

## Introduction

- Do you know the difference between  [\$\alpha\$ -quartz](#),  [\$\beta\$ -quartz](#)? Or why does quartz have these different forms?
- Certain [chemical elements](#), can exist in two or more different forms . For example, iron exists in three forms namely ‘ $\alpha$ ’ iron, ‘ $\gamma$ ’ iron and ‘ $\delta$ ’ iron and they behave slightly different from the elements mentioned in the first question . What are they?
- Do you know the meaning of ‘crystal imperfections’?

## Learning Objectives

On completion of this topic you will be able to understand:

1. Poly morphism
2. Allotropy
3. Point defects in crystal
4. Dislocations in crystals.
5. Grain boundary in crystals
6. Crystal twinning
7. Stacking default

## Polymorphism

**Polymorphism** in [materials science](#) is the ability of a solid material to exist in more than one form or [crystal](#) structure. Polymorphism can potentially be found in any crystalline material including [polymers](#), [minerals](#), and [metals](#), and is related to [allotropy](#), which refers to [elemental solids](#). Together with polymorphism the complete morphology of a material is described by other variables such as [crystal habit](#), [amorphous fraction](#) or [Crystallographic defects](#). Polymorphism is relevant to the fields of [pharmaceuticals](#), [agrochemicals](#), [pigments](#), [dyestuffs](#), [foods](#), and [explosives](#).

When polymorphism exists as a result of difference in crystal packing, it is called **packing polymorphism**. Polymorphism can also result from the existence of different [conformers](#) of the same molecule in **conformational polymorphism**. In **pseudopolymorphism** the different crystal types are the result of [hydration](#) or [solvation](#). An example of an organic polymorph is [glycine](#), which is able to form [monoclinic](#) and [hexagonal](#) crystals. [Silica](#) is known to form many polymorphs, the most important of which are;  [\$\alpha\$ -quartz](#),  [\$\beta\$ -quartz](#), [tridymite](#), [cristobalite](#), [coesite](#), and [stishovite](#).

In terms of [thermodynamics](#), there are two types of polymorphism. For a monotropic system, a plot of the free energy of the various polymorphs against temperature do not cross before all polymorphs melt--in other words, any transition from one polymorph to another will be irreversible. For an enantiotropic system, a plot of the free energy against temperature shows a crossing point before the various melting points, and it may be possible to convert reversibly between the two polymorphs on heating and cooling.

## Allotropy

If the change in structure is reversible then the polymorphism is known as 'allotropy'. **Allotropy** (Gr. *allos*, other, and *tropos*, manner) is a behavior exhibited by certain [chemical elements](#): these elements can exist in two or more different forms, known as *allotropes* of that element. In each allotrope, the element's [atoms](#) are [bonded](#) together in a different manner. Allotropes are different structural modifications of an element.<sup>[1]</sup> The phenomenon of allotropy is sometimes also called allotropism.

For example, the element [carbon](#) has two common allotropes: [diamond](#), where the carbon atoms are bonded together in a [tetrahedral](#) lattice arrangement, and [graphite](#), where the carbon atoms are bonded together in sheets of a hexagonal lattice.

Note that allotropy refers only to different forms of an element within the same phase or [state of matter](#) (i.e. different [solid](#), [liquid](#) or [gas](#) forms) - the changes of state between solid, liquid and gas in themselves are not considered allotropy. For some elements, allotropes have different molecular formulae which can persist in different phases - for example, the two allotropes of [oxygen](#) ([dioxygen](#), O<sub>2</sub> and [ozone](#), O<sub>3</sub>), can both exist in the solid, liquid and gaseous states. Conversely, some elements do not maintain distinct allotropes in different phases: for example [phosphorus](#) has numerous solid allotropes, which all revert to the same P<sub>4</sub> form when melted to the liquid state.

By 1912, [Ostwald](#) noted that the allotropy of elements is just a special case of the phenomenon of [polymorphism](#) known for compounds, and proposed that the terms allotrope and allotropy be abandoned and replaced by polymorph and polymorphism. Although many other chemists have repeated this advice, [IUPAC](#) and most chemistry texts still favour the usage of allotrope and allotropy for elements only.

