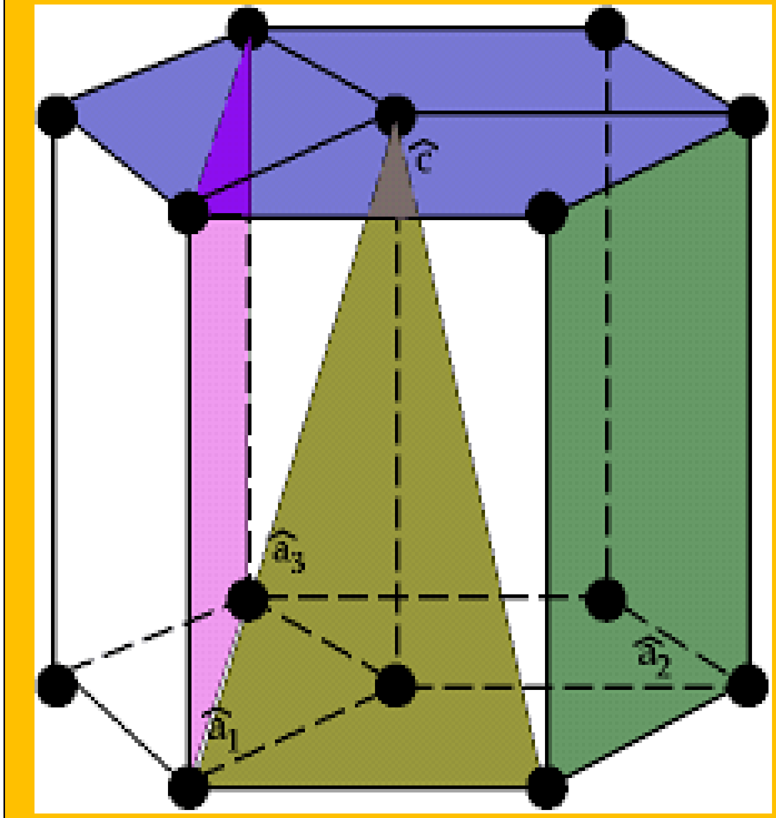
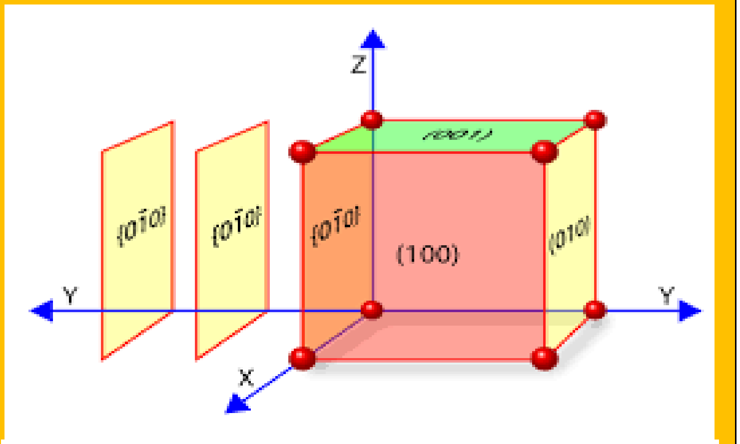
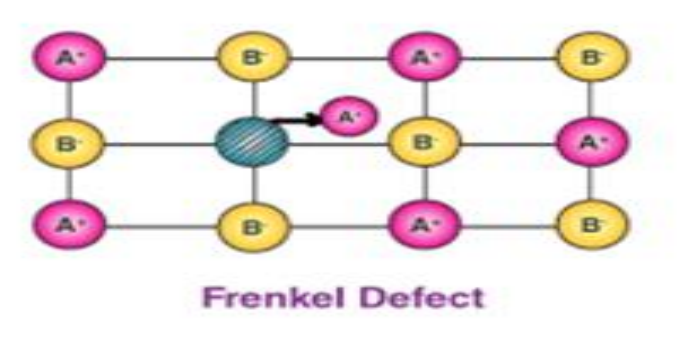
MSCCH-601
M.Sc III Semester
SOLID STATE AND MATERIAL CHEMISTRY







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Block I Solid-State

Block II Soft Materials

UNIT 1 RECAPITULATION OF FUNDAMENTAL PRINCIPLES OF SOLID STATES:

CONTENTS

1.1 OBJECTIVES

- Describe the basic and advance solid material characteristics'
- Knowledge of basic theories of solid-state structure
- Understanding of Crystal Symmetry
- Learning of crystal lattices and to understand the concept of a lattice plane
- Be aware of how knowledge of lattice planes and their Miller indices can help to understand other concepts in materials science.

1.2 INTRODUCTION

Solids have definite mass, volume, and shape because the constituent particles of matter are held together by strong intermolecular forces. Solids mainly have the following characteristics. Like.

- Short Intermolecular distance
- Strong Intermolecular Forces
- The constituent particles remain fixed at their positions and can only oscillate about their mean positions
- Have fixed boundaries
- Solids are incompressible and rigid
- High Density

Depending on the nature of the acting interatomic forces, all solids may be subdivided into:

(a) Ionic solids (NaCl)

(b) Covalent solids (Diamond)

(c) Metallic solids (Fe, Ni, etc.)

(d) Vander Waals solids (ice, solid He)

1.3 CRYSTAL LATTICE OR SPACE LATTICE AND UNIT CELL

According to Hauy (1784) a crystal is built up by a number of small crystals having the shape of the original crystal as a whole. This led to the concept of space lattice or crystal lattice.

“A space lattice is an array of points showing how particles (atoms, ions or molecules) are arranged at different sites in three dimensional spaces.”

The unit cell may also be defined as, “the smallest repeating unit in space lattice which, when repeated over again, results in a crystal of the given substance”.

A crystal is a three-dimensional design in which identical points form a 3-dimensional network of cells each representing the unit and through which whole crystal can be built up. The lattice points can be connected by a regular network of lines in various ways. Thus, the lattice is broken up into a number of unit cells. This is done by connecting the points by a regular network of lines as shown in Fig. 1.1 [1].

Therefore, space lattice of a crystal has been likened to a wall-paper on which a single pattern is continuously repeated. Each unit cell requires two vectors a and b for its description. A three-dimensional space lattice can be similarly divided into unit cells described by three vectors. The exact location of particles in a unit cell can be obtained by X-ray diffraction.

It should be understood that the choice of unit cell is by no means unique. There are various ways in which a cell can be drawn in a unique space lattice. However, it is usually convenient to choose a parallel pipe whose edges are parallel with the crystallographic axes (a, b and c) and with the 7 types of unit cells, defined by edge lengths (a,b,c) respectively along the x,y,z axis and angles αα, ββ, and γγ.

The smallest unit of a structure that can be indefinitely repeated to generate the whole structure. The simplest repeating unit in a crystal is called a unit cell (Fig. 1.1).

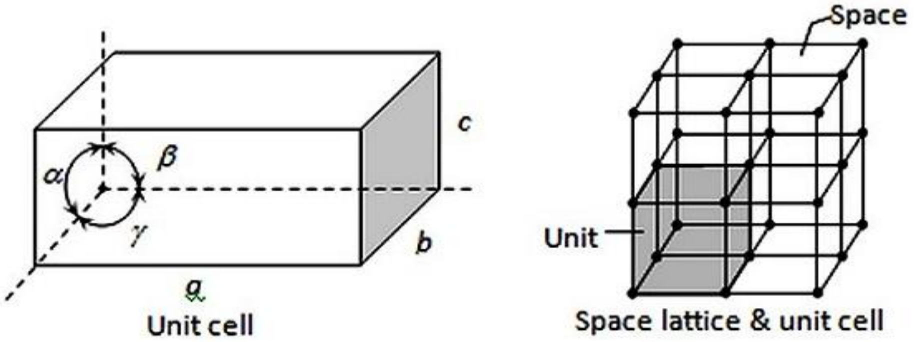


Fig. 1.1 Structure of Space Lattice and Unit Cell

There are following types of unit cells:

1.3.1 Primitive Unit Cells

When the constituent particles occupy only the corner positions, it is known as Primitive Unit Cells. A crystal can be classified according to its elements of symmetry; for example, it may belong to one of 230 space groups, 32-point groups, 14 Bravais lattices, and 7 crystal systems. A crystal can be represented diagrammatically by an orderly stacking of unit cells; the shape of the unit cell determines which of the seven crystal systems the crystal belongs to. Unit cells of the same shape may have points (each representing an atom or a group of atoms) at their centres or on their faces, in addition to those at their corners. These additional lattice points divide the 7 crystal systems into 14 Bravais lattices; the Bravais lattices are subdivided into 32 crystal classes, or point groups. Each point group corresponds to one of the possible combinations of rotations, reflections, inversions, and improper rotations; with the inclusion of translational elements, 230 space groups are produced (Fig. 1.2) [2].

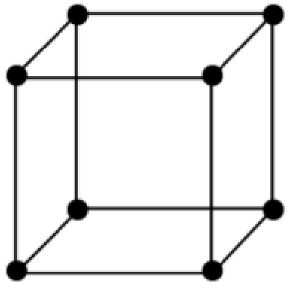
1.3.2 Centered Unit Cells

When the constituent particles occupy other positions in addition to those at corners, it is known as Centred Unit Cell. There are 3 types of Centred Unit Cells (Fig. 1.3):

Body Centred: When the constituent particle at the centre of the body, it is known as Body Centred Unit cell.

Face Centred: When the constituent particle present at the centre of each face, it is known as Face Centred Unit cell.

End Centred: When the constituent particle present at the centre of two opposite faces, it is known as an End Centred Unit cell.



