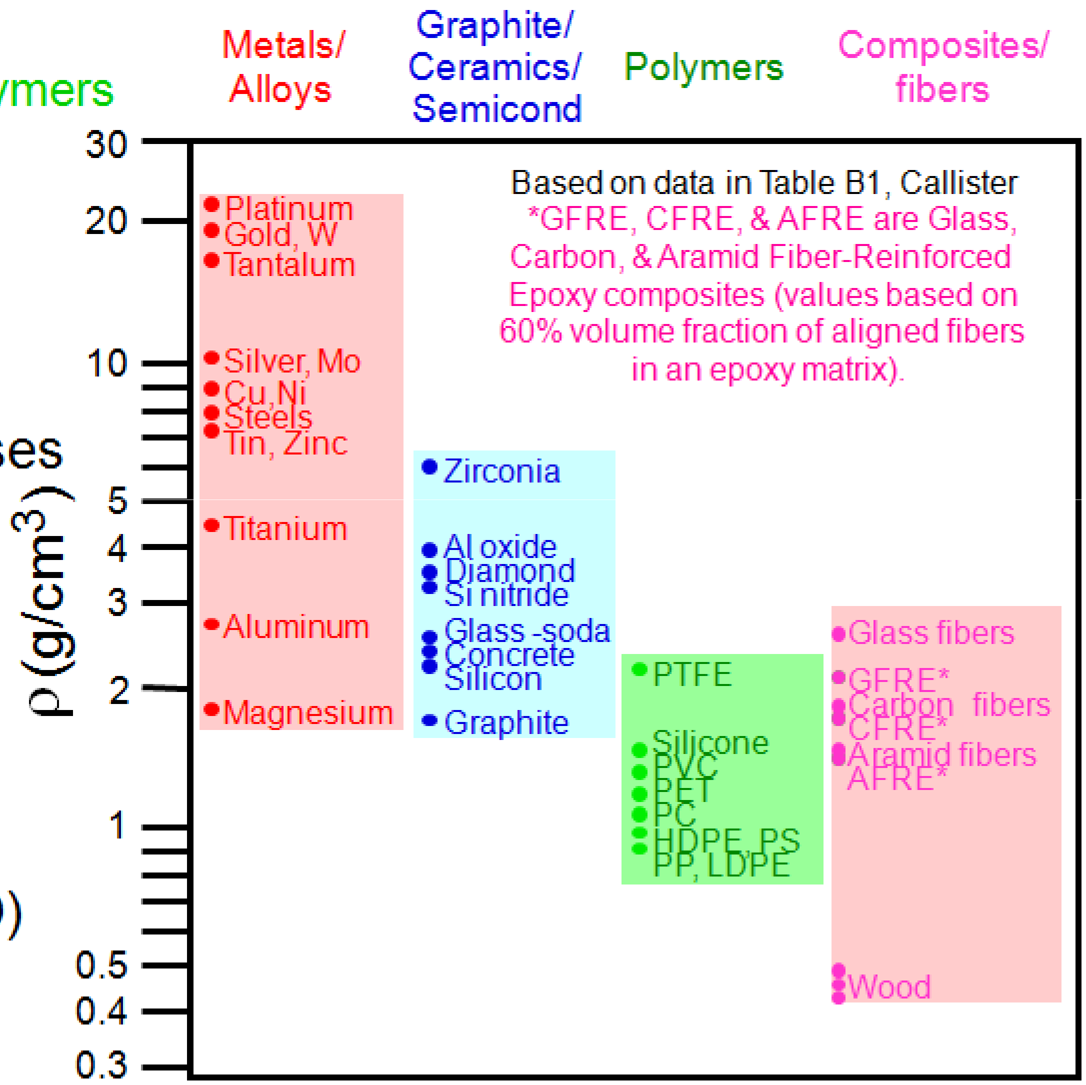
Why?

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



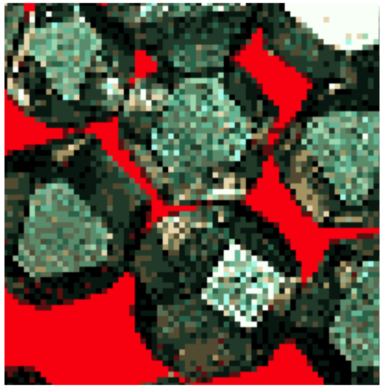
Based on data in Table B1, Callister

*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

- Properties of crystalline materials often related to crystal structure.

Ex: Quartz fractures more easily along some crystal planes than others.

Polycrystalline Materials

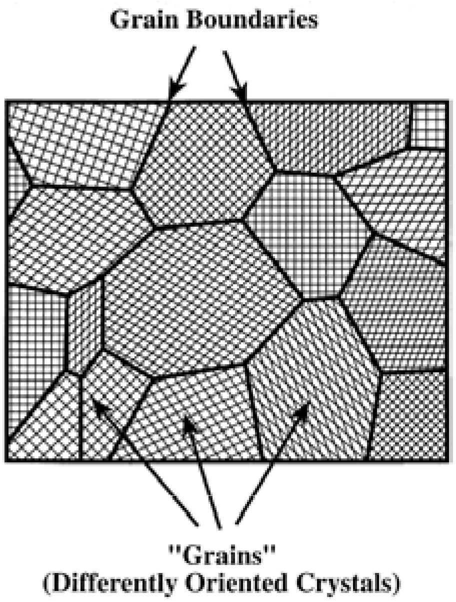
- Most engineering materials are polycrystals.

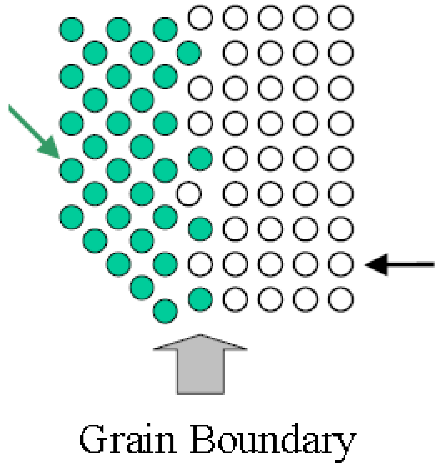
- In polycrystalline materials, grain orientations are random, so bulk material properties are isotropic
- Some polycrystalline materials have grains with preferred orientations (texture), so properties are dominated by those relevant to the texture orientation

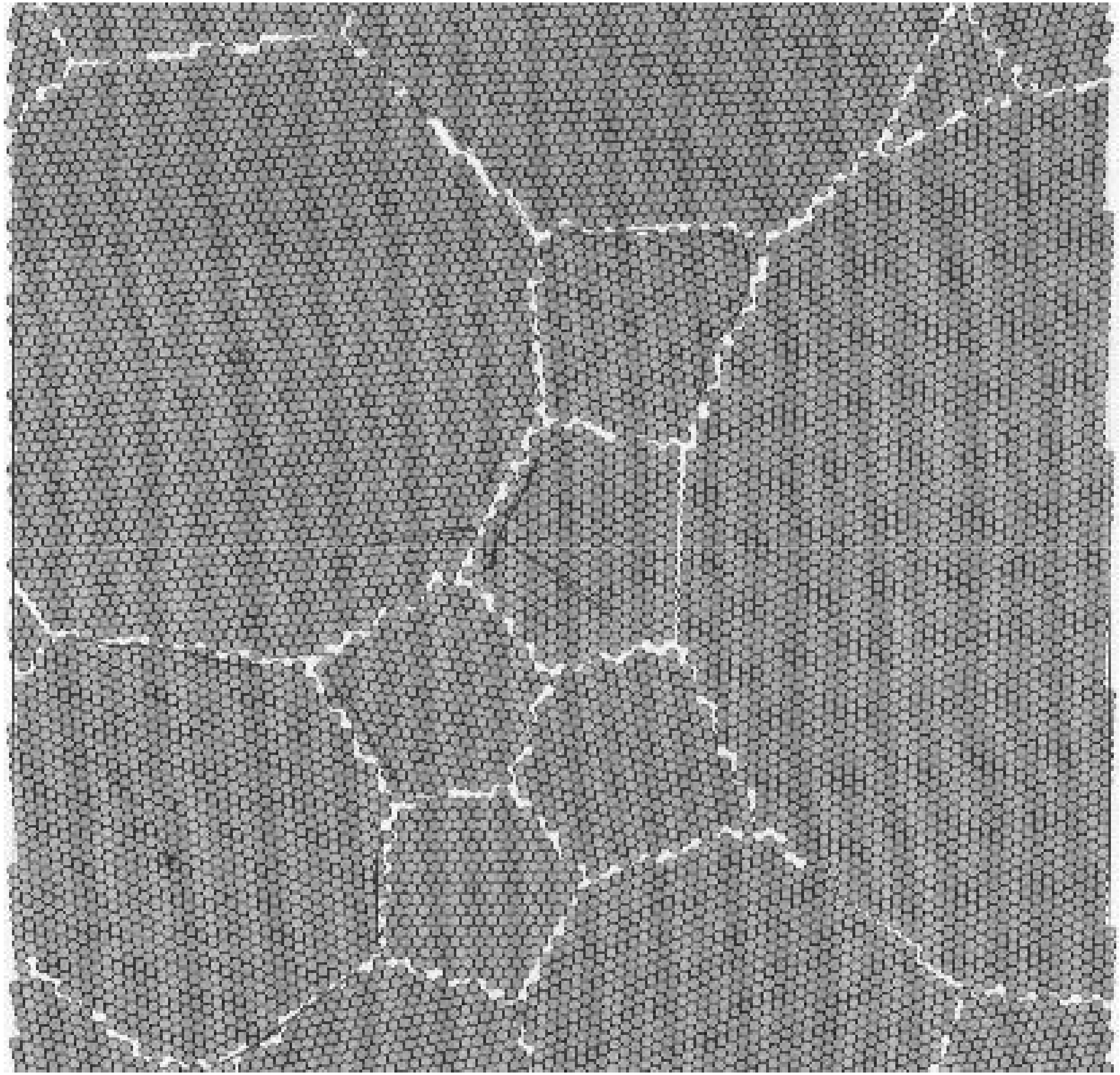
- If grains are randomly oriented, overall component properties are not directional.

