Institute Core Course for BTech Program

IC250: Materials Chemistry II

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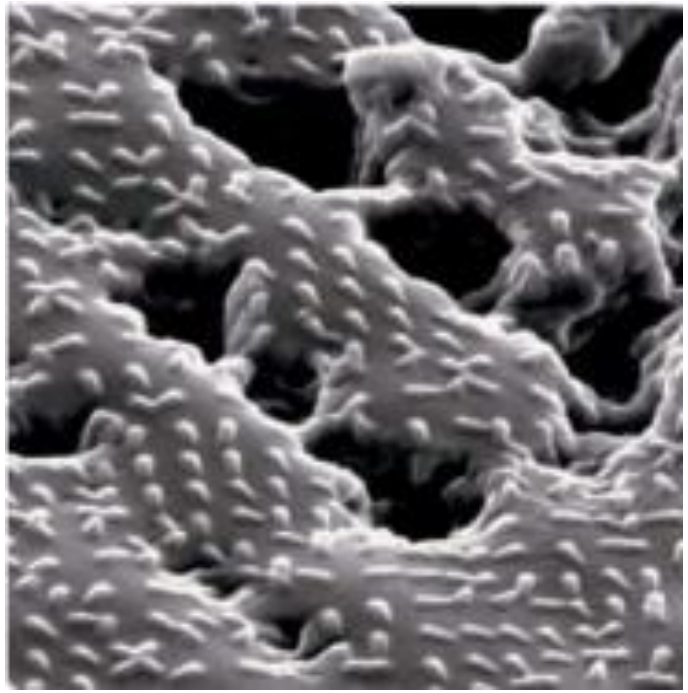
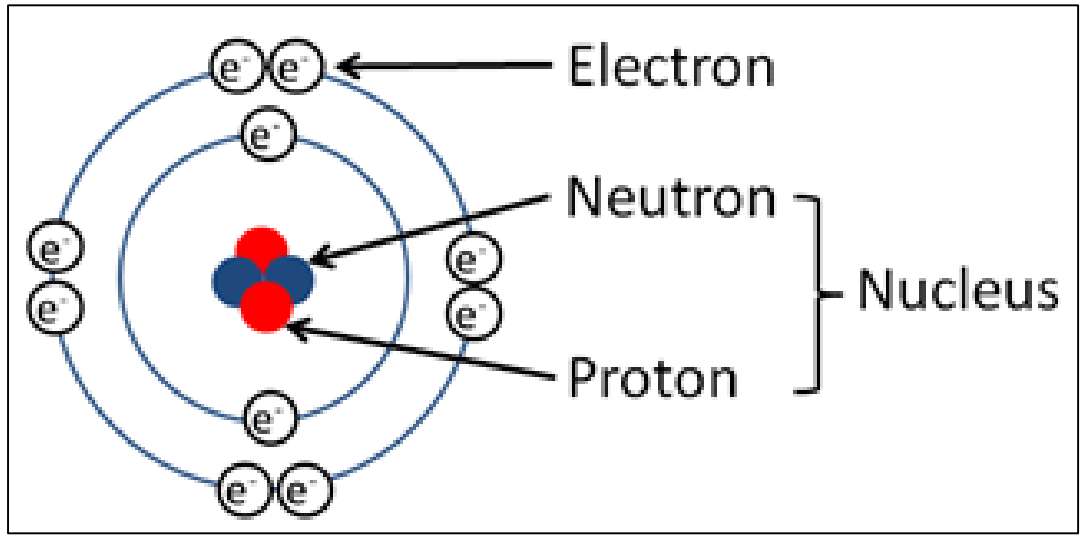
Atomic Structures, Interatomic Bonding and Structure of Crystalline Solids

Introduction



Atomic Structure

- Every atom consists of a small nucleus composed of protons and neutrons, which is encircled by moving electrons in their orbitals, specific energy levels.
- The top most orbital electrons, valence electrons, **affect most material properties that are of interest to engineers**, e.g.: chemical properties, nature of bonding, size of atom, optical/magnetic/electrical properties etc.



