Chemical Engineering 378

Science of Materials Engineering

Lecture 6

Point Defects, Solid Solutions

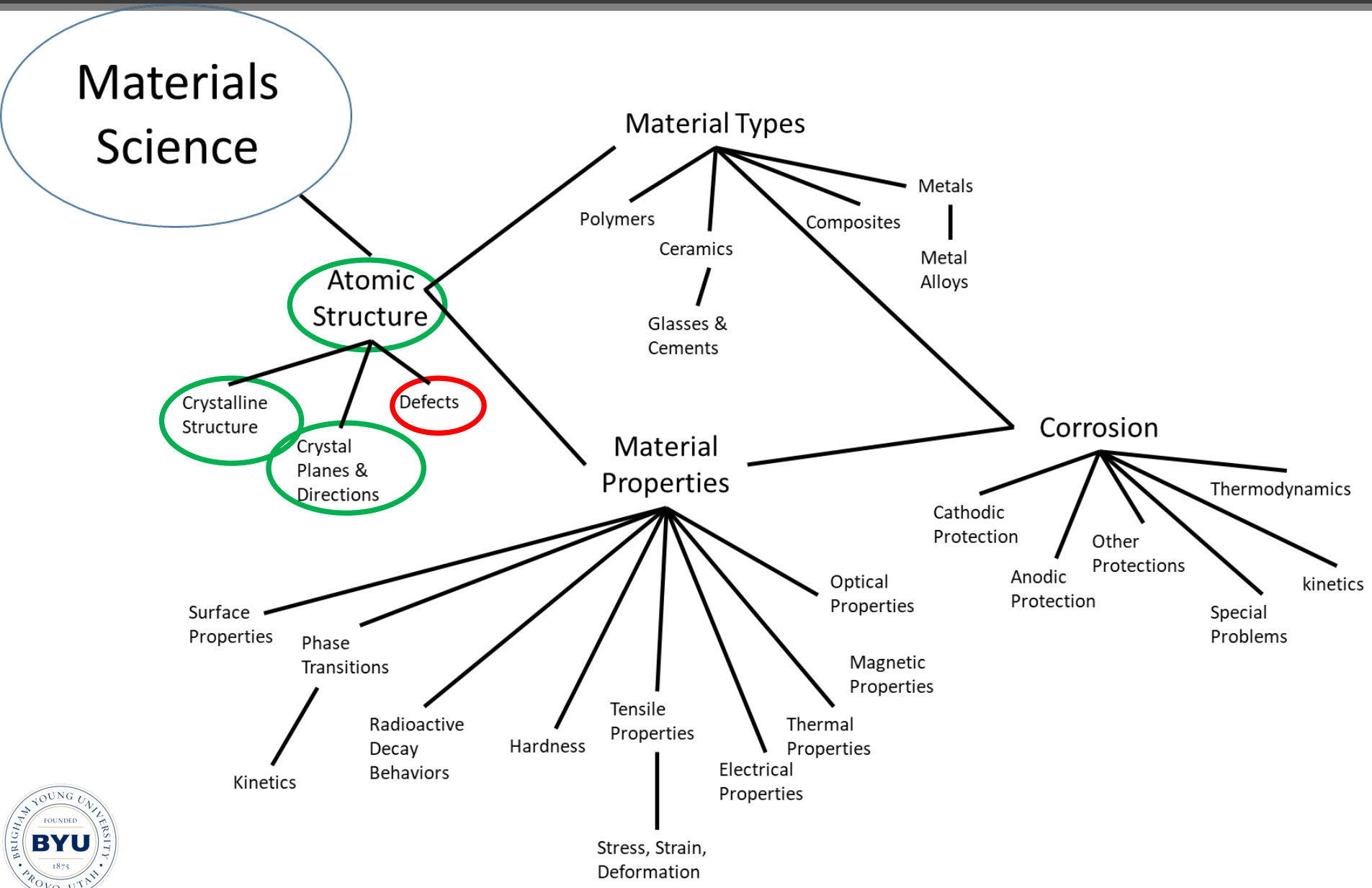
Spiritual Thought

"Why do any of us have to be so mean and unkind to others? Why can't all of us reach out in friendship to everyone about us? Why is there so much bitterness and animosity? It is not a part of the gospel of Jesus Christ… There is no end to the good we can do, to the influence we can have with others. Let us not dwell on the critical or the negative. Let us pray for strength; let us pray for capacity and desire to assist others. Let us radiate the light of the gospel at all times and all places, that the Spirit of the Redeemer may radiate from us."