Single Crystals and Polycrystalline Materials

- Single crystal: atoms are in a repeating or periodic array over the entire extent of the material.
- Polycrystalline material: comprised of many small crystals or grains. The grains have different crystallographic orientation.
- There exist atomic mismatch within the regions where grains meet. These regions are called grain boundaries.

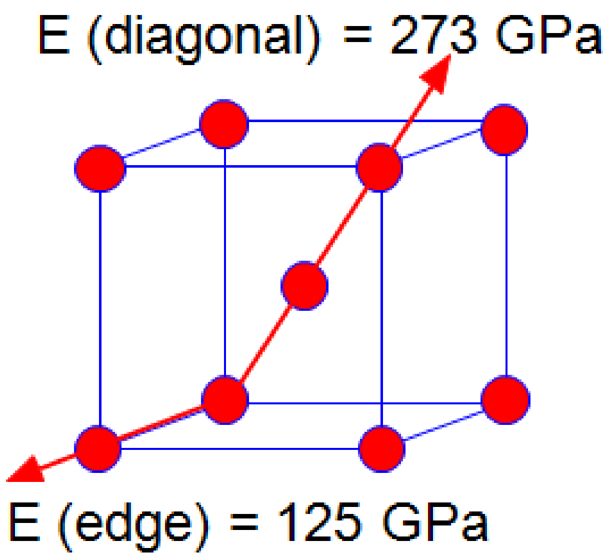




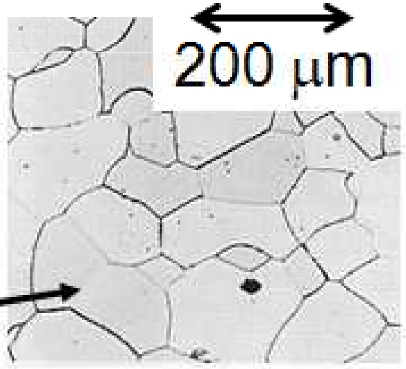


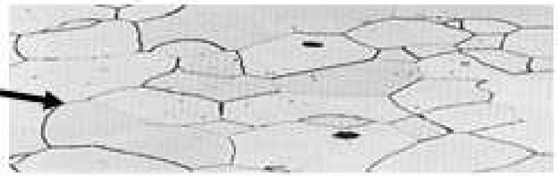
Polycrystalline Materials

- 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.





Anisotropic exhibiting properties with different values when measured along axes in different directions.

Isotropic exhibiting properties with the same values when measured along axes in all directions.

Anisotropy

- Different directions in a crystal have different packing.
- For instance, atoms along the edge of FCC unit cell are more separated than along the face diagonal.
- This causes anisotropy in the properties of crystals, for instance, the deformation depends on the direction in which a stress is applied.

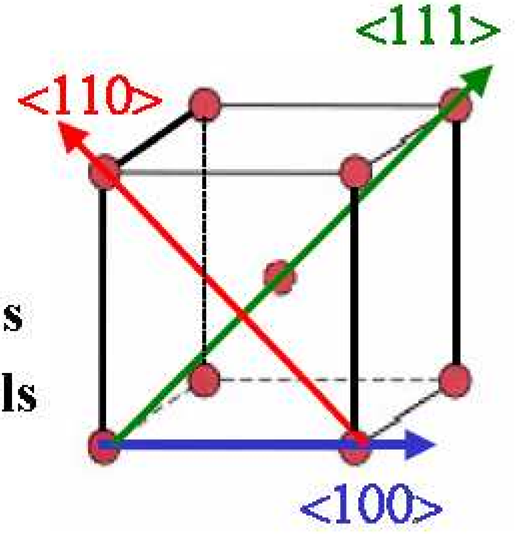
Anisotropy

- In some polycrystalline materials, grain orientations are random, so bulk material properties are isotropic
- Some polycrystalline materials have grains with preferred orientations (texture), so properties are dominated by those relevant to the texture orientation and the material exhibits anisotropic properties.

Anisotropy

Properties of crystals may be different along different directions, because atomic periodicities are different. E.g. in single crystal cubic system:

- <100> Cube edges
- <110> Face diagonals
- <111> Body diagonals



Polymorphism and Allotropy

- Some materials may exist in more than one crystal structure, this is called **polymorphism**.
- If the material is an elemental solid, it is called **allotropy**.
- Allotropy means the existence of a substance in two or more different forms in the same phase.
- An example of allotropy is carbon, which can exist as diamond, graphite, and amorphous carbon.

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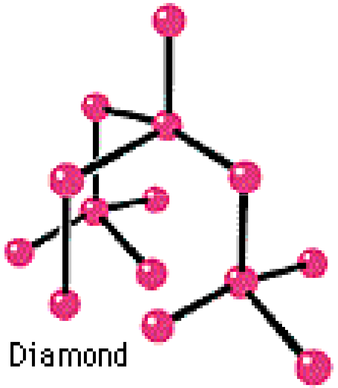
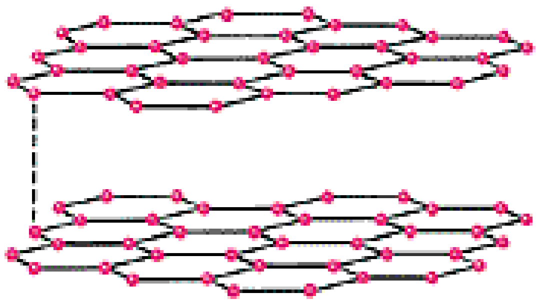
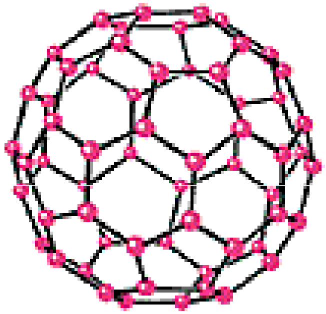
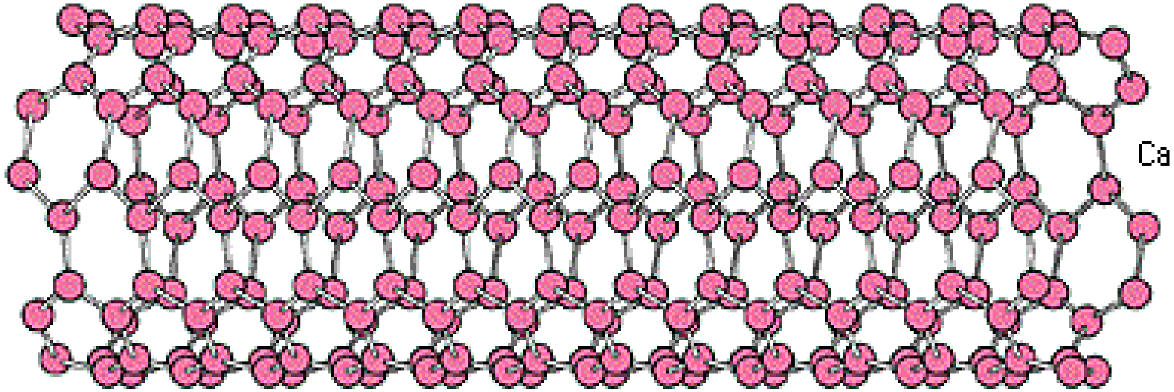
- An example of allotropy is carbon, which can exist as diamond, graphite, and amorphous carbon.