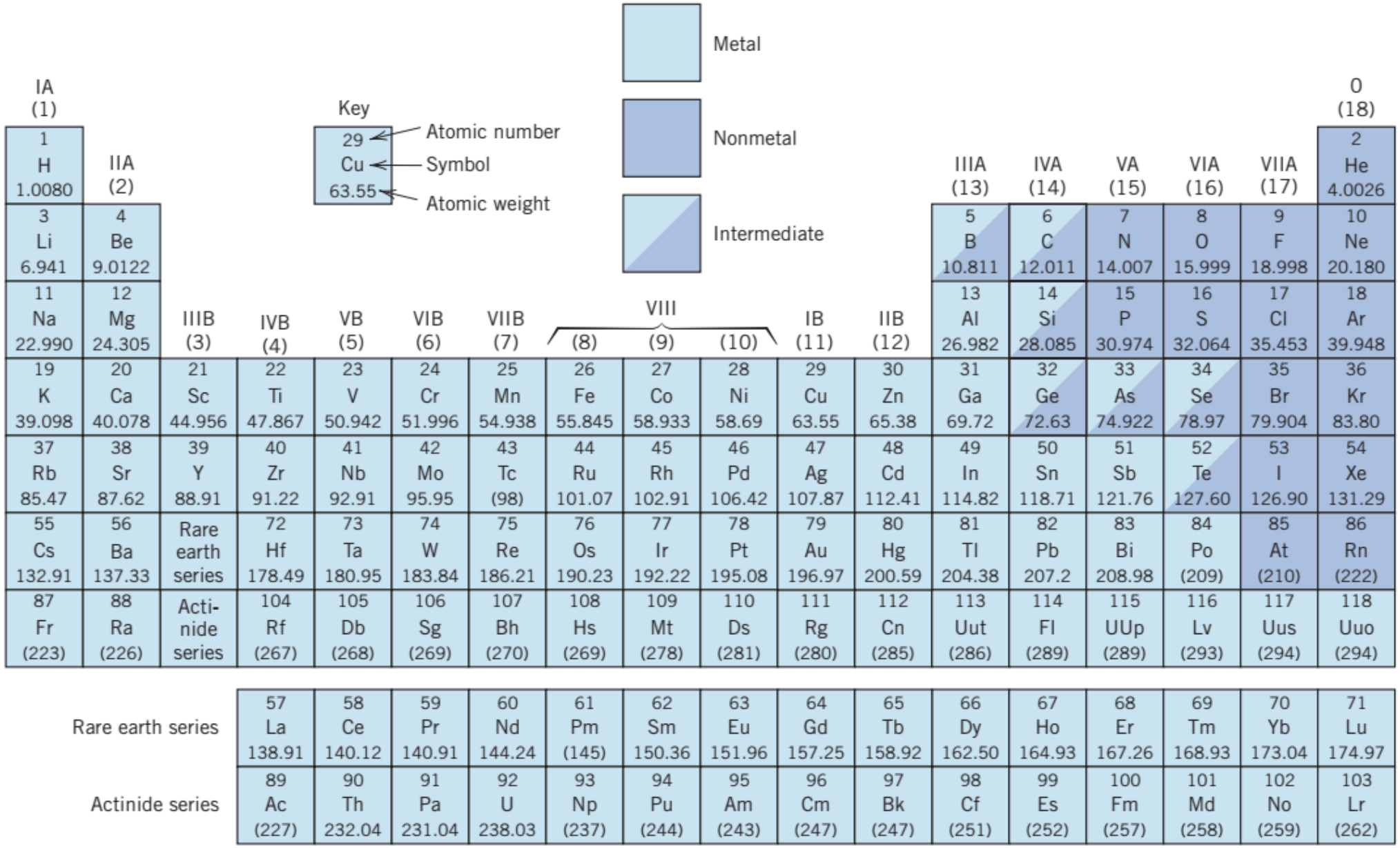
Atomic Structure

- Electrons and protons are negative and positive charges of the same magnitude being 1.60×10^{-19} coulomb. Neutrons are electrically neutral.
- Protons and neutrons have approximately the mass, 1.67×10^{-27} kg, which is significantly larger than that of an electron, 9.11×10^{-31} kg.
- **Atomic number (Z)** is the number of protons per atoms.
- **Atomic mass (A)** is the sum of the masses of protons and neutrons within the nucleus.
- Atomic mass is measured in atomic mass unit (amu), where 1amu = (1/12) the mass of most common isotope of carbon atom, measured in grams.

Atomic Structure

- $A \cong Z+N$, where N is number of neutrons.
- **Isotopes**: Atoms with same atomic number but different atomic masses.
- A **mole** is the amount of matter that has a mass in grams equal to the atomic mass in amu of the atoms. Thus a mole of carbon has a mass of 12 grams.
- The number of atoms or molecules in a mole of substance is called the Avogadro's number = 6.023×10^{23}.
- Most solid materials will have atomic density in the order of 6×10^{22}, that's about 39 million atoms per centimeter.

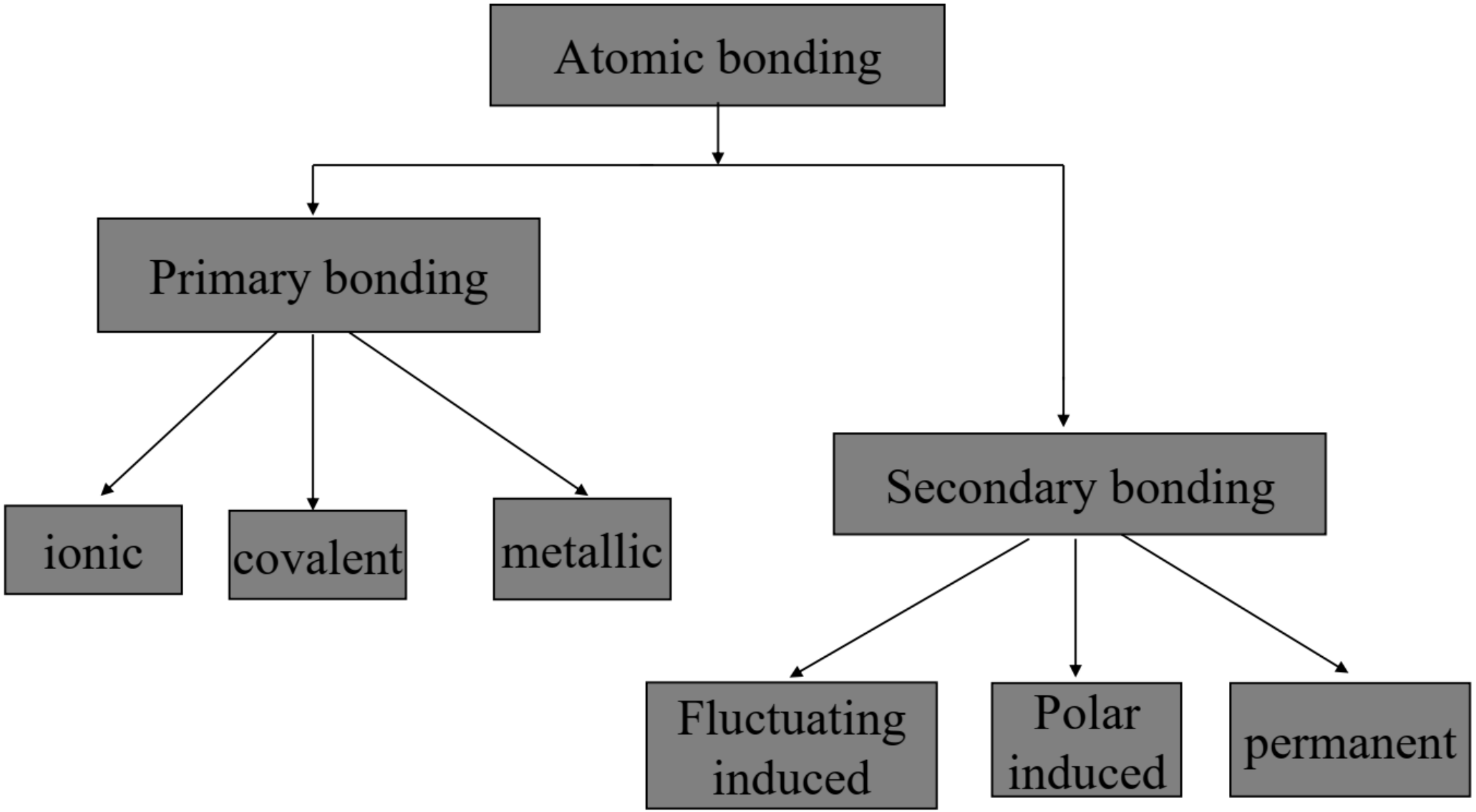
The Periodic Table



IA (1)	IIA (2)	IIIB (3)	IVB (4)	VB (5)	VIB (6)	VIIB (7)	VIII (8)	VIII (9)	VIII (10)	IB (11)	IIB (12)	IIIA (13)	IVA (14)	VA (15)	VIA (16)	VIIA (17)	0 (18)
1 H 1.0080																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.085	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.922	34 Se 78.97	35 Br 79.904	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	Rare earth series	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	Acti-nide series	104 Rf (267)	105 Db (268)	106 Sg (269)	107 Bh (270)	108 Hs (269)	109 Mt (278)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Uut (286)	114 Fl (289)	115 UUp (289)	116 Lv (293)	117 Uus (294)	118 Uuo (294)