-President Gordon B. Hinkley

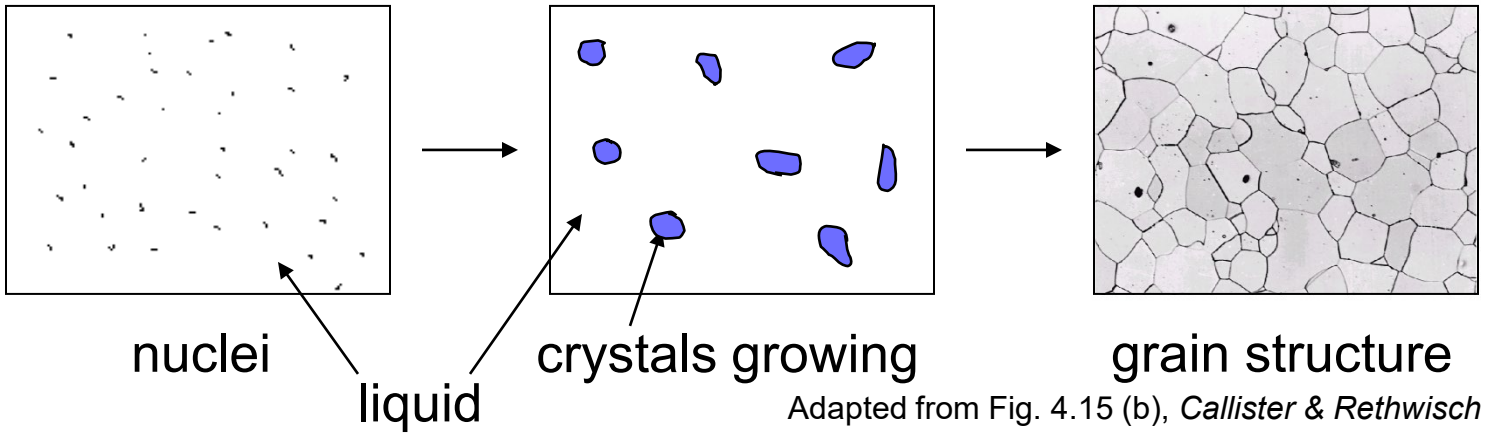
"The Need for Greater Kindness"

Materials Roadmap



Solidification

- Solidification- result of casting of molten material
  - 2 steps
    - Nuclei of the solid phase form
    - Crystals grow until their boundaries meet each other – the crystals become grains
- Start with a molten material – all liquid



[Photomicrograph 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.)]

Adapted from Fig. 4.15 (b), *Callister & Rethwisch 10e.*

Grains and Grain Boundaries

Grain Boundaries

- regions between grains (crystals)
- crystallographic misalignment across a grain boundary
- Slight atomic disorder
  - high atomic mobility
  - high chemical reactivity

