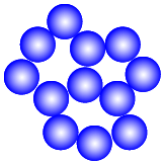
Chapter 3: Structures of Metals & Ceramics

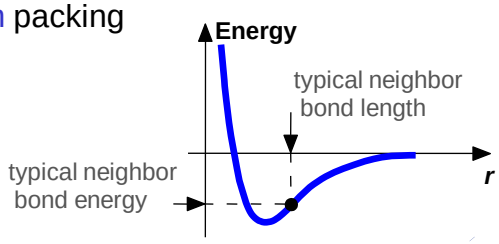
ISSUES TO ADDRESS...

- What is the difference in atomic arrangement between crystalline and noncrystalline solids?
- What features of a metal's/ceramic's atomic structure determine its density?
- How do the crystal structures of ceramic materials differ from those for metals?
- Under what circumstances does a material property vary with the measurement direction?

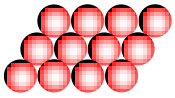
Energy and Packing

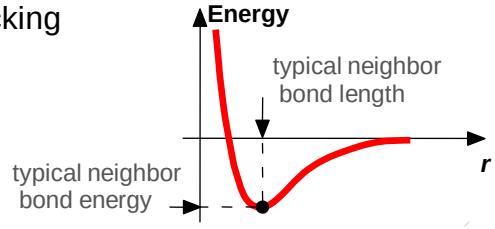
- Non dense, random packing





- Dense, ordered packing

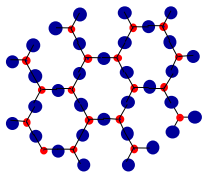




Dense, ordered packed structures tend to have lower energies.

Materials and Packing

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

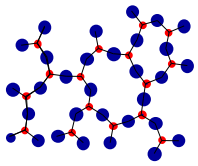


crystalline SiO_2
Adapted from Fig. 3.41(a), *Callister & Rethwisch 4e.*

• Si ● Oxygen

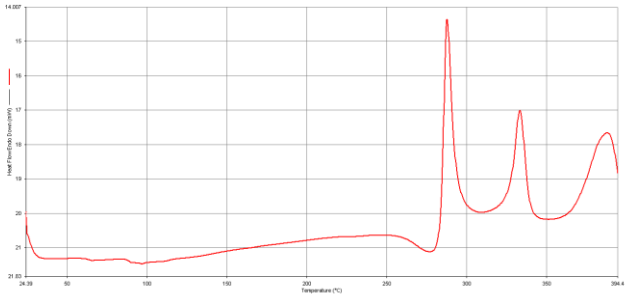
Noncrystalline materials...
- atoms have no periodic packing
- occurs for: -complex structures
  -rapid cooling

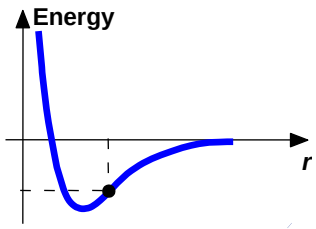
"Amorphous" = Noncrystalline



noncrystalline SiO_2
Adapted from Fig. 3.41(b), *Callister & Rethwisch 4e.*

DSC profile of amorphous materials
(Differential scanning calorimetry)

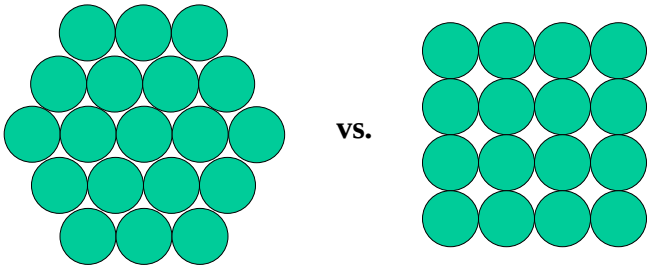




Metallic Crystal Structures

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

2-dimensions



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

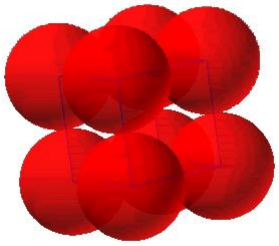
Metallic Crystal Structures

- Tend to be densely packed.
- Reasons for dense packing:
  - Typically, only one element is present, so all atomic radii are the same.
  - Metallic bonding is not directional.
  - Nearest neighbor distances tend to be small in order to lower bond energy.
- Metals have the simplest crystal structures.

We will examine three such structures...

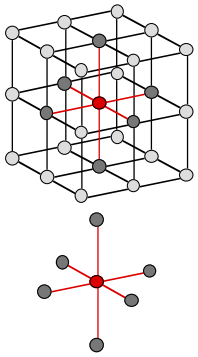
Simple Cubic Structure (SC)

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



(Courtesy P.M. Anderson)

- Coordination # = 6
  (# nearest neighbors)

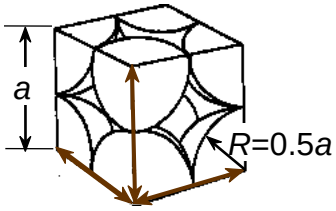


Atomic Packing Factor (APF)

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

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

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

Adapted from Fig. 3.43,
Callister & Rethwisch 4e.

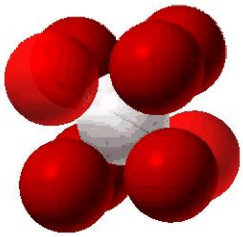
$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{1 \cdot \frac{4}{3}\pi (0.5a)^3}{a^3}$$

Body Centered Cubic Structure (BCC)

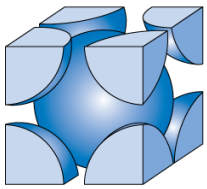
- Atoms touch each other along cube diagonals.
  --Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

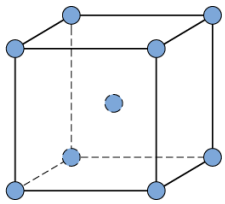
ex: Cr, W, Fe (α), Tantalum, Molybdenum

- Coordination # = 8



(Courtesy P.M. Anderson)



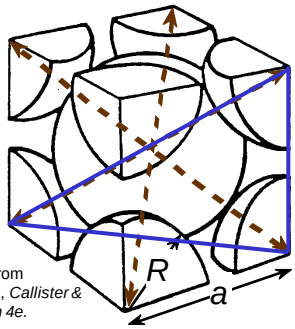


Adapted from Fig. 3.2, *Callister & Rethwisch 4e.*

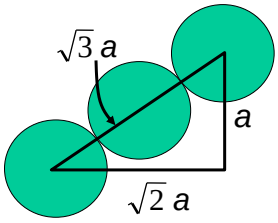
2 atoms/unit cell: 1 center + 8 corners x 1/8

Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68



Adapted from Fig. 3.2(a), *Callister & Rethwisch 4e.*



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

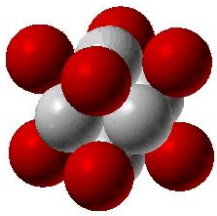
$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{2\left(\frac{4}{3}\pi\left(\frac{\sqrt{3}a}{4}\right)^3\right)}{a^3}$$

