Material Science
ME 221

Fall 2020

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Chapter 3: The *Structure of Crystalline Solids*

- Crystal Structures
- Theoretical Density Computations
- Crystal Systems
- Crystallographic Points, Directions, and Planes
- Linear and Planner Density
- Crystalline and Noncrystalline Materials

Materials Contents in this Slides adapted from : Materials science and engineering: an introduction / William D. Callister, Jr., David G. Rethwisch.–8th ed.

WHY STUDY The *Structure of Crystalline Solids?*

- Affect the properties of some materials.
    - Pure and undeformed magnesium, much more brittle than are pure and undeformed metals such as gold due to different crystal structure they have.

- Ceramics and Polymers
    - Noncrystalline normally are optically transparent
    - Crystalline (or semicrystalline) opaque or, at best, translucent.

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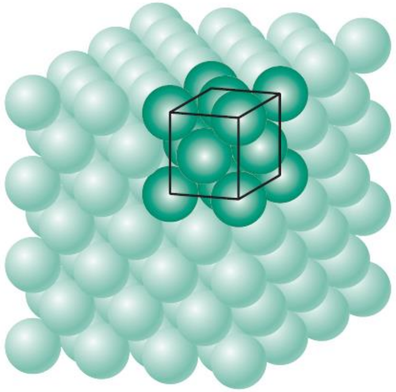
Crystal Structures

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

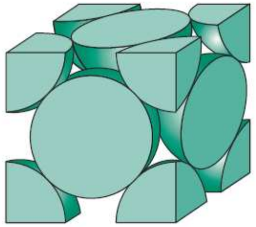
- **Non-crystalline or amorphous**

- **Crystal structure**: Spatial arrangement of atoms
- ***Lattice****:* three-dimensional array of points coinciding with atom positions (or sphere centers).

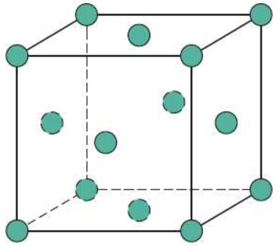


- **Lattice structure**: 3D array of points *(lattice points) with infinite repetition.*

- **Unit cell:** small groups of atoms form a repetitive pattern, The basic structural unit of the lattice structure.
- ***Atomic hard-sphere model****:* atoms (or ions) are thought of as being solid spheres having well-defined diameters.



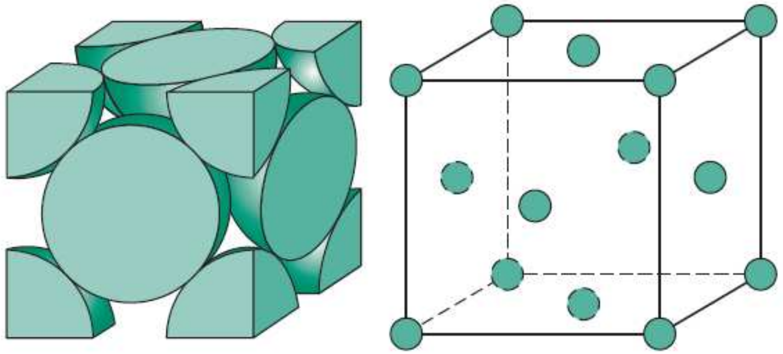
- **Reduced-sphere unit cell**

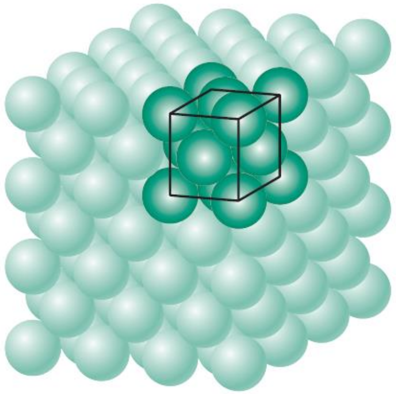


The Face-Centered Cubic Crystal Structure

- **Coordination number:** number of nearest-neighbor or touching atoms

$$a = 2R\sqrt{2}$$





- **Atomic packing factor (APF).**

$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}}$$

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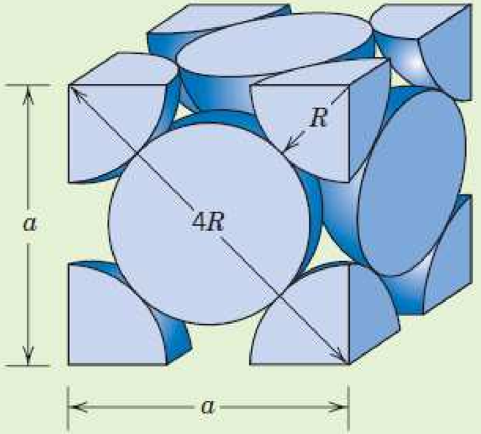
Determination of FCC Unit Cell Volume

Calculate the volume of an FCC unit cell in terms of the atomic radius R.

Solution

In the FCC unit cell illustrated,



the atoms touch one another across a face-diagonal the length of which is $4R$. Because the unit cell is a cube, its volume is a^3, where a is the cell edge length. From the right triangle on the face,

$$a^2 + a^2 = (4R)^2$$

or, solving for a,

$$a = 2R\sqrt{2} \qquad (3.1)$$

The FCC unit cell volume V_C may be computed from

$$V_C = a^3 = (2R\sqrt{2})^3 = 16R^3\sqrt{2} \qquad (3.4)$$

Computation of the Atomic Packing Factor for FCC

Show that the atomic packing factor for the FCC crystal structure is 0.74.

Solution

The APF is defined as the fraction of solid sphere volume in a unit cell, or

$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} = \frac{V_S}{V_C}$$

Both the total atom and unit cell volumes may be calculated in terms of the atomic radius R. The volume for a sphere is $\frac{4}{3}\pi R^3$, and because there are four atoms per FCC unit cell, the total FCC atom (or sphere) volume is

$$V_S = (4)\tfrac{4}{3}\pi R^3 = \tfrac{16}{3}\pi R^3$$

From Example Problem 3.1, the total unit cell volume is

$$V_C = 16R^3\sqrt{2}$$

Therefore, the atomic packing factor is

$$\text{APF} = \frac{V_S}{V_C} = \frac{(\frac{16}{3})\pi R^3}{16R^3\sqrt{2}} = 0.74$$

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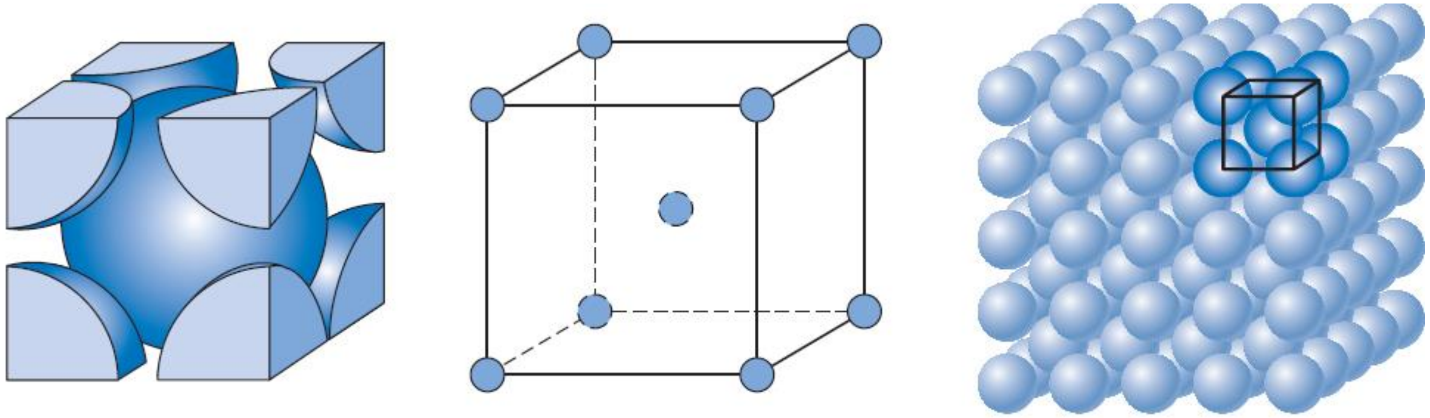
The Body-Centered Cubic Crystal Structure

- CN: 8
- APF = 0.68

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



The Body-Centered Cubic Crystal Structure

- *Show for the body-centered cubic crystal structure that the unit cell edge length a and the atomic radius R are related through* $a = 4R/\sqrt{3}$

NOP triangle

$$(\overline{NP})^2 = a^2 + a^2 = 2a^2$$

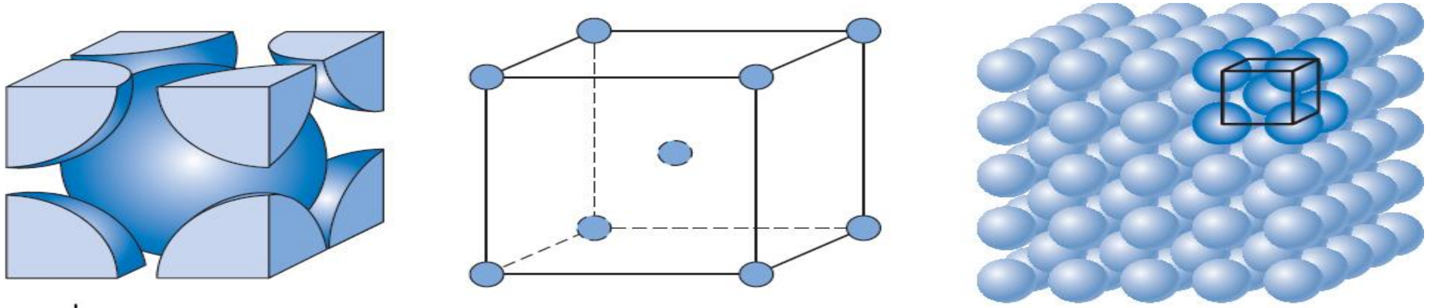
NPQ triangle

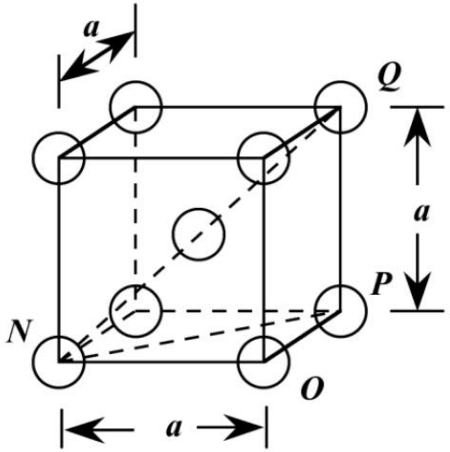
$$(\overline{NQ})^2 = (\overline{QP})^2 + (\overline{NP})^2$$

$$\overline{NQ} = 4R \qquad \overline{QP} = a$$

$$(4R)^2 = a^2 + 2a^2$$

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





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The Body-Centered Cubic Crystal Structure