P (Primitive)

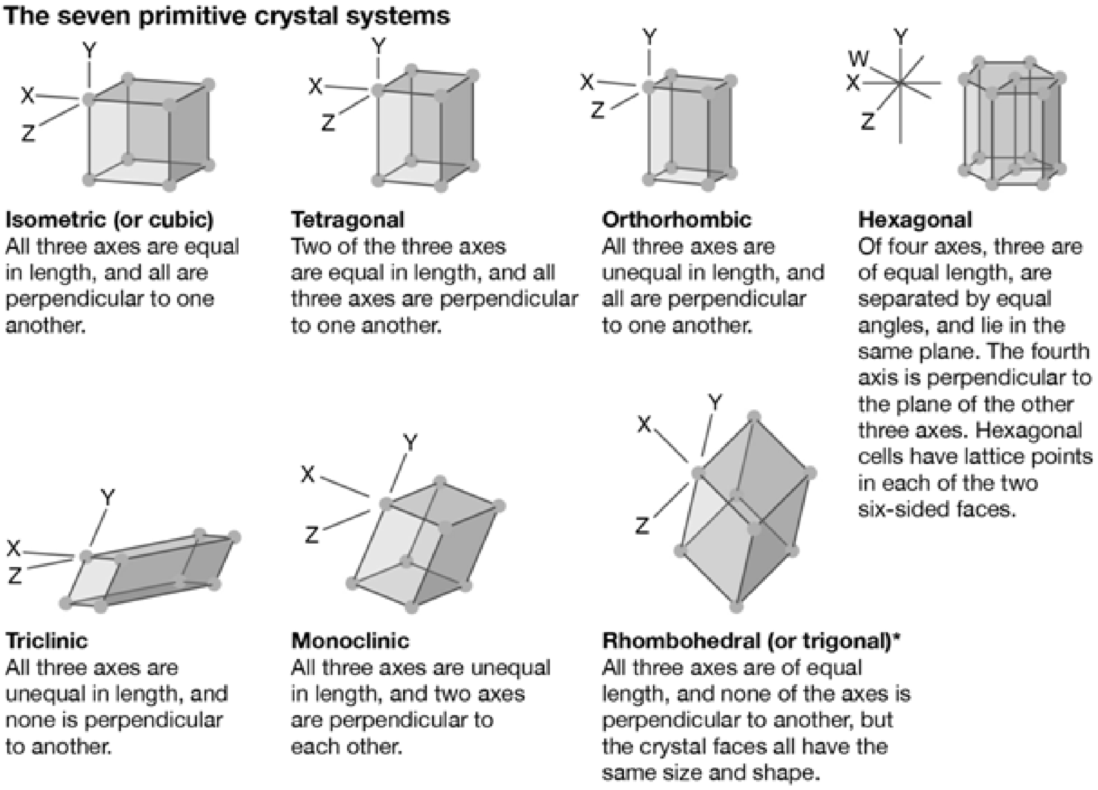


Fig. 1.2 Structure of primitive unit cells

1.4 CRYSTAL SYMMETRY

Symmetry, in crystallography, fundamental property of the orderly arrangements of atoms found in crystalline solids. Each arrangement of atoms has a certain number of elements of symmetry; *i.e.*, changes in the orientation of the arrangement of atoms seem to leave the atoms unmoved. One such element of symmetry is rotation; other elements are translation, reflection, and inversion. The elements of symmetry present in a particular crystalline solid determine its shape and affect its physical properties.

Translations involve displacement of the crystal in a direction that replaces each atom by one of its identical neighbors, so that the atoms seem unmoved. Rotations turn the crystal around an axis of symmetry passing through the crystal; the only rotations compatible with translational symmetry move the crystal through an angle of 360° divided by n, with n equal to 1, 2, 3, 4, or 6. Reflections exchange the parts of the crystal on the two sides of a plane of symmetry (mirror plane) within the solid. Inversions move every atom to another position in the crystal; the old and new positions of the atom lie upon a line, at the middle of which is the centre of inversion. So-called improper rotations are rotations followed by reflections (known as roto reflections) or rotations followed by inversions (called roto inversions) (Fig.1.4) [3].

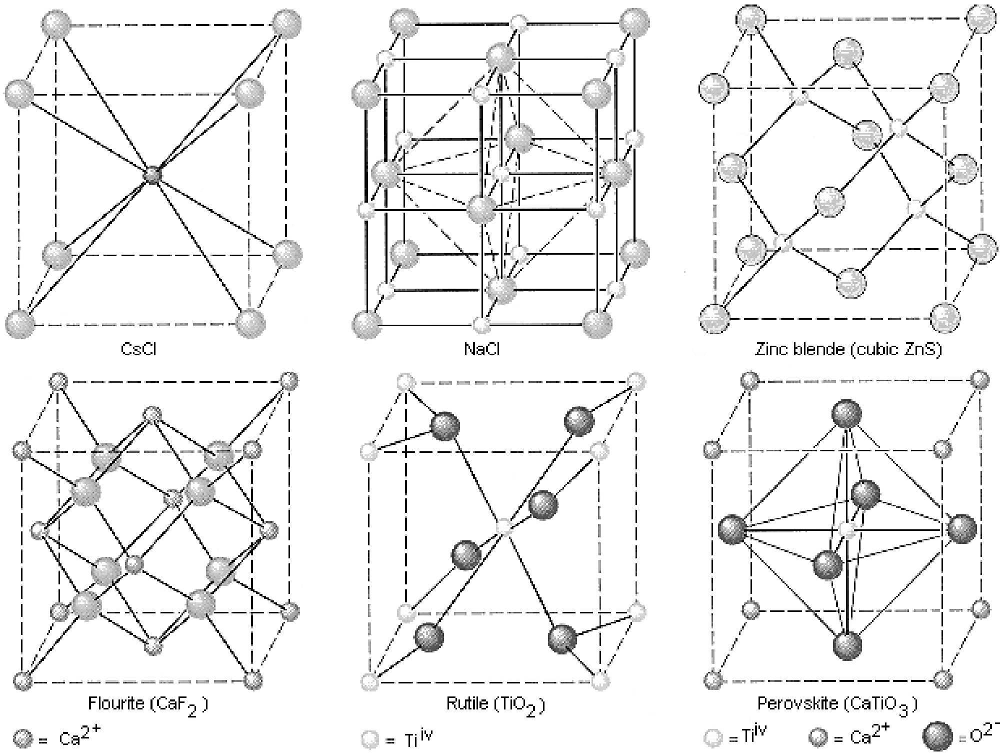


Fig. 1.3 Structures of the unit cell for a variety of salts

1.4.1 Screw Axis

Screw axes are like spiral staircases. The rotation is combined with a translation in a defined crystallographic direction by a defined step (half a unit cell for twofold screw axes, a third of a unit cell for threefold screw axes, etc.

The screw axes can be either right-handed (advances away from observer when rotated clockwise) or left-handed (advances away from observer when rotated counterclockwise)

Screw axis (nm) = rotation (n) + translation (m/n)

A screw axis have the notation nm where n is the rotation axis “fold” and m/n is the translation given as a fraction of the unit translation parallel to the rotation axis. There are e.g. 2_1, 4_1 and 6_3 screw axes. Subscripts indicate the magnitude of translation – 4_2 indicates a 4-fold axis translated every 2/4 t – 4_3 indicates a 4-fold axis translated every 3/4 t – 4 indicates a 4-fold axis translated every t. Can have 2, 3, 4, or 6- fold rotation (360º/n) and translation of some magnitude (rational fraction) of t (unit cell edge length).

A 2_1 screw axis translates an object by half a unit cell in the direction of the screw axis, followed by a 180° rotation (Fig. 1.5) [4].

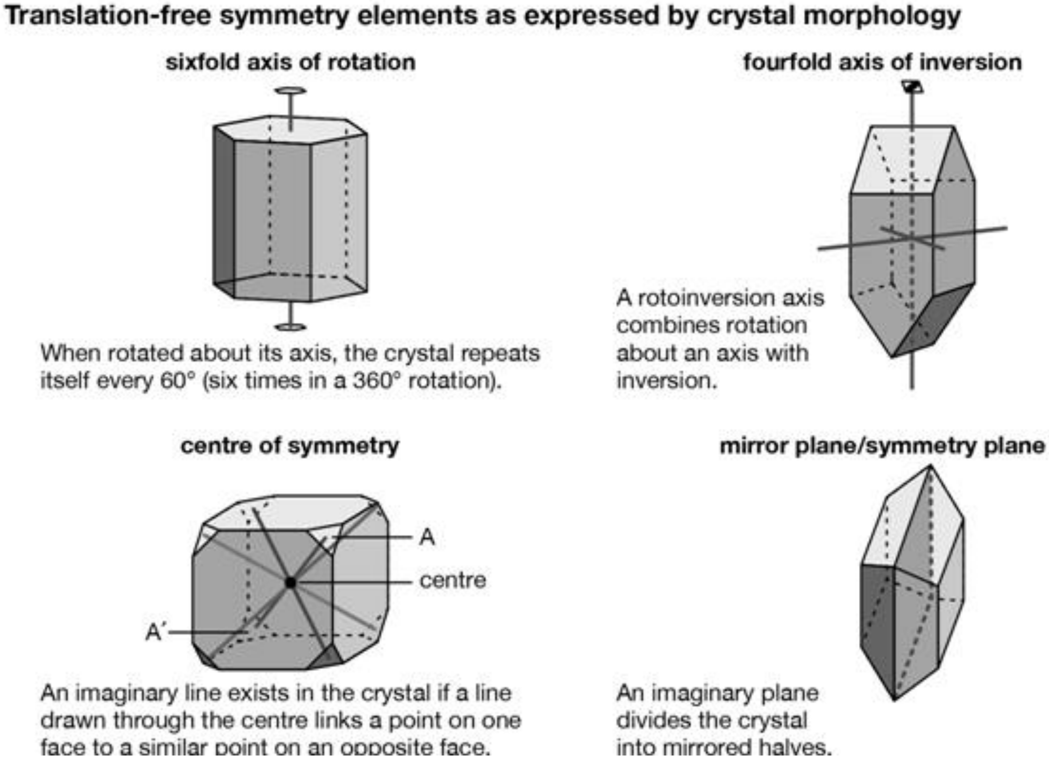


Fig. 1.4. Schematic representation of the unit cells for the seven crystal systems

