

# ***Ch. 4: Imperfections in Solids***

## ***Part 1***

Dr. Feras Fraige

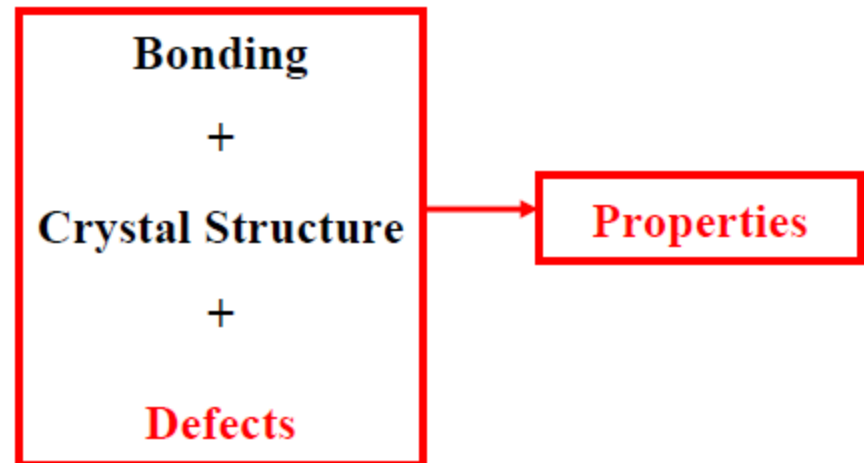
# Outline

- **Defects in Solids**
  - **0D, Point defects**
    - ✓ vacancies
    - ✓ Interstitials
    - ✓ impurities, weight and atomic composition
  - **1D, Dislocations**
    - ✓ edge
    - ✓ screw
  - **2D, Grain boundaries**
    - ✓ tilt
    - ✓ twist
  - **3D, Bulk or Volume defects**
  - **Atomic vibrations**

# Why are defects important?

- Defects have a profound impact on the various properties of
- materials:
- Production of advanced semiconductor devices require not only a rather perfect Si crystal as starting material, but also involve introduction of specific defects in small areas of the sample.
- Defects are responsible for color (& price) of a diamond crystal.
- **Forging** a metal tool introduces defects ... and increases strength of the tool.

