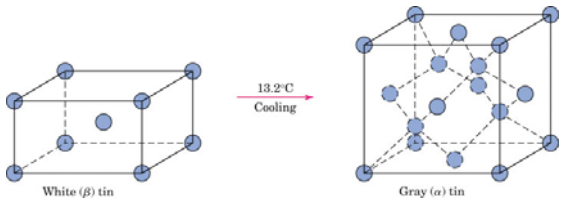
Structure of Crystalline Solids

Instructor:
Prof. Sujoy Kumar Kar



What are we going to discuss?

- Atomic arrangement in the solid state
- Concepts of crystallinity and noncrystallinity
- Notion of crystal structure, specified in terms of a unit cell
- The scheme by which crystallographic directions and planes are designated

Fundamental Concepts

- **Crystalline material:** One in which the atoms/ molecules/ ions are situated in a 3-dimensional repeating or periodic array over large atomic distances
  - All metals, many ceramic materials, and certain polymers form crystalline structures under normal solidification conditions
- **Noncrystalline or amorphous materials:**
  - *Do not crystallize*
  - *Long range atomic order absent*

Fundamental Concepts (Continued….)

Lattice:

- An imaginary pattern of points in which every point has an environment that is identical to that of any other point in the pattern.
- A lattice has no specific origin, as it can be shifted parallel to itself.
- Although it is an imaginary construct, the lattice is used to describe the structure of real materials.

Fundamental Concepts (Continued….)

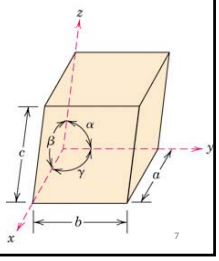
Unit cells:

- Small repeat units of lattice or, crystal structure
  - Defines the lattice/ crystal structure by virtue of its geometry and the atom positions within
- Parallelepipeds having three sets of parallel faces
- Chosen to represent the symmetry of the lattice/ crystal structure,
  - Not unique. Generally use the unit cell having the highest level of geometrical symmetry
- All the lattice points or atom positions in the crystal may be generated by translations of the unit cell integral distances along each of its edges.

Fundamental Concepts (Continued….)

Lattice Parameters:

- An x, y, z coordinate system is established with its origin at one of the unit cell corners; each of the x, y, and z axes coincides with one of the three parallelepiped edges that extend from this corner
- The unit cell geometry is completely defined in terms of six parameters: the three edge lengths a, b, and c, and the three inter-axial angles α, β, and γ. They are termed as **Lattice Parameters**



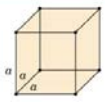
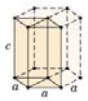
Fundamental Concepts (Continued….)

Crystal systems:

- Classification of crystals according to unit cell geometry.
- There are **seven** different possible combinations of a, b, and c, and α, β, and γ, each of which represents a distinct crystal system

1. **Cubic**
2. **Hexagonal**
3. **Tetragonal**
4. **Trigonal**
5. **Orthorhombic**
6. **Monoclinic**
7. **Triclinic**

- Defined in terms of highest symmetry elements present

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

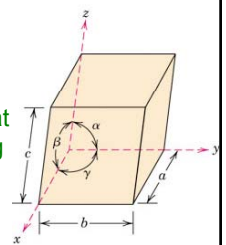
Crystal System	Axial Relationships	Interaxial Angles	Unit Cell Geometry
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c$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

Crystallographic Directions and Planes

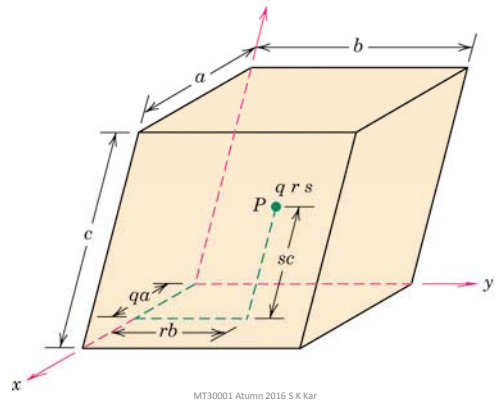
- All directions and planes are represented in the crystallographic coordinate system.
- This is always a right-handed coordinate system based on the unit cell.

Labeling conventions of crystallographic planes and directions

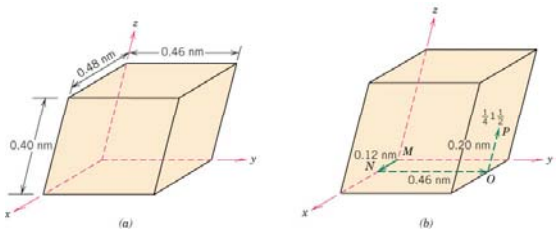
- Three integers or indices are used to designate directions and planes.
- The basis for determining index values is the unit cell, with a coordinate system consisting of three (*x, y, and z)* axes situated at one of the corners and coinciding with the unit cell edges
- For hexagonal, rhombohedral, monoclinic, and triclinic—the three axes are *not mutually perpendicular*



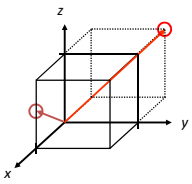
Point Coordinates



Point Coordinates



Crystallographic Directions



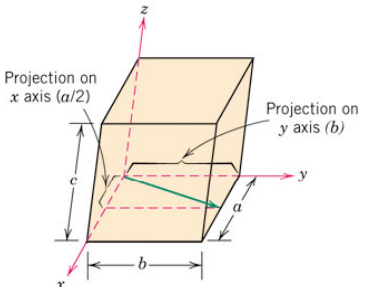
Algorithm

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 (Multiply or divide by a common factor)
4. Enclose in square brackets, no commas

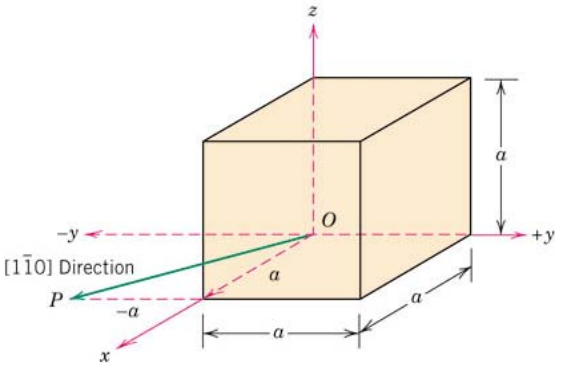
[*uvw*]

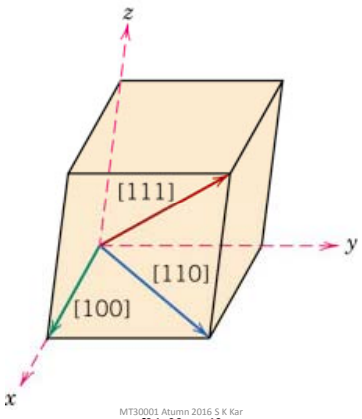
ex: 1, 0, ½ => 2, 0, 1 => [201]

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



	x	*y*	*z*
Projections	*a*/2	*b*	0*c*
Projections (in terms of *a*, *b*, and *c*)	½	1	0
Reduction	1	2	0
Enclosure	[120]		