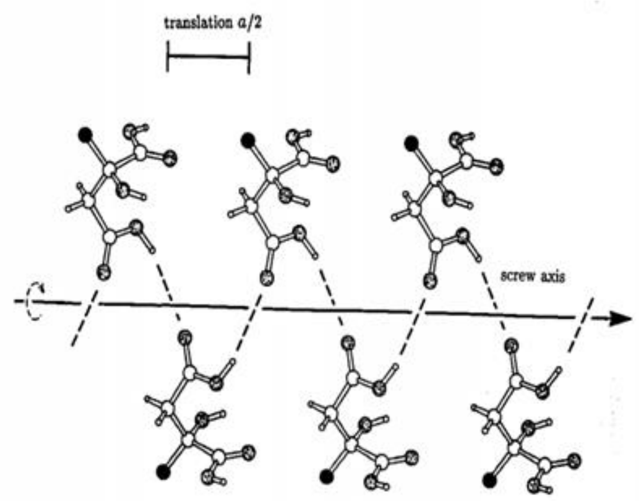
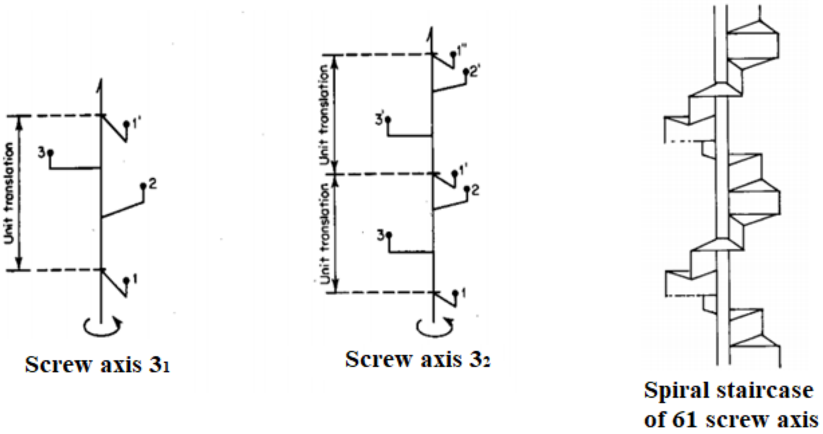


Fig. 1.5 2_1 screw axis

A C_n screw axis translates an object by the unit cell dimension multiplied by n/C along the direction of the screw axis, followed by a C-fold rotation



Screw axis 3_1

Screw axis 3_2

Spiral staircase of 61 screw axis

Fig. 1.6 C_n screw axis

1.4.2 Glide Plane

Glide plane (or transflection) is a symmetry operation describing how a reflection in a plane, followed by a translation parallel with that plane, may leave the crystal unchanged. Combine translation with a mirror plane (Fig. 1.7). There are a, b, c, n and d glide planes

Glide plane (a, b, c, n, d) = mirroring + ½ translation along an axis (or more axes)

A glide plane corresponds to a reflection-translation operation

- reflection through the glide plane

- translation within/parallel to the glide plane

- exact translation depends on type of glide

Glide plane are of three types

- Axial glide plane - a, b and c glides correspond to translations of ½ a, ½ b and ½ c respectively - called “axial glide planes”.

- Diagonal glide plane- n glide corresponds to a translation of ½ a + ½ b, ½ a + ½ c, or ½ b + ½ c - called “diagonal glide plane”

- Diamond glide plane-d glide corresponds to a translation of ¼ a + ¼ b, ¼ a + ¼ c, or ¼ b + ¼ c - called “diamond glide plane”

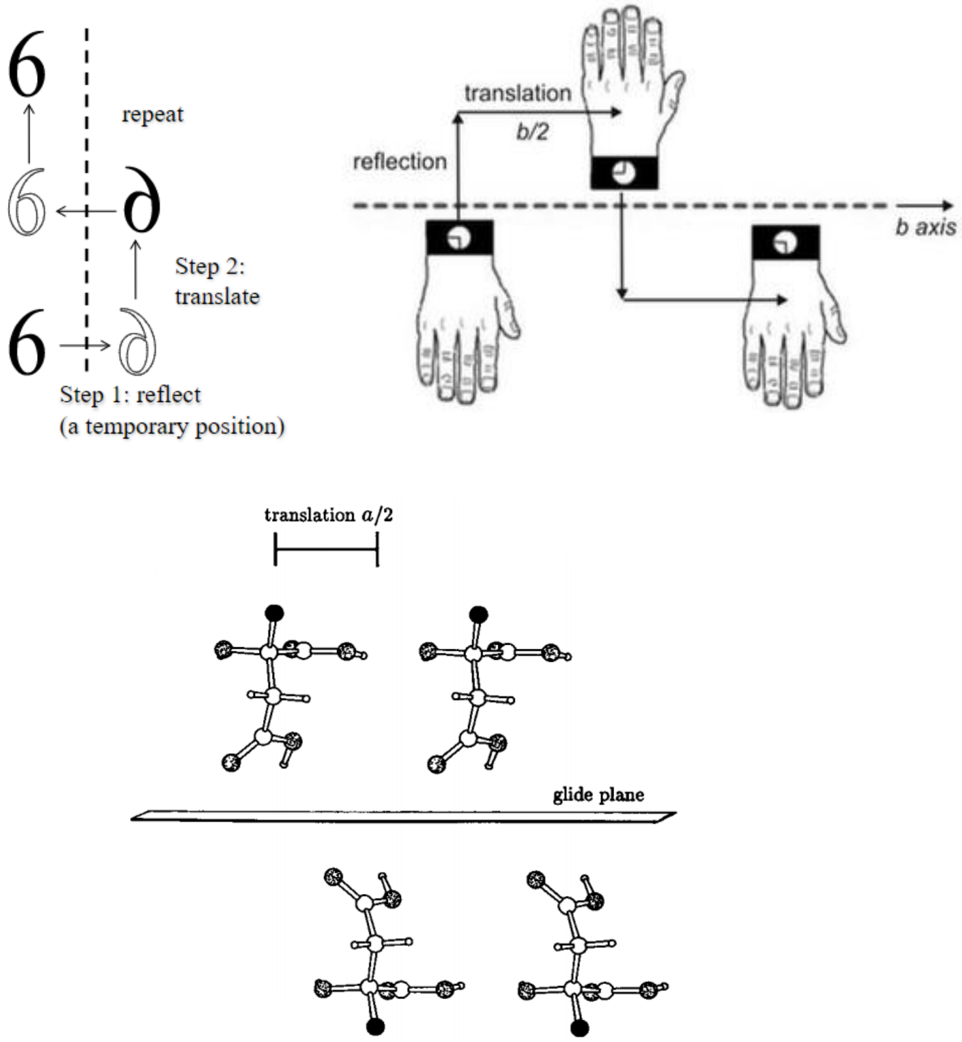


Fig. 1.7 Examples of Glide Planes

1.5 CRYSTALLOGRAPHIC POINTS

Labeling points in a unit cell follows the same procedure for listing points in any Cartesian coordinate system. The indices used to refer to points are q, r, and s. They are listed without commas, parentheses, or brackets. Consider point P in Fig. 1.7 [5,6]. If you were standing at the origin of the unit cell, you could travel q·a in the x-direction, r·v in the y-direction, and s·c in the z-direction to get to point P. Thus we would say that point P corresponds to the qrs point coordinates.

To find q, r, and s when you are shown a drawing with a point:

1. Start with your pencil at the origin.

2. Count the number lattice constants you must move in the x-, y-, and z-directions to reach the point.

3. Write the point as qrs without commas, parentheses, or brackets. Do not convert the coordinates to reduced integers.

To draw a point given qrs:

1. Start with your pencil at the origin.

2. Count q · a in the x-direction, r · v in the y-direction, and s · c in the z-direction.

3. Draw and label the point.

To draw a point given qrs:

1. Start with your pencil at the origin.

2. Count q · a in the x-direction, r · v in the y-direction, and s · c in the z-direction.

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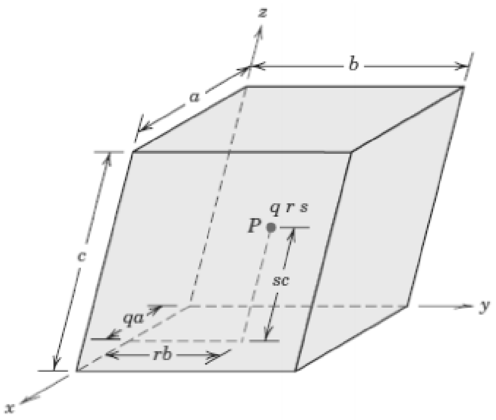


Fig. 1.7 Point coordinate of point P

1.6 CRYSTALLOGRAPHIC DIRECTIONS

To draw a direction given the [uvw] indices:

1. Choose a point for the origin of your vector. Simple directions, such as those shown in Figure 1.8, are easy to draw using the 000 crystallographic point as the origin. For more complicated directions (Fig. 1.8), it is more convenient to translate (add or subtract) or scale (multiply or divide) the indices of the direction. If you translate your origin to the point 001 for example, the tail of your direction vector will be at this point.

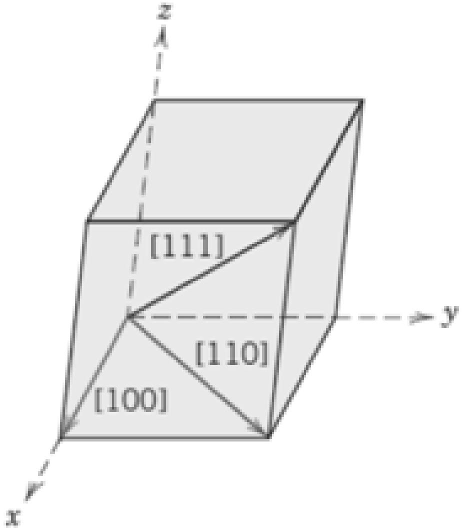


Fig. 1.8 The [111], [110], and [100] directions.

2. Start with your pencil on your chosen origin. Move your pencil u · a in the x-direction, v · b in the y-direction, and w · c in the z-direction. If u, v, or w are negative, move in the negative direction on that axis.

3. Draw and label a point.

4. Draw a line from your chosen origin to the point you just drew. Add an arrow head at the point. It is extremely important when drawing directions that you label the point that lies at the end of your direction vector. If the TAs cannot tell where your direction is ending, you will not receive full credit. Is it also highly preferred that you shift the origin and scale of the direction vector so that it is contained inside the unit cell [6].

If you shifted the origin, a way to check that you drew your direction properly is to subtract the point coordinates of the arrowhead from those of its tail. The resulting indices should be [uvw] (Fig. 1.9). To write the [uvw] indices given a drawing of a direction:

1. Place your pencil at the tail of the given vector.

2. Count how many lattice constants you must move in the x-, y-, and z-directions to reach the head of the vector. Write them down. Be mindful of negatives.

