DEFECTS IN SOLIDS

NILESH PANCHOLI

B.E. (Mech.), M.E. (Mech.), Ph. D.

Email: *nhpancholi@gmail.com*

www.nileshpancholi.com

DEFECTS IN SOLIDS

1 mole Fe = 55.85g; V= 7.10 cm^3 (D=7.87g/cm^3); ~ 6 x 10^{23} atoms

It would be nearly impossible to arrange so many atoms in exact 3D periodicity. So, formation of defects is not unexpected!

ISSUES TO ADDRESS...

- What types of defects arise in solids?
- How do defects affect material properties?
- Are defects undesirable?

Defects 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 DEFECTS IN SOLIDS

Perfect crystals do not exist

Defect: imperfection or "mistake" in the regular periodic arrangement of atoms in a crystal

Defects, even in very small concentrations, can have a serious effect on the properties of a material.

Point defects — Confined to single crystallographic sites

→ ***Intrinsic defects*** — Occur in pure substances

→ ***Extrinsic defects*** — Due to impurities

Line Defect

Area (Surface) Defect

Throughout the whole crystal

Types of Imperfections

- Vacancy atoms
- Interstitial atoms
- Substitutional atoms

Point defects

- Dislocations

Line defects

- Grain Boundaries

Area defects

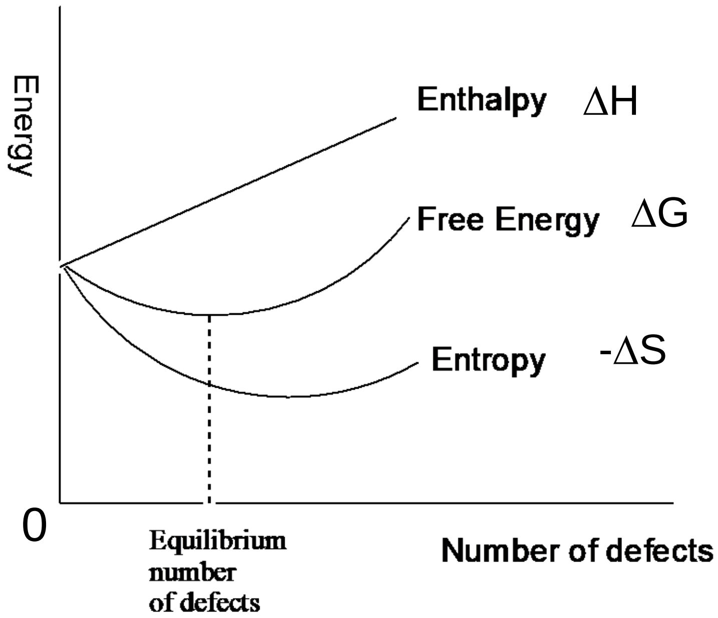
Point defects

Intrinsic defects do not involve changes in the overall composition

Extrinsic defects involve changes in the overall composition

Why do defects form?

The introduction of defects increases entropy ΔS and decreases free energy ΔG



$$\Delta G = \Delta H - T\Delta S$$

A minimum value for ΔG is reached for an optimum concentration of defects

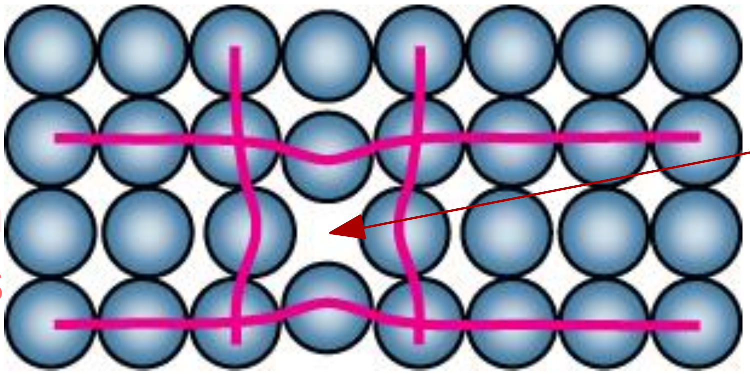
⇩

A structure with defects is more stable

Point Defects (*Intrinsic*)

- Vacancies:
  -vacant atomic sites in a structure.

