Chapter 4

IMPERFECTIONS IN SOLIDS

The University of Jordan
Chemical Engineering Department
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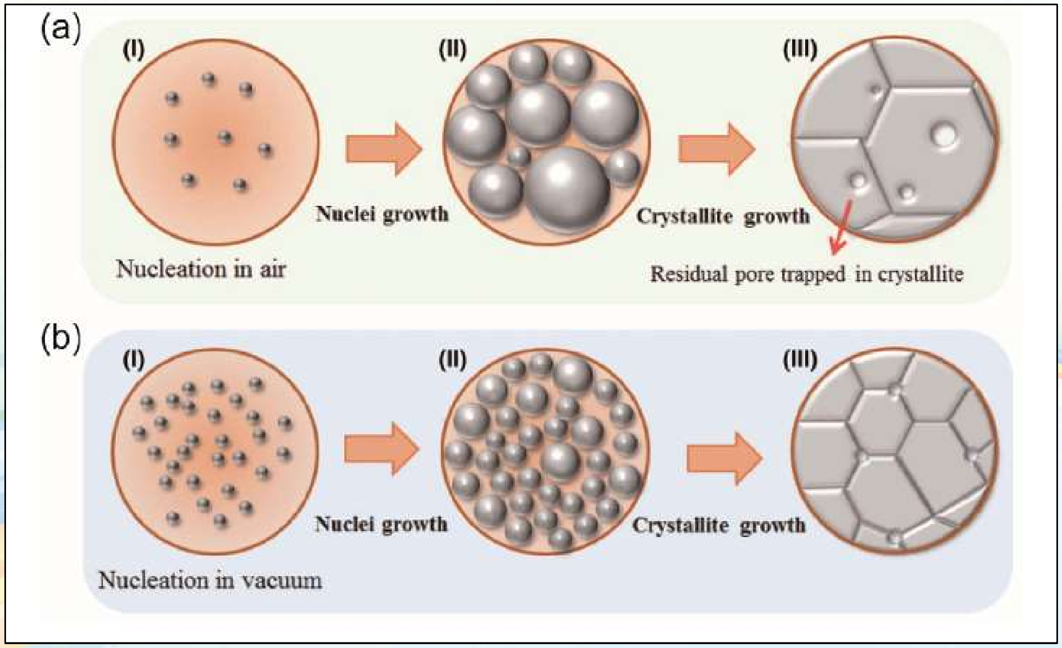
Outline

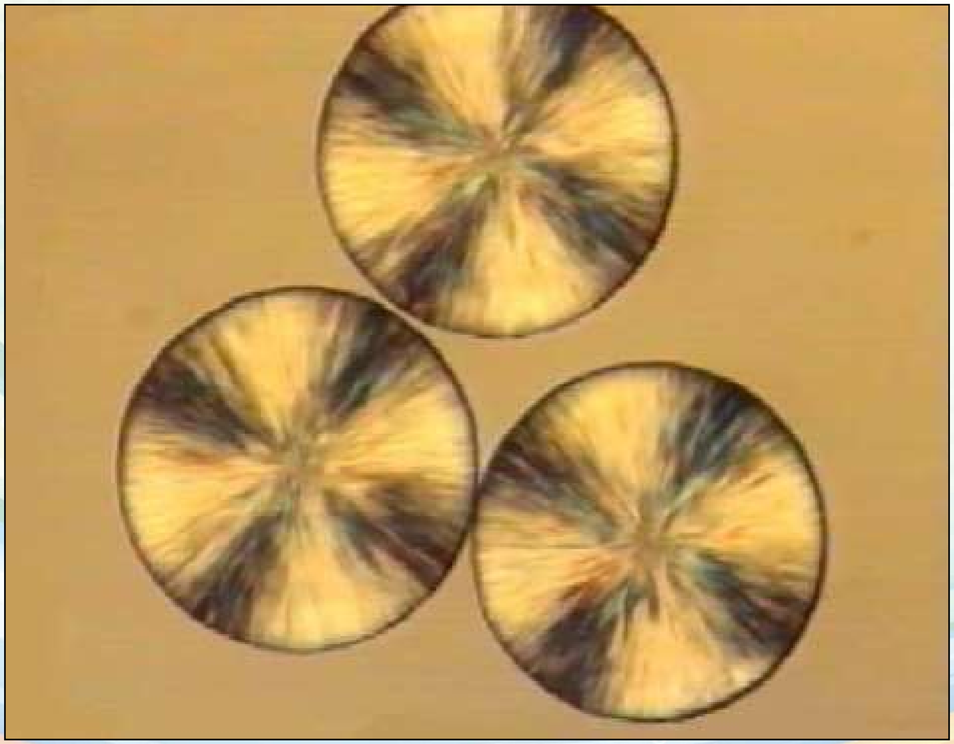
- What are the solidification mechanisms?
- What types of defects arise in solids?
- Can the number and type of defects be varied and controlled?
- How do defects affect material properties?
- Are defects undesirable?

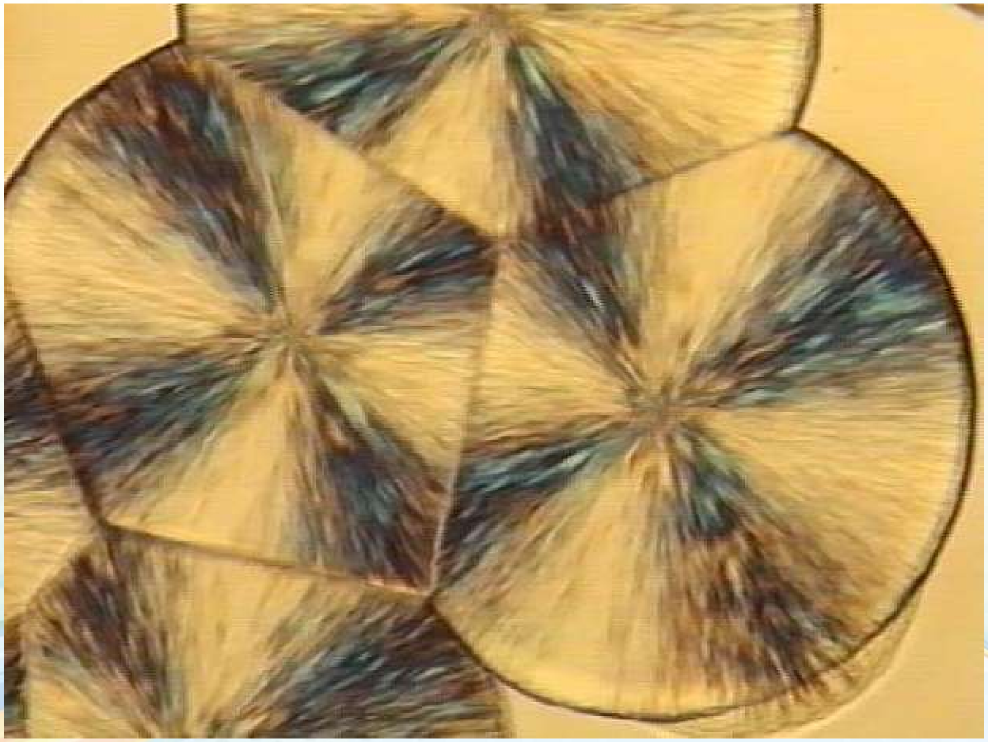
Solidification

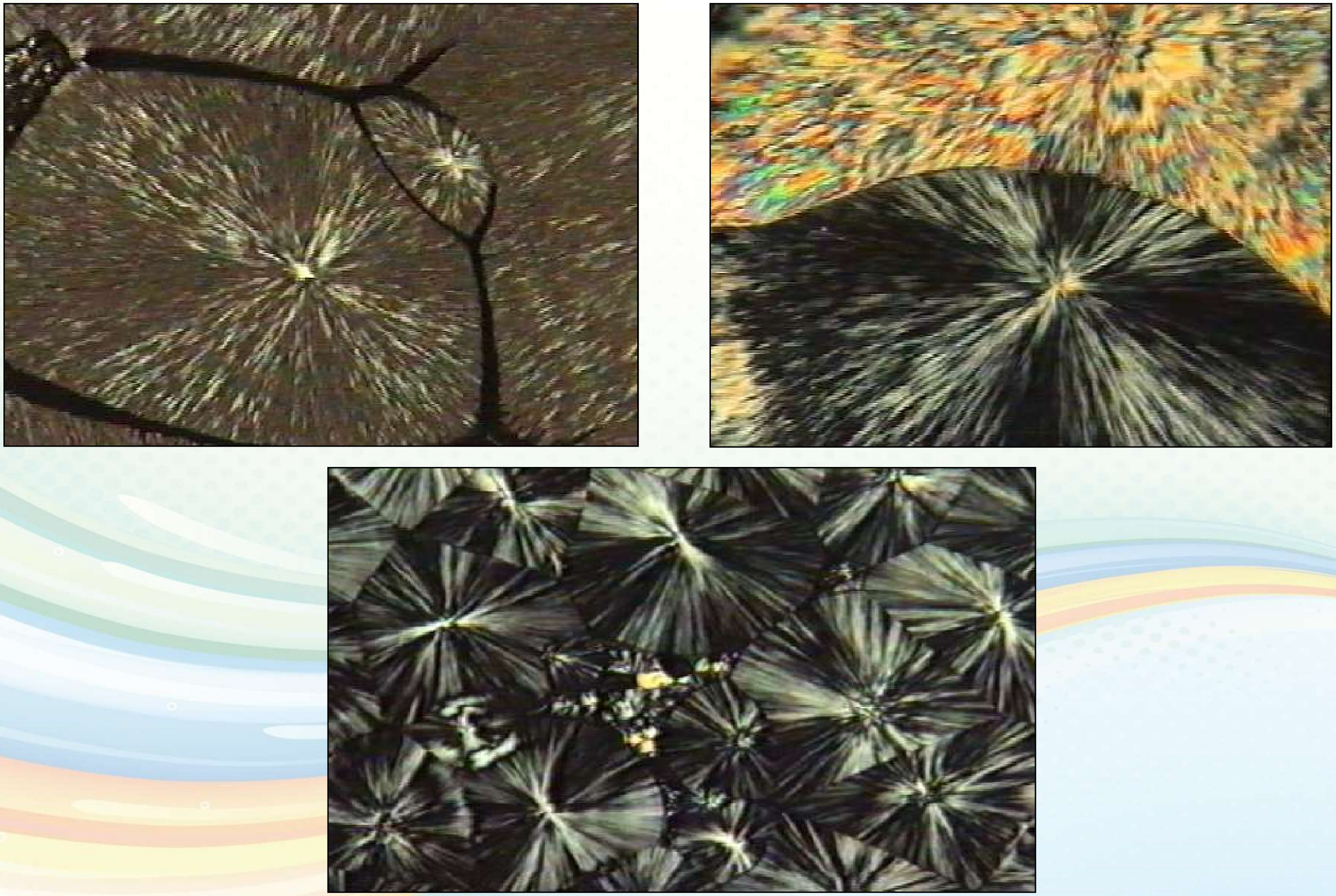
- Start with a molten material – all liquid
  Result of casting of molten material:

1. Nuclei form.
2. Nuclei grow to form crystals – grain structure.
2. Crystals grow until they meet each other.





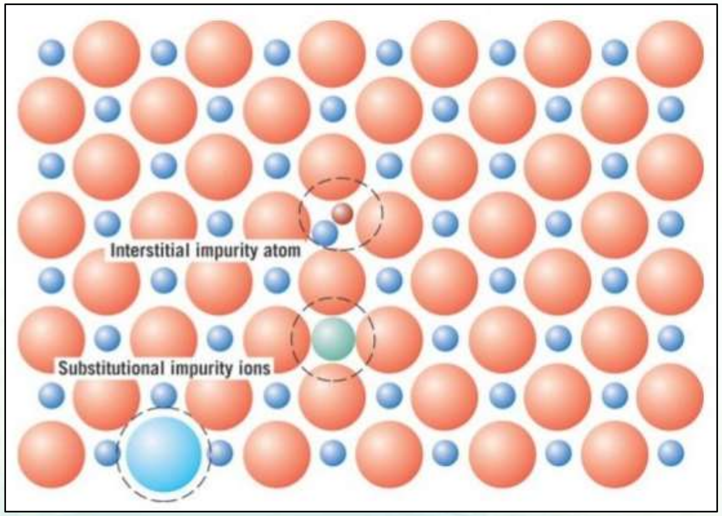


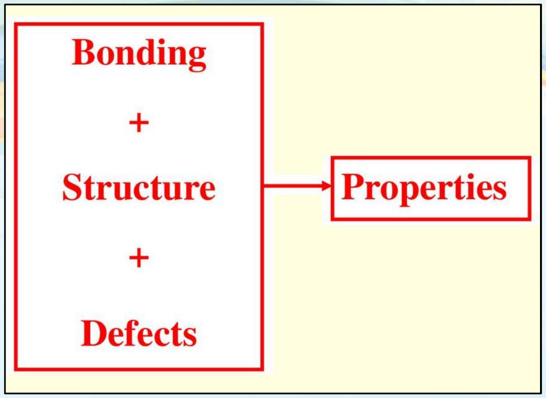


Experiment 2
Hot Ice Sea Urchin

Imperfections in Solids

- There is no such thing as a perfect crystal.
  - ✓ What are these imperfections?
  - ✓ Why are they important?
- Many of the important properties of materials are due to the presence of imperfections.
- Defects have a profound impact on the macroscopic properties of materials.
  - ✓ Semiconducting properties
  - ✓ Yield stress
  - ✓ Fracture strength
  - ✓ Electrical conductivity





Bonding

+

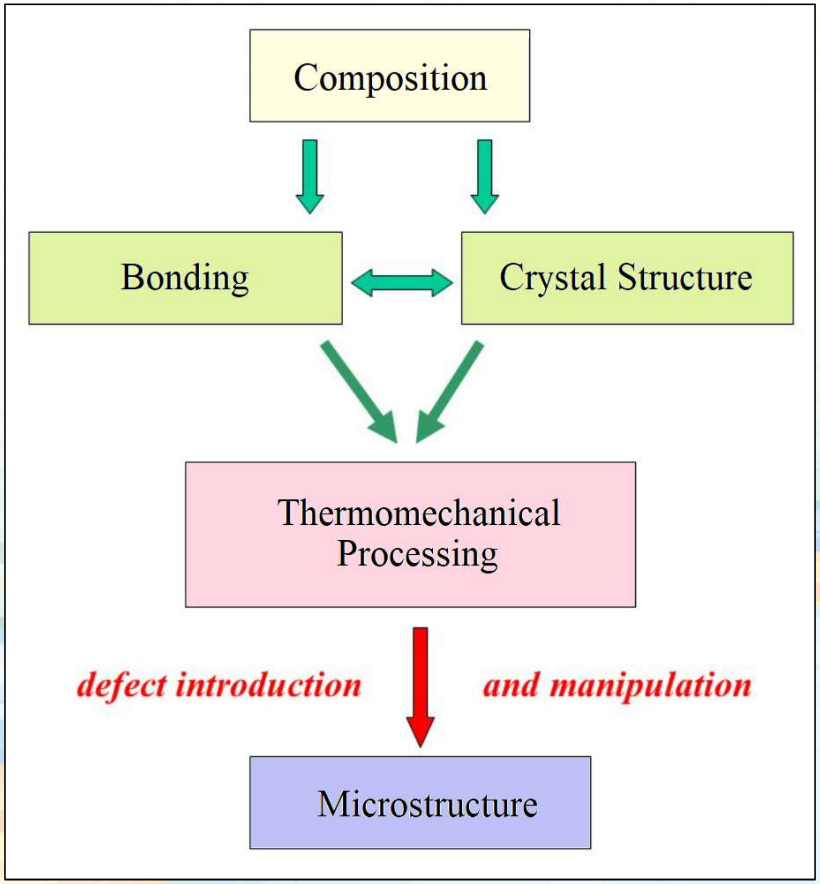
Structure

+

Defects

Properties

- *The processing determines the defects imperfections*



Composition

Bonding

Crystal Structure

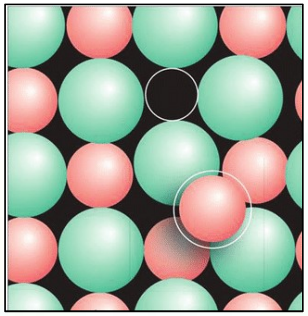
Thermomechanical Processing

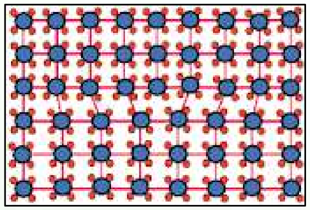
defect introduction ***and manipulation***

Microstructure

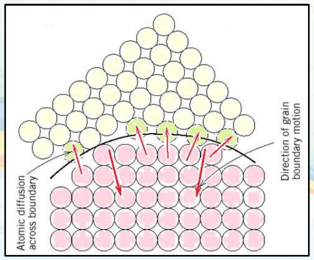
Types of Imperfections

1. **Point defects:** atoms missing or in irregular places in the lattice
   - Vacancies
   - Interstitials (space that intervenes between things).
   - Impurities, weight and atomic composition

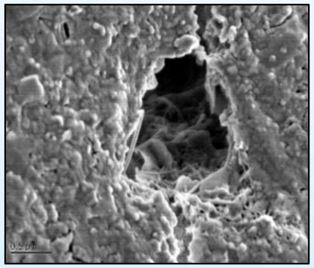




2. **Line defects:** groups of atoms in Irregular Positions: edge dislocations and screw dislocations
3. **Area defects:** the interfaces between homogeneous regions of the material
   - Grain boundaries



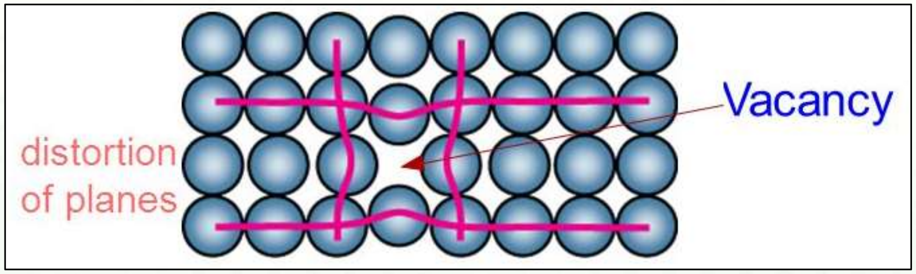
4. **Bulk or Volume defects:**
   - Pores
   - Cracks



Point Defects

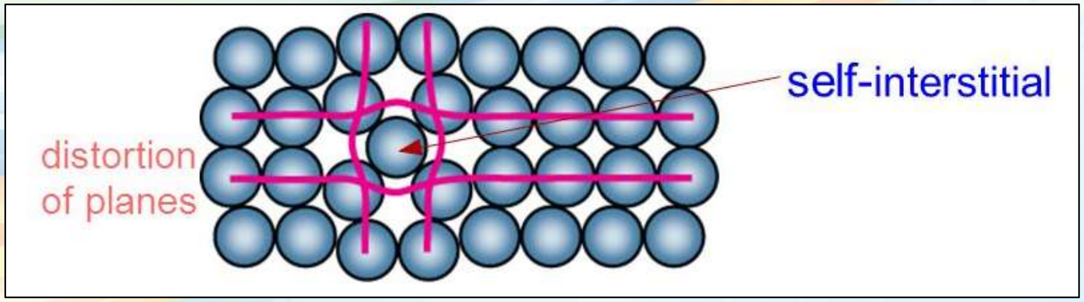
- **Vacancies**

  This figure shows a vacant atomic sites in a structure.



- **Self-Interstitials**

  "Extra" atoms positioned between atomic sites.



How many vacancies are there?

