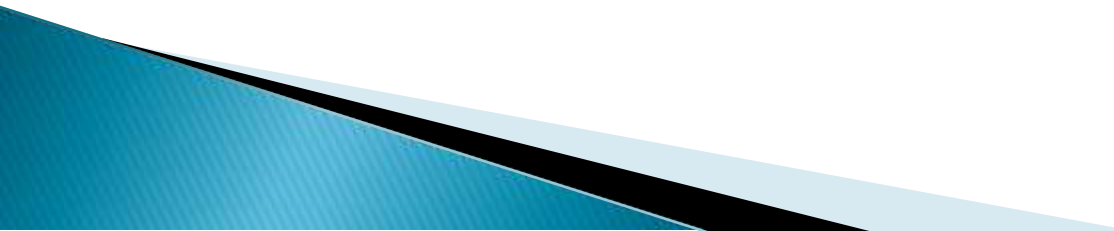# Crystaline defects

By: Assi . Lec
Ihab Adnan Thabet

# INTRODUCTION

A perfect crystal is an idealization; there is no such thing in nature. Atom arrangements in real materials do not follow perfect crystalline patterns. Nonetheless, most of the materials that are useful in engineering are crystalline to a very good approximation. There is fundamental physical reason for this. The preferred structures of solids at low temperature are those that minimize the energy. The low-energy atomic configurations are almost invariably crystalline since the regular pattern of the crystal lattice repeats whatever local configuration is most favorable for bonding. There is also a fundamental physical reason why the crystal is imperfect. While a perfect crystalline structure may be preferred energetically, at least in the limit of low temperature, atoms are relatively immobile in solids and it is, therefore, difficult to eliminate whatever imperfections are introduced into the crystal during its growth, processing or use.
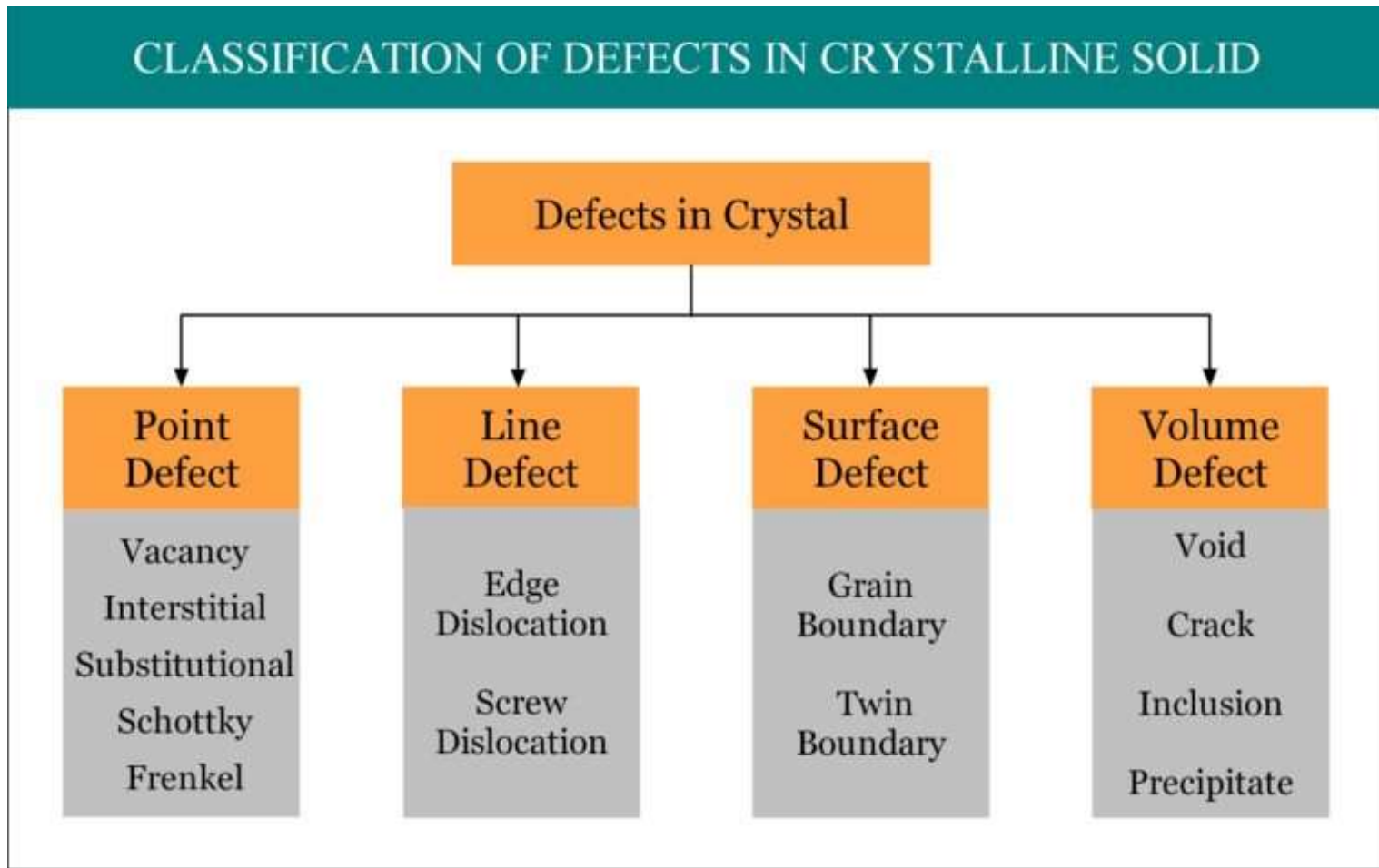
# Various crystal defects
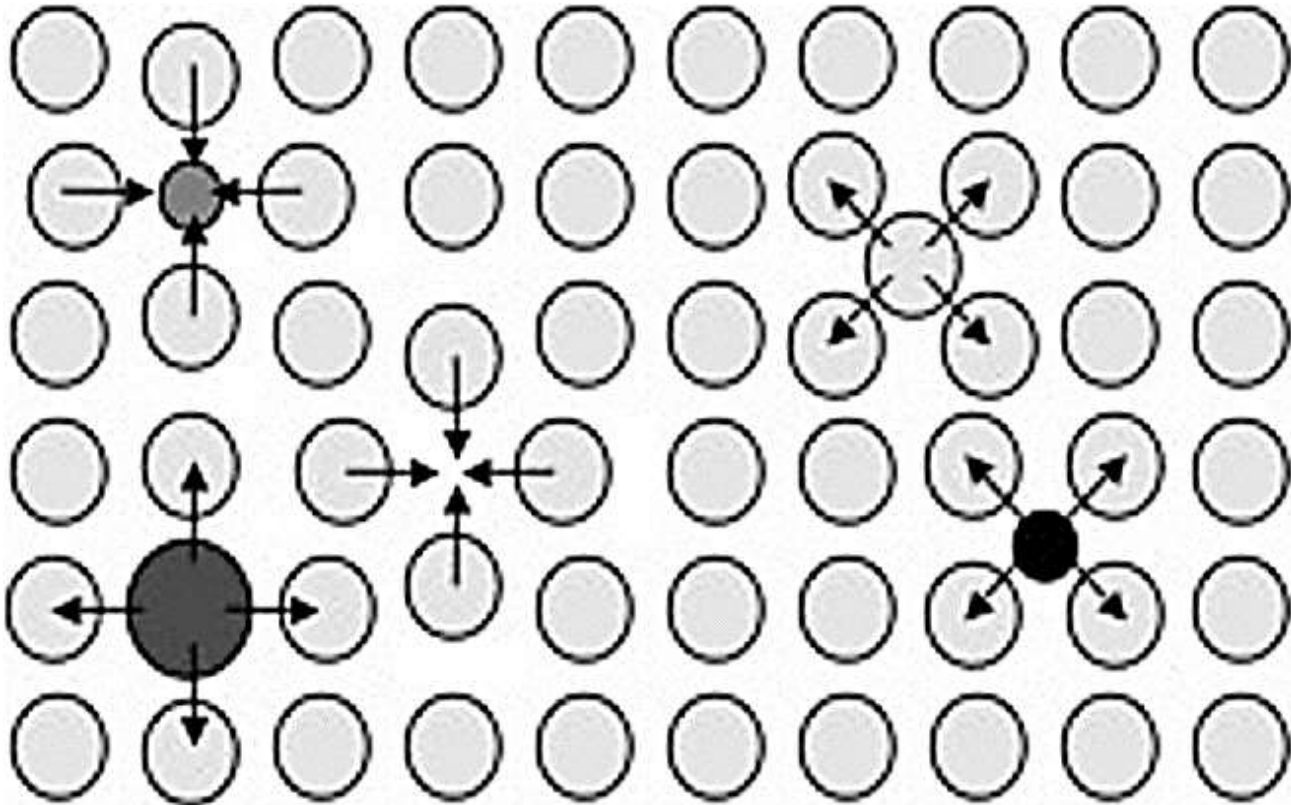