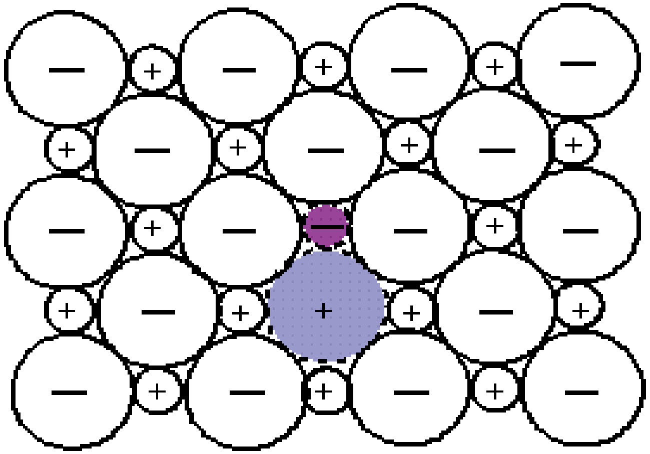
distortion of planes



absence of an atom (ion) from its location in a perfect crystal

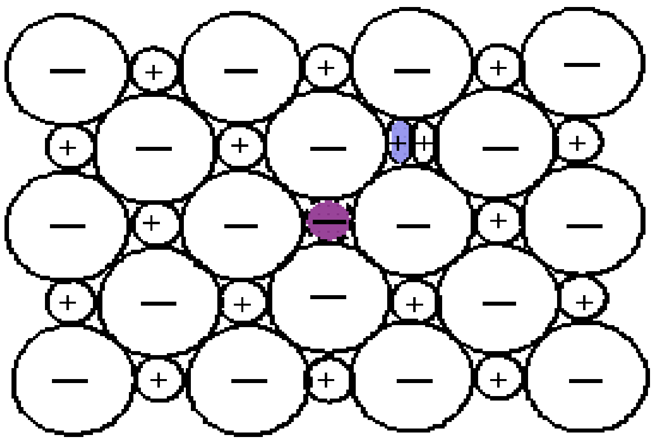
Schottky defects

A vacant cation site and a vacant anion site. In NaCl: one Na^+ and one Cl^- missing



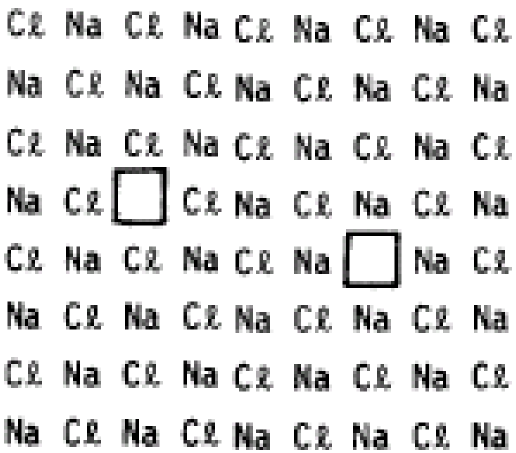
Charge neutrality is maintained within the crystal and there is no change in the composition

Frenkel defects



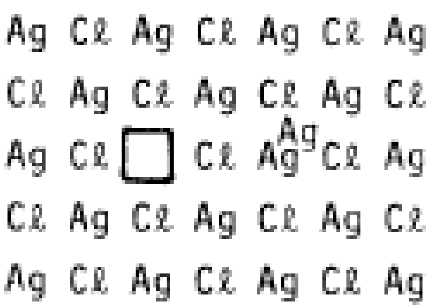
an atom (ion) moving into an interstitial site and creating a vacancy

