2019 Fall

Introduction to Materials Science and Engineering

10. 08. 2019

Eun Soo Park

Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by appointment

Contents for previous class

CHAPTER 4 & 5 The Structure of Crystalline Solids

- **Common metallic crystal structures** are FCC, BCC, and HCP. Coordination number and atomic packing factor are the same for both FCC and HCP crystal structures.

- **Interatomic bonding in ceramics** is ionic and/or covalent.

- **Ceramic crystal structures** are based on:
  -- maintaining charge neutrality
  -- cation-anion radii ratios.

- Some materials can have more than one crystal structure. This is referred to as polymorphism (or allotropy).

- **Polymer (= many mer)** is a substance composed of molecules characterized by the multiple repetition of one or more species of atoms or groups of atoms (constitutional repeating units) linked to each other in amounts sufficient to provide a set of properties. Most polymers are hydrocarbons – i.e., made up of H and C.

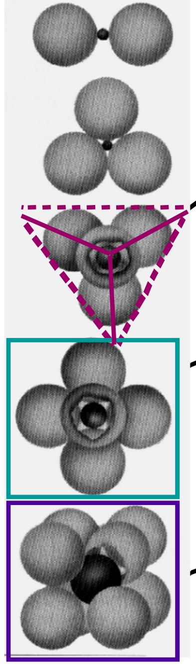
- **X-ray diffraction** is used for crystal structure and interplanar spacing determinations.

Coordination Number and Ionic Radii

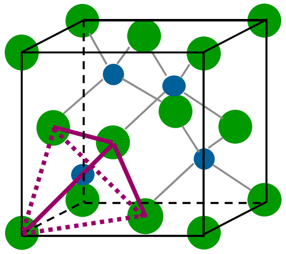
- Coordination Number increases with $\dfrac{r_{cation}}{r_{anion}}$

To form a stable structure, how many anions can surround around a cation?

$\dfrac{r_{cation}}{r_{anion}}$	Coord. Number	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	tetrahedral
0.414 - 0.732	6	octahedral
0.732 - 1.0	8	cubic

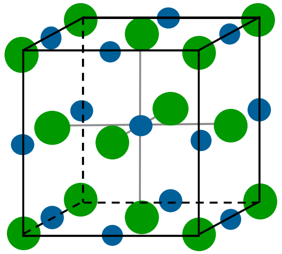


Adapted from Table 4.3, *Callister & Rethwisch 9e.*



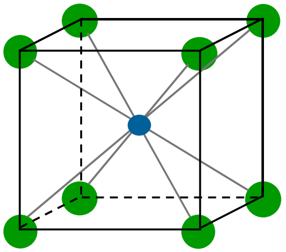
ZnS (zinc blende)

Adapted from Fig. 4.7, *Callister & Rethwisch 9e.*



NaCl (sodium chloride)

Adapted from Fig. 4.5, *Callister & Rethwisch 9e.*



CsCl (cesium chloride)

Adapted from Fig. 4.6, *Callister & Rethwisch 9e.*

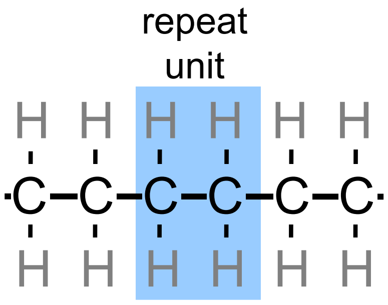
Chapter 5: Structures of Polymers

What is a Polymer?

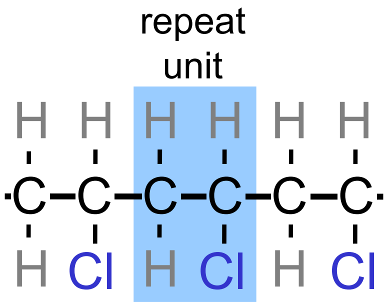
Polymer (= many mer) : a substance composed of molecules characterized by the multiple repetition of one or more species of atoms or groups of atoms (constitutional repeating units) linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with the addition of one or a few of the constitutional repeating units

Poly mer

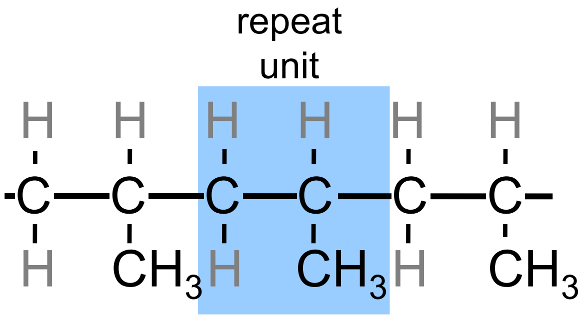
many repeat unit



Polyethylene (PE)



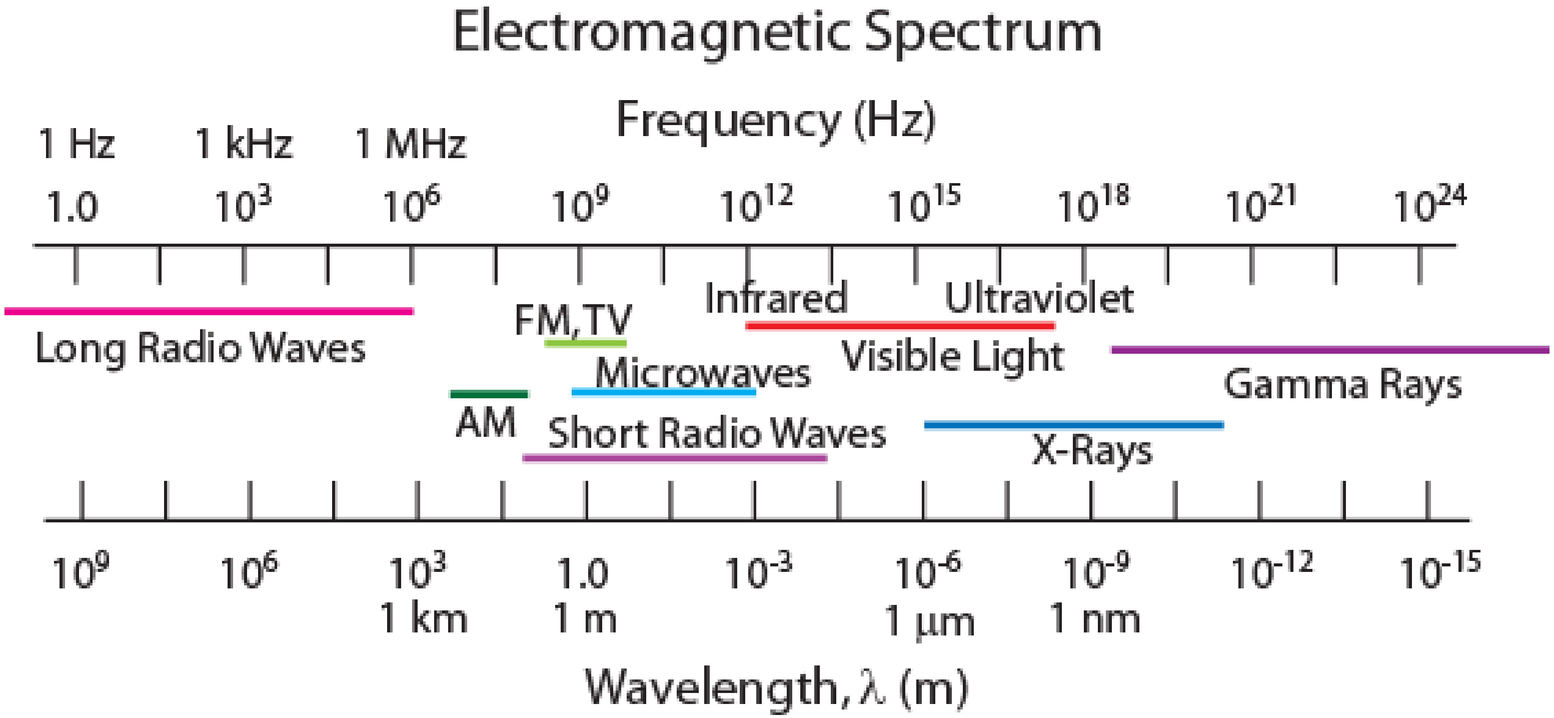
Poly(vinyl chloride) (PVC)



Polypropylene (PP)

Adapted from Fig. 5.2, *Callister & Rethwisch 9e.*

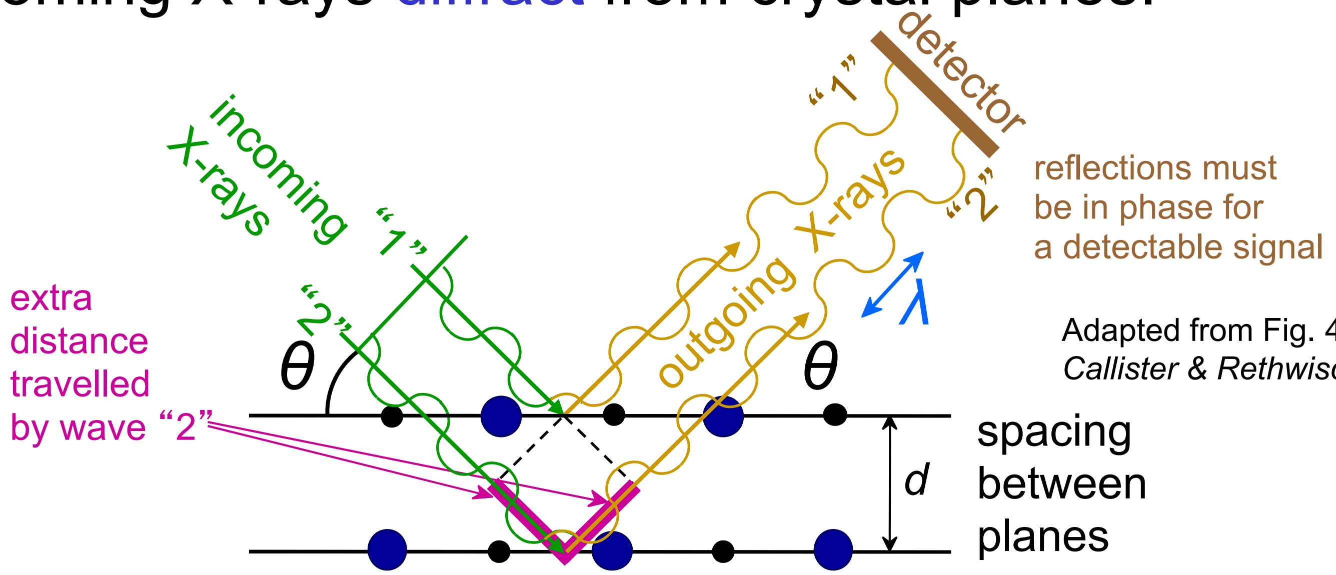
X-Ray Diffraction



- Diffraction gratings must have spacings comparable to the wavelength of diffracted radiation.
- Can't resolve spacings $< \lambda$
- Spacing is the distance between parallel planes of atoms.

