Crystal Defects

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

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

- **Intrinsic** defects – present for thermodynamic reasons
- **Extrinsic** defects – not required by thermodynamics, can be controlled by purification or synthetic conditions

- Chemical defects (foreign atom, mixed crystals, nonstoichiometry)
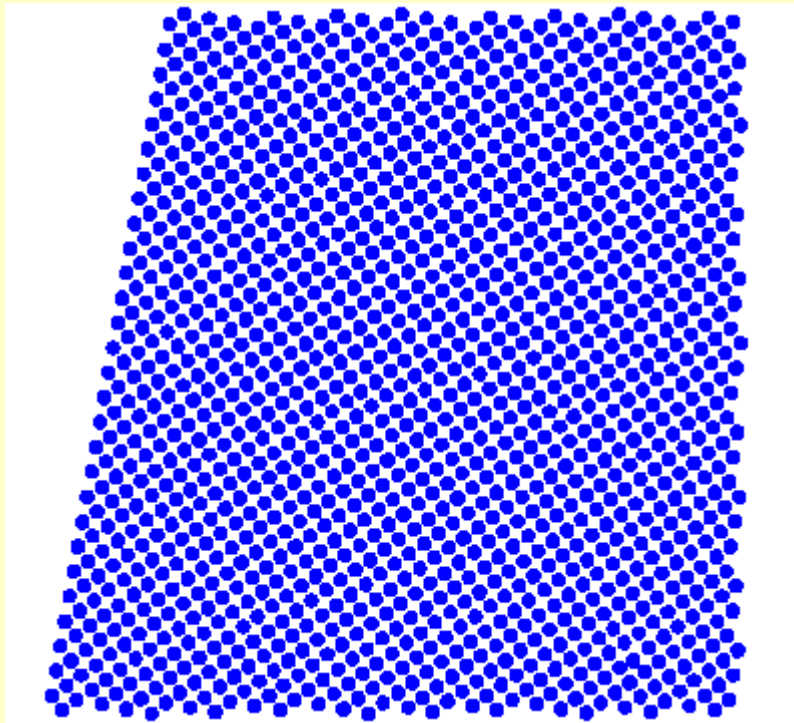- Geometrical defects (vacancy, interstitials, dislocations, boundaries, surface)

Defects dominate the material properties:

                        Mechanical, Chemical, Electrical, Diffusion
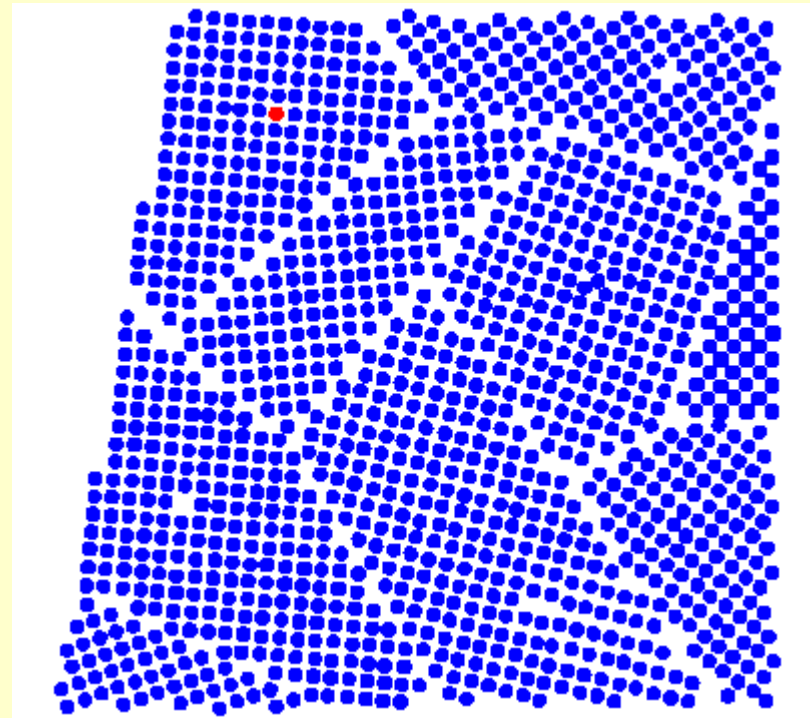
Defects can be added intentionally

Crystal Defects

Perfect crystal

Real crystal

does not exist at T > 0 K

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

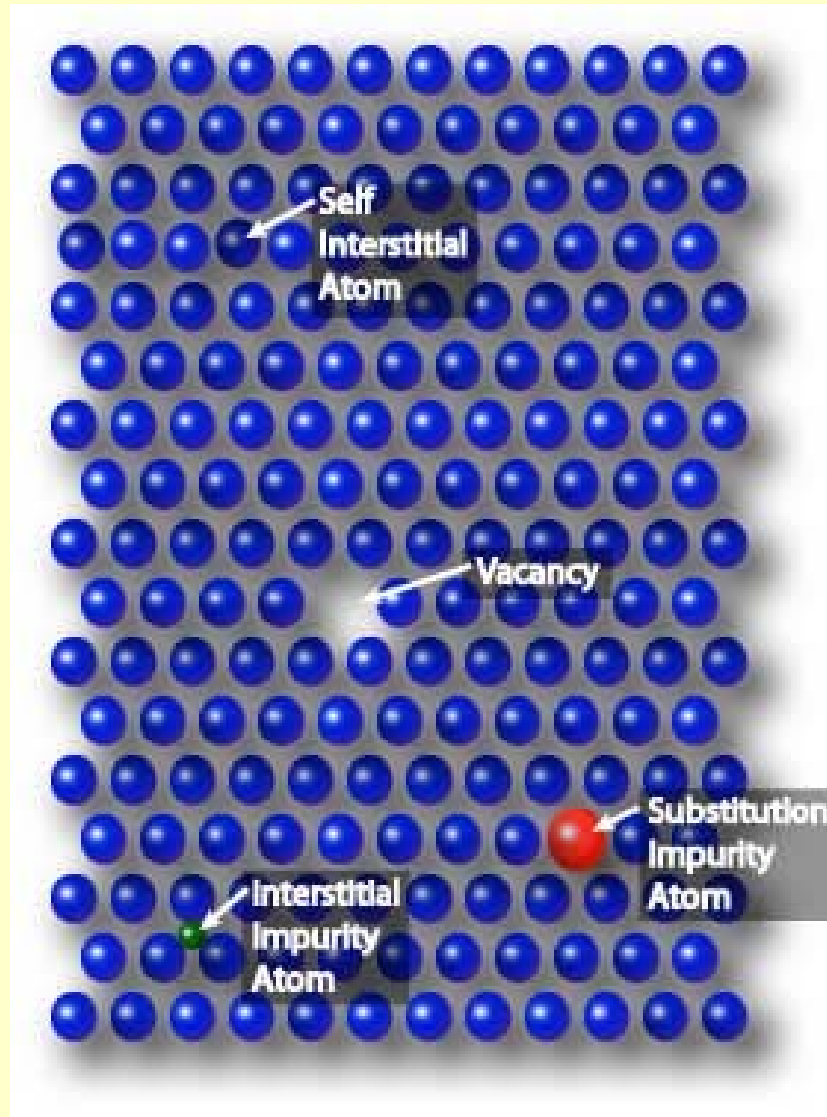**Linear defects** (1D) groups of atoms in irregular positions – dislocations

Planar defects (2D) interfaces between homogeneous regions of the material - grain boundaries, stacking faults, external surfaces

Volume defects (3D) spaces of foreign matter – pores, inclusions

3

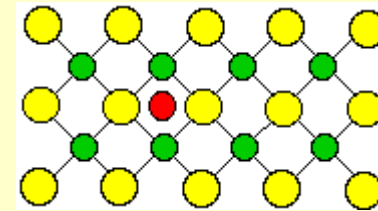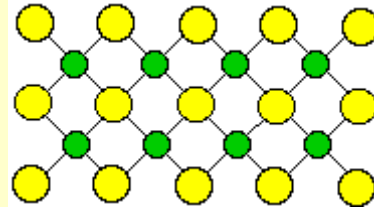# Classes of Crystal Defects
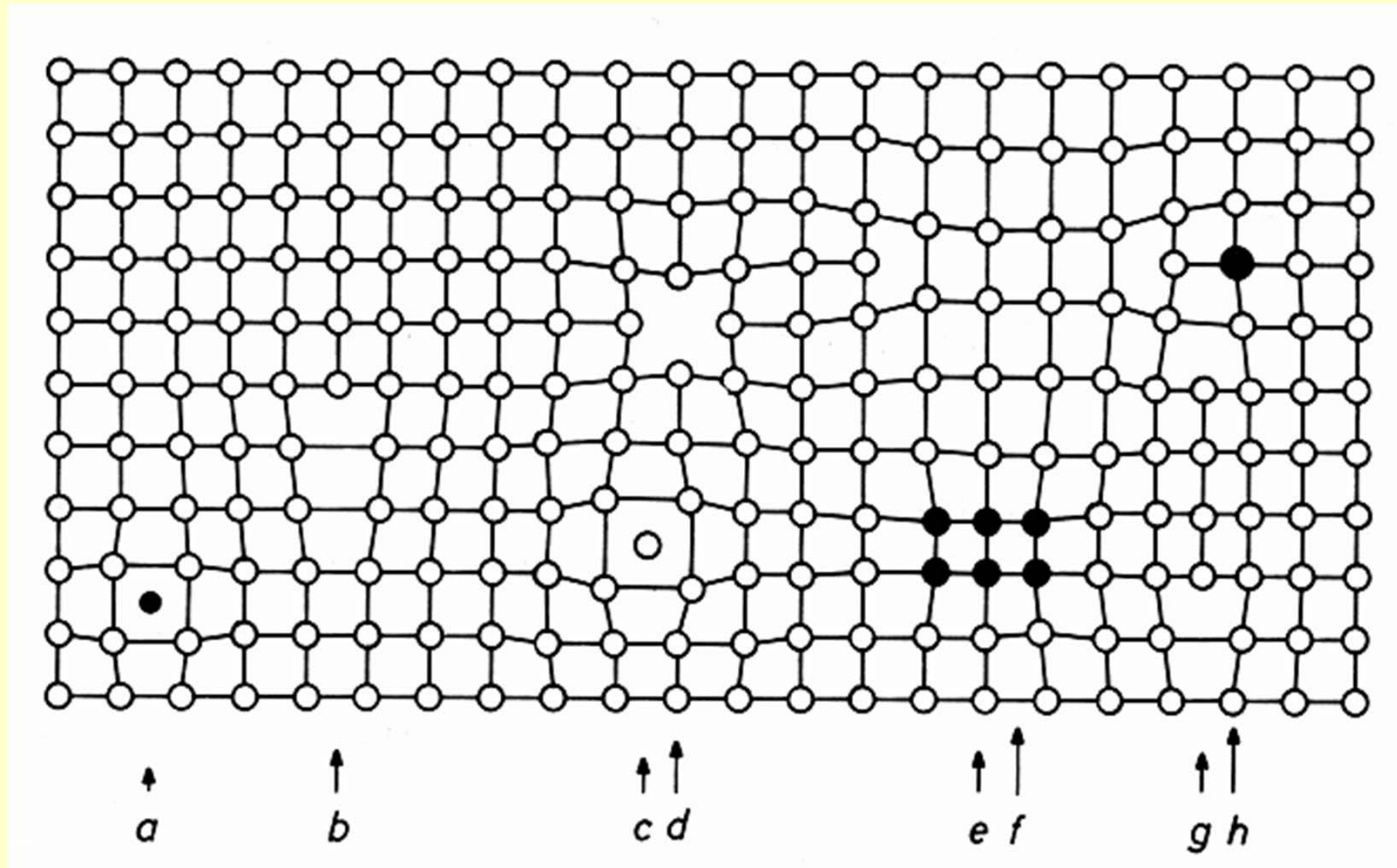
Point Defects

Point defects - an atom is missing or is in an irregular position in the lattice

- self interstitial atoms

- interstitial impurity atoms

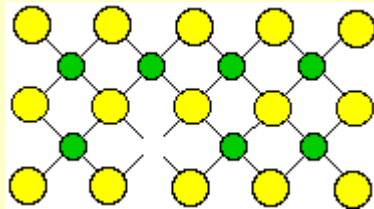- substitutional impurity atoms

- vacancies

5

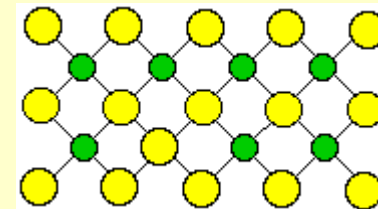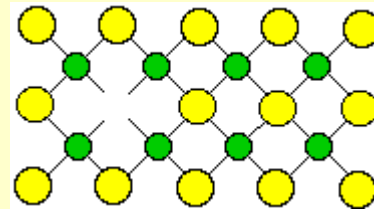# Point Defects – Ionic Compounds
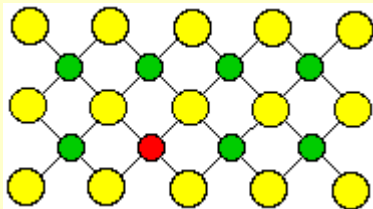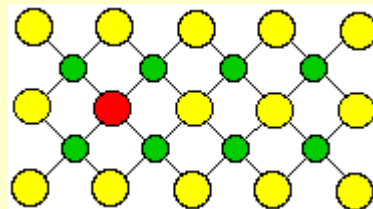
perfect crystal lattice AB
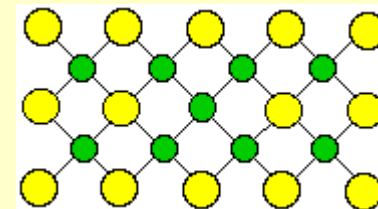
interstitial imputity

cation vacancy   anion vacancy

B_A antisite defect

substitution of a cation   substitution of an anion

A_B antisite defect

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Point Defects – Ionic Compounds

