

# CRYSTAL DEFECTS

***A perfect crystal is an idealization; there is no such thing in nature. Atom arrangements in real materials do not follow perfect crystalline patterns***

- What types of defects arise in solids?
- Can the number and type of defects be varied and controlled?
- How do defects affect material properties?
- Are defects undesirable?

# Crystal Defects And Imperfections

*Most real materials have one or more “errors in perfection” with dimensions on the order of an atomic diameter to many lattice sites*

- ❖ The term “**defect**” or “**imperfection**” is generally used to describe any deviation from the perfect periodic array of atoms in the crystal.
- ❖ metals are not perfect neither at the **macro-level** and nor at the **micro-level**
- ❖ contain a number of different types of crystalline defects (at the atomic level)
- ❖ defects are important in many processes e.g. diffusion, deformation

# Many of the important properties of materials are due to the presence of imperfections.

- ☐ The conductivity of some semiconductors is due entirely to trace amount of chemical impurities.
- ☐ Color, luminescence of many crystals arise from impurities and imperfections
- ☐ Atomic diffusion may be accelerated enormously by impurities or imperfections
- ☐ Mechanical and plastic properties are usually controlled by imperfections

**The preferred structures of solids at low temperature are those that minimize the energy.**

- Principles of thermodynamics is used explain the necessity of the existence of vacancies in crystalline solids.

- The Gibbs free energy for the function of vacancies is given by:

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

where  $\Delta H$  is the change in enthalpy and  $\Delta S$  the change in entropy of the reaction and  $T$  is the absolute temperature.

- Vacancy increases  $H$  of the crystal due to energy required to break bonds
- The creation of single point defect in a crystalline solid increases the internal energy of the system and the enthalpy of the defect formation is positive. But the configurational entropy of the system also increases, and the equilibrium concentration of the defects will be reached when the Gibbs energy of the system is at minimum



## Defects can be classification:

1. according to geometry  
(point, line or plane)
2. dimensions of the defect

### ➤ 0D, Point defects:

atoms missing or in irregular places in the lattice (vacancies, interstitials, impurities)

### ➤ 1D, Linear defects:

groups of atoms in irregular positions (e.g. screw and edge dislocations)

### ➤ 2D, Planar defects:

interfaces between homogeneous regions of the material (grain boundaries, external surfaces)

### ➤ 3D, Volume defects:

extended defects (pores, cracks)

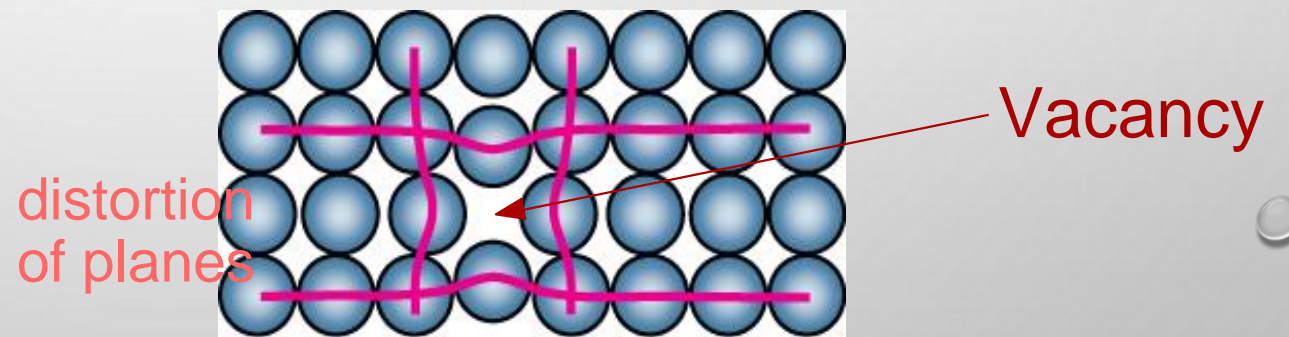
# Point Defects In Metals

- They are imperfect point- like regions, one or two atomic diameters in size and hence referred to as 'zero dimensional imperfections'.
- There are different kinds of point imperfections.

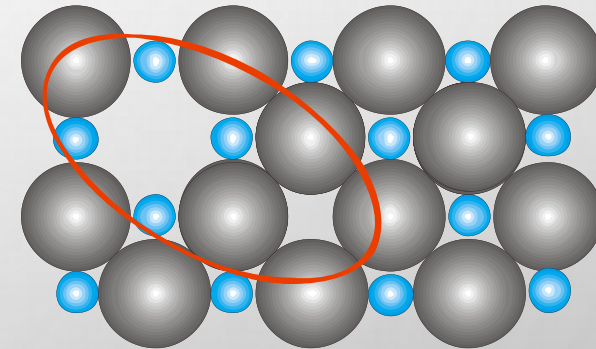
## *First :In Pure metals*

### **Vacancies:**

-vacant atomic sites in a structure.



- In metals vacancies created by thermal excitation.
- When the temperature is sufficiently high, as the atoms vibrate around their regular positions, some acquire enough energy to leave the site completely.
- When the regular atom leaves, migrates through successive steps and eventually settles at the crystal surface. This is called **Schottky imperfection**
- In ionic crystals, a pair of one cation and one anion can be missed from an ionic crystal.
- This type of defect is dominant in alkali halides.