### Carbon and its allotropes

- [Diamond](#) - an extremely hard, transparent crystal, with the carbon atoms arranged in a tetrahedral lattice. A poor electrical conductor. An excellent thermal conductor.
- [Graphite](#) - a soft, black, flaky solid, a moderate electrical conductor. The C atoms are bonded in flat hexagonal lattices, which are then layered in sheets.
- [Amorphous carbon](#)
- [Fullerenes](#), including "[buckyballs](#)", such as C<sub>60</sub>, and [carbon nanotubes](#)

### Phosphorous and its allotropes

- White phosphorus - crystalline solid P<sub>4</sub>
- Red phosphorus - polymeric solid
- Scarlet phosphorus
- Violet phosphorus
- Black phosphorus - semiconductor, analogous to graphite

- [Diphosphorus](#)

Oxygen and its allotropes

- [dioxygen](#), O<sub>2</sub> - colorless
- [Ozone](#), O<sub>3</sub> - blue
- [Tetra oxygen](#), O<sub>4</sub> - metastable
- [Octaoxygen](#), O<sub>8</sub> - red

Nitrogen and its allotropes

- [Dinitrogen](#)
- [Tetra nitrogen](#)
- Trinitrogen
- Two solid forms: one hexagonal close-packed and the other alpha cubic

Boron and its allotropes

- Amorphous boron - brown powder
- Crystalline boron - black, hard (9.3 on Mohs' scale), and a weak conductor at room temperature

Germanium and its allotropes

- $\alpha$ -germanium -
- $\beta$ -germanium - at high pressures

## Imperfections in Solids

### Introduction

Materials are often stronger when they have defects. The study of defects is divided according to their dimension:

0D (zero dimension) – point defects: vacancies and interstitials. Impurities.

1D – linear defects: dislocations (edge, screw, mixed)

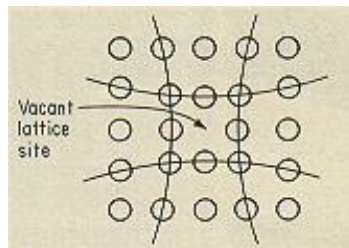
2D – grain boundaries, surfaces.

3D – extended defects: pores, cracks.

## Point Defects

### Vacancies

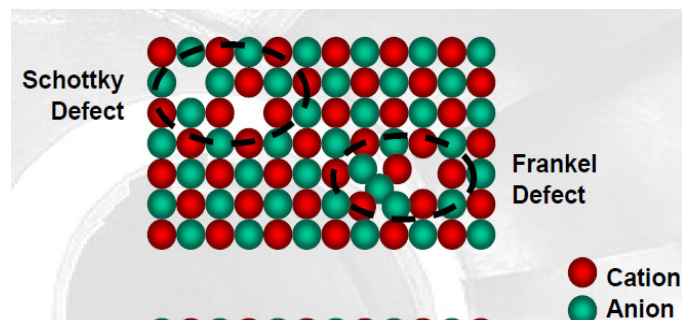
A vacancy is a lattice position that is vacant because the atom is missing. It is created when the solid is formed. Vacancies are simply empty atom sites as shown in Figure 1.



**Figure 1. Vacancy crystal defect.**

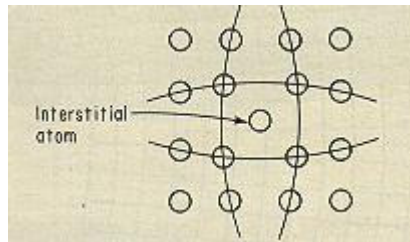
The lattice vacancies are a stable feature of metals at all temperatures above absolute zero. By successive jumps of atoms, just like playing Chinese checkers, it is possible for a vacancy to move in the lattice structure and therefore play an important part in diffusion of atoms through the lattice. Vacancies are not only present as a result of solidification but can be produced by raising the temperature or by irradiation with fast moving nuclear particles.

A pair of one cation and one anion can be missing from an ionic crystal as shown in the following figure. Such a pair of vacant sites is called **Schottky defects**. Also, in ionic crystals, an ion displaced from a regular site to an interstitial site is called **Frenkel defect**. As cations are generally the smaller in size, it is possible for them to get displaced into void space. A Frenkel defect does not change the overall electrical neutrality of the crystal. These types of defect are dominant in alkali halides.

