

MME211 – SCIENCE OF MATERIALS

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- Course Outline

SESSION	TOPIC
WEEK 1	<ul style="list-style-type: none">• Course Outline, Laboratory Experiments, Term Paper Topics• Types of Materials• Material Properties• <u>Laboratory</u>: Introduction to Laboratory Experiments
WEEK 2	<ul style="list-style-type: none">• Material Structure<ul style="list-style-type: none">– Atomic structure– Electronic Structure– Nuclear Model of the atom• Atomic Bonds

WEEK 3	<ul style="list-style-type: none">• Crystal Structure• Crystallization• Crystal Imperfections• Laboratory: Rockwell and Brinell Hardness Tests
WEEK 4	<ul style="list-style-type: none">• Plastic Deformation (Slip and Twinning)• Cold Work• Annealing• Laboratory: Cold Working
WEEK 5	<ul style="list-style-type: none">• Phase Diagrams (Part 1)• Phase Diagrams (Part 2)• Laboratory: Annealing

WEEK 6	<ul style="list-style-type: none"> • Polymorphism and Allotropy <ul style="list-style-type: none"> – Iron-Iron Carbide Diagrams – Iron-Iron Carbide Applications – Optical Microscope and the Crystal Structures found in Iron-Iron Carbide Diagrams • Definition of Structures on the Iron-iron carbide diagram • Sample Preparation, Etching and Preparation Artifacts • <u>Laboratory:</u> Metallography
WEEK 7	<ul style="list-style-type: none"> • Effect of Carbon on the Strength and Hardness of Steel • Effect of Alloying on the Properties of Steel Cast iron • Classification of Steels • Stainless Steels • <u>Laboratory:</u> Coldwork micrographs • <u>Laboratory:</u> Annealing Micrographs

WEEK 8	<ul style="list-style-type: none"> •TTT Diagrams •Heat Treatment of Steel • Annealing • Normalizing •Review for the test •<u>Laboratory:</u> Phase Diagram of Lead and Tin Alloys
WEEK 9	<ul style="list-style-type: none"> •TEST 1
WEEK 10	<ul style="list-style-type: none"> •Quenching and Tempering • Case Hardening • Deep Cryogenic Tempering •Solution Heat Treatment and Age Hardening •<u>Laboratory:</u> Nondestructive Testing Methods

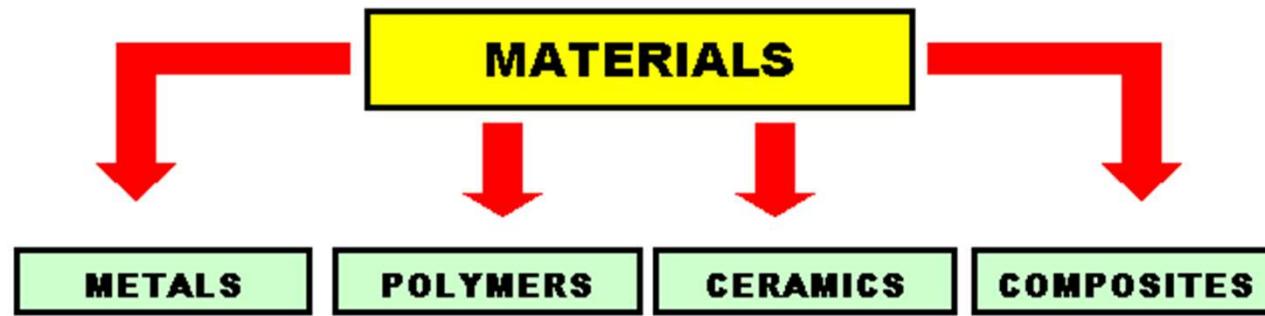
WEEK 11	<ul style="list-style-type: none"> • Tool Steels • Nonferrous Metal Alloys • Laboratory: Solution Heat Treatment and Age Hardening • <u>Laboratory:</u> Conventional Quenching and Tempering
WEEK 12	<ul style="list-style-type: none"> • Composites • Ceramics • Polymers • Thermoplastics and Thermosets • <u>Laboratory:</u> Jominy End Quench Test
WEEK 13	TERM PAPER PRESENTATIONS
WEEK 14	Review
WEEK 15	FINAL EXAM

- Grading
- Test 15 %
- Final Exam 60 %
- Lab reports 15 %
- Term Papars (Assignment) 10 %

REFERENCES

- 1 James P. Schaffer et al. The Science and Design of Engineering Materials. 2nd Edition, McGraw-Hill, 1999
- 2 J.C. Anderson et al. Materials Science. 2nd Edition, E.L.B.S., 1974
- 3 John, Introduction to Engineering Materials. Macmillian
- 4 D.J. Davies, L.A. Oelmann. The Structure, Properties and Heat Treatment of Metals. Pitman, 1983
- 5 Atkins, Physical Chemistry
- Khanna O.P. material Science & Metallurgy. Dhanpat Rai Pub. Ltd. New Delhi, 2008
- Rajput R.K. Material Science & Engineering. S. K. Kataria & Sons. Delhi, 2007

Types of Materials



Metals:

good **electrical** and **thermal conductivity**,
high **strength**, high **stiffness**, and have good
ductility.

Some metals, such as Fe, Co and Ni are **magnetic**.
At extremely low temperatures, some metals and
intermetallic compounds become superconductors.

*(5 categories of Engineering Materials): Metals, Polymers,
Ceramics, Semi-conductors & Composites.*

Pure metals:

- Pure metals are elements which come from a particular area of the periodic table.

Examples of pure metals include copper in electrical wires and aluminum in cooking foil and beverage cans.

Metal Alloys:

- Metal Alloys contain more than one metallic element. Their properties can be changed by changing the elements present in the alloy.

Examples of metal alloys include stainless steel which is an alloy of iron, nickel, and chromium; and gold jewelry which usually contains an alloy of gold and nickel.

- The most important properties of metals include density, fracture toughness, strength and plastic deformation. The atomic bonding of metals also affects their properties. In metals, the outer valence electrons are shared among all atoms, and are free to travel everywhere. Since electrons conduct heat and electricity, metals make good cooking pans and electrical wires.
- Many metals and alloys have high densities and are used in applications which require a high mass-to-volume ratio.
- Some metal alloys, such as those based on Aluminum, have low densities and are used in aerospace applications for fuel economy.
- Many metal alloys also have high fracture toughness, which means they can withstand impact and are durable.

Polymers

- A polymer has a **repeating structure**, usually based on a **carbon backbone**. The repeating structure results in large chainlike molecules.
- Polymers are useful because they are **lightweight**, are **corrosion resistant**, are easy to **process at low temperatures**, and are generally **inexpensive**.
- Some important characteristics of polymers include their **size (or molecular weight)**, **softening and melting points**, **crystallinity**, and **structure**. The mechanical properties of polymers generally include **low strength and high toughness**. Their strength is often improved using reinforced composite structures.
- One of the distinct properties of polymers is that they are **poor conductors of electricity and heat**, which makes them good **insulators**.

Ceramics

- A ceramic is often broadly defined as any **inorganic nonmetallic material**. Examples of such materials can be anything from NaCl (table salt) to clay (a complex silicate). Some of the useful properties of ceramics and glasses include **high melting temperature, low density, high strength, stiffness, hardness, wear resistance, and corrosion resistance**. Many ceramics are good **electrical and thermal insulators**.
- Some ceramics have special properties: some ceramics are **magnetic materials**; some are **piezoelectric materials**; and a few special ceramics are **superconductors at very low temperatures**.
- Ceramics and glasses have one major drawback: they are **brittle**

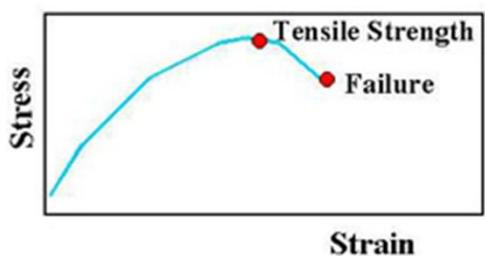
Glasses

- A glass is an **inorganic non-metallic** material that does not have a crystalline structure. Such materials are said to be amorphous.
- Examples of glasses range from the soda-lime silicate glass in soda bottles to the extremely high purity silica glass in optical fibers.

Composites

- Composites are formed from two or more types of materials. Examples include polymer/ceramic and metal/ceramic composites.
- Composites are used because overall properties of the composites are superior to those of the individual components. For example: polymer/ceramic composites have a greater modulus than the polymer component, but aren't as brittle as ceramics.

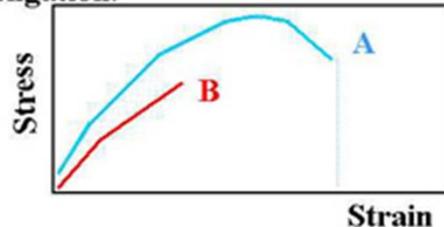
Tensile strength is defined as the highest stress that a material can withstand before failure occurs.



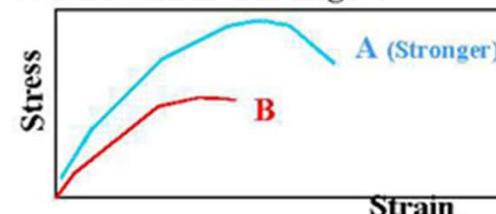
Toughness is defined as the total area under the stress -strain curve. It indicates the amount of energy absorbed before failure.



Ductility is measured by the amount of elongation that can be applied to the material before the failure occurs. Strain is directly proportional to elongation.

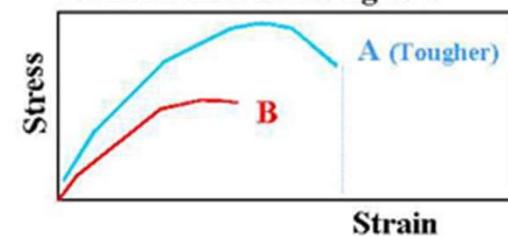


Which material is stronger?



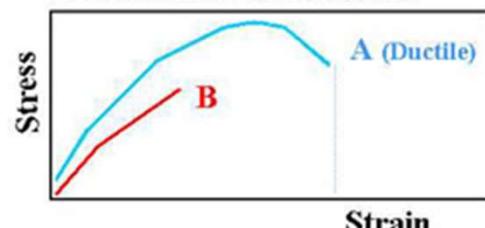
A is stronger. Because it withstands a higher stress before failure than material **B**. (Compare the peak stress levels of the two curves)

Which material is tougher?



A is tougher, because the area under curve **A** is greater than **B**. This indicates that **A** absorbs more energy than **B** before failure.

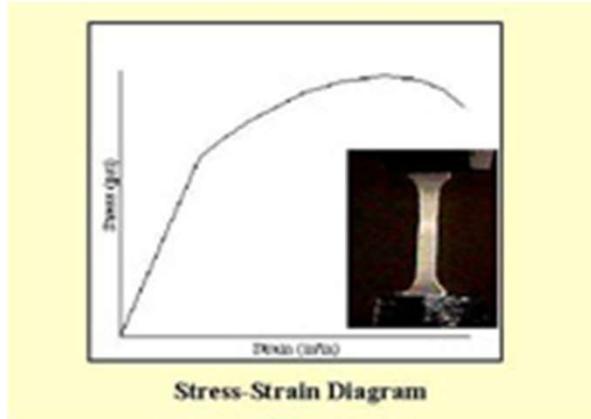
Which material is ductile?



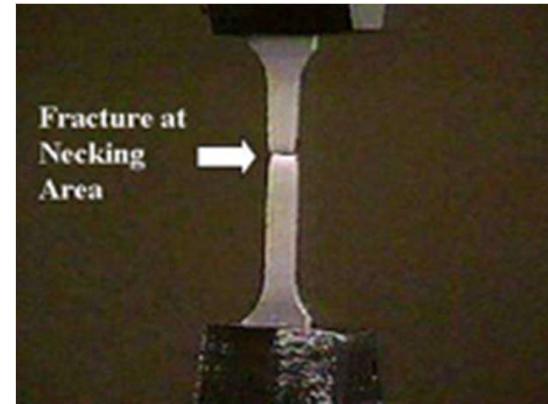
A is ductile, because the strain under curve **A** is greater than **B**. This indicates that **A** shows more elongation than **B** before failure.

Tensile Test:

- Tensile test determines the strength of the material when subjected to a simple stretching operation. Typically, standard dimension test samples are pulled slowly at a uniform rate in a testing machine while the strain is defined as :
- *Engineering Strain = Change in Length / Original Length*
- The engineering stress is defined as:
- *Engineering Stress = Applied Force / Original Area*



Slide 1. Stress-strain diagram

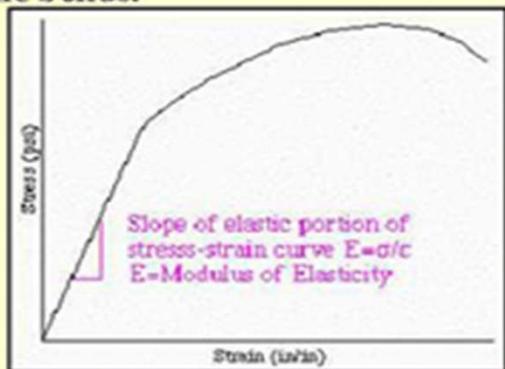


Slide 2. Fracture of a flat tensile test specimen

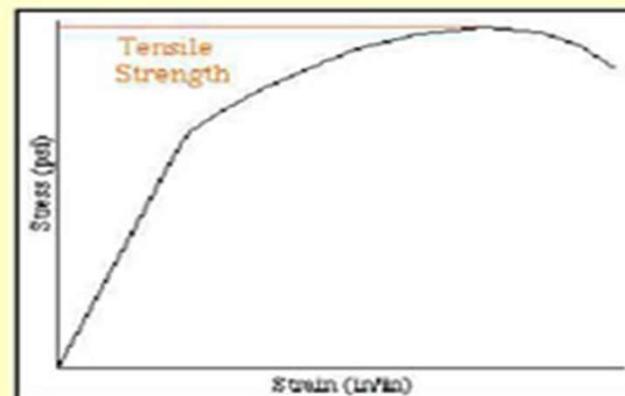
- Slide 1 shows the stress-strain diagram of a ductile material where the linear portion of the graph indicates elastic deformation.
- **Modulus of Elasticity:** The initial slope of the curve, related directly to the strength of the atomic bonds. This modulus indicates the **stiffness** of the material. (Modulus Elasticity is also known as Young's Modulus)
 - *Modulus of Elasticity, $E = \text{Change in Stress} / \text{Change in Strain}$*

Tensile Strength: The maximum stress applied to the specimen. Tensile strength is also known as Ultimate Strength. (The highest point on the stress-strain diagram)

Modulus of elasticity - the initial slope of the curve, related directly to the strength of the atomic bonds.



Tensile strength - the maximum stress applied to the specimen.



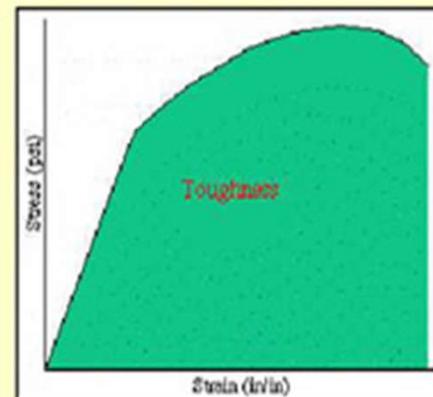
Ductility: The total elongation of the specimen due to plastic deformation, neglecting the elastic stretching.

Toughness: The total area under the curve, which indicates the energy absorbed by the specimen in the process of breaking.

Ductility - the total elongation of the specimen due to plastic deformation, neglecting the elastic stretching (the broken ends snap back and separate after failure).



Toughness - the total area under the curve, which measures the energy absorbed by the specimen in the process of breaking.

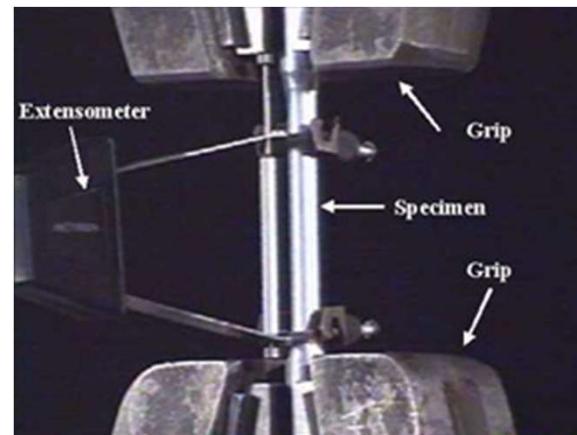


Extensometer

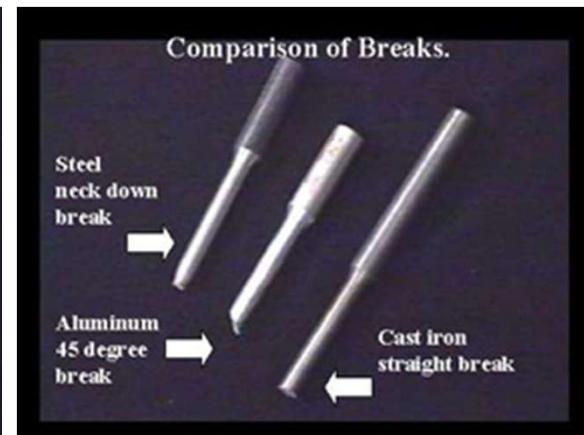
- **Extensometer:** The instrument that measures the elongation of a material while applying tension.



Tensile Test Machine



Measurement of Elongation



Comparison of Breaks.

Material Structure

- All **matter** is considered to be composed of unit substances known as **chemical elements**. These are the smallest units that are distinguishable on the basis of their **chemical activity and physical properties**. The elements are composed of **atoms** which have distinct structure characteristic of each **element**.
- **Matter:** Anything that has **weight** and that takes up **space**.
- **Forms of Matter:** Solid, Liquid, Gas
- **Molecule:** The smallest particle of matter that retains the same properties of that matter. Example: Water
- **Compound:** A substance that can be broken down into two or more simpler substances. (A compound is made of millions of molecules)
- **Element:** The smallest part of a substance that retains the same properties of that substance and can not be broken down any further. Elements are composed of atoms which have a distinct structure characteristic of each element.
- **Atom:** The smallest particle of an element which retains the distinct structure characteristic of an element.

Atomic Structure:

- The free atom is composed of **electrons**, **protons**, and **neutrons**. Almost the entire mass of the atom is concentrated in the **nucleus**, which contains the **protons (positive charges)** and **neutrons (electrically neutral particles)**. The electrical charge **q** carried by each **e** and **p** is **1.60×10^{-19} coulombs**. An atom consists of a minute **positively charged nucleus** surrounded by a sufficient number of **electrons (negative charges)** to keep the **atom as a whole neutral**. The nucleus is **10^{-14}m** in diameter. Since the electron and proton have equal but opposite electrical charge, the neutral atom must contain an equal number of electrons and protons.

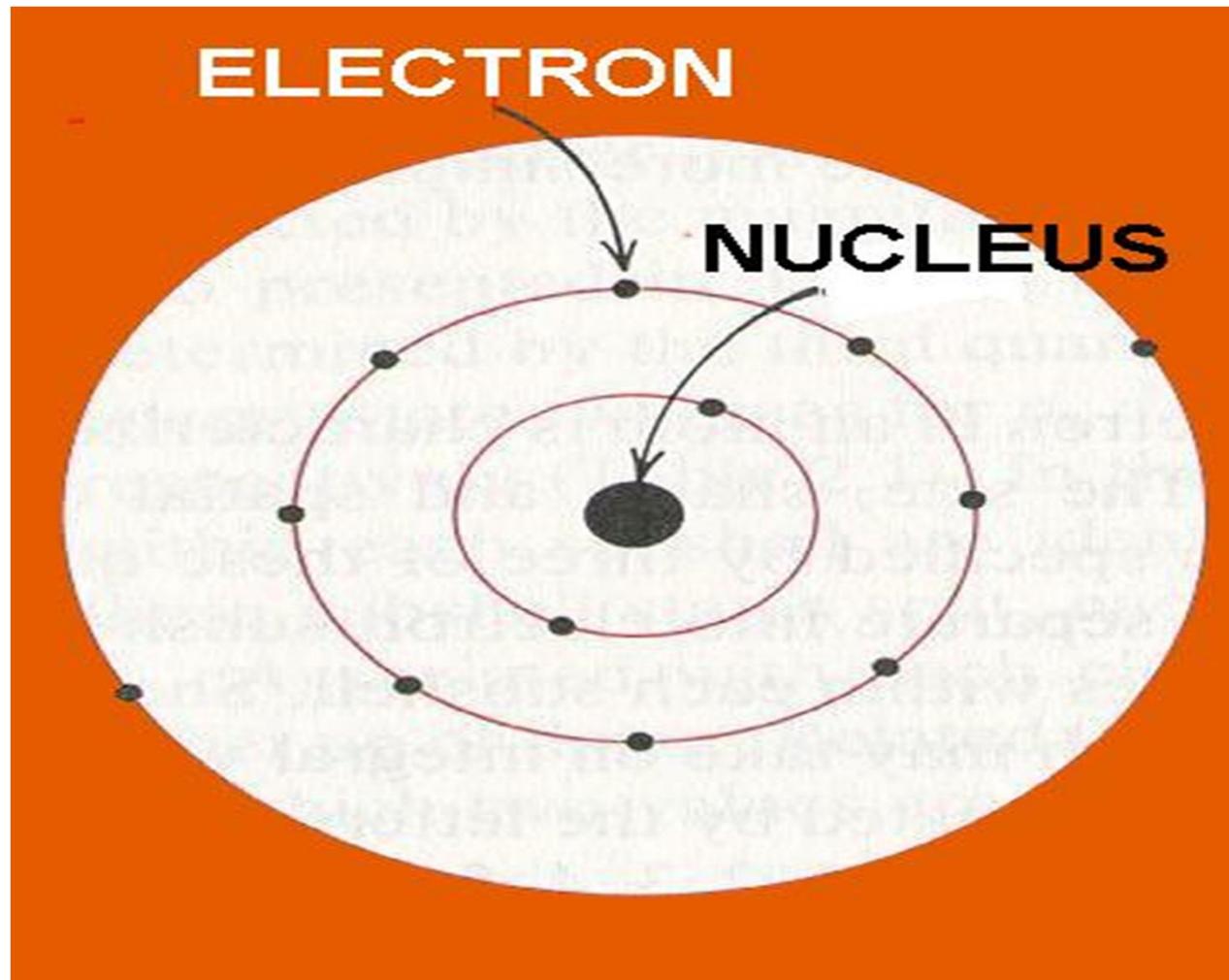


Figure 1. Atomic Model

Atomic Mass Number:

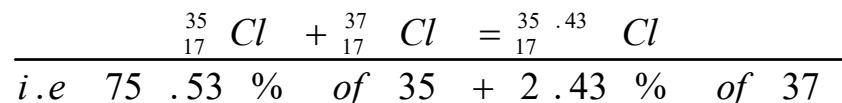
- **Atomic Mass Number, A** = Number of electrons, **e** + Number of neutrons, **N** or it can be equal to Number of Protons, **p** + Number of Neutrons, **N** i.e.
- **A = e + N or A = p + N**
- The **mass** of each proton and neutron is about 1.67×10^{-24} g which is referred to **a.m.u**, but the mass of each electron is 9.11×10^{-28} g which makes a negligible contribute to the atomic mass of the element.
- **M_p is greater than M_e by 1876**
- Mass Number has a mass very close to the atomic mass unit. **The mass number of an atom approximately expresses its ATOMIC MASS.**
- Mass Number is the mass of Avogadro number, **N_A = 6.02×10^{23} mol⁻¹** is the number of atoms or molecule in a **g mole**. The **unit** of atomic mass is **g/g mole or a.m.u**, which is the mass of carbon 12.
- **Atomic Number:**
- Atomic Number, **Z** = Number of electrons = Number of protons
- **Z = e = p.**
- The number of **p** in the nucleus of an atom is the **characteristic of the element in which that atom belongs** and is called the **ATOMIC NUMBER** of that element.

	Proton	Neutron	Electron
Symbol	p	N	e
Mass , kg	1.67x10⁻²⁷	1.67x10⁻²⁷	9.11x10⁻³¹
Charge, C	1.6x10⁻¹⁹	0	1.6x10⁻¹⁹
Mass relative to e	1876	1876	1
Charge relative to p	+1	0	-1

- The electrons, spinning on their own axes as they rotate around the nucleus, are arranged in definite shells. The **maximum number of electrons** that can fit in each shell is $2n^2$ where n is the shell number.
- The maximum number of electrons that can fit in the first shell (K) is two, the second shell (L) eight, the third shell (M) eighteen, the fourth shell (N) thirty two, etc.

ISOTOPES

- Atoms of the same element that contain a different number of N in the nucleus, and thus have different atomic mass.
- Atomic mass = average (means) of the proportion (abundances) isotopes.



