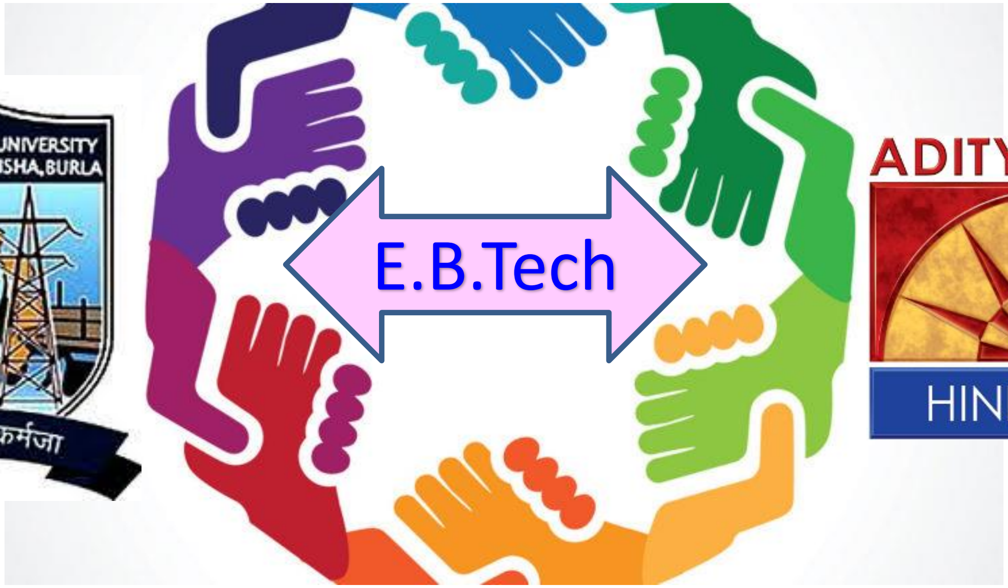
EXECUTIVE B.TECH PROGRAMME

LECTURE NOTES

INTRODUCTION TO PHYSICAL METALLURGY



INTRODUCTION TO PHYSICAL METALLURGY

Course Coordinator(s)

Avala Lava Kumar
Department of Metallurgical & Materials Engineering (MME)
Veer Surendra Sai University of Technology (VSSUT), Burla-768018
E-mail : lavakumar.vssut@gmail.com Phone: (+91) (7077110110)

INTRODUCTION TO PHYSICAL METALLURGY

The course aims to provide a general introduction to the field of Physical Metallurgy. The course covers crystal structures, solidification, equilibrium phase diagrams, transformation diagrams, diffusion, liquid to solid transformations, ferrous and non-ferrous materials, cold work, recovery and Recrystallization.

Course Overview

The module provides a systematic overview of the major principles of physical metallurgy. Students successfully completing the module will have a critical awareness of how these principles relate to current issues in exploiting structural alloys in engineering applications.

Learning Outcomes

Upon successful completion of the module, students should be able to ►Show a systematic understanding of the role that crystal structures play in material properties. ►Evaluate critically the relevance of phase diagrams, isothermal transformation diagrams and continuous cooling transformation diagrams to understanding real alloys and their microstructure.► Display a critical awareness of the relevance of key areas, e.g. diffusion, defects, transformation type, to current problems in designing, processing and exploiting real alloys. ►Show a systematic understanding of the complex interplay between microstructure, processing and engineering properties in metallic materials.

INTRODUCTION TO PHYSICAL METALLURGY

CONTENTS

INTRODUCTION TO PHYSICAL METALLURGY

References

- Introduction to Physical Metallurgy (*This is the major reference for this course*)

  Sidney H. Avner

  McGraw Hill Education (India) Private Limited

- Materials Science & Engineering E-book (A *learners guide*) (*This is the major reference for this Notes, we directly taken these slides with slight modifications, our sincere thanks to authors*)

  Anandh Subramaniam & Kantesh Balani (IITK)

  MHRD, Govt. of India through NMEICT

- Materials Science and Engineering (5th Edition)
  V. Raghavan
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- Callister's Materials Science and Engienering
  William D Callister (Adapted by R. Balasubramaniam)
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- The Science and Engineering of Materials
  Donald. R. Askeland & Pradeep Phulé
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- Materials Science & Engineering (NPTEL Course)

  Ranjit Bauri (IITM)

Introduction

Avala Lava Kumar *

Department of Metallurgical & Materials Engineering (MME)

Veer Surendra Sai University of Technology (VSSUT), Burla -768018

**E-mail : lavakumaravala@gmail.com*

Introduction

What is physical metallurgy?

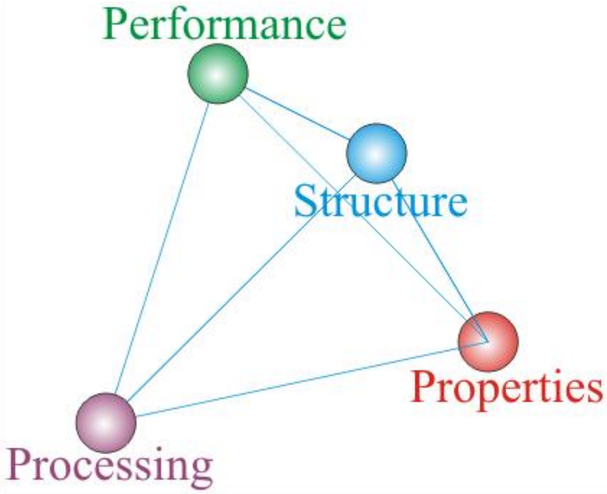
- Evolution of structures in solid as it from liquid
- Effect of alloy elements/ impurities on the transformation processes
- Effect of processing techniques on evolution of structure
- Structure property relation.

Objectives

- At some point of time or the other an engineering problem involves issues related to material selection.
- Understanding the behavior of materials, particularly structure-property correlation, will help selecting suitable materials for a particular application.
- To provide a basic understanding of the underlying principles that determines the evolution the evolution of structures in metals and alloys during their processing and its relation with their properties & performance in service.

The Materials Tetrahedron

- A materials scientist has to consider four 'intertwined' concepts, which are schematically shown as the 'Materials Tetrahedron'.
  - When a certain performance is expected from a component (and hence the material constituting the same), the 'expectation' is put forth as a set of properties.
  - The material is synthesized and further made into a component by a set of processing methods (casting, forming, welding, powder metallurgy etc.).
  - The structure (at various length scales) is determined by this processing.
  - The structure in turn determines the properties, which will dictate the performance of the component.
- Hence each of these aspects is dependent on the others.

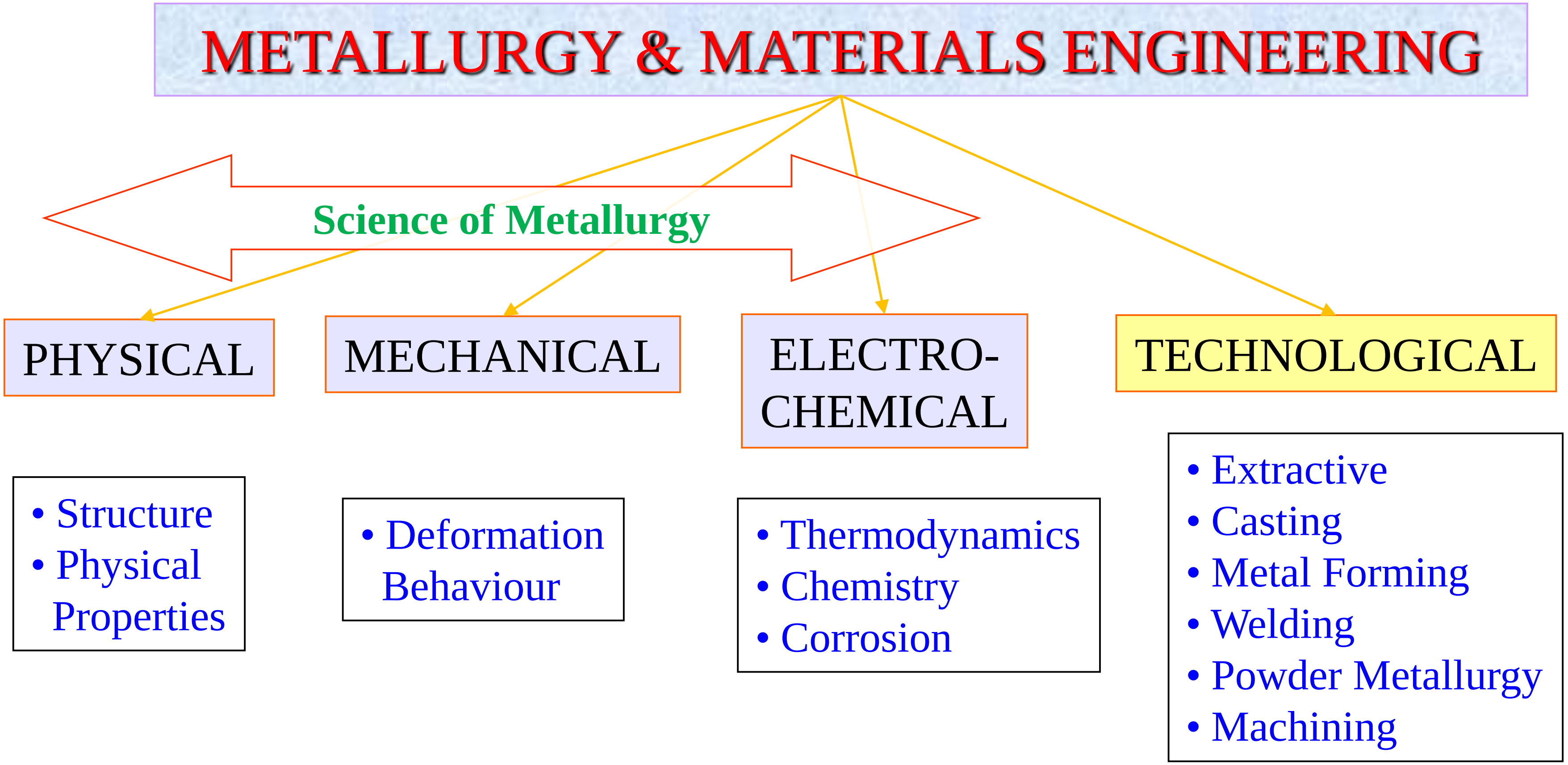


The Materials Tetrahedron

The broad goal of Metallurgy & Materials Engineering is to understand and 'Engineer' this Tetrahedron

A General Classification

- The broad scientific and technological segments of Metallurgy & Materials Science are shown in the diagram below.
- To gain a comprehensive understanding of Metallurgy, all these aspects have to be studied.



METALLURGY & MATERIALS ENGINEERING

Science of Metallurgy

PHYSICAL
- Structure
- Physical Properties

MECHANICAL
- Deformation Behaviour

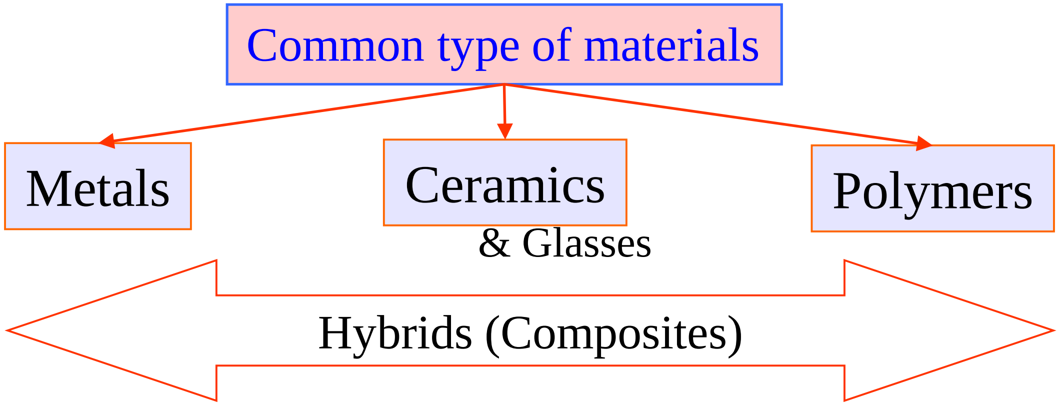
ELECTRO-CHEMICAL
- Thermodynamics
- Chemistry
- Corrosion

TECHNOLOGICAL
- Extractive
- Casting
- Metal Forming
- Welding
- Powder Metallurgy
- Machining

A Broad Overview

- Based on state (phase) a given material can be Gas, Liquid or Solid
- Based on structure (arrangement of atoms/molecules/ions) materials can be Crystalline, Quasicrystalline or Amorphous.
- Based on Band Structure we can classify materials into Metals, Semiconductors and Insulators.
- Based on the size of the entity in question we can Nanocrystals, Nanoquasicrystals etc.

Let us consider the common types of Engineering Materials.



Common type of materials

Metals

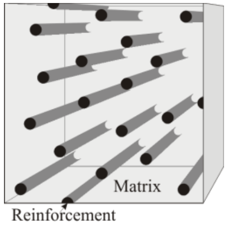
Ceramics & Glasses

Polymers

Hybrids (Composites)

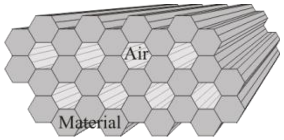
Classification of materials based on form of usage

- Materials
  - Monolithic
    - Metals (& Alloys)
    - Ceramics & Glasses
    - Polymers (& Elastomers)
  - Hybrids
    - Composite
    - Sandwich
    - Lattice
    - Segment

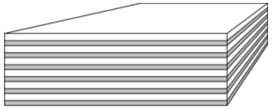


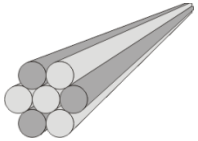
Composites: have two (or more) solid components; usually one is a matrix and other is a reinforcement

Sandwich structures: have a material on the surface (one or more sides) of a core material



Lattice* Structures: typically a combination of material and space (e.g. metallic or ceramic forms, aerogels etc.).



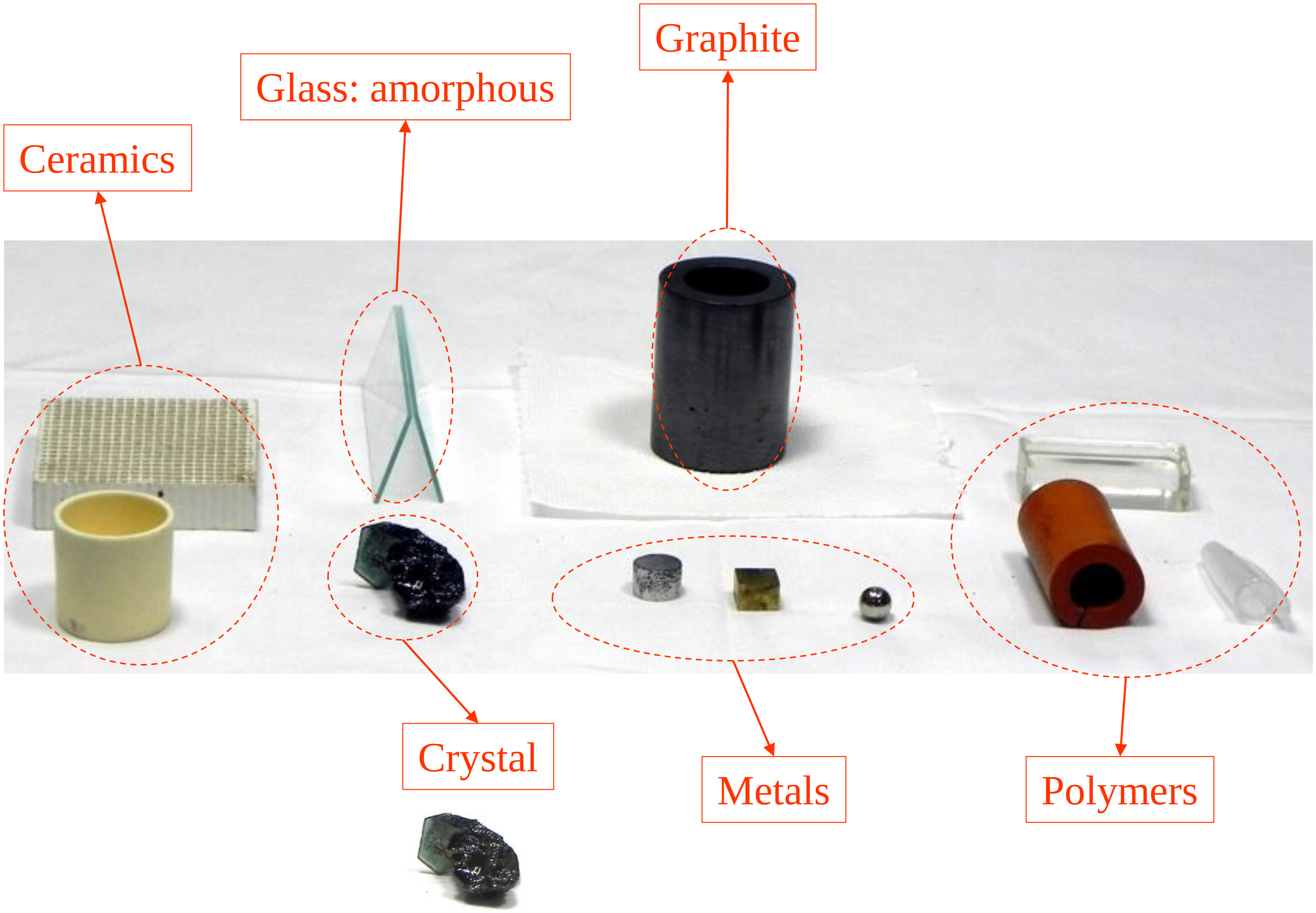


Segmented Structures: are divided in 1D, 2D or 3D (may consist of one or more materials).

Hybrids are designed to improve certain properties of monolithic materials

Note: this use of the word 'lattice' should not be confused with the use of the word in connection with crystallography.

Common materials : with various 'viewpoints'



Ceramics

Glass: amorphous

Graphite

Crystal

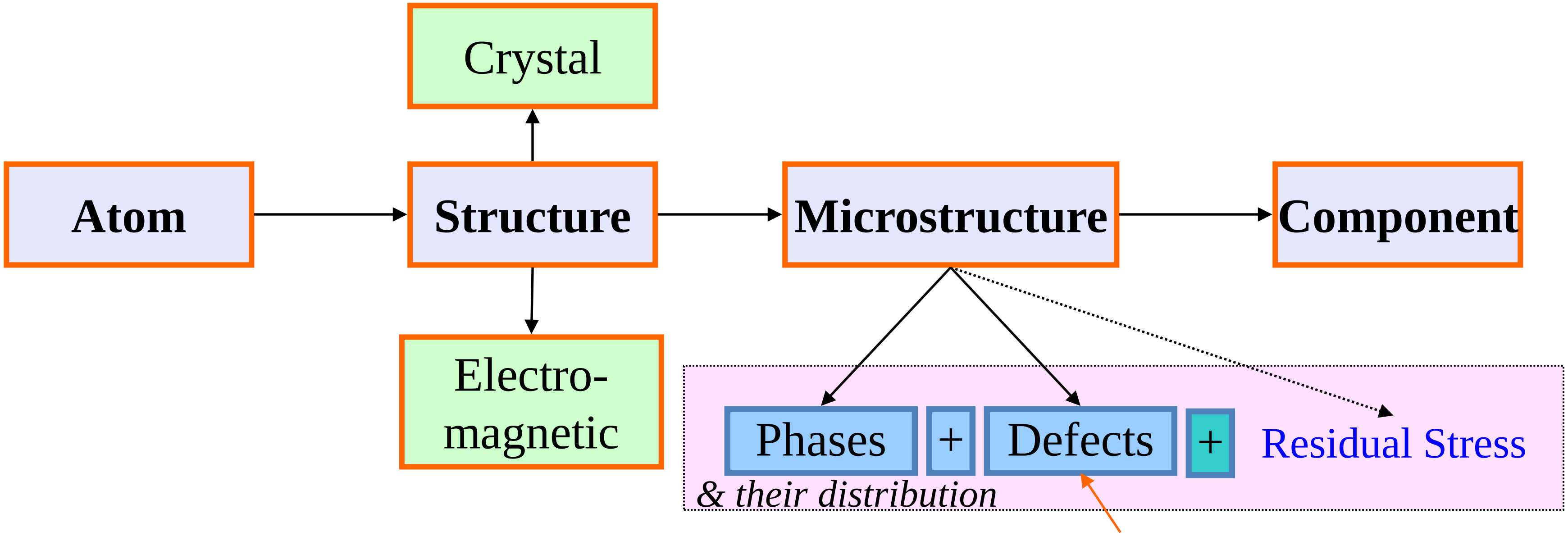
Metals

Polymers

Classes of property

Economic	Price and Availability, Recyclability
General Physical	Density
Mechanical	Modulus, Yield and Tensile strength, Hardness, Fracture strength, Fatigue strength, Creep strength, Damping
Thermal	Thermal conductivity, Specific Heat
Electric & Magnetic	Resistivity, Dielectric constant, Magnetic permeability
Environmental interactions	Oxidation, corrosion and wear
Production	Ease of manufacturer, joining, finishing
Aesthetic (Appearance)	Colour, Texture, Feel.

Length scales in metallurgy



Atom → **Structure** → **Microstructure** → **Component**

Structure → Crystal

Structure → Electro-magnetic

Microstructure → Phases + Defects + Residual Stress

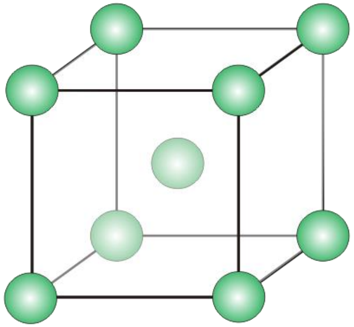
& their distribution

- Vacancies
- Dislocations
- Twins
- Stacking Faults
- Grain Boundaries
- Voids
- Cracks

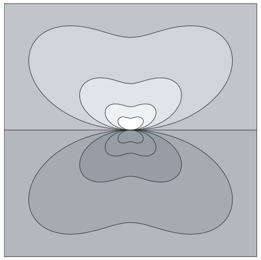
- ❑ Structure could imply two types of structure:
  - ➢ Crystal structure
  - ➢ Electromagnetic structure
- ❑ Microstructure can be defined as: (Phases + Defect Structure + Residual Stress) *and their distributions*

Length scales in metallurgy

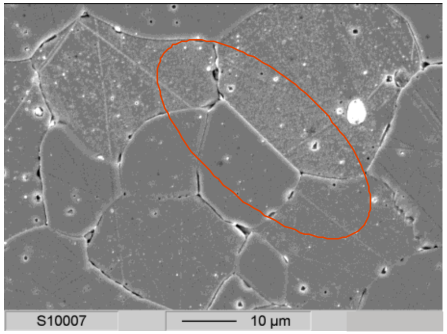
Let us start with a cursory look at the lengthscales involved in Materials Science



Angstroms



Dislocation Stress fields
→ Nanometers

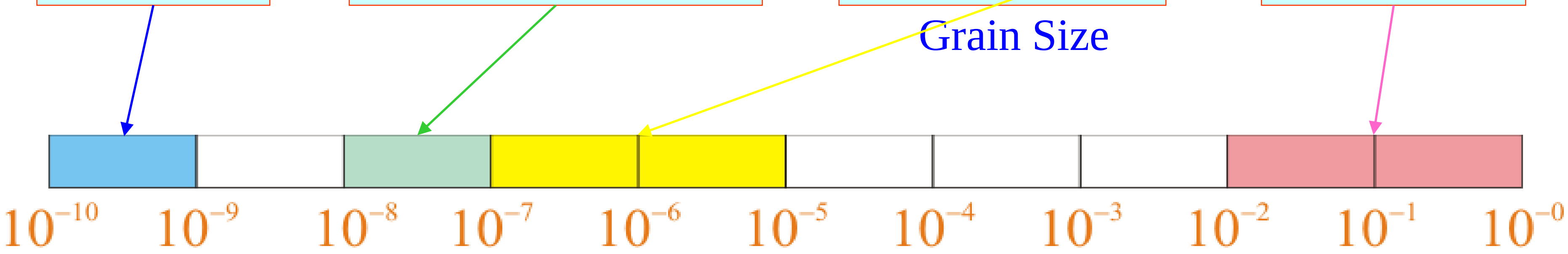


Microns

Centimeters

Unit Cell* → Crystalline Defects → Microstructure → Component

Grain Size

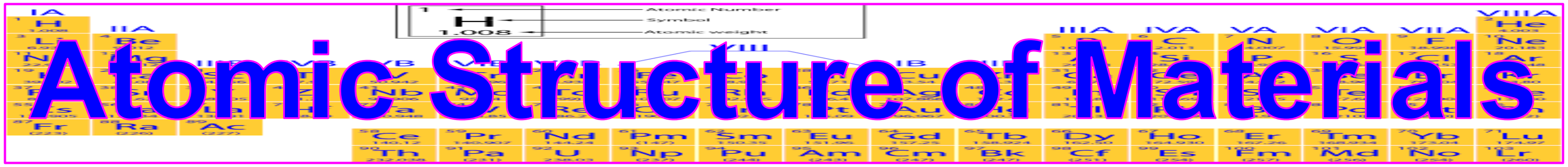


← Metres →

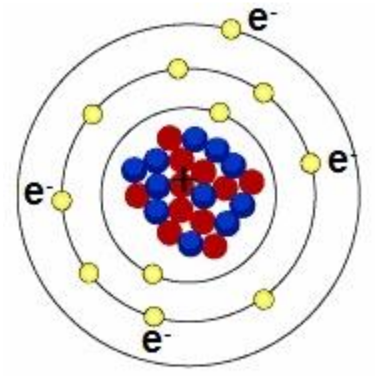
Questions?

1. What is Physical Metallurgy?
2. Give the broad classification of Materials?
3. Define Metal, Ceramic and Composite.
4. Define Macrostructure and Microstructure?
5. What is Grain and Grain boundary?
6. Give some of important properties of materials.
7. What is composite?
8. What is Bio-materials?
9. What is smart materials?
10. Give some of the types of advanced materials and its applications.


Thank You!



Atomic Structure of Materials



Avala Lava Kumar *

Department of Metallurgical & Materials Engineering (MME)

Veer Surendra Sai University of Technology (VSSUT), Burla -768018

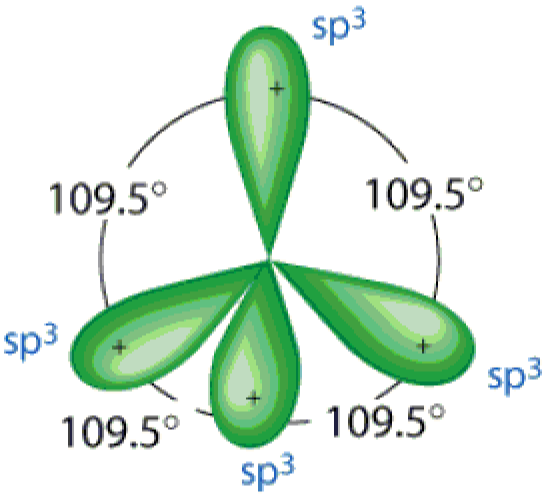
**E-mail : lavakumaravala@gmail.com*

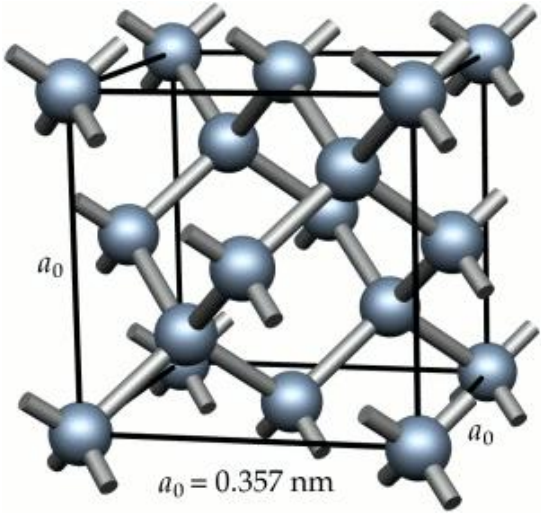
Introduction

- *In order to understand the structure of materials and its correlation to property, we have to start form the basic element of matter – The Atom*
- An atom consists of a nucleus composed of protons and neutrons and electrons which encircle the nucleus.
- Protons and electrons have same and opposite charge of 1.6 x10^{-19} C.
- Atomic number (Z) = Number protons = number of electrons
- Atomic mass (A) = proton mass + neutron mass
- Isotopes are the same element having different atomic masses. Number of protons in isotopes remains same while number of neutrons varies.
- Atomic mass unit (amu) = 1/12 mass of Carbon 12 (^{12}C)
- 1 mol of substance contains 6.023 x 10^{23} (Avogadro's number) atoms or molecules.
- Atomic weight = 1 amu/atom (or molecule) = 1 g/mol = Wt. of 6.023 x 10^{23} atoms or molecules.
  - For example, atomic weight of copper is 63.54 amu/atom or 63.54 g/mole

Role of atomic structure in materials

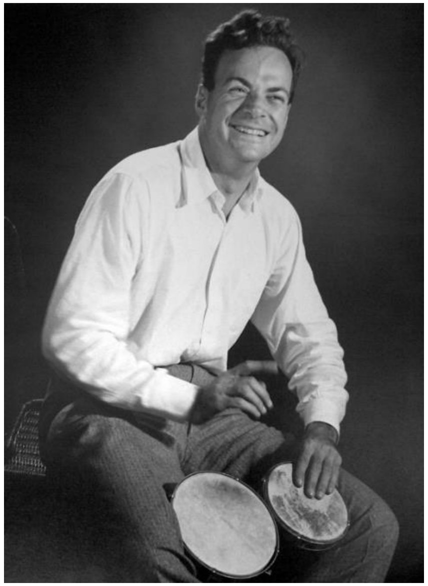
- As we know, common to all materials is that they are composed of **atoms**.
- The properties (whether mechanical, electrical, chemical etc) of all solid materials are dependent upon the relative positions of the atoms in the solid (in other words the atomic structure of the material) and their mutual interaction i.e. the nature of the bonding (whether e.g. covalent, ionic, metallic, van der Waals).
- There are examples of where the atom-atom interactions is strongly reflected in the atomic structure. An example is diamond. Here the carbon-carbon interactions lead to a very directional covalent bond called a sp^3 bond which has tetrahedral symmetry – this leads to an open structure as shown below.