- Vacancy

- Interstitial

- Substitutional

- Frenkel

- Schottky

Schottky imperfection

Frenkel imperfection
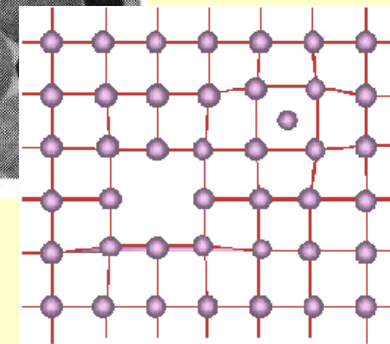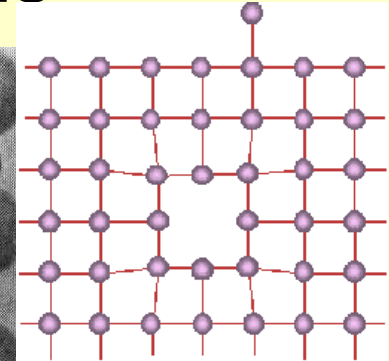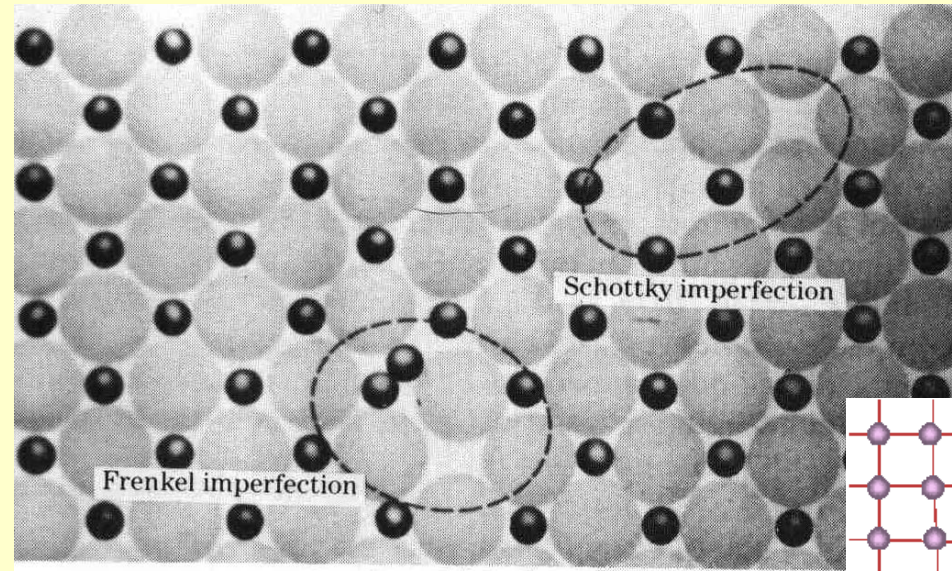
Schottky: a pair of vacancies, missing cation/anion moved to the surface, equal numbers of vacancies at both A and B sites preserving charge balance, found in compounds where metal ions are able to assume multiple oxidation states

Frenkel: ions moved to interstitial positions, vacancies, found in open structures (wurtzite, sphalerite, etc) with low coordination numbers, open structure provides room for interstital sites to be occupied

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:

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

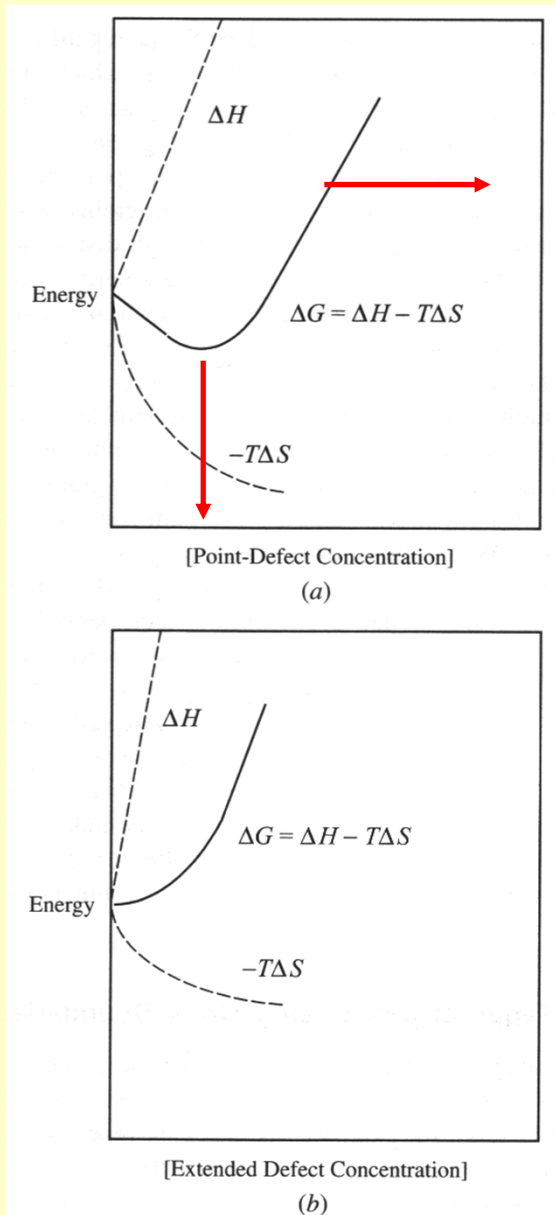- N = the total number of sites in a crystal
- N_v = the number of vacancies
- ΔH^a = the activation energy for the formation of a vacancy
- R = the gas constant

N_v goes up exponentially with temperature T

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

Crystal Energies

ΔH

Energy

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

−TΔS

[Point-Defect Concentration]

(a)

ΔH

Energy

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

−TΔS

[Extended Defect Concentration]

(b)

Point defects = equilibrium concentration
Enthalpy ΔH is positive but configurational entropy ΔS is positive – defects = disorder
Minimum on free energy ΔG – equilibrium conc. of defects
The concentration of vacancies grows as the temperature increases

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

Metastable defects – dislocations, grain boundaries, surface

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

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Typical Point Defects in Crystals

Alkali halides   Schottky (cations and anions)
Alkaline earth oxides   Schottky (cations and anions)
Silver halides   Frenkel (cations)
Alkaline earth fluorides   Frenkel (anions)

Typical activation energies for ion diffusion

Na^+ in NaCl $\sim$ 0,7 eV
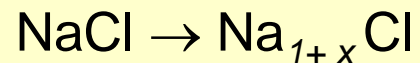Cl^- in NaCl $\sim$ 1 eV
Schottky pair $\sim$ 2,3 eV

(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 compostion

$$NaCl \rightarrow Na_{1+x}Cl$$

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

This 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^-

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 $VO_{0.79}$ to $VO_{1.29}$

What oxidation states?

other examples: TiO_x, Ni_xO, UO_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 composition

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

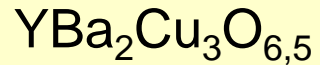# Non-Stoichiometric Compounds

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.

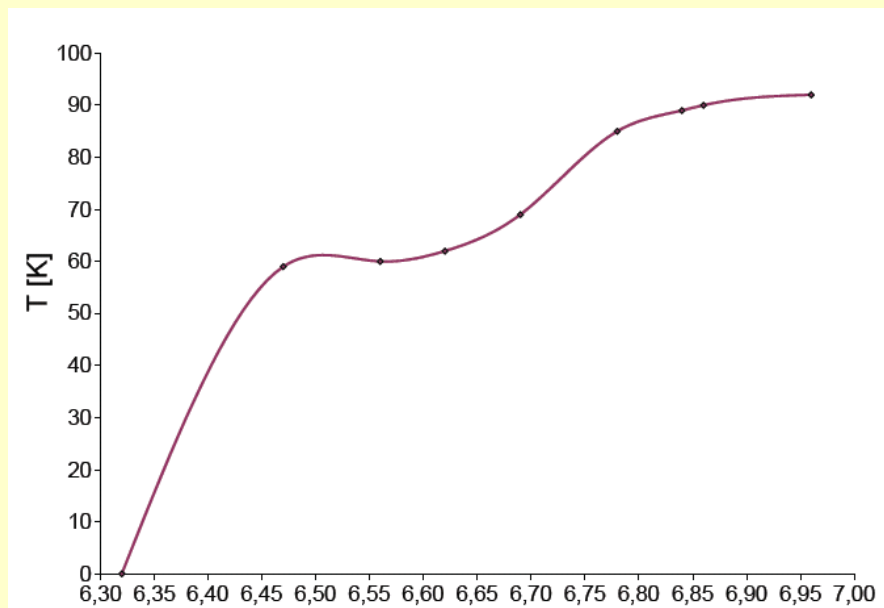# Non-Stoichiometric Compounds

Non-stoichiometric superconductor YBCO
$YBa_2Cu_3O_{6,5}$
a multi-valent element = Cu

$YBa_2Cu_3O_{6,8-7,0}$ **90 K superconductor**
$YBa_2Cu_3O_{6,45-6,7}$ **60 K superconductor**
$YBa_2Cu_3O_{6,0-6,45}$ **antiferromagnetic semiconductor**
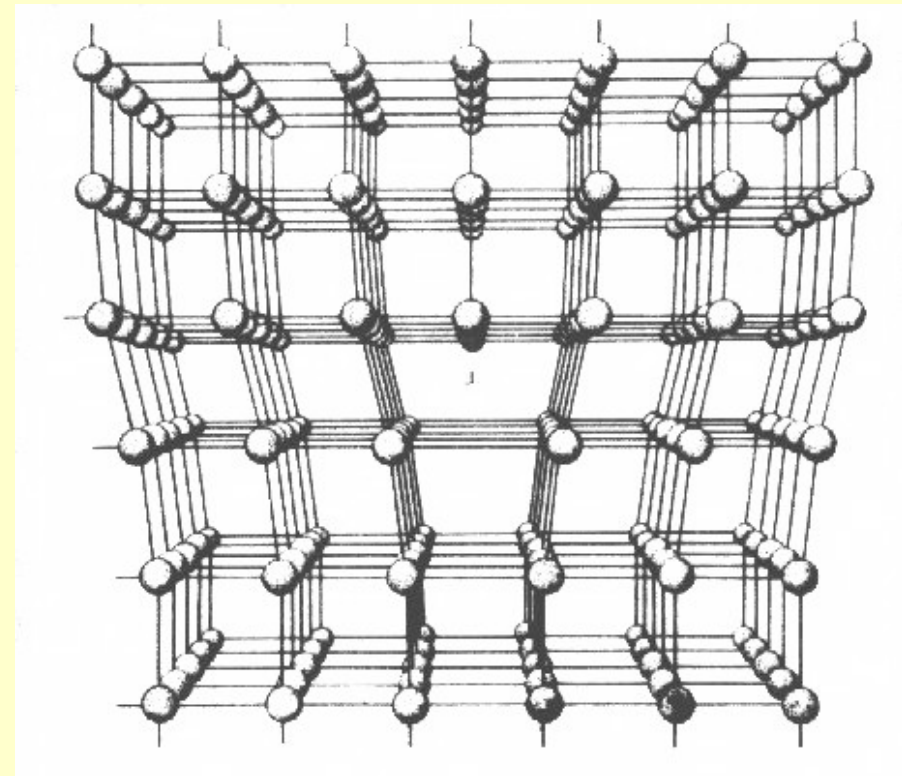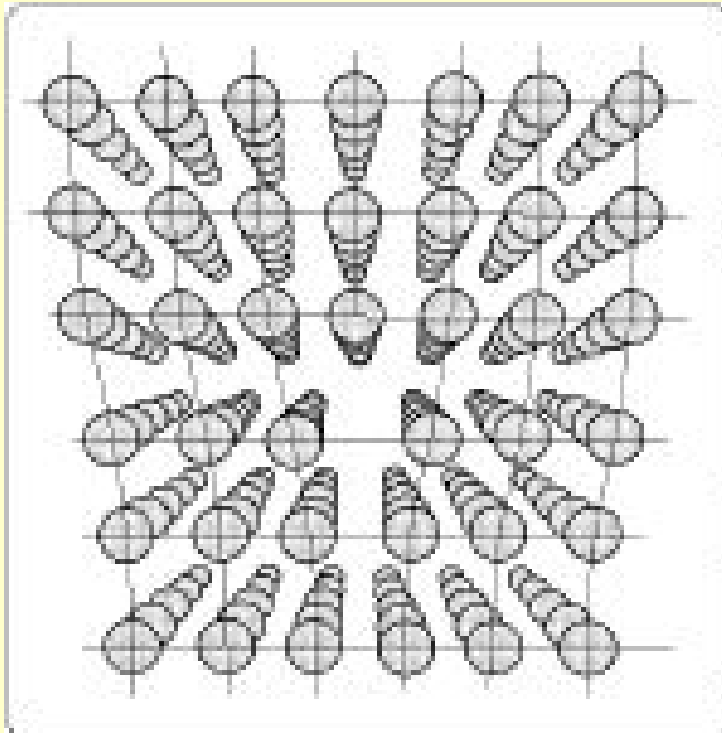