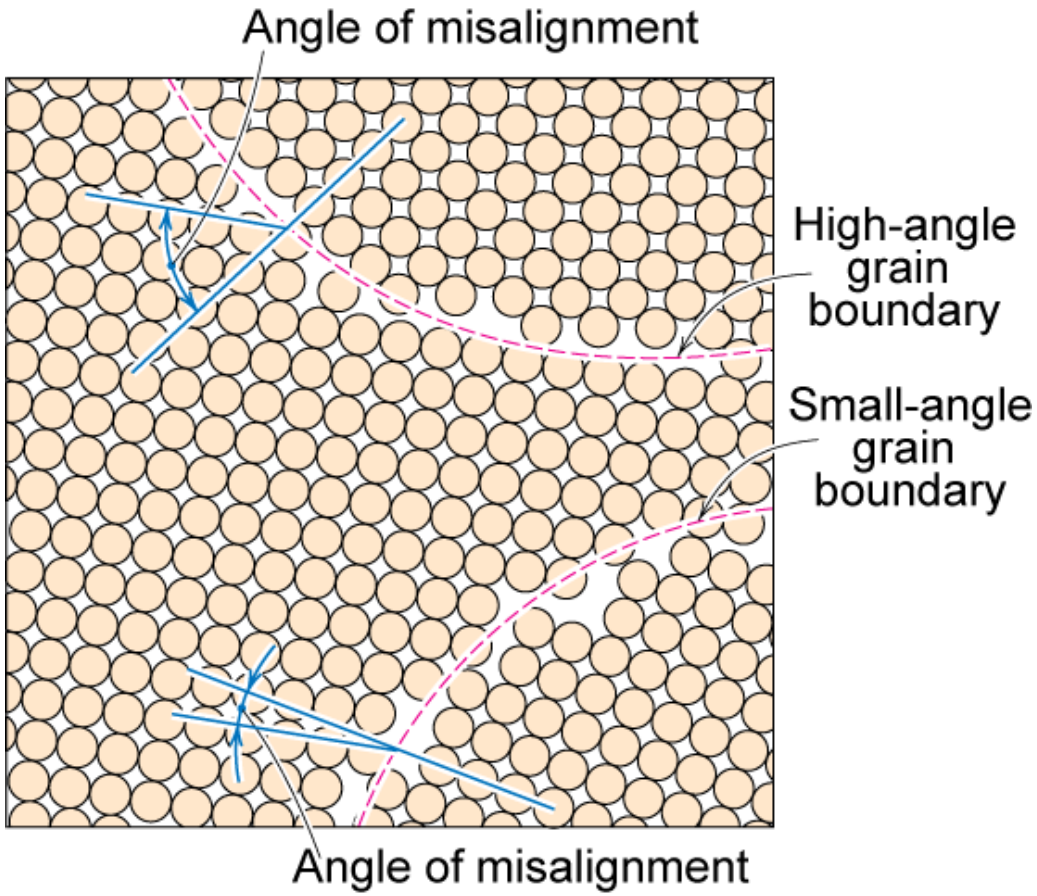


Fig. 4.8, *Callister & Rethwisch 10e.*

Imperfections in Solids

There is no such thing as a perfect crystal!

Crystalline imperfections (or defects) are always present.

- Impact Material Properties
- Crystalline defect →lattice irregularity →atom diameter
- Types?

Types of Imperfections

- Vacancies
- Interstitial atoms
- Substitutional impurity atoms

Point defects (0-Dimensional)

- Dislocations

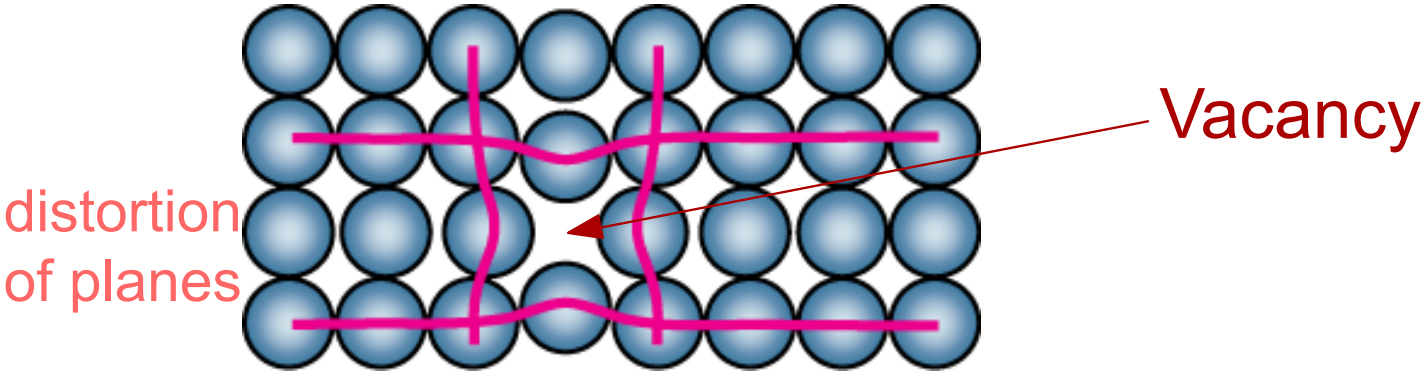
Linear defects (1-Dimensional)

- Grain Boundaries

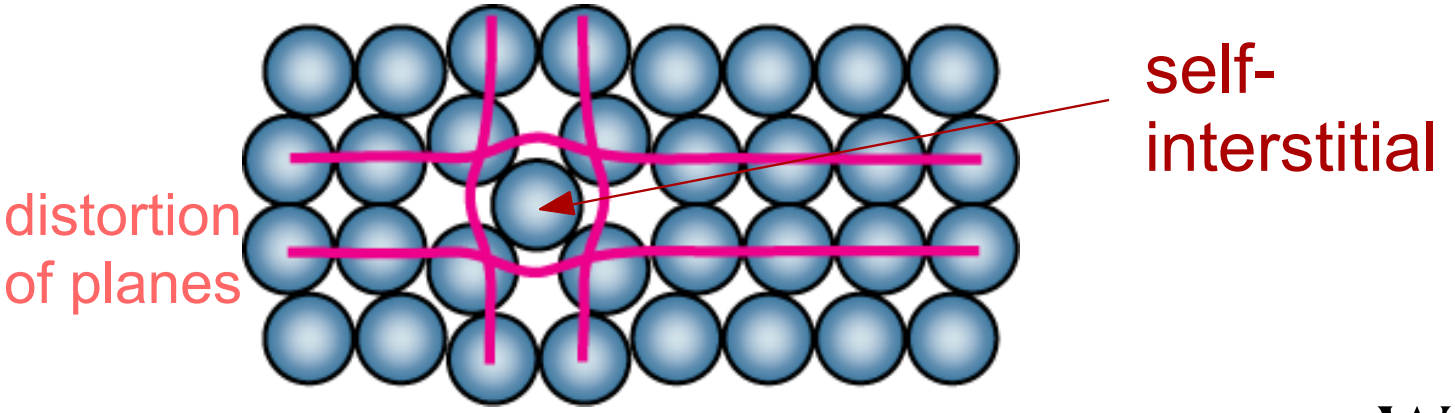
Interfacial defects (2-Dimensional)