Role of atomic structure in materials

- Of course carbon can also take the form of graphite. Here the carbon atoms are arranged in a rather different structure and graphite has very different properties to diamond!
- In other solid systems (for example many of the metallic elements) the atomic structure is dictated by how well we can 'pack' the atoms into 3D space – 'packing efficiency' – this leads to dense close-packed structures as we will also discuss in *crystal structure* chapter.
- So it is vital that to understand the properties of material, and to improve those properties for example by adding or removing atoms, we need to know the material's atomic structure.



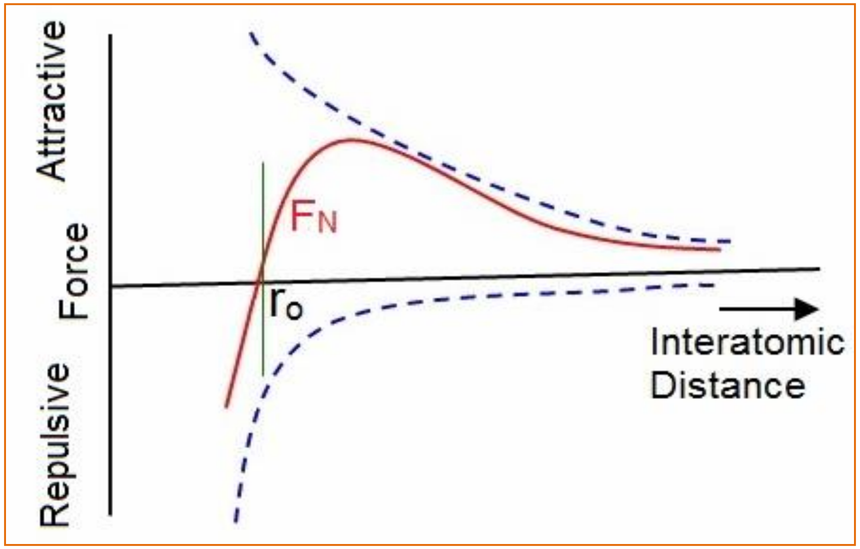
As Richard Feynman said….!

> ***"It would be very easy to make an analysis of any complicated chemical substance; all one would have to do would be to look at it and see where the atoms are…"***

Atomic Interaction

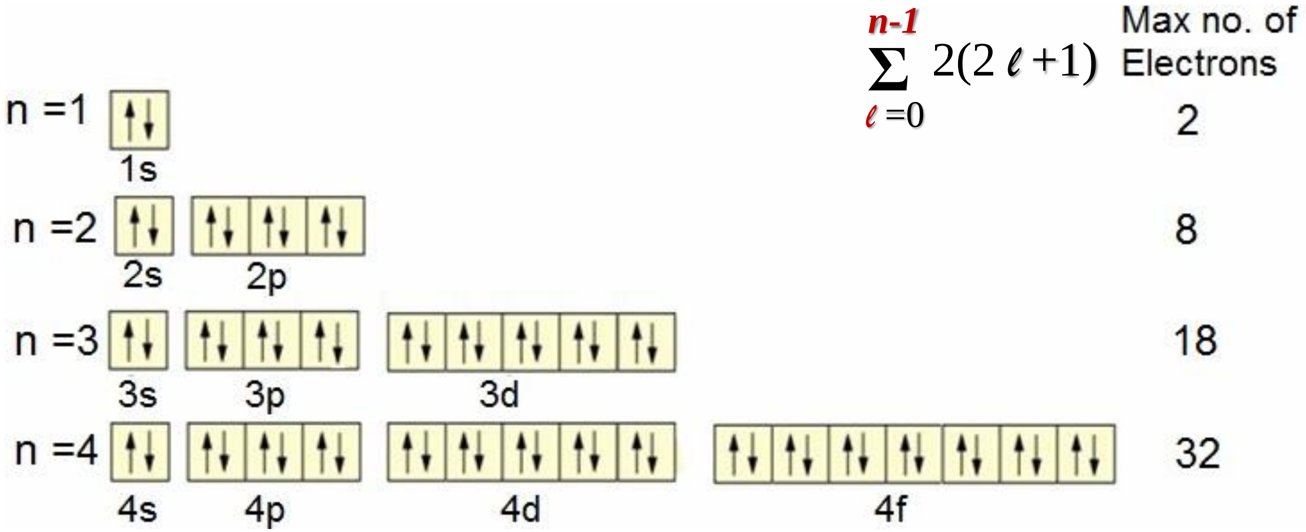
- ☐ When two neutral atoms are brought close to each other, they experience attractive and or repulsive force.
- ☐ Attractive force is due to electrostatic attraction between electrons of one atom and the nucleus of the other.
- ☐ Repulsive force arises due to repulsion between electrons and nuclei of the atoms.
- ☐ The net force, F_N (Fig) acting on the atoms is the summation of attractive and repulsive forces.
- ☐ The distance, at which the attraction and repulsion forces are equal and the net force is zero, is the equilibrium interatomic distance, r_o . The atoms have lowest energy at this position.

- ☐ Attraction is predominant above r_o and repulsion is dominant below $r_{o.}$



Electron Configuration

The quantum mechanic principles as discussed before allow determination of electron configuration i.e. the manner in which electron states are occupied in a given atom.Σ



$$\sum_{\ell=0}^{n-1} 2(2\ell+1)$$

Electron configuration based on quantum numbers. Total number of electrons in a shell is $2n^2$ or

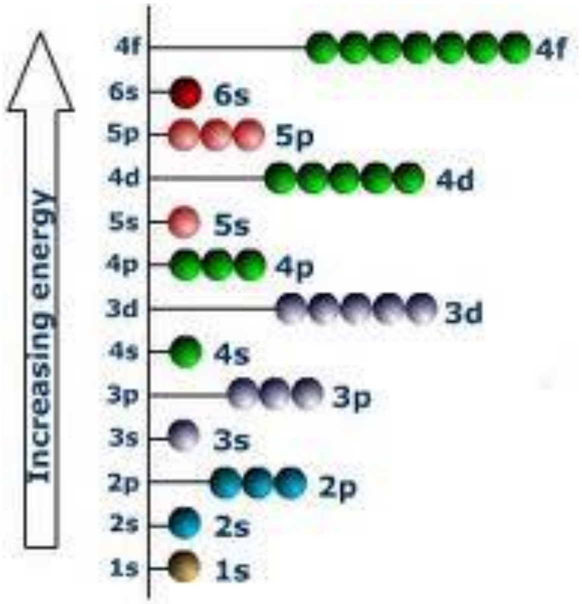
$$\sum_{\ell=0}^{n-1} 2(2\ell+1)$$

The manner or sequence of filling of electron orbital's is decided a by a set of two principles / rules:

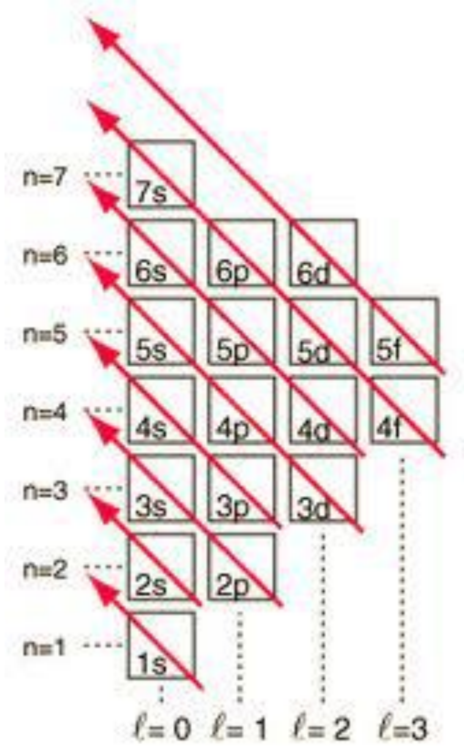
- Aufbau principle
- Madelung's rule

Electron Configuration

- Aufbau principle (German meaning is *building up*) : it states that lower energy states will be filled up first.
- Madelung's rule : Orbitals fill in the order of increasing (n+ℓ). 4s (n+ℓ = 4+0 = 4) will be filled before 3d (n+ℓ= 3+2 = 5) and 5s (n+ℓ = 5+0 = 5)
- For orbital with same values of (n+ℓ), the one with lower 'n' will be filled first. 3d will be filled before 4p.



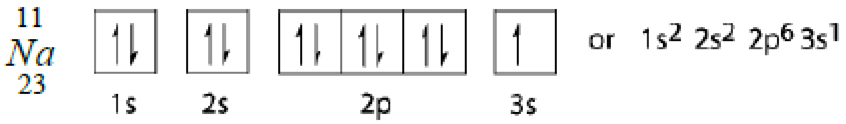
Aufbau principle

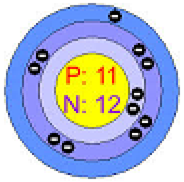


Madelung rule

Electron Configuration

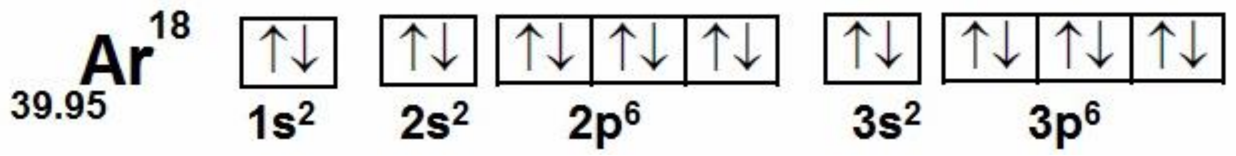
- Based on the foregoing discussion, it is now possible to find the electron configuration for a given atom.
- For example, sodium Na^{11}_{23} has 11 electrons – the configuration is shown in the first figure. The second picture shows the Bohr configuration.

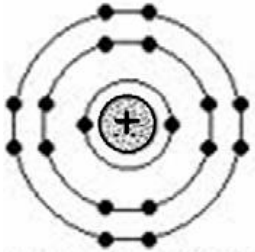




Valence electrons

- The electrons in the outer most shell are known as valence electrons. Na has one valence electron (the 3s electron). These electrons are responsible for chemical reaction and atomic bonding.
- Look at the electron configuration of inert gases (He, Ne, Ar, Kr, Xe) in the previous table. Their valence electron cell is completely filled unlike any other element.



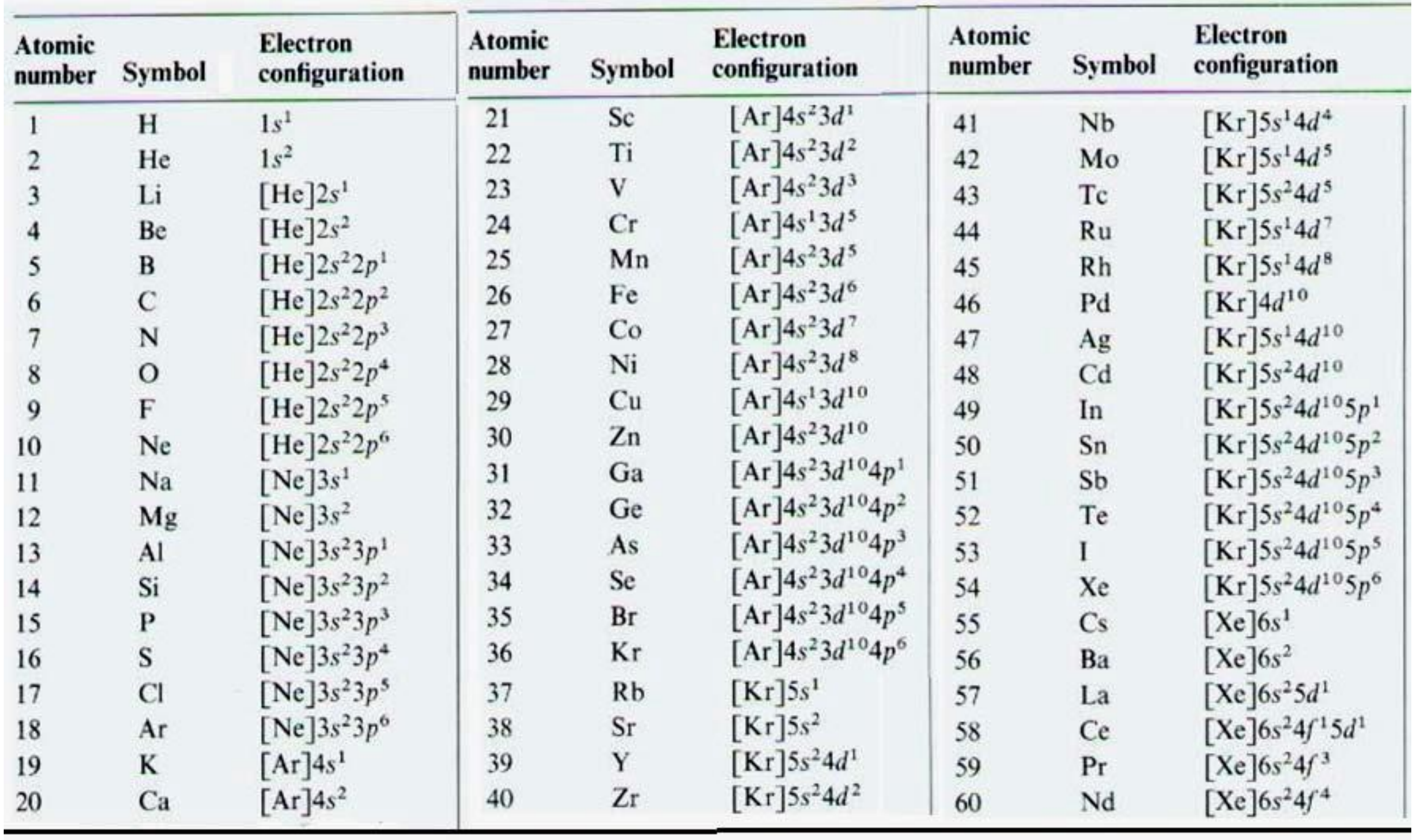


Ar (18) 2.8.8

Electron Configuration

- Note that the configuration of higher atomic number elements can be expressed by the previous inert element configuration.
- It is the tendency of every element to attain the lowest energy stable configuration that forms the basis of chemical reactions and atomic bonding.

Electron Configuration of Elements

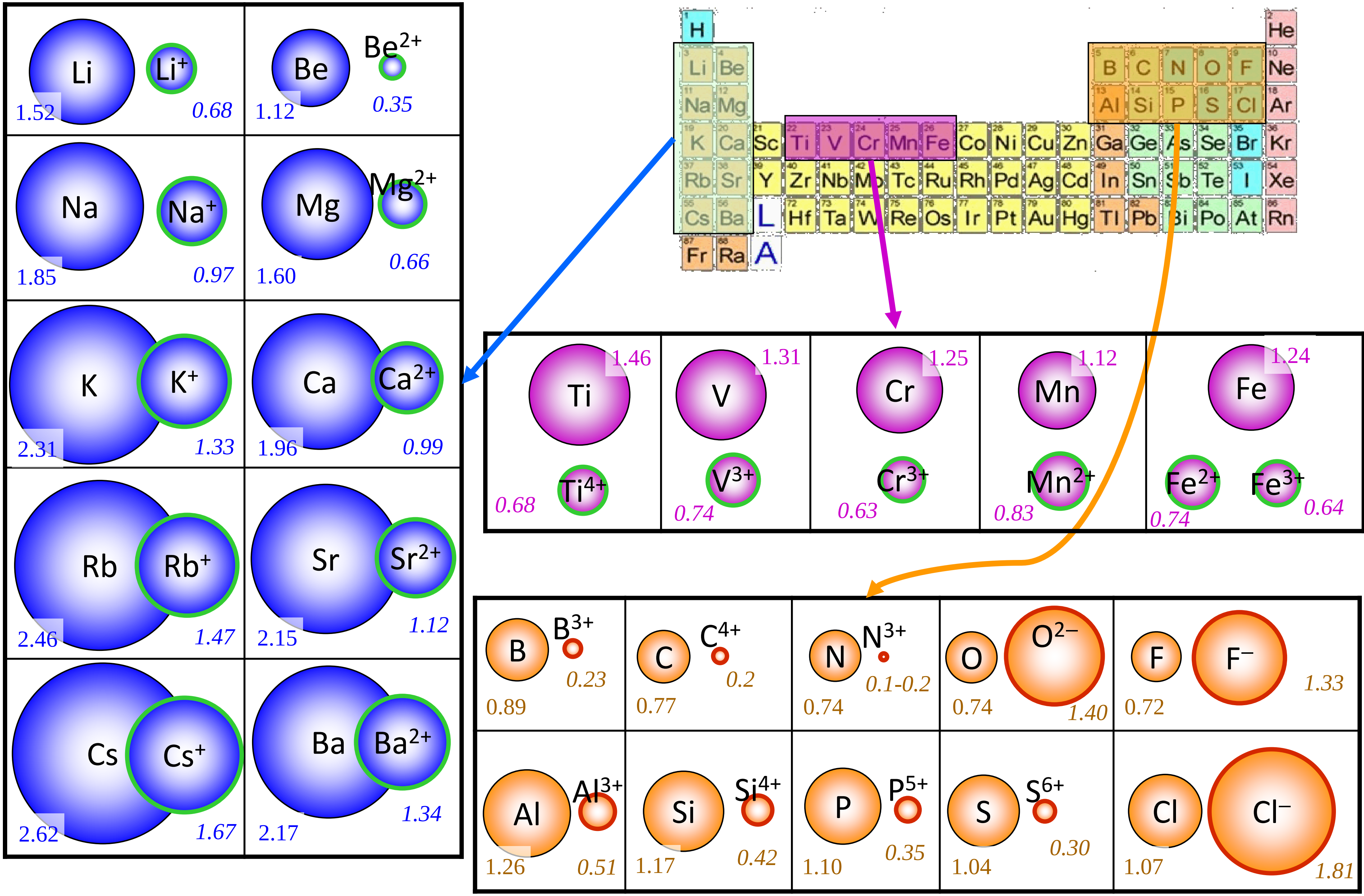


Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration
1	H	$1s^1$	21	Sc	[Ar]$4s^2 3d^1$	41	Nb	[Kr]$5s^1 4d^4$
2	He	$1s^2$	22	Ti	[Ar]$4s^2 3d^2$	42	Mo	[Kr]$5s^1 4d^5$
3	Li	[He]$2s^1$	23	V	[Ar]$4s^2 3d^3$	43	Tc	[Kr]$5s^2 4d^5$
4	Be	[He]$2s^2$	24	Cr	[Ar]$4s^1 3d^5$	44	Ru	[Kr]$5s^1 4d^7$
5	B	[He]$2s^2 2p^1$	25	Mn	[Ar]$4s^2 3d^5$	45	Rh	[Kr]$5s^1 4d^8$
6	C	[He]$2s^2 2p^2$	26	Fe	[Ar]$4s^2 3d^6$	46	Pd	[Kr]$4d^{10}$
7	N	[He]$2s^2 2p^3$	27	Co	[Ar]$4s^2 3d^7$	47	Ag	[Kr]$5s^1 4d^{10}$
8	O	[He]$2s^2 2p^4$	28	Ni	[Ar]$4s^2 3d^8$	48	Cd	[Kr]$5s^2 4d^{10}$
9	F	[He]$2s^2 2p^5$	29	Cu	[Ar]$4s^1 3d^{10}$	49	In	[Kr]$5s^2 4d^{10} 5p^1$
10	Ne	[He]$2s^2 2p^6$	30	Zn	[Ar]$4s^2 3d^{10}$	50	Sn	[Kr]$5s^2 4d^{10} 5p^2$
11	Na	[Ne]$3s^1$	31	Ga	[Ar]$4s^2 3d^{10} 4p^1$	51	Sb	[Kr]$5s^2 4d^{10} 5p^3$
12	Mg	[Ne]$3s^2$	32	Ge	[Ar]$4s^2 3d^{10} 4p^2$	52	Te	[Kr]$5s^2 4d^{10} 5p^4$
13	Al	[Ne]$3s^2 3p^1$	33	As	[Ar]$4s^2 3d^{10} 4p^3$	53	I	[Kr]$5s^2 4d^{10} 5p^5$
14	Si	[Ne]$3s^2 3p^2$	34	Se	[Ar]$4s^2 3d^{10} 4p^4$	54	Xe	[Kr]$5s^2 4d^{10} 5p^6$
15	P	[Ne]$3s^2 3p^3$	35	Br	[Ar]$4s^2 3d^{10} 4p^5$	55	Cs	[Xe]$6s^1$
16	S	[Ne]$3s^2 3p^4$	36	Kr	[Ar]$4s^2 3d^{10} 4p^6$	56	Ba	[Xe]$6s^2$
17	Cl	[Ne]$3s^2 3p^5$	37	Rb	[Kr]$5s^1$	57	La	[Xe]$6s^2 5d^1$
18	Ar	[Ne]$3s^2 3p^6$	38	Sr	[Kr]$5s^2$	58	Ce	[Xe]$6s^2 4f^1 5d^1$
19	K	[Ar]$4s^1$	39	Y	[Kr]$5s^2 4d^1$	59	Pr	[Xe]$6s^2 4f^3$
20	Ca	[Ar]$4s^2$	40	Zr	[Kr]$5s^2 4d^2$	60	Nd	[Xe]$6s^2 4f^4$

Ionization Potential, Electron Affinity, Electronegativity

- If sufficient energy is supplied, an electron in the outer orbital can break away completely from the atom and become free. The energy required to remove an electron in this manner is known as the Ionization potential.
- When the extra electron is attracted from infinity to the outer orbital of the neutral atom, is known as the electron affinity of the atom.
- The tendency of an atom to attract electrons to itself during the formation of bonds with other atoms is measured by the electronegativity of the atom.

Let us start by looking at the relative sizes of some ions in the periodic table

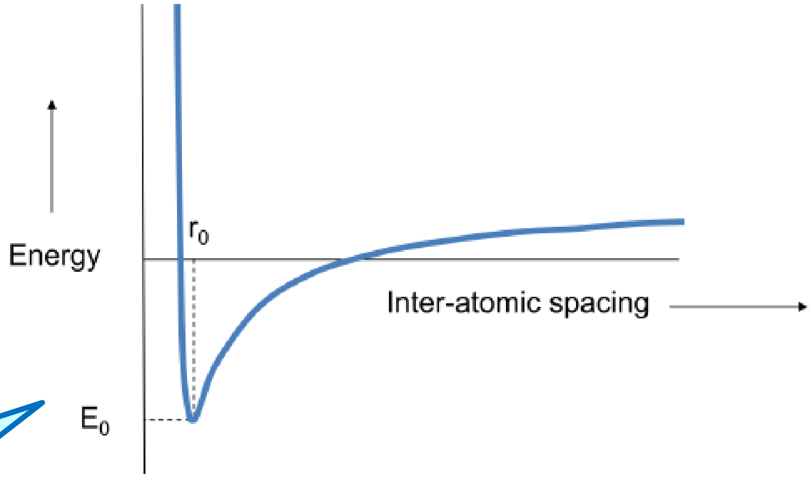


Values are: Pauling-Ahrens Radii in Å

Concept of Thermal Expansion

- The length of a bond is defined as the center-to-center distance of the bonding atoms. Strong bonds pull the bonding atoms closer together and so have smaller bond lengths as compared to weak bonds.
- Primary bonds have lengths in the range 1-2 Å (0.1-0.2 nm). Secondary bond lengths are larger, in the range 2-5Å (0.2-0.5 nm)
- Some ambiguity in this definition arises if the element in question, exhibits different crystal forms.
- *For example, the diameter of the iron atom is 2.48 Å when it is surrounded by eight neighbours in the BCC crystal and 2.54Å when it has 12 nearest neighbours in the FCC crystal.*

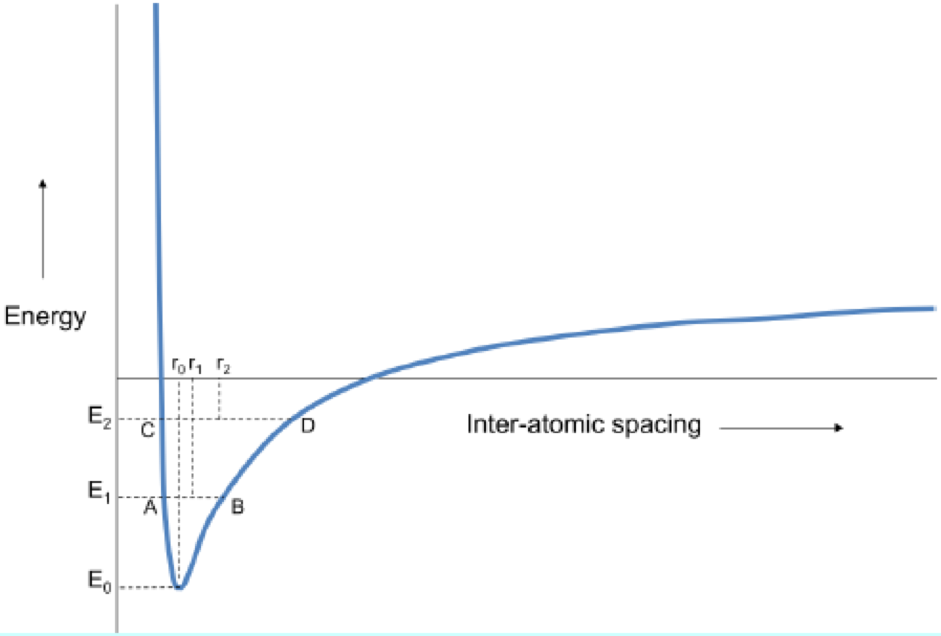
- If the inter-ionic separation is fixed, it means the atoms are stationary, and this can occur only at 0 Kelvin. Therefore the atoms are at their minimum energy E_0, and inter-ionic separation r_0, at 0 Kelvin.



The minimum energy E_0, and equilibrium inter-ionic spacing r_0, at 0 Kelvin.

Concept of Thermal Expansion

- As the temperature of the system is raised to T_1, and then further to T_2, the solid becomes consistent with the higher temperatures by having the ions gain energy, and vibrate with increased amplitudes. Therefore, as shown in Figure(below), at T_1, when the energy is E_1, the ions are able to vibrate between the positions “A” and “B”. Similarly, at T_2, when the energy is E_2, the ions are able to vibrate between the positions “C” and “D”.

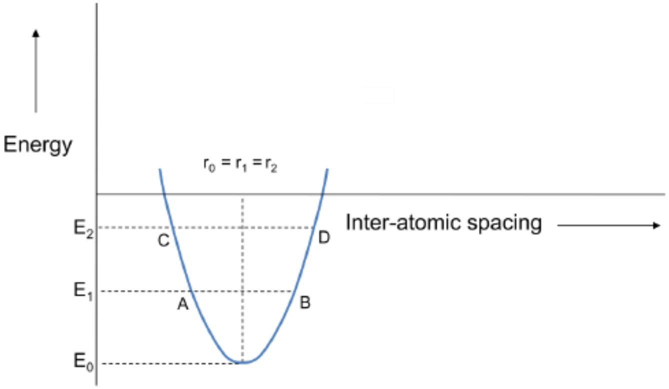


Effect of increasing temperature on the vibration of the ions and hence on the inter-ionic separation. The system is raised to temperature T_1, and then further to T_2. At T_1, when the energy is E_1, the ions are able to vibrate between the positions “A” and “B”. Similarly, at T_2, when the energy is E_2, the ions are able to vibrate between the positions “C” and “D” .

Concept of Thermal Expansion

- It is important to note from the Figure (previous slide) that, the midpoint between “A” and “B”, which represents the mean inter-ionic distance at T_1, is r_1 which is greater than r_0. This is a direct result of the fact that the solid curve in Figure, is asymmetric.
- ***It is therefore important to note that thermal expansion occurs as a direct result of the fact that the ‘E Vs R’ curve is asymmetric.***
- It is also important to note that while the general approach used here can be extended to many systems, the exact shape of the resultant curve obtained will depend on the details of the specific system. In some cases, such as ceramic materials, the resultant curve will have a very deep and narrow trough, such materials will have a very low coefficient of thermal expansion. In other cases, the resultant curve will have a shallow and wide trough, which will cause the material to display a high coefficient of thermal expansion.

A hypothetical solid, in which the E Vs R curve is exactly symmetric. In this case when the temperature is raised, E increases, and the amplitude of vibration of the ions increase, but there is no thermal expansion since the mean inter-ionic distance is exactly the same at all temperatures



Atomic Bonding

- The mechanisms of bonding between the atoms are based on the foregoing discussion on electrostatic inter- atomic interaction.
- The types of bond and bond strength are determined by the electronic structures of the atoms involved.
- The valence electrons take part in bonding. The atoms involved acquire, loose or share valence electrons to achieve the lowest energy or stable configuration of noble gases.
- Atomic bonding can be broadly classified as i) primary bonding ii) secondary bonding

Primary Bonds

Ionic

Covalent

Metalic

Secondary Bonds

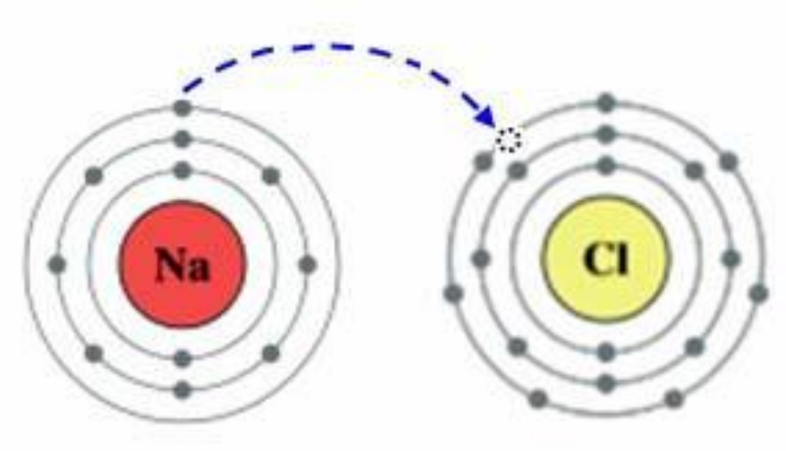
Vanderwaals

Hydrogen

- Majority of the engineering materials consist of one of these bonds. Many properties of the materials depend on the specific kind of bond and the bond energy.

Ionic Bond

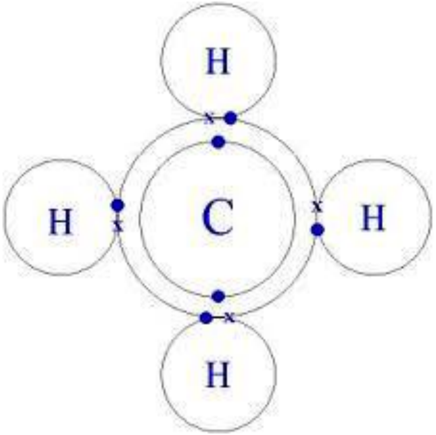
- Ionic bonds are generally found in compounds composed of metal and non-metal and arise out of electrostatic attraction between oppositely charged atoms (ions).
- Number of electron in outer shell is 1 in Na and 7 in Cl . Therefore, Na will tend to reject one electron to get stable configuration of Ne and Cl will accept one electron to obtain Ar configuration.
- The columbic attraction between Na+ and Cl^- ions thus formed will make an ionic bond to produce NaCl.

