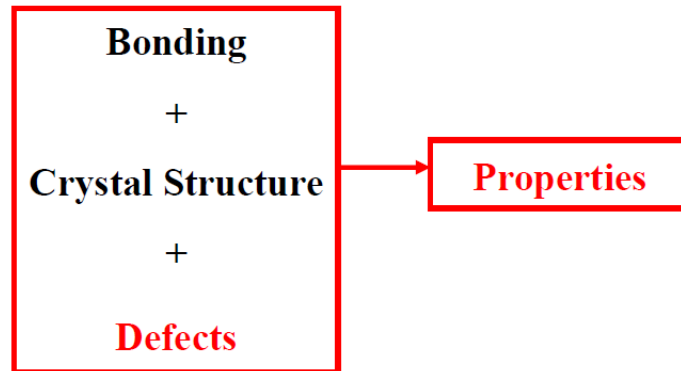


**Imperfections in Solids**

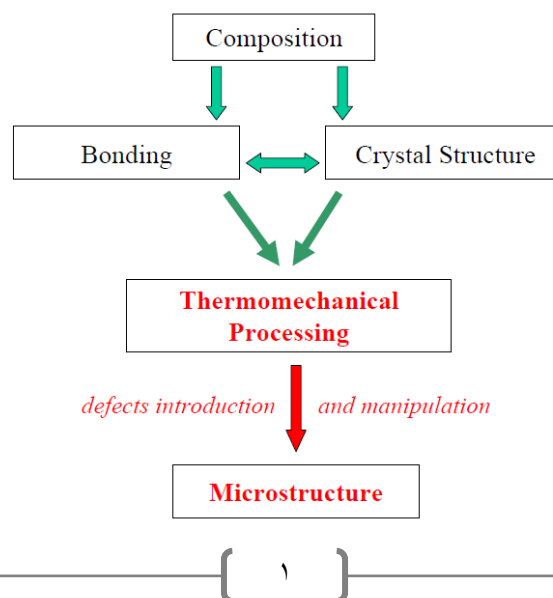
Why are defects important?



**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.

**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.**

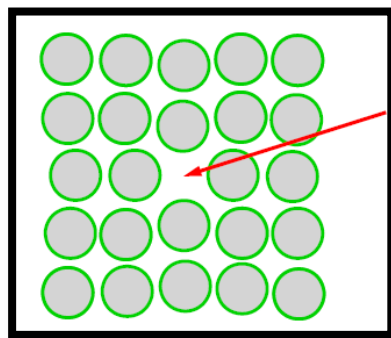
### **Types of Defects**

Defects may be classified into four categories depending on their dimension:

- 1- **0D, Point defects:** atoms missing or in irregular places in the lattice (lattice vacancies, substitutional and interstitial impurities, self-interstitials)
- 2- **1D, Linear defects:** groups of atoms in irregular positions (e.g. screw and edge dislocations)
- 3- **2D, Planar defects:** the interfaces between homogeneous regions of the material (e.g. grain boundaries, stacking faults, external surfaces)
- 4- **3D, Volume defects:** extended defects (pores, cracks)

### **Point Defects: Vacancies**

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



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  $^{\circ}\text{C}$  or  $^{\circ}\text{F}$ ).

- **Vacancies are required to be present in a crystal at any temperature.**
- **The concentration of vacancies increases sharply with temperature.**

**Example:** number of vacancies in Cu at room T:

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

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  $N_s = N_A \rho / A_{\text{Cu}}$

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

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

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

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

$$N_v = 8 \times 10^{22} \frac{\text{atoms}}{\text{cm}^3} \exp\left(-\frac{0.9 \text{ eV/atom}}{0.026 \text{ eV/atom}}\right) = 7.4 \times 10^7 \text{ vacancies/cm}^3$$

### 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.

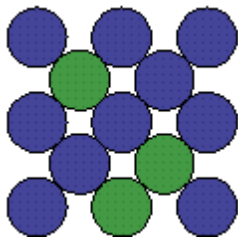
Due to the local stresses introduced by point defects, they can feel each other (interact) and feel external stresses.

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

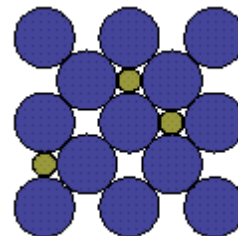
## Impurities

### Impurities - atoms which are different from the host

- All real solids are impure. Very pure metals 99.9999% - one impurity per 10<sup>6</sup> 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:**

1. homogeneous
2. maintain crystal structure
3. contain randomly dispersed impurities (substitutional or interstitial)

- **Second Phase:** as solute atoms are added, new compounds / structures are formed, or solute forms local *precipitates* .

