

Chapter Outline

“Crystals are like people, it is the defects in them which tend to make them interesting!” - Colin Humphreys.

- **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**

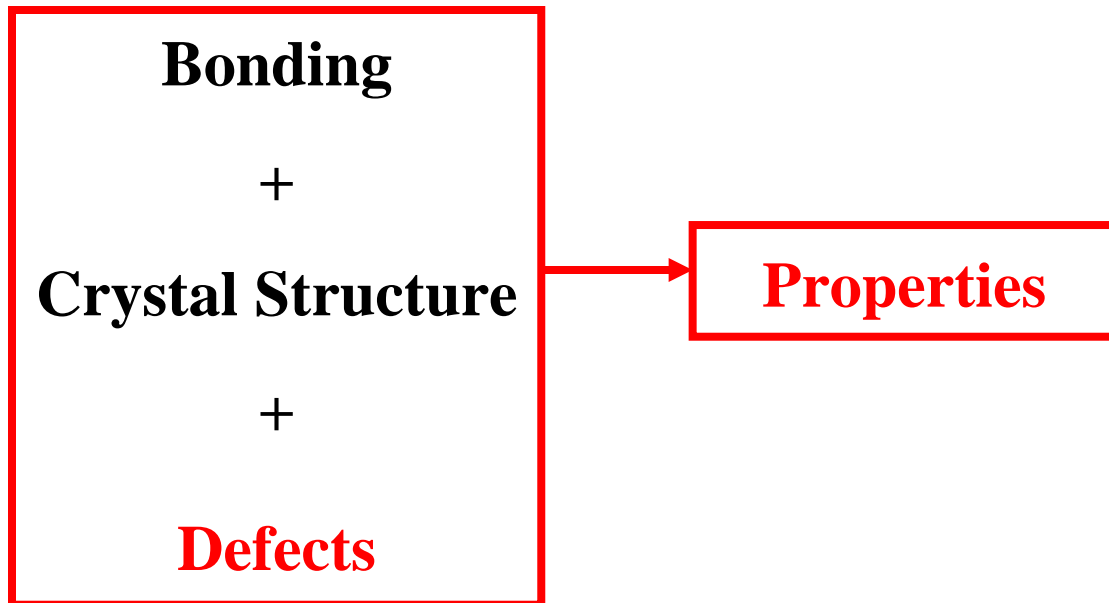
- **Atomic vibrations**

Optional reading (Parts that are not covered / not tested):

4.9 – 4.10 Microscopy

4.11 Grain size determination

Why are defects important?



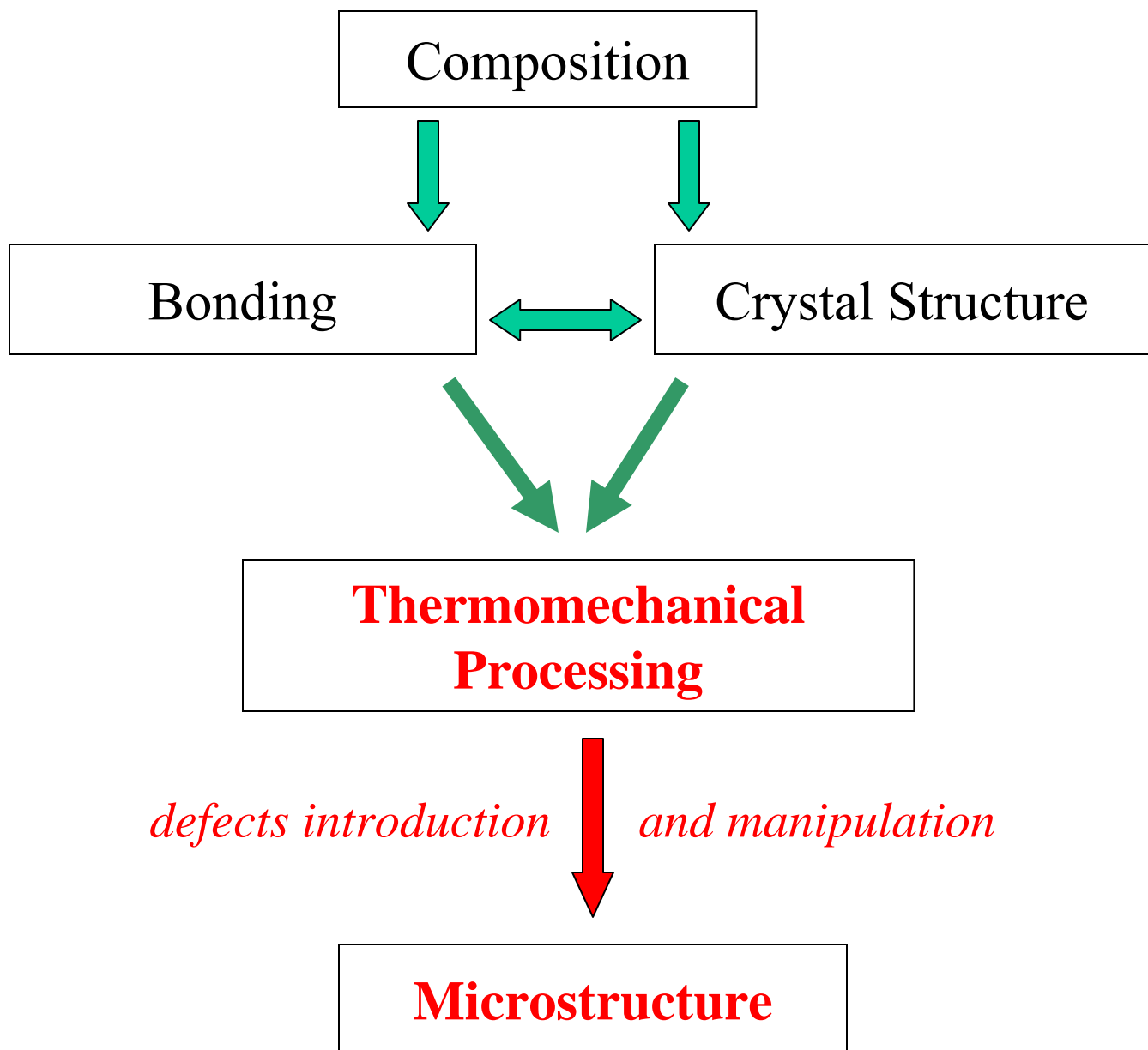
Defects have a profound impact on the various properties of materials:

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.

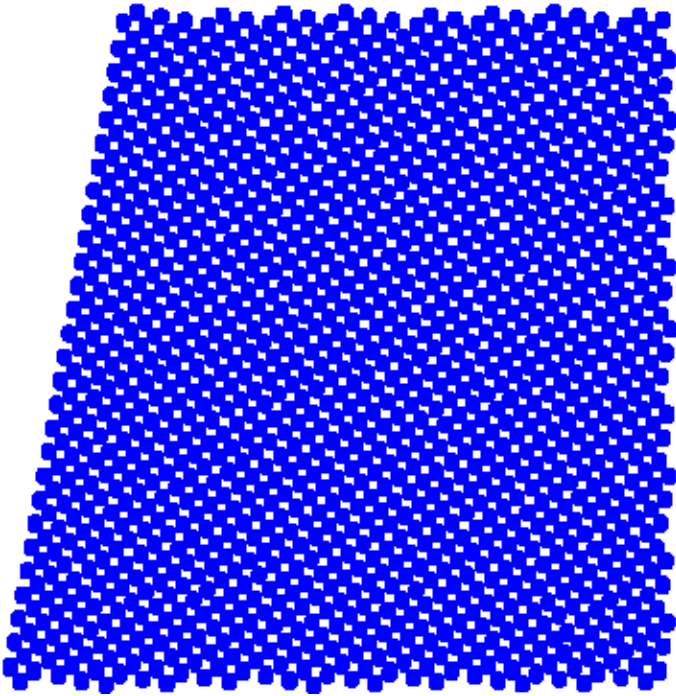
Defects can be introduced/removed during processing



Processing allows one to achieve the required properties **without changes in composition of the material, but just by manipulating the crystal defects.**

