

Chapter 3: The Structure of Crystalline Solids

ISSUES TO EXPLORE...

- What is the difference in atomic arrangement between crystalline and noncrystalline solids?
結晶結構
- What are the crystal structures of metals/ceramics?
- What are the characteristics of crystal structures?
- How are crystallographic points, directions, and planes specified?
- What characteristics of a material's atomic structure determine its density?

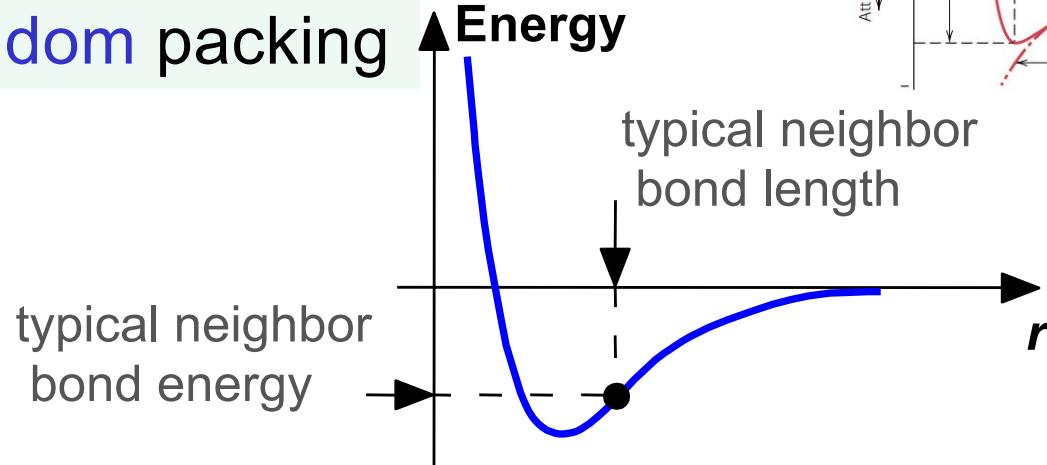
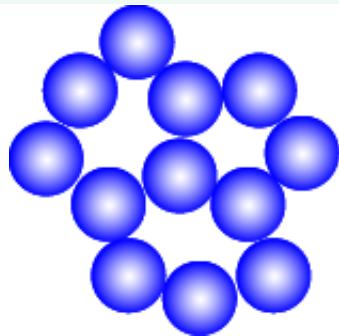
Crystal Structures

Fundamental concepts

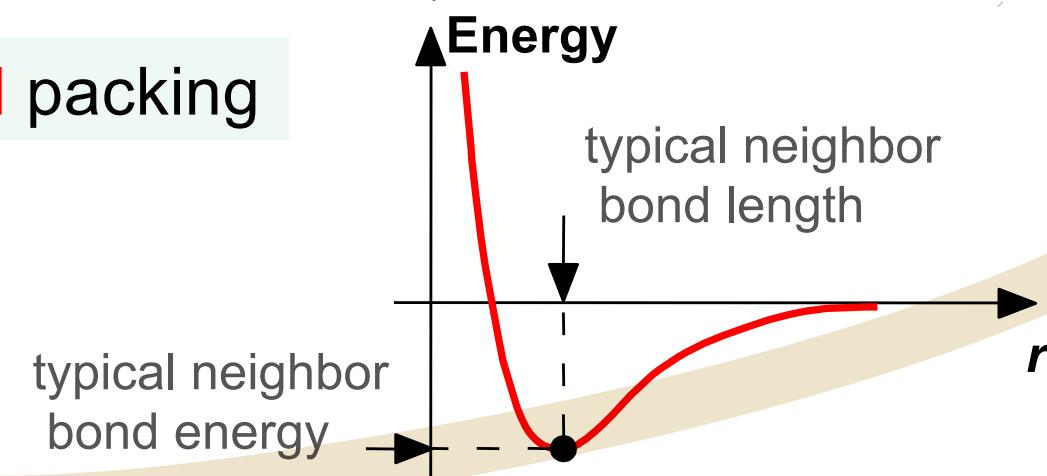
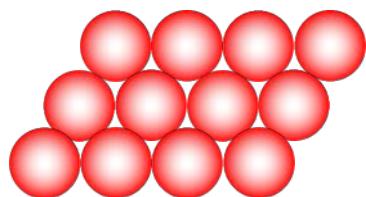
- Solid materials can be classified according to the **regularity of atoms** or ions.
- A **crystalline material** is the **atoms are situated in a repeating or periodic array over large atomic distances**, in which each atom is bonded to its nearest-neighbor atoms.
- The properties of crystalline solids depend on the crystal structure.
- For those that **do not crystallize (amorphous materials)**, this long-range atomic order is absent
非結晶

Energy and Packing

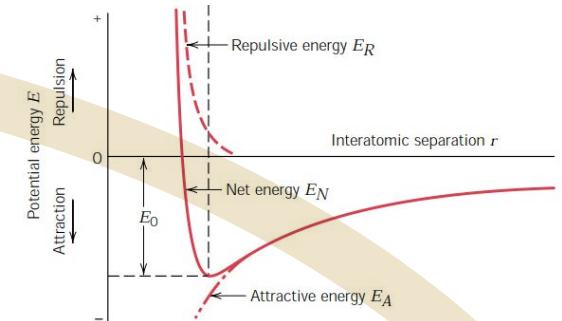
- Non dense, random packing



- Dense, ordered packing



Ordered structures tend to be nearer the minimum in bonding energy and are more stable.



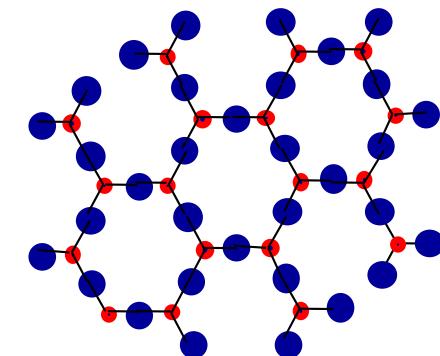
Materials and Atomic Arrangements

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Crystalline materials...

- atoms arranged **in periodic**, 3D arrays
- typical of:
 - metals
 - many ceramics
 - some polymers

週期性



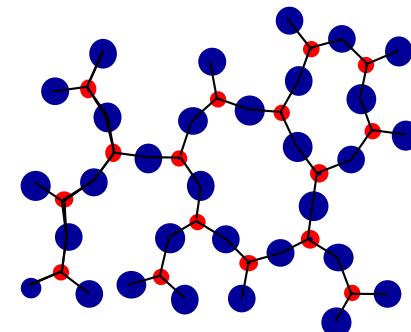
crystalline SiO_2

Adapted from Fig. 3.40(a),
Callister & Rethwisch 5e.

• Si • Oxygen

Noncrystalline materials...

- atoms have **no periodic** arrangement
- occurs for:
 - complex structures
 - rapid cooling



noncrystalline SiO_2

Adapted from Fig. 3.40(b),
Callister & Rethwisch 5e.

"**Amorphous**" = Noncrystalline

Y

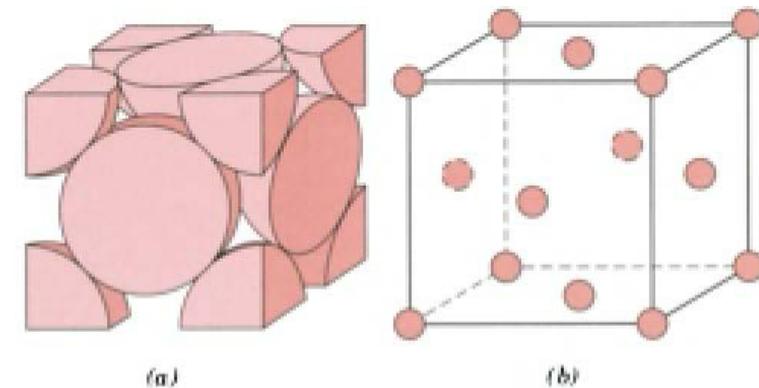
Metallic Crystal Structures: Atomic Packing

- Dense atomic packing for crystal structures of metals.
- **Reasons for dense packing:** 原子鍵結(?)
 - Atomic bonding between metal atoms are metallic (**nondirectional**). 無方向性 → packing density 最高 兩原子間距離最短
 - Nearest neighbor distances tend to be small in order to lower bond energy.
 - Metals typically have relatively large atomic packing factors to maximize the shielding provided by the free electron cloud.
- Crystal structures for metals simpler than structures for ceramics and polymers.

Unit Cell and Atomic Hard Sphere Model

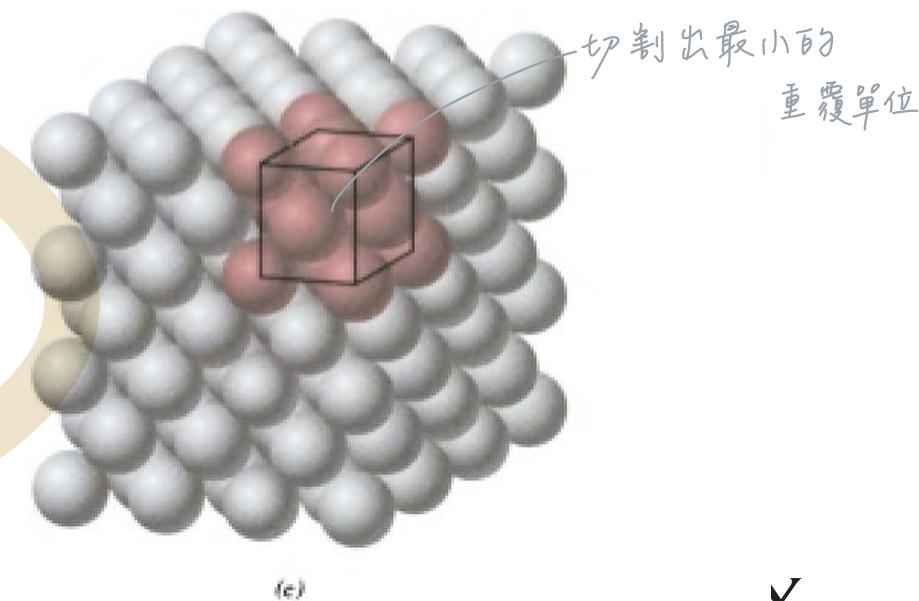
Unit cells 單位晶胞

- to represent the symmetry of the crystal structure, wherein all the atom positions in the crystal may be generated by translations of the unit cell integral distances along each of its edges.



Atomic hard sphere model

- When describing crystalline structures, **atoms** (or ions) are thought of as being solid spheres having well-defined diameters which termed the “**atomic hard sphere model**”.



Coordination Number and Atomic Packing Factor

Coordination Number (配位數)

Coordination Number = number of nearest-neighbor
or touching atoms

Atomic Packing Factor (APF) (原子堆積因子)

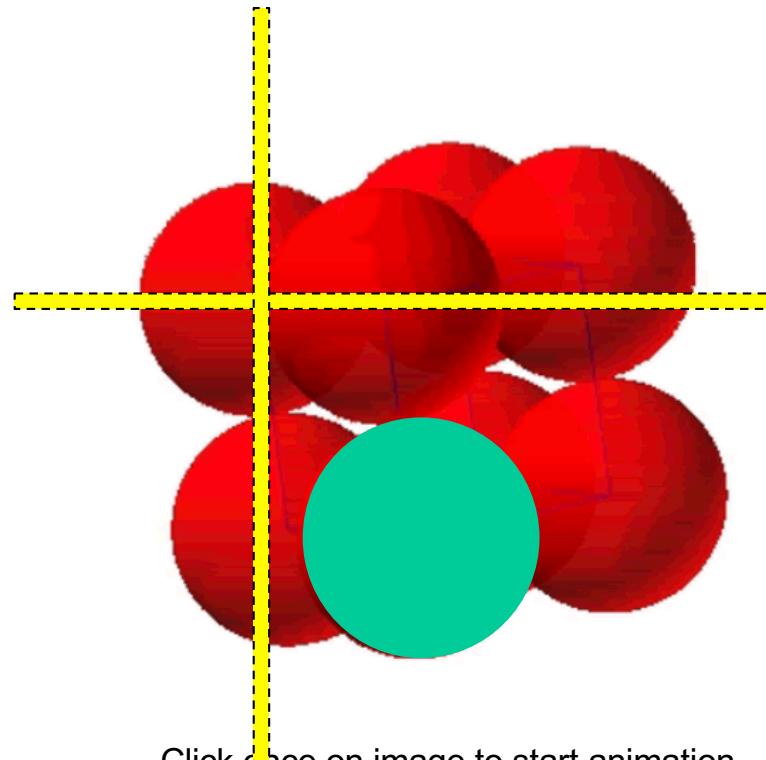
$$\text{APF} = \frac{\text{Volume of atoms in unit cell}^*}{\text{Volume of unit cell}}$$

*assume hard spheres

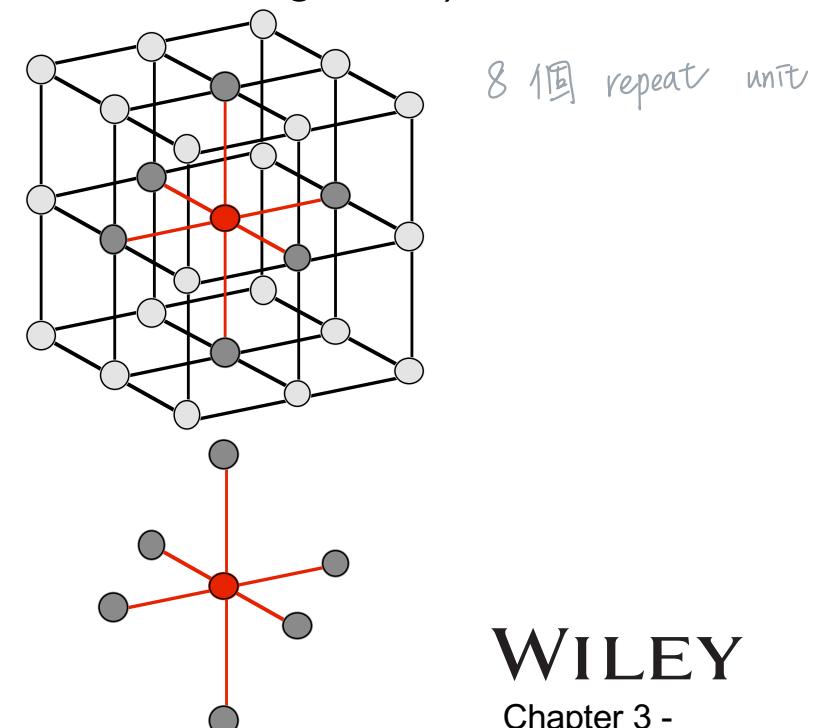
Simple Cubic (SC) Crystal Structure

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- Centers of atoms located at the eight corners of a cube
- Rare due to low packing density (only Po has this structure)
- **Close-packed directions** are cube edges.



- Coordination # = 6
(# nearest neighbors)

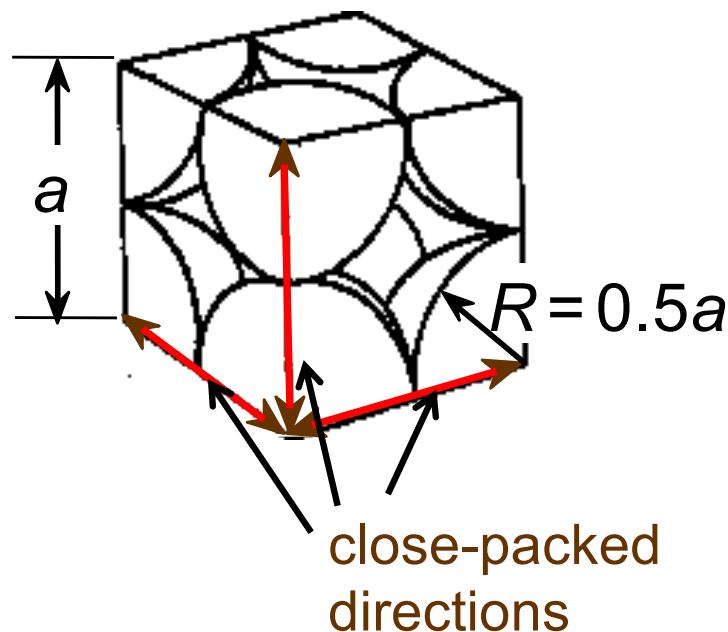


Atomic Packing Factor (APF) for Simple Cubic

Q3

$\frac{4}{3}\pi R^3$

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



$$APF = \frac{\frac{\text{atoms}}{\text{unit cell}} \times \frac{4}{3}\pi(0.5a)^3}{a^3}$$

$= 0.52$

The diagram shows the calculation of APF for a simple cubic unit cell. It starts with the formula $APF = \frac{\text{atoms}/\text{unit cell} \times \text{volume/atom}}{\text{volume}/\text{unit cell}}$. The 'atoms/unit cell' term is shown as 1. The 'volume/atom' term is shown as $\frac{4}{3}\pi(0.5a)^3$. The 'volume/unit cell' term is shown as a^3 . The result is calculated as $= 0.52$.

Unit cell contains 1 atom = $8 \times 1/8 = 1$ atom/unit cell

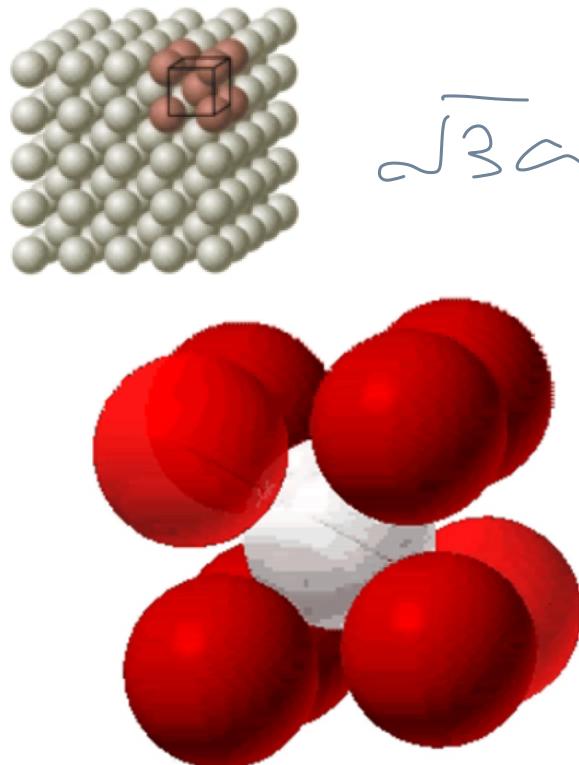
SC AFP: 0.52

Body-Centered Cubic Structure (BCC)

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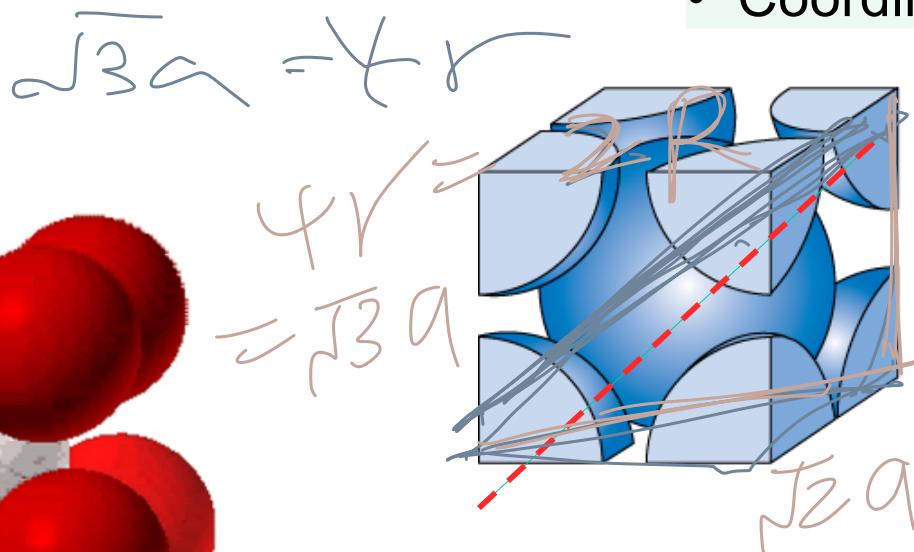
- Atoms located at 8 cube corners with a single atom at cube center.

