BEEE201L- Electronic Materials

Winter Semester 2023-24 (General Freshers)

Slot: F1+TF1 & C2+TC2

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INTRODUCTION TO COURSE:

BEEE201L	Electronic Materials	L	T	P	C
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Pre-requisite	**NIL**	**Syllabus version**			
		1.0			

Course Objectives

1. Familiarize the relevant concepts, principles and characteristics of electronic materials.
2. Understand and comprehend the various laws and mechanisms of semiconductor, dielectric and magnetic materials.
3. Analyze and compare the unique properties, characteristics and applications of materials in electronic devices.

Course Outcomes

On completion of this course, the students will be able to:

1. Understand the fundamental physics of electronic materials.
2. Classify and interpret various types of current carrying mechanisms in semiconductor materials.
3. Comprehend the categories of magnetic materials and its characteristics.
4. Analyze the various types of dielectric materials based on the nature of electric field.
5. Distinguish and examine the various optical properties of materials.

Syllabus :

Module:1	Physics of Materials	6 hours
Atomic structure and atomic number, electron spin and Pauli's exclusion principle, bonding and types of solids, concepts of Fermi level, energy bands in solids; Classification of materials – metals, semiconductors and insulators; Potential barrier problems, crystal directions and planes, crystal properties, defects and vacancies.		
Module:2	**Semiconductor Materials**	**10 hours**
Classification of semiconductors, doping of semiconductor, temperature dependence, metal-semiconductor junction; Carrier concentration, carrier generation and recombination, Carrier actions, diffusion and conduction equations, continuity equation; Organic semiconductor; Direct and indirect band gaps, optical absorption, Piezo-resistivity; Applications of semiconductor materials: PN junction diodes, BJT, JFET, MOSFET.		

Module:3	Magnetic Materials	6 hours
Classification of magnetic materials, concept of ferromagnetism, saturation magnetization, Curie and Neel temperature; Temperature dependence of conductivity materials; Magnetostriction, magnetic anisotropy, spin-orbit interaction; Superconductivity.		
Module:4	**Dielectric Materials and Insulation**	**8 hours**
Requirements of insulating materials: Electrical and molecular properties, dependence of permittivity on temperature, pressure & humidity; Dipole moment and electronic polarization, Clausius–Mossotti equation, polarization mechanisms; Behaviour of dielectrics under static and alternating fields; Frequency dependence; Complex dielectric constants and dielectric loss, bipolar relaxation and characteristics.		
Module:5	**Optical Properties of Materials**	**8 hours**
Light propagation in a homogeneous medium, refractive index, group velocity and group index, complex refractive index and light absorption; Light scattering, attenuation in optical fibers; Luminescence, phosphors, Light Emitting Diode (LED), Liquid Colour Display (LCD), electro optic effects.		

Module:6	**Semiconductor Nanomaterials**	**5 hours**
Flexible energy storage devices, flexible chemical sensors, flexible solar cells		
Module:7	**Contemporary Issues**	**2 hours**
	Total Lecture hours:	**45 hours**
Text Book(s)		
1.	S.O. Kasap, Principles of Electronic Materials and Devices, 2018, 4th Edition, McGraw Hill Education	
2.	Yugang Sung, John A Rogers, William Andrew, Semiconductor Nanomaterials for Flexible Technologies: From Photovoltaics and Electronics to Sensors and Energy Storage/ Harvesting Devices, 2010, 1st Edition, Elsevier	
Reference Books		
1.	T.K. Basak, Electrical Engineering Materials, 2012, 1st Edition, New Academic Science Limited	
2.	Rolf E. Hummel,Electronic Properties of Materials, 2001, 3rd Edition, Springer	
3.	C. S. Indulkar, S. Thiruvengadam, An Introduction to Electrical Engineering Materials,2011, 6th Edition, S. Chand & Company	
Mode of Evaluation: CAT, Digital Assignments, Quiz and FAT		

ASSESMENT METHOD

S.No	Assessment Title	Max.Mark	Weightage %
1	Digital Assignment-1	20	10
2	CAT-1	50	15
3	Digital Assignment-2	20	10
4	CAT-2	50	15
5	Digital Assignment-3/Quiz	20	10
6	FAT	100	40
			100

*Tentative

What are electronic materials?

Those materials that are useful in the applications related to electronics are electronic materials.

- Basic electronics
- Microelectronics
- Power electronics
- Consumer electronics
- Medical electronics
- Flexible and wearable electronics
- Energy electronics

Applications of Electronic Materials

- All electronic elements like resistors, capacitors, inductors, transistors, diodes, thyristors etc.
- All machines like transformers, motors, generators, etc.
- Power electronics like power transistors, power MOSFETs, IGBTs and diodes.
- Solar cells and semiconductors for solar panels, photovoltaics, heating elements etc.
- Integrated circuits, IC packaging, MOSFETs, on-chip elements, PCBs, microstrip lines, antennas.
- Consumer electronics, laptops, mobiles and other electronic gadgets.
- Future devices like Nano transistors, flexible and wearable electronics, Nano materials etc..
- Energy electronics like batteries, supercapacitors, electrodes, packaging, etc.

Why Electronic Material?

The type of material selected for a particular application can affect its performance.

- Electronic properties
- Band gap
- Dielectric constant
- Electrical Conductivity
- Thermal conductivity
- Magnetic properties including spin
- Electron mobility
- Electron density
- Structure effects

Intended Learning Outcomes

At the end of this section, students will be able to:-

- Identify with examples the different classes of materials.
- Describe the distinctive chemical features of different materials.
- Identify ‘Advanced Materials’ and how these differ from the classical material classes.

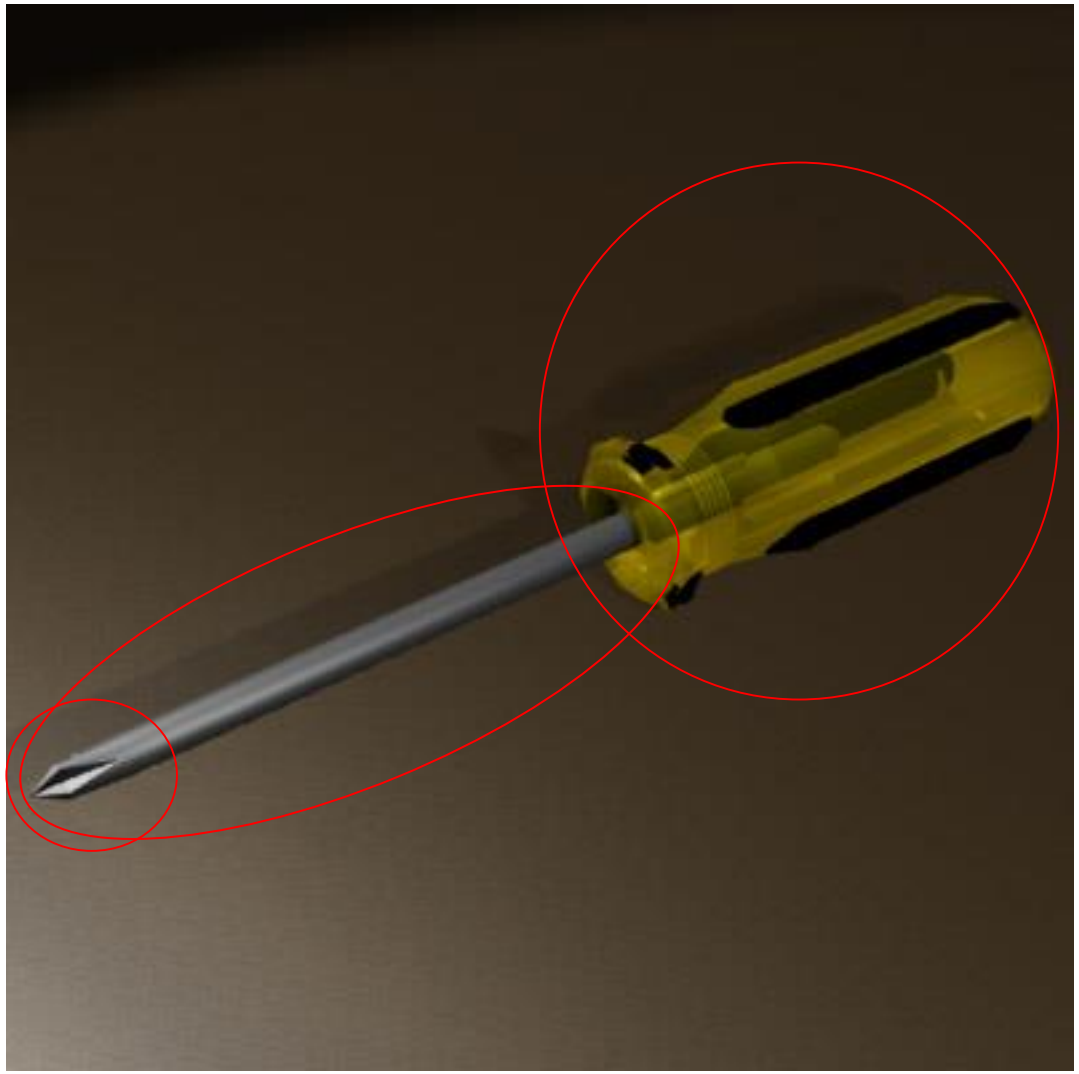
What is Materials science and engineering?

Materials science: Studies the relationships that exist between the structures and properties of materials.

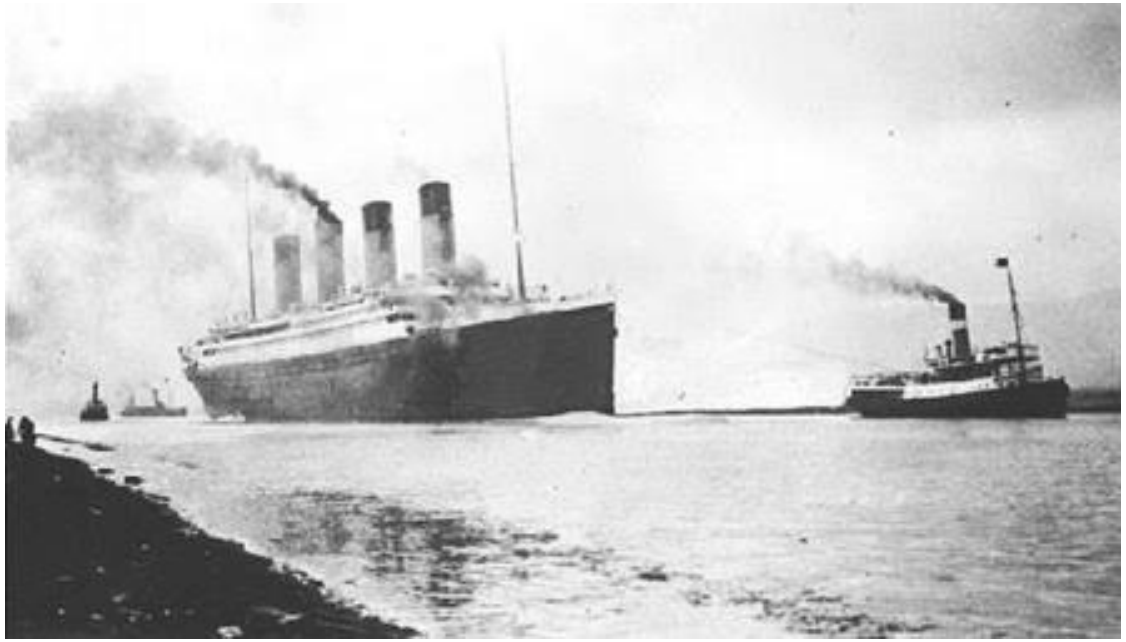
Materials engineering: Designing or engineering a material with a predetermined set of properties on the basis of the structure property correlations.

Why should we know about materials? Because it is the job of the engineer to select materials for given application based of materials structure, properties, processing, performance and cost.

Example - Screwdriver



What happens when we get it wrong?



Why did Titanic sink in 1912?

It was built with the wrong steel (containing excessive ratios of sulphur and phosphor) which undergo brittle fracture at low temperature.

What happens when we get it wrong?

Train disaster:

Caused by metal fatigue of the wheels.

Recent example: CHANDRAYAAN-3

Things we need to know about materials

Structure:

The structure of a material is usually the arrangement of its internal components.

Atomic structure: the organisation of atoms or molecules relative to one another.

Microscopic structure: a larger structural realm, which contains large groups of atoms that are normally agglomerated together, which is subject to direct observation using some type of microscope.

Macroscopic structure: comprises structural elements that may be viewed with the naked eye.

Properties:

“A property is a material trait in terms of the kind and magnitude of response to a specific imposed stimulus.”

Mechanical properties: for example, would relate deformation to an applied load or force; examples include elastic modulus and strength.

Electrical properties: such as electrical conductivity and dielectric constant, the stimulus is an electric field.

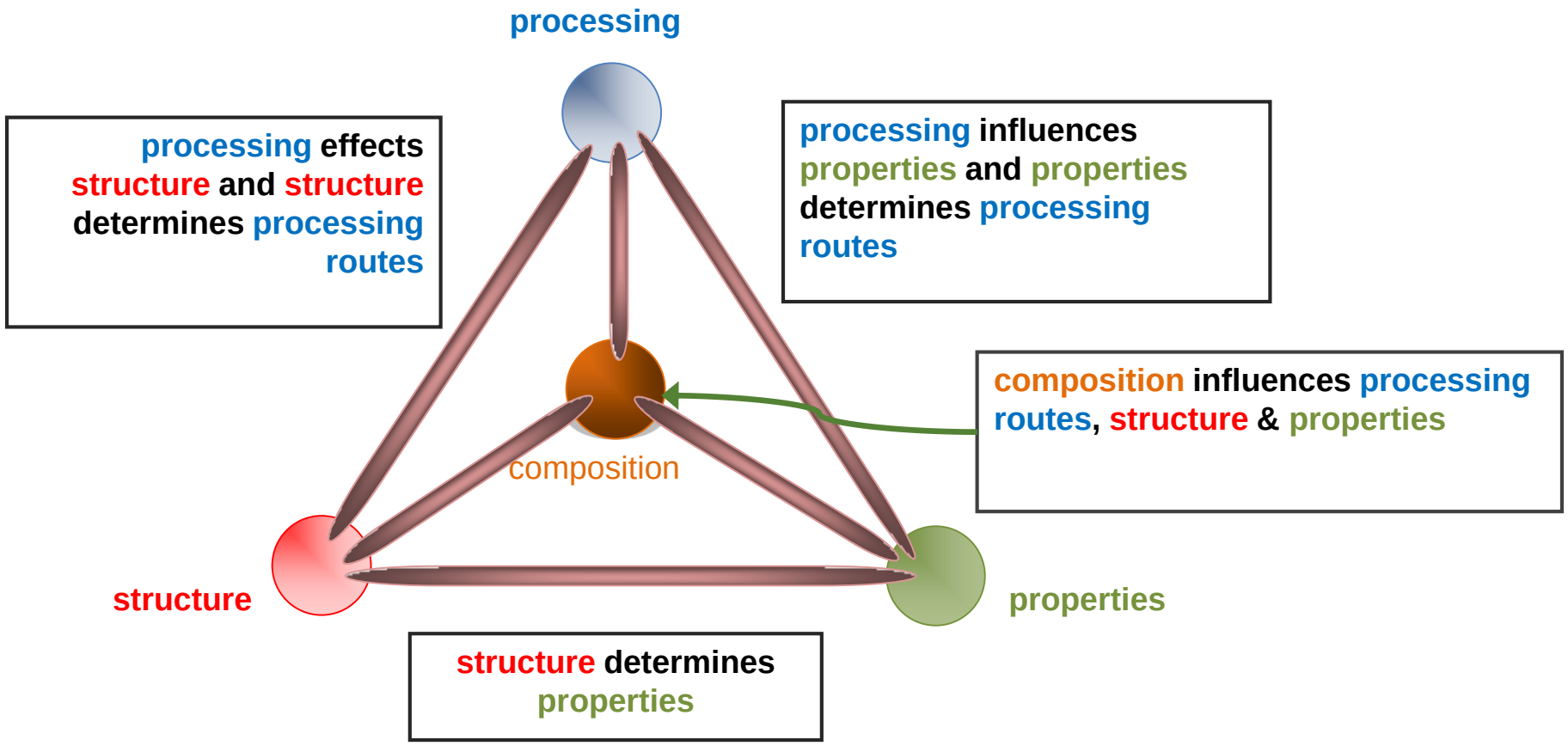
Thermal properties: measure for the behaviour of a material in response to temperature such as heat capacity and thermal conductivity.

Magnetic properties: the response of a material to the application of a magnetic field.

Optical properties: the stimulus is electromagnetic or light radiation. Index of refraction and reflectivity are representative optical properties.

Processing: The series of operations that transforms industrial materials from a raw-material state into finished parts or products.

Performance:



Structure, Processing, & Properties are mutually related

Same material – aluminium oxide – different processing method – different structure

Adapted from Fig. 1.2, *Callister & Rethwisch 8e.* (Specimen preparation, P.A. Lessing; photo by S. Tanner.)

Single crystal

Polycrystalline made of very small single crystals

Polycrystalline with pores

TEXT BOOK: S.O. Kasap "Principles of Electronic Materials and Devices" Second Edition, McGraw-Hill, New York. (Click below link to download).

https://drive.google.com/file/d/1e2qhsOdr2tMLy4PlUN5ZIKzfr6HmB02J/view?usp=sharing

BEEE102L- Basic Electrical and Electronics Engineering

Module-1 : Physics of material

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Content of Module-1:

Atomic structure and atomic number,

Electron spin and Pauli's exclusion principle, bonding and types of solids,

Concept of Fermi level, Energy bands in solids;

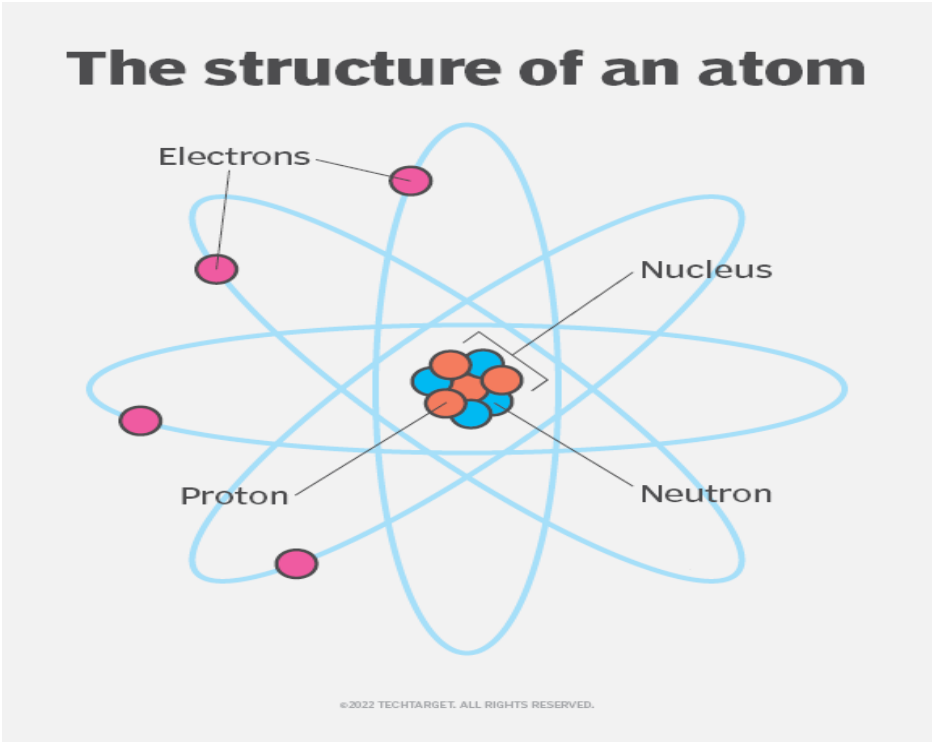
Classification of materials- Metals, Semiconductors and insulators;

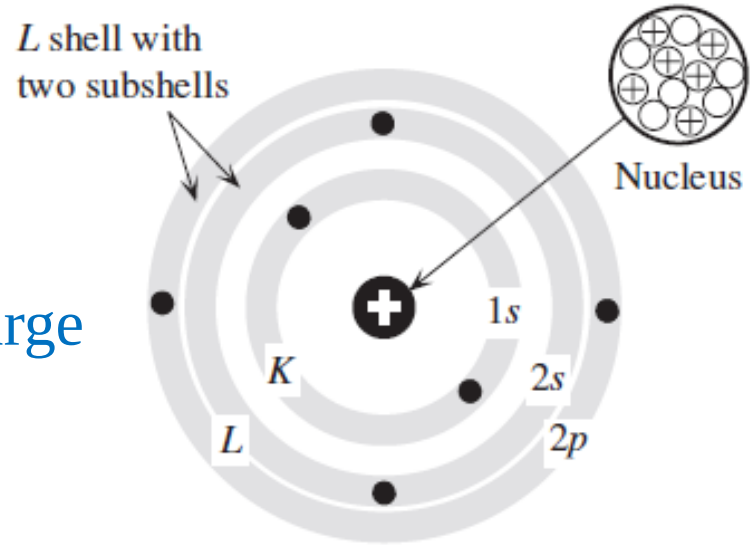
Potential barrier problems,

crystal directions and planes, crystal properties, defects and vacancies.

Atomic structure and atomic number

- The model of an atom is called as shell model is based on the **Bohr Model** (1913)
- Mass of the atom is concentrated at the nucleus, which contains protons and neutrons
- Protons are positively charged particles, whereas neutrons are neutral particles, and both protons and neutrons have about the same mass.
- Atomic Number (Z): Number of protons in the nucleus of an atom = Number of electrons in a neutral atom.





- Electrons are assumed to be orbiting the nucleus at very large distances compared to the size of the nucleus.
- No of electrons orbiting is same as the number of protons.
- Certain orbits with fixed radii are stable around the nucleus
- For example the closest orbit for hydrogen atom can only have a radius of 0.053nm
- Electron is constantly moving around an orbit, the electron would appear as a spherical negative-charge cloud around the nucleus (Shell) and not as a single dot representing a finite particle.

Table 1 Properties of Fundamental Particles

Name	Symbol	Absolute charge/C	Relative charge	Mass/kg	Mass/u	Approx. mass/u
Electron	e	-1.602176×10^{-19}	−1	9.109382×10^{-31}	0.00054	0
Proton	p	$+1.602176\times10^{-19}$	+1	1.6726216×10^{-27}	1.00727	1
Neutron	n	0	0	1.674927×10^{-27}	1.00867	1

Atom Structure

Dual Behaviour of Matter

The French physicist, de Broglie, in 1924 proposed that matter, like radiation, should also exhibit dual behavior i.e., both **particle and wavelike properties**.

This means that just as the photon has momentum as well as wavelength, electrons should also have momentum as well as wavelength,

De Broglie's equation

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

Where λ is wavelength in m, mass in kg, v is velocity in m/s.

Planck constant h is equal to exactly 6.626×10^{-34} Joule seconds.

Exercise

- 1. What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 m s–1 ?
- 2. The mass of an electron is 9.1×10–31 kg. If its K.E. is 3.0×10–25 J, calculate its wavelength.
- Microscopic particle motion have wave like properties are significant.

Heisenberg Uncertainty Principle

Werner Heisenberg a German physicist in 1927, stated uncertainty principle which is the consequence of dual behavior of matter and radiation.

It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron.

$$\Delta x \, \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \, m\Delta v \geq \frac{h}{4\pi}$$

$$\Delta x \, \Delta v \geq \frac{h}{4\pi m}$$

Heisenberg Uncertainty Principle

where Δx is the uncertainty in position and Δp (or Δv) is the uncertainty in momentum (or velocity) of the particle.

If the position of the electron is known with high degree of accuracy (Δx is small), then the velocity of the electron will be uncertain [$\Delta(v)$ is large].

On the other hand, if the velocity of the electron is known precisely ($\Delta(v)$ is small), then the position of the electron will be uncertain (Δx will be large).

Thus, if we carry out some physical measurements on the electron's position or velocity, the outcome will always depict a fuzzy or blur picture.

Atom Structure

Significance of Uncertainty Principle

One of the important implications of the Heisenberg Uncertainty Principle is that it rules out existence of **definite paths or trajectories** of electrons and other similar particles.

The trajectory of an object is determined by its location and velocity at various moments.

The effect of Heisenberg Uncertainty Principle is significant only for motion of **microscopic** objects and is negligible for that of **macroscopic** objects.

Orbit and Orbital

An orbit, as proposed by Bohr, is a circular path around the nucleus in which an electron moves, its two dimensional representation. An orbital is the probable area of finding the maximum density of electrons in an atom, it's a three dimensional representation.

A precise description of this path of the electron is impossible according to **Heisenberg uncertainty principle.** Bohr orbits, therefore, have no real meaning and their existence can never be demonstrated experimentally.

An atomic orbital, on the other hand, is a quantum mechanical concept and refers to the one electron wave function ψ in an atom. It is characterized by three quantum numbers (n, l and m_l) and its value depends upon the coordinates of the electron.

$|\psi|^2$ at any point in an atom gives the value of probability density of finding the electron at that point.

Exercise

1. A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1 Å. What is the uncertainty involved in the measurement of its velocity?

1 Å (Angstrom)= 10^{-10}m

2. A golf ball has a mass of 40g, and a speed of 45 m/s. If the speed can be measured within accuracy of 2%, calculate the uncertainty in the position.

Quantum Mechanical Model of Atom

Quantum mechanics is a theoretical science that deals with the study of the motions of the **microscopic objects** that have both observable **wave like and particle like properties**.

The fundamental equation of quantum mechanics was developed by **Schrödinger** and it won him the Nobel Prize in Physics in 1933.

Quantum Mechanical Model of Atom

When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) (ψ) of the electron associated with each energy level.

These quantized energy states and corresponding wave functions which are characterized by **a set of three quantum numbers (principal quantum number n, azimuthal quantum number l and magnetic quantum number m_l)** arise as a natural consequence in the solution of the Schrödinger equation.

When an electron is in any energy state, the wave function corresponding to that energy state contains all information about the electron.

Quantum Mechanical Model of Atom

$$E_n = \frac{-m_0 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}$$

Where n=1,2, 3, …. n is Principal quantum number

- The negative energy indicates that the electron is bound to the nucleus, and we again see that the energy of the bound electron is quantized.
- If the energy were to become positive, then the electron would no longer be a bound particle and the total energy would no longer be quantized.

Quantum Mechanical Model of Atom

Orbitals and Quantum Numbers

A large number of orbitals are possible in an atom.

Qualitatively these orbitals can be distinguished by their size, shape and orientation.

Atomic orbitals are precisely distinguished by what are known as quantum numbers.

Each orbital is designated by three quantum numbers labelled as n, l and m_l.

Quantum Mechanical Model of Atom

Principal Quantum Number (n)

Size of an orbital increases with increase of principal quantum number ‘n’. It represents the main energy level occupied by the electron. In other words, the electron will be located away from the nucleus.

Since energy is required in shifting away the negatively charged electron from the positively charged nucleus, the energy of the orbital will increase with increase of n.

The principal quantum number ‘n’ is a positive integer with value of n = 1,2,3.....

The principal quantum number determines the size and to large extent the energy of the orbital.

The principal quantum number also identifies the shell.

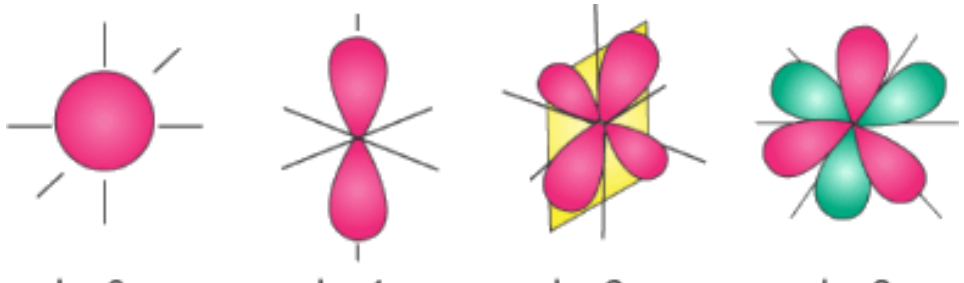
Quantum Mechanical Model of Atom

Azimuthal Quantum Number (l)

Azimuthal quantum number. 'l' is also known as orbital angular momentum.