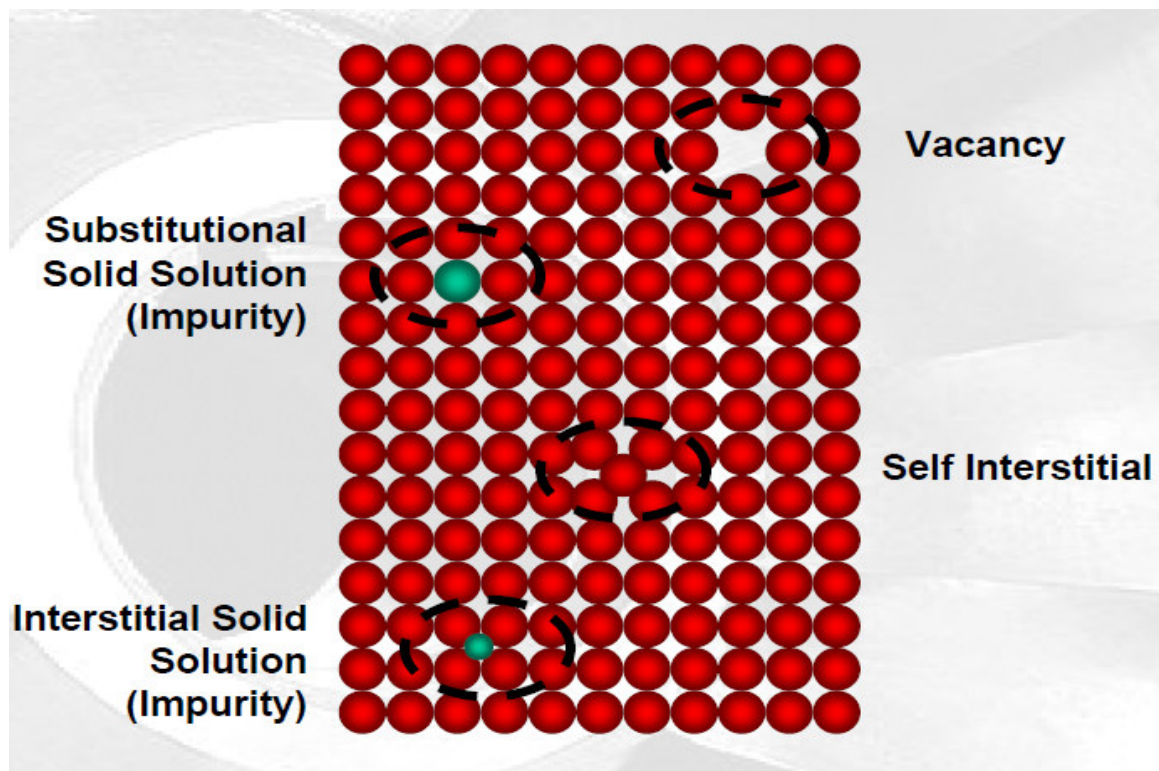


**Interstitials:**

An interstitial is an atom that occupies a place outside the normal lattice position. It may be the same type of atom as the others (self interstitial) or an impurity atom.



**Figure 2. Interstitial crystal defect.**



Interstitials tend to push the surrounding atoms farther apart and also produce distortion of the lattice planes.

Interstitial atoms may be produced by the severe local distortion during plastic deformation as well as by irradiation.

In the case of vacancies and interstitials, there is a change in the coordination of atoms around the defect. This means that the forces are not balanced in the same way as for other atoms in the solid, which results in lattice distortion around the defect.

The number of vacancies formed by thermal agitation follows the law:

$$N_V = N_A \times \exp(-Q_V/kT)$$

Where  $N_A$  is the total number of atoms in the solid,  $Q_V$  is the energy required to form a vacancy;  $k$  is Boltzmann constant, and  $T$  the temperature in Kelvin (note, not in °C or °F).

When  $Q_V$  is given in joules,  $k = 1.38 \times 10^{-23}$  J/atom-K. When using eV as the unit of energy,  $k = 8.62 \times 10^{-5}$  eV/atom-K.

Note that  $kT$  (300 K) = 0.025 eV (room temperature) is much smaller than typical vacancy formation energies. For instance,  $Q_V$  (Cu) = 0.9 eV/atom. This means that  $N_V/N_A$  at room temperature is  $\exp(-36) = 2.3 \times 10^{-16}$ , an insignificant number. Thus, a high temperature is needed to have a high *thermal* concentration of vacancies. Even so,  $N_V/N_A$  is typically only about 0.0001 at the melting point.