Various Crystal Defects
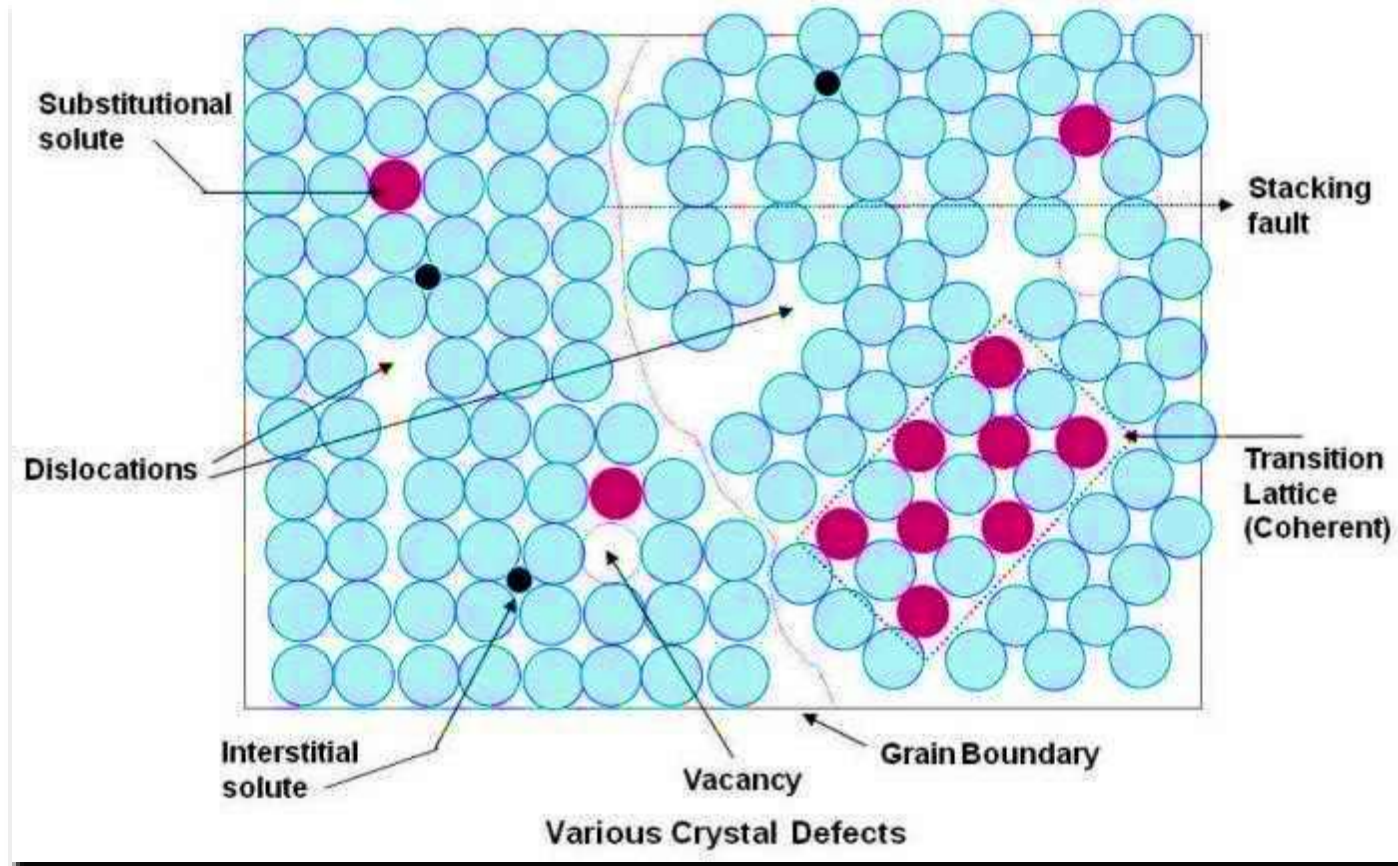
# WHY STUDY Imperfections in Solids?

- The properties of some materials are profoundly influenced by the presence of imperfections. Consequently, it is important to have a knowledge about the types of imperfections that exist and the roles they play in affecting the behavior of materials. For example, the mechanical properties of pure metals experience significant alterations when alloyed. Adding alloying elements to a metal is one way of introducing a crystal defect.

- Crystal imperfections have strong influence upon many properties of crystals, such as strength, electrical conductivity and hysteresis loss of ferromagnets. Thus some important properties of crystals are controlled by as much as by imperfections and by the nature of the host crystals.

# Types of Crystalline Defects

## CLASSIFICATION OF DEFECTS IN CRYSTALLINE SOLID

Defects in Crystal

| Point Defect | Line Defect | Surface Defect | Volume Defect |
|---|---|---|---|
| Vacancy | Edge Dislocation | Grain Boundary | Void |
| Interstitial | | | Crack |
| Substitutional | Screw Dislocation | Twin Boundary | Inclusion |
| Schottky | | | Precipitate |
| Frenkel | | | |

# Point defects

# Point defects

**<u>Intrinsic point defects</u> :**

The presence of intrinsic point defects is related to the nature of the atom. Atoms in a solid are subject to thermal vibrations at any temperature. The average amplitude of the atomic displacements increases with increasing temperature. Therefore, it is easy to imagine a localized area within the crystal where the vibrations are intense enough to cause a single atom to jump to a different location, either to the surface of the crystal or to an intermediate or interstitial position within the crystal. If the atom moves to the surface of the crystal, a Schottky defect is said to have formed, leaving a vacancy as the defect. However if the atom jumps to an interstitial position within the crystal lattice, it is said to have formed a Frenkel defect, creating both a vacancy and a self-interstitial.

# Point defects

This leads to the conclusion that the imperfect crystal has a lower free energy than a perfect crystal. From thermodynamics, we know that the change in the free energy of a system, $\Delta G$, is related to the changes in enthalpy, $\Delta H$, and entropy, $\Delta S$, as shown in Eq, where T is absolute temperature:

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

# Point defects

The energy to form a defect, $E_D$, is a positive contribution to the enthalpy term, thus increasing the free energy of the system. However, the creation of the defect increases the disorder of the crystal, thus increasing the entropy of the system and causing a decrease in the free energy of the system. The balance of these two factors leads to an equilibrium number of defects naturally occurring within the crystalline lattice. Through calculating the minimum free energy condition as a function of temperature, Boltzmann determined that the equilibrium number of defects, ne, can be written according to Eq.

$$n_e = NA \exp\left(\frac{-E_D}{k_b T}\right)$$

, where $N$ is the number of atoms
in the crystal, A is a constant often taken as unity, T is the absolute temperature, and $k_b$ is Boltzmann's constant. By dividing $n_e$ by $N$, the equilibrium concentration of defects, $n_e$, may be found.

# Concentration:Point defects

• varies with temperature!

No. of defects

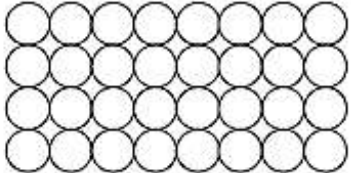Activation energy

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)$$

No. of potential defect sites.

Each lattice site is a potential vacancy site

Boltzmann's constant

Temperature

$(1.38 \times 10^{-23}$ J/atom K$)$

$(8.62 \times 10^{-5}$ eV/atom K$)$

Activation energies may also be quoted in J per mole, or cal/mol, then the product of Boltzmann's constant and Avogadro's constant is to be used in order to consider single atoms
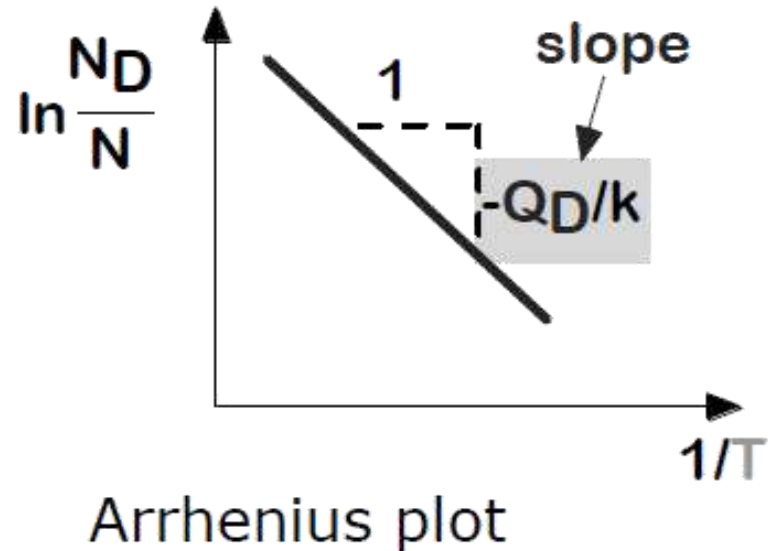
# Measuring Activation Energy

- We can get Q from an experiment.

- Measure this...

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)$$

- Replot it...



defect concentration
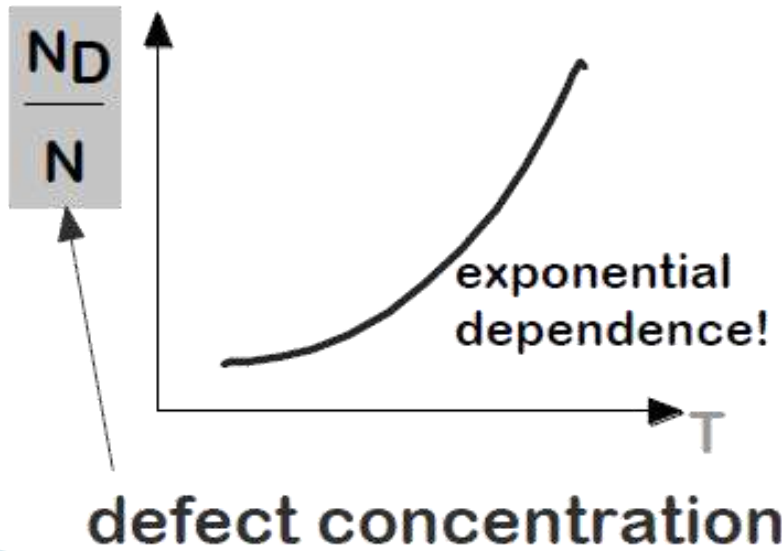
Arrhenius plot

# Intrinsic point defects

## **Vacancies**

A vacancy is produced when an atom or an ion is missing from its normal site in the crystal structure, as in Figure. When atoms or ions are missing (i.e., when vacancies are present), the overall randomness or entropy of the material increases, which increases the thermodynamic stability of a crystalline material.
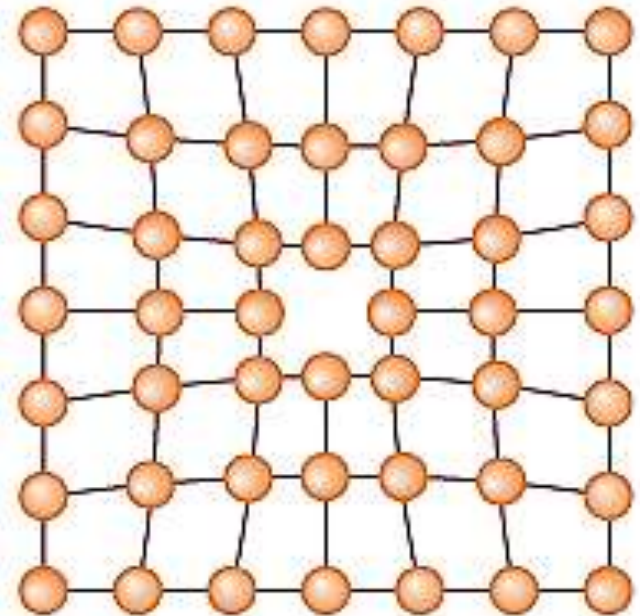
# Vacancies

- All crystalline materials have vacancy defects. Vacancies are introduced into metals and alloys during solidification, at high temperatures, or as a consequence of radiation damage. Vacancies play an important role in determining the rate at which atoms or ions can move around, or diffuse in a solid material, especially in pure metals.