X-Rays to Determine Crystal Structure

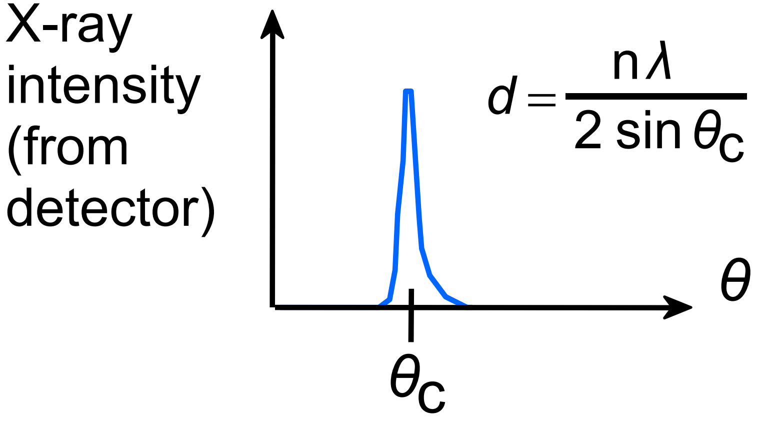
- Incoming X-rays diffract from crystal planes.



reflections must be in phase for a detectable signal

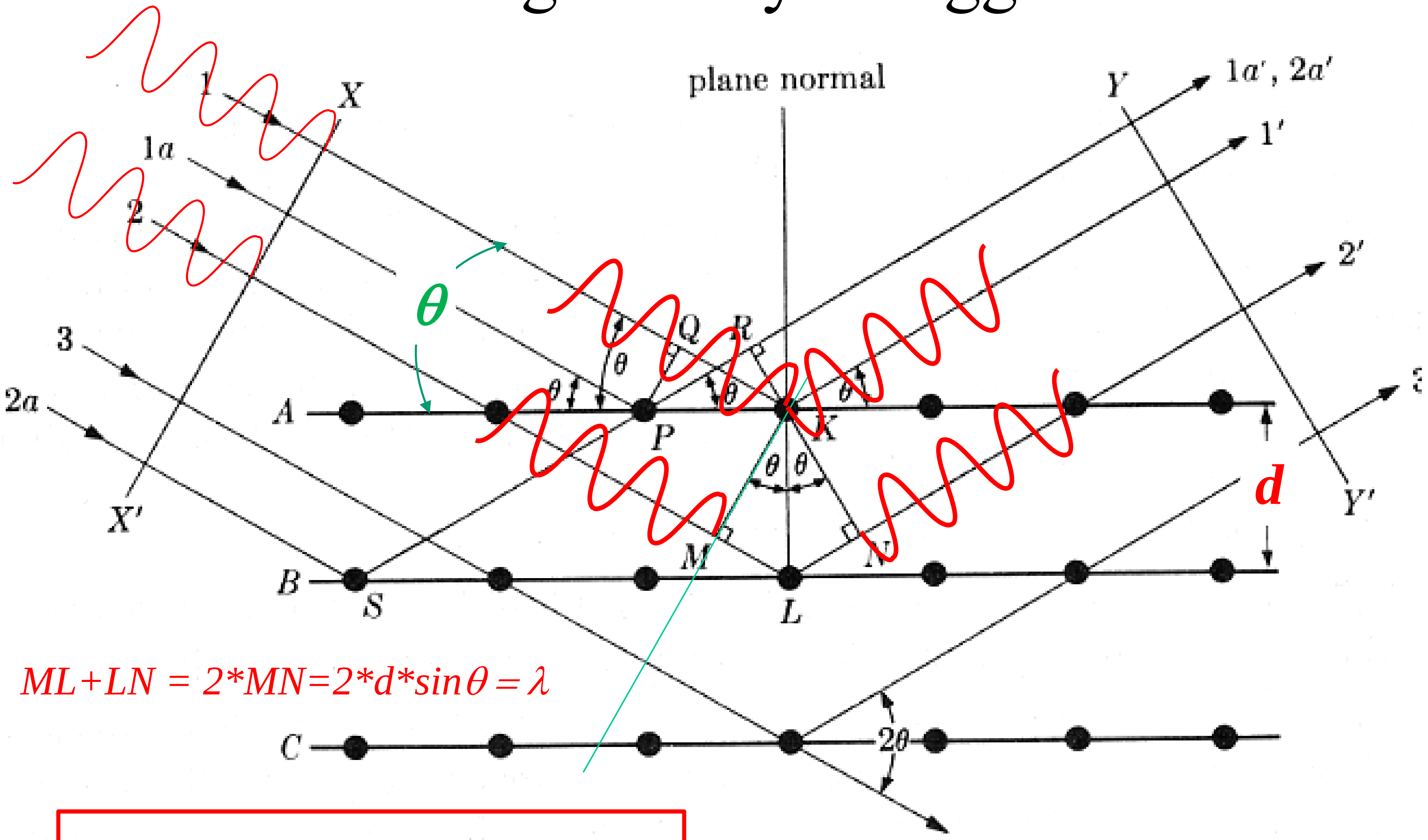
Adapted from Fig. 4.29, *Callister & Rethwisch 9e*.

Measurement of critical angle, θ_c, allows computation of planar spacing, *d*.



$$d = \frac{n\lambda}{2\sin\theta_c}$$

Diffraction geometry: Bragg’s Law



ML+LN = 2*MN=2*d*sin$\theta = \lambda$

$$\boxed{\lambda = 2d\sin\theta_B}$$

Structure Determination (X-Ray)

Crystal structure	**Diffraction does not occur when**	**Diffraction occurs when**
Body-centered cubic (bcc)	$h + k + l =$ odd number	$h + k + l =$ even number
Face-centered cubic (fcc)	h, k, l mixed (i.e., both even and odd numbers)	h, k, l unmixed (i.e., are all even numbers or all odd numbers)
Hexagonal close packed (hcp)	$(h + 2k) = 3n$, l odd (n is an integer)	All other cases

diffraction line	$h^2+k^2+l^2$ (cubic)		
	sc	bcc	fcc
100	1		
110	2	2	
111	3		3
200	4	4	4
210	5		
211	6	6	
220	8	8	8
221	9		

$$2d \sin \theta = \lambda$$

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

(interplanar spacing)

Contents for today's class

Chapter 6: Imperfections in Solids

I. Point defects

- Point defects in metals/ceramics/polymers, impurities in solids

II. Dislocations-Linear defects

- Edge/ Screw/ Mix dislocation

III. Interfacial defects

- External surfaces/ Grain boundaries/ Phase boundaries (stacking fault)/ Twin boundaries/ domain boundaries

IV. Bulk or Volume defects

- pores/ cracks/ foreign inclusions, and other phases

V. Microscopic Examination

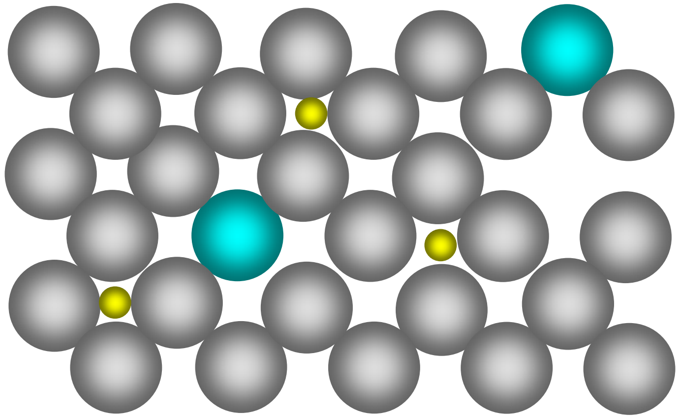
- Basic concepts of microscopy
- Microscopic techniques : Optical microscopy (Grain-size determination) / Electron microscopy/ Scanning probe microscopy

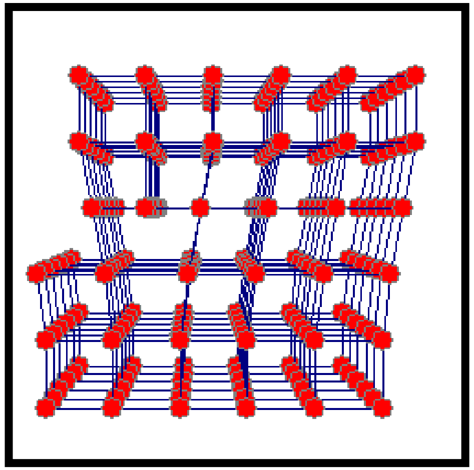
Chapter 6: Imperfections in Solids

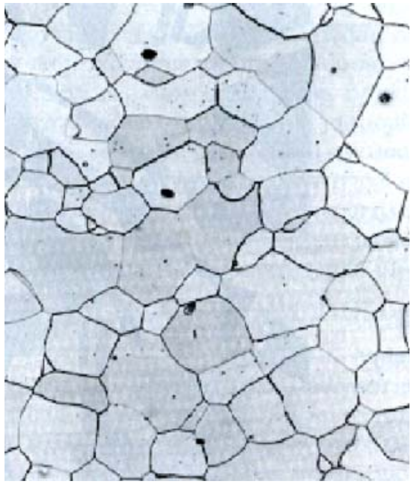
- Perfect and extensive ordering does not exist.
- Crystalline imperfections have a profound effect on materials behavior
- If we can control imperfections, it is possible to produce
  - stronger metals and alloys
  - more powerful magnets
  - improved transistors and solar cells
  - glassware of striking colors

Types of Imperfections

0-dimensional	Point defects	Vacancy atoms Interstitial atoms Substitutional atoms
1-dimensional	Line defects	Dislocations
2-dimensional	Planar (Area) defects	Surface Grain boundary Stacking fault