### **Impurities in Solids**

All real solids are impure. A very high purity material, say 99.9999% pure (called 6N – six nines) contains  $\sim 6 \times 10^{16}$  impurities per  $\text{cm}^3$ .

Impurities are often added to materials to improve the properties. For instance, carbon added in small amounts to iron makes steel, which is stronger than iron. Boron impurities added to silicon drastically change its electrical properties.

Solid solutions are made of a host, the solvent or matrix) which dissolves the solute (minor component). The ability to dissolve is called *solubility*. Solid solutions are:

- homogeneous
- maintain crystal structure
- contain randomly dispersed impurities (substitutional or interstitial)

Factors for high solubility

- Similar atomic size (to within 15%)
- Similar crystal structure
- Similar electro negativity (otherwise a compound is formed)
- Similar valence

Composition can be expressed in weight percent, useful when making the solution, and in atomic percent, useful when trying to understand the material at the atomic level.

### Dislocations—Linear Defects

Dislocations are abrupt changes in the regular ordering of atoms, along a line (dislocation line) in the solid. They occur in high density and are very important in mechanical properties of material. The Burgers vector, found by doing a loop around the dislocation line and noticing the extra interatomic spacing needed to close the loop, characterizes them. The Burgers vector in metals points in a close packed direction.

Edge dislocations occur when an extra plane is inserted. The dislocation line is at the end of the plane. In an edge dislocation, the Burgers vector is perpendicular to the dislocation line.

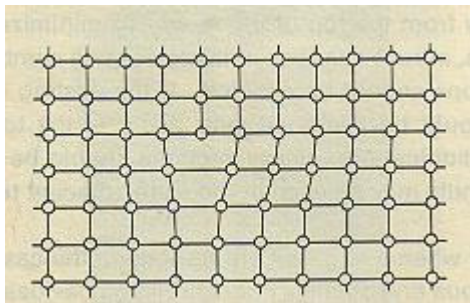
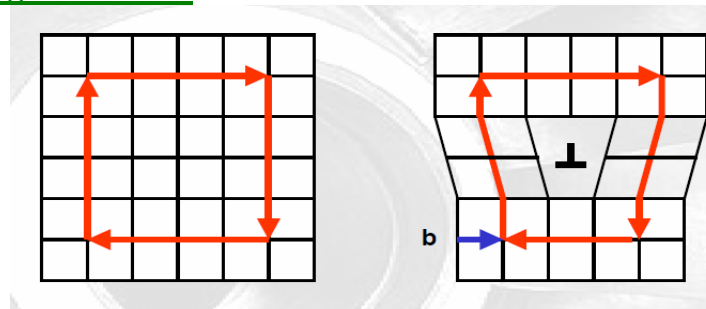


Figure 3. Edge dislocation

### Burgers vector in edge dislocation



Screw dislocations result when displacing planes relative to each other through shear. In this case, the Burgers vector is parallel to the dislocation line.

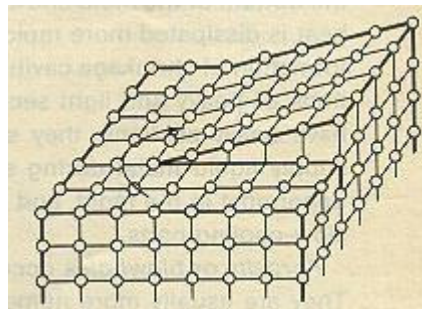
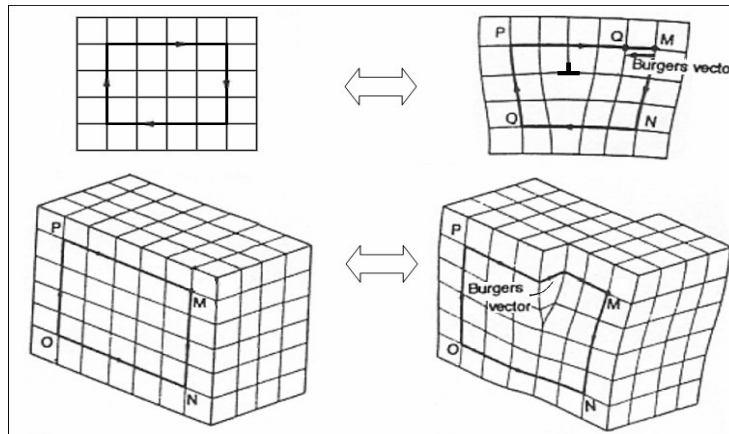


