Imperfections in solids

Textbook: Ch 4, Fundamentals of Materials Science and Engineering, Callister Jr., 5th edition, John Wiley and Sons Inc
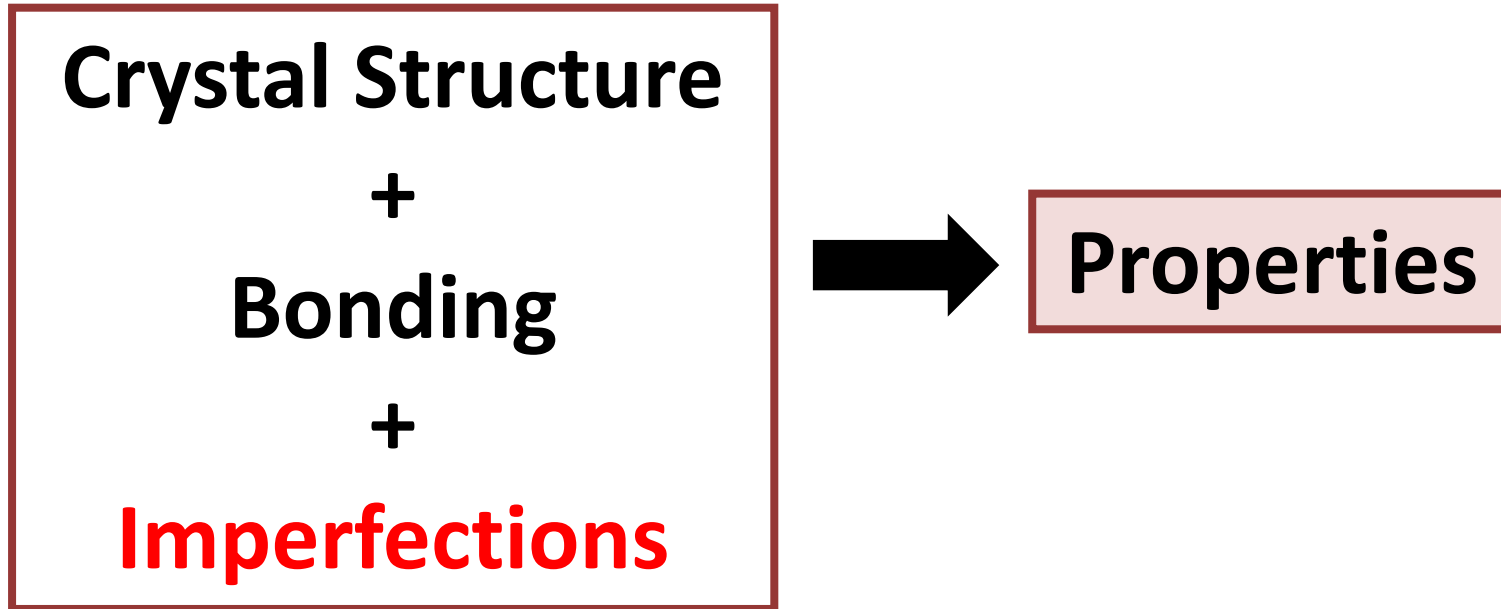
QUIZ-1

Sep 5/6, 2014 (Monday), LBC102

Syllabus:

- Atomic Structure and Bonding
- Structure of Crystalline Solids

Why are imperfections important?

Crystal Structure

+

Bonding

+

Imperfections

➡️ **Properties**

Examples:
Doping in Si
Formation of alloy
Secondary processing of metals (rolling, forging etc.)
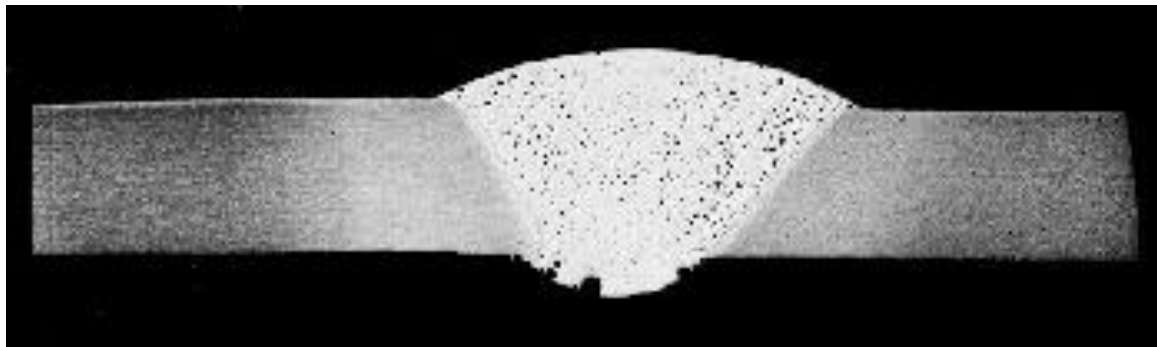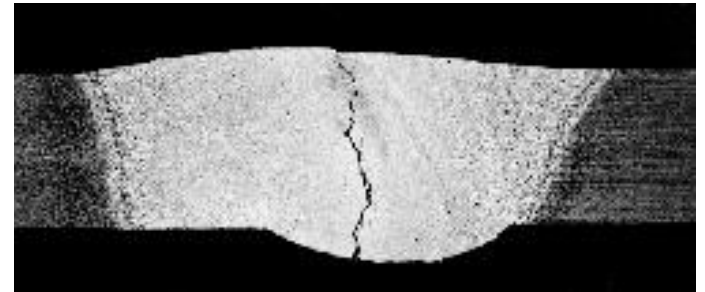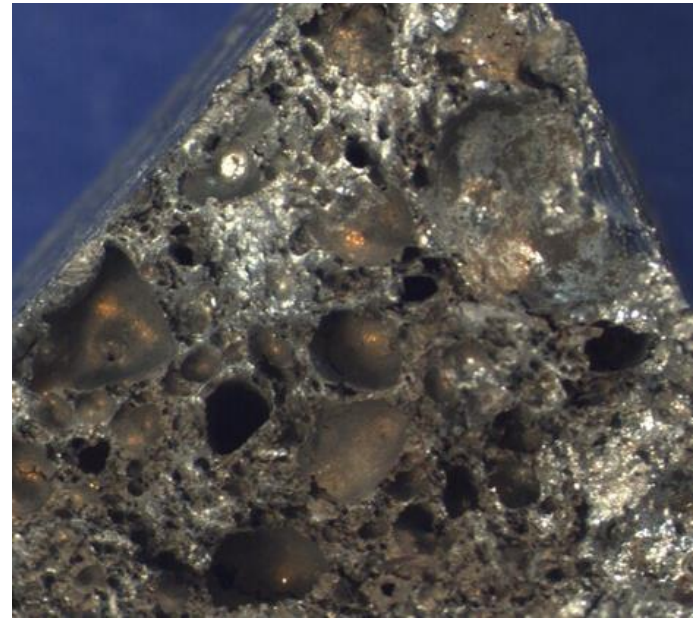
Classification based on dimensionality

o **Point Defects (0-D)**

o **Linear Defects (1-D)**

o **Interfacial Defects (2-D)**

o **Bulk or volume Defects (3-D)**

Outline

- **Pores**

- **Cracks**

- **Foreign inclusions**

Outline

o **Point Defects**

o **Linear Defects**

o **Interfacial Defects**

o **Bulk or volume Defects**

Macrostructure

Microstructure

Figure: High purity polycrystalline lead ingot. The individual grains are of macroscopic dimensions and are visible to unaided eye i.e., without using a microscope
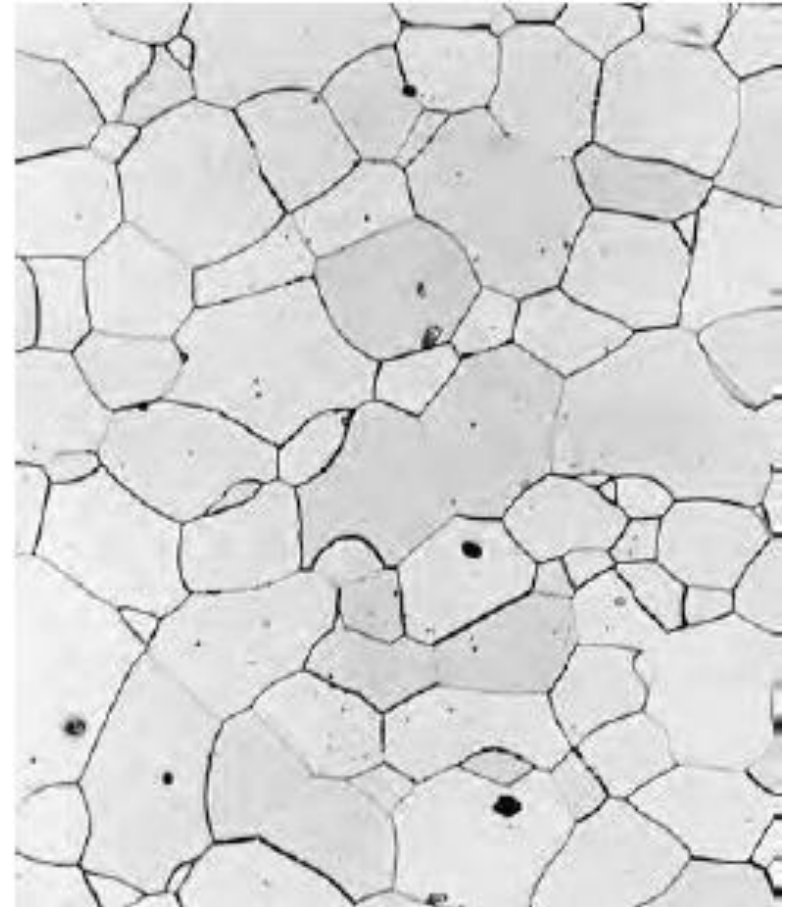
Most materials have grains of diameters on the order of microns. Need a microscope to investigate the microstructure.

- **interfacial** or **planar defects**
  - occupy an area or surface and are therefore bidimensional.
- Other examples of this form of defects include:
  - grain boundaries
  - twin boundaries
  - anti-phase boundaries
  - free surface of materials
- Of all these, the **grain boundaries** are the most important from the **mechanical properties point of view**.

External surfaces

External surface is one along which the crystal

structure terminates.
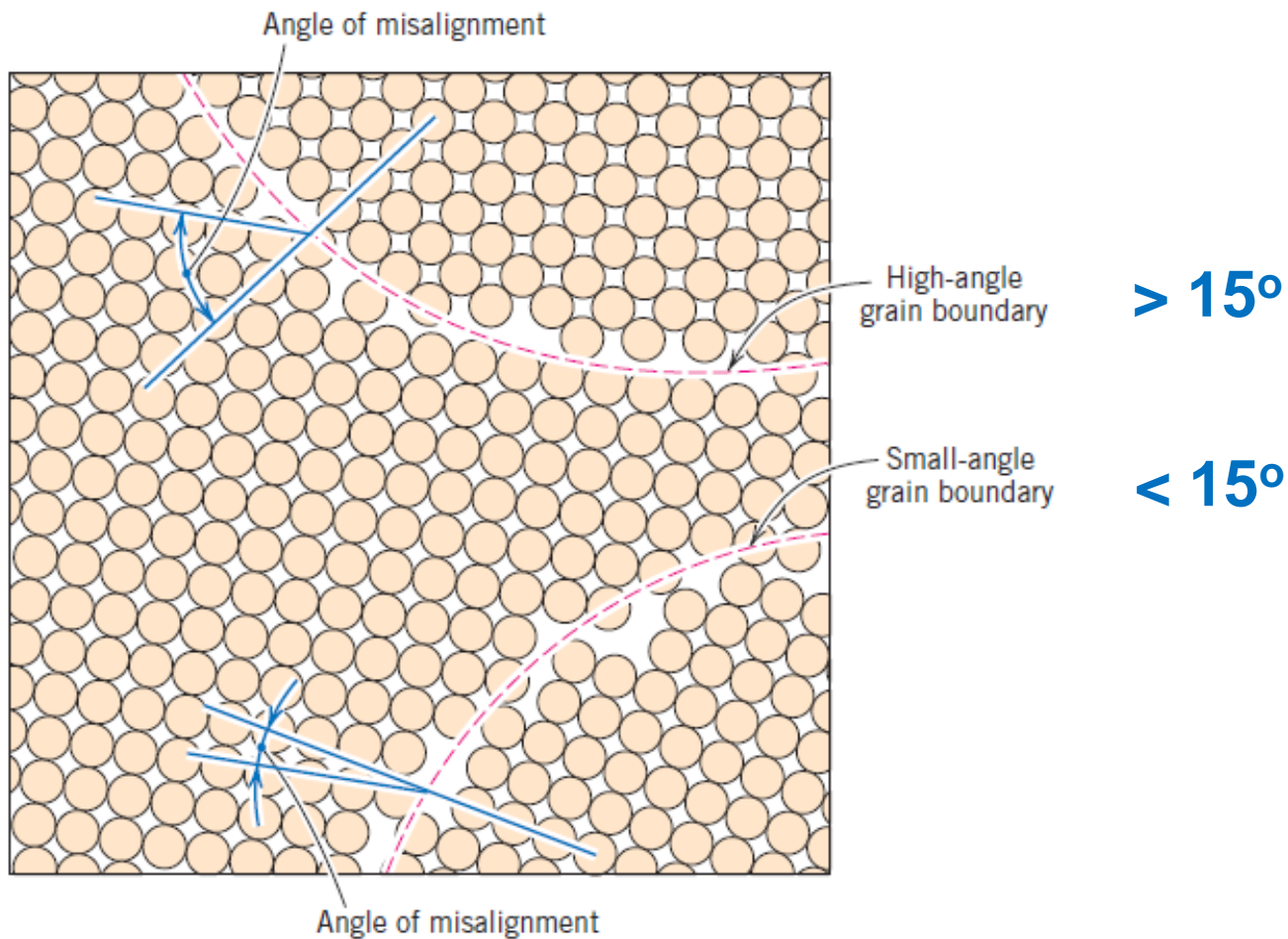
Grain boundaries

- Crystalline solids (most materials) generally consist of millions of individual grains separated by boundaries.