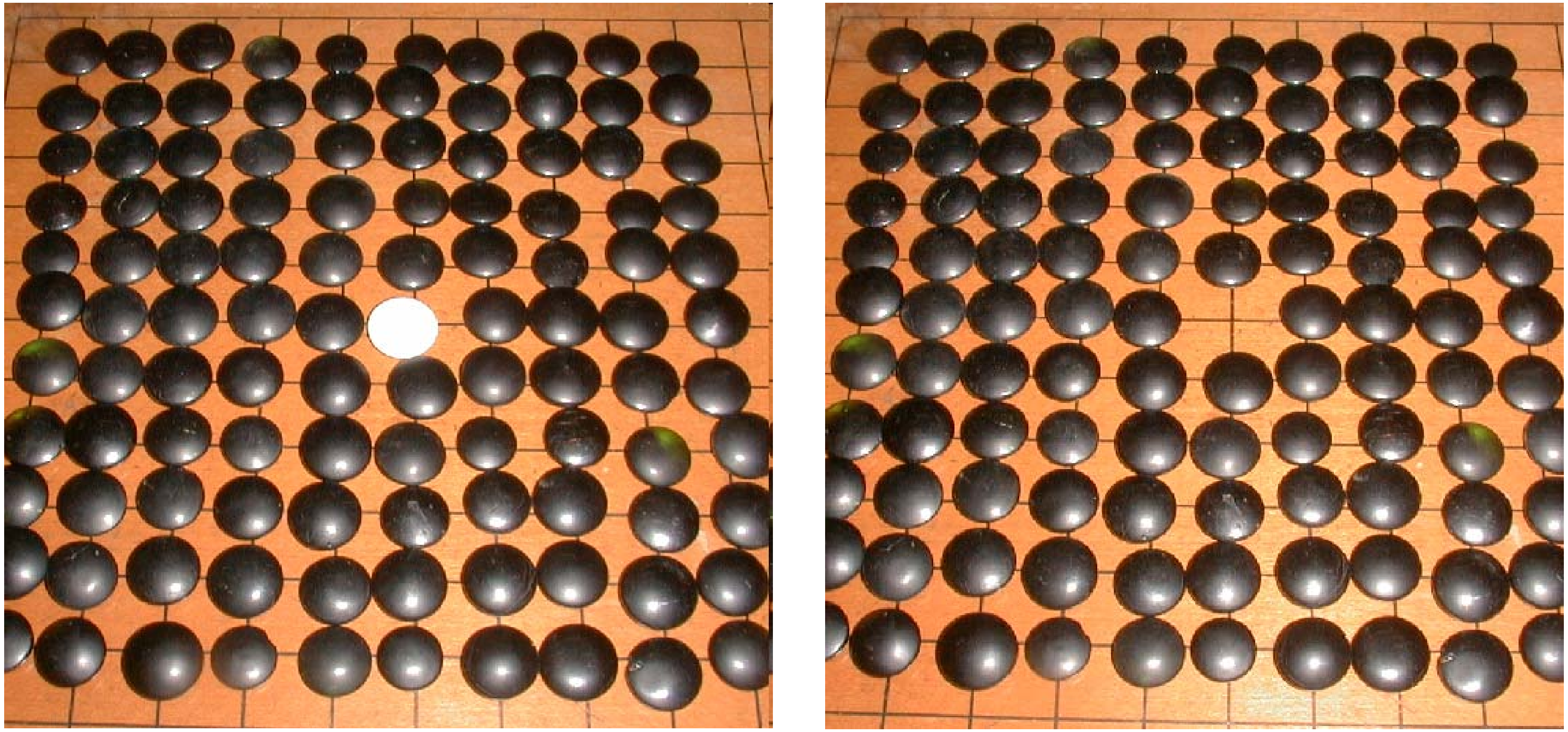






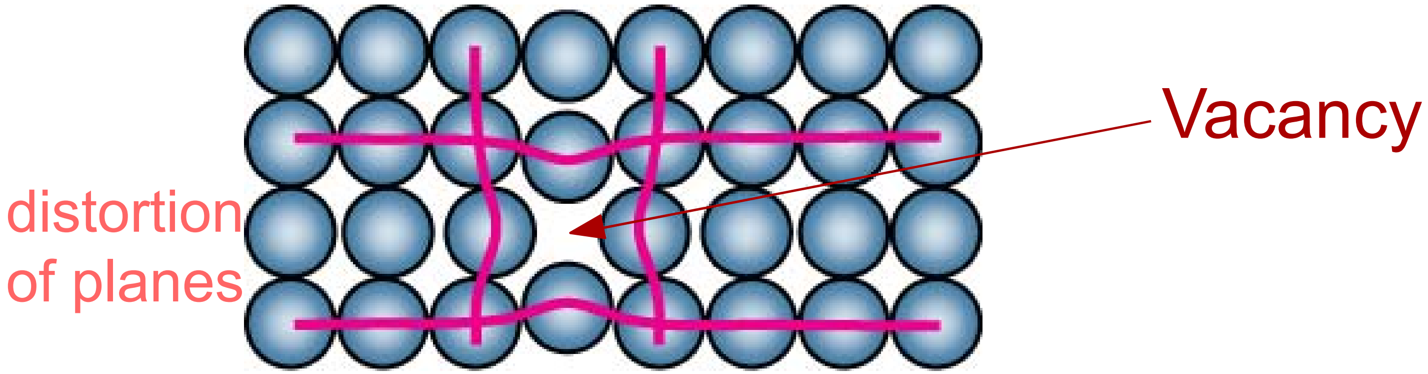
I. Point Defects

- What is a point defect?

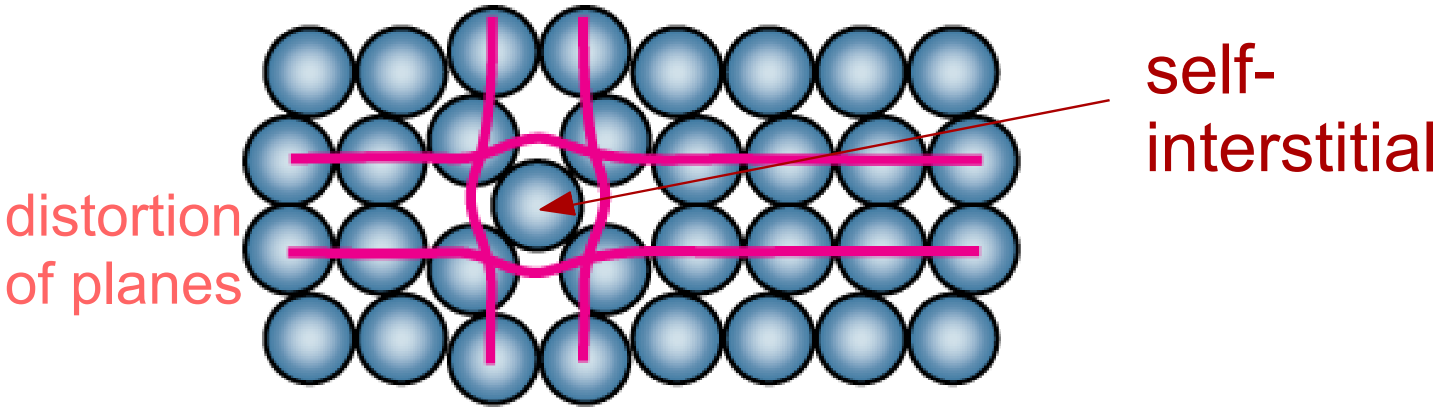


Point Defects in Metals

- **Vacancies**:
  -vacant atomic sites in a structure.

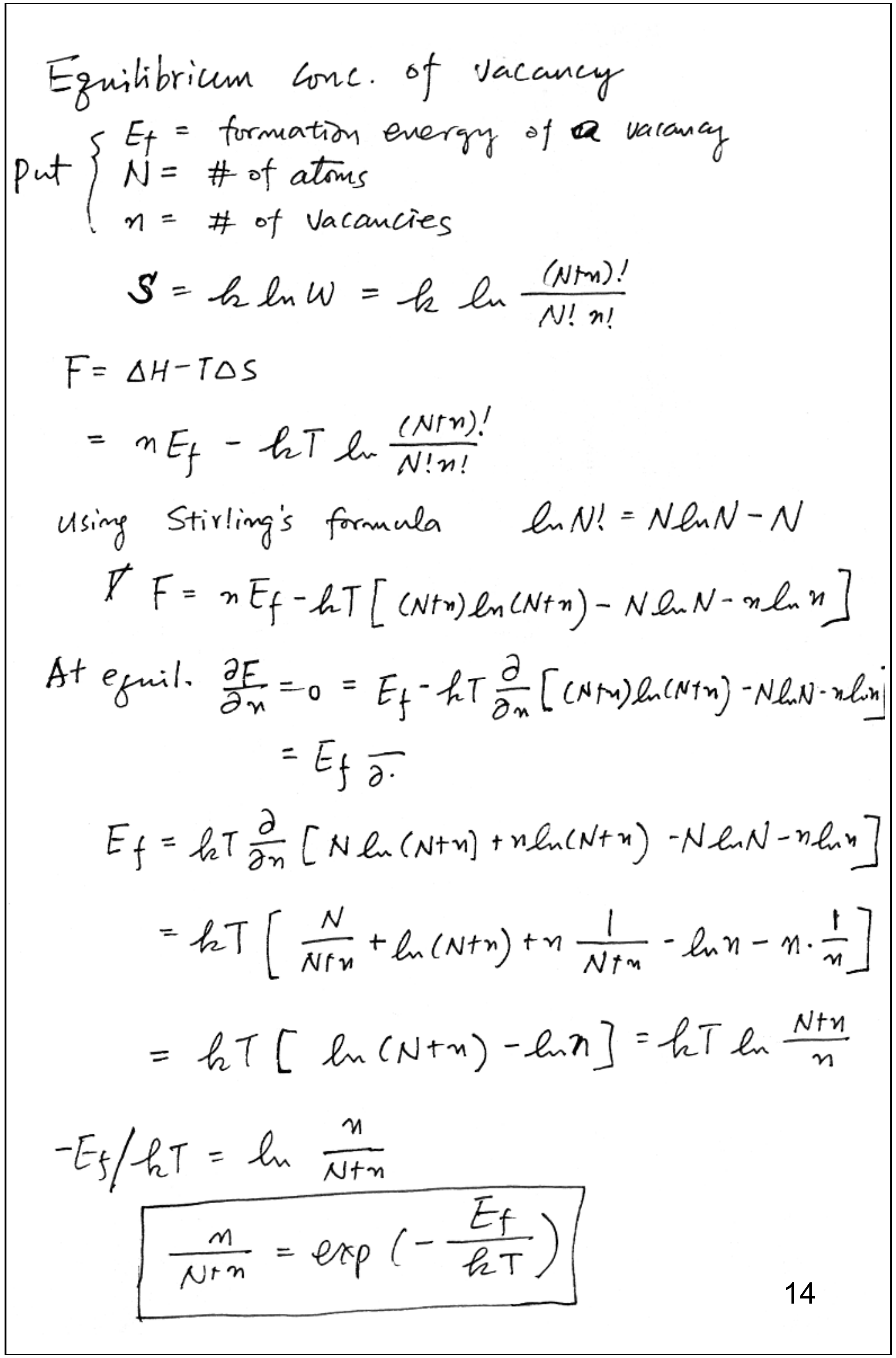


- **Self-Interstitials**:
  -"extra" atoms positioned between atomic sites.



Point defect thermodynamically predictable!

Thermodynamic arguments not only suggest that point defects may be present, but actually demand their presence and imply that it is impossible to create a stable single crystal without point defects.



Equilibrium conc. of vacancy

Put $\begin{cases} E_f = \text{formation energy of a vacancy} \\ N = \#\text{ of atoms} \\ n = \#\text{ of vacancies} \end{cases}$

$$S = k \ln W = k \ln \frac{(N+n)!}{N!\,n!}$$

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

$$= nE_f - kT \ln \frac{(N+n)!}{N!\,n!}$$

using Stirling's formula $\ln N! = N\ln N - N$

$$\therefore F = nE_f - kT\left[(N+n)\ln(N+n) - N\ln N - n\ln n\right]$$

At equil. $\frac{\partial E}{\partial n} = 0 = E_f - kT\frac{\partial}{\partial n}\left[(N+n)\ln(N+n) - N\ln N - n\ln n\right]$

$$= E_f \frac{}{\partial\cdot}$$

$$E_f = kT\frac{\partial}{\partial n}\left[N\ln(N+n) + n\ln(N+n) - N\ln N - n\ln n\right]$$

$$= kT\left[\frac{N}{N+n} + \ln(N+n) + n\frac{1}{N+n} - \ln n - n\cdot\frac{1}{n}\right]$$

$$= kT\left[\ln(N+n) - \ln n\right] = kT\ln\frac{N+n}{n}$$

$$-E_f/kT = \ln\frac{n}{N+n}$$

$$\boxed{\frac{n}{N+n} = \exp\left(-\frac{E_f}{kT}\right)}$$

a) 평형에 미치는 공공의 영향

1.5.8. Equilibrium Vacancy Concentration

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

G of the alloy will depend on the concentration of vacancies and X_V^e will be that which gives the minimum free energy.

1) Vacancies increase the internal energy of crystalline metal due to broken bonds formation. (Here, vacancy-vacancy interactions are ignored.)

$$\Delta H \cong \Delta H_V X_V$$

2) Vacancies increase entropy because they change the **thermal vibration frequency** and also the **configurational entropy**.

Small change due to changes in the vibrational frequencies

"Largest contribution"

- Total entropy change is thus

$$\Delta S = \Delta S_V X_V - R\{X_V \ln X_V + (1 - X_V)\ln(1 - X_V)\}$$

The molar free energy of the crystal containing X_V mol of vacancies

$$G = G_A + \Delta G = G_A + \Delta H_V X_V - T\Delta S_V X_V + RT\{X_V \ln X_V + (1 - X_V)\ln(1 - X_V)\}$$

➡ With this information,
estimate the equilibrium vacancy concentration.

