Crystal Defect (Imperfection)

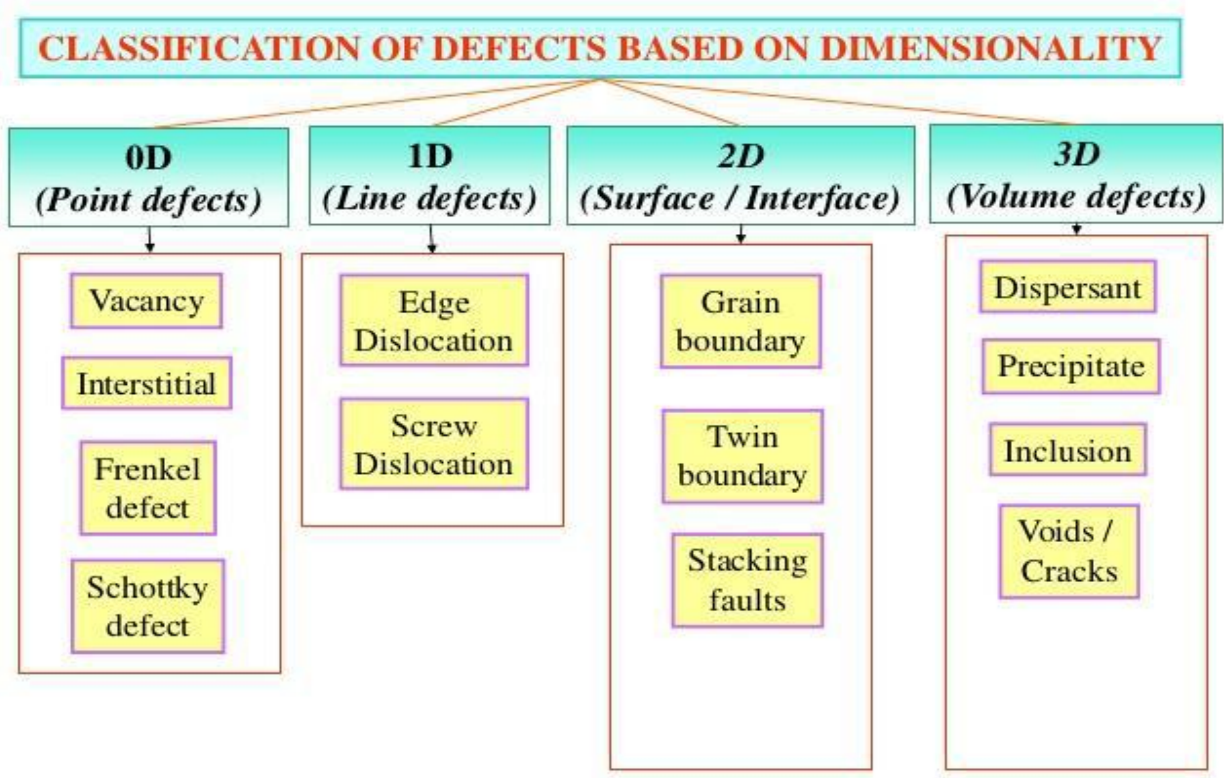
Is imperfection in the regular geometrical arrangement of the atoms in a crystalline solid. These imperfections result from deformation of the solid by: rapid cooling from high temperature, or high-energy radiation (X-rays or neutrons) striking the solid, foreign atoms, external stresses, thermal effect. Real crystals are never perfect, there are always defects. These defects influence its mechanical, electrical, and optical behavior. Defects or imperfections in crystalline solids are normally classified according to their dimension as follows