- Each grain (or subgrain) is a **single crystal**.

- Within each individual grain there is a **systematic packing of atoms**. Therefore each grain has **different orientation** (see Figure) and is separated from the neighboring grain by grain boundary.

- When the **misorientation between two grains is small**, the grain boundary can be described by a relatively simple configuration of dislocations (e.g., an edge dislocation wall) and is, fittingly, called a **low-angle boundary**.
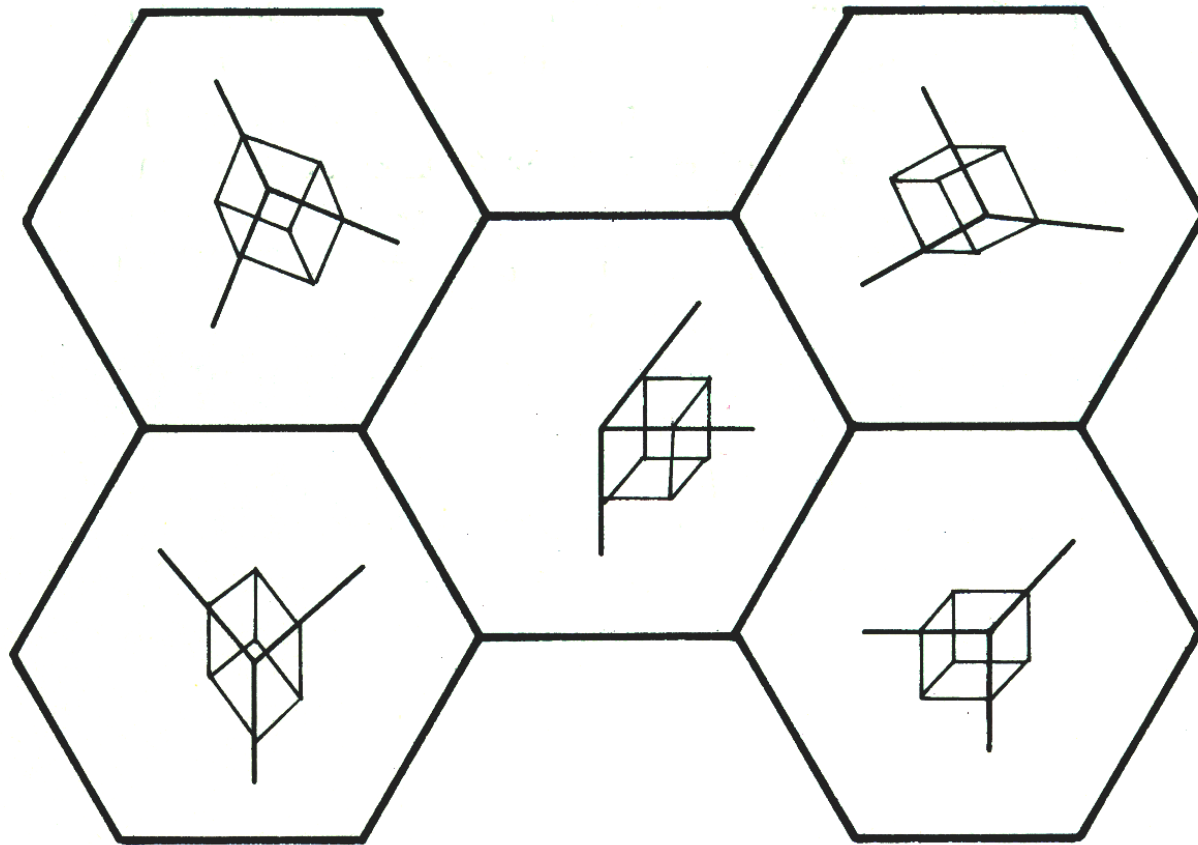
Grains in a metal or ceramic; the cube depicted in each grain indicates the crystallographic orientation of the grain in schematic fashion

- When the misorientation is large (high-angle grain boundary), more complicated structures are involved (as in a configuration of soap bubbles simulating the atomic planes in crystal lattices).

- The grain boundaries are therefore:
  - where grains meet in a solid.
  - transition regions between the neighboring crystals.
  - Where there is a disturbance in the atomic packing, as shown in Figure.

- These **transition regions** (grain boundaries) may consist of various kinds of **dislocation arrangements**.

A boundary separating two grains or crystals having different crystallographic orientations in polycrystalline materials

Angle of misalignment

High-angle grain boundary **> 15º**

Small-angle grain boundary **< 15º**

Angle of misalignment
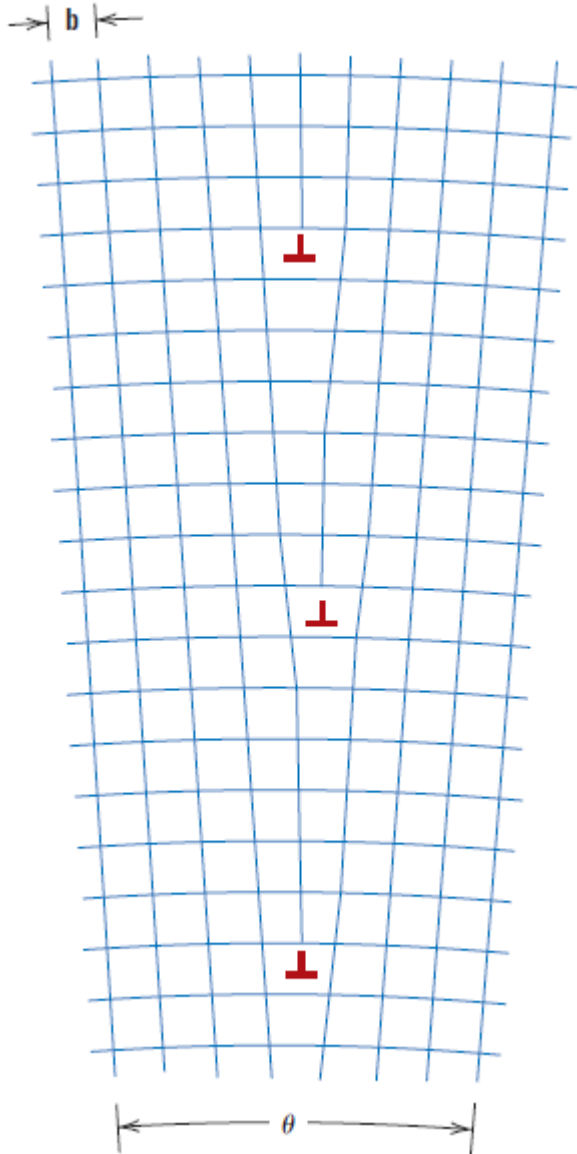
Tilt boundaries

Small angle grain boundaries consisting entirely of edge dislocations are called tilt boundaries.

The angle of misrientation: Θ

Characteristics of grain boundaries

▪ The grain boundary is associated with energy which is called grain boundary energy (GBE) or interfacial energy. The magnitude of this energy is a function of the degree of misorientation.

$$GBE_{\text{high-angle boundaries}} > GBE_{\text{low-angle boundaries}}$$

▪ Grain boundaries are more chemically reactive than the grains themselves as a consequence of this boundary energy. Furthermore, impurity atoms often preferentially segregate along these boundaries because of their higher energy state.

▪ The total interfacial energy is lower in large or coarse-grained materials than in fine-grained ones, because there is less total boundary area in the former.

▪ Grains grow at elevated temperatures to reduce the total boundary energy.

Twin boundaries

A twin boundary is a special type of grain boundary across which atoms on one side of the boundary are located in mirror-image positions of the atoms on the other side. The material between two such boundaries is appropriately termed a **twin**.

two types of twins:

- Mechanical Twins

- Annealing Twins

Plane of Paper ($\bar{1}10$)

(111) Twin Plane
[11$\bar{2}$] Twin Direction
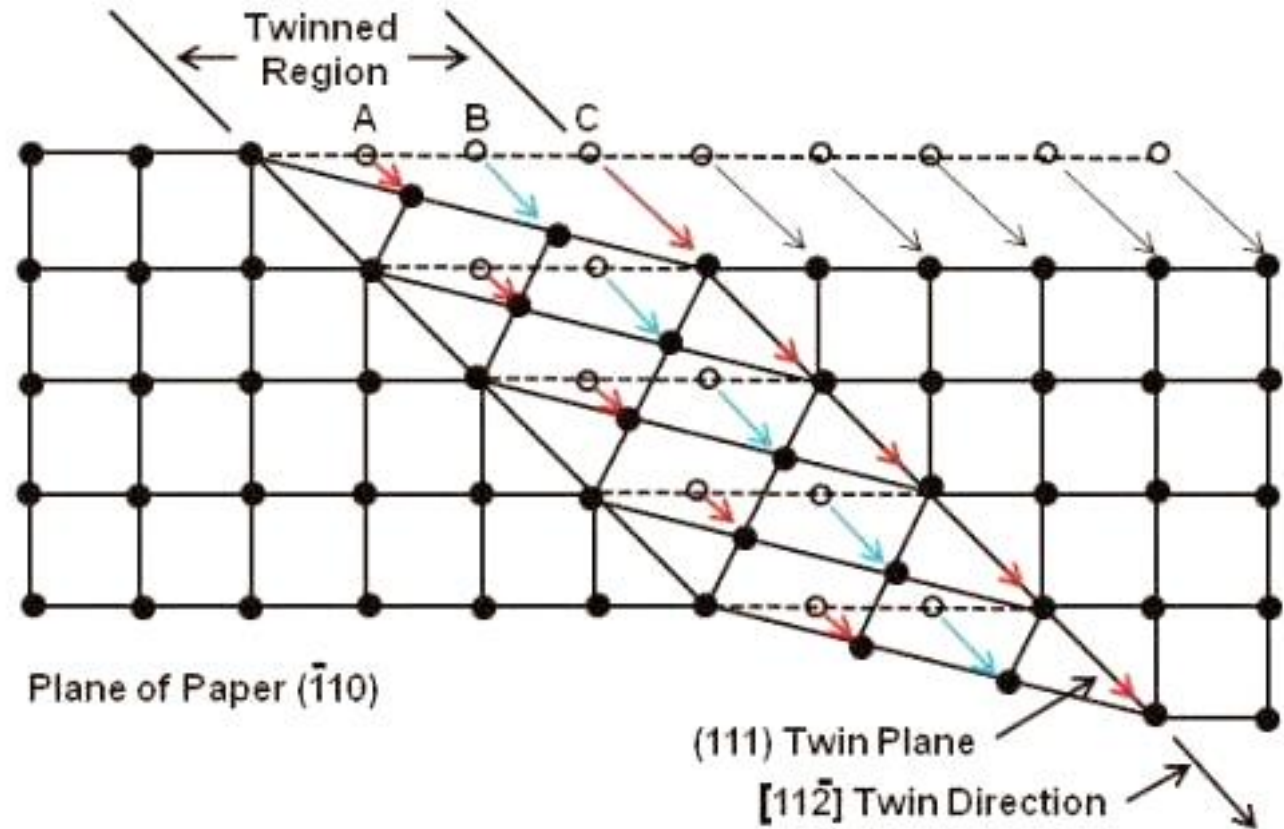
- Mechanical twins: Twins resulting from atomic displacements that are produced from applied mechanical shear forces.

