

Crystal Defects

The crystal lattices = an idealized, simplified system of geometrical points used to understand important principles governing the behavior of solids

Real crystals - contain large numbers of defects, e.g., variable amounts of impurities, missing or misplaced atoms or ions

These defects occur for three main reasons:

- 1) It is impossible to obtain any substance in 100% pure for, some **impurities** are always present
- 2) Even if a substance were 100% pure, forming a perfect crystal would require **cooling** the liquid phase infinitely slowly to allow all atoms, ions, or molecules to find their proper positions. Cooling at more realistic rates usually results in one or more components being trapped in the “wrong” place in a lattice or in areas where two lattices that grew separately intersect
- 3) Applying an **external stress** to a crystal can cause microscopic regions of the lattice to move with respect to the rest, thus resulting in imperfect alignment

Crystal Defects

Perfect crystals - every atom of the same type in the correct equilibrium position in the cell (does not exist at $T > 0$ K)

Real crystals - all crystals have some imperfections - defects
most atoms are in ideal locations, a small number are out of place

- **Intrinsic** – present for thermodynamic reasons
- **Extrinsic** – not required by thermodynamics, can be controlled by purification or synthetic conditions
- **Chemical** – foreign atom, mixed crystals, nonstoichiometry
- **Geometrical** – vacancy, interstitials, dislocations, boundaries, surface

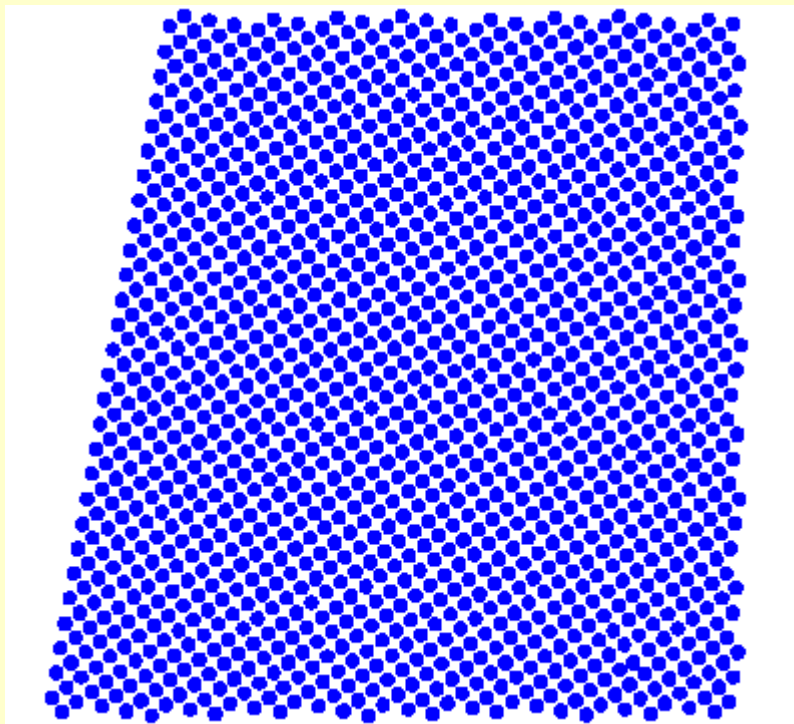
Defects dominate the material properties:

Mechanical, Chemical, Electrical, Diffusion

Defects can be added intentionally

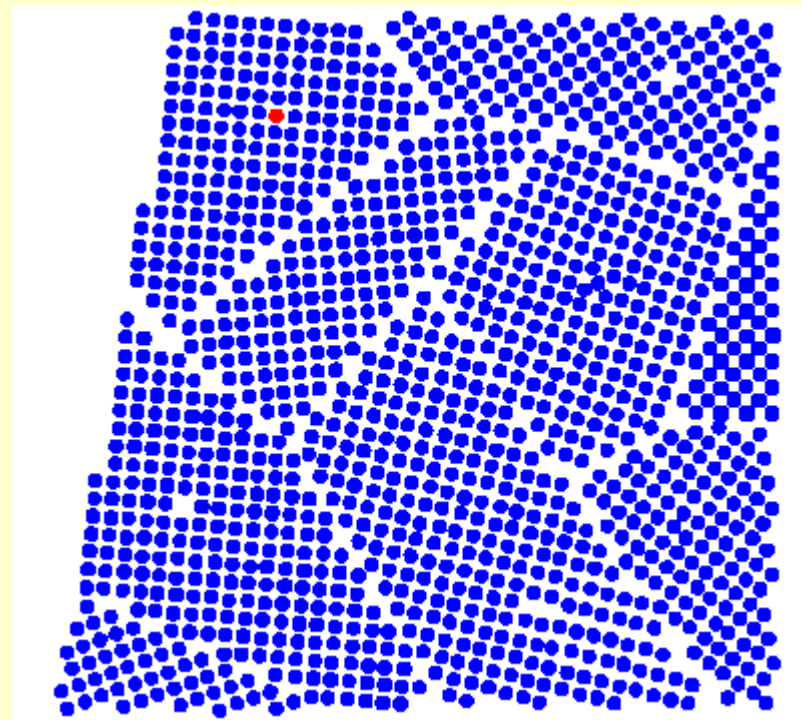
Crystal Defects

Perfect crystal



Does not exist at $T > 0$ K

Real crystal



Classes of Crystal Defects

Point defects (0D)

places where an atom is missing or irregularly placed in the lattice structure – lattice vacancies, self-interstitial atoms, substitution impurity atoms, interstitial impurity atoms

Linear defects (1D)

groups of atoms in irregular positions – dislocations

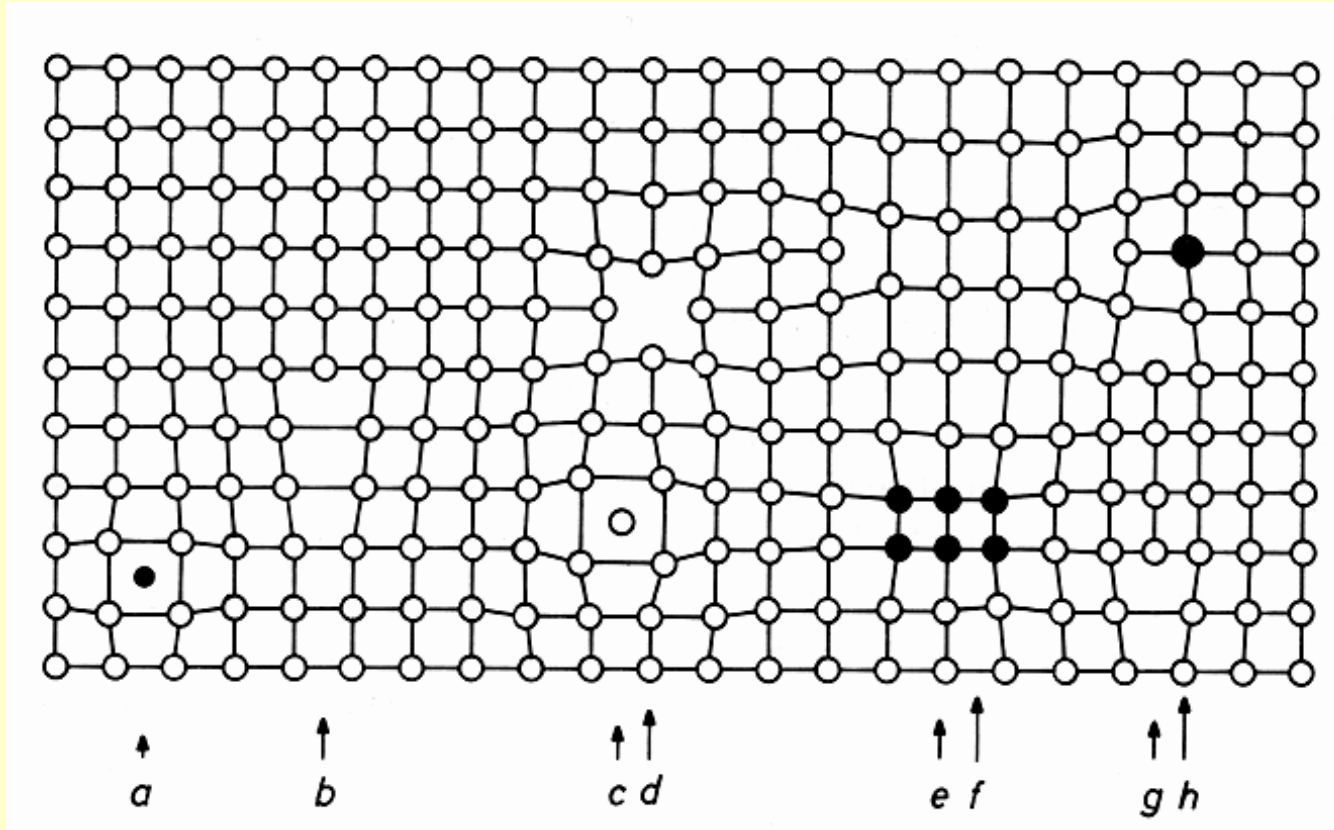
Planar defects (2D)

interfaces between homogeneous regions of the material - grain boundaries, stacking faults, shear planes, external surfaces

Volume defects (3D)

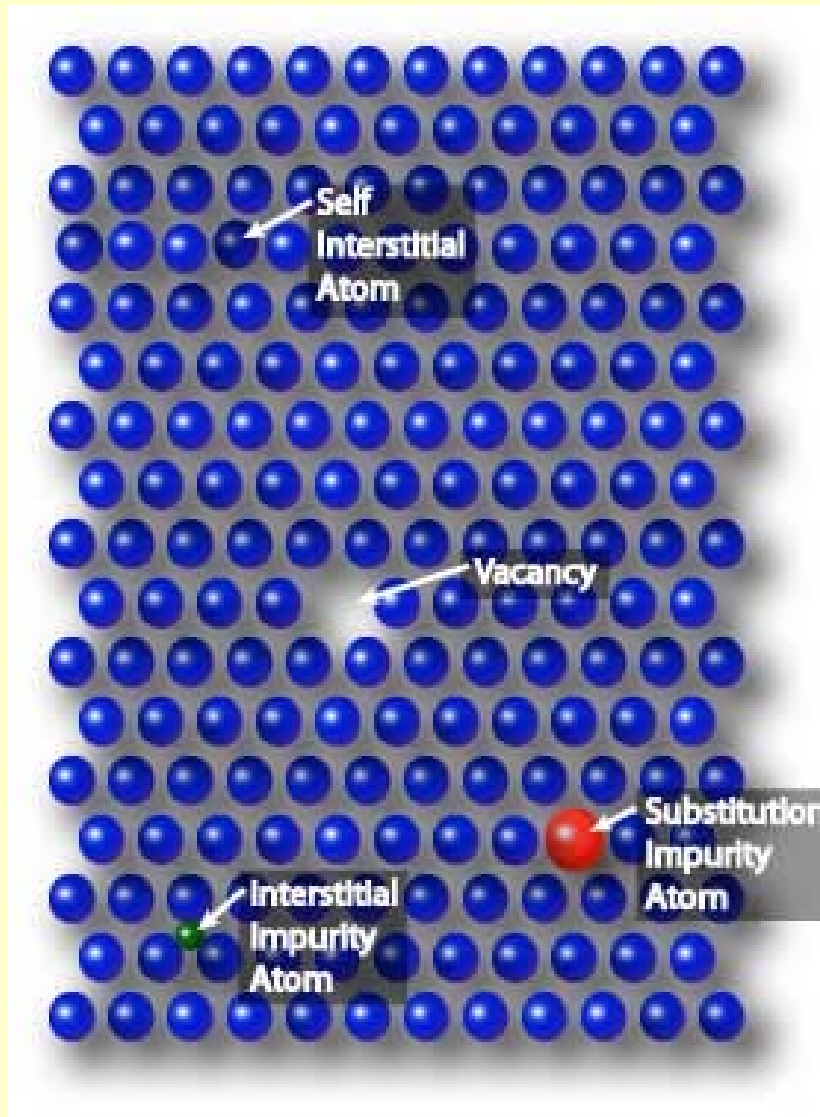
spaces of foreign matter – pores, inclusions, mosaic, domains

Classes of Crystal Defects



a - interstitial impurity atoms, b, g - dislocations, c - self-interstitial atom, d - vacancy, e,f - inclusions, h - substitution impurity atom

Point Defects



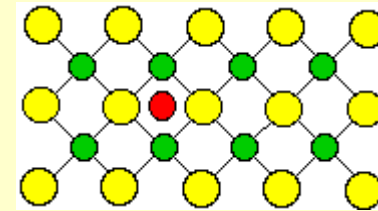
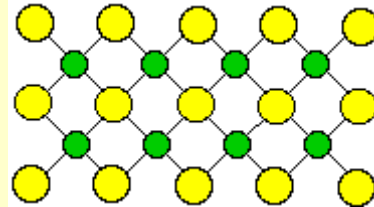
Point defects

an atom is missing or is in an irregular position in the lattice

- self interstitial atoms
- interstitial impurity atoms
- substitutional impurity atoms
- vacancies

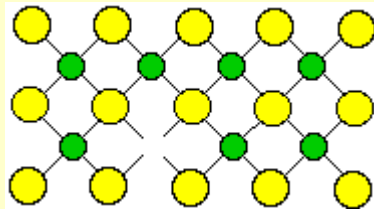
Point Defects – Ionic Compounds

perfect crystal lattice AB

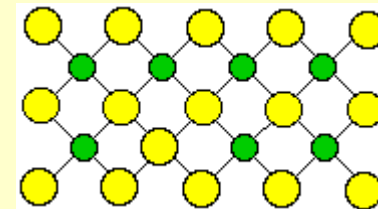
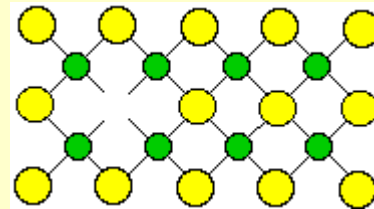


interstitial impurity

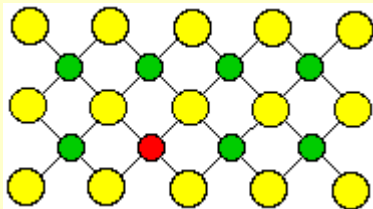
cation vacancy



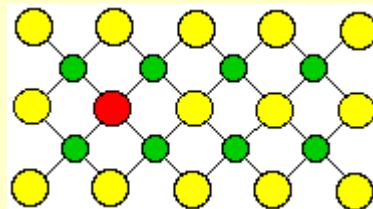
anion vacancy



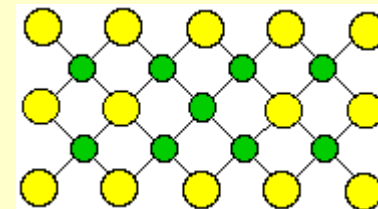
B_A antisite defect



substitution of a cation



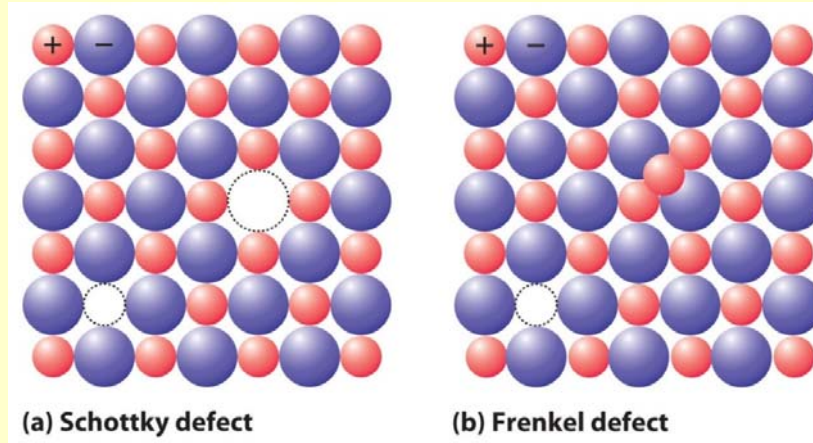
substitution of an anion



A_B antisite defect

Point Defects – Ionic Compounds

- Vacancy
- Interstitial
- Substitutional
- Frenkel
- Schottky



Schottky: a pair of vacancies, missing cation/anion moved to the surface, **equal numbers of vacancies at both A and B sites** preserving charge balance, found in highly ionic compounds where cation and anion have comparable size and high coordination numbers (NaCl), metal ions are able to assume multiple oxidation states