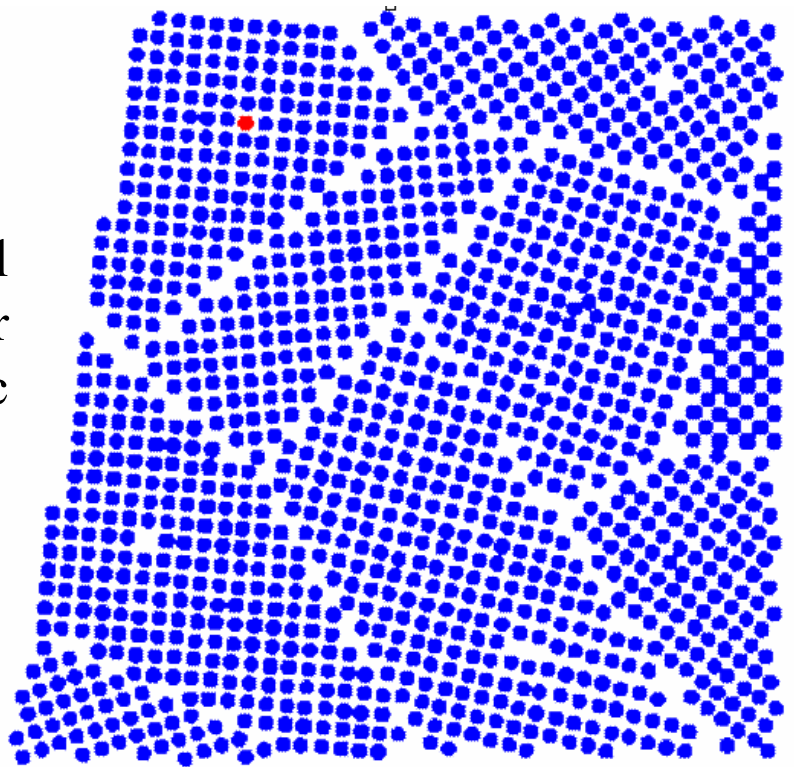
Control (and intentional introduction) of defects is in the core of many types of material processing.

Defects in Crystals



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

But ... structures of real materials can be better represented by the schematic drawing to the left.



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

Real crystals are never perfect, there are always defects

Types of Defects

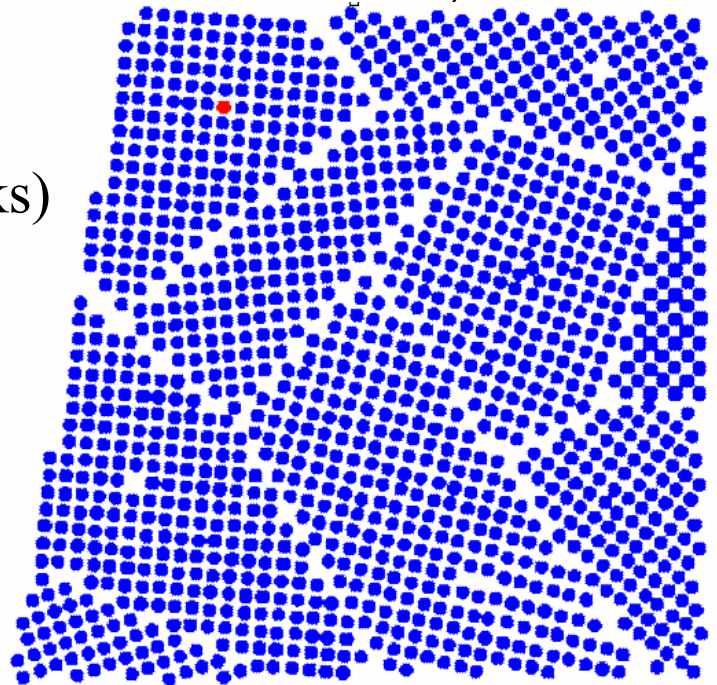
Defects may be classified into four categories depending on their dimension:

➤ **0D, Point defects:** atoms missing or in irregular places in the lattice (lattice vacancies, substitutional and interstitial impurities, self-interstitials)

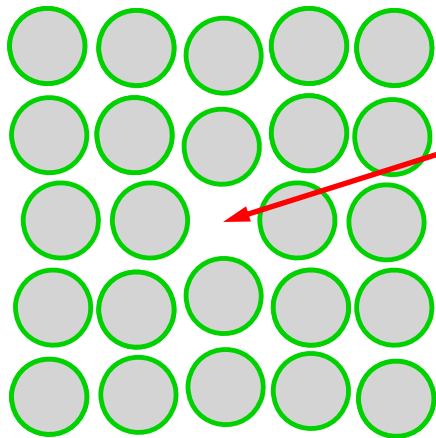
➤ **1D, Linear defects:** groups of atoms in irregular positions (e.g. screw and edge dislocations)

➤ **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



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 °C or °F**).

Equilibrium number of vacancies (continued)

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

- **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.

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

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

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

The temperature in Kelvin $T = 27^\circ \text{C} + 273 = 300$ 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 $Q_v = 0.9$ eV/atom

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

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

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

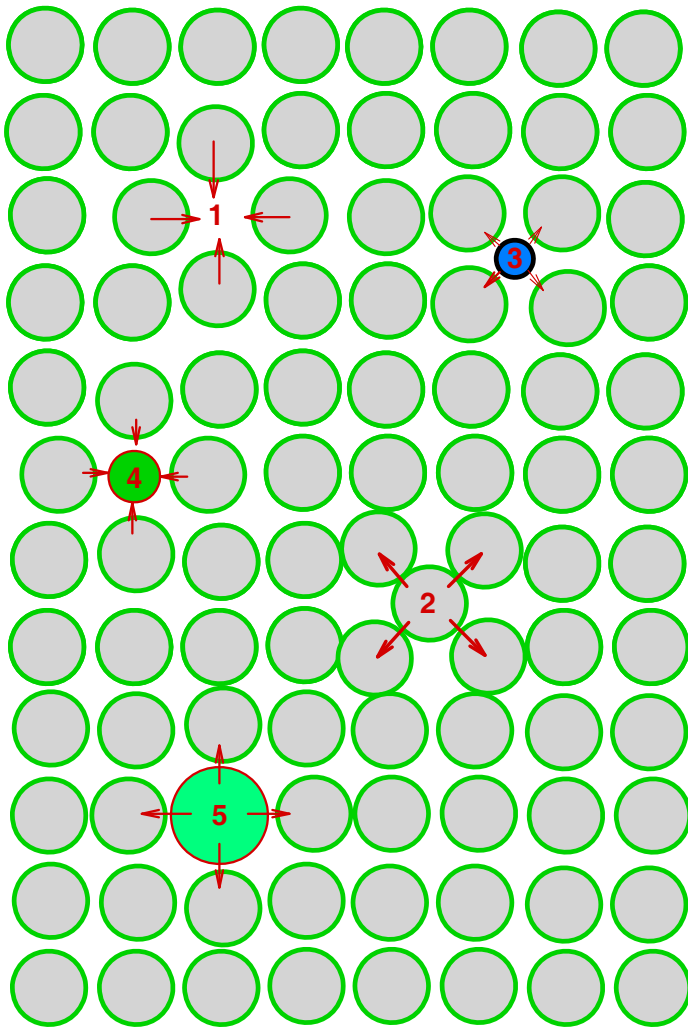
$$A_{\text{cu}} = 63.5 \text{ g/mol}$$

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

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

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

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.

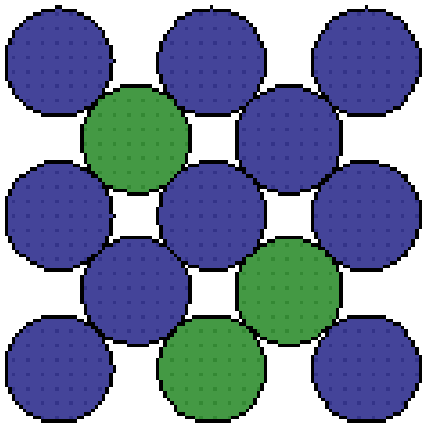
Self-interstitials:

Self-interstitials in metals introduce large distortions in the surrounding lattice \Rightarrow the energy of self-interstitial formation is ~ 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 cm^3 at room T).