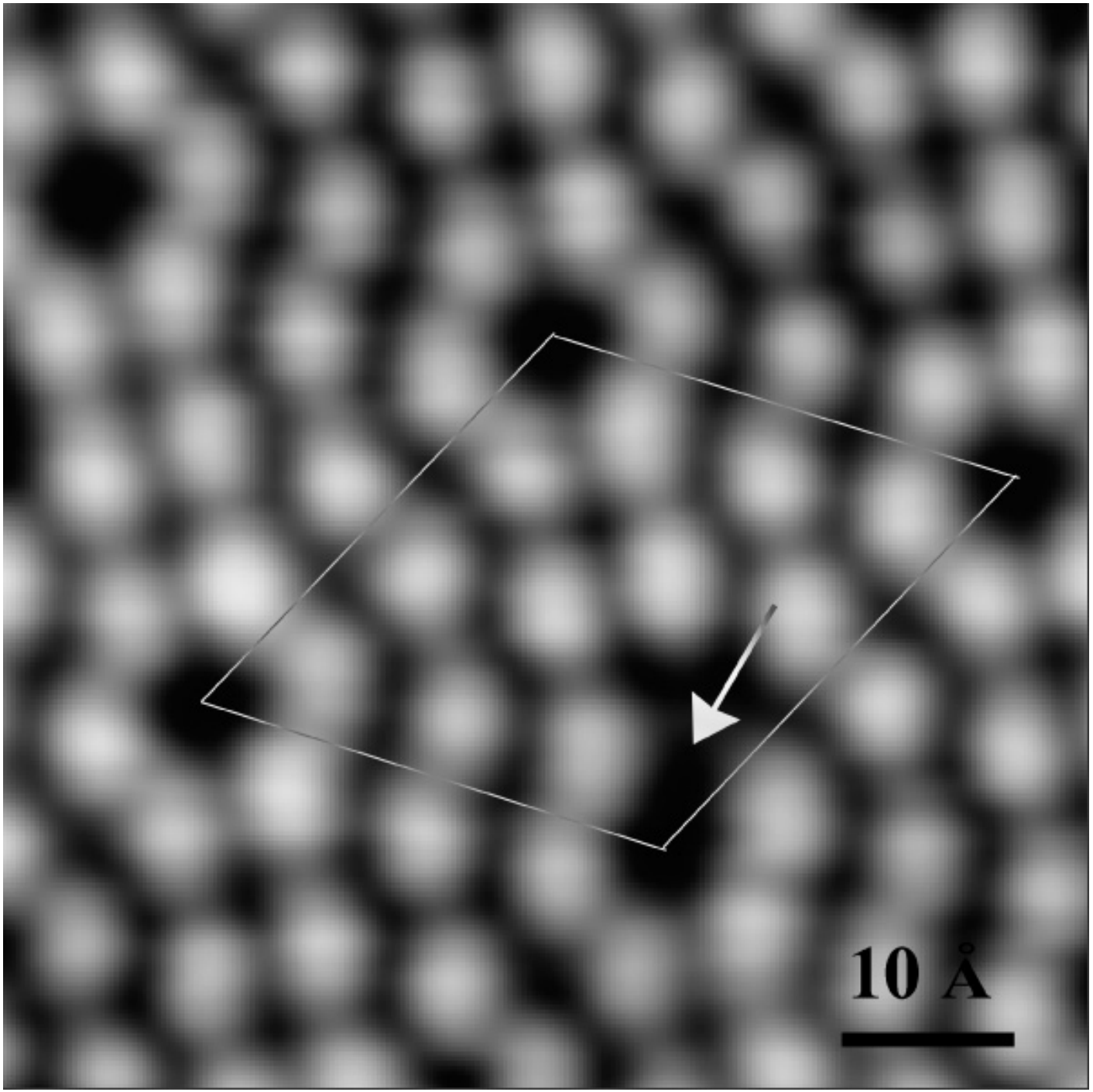
Point Defects in Metals

- Vacancies:
  -vacant atomic sites.



