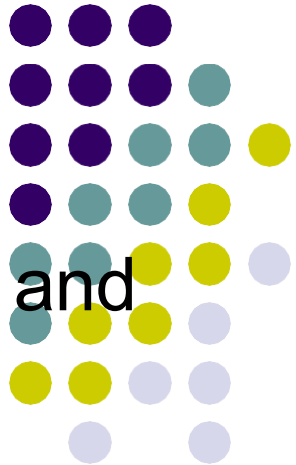
Physics of Materials: Defects in Solids

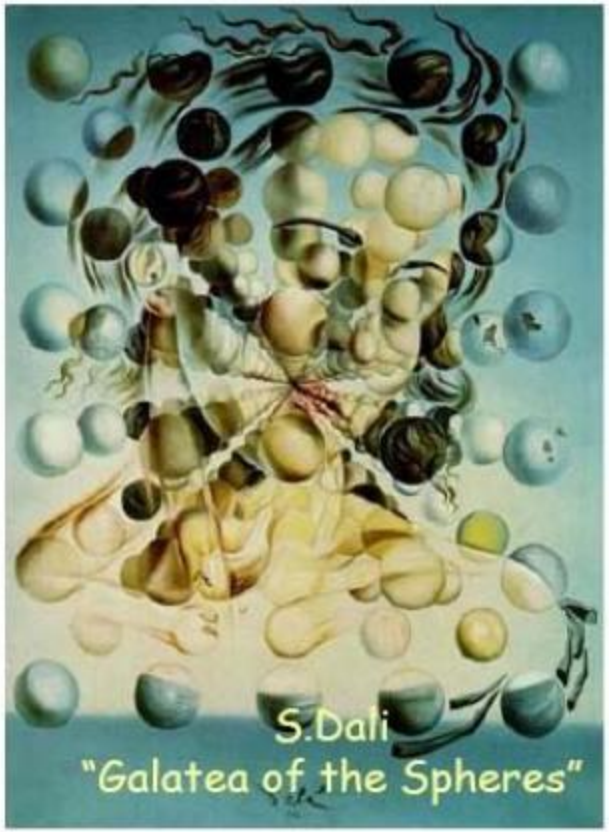
Dr. Anurag Srivastava

Atal Bihari Vajpayee

Indian Institute of Information Technology and Manegement, Gwalior



"Defects" in Solids



"Solids are like people - imperfect!

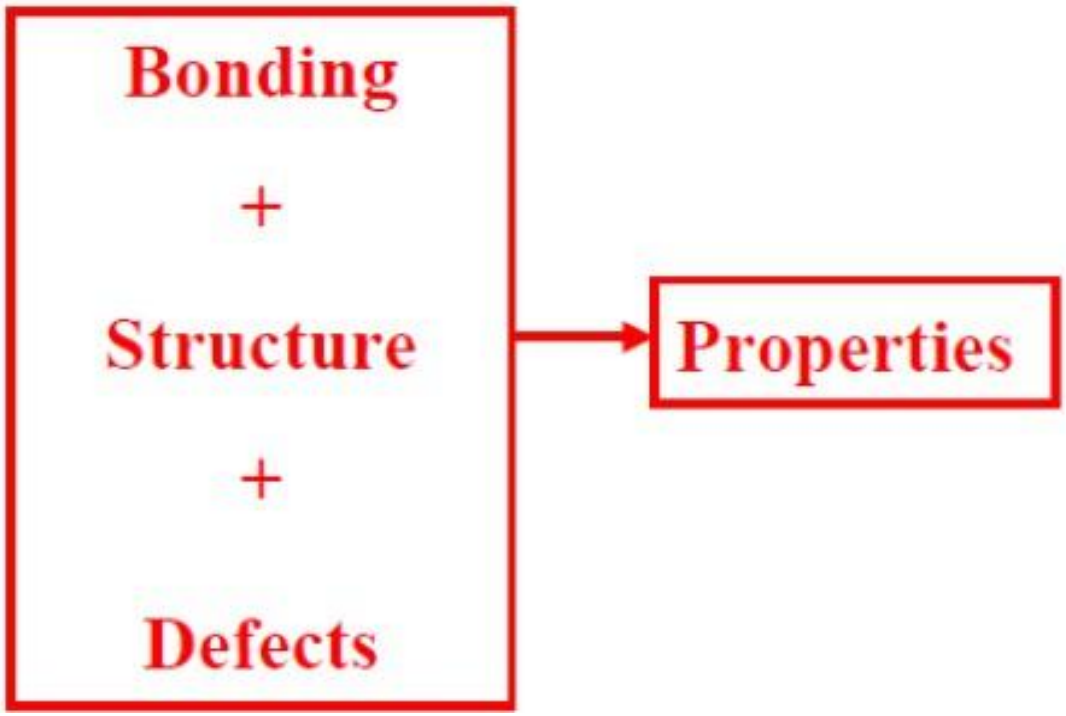
It's the defects that make them unique & interesting"

(J. Corish)

http://www.bath.ac.uk/podcast/powerpoint/Inaugural_lecture_250407.pdf

In real crystals, lattices are not perfect. They contain imperfections and impurities, which can alter the electrical properties of solid materials.

Defects have a profound impact on the macroscopic properties of materials



http://web.utk.edu/~prack/mse201/Chapter%204%20Defects.pdf

Impact on Properties

Mechanical Properties:

Defects like dislocations and pores can disrupt the regular atomic arrangement, making materials weaker, more brittle, or increasing their yield strength.

Electrical/Electronic Properties:

Defects influence electrical conductivity by scattering charge carriers and creating localized energy levels within the material's band structure.

Optical Properties:

Defects can lead to new light absorptions, shifts in resonances, and changes in transparency by creating new energy states that interact with photons.

Thermal Properties:

The presence of defects, such as vacancies or dislocations, can hinder the movement of phonons, which are the primary carriers of heat in a material. This scattering reduces the material's thermal conductivity and alters its specific heat capacity.

Magnetic properties

In magnetic materials, defects can change the local magnetic environment, affecting magnetic behavior.

Properties of Materials affected by defects

Mechanical: Dislocation

Electronic: Conduction in electronic ceramic (vacancies)
Mobility in semiconductors

Diffusions: Vacancies and Interstitials

Optical: recombination centers

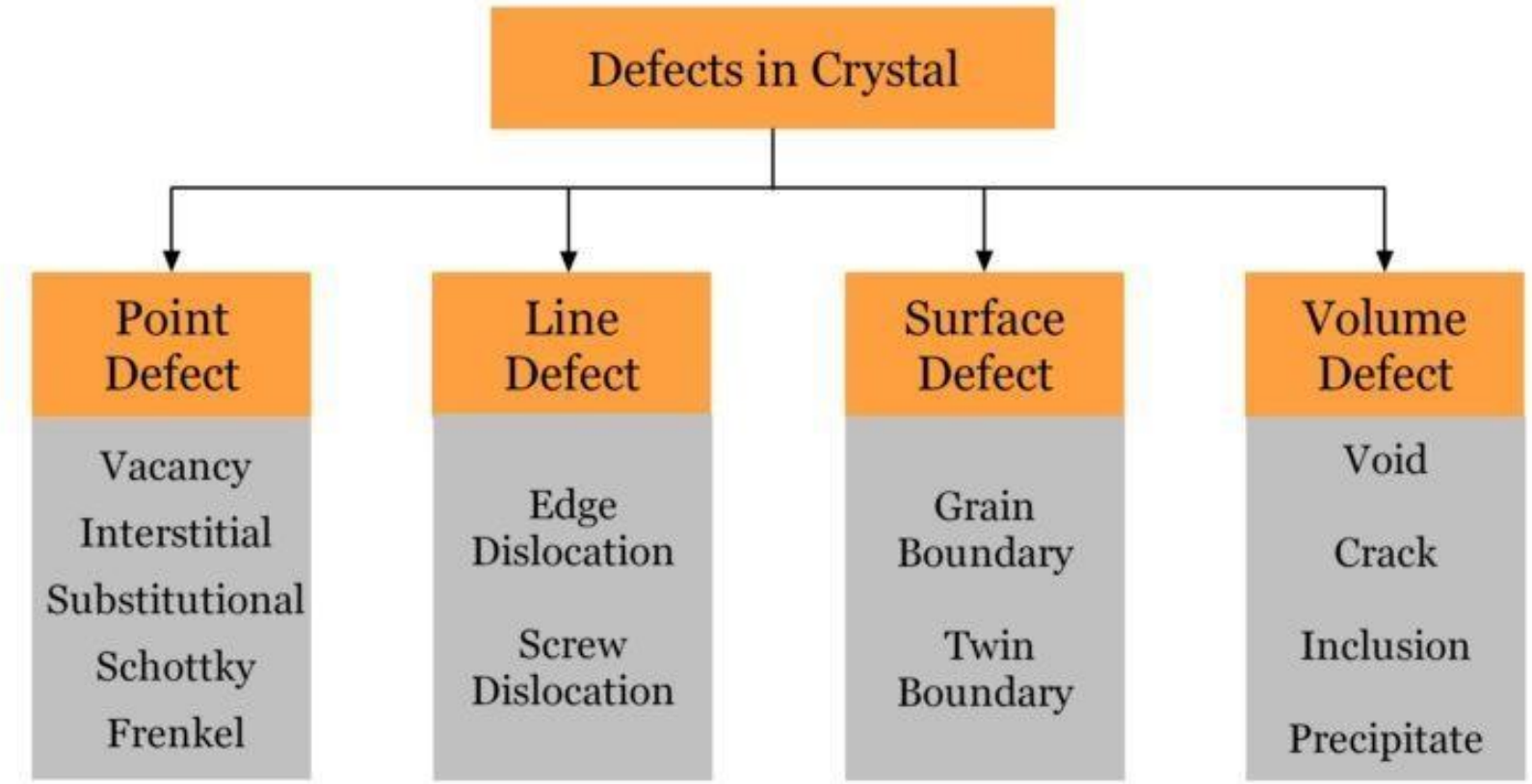
How Bonding affects

The nature and strength of chemical bonds, as well as intermolecular forces, directly influence a substance's properties such as its **melting point, boiling point, solubility, and electrical conductivity**.

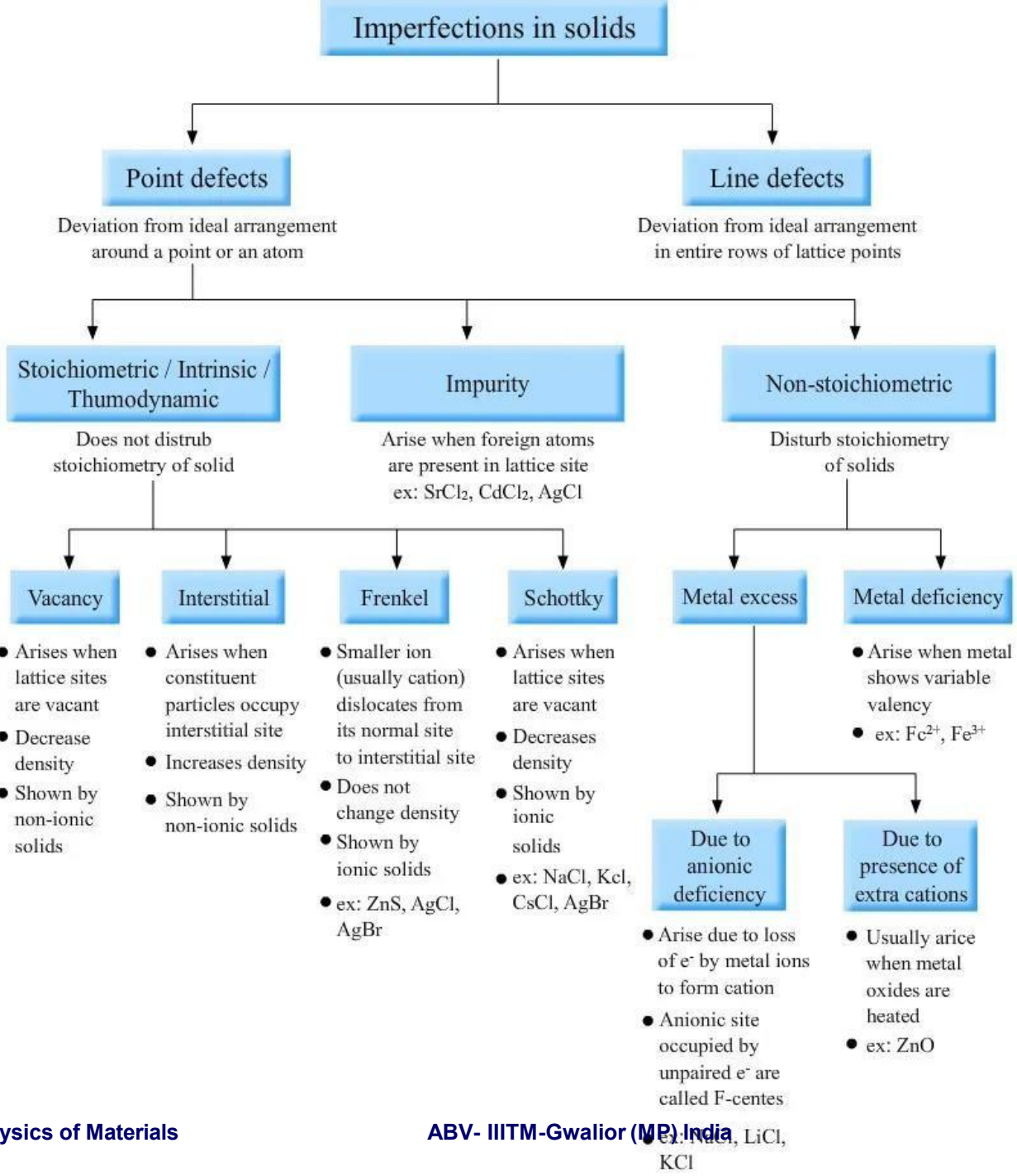
For instance, **strong ionic bonds** result in **high melting points and electrical conductivity** in molten or dissolved states, while the weak but numerous hydrogen bonds in water give it a high boiling point and surface tension.

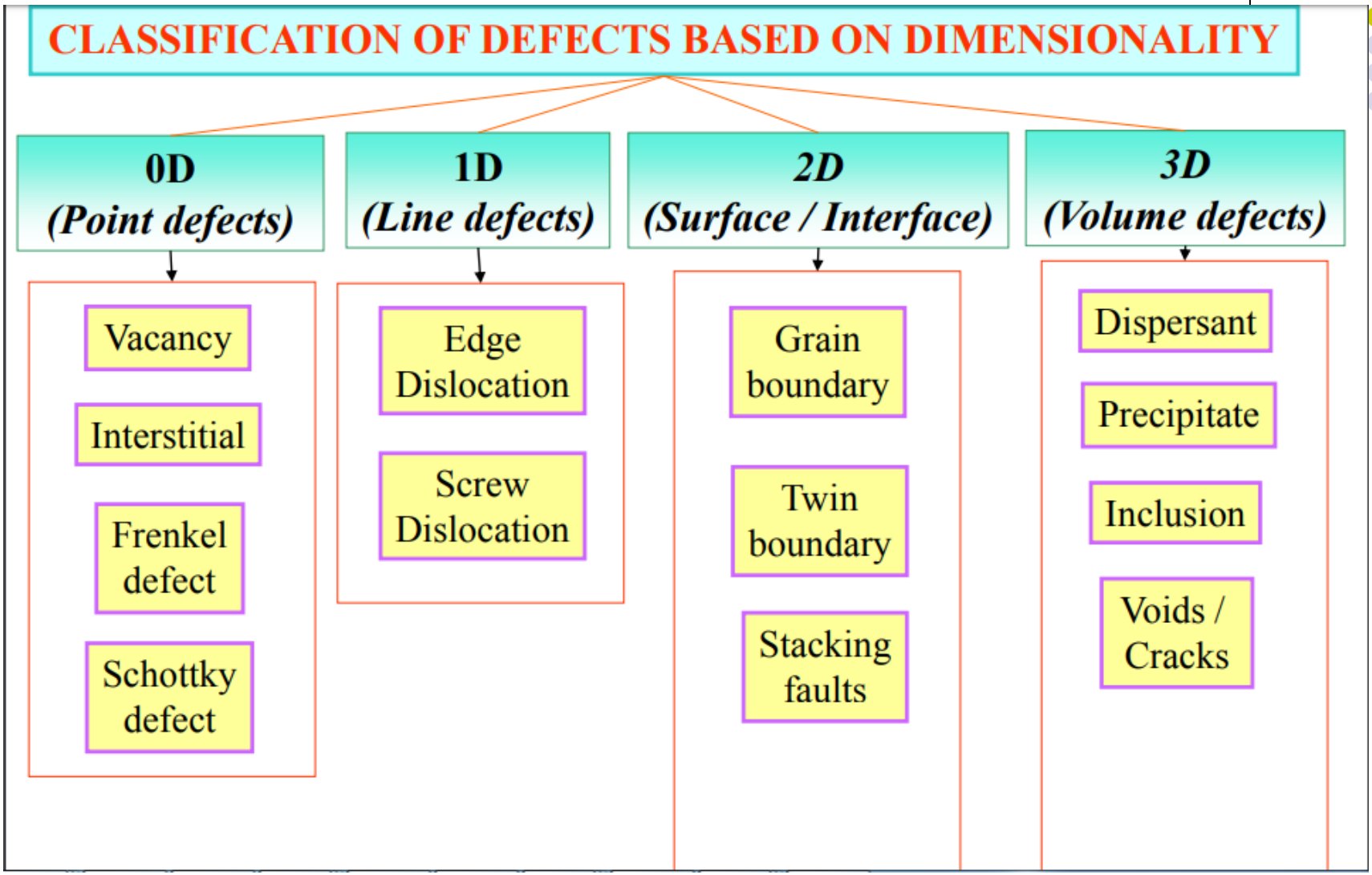
Metallic bonds enable electrical and thermal conductivity and malleability due to delocalized electrons.