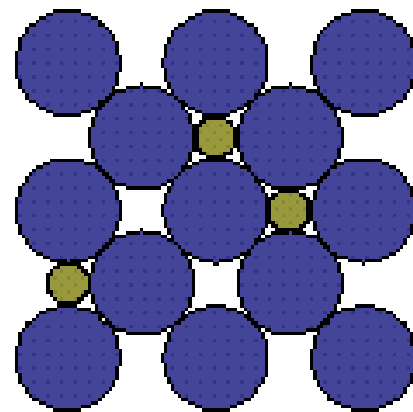
Impurities

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

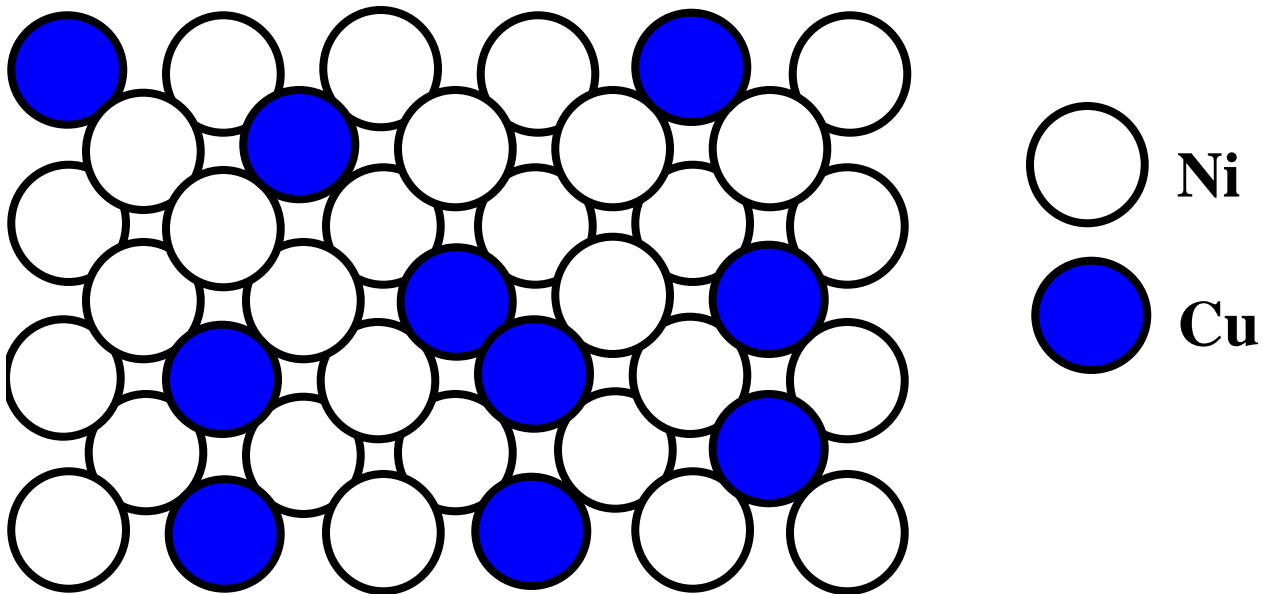
Solids with impurities - Solid Solutions

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...

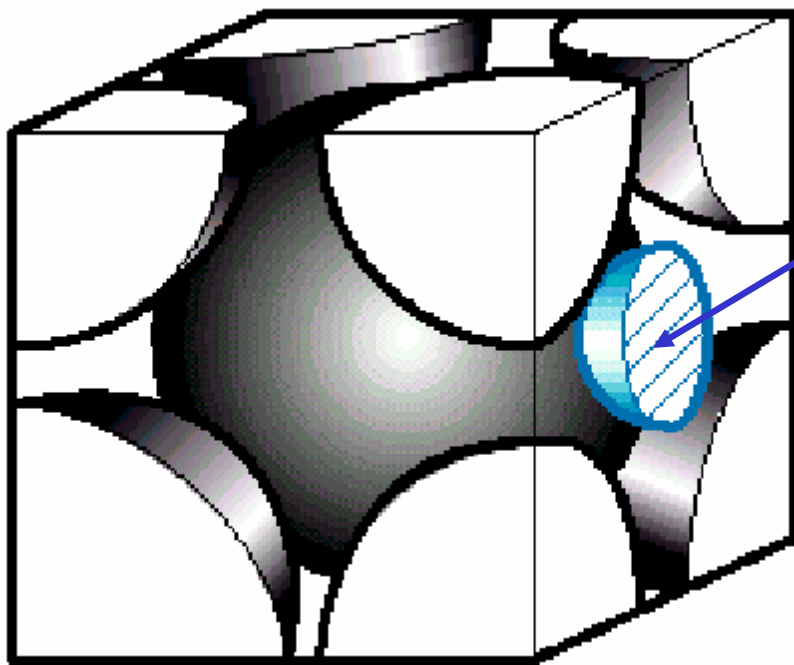
Substitutional Solid Solutions



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



Carbon interstitial atom in BCC iron

Interstitial solid solution of C in α -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 α -Fe (BCC), 2.06 wt.% for C in γ -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

□ **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 %:

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

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

Atomic % to Weight %:

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

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

Textbook, pp. 96-99

Composition Conversions

From Weight % to mass per unit volume (g/cm³):