Schottky defect



## Equilibrium Concentration: Point Defects (an Arrhenius model)

- Equilibrium concentration varies with temperature!

No. of defects  $\rightarrow N_v$

No. of potential defect sites  $\rightarrow N$

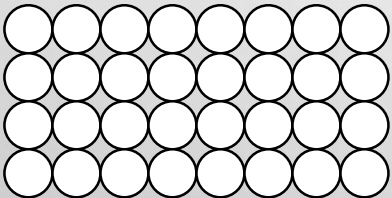
Activation energy (Energy required to form vacancy)  $\rightarrow Q_v$

Boltzmann's constant  $\rightarrow k$

Temperature  $\rightarrow T$

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

Each lattice site is a potential vacancy site



## Example: Estimating vacancy concentration

- Find the equil. # of vacancies in 1 m<sup>3</sup> of Cu at 1000°C.

- Given:

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

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

$$\frac{N_V}{N} = \exp\left(\frac{-Q_V}{kT}\right) = 2.7 \times 10^{-4}$$

Annotations:  $Q_V = 0.9 \text{ eV/atom}$  (red),  $kT = 8.62 \times 10^{-5} \text{ eV/atom-K} \times 1273 \text{ K}$  (green)

For 1 m<sup>3</sup>,  $N = \rho \times \frac{N_A}{A_{\text{Cu}}} \times 1 \text{ m}^3 = 8.0 \times 10^{28} \text{ sites}$

- Answer:

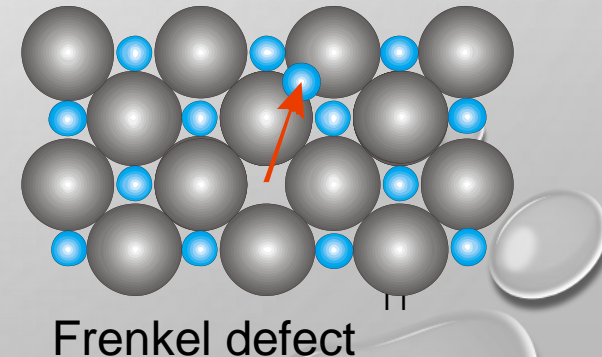
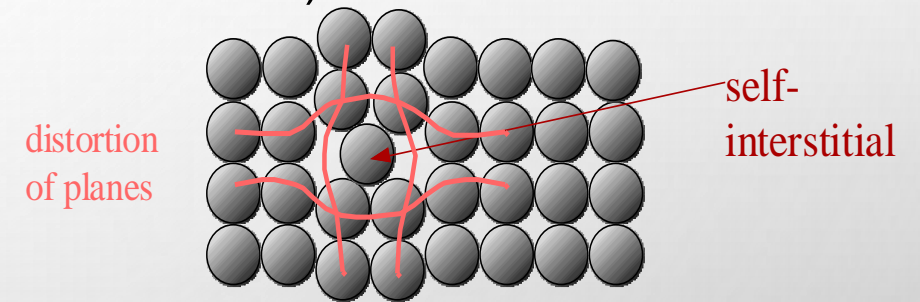
$$N_V = (2.7 \times 10^{-4})(8.0 \times 10^{28}) \text{ sites} = 2.2 \times 10^{25} \text{ vacancies}$$

But at room temperature  $N_V = 7.4 \times 10^7 \text{ vacancies/cm}^3$

## Self-Interstitials:

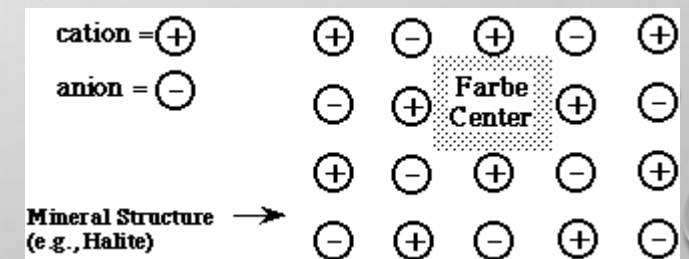
"extra" atoms positioned between atomic sites.

- An interstitial defect arises when an atom occupies a definite position in the lattice that is not normally occupied in the perfect crystal.
- Energy of self-interstitial formation is~ **3 x larger** than for vacancies ( $Q_i \sim 3 \times Q_v$ )  
⇒ equilibrium concentration of self-interstitials is very low( $< 1/ \text{cm}^3$  at 300K)
- In ionic crystals, an ion displaced from a regular site to an interstitial site is called '**Frenkel imperfection**'.
- As cations are generally the smaller ones, it is possible for them to get displaced into the void space.
- Anions do not get displaced as the void space is too small compared to the size of the anions.
- **A Frenkel imperfection** does not change the overall electrical neutrality of the crystal. This type of defect occurs in silver halides and  $\text{CaF}_2$ .



