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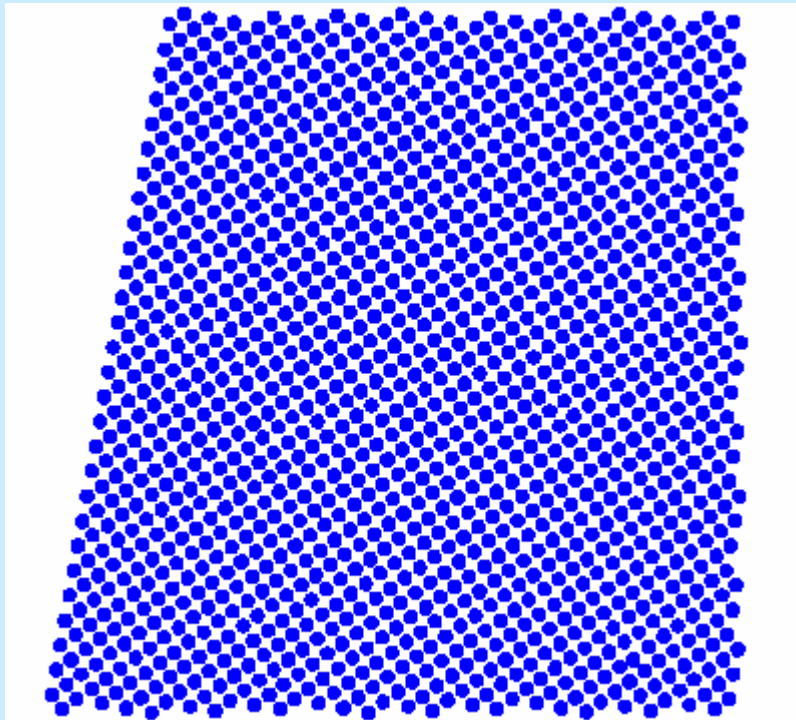
  • Chemical defects (foreign atom, mixed crystals, nonstoichiometry)
  • Geometrical defects (vacancy, interstitials, dislocations, boundaries, surface)

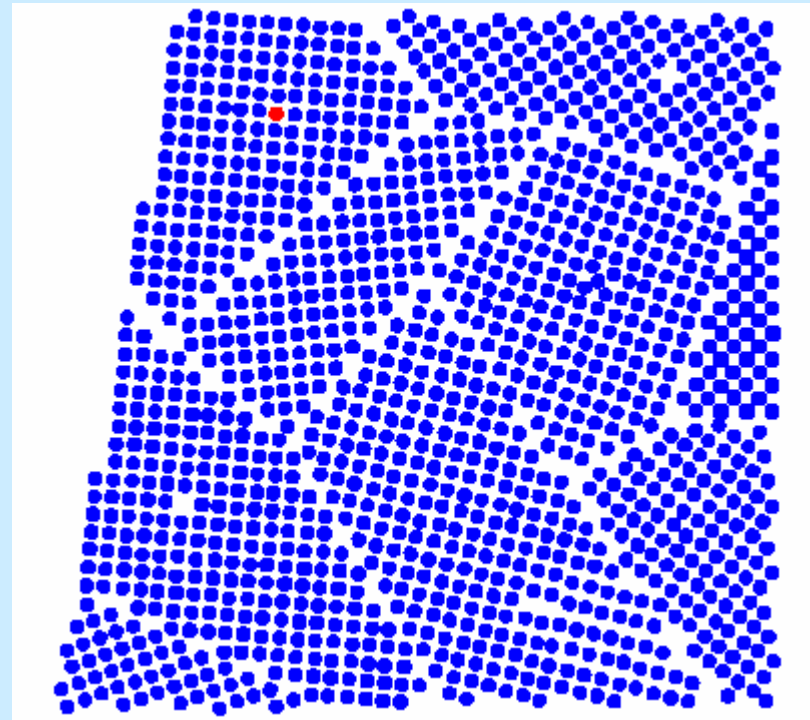Defects dominate the material properties, contribute to:

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

Crystal Defects

Perfect crystal

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

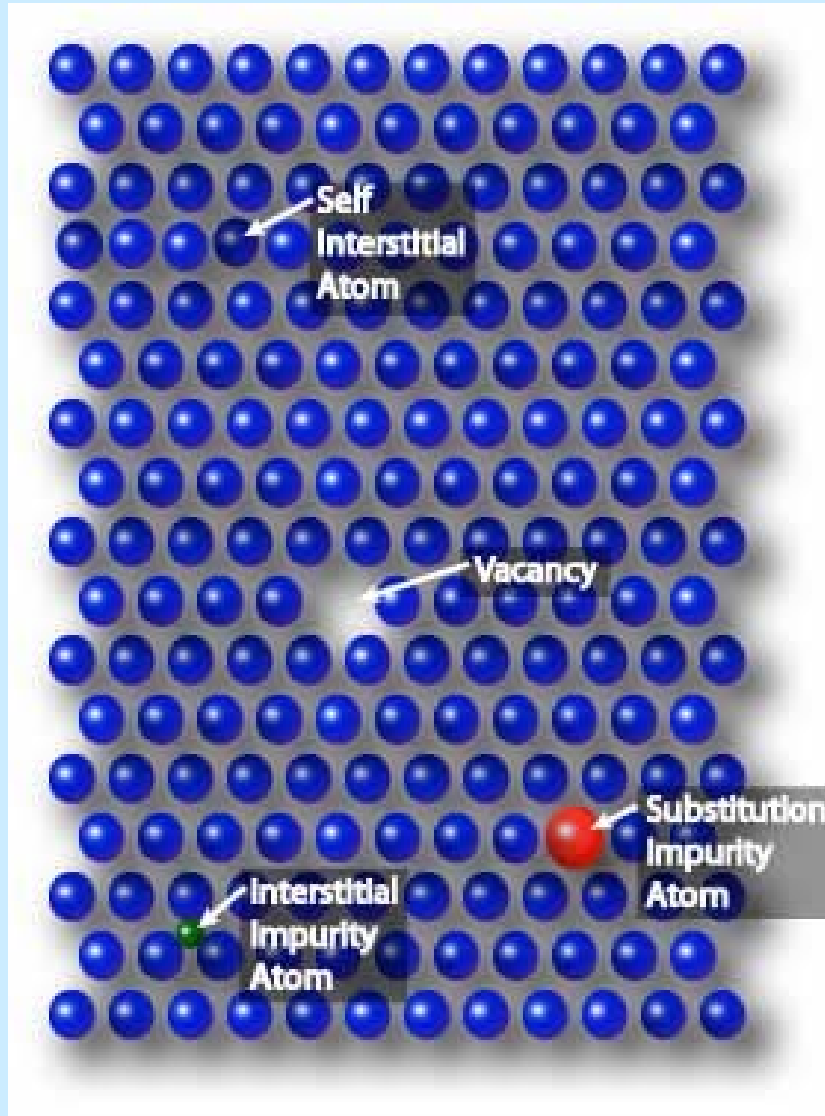**Linear defects** (1D) groups of atoms in irregular positions – dislocations