It defines the three-dimensional shape of the orbital.

For a given value of n, l can have n values ranging from 0 to n – 1, that is, for a given value of n, the possible value of l are : l = 0, 1, 2, ... (n–1).



Each shell consists of one or more subshells or sub-levels. The number of sub-shells in a principal shell is equal to the value of n.

Quantum Mechanical Model of Atom

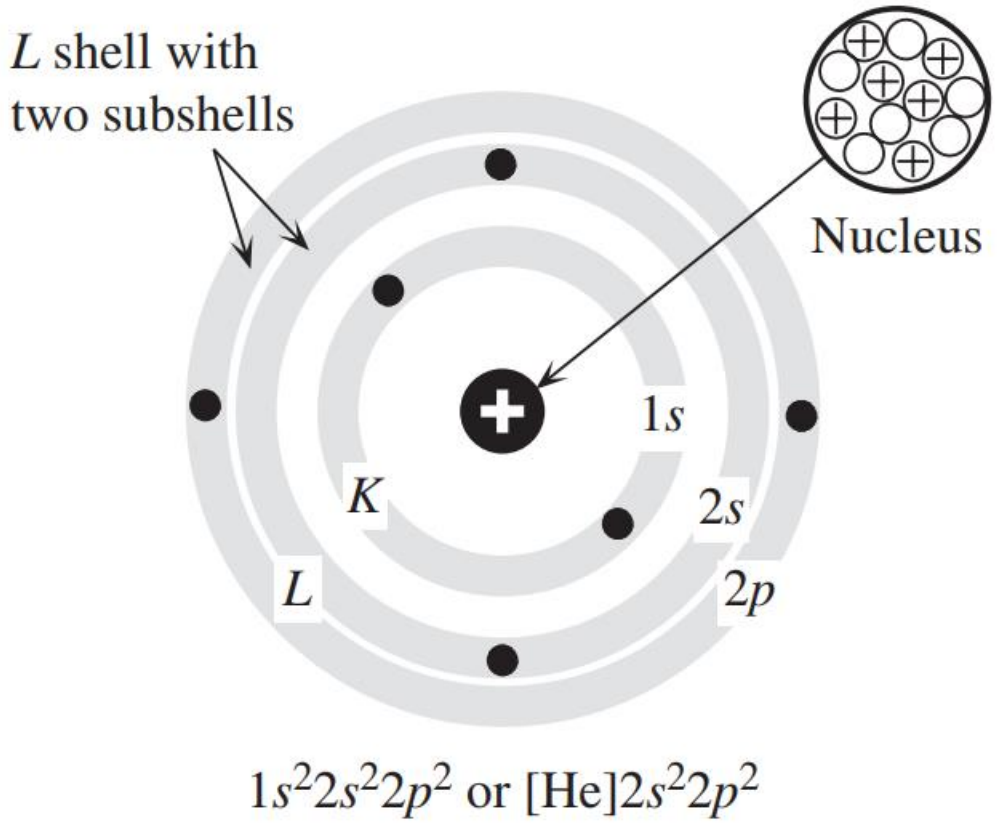


Figure: The shell model of the carbon atom, in which the electrons are confined to certain shells and subshells within shells.

Quantum Mechanical Model of Atom

Table 1.1 Maximum possible number of electrons in the shells and subshells of an atom

		Subshell			
		$\ell = 0$	1	2	3
n	Shell	s	p	d	f
1	K	2			
2	L	2	6		
3	M	2	6	10	
4	N	2	6	10	14

Quantum Mechanical Model of Atom

n	l	Subshell notation
1	0	$1s$
2	0	$2s$
2	1	$2p$
3	0	$3s$
3	1	$3p$
3	2	$3d$
4	0	$4s$
4	1	$4p$
4	2	$4d$
4	3	$4f$

Quantum Mechanical Model of Atom

Magnetic orbital Quantum Number (m_l)

<u>Gives information about the spatial orientation of the orbital with respect to standard set of co-ordinate axis.</u>

For any sub-shell (defined by 'l' value) **2l+1 values of m_l** are possible and these values are given by

$m_l = -l, -(l-1), -(l-2) \ldots 0, 1 \ldots (l-2), (l-1), l$

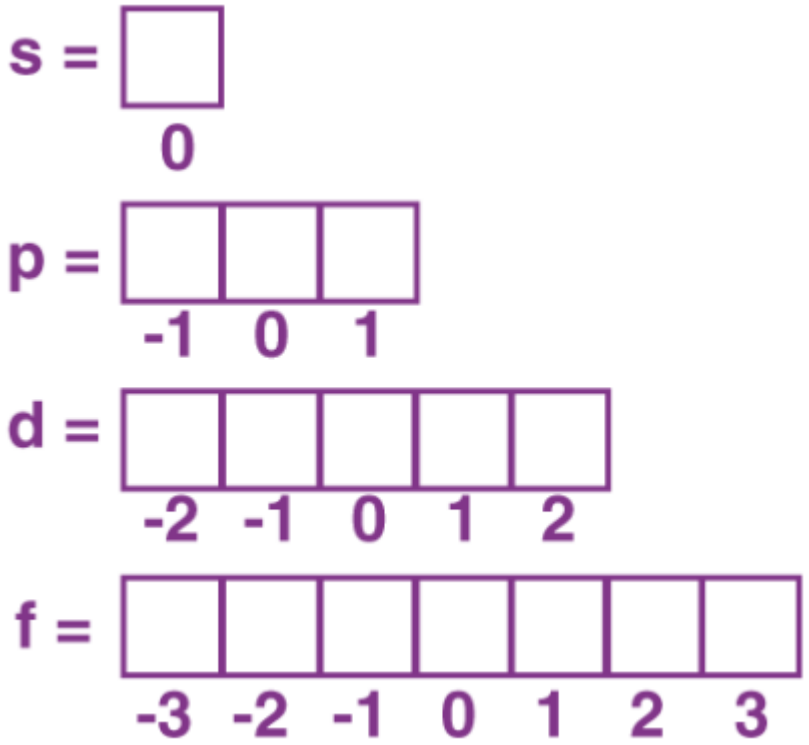
It should be noted that the values of m_l are derived from l and that the value of l are derived from n.

Sublevel	s	p	d	f
'l' value	0	1	2	3
'ml' value	0	-1, 0, +1	-2,-1, 0, +1, +2	-3, -2,-1, 0, +1, +2, +3

Quantum Mechanical Model of Atom

Magnetic orbital Quantum Number (m_l)

Value of l	0	1	2	3	4	5
Subshell notation	s	p	d	f	g	h
number of orbitals	1	3	5	7	9	11



Distribution of electrons in different orbits

Element			Electron per shel										
Atomic number	Symbol	Name	K	L		M			N				
			1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s
1	H	Hydrogen	1										
2	He	Helium	2										
3	Li	Lithium	2	1									
4	Be	Beryllium	2	2									
5	B	Boron	2	2	1								
6	C	Carbon	2	2	2								
7	N	Nitrogen	2	2	3								
8	O	Oxygen	2	2	4								
9	F	Fluorine	2	2	5								
10	Ne	Neon	2	2	6								
11	Na	Sodium	2	2	6	1							
12	Mg	Magnesium	2	2	6	2							
13	Al	Aluminum	2	2	6	2	1						
14	Si	Silicon	2	2	6	2	2						
15	P	Phosphorus	2	2	6	2	3						
18	Ar	Argon	2	2	6	2	6						
19	K	Potassium	2	2	6	2	6		1				
20	Ca	Calcium	2	2	6	2	6		2				
21	Sc	Scandium	2	2	6	2	6	1	2				
22	Ti	Titanium	2	2	6	2	6	2	2				
23	V	Vanadium	2	2	6	2	6	3	2				
24	Cr	Chromium	2	2	6	2	6	5	1				
25	Mn	Manganese	2	2	6	2	6	5	2				
26	Fe	Iron	2	2	6	2	6	6	2				
27	Co	Cobalt	2	2	6	2	6	7	2				
28	Ni	Nickel	2	2	6	2	6	8	2				
29	Cu	Copper	2	2	6	2	6	10	1				
30	Zn	Zinc	2	2	6	2	6	10	2				
31	Ga	Gallium	2	2	6	2	6	10	2	1			
32	Ge	Germanium	2	2	6	2	6	10	2	2			
33	As	Arsenic	2	2	6	2	6	10	2	3			

la, As

Quantum Mechanical Model of Atom

Electron spin quantum number (m_s)

The three quantum numbers labelling an atomic orbital can be used equally well to define its **energy, shape and orientation**.

An electron spins around its own axis, much in a similar way as earth spins around its own axis while revolving around the sun.

In other words, an electron has, besides charge and mass, intrinsic spin angular quantum number.

Spin angular momentum of the electron — a vector quantity, can have two orientations relative to the chosen axis.

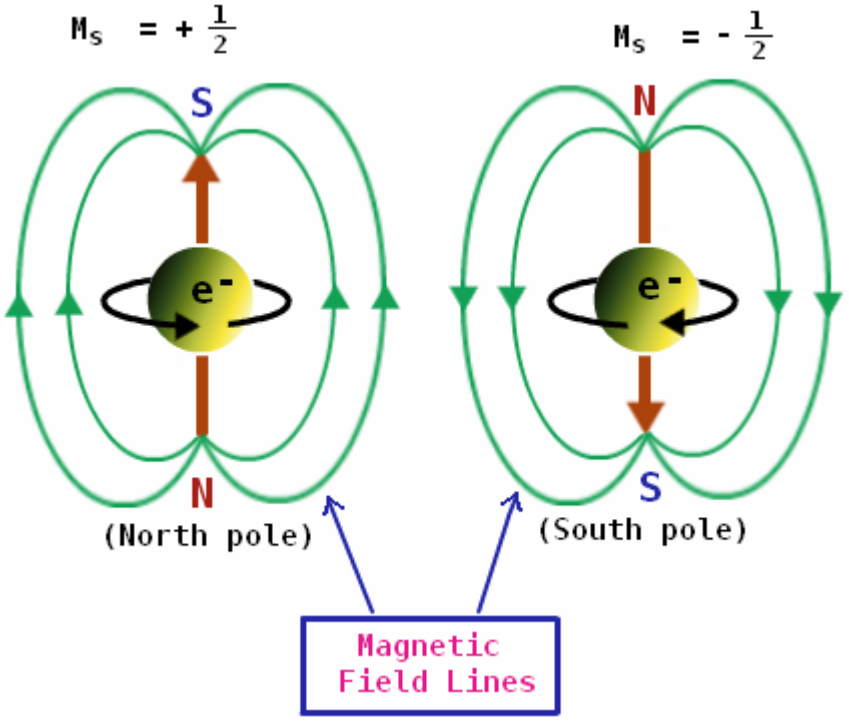
Quantum Mechanical Model of Atom

Electron spin quantum number (m_s)

These two orientations are distinguished by the spin quantum numbers **ms** which can take the values of +½ or –½. **These are called the two spin states of the electron and are normally represented by two arrows, ↑ (spin up) and ↓ (spin down).**

Two electrons that have different ms values (one +½ and the other –½) are said to have opposite spins.

An orbital cannot hold more than two electrons and these two electrons should have opposite spins.



Highlights

To sum up, the four quantum numbers provide the following information :

i) n defines the shell, determines the size of the orbital and also to a large extent the energy of the orbital.

ii) There are n subshells in the nth shell. l identifies the subshell and determines the shape of the orbital. There are (2l+1) orbitals of each type in a subshell, that is, one s orbital (l = 0), three p orbitals (l = 1) and five d orbitals (l = 2) per subshell.

To some extent l also determines the energy of the orbital in a multi-electron atom.

iii) m_l designates the orientation of the orbital. For a given value of l, m_l has (2l+1) values, the same as the number of orbitals per subshell. It means that the number of orbitals is equal to the number of ways in which they are oriented.

iv) m_s refers to orientation of the spin of the electron.

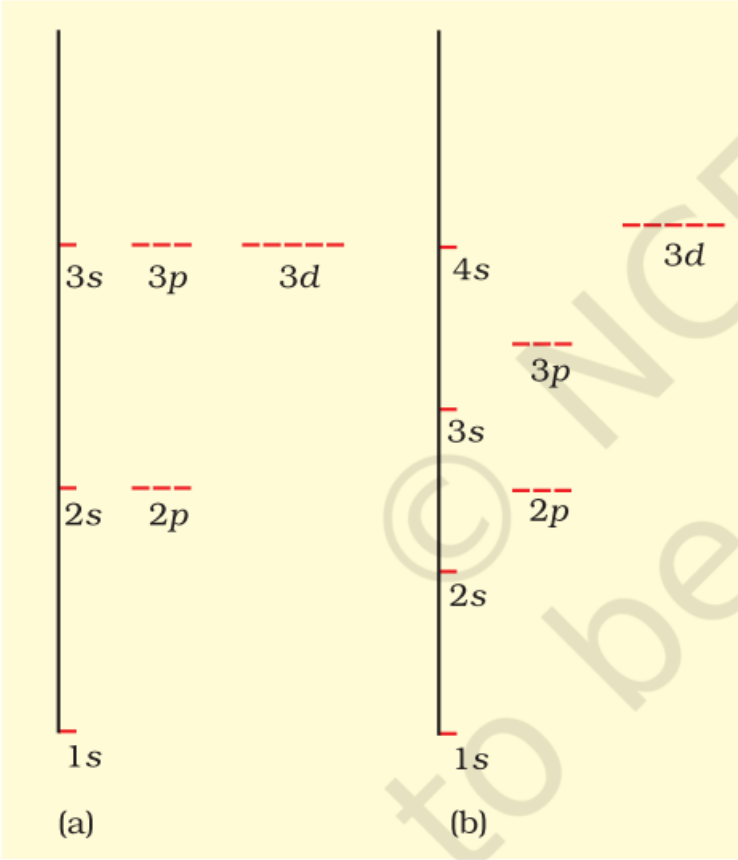
Exercise

1. What are four quantum numbers? What is the importance of each quantum number? How are they mathematically related?

2. What is the total number of orbitals associated with the principal quantum number n = 3?

Quantum Mechanical Model of Atom

Energies of Orbitals



- Note that orbitals for the same value of principal quantum number, have the same energies even for different azimuthal quantum number for hydrogen atom.
- In case of multi-electron atoms, orbitals with same principal quantum number possess different energies for different azimuthal quantum numbers.

Figure: Energy level diagrams for the few electronic shells of (a) hydrogen atom and (b) multi-electronic atoms.

Quantum Mechanical Model of Atom

Energies of Orbitals

The energy of an electron in a multielectron atom, unlike that of the hydrogen atom, depends not only on its principal quantum number (shell), but also on its azimuthal quantum number (subshell).

Within a given principal quantum number, the energy of orbitals increases in the order **s<p<d<f**

The main reason for having different energies of the subshells is the mutual repulsion among the electrons in multielectron atoms.

The energy of orbitals refers to the energy required to take an electron present in that orbital to infinity or the energy released when an electron is added to that orbital from infinity.

Quantum Mechanical Model of Atom

Energies of Orbitals

Due to the presence of electrons in the inner shells, the electron in the outer shell will not experience the full positive charge of the nucleus (Ze).

The effect will be lowered due to the partial screening of positive charge on the nucleus by the inner shell electrons. This is known as the shielding of the outer shell electrons from the nucleus by the inner shell electrons, and the net positive charge experienced by the outer electrons is known as effective nuclear charge (**Zeff e**).

Quantum Mechanical Model of Atom

Energies of Orbitals

For a given shell (principal quantum number), the Zeff experienced by the electron decreases with increase of azimuthal quantum number (l), that is, the s orbital electron will be more tightly bound to the nucleus than p orbital electron which in turn will be better tightly bound than the d orbital electron.

The energy of electrons in s orbital will be lower (more negative) than that of p orbital electron which will have less energy than that of d orbital electron and so on.

The lower the value of (n + l) for an orbital, the lower is its energy. If two orbitals have the same value of (n + l), the orbital with lower value of n will have the lower energy.

Quantum Mechanical Model of Atom

Orbital	Value of n	Value of l	Value of $(n + l)$	
1s	1	0	1 + 0 = 1	
2s	2	0	2 + 0 = 2	
2p	2	1	2 + 1 = 3	2p (n=2) has lower energy than
3s	3	0	3 + 0 = 3	3s (n=3)
3p	3	1	3 + 1 = 4	3p (n =3) has lower energy than
4s	4	0	4 + 0 = 4	4s (n =4)
3d	3	2	3 + 2 = 5	3d (n =3) has lower energy than
4p	4	1	4 + 1 =5	4p (n =4)

Table: Arrangement of Orbitals with Increasing Energy on the Basis of (n+l) Rule

Quantum Mechanical Model of Atom

Energies of Orbitals

Energies of the orbitals in the same subshell decrease with increase in the atomic number (Z_{eff}).

For example, energy of 2s orbital of hydrogen atom is greater than that of 2s orbital of lithium and that of lithium is greater than that of sodium and so on, that is, E_{2s} (H) > E_{2s} (Li) > E_{2s} (Na) > E_{2s} (K).

Filling of Orbitals in Atom

Aufbau Principle: In the ground state of the atoms, the orbitals are filled in order of their increasing energies.

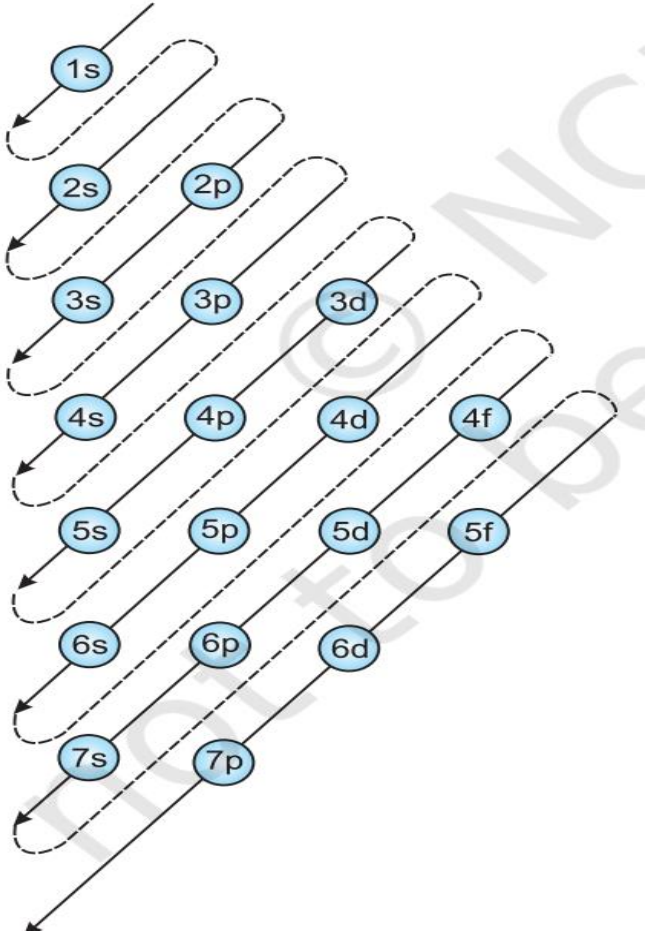
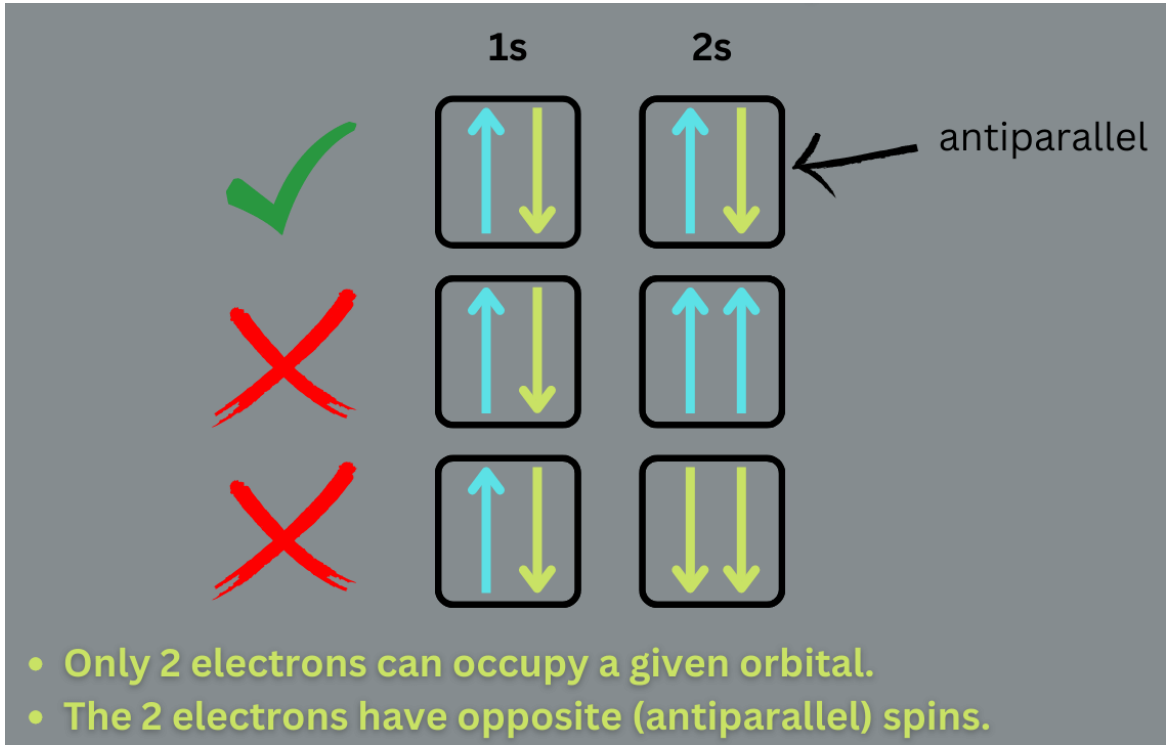


Fig. Order of filling of orbitals

Filling of Orbitals in Atom

Pauli Exclusion Principle:

No two electrons in an atom can have the same set of four quantum numbers.



"Only two electrons may exist in the same orbital and these electrons must have opposite spin."

This means that the two electrons can have the same value of three quantum numbers n, l and ml, but must have the opposite spin quantum number.

Filling of Orbitals in Atom

Hund's Rule of Maximum Multiplicity:

This rule deals with the filling of electrons into the orbitals belonging to the same subshell

It states: Pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.

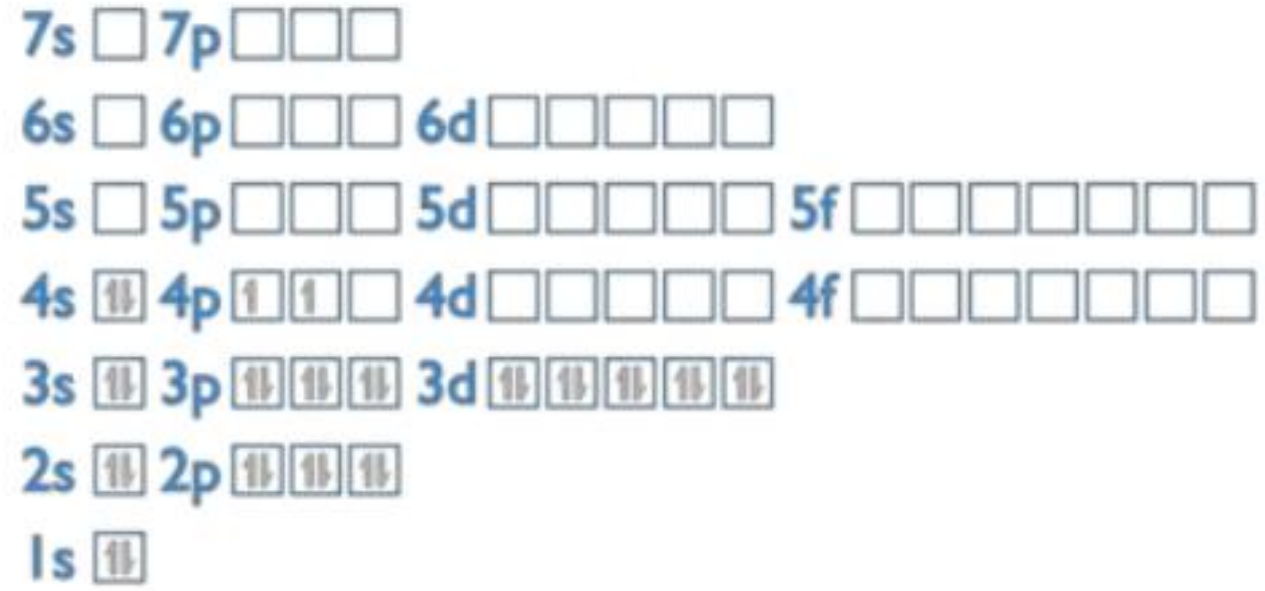
Table Representation of arrangements of electrons

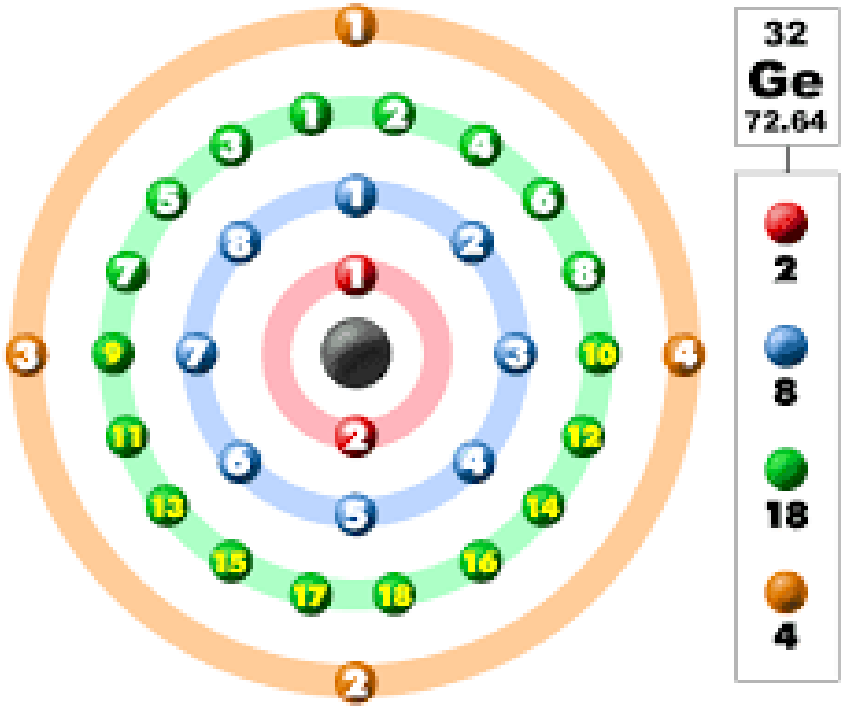
Atomic Number	Element	1s	2s	$2p_x$	$2p_y$	$2p_z$	Number of unpaired electrons
1	H	↑					1
2	He	↑↓					0
3	Li	↑↓	↑				1
4	Be	↑↓	↑↓				0
5	B	↑↓	↑↓	↑	↑		1
6	C	↑↓	↑↓	↑	↑		2
7	N	↑↓	↑↓	↑	↑	↑	3
8	O	↑↓	↑↓	↑↓	↑	↑	2
9	F	↑↓	↑↓	↑↓	↑↓	↑	1
10	Ne	↑↓	↑↓	↑↓	↑↓	↑↓	0

Filling of Orbitals in Atom

- The electrons in the completely filled shells are known as core electrons and the electrons that are added to the electronic shell with the **highest principal quantum number** are called **valence electrons**.

- Valence electrons occupy the outermost shell or highest energy level of an atom while core electrons are those occupying the innermost shell or lowest energy levels.