## F-center

- Farbe center or color center is a type of crystallographic defect in which an anionic vacancy in a crystal is filled by one or more unpaired electrons.
- Electrons in such a vacancy tend to absorb light in the visible spectrum such that a material that is usually transparent becomes colored. This is used to identify many compounds, especially zinc oxide (yellow).
- Color centers can occur naturally in compounds (particularly metallic oxides) because when heated to high temperature the ions become excited and are displaced from their normal crystallographic positions, leaving behind some electrons in the vacated spaces.
- The greater the number of F-centers, the more intense is the color of the compound.
- A way of producing F-centers is to heat a crystal in the presence of an atmosphere of the metal that constitutes the material, e.g., **NaCl** heated in a metallic **Na** atmosphere.

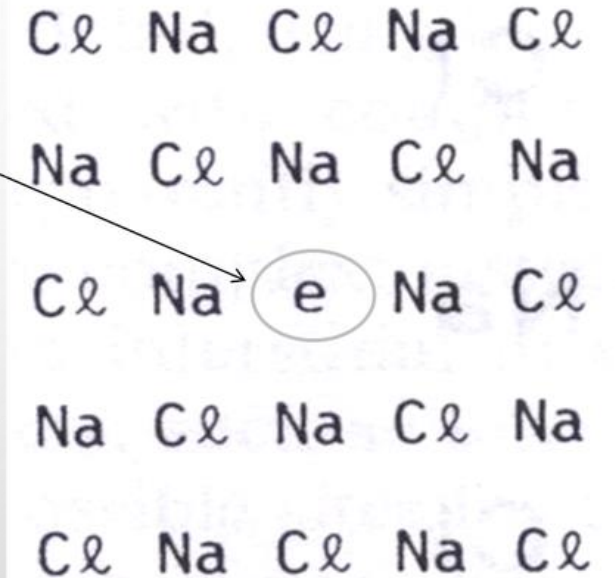




## How does F center happen?

when the crystals are heated in Na vapour, the Na atoms are deposited on the surface of the crystal. The Cl<sup>-</sup> ions diffuse to the surface and combine with Na to give NaCl. This happens by the loss of e<sup>-</sup> by Na atoms to form Na<sup>+</sup> ions. The released e<sup>-</sup> diffuse into the crystal and occupy anionic sites. As a result the crystal has excess of Na. the anionic sites occupied by the unpaired e<sup>-</sup> are called F-Centers

F-center  
(e<sup>-</sup> trapped  
in anionic  
vacancy)



This is the reason that some crystals like lithium chloride, potassium chloride, and zinc oxide become pink, lilac and yellow, respectively on heating them



## Second :In Alloys

Impurities → atoms which differ from host

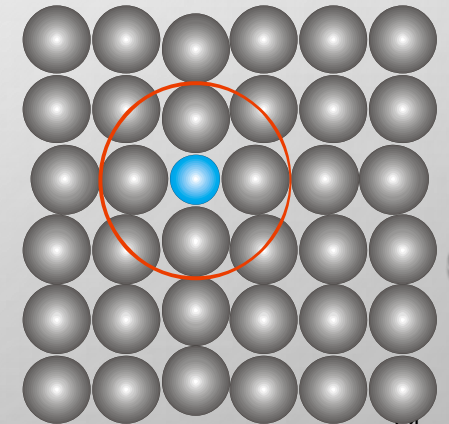
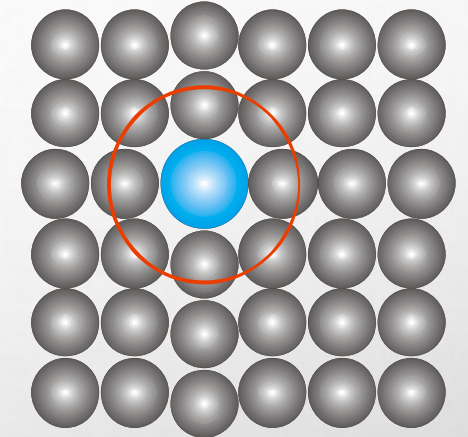
### Substitutional Impurity

Foreign atom replacing the parent atom in the crystal

- E.g. **Cu** sitting in the lattice site of FCC-**Ni**

### Interstitial Impurity

- Foreign atom sitting in the void of a crystal
  - E.g. **C** sitting in the octahedral void in HT FCC-**Fe**



➤ **All real solids are impure.** Very pure metals 99.9999%  
- one impurity per  $10^6$  atoms

➤ **May be intentional or unintentional**

Carbon in small amounts in iron makes steel. It is stronger.  
Boron in silicon change its electrical properties.

➤ **Alloys** - deliberate mixtures of metals

Sterling silver is 92.5% silver – 7.5% copper alloy.  
Stronger than pure silver.