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

C_1 and C_2 are concentrations of the first and second components in g/cm³

Average density & average atomic weight in a binary alloy

Average density
of a binary alloy

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

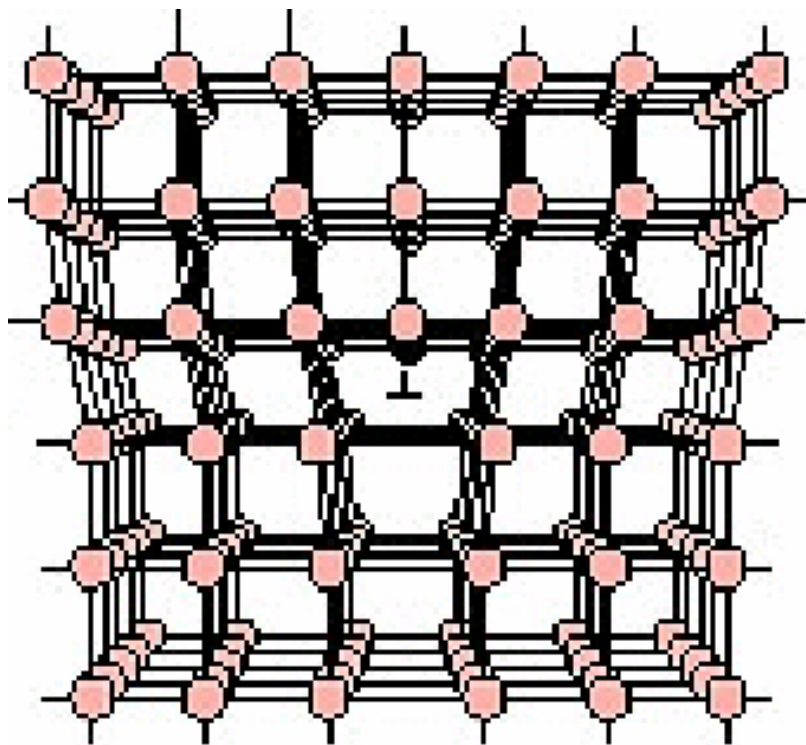
Average atomic weight
of a binary alloy

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

Textbook, p. 97

Dislocations—Linear Defects

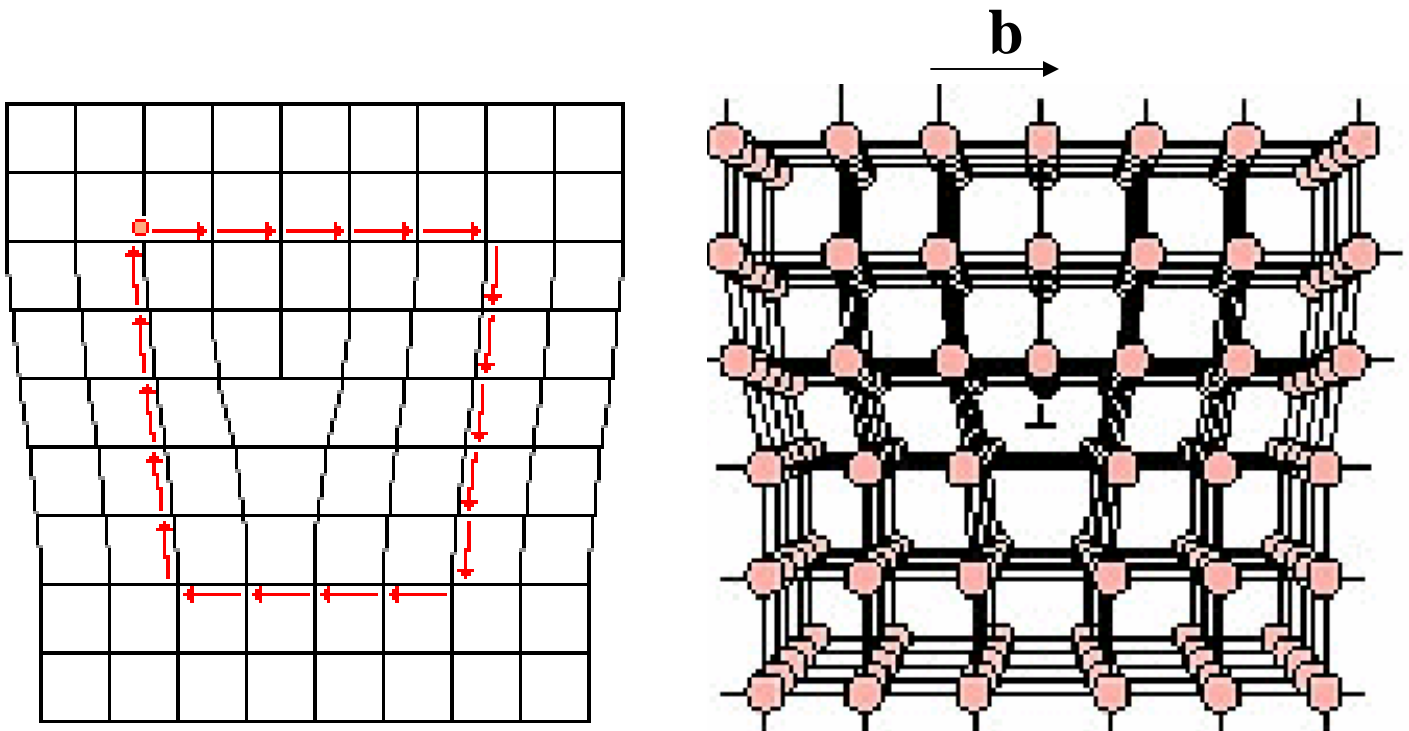
Dislocations are linear defects: the interatomic bonds are significantly distorted only in the immediate vicinity of the dislocation line. This area is called the **dislocation core**. Dislocations also create small elastic deformations of the lattice at large distances.



Dislocations are very important in mechanical properties of material (Chapters 6, 7, 8). Introduction/discovery of dislocations in 1934 by Taylor, Orowan and Polanyi marked the beginning of our understanding of mechanical properties of materials.

Description of Dislocations—Burgers Vector

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} .

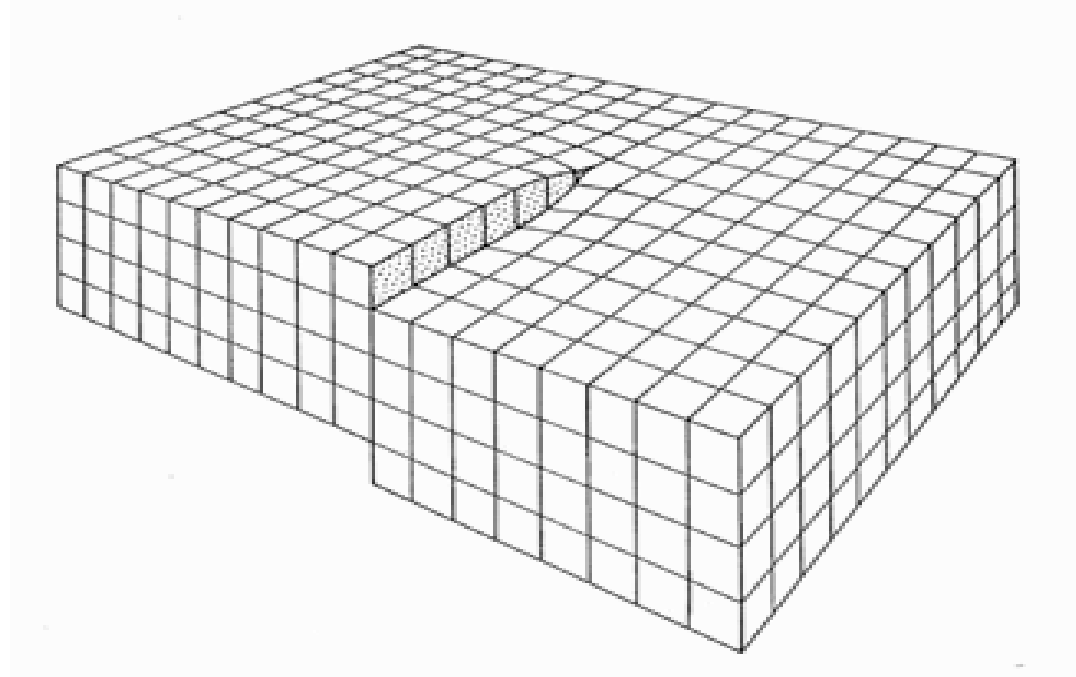


Dislocations shown above have **Burgers vector directed perpendicular to the dislocation line**. These dislocations are called **edge dislocations**.

Edge and screw dislocations

Dislocations shown in previous slide are **edge dislocations**. They have Burgers vector directed perpendicular to the dislocation line.

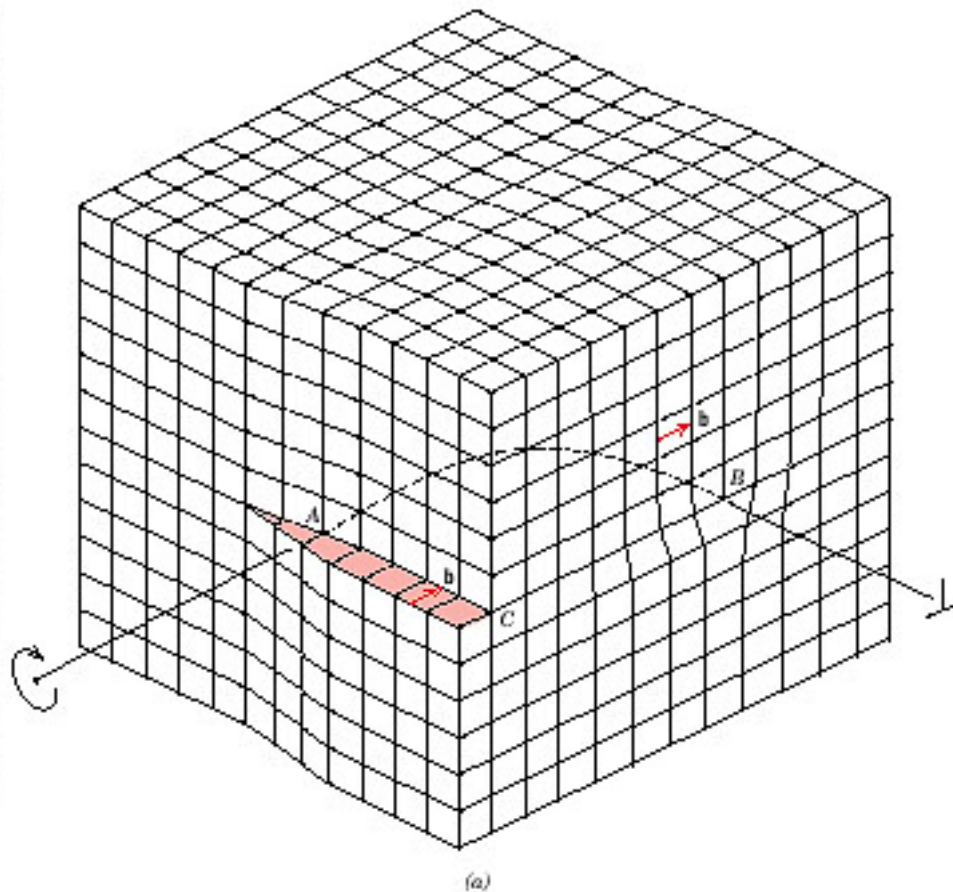
There is a second basic type of dislocation, called **screw dislocation**. The screw dislocation is parallel to the direction in which the crystal is being displaced (Burgers vector is parallel to the dislocation line).