Face Centered Cubic Structure (FCC)

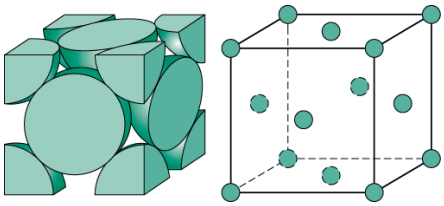
- Atoms touch each other along face diagonals.
  --Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

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

- Coordination # = 12



(Courtesy P.M. Anderson)



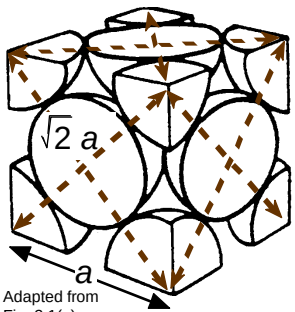
Adapted from Fig. 3.1, *Callister & Rethwisch 4e.*

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



Adapted from Fig. 3.1(a), *Callister & Rethwisch 4e.*

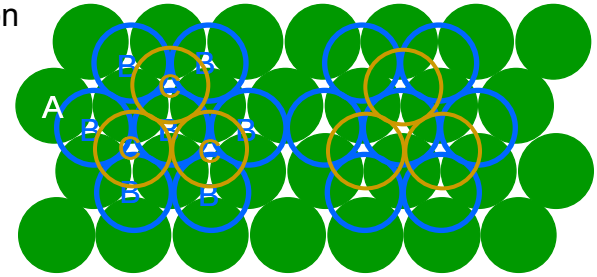
Close-packed directions:
length = $4R = \sqrt{2}\,a$

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

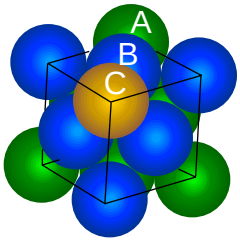
$$APF = \frac{\left(\frac{\text{atoms}}{\text{unit cell}}\right)\left(\frac{\text{volume}}{\text{atom}}\right)}{\frac{\text{volume}}{\text{unit cell}}} = \frac{4\left(\frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3\right)}{a^3}$$

FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

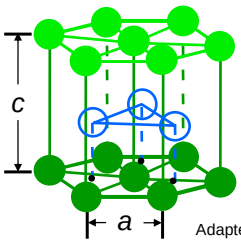


- FCC Unit Cell



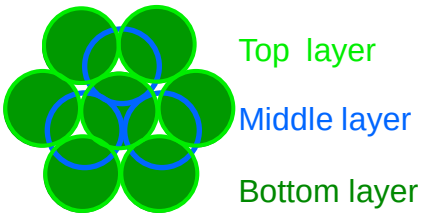
Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection



Adapted from Fig. 3.3(a), *Callister & Rethwisch 4e.*

- 2D Projection



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

6 atoms/unit cell

ex: Cd, Mg, Ti, Zn

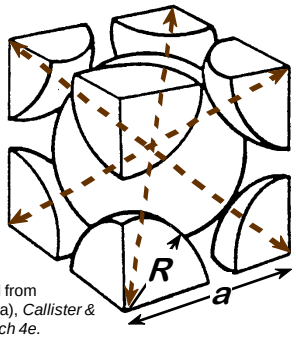
Theoretical Density, ρ

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

$$\rho = \frac{n A}{V_C N_A}$$

where n = number of atoms/unit cell
A = atomic weight (g/mol)
V_C = Volume of unit cell = a^3 for cubic
N_A = Avogadro's number
= 6.022×10^{23} atoms/mol

Theoretical Density, ρ



Adapted from Fig. 3.2(a), *Callister & Rethwisch 4e.*

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

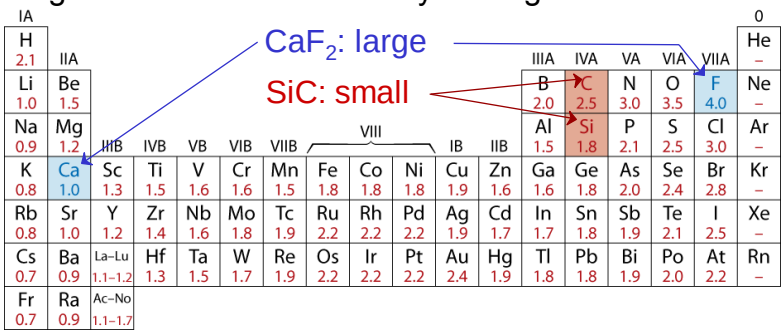
$a = 4R/\sqrt{3} = 0.2887$ nm

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

$\rho_{theoretical}$	= 7.18 g/cm^3
ρ_{actual}	= 7.19 g/cm^3

Atomic Bonding in Ceramics

- Bonding:
  -- Can be ionic and/or covalent in character.
  -- % ionic character increases with difference in electronegativity of atoms.
- Degree of ionic character may be large or small:



Adapted from Fig. 2.7, *Callister & Rethwisch 4e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition. Copyright 1939 and 1940, 3rd edition copyright © 1960 by Cornell University.

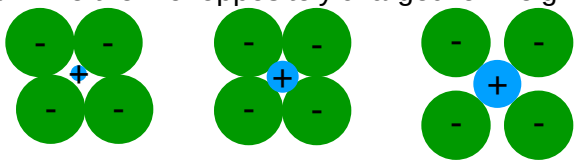
Ceramic Crystal Structures

Oxide structures

- oxygen anions larger than metal cations
- close packed oxygen in a lattice (usually FCC)
- cations fit into interstitial sites among oxygen ions

Factors that Determine Crystal Structure

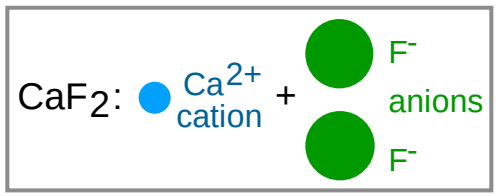
1. Relative sizes of ions – Formation of stable structures:
--maximize the # of oppositely charged ion neighbors.



unstable stable stable

Adapted from Fig. 3.4, *Callister & Rethwisch 4e.*

2. Maintenance of Charge Neutrality :
--Net charge in ceramic should be zero.
--Reflected in chemical formula: $A_m X_p$



m, p values to achieve charge neutrality

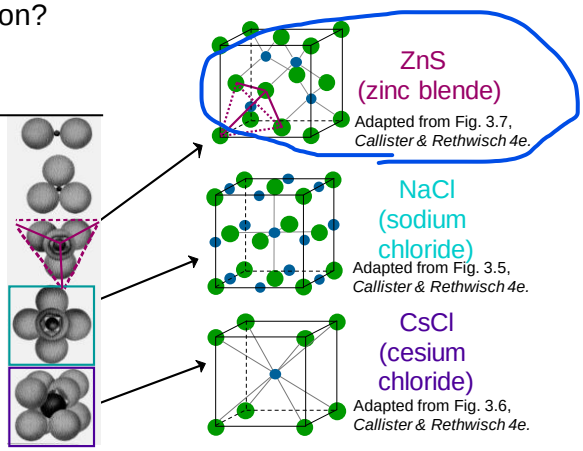
Coordination Number and Ionic Radii

- Coordination Number increases with $\frac{r_{cation}}{r_{anion}}$

To form a stable structure, how many anions can surround around a cation?