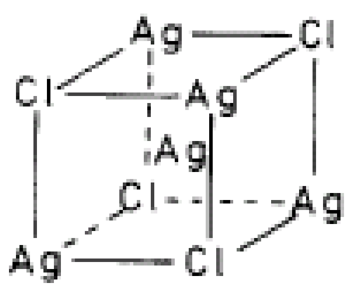
Frenkel defects are common in fluorite structures (CaF_2, ZrO_2) and AgCl



Schottky defects

-200 $kJmol^{-1}$ creation energy





Frenkel defects

-130 $kJmol^{-1}$ creation energy

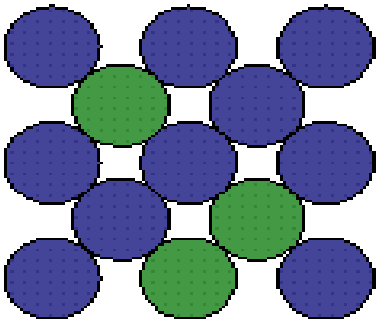
Extrinsic defects (due to impurities)

Impurities in a solid are any atom(s) of a type that do not belong in the perfect crystal structure (see 'extrinsic semiconductors')

Substitutional solid solutions

Impurity atoms occupy the same sites of the **host atoms**

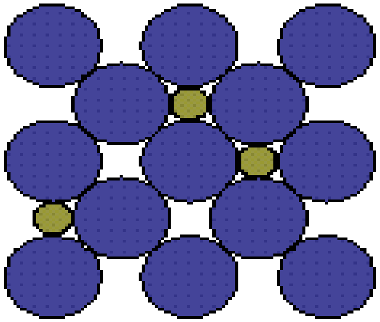
Impurities "substitute" for the host atoms



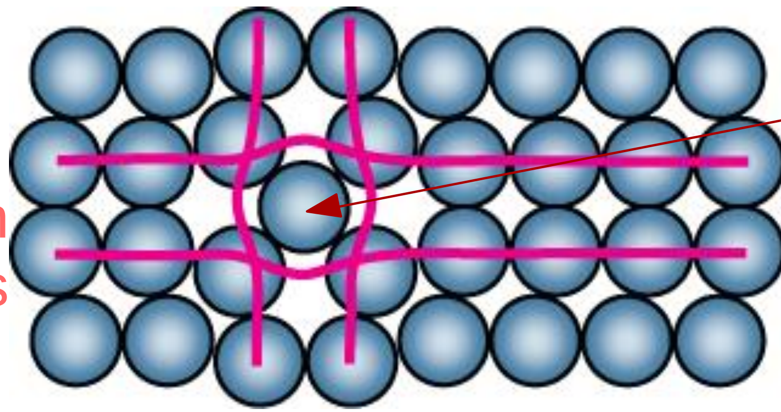
Interstitial solid solutions

Impurity atoms occupy interstices in the **host crystal** structure

Impurities usually have a small size compared to the host atoms



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



Equilibrium Concentration: Point Defects

- Equilibrium concentration varies with temperature!

No. of defects

Activation energy

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

No. of potential defect sites.

unitless; probability

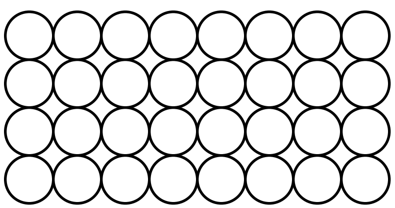
Boltzmann's constant

Absolute Temperature

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

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

1 eV = 1.6 x 10^{-19} J



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:

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

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

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

Q_V: 0.9 eV/atom

T: 1273K

k: 8.62×10^{-5} eV/atom-K

Cu T_m=1083 °C, **so at $T \sim T_m$ ~ 1/10^4 sites are vacant (general rule)**

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

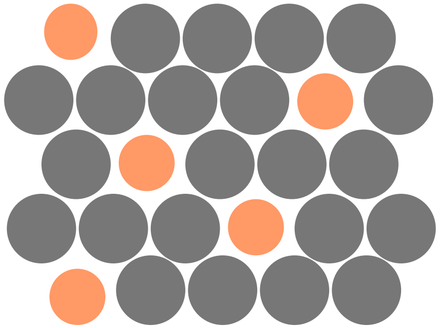
- Answer:

