Chpt 5: Imperfections in Solids

ISSUES TO ADDRESS...

• **What types of defects arise in solids? Describe them.**

• **Can the number and type of defects be varied and controlled?**

• **How do defects affect material properties?**

• **Are defects undesirable?**

Given masses or atomic weights of two or more elements in an alloy, calculate weight or atomic percentages.

Lattice Defects

The concept of a perfect lattice is adequate for explaining *structure-insensitive* properties (esp. for metals).

But, to understand *structure-sensitive* properties, it is necessary to consider numerous lattice defects.

Practically all mechanical properties are structure-sensitive properties.

(almost) structure-insensitive	*structure-sensitive*
elastic constants	Electrical conductivity
Melting points	Semiconducting properties
density	Yield stress
Specific heat	Fracture strength
coefficient of thermal expansion	Creep strength

Types of Imperfections

• **Vacancy atoms**
• **Interstitial atoms**   **Point defects**
• **Substitutional atoms**

• **Dislocations**   **Line defects**
   Edges, Screws, Mixed

• **Grain Boundaries**   **Planar defects**
• **Stacking Faults**
• **Anti-Phase and Twin Boundaries**
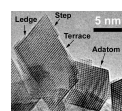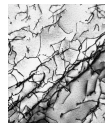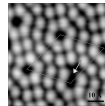
We need to describe them and understand their effects.

Length Scale of Imperfections

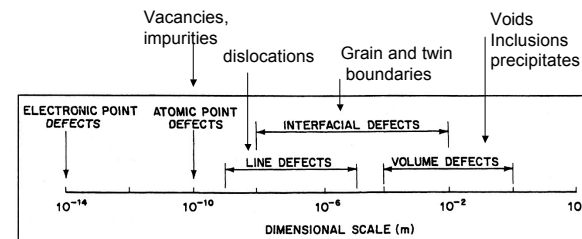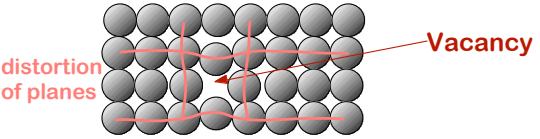**point, line, planar, and volumetric defects**

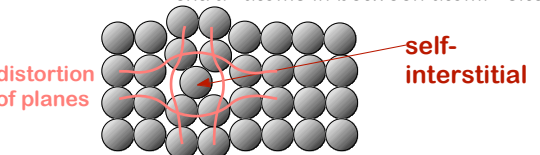**Figure 4.1** Dimensional ranges of different classes of defects.

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Point Defects

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

distortion of planes → **Vacancy**

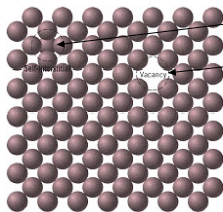- **Self-Interstitials**: "extra" atoms in between atomic sites.

distortion of planes → **self-interstitial**

Point Defects

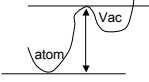**Self-interstitial**: atom crowded in 'holes'

Vacancy: a vacant lattice site

It is not possible to create a crystal free of vacancies. About 1 out of 10,000 sites are vacant near melting.

Self-interstitials are much less likely in metals, e.g.,, as it is hard to get big atom into small hole - there is large distortions in lattice required that costs energy.

Thermodynamics (temperature and counting) provides an expression for
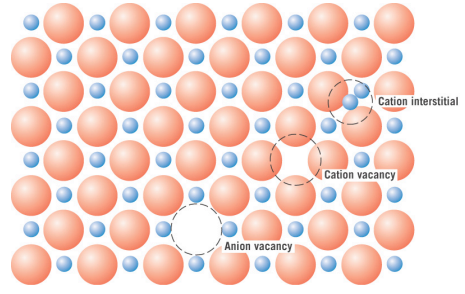
Vacancy Concentration: (see handout)
$$\frac{N_v}{N} = \exp\left(-\frac{Q_v}{k_B T}\right)$$

Q_v=vacancy formation energy
k_B= 1.38 x 10^{-23} J/atom-K = 8.62 x 10^{-5} eV/atom-K
k_B/mole = R = 1.987 cal/mol-K

Defects ALWAYS cost energy!