- The equilibrium number of vacancies formed as a result of thermal vibrations may be calculated from thermodynamics:

$$\frac{N_v}{N_s} = exp\left(\frac{-Q_v}{kT}\right)$$

Where:

N_v: Number defects

N_s: Number of potential defect sites

K: Boltzmann's constant; 1.38×10^{-23} J/atom-K or 8.62×10^{-5} eV/atom-K

T: Temperature

Q_v: Activation energy

Each lattice site is a potential vacancy site

Example:

Estimate the number of vacancies in Cu at room temperature.

$$N_v = N_s exp\left(\frac{-Q_v}{k_B T}\right)$$

- The Boltzmann's constant $k_B = 1.38\times10^{-23}$ J/atom-K or 8.62×10^{-5} eV/atom-K
- The temperature in Kelvin $T = 27\ ^oC + 273 = 300$ K
- $k_B T = 300\ K \times 8.62 \times 10^{-5}\ eV/K = 0.02586\ eV$
- The energy for vacancy formation $Q_v = 0.9$ eV/atom
- The number of regular lattice sites $N_s = \frac{N_A \rho}{A_{Cu}}$
- $N_A = 6.023 \times 10^{23}$ atoms/mol
- $\rho = 8.4\ g/cm^3$
- $A_{Cu} = 63.5$ g/mol

$$N_s = \frac{6.023 \times 10^{23}\ atoms/mol \times 8.4\ g/cm^3}{63.5\ g/mol} = 7.967 \times 10^{22}\ \frac{atoms}{cm^3}$$

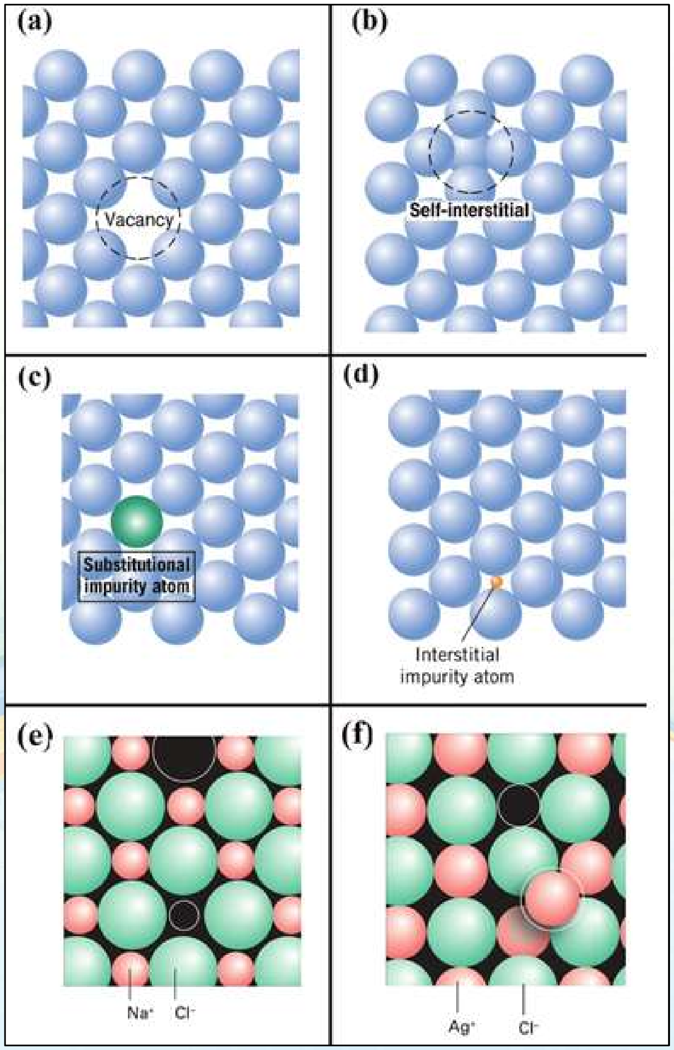
$$N_v = 7.967 \times 10^{22}\ \frac{atoms}{cm^3}\ exp\left(\frac{-0.9\ eV/atom}{0.02586\ eV/atom}\right)$$

$$= 6.12 \times 10^{7}\ \frac{vacancies}{cm^3}$$

Temperature °C	N_v	Weight %
27	6.12×10^{7}	$7.68\ 10^{-14}$
40	259.67×10^{7}	$3.26\ 10^{-13}$
100	5.556×10^{10}	$6.97\ 10^{-11}$
400	1.458×10^{16}	$1.83\ 10^{-5}$
600	5.096×10^{17}	0.00064
900	1.086×10^{19}	0.01363
1700	4.01×10^{20}	0.5032

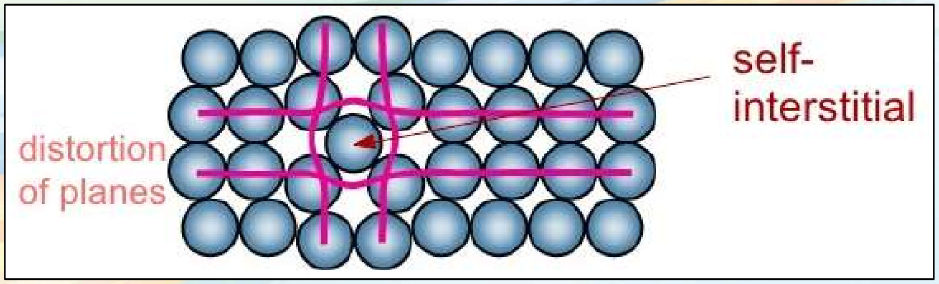
Other point defects: self-interstitials, impurities

- Schematic representation of different point defects:
  - (a) Vacancy
  - (b) Self-interstitial
  - (c) Substitutional impurities
  - (d) Interstitial impurity



Self-interstitials

- *Self-interstitials in metals introduce large distortions in the surrounding lattice .*
- *The energy of self-interstitial formation is ~ 3 times larger as compared to vacancies ($Q_i \sim 3 \times Q_v$).*
- *Equilibrium concentration of self-interstitials is very low (less than one self-interstitial per cm^3 at room T).*



Impurities

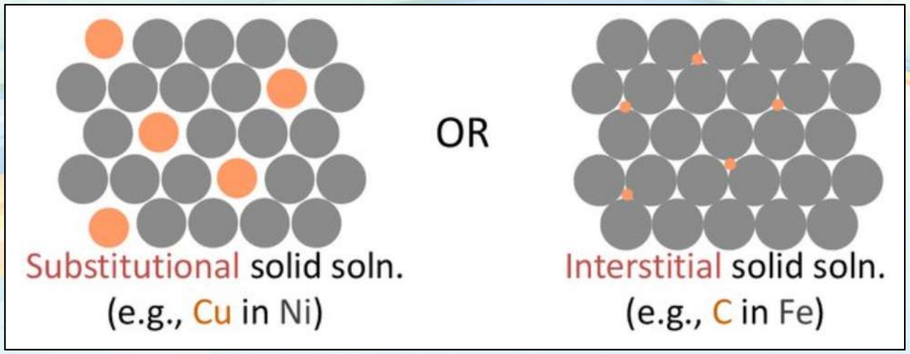
- Impurities - atoms which are different from the host.
  - ✓ All real solids are impure.
  - ✓ Very pure metals 99.9999% - one impurity per 10^6 atoms.
  - ✓ May be intentional or unintentional.
- Examples:
  - ✓ Carbon added in small amounts to iron makes steel, which is stronger than pure iron.
  - ✓ Boron added to silicon change its electrical properties.
- Alloys: deliberate mixtures of metals.
- Example: sterling silver is 92.5% silver – 7.5% copper alloy. Stronger than pure silver.

Solid Solutions

- *Solid solutions are made of a host (the solvent or matrix) which dissolves the minor component (solute).*
- *The ability to dissolve is called solubility.*
- *Solvent: in an alloy, the element or compound present in greater amount.*
- *Solute: in an alloy, the element or compound present in lesser amount.*

1. Solid Solution

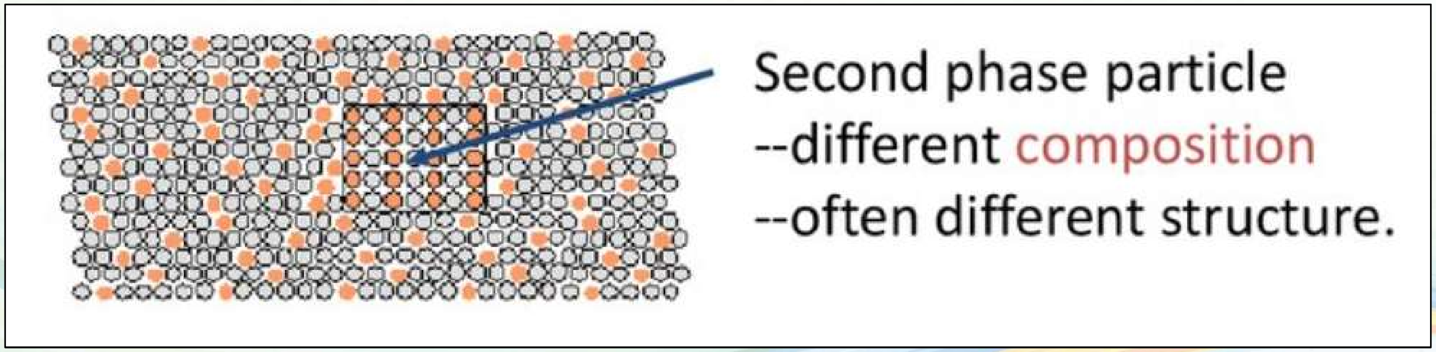
- ✓ *Homogeneous*
- ✓ *Maintain crystal structure*
- ✓ *Contain randomly dispersed impurities (substitutional or interstitial)*



Solid Solutions

2. Second Phase:

As solute atoms are added, new compounds / structures are formed, or solute forms local precipitates.



Second phase particle
--different composition
--often different structure.

- Whether the addition of impurities results in formation of solid solution or second phase depends on the nature of the impurities, their concentration and temperature, pressure…

Substitutional Solid Solutions

Factors for high solubility: (Hume – Rothery rule)

- **Atomic size factor** - atoms need to "fit" solute and solvent atomic radii should be within ~ ±15%. If size difference of elements are greater than 15%, the lattice distortions (local lattice strain) are too big and solid-solution will not be favored.

$$DR\% = \frac{r_{solute} - r_{solvent}}{r_{solvent}} \times 100\%$$

- **Crystal structures:** like elemental crystal structure are better. For appreciable solubility, the crystal structure for metals must be the same, i.e. solute and solvent should be the same.

Substitutional Solid Solutions

- Electronegativity: DE ~ 0 favors solid-solution.

$$DR\% = \frac{E_{solute} - E_{solvent}}{E_{solvent}} \times 100\%$$

The more electropositive one element and the more electronegative the other, then intermetallic compounds are more likely.

- Valence: Generally more solute goes into solution when it has higher valency than solvent.