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

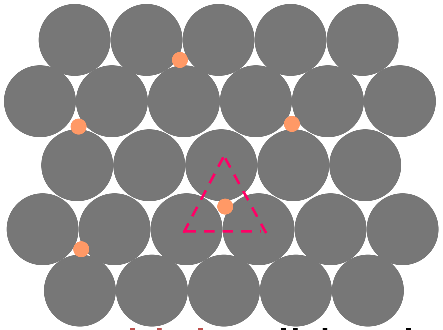
Point Defects in Alloys

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

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



OR

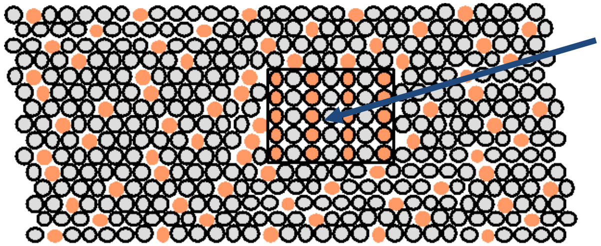


Insterstitial site can be calculated using simple geometry.

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.

Line Defects in Solids

Linear Defects (Dislocations)

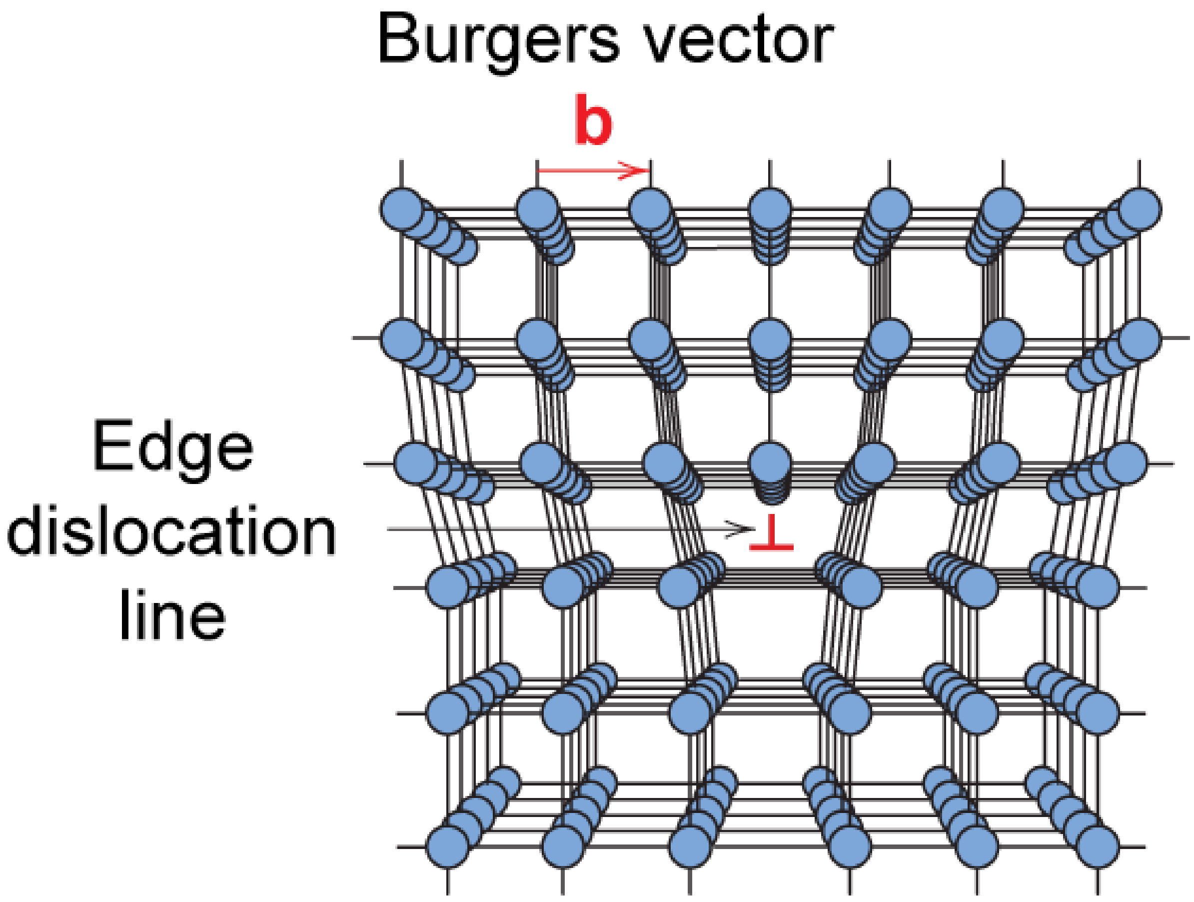
- Are one-dimensional defects around which atoms are misaligned