Figure 4. Screw dislocation

## Burgers vector in screw dislocation

The **Burgers vector**, often denoted by **b**, is a vector that represents the magnitude and direction of the lattice distortion of dislocation in a crystal lattice. The vector's magnitude and direction is best understood when the dislocation-bearing crystal structure is first visualized *without* the dislocation, that is, the *perfect* crystal structure. In this perfect crystal structure, a rectangle whose lengths and widths are integer multiples of "a" (the unit cell length) is drawn *encompassing* the site of the original dislocation's origin. Once this encompassing rectangle is drawn, the dislocation can be introduced. This dislocation will have the effect of deforming, not only the perfect crystal structure, but the rectangle as well. Said rectangle could have one of its sides disjoined from the perpendicular side, severing the connection of the length and width line segments of the rectangle at one of the rectangle's corners, and displacing each line segment from each other. What was once a rectangle before the dislocation was introduced is now an open geometric figure, whose opening defines the direction and magnitude of the Burgers vector. Specifically, the breadth of the opening defines the magnitude of the Burgers vector, and, when a set of fixed coordinates is introduced, an angle between the termini of the dislocated rectangle's length line segment and width line segment may be specified. The direction of the vector depends on the plane of dislocation, which is usually on the closest-packed plane of unit cell.



In edge dislocations, the Burgers vector and dislocation line are at right angles to one another. In screw dislocations, they are parallel. The Burgers Vector is significant in determining the strength of a material: it affects solute hardening, precipitation hardening and work hardening, all of which affect yield strength.

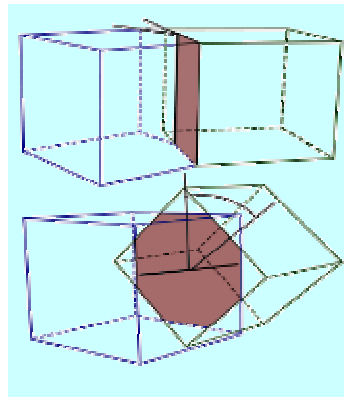
## Interfacial Defects

Grain boundaries are interfaces where crystals of different orientations meet. A grain boundary is a single-phase interface, with crystals on each side of the boundary being identical except in orientation. The term "crystallite boundary" is sometimes, though rarely, used. Grain boundary areas contain those atoms that have been perturbed from their original lattice sites, dislocations, and impurities that have migrated to the lower energy grain boundary.

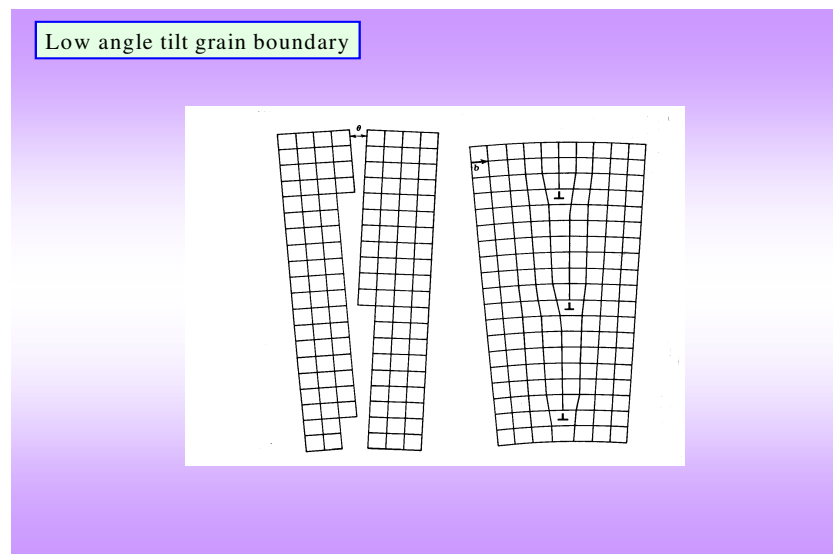


Grain boundaries disrupt the motion of dislocations through a material, so reducing crystallite size is a common way to improve strength. Since grain boundaries are defects in the crystal structure they tend to decrease the electrical and thermal conductivity of the material. The high interfacial energy and relatively weak bonding in most grain boundaries often makes them preferred sites for the onset of corrosion and for the precipitation of new phases from the solid. They are also important to many of the mechanisms of creep.