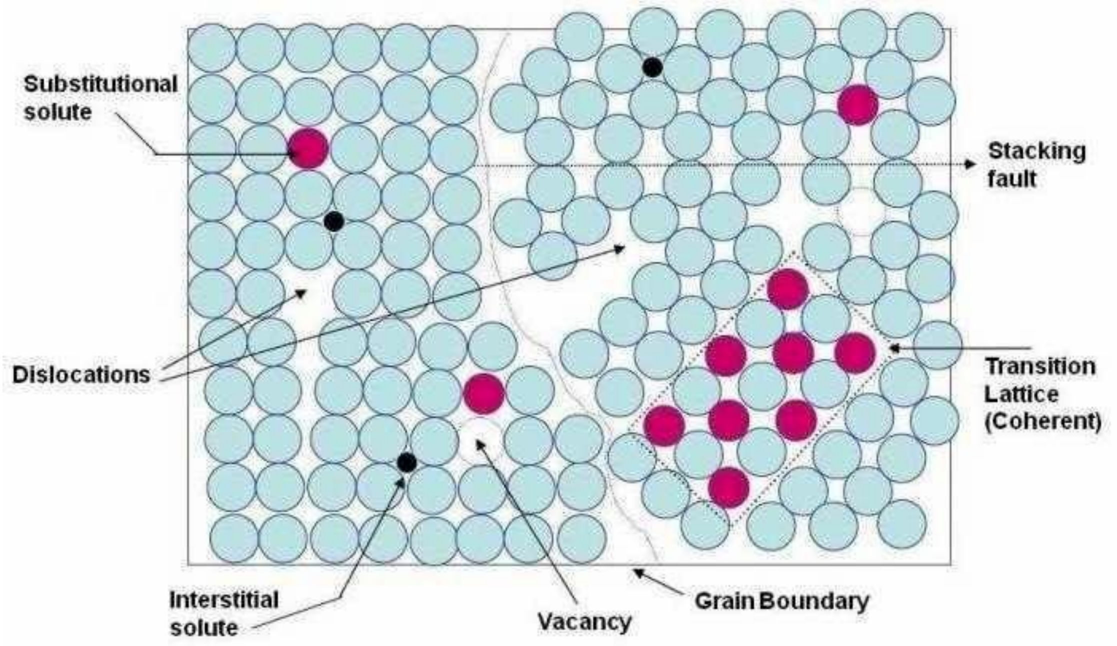
1. Point imperfections (Zero dimensional defects)
2. Line imperfections (one dimensional defects)
3. Plane or surface imperfections (Two dimensional defects)
4. Volume imperfections (three dimensional defects)

Why defect is important?

There are a lot of properties that are controlled or affected by defects, for example:

- Electric and thermal conductivity in metals (strongly reduced by point defects).
- Electronic conductivity in semiconductors (controlled by substitution defects). The conductivity of some semiconductors is due entirely to trace amount of chemical impurities.
- Diffusion (controlled by vacancies)
- Ionic conductivity (controlled by vacancies).
- Plastic deformation in crystalline materials (controlled by dislocation).
- Colors (affected by defects). luminescence of many crystals arise from impurities and imperfections
- Mechanical strength (strongly depended on defects). Mechanical and plastic properties are usually controlled by imperfections





Various Crystal Defects

1- Point defects

Point defects are the loss of one or a few atoms. Point defects are defects that occur only at or around a single lattice point. They are not extended in space in any dimension. The size of the defect could be one atom, or two atomic diameters, which is just like a point. A point defect extends its influence only a few atomic diameters beyond its lattice position. Point defects include vacancies, self-interstitial atoms, interstitial impurity atoms, and substitutional atoms.

1- Vacancy defect

is simplest of the point defects. Vacancy is produced when an atom is missing from a normal site see above Figure. It is created when the solid is formed.

At R.T, very few vacancies are present, but this number increases exponentially as we increase the temperature (see Eq. 1).

The creation of vacancies becomes easier with the increase of temperature as thermal energy helps in the diffusion of the atoms.