Show that the atomic packing factor for BCC is 0.68

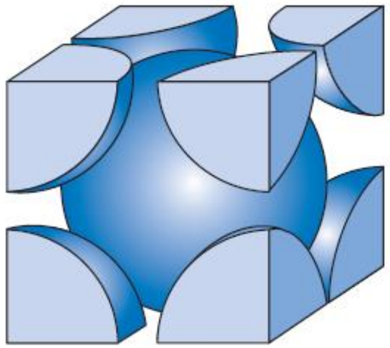
$$\text{APF} = \frac{V_S}{V_C}$$

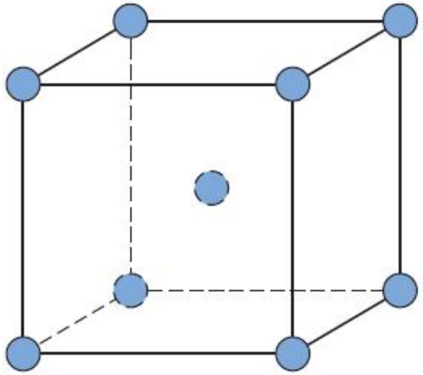
$$V_S = 2(\text{sphere volume}) = 2\left(\frac{4\pi R^3}{3}\right) = \frac{8\pi R^3}{3}$$

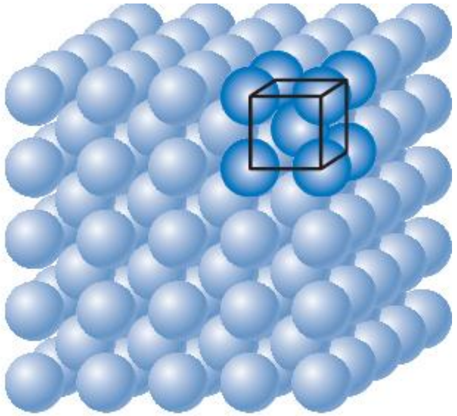
$$V_C = a^3 \longrightarrow a = \frac{4R}{\sqrt{3}}$$

$$V_C = \left(\frac{4R}{\sqrt{3}}\right)^3 = \frac{64R^3}{3\sqrt{3}}$$

$$\text{APF} = \frac{V_S}{V_C} = \frac{8\pi R^3/3}{64R^3/3\sqrt{3}} = 0.68$$







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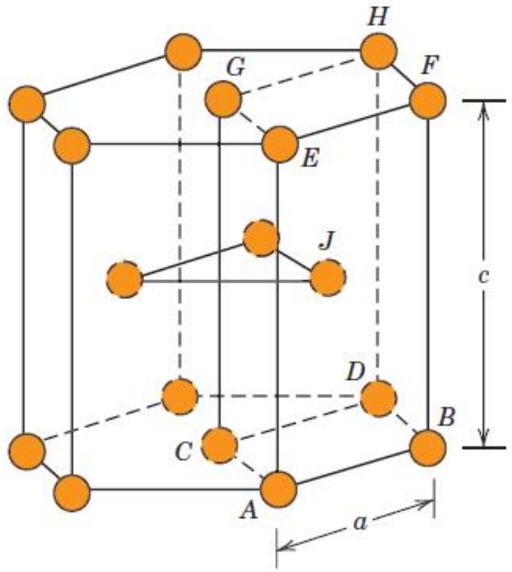
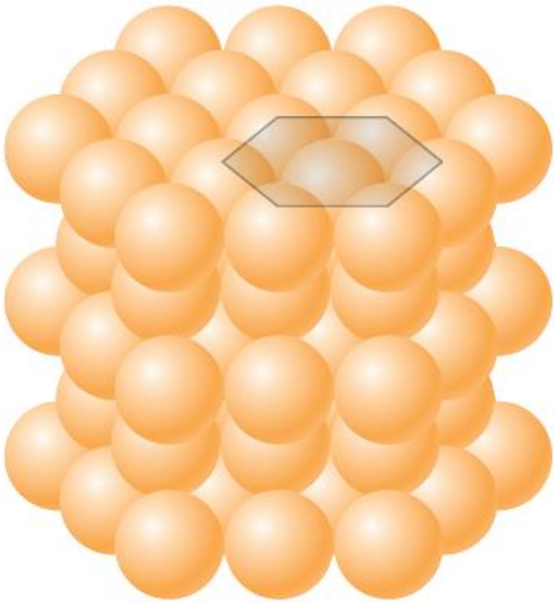
The Hexagonal Close-Packed Crystal Structure

- CN & APF = FCC
- c/a must be 1.633





Theoretical Density Computations

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

n = number of atoms associated with each unit cell
A = atomic weight
V_C = volume of the unit cell
N_A = Avogadro's number (6.022×10^{23} atoms/mol)

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Example

Theoretical Density Computation for Copper

Copper has an atomic radius of 0.128 nm, an FCC crystal structure, and an atomic weight of 63.5 g/mol. Compute its theoretical density and compare the answer with its measured density.

Solution

Equation 3.5 is employed in the solution of this problem. Because the crystal structure is FCC, n, the number of atoms per unit cell, is 4. Furthermore, the atomic weight A_{Cu} is given as 63.5 g/mol. The unit cell volume V_C for FCC was determined in Example Problem 3.1 as $16R^3\sqrt{2}$, where R, the atomic radius, is 0.128 nm.

Substitution for the various parameters into Equation 3.5 yields

$$\rho = \frac{nA_{Cu}}{V_C N_A} = \frac{nA_{Cu}}{(16R^3\sqrt{2})N_A}$$

$$= \frac{(4 \text{ atoms/unit cell})(63.5 \text{ g/mol})}{[16\sqrt{2}(1.28 \times 10^{-8} \text{ cm})^3/\text{unit cell}](6.022 \times 10^{23} \text{ atoms/mol})}$$

$$= 8.89 \text{ g/cm}^3$$

The literature value for the density of copper is 8.94 g/cm^3, which is in very close agreement with the foregoing result.

Example

- *Calculate the radius of an iridium atom, given that Ir has an FCC crystal structure, a density of 22.4 g/ cm³, and an atomic weight of 192.2 g/mol*

$n = 4$ atoms/unit cell, $\quad V_C = 16R^3\sqrt{2}$

$$\rho = \frac{nA_{Ir}}{V_C N_A}$$

$$= \frac{nA_{Ir}}{(16R^3\sqrt{2})N_A}$$

$$R = \left(\frac{nA_{Ir}}{16\rho N_A\sqrt{2}}\right)^{1/3}$$

$$= \left[\frac{(4 \text{ atoms/unit cell})(192.2 \text{ g/mol})}{(16)(22.4 \text{ g/cm}^3)(6.022 \times 10^{23} \text{ atoms/mol})(\sqrt{2})}\right]^{1/3}$$

$$= 1.36 \times 10^{-8} \text{ cm} = 0.136 \text{ nm}$$

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Example

- *Rhodium has an atomic radius of 0.1345 nm and a density of 12.41 g/cm3. Determine whether it has an FCC or BCC crystal structure*

Calculate the density using FCC parameters (n & a)

$$\rho = \frac{nA_{\text{Rh}}}{a^3 N_A} = \frac{nA_{\text{Rh}}}{(2R\sqrt{2})^3 N_A}$$

$$= \frac{(4\ \text{atoms/unit cell})(102.91\ \text{g/mol})}{\left\{\left[(2)(1.345 \times 10^{-8}\ \text{cm})(\sqrt{2})\right]^3 / (\text{unit cell})\right\}(6.022 \times 10^{23}\ \text{atoms/mol})}$$

$$= 12.41\ \text{g/cm}^3$$

Rh has the FCC crystal structure

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Polymorphism and Allotropy

- **Polymorphism** : Material have more than one crystal structure
  - In solid often termed **Allotropy**

- Most crystal structure depends on
  - temperature
  - external pressure.

  - Carbon:
    - Graphite: stable polymorph at ambient conditions
    - Diamond: formed at extremely high pressures

  - Pure iron
    - Has a BCC crystal structure at room temperature
    - Has FCC crystal structure at 912 ^{o} C

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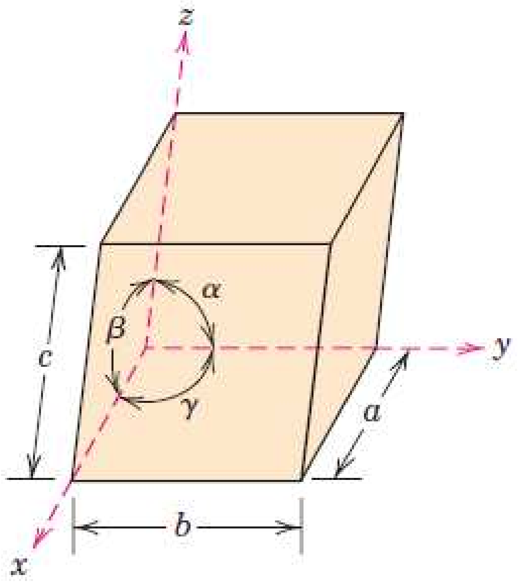
Crystal Systems

- Crystal structures: it is sometimes convenient to divide them into groups according to unit cell configurations and/or atomic Arrangements = > Lattice parameters



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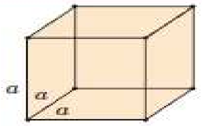
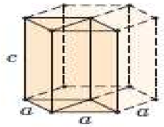
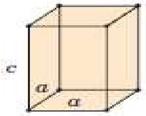
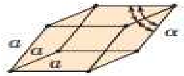
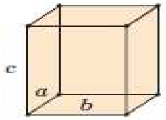
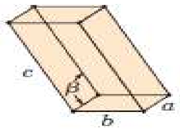
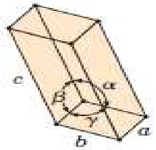
Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta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