- All the elements in the periodic table exhibit isotopic character except Be, Fe, Na, Al, P, Sc, Mn, Co, As, Y, Nb, Rh, I Cs, Pr, Ts, Ho, Tm, Au. ISOTOPES
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PHYSICAL MODELS OF THE ATOM (ELECTRONIC STRUCTURE)

- An **e** has the **lowest energy** when it is in the orbit **closest to the nucleus** (i.e. normal or ground state of an atom)
- The energy of an **e** can take on **only definite “allowed” values**, in other words it is quantized i.e. electron occupy discrete energy levels within the atom. Each **e** possesses a particular energy, with **no more than 2 e in each atom having the same energy**.
- The energy level to which each **e** belongs determined by the **4 quantum number**.
- The number of **POSSIBLE ENERGY** levels is determined by the **1st 3 quantum number**

FIRST (PRINCIPAL) QUANTUM number, n

- The **possible energy states** of an electron in an atom are determined by the volume of the principal quantum number, n that can take 1,2,3...., etc. An e has the smallest energy at n=1. It grows with n increases. At n=1, e is the 1st on ground energy level, at n=2, it is at 2nd level etc .
- **n determines the dimension of the electron cloud.** A greater value of n corresponds to greater dimensions of the dimensions of the electron cloud (layers or shells).
- A DISCRETE number of e is situated in every level and is equal to
 - $N = 2n^2$ where N – total number of e
 - 1st level $N = 2 \times 1^2 = 2$ electrons
 - 2nd level $N = 2 \times 2^2 = 8$ electrons
 - 3rd level $N = 2 \times 3^2 = 18$ electrons and etc.
- Principal quantum number, n 1 2 3 4 5 6 7
- Designation of energy level K L M N O P Q

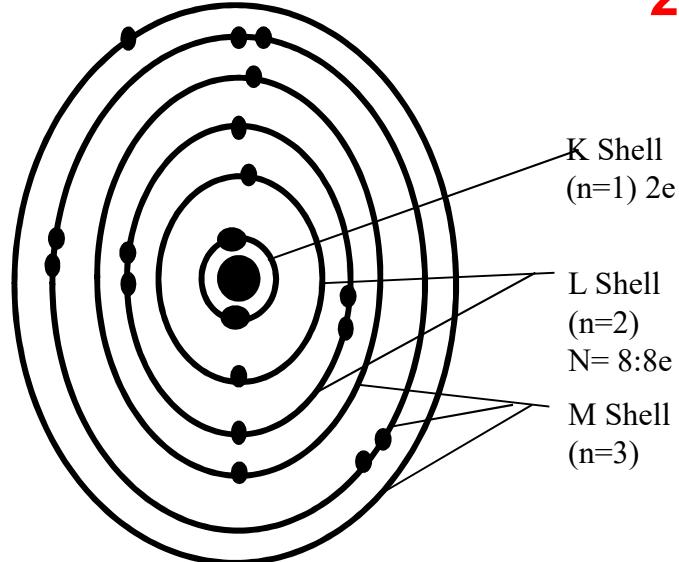
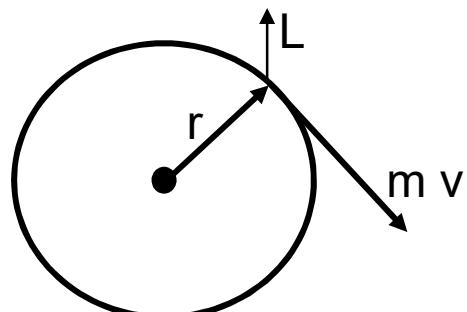


Figure 1. The atomic structure of sodium²³



2nd (ORBITAL) or AZIMUTHAL Quantum number, l
The shape of the e cloud is determined l

that can take the value of 0 to (n-1). It determines the value of **ORBITAL ANGULAR MOMENTUM** of an electron.

$l=0$ when $n=1$ does not mean an electron at rest, but a motion that does not give rise to a resultant angular momentum, L

$$L = m v r$$

m is the mass of the particle, v is the velocity and r is the position vector connecting the center of revolution to the particle.

Na

The angular momentum of the electron

$$L_m = \frac{h}{2n} \sqrt{(q(q+1))} \quad \text{-----} (1)$$

h -plank's constant = 6.626×10^{-34} Js

q – the charge of the electron.

- The azimuthal quantum numbers are customarily called the **ENERGY SUBLVELS OR SUBSHELLS** of an electron in an atom. They are designated by lowercase letters

Orbital q. no	0	1	2	3	4	5	6	7
Designation of energy level	s	p	d	f	g	h	i	j

- s-sharp, p-principal, d-diffuse, f-fundamental.
- when $n=2$ we have either 0 or -1 i.e. 2 sublevels
- In general, in the nth level, there will be n sublevels with equals to 0, 1, 2, 3,..., n-1

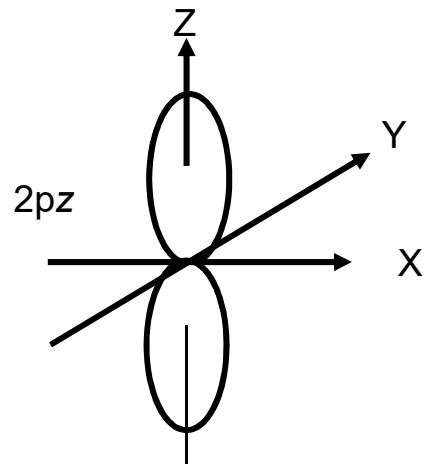
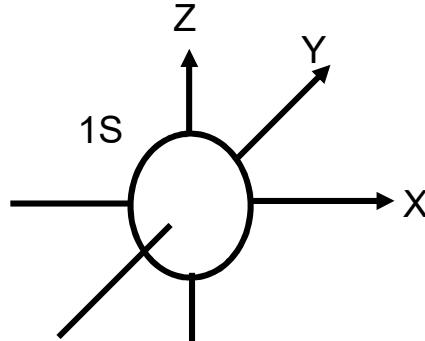
THIRD (MAGNETIC) QUANTUM number, m_l ,

- indicates the **orientation of an electron**. It gives the number of energy levels or orbital for each azimuthal quantum number. The total of for each l is $2l+1$. The values of m_l are given by whole numbers between $-l$ and $+l$. for example 3 different values of (-1, 0, +1) are possible for p electron ($=1$) and s for M, (-2,-1,0,+1,+2) for d electron ($=2$) which is $2(2)+1=5$.
- m_l is called magnetic because of the interact of the magnetic field set up by an electron with which the external magnetic field depends on its value.

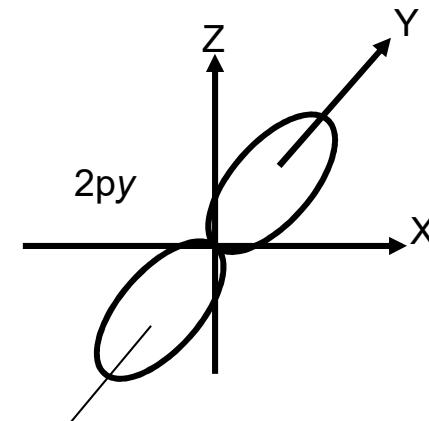
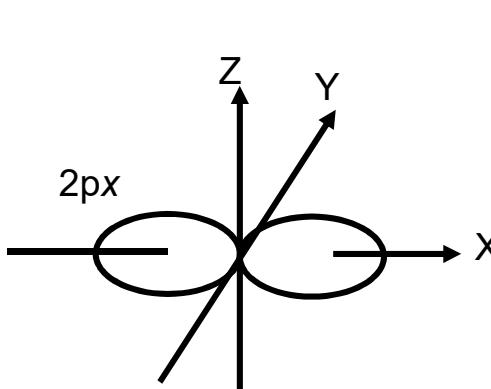
SHAPE AND ARRANGEMENT OF ELECTRONS IN SPACE

Electron clouds of 1s, 2p and 3d electrons

i) Since $m_l = (0) = 1$ for "s" state $l = 0$, then any possible arrangement of an S electron cloud in space are identical



ii) p orbital $l = 1$; $m_l (-1, 0, 1) = 3$, accordingly they can be arranged in space in 3 ways



The 3 p electron clouds are oriented along mutually perpendicular direction, which are conventionally taken as the direction of the coordinate axes (x, y or z); the corresponding states of the electrons are designated p_x , p_y , and p_z

iii) For d orbital $l = 5$; $m_l = (-2, -1, 0, +1, +2) = 5$ values of the magnetic quantum number are possible and accordingly, 5 different orientations of the d electron clouds in space.

FOURTH QUANTUM NUMBER, (SPIN QUANTUM NUMBER)

- m_s or simply the spin is used to determine the **INTRINSIC state of an electron**. Unlike n , l , and m_l , m_s is not associated with motion of the electron about the nucleus. can be loosely associated with the spin of the electron about its own axis. This can have only 2 values $+\frac{1}{2}$ or $-\frac{1}{2}$ depending on the direction of rotation of the electron about its axis ($m_s = +\frac{1}{2}$ or $-\frac{1}{2}$). Two electrons in the same orbital having values of $+\frac{1}{2}$ and $-\frac{1}{2}$ are said to be paired; both of them would have the same amount of energy.
- NOTE: The possible values of the spin quantum number differ by **UNITY**.

PAULI EXCLUSION PRINCIPLE

It specifies that **no more than 2 electrons**, each with oppositely electronic spins, may be present in each orbital. The spin quantum number is assigned values $\pm \frac{1}{2}$ to reflect the different spins .

Summary

Table 1.2 Maximum number of electrons in atom energy levels and sublevels

Energy Level	Energy sublevel	Possible Values of Magnetic Quantum Number	Number of orbitals		Number of electrons	
			In sublevel	In level	In sublevel	In level
K (n=1)	s($l=0$)	0	1	1	2	2
L (n=2)	s($l=0$) p($l=1$)	0 -1, 0, +1	1 3	4	2 6	8
M (n=3)	s($l=0$) p($l=1$) d($l=2$)	0 -1, 0, +1 -2,-1,0,+1,+2	1 3 5	9	2 6 10	18
N=(n=4)	s($l=0$) p($l=1$) d($l=2$) f($l=3$)	0 -1, 0, +1 -2,-1,0,+1,+2 -3,-2,-1,0,+1,+2,+3	1 3 5 7	16	2 6 10 14	32

CONCLUSION

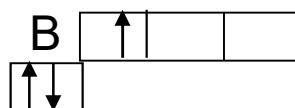
- Each principal level of quantum number, n contains a total n sublevels
- Each sublevel of quantum No, l contains a total $2l + 1$ orbitals
- Each orbital can hold two electrons
- The maximum number of e in each energy level is $2n^2$
- The shorthand notation frequently used to denote the electronic structure of an atom combines the numerical value of the principal quantum No, n, the lowercase letter rotation for the azimuthal quantum No and a superscript showing the number of electrons in each orbital. Thus, the shorthand notation for the electronic structure of bromine which has an atomic number of 35 is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2 4p^5$

NOTE

The energy state of the electrons **depends not only on the principal quantum number n, but also on the orbital quantum number**. This is associated with the circumstance that an electron in an atom is **not only attracted** by the nucleus, but is also **repelled** by the electrons between the given electron and the nucleus. The internal electron layers form a peculiar shield that weakens the attraction to the nucleus

ORBITAL DIAGRAMS HUND'S RULE

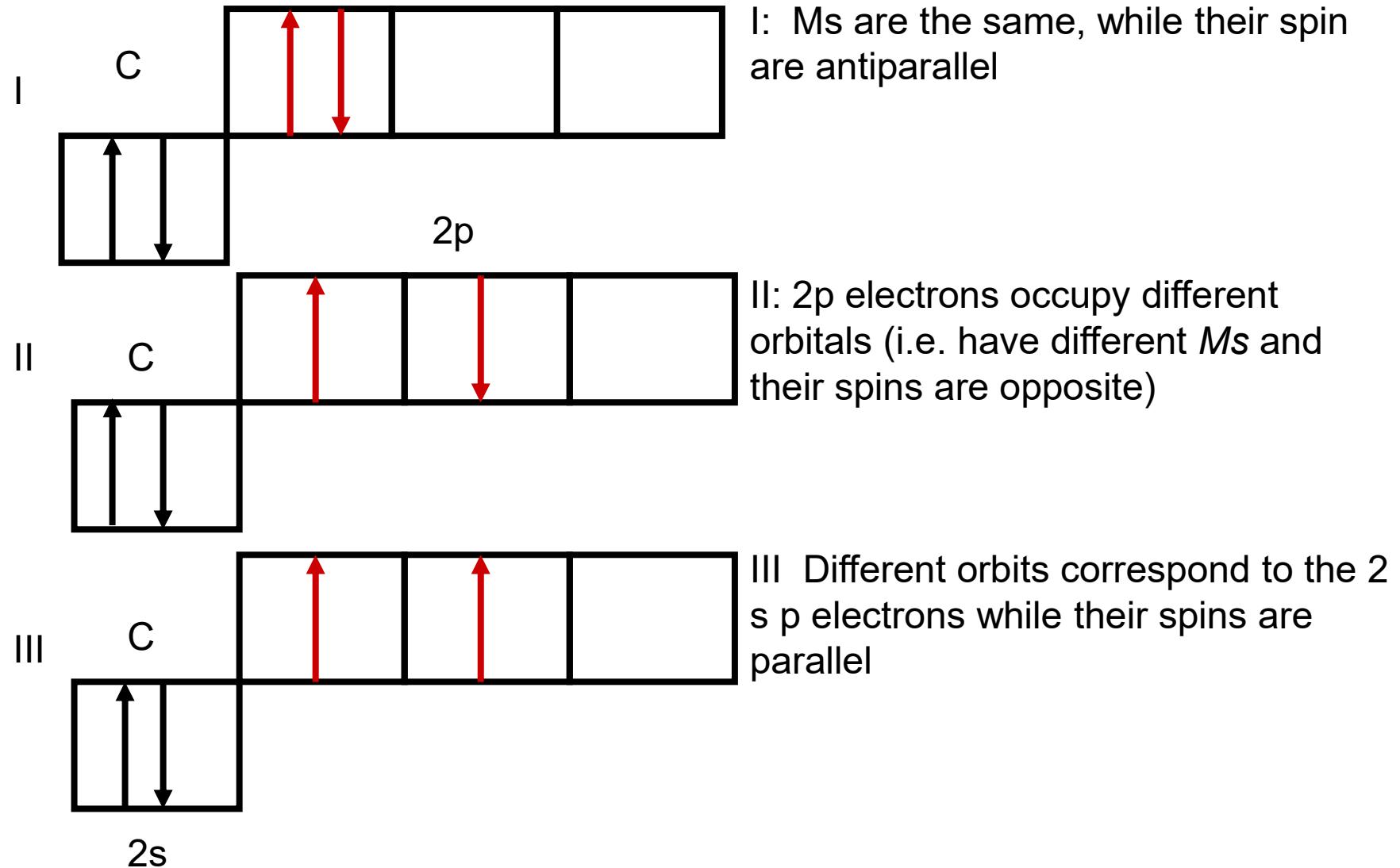
- Orbital diagram indicates the number of electrons in each orbital and their respective spins:



Electron configuration of boron

Definition (Hund's Rule)

In an atom in which orbitals of equal energy are to be filled by electrons, the order of filling is such that as many electrons **remain unpaired as possible**



Among the 3 diagrams, the third is correct and it corresponds to the greatest value of the total spin of an atom. (In I & II the sum of the spin of all electrons is zero while, for the third diagram it is unity.)

- Therefore Hund's rule states that the maximum value of the total spin of an atom corresponds to the stable i.e. unexcited state in which the atom has the smallest possible energy; at any other distribution of the electrons, the energy of the atom will be higher, so that it will be in an excited, unstable state. In other words the distribution of the electrons within the limits of an energy sublevel at which the absolute value of the total spin of the atom is maximum corresponds to the stable state of an atom.

1st Rule

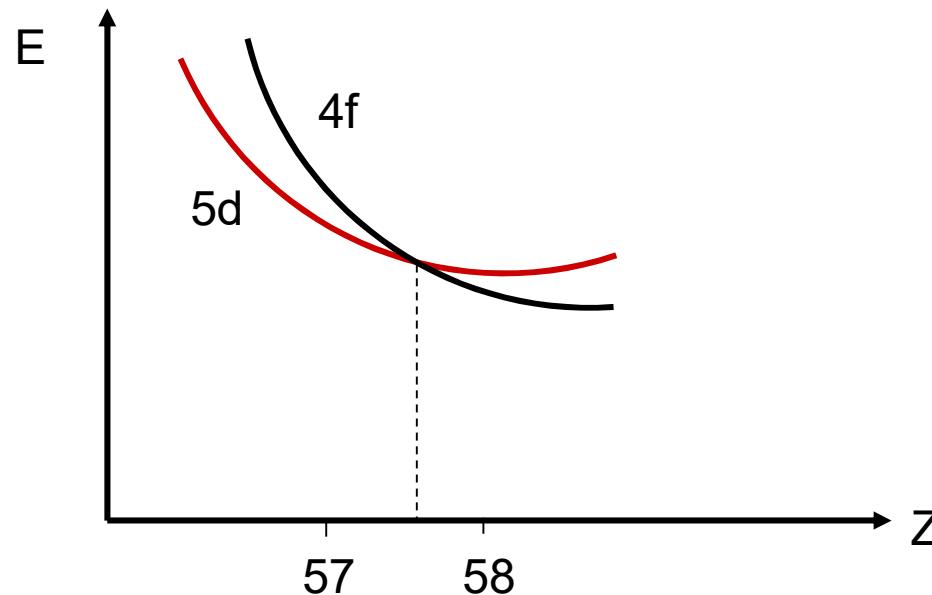
- The sequence of filling of the atomic electron orbitals depends on the values of the principal and orbital quantum number. And the energy of an electron rises as the sum of these 2 quantum number increases, i.e. with increasing $n+l$. With an increase in the charge of the nucleus of an atom, the electron orbitals are filled consecutively from orbitals with a smaller value of the sum of the principal and orbital quantum ($n + l$) to orbitals with a greater value of this sum.

2nd Rule

- At identical values of the sum $n+l$ the orbital are filled consecutively in the direction of the growth in the value of the principal quantum number, n

- Note:
- The chemical properties of the elements are determined first of all by the structure of the outer electron layer of their atom and depend only to a smaller content on the content on the structure of the preceding (inner) electron layers.
- All the **d (transition) elements are METALS** whereas the filling of the outer P sublevel result in a transit from a metal to a typical non-metal and finally, to a noble gas.
- The outer orbitals of d metals are filled in order of energy stability and an increased energy stability is a property of electrons configurations with exactly a **HALF-FILLED or TOTAL-FILLED sublevel** (e.g. structures containing 3 electrons in the outer layer, five d electrons in the layer preceding the outer one, or seven f electrons in a still deeper layer).

- **Violation**
- The violations of the “normal” sequence of filling the energy states in (lanthanum ($Z = 57$) (the appearances of a 5d instead of a 4f electron) and cesium (the simultaneous appearance of two 4f election). This can be explained as follows: upon an increase in the charge of the nucleus the electrostatic attraction to it of an electron in a given energy sublevel becomes **stronger** and the **energy** of the electron **diminishes**. The energy of the electron in different sublevels changes differently because the charge of the nucleus is increased to a different extent with respect to these electrons. In particular, the energy of 4f of electrons diminishes with a growth in the charge of the nucleus more sharply than the energy of the 5d electrons.



Dependence of the energy of the 4f and 5d electrons on the nuclear charge.

- Consequently in La ($Z = 57$), the energy of the 5d electrons is found to be lower and in cesium ($Z=58$) higher than that of the 4f electrons.
Accordingly, the electron that in La is in the sublevel 5d in cesium passes to the sublevel 4f
- ${}^{57}\text{La}$ $1\text{s}^2 \ 2\text{s}^2 \ 2\text{p}^6 \ 3\text{s}^2 \ 3\text{p}^6 \ 3\text{d}^{10} \ 4\text{s}^2 \ 4\text{p}^6 \ 4\text{d}^{10}$
 $5\text{s}^2 \ 5\text{p}^6 \ \textbf{5d}^1 \ 6\text{s}^2$
- ${}^{58}\text{Ce}$ $1\text{s}^2 \ 2\text{s}^2 \ 2\text{p}^6 \ 3\text{s}^2 \ 3\text{p}^6 \ 3\text{d}^{10} \ 4\text{s}^2 \ 4\text{p}^6 \ 4\text{d}^{10}$
4f²
 $5\text{s}^2 \ 5\text{p}^6 \ 6\text{s}^2$
- The most stable state of an electron in an atom corresponds to the minimum possible value of its energy

Periodic Table

- **Valence:** The valence of an atom is the **ability** of the atom to enter into **chemical combination** with other elements and is often determined by the number of electron in the outer most combined **s p level**. O_2 -referred valence and H_2 -referred Mg-2; Al-3; Ge-4; Na-1; P-3,5; Mn-2,3,4,6,7
- **ELECTRONEGATIVITY:** Describes the tendency of an atom **to gain an electron**. Atoms with almost completely filled outer energy level, like Cl are strongly electronegative and readily accept electron.
- **EXCITATION, IONIZATION AND IONIZATION ENERGIES:** When atoms are exposed to high energy high temperature or exposed to fast-moving electrons from nearly any source, they tend to become excited and to give off energy in the form of radiation. The nature of the radiation emitted depends on the excitation which is used. When atoms through collisions, **absorb energy and become excited, they move in the process to higher allowed electronic energy levels**. Once excited the atoms will be unstable and will tend to return to lower electronic energy levels, ultimately reaching the lower energy level, the ground state of the atom. Under excitation the atom will quickly reach a **state of dynamic equilibrium** in which some atoms are releasing energy at the same rate that it is being absorbed by other.

- In a process in which an excited atom makes a transition to a lower energy level, **a photon of light may be emitted** (A ray of light can be considered to consist of photons which appear to have some properties characteristic of particles).
- The wavelength of the photon is related to the magnitude of the change in energy (ΔE) of the atom by

$$|\Delta E_{atom}| = E_{Photon} = \frac{hc}{\lambda} \quad \dots \quad (2)$$

where h is a physical constant, called = Planck's constant 6.626×10^{-34} J.S, c is the speed of light = 2.998×10^8 m/s and λ the wavelength of the photon in meters.

IONIZATION ENERGY and AFFINITY ELECRON

- The amount of energy needed to detach an electron from an atom with conversion of the latter into a positive ion is called ionization energy.
- The smallest voltage of the field at which the speed of the electrons becomes sufficient for ionization of the atoms is the ionization potential of the atoms and is expressed in volts.
- The energy of an electron is often expressed in electron volts (eV)
- 1eV is the energy acquired by an electron in an accelerating electric field with a potential difference of one volt
- $1\text{eV} = 1.6 \times 10^{-19}\text{J} = 96.5\text{KJ/mol}$
- The ionization energy expressed in electron-volts numerically equals the ionization potential expressed in volts.
- The first ionization energy, of an atom is the energy change of the formation of positive ion from the gaseous atom;



- The magnitude of the E, can be a measure of the greater as smaller “**metallicity**” of an element the smaller the E, the easier it is to detach an electron from the atom and the stronger should the metallic properties of the element be empresses.
- An increase in the **atomic number of element is attended by diminishing of the ionization energy** in the groups. This fronts to an increase in the metallic properties and accordingly, a decrease in the non-metallic properties of the relevant element.
- This regularity is associated with the growth in the atomic radii. - **the smaller the atom, the more tightly its electrons are held to the nucleus and the more difficulty they are to be removed**. In addition, an increase in the number of intermediate electron layers between the nucleus of an atom and the outer electrons leads to greater screaming of the nucleus, i.e. diminishing its effective charge. Both these factors (the growing of its effective charge) lead to weakening of the bond of the outer electrons with the nucleus and consequently, to lowering of the ionization energy. Large atoms such as those of the alkali metals have relatively **low ionization energies** because the **outer electrons are far away from the positive charge of the nucleus**.

Summary

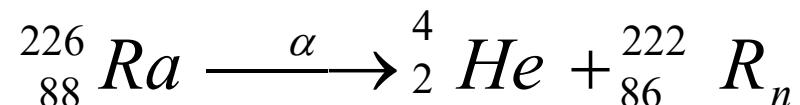
- The properties of an atom are determined by the following factors:
 - The **atomic number** that corresponds to the number of electrons or protons in a neutral atom
 - The **mass of the atom**
 - The **spatial distribution of the electrons** in orbits around the nucleus
 - The **energy of the electrons** in the atom and
 - The **ease of adding or removing** one or more **electrons** from the atom to create a **charged ion**.

Problem: Determine the electron configuration for a sulfur atom, a selenium atom and a tellurium atom. Explain why these three elements display similar characteristics?

STRUCTURE AND PROPERTIES OF ATOMIC NUCLEI. RADIOACTIVITY

- **Radioactivity:** This is the name given to the phenomenon of the emission of radiation by certain element capable of penetrating through a substance, ionizing air, and of causing photographic plates to dasher. This phenomenon was first discovered in uranium compounds by the French physicist **A. Becquerel**.
- Investigation of the Curies (Pierre) and of the British physicist **Rutherford** showed that radioactive radiation is not homogeneous: a magnetic field causes it to divide into **three beams**, one of which does not change its original direction, while the other 2 deviate in opposite directions.
- The **rays that do no deviate** in a magnetic field and, consequently, have **no electric charge**, were called **GRAMMA RAYS**. They are electromagnetic radiation similar to **X-rays** and having a very high **penetrability**.
- The deflection of the other outer 2 teams under the action of magnetic field indicates that these beams consist of electrically charged particles. The opposite direction of the observed deflecting witness that one beam contains **negatively charged particles (BETA RAYS)**, while the other **(ALPHA RAYS) CONTAINS POSITIVELY CHARGED PARTICLES**. The **beta rays** were found to be a stream of rapidly moving **electrons**.
- The positively charged **alpha rays** were found to consist of particles whose **mass equals that of a helium atom** and whose charge is absolute value is **double that of an electron**.

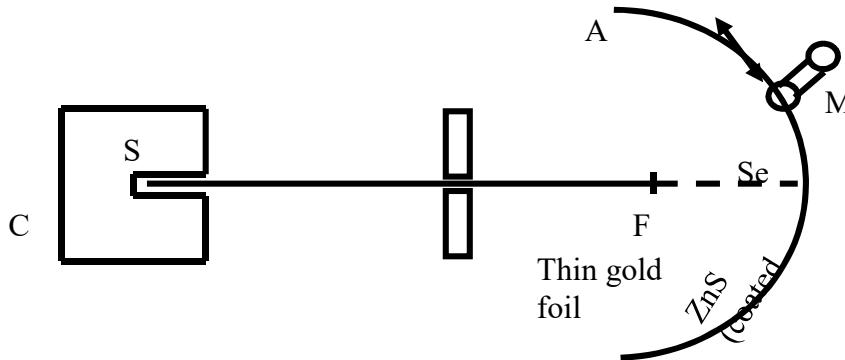
- Rutherford proved by direct experiments that these particles are charged helium atoms. The results of the experiment proved that Radium atoms in the process of radioactive mission disintegrate (decay), transforming into atom of other elements, particularly into helium atoms



NUCLEAR MODEL OF THE ATOM

According to the model proposed in 1903 by J.J Thomas, an atom consists of a positive charge uniformly distributed over the entire volume of the atom and electron migrating inside this charge.