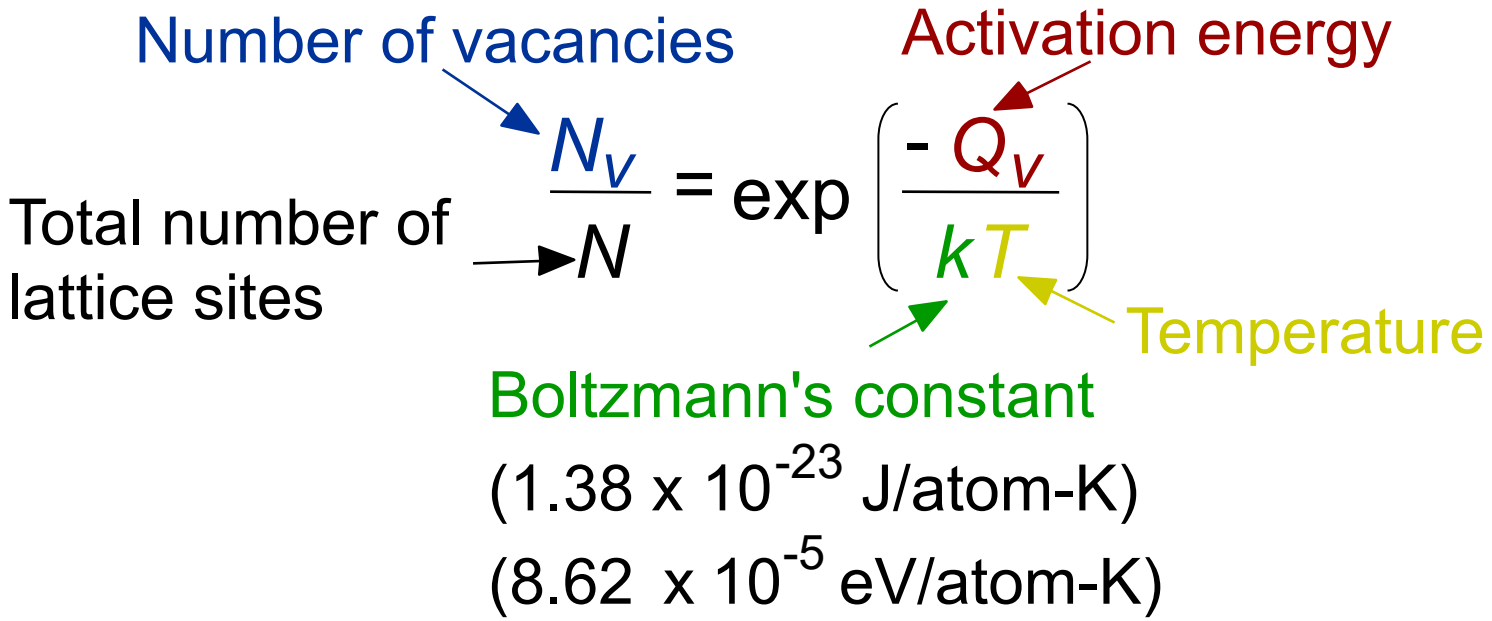
- Self-Interstitials:
  -Host atoms positioned in interstitial positions between atoms.




10 Å

Vacancies – How Many? Equilibrium Concentration

- Equilibrium concentration varies with temperature



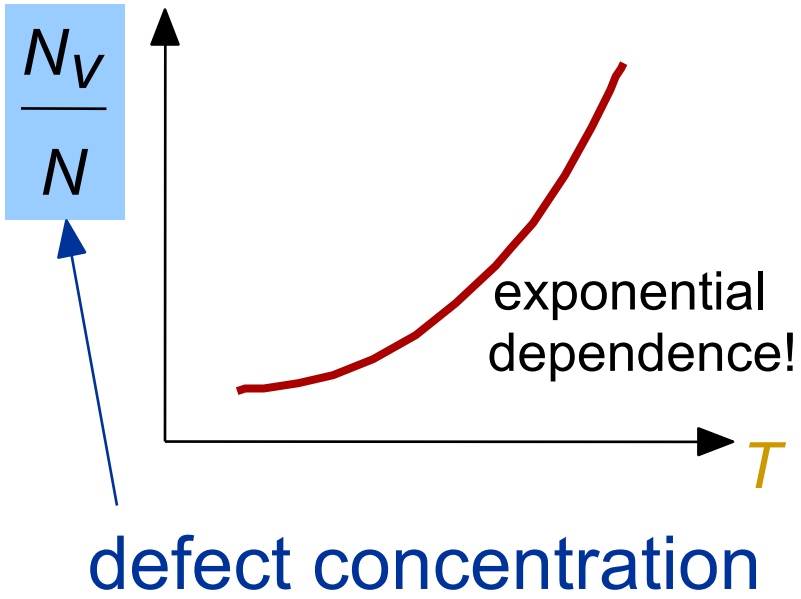
Note: Each lattice site is a potential vacancy.