- Annealing twins: Twins which appear during annealing heat treatments following mechanical deformation.

- Twinning occurs on a definite crystallographic plane and in a specific direction.

- Annealing twins are found in FCC metals.

- Mechanical twins are observed in BCC and HCP metals.
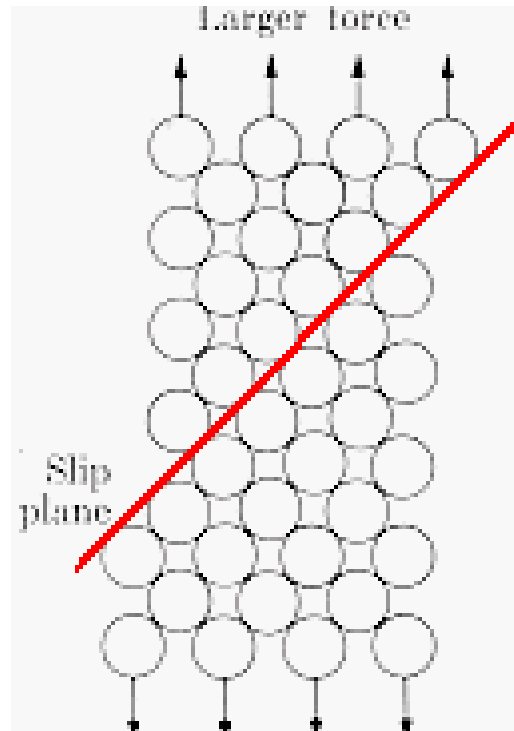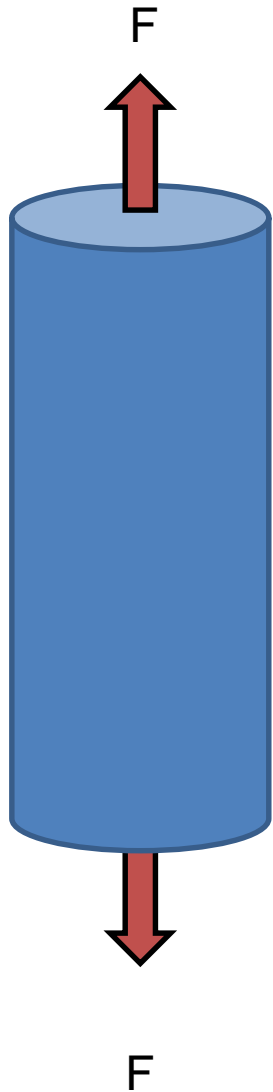
Annealing Twins in FCC brass

(c) 200 μm

The twins correspond to those regions having relatively straight and parallel sides.

There is a different visual contrast compared to untwinned regions of the grains within which they reside.
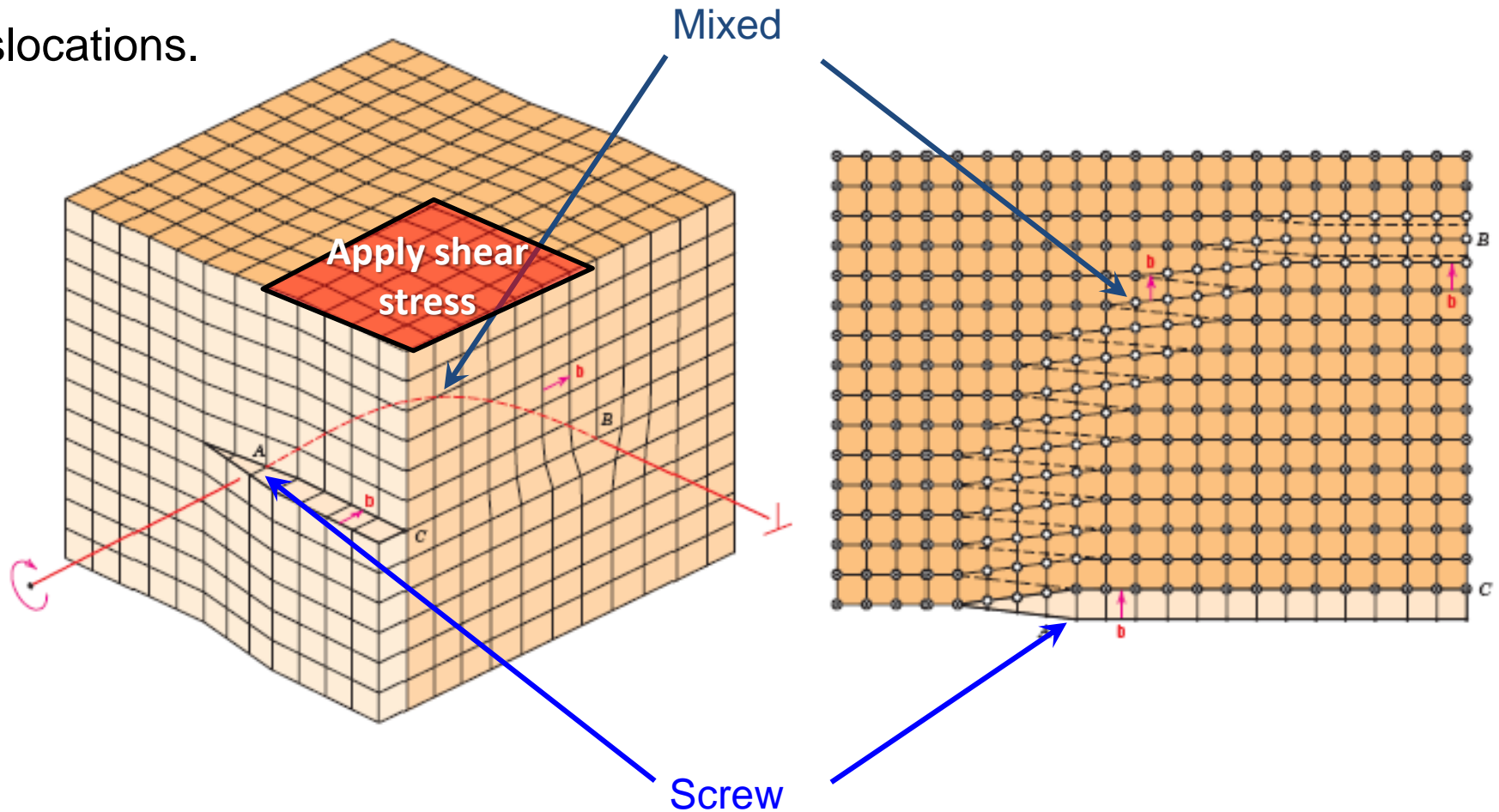
Outline

Plastic deformation is mediated by slip

F

F

Larger force

Slip plane
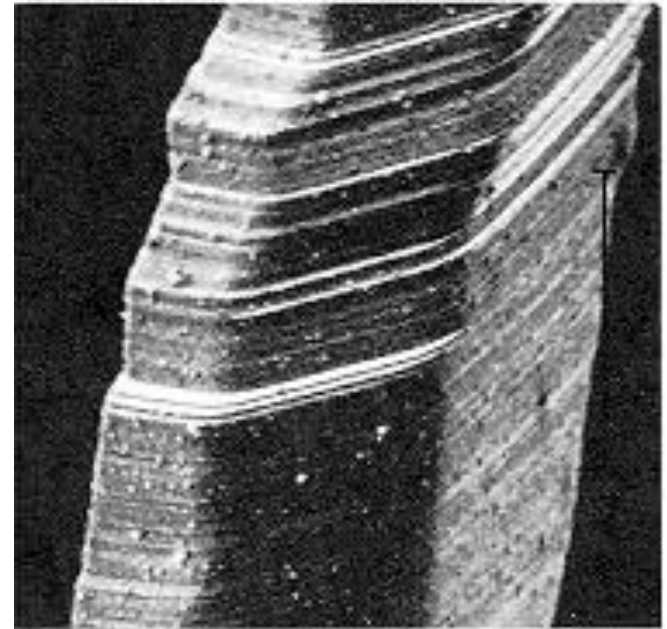
Deformation in single crystals

Mixed Dislocation: The reality

Mixed dislocations are intermediate between edge dislocations and screw dislocations.

Mixed

Apply shear stress

Screw

Adapted from Fig. 4.5, *Callister & Rethwisch 8e.*

Burgers vector is neither perpendicular nor parallel to dislocation line.
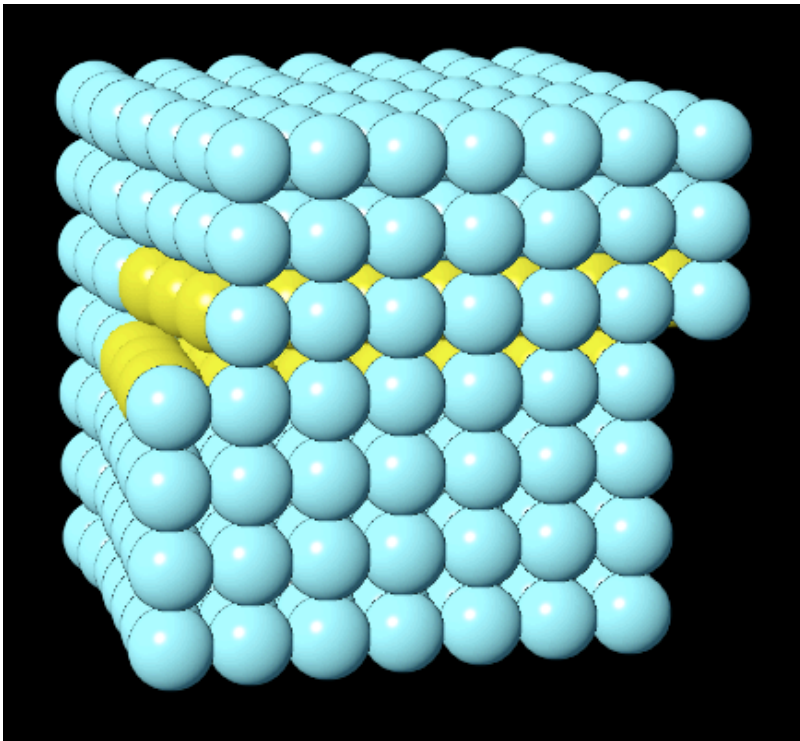
Slip caused by movement of edge dislocation
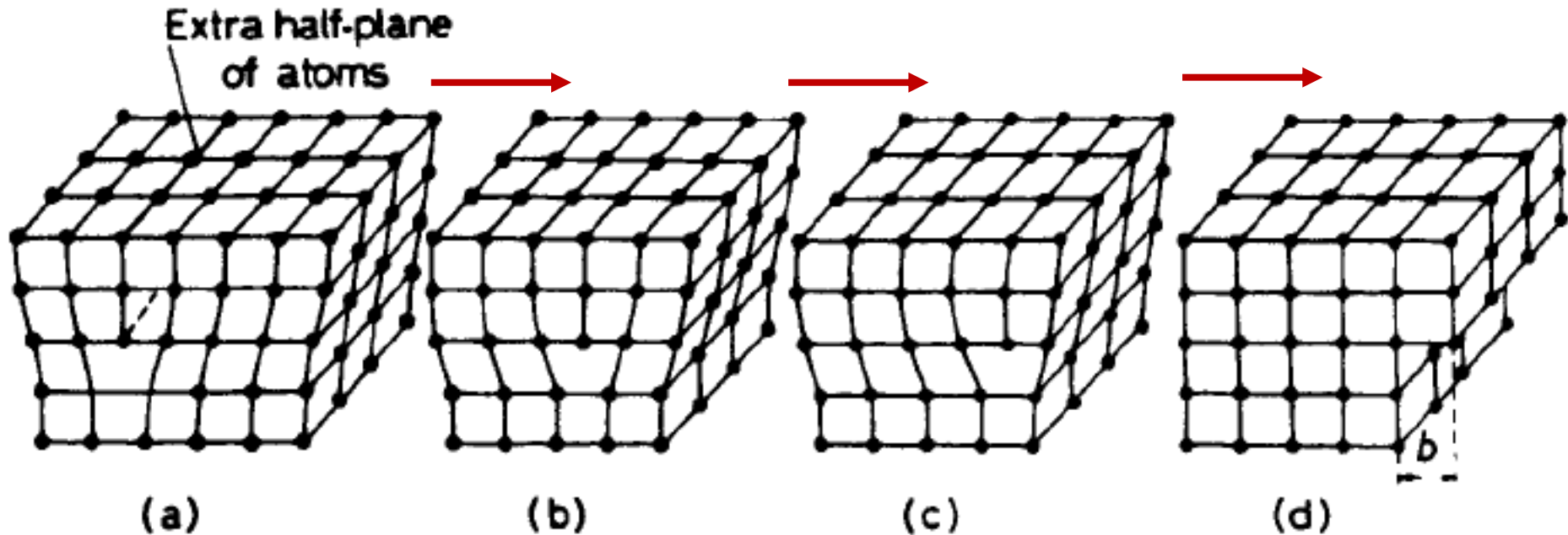
Plastic deformation occurs due to slip on close packed planes along close packed directions.
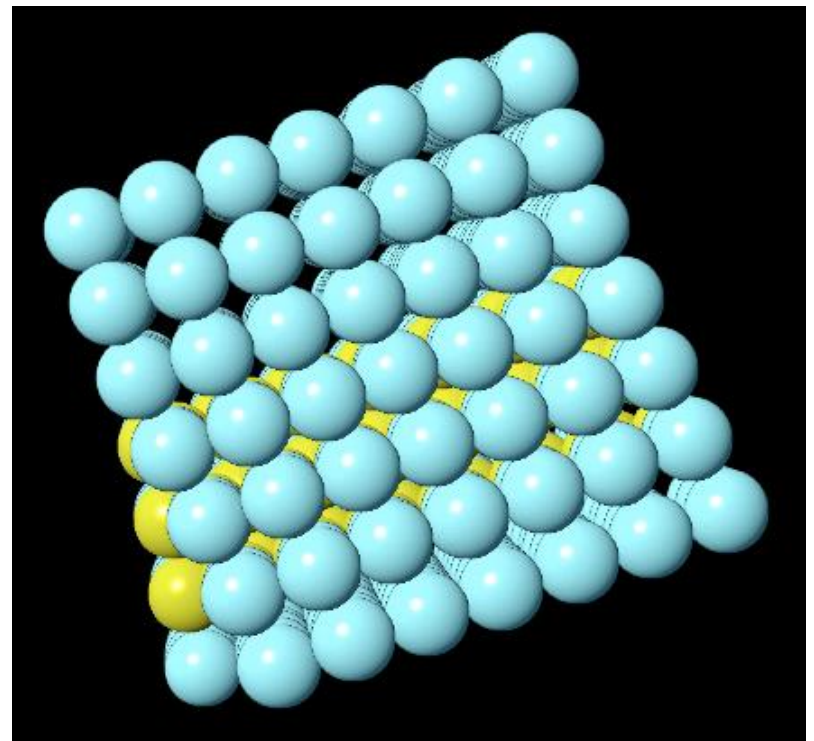
Slip due to the movement of screw dislocation