CLASSIFICATION OF DEFECTS IN CRYSTALLINE SOLID



It is practically impossible to obtain any substance in 100% pure form. Some impurities will always present in it.


Imperfections in solids
Point defects
Deviation from ideal arrangement around a point or an atom
Line defects
Deviation from ideal arrangement in entire rows of lattice points
Stoichiometric / Intrinsic / Thumodynamic
Does not distrub stoichiometry of solid
Impurity
Arise when foreign atoms are present in lattice site ex: $SrCl_2$, $CdCl_2$, AgCl
Non-stoichiometric
Disturb stoichiometry of solids
Vacancy
Arises when lattice sites are vacant
Decrease density
Shown by non-ionic solids
Interstitial
Arises when constituent particles occupy interstitial site
Increases density
Shown by non-ionic solids
Frenkel
Smaller ion (usually cation) dislocates from its normal site to interstitial site
Does not change density
Shown by ionic solids
ex: ZnS, AgCl, AgBr
Schottky
Arises when lattice sites are vacant
Decreases density
Shown by ionic solids
ex: NaCl, Kcl, CsCl, AgBr
Metal excess
Due to anionic deficiency
Arise due to loss of e^- by metal ions to form cation
Anionic site occupied by unpaired e^- are called F-centes
ex: NaCl, LiCl, KCl
Due to presence of extra cations
Usually arice when metal oxides are heated
ex: ZnO
Metal deficiency
Arise when metal shows variable valency
ex: Fc^{2+}, Fe^{3+}


CLASSIFICATION OF DEFECTS BASED ON DIMENSIONALITY
0D
(Point defects)
1D
(Line defects)
2D
(Surface / Interface)
3D
(Volume defects)
Vacancy
Interstitial
Frenkel defect
Schottky defect
Edge Dislocation
Screw Dislocation
Grain boundary
Twin boundary
Stacking faults
Dispersant
Precipitate
Inclusion
Voids / Cracks

Definition of Point Defect:

A point defect occurs when one or more atoms of a crystalline solid leave their original lattice site and/or foreign atoms occupy the interstitial position of the crystal. So there exist three possibilities by which point defect may occur, as provided below:

- One or more original atoms of the crystal are missing from their corresponding lattice site.
- One or more original atoms are shifted from the original lattice site to the interstitial position in same crystal.
- One or more foreign atoms occupied the interstitial position of the crystalline solid.
- One or more foreign atoms replaced the original atom of the crystal and subsequently occupied the interstitial position.

Causes of Point Defect in Crystalline Solid:

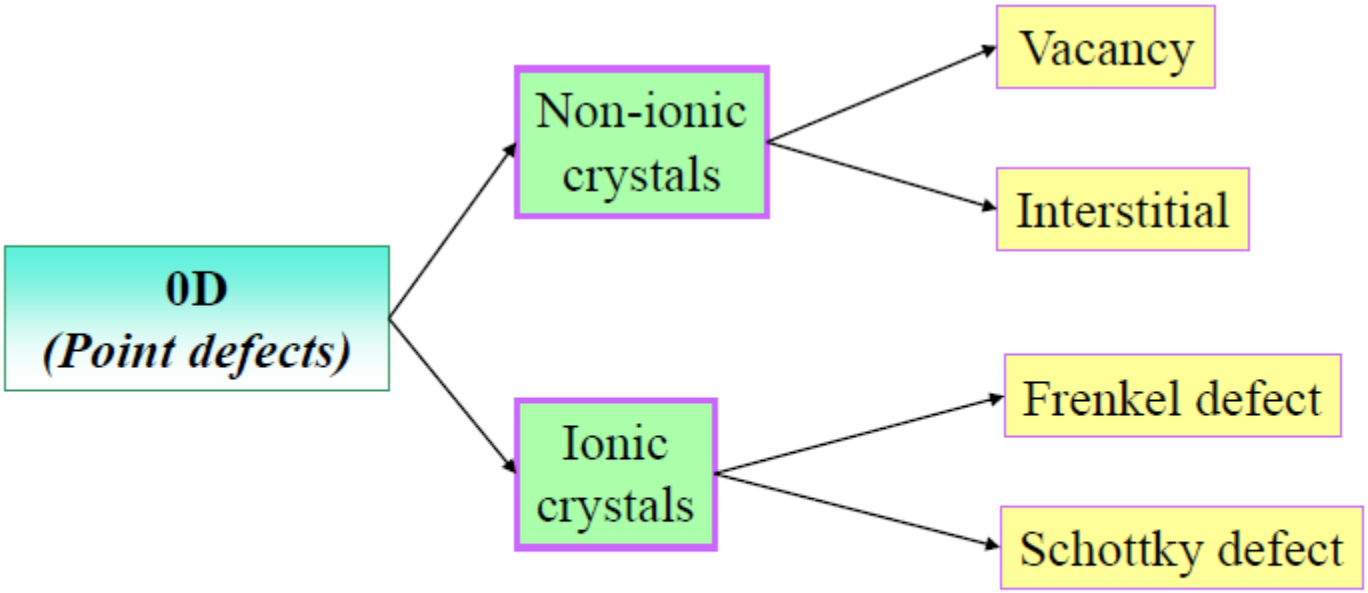
- Diffusion (solid-solid).
- Increase or decrease in temperature in presence of other medium.
- Plastic deformation.
- Particle or ion bombarding, such as sputtering or ion irradiation.
- Deliberate alloying to enhance properties.
- Presence of residual stress.

Types of Point Defect in Crystalline Solid:

Point defect can be primarily classified into three categories, viz. Vacancy, Interstitial, and Substitutional. Sometime Self-Interstitial defect is also considered another one category. However, in case of ionic crystals (ceramics), Schottky defect and Frenkel defect can occur, which are nothing but the combination of two different types of the above mentioned four basic types of point defects. The details of these point defects are discussed in the following section.

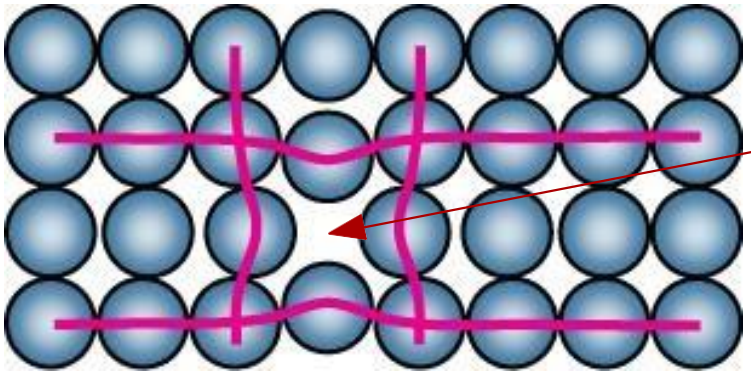
POINT DEFECTS

Point Defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance.

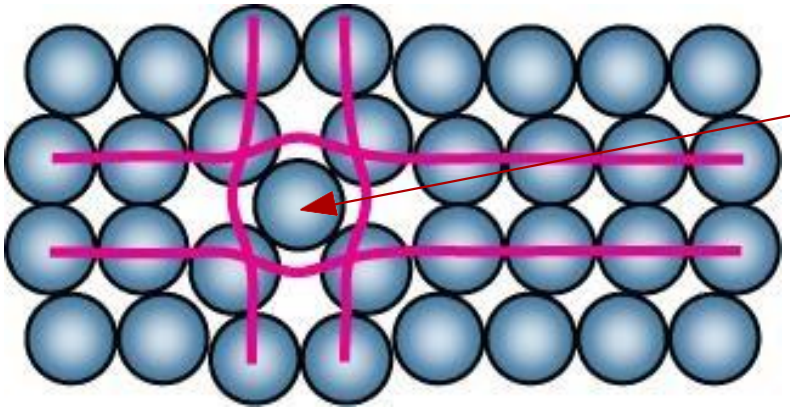


Point Defects in Metals

- Vacancies:
  -vacant atomic sites in a structure.



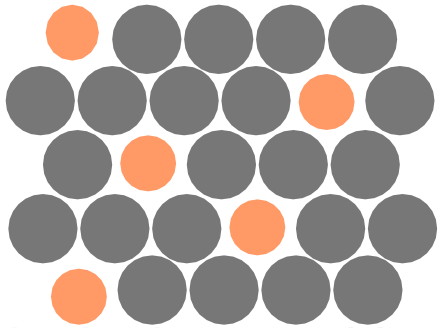
- Self-Interstitials:
  -"extra" atoms positioned between atomic sites.



Imperfections in Metals (i)

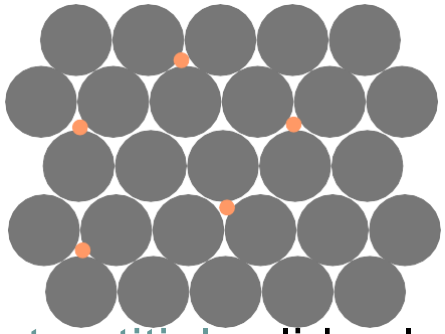
Two outcomes if impurity (B) added to host (A):

- Solid solution of B in A (i.e., random dist. of point defects)



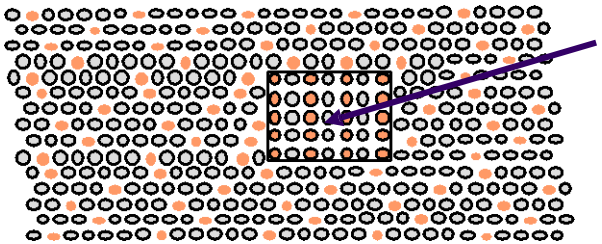
Substitutional solid soln.
(e.g., Cu in Ni)

OR



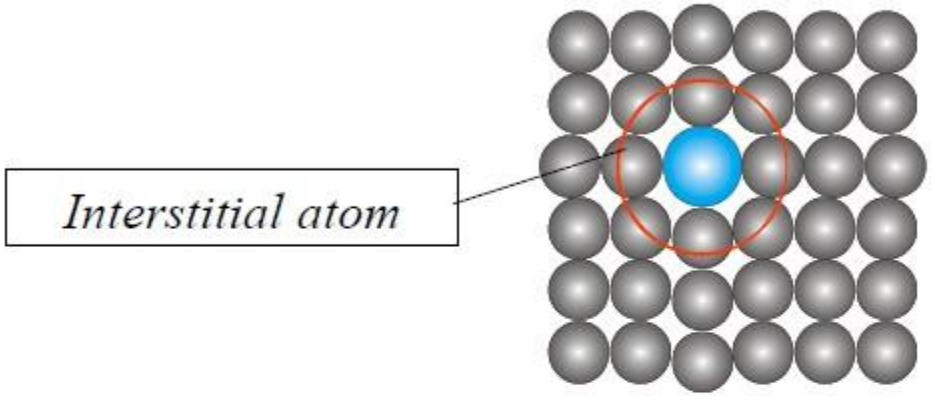
Interstitial solid soln.
(e.g., C in Fe)

- Solid solution of B in A plus particles of a new phase (usually for a larger amount of B)

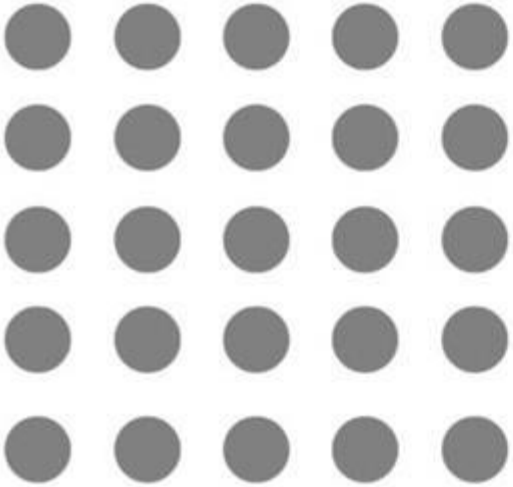


Second phase particle
-- different composition
-- often different structure.

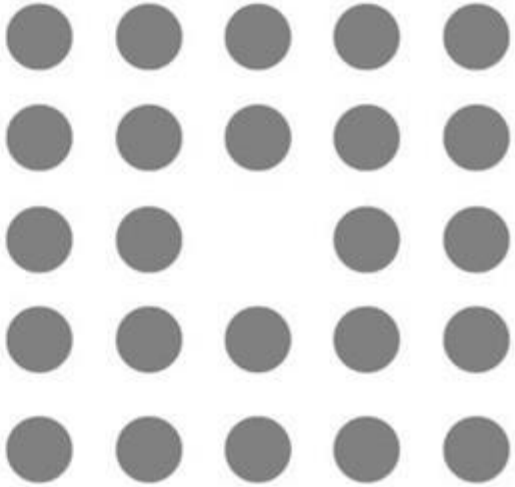
INTERSTITIALS DEFECT



- Addition of an extra atom within a crystal structure
- This defect increases the density of the substance
- Causes atomic distortion
- Vacancy and interstitials are inverse phenomena



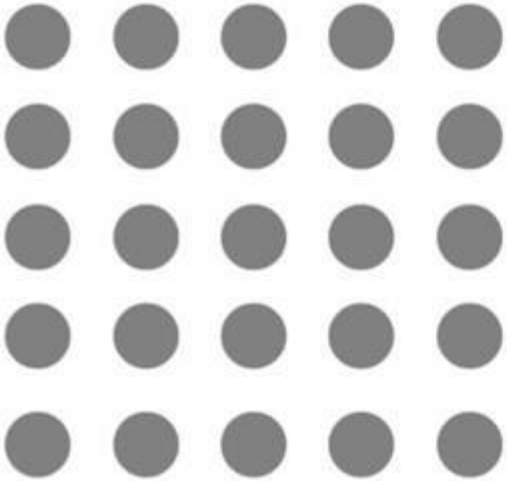
Perfect Crystal



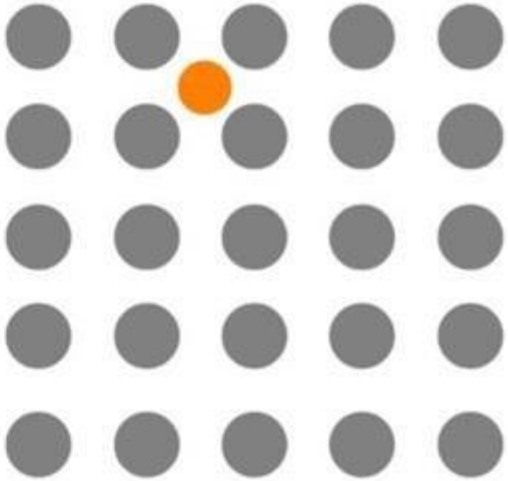
Vacancy - Point Defect

Vacancy – A Point Defect

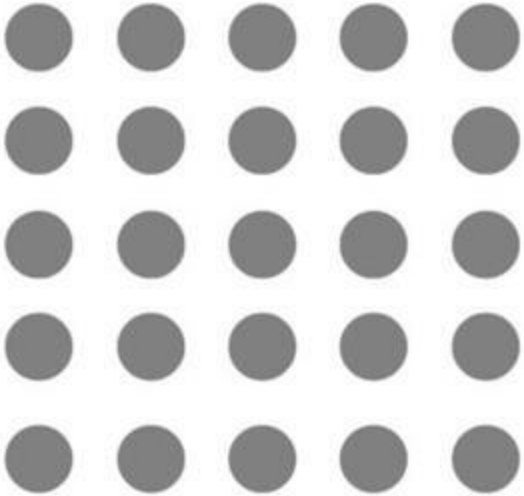
A vacancy is produced when an atom is missing from its original lattice site. So vacancy creates an empty lattice site as depicted below. Like other point defects, vacancy is also a zero-dimensional defect. Vacancy defect puts the neighboring atoms under tension. Due to the reduction in number of atoms in the crystalline solid, vacancy defect results in reduction of the density. However, hardness of the solid may increase. The number of vacancies present within a crystalline solid depends exponentially with temperature, thus with increase in temperature of solid, number of vacancies also increases. You can learn more and solve problems regarding vacancy defect.



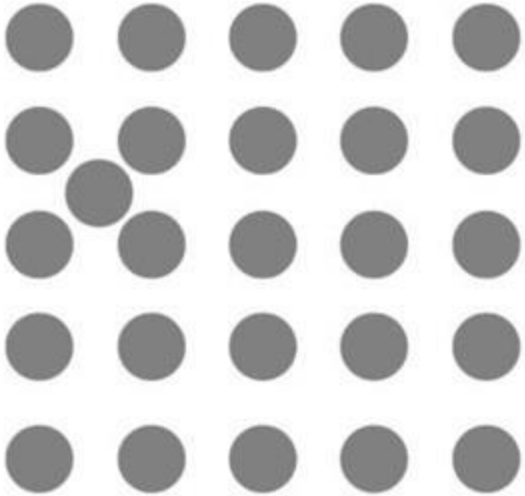
Perfect Crystal



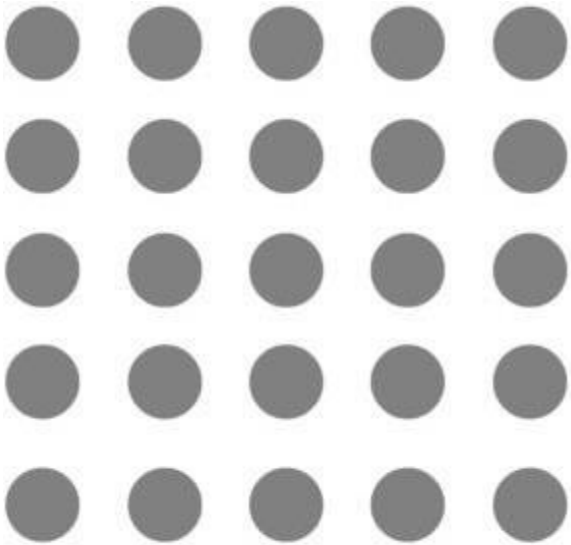
Interstitial Atom - Point Defect



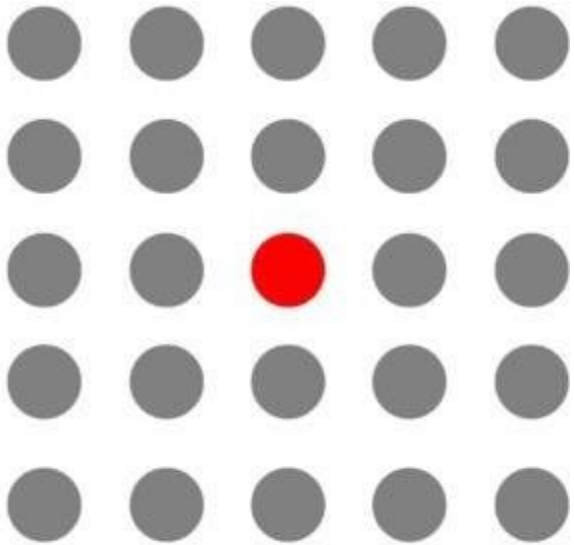
Perfect Crystal



Self-Interstitial Atom - Point Defect



Perfect Crystal



Substitutional Atom - Point Defect

Equilibrium Concentration: Point Defects

- Equilibrium concentration varies with temperature!

