



# Imperfections in Solids

In this topic we will try to answer the following questions:

- What types of defects arise in solids?
- Are these defects undesirable?
- How do defects affect material properties?
- Can the number and type of defects be varied and controlled?



# Imperfections in Solids

**There is no such thing as a perfect crystal!**

- Thermodynamically “impossible”
- “*defects*” lower the energy of a crystal & make it more stable
- always have vacancies and impurities, to some extent

**Defect does not necessarily imply a bad thing**

- addition of C to Fe to make steel
- addition of Cu to Ni to make thermocouple wires
- addition of Ge to Si to make thermoelectric materials
- addition of Cr to Fe for corrosion resistance
- introduction of grain boundaries to strengthen materials
- ..... and so on

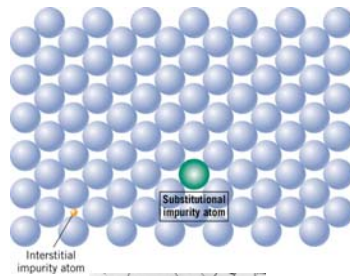
*“Defect” (in this context) can be either desirable or undesirable. In general, a defect simply refers to a disruption in the crystalline order of an otherwise periodic material.*



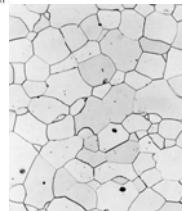
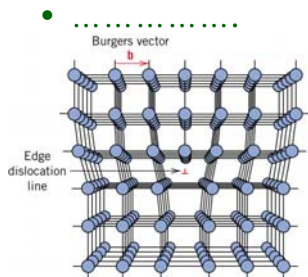
## Types of Imperfections

1- Point defects:

- *Vacancy atoms*
- *Interstitial atoms*
- *Substitutional atoms*



2- Line defects



3- Area defects:

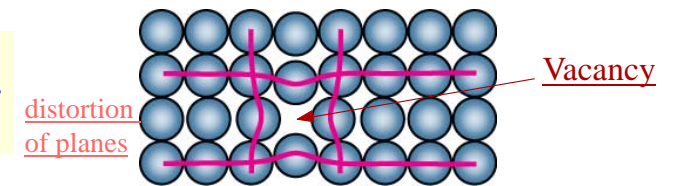
- .....



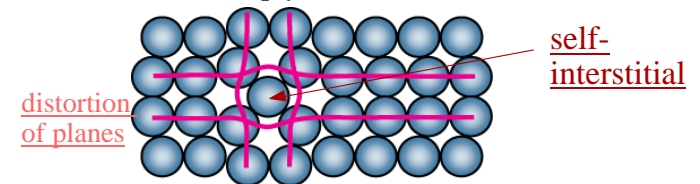
## Point Defects

*vacancy* → a lattice site that is missing an atom:

All crystals contain some vacancies.



*self-interstitial* → an atom from the crystal that crowds its way into an otherwise empty void between atoms



*Self-interstitials are far less common than vacancies because of the relatively large energy required to squeeze an atom into the small voids between existing sites.*



## Equil. Concentration: Point Defects

- Equilibrium concentration varies with temperature!

No. of defects  $N_D = \exp\left(\frac{-Q_D}{kT}\right)$

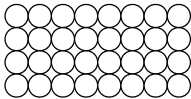
No. of potential defect sites.  $N$

Activation energy  $Q_D$

Temperature  $T$

Boltzmann's constant  $k$   
 $(1.38 \times 10^{-23} \text{ J/atom K})$   
 $(8.62 \times 10^{-5} \text{ eV/atom K})$

Each lattice site is a potential vacancy site



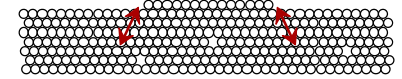
This is called an *Arrhenius equation*, after Svante August Arrhenius, a Swedish chemist who won the Nobel prize in chemistry in 1903.



## Observing Equil. Vacancy Conc.

- Increasing temp. causes surface island of atoms to grow.

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

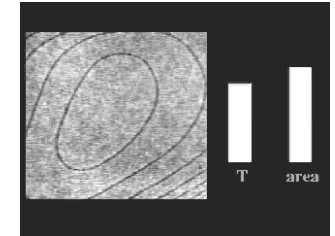


- Why?**  
- Because the equil. Vacancy conc. increases via atom motion from the crystal to the surface, where they join the island.

So, can we observe this?

.....

For e.g. the low energy electron microscope view of a (110) surface of NiAl shows how the surface islands grow with temp.