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

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

Classes of Crystal Defects
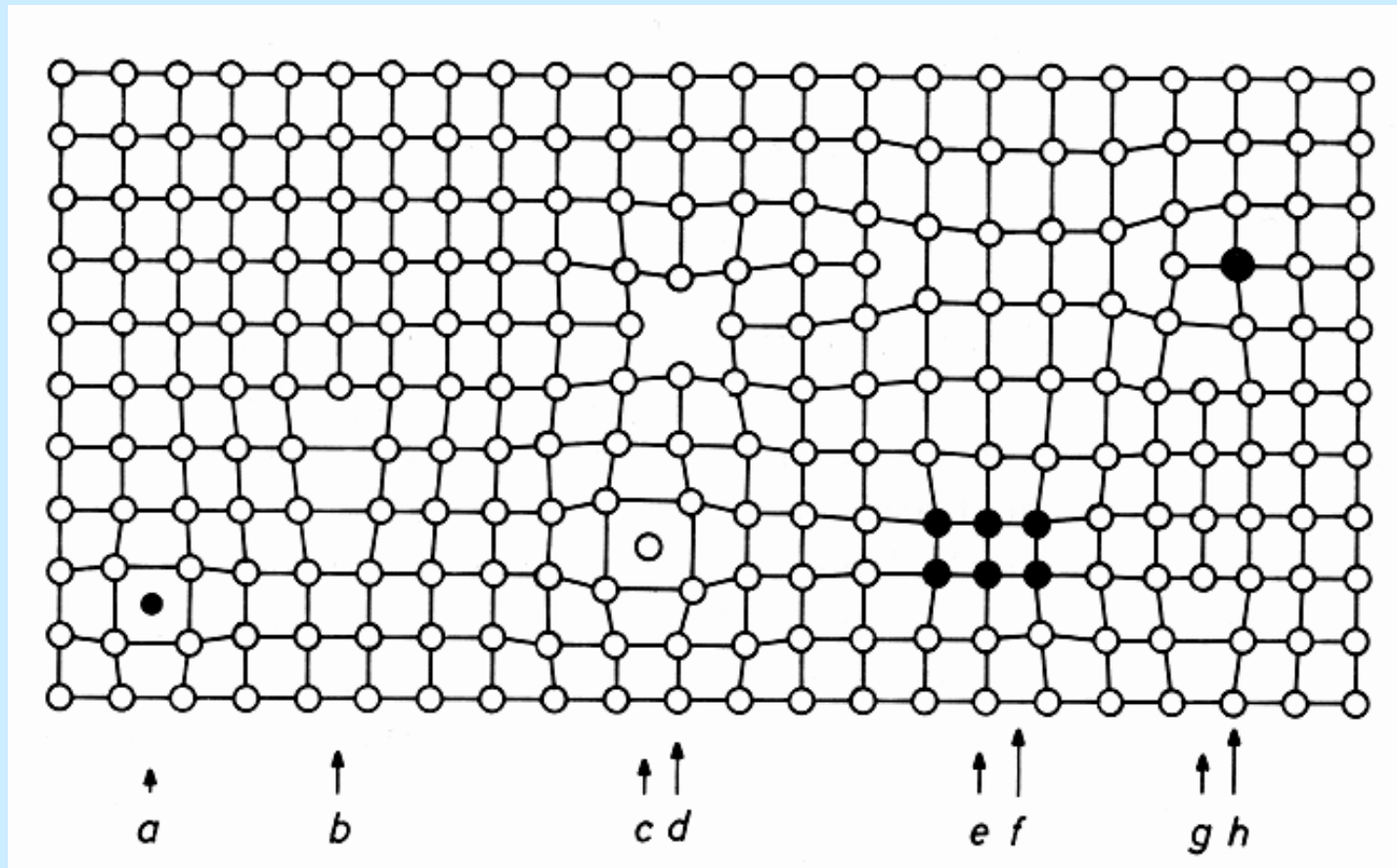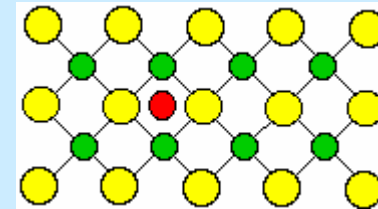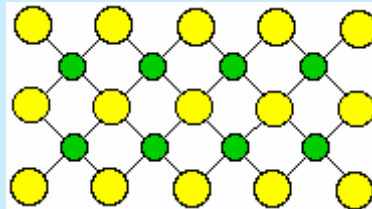
Point Defects – Metals

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

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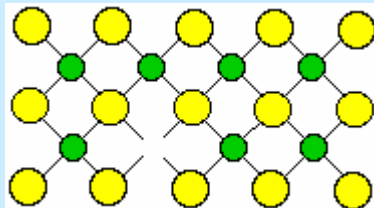- substitutional atoms
- vacancies

5
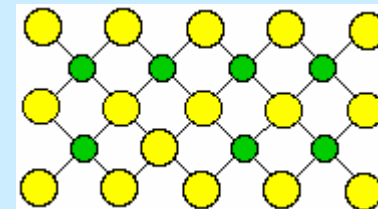
Point Defects – Ionic Compounds

perfect crystal lattice AB

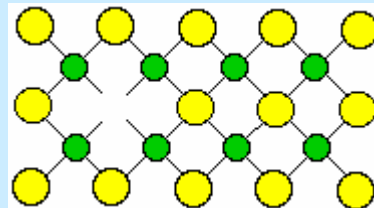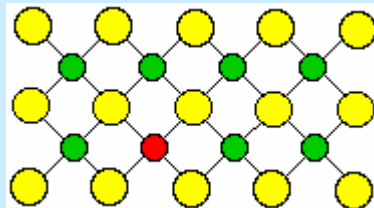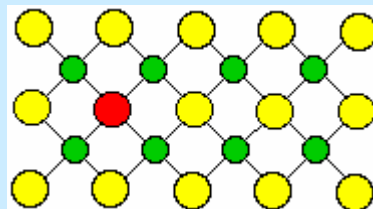interstitial imputity

cation vacancy

anion vacancy

B_A antisite defect

substitution of a cation

substitution of an anion
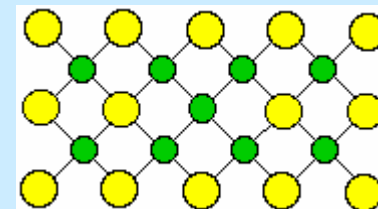
A_B antisite defect

6

Types of Point Defects in Ionic Compounds

- Vacancy

- Interstitial

- Substitutional

- Frenkel

- Schottky
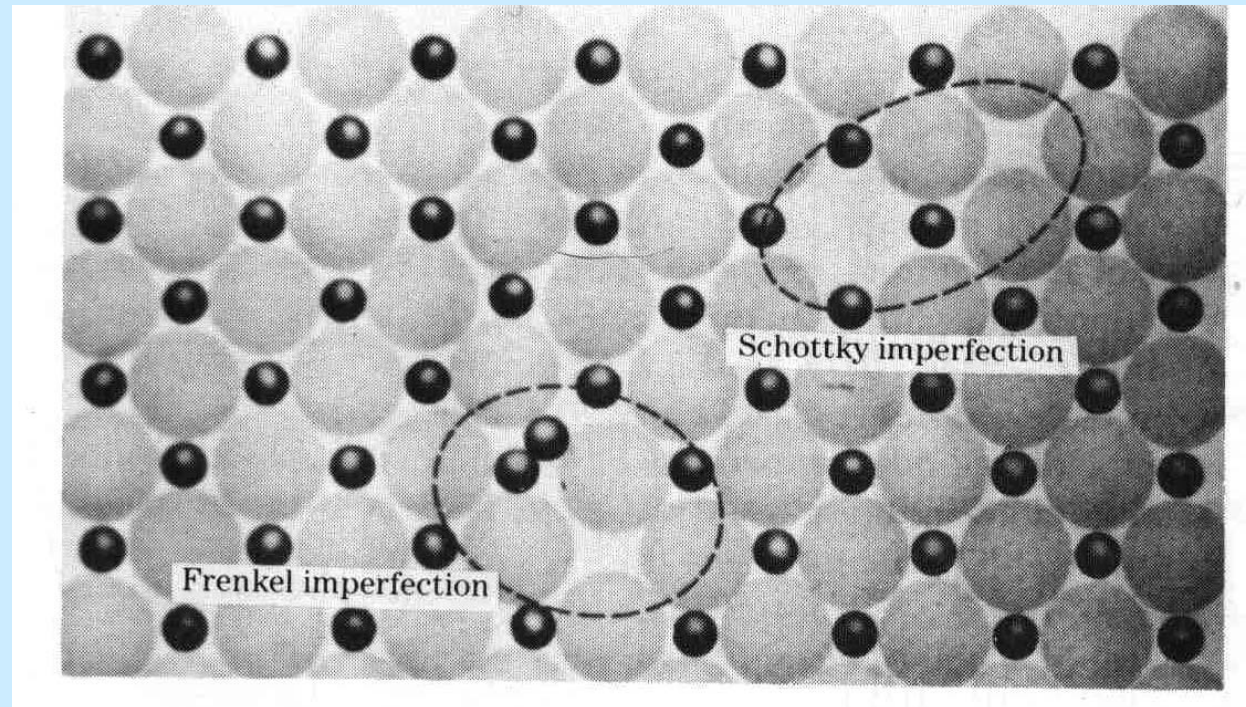
Schottky: a pair of vacancies, missing cation/anion moved to the surface

Frenkel: ions moved to interstitial positions, vacancies

Point Defects

Schottky - equal numbers of vacancies at both A and B sites preserving charge balance. Encountered more commonly when metal ions are able to easily assume multiple oxidation states.