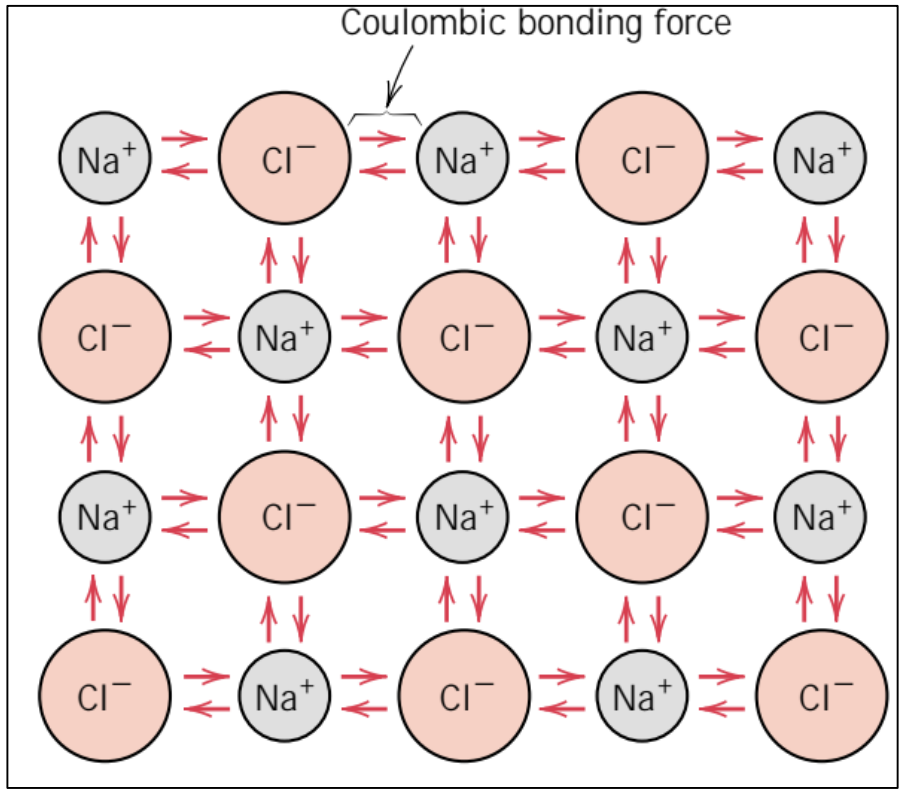
Rare earth series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinide series	89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

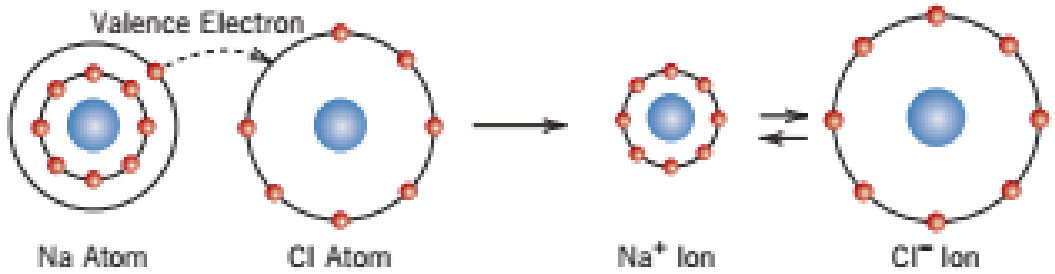
Atomic Bonding in Solids



Ionic Bonding

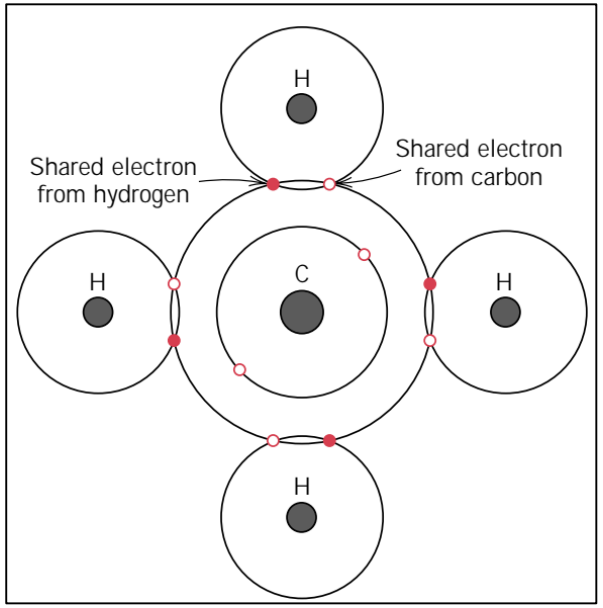
- This primary bond exists between two atoms when transfer of electron(s) results in one of the atoms to become negative (has an extra electron) and another positive (has lost an electron).
- This bond is a direct consequence of strong coulombic attraction between charged atoms.
- **Ionic bonds are non-directional** in nature.





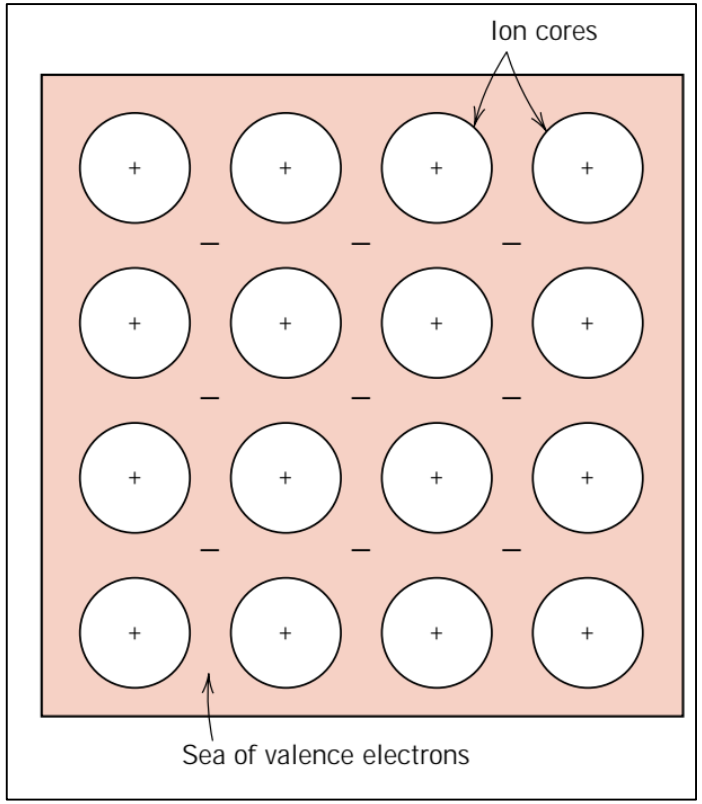
Covalent Bonding

- This bond comes into existence if valence electrons are shared between a pair of atoms, thus acquire stability by saturating the valence configuration.
- Covalent bonds are stereospecific, *i.e.* each bond is between a specific pair of atoms, which share a pair of electrons (of opposite magnetic spins).
- Typically, covalent bonds are very strong, and **directional** in nature.



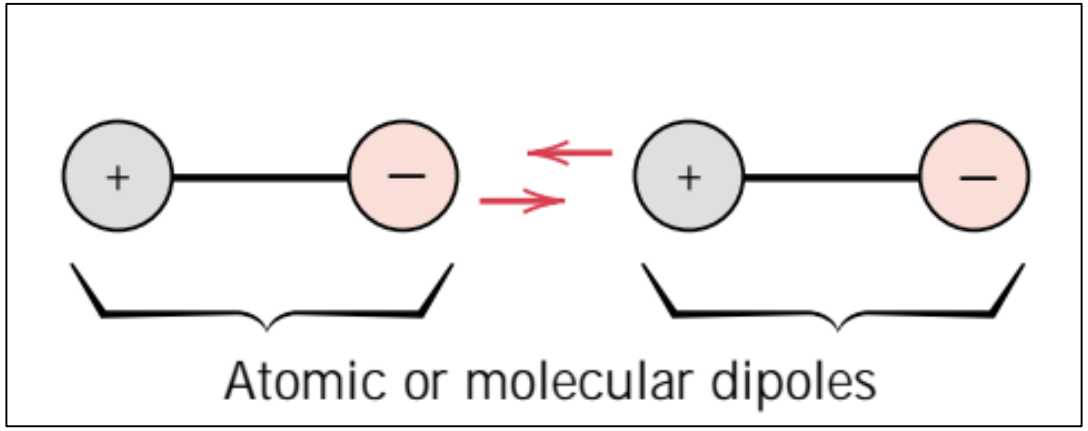
Metallic Bonding

- This bond comes into existence if valence electrons are shared between number of atoms, *i.e.* arranged positive nucleuses are surrounded by electron pool.
- Shared electrons are not specific to a pair of atoms, in contrast to covalent bond, *i.e.* electrons are delocalized.
- As shared electrons are delocalized, metallic bonds are **non-directional**.
- Very characteristic properties of metals like high thermal and electrical conductivities are result of presence of delocalized electron pool.