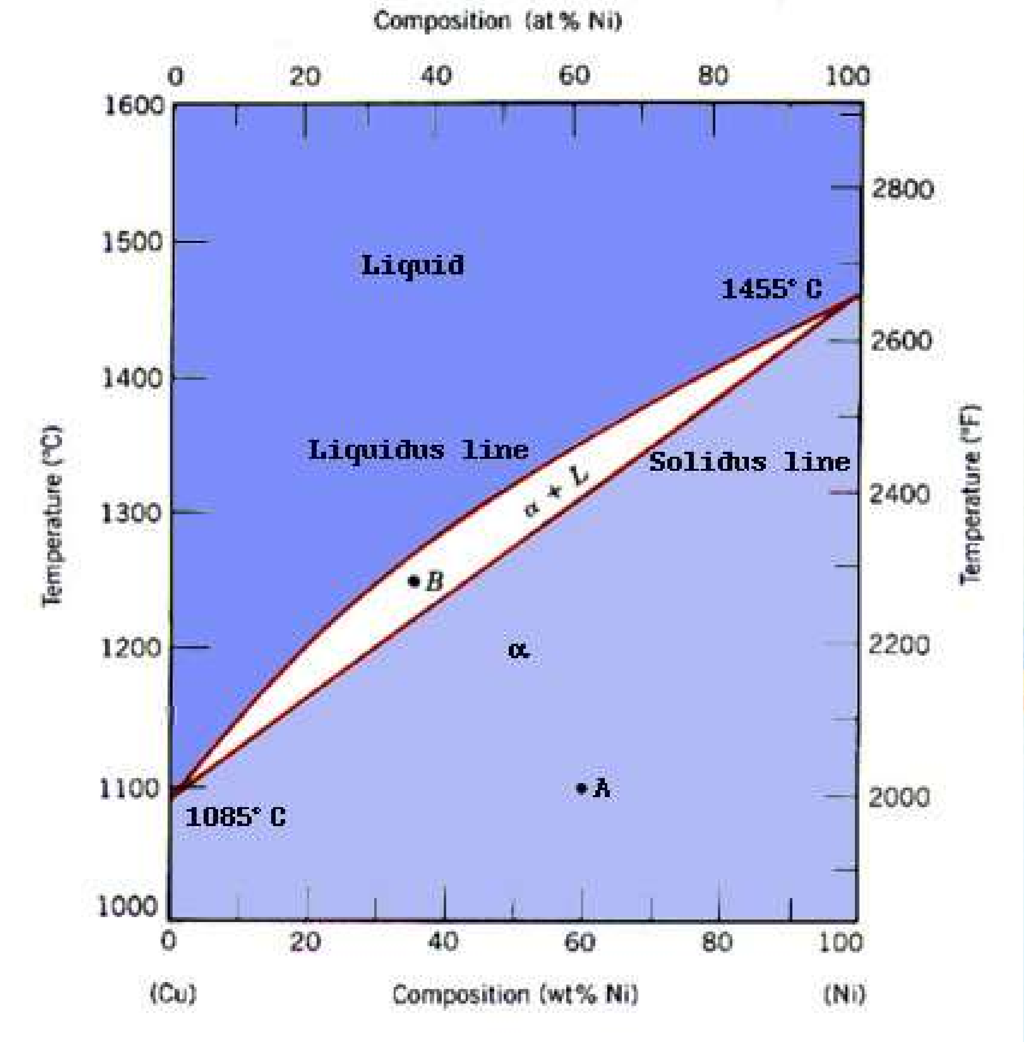
Higher in lower alright. Lower in higher, it's a fight.

Example

Is solid-solution favorable, or not for Cu-Ni alloys?

- ✓ Rule 1: r_{Cu} = 0.1278 nm and r_{Ni} = 0.1246 nm
  DR% = (0.1246-0.1278)/0.1278*100% = 2.5% (Favorable)
- ✓ Rule 2: Ni and Cu have the FCC crystal structure (Favorable)
- ✓ Rule 3: E_{Cu} = 1.9 and E_{Ni} = 1.8. Thus,
  DE% = (1.8-1.9)/1.9*100% = -5.2 % (Favorable)
- ✓ Rule 4: Valency of Ni and Cu are both +2. (Favorable)

- ➢ Expect Ni and Cu forms S.S. over wide composition range

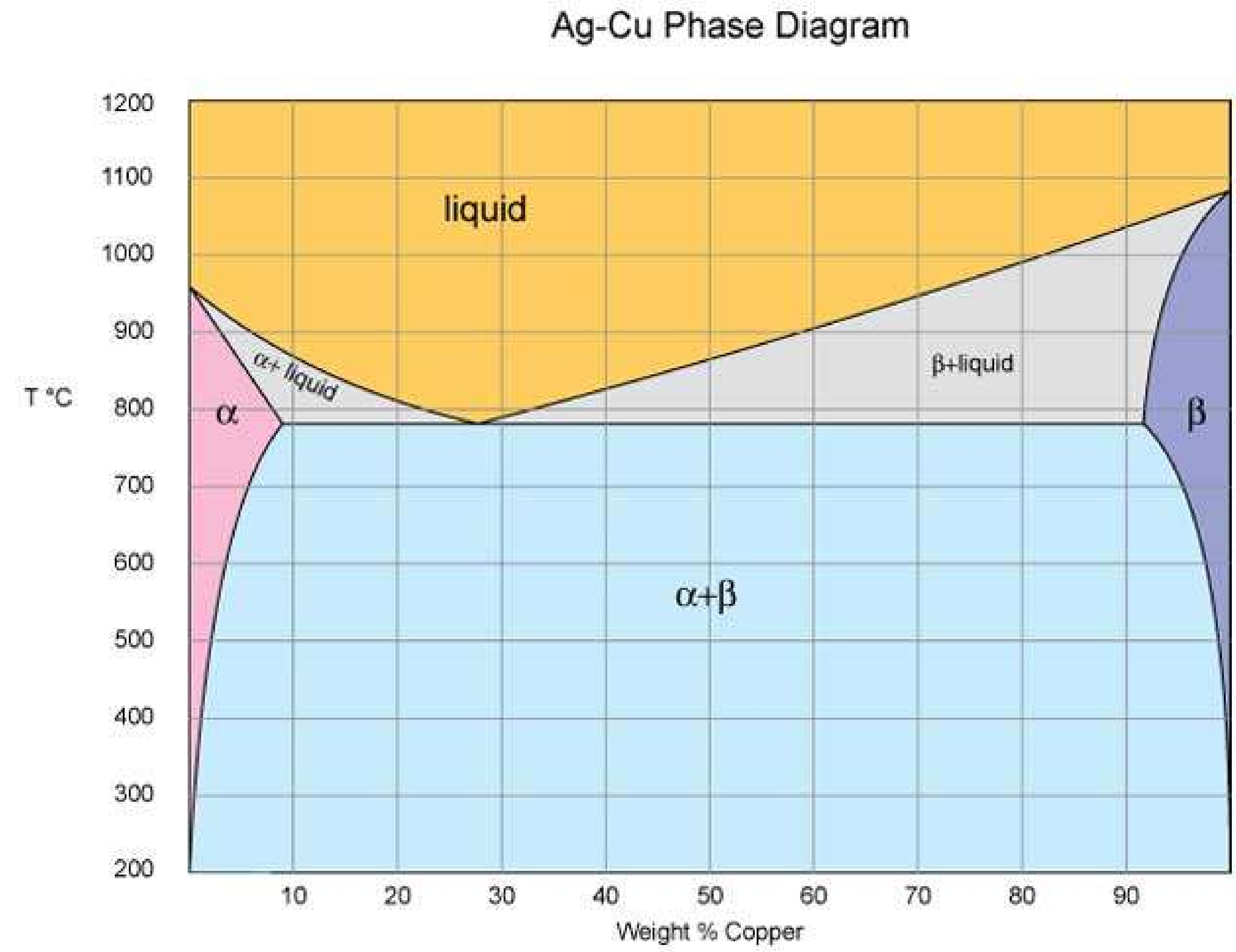

Composition (at % Ni)
0
20
40
60
80
100
1600
1500
1400
1300
1200
1100
1000
Temperature (°C)
2800
2600
2400
2200
2000
Temperature (°F)
Liquid
1455° C
Liquidus line
α + L
Solidus line
B
α
A
1085° C
0
20
40
60
80
100
(Cu)
Composition (wt% Ni)
(Ni)

Example

Is solid-solution favorable, or not for Cu-Ag alloys?

- ✓ Rule 1: r_{Cu} = 0.1278 nm and r_{Ni} = 0.1445 nm
  DR% = (0.1445-0.1278)/0.1278*100% = 13% (Favorable)
- ✓ Rule 2: Ag and Cu have the FCC crystal structure (Favorable)
- ✓ Rule 3: E_{Cu} = 1.9 and E_{Ni} = 1.9. Thus,
  DE% = 0% (Favorable)
- ✓ Rule 4: Valency of Cu is +2 and Ag is +1 (Not favorable)

- ➢ Expect Ag and Cu have limited solubility.
- ➢ In fact, the Cu-Ag phase diagram shows that a solubility of only 18% Ag can be achieved at high T in the Cu-rich alloys.


Ag-Cu Phase Diagram
1200
1100
1000
900
800
700
600
500
400
300
200
T °C
liquid
α+ liquid
α
β+liquid
β
α+β
10
20
30
40
50
60
70
80
90
Weight % Copper

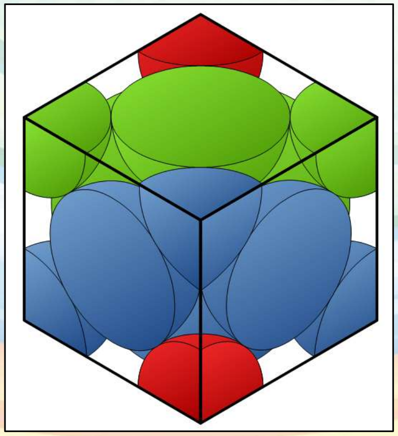
Solid Solutions

Application of Hume – Rothery rules – Solid Solutions.

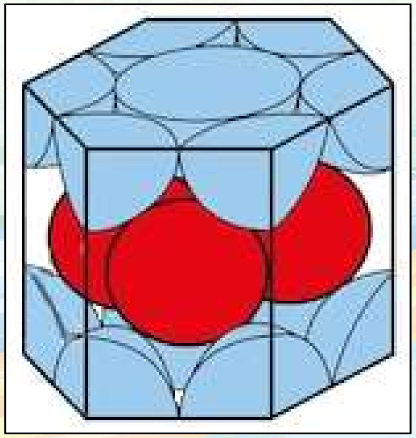
1. Would you predict more Al or Ag to dissolve in Zn?