Frenkel - encountered in open structures (wurtzite, sphalerite, etc) where coordination numbers are low and open structure provides room for interstital sites to be occupied

Schottky
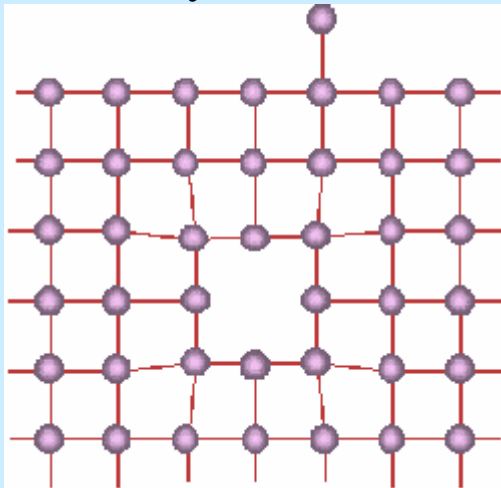
Frenkel
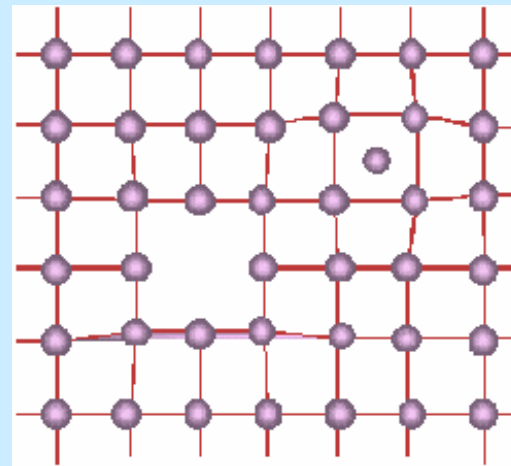
Vacancies

- There are naturally occurring vacancies in all crystals
- Equilibrium defects – thermal oscillations of atoms at T > 0 K
- The number of vacancies increases as the temperature goes up
- The number of vacancies

$$N_v = N \exp(-\Delta H^a / RT)$$

- – N is the total number of sites in a crystal
- – N_v is the number of vacancies
- – ΔH^a is the activation energy for the formation of a vacancy
- – R is the gas constant
- – N_v goes up exponentially with temperature T

Crystal Energies
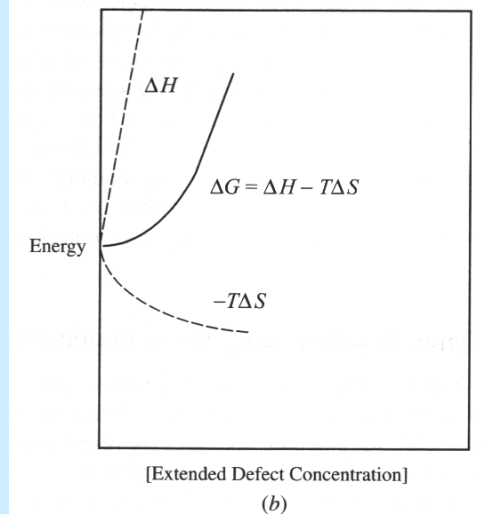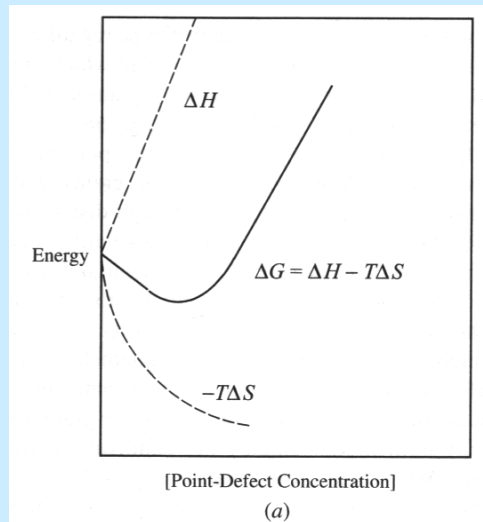
[Point-Defect Concentration]
(a)

[Extended Defect Concentration]
(b)

Point defects = equilibrium concentration, Enthalpy is positive, configurational entropy positive Minimum on free energy

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

Metastable – dislocations, grain boundaries, surface

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

10

Interstitial Atoms

- An atom must be fairly small to fit into the interstitial voids
- Hydrogen and Helium can diffuse rapidly through metals by moving through the interstitial voids
- Interstitial Carbon is used to strengthen iron - it distorts the matrix
- The ratio of r/R is 0.57 – therefore it needs an octahedral hole
- There are octahedral and tetrahedral holes in both FCC and BCC – however the holes in BCC are not regular polyhedra
- The solubility of Carbon in FCC iron is much higher than in BCC iron

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   ~ 0,7 eV
Cl^- in NaCl   ~ 1 eV
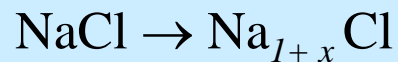Schottky pair   ~ 2,3 eV

(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 the 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

Non-stoichiometric Compounds

Vanadium oxide
varies from $VO_{0.79}$ to $VO_{1.29}$

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-stoichiometry can be caused by doping or by a multi-valent element

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.

They are formed by introducing an impurity (doping) or by the ability of an element to show multi-valent character. The electronic, optical, magnetic and mechanical properties of non-stoichiometric compounds can be controlled by varying their composition.
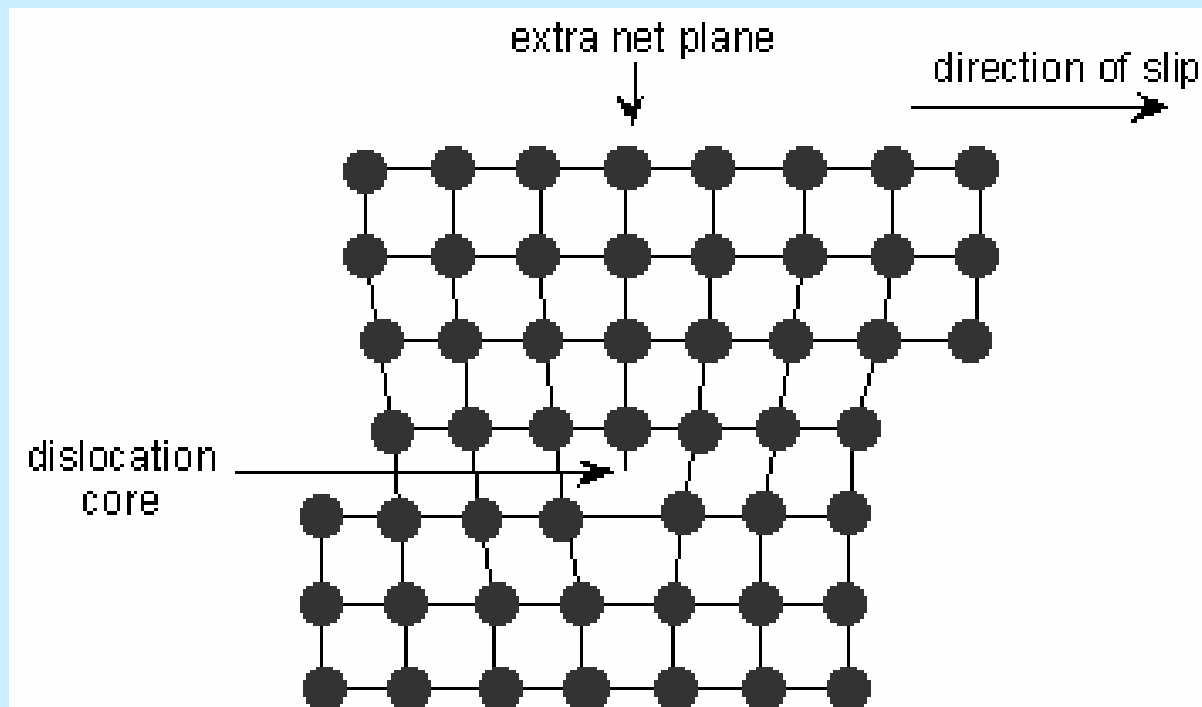
Dislocations