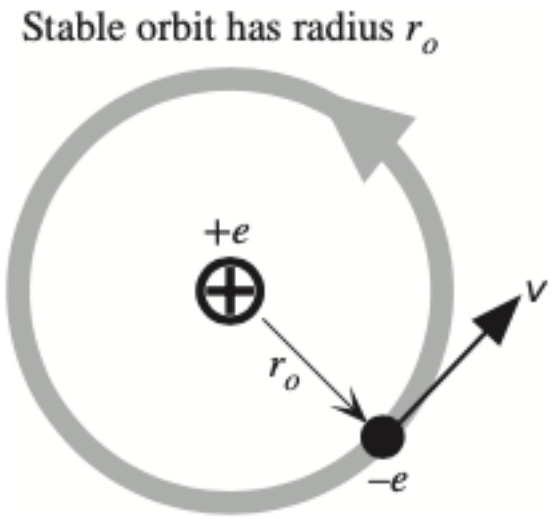
Virial Theorem

- Virial theorem allows us to relate the average kinetic energy KE, average potential energy PE, and average total or overall energy E of an electron in an atom, or electrons and nuclei in a molecule

$$\overline{E} = \overline{KE} + \overline{PE} \qquad \text{and} \qquad \overline{KE} = -\frac{1}{2}\overline{PE}$$

Numerical

Consider the hydrogen atom in Figure 1.2 in which the electron is in the stable 1s orbit with a radius r_0. The ionization energy of the hydrogen atom is 13.6 eV.



a). It takes 13.6 eV to ionize the hydrogen atom, i.e., to remove the electron to infinity. If the condition when the electron is far removed from the hydrogen nucleus defines the zero reference of energy, then the total energy of the electron within the H atom is −13.6 eV. Calculate the average PE and average KE of the electron.

b). Assume that the electron is in a stable orbit of radius r_0 around the positive nucleus. What is the Coulombic PE of the electron? Hence, what is the radius r_0 of the electron orbit?

c). What is the velocity of the electron?

d). What is the frequency of rotation (oscillation) of the electron around the nucleus?

SOLUTION

a. From Equation 1.1 we obtain

$$\bar{E} = \overline{PE} + \overline{KE} = \frac{1}{2}\overline{PE}$$

or
$$\overline{PE} = 2\bar{E} = 2 \times (-13.6\ \text{eV}) = -27.2\ \text{eV}$$

The average kinetic energy is

$$\overline{KE} = -\frac{1}{2}\overline{PE} = 13.6\ \text{eV}$$

b. The Coulombic *PE* of interaction between two charges Q_1 and Q_2 separated by a distance r_o, from elementary electrostatics, is given by

$$PE = \frac{Q_1 Q_2}{4\pi\varepsilon_o r_o} = \frac{(-e)(+e)}{4\pi\varepsilon_o r_o} = -\frac{e^2}{4\pi\varepsilon_o r_o}$$

where we substituted $Q_1 = -e$ (electron's charge), and $Q_2 = +e$ (charge of the nucleus). Thus the radius r_o is

$$r_o = -\frac{(1.6 \times 10^{-19}\ \text{C})^2}{4\pi(8.85 \times 10^{-12}\ \text{F m}^{-1})(-27.2\ \text{eV} \times 1.6 \times 10^{-19}\ \text{J/eV})}$$
$$= 5.29 \times 10^{-11}\ \text{m} \quad \text{or} \quad 0.0529\ \text{nm}$$

which is called the **Bohr radius** (also denoted a_o).

c. Since $KE = \frac{1}{2}m_e v^2$, the average velocity is

$$v = \sqrt{\frac{\overline{KE}}{\frac{1}{2}m_e}} = \sqrt{\frac{13.6\text{ eV} \times 1.6 \times 10^{-19}\text{ J/eV}}{\frac{1}{2}(9.1 \times 10^{-31}\text{ kg})}} = 2.19 \times 10^{6}\text{ m s}^{-1}$$

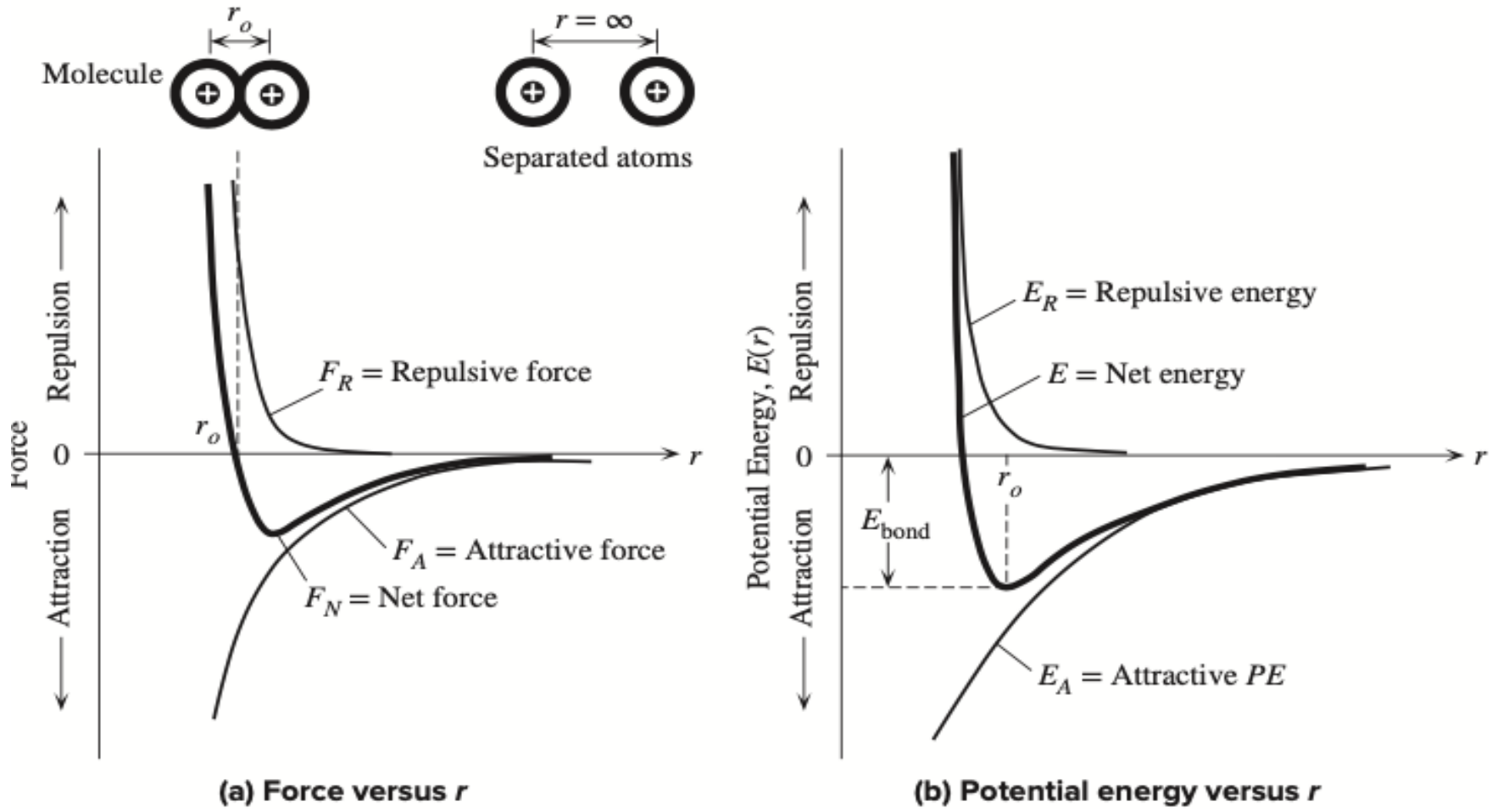
d. The period of orbital rotation T is

$$T = \frac{2\pi r_o}{v} = \frac{2\pi(0.0529 \times 10^{-9}\text{ m})}{2.19 \times 10^{6}\text{ m s}^{-1}} = 1.52 \times 10^{-16}\text{ seconds}$$

The orbital frequency $f = 1/T = 6.59 \times 10^{15}\text{ s}^{-1}$ (Hz).

Bonding and Types of Solids

The attraction and repulsion forces that tend to hold the adjacent atoms, molecules, or ions at a certain spacing to keep a balance between the opposing forces are known as bonds.



- When the distance between atoms is very high, then the force of attraction F_A will be more than the force of repulsion F_R.
- As the distance between atoms reduces, the force of repulsion increases and F_N resultant force at Equilibrium

$$F_N = F_A + F_R = 0$$

- This distance is called the equilibrium separation and is effectively the bond length.
- On the energy diagram, F_N = 0 means dE/dr = 0, which means that the equilibrium of two atoms corresponds to the potential energy of the system acquiring its minimum value.

- When two atoms are brought together, the valence electrons interact with each other and with the neighbor's positively charged nucleus.
- The result of this interaction is often the formation of a bond between the two atoms, producing a molecule.
- The formation of a bond means that the energy of the system of two atoms together must be less than that of the two atoms separated, so that the molecule formation is energetically favorable, that is, more stable.
- Atoms when brough together experience forces of attraction and repulsion, the state of equilibrium is reached when:

$$F_N = F_R + F_A = 0 \ldots\ldots (1)$$

- The potential energy (PE(r)) of the atoms can be found by

$$PE(r) = -\int F_N dr \ldots\ldots (2)$$

- **Equilibrium distance:** The distance between the atoms when they are in state of equilibrium and is also known as bond length.
- **Bond Energy:** Energy required to separate the two atoms from the state of equilibrium is termed as bond energy.
- The argument discussed here is applicable to between many atoms.

Types of Bonding's

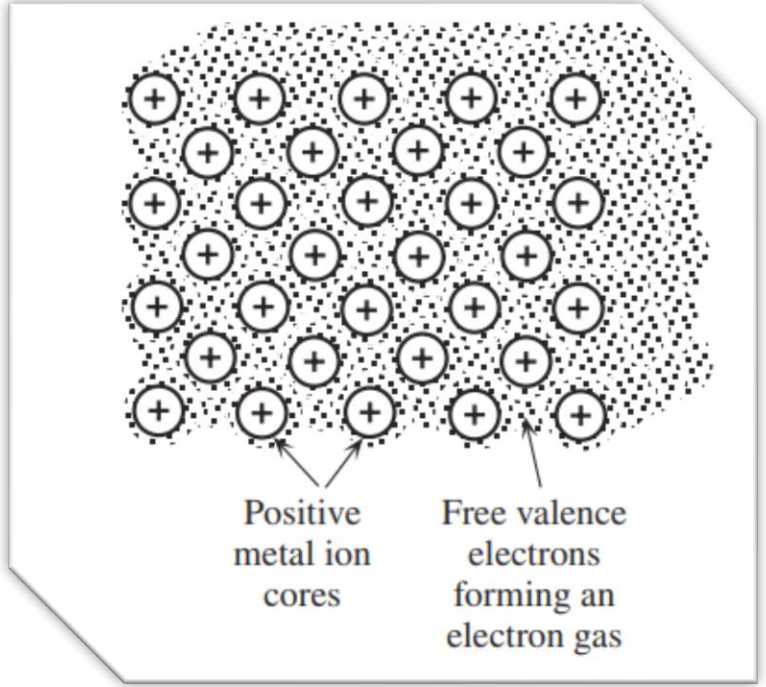
1. Metallic Bonding: (Metals)

Metallic bonding is a type of chemical bonding that arises from the electrostatic attractive force between conduction electrons (in the form of an electron cloud of delocalized electrons) and positively charged metal ions.

Ex:- Al, Cu, Mg (magnesium), Ca (Calcium)

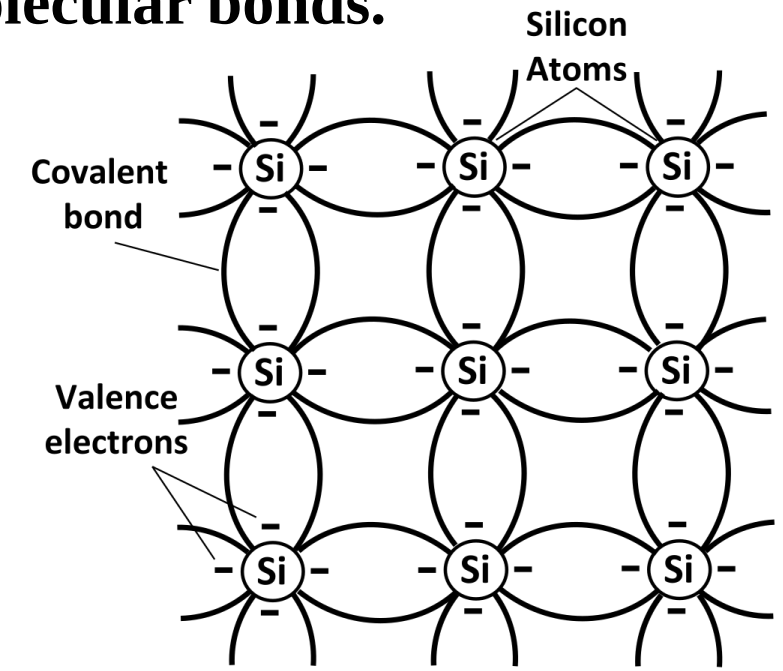
- Metal atoms have only a few valence electrons, which are not very difficult to remove.
- When many metal atoms are brought together to form a solid, these valence electrons are lost from individual atoms and become collectively shared by all the ions.
- The valence electrons therefore become delocalized and form an electron gas or electron cloud, permeating the space between the ions.
- Bonding in a metal is essentially due to the attraction between the stationary metal ions and the freely wandering electrons between the ions.
- The bond is a collective sharing of electrons and is therefore nondirectional.
- Consequently, the metal ions try to get as close as possible, which leads to close-packed crystal structures with high coordination numbers, compared to covalently bonded solids.

- Very good conductors, as electrons can move freely under the externally applied electric field.
- Good conductor of heat: If there is a temperature gradient along a metal bar, the free electrons can also contribute to the energy transfer from the hot to the cold regions, since they frequently collide with the metal ions and thereby transfer energy.

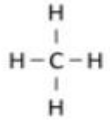


2. Covalent (Non-Metals)

A covalent bond is formed by equal sharing of electrons from both the participating atoms. The pair of electrons participating in this type of bonding is called shared pair or bonding pair. The covalent bonds are also termed as molecular bonds.



COVALENT - non-metals only



SIMPLE COVALENT (most covalent compounds)

GIANT COVALENT (a few covalent compounds)

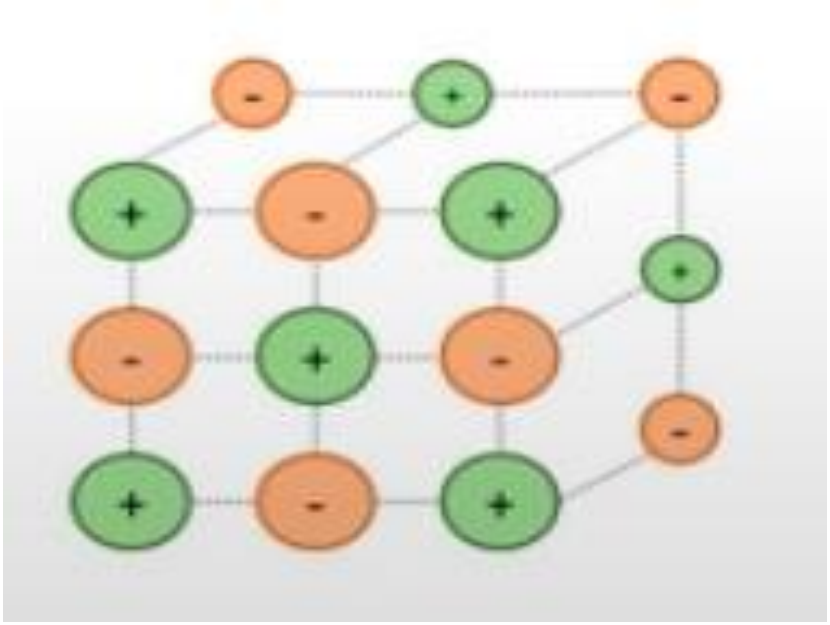
Covalently bonded solids:

- Two atoms can form a bond with each other by sharing some or all of their valence electrons and thereby reducing the overall potential energy of the combination.
- The covalent bond results from the sharing of valence electrons to complete the subshells of each atom.
- Due to the strong Coulombic attraction between the shared electrons and the positive nuclei, the covalent bond energy is usually the highest for all bond types, leading to very high melting temperatures and very hard solids: diamond is one of the hardest known materials.
- As all the valence electrons are locked in the bonds between the atoms, these electrons are not free to drift in the crystal when an electric field is applied. Consequently, the electrical conductivity of such materials is very poor.

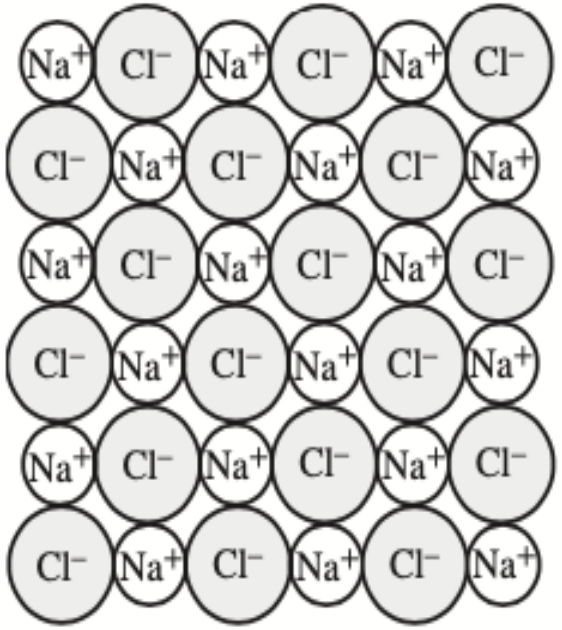
3. Ionic (Metals and Non-Metals)

The electrostatic force of attraction which holds the two oppositely charged ions together is called the ionic bond.

IONIC - both metals and non-metals 'giant ionic lattice'



- In ionic bonds, the complete transfer of one or more electrons occurs between the donor and acceptor elements.
- There are few factors that cause the formation of ionic bonds; one of them is the **large differences in electronegativity of atoms**, which attract other atoms for the transfer of their electrons.
- An ionic bond is formed by the complete transfer of some electrons from one atom to another.
- **The atom losing one or more electrons becomes a cation—a positively charged ion.**
- **The atom gaining one or more electron becomes an anion—a negatively charged ion.**
- When the transfer of electrons occurs, an electrostatic attraction between the two ions of opposite charge takes place and an ionic bond is formed.



Classification of Materials

- Materials can be mainly classified as **metals, semiconductors or insulators** based on conductivity or resistivity and energy bands in electronics.
- This concept also helps in understanding the band theory and importance of valance and covalent bands in solids.

- Metals have very high conductivity and low resistivity, hence,

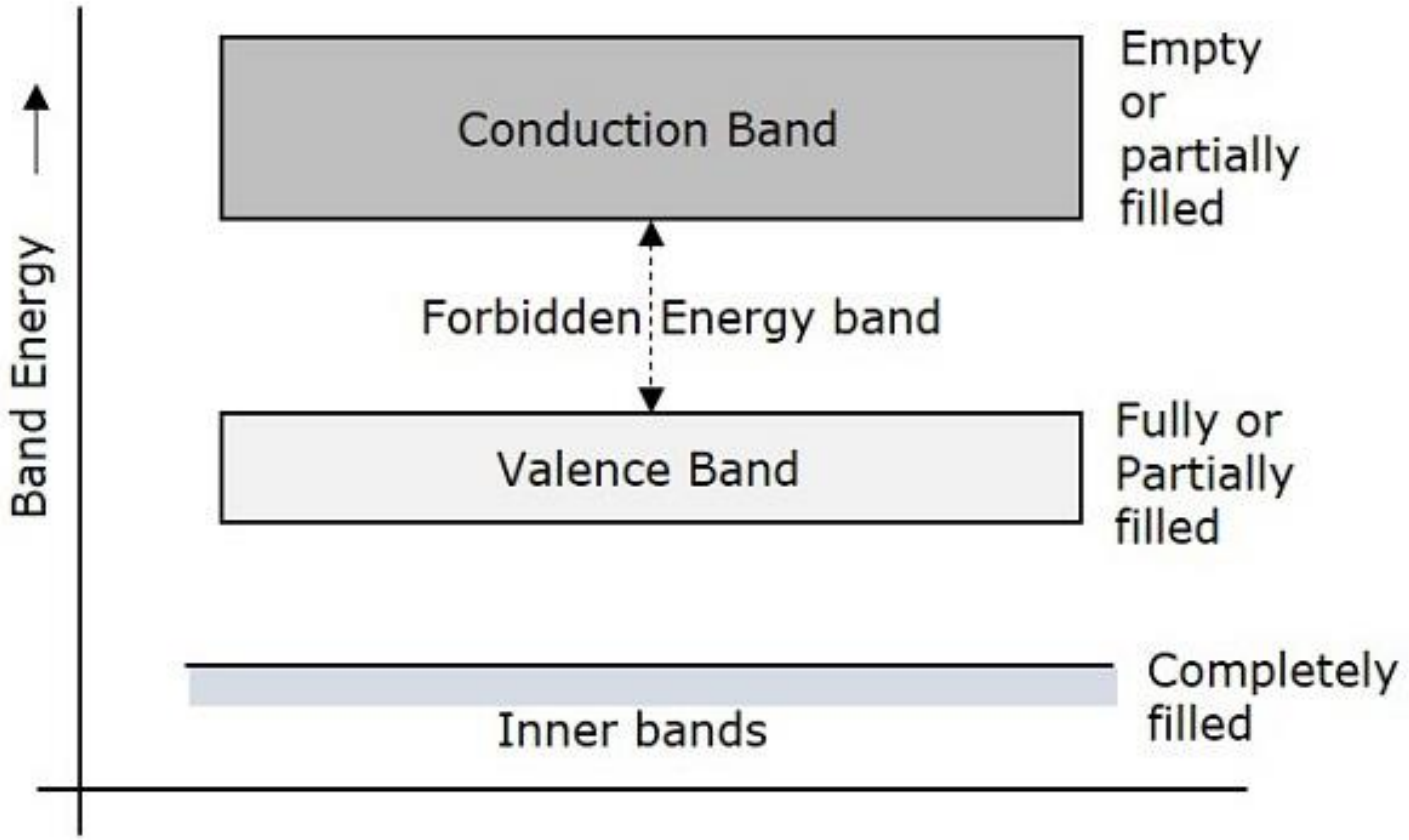
Metals: $\sigma \sim 10^{2}\ to 10^{8}\ S/m$ and $\boldsymbol{\rho} \sim 10^{-2}\ to 10^{-8}\ Ohm * m$

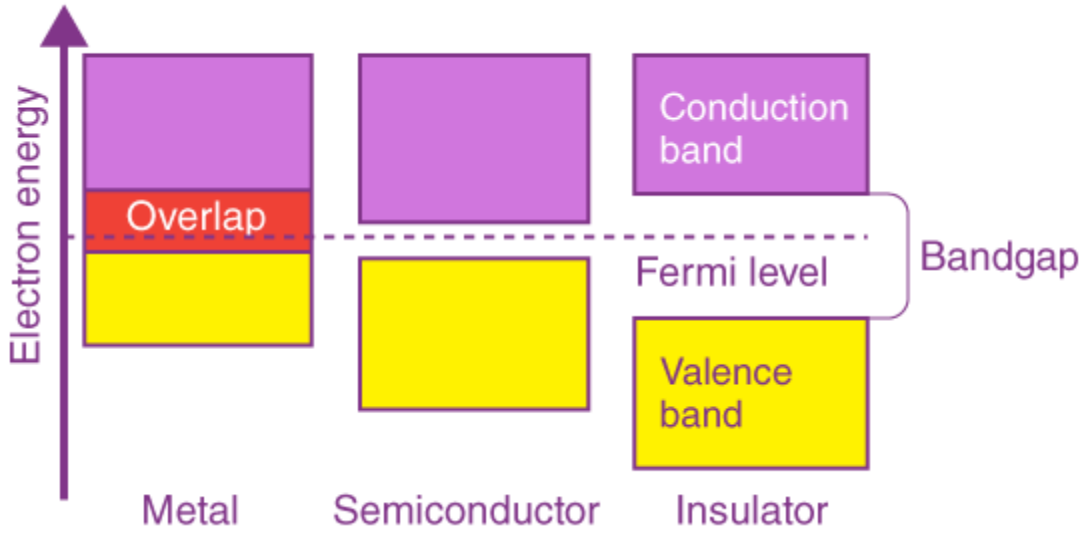
Semiconductors: $\sigma \sim 10^{5}\ to 10^{-6}\ S/m$ and $\boldsymbol{\rho} \sim 10^{-5}\ to 10^{6}\ Ohm * m$

Insulators: $\sigma \sim 10^{-11}\ to 10^{-19}\ S/m$ and $\boldsymbol{\rho} \sim 10^{11}\ to 10^{19}\ Ohm * m$

Classification based on Energy Band

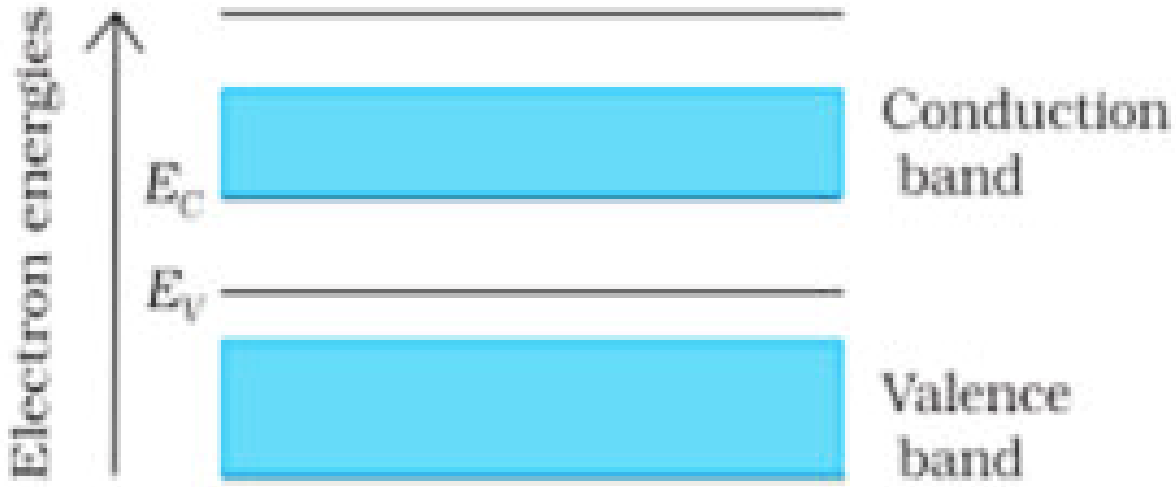
- In case of **metallic conductors**, conduction band overlaps on the electrons in the valence band. The **energy gap is $e_g = 0ev$.**
- **Semiconductors** have a small gap between both these bands. Some valence electrons gain energy from external sources and cross the gap between the valence and conduction bands. By this movement, they create a free electron in the conduction band and a vacant energy level in the valence band for other valence electrons to move. This creates the possibility of conduction. The **energy gap is $e_g = 1ev$.**
- **In insulators**, there is a large gap between both these bands. Hence, the electrons in the valence band remain bound and no free electrons are available in the conduction band. The **energy gap is $e_g > 5ev$.**





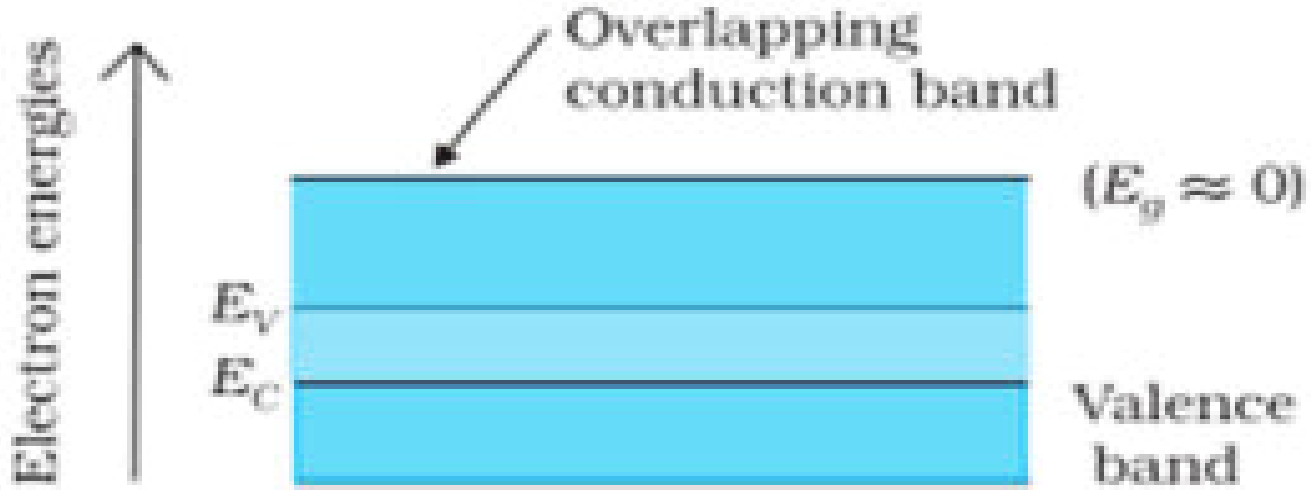
The conduction band is the band of electron orbitals that electrons can bounce up into from the valence band when energized. At the point when the electrons are in these orbitals, they have enough energy to move freely in the material. This movement of electrons makes an electric current flow.

