Chapter 4:
Imperfections in Solids

- 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?

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.

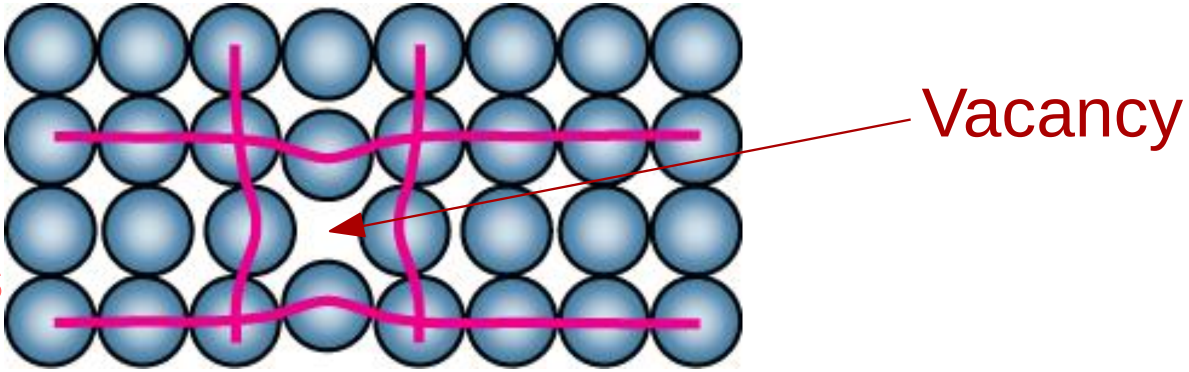
Types of Imperfections

• Vacancy atoms • Interstitial atoms • Substitutional atoms	Point defects
• Dislocations	Line defects
• Grain Boundaries	Planar defects

Point Defects in Metals

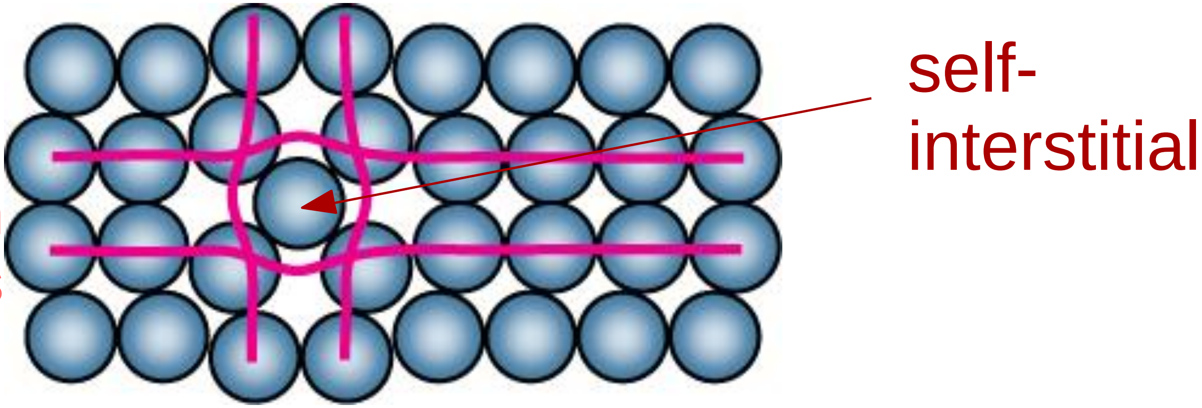
- Vacancies:
  -vacant atomic sites in a structure.

distortion
of planes



- Self-Interstitials:
  -"extra" atoms positioned between atomic sites.

distortion
of planes



Equilibrium Concentration: Point Defects

- Equilibrium concentration varies with temperature!

No. of defects

Activation energy

No. of potential defect sites

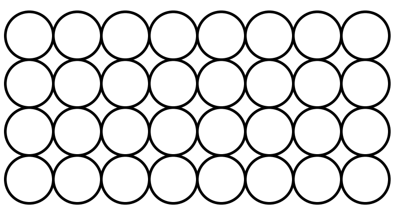
$$\frac{N_v}{N} = \exp\left(\frac{-Q_v}{kT}\right)$$

Temperature

Boltzmann's constant

$(1.38 \times 10^{-23}$ J/atom-K)

$(8.62 \times 10^{-5}$ eV/atom-K)



Each lattice site is a potential vacancy site

Estimating Vacancy Concentration

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

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

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

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

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

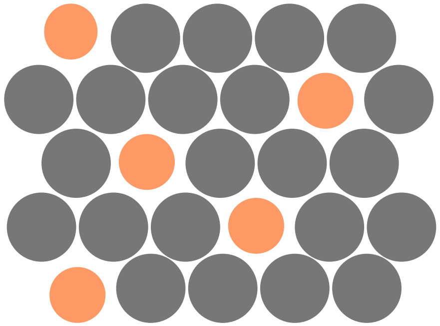
- Answer:

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

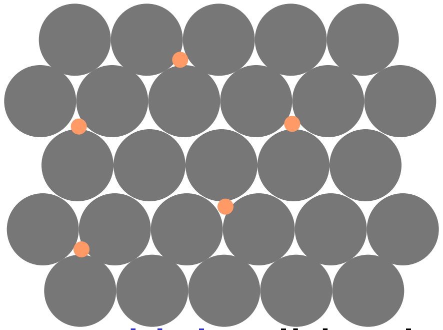
Imperfections in Metals (i)

Two outcomes if impurity (B) added to host (A):

- Solid solution of B in A (i.e., random dist. of point defects)



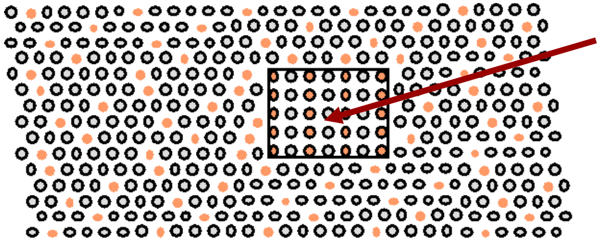
OR



Substitutional solid soln.
(e.g., Cu in Ni)

Interstitial solid soln.
(e.g., C in Fe)

- Solid solution of B in A plus particles of a new phase (usually for a larger amount of B)



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

Imperfections in Metals (ii)

Conditions for substitutional solid solution (S.S.)

- W. Hume – Rothery rule
  - 1. Δr (atomic radius) < 15%
  - 2. Proximity in periodic table
    - i.e., similar electronegativities
  - 3. Same crystal structure for pure metals
  - 4. Valency
    - All else being equal, a metal will have a greater tendency to dissolve a metal of higher valency than one of lower valency

Imperfections in Metals (iii)

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-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

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

Impurities in Solids

- Specification of composition

  – weight percent

$$C_1 = \frac{m_1}{m_1 + m_2} \text{x} 100$$

m_1 = mass of component 1

  – atom percent

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

n_{m1} = number of moles of component 1

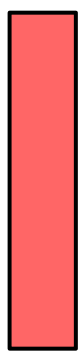
Line Defects

Dislocations:

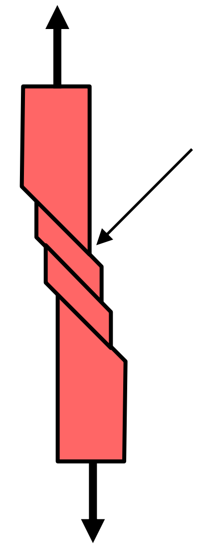
- are line defects,
- slip between crystal planes result when dislocations move,
- produce permanent (plastic) deformation.

Schematic of Zinc (HCP):

- before deformation



- after tensile elongation



Imperfections in Solids

Linear Defects (Dislocations)

- Are one-dimensional defects around which atoms are misaligned

- Edge dislocation:
  - extra half-plane of atoms inserted in a crystal structure
  - **b** perpendicular ($\perp$) 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