- In some other applications, we make use of the vacancies created in a ceramic material to tune its electrical properties. At room temperature (~300 K), the concentration of vacancies is small, but the concentration of vacancies increases exponentially as we increase the temperature, as shown by the following Arrhenius type behavior

# Vacancies

$$n_v = n \exp\left(\frac{-Q_v}{RT}\right)$$

$n_v$ is the number of vacancies per cm$^3$;

$n$ is the number of atoms per cm$^3$;

$Q_v$ is the energy required to produce one mole of vacancies, in cal/mol or Joules/mol ;

R is the gas constant, (1.987 cal / mol – K) or (8.31 Joules / mol – K) ;and

T is the temperature in degrees Kelvin.

# Vacancies

The probability that a given site is vacant is proportional to the Boltzmann factor for thermal equilibrium:

$$P = \exp(-E_V/k_B T),$$

Where $E_V$ is the energy required to take an atom from a lattice site inside the crystal to a lattice site on the surface. If there are N atoms, the equilibrium number n of vacancies is given by the Boltzmann factor :
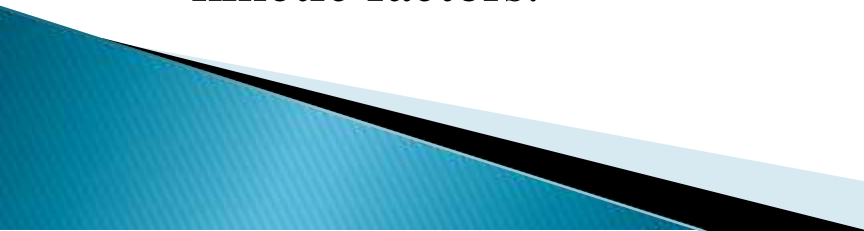
$$\frac{n}{N-n} = \exp(-E_V/k_B T) \ .$$

If $n \ll N$, then

$$n/N \cong \exp(-E_V/k_B T) \ .$$

If $E_V \approx 1$ eV and $T \approx 1000$ K, then $n/N \approx e^{-12} \approx 10^{-5}$.

# Vacancies

- Due to the large thermal energy atoms have near the melting temperature of a material, there may be as many as one vacancy per 1000 atoms. Note that this equation provides for equilibrium concentration of vacancies at a given temperature.

- It is also possible to retain a non-equilibrium concentration of vacancies produced at a high temperature by quenching the material rapidly. Thus, in many situations the concentration of vacancies observed at room temperature is not the equilibrium concentration predicted by Equation.

- Vacancies trapped in the structure may be one thousand times greater than the equilibrium number of vacancies at room temperature. Thus, vacancy concentrations encountered in relatively pure materials are often dictated by both the thermodynamic and kinetic factors.

# Estimating Vacancy Concentration

**Q/** Find equilibrium of vacancies in $1m^3$ of Cu at 1000 °C.

- Given:

$$\rho = 8.4 \text{ g/cm}^3 \qquad A_{Cu} = 63.5 \text{g/mol}$$

$$Q_V = 0.9 \text{eV/atom} \quad N_A = 6.02 \times 10^{23} \text{ atoms/mole}$$

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right) = 2.7 \cdot 10^{-4}$$

0.9eV/atom

1273K

8.62 x $10^{-5}$ eV/atom-K

For $1m^3$, $N = \rho \times \dfrac{N_A}{A_{Cu}} \times 1m^3 = 8.0 \times 10^{28}$ sites

- Answer:

$$N_D = 2.7 \cdot 10^{-4} \cdot 8.0 \times 10^{28} \text{ sites} = 2.2 \times 10^{25} \text{ vacancies}$$

# Vacancies

## The Effect of Temperature on Vacancy Concentrations

Calculate the concentration of vacancies in copper at 25°C. What temperature will be needed to heat treat copper such that the concentration of vacancies produced will be 1000 times more than the equilibrium concentration of vacancies at room temperature? Assume that 20,000 cal are required to produce a mole of vacancies in copper.

## SOLUTION

The lattice parameter of FCC copper is 0.36151 nm. The basis is 1, therefore, the number of copper atoms, or lattice points, per $cm^3$ is:

$$n = \frac{4 \text{ atoms/cell}}{(3.6151 \times 10^{-8} \text{ cm})^3} = 8.47 \times 10^{22} \text{ copper atoms/cm}^3$$

At 25°C, $T = 25 + 273 = 298$ K:

$$n_v = n \exp\left(\frac{-Q_v}{RT}\right)$$

$$= \left(8.47 \times 10^{22} \frac{\text{atoms}}{\text{cm}^3}\right) \cdot \exp\left(\frac{-20{,}000 \frac{\text{cal}}{\text{mol}}}{1.987 \frac{\text{cal}}{\text{mol} - \text{K}} \times 298 \text{ K}}\right)$$

$$= 1.815 \times 10^8 \text{ vacancies/cm}^3$$

# Vacancies

We wish to find a heat treatment temperature that will lead to a concentration of vacancies which is 1000 times higher than this number, or $n_v = 1.815 \times 10^{11}$ vacancies/cm$^3$.

We could do this by heating the copper to a temperature at which this number of vacancies forms:

$$n_v = 1.815 \times 10^{11} = n \exp\left(\frac{-Q_v}{RT}\right)$$

$$= (8.47 \times 10^{22}) \exp(-20,000/(1.987 \times T))$$

$$\exp\left(\frac{-20,000}{1.987 \times T}\right) = \frac{1.815 \times 10^{11}}{8.47 \times 10^{22}} = 0.214 \times 10^{-11}$$

$$\frac{-20,000}{1.987T} = \ln(0.214 \times 10^{-11}) = -26.87$$

$$T = \frac{20,000}{(1.987)(26.87)} = 375 \text{ K} = 102°\text{C}$$

# Intrinsic point defects

**Interstitial Defects**

An interstitial defect is formed when an extra atom or ion is inserted into the crystal structure at a normally unoccupied position, as in Figure.
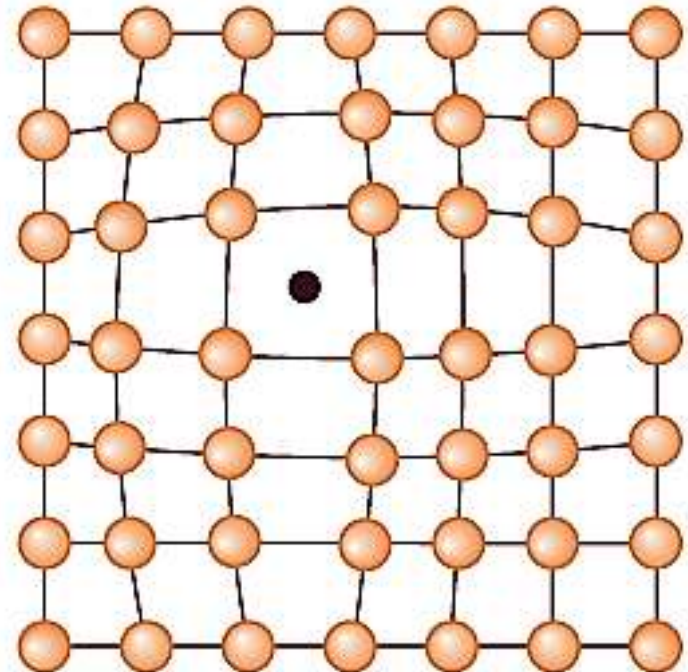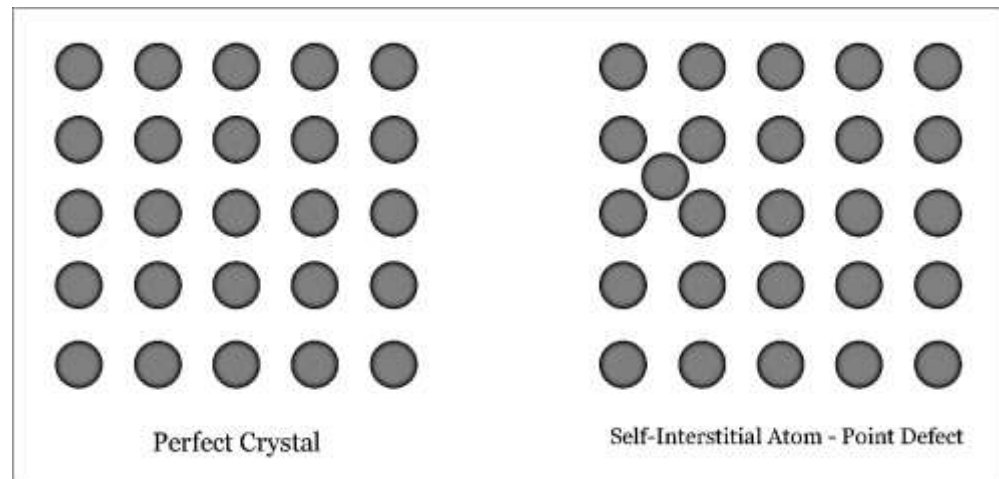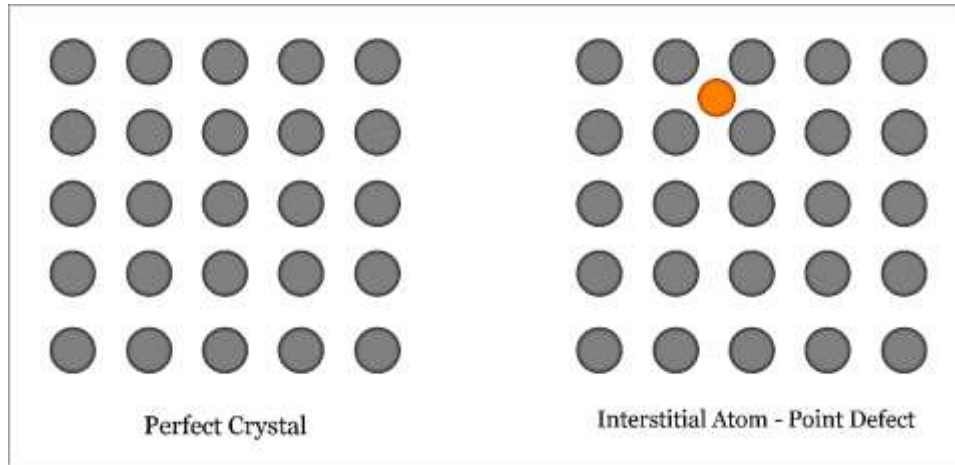
# Interstitial Defects

- Interstitial atoms or ions, although much smaller than the atoms or ions located at the lattice points, are still larger than the interstitial sites that they occupy. Consequently, the surrounding crystal region is compressed and distorted.