3. If necessary, multiply by a common number to make the indices integers.

4. Rewrite the indices and enclose them in square brackets [uvw].

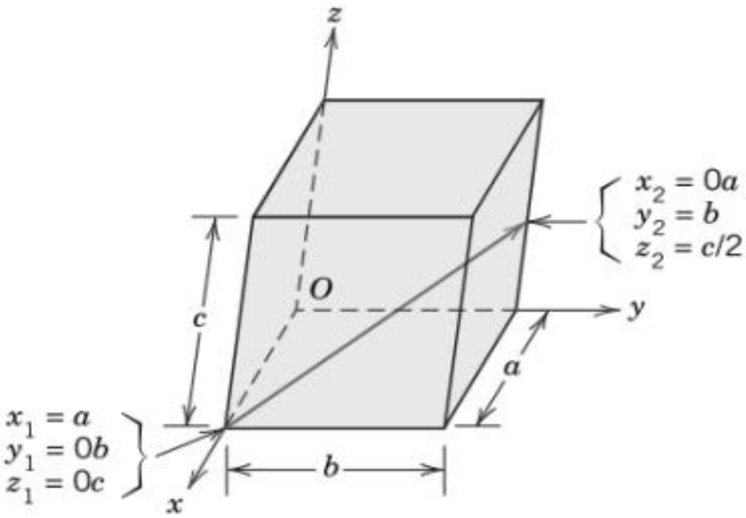


Fig. 1.9 The [¯221] direction shown with a 100 origin

1.7 CRYSTALLOGRAPHIC PLANES

To draw a plane given the (hkl) indices:

1. Find the reciprocal of (hkl). If one or more of the indices is zero, consider the reciprocal to be infinity. The values 1/ h, 1/ k, and 1/ l are the intercepts of the x-, y-, and z-axes, respectively. If one or more intercept is infinity, this means that the plane will never intercept that axis (it is parallel to that axis). For the (221) plane shown in Fig.1.10a, the reciprocals would be 1/2, 1/2, and 1.

2. For all non-zero indices, draw a point on the x-axis at a/h, a point on the y-axis at b/k, and a point on the z-axis at c/l.

3. Connect the dots.

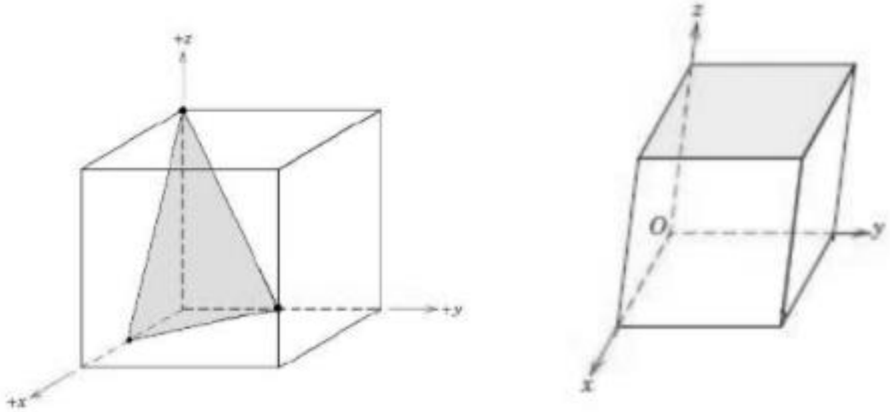
4. If you had a zero index - for example, the (001) plane in Fig.1.10b - draw two points at 111 and 011, and 110, then connect the dots.

To list the (hkl) indices given a drawing of a plane:

1. Check to see if the plane goes through the origin, as in Fig.1.11a. If not, proceed to step 2. If it does, shift the plane 1 lattice constant in an axis such that it no longer passes through the origin (see Fig.1.11b). This new plane is equivalent to the first.

2. Find the coefficients by which you would multiply the lattice constants to identify where the plane intercepts the x-, y-, and z-axes. Be mindful of negative intercepts. If the plane doesn't intercept an axis (it is parallel to that axis), call the intercept infinity. Write down these values.

3. Take the reciprocal of these intercepts. The value of 1 ∞ is zero.

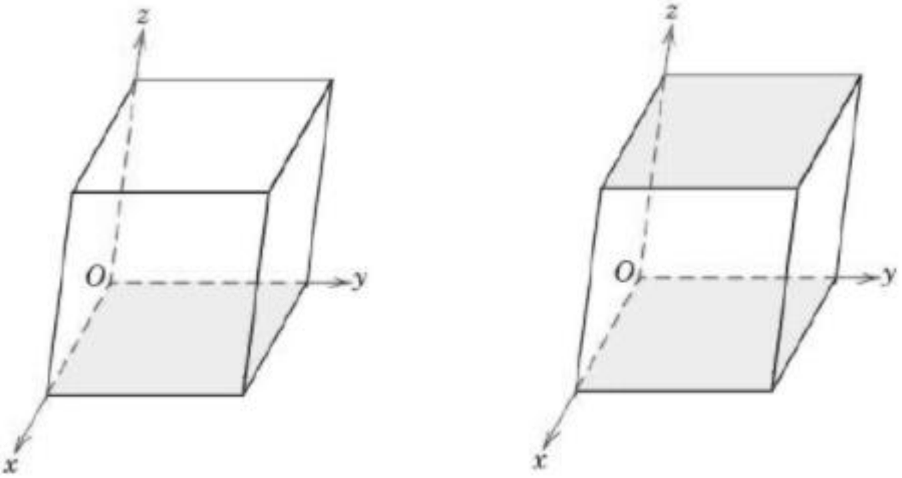


(a) The (221) plane (b) The (001) plane

Fig. 1.10 Crystallographic planes

4. If necessary, multiply or divide by a common number to put the indices in the most reduced integer form. Sometimes you will be asked to leave the indices unreduced - for example, (220) instead of (110) - for use in x-ray diffraction questions.
5. Enclose the indices in parentheses without commas (hkl).

It is extremely important when drawing planes that you label where the plane intersects the axes. If the TAs cannot tell where your plane intersects the axis, you will not receive full credit. Note: The hkl indices define a vector that starts at the origin and it perpendicular to the plane. Recall from your multi-variable or vector calculus class that the equation of a plane can be written as $a\vec{x} + b\vec{y} + c\vec{z} = d,$ where the vector [abc] is perpendicular to the plane. In our case, a crystallographic plane can be written as $h\vec{a} + k\vec{b} + l\vec{c} = d.$



(a) Plane that passes through the origin (b) The plane shifted +1 lattice constant in the z-direction

Fig.1.11: The method used to determine the indices of a plane that passes through the origin

1.8 MILLER INDICES

Miller indices are used to specify directions and planes, these directions and planes could be in lattices or in crystals. The number of indices will match with the dimension of the lattice or the crystal. Miller indices used to express lattice planes and directions. indices are used to express the Miller Indices are a symbolic vector representation for the orientation of an atomic plane in a crystal lattice and are defined as the reciprocals of the fractional intercepts which the plane makes with the crystallographic axes (Fig.1.12) [6].

- x, y, z are the axes (on arbitrarily positioned origin).

- a, b, c are lattice parameters (length of unit cell along a side) h, k, l are the Miller indices for planes and directions - expressed as planes: (hkl) and directions: [hkl].

- There are no commas between numbers

- Negative values are expressed with a bar over the number.

If you want to describe the orientation of a crystal face or a plane of atoms within a crystal lattice, then there are series of steps that will lead you to its notation using Miller indices.

1. The first step is to determine the fractional intercepts that the plane/face makes with each crystallographic axis. In other words, how far along the unit cell lengths does the plane intersect the axis. In the figure above, the plane intercepts each axis at exact one unit length.

2. Step two involves taking the reciprocal of the fractional intercept of each unit length for each axis. In the figure above, the values are all 1/1.

3. Finally, the fractions are cleared (*i.e.,* make 1 as the common denominator). The cleared fractions result in 3 integer values. These integers are designated *h, k* and *l.*

4. These integer numbers are then parenthetically enclosed *(hkl)* to indicate the specific crystallographic plane within the lattice. Since the unit cell repeats in space, the *(hkl)* notation actually represents a family of planes, all with the same orientation. In the figure above, the Miller indices for the plane are (111) (Fig.1.13).

5. This becomes immediately apparent when we consider the case of the (101). In this case, the plane intercepts a axis at one unit length and also the *c* axis at one unit length. The plane, however, never intersects the *b* axis. In other words, it can be said that the intercept to the *b* axis is infinity. The intercepts are then designated as 1, infinity, 1. The reciprocals are

then 1/1, 1/infinity, 1/1. Knowing 1/infinity = 0 then the indices become (101) (Fig.1.14 to 1.16).

In brief

- (h,k,l) represents a point – note the exclusive use of commas
- Negative numbers/directions are denoted with a bar on top of the number
- [hkl] represents a direction • represents a family of directions
- (hkl) represents a plane • {hkl} represents a family of planes

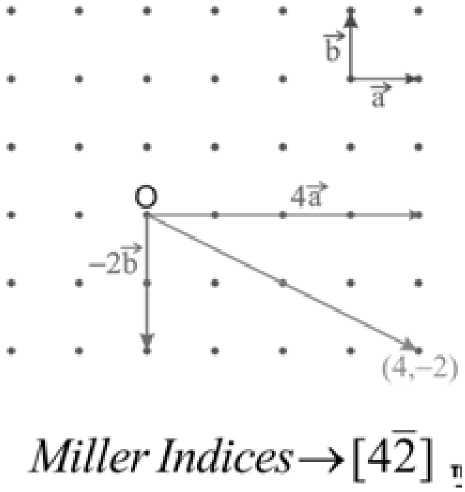


Fig. 1.12: Miller Indices for points

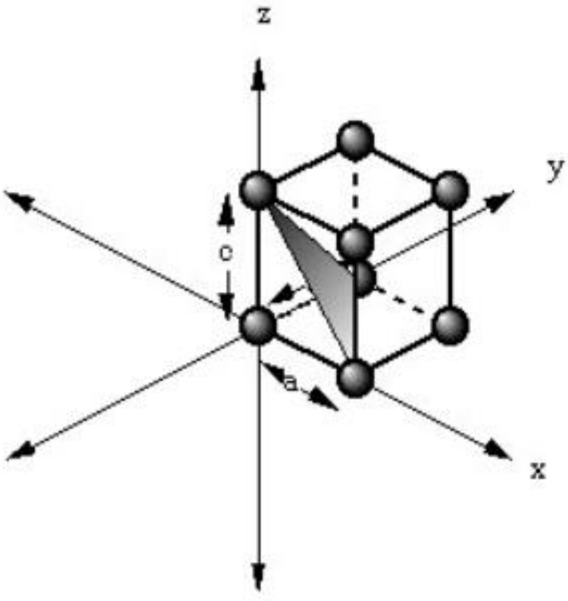


Fig.1.13 Example of the (111) plane

	a	**b**	**c**
Intercept length	1	1	1
Reciprocal	1/1	1/1	1/1
Cleared fraction	1	1	1
Miller Indice	**111**		