- Edge dislocation:
  - extra half-plane of atoms inserted in a crystal structure
  - **b** $\perp$ to dislocation line
- Screw dislocation:
  - spiral planar ramp resulting from shear deformation
  - **b** $||$ to dislocation line

Burger's vector, **b**: measure of lattice distortion

Line Defects in Solids

One dimensional defect in which atoms are mispositioned.

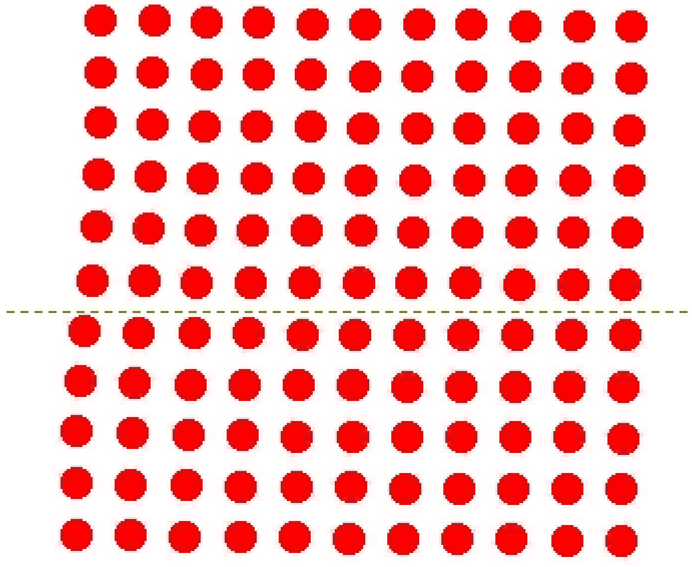


Edge Dislocation

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.