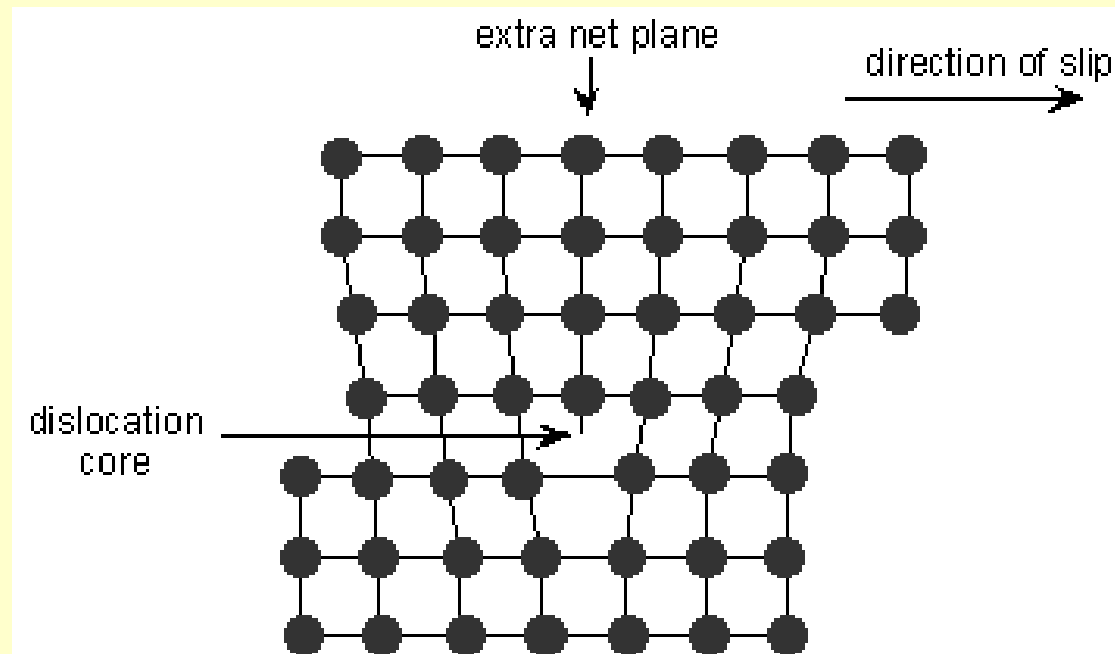
T$_{critical}$

Kelvin

Oxygen content
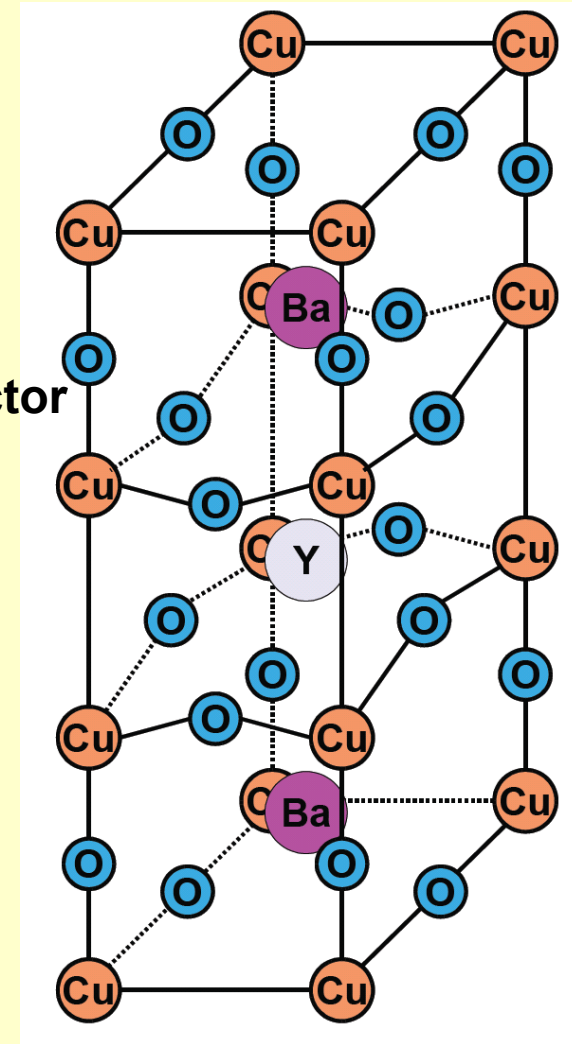
Dislocations

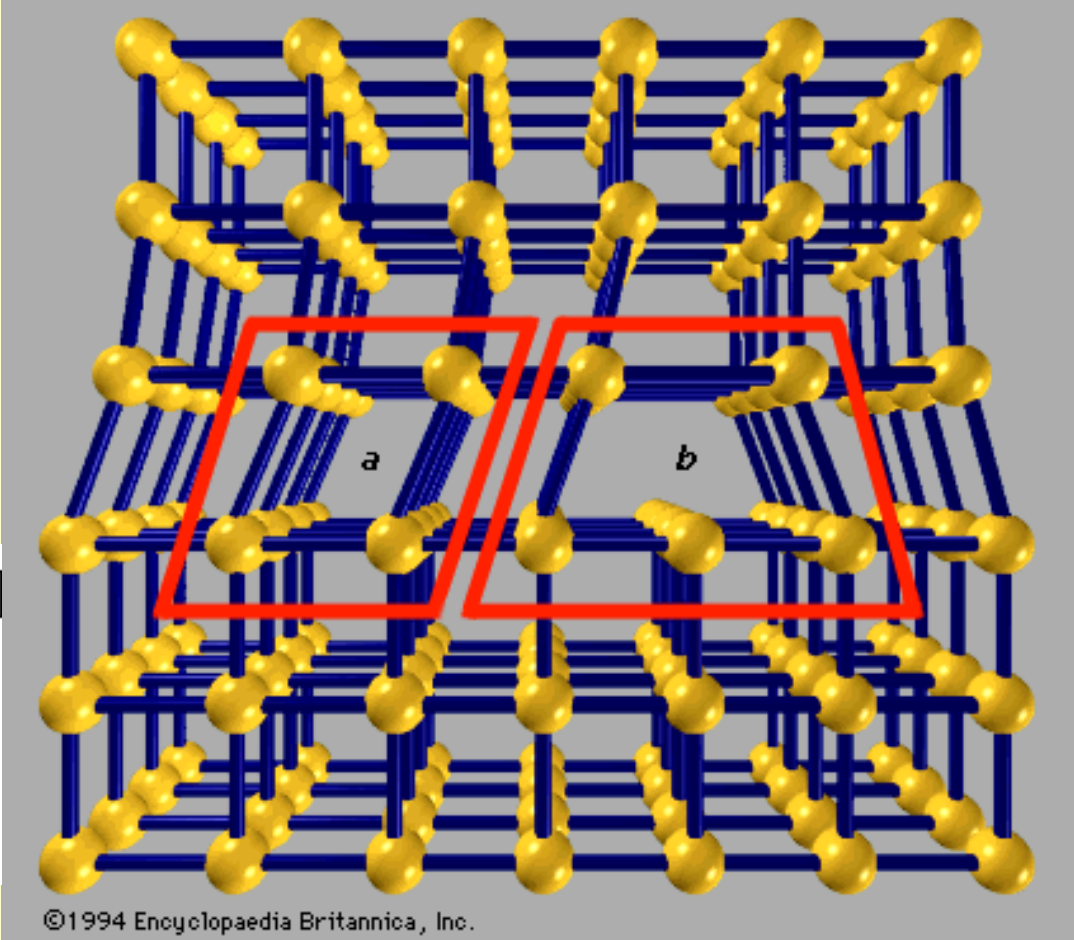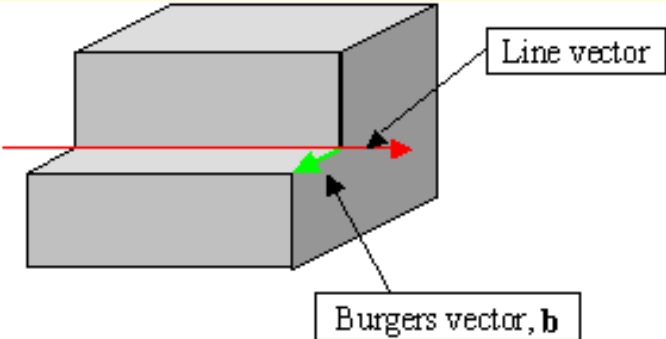Line imperfections in a 3D lattice

- Edge
- Screw
- Mixed

Edge Dislocation

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

Edge Dislocation

Line vector

Burgers vector, **b**

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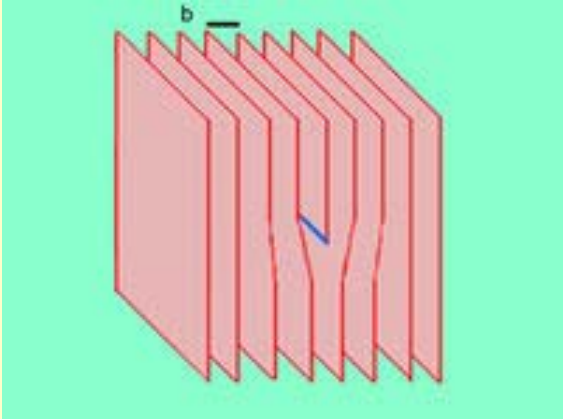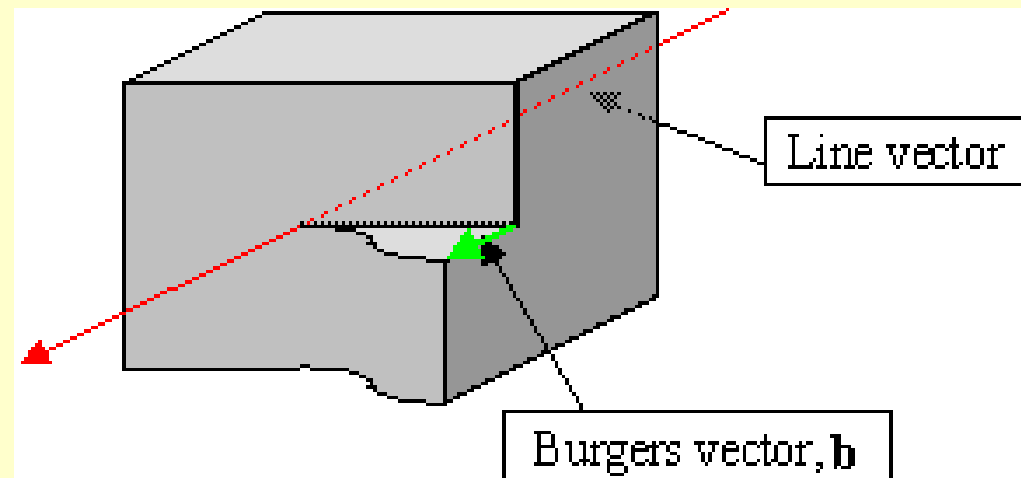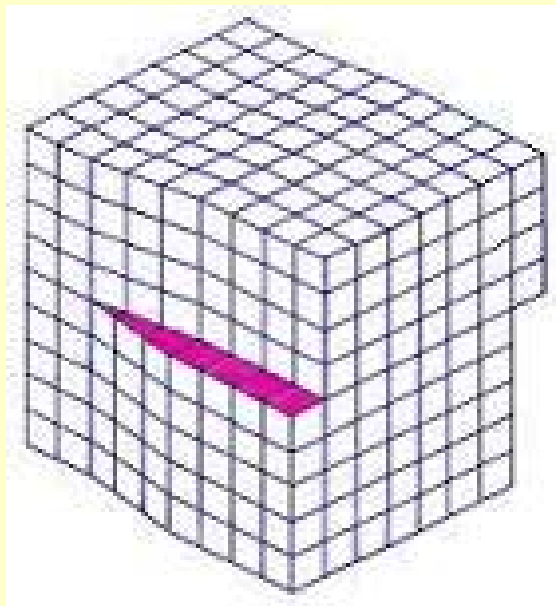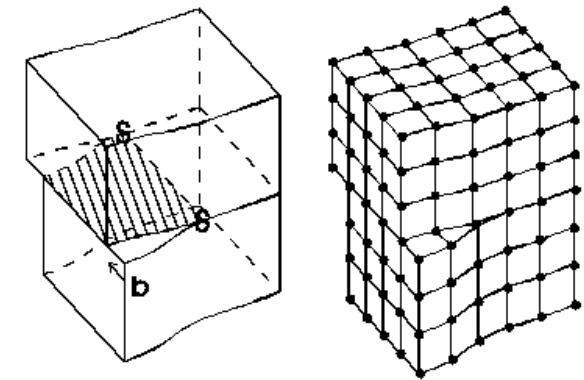
Screw Dislocation