(a)   (b)   (c)
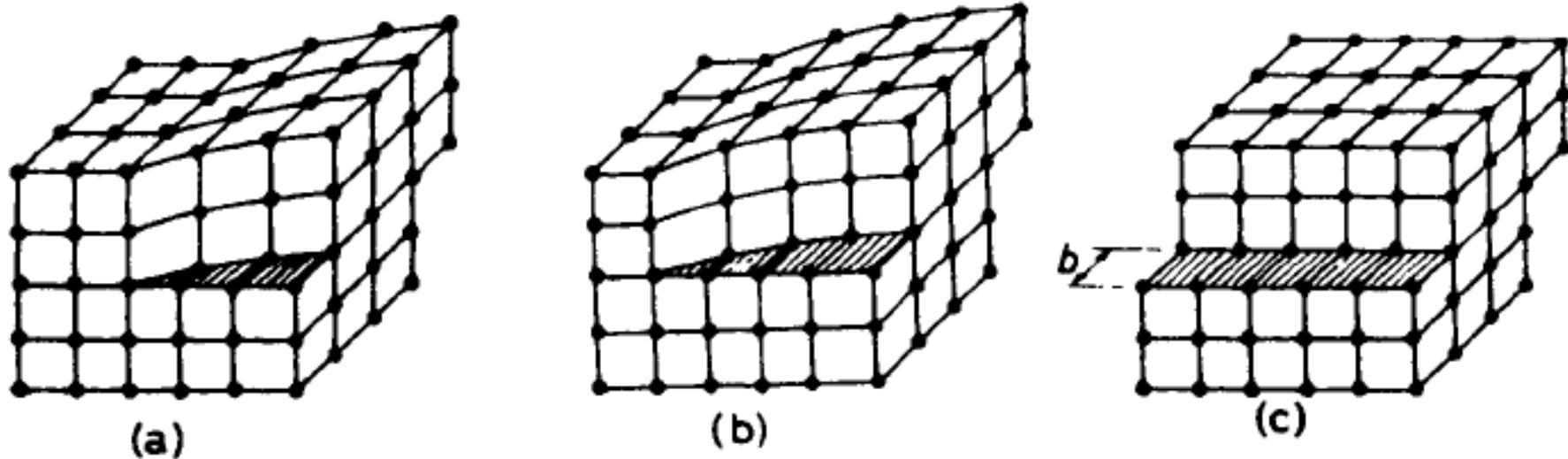
VMSE: Screw Dislocation

- In VMSE:
  - a region of crystal containing a dislocation can be rotated in 3D
  - dislocation motion may be animated

Front View

Top View

VMSE Screen Shots

Dislocations

- A dislocation is a linear or one-dimensional defect around which some of the atoms are misaligned.
- A dislocation is a boundary between slipped and unslipped parts of the crystal lying on a slip plane.
- A dislocation is characterized by dislocation line and Burgers vector.
- Dislocations are associated with lattice distortions. The magnitude and direction of the lattice distortion associated with a dislocation is expressed in terms of a Burgers vector, denoted by **b**.

There are **two** types of dislocation:
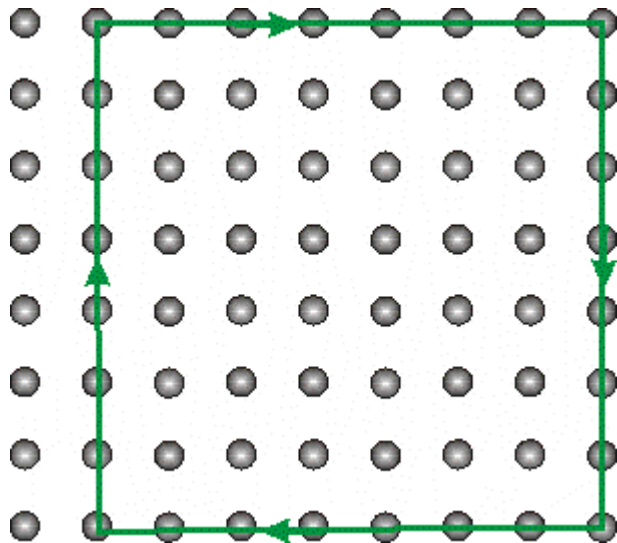
o Edge dislocation

o Screw dislocation

Edge Dislocation

An edge dislocation is a defect where an extra half-plane of atoms is introduced mid way through the crystal, distorting nearby planes of atoms.
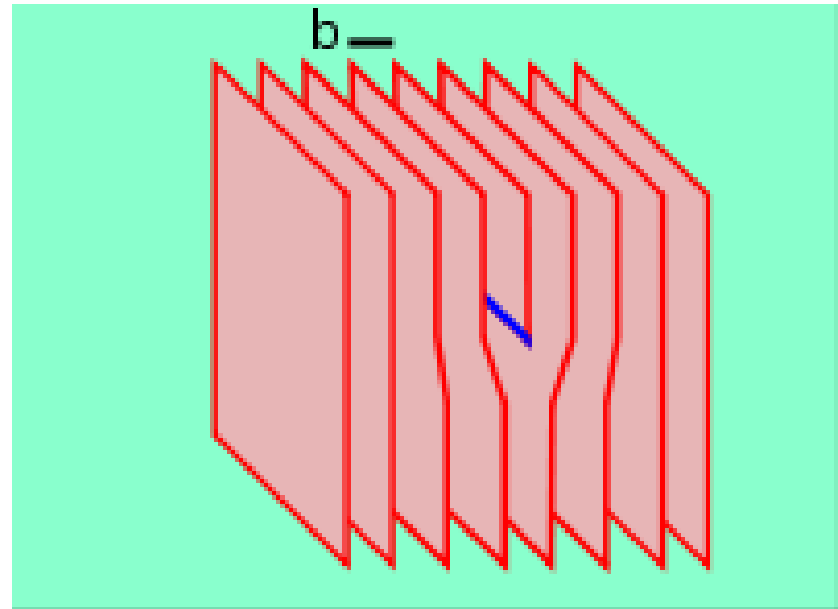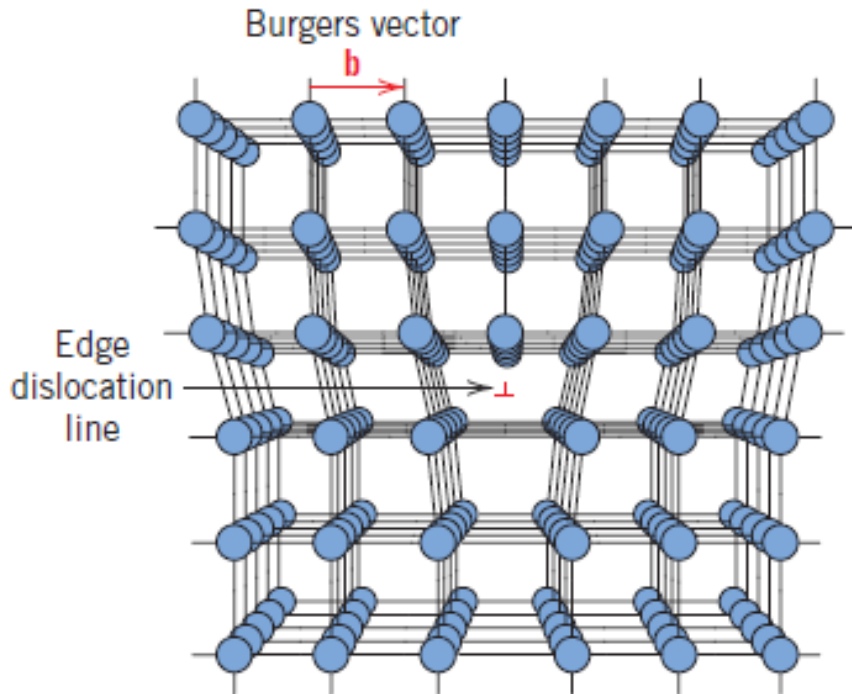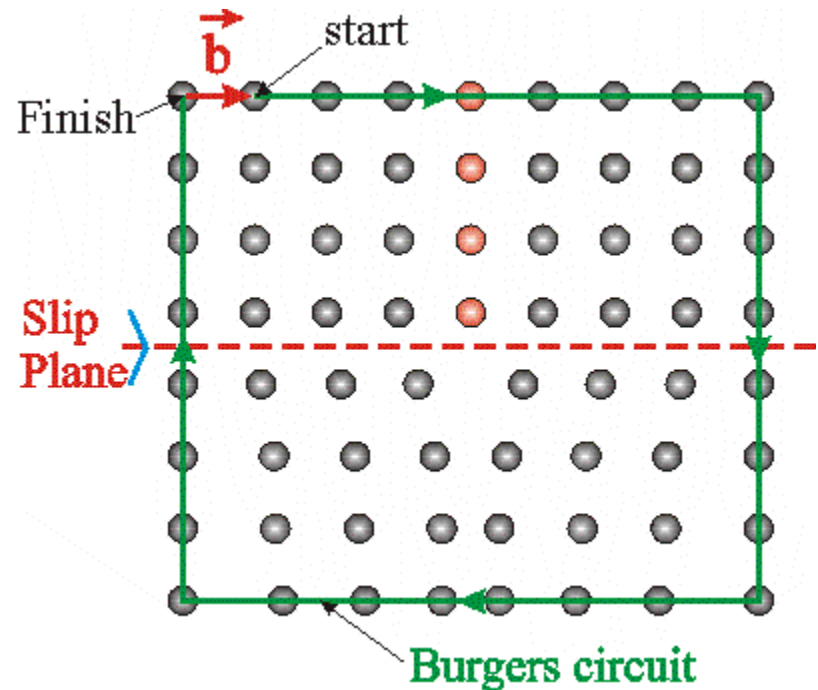

Burgers vector is perpendicular to dislocation line.