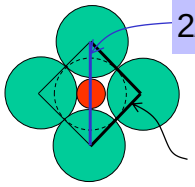
$\frac{r_{cation}}{r_{anion}}$	Coord. Number	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	tetrahedral
0.414 - 0.732	6	octahedral
0.732 - 1.0	8	cubic

Adapted from Table 3.3, *Callister & Rethwisch 4e.*



Computation of Minimum Cation-Anion Radius Ratio

- Determine minimum r_{cation}/r_{anion} for an octahedral site (C.N. = 6)



$$2r_{anion} + 2r_{cation} = \sqrt{2}a$$

$$a = 2r_{anion}$$

$$2r_{anion} + 2r_{cation} = 2\sqrt{2}r_{anion}$$

$$r_{anion} + r_{cation} = \sqrt{2}r_{anion} \qquad r_{cation} = (\sqrt{2} - 1)r_{anion}$$

$$\frac{r_{cation}}{r_{anion}} = \sqrt{2} - 1 = 0.414$$

Bond Hybridization

3s 3p 가 혼성궤도

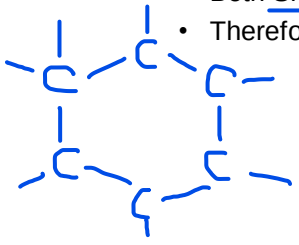
Bond Hybridization is possible when there is significant covalent bonding

- hybrid electron orbitals form
- For example for SiC
  - $X_{Si} = 1.8$ and $X_C = 2.5$

C. Si 다이아몬드 구조

$$\% \text{ ionic character} = 100\{1 - \exp[-0.25(X_{Si} - X_C)^2]\} = 11.5\%$$

- ~ 89% covalent bonding
- Both Si and C prefer sp^3 hybridization
- Therefore, for SiC, Si atoms occupy tetrahedral sites



그래핀도

Example Problem: Predicting the Crystal Structure of FeO

- On the basis of ionic radii, what crystal structure would you predict for FeO?

Cation	Ionic radius (nm)
Al^{3+}	0.053
Fe^{2+}	0.077
Fe^{3+}	0.069
Ca^{2+}	0.100
Anion	
O^{2-}	0.140
Cl^{-}	0.181
F^{-}	0.133

Data from Table 3.4, *Callister & Rethwisch 4e.*

- Answer:

$$\frac{r_{cation}}{r_{anion}} = \frac{0.077}{0.140} = 0.550$$

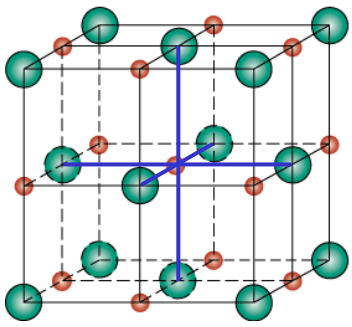
based on this ratio,
-- coord # = 6 because

$0.414 < 0.550 < 0.732$

-- crystal structure is NaCl

Rock Salt Structure

Same concepts can be applied to ionic solids in general.
Example: NaCl (rock salt) structure



Adapted from Fig. 3.5, *Callister & Rethwisch 4e.*

Na^+ $r_{Na} = 0.102$ nm

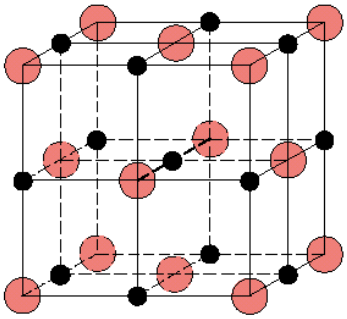
Cl^- $r_{Cl} = 0.181$ nm

$r_{Na}/r_{Cl} = 0.564$

$\therefore$ cations (Na^+) prefer octahedral sites

MgO and FeO

MgO and FeO also have the NaCl structure



Adapted from Fig. 3.5, *Callister & Rethwisch 4e.*

O^{2-} $r_O = 0.140$ nm

Mg^{2+} $r_{Mg} = 0.072$ nm

$r_{Mg}/r_O = 0.514$

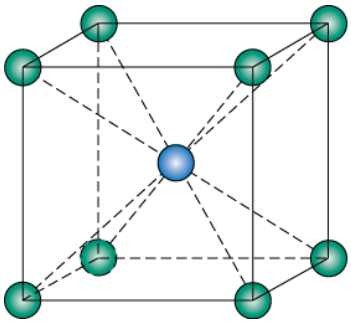
$\therefore$ cations prefer octahedral sites

So each Mg^{2+} (or Fe^{2+}) has 6 neighbor oxygen atoms

AX Crystal Structures

AX–Type Crystal Structures include NaCl, CsCl, and zinc blende

Cesium Chloride structure:



Adapted from Fig. 3.6, *Callister & Rethwisch 4e.*

Cs^+

Cl^-

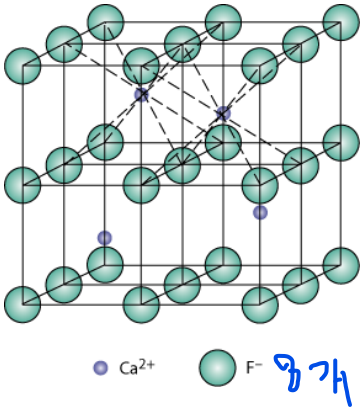
$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{0.170}{0.181} = 0.939$$

$\therefore$ Since $0.732 < 0.939 < 1.0$, cubic sites preferred

So each Cs^+ has 8 neighbor Cl^-

AX_2 Crystal Structures

Fluorite structure



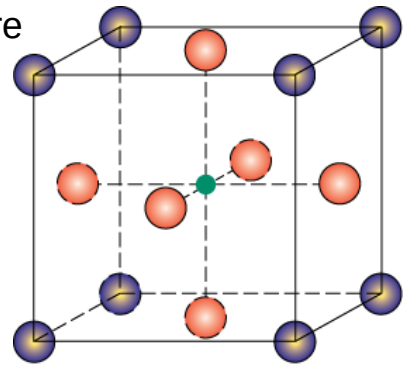
Adapted from Fig. 3.8, *Callister & Rethwisch 4e.*

- Calcium Fluorite (CaF_2)
- Cations in cubic sites
- UO_2, ThO_2, ZrO_2, CeO_2
- Antifluorite structure – positions of cations and anions reversed