- 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

Line vector

Burgers vector, **b**

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**

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
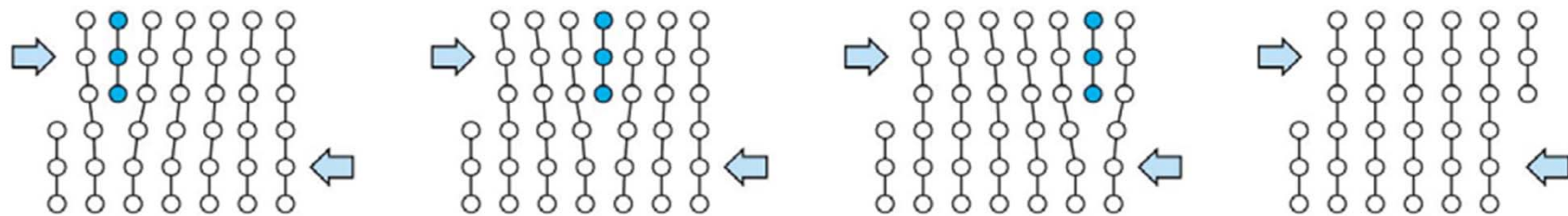
Deformation

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

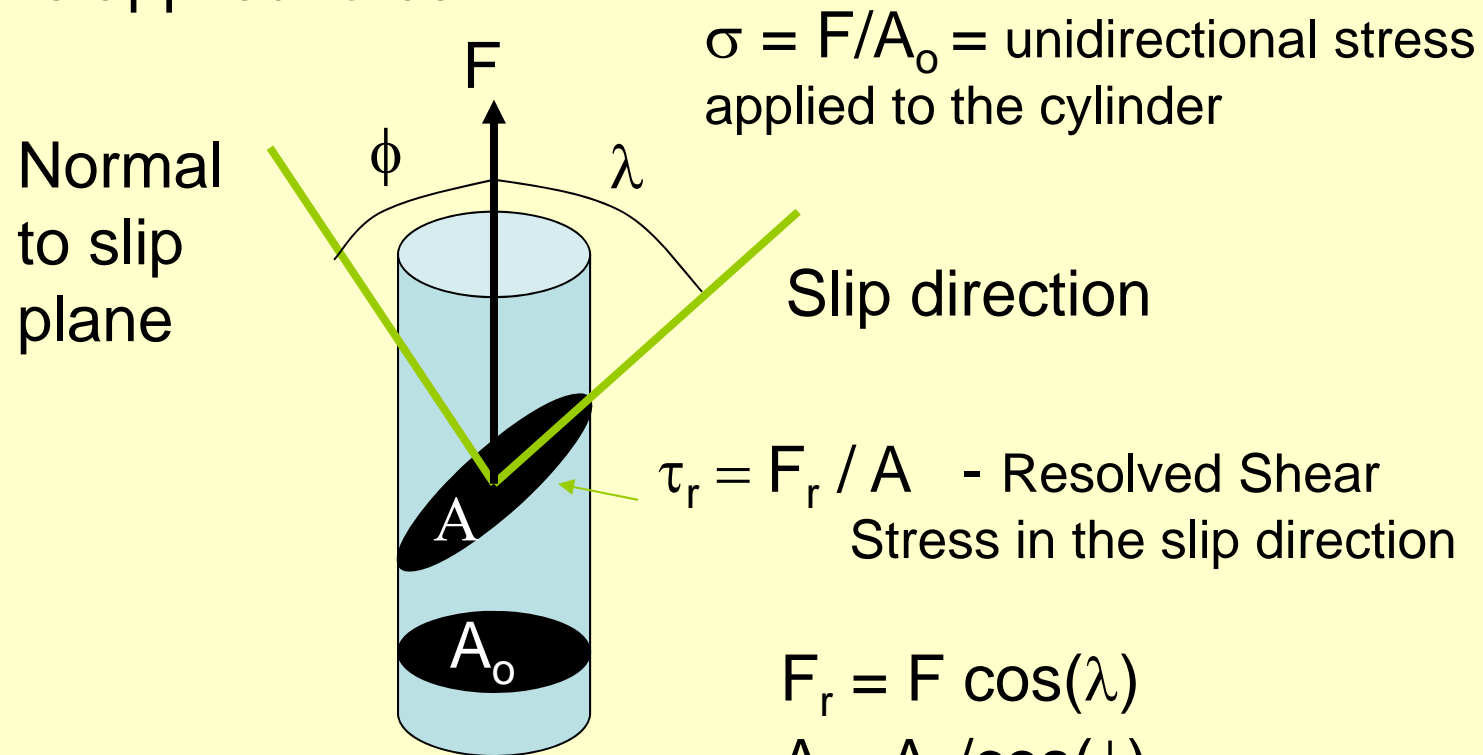Called "strain hardening" or "cold work"

Slip

- When dislocations move slip occurs
    - Direction of movement – same as the Burgers vector
- Slip is easiest on close packed **planes**
- Slip is easiest in the close packed **direction**

- Affects
    - Ductility
    - Material Strength

Schmidt's Law

- In order for a dislocation to move in its slip system, a shear force acting in the slip direction must be produced by the applied force.

$\sigma = F/A_o$ = unidirectional stress applied to the cylinder

F

Normal to slip plane

ϕ

λ

Slip direction

$\tau_r = F_r / A$ - Resolved Shear Stress in the slip direction

A

A_o

$F_r = F \cos(\lambda)$
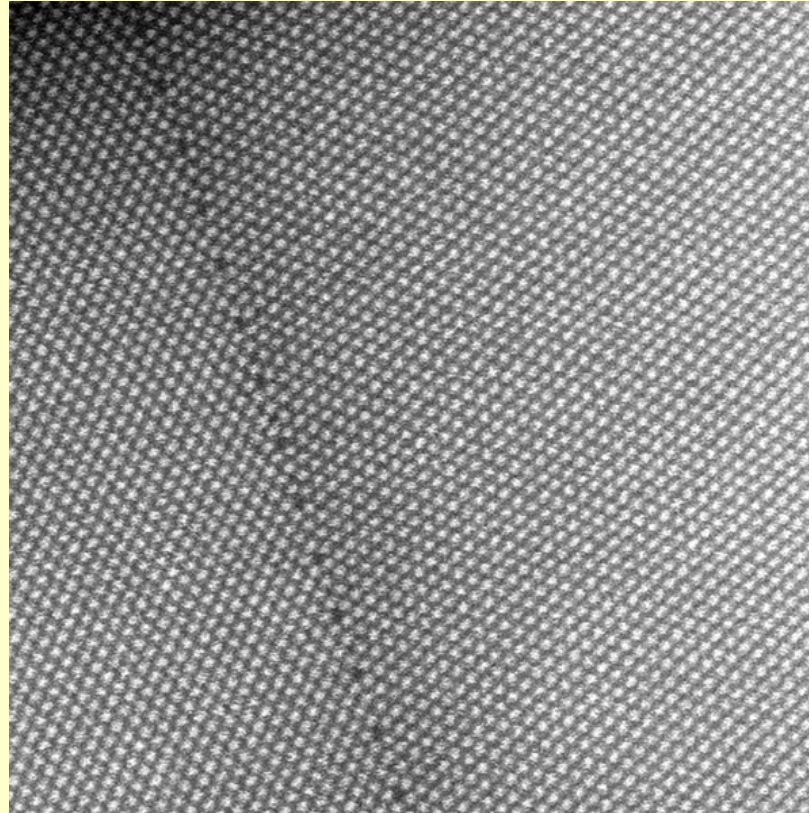
$A = A_0/\cos(\phi)$

$\tau = \sigma \cos(\phi) \cos(\lambda)$

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Surface and Grain Boundaries

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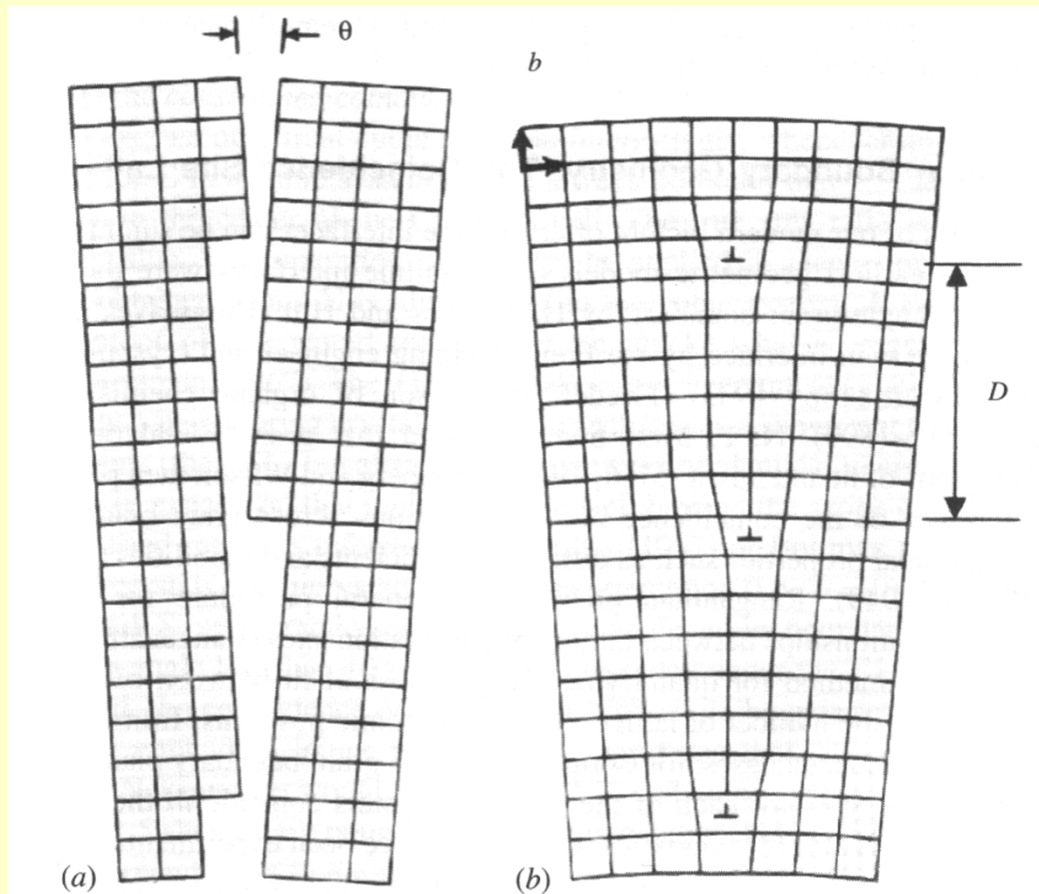- Low and High angle boundaries

23
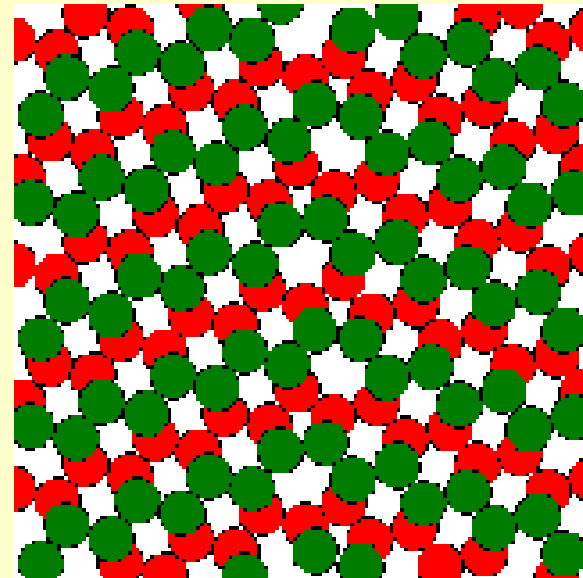
Grain Boundaries

High resolution STEM image from a grain boundary in gold at the atomic level, imaged on an FEI Titan STEM 80-300.
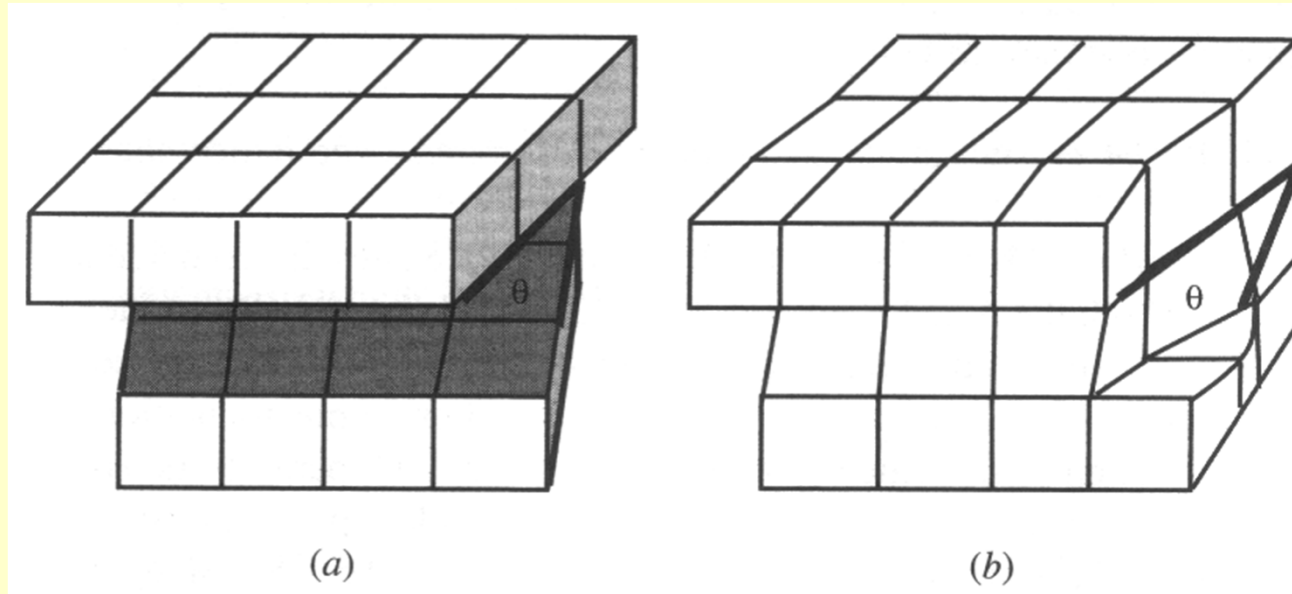
Low Angle Tilt Boundary