No. of defects

Activation energy

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

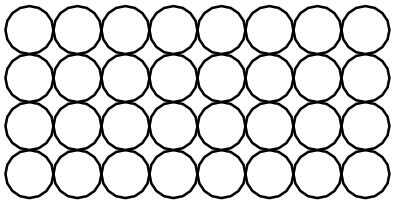
No. of potential defect sites

Temperature

Boltzmann's constant

(1.38 x 10^{-23} J/atom-K)

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



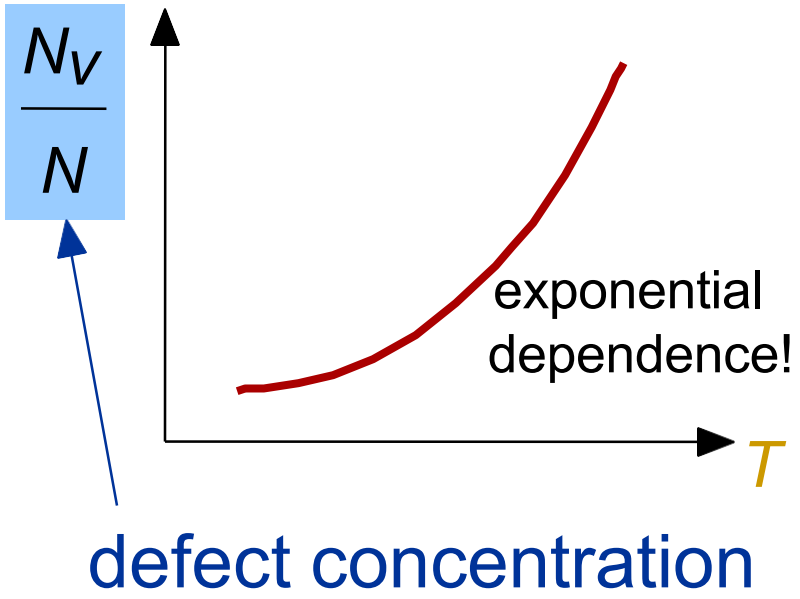
Each lattice site is a potential vacancy site

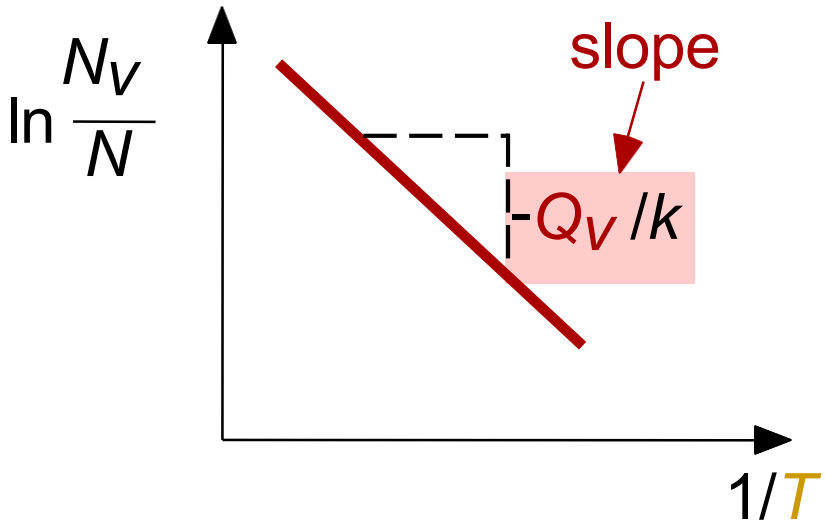
Measuring Activation Energy

- We can get Q_v from an experiment.
- Measure this...

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

- Replot it...





VACANCY DEFECT

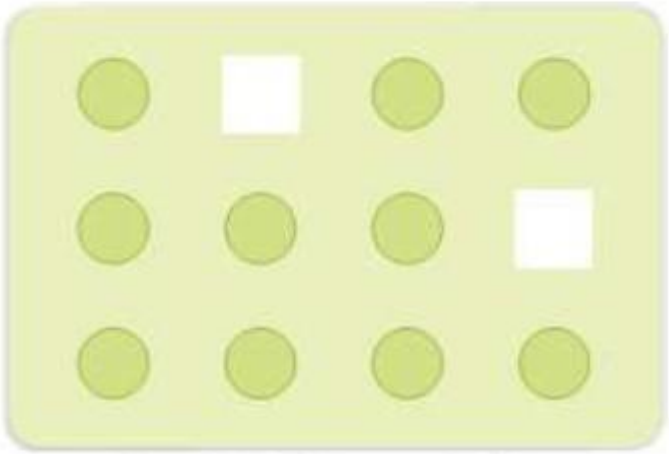
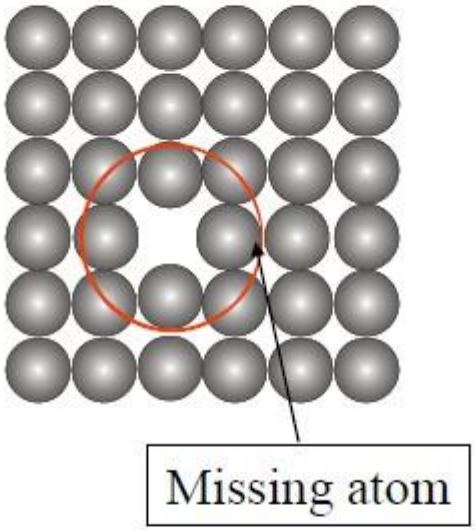


Fig. 1.23: Vacancy defects



- Atom missing from an atomic site
- Occur due to imperfect packing during crystallisation
- This results in decrease in density of the substance
- Number of vacancy defects depend on temperature

Estimating Vacancy Concentration

- Find the equil. # of vacancies in 1 m^3 of Cu at 1000°C.
- Given:

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

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

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

0.9 eV/atom

1273 K

8.62×10^{-5} eV/atom-K

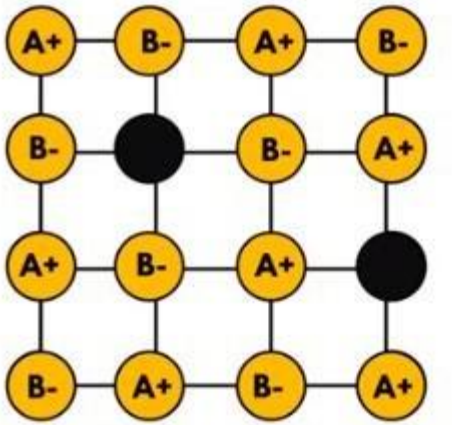
For 1 m^3, $N = \rho \times \frac{N_A}{A_{Cu}} \times 1\ m^3 = 8.0 \times 10^{28}$ sites

- Answer:

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

IMPERFECTION

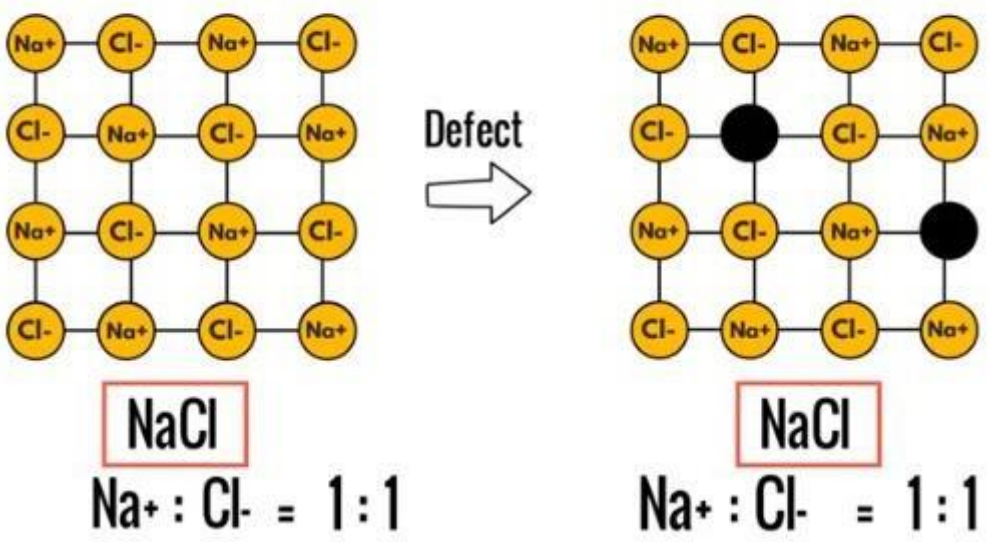
Defects in Solids



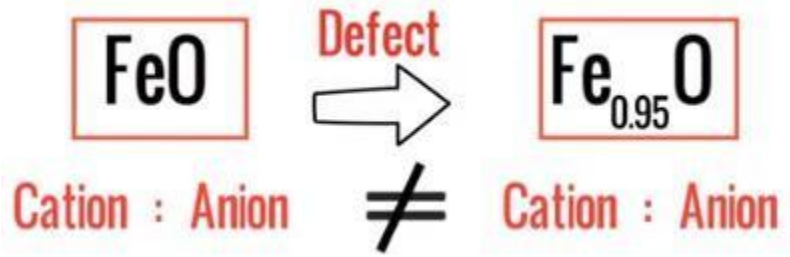
- Stoichiometry
- Non - Stoichiometry
- Impurity

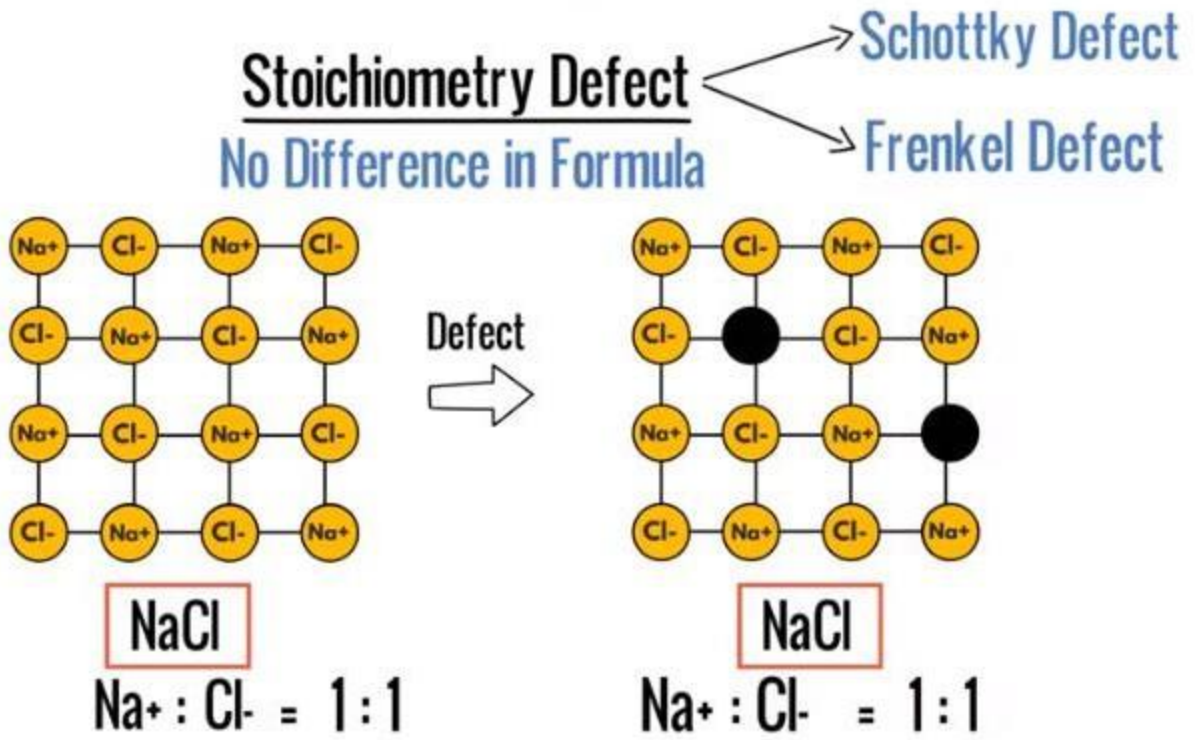
Stoichiometry Defect

No Difference in Formula

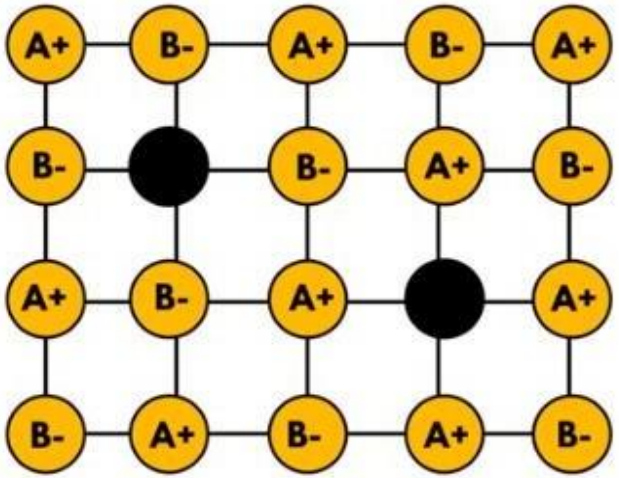


Non - Stoichiometry Defect




Stoichiometry Defect
Schottky Defect
Frenkel Defect
No Difference in Formula
Na+
Cl-
Defect
NaCl
Na+ : Cl- = 1 : 1
NaCl
Na+ : Cl- = 1 : 1

SCHOTTKY DEFECT



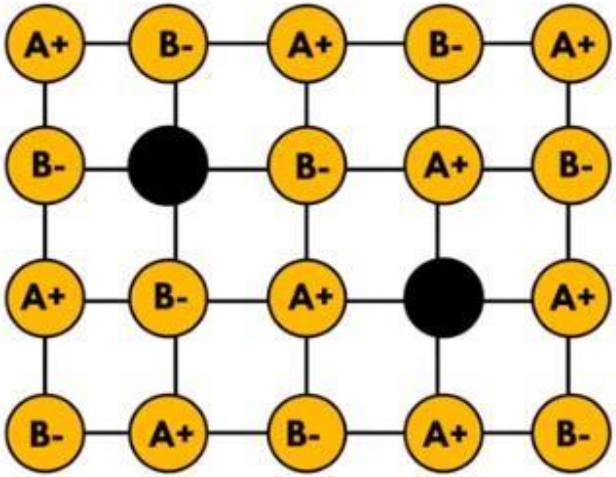
cation missing = anion missing — STOICHIOMETRIC DEFECT

$A^+ = B^- \Rightarrow$ Neutral

$A^+ > B^- \Rightarrow$ +ve charge

$B^- > A^+ \Rightarrow$ -ve charge

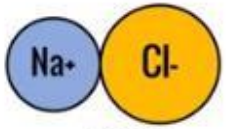
SCHOTTKY DEFECT



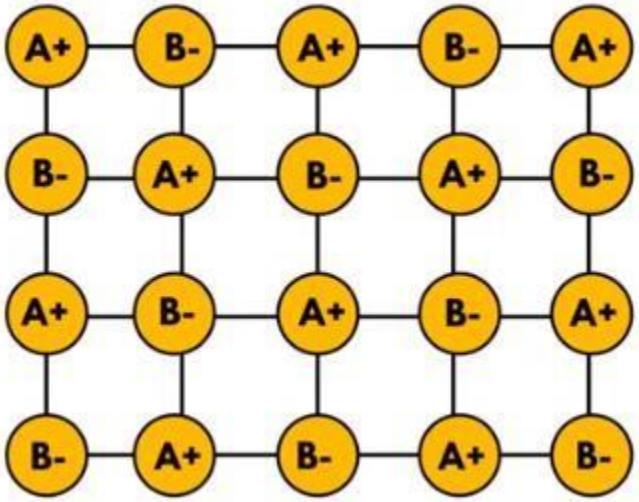
EXAMPLES

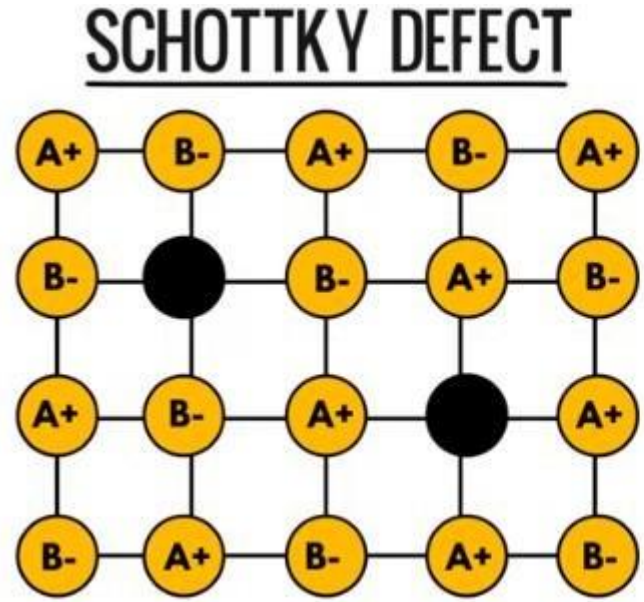
1. High Coordination No.