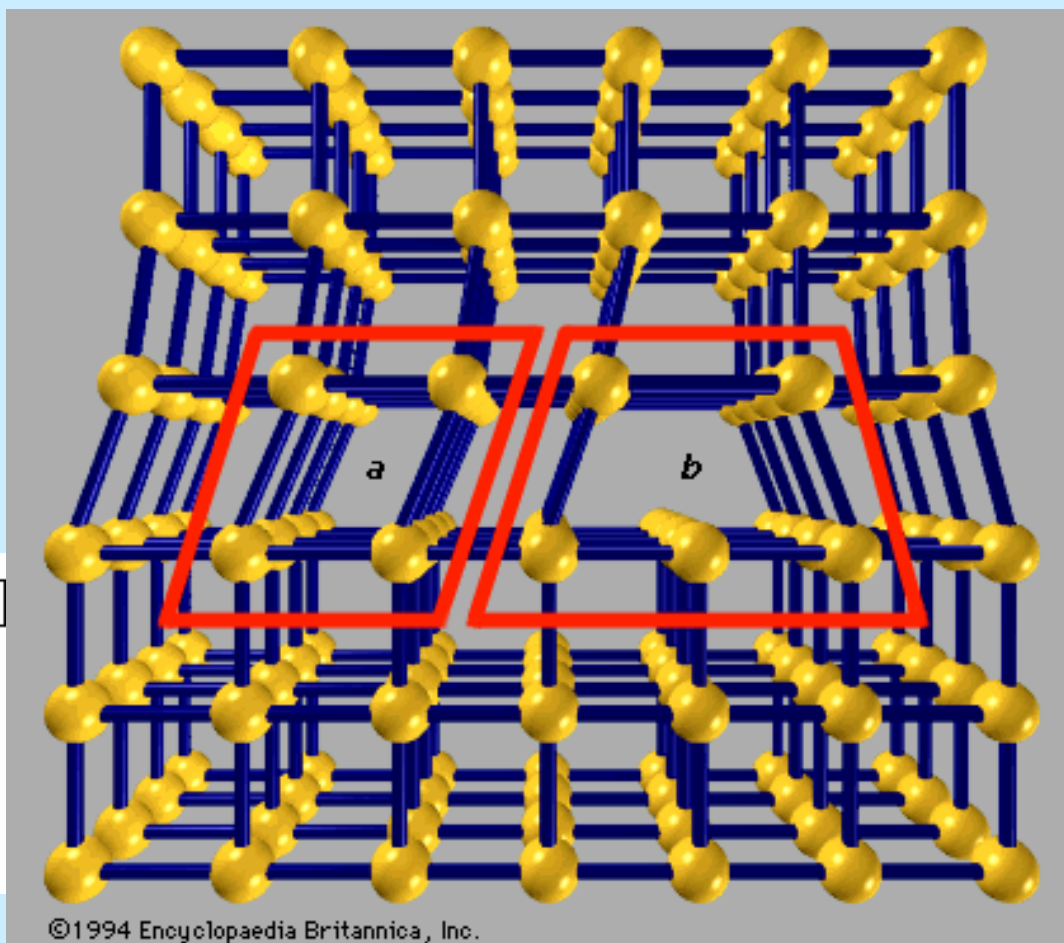Line imperfections in a 3D lattice

- Edge
- Screw
- Mixed
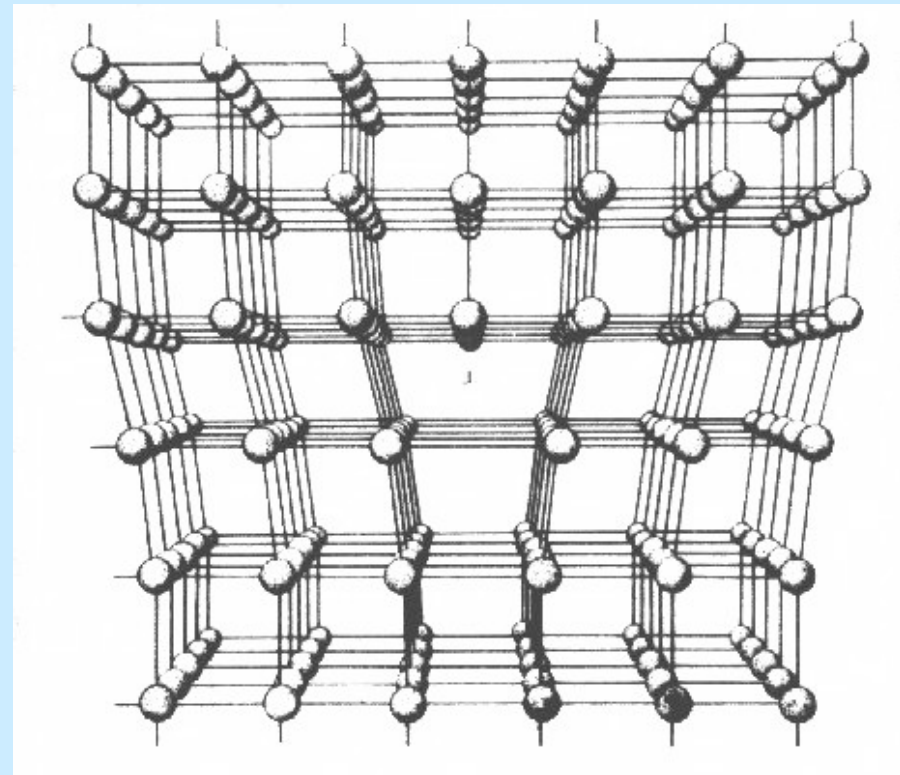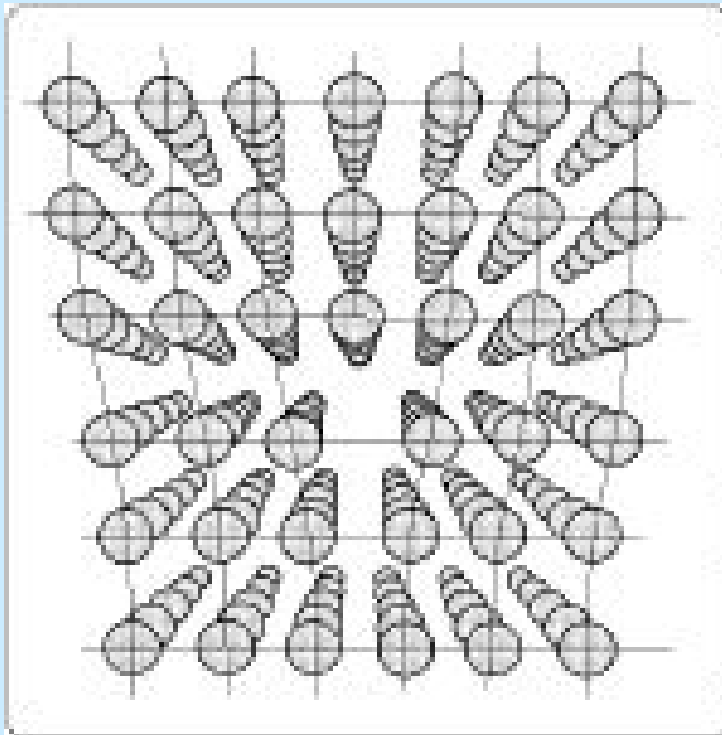
Edge Dislocation

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

Edge Dislocation
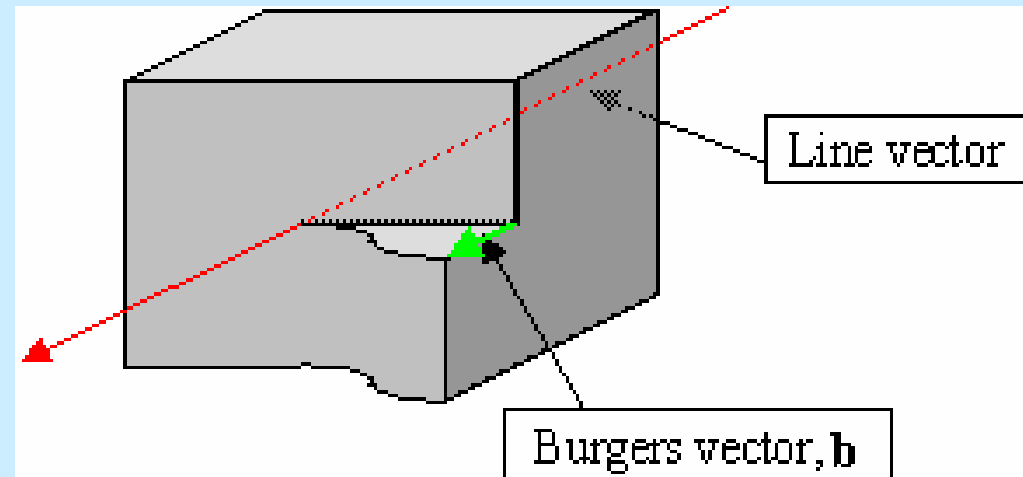

Line vector
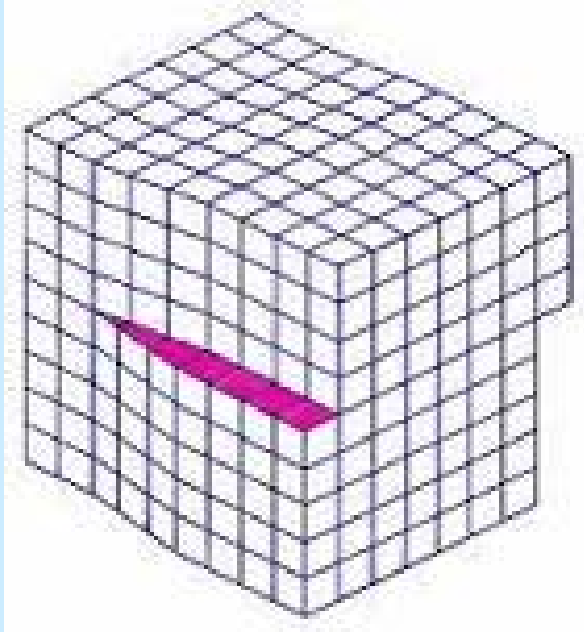
Burgers vector, **b**

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18
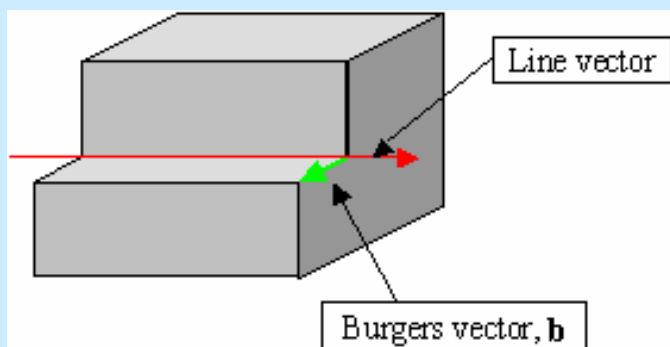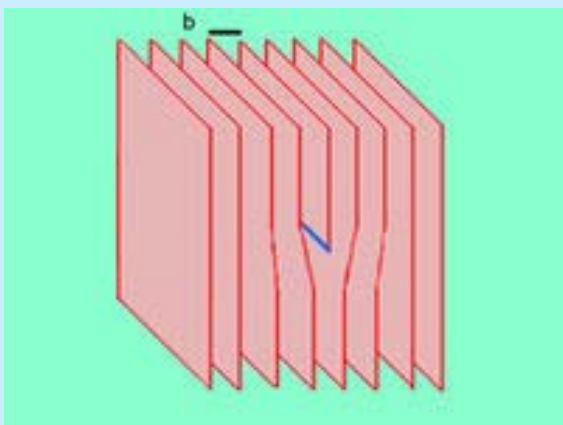
Screw Dislocation