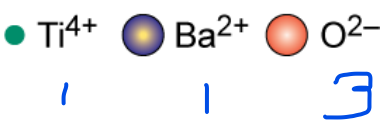
ABX_3 Crystal Structures

- Perovskite structure

Ex: complex oxide
$BaTiO_3$



Adapted from Fig. 3.9, *Callister & Rethwisch 4e.*



Density Computations for Ceramics

Number of formula units/unit cell

$$r = \frac{n'(SA_C + SA_A)}{V_C N_A}$$

Avogadro's number

Volume of unit cell

SA_C = sum of atomic weights of all cations in formula unit

SA_A = sum of atomic weights of all anions in formula unit

Densities of Material Classes

In general

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

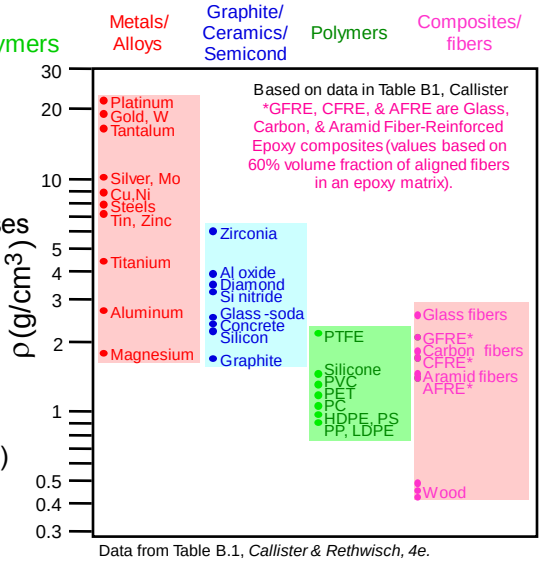
Why?

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

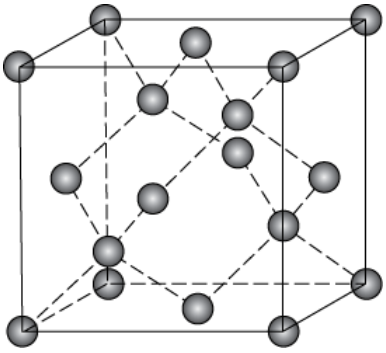


Data from Table B.1, *Callister & Rethwisch, 4e.*

Polymorphic Forms of Carbon

Diamond

- tetrahedral bonding of carbon
  - hardest material known
  - very high thermal conductivity
- large single crystals – gem stones
- small crystals – used to grind/cut other materials
- diamond thin films
  - hard surface coatings – used for cutting tools, medical devices, etc.

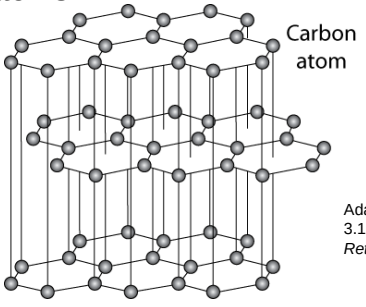


Adapted from Fig. 3.16, *Callister & Rethwisch 4e.*

Polymorphic Forms of Carbon (cont)

Graphite

- layered structure – parallel hexagonal arrays of carbon atoms

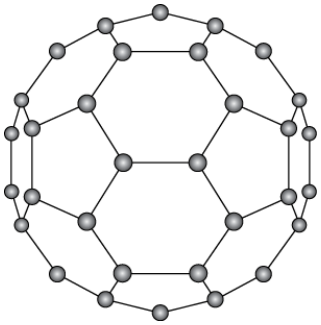


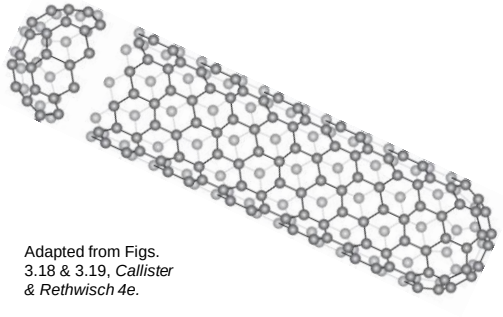
Adapted from Fig. 3.17, *Callister & Rethwisch 4e.*

- weak van der Waal's forces between layers
- planes slide easily over one another -- good lubricant

Polymorphic Forms of Carbon (cont)
Fullerenes and Nanotubes

- Fullerenes – spherical cluster of 60 carbon atoms, C_{60}
  - Like a soccer ball
- Carbon nanotubes – sheet of graphite rolled into a tube
  - Ends capped with fullerene hemispheres





Adapted from Figs. 3.18 & 3.19, *Callister & Rethwisch 4e.*

Polymorphism

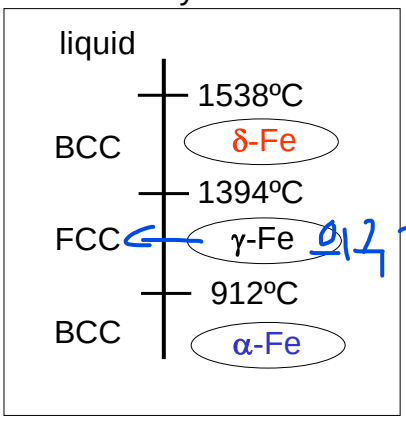
BCC → FCC → BCC

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

titanium
α, β-Ti

carbon
diamond, graphite

iron system



상온 FCC

Polycrystals

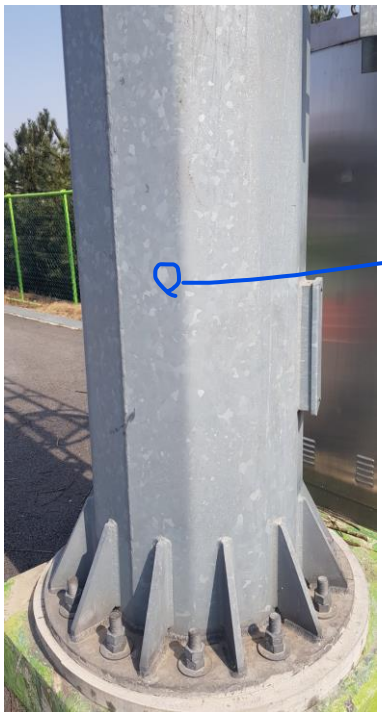
- *Most* engineering materials are polycrystals.

Anisotropic

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

Isotropic

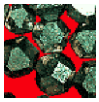
- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- If grains are randomly oriented, overall component properties are not directional.
- Grain sizes typ. range from 1 nm to 2 cm (i.e., from a few to millions of atomic layers).



A light tower next to the football field in Koreatech

Crystals as Building Blocks

- *Some* engineering applications require single crystals:
  - -- diamond single crystals for abrasives



(Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.)

  - -- turbine blades

Fig. 9.40(c), *Callister & Rethwisch 4e.* (Fig. 9.40(c) courtesy of Pratt and Whitney).