The higher is the temperature, more often atoms are jumping from one equilibrium position to another and larger number of vacancies can be found in a crystal. Actually, the equilibrium number of vacancies, N_v, increases exponentially with the absolute temperature T, and can be estimated using the equation (Boltzmann Distribution):

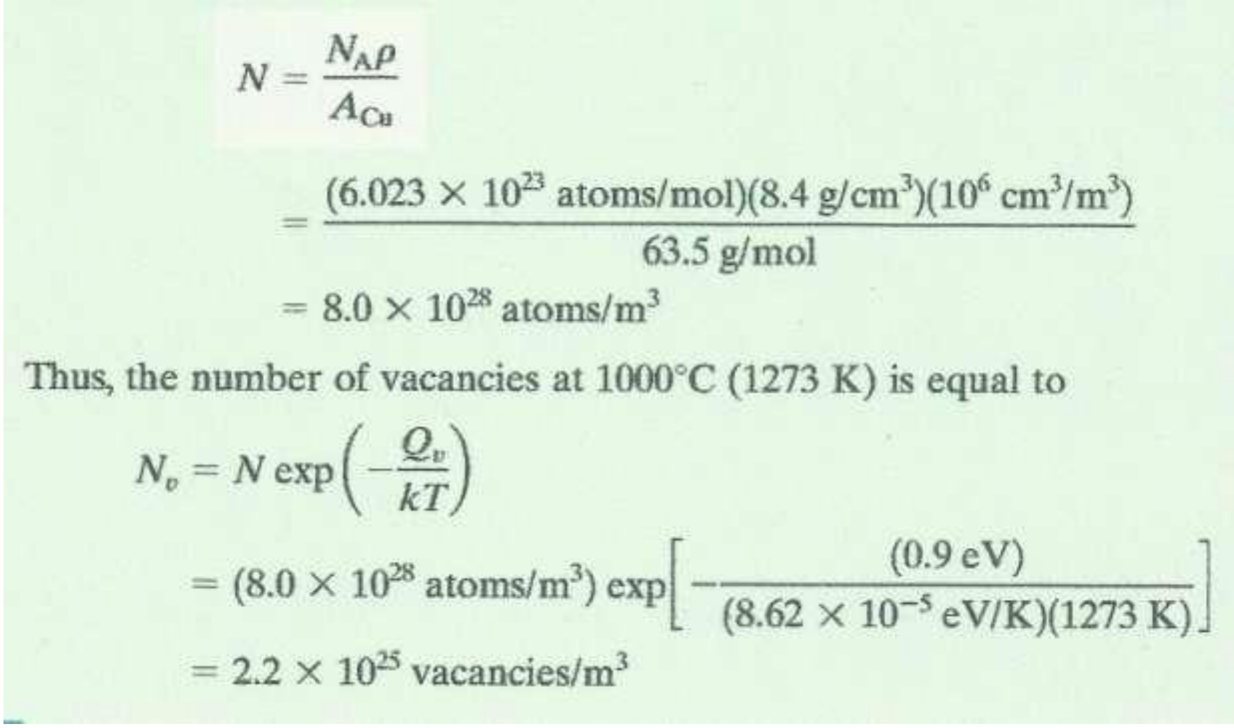
$$N_v = N \exp(-Q_v/kT) \;\ldots\ldots\quad 1$$

Where N is the number of regular lattice sites, k is the Boltzmann constant ($1.38 * 10^{-23}$ J/atom. K), and Q_v is the energy needed to form a vacancy in a perfect crystal.

Using this simple equation, we can estimate that at room temperature in copper there is one vacancy per 10^{15} lattice atoms, whereas at high temperature, just below the melting point (1358 K) there is one vacancy for every 10,000 atoms. These are the lower end estimations, a large numbers of additional vacancies can be introduced in a growth process or as a result of further treatment (plastic deformation, quenching from high temperature to the ambient one, etc.).