- 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

Screw Dislocation
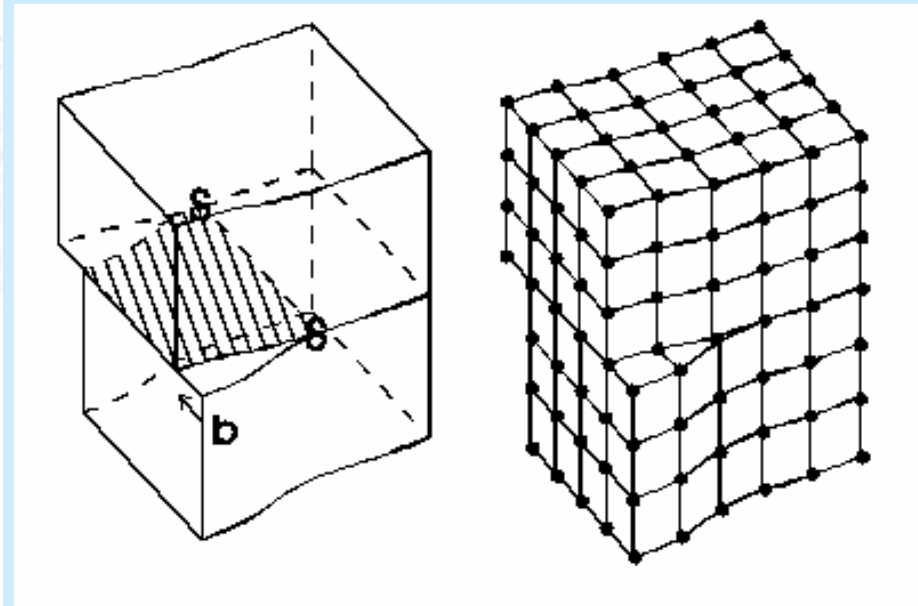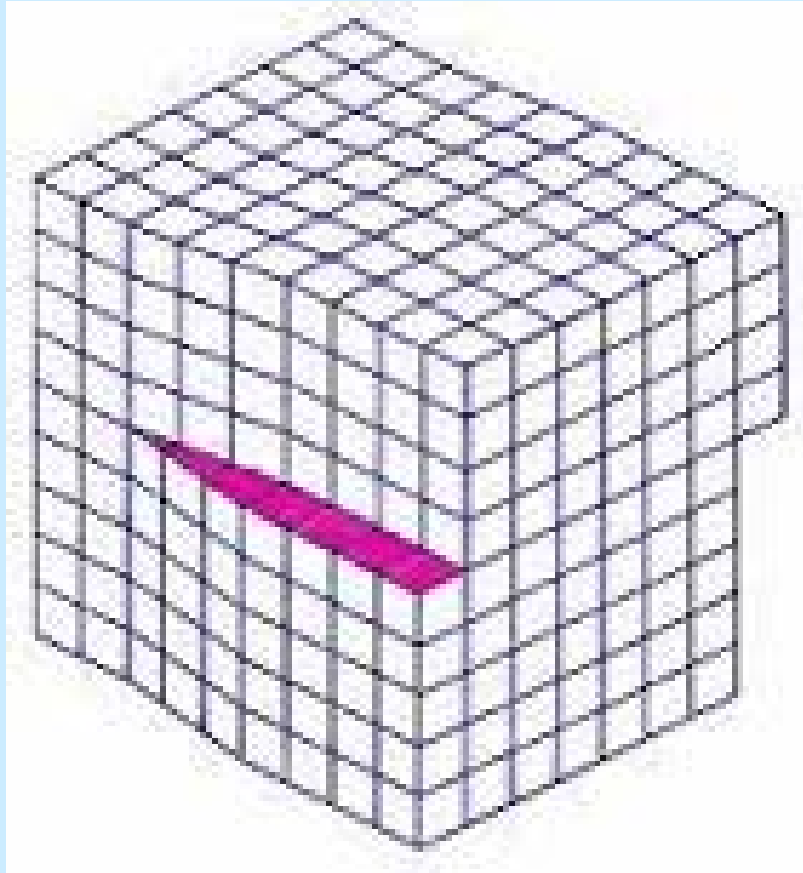
Deformation

When a shear force is applied to a material, the dislocations move
Plastic deformation in a material occurs due to 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 result from plastic forming operations such
as rolling and 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 - drives up the force needed to move the dislocation - strengthens the material

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.

$$\sigma = F/A$$

Normal to slip plane

ϕ λ

Slip direction

$$\tau_r = F_r / A \quad \text{- Resolved Shear}$$
$$\text{Stress}$$

A

A_o
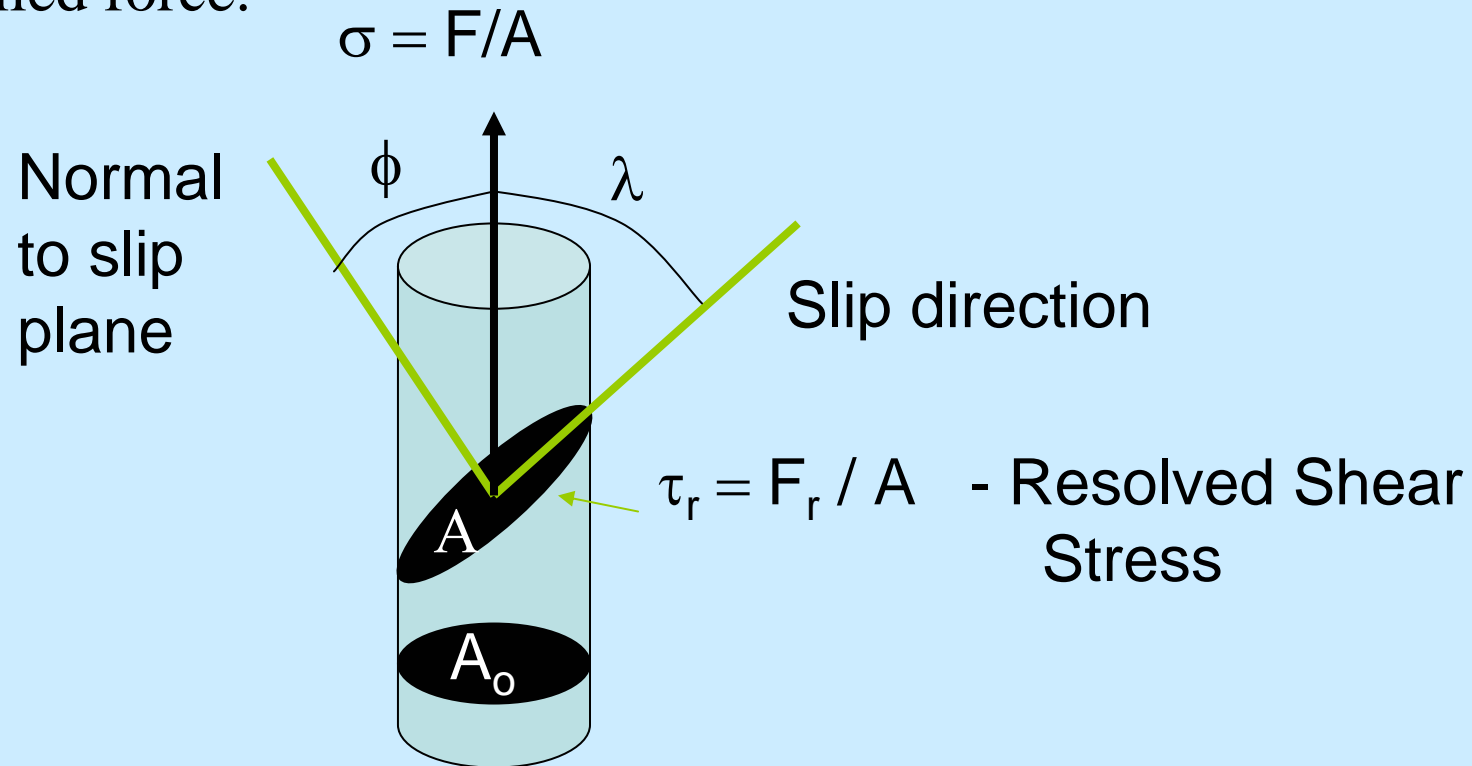
Schmidt's Law

- $F_r = F \cos(\lambda)$

$A = A_0/\cos(\phi)$

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

Where:

$\quad \tau = F_r / A$ = resolved shear stress in the slip direction

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

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 usually not cross grain boundaries

- Tilt and Twist boundaries

- Low and High angle boundaries
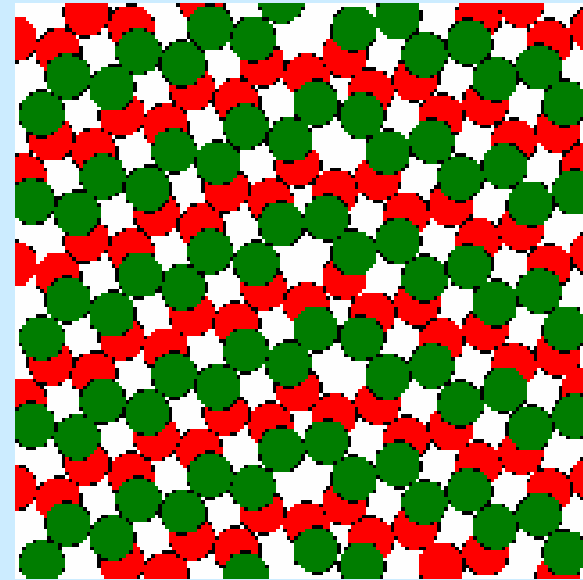
Low Angle Tilt Boundary
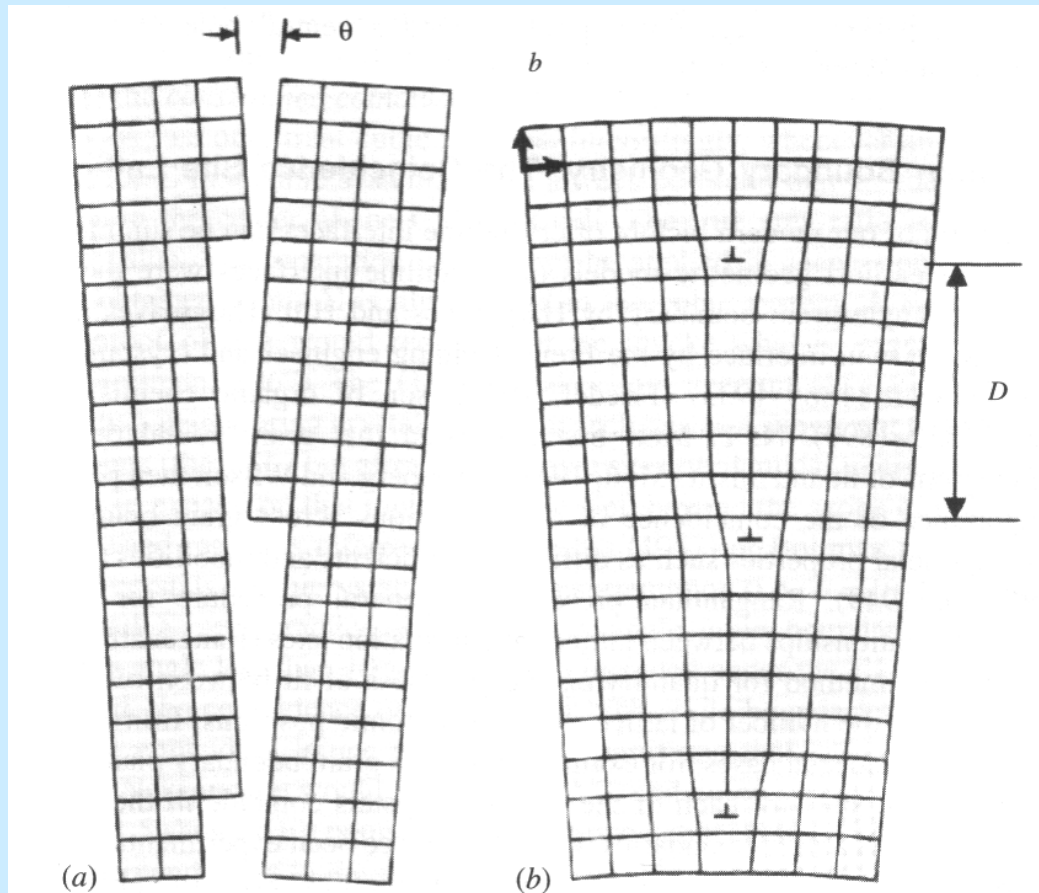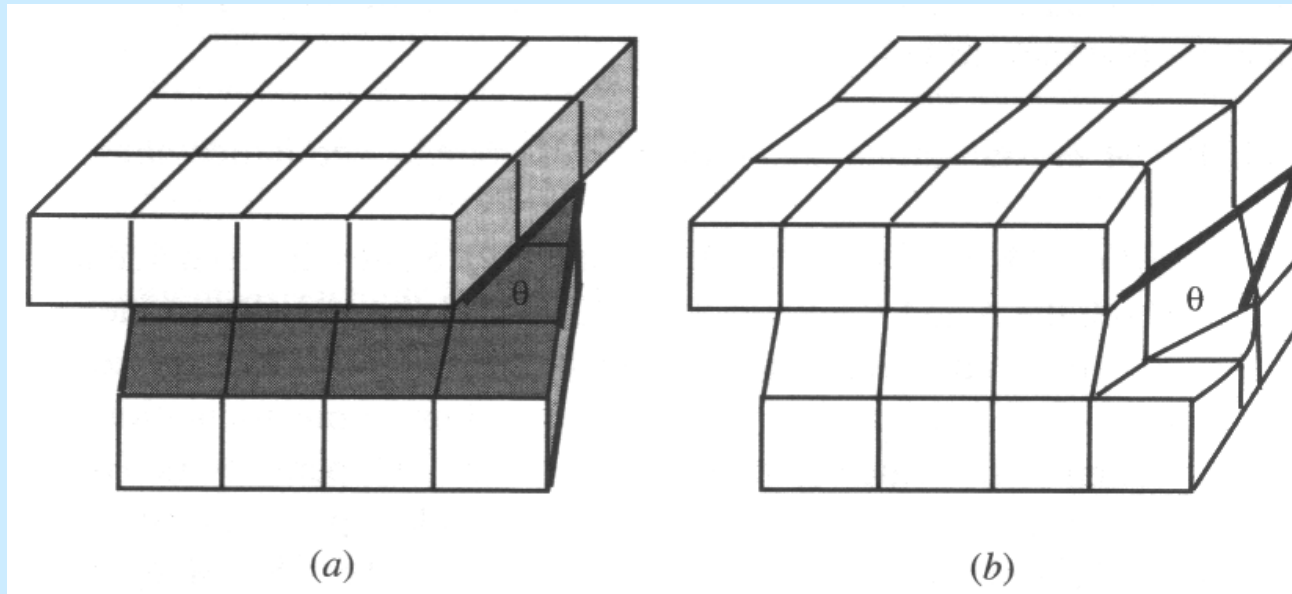

**Low Angle Tilt Boundary =
Array of Edge dislocations**
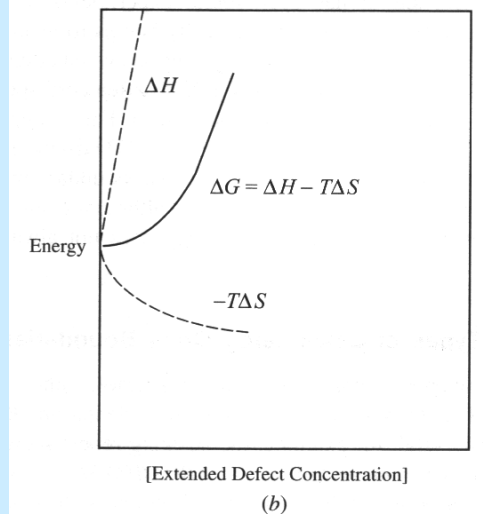
$$D = \frac{b}{\sin \theta}$$

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

Low Angle Twist Boundary

(a)   (b)