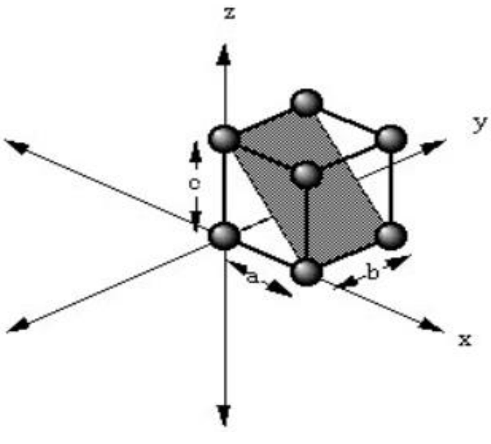


Fig.1.14 Example of the (101) plane

	a	**b**	**c**
Intercept length	1	∞	1
Reciprocal	1/1	1/∞	1/1
Cleared fraction	1	0	1
Miller Indice	**101**		

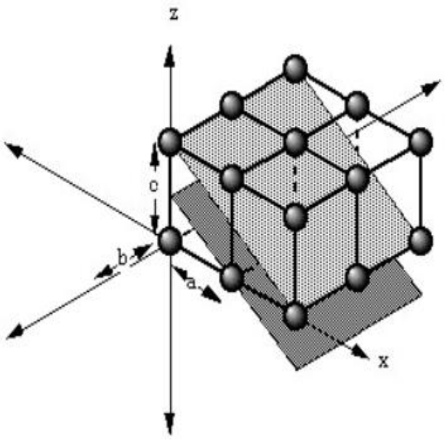


Fig. 1.15 Example of the (102) plane

	a	**b**	**c**
Intercept length	1	∞	1/2
Reciprocal	1/1	1/∞	1/1/2
Cleared fraction	1	0	2
Miller Indice	**102**		

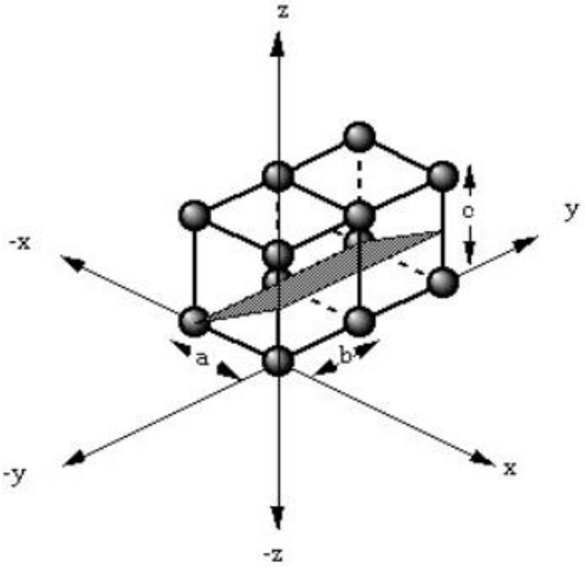


Fig. 1.16 Examples of -102 plane

	a	**b**	**c**
Intercept length	-1	∞	1/2
Reciprocal	1/-1	1/∞	1/1/2
Cleared fraction	-1	0	2
Miller Indice	**-102**		

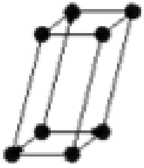
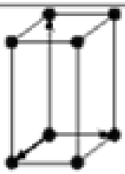
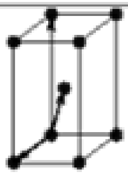
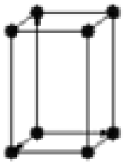
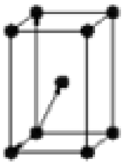
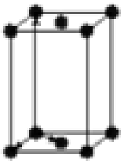
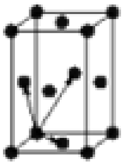
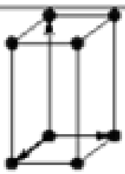
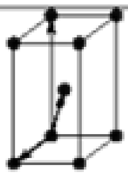
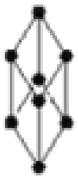
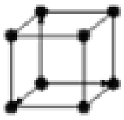
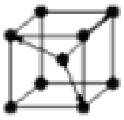
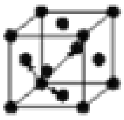
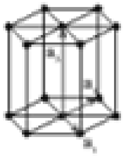
1.9 BRAVAIS LATTICES

The unit vectors a,b and c are lattice parameters.Based on their length equality or inequality and their orientation (the angles between them, α, β and ɣ) a total of 7 crystal systems can be defined. With the centering (face, base and body centering) added to these, 14 kinds of 3D lattices, known as Bravais lattices. There are several ways to describe a lattice. The most fundamental description is known as the Bravais lattice. In words, a Bravais lattice is an array of discrete points with an arrangement and orientation that look exactly the same from any of the discrete points, that is the lattice points are indistinguishable from one another.

Thus, a Bravais lattice can refer to one of the 14 different types of unit cells that a crystal structure can be made up of. These lattices are named after the French physicist Auguste Bravais.

Out of 14 types of Bravais lattices some 7 types of Bravais lattices in three-dimensional space are listed in this subsection. Note that the letters a, b, and c have been used to denote the dimensions of the unit cells whereas the letters α, β, and γ denote the corresponding angles in the unit cells (Table.1.1) [5].

Table.1.1 The fourteen lattice types

Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				

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5. D. McKie and C. McKie, Crystalline Solids, Thomas Nelson and Sons, 1974. A very comprehensive crystallography text.

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Chapter 5 covers lattice planes and directions. The rest of the book gives an introduction to crystallography and diffraction in general.

1.11 QUESTIONS

1. How many atoms of each type are contained in a conventional unit cell?

2. What is the Bravais lattice?

3. Draw the following crystal structures: simple cubic, fcc, bcc, NaCl, CsCl, hexagonal, tetragonal, and orthorhombic.

4. Calculate the angle between the [110] direction and the [111] direction for a monoclinic lattice with $a = 0.3$ nm, $b = 0.4$ nm, $c = 0.5$ nm, and $\beta = 107°$.

5. Consider a cubic lattice. Give a single crystallographic direction [uvw] which is within the (111) plane. Note, there many directions within the (111) plane.

6. Practice sketching some lattice planes. Make sure you can draw the {100}, {110} and {111} type planes in a cubic system.

7.Draw the trace of all the (121) planes intersecting a block 2 × 2 × 2 block of orthorhombic ($a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$) unit cells.

UNIT 2 SOLID STATE REACTIONS, CRYSTAL DEFECTS AND NON-STOICHIOMETRY

CONTENTS

2.1 OBJECTIVES

- Knowledge of basic concepts of solid-state reactions.
- Understanding of experimental procedure and kinetics of solid-state reactions
- To understand the origin and nature of defects in crystals.
- Describe the imperfections in solids and their effect on properties

2.2 INTRODUCTION

Reactions between or within solid reactants to yield a solid product are prototypical of solvent free reactions. Solid state reactions shall refer to all solventless processes leading from a solid reactant to a solid product. Solid state reactions occur within the rigid constraining environment of the crystal lattice and therefore provide an extreme case for evaluating the effect of intermolecular forces on a reaction and their influence on reaction mechanism and direction. The confined environment of the reactant crystal lattice can control the kinetic features of a reaction and hence the nature of products.

2.3 SOLID STATE REACTIONS

Solid state reactions may have the following advantages over solution phase reactions:

(i) The atom economic nature of the solid-state reactions and the limited formation of side products.

(ii) No solvents are needed in the reaction and hence no waste disposal issues associated with the solvent need be considered. This is of considerable importance in the rapidly emerging field of Green Chemistry and products do not require extensive purification to remove traces of solvent and impurities.

(iii) The constrained environment in a ‘reaction cavity’ can lead to novel chemical reactions, with product selectivity different from that expected in the liquid phase. It is expected that the crystalline solid state may affect the product selectivity of chemical reactions, not only by rate accelerations but also by slowing down rates of competing processes. Manipulating rates and selectivity by changing activation energies in the liquid phase can be thought of as a low-resolution approach to controlling chemical reactivity. It is therefore possible that solid state reactions may occur with both control and yields not achievable by any other media, indeed quantitative yields have been observed with solid state reactions. These reactions are often faster, taking just a few minutes rather than hours to complete because the reactants are in intimate contact with each other.

(iv) Enantioselective reactions are feasible in a chiral cavity. In such reactions the asymmetry is only determined by its physical origin without any chemical reagent - the chiral source being the chiral crystal packing.

(v) Kinetic trapping of highly reactive intermediates.

(vi) Crystal engineering using organometallic complexes is possible in the solid state.

(vii) Cascade reactions can be carried out quite easily and with high yields.

2.4 EXPERIMENTAL PROCEDURES OF SOLID-STATE REACTIONS

The potential of solid-state chemistry for mechanistic studies, solvent free synthesis and materials applications is now fully recognized. A general experimental procedure scheme is presented in Fig. 2.1.