Low Angle Tilt Boundary = Array of Edge dislocations

$$D = \frac{b}{\sin \theta}$$

D = dislocation spacing
b = Burgers vector
θ = misorientation angle

Low Angle Twist Boundary

(a)   (b)

Low Angle Twist Boundary = a Screw dislocation

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 = stress
K = unpinning constant
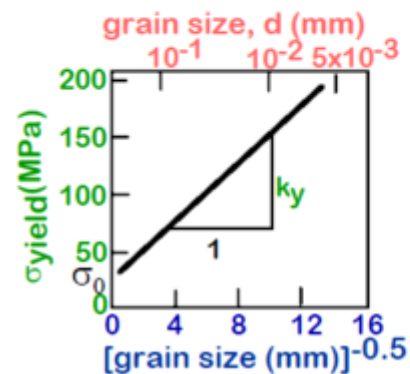

Grain Size Strengthening: Example

0.75mm

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

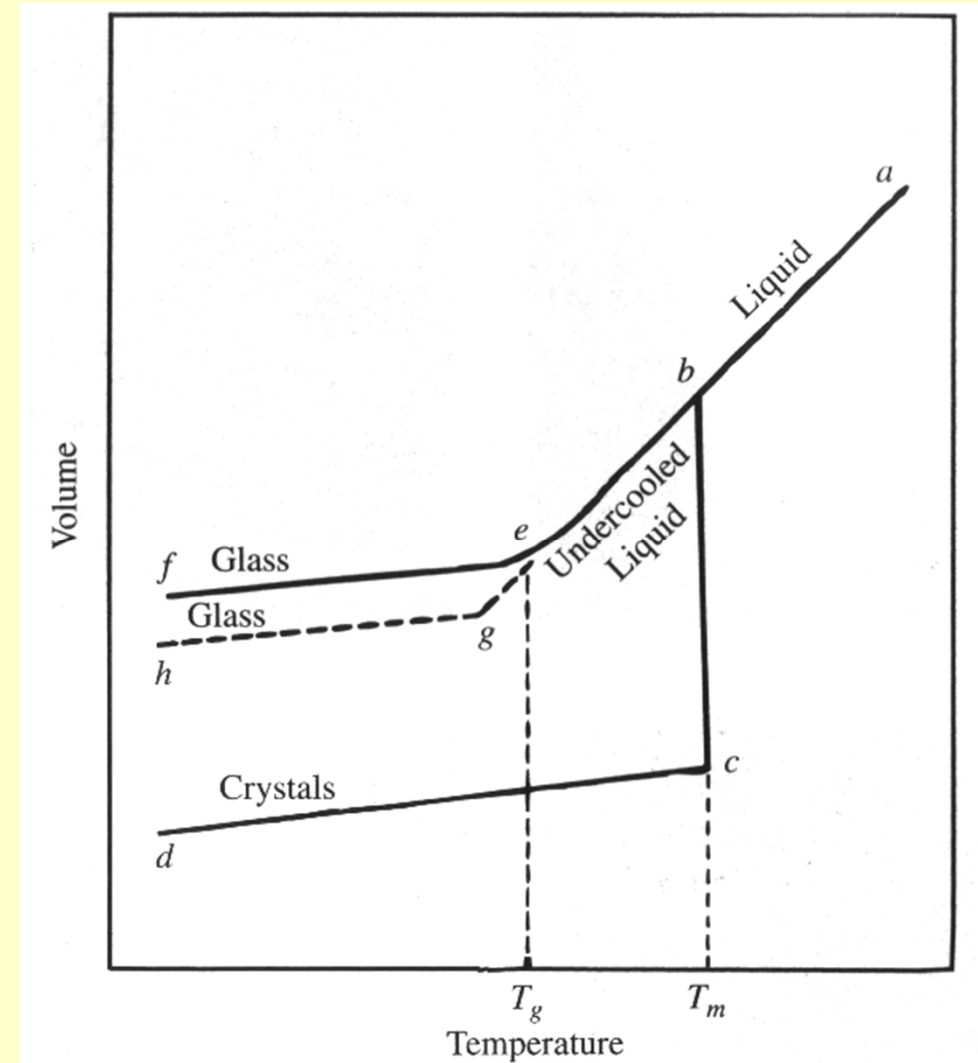$$\sigma_{yield} = \sigma_o + k_y d^{-1/2}$$

- Data:

Control of the Slip Process

- Strain hardening
- Solid Solution strengthening
- Grain Size strengthening

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
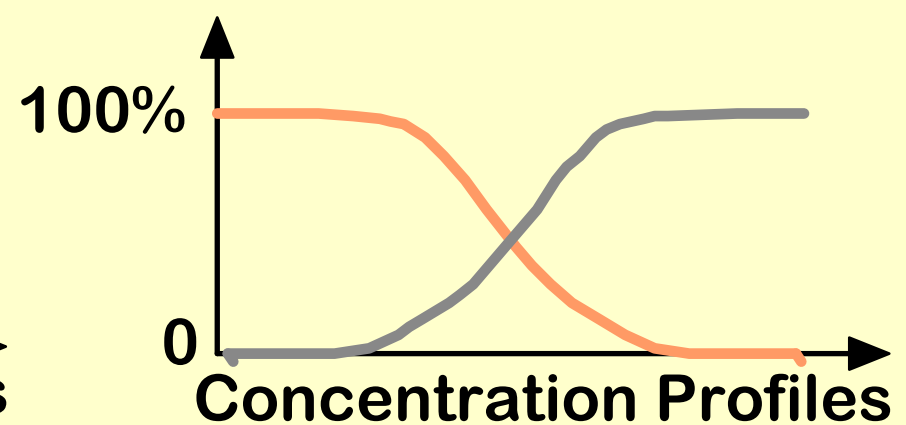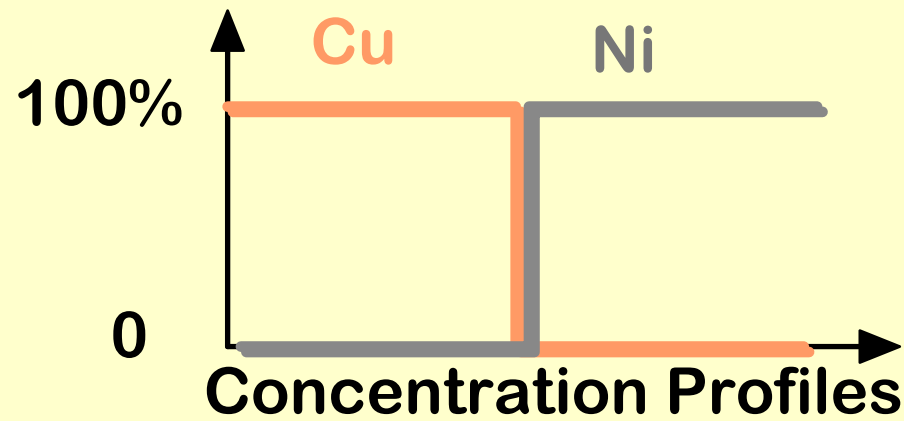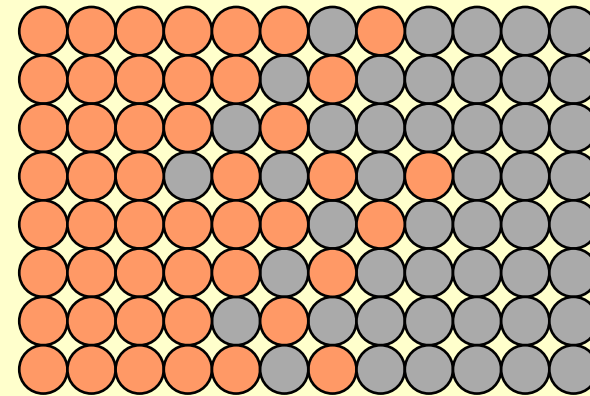
Diffusion

Interdiffusion: atoms migrate from regions of large to lower concentration

Initial state (diffusion couple)

After elapsed time

Concentration Profiles

Concentration Profiles
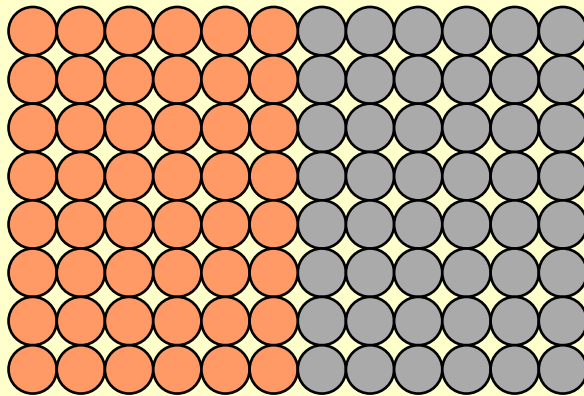
Diffusion Couple Experiments
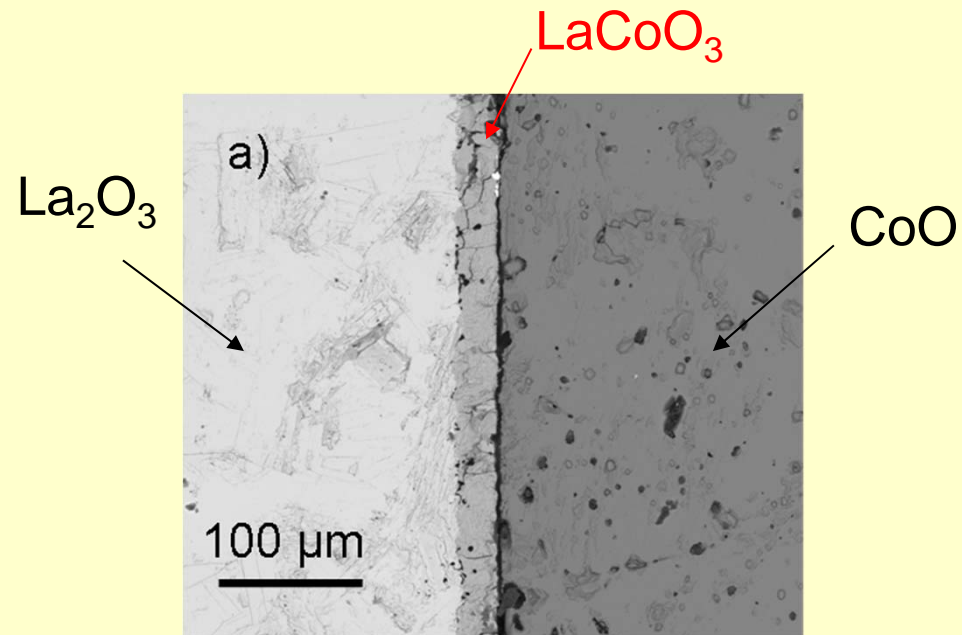
Experimental conditions: T = 1370 – 1673 K
pO$_2$ = 40 Pa – 50 kPa

Diffusion
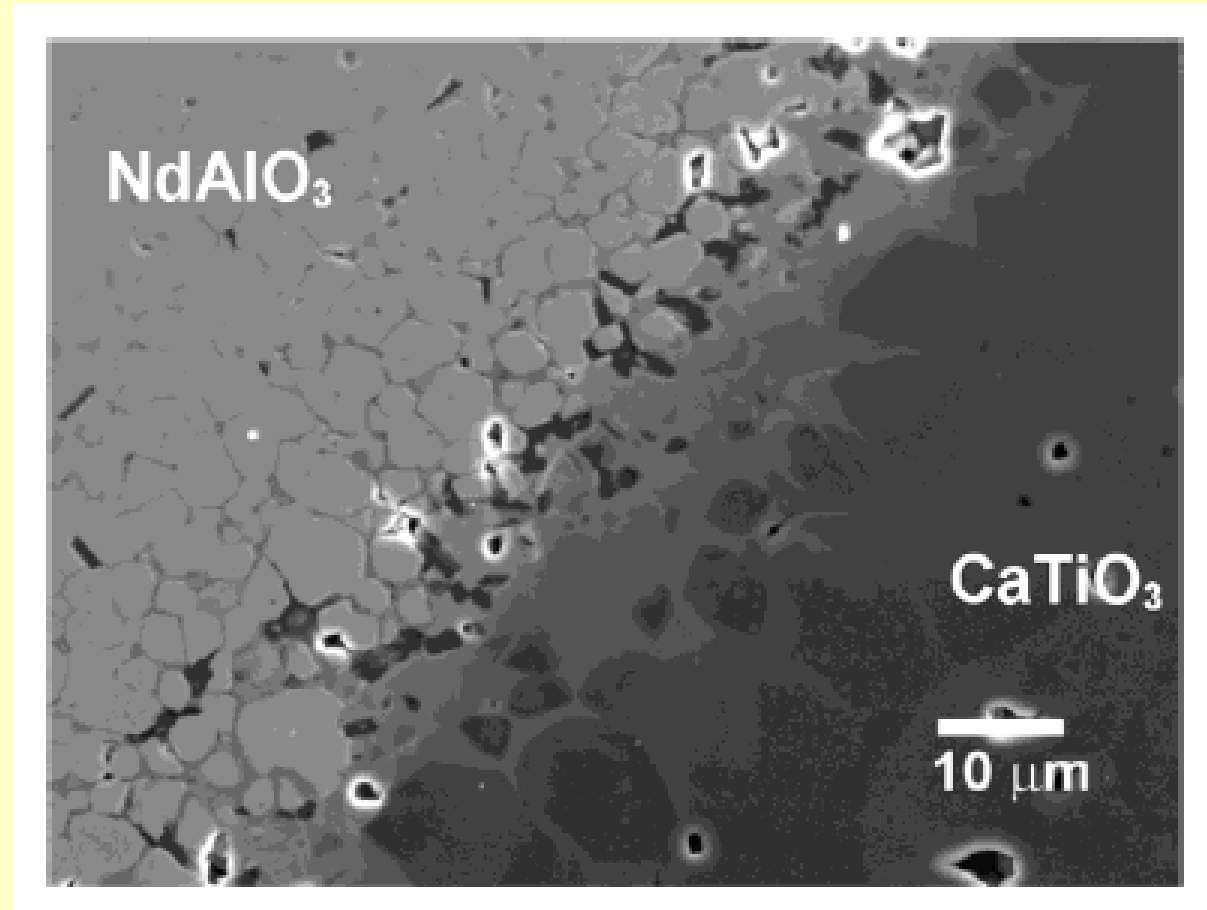
CaTiO$_3$-NdAlO$_3$ diffusion couple fired at 1350 °C/ 6 h