Equilibrium concentration X_V^e will be that which gives the minimum free energy.

at equilibrium $$\left(\frac{dG}{dX_V}\right)_{X_V = X_V^e} = 0$$

$$\Delta H_V - T\Delta S_V + RT \ln X_V^e = 0$$

A constant ~3, independent of T

Rapidly increases with increasing T

$$X_V^e = \boxed{\exp\frac{\Delta S_V}{R}} \cdot \exp\frac{-\Delta H_V}{RT}$$

putting $\Delta G_V = \Delta H_V - T\Delta S_V$

$$\boxed{X_V^e = \exp\frac{-\Delta G_V}{RT}}$$

- **In practice, ΔH_V is of the order of 1 eV per atom and $X_V{}^e$ reaches a value of about 10^{-4}~10^{-3} at the melting point of the solid**

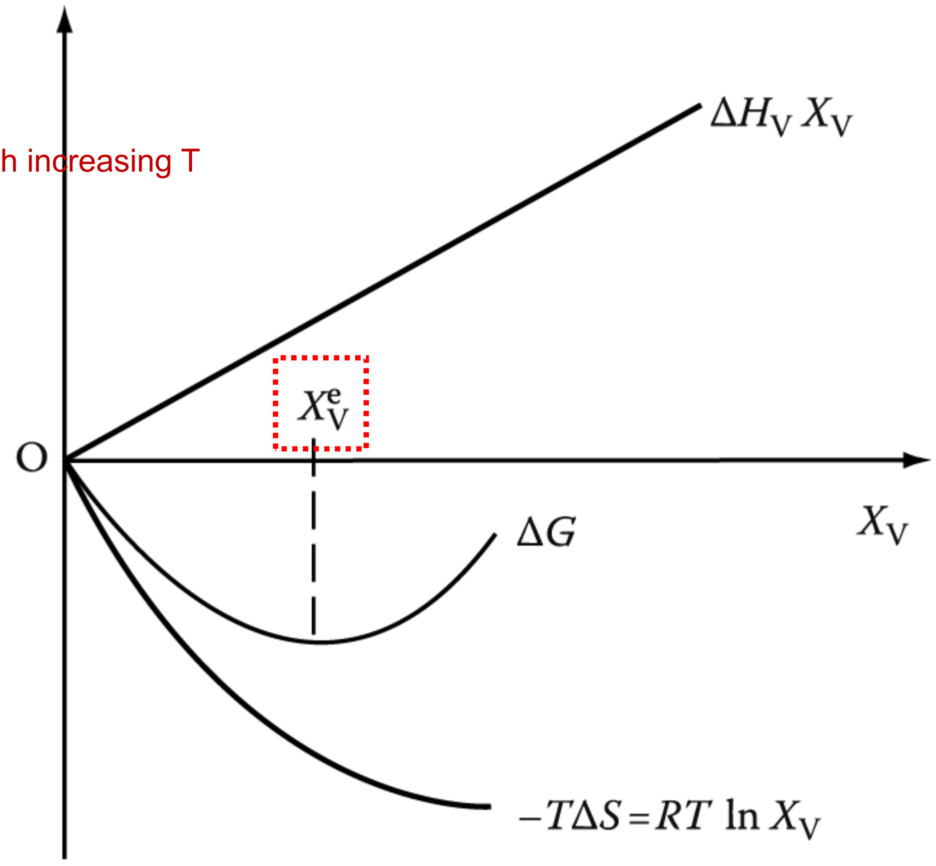


Fig. 1.37 Equilibrium vacancy concentration.

: adjust so as to reduce G to a minimum

Equilibrium Concentration: Point Defects

- Equilibrium concentration varies with temperature!

No. of defects

Activation energy

No. of potential defect sites

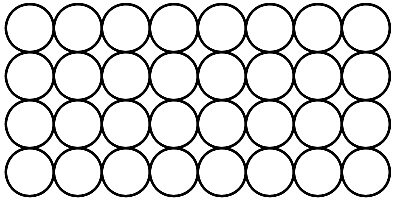
$$\frac{N_v}{N} = \exp\left(\frac{-Q_v}{kT}\right)$$

Temperature

Boltzmann's constant

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

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



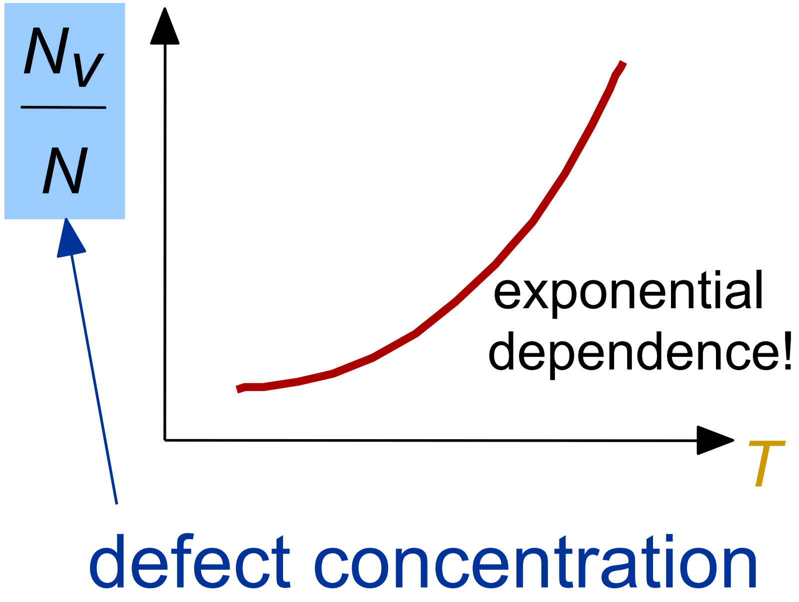
Each lattice site is a potential vacancy site

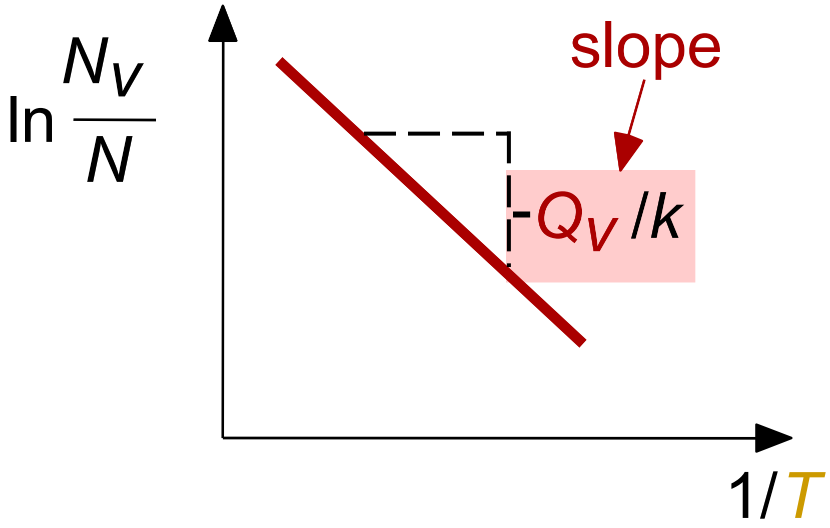
Measuring Activation Energy

- <u>We can get Q_v from an experiment.</u>

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

- Measure this...
- Replot it...





Estimating Vacancy Concentration

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

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

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

0.9 eV/atom

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

1273 K

8.62×10^{-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:

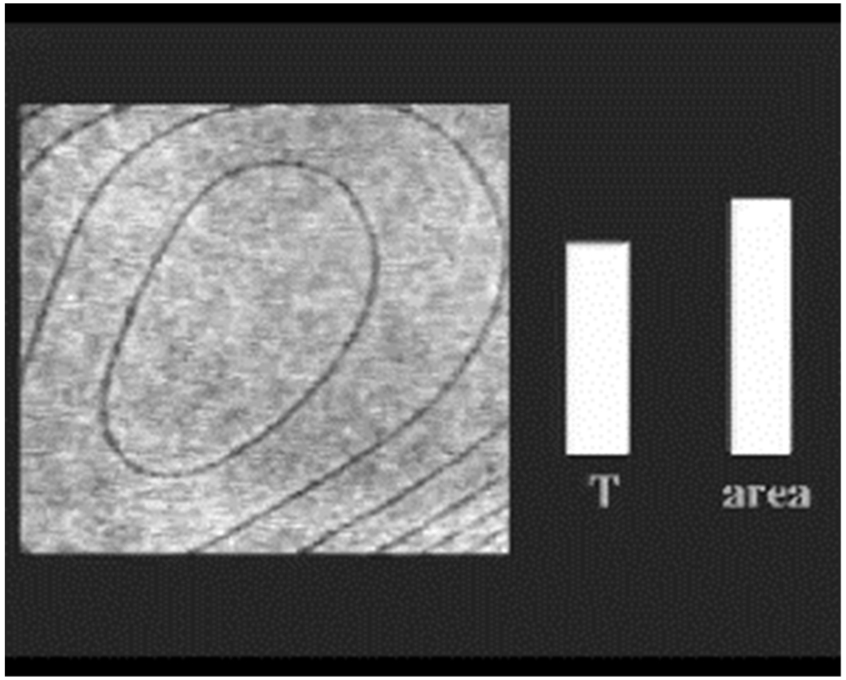
$N_v = (2.7 \times 10^{-4})(8.0 \times 10^{28})$ sites $= 2.2 \times 10^{25}$ vacancies

T_m of Cu= 1085 °C

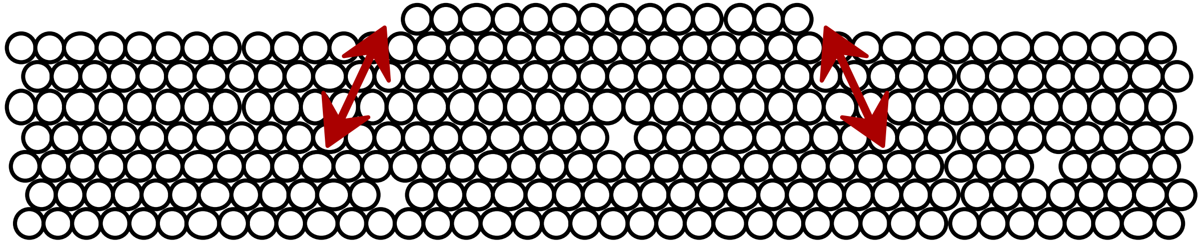
25 °C 의 $N_v = 4.9 \times 10^{13}$ vacancies

Observing Equilibrium Vacancy Concentration

- Low energy electron microscope view of a (110) surface of NiAl
- Increasing T causes surface island of atoms to grow
- Why? The equil. vacancy conc. increases via atom motion from the crystal to the surface, where they join the island



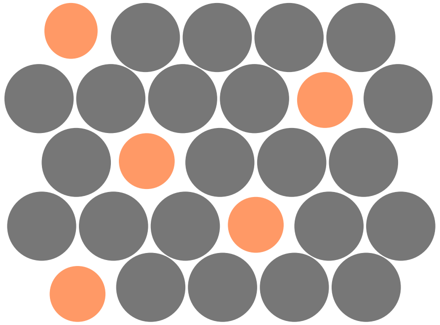
Island grows/shrinks to maintain equil. vancancy conc. in the bulk.