It is convenient to separate grain boundaries by the extent of the mis-orientation between the two grains. *Low angle grain boundaries* (LAGBs) are those with a misorientation less than about 11 degrees. Generally speaking they are composed of an array of dislocations and their properties and structure are a function of the misorientation. In contrast the properties of *high angle grain boundaries* (HAGBs) whose misorientation is greater than about 11 degrees (the transition angle varies from 10-15 degrees depending on the material) are normally found to be independent of the misorientation. However there are 'special boundaries' at particular orientations whose interfacial energies are notably lower than those of general HAGBs.



**Schematic representations of a tilt boundary (top) and a twist boundary between two idealised grains.**



$$\frac{b}{2h} = \sin\left(\frac{\theta}{2}\right)$$

$$\frac{b}{h} \sim \theta$$

$$\frac{b}{h} = \tan \theta$$

Book

~8° TILT BOUNDARY IN SrTiO<sub>3</sub> POLYCRYSTAL

No visible Grain Boundary

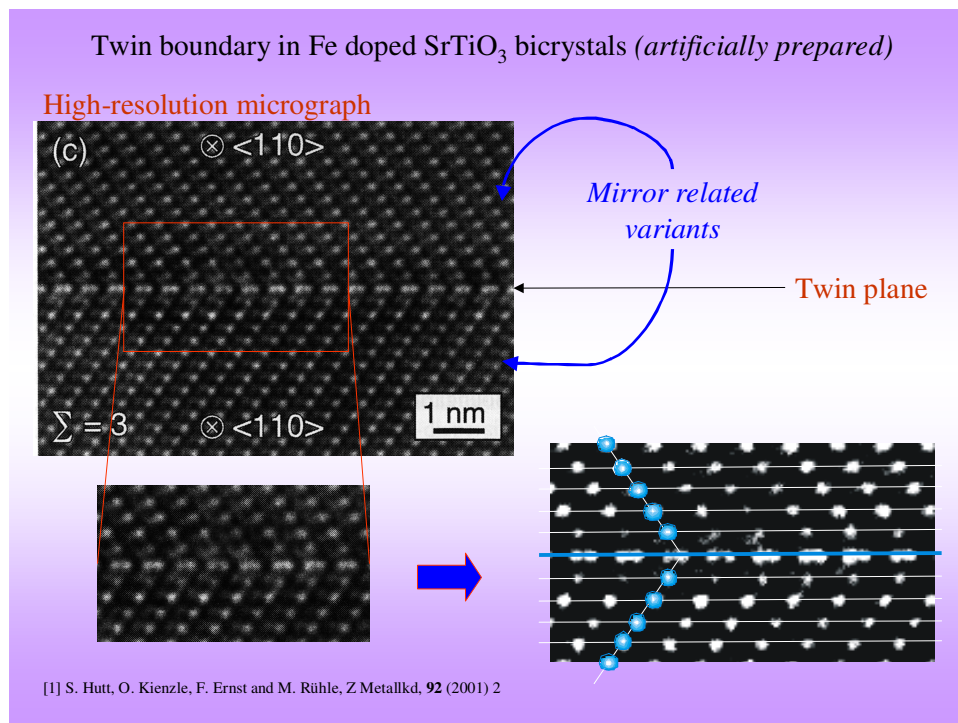
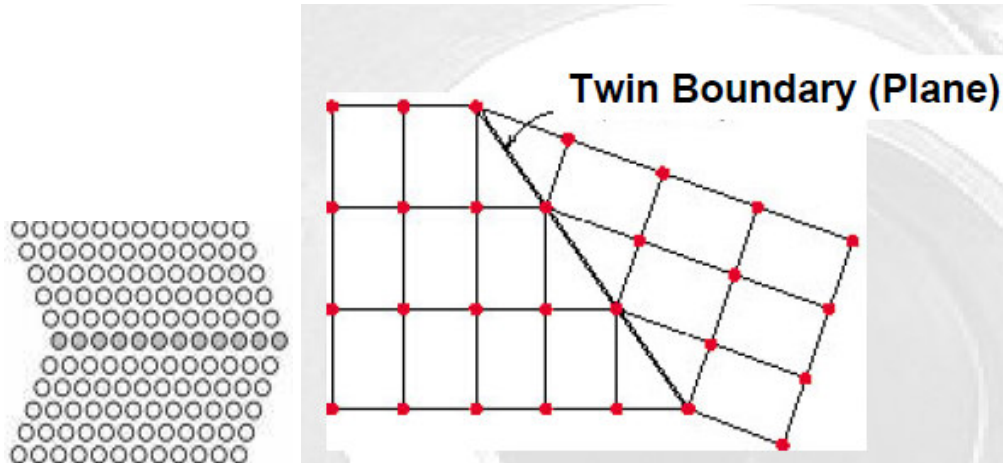
2.761 Å

