Nanomaterials

2nd year Medical Physics

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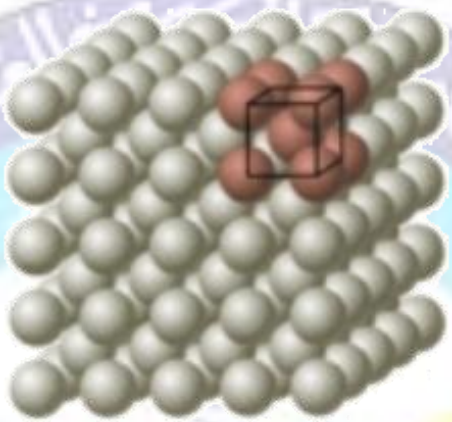
Lecture 2: Crystal Structure



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2.1 The Wave-Mechanical model

An electron is no longer treated as a particle moving in a discrete orbital; but rather, position is considered to be the probability of an electron's being at various locations around the nucleus. In other words, position is described by a probability distribution or electron cloud. Look at figure 2.1 below for elaboration.

Using wave mechanics, every electron in an atom is characterized by four quantum numbers:

- *n* = principal quantum number, n is like the Bohr shells (n = 1, 2, 3….).
- *l* = angular momentum quantum number, *l* governs orbital shape, l = 0, 1,….(n-1)
  (l = 0 is an s orbital - spherical, l = 1 is a p orbital – dumbbell shape, l = 2 is a d orbital – double dumbbell etc.)
- *m* = magnetic quantum number, m = 0, ±1,… ±*l*.
- s = spin quantum number, s = ±1/2. Each orbital can contain two electrons of opposite spin.

No two electrons can have the same four quantum numbers.

Each shell contains sub-shells. The higher the principal number the greater the number of sub-shells. Each sub-shell can contain a number of equivalent states, each state occupied by spin-up & spin-down electrons.

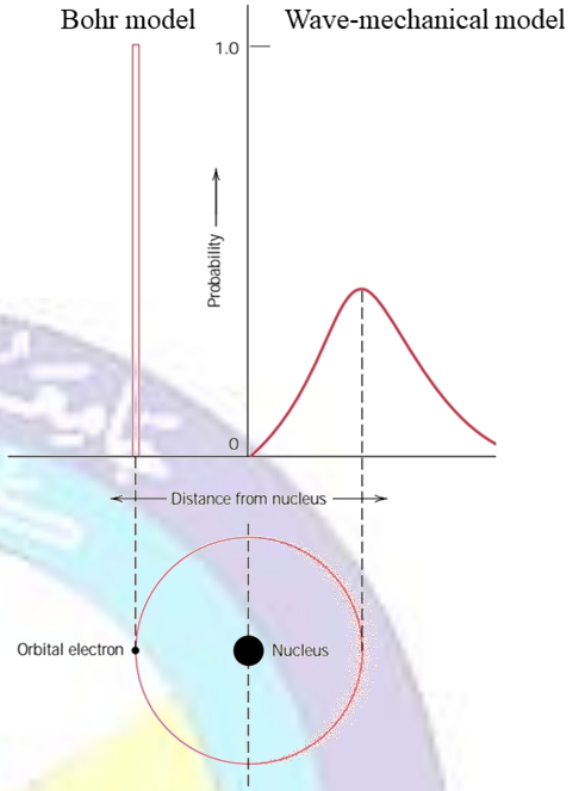


Figure 2.1 the probability of electron location according to Bohr and wave-mechanical models

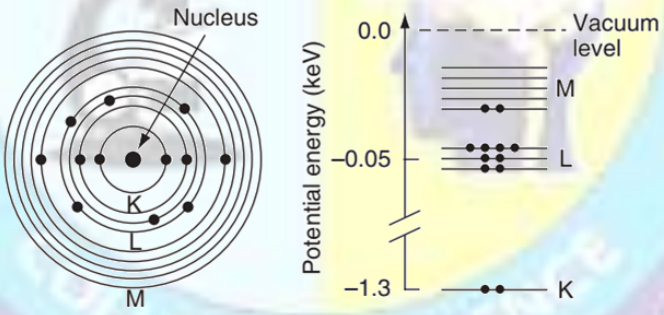


Figure 2.2 a schematic illustration of the atomic shells and subshells

Of course, not all possible states in an atom are filled with electrons. For most atoms, the electrons fill up the lowest possible energy states in the electron shells and subshells, two electrons (having opposite spins) per state.