Low Angle Twist Boundary = a Screw dislocation

Crystal Energies
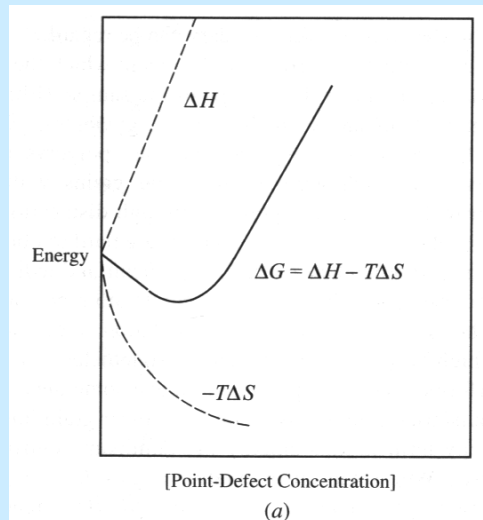
[Point-Defect Concentration]
(a)

[Extended Defect Concentration]
(b)

Point defects = equilibrium concentration, Enthalpy is positive, configurational entropy positive Minimum on free energy

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

Metastable – dislocations, grain boundaries, surface

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

29

Effect of Grain Size on Strength

- In a small grain, a dislocation gets to the boundary and stops – slip stops

- In a large grain, the dislocation can travel farther

- Small grain size equates to more strength

30

Hall-Petch Equation

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

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

d = average diameter of the grains

σ_0 = constant
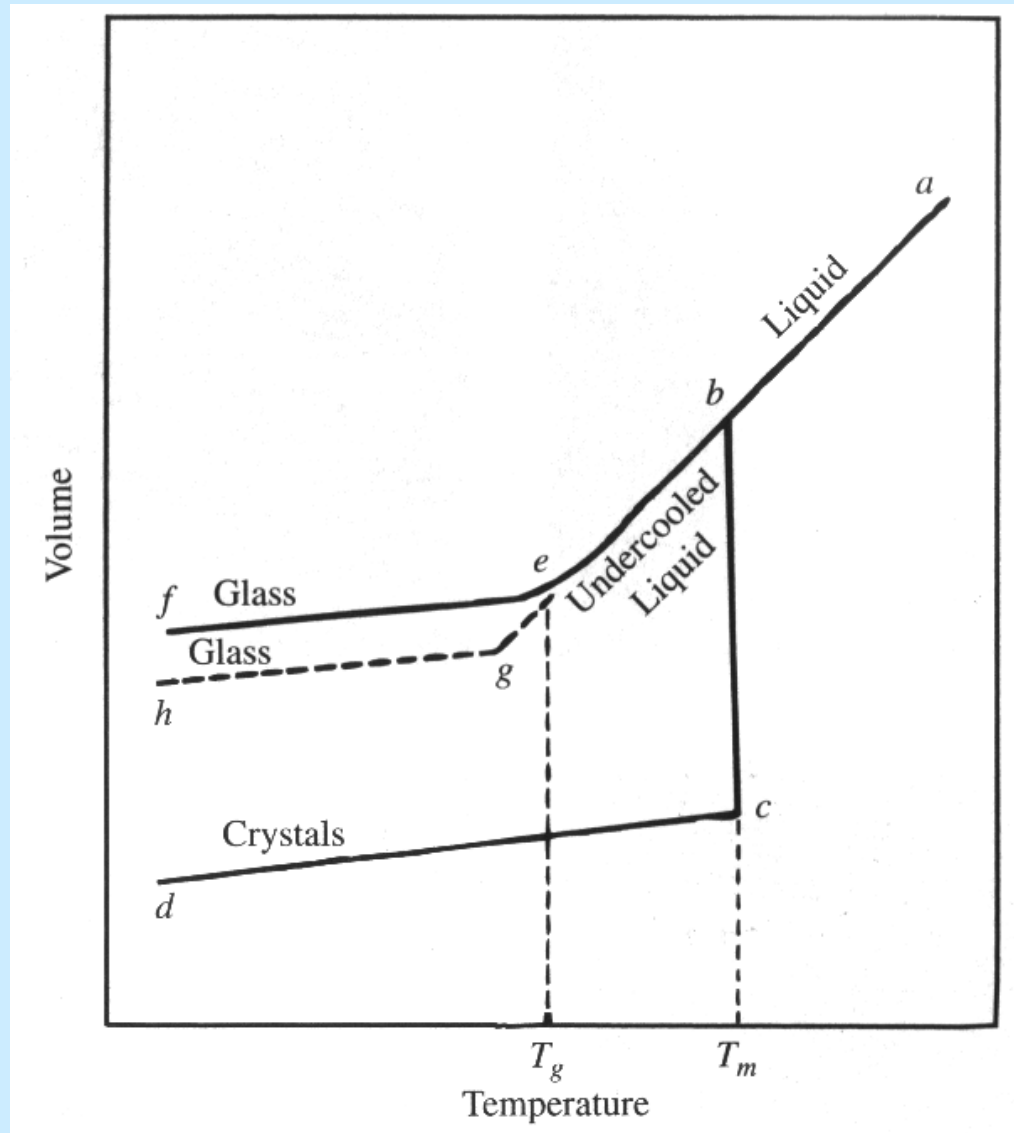
K = constant

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

Amorphous Structures

Diffusion

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

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

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

Diffusion - Fick's First Law

Fick's first law describes steady state diffusion

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

diffusion flux

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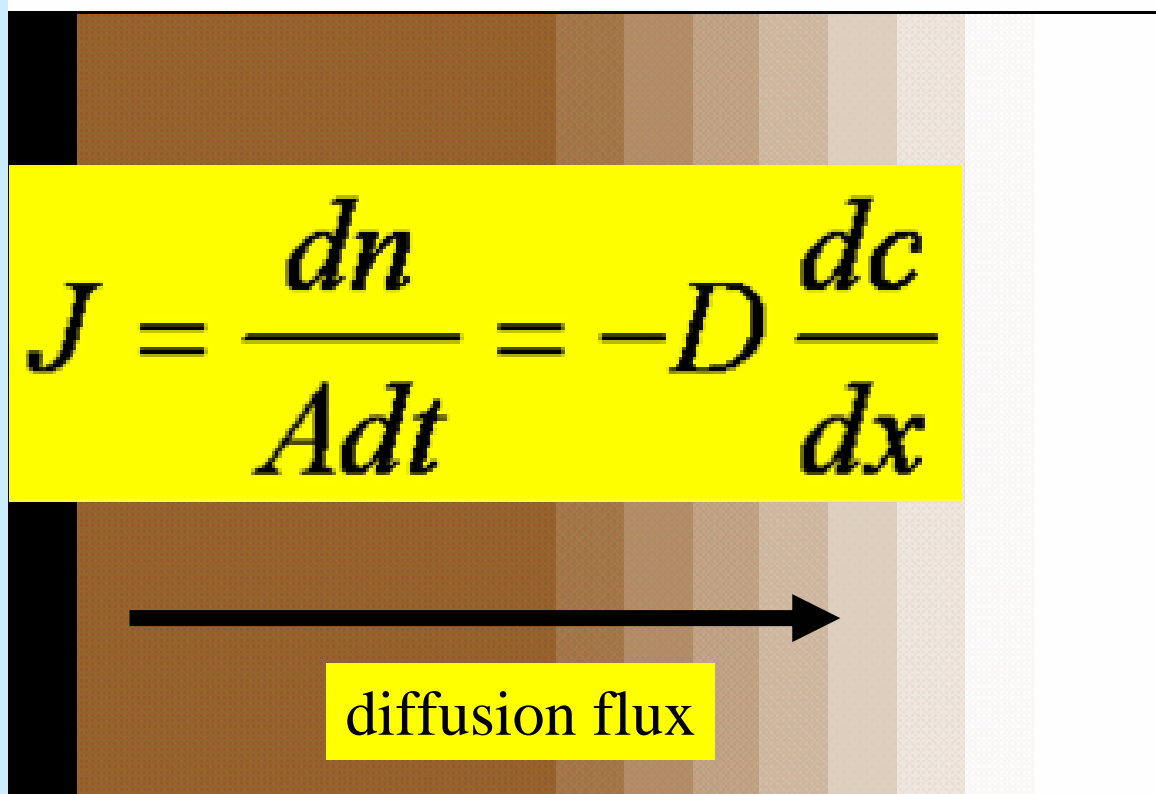
J = diffusion flux
[mol s^{-1} m^{-2}]

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

dc/dx = concentration
gradient

A = area [m^2]

Typical diffusion coefficients for ions (atoms) in a solid at room temperature are about 10^{-13} cm^2 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})

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 coefficients show an exponential temperature dependence (Arrhenius type):

$$D = D_\infty \exp(-Q/kT)$$ (D_∞: D for $T \rightarrow \infty$, Q: activation energy of diffusion, k: Boltzmann-faktor)