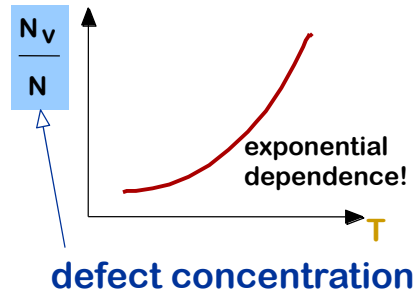
Reprinted with permission from [Nature](#) (K.F. McCarty, J.A. Nobel, and N.C. Bartelt, "Vacancies in Solids and the Stability of Surface Morphology", Nature, Vol. 412, pp. 622-625 (2001). Image is 5.75 mm by 5.75 mm.) Copyright (2001) Macmillan Publishers, Ltd.



## MEASURING ACTIVATION ENERGY

$$N_v = N_o \exp\left(-\frac{Q}{kT}\right)$$

- We can get Q from an experiment.

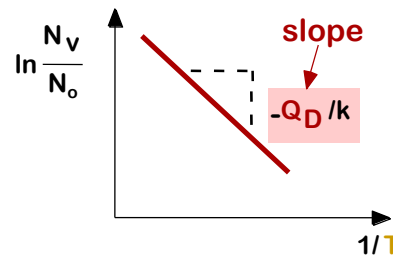


Note:  $\exp(-Q/kT)$  is a strong function of temperature

taking logarithms of both sides of the above equation:

$$\ln\left[\frac{N_v}{N_o}\right] = -\frac{Q}{kT}$$

plot  $\ln\left[\frac{N_v}{N_o}\right]$  versus  $\frac{1}{T}$ :



## Example:

Calculate the fraction of atom sites that are vacant for lead at its melting temperature of 327°C (=600 K). Assume an activation energy of 0.55 eV/atom.

*In order to compute the fraction of atom sites that are vacant in lead at 600 K, we must employ Arrhenius Equation (eqn. 4.1).*

- As stated in the problem,  $Q_v = 0.55 \text{ eV/atom}$ . Thus,

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



## Point Defects

**impurity** → addition of an atom of a different species than the “host” or matrix

- **Alloys** – other types of atoms are deliberately added to give the material certain properties
  - *May or may not result in the same crystal structure*
  - *May or may not result in secondary phases*

**Example 1:** add 1% Sn to Pb  
*i.e., of every 100 Pb lattice sites, 1 is occupied by an Sn atom*

**Result:** .....  
*same crystal structure as pure Pb*

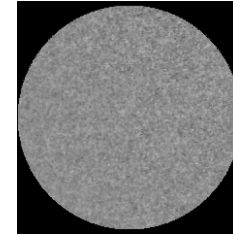
**Example 2:** add 25% Sn to Pb

**Result:** a ..... microstructure (distinct regions of Sn)  
*“solubility” of Pb (in the solid state) is exceeded*



## Alloying a Surface

- Low energy electron microscope view of a (111) surface of Cu.
- Sn islands move along the surface and **alloy** the Cu with Sn atoms, to make .....
- The islands continually move into ..... regions and leave tiny bronze particles in their wake.
- Eventually, the islands disappear.



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.



## Solid Solution

- A homogeneous distribution of two or more elements.
- “**solute**” atoms are added without altering the crystal structure or resulting in formation of a new phase.
- Solid solution is a particular type of alloy
- Two types: **substitutional** and **interstitial**

“**solvent**” – the host material, usually the element or compound present in the greatest amount.

“**solute**” – the minor phase, added to the solvent. Usually the element or compound present in minor concentrations.

“**phase**” is a region of uniform composition or crystal structure

What would a solid solution look like?



## Point Defects in Alloys

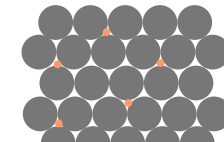
Two outcomes if impurity (B) added to host (A):

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



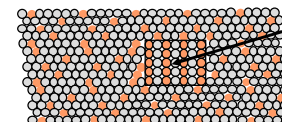
Substitutional solid soln.  
*(e.g., Cu in Ni)*

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)



Second phase particle  
• *different composition*  
• *often different structure.*



## Solid Solution

Not all elements form solid solutions. There are very specific rules that govern the extent to which solid solutions can form.

For **appreciable** solubility to occur the following factors must hold:

- **Atomic size factor**

the difference in atomic radii between the two atoms must be  $\leq \dots\dots\dots$

- **Electronegativity**

the difference in electronegativity between the two atoms must be  $\leq \pm 0.4$  eV (i.e. large differences  $\rightarrow$  compound formation (intermetallics))

- **Crystal structure**

The crystal structure of each element must be the  $\dots\dots\dots$

- **Valence**

For a given solvent, a solute with a higher valency is more likely to be soluble than one of lower valency, all other factors being equal.