When all the electrons occupy the lowest possible energies in accord with the foregoing restrictions, an atom is said to be in its **ground state**.

In the conventional notation the number of electrons in each subshell is indicated by a superscript after the shell–subshell designation. For example, the electron configurations for hydrogen, helium, and sodium are, respectively, $1s^1$, $1s^2$, and $1s^2 2s^2 2p^6 3s^1$.

The valence electrons are those that occupy the outermost filled shell. **These electrons are extremely important**; as will be seen, they participate in the bonding between atoms to form atomic and molecular aggregates.

Furthermore, many of the physical and chemical properties of solids are based on these valence electrons.

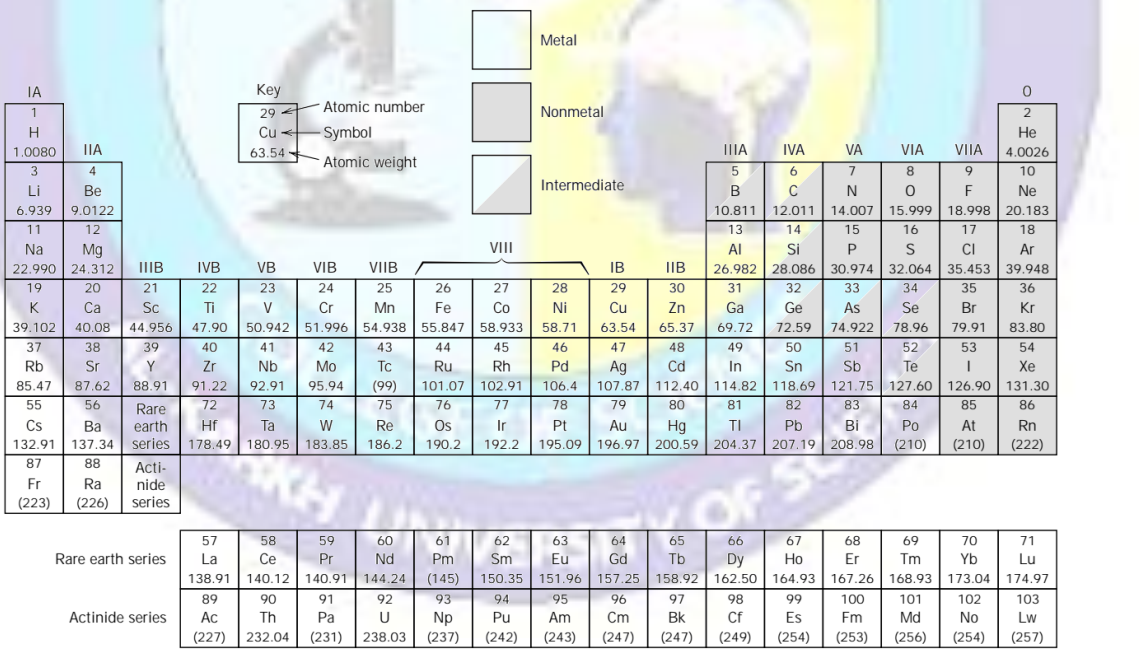
Some atoms have states within the outermost or valence electron shell are completely filled. These elements (Ne, Ar, Kr, and He) are the inert, or noble, gases, which are virtually unreactive chemically.

2.2 The Periodic Table

All the elements have been classified according to electron configuration in the periodic table. Here, the elements are situated, with increasing atomic number, in seven horizontal rows called periods.

The arrangement is such that all elements that are arrayed in a given column or group have similar valence electron structures, as well as chemical and physical properties. These properties change gradually and systematically, moving horizontally across each period.

The elements positioned in Group 0, the rightmost group, are the inert gases, which have filled electron shells and stable electron configurations.



IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 H 1.0080																	2 He 4.0026
3 Li 6.939	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 20.183
11 Na 22.990	12 Mg 24.312											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.91	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 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	Rare earth series	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	Acti-nide series															

Rare earth series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.35	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)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lw (257)

Figure 2.3 the periodic table of elements

Group VIIA and VIA elements are one and two electrons deficient, respectively, from having stable structures.

The alkali and the alkaline earth metals (Li, Na, K, Be, Mg, Ca, etc.) are labelled as Groups IA and IIA, having, respectively, one and two electrons in excess of stable structures.

The elements in the three long periods, Groups IIIB through IIB, are termed the transition metals, which have partially filled d electron states and in some cases one or two electrons in the next higher energy shell.

Groups IIIA, IVA, and VA (B, Si, Ge, As, etc.) display characteristics that are intermediate between the metals and non-metals by virtue of their valence electron structures.

2.3 Bonding between Atoms

An understanding of many of the physical properties of materials is predicated on a knowledge of the interatomic forces that bind the atoms together. Perhaps the principles of atomic bonding are best illustrated by considering the interaction between two isolated atoms as they are brought into close proximity from an infinite separation. At large distances, the interactions are negligible; but as the atoms approach, each exerts forces on the other. These forces are of two types, attractive and repulsive, and the magnitude of each is a function of the separation or interatomic distance.

The bonding energy for these two atoms corresponds to the energy at this minimum point; it represents the energy that would be required to separate these two atoms to an infinite separation.

For example, materials having large bonding energies typically also have high melting temperatures; at room temperature, solid substances are formed for large bonding energies, whereas for small energies the gaseous state is favoured; liquids prevail when the energies are of intermediate magnitude. In addition, the mechanical stiffness (or modulus of elasticity) of a material is dependent on the shape of its force-versus-interatomic separation curve. The main three types of strong bonding found in compounds are discussed briefly hereafter.

2.3.1 Ionic Bonds

Ionic bonding is the easiest to describe and visualize. It is always found in compounds that are composed of both metallic and non-metallic elements, elements that are situated at the horizontal extremities of the periodic table. Atoms of a metallic element easily give up their valence electrons to the non-metallic atoms. In the process all the atoms acquire stable or inert gas configurations and, in addition, an electrical charge; that is, they become ions. Sodium chloride (NaCl) is the classical ionic material.

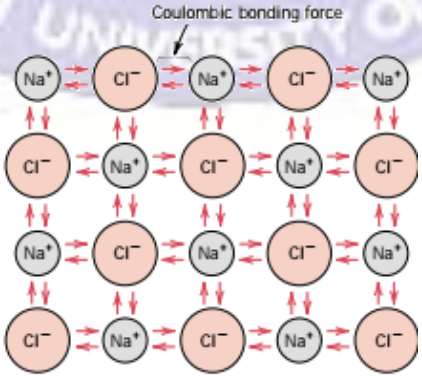


Figure 2.4 a schematic illustration of ionic bonds NaCl

2.3.2 Covalent Bonds

In covalent bonding stable electron configurations are assumed by the sharing of electrons between adjacent atoms. Two atoms that are covalently bonded will each contribute at least one electron to the bond, and the shared electrons may be considered to belong to both atoms. The carbon atom has four valence electrons, whereas each of the four hydrogen atoms has a single valence electron. An example of covalent bonding is illustrated the molecule of methane (CH4) in the figure 2.5 below.

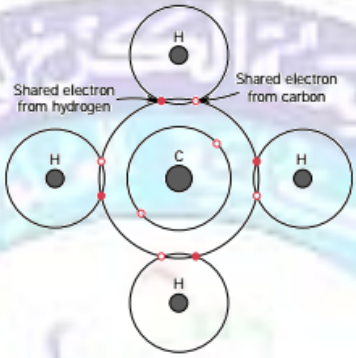


Figure 2.5 a schematic illustration of the covalent bonds in Methane CH_4

2.3.3 Metallic Bonds

Metallic bonding, the final primary bonding type, is found in metals and their alloys.

Metallic materials have one, two, or at most, three valence electrons. With this model, these valence electrons are not bound to any particular atom in the solid and are more or less free to drift throughout the entire metal.

They may be thought of as belonging to the metal as a whole, or forming a ‘‘sea of electrons’’ or an ‘‘electron cloud.’’