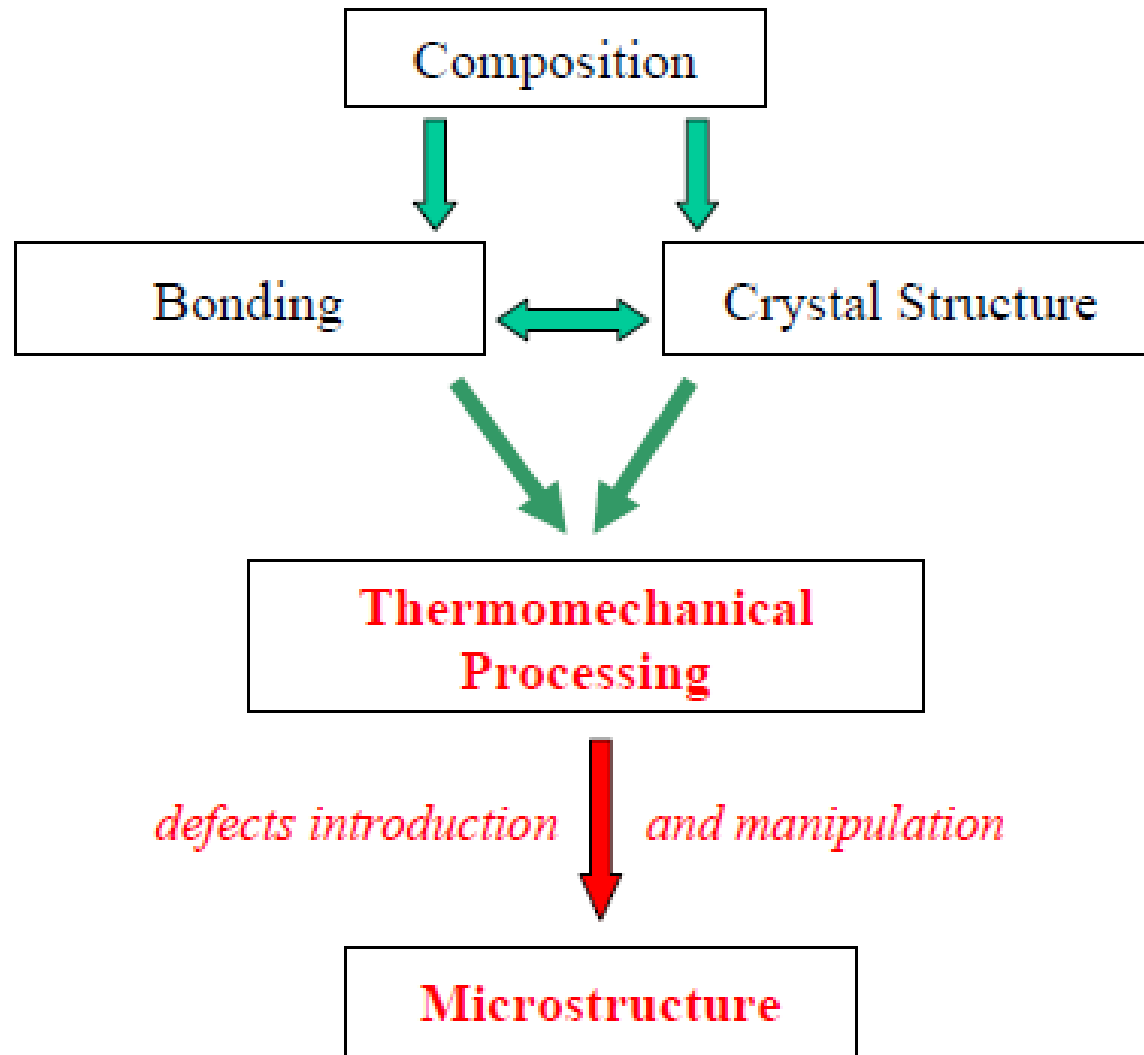
**Metal forging** is a metal forming process that involves applying compressive forces to a work piece to deform it, and create a desired geometric change to the material. The forging process is very important in industrial metal manufacture, particularly in the extensive iron and steel manufacturing industry.



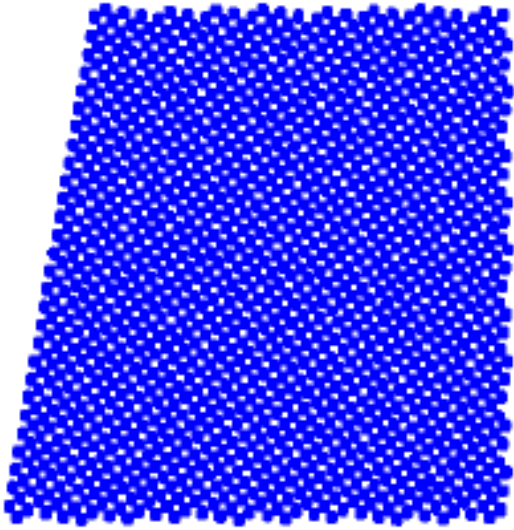
# Defects can be introduced/removed during processing

- Processing allows one to achieve the required properties **without changes in composition of the material, but just by manipulating the crystal defects.**
- Control (and intentional introduction) of defects is in the core of many types of material processing.