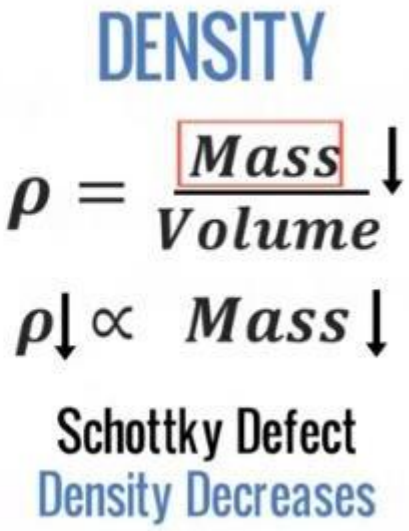
2. Small Difference in Size of Cation to Anion



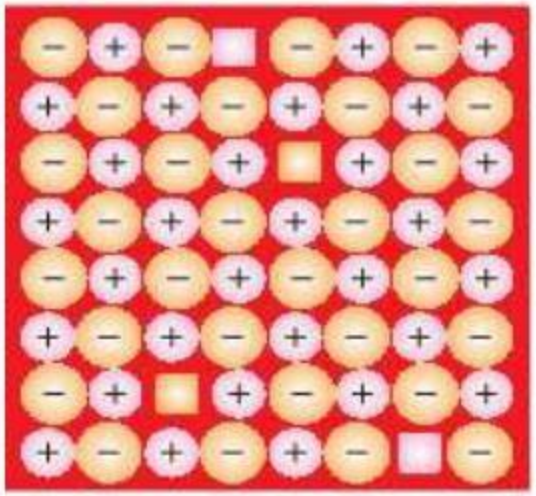
NaCl KCl CsCl


A+ B- A+ B- A+
B- A+ B- A+ B-
A+ B- A+ B- A+
B- A+ B- A+ B-


SCHOTTKY DEFECT
A+ B- A+ B- A+
B- B- A+ B-
A+ B- A+ A+
B- A+ B- A+ B-


DENSITY
$\rho = \frac{Mass}{Volume}\downarrow$
$\rho\downarrow \propto Mass\downarrow$
Schottky Defect
Density Decreases

SCHOTTKY DEFECT



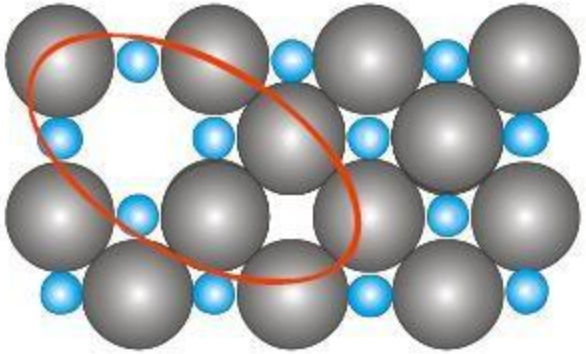
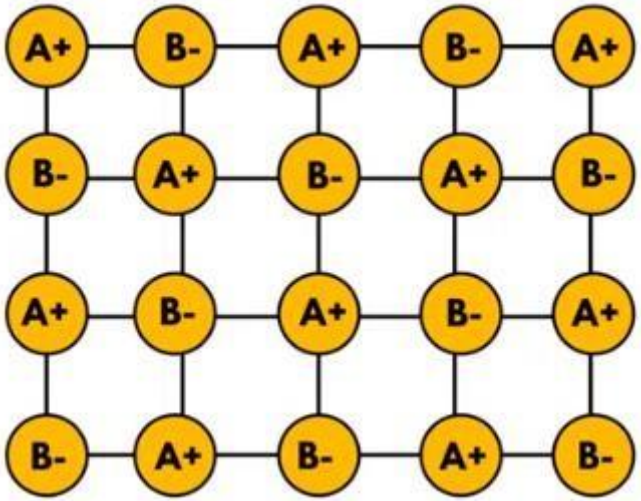
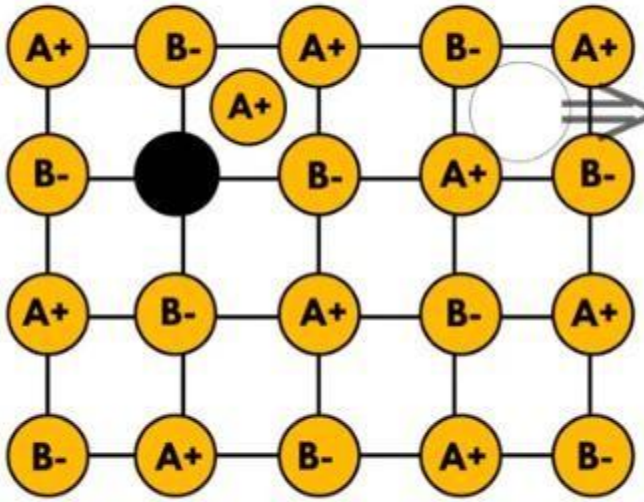


Fig. 1.26: Schottky defects

- Pair of anion and cation vacancies
- In order to maintain electrical neutrality, the number of missing cations and anions are equal
- It also decreases the density of crystal
- E.g. Alkali halides such as NaCl, KF, etc.



FRENKEL DEFECT



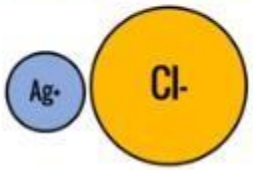
No Difference in Formula

Examples

interstitial site

ZnS AgCl AgBr

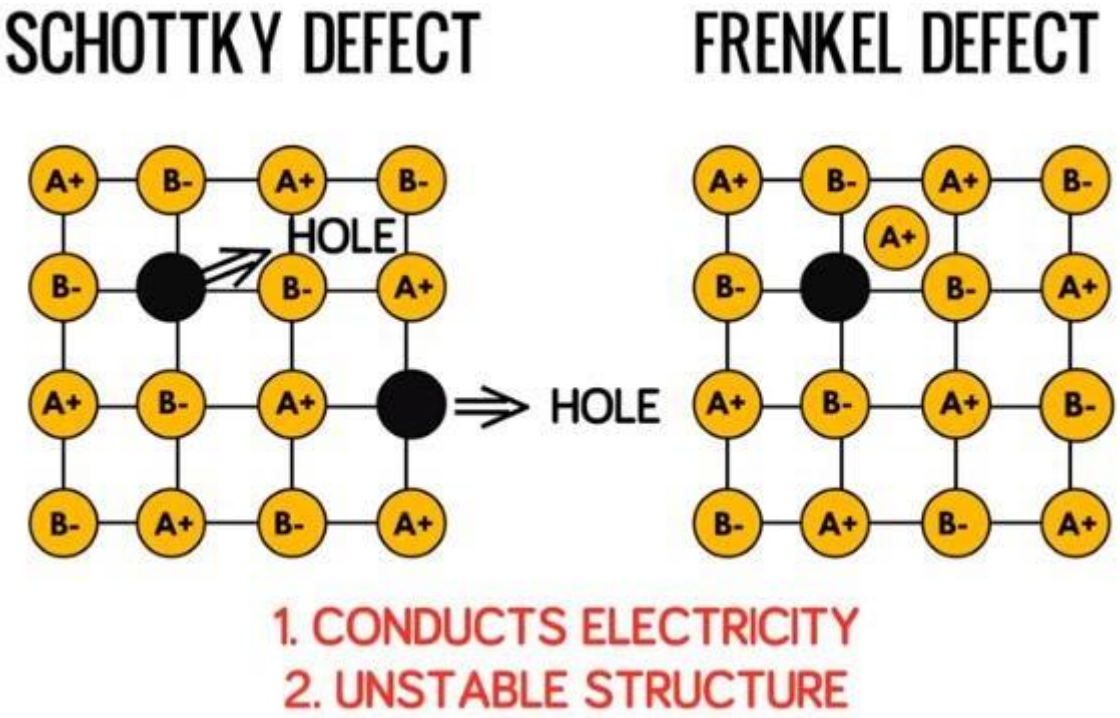
1. Low Coordination No.
2. Large Difference in Size of Cation to Anion

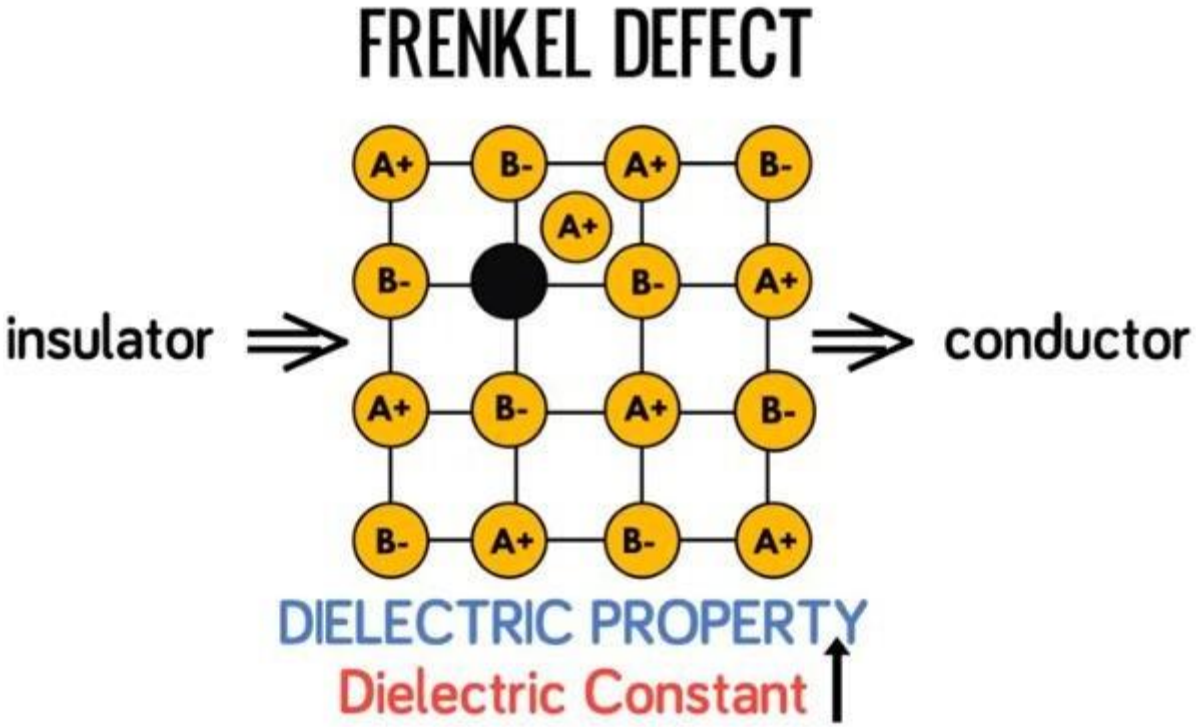


DENSITY

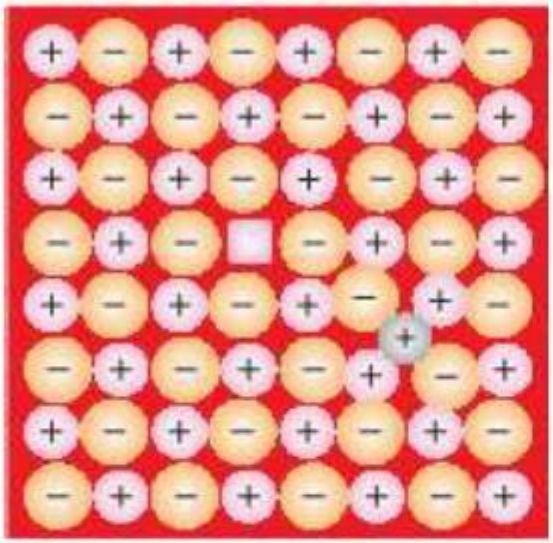
$$\rho = \frac{Mass}{Volume}$$

NO IMPACT


SCHOTTKY DEFECT
FRENKEL DEFECT
A+
B-
HOLE
HOLE
1. CONDUCTS ELECTRICITY
2. UNSTABLE STRUCTURE


FRENKEL DEFECT
A+
B-
A+
B-
A+
B-
B-
A+
B-
A+
A+
B-
A+
B-
B-
A+
B-
A+
insulator
conductor
DIELECTRIC PROPERTY
Dielectric Constant

FRENKEL DEFECTS



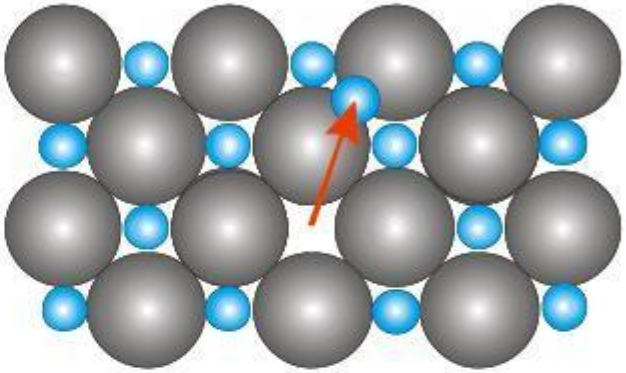


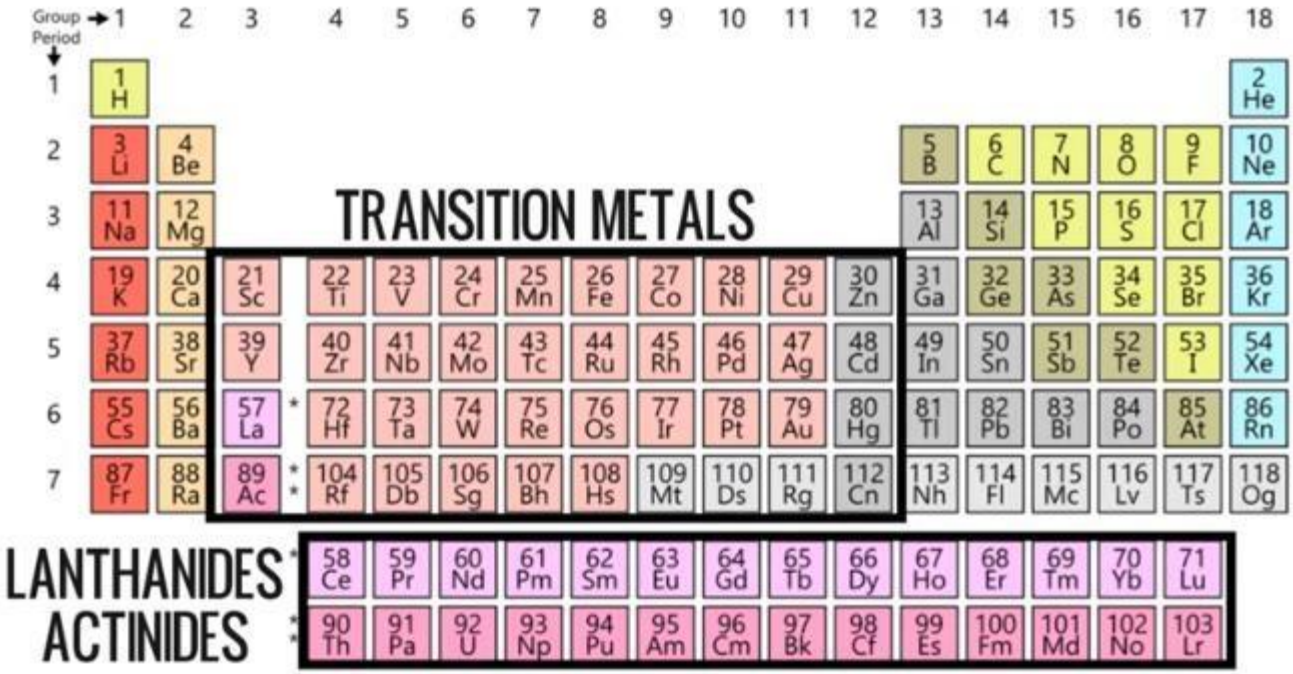
Fig. 1.25: Frenkel defects

- Cation (being smaller get displaced to interstitial voids
- Combination of vacancy and interstitial atom
- No change in the density
- E.g. AgI, CaF_2