Pure, solid carbon occurs in three crystalline forms – diamond, graphite; and large, hollow **fullerenes**. Two kinds of fullerenes are shown here: buckminsterfullerene (buckyball) and carbon nanotube.


Diamond

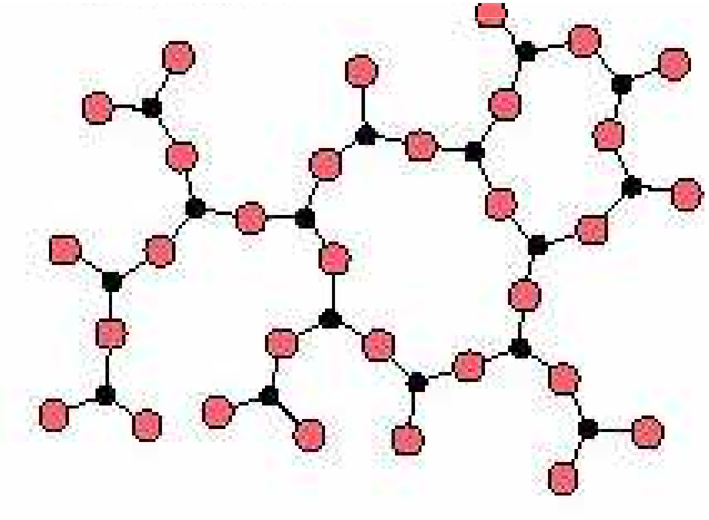

Graphite


Buckminsterfullerene

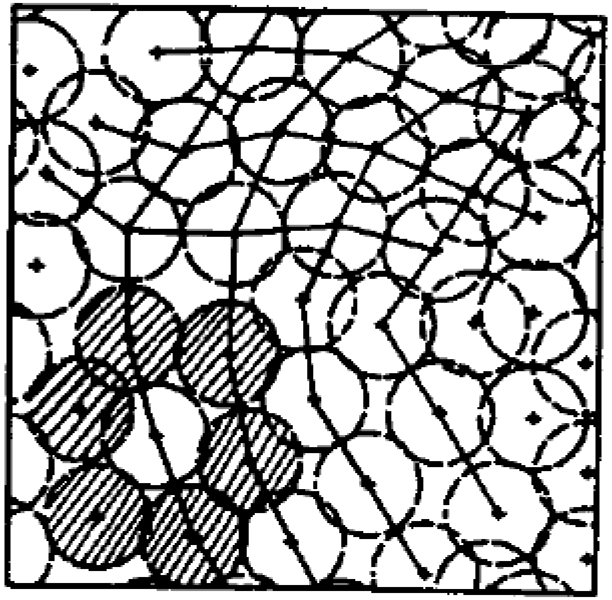

Carbon nanotube

Non-Crystalline (Amorphous) Solids

- In amorphous solids, there is no long-range order.
- But amorphous does not mean random, in many cases there is some form of short-range order.



Schematic picture of amorphous SiO_2 structure



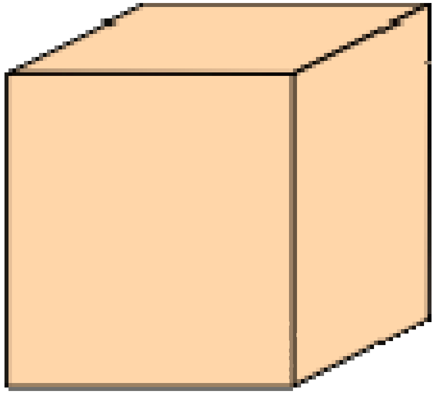
Amorphous structure

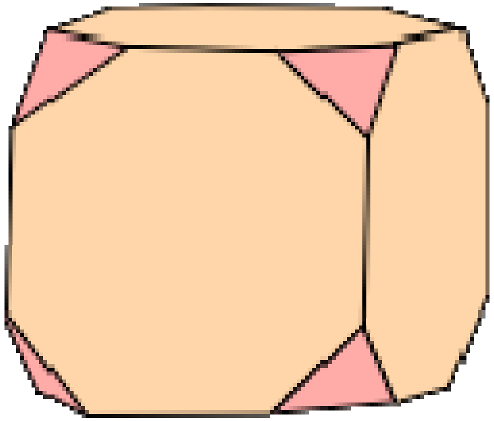
Crystallographic Points, Directions, and Planes.

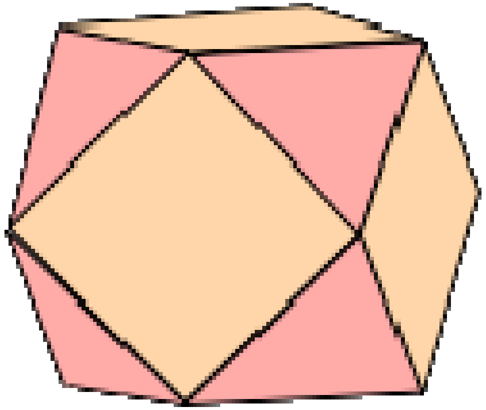
How to define points, directions, planes, as well as linear, planar, and volume densities.

- Points (atomic positions)
- Vectors (defines a particular direction - plane normal)
- Miller Indices (defines a particular plane)
- relation to diffraction
- 3-index for cubic and 4-index notation for HCP

Symmetry Equivalent Directions


①


②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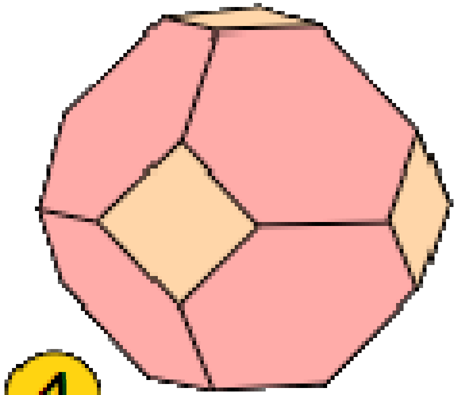
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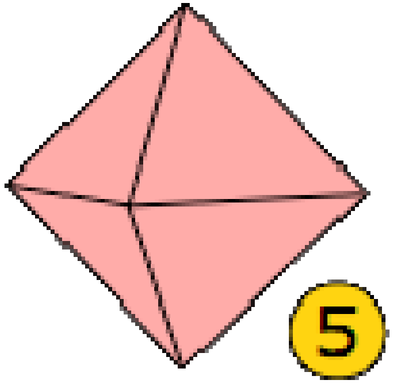
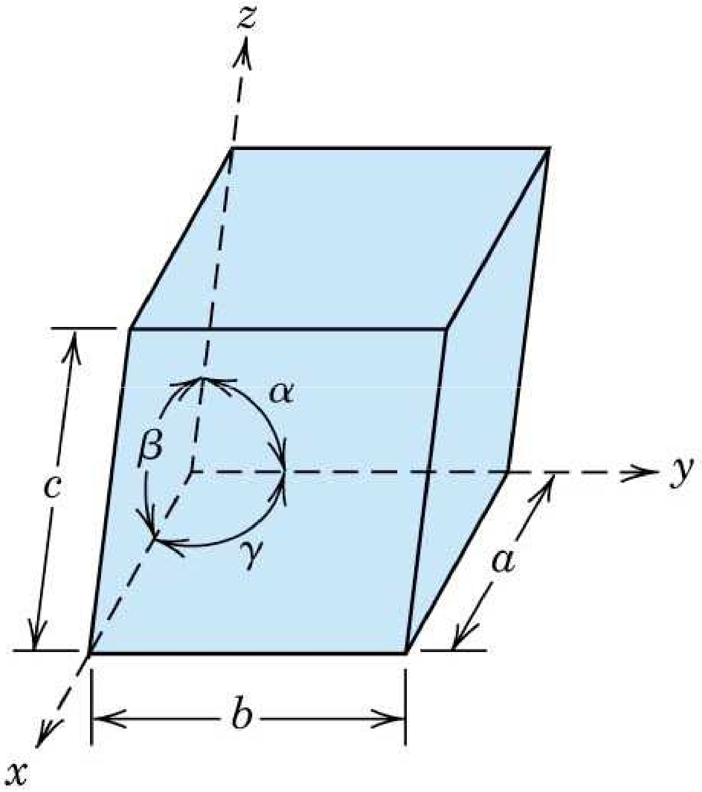

⑤

All periodic unit cells may be described via these vectors and angles, if and only if

- a, b, and c define axes of a 3D coordinate system.
- coordinate system is Right-Handed.
- We can define points, directions and planes with a “triplet” of numbers in units of a, b, and c unit cell vectors.
- For HCP we need a “quad” of numbers.