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>.
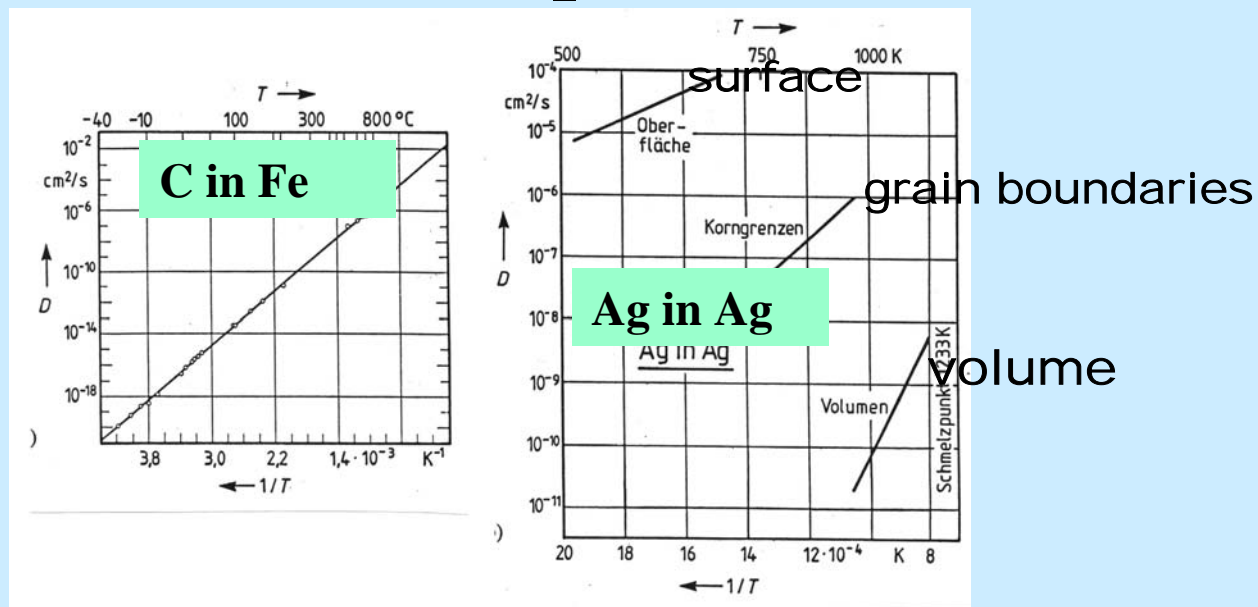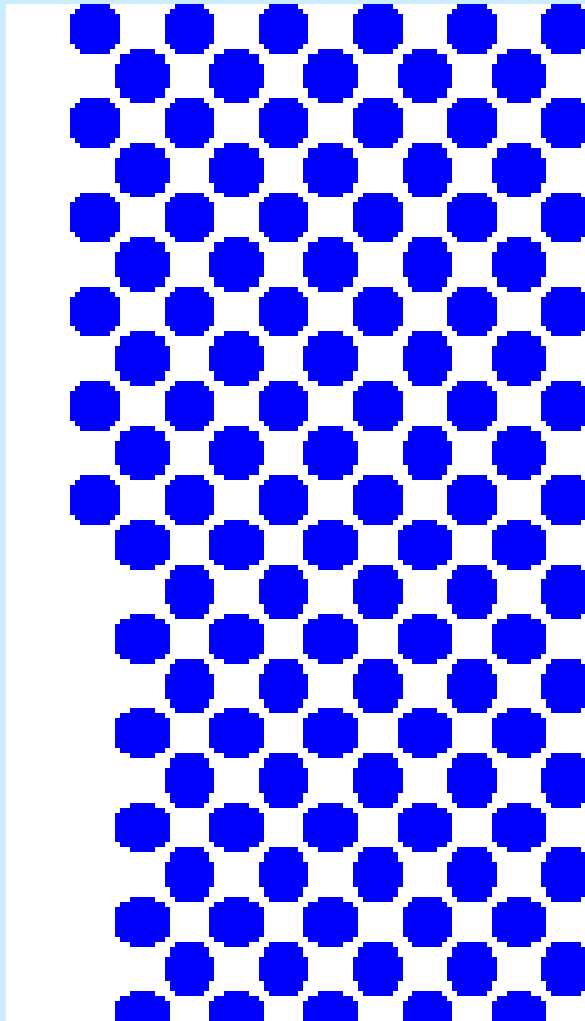
Mechanics of Diffusion

- Primarily At Defects
  - Point Defects
  - Line Defects
  - Edge Defects
- Through Interstitial Spaces

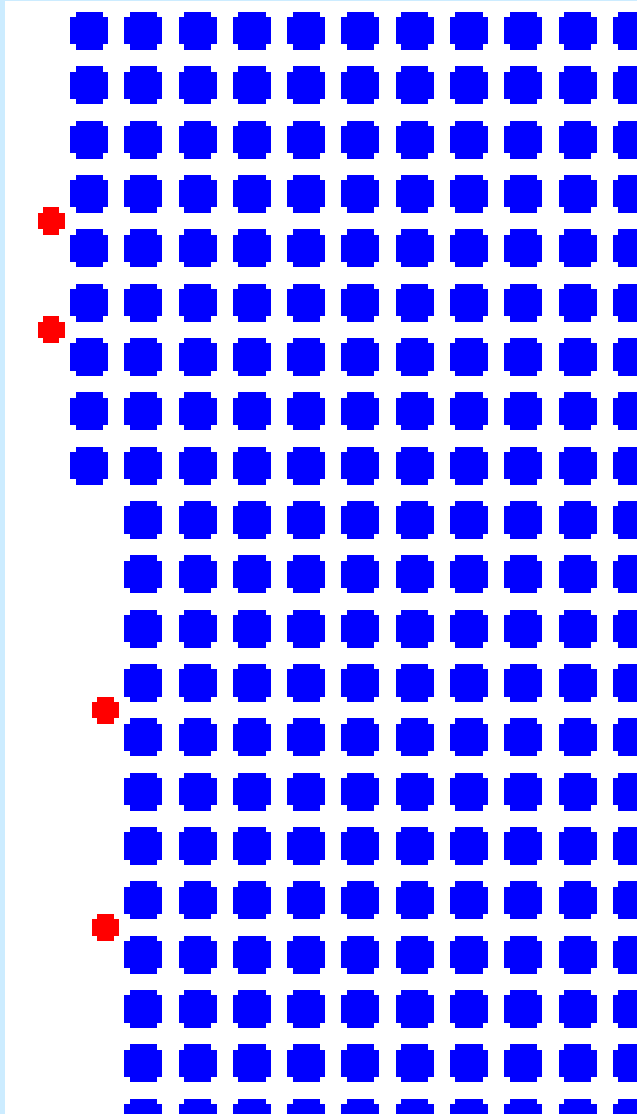Interstitial   Substitutional
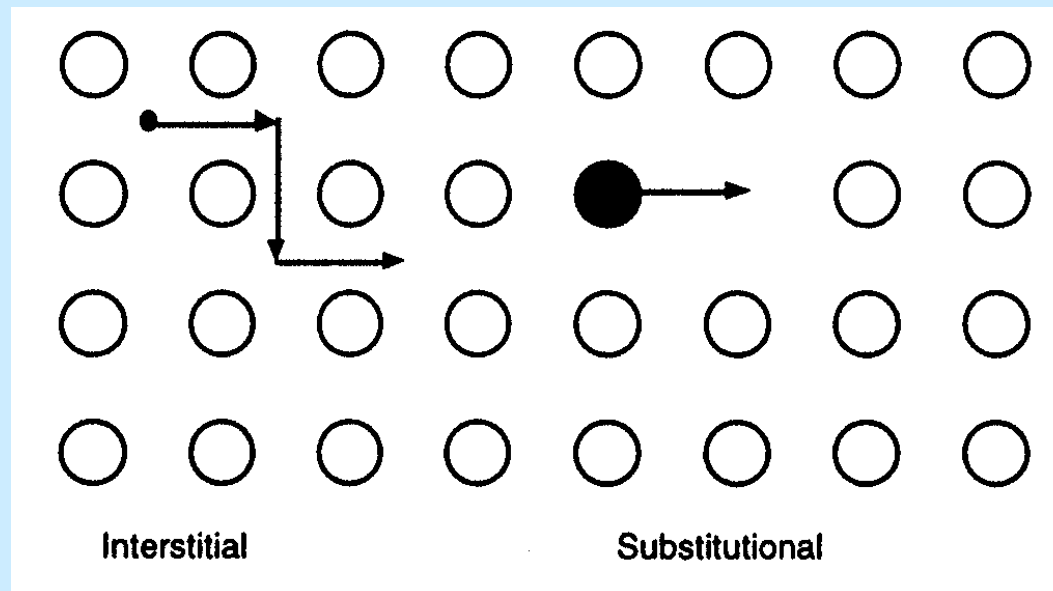
Vacancy Diffusion

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

Interstitial Diffusion

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

Other Mechanisms

- Grain Boundaries

- Surface

Activation Energy

- All the kinds of diffusion 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

Diffusion Rate

- High activation energy corresponds to low diffusion rates
- $D = D_0 * \exp(-Q/RT)$
  - Where D is the diffusivity, which is proportional to the diffusion rate
  - Q is the activation energy
  - R is the gas constant
  - T is the absolute temperature

Diffusivity

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

Diffusivity of Fe and Carbon in Iron