Non - Stoichiometry Defect

FeO $\xrightarrow{\text{Defect}}$ $Fe_{0.95}O$

Cation : Anion $\neq$ Cation : Anion



Non - Stoichiometry Defect

- **Metal Excess**
  Cation > Anion
- **Metal Deficient**
  Anion > Cation

Metal ⇒ Cation

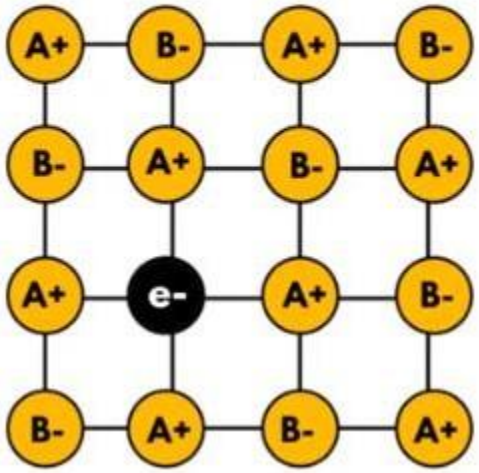
Na → Na^+

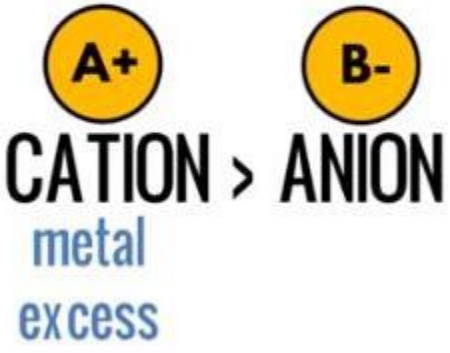
Metal Excess

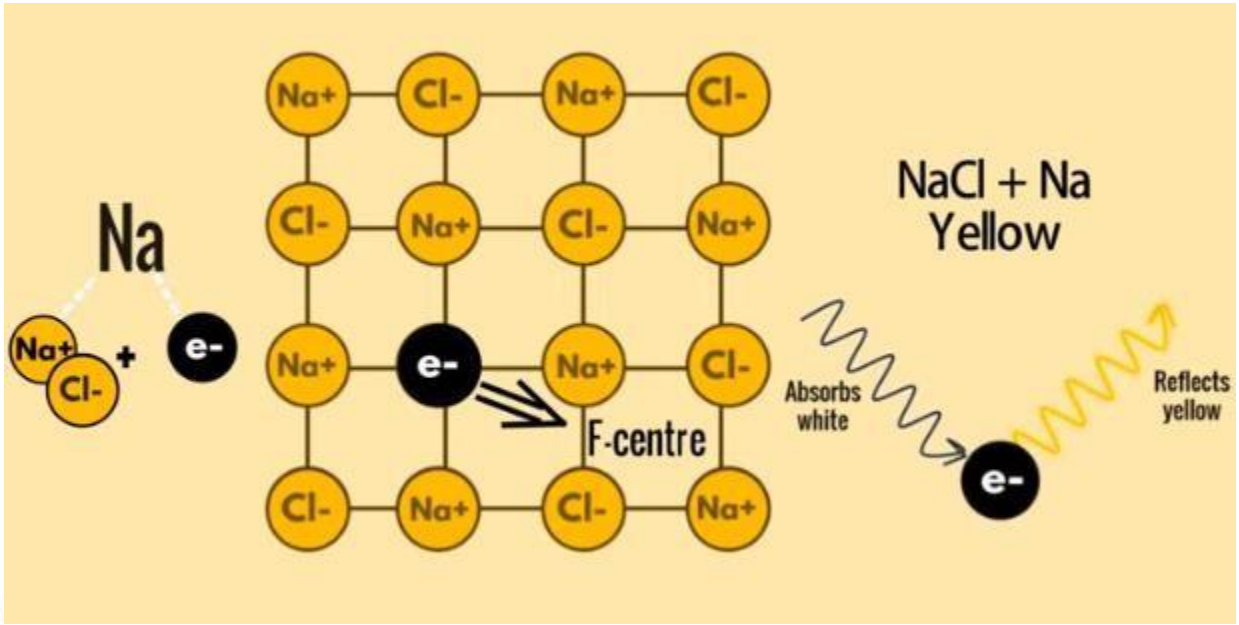
- **Anion Vaccancy**
- **Extra Cation**

METAL EXCESS

ANION VACCANCIES







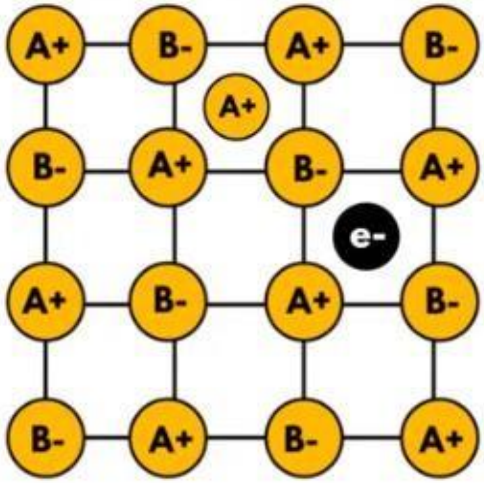
NaCl + Na ⇒ YELLOW

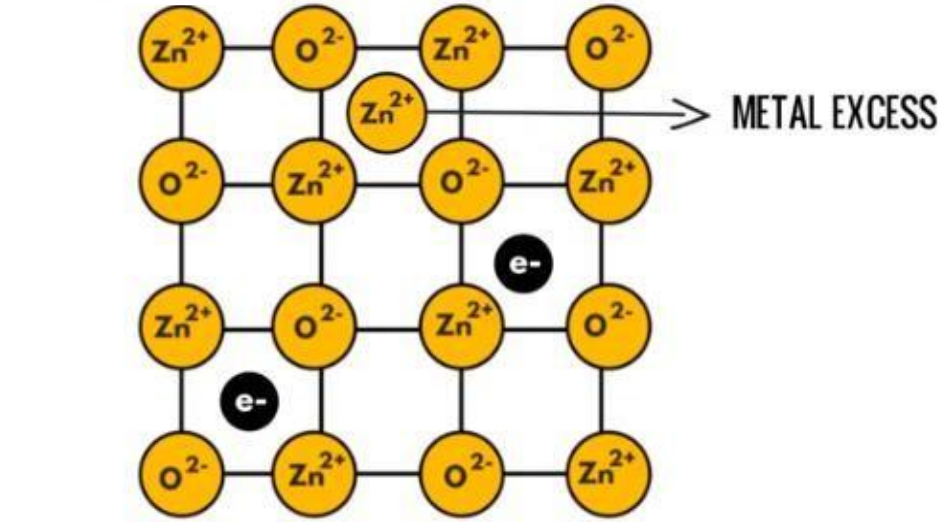
LiCl + Li ⇒ PINK

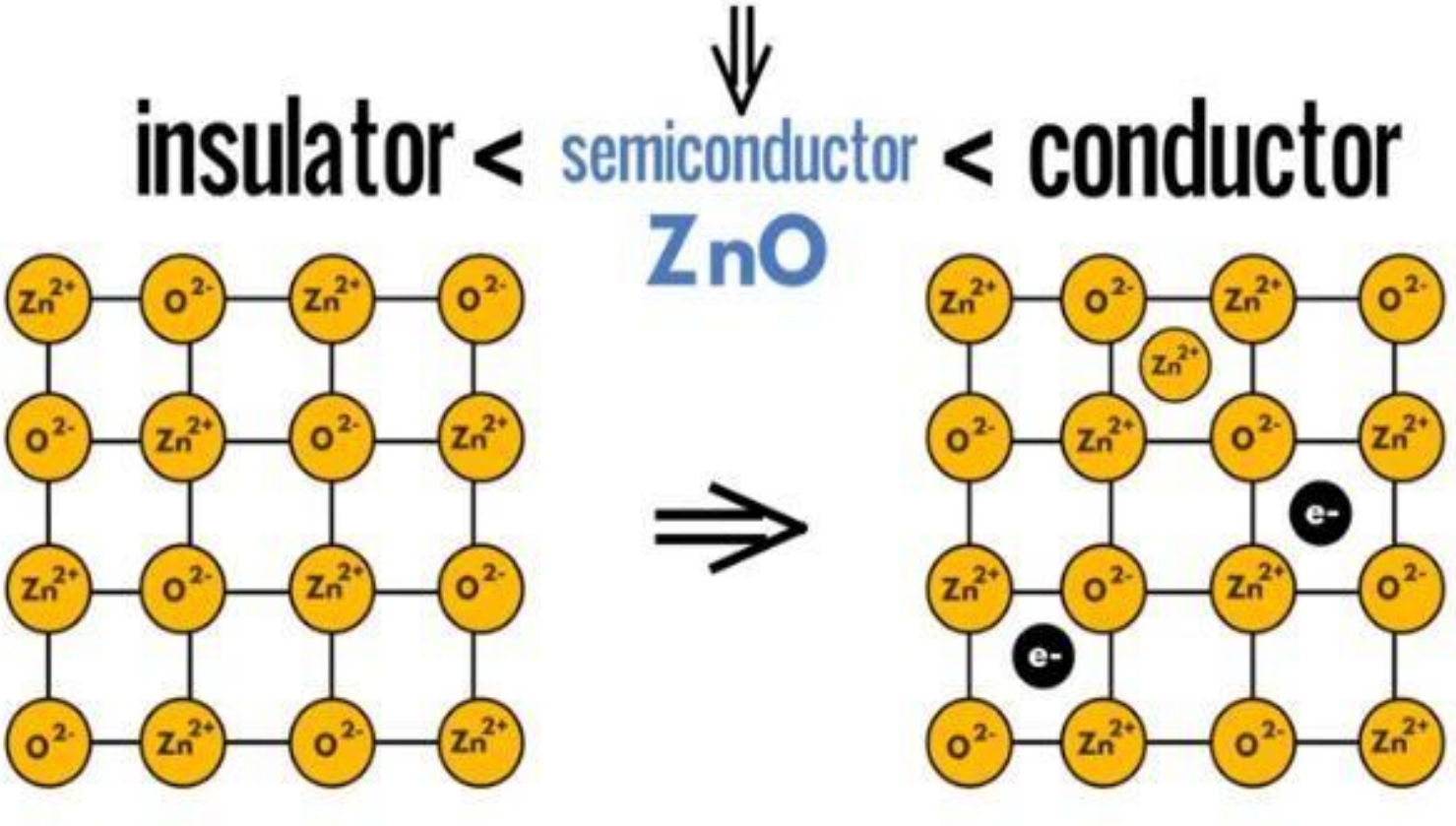
KCl + K ⇒ VOILET

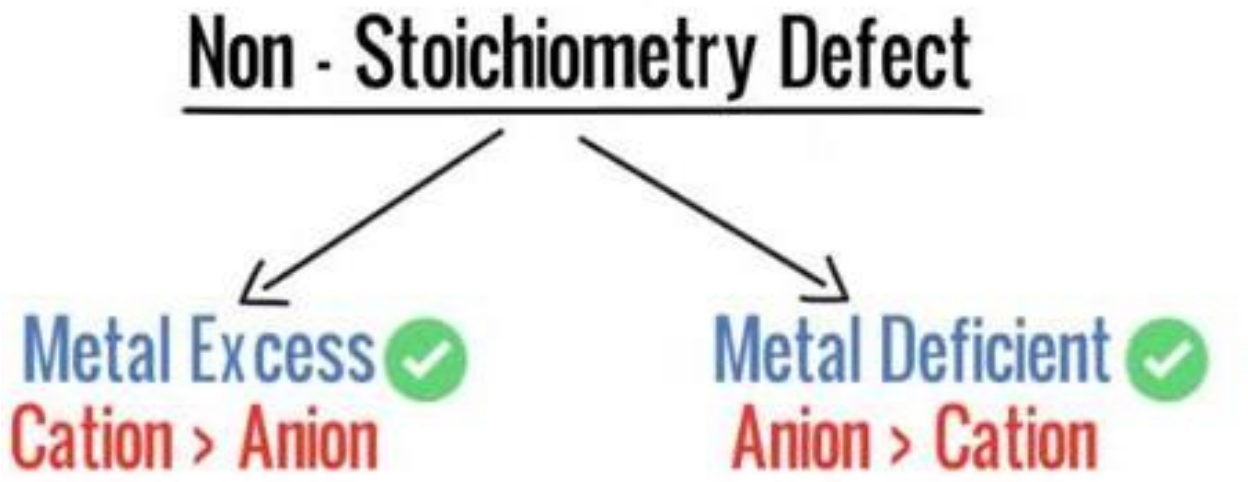
METAL EXCESS

EXTRA CATION IN INTERSTITIAL SITES

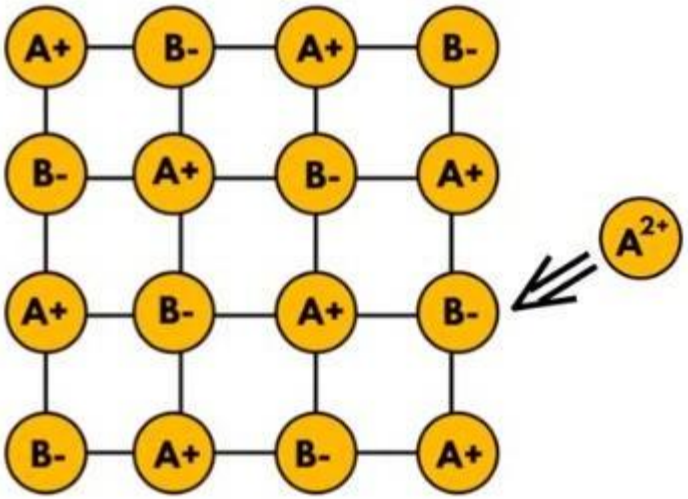


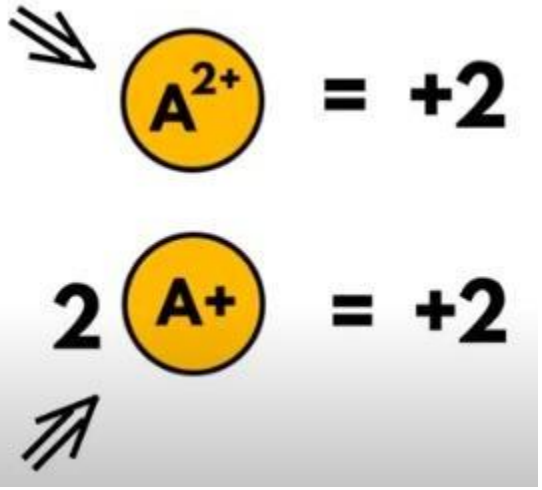



insulator < semiconductor < conductor
ZnO
Zn2+
O2-
e-

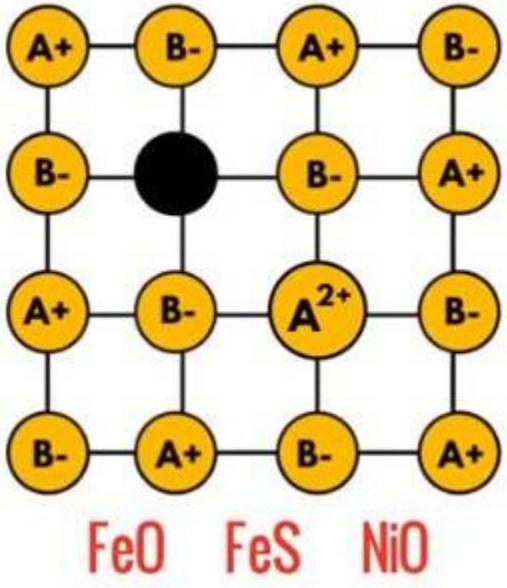

Non - Stoichiometry Defect
Metal Excess
Cation > Anion
Metal Deficient
Anion > Cation