Burgers vector and Burgers circuit


Perfect crystal

Crystal with edge dislocation

- The closure failure is the Burgers vector.
- Right-hand/ Finish-Start convention
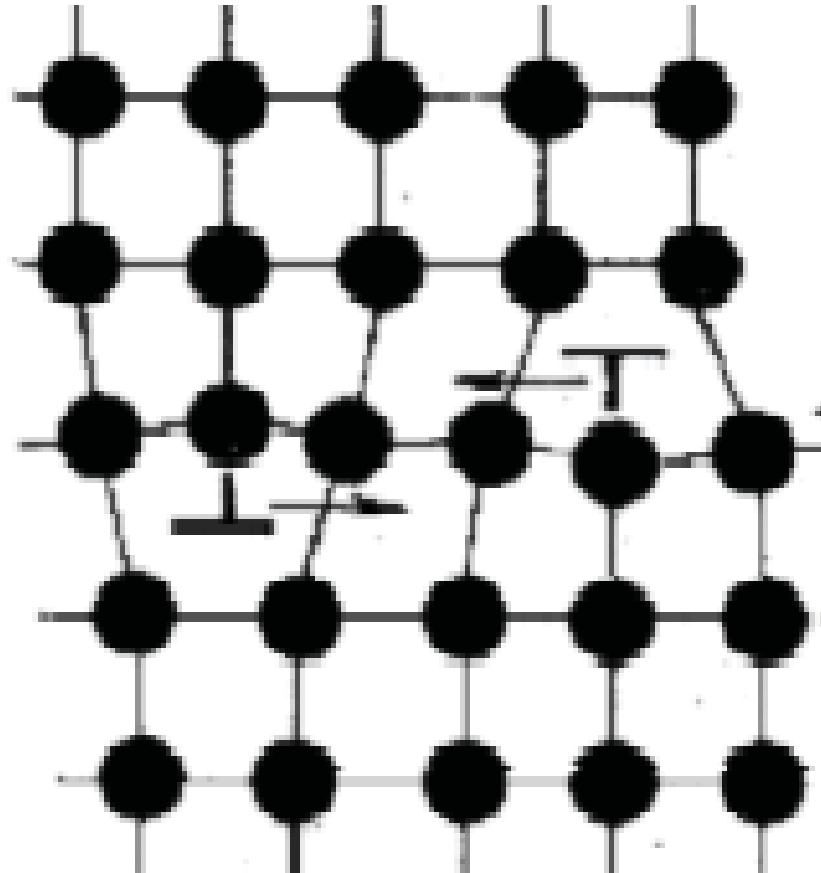
Burgers vector

- For metallic materials, Burgers vector for a dislocation will point in a close-packed crystallographic direction, and will be of magnitude equal to the interatomic spacing.

- Burgers vector remains unchanged at all points on the dislocation line.
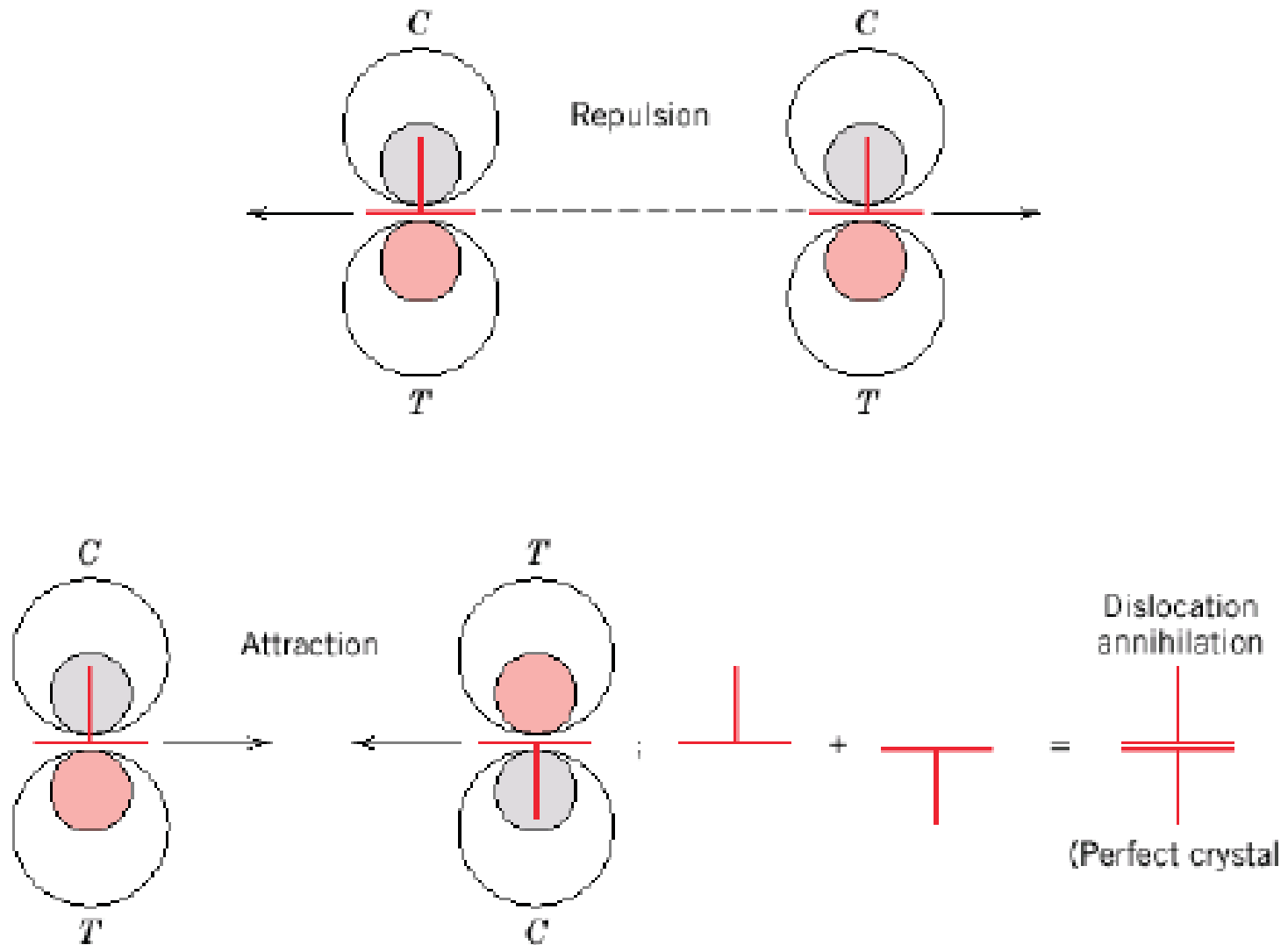
Summary: Edge Dislocation

- Has an extra half plane.
- The edge dislocation centers around the line that is defined along the end of the extra half plane of atoms. This is called the dislocation line.
- For a positive dislocation, the atoms above the dislocation line are squeezed together, and those below the line are pulled apart. The magnitude of this distortion is maximum at the dislocation line and decreases with distance away from the dislocation line.
- A positive edge dislocation is represented by the symbol ⊥
- A negative edge dislocation is formed by an extra plane of atoms that is included in the bottom portion of the crystal.
- A negative edge dislocation is designated by the symbol ⊤
- Burgers vector of an edge dislocation is perpendicular to the dislocation line.
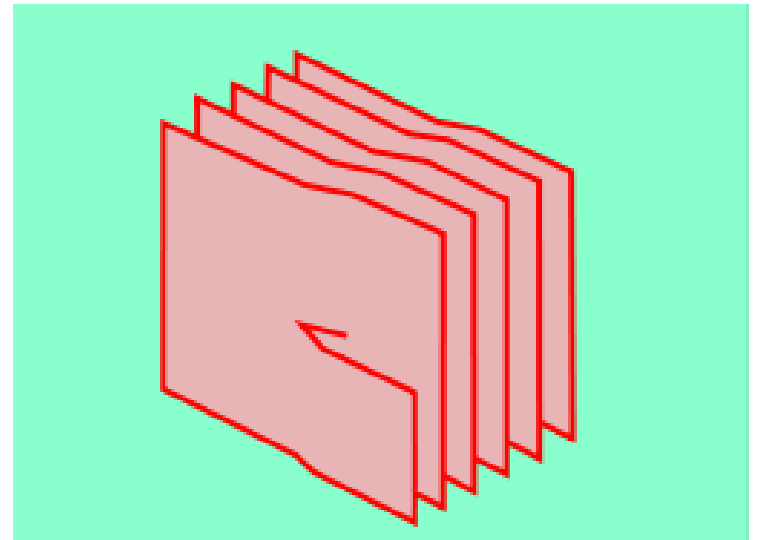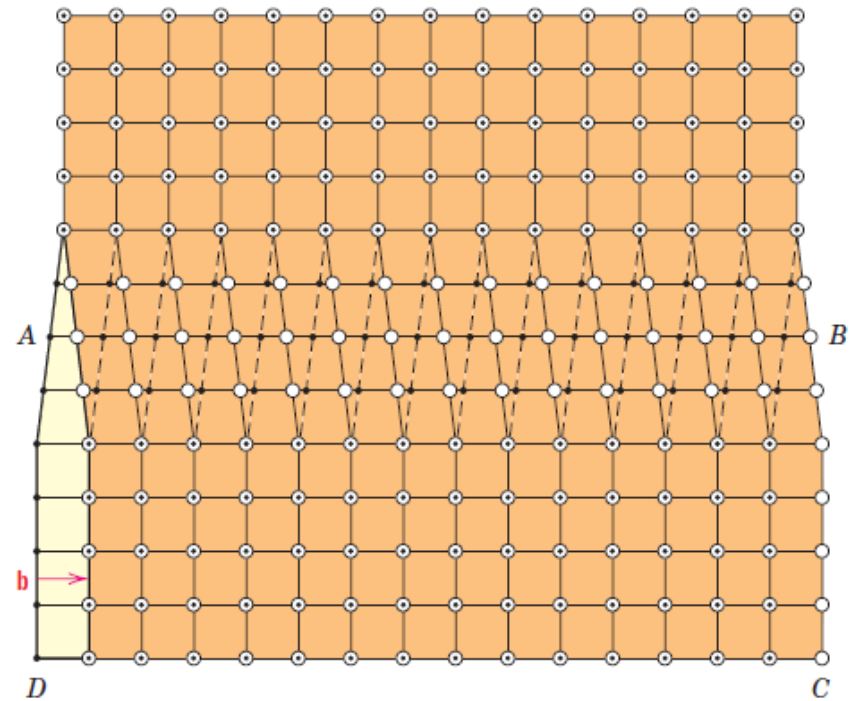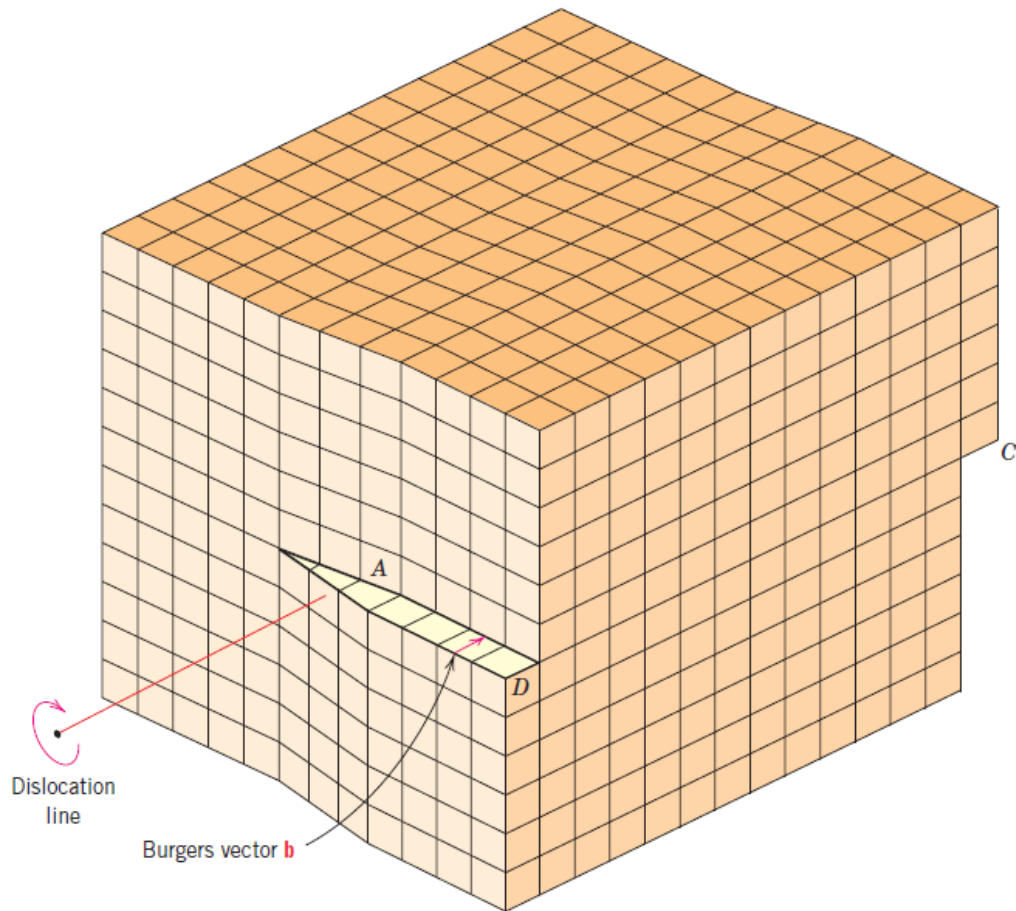- The dislocation line moves parallel to the Burgers vector.
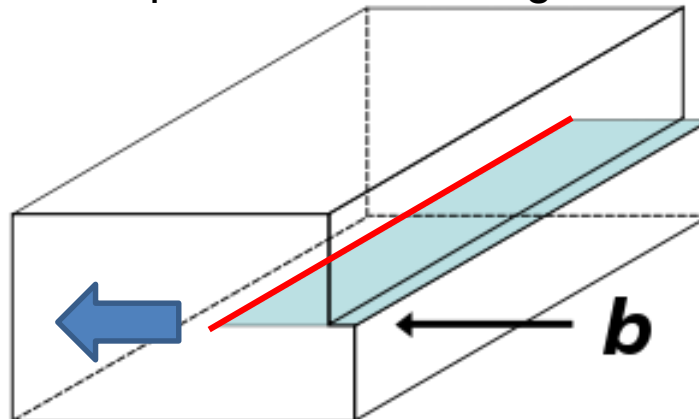
o Positive Edge dislocation