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Example

- *The unit cell for tin (Sn) has **tetragonal** symmetry, with a and b lattice parameters of 0.583 and 0.318 nm, respectively. If its density, atomic weight, and atomic radius are 7.30 g/cm3, 118.69 g/mol, and 0.151 nm, respectively, compute the atomic packing factor*

$$n = \frac{\rho V_C N_A}{A_{Sn}}$$

$$= \frac{(7.30\ \text{g/cm}^3)(5.83)^2(3.18)(\times 10^{-24}\ \text{cm}^3)(6.022 \times 10^{23}\ \text{atoms/mol})}{118.69\ \text{g/mol}}$$

$$= 4.00\ \text{atoms/unit cell}$$

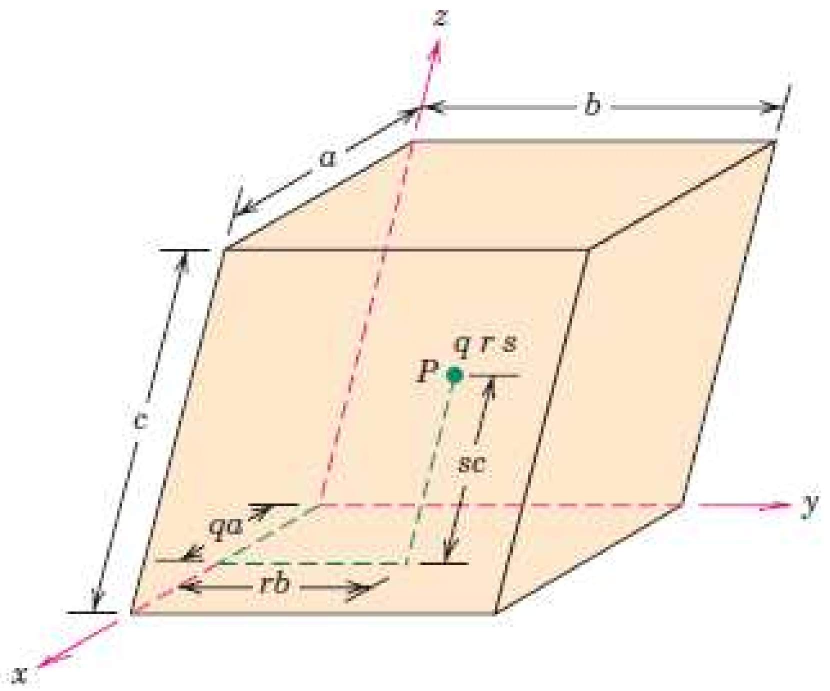
$$\text{APF} = \frac{V_S}{V_C} = \frac{(4)\left(\frac{4}{3}\pi R^3\right)}{(a)^2(c)}$$

$$= \frac{(4)\left[\frac{4}{3}(\pi)(1.51 \times 10^{-8}\ \text{cm})^3\right]}{(5.83 \times 10^{-8}\ \text{cm})^2(3.18 \times 10^{-8}\ \text{cm})}$$

$$= 0.534$$

Crystallographic Points, Directions, and Planes

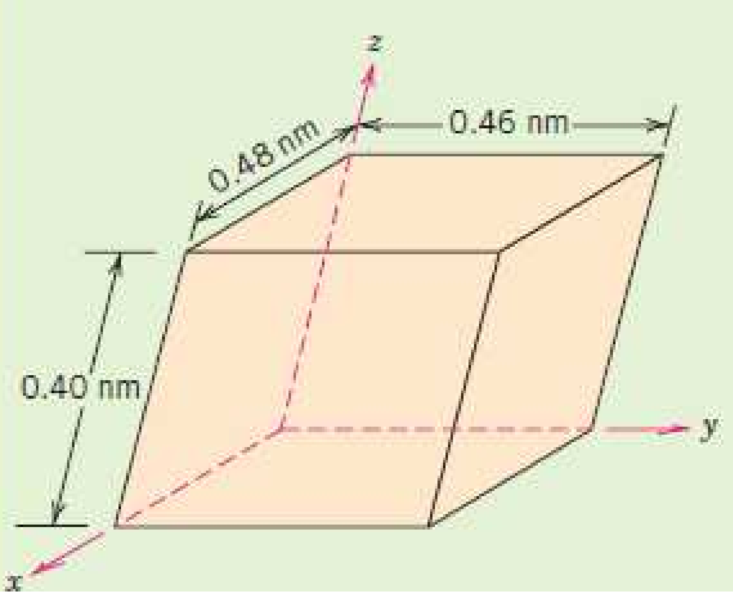
- **Points Coordinates**

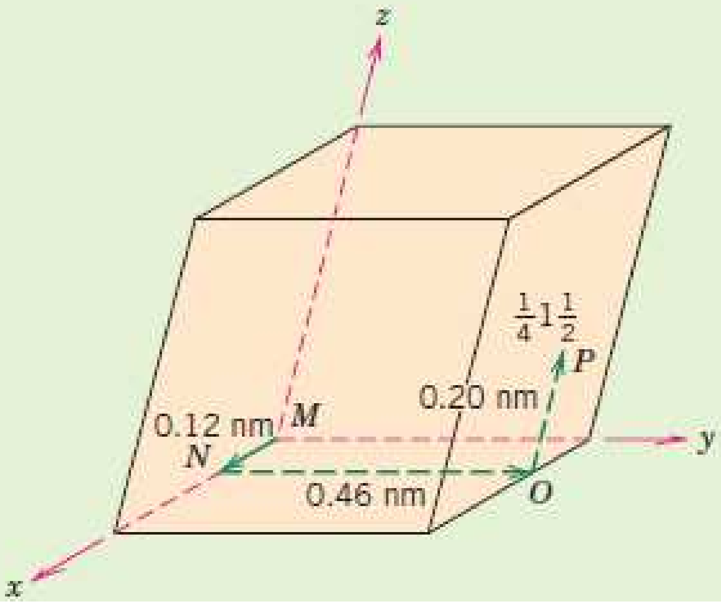


Example

Location of Point Having Specified Coordinates

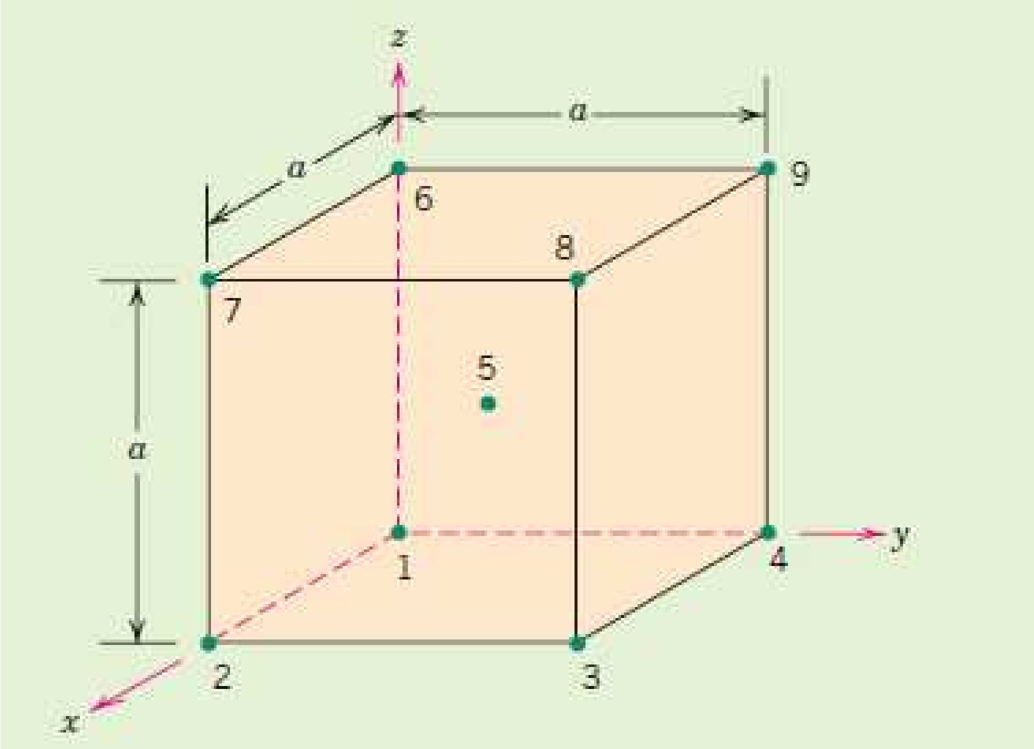
For the unit cell shown in the accompanying sketch (*a*), locate the point having coordinates $\frac{1}{4}\ 1\ \frac{1}{2}$.



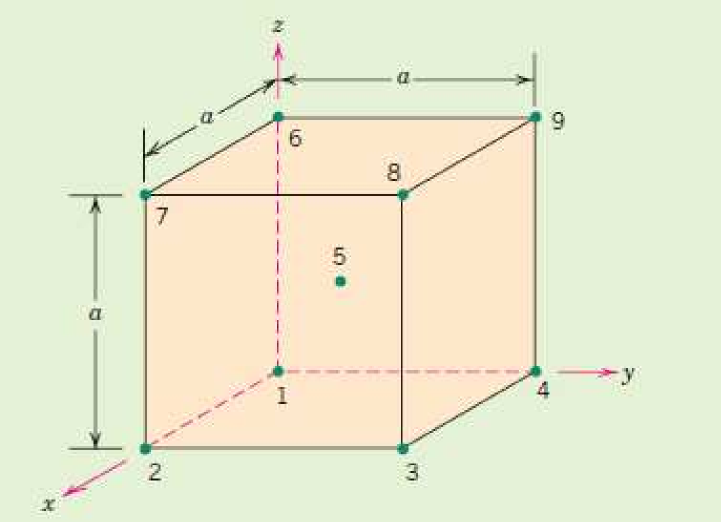


Example

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



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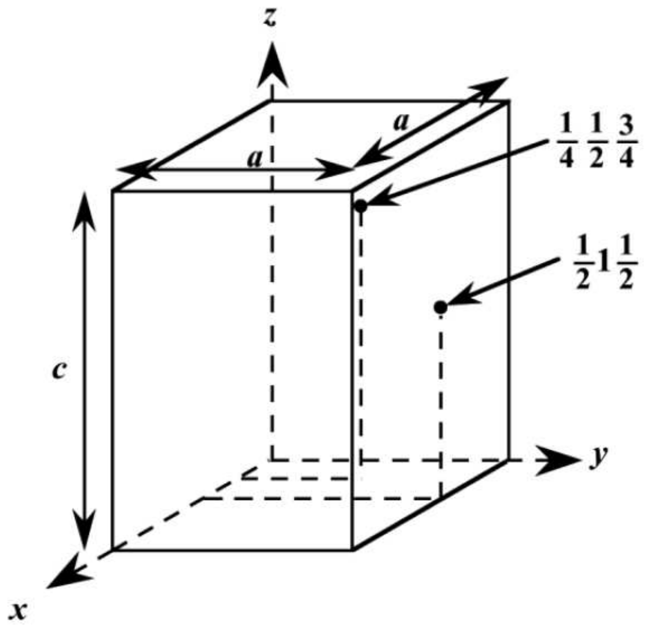
Example