Case 1



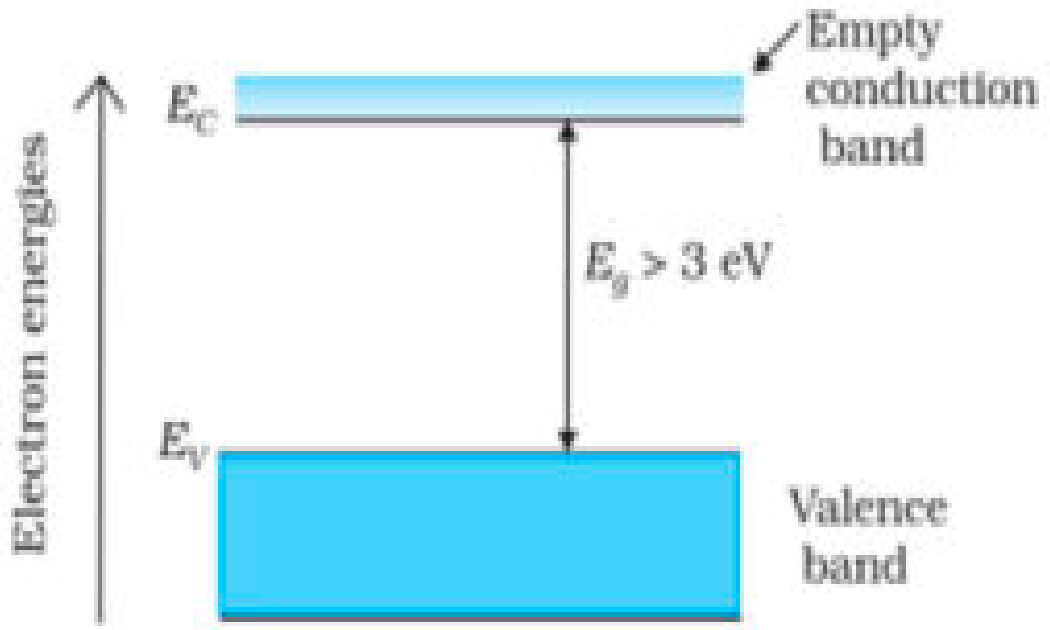
E_c denotes the lowest energy level of the conduction band and E_v denotes the highest energy level of the valence band. The above diagram describes a **solid** where the valence band is partially empty. Hence, electrons from the lower energy levels can move to the higher levels making conduction possible. Also, the resistivity of such solids is low or the conductivity is high

Case 2



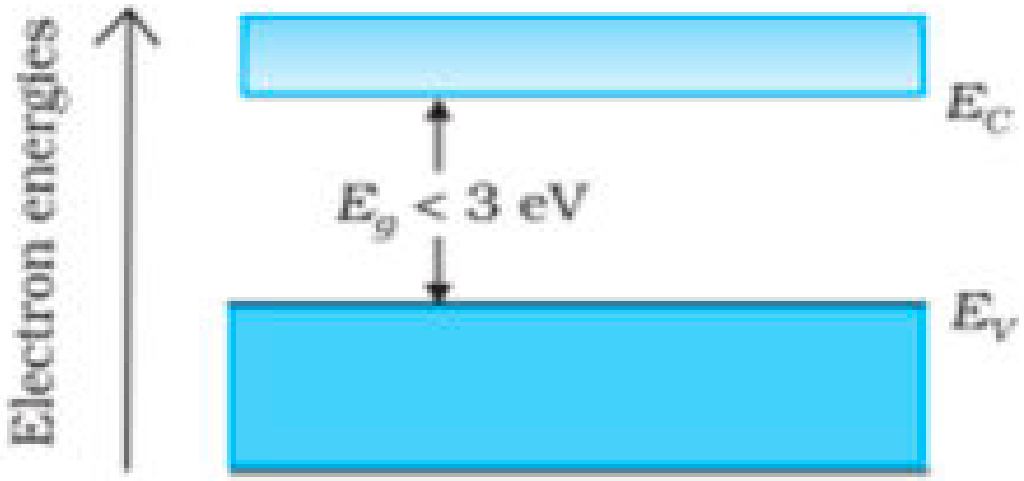
E_c and E_v are the same as case 1 and E_g is the energy gap. This diagram describes a **solid** where the conduction and valence bands overlap each other. Hence, electrons can easily move from the valence to the conduction band. This makes a large number of electrons available for conduction. Also, the resistivity of such solids is low or the conductivity is high.

Case 3



This diagram describes a solid where the energy gap (E_g) is very large (>3 eV). Due to this large gap, electrons cannot be excited to move from the valence to the conduction band by thermal excitation. Hence, there are no free electrons in the conduction band and no conductivity. These are insulators.

Case 4

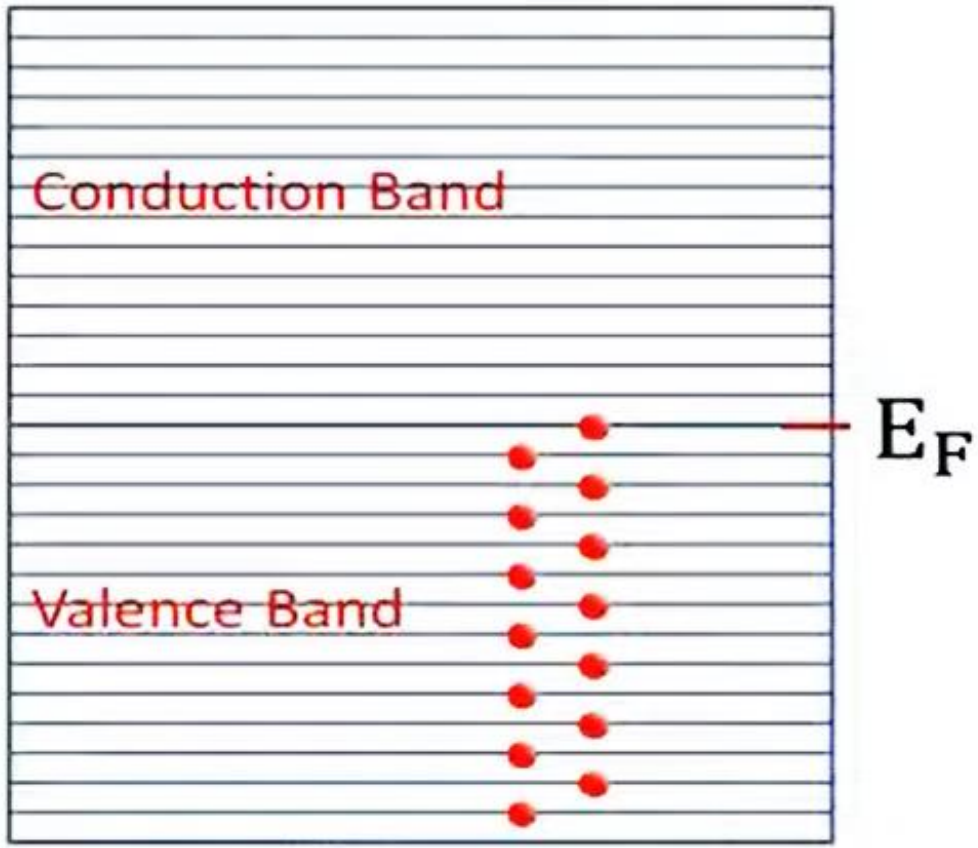


This diagram describes a solid where the energy gap is small (< 3 eV). Since the gap is small, some electrons acquire enough energy even at room temperature and enter the conduction band. These electrons can move in the conduction band increasing the conductivity of the solid. These are **semiconductors**. The resistivity of semiconductors is lower than that of insulators but higher than that of metals.

Concept of Fermi Level

Fermi Energy:

- A Fermi level is the measure of the energy of the least tightly held electrons within a solid. It is important in determining the thermal and electrical properties of solids. It can be defined as:
  - Fermi energy is a concept in quantum mechanics that usually refers to the energy difference between the highest and lowest occupied single-particle states in a quantum system of non-interacting fermions at absolute zero temperature.
- The **highest energy level that an electron can occupy at the absolute zero temperature is known as the Fermi Level**. **The Fermi level lies between the valence band and conduction band because at absolute zero temperature (−273.15 °C or 0K)**, **the electrons are all in the lowest energy state**.
- Fermi energy is constant for each solid.



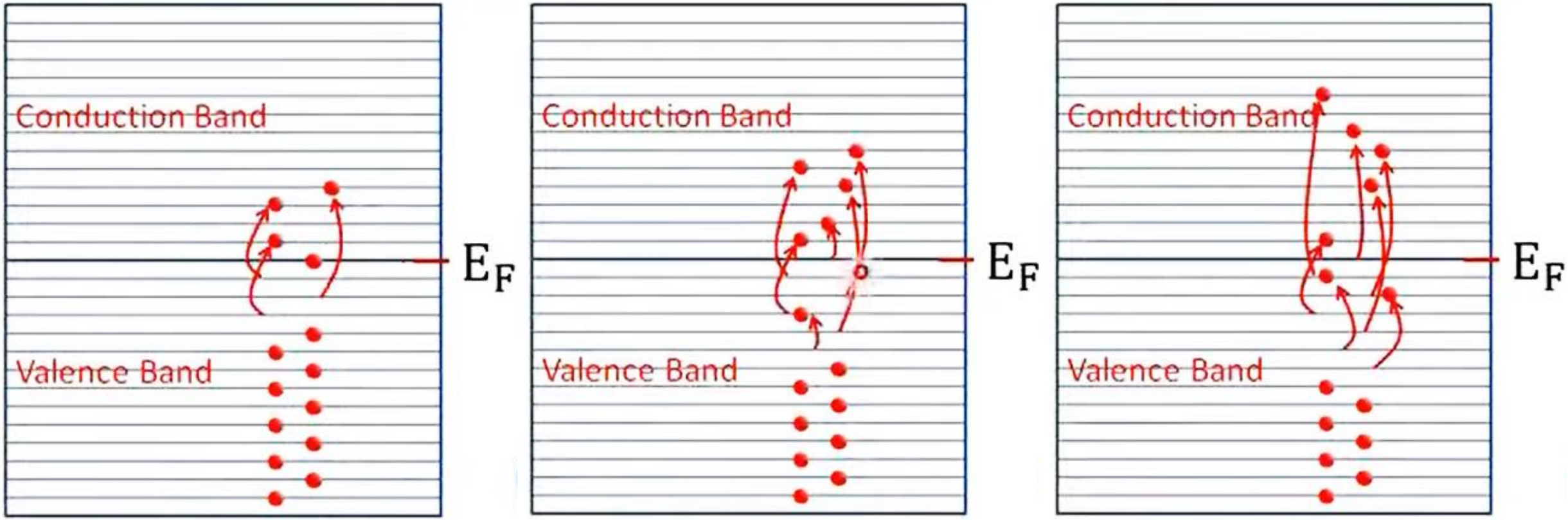
Metal (Conductor)

$T = 0\ K$

- In metal, there is one partially filled band which is a result of conduction band overlapping with valence band.
- In this band lowest energy levels are filled first.
- The highest occupied energy level at absolute zero temperature (0K) is called as Fermi level.
- Energy corresponding to it is called as **Fermi energy denoted by E_F**

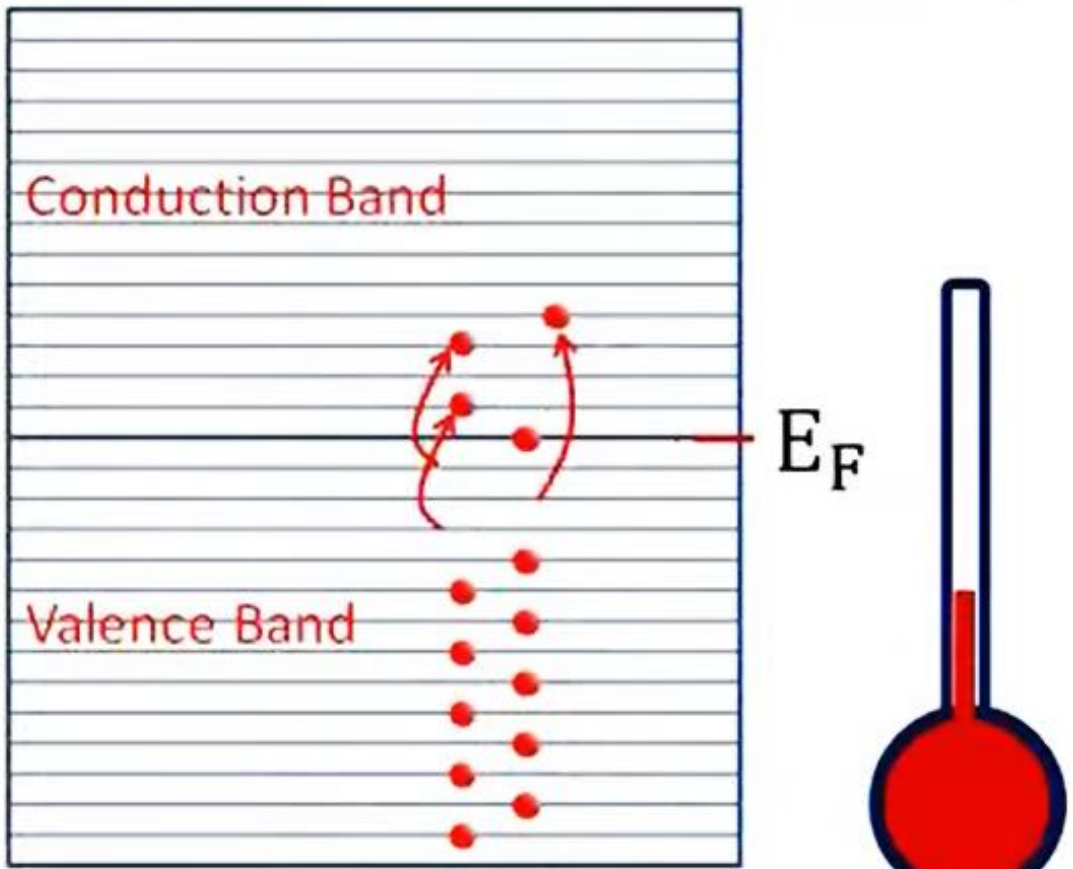
Metal Conductor at T > 0

$T_1 < T_2 < T_3$



At T_1 **At T_2** **At T_3**

Fermi Level and Fermi-Dirac Distribution Function



Metal (Conductor)

$T > 0\ K$

- At temperature $T > 0K$, the distribution of electrons over a range of allowed energy levels at thermal equilibrium is given by Fermi-Dirac Distribution function

$$f(E) = \frac{1}{1+e^{\left(\frac{E-E_F}{kT}\right)}}$$

f(E) is the probability of occupancy for energy level E

E_F is Fermi energy

T is temperature in ^0K and

$k = 1.38 \times 10^{-23} J/K = 8.625 \times 10^{-5} eV/K$

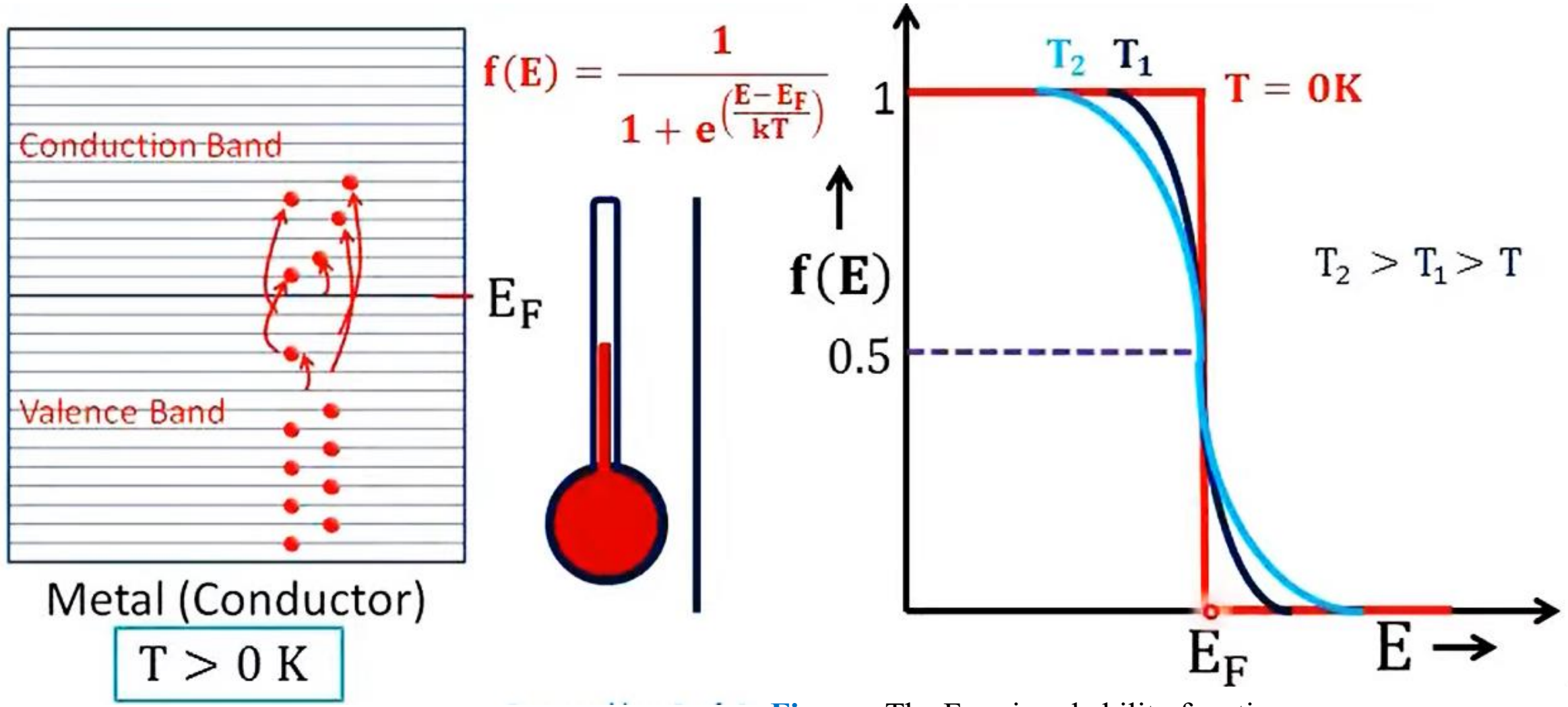


Figure . The Fermi probability function versus energy for different temperatures.

At $T = 0$ K, For $E < E_F$

$$e^{\left(\frac{E-E_F}{kT}\right)} = e^{\frac{-\text{ve number}}{0}} = e^{-\infty} = \frac{1}{e^{\infty}} = \frac{1}{\infty} = 0$$

$$\therefore f(E) = \frac{1}{1 + e^{\left(\frac{E-E_F}{kT}\right)}} = \frac{1}{1+0} = 1$$

This indicates all energy levels below E_F are completely **filled** at absolute zero temperature

At $T = 0$ K, For $E > E_F$

$$e^{\left(\frac{E-E_F}{kT}\right)} = e^{\frac{+\text{ve number}}{0}} = e^{+\infty} = \infty$$

$$\therefore f(E) = \frac{1}{1 + e^{\left(\frac{E-E_F}{kT}\right)}} = \frac{1}{1+\infty} = 0$$

This indicates all energy levels above E_F are completely **empty** at absolute zero temperature

At $T > 0$ K, For $E = E_F$

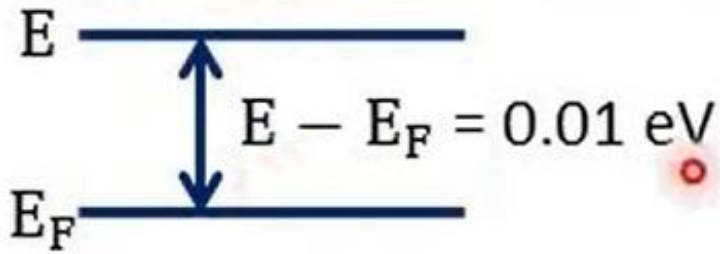
$$e^{\left(\frac{E-E_F}{kT}\right)} = e^{\frac{0}{kT}} = e^{0} = 1$$

$$\therefore f(E) = \frac{1}{1 + e^{\left(\frac{E-E_F}{kT}\right)}} = \frac{1}{1+1} = \frac{1}{2}$$

At $T > 0$ K, probability of occupancy for Fermi level is always half

Calculate probability of non-occupancy for the energy level which lies 0.01 eV above the Fermi energy level at 27 ^{0}C.

Given : T = 27 ^{0}C = 300 ^{0}K, $k = 8.625 \times 10^{-5} \frac{eV}{^0K}$



$$\text{Probability of occupancy } f(E) = \frac{1}{1+e^{\left(\frac{E-E_F}{kT}\right)}}$$

$$\therefore \text{Probability of non} - \text{occupancy} = 1 - f(E) = 1 - \frac{1}{1+e^{\left(\frac{E-E_F}{kT}\right)}}$$

$$= 1 - \frac{1}{1+e^{\left(\frac{0.01}{8.625\times10^{-5}\times300}\right)}}$$

$$= 0.595$$

Fermi level for silver is 5.5 eV. Find out the energy for which the probability of occupancy at 300 K is 0.9.

Given : $T = 27\,^{\circ}C = 300^{0}K$, $k = 8.625 \times 10^{-5}\,\frac{eV}{^{\circ}K}$, $E_F = 5.5\ eV$

when $f(E) = 0.9$, E =?

Probability of occupancy $f(E) = \dfrac{1}{1+e^{\left(\frac{E-E_F}{kT}\right)}}$

$$\therefore 1 + e^{\left(\frac{E-E_F}{kT}\right)} = \frac{1}{f(E)}$$

$$\therefore e^{\left(\frac{E-E_F}{kT}\right)} = \frac{1}{f(E)} - 1$$

$$\therefore \frac{E - E_F}{kT} = \ln\left(\frac{1}{f(E)} - 1\right)$$

$$\therefore E - E_F = kT \ln\left(\frac{1}{f(E)} - 1\right)$$

$$\therefore E = E_F + kT \ln\left(\frac{1}{f(E)} - 1\right)$$

For $f(E) = 0.9$

$$E = 5.5 + 8.625 \times 10^{-5} \times 300 \ln\left(\frac{1}{0.9} - 1\right)$$

$$= 5.443\ eV$$

Fermi level in potassium is 2.1 eV. What are the energies for which the probability of occupancy at 300 K are 0.99 and 0.01.

Given :$T = 27\,^{\circ}C = 300^{0}K$, $k = 8.625 \times 10^{-5}\,\frac{eV}{^{0}K}$, $E_F = 2.1$ eV

when $f(E) = 0.99$ and $f(E) = 0.01$, $E = ?$

Probability of occupancy $f(E) = \frac{1}{1+e^{\left(\frac{E-E_F}{kT}\right)}}$

$$\therefore E = E_F + kT \ln\left(\frac{1}{f(E)} - 1\right)$$

$$\therefore 1 + e^{\left(\frac{E-E_F}{kT}\right)} = \frac{1}{f(E)}$$

$$\therefore e^{\left(\frac{E-E_F}{kT}\right)} = \frac{1}{f(E)} - 1$$

$$\therefore \frac{E - E_F}{kT} = \ln\left(\frac{1}{f(E)} - 1\right)$$

For $f(E) = 0.99$

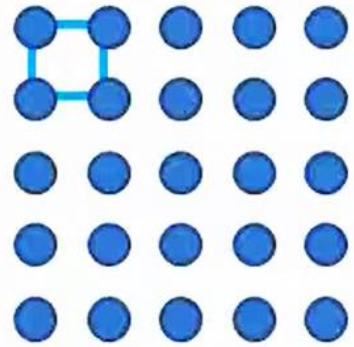
$$E = 2.1 + 8.625 \times 10^{-5} \times 300 \ln\left(\frac{1}{0.99} - 1\right) = 1.981 \text{ eV}$$

For $f(E) = 0.01$

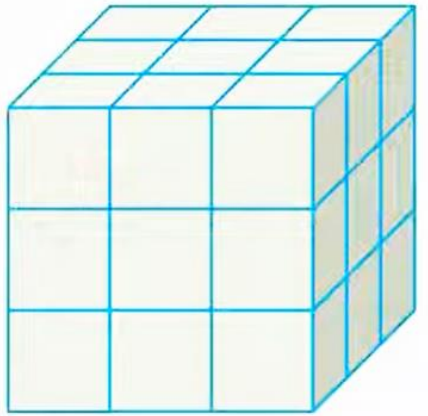
$$E = 2.1 + 8.625 \times 10^{-5} \times 300 \ln\left(\frac{1}{0.01} - 1\right) = 2.218 \text{ eV}$$

Crystal directions and Planes, Crystal Properties, Defects and Vacancies

- In solids, the constituent atoms or molecules are very tightly packed and strongly bonded to each other. Solid constituent a very large preparation of materials used in engineering and technology. Therefore, it is necessary to study their properties.
- A crystal consists of three dimensional arrays of regularly spaced atoms.
- As the separation between the atoms is of the order of 1A°
- Diffraction pattern can be obtained by making X-rays incident on the atomic planes, by analyzing the diffraction pattern, crystal structure can be studied.
- The smallest fundamental building unit having definite arrangement of atoms, ions or molecules which is repeated to form a crystal is called as the **unit cell**.

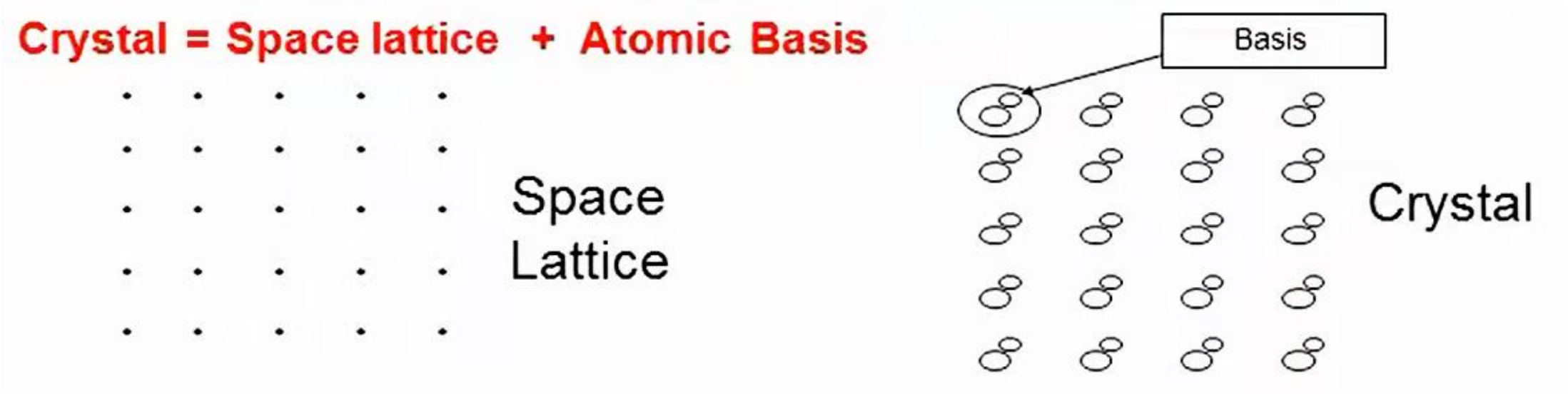


Two dimensional space lattice



Three dimensional space lattice

- The most important property of a crystal is periodicity, which leads to what is termed long-range order. In a crystal, the local bonding geometry is repeated many times at regular intervals, to produce a periodic array of atoms that constitutes the crystal structure.
- All crystals can be described in terms of a lattice and a basis.
- A lattice is an infinite periodic array of geometric points in space, without any atoms.
- When we place an identical group of atoms (or molecules), called a basis, at each lattice point, we obtain the actual crystal structure.
- Crystal = Lattice + basis @ each lattice point.