- interstitial defect can be of two types:

<u>Self-Interstitial Defect</u>: occurs when atom of the same crystalline solid occupies the interstitial position leaving its original lattice site.
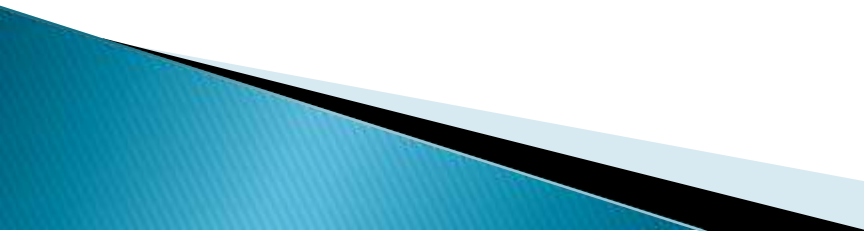
<u>Interstitial Defect</u>: occurs when a foreign atom occupies the interstitial position.

# Interstitial Defects

Perfect Crystal

Interstitial Atom - Point Defect

Perfect Crystal

Self-Interstitial Atom - Point Defect

# Interstitial Defects

**Effects of interstitial defects:**

- Although an extra atom occupies the empty interstitial space, the atom's size is typically more than that of the space. As a result, the atoms in the vicinity are squeezed and deformed.

- The presence of a large number of interstitial atoms can alter the solid's mechanical and thermal properties. However, this might be advantageous at times, and so interstitial flaws can be used in a regulated manner to improve certain aspects of the solid.

- A sufficient number of interstitial atoms can help in changing an electrically non-conductive material into a conductive one.

# Interstitial Defects

**Q/** Calculate the equilibrium number of vacancies per cubic meter for copper at 1000°C. The energy for vacancy formation is 0.9 eV/atom; the atomic weight and density (at 1000°C) for copper are 63.5 g/mol and 8.4 g/cm³, respectively.

*Solution*

to determine the value of $N$, the number of atomic sites per cubic meter for copper, from its atomic weight $A_{Cu}$, its density $\rho$, and Avogadro's number $N_A$, according to

$$N = \frac{N_A \rho}{A_{Cu}} = \frac{(6.023 \times 10^{23} \text{ atoms/mol})(8.4 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{63.5 \text{ g/mol}}$$

$$= 8.0 \times 10^{28} \text{ atoms/m}^3$$

Thus, the number of vacancies at 1000°C (1273 K) is equal to

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

$$= (8.0 \times 10^{28} \text{ atoms/m}^3) \exp\left[-\frac{(0.9 \text{ eV})}{(8.62 \times 10^{-5} \text{ eV/K})(1273 \text{ K})}\right]$$

$$= 2.2 \times 10^{25} \text{ vacancies/m}^3$$

# Schottky & Frenkel defects

**Schottky defect** it is one type of Point Defect that occurs in ionic crystals. Schottky defect occurs when oppositely charged atoms (cation and anion) leave their corresponding lattice sites and create a pair of Vacancy Defects. Since both cation and anion leave the lattice sites at the same time, so overall electrical neutrality of the crystal is maintained; however, density reduces because of the vacancies.

**Frenkel Defect** is one type of Point Defect; in fact, it is a combination of both Vacancy and Interstitial type of point defects. Usually, this type of defect is observed in ionic solids, where size of anion is substantially larger than the size of cation. Basically, a Frenkel Defect is one type of point defect where an atom (better to say ion, especially cation) leaves its original lattice site and occupies an interstitial position on the same crystal. When an atom leaves the original lattice site then Vacancy Defect is created. Alternatively, when an atom (of same crystal or foreign crystal) occupies the interstitial site then Interstitial Defect is created. Since, in Frenkel Defect, one atom leaves the original lattice site and occupies an interstitial site in the same crystal, so Frenkel Defect is a pair of Vacancy & Self-interstitial Defects. The following image depicts a typical crystal with Frenkel Defect.

# Frenkel & Schottky defects
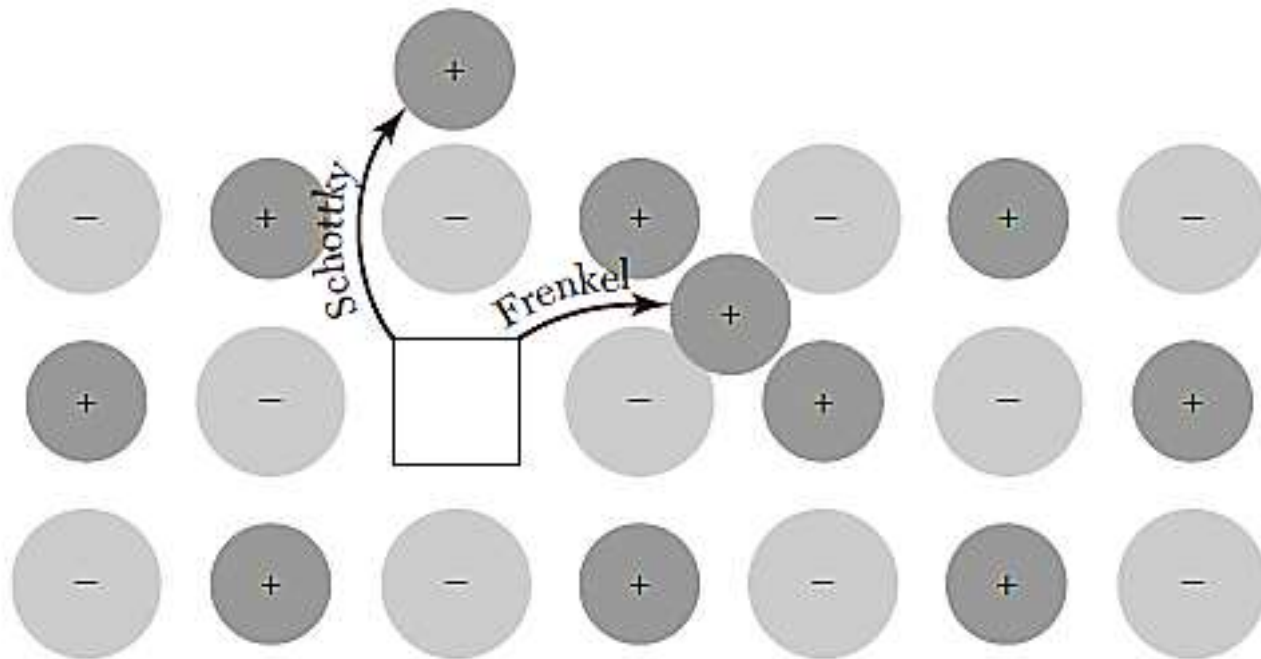
# Frenkel defects

**characteristics of the Frenkel Defect**

- The lattices formed in a Frenkel Defect are relatively open.
- The Frenkel Defect occurs when the size of cations is smaller in comparison to the anions.
- The coordination number of a solid-state in the Frenkel Defect is low.
- The Frenkel Defect does not change the chemical properties of a substance.
- Frenkel Defect has no impact on the density of the structure, therefore it preserves the mass and volume of the solid.
- Substances maintain their electrical neutrality in the undertaking of the Frenkel Defect.
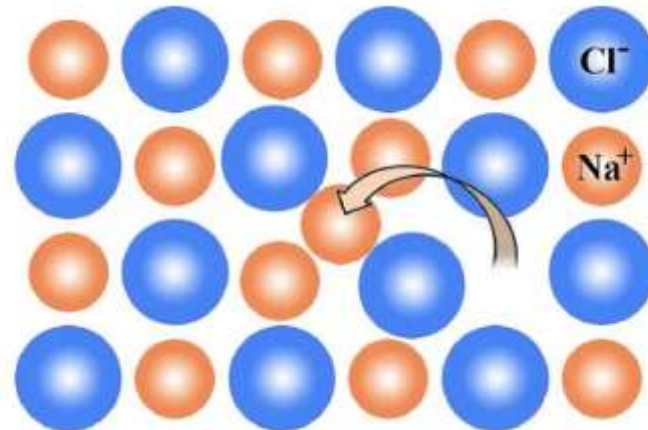
# Frenkel defects

**The formula for calculating the Frenkel defect is given by:**

$$n = \sqrt{NN'}\, e^{\frac{\Delta H}{2RT}}$$

Where,

N= Normally occupied positions   ,   N'= Number of available positions

$\Delta H$= One Frenkel Defect's enthalpy formation

R = Gas constant   ,   T = Temperature

n of Frenkel defects is much smaller than the number of lattice sites N and the number of interstitial sites N', the result is:

$$n = (NN')^{1/2} \exp(-E_I / 2kBT)$$

where $E_I$ is the energy necessary to remove an atom from a lattice site to an interstitial position. Lattice vacancies

# Schottky defects

**What are the Characteristics of Schottky Defect?**
•There is a small difference between the size of the anion and cation.
•Usually, two vacancies are formed.
•Anion and Cation both leave the solid crystal at the same time.
•Atoms also move out of the crystal permanently.
•The density of the solid reduces considerably.
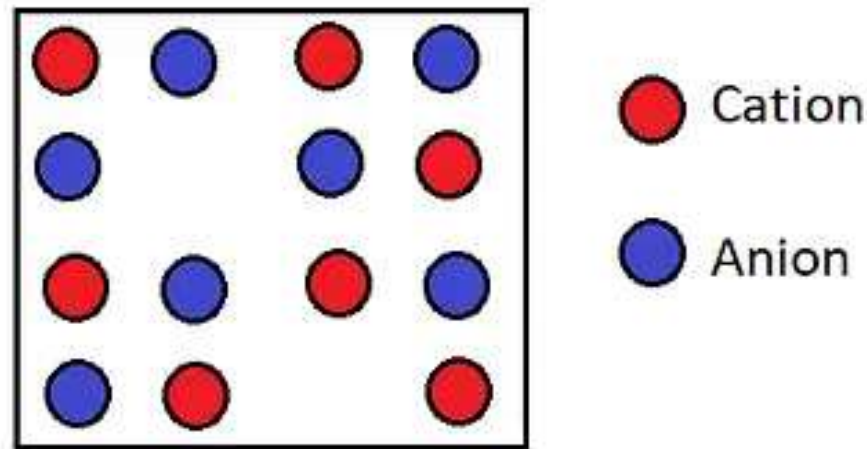


Schottky defect

# Schottky defects

**<u>Schottky Defect Formula :</u>**
Schottky defects are formed by applying heat to the solid crystal. At a given temperature, following formula can be used for calculating Schottky Defect:

$$n_s \approx N \, exp \left( \frac{-\Delta H_s}{2RT} \right)$$

Where,
$n_s$ = number of Schottky defects per unit volume at temperature T (in Kelvins)
$\Delta H_s$ = Enthalpy for creating one defect.
R = Gas constant
T = Absolute temperature (in K)
N can be computed by using the following formula:

$$\mathbf{N} = \frac{Density of the ionic crystal compound \times NA}{Molar mass of the Ionic Crystal Compound}$$

# Schottky defects

In ionic crystals it is usually energetically favorable to form roughly equal numbers of positive and negative ion vacancies. The formation of pairs of vacancies keeps the crystal electrostatically neutral on a local scale. From a statistical calculation we obtain:

$$n \cong N \exp(-E_p/2k_B T)$$

for the number of pairs, where $E_p$ is the energy of formation of a pair.