## ***line defects***

- ❑ The defects, which take place due to dislocation or distortion of atoms along a line, in some direction
- ❑ Line defects are also called **dislocations**. In the geometric sense, they may be called as 'one dimensional defects'.
- ❑ A dislocation may be defined as a disturbed region between two substantially perfect parts of a crystal.
- ❑ It is responsible for the phenomenon of slip by which most metals deform plastically.
- ❑ Dislocations strongly affect the mechanical, electronic and photonic properties of materials

### **Dislocation Line:**

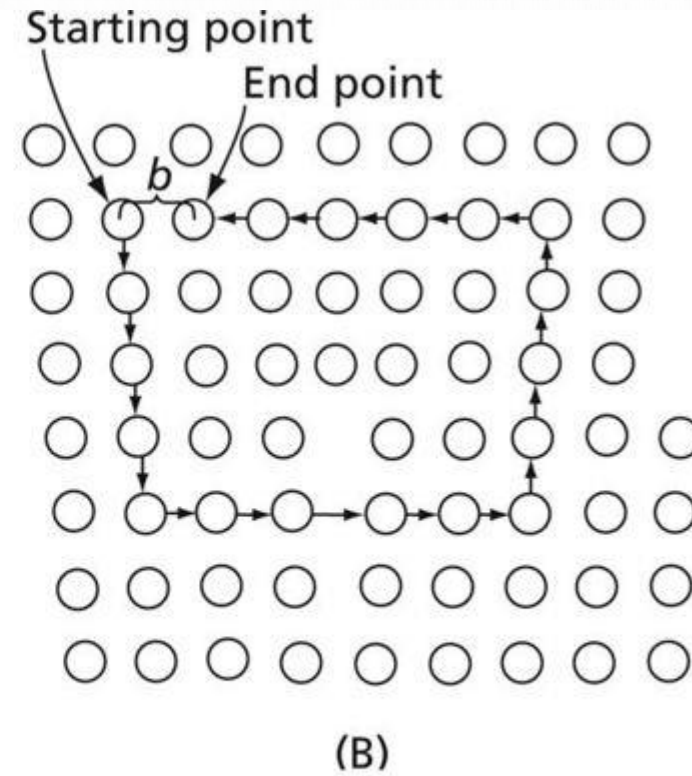
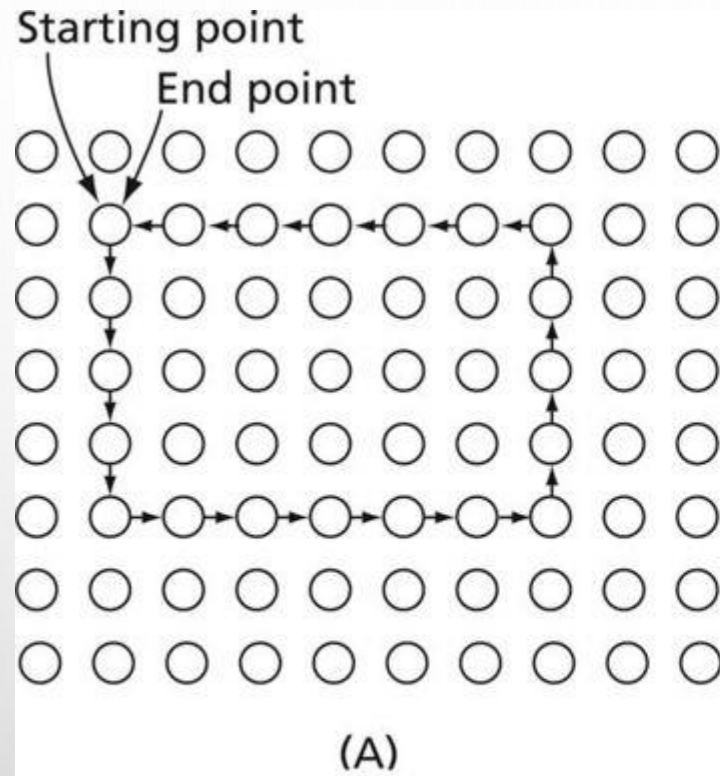
A dislocation line is the boundary between slip and no slip regions of a crystal

### **Burgers vector:**

The magnitude and the direction of the slip is represented by a vector **b** called the Burgers vector,

### **Line vector**

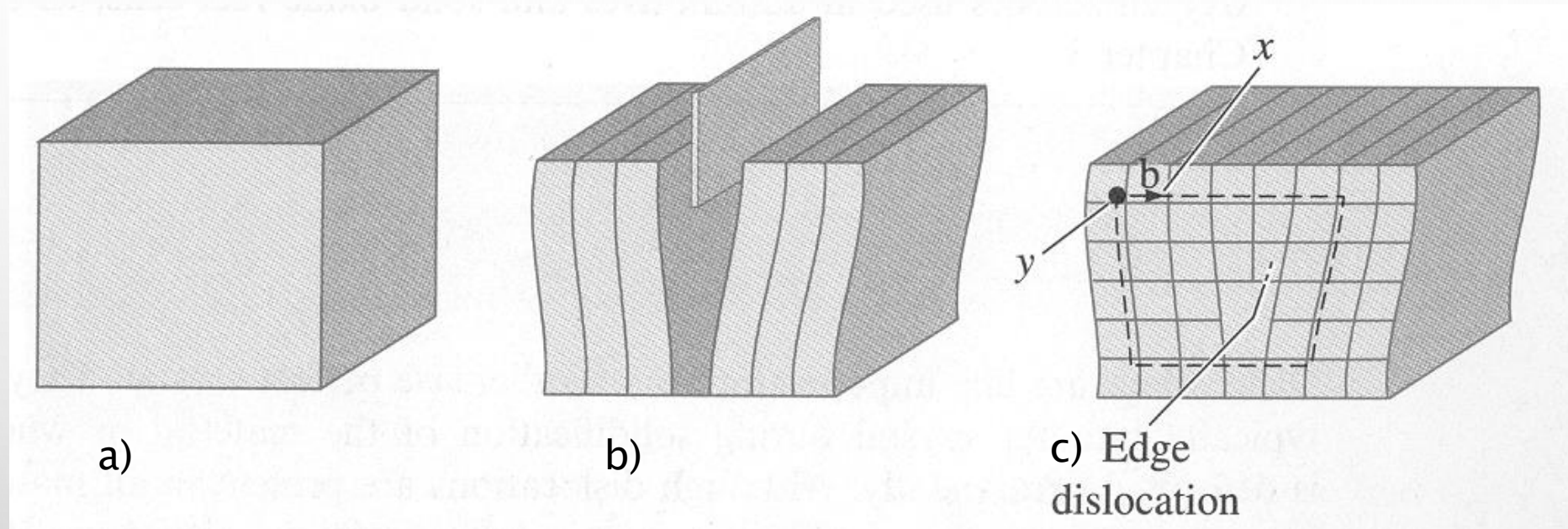
A unit vector **t** tangent to the dislocation line is called a tangent vector or the line vector.