- *Sketch a tetragonal unit cell, and within that cell indicate locations of the* and *point indices.* ½ 1 ½ , ¼ ½ ¾



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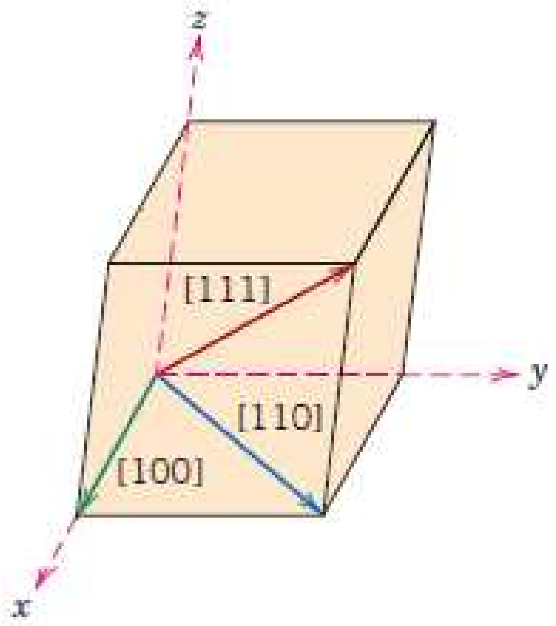
Crystallographic Direction

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

- The [100], [110], and [111] directions

  within a unit cell.



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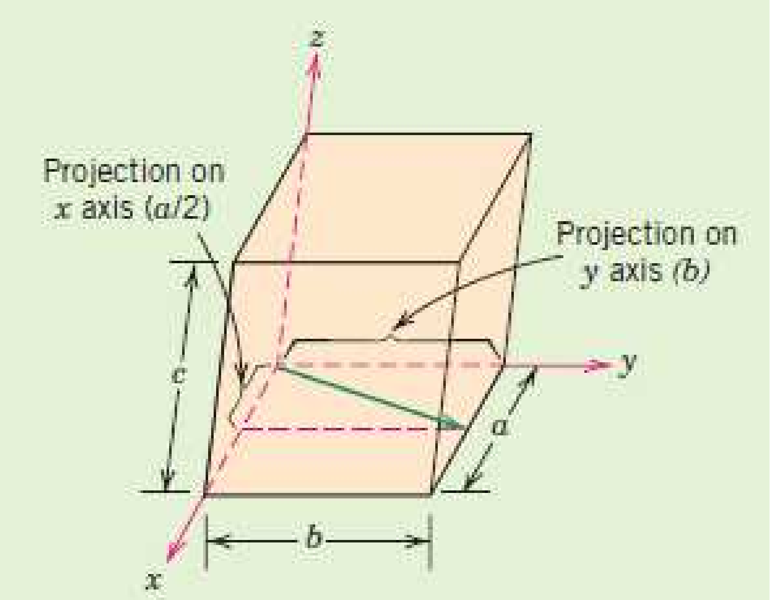
Example

- Determine the indices for the direction shown in figure below:



	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]	

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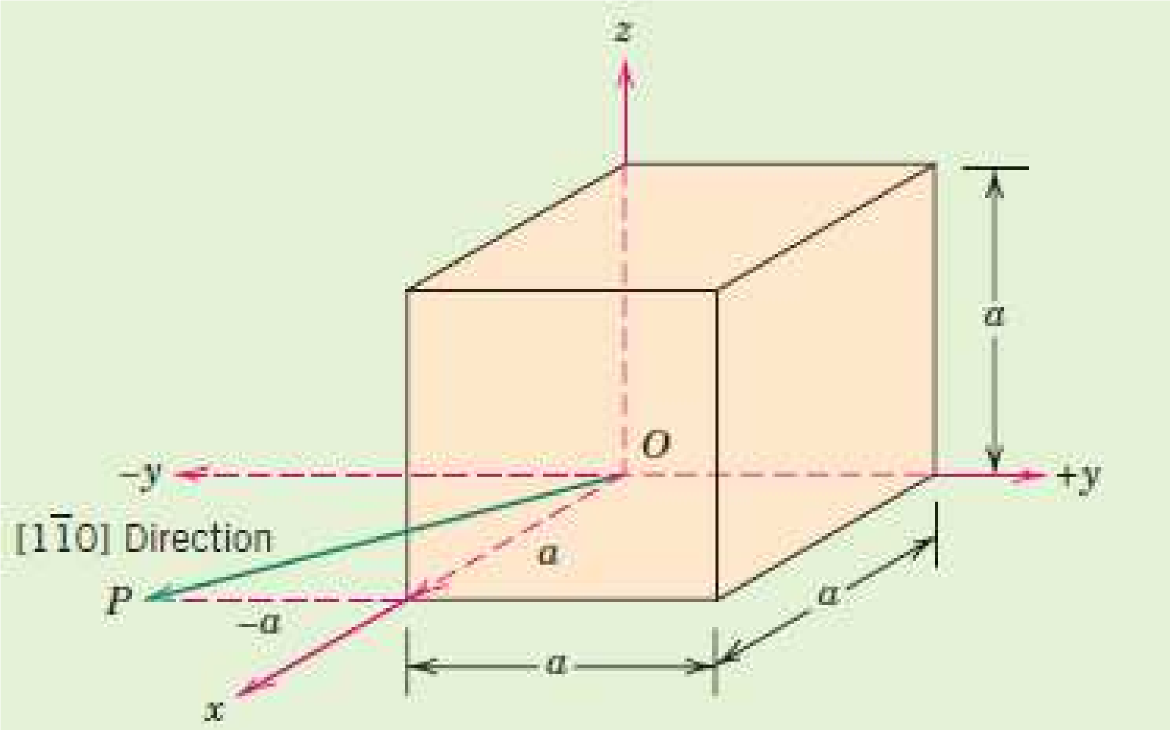
Example

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



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Directions for Hexagonal Crystals

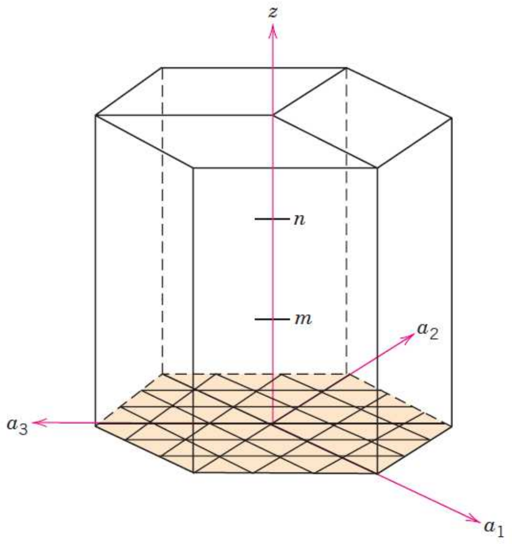
$$[u'v'w'] \longrightarrow [uvtw]$$

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

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

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

$$w = w'$$



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Example

- Draw [111] direction within a reduced-scale hexagonal crystals coordinate system

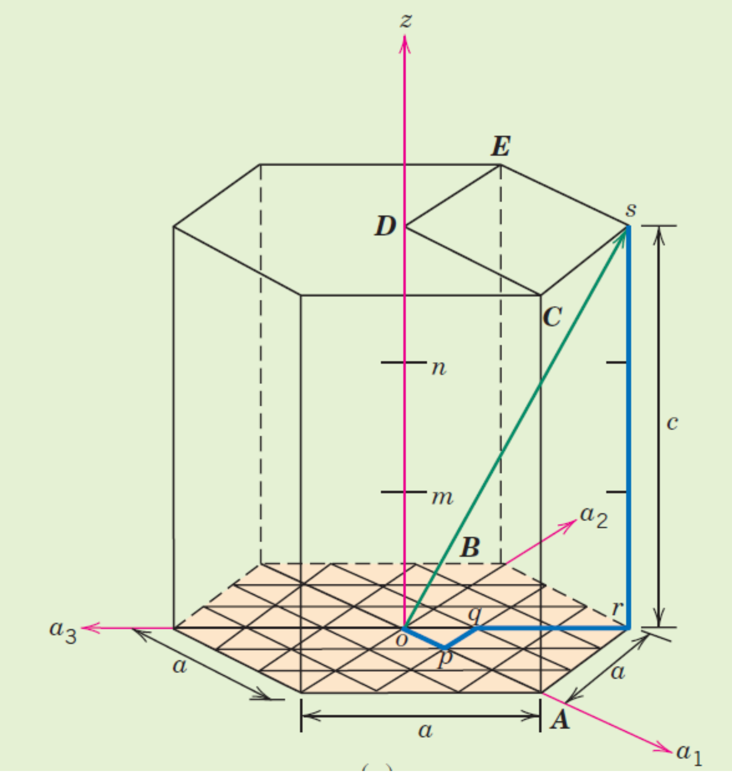
$$u' = 1 \quad v' = 1 \quad w' = 1$$

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

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

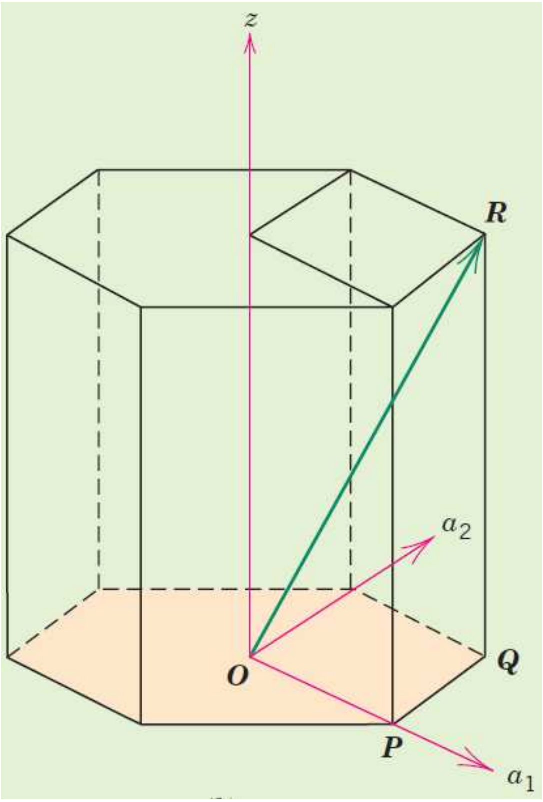
$$t = -(u + v) = -\left(\frac{1}{3} + \frac{1}{3}\right) = -\frac{2}{3}$$