Imperfections in Metals (i)

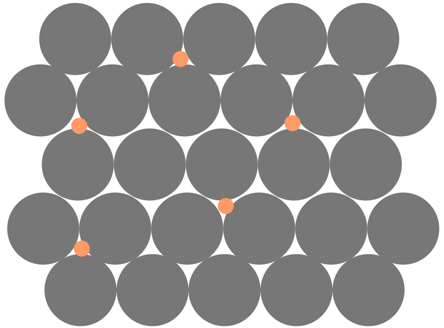
Two outcomes if impurity (B) added to host (A):

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



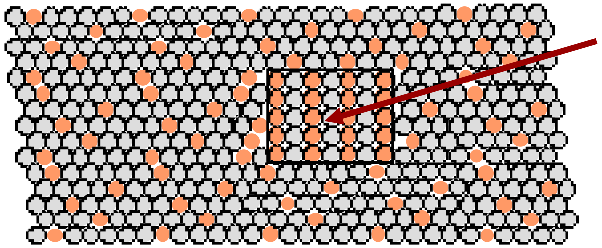
Substitutional solid soln.
(e.g., Cu in Ni)

OR



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

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



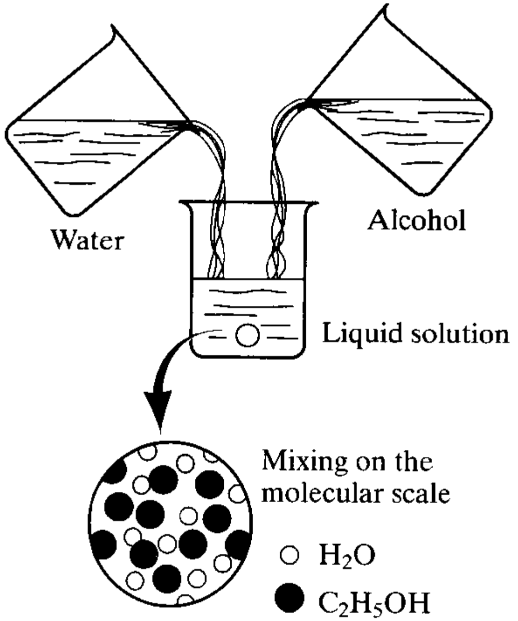
Second phase particle
-- different composition
-- often different structure.

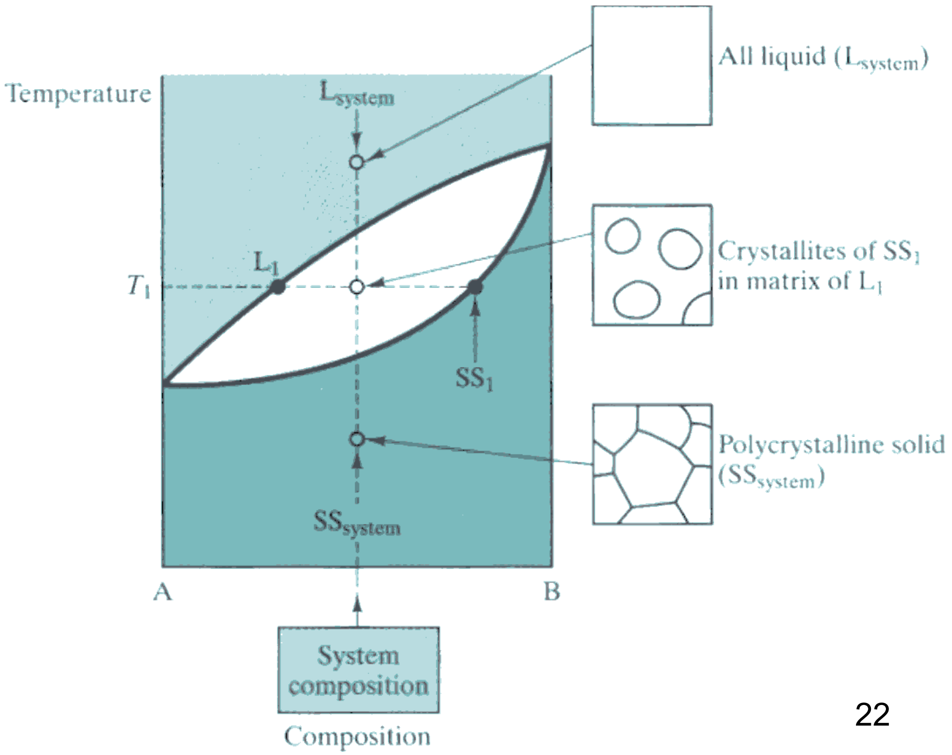
Solubility

- Unlimited Solubility
  - Hume Rothery' Conditions
    - Similar Size
    - Same Crystal Structure
    - Same Valance
    - Similar Electronegativity
  - Implies <u>single phase</u>

- Limited Solubility
  - Implies <u>multiple phases</u>

- No Solubility
  - oil and water region





Hume-Rothery Rules for Mixing

Empirical rules for substitutional solid-solution formation were identified from experiment that are not exact, but give an expectation of formation. Briefly,

1) Atomic Size Factor **The 15% Rule**

If "size difference" of elements are greater than ±15%, the lattice distortions (i.e. local lattice strain) are too big and solid-solution will not be favored.

$$\mathrm{DR\%} = \frac{r_{solute} - r_{solvent}}{r_{solvent}} \mathrm{x}100\% \quad < \pm 15\% \text{ will not disallow formation.}$$

2) Crystal Structure **Like elemental crystal structures are better**

For appreciable solubility, the crystal structure for metals must be the same.

3) Electronegativity **ΔE ~ 0 favors solid-solution.**

The more electropositive one element and the more electronegative the other, then "intermetallic compounds" (order alloys) are more likely.

4) Valences **Higher in lower alright. Lower in higher, it's a fight.**

A metal will dissolve another metal of higher valency more than one of lower valency.

Hume-Rothery Empirical Rules in Action

Is solid-solution favorable, or not?

- **Cu-Ni Alloys**

Rule 1: r_{Cu} = 0.128 nm and r_{Ni}= 0.125 nm.

DR%= $\frac{r_{solute} - r_{solvent}}{r_{solvent}} x100\%$ **= 2.3%** **favorable √**

Rule 2: Ni and Cu have the FCC crystal structure. **favorable √**

Rule 3: E_{Cu} = 1.90 and E_{Ni}= 1.80. Thus, ΔE%= -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.

At high T, it does (helpful processing info), but actually phase separates at low T due to energetics (quantum mechanics).

Hume-Rothery Empirical Rules in Action

Is solid-solution favorable, or not?

- **Cu-Ag Alloys**

Rule 1: r_{Cu} = 0.128 nm and r_{Ag}= 0.144 nm.

DR%= $\frac{r_{solute} - r_{solvent}}{r_{solvent}} x100\%$ **= 9.4%** **favorable √**

Rule 2: Ag and Cu have the FCC crystal structure. **favorable √**

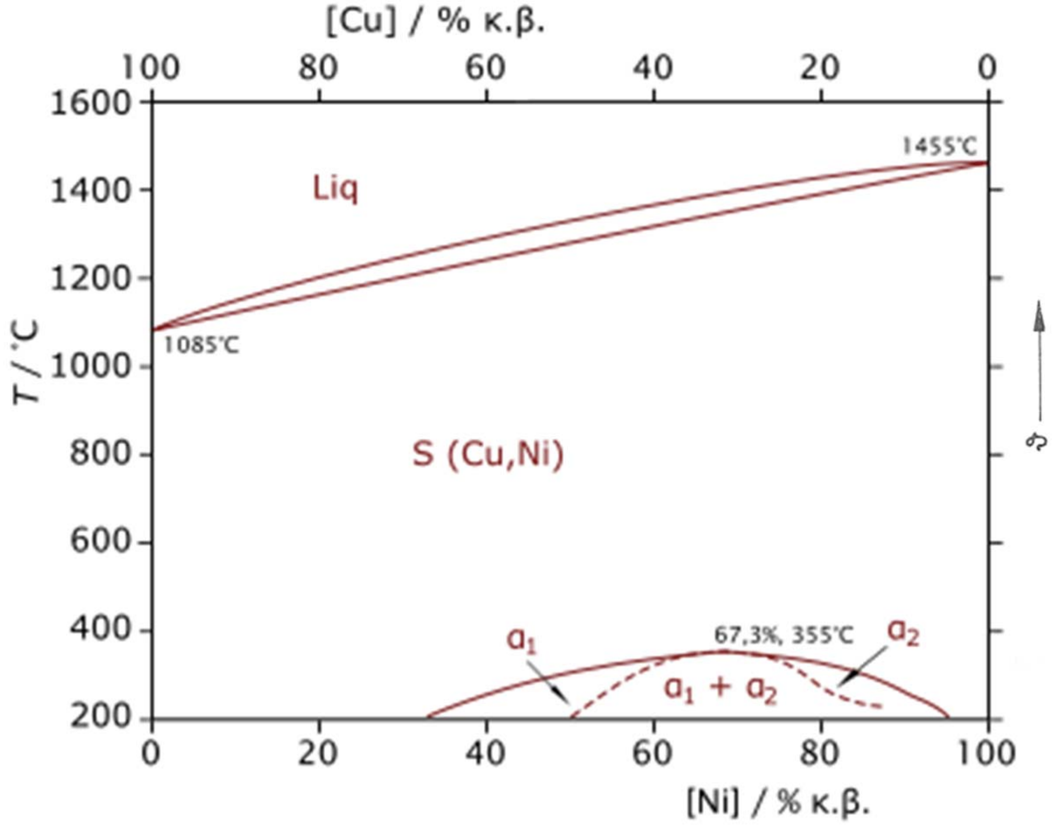
Rule 3: E_{Cu} = 1.90 and E_{Ni}= 1.80. Thus, DE%= -5.2% **favorable √**

Rule 4: Valency of Cu is +2 and Ag is +1. **NOT favorable**

Expect Ag and Cu have <u>limited solubility</u>.

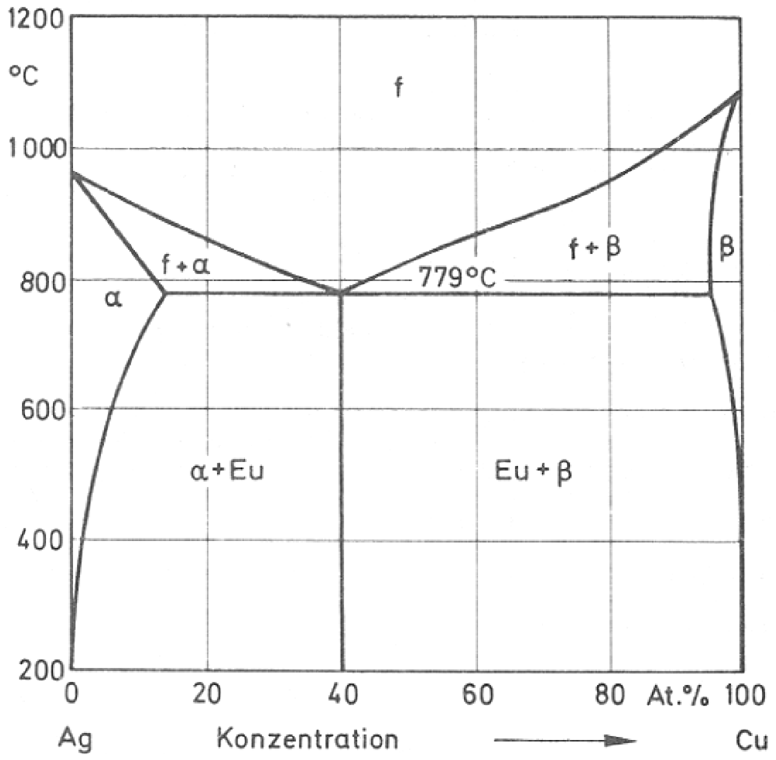
In fact, the Cu-Ag phase diagram (T vs. c) shows that a solubility of only 18% Ag can be achieved at high T in the Cu-rich alloys.