2.4.1 Solid State reaction method of $Co_{0.5}Zn_{0.5}Cd_{0.2}Fe_{1.8}O_4$ ferrite synthesis

All of the starting materials like $CdCl_2.H_2O$, $ZnCl_2$, $FeCl_3.6H_2O$ and $CoCl_2.6H_2O$ were analytical grade in stoichiometry, used to synthesis the ($Co_{0.5}Zn_{0.5}Cd_{0.2}Fe_{1.8}O_4$) by standard solid state reaction method (shown in Fig. 2.2). The mixture of chemicals were grind in the agate-mortar for 5 hour to get homogeneous finely powdered and heated in a muffle furnace in silica crucible sintered at 800°C for 3 hours and at 1000°C for 3 hours for another sample. Structural characterization of the ferrite powders was carried out X-ray Diffractometer, (with Cu-Kα radiation, 1.5406 Å) = l wavelength [1].

$$CoCl_2.6H_2O + ZnCl_2 + FeCl_3.6H_2O + CdCl_2.H_2O \rightarrow Co_{0.5}Zn_{0.5}Cd_{0.2}Fe_{1.8}O_4 + nH_2O\uparrow + nCl_2\uparrow$$

2.4.2 Co-precipitation as a precursor to solid state reactions

Co-precipitation involves taking a stoichiometric mixture of soluble salts of the metal and precipitating them as hydroxides, citrates, oxalates, or formates. The mixture is filtered, dried, and then heated to give the final product. Precursor method involves atomic level mixing by forming a solid compound (precursor) in which the metals of the desired compound are present in the proper stoichiometry. Precursors such as nitrates and carbonates can be used as starting materials instead of oxides. For example, a mixed salt of an oxyacid (e.g. acetate) containing M and M' in the ratio of 1:2 is formed in the case of formation of MM'_2O_4. The precursor is heated to decompose it to the desired product and the homogeneous products are formed at relatively low temperatures. It is not always possible to find a suitable precursor Co-precipitation and precursor methods some precursor method example are as follows

$$Ti(OBu)_4(aq) + 4H_2O(l) \rightarrow Ti(OH)_4(s) + 4BuOH(aq)$$

Excess oxalic acid redissolves the precipitate.

$$Ti(OH)_4(s) + (COO)_2^{2-}(aq) \rightarrow TiO(COO)_2(aq) + 2OH^-(aq) + H_2O(l)$$

$$Ba^{2+}(aq) + (COO)_2^{2-}(aq) + TiO(COO)_2(aq) \rightarrow Ba[TiO((COO)_2)_2](s)$$

Decomposition by heating (920 K) gives the desired oxide phase.

$$Ba[TiO((COO)_2)_2](s) \rightarrow BaTiO_3(s) + 2CO2(g) + 2CO(g)$$

Decomposition of oxalates is also used to form ferrites (MFe_2O_4). Products from precursor methods often contain small particles with a large surface area, which is desired for certain applications.

2.5 KINETICS OF SOLID STATE REACTIONS

Chemical kinetic concepts were originally based on generalizations from empirical studies of homogenous reactions first in the gas phase. These concepts were later applied to solution phase processes and eventually to solid-state reactions. Solid-state kinetic concepts was justified in the solid-state because of similarities to some homogenous reactions. For example, the Arrhenius equation was historically developed empirically, after which theoretical justification for its use was later introduced in gases through the collision theory and in solutions through the transition-state theory [1,2].

The rate of a solid-state reaction can be generally described by:

$$\frac{d\alpha}{dt} = Ae^{-(E_a/RT)} f(\alpha) \qquad (1)$$

where, A is the preexponential (frequency) factor, E_a is the activation energy, T is absolute temperature, R is the gas constant, f(R) is the reaction model, and R is the conversion fraction. For a gravimetric measurement, R is defined by

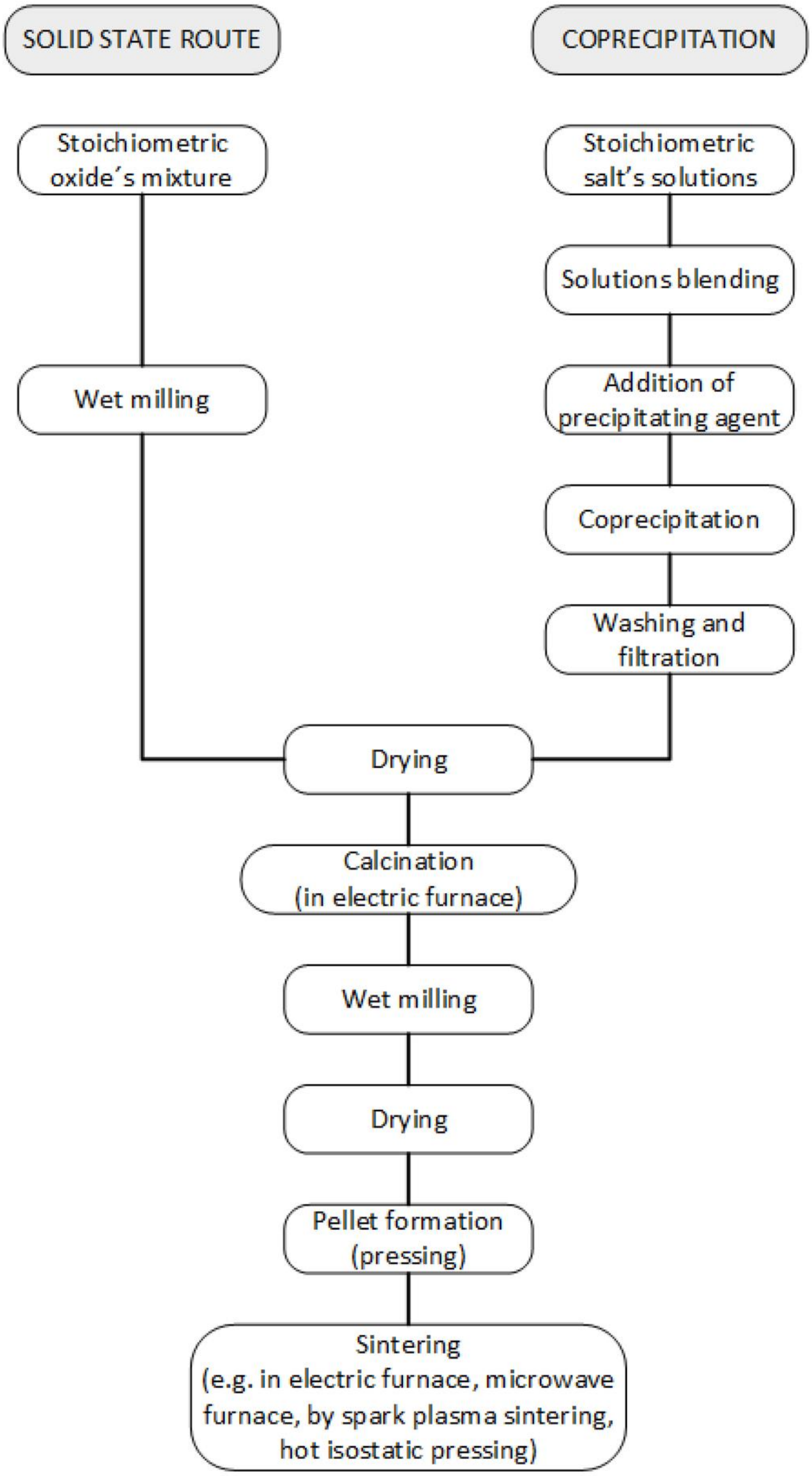


Fig. 2.1 General scheme for solid state reaction synthesis

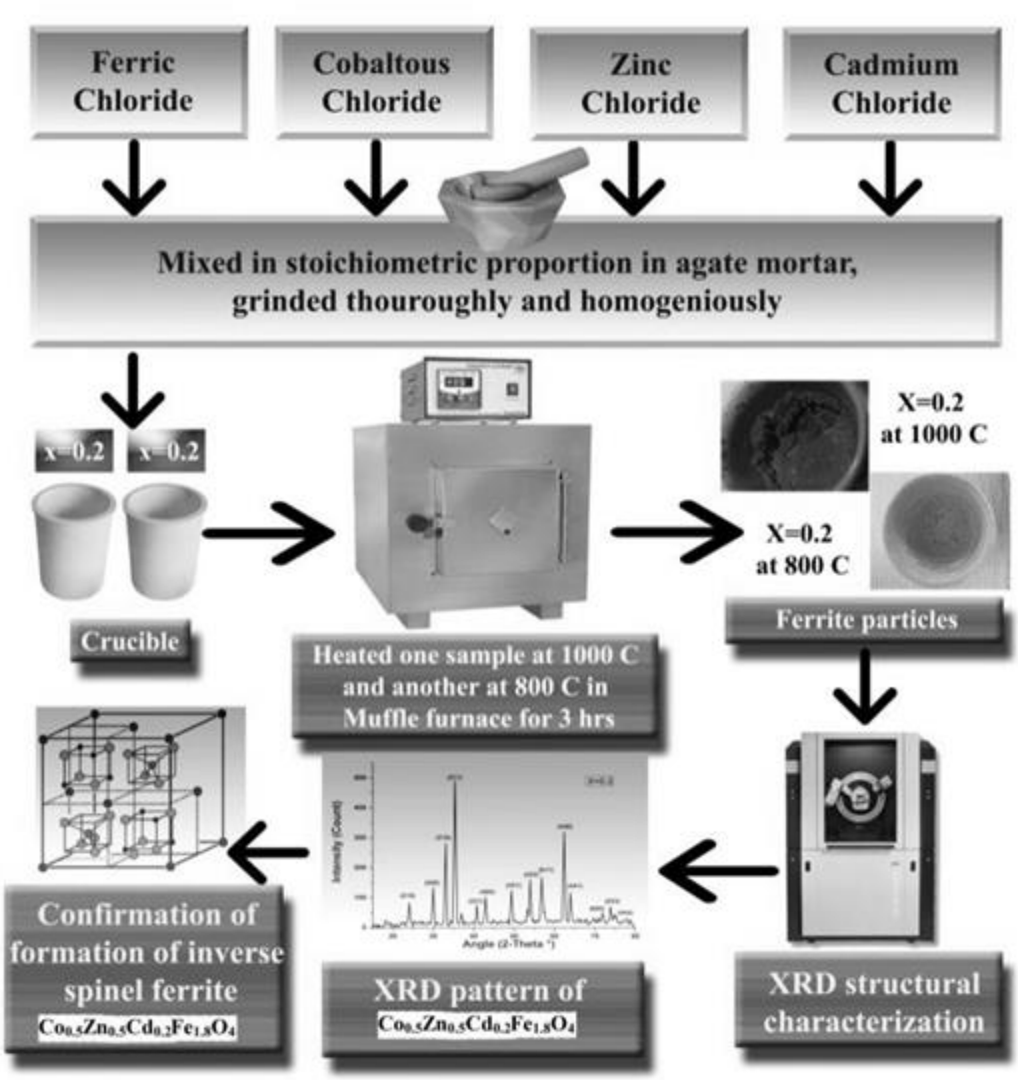


Fig. 2.2 Schematic diagram of Solid-State reaction method of $Co_{0.5}Zn_{0.5}Cd_{0.2}Fe_{1.8}O_4$ ferrite for 800°C and 1000°C sintering temperatures

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \qquad (2)$$

where, m_0 is initial weight, m_t is weight at time t, and m_∞ is final weight. Kinetic parameters (model, A, E_a) can be obtained from isothermal kinetic data by applying the above rate law (eq 1). Alternatively, eq 1 can be transformed into a non-isothermal rate expression describing reaction rate as a function of temperature at a constant heating rate by utilizing the following:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\frac{dt}{dT} \qquad (3)$$

where, dR/dT is the nonisothermal reaction rate, dR/dt is the isothermal reaction rate, and dT/dt is the heating rate (â). Substituting eq 1 into eq 3 gives the differential form of the non-isothermal rate law,

$$\frac{d\alpha}{dT} = \frac{A}{\beta}e^{-(E_a/RT)}f(\alpha) \qquad (4)$$

Separating variables and integrating eqs. 1 and 4 gives the integral forms of the isothermal and non-isothermal rate laws, respectively:

$$g(\alpha) = Ae^{-(E_a/RT)}\,t \qquad (5)$$

and

$$g(\alpha) = \frac{A}{\beta}\int_0^T e^{-(E_a/RT)}\,dT \qquad (6)$$

where, g(R) is the integral reaction model, defined by

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$$

Reaction kinetics in the solid-state are often studied by thermogravimetry, but they can also be studied by other analytical methods such as differential scanning calorimetry (DSC), powder X-ray diffraction (PXRD), and nuclear magnetic resonance (NMR). For any analytical method, the measured parameter must be able to be transformed into a conversion fraction (R) that can be used in the kinetic equations.