$$w = w' = 1$$



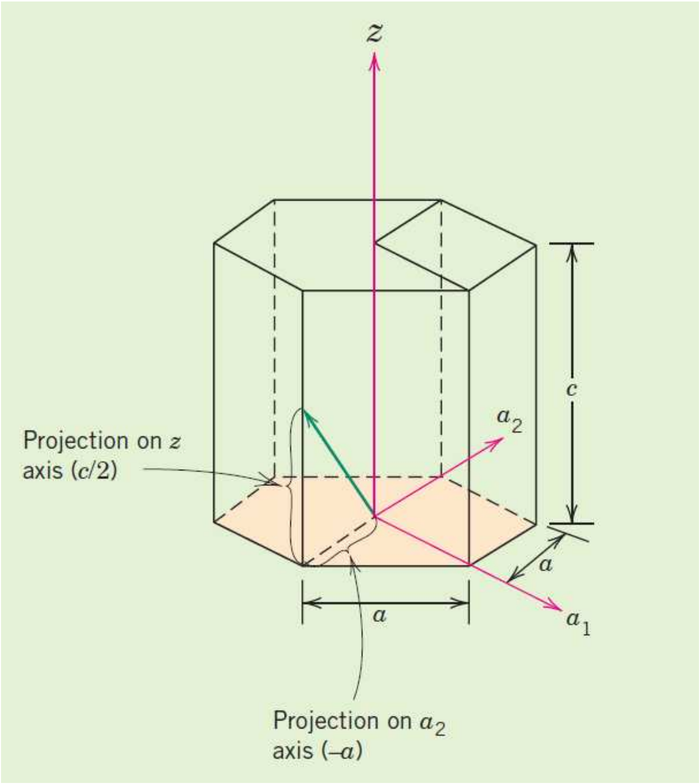
Example

- Draw the [111] direction within a hexagonal unit cell that utilizes a
- three-axis (a1, a2, z) coordinate system.



Example

- Determine the directional indices (four-index system) for the direction shown in figure below:



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Example

$$u' = 0 \quad v' = -2 \quad w' = 1$$

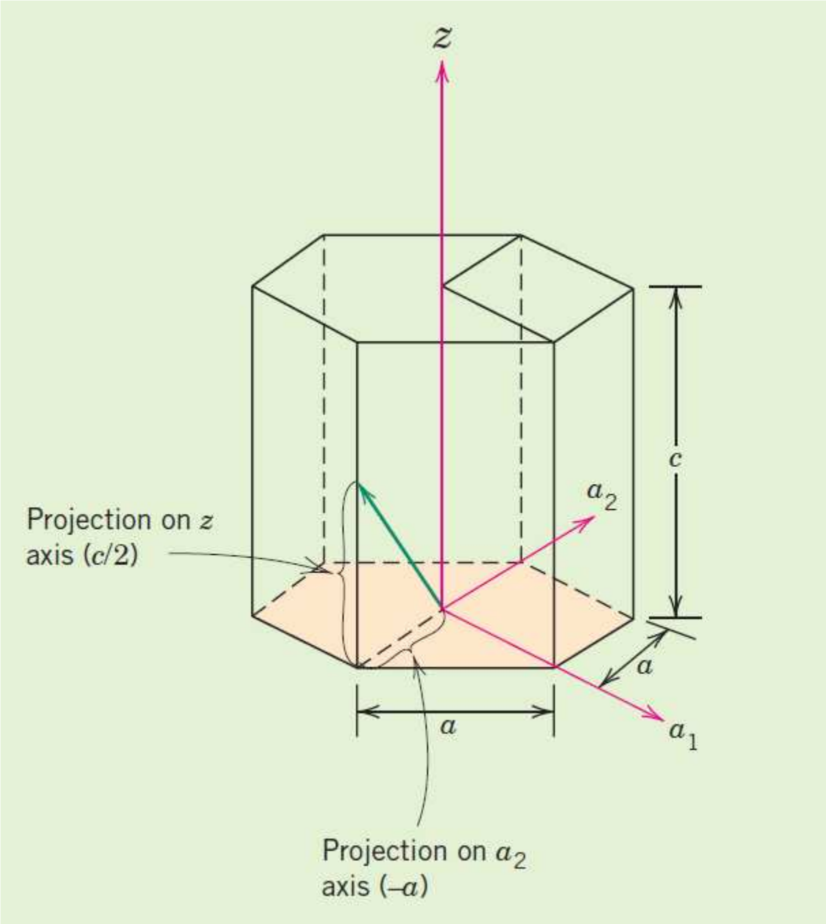
$$u = \frac{1}{3}(2u' - v') = \frac{1}{3}[(2)(0) - (-2)] = \frac{2}{3}$$

$$v = \frac{1}{3}(2v' - u') = \frac{1}{3}[(2)(-2) - 0] = -\frac{4}{3}$$

$$t = -(u + v) = -\left(\frac{2}{3} - \frac{4}{3}\right) = \frac{2}{3}$$

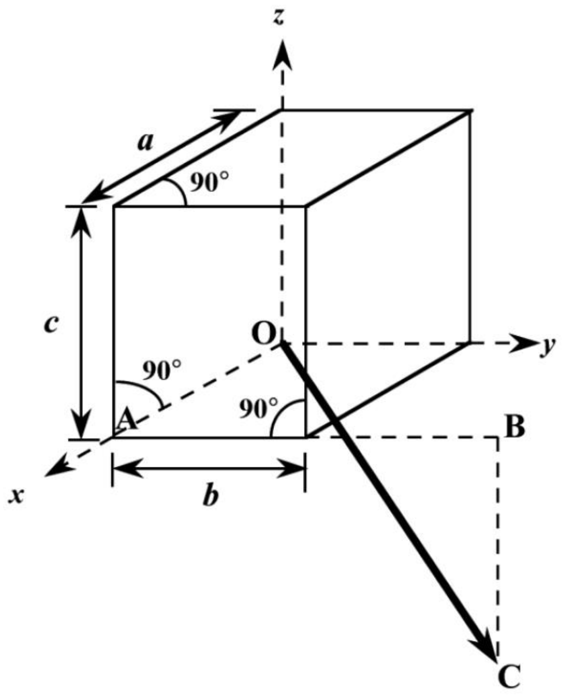
$$w = w' = 1$$

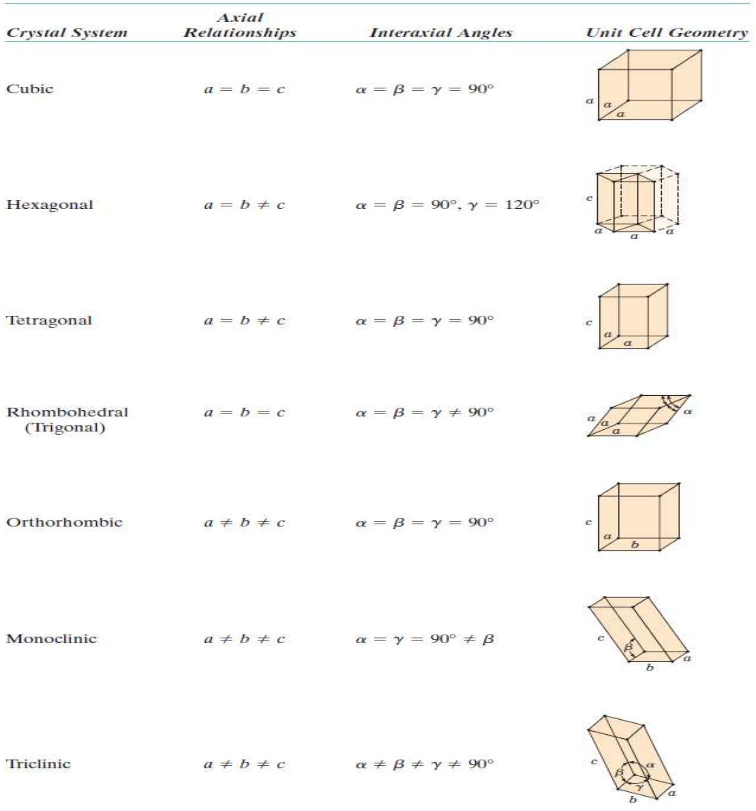
$$[2\bar{4}23]$$



Example

- Draw an orthorhombic unit cell, and within that cell a $[12\bar{1}]$ direction





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

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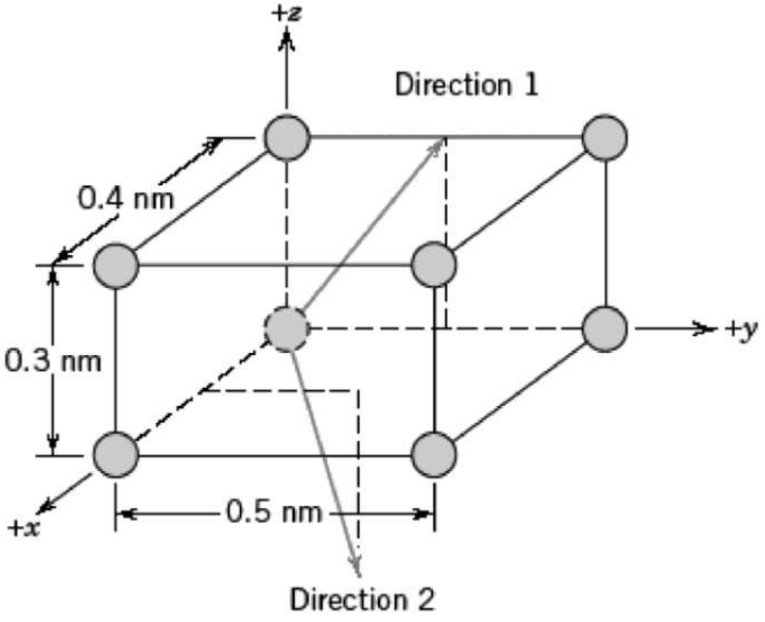
Exercise (10 min)

- *What are the indices for the directions indicated by the two vectors in the sketch below?*



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Crystallographic Plane

“**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.