Frenkel: ions moved to interstitial positions, vacancies, found in open structures (wurtzite, sphalerite, AgX, etc.) with low coordination numbers, open structure provides room for interstitial sites to be occupied, cations much smaller than anions, more covalent bonding

Vacancies

There are naturally occurring vacancies in all crystals

Equilibrium defects – thermal oscillations of atoms at $T > 0$ K

The number of vacancies grows as the temperature increases

The number of vacancies:

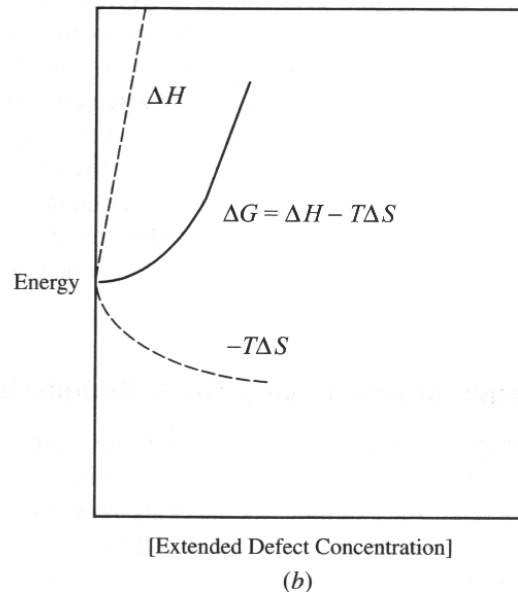
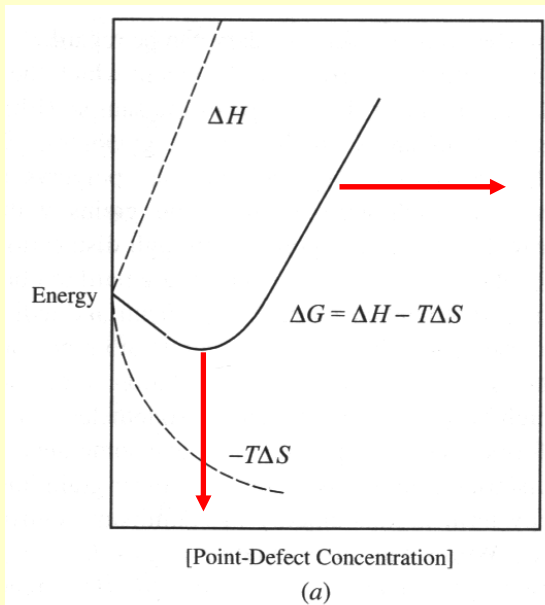
$$N_v = N \exp\left(-\frac{\Delta H^a}{RT}\right)$$

- N = the total number of sites in a crystal
- N_v = the number of vacancies
- ΔH^a = the activation energy for the formation of a vacancy
- R = the gas constant

N_v goes up exponentially with temperature T

$$\Delta G = \Delta H - T\Delta S$$

Crystal Energies



Point defects = equilibrium concentration
 Enthalpy ΔH is positive but configurational entropy ΔS is positive – defects = disorder
 Minimum on free energy $\Delta G =$ equilibrium concentration of defects
 The concentration of vacancies grows as the temperature increases

Extended defects = no equilibrium concentration
 Enthalpy is HIGHLY positive, configurational entropy cannot outweigh
 No minimum on free energy ΔG

Metastable defects – dislocations, grain boundaries, surface

Heating = minimize free energy:
 polycrystalline \rightarrow single crystal grain growth
 Grains with high dislocation density consumed
 Atoms move across grain boundary

Typical Point Defects in Crystals

Alkali halides

Alkaline earth oxides

Silver halides

Alkaline earth fluorides

Schottky (cations and anions)

Schottky (cations and anions)

Frenkel (cations)

Frenkel (anions)

Typical activation energies for ion diffusion

Na⁺ in NaCl ~ 0,7 eV

Cl⁻ in NaCl ~ 1 eV

Schottky pair ~ 2,3 eV

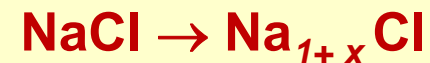
(1 eV/molecule = 96.49 kJ/mol)

Extrinsic Defects

The addition of **the dopant** (an impurity) into a perfect crystal = point defects in the crystal

NaCl heated in Na vapors

Na is taken into the crystal and changes its composition



Na atoms occupy cation sites, an equivalent number of unoccupied anion sites, Na atoms ionize, Na^+ ions occupy the cation sites, the electrons occupy the anion vacancies – F centers – color (Farbe)

Such solid is now a non-stoichiometric compound as the ratio of atoms is no longer the simple integer

Violet color of Fluorite (CaF_2) = missing F^- anions replaced by e^-



Solid Solutions

Substitution (mixing, solution) of ions on specific sites

Forsterite: Mg_2SiO_4

Can substitute Fe for Mg

Fayalite: Fe_2SiO_4

Olivine - the substitution is very readily accomplished and any intermediate composition is possible

Olivine: $(\text{Mg}, \text{Fe})_2\text{SiO}_4$

Olivine is a solid-solution series in which any ratio of Mg/Fe is possible as long as they sum to two ions per formula unit required for electric neutrality

Non-Stoichiometric Compounds

Non-stoichiometry can be caused by

- introducing an impurity (doping)
- the ability of an element to show **multiple valencies**

Vanadium oxide varies from $\text{VO}_{0.79}$ to $\text{VO}_{1.29}$

What oxidation states?

other examples: TiO_x , Ni_xO , UO_x , WO_x , and Li_xWO_3

Covalent compounds - held to together by very strong covalent bonds which are difficult to break, do not show a wide range of compositions

Ionic compounds - do not show a wide range because a large amount of energy is required to remove / add ions

Non-Stoichiometric Compounds

Non-stoichiometric ionic crystals

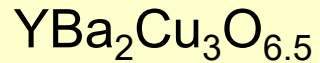
a multi-valent element - changes in the number of ions can be compensated for by changes in the charge on the ions, therefore maintaining **charge balance** but changing the stoichiometry

Non-stoichiometric compounds have formulae with non-integer ratios and can exhibit a range of compositions

The electronic, optical, magnetic and mechanical **properties** of non-stoichiometric compounds can be **controlled** by varying their **composition**

Non-Stoichiometric Compounds

Non-stoichiometric superconductor YBCO



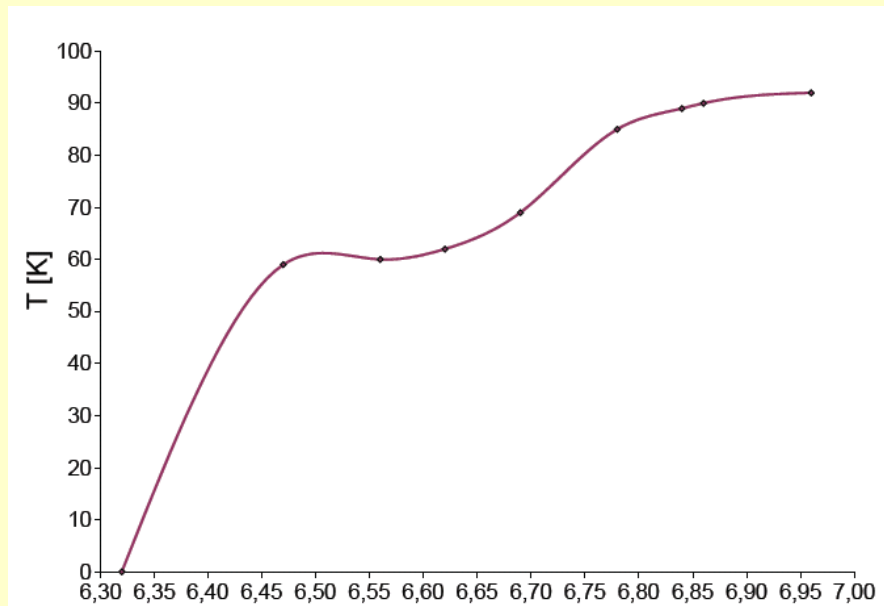
a multi-valent element = Cu

$\text{YBa}_2\text{Cu}_3\text{O}_{6.8-7.0}$ 90 K superconductor

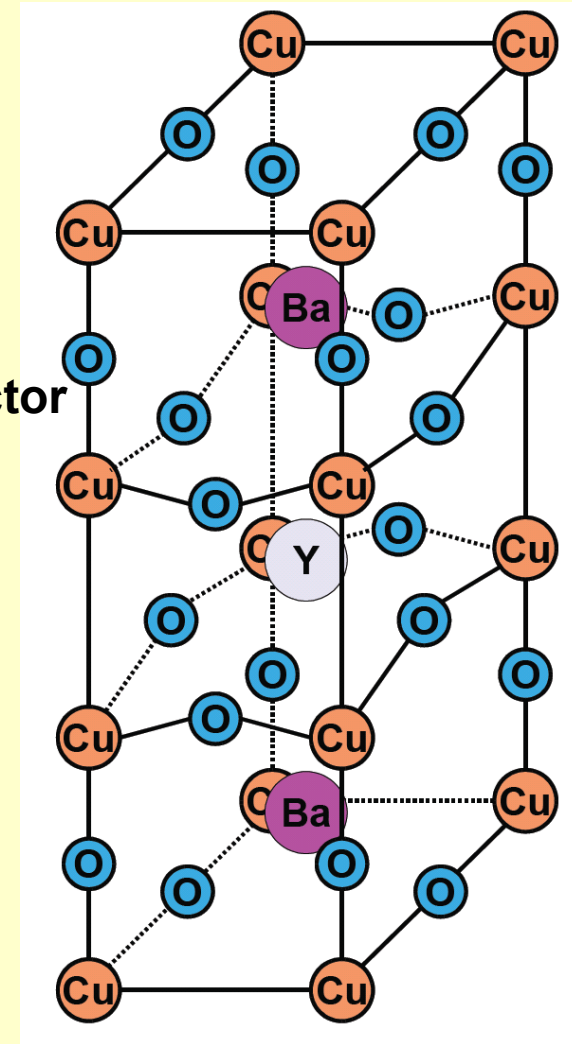
$\text{YBa}_2\text{Cu}_3\text{O}_{6.45-6.7}$ 60 K superconductor

$\text{YBa}_2\text{Cu}_3\text{O}_{6.0-6.45}$ antiferromagnetic semiconductor

T_{critical}
Kelvin



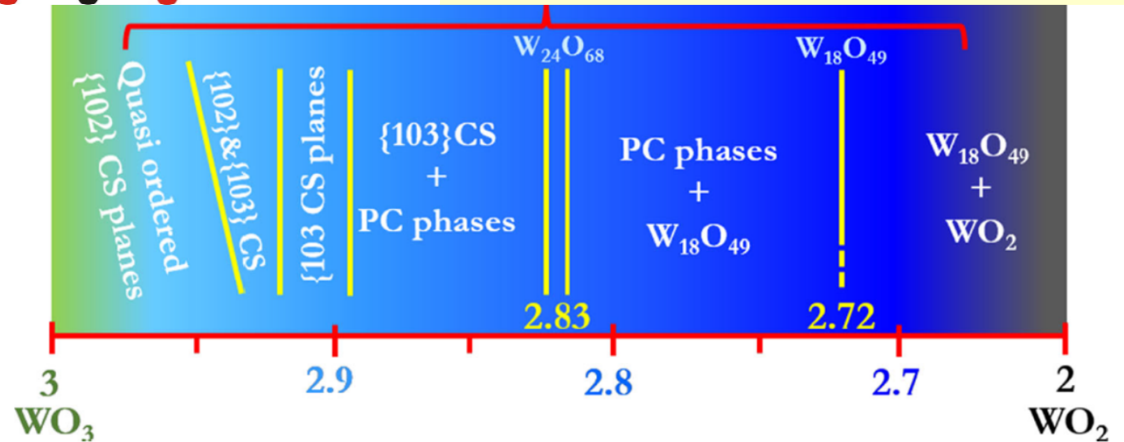
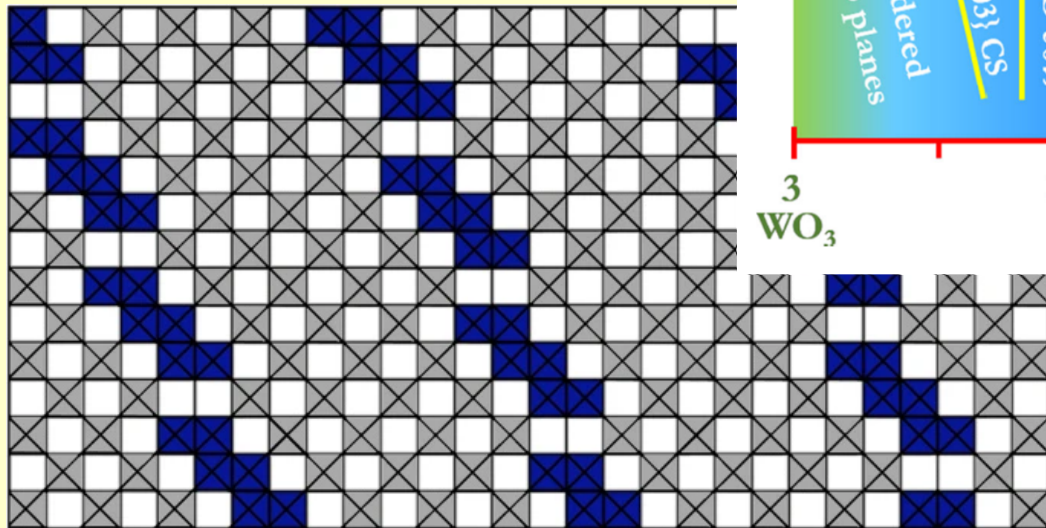
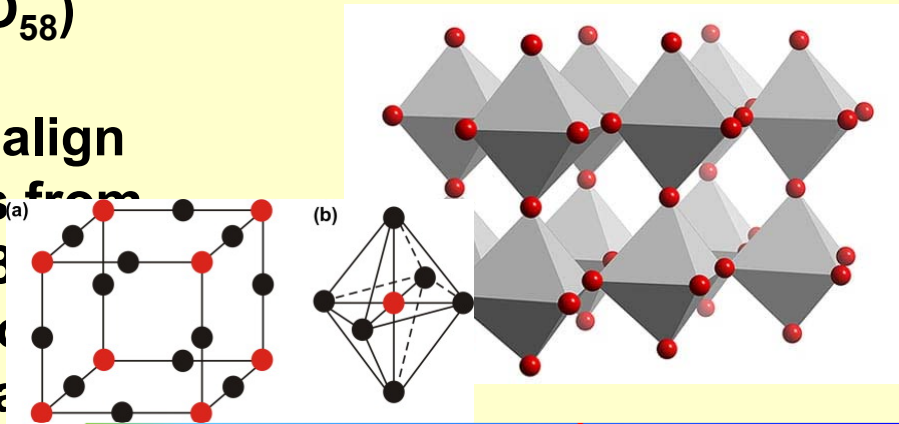
Oxygen content