# Schottky defects

The number of Vacancies with a positive charge ($n_c$) is equal to the number of Vacancies with a negative charge ($n_a$), meaning that:

$n_c = n_a = n$

The $\omega_c$ probabbility of the different ways in which a positive ion can be removed and expelled out of the crystal to be replaced by a positive vacacies is given by the mathematical relationship:

$$\omega_c = \frac{N(N-1)(N-2)...(N-n_c+1)}{n_c!} = \frac{N!}{(N-n_c)!\,n_c!}$$

In the same way, the probability $\omega_a$ of extracting a negative ion and expelling it outside the crystal to replace it with a negative vacancy is given by the following relationship:

$$\omega_a = \frac{N(N-1)(N-2)...(N-n_a-1)}{n_a!} = \frac{N!}{(N-n_a)!\,n_a!}$$

# Schottky defects

The total probability that a pair of positive and negative vacancies can be formed is:

$$\omega = \omega_c \, \omega_a$$

From the above equations, we find that:

$$\omega = \left[ \frac{N!}{(N-n)!\,n!} \right]^2$$

The occurrence of voids inside the crystal leads to a change in the free energy (H) of Helmholtz, which in turn depends on the change of both the enthalpy E and the entropy S, as mentioned in the equation:

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

Where: E is the internal energy of the crystal

T is the absolute temperature

S entropy in relation:

$$S = k_B \, ln \, \omega$$

# Schottky defects

Where: $K_B$ is the Boltzmann constant

   $\omega$ is the probability

Increasing the number of vacancy formed leads to an increase in entropy, and therefore entropy can be calculated from the relationship:

$$\therefore S = k_B \, ln\left[\frac{N!}{(N-n)!n!}\right]^2$$

What is meant by internal energy here is the formation energy of pair vacancies it is symbolized by $E_P$, and therefore the formation energy is defined as the energy required to form a pair of positive and negative vacancies. Since the occurrence of n pairs of vacancies, the internal energy can be written instead of the formation energy:

$$E = n\, E_P$$

Substituting the above equations into each other:

$$H = nE_P - k_B T \, ln\left[\frac{N!}{(N-n)!n!}\right]^2$$

# Schottky defects

Using stirling's formula:

$$Ln\ x! = x\ lnx - x$$

so

$$ln\left[\frac{N!}{(N-n)!\,n!}\right]^{2} = 2[NlnN-(N-n)\ ln\ (N-n)-n\ ln\ n]$$

By Substituting we get

$$H = nE_{P} - 2K_{B}T\,[\,N\ ln\ N - (N-n)\ ln\,(N-n) - n\ ln\ n\,]$$

If the temperature of the crystal rises from T1 to T2, the number of vacancies will gradually increase to a point where the increase stops, i.e. the vacancies reach the saturation limit, and this means that the number of vacancies becomes a constant quantity in the case of thermal equilibrium, and the first derivative of the free energy in relation to the number of vacancies is equal to zero.

# Schottky defects

$$\therefore \frac{dH}{dn} = 0 = E_P - 2k_B T [ \ln ( N - n ) - \ln n$$

$$\frac{N - n}{n} = e^{E_P / 2k_B T}$$

And since the number of vacancies in the crystal is usually much smaller than the number of ions in the crystal, that is, n<<N on it, (n) can be neglected from the numerator so that the equation becomes as follows:

$$\boxed{n = N e^{- E_P / 2k_B T}}$$

The equation is called the **Schottky equation**

# Frenkel defects

Suppose that the crystal consists of (N) number of atoms. When an atom is displaced from its position to an interstitial site, it will work to create a vacancy, so the number of vacancies ($n_v$) will be equal to the number of interstitial atoms ($n_i$), meaning that:

$$n_v = n_i = n$$

We suppose that the interstitial atom can occupy one site out of the total number ($N_i$) of the interstitial sites, the probability ($\omega_v$) of the different methods of displacing an atom from its original position to replace it with a vacancy is:

$$\omega_v = \frac{N!}{(N - n_v)! \, n_v!}$$

The probability ($\omega_i$) of the different ways that the interstitial atom can occupy in ($N_i$) sites is:

$$\omega_i = \frac{N_i!}{(N_i - n_i)! \, n_i!}$$

The total probability ($\omega$) with which vacancy-interstitial atom pairs can be formed is:

$$\omega = \omega_v \, \omega_i$$

# Frenkel defects

Substituting the equations together, we get:

$$\omega = \frac{N!}{(N-n)!\,n!} \cdot \frac{N_i!}{(N_i-n)!\,n!}$$

The occurrence of vacancy- interstitial atom pairs inside the crystal leads to a change in the free energy (H) of Helmholtz, which in turn depends on the change of both the internal energy E and the entropy S, which was mentioned in an equation previously. The change in entropy can be calculated from the following equation:

$$S = k_B \ln\left[\frac{N!}{(N-n)!\,n!} \cdot \frac{N_i!}{(N_i-n)!\,n!}\right]$$

The internal energy E in Frenkel defects is represented by the Frenkel formation energy $E_i$, which is defined as the energy required to move an atom from its original position to an interstitial site. Since the occurrence of (n) vacancy-interstitial atom pairs is, the internal energy can be written in terms of the formation energy, that is:

$$E = n\,E_i$$

# Frenkel defects

Substituting the two equations above, we get:

$$H = nE_i - k_B T \ln \left[ \frac{N!}{(N-n)!n!} \cdot \frac{N_i!}{(N_i-n)!n!} \right]$$

Using stirling's formula we get :

$$H = nE_i - k_B T \left( N \ln N + N_i \ln N_i - (N-n) \ln (N-n) - (N_i - n) \ln (N_i - n) - 2n \ln n \right]$$

In the case of thermal equilibrium, the first derivative of the free energy with respect to the number (n) is zero:

$$\therefore \frac{dH}{dn} = 0 = E_i - k_B T \ln \frac{(N-n)(N_i-n)}{n^2}$$

$$\frac{(N-n)(N_i-n)}{n^2} = e^{E_i / k_B T}$$

And when (n) is much smaller than (N) and also much smaller than ($N_i$), then (n) can be neglected from the numerator to become the equation

# Frenkel defects

Substituting the two equations above, we get:

$$\frac{NN_i}{n^2} = e^{E_i / k_B T}$$

$$n^2 = NN_i\, e^{-\dfrac{E_i}{2k_B T}}$$

$$n = \sqrt{NN_i}\; e^{-\dfrac{E_i}{2k_B T}}$$

The equation is called the **Frenkel equation**

# Frenkel defects & Schottky defects

| Schottky defect | Frenkel defect |
|---|---|
| It occurs when the atoms are totally missing from the crystal lattice. | It occurs when the atoms are just displaced from their position to some voids or interstitial sites of the crystal lattice. |
| It generally occurs in crystal lattice where the size ratio of cation and anion is nearly 1 | It occurs generally in the lattice where the size ratio of cation and anion is large |
| In this, both the cation and the anion leave the lattice, thus ensuring that the overall crystal is neutral. | In this, only the smaller ion is displaced. Cation is smaller and so it gets displaced in interstitial sites. |
| Two atoms are removed from the lattice for 1 single defect | Number of atoms remain same before and after the defect. |
| Thus,there is decrease in the density of the crystal | Thus,the density of the crystal is unaffected |
| Two vacancies are created when 1 pair of ions are removed | One vacancy is created and one interstitial site is occupied |
| Eg NaCl, KCl, KBr | Eg ZnS, AgCl, AgBr |

# Point defects

## **Extrinsic point defects :**

Extrinsic point defects, are caused by an outside source, such as growth conditions or processing factors. They are created when a foreign atom embeds itself within the crystal. If the atom is located on a lattice site, i.e. replacing the native atom, then it is called a substitutional impurity. The foreign atom may also be located at an interstitial site, and is thus termed an interstitial impurity.

# Extrinsic point defects

**Substitutional Defects** A substitutional defect is introduced when one atom or ion is replaced by a different type of atom or ion as in Figures. The substitutional atoms or ions occupy the normal lattice sites. Substitutional atoms or ions may either be larger than the normal atoms or ions in the crystal structure, in which case the surrounding interatomic spacings are reduced, or smaller causing the surrounding atoms to have larger interatomic spacings. In either case, the substitutional defects alter the interatomic distances in the surrounding crystal. Again, the substitutional defect can be introduced either as an impurity or as a deliberate alloying addition, and, once introduced, the number of defects is relatively independent of temperature.