Diffusion - Fick's First Law

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

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

diffusion flux

x
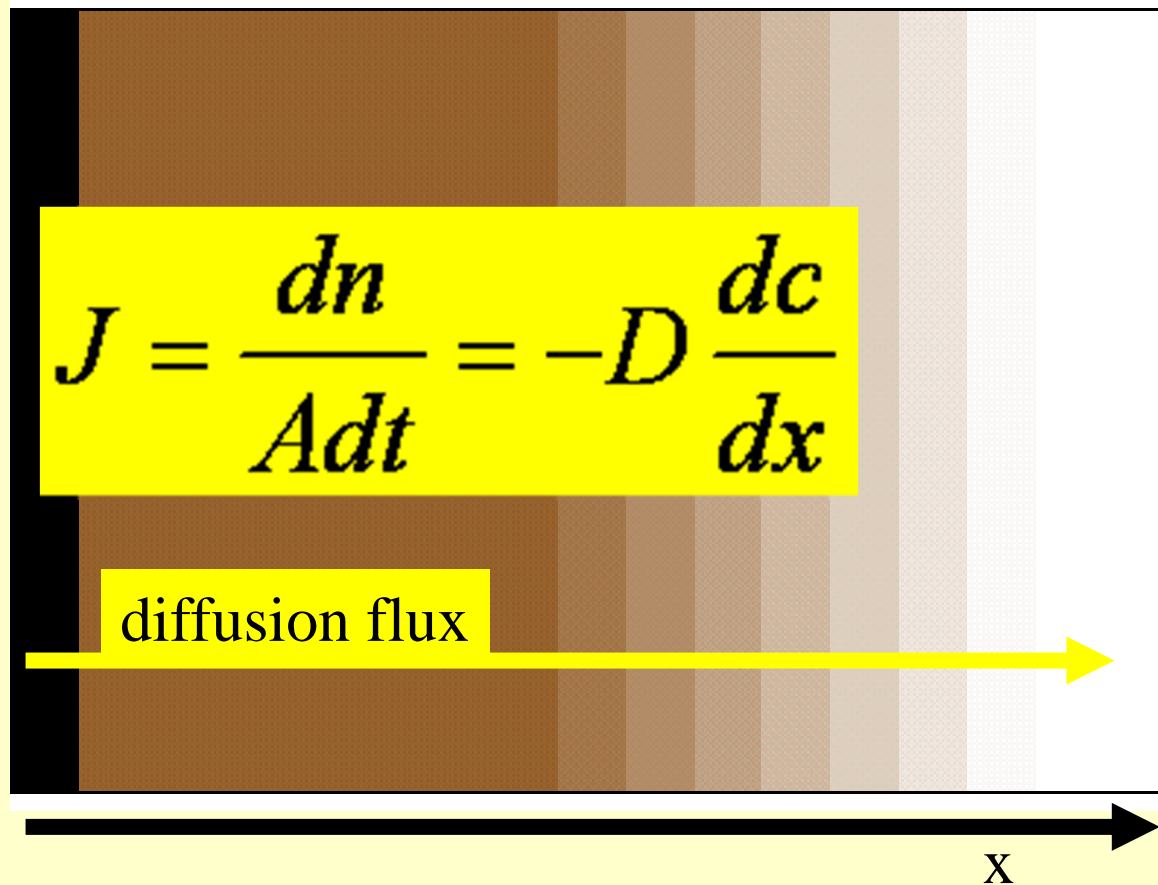
J = diffusion flux
[mol s^{-1} m^{-2}]

D = diffusion coefficient
diffusivity
[m^2 s^{-1}]

dc/dx = concentration
gradient [mol m^{-3} m^{-1}]

A = area [m^2]

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

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Diffusion - Fick's First Law

Typical diffusion coefficients for ions (atoms) in a solid at room temperature

$$10^{-13} \text{ cm}^2 \text{ s}^{-1}$$

In solid state ionic conductors (e.g. Ag-ions in α-AgI) the values are greater by orders of magnitude ($\approx 10^{-6}$ cm^2 s^{-1})

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**

Interstitial   Substitutional
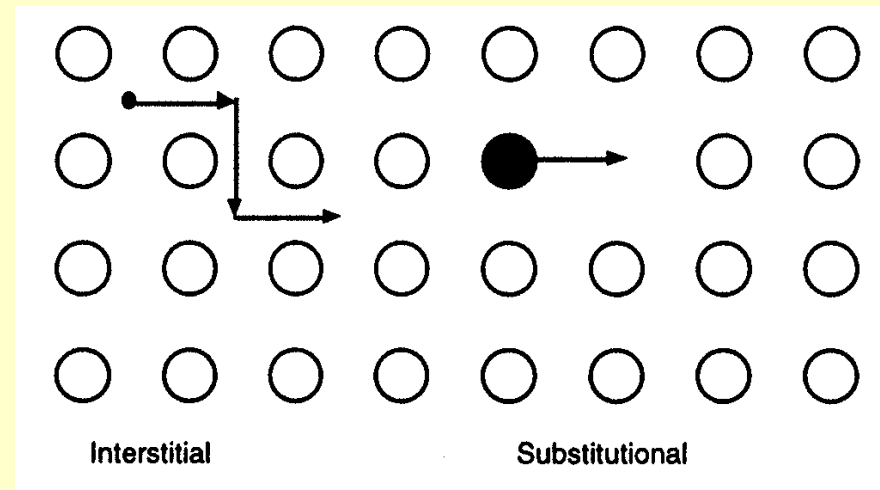
Vacancy Mechanisms of Diffusion
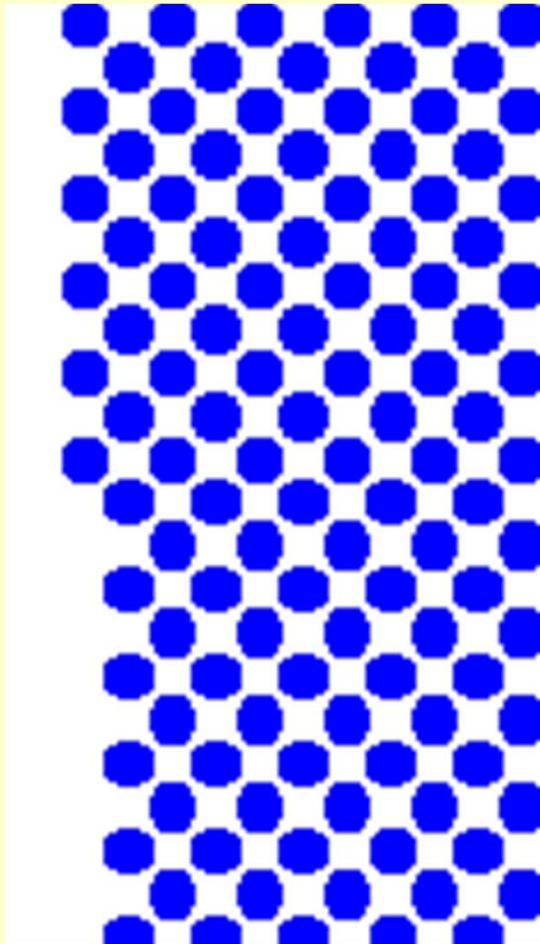
- Vacancies are holes in the matrix
- Vacancies are always moving
- An impurity can move into the vacancy
- Diffuse through the material

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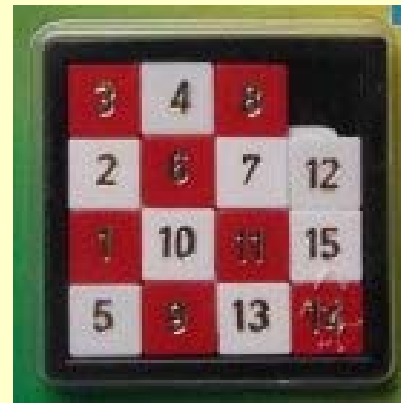
The activation energy for diffusion is the sum of the energy required to form a vacancy and the energy to move the vacancy.

increasing elapsed time
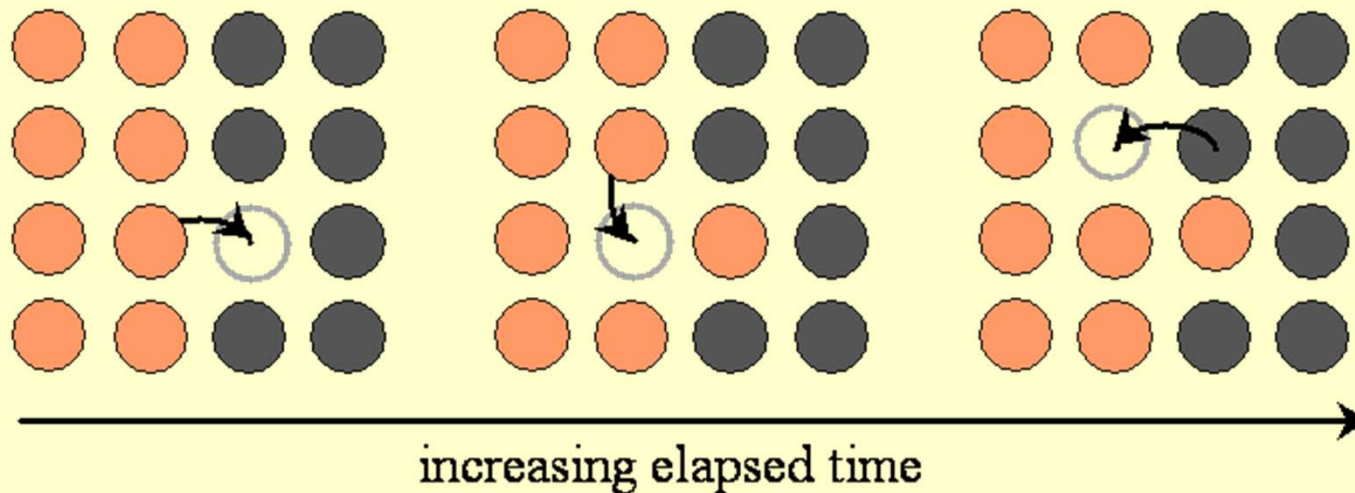
Interstitial Mechanisms of Diffusion
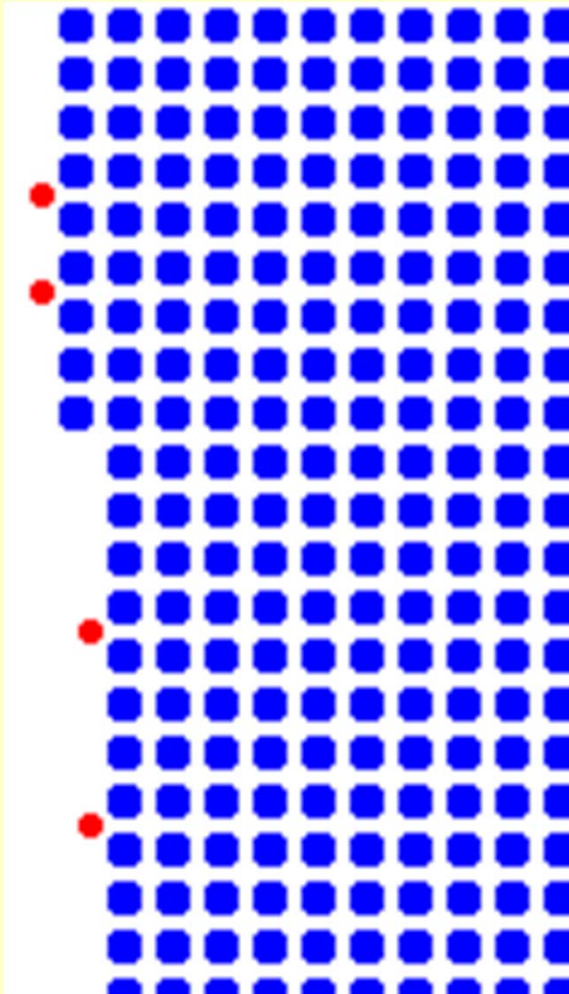
- **There are holes between the atoms in the matrix**
- **If the atoms are small enough, they can diffuse through the interstitial holes**
- **Fast diffusion**