Non-Stoichiometric Compounds

Magnéli phase $WO_{2.9}$ ($W_{20}O_{58}$)

W_nO_{3n-1} the shear planes align along (102) where 'n' varies from 30 to 19 $WO_{2.96}$ to $WO_{2.93}$
 W_nO_{3n-2} the reduction below $WO_{2.92}$, the defect planes are along (103) for 'n' values between 20 and 15

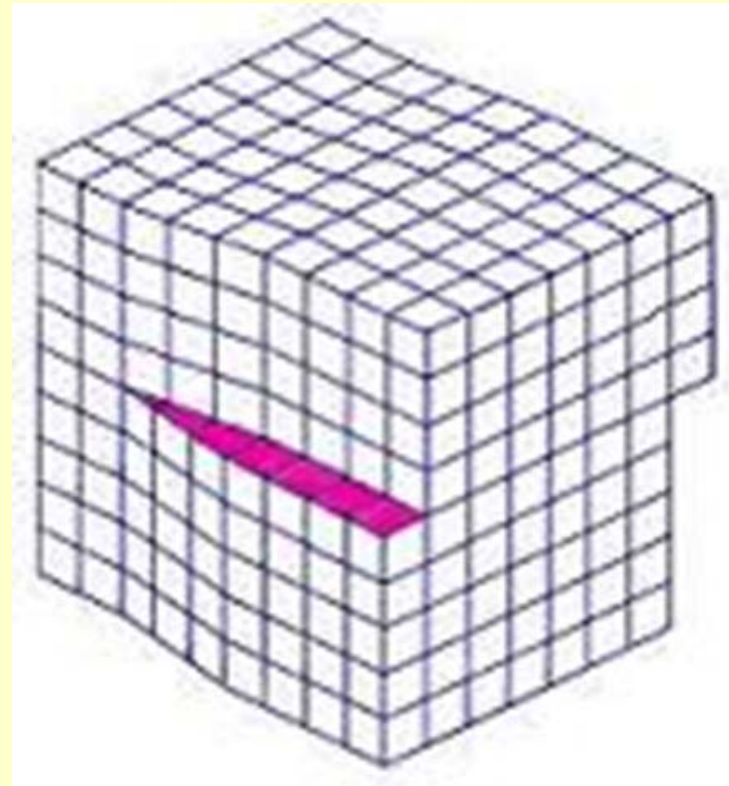
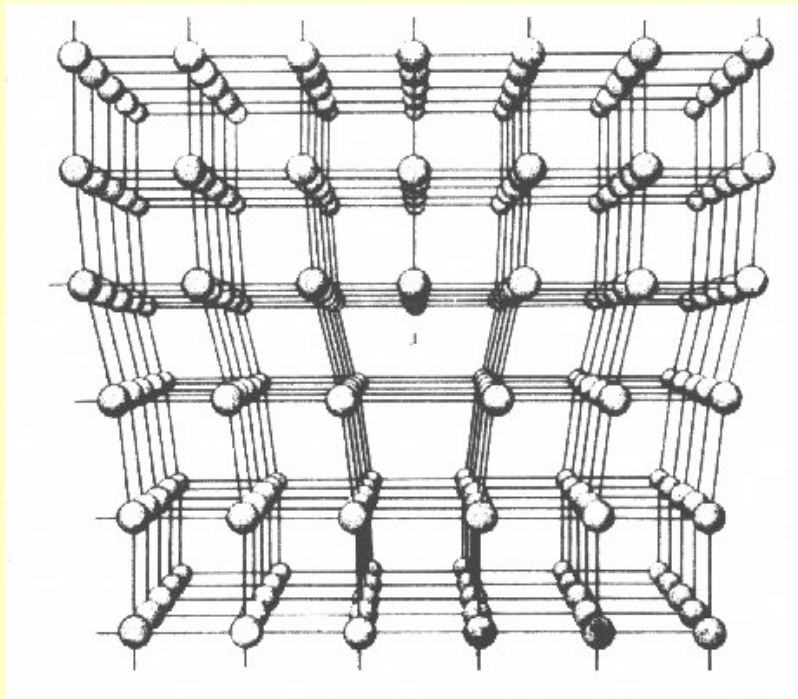


W₂₀O₅₈ ($WO_{2.9}$), **W₅O₁₄** ($WO_{2.8}$), **W₄O₁₁** ($WO_{2.75}$), **W₁₈O₄₉** ($WO_{2.72}$), **W₃O₈** ($WO_{2.67}$), **W₂O₅** ($WO_{2.5}$),

Dislocations

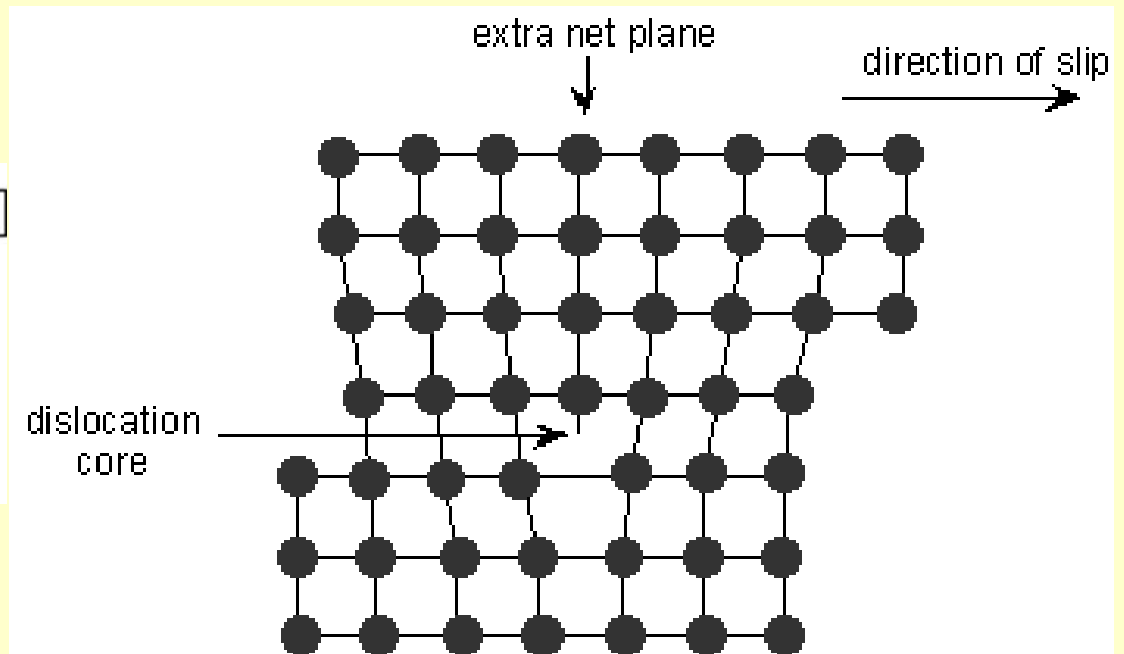
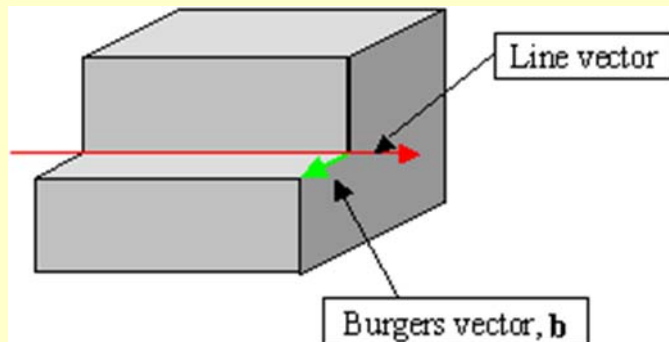
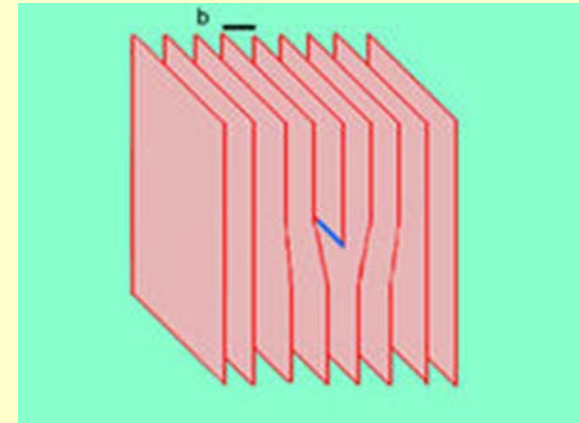
Line imperfections in a 3D lattice

- Edge
- Screw
- Mixed



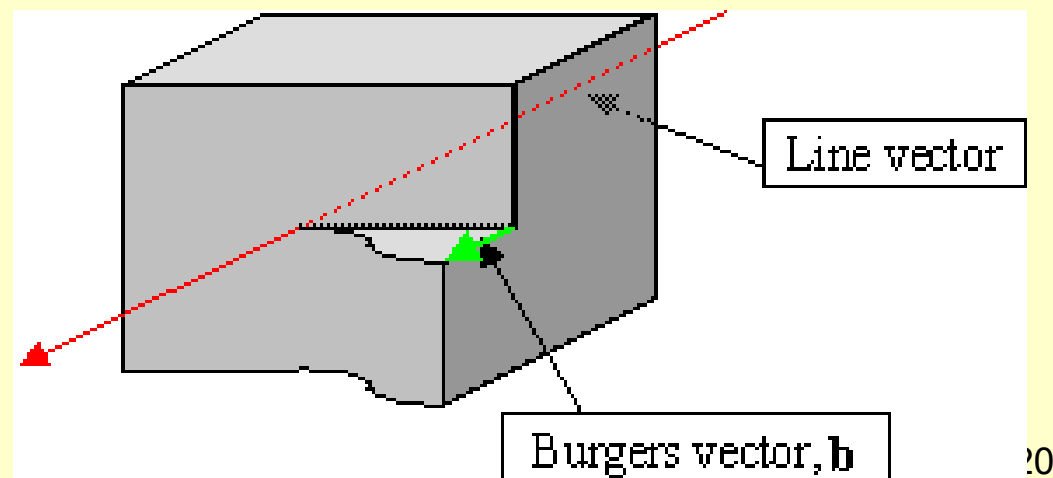
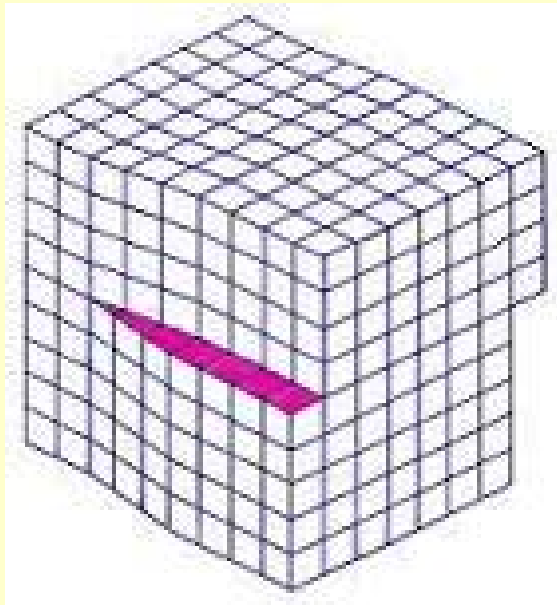
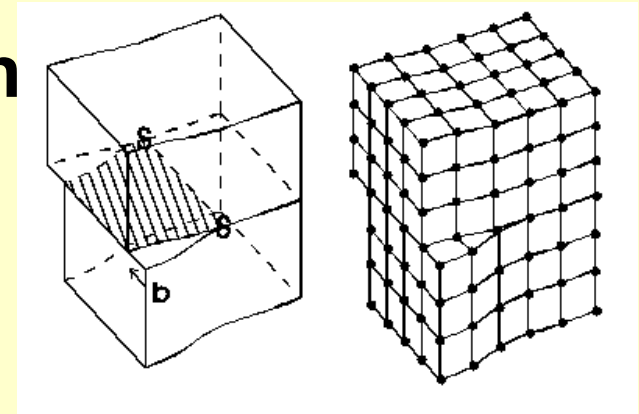
Edge Dislocation

- Extra plane of atoms
- Burgers vector
 - Deformation direction
 - For edge dislocations it is perpendicular to the dislocation line



Screw Dislocation

- A ramped step
- Burgers vector
 - Direction of the displacement of the atoms
 - For a screw dislocation it is parallel to the line of the dislocation

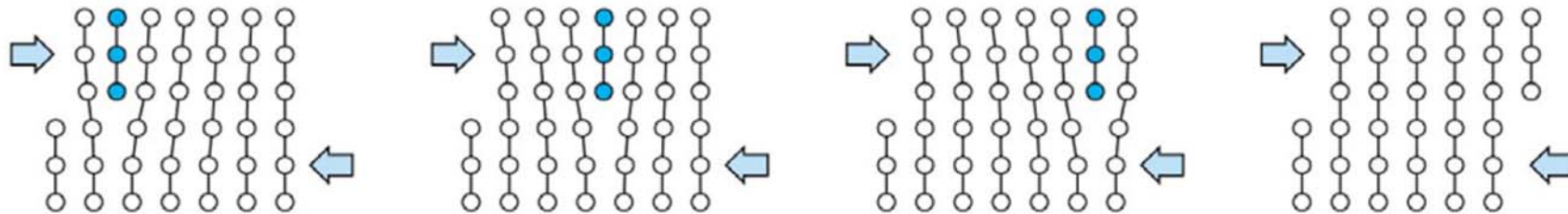


Deformation

When a **shear force** is applied to a material, the dislocations move

Plastic deformation = the movement of dislocations (linear defects)

The **strength** of the material depends on the force required to make the dislocation move, not the bonding energy



Deformation

Millions of dislocations in a material - result of plastic forming operations (rolling, extruding,...)