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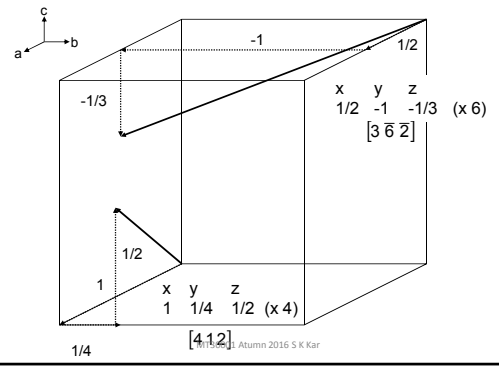
Miller Indices - Directions



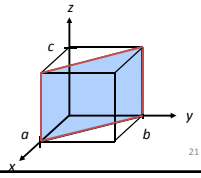
Equivalent directions

- Equivalent directions -- The spacing of atoms along each direction is the same.
- In cubic crystals, [100], [$\bar{1}$00], [010], [0$\bar{1}$0], [001], and [00$\bar{1}$] are equivalent.
- Equivalent directions are grouped together into a *family,* enclosed in angle brackets, thus: <100>.
- Directions in cubic crystals having the same indices without regard to order or sign, for example, [123] and [213], are equivalent.
- In general, not true for other crystal systems. In tetragonal crystal system, [100] and [010] directions are equivalent, whereas [100] and [001] are not.

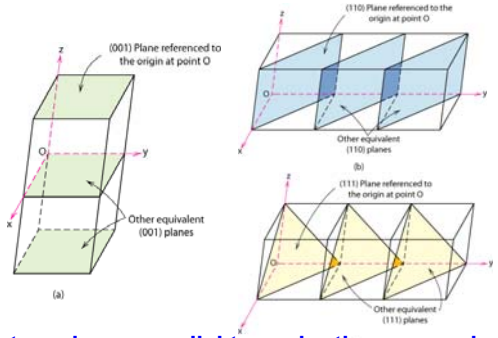
Crystallographic Planes

- Algorithm
  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, new origin must be established at the corner of another unit cell. At this point the crystallographic plane either intersects or parallels each of the three axes
  2. Read off intercepts of plane with axes in terms of *a*, *b*, *c*
  3. Take reciprocals of intercepts
  4. Reduce to smallest integer values
  5. Enclose in parentheses, no commas i.e., (*hkl*)

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)		



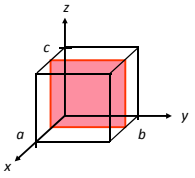
Crystallographic Planes



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

Crystallographic Planes

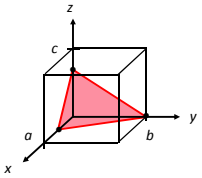
example		*a*	*b*	*c*
1.	Intercepts	1/2	∞	∞
2.	Reciprocals	1/½	1/∞	1/∞
		2	0	0
3.	Reduction	2	0	0
4.	Miller Indices	(200)		



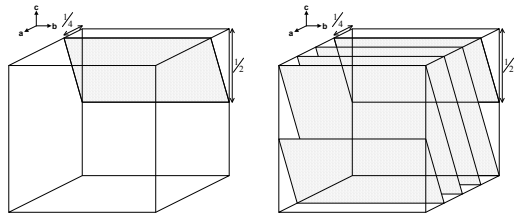
Crystallographic Planes

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)		



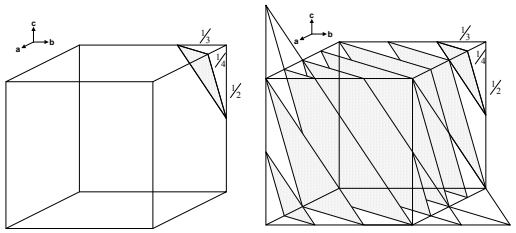
Miller Indices - Planes



	x	y	z
intercept	1/4	∞	-1/2
reciprocal	4	0	-2

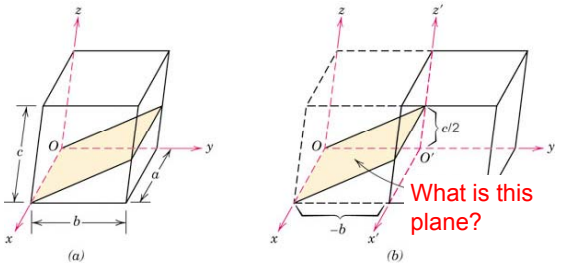
$(4\,0\,\bar{2})$

Miller Indices - Planes



	x	y	z
intercept	1/4	-1/3	-1/2
reciprocal	4	-3	-2

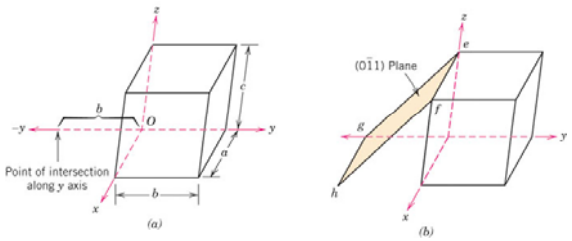
$(4\,\bar{3}\,\bar{2})$



$(0\bar{1}2)$

Which one is the $(0\bar{1}1)$ plane?

Follow the steps in reverse order: 1) Take reciprocal 2) Determine the intercepts.



Miller Indices

Planes	(hkl)	specific
	{hkl}	family
Directions	[uvw]	specific
	<uvw>	family

- No commas
- No fractions
- Negative indicated by bar over number

Reversing the directions of all indices specifies another plane parallel to, on the opposite side of and equidistant from, the origin.

Family of Planes {*hkl*}

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

Equivalent Planes

A family of planes includes all planes which are equivalent by symmetry (Same atomic packing) - depends on crystal system.

- For cubic: (110),(011) and (101) are all {110}
- For tetragonal: (011) and (101) are {101} but (110) is not (c≠a)

- In the cubic system only, planes having the same indices, irrespective of order and sign, are equivalent
- Both $(1\bar{2}3)$ and $(3\bar{1}2)$ belong to the {123} family

Cubic crystals

- One interesting and **unique** characteristic **of cubic crystals** is that **planes and directions having the same indices are perpendicular to one another**
- For other crystal systems there are no simple geometrical relationships between planes and directions having the same indices

Why 4-index notation for Hexagonal crystals ?

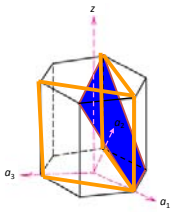
The third index is included to emphasize the symmetry; if the third index were not included, you might not realize that, e.g., the *(2 $\bar{1}$ 0)* and **(1 1 0)** are crystallographically equivalent.

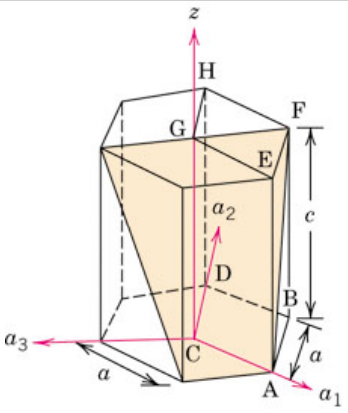
What are these planes in hexagonal unit cell? : *(2 $\bar{1}$ 0)* and **(1 1 0)**

Crystallographic Planes (Hexagonal)

- In hexagonal unit cells the same idea is used

example	a_1	a_2	c
1. Intercepts	1	∞	1
2. Reciprocals	1	1/∞	1
	1	0	1
3. Reduction	1	0	1
4. Miller Indices	(101)		

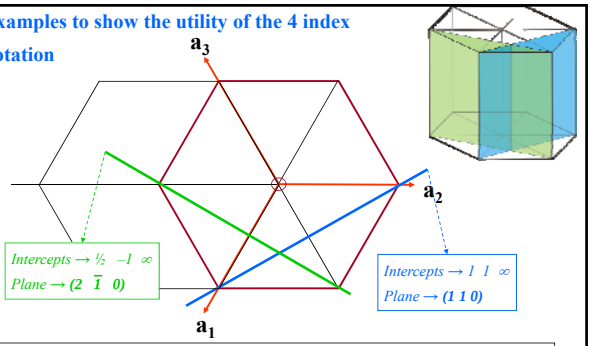




What is the Miller-Bravais indices of the plane?