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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
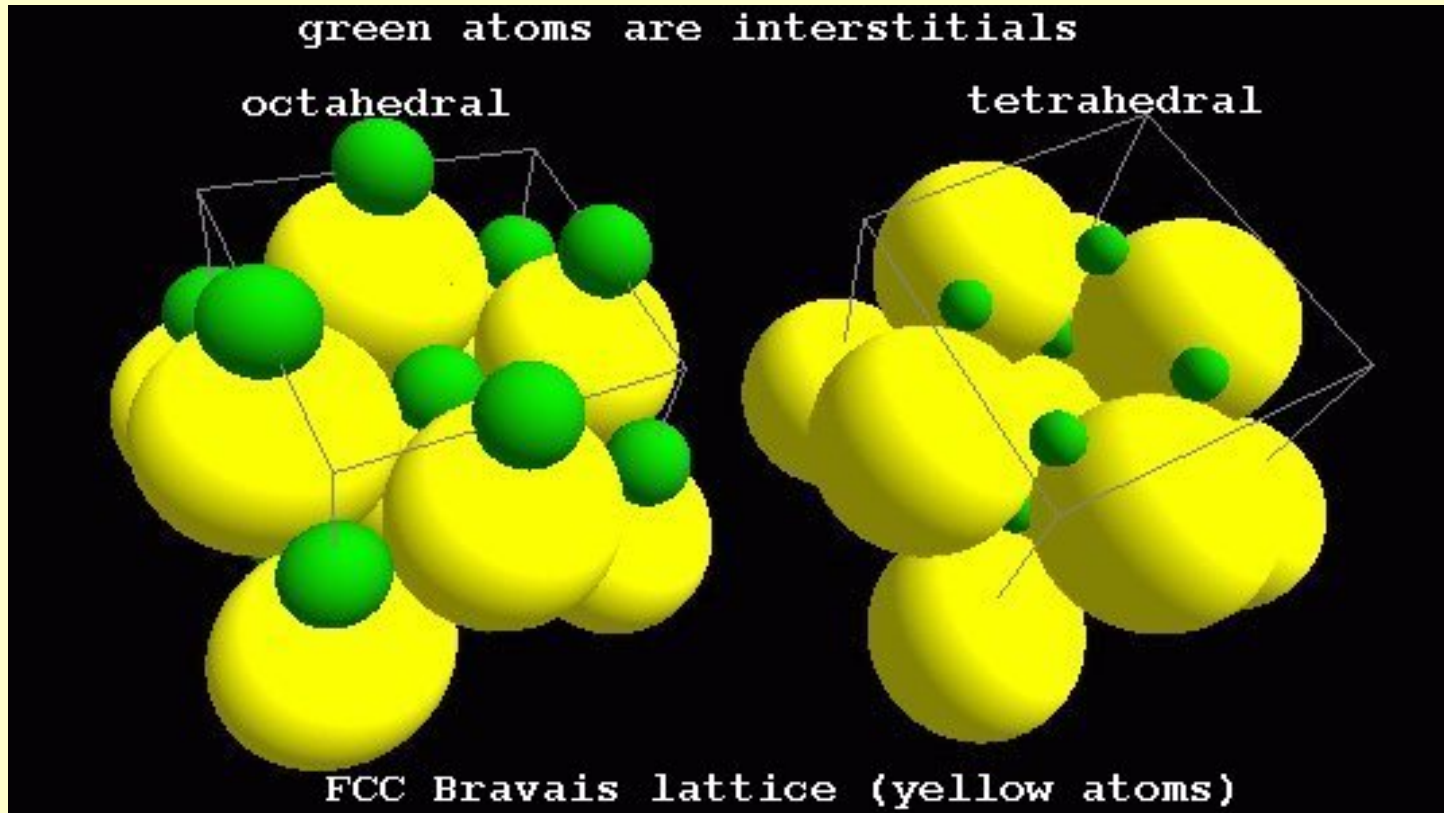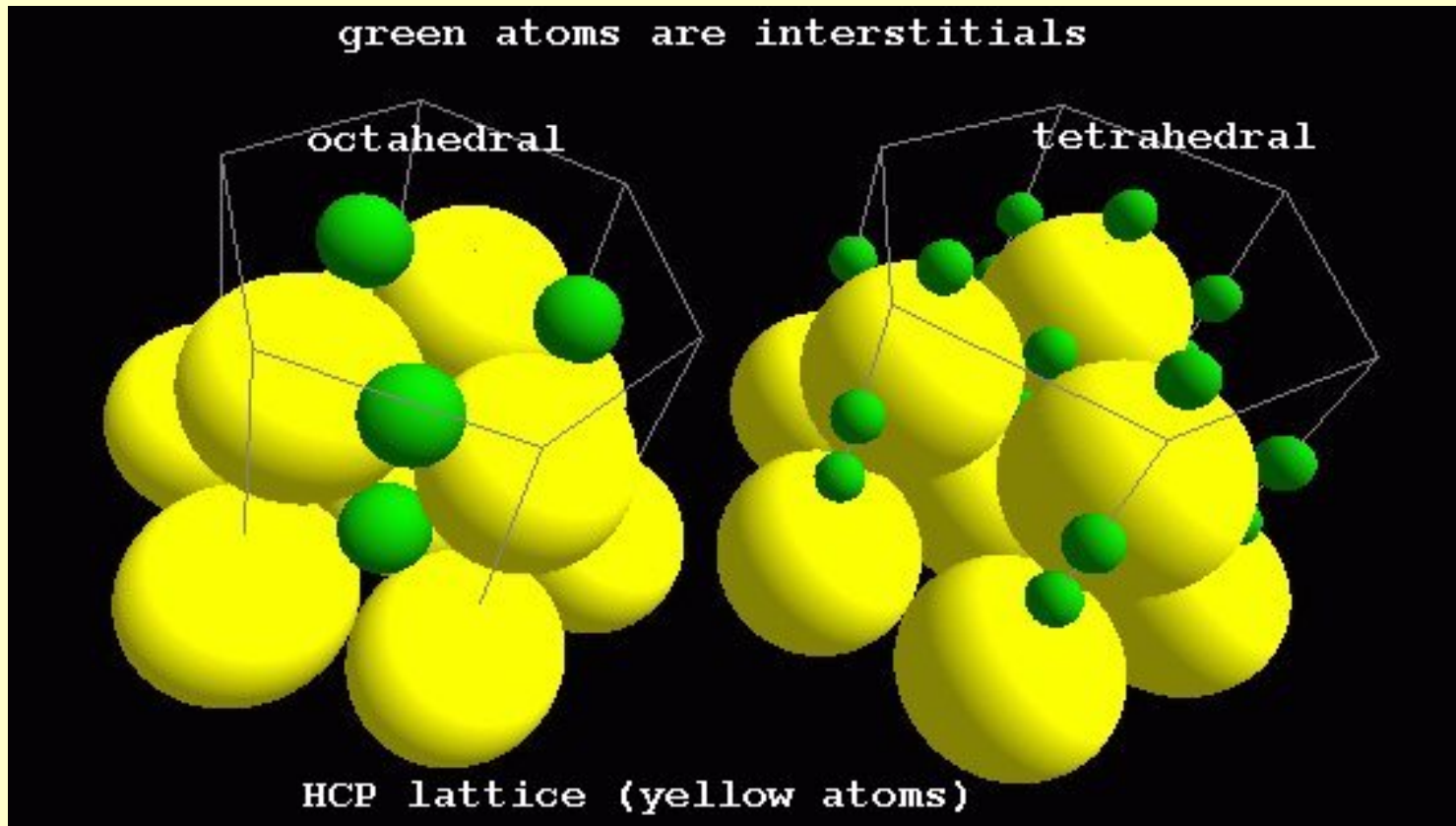- Interstitial atoms like hydrogen, helium, carbon, nitrogen, etc. must squeeze through openings between interstitial sites to diffuse around in a crystal
- The activation energy for diffusion is the energy required for these atoms to squeeze through the small openings between the host lattice atoms.

- 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

green atoms are interstitials

octahedral   tetrahedral

FCC Bravais lattice (yellow atoms)

Interstitial Atoms

green atoms are interstitials

octahedral

tetrahedral

HCP lattice (yellow atoms)

Interstitial Atoms

green atoms are interstitials

octahedral   tetrahedral

BCC Bravais lattice (yellow atoms)
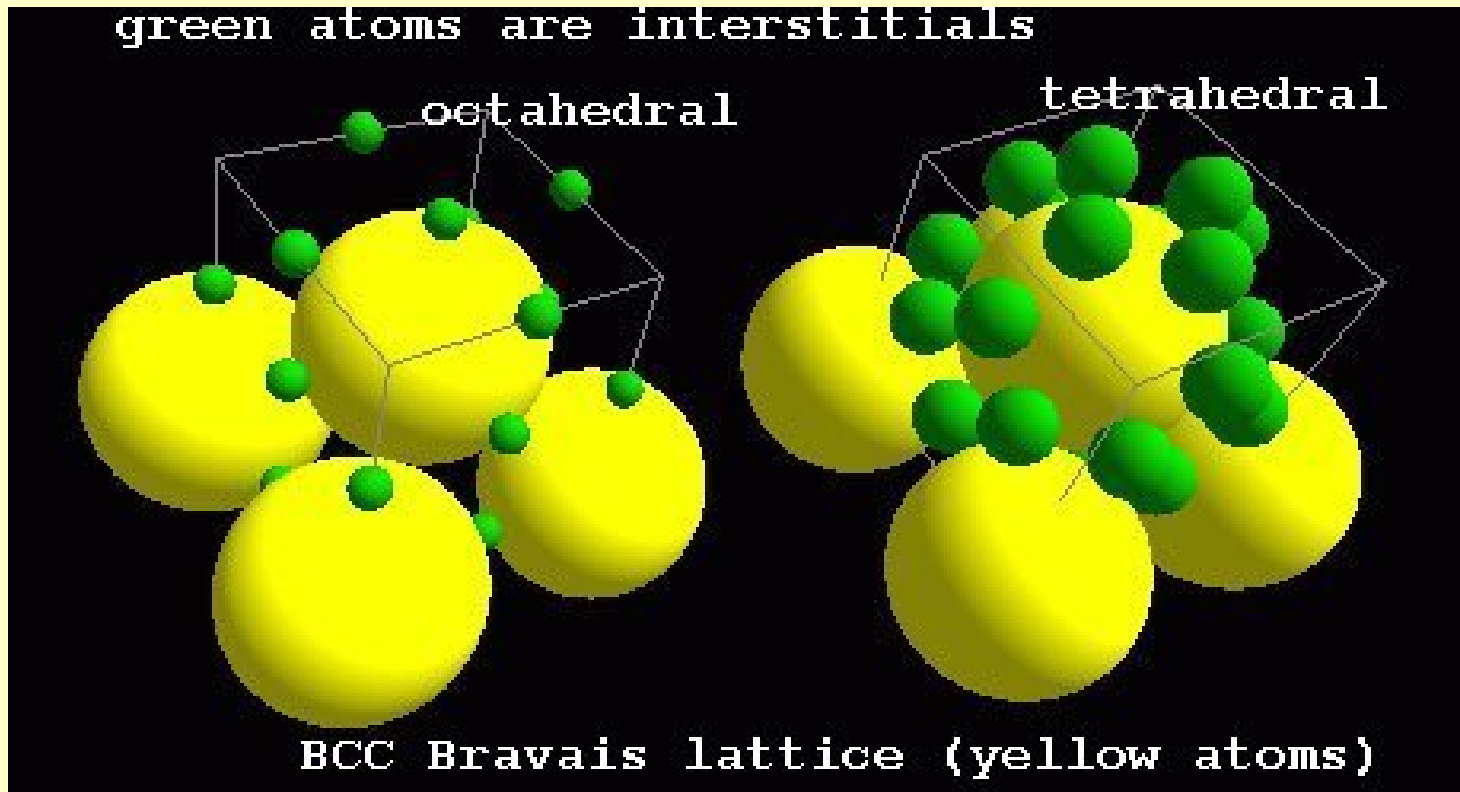
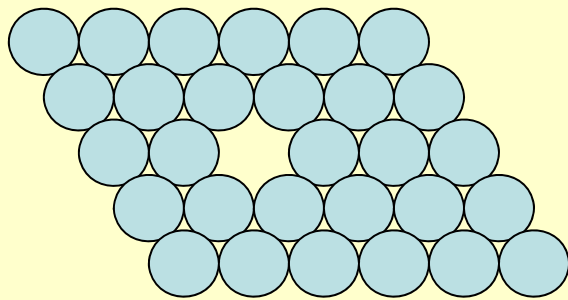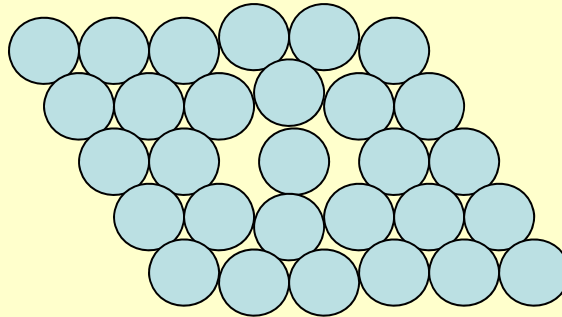# Activation Energy

- **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 highest energy is for volume diffusion**