# Substitutional Defects
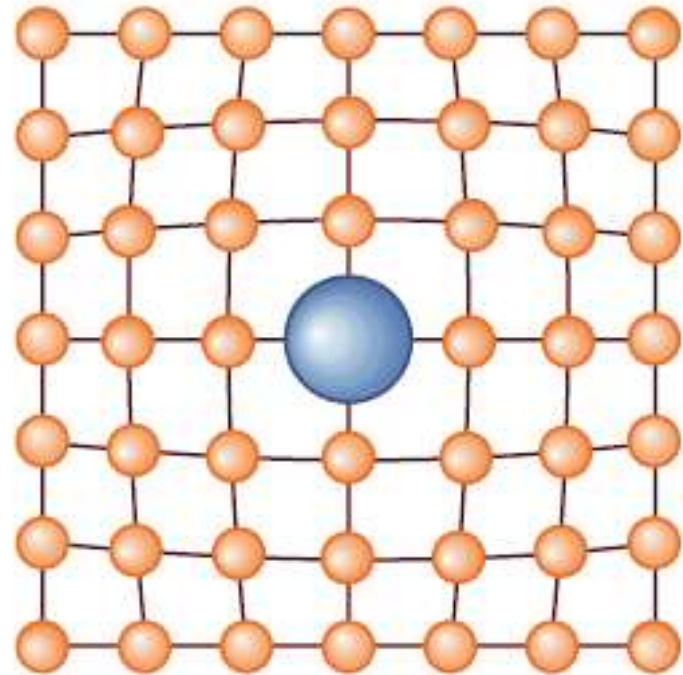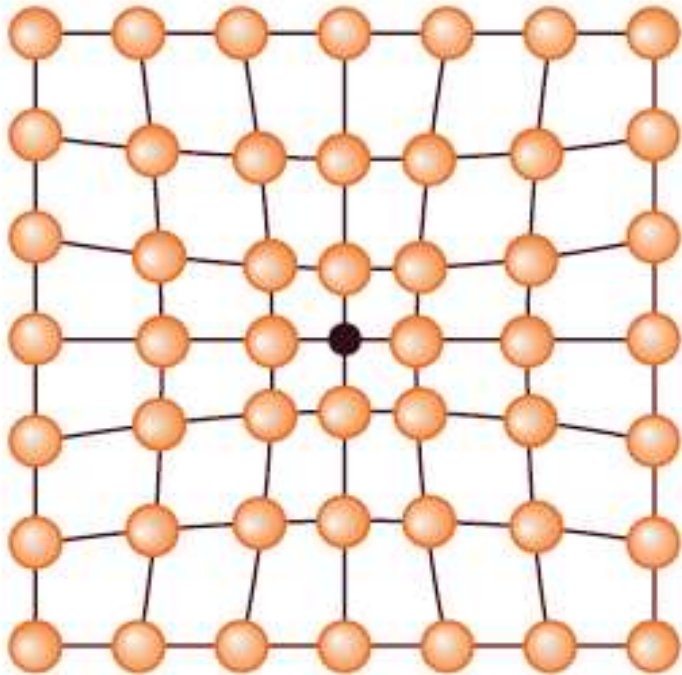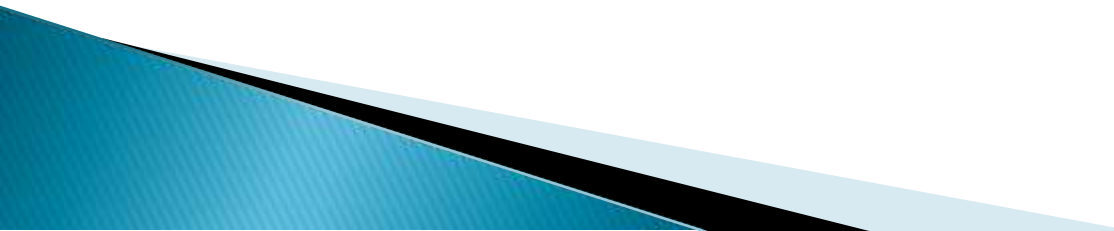
# Extrinsic point defects

**Where Substitutional defects can be found?**

- Substitutional defects can be found in brass, where zinc atoms replace copper atoms.
- In semiconductor materials also.

**Causes of Substitutional defect in solids:**

- Presence of foreign atoms as natural impurities within the solid.
- Deliberate addition, such as during iron to steel conversion, heat treatment, sputtering, etc.
- Diffusion, caused by close contact between two different materials.

# Extrinsic point defects

**Effects of Substitutional defects in solids:**

- If the foreign atom is smaller in size as compared to the original atom of the solid, the neighboring atoms will remain in tensile stress.

- If the foreign atom is larger in size as compared to the original atom of the solid, the neighboring atoms will remain in compressive stress.

- So, presence of foreign atom may distort the original lattice structure

- Presence of substantial number of foreign atoms can change the mechanical and thermal properties of the solid. However, this is sometime beneficial, and thus substitutional defects can be applied in a controlled way to enhance various properties of the solid.

# Linear defects

- In linear defects groups of atoms are in irregular positions. Linear defects are commonly called dislocations. Any deviation from perfectly periodic arrangement of atoms along a line is called the line imperfection. In this case, the distortion is centered only along a line and therefore the imperfection can be considered as the boundary between two regions of a surface which are perfect themselves but are out of register with each other. The line imperfection acting as boundary between the slipped and un-slipped region, lies in the slip plane and is called a dislocation. Dislocations are generated and move when a stress is applied.

- **Dislocations** are line imperfections in an otherwise perfect crystal. They are introduced typically into the crystal during solidification of the material or when the material is deformed permanently. Although dislocations are present in all materials, including ceramics and polymers, they are particularly useful in explaining deformation and strengthening in metallic materials. to extreme types of dislocations are distinguish as :

1. Edge dislocations
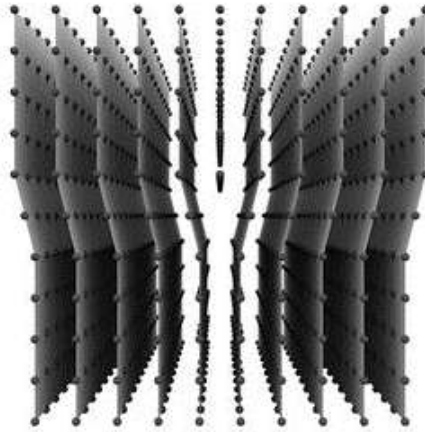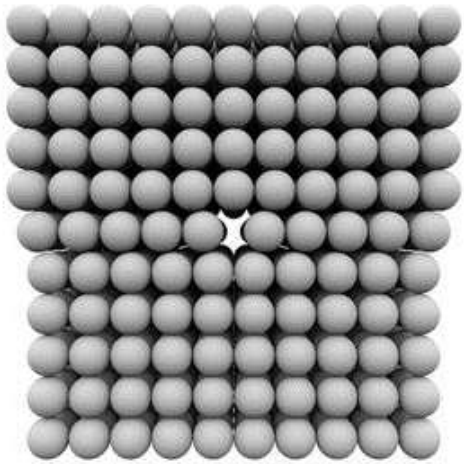2. Screw dislocations
3. mixed dislocation

# Linear defects

**Screw Dislocations** the screw dislocation can be illustrated by cutting partway through a perfect crystal, then skewing the crystal one atom spacing. If we follow a crystallographic plane one revolution around the axis on which the crystal was skewed, starting at point x and traveling equal atom spacing's in each direction, we finish one atom spacing below our starting point (point y). The vector required to complete the loop and return us to our starting point is the **Burgers vector b**. If we continued our rotation, we would trace out a spiral path. The axis, or line around which we trace out this path, is the screw dislocation.

The magnitude and direction of the lattice distortion associated with a dislocationis expressed in terms of a **Burgers vector**

**Edge Dislocations** An edge dislocation can be illustrated by slicing partway through a perfect crystal, spreading the crystal apart, and partly filling the cut with an extra plane of atoms.
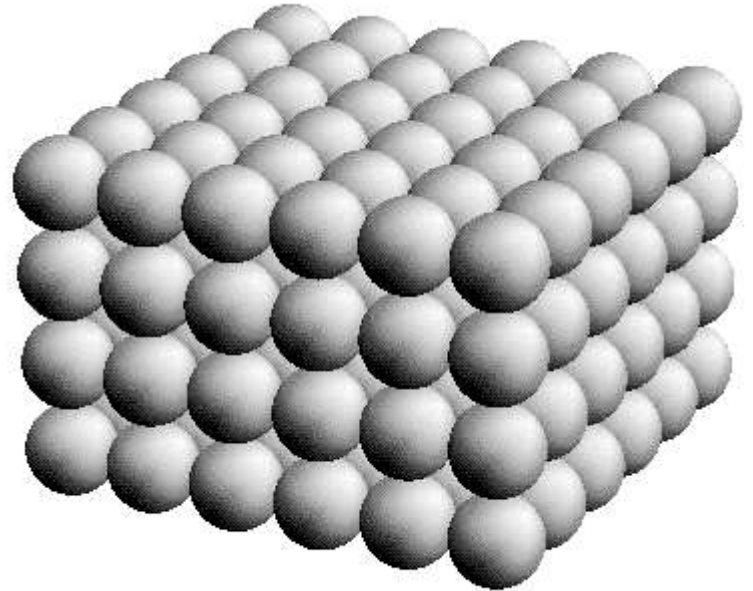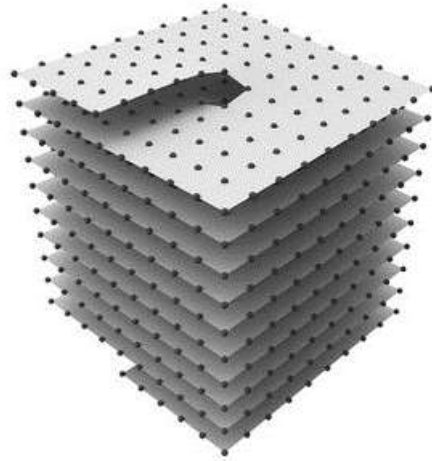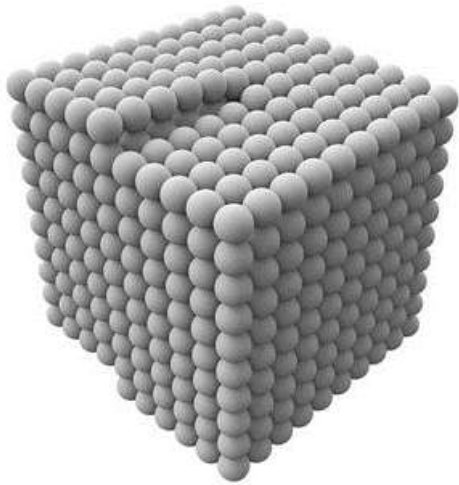
# Linear defects



Edge
dislocation
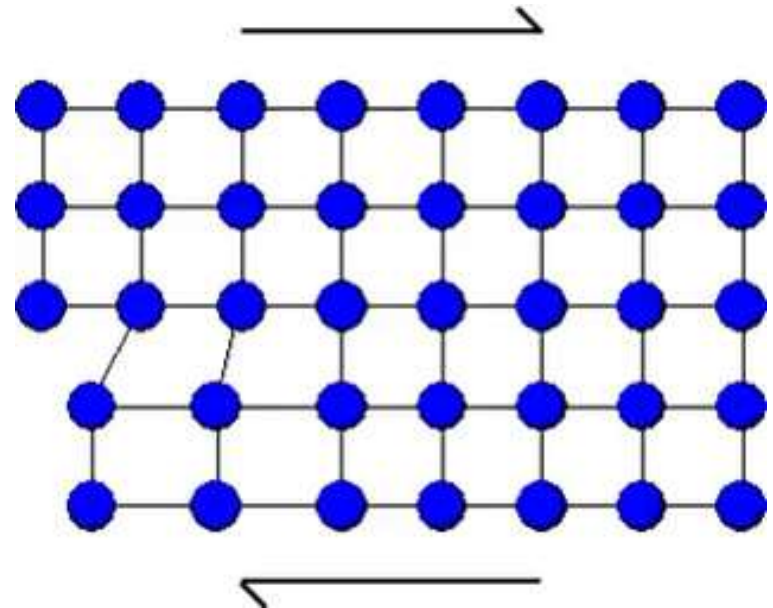
# Linear defects

# Linear defects

The bottom edge of this inserted plane represents the edge dislocation. If we describe a clockwise loop around the edge dislocation, starting at point x and going an equal number of atoms spacings in each direction, we finish, at point y, one atom spacing from the starting point. The vector required to complete the loop is, again, the Burgers vector. In this case, the Burgers vector is perpendicular to the dislocation. By introducing the dislocation, the atoms above the dislocation line are squeezed too closely together, while the atoms below the dislocation are stretched too far apart. The surrounding region of the crystal has been disturbed by the presence of the dislocation. Unlike an edge dislocation, a screw dislocation cannot be visualized as an extra half plane of atoms.