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

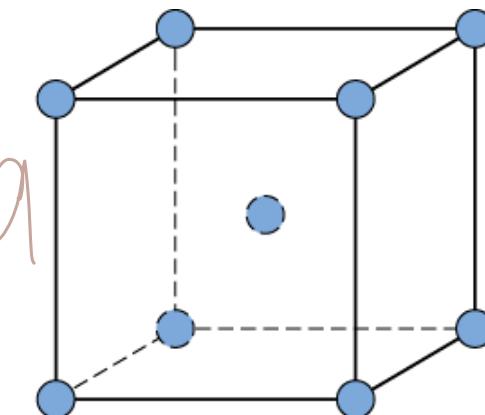


Click once on image to start animation

(Courtesy P.M. Anderson)



- Coordination # = 8



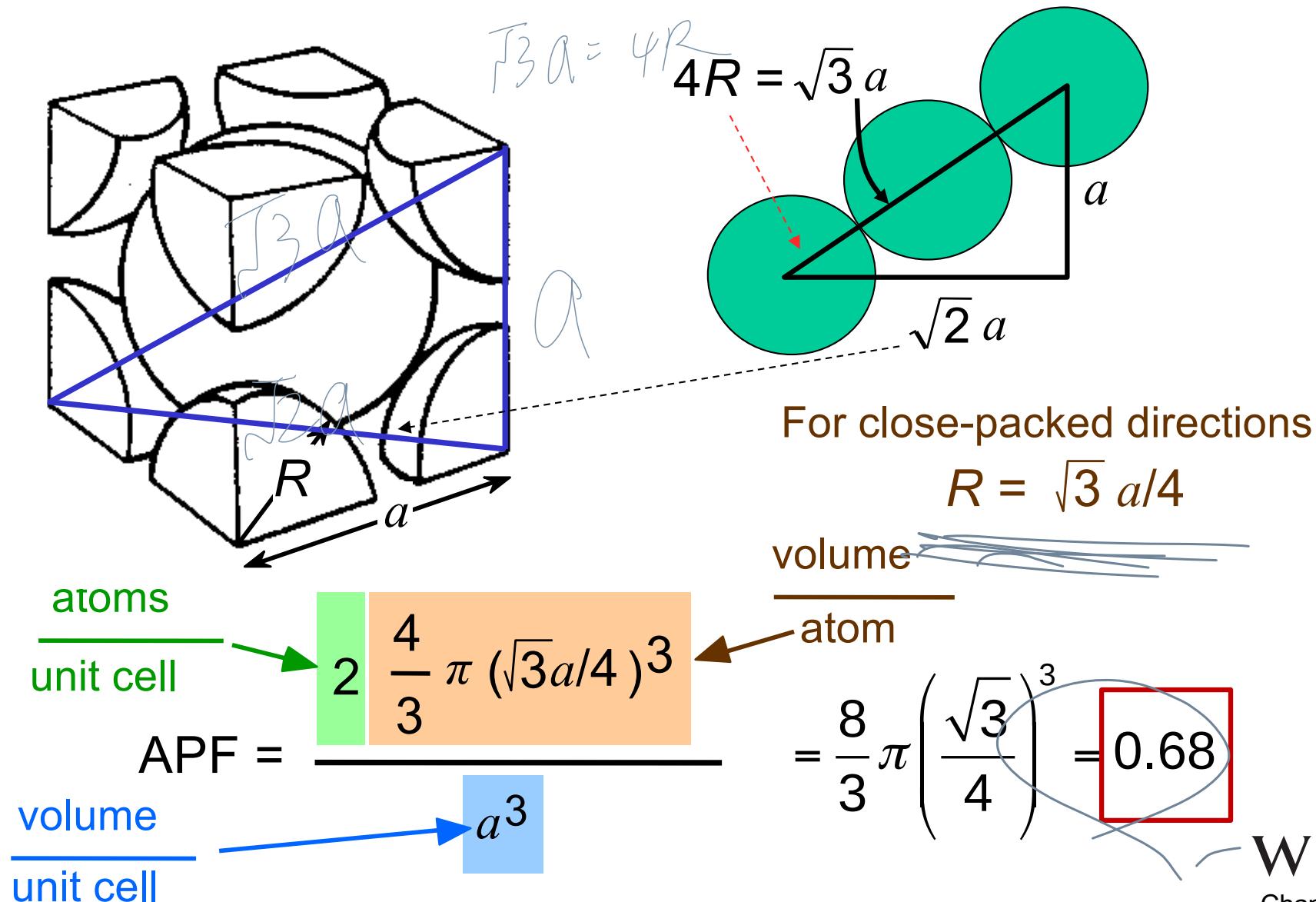
Adapted from Fig. 3.2,
Callister & Rethwisch 5e.

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

ex: Cr, W, Fe (α), Ta, Mo

Atomic Packing Factor: BCC

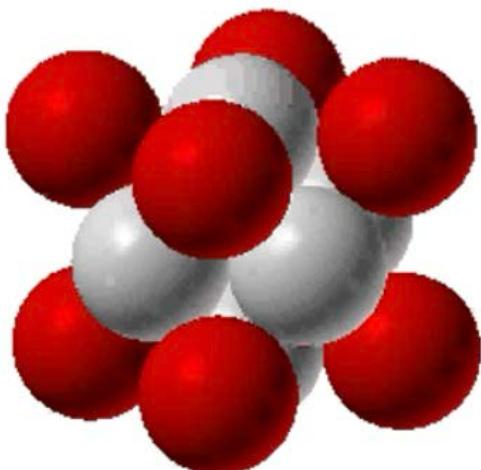
- APF for the body-centered cubic structure = **0.68**



面心立方

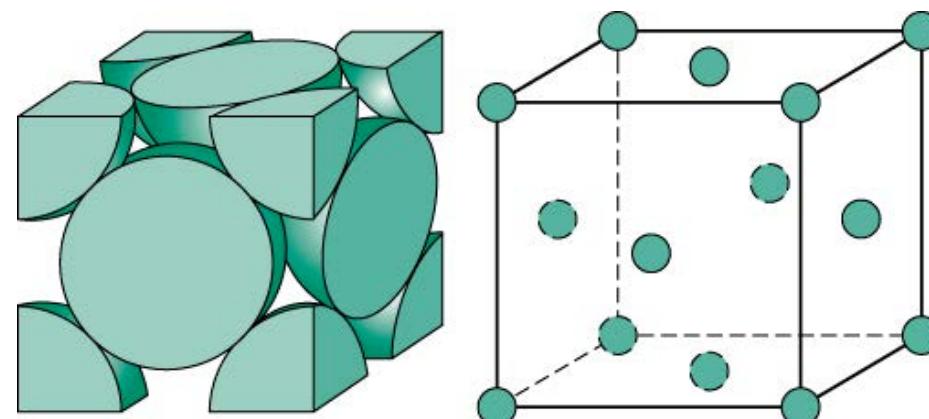
Face-Centered Cubic Structure (FCC)

- Atoms located at 8 cube corners and at the centers of the 6 faces.



Click once on image to start animation
(Courtesy P.M. Anderson)

- Coordination # = 12



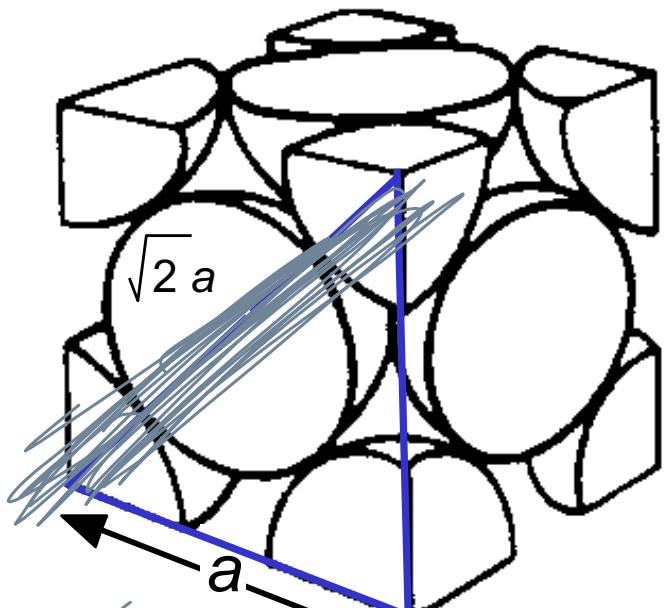
Adapted from Fig. 3.1, Callister & Rethwisch 5e.

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

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

Atomic Packing Factor: FCC

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



$$\sqrt{2}a = 4R \quad \text{maximum achievable APF}$$

For close-packed directions:

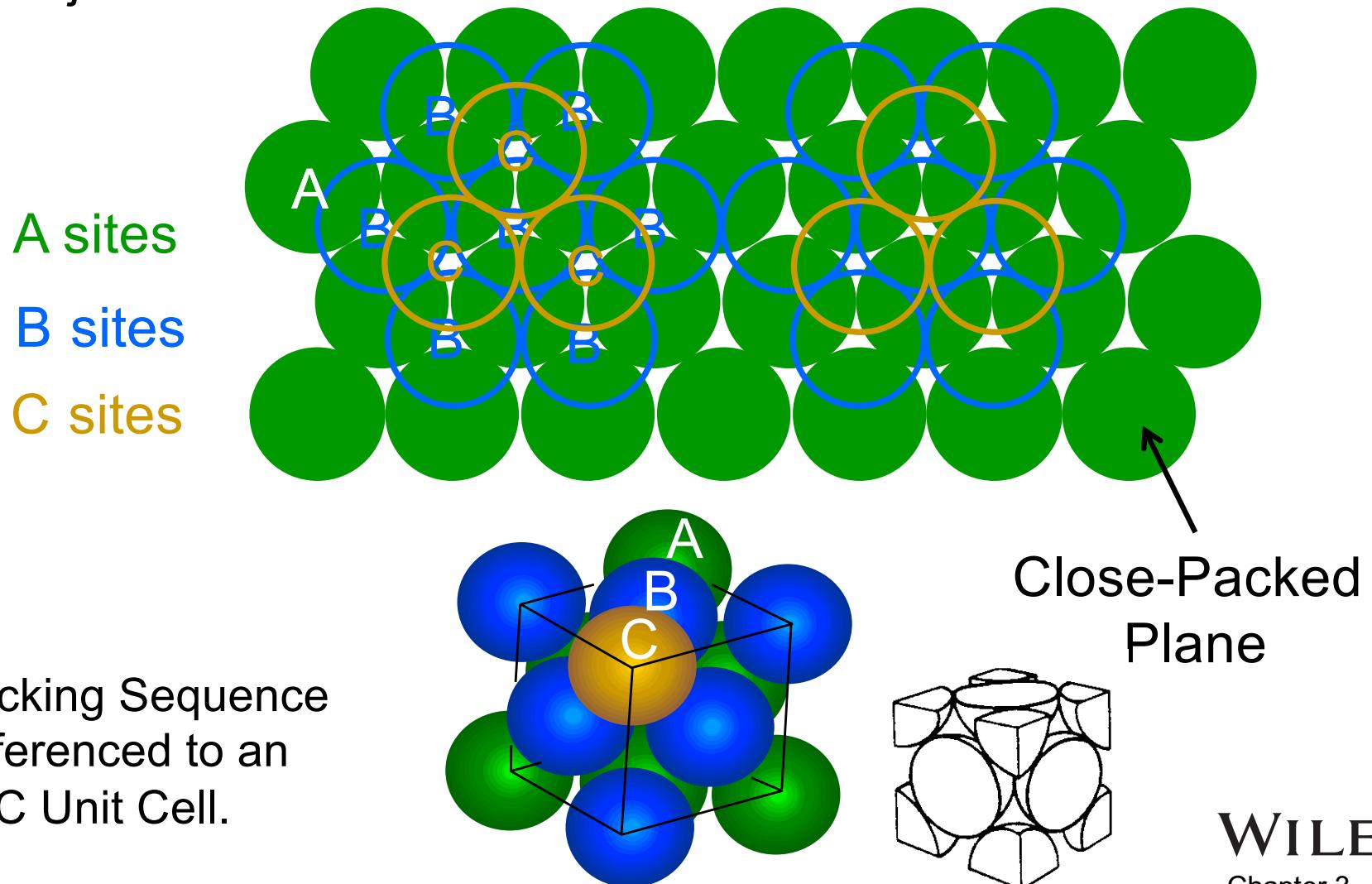
$$4R = \sqrt{2}a \quad \left(\text{i.e., } R = \frac{\sqrt{2}a}{4}\right)$$

$$\text{APF} = \frac{\frac{\text{atoms}}{\text{unit cell}} \times \frac{4}{3} \pi (\sqrt{2}a/4)^3}{\frac{\text{volume}}{\text{atom}} \times \frac{\text{volume}}{\text{unit cell}}} = 0.74$$

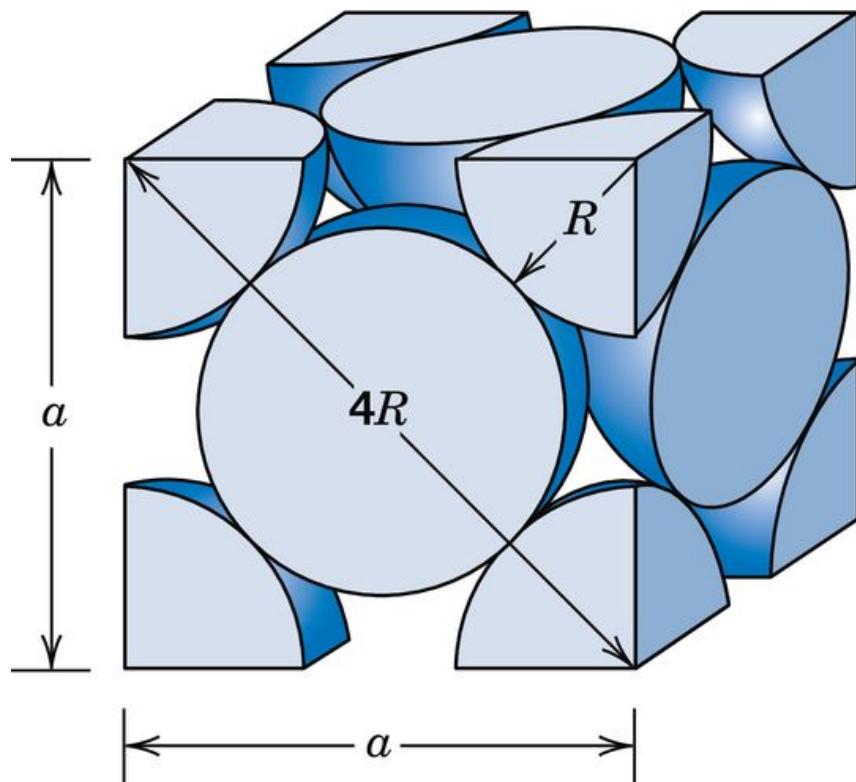
Unit cell contains: $6 \times 1/2 + 8 \times 1/8$
= 4 atoms/unit cell

FCC Plane Stacking Sequence

- ABCABC... Stacking Sequence—Close-Packed Planes of Atoms
- 2D Projection



Calculate the **volume** of FCC unit cells of the atomic radius R



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

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

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

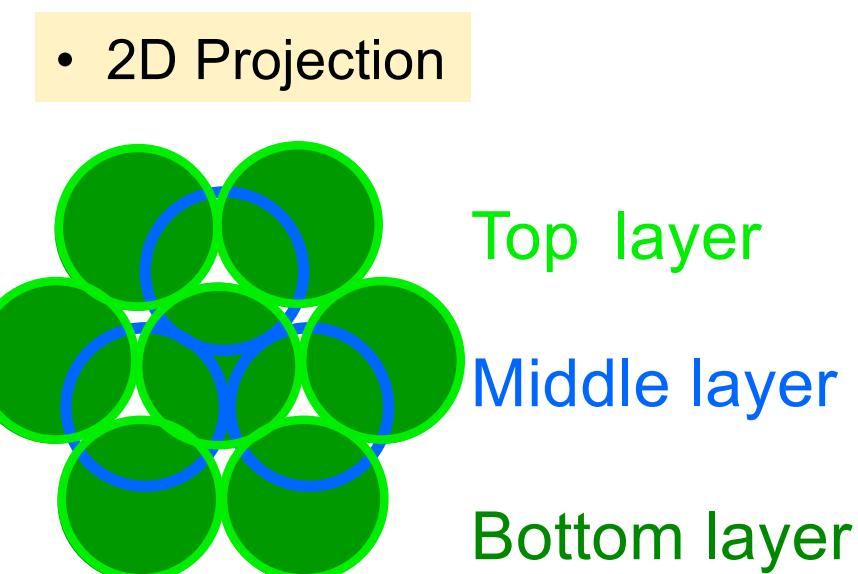
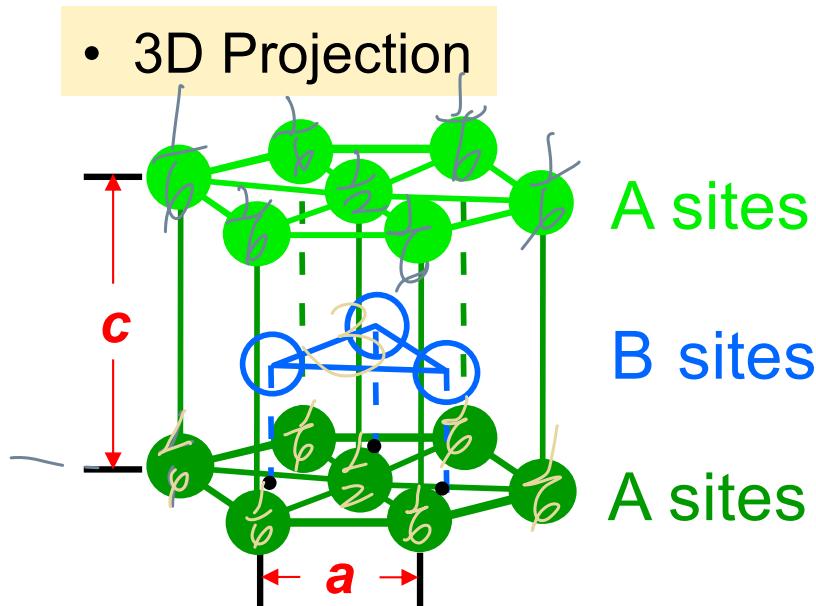
$$\mathbf{Vc} = a^3 = (2R\sqrt{2})^3 = 16 \mathbf{R}^3 \sqrt{2}$$

	Coordination Number	<u>atoms</u> unit cell
Simple Cubic (SC)	6	1
Body-Centered Cubic (BCC)	8	2
Face-Centered Cubic (Fcc)	12	4

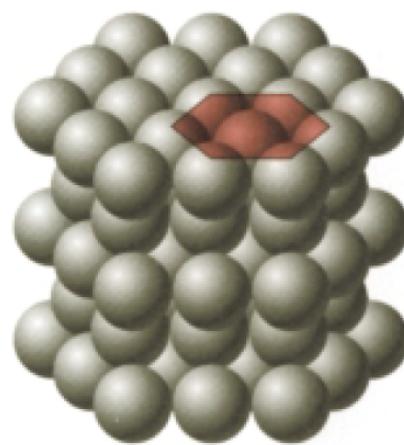
Hexagonal Close-Packed Structure (HCP)

六方最密堆積

- **ABAB...** Stacking Sequence – Close-Packed Planes of Atoms



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



6 atoms/unit cell
ex: Cd, Mg, Ti, Zn

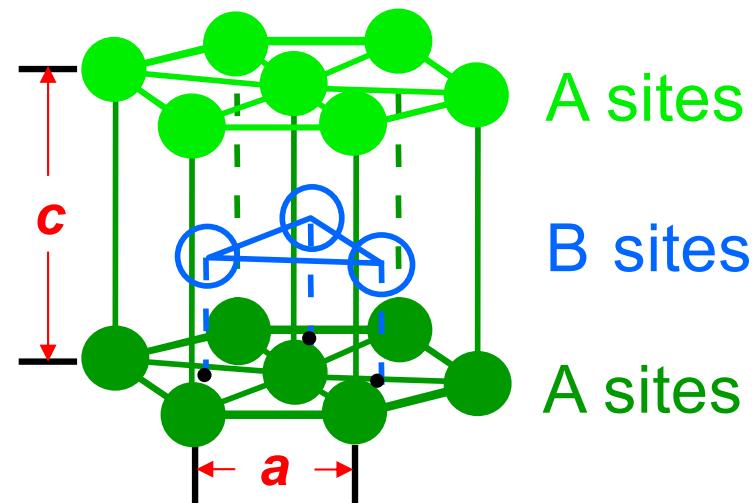
Hexagonal Close-Packed Structure (HCP)

6 atoms/unit cell

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{6} \quad (3.5)$$

$$N = 3 + \frac{2}{2} + \frac{12}{6}$$

$$N = 6$$

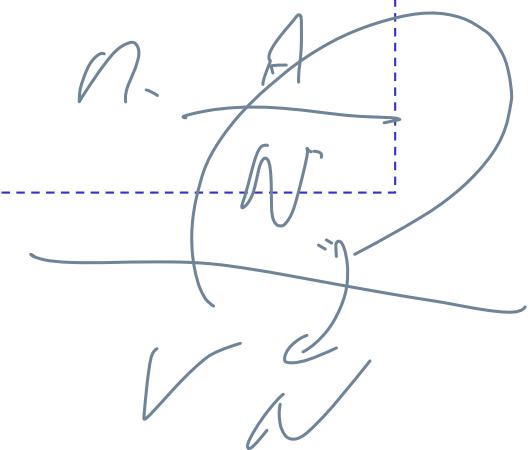


$$1 \text{ mol} < 12 \text{ g} \quad \frac{12}{6.022 \times 10^{23}}$$

Theoretical Density for Metals, ρ

$$\text{Density} = \rho = \frac{\text{Mass of Atoms in Unit Cell}}{\text{Total Volume of Unit Cell}} = \frac{(nA) / N_A}{V_c}$$

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



where

n = number of atoms/unit cell

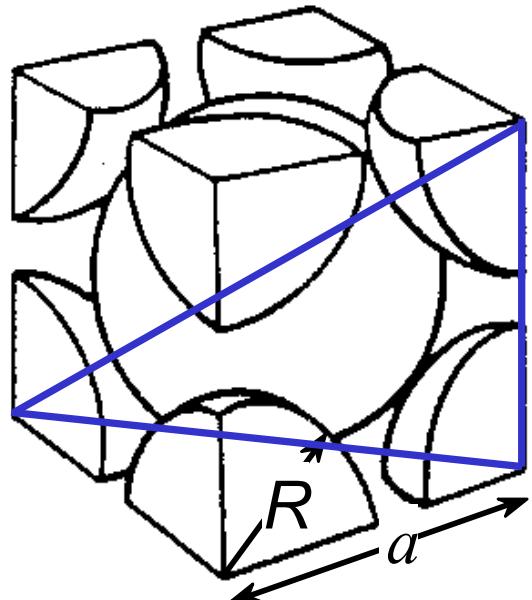
A = atomic weight

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

N_A = Avogadro's number

= 6.022×10^{23} atoms/mol

Theoretical Density Computation for Chromium (Cr)



- Cr has **BCC** crystal structure

$$A = 52.00 \text{ g/mol}$$

$$R = 0.125 \text{ nm}$$

$$n = 2 \text{ atoms/unit cell}$$

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

$$V_C = a^3 = 2.406 \times 10^{-23} \text{ cm}^3$$

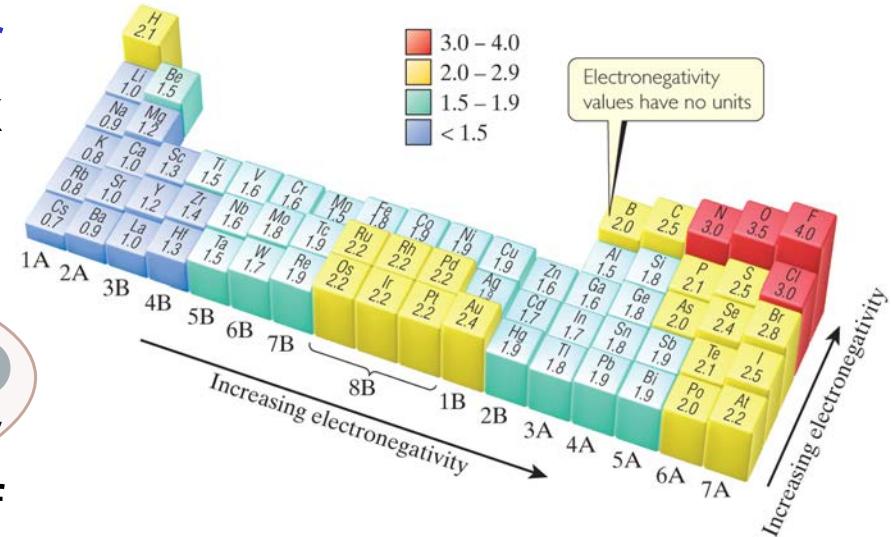
$$\rho = \frac{\frac{n}{\text{unit cell}} A}{\frac{V_C N_A}{\text{volume unit cell}}} = \frac{2 \text{ atoms}}{2.406 \times 10^{-23} \text{ cm}^3 \frac{6.022 \times 10^{23}}{\text{mol}}} = 7.19 \text{ g/cm}^3$$

atoms
mol

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

Ceramic Crystal Structures

- Ceramics are composed of two or more elements with a complex crystal structure. 比亞屬複雜
- The atomic bonding in these materials ranges from **purely ionic, hybrid, to totally covalent**; many ceramics exhibit a combination of these two bonding types.



$$\% \text{ ionic character} = \{1 - \exp[-(0.25)(X_A - X_B)^2]\} \times 100 \quad (2.10)$$

where X_A and X_B are the electronegativities for the respective elements.