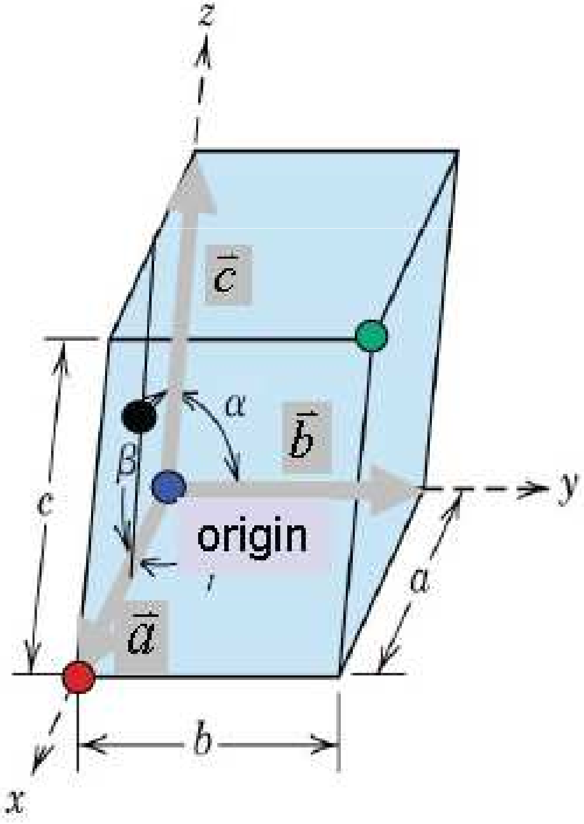


POINT Coordinates

To define a point within a unit cell….
Express the coordinates uvw as fractions of unit cell vectors a, b, and c (so that the axes x, y, and z do not have to be orthogonal).

pt. coord.

pt.	**x (*a*)**	**y (*b*)**	**z (*c*)**
🔵	0	0	0
🔴	1	0	0
🟢	1	1	1
⚫	1/2	0	1/2

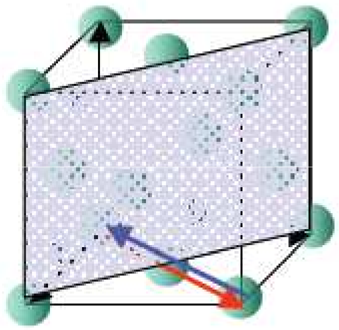


Point Coordinates

Procedure:

1. Any line (or vector direction) is specified by 2 points.
    - The first point is, typically, at the origin (000).
2. Determine length of vector projection in each of 3 axes in units (or fractions) of a, b, and c.

X (a)	Y(b)	Z(c)
1	1	0



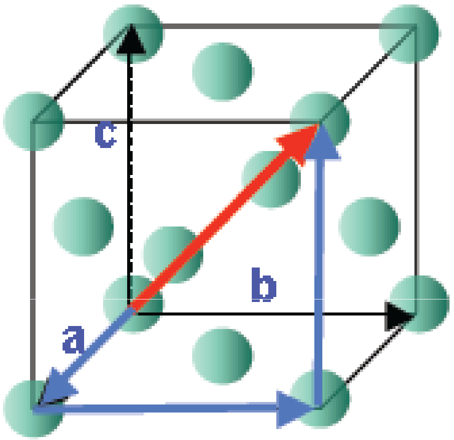
3. Multiply or divide by a common factor to reduce the lengths to the smallest integer values, u v w.
4. Enclose in square brackets: [u v w]: [110] direction.
5. Designate negative numbers by a bar $\left[\bar{1}\,\bar{1}\,0\right]$

- Pronounced "bar 1", "bar 1", "zero" direction.

6. "Family" of [110] directions is designated as <110>.

Point Coordinates

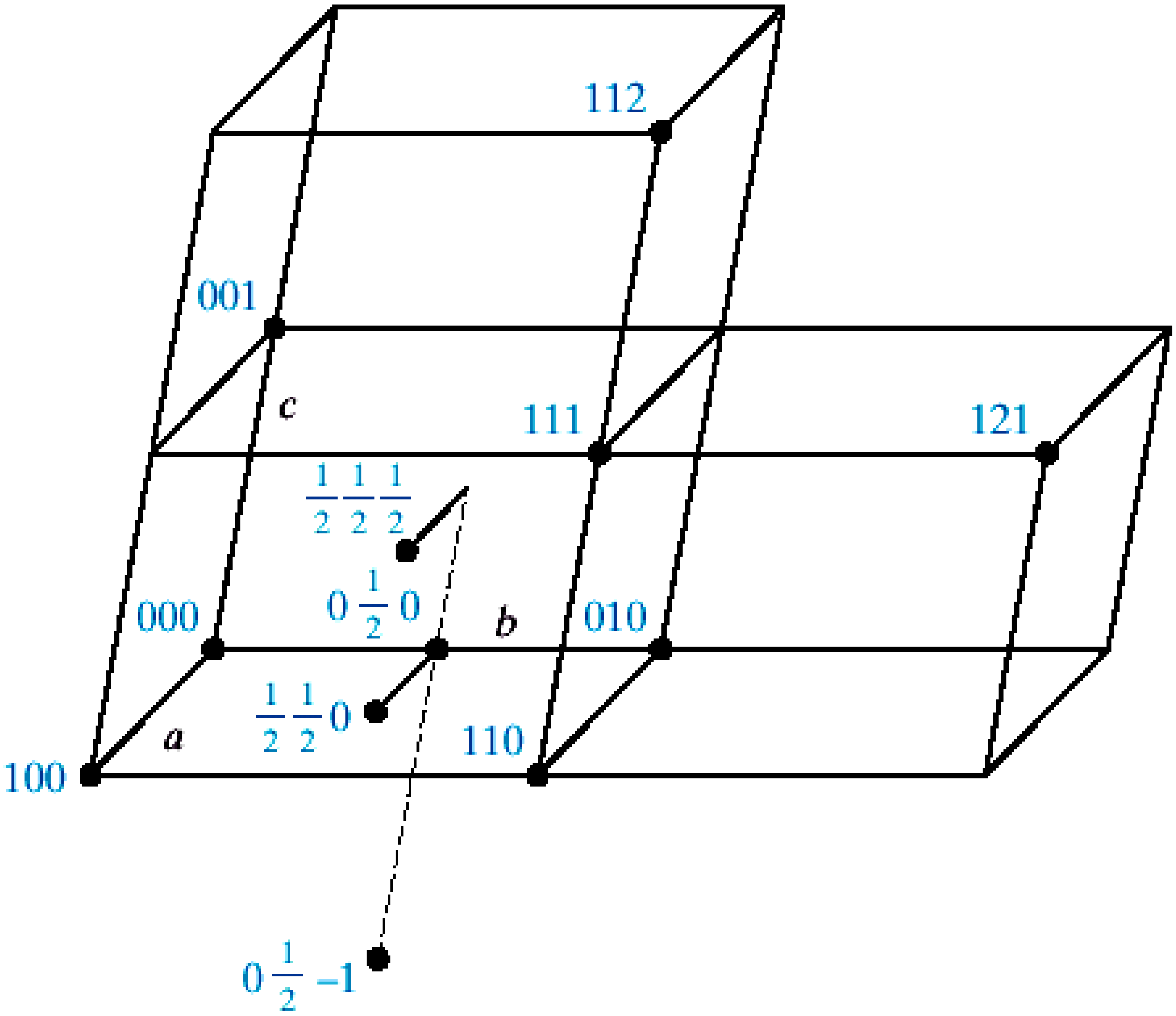
Example 1: What is crystallographic direction?