To verify Thomson's hypothesis and establish more accurately the internal structure of an atom, E-Rutherford performed series of experiments involving scattering of alpha particles by thin metal plates (gold foil)



Set-up of alpha particle scattering experiment

- Source S of alpha rays was placed in lead capsule C with a borehole drilled in it in order to obtain a pencil of alpha particles flying in a definite direction. Upon reaching screen be coated with zinc sulphide, the alpha particles cause to grow this gold foil F was placed between the radiation source and the screen. The flashes on the screen allowed the experimentalist to assess the deflection of the particles from the original direction, although the thickness of the foil was hundreds of thousands of atomic diameters. But a certain fraction of the particles was nevertheless deflected through small angles while from time to time the particles sharply changed the direction of their motion, and some of them even rebounded from the foil as if they had encountered a massive obstacle.
- It followed from these results that the predominating part of the space occupied by an atom of a metal contains no heavy particles only electrons can there. And the mass of main alpha particles is almost 7500 times greater than that of an electron, so that a collision with the latter cannot virtually affect the direction of the motion. Cases of where deflection and even rebounding of the alpha particles however signify that an atom contains heavy particles in which the predominating part of the entire mass of the atom is concentrated. This nucleus occupies a very small volume and must have a positive charge. This is why that nucleus repels the positively charged alpha particles.

- On the basis of these considerations, Rutherford in 1911 proposed the following **model of the structure of an atom** which is known as the structure of an atom which is known as the **nuclear model of the atom**. An atom consists of a positively charged nucleus in which the predominating part of the atom's mass is concentrated, and of electrons orbiting around it. The positive charged of the nucleus is neutralized by the total negative charge of the electrons, so that the atom as a whole is electrically neutral. The centrifugal force produced owing to rotation of the electrons around the nucleus is balanced by the force or electrostatic attraction of the electrons to the appositively charged nucleus. The size of the nucleus is very small in comparison with that of an atom is of the order of 10^{-8} cm, whereas the diameter of the nucleus is of the order of 10^{-13} to 10^{-12} cm.
- This experiment made it possible not only to detect an atomic nucleus, but also to determine its charge. It followed that the **charge of a nucleus (expressed in units of electron charge of a nucleus (expressed in units of electron charge) numerically equals the atomic number) of the element in the periodic table.**

- The physical meaning of the atomic number of an element in the periodic table was found to be a very important constant of an element expressing the positive charge of its atom's nucleus. It can be seen from their electrons orbiting about the nucleus also equals to the atomic number of the element.
- This discovery eliminated an apparent contradiction in the periodic table the position of some of the elements with a greater atomic mass ahead of elements with a smaller atomic mass



- There is no contradiction here because the placement of an element in the table is determined by the charge of the atomic nucleus. The charge of a Fe atom is 52, and that of an iodine atom 53-established experimentally.
- Thus, the charge of the atomic nucleus is the basic quantity determining the properties of an element and its position in the periodic table.
- The determination of the atomic number of the element according to the charges of the nuclei of their atoms made it possible to establish the total number of position in the periodic table.

CONTRADICTIONS IN RUTHERFORD'S THEORY

- The theory could **not explain the stability of the atom**. An electron orbiting about a positively charged nucleus ought to emit electromagnetic energy in the form of high waves. And by so doing, the electron lose part of its energy which would result in the violation of equilibrium between the centrifugal force associated with the rotation of the electron and the force of electrostatic attraction of the electron to the nucleus. To restore equilibrium, the electron must move closer to the nucleus. Thus, an electron continuously emitting electromagnetic energy and moving along spiral will approach the nucleus. After exhausting all its energy, it should “fall” onto the nucleus, and the atom will stop existing. This conclusion contradicts the real properties of atomic, without decay for an exceedingly long time.
- The model led to **improper conclusions on the nature of atomic spectra**. The radiation of a glowing solid or liquid body consists of electromagnetic waves of every possible frequency continuous spectrum.
- An appreciable step in the development of the atomic structure concept was made by **NEILS BOHR** who proposed a theory **combining the nuclear model of the atom with the quantum theory of light**.

QUANTUM THEORY OF LIGHT

- Max Planck showed that radiant energy is emitted and absorbed by bodies **not continuously, but discretely** i.e. in separate portions (quanta).
- Frequency of the energy emitted or absorbed, ϑ is given by the Einstein equation (Planck)
- $\Delta E = E_2 - E_1 = h\vartheta$.----- (3)
- The proportionality constant h -the Planck constant, E_2 -the final energy of the atom after the jump, E_1 - the initial energy of the atom before the jump, a negative ΔE means that energy is emitted.
- Einstein concluded that electromagnetic (radian) energy exists only in the form of quanta and that consequently radiation is a stream of indivisible material “particles” (photons) whose energy is determined by the Planck equation.
- It follows from the quantum theory of light that a **photon behaves like a particle i.e. displays corpuscular properties**. It however, also has wave properties. It has **wave - particle duality**
- Bohr theory failed to predict properly the energy levels of some other simple systems such as vibrating or rotating diatomic molecules.

WAVE MECHANICS QUANTUM MECHANICS AND WAVE FUNCTION

The **particle properties** of the photon are expressed by the **Planck equation**

$$E = h\vartheta \text{ ----- (4)}$$

according to which the **photon is indivisible and exists as a discrete formation**. The wave properties of the photon, on the other hand are expressed in the equation.

$$\lambda\vartheta = c \text{ ----- (5)}$$

- Relating the wavelength of electromagnetic oscillation to its frequency ϑ and the speed of propagation, c
- Thus

$$E = \frac{hc}{\lambda} \text{ ----- (6)}$$

- But a photon having the energy, E also possesses a certain mass in accordance with the Einstein equation

$$E = mc^2 \quad \dots \quad (7)$$

- but $mc^2 = \frac{hc}{\lambda}$

- Whence

$$\lambda = \frac{h}{mc}$$

- The product mc is called the momentum of the body

- $\lambda = \frac{h}{p} \quad \dots \quad (8)$

- Eq. 8 was first derived by **de Broglie** by assuming that a photon has both wave and particle properties.
- He assumed that wave-particle duality is a property of electrons in addition to photons. Consequently, an electron must display wave properties and like a photon, it must obey the last equation, which is often **called de Broglie equation**
- The fact that an electron has a wavelength does not necessarily mean that it is a wave; it does mean that **the motion of the electron is governed by the same differential equations that describe wave motion**

- $$\frac{d^2 s}{dx^2} + \frac{4\pi^2}{\lambda^2} s = 0 \quad \dots \quad (9)$$

- Eq 9 Schrodinger standing waves equation. Where s is the max. transverse displacement, or amplitude, of a segment of string dx , x is the distance along the string, and λ is the wavelength.

WAVE FUNCTION

- Based on the concept of Schrödinger that the state of an electron moving in an atom must be described by the equation of a standing electromagnetic wave.
- By substituting the wave function ψ for the amplitude s , the de Broglie wavelength, $h/(mv) = h/p$, for λ , and $E-V$ for the kinetic energy $\frac{1}{2} mv^2$. The result is

- $$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}(E-V)\psi = 0 \quad \text{-----(10)}$$

- where E -represents total energy and V represents potential energy.
- The three - dimensional form will be

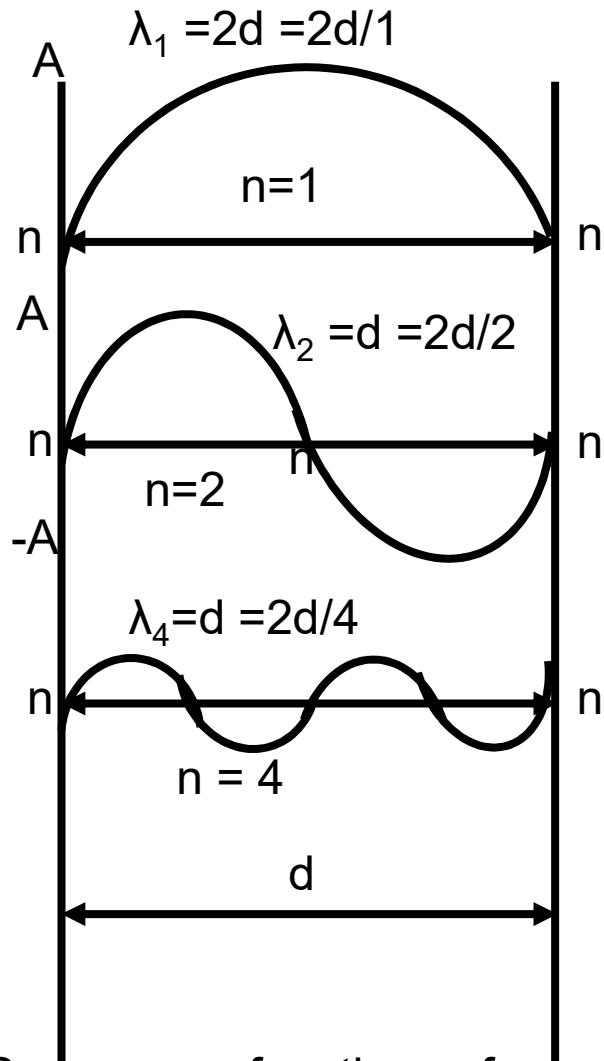
- $$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2m}{h^2}(E-V)\psi = 0 \quad \text{-----(11)}$$

- **wave functions are sinusoidal** for the particle in the given system.
- The wave function ψ is of special significance for characterizing the state of an electron. Like the amplitude of any wave process, it can take on both positive and negative values.
- The quantity ψ^2 however, is always positive. The **higher the values ψ^2 in a given region, the greater is the probability of an electron displaying its action here** i.e. if its existence being detected in a physical process.
- To be more precisely, the probability of detecting an electron in a certain small volume is expressed by $\psi^2 \Delta V$. Thus, **the quantity ψ^2 itself expresses the DENSITY OF THE PROBABILITY** of finding an electron in the corresponding region of space. **The density of an electron cloud is proportional to the square of the wave function.**
- From the properties of waves, the latter can have finite amplitudes only inside the system, the amplitude at the walls must be zero.

Antinodes – maximum amplitude

Nodes n – amplitude of the oscillation vanishes

If the length of a one-dimensional atom (the distance between the walls is d and n is an integer equal to 1,2,3,...
The wavelength, λ of the allowed waves



Some wave functions of a particle in one-dimensional box

$$\boxed{\lambda = \frac{2d}{n}} \quad \text{-----(12)}$$

By combining de Broglie's equation

$$\lambda = \frac{h}{mv} = \frac{2d}{n} \quad \text{or} \quad \lambda = \frac{nh}{2d}$$

Energy, E to certain allowed values

$$E = \left(\frac{1}{2}\right)mv^2 = \frac{1}{2}(mv)^2$$

$$\boxed{E = \frac{1}{2m} \left(\frac{nh}{2d}\right)^2 = \frac{h^2}{8md^2} n^2} \quad \text{---(13)}$$

- This equation tells us that a particle, of any kind confined to move in a region of any length will have only certain energies allowed to it.
- Those energies (from Eq. 13) depend on the mass, m of the particle, the interval d through which it can move, and the quantum number, n .

Implications of de Broglie relation

1. A confined particle cannot have zero energy since n cannot be zero if a wave is to be present. Since n can equal 1,2,3.. the particles may take on many energies, the lowest value will be when $n=1$
2. The lowest energy available to a particle depends markedly on its mass and on the size of the space to which it is confined. This energy varies inversely with the mass every time the mass is decreased by a factor of 2 the energy is doubled. The minimum energy also varies inversely with the square of the length through which the particle can move.

ISOTOPES

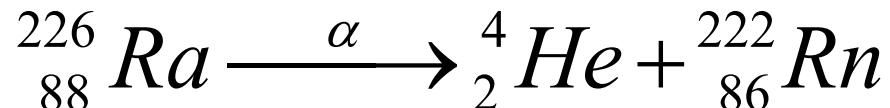
- From the Greek words “**isos**” which means **same** and “**topes**” – **place**.
- Atoms having an identical charge of their nucleus (and, consequently, identical chemical properties) , but a different numbers of neutron and (and, therefore, a different mass number) are known as isotopes.
- The **chemical properties of isotopes are identical**. This means that if there does exist a certain difference between isotopes with respect to their chemical properties, it is so small that it is virtually not detected, only those involving mass effects would be noticed.
- **An exception is the hydrogen isotopes ^1H and ^2H** . Owing to the **enormous relative difference in their atomic masses** (the mass of an atom of one isotope is double that of an atom of the other isotope) the properties of these isotopes differ quite appreciable. The ^2H is called Deuterium (D). The deuterium content in ordinary hydrogen is about 0.015%.
- Also known is the radioactive hydrogen isotope ^3H -Tritium (T) (with half-life of about 12 years) prepared only artificially. Tritium is unstable. The elements of higher Z contain at least as many neutrons as protons, but because of the shielding effect of the innermost electrons this does not affect the material properties. In the atoms of higher Z, the number of neutrons considerable exceeds the number of protons, and these elements are often referred to as the heavy elements. E.g. ^{238}U – 99 % of natural uranium 0 .7 % $^{235}_{92}\text{U}$ and $^{233}_{92}\text{U}$ which is artificially produced by neutron bombardment of thorium.
- The nucleus itself eventually becomes unstable and the addition of a further neutron may cause nuclear “fission”. The atom then disintegrates with the production of two new atoms and a debris of elementary particles and radiations.

ISOTOPIC INDICATORS (TRACERS)

- Isotopic indicators or “labeled atoms” (tracer atom) are widely used in studying the mechanism of chemical and biological processes. This use is based on the possibility of tracing the ways of transition of an element in chemical transformation by measuring the concentration of one of its isotopes in one of the substances taken for a reaction. Since all the isotopes of the same element behave virtually identically in chemical reactions, by determining the change in the composition of the isotopes of a given element in the various products, we can trace its path.
- For example, the use of the heavy oxygen isotope ^{18}O in studying how carbon dioxide is assimilated by plants. (Carbon dioxide and water enriched with ^{18}O were used for the experiments) showed that the process occurs according to the following reaction, in which the isotope ^{18}O is marked with an asterisk.
- $6\text{CO}_2 + 12\text{H}_2\text{O}^* = \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O} + 6\text{O}_2^*$
- $6\text{CO}_2^* + 12\text{H}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6^* + 6\text{H}_2\text{O}^* + 6\text{O}_2$
- It was thus established that the oxygen returned by plants to the atmosphere is taken completely from water and not from carbon dioxide.
- ^{18}O a stable isotope which is quite rare in nature (abundance = 0.20%). This isotope is readily detected by using a mass spectrometer.
- Carbon-14 can be used also.
- In Medicine: The high-energy radiation given off by Radium is used in the treatment of cancer.

RADIOACTIVITY NUCLEAR REACTIONS

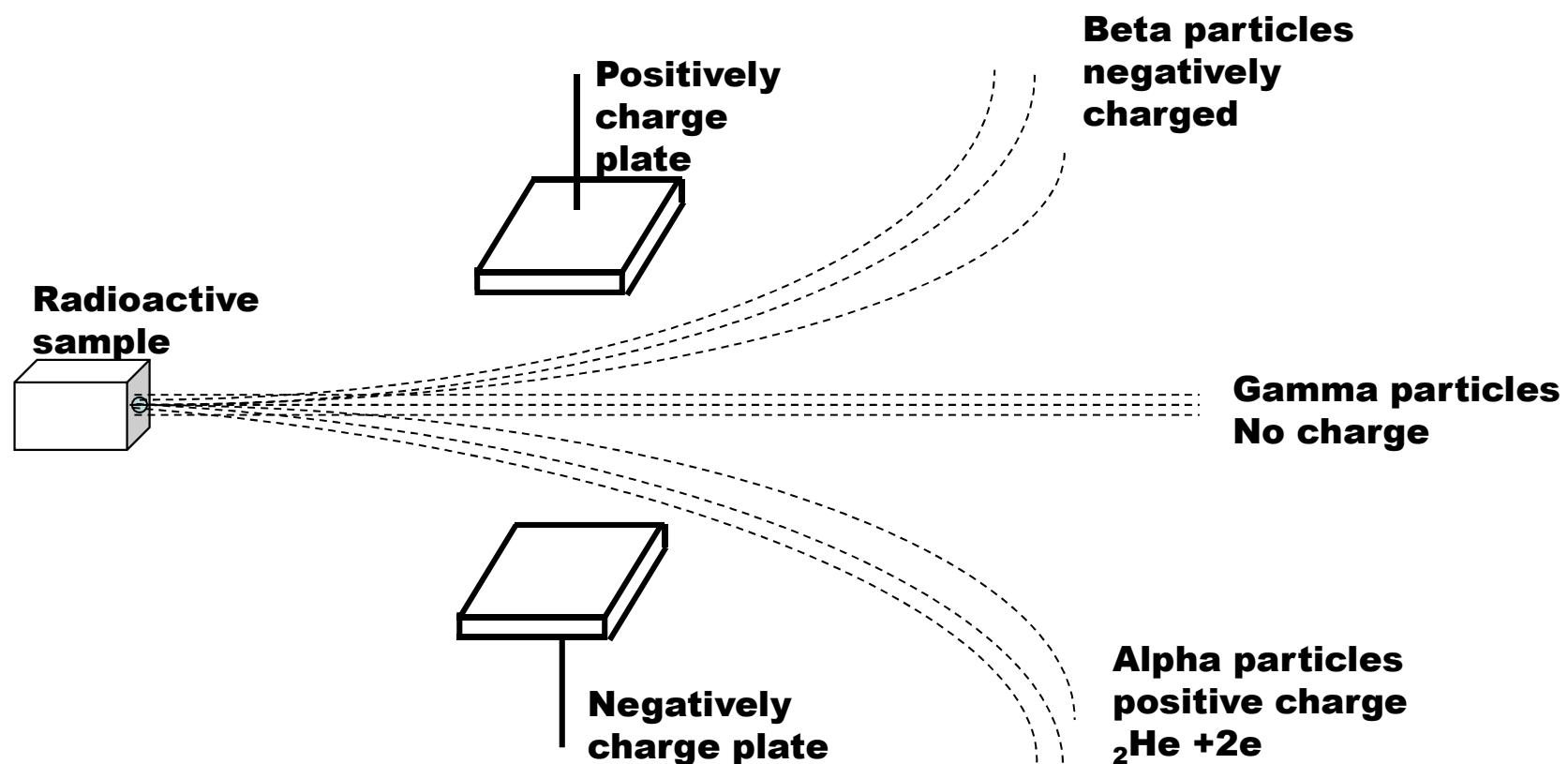
- Nuclear reactions differ from ordinary chemical reactions.
- 1. In ordinary reactions, the different isotopes of an element show virtually identical chemical properties; in nuclear reactions they behave quite differently.
- The chemical properties of $^{12}_6C$ and $^{14}_6C$ are very similar but the $^{12}_6C$ nucleus is extremely stable while the $^{14}_6C$ nucleus decomposes spontaneously.
- 2. The nuclear reactivity of an element is essentially independent of its state of chemical combination. E.g. Ra^{2+} ion in RaCl_2 and elementary Radium behave similarly from a nuclear stand point. In ordinary chemical reaction on the other hand, the radium atom and the Ra^{2+} ion behave quite differently since they have different outer electronic structures.
- 3. Nuclear reaction frequently involve the conversion of one element to another (with a change in the number of protons in the nucleus. Elements in ordinary chemical reaction retain their identity.



- 4. Nuclear reactions are accompanied by energy changes which exceed by several orders of magnitude, those associated with ordinary chemical reaction. The energy evolved when a gram of radium undergo radioactive decay is about 500,000 times as great as that given off when an equal amount of radium reacts with chlorine to form radium chloride.

RADIOACTIVITY

- By radioactivity is meant the spontaneous transformation of an unstable isotope of one chemical element into an isotope of another element attended by the emission of elementary particles or nuclei (for instance alpha particles).
- The rate of radioactive transformations is characterized by the radioactive decay constant which shows part of the total number of atom of a radioactive isotopes decays in one second. The greater the radioactive decays, the more rapidly does an isotope decay.
- The number of atoms of a radioactive isotope decaying in unit time is proportional to the total number of atom of this isotope present at the given moment.
- The time needed for half of the original amount of a radioactive element to decay is called the HALF-LIFE. This quantity characterizes the lifetime of an element. It ranges from fraction of a second to hundreds of millions of years. E.g., the half-life of Radium is 3.85 days, of Radium is 1620 years, of uranium 4500 million years.
- The main kinds of radioactive radiation include alpha, beta and gamma radiation.



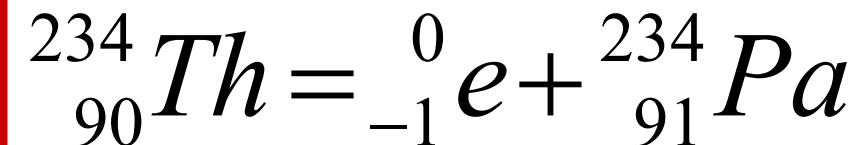
- **Alpha Radiation** which consists of a stream of **positively charge particles** (alpha particles) that carry a charge of +2 and have a mass of 4 on the atomic mass scale. In alpha decay, the nucleus of an atom emits 2 protons and 2 neutrons bound in a nucleus of the helium atom ${}^4_2\text{He}$. The result is lowering of the charge of the initial radioactive nucleus by 2, and of its mass number by 4. Thus **alpha decay results in the formation of an atom of an element having an atomic number two less than the original isotope.**



Beta Radiation (decay) which is made up of a stream of **negatively charged particles** (beta particles) that have all the **properties of electrons**. (mass charge ≈ -1)

Beta particles results from the transformation of a neutron (mass = 1 charge = 0) at the surface of the nucleus into a proton (mass = 1, charge = +1).

Consequently beta-emission leaves the **mass number unchanged but increases the atomic number by one unit**



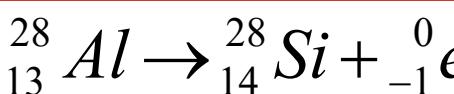
The process of beta decay can be written as neutron \rightarrow proton + electron or $n \rightarrow P + e^-$. The electron appearing in this transformation flies out of the nucleus, and the positive charge of the letter grows by unity.

A proton may also transform into a neutron as:

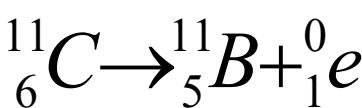
- Protons → neutron +Positron or $P \rightarrow n + e^+$
- A positron, whose symbol is e^+ , is an elementary particle with a mass equal to that of an electron, but carrying a positive electric charge. The charges of an electron and a positron are identical in absolute value.
- A proton may transform into a neutron with the formation of a positron when the instability of the nucleus is due to an excess content of protons in it. One of the protons in the nucleus transforms into a neutron, the positron that appears flies out of the nucleus, and the charge of the nucleus diminishes by unity. This kind of radioactive decay is called POSITRON. BETA DECAY (β^+ decay) in contrast to the previously considered ELECTRON BETA DECAY (β^- decay).
- As a result of beta decay the atom is transformed into a new element whose atomic number is one greater (with β^- decay) or one less (with β^+ decay) than that of the original isotope.



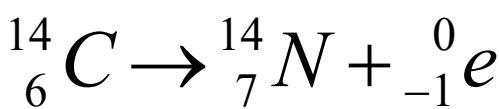
(β^+ decay)



(β^- decay)



(β^+ decay)



(β^- decay)

- **GAMMA Radiation**, electromagnetic radiation of very short wavelength ($\lambda=0.0005$ to 0.1nm) i.e. high –energy photons. The emission of gamma radiation accompanies virtually all nuclear reaction as the result of an energy change within the nucleus, whereby an unstable, excited nucleus remitting from alpha – or beta-emission given off a photon and drop to a lower more stable energy state (no mass change, no change in Z).

INTERACTION OF RADIATION

- The commonly instrument used to detect and measure radiation is the Scintillation counter. We have also Geiger Muller counter.
- The harmful effect of radiation upon human beings is caused by its ability to ionize and ultimately destroy the organic molecules of which body cells are composed. The extent of damage depends upon
 - 1. the energy and the
 - 2. types of radiation. The former is expressed in GRAYS. A gray corresponds to the absorption of one joule per kilogram of tissue. The total biological effect of radiation is expressed in rems.
 - Number of Re却s = $n \times$ (number of grays) where n is 100 for β , γ , and x radiation and 1000 for α radiation or high –energy neutrons.
 - **Effect of exposure to a single dose of radiation**
 - **Dose (Re却s)** **Probable effect**

• 0 to 25	No observable effect
• 25 to 50	Small decrease in white blood cell count
• 50 to 100	Lesions, marked decrease in white blood cells
• 100 to 200	Nausea, vomiting, loss of hair
• 200 to 500	Hemorrhaging, ulcers, possible death
• 5000 +	Fatal.
 - Radiation can produce mutations in plants and animals by bringing about changes in chromosomes. Federal research council has set an upper limit of 0.17 per year above background as the max. dosage to which major population group can be exposed.

USEFULNESS

- In Medicine
- Treatment of cancer to destroy or arrest the growth of malignant tissue (Radium). Even cheaper cobalt-60. Sodium iodine containing radioactive iodine (^{131}I or ^{126}I) used to destroy the malignant cells (cancer of the thyroid) in human beings.