o Negative Edge dislocation

Annihilation of dislocation
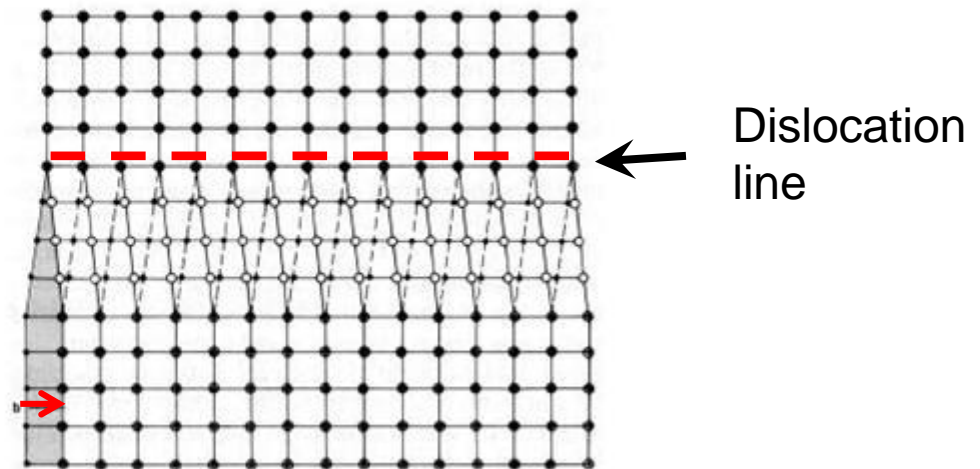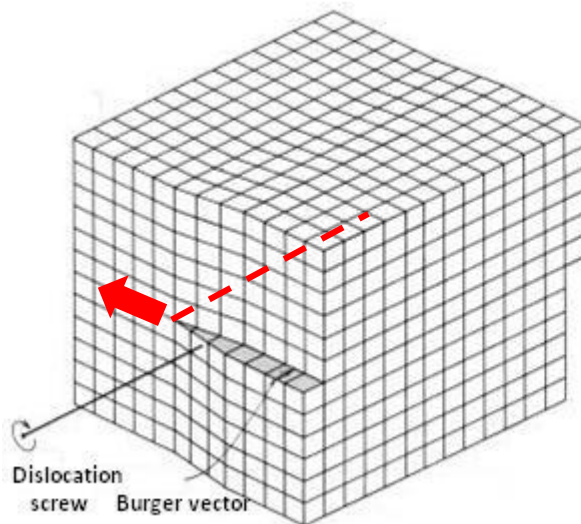
Screw Dislocation

Dislocation line

Burgers vector **b**

Burgers vector is parallel to dislocation line.

Summary: Screw Dislocation

- Formed by a shear stress
- Burgers vector is parallel to the dislocation line.
- Direction of motion of dislocation line is perpendicular to Burgers vector.
- The upper front of the crystal is shifted one atomic distance right with respect to the bottom portion.
- Line AB is the dislocation line.
- The atomic distortion associated with edge dislocation is also linear.
- The screw dislocation gets its name from the spiral or helical path that is traced around the dislocation line.
- A screw dislocation is designated by ↻

Dislocation screw   Burger vector

Dislocation line

How many dislocations?

	Dislocation density, cm^{-2}
Slowly solidified metal	10^5
Heavily cold worked metal	10^{12}
Completely annealed metal	10^6

"Seeing" dislocations

o Etch pit Technique

o Transmission Electron Microscopy

o Field Ion Microscopy

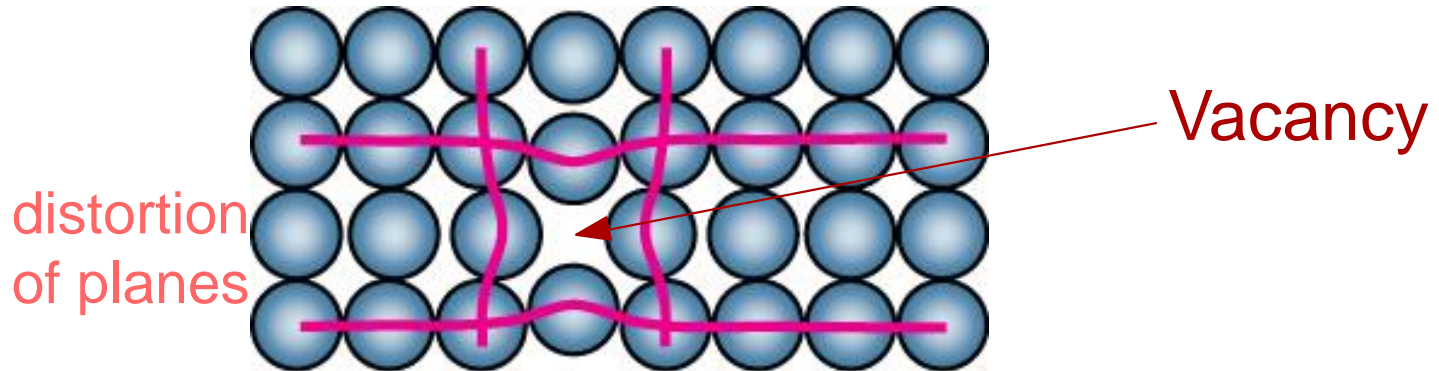o Atom Probe Techniques

How dislocations look?
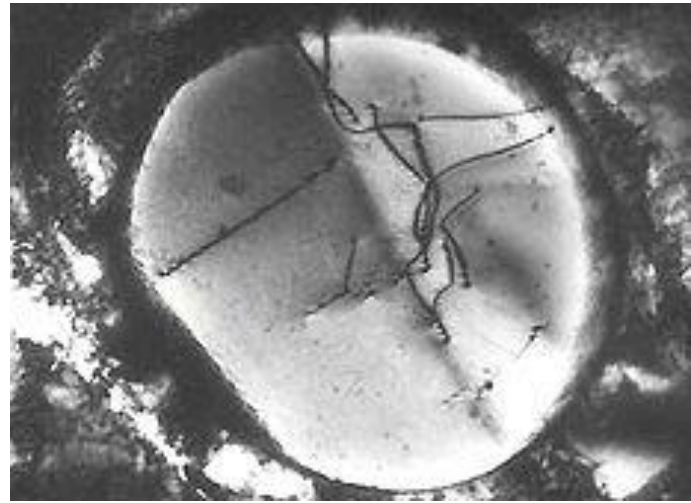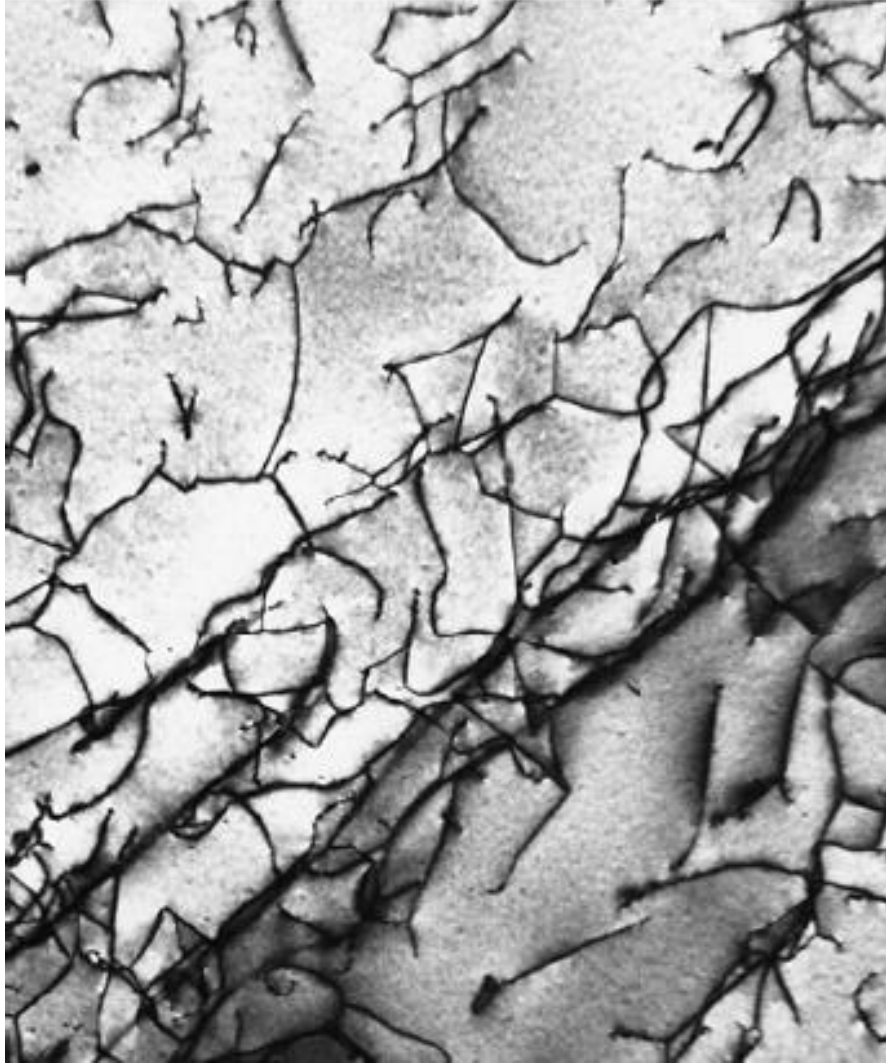
Outline

o **Point Defects**

o Linear Defects

o Interfacial Defects

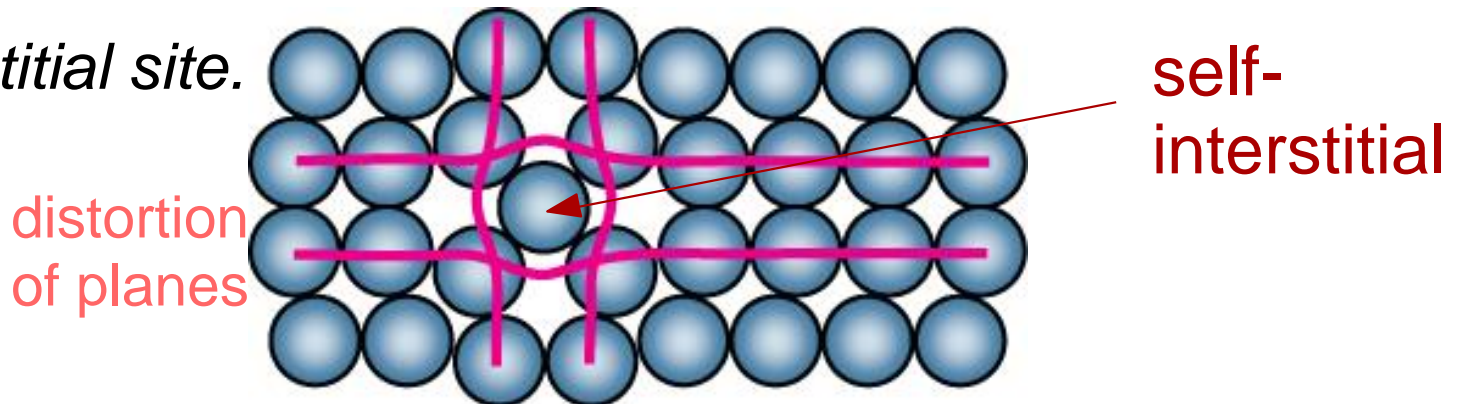o Bulk or volume Defects

Point Defects (0-D)

1. Vacancies

When an atom is missing from lattice site, vacancy is created.

distortion of planes — Vacancy

2. Self Interstitial

A self-interstitial is an atom from the crystal that is crowded into an interstitial site.