Magnitude along

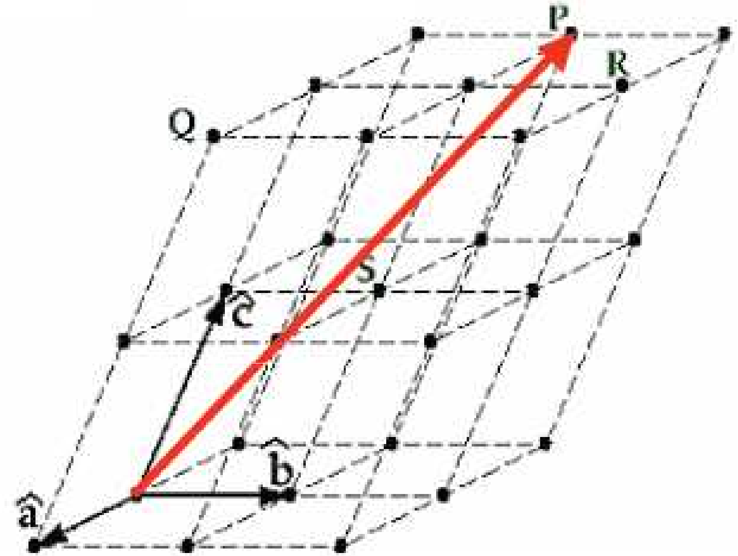
Along x: 1 a	X
Along y: 1 b	Y
Along z: 1 c	Z

DIRECTION = [1 1 1]


112
001
c
111
121
$\frac{1}{2}\frac{1}{2}\frac{1}{2}$
000
$0\frac{1}{2}0$
b
010
$\frac{1}{2}\frac{1}{2}0$
a
110
100
$0\frac{1}{2}-1$

Point Coordinates

Example 2:



(a) What is the lattice point given by point P?

$[\bar{1}12]$

(b) What is crystallographic direction for the origin to P?

$[\bar{1}12]$

Example 3: What lattice direction does the lattice point **264** correspond?

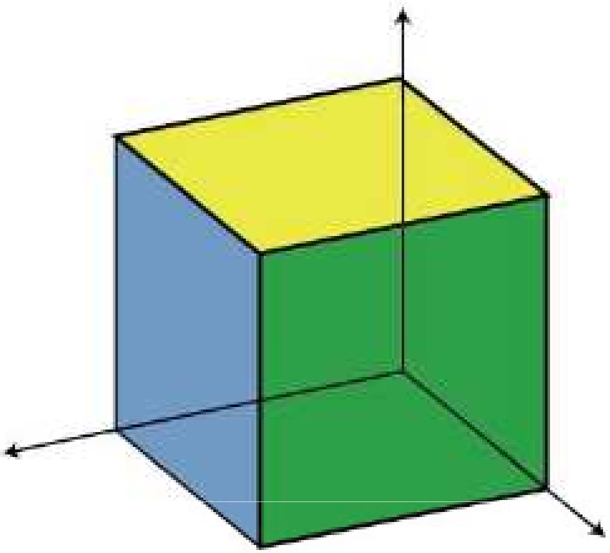
The lattice direction [132] from the origin.

Symmetry Equivalent Directions

Note: for some crystal structures, different directions can be equivalent.

e.g. For cubic crystals, the directions are all equivalent by symmetry:

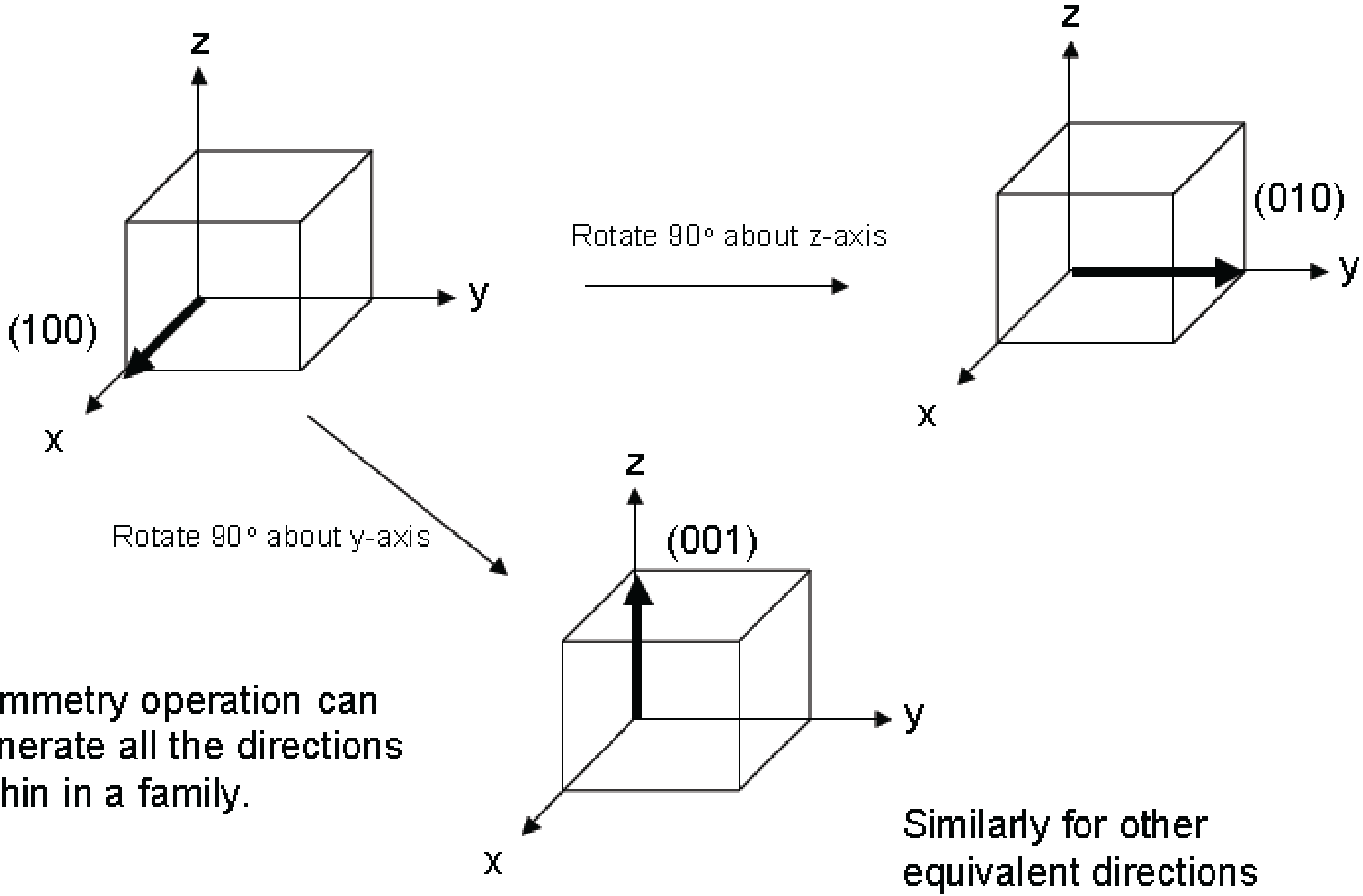
[1 0 0], [$\bar{1}$ 0 0], [0 1 0], [0 $\bar{1}$ 0], [0 0 1], [0 0 $\bar{1}$]



Families of crystallographic directions
e.g. <1 0 0>

Angled brackets denote a family of crystallographic directions.

Symmetry Equivalent Directions



Symmetry operation can generate all the directions within in a family.

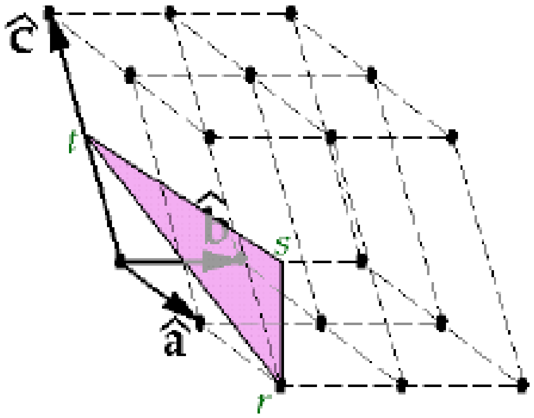
Similarly for other equivalent directions

How Do We Designate Lattice Planes?