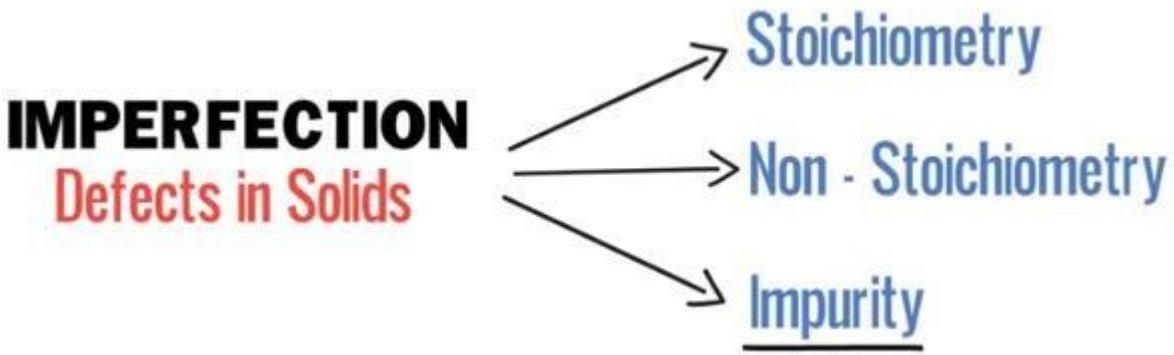
METAL DEFICIENCY



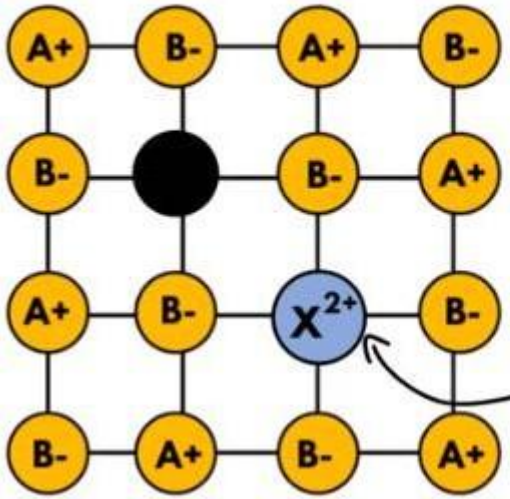


METAL DEFICIENCY

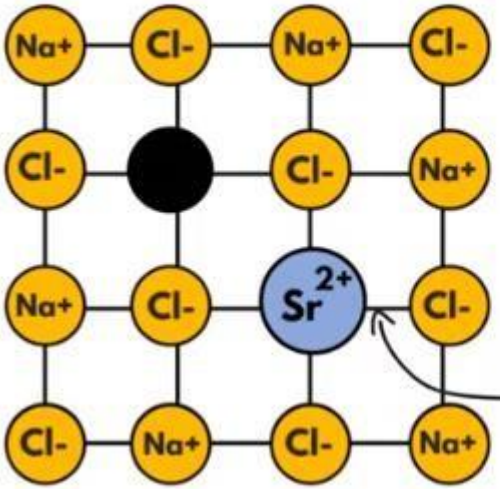



IMPERFECTION
Defects in Solids
Stoichiometry
Non - Stoichiometry
Impurity

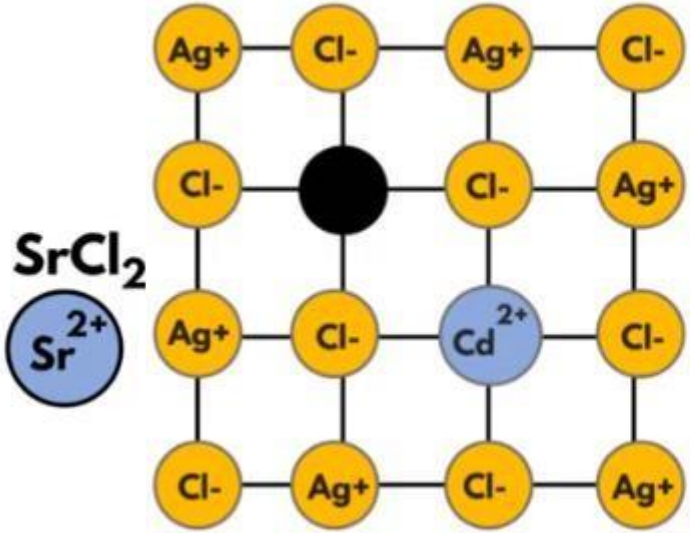
IMPURITY DEFECT



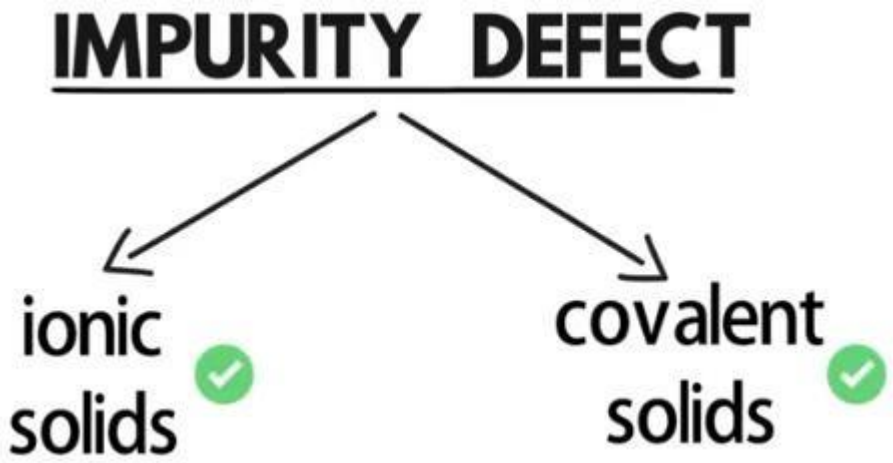
IMPURITY DEFECT

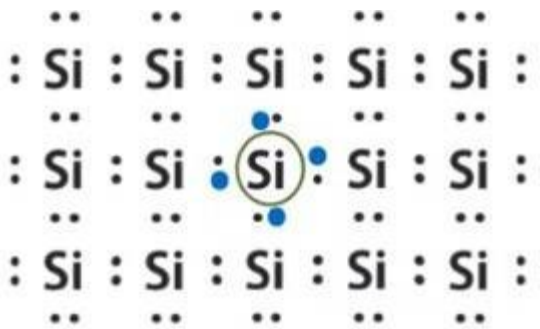


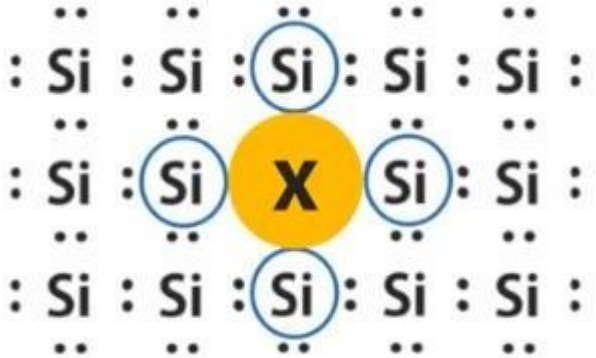
$NaCl + SrCl_2$

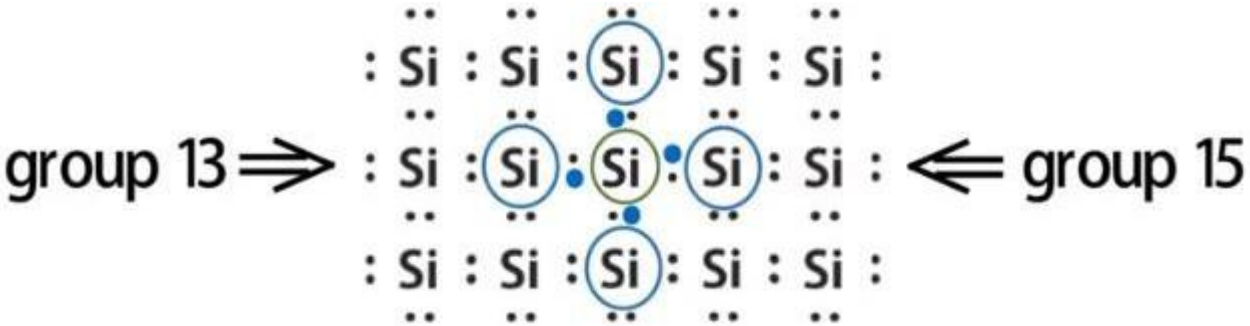


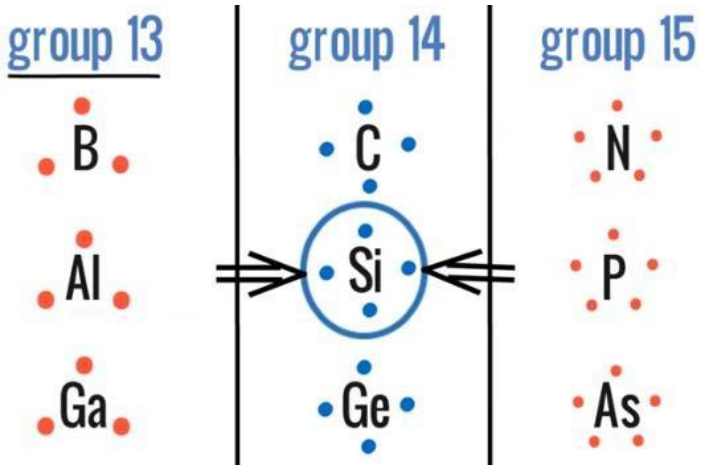
$AgCl + CdCl_2$

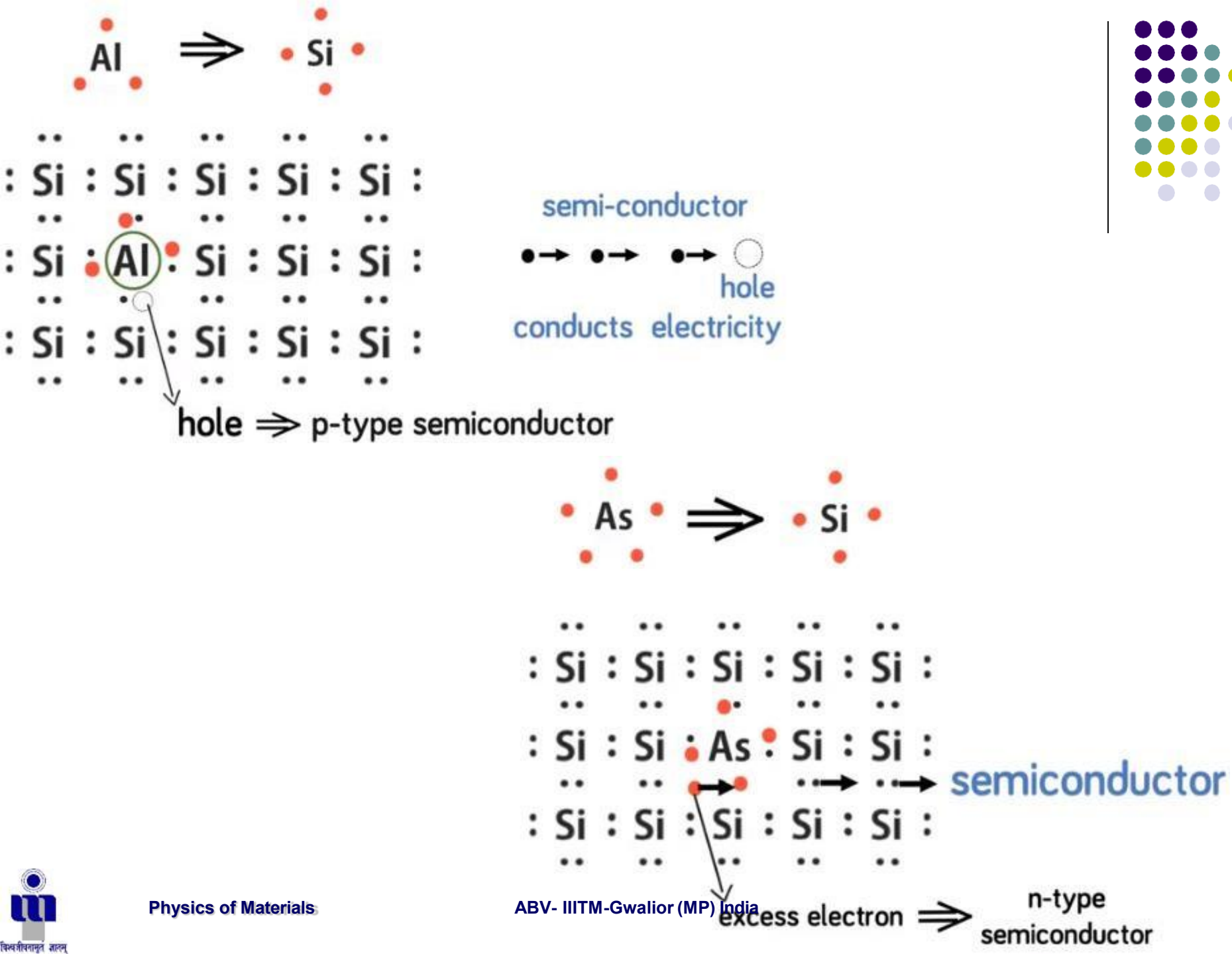

IMPURITY DEFECT
ionic solids
covalent solids


Si


Si
X

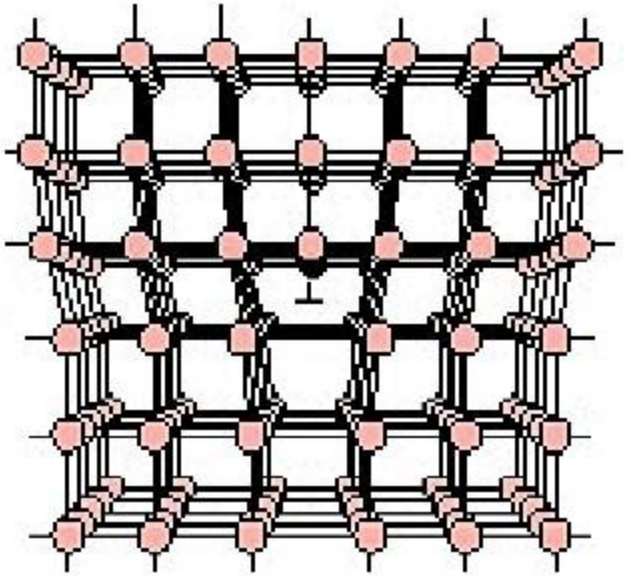

group 13
Si
group 15


group 13
group 14
group 15
B
Al
Ga
C
Si
Ge
N
P
As


Al
Si
Si Si Si Si Si
Si Al Si Si Si
Si Si Si Si Si
semi-conductor
hole
conducts electricity
hole ⇒ p-type semiconductor
As
Si
Si Si Si Si Si
Si Si As Si Si
Si Si Si Si Si
semiconductor
excess electron ⇒ n-type semiconductor

LINE DEFECTS

- Line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points.



- Interatomic bonds significantly distorted in immediate vicinity of dislocation line.
- Dislocation affects the mechanical properties.

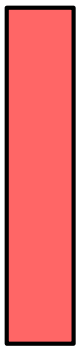
Line Defects

Dislocations:

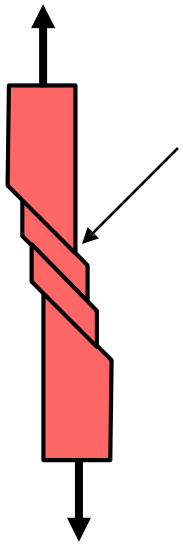
- are line defects,
- slip between crystal planes result when dislocations move,
- produce permanent (plastic) deformation.

Schematic of Zinc (HCP):

- before deformation



- after tensile elongation



Imperfections in Solids

Linear Defects (Dislocations)

- Are one-dimensional defects around which atoms are misaligned

- Edge dislocation:
  - extra half-plane of atoms inserted in a crystal structure
  - **b** perpendicular ($\perp$) to dislocation line
- Screw dislocation:
  - spiral planar ramp resulting from shear deformation
  - **b** parallel ($\parallel$) to dislocation line

Burger's vector, **b**: measure of lattice distortion

Imperfections in Solids

Edge Dislocation

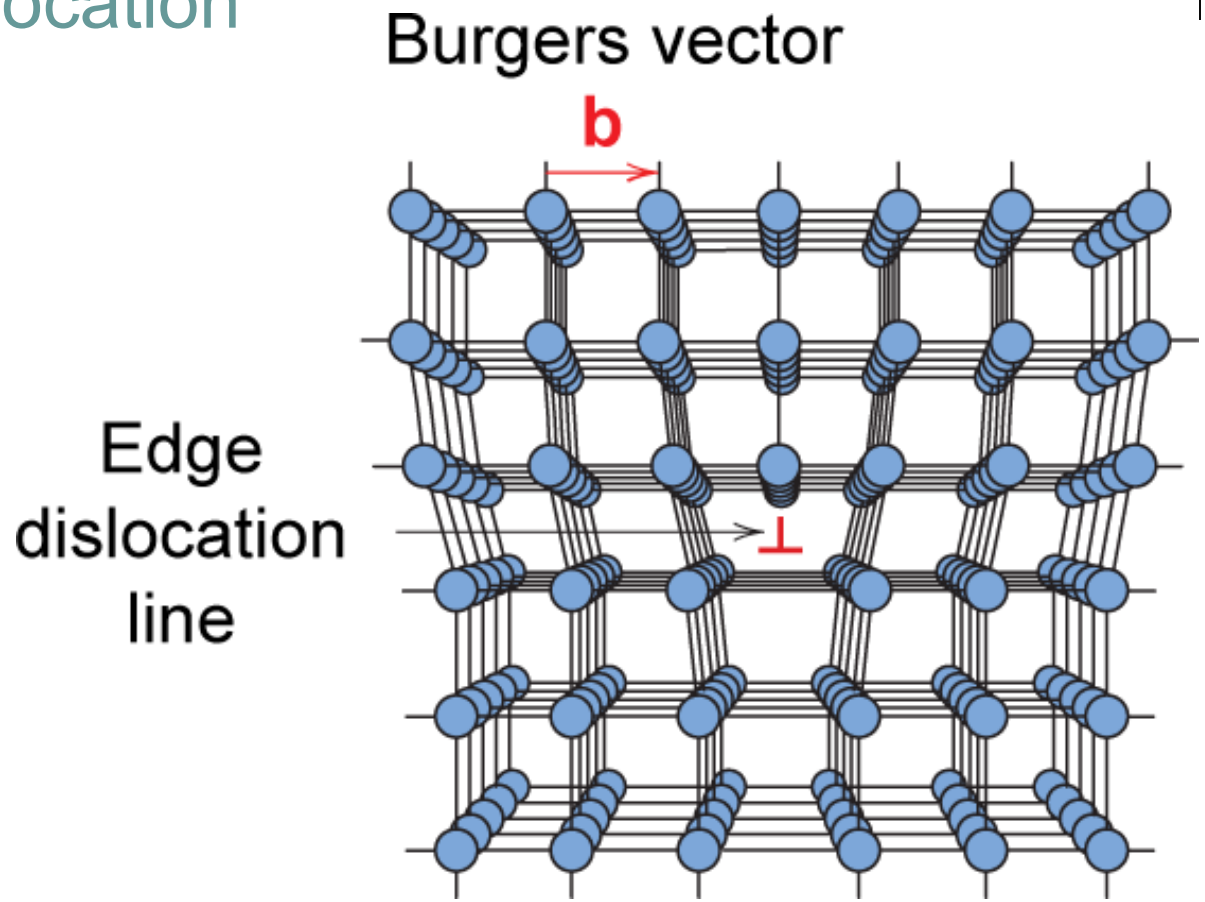
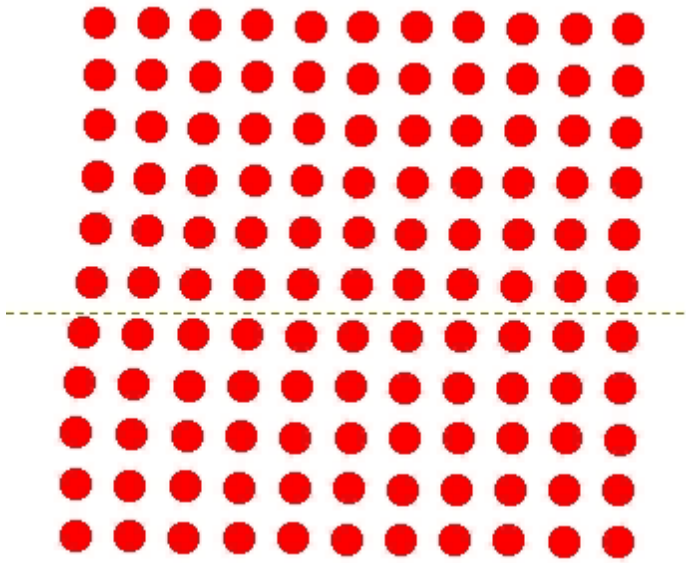


Fig. 4.3, *Callister & Rethwisch 8e.*

Motion of Edge Dislocation

- Dislocation motion requires the successive bumping of a half plane of atoms (from left to right here).
- Bonds across the slipping planes are broken and remade in succession.