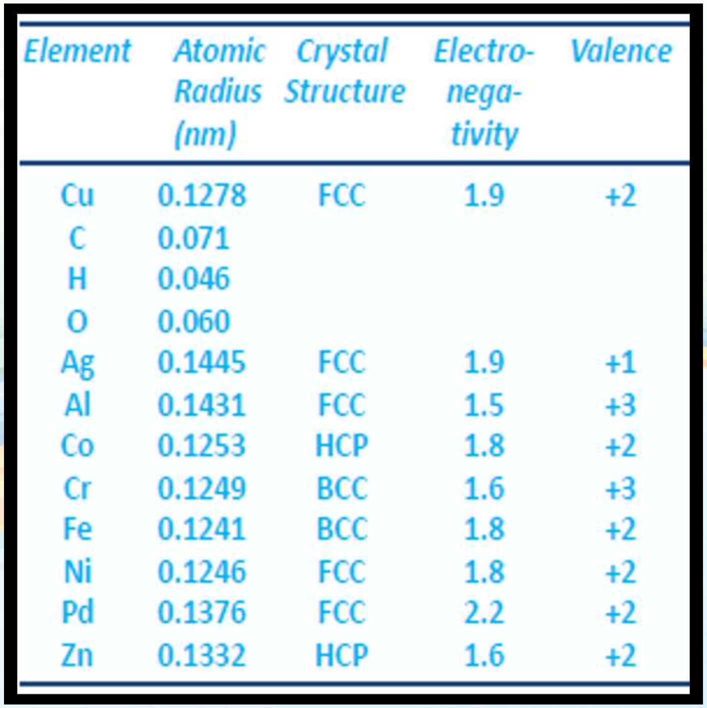
2. More than Zn or Al in Cu?

Al and Ag



Zn





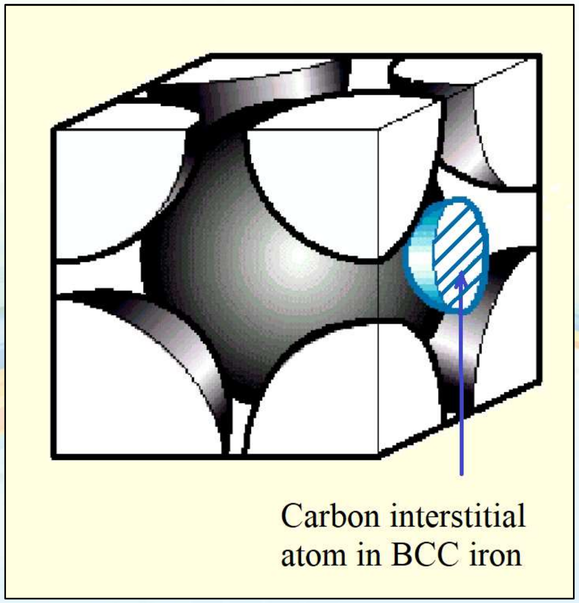
Element	Atomic Radius (nm)	Crystal Structure	Electro-nega-tivity	Valence
Cu	0.1278	FCC	1.9	+2
C	0.071			
H	0.046			
O	0.060			
Ag	0.1445	FCC	1.9	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.8	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.8	+2
Ni	0.1246	FCC	1.8	+2
Pd	0.1376	FCC	2.2	+2
Zn	0.1332	HCP	1.6	+2

Interstitial Solid Solutions

- Interstitial solid solution of C in α-Fe. The C atom is small enough to fit, after introducing some strain into the BCC lattice.

Factors for high solubility:

- For FCC, BCC, HCP structures the voids (or interstices) between the host atoms are relatively small, atomic radius of solute should be significantly less than solvent.
- Normally, max. solute concentration ≤ 10%, (2% for C-Fe)



Composition / Concentration

Composition can be expressed in:

- Weight percent, useful when making the solution.
- Atom percent, useful when trying to understand the material at the atomic level.
- Weight percent (wt %): weight of a particular element relative to the total alloy weight.
- For two-component system, concentration of element 1 in wt. % is

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100$$

Composition / Concentration

- Atom percent (at %): number of moles (atoms)) of a particular element relative to the total number of moles (atoms) in alloy.
- For two-component system, concentration of element 1 in at. % is:

$$C_1' = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100$$

where $n_{m1} = m'_1/A_1$

m'_1 is weight in grams of element 1.

A_1 is atomic weight of element 1.

Composition Conversions

- Weight % to Atomic %

$$C_1' = \frac{C_1A_2}{C_1A_2 + C_2A_1} \times 100$$

$$C_2' = \frac{C_2A_1}{C_1A_2 + C_2A_1} \times 100$$

- Atomic % to Weight %

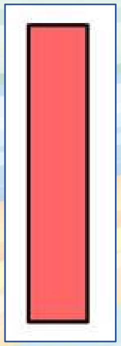
$$C_1 = \frac{C_1'A_1}{C_1'A_1 + C_2'A_2} \times 100$$

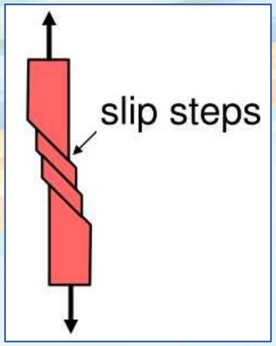
$$C_2 = \frac{C_2'A_2}{C_1'A_1 + C_2'A_2} \times 100$$

Dislocations —Linear Defects

- Dislocations are very important in mechanical properties of material.
- Introduction/discovery of dislocations in 1934 by Taylor, Orowan and Polyani marked the beginning of understanding of mechanical properties of materials.
- Dislocations are line defects.
- Slip between crystal planes result when dislocations move.
- Dislocations produce permanent (plastic) deformation.

Before deformation





After tensile elongation

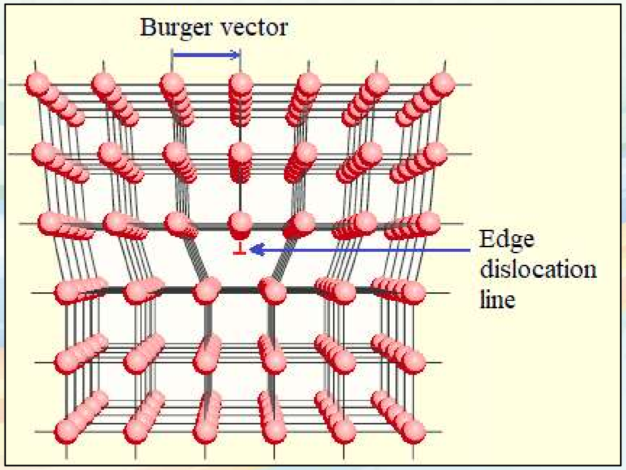
Dislocations —Linear Defects

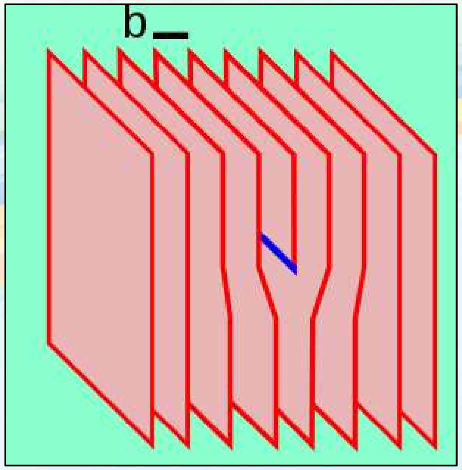
- ✓ Are one-dimensional defects around which atoms are misaligned
- ➢ Edge dislocation:
  - ✓ Extra half-plane of atoms inserted in a crystal structure.
  - ✓ b perpendicular to dislocation line.
- ➢ Screw dislocation:
  - ✓ Spiral planar ramp resulting from shear deformation.
  - ✓ b parallel to dislocation line

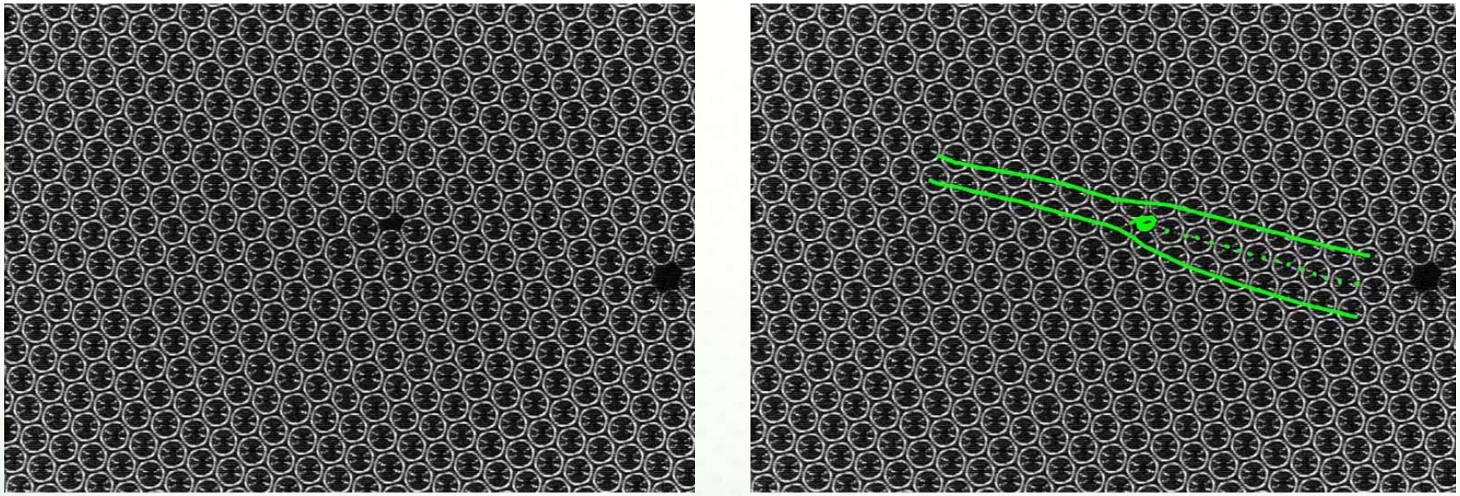
Burger's vector b: measure of lattice distortion.