Imperfections in Solids

Edge Dislocation

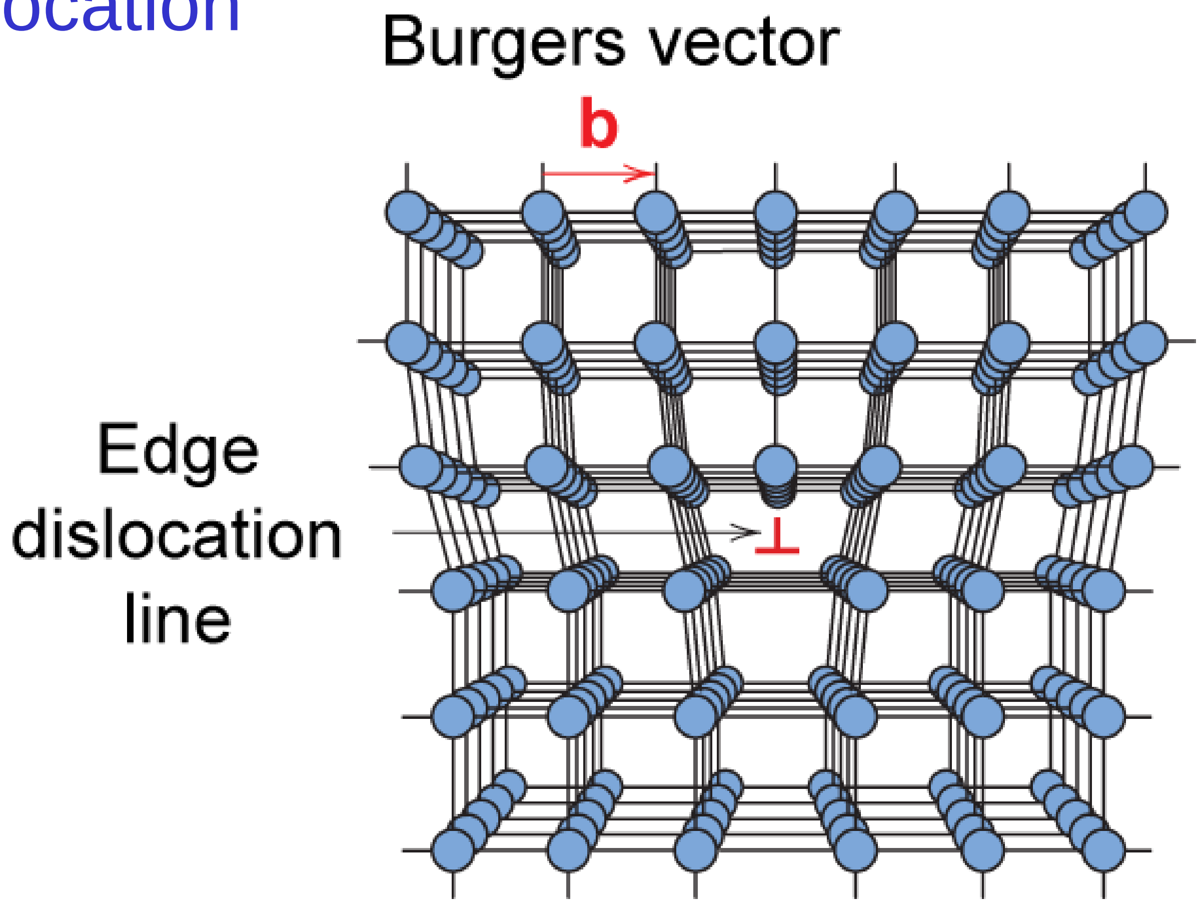
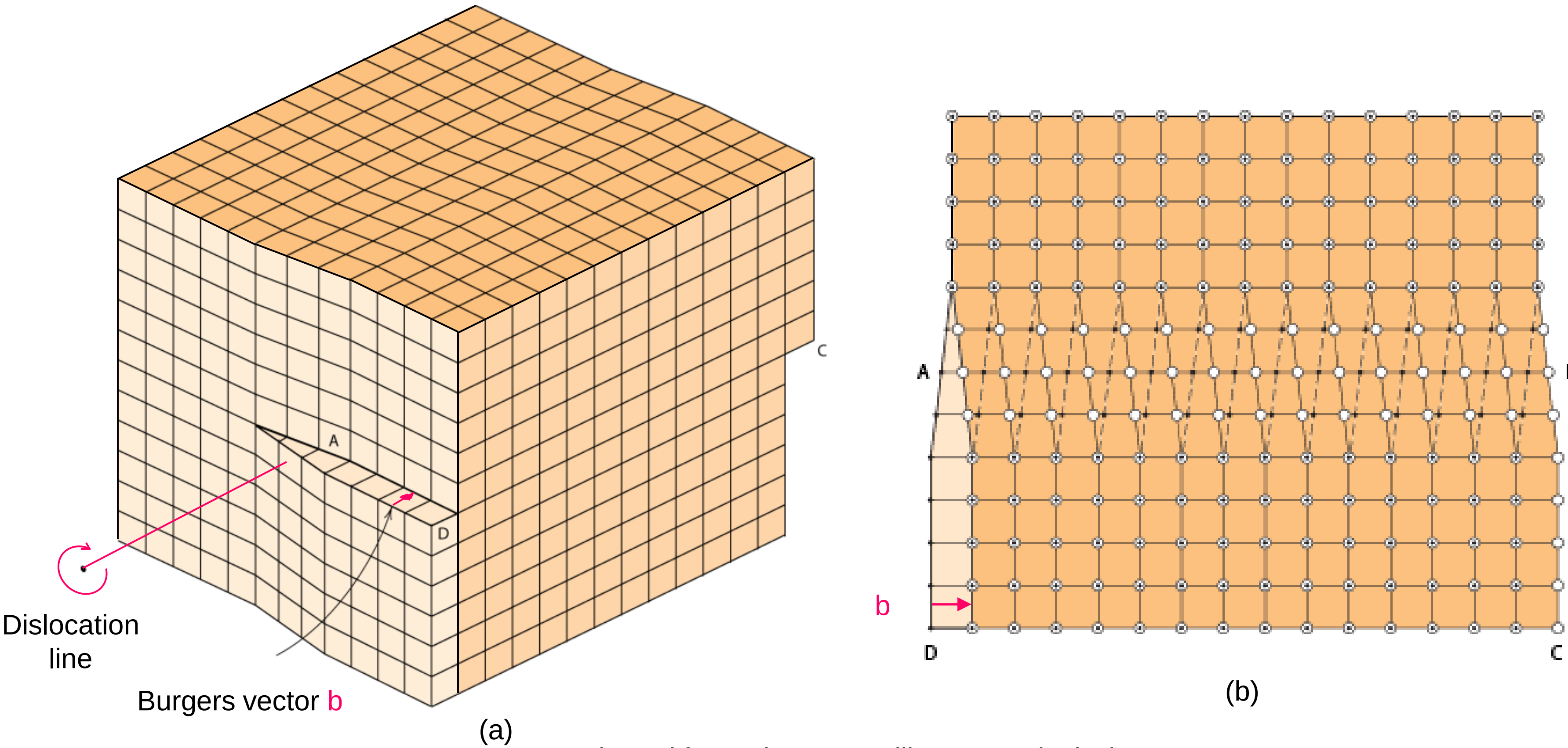