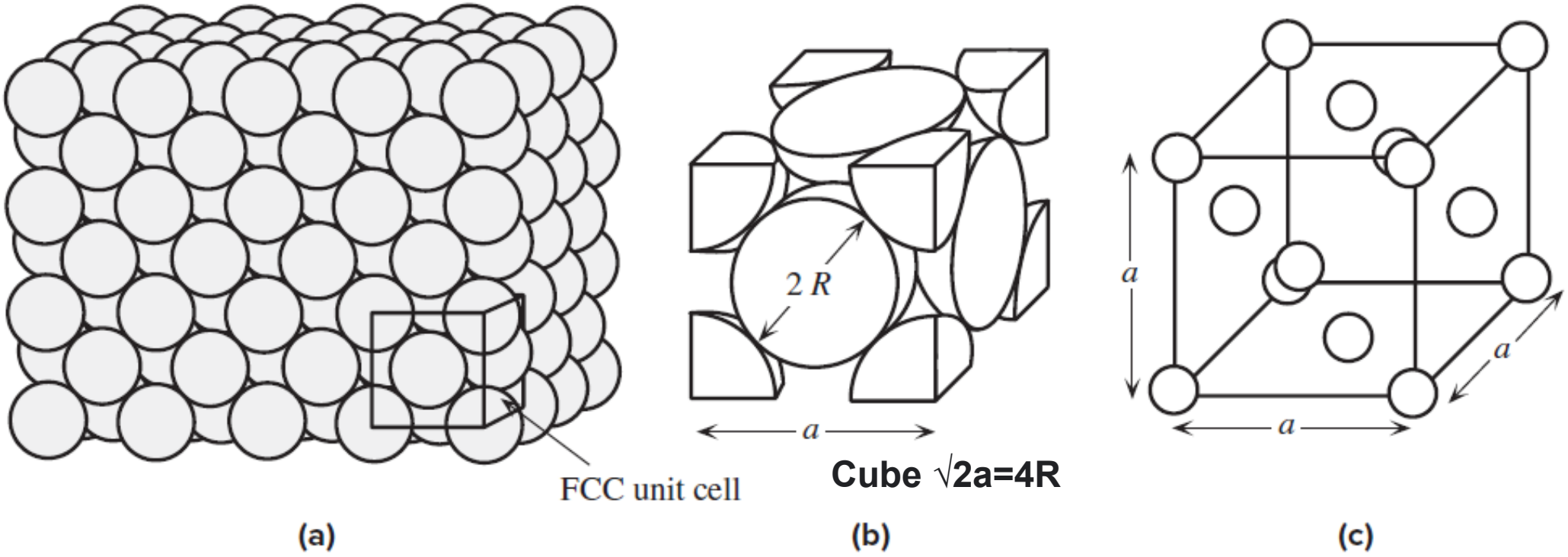


Figure 1.32 (a) The crystal structure of copper which is face-centered cubic (FCC). The atoms are positioned at well-defined sites arranged periodically, and there is a long-range order in the crystal. (b) An FCC unit cell with close-packed spheres. (c) Reduced-sphere representation of the FCC unit cell. Examples: Ag, Al, Au, Ca, Cu, γ-Fe (>912 °C), Ni, Pd, Pt, and Rh.

- A crystalline solid is a solid in which the atoms bond with each other in a regular pattern to form a periodic collection (or array) of atoms, as shown for the copper crystal in Figure 1.32.

- The most important property of a crystal is periodicity, which leads to what is termed long-range order. In a crystal, the local bonding geometry is repeated many times at regular intervals, to produce a periodic array of atoms that constitutes the crystal structure.
- The unit cell of Cu is thus said to have a face-centered cubic (FCC) structure. The Cu atoms are shared with neighboring unit cells.
- Effectively, then, only one-eighth of a corner atom is in the unit cell and one-half of the face-centered atom belongs to the unit cell, as shown in Figure 1.32b.
- This means there are effectively four atoms in the unit cell. The length of the cubic unit cell is termed the lattice parameter a of the crystal structure.
- For Cu, for example, a is 0.362 nm, whereas the radius R of the Cu atom in the crystal is 0.128 nm. Assuming the Cu atoms are spheres that touch each other, we can geometrically relate a and R. For clarity, it is often more convenient to draw the unit cell with the spheres reduced, as in Figure 1.32c.

EXAMPLE 1.16 **THE COPPER (FCC) CRYSTAL** Consider the FCC unit cell of the copper crystal shown in Figure 1.40.

a. How many atoms are there per unit cell?

b. If R is the radius of the Cu atom, show that the lattice parameter a is given by $a = R2\sqrt{2}$.

c. Calculate the **atomic packing factor** (APF) defined by

$$\text{APF} = \frac{\text{Volume of atoms in unit cell}}{\text{Volume of unit cell}}$$

d. Calculate the **atomic concentration** (number of atoms per unit volume) in Cu and the density of the crystal given that the atomic mass of Cu is 63.55 g mol^{-1} and the radius of the Cu atom is 0.128 nm.

Solution

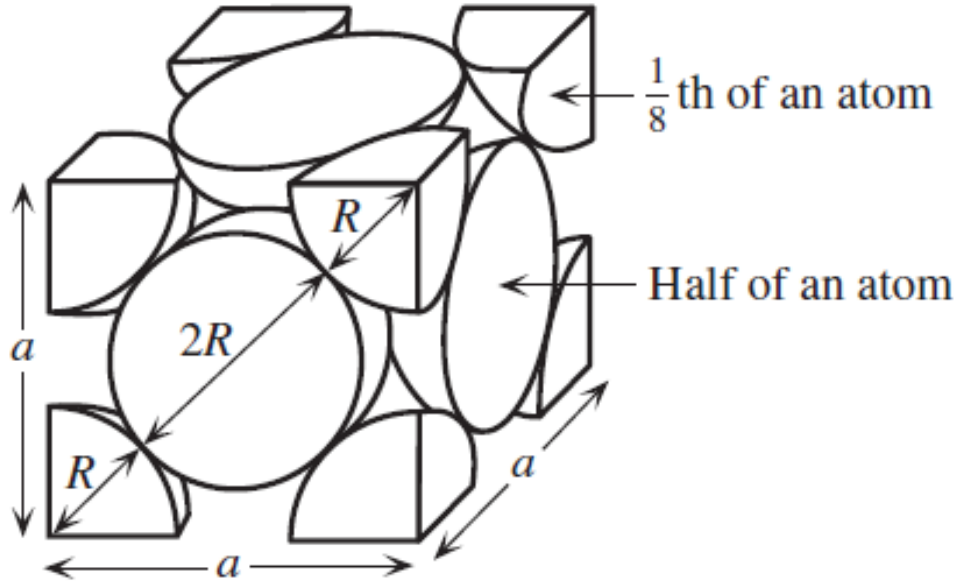


Figure 1.40 The FCC unit cell.
The atomic radius is R and the lattice parameter is a.

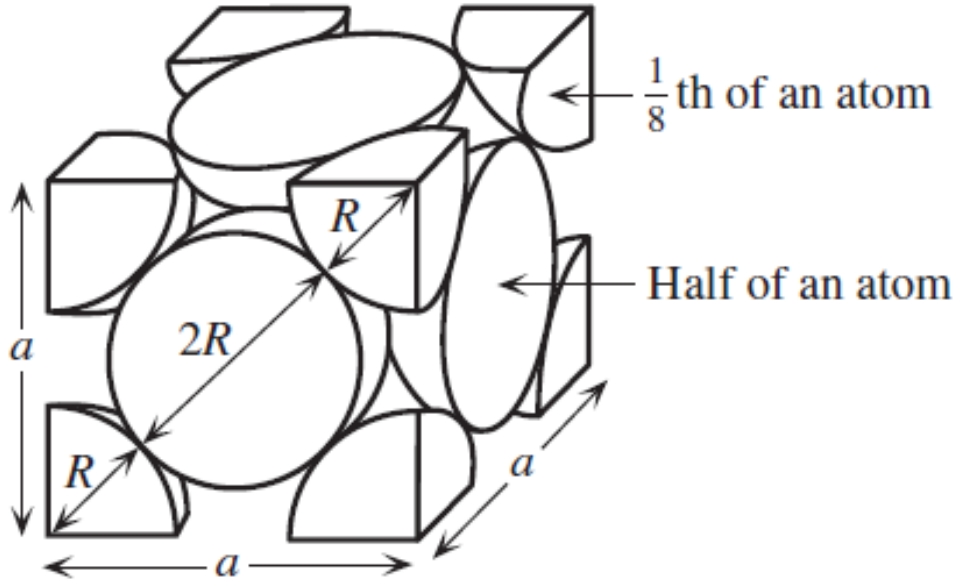


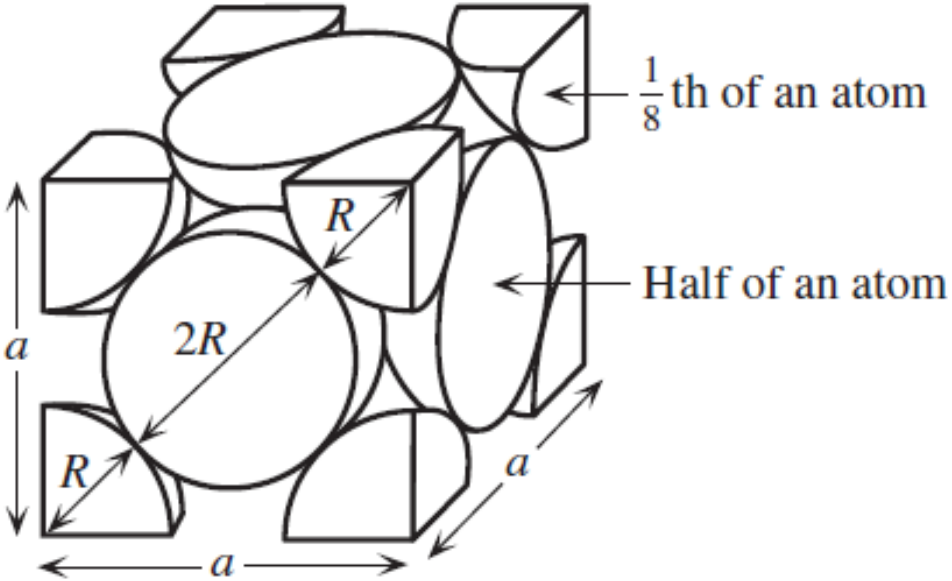
Figure 1.40 The FCC unit cell.
The atomic radius is R and the lattice parameter is a.

a. There are four atoms per unit cell. The Cu atom at each corner is shared with eight other adjoining unit cells. Each Cu atom at the face center is shared with the neighboring unit cell. Thus, the number of atoms in the unit cell = 8 corners ($\frac{1}{8}$ atom) + 6 faces ($\frac{1}{2}$ atom) = 4 atoms.

b. Consider the unit cell shown in Figure 1.40 and one of the cubic faces. The face is a square of side a and the diagonal is $\sqrt{a^2 + a^2}$ or $a\sqrt{2}$. The diagonal has one atom at the center of diameter $2R$, which touches two atoms centered at the corners. The diagonal, going from corner to corner, is therefore $R + 2R + R$. Thus, $4R = a\sqrt{2}$ and $a = 4R/\sqrt{2} = R2\sqrt{2}$. Therefore, $a = 0.3620$ nm.

c. $$\text{APF} = \frac{(\text{Number of atoms in unit cell}) \times (\text{Volume of atom})}{\text{Volume of unit cell}}$$

$$= \frac{4 \times \frac{4}{3}\pi R^3}{a^3} = \frac{\frac{4^2}{3}\pi R^3}{(R2\sqrt{2})^3} = \frac{4^2\pi}{3(2\sqrt{2})^3} = 0.74$$



d. In general, if there are x atoms in the unit cell, the atomic concentration is

$$n_{\text{at}} = \frac{\text{Number of atoms in unit cell}}{\text{Volume of unit cell}} = \frac{x}{a^3}$$

Thus, for Cu

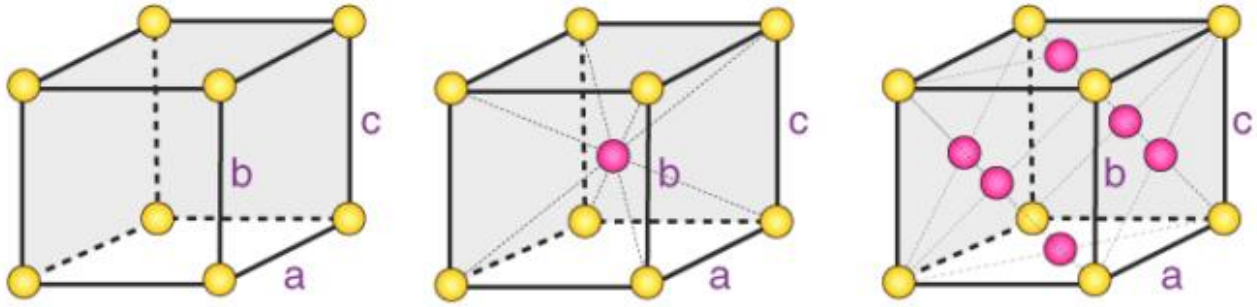
$$n_{\text{at}} = \frac{4}{(0.3620 \times 10^{-7}\ \text{cm})^3} = 8.43 \times 10^{22}\ \text{cm}^{-3}$$

There are x atoms in the unit cell, and each atom has a mass of M_{at}/N_A grams. The density ρ is

$$\rho = \frac{\text{Mass of all atoms in unit cell}}{\text{Volume of unit cell}} = \frac{x\left(\frac{M_{\text{at}}}{N_A}\right)}{a^3}$$

that is,

$$\rho = \frac{n_{\text{at}} M_{\text{at}}}{N_A} = \frac{(8.43 \times 10^{22}\ \text{cm}^{-3})(63.55\ \text{g mol}^{-1})}{6.022 \times 10^{23}\ \text{mol}^{-1}} = 8.9\ \text{g cm}^{-3}$$

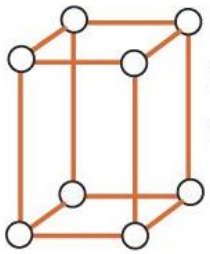


Simple cubic

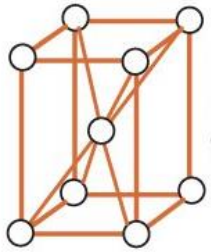
Body-centred Cubic Unit Cell (BCC)

Face-centred Cubic Unit Cell (FCC)

Tetragonal: a = b ≠ c, α = β = γ = 90°

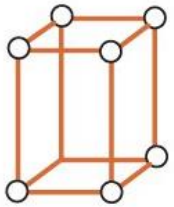


Simple tetragonal

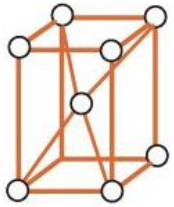


Body-centered tetragonal (BCT)

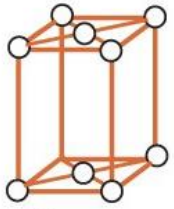
Orthorhombic: a ≠ b ≠ c, α = β = γ = 90°



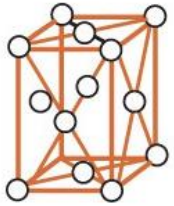
Simple



Body-centered

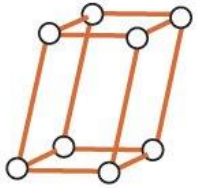


Base-centered

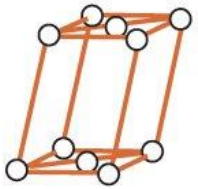


Face-centered

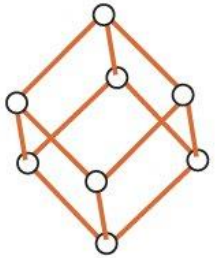
Monoclinic: a ≠ b ≠ c, α = γ = 90° ≠ β



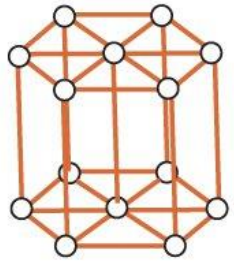
Simple monoclinic



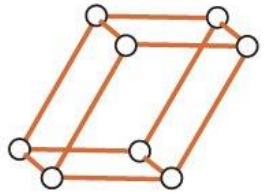
Base-centered monoclinic



Rhombohedral
a = b = c
α = β = γ = 90°

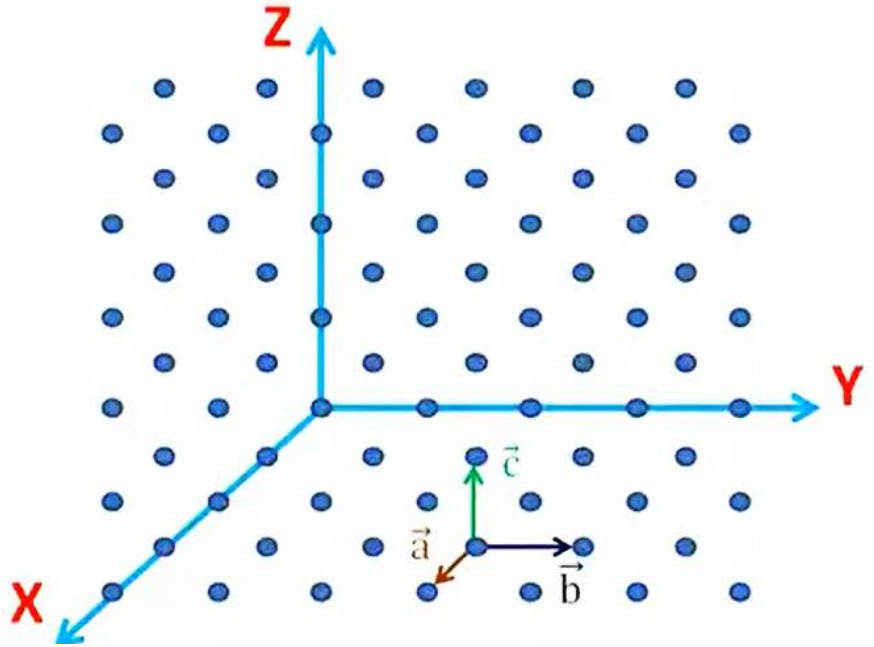


Hexagonal
a = b ≠ c
α = β = 90° γ = 120°

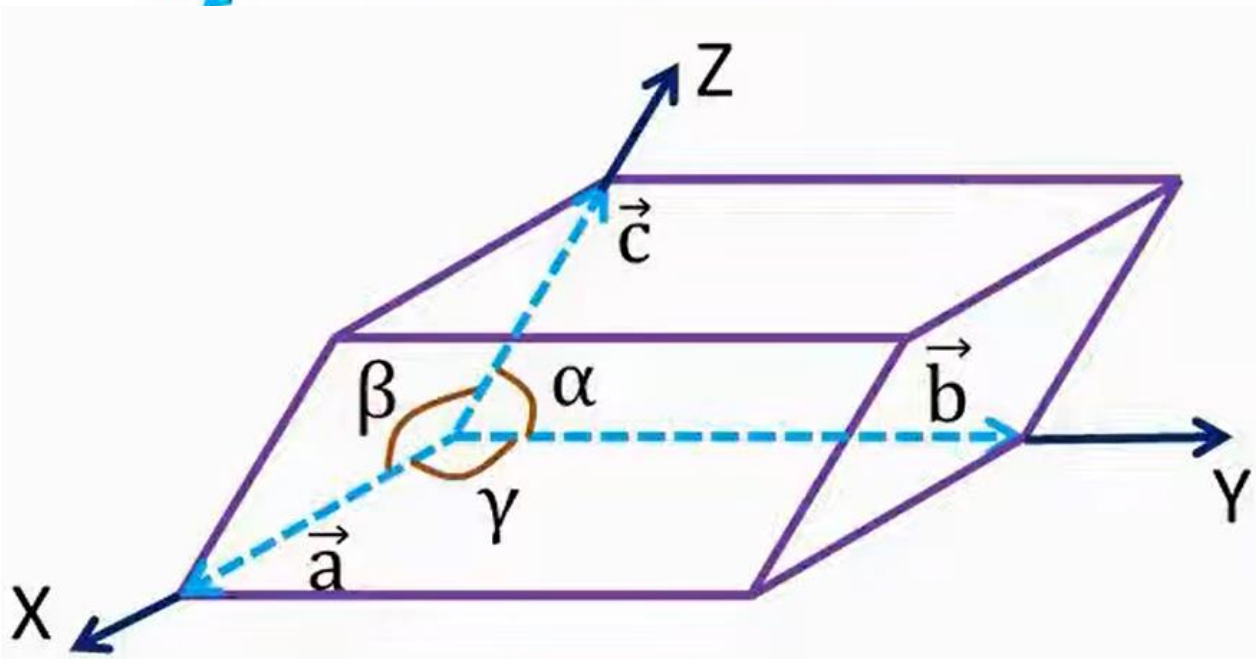


Triclinic
a ≠ b ≠ c
α ≠ β ≠ γ ≠ 90°

Crystal axes or Lattice axes

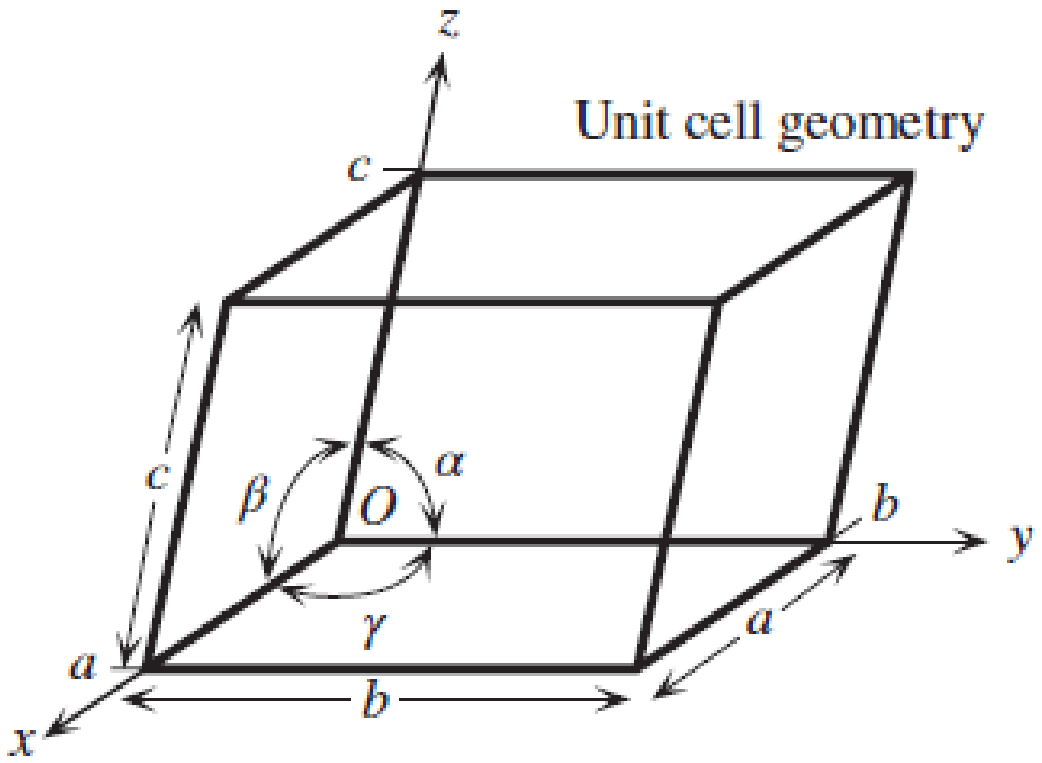


$\vec{a}, \vec{b}$ and $\vec{c}$ are basis vectors or lattice vectors along X, Y and Z axis respectively

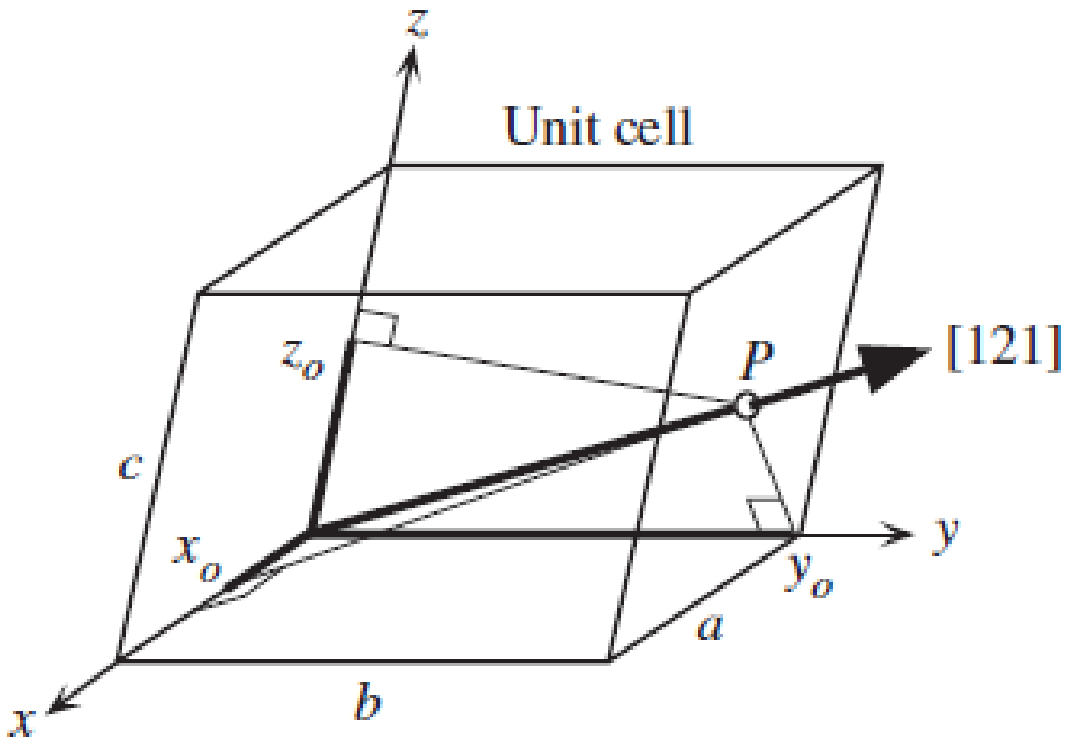


$\vec{a}, \vec{b}$ and $\vec{c}$ are basis vectors

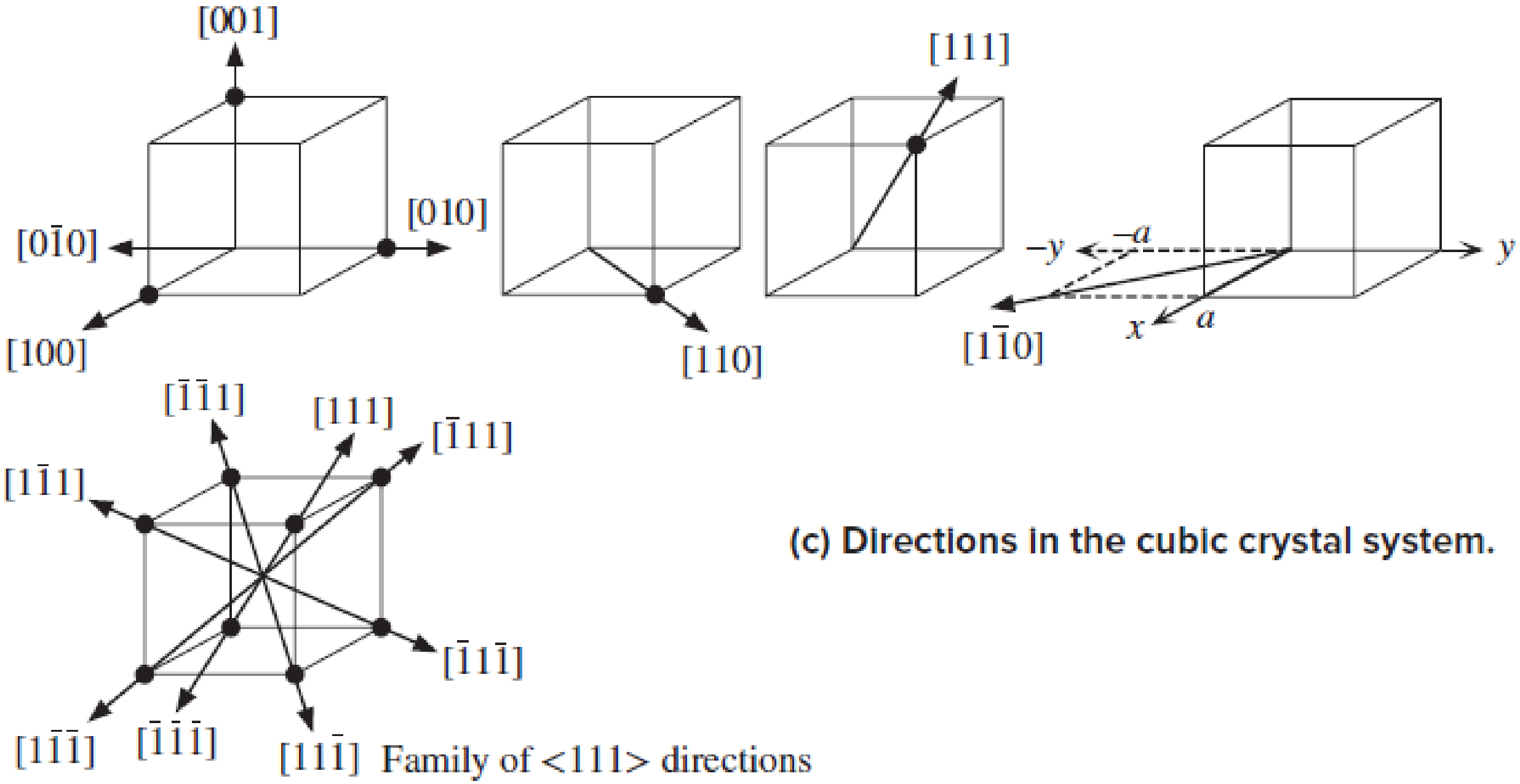
α, β and γ are interfacial angles



(a) A parallelepiped is chosen to describe the *geometry* of a unit cell. We line the *x*, *y*, and *z* axes with the edges of the parallelepiped taking the lower-left rear corner as the origin.