RATE OF RADIOACTIVE DECAY

- **FIRST ORDER RATE LAW**
- The first order equation reaction
- X- products; rate = $\frac{-\Delta \text{conc. } x}{\Delta t} = k(\text{conc. } X)$
$$\frac{-\Delta \text{conc. } x}{\text{conc. } x} = -k\Delta t$$
- $\log_{10} \text{conc. } X = \log_{10} (\text{conc. } X)_0 - Kt / 2.30$
- ($\Delta \text{Conc } x = \text{conc of } x \text{ at } t - \text{conc of } x \text{ at } t = \text{zero}; \text{conc } x - (\text{conc } x)_0$)
- ($\Delta t = t - 0 = t$)
- where $(\text{conc. } X)_0$ is the initial concentration and t is the elapsed time (X_0 is the amount of radioactive substance at zero time (when the counting process starts) and X is the amount remaining after time t . The first order rate constant K , is the characteristic of the isotope undergoing radioactive decay.

$$\log_{10} \frac{(\text{conc. } x)_0}{\text{Conc. } x} = \frac{kt}{2.30} \quad \text{-----(14)}$$

- Derivation of Eq. 14 is as follows:

$$\text{Rate} = -\frac{dx}{dt} = kx$$

$$\frac{dx}{x} = -kdt$$

- Integrating from $t = 0$ to t and from x_0 to x

$$\int_{x_0}^x \frac{dx}{x} = -K \int_0^t dt$$

$$\ln x - \ln x_0 = -Kt \text{ and } \ln X = 2.30 \log_{10} X$$

$$\log_{10} x - \log_{10} x_0 = -\frac{Kt}{2.30}$$

$$\log_{10} \frac{x_0}{x} = \frac{Kt}{2.30} \quad \text{or} \quad \frac{2.30}{K} \log_{10} \frac{x_0}{x} = t$$

Since $X = x_0/2$;

$x_0 = 2X$;

$x_0/X = 2$

$$t_{0.5} = \frac{2.30}{K} \log_{10} 2 = \frac{0.693}{K}$$

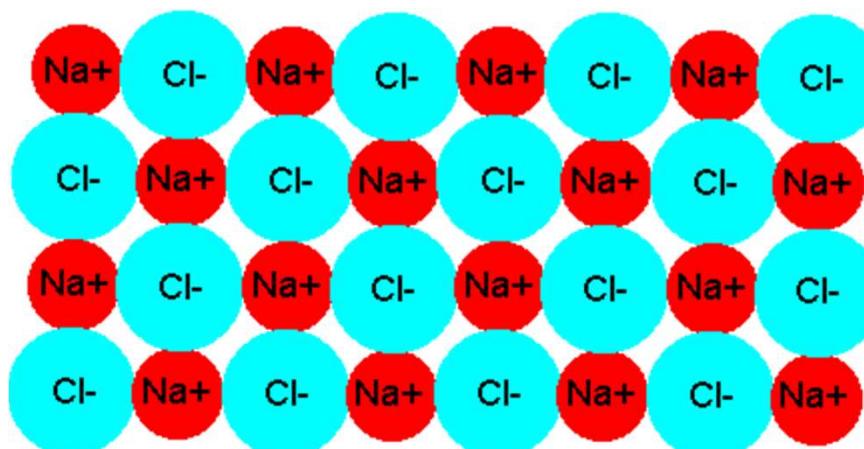
----- (15)

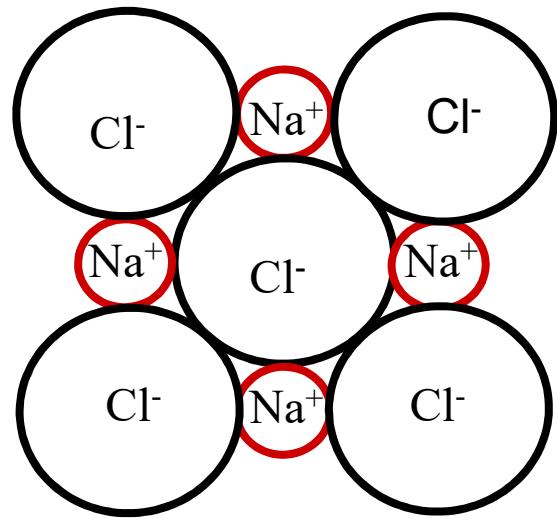
ATOMIC BONDING

- There are two types of bonds:
- Primary
- Secondary
- Primary Bonds:
- Primary bonds are the strongest bonds which hold atoms together. The three types of primary bonds are:
 - **Ionic Bonds**
 - **Covalent Bonds**
 - **Metallic Bonds**
- bonding is achieved when atoms fill their outer s and p levels.

THE IONIC BOND

- Lost and gain of electrons
- Ionic bond is created between 2 unlike atoms with different electronegativities i.e. one atom donate its valence electrons to a different atom. Both atoms now have filled (or empty) outer energy levels but both have acquired an electrical charge and as ions.
- The donor of the electron is left with a positive charge and is a cation while the electron accepter acquires a net negative charge and is an anion. The oppositely charged ions are then attracted to one another to produce the ionic bond.





The ionic bond between Na and Cl

When a force is applied to NaCl crystal the electrical balance between the ions is upset. Partly for this reason, ionically bonded materials behave in a brittle manner. Electrical conductivity is also poor; when a voltage is applied the electrical charge is transferred by the movement of entire ion which does not move as easily as electrons.

Ionic bond does **not have saturability**. The oppositely attracted charge ions retain their ability to interact electrostatically with other ions.

The forces of attraction of oppositely charged ions must predominate over the force of mutual repulsion exerted between ions of the same sign.

The **absence of directionality and saturability** in an ionic bond is the reason why ionic molecules tends to associate i.e. to combine with one another.

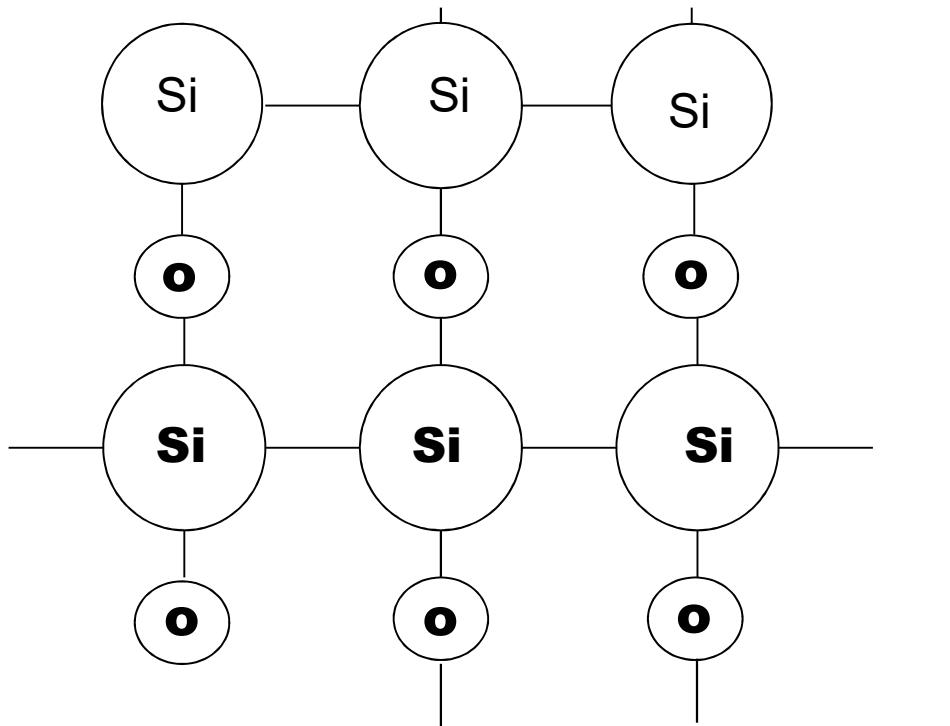
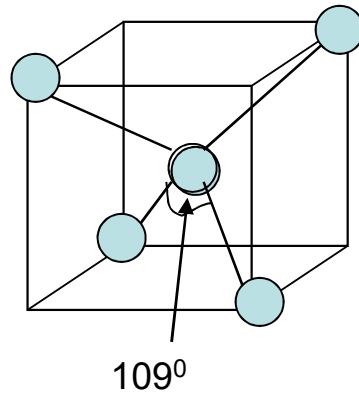
The ionic bond is **non-directional**. A positively charged Na^+ will attract any adjacent Cl^- equally in all directions.

The more electropositive the metal and the more electronegative the non-metal, the greater the ionic contribution to bonding. LiF is almost completely ionic MgO has a little covalent character in its bond sand SiO_2 is about half ionic half covalent.

The non-directional of ionic bond is due to the spherically symmetry of the electric field of an ion, i.e. diminishes with the distance according to the same way regardless of directions.

COVALENT BOND

- Covalent bonding requires that **electron** be shared between atoms in such a way that each atom has its outer sp orbital filled. For example, a silicon atom, which has a valence of 4 obtains 8 electrons in its outer energy shell by sharing its electrons with 4 surrounding silicon atoms. Therefore in Si 4 covalent bonds must be formed.
- In order for the covalent bonds to occur the Si atoms must be arranged as the bonds have a fixed **DIRECTIONAL relationship with one another**. In Si, C the arrangement produces a tetrahedron with angles of about 109° between the covalent



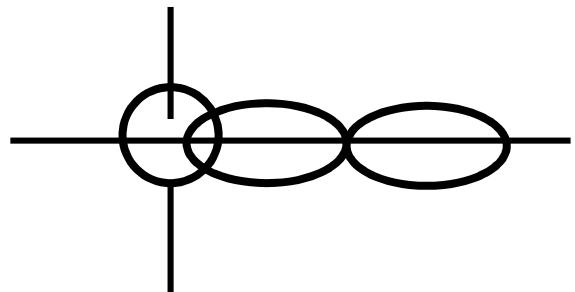
In Si, C a tetrahedral structure is formed with angles of about 109° required between ach covalent bond.

A covalent chemical bond is formed by 2 electrons with anti parallel spins , this electron pair belonging to 2 atoms. The strength of a covalent bond grows with an increasing degree of overlapping of the interaction electron clouds.

The ability of atoms to participate in the formation of a restricted number of covalent bonds is called **SATURABILITY** of covalent bond.

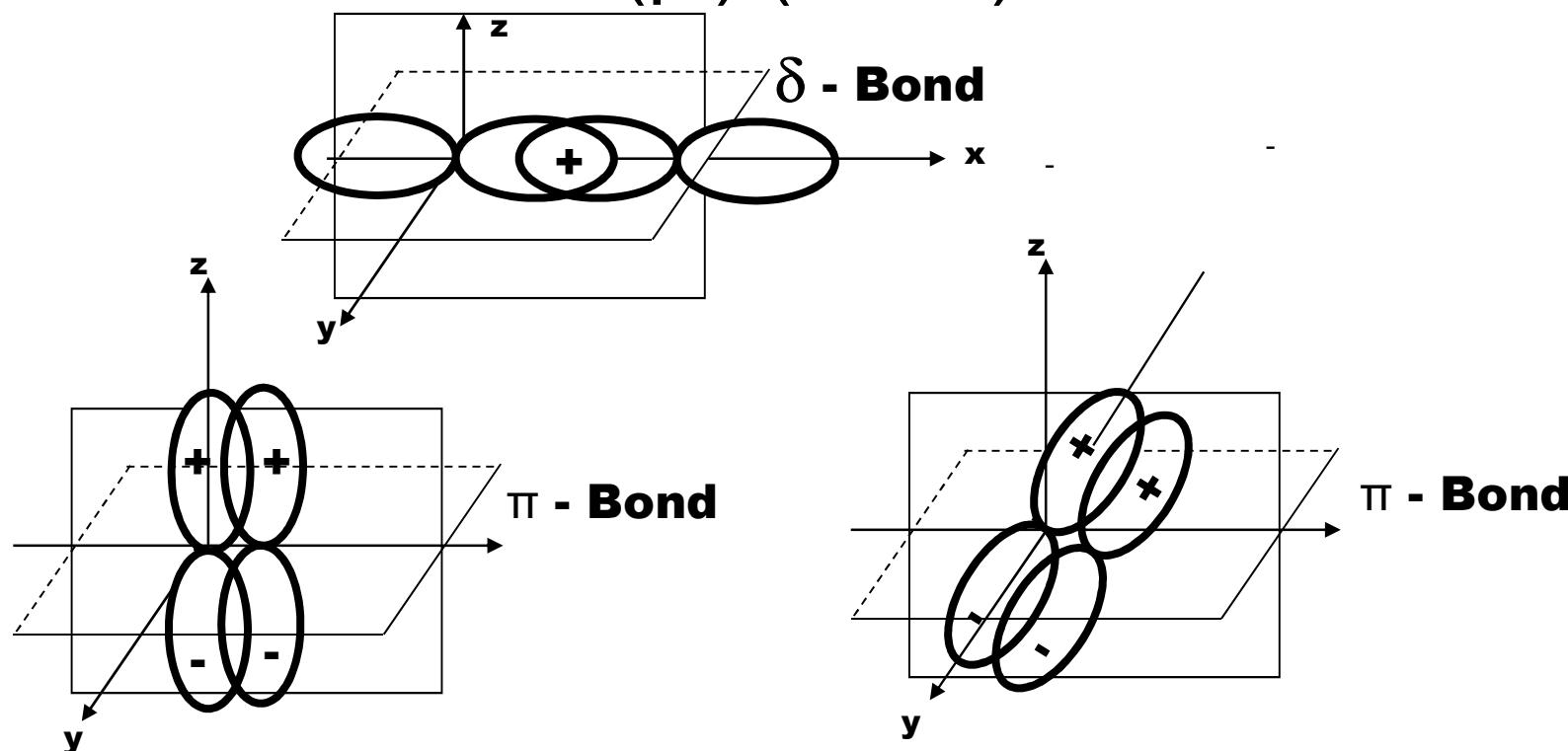
The formation of a covalent bond is a result of overlapping of the valence electron clouds of the interaction atoms. But such overlapping is possible only with a definite mutual orientation of the electron cloud; here the **overlap region is arranged in a definite direction with respect to the interacting atoms**. In other words, a covalent bond is **DIRECTIONAL**.

- **DIRECTION OF A COVALENT BOND**
- The properties of a molecule, its ability to enter into chemical reactions with other molecules (its reactivity) depend not only on the strength of the chemical bonds in the molecule, but to a considerable extent on its dimensional structure too.
- In a hydrogen molecule, the atomic S-electron clouds overlaps near the imaginary straight line joining the nuclei of the interacting atoms (i.e. the bond axis). A covalent bond formed in such a way is known as a δ (sigma) bonds.
-  **overlapping of atomic electron clouds in a hydrogen molecule.**
- If p-electron clouds are oriented along the bond axis, they can also participate in the formation of a sigma bond. **Overlapping of the 2p-electron cloud of the fluorine atom and the 1s-electron cloud of the hydrogen atom in the formation of a sigma bond in the molecule HF**
- **Note:** In the formation of a chemical bond energy is always evolved as a result of the decrease in the potential energy of the system of interacting electrons and nuclei this is why the potential energy of a particle formed a (a molecule or crystal) is always less than the total potential energy of the initial free atom.
- The chemical bond in the molecule F_2 is also sigma bond, it is formed by the 2p-electron clouds of the F atoms.



Overlapping of the 2p-electron cloud of the fluorine atom and the 1s-electron cloud of the hydrogen atom in the formation of a sigma bond in the molecule HF

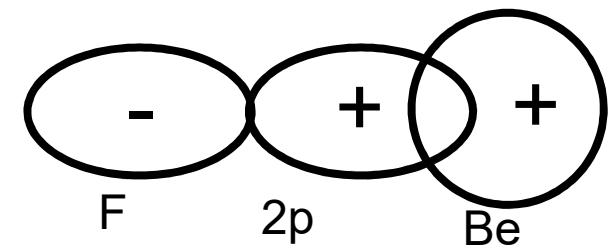
- When P- electron clouds oriented perpendicularly to the bond axis interact, two overlaps regions are formed at both sides of this axis instead of a single region. Such a covalent bond is called a π (pi) (Bond)



Overlapping of the 2p-electron clouds in the molecule N_2 a – sigma bond and 2-pi bonds

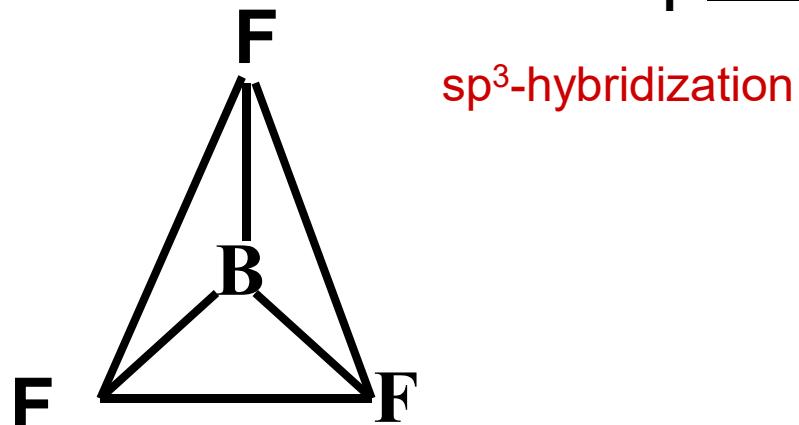
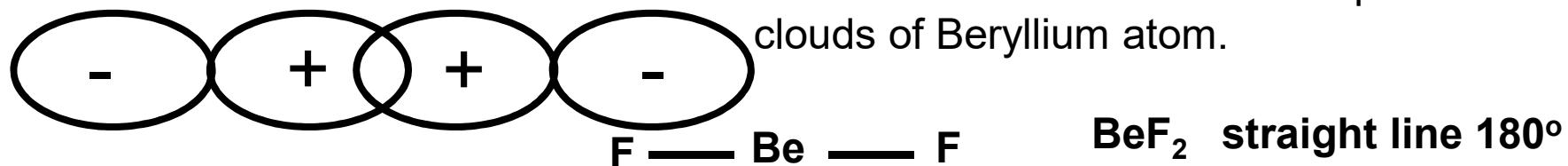
HYBRIDIZATION OF ATOMIC ELECTRON ORBITALS

- The method of hybridization of atomic orbital proceeds from the assumption that in the formation of a molecule, instead of the initial atomic s-, p-, and d-electron clouds, equivalent “blended” or hybrid electron clouds are formed that are stretched out in a direction towards the neighboring atoms, the result being their more complete overlapping with the electron clouds of these atoms. The more complete overlapping of the valence electron clouds the stronger the chemical bond formed and consequently to additional gain in energy. If this gain in energy is sufficient to more than compensate the expenditure of energy for the deformation of initial atomic electron clouds, such hybridization in the long run leads to diminishing of potential energy of the molecule formed and consequently to an increase in its stability.



sp-hybridization – Hybridization of 1s and 2p orbital leading to the formation of two sp orbital
 BeF_2 linear orientation

Overlapping of the 2p electron clouds of the fluorine atoms with the 2s and 2p electron clouds of Beryllium atom.



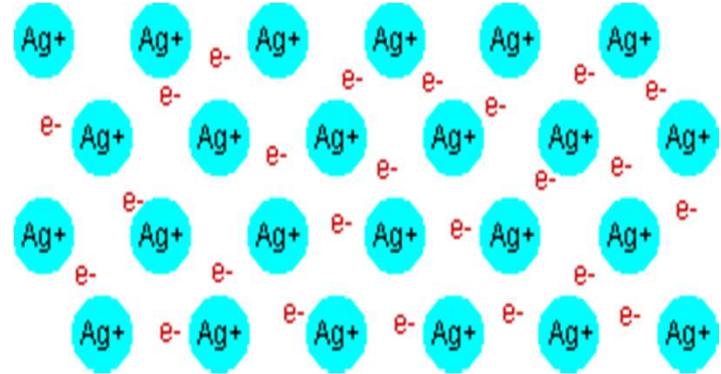
equilateral triangle 120° BF_3

CH_4 Tetrahedron 109.5°

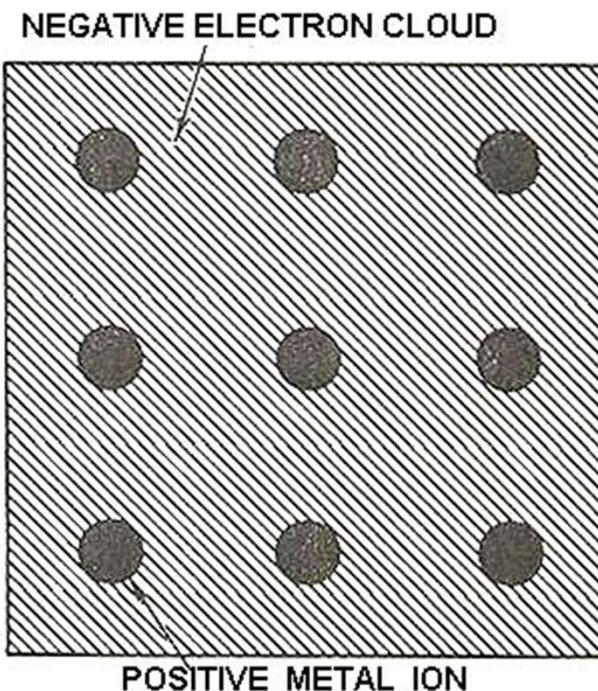
- i) 4 pairs of electrons around the central atom are all shared, the molecule is tetrahedral
- ii) when one pair is unshared, the structure is that of a pyramid with an equilateral triangle as large
- iii) 2 unshared pairs lead to a bent.

METALLIC BOND

- The metallic bond involves sharing of **delocalized electron** given a non-directional bond high electrical conductivity. The metallic bond forms when **atom give up their valence electron**, which then form an **electron sea (or gas)** leaving behind a core consisting of the nucleus and inner electron and the core becomes an ion with a positive charge. The positively charge atom cores are bonded by mutual attraction to the negatively charged electron.
- Metallic bonds are **non directional**; the electron holding the atoms together are not fixed in one position. This properly permit metals to have **good ductility** and to be deformed into useful shapes since when the former is bent and the atoms attempt to change their relationships to one another, the **direction of the bond merely shifts** rather than the bond breaking.
- Since the **electrons are free to move**, they lead to **good thermal and electrical conductivity**.



Metallic bond.

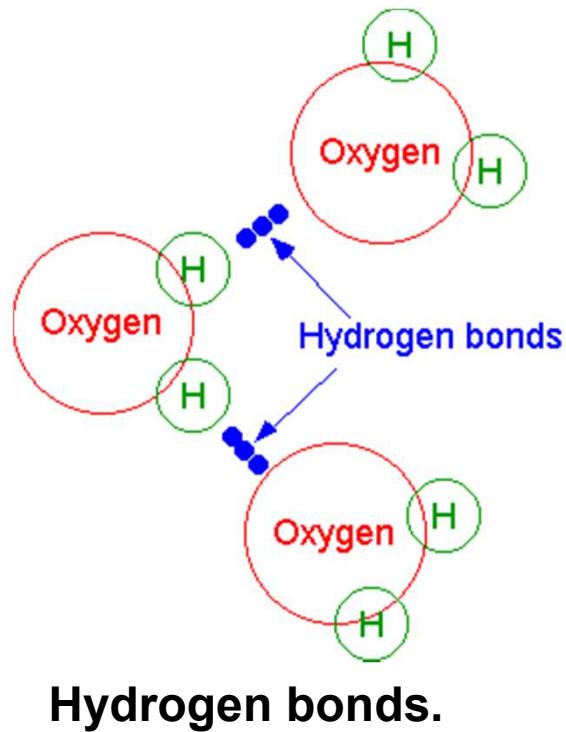


Metallic bond and electron cloud

Secondary Bonds:

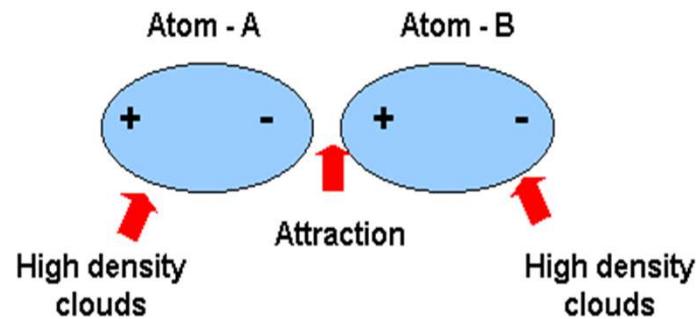
- Secondary bonds are much weaker than primary bonds. They often provide a "weak link" for deformation or fracture. Example for secondary bonds are: **Hydrogen Bonds and Van der Waals Bonds**

Hydrogen Bonds



Hydrogen bonds are common in covalently bonded molecules which contain hydrogen, such as water (H_2O). Since the bonds are primarily covalent, the electrons are shared between the hydrogen and oxygen atoms. However, the electrons tend to spend more time around the oxygen atom. This leads to a small positive charge around the hydrogen atoms, and a negative charge around the oxygen atom. When other molecules with this type of charge transfer are nearby, the negatively charged end of one molecule will be weakly attracted to the positively charged end of the other molecule. The attraction is weak because the charge transfer is small.

Van der Waals Bonds



Van der Waals bonds are very weak compared to other types of bonds. These bonds are especially important in noble gases which are cooled to very low temperatures. The electrons surrounding an atom are always moving. At any given point in time, the electrons may be slightly shifted to one side of an atom, giving that side a very small negative charge. This may cause an attraction to a slightly positively charged atom nearby, creating a very weak bond. At most temperatures, thermal energy overwhelms the effects of Van der Waals bonds.

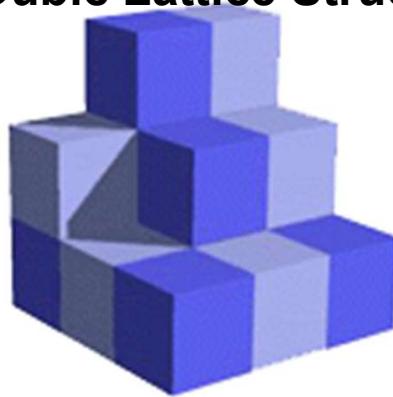
Van Der Waals bonding is a secondary bonding, which exists between virtually all atoms or molecules, but its presence may be obscured if any of the three primary bonding types is present. Secondary bonding forces arise from atomic or molecular dipoles. In essence, an electron dipole exists whenever there is some separation of positive and negative portions of an atom or molecule. When an electron cloud density occurs at one side of an atom or molecule during the electron flight about the nucleus, Van Der Waals forces are generated. This creates a dipole wherein one side of the atom becomes electrically charged and the other side has deficiency of electrons and is considerably charged positive.

Crystal Lattice Structures

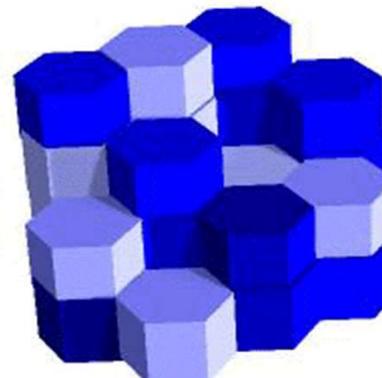
- Atoms are the building blocks of all materials.
- They are **bonded or "held together"** by cohesive forces in a manner characteristic of a particular material.
- In a **liquid state** the atoms of metal are of **random arrangement**, having **short-range order**. At times several unlike atoms will arrange themselves in the characteristic pattern of a particular metal.
- There is the phenomenon of **random grouping, scattering, and regrouping** for **short periods of time** is characteristic of the liquid state. As the **random grouping mechanism becomes less frequent** and the **atomic movement** of unlike atoms become **more agitated**, the material may become a **gas**.
- As the **energy input decreases**, the **random movement** of the unlike atoms becomes **less frequent**, the **bonding becomes stronger**, and **ordered arrays** of atoms form lattices.
- **A crystal** is a **repeating array**. In describing this structure we must distinguish between the pattern of repetition (the lattice type) and what is repeated (the unit cell). **The most fundamental property of a crystal lattice is its symmetry**. In three-dimensions, unit cells stack like boxes, filling the space, making the crystal. **A Crystal: A repetitive, three dimensional arrangement of atoms or ions in a solid. It possess a periodicity that produces long-range order i.e. the local atomic (ionic) arrangement is repeated at regular intervals millions of times in the 3 dimensions of space.**

- The **most stable** arrangement of atoms in a crystal will be that which **minimizes the energy per unit volume** or in other words, the one that
 - Preserves electrical neutrality
 - Satisfies the directionality and discreteness of all covalent bonds
 - Minimizes strong-ion-ion repulsion
 - Packs the atoms as closely as possible consistent with (1), (2) and (3)

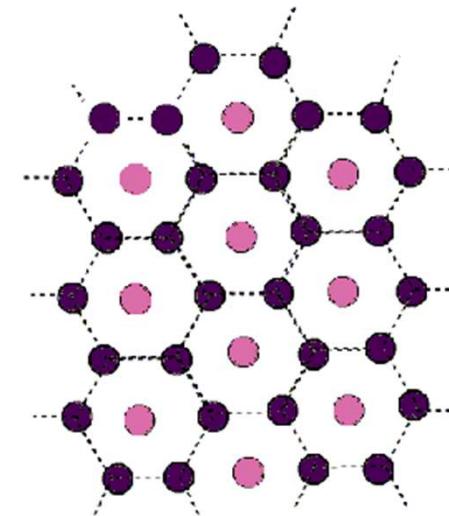
Cubic Lattice Structure



Orientation of the unit cells in a lattice.