Find the Burgers vector of a screw dislocation.
How a screw dislocation got its name?

Mixed/partial dislocations (*not tested*)

The exact structure of dislocations in real crystals is usually more complicated than the ones shown in this pages. Edge and screw dislocations are just extreme forms of the possible dislocation structures. Most dislocations have mixed edge/screw character.



To add to the complexity to real defect structures, dislocation are often split in "partial" dislocations that have their cores spread out over a larger area.

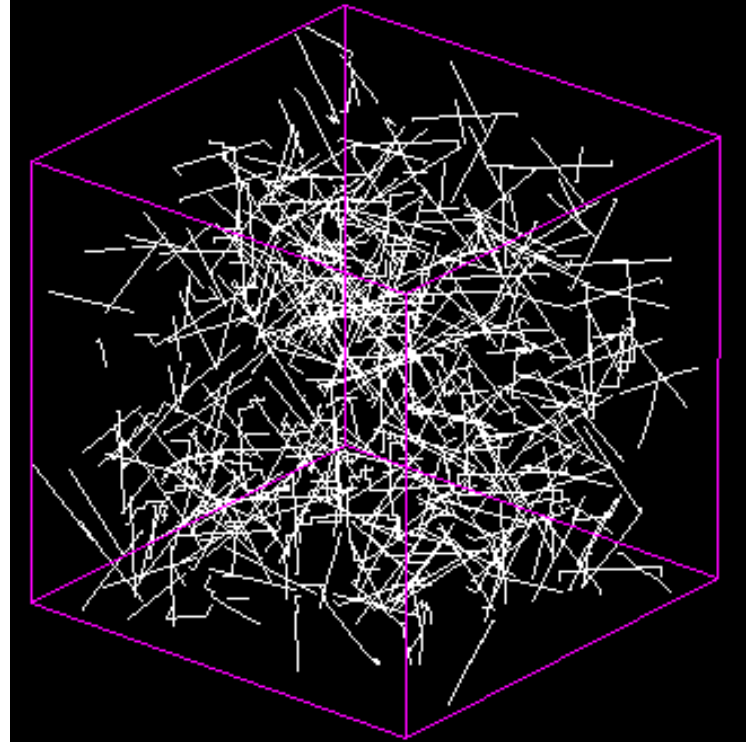
Where do dislocations come from ?

The number of dislocations in a material is expressed as the **dislocation density** - the total dislocation length per unit volume or the number of dislocations intersecting a unit area. Dislocation densities can vary from 10^5 cm^{-2} in carefully solidified metal crystals to 10^{12} cm^{-2} in heavily deformed metals.

Most crystalline materials, especially metals, have dislocations in their as-formed state, mainly as a result of stresses (mechanical, thermal...) associated with the forming process.

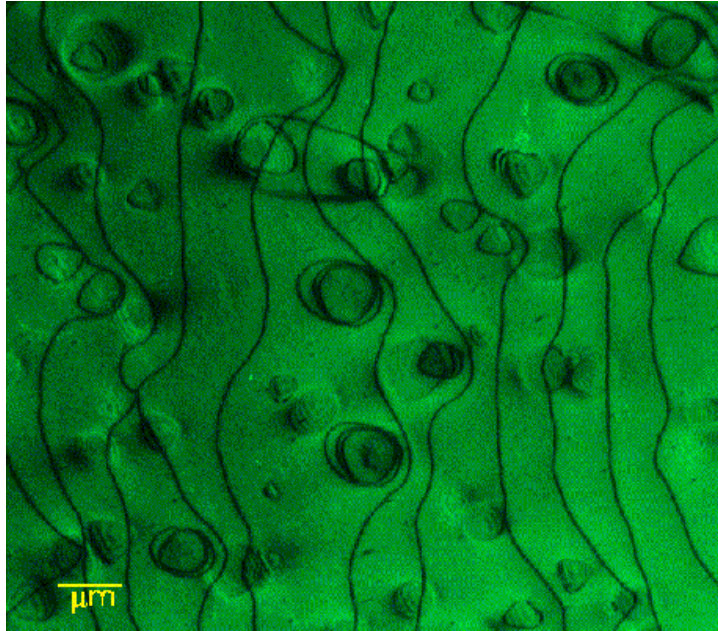
The number of dislocations increases dramatically during plastic deformation (Ch.7). Dislocations spawn from existing dislocations, grain boundaries & surfaces

This picture is a snapshot from simulation of plastic deformation in a fcc single crystal (Cu) of linear dimension 15 micrometers.

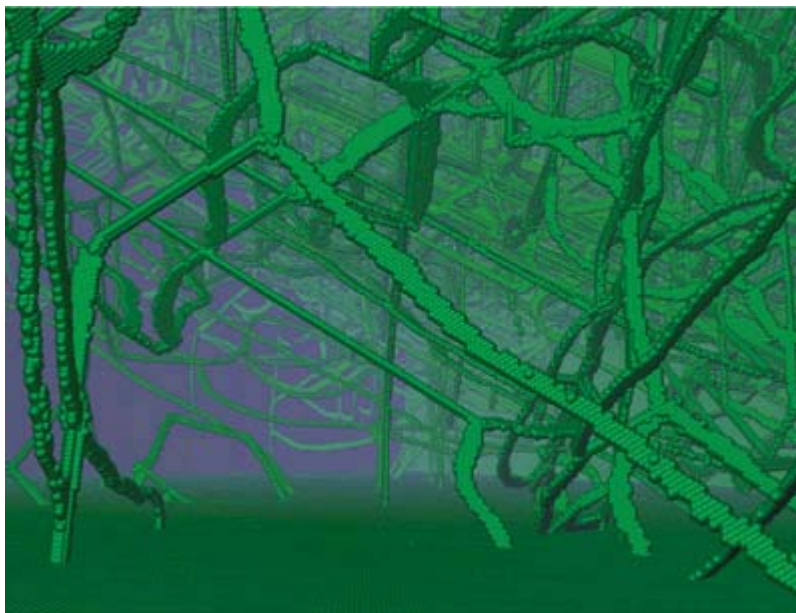


<http://zig.onera.fr/DisGallery/3D.html>

Experimental and computational images of dislocation structures



Dislocations in Ni (the dark lines and loops), transmission electron microscopy image, Manchester Materials Science Center.



Atomistic simulation of work-hardening in a FCC solid, IBM-LLNL collaboration.