Example:

Calculate the equilibrium number of vacancies per cubic meter for copper at 1000^oC. The energy for vacancy formation is 0.9 eV/atom; the atomic weight and density (at 1000^oC) for copper are 63.5 g/mol and 8.4 g/cm^3, respectively.



$$
\begin{aligned}
N &= \frac{N_A \rho}{A_{Cu}} \\
&= \frac{(6.023 \times 10^{23} \text{ atoms/mol})(8.4 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{63.5 \text{ g/mol}} \\
&= 8.0 \times 10^{28} \text{ atoms/m}^3
\end{aligned}
$$

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

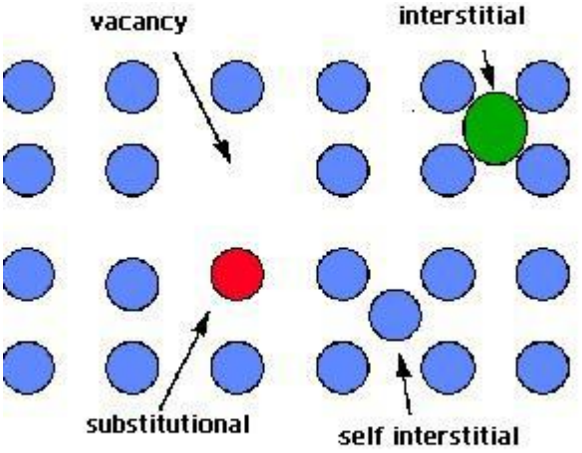
$$
\begin{aligned}
N_v &= N \exp\left(-\frac{Q_v}{kT}\right) \\
&= (8.0 \times 10^{28} \text{ atoms/m}^3) \exp\left[-\frac{(0.9 \text{ eV})}{(8.62 \times 10^{-5} \text{ eV/K})(1273 \text{ K})}\right] \\
&= 2.2 \times 10^{25} \text{ vacancies/m}^3
\end{aligned}
$$

2- Interstitial defect

An interstitial defect is formed when an extra atom is inserted into the lattice structure in a place between atoms. The number of this defects is independent of temperature.

3- Substitutional defect

A substitutional defect is formed when an atom is replaced different type of atom. The substitutional atom remains at the original normal lattice point. The number of this defects is independent of temperature.



4- Schottky defect

A vacancy can be formed by an atom migrating from a normal lattice site in the bulk to the surface of the crystal. This is known as a schottky defect (see Fig.). Schottky defect occurs in ionic crystals such as NaCl.

Schottky got a mathematical relationship to calculate the concentration of the vacancies (n) in ionic crystals at different temperatures, so suppose that the real ionic crystals composed of equal numbers (N) of the positive and negative ions:

$$n = N\, e^{-E_p/2k_BT} \qquad (1)$$

Where n<<N

Ep represented energy required to form a pair of vacancies

E = n Ep (E represented internal energy)

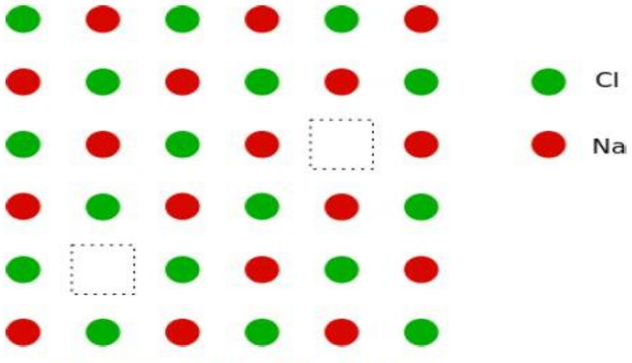


Fig. Schottky defect

5- Frenkel defect

A Frenkel defect is a vacancy-interstitial atom pair formed when an ion jumps from a normal lattice point to an interstitial site, leaving behind a vacancy see Fig. 5. Frenkel defect occurs in metallic and semiconductor crystals.

Frenkel got a mathematical relationship to calculate the concentration of the number of pairs from the vacancy-interstitial at different temperatures:

$$n = \sqrt{NN_i}\, e^{-E_i/2k_BT} \qquad (2)$$

Where N_i is the number of intra-sites.

Ei represented energy required to form a pair of vacancy-interstitial atom.