Determination of Activation Energy for Vacancy Formation

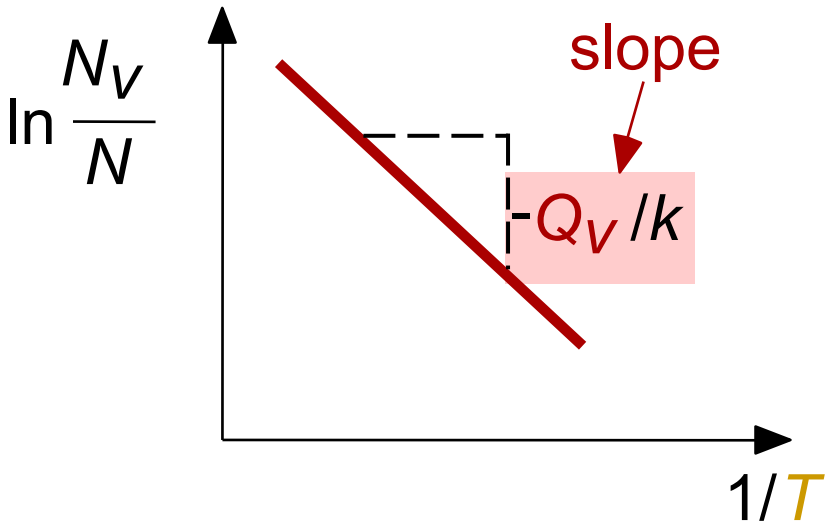
- Q_v can be determined experimentally.

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

- Data may be plotted as...



- Replot data as follows...



Example Problem

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

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

$Q_V = 0.9\ eV/atom$ $\quad N_A = 6.022 \times 10^{23}\ atoms/mol$

Solution: The first step is to determine the total number of lattice sites *N* using Equation 4.2

$$N = \frac{N_A \rho}{A_{Cu}} = \frac{(6.022 \times 10^{23}\ sites/mol)(8.4\ g/cm^3)}{63.5\ g/mol}\left(\frac{10^6 cm^3}{m^3}\right)$$

$$N = 8.0 \times 10^{28}\ sites/m^3$$

Computation of Equilibrium Vacancy Concentration (continued)

The second step is to determine the equilibrium vacancy concentration N_V using Equation 4.1.

$$N_V = N \exp\left(\frac{-Q_V}{kT}\right) = N \exp\left(\frac{-0.9 \text{ eV/atom}}{(8.62 \times 10^{-5} \text{ eV/atom-K})(1273 \text{ K})}\right)$$

$$= (2.7 \times 10^{-4})\, N$$

- Answer:

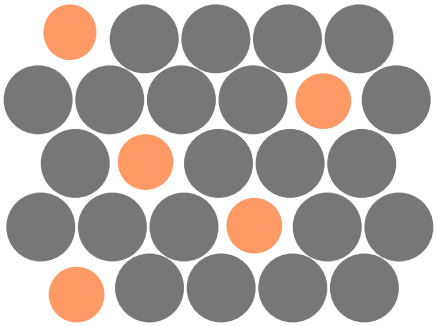
$$N_V = (2.7 \times 10^{-4})(8.0 \times 10^{28}) \text{ sites/m}^3$$

$$= 2.2 \times 10^{25} \text{ vacancies/m}^3$$

Impurities in Metals

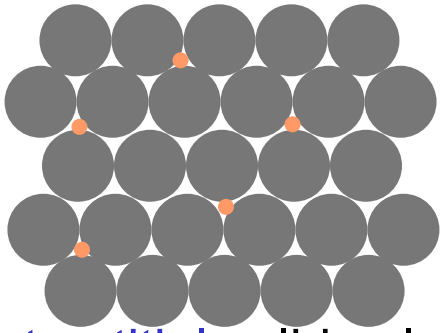
Two outcomes if impurity B atoms are added to a solid composed of host A atoms:

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



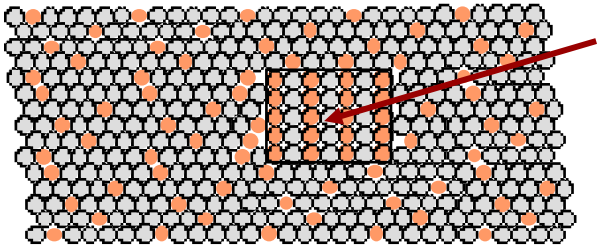
Substitutional solid soln.
(e.g., Cu in Ni)