(1 -1 0 1)

Examples to show the utility of the 4 index notation



These planes are crystallographically equivalent. – Not apparent from the 3 index notation

In 4 index system (2 $\bar{1}$ $\bar{1}$ 0)

In 4 index system Plane → (1 1 $\bar{2}$ 0)

Miller-Bravais indices

(hkl) → (hkil)

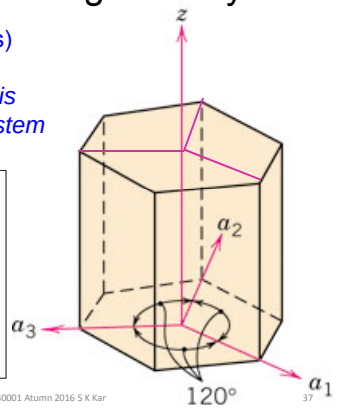
i = -(h+k)

Directions in Hexagonal Crystal

3-indices (Miller indices)
and
4-indices (*Miller–Bravais indices), coordinate system*

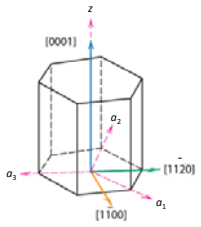
Why we need 4 index system?

In 4 index system, Indices reveal crystallographically equivalent directions



3 index (Miller indices) to 4 index (Miller-Bravais indices)

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



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

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

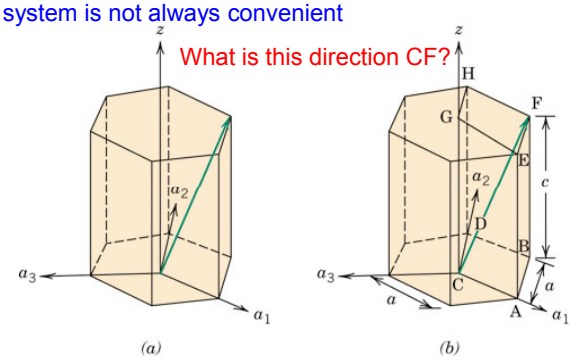
$$v = \frac{1}{3}(2v' - u')$$

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

$$w = w'$$

Finding perpendicular projections in Hexagonal crystal system is not always convenient

What is this direction CF?



In three index system: [1 1 1]

What is the index of the direction CE?

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

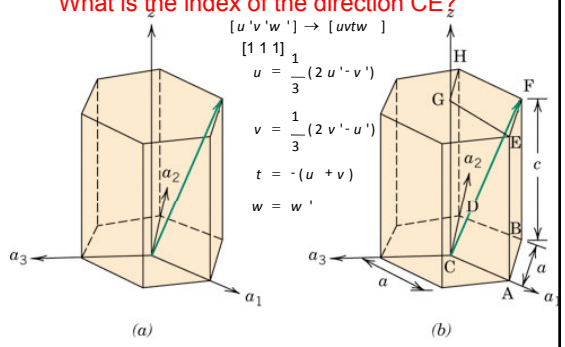
[1 1 1]

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

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

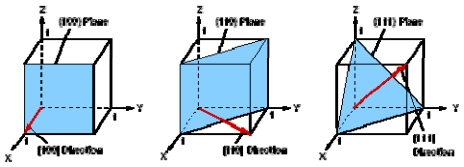
$$t = -(u + v)$$

$$w = w'$$



In Four index system: $[11\bar{2}3]$

MILLER INDICES OF SOME IMPORTANT PLANES



Angle θ between two cystallographic directions
$[u_1\ v_1\ w_1]$ and $[u_2\ v_2\ w_2]$

$$\cos\theta = \frac{u_1u_2 + v_1v_2 + w_1w_2}{(u_1^2 + v_1^2 + w_1^2)^{1/2} \times (u_2^2 + v_2^2 + w_2^2)^{1/2}}$$

Worked Example
Find the angle between the directions [2 1 1] and [1 1 2] in a cubic crystal.

The two directions are [2 1 1] and [1 1 2]

In this case, $u_1 = 2$, $v_1 = 1$, $w_1 = 1$, $u_2 = 1$, $v_2 = 1$, $w_2 = 2$

$$\therefore \cos\theta = \frac{(2 \times 1) \times (1 \times 1) + (1 \times 2)}{\sqrt{2^2 + 1^2 + 1^2} \times \sqrt{1^2 + 1^2 + 2^2}} = \frac{5}{6}$$

(or) $\cos\theta = 0.833 \rightarrow \theta = 35°35'30''$

Interplanar Distance

$$d_{hkl} = \frac{a}{\sqrt{\left(h^2 + k^2 + l^2\right)}}$$

If (h k l) is the Miller indices of a crystal plane then the intercepts made by the plane with the crystallographic axes are given as $\frac{a}{h}, \frac{b}{k}$ and $\frac{c}{l}$

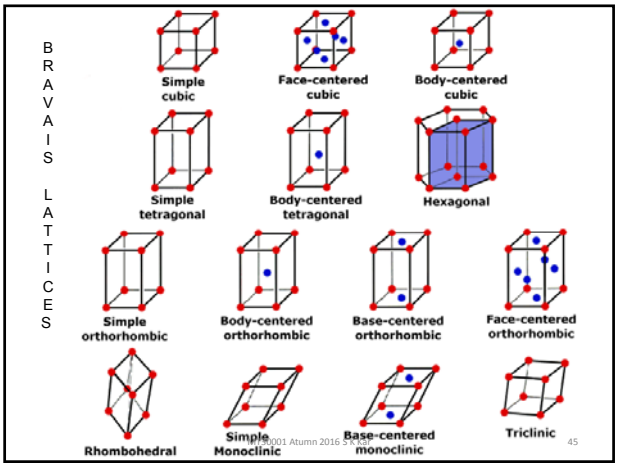
where a, b and c are lattice parameters

Bravais Lattices

Named after named after Auguste Bravais

7 Crystal Systems → (Centering) → 14 Bravais Lattices

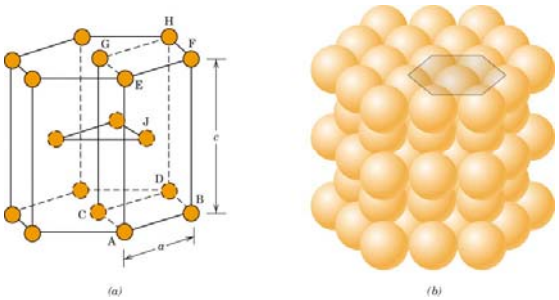
- Primitive
- Body Centering
- Face Centering
- Base Centering