    - **Vacancy**

    - **Interstitial**

- **Grain Boundary diffusion requires less energy**

- **Surface Diffusion requires the least**

Activation Energy

Initial state   **Intermediate state**   **Final state**
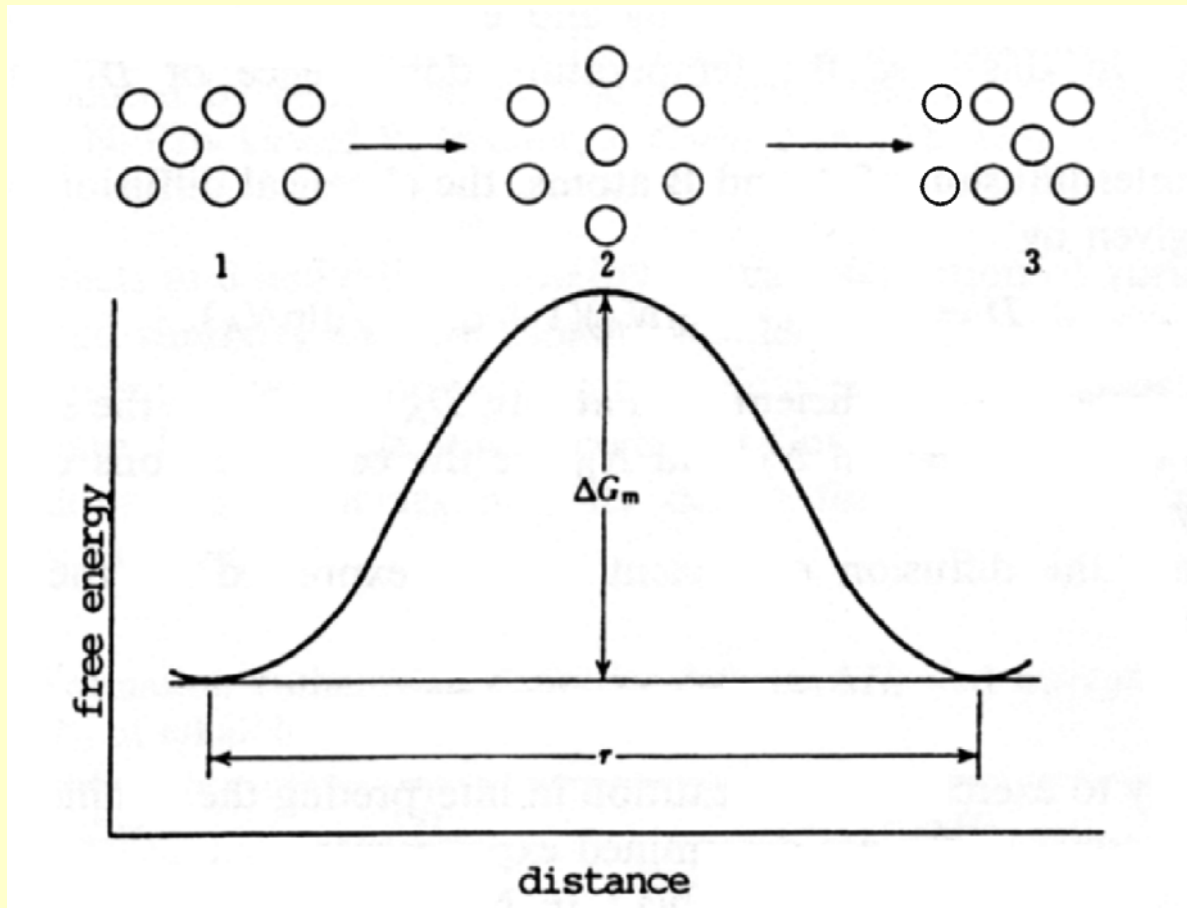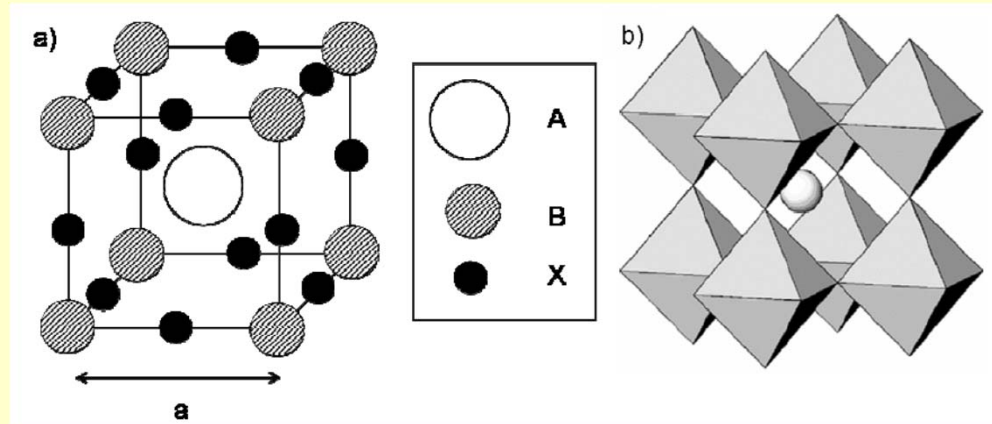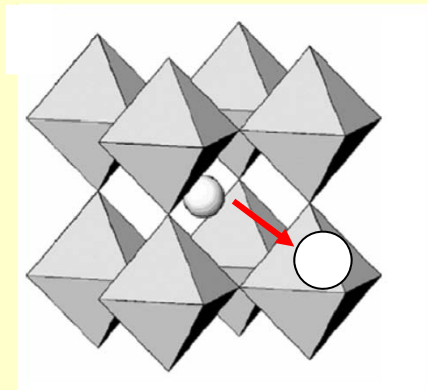

E
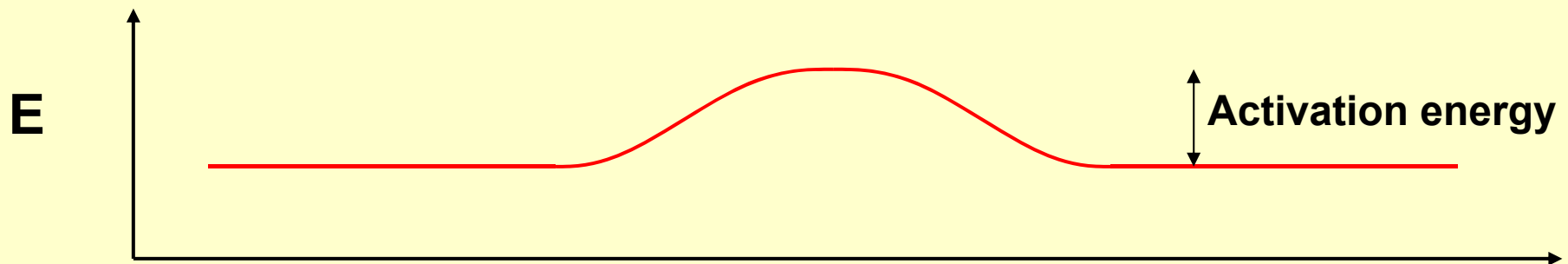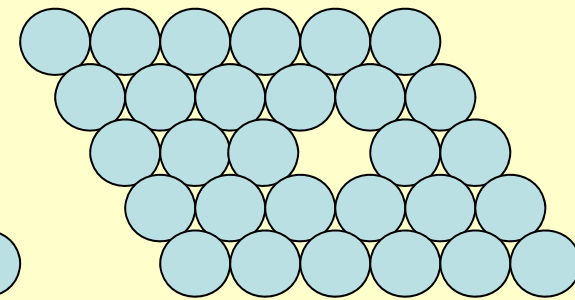
Activation energy

Energy barrier for diffusion

Energy Barrier for Diffusion

Diffusion in Perovskites ABX$_3$

A cation diffusion

B cation diffusion

The A cation diffusion is easier

$E_A = 379$

(100)$_{Cubic}$ plane
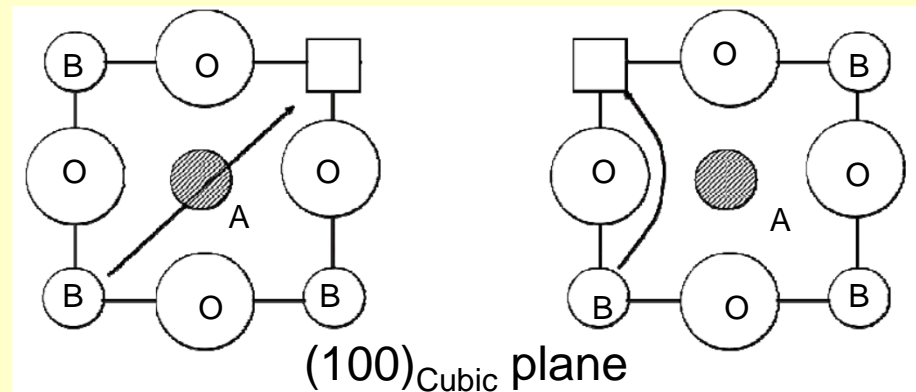
$E_A = 1420$ $E_A = 746$

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_∞ = D for T$\rightarrow \infty$
Q = the activation energy
R = the gas constant
T = the absolute temperature

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 verus 1/T is linear, the <u>slope</u> corresponds to the <u>activation energy</u> and the <u>intercept</u> to <u>D_∞</u>

Diffusion Coefficients

C in Fe

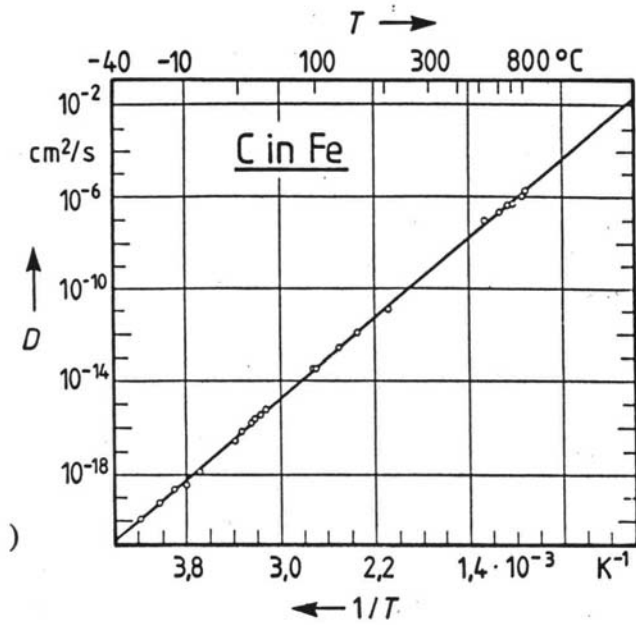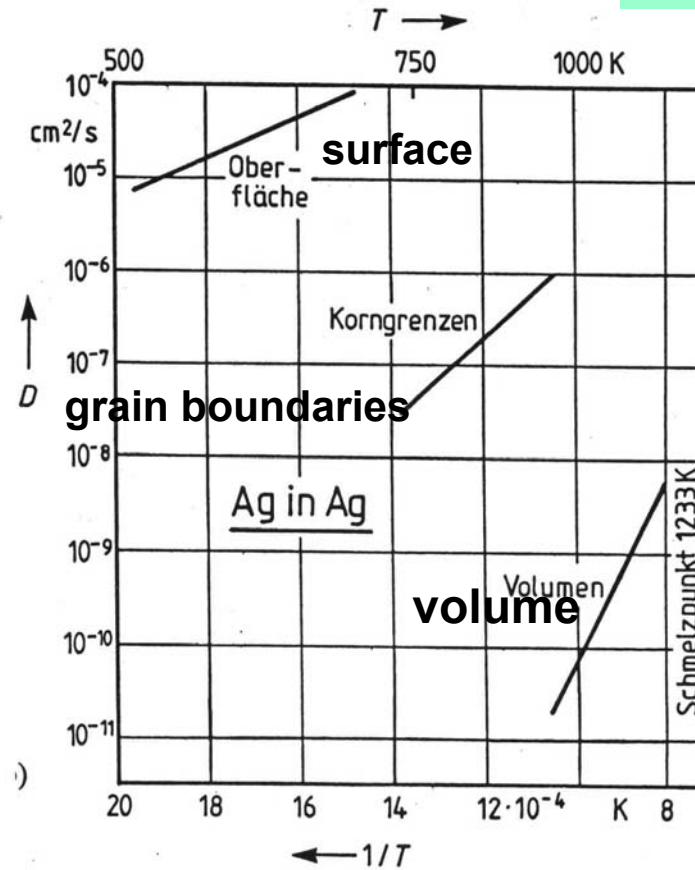**Ag in Ag**

surface

grain boundaries

volume

Diffusion

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

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

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

J_i: flow of diffusion (mol s^{-1} cm^{-2}); D_i: diffusion coefficient (cm^2 s^{-1})
$\delta c_i / \delta x$: concentration gradient (mol cm^{-3} cm^{-1}) (i.e. change of concentration along a line in the solid)

Knowledge of D allows an estimation of the <u>average diffusion length</u> for the migrating particles:

$\langle x^2 \rangle$ = 2Dt ($\langle x^2 \rangle$: average square of diffusion area; t: 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.

Consider diffusion in from a surface where the concentration of diffusing species is always constant. This solution applies to gas diffusion into a solid as in carburization of steels or doping of semiconductors.

Boundary Conditions

For   t = 0, $C = C_o$ at $0 < x$
For   t > 0 $C = C_s$ at $x = 0$
                    $C = C_o$ 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

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

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

Fick's Second Law of Diffusion

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