Cu-Ni Alloys



complete solid solution

Cu-Ag Alloys

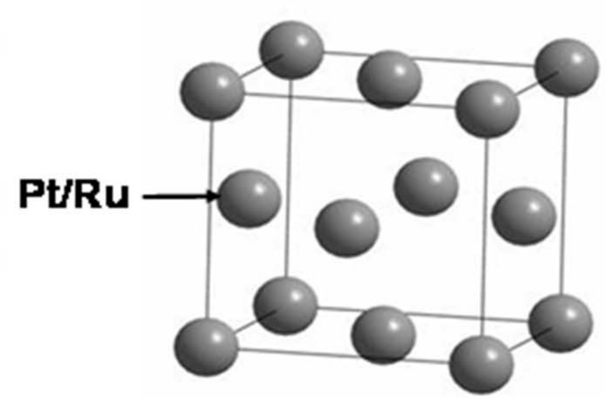


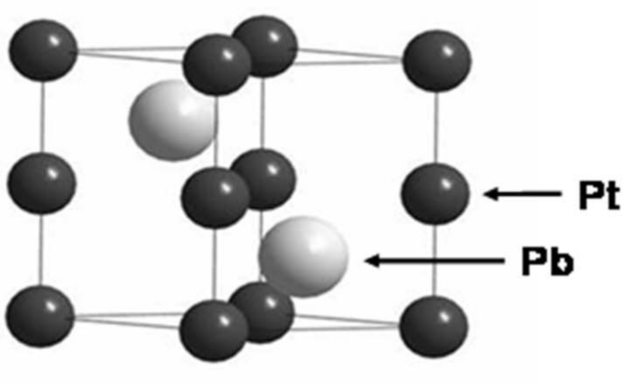
limited solid solution

Alloying: atoms mixed on a lattice ➡ solid solution and ordered compound

Solid Solution vs. Intermetallic Compound

Crystal structure

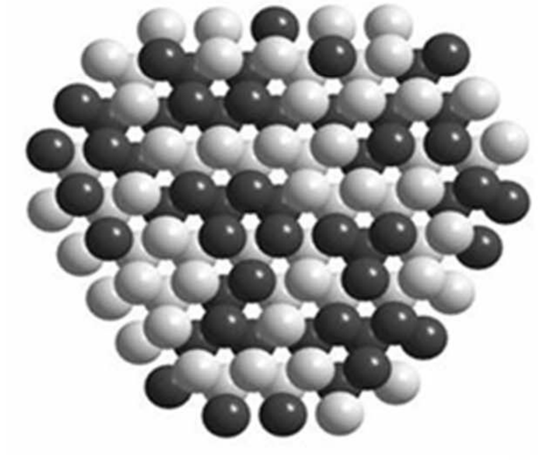


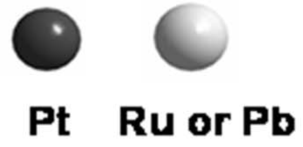


$Pt_{0.5}Ru_{0.5}$ – Pt structure (fcc)

PtPb – NiAS structure

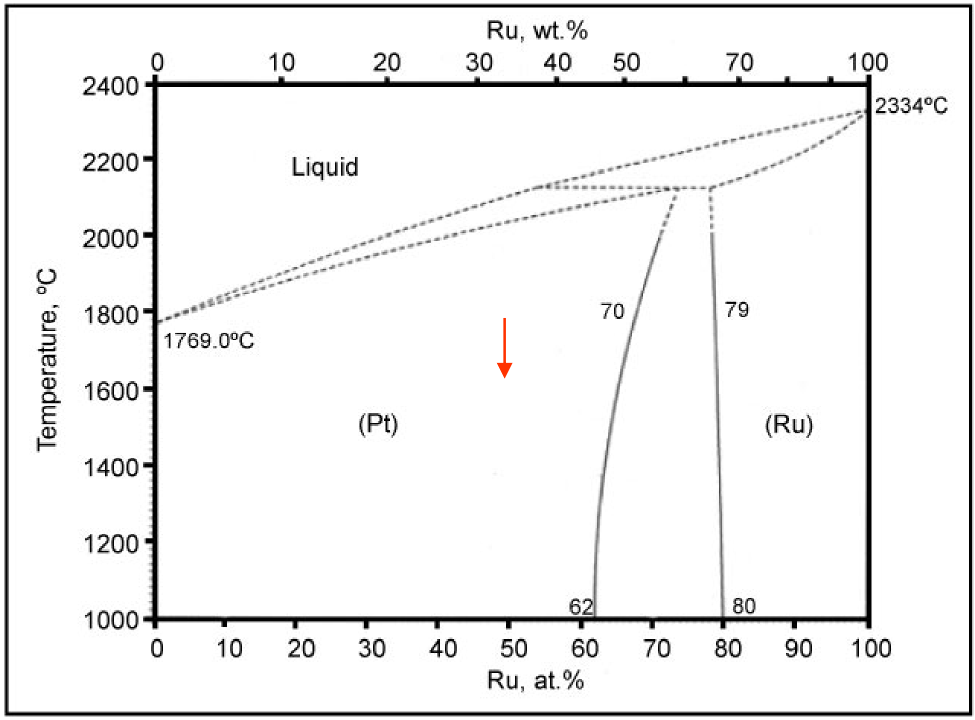
Surface

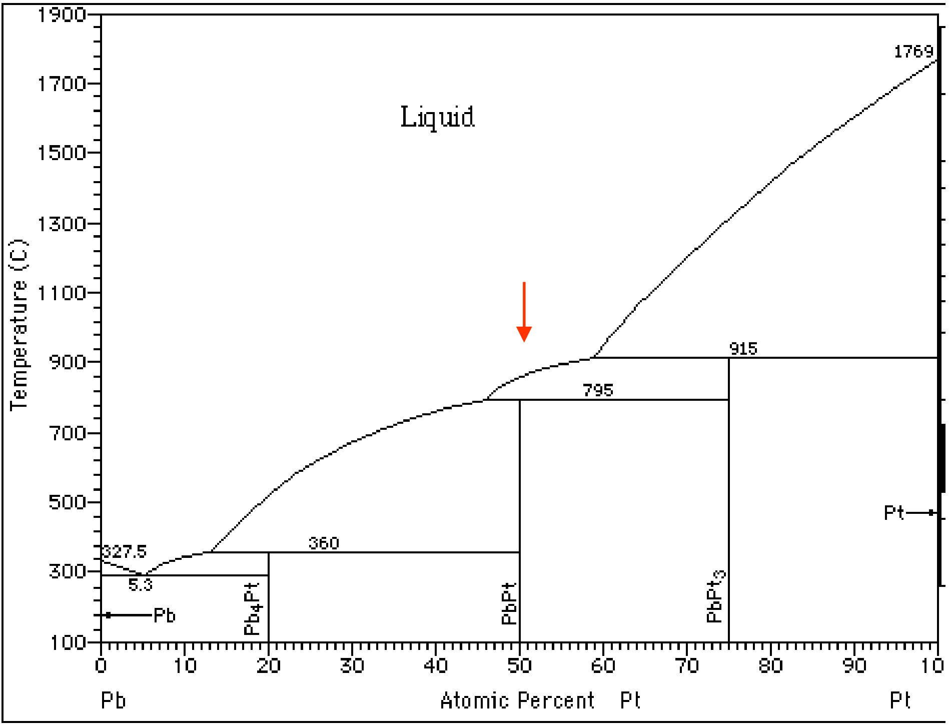




ruthenium 루테늄《백금류의 금속 원소;기호 Ru, 번호 44》

Solid Solution vs. Intermetallic Compounds





$Pt_{0.5}Ru_{0.5}$ **– Pt structure (fcc)**

PbPt – NiAS structure

Assumption: a simple physical model for "binary solid solutions"

: in order to introduce some of the basic concepts of the thermodynamics of alloys

Composition

- Definition: Amount of impurity (B) and host (A) in the system
- Two descriptions:

  - Weight %

$$C_B = \frac{\text{mass of B}}{\text{total mass}} \times 100$$

  - Atom %

$$C'_B = \frac{\text{\# atoms of B}}{\text{total \# atoms}} \times 100$$

  - Conversion between wt % and at% in an A-B alloy:

$$C_B = \frac{C'_B A_B}{C'_A A_A + C'_B A_B} \times 100 \qquad C'_B = \frac{C_B/A_B}{C_A/A_A + C_B/A_B}$$

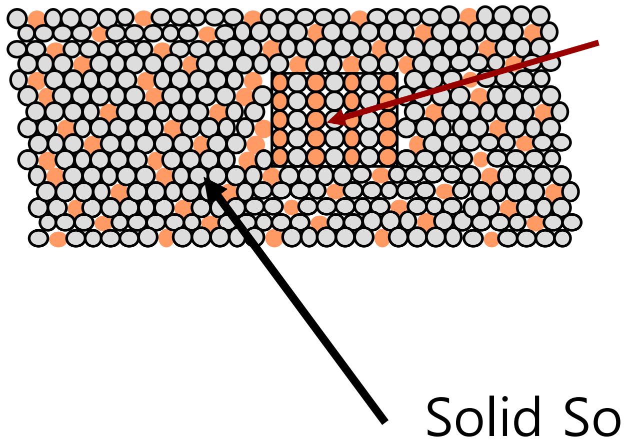
  - Basis for conversion:

$$\text{mass of B} = \text{moles of B} \times A_B \xleftarrow{} \text{atomic weight of B}$$

$$\text{mass of A} = \text{moles of A} \times A_A \xleftarrow{} \text{atomic weight of A}$$