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.

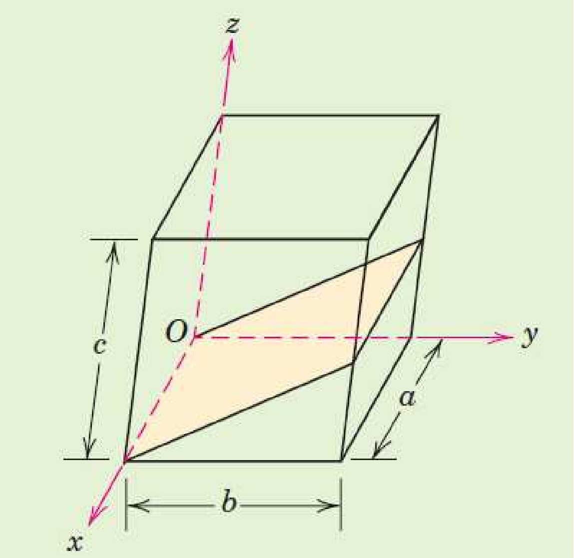
4. If necessary, these three numbers are changed to the

set of smallest integers by multiplication or division by

a common factor.

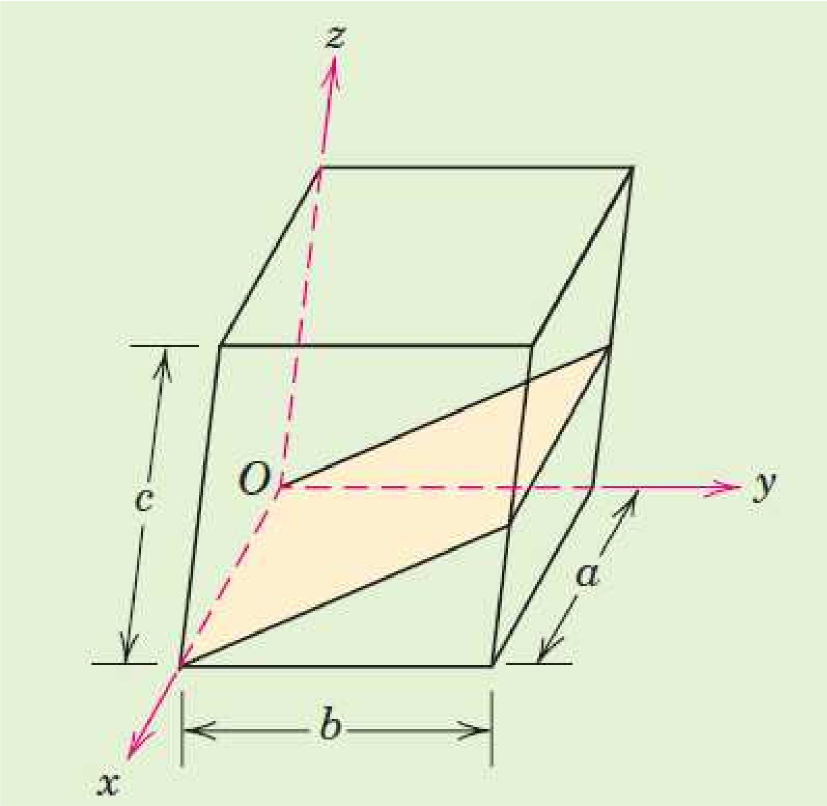
5. Finally, the integer indices, not separated by commas,

are enclosed withinparentheses, thus: (*hkl*).”



Example

- Determine the Miller indices for the plane shown.



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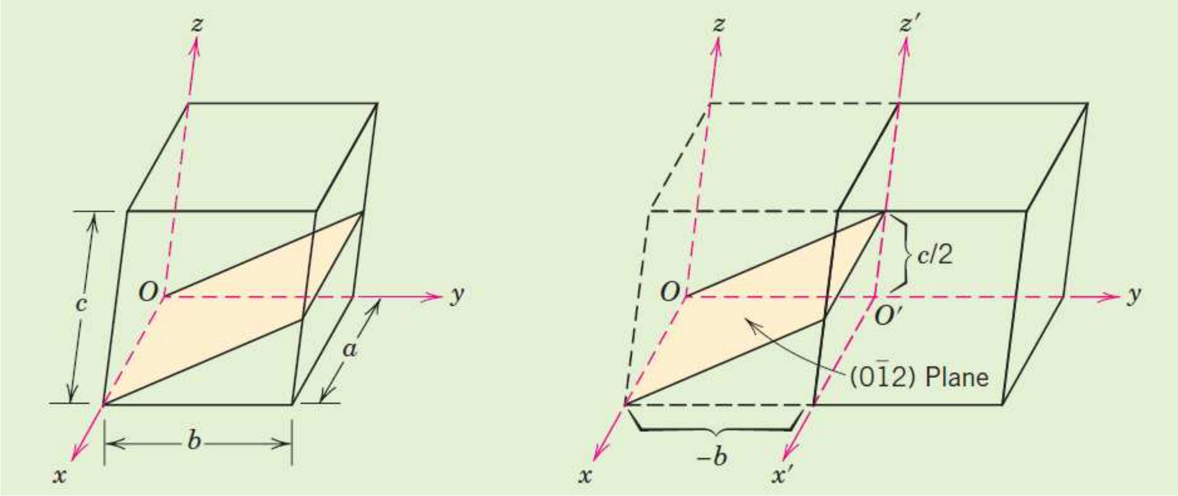
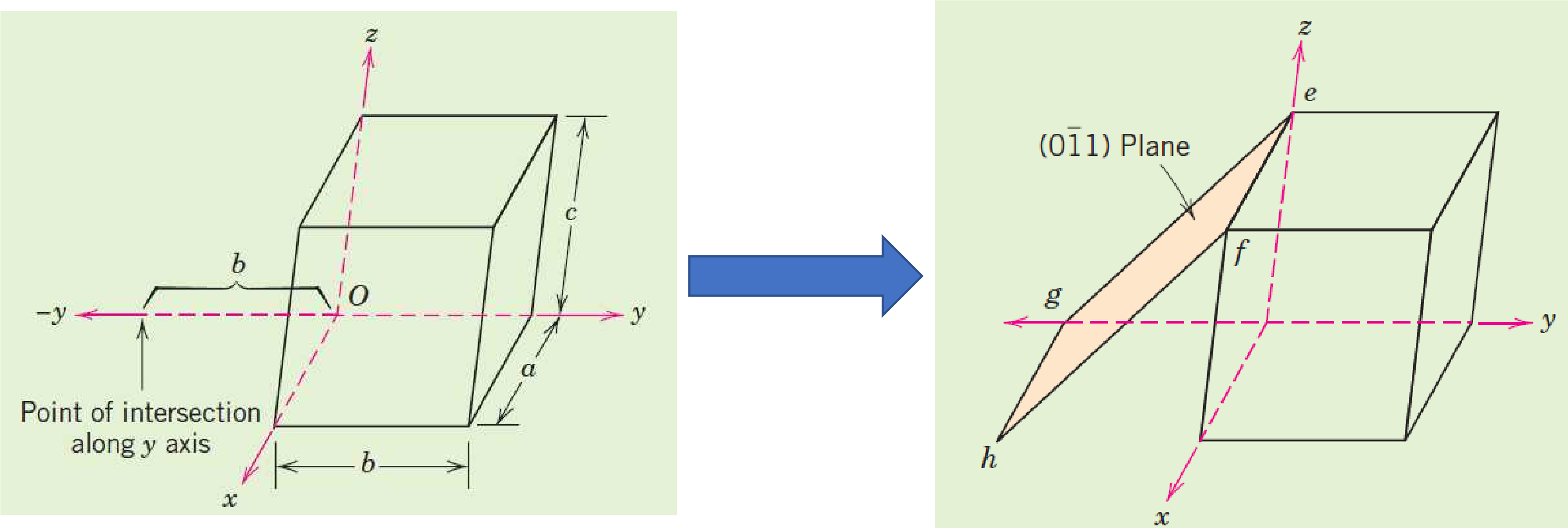
Example

- The plane passes through the origin, thus, choose a new origin point at the corner of another unit cell.