E = n Ei (E represented internal energy)

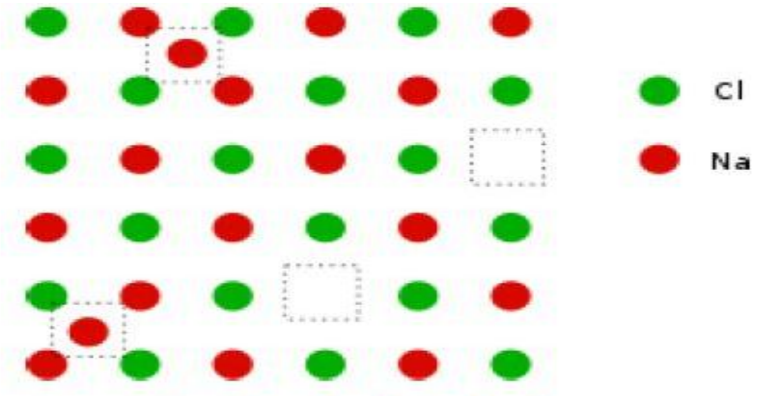
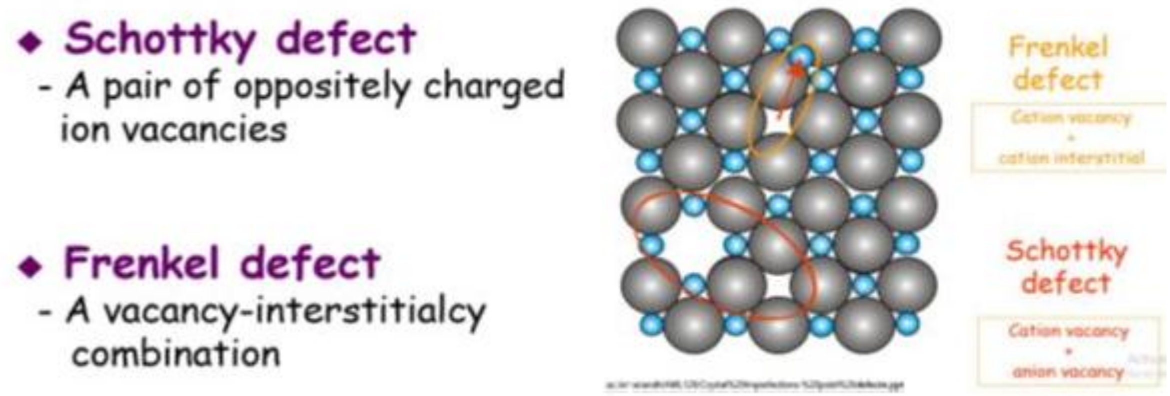
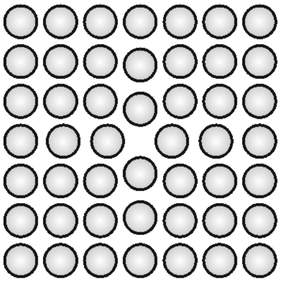


Fig Frenkel defect

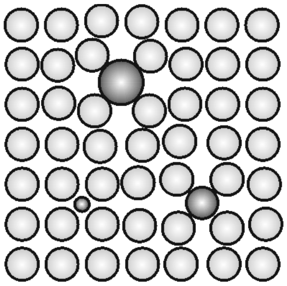
The combination of anion - cation vacancies (in pairs) is called Schottkey imperfections. The combination of a vacancy and interstitial is called a Frankel imperfection. Figure -6- represents the crystalline defects group.