Fig. 4.3, *Callister & Rethwisch 8e.*

Imperfections in Solids

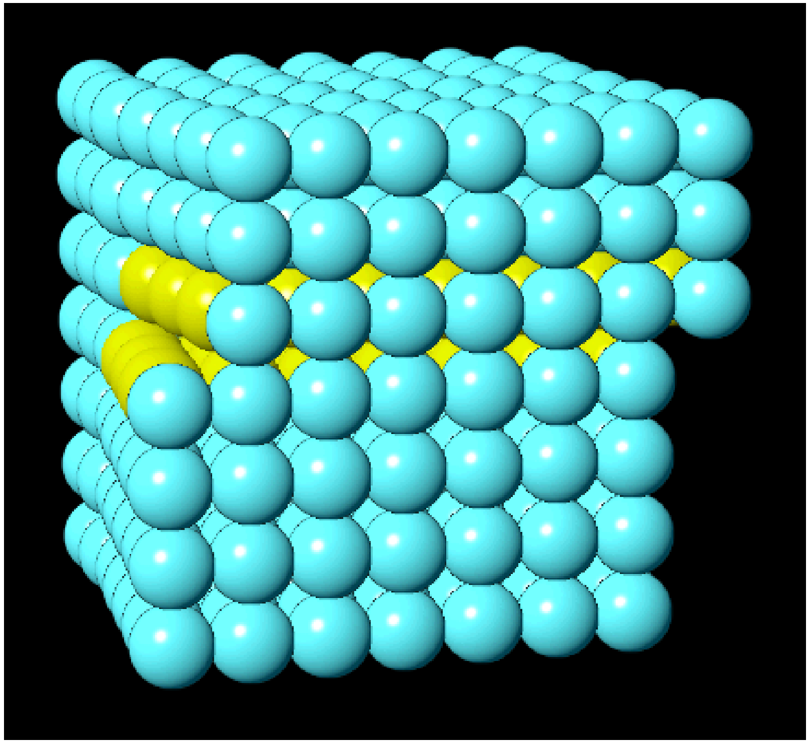
Screw Dislocation



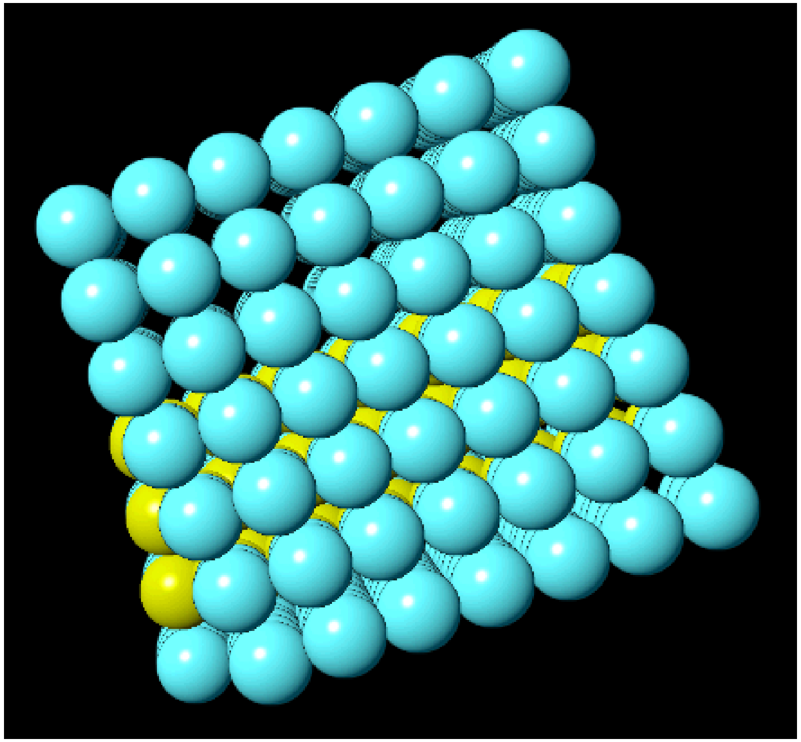
Adapted from Fig. 4.4, *Callister & Rethwisch 8e.*