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

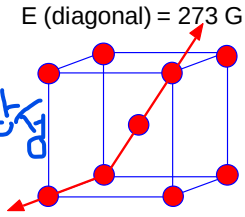
(Courtesy P.M. Anderson)

Czochralski method of silicon
https://youtu.be/xftnhfa-Dmo

grain 이 1개

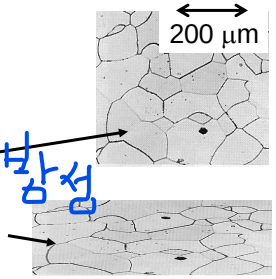
Single vs Polycrystals

- Single Crystals
  - -Properties vary with direction: anisotropic. 이방성
  - -Example: the modulus of elasticity (E) in BCC iron:



Data from Table 3.7, *Callister & Rethwisch 4e.* (Source of data is R.W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd ed., John Wiley and Sons, 1989.)

- Polycrystals
  - -Properties may/may not vary with direction.
  - -If grains are randomly oriented: isotropic. 등방성 ($E_{poly\ iron}$ = 210 GPa)
  - -If grains are textured, anisotropic.



Adapted from Fig. 5.19(b), *Callister & Rethwisch 4e.* (Fig. 5.19(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC [now the National Institute of Standards and Technology, Gaithersburg, MD].)

Crystal Systems

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

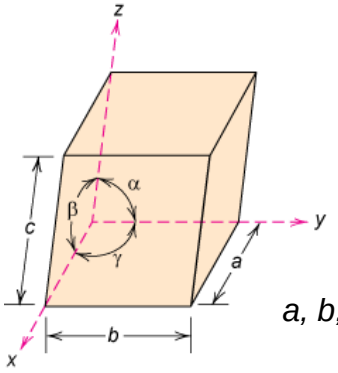


Fig. 3.20, *Callister & Rethwisch 4e.*

7 crystal systems

14 crystal lattices

a, b, and *c* are the lattice constants

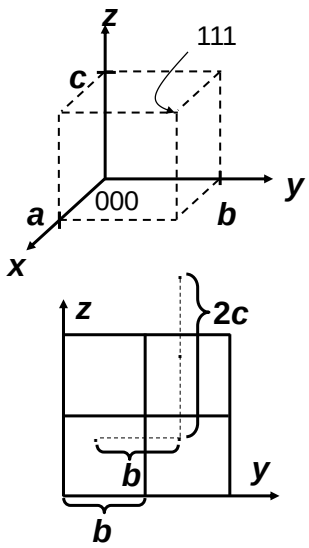
14 Bravais Lattices in 3D

The 7 lattice systems	The 14 Bravais lattices			
Triclinic	P $\alpha, \beta, \gamma \neq 90°$			$a \neq b \neq c$
Monoclinic	P $\beta \neq 90°$ $\alpha, \gamma = 90°$	C $\beta \neq 90°$ $\alpha, \gamma = 90°$		$a \neq b \neq c$
Orthorhombic	P $a \neq b \neq c$	C $a \neq b \neq c$	I $a \neq b \neq c$	F $a \neq b \neq c$

Tetragonal	P $a \neq c$	I $a \neq c$	
Rhombohedral	P $\alpha = \beta = \gamma \neq 90°$		
Hexagonal	P		
Cubic	P (scc)	I (bcc)	F (fcc)

http://en.wikipedia.org/wiki/Bravais_lattice

Point Coordinates



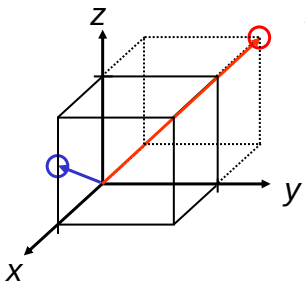
Point coordinates for unit cell center are

a/2, *b*/2, *c*/2 ½½½

Point coordinates for unit cell corner are 111

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

Crystallographic Directions



Algorithm

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

[*uvw*]

ex: 1, 0, ½ => 2, 0, 1 => [201]

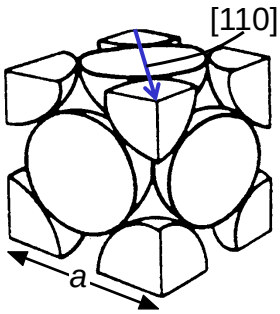
-1, 1, 1 => $[\bar{1}11]$ where overbar represents a negative index

families of directions <*uvw*> <angle bracket>

방향의 family

Linear Density

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



Adapted from Fig. 3.1(a), *Callister & Rethwisch 4e.*

ex: linear density of Al in [110] direction

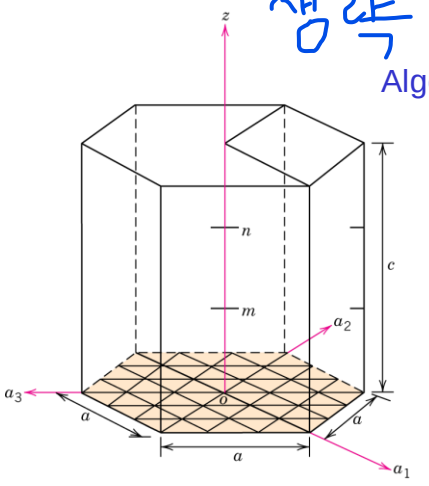
a = 0.405 nm

atoms → 2

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

length → $\sqrt{2}a$

Drawing HCP Crystallographic Directions (i)



Adapted from Figure 3.25, *Callister & Rethwisch 4e.*

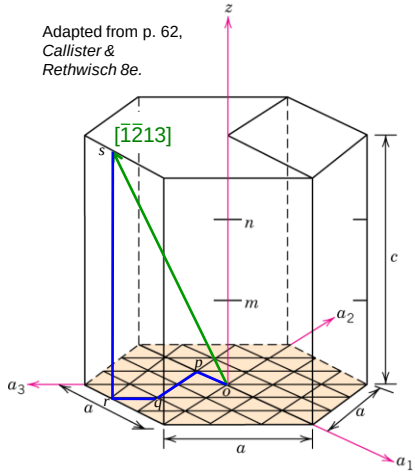
Algorithm (Miller-Bravais coordinates)

1. Remove brackets
2. Divide by largest integer so all values are ≤ 1
3. Multiply terms by appropriate unit cell dimension a (for a_1, a_2, and a_3 axes) or c (for z-axis) to produce projections
4. Construct vector by stepping off these projections

Drawing HCP Crystallographic Directions (ii)

- Draw the $[\bar{1}\,\bar{2}13]$ direction in a hexagonal unit cell.