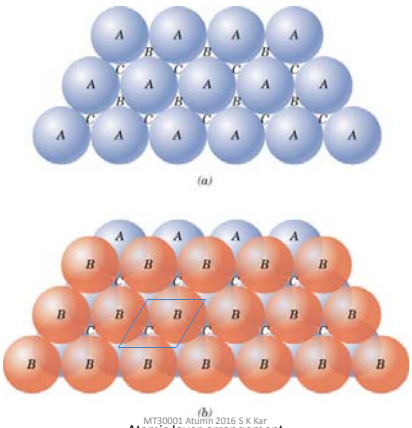
Bravais Lattices (14)

Crystal System	Parameters	Primitive (Simple)	Body-Centered	Face-Centered	Base-Centered
Cubic	a=b=c α=β=γ=90°	X	X	X	
Tetragonal	a=b≠c α=β=γ=90°	X	X		
Orthorhombic	a≠b≠c α=β=γ=90°	X	X	X	X
Rhombohedral	a=b=c α=β=γ≠90°	X			
Hexagonal	a=b≠c α=β=90°, γ=120°	X			
Monoclinic	a≠b≠c α=γ=90°≠β	X			X
Triclinic	a≠b≠c α≠β≠γ≠90°	X			

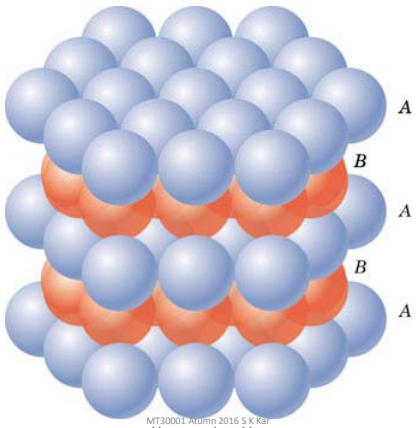
HCP Structure



Hexagonal unit cell



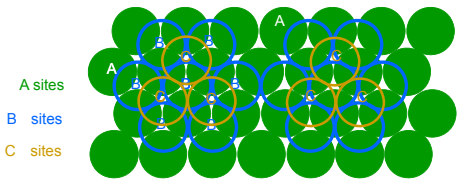
Atomic layer arrangement



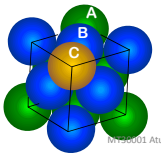
Hexagonal packing

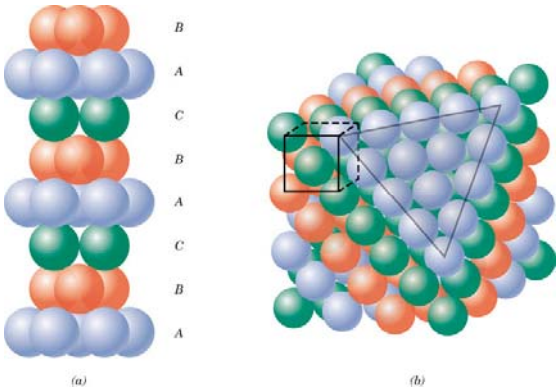
Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

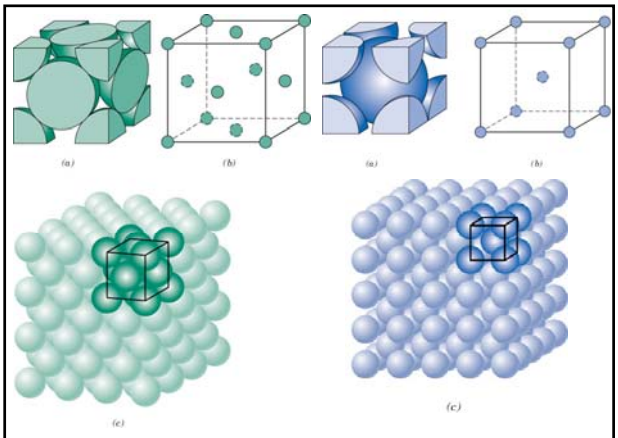


- FCC Unit Cell





Cubic closed packing

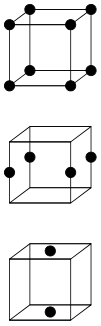


FCC unit cell

BCC unit Cell

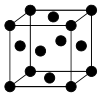
Atoms Per Unit Cell

- Corners - shared by eight unit cells (x 1/8)
- Edges - shared by four unit cells (x 1/4)
- Faces - shared by two unit cells (x 1/2)

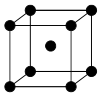


Common Metal Structures

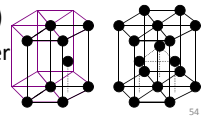
- Face-Centered Cubic (FCC)
  - 8 corners x 1/8 + 6 faces x 1/2
  - 1 + 3 = 4 atoms/u.c.



- Body-Centered Cubic (BCC)
  - 8 corners x 1/8 + 1 center
  - 1 + 1 = 2 atoms/u.c.



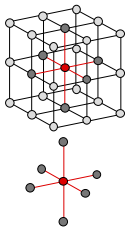
- Hexagonal Close-Packed (HCP)
  - (4 x (1/6) + 4 x (1/12)) = 1 corner + 1 middle
  - 1 + 1 = 2 atoms/u.c.



Simple Cubic Structure (SC)

- Rare due to low packing density (only Po has this structure)
  - Close-packed directions are cube edges.

- Coordination # = 6
  (# nearest neighbors)

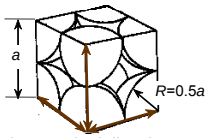


Atomic Packing Factor (APF)

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

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions
contains 8 x 1/8 =
1 atom/unit cell

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

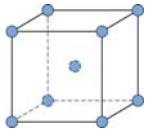
Body Centered Cubic Structure (BCC)

- Atoms touch each other along cube diagonals.

--Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

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

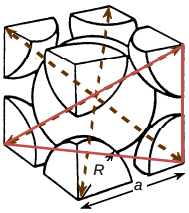
- Coordination # = 8

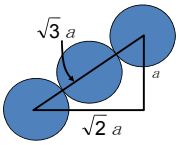


2 atoms/unit cell: 1 center + 8 corners x 1/8

Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68





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

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

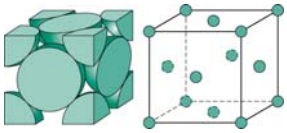
Face Centered Cubic Structure (FCC)

- Atoms touch each other along face diagonals.

--Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

ex: Al, Cu, Au, Pb, Ni, Pt, Ag

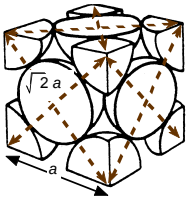
- Coordination # = 12



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

Atomic Packing Factor: FCC

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



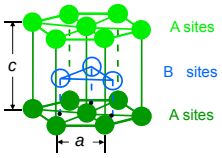
Close-packed directions:
length = $4R = \sqrt{2}\,a$

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

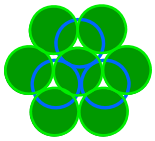
$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} = \frac{4 \cdot \frac{4}{3}\pi (\sqrt{2}\,a/4)^3}{a^3} \cdot \frac{\text{volume}}{\text{unit cell}}$$

Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection



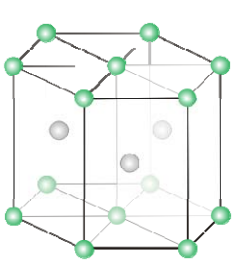
- 2D Projection

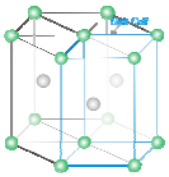


- Coordination # = 12
- APF = 0.74
- c/a = 1.633

6 atoms/unit cell

ex: Cd, Mg, Ti, Zn





c/a = sqrt(8/3)