Hexagonal Lattice Structure



Unit Cell: When a solid has a crystalline structure, the atoms are arranged in repeating structures called unit cells, which are the smallest units that show the full symmetry of a crystal.

Lattice: The three dimensional array formed by the unit cells of a crystal is called lattice.

- Face-centered cubic (F.C.C.)
- Body-centered cubic (B.C.C.)
- Hexagonal-close-packed (H.C.P.)

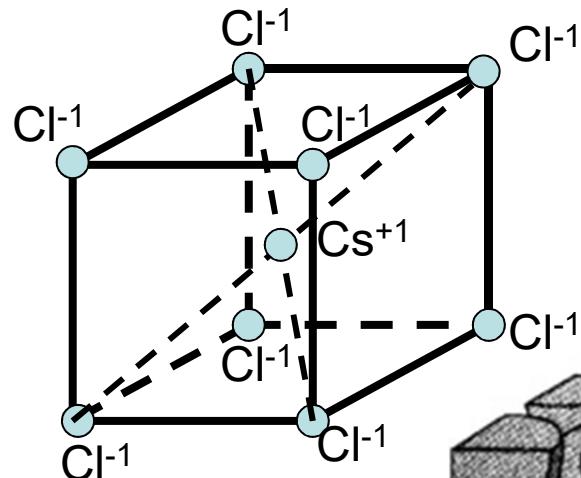
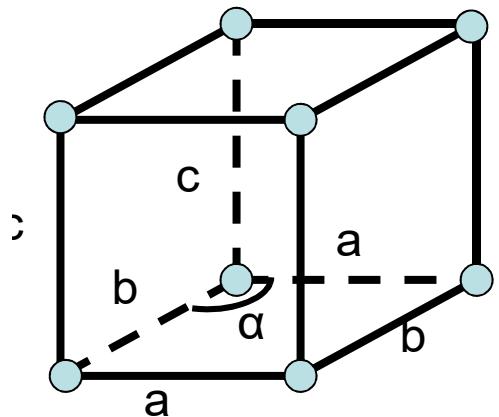
Crystal Systems

7 systems (7 unique unit cell shapes) to describe crystal structures. Lattice pts can be arranged in only 14 different arrays called Bravais lattices

- **Lattice pt:** The vertices of the unit cell
- **Lattice parameter:** The length of the unit cell edges
- The angles and lengths within the repeat unit determine the class to which the lattice cell belongs

Basis: “group of things” located on a lattice

Lattice + Basis = Crystal Structure



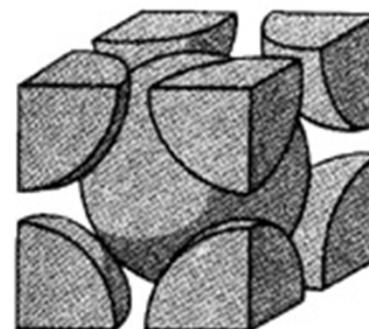
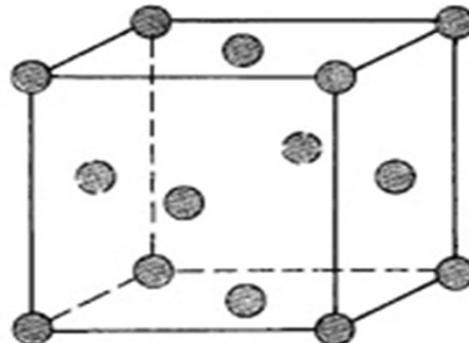
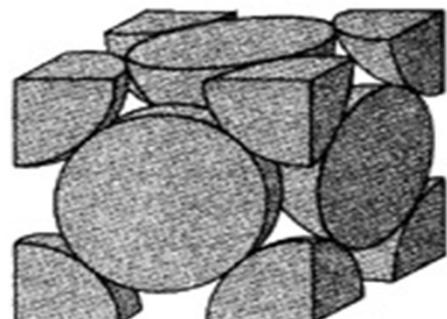
Simple Cubic (S.C)
CN = 8

Brass – SC $r/R > 0.73$

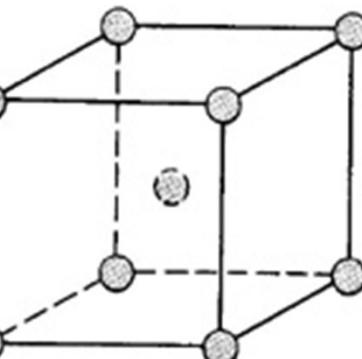
CaTiO_3 – SC

$$a_{\text{SC}} = 2(r_{\text{Cs}^+} + R_{\text{Cl}^-})/\sqrt{3}$$

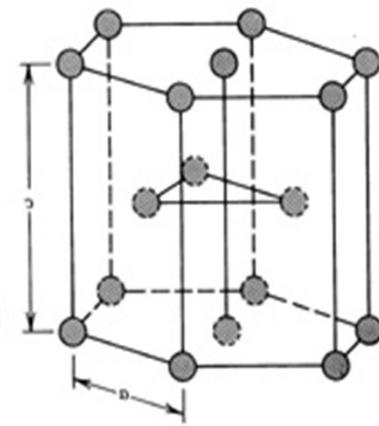
Face Centered Cubic (F.C.C) Lattice Structure



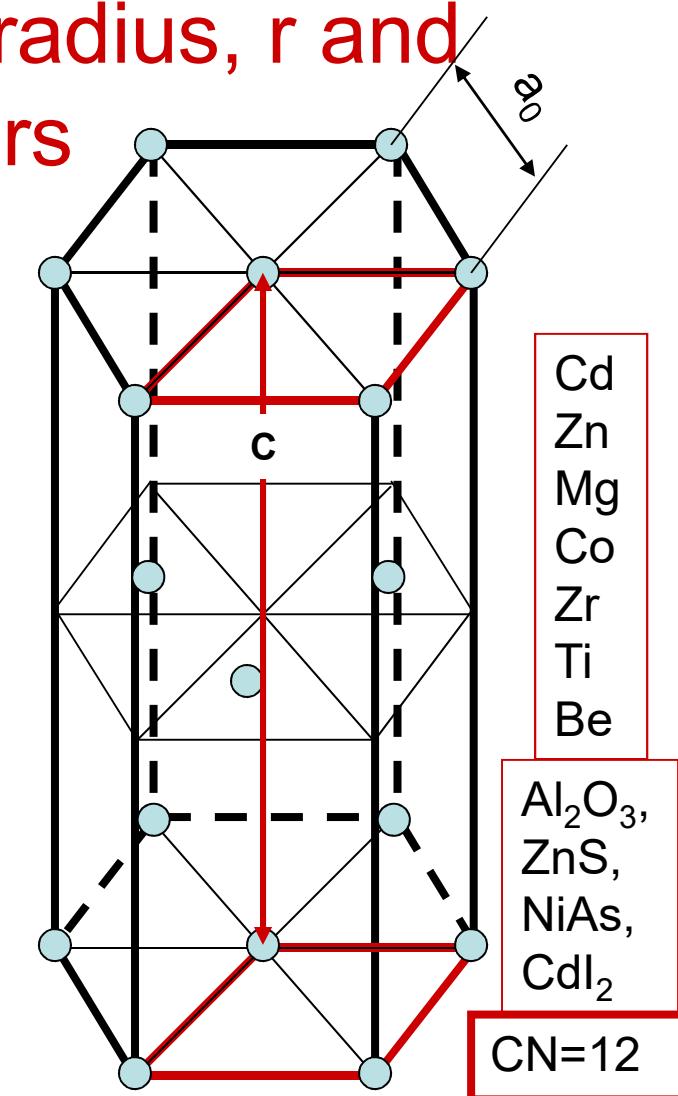
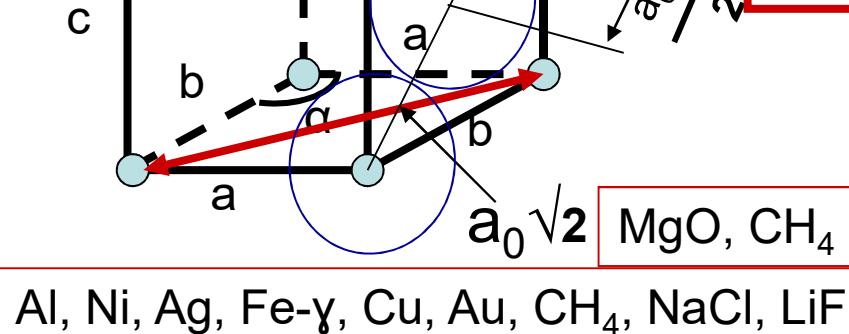
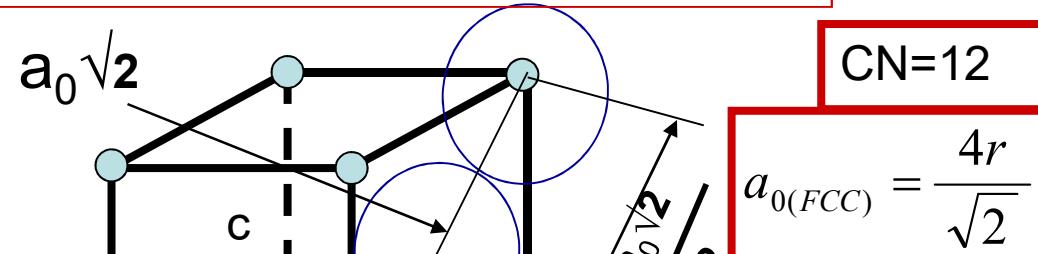
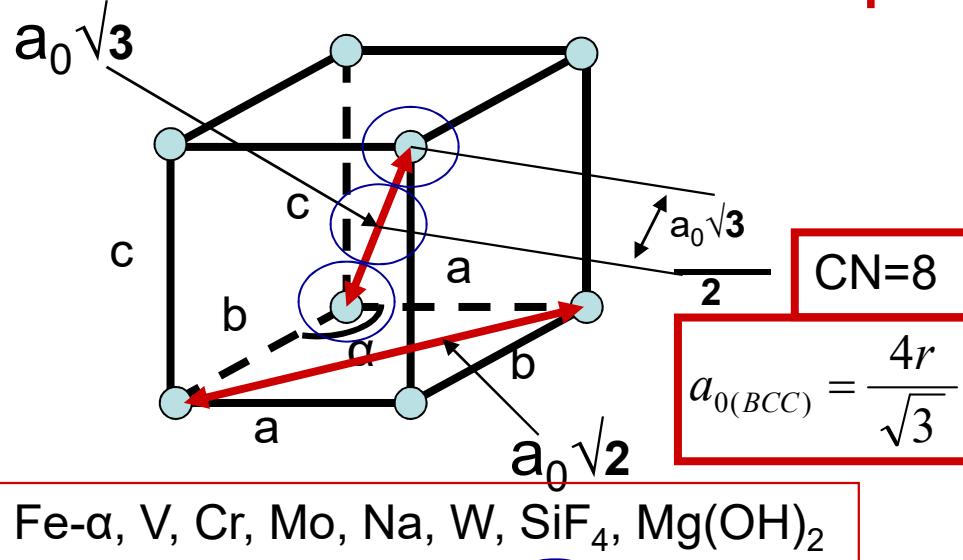
**Body Centered Cubic (B.C.C)
Lattice Structure**



**Closed Packed Hexagonal (C.P.H)
Lattice Structure**



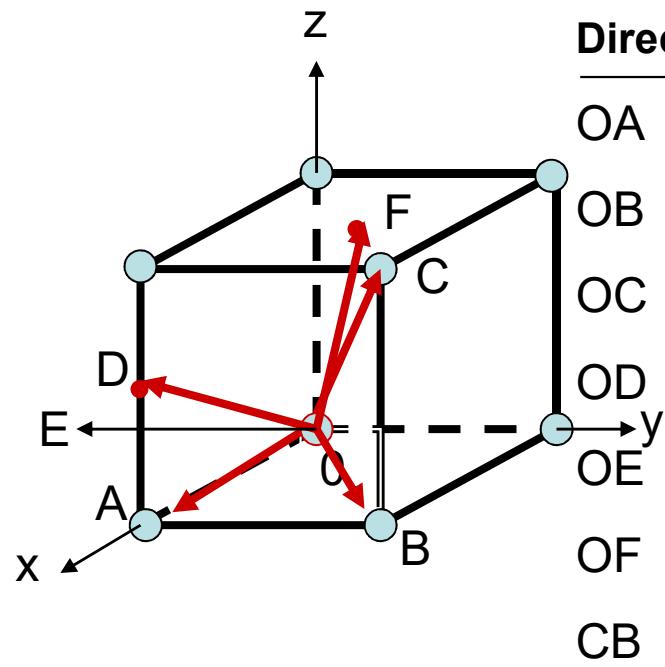
Relationship between the radius, r and lattice parameters



Miller Indices

- Indices of Directions

- Determine the coordinates of 2 pts that lie in the direction of interest – h_1, k_1, l_1 and h_2, k_2, l_2
- Subtract the coordinates of the 2nd pt from those of the 1st pt: $h' = h_2 - h_1$, $k' = k_2 - k_1$ and $l' = l_2 - l_1$,
- Clear fractions from the differences – h' , k' and l' – to give indices in lowest integer values, h, k, l
- Write the indices in square brackets without commas: $[h \ k \ l]$
- If $h < 0$, we write $[\bar{h} \ k \ l]$



Directions	Indices $[h \ k \ l]$
OA	$[1 \ 0 \ 0]$
OB	$[1 \ 1 \ 0]$
OC	$[1 \ 1 \ 1]$
OD	$[2 \ 0 \ 1]$
OE	$[0 \ 1 \ 0]$
OF	$[1 \ 1 \ 2]$
CB	$[0 \ 0 \ \bar{1}]$

To determine the angle between directions

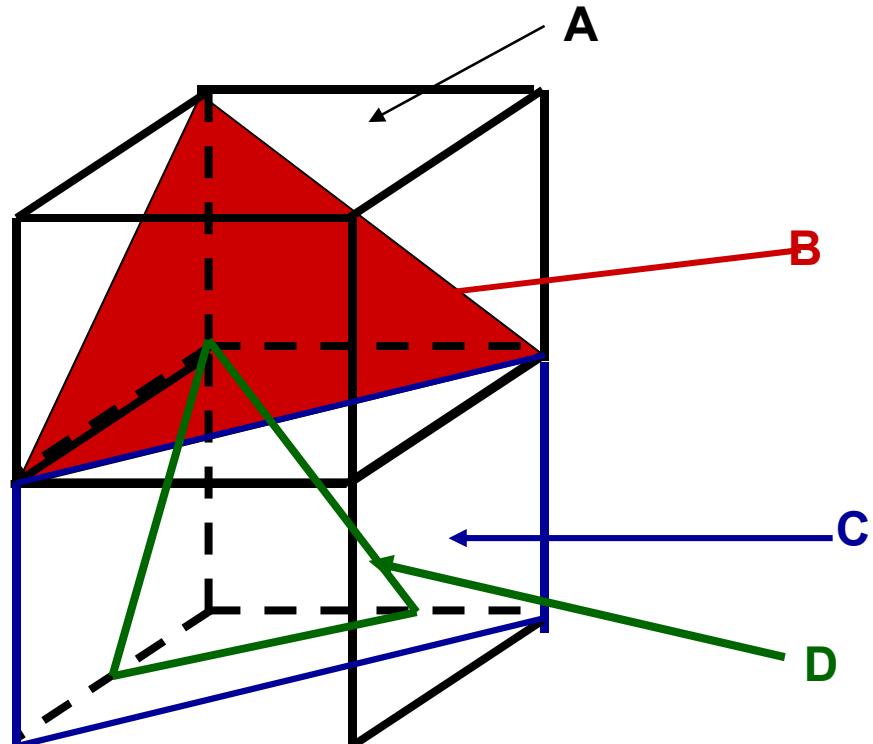
If $A = u\mathbf{i} + v\mathbf{j} + w\mathbf{k}$ and $B = u'\mathbf{i} + v'\mathbf{j} + w'\mathbf{k}$, then,

$A \cdot B = |A||B| \cos \varphi$ where
 φ is the angle between
the 2 vectors

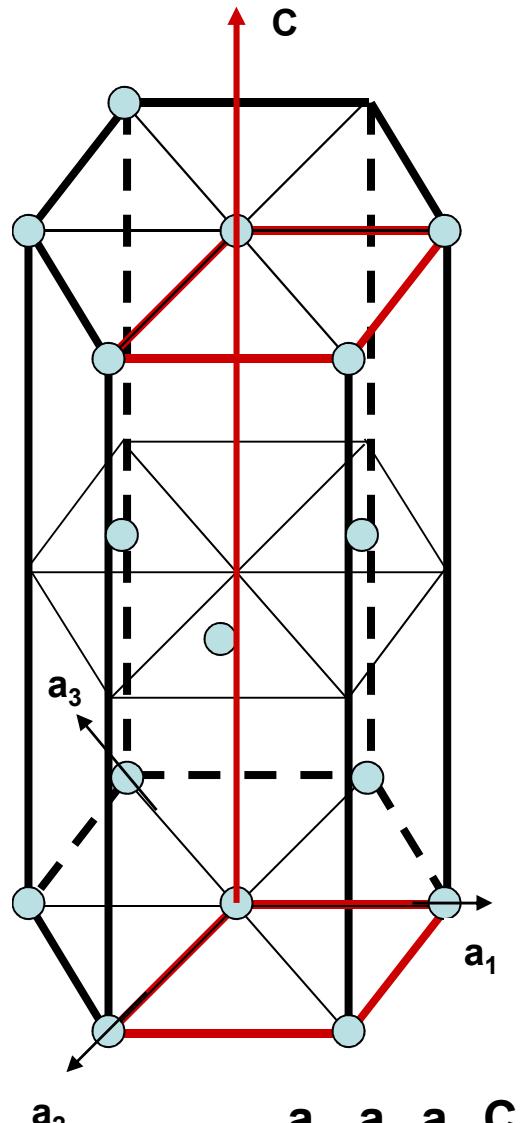
$$\varphi = \cos^{-1} \left[\frac{uu^1 + vv^1 + ww^1}{(u^2 + v^2 + w^2)^{\frac{1}{2}}(u^{12} + v^{12} + w^{12})^{\frac{1}{2}}} \right]$$

Indices of Planes

- Identify the coordinates intercepts of the plane. If the plane is parallel to one of the axes, the intercept is taken as infinity
- Take the reciprocal of the intercepts
- Clear fractions, but do not reduce to lowest integers
- Cite planes in parentheses – (h k l).



Plane	Intercepts	Indices
A	$\infty, \infty, 1$	(0 0 1)
B	1, 1, 1	(1 1 1)
C	1, 1, ∞	(1 1 0)
D	$\frac{1}{2}, \frac{2}{3}, 1$	(3 4 6)



Linear density, ρ_L is the ratio of the number of atoms centered along direction within one unit to the length of the line contained within one unit

Planar density, ρ_P is the ratio of the number of atoms centered on a plane within one unit to the area of the plane contained within one unit

Volumetric density, ρ_V is the number of atoms per unit volume

Atomic Packing Factor, APF is the ratio of the volume of atoms in a unit cell to the volume of unit cell; or **APF** is the product of atoms in cell and volume of an atom per unit volume of the cell; or

$$APF = \rho_V \left[\left(\frac{4}{3} \right) \pi r^3 \right]$$

DCS, Perovskite Structure
SC, Crystobalite Structure

- **Significance of local packing arrangement**
- A coordination polyhedron behaves as a tightly bound unit when the **valence of the central atom is more than half the total valence of the atoms bonded to it**. If the valence of the central atom equals the total valence of the surrounding atoms, the subunit is really a **molecule**
- When polyhedral subunits are discrete atomic groups bonded to one another by **secondary bonds** than when they are bonded together with primary bonds, the **melting or softening temperature will be lower**. For example in SiF_4 each silicon is tetrahedrally coordinated by 4 fluorine atoms and in SiO_2 each silicon is tetrahedrally coordinated by 4 oxygen atoms yet SiF_4 melts at -90°C and SiO_2 melts at 1710°C
- Polyethylene melts at about 125°C . But if adjacent polyethylene chains are bonded together by some C-C bonds produced by irradiation, the polymer may keep its shape and thermal stability up to 300°C

Influence of bond type on structure and properties

The non-directionality of metallic and ionic bond allows metal atoms to be packed closely together in a regular crystalline array. The major of them have ligancy of either 12 (CPH or FCC systems) or 8 (BCC systems). The CN of ionic crystals is frequency of 4, 6, or 8 and so, on average, ionic crystals possess lower packing densities than metals. This is due to the fact that ionic compound contains at least 2 types of ion which may be of different sizes, compared to a pure metal where all atoms are identical, and secondly the ions possess opposing charges.

Metals and ceramics are fully crystalline but polymers and glasses are either partially crystalline or completely amorphous. In amorphous structures, the atoms or molecules are not packed in a regular and symmetrical pattern and the amount of void space is greater than within a crystal.

As the atomic number of the element increases and the distance of the outer shell or valence, electrons from the nucleus becomes greater, the bond strength of covalently bonded crystals reduces.

The melting pt of C, Si, Ge, Sn are 3800, 1420, 937 and 232oC respectively.

The melting pt of ceramics materials mainly oxides, carbides and nitrides of the lower atomic number elements such as Al, B, Mg, Si are all high being in the order of 1000 – 3000oC. The presence of weak van der waals bond within the covalently bonded molecules influences the melting temperatures.

The polyimides (nylons) have higher m.p than other polymers such as polyethylene because of the presence of hydrogen bonds.

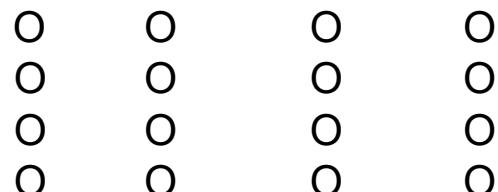
The close packing of atoms in metals leads towards relatively high m.p. the strength of bond may be less compare to that of ionic and covalent bonds

Crystal Imperfections

- **Point Defects**

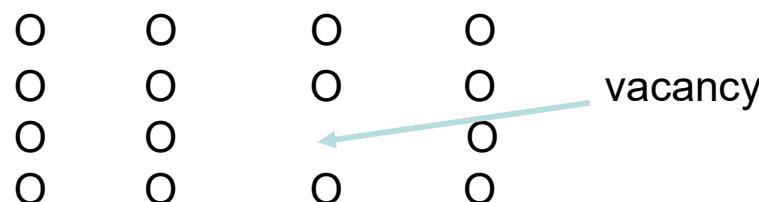
Point defects are localized disruption of the lattice involving one as possibly several atoms

- . Consider a hypothetical crystal structure.



VACANCIES

- A vacancy is produced when an atom is missing from a lattice point (i.e. from a normal site)



Crystal Imperfections

A vacancy is produced into the crystal during solidification at high temperature or as a result of radiation change volume, Ω_v is expressed as

$$n_v = n \exp\left(\frac{-Q}{RT}\right) \Rightarrow n_v \alpha T$$

Where

Ω_v – the number of vacancies per cm^3

Ω – the number of lattice points per cm^3

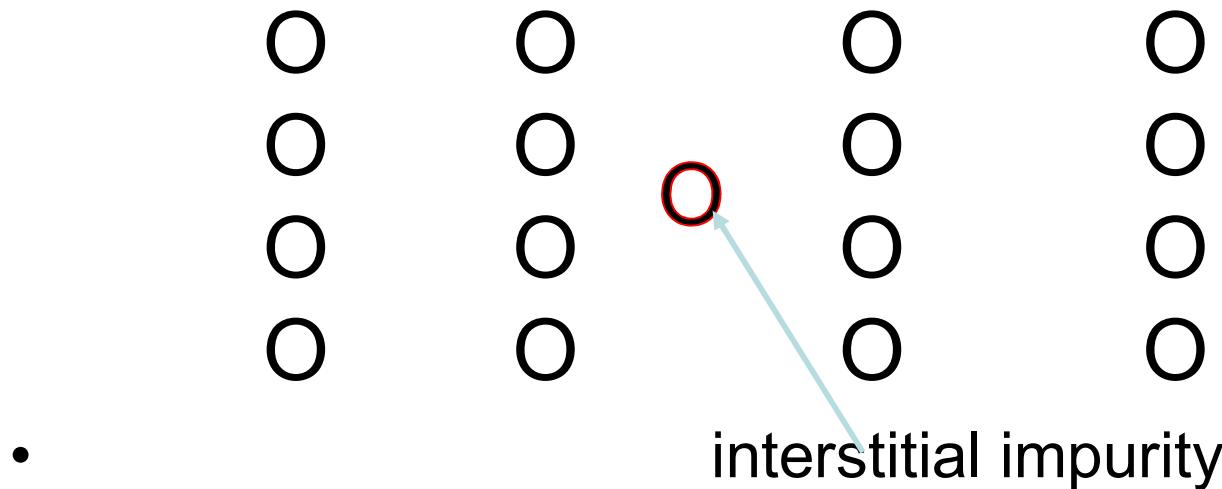
Q is the energy required to produce a vacancy in J/mole .