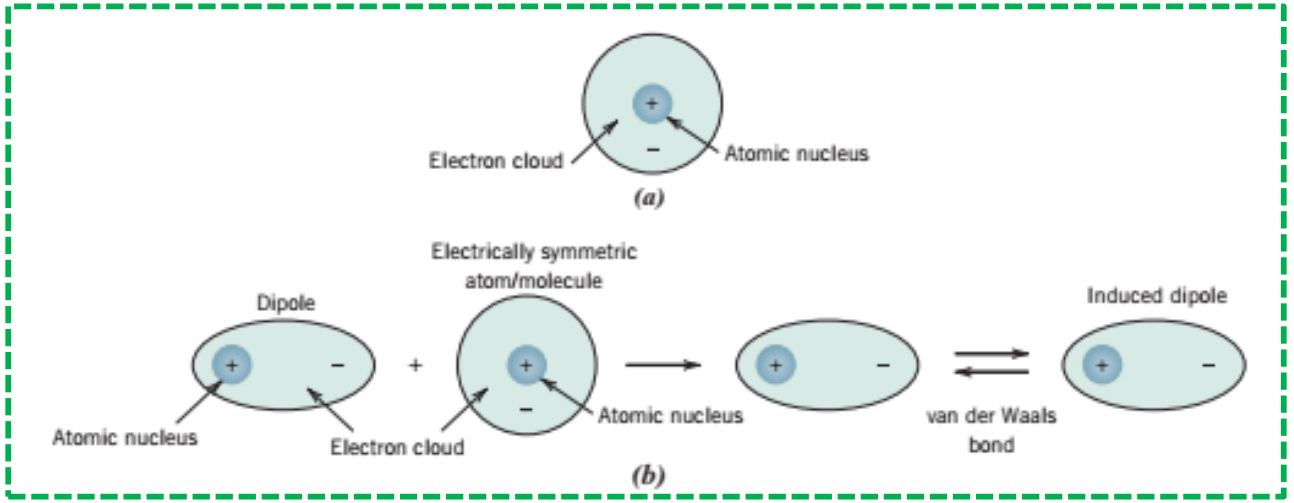
Secondary Bonding

- These bonds involves atomic or molecular dipoles.
- Bonds can exists between induced and permanent dipoles (polar molecules).
- Bond comes into existence because of Columbic attraction between positive end of one dipole and negative end of another dipole.
- Bond energies range between about 4 and 30 kJ/mol.



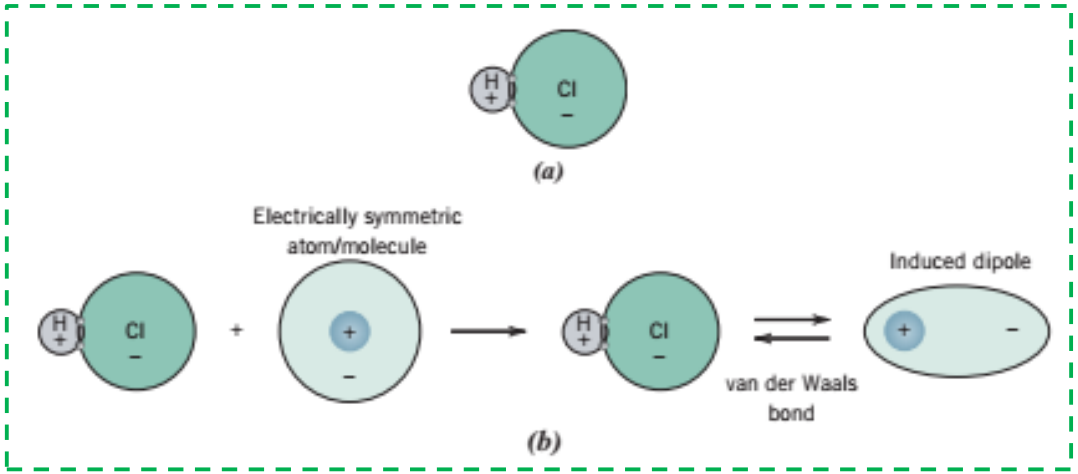
Fluctuating Induced Dipole Bonds

- A dipole may be created or induced in an atom or molecule that is normally electrically symmetric; that is, the overall spatial distribution of the electrons is symmetric with respect to the positively charged nucleus.
- All atoms are experiencing constant vibrational motion that can cause instantaneous and short-lived distortions of this electrical symmetry for some of the atoms or molecules, and the creation of small electric dipoles.



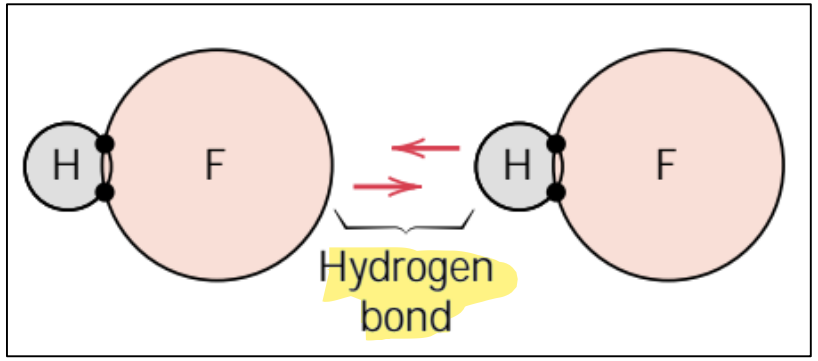
Polar-Molecule Dipole Bonds

- Permanent dipole moments exist in some molecules by virtue of an asymmetrical arrangement of positively and negatively charged regions; such molecules are termed polar molecules.
- Polar molecules can also induce dipoles in adjacent nonpolar molecules, and a bond will form as a result of attractive forces between the two molecules.
- Furthermore, the magnitude of this bond will be greater than for fluctuating induced dipoles.