# Defects can be introduced/removed during processing

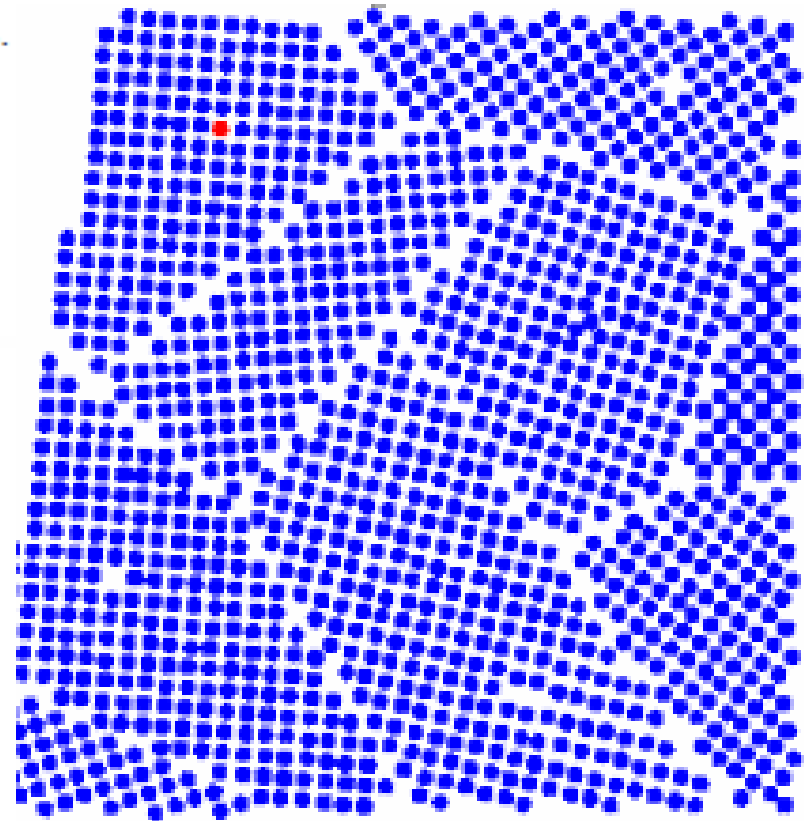


# Defects in Crystals



A 2D representation of a perfect single crystal with regular arrangement of atoms.

**Real crystals are never perfect, there are always defects**



Schematic drawing of a poly-crystal with defects by Helmut Föll, University of Kiel, Germany.

# Types of Defects

- Defects may be classified into four categories depending on their dimension:
  - **0D, Point defects: atoms missing or in irregular places** in the lattice (lattice vacancies, substitutional and interstitial impurities, self-interstitials)
  - **1D, Linear defects: groups of atoms in irregular positions** (e.g. screw and edge dislocations)
  - **2D, Planar defects: the interfaces between** homogeneous regions of the material (e.g. grain boundaries, stacking faults, external surfaces)
  - **3D, Volume defects: extended defects** (pores, cracks)

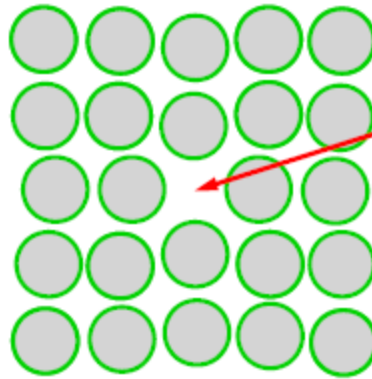
# Point Defects: Vacancies

- Vacancies are always present in crystals and they are particularly numerous at high temperatures, when atoms are frequently and randomly change their positions leaving behind empty lattice sites (vacancies).
- **How many vacancies are there?**
- Statistical thermodynamics predicts that the number of vacancies,  $N_v$ , have very strong dependence on temperature,  $T$ , and can be estimated using the Boltzmann distribution:

$$N_v = N_s \exp\left(-\frac{Q_v}{k_B T}\right)$$

- where  $N_s$  is the number of regular lattice sites,  $k_B$  is the Boltzmann constant,  $Q_v$  is the energy needed to form a vacant lattice site in a perfect crystal, and  $T$  the temperature in **Kelvin** (note, not in °C or °F).





**Vacancy = absence of an atom from its normal location in a perfect crystal structure**

- **Vacancies are required to be present in a crystal at any temperature!**
- **The concentration of vacancies increases sharply with temperature.**
- We can estimate for copper:  
at room temperature - one vacancy per  $10^{15}$  lattice sites
- at high temperature, just below the melting point – one vacancy for every 10,000 atoms.

$$N_v = N_s \exp\left(-\frac{Q_v}{k_B T}\right)$$

- Note, that the above equation gives the lower end estimation of the number of vacancies in real materials, a large numbers of additional (non-equilibrium) vacancies can be introduced in a growth process or as a result of further treatment (plastic deformation, quenching from high temperature to the ambient one, etc.)