VMSE: Screw Dislocation

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



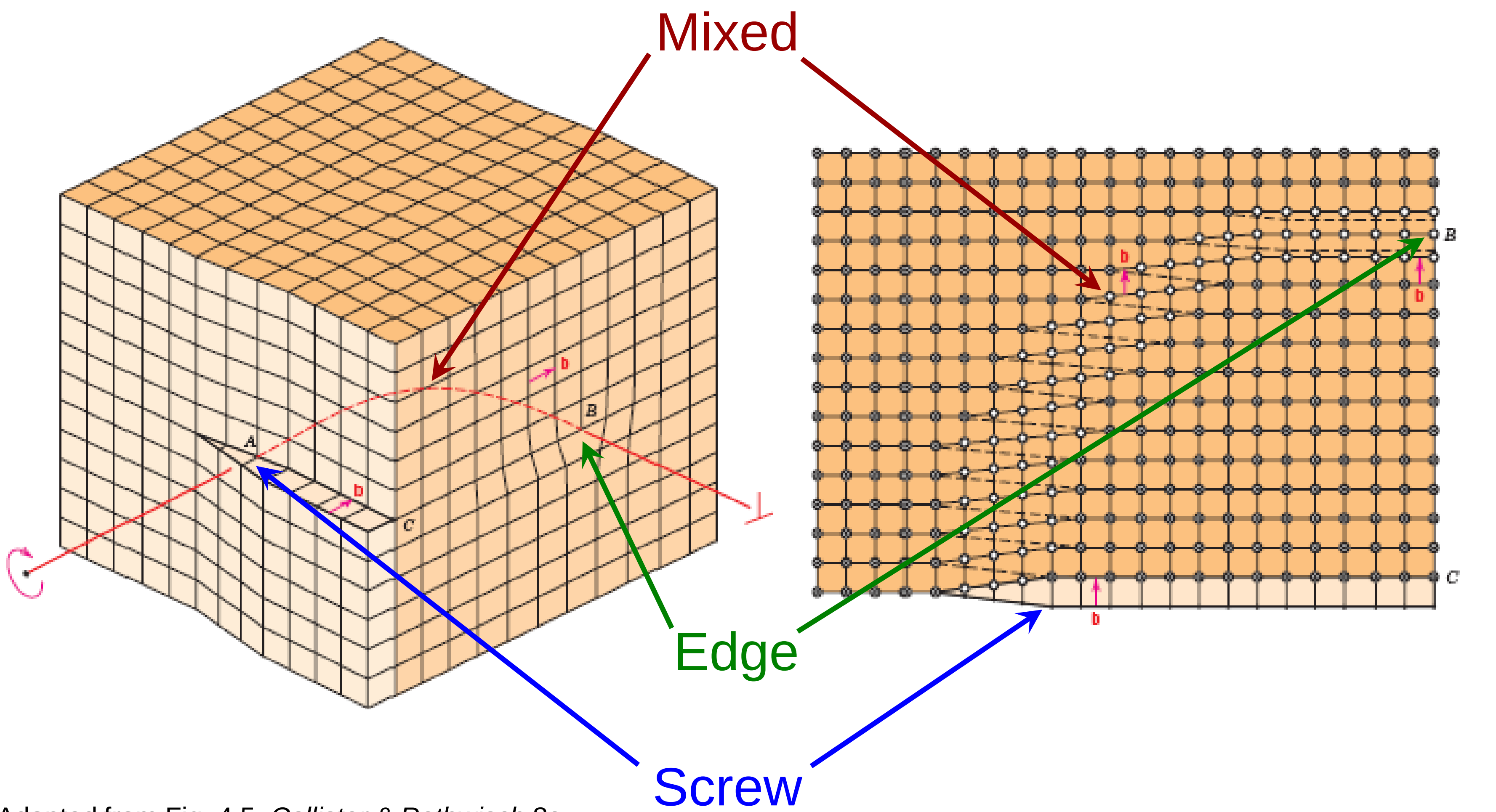
Front View



Top View

VMSE Screen Shots

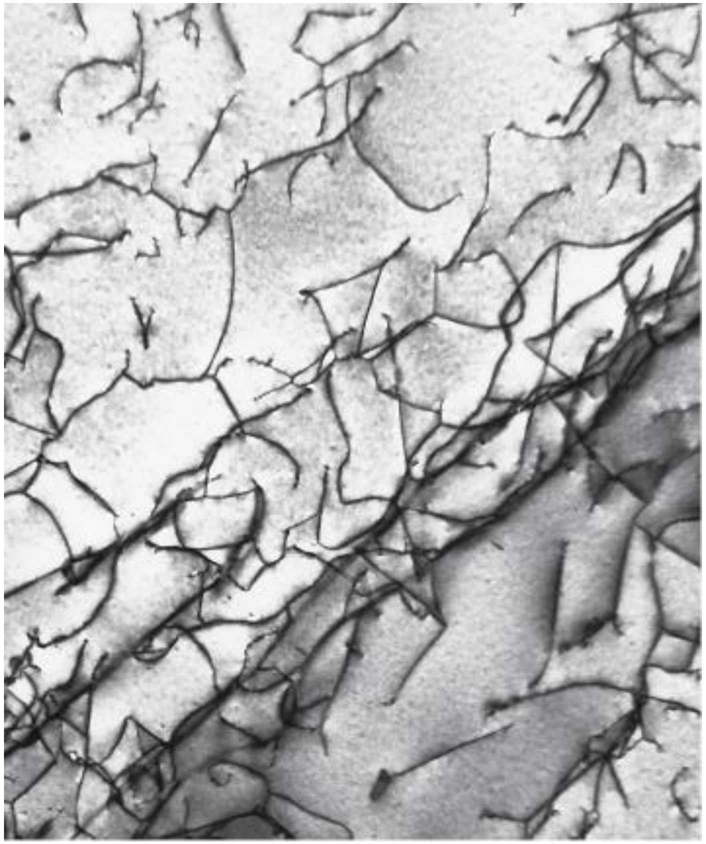
Edge, Screw, and Mixed Dislocations



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

Imperfections in Solids

Dislocations are visible in electron micrographs



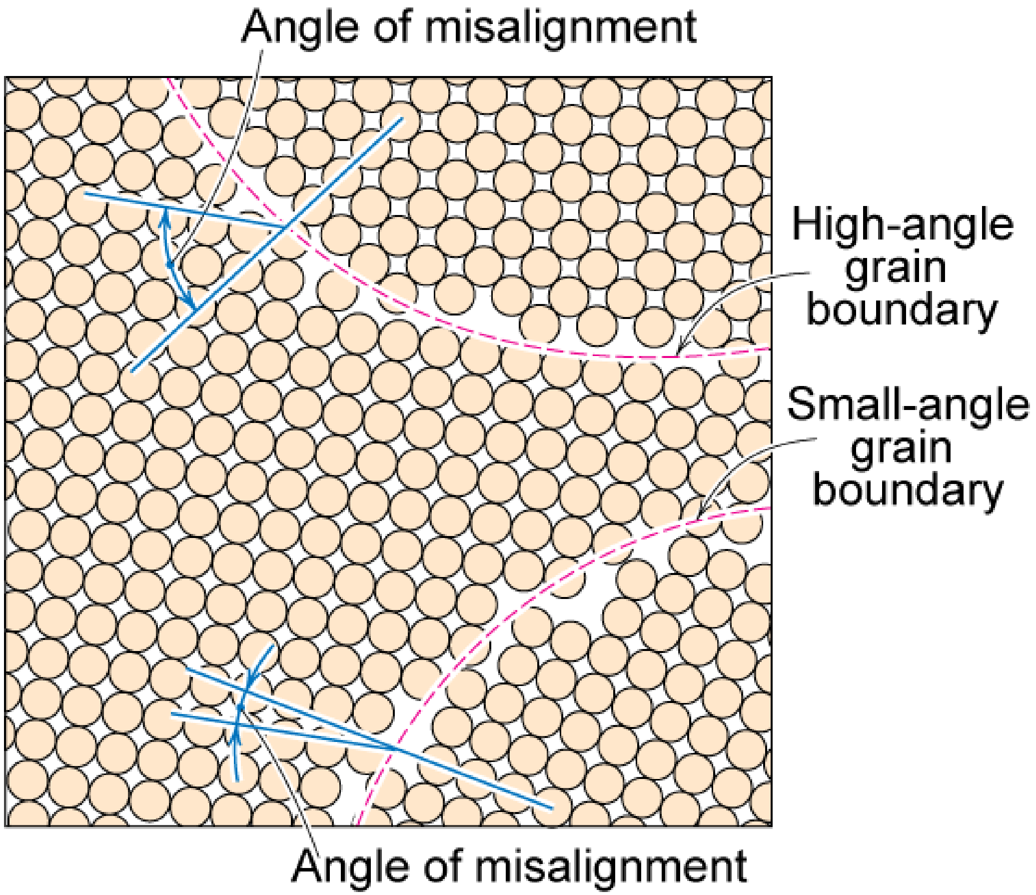
0.2 μm

Fig. 4.6, *Callister & Rethwisch 8e.*