Any **defect** in the regular lattice structure (point, planar defects, other dislocations) **disrupts the motion of dislocation** - makes slip or plastic deformation more difficult

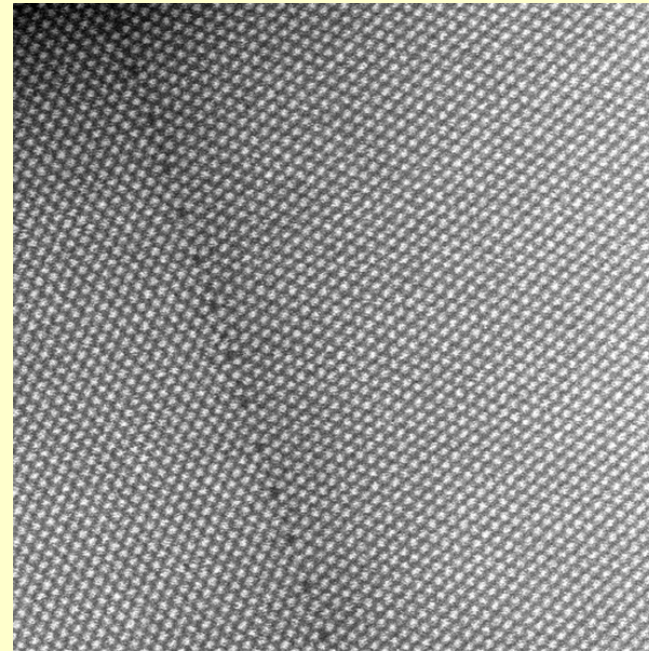
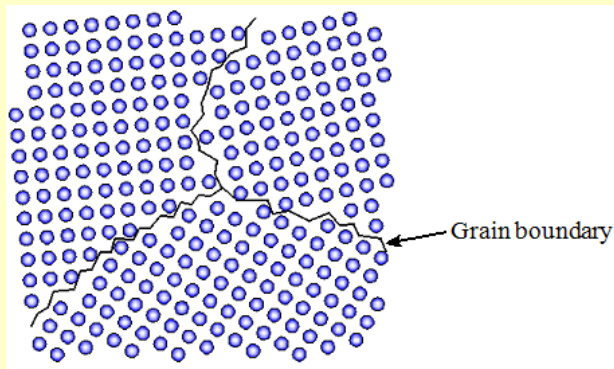
Dislocation movement produces additional dislocations

Dislocations collide – **entangle** – impede movement of other dislocations - the force needed to move the dislocation increases - the material is **strengthened**

Applying a force to the material increases the number of dislocations
Called “strain hardening” or “cold work”

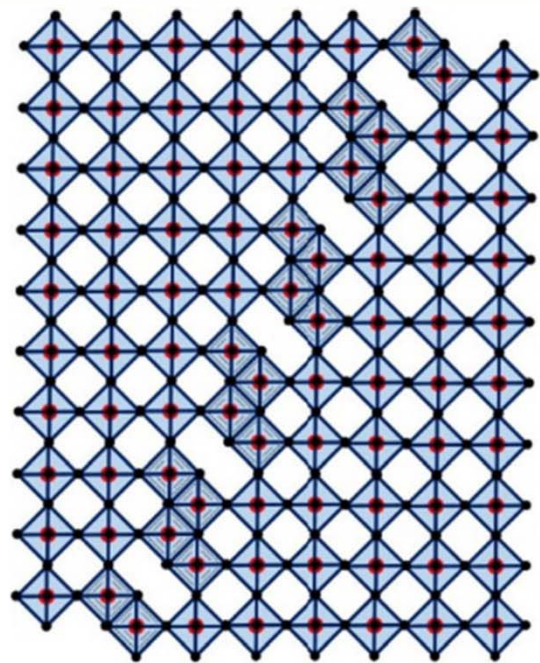
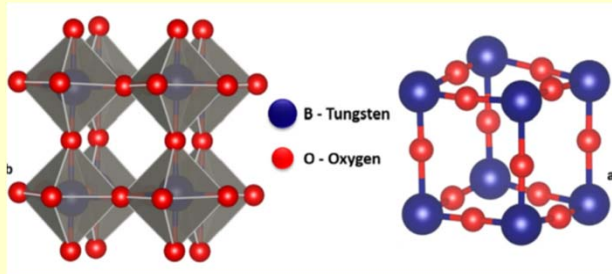
Surface and Grain Boundaries

- The atoms at the boundary of a grain or on the surface are not surrounded by other atoms – lower coordination number (CN), weaker bonding
- Grains line up imperfectly where the grain boundaries meet
- Dislocations can not cross grain boundaries
- Tilt and Twist boundaries
- Low and High angle boundaries

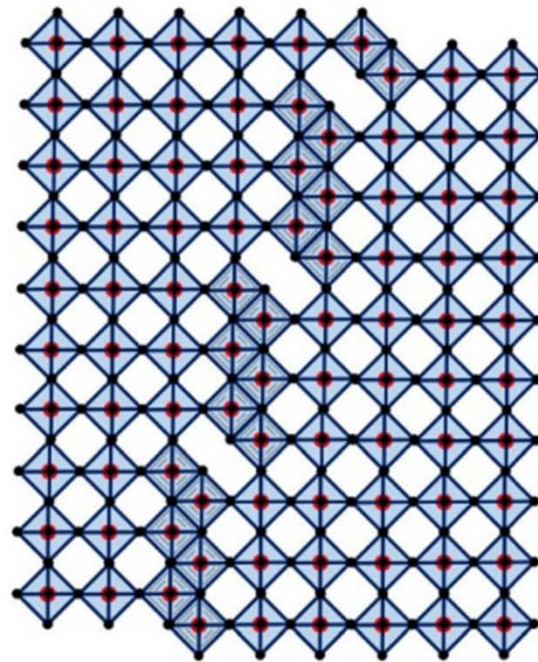


High resolution STEM image from a grain boundary in Au 23
at the atomic level, imaged on an FEI Titan STEM 80-300

Crystal Shear Planes



CS planes aligned in {102}



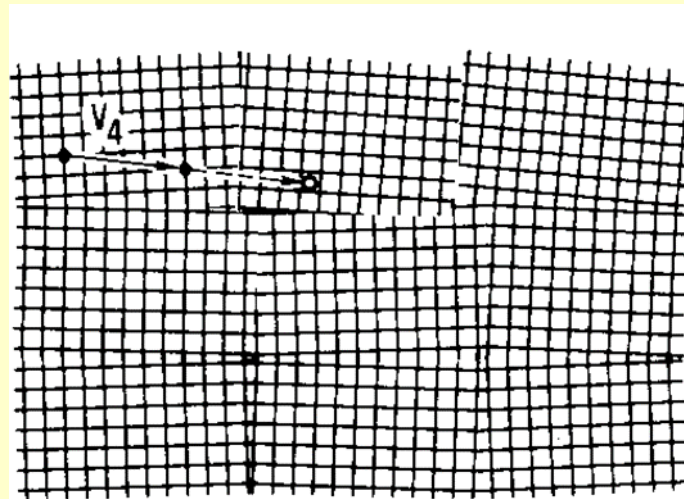
CS planes aligned in {103}

Mosaic Crystals

Boundary of slightly mis-oriented volumes within a single crystal

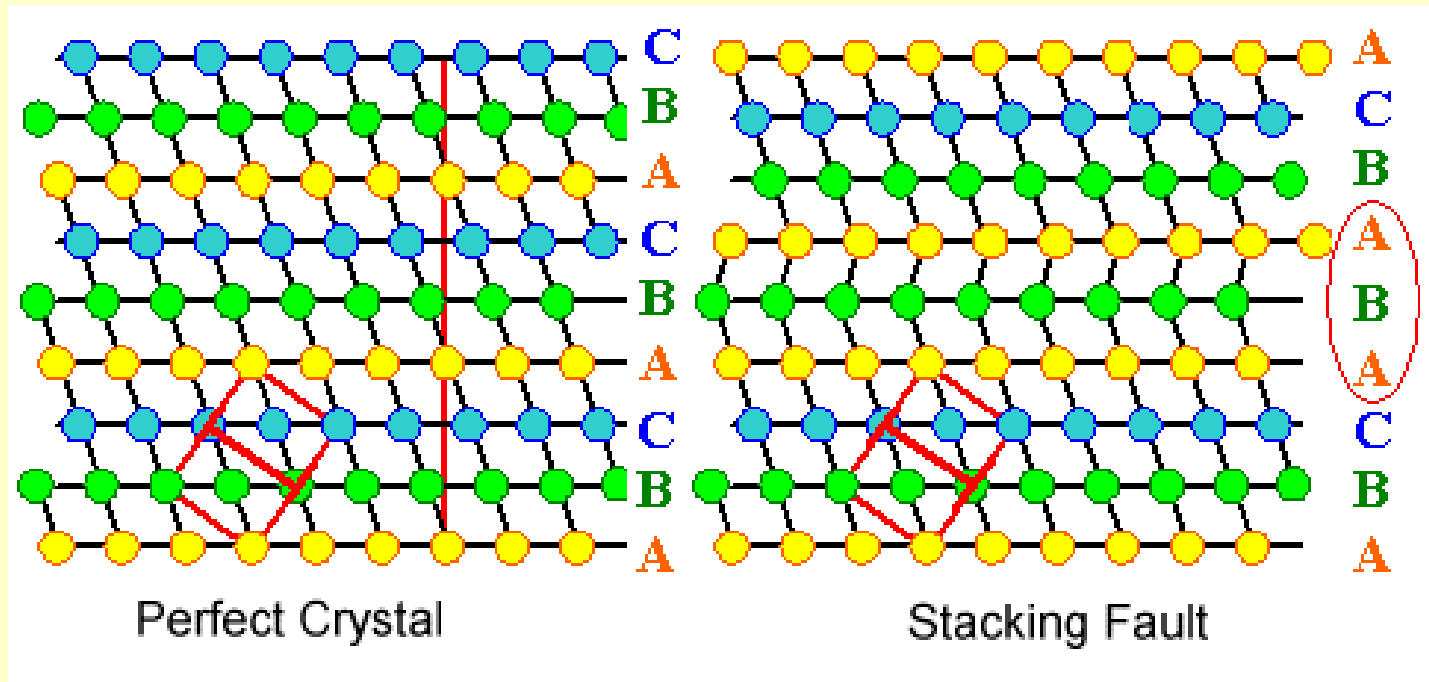
Lattices are close enough to provide continuity (so not separate crystals)

Has short-range order, but not long-range order



LATTICE : MOSAIC CRYSTAL

Stacking Faults



ABCABCABC**AB**ABCABC

AAAAAA**B**AAAAAAA

ABABABAB**ABC**ABABAB

Effect of Grain Size on Strength

- Material with a small grain = a dislocation moves to the boundary and stops – slip stops
- Material with a large grain = the dislocation can travel farther
- Small grain size = more strength
- Hall-Petch Equation

$$\sigma_y = \sigma_0 + K d^{-1/2}$$

σ_y = yield strength
(stress at which the material permanently deforms)

d = average grain diameter

σ_0 = yield stress for bulk single crystal

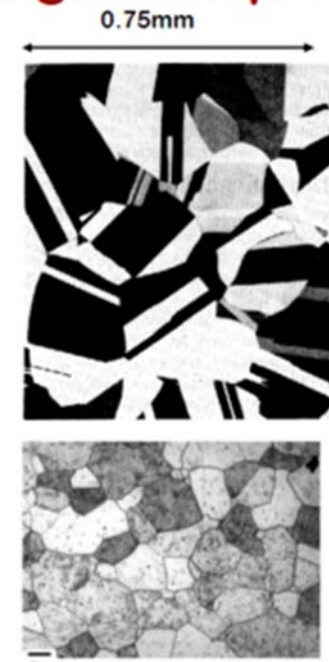
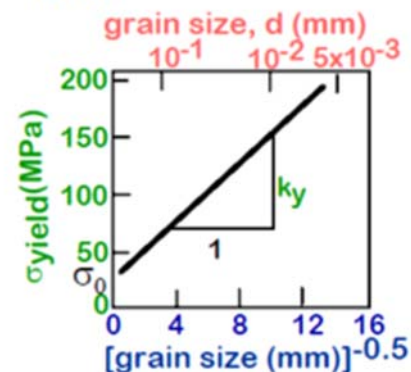
K = unpinning constant

Grain Size Strengthening: Example

- 70wt%Cu-30wt%Zn brass alloy

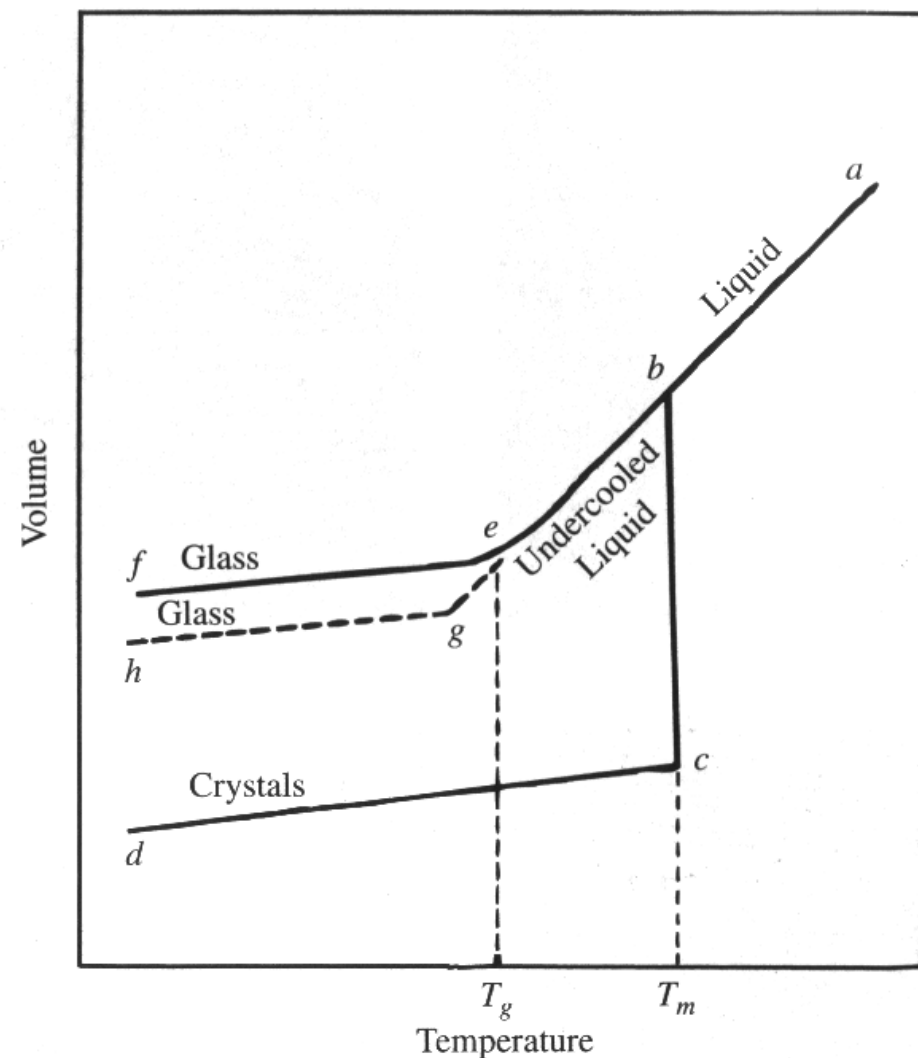
$$\sigma_{\text{yield}} = \sigma_0 + k_y d^{-1/2}$$