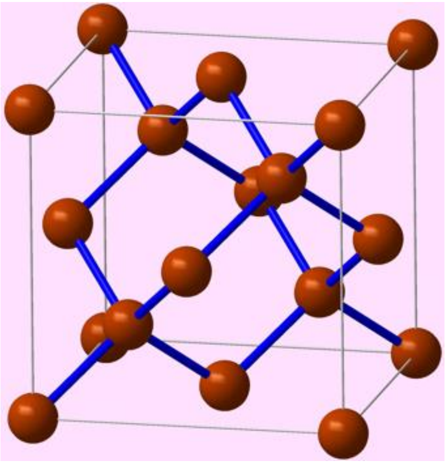


- Some other examples are CaF_2 , CsCl, MgO, Al_2O_3

Covalent Bond

- In this type of bonding, atoms share their valence electrons to get a stable configuration.
- Methane (CH_4): Four hydrogen atoms share their valence electrons with one carbon atom and the carbon atom in turn shares one valence electron with each of the four hydrogen atoms. In the process both H and C atoms get stable configuration and form a covalent bond.

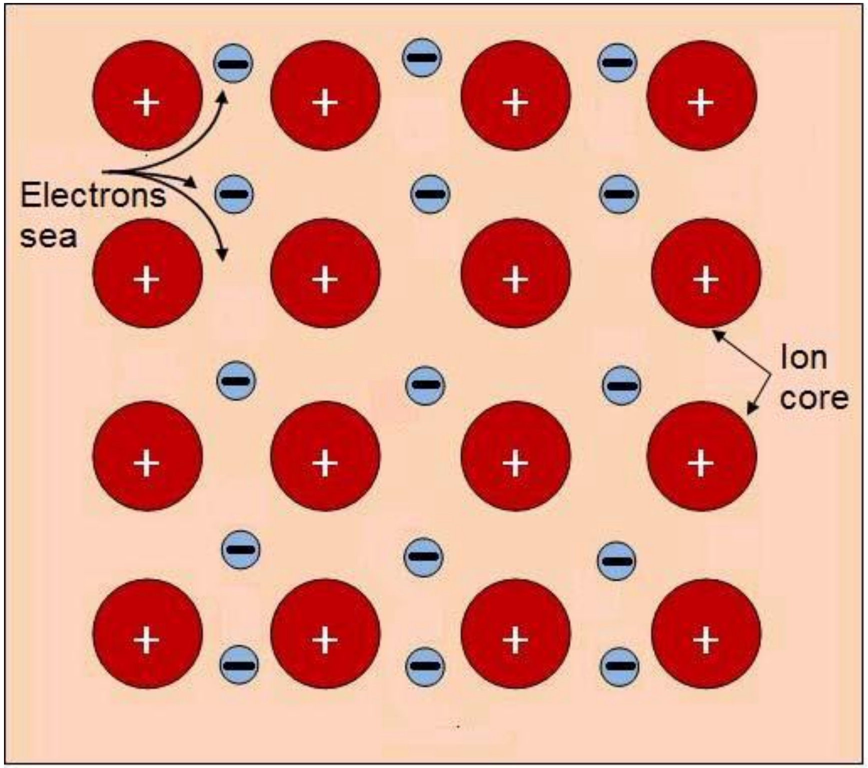




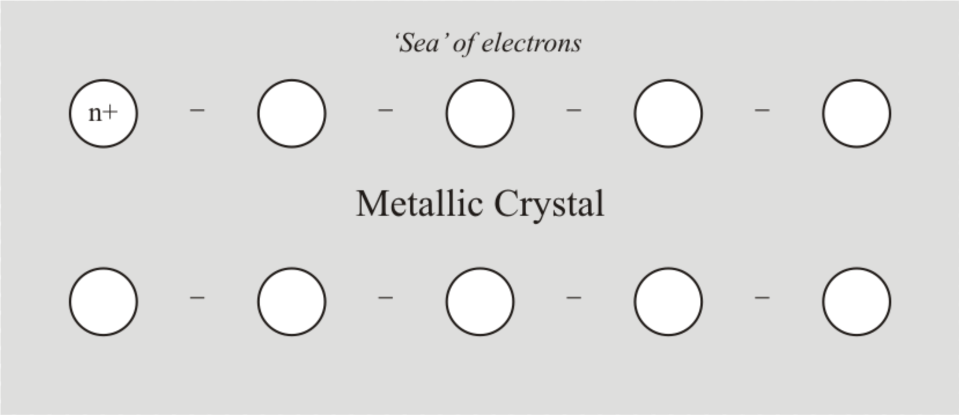
- Covalent bonds are formed between atoms of similar electro negativity.
- C atoms in diamond are covalently bonded to each other.
- Si also has valency of four and forms SiC through covalent bonding with C atoms.

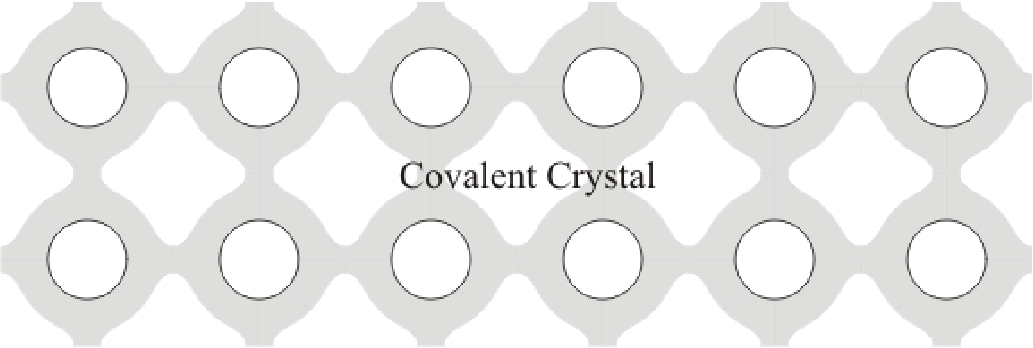
Metallic Bond

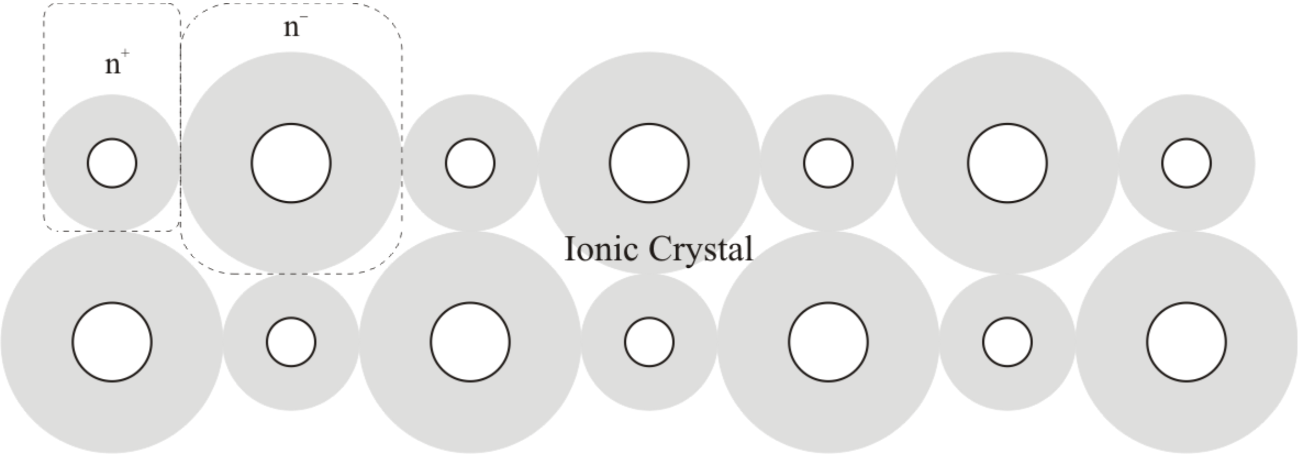
- In metals the valence electrons are not really bound to one particular atom, instead they form a sea or cloud of valence electrons which are shared by all the atoms. The remaining electrons and the nuclei form what is called the ion core which is positively charged. The metallic bond arises out of the columbic attraction between these two oppositely charged species – the electron cloud and the ion cores.



Electron cloud distribution in various kinds of bonding





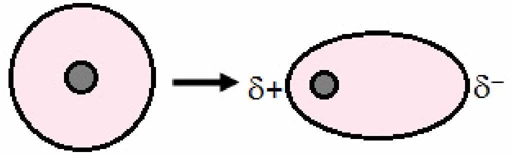


Characteristics of primary bonds

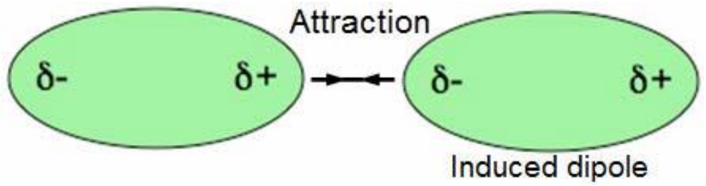
- Ionic and covalent bonds posses high bond energy : 450-1000 KJ/mole
- High bond strength in ionic and covalent solids results in high melting point, high strength and hardness. e.g. diamond
- As the electrons are tightly bound to the atoms they are generally poor conductors of heat and electricity.
- Are brittle in nature
- Most of the ceramics consist of covalent (SiC) or ionic bonds (Al_2O_3) or a mix of both and hence, exhibit all the properties described above.
- Metallic bonds on the other hand provide good thermal and electrical conductivities as the valence electrons are free to move.
- The metallic bond energy is 68 kJ/mol (Hg) on the lower side and 850 kJ/mol (W, tungsten) on the higher side.
- Bond strength increases with atomic number as more electrons are available to form the bonds with the ion cores. As a result melting point, hardness and strength increases with atomic number.
- Metals are ductile as the free moving electrons provides agility to the bonds and allows plastic deformation.

Vanderwaals bonding

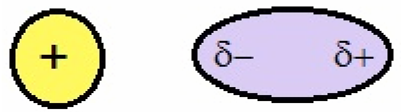
- Vanderwaals bonding between molecules or atoms arise due to weak attraction forces between dipoles.
- The natural oscillation of atoms leading to momentary break down of charge symmetry can generate temporary dipoles.



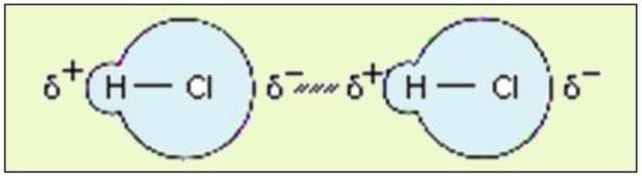
- Dipoles can induce dipoles and attraction between opposites ends of the dipoles leads to weak bonding.



- An ion can also induce a dipole

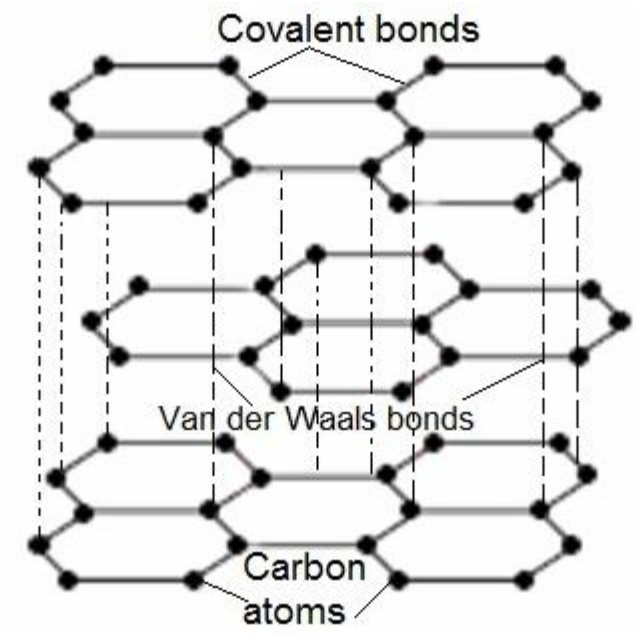


- Some molecules like HCl have permanent dipoles due to asymmetrical arrangement of +ve and –ve charges.



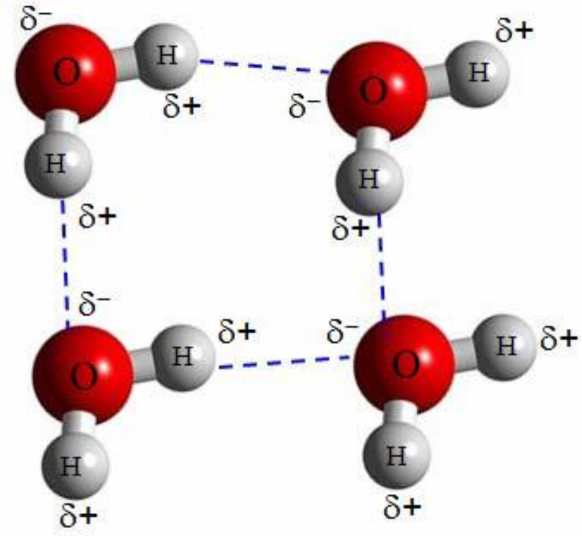
Vanderwaals bonding

- ❑ Van der Waals bonding is much weaker compared to primary bonds. Bond energy lies in the range of 2 – 10 kJ/mol
- ❑ Molecules in liquid and gas are held by weak Vanderwaals forces.
- ❑ The atomic layers in graphite are held together by weak vanderwaals bonds. Therefore, the layers can move easily over each other and this imparts the lubricating property graphite is known for.



Hydrogen bonding

- Hydrogen bond is a type of secondary bond found in molecules containing hydrogen as a constituent.
- The bond originates from electrostatic interaction between hydrogen and another atom of high electro-negativity such as fluorine or oxygen.
- The strength of hydrogen bonds is in the range of 10 - 50 kJ/mol.
- Water molecules, for example, are connected by hydrogen bonds (dashed lines in the picture).



Mixed bonding

- Many materials have a mixed bonding characteristics, between covalent and ionic bonding. Examples are as below.

Oxides:	% ionic bonding	~ 70%
Nitrides:	% ionic bonding	~ 40%
Carbides:	% ionic bonding	~ 15~20%

- Metallic-covalent Mixed Bonding: The transition metals are an example where s,p,d-bonding orbital's lead to high melting points.

Binding Energies of Bonds

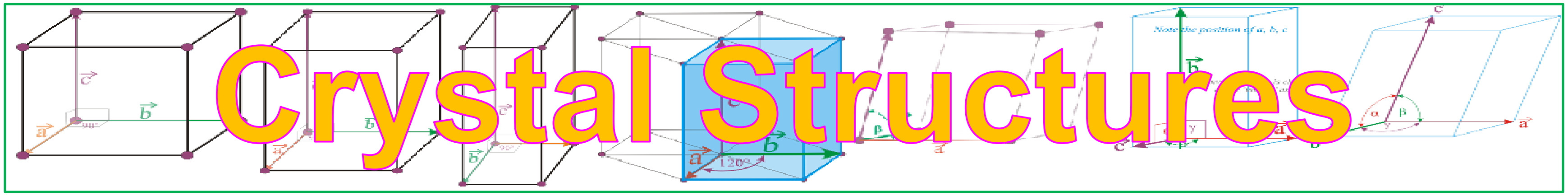
Bond Type	Energy (eV)	Energy (kJ/mole)	Energy (kJ/mole)
Ionic	~5-15 (strong)	~500-1000	NaCl: 640
Covalent	~1-10 (strong)	~100-1000	Diamond: ~710
Metallic	~0.5-8.5 (strong)	~50-850	Fe: 406
Hydrogen	~0.05-1.5	~5-155	H_2O: 51
Van der Walls	~0.01-0.5	~1-50	Ar:7.7

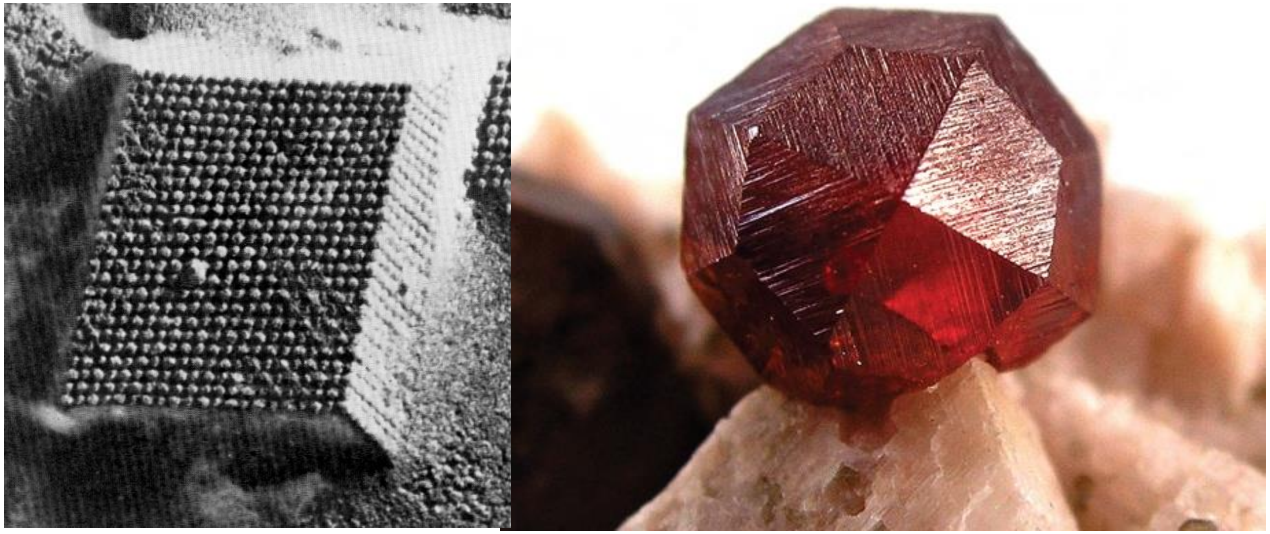
Questions?

1. Define atom, electron, proton and neutron
2. What is Pauli’s exclusion principle.
3. Define a solid. Glass is not considered as true solid
4. Why are noble gases inert?
5. Briefly explain the primary bonds in solids.
6. How do secondary bonds form? What is hydrogen bond?
7. Why is graphite lubricating?
8. Why are ceramics hard and brittle? Why are they not conductive?
9. How many atoms are there in 1 g of copper?
10. Why are some elements known as transition elements
11. Why is Tungsten (74) much stronger than Aluminium (13) though both are metallic?
12. Explain the arrangement of the elements in the periodic table


Thank You!

Crystal Structures





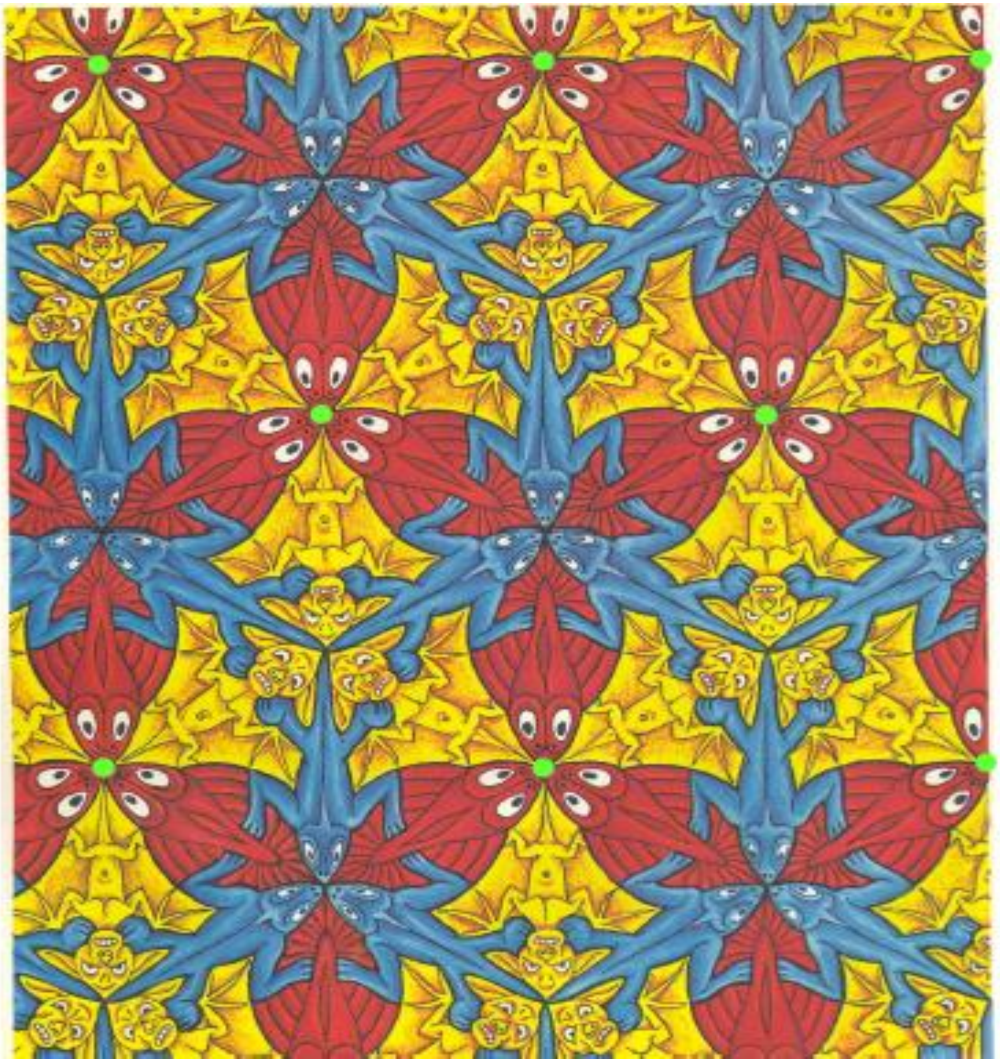
Avala Lava Kumar*

Department of Metallurgical & Materials Engineering (MME)

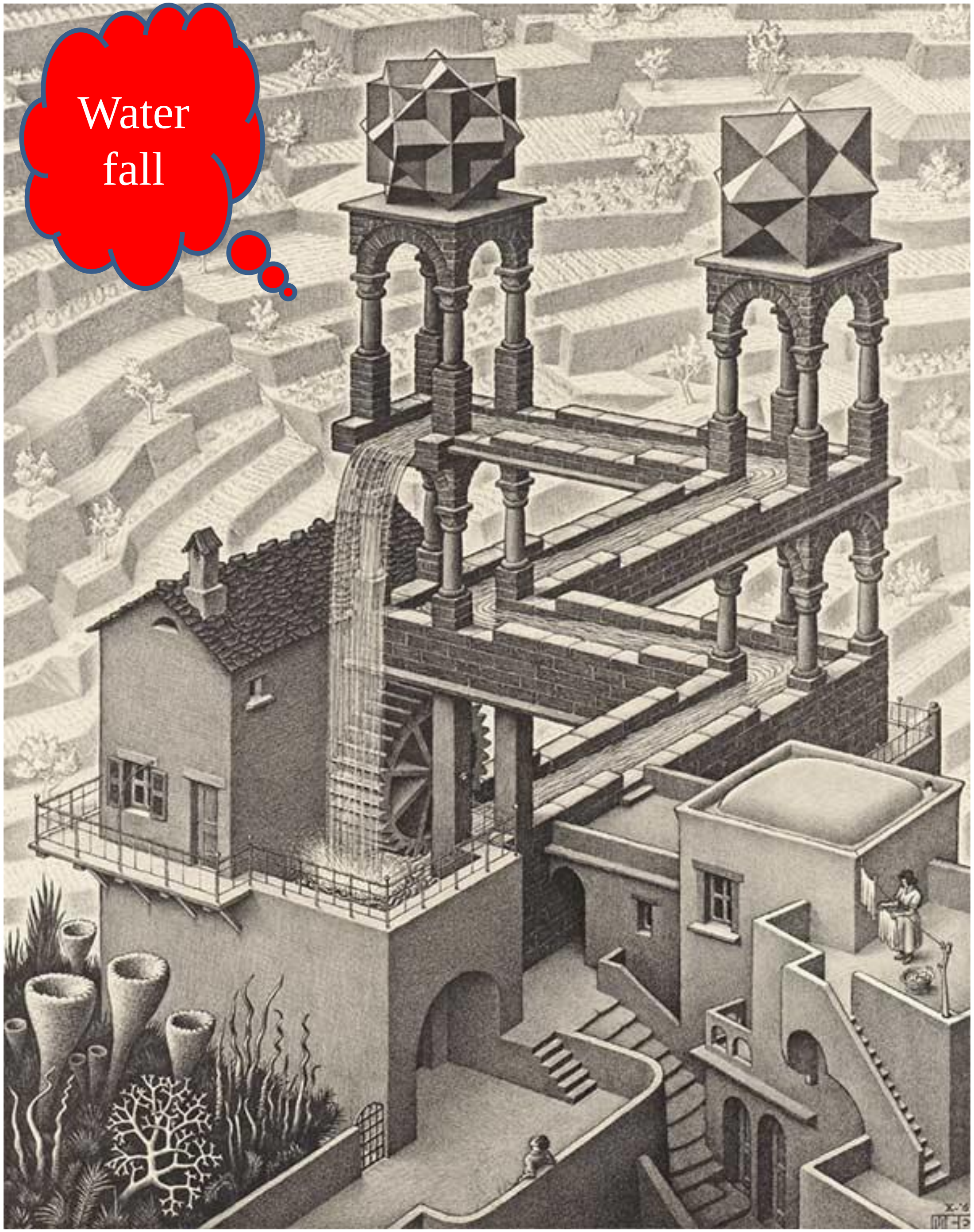
Veer Surendra Sai University of Technology (VSSUT), Burla -768018

**E-mail : lavakumaravala@gmail.com*

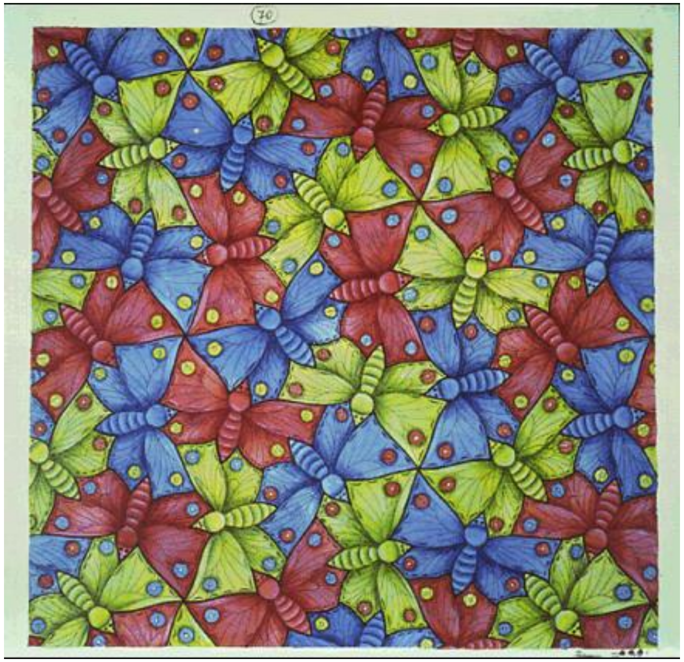
M.C. Esher : Art with Science



Every periodic pattern (and hence a Crystal) has a unique lattice associate with it.



Water fall



Why study crystal structures?

- ❑ When we look around much of what we see is non-crystalline (organic things like wood, paper, sand; concrete walls, etc. → some of the things may have some crystalline parts!).
- ❑ But, many of the common 'inorganic' materials are *'usually***'* crystalline:
  - ◘ Metals: Cu, Zn, Fe, Cu-Zn alloys
  - ◘ Semiconductors: Si, Ge, GaAs
  - ◘ Ceramics: Alumina (Al_2O_3), Zirconia (Zr_2O_3), SiC, $SrTiO_3$
- ❑ Also, the usual form of crystalline materials (say a Cu wire or a piece of alumina) is polycrystalline and special care has to be taken to produce single crystals
- ❑ Polymeric materials are *usually* not 'fully' crystalline
- ❑ The crystal structure directly influences the properties of the material

Why study crystallography?