Adapted from p. 62, *Callister & Rethwisch 8e.*



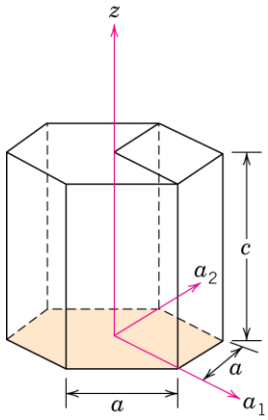
Algorithm

	a_1	a_2	a_3	z
1. Remove brackets	-1	-2	1	3
2. Divide by 3	$-\frac{1}{3}$	$-\frac{2}{3}$	$\frac{1}{3}$	1
3. Projections	$-\frac{a}{3}$	$-\frac{2a}{3}$	$\frac{a}{3}$	c

4. Construct Vector
   - start at point o
   - proceed $-a/3$ units along a_1 axis to point p
   - $-2a/3$ units parallel to a_2 axis to point q
   - $a/3$ units parallel to a_3 axis to point r
   - c units parallel to z axis to point s

$[\bar{1}\bar{2}13]$ direction represented by vector from point o to point s

Determination of HCP Crystallographic Directions (ii)



Adapted from p. 74, *Callister & Rethwisch 4e.*

Algorithm

1. Vector repositioned (if necessary) to pass through origin.
2. Read off projections in terms of three-axis (a_1, a_2, and z) unit cell dimensions a and c
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas, for three-axis coordinates $[u'v'w']$
5. Convert to four-axis Miller-Bravais lattice coordinates using equations below:

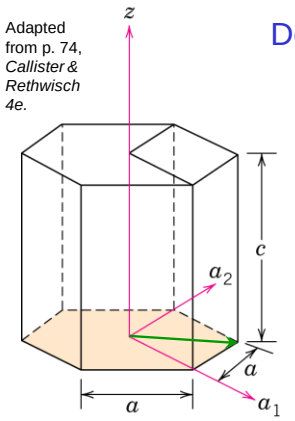
$$u = \frac{1}{3}(2u' - v') \quad v = \frac{1}{3}(2v' - u')$$

$$t = -(u+v) \quad w = w'$$

6. Adjust to smallest integer values and enclose in brackets $[uvtw]$

[-4-53]

Determination of HCP Crystallographic Directions (ii)



Adapted from p. 74, *Callister & Rethwisch 4e.*

Determine indices for green vector

Example	a_1	a_2	z
1. Reposition	not needed		
2. Projections	a	a	$0c$
	1	1	0
3. Reduction	1	1	0
4. Brackets		[110]	

5. Convert to 4-axis parameters

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

$$t = -(\frac{1}{3} + \frac{1}{3}) = -\frac{2}{3} \qquad w = 0$$

6. Reduction & Brackets

1/3, 1/3, -2/3, 0 => 1, 1, -2, 0 => $[11\bar{2}0]$

Quiz

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

Quiz

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

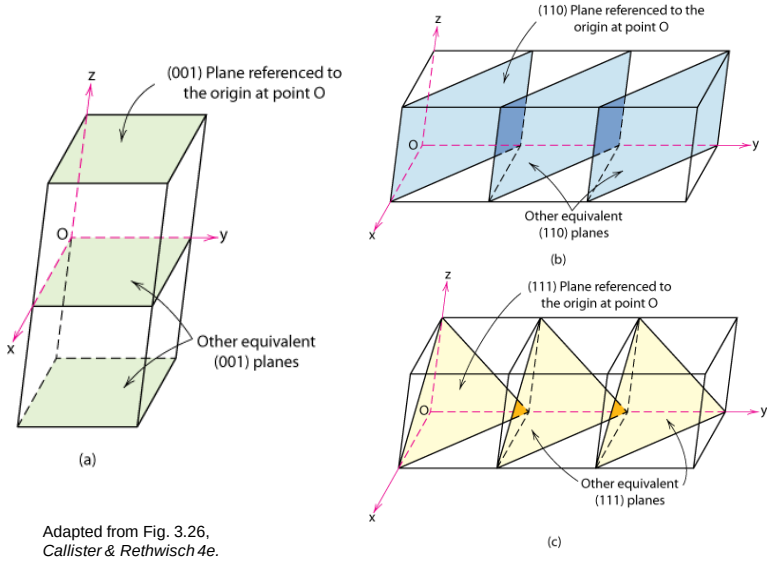
(a) $[\bar{1}10]$, (e) $[\bar{1}\bar{1}1]$,

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

(c) $[0\bar{1}2]$, (g) $[1\bar{2}\bar{3}]$,

(d) $[1\bar{3}3]$, (h) $[\bar{1}03]$.

Crystallographic Planes



Adapted from Fig. 3.26, *Callister & Rethwisch 4e.*

Crystallographic Planes

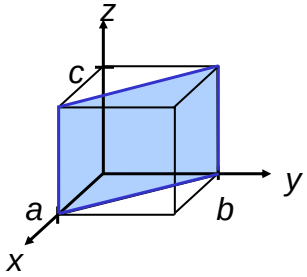
- Miller Indices: Reciprocals of the (three) axial intercepts for a plane, cleared of fractions & common multiples. All parallel planes have same Miller indices.

- 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*)

교차점
역수

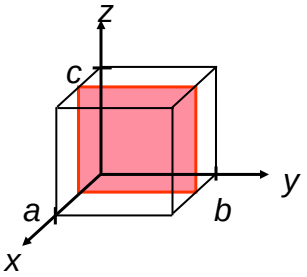
Crystallographic Planes

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)		

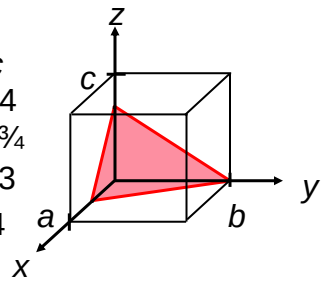
(200)



같은원자배열 구조
면기능비는 다르다

Crystallographic Planes

example		*a*	*b*	*c*
1.	Intercepts	1/2	1	3/4
2.	Reciprocals	1/½	1/1	1/¾
		2	1	4/3
3.	Reduction	6	3	4
4.	Miller Indices	(634)		



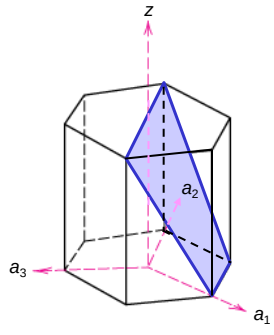
Family of Planes $\{hkl\}$ Curly bracket

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

Crystallographic Planes (HCP)

- In hexagonal unit cells the same idea is used

example		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	$(10\bar{1}1)$			



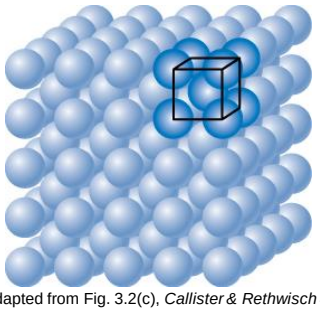
Adapted from Fig. 3.24(b), *Callister & Rethwisch 4e.*

Crystallographic Planes

- We want to examine the atomic packing of crystallographic planes
- Iron foil can be used as a catalyst. The atomic packing of the exposed planes is important.
  a) Draw (100) and (111) crystallographic planes for Fe.
  b) Calculate the planar density for each of these planes.