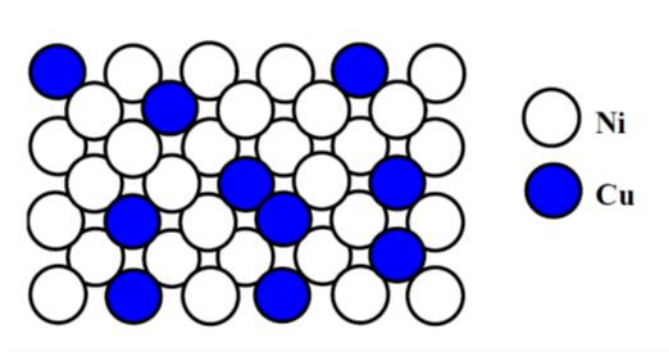
Whether the addition of impurities results in formation of solid solution or second phase depends the nature of the impurities, their concentration and temperature, pressure.

### **Types of solid solutions:**

#### 1- 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



## 2- Interstitial Solid Solutions:

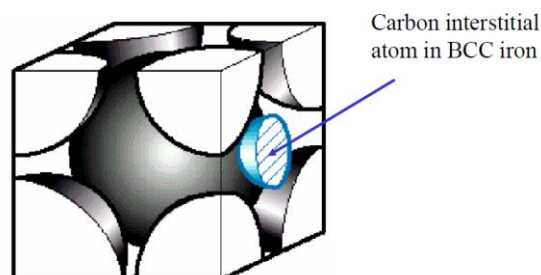
### *Factors for high solubility:*

□ 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 Carbon interstitial atom in BCC iron

Interstitial solid solution of C in  $\alpha$ -Fe. The C atom is small enough to fit, after introducing some strain into the BCC lattice.

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).



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**Dislocations—Linear Defects**

**Dislocations are linear defects:** the interatomic bonds are significantly distorted only in the immediate vicinity of the dislocation line. This area is called the **dislocation core**.

-Dislocations also create small elastic deformations of the lattice at large distances.

-To describe the size and the direction of the lattice distortion caused by a dislocation we should introduce so called **Burgers vector  $\mathbf{b}$** .

-To find the Burgers vector, we should make a circuit from atom to atom counting the same number of atomic distances in all directions. If the

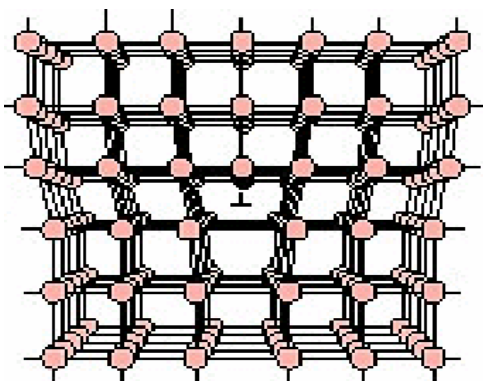
-circuit encloses a dislocation it will not close.

-The vector that closes the loop is the Burgers vector  $\mathbf{b}$ .

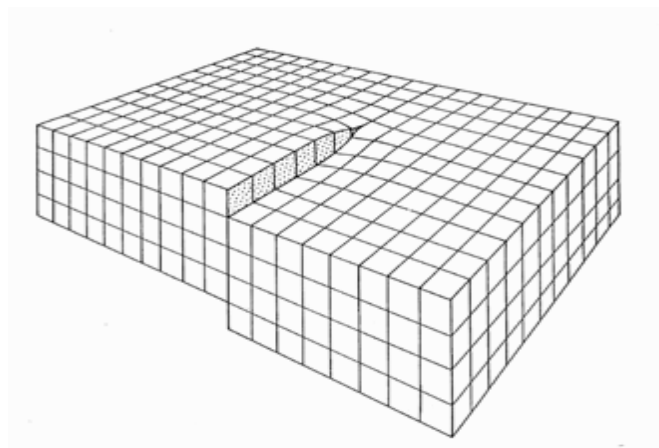
**Edge and screw dislocations**

**Edge dislocations:** They have Burgers vector directed perpendicular to the dislocation line.

**Screw dislocation:** The screw dislocation is parallel to the direction in which the crystal is being displaced (Burgers vector is parallel to the dislocation line).



Edge



Screw



**Planar (interfacial) defects****External Surfaces:**

Surface atoms have unsatisfied atomic bonds, and higher energies than the bulk atoms  $\Rightarrow$  Surface energy,  $\gamma$  (J/m<sup>2</sup>)

- Minimization of surface areas reduces the energy of the system (e.g. liquid drop)
- Solid surfaces can “reconstruct” to satisfy atomic bonds at surfaces.

**Grain Boundaries**

Polycrystalline material comprised of many small crystals or grains. The grains have different crystallographic orientation. There exist atomic mismatch within the regions where grains meet. These regions are called **grain boundaries**.