**FIG. 4.19** The Burgers circuit for an edge dislocation: **(A)** Perfect crystal and **(B)** crystal with dislocation



## Edge dislocation

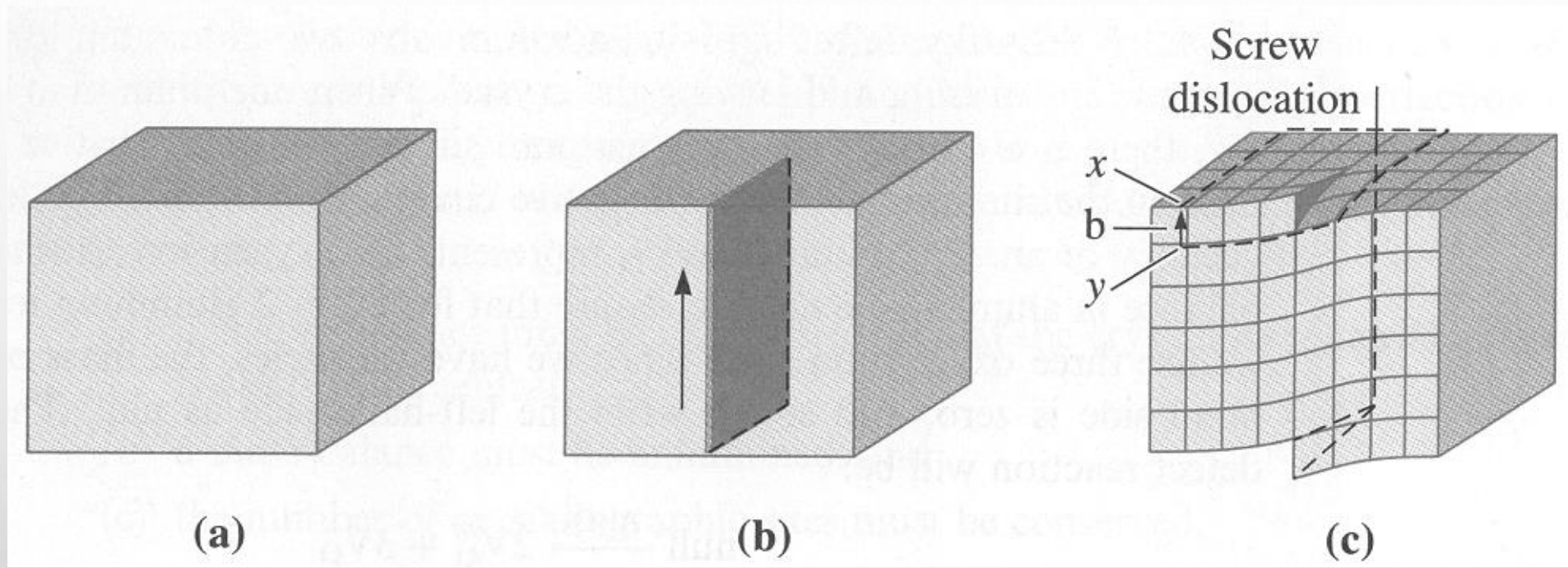


The perfect crystal in a) is cut and an extra plane of atoms is inserted in b). The bottom edge of the extra plane is an edge dislocation in c). A Burgers vector **b** is required to close a loop of equal atom spacing around the edge dislocation.