Spheres at: (0,0,0), (⅔, ⅓,½)

Note: Atoms are coloured differently but are the same

Atomic Packing Factor: HCP

Close-packed directions:

length = 2R = a

c/a = $\sqrt{8/3}$

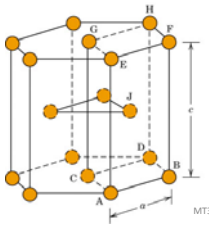
Unit cell contains:

4 x 1/(3 x 2) + 4 x 1/(6 x 2) + 1

= 2 atoms/unit cell

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

$$\approx 0.74.$$



Theoretical Density, ρ

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

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

where

n = number of atoms/unit cell

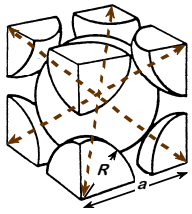
A = atomic weight

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

N_A = Avogadro's number

= 6.023 x 10^{23} 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

$$\rho = \frac{\frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{g}}{\text{mol}}}{\text{volume} \cdot \frac{\text{atoms}}{\text{mol}}} = \frac{2 \cdot 52.00}{a^3 \cdot 6.023 \times 10^{23}}$$

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

ρ_{actual} = 7.19 g/cm^3

Linear and Planar density

- Linear Density

– Number of atoms per length whose centers lie on the direction vector for a specific crystallographic direction.

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

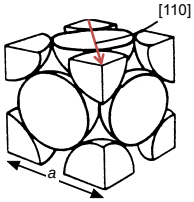
- Planar Density

– Number of atoms per unit area that are centered on a particular crystallographic plane.

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

Linear Density

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



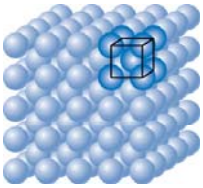
ex: linear density of Al in [110] direction
a = 0.405 nm

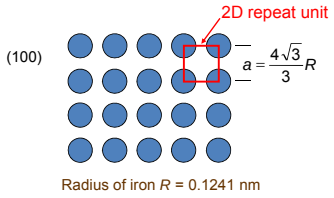
atoms: 2
length: $\sqrt{2}a$

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

Planar Density of (100) Iron

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





Radius of iron R = 0.1241 nm

atoms in 2D repeat unit: 1
area of 2D repeat unit: a^2

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

Linear and Planar Density

- Why do we care?
  - Properties, in general, depend on linear and planar density.
- Examples:

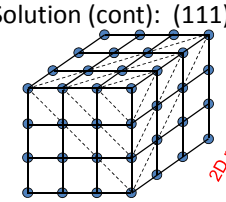
  Speed of sound along directions
  - Slip (deformation in metals) depends on linear and planar density
  - Slip occurs on planes that have the greatest density of atoms in direction with highest density (*we would say along closest packed directions on the closest packed planes*)

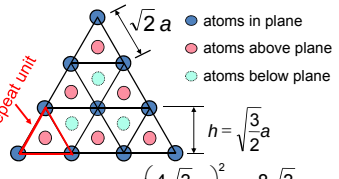
Class Work

Find out the Planar Density of (111) plane of Iron

Planar Density of (111) Iron

Solution (cont): (111) plane 1 atom in plane/ unit surface cell





$$\text{area} = \frac{\sqrt{3}}{4}2a^2 = \frac{\sqrt{3}}{2}a^2 = \frac{\sqrt{3}}{2}\left(\frac{4\sqrt{3}}{3}R\right)^2 = \frac{8\sqrt{3}}{3}R^2$$

atoms in 2D repeat unit: 1/2
area of 2D repeat unit: $\frac{8\sqrt{3}}{3}R^2$

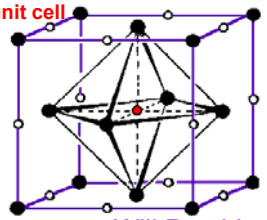
$$\text{Planar Density} = \frac{1/2}{\frac{8\sqrt{3}}{3}R^2} = 7.0\ \frac{\text{atoms}}{\text{nm}^2} = 0.70 \times 10^{19}\ \frac{\text{atoms}}{\text{m}^2}$$

Octahedral interstitial sites

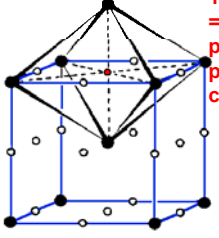
The space in the interstices between **6** regular atoms that form an octahedron.

Four regular atoms are positioned in a plane, the other two are in a symmetrical position just above or below.

FCC
12/4 +1 = 4 positions per unit cell



BCC



12/4 + 6/2 = 6 positions per unit cell

Will Provide you this slide

Tetrahedral interstitial sites

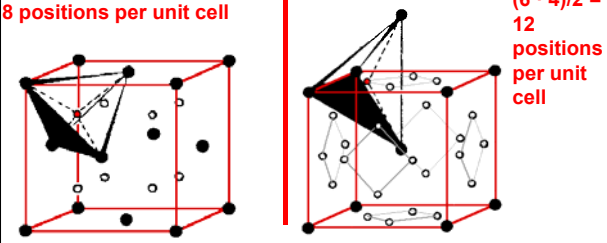
The center of a tetrahedra formed by four lattice atoms.

Three atoms, touching each other, are in plane; the fourth atom sits in the symmetrical position on top.

FCC
8 positions per unit cell

BCC

(6 · 4)/2 = 12 positions per unit cell



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Ceramic Crystal Structures

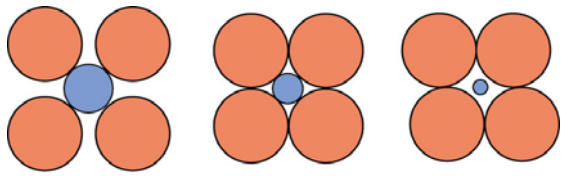
- Greek word "Keramikos" (= burnt stuff) → Ceramics
  - Desired properties obtained through a high temperature heat treatment process called "Firing"
- Composed of atleast two elements –
  - Crystal structures are more complex than metals
- Bonding is ionic to covalent
  - Depending on the electro-negativities of the atoms

Bond characters of ceramics

Material	*Percent Ionic Character*
CaF_2	89
MgO	73
NaCl	67
Al_2O_3	63
SiO_2	51
Si_3N_4	30
ZnS	18
SiC	12

For ceramics having ionic bonding

- Cation and anions
- Charges on them and relative sizes determine the crystal structure
- Cations are smaller than anions
- Ions prefer to have maximum number of oppositely charged ion nearest neighbours
- Stable ceramic structure forms when those anions surrounding a cation are all in contact with that cation

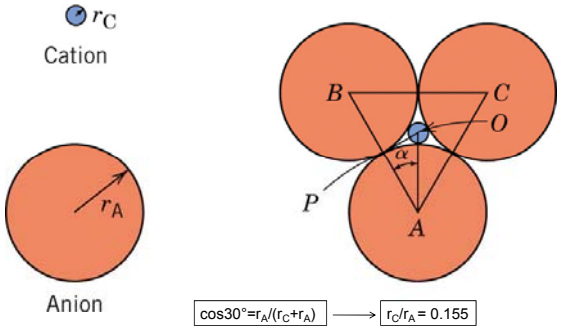


Stable Stable Unstable

Radius Ratio Rules

- The coordination number (number of anion nearest neighbours for a cation) is related to the cation-anion radius ratio.
- For a specific coordination number, there is a critical or minimum r_C/r_A ratio for which the cation-anion contact is established.