Polycrystalline Materials

Grain Boundaries

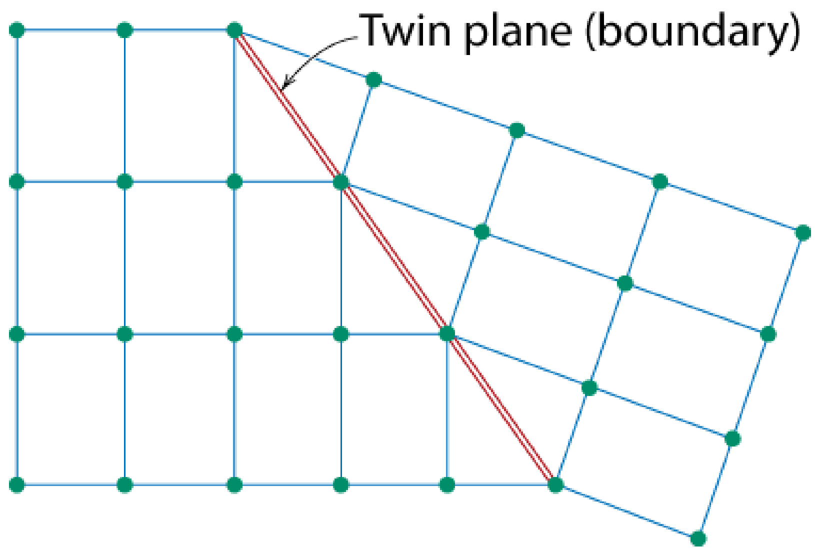
- regions between crystals
- transition from lattice of one region to that of the other
- slightly disordered
- low density in grain boundaries
  - high mobility
  - high diffusivity
  - high chemical reactivity



Adapted from Fig. 4.7, *Callister & Rethwisch 8e.*

Planar Defects in Solids

- One case is a twin boundary (plane)
  - Essentially a reflection of atom positions across the twin plane.