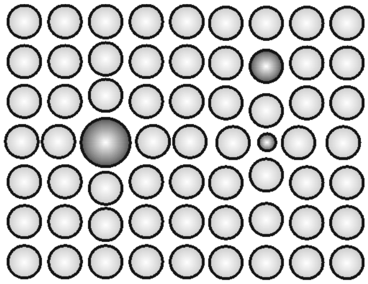
- **Schottky defect**
  - A pair of oppositely charged ion vacancies
- **Frenkel defect**
  - A vacancy-interstitialcy combination



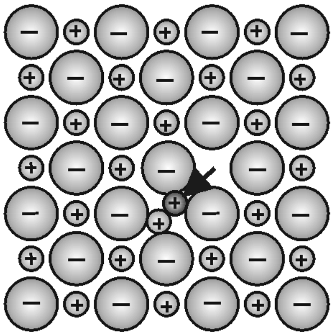
(a) vacancy



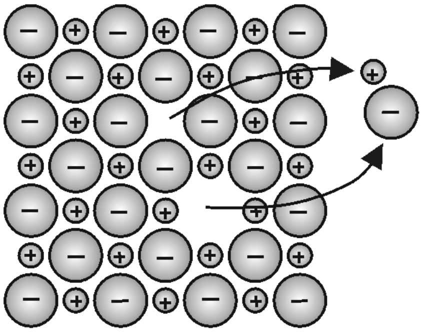
(b) interstitial defects



(c) substitutional defects



(d) Frenkel imperfection



(e) Schottky imperfection

Exercise1:

Why it was called point defects?

Solution:

Because the maximum dimension of a point defect in every direction is no more than a few atomic spacing’s.

Exercise2:

Calculate the number of vacancies per cubic centimeter and the number of vacancies per copper atom when copper is a (a) R.T and (b) 1084^{0}C. About 20000 cal/mole required to produce a vacancy in copper.

Solution:

The lattice parameter of FCC copper is $3.6151*10^{-8}$cm. The number of copper atoms or lattice points per cm^3 is:

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

a) At room temperature, T=25+273=298K

$$n = N\, e^{-E_p/2k_BT} = 8.47*10^{22} \exp \frac{-20000}{(1.987)(298)}$$

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

$$\frac{n}{N} = \frac{1.815\ 10^{8}}{8.47*10^{22}} = 2.14\ 10^{-15}$$

b) T=1084+273=1357K

$$n = N\, e^{-E_p/2k_BT} = 8.47*10^{22} \exp \frac{-20000}{(1.987)(1357)}$$

$$= 5.09*\ 10^{19} \text{ vacancies/cm}^3$$

$$\frac{n}{N} = \frac{5.09*10^{19}}{8.47*10^{22}} = 6\ *10^{-4}$$

2- Line Defect or Imperfections:

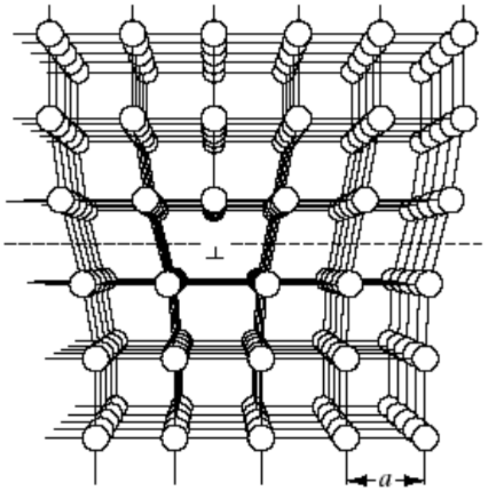
In linear defects groups of atoms are in irregular positions. Linear defects are commonly called dislocations. Any deviation from perfectly periodic arrangement of atoms along a line is called the line imperfection. In this case, the distortion is centered only along a line and therefore the imperfection 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. The strength and ductility of metals are controlled by dislocations.