- ❑ Gives a terse (concise) representation of a large assemblage of species
- ❑ Gives the 'first view' towards understanding of the properties of the crystal

---

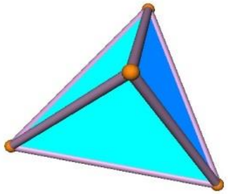
* *Many of the materials which are usually crystalline can also be obtained in an amorphous form*

Platonic Solids

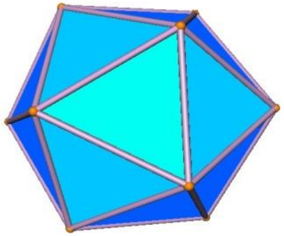
- ❑ In 387B.C. scientist called “PLATO” most famous student of Socrates thought that whole universe is made up of five solids. Whole universe is periodic arrangement of five solids named as Platonic Solids.
  - Tetrahedron - 4 *faces* - *Fire*
  - Hexahedron - 6 *faces* - *Earth*
  - Octahedron - 8 *faces* - *Air*
  - Dodecahedron - 12 *faces* - *GOD*
  - Icosahedron - 20 *faces* - *Water*

He had a some philosophical thought; in the universe we have 5 elements made up of these five solids

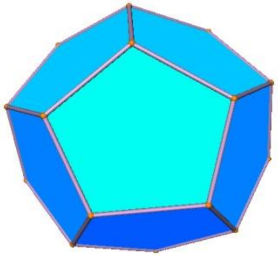
- ❑ In icosahedron, we will get best packing as for we concerned. But only problem is, if we try to translate it in 3D we can’t get continuous structure, without any voids left. This voids in crystallography is called *frustation.*
- ❑ Long back people thought, it is not possible to have solids with Icosahedron packing; but it is possible when Quasicrystals are discovered in 1984. (Al-Mn)



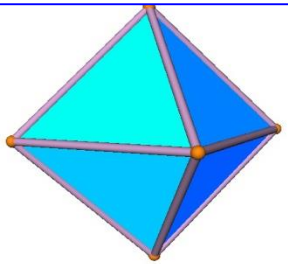
Tetrahedron



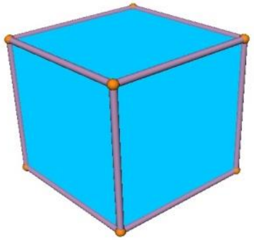
Icosahedron



Dodecahedron

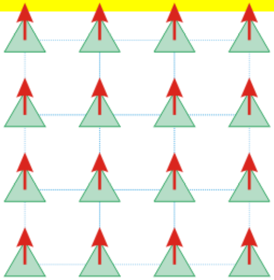


Octahedron



Cube

Ideal Crystals → Real Crystals → Microstructures → Material → Component

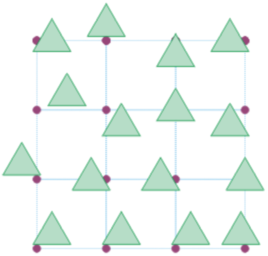


Ideal Mathematical Crystal

Ideal Crystal

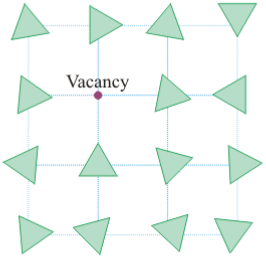
Consider only the Orientational
or
Positional Order

Crystal



Put in Crystalline defects
& Free Surface
& Thermal Vibration

'Real Crystal'



Put in Multiple Crystals *(Phases)*
giving rise to interfacial defects

~Microconstituents

Put multiple ~microconstituents
Add additional residual stress[†]

Microstructure

Material

Material or Hybrid

Component

Real materials are usually complex and we start with ideal descriptions

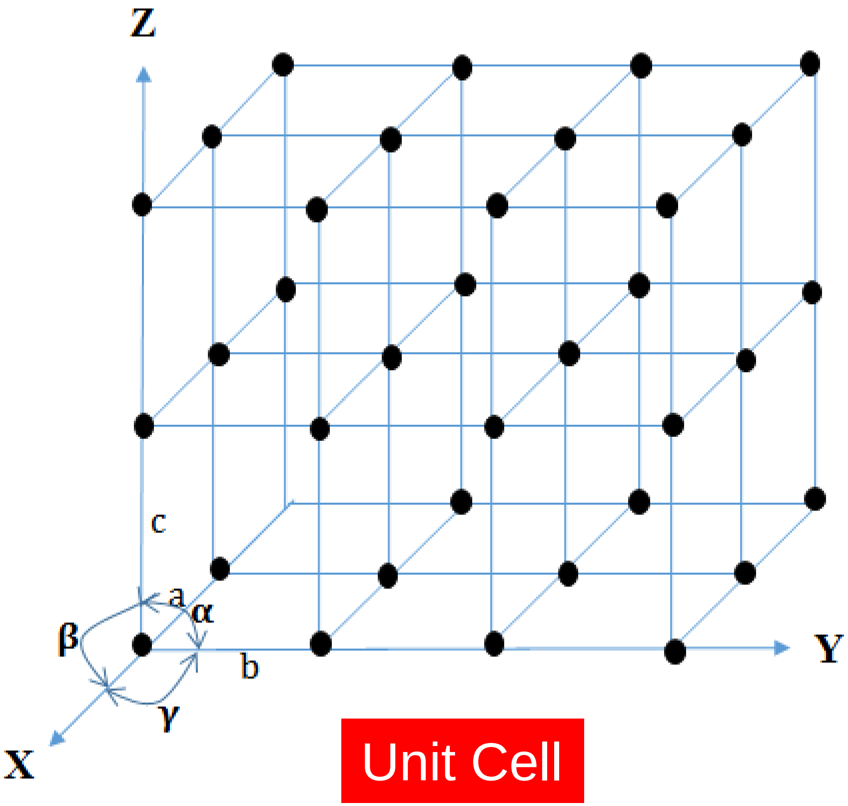
How to define a Crystal?

Crystal

A 3D translationally periodic arrangement of atoms in a space is called a crystal.

Lattice

A 3D translationally periodic arrangement of points in a space is called a crystal.



Unit Cell

What is the relation between the two ?

Crystal = Lattice + Motif

***Motif* or *Basis*:**

typically an atom or a group of atoms associated with each lattice point

Lattice ➢ The underlying periodicity of the crystal

Basis ➢ Entity associated with each lattice points

Lattice ➢ how to repeat

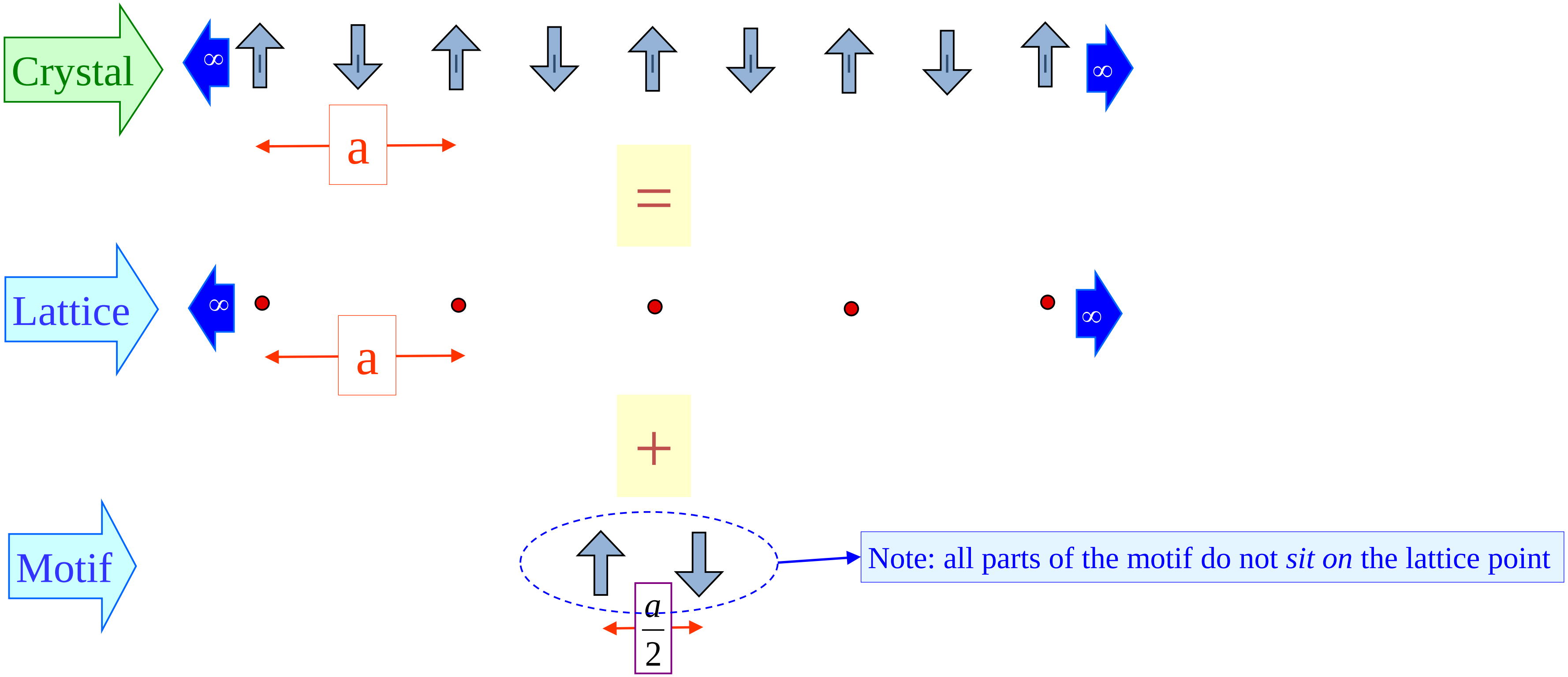
Motif ➢ what to repeat

Lattice	Crystal
Translationally periodic arrangement of points	**Translationally periodic arrangement of motifs**

What is the relation between the two ?

Crystal =

Lattice *(Where to repeat)*+**Motif** *(What to repeat)*

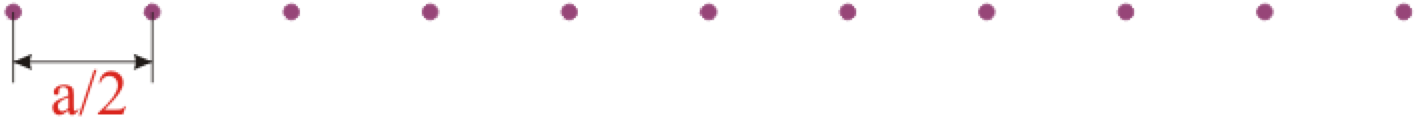


Note: all parts of the motif do not *sit on* the lattice point

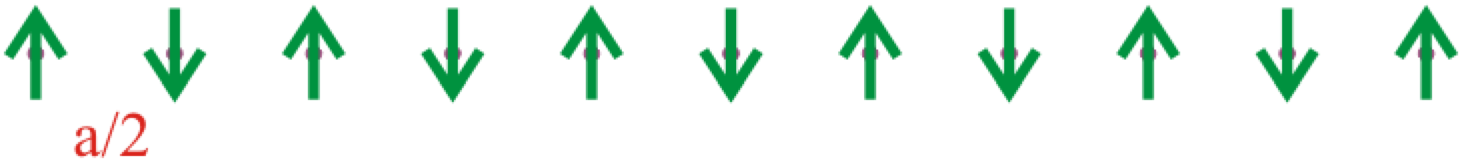
Motifs are associated with lattice points → they need NOT *sit* physically at the lattice point

Example

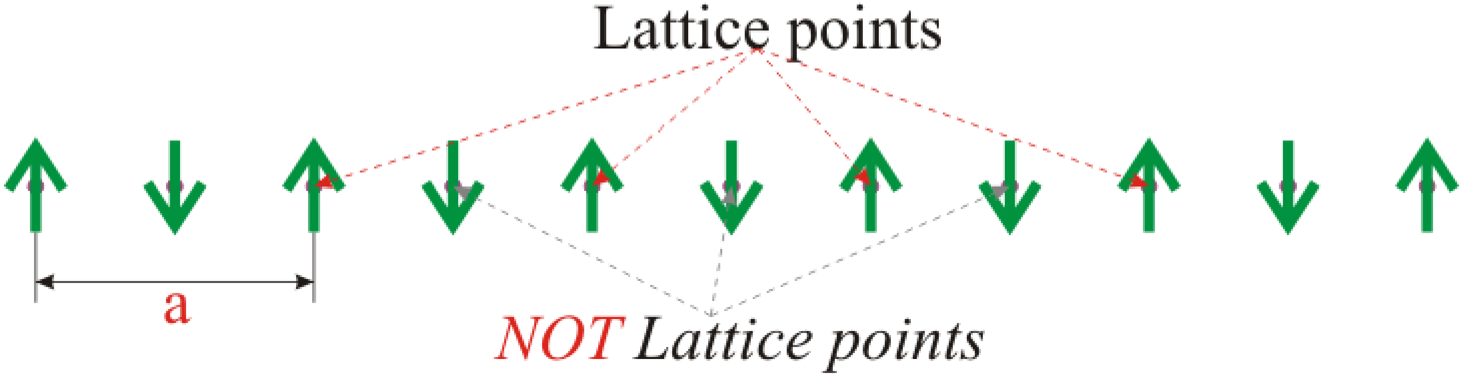
Let us construct the crystal considered before starting with an infinite array of points spaced a/2 apart



Put arrow marks pointing up and down alternately on the points:



What we get is a crystal of lattice parameter 'a' and not 'a/2'! → *as this lattice parameter is a measure of the repeat distance!*



And the motif is:
↑ + ↓

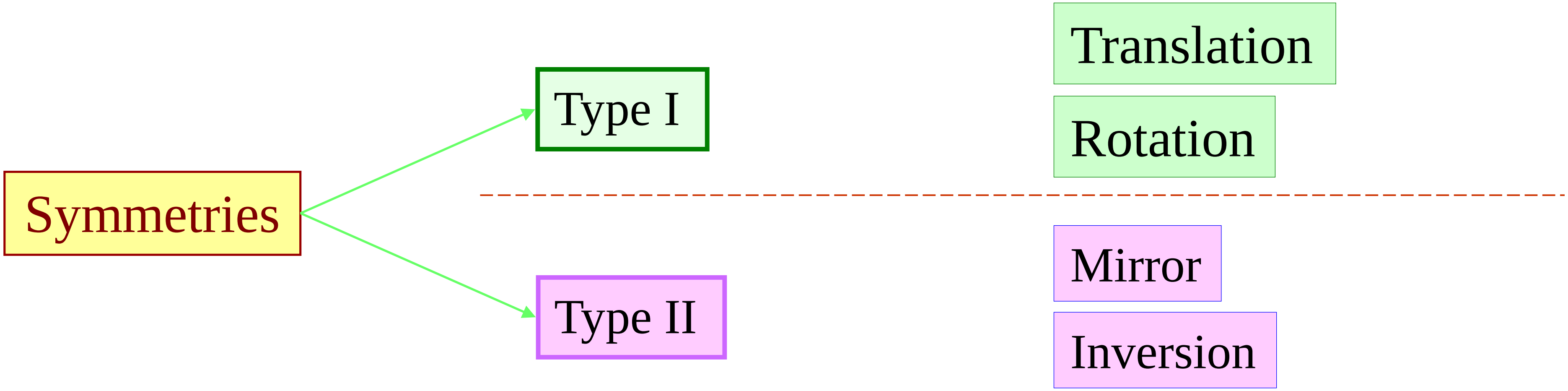
Note: we could have alternately chosen the centres of bottom arrows as lattice points!

Why study symmetry..?

- Crystals are an important class of materials.
- Crystals (and in fact quasicrystals) are defined based on symmetry.
- Symmetry helps reduce the *'infinite'* amount of information required to describe a crystal into a finite *(preferably small)* amount of information.
- In crystallography (the language of describing crystals) when we talk of Symmetry; the natural question which arises is: *Symmetry of What?*
- The symmetry under consideration could be of one the following entities:

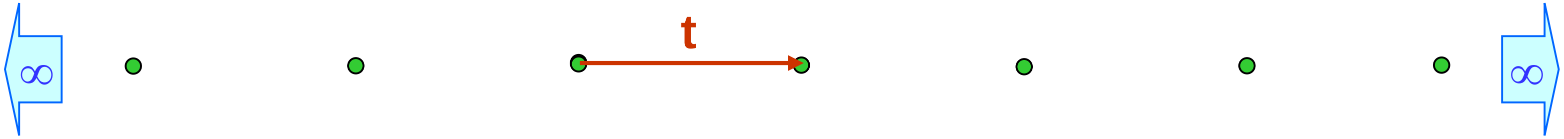
➢ Lattice ➢ Crystal ➢ Motif ➢ Unit cell

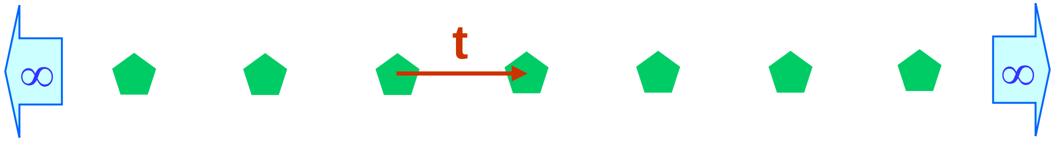
Symmetry can be defined as, if an object is brought into self-coincidence after some operation it said to possess symmetry with respect to that operation.



Translation

- The translation symmetry operator (t) moves an point or an object by a displacement **t** or a distance t.
- A periodic array of points or objects is said to posses translational symmetry.
- Translational symmetry could be in 2D or 3D (or in general nD).
- If we have translational symmetry in a pattern then instead of describing the entire pattern we can describe the 'repeat unit' and the translation vector(s).

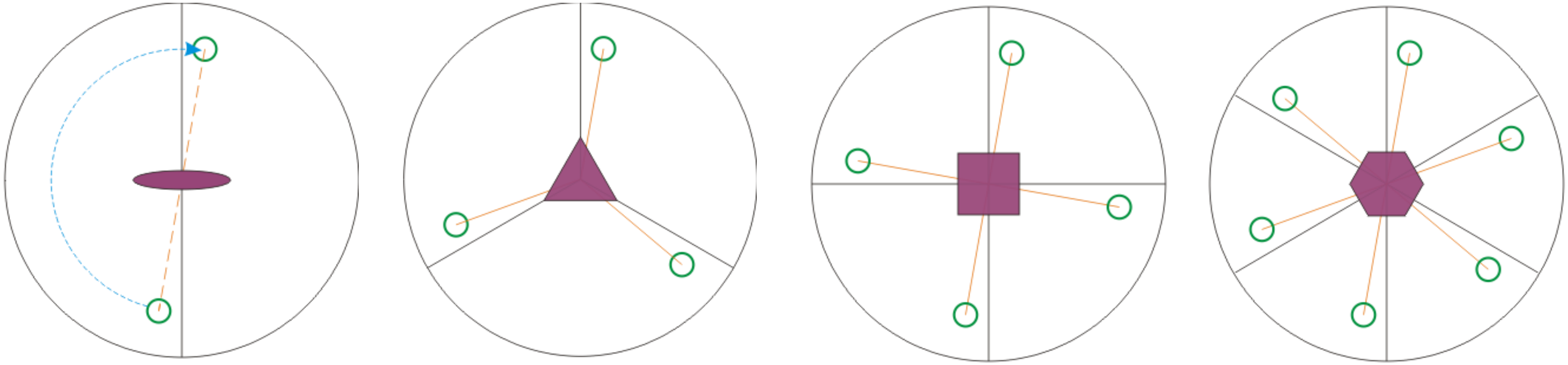




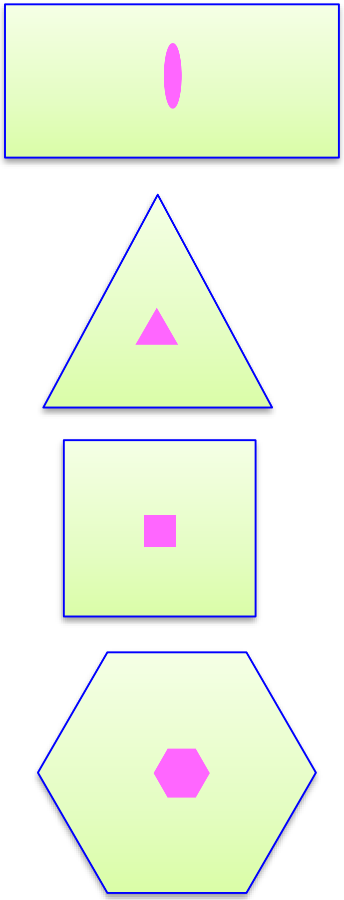
Rotation Axis

- Rotation axis rotates a general point (and hence entire space) around the axis by a certain angle
- On repeated operation (rotation) the 'starting' point leaves a set of 'identity-points' before coming into coincidence with itself.
- As we are interested mainly with crystals, we are interested in those rotations axes which are compatible with translational symmetry → these are the (1), 2, 3, 4, 6 – fold axis.
- If an object come into self-coincidence through smallest non-zero rotation angle of θ then it is said to have an n-fold rotation axis where:

$$n = \frac{360^0}{\theta}$$



Rotational Symmetry



θ=180°	n=2	2-fold rotation axis
θ=120°	n=3	3-fold rotation axis
θ=90°	n=4	4-fold rotation axis
θ=60°	n=6	6-fold rotation axis

The rotations compatible with translational symmetry are ⇨ (1, 2, 3, 4, 6)

⇒ Crystals can *only* have 1, 2, 3, 4 or 6 fold symmetry

Examples of Rotational Symmetry

Angles

180° 120° 90° 72 ° 60° 45°

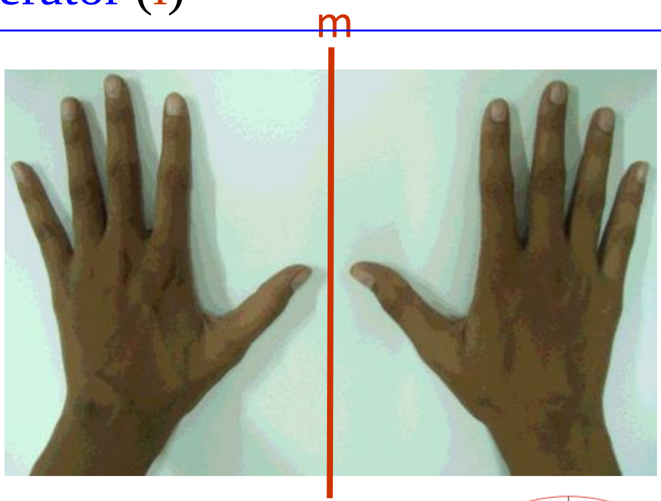
Fold

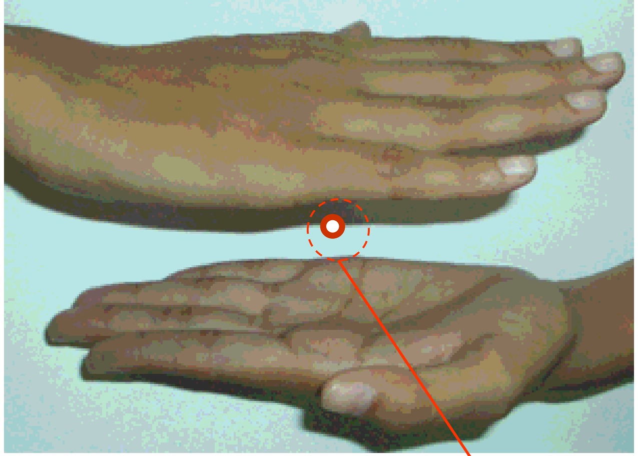
2 3 4 5 6 8

Graphic Symbol

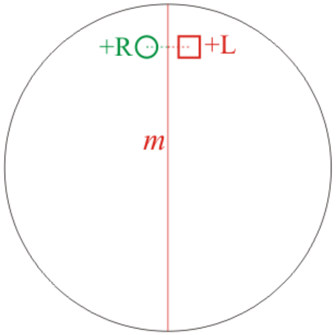
Mirror and Inversion

- The left hand of a human being cannot be superimposed on the right hand by mere translations and rotations
- The left hand is related to the right hand by a mirror symmetry operation (m)
- The right hand is called the *enantiomorphic form* of the left hand
- Another operator which takes objects to enantiomorphic forms is the inversion operator (i)

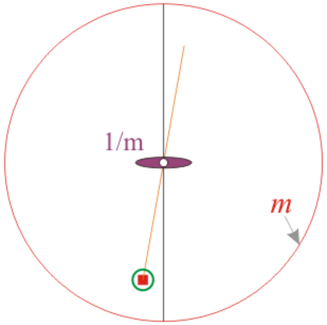




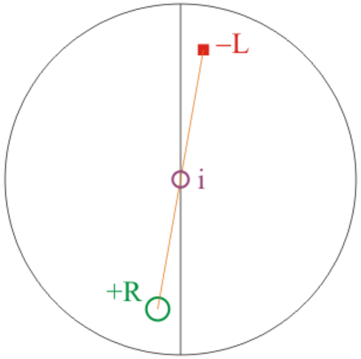
Inversion operator



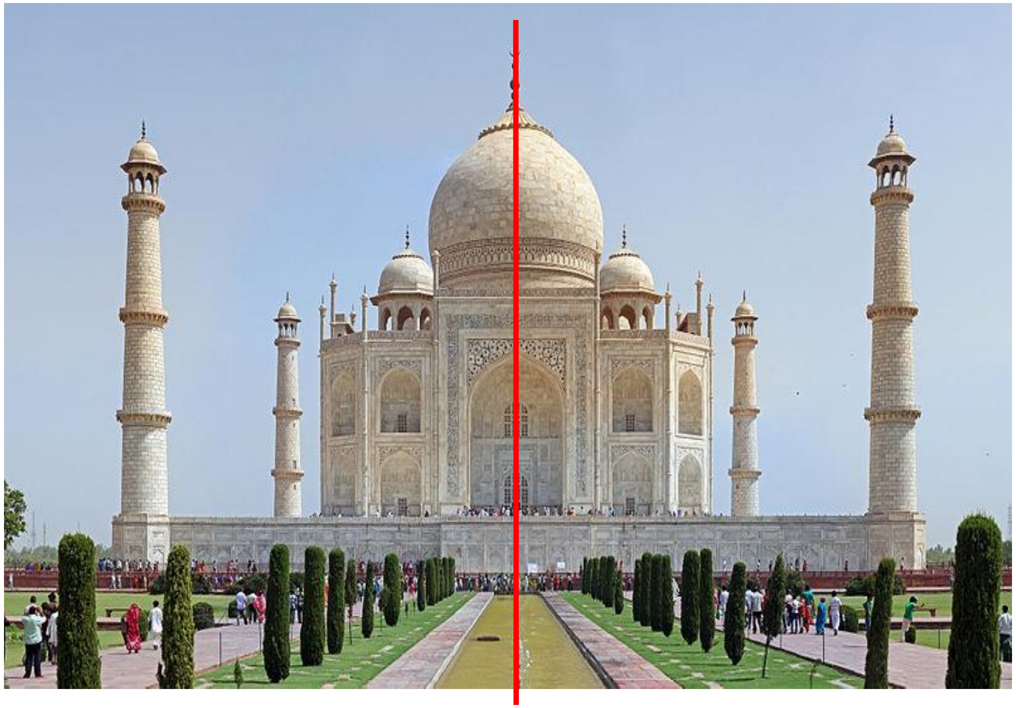
Vertical Mirror



Horizontal Mirror



Reflection (or mirror symmetry)

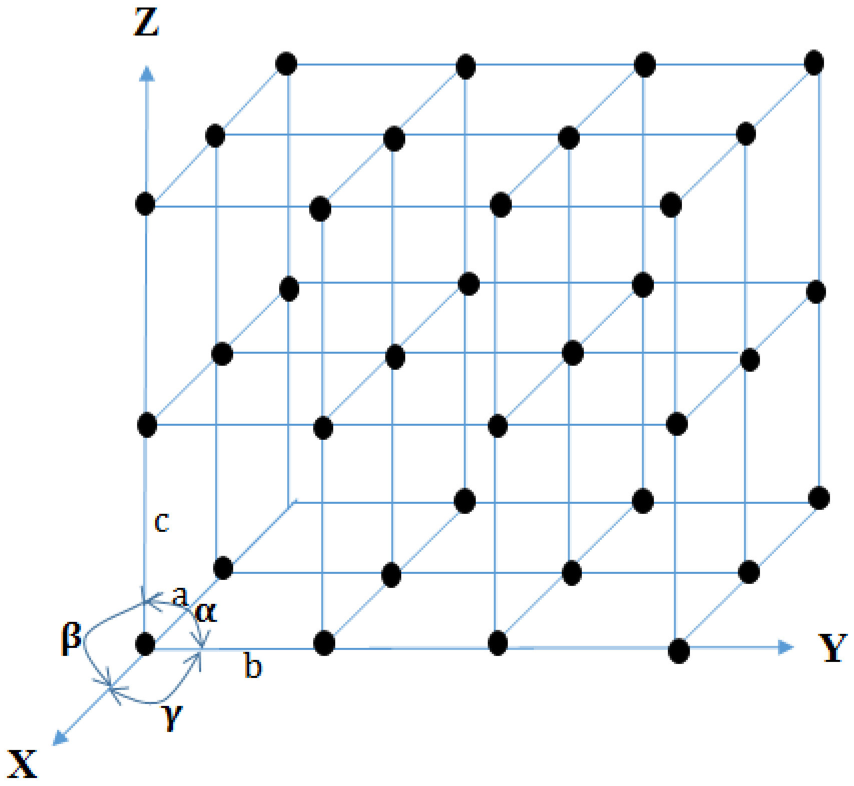


Unit Cells (UC)

- An unit cell *(also sometimes causally referred to as a cell)* is a representative unit of the structure
  - ✓ Instead of drawing the whole structure I can draw a representative part and specify the repetition pattern
- If the structure under considerations is a crystal, then the unit cell will also contain atoms (or ions or molecules etc.)
- The dimension of the unit cell will match the dimension of the structure; If the lattice is 1D the unit cell will be 1D, if the crystal is 3D then the unit cell will be 3D, if the lattice is nD the unit cell will be nD.
- If the lattice points are *only* at the corners, the cell is **primitive**.
- If there are lattice points in the cell other than the corners, the cell is **non-primitive**.

3D Unit Cell

- In order to define translations in 3-D space, we need 3 non-coplanar vectors
- Conventionally, the fundamental translation vector is taken from one lattice point to the next in the chosen direction
- With the help of these three vectors, it is possible to construct a parallelopiped called a UNIT CELL



Crystal Structures (or) 14 Bravais Lattices

A Symmetry based concept

‘Translation’ based concept

	Crystal System	Lattice Parameters	Bravais Lattices			
			P	I	F	C
1	Cubic	$(a = b = c, \alpha = \beta = \gamma = 90^\circ)$	✓	✓	✓	
2	Tetragonal	$(a = b \neq c, \alpha = \beta = \gamma = 90^\circ)$	✓	✓		
3	Orthorhombic	$(a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ)$	✓	✓	✓	✓
4	Hexagonal	$(a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ)$	✓			
5	Trigonal	$(a = b = c, \alpha = \beta = \gamma \neq 90^\circ)$	✓			
6	Monoclinic	$(a \neq b \neq c, \alpha = \gamma = 90^\circ \neq \beta)$	✓			✓
7	Triclinic	$(a \neq b \neq c, \alpha \neq \beta \neq \gamma)$	✓			

P	Primitive
I	Body Centred
F	Face Centred
C	End Centred

Bravais Lattice: various viewpoints

- A lattice is a set of points constructed by translating a single point in discrete steps by a set of basis vectors.

- In three dimensions, there are 14 unique **Bravais** lattices (distinct from one another) in three dimensions. All crystalline materials recognized till now fit in one of these arrangements.

- In geometry and crystallography, a **Bravais lattice** is an infinite set of points generated by a set of discrete translation operations.

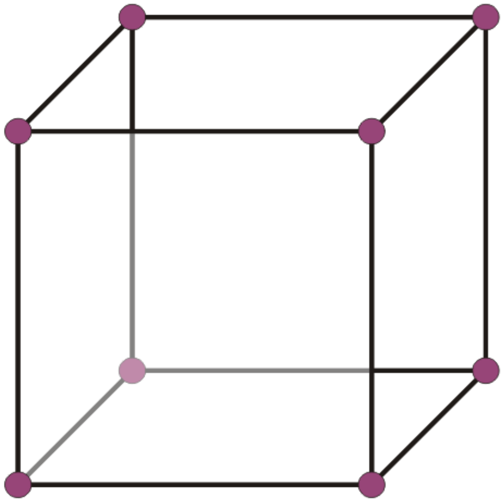
- A Bravais lattice looks exactly the same no matter from which point in the lattice one views it.