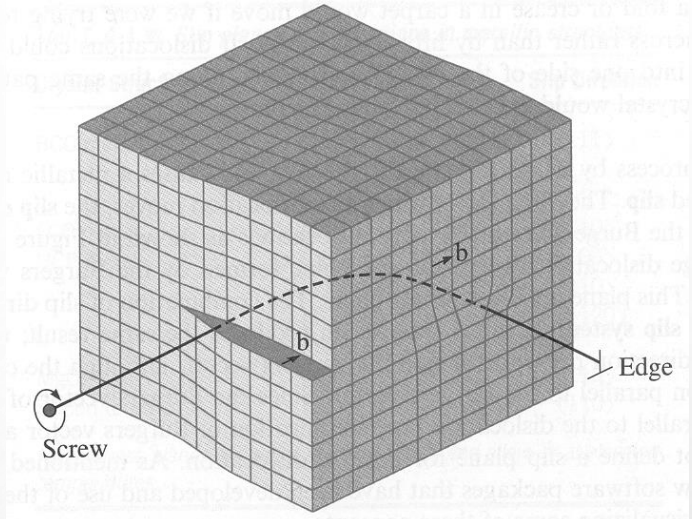
- In perfect crystal, atoms are arranged in both vertical and horizontal planes parallel to the side faces.
- If one of these vertical planes does not extend to the full length, but ends in between within the crystal it is called '**edge dislocation**'.
- In the perfect crystal, just above the edge of the incomplete plane the atoms are squeezed and are in a state of compression.
- Just below the edge of the incomplete plane, the atoms are pulled apart and are in a state of tension.
- Edge dislocations are represented by ' $\perp$ ' or 'T' depending on whether the incomplete plane starts from the top or from the bottom of the crystal.
- These two configurations are referred to as positive and negative edge dislocations respectively.

## *Screw dislocation*



The perfect crystal in a) is cut and sheared one atom spacing in b) and c). The line along which the shearing occurs is a screw dislocation. A Burgers vector  $\mathbf{b}$  is required to close a loop of equal atom spacing around the screw dislocation.

**A mixed dislocation** showing a screw dislocation at the front of the crystal gradually changing to an edge dislocation at the side of the crystal. Note that the line direction of the dislocation is parallel to the Burgers vector of the screw dislocation and perpendicular to the edge dislocation.



- Speed of movement of a screw dislocation is lesser compared to edge dislocation. Normally, the real dislocations in the crystals are the mixtures of edge and screw dislocation.
- In general, there can be any angle between the Burgers vector **b** (magnitude and the direction of slip) and the line vector **t** (unit vector tangent to the dislocation line)

$\mathbf{b} \perp \mathbf{t} \Rightarrow$  Edge dislocation

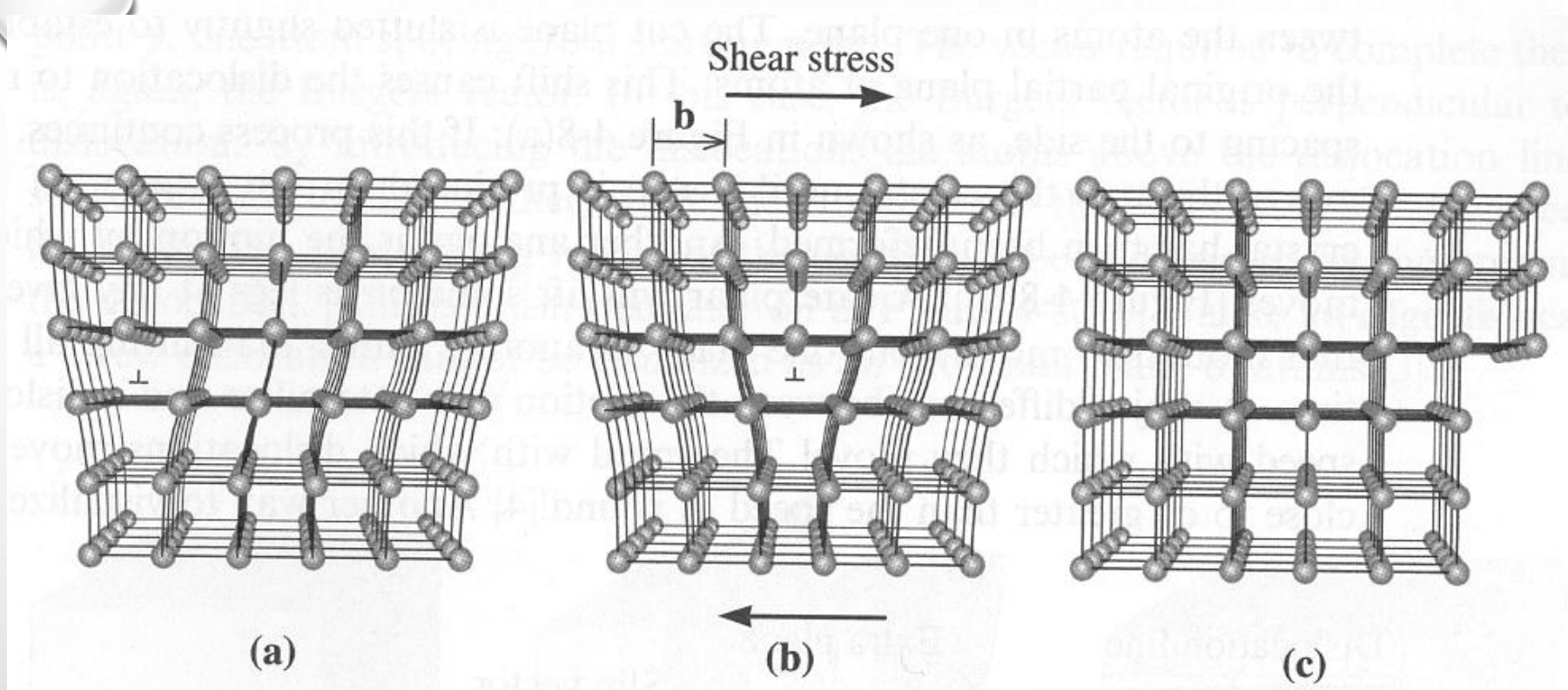
$\mathbf{b} \parallel \mathbf{t} \Rightarrow$  Screw dislocation