Example: number of vacancies in Cu at room T

The Boltzmann's constant  $k_B = 1.38 \times 10^{-23} \text{ J/atom-K} = 8.62 \times 10^{-5} \text{ eV/atom-K}$

The temperature in Kelvin  $T = 27^\circ \text{ C} + 273 = 300 \text{ K}$ .

$k_B T = 300 \text{ K} \times 8.62 \times 10^{-5} \text{ eV/K} = 0.026 \text{ eV}$

The energy for vacancy formation  $Q_v = 0.9 \text{ eV/atom}$

The number of regular lattice sites  $N_s = N_A \rho / A_{\text{cu}}$

$N_A = 6.023 \times 10^{23} \text{ atoms/mol}$

$\rho = 8.4 \text{ g/cm}^3$

$A_{\text{cu}} = 63.5 \text{ g/mol}$

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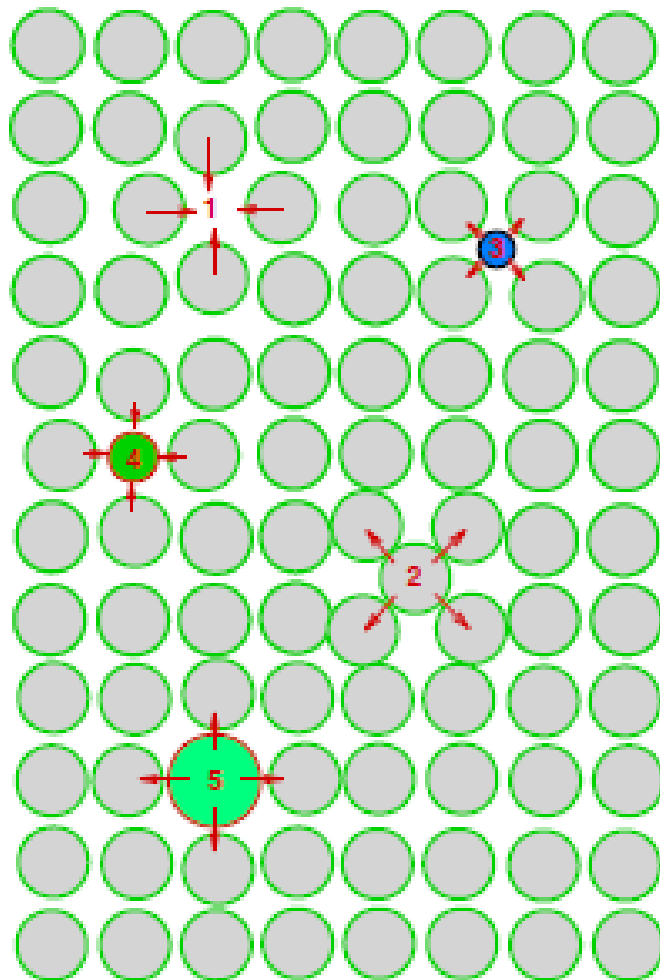
$$N_v = N_s \exp\left(-\frac{Q_v}{k_B T}\right)$$

$$N_s = \frac{\left(6.023 \times 10^{23} \text{ atoms/mol}\right) \times \left(8.4 \text{ g/cm}^3\right)}{63.5 \text{ g/mol}} = 8 \times 10^{22} \text{ atoms/cm}^3$$

$$N_v = 8 \times 10^{22} \frac{\text{atoms}}{\text{cm}^3} \exp\left(-\frac{0.9 \text{ eV/atom}}{0.026 \text{ eV/atom}}\right) =$$

$$= 7.4 \times 10^7 \text{ vacancies/cm}^3$$

# Other point defects: self-interstitials, impurities



Schematic representation of different point defects:

- (1) vacancy;
- (2) self-interstitial;
- (3) interstitial impurity;
- (4,5) substitutional impurities

The arrows show the local stresses introduced by the point defects.