An important property of a lattice

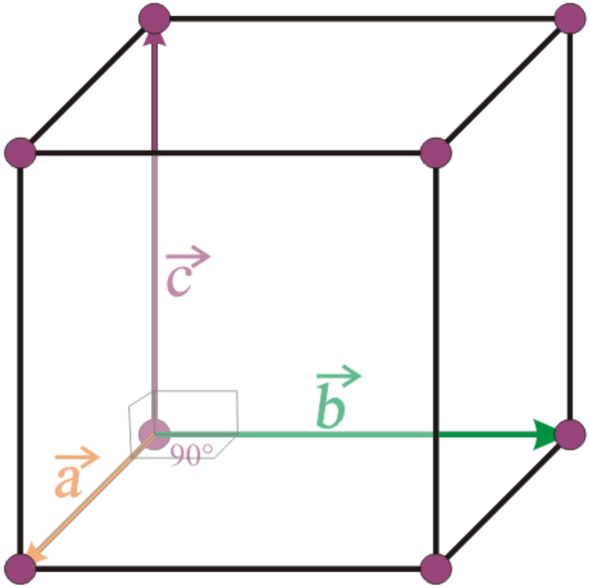
- Bravais concluded that there are only **14** possible Space Lattices (with Unit Cells to represent them). These belong to **7** Crystal systems.

- There are 14 Bravais Lattices which are the Space Group symmetries of lattices

			P	I	F	C
1	Cubic	Cube	✓	✓	✓	

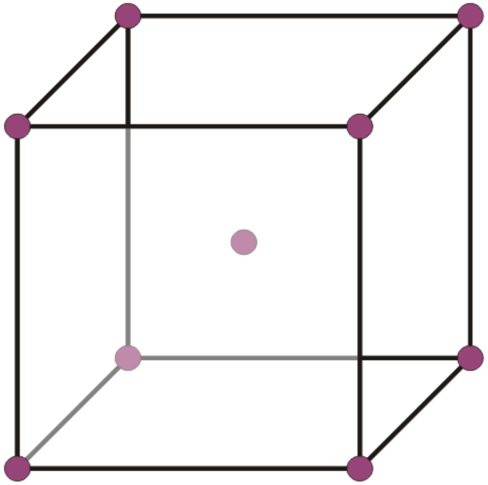


P



$a = b = c$

$\alpha = \beta = \gamma = 90°$



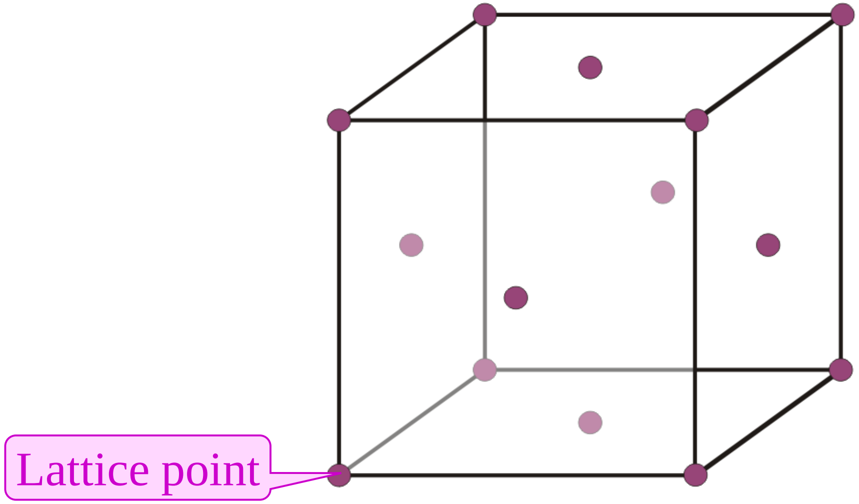
I

- Elements with Cubic structure →

  SC: F, O, Po

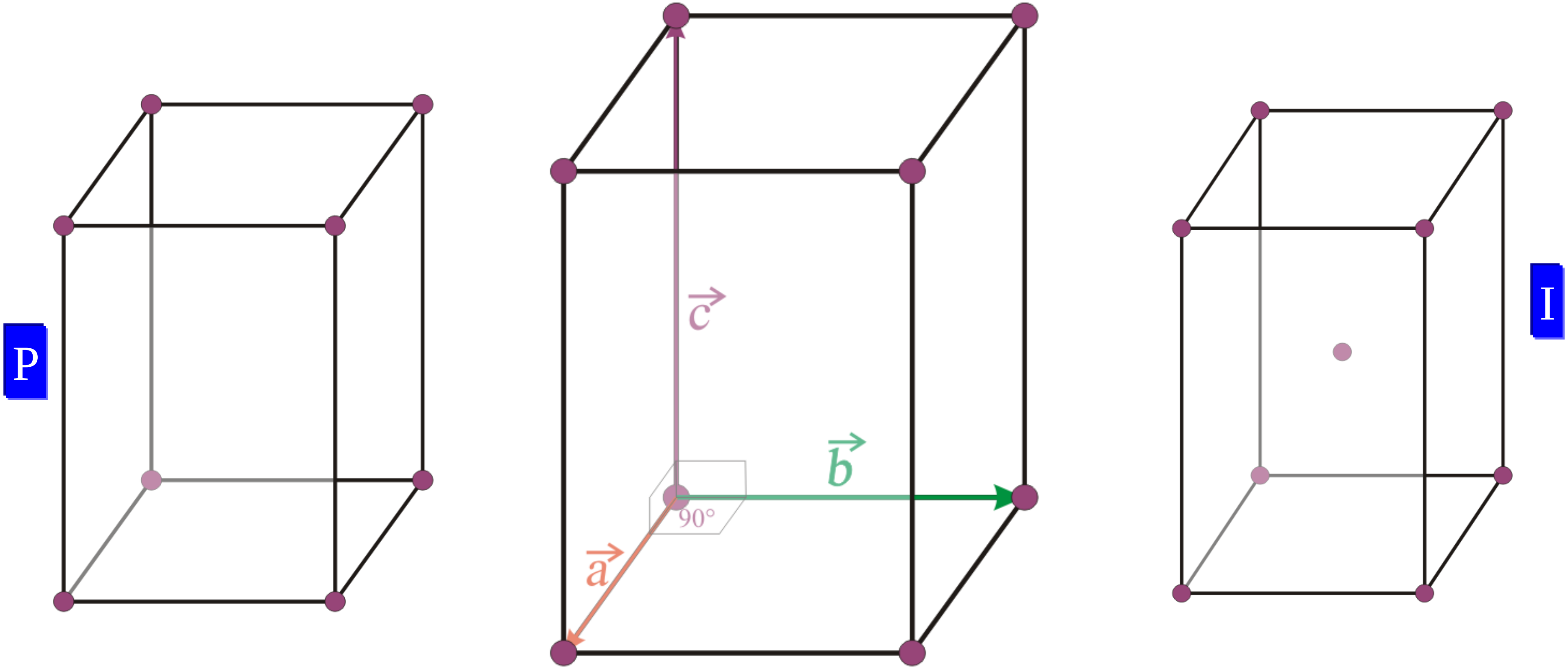
  BCC: Cr, Fe, Nb, K, W, V

  FCC: Al, Ar, Pb, Ni, Pd, Pt, Ge



F

			P	I	F	C
2	Tetragonal	Square Prism (general height)	✓	✓		

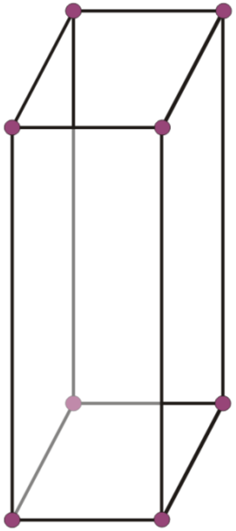


$$\boxed{a = b \neq c}$$

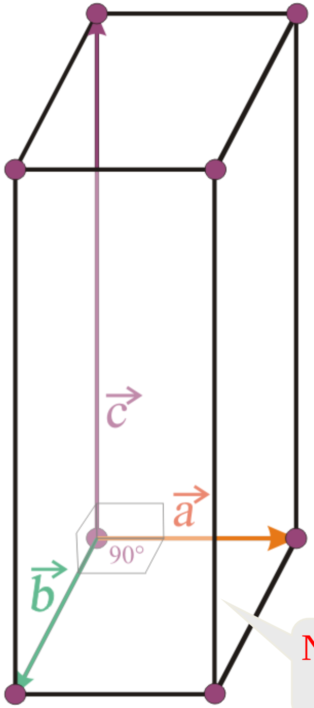
$$\boxed{\alpha = \beta = \gamma = 90^\circ}$$

- Elements with Tetragonal structure → In, Sn

			P	I	F	C
3	Orthorhombic	Rectangular Prism (general height)	✓	✓	✓	✓

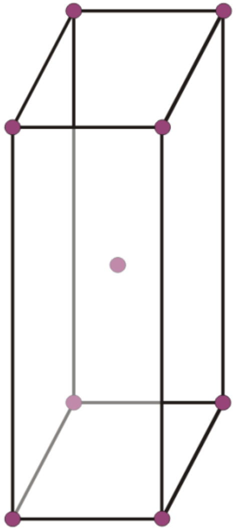


P



One convention

$a < b < c$

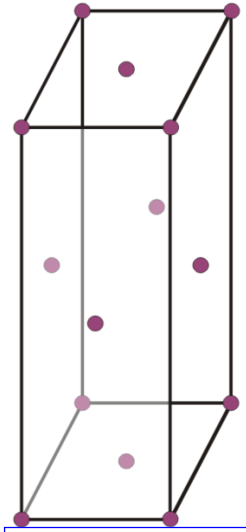


I

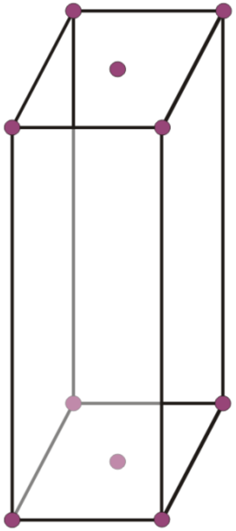
Note the position of ‘a’ and ‘b’

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90°$



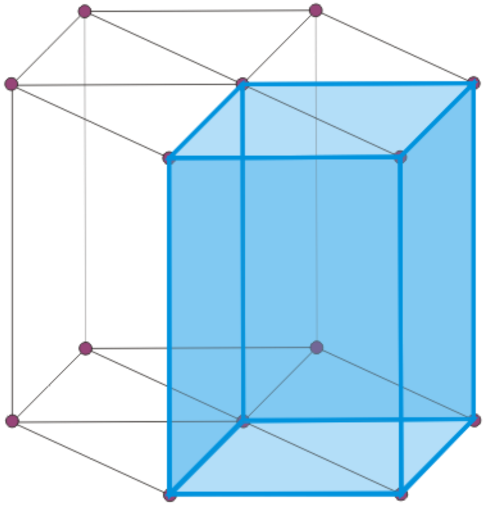
F



C

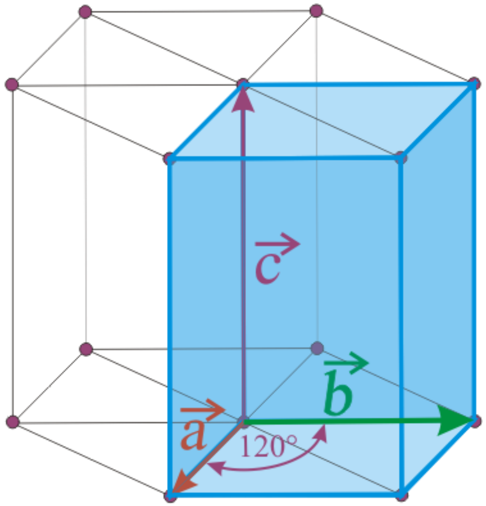
- Elements with Orthorhombic structure → Br, Cl, Ga, I, Su

			P	I	F	C
4	Hexagonal	120° Rhombic Prism	✓			



$$a = b \neq c$$

$$\alpha = \beta = 90^\circ,\ \gamma = 120^\circ$$



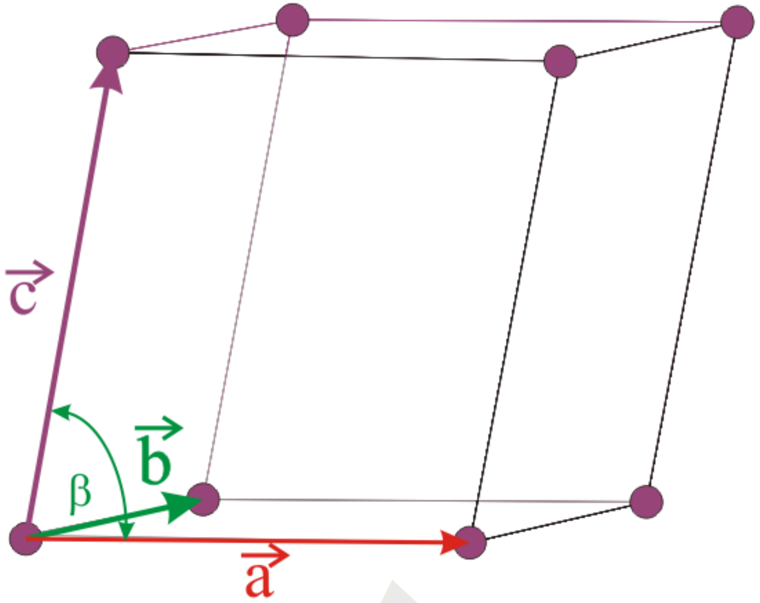
A single unit cell *(marked in blue) along with a 3-unit cells forming a hexagonal prism*

- Elements with Hexagonal structure → Be, Cd, Co, Ti, Zn

Note: there is only one type of hexagonal lattice *(the primitive one)*

What about the HCP?
(Does it not have an additional atom somewhere in the middle?)

			P	I	F	C
5	Trigonal / *Rhombohedral*	Parallelepiped (Equilateral, Equiangular)	✓			



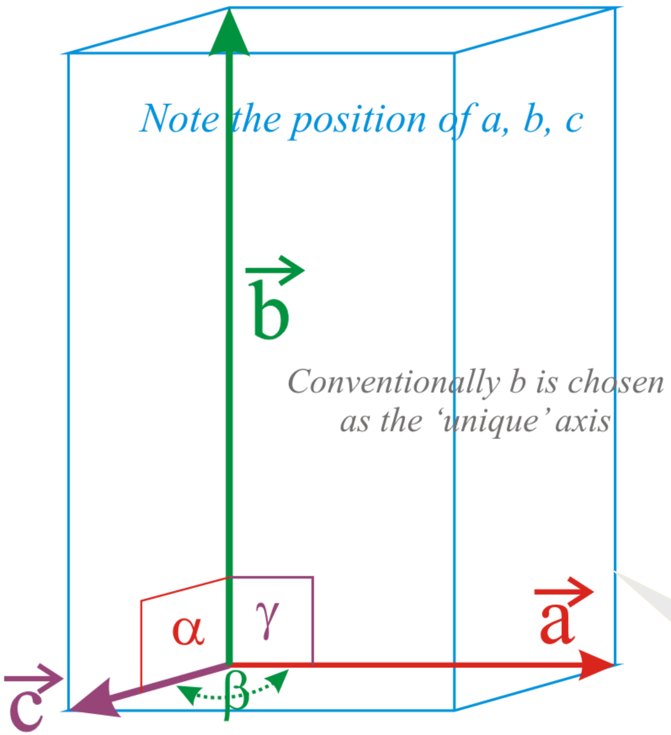
Note the position of the origin and of ‘a’, ‘b’ & ‘c’

$$\boxed{a = b = c}$$

$$\boxed{\alpha = \beta = \gamma \neq 90^\circ}$$

- Elements with Trigonal structure → As, B, Bi, Hg, Sb, Sm

			P	I	F	C
6	Monoclinic	Parallogramic Prism	✓			✓



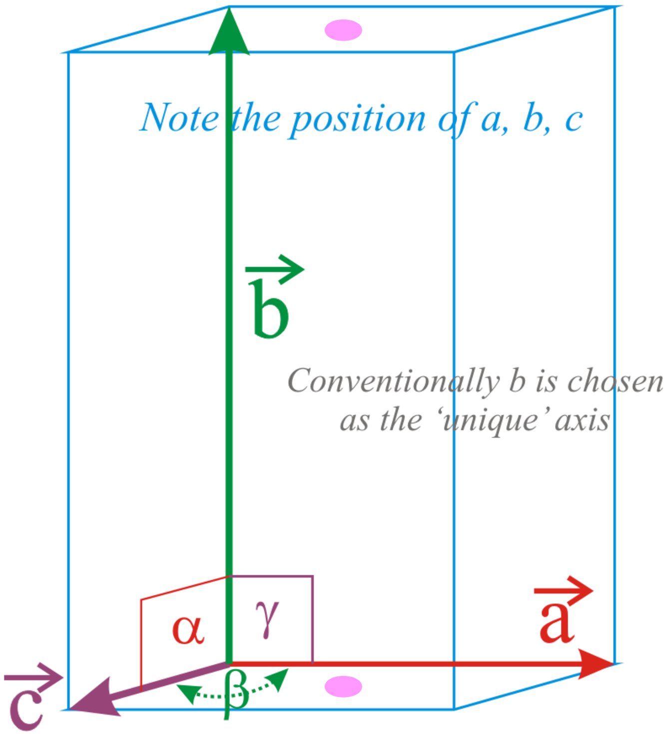
Note the position of 'a', 'b' & 'c'

One convention

$$a < b < c$$

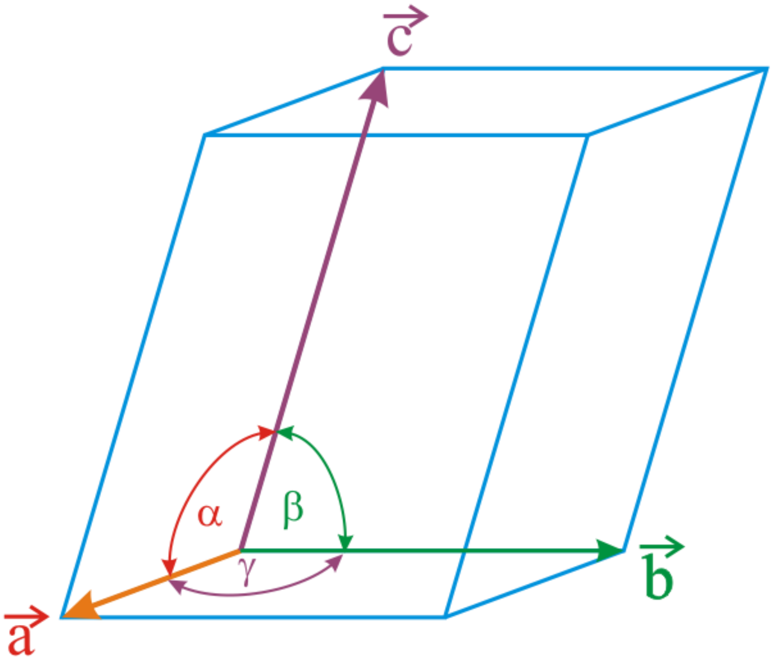
$$\boxed{a \neq b \neq c}$$

$$\boxed{\alpha = \gamma = 90^\circ \neq \beta}$$



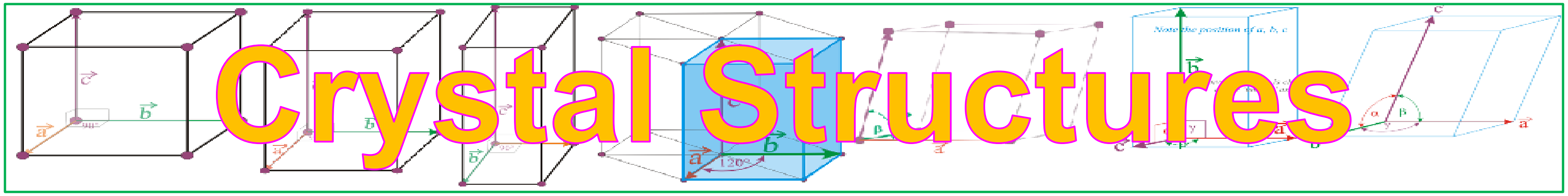
- Elements with Monoclinic structure → P, Pu, Po

			P	I	F	C
7	Triclinic	Parallelepiped (general)	✓			



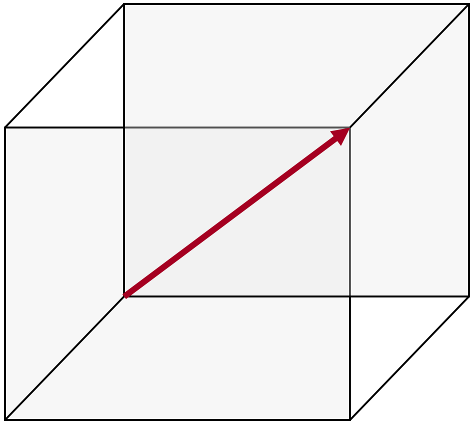
$\boxed{a \neq b \neq c}$

$\boxed{\alpha \neq \beta \neq \gamma}$

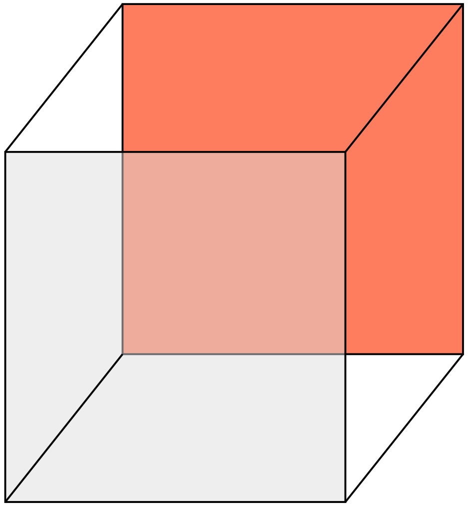


Crystal Structures

MILLER INDICES



- PLANES
- DIRECTIONS

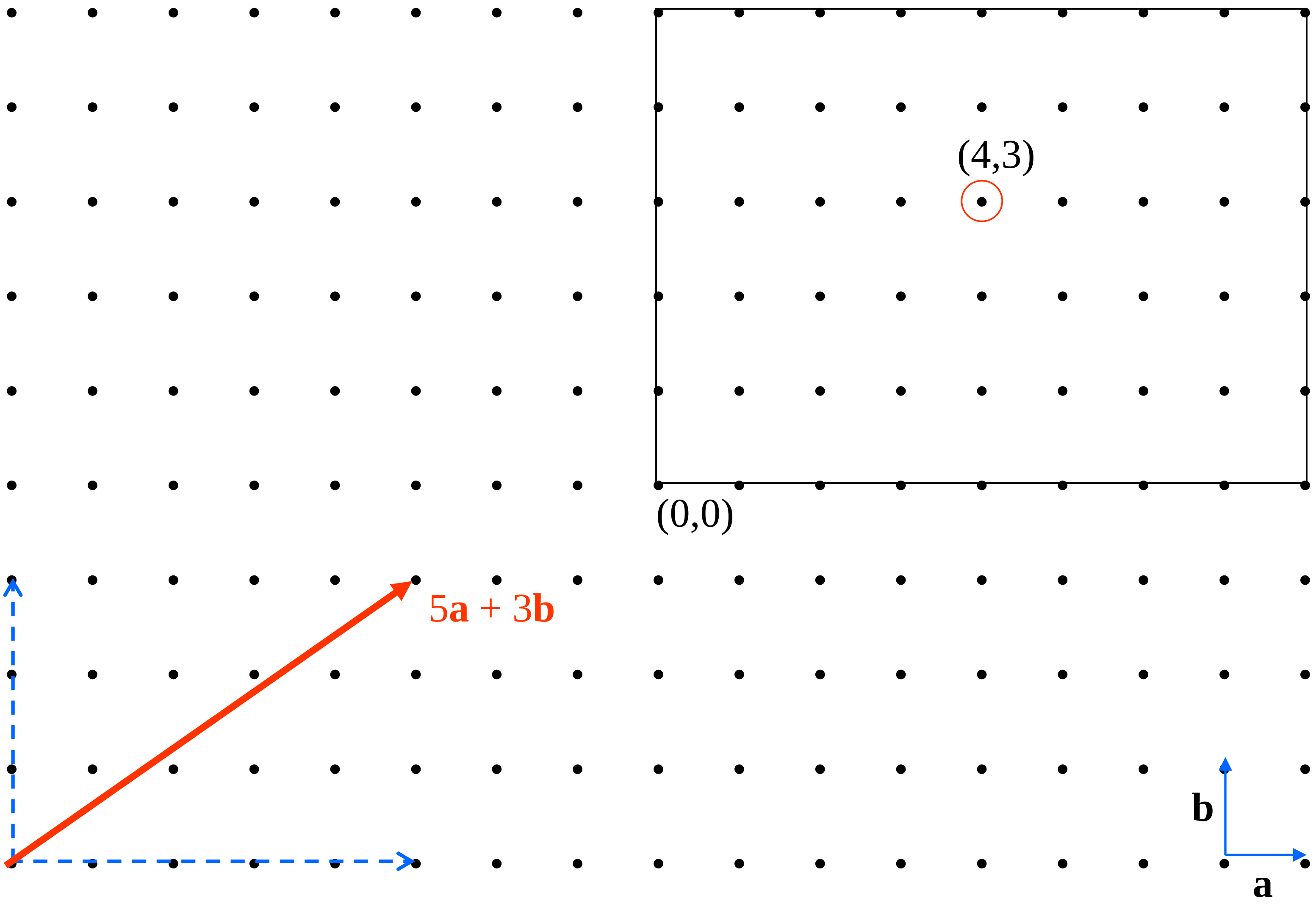


From the law of rational indices developed by French Physicist and mineralogist
Abbé René Just Haüy
and popularized by
William Hallowes Miller

Miller Indices

- Miller indices are used to specify directions and planes.
- These directions and planes could be in lattices or in crystals.
- The number of indices will match with the dimension of the lattice or the crystal: in 1D there will be 1 index and 2D there will be two indices etc.
- Some aspects of Miller indices, especially those for planes, are not intuitively understood and hence some time has to be spent to familiarize oneself with the notation.

Miller Indices for directions in 2D

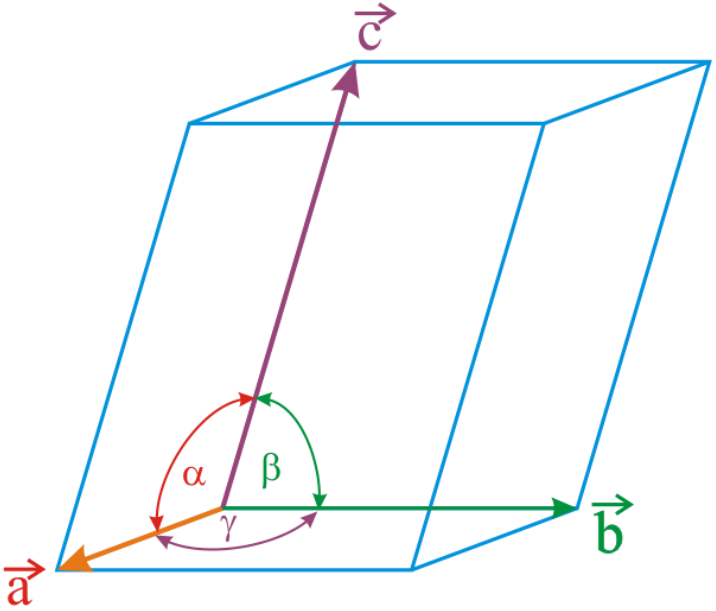


Miller indices → [53]