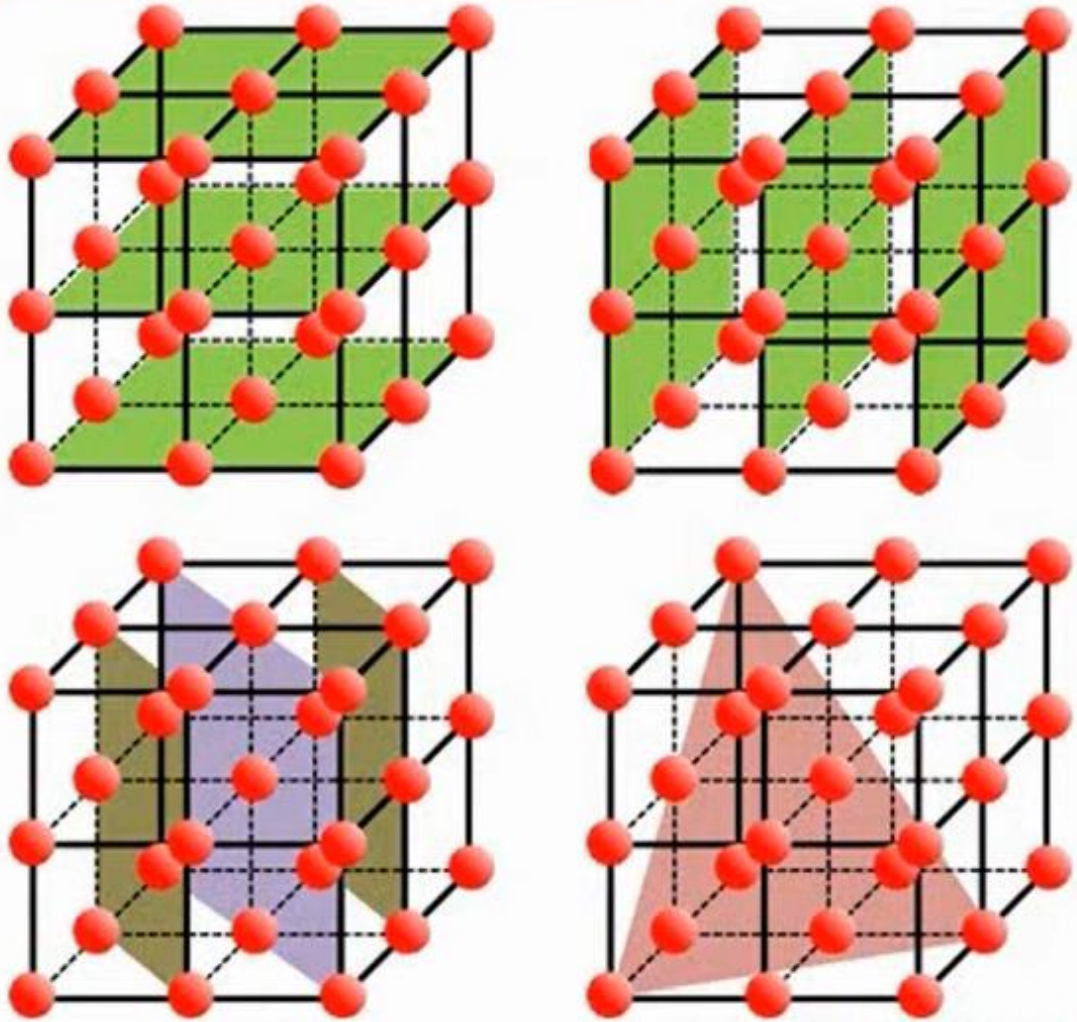


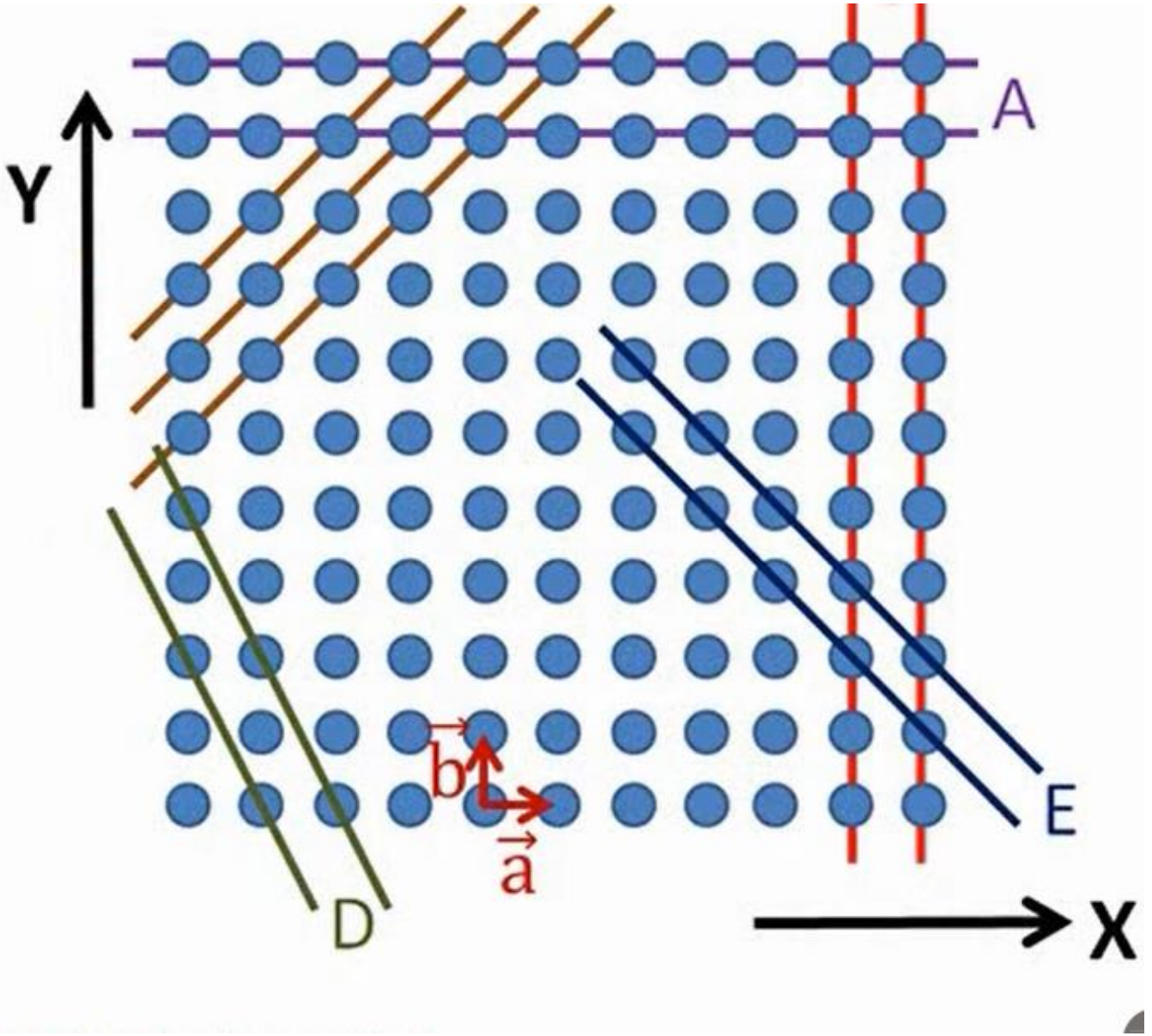
(b) Identification of a direction in a crystal.



(c) Directions in the cubic crystal system.

Lattice Planes



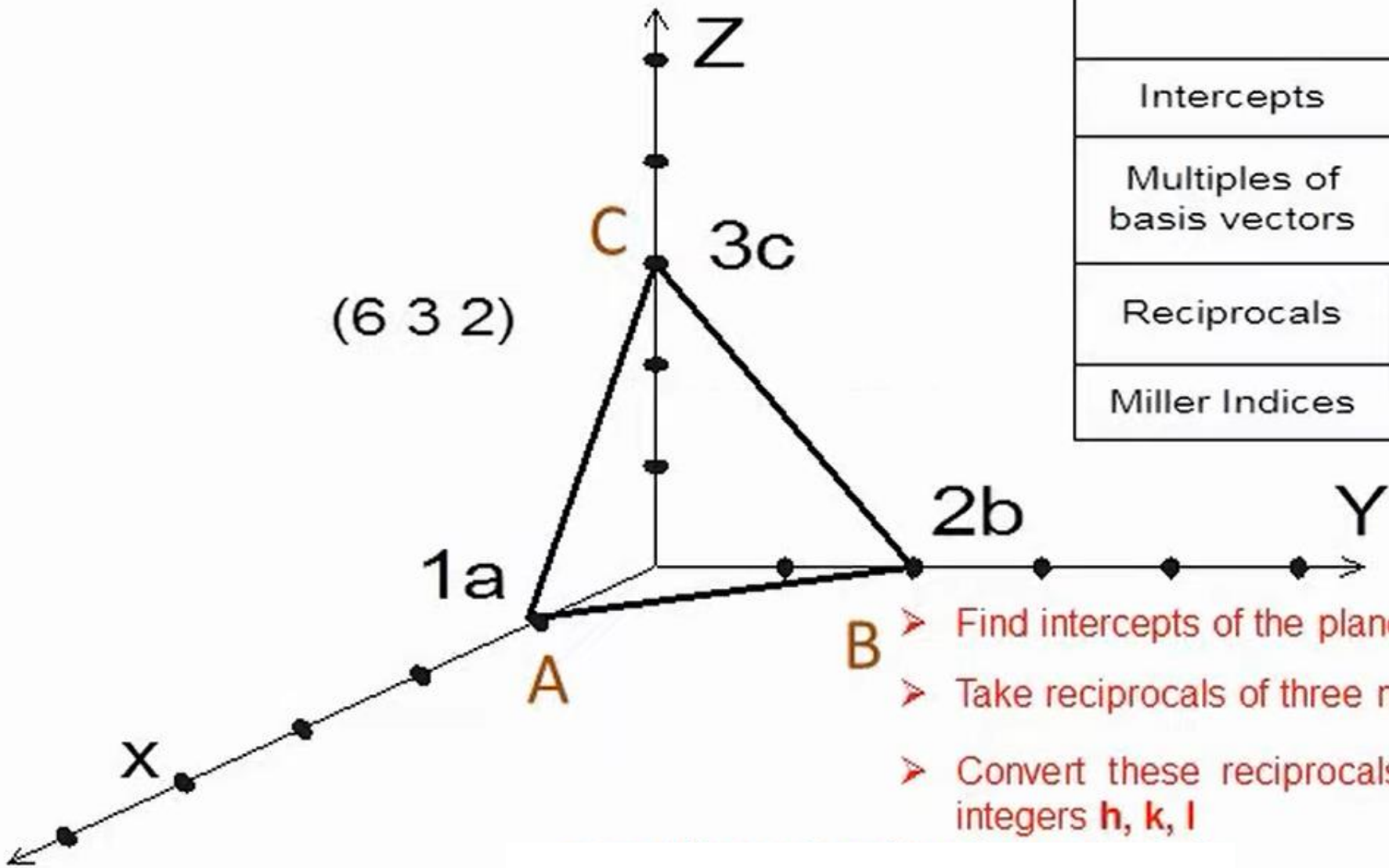


Miller Indices of Planes

The notation system generally adopted uses a set of three integers to describe the position of a plane inside the lattice.

The three integers describing a particular plane are found in the following way –

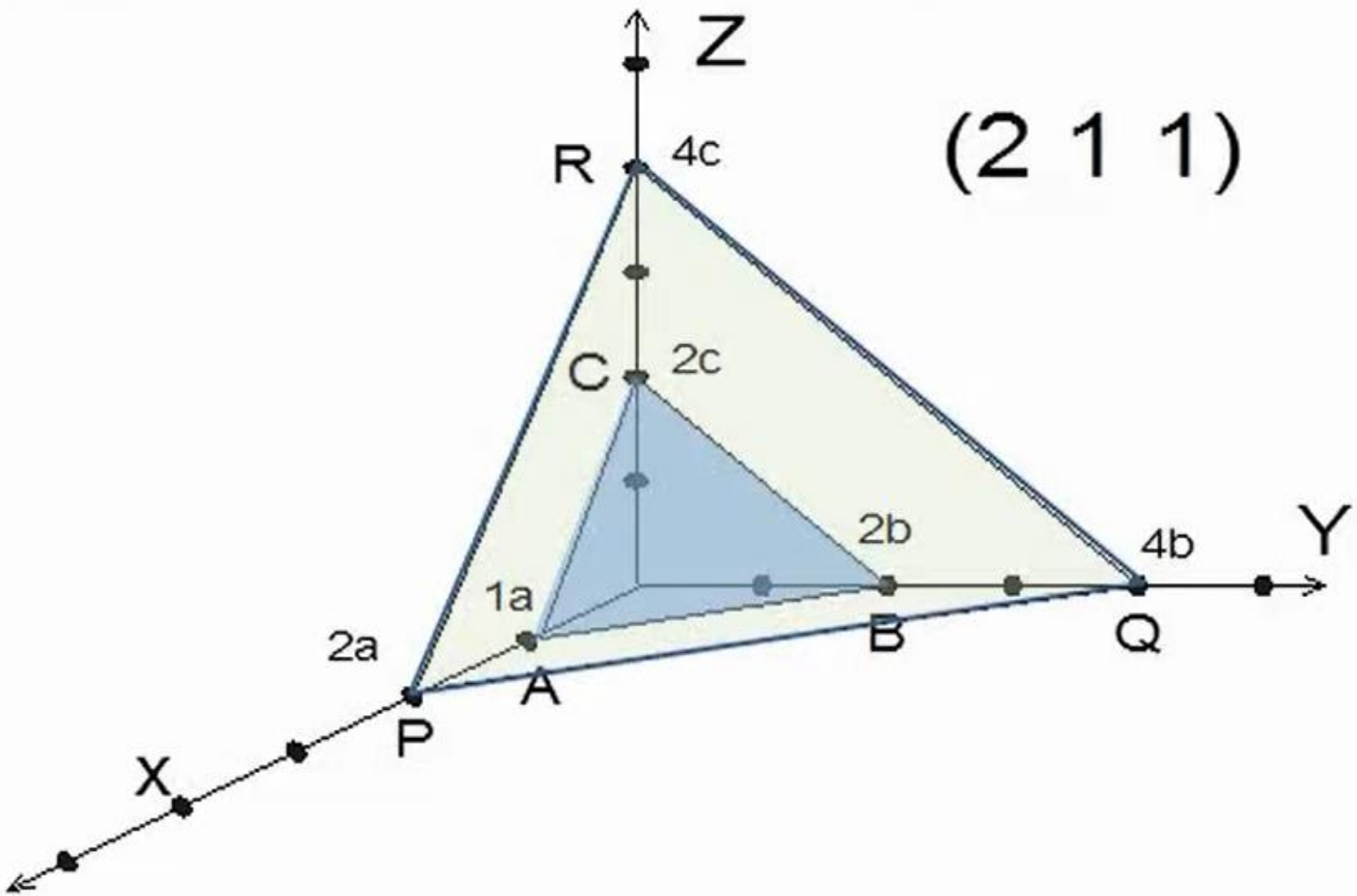
- Find the intercepts of the plane on three crystal axes (say X, Y, Z axes). Let these intercepts be $p\vec{a}, q\vec{b}, r\vec{c}$. Express these intercepts as multiples of basis vectors i.e. **p, q and r**.
- Take reciprocals of three numbers $\frac{1}{p}, \frac{1}{q}, \frac{1}{r}$
- Convert these reciprocals into smallest set of integers **h, k, l** which will have same ratio relationship to each other as the three reciprocals.
- Three integers h, k and l are called as miller indices. Write these as **(h k l)**.



	X	Y	Z
Intercepts	1a	2b	3c
Multiples of basis vectors	1	2	3
Reciprocals	1	1/2	1/3
Miller Indices	6	3	2

- Find intercepts of the plane on three axes.
- Take reciprocals of three numbers $\frac{1}{p}, \frac{1}{q}, \frac{1}{r}$
- Convert these reciprocals into smallest set of integers **h, k, l**

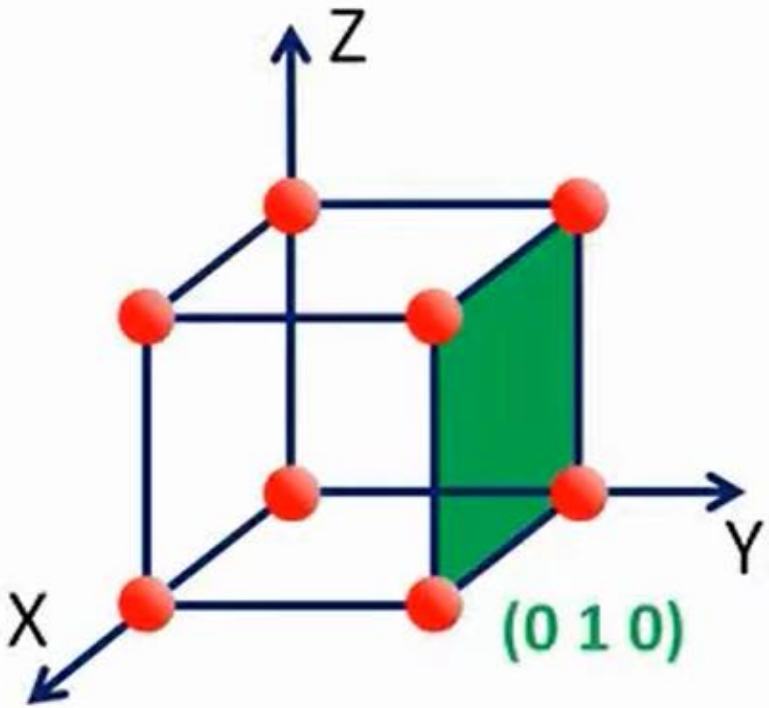
Miller Indices of Parallel planes are same (Example)

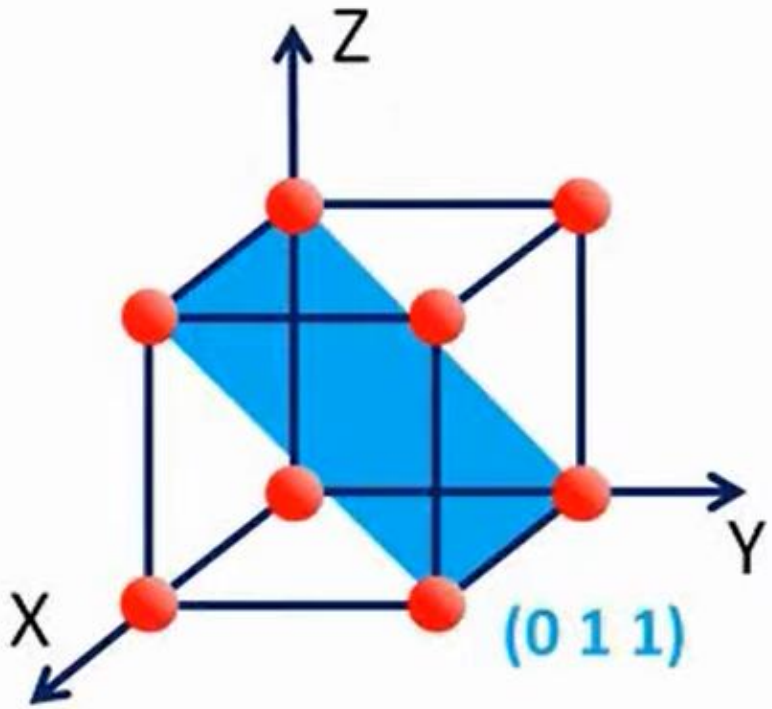


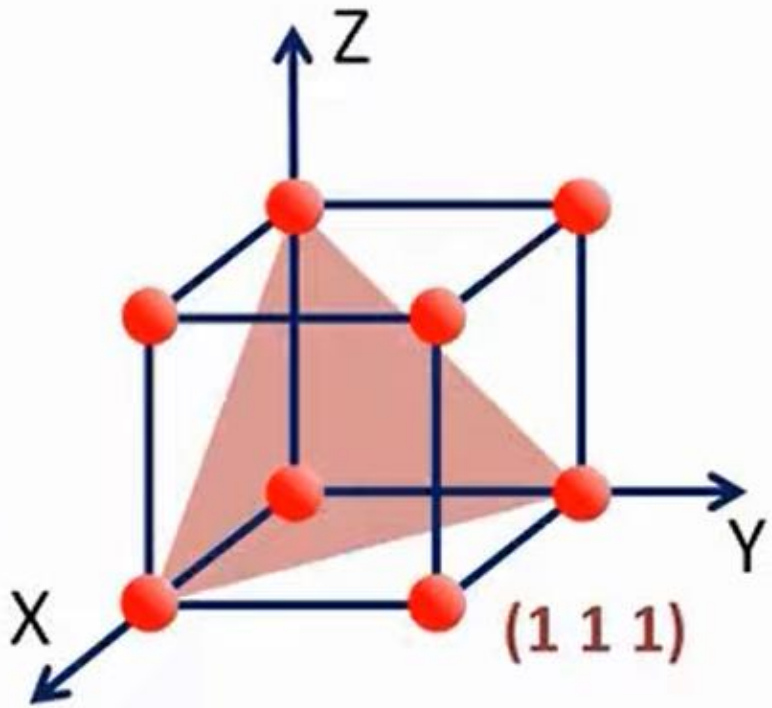
plane ABC	X	Y	Z
Intercepts	1a	2b	2c
Multiples of basis vectors	1	2	2
Reciprocals	1	1/2	1/2
Miller Indices	2	1	1

plane PQR	X	Y	Z
Intercepts	2a	4b	4c
Multiples of basis vectors	2	4	4
Reciprocals	1/2	1/4	1/4
Miller Indices	2	1	1