Particles of New Phase in Solid-Solution Alloys

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

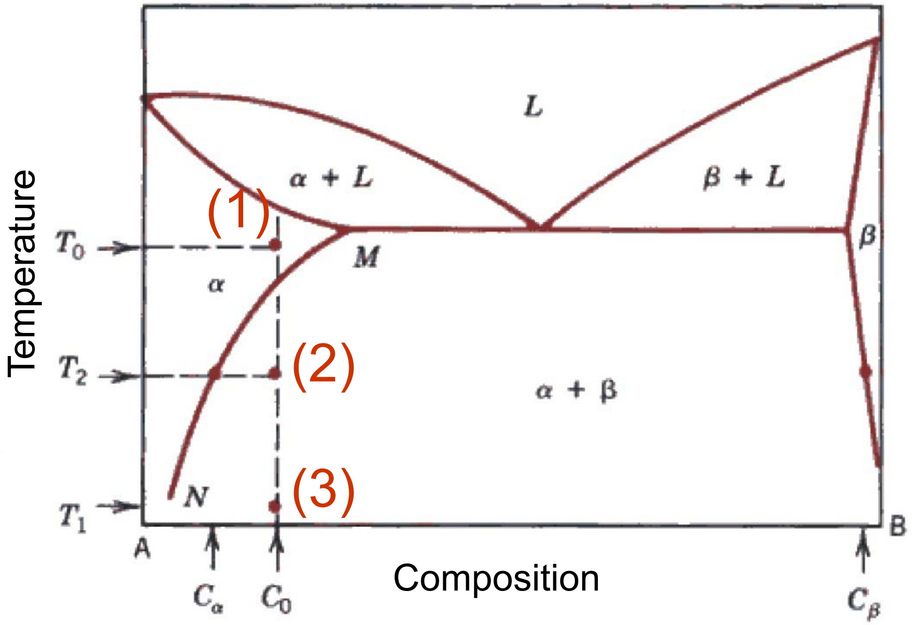


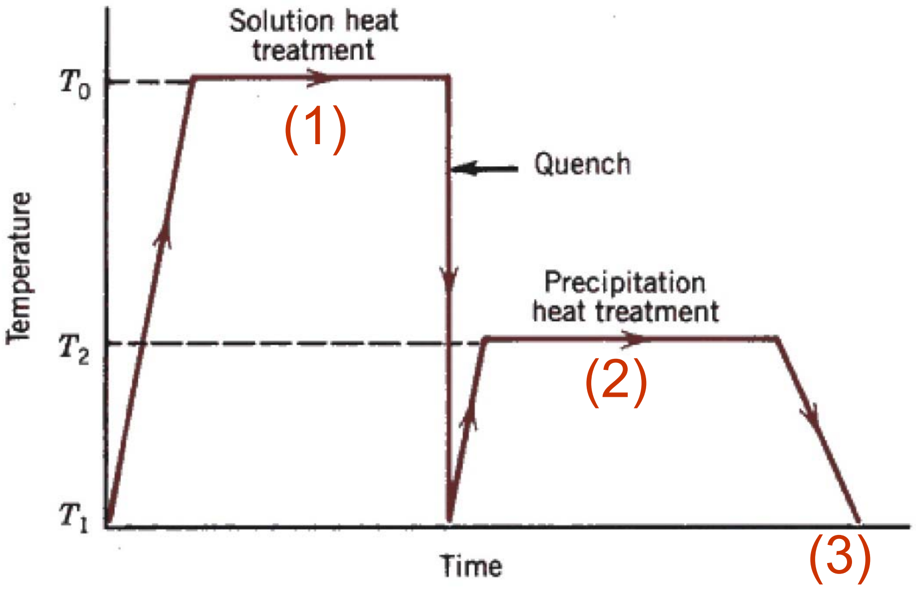
Second phase particle
--different composition
--often different structure.

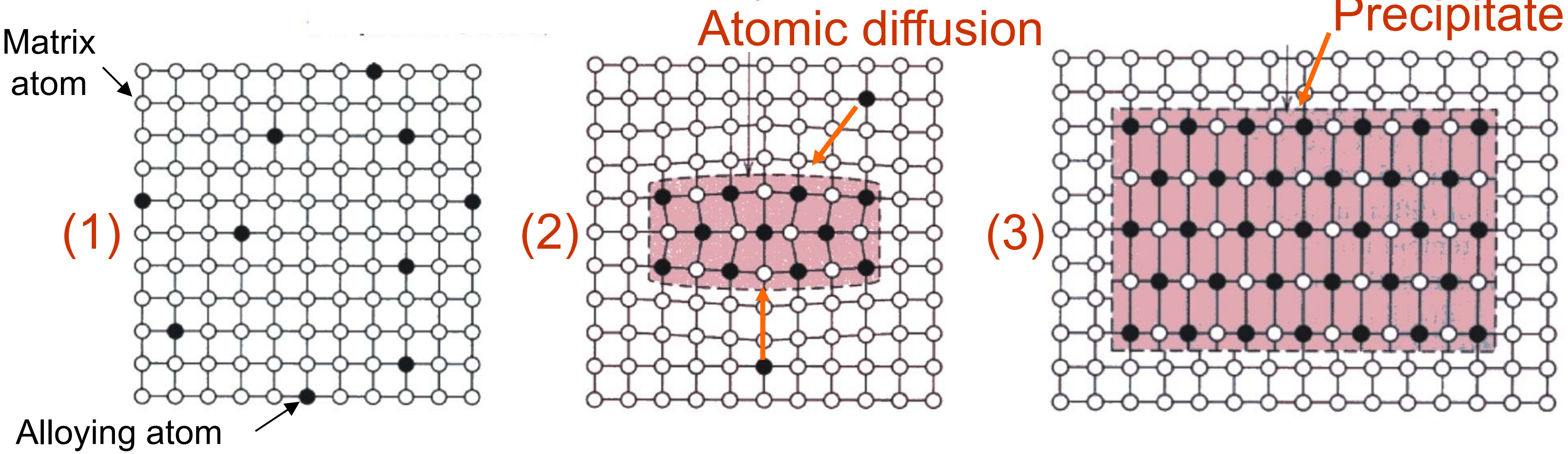
Solid Solution phase: B atoms in A

* Microstructure control : Secondary phase control

Mechanism of Precipitation





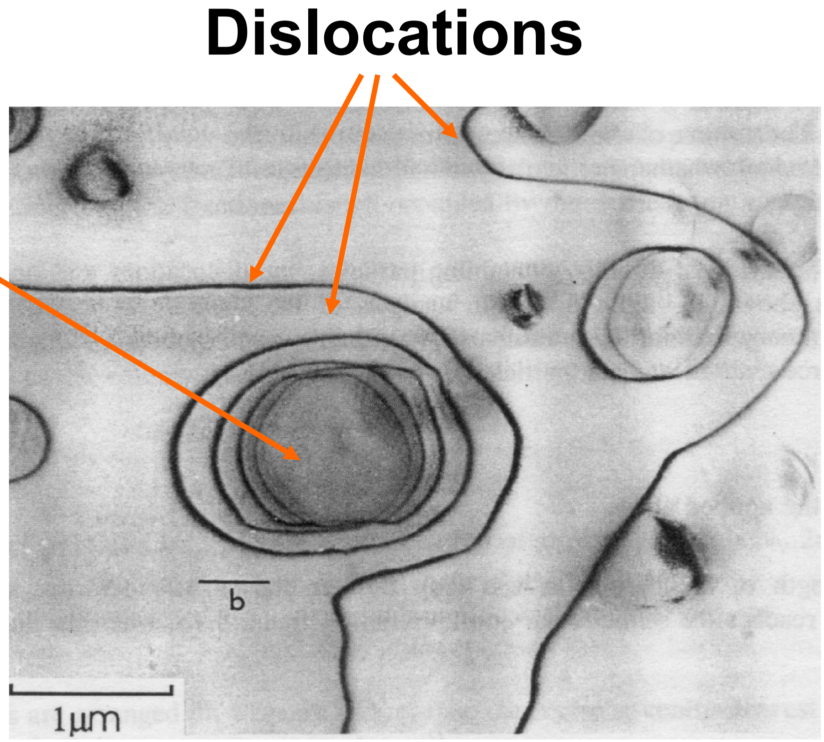


Effect of Second Phase Particle on Mechanical Property

Second phase particle in matrix material

Obstacle of dislocation slip & grain growth

High strength



Ni_3Si particles in Ni-6%Si single crystal

Point Defects in Ceramics (i)

- Vacancies
  - -- vacancies exist in ceramics for both cations and anions
- Interstitials
  - -- interstitials exist for cations
  - -- interstitials are not normally observed for anions because anions are large relative to the interstitial sites

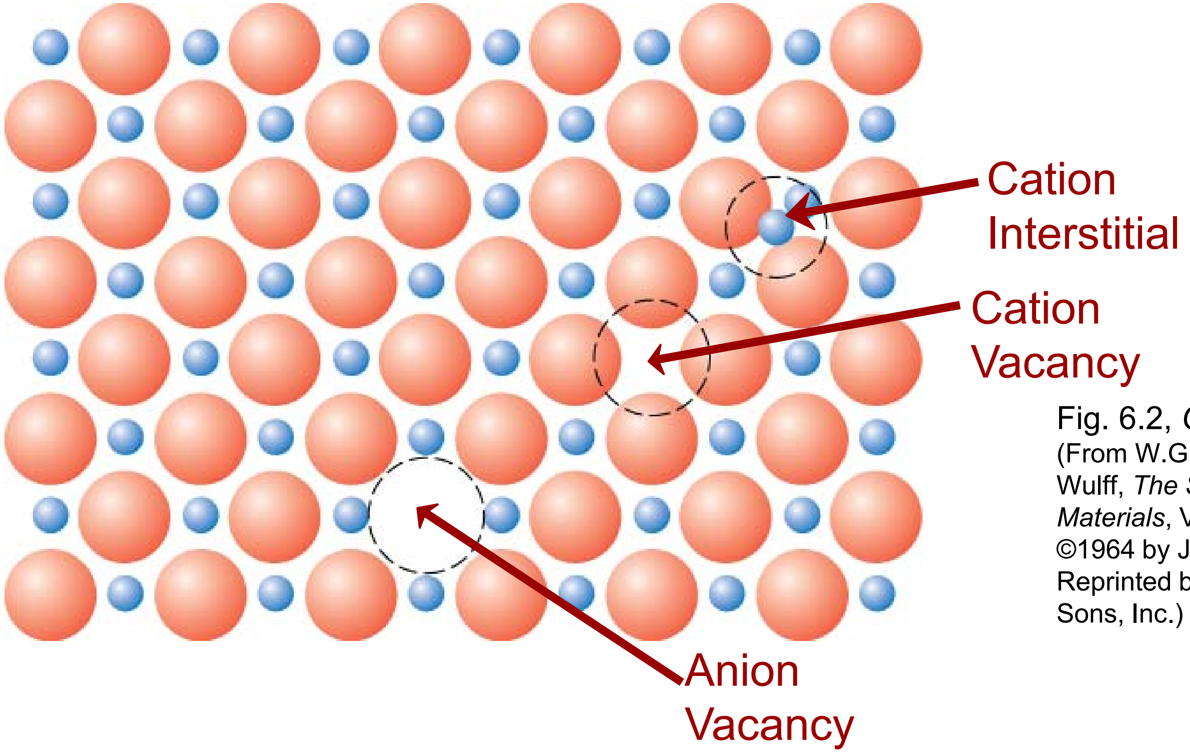


Fig. 6.2, *Callister & Rethwisch 9e.* (From W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, p.78. Copyright ©1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley and Sons, Inc.)

Point Defects in Ceramics (ii)

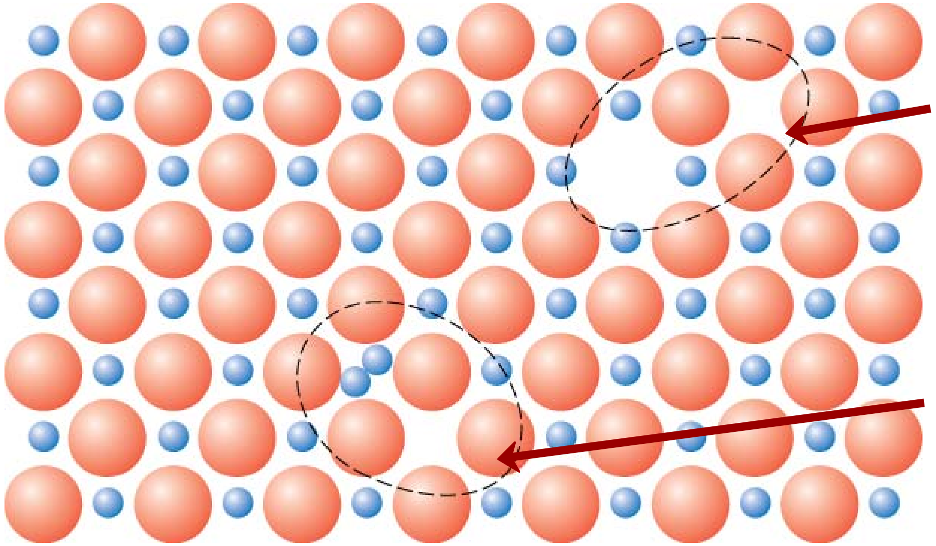
Should consider : Electrical charge neutrality

- Frenkel Defect

  -- a cation vacancy-cation interstitial pair.