- The **degree of ionic character** depends on the **electronegativities** of the atoms.
- Ceramic materials which the atomic bonding is predominantly ionic, the crystal structures are composed of **electrically charged ions** instead of atoms.

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:

離子
CaF₂: large

共價
SiC: small

IA		IIA														0	
H 2.1		Be 1.5														He -	
Li 1.0		Mg 1.2														Ne -	
Na 0.9																Ar -	
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr -
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe -
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn -
Fr 0.7	Ra 0.9	Ac-No 1.1-1.7															

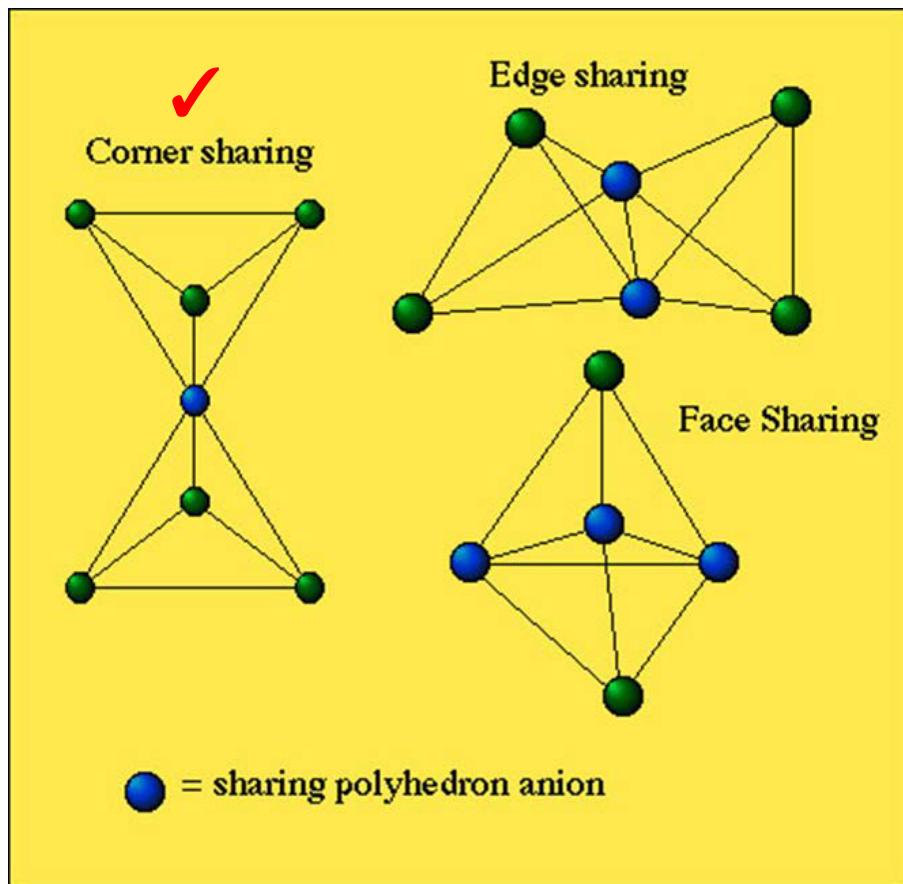
Bond Hybridization is possible when there is significant covalent bonding

- hybrid electron orbitals form
- For example for SiC
 - $X_{\text{Si}} = 1.8$ and $X_{\text{C}} = 2.5$
 - % ionic character = $100 \{1 - \exp[-0.25(X_{\text{Si}} - X_{\text{C}})^2]\} = 11.5\%$
 - ~ 89% covalent bonding

Ceramic Crystal Structures

- The **relative sizes of the cations and anions**, and the **electrical charge** on each of the component ions in crystalline ceramic materials influence the crystal structure.
- Oxide structures
 - Size: oxygen anions > metal cations
 - Close packed oxygen in a lattice (usually FCC)
 - Cations fit into interstitial sites among oxygen ions
- **Pauling's rules:** for predicting and rationalizing the crystal structures of ionic compounds.

Pauling's Rules



For predicting and rationalizing the crystal structures of ionic compounds

- 1st rule: the radius ratio rule (CN)
- 2nd rule: the electrostatic valence rule
- 3rd rule: sharing of polyhedron
電荷平衡 corners, edges and faces
- 4th rule: crystals containing different cations
陽離子
- 5th rule: the rule of parsimony

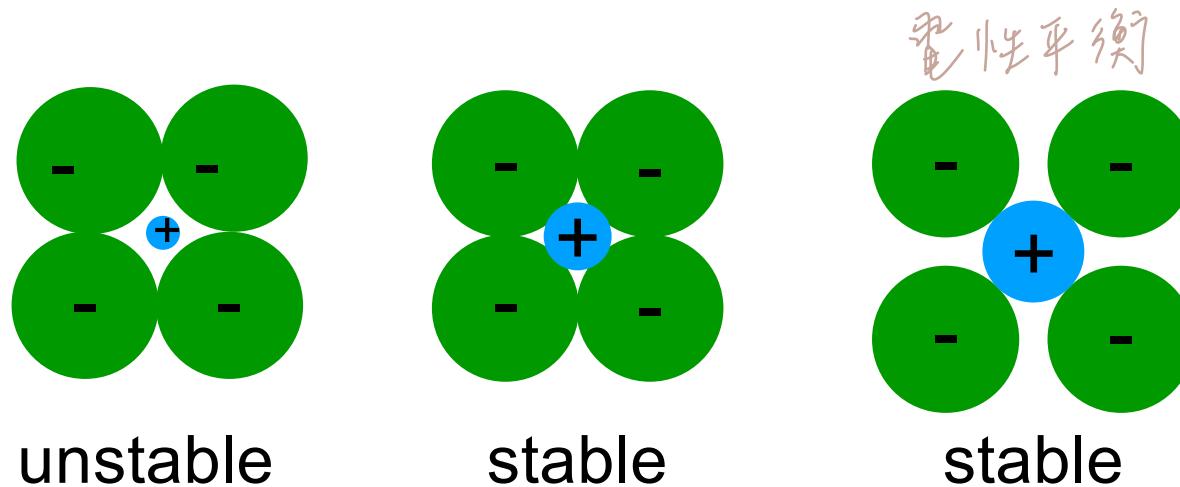
3S:3°

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Chapter 3 - 25

Factors that Determine Crystal Structure

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



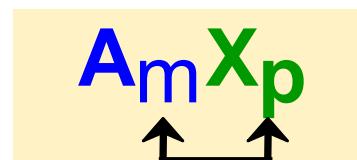
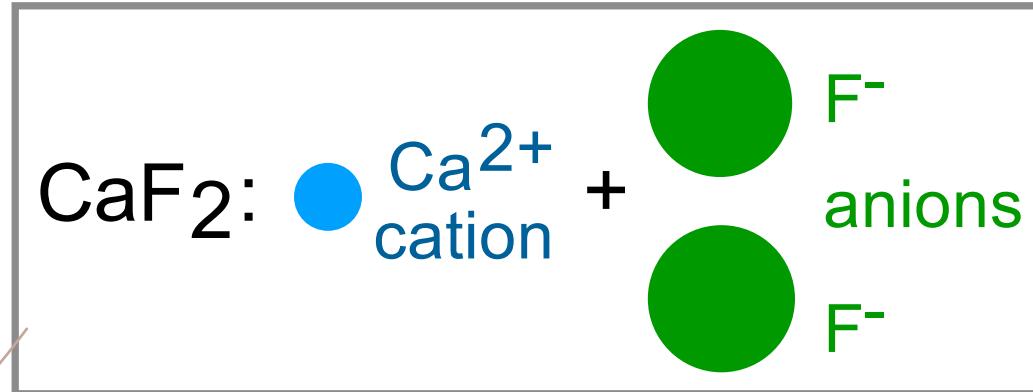
Adapted from Fig. 3.5,
Callister & Rethwisch 5e.

- Because the metallic elements give up electrons when ionized, **cations are ordinarily smaller than anions**, and, consequently, the ratio r_C/r_A is less than unity **陽離子が小**
- Each cation prefers to have as many nearest-neighbor anions as possible.
- The anions also desire a maximum number of cation nearest neighbors.

Factors that Determine Crystal Structure

2. Maintenance of Charge Neutrality :

- Net charge in ceramic should be zero. *不带电*
- Reflected in chemical formula:



m, p values to achieve charge neutrality

- The crystal must be **electrically neutral**; all the cation positive charges must be balanced by an equal number of anion negative charges.
- The chemical formula of a compound indicates the **ratio of cations to anions**, or the composition that achieves this **charge balance**.

Coordination Number & Ionic Radii

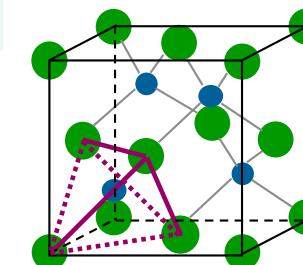
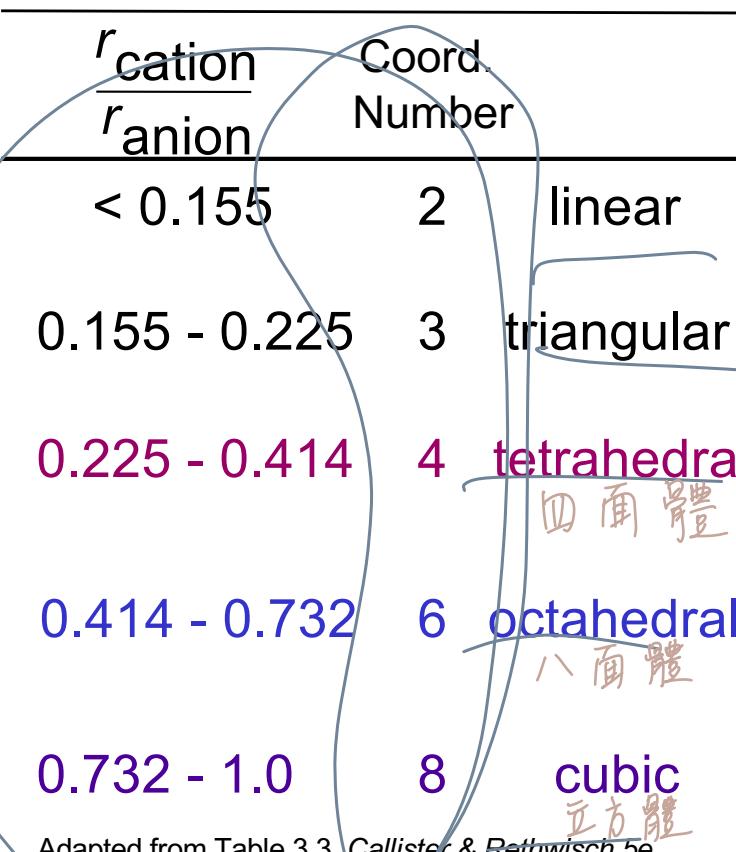
配位數

- Coordination Number increases with

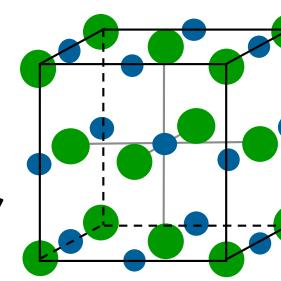
To form a stable structure, how many anions can surround around a cation?

$$\frac{r_{\text{cation}}}{r_{\text{anion}}}$$

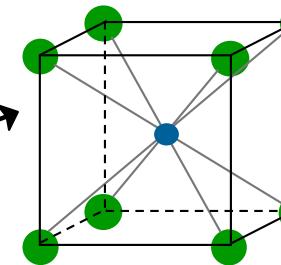
Adapted from Fig. 3.8, Callister & Rethwisch 5e.



ZnS
(zinc blende)



NaCl
(sodium chloride)



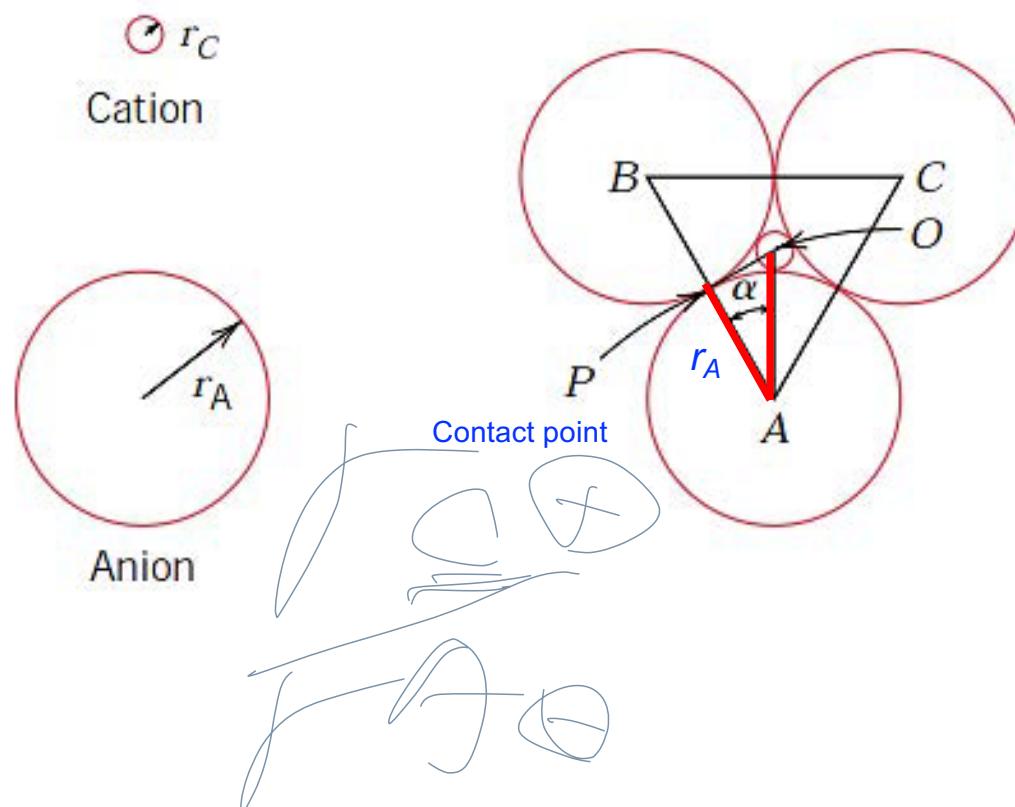
CsCl
(cesium chloride)

Adapted from Fig. 3.7, Callister & Rethwisch 5e.

The coordination number is related to the cation–anion radius ratio.

Computation of Minimum Cation-Anion Radius Ratio

- Determine minimum $r_{\text{cation}}/r_{\text{anion}}$ for an **triangular site** (C.N. = 3)



$$AP = r_A$$

$$AO = r_A + r_C$$

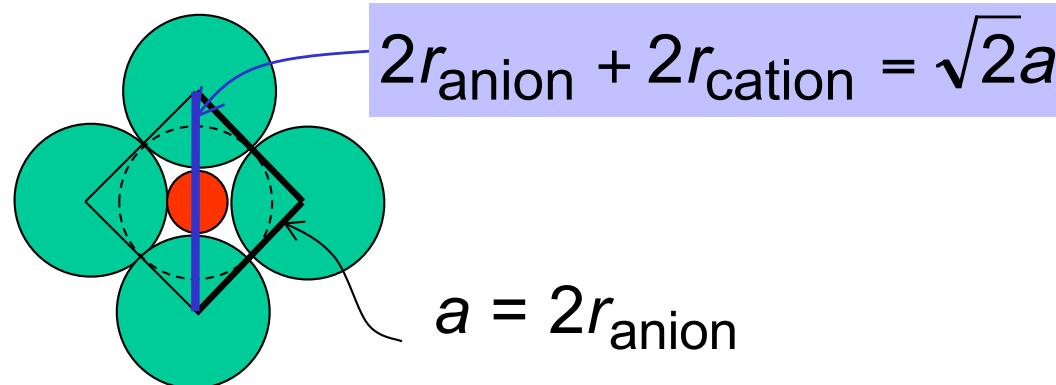
$$AP/AO = \cos^\circ 30 = \sqrt{3}/2$$

$$r_A / r_A + r_C = \sqrt{3}/2$$

$$\begin{aligned} r_C/r_A &= (1 - \sqrt{3}/2) / \sqrt{3}/2 \\ &= 0.155 \end{aligned}$$

Computation of Minimum Cation-Anion Radius Ratio

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



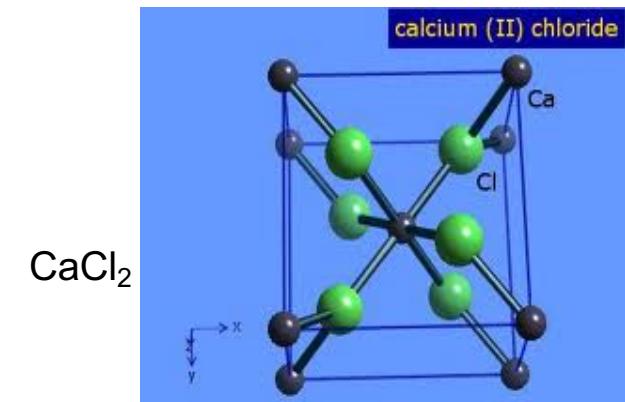
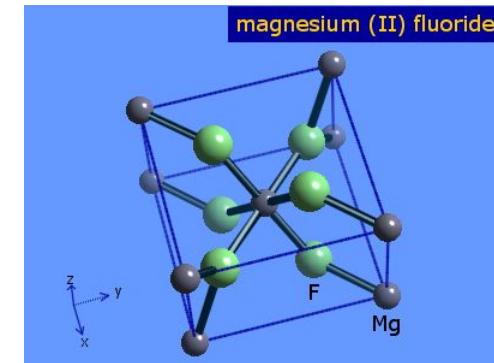
$$2r_{\text{anion}} + 2r_{\text{cation}} = 2\sqrt{2}r_{\text{anion}}$$

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

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

Ionic Radii for Several Cations and Anions

Cation	<i>Ionic Radius (nm)</i>	Anion	<i>Ionic Radius (nm)</i>
Al^{3+}	0.053	Br^-	0.196
Ba^{2+}	0.136	Cl^-	0.181
Ca^{2+}	0.100	F^-	0.133
Cs^+	0.170	I^-	0.220
Fe^{2+}	0.077	O^{2-}	0.140
Fe^{3+}	0.069	S^{2-}	0.184
K^+	0.138		
Mg^{2+}	0.072		
Mn^{2+}	0.067		
Na^+	0.102		
Ni^{2+}	0.069		
Si^{4+}	0.040		
Ti^{4+}	0.061		



- The most common coordination numbers for ceramic materials are 4, 6, and 8.
- For a coordination number of 6 (r_C/r_A ranges 0.414–0.732)
 - $\text{MgF}_2 = 0.072/0.133 = 0.541$
 - $\text{CaCl}_2 = 0.100/0.181 = 0.552$

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

- Answer:

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

based on this ratio,

-- CN = 6 because

$$0.414 < 0.550 < 0.732$$

-- crystal structure is **NaCl Octahedral**

Some Common Ceramic Crystal Structures

Structure Name	Type	Anion Packing	Coordination Numbers		Examples
			Cation	Anion	
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	Simple cubic	8	4	CaF_2 , UO_2 , ThO_2
Perovskite	ABX_3	FCC	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

- 岩鹽結構 (Rock salt structure)
AX • 氯化銫 (CsCl)

- 閃鋅礦 (ZnS structure)



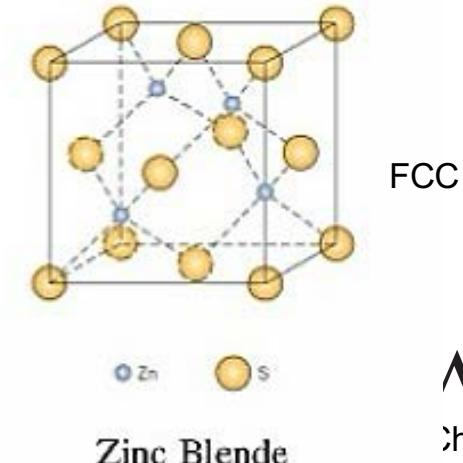
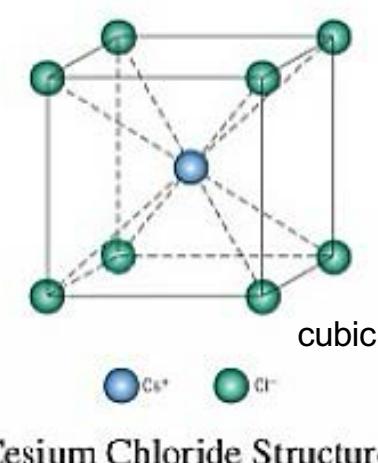
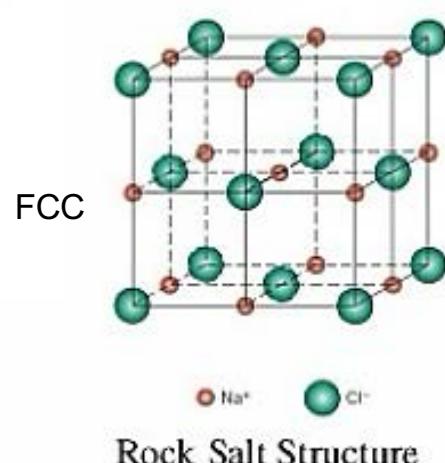
- CaF_2 ,
- TiO_2



BaTiO_3
鈣鈦礦
(perovskite)

AX Crystal Structures

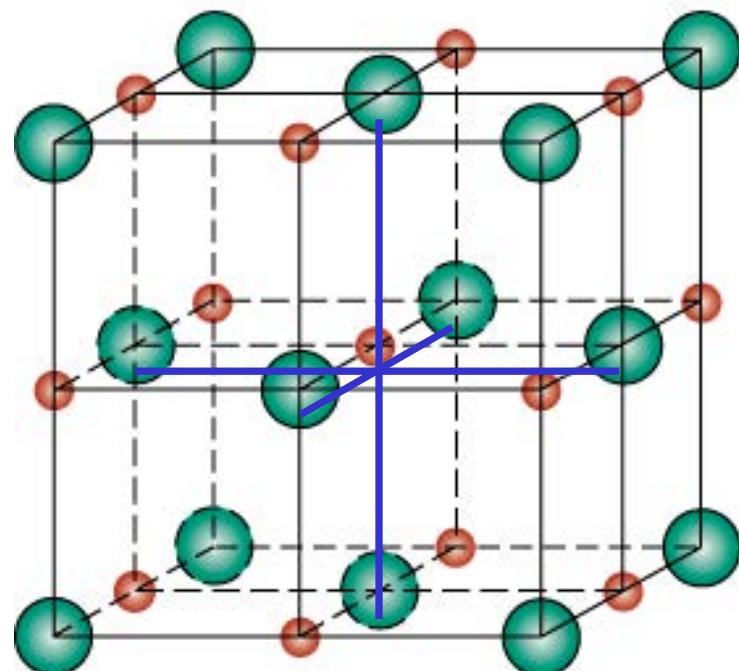
- AX compounds **ceramic** materials are those in which there are **equal numbers** of **cations** and **anions** (A denotes the **cation** and X the **anion**).
- There are several different crystal structures for AX compounds; each is normally named after a common material that assumes the particular structure.
- AX-type crystal structures include **rock salt (NaCl)**, **cesium chloride (CsCl)**, and **zinc blende (ZnS)**



Rock Salt Structure

Same concepts can be applied to ionic solids in general.