Planar (interfacial) defects

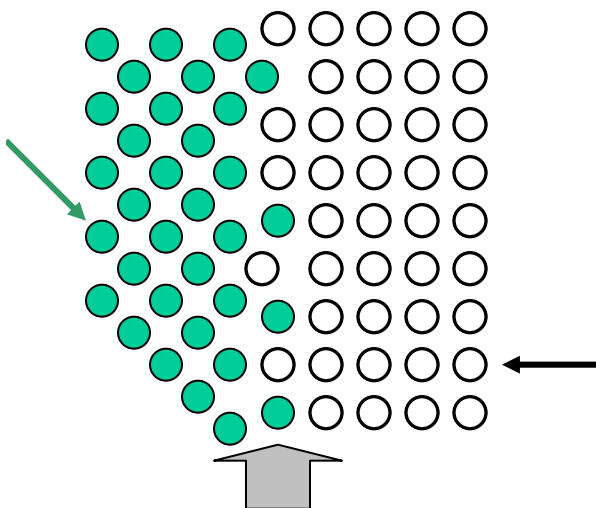
External Surfaces

Surface atoms have have unsatisfied atomic bonds, and higher energies than the bulk atoms \Rightarrow Surface energy, γ (J/m^2)

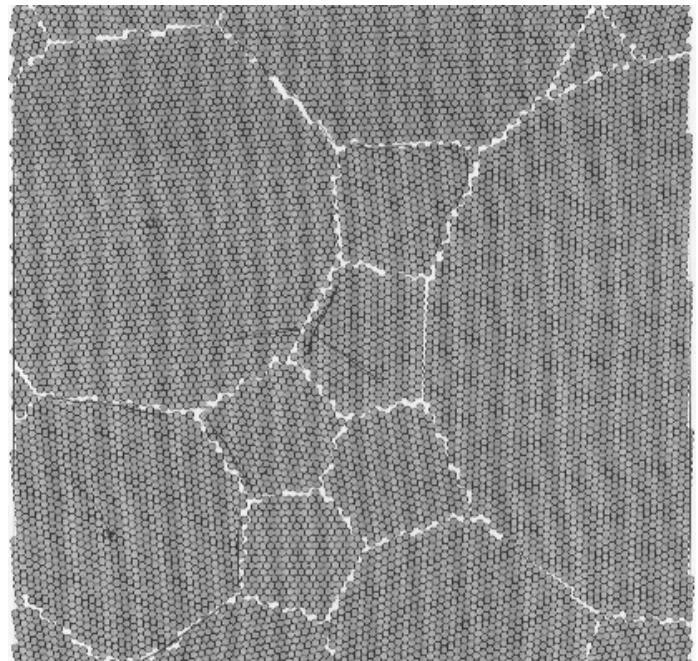
- Minimization of surface areas reduces the energy of the system (e.g. liquid drop)
- Solid surfaces can “reconstruct” to satisfy atomic bonds at surfaces.

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**.



Grain Boundary

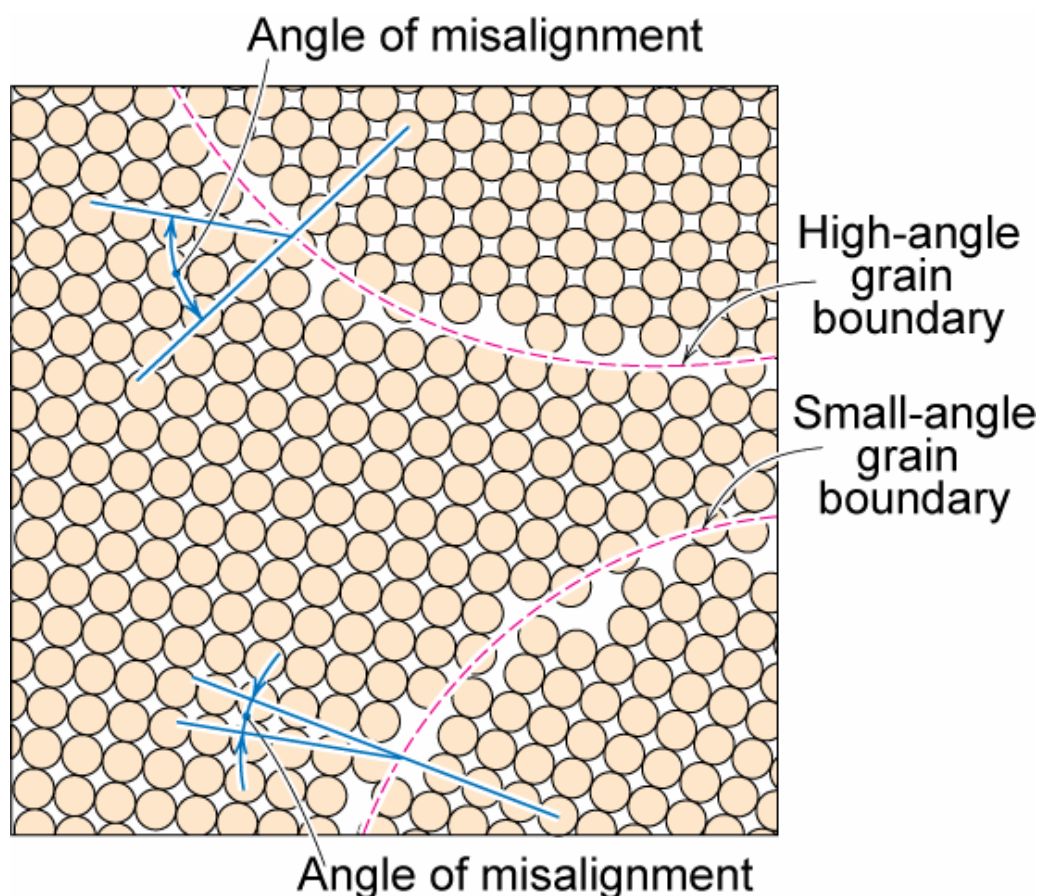


Surfaces and interfaces have structure that is different from the bulk and can be reactive → impurities tend to segregate there.

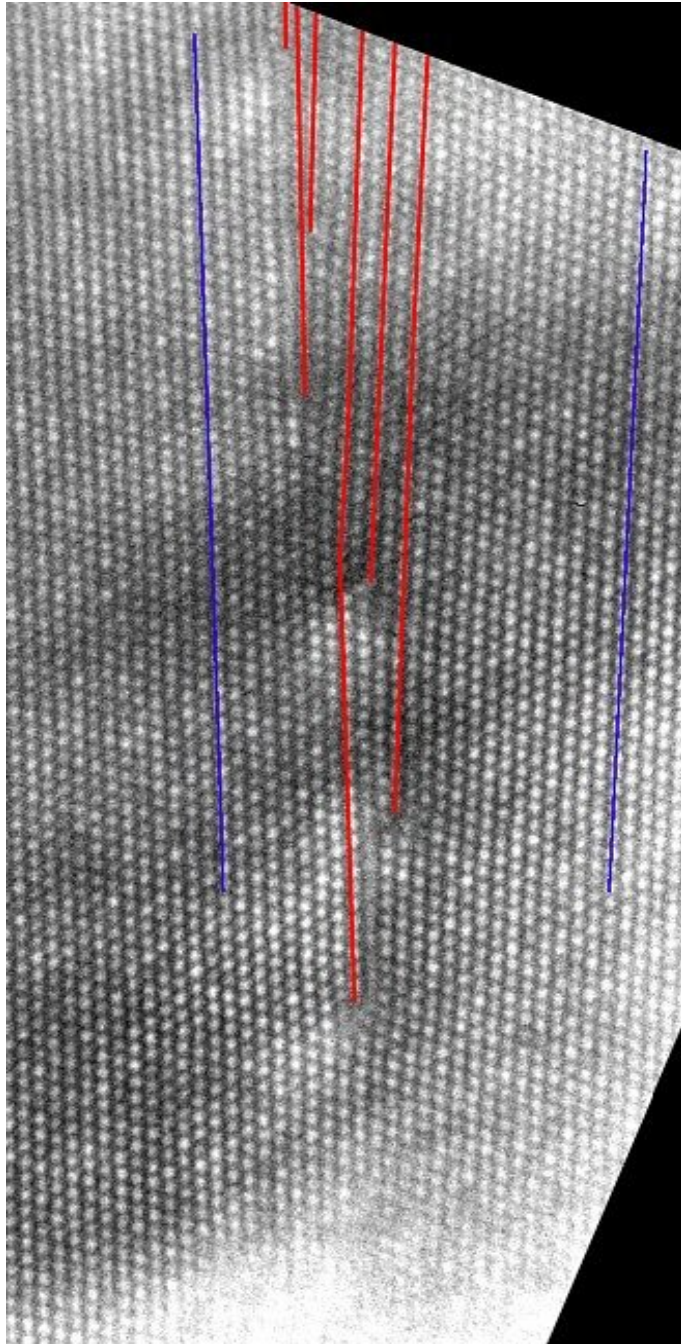
Since energy is associated with interfaces, grains tend to grow in size at the expense of smaller grains to minimize energy. This occurs by diffusion (Chapter 5), which is accelerated at high temperatures.