→ materials can be deformed rather easily……

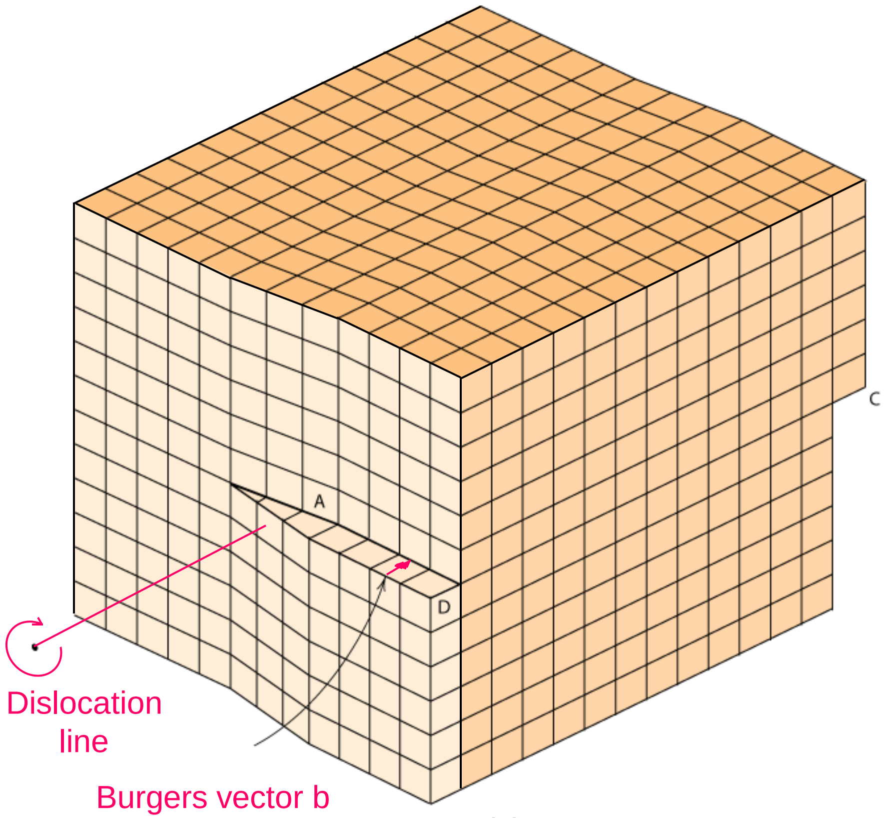


Atomic view of edge dislocation motion from left to right as a crystal is sheared.

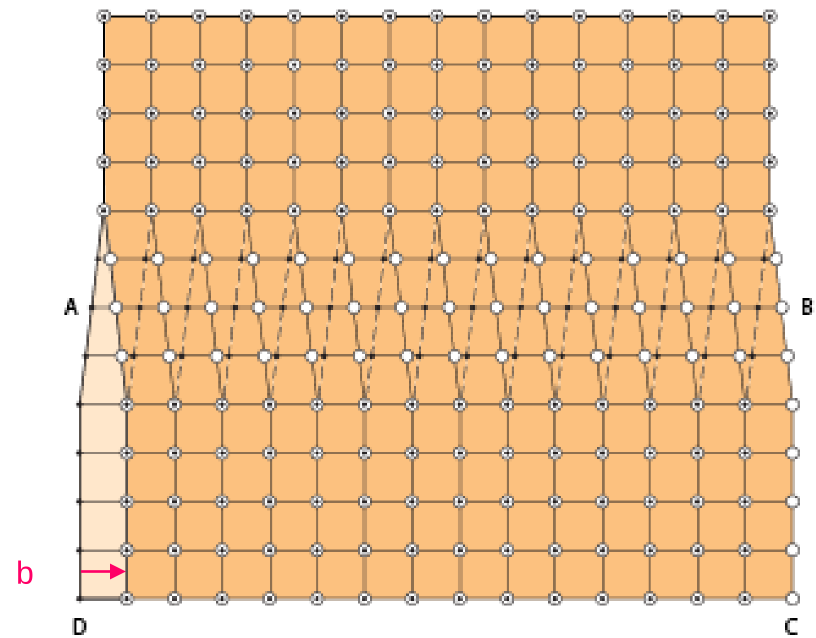
(Courtesy P.M. Anderson)