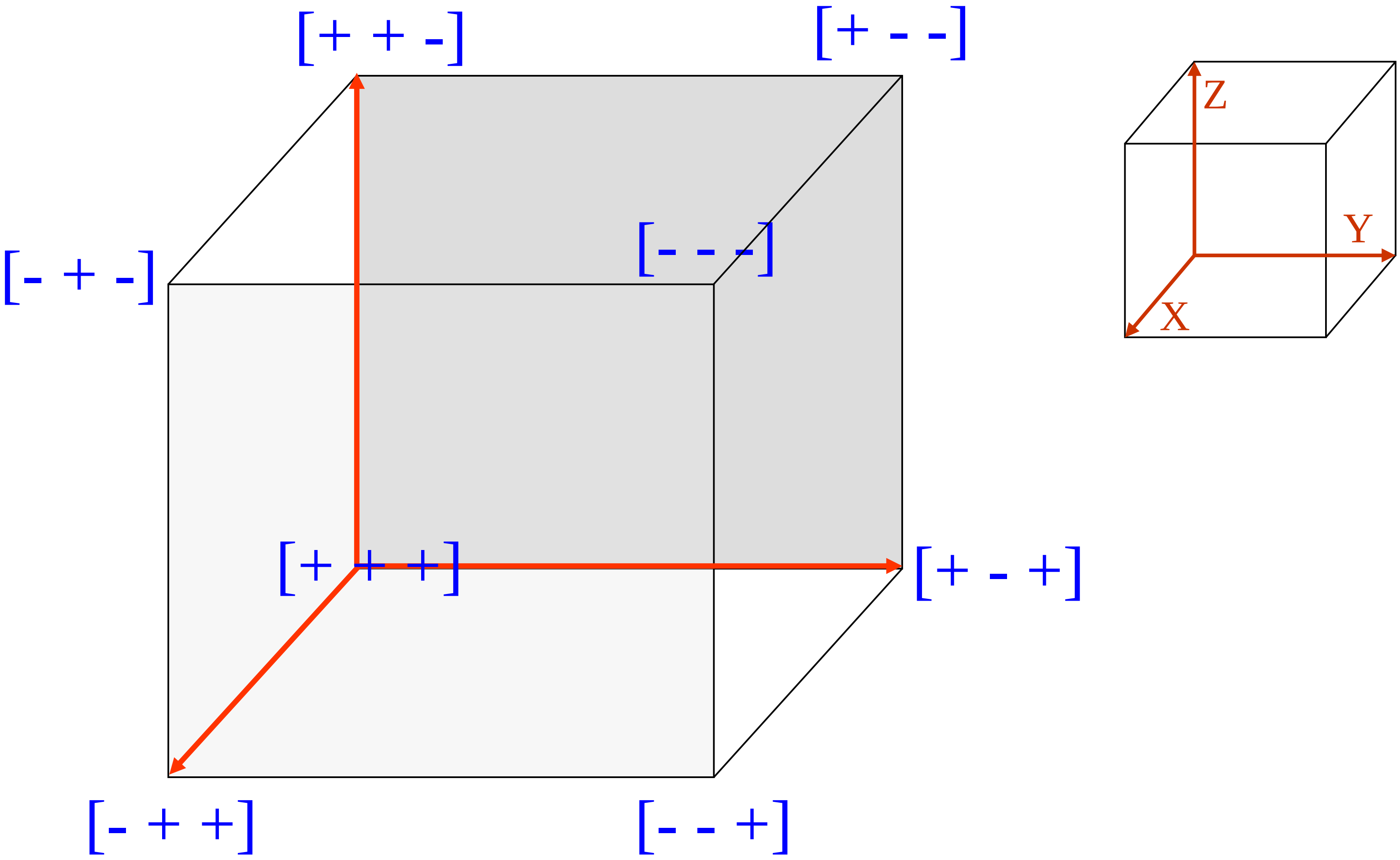
Miller indices for directions in 3D

- ❑ A vector **r** passing from the origin to a lattice point can be written as
- ❑ **r** = r_1 **a** + r_2 **b** + r_3 **c**
- ❑ Where, **a**, **b**, **c** → basic vectors
- ❑ Basis vectors are unit lattice translation vectors which define the coordinate axis *(as in the figure below).*
- ❑ *Note their length is not 1 unit! (like for the basis vectors of a coordinate axis).*

$$\boxed{r = r_1\,\vec{a} + r_2\,\vec{b} + r_3\,\vec{c}}$$



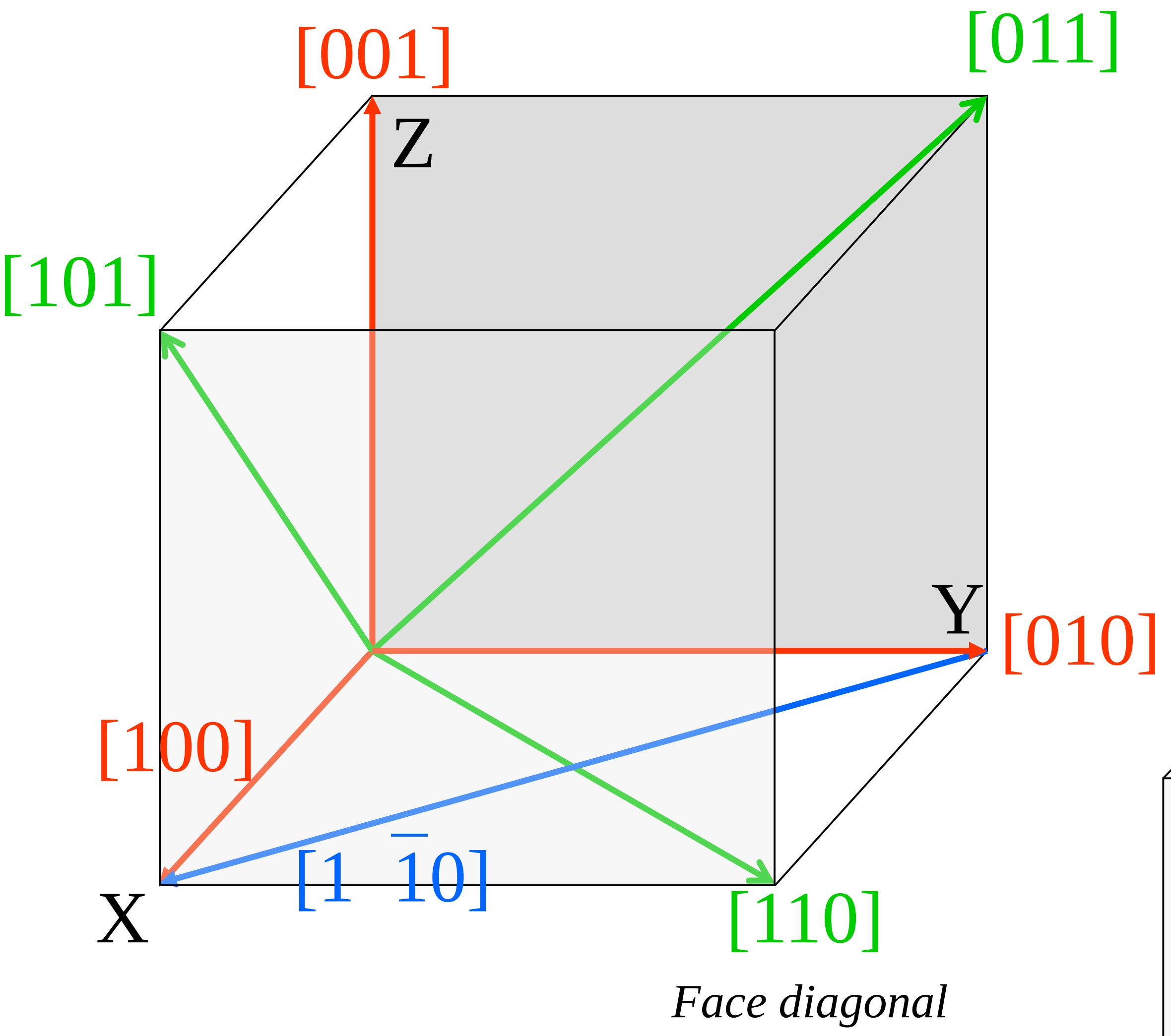
Possible coordinates in 3D

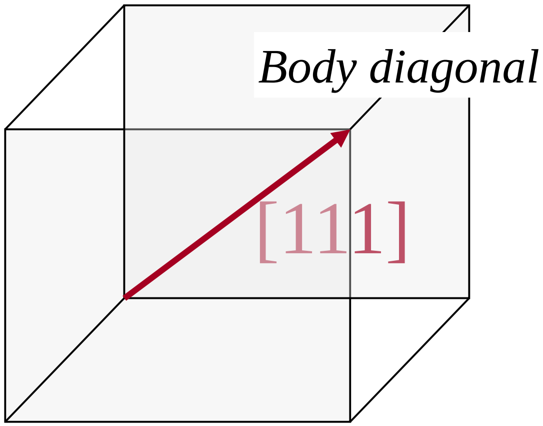


If you have confusion while selecting origin in negative indices refer this figure

Important directions in 3D represented by Miller Indices (cubic lattice)

Memorize these





Procedure as before:

- (Coordinates of the final point – coordinates of the initial point)
- Reduce to smallest integer values

Family of directions

- ☐ A set of directions related by symmetry operations of the lattice or the crystal is called a family of directions
- ☐ A family of directions is represented (Miller Index notation) as: <u v w>

Index	Members in family for **cubic lattice**	Number
<100>	$[100],[\bar{1}00],[010],[0\bar{1}0],[001],[00\bar{1}]$	3 x 2 = 6
<110>	$[110],[\bar{1}10],[1\bar{1}0],[\bar{1}\bar{1}0],[101],[\bar{1}01],[10\bar{1}],[\bar{1}0\bar{1}],[011],[0\bar{1}1],[01\bar{1}],[0\bar{1}\bar{1}]$	6 x 2 = 12
<111>	$[111],[\bar{1}11],[1\bar{1}1],[11\bar{1}],[\bar{1}\bar{1}1],[\bar{1}1\bar{1}],[1\bar{1}\bar{1}],[\bar{1}\bar{1}\bar{1}]$	4 x 2 = 8

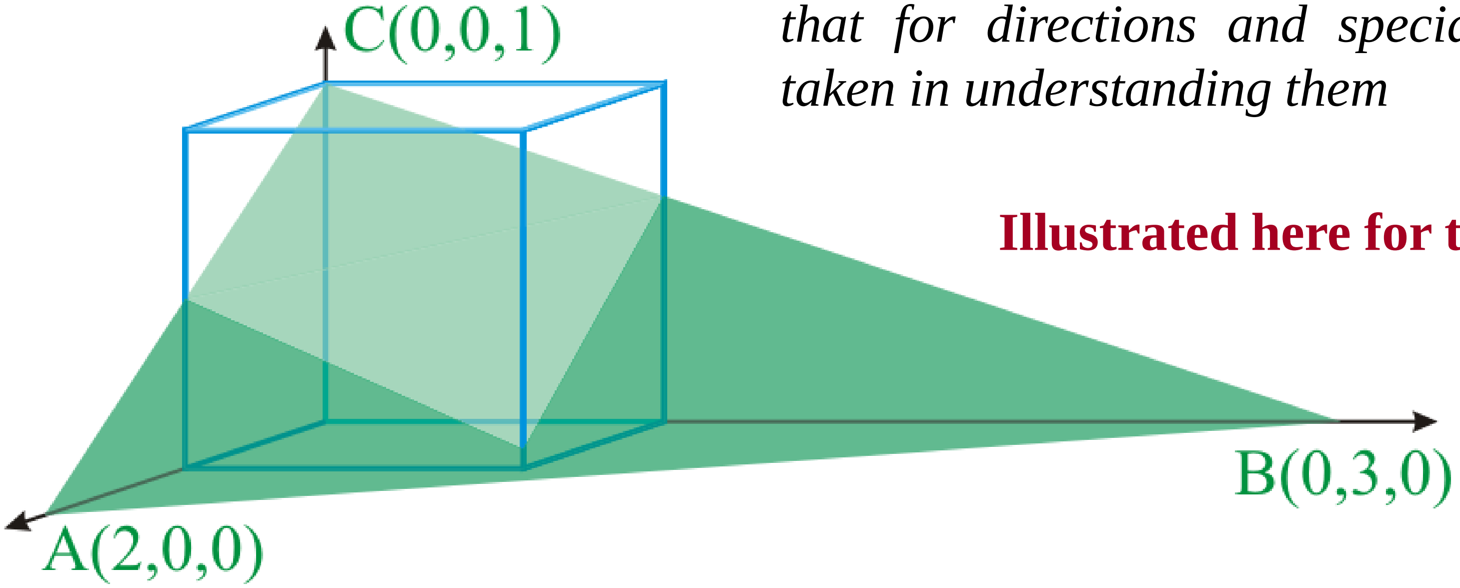
the 'negatives' (opposite direction)

Symbol	Alternate symbol		
[ ]		→	Particular direction
< >	[[ ]]	→	Family of directions

Miller Indices for Planes

Miller indices for planes is not as intuitive as that for directions and special care must be taken in understanding them

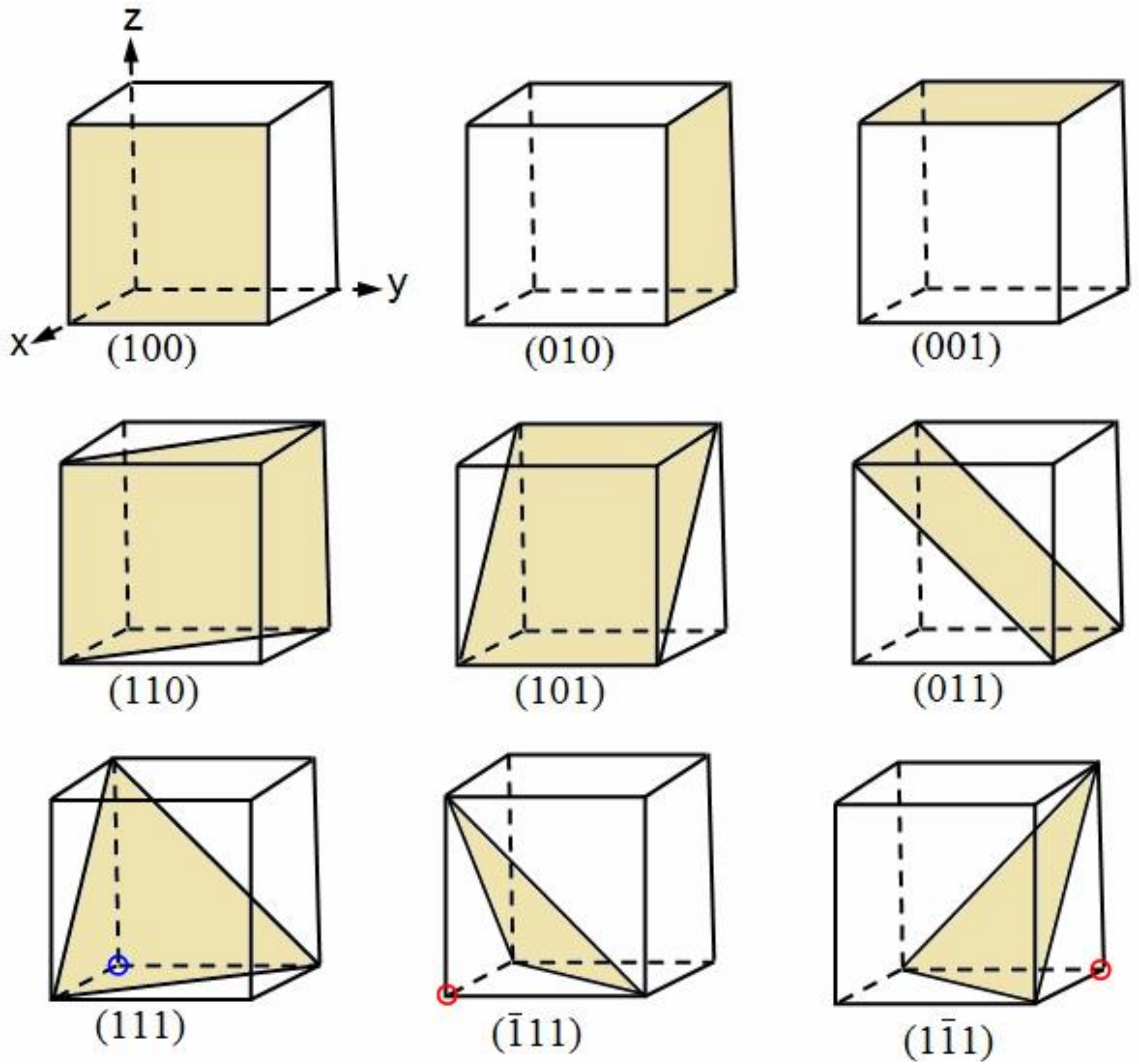
Illustrated here for the cubic lattice



- Find intercepts along axes → 2 3 1
- Take reciprocal* → 1/2 1/3 1
- Convert to smallest integers in the same ratio → 3 2 6
- Enclose in parenthesis → (326)

**The reciprocal procedure avoids the intercept of ∞ for a plane parallel to an axis, by making it 0*

Important Planes in 3D represented by Miller Indices (cubic lattice)



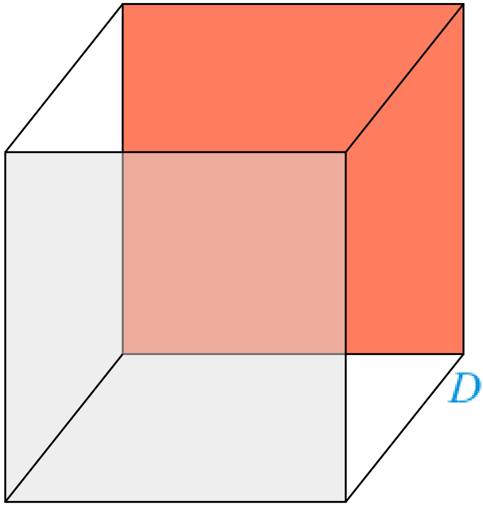
(100) (010) (001)

(110) (101) (011)

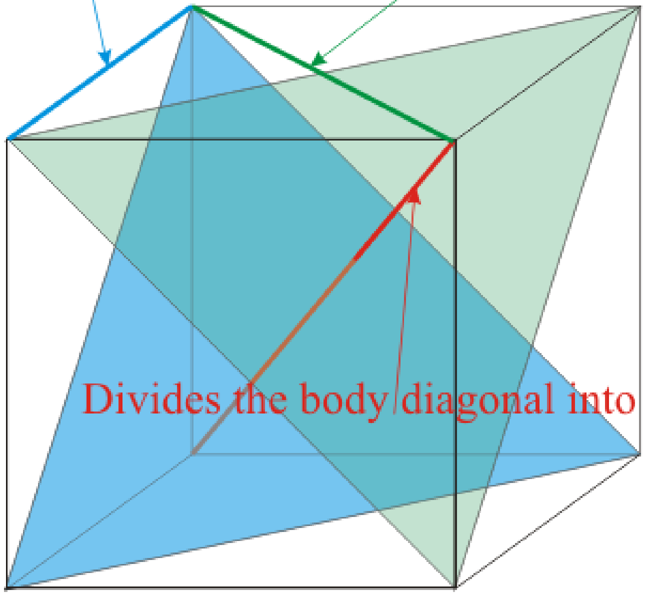
(111) $(\bar{1}11)$ $(1\bar{1}1)$

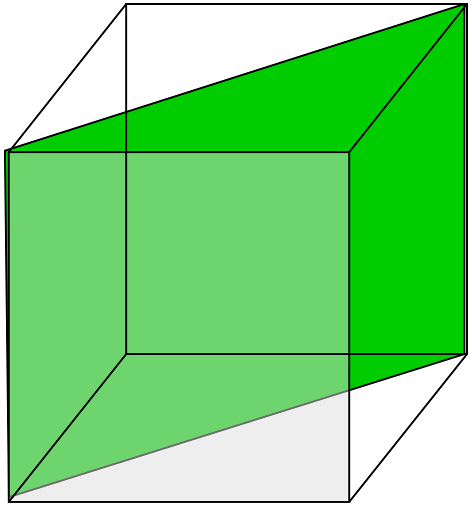
- A set of planes related by symmetry operations of the lattice or the crystal is called a family of planes
- All the points which one should keep in mind while dealing with directions to get the members of a family, should also be kept in mind when dealing with planes

Family of planes



Intercepts → 1 ∞ ∞
Plane → (100)
Family → {100} → 6





Intercepts → 1 1 ∞
Plane → (110)
Family → {110} → 6

Intercepts → 1 1 1
Plane → (111)
Family → {111} → 8
(Octahedral plane)

The purpose of using reciprocal of intercepts and not intercepts themselves in Miller indices becomes clear → the ∞ are removed

Summary on planes and directions

- Unknown direction → [uvw]
- Unknown plane → (hkl)
- Double digit indices should be separated by commas → (12,22,3)
- In cubic lattices/crystals [hkl] ⊥ (hkl)

Interplanar spacing (d_{hkl}) in cubic lattice (& crystals)

$$d_{hkl}^{cubic\ lattice} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

	Symbol		Alternate symbols		
Direction	[ ]	[uvw]		→	Particular direction
	< >	<uvw>	[[ ]]	→	Family of directions
Plane	( )	(hkl)		→	Particular plane
	{ }	{hkl}	(( ))	→	Family of planes

Directions ⊥ Planes

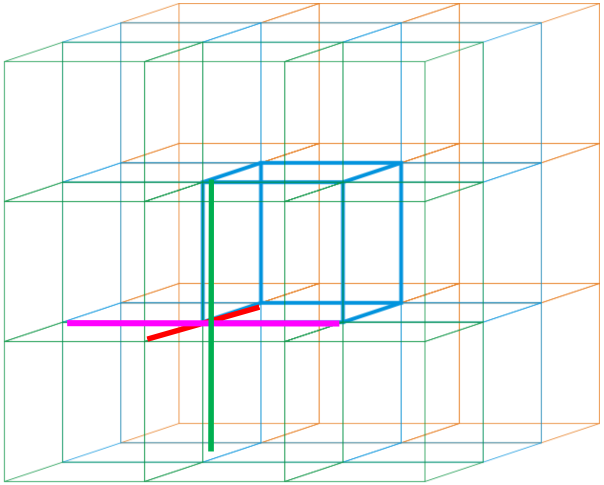
- Cubic system: (hkl) ⊥ [hkl]
- Tetragonal system: only special planes are ⊥ to the direction with same indices:
  [100] ⊥ (100), [010] ⊥ (010), [001] ⊥ (001), [110] ⊥ (110)
  ([101] not ⊥ (101))
- Orthorhombic system:
  [100] ⊥ (100), [010] ⊥ (010), [001] ⊥ (001)
- Hexagonal system: [0001] ⊥ (0001)
  (this is for a general c/a ratio; for a Hexagonal crystal with the special c/a ratio = √(3/2) the cubic rule is followed)
- Monoclinic system: [010] ⊥ (010)
- Other than these a general [hkl] is NOT ⊥ (hkl)

Coordination Number

Coordination number is defined as the total number of nearest neighboring atoms

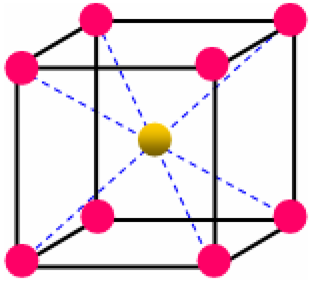
Simple cubic

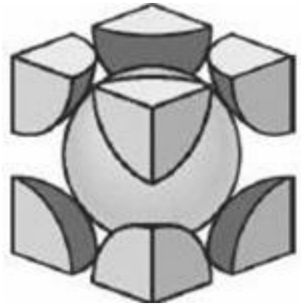
The coordination number of simple cubic crystal is ‘6’ It is shown in figure. In this figure we are considered one corner and drawn 3 lines connecting to six points.



Body Centered cubic

The coordination number of BCC crystal is 8. The body centered atom is in contact with all the eight corner atoms. Each corner atom is shared by eight unit cells and hence, each of these atoms is in touch with eight body centered atoms.

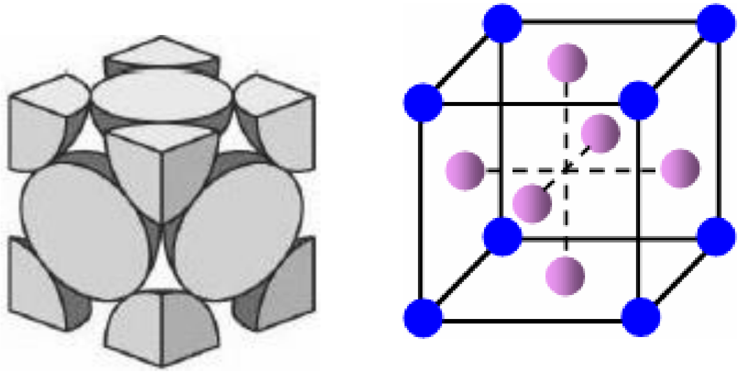




Coordination Number

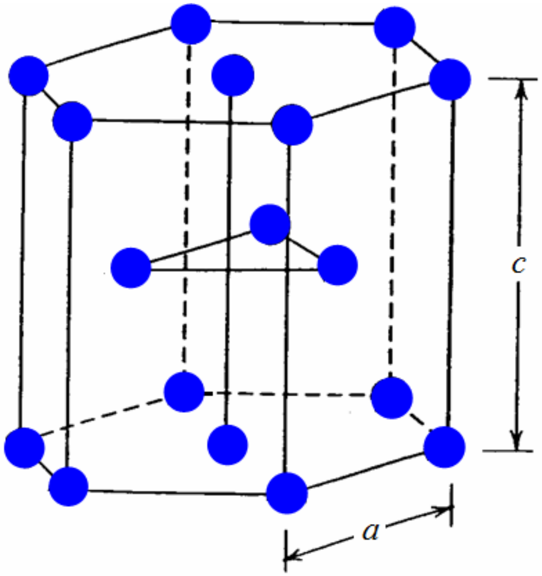
Face Centered cubic

In the FCC lattice each atom is in contact with 12 neighbor atoms. FCC coordination number Z = 12 . For example, the face centered atom in the front face is in contact with four corner atoms and four other face-centered atoms behind it (two sides, top and bottom) and is also touching four face-centered atoms of the unit cell in front of it.



Hexagonal close pack structure

In Hexagonal lattice Z = 12. The center atom of the top face is in touch with six corner atoms, three atoms of the mid layer and other three atoms of the mid layer of the unit cell above it.



Average number of atoms per unit cell

		Position of atoms	Effective number of atoms
1	SC	8 Corners	= [8 × (1/8)] = 1
2	BCC	8 Corners + 1 body centre	= [1 (for corners)] + [1 (BC)] = 2
3	FCC	8 Corners + 6 face centres	= [1 (for corners)] + [6 × (1/2)] = 4
4	HCP	12 corners (6 bottom+6 top) + 2 atoms at face centers + 3 atoms in the interior	= [12 × (1/6)] + [2 × (1/2)] + [3 (interior)] = 6

Atomic packing factor

Atomic packing factor (APF) or packing efficiency indicates how closely atoms are packed in a unit cell and is given by the ratio of volume of atoms in the unit cell and volume of the unit cell.

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

Simple Cubic

In a simple cubic structures, the atoms are assumed to be placed in such a way that any two adjacent atoms touch each other. If ‘a’ is the lattice parameter of simple cubic structure and ‘r’ the radius of atoms. From the figure it is clear that

Atomic radius (r) $= a/2$

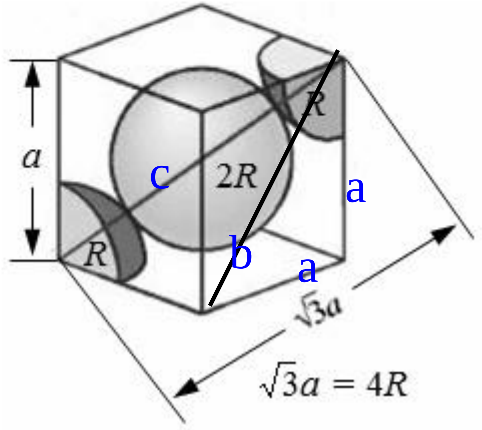
$$APF = \frac{Avg. no of atoms per unit cell \times Volume of an atom}{Volume of the unit cell}$$

$$APF = \frac{1 \times \frac{4}{3}\prod r^3}{a^3} = \frac{\frac{4}{3}\prod r^3}{(2r)^3} = \frac{4\prod}{24} \times 100 = 0.52 = 52\%$$

Atomic packing factor

Body Centered Cubic

In body centered cubic structures the center atom touches the corner atoms as shown in Figure



From the figure

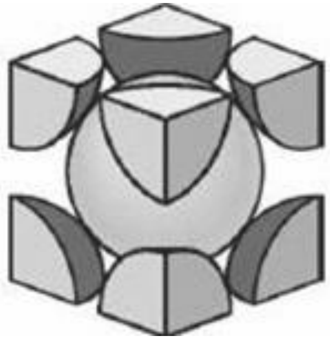
$$b^2 = a^2 + a^2 = 2a^2$$

$$c^2 = b^2 + a^2 \rightarrow c^2 = 2a^2 + a^2$$

$$c^2 = 3a^2 \rightarrow (4r)^2 = 3a^2 \rightarrow r^2 = \frac{3a^2}{16}$$

$$r = \frac{\sqrt{3}a}{4}, a = \frac{4r}{\sqrt{3}}$$

r = atomic radius
a = lattice parameter



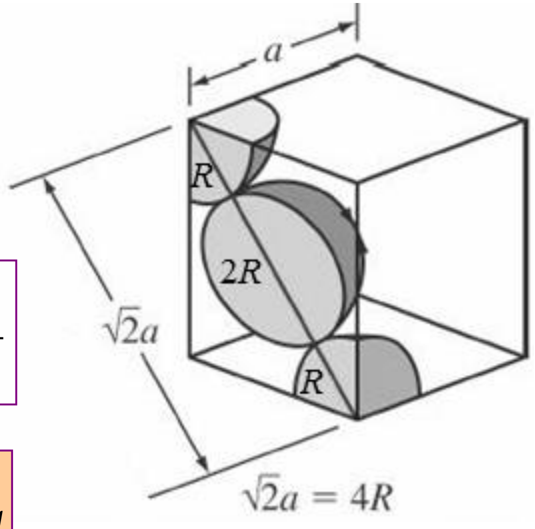
$$APF = \frac{2 \times \frac{4}{3} \prod r^3}{a^3} = \frac{2 \times \frac{4}{3} \prod \left(\frac{\sqrt{3}a}{4} \right)^3}{a^3} = \frac{8 \times 3\sqrt{3} \prod a^3}{3 \times 64 a^3}$$

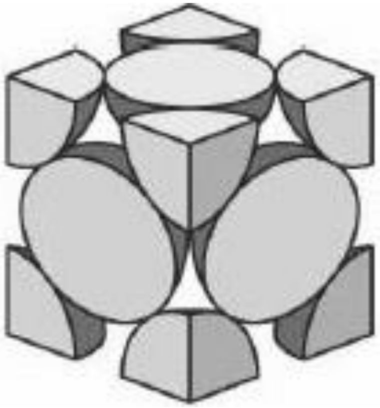
$$APF = 0.68 (or) 68\%$$

Atomic packing factor

Face Centered Cubic

From this figure; first we can calculate atomic radius:





$$(4r)^2 = a^2 + a^2 \rightarrow 16r^2 = 2a^2 \rightarrow r^2 = \frac{2a^2}{16}$$

$$r = \frac{a\sqrt{2}}{4} = \frac{a}{2\sqrt{2}}$$

$$a = \frac{4r}{\sqrt{2}} \rightarrow 4r = \sqrt{2}a$$

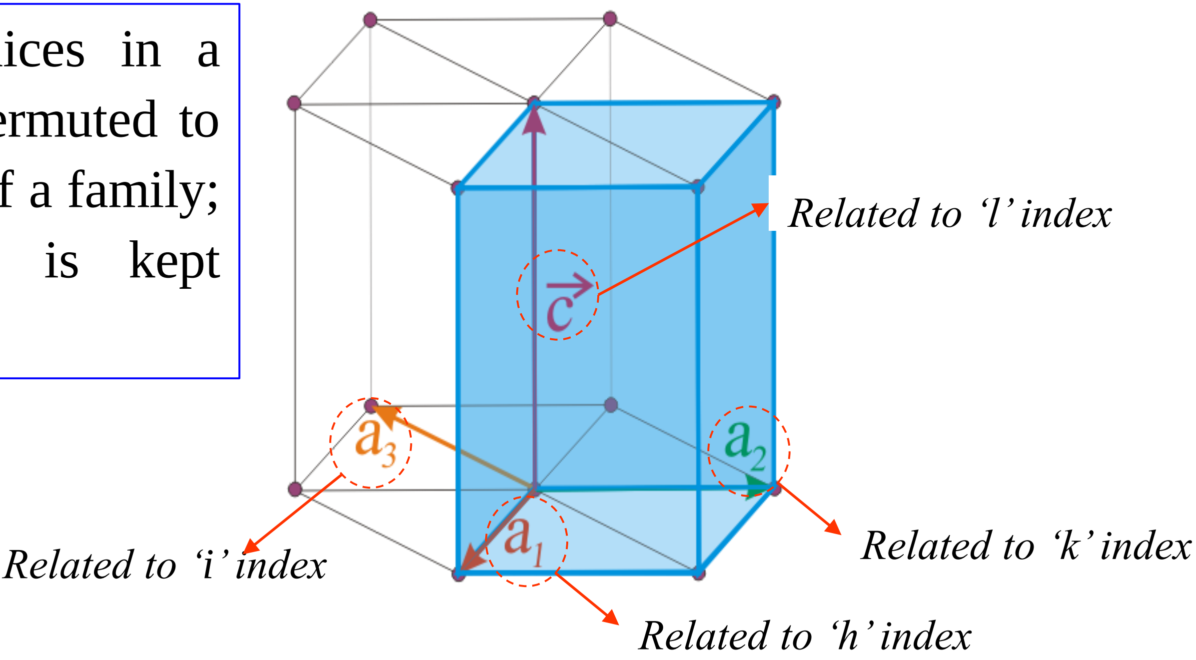
$$APF = \frac{4\times\frac{4}{3}\prod r^3}{a^3} = \frac{4\times\frac{4}{3}\prod\left(\frac{a}{2\sqrt{2}}\right)^3}{a^3} = \frac{16\times 2\sqrt{2}\prod a^3}{3\times 64a^3} = 0.74$$

$$APF_{FCC} = 0.74(or)74\%$$

Hexagonal crystals → Miller-Bravais Indices : Planes

- ❑ Directions and planes in hexagonal lattices and crystals are designated by the 4-index Miller-Bravais notation
- ❑ In the four index notation:
  - ➢ the first three indices are a symmetrically related set on the basal plane
  - ➢ the third index is a *redundant one* (which can be derived from the first two) and is introduced to make sure that members of a family of directions or planes have a set of numbers which are identical
  - ➢ the fourth index represents the 'c' axis *(⊥ to the basal plane)*

- ❑ Hence the first three indices in a hexagonal lattice can be permuted to get the different members of a family; while, the fourth index is kept separate.