Point Defects in Ceramics

Cation interstitial

Cation vacancy
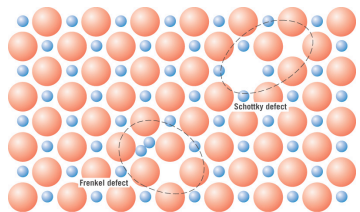
Anion vacancy

Why is it rather improbable that anion interstitials exist?

Frenkel and Schottky Defects: paired anions and cations

- Electronic neutrality *must be maintained* in crystal.
- Defects must come in pairs to maintain ΔQ=0.

- Cation-vacancy + Cation-interstitial = **Frenkel Defect**   (ΔQ=0)

- In AX-type crystals,
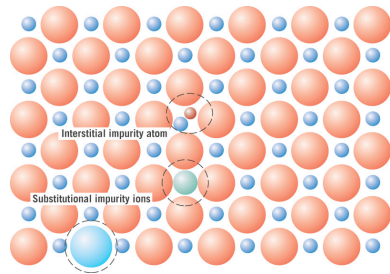 Cation-vacancy + Anion-vacancy   = **Schottky Defect**   (ΔQ=0)

Schottky defect

Frenkel defect

Color centers: Balancing missing cation by bound extra electron is also possible.

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Ionic Crystals and Impurities:
Interstitial, anion-substitutional, cation-substitutional

Interstitial impurity atom

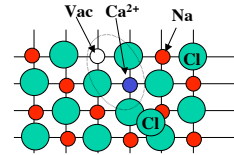Substitutional impurity ions

Consider NaCl. (use charge neutrality)
• What point defects are possible when a Ca^{2+} substitutes for Na^+?
• How many of these defects exits for every Ca^{2+} ion?

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Ionic Crystals and Impurities:
Interstitial, anion-substitutional, cation-substitutional

Consider NaCl. (use charge neutrality)

• **What point defects are possible when a Ca^{2+} substitutes for Na^+?**
• **How many of these defects exits for every Ca^{2+} ion?**

• **Replacement of Na^+ by a Ca^{2+} introduces 1 excess positive (+1).**

ΔQ=0 only if
• **a single positive charge is eliminated.**   **(Make a Na^+ vacancy. –1)**
• **a single negative charge is added.**   **(Make a Cl^- interstitial, –1)**

Vac Ca^{2+} Na

Cl

Cl

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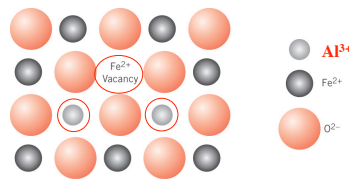
Ionic Crystals and Impurities:
Interstitial, anion-substitutional, cation-substitutional

• **With multiple valances, it is possible not to have correct cation/anion ratio.**
• **e.g., NaCl or FeO are 1-to-1 ratio.**

Consider $Fe^{2+} O^{2-}$ and add Al^{3+} (via Al_2O_3) to replace Fe^{2+} .

• **Add Al^{3+} in place Fe^{2+} (not neutral), so excess charge of +1 must be offset.**

• **What happens?   With two Al^{3+} defects, need one Fe^{2+} vacancy for neutrality,**
      i.e., 2(+1) - (+2) = 0.

Fe^{2+} Vacancy

Al^{3+}

Fe^{2+}

O^{2-}

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Equilibrium Concentration of Point Defects

• **Equilibrium concentration varies with temperature!**

No. of defects   **Activation energy**

$$C_V = \frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)$$

No. of potential defect sites.

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 from an experiment.

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)$$

- Measure this...

- Replot it...

$\frac{N_D}{N}$

exponential dependence!