Line Defects in Solids

Screw Dislocation

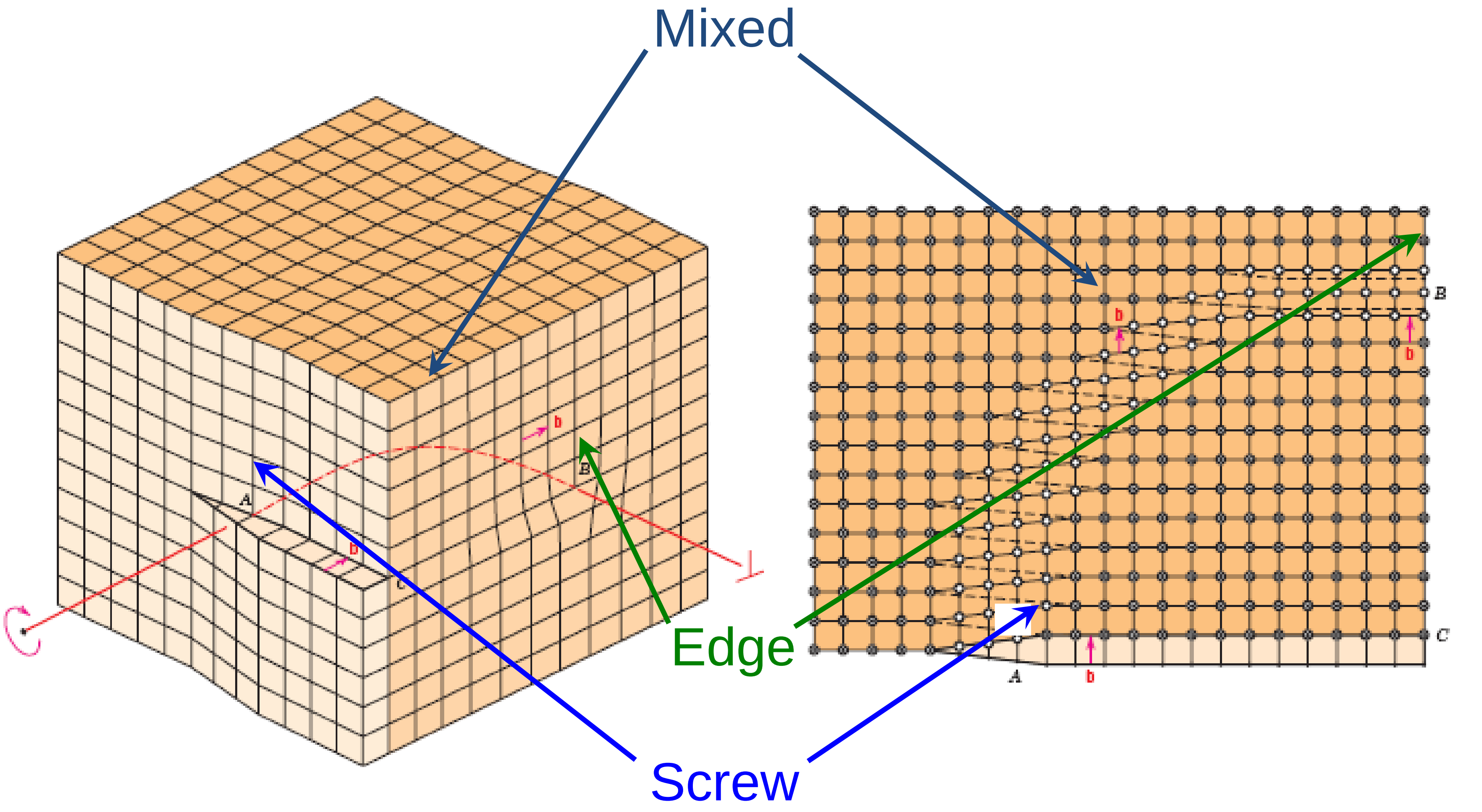


(a)



(b)