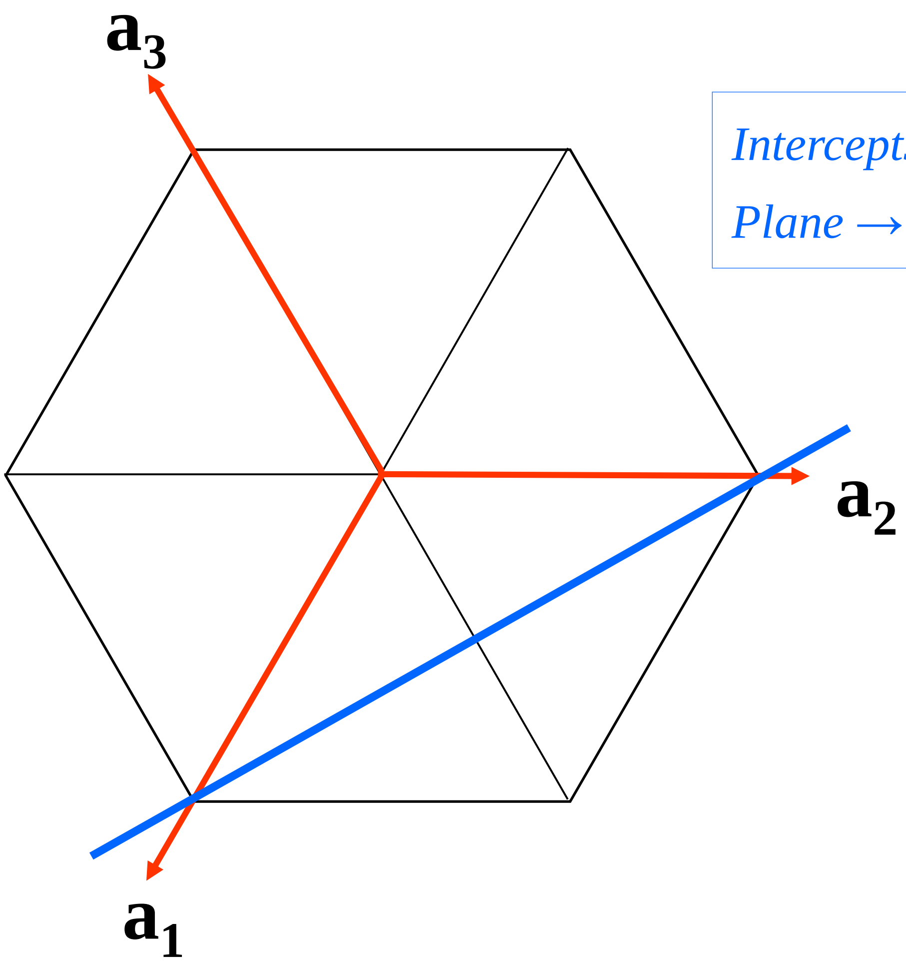
Related to 'l' index

Related to 'i' index

Related to 'k' index

Related to 'h' index

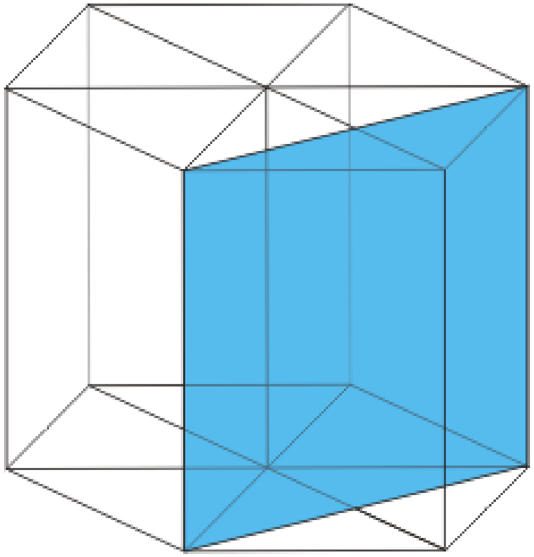
Hexagonal crystals → Miller-Bravais Indices : PLANES



Intercepts → 1 1 - ½ ∞

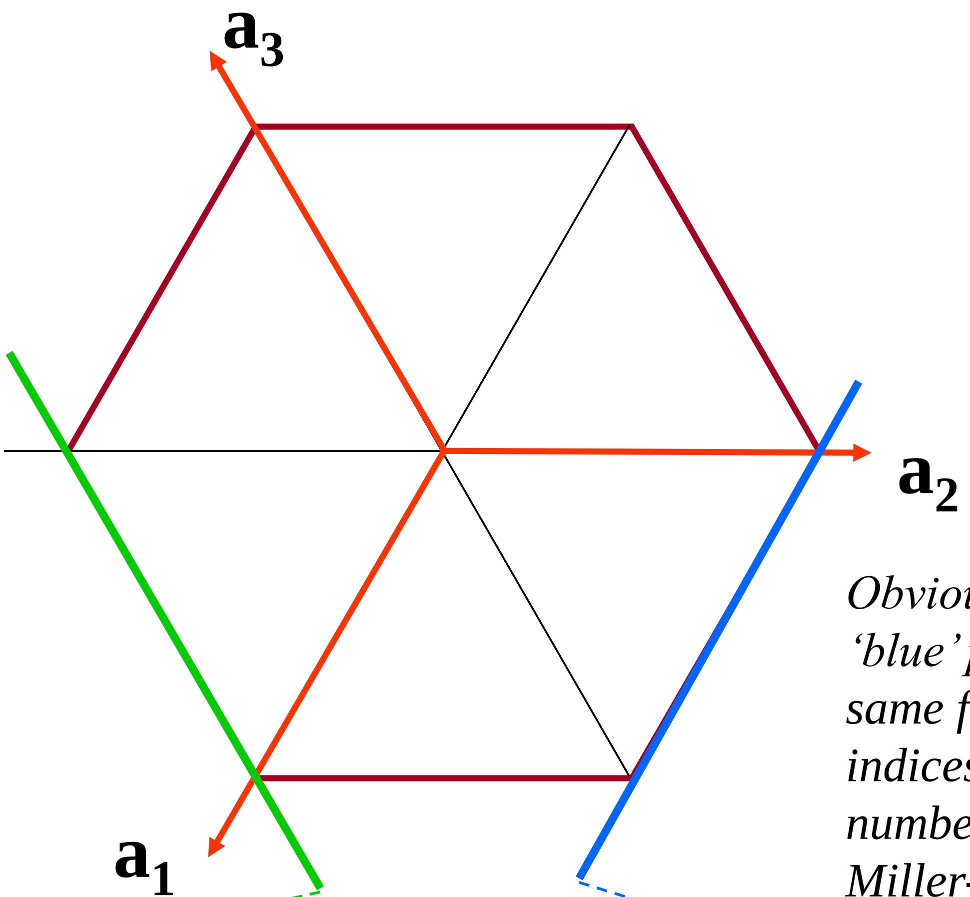
Plane → $(1\ 1\ \bar{2}\ 0)$

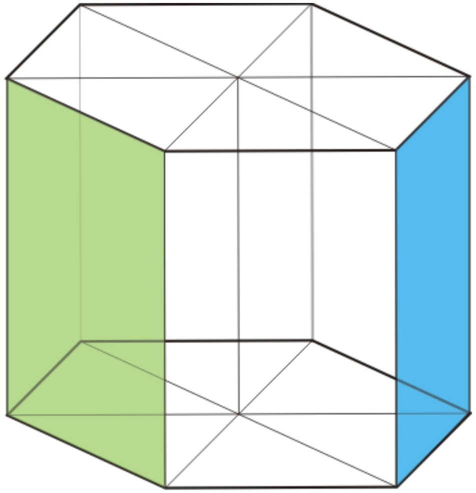
(h k i l)
i = –(h + k)



In general three indices point is denoted as miller indices i.e., (h k l). But hexagonal crystals we are using 4 indices point is denoted by miller-bravais indices i.e., (h k i l)The use of the 4 index notation is to bring out the equivalence between crystallographically equivalent planes and directions.

Hexagonal crystals → Miller-Bravais Indices : PLANES





Obviously the 'green' and 'blue' planes belong to the same family and first three indices have the same set of numbers (as brought out by the Miller-Bravais system)

Intercepts → $1\ -1\ \infty\ \infty$

Miller → $(1\ \bar{1}\ 0)$

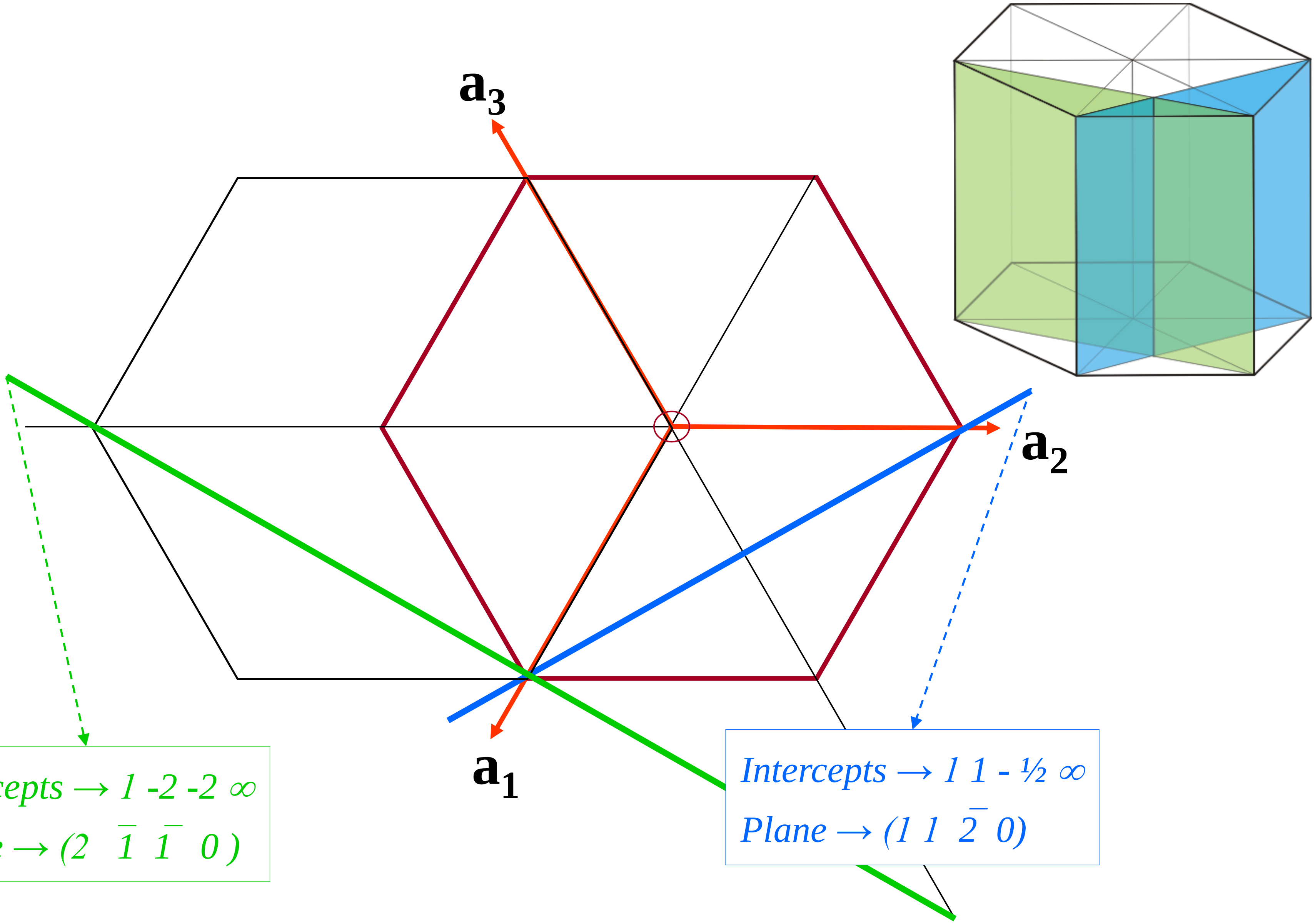
Miller-Bravais → $(1\ \bar{1}\ 0\ 0)$

Intercepts → $\infty\ 1\ -1\ \infty$

Miller → $(0\ 1\ 0)$

Miller-Bravais → $(0\ 1\ \bar{1}\ 0)$

Hexagonal crystals → Miller-Bravais Indices : PLANES



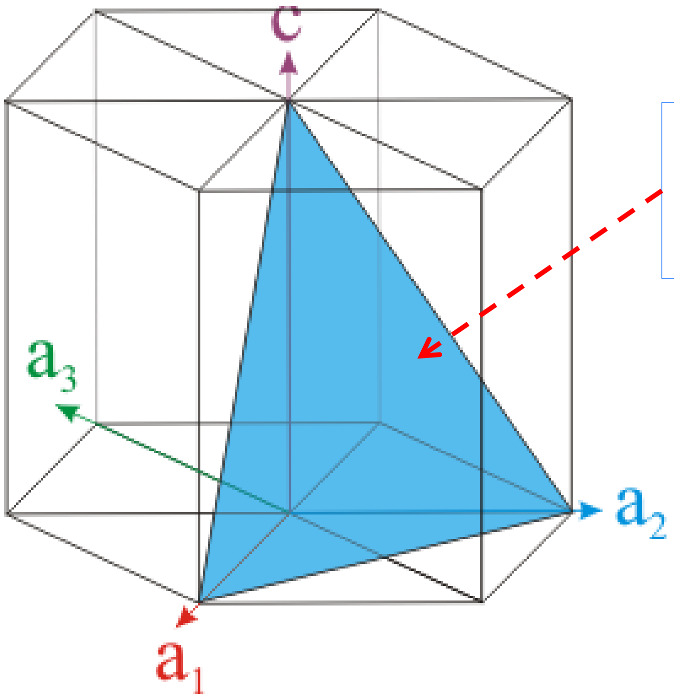
Intercepts → 1 -2 -2 ∞

Plane → $(2\ \bar{1}\ \bar{1}\ 0)$

Intercepts → 1 1 - ½ ∞

Plane → $(1\ 1\ \bar{2}\ 0)$

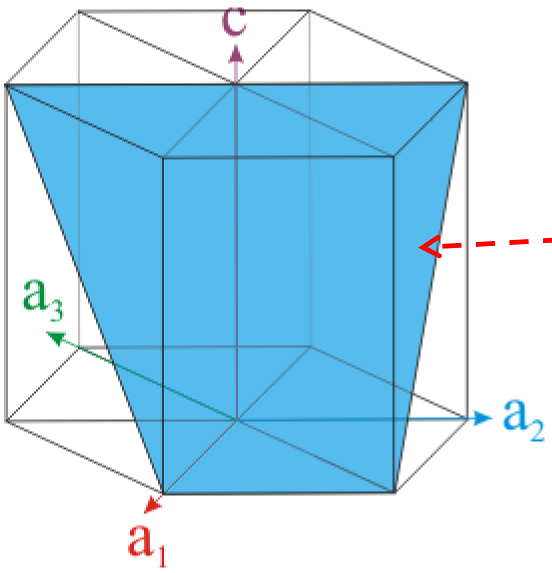
Hexagonal crystals → Miller-Bravais Indices : PLANES



Intercepts → 1 1 - ½ 1

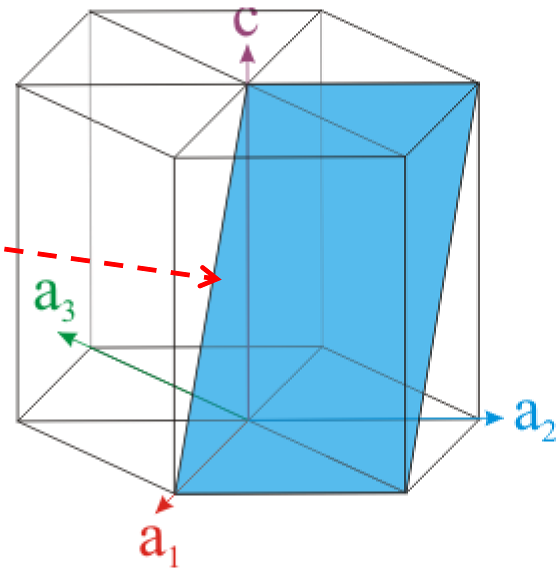
Plane → $(1\ 1\ \bar{2}\ 1)$

Both planes contain same intercepts. The common thing in these planes is $\mathbf{a_2}$ axis is infinite



Intercepts → $1\ \infty\ -1\ 1$

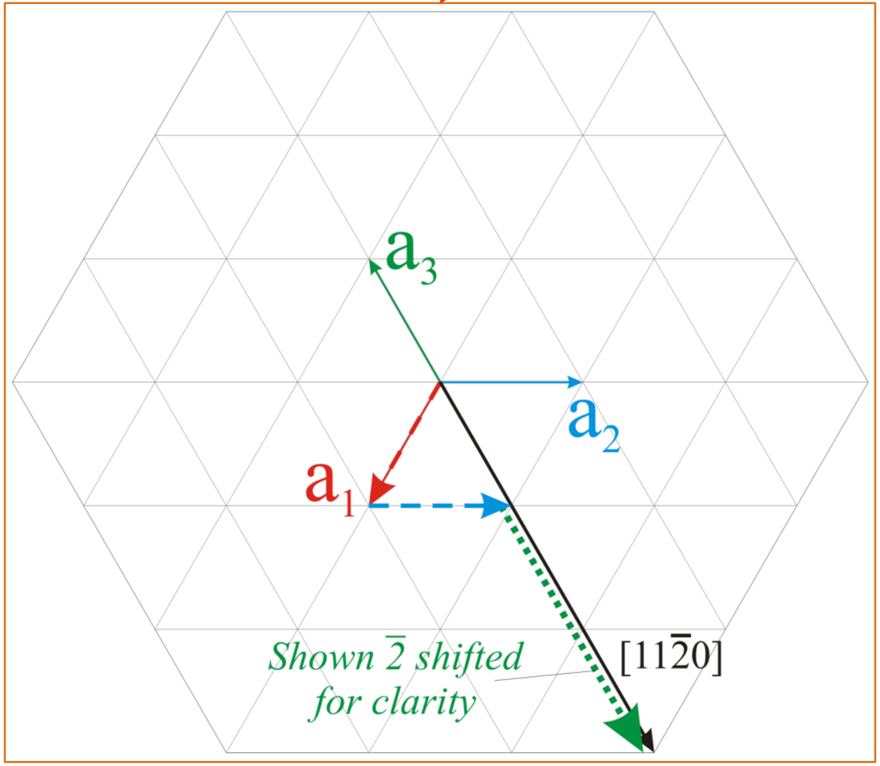
Plane → $(1\ 0\ \bar{1}\ 1)$



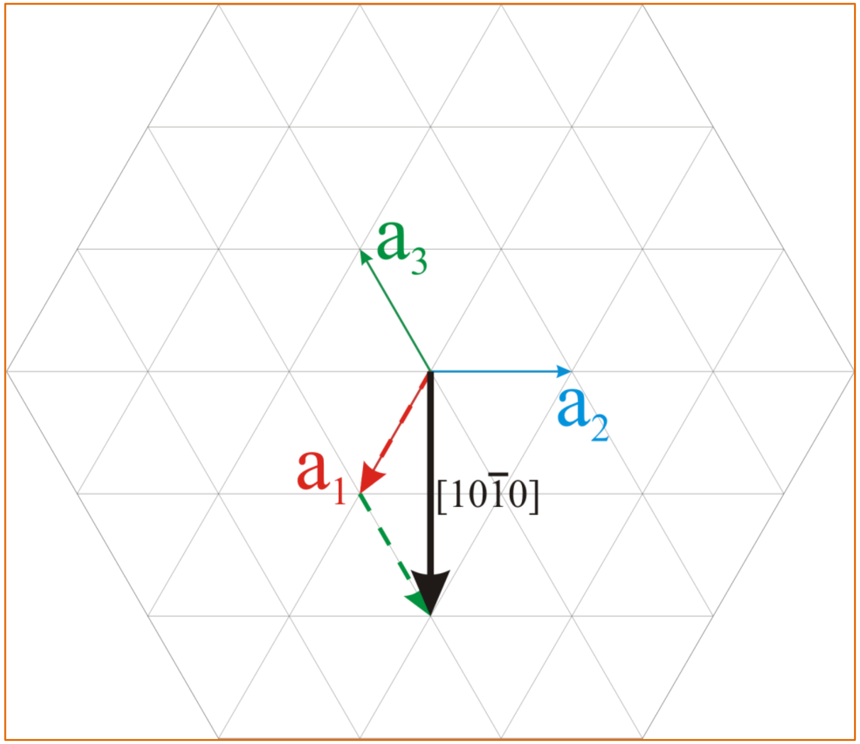
Hexagonal crystals → Miller-Bravais Indices : DIRECTIONS

Drawing the $[11\bar{2}0]$ *direction*

- Trace a path along the basis vectors as required by the direction. In the current example move 1unit along a_1, 1unit along a_2 and –2 units along a_3.
- Directions are projected onto the basis vectors to determine the components and hence the Miller-Bravais indices can be determined as in the table.



Drawing the $[10\bar{1}0]$ direction



Hexagonal crystals → Miller-Bravais Indices : DIRECTIONS

Transformation between 3-index *[UVW]* and 4-index *[uvtw]* notations

$$U = u - t$$

$$V = v - t$$

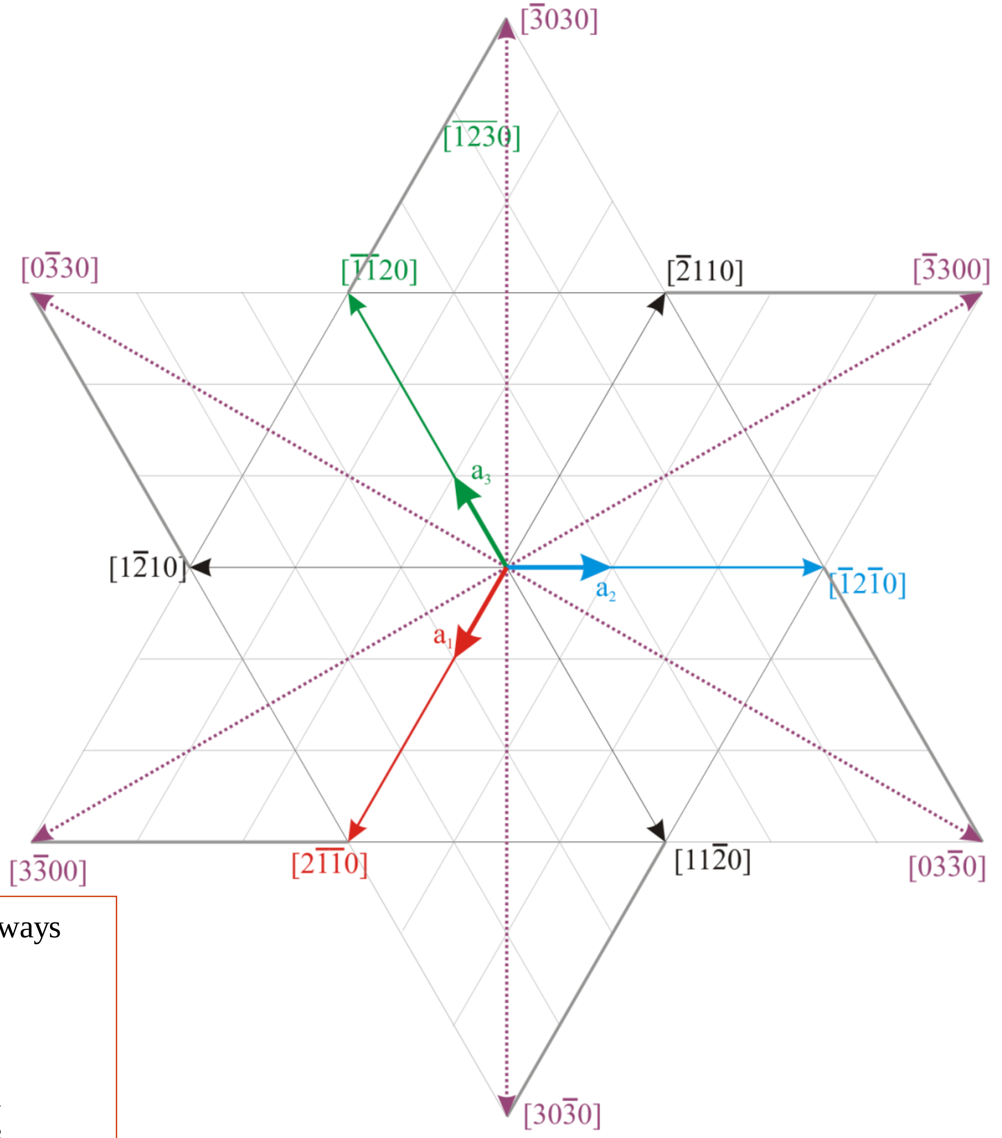
$$W = w$$

$$u = \frac{1}{3}(2U - V)$$

$$v = \frac{1}{3}(2V - U)$$

$$t = -(u + v)$$

$$w = W$$

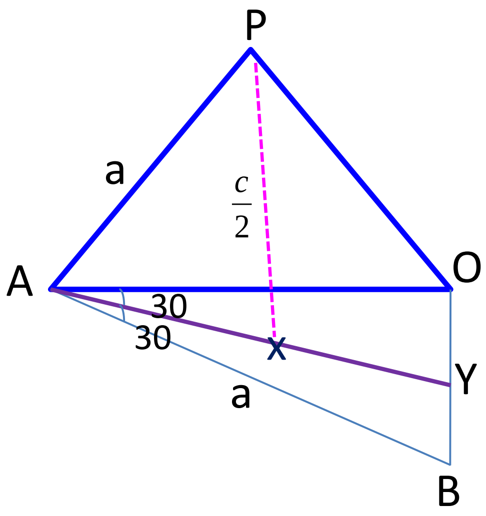


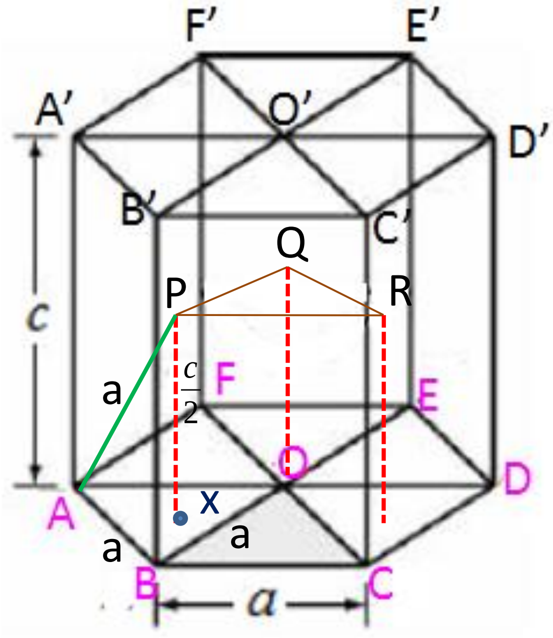
- Directions in the hexagonal system can be expressed in many ways
- 3-indices:
  By the three vector components along a_1, a_2 and c:
  $r_{UVW} = Ua_1 + Va_2 + Wc$
- In the three index notation equivalent directions may not seem equivalent; while, in the four index notation the equivalence is brought out.