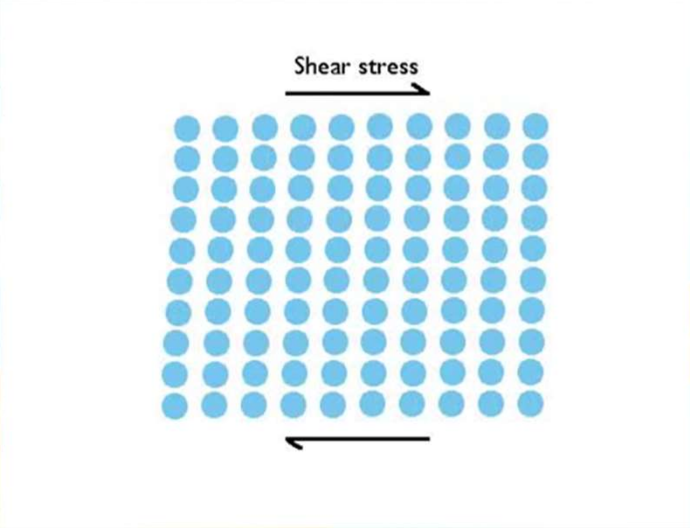
Edge dislocation

- *Dislocations are linear defects: the interatomic bonds are significantly distorted only in the immediate vicinity of the dislocation line*
- *This area is called the dislocation core.*
- *Dislocations also create small elastic deformations of the lattice at large distances.*



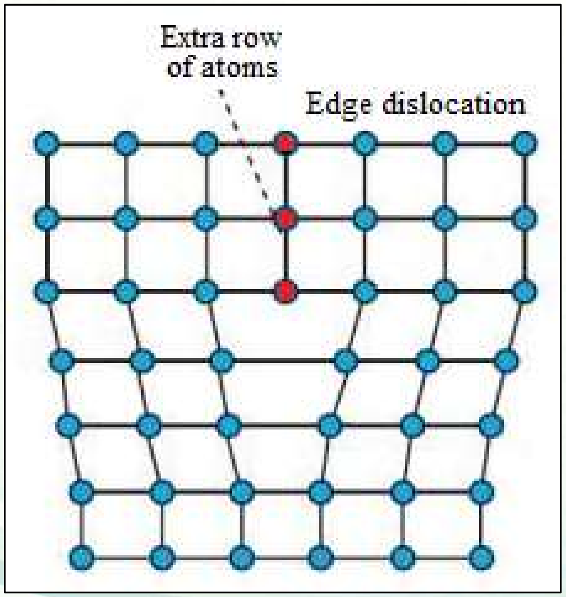


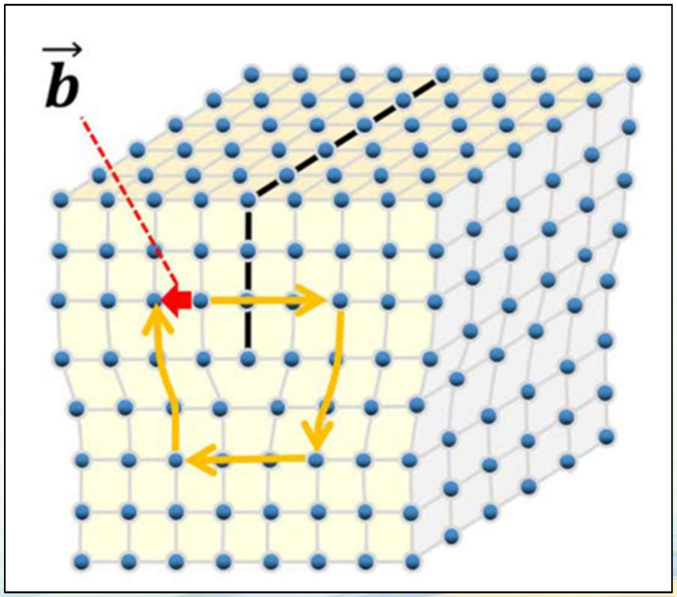



Shear stress

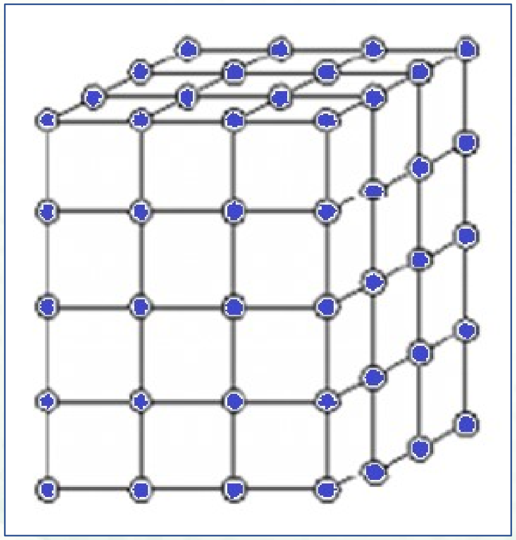
Motion of Edge Dislocation

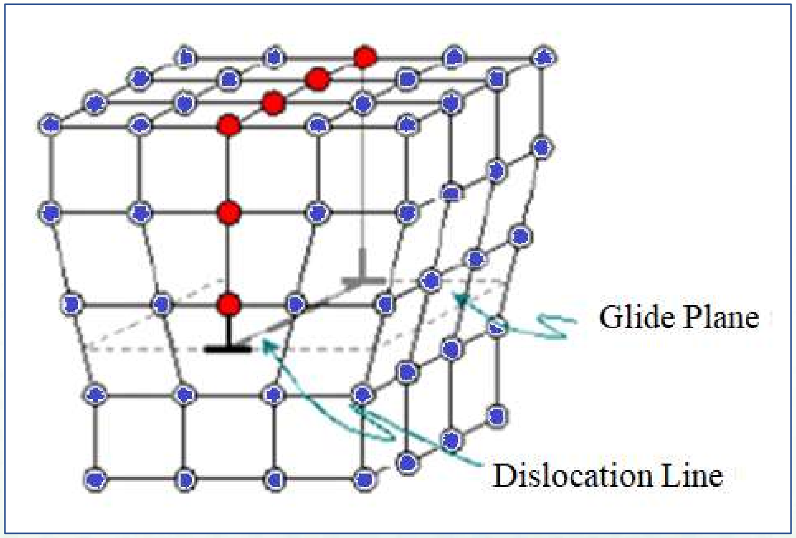
- Dislocation motion requires the successive bumping of a half plane of atoms.
- Bonds across the slipping planes are broken and remade in succession
- To describe the size and the direction of the main lattice distortion caused by a dislocation we should introduce so-called Burgers vector b.
- To find the Burgers vector, we should make a circuit from atom to atom counting the same number of atomic distances in all directions.
- If the circuit encloses a dislocation it will not close.
- The vector that closes the loop is the Burgers vector b.





- *Dislocations shown above have Burgers vector directed perpendicular to the dislocation line.*
- *These dislocations are called edge dislocations.*

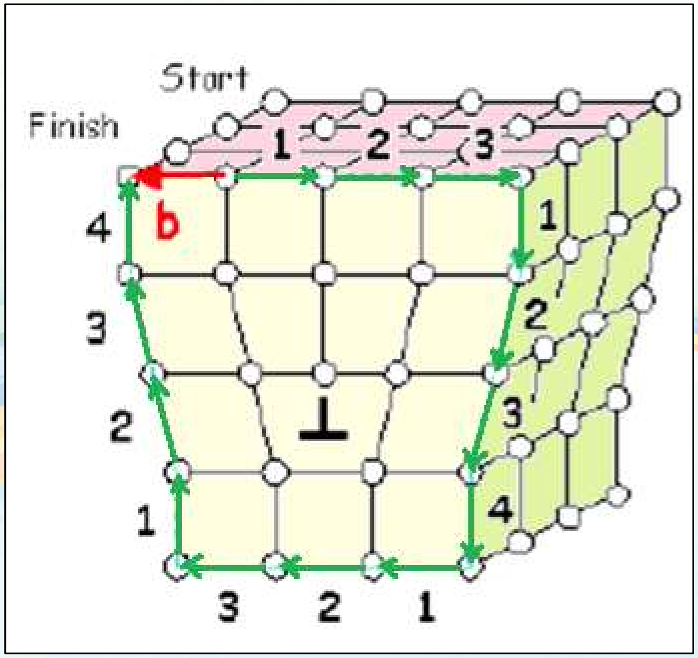




- *Introducing a dislocation into a crystal lattice by cramming in an extra half-plane.*
- *The dislocation line marks the edge of the half-plane. The inverted T symbol shows the location of the half-plane.*