Some Basic Planes

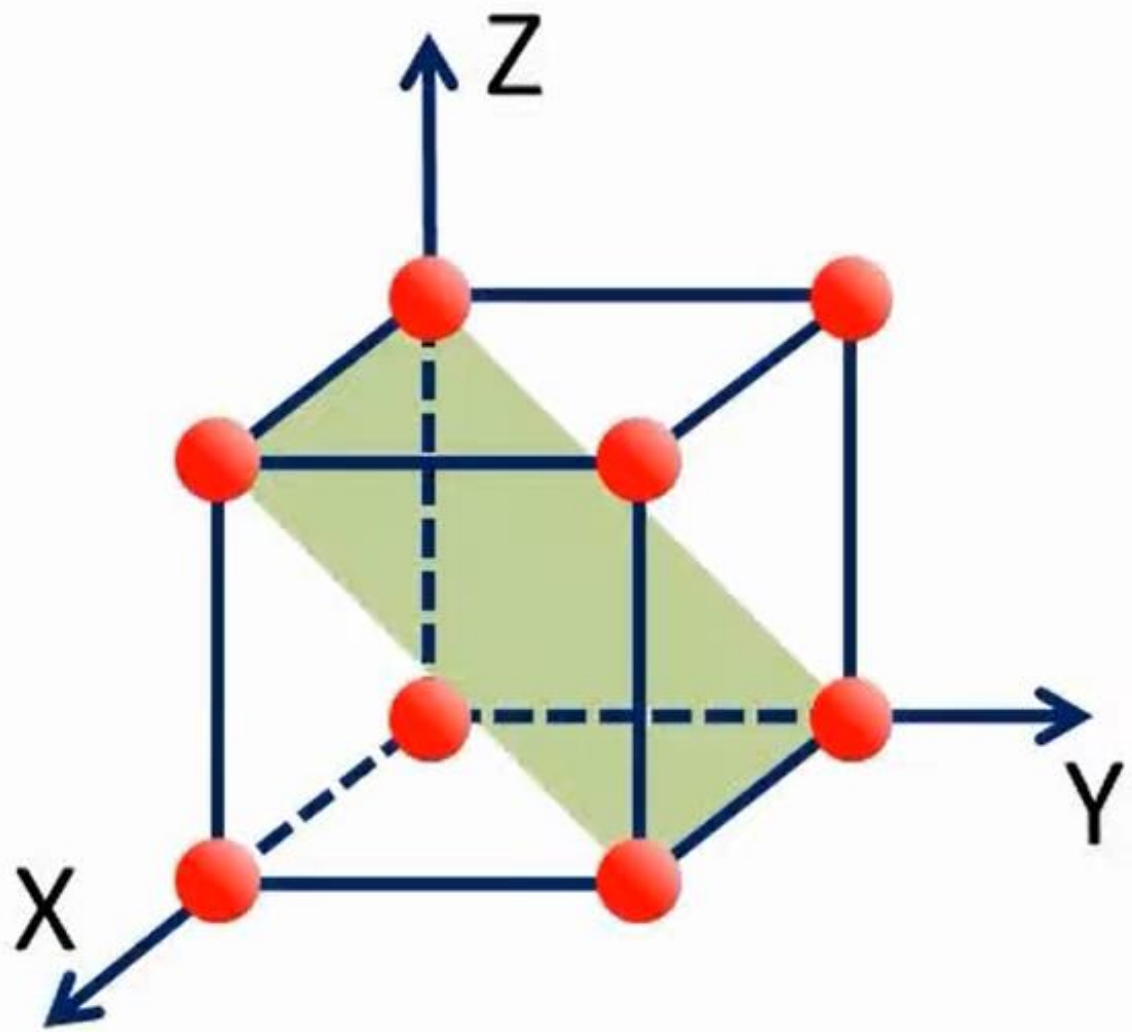






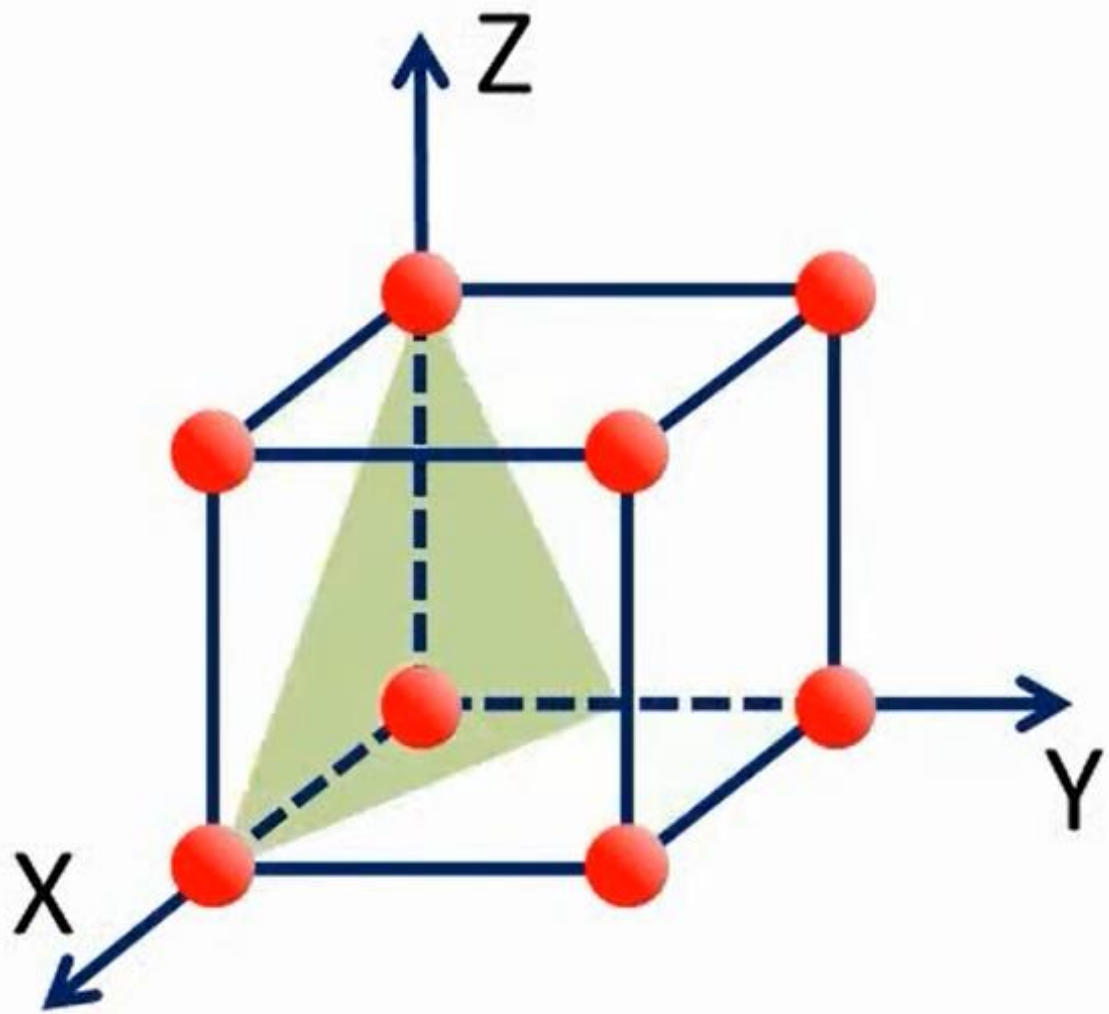
Drawing the Plane in Unit Cell

(0 1 1)			
	X	Y	Z
Miller Index	0	1	1
Reciprocal / Intercept	∞	1	1



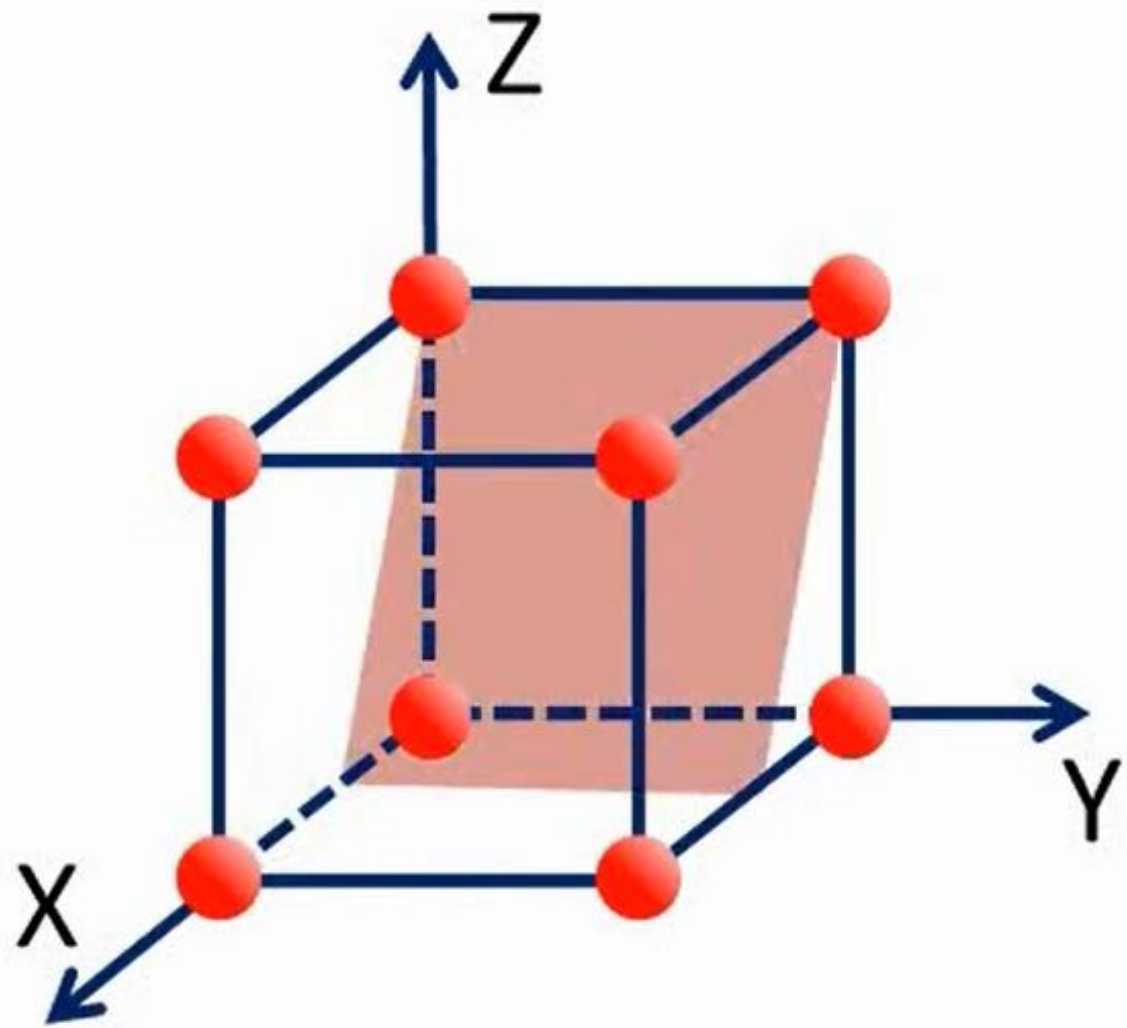
Drawing the Plane in Unit Cell

(1 2 1)			
	X	Y	Z
Miller Index	1	2	1
Reciprocal / Intercept	1	$\frac{1}{2}$	1



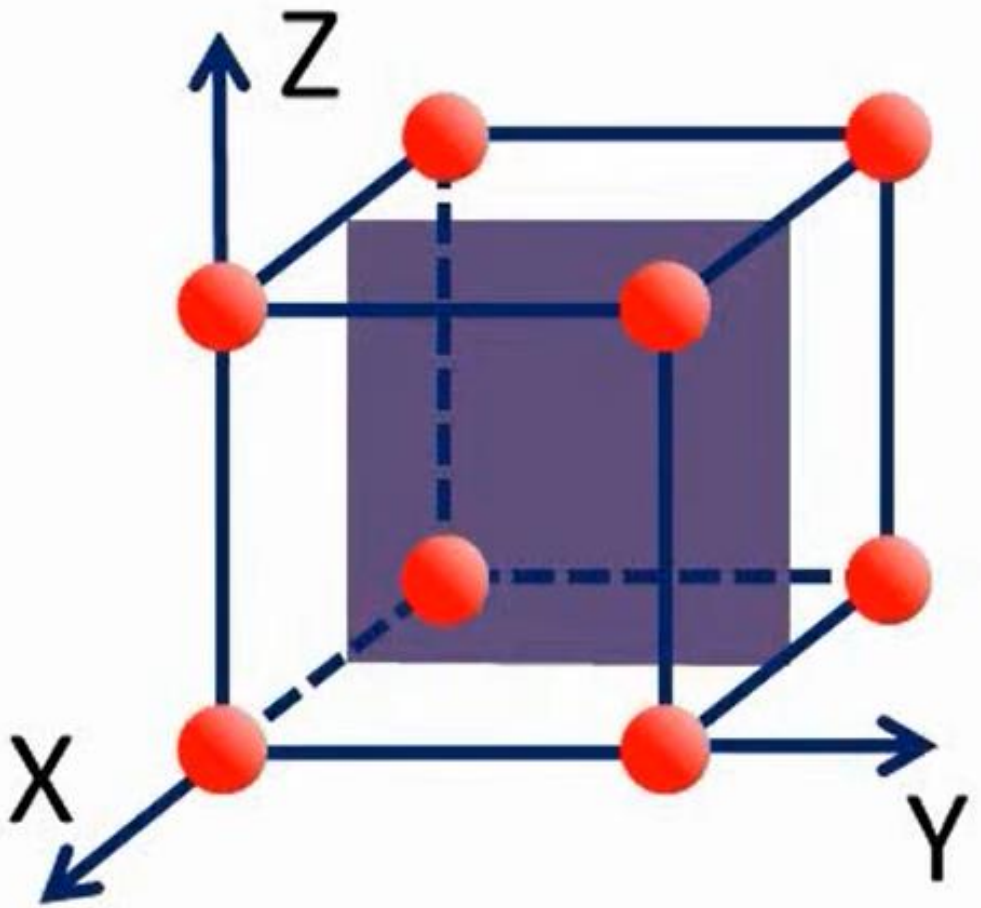
Drawing the Plane in Unit Cell

(2 0 1)			
	X	Y	Z
Miller Index	2	0	1
Reciprocal / Intercept	$\frac{1}{2}$	∞	1



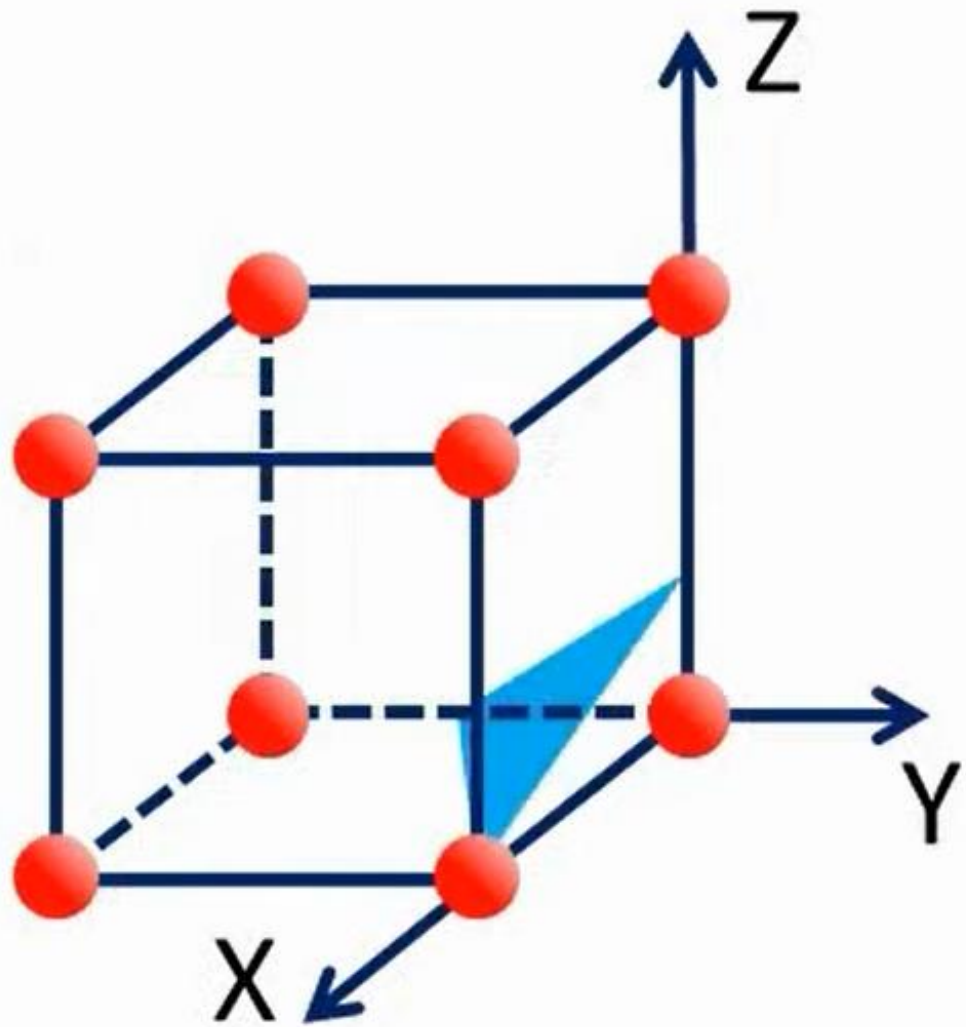
Drawing the Plane in Unit Cell

$(\bar{2}\,0\,0)$			
	X	Y	Z
Miller Index	$\bar{2}$	0	0
Reciprocal / Intercept	$-\frac{1}{2}$	∞	∞



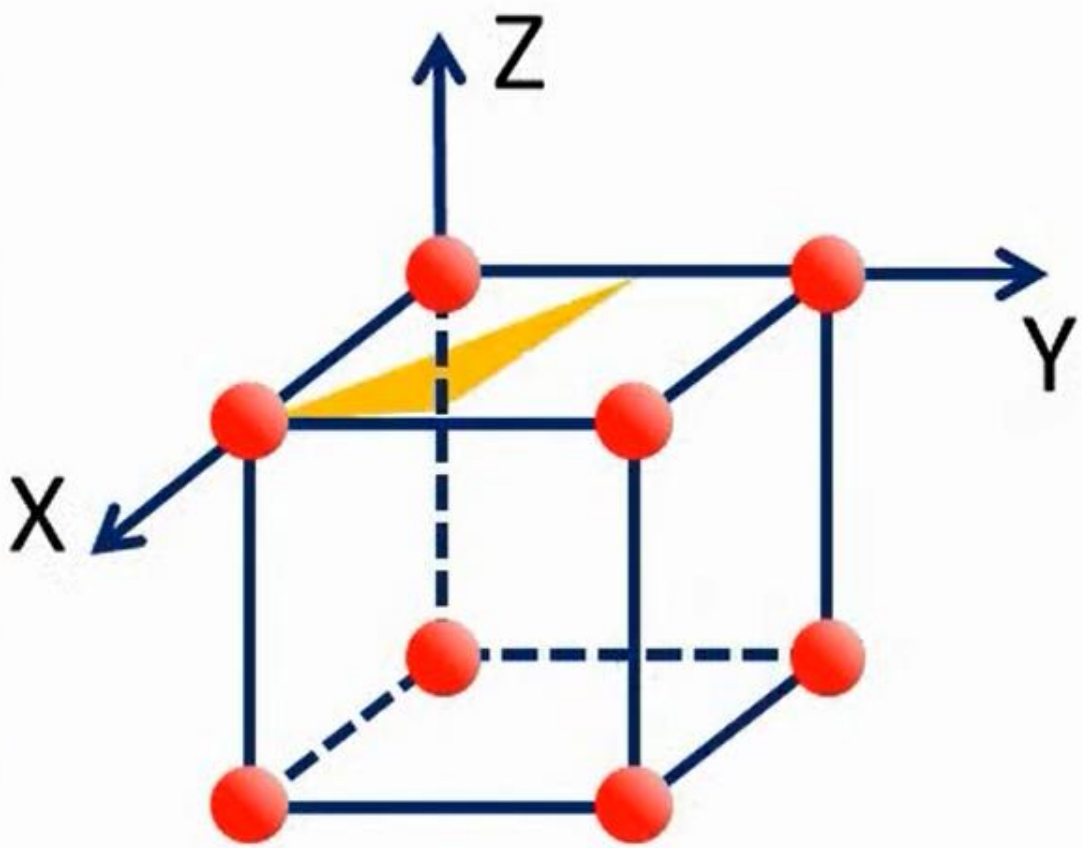
Drawing the Plane in Unit Cell

$(1\ \bar{2}\ 3)$			
	X	**Y**	**Z**
Miller Index	1	$\bar{2}$	3
Reciprocal / Intercept	1	$-\frac{1}{2}$	$\frac{1}{3}$



Drawing the Plane in Unit Cell

$(1\ 2\ \bar{3})$			
	X	Y	Z
Miller Index	1	2	$\bar{3}$
Reciprocal / Intercept	1	$\frac{1}{2}$	$-\frac{1}{3}$



Go through **EXAMPLE 1.17** in Kasap Text Book

Go through **TABLE 1.3** in Kasap Text Book

Crystal Defects and Vacancies

Ideal Crystal =Lattice + Basic

Real Crystal=deviation from ideality

Controls the physical and mechanical properties

Classification of Defects:

Based on Dimensionality

1. Zero Dimensional or Point Defects: Vacancies and Impurities.

2. One dimensional or Line defects : Edge and Screw Dislocation.

3. Two dimensional or Surface defects: Free Surface, Grain boundary, Twin boundary, stacking fault.

Real crystal are finite crystal has a boundary line and that boundary has an external surface or free surface

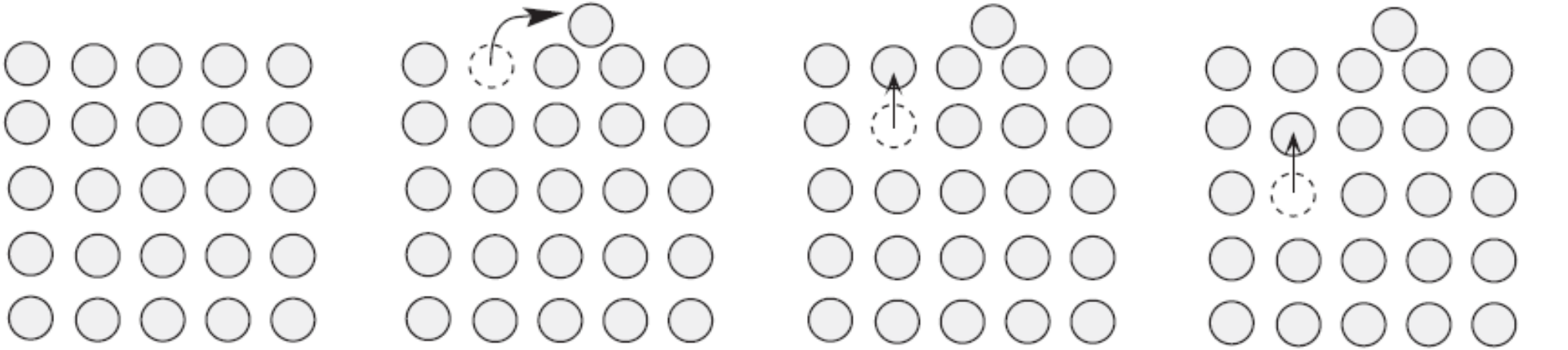
What happens when the crystal is grown from a liquid or vapor?
Do you always get a perfect crystal?
What happens when the temperature is raised?
What happens when impurities are added to the solid?

We must therefore understand the types of defects that can exist in a given crystal structure. Quite often, key mechanical and electrical properties are controlled by these defects.

Above the absolute zero temperature, all crystals have atomic vacancies or atoms missing from lattice sites in the crystal structure. The vacancies exist as a requirement of thermal equilibrium and are called **thermodynamic defects.** Vacancies introduce disorder into the crystal by upsetting the perfect periodicity of atomic arrangements.

1. Zero Dimensional or Point Defects: Vacancies and Impurities

At some instant, there may be **one atom with sufficient energy to break its bonds and jump to an adjoining site on the surface**, as depicted in Figure 1.45. **This leaves a vacancy behind**, just below the surface. This vacancy can then diffuse into the bulk of the crystal, because a neighboring atom can diffuse into it.



(a) Perfect crystal without vacancies

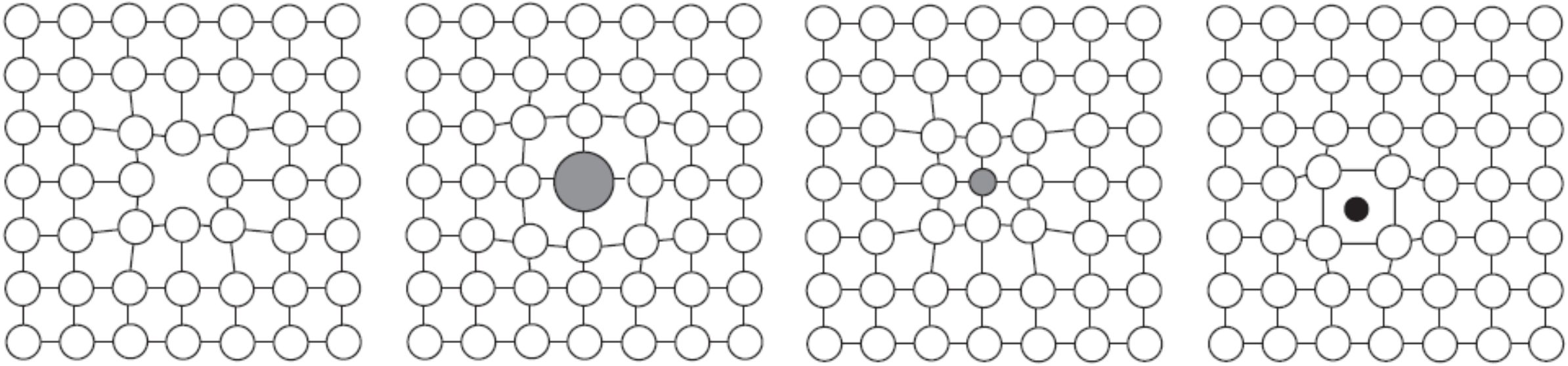
(b) An energetic atom at the surface breaks bonds and jumps on to a new adjoining position on the surface. This leaves behind a vacancy.

(c) An atom in the bulk diffuses to fill the vacancy thereby displacing the vacancy toward the bulk.

(d) Atomic diffusions cause the vacancy to diffuse into the bulk.

Figure 1.45 Generation of a vacancy by the diffusion of an atom to the surface and the subsequent diffusion of the vacancy into the bulk.

Vacancies are only one type of **point defect** in a crystal structure. Point defects generally involve lattice changes or distortions of a few atomic distances, as depicted in Figure 1.46a. The crystal structure may contain impurities, either naturally or as a consequence of intentional addition, as in the case of silicon crystals grown for microelectronics. If the impurity atom substitutes directly for the host atom, the result is called a **substitutional impurity** and the resulting crystal structure is that of a **substitutional solid solution,** as shown in Figure 1.46b and c. When a Si crystal is "doped" with small amounts of arsenic (As) atoms, the As atoms substitute directly for the Si atoms in the Si crystal; that is, the arsenic atoms are substitutional impurities. The impurity atom can also place itself in an interstitial site, that is, in a void between



(a) A vacancy in the crystal.

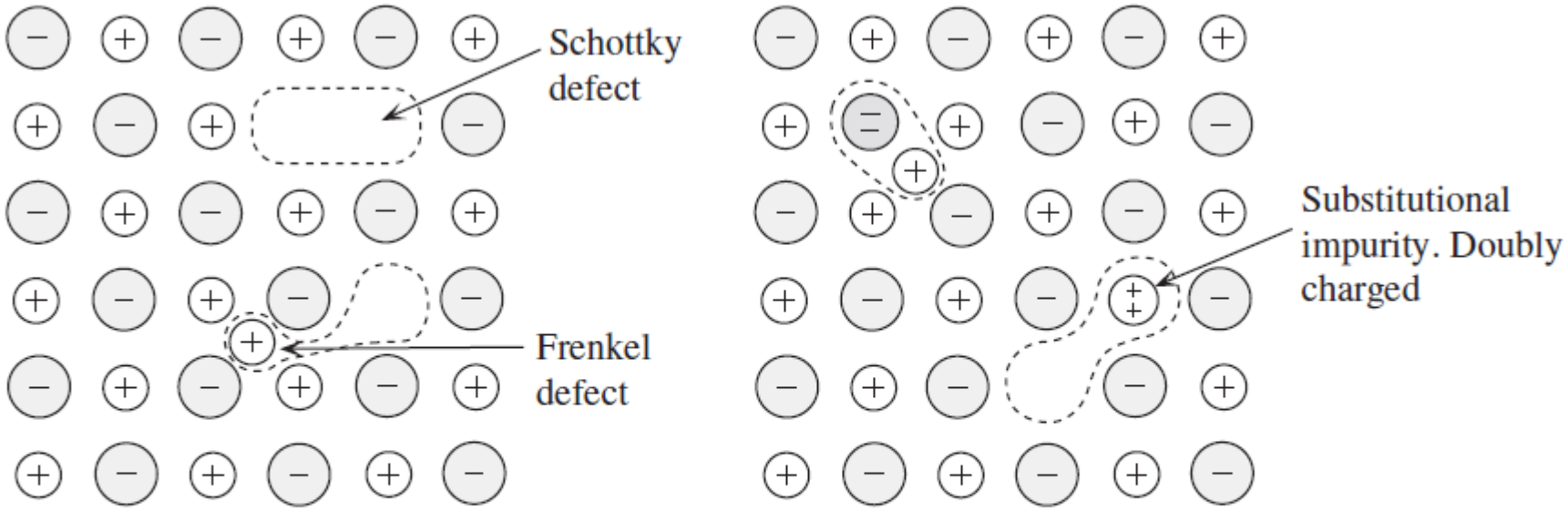
(b) A substitutional impurity in the crystal. The impurity atom is larger than the host atom.

(c) A substitutional impurity in the crystal. The impurity atom is smaller than the host atom.

(d) An interstitial impurity in the crystal. The impurity occupies an empty space between host atoms.

In an ionic crystal, such as NaCl, which consists of anions (Cl−) and cations (Na+), one common type of defect is called a **Schottky defect. This involves a missing cation–anion pair** (which may have migrated to the surface), so the neutrality is maintained, as indicated in Figure 1.47a.

Another type of defect in the ionic crystal is **the Frenkel defect, which occurs when a host ion is displaced into an interstitial position, leaving a vacancy at its original site.** The interstitial ion and the vacancy pair constitute the Frenkel defect, as identified in Figure 1.47a.



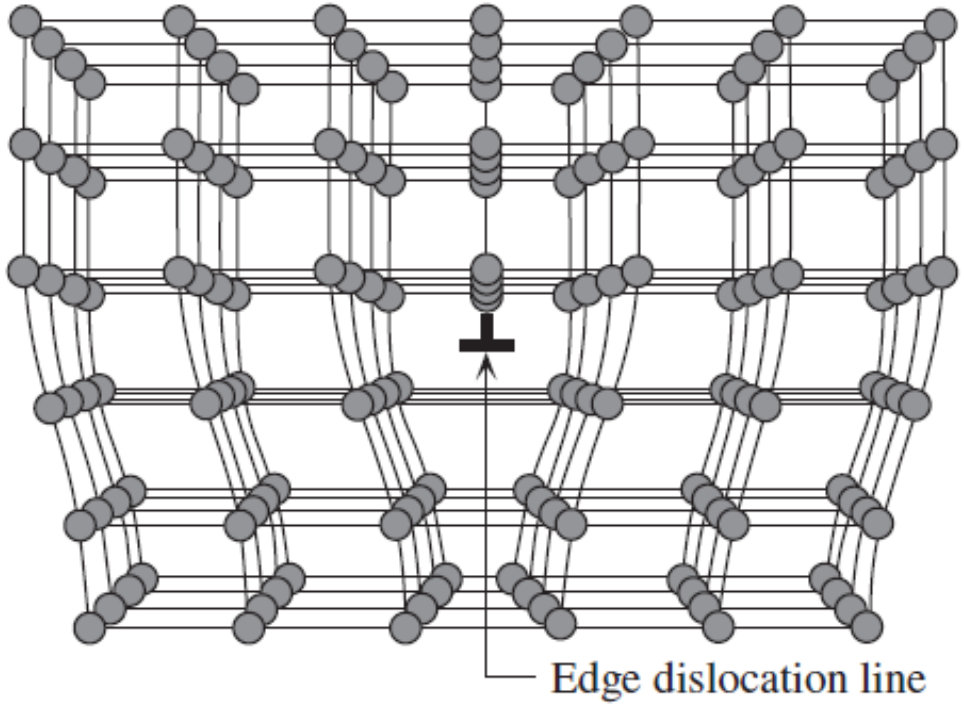
(a) Schottky and Frenkel defects in an ionic crystal.