Fourier filtered image

Dislocation structures at the Grain boundary

## Crystal twinning

**Crystal twinning** occurs when two separate crystals share some of the same [crystal lattice](#) points in a symmetrical manner. The result is an intergrowth of two separate crystals in a variety of specific configurations. A twin boundary or composition surface separates the two crystals. [Crystallographers](#) classify twinned crystals by a number of [twin laws](#). These twin laws are specific to the [crystal system](#). The type of twinning can be a diagnostic tool in mineral identification. Simple twinned crystals may be *contact twins or penetration twins*.

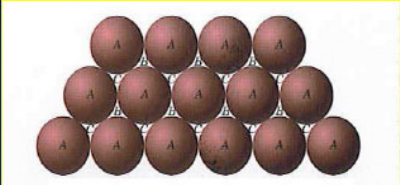


## Stacking fault

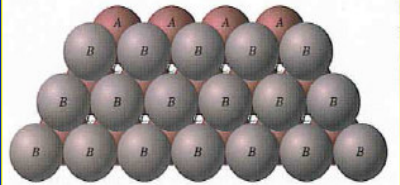
Stacking faults occur in a number of crystal structures, but the common example is in close-packed structures. Face-centered cubic (fcc) structures differ from hexagonal close packed (hcp) structures only in stacking order: both structures have close packed atomic planes with sixfold symmetry -- the atoms form equilateral triangles. When stacking one of these layers on top of another, the atoms are not directly on top of one another -- the first two layers are identical for hcp and fcc, and labelled AB. If the third layer is placed so that its atoms are directly above those of the first layer, the stacking will be ABA -- this is the hcp structure, and it continues ABABABAB. However there is another location for the third layer, such that its atoms are not above the first layer. Instead, the fourth layer is placed so that its atoms are directly above the first layer. This produces the stacking ABCABCABC, and is actually a cubic arrangement of the atoms. A stacking fault is a one or two layer interruption in the stacking sequence, for example if the sequence ABCABABCAB were found in an fcc structure.

### Close packed structures

The **fcc** and the **hcp** structures are both **close-packed structures** **APF** = 0.74, whereas a **bcc** structure has **APF** = 0.68 and a **simple cubic** unit has **APF** = 0.52.

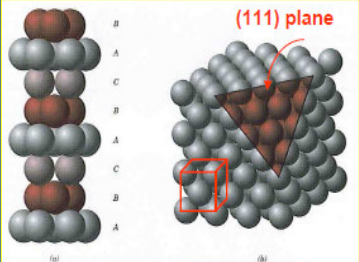


(a) Close-packed plane stacking ABC



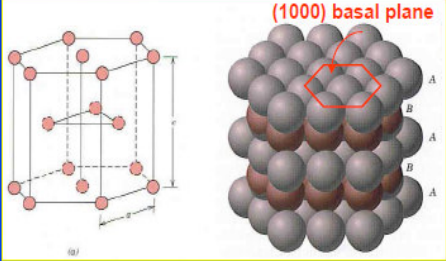
(b) Close-packed plane stacking AB

**Close-packed plane stacking sequence of FCC structure. ABCABC → {111} plane.**




(c)

**Close-packed plane stacking sequence of HCP structure. ABAB → (100) basal plane.**



(d)



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May-Aug 2007

**Stacking Fault**

- ❑ Error in the sequence of stacking atomic planes ? Stacking fault
- ❑ Defined by a shift vector

FCC stacking → ...ABC ABC ABC ABC...