Crystallographic Planes

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

- Algorithm
  1. 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*)



Planes intersects axes at:

- a axis at r= 2
- b axis at s= 4/3
- c axis at t= 1/2

How do we symbolically designate planes in a lattice?

Possibility #2: THE ACCEPTED ONE

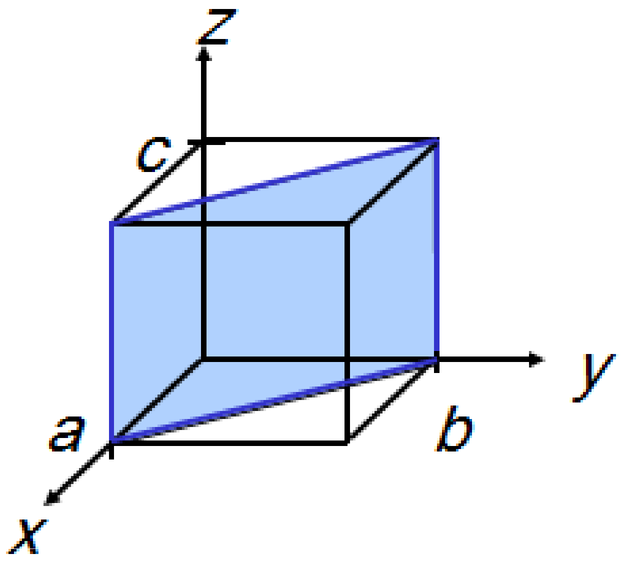
1. Take the reciprocal of r, s, and t.
   - Here: 1/r = 1/2 , 1/s = 3/4 , and 1/r = 2
2. Find the *least common multiple* that converts all reciprocals to integers.
   - With LCM = 4, h = 4/r = 2 , k= 4/s = 3 , and l= 4/r = 8
3. Enclose the new triple (h,k,l) in parentheses: (238)
4. This notation is called the Miller Index.

** Note: If a plane does not intercept an axes (I.e., it is at ∞), then you get 0.*

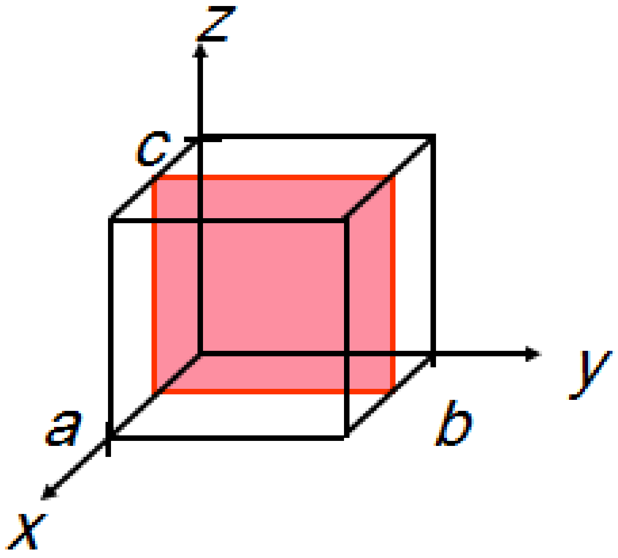
** Note: All parallel planes at similar staggered distances have the same Miller index.*

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)		



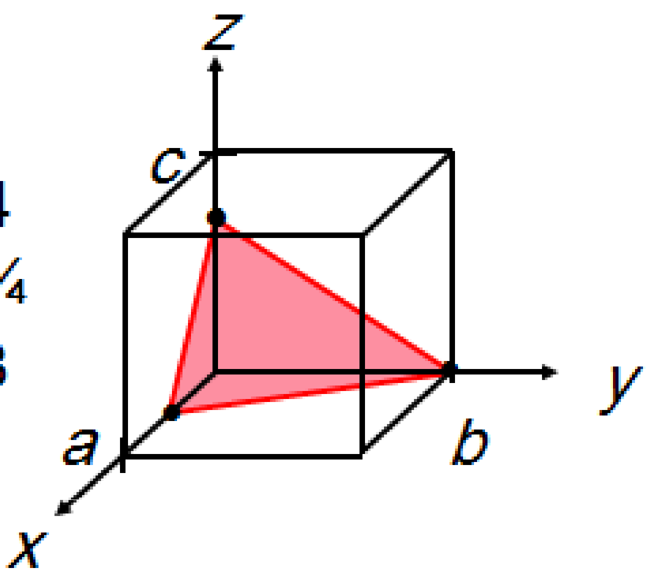
example		a	b	c
1.	Intercepts	1/2	∞	∞
2.	Reciprocals	1/½	1/∞	1/∞
		2	0	0
3.	Reduction	2	0	0
4.	Miller Indices	(100)		



Crystallographic Planes

	<u>example</u>	*a*	*b*	*c*
1.	Intercepts	1/2	1	3/4
2.	Reciprocals	1/½	1/1	1/¾
		2	1	4/3
3.	Reduction	6	3	4

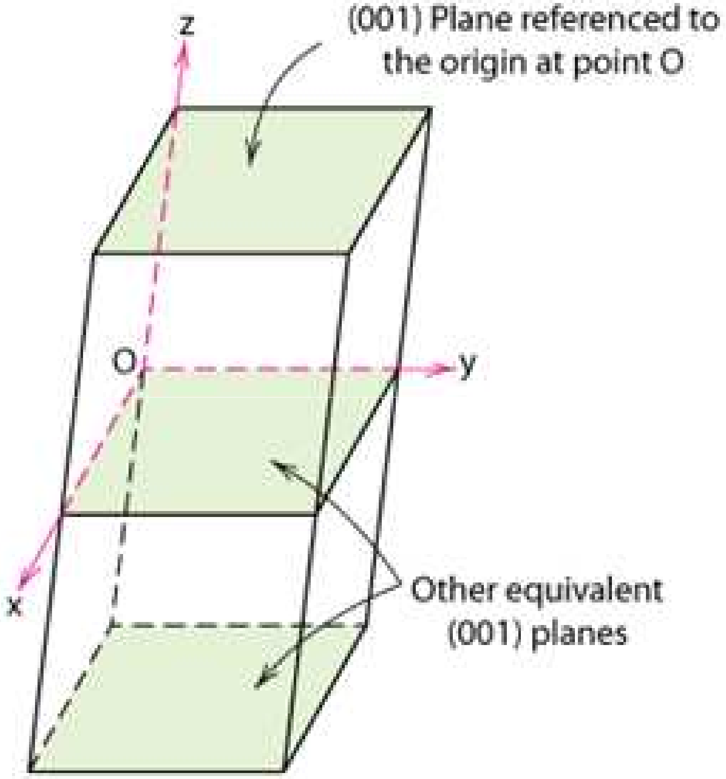
4. Miller Indices (634)