	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		$(0\bar{1}2)$	

- Construct a $(0\bar{1}1)$ plane within a cubic unit cell



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Example

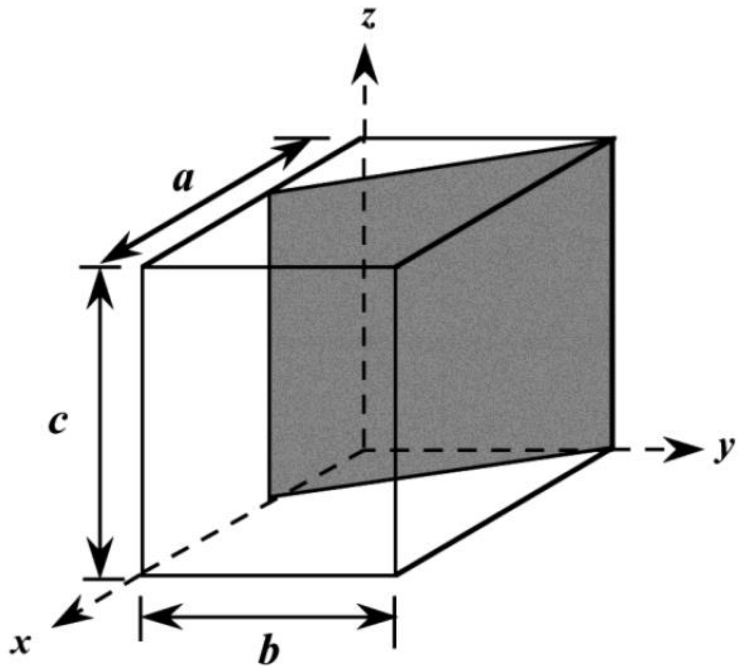
- *Draw an orthorhombic unit cell, and within that cell a (210) plane.*

Intercepts

$$A = \frac{na}{h} = \frac{(1)a}{2} = \frac{a}{2}$$

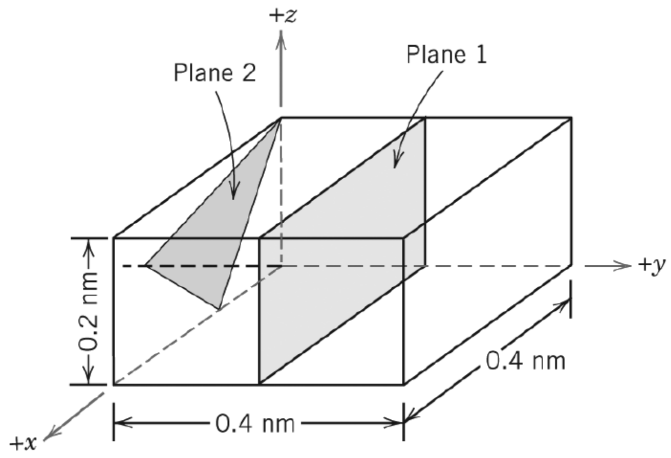
$$B = \frac{nb}{k} = \frac{(1)b}{1} = b$$

$$C = \frac{nc}{l} = \frac{(1)c}{0} = \infty c$$



Exercise

What are the indices for the plane 1 drawn in the sketch below?



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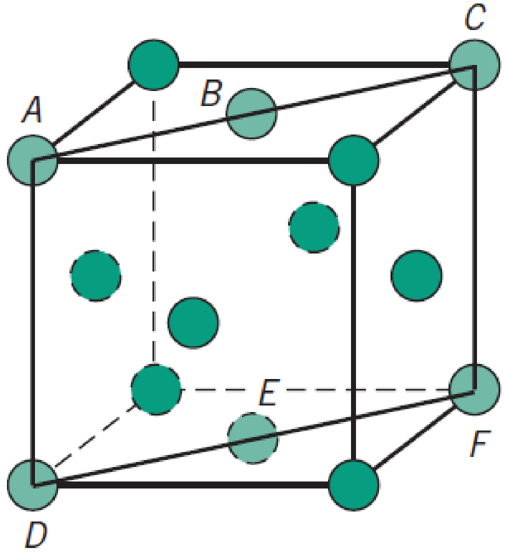
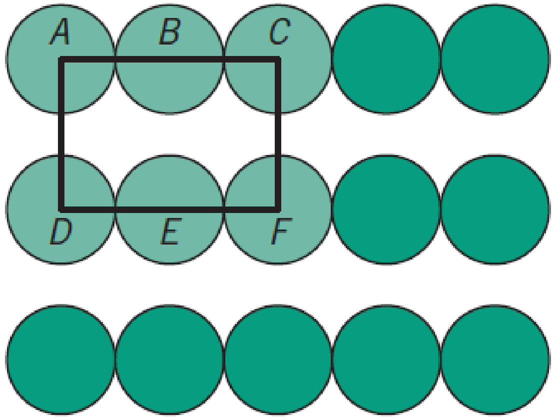
Atomic Arrangements

- Atomic packing of an FCC (110) plane





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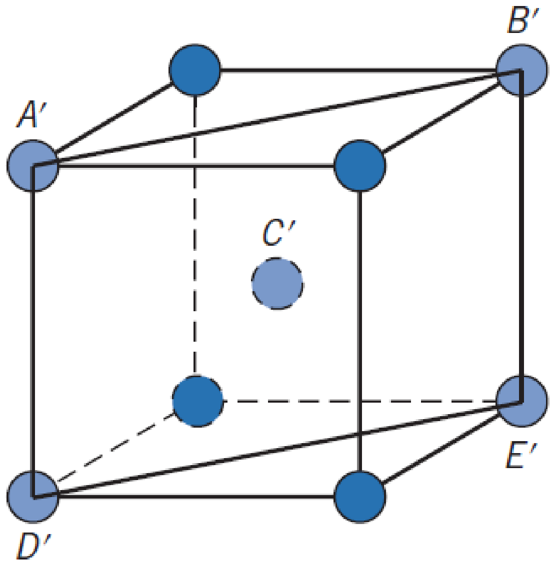
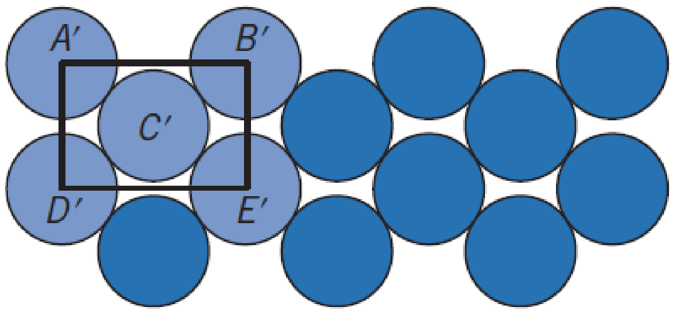
Atomic Arrangements

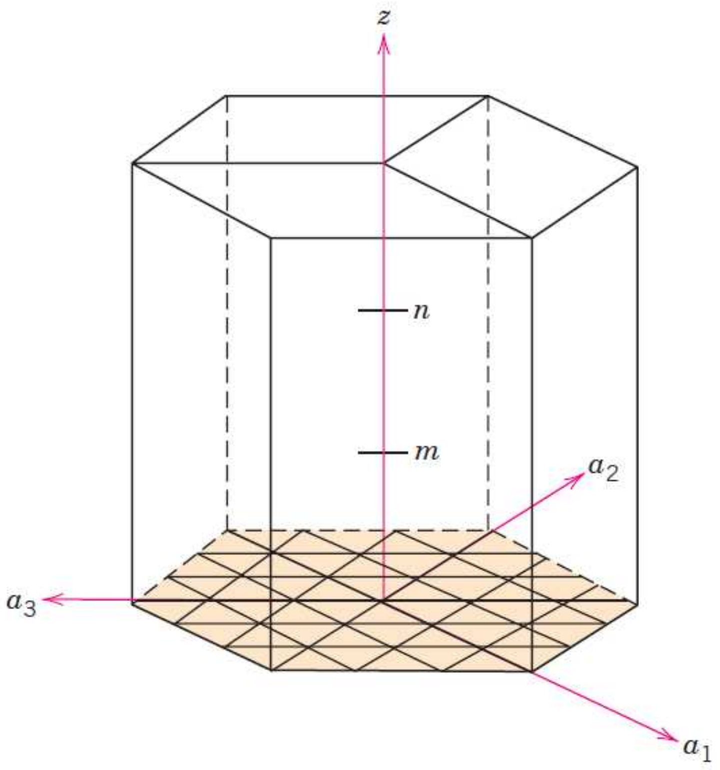
- Atomic packing of a BCC (110) plane





Plane of Hexagonal Crystals

- $(hkil) = (a_1, a_2, a_3, z)$
- $i = -(h+k)$.

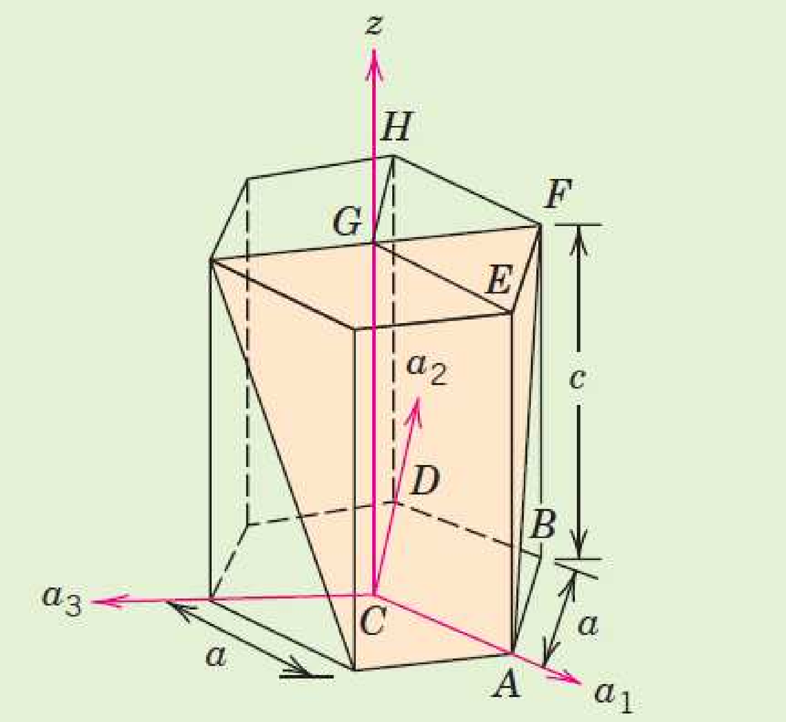


Example

$$h = 1$$
$$k = -1$$
$$l = 1$$

$$i = -(h + k)$$
$$= -(1 - 1) = 0$$

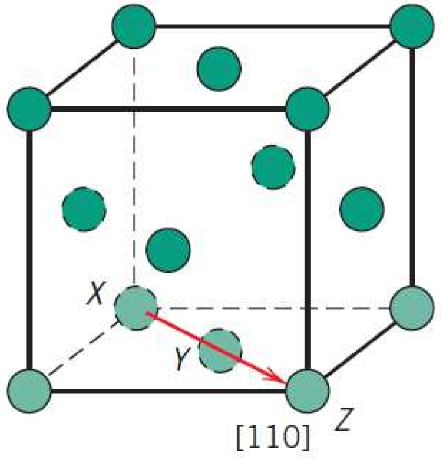
$$(1\bar{1}01)$$

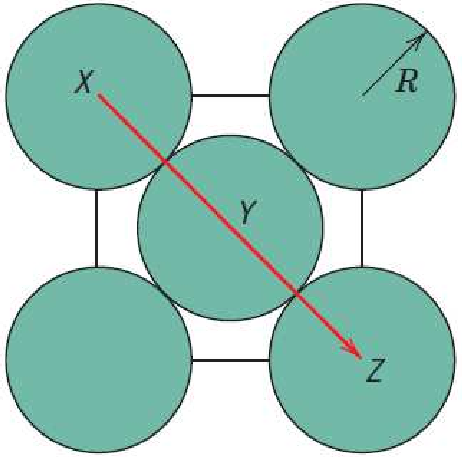


Linear Density

"number of atoms per unit length whose centers lie on the direction vector for a specific crystallographic direction"