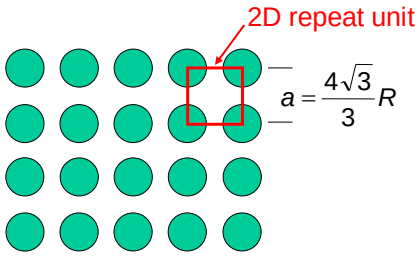
Planar Density of (100) Iron

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



Adapted from Fig. 3.2(c), *Callister & Rethwisch 4e.*

(100)



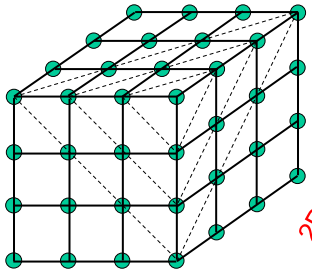
Radius of iron R = 0.1241 nm

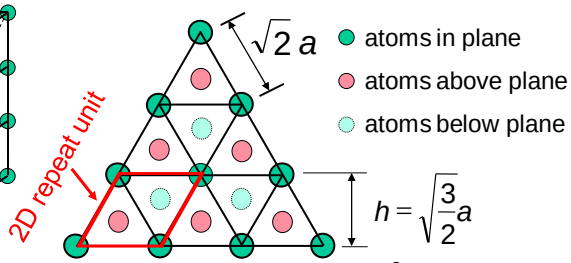
$$\text{Planar Density} = \frac{\dfrac{\text{atoms}}{\text{2D repeat unit}}}{\dfrac{\text{area}}{\text{2D repeat unit}}} = \frac{1}{a^2} = \frac{1}{\left(\frac{4\sqrt{3}}{3}R\right)^2} = 12.1\,\frac{\text{atoms}}{\text{nm}^2} = 1.2 \times 10^{19}\,\frac{\text{atoms}}{\text{m}^2}$$

Planar Density of (111) Iron

Solution (cont): (111) plane

1 atom in plane/ unit surface cell

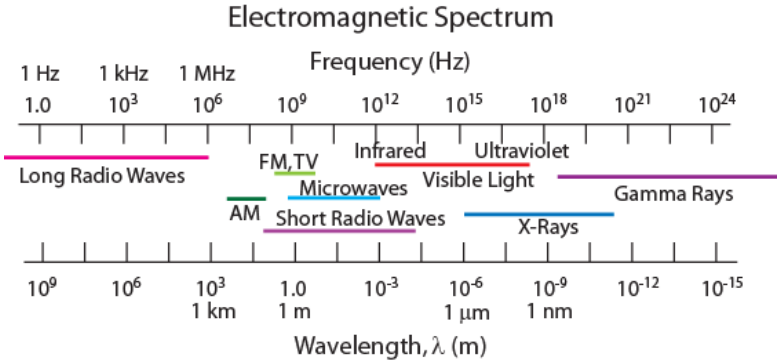




$$\text{area} = \sqrt{2}\,ah = \sqrt{3}\,a^2 = \sqrt{3}\left(\frac{4\sqrt{3}}{3}R\right)^2 = \frac{16\sqrt{3}}{3}R^2$$

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

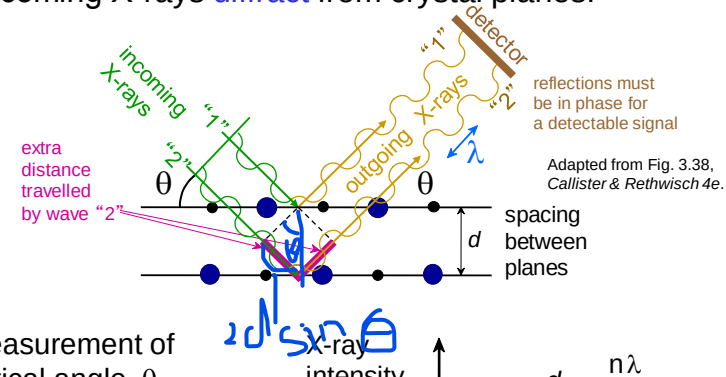
X-Ray Diffraction



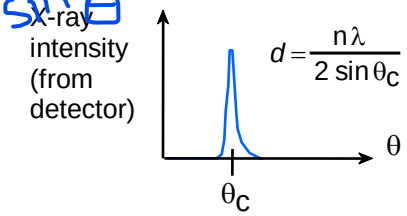
- Diffraction gratings must have spacings comparable to the wavelength of diffracted radiation.
- Can't resolve spacings $< \lambda$
- Spacing is the distance between parallel planes of atoms.

X-Rays to Determine Crystal Structure

- Incoming X-rays diffract from crystal planes.



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



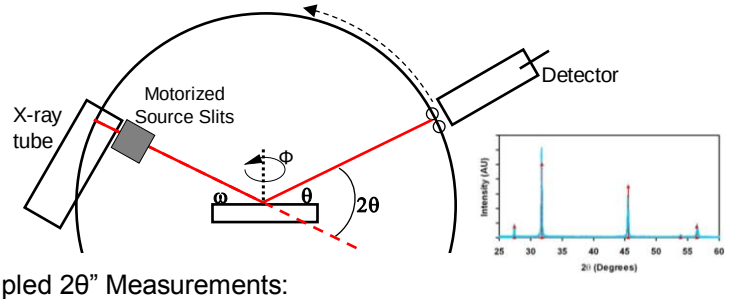
$$d = \frac{n\lambda}{2 \sin \theta_c}$$

Instrument Settings

- Source
  - Cu K_α
- Type of measurement
  - Coupled 2θ
  - Detector scan
  - Etc.

Bruker D8 Focus

Coupled 2θ Measurements



- In "Coupled 2θ" Measurements:
  - The incident angle ω is always ½ of the detector angle 2θ .
  - The x-ray source is fixed, the sample rotates at θ °/min and the detector rotates at 2θ °/min.
- Angles
  - The incident angle (ω) is between the X-ray source and the sample.
  - The diffracted angle (2θ) is between the incident beam and the detector.
  - In plane rotation angle (Φ)

ANALYSIS OF POWDERS

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Powder diffraction

- ✓ For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract
- ✓ Basic assumptions of powder diffraction:
  - ➢ For every set of planes, there is an equal number of crystallites that will diffract
  - ➢ There is a statistically relevant number of crystallites

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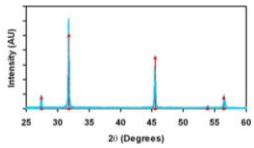
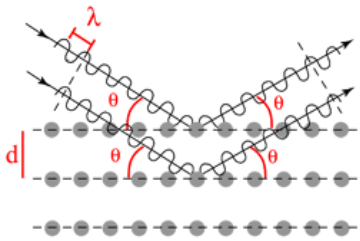
https://www.list.lu/fileadmin//files/Event/sites/tudor/files/event/4_Presentation_Dr_Yves_Fleming.pdf

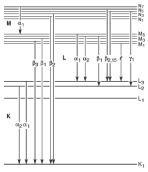
Bragg's law and Peak Positions.