- Data:



Amorphous Structures

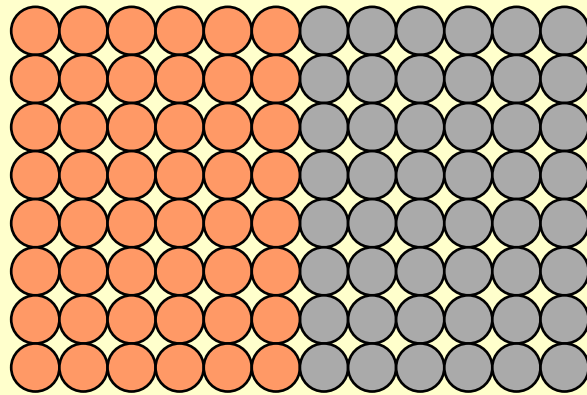
- Cooling a material off too fast - it does not have a chance to crystallize
- Forms a glass
- Easy to make a ceramic glass
- Hard to make a metallic glass
- There are no slip planes, grain boundaries in a glass



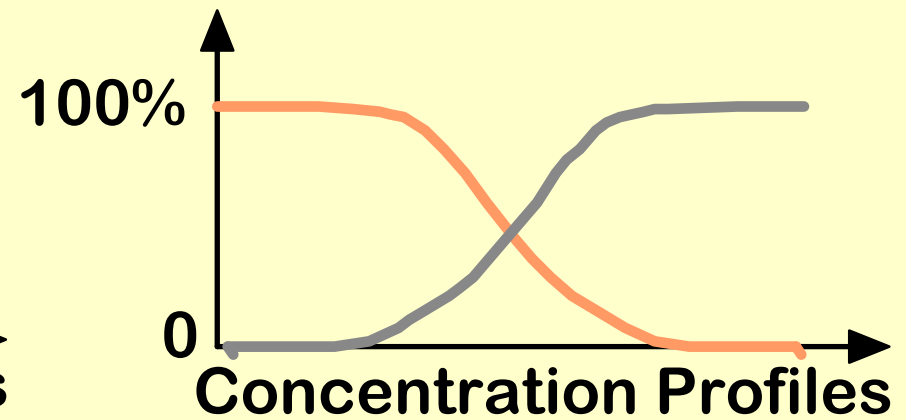
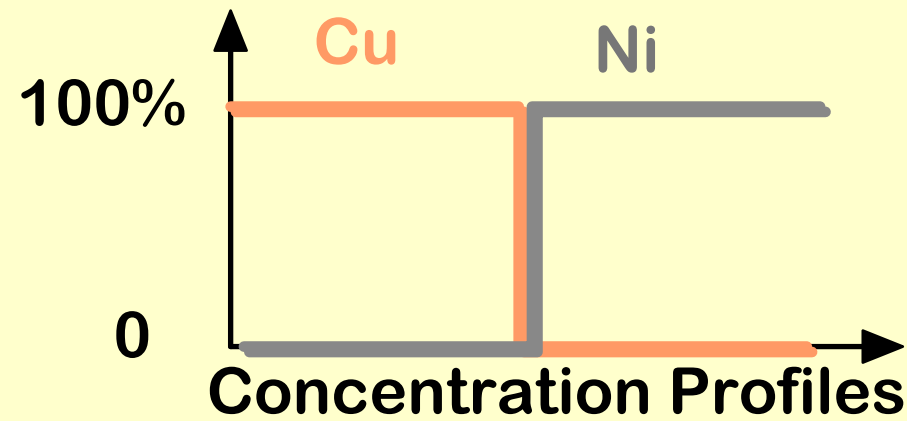
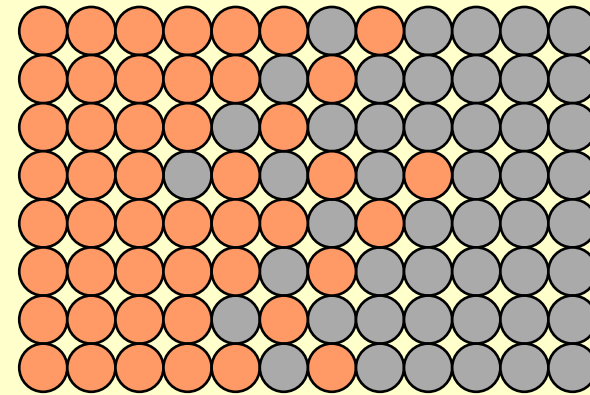
Diffusion

Interdiffusion:
atoms migrate from regions of large to lower concentration

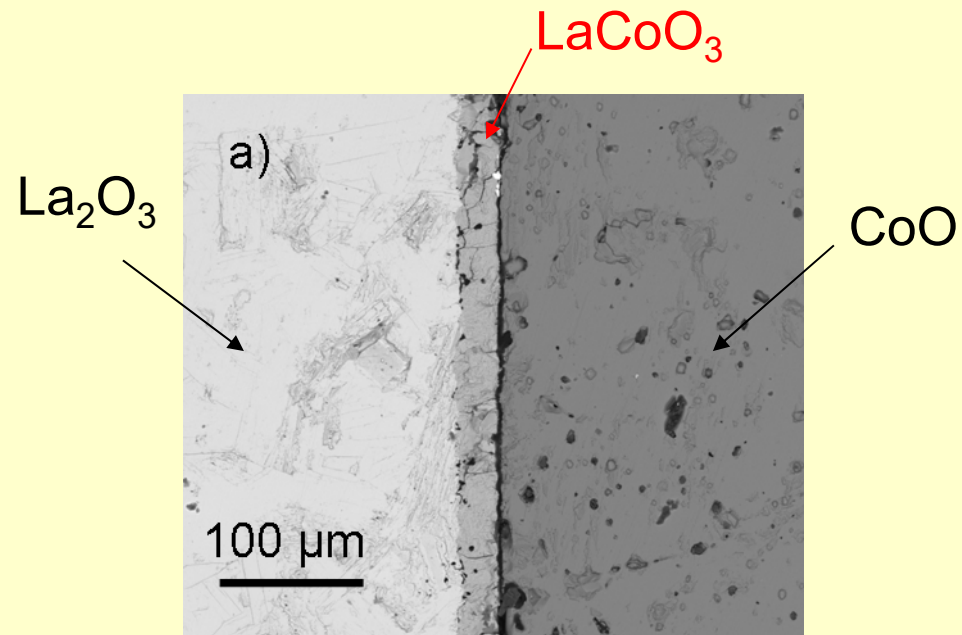
Initial state (diffusion couple)



After elapsed time



Diffusion Couple Experiments

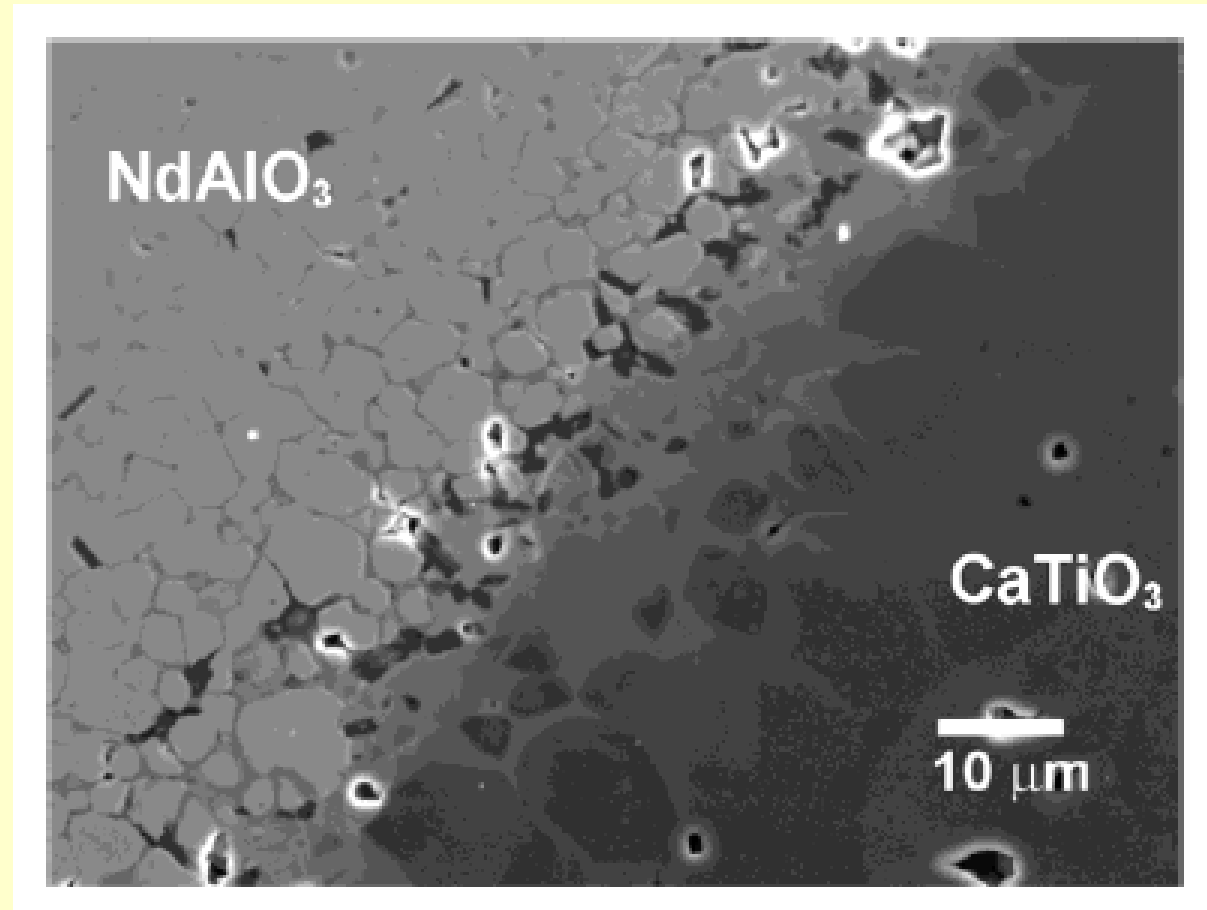


Experimental conditions:

$T = 1370 - 1673 \text{ K}$

$p\text{O}_2 = 40 \text{ Pa} - 50 \text{ kPa}$

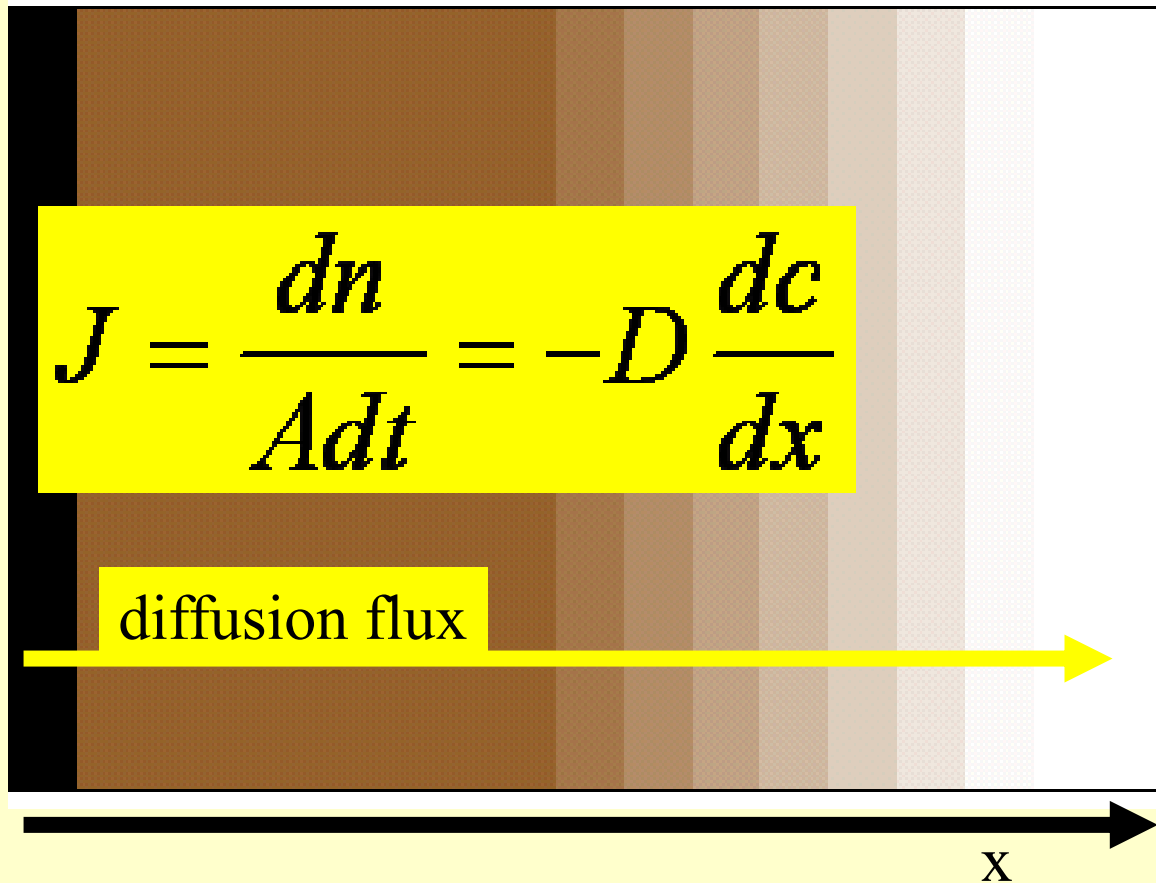
Diffusion Couple Experiments



CaTiO₃-NdAlO₃ diffusion couple fired at 1350 °C/ 6 h

Diffusion - Fick's First Law

Fick's first law describes **steady-state** diffusion



$$J = \frac{dn}{A dt} = -D \frac{dc}{dx}$$

J = diffusion flux
[mol s⁻¹ m⁻²]