Minimum r_C/r_A ratio for CN=3



$\cos 30° = r_A/(r_C + r_A) \longrightarrow r_C/r_A = 0.155$

Radius Ratio Rules

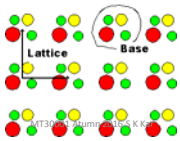
Coordination Number	Cation–Anion Radius Ratio	Coordination Geometry
2	<0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	

Common Ceramic Crystal Structures

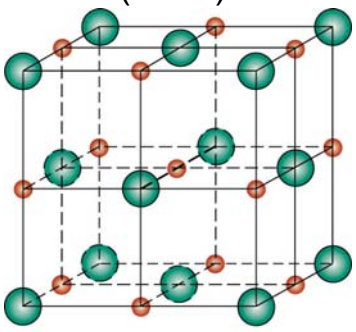
Structure Name	Structure Type	Anion Packing	Coordination Numbers: Cation	Coordination Numbers: Anion	Examples
Rock salt (sodium chloride)	AX	FCC	6	6	NaCl, MgO, FeO
Cesium chloride	AX	Simple cubic	8	8	CsCl
Zinc blende (sphalerite)	AX	FCC	4	4	ZnS, SiC
Fluorite	AX_2	FCC	8	4	CaF_2, UO_2, ThO_2
Perovskite	ABX_3	SC	12(A) 6(B)	6	$BaTiO_3$, $SrZrO_3$, $SrSnO_3$
Spinel	AB_2X_4	FCC	4(A) 6(B)	4	$MgAl_2O_4$, $FeAl_2O_4$

Crystal = Bravais lattice + Base

- A *crystal* now is obtained by taking a **Bravais lattice** *and* adding a **base**! The base can just be one atom (as in the case of many elemental crystals, most noteworthy the metals), two identical atoms (e.g. **Si**, **Ge**, **C**(diamond)), two different atoms (**NaCl**, **GaAs**, ...) three atoms, ... up to huge complex molecules as in the case of protein crystals.



Rock Salt (NaCl) Structure

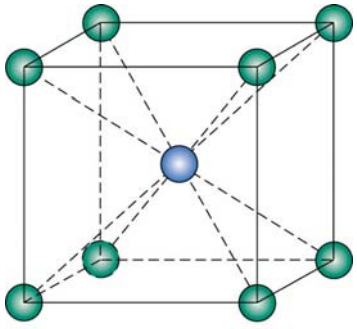


(fcc), with *two* atoms in the base: one at **(0, 0, 0)**, the other one at **(½, ½, ½)**

Many salts and oxides have this structure, e.g. **KCl**, **AgBr**, **KBr**, **PbS**, ... or **MgO**, **FeO**, ...

Na^+ Cl^-

CsCl Crystal Structure

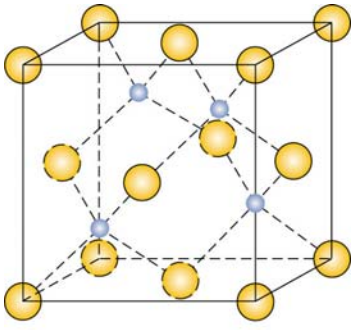


cubic primitive with *two* atoms in the base at **(0,0,0)** and **(½, ½, ½)**

Intermetallic compounds (not necessarily ionic crystals), but also common salts assume this structure; e.g. **CsCl**, ..., or **AlNi**, **CuZn**

Cs^+ Cl^-

ZnS (Zinc Blende) Structure

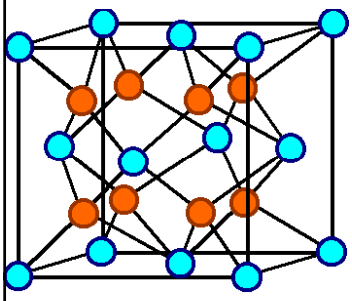


(fcc) with two atoms in the base at **(0,0,0)** and **(¼, ¼, ¼)**

typical lattice of *covalently bonded group IV semiconductors* (**C** (diamond form), **Si**, **Ge**) or III-V compounds semiconductors (**GaAs, GaP, InSb, InP,** ..)

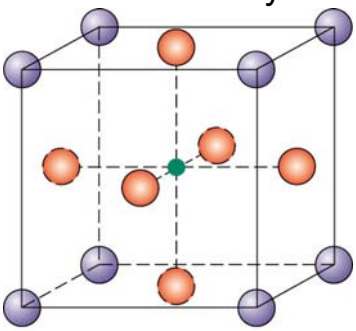
Zn S

CaF_2 (Fluorite) Structure



(fcc) with *three* atoms in the base, one kind (the cations) at **(0,0,0)**, and the other two (anions of the same kind) at **(¼, ¼, ¼)**, and **(-¼, -¼, -¼)**

Perovskite crystal Structure

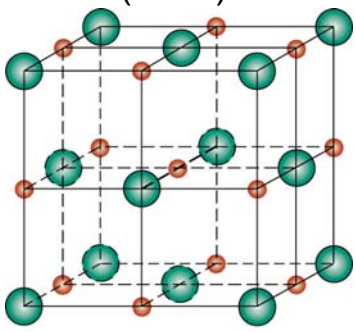


cubic primitive: *three* different atoms in the base. In the example it would be **Ba** at **(0,0,0)**, **O** at **(½, ½, ,0),** at **(½, 0, ½),** at **(0, ½, ½)** and **Ti** at **(½, ½, ½)**.

Barium titanate ($BaTiO_3$), having both Ba^{2+} and Ti^{4+} cations

Ti^{4+} Ba^{2+} O^{2-}

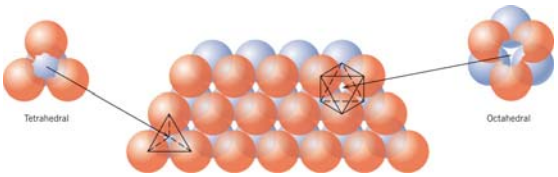
Rock Salt (NaCl) Structure



Na^+ Cl^-

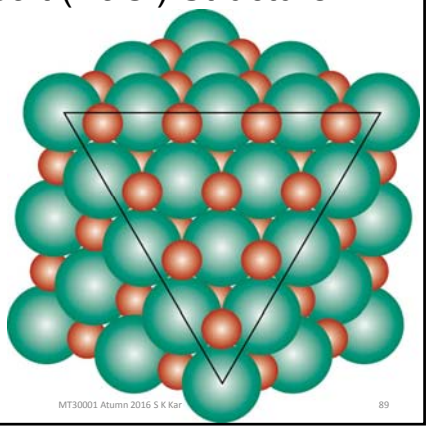
Close Packed Structure in ceramics

- Close packed planes of anions
- Cations reside at Tetrahedral and/ or Octrahedral interstitial sites



Rock Salt (NaCl) Structure

- Close packed arrangement of Cl ions on {111} planes
- Na+ ions are at Octahedral sites