2.6 PERFECT AND IMPERFECT CRYSTALS

Real crystals are never perfect; they always contain a considerable density of defects and imperfections that affect their physical, chemical, mechanical, and electronic properties.

Imperfections make them unique and responsible for the existence of defects also plays an important role in various technological processes and phenomena such as annealing, precipitation, diffusion, sintering, oxidation, and others. It should be noted that defects do not necessarily have adverse effects on the properties of materials

All the atoms in the ideal lattice positions at 0K behave as perfect crystals. Defects do not necessarily have adverse effects on the properties of materials. It is very rare to have a perfect crystal, even a careful control of the types and amounts of imperfections can bring about specific characteristics to improve a system.

An incontrovertible law of nature states: “nothing is perfect”. This law applies to humans as well as to the inorganic world of crystalline solids and can be formulated as the second law of thermodynamics: $F = H - TS$, where F is the free energy of a given system, H is the heat content or enthalpy and TS is the entropy, or disorder, term.

Real crystals always contain a considerable amount of defects and imperfections that affect their physical, chemical, mechanical and electronic properties. These imperfections give those unique properties to play an important role in various technological processes such as annealing, precipitation, diffusion, sintering, oxidation and others.

2.7 TYPES OF DEFECTS

The three basic classes of defects in crystals:

2.7.1 Point defects **-** atoms missing or in irregular places in the lattice (lattice vacancies, substitutional and interstitial impurities, self-interstitials).

Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance. Point defects can be considered as 0D (zero dimensional) defects (Fig. 2.3).

Vacancy: When an atom is missing from a position where it should be.

Interstitial: An atom from the crystal occupies the place of an interstitial (self-interstitial or interstitialcy)

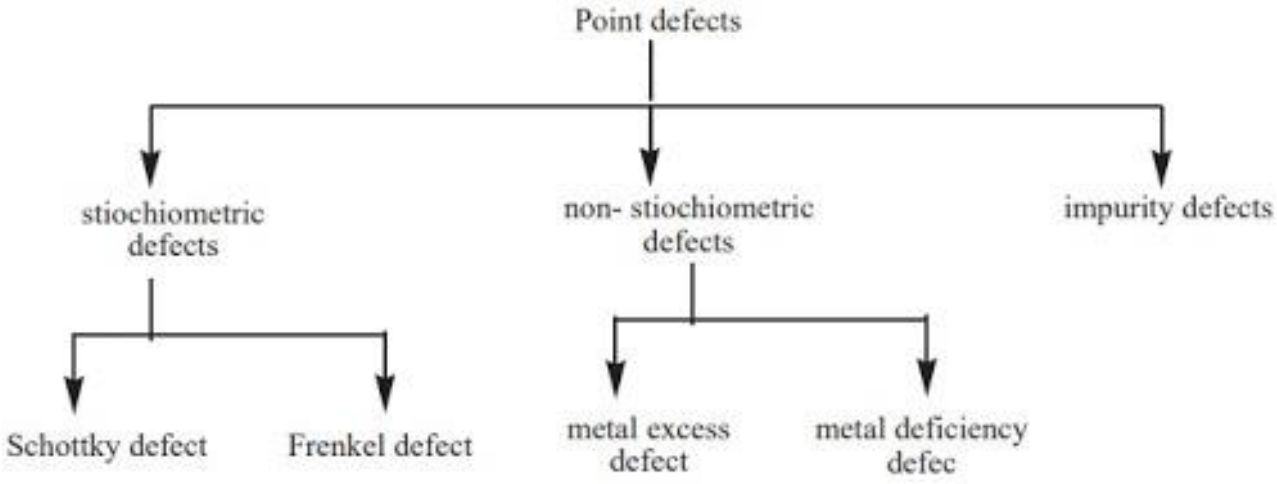
Point defects occur in single letter sites that's why point defects are known as zero dimension defects. Such imperfections are localised in some points like regions in the Crystal. Point defects are created by thermal fluctuation and quenching (high rate of cooling), severe deformation. It may arise due to the

(i) Vacancies in the lettice sites.

(ii) Substitution impurity

(iii) Occurrence of constituent ions in the interstitial spaces.

(iv) Non stoichiometric proportions of the constituent ions.



However, the point defects in the ionic crystal can be classified into different groups.

Fig. 2.3 Classification of point's defects

2.7.1.1 Stoichiometric or Intrinsic defect

These defects in a crystal run in such a way that the ratio of the number of constituent positive and negative ions remain the same as indicated by their chemical formula. These are further divided in two types (Table 2.1)

(a) Schottky defect

In this defect both missing cations and anions are in equivalent proportion, and it maintains the electrical neutrality of Crystal. In this type the missing cation disappears and produces a pair of holes leading to Schottky defects. In NaCl crystal the missing number of one sodium ion requires one chloride ion to disappear and to make a hole, while in the case of calcium chloride crystal the missing calcium ions requires two chloride ions in making hole to maintain the electrical neutrality in the crystal (Fig. 2.4). In the case of metallic crystals there is no question of missing lattice points in pairs stoichiometric proportion, because they consist of electrically neutral constituents of the same type.

Briefly it can be noted this type of defect is shown by highly ionic compounds which have

- High Co – ordination number and
- Small difference in the sizes of cations and anions
- A few examples of ionic compounds exhibiting Schottky defects are NaCl, KCl, KBr and CsCl.

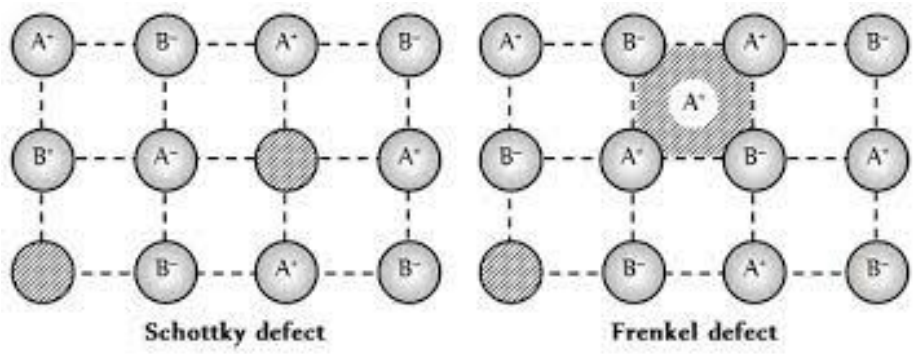


Fig. 2.4 Schottky defect and Frenkel defects

Effects of Schottky Defect

- As the number of ions decreases as a result of this defect, the mass decreases whereas the volume remains the same. Hence density of the solid decreases
- The crystal begins to conduct electricity to a small extent by ionic mechanism
- The presence of too many voids lowers lattice energy and the stability of the crystal

(a) Frenkel defect

Frenkel defects arise due to displacement of ions generally cations to the interstitial positions from the lattice sites. When some of the constituent the interstitial position rather than their letters sites, it may lead to Frenkel defects (Fig. 2.4). Generally, the smaller size cations tend to occupy interstitial sites. Such defects are predominant in the lattices, where ions have coordination numbers due to low value of cationic and anionic radii ratio. Low coordination numbers are preferred in this defect, because it requires a lower amount of energy to break down the less number of attractive interactions. Because the r+/r- values i.e., small, and large anion the polarization is significant to produce a good number of covalency in the compound. Examples of such compounds are like silver bromide (4:4), silver iodide (4:4), zinc sulphide (4:4) etc.

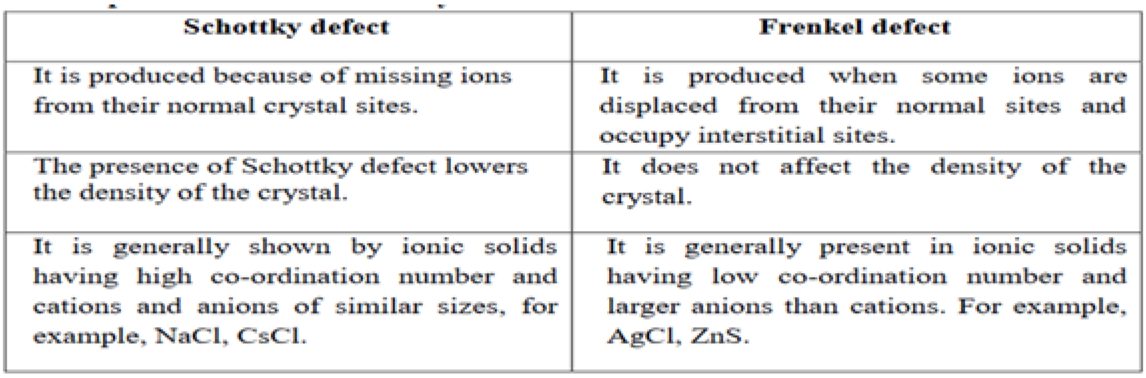
Briefly it can be noted that this type of defect is present in ionic compounds which have

- Low coordination number
- Larger difference in size of cation and anions
- Compounds having highly polarizing cation and easily polarizable anion. A few examples of ionic compounds exhibiting this defect are AgCl, AgBr, AgI, ZnS etc.