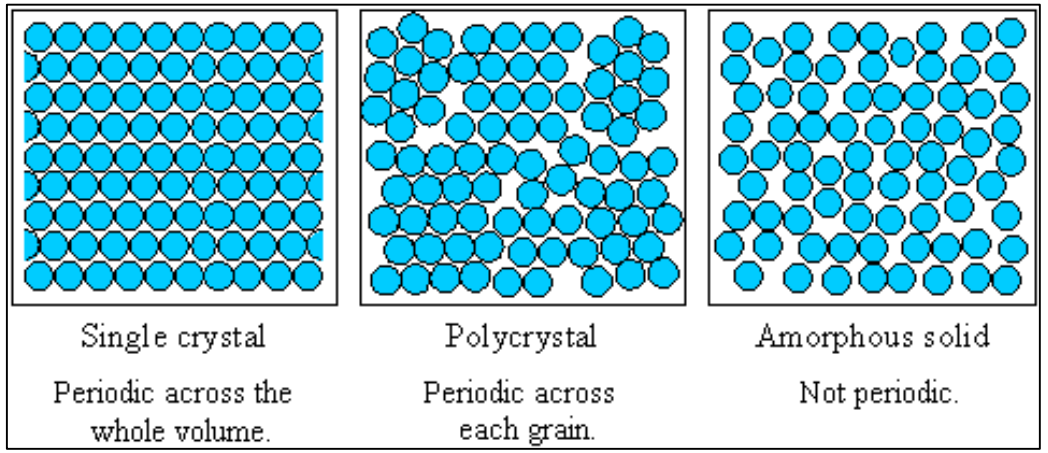
Permanent Dipole Bonds

- It occurs between molecules in which hydrogen is covalently bonded to fluorine (as in HF), oxygen (as in H_2O), and nitrogen (as in NH_3).
- For each H–F, H–O, or H–N bond, the single hydrogen electron is shared with the other atom. Thus, the hydrogen end of the bond is essentially a positively charged bare proton that is unscreened by any electrons.
- This highly positively charged end of the molecule is capable of a strong attractive force with the negative end of an adjacent molecule.



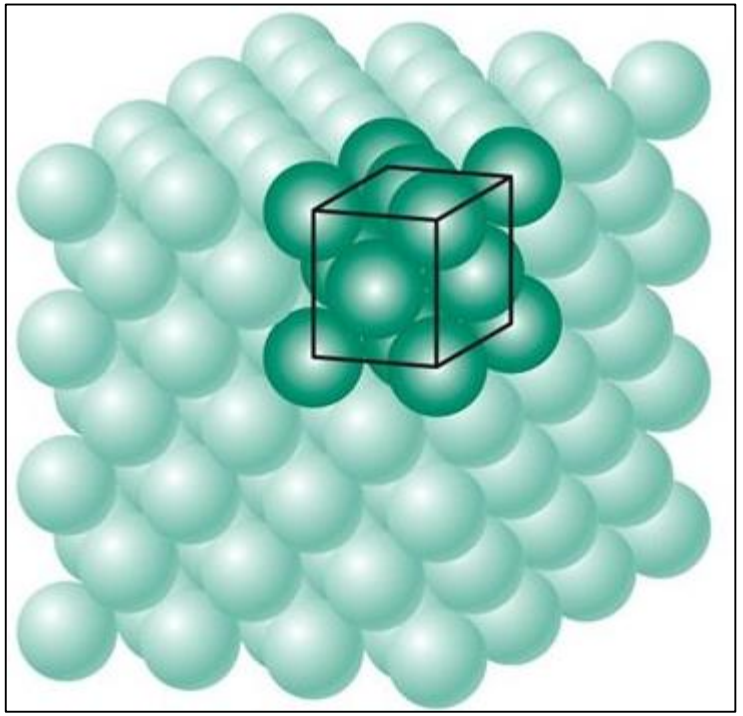
Crystal Structures

- All solid materials are made of atoms/molecules, which are arranged in specific order in some materials, called crystalline solids.
- Else, non-crystalline or amorphous solids.

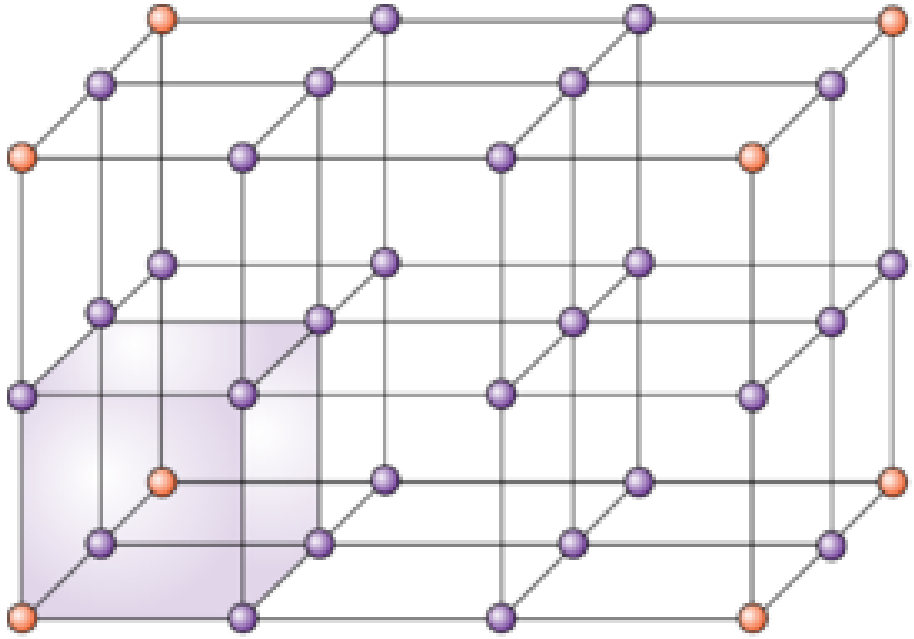


- Groups of atoms/molecules specifically arranged – **crystal**.
- **Unit cell** is smallest repeatable entity that can be used to completely represent a crystal structure. It is the building block of crystal structure.
- **Lattice** is used to represent a three-dimensional periodic array of points coinciding with atom positions.

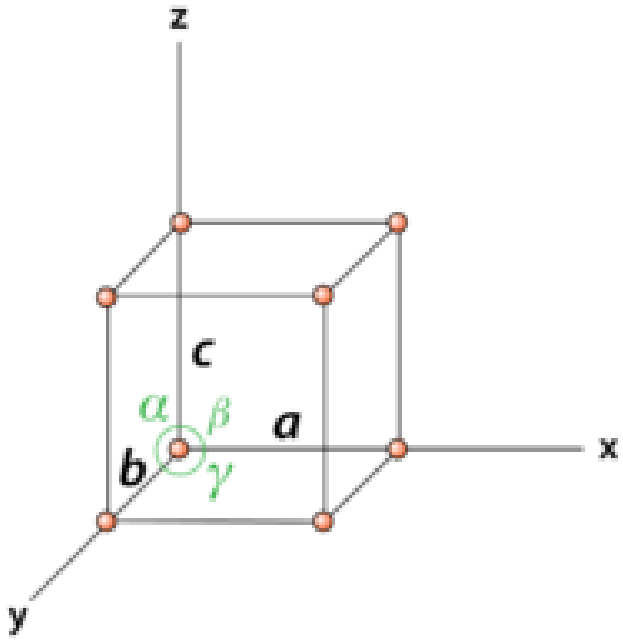
Crystal Structures



Atomic hard sphere model



Crystal Lattice



Unit Cell

Unit Cells

It is characterized by:

- Type of atom and their radii, R
- Cell dimensions, a and c (for hexagonal structures)
- Number of atoms per unit cell, n
- Coordination number (CN)– closest neighbors to an atom
- Atomic packing factor, APF
- **Most common unit cells**:

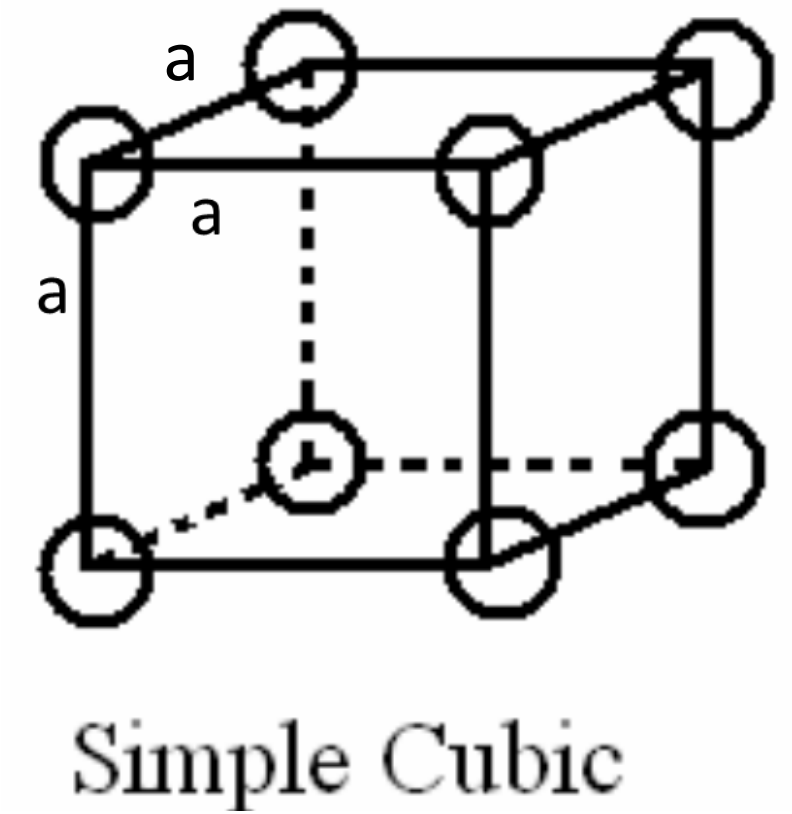
a) Simple Cubic (SC)

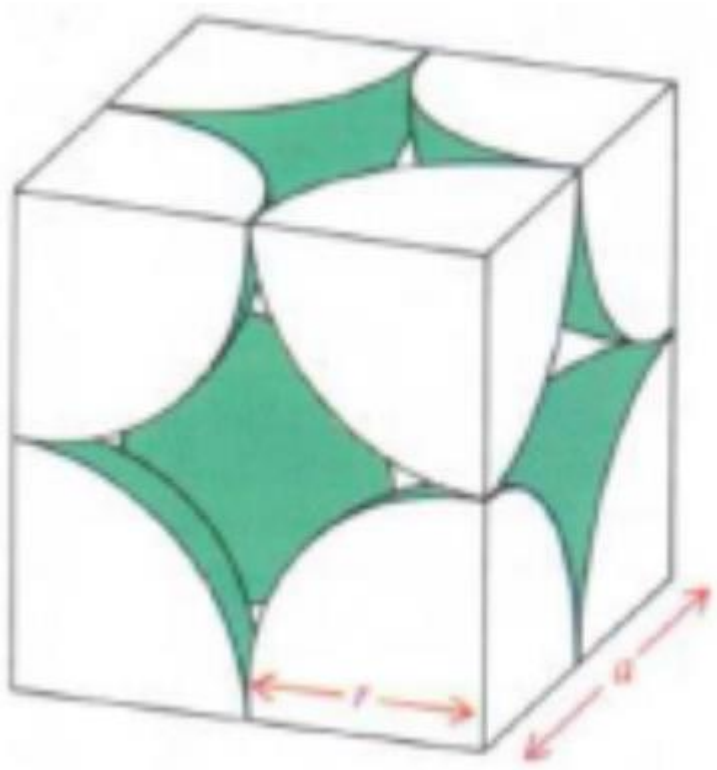
b) Body-centered cubic (BCC)

c) Face-centered Cubic (FCC)

d) Hexagonal close-packed (HCP)