DENSITY COMPUTATIONS—CERAMICS

$$\rho = \frac{n'(\Sigma A_C + \Sigma A_A)}{V_C N_A}$$

where

n' = the number of formula units[1] within the unit cell

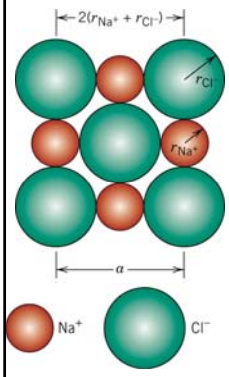
ΣA_C = the sum of the atomic weights of all cations in the formula unit

ΣA_A = the sum of the atomic weights of all anions in the formula unit

V_C = the unit cell volume

N_A = Avogadro's number, 6.023×10^{23} formula units/mol

DENSITY COMPUTATIONS—CERAMICS



$$\Sigma A_C = A_{Na} = 22.99 \text{ g/mol}$$

$$\Sigma A_A = A_{Cl} = 35.45 \text{ g/mol}$$

$$V_C = a^3 = (2r_{Na^+} + 2r_{Cl^-})^3$$

n' = 4; FCC lattice

$$\rho = \frac{n'(A_{Na} + A_{Cl})}{(2r_{Na^+} + 2r_{Cl^-})^3 N_A}$$

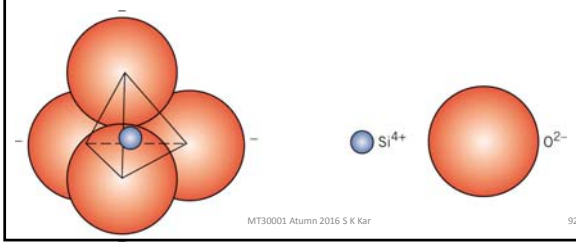
$$= \frac{4(22.99 + 35.45)}{[2(0.102 \times 10^{-7}) + 2(0.181 \times 10^{-7})]^3 (6.023 \times 10^{23})}$$

$$= 2.14 \text{ g/cm}^3$$

Experimental value: 2.16 gm/cc

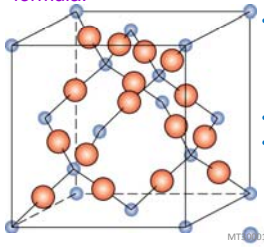
Silicate Ceramics

- Bulk of soils, rocks, clays, and sand come under the silicate classification
- Characterize crystal structure in terms of various arrangements of an SiO_4^{4-} tetrahedron
- Basic unit of the silicates



Silica (SiO_2)

- Chemically, the most simple silicate
- Structurally, it is a 3d network generated when every corner O atom in each tetrahedron is shared by adjacent tetrahedra.
- Electrically neutral
- The ratio of Si to O atoms is 1 : 2, as indicated by the chemical formula.



- Three primary polymorphic crystalline forms of silica: quartz, cristobalite and tridymite.
- Strong Si-O bonds → high mp
- Relatively open str. → Low density

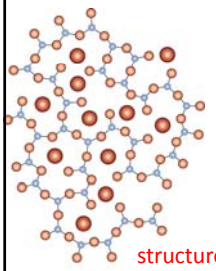
Si^{4+} O^{2-}

SILICA GLASSES

Silicon dioxide (or silica, SiO_2) in the noncrystalline state is called *fused silica, or vitreous silica*

Other oxides (e.g., B_2O_3 and GeO_2) may also form glassy structures

Network formers



The common inorganic glasses used for containers → Silica glasses to which have been added other oxides such as CaO and Na_2O

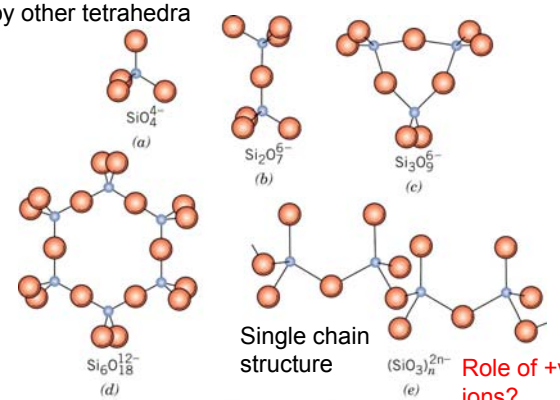
Cations are incorporated within and modify the SiO_4^{4-} network

Network modifiers

Lowers the mp and viscosity of glasses → easy formation at low temp

structure of a sodium–silicate glass

One or two or three corner oxygen atoms are shared by other tetrahedra



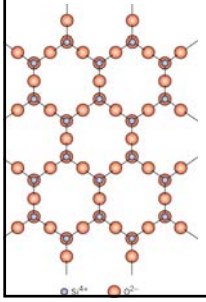
Single chain structure

Role of +ve ions?

Si^{4+} O^{2-}

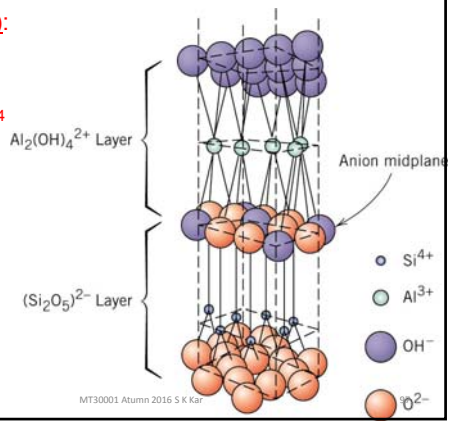
Sheet or layered silicates

- A 2d sheet or layered structure
- By sharing of 3 O ions in each of the tetrahedra
- A second planar sheet structure having an excess of cations → Charge neutrality

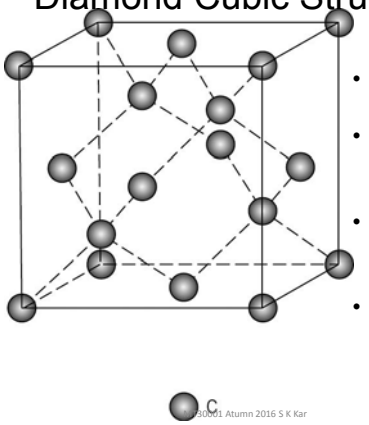


Their basic structure is characteristic of clays and other minerals

Keolinite (Clay):
2 layer silicate sheet structure
$Al_2(Si_2O_5)(OH)_4$
Talc
Mica

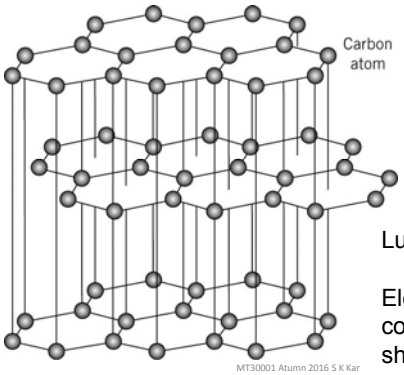


Diamond Cubic Structure



- Extremely hard
- Low electrical conductivity
- Optically Transparent
- High index of refraction