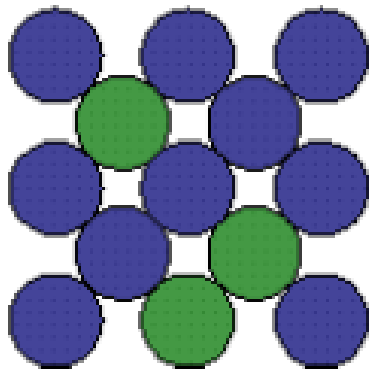
Due to the local stresses introduced by point defects, they can feel each other (interact) and feel external stresses.

The interactions can give a directionality to otherwise random jumps of atoms.

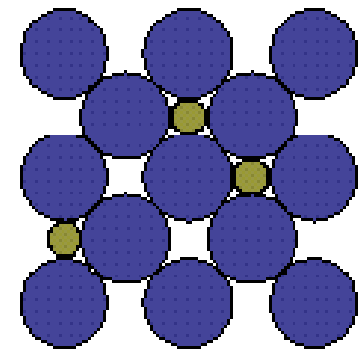
- Self-interstitials in metals introduce large distortions in the surrounding lattice  $\Rightarrow$  the energy of self-interstitial formation is  $\sim 3$  times larger as compared to vacancies ( $Q_i \sim 3 \times Q_v$ )  $\Rightarrow$  equilibrium concentration of self-interstitials is very low (less than one self-interstitial per  $\text{cm}^3$  at room T).

# Impurities

- **Impurities - atoms which are different from the host**
- All real solids are impure. Very pure metals 99.9999% one impurity per  $10^6$  atoms
- May be intentional or unintentional
- Examples: carbon added in small amounts to iron makes steel, which is stronger than pure iron. Boron added to silicon change its electrical properties.
- **Alloys - deliberate mixtures of metals**
- Example: sterling silver is 92.5% silver – 7.5% copper alloy. Stronger than pure silver.



**substitutional impurity**



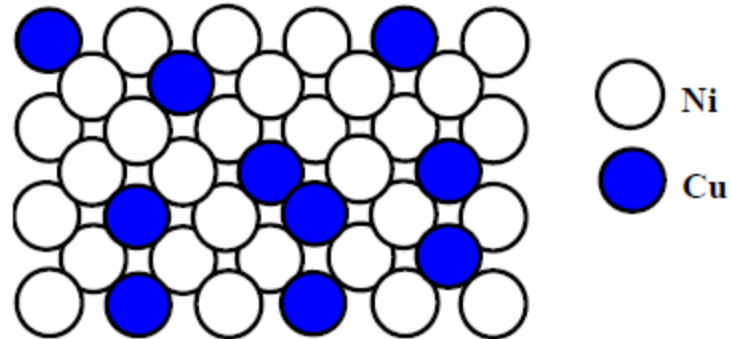
**interstitial impurities**



# Solids with impurities - Solid Solutions

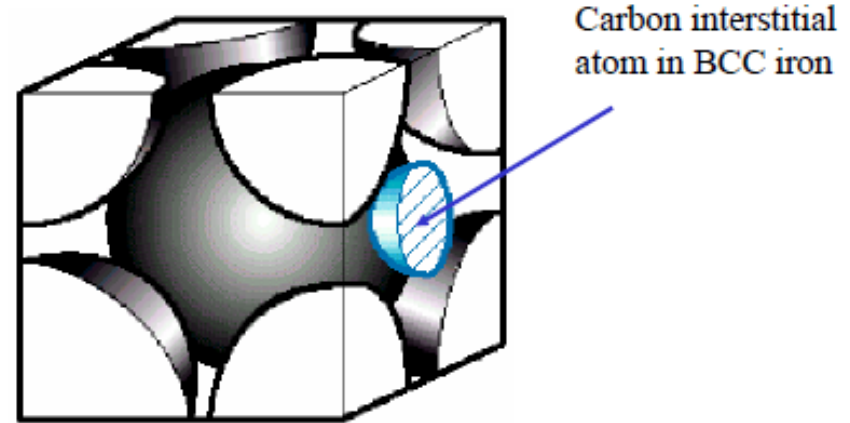
- Solid solutions are made of a host (the solvent or matrix) which dissolves the minor component (solute). The ability to dissolve is called solubility.
- **Solvent:** in an alloy, the element or compound present in greater amount
- **Solute:** in an alloy, the element or compound present in lesser amount
- **Solid Solution:**
  - homogeneous
  - maintain crystal structure
  - contain randomly dispersed impurities (substitutional or interstitial)
- **Second Phase:** as solute atoms are added, new compounds / structures are formed, or solute forms local *precipitates* (*discussed in Chapter 9*)
- Whether the addition of impurities results in formation of solid solution or second phase depends the nature of the impurities, their concentration and temperature, pressure...