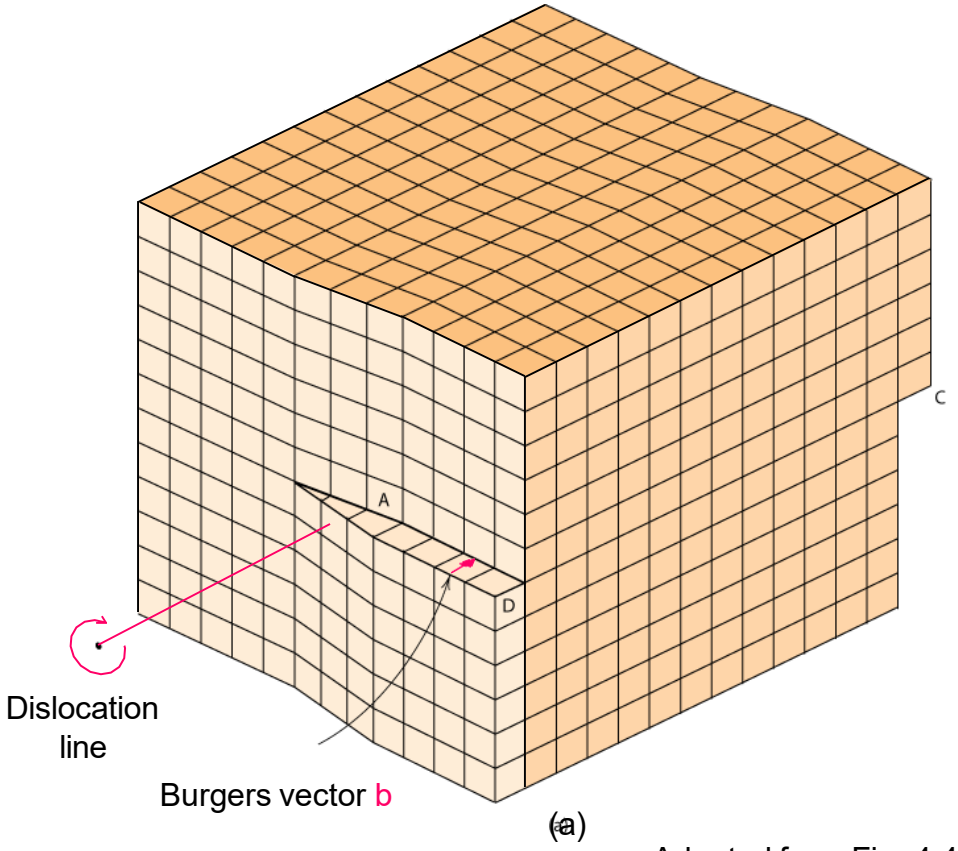
Click once on image to start animation

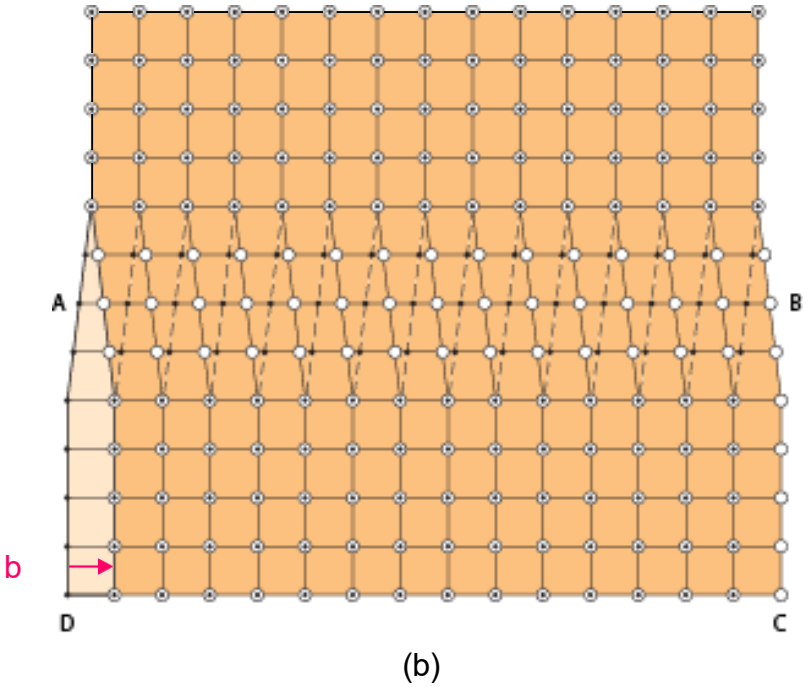
(Courtesy P.M. Anderson)

Atomic view of edge dislocation motion from left to right as a crystal is sheared.

Imperfections in Solids

Screw Dislocation



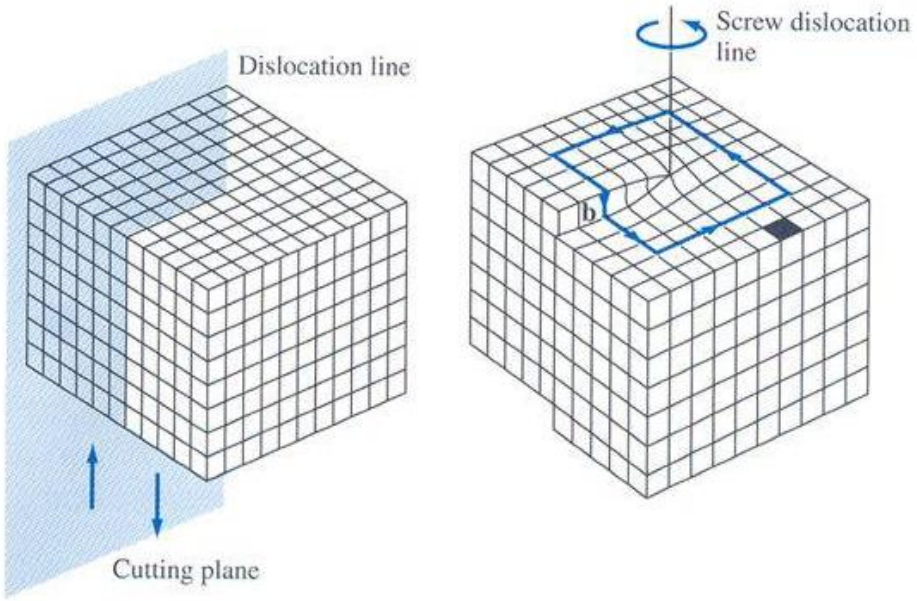


Adapted from Fig. 4.4, *Callister & Rethwisch 8e.*

Imperfections in Solids

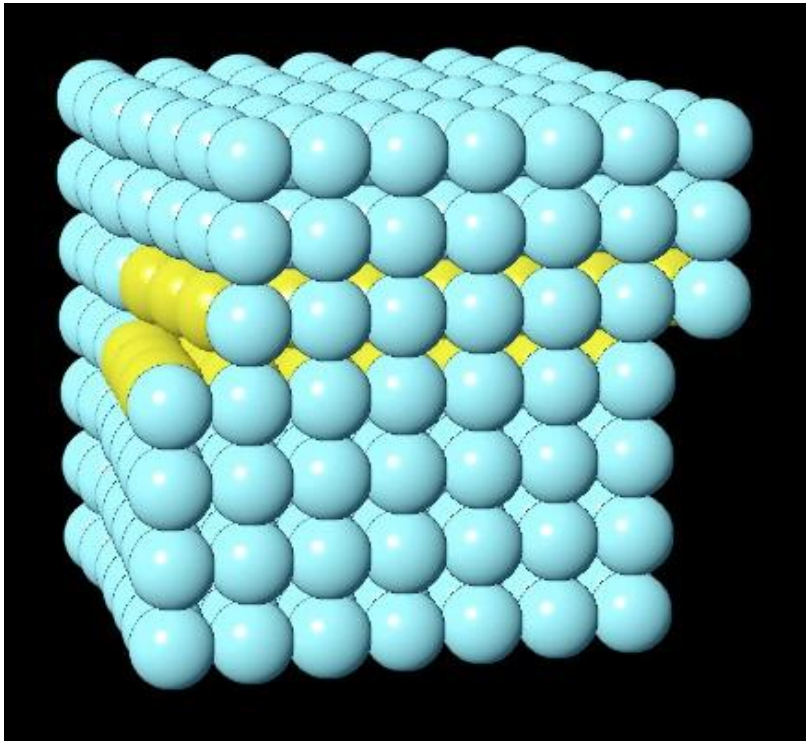
Screw Dislocation

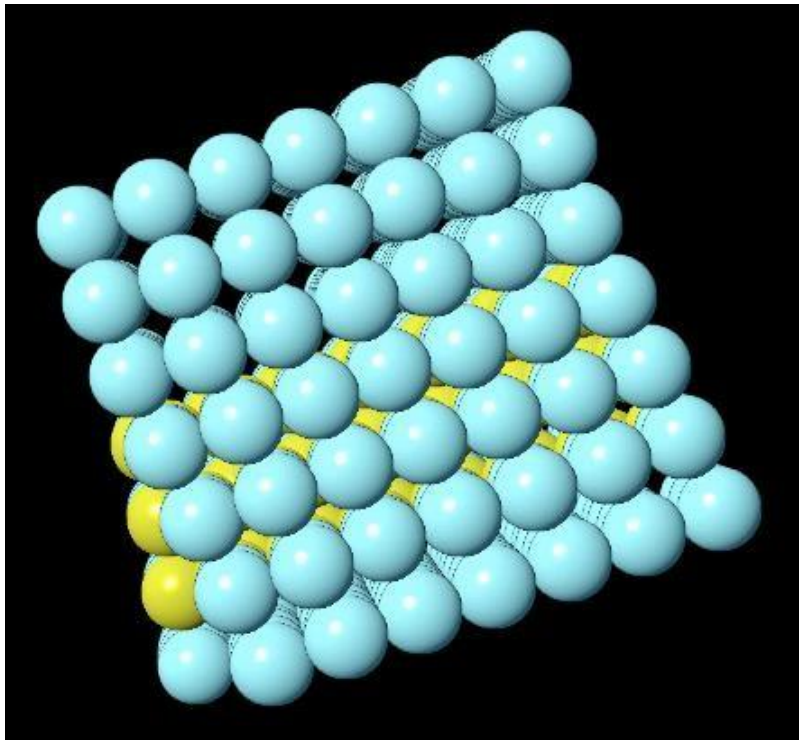
- **Created due to shear stresses applied to regions of a perfect crystal separated by cutting plane.**
- **Distortion of lattice in form of a spiral ramp.**
- **Burgers vector is parallel to dislocation line.**



VMSE: Screw Dislocation

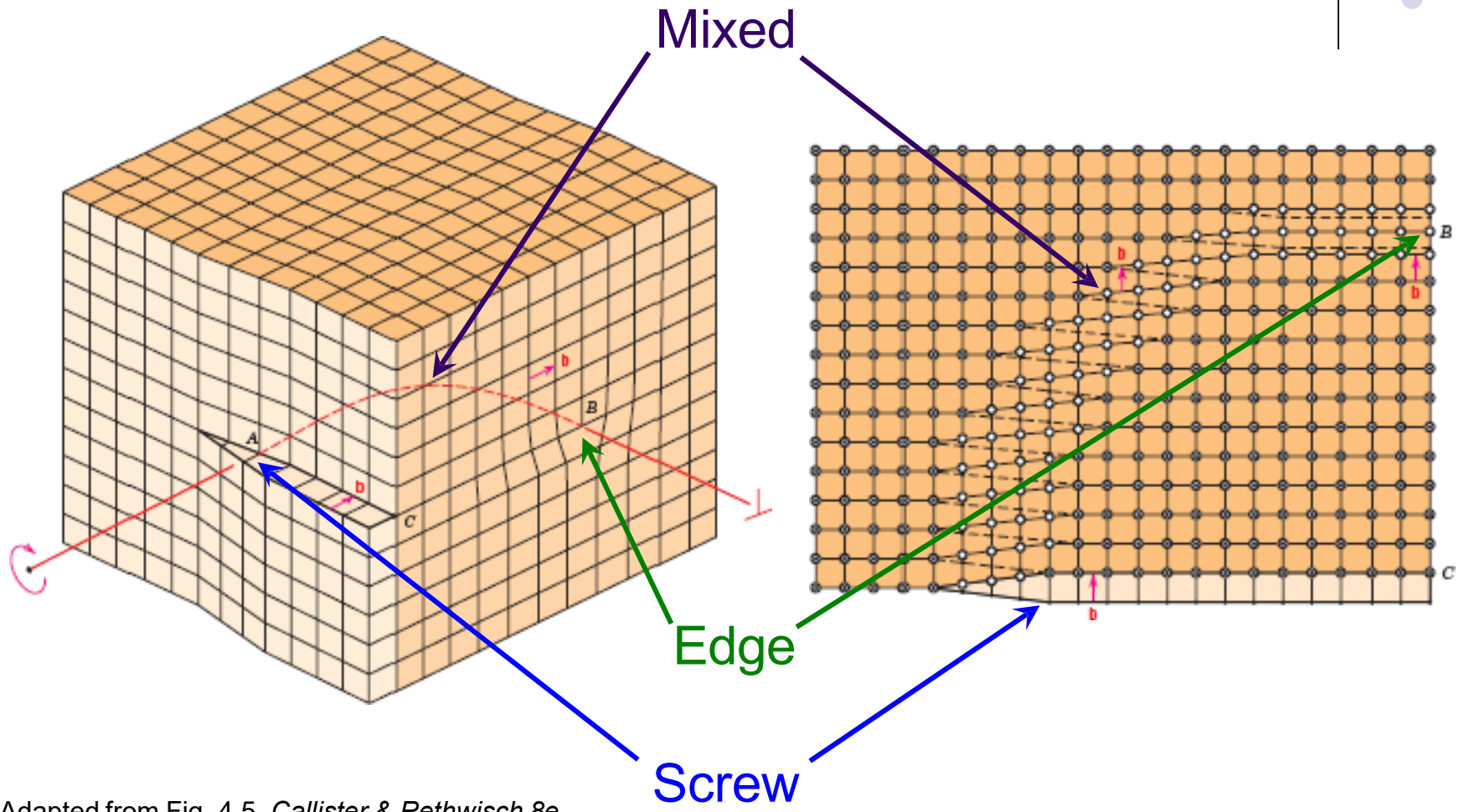
- In VMSE:
  - a region of crystal containing a dislocation can be rotated in 3D
  - dislocation motion may be animated





Front View VMSE Screen Shots Top View

Dislocations



Adapted from Fig. 4.5, *Callister & Rethwisch 8e.*

Imperfections in Solids

Dislocations are visible in electron micrographs

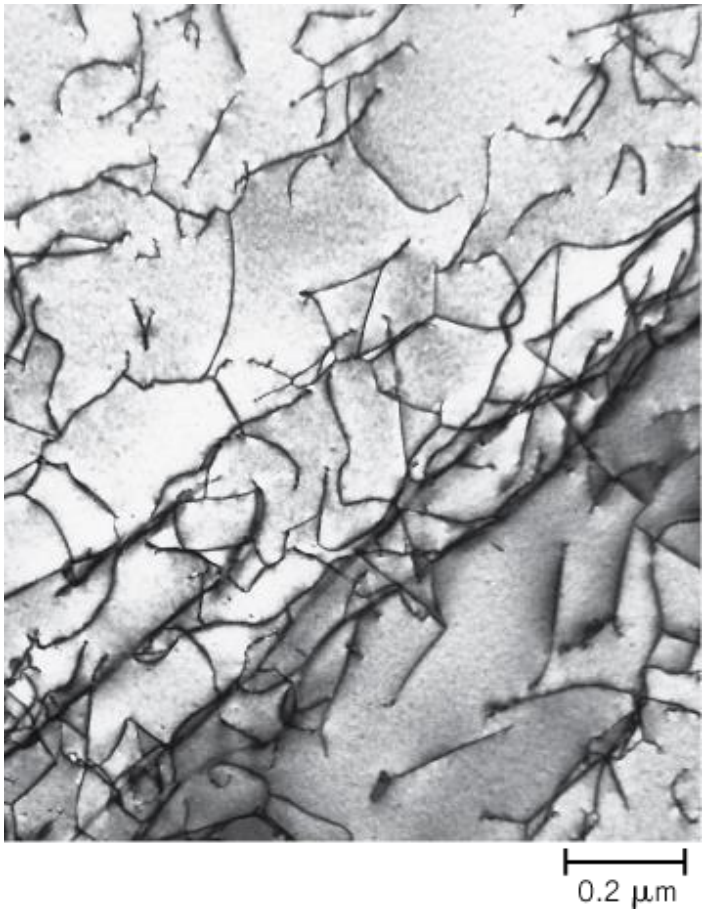
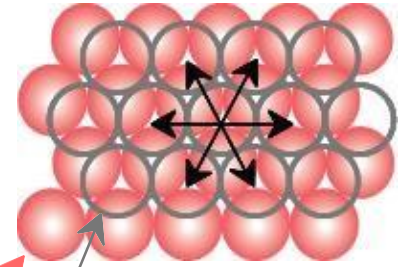


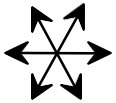
Fig. 4.6, *Callister & Rethwisch 8e.*

Dislocations & Crystal Structures

- Structure: close-packed planes & directions are preferred.



view onto two close-packed planes.



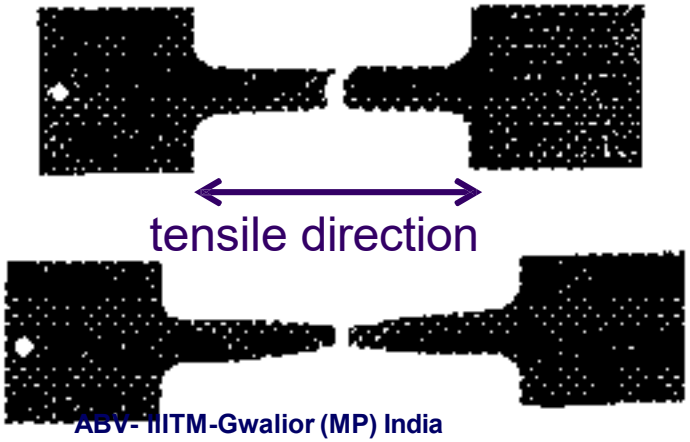
close-packed directions

close-packed plane (bottom)

close-packed plane (top)

- Comparison among crystal structures:
  - FCC: many close-packed planes/directions;
  - HCP: only one plane, 3 directions;
  - BCC: none

- Specimens that were tensile tested.