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





$$\text{LD}_{110} = \frac{2 \text{ atoms}}{4R} = \frac{1}{2R}$$

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Planner Density

“number of atoms per unit area that are centered on a particular crystallographic plane”

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

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

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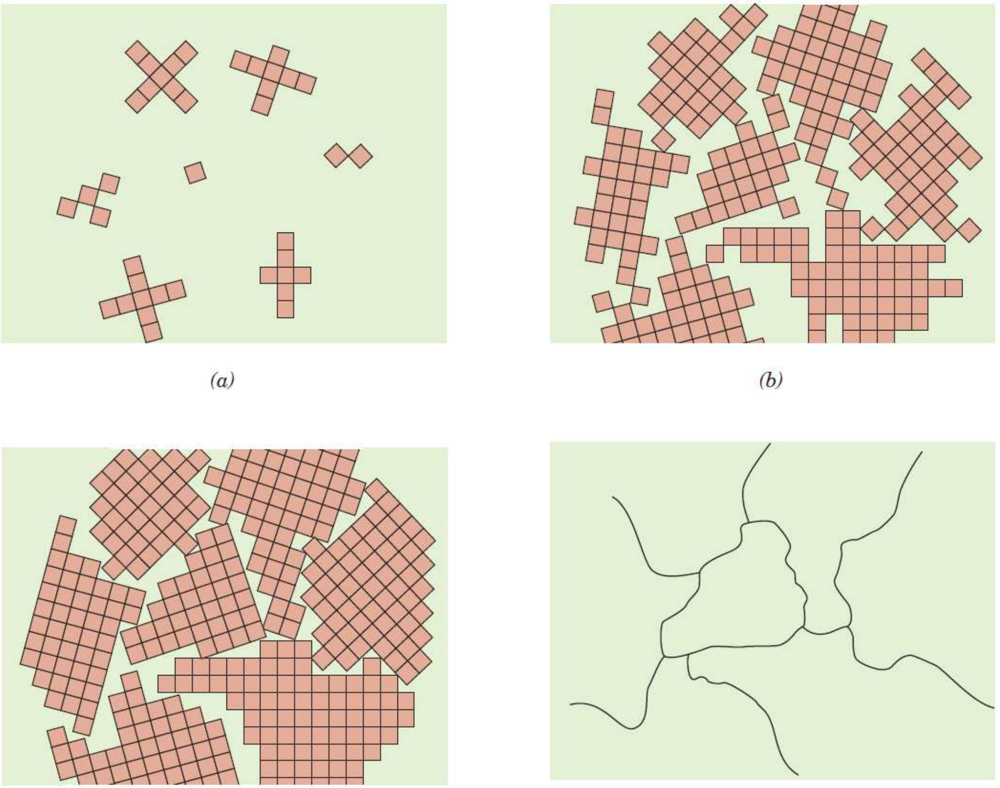
Polycrystalline Material

- **Polycrystalline :** Most crystalline solids are composed of a collection of many small crystals or **grains**



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Anisotropy

- For Single Crystal: Material properties depend on the direction.

	Modulus of Elasticity (GPa)		
Metal	*[100]*	*[110]*	*[111]*
Aluminum	63.7	72.6	76.1
Copper	66.7	130.3	191.1
Iron	125.0	210.5	272.7
Tungsten	384.6	384.6	384.6

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NonCrystalline Solids

- Also called **Amorphous**

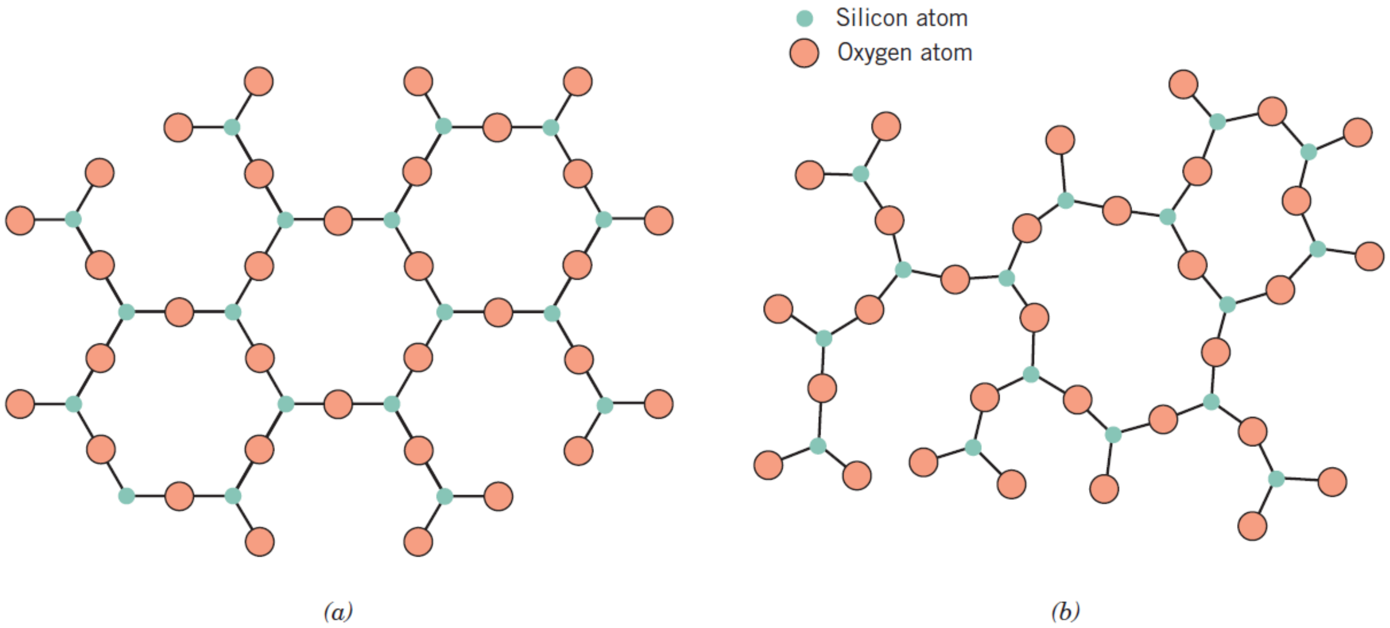

Figure 3.23 Two-dimensional schemes of the structure of (*a*) crystalline silicon dioxide and (*b*) noncrystalline silicon dioxide.

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Homework

1- What is the difference between atomic structure and crystal structure?

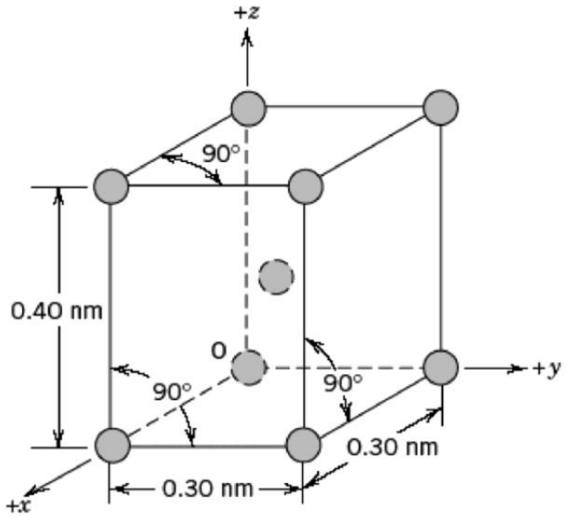
2- The atomic weight, density, and atomic radius for three hypothetical alloys are listed in the following table. For each determine whether its crystal structure is FCC, BCC, or simple cubic and then justify your determination.

Alloy	*Atomic Weight (g/mol)*	*Density (g/cm^3)*	*Atomic Radius (nm)*
A	77.4	8.22	0.125
B	107.6	13.42	0.133
C	127.3	9.23	0.142

Homework

3- Accompanying figure shows a unit cell for a hypothetical metal.

- (a) To which crystal system does this unit cell belong?
- (b) What would this crystal structure be called?
- (c) Calculate the density of the material, given that its atomic weight is 141 g/mol.



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Homework

4- Within a cubic unit cell, sketch the following directions:

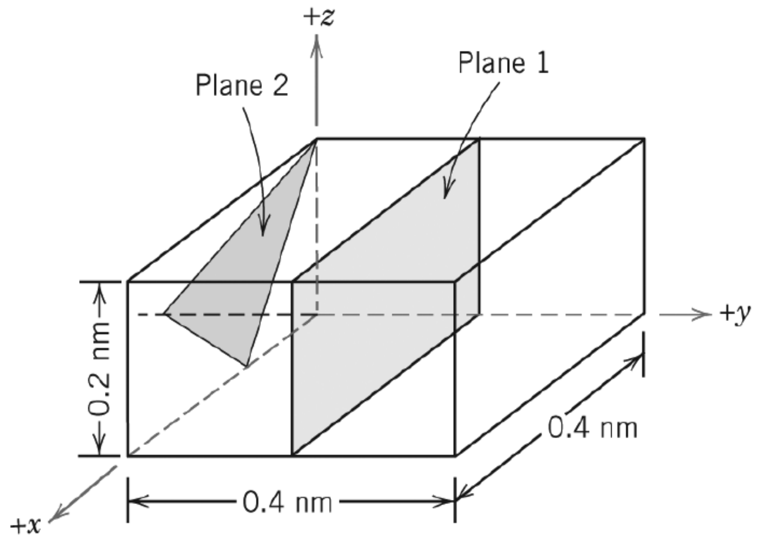
(a) $[\bar{1}10]$ (e) $[\bar{1}\bar{1}1]$

(b) $[\bar{1}\bar{2}1]$ (f) $[\bar{1}22]$

5- Draw an orthorhombic unit cell, and within that cell a (210) plane.

Homework

6- What are the indices for the two planes drawn in the sketch below?



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