**Mixed Dislocations** mixed dislocations have both edge and screw components, with a transition region between them. The Burgers vector, however, remains the same for all portions of the mixed dislocation.

# Linear defects

(a) Schematic representation of a dislocation that has edge, screw, and mixed character.
(b) Top view, where open circles denote atom positions above the slip plane. Solid circles, atom positions below.
At point A, the dislocation is pure screw, while at point B, it is pure edge. For regions in between where there is curvature in the dislocation line, the character is mixed edge and screw.
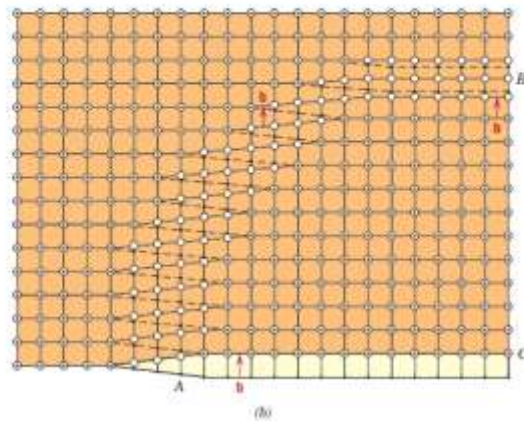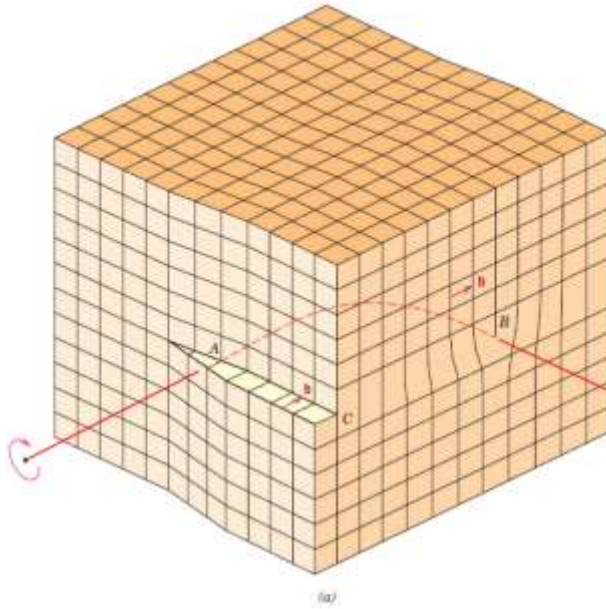
(a) A screw dislocation within a crystal.
(b) The screw dislocation in (a) as viewed from above. The dislocation line extends along line AB. Atom positions above the slip plane are designated by open circles, those below by solid circles.
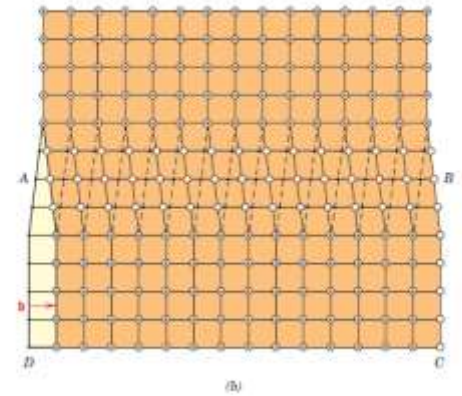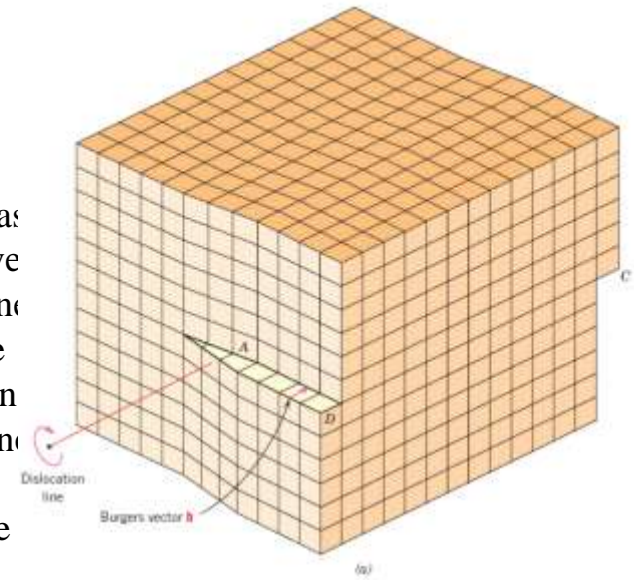
# Linear defects

**Slip** The process by which a dislocation moves and causes a metallic material to deform is called slip. The direction in which the dislocation moves, the slip direction, is the direction of the Burgers vector for edge dislocations. During slip, the edge dislocation sweeps out the plane formed by the Burgers vector and the dislocation. This plane is called the slip plane. The combination of slip direction and slip plane is the slip system. A screw dislocation produces the same result; the dislocation moves in a direction perpendicular to the Burgers vector, although the crystal deforms in a direction parallel to the Burgers vector. The Peierls-Nabarro stress is required to move the dislocation from one equilibrium location to another,

$$\tau = c \exp(-kd/b)$$

where $\tau$ is the shear stress required to move the dislocation, $d$ is the interplanar spacing between adjacent slip planes, $b$ is the magnitude of the Burgers vector, and both $c$ and $k$ are constants for the material.

# Linear defects

It is assumed that there is a periodic shearing force required to move the top row of atoms across the bottom row which is given by the

$$\tau = \frac{Gb}{2\pi a}\sin\frac{2\pi x}{b}$$
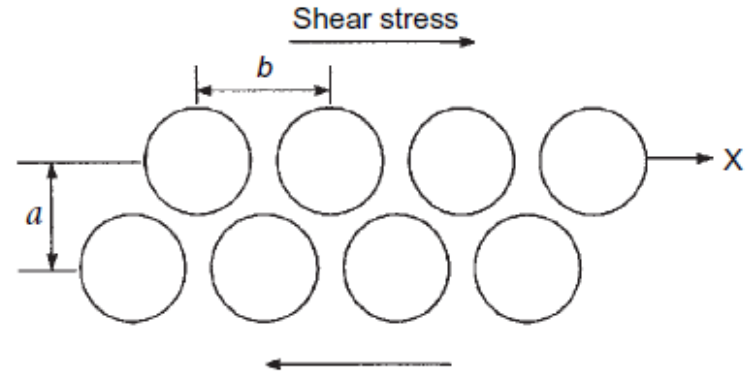
where $\tau$ is the applied shear stress, G is the shear modulus, b the spacing between atoms in the direction of the shear stress, a the spacing of the rows of atoms and x is the shear translation of the two rows away from the low-energy position of stable equilibrium (x=0)

# Linear defects
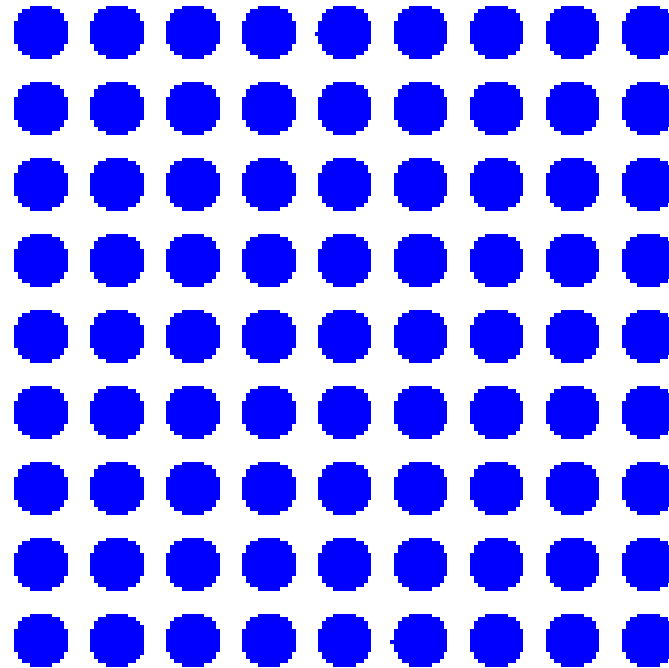
As a first approximation the stress-displacement curve can be written as

$$\tau = \tau_m Sin\left(\frac{2\pi x}{b}\right)$$

At small values of displacement Hooke's law should apply

$$\tau = G\gamma = G\frac{x}{a}$$

$$\Rightarrow \text{For small values of x/b}$$

$$\tau = \tau_m\left(\frac{2\pi x}{b}\right)$$

$$G\frac{x}{a} = \tau_m\left(\frac{2\pi x}{b}\right)$$

Hence the maximum shear stress at which slip should occur

$$\tau_m = \frac{G}{2\pi}\frac{b}{a}$$

If b ~ a

$$\tau_m \square \frac{G}{2\pi}$$

$$\tau_m \simeq \frac{G}{2\pi}$$

➡ ❏ The theoretical shear stress will be in the range 3 – 30 GPa

# Surface defects

are the boundaries, or planes, that separate a material into regions, each region having the same crystal structure but different orientations. Or two-dimensional defects, refer to irregularities in the crystalline lattice that occur across a planar surface of the crystal. These may be due to an internal error in the crystal structure, or interfaces between two different materials, including interfaces with different phases of matter. Include:

1-Internal planar defects

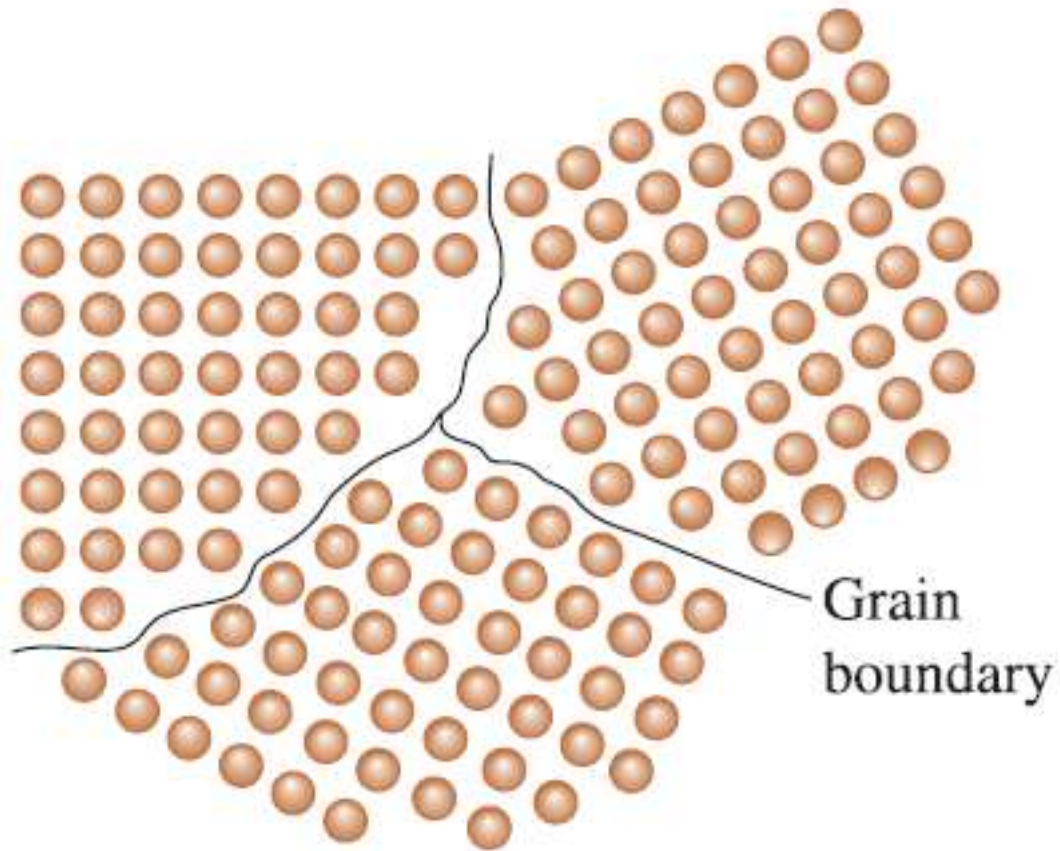- Twin boundaries,

- Grain boundaries,

-  Stacking fault

2-external planar defects

# Surface defects

**Grain Boundaries**

Another type of planer defect is the grain boundary. solids generally consist of a number of crystallites or grains. Grains can range in size from nanometers to millimeters across and their orientations are usually rotated with respect to neighboring grains. Where one grain stops and another begins is known as a grain boundary. Grain boundaries limit the lengths and motions of dislocations. Therefore, having smaller grains (more grain boundary surface area) strengthens a material. The size of the grains can be controlled by the cooling rate when the material cast or heat treated. Generally, rapid cooling produces smaller grains whereas slow cooling result in larger grains. By reducing the grain size, we increase the number of grains and, hence, increase the amount of grain boundary area.

# Grain boundaries



Grain boundary

# Grain boundaries

Any dislocation moves only a short distance before encountering a grain boundary and being stopped, and the strength of the metallic material is increased. The Hall-Petch equation relates the grain size to the yield strength ($\sigma_y$)

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

where d is the average diameter of the grains, and s0 and K are constants for the metal. Recall that yield strength ($\sigma_y$) of a metallic material is the minimum level of stress that is needed to initiate plastic (permanent) deformation.

**Q/** The yield strength of mild steel with an average grain size of 0.05 mm is 20,000 psi. The yield stress of the same steel with a grain size of 0.007 mm is 40,000 psi. What will be the average grain size of the same steel with a yield stress of 30,000 psi? Assume the Hall-Petch equation is valid and that changes in the observed yield stress are due to changes in grain size.

## SOLUTION

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

Thus, for a grain size of 0.05 mm the yield stress is

$$20 \times 6.895 \text{ MPa} = 137.9 \text{ MPa}.$$

(*Note*: 1,000 psi = 6.895 MPa). Using the Hall-Petch equation

$$137.9 = \sigma_0 + \frac{K}{\sqrt{0.05}}$$

For the grain size of 0.007 mm, the yield stress is $40 \times 6.895$ MPa = 275.8 MPa. Therefore, again using the Hall-Petch equation:

$$275.8 = \sigma_0 + \frac{K}{\sqrt{0.007}}$$

Solving these two equations $K = 18.43$ MPa-mm$^{1/2}$, and $\sigma_0 = 55.5$ MPa. Now we have the Hall-Petch equation as

$$\sigma_y = 55.5 + 18.43 \times d^{-1/2}$$

If we want a yield stress of 30,000 psi or $30 \times 6.895 = 206.9$ MPa, the grain size will be 0.0148 mm or 14.8 $\mu$m.
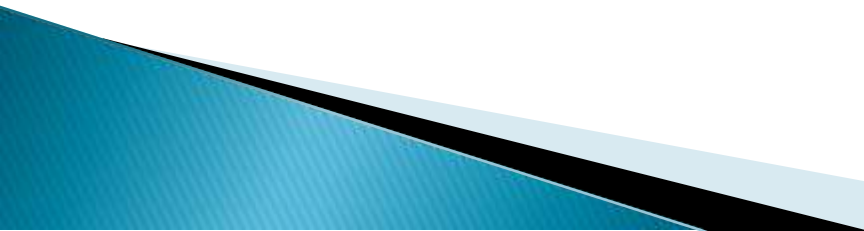
# Twin Boundaries

A **twin boundary** is a plane across which there is a special mirror image misorientation of the crystal structure. Twins can be produced when a shear force, acting along the twin boundary, causes the atoms to shift out of position. Twinning occurs during deformation or heat treatment of certain metals or alloys. The twin boundaries interfere with the slip process and increase the strength of the metal. Movement of twin boundaries can also cause a metal to deform.
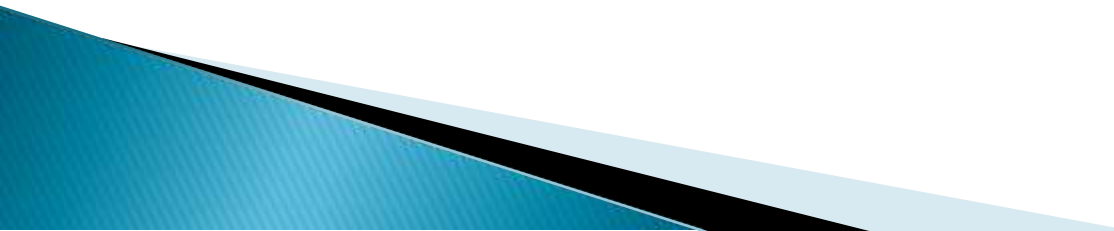


Twin
Boundary    Boundary
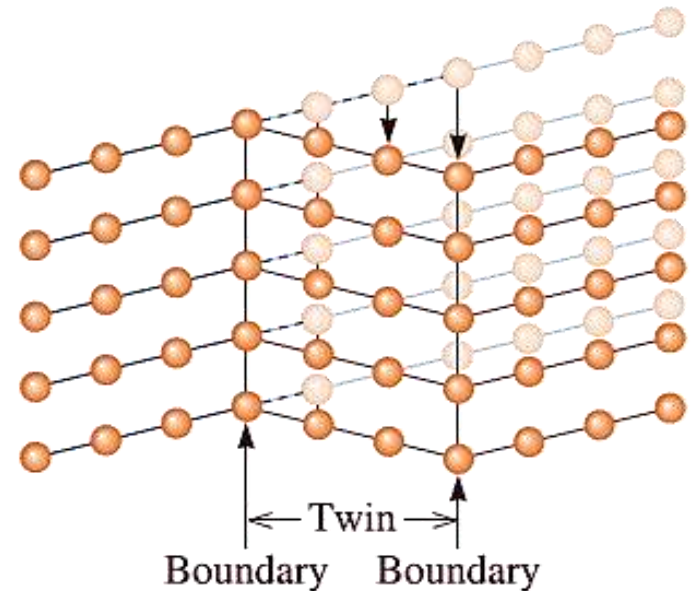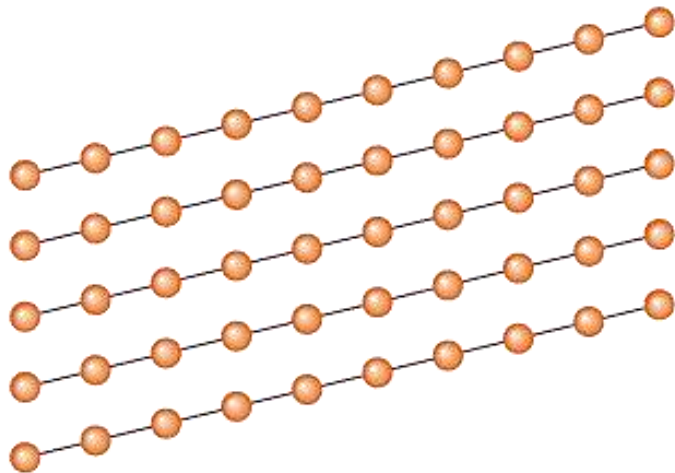
# Volume defects

**Volume defects**, also known as bulk defects, are clusters of point defects. Clusters of defects are produced when the crystal become supersaturated. Each point defect introduced into a crystal has a certain level of solubility, which defines the maximum concentration of the impurity in the host crystal. In general, solubility is temperature dependent and decreases as the crystal is cooled down. When the concentrations of defects exceed their solubility limit or the crystal is cooled down after it gets saturated, it becomes supersaturated with that defect. The crystal under a supersaturated condition tries to achieve an equilibrium condition by condensing the excess defects into clusters with different phase regions.

# Volume defects

- Volume defects are two-dimensional defects
- Volume defects such as cracks may arise in crystals during the process of crystal growth.
- While growing, any possible small electrostatic dissimilarity between the stacking layers may result in crack.
- A large vacancy may arise due to missing of clusters of atoms which is a volume defect.
- Inclusion of foreign particles or non-crystalline regions of dimensions of at least 10-30Å also belong to the category of volume defects.
- Using optical microscopes, presence of volume defects can be detected.
- Interferometric techniques can also be applied to study the volume defects.

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# THANK YOU
## FOR LISTENING