OR

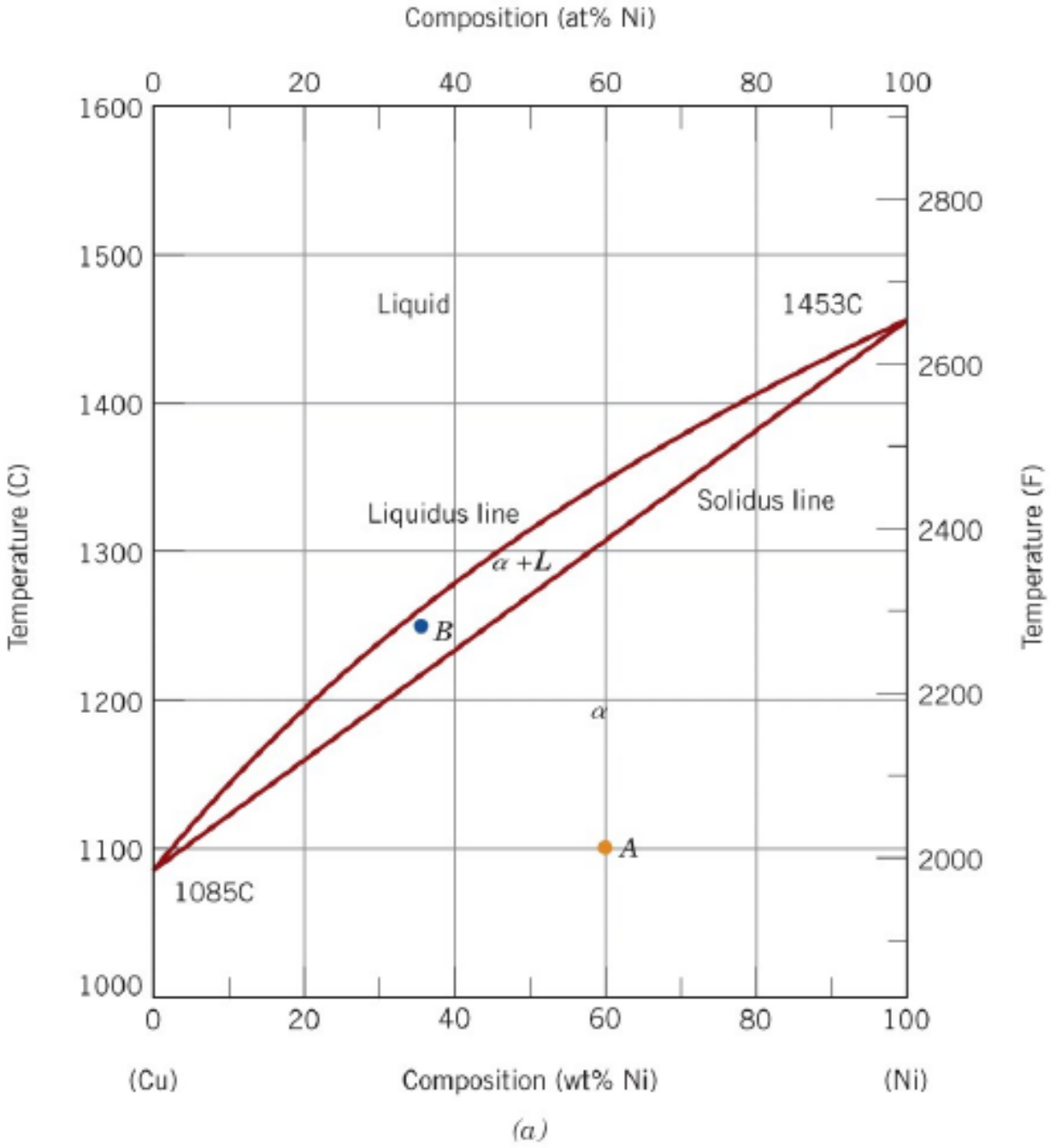


Interstitial solid soln.
(e.g., C in Fe)

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



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


Composition (at% Ni)
0
20
40
60
80
100
1600
1500
1400
1300
1200
1100
1000
2800
2600
2400
2200
2000
Temperature (C)
Temperature (F)
Liquid
1453C
Liquidus line
Solidus line
α +L
B
α
A
1085C
(Cu)
Composition (wt% Ni)
(Ni)
(a)

Impurities in Metals (continued)

Conditions for formation of substitutional solid solutions

W. Hume – Rothery rules

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

Impurities in Metals (continued)

Application of Hume–Rothery rules – Solid Solutions

Ex: Would you predict more Al or Ag to dissolve in Zn?

1. Δr – slightly favors Al
2. Electronegativity – favors Al
3. Crystal structure – tie
4. Valences –higher valance more soluble so favors Al

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. 135, *Callister & Rethwisch 9e.*

This suggests Al is more soluble in Zn. This agrees with experimental observations.