## Composition and Conversion wt% $\leftrightarrow$ at.%

Mixtures or alloys of two (or more) elements, are quantitatively described in terms of composition:

Consider a mixture of B in A:

$$\text{weight percent B} = \frac{\text{mass of B}}{\text{total mass of A + B}} \times 100\% = C_B$$

$$\text{atomic percent B} = \frac{\# \text{ moles of B}}{\text{total \# moles of A + B}} \times 100\% = C'_B$$

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

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

- **Basis for conversion:**

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

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

• Industry usually uses weight % for alloys: easier to add (x) kg's of Mg to (Y) tonnes of Al.  
• For chemical/scientific measures often need atomic %



## Linear Defects

### Dislocations

- Dislocations result from solidification from the melt, from mechanical work (e.g., rolling, drawing, compressive impact, tensile or shear stress), or from thermal stresses

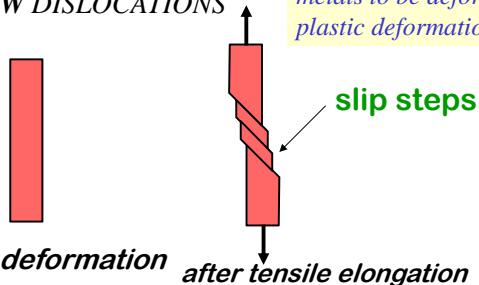
- It is very difficult to prepare a **dislocation-free** crystal!!!

- 2 Types:

- **EDGE DISLOCATIONS**

- **SCREW DISLOCATIONS**

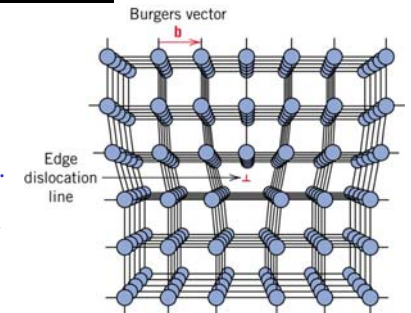
Dislocations make metals weaker than they should be, BUT also allow metals to be deformed (ie. allow plastic deformation). (Chp. 6)



## Edge Dislocation

- Think of edge dislocation as an extra half-plane of atoms inserted in a crystal.

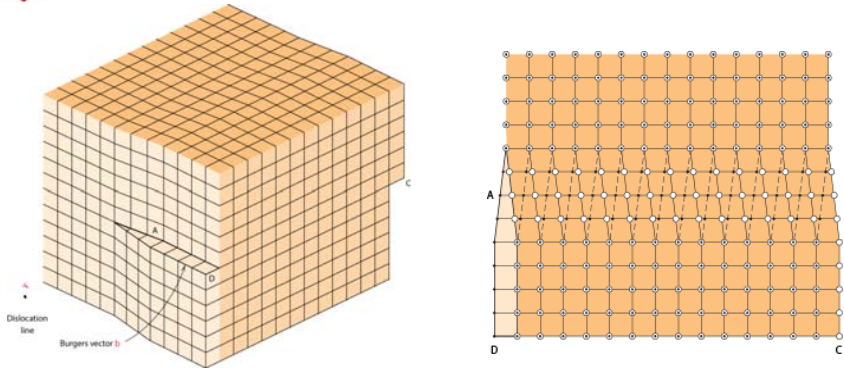
- Misalignment of atomic planes due to the extra half plane.



**Burger's vector (b)** = magnitude + direction of lattice distortion.



## Screw Dislocation

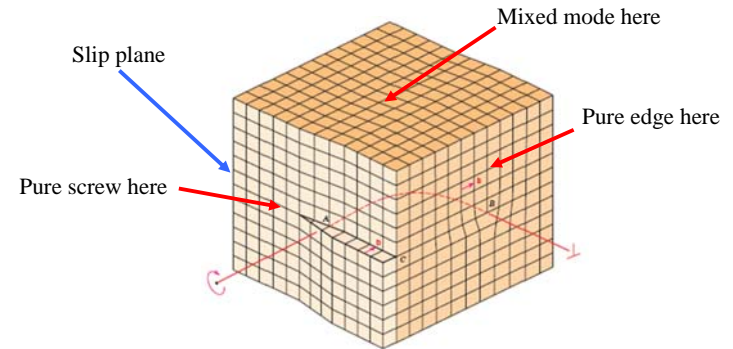


- *Crystal* is "cut halfway through and then slide sideways"  
*helical path through structure hence "screw"*.
- The motion of a screw dislocation can be thought of in terms of tearing a sheet of paper.



## Dislocations

Usually, dislocations have both an edge and a screw character;  
i.e., they are ..... **dislocations**:



Next time:

## Grain Boundaries and Microstructure