R is the gas constant, 8.31 J/mole K and

T is the temperature in degrees Kelvin .

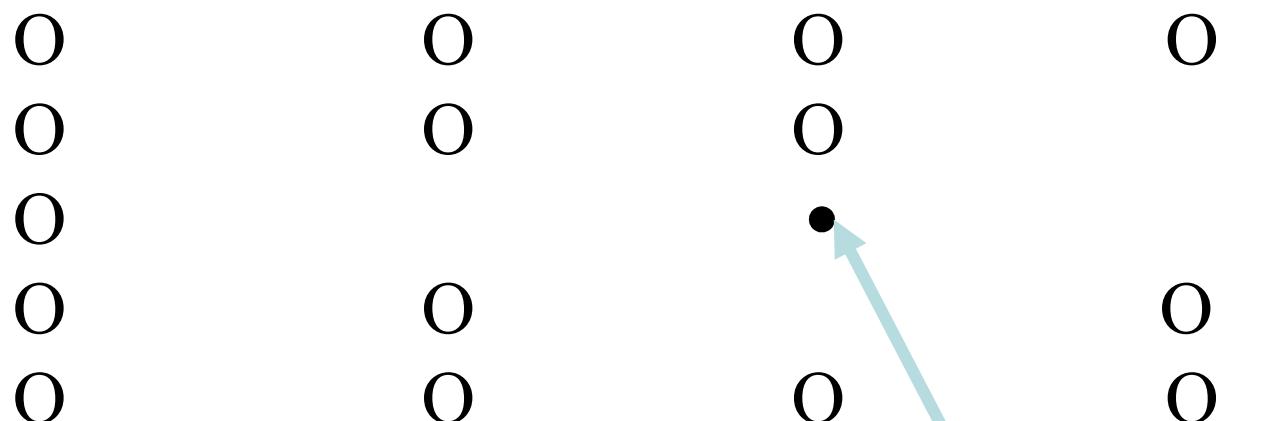
Crystal Imperfections

- INTERSTITIAL
- An interstitial defect is formed when an extra atom is placed into the lattice at a site that is normally not a lattice point.



Crystal Imperfections

- SUBSTITUTIONAL
- A point defect produced when an atom is removed from a regular point and replaced with a different atom, usually of a different size.



Substitutional (smaller or
bigger than the regular

Crystal Imperfections

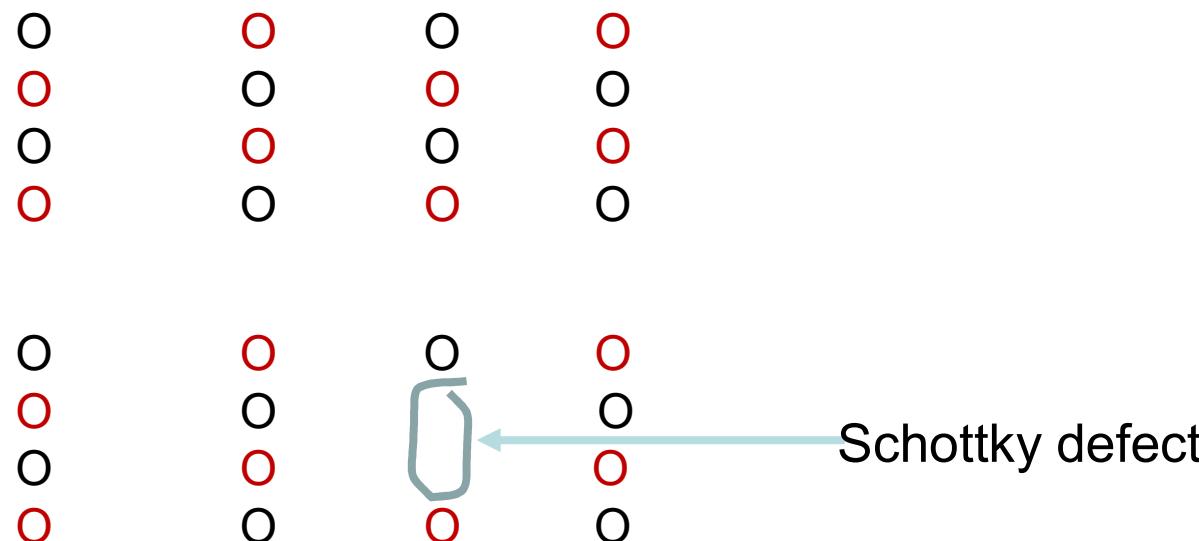
- The interstitial and substitutional defects are present in materials as impurities and may also be intentionally introduced as alloying elements. The number of these defects are independent of temperature

Crystal Imperfections

SCHOTTKY DEFECT

A Schottky defect is a pair of vacancies in an ionically bonded material.

Consider crystal structure below



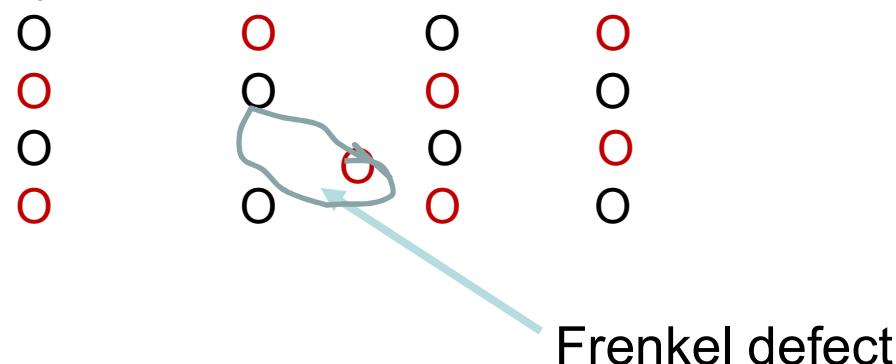
If a vacancy should occur on two adjacent ion and cation we have a schottky defect

Crystal Imperfections

FRENKEL DEFECT

A Frenkel defect is a vacancy – interstitial pair formed when an ion jumps from a normal lattice point to an interstitial site, leaving behind a vacanc.

Consider crystal structure below



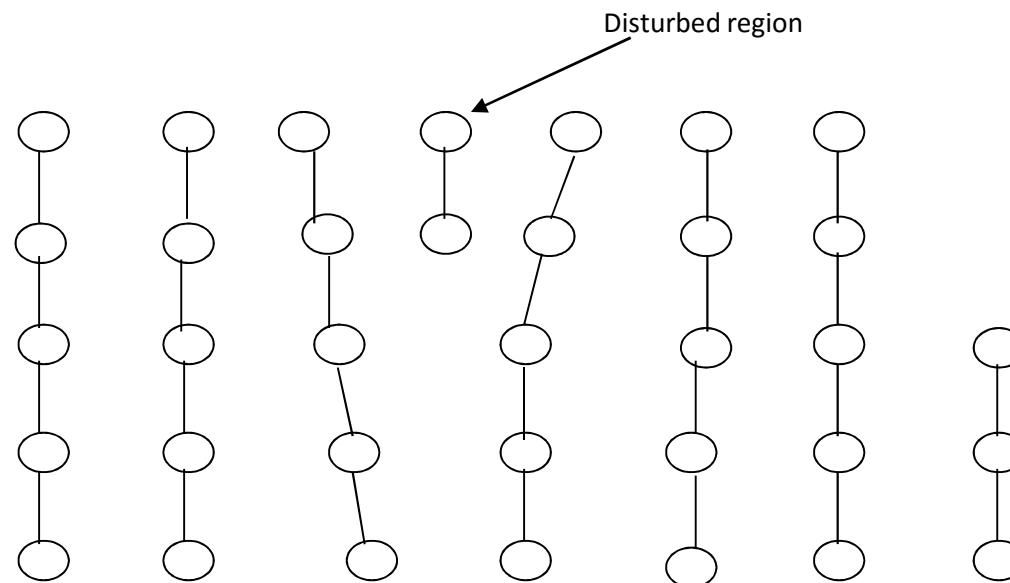
Crystal Imperfections

Point defects disturb the perfect arrangement of the surrounding atom. When a vacancy or a small substitutional atom is present, the surrounding atom collapse towards the point defect, stretching the bonds between the surrounding atom and producing a tensile stress field. An interstitial and large substitutional atom produce the surrounding atoms together, producing a compressive stress field. The disruption accounts for the strength of the metal.

Crystal Imperfections

LINE DEFECT (DISLOCATIONS)

Dislocations are line imperfections in a perfect lattice. A Dislocation is a disturbed region between two substantially perfect parts of a crystal.



The dislocation is responsible for the phenomenon of slip, by which most metals deform plastically. The dislocation is responsible for the phenomenon of slip, by which most metals deform plastically

Crystal Imperfections

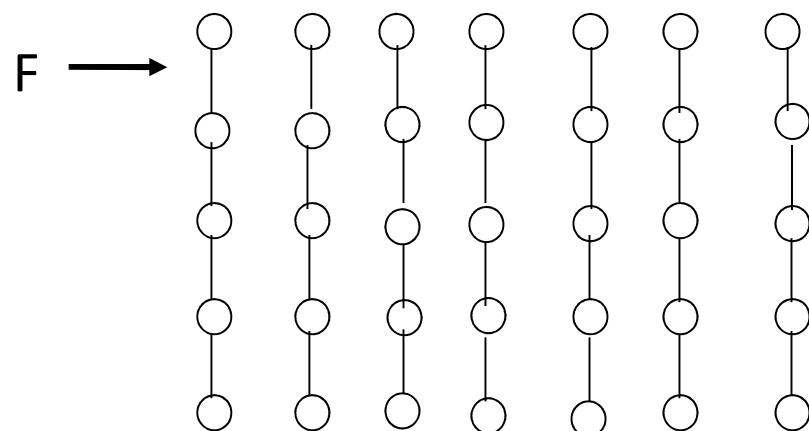
CONCEPT OF EDGE AND SCREW DISLOCATION

In edge dislocation the Burger's vector lies at an angle to the line of the dislocation, along the axis of rows of atoms in the same plane, whereas in screw dislocation, Burger's vector lies parallel to the dislocation line along the axis of a line of atoms in the same plane.

Crystal Imperfections

EDGE DISLOCATIONS

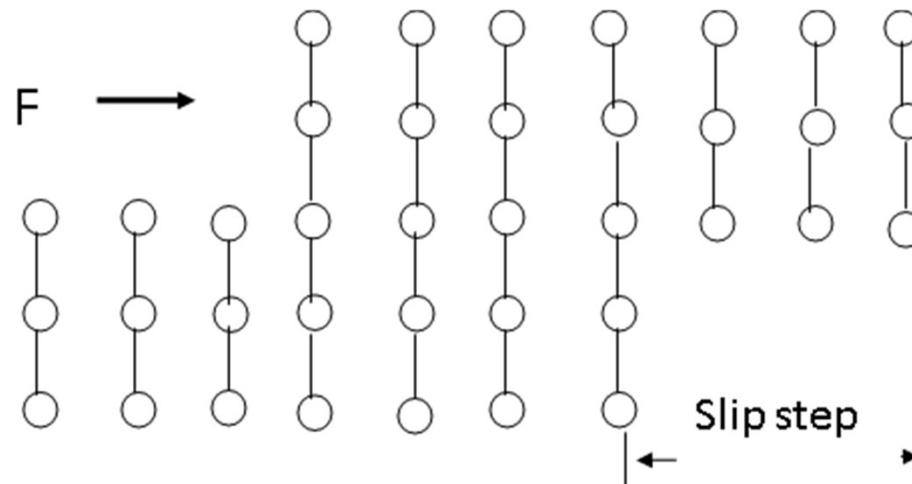
Considering the diagram below, if a force or stress “F” is applied parallel to and along the x- axis, we have a motion.



The dislocation is responsible for the phenomenon of slip, by which most metals deform plastically. The dislocation is responsible for the phenomenon of slip, by which most metals deform plastically.

EDGE DISLOCATIONS

An edge dislocation lies perpendicular to its Burger's vector.



An edge dislocation moves (in its slip plane) in the direction of the Burger's vector (slip direction)

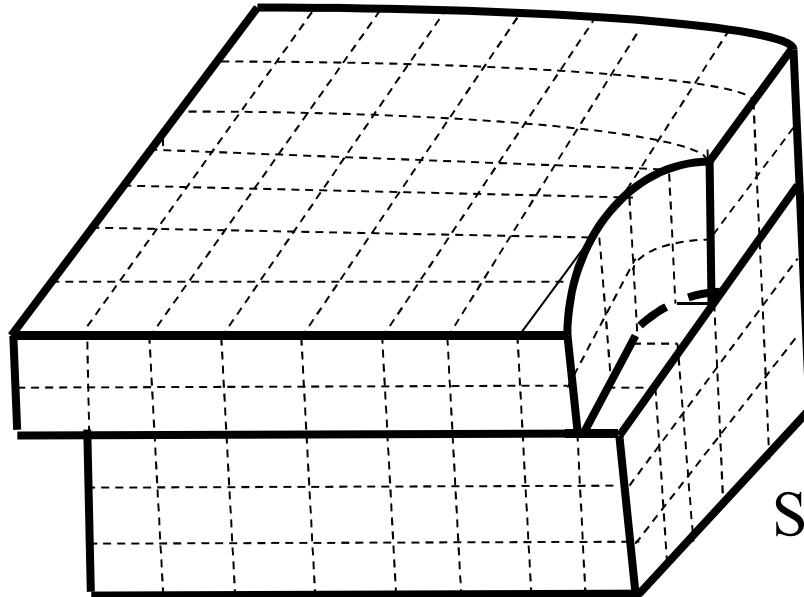
An edge dislocation involves an extra row of atoms, either above (positive sign) or below (negative sign) the slip plane.

The presence of this extra row means that adjacent atoms are displaced elastically, and consequently from both sides elastic forces are exerted on the dislocation

SHEAR Stress = +ve dislocation moves to the right, -ve to the left

SCREW DISLOCATIONS

A screw dislocation lies parallel to its Burger's vector.



Shearing occurs in a screw dislocation

A screw dislocation moves (in the slip plane) in the direction perpendicular to the Burger's vector (slip direction)

In the screw dislocation, the distortion follows a helical or screw path and both right hand and left hand senses are possible.

A dislocation produced by skewing a crystal so that one atomic plane produces a special ramp about the dislocation

The direction and distance that a dislocation moves in each step is known as burger's vector i.e. the vector requested to complete the loop and return to the starting point.

Screw and edge dislocation can occur in different form among which are:

Dislocation slide : if a force causes the movement of atoms in the horizontal direction

Dislocation jump: this could be either +ve or – ve. It is the vertical movement of the atom within the crystal structure (+ ve for upward and – ve for downward)

Dislocation jog: when a force is applied not all the planes move in the direction of the force.

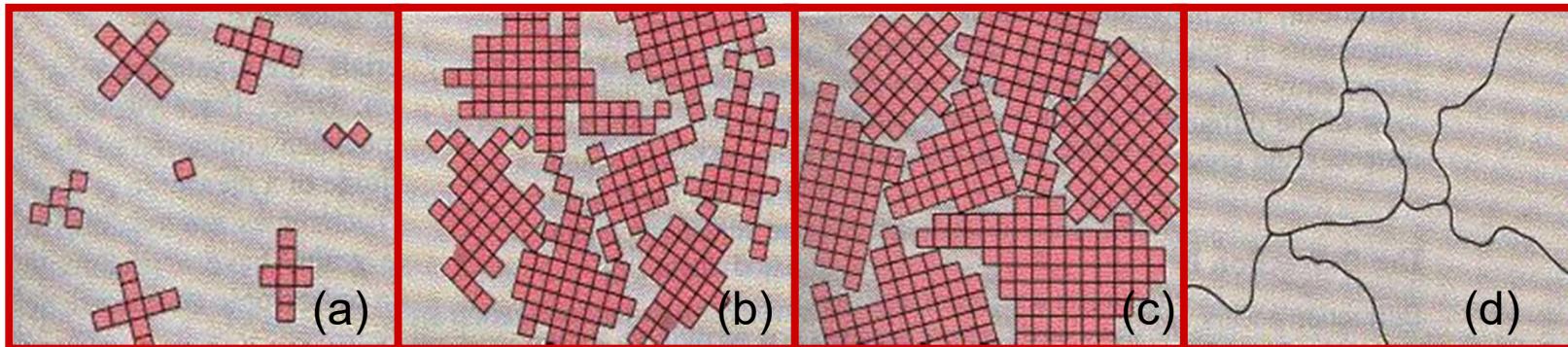
- **SIGNIFICANCE OF DISLOCATIONS**
- The process by which dislocation moves and causes a metal to deposition is called slip.
- This slip explain why the strength of metals is much lower than the value predicted from metallic bond
- Slip provides ductility in metals, if no dislocation were present, the metal (Bar) is brittle, the materials can not be shaped by various metalworking processes such as forging into useful shapes.
- The mechanical properties of a meta; or alloy can be control by interfering with the movement of dislocations. An alloy or obstacle introduced into the crystal presents a dislocation from slipping.
- Dislocation densities of 10^6 cm/cm^3 are typical of the softer metals while densities upto 10^{12} cm/ cm^3 can be achieved by deformina the materials.

SCHMID'S LAW

Crystal Formation

Crystallization

- Crystallization is the transition from the liquid to the solid state and occurs in two stages:
 - 1. Nucleus formation
 - 2. Crystal growth
- Atomic motion in the liquid state of a metal is almost completely disordered. Although the atoms in the liquid state do not have any definite arrangement, it is possible that some atoms at any given instant are in positions exactly corresponding to the space lattice they assume when solidified. As the energy in the liquid system decreases, the movement of the atoms decreases and the probability increases for the arrangement of a number of atoms into a characteristic lattice for that material. The energy level at which these isolated lattices form is called the *freezing point*.



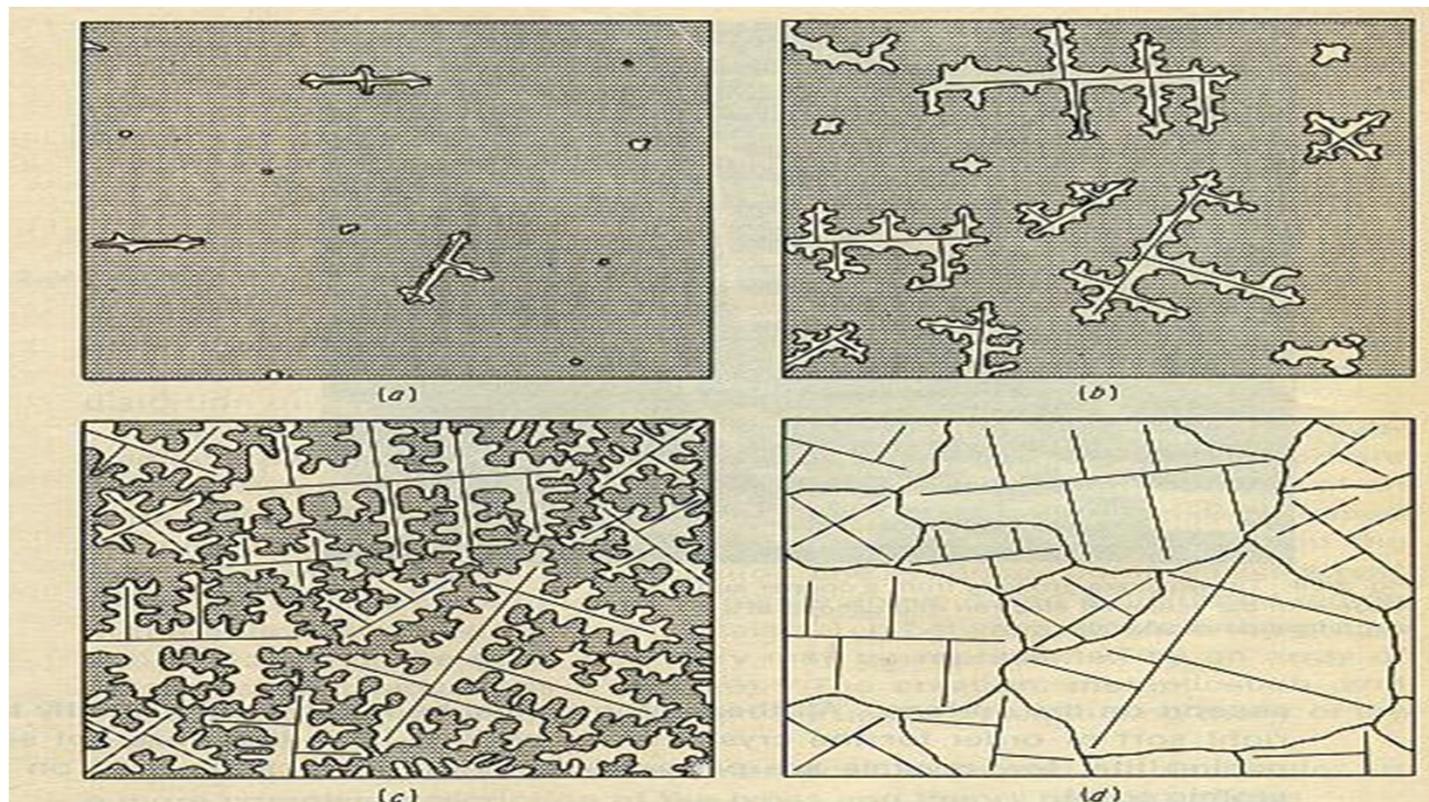
Mechanism of solidification (square grids represent the unit cells)

(a) Nucleus formation; (b), (c) Growth of the crystallites; (d) Grain boundaries

Now consider a pure metal at its *freezing point* where both the liquid and solid states are at the same temperature. The kinetic energy of the atoms in the liquid and the solid must be the same, but there is a significant difference in potential energy. *Kinetic energy* is related to the speed at which the atoms move and is strictly a function of temperature. The higher the temperature, the more active are the atoms and the greater is their kinetic energy. *Potential energy*, on the other hand, is related to the distance between atoms. The greater the average distance between the atoms, the greater is their potential energy. The atoms in the solid are much closer together, so that solidification occurs with a release of energy. This difference in potential energy between the liquid and solid states is known as the *latent heat of fusion*.

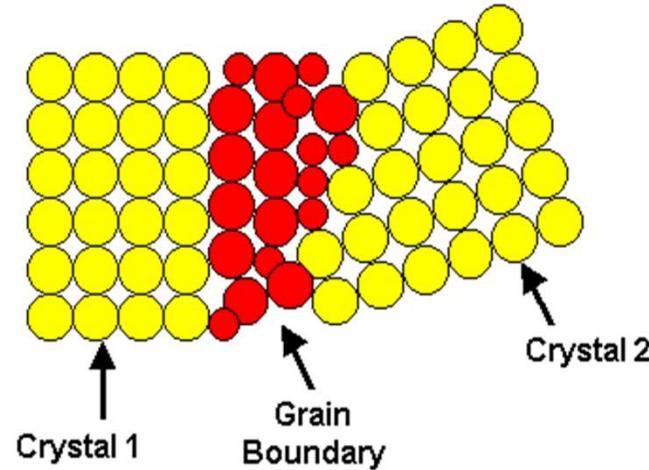
When the temperature of the liquid metal has dropped sufficiently below its freezing point, stable aggregates or nuclei appear spontaneously at various points in the liquid. These nuclei, which have now solidified, act as centers for further crystallization. As cooling continues, more atoms tend to freeze, and they may attach themselves to already existing nuclei or form new nuclei of their own. Each nucleus grows by the attraction of atoms from the liquid into its space lattice.

- Crystal growth continues in three dimensions, the atoms attaching themselves in certain preferred directions, usually along the axes of a crystal. This gives rise to a characteristic treelike structure which is called *dendrite*. Crystal growth continues in three dimensions, the atoms attaching themselves in certain preferred directions, usually along the axes of a crystal. This gives rise to a characteristic treelike structure which is called *dendrite*.

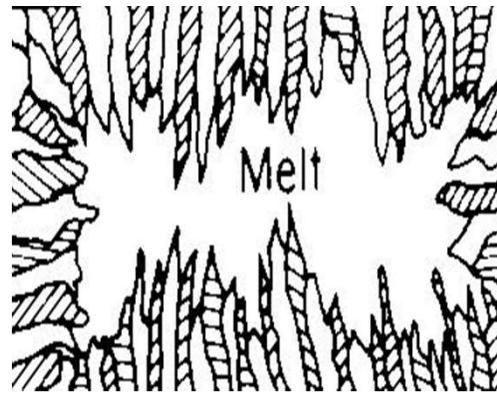


Process of crystallization by nucleation and dendritic growth.

- The crystal axes are pointed at random because Each nucleus is formed by chance, and therefore the dendrites will grow in different directions in each crystal. As the amount of liquid decreases, the gaps between the arms of the dendrite will be filled and the growth of the dendrite will be mutually obstructed by that of its neighbors. This leads to a very irregular external shape. The crystals found in all commercial metals are commonly called *grains* because of this variation in external shape. The area along which crystals meet, known as the *grain boundary*, is a region of mismatch. The boundaries are formed by materials that are not part of a lattice, such as impurities, which do not show a specific grain pattern. This leads to a *noncrystalline (amorphous) structure* at the grain boundary with the atoms irregularly spaced. Since the last liquid to solidify is generally along the grain boundaries, there tends to be a higher concentration of impurity atoms in that area.



Grain Boundary



Formation of dendrites in a molten metal.