High and low angle grain boundaries

Depending on misalignments of atomic planes between adjacent grains we can distinguish between the low and high angle grain boundaries



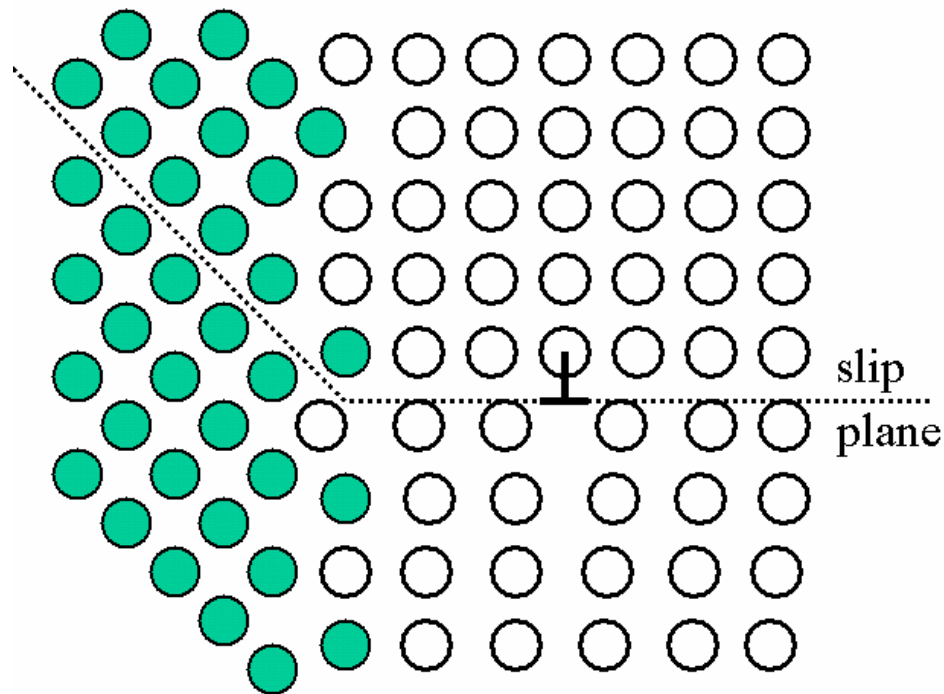
Low angle grain boundaries



Small angle grain boundaries can be described as arrays of dislocations. This is a transmission electron microscope image of a small angle **tilt** boundary in Si. The red lines mark the edge dislocations, the angle between the blue lines corresponds to the tilt angle.

Interaction between dislocations and grain boundaries

Motion of dislocations can be impeded by grain boundaries – increase of the force needed to move them (strengthening the material).



Grain boundary present a barrier to dislocation motion: slip plane discontinues or change orientation.

Small angle grain boundaries are not very effective in blocking dislocations.

High-angle grain boundaries block slip and increase strength of the material. A stress concentration at end of a slip plane may trigger new dislocations in an adjacent grain.

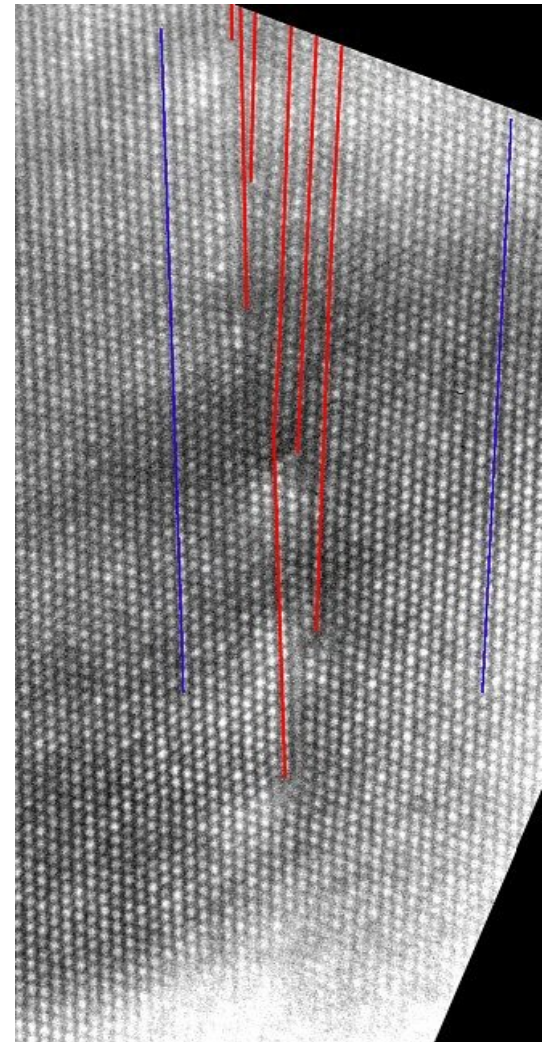
Tilt and twist grain boundaries

If the rotation axis that corresponds to the angle of misorientation between the adjacent grains is parallel to the boundary plane, the grain boundary is called **tilt boundary** (consider joint of two wedges).

A small-angle tilt grain boundary can be represented as an array of aligned edge dislocations.



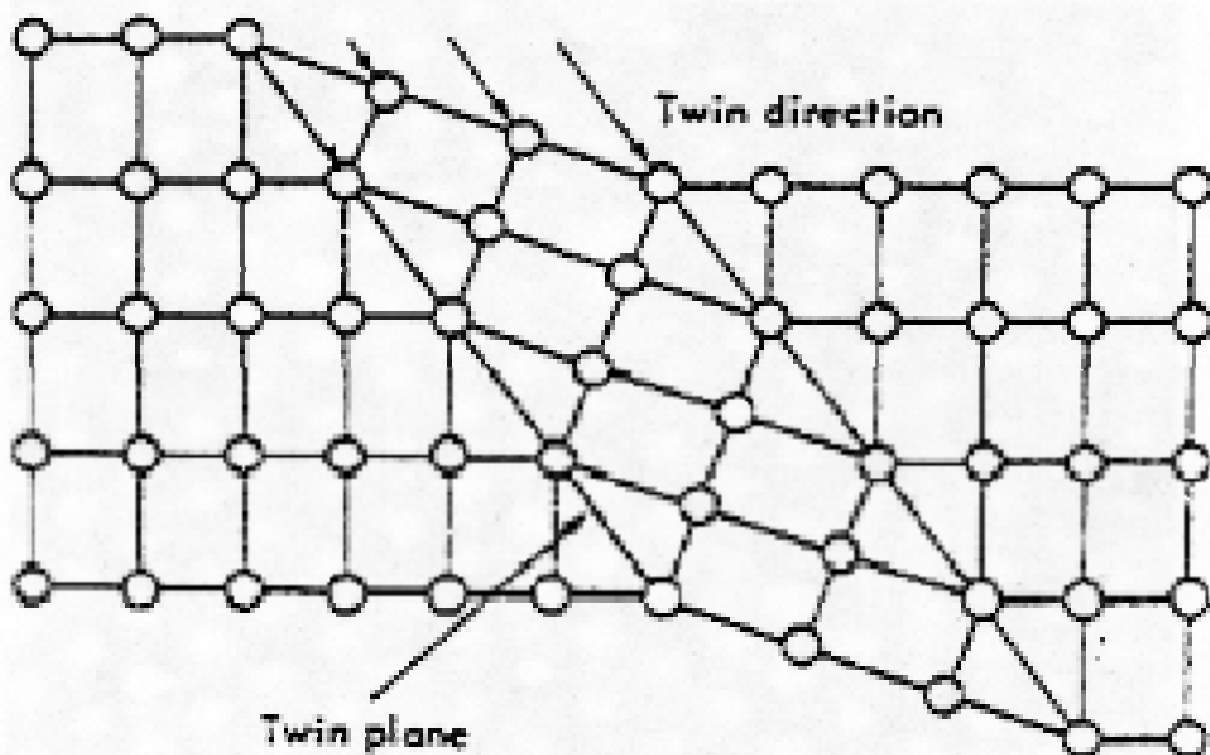
If the misorientation occurs around an axis that is perpendicular to the boundary plane, the grain boundary is called **twist grain boundary**



Small angle twist boundary can be represented by an array of screw dislocations (consider joint of two halves of a cube and twist an angle around the cross section normal)

Twin Boundaries (*not tested*)

Low-energy **twin boundaries** with mirrored atomic positions across boundary may be produced by deformation of materials. This gives rise to **shape memory metals**, which can recover their original shape if heated to a high temperature. Shape-memory alloys are twinned and when deformed they untwin. At high temperature the alloy returns back to the original twin configuration and restore the original shape.