# Substitutional Solid Solutions



- Factors for high solubility:
- Atomic size factor - atoms need to “fit”  $\Rightarrow$  solute and solvent atomic radii should be within  $\sim 15\%$
- Crystal structures of solute and solvent should be the same
- Electronegativities of solute and solvent should be comparable (otherwise new inter-metallic phases are encouraged)
- Generally, in metals, more solute goes into solution when it has higher valency than solvent

# Interstitial Solid Solutions



- Interstitial solid solution of C in  $\alpha$ -Fe. The C atom is small enough to fit, after introducing some strain into the BCC lattice.
- Factors for high solubility:
- For fcc, bcc, hcp structures the voids (or interstices) between the host atoms are relatively small  $\Rightarrow$  atomic radius of solute should be significantly less than solvent
- Normally, maximum solute concentration  $\leq 10\%$ , e.g. 0.25 wt.% for C in  $\alpha$ -Fe (BCC), 2.06 wt.% for C in  $\gamma$ -Fe (FCC).

# Composition / Concentration

- Composition can be expressed in
- **weight percent, useful when making the solution**
- **atom percent, useful when trying to understand the material at the atomic level**
- **Weight percent (wt %): weight of a particular element relative to the total alloy weight. For two-component system, concentration of element 1 in wt. % is**

$$C_1^{wt} = \frac{m_1}{m_1 + m_2} \times 100$$

- $m_1$  and  $m_2$  are masses of the two components

# Composition / Concentration

- **Atom percent (at %):** number of moles (atoms) of a particular element relative to the total number of moles (atoms) in alloy. For two-component system, concentration of component 1 in at. % is

$$C_1^{at} = \frac{n_{m_1}}{n_{m_1} + n_{m_2}} \times 100$$

- where  $n_{m_1} = m'_1/A_1$ ,  $m'_1$  is mass in grams of component 1 ,  $A_1$  is atomic mass of component 1

# Composition Conversions

Weight % to Atomic %:

$$C_1^{at} = \frac{C_1^{wt} A_2}{C_1^{wt} A_2 + C_2^{wt} A_1} \times 100$$

$$C_2^{at} = \frac{C_2^{wt} A_1}{C_1^{wt} A_2 + C_2^{wt} A_1} \times 100$$

- See pp 96-99 in textbook
- For more details

Atomic % to Weight %:

$$C_1^{wt} = \frac{C_1^{at} A_1}{C_1^{at} A_1 + C_2^{at} A_2} \times 100$$

$$C_2^{wt} = \frac{C_2^{at} A_2}{C_1^{at} A_1 + C_2^{at} A_2} \times 100$$

# Composition Conversions

From Weight % to mass per unit volume (g/cm<sup>3</sup>):

$$C_1 = \frac{C_1^{wt}}{\frac{C_1^{wt}}{\rho_1} + \frac{C_2^{wt}}{\rho_2}} \quad C_2 = \frac{C_2^{wt}}{\frac{C_1^{wt}}{\rho_1} + \frac{C_2^{wt}}{\rho_2}}$$

$C_1$  and  $C_2$  are concentrations of the first and second components in g/cm<sup>3</sup>

Average density & average atomic weight in a binary alloy

Average density  
of a binary alloy

$$\rho_{ave} = \frac{100}{\frac{C_1^{wt}}{\rho_1} + \frac{C_2^{wt}}{\rho_2}}$$

Average atomic weight  
of a binary alloy

$$A_{ave} = \frac{C_1^{at} A_1 + C_2^{at} A_2}{100}$$