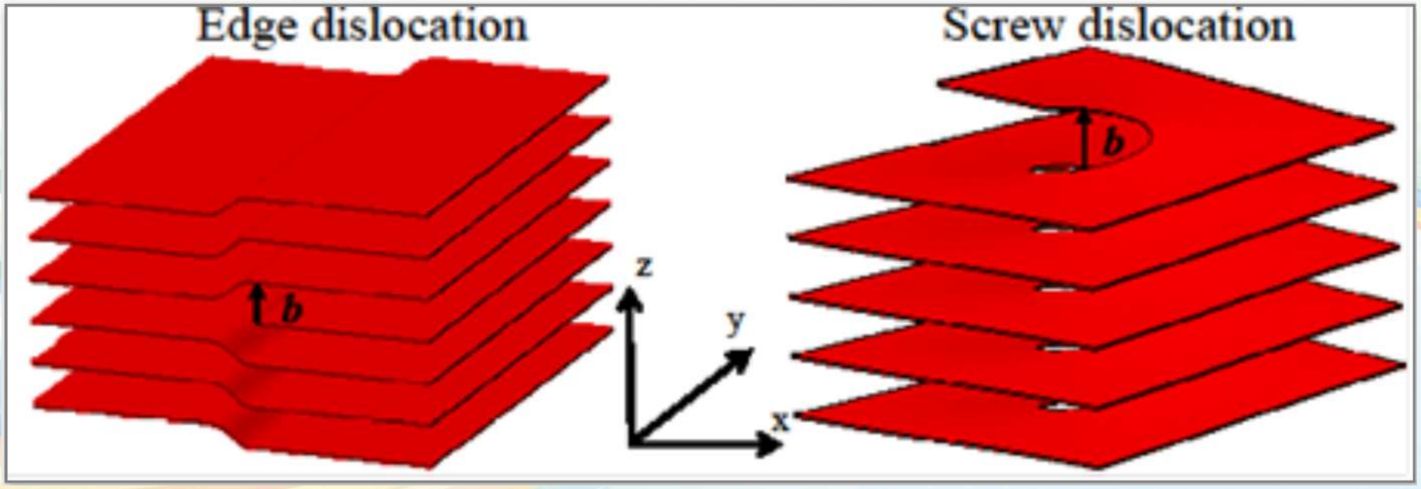
Burgers vector

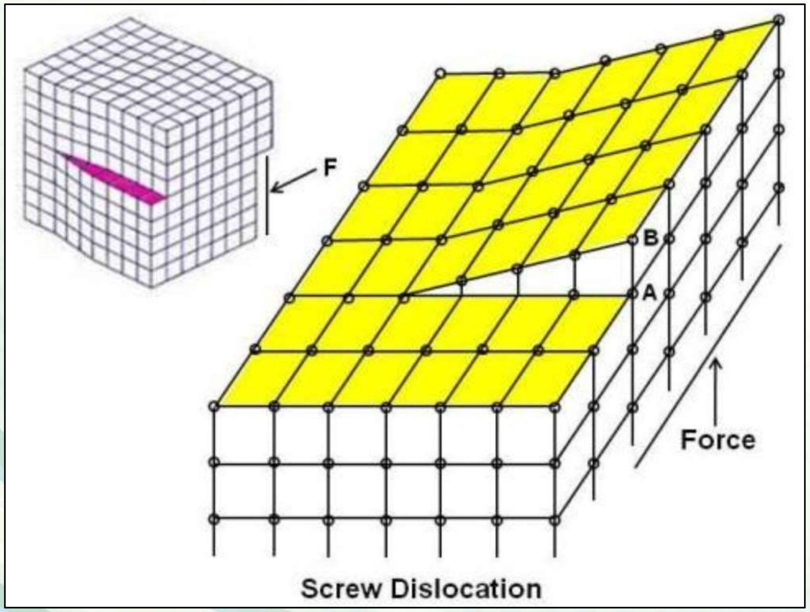
- Start at some point, going clockwise around the dislocation and counting our steps so that we take the same number right as we took left, the same number down as we took up and so on.
- Once we have circled the dislocation and our steps match up, the Burgers vector is the vector which points from Start to Finish.

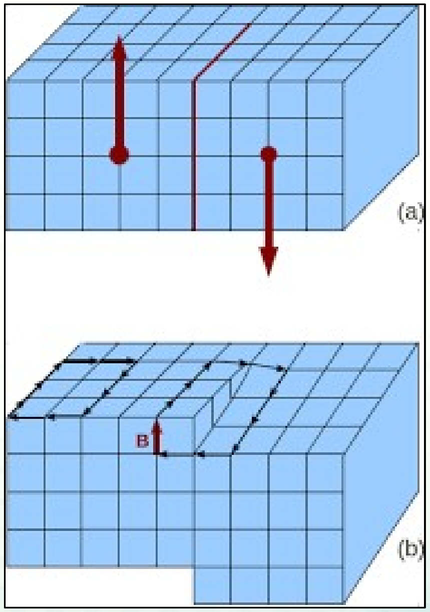


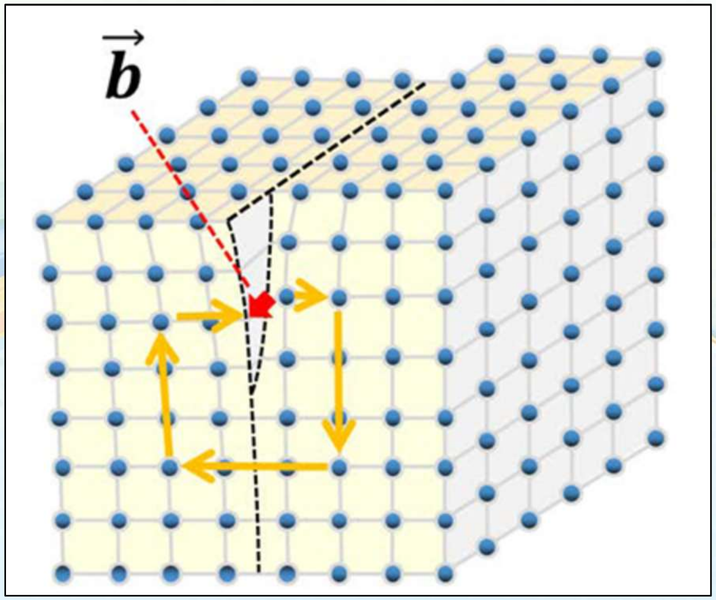
Screw dislocations

- Dislocations shown in previous slide are edge dislocations, have Burgers vector directed perpendicular to the dislocation line.
- There is a second basic type of dislocation, called screw dislocation

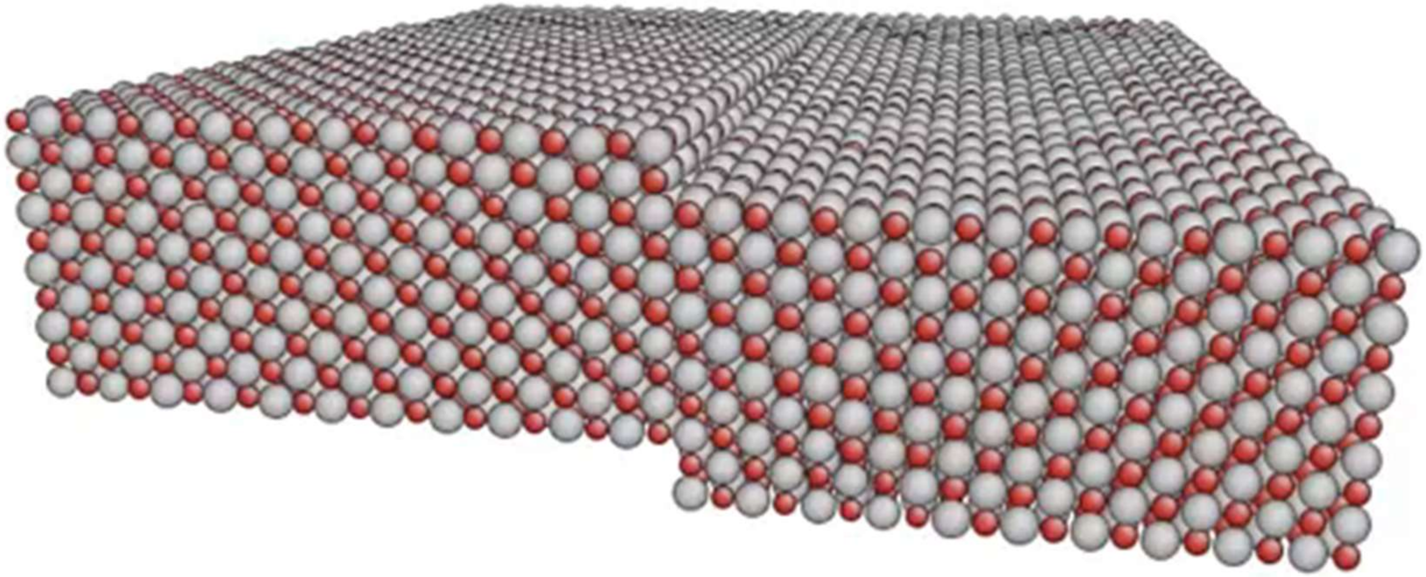


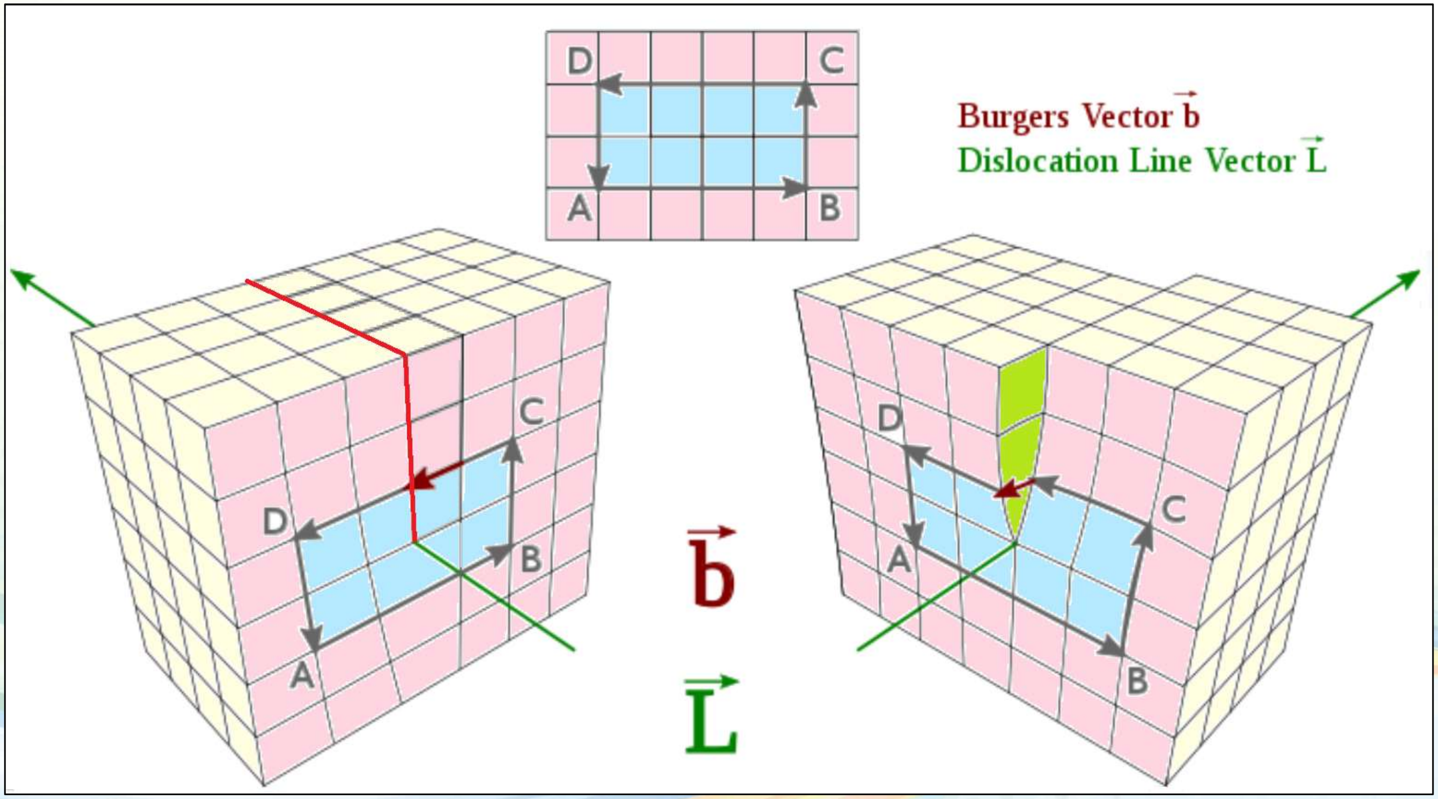






- *The screw dislocation is parallel to the direction in which the crystal is being displaced (Burgers vector is parallel to the dislocation line).*