Example: **NaCl** (rock salt) is the most common **AX** crystal structure



$$r_{\text{Na}} = 0.102 \text{ nm}$$



$$r_{\text{Cl}} = 0.181 \text{ nm}$$

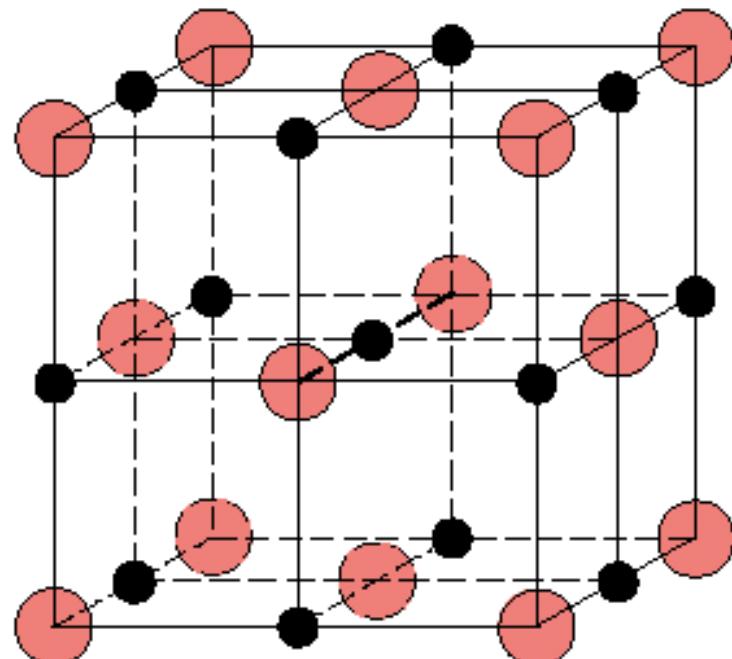
$$r_{\text{Na}}/r_{\text{Cl}} = 0.564$$

∴ cations (Na^+) prefer octahedral sites

- FCC, the CN for both cations and anions is 6, and the cation–anion radius ratio is between approximately 0.414 and 0.732.
- Such as NaCl, MgO, MnS, LiF, and FeO.

MgO and FeO

MgO and FeO also have the NaCl structure



Adapted from Fig. 3.6,
Callister & Rethwisch 5e.

● O²⁻ $r_O = 0.140 \text{ nm}$
● Mg²⁺ $r_{Mg} = 0.072 \text{ nm}$

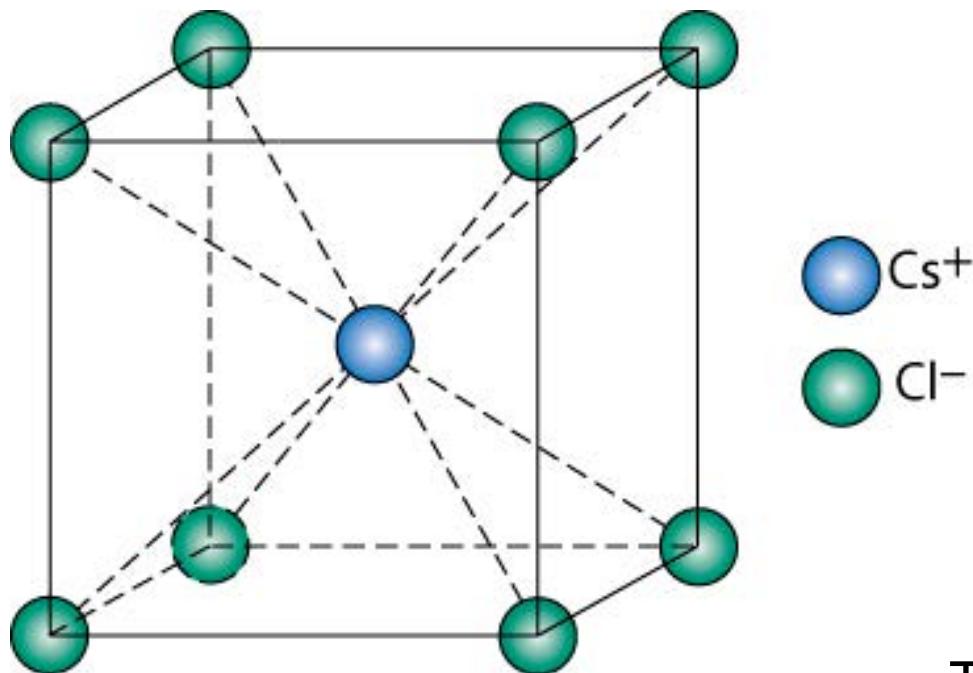
$$r_{Mg}/r_O = 0.514$$

∴ cations prefer octahedral sites

So each Mg²⁺ (or Fe²⁺) has 6 neighbor oxygen atoms

Cesium Chloride Structure

Cesium Chloride structure:



Adapted from Fig. 3.7, Callister & Rethwisch 5e.

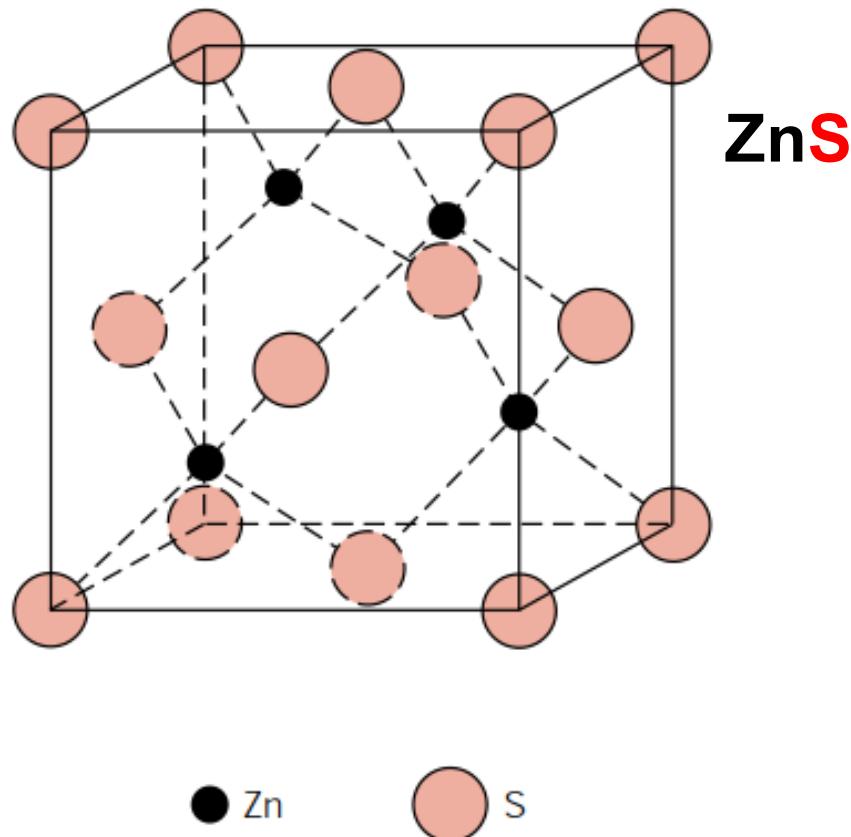
$$\frac{r_{\text{Cs}^+}}{r_{\text{Cl}^-}} = \frac{0.170}{0.181} = 0.939$$

∴ Since $0.732 < 0.939 < 1.0$,
cubic sites preferred

So each **Cs⁺** has 8 neighbor **Cl⁻**

- The CN for both cations and anions is **8**, and the cation–anion radius ratio is between approximately 0.732 and 1.0.

Zinc Blende Structure



- $r_{\text{Zn}}/r_{\text{S}} = 0.6/1.84 = 0.326$
- Since $0.255 < 0.326 < 0.414$, **tetrahedral sites** preferred ($\text{CN}=4$).

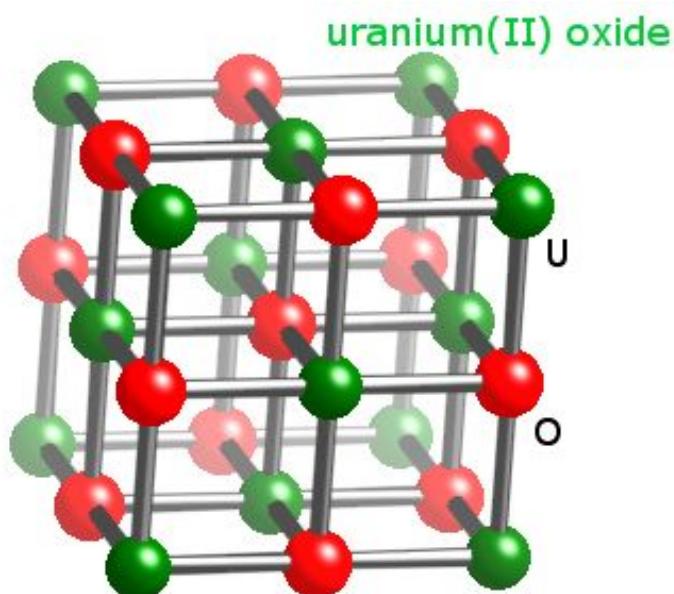
Table 3.2 For Several Ceramic Materials, Percent Ionic Character of the Interatomic Bonds

<i>Material</i>	<i>Percent Ionic Character</i>
CaF_2	89
MgO	73
NaCl	67
Al_2O_3	63
SiO_2	51
Si_3N_4	30
<u>ZnS</u>	18
<u>SiC</u>	12

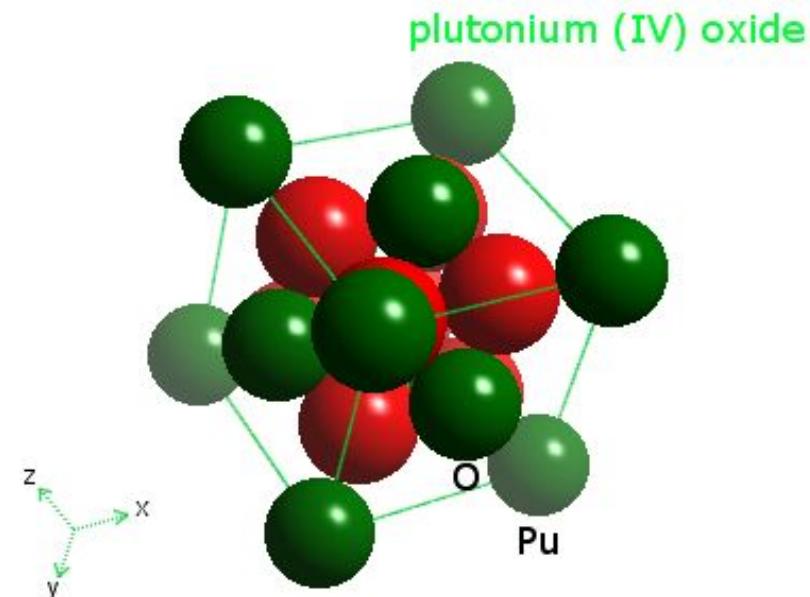
- Most often the atomic bonding is highly **covalent** in this crystal structure, which include ZnS, ZnTe, and SiC.

A_mX_p -type Crystal Structures

- If the **charges** on the cations and anions **are not the same**, a compound can exist with the chemical formula A_mX_p , where m and/or $p \neq 1$.
- Compounds such as CaF_2 , UO_2 , PuO_2 , and ThO_2 have this crystal structure.



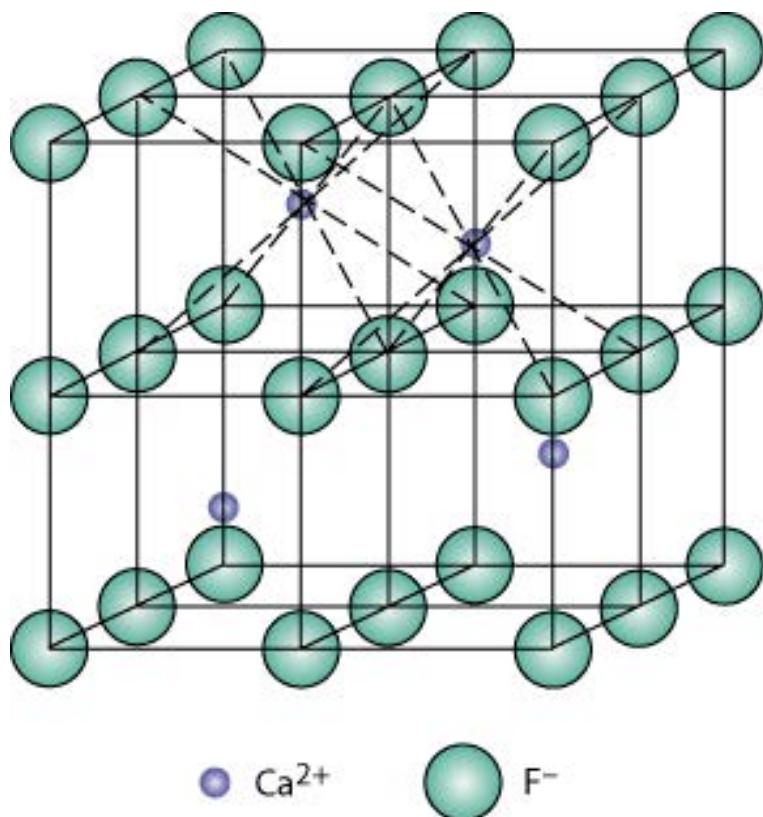
Uranium (2⁺) oxide (UO_2)



Plutonium (4+) O₂ (PuO_2)

AX_2 Crystal Structures

Fluorite structure



- Calcium Fluorite (CaF_2)
- The ionic radii ratio $r_{\text{C}}/r_{\text{A}}$ for CaF_2 is about 0.8 which has a coordination number of 8.
- Cations in cubic sites
- UO_2 , ThO_2 , ZrO_2 , CeO_2

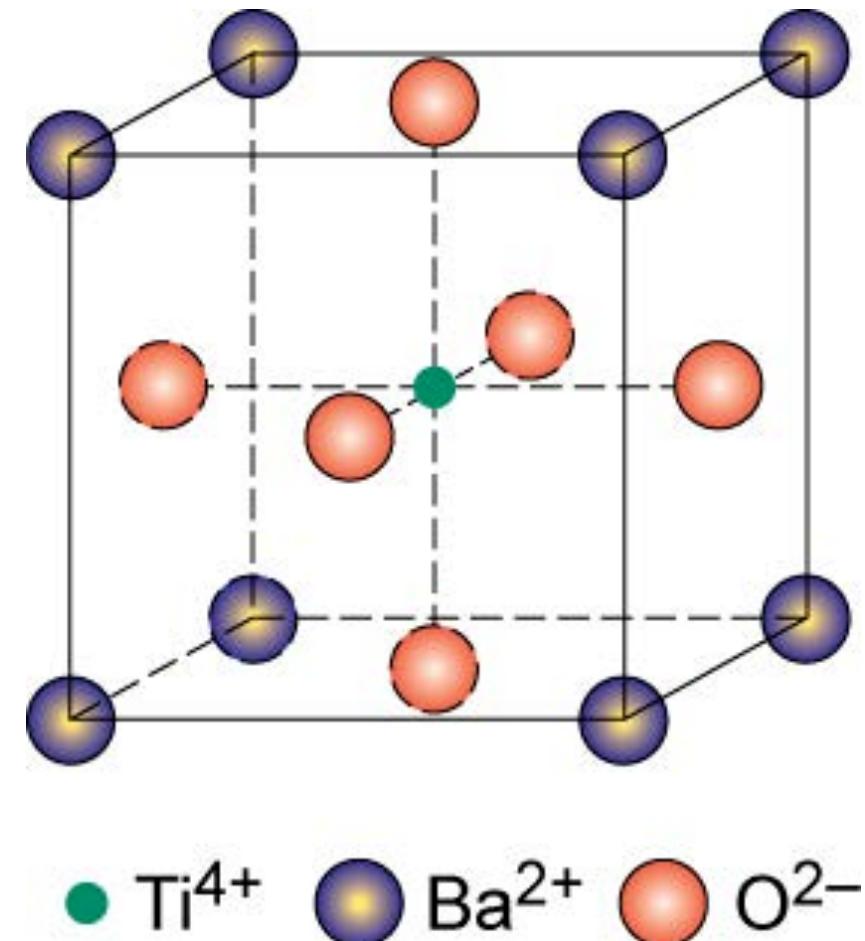
Adapted from Fig. 3.9,
Callister & Rethwisch 5e.

ABX_3 Crystal Structures

- **Perovskite** structure

鈣鈦礦

Ex: complex oxide



Adapted from Fig. 3.10,
Callister & Rethwisch 5e.

Density Computations for Ceramics

Number of formula units/unit cell

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

Avogadro's number

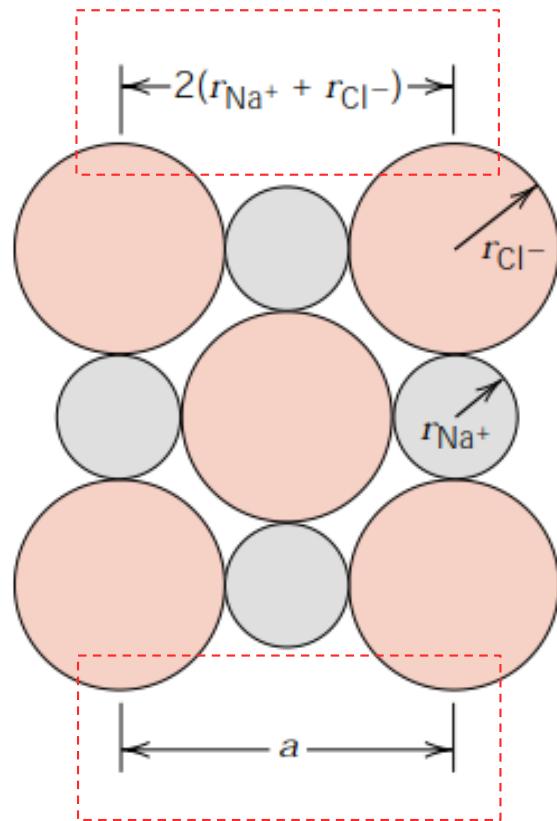
Volume of unit cell

$\sum A_C$ = sum of atomic weights of **all cations** in formula unit

$\sum A_A$ = sum of atomic weights of **all anions** in formula unit

Example Problem

Compute the theoretical density for sodium chloride ((NaCl))



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

- $\Sigma A_C = A_{\text{Na}} = 22.99 \text{ g/mol}$
- $\Sigma A_A = A_{\text{Cl}} = 35.45 \text{ g/mol}$
- $a = 2r_{\text{Na}^+} + 2r_{\text{Cl}^-}$
- $V_C = a^3 = (2r_{\text{Na}^+} + 2r_{\text{Cl}^-})^3$

$$\begin{aligned}\rho &= \frac{n'(A_{\text{Na}} + A_{\text{Cl}})}{(2r_{\text{Na}^+} + 2r_{\text{Cl}^-})^3 N_A} \\ &= \frac{4(22.99 + 35.45)}{[2(0.102 \times 10^{-7}) + 2(0.181 \times 10^{-7})]^3 (6.023 \times 10^{23})} \\ &= 2.14 \text{ g/cm}^3\end{aligned}$$

- experimental value is 2.14 g/cm^3

Densities Comparison for Four Material Types

In general
高密度

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

高密度

Why?

Metals have...

- **close-packing**
(metallic bonding)
- often **large atomic masses**

Ceramics have...

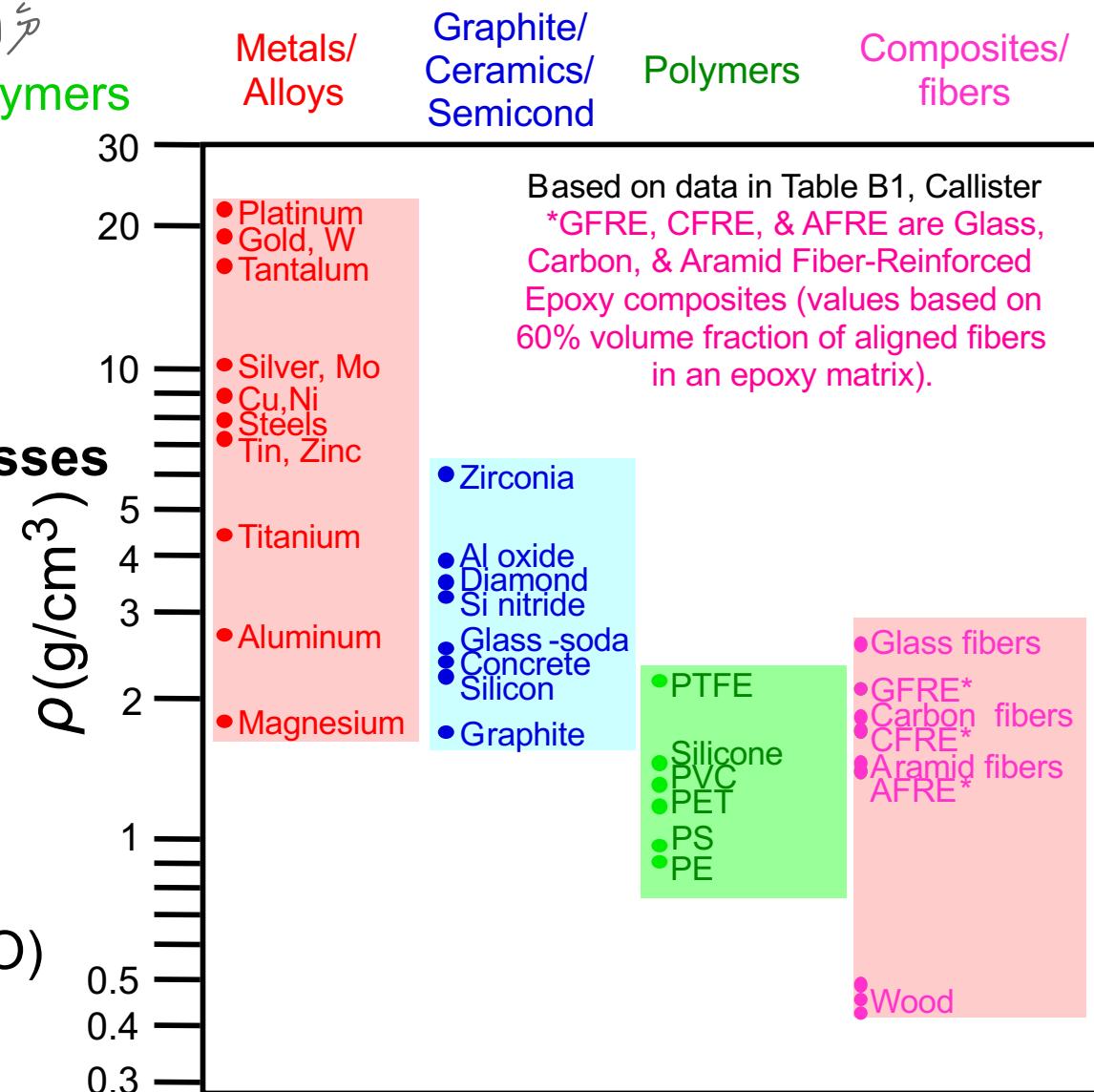
- often lighter elements

Polymers have...

- **low packing density**
(often amorphous)
- **lighter elements** (C,H,O)

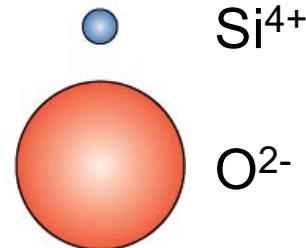
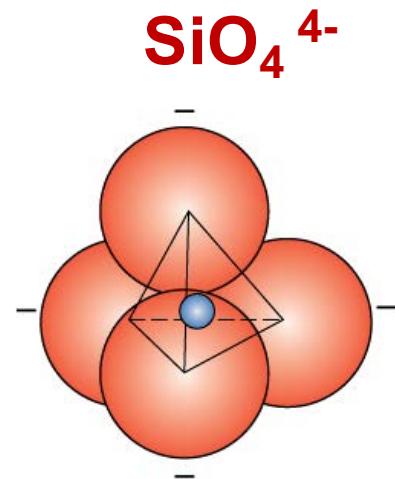
Composites have...

- moderate to low densities

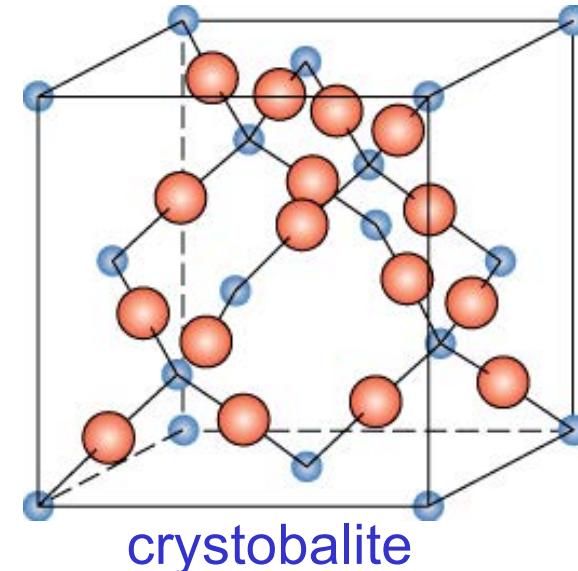
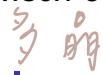


Silicate Ceramics

Most common elements on earth are Si & O



Figs. 3.11 & 3.10, Callister &
Rethwisch 5e



cristobalite

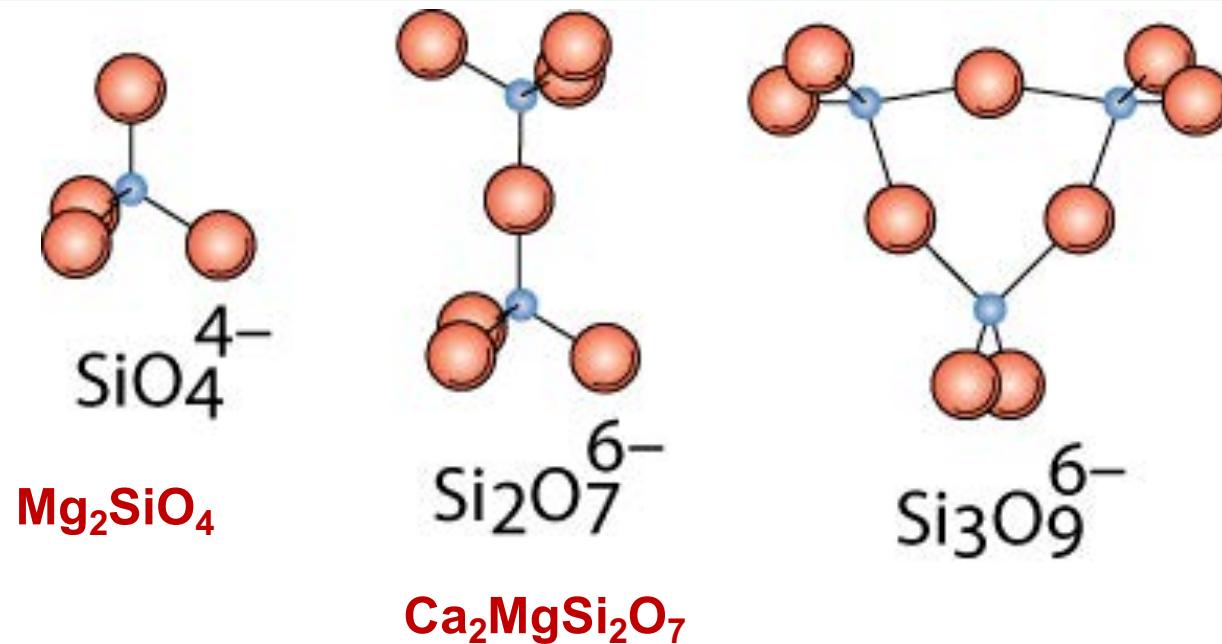
- SiO_2 (silica) polymorphic forms are *quartz* (石英), *cristobalite* (石英), & *tridymite* (鳞石英)



- The **strong Si-O bonds** lead to a **high melting temp.** ($1710^{\circ}C$) for this material

Silicate Ceramics

Bonding of adjacent SiO_4^{4-} accomplished by the sharing of common corners, edges, or faces



Adapted from Fig.
3.13, Callister &
Rethwisch 5e.

Presence of cations such as Ca^{2+} , Mg^{2+} , & Al^{3+}

1. maintain charge neutrality,
2. ionically bond SiO_4^{4-} to one another

Layered Silicates

層狀

- Layered silicates (e.g., clays, mica, talc)
 - SiO_4 tetrahedra connected together to form 2-D plane 平面
- A net negative charge is associated with each $(\text{Si}_2\text{O}_5)^{2-}$ unit
- Negative charge balanced by adjacent plane rich in positively charged cations

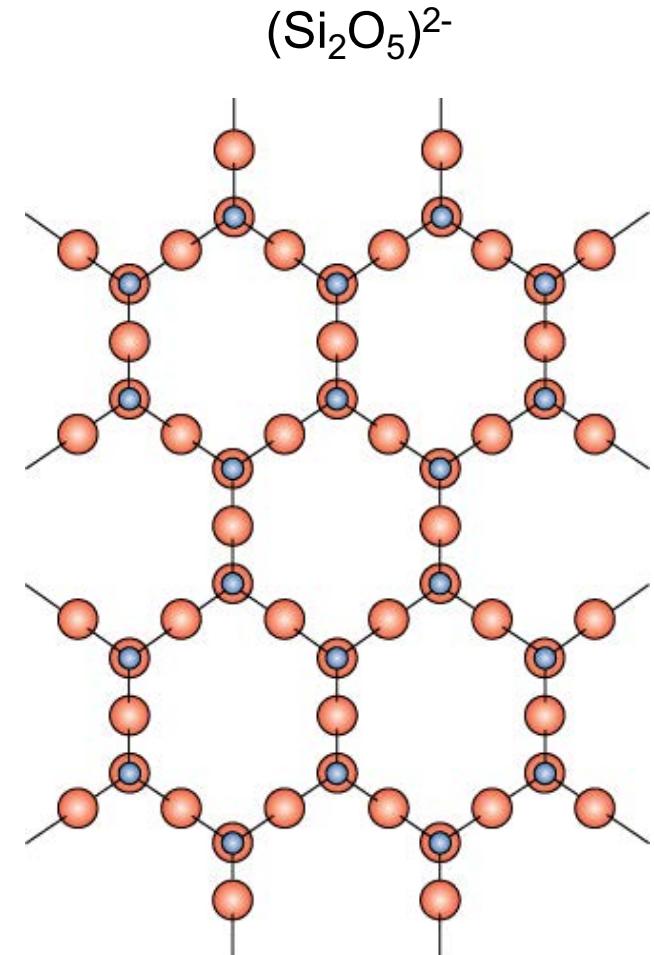
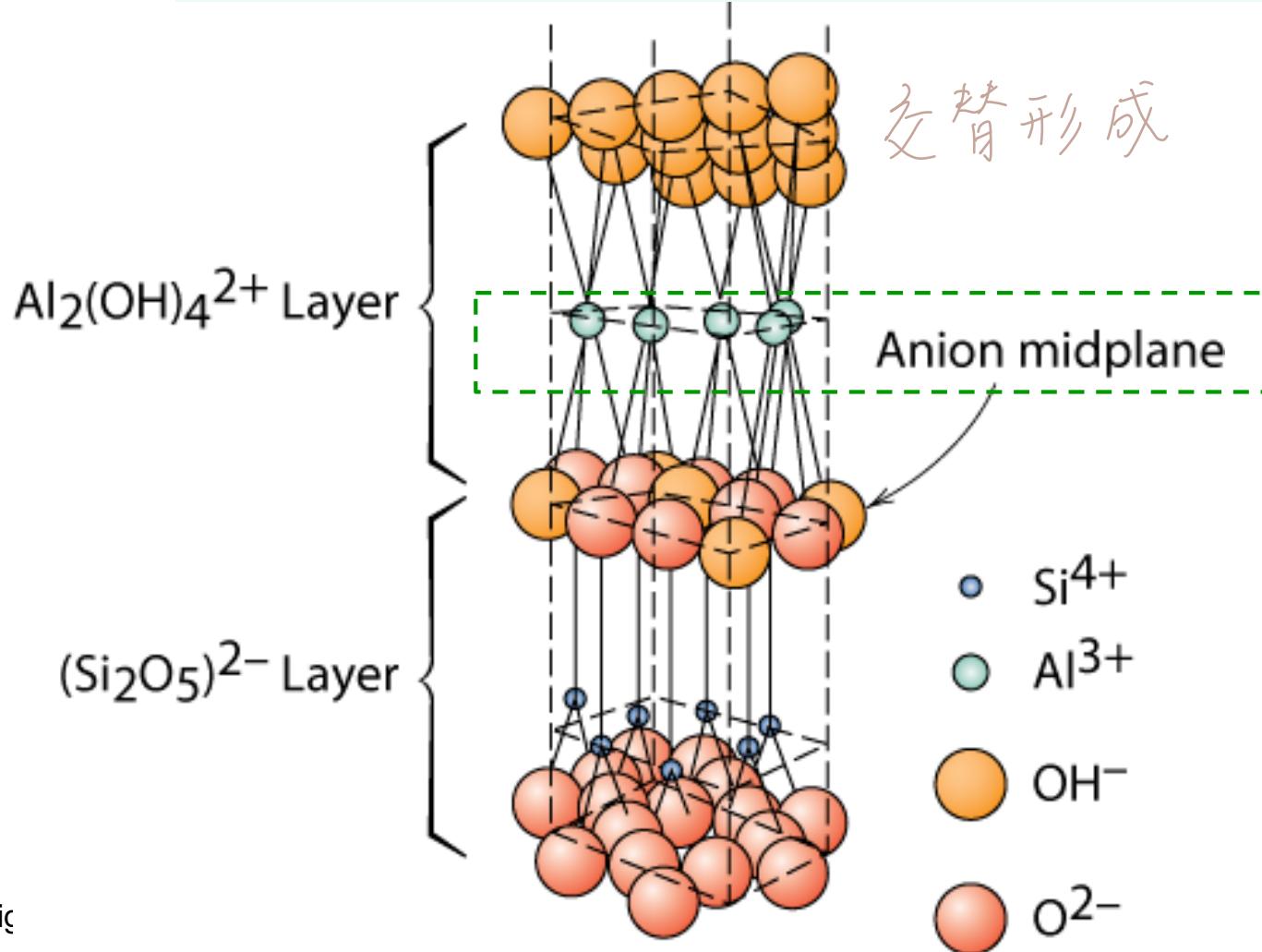


Fig. 3.14, Callister & Rethwisch 5e.

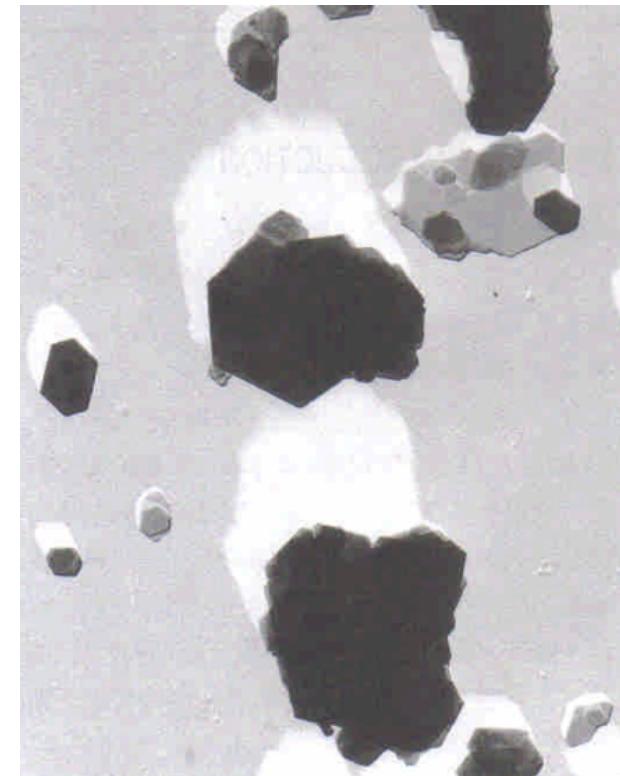
Layered Silicates

- Kaolinite clay alternates $(\text{Si}_2\text{O}_5)^{2-}$ layer with $\text{Al}_2(\text{OH})_4^{2+}$ layer

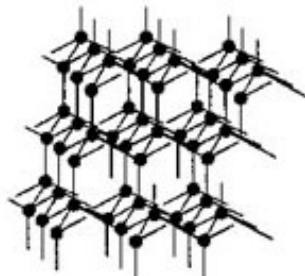


Fig

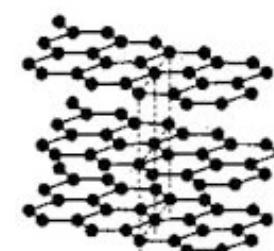
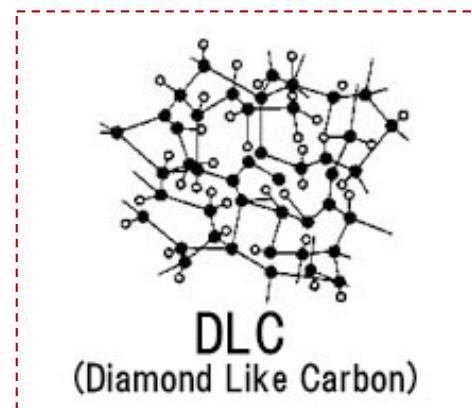
Note: Adjacent sheets of this type are loosely bound to one another by van der Waal's forces.



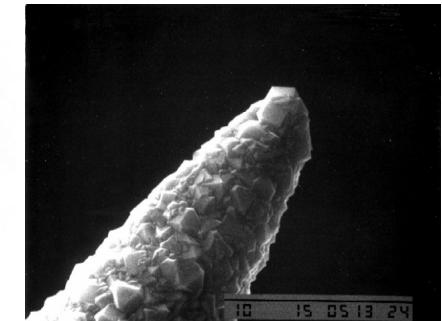
Diamond-like Carbon



Diamond



Graphite



Diamond-coated microtip



- **DLC** (diamond-like carbon) is a hydrogen-containing amorphous carbon coating, which feature is close to tough diamond.

Single Crystals

- When the periodic arrangement of atoms (**crystal structure**) extends without interruption throughout the entire specimen.

-- diamond single crystals for abrasives



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

-- single crystal for turbine blade



-- Quartz single crystal

Courtesy P.M. Anderson



Garnet (石榴石)



Photograph courtesy of irocks.com, Megan Foreman photo.

Fig. 9.42(c),
Callister & Rethwisch 5e.
(courtesy of Pratt and Whitney)

Polycrystalline Materials

- Most engineering materials are composed of many small, single crystals (i.e., are *polycrystalline*).

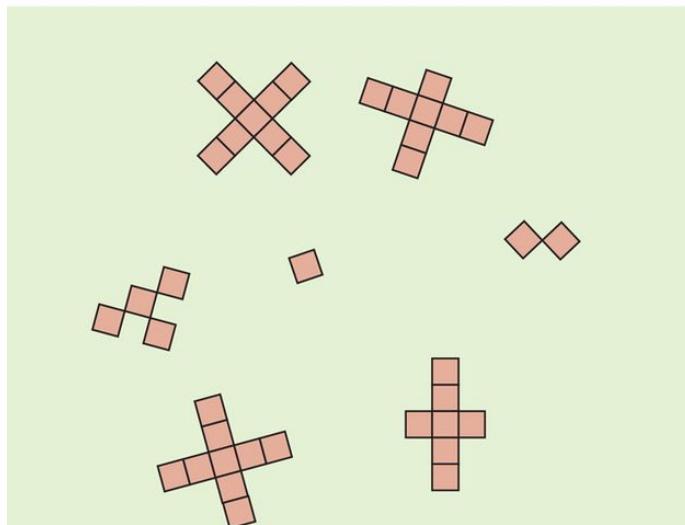
Courtesy of Paul E. Danielson, Teledyne Wah Chang Albany



- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- Grain sizes typically range from 1 nm to 2 cm (i.e., from a few to millions of atomic layers).

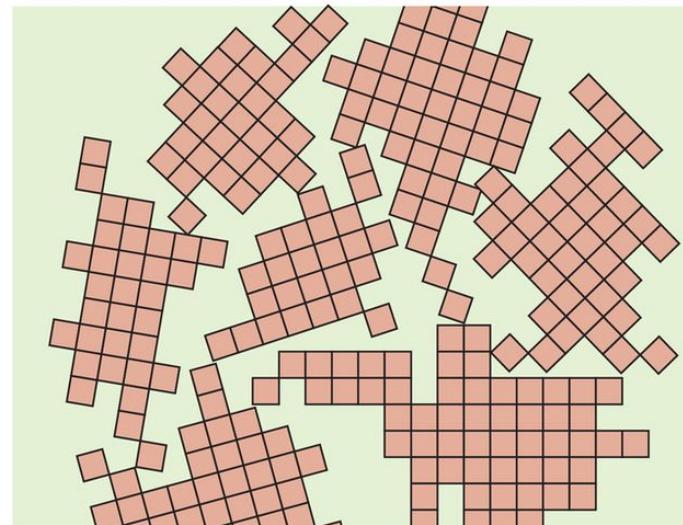
(niobium-hafnium-Wolfram plate)

Small crystallite nuclei



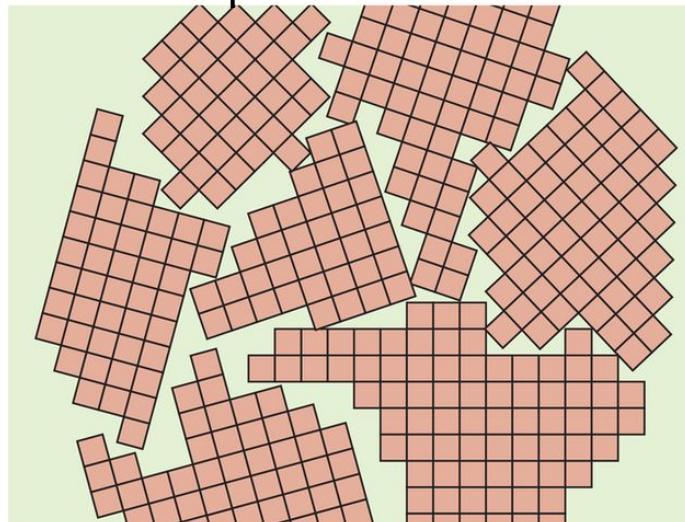
(a)

Growth of crystallites



(b)

Complete solidification



(c)



(d)

Adapted from W. Rosenhain, An Introduction to the Study of Physical Metallurgy, 2nd edition, Constable & Company Ltd., London, 1915.

Anisotropy 異向性

- Anisotropy — Physical property value depends on crystallographic direction of measurement.

有方向性

- Observed in **single crystals**.

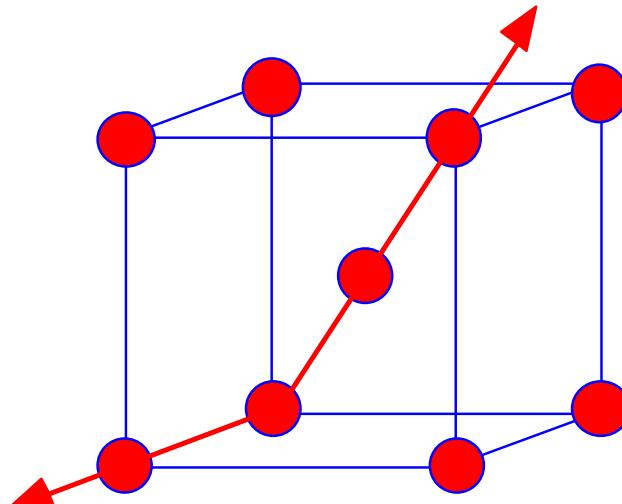
- Example: modulus of elasticity (E) in BCC iron

$$E(\text{edge}) \neq E(\text{diagonal})$$

Metal	Modulus of Elasticity (GPa)		
	[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

Unit cell of BCC iron

$$E(\text{diagonal}) = 273 \text{ GPa}$$



$$E(\text{edge}) = 125 \text{ GPa}$$

Isotropy 等向性

- **Polycrystals**

- Properties may/may not vary with direction.

- If grains randomly oriented:
properties **isotropic**.

($E_{\text{poly iron}} = 210 \text{ GPa}$)

- If grains textured
(e.g., deformed grains have preferential crystallographic orientation):
properties **anisotropic**.

異向性

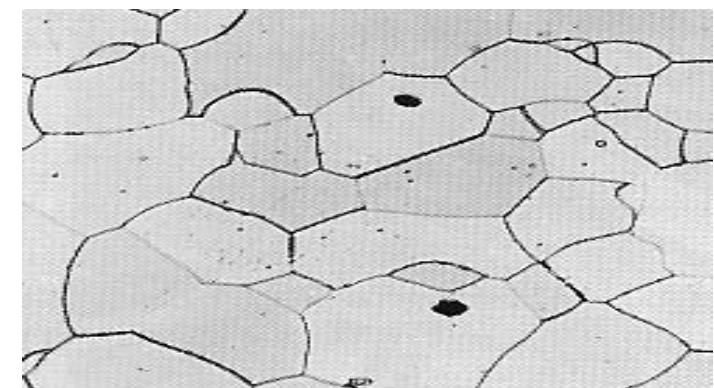
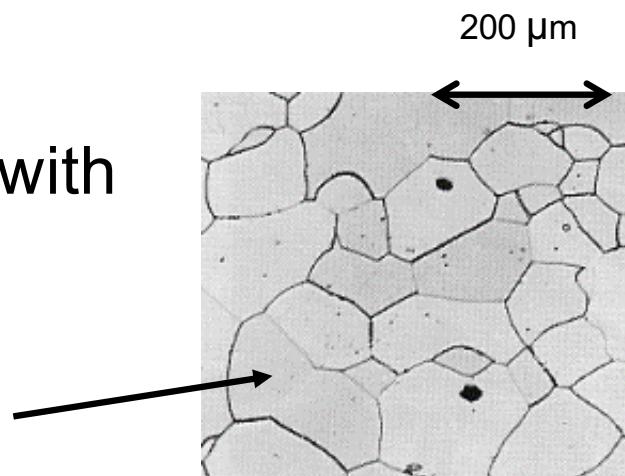


Fig. 5.20(b), Callister & Rethwisch 5e.
[Fig. 4.15(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC (now the National Institute of Standards and Technology, Gaithersburg, MD).]

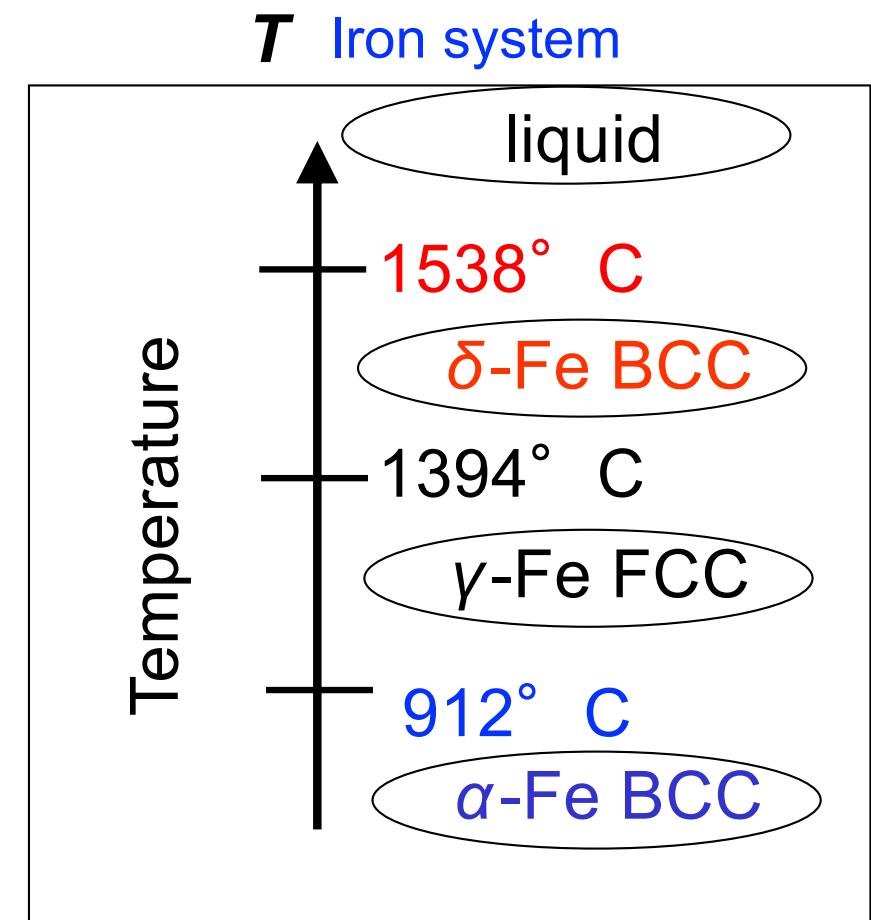
多形體

同素異形體

Polymorphism/Allotropy

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

- Iron: α to δ forms
- Titanium: α or β forms
- Carbon: diamond, graphite



Crystal systems

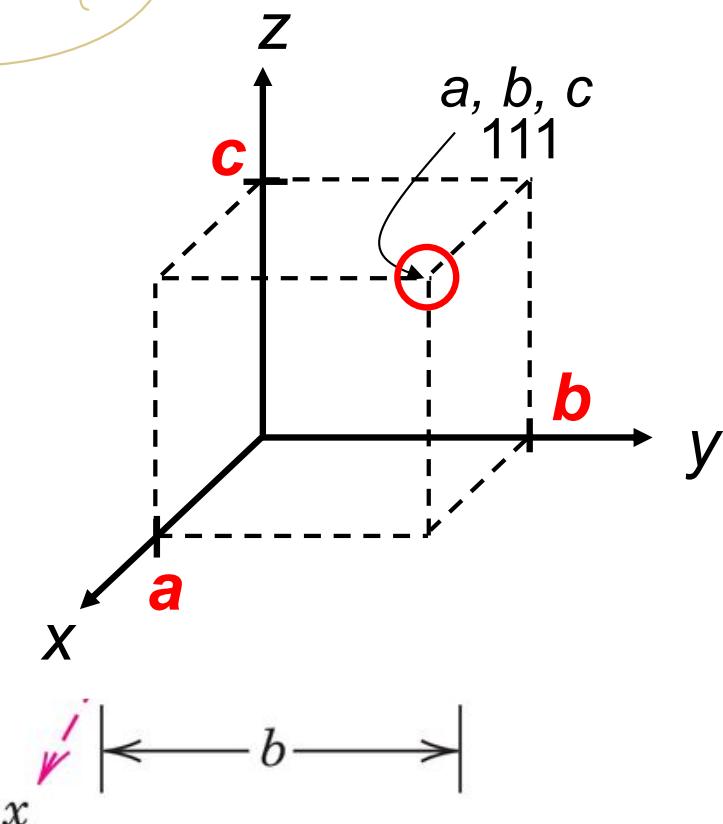
- Crystallographic Points
- Crystallographic Direction
- Crystallographic Planes

Point Coordinates

晶格點座標

A point coordinate is a **lattice position in a unit cell**

Determined as fractional multiples of **a**, **b**, and **c** unit cell edge lengths



Example: Unit cell upper corner

1. Lattice position is

a, b, c

2. Divide by unit cell edge lengths

(**a**, **b**, and **c**) and remove commas

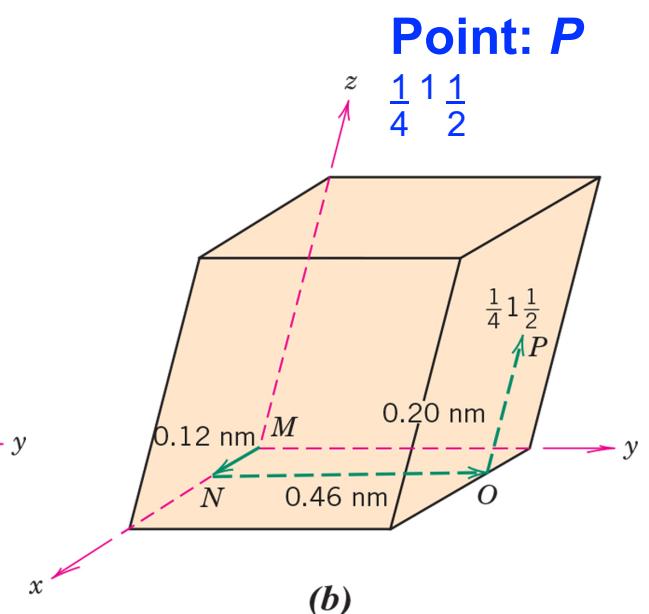
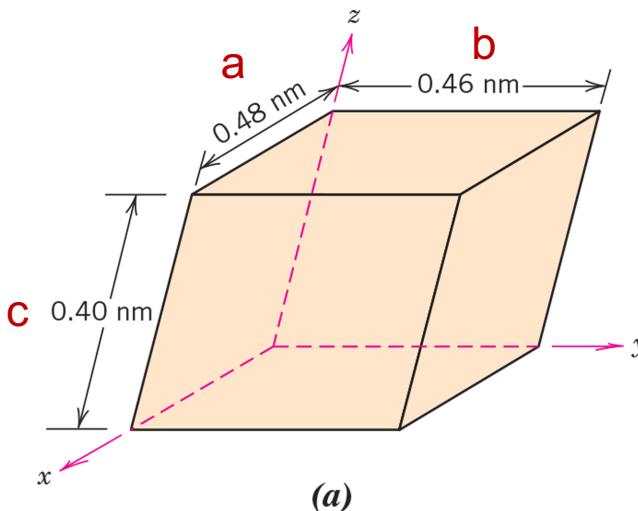
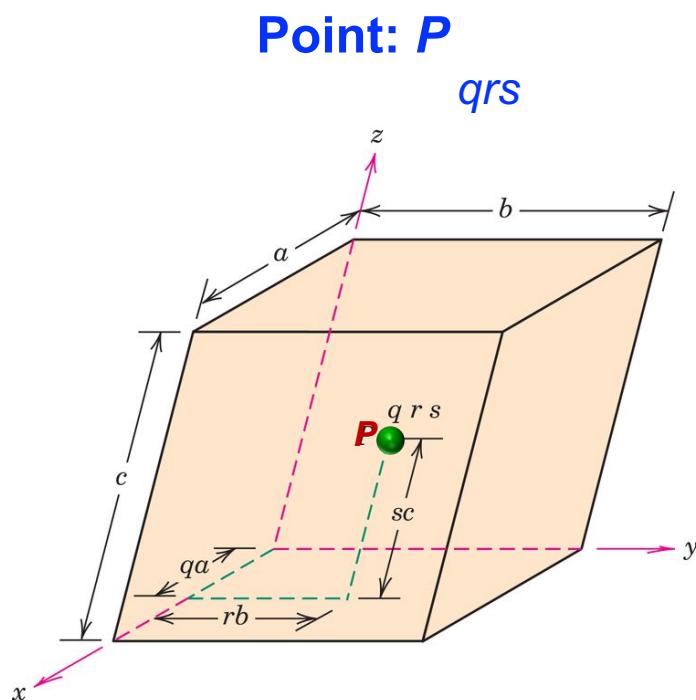
$$\frac{a}{a} \frac{b}{b} \frac{c}{c} = 111$$

3. Point coordinates for unit cell corner

are: **111**

單位晶胞 角落點座標

Point Coordinates



$$qa = (1/4) a = (1/4)(0.48 \text{ nm}) = 0.12 \text{ nm}$$

$$rb = (1) b = (1)(0.46 \text{ nm}) = 0.46 \text{ nm}$$

$$sc = (1/2) c = (1/2)(0.40 \text{ nm}) = 0.2 \text{ nm}$$

qa = lattice position referenced to the x axis (3.10a)

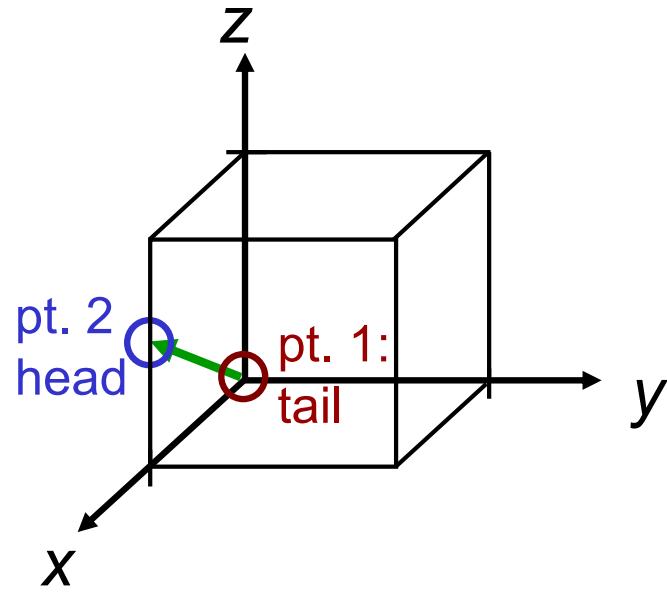
rb = lattice position referenced to the y axis (3.10b)

sc = lattice position referenced to the z axis (3.10c)

Crystallographic Directions I.

Example Problem I

Algorithm – determine direction indices



ex:

$$\text{pt. 1 } x_1 = 0, y_1 = 0, z_1 = 0$$

$$\text{pt. 2 } x_2 = a, y_2 = 0, z_2 = c/2$$

$$\frac{a - 0}{a} \quad \frac{0 - 0}{b} \quad \frac{c/2 - 0}{c}$$

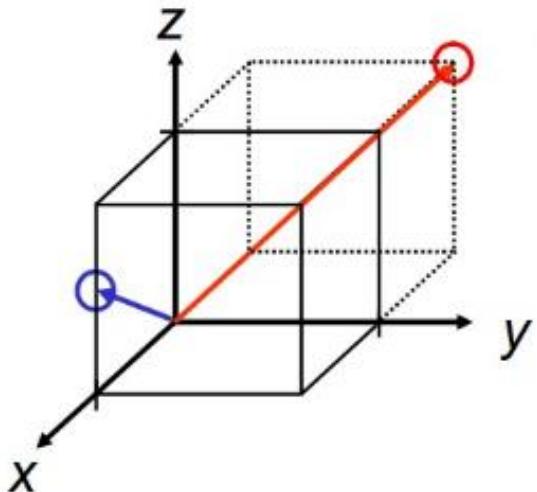
1. Determine coordinates of vector tail, pt. 1: $x_1, y_1, \& z_1$; and vector head, pt. 2: $x_2, y_2, \& z_2$.
2. Tail point coordinates subtracted from head point coordinates.
3. Normalize coordinate differences in terms of lattice parameters a, b , and c :

$$\frac{x_2 - x_1}{a} \quad \frac{y_2 - y_1}{b} \quad \frac{z_2 - z_1}{c}$$

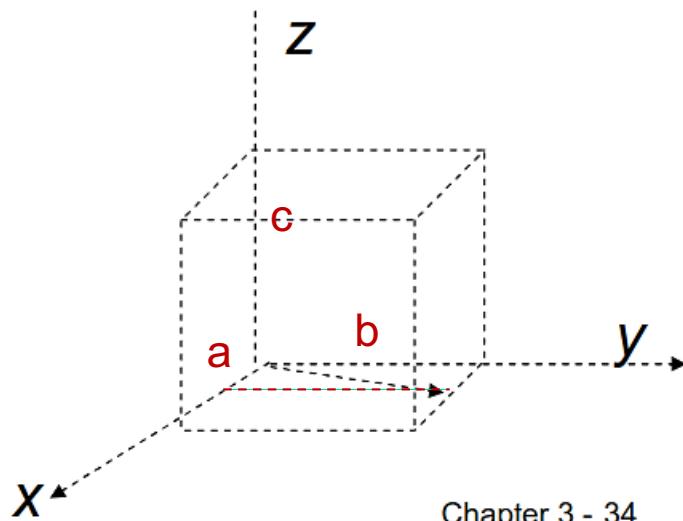
4. Reduce to smallest integer values
 5. Enclose indices in **square brackets**, no commas $[uvw]$
- $\Rightarrow 1, 0, 1/2 \Rightarrow 2, 0, 1$
- $\Rightarrow [201]$

Crystallographic Directions II:

Example Problem 2



- $-\mathbf{a}, \mathbf{b}, \mathbf{c}$
- $[-1, 1, 1]$
- $[\bar{1}11]$



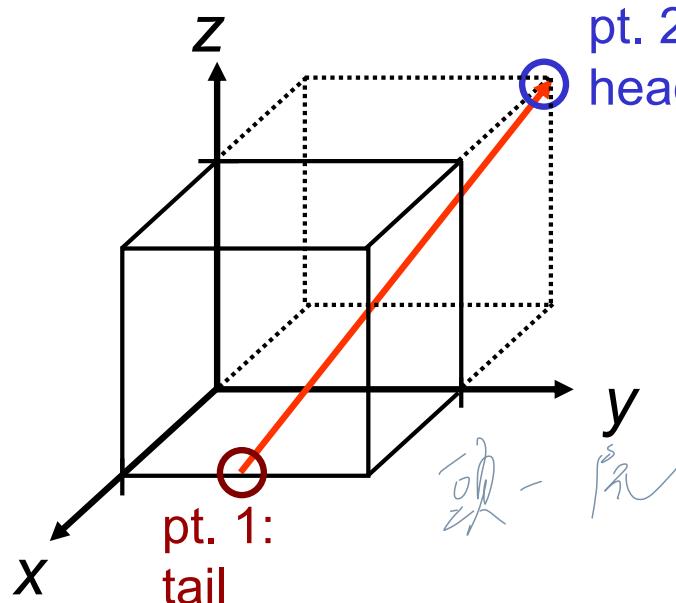
$\frac{1}{2}, 1, 0$

- $a/2, b, 0$
- $[1/2, 1, 0]$
- $[120]$

$1, 2, 0$

Crystallographic Directions III:

Example Problem 3



1. Point coordinates of tail and head

$$\begin{array}{lll} \text{tail pt. 1 } & x_1 = a, & y_1 = b/2, z_1 = 0 \\ \text{head pt. 2 } & x_2 = -a, & y_2 = b, z_2 = c \end{array}$$

2 & 3. Subtract and normalize

$$\frac{-a-a}{a} = -2; \quad \frac{b-b/2}{b} = 1/2; \quad \frac{c-0}{c} = 1$$

$\Rightarrow -2, 1/2, 1$

4 & 5. Multiply by 2 to eliminate the fraction, then place in square brackets (no commas)

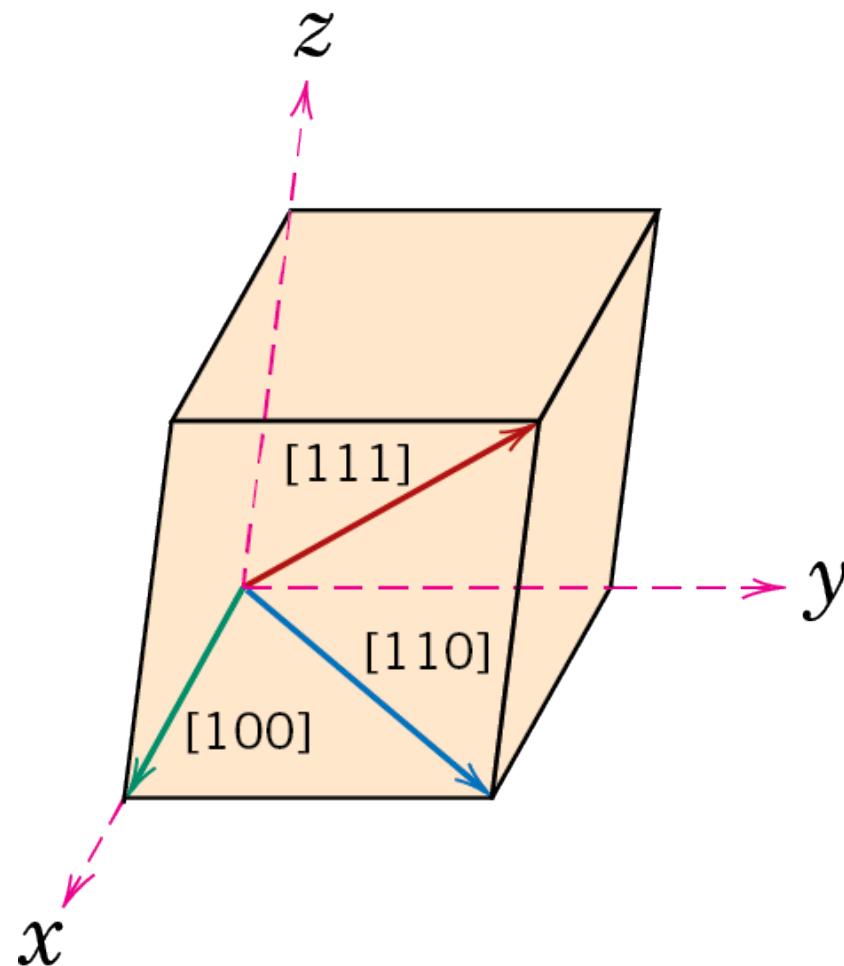
$$-4, 1, 2 \Rightarrow [\bar{4}12]$$

where the overbar represents a negative index

Family of directions – all directions that are crystallographically equivalent (have the same atomic spacing) – indicated by indices in **angle brackets**

$$\text{Ex: } \langle 100 \rangle = [100], [\bar{1}00], [010], [0\bar{1}0], [001], [00\bar{1}]$$

Common Crystallographic Directions



Adapted from Fig. 3.21,
Callister & Rethwisch 5e.

$[\bar{1}\bar{1}\bar{1}]$ is directly opposite to $[1\bar{1}1]$

Crystal System

Unit Cells

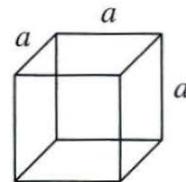
TABLE 2.2

The Seven Main Crystal Systems and their Corresponding Lattice Parameters and Angles

System	Axial lengths and angles ^a	Unit cell geometry
--------	---------------------------------------	--------------------

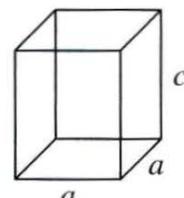
Cubic
立方晶系

$$a = b = c, \alpha = \beta = \gamma = 90^\circ$$



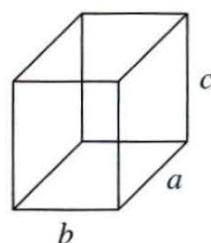
Tetragonal
四方晶系

$$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$$



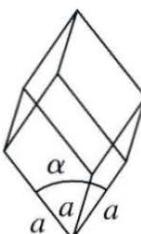
Orthorhombic
正交晶系

$$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$$

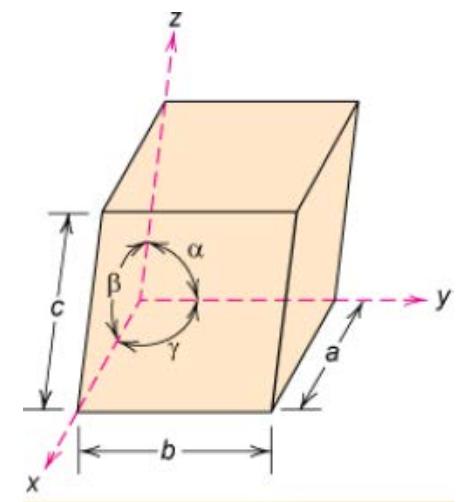


Rhombohedral
菱形晶系

$$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$$



- Lattice constant: a , b , c are unit of cell edge lengths.
- α , β , ρ , are angles between adjacent unit cells axes

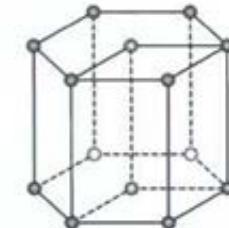


Crystal Structure

Unit Cells

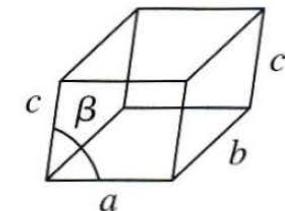
Hexagonal
六方晶系

$$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$$



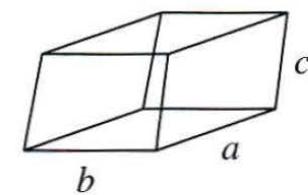
Monoclinic
單斜晶系

$$a \neq b \neq c, \alpha = \gamma = 90^\circ \neq \beta$$



Triclinic
三斜晶系

$$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$$



^aThe lattice parameters, a , b , and c are unit cell edge lengths. The lattice parameters α , β , and γ are angles between adjacent unit cell axes where α is the angle viewed *along* the a axis (i.e., the angle *between* the b and c axes). The inequality sign (\neq) means that equality is not required. Accidental equality occasionally occurs in some structures.

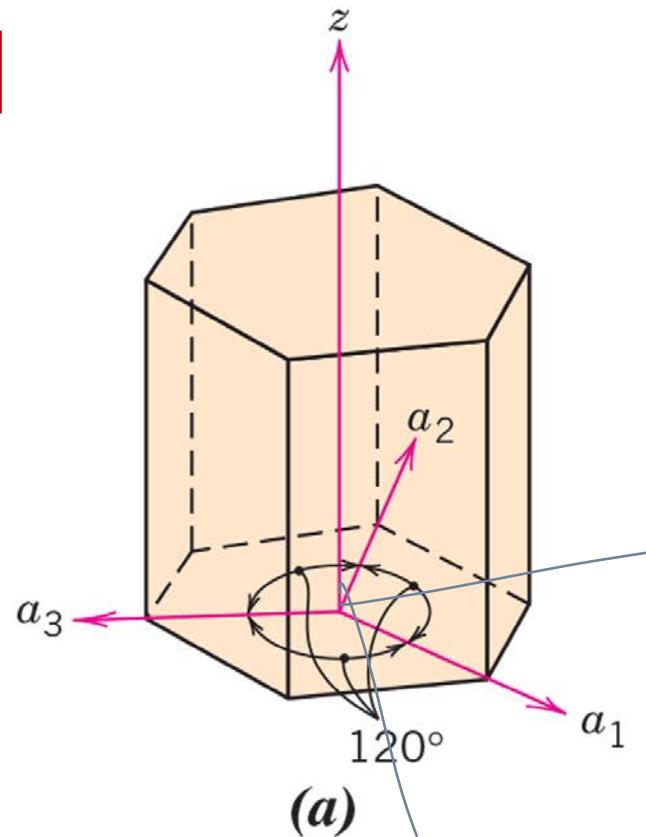
(Reprinted with permission from [1].)

Coordinate axis systems for a hexagonal unit cell

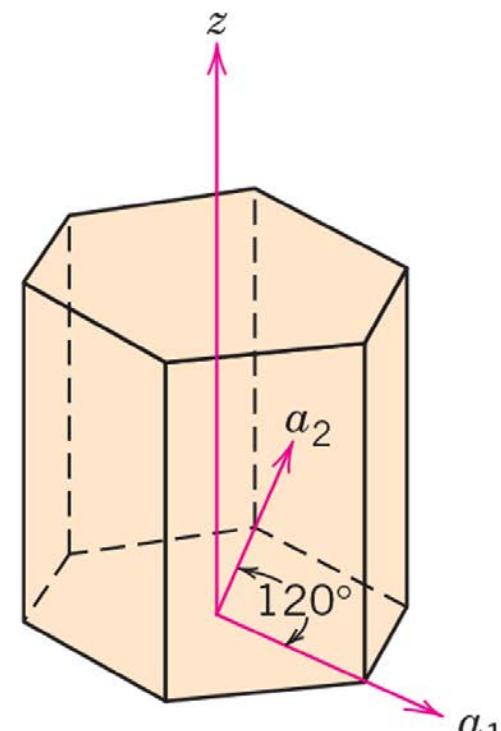
(a) four-axis Miller-Bravais

[$uvtw$]

x y z



(b) three-axis



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

$$t = -(u + v) \quad w = W(z)$$

Crystallographic Direction of HCP

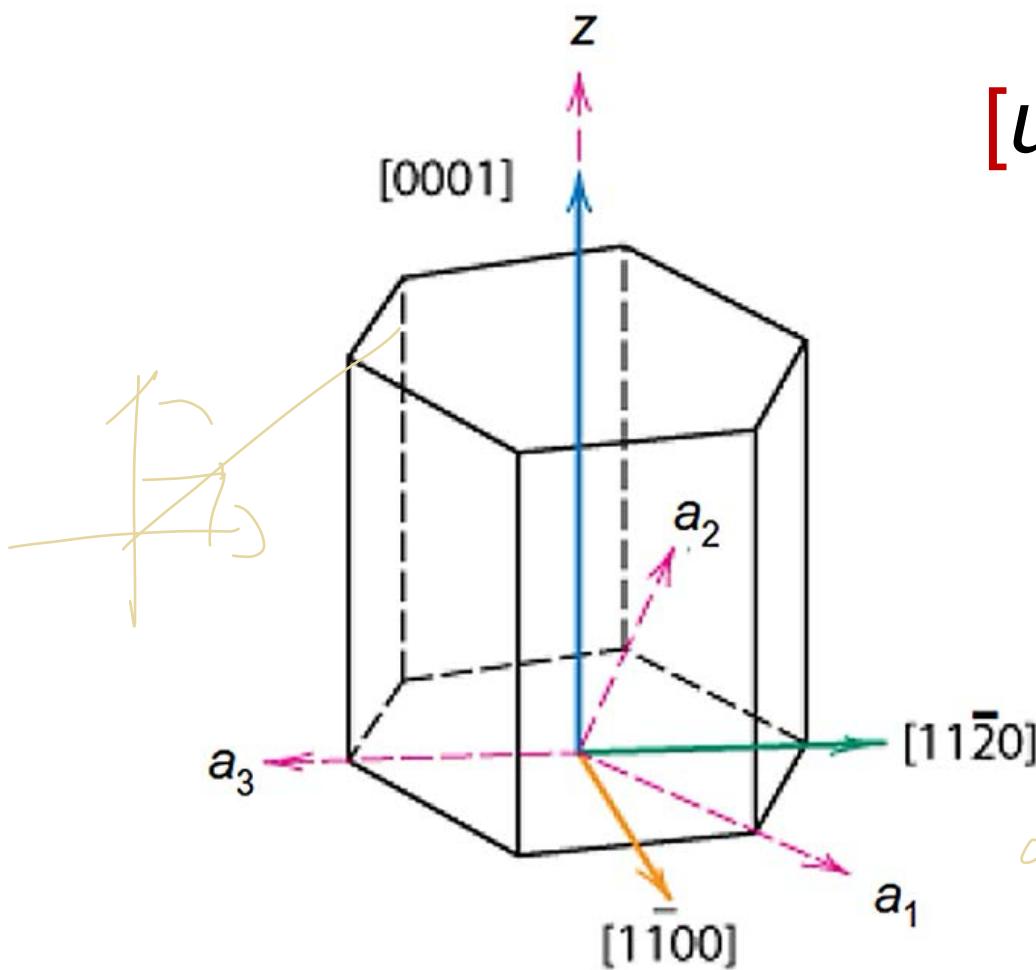
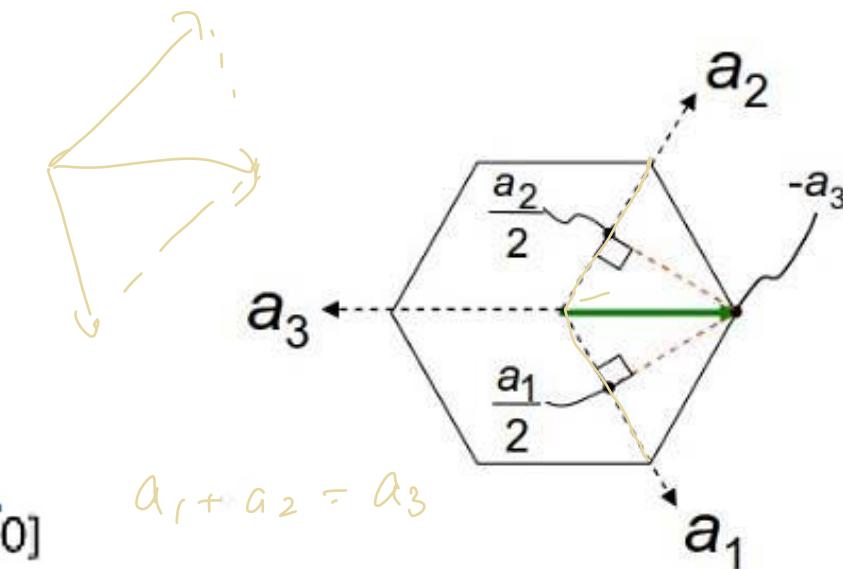


Fig. 3.8(a), Callister 7e.

$[uvw]$



$$\frac{1}{2}, \frac{1}{2}, -1, 0 \Rightarrow [1\bar{1}20]$$

Crystallographic Planes

晶面指數

Algorithm for determining the **Miller Indices** of a plane

1. If plane passes through selected origin, establish a new origin in another unit cell
2. Read off values of intercepts of plane (designated A, B, C) with x, y , and z axes in terms of a, b, c
3. Take reciprocals of intercepts
4. Normalize reciprocals of intercepts by multiplying by lattice parameters a, b , and c
5. Reduce to smallest integer values
6. Enclose resulting Miller Indices in **parentheses**, no commas i.e., (hkl)

Common Crystallographic Planes

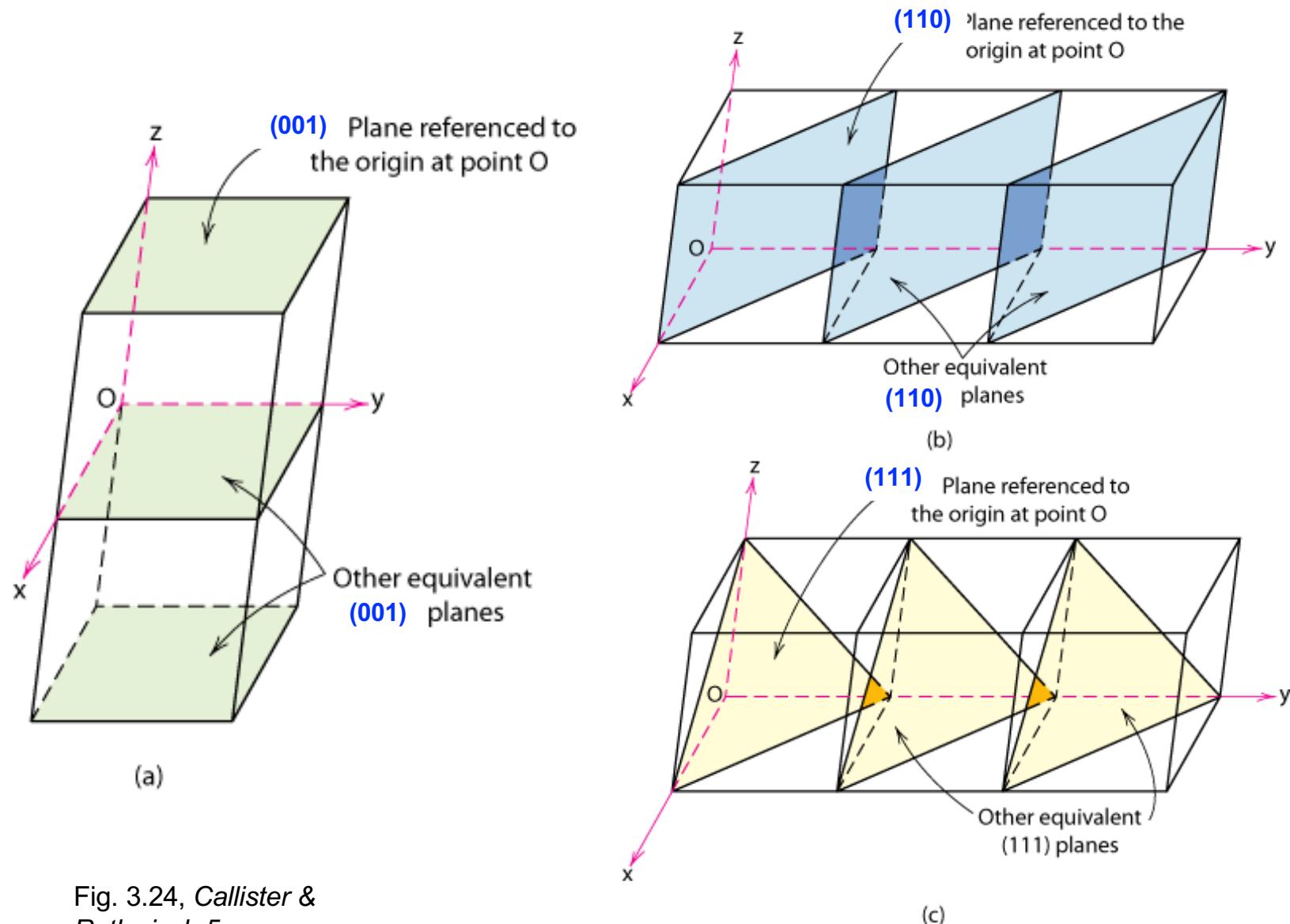
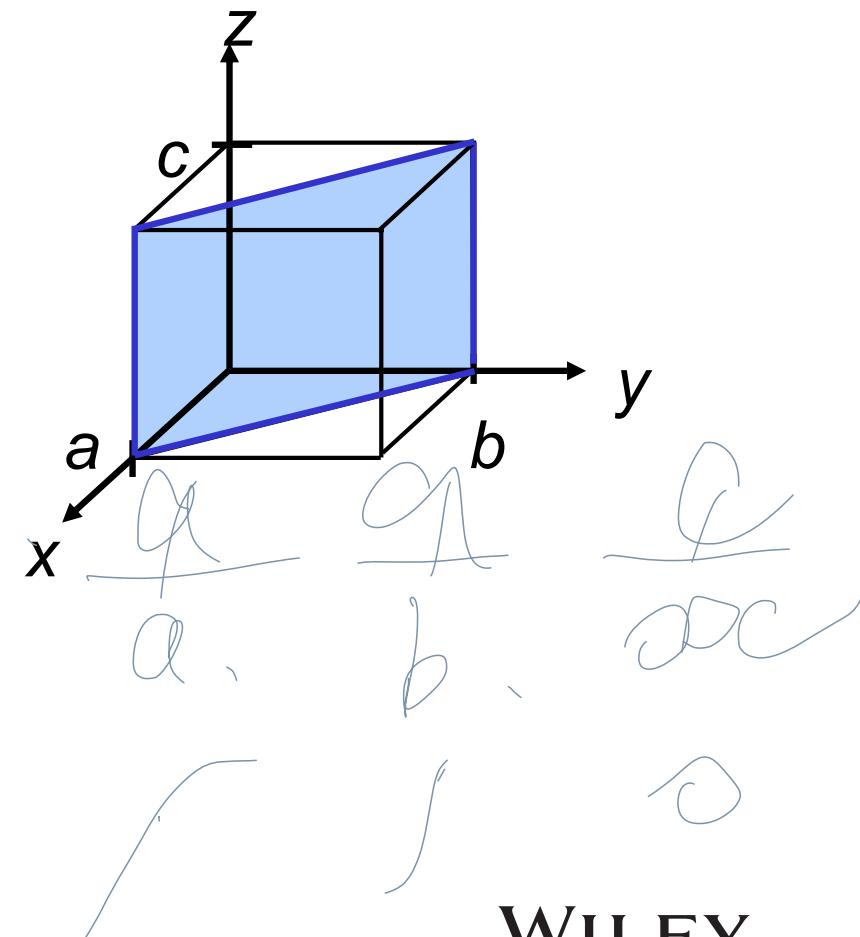


Fig. 3.24, Callister & Rethwisch 5e.

Crystallographic Planes

Example Problem I

	x	y	z
1. Relocate origin – not needed			
2. Intercepts	a	b	∞c
3. Reciprocals	$1/a$	$1/b$	$1/\infty c$
4. Normalize	a/a	b/b	$c/\infty c$
	1	1	0
5. Reduction	1	1	0
6. Miller Indices	(110)		

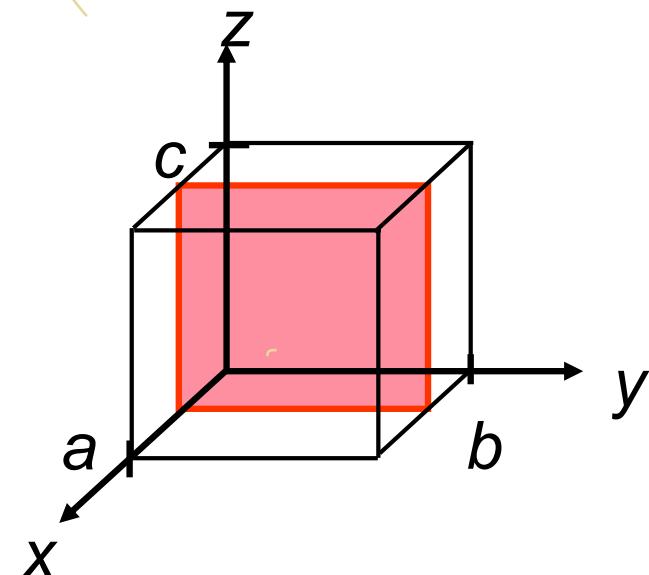


Crystallographic Planes

Example Problem II

	x	y	z
1. Relocate origin – not needed			
2. Intercepts	$a/2$	∞b	∞c
3. Reciprocals	$2/a$	$1/\infty b$	$1/\infty c$
4. Normalize	$2a/a$	$b/\infty b$	$c/\infty c$
	2	0	0
5. Reduction	2	0	0
6. Miller Indices	(200)		

$(\frac{1}{2}a, \infty b, \infty c)$



$\frac{1}{2}a$

∞b ∞c

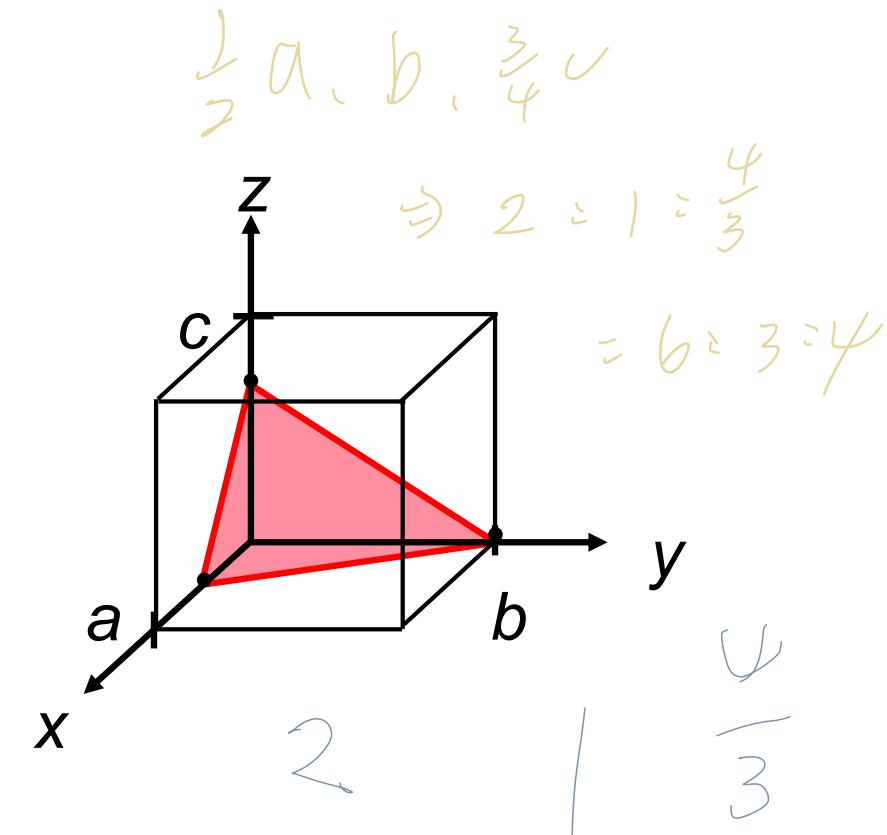
2

0 1

Crystallographic Planes

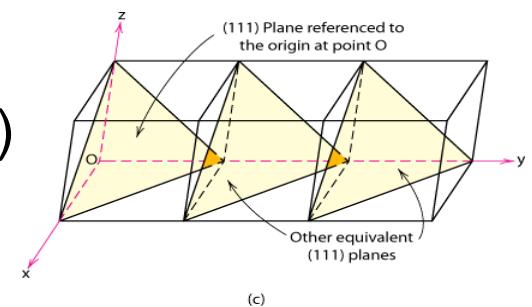
Example Problem III

- | | x | y | z |
|---------------------------------|--------|-------|---------|
| 1. Relocate origin – not needed | | | |
| 2. Intercepts | $a/2$ | b | $3c/4$ |
| 3. Reciprocals | $2/a$ | $1/b$ | $4/3c$ |
| 4. Normalize | $2a/a$ | b/b | $4c/3c$ |
| | 2 | 1 | $4/3$ |
| 5. Reduction (x3) | 6 | 3 | 4 |
| 6. Miller Indices | (634) | | |



Family of planes – all planes that are crystallographically equivalent (have the same atomic packing) – indicated by indices in **braces**

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

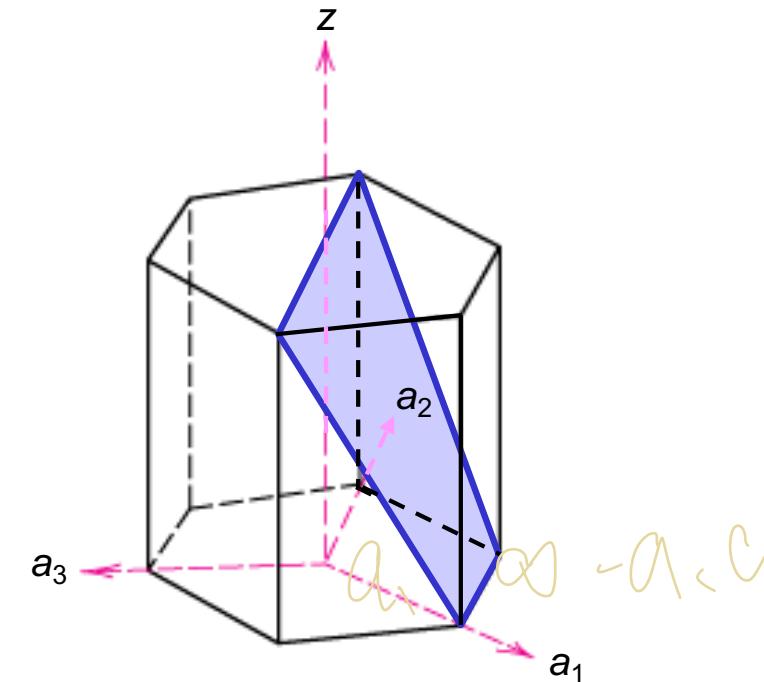


Crystallographic Planes (HCP)

- For **hexagonal unit cells** a similar procedure is used
 - Determine the intercepts with the a_1 , a_2 , and z axes, then determine the **Miller-Bravais Indices h , k , i , and l**

example

	a_1	a_2	a_3	c
1. Relocate origin – not needed				
2. Intercepts	a	∞	$-a$	c
3. Reciprocals	$1/a$	$1/\infty$	$-1/a$	$1/c$
4. Normalize	a/a	a/∞	$-a/a$	c/c
5. Reduction	1	0	-1	1
6. Miller-Bravais Indices	$(10\bar{1}1)$			



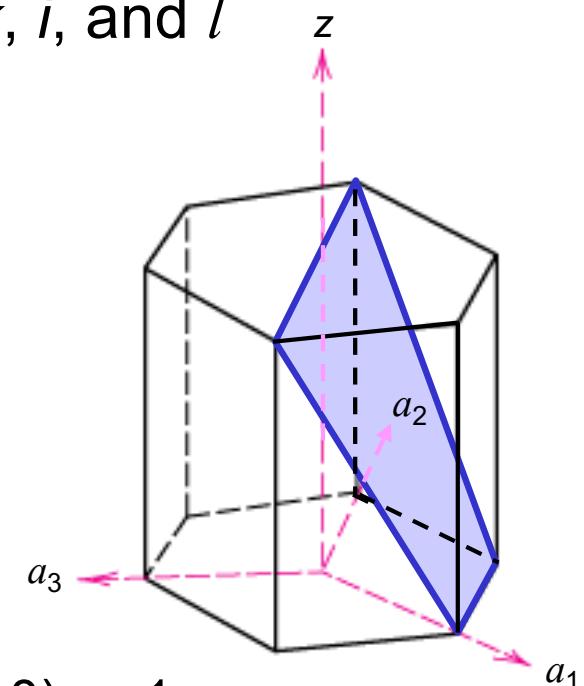
Crystallographic Planes (HCP)

- For hexagonal unit cells a similar procedure is used
 - Determine the intercepts with the a_1 , a_2 , and z axes, then determine the Miller-Bravais Indices h , k , i , and l

example

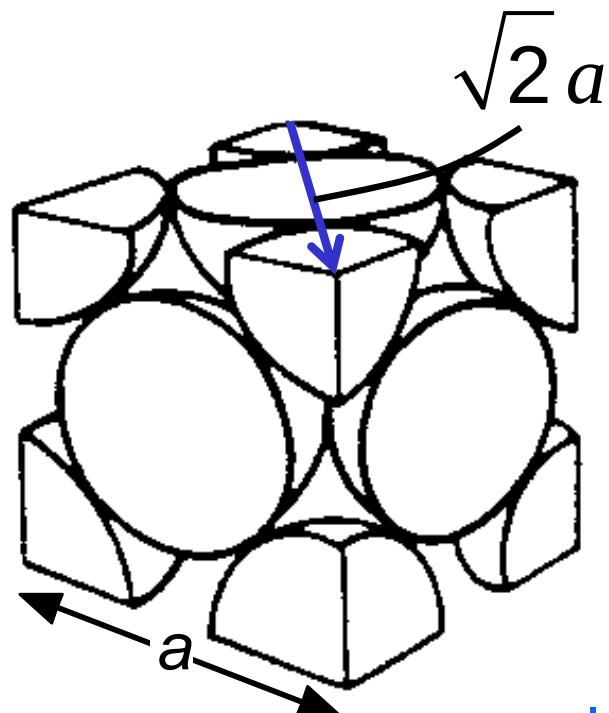
$a_1 \quad a_2 \quad c$

1. Relocate origin – not needed
2. Intercepts $a \quad \infty a \quad c$
3. Reciprocals $1/a \quad 1/\infty a \quad 1/c$
4. Normalize $a/a \quad a/\infty a \quad c/c$
 $1 \quad 0 \quad 1$
5. Reduction $h = 1 \quad k = 0 \quad l = 1$
6. Determine index $i = -(h + k) \quad i = -(1 + 0) = -1$
7. Miller-Bravais Indices $(10\bar{1}1)$



Linear Density of Atoms (LD)

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



ex:

linear density of Al in [110] direction

There are 2 half atoms and 1 full atom
= 2 atoms centered on vector

atoms

$$LD = \frac{2}{\sqrt{2}a} = \frac{2}{\sqrt{2}(0.405 \text{ nm})} = 3.5 \text{ nm}^{-1}$$

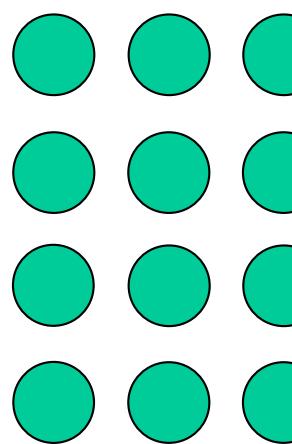
length

$a = 0.405 \text{ nm}$

Planar Density of Atoms (PD)

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

2D repeat unit



ex: planar density of (100) plane of BCC Fe

There are 4 quarter atoms
= 1 atom centered on plane

$$a = \frac{4}{\sqrt{3}} R = \frac{4}{\sqrt{3}} (0.1241 \text{ nm}) = 0.287 \text{ nm}$$

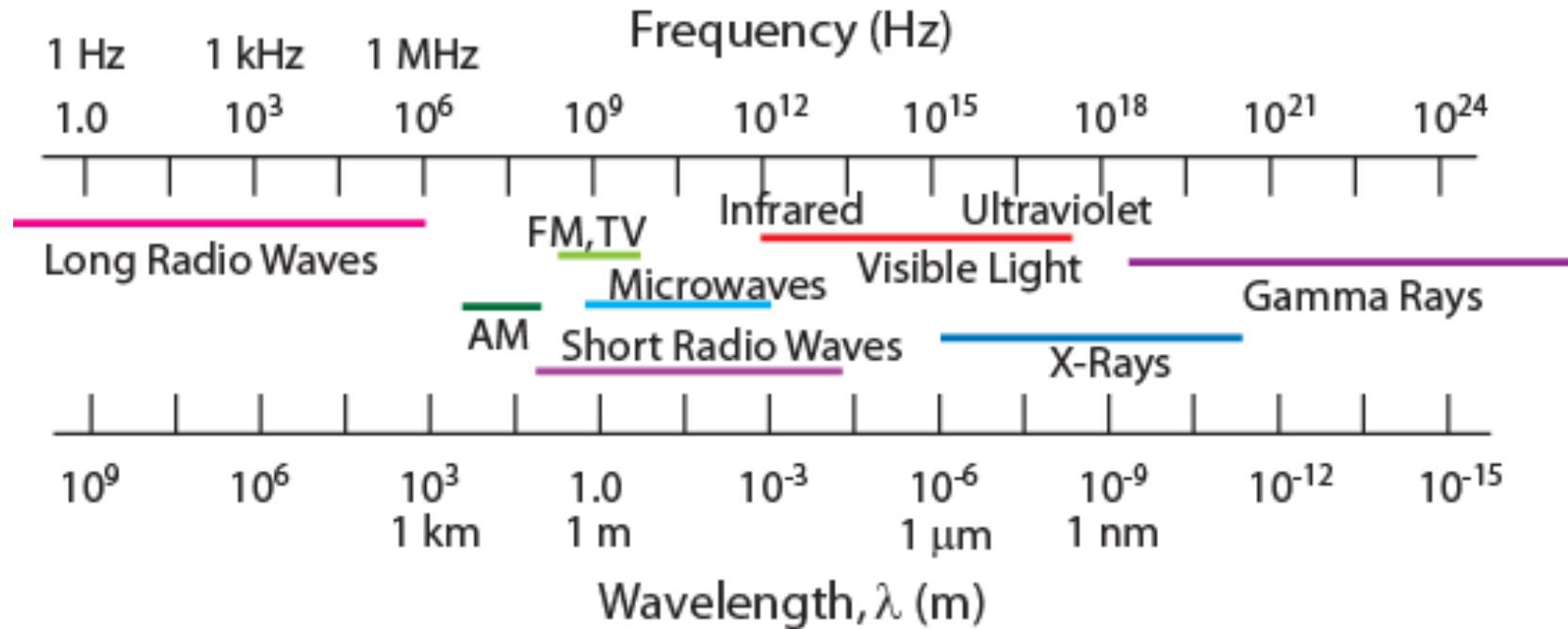
Radius of iron,
 $R = 0.1241 \text{ nm}$

atoms

$$PD = \frac{1}{a^2} = \frac{1 \text{ atom}}{(0.287 \text{ nm})^2} = 12.1 \frac{\text{atoms}}{\text{nm}^2}$$

X-Ray Diffraction

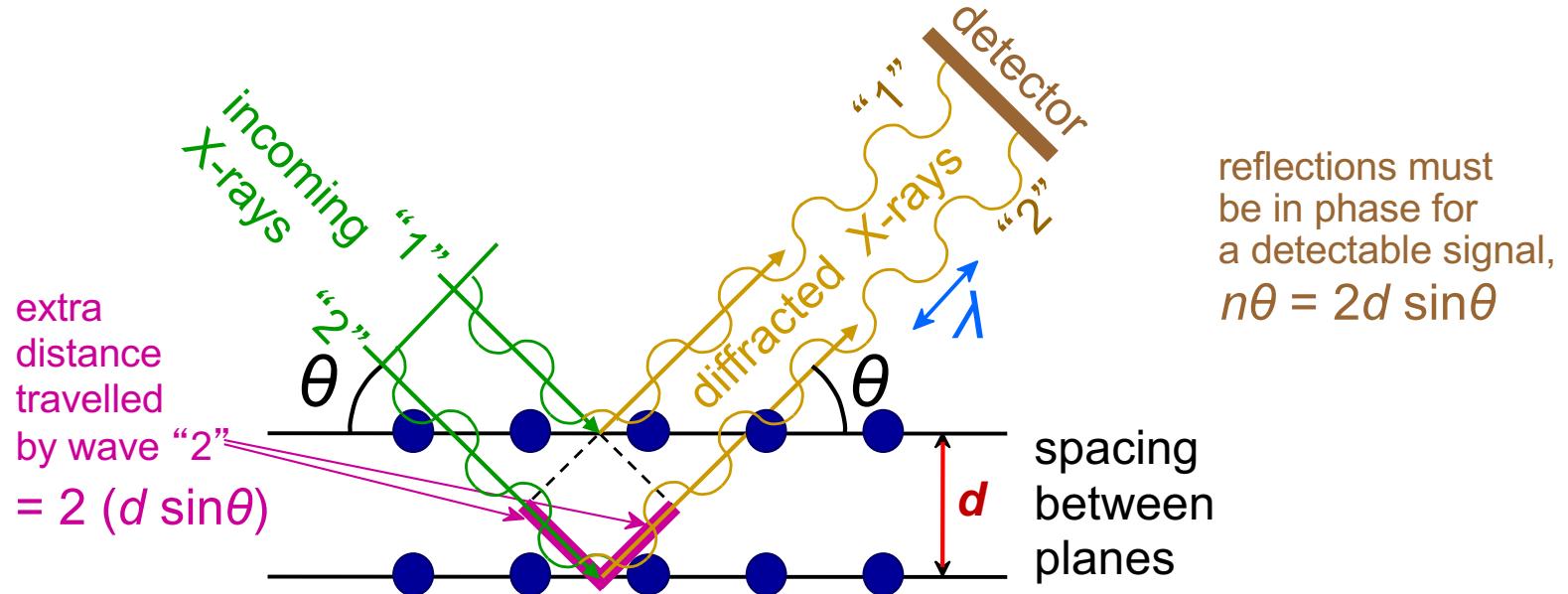
Electromagnetic Spectrum



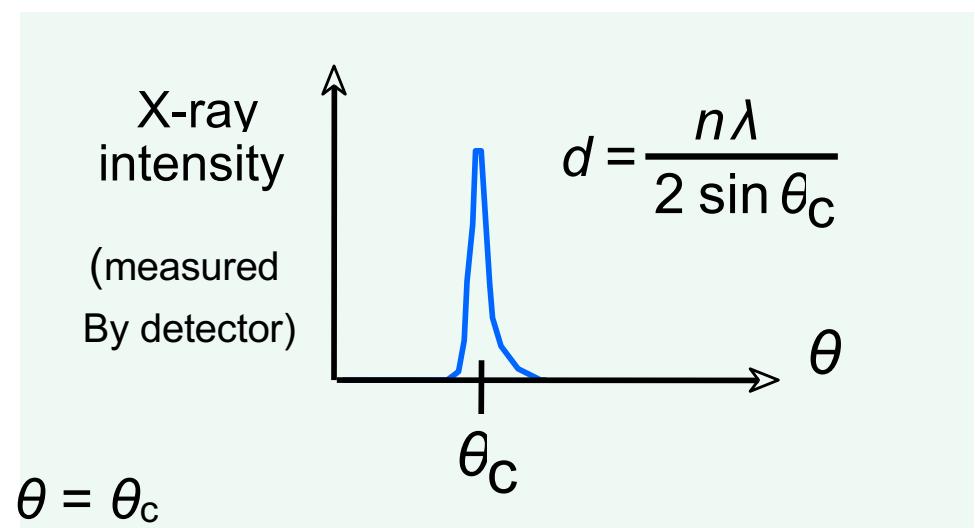
- To diffract light, the diffraction grating spacing must be comparable to the light wavelength.
- X-rays are diffracted by planes of atoms.
- Interplanar spacing is the distance between parallel planes of atoms.

X-Rays to Determine Crystal Structure

- Crystallographic planes diffract incoming X-rays

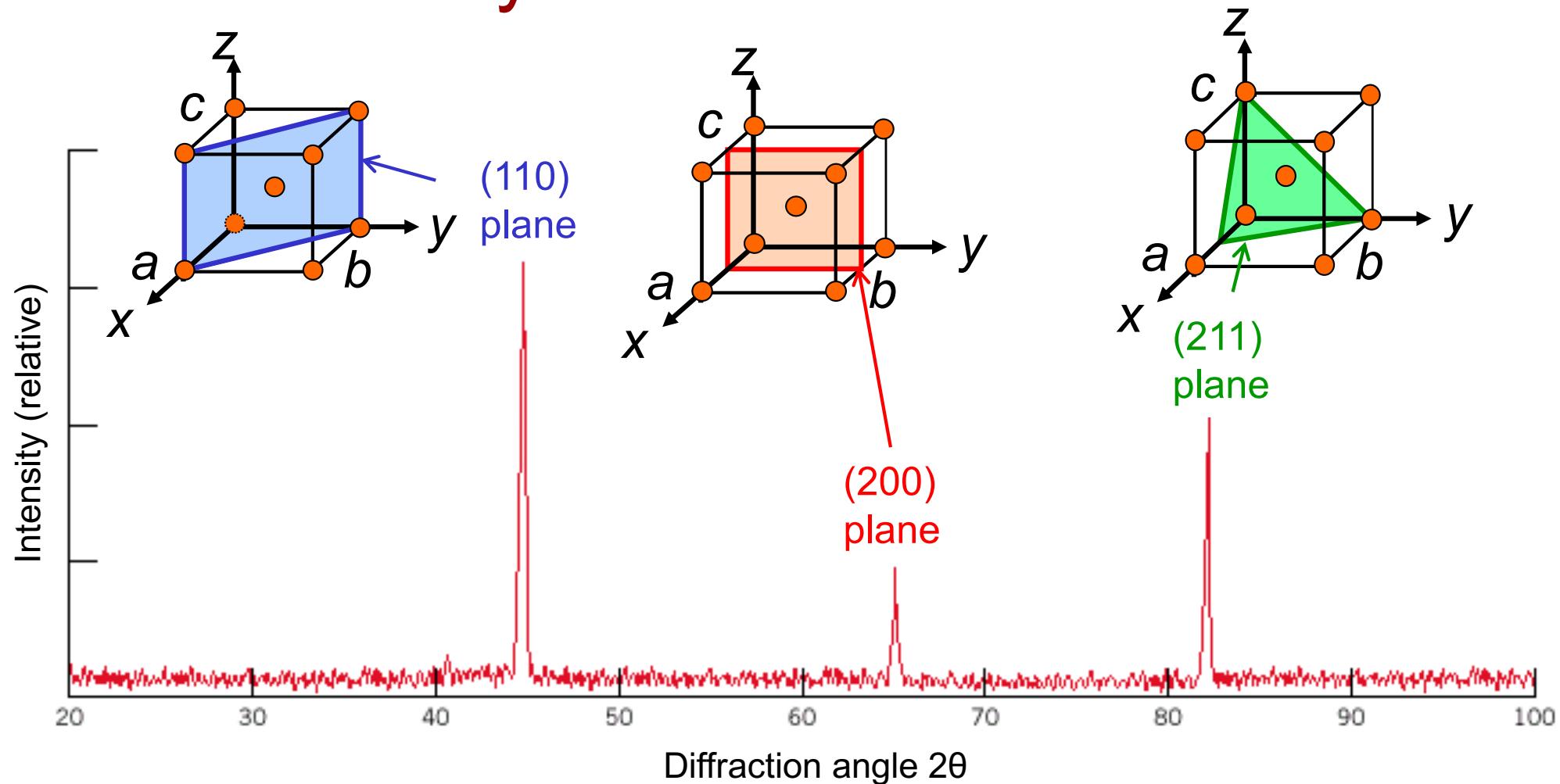


Measurement of diffraction angle, θ_c ,
allows computation of interplanar spacing, d .



Diffraction occurs when $\theta = \theta_c$

X-Ray Diffraction Pattern



Diffraction pattern for polycrystalline α -iron (BCC)

Summary

- Atoms may assemble into **crystalline** (ordered) or **amorphous** (disordered) 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 calculate the **theoretical density** of a metal, given its **crystal structure**, **atomic weight**, and **unit cell lattice parameters**.
- **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

- Crystallographic points, directions and planes may be specified in terms of indexing schemes.
- Atomic and planar densities are related to crystallographic directions and planes, respectively.
- Materials can exist as single crystals or polycrystalline.
- For most single crystals, properties vary with crystallographic orientation (i.e., are anisotropic).
- For polycrystalline materials having randomly oriented grains, properties are independent of crystallographic orientation (i.e., they are isotropic).
 - X-ray diffraction is used for crystal structure and interplanar spacing determinations.