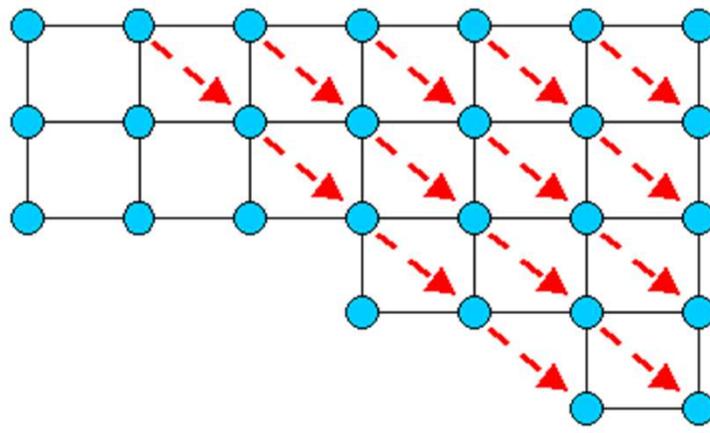
Dendrites observed at a magnification of 250x

Plastic Deformation

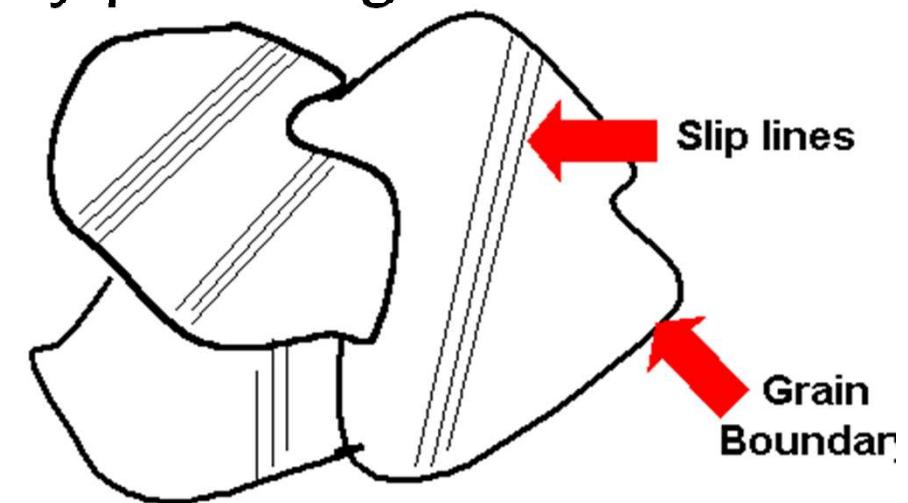
- When a material is stressed below its **elastic limit**, the resulting deformation or strain is temporary. Removal of stress results in a gradual return of the object to **its original dimensions**. When a material is stressed **beyond its elastic limit**, **plastic or permanent deformation** takes place, and it will **not return to its original shape** by the application of force alone. All shaping operations such as stamping, pressing, spinning, rolling, forging, drawing, and extruding involve plastic deformation of metals. Various machining operations such as milling, turning, sawing, and punching also involve plastic deformation.

- Plastic deformation may take place by :
 - » Slip
 - » Twinning
 - » Combination of slip and twinning
- Deformation by Slip:

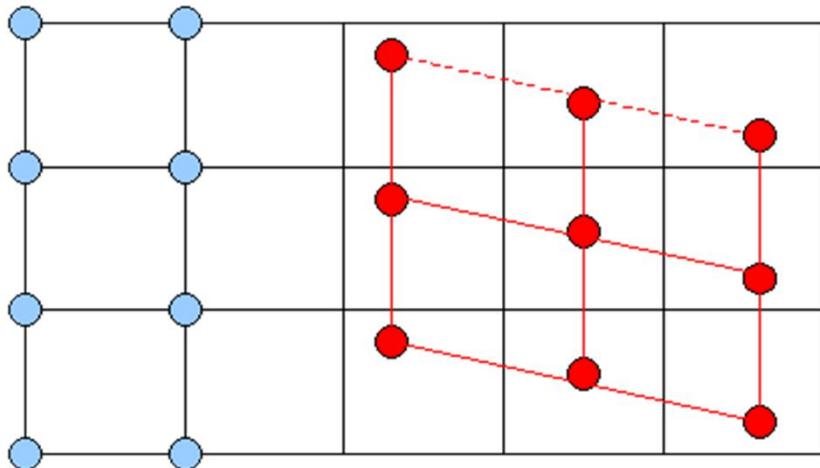
When the plastic deformation is due to slip, the atoms move a whole interatomic space (moving from one corner to another corner of the unit cell). This means that overall lattice structure remains the same. Slip is observed as thin lines under the microscopes and these lines can be removed by polishing.



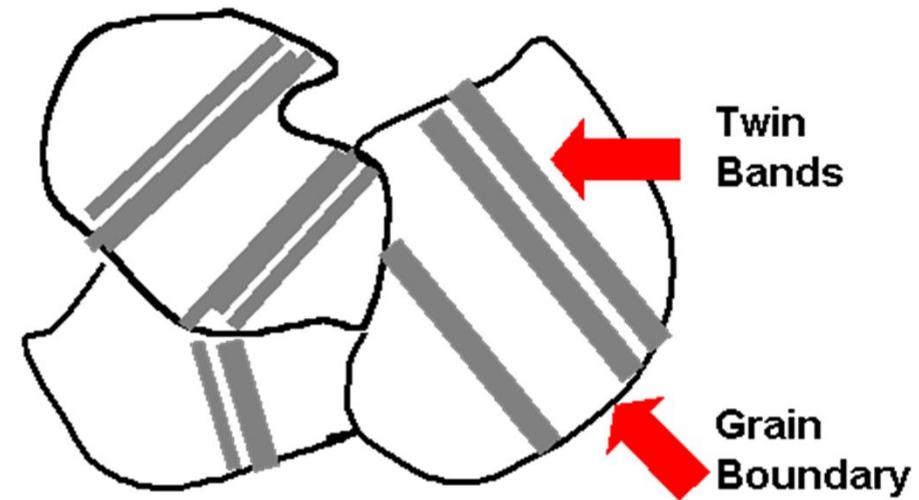
The effect of slip on the lattice structure.



- Deformation by Twinning:
- When mechanical deformation is created by twinning, the lattice structure changes. **The atoms move only a fraction of an interatomic space and this leads to a rearrangement of the lattice structure.** Twinning is observed as wide bands under the microscope. These wide bands can not be removed by polishing.
- Two kinds of twins are of interest to the metallurgists:
 - 1. **Deformation or mechanical twins**, most prevalent in **close packed hexagonal metals** (magnesium, zinc, iron with large amount of ferrite)
 - 2. **Annealing twins**, most prevalent in F.C.C. (Face centered cubic) metals (aluminum, copper, brass, iron with austenite). These metals have been previously worked and heat treated. The twins are formed because of a change in the normal growth mechanism.



The effect of twinning on the lattice structure.



Twin bands



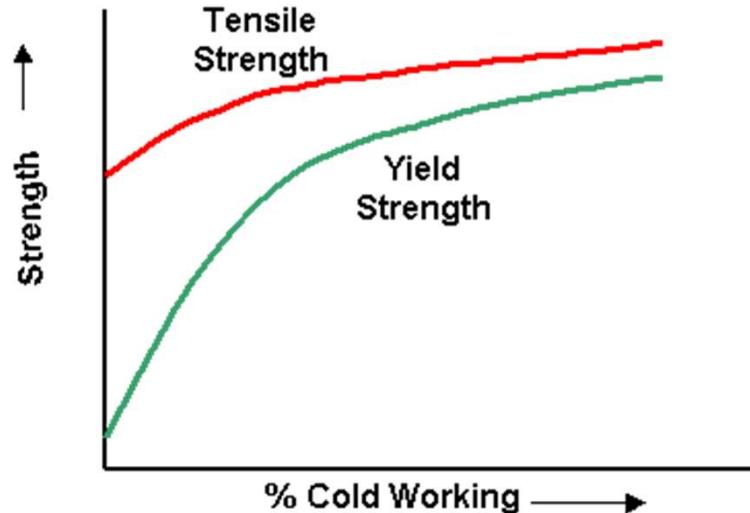
Twin bands in zinc.

Slip versus Twinning

	Slip	Twinning
Atomic movement	Atoms move a whole number of atomic spacing.	Atoms move fractional atomic spacing.
Microscopic appearance	Thin lines	Wide bands or broad lines
Lattice orientation	No change in lattice orientation. The steps are only visible on the surface of the crystal and can be removed by polishing. After polishing there is no evidence of slip.	Lattice orientation changes. Surface polishing will not destroy the evidence of twinning.

Cold Work

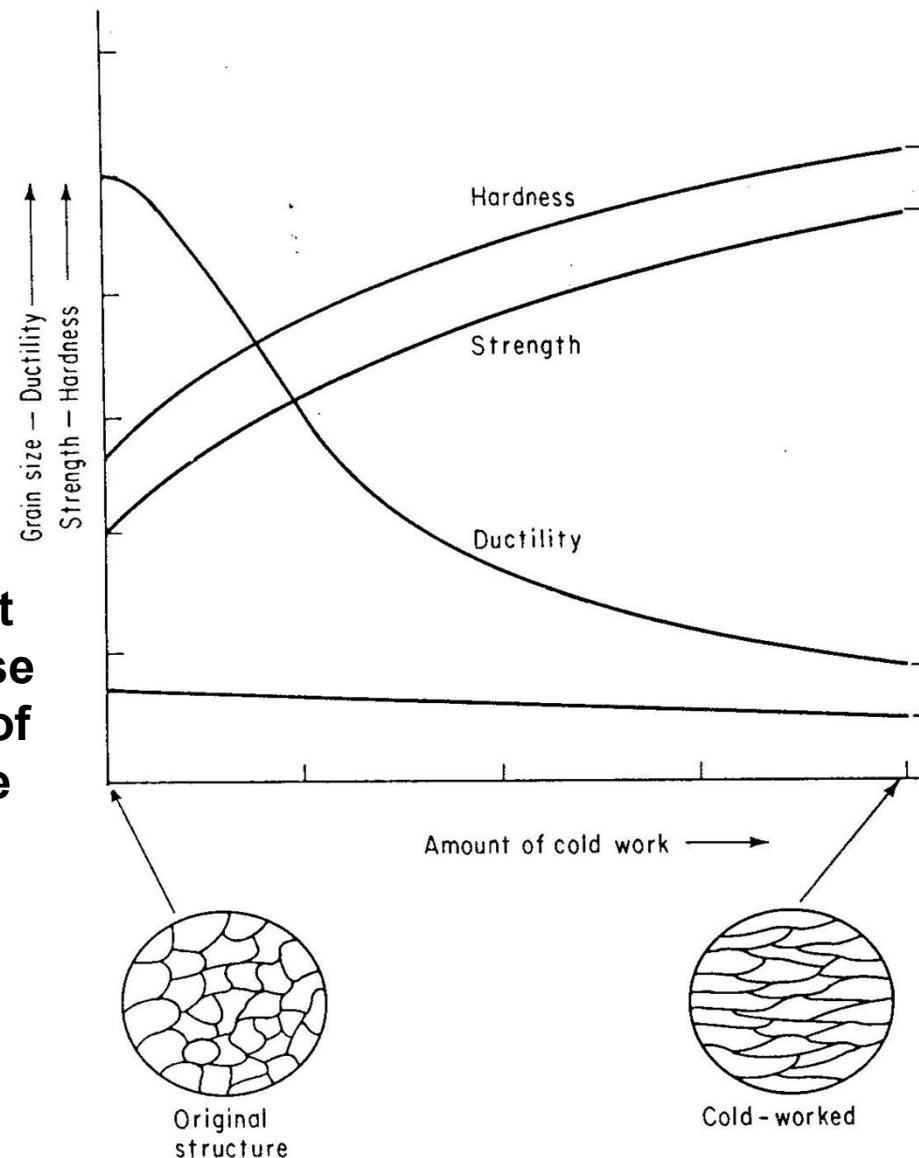
- A material is considered to be cold worked if its grains are in a **distorted condition after plastic deformation is completed**. All the properties of a metal that are dependent on the lattice structure are affected by plastic deformation or cold working. The following properties are affected by cold work significantly:
 - Tensile Strength
 - Hardness
 - Yield Strength
 - Ductility
 - **Tensile strength, yield strength and hardness are increased, while ductility is decreased.** Although both strength and hardness increase, the rate of change is not the same. Hardness generally increases most rapidly in the first 10 percent reduction (cold work), whereas the tensile strength increases more or less linearly. The yield strength increases more rapidly than the tensile strength, so that, as the amount of plastic deformation is increased, the gap between the yield and tensile strengths decreases. This is important in certain forming operations where appreciable deformation is required. In drawing, for example, the load must be above the yield point to obtain appreciable deformation but below the tensile strength to avoid failure. If the gap is narrow, very close control of the load is required.



Effect of cold working on tensile and yield strength of copper.

Ductility follows a path opposite to that of hardness. A large decrease in the first 10 percent reduction and then a decrease at a slower rate is observed. Distortion of the lattice structure hinders the passage of electrons and decreases electrical conductivity in alloys. The increase in internal energy, particularly at the grain boundaries, makes the material more susceptible to inter granular corrosion, SCC

Effect of cold working on tensile strength, hardness, ductility and grain size. (The curve below ductility represents the change in grain size)



Annealing

- As a result of cold working, the hardness, tensile strength, and electrical resistance increase, while ductility decreases. There is also a large increase in the number of dislocations, and certain planes in the crystal structure are severely distorted. Most of the energy used to cold work the metal is dissipated in heat, and a finite amount of energy is stored in the crystal structure as internal energy associated with the lattice defects created by the deformation.
- **Full annealing** is the process by which the distorted cold worked lattice structure is changed back to one which is strain free through the application of heat. This process is carried out entirely in the solid state and is usually followed by slow cooling in the furnace from the desired temperature.

- The annealing process may be divided into three stages:
 - Recovery
 - Recrystallization
 - Grain growth
- **Recovery:**
- This is primarily a low temperature process, and the property changes produced do not cause appreciable change in microstructure or the properties, such as tensile strength, yield strength, hardness and ductility. The principal effect of recovery is the relief of internal stresses due to cold working.
- When the load which causes plastic deformation is released, all the elastic deformation does not disappear. This is due to the different orientation of crystals, which will not allow some of them to move back when the load is released. As the temperature is increased, there is some spring back of these elastically displaced atoms which relieve most of the internal stresses. Electrical conductivity is also increased appreciably during the recovery stage.
- Since the mechanical properties of the metal are essentially unchanged, the main purpose of heating in the recovery range is stress relieving cold worked alloys to prevent stress corrosion cracking or to minimize the distortion produced by residual stresses. Commercially, this low temperature treatment in the recovery range is known as **stress relief annealing or process annealing**.

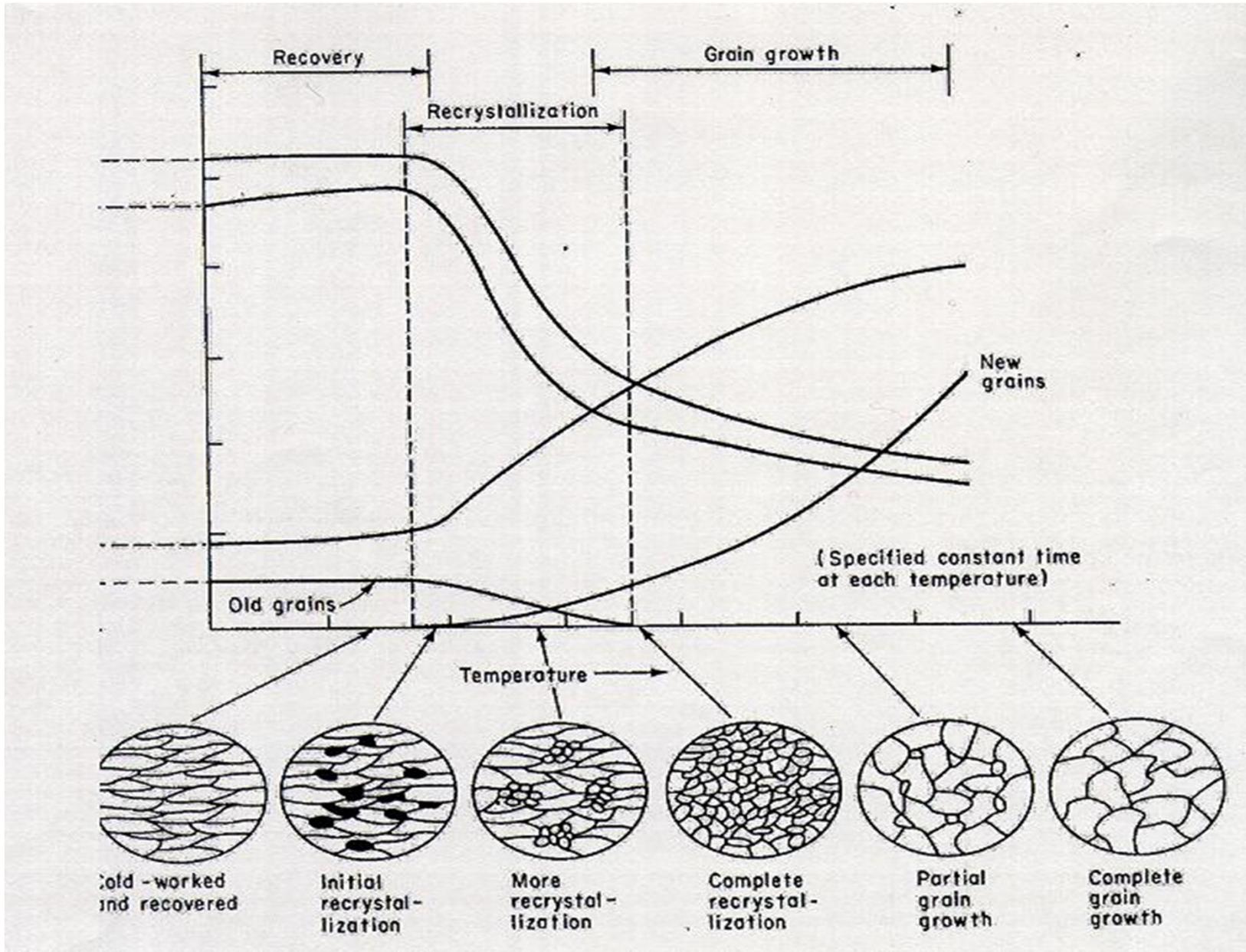
- **Recrystallization:**
- As the temperature of the recovery range is reached, minute new crystals appear in the microstructure. These new crystals have the same composition and lattice structure as the original undeformed grains and are not elongated but are uniform in dimensions. The new crystals generally appear at the most drastically deformed portions of the grain, usually the grain boundaries and slip planes. The cluster of atoms from which the new grains are formed is called a nucleus. **Recrystallization takes place by a combination of nucleation of strain free grains and the growth of these nuclei to absorb the entire cold worked material.**
- The term recrystallization temperature does not refer to a definite temperature below which recrystallization will not occur, but refers to the approximate temperature at which a highly cold worked material completely recrystallizes in one hour.

Material	Recrystallization Temperature (°F)
Copper (99.99 %)	250
Copper (5 % Zinc)	600
Aluminum (99.99 %)	175
Aluminum alloys	600
Low carbon steel	1000
Zinc	50
Tin	25
Lead	25

Recrystallization temperatures for various metals and alloys.

Material	Recrystallization Temperature (°F)
Copper (99.99 %)	250
Copper (5 % Zinc)	600
Aluminum (99.99 %)	175
Aluminum alloys	600
Low carbon steel	1000
Zinc	50
Tin	25
Lead	25

- The greater the prior deformation, the lower the temperature for the start of recrystallization.
- Increasing the annealing time decreases the recrystallization temperature for the start of recrystallization.
- During recrystallization stage, there is a significant drop in tensile strength, hardness and a large increase in the ductility of the material.
- **Grain Growth:**
- In this stage the tensile strength and hardness continue to decrease but at a much less rate than the recrystallization stage. The major change observed during this stage is the growth of the grain boundaries and reaching the original grain size (See Figure below).



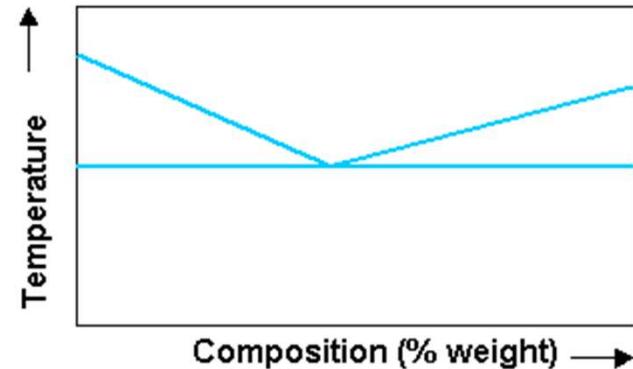
Effect of annealing on tensile strength, hardness, ductility and grain size.

Phase Diagrams

Part 1

The properties of a material depend on the type, number, amount, and form of the phases present, and can be changed by altering these quantities. In order to make these changes, it is essential to know the conditions under which these quantities exist and the conditions under which a change in phase will occur. The best method to record the data related to phase changes in many alloy systems is in the form of *phase diagrams*, also known as *equilibrium diagrams* or *constitutional diagrams*.

In order to specify completely the state of a system in equilibrium, it is necessary to specify three independent variables. These variables, which are externally controllable, are *temperature*, *pressure* and *composition*. With pressure assumed to be constant at atmospheric value, the equilibrium diagram indicates the structural changes due to variation of temperature and composition. Phase diagrams show the phase relationships under equilibrium conditions, that is, under conditions in which there will be no change with time. Equilibrium conditions may be approached by extremely slow heating and cooling, so that if a phase change is to occur, sufficient time is allowed. Phase diagrams are usually plotted with temperature as the ordinate, and the alloy composition as the abscissa as shown in the Figure above.

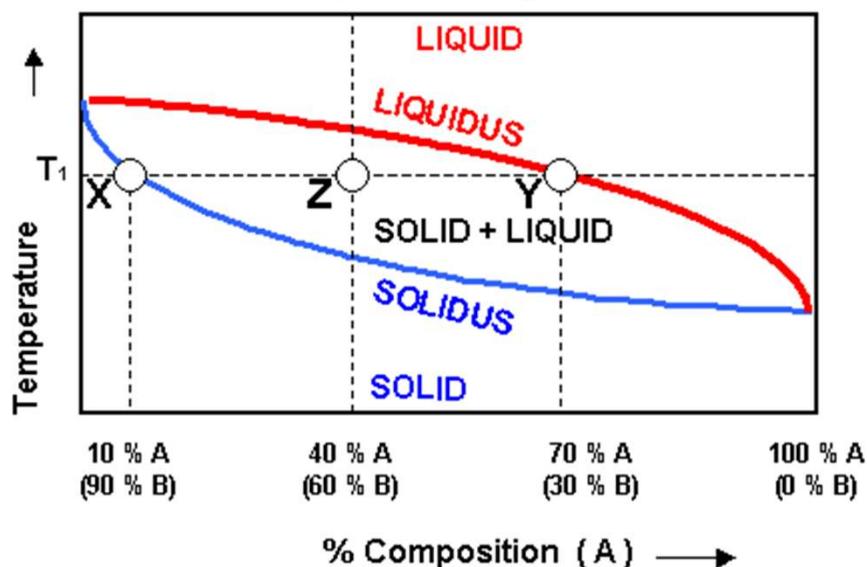


Sample Phase Diagram

Phase Diagrams

Part 2

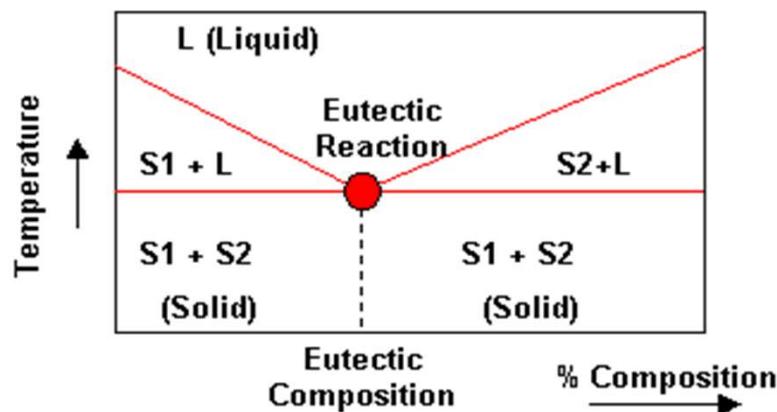
- Inverse Lever Rule:
- Inverse lever rule is used to determine the percentage of each phase that is present at various temperatures.
- The length of line XY represents the sum of the two phases as 100 percent. The inverse lever rule states that liquid phase can be calculated by taking the length of the line XZ and dividing this by XY.
- The solid phase can be calculated by taking the length of the line ZY and dividing it by XY. To get the percentages, the values are multiplied by 100.



Phase diagram of a mixture with complete solubility in liquid and solid states.

- **Eutectic System:**

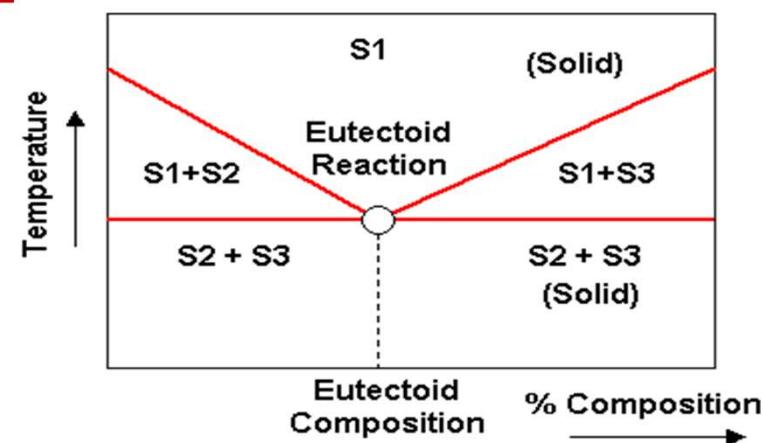
- Eutectic system is a phase transformation that takes place when a single-phase liquid transforms directly to a two-phase solid.
- $L \rightarrow S_1 + S_2$
- Liquid \rightarrow Solid 1 + Solid 2
- (This is a reversible phase transformation)



Eutectic phase transformation

- **Eutectoid System:**

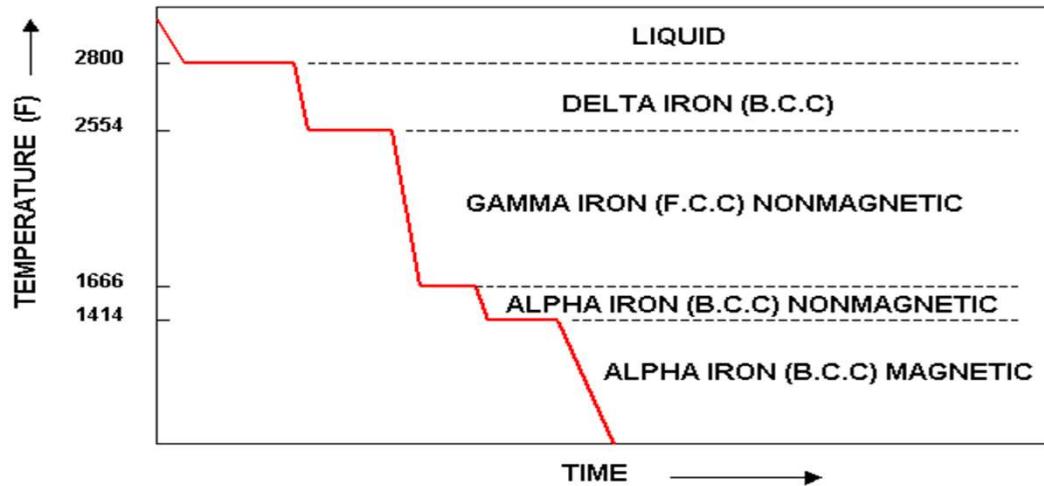
- The eutectoid phase transformation occurs when a single-phase solid transforms directly to two-phase solid.
- $S_1 \rightarrow S_2 + S_3$
- Solid 1 \rightarrow Solid 2 + Solid 3
- (This is a reversible phase transformation)



Eutectoid phase transformation

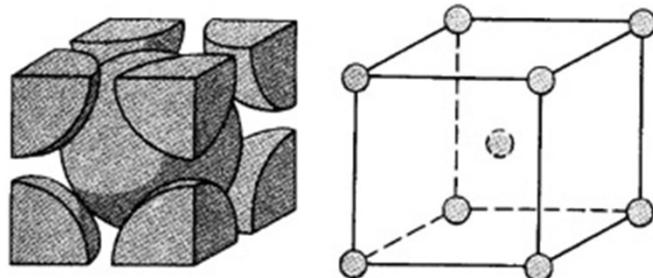
Polymorphism and Allotropy

- **Polymorphism** is a physical phenomenon where a material may have more than one crystal structure. A material that shows polymorphism exists in more than one type of space lattice in the solid state. If the change in structure is reversible, then the polymorphic change is known as **allotropy**. The prevailing crystal structure depends on both the temperature and the external pressure.
- One familiar example is found in carbon: graphite is the stable polymorph at ambient conditions, whereas diamond is formed at extremely high pressures.
- The best known example for allotropy is iron. When iron crystallizes at 2800 °F it is B.C.C. (δ -iron), at 2554 °F the structure changes to F.C.C. (γ -iron or austenite), and at 1670 °F it again becomes B.C.C. (α -iron or ferrite).