Bulk or volume defects

- Pores
- Cracks
- Foreign inclusions

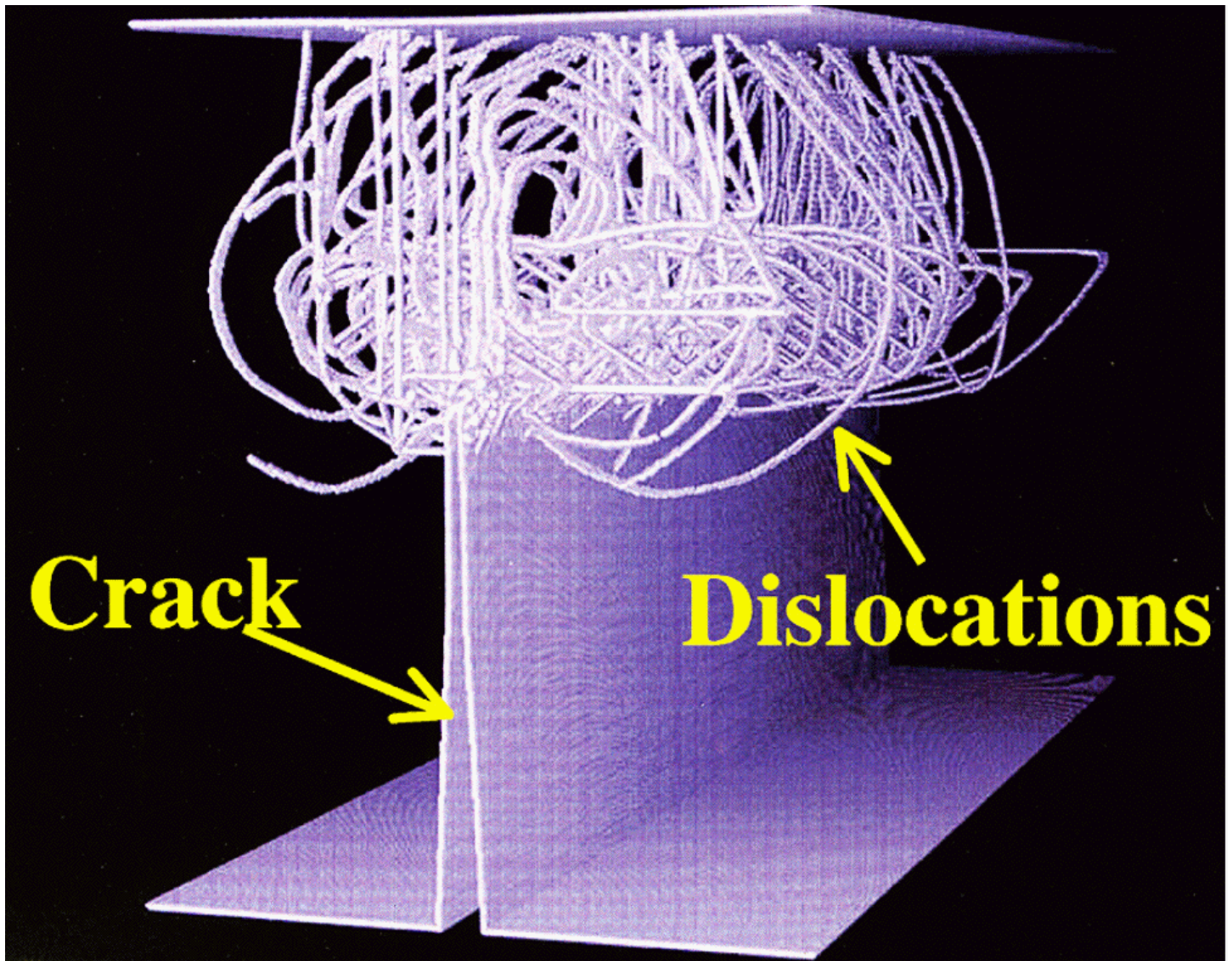
Presence of volume defects can greatly affect electrical, mechanical, thermal, and optical properties of the material



A cluster of microcracks in a melanin granule irradiated by a short laser pulse.

Computer simulation by Zhigilei and Garrison.

Atomistic simulation of crack propagation



V. Bulatov et al., Nature 391, #6668, 669 (1998)

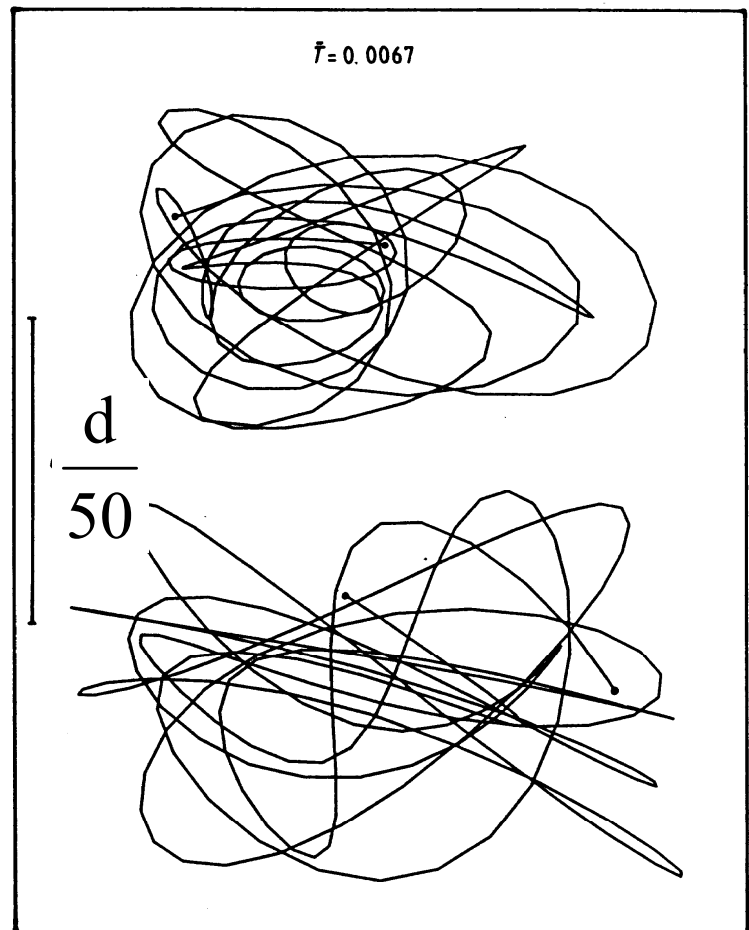
Atomic Vibrations

- Thermal energy (heat) causes atoms to vibrate
- Vibration amplitude increases with temperature
- Melting occurs when vibrations are sufficient to rupture bonds
- Vibrational frequency $\sim 10^{13}$ Hz (10^{13} vibrations per second)
- Average atomic energy due to the thermal excitation is of order $k_B T$

Atomic paths of two atoms in FCC lattice.

MD simulations by Brandt, J. Phys: Condens. Matter **1**, 10002, 1989.

d – equilibrium interatomic distance



Summary

Make sure you understand language and concepts:

- Alloy
- Atom percent
- Atomic vibration
- Boltzmann's constant
- Burgers vector
- Composition
- Dislocation line
- Edge dislocation
- Grain boundary
- Imperfection
- Impurity
- Interstitial solid solution
- Microstructure
- Point defect
- Screw dislocation
- Self-interstitial
- Solid solution
- Solute
- Solvent
- Substitutional solid solution
- Vacancy
- Weight percent

Homework #2: 4.2, 4.9, 4.11, 4.18, and 4.D2

Due date: Monday, September 13.

Reading for next class:

Chapter 5: Diffusion

Diffusion mechanisms (vacancy, interstitial)

Steady-state diffusion (Fick's first law)

Nonsteady-state diffusion (Fick's second law)

Factors that influence diffusion

Other diffusion paths