$\mathbf{b} \not\perp \mathbf{t}, \mathbf{b} \not\parallel \mathbf{t} \Rightarrow$  Mixed dislocation



## Control of Dislocations

- Control of dislocations allow us to manipulate **mechanical properties** and understand their temperature dependence.
- When a **shear force** acting in the direction of the Burger's vector is applied to a crystal containing a dislocation, the dislocation can move by **breaking bonds** between the atoms in one plane.
- By this process, the dislocation moves through the crystal to produce a **step** on the exterior of the crystal.
- The process by which the dislocation moves and causes a solid to deform is called **slip**.



When a shear stress is applied to the dislocation in a) the atoms are displaced, causing the dislocation to move one Burgers vector in the slip direction b). Continued movement of the dislocation creates a step c) and the crystal is deformed. Motion of a caterpillar (or a fold in a rug) is analogous to the motion of a dislocation.

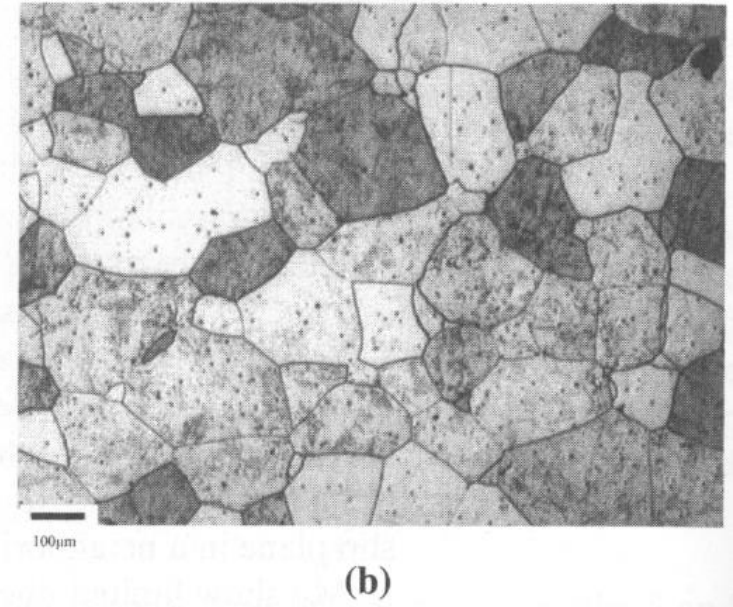
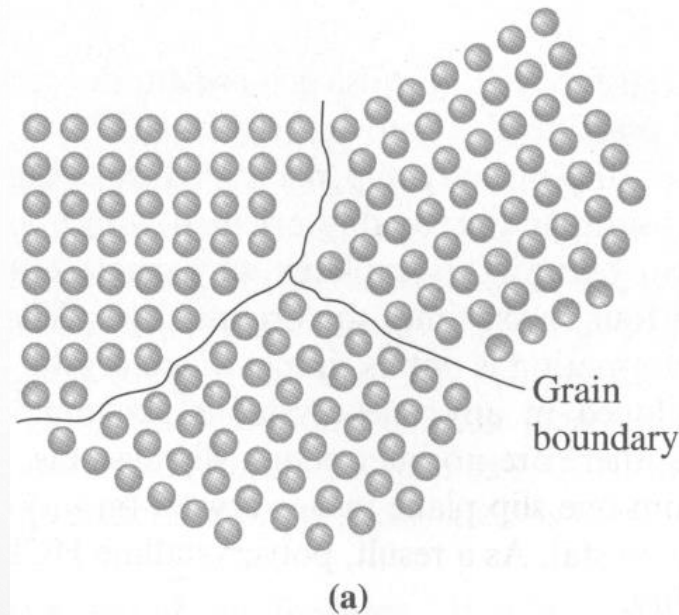
Note: the slip direction is **always** in the direction of the Burgers vector of the dislocation.



## Surface (plane) Defects

- Surface defects are another type of imperfection in real materials.
- They consist of the **boundaries** or **planes** that separate a material into regions of different crystal structure or orientation.
  - The **material's surface** is one example
  - **Grain boundaries** are another example of a surface defect.
  - Others are **stacking faults**, **twin boundaries** and **magnetic domain boundaries**
- ❖ The environment of an atom **at a surface** differs from that of an atom in the bulk, in that the number of neighbors (coordination) decreases. This introduces unbalanced forces which result in **relaxation** (the lattice spacing is decreased) or **reconstruction** (the crystal structure changes)
- ❖ Since these surface atoms are not surrounded by others, they possess higher energy than that of internal atoms.