To extreme types of dislocations are distinguish as

1. Edge dislocations and

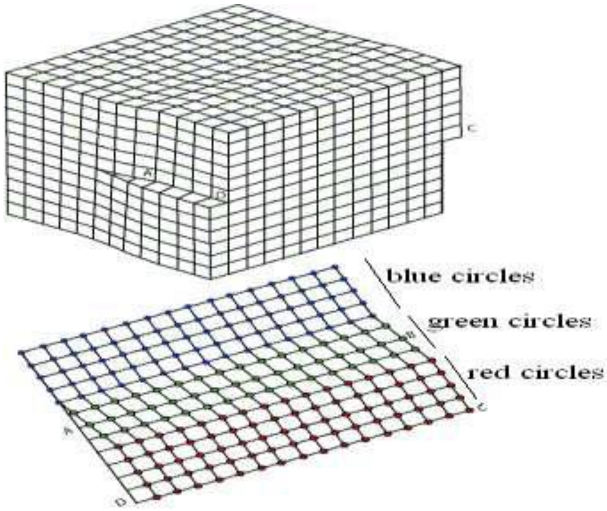
2. Screw dislocations.

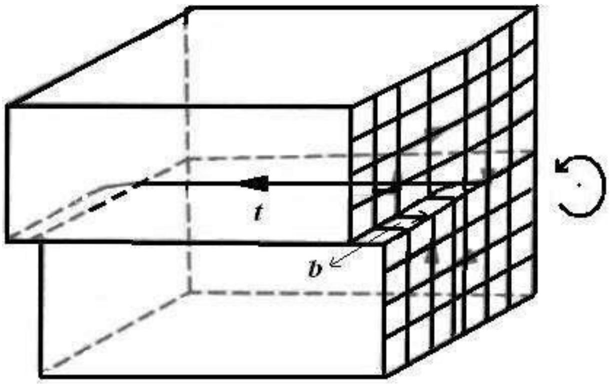
1- Edge Dislocations: An Edge dislocation in a metal may be regarded as the insertion (or removal) of an extra half plane of atoms in the crystal structure. This is termed an edge dislocation; it is a linear defect that centers on the line that is defined along the end of the extra half-plane of atoms. This is sometimes termed the dislocation line, which, for the edge dislocation in Figure is perpendicular to the plane of the page. Within the region around the dislocation line there is some localized lattice distortion The magnitude of this distortion decreases with distance away from the dislocation line. An edge dislocation may also be formed by an extra half plane of atoms that is included in the bottom portion of the crystal; its designation is a ⊤. Burgers vector is the magnitude and direction of the lattice distortion associated with a dislocation denoted by b. For an edge dislocation, it is perpendicular orientations of dislocation line.



⊥
Represents the edge of an
extra half plane of atoms

2- Screw Dislocations: The screw dislocation is slightly more difficult to visualize. The motion of a screw dislocation is also a result of shear stress, but the defect line movement is perpendicular to direction of the stress and the atom displacement, rather than parallel. To visualize a screw dislocation, imagine a block of metal with a shear stress applied across one end so that the metal begins to rip. **i** The upper front region of the crystal is shifted one atomic distance to the right relative to the bottom portion. A Screw Dislocation changes the character of the atom planes.



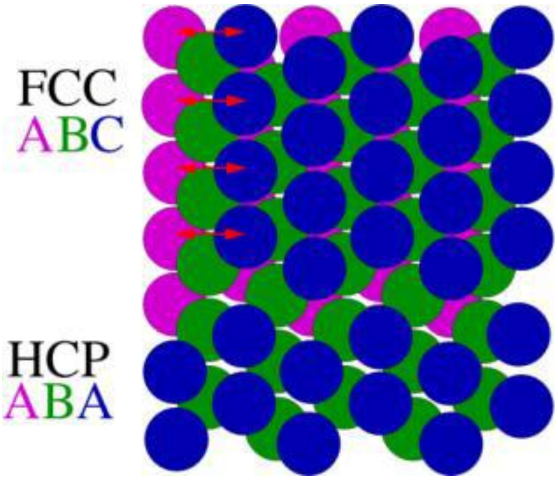


3- Planar defects, which are interfaces between homogeneous regions of the material. Planar defects include grain boundaries, stacking faults and twin boundaries.