- Shottky Defect

  -- a paired set of cation and anion vacancies.



Shottky Defect:

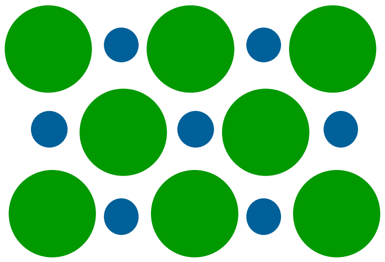
Frenkel Defect

Fig. 6.3, *Callister & Rethwisch 9e.* (From W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, p.78. Copyright ©1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley and Sons, Inc.)

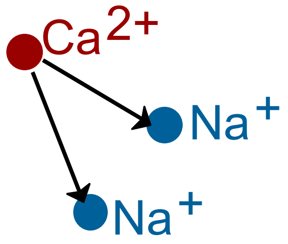
- Equilibrium concentration of defects $\propto e^{-Q_D/kT}$

Imperfections in Ceramics

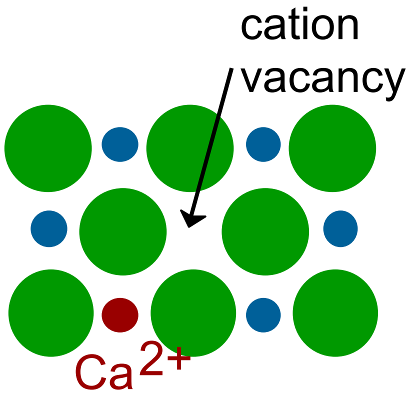
- Electroneutrality (charge balance) must be maintained when impurities are present
- Ex: NaCl Na^+ ● Cl^- ●
- Substitutional cation impurity



without impurity

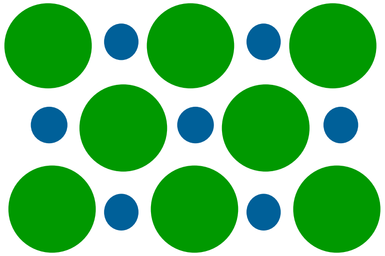


Ca^{2+} impurity

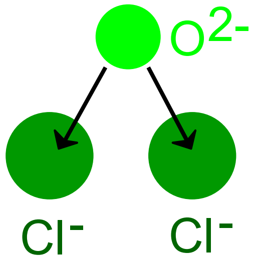


with impurity

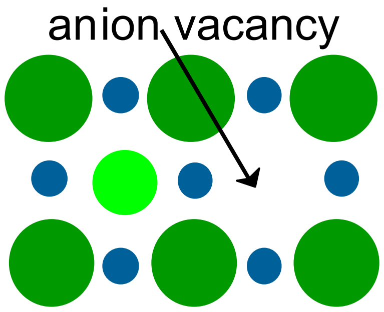
- Substitutional anion impurity



without impurity



O^{2-} impurity



with impurity

The value of seeing nothing

Jochen Mannhart and Darrell G. Schlom

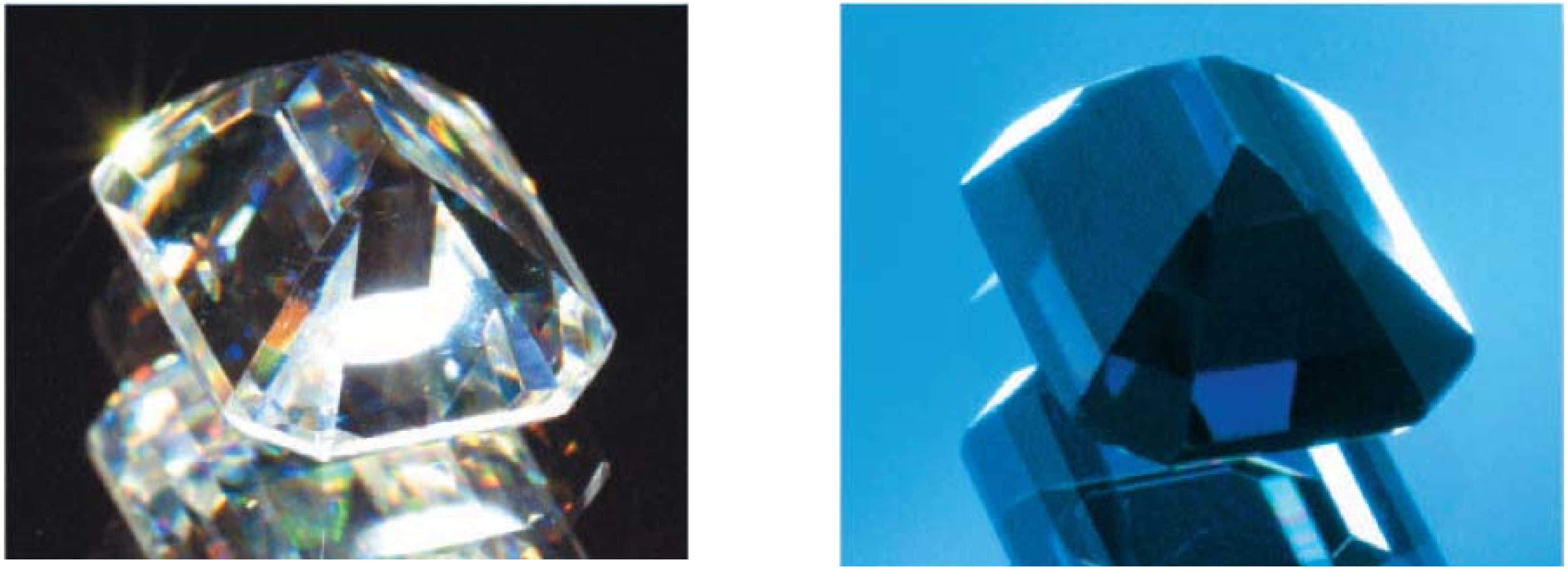


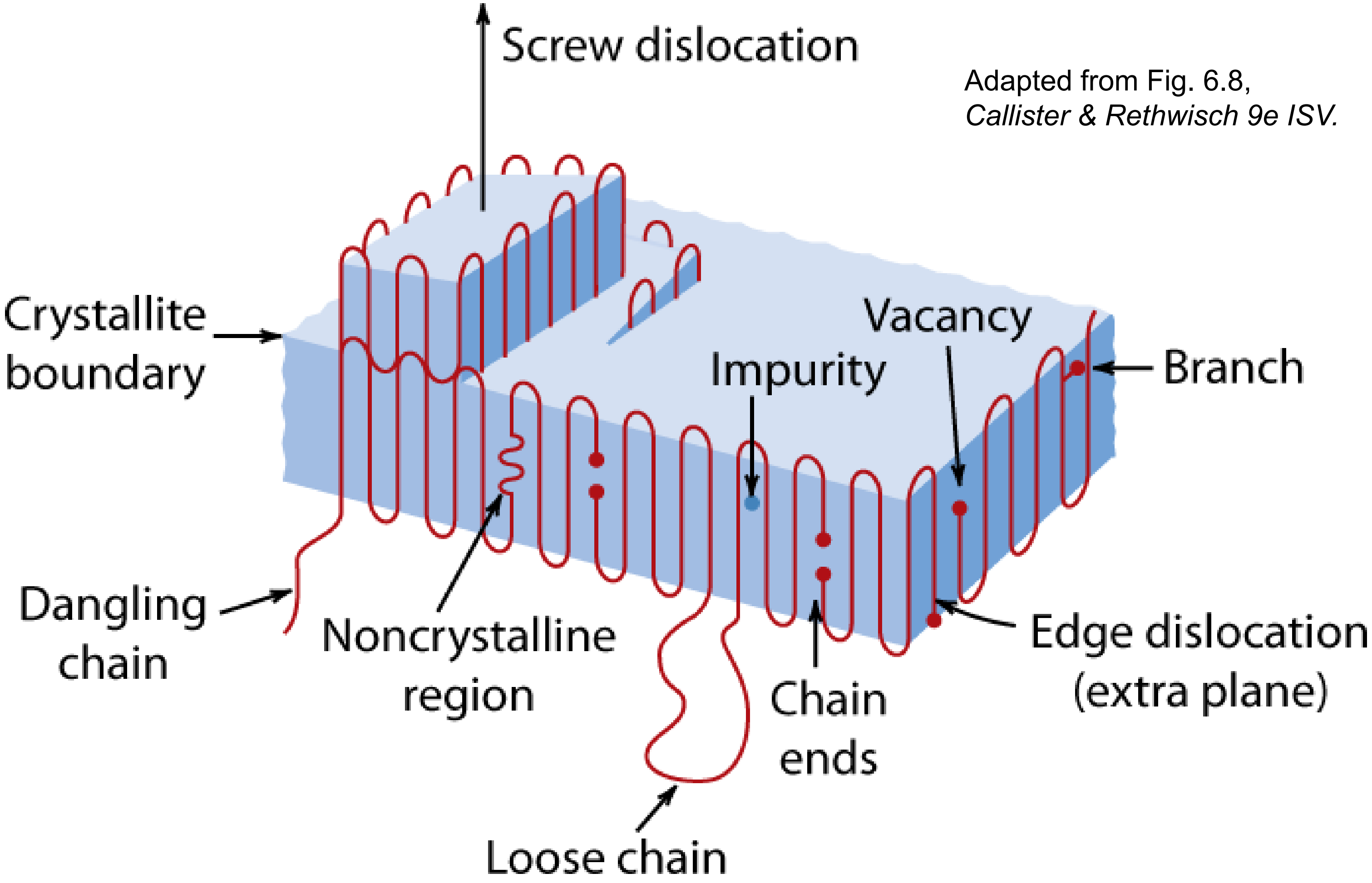
Figure now you see it, now you don’t. These micrographs of a **$SrTiO_3$ crystal** show the effect of removing oxygen atoms, leaving vacancies in the crystal lattice: the glistening oxidized gem (left) is transformed into **a dull blue, conductive crystal** (right).

Oxygen vacancy $V_o + 2e'$

NATURE | VOL 430 | 5 AUGUST 2004 | www.nature.com/nature

Point Defects in Polymers

- Defects due in part to chain packing errors and impurities such as chain ends and side chains



Adapted from Fig. 6.8, *Callister & Rethwisch 9e ISV.*

Contents for today's class

Chapter 6: Imperfections in Solids

I. Point defects

- Point defects in metals/ceramics/polymers, impurities in solids

- Equilibrium concentration varies with temperature!

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

- Two outcomes if impurity (B) added to host (A):
  - Solid solution of B in A (i.e., random dist.) _ **Hume-Rothery Rules**
  - Solid solution of B in A plus particles of a new phase (usually for a larger amount of B) _ **Precipitation!**

➢ Weight % $C_B = \frac{\text{mass of B}}{\text{total mass}} \times 100$ ➢ Atom % $C'_B = \frac{\text{\# atoms of B}}{\text{total \# atoms}} \times 100$

- Imperfection in Ceramics: Electroneutrality (charge balance) must be maintained when impurities are present.

- Point defects in polymer: defects due in part to chain packing errors and impurities such as chain ends and side chains