T

defect concentration

$\ln\frac{N_D}{N}$

slope

1

$-Q_D/k$
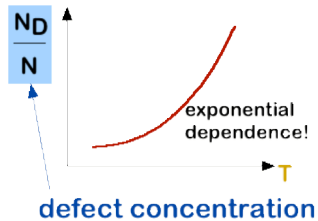
1/T
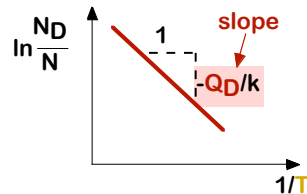
Estimating Vacancy Concentration

- Find the equil. # of vacancies in 1m^3 of Cu at 1000C.
- Given: ρ = 8.4 g/cm^3 A_{Cu} = 63.5g/mol

  Q_V = 0.9eV/atom N_A = 6.02 x 10^{23} atoms/mole

$$C_V = \frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right) = 2.7 \cdot 10^{-4}$$

0.9eV/atom

1273K

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

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

- Solve: N_D = 2.7 · 10^{-4} · 8.0 x 10^{28} sites = 2.2x 10^{25} vacancies

* What happens when temperature is slowly reduced to 500 C, or is rapidly quenched to 500 C?   10^6 cm^3 = 1 m^3


Observing Equil. Vacancy Concentration

- Low-energy electron microscope view of (110) surface of NiAl.
- Larger T causes surface island of atoms to grow.
- **Why?** Equilibrium vacancy conc. increases via atom motion from the crystal to the surface, where they join the island.
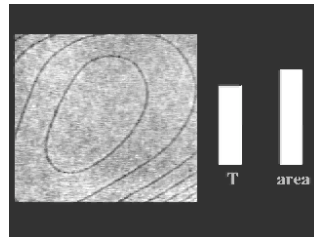
Reprinted with permission from Nature (K.F. McCarty, J.A. Nobel, and N.C. Bartelt, "Vacancies in Solids and the Stability of Surface Morphology", Nature, 412, 622-625 (2001). Image is 5.75 μm by 5.75 μm.) Copyright (2001) Macmillan Publishers, Ltd.

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

Terrace   Kink   Ledge

Step   Vacancy   Adatom
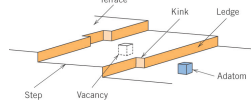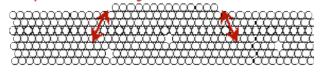
Radiation damage creates numerous defects
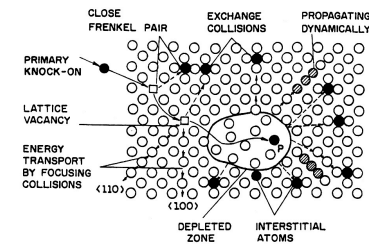

Figure 4.9 Seeger model of damage produced by irradiation. *P* indicates the position where the first "knock-on" terminates. (Reprinted with permission from A. Seeger, in *Proc. Symp. Radiat. Damage Solids React.*, Vol. 1, IAEA, Vienna, 1962, pp. 101, 105)

In nuclear reactor, this effects causes expected lifetime and failures. In space, charged particles bombard objects always.

Volumetric Defects from Radiation Damage

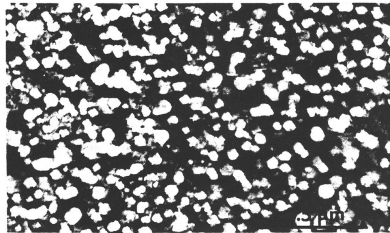**Cracks, voids, inclusions, pores, other phases usually caused by processing.**

Figure 4.10 Voids formed in nickel irradiated using 400 keV $^{14}N_2^+$ ions to a dose of 40 dpa at 500°C; notice the voids with polyhedral shape. (Courtesy L. J. Chen and A. J. Ardell)
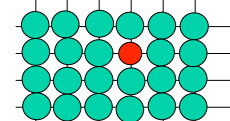
**In nuclear reactor, this effects causes expected lifetime and failures.
In space, charged particles bombard objects always.**

Alloying: atoms mixed on a lattice
Solid Solutions and Ordered Compounds

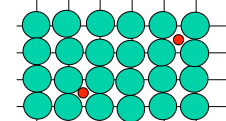**Two Possibilities for Solid Solutions: B atoms in A atoms**

Substitutional	Interstitials
'new element replaces host atoms'	'new element goes in holes'

e.g. Ni in Cu, steels	e.g. semiconductor devices: doped-Si C in Fe

Can we roughly estimate what atoms will form solid solutions?