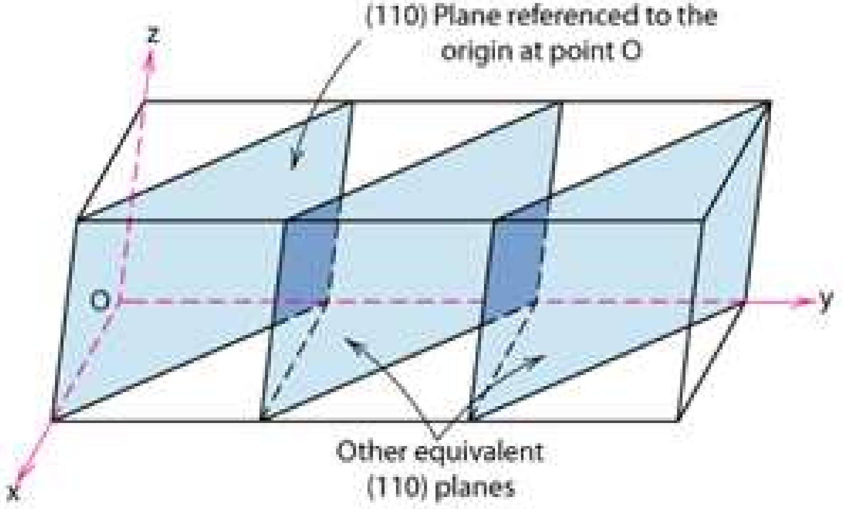


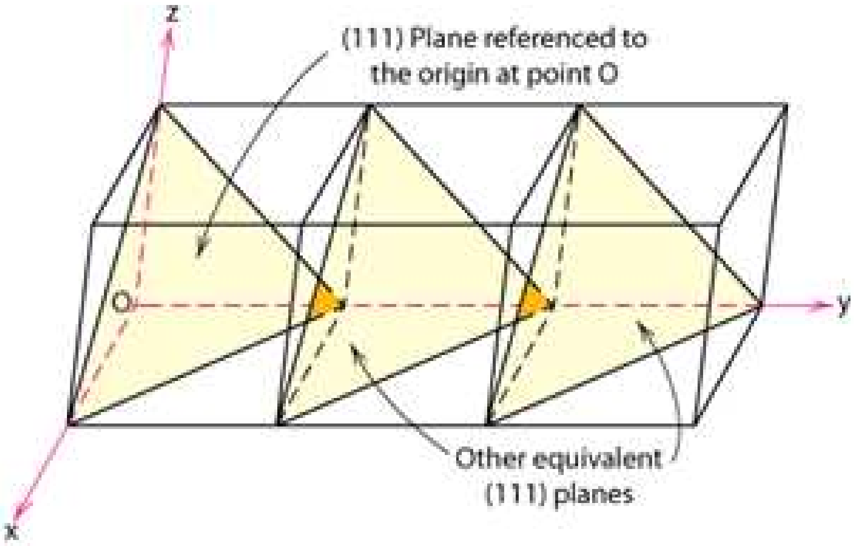
Family of Planes {*hkl*}

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

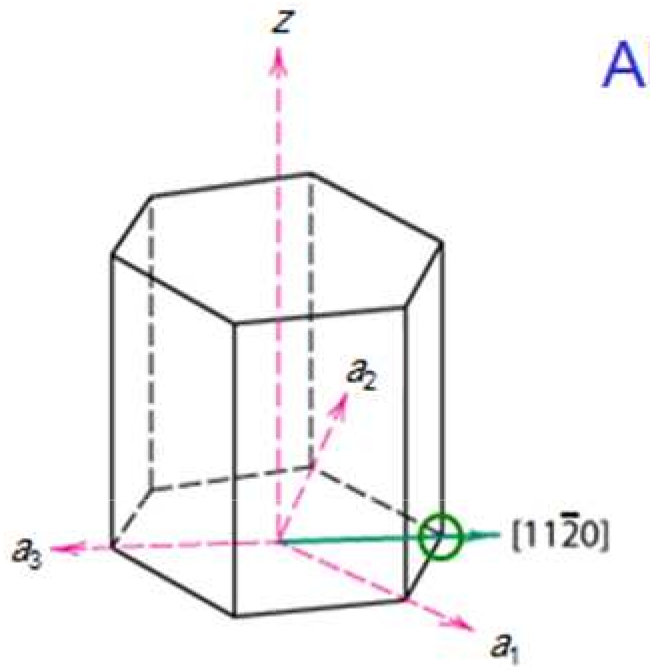
Crystallographic Planes







HCP Crystallographic Directions

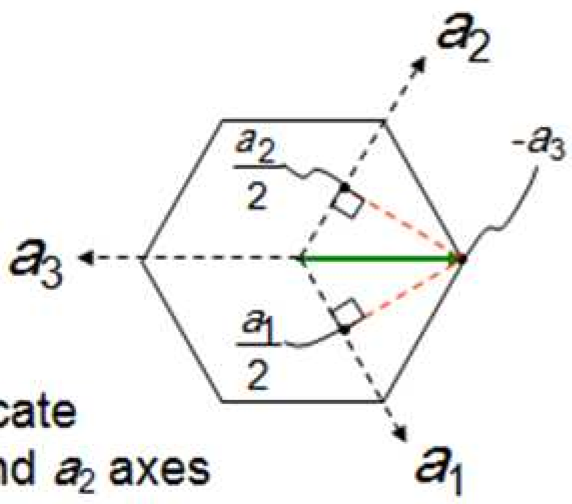


Algorithm

1. Vector repositioned (if necessary) to pass through origin.
2. Read off projections in terms of unit cell dimensions a_1, a_2, a_3, or c
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas

$[uvtw]$

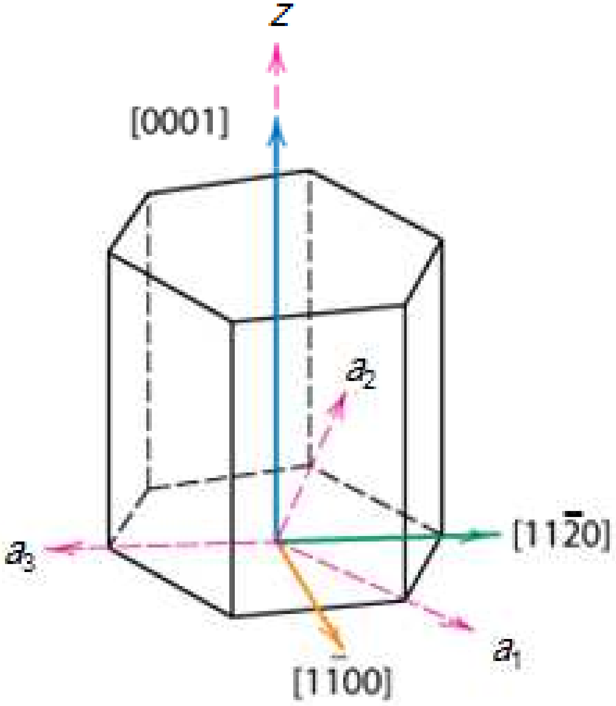
ex: $\frac{1}{2}, \frac{1}{2}, -1, 0 \quad \Rightarrow \quad [11\bar{2}0]$



dashed red lines indicate projections onto a_1 and a_2 axes

HCP Crystallographic Directions

- <u>Hexagonal Crystals</u>
  - 4 parameter Miller-Bravais lattice coordinates are related to the direction indices (i.e., $u'v'w'$) as follows.



$$[u'v'w'] \rightarrow [uvtw]$$

$$u = \frac{1}{3}(2u' - v')$$

$$v = \frac{1}{3}(2v' - u')$$

$$t = -(u + v)$$

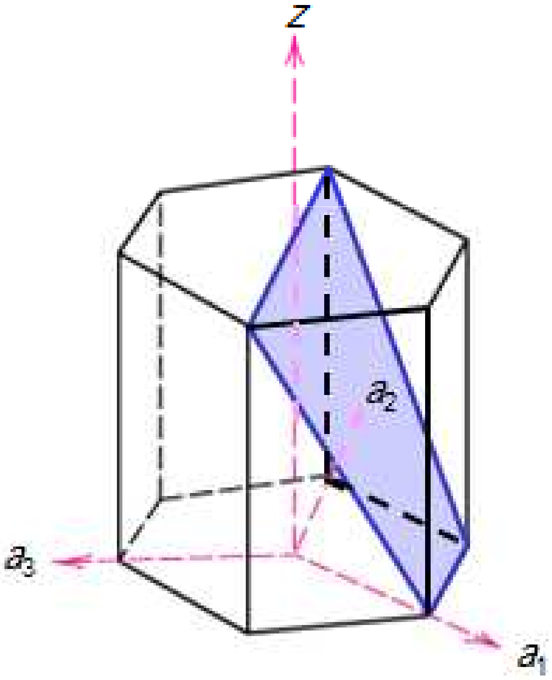
$$w = w'$$

Crystallographic Planes (HCP)

- In hexagonal unit cells the same idea is used

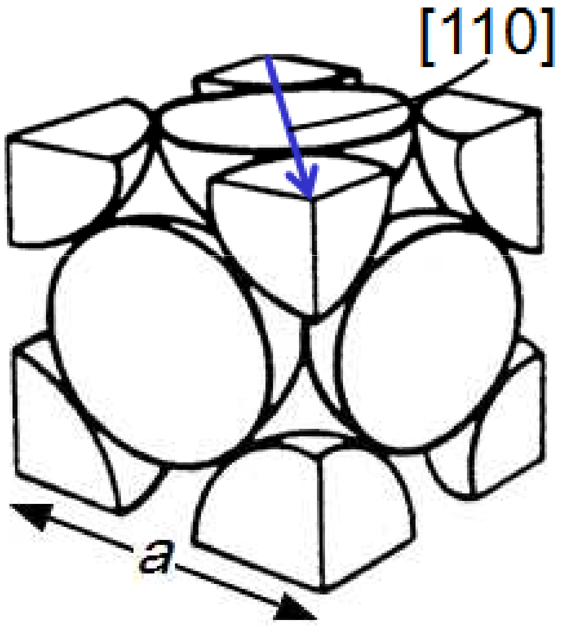
<u>example</u>	a_1	a_2	a_3	c
1. Intercepts	1	∞	-1	1
2. Reciprocals	1	1/∞	-1	1
	1	0	-1	1
3. Reduction	1	0	-1	1