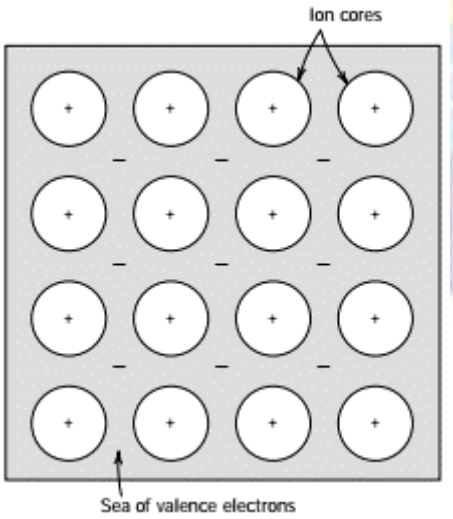


Figure 2.6 a schematic representation of metallic bonding

2.4 Crystalline Structure

Solid materials may be classified according to the regularity with which atoms or ions are arranged with respect to one another. A **crystalline material** is one in which the atoms are situated in a repeating or periodic array over large atomic distances; that is, long-range order exists, such that upon solidification, the atoms will position themselves in a repetitive three-dimensional pattern, in which each atom is bonded to its nearest-neighbour atoms. All metals, many ceramic materials, and certain polymers form crystalline structures under normal solidification conditions. For those that do not crystallize, this long-range atomic order is absent; such materials are known as being **non-crystalline** or **amorphous** materials.

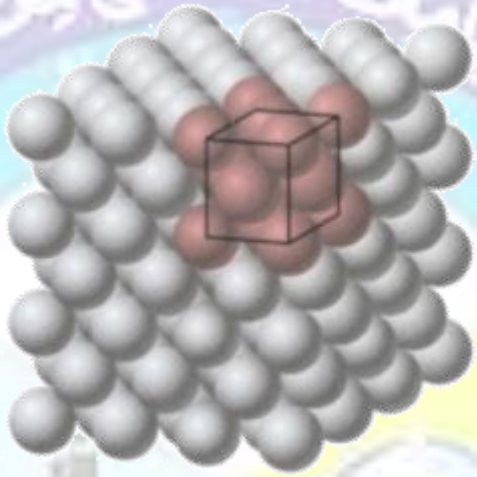


Figure 2.7 an aggregate of atoms in repetitive & cubic pattern

Some of the properties of crystalline solids depend on the crystal structure of the material, the manner in which atoms, ions, or molecules are spatially arranged.

There is an extremely large number of different crystal structures all having long range atomic order; these vary from relatively simple structures for metals, to exceedingly complex ones, as displayed by some of the ceramic and polymeric materials.

When describing crystalline structures, atoms (or ions) are thought of as being solid spheres having well-defined diameters. This is termed the atomic hard sphere model in which spheres representing nearest-neighbour atoms touch one another.

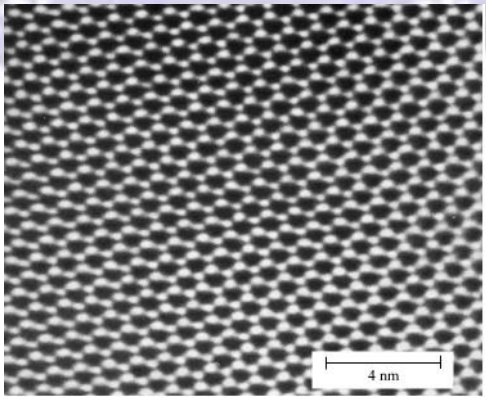


Figure 2.8 an illustration of an atomic lattice

Sometimes the term lattice is used in the context of crystal structures; in this sense ‘‘lattice’’ means a three-dimensional array of points coinciding with atom positions (or sphere centres).

2.5 Unit Cell

The atomic order in crystalline solids indicates that small groups of atoms form a repetitive pattern. Thus, in describing crystal structures, it is often convenient to subdivide the structure into small repeat entities called **unit cells**. A unit cell is chosen to represent the symmetry of the crystal structure, wherein all the atom positions in the crystal may be generated by translations of the unit cell integral distances along each of its edges. Thus, the unit cell is the basic structural unit or building block of the crystal structure and defines the crystal structure by virtue of its geometry and the atom positions within.