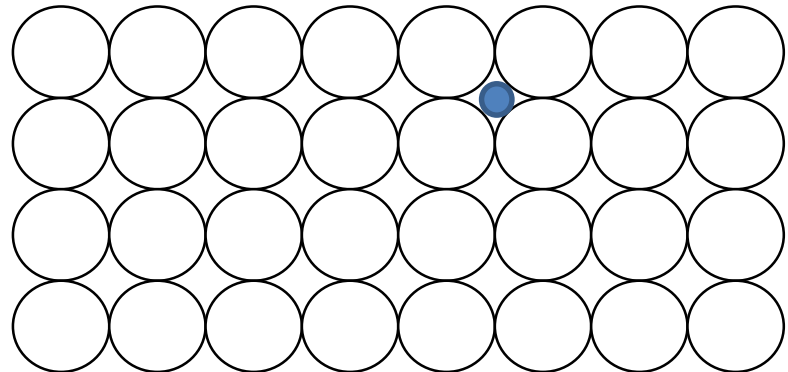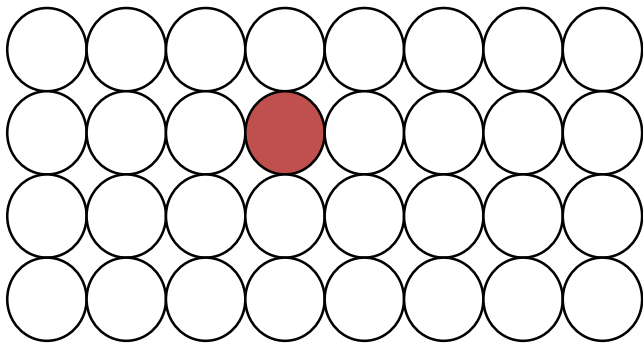distortion of planes — self-interstitial

Point Defects

3. Impurities in solids

Addition of alloying element may be considered as an impurity in solids.

(A metal of 99.9999% purity contains 10^{22}-10^{23} impurity atoms per cubic metre)

Equilibrium Concentration: Point Defects

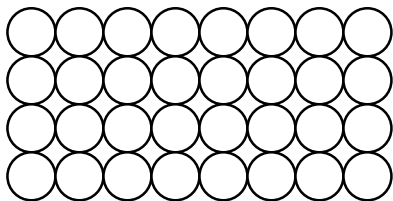• Equilibrium concentration varies with temperature!

No. of defects

Activation energy

No. of potential defect sites

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

Temperature

Boltzmann's constant

(1.38 x 10^{-23} J/atom-K)

(8.62 x 10^{-5} eV/atom-K)

Each lattice site is a potential vacancy site
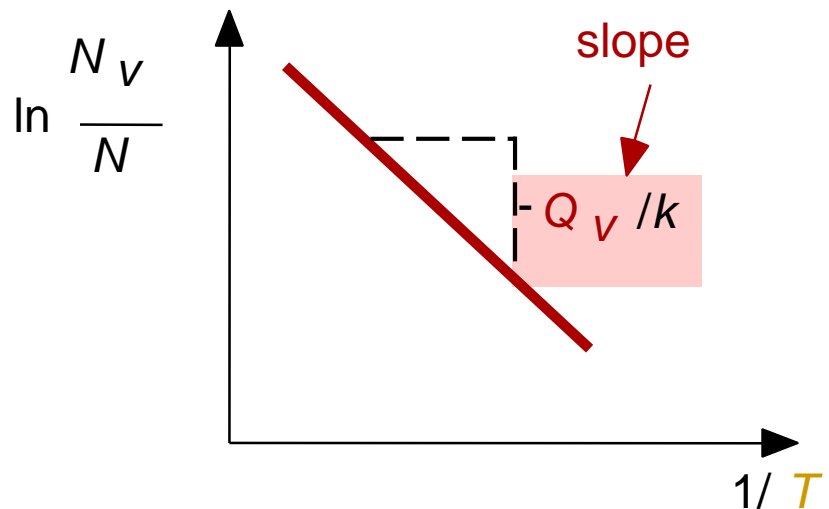
Measuring Activation Energy

- We can get Q_v from an experiment.

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

- Measure this...

- Replot it...

$\frac{N_v}{N}$

exponential dependence!

T

defect concentration

$\ln \frac{N_v}{N}$

slope

$-Q_v/k$
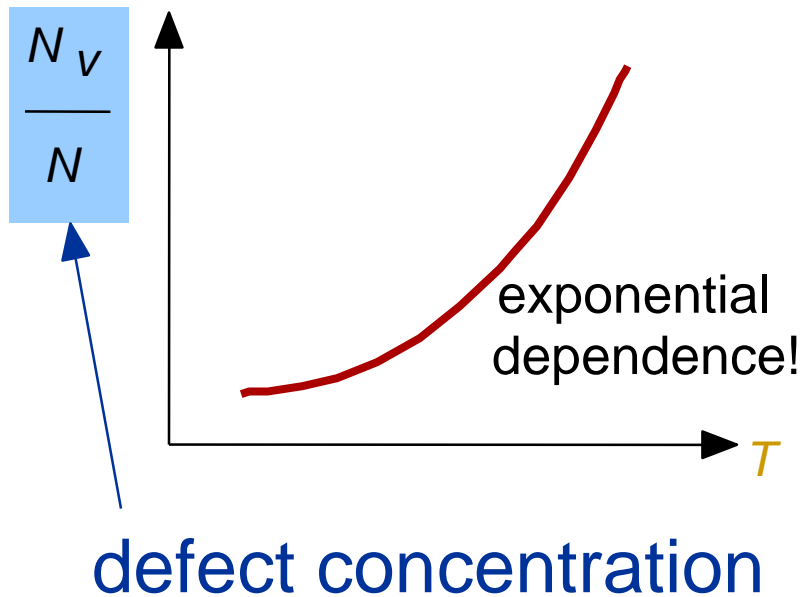
$1/T$

Estimating Vacancy Concentration

- Find the equil. # of vacancies in 1 m^3 of Cu at 1000°C.
- Given:

$$\rho = 8.4 \text{ g/cm}^3 \qquad A_{Cu} = 63.5 \text{ g/mol}$$

$$Q_v = 0.9 \text{ eV/atom} \qquad N_A = 6.02 \times 10^{23} \text{ atoms/mol}$$

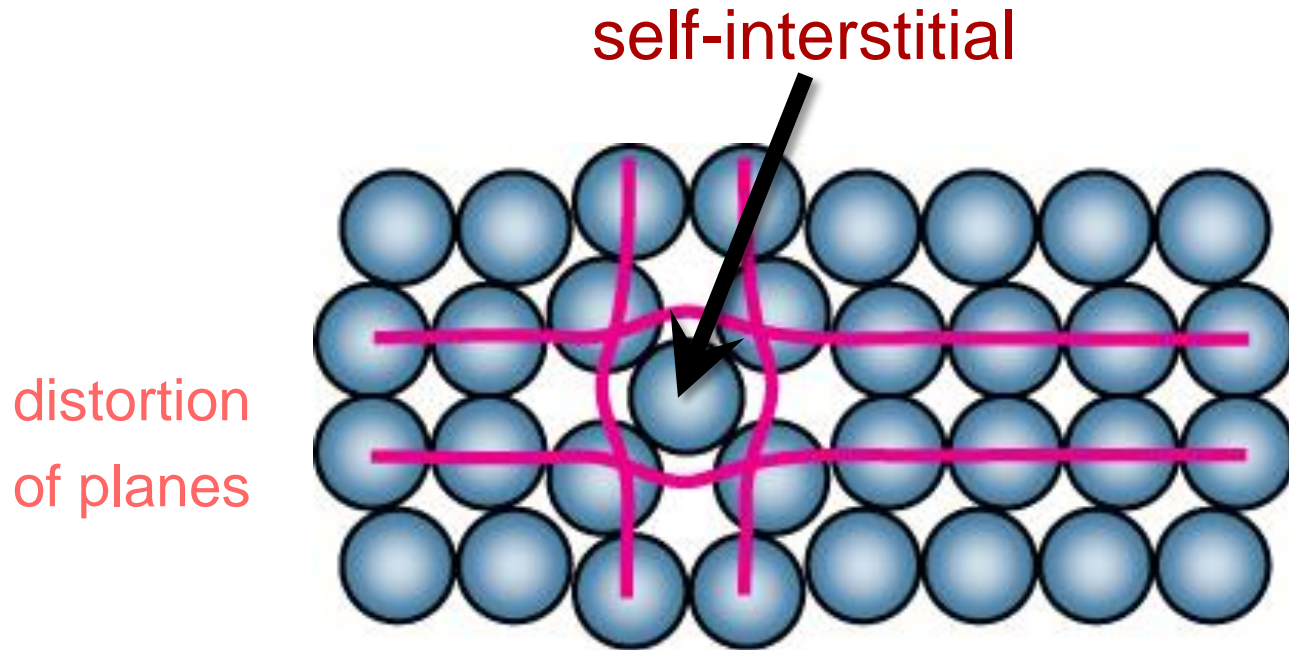$$\frac{N_v}{N} = \exp\left(\frac{-Q_v}{kT}\right) = 2.7 \times 10^{-4}$$

0.9 eV/atom

1273 K

8.62 x 10^{-5} eV/atom-K

For 1 m^3, $N = \rho \times \dfrac{N_A}{A_{Cu}} \times 1 \text{ m}^3 = 8.0 \times 10^{28}$ sites

- Answer:

$$N_v = (2.7 \times 10^{-4})(8.0 \times 10^{28}) \text{ sites} = 2.2 \times 10^{25} \text{ vacancies}$$

Self-interstitial

self-interstitial

distortion
of planes

In metals:

- relatively large distortions in the surrounding lattice
- since the radius of the atom > radius of interstitial void

less probable defect => very small concentrations, significantly lower than vacancies.

Impurities in solids and the concept of alloys

o Impurity atoms are added intentionally to a pure metal to impart specific characteristics to the metal.

o **Solid solution** forms when the solute atoms are added to the solvent atoms (host atoms), the crystal structure is maintained, and no new structures are formed. It is compositionally homogeneous; the impurity atoms are randomly and uniformly dispersed within the solid.