D = diffusion coefficient
diffusivity
[m² s⁻¹]

dc/dx = concentration
gradient [mol m⁻³ m⁻¹]

A = area [m²]

Velocity of diffusion of particles (ions, atoms ...) in a solid
mass transport and concentration gradient for a given point in a solid

Mechanisms of Diffusion

Diffusion = the mechanism by which matter is transported into or through matter

Diffusion at the atomic level is a step-wise migration of atoms from lattice site to lattice site

Conditions for diffusion:

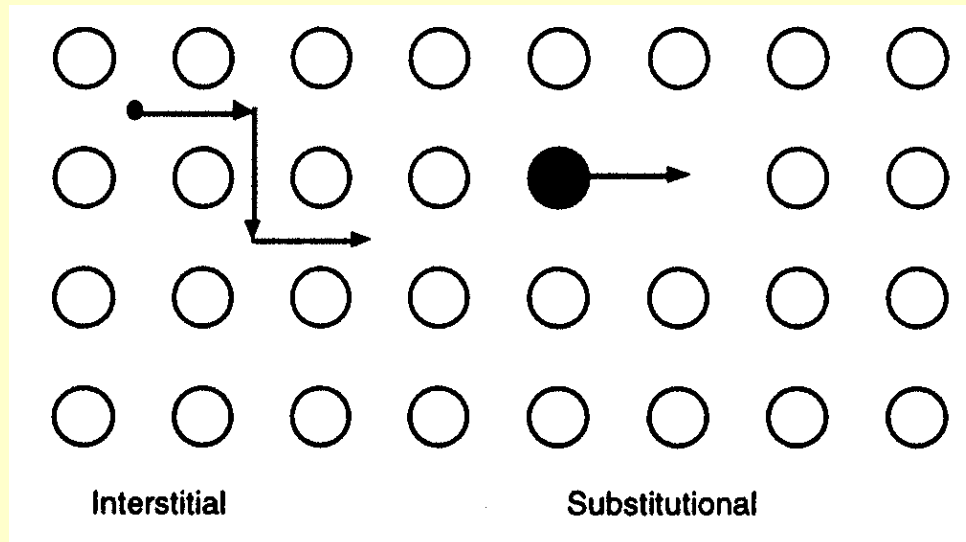
- an adjacent **empty site**
- atom possesses **sufficient energy** to break bonds with its neighbors and migrate to adjacent site (activation energy)

The higher the temperature, the higher is the probability that an atom will have sufficient energy

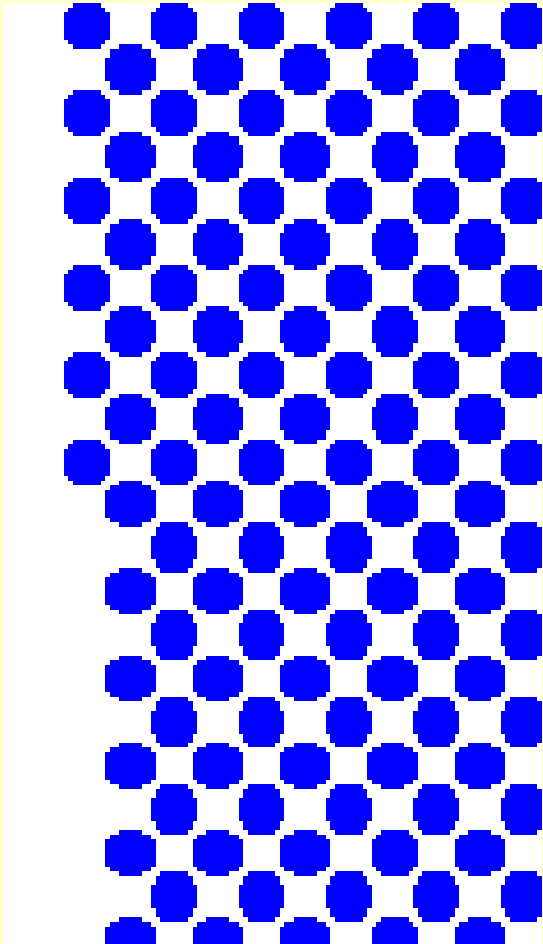
Diffusion rates increase with temperature

Mechanisms of Diffusion

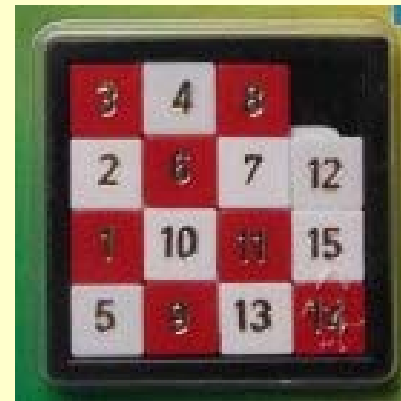
- Along **Defects** = Vacancy (or Substitutional) mechanism
 - Point Defects
 - Line Defects
- Through **Interstitial** Spaces = Interstitial mechanism
- Along **Grain Boundaries**
- On the **Surface**



Vacancy Mechanisms of Diffusion



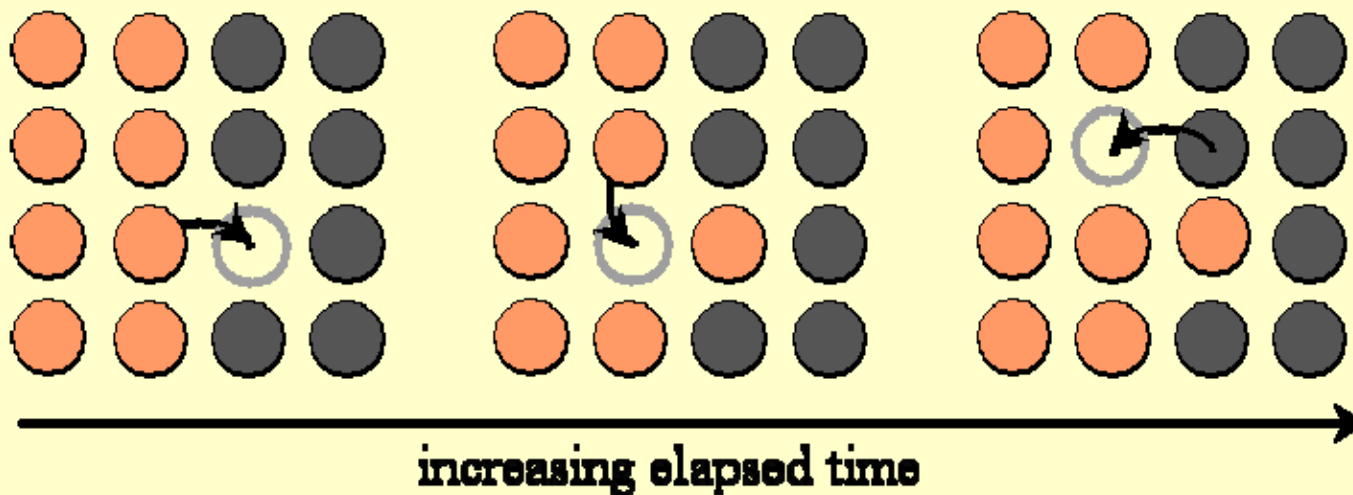
- Vacancies are holes in the matrix
- Vacancies are always moving
- An impurity can move into the vacancy
- Diffuse through the material



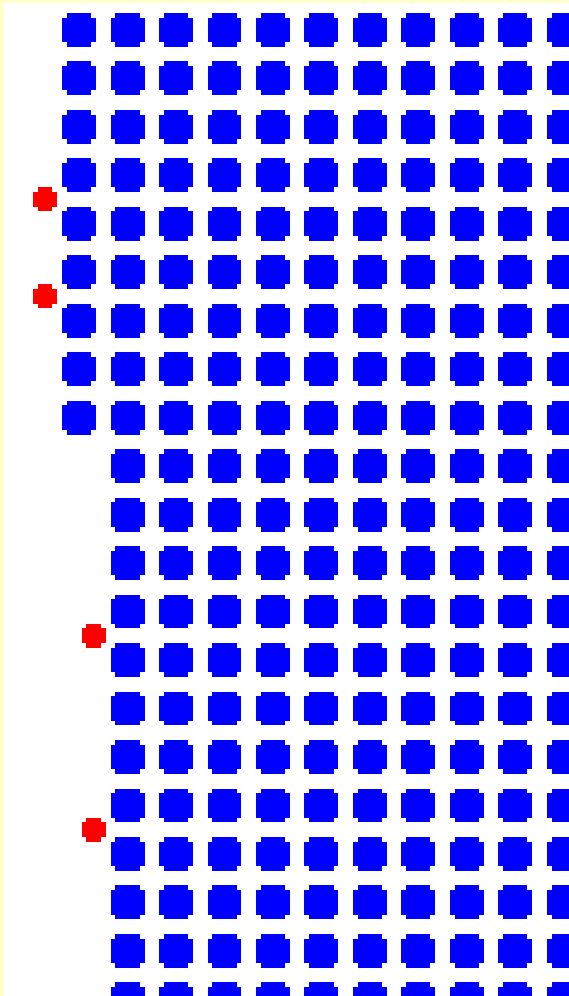
Vacancy Mechanisms of Diffusion

Atoms can move from one site to another if there is sufficient energy present for the atoms to overcome a local activation energy barrier and if there are vacancies present for the atoms to move into

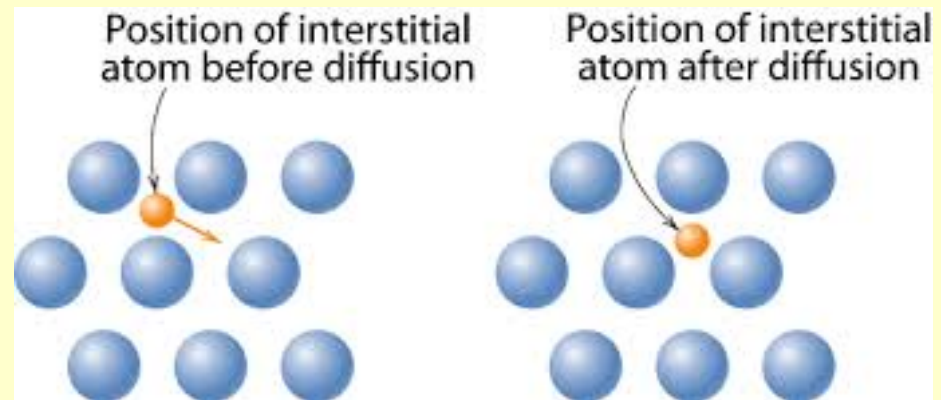
The activation energy for diffusion is the sum of the energy required to form a vacancy and the energy to move the vacancy



Interstitial Mechanisms of Diffusion



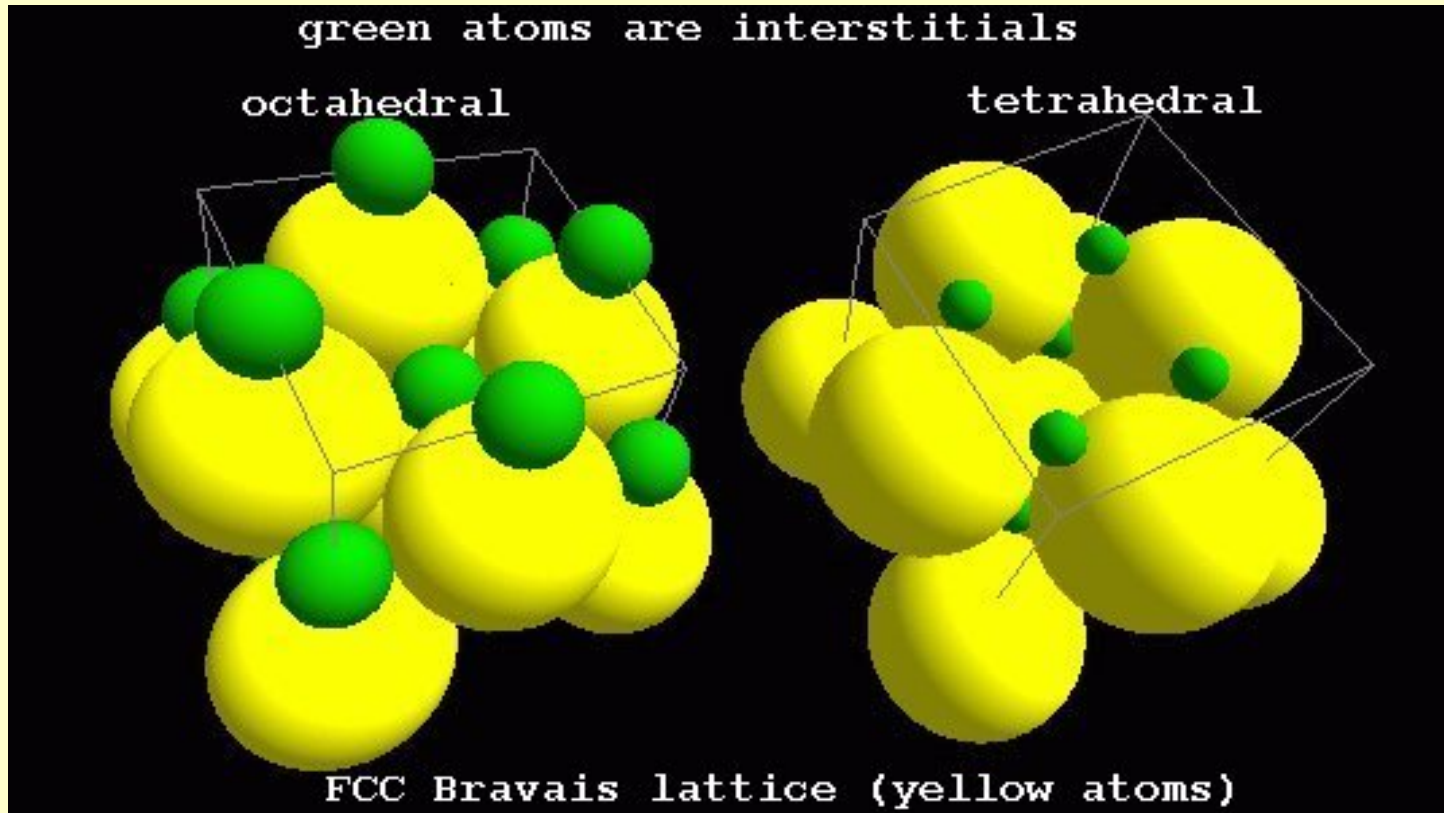
- There are holes between the atoms in the matrix
- If the atoms are small enough, they can diffuse through the interstitial holes
- Fast diffusion