1-Stacking Faults

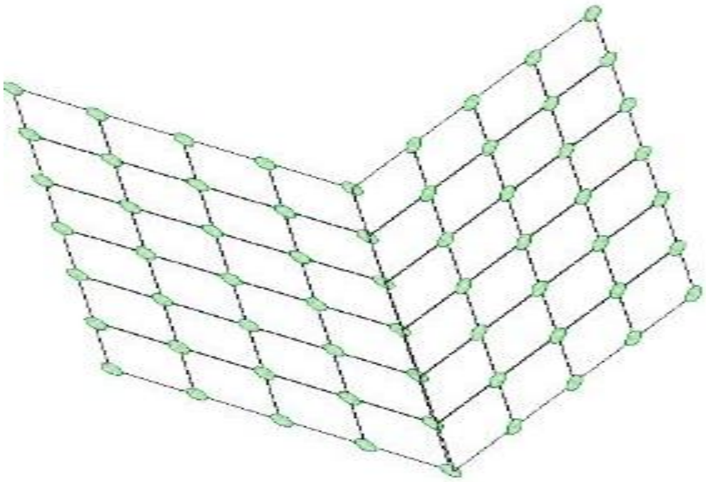
A disruption of the long-range stacking sequence can produce two other common types of crystal defects: 1) a stacking fault and 2) a twin region. A change in the stacking sequence over a few atomic spacing produces a stacking fault whereas a change over many atomic spacing produces a twin region. A stacking fault is a one or two-layer interruption in the stacking sequence of atom planes. Stacking faults occur in a number of crystal structures, but it is easiest to see how they occur in close packed structures. For example, it is knowing from a previous discussion that face centered cubic (fcc) structures differ from hexagonal close packed (hcp) structures only in their stacking order. For hcp and fcc structures, the first two layers arrange themselves identically, and are said to have an AB arrangement. If the third layer is placed so that its atoms are directly above those of the first (A) layer, the stacking will be ABA. This is the hcp structure, and it continues ABABABAB. However it is possible for the third layer atoms to arrange themselves so that they are in line with the first layer to produce an ABC arrangement which is that of the fcc structure. So, if the hcp structure is going along as ABABAB and suddenly switches to ABABABCABAB, there is a stacking fault present.

Alternately, in the fcc arrangement the pattern is ABCABCABC. A stacking fault in an fcc structure would appear as one of the C planes missing. In other words the pattern would become ABCABCAB_ABCABC.



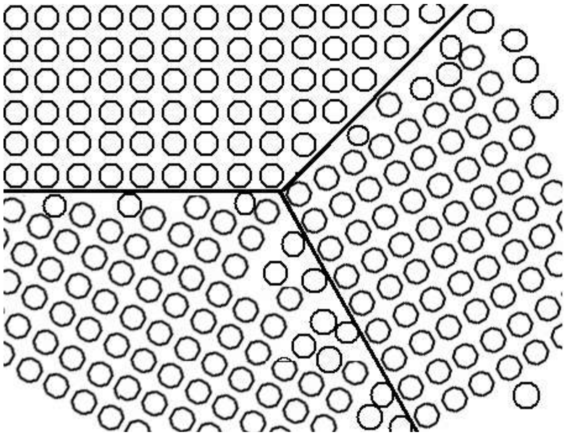
2- Twin boundaries

A Twin Boundary happens when the crystals on either side of a plane are mirror images of each other. The boundary between the twinned crystals will be a single plane of atoms. There is no region of disorder and the boundary atoms can be viewed as belonging to the crystal structures of both twins. Twins are either grown-in during crystallization, or the result of mechanical or thermal work.



3- 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.



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4- Volume defects

Volume defects as name suggests are defects in 3-dimensions. These include pores, cracks, foreign inclusions and other phases.

- Cracks may arise in crystals during the process of crystal growth. During growth, 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 called Voids.
- Inclusion of foreign particles or non- crystalline regions of dimensions of at least 10-30Å also belong to the category of volume defects.
- When voids occur due to air bubbles becoming trapped when a material solidifies, it is commonly called porosity.
- When a void occurs due to the shrinkage of a material as it solidifies, it is called cavitation.

These defects are normally introduced during processing and fabrication steps.