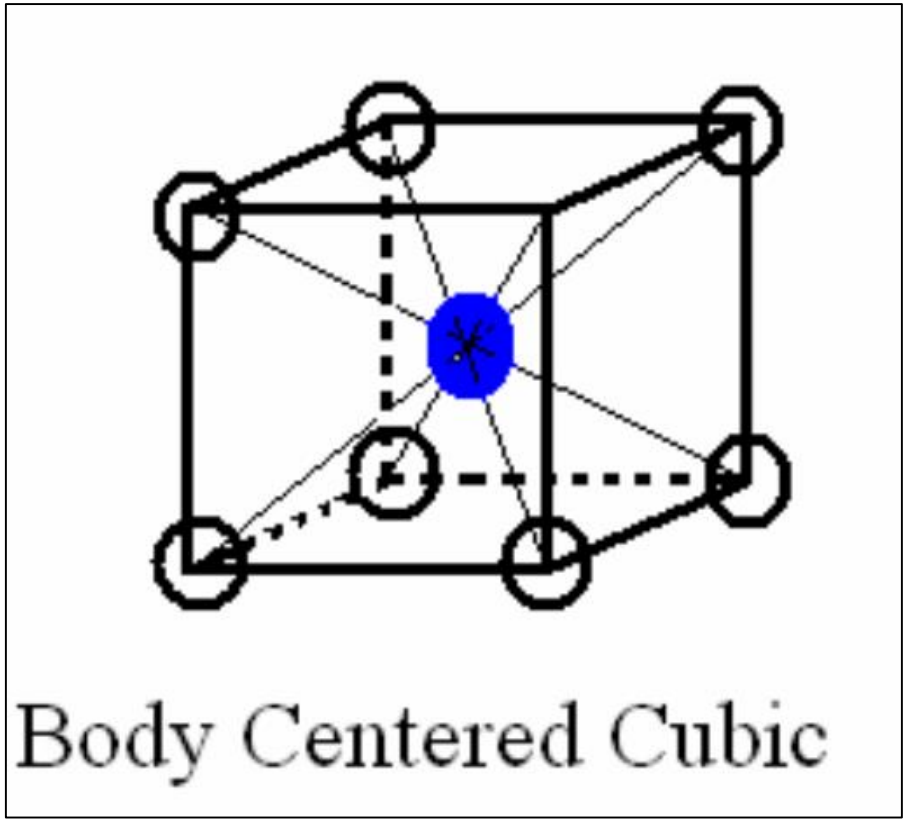
Simple Cubic (SC) Unit Cell

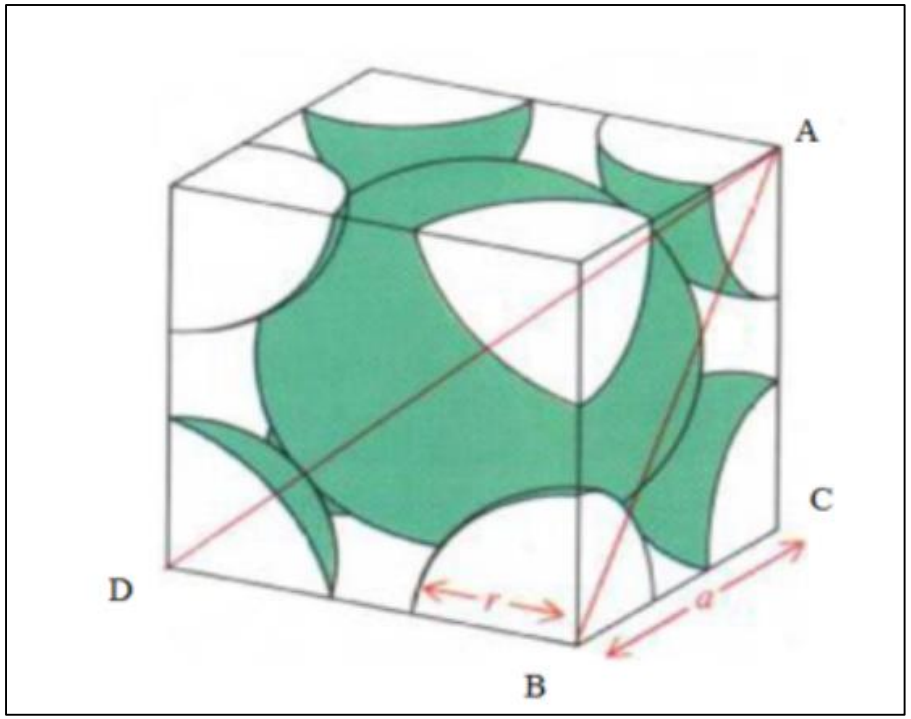




% space occupied= 52

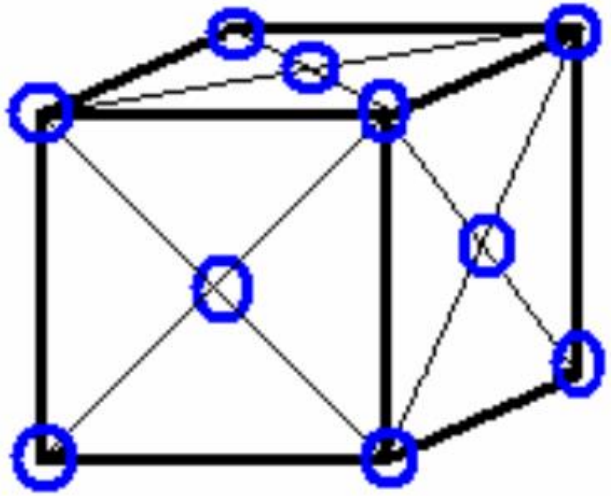
Body Centered Cubic (BCC) Unit Cell



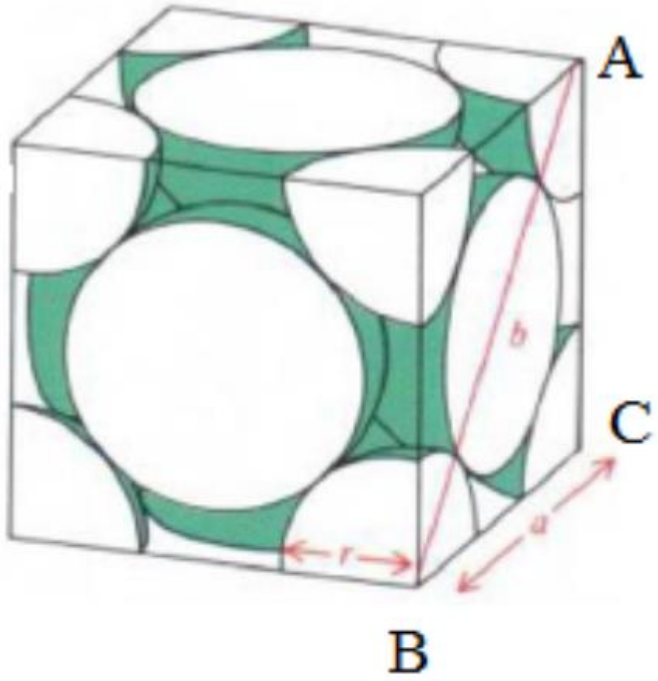


% space occupied = 68

Face Centered Cubic (BCC) Unit Cell

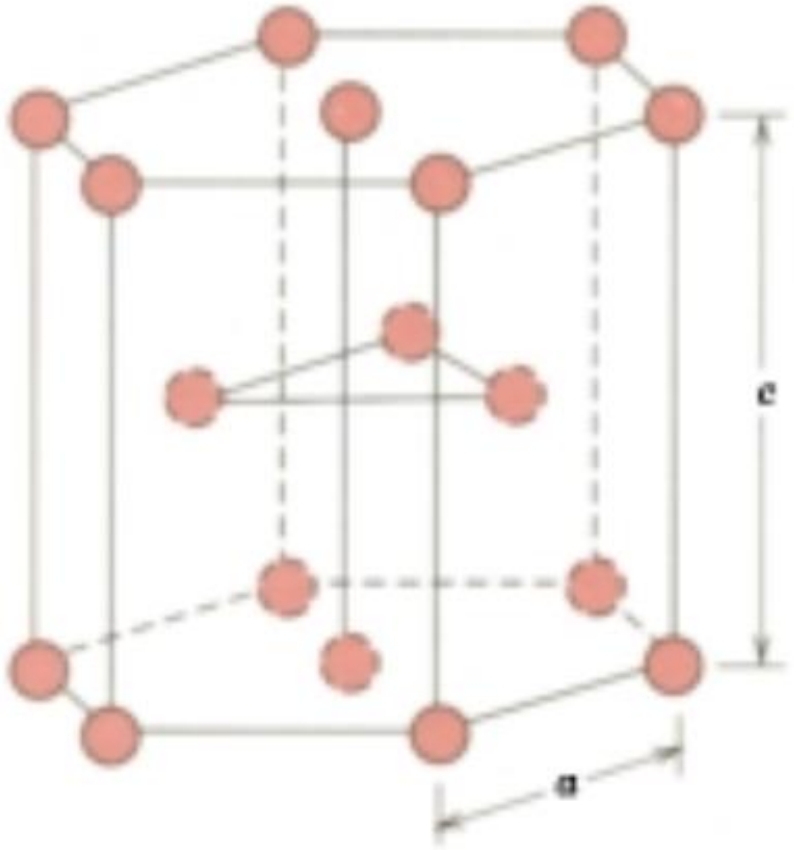


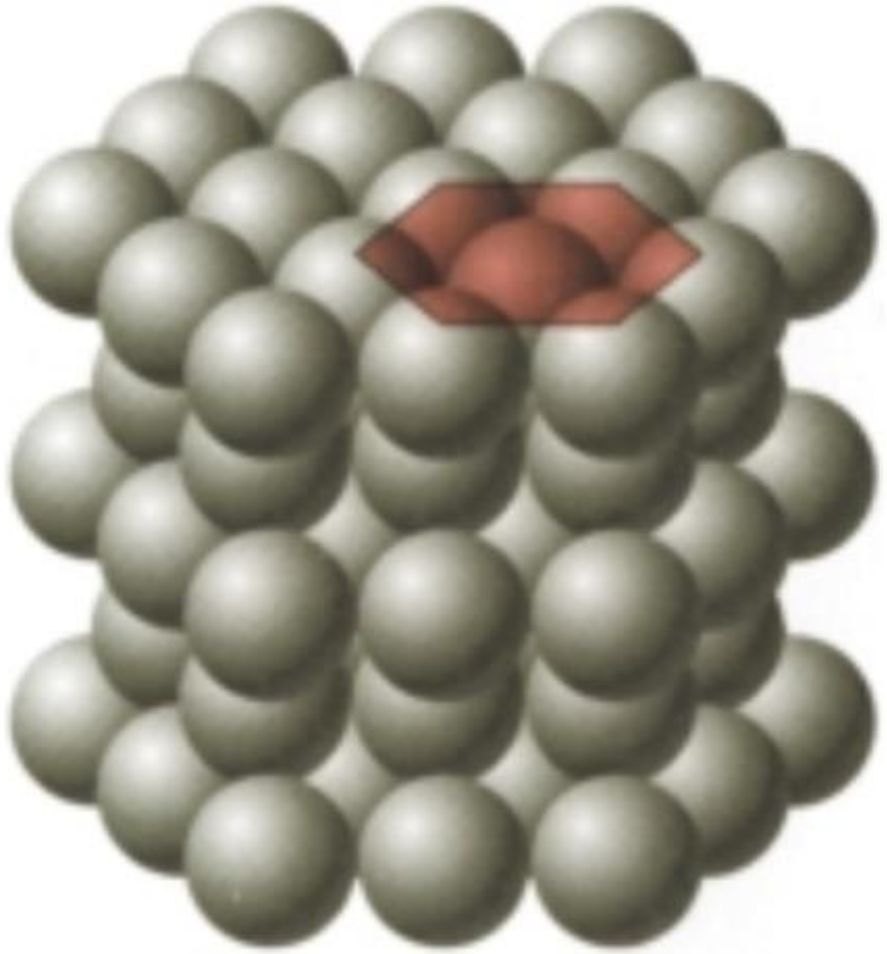
Face Centered Cubic



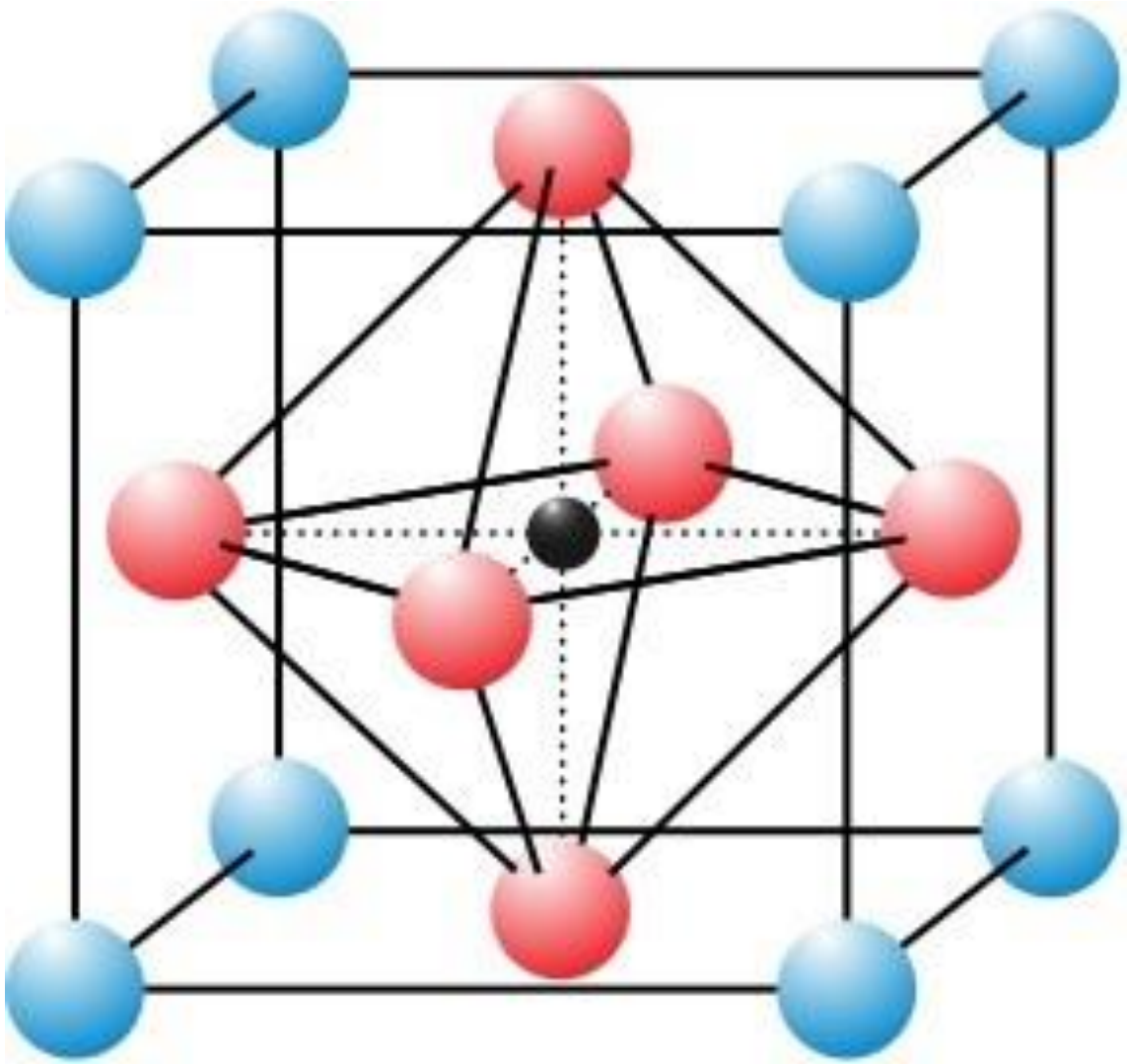
% space occupied = 74

Hexagonal Close Packed (HCP) Unit Cell





Perovskite Structure



ABX_3

- Physical properties of interest to materials science among perovskites include superconductivity, magnetoresistance, ionic conductivity, and a multitude of dielectric properties, which are of great importance in microelectronics and telecommunication.

Summary of the Crystal Systems

Structure Name	Structure Type	Anion Packing	Coordination Numbers		Examples
			Cation	Anion	
Rock salt (sodium chloride)	AX	FCC	6	6	NaCl, MgO, FeO
Cesium chloride	AX	Simple cubic	8	8	CsCl
Zinc blende (sphalerite)	AX	FCC	4	4	ZnS, SiC
Fluorite	AX_2	Simple cubic	8	4	CaF_2, UO_2, ThO_2
Perovskite	ABX_3	FCC	12(A) 6(B)	6	$BaTiO_3$, $SrZrO_3$, $SrSnO_3$
Spinel	AB_2X_4	FCC	4(A) 6(B)	4	$MgAl_2O_4$, $FeAl_2O_4$

- Examples of metals with the bcc structure are **alpha iron, tungsten, chromium, and beta titanium.**

Cation-Anion Radius Ratios

Coordination Number	Cation–Anion Radius Ratio	Coordination Geometry
2	<0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0