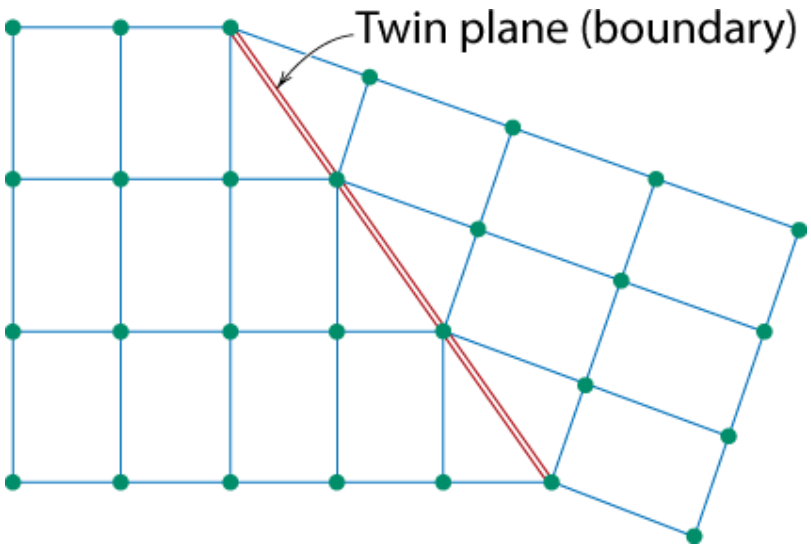


Mg (HCP)

Al (FCC)

Planar Defects in Solids

- One case is a twin boundary (plane)
  - Essentially a reflection of atom positions across the twin plane.



Adapted from Fig. 4.9,
Callister & Rethwisch 8e.

In crystallography, a twin plane (also known as a composition plane or mirror plane) is the boundary or interface between two otherwise identical crystal lattices that have been joined in a twinned structure. This plane is where the crystal lattice points are shared between the individual crystals, creating a symmetrical intergrowth where one part of the crystal is a reflection or mirror image of the other across this plane.

- Stacking faults
  - For FCC metals an error in ABCABC packing sequence
  - Ex: ABCABABC

SURFACE DEFECTS

- Surface defects are associated with boundaries that are separate regions of the materials and have different crystal structure.
- Two Dimensional defect.
- Due to change in orientation of the atomic planes and stacking sequence of atomic planes.
- Caused during solidification or mechanical or thermal treatment of material.
- Effect the mechanical properties, electrical resistance and corrosion resistance.

Catalysts and Surface Defects

- A catalyst increases the rate of a chemical reaction without being consumed
- Active sites on catalysts are normally surface defects

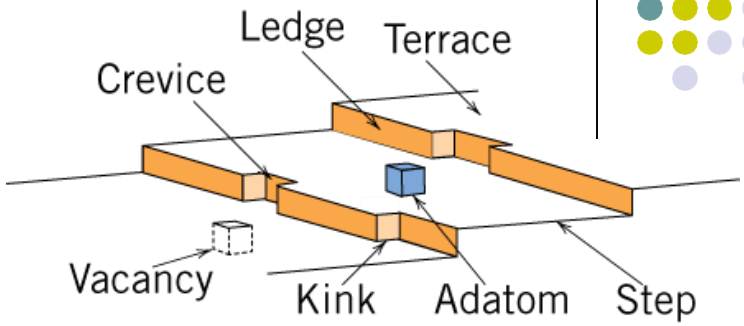


Fig. 4.10, *Callister & Rethwisch 8e.*

Single crystals of $(Ce_{0.5}Zr_{0.5})O_2$ used in an automotive catalytic converter

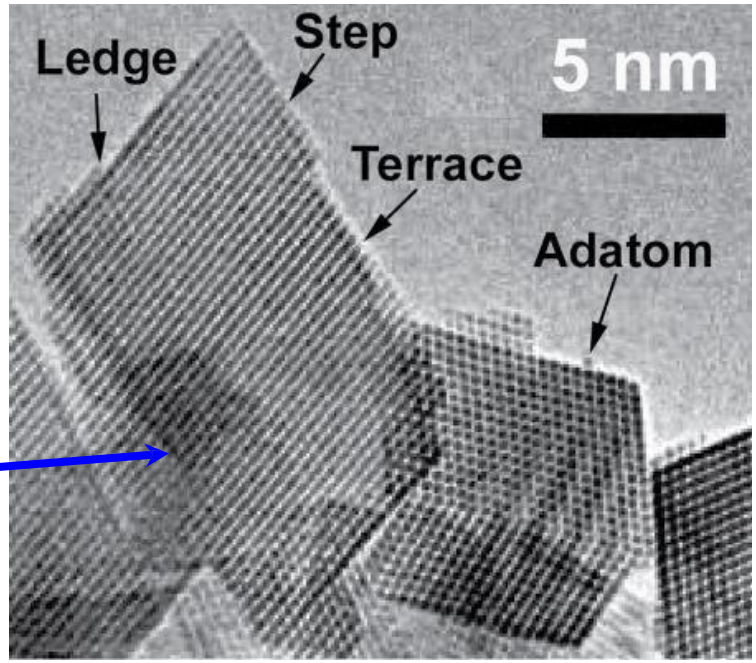
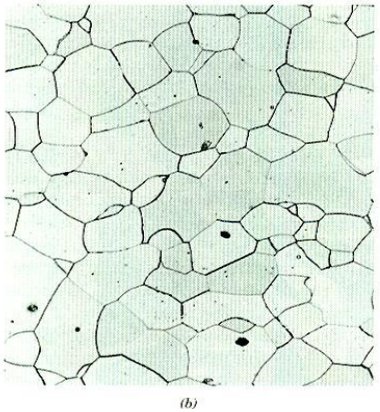


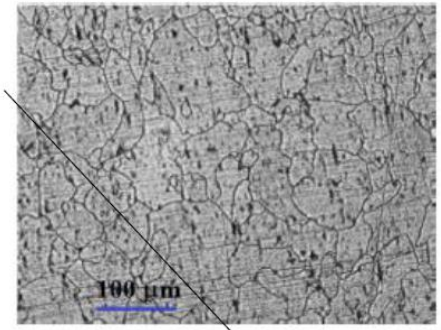
Fig. 4.11, *Callister & Rethwisch 8e.*

Surface defects

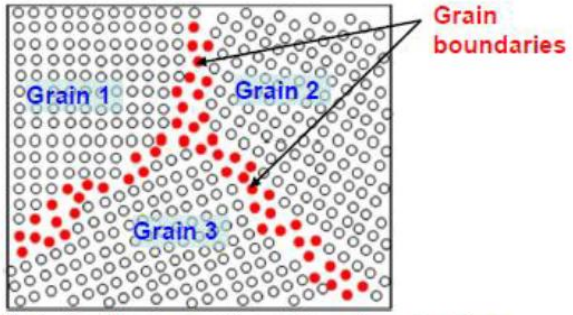
Grain Boundaries

- Most crystalline solids are an aggregate of several crystals. Such materials are called polycrystalline.
- Each crystal is known as a grain. The boundary between the grains is the grain boundary (the irregular lines in Fig.a)
- A grain boundary is a region of atomic disorder in the lattice only a few atomic diameter wide.
- The orientation of the crystals changes across the grain boundary as shown schematically in Fig. b.
- Grain boundaries act as obstacles to dislocation motion. Hence, presence of more grain boundaries (finer grain size) will increase the strength.



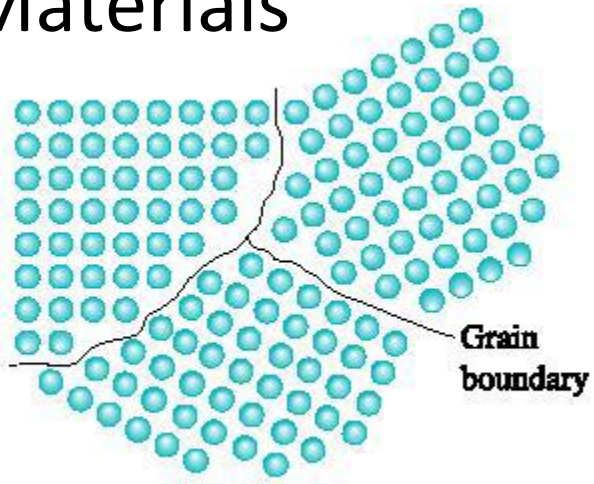


(a) Optical micrograph of a polycrystalline material

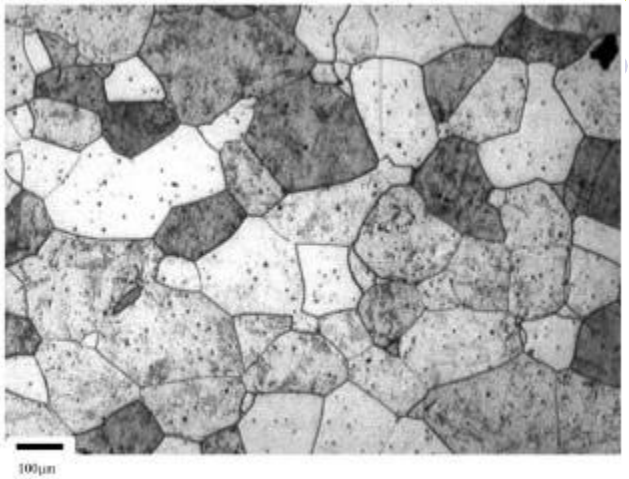


(b) Schematic of orientation change across the grain boundary

Polycrystalline Materials



(a)



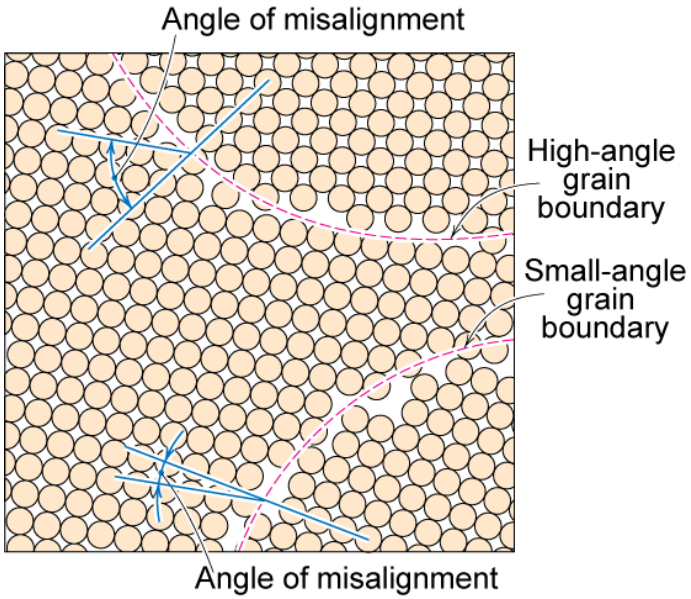
(b)

Grain Boundaries

- regions between crystals
- transition from lattice of one region to another

(a) The atoms near the boundaries of the 3 grains do not have an equilibrium spacing or arrangement; slightly disordered.

(b) Grains and grain boundaries in a stainless steel sample. low density in grain boundaries



Bulk and Volume Defect

Bulk or volume defects are three-dimensional imperfections within a material's crystal lattice, occurring at a larger scale than point or line defects, and include
voids, inclusions, pores, cracks, and other foreign particles.
These defects are typically introduced during material processing and can significantly affect mechanical properties by acting as "stress raisers," but in some cases, foreign particles can also be added to strengthen the material through mechanisms like dispersion hardening.

Bulk or volume defects
- Porosity
- Inclusions
- Cracks
- These defects form during manufacturing processes for various reasons and are harmful to the material.

Bulk defects

Weld defect

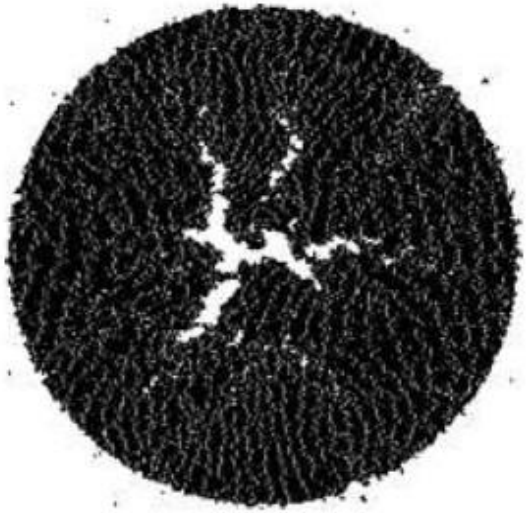
Casting defect

Shrinkage cavity

- Casting blow holes, porosity – Gas entrapment during melting and pouring. Improper welding parameters/practice
- Shrinkage cavity due to improper risering
- Non-metallic inclusions – Slag, oxide particles or sand entrapment
- Cracks – Uneven heating/cooling, thermal mismatch, constrained expansion/contraction all leading to stress development

Bulk or Volume Defects

- **PERCIPITATES** : Fraction of a micron in size
- **DISPERSANTS** : may be large precipitates, grains, or polygranular particles distributed through microstructure
- **INCLUSIONS** : foreign particles or large precipitate particles ; undesirable ; harmful
- **VOIDS** : Trapped Gases ; Decreases mechanical strength



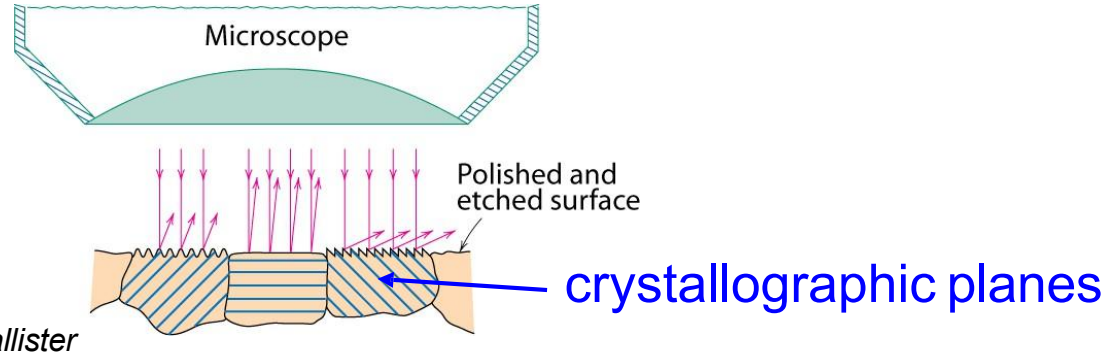
Cluster of microcracks in a melanin granule irradiated by a short laser pulse.

Microscopic Examination

- Crystallites (grains) and grain boundaries. Vary considerably in size. Can be quite large.
  - ex: Large single crystal of quartz or diamond or Si
  - ex: Aluminum light post or garbage can - see the individual grains
- Crystallites (grains) can be quite small (mm or less) – necessary to observe with a microscope.

Optical Microscopy

- Useful up to 2000X magnification.
- Polishing removes surface features (e.g., scratches)
- Etching changes reflectance, depending on crystal orientation.



Adapted from Fig. 4.13(b) and (c), *Callister & Rethwisch 8e.* (Fig. 4.13(c) is courtesy of J.E. Burke, General Electric Co.)

Micrograph of brass (a Cu-Zn alloy)

Optical Microscopy

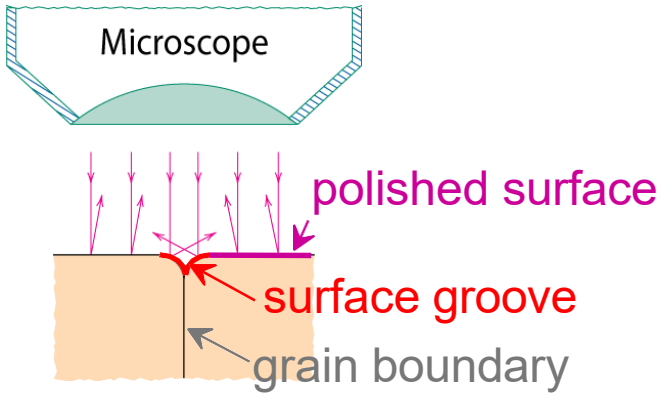
Grain boundaries...

- are imperfections,
- are more susceptible to etching,
- may be revealed as dark lines,
- change in crystal orientation across boundary.

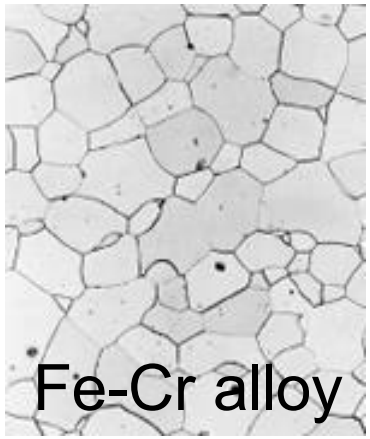
ASTM grain size number

$N = 2^{n-1}$

number of grains/in^2 at 100x magnification



(a)



(b)

Adapted from Fig. 4.14(a) and (b), *Callister & Rethwisch 8e.* (Fig. 4.14(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC [now the National Institute of Standards and Technology, Gaithersburg, MD].)

Optical Microscopy

- Polarized light
  - metallographic scopes often use polarized light to increase contrast
  - Also used for transparent samples such as polymers

Microscopy

Optical resolution ca. 10^{-7} m = 0.1 μm = 100 nm

For higher resolution need higher frequency

- X-Rays? Difficult to focus.
- Electrons
  - wavelengths ca. 3 pm (0.003 nm)
    - (Magnification - 1,000,000X)
  - Atomic resolution possible
  - Electron beam focused by magnetic lenses.