Effects of Frenkel defect

- As no ions are missing from the crystal lattice, therefore density of the solid remains the same
- The closeness of like charges tends to increases the dielectric constant of the crystal
- The crystal conducts electricity to a small extent by ionic mechanism

Table 2.1 Comparative details of Schottky and Frenkel defects



Schottky defect	Frenkel defect
It is produced because of missing ions from their normal crystal sites.	It is produced when some ions are displaced from their normal sites and occupy interstitial sites.
The presence of Schottky defect lowers the density of the crystal.	It does not affect the density of the crystal.
It is generally shown by ionic solids having high co-ordination number and cations and anions of similar sizes, for example, NaCl, CsCl.	It is generally present in ionic solids having low co-ordination number and larger anions than cations. For example, AgCl, ZnS.

2.7.1.2 Non-Stoichiometric Defects/Extrinsic Defects

It arises as a result of imperfection, the ratio of number of cation to anion becomes different from that indicated by the ideal chemical formula, the defects are called non – stoichiometric defects [2].

These defects arise either due to excess of metal atoms or nonmetal atoms or presence of impurities /foreign particles.

This can be divided into following types:

(i) Metal excess defect

(ii) Metal deficiency

(iii) Substitution by impurities

(i) Metal excess defect or Nonmetal deficiency

It can occur by two ways

(a) Excess defect by replacement of anion by electron

When the lattice site an anion is occupied by the electron instead of the anion it can lead to metal excess in the Crystal. The trapped electron maintains electrical neutrality. The lattice site in which the electron strap is called a F-centre (where F is a German word farbe with means colour). The trapped electron at the F-centre can absorb light in the visible range for its transition to a higher energy level and responsible for colour production from that crystal.

Like a crystal of NaCl is heated in sodium vapour, it acquires a yellow colour. This yellow colour is due to the formation of a non-stoichiometric compound of sodium chloride in which there is a slight excess of sodium ions.

What happens in this case is that some sodium metal gets doped into sodium chloride crystal which, due to the crystal energy, gets ionized into Na^+ and e^-. This electron occupies a site that would otherwise be filled by a chloride ion, as illustrated in figure.

There is evidently an excess of metal ions although the crystal as a whole is neutral. A little reflection would show that there are six Na^+ sites adjacent to the vacant site occupied by the electron.

The extra electron is thus shared between all the six Na^+ ions which implies that this electron is not localized at the vacant Cl^- site. On the other hand, this electron is similar to the delocalized p electrons present in molecules containing conjugated double bonds.

Light is absorbed when this delocalized electron makes an easy transition from its ground state to an excited state. As a result, the non – stoichiometric form of sodium chloride appears coloured. Because of this, the sites occupied by the extra electrons are known as colour centres. These are also called F-centres (Fig. 2.5). This name comes from the German word Farbe meaning colour.

The non-schiometric sodium chloride may be represented by the formula Na(1+d)Cl where d is the excess sodium metal doped in the crystal because of its exposure to sodium vapour.

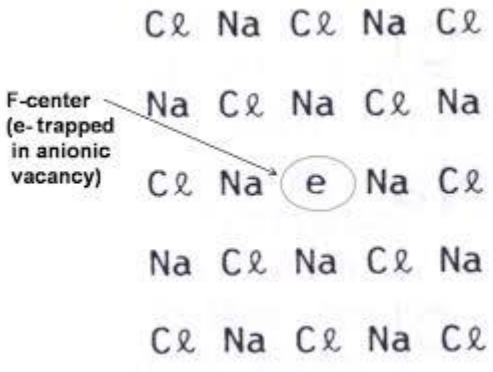


Fig. 2.5 Replacement of anion by electron

Another common example of metal excess defects is the formation of a magenta coloured non-stoichiometric compound of potassium chloride by exposing the crystals of KCl to K metal vapour.

The coloured compound contains an excess of K^+ ions, the vacant Cl^- sites being filled by electrons obtained by the ionization of the excess K metal doped into the crystal.

(b) Excess defect produced by the presence of extra cation

When one or more cations occupy the interstitial site and in order to maintain the electrical neutrality of Crystal equal number of electrons are trapped into other interstitial sites. So the Crystal as a whole is electrically neutral and the number of metal ions become greater than the number of anions that's why there is an excess of metal ions in the Crystal and hence this defect is also called as metal excess defect.

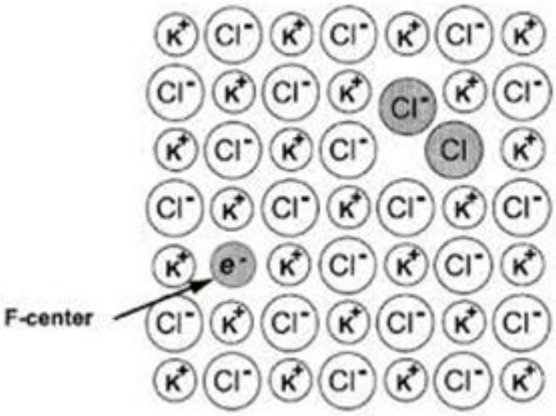


Fig. 2.6 Excess defect produced by the presence of extra cation

This defect is found in those crystals in particular which have a frenkel defect. The crystals having this type of defect have advanced electrical conductivity due to the presence of special electrons (Fig. 2.6).

Like this defect is found in zinc oxide. ZnO loses oxygen reversible at high temperatures and becomes yellow in colour. The excess of zinc cations get trapped into the interstitial sites and an equal number of electrons cat prapt into the The Other interstitial sites to maintain the electrical charge neutrality.

Consequences of metal excess defects:

- Electrical conductivity of non-stoichiometric crystals having metal excess defects increases and the conduct electricity through them. Since the number of electrons is low the crystals show low electrical conductivity hence are n type semiconductors.

- Colours of the non-Striker metric crystals since the free electrons present in the non-static metric crystals have metal excess defect can be excited to higher energy level by the absorption of radiation in the visible range of spectrum these crystals are generally coloured like yellow colour crystals of non-stoichiometric sodium chloride and lilac colour of non-stoichiometric KCl.

(ii) Metal deficiency defects

These defects occur when the crystal contains less number of positive ions then negative ions. These defects can arise due to the following two reasons:

(a)Cation vacancies

(b) Extra anions occupying interstitial sites.

(a) Cation vacancies: In some cases, the positive ions may be missing from their lattice sites. The extra negative charge may be balanced by some nearby metal ion acquiring two positive charges instead of one. This type of defect is possible in metals which show variable oxidation state. The common example of compounds having this defect are ferrous oxide, ferrous sulphide and nickel oxide. In case iron pyrites (FeS), two out of three ferrous ions in a lattice may be converted into Fe3+ state and the third Fe2+ ion may be missing from its lattice site. Therefore, the crystal contains Fe^{2+} to Fe^{3+} ions. This gives rise to exchange of electrons from one Fe^{2+} to Fe^{3+} ion in which Fe^{2+}changes to Fe^{2+} to Fe^{3+} changes to Fe^{2+} ion. As a result, the crystal has metallic luster. Because of the natural colour of iron pyrites and metallic lustre some samples of minerals shine like gold and have been nick named as fool's gold. Similarly, FeO is mostly found with a composition of 0.95. It may actually range from 0.93 to 0.96. In crystals of FeO, some $Fe^{2+}$are missing and the loss of positive charge is made up by the presence of a required number of Fe^{3+} ions. Moreover, since there is exchange of electrons, the substances become conductors.

2.7.1.3 Impurities defects/Substitution by impurities

A general method of introducing defects in ionic solids is by adding impurity ions. If the impurity ions are in different valence states from that of host, vacancies are created in the crystal lattice of the host. For example, addition of $CdCl_2$ to silver chloride yields solid solutions where the divalent cation Cd^{2+} occupies the position of Ag^+. This will disturb the electrical neutrality of the crystal. In order to maintain the same, proportional number of Ag^+ ions leaves the lattice. This produces a cation vacancy in the lattice, such kind of crystal defects are called impurity defects.

2.7.1.4 Summary of Points Defects

- Any departure from a perfectly ordered arrangement of constituent particles (atoms, molecules, or ions) in crystal is called imperfection or defect.
- Imperfections/defects occur due to the fast rate of crystallization because constituent particles (atoms, molecules, ions) do not get sufficient time to arrange themselves in a perfect order.
- Even during the preparation of a single crystal, by carrying out the crystallization at an extremely slow rate, the crystal may not have a perfect arrangement.
- There are two types of defects, namely point defects and line defects.
- When the deviations or irregularities exist from the ideal arrangement around a point or an atom in a crystalline substance the defects are called Point defects.
- When the deviation from the ideal arrangement exists in the entire row of lattice points, the defect is called line defect.
- If defects in the crystals are such that the ratio between the cations and anions remains the same as represented by the molecular formula, i.e., the stoichiometry of the solid is not disturbed, the defects are called stoichiometric defects.
- These are also called intrinsic defects (deviation within the crystal) or thermodynamic defects (due to absorption of heat from the surrounding).

- When in crystalline substance, some of the lattice sites are vacant, the crystal is said to have vacancy defects. It results in the decrease in the density of the substance. This defect is shown by non-ionic solids.

- When some constituent particles (atoms, molecules) are present in the interstitial sites, the crystals are said to have interstitial defects. This defect increases the density of substance (because mass increases but volume remains same). This defect is shown in non-ionic solids.

- In Frenkel defect the smaller ion, usually cation, is missing from its lattice site causing a vacancy or a hole there and occupies the interstitial site. In this defect electrical neutrality as well as the stoichiometry of the compound is maintained. This defect is a combination of vacancy defect and interstitial defect.

- In Schottky defect equal numbers of cations and anions are missing from the lattice site.

- Impurity defects arise when foreign atoms are present at the lattice site in place of host atoms (substitutional solid solutions) or at the vacant interstitial site (interstitial solid solution).

- In non-stoichiometric defects the ratio of the number of cations to the number of anions is different from that indicated by the ideal chemical formula. That is, the stoichiometry of the compound is disturbed.

- In metal excess defect by anion, a negative ion may be missing from its lattice site, leaving a hole which is occupied by an electron thereby maintaining the electrical neutrality. These sites containing the electron are called F-centres (F-Farbenzenter a German Word for colour).

- In another type of metal excess defect an extra cation may occupy an interstitial site and an extra electron may be present in an interstitial site.

- Metal deficiency defect occurs in those solids which contain less amount of metals compared to stoichiometric composition. This occurs in metals which show variable valency like transition metals. This defