

MATERIALS SCIENCE

SSP 2412

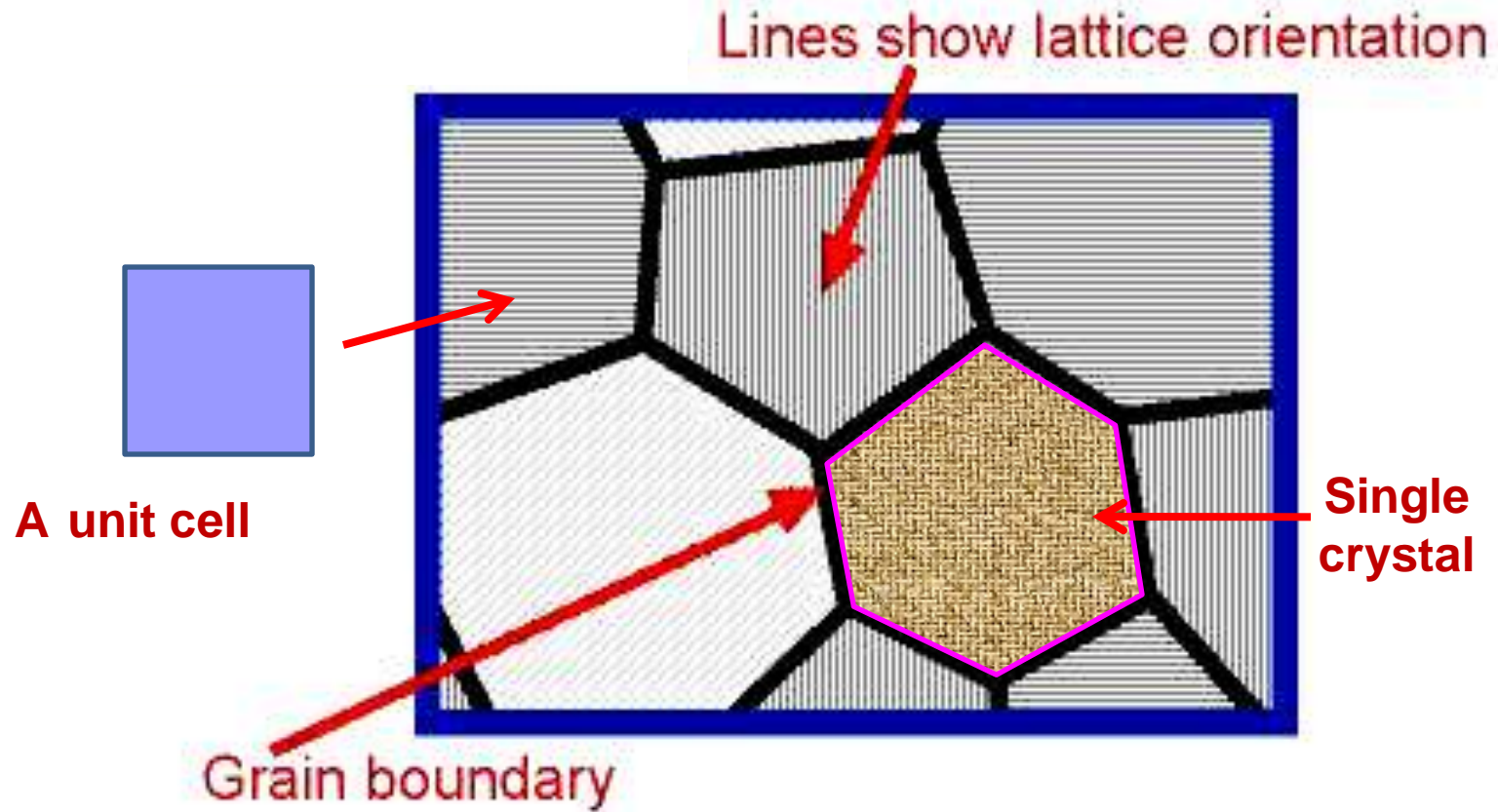
CRYSTAL STRUCTURES AND DEFECTS

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STRUCTURE - Introduction

Solid materials can exist in either **crystal** or **amorphous** or a combination of both

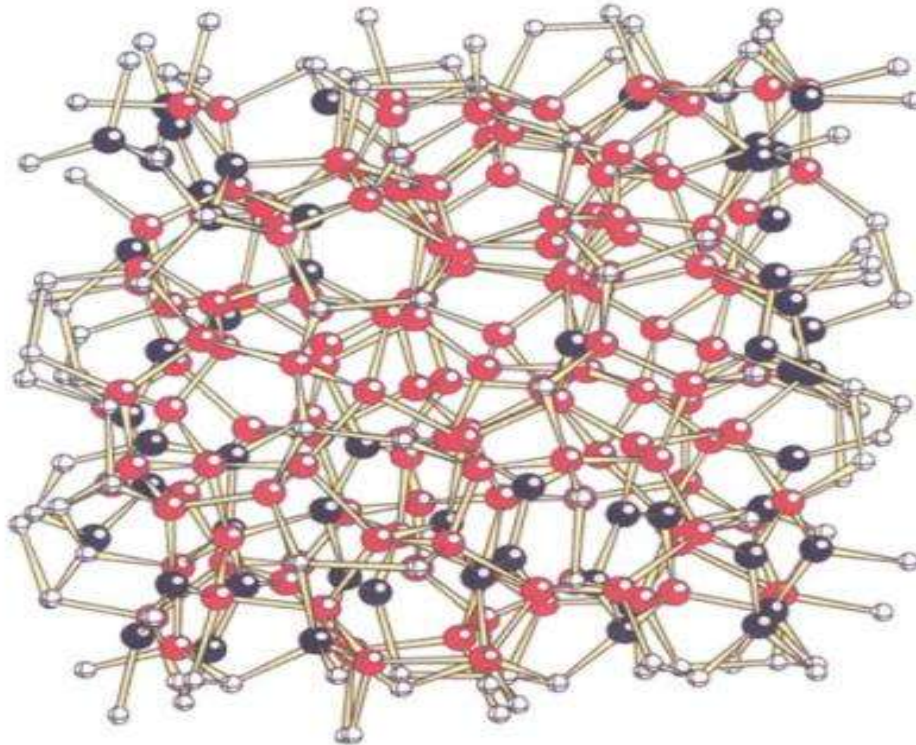
A **crystal** or crystalline solid is a solid material, whose constituent atoms, molecules, or ions are arranged in an orderly repeating pattern extending in all three spatial dimensions. It has long-range atomic order due to periodic arrangement (i.e. crystalline or amorphous). Most metals and semiconductors are crystalline solids



Polycrystalline

An **amorphous** solid is a solid in which there is no long-range order of the positions of the atoms. In other word it has no definite form or distinct shape due to random (irregular) atomic arrangement. Glass and plastic are examples of amorphous solids

Polycrystalline materials are solids that are composed of many crystallites of varying size and orientation. The variation in direction can be random (random texture) or directed, possibly due to growth and processing conditions. Most metals and ceramics exist in this polycrystalline form

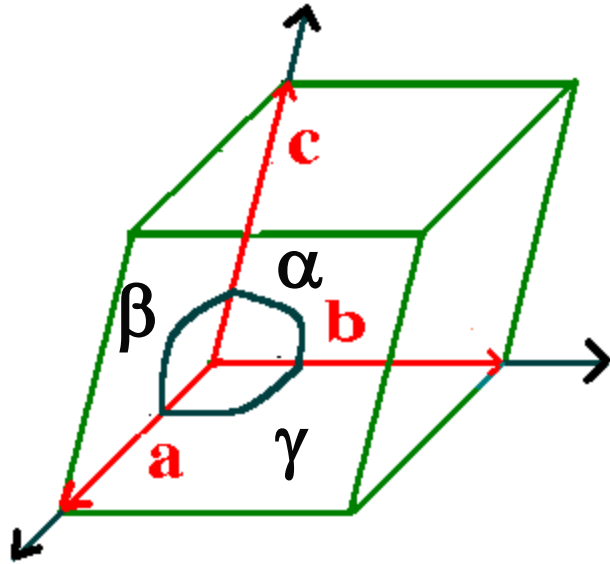


Amorphous (non-crystalline)

CRYSTAL – general features

- ✘ **Crystal consists of 3-D periodic arrangement of atoms/ combination of atoms/molecules**
- ✘ **Each repeating 3-D unit is the UNIT CELL of that crystal**

3-D Unit Cell



$\alpha = \angle$ between \vec{b} and \vec{c}

$\beta = \angle$ between \vec{c} and \vec{a}

$\gamma = \angle$ between \vec{a} and \vec{b}

A **parallelepiped** is generated by the vectors

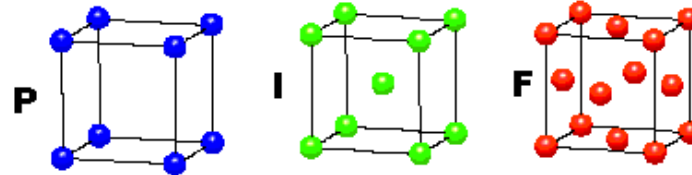
\vec{a} , \vec{b} and \vec{c}

CRYSTAL SYSTEMS

CUBIC

$$a = b = c$$

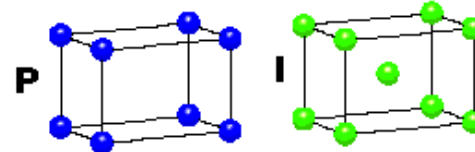
$$\alpha = \beta = \gamma = 90^\circ$$



TETRAGONAL

$$a = b \neq c$$

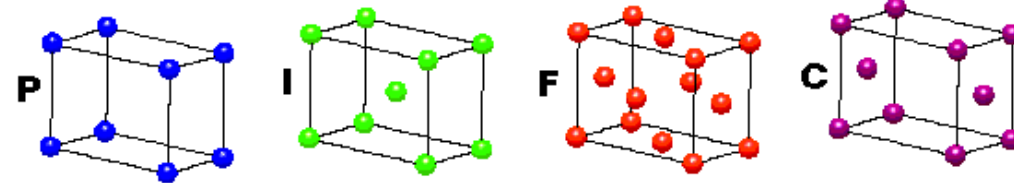
$$\alpha = \beta = \gamma = 90^\circ$$



ORTHORHOMBIC

$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

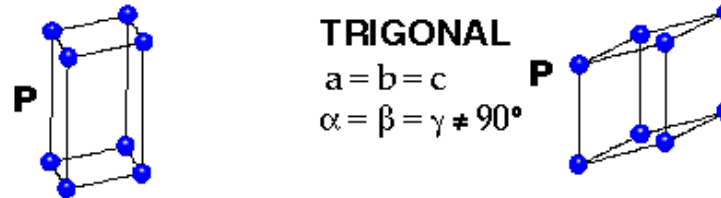


HEXAGONAL

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ$$

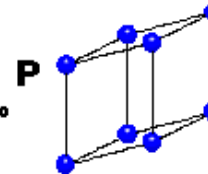
$$\gamma = 120^\circ$$



TRIGONAL

$$a = b = c$$

$$\alpha = \beta = \gamma \neq 90^\circ$$

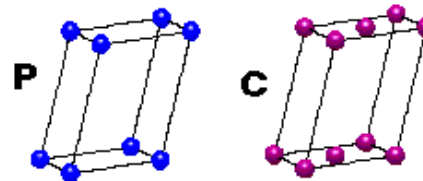


MONOCLINIC

$$a \neq b \neq c$$

$$\alpha = \gamma = 90^\circ$$

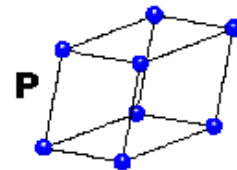
$$\beta \neq 120^\circ$$



TRICLINIC

$$a \neq b \neq c$$

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



4 Types of Unit Cell

P = Primitive

I = Body-Centred

F = Face-Centred

C = Side-Centred

+

7 Crystal Classes

→ 14 Bravais Lattices

A complete analysis based on mathematics and geometry has shown that a single **lattice system** can have at the most **FOUR** types.

In all the seven lattice systems have a total of **14** types.

These are called the **BRAVAIS LATTICES.**

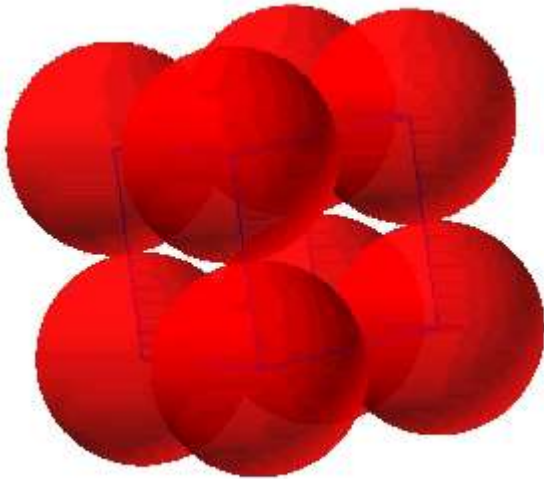
Seven systems divide into 14 Bravais lattices :

1. Cubic	P, I, F
2. Orthorhombic	P, C, I, F
3. Tetragonal	P, I
4. Trigonal (Rhombohedral)	P
5. Monoclinic	P, C
6. Triclinic	P
7. Hexagonal	P

SIMPLE CUBIC STRUCTURE (SC)

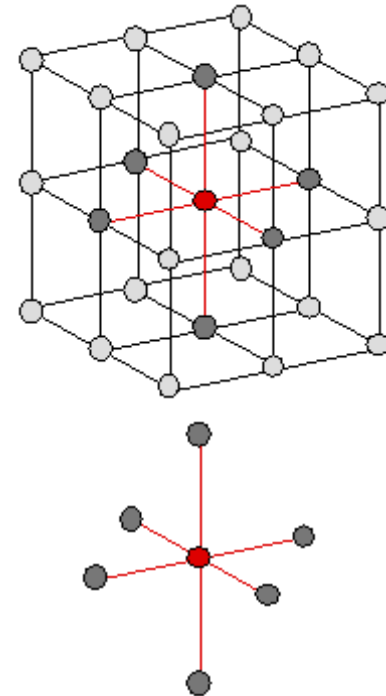
- Rare due to poor packing (only Po has this structure)
- **Close-packed directions** are cube edges.

Closed packed direction is where the atoms touch each other



(Courtesy P.M. Anderson)

- **Coordination # = 6**
(# nearest neighbors)

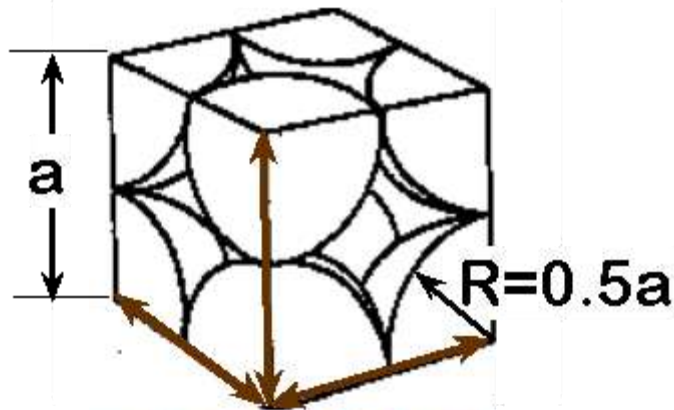


ATOMIC PACKING FACTOR

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

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

contains $8 \times 1/8 =$

1 atom/unit cell

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

Annotations for the APF equation:

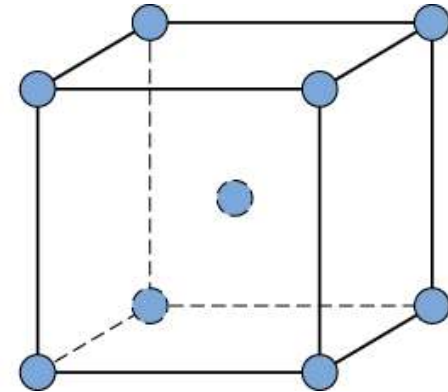
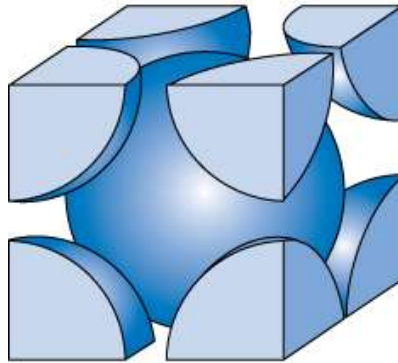
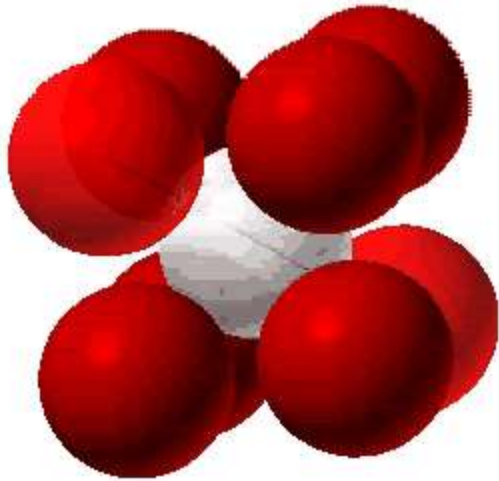
- atoms unit cell: 1
- volume atom: $\frac{4}{3} \pi (0.5a)^3$
- volume unit cell: a^3

BODY CENTERED CUBIC STRUCTURE (BCC)

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

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

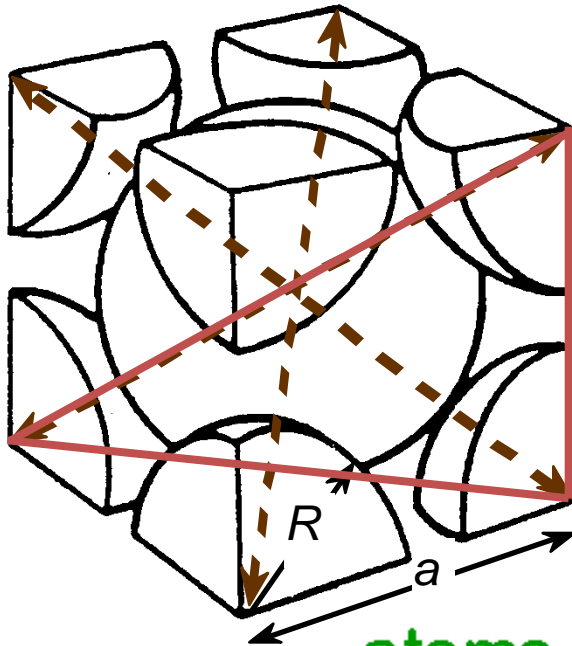
- **Coordination # = 8**



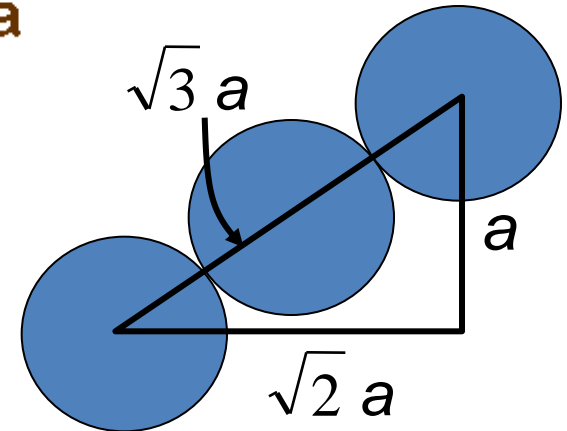
2 atoms/unit cell: 1 center + 8 corners \times 1/8

ATOMIC PACKING FACTOR: BCC

- APF for a body-centered cubic structure = 0.68



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

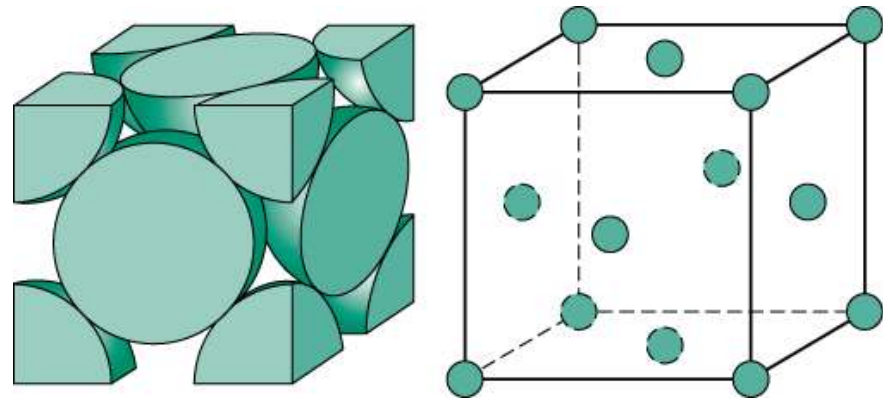
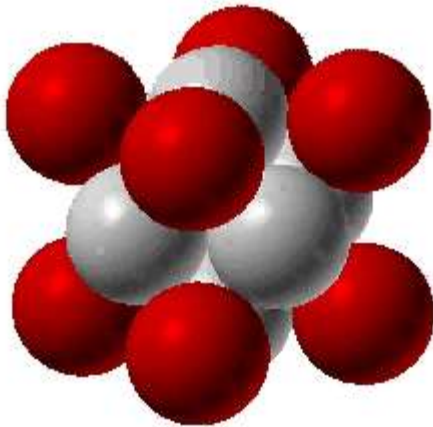


$$\text{APF} = \frac{\text{atoms unit cell} \times \text{volume atom}}{\text{volume unit cell}}$$

$$\text{APF} = \frac{2 \times \frac{4}{3} \pi \left(\frac{\sqrt{3}a}{4}\right)^3}{a^3}$$

FACE CENTERED CUBIC STRUCTURE (FCC)

- Close packed directions are 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



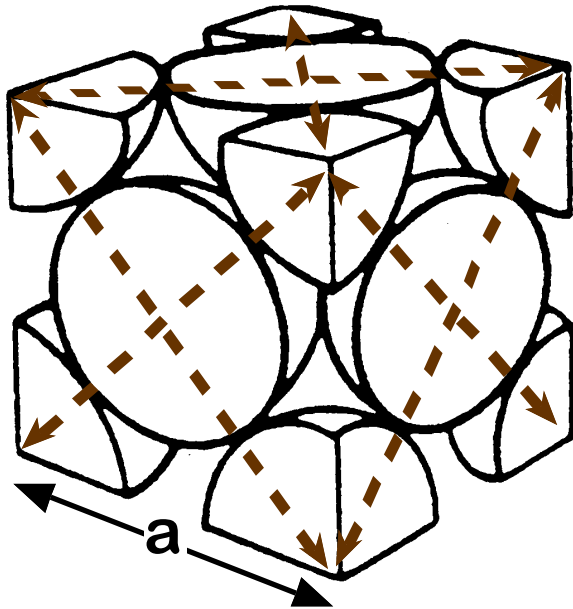
Adapted from Fig. 3.1, *Callister 7e*.

4 atoms/unit cell: $6 \text{ face} \times 1/2 + 8 \text{ corners} \times 1/8$

(Courtesy P.M. Anderson)

ATOMIC PACKING FACTOR: FCC

- APF for a body-centered cubic structure = 0.74



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

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

$$\text{APF} = \frac{\text{atoms/unit cell} \times \text{volume/atom}}{\text{volume/unit cell}}$$

$$\text{APF} = \frac{4 \times \frac{4}{3} \pi \left(\frac{\sqrt{2}a}{4}\right)^3}{a^3}$$

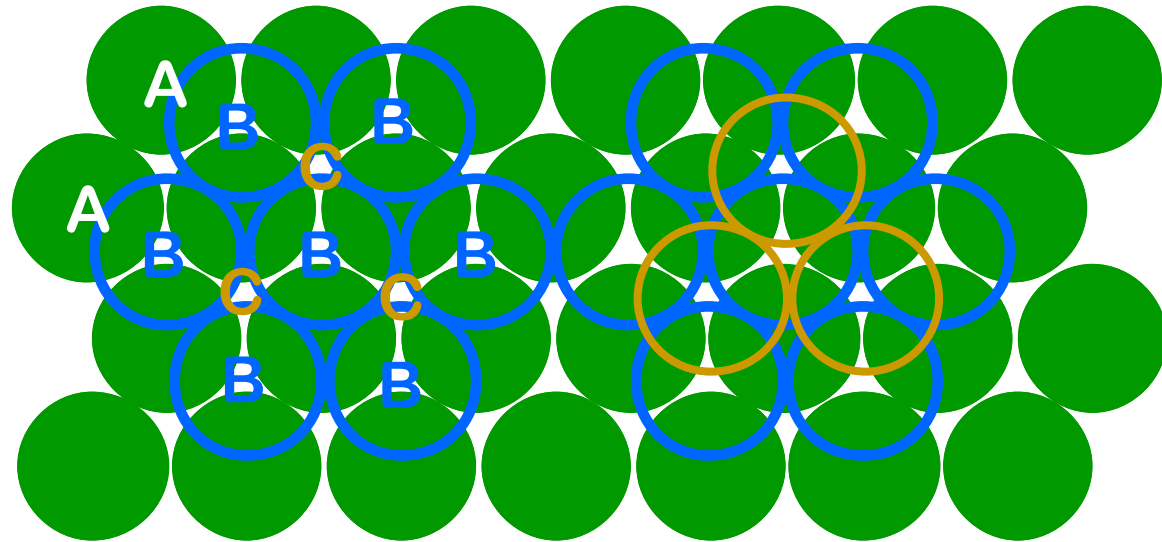
FCC STACKING SEQUENCE

- ABCABC... Stacking Sequence
- 2D Projection

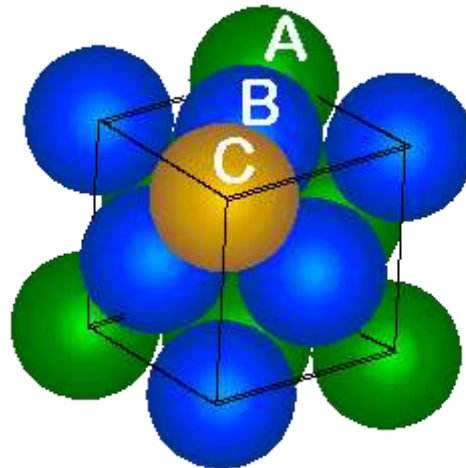
A sites

B sites

C sites

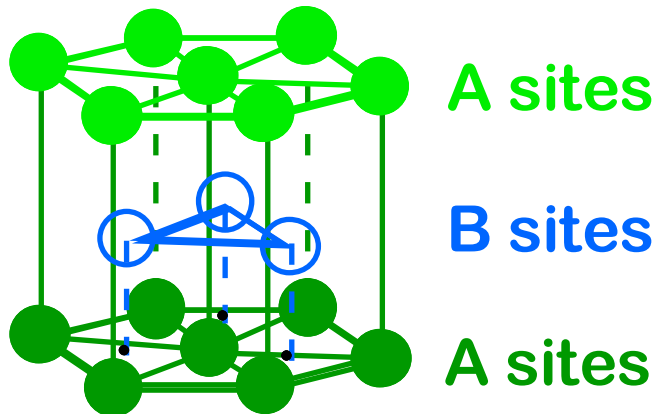


- FCC Unit Cell



HEXAGONAL CLOSE-PACKED STRUCTURE (HCP)

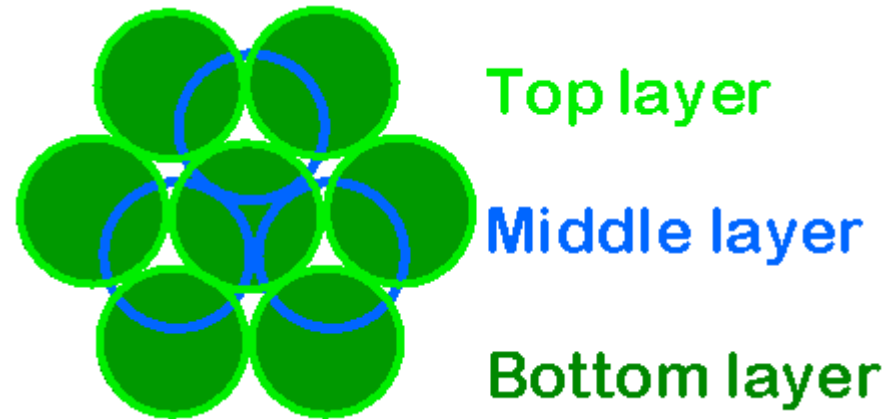
- ABAB... Stacking Sequence
- 3D Projection



Adapted from Fig. 3.3,
Callister 6e.

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

- 2D Projection



6 atoms/unit cell

ex: Cd, Mg, Ti, Zn

THEORETICAL DENSITY, ρ

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

atoms/unit cell \rightarrow n Atomic weight (g/mol) \rightarrow A
 Volume/unit cell \rightarrow V_c Avogadro's number \rightarrow N_A
 ($\text{cm}^3/\text{unit cell}$) (6.023×10^{23} atoms/mol)

Example: Copper

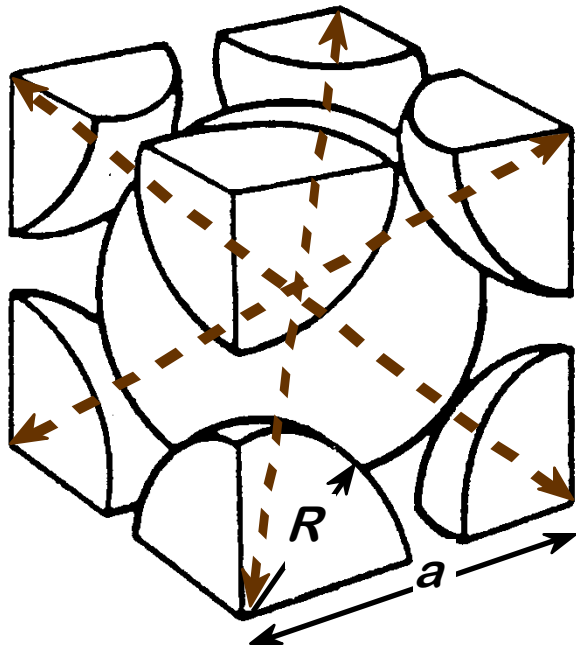
Data from Table inside front cover of Callister (see next slide):

- crystal structure = FCC: **4 atoms/unit cell**
- atomic weight = **63.55 g/mol** (1 amu = 1 g/mol)
- atomic radius $R = 0.128$ nm (1 nm = 10^7 cm)
 $V_c = a^3$; For FCC, $a = 4R\sqrt{2}$; $V_c = 4.75 \times 10^{-23} \text{cm}^3$

Result: theoretical $\rho_{\text{Cu}} = 8.89 \text{ g/cm}^3$

Compare to actual: $\rho_{\text{Cu}} = 8.94 \text{ g/cm}^3$

Theoretical Density, ρ



- Ex: Cr (BCC)

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

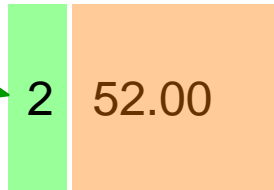
$$R = 0.125 \text{ nm}$$

$$n = 2$$

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

atoms

unit cell

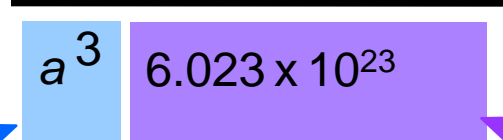


g

mol

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

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

 $\rho =$ 

volume

unit cell

atoms

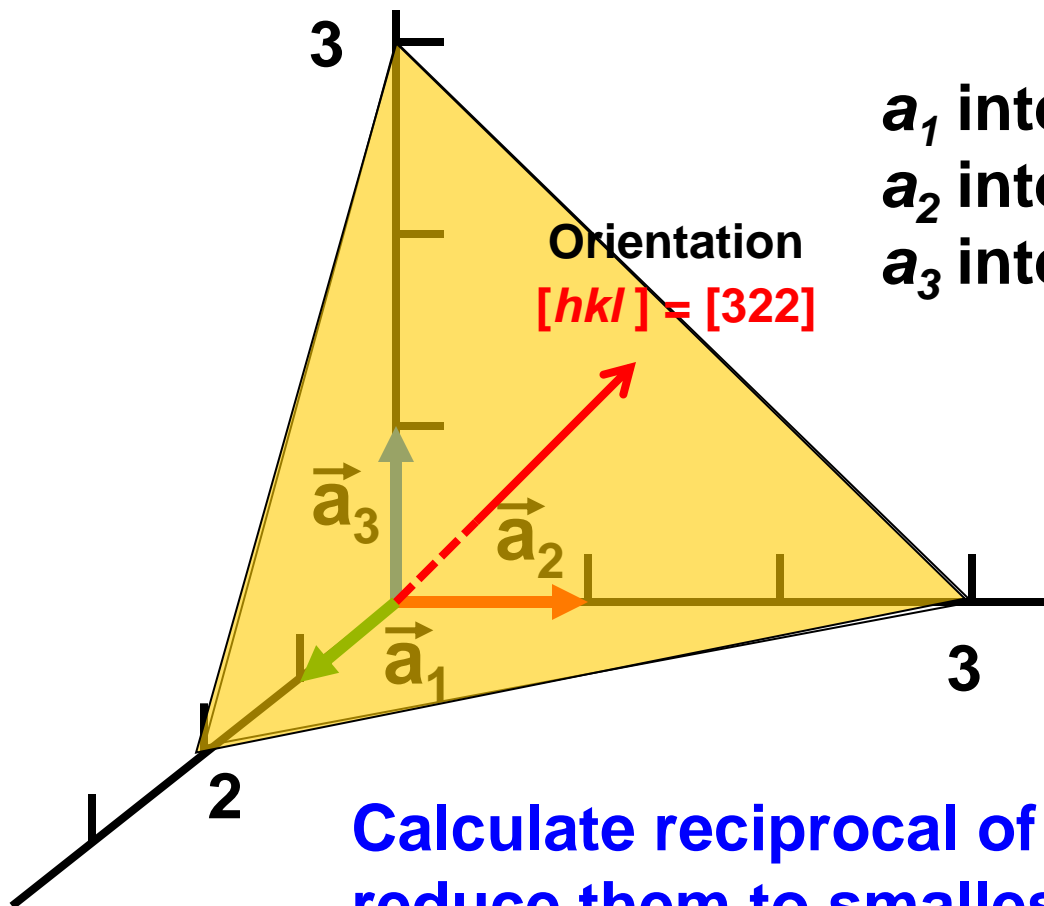
mol

Characteristics of Selected Elements at 20C

Element	Symbol	At. Weight (amu)	Density (g/cm ³)	Crystal Structure	Atomic radius (nm)
Aluminum	Al	26.98	2.71	FCC	0.143
Argon	Ar	39.95	-----	-----	-----
Barium	Ba	137.33	3.5	BCC	0.217
Beryllium	Be	9.012	1.85	HCP	0.114
Boron	B	10.81	2.34	Rhomb	-----
Bromine	Br	79.90	-----	-----	-----
Cadmium	Cd	112.41	8.65	HCP	0.149
Calcium	Ca	40.08	1.55	FCC	0.197
Carbon	C	12.011	2.25	Hex	0.071
Cesium	Cs	132.91	1.87	BCC	0.265
Chlorine	Cl	35.45	-----	-----	-----
Chromium	Cr	52.00	7.19	BCC	0.125
Cobalt	Co	58.93	8.9	HCP	0.125
Copper	Cu	63.55	8.94	FCC	0.128
Flourine	F	19.00	-----	-----	-----
Gallium	Ga	69.72	5.90	Ortho.	0.122
Germanium	Ge	72.59	5.32	Dia. cubic	0.122
Gold	Au	196.97	19.32	FCC	0.144
Helium	He	4.003	-----	-----	-----
Hydrogen	H	1.008	-----	-----	-----

Adapted from Table, "Characteristics of Selected Elements", inside front cover, *Callister 6e.*

Miller index



Reciprocal

a_1 intercept is 2 \rightarrow $1/2$

a_2 intercept is 3 \rightarrow $1/3$

a_3 intercept is 3 \rightarrow $1/3$

Hence Miller indices
are 3,2,2 and are
depicted by

$(hkl) = (322)$

Calculate reciprocal of these intercepts and
reduce them to smallest three integers
having same ratio.

Definition of Miller Index

Miller indices are a notation system in crystallography for planes and directions in crystal (Bravais) lattices

Miller Indices (hkl) are a symbolic vector representation for the orientation of an atomic plane in a crystal lattice and are defined as the reciprocals of the fractional intercepts which the plane makes with the crystallographic axes

Inter-planer Distance

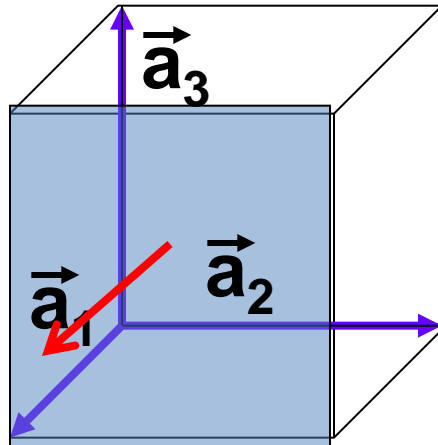
(hkl) represent a family of planes. All parallel crystal planes have the same Miller index. **These planes are equally spaced at distance d_{hkl} .** This distance is defined as:

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

Crystal planes in a cubic unit cell

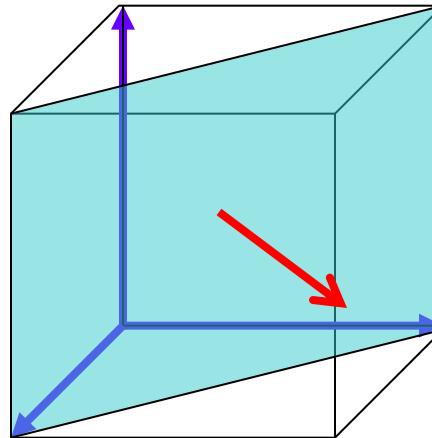


Orientation/Direction
[...]



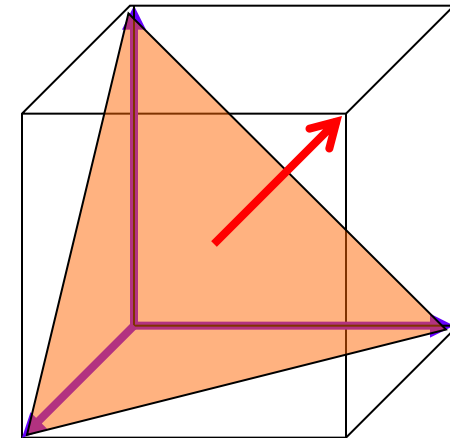
(100)

$$d_{hkl} = a$$



(110)

$$d_{hkl} = a/\sqrt{2}$$



(111)

$$d_{hkl} = a/\sqrt{3}$$

Prepare a Table

θ	$\sin \theta$	$\sin^2 \theta$	$\sin^2 \theta / N$		
			1	2	3
10.83°	0.1879	0.0353	0.0353	0.0177	0.0118
15.39°	0.2654	0.0704	0.0704	0.0352	0.0235
18.99°	0.3254	0.1059	0.1059	0.0529	0.0353

$$\frac{\sin^2 \theta}{N} = \frac{\lambda^2}{4 a^2} = 0.0353$$

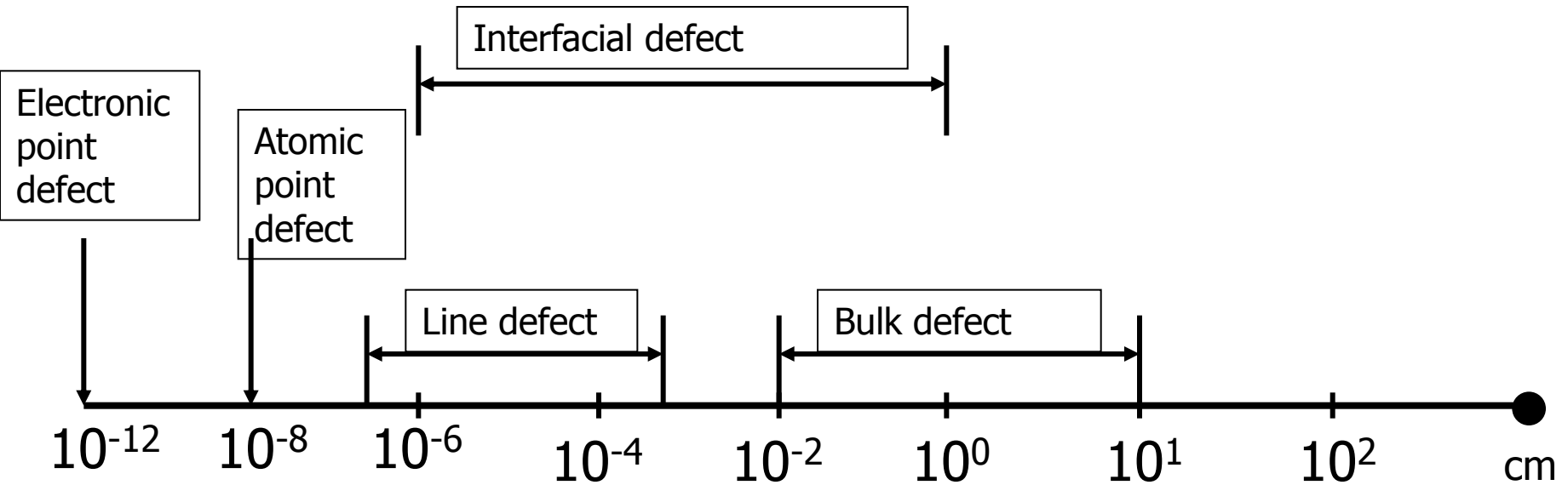
$$\text{For } \lambda = 1.5404 \text{ \AA}, \\ a = 4.10 \text{ \AA}$$

DEFECTS - Introduction

Real Crystalline solids are almost never perfect. These imperfections can be classified according to their dimensionality:

1. Point defects (0-Dimension)
2. Line defects (1-D)
3. Interfacial defects (2-D)
4. Bulk defects (3-D)

Relative Size Ranges of Defects



1. POINT DEFECTS

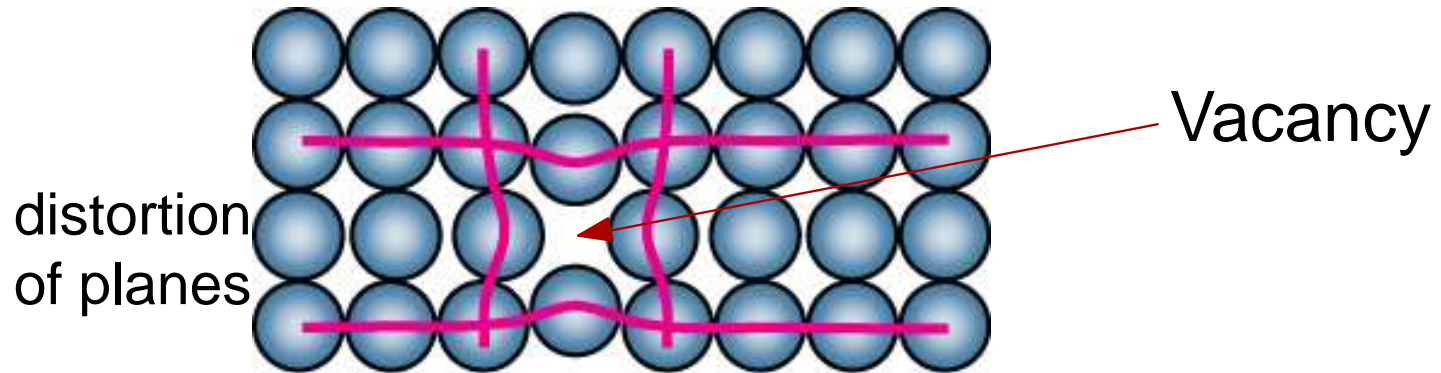
These are defects of atomic dimensions that usually result from:

1. The presence of an impurity atom
 - ❑ Substitutional → larger atoms
 - ❑ Interstitial → smaller atoms
2. The absence of a matrix atom (vacancy)
3. The presence of a matrix atom in a wrong place (self-interstitial)

Point Defects

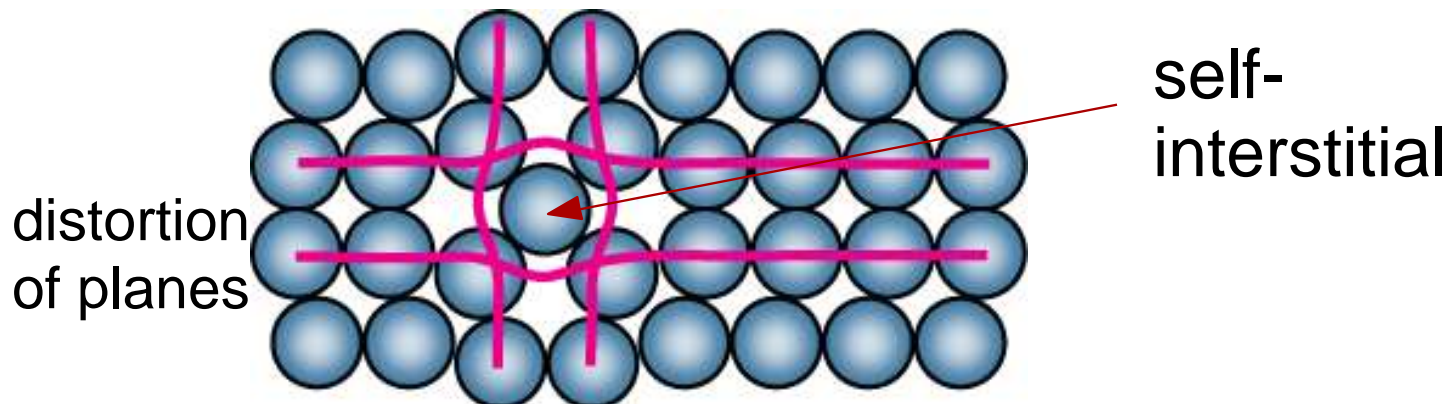
- **Vacancies:**

-vacant atomic sites in a structure.



- **Self-Interstitials:**

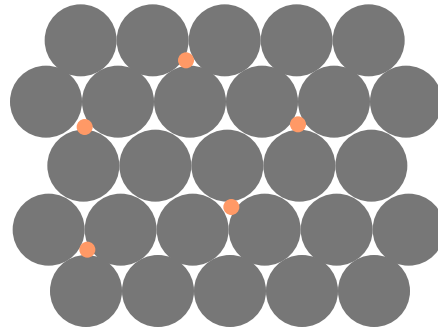
-"extra" atoms positioned between atomic sites.



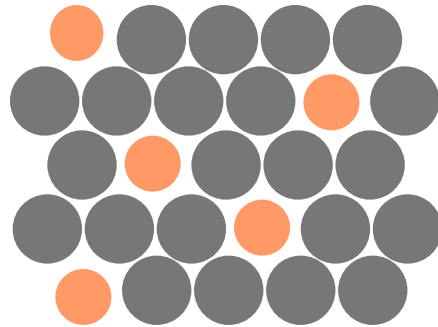
Presence of an impurity atom:

- "extra" atoms positioned between atomic sites.

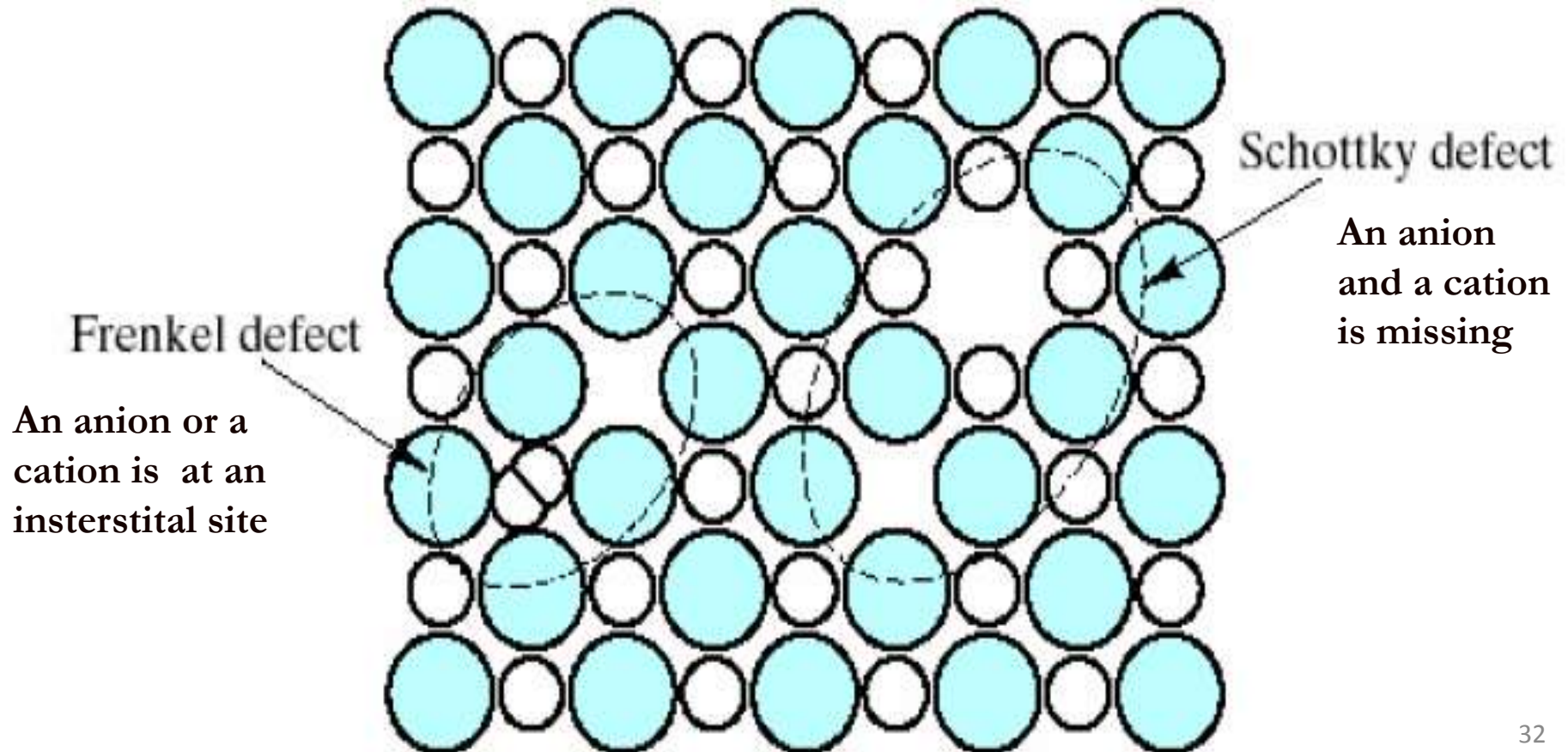
Interstitial



Substitutional



The point defects discussed so far occur in metallic structures. Those in ionic structures differ because of the charge neutrality requirement.



2. Line Defects (Dislocations)

Dislocations:

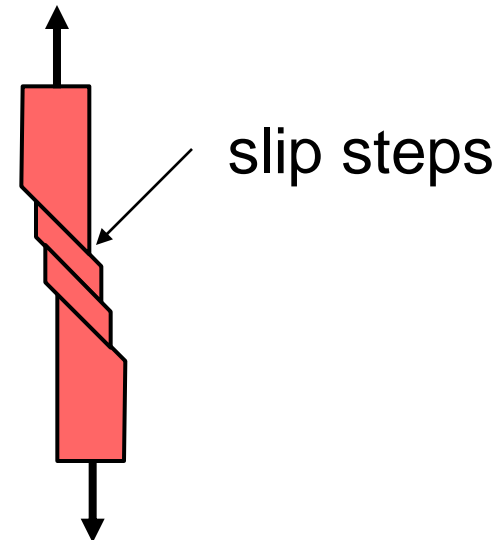
- are line defects,
- slip between crystal planes result when dislocations move,
- produce permanent (plastic) deformation.

Schematic of Zinc (HCP):

- before deformation



- after tensile elongation



Linear Defects (**Dislocations**)

- Are one-dimensional defects around which atoms are misaligned
- **Edge dislocation:**
 - extra half-plane of atoms inserted in a crystal structure
 - $\mathbf{b} \perp$ to dislocation line
- **Screw dislocation:**
 - spiral planar ramp resulting from shear deformation
 - $\mathbf{b} \parallel$ to dislocation line

Burger's vector, \mathbf{b} : measure of lattice distortion

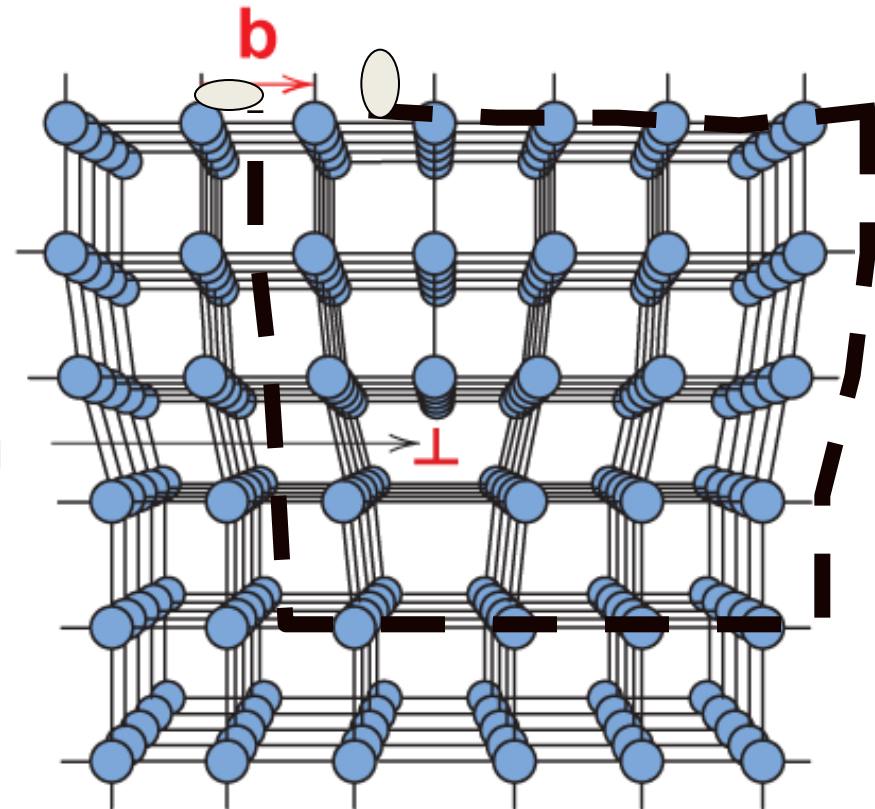
- ❑ First a closed circuit is drawn around the dislocation by jumping from one atom to another.
- ❑ The same number of jumps will be made in a perfect system.
- ❑ The vector needed to complete the circuit is called **BURGER VECTOR**.

Edge Dislocations

Burger's vector is perpendicular to dislocation in edge dislocations.

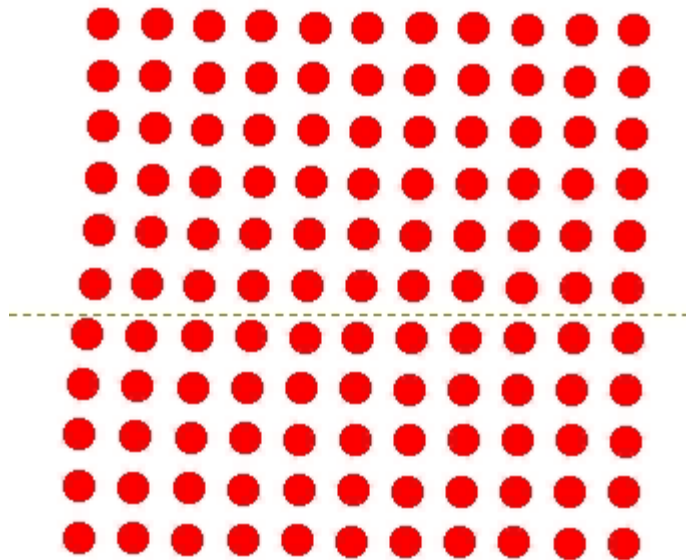
Edge dislocation line

Burgers vector



Motion of Edge Dislocation

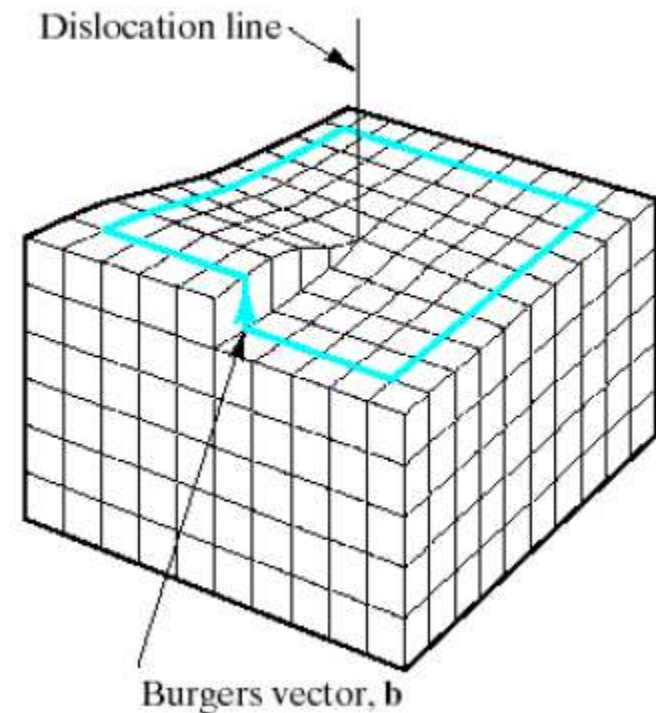
- Dislocation motion requires the successive bumping of a half plane of atoms (from left to right here).
- Bonds across the slipping planes are broken and remade in succession.



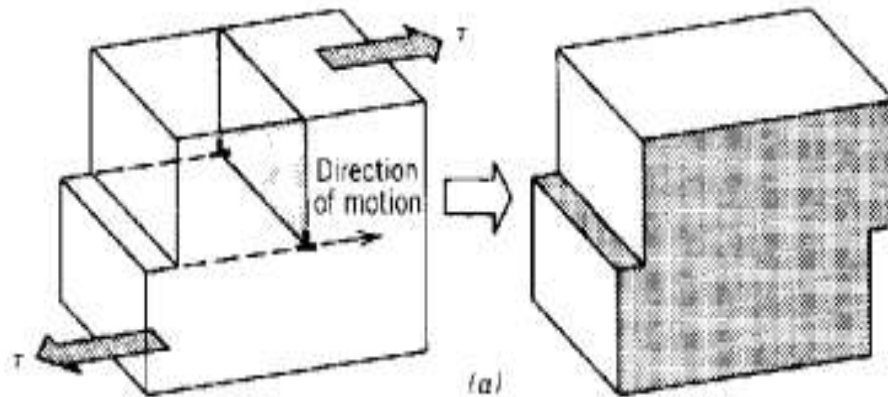
Atomic view of edge dislocation motion from left to right as a crystal is sheared.

Screw Dislocations

Burger's vector is parallel to dislocation in screw dislocations.

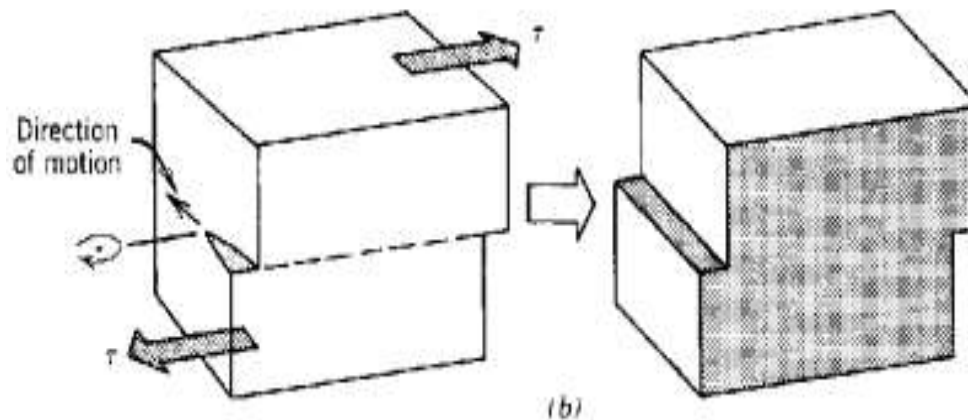


Formation of a step on the surface of a crystal due to:



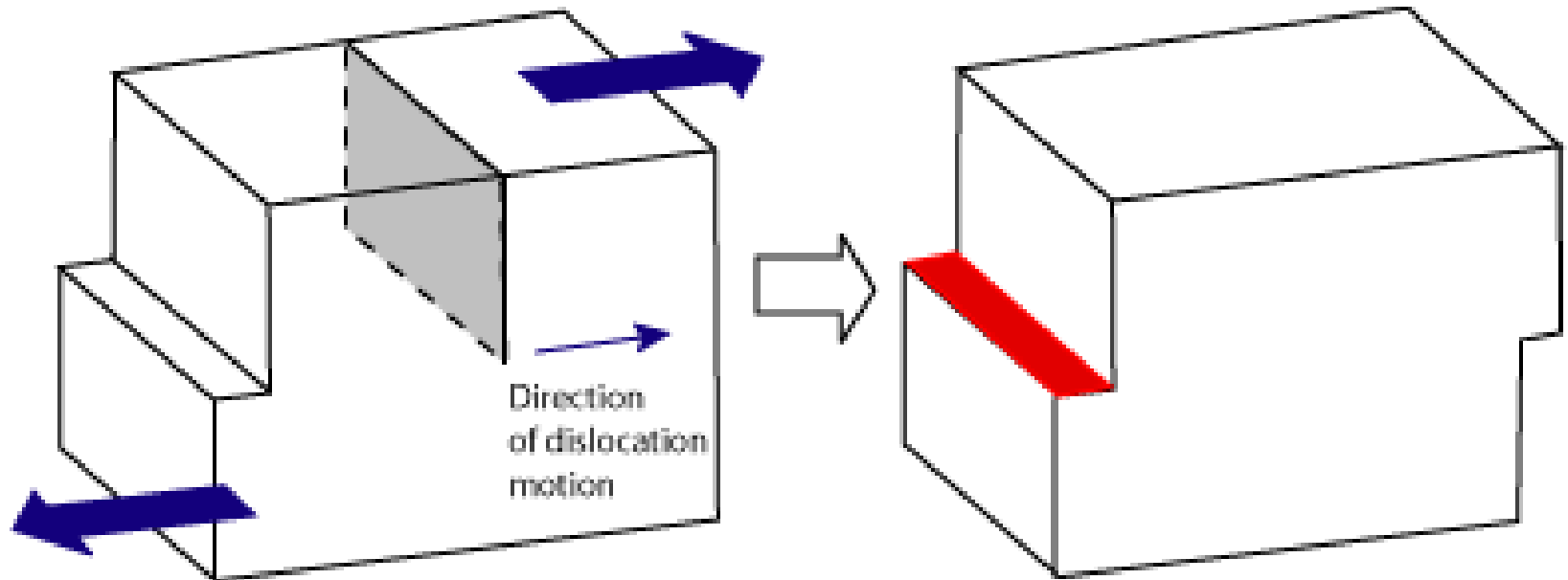
Edge Dislocation:

Dislocation moves in direction of applied shear stress



Screw Dislocation:

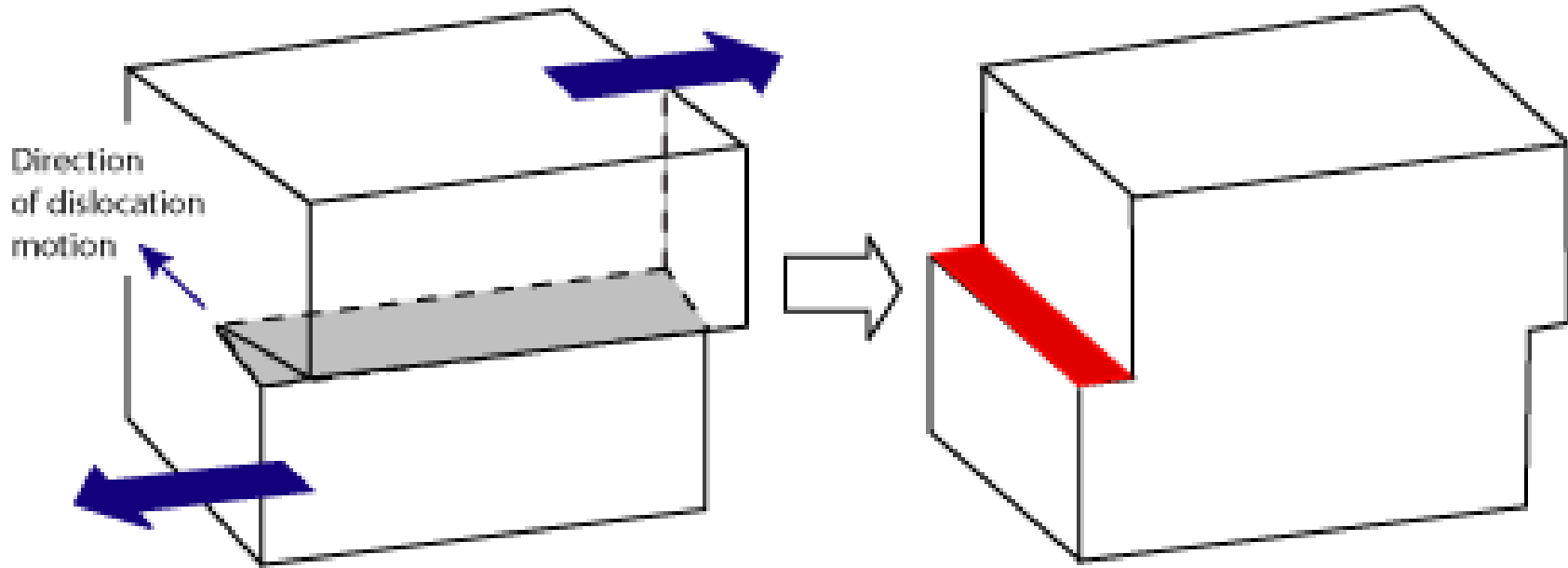
Dislocation motion is perpendicular to applied shear stress



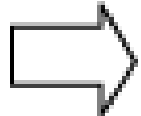
Direction of dislocation motion



Edge Dislocation



Direction of dislocation motion

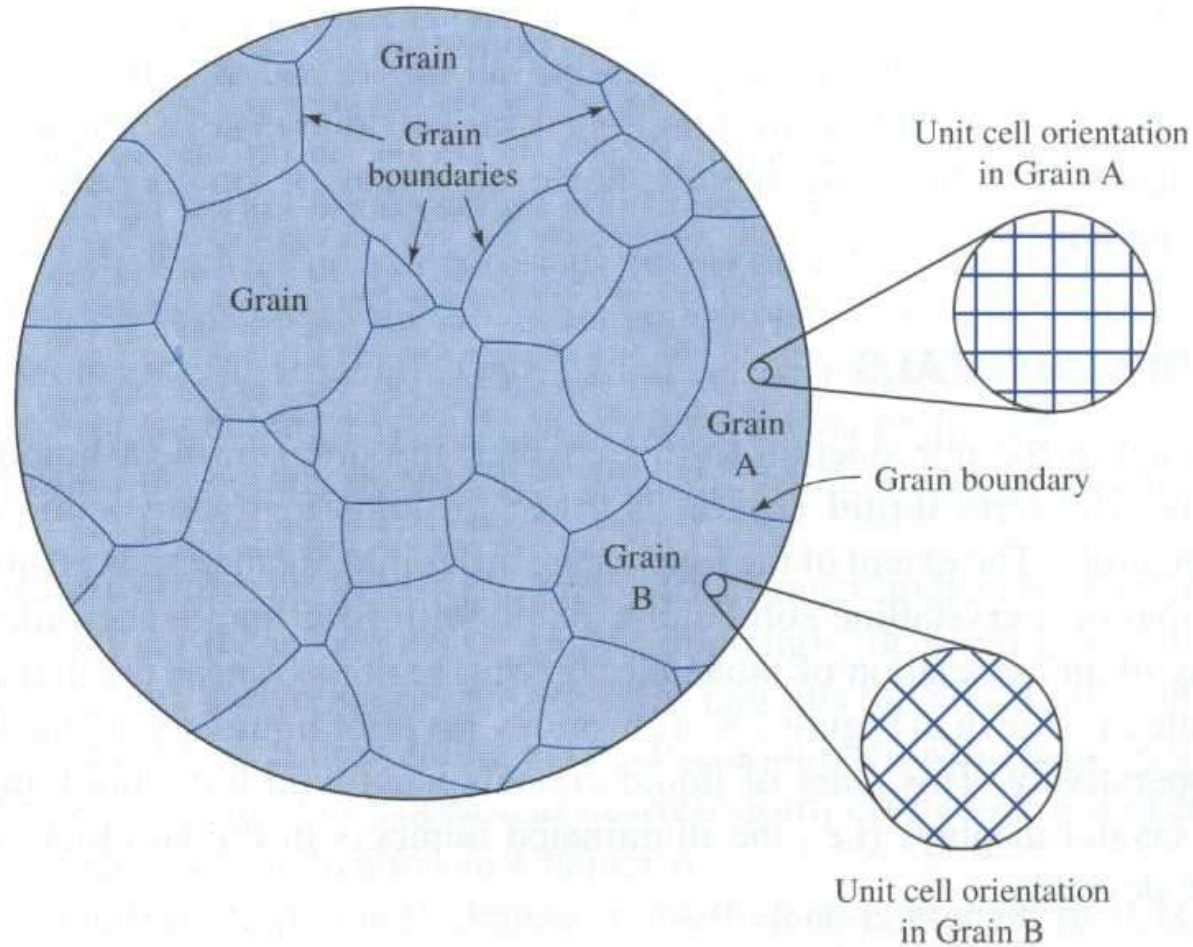


Screw Dislocation

- Dislocations are simply slide or slip of one portion of crystal system over another as dislocations move one part of the system relative to the other.
- When dislocations pass through the whole system, the system permanently deforms.
- Dislocations are on boundary between the regions where slip has occurred and where it has not.
- On either side of the dislocation crystalline system is essentially perfect.