(b) Two possible imperfections caused by ionized substitutional impurity atoms in an ionic crystal.

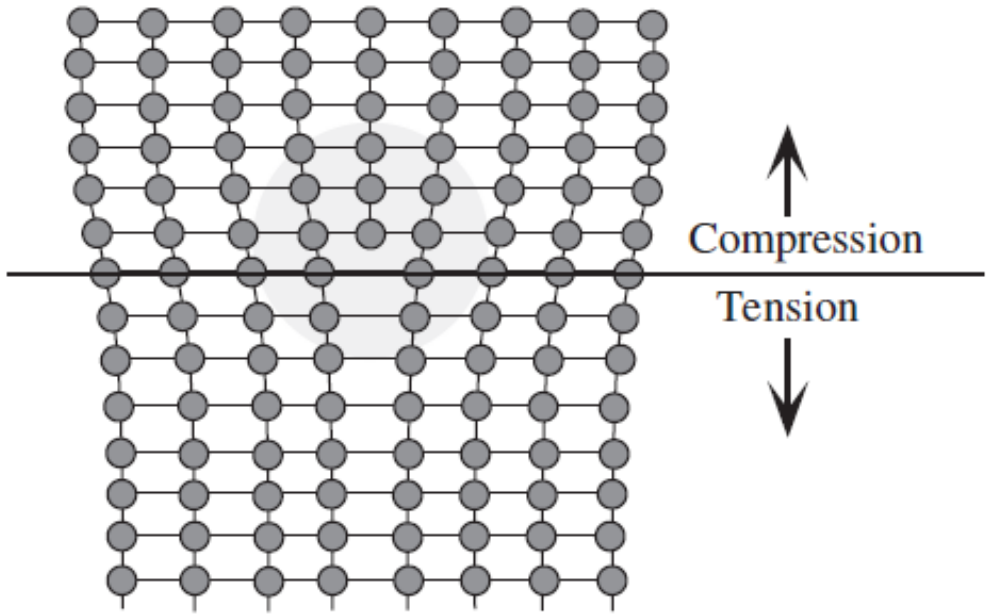
Figure 1.47 Point defects in ionic crystals.

2. One dimensional or Line defects : Edge and Screw Dislocation

A line defect is formed in a crystal when an atomic plane terminates within the crystal instead of passing all the way to the end of the crystal, as depicted in Figure 1.48a. The edge of this short plane of atoms is therefore like a line running inside the crystal. The planes neighboring (*i.e.*, above) this short plane are dislocated with respect to those below the line. We therefore call this type of defect an **edge dislocation** and use an inverted T symbol.



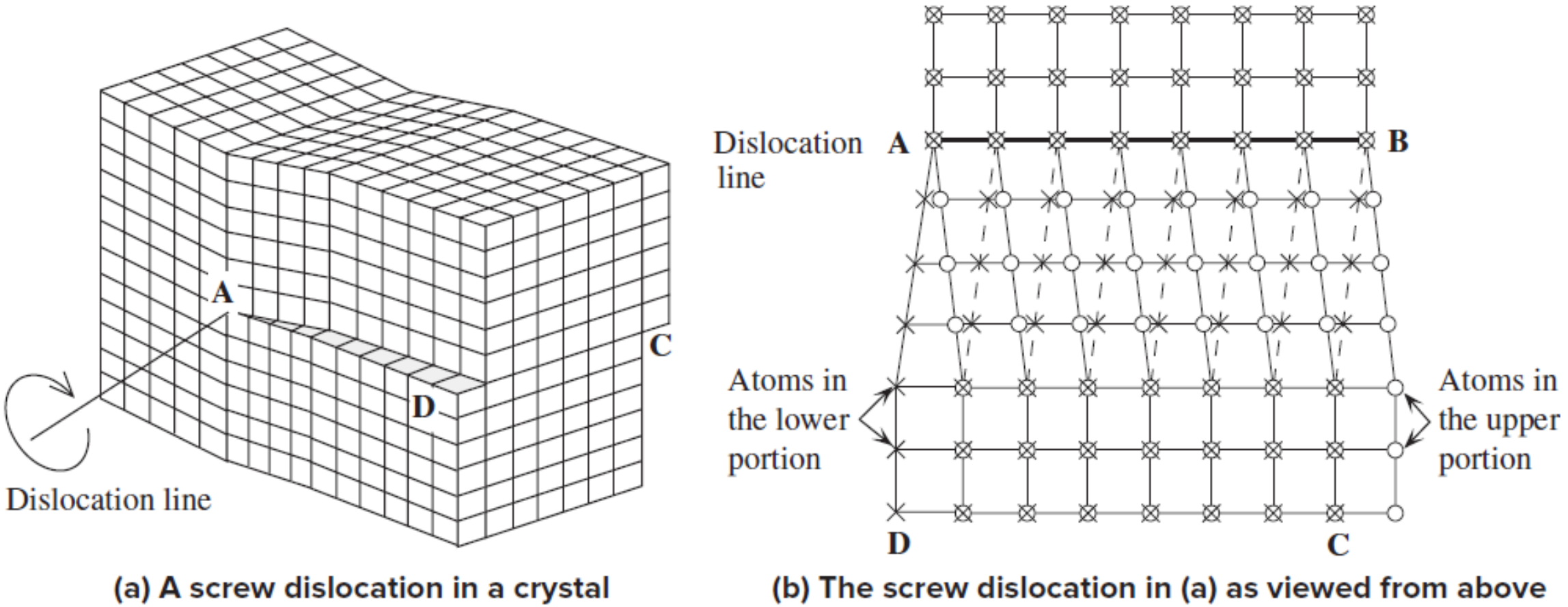
(a) Dislocation is a line defect. The dislocation shown runs into the paper.



(b) Around the dislocation there is a strain field as the atomic bonds have been compressed above and stretched below the dislocation line.

Figure 1.48 Dislocation in a crystal. This is a line defect, which is accompanied by lattice distortion and hence a lattice strain around it.

Another type of dislocation is the screw dislocation, which is essentially a shearing of one portion of the crystal with respect to another, by one atomic distance, as illustrated in Figure 1.49a. The displacement occurs on either side of the **screw dislocation line.**



(a) A screw dislocation in a crystal

(b) The screw dislocation in (a) as viewed from above

Figure 1.49 A screw dislocation, which involves shearing one portion of a perfect crystal with respect to another, on one side of a line (AB).

3. Two dimensional or Surface defects: Free Surface, Grain boundary, Twin boundary, Stacking fault.

When the crystal lattice is abruptly terminated by a surface, the atoms at the surface cannot fulfill their bonding requirements as illustrated in Figure 1.55. For simplicity, the figure shows a Si crystal schematically sketched in two dimensions where each atom in the bulk of the crystal has four covalent bonds, each covalent bond having two electrons.

Free Surface:

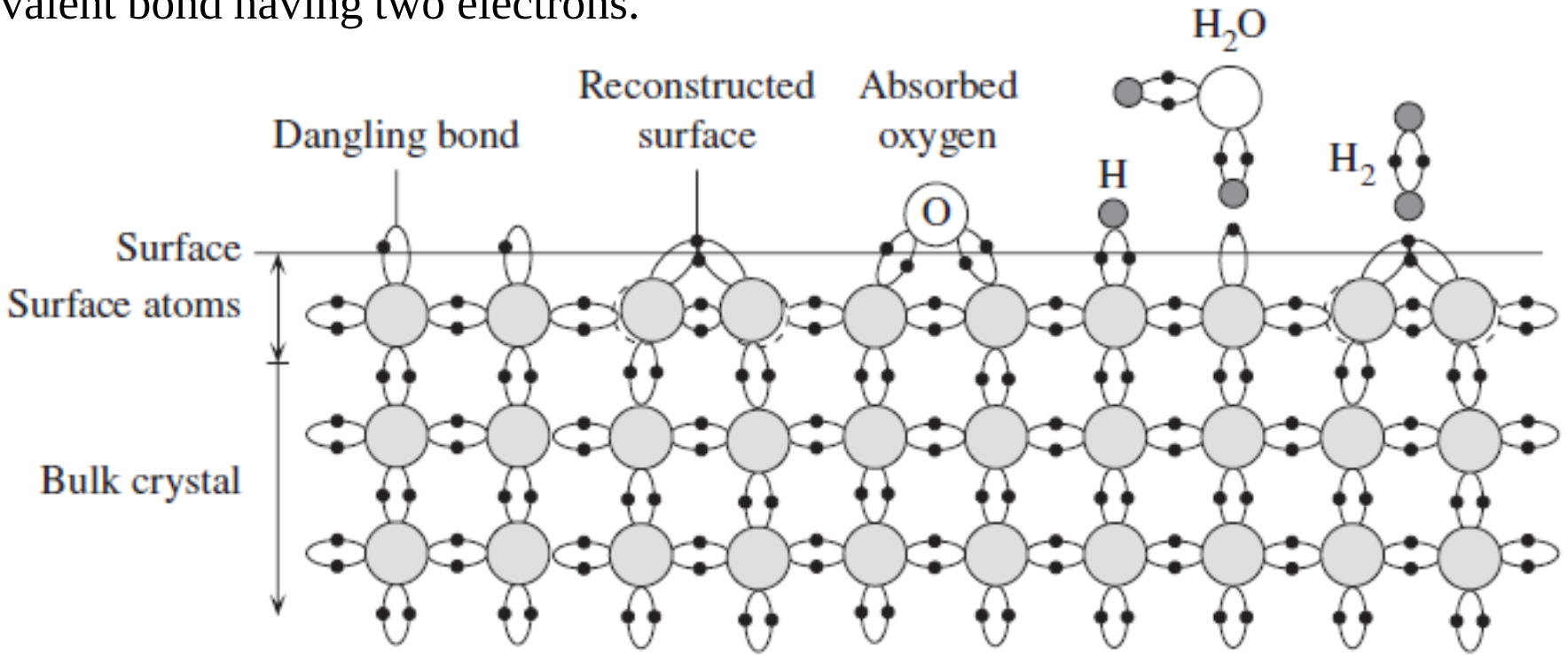


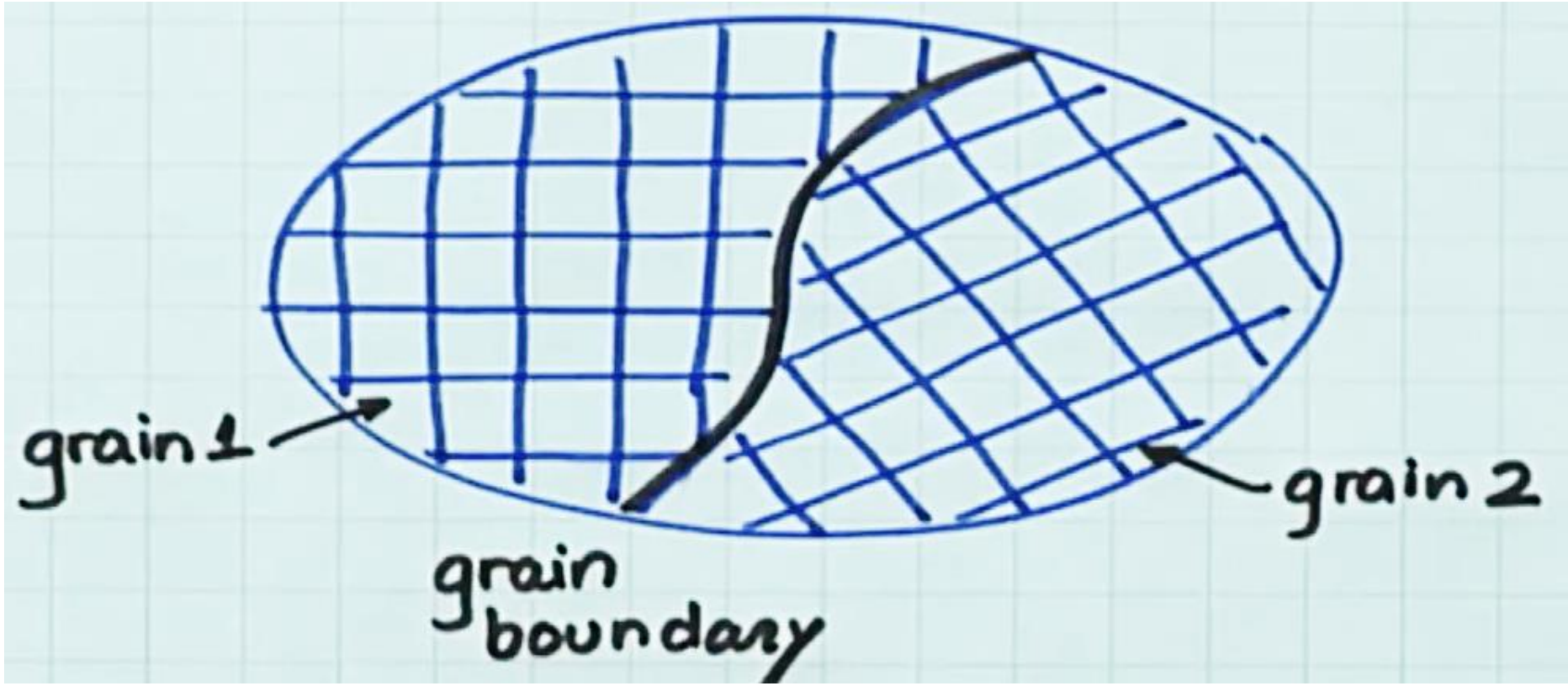
Figure 1.55 At the surface of a hypothetical two-dimensional crystal, the atoms cannot fulfill their bonding requirements and therefore have broken, or dangling, bonds.

Some of the surface atoms bond with each other; the surface becomes reconstructed. The surface can have physisorbed and chemisorbed atoms.

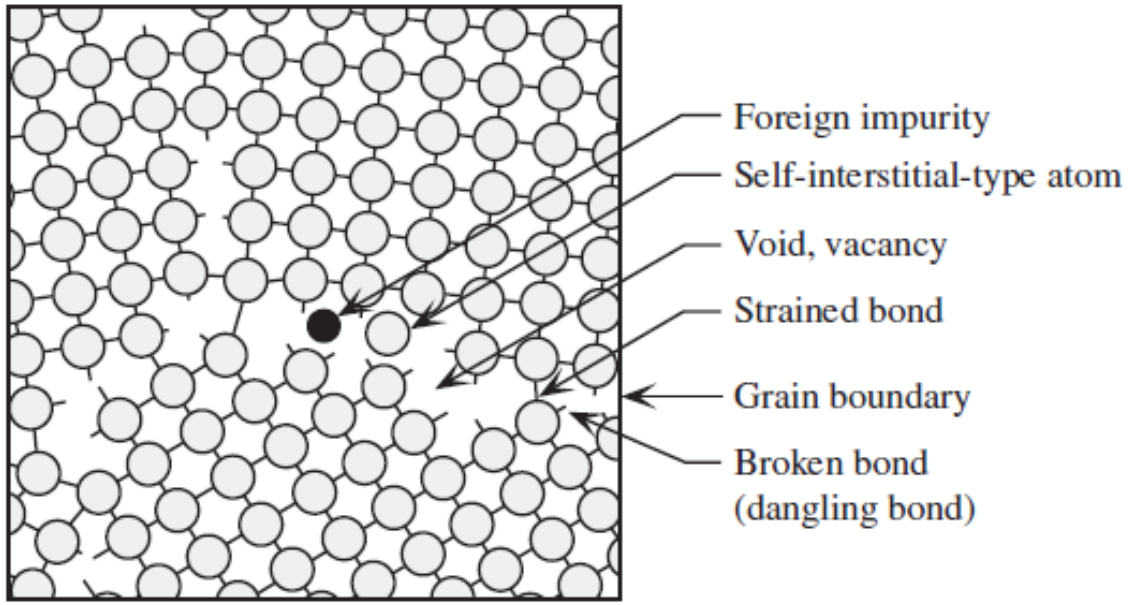
- The atoms at the surface are left with **dangling bonds,** bonds that are half full, only having one electron. These dangling bonds are looking for atoms to which they can bond. Two neighboring surface atoms can share each other's dangling bond electrons. This bonding between surface atoms causes a slight displacement of the surface atoms and leads to a surface that has been **reconstructed**.
- Atoms from the environment can also bond with the atoms on the crystal surface. For example, a hydrogen atom can be captured by a dangling bond at the surface to form a chemical bond as a result of which **hydrogen** becomes **absorbed**.
- The H atom in Figure 1.55 forms a covalent bond with a Si atom and hence becomes **chemisorbed**.
- However, the H_2O molecule cannot form a covalent bond, but, because of hydrogen bonding, it can form a **secondary bond with a surface Si atom and become adsorbed**.
- Water molecules in the air can readily become adsorbed at the surface of a crystal. Although the figure also shows a physisorbed H_2 molecule as an example.

Grain boundary defects

- Grain boundaries are internal boundaries inside a crystal. Dislocation inside a crystal can end an grain boundary.
- If the sample has same orientation of crystal right through, all the units are parallel act as single crystal.
- Instead, if it has internal boundary, if crystal has one side oriented in one way, another side orientation is different. This boundary as grain boundary between two grains. Its called **biocrystal**.



- **Many materials are polycrystalline**; that is, they are composed of many small crystals oriented in different directions. They have multiple grains separated by grain boundaries.



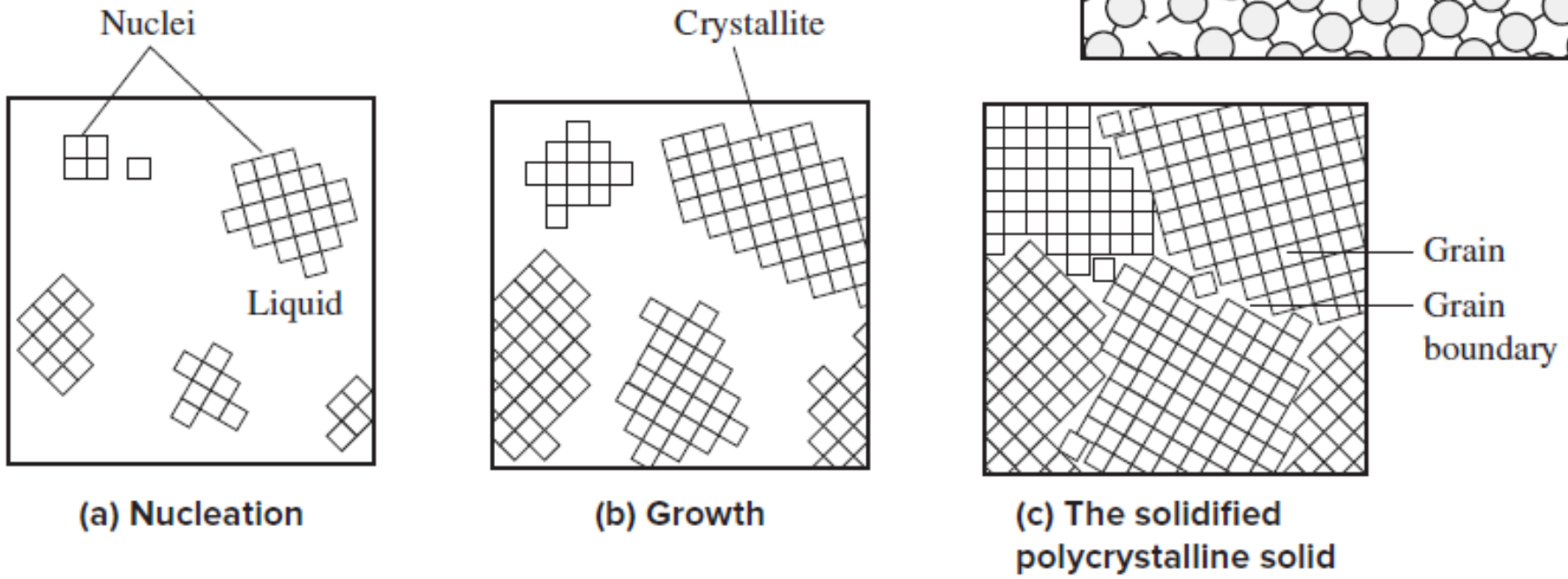
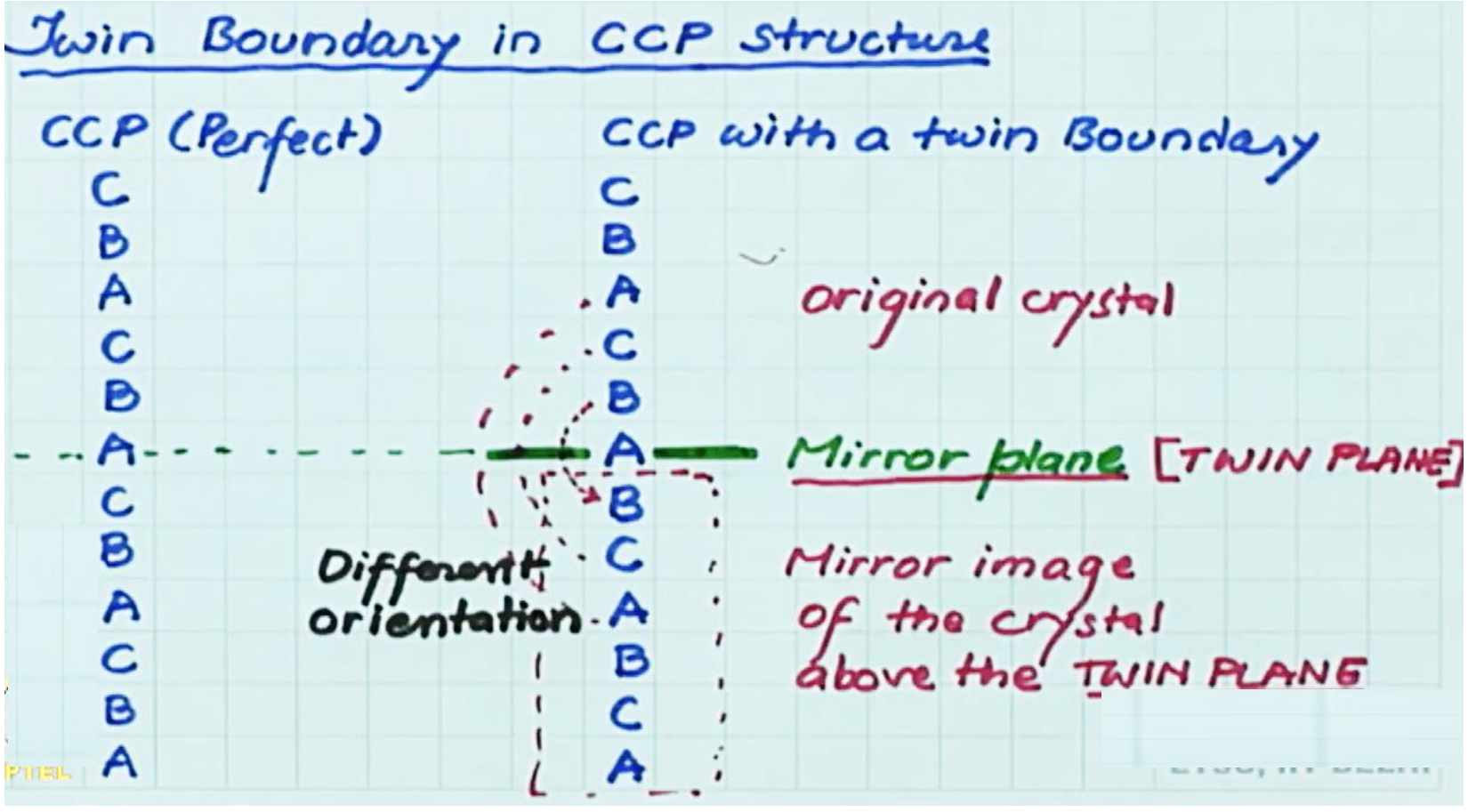


Figure 1.53 Solidification of a polycrystalline solid from the melt. For simplicity, cubes represent atoms.

Twin boundary defects

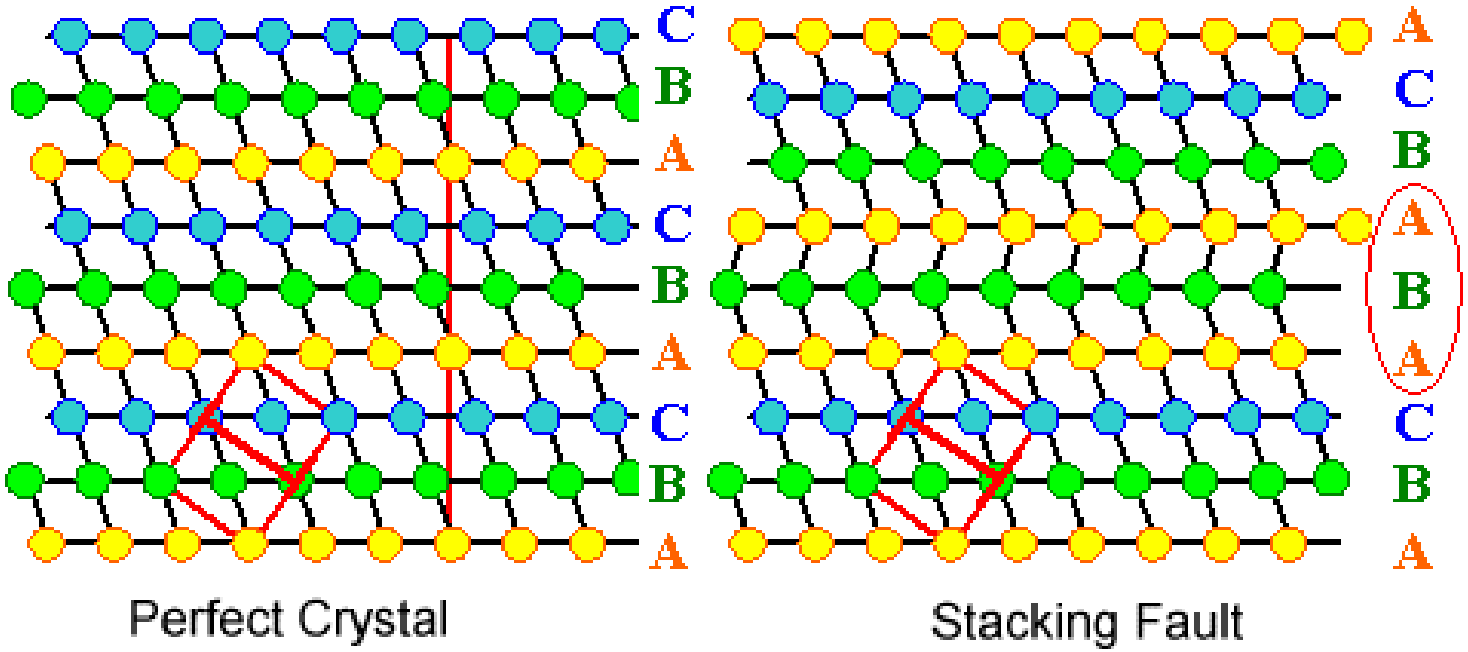
- Twin boundaries are types of planar surface defects.
- The atomic arrangement on one side of a twin boundary is a mirror reflection of the arrangement on the other side.
- Twin boundaries occur in pairs such that the orientation change introduced by one boundary is restored by the other.

Tilt boundary defects with perpendicular to each other



Stacking Fault

- Fault in the stacking sequence of a crystal.
- **For a perfect crystal** the stacking sequence of plains is **ABCABCABC…. (from bottom to top)**, it produce FCC crystal.
- **In Faulted structure**, the C plane is missing and remaining will continue the same. It produce ABCABABCA…., The fault plane ABA produce HCP crystal and before and after produce FCC only.




Thank You!