Adapted from Fig. 4.9, *Callister & Rethwisch 8e.*

- Stacking faults
  - For FCC metals an error in ABCABC packing sequence
  - Ex: ABCABABC

Catalysts and Surface Defects

- A catalyst increases the rate of a chemical reaction without being consumed
- Active sites on catalysts are normally surface defects

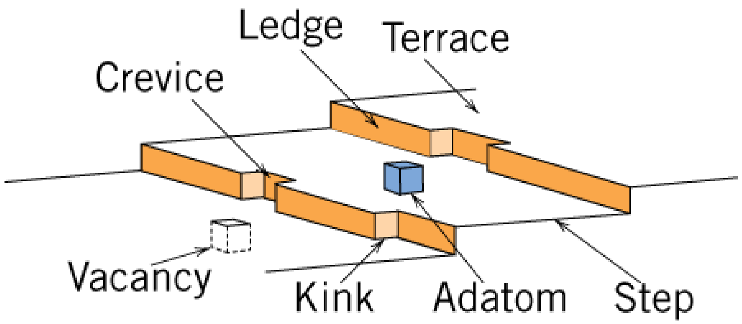


Fig. 4.10, *Callister & Rethwisch 8e.*

Single crystals of $(Ce_{0.5}Zr_{0.5})O_2$ used in an automotive catalytic converter