Atomic packing factor

Hexagonal Close Packed Structure

Consider any one triangle
Let us consider ΔAOB;
‘P’ is center of triangle
APOB - Tetrahedron





In the Δ AYB

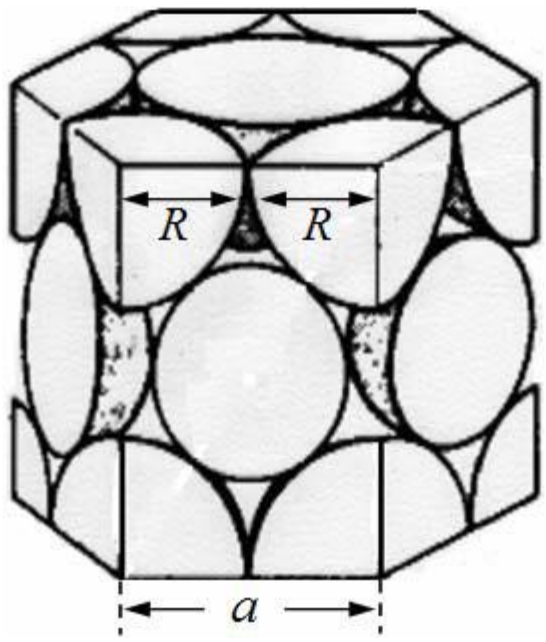
$$Cos30^0 = \frac{AY}{AB}$$

The distance between any neighboring atoms is ‘a’ from the figure ‘AB’ = a

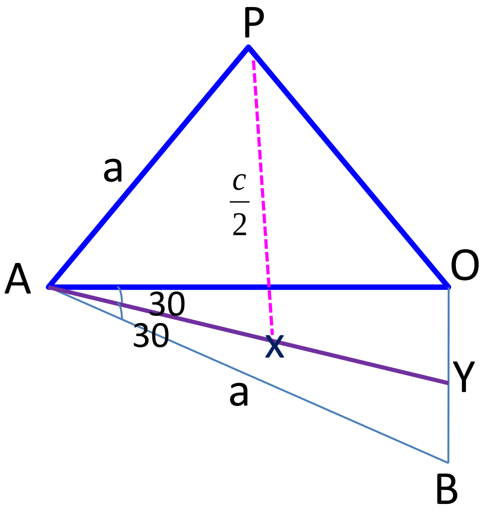
$$AY = AB\cos 30^0 = \frac{a\sqrt{3}}{2}$$

From the figure ‘Ax’ is orthocenter; so,

$$Ax = \frac{2}{3}AY = \frac{2}{3}\times\frac{a\sqrt{3}}{2} = \frac{a}{\sqrt{3}}$$



Hexagonal Close Packed Structure



Consider Δ APx

$$(AP)^2 = (Ax)^2 + (xP)^2$$

$$a^2 = \frac{a^2}{3} + \frac{c^2}{4} \rightarrow a^2 - \frac{a^2}{3} = \frac{c^2}{4} \rightarrow \frac{c^2}{4} = \frac{2a^2}{3}$$

$$\boxed{\frac{c^2}{a^2} = \frac{8}{3} \rightarrow \frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633}$$

$$APF = \frac{Avg.noofatomsperunitcell \times Volumeofanatom}{Volumeoftheunitcell}$$

$$APF = \frac{6 \times \frac{4}{3} \prod r^3}{Volumeoftheunitcell}$$

In cubic a=b=c, so volume is a^3 but in this case, it is H.C.P so here a=b≠c

Volume of unitcell = Area of base of hexagonal × Height

Hexagonal Close Packed Structure

Volume of unitcell = Area of base of hexagonal × Height

$$\text{Volume of unit cell} = 6 \times \text{area of } \Delta AOB \times c$$

$$\text{Volume of unit cell} = 6 \times \frac{1}{2} \times OB \times AY \times c$$

$$\text{Volume of unit cell} = 6 \times \frac{1}{2} \times a \times \frac{a\sqrt{3}}{2} \times c = ca^2 \frac{3\sqrt{3}}{2}$$

$$APF = \frac{6 \times \frac{4}{3} \prod r^3}{ca^2 \frac{3\sqrt{3}}{2}}$$

$$APF = \frac{6 \times \frac{4}{3} \prod r^3}{ca^2 \frac{3\sqrt{3}}{2}} = \frac{6 \times \frac{4}{3} \prod \times \frac{a^3}{8}}{ca^2 \frac{3\sqrt{3}}{2}} = \frac{2 \prod a}{c \times 3\sqrt{3}} = 0.74$$

$$APF_{HCP} = 0.74 (or) 74\%$$

Summary on PACKING FRACTION / Efficiency

$$\text{Packing Fraction} = \frac{\text{Volume occupied by atoms}}{\text{Volume of Cell}}$$

	SC*	**BCC***	**CCP**	**DC**	**HCP**
Relation between atomic radius (r) and lattice parameter (a)	a = 2r	$\sqrt{3}a = 4r$	$\sqrt{2}a = 4r$	$\frac{\sqrt{3}}{4}a = 2r$	a = 2r $c = 4r\sqrt{\frac{2}{3}}$
Atoms / cell	1	2	4	8	2
Lattice points / cell	1	2	4	4	1
No. of nearest neighbours	6	8	12	4	12
Packing fraction	$\frac{\pi}{6}$	$\frac{\sqrt{3}\pi}{8}$	$\frac{\sqrt{2}\pi}{6}$	$\frac{\sqrt{3}\pi}{16}$	$\frac{\sqrt{2}\pi}{6}$
	~ 0.52	~ 0.68	~ 0.74	~ 0.34	~ 0.74

* *Crystal formed by monoatomic decoration of the lattice*

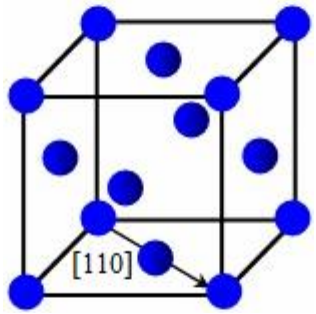
Density

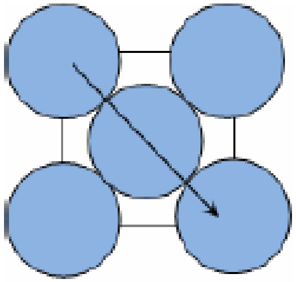
- The usual density is mass/volume
- In materials science various other kinds of density and occupation ratios are defined. These include:
  - Linear density: mass/length [kg/m]
    atoms/length [/m] *or number/length*
    length occupied/length [m/m]
  - Planar(Areal) density: mass/area [kg/m^2]
    atoms/area [/m^2] *or number/area*
    area occupied/area [m^2/m^2]
  - Volume density: mass/volume [kg/m^3]
    atoms/volume [/m^3] *or number/volume*
    volume occupied/volume [m^3/m^3]
- The volume occupied/volume of space [m^3/m^3] is also called the packing fraction
- In this context other important quantities include:
  - Length/area [m/m^2] → e.g. length of dislocation lines per unit area of interface (interfacial dislocations)
  - Length/volume [m/m^3] → e.g. length of dislocation lines per unit volume of material
  - Area/volume [m^2/m^3] → e.g. grain boundary area per unit volume of material
- The 'useful' way to write these quantities is to NOT factor out the common terms: i.e. write [m/m^3] '*as it is*' and *not as* [1/m^2]

Linear density

Linear density (LD) is the number of atoms per unit length along a particular direction

$$\mathit{LinearDensity} = \frac{\mathit{Numberofatomsonthedirectionvector}}{\mathit{Lengthofthedirectionvector}}$$





<110> directions in the FCC lattice have 2 atoms (1/2 x 2 corner atoms + 1 center atom) and the length is

$$LD_{[110]} = \frac{2}{\sqrt{2}a} = \frac{\sqrt{2}}{a}$$

This is the most densely packed direction in the FCC lattice

Planar(Areal) density

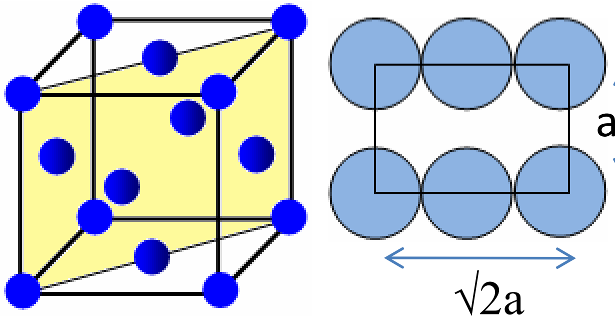
Planar density (PD) refers to density of atomic packing on a particular plane.

$$PlanarDensity = \frac{Numberofatomsonaplane}{Areaofplane}$$

For example, there are 2 atoms (1/4 x 4 corner atoms + 1/2 x 2 side atoms) in the {110} planes in the FCC lattice.

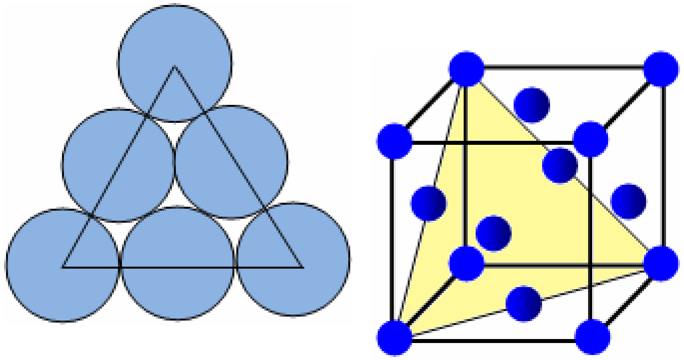
Planar density of {110} planes in the FCC crystal

$$PD_{(110)} = \frac{2}{a\sqrt{2}a} = \frac{\sqrt{2}}{a^2}$$



In the {111} planes of the FCC lattice there are 2 atoms (1/6 x 3 corner atoms + 1/2 x 3 side atoms). Planar density of {111} planes in the FCC crystal

$$PD_{(111)} = \frac{2}{\frac{1}{2}\sqrt{2}a \times \sqrt{2}a\frac{\sqrt{3}}{2}} = \frac{4}{\sqrt{3}a^2}$$



This is higher than {110} and any other plane. Therefore, {111} planes are most densely packed planes in the FCC crystal

Theoretical (Volume) density

Theoretical density calculation from crystal structure

Theoretical density $$\rho = \frac{nA}{V_C N_A}$$

n = number of atoms in the unit cell

A = atomic weight

V_C = Volume of unitcell

N_A = Avogadro's number (6.023×10^{23})

Calculate the theoretical density of Aluminum (Al)

Given : Al is FCC structure; Lattice parameter is $4.05A^0$; n=4;
Atomic weight of Al is 26.98 g/mol

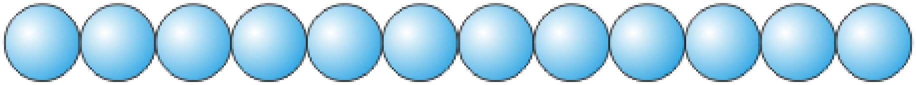
$$\rho = \frac{4 \times 26.98}{(4.05 \times 10^{-8})^3 \times 6.023 \times 10^{23}} = 2.697 g/cc$$

CCP=FCC

Closed Packed Structures : FCC

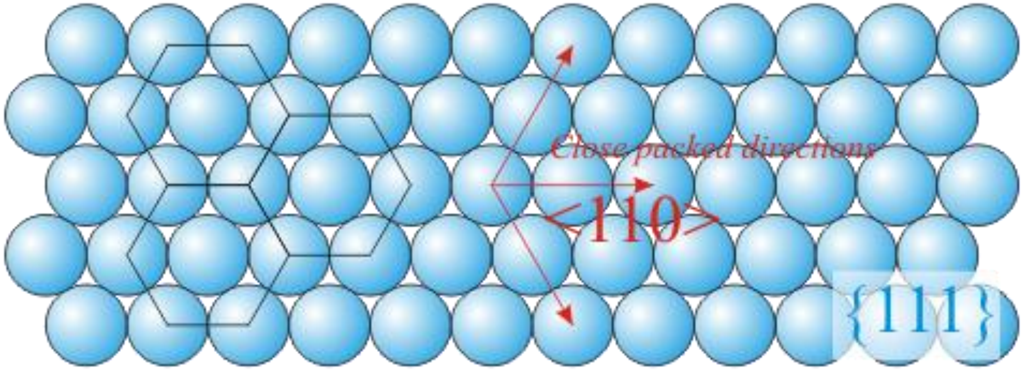
CCP=FCC

Start with a row of atoms *(close packed in 1D)*



Monatomic decoration of FCC lattice

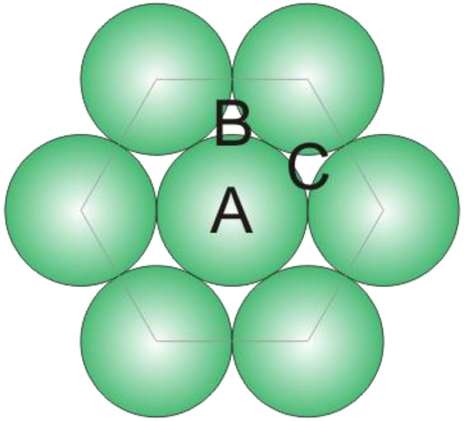
Make a 2D hexagonal close packed array (the A layer)

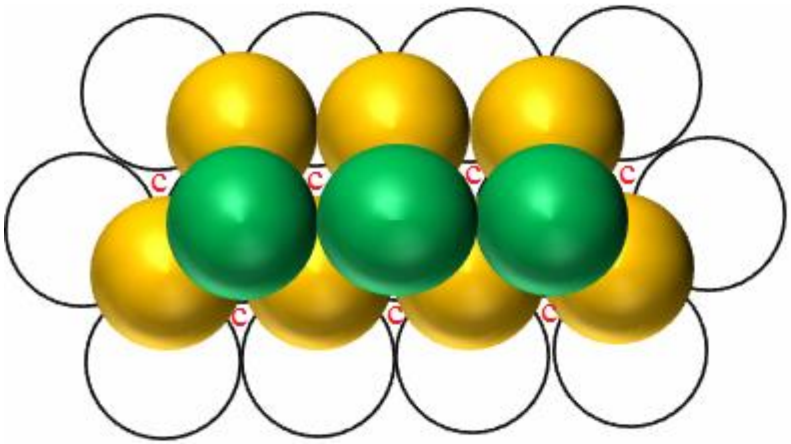


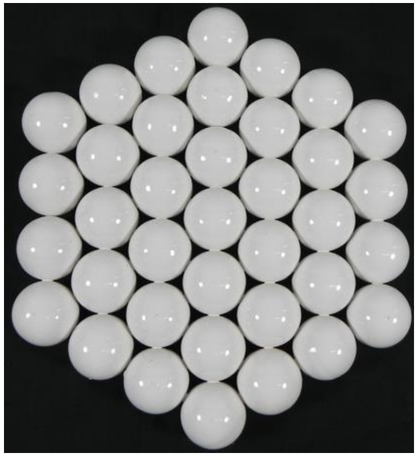
There is only one way of doing so!

- This is a close packed layer with close packed directions (like <110> directions represented using cubic indices)
- As we shall see this becomes the {111} plane in the FCC crystal

To build the next layer → leading to the 3D structure, there are 2 stable positions where atoms can be put → called the B and C positions. If atoms are put in the B position than we cannot put atoms in the C position (no space!)

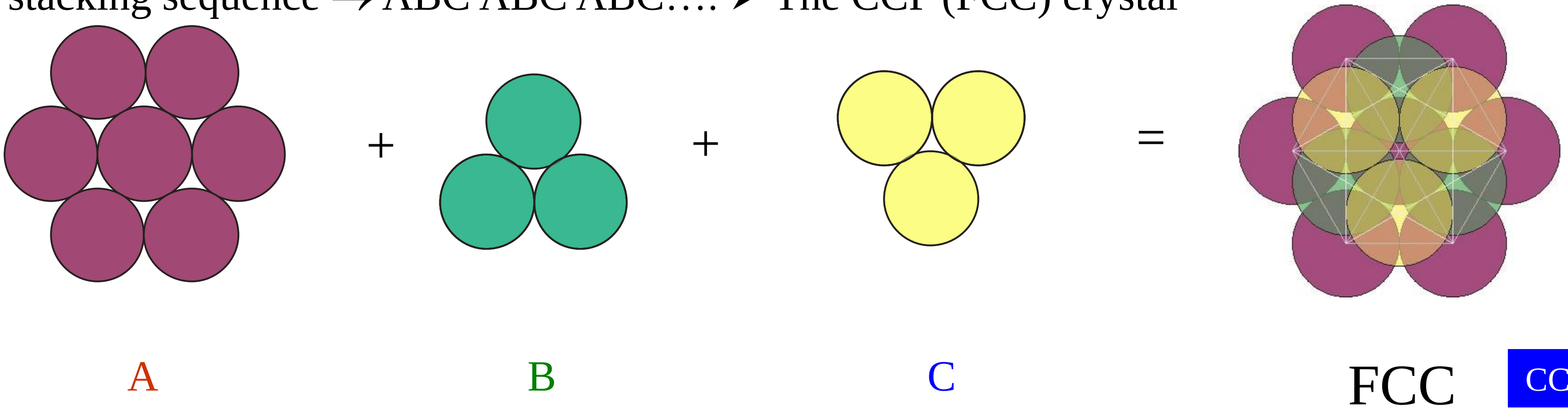




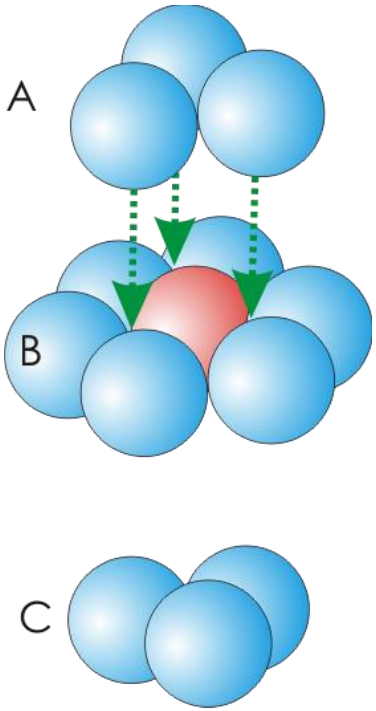


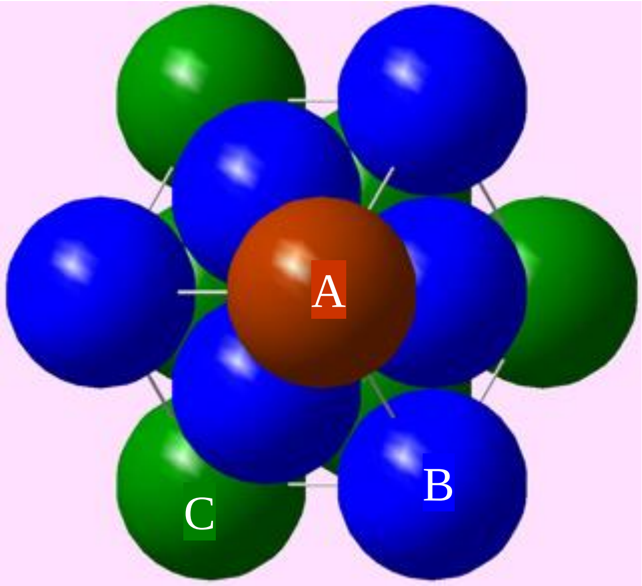
Closed Packed Structures : FCC

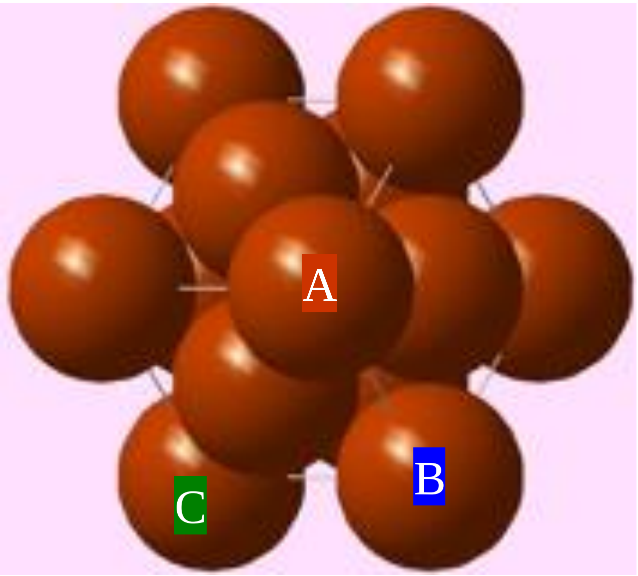
Putting atoms in the B position in the II layer and in C positions in the III layer we get a stacking sequence → ABC ABC ABC…. ➢ The CCP (FCC) crystal



CCP=FCC



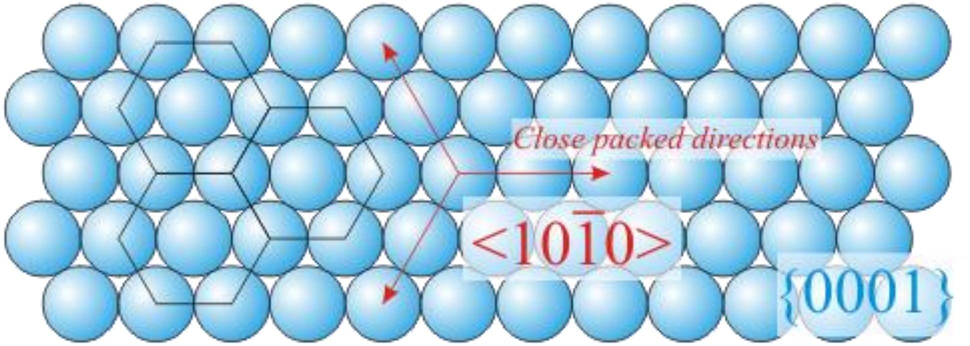




Closed Packed Structures : HCP

An alternate packing (one amongst an infinite possibilities) is where in the III layer coincides with the I layer → giving rise to a AB AB AB … packing → The Hexagonal Close Packed Crystal *(this arrangement is close packed only for ideal c/a ratio; i.e. for 'hard sphere' packing)*

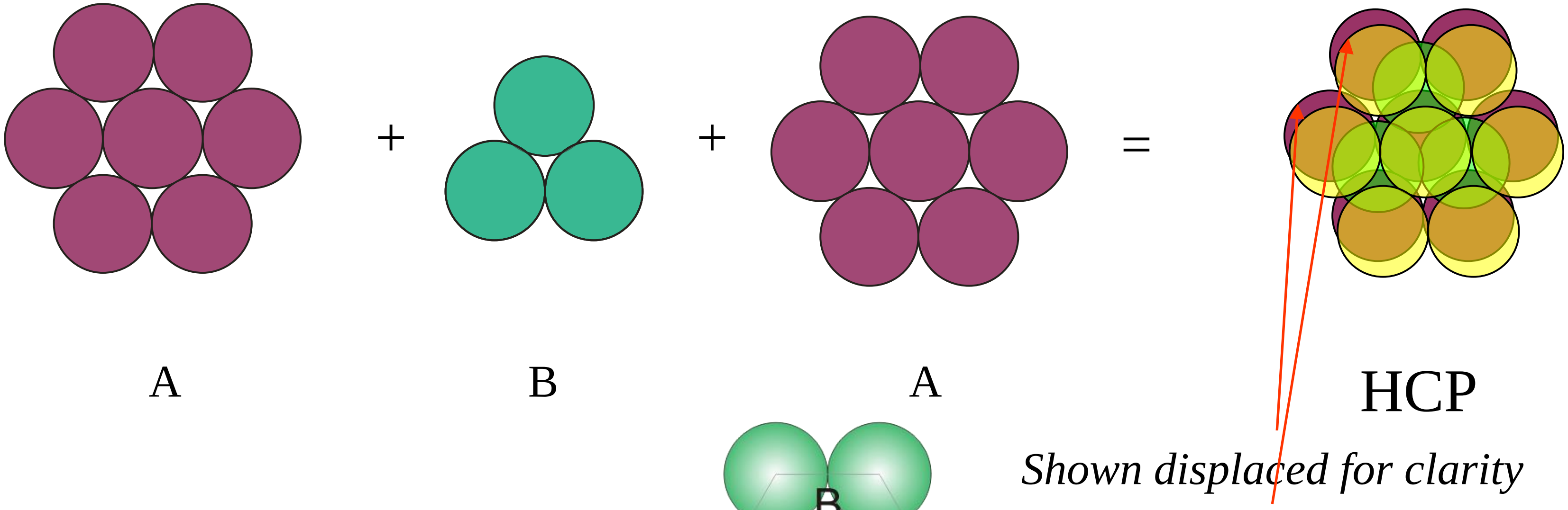
As before we make a 2D hexagonal close packed array (the A layer)



- This is a close packed layer with close packed directions (like $<11\bar{2}0>$ directions)
- As we shall see this becomes the {0001} plane in the HCP crystal

Metals which adopt HCP structure ➢
Mg, Zn, Ti, Co, Be, Cd, Zr, Y, Sc, Tc, Ru, Gd, Tb, Dy, Ho, Er, Tm, Lu, Hf, Re, Os, Tl

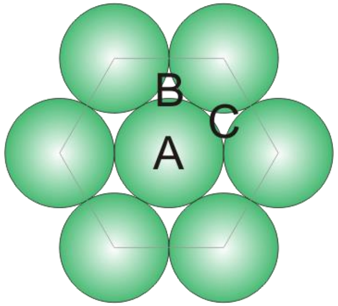
Closed Packed Structures : HCP

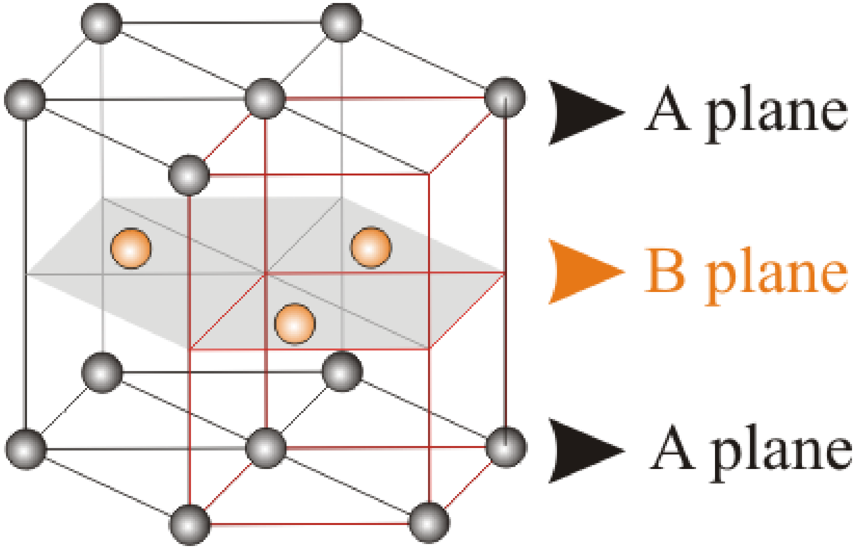


Shown displaced for clarity

The C position is vacant and we can pass a line through this position without intersecting any atoms

As we shall see in one of the upcoming slides that this is special line





HCP

Structure-Property Correlation

- Aluminum (Al) is ductile while iron (Fe) and magnesium (Mg) are not. This can be explained from their crystal structures.
- Al is FCC where as Fe is BCC and Mg is HCP.
- Plastic deformation in metals takes place mainly by a process called slip. Slip can broadly be visualized as sliding of crystal planes over one another. Slip occurs on most densely packed planes in the most closely packed directions lying on that plane.
- The slip plane and the direction together is called a Slip system
- In FCC, {111} planes are close-packed and there are four unique {111} planes. Each of these planes contains three closely packed <110> directions. Therefore, there are 4 x 3 = 12 slip systems
- In HCP, the basal plane, (0001) is the close-packed and it contains three $\langle 11\bar{2}0 \rangle$ directions. Hence, number of slip system = 1 x 3 = 3
- Slip in more number of slip systems allows greater plastic deformation before fracture imparting ductility to FCC materials.
- Close-packed planes are also planes with greatest interplanar spacing and this allows slip to take place easily on these planes.
- BCC structure on the other hand has 48 possible slip systems. However, there is no close-packed plane. Hence, plastic deformation before fracture is not significant. Slip might occur in {110}, {112} and {123} planes in the <111> directions.

Questions?

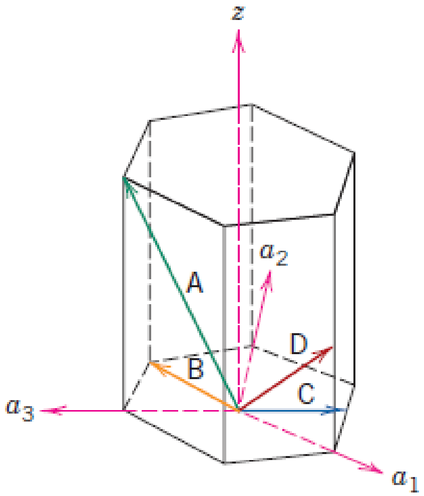
1. What is unit cell? What is lattice parameter?
2. What is Bravais lattice? How are the Bravais lattices obtained from the primitive cell? How many types of Bravais lattices are there?
3. Draw two adjacent FCC unit cells and join the top and bottom face centers of each cell. Also join these four face centers to the nearest common corners.
    i. What is the unitcell outlined by this procedure?
    ii. Is it in the Bravais list?
4. Show that packing efficiency of FCC is 74% and that of BCC is 68%.
5. Show that the ideal c/a ratio in a hexagonal unit cell is 1.633 and calculate the packing efficiency.
6. What is miller index? How is it obtained?
7. Draw the planes $(\bar{1}\,\bar{1}0),(1\bar{2}1),(2\bar{3}4),(\bar{1}12)$ and directions $[11\bar{1}],[123],[120],[1\bar{2}1]$ in a cubic unit cell.
8. If the lattice parameter of Alpha iron is 286 pm, what is its atomic radius?
9. Lattice constant of Al is 4.05 Å. What is the atomic radius of Al?
10. What is the difference between atomic structure and crystal structure?

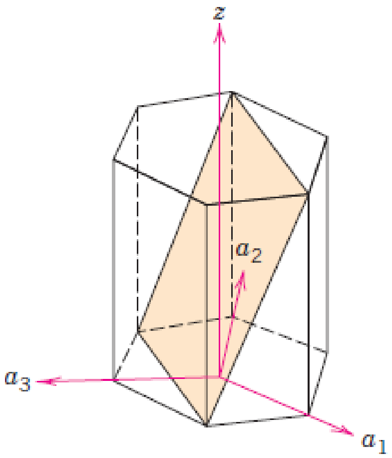
Questions?

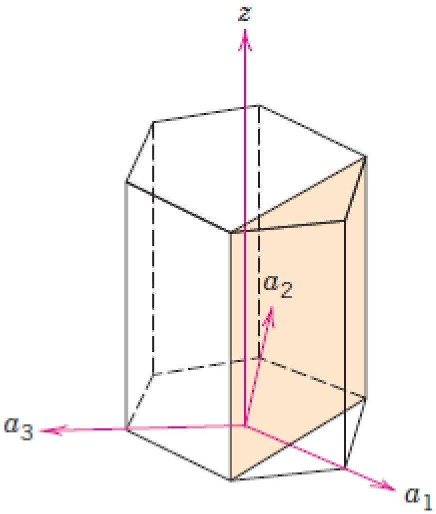
11. Why it is necessary to include a fourth miller index in the hexagonal system?
12. Convert the directions [112], [1$\bar{2}$3], [110], [111], to four indices in a hexagonal lattice.
13. A metal has a density of 10.22 g/cc, atomic weight of 95.94 and atomic radius of 0.136 nm. Is it BCC or FCC?
14. Calculate the volume of the unit cell of Zn crystal. a and c of Zn are 266.5 pm and 494.7 pm respectively.
15. Some hypothetical metal has the simple cubic crystal structure. If its atomic weight is 74.5 g/mol and the atomic radius is 0.145 nm, compute its density.
16. Calculate the planar density of {110} planes in α-Fe (BCC) crystal. *a = 0.287 nm.*
17. Calculate the linear density of [110] direction in a Cu crystal. a = 0.361 nm.
18. What are the miller indices of a plane that intersects the X axis at 2 and the Y axis at ½ and is parallel to the z axis? The structure is cubic.
19. Copper has FCC crystal structure and the unit cell with a lattice constant of 0.361 nm. What is the inter-planar spacing of d111 planes?

Questions?

20. Determine the indices for the directions and plane shown in the following hexagonal unit cell:








Thank You!