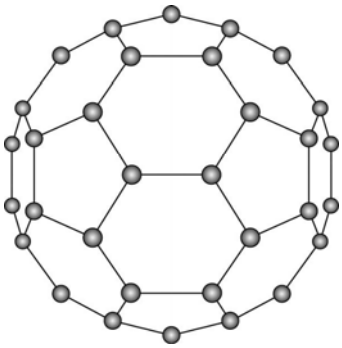
Graphite



Lubricative property

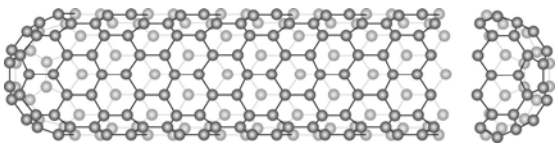
Electrical conductivity along sheet

Fullerenes

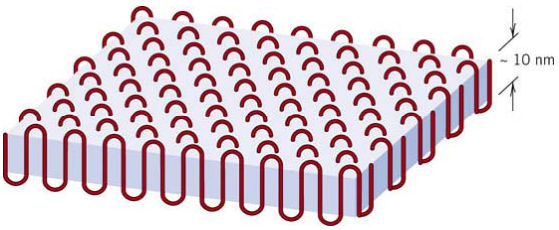


Buckminsterfullerene
Buckyball

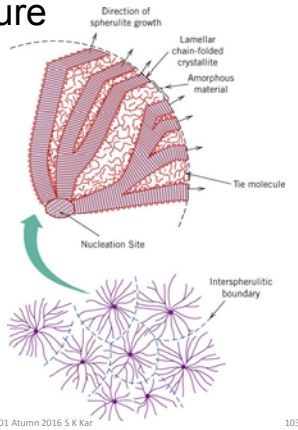
Carbon Nanotube

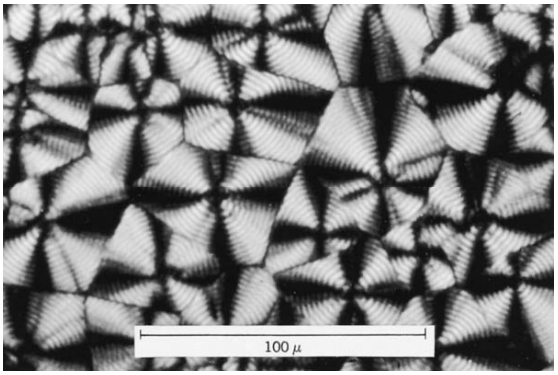


Chain Folded model of Polymer crystallite



Spherulite sructure





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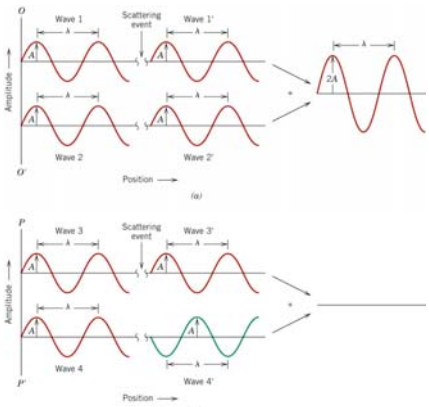
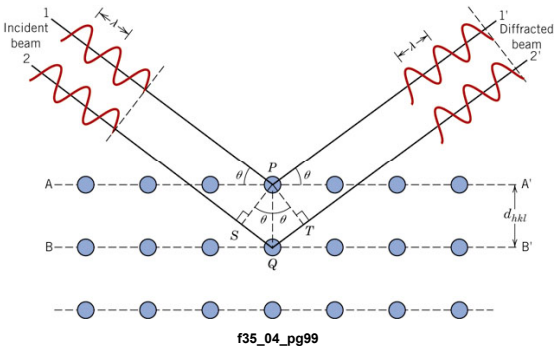
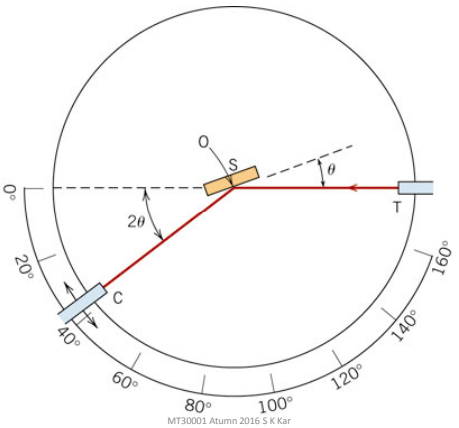
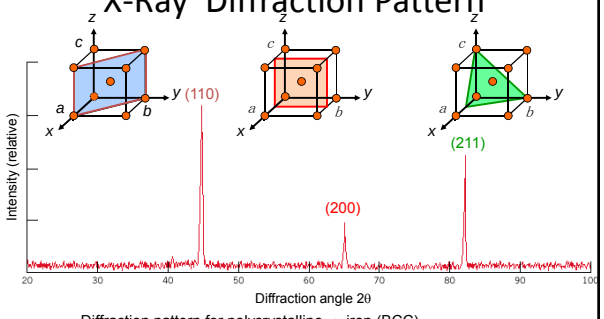




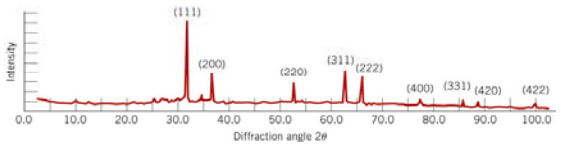
f35_04_pg99



X-Ray Diffraction Pattern



Diffraction pattern for polycrystalline α-iron (BCC)

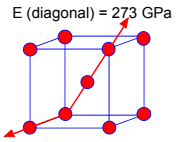


Single vs Polycrystals

- Single Crystals

-Properties vary with direction: anisotropic.

-Example: the modulus of elasticity (E) in BCC iron:

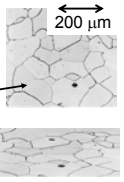


- Polycrystals

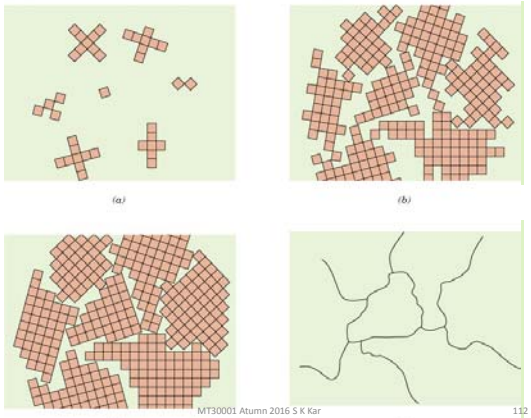
-Properties may/may not vary with direction.

-If grains are randomly oriented: isotropic. ($E_{poly\ iron}$ = 210 GPa)

-If grains are textured, anisotropic.



Concept of Grains and Grain Boundary: Single crystal vs. polycrystalline



Modulus of Elasticity values for several metals at various crystallographic orientations

	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

Questions

1. If you are given plots of interatomic force vs. interatomic distance for two different metal systems, then how would you determine which metal has higher stiffness among the two from the plots?
2. Why are metals electrically conductive while ceramics are not?
3. How is bond energy related to coefficient of thermal expansion?
4. How many valence electrons are there for Boron?
5. What are the relations between lattice parameters for Monoclinic system?
6. For which four crystal systems, the three axes along unit cell edges are not mutually perpendicular?

Clarifications:

Indexing of Crystallographic planes

- Convert to smallest integers (**Optional step**)

Index reduction is not carried out (e.g., for x-ray or electron diffraction studies); for example, (002) is not reduced to (001). In addition, for ceramic materials, the ionic arrangement for a reduced-index plane may be different from that for a nonreduced one.

Clarification

Can the indices representing directions be irrational numbers? YES
→

Can the directions represented by irrational numbers be lattice vectors? **NO**

So, For lattice vectors, indices have to be integers → Miller indices of the Crystallographic directions would be integers