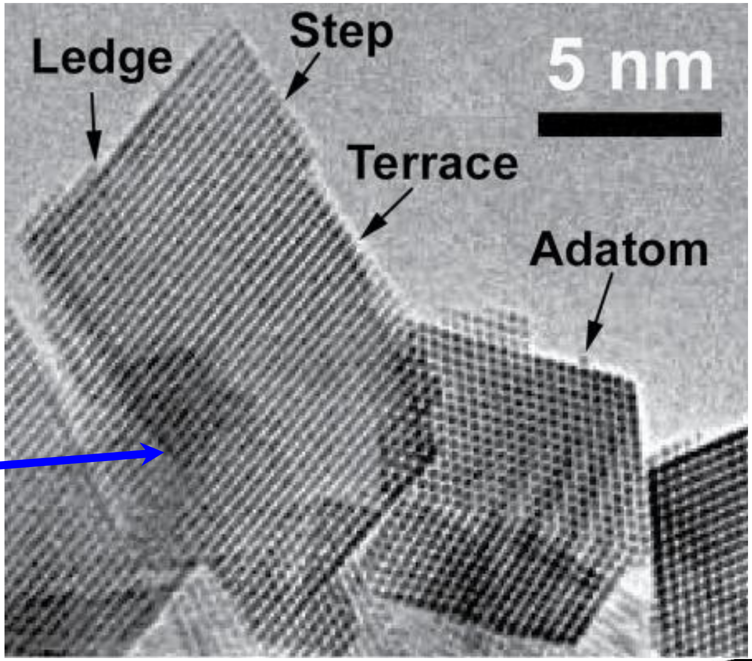


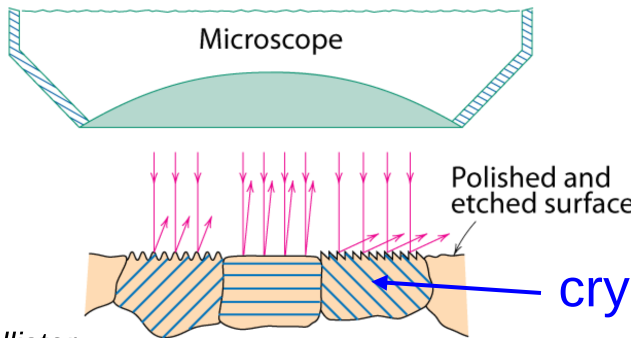
Fig. 4.11, *Callister & Rethwisch 8e.*

Microscopic Examination

- Crystallites (grains) and grain boundaries. Vary considerably in size. Can be quite large.
  - ex: Large single crystal of quartz or diamond or Si
  - ex: Aluminum light post or garbage can - see the individual grains
- Crystallites (grains) can be quite small (mm or less) – necessary to observe with a microscope.

Optical Microscopy

- Useful up to 2000X magnification.
- Polishing removes surface features (e.g., scratches)
- Etching changes reflectance, depending on crystal orientation.



crystallographic planes

Adapted from Fig. 4.13(b) and (c), *Callister & Rethwisch 8e.* (Fig. 4.13(c) is courtesy of J.E. Burke, General Electric Co.)

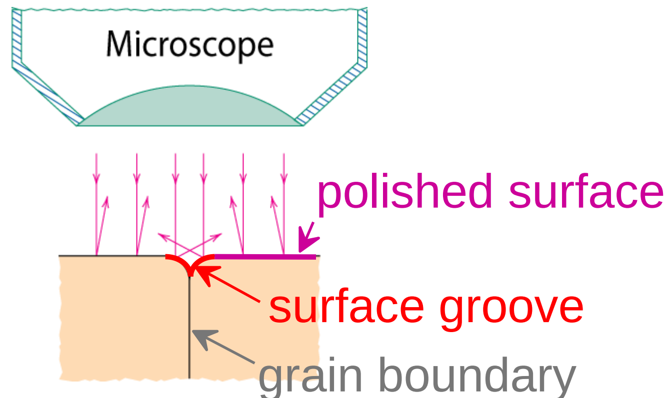
0.75mm

Micrograph of brass (a Cu-Zn alloy)

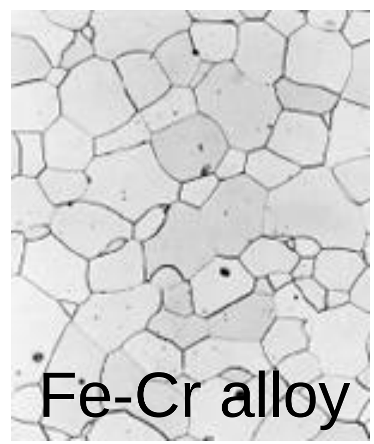
Optical Microscopy

Grain boundaries...

- are imperfections,
- are more susceptible to etching,
- may be revealed as dark lines,
- change in crystal orientation across boundary.



(a)



(b)

Adapted from Fig. 4.14(a) and (b), *Callister & Rethwisch 8e.* (Fig. 4.14(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].)

ASTM grain size number

$$N = 2^{n-1}$$

number of grains/in^2 at 100x magnification

Optical Microscopy

- Polarized light
  - metallographic scopes often use polarized light to increase contrast
  - Also used for transparent samples such as polymers

Microscopy

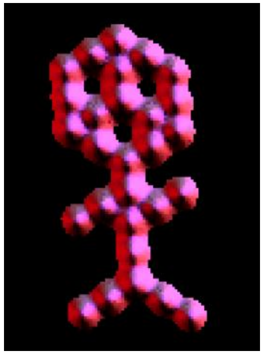
Optical resolution ca. 10^{-7} m = 0.1 μm = 100 nm

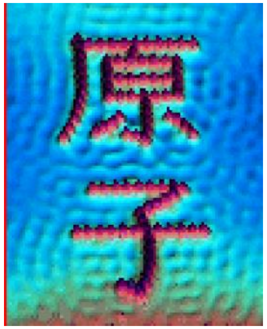
For higher resolution need higher frequency

- X-Rays? Difficult to focus.
- Electrons
  - wavelengths ca. 3 pm (0.003 nm)
    - (Magnification - 1,000,000X)
  - Atomic resolution possible
  - Electron beam focused by magnetic lenses.

Scanning Tunneling Microscopy (STM)

- Atoms can be arranged and imaged!





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Carbon monoxide molecules arranged on a platinum (111) surface.

Iron atoms arranged on a copper (111) surface. These Kanji characters represent the word “atom”.

Summary

- Point, Line, and Area defects exist in solids.
- The number and type of defects can be varied and controlled (e.g., *T* controls vacancy conc.)
- Defects affect material properties (e.g., grain boundaries control crystal slip).
- Defects may be desirable or undesirable (e.g., dislocations may be good or bad, depending on whether plastic deformation is desirable or not.)