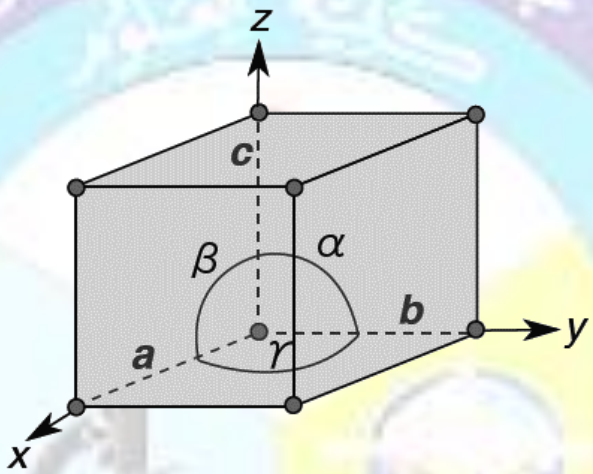


Figure 2.9 an illustration of a crystalline unit cell

2.6 Crystal Structure Types

Three relatively simple crystal structures are found for most of the common metals: face-centred cubic, body-centred cubic, and hexagonal close-packed.

2.6.1 Face-Centred Cubic Structure

The crystal structure found for many metals has a unit cell of cubic geometry, with atoms located at each of the corners and the centres of all the cube faces. That’s why it’s called the **face centred cubic** (FCC) crystal structure. Some of the familiar metals having this crystal structure are copper, aluminium, silver, and gold. Figure 2.10 shows a hard sphere model for the FCC unit cell. The aggregate of atoms in the figure represents a section of crystal consisting of many FCC unit cells. These spheres or ion cores touch one another across a face diagonal; the cube edge length (**a)** and the atomic radius (**R)** are related through

$$a = 2R\sqrt{2}$$

For the FCC crystal structure, each corner atom is shared among eight unit cells, whereas a face-centred atom belongs to only two. Therefore, one eighth of each of the eight corner atoms and one half of each of the six face atoms, or a total of four whole atoms, may be assigned to a given unit cell.

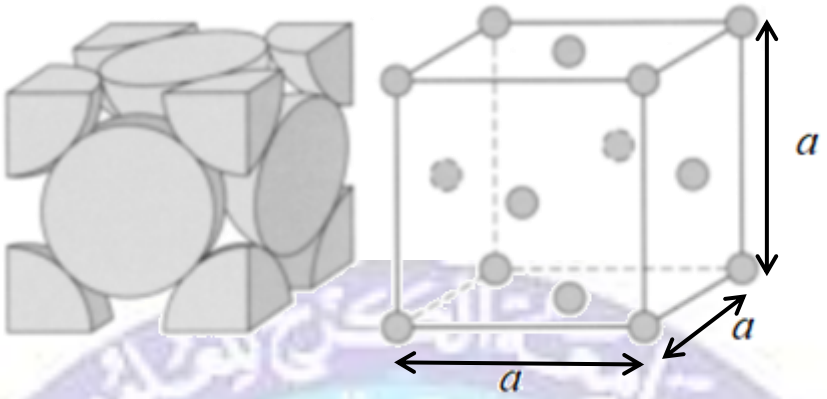


Figure 2.10 a Face-Centred Cubic (FCC) unit cell

Two other important characteristics of a crystal structure are the coordination number and the atomic packing factor (APF). For metals, each atom has the same number of nearest-neighbour or touching atoms, which is the coordination number.

For face-centred cubic, the coordination number is 12. The front face atom has four corner nearest-neighbour atoms surrounding it, four face atoms that are in contact from behind, and four other equivalent face atoms residing in the next unit cell to the front, which is not shown.

The APF is the fraction of solid sphere volume in a unit cell, assuming the atomic hard sphere model, or:

$$APF = \frac{volume\ of\ atoms\ in\ unit\ cell}{total\ unit\ cell\ volume}$$

For the FCC structure, the atomic packing factor is 0.74, which is the maximum packing possible for spheres all having the same diameter. Metals typically have relatively large atomic packing factors to maximise the shielding provided by the free electron cloud.