↓

FCC stacking with a stacking fault → ...ABC AB AB ABC...

↑

*Thin region of HCP type of stacking*

- ❑ In above the number of nearest neighbours remains the same but next-nearest neighbours are different than that in FCC
- ❑ Stacking fault energy  $\sim 0.01 - 0.05 \text{ J/m}^2$
- ❑ Stacking fault in HCP can lead to thin region of FCC kind of stacking

### Check your understanding

1. Explain polymorphism and give examples for the same.
2. Explain allotropy and give examples for the same.
3. Mention the various point defects in crystals.
4. Mention the various dislocations in crystals.
5. What is meant by 'grain boundary'?
6. What does 'crystal twinning' mean?
7. What does 'stacking default' mean?

Check the correct answers on page 13 and 14.

### Summary

On completion of this topic you have learned that:

1. **Polymorphism** in [materials science](#) is the ability of a solid material to exist in more than one form or [crystal](#) structure. Polymorphism can potentially be found in any crystalline material including [polymers](#), [minerals](#), and [metals](#).
  - An example of an organic polymorph is [glycine](#), which is able to form [monoclinic](#) and [hexagonal](#) crystals. [Silica](#) is known to form many polymorphs, the most important of which are;  [\$\alpha\$ -quartz](#),  [\$\beta\$ -quartz](#), [tridymite](#), [cristobalite](#), [coesite](#), and [stishovite](#).

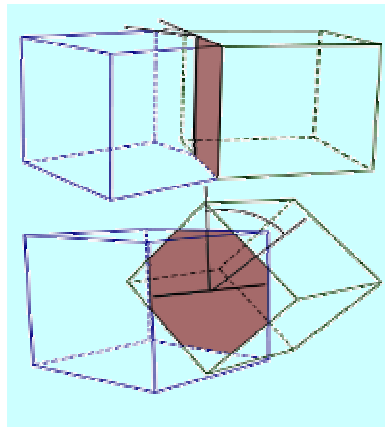
2. If the change in structure is reversible then the polymorphism is known as ‘allotropy’.
  - For example, the element [carbon](#) has two common allotropes: [diamond](#), where the carbon atoms are bonded together in a [tetrahedral](#) lattice arrangement, and [graphite](#), where the carbon atoms are bonded together in sheets of a hexagonal lattice.
3. The point defects in crystals are (i) Vacancies and (ii) Interstitials.

A vacancy is a lattice position that is vacant because the atom is missing. It is created when the solid is formed. Vacancies are simply empty atom sites.

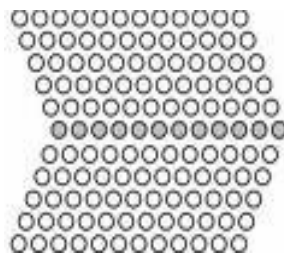
An interstitial is an atom that occupies a place outside the normal lattice position. It may be the same type of atom as the others (self interstitial) or an impurity atom.
4. The types of dislocations in crystals are (i) Edge dislocation and (ii) Screw dislocation.

Edge dislocations occur when an extra plane is inserted. The dislocation line is at the end of the plane. In an edge dislocation, the Burgers vector is perpendicular to the dislocation line.

Screw dislocations result when displacing planes relative to each other through shear. In this case, the Burgers vector is parallel to the dislocation line.
5. Grain boundary is an interfacial defect. Grain boundaries are interfaces where crystals of different orientations meet. A grain boundary is a single-phase interface, with crystals on each side of the boundary being identical except in orientation.



6. **Crystal twinning** occurs when two separate crystals share some of the same [crystal lattice](#) points in a symmetrical manner. The result is an intergrowth of two separate crystals in a variety of specific configurations.



7. ‘Stacking default’ means error in the sequence of stacking of atomic planes.

### **Activity**

Students can try to understand the above concepts by doing as explained with balls of different colors and required materials.

### **Suggested Reading**

Solid state Physics by Gupta and Kumar

### **Answers to CYU.**

The answers to all questions are available in summary completely.