3. INTERFACIAL DEFECTS (BOUNDARIES)

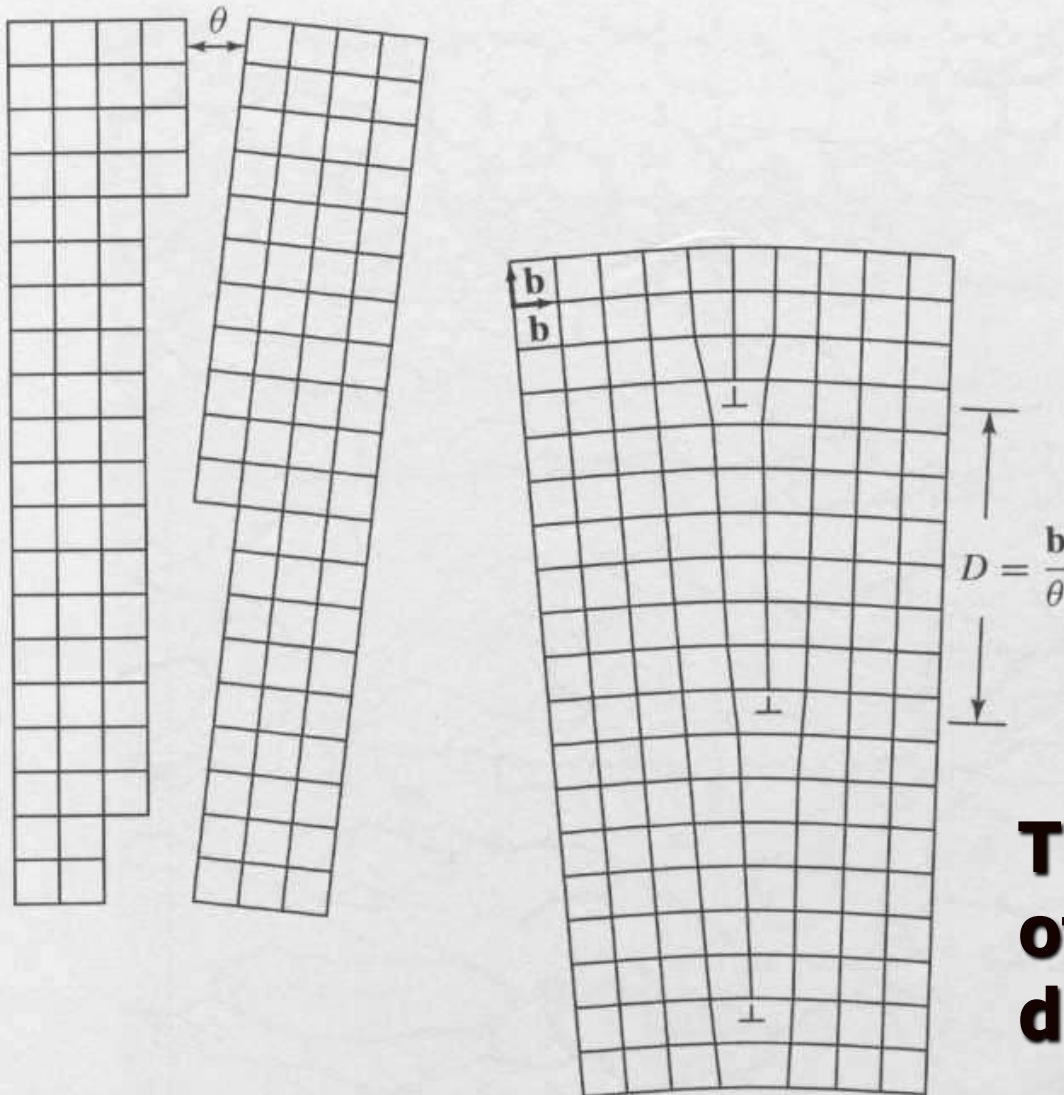
- Boundaries could be summarized into three:
 1. **Free surfaces:** Interfaces between liquids and gases.
 2. **Grain boundaries:** Interfaces between crystal systems having different orientation.
In each crystal system the atoms are arranged orderly. However, at the boundary there is a transition zone which is not aligned with either of the crystal systems.



A schematic illustration of a polycrystalline sample. The polycrystal is composed of many grains separated by regions of disorder known as grain boundaries. Note that the unit cell alignment within Grain A (shown in the high magnification insert) is different from that in Grain B.

3. **Interphase boundaries:** similar to grain boundaries both in shape and behavior. However, in these systems there are two or more materials having different crystal structures. Multiphase materials having a change in physical and/or chemical characteristics will also have interphase boundaries. (**Ex:** ice-water)

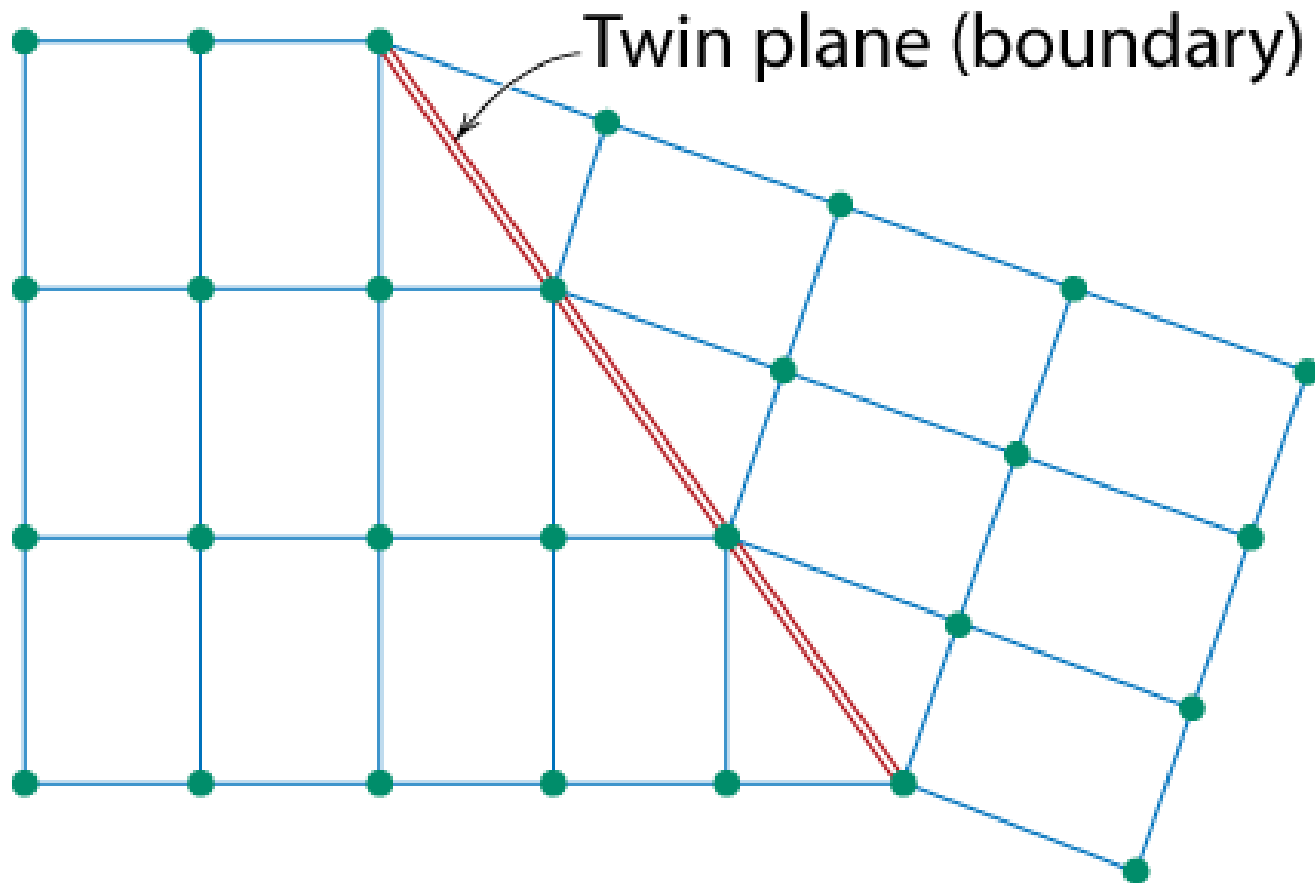
Grain Boundaries



Simple grain boundary structure. This is termed a tilt boundary because it is formed when two adjacent crystalline grains are tilted relative to each other by a few degrees (θ). The resulting structure is equivalent to isolated edge dislocations separated by the distance b/θ , where b is the length of the Burgers vector, b . (From W. T. Read, Dislocations in Crystals, McGraw-Hill Book Company, New York, 1953. Reprinted with permission of the McGraw-Hill Book Company.)

Tilt boundary: Result of a set of edge dislocations.

Grain Boundaries



Twist boundary: Result of a set of screw dislocations

4. BULK DEFECTS

- They are either introduced during the production of the material or during its fabrication.
- For example → inclusions (cracks, notches, air bubbles & etc.) added during production.

IMPORTANCE OF IMPERFECTIONS

Most of the properties of materials are affected by imperfections:

- ❑ Small amount of impurity atoms may increase the electrical conductivity of semi-conductors.
- ❑ Dislocations are responsible for ductility. Strength of materials can be increased to a large extent by the mechanism “strain-hardening” which produces line defects that act as a barrier to control the growth of other imperfections.
- ❑ Presence of bulk defects such as cracks, notches, holes causes brittle materials, which break at very low stresses without showing large deformations.