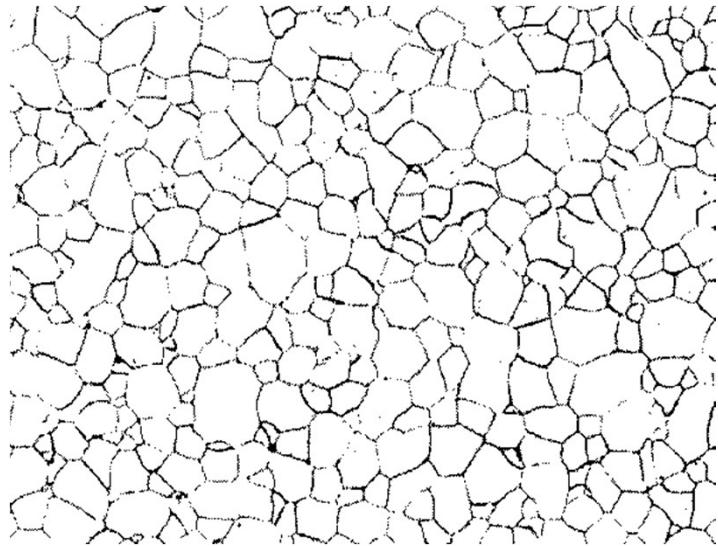


Cooling curve for pure iron. (Allotropic behavior of pure iron)

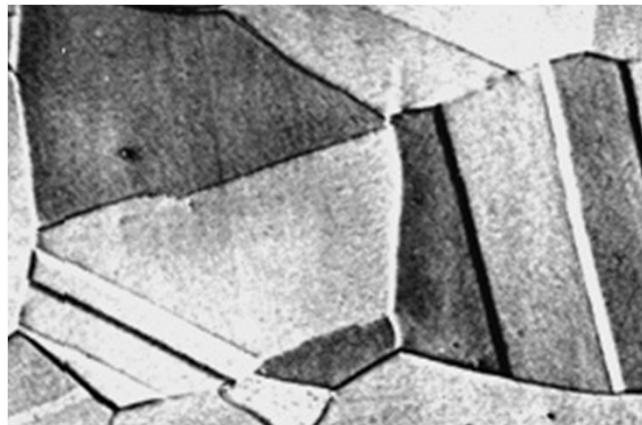
- a -iron (alpha) :
- Figure 2. Alpha iron (B.C.C) unit cell
- The other name for a -iron is ferrite. This crystal has body centered cubic structure. The unit cell and the micrograph of the crystal are shown in the Figures below.



Alpha iron (B.C.C) unit cell

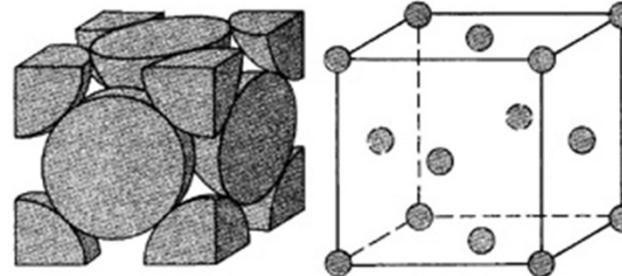


Ferrite crystals.



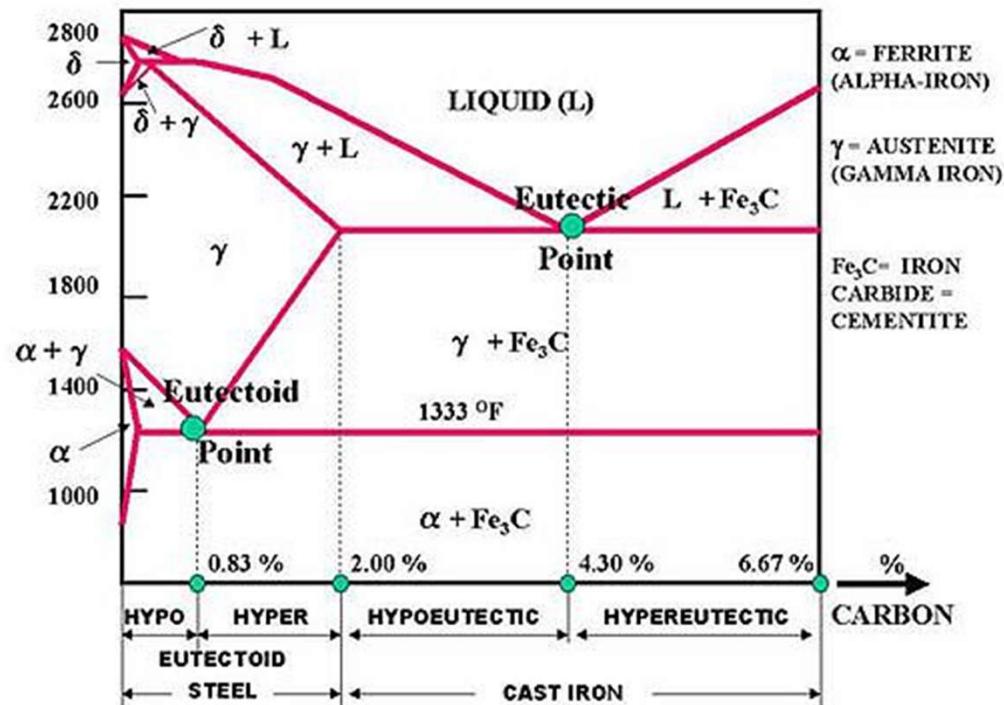
Austenite crystals.

γ -iron (Gamma):



Face centered cubic crystal unit cell.
The other name for γ -iron is austenite. This crystal has face centered cubic (F.C.C) structure. The unit cell and the micrograph of the crystal are shown in the Figures below.

Iron-Iron Carbide Diagram



Iron-iron carbide diagram

CEMENTITE (Fe_3C):

Cementite is also known as iron carbide which has a chemical formula, Fe_3C . It contains 6.67 % Carbon by weight. It is a typical hard and brittle interstitial compound of low tensile strength (approximately 5,000 psi) but high compressive strength. Its crystal structure is orthorhombic.

AUSTENITE (γ iron):

It is also known as (γ) gamma-iron, which is an interstitial solid solution of carbon dissolved in iron with a face centered cubic crystal (F.C.C) structure. Average properties of austenite are:

Table 1. Properties of Austenite

Tensile strength	150,000 psi.
Elongation	10 % in 2 in gage length.
Hardness	Rockwell C 40
Toughness	High



Austenite (gamma iron) crystal structure

Austenite is normally unstable at room temperature. Under certain conditions it is possible to obtain austenite at room temperature.

FERRITE (α iron):

It is also known as (α) alpha -iron, which is an interstitial solid solution of a small amount of carbon dissolved in iron with a Body Centered Cubic (B.C.C.) crystal structure. It is the softest structure on the iron-iron carbide diagram. Average properties are:

Table 2. Properties of Ferrite.

Tensile Strength	40,000 psi
Elongation	40 % in 2 in gage length
Hardness	Less than Rockwell C 0 or less than Rockwell B 90.
Toughness	Low



Ferrite (alpha iron) crystal structure

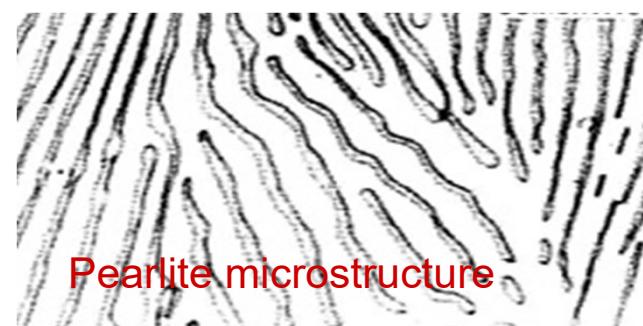
PEARLITE (α + Fe_3C)

It is the eutectoid mixture containing 0.83 % Carbon and is formed at 1333°F on very slow cooling. It is very fine platelike or lamellar mixture of ferrite and cementite. The structure of pearlite includes a white matrix (ferritic background) which includes thin plates of cementite. Average properties are:

Table 3. Properties of pearlite.

Tensile Strength	120,000 psi
Elongation	20 % in 2 in gage length
Hardness	Rockwell C 20 or BHN 250-300

(Light background is the ferrite matrix, dark lines are the cementite network)

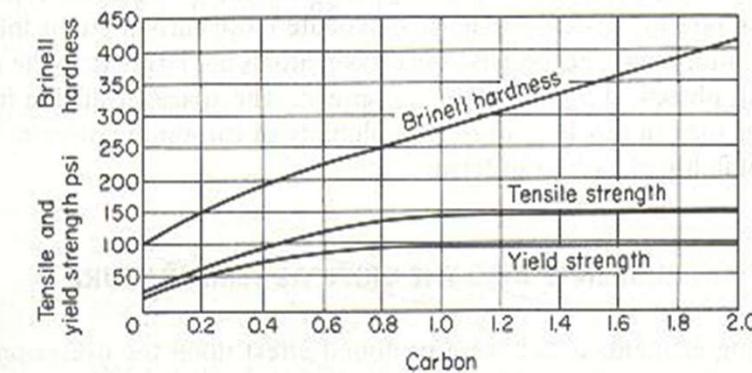


Pearlite microstructure

A fixed amount of carbon and a fixed amount of iron are needed to form cementite (Fe_3C). Also, pearlite needs fixed amounts of cementite and ferrite. If there is not enough carbon, that is less than 0.83 %, the C and the Fe will combine to form Fe_3C until all the C is consumed. This cementite will combine with the required amount of ferrite to form pearlite. The remaining amount of ferrite will stay in the structure as free ferrite. Free ferrite is also known as proeutectoid ferrite. The steel that contains proeutectoid ferrite is referred to as hypoeutectoid steel. If, however, there is an excess of C above 0.83 % in the austenite, pearlite will form, and the excess C above 0.83 % will form cementite. The excess cementite deposits in the grain boundaries. This excess cementite is also known as proeutectoid cementite

- LEDEBURITE (α + Fe₃C)
- It is the eutectic mixture of austenite and cementite. It contains 4.3 % Carbon and represents the eutectic of cast iron. Ledeburite exists when the carbon content is greater than 2 %, which represents the dividing line on the equilibrium diagram between steel and cast iron.
- (δ) DELTA IRON:
- Delta iron exists between 2552 and 2802 oF. It may exist in combination with the melt to about 0.50 % Carbon, in combination with austenite to about 0.18 % Carbon and in a single phase state out to about 0.10 % carbon. Delta iron has the Body Centered Cubic (B.C.C) crystal structure and is magnetic.

- **Effect of Carbon on the Physical Properties of Steel**
- In general, as the carbon content increases the hardness of the steel also increases. The tensile strength and the yield strength also increase to about 0.83 % carbon. Thereafter, they level out. This is shown in Figure 1.



- Figure 1. Effect of carbon on hardness, tensile strength and yield strength of steels.
- The tensile strength and hardness are affected as the ratio of ferrite to cementite in the structure of steel changes. As the percentage of pearlite increases in the hypoeutectoid steels, the tensile strength increases. The hardness does not increase dramatically. The hypereutectoid steels show only a slight increase in strength as the cementite-to-ferrite ratio increases.

- The elongation and the reduction in area represent how ductile or brittle a material is. Figure 2 indicates the effect of carbon on the ductility and impact resistance (toughness) of steels. The elongation and the reduction in area drop sharply with increase in carbon content, going almost to zero at about 1.5 % carbon. This indicates that the carbon content of 1.5 % or more will cause high brittleness. The impact resistance also decreases very sharply up to about 0.83 % carbon and then levels out.

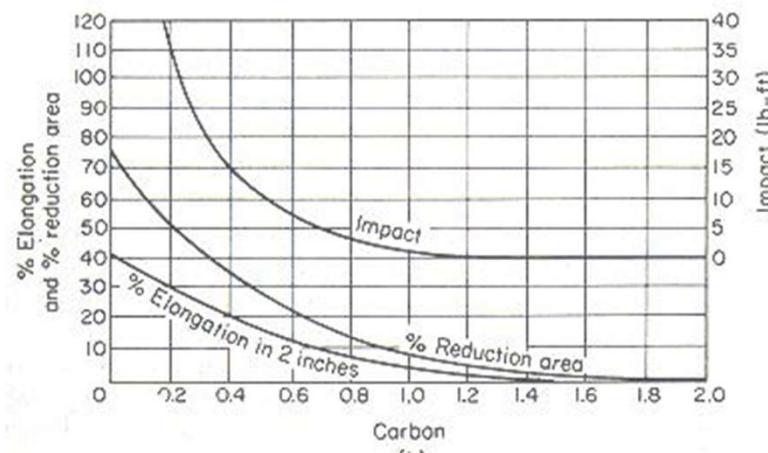


Figure 2. Effect of carbon on the impact resistance and ductility of steels.

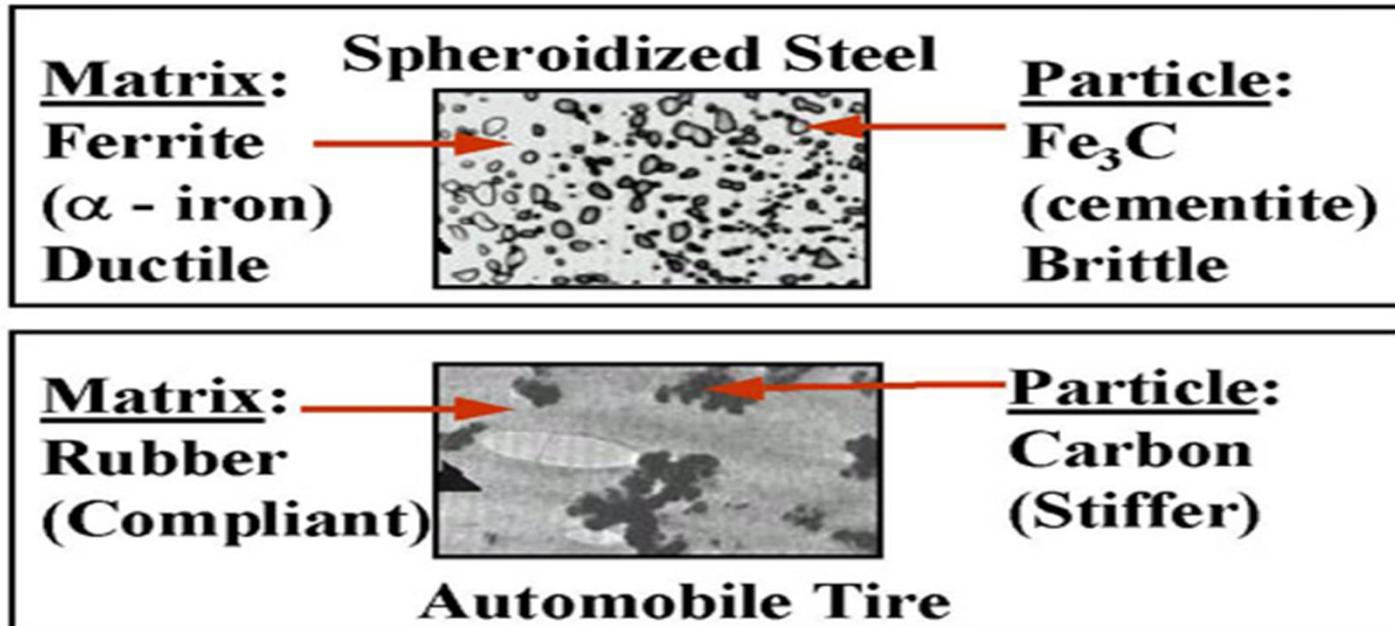
- Composites
- Composites are combinations of two materials in which one of the materials, called the reinforcing phase, is in the form of fibers, sheets, or particles, and is embedded in the other materials called the matrix phase. The reinforcing material and the matrix material can be metal, ceramic, or polymer. Composites are used because overall properties of the composites are superior to those of the individual components. For example: polymer/ceramic composites have a greater modulus than the polymer component, but aren't as brittle as ceramics. The following are some of the reasons why composites are selected for certain applications:
 - High strength to weight ratio (low density high tensile strength)
 - High creep resistance
 - High tensile strength at elevated temperatures
 - High toughness
 - Typically, reinforcing materials are strong with low densities while the matrix is usually a ductile, or tough, material. If the composite is designed and fabricated correctly, it combines the strength of the reinforcement with the toughness of the matrix to achieve a combination of desirable properties not available in any single conventional material. The downside is that such composites are often more expensive than conventional materials. Examples of some current application of composites include the diesel piston, brake-shoes and pads, tires and the Beechcraft aircraft in which 100% of the structural components are composites.

- The strength of the composite depends primarily on the amount, arrangement and type of fiber (or particle) reinforcement in the resin. Typically, the higher the reinforcement content, the greater the strength. In some cases, glass fibers are combined with other fibers, such as carbon or aramid (Kevlar29 and Kevlar49), to create a "hybrid" composite that combines the properties of more than one reinforcing material. In addition, the composite is often formulated with fillers and additives that change processing or performance parameters.
- Three types of composites are:
- Particle-reinforced composites
- Fiber-reinforced composites
- Structural composites

Particle Reinforced Composites:

- Particles used for reinforcing include ceramics and glasses such as small mineral particles, metal particles such as aluminum, and amorphous materials, including polymers and carbon black. Particles are used to increase the modulus of the matrix, to decrease the permeability of the matrix, to decrease the ductility of the matrix. Particles are also used to produce inexpensive composites. Reinforcers and matrices can be common, inexpensive materials and are easily processed. An example of particle reinforced composites is an automobile tire which has carbon black particles in a matrix of polyisobutylene elastomeric polymer. Another example is spheroidized steel where cementite is transformed into a spherical shape which improves the machinability of the material. Another example for particle-reinforced composite is concrete where the aggregates (sand and gravel) are the particles and cement is the matrix. Particle reinforced composites support higher tensile, compressive and shear stresses.

Particle Reinforced Composites

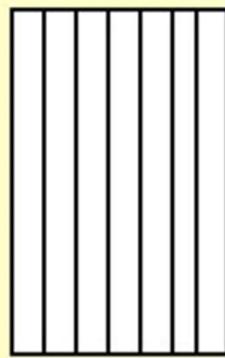


Fiber-reinforced Composites:

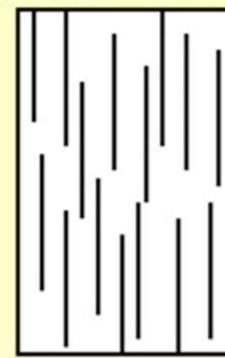
- Reinforcing fibers can be made of metals, ceramics, glasses, or polymers that have been turned into graphite and known as carbon fibers. Fibers increase the modulus of the matrix material. The strong covalent bonds along the fiber's length gives them a very high modulus in this direction because to break or extend the fiber the bonds must also be broken or moved. Fibers are difficult to process into composites which makes fiber-reinforced composites relatively expensive.

- Fiber-reinforced composites are used in some of the most advanced, and therefore most expensive, sports equipment, such as a time-trial racing bicycle frame which consists of carbon fibers in a thermoset polymer matrix. Body parts of race cars and some automobiles are composites made of glass fibers (or fiberglass) in a thermoset matrix.
- The arrangement or orientation of the fibers relative to one another, the fiber concentration, and the distribution all have a significant influence on the strength and other properties of fiber-reinforced composites. Applications involving totally multidirectional applied stresses normally use discontinuous fibers, which are randomly oriented in the matrix material. Consideration of orientation and fiber length for a particular composites depends on the level and nature of the applied stress as well as fabrication cost. Production rates for short-fiber composites (both aligned and randomly oriented) are rapid, and intricate shapes can be formed which are not possible with continuous fiber reinforcement.

Fiber Orientations in Fiber Reinforced Composites



Continuous
and aligned
fibers



Discontinuous
and aligned
fibers



Discontinuous
and randomly
oriented fibers

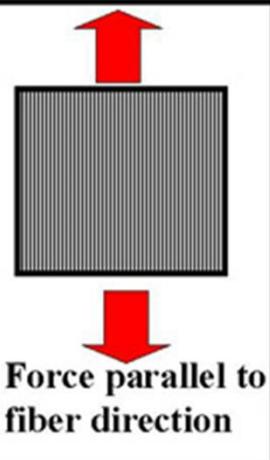
Modulus of Fiber-Reinforced Composites:

- Fibers have a very high modulus along their axis, but have a low modulus perpendicular to their axis. If the fibers are all parallel, the modulus of a fiber reinforced composite depends upon which direction you're measuring. The modulus of the entire composite, matrix plus reinforcer, is governed by the rule of mixtures when measuring along the length of the fiber:

- $E_c = E_f V_f + E_m V_m$
- E_c is the modulus of the entire composite along the length of the fiber.
- E_f is the modulus of the fiber along the length of the fiber.
- V_f is the volume percent occupied by the fibers.
- E_m is the modulus of the matrix (usually not dependent upon direction)
- V_m is the volume percent occupied by the matrix (equal to $(1-V_f)$).

LONGITUDINAL LOADING

ISOSTRAIN CONDITION: Deformation of matrix and fibers is the same.



$$S_c = S_m * V_m + S_f * V_f$$

$$E_c = E_m * V_m + E_f * V_f$$

S = Tensile Strength

E = Modulus of Elasticity

V = Volume Fraction

m = Matrix

f = Fiber

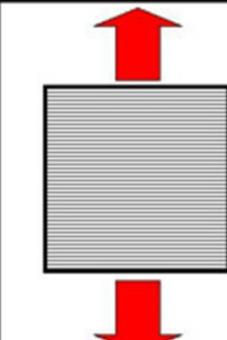
c = Composite

Tensile strength and elastic modulus when fibers are parallel to the direction of stress.

tensile strength and elastic modulus when fibers are perpendicular to the direction of stress.

TRANSVERSE LOADING

ISOSTRESS CONDITION: Matrix and fibers are under the same stress. ($S_c = S_m = S_f$)



$$E_c = \frac{E_m E_f}{V_m E_f + V_f E_m}$$

S = Tensile Strength

E = Modulus of Elasticity

V = Volume Fraction

m = Matrix

f = Fiber

c = Composite

Polymer	Trade Names	Major Application Characteristics	Typical Applications
Acrylics (Polymethyl methacrylate)	Lucite, Plexiglas	Outstanding light transmission and resistance to weathering	Lenses, transparent aircraft enclosures, drafting equipment, outdoor signs
Fluorocarbons (PTFE or TFE)	Teflon, TFE, Halon TFE	Chemically inert in almost all environments; excellent electrical properties; low coefficient of friction; may be used to 500 F; relatively weak	Anticorrosive seals, chemical pipes and valves, bearings, antiadhesive coatings, high temperature electronic parts
Nylons	Zytel, Plaskon	Good mechanical strength, abrasion resistance, and toughness; low coefficient of friction; absorbs water and some other Liquid	Bearings, gears, cams, bushings, handles, and jacketing for wires and cables
Polycarbonates	Merlon, Lexan	Dimensionally stable; low water absorbtion; transparent; very good impact resistance and ductility; chemical resistance not outstanding	Safety helmets; lenses, light globes, base for photographic film
Polyethylene	Alathon, Petrothene, Hi-fax	Chemically resistant, and electrically insulating; tough and relatively low coefficient of friction; low strength and poor resistance to weathering	Flexible bottles, toys, tumblers, battery parts, ice trays, film wrapping materials
Polypropylene	Pro-fax, Tenite, Moplen	Resistant to heat distortion; excellent electrical properties and fatigue strength; chemically inert; relatively inexpensive; poor resistance to UV light	Sterilizable bottles, packaging film, TV cabinets, luggage
Polystyrene	Dtyron, Lustrex, Rexolite	Excellent electrical properties and optical clarity; good thermal and dimensional stability; relatively inexpensive	Wall tile, battery cases, toys, indoor lighting panels, appliance housings
Vinyls	PVC, Pliovic, Saran, Tygon	Good low cost, general purpose materials; ordinarily rigid, but may be made flexible with plasticizers; often copolymerized; susceptible to heat distortion	Floor coverings, pipe, electrical wire insulation, garden hose
Polyester (PET)	Mylar, Dacron, Celanar	One of the toughest of plastic films; excellent fatigue and tear strength, and resistance to humidity, acids, greases, oils, and solvents	Magnetic recording tapes, clothing, auomotive tire cords