4. Miller-Bravais Indices $(10\bar{1}1)$



Linear Density

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



ex: linear density of Al in [110] direction

$a = 0.405$ nm

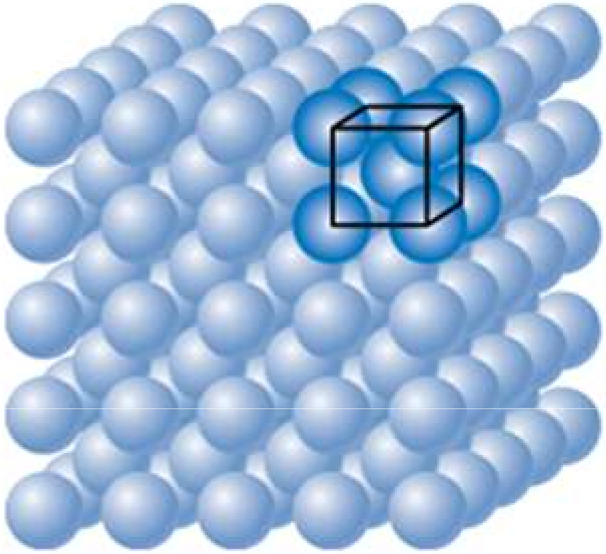
atoms

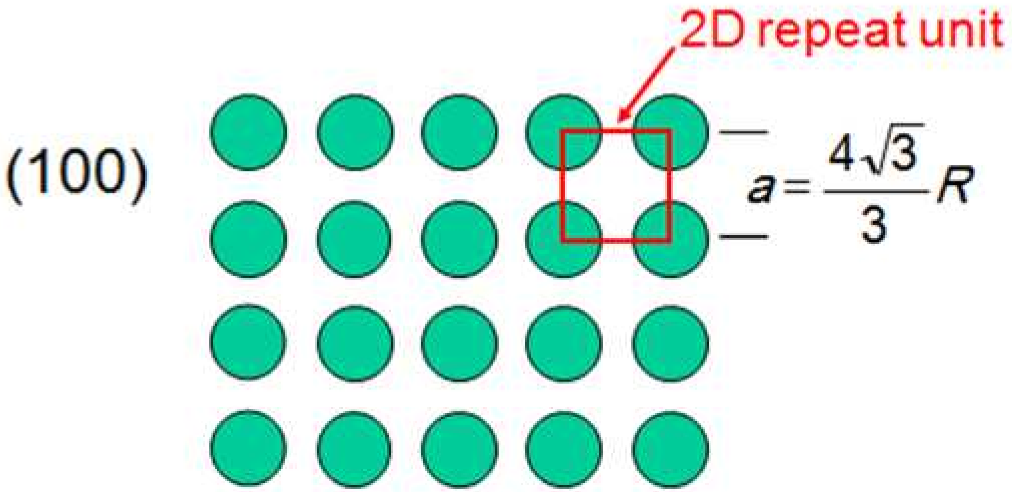
$$\mathrm{LD} = \frac{2}{\sqrt{2}a} = \boxed{3.5\ \mathrm{nm}^{-1}}$$

length

Planar Density of (100) Iron

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





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

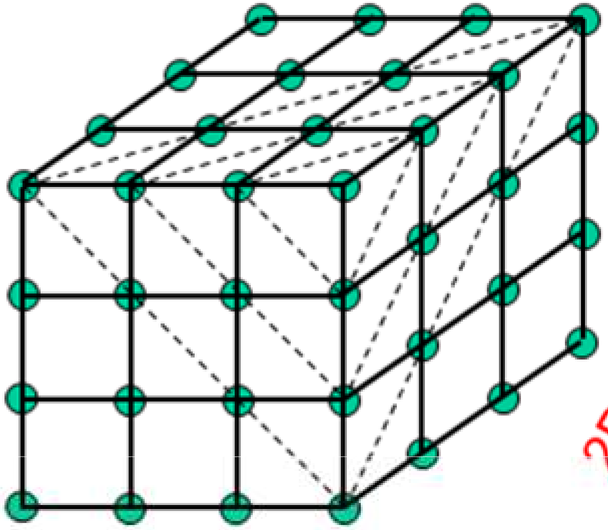
Radius of iron $R = 0.1241$ nm

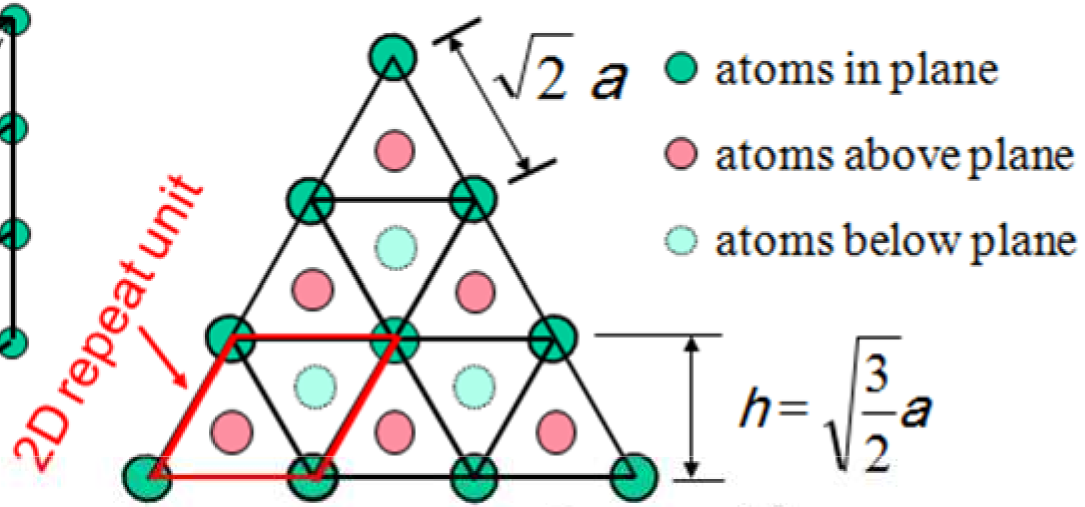
$$\text{Planar Density} = \frac{\overset{\frac{\text{atoms}}{\text{2D repeat unit}}}{1}}{\underset{\frac{\text{area}}{\text{2D repeat unit}}}{a^2}} = \frac{1}{\left(\frac{4\sqrt{3}}{3}R\right)^2} = 12.1\,\frac{\text{atoms}}{\text{nm}^2} = \boxed{1.2 \times 10^{19}\,\frac{\text{atoms}}{\text{m}^2}}$$

Planar Density of (111) Iron

(111) plane

1 atom in plane/ unit surface cell





$$\text{area} = \sqrt{2}\ ah = \sqrt{3}\ a^2 = \sqrt{3}\left(\frac{4\sqrt{3}}{3}R\right)^2 = \frac{16\sqrt{3}}{3}R^2$$

$$\text{Planar Density} = \frac{\dfrac{\text{atoms}}{\text{2D repeat unit}}}{\dfrac{\text{area}}{\text{2D repeat unit}}} = \frac{1}{\dfrac{16\sqrt{3}}{3}R^2} = 7.0\,\frac{\text{atoms}}{\text{nm}^2} = \boxed{0.70 \times 10^{19}\ \frac{\text{atoms}}{\text{m}^2}}$$

Designating Lattice Planes

Why are planes in a lattice important?

(A) Determining crystal structure:

* Diffraction methods measure the distance between parallel lattice planes of atoms. This information is used to determine the lattice parameters in a crystal.

* Diffraction methods also measure the angles between lattice planes.

(B) Plastic deformation

* Plastic deformation in metals occurs by the slip of atoms past each other in the crystal.

* This slip tends to occur preferentially along specific crystal-dependent planes.

(C) Transport Properties

* In certain materials, atomic structure in some planes causes the transport of electrons and/or heat to be particularly rapid in that plane, and relatively slow not in the plane.

- Example: Graphite: heat conduction is more in sp^2-bonded plane.