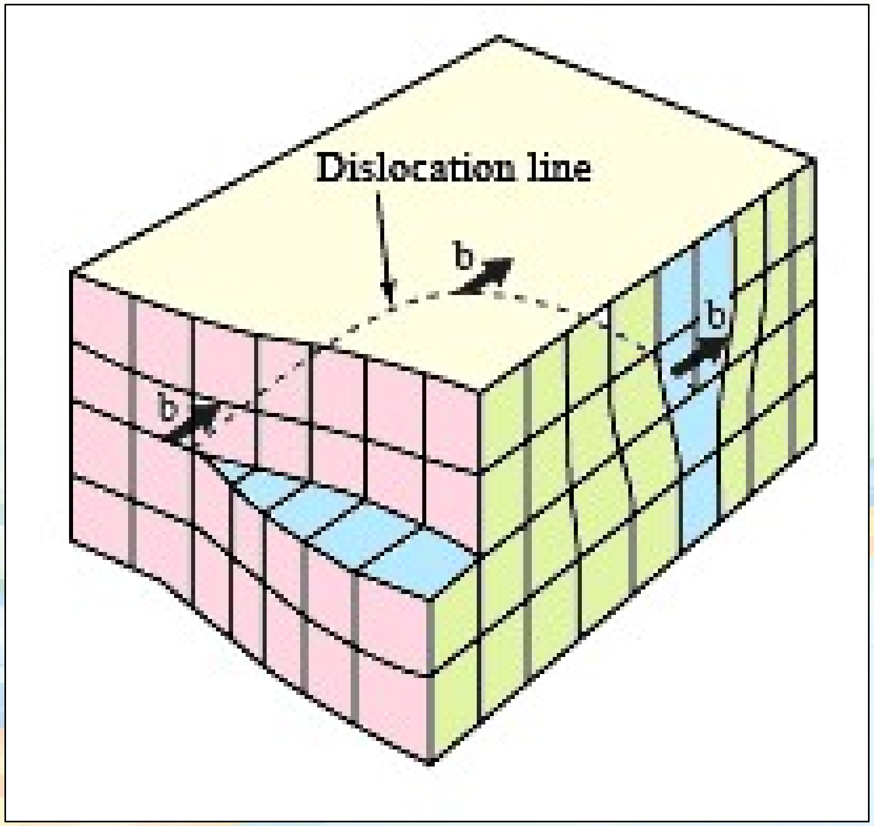


A screw dislocation is like a spiral staircase or a parking garage. The dislocation line is the axis of the helix.

Mixed/partial dislocations (not tested)

- The exact structure of dislocations in real crystals is usually more complicated than the ones shown in the edge and screw dislocations.
- Edge and screw dislocations are just extreme forms of the possible dislocation structures.
- Most dislocations have mixed edge/screw Character.

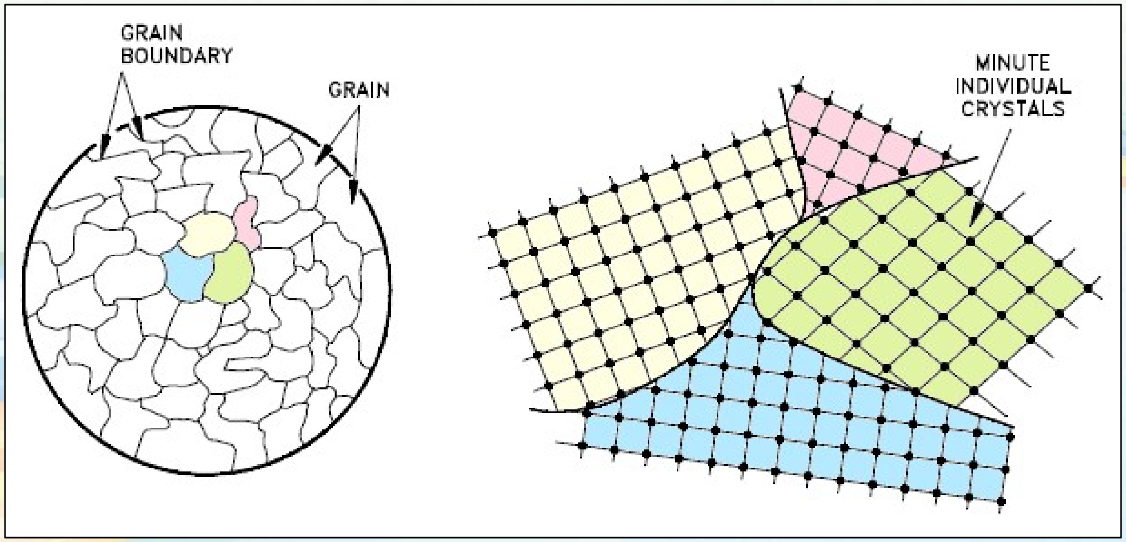
Edge, Screw, and Mixed Dislocations



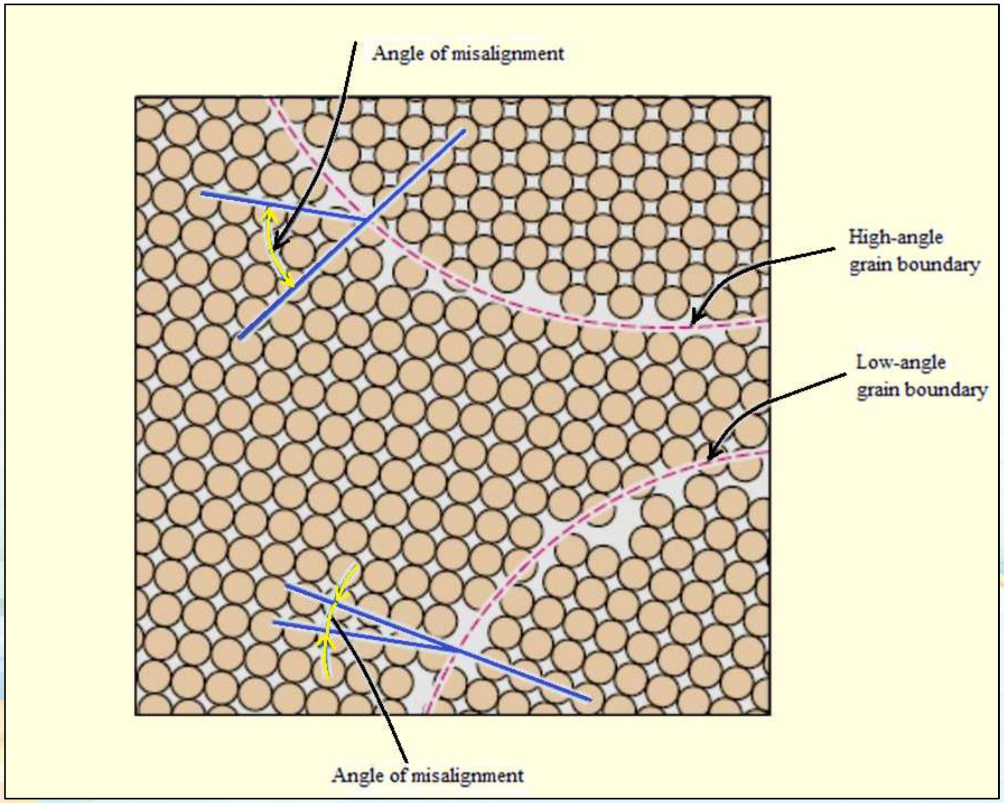
Interfacial Defects

- Interfacial defects are two dimensional boundaries with different crystal structures and/or orientations.
- External surface: where the crystal terminates.
- Grain boundaries: crystal often form groups of atoms known as grains, which when combined with other grains in a large crystal, often have misalignments that form boundaries.
- Phase boundaries: where a crystal forms more than one phase (i.e. solid and liquid)
- Polycrystalline material comprised of many small crystals or grains.
- The grains have different crystallographic orientation.

- *There exist atomic mismatch within the regions where grains meet. These regions are called grain boundaries.*
- *Surfaces and interfaces are reactive and impurities tend to segregate there. Since energy is associated with interfaces, grains tend to grow in size at the expense of smaller grains to minimize energy.*

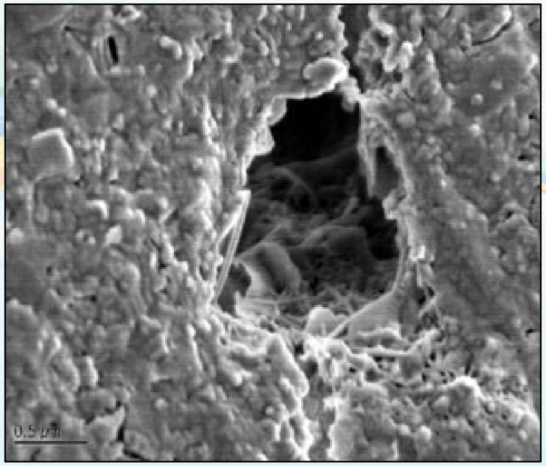


- *High and Low Angle Grain Boundaries:*
- *Depending on misalignments of atomic planes between adjacent grains we can distinguish between the low and high angle grain boundaries*



Bulk or Volume Defects

- Bulk defects occur on a much bigger scale than the rest of the crystal defects discussed.
- Voids are regions where there are a large number of atoms missing from the lattice.
- Pores - can greatly affect optical, thermal, mechanical properties.
- Cracks - can greatly affect mechanical properties.
- Foreign inclusions - can greatly affect electrical, mechanical, optical properties
- The image is a void in a piece of metal. The image was acquired using a Scanning Electron Microscope (SEM).



Atomic Vibrations

- Heat causes atoms to vibrate.
- Vibration amplitude increases with temperature.
- Melting occurs when vibrations are sufficient to rupture bonds.
- Vibrational frequency ~ 10^{13} Hz.
- Average atomic energy due to thermal excitation is of order kT.