Solid Solutions

○ **Substitutional solid solution**
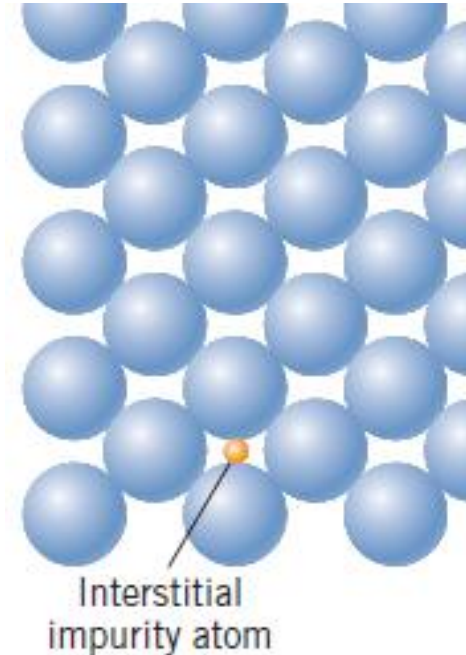
Solute atoms substitute for the solvent atoms
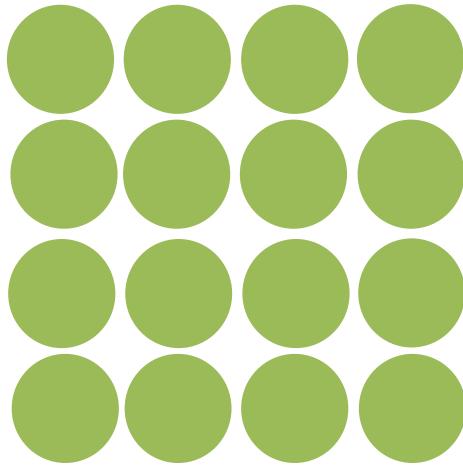Ex. Cu-Ni, Bi-Sb, Pt-Au

Substitutional impurity atom
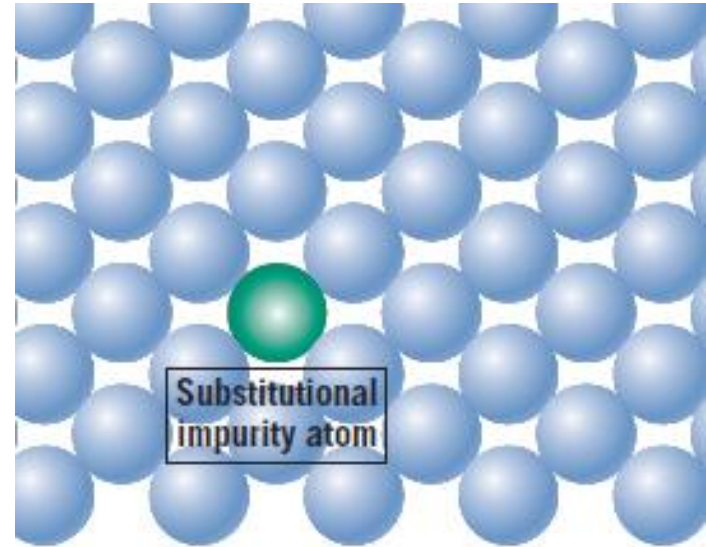
○ **Interstitial solid solution**

Solute atoms fill the voids or interstices among solvent atoms
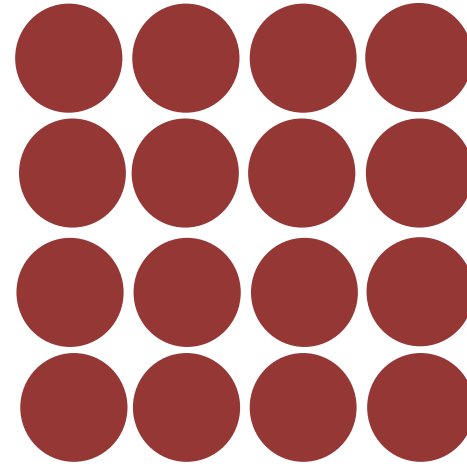Ex. Fe-C, Ti-B

Interstitial impurity atom
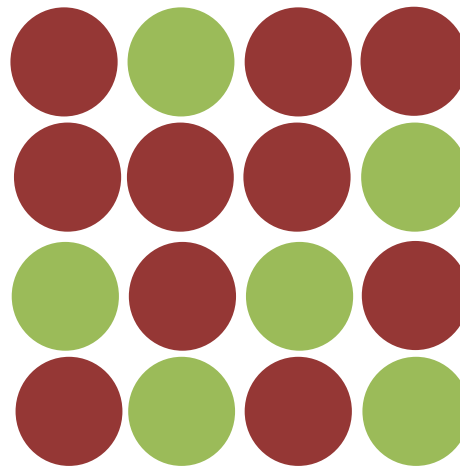
Formation of substitutional solid solution

Pure element A

$+$

Pure element B

Alloy A-B

Hume-Rothery Rules for substitutional solid solution

Difference in atomic Radii <15%

Cu-Ni : r_{Cu} = 0.128 nm, r_{Ni} = 0.125 nm;

Fe-C : r_{Fe} = 0.124 nm, r_C = 0.071 nm

Crystal structure ≡

Electronegativity difference → small

Solute's valency: higher the better

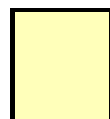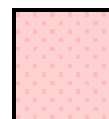Primitive cubic

Cubic close packing
(Face centered cubic)

Body centered cubic

Hexagonal close packing

Hume-Rothery Rules for substitutional solid solution

- **Atomic size factor**: the difference in atomic radii between the two atom types should be less than about $\pm15\%$, else the solute atoms will create substantial lattice distortions and a new phase will form.

  Cu-Ni : r_{Cu} = 0.128 nm, r_{Ni} = 0.125 nm;   **Fe-C :** r_{Fe} = 0.124 nm, r_C = 0.071 nm

- **Crystal structure**: the crystal structures for metals of both atom types must be the same. (Cu and Ni are FCC)

- **Electronegativity**: The more electropositive one element and the more electronegative the other, the greater the likelihood that they will form an inter-metallic compound instead of a substitutional solid solution.

- **Valences**: Other factors being equal, a metal will have more of a tendency to dissolve another metal of higher valency than one of a lower valency.

Hume-Rothery Rules for interstitial solid solution

1. Solute atoms must be smaller than the interstitial sites in the solvent lattice.

2. The solute and solvent should have similar electronegativity.

Imperfections in Metals

Application of Hume–Rothery rules – Solid Solutions

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

2. More Zn or Al in Cu?

Element	Atomic Radius (nm)	Crystal Structure	Electro-negativity	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

Table on p. 118, *Callister & Rethwisch 8e.*

Impurities in Solids

- Specification of composition (Binary alloy)

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

  m_1 = mass of component 1

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

  n_{m1} = number of moles of component 1

  $$= \frac{m_1}{A_1}$$

  A_1 is the atomic weight of component 1

Composition conversions

Conversion of weight percent to atom percent (for a two-element alloy)

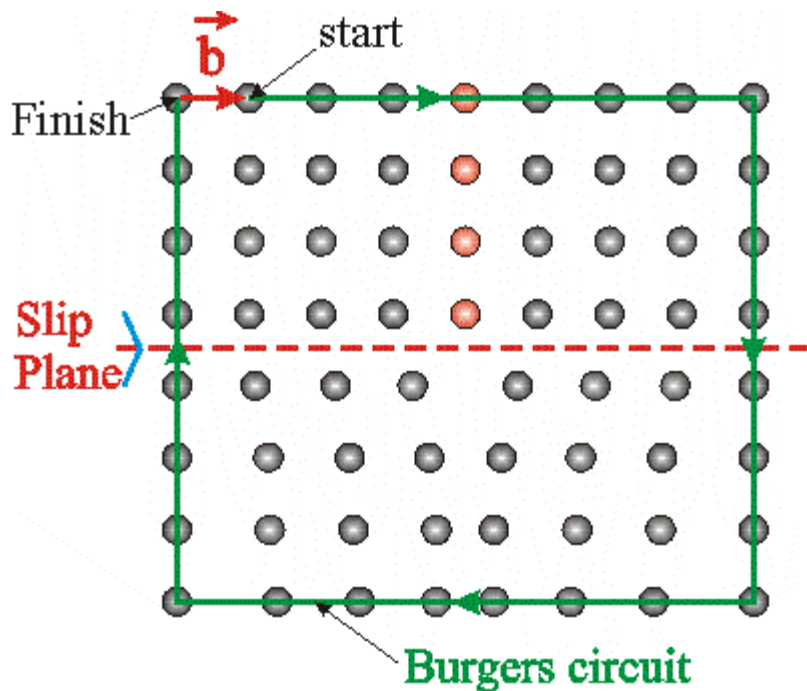$$C_1' = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

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

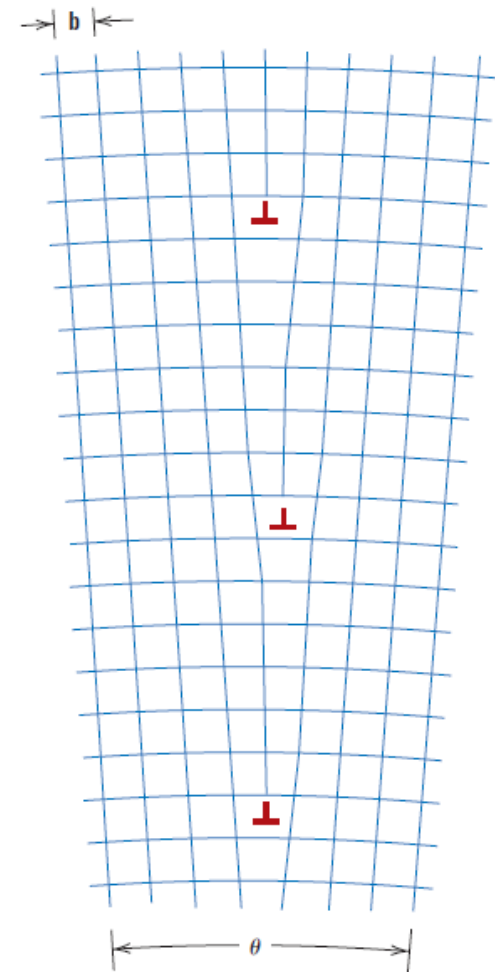Conversion of atom percent to weight percent (for a two-element alloy)

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

$$C_2 = \frac{C_2' A_2}{C_1' A_1 + C_2' A_2} \times 100$$
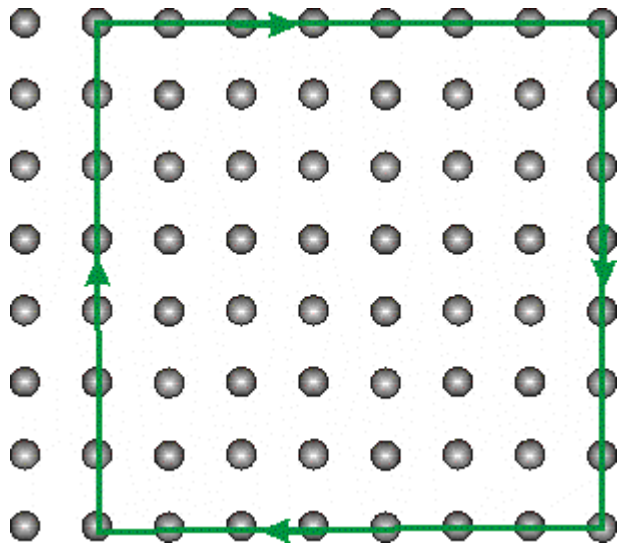
Putting it all together …

Edge dislocation can be thought of a collection of point defects (self-interstitials or vacancies)
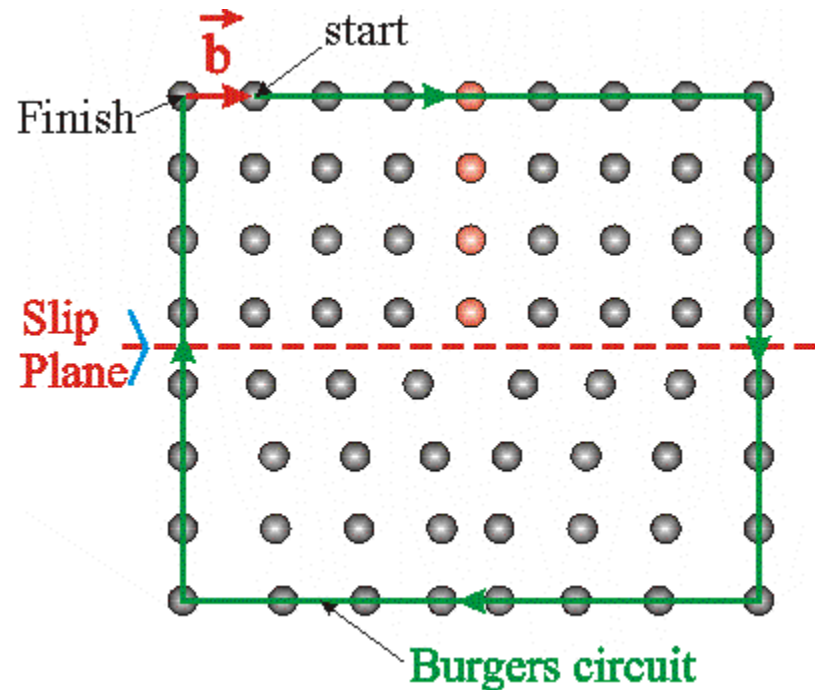

Tilt boundaries are array of dislocations

Extra half-plane as diffusion of vacancies or self-interstitials

Perfect crystal

Crystal with edge dislocation