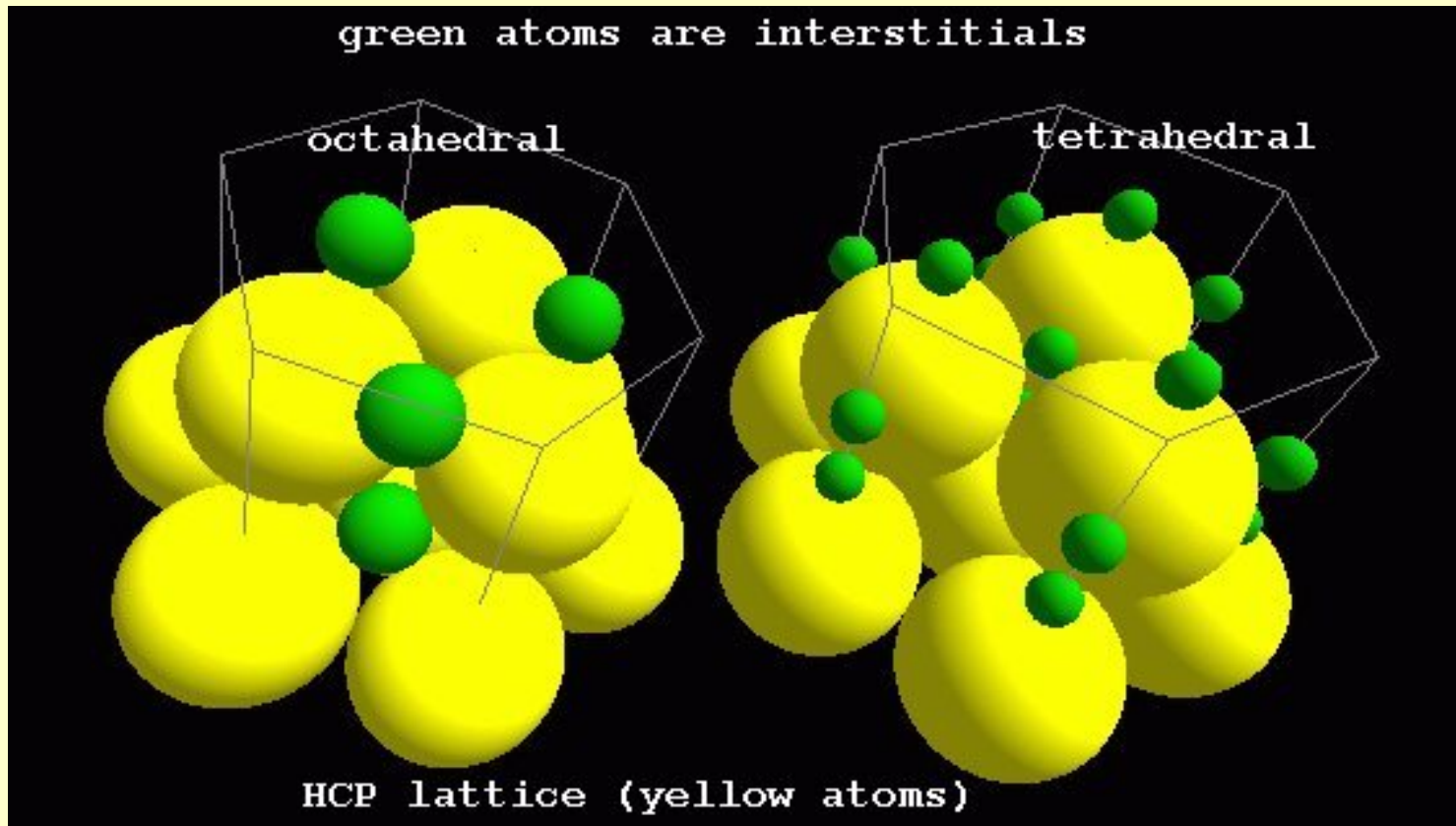
Interstitial Atoms

- An atom must be small to fit into the interstitial voids
 - H and He can diffuse rapidly through metals by moving through the interstitial voids
 - Interstitial atoms like hydrogen, helium, carbon, nitrogen, etc. must squeeze through openings between interstitial sites to diffuse around in a crystal
 - The activation energy for diffusion is the energy required for these atoms to squeeze through the small openings between the host lattice atoms
-
- Interstitial C is used to strengthen Fe = steel, it distorts the matrix
 - The ratio of r/R is 0.57 – needs an octahedral hole
 - Octahedral and tetrahedral holes in both FCC and BCC – however the holes in BCC are not regular polyhedra
 - The solubility of C in FCC-Fe is much higher than in BCC-Fe

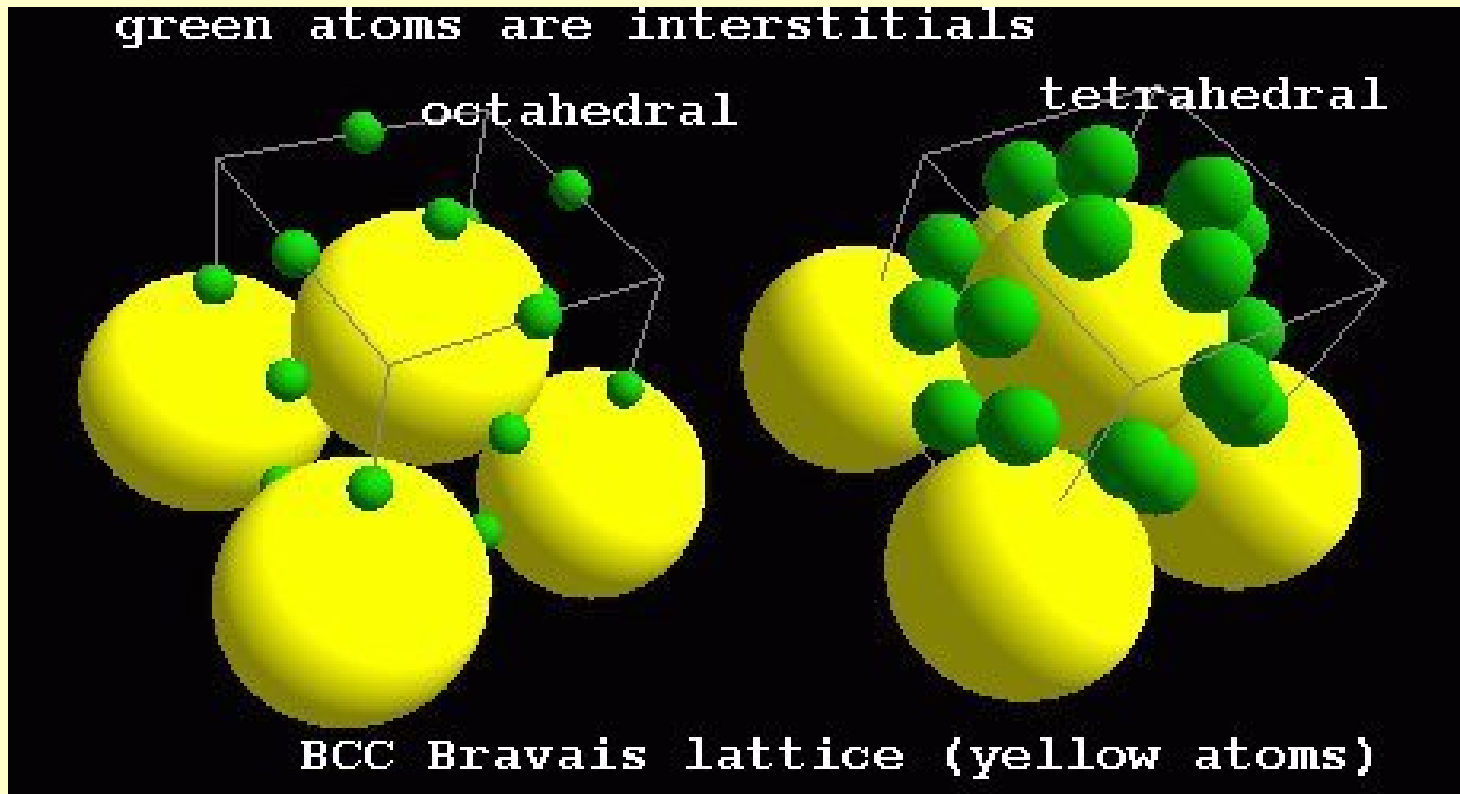
Interstitial Atoms



Interstitial Atoms

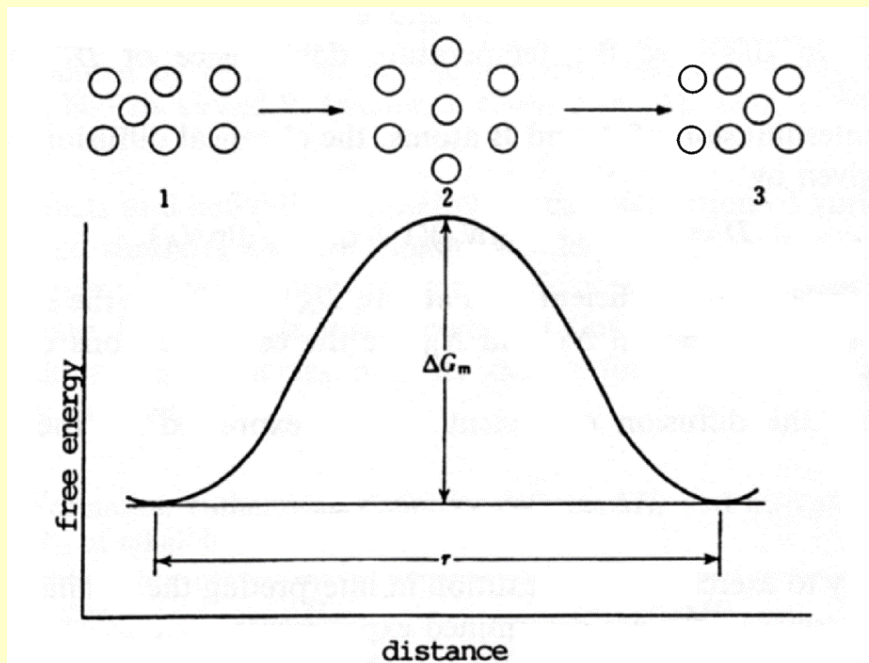


Interstitial Atoms



Activation Energy

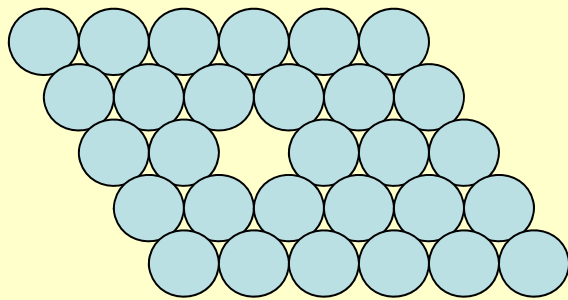
- All the diffusion mechanisms require a certain minimum energy to occur - the activation energy
- The higher the activation energy, the harder it is for diffusion to occur
- The order of energy for diffusion types:
Volume (Vacancy, Interstitial) > Grain Boundary > Surface



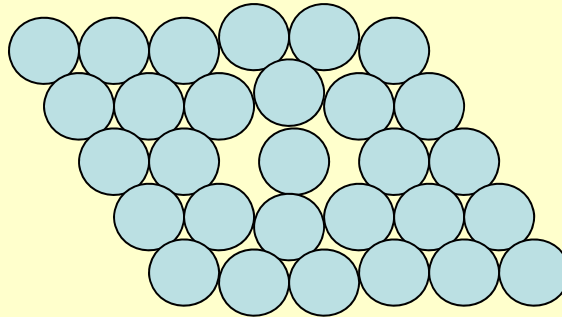
The activation energy =
Energy barrier for diffusion

Activation Energy

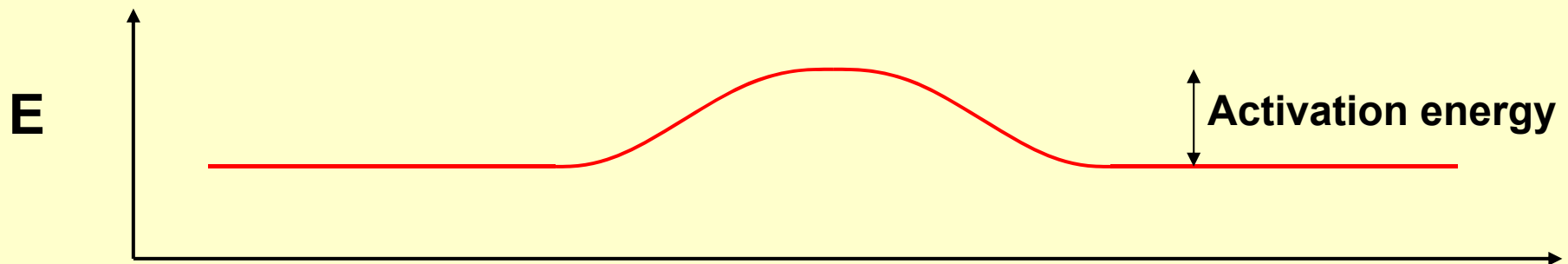
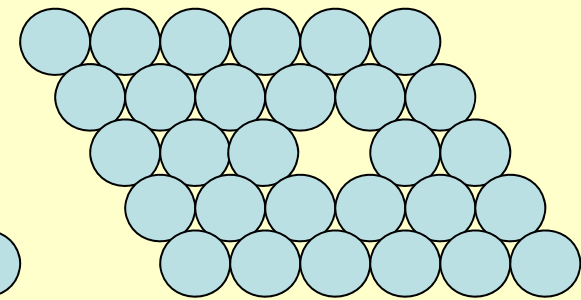
Initial state