Example

Class Exercise 2: Application of Hume–Rothery rules – Solid Solutions

a) Would you predict more Al or Cu to dissolve in Zn?

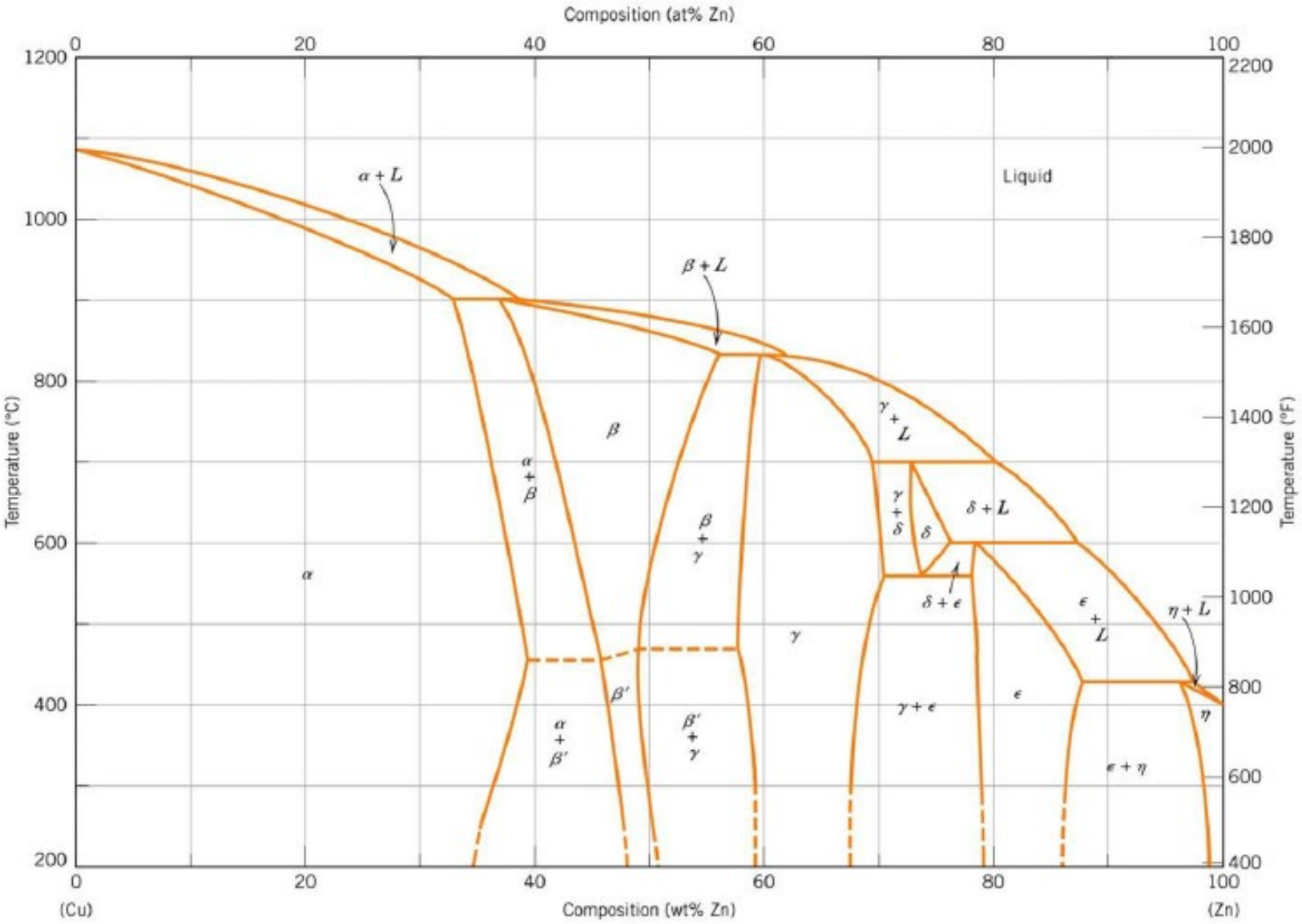
b) More Co or Cr in Fe?

c) More Ag or Al in Zn?

Element	*Atomic Radius (nm)*	*Crystal Structure*	*Electro-nega-tivity*	*Valence*
Cu	0.1278	FCC	1.8	+2
C	0.071			
H	0.046			
O	0.060			
Ag	0.1445	FCC	1.4	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.7	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.7	+2
Ni	0.1246	FCC	1.8	+2
Pd	0.1376	FCC	1.4	+2
Zn	0.1332	HCP	1.7	+2

Table on p. 29, *Callister & Rethwisch 9e.*

Cu-Zn Phase Diagram



Specification of Composition

– 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

– conversion

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

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