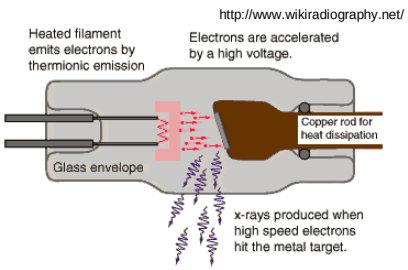
$$\lambda = 2d_{hkl}\sin\theta$$

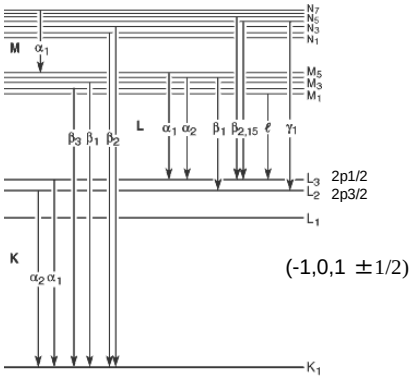




- For parallel planes of atoms, with a space d_{hkl} between the planes, constructive interference only occurs when Bragg's law is satisfied.
-
  - X-ray wavelengths λ are:
    - Cu $K_{\alpha 1}$=1.540598 Å and Cu $K_{\alpha 2}$=1.544426 Å
    - Or Cu $K_{\alpha(avg)}$=1.54278 Å
  - d_{hkl} is dependent on the lattice parameter (atomic/ionic radii) and the crystal structure

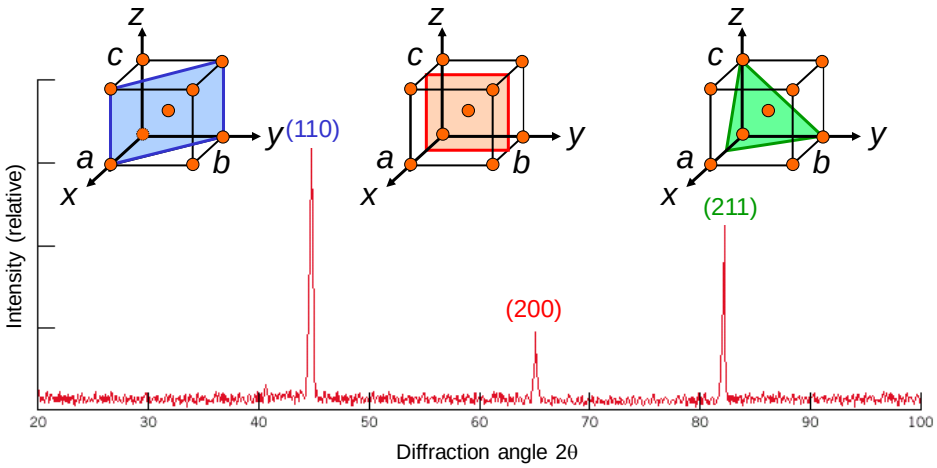






1. W filament generate electrons (cathode)
2. Electrons heat Cu target (anode)
3. Cu target generate x-ray

X-Ray Diffraction Pattern



Diffraction pattern for polycrystalline α-iron (BCC)

Adapted from Fig. 3.40, *Callister 4e.*

Lattice spacing

The value of d, the distance between adjacent planes in the set (hkl), may be found from the following equations.

Cubic:
$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal:
$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Hexagonal:
$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

Rhombohedral:
$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + hl)(\cos^2\alpha - \cos\alpha)}{a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)}$$

Orthorhombic:
$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

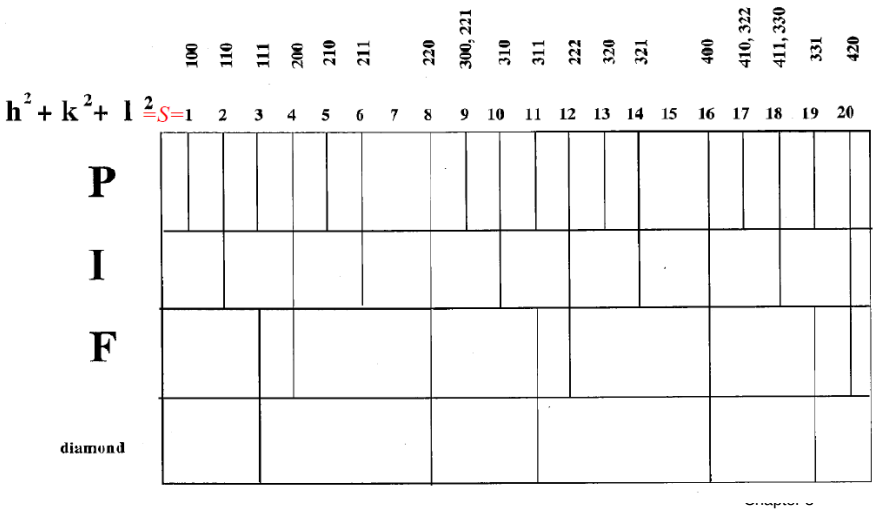
Monoclinic:
$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

Triclinic:
$$\frac{1}{d^2} = \frac{1}{V^2}(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl)$$

Selection rules for cubic

P		I		F	
S	(hkl)	S	(hkl)	S	(hkl)
1	100	-	-	-	-
2	110	2	110	-	-
3	111	-		3	111
4	200	4	200	4	200
5	210	-	-	-	-
6	211	6	211	-	-
7	-	-	-	-	-
8	220	8	220	8	220
9	221,300	-	-		
10	310	10	310		
11	311	-	-	11	311
12	222	12	222	12	222

Review of Systematic Absences in the Diffraction Patterns of 4 Cubic Structures



SUMMARY

- Atoms may assemble into crystalline or amorphous structures.
- Common metallic crystal structures are FCC, BCC, and HCP. Coordination number and atomic packing factor are the same for both FCC and HCP crystal structures.
- We can predict the density of a material, provided we know the atomic weight, atomic radius, and crystal geometry (e.g., FCC, BCC, HCP).
- Interatomic bonding in ceramics is ionic and/or covalent.
- Ceramic crystal structures are based on:
  -- maintaining charge neutrality
  -- cation-anion radii ratios.
- Crystallographic points, directions and planes are specified in terms of indexing schemes. Crystallographic directions and planes are related to atomic linear densities and planar densities.

SUMMARY

- Materials can be single crystals or polycrystalline. Material properties generally vary with single crystal orientation (i.e., they are anisotropic), but are generally non-directional (i.e., they are isotropic) in polycrystals with randomly oriented grains.
- Some materials can have more than one crystal structure. This is referred to as polymorphism (or allotropy).
- X-ray diffraction is used for crystal structure and interplanar spacing determinations.