Edge, Screw, and Mixed Dislocations



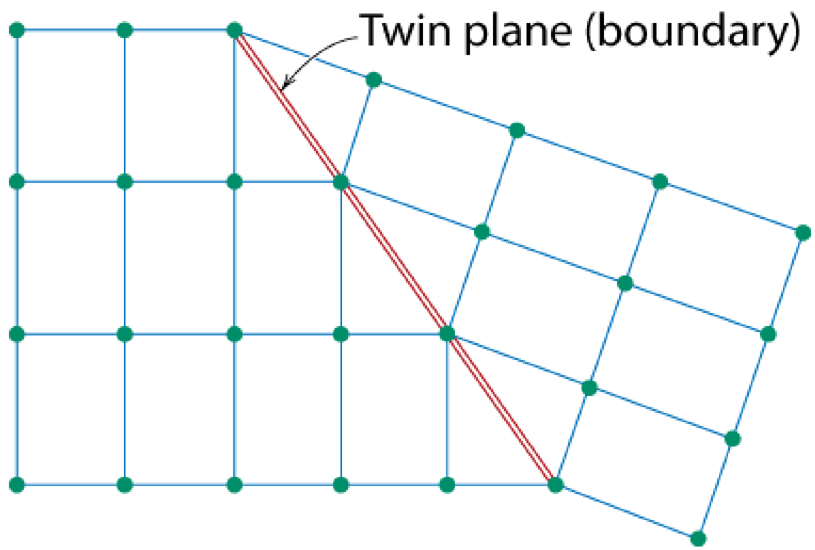
Imperfections in Solids

Dislocations are visible in electron micrographs

Planar Defects in Solids

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

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

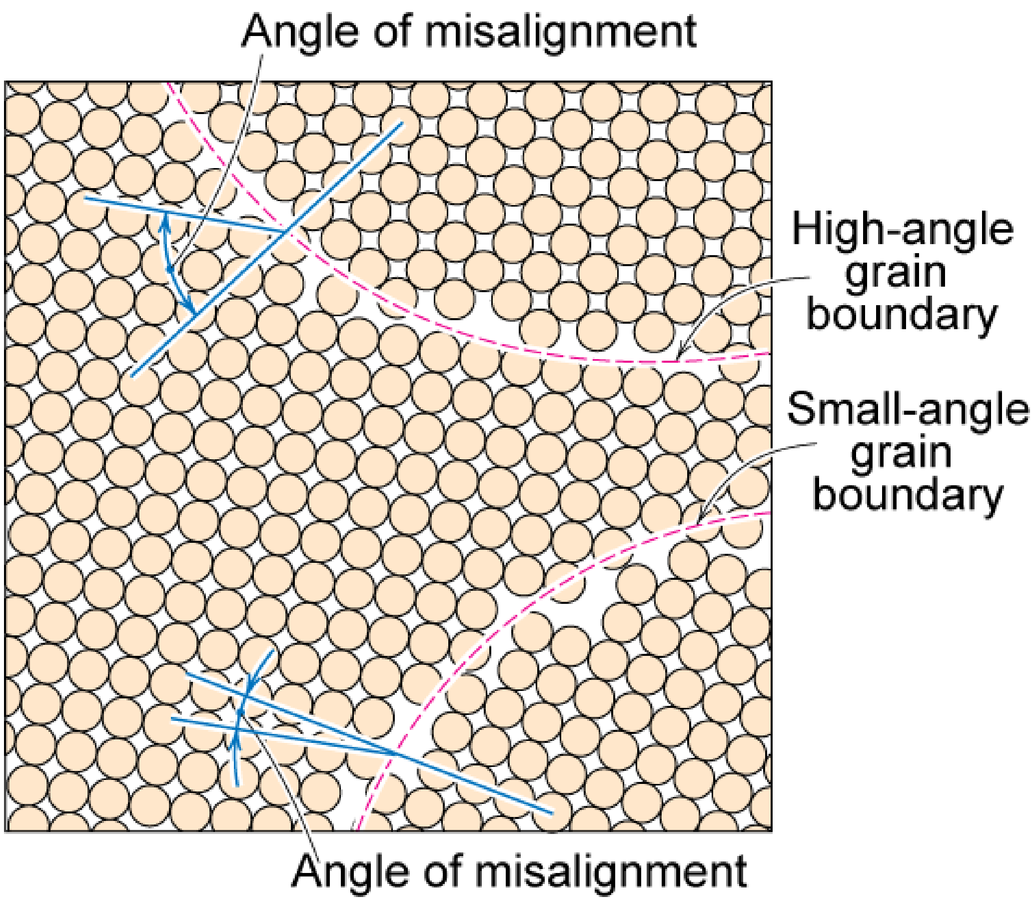


Adapted from Fig. 4.9, *Callister 7e.*

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 7e.*

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.)