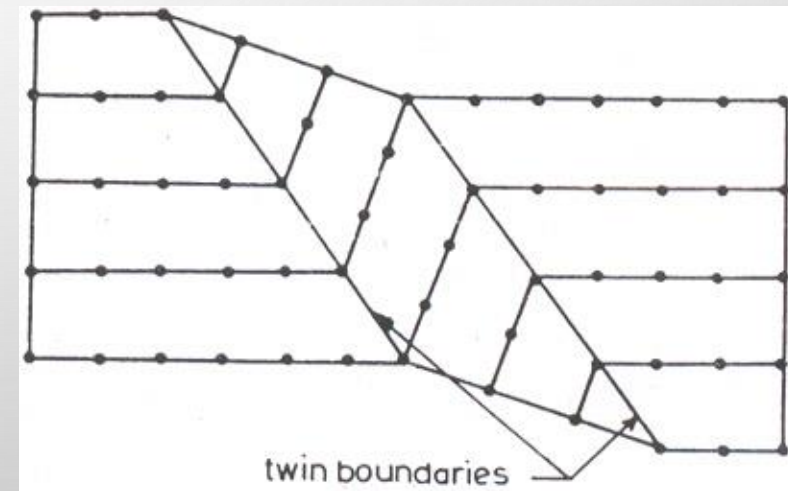
- ❑ **Polycrystalline** material comprised of many small crystals or grains. The **grains** have different crystallographic orientation. There exist atomic mismatch within the regions where grains meet. These regions are called **grain boundaries**.



Grain boundaries showing in a) that the atoms at the boundaries near the three grains (referred to as a triple point) do not have an equilibrium spacing and in b) grains in a stainless steel sample.

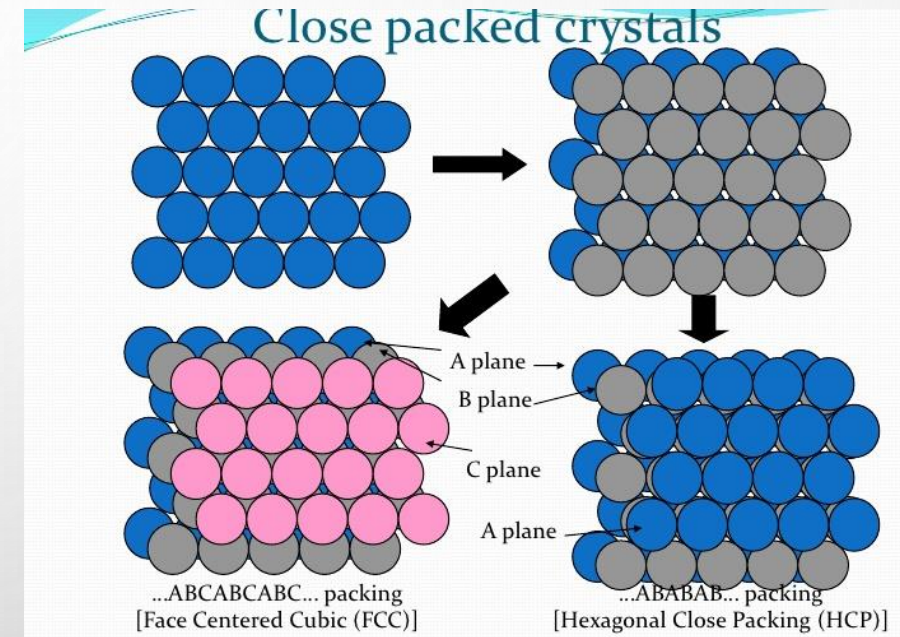
- ❑ As we saw in the electron images of the atoms (lattice images), **grain boundaries** are narrow zones where the atoms are not properly spaced in which tension or compression exists.
- ❑ **Grain size** influences many material properties such as strength and electrical conductivity.

- ❖ If the atomic arrangement on one side of a boundary is a mirror reflection of the arrangement on the other side, then it is called as ***twin boundary***.
- ❖ These boundaries are easily identified under an optical microscope.
- ❖ The plane of symmetry between the two portions is called the *twinning plane*.





- ❖ Whenever the stacking of atomic planes is not in a proper sequence throughout the crystal, the fault caused is known as **stacking fault**.
- ❖ For example, the stacking sequence in an ideal FCC crystal may be described as A-B-C-A-B-C-A-B-C-..... But the stacking fault may change the sequence to A-B-C-A-B-A-B-A-B-C. The region in which the stacking fault occurs (A-B-A-B) forms a thin region and it becomes HCP.
- ❖ This thin region is a surface imperfection and is called a **stacking fault**.



## ***Volume defects***

- ❖ Volume defects such as **cracks** may arise in crystals when there is only small electrostatic dissimilarity between the stacking sequences of close packed planes in metals.
- ❖ Presence of a **large vacancy** or **void space**, when **cluster of atoms** are missed is also considered as a volume imperfection.
- ❖ **Foreign particle** inclusions and **non crystalline** regions which have the dimensions of the order of 0.20 nm are also called as volume imperfections.