Intermediate state

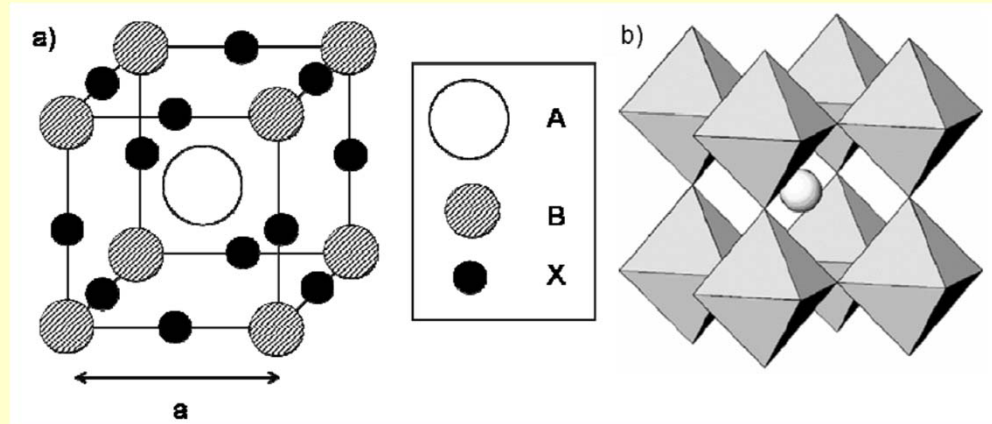


Final state

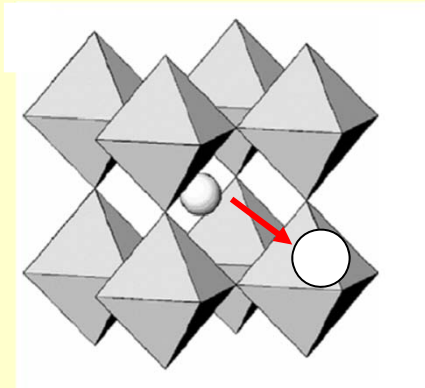


Energy barrier for diffusion

Diffusion in Perovskites ABX_3



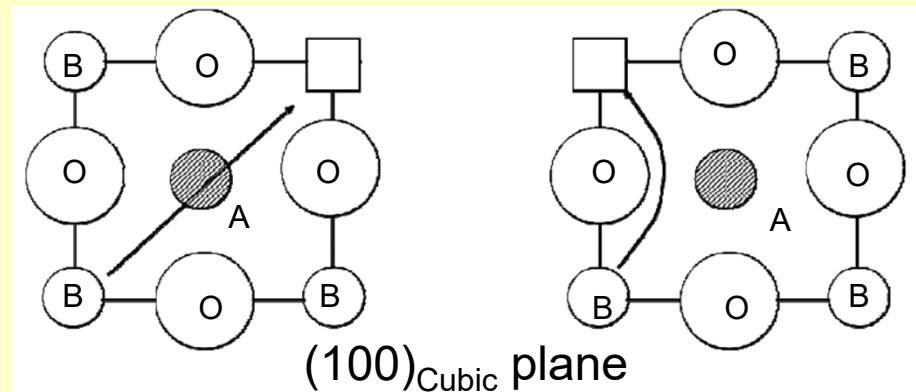
A cation diffusion



The A cation diffusion is easier

$$E_A = 379$$

B cation diffusion



$$E_A = 1420$$

$$E_A = 746$$

Activation energies (kJ mol^{-1})

Diffusion Rate

$$D = D_{\infty} \exp\left(-\frac{Q}{RT}\right)$$

Diffusion coefficients show an exponential temperature dependence (Arrhenius type)

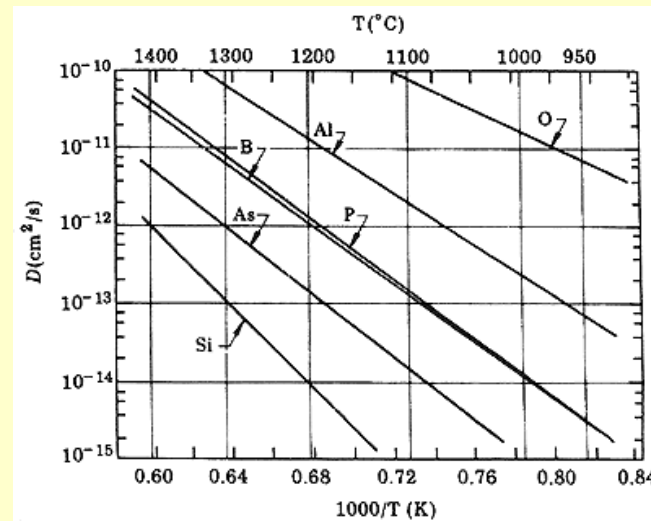
D = the diffusivity, which is proportional to the diffusion rate

$D_{\infty} = D$ for $T \rightarrow \infty$

Q = the activation energy

R = the gas constant

T = the absolute temperature



Diffusion coefficients for impurities in Si

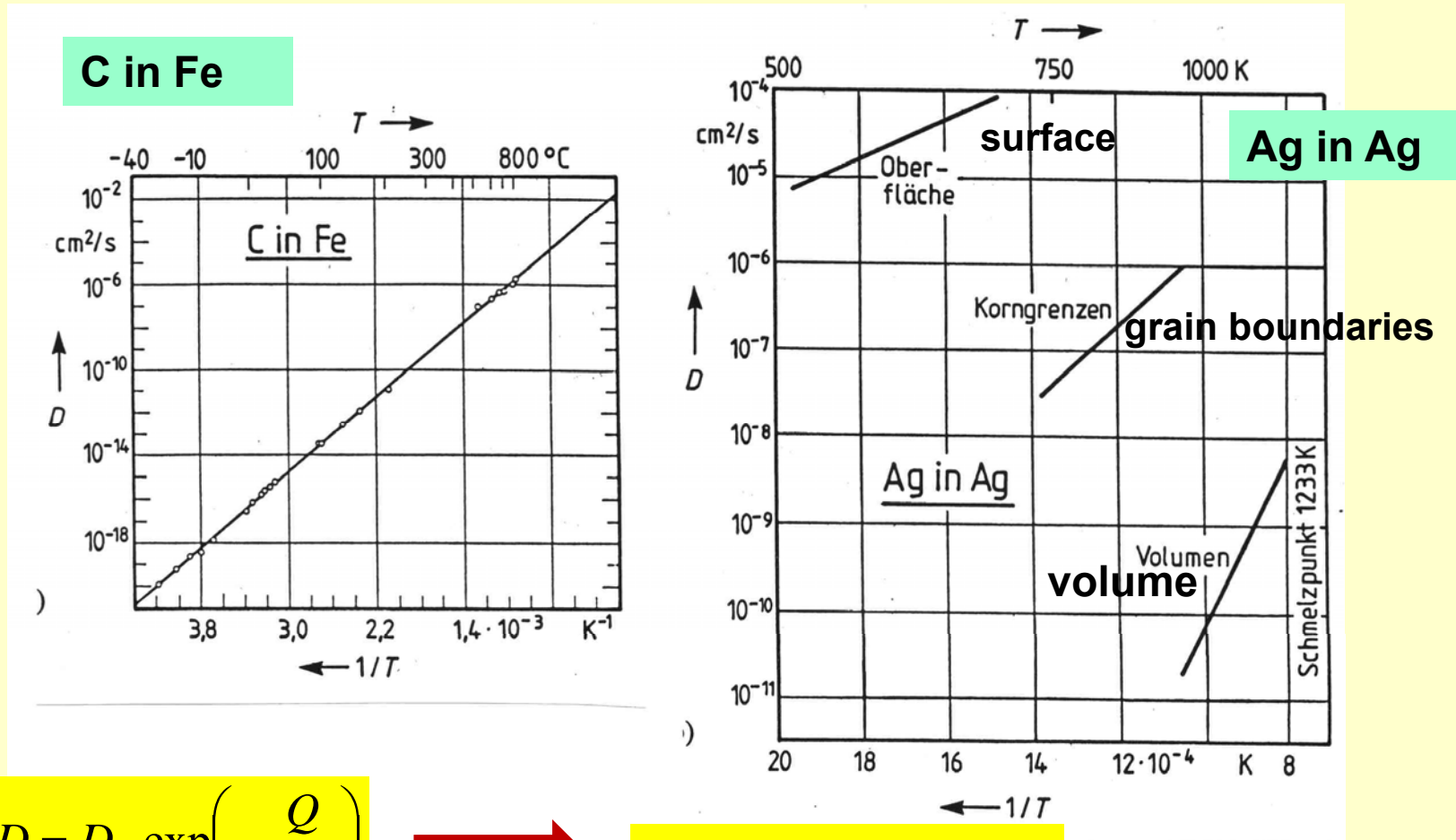
D is a function of temperature

Thus the flux (**J**) is also a function of temperature

High activation energy corresponds to low diffusion rates

The logarithmic representation of **D** versus $1/T$ is linear, the slope corresponds to the activation energy and the intercept to D_{∞}

Diffusion Coefficients



$$D = D_{\infty} \exp\left(-\frac{Q}{RT}\right)$$



$$\ln D = \ln D_{\infty} - Q/RT$$

Diffusion

Velocity of diffusion of particles (ions, atoms ...) in a solid

- mass transport and concentration gradient for a given point in a solid

$$J = \frac{dn}{A dt} = -D \frac{dc}{dx} \quad [\text{mol cm}^{-2} \text{ s}^{-1}] \quad (\text{const. T})$$

J_i : flow of diffusion ($\text{mol s}^{-1} \text{ cm}^{-2}$); D_i : diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$)

$\delta c_i / \delta x$: concentration gradient ($\text{mol cm}^{-3} \text{ cm}^{-1}$) (i.e. change of concentration along a line in the solid)

Knowledge of D allows an estimation of the average diffusion length for the migrating particles:

$$\langle x^2 \rangle = 2Dt \quad (\langle x^2 \rangle: \text{average square of diffusion area; } t: \text{time})$$

Diffusion

Diffusion FASTER for:

- open crystal structures
- lower melting T materials
- materials w/secondary bonding
- smaller diffusing atoms
- lower density materials

Diffusion SLOWER for:

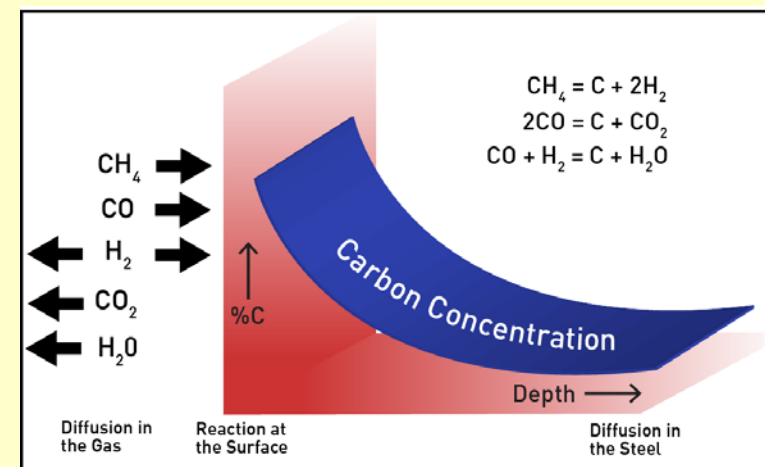
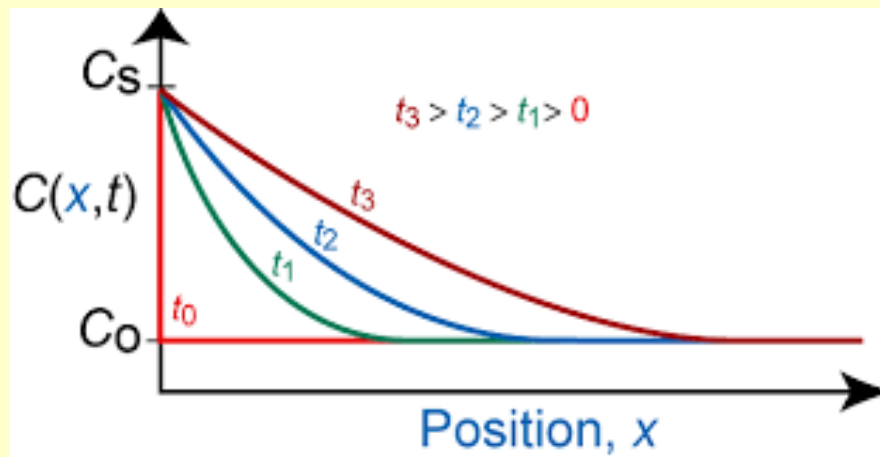
- close-packed structures
- higher melting T materials
- materials w/covalent bonding
- larger diffusing atoms
- higher density materials

Non-Steady-State Diffusion

Fick's Second Law of Diffusion

$$\frac{d C_x}{d t} = \frac{d}{d x} \left(D \frac{d C_x}{d x} \right)$$

The rate of change of composition at position x with time, t , is equal to the rate of change of the product of the diffusivity, D , times the rate of change of the concentration gradient, dC_x/dx , with respect to distance, x



Fick's Second Law of Diffusion

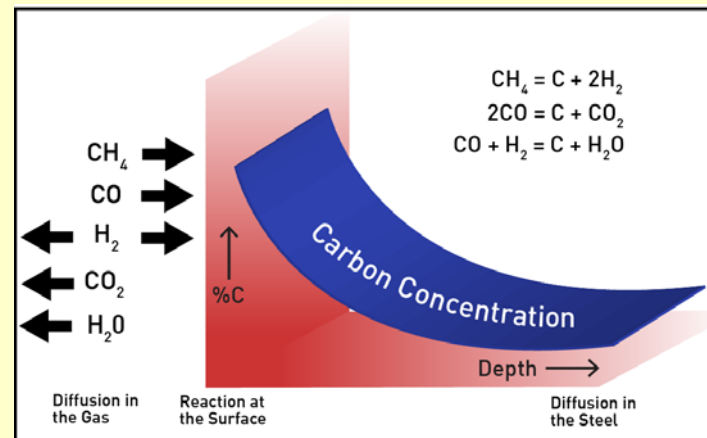
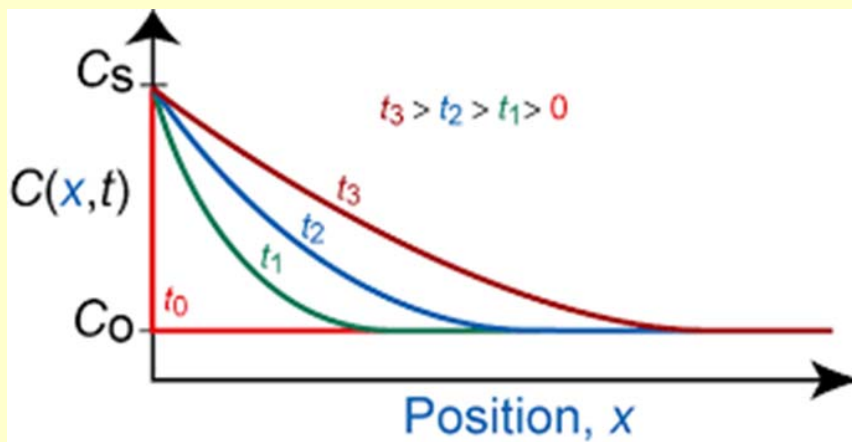
Second order differential equations are nontrivial

Diffusion in from a surface where the concentration of diffusing species is always constant, e.g. :

- gas diffusion into a solid as in carburization of steels
- doping of semiconductors

Boundary Conditions

For $t = 0$, $C = C_0$ at $0 < x$
 For $t > 0$ $C = C_s$ at $x = 0$
 $C = C_0$ at $x = \infty$



Fick's Second Law of Diffusion

The solution to Fick's second law is the relationship between the concentration C_x at a distance x below the surface at time t

$$\frac{C_x - C_o}{C_s - C_o} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

C_s = surface concentration
 C_o = initial uniform bulk concentration
 C_x = concentration of element at distance x from surface at time t
 x = distance from surface
 D = diffusivity of diffusing species in host lattice
 t = time
erf = error function