Alloying: atoms mixed on a lattice
Solid Solutions and Ordered Compounds

Ordered Substitutional and Interstititials Compounds

Substitutional element replaces host atoms in an orderly arrangement	Interstitial element goes into holes in an orderly arrangement
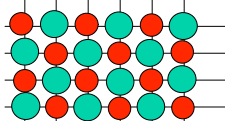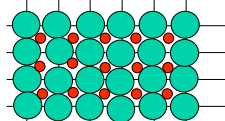
e.g., Ni_3Al (hi-T yield strength), $Al_3(Li,Zr)$ (strengthening)	e.g., small impurities, clays ionic crystals, ceramics.

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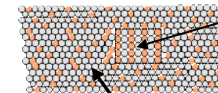
Second phase particle
--different composition
--often different structure.

Solid Solution phase B atoms in A

Hume-Rothery Rules for Alloys (atoms mixing on a lattice)

Will mixing 2 (or more) different types of atoms lead to a solid-solution phase?

Empirical observations have identified 4 major contributors through :

Atomic Size Factor , Crystal Structure, Electronegativity, Valences

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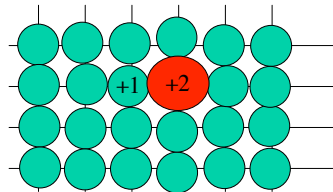
Empirical rules for substitutional solid-solution formation were identified from experiment that are not exact, but give an expectation of formation. Briefly,

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.

$$DR\% = \frac{r_{solute} - r_{solvent}}{r_{solvent}} x100\%$$ **< ±15% 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   DE ~ 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

Example Applications   Si-Ge semiconductor, Cu-Ni and Cu-Ag metal alloys.
Is solid-solution favorable, or not?

• **Si-Ge Alloys**
Rule 1: r_{Si} = 0.117 nm and r_{Ge}= 0.122 nm.

DR%= $\frac{r_{solute} - r_{solvent}}{r_{solvent}} x100\%$ = 4%   **favorable √**

Rule 2: Si and Ge have the diamond crystal structure.   **favorable √**

Rule 3: E_{Si} = 1.90 and E_{Ge}= 2.01. Thus, DE%= 5.8%   **favorable √**

Rule 4: Valency of Si and Ge are both 4.   **favorable √**

Expect Si and Ge to form S.S. over wide composition range.

In fact, S.S. forms over entire composition at high temperature.

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, DE%= -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%= $\dfrac{r_{solute} - r_{solvent}}{r_{solvent}} x100\%$ = 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.

Alloying A Surface: Sn on Cu

- **Low-energy electron microscope view of a (111) surface of Cu.**

- **Sn islands move on surface and "alloy" Cu with Sn making "bronze".**

- **Islands continually move into "unalloyed" regions and leave tiny bronze particles in their wake.**

- **Eventually, the islands disappear.**
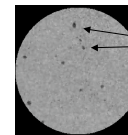
"Bronze"

Reprinted with permission from: A.K. Schmid, N.C. Bartelt, and R.Q. Hwang, **"Alloying at Surfaces by the Migration of Reactive Two-Dimensional Islands"**, Science, Vol. 290, No. 5496, pp. 1561-64 (2000). Field of view is 1.5 μm and the temperature is 290K.

Defining Composition of Alloy

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:**

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

mass of B = moles of B x A_B ← atomic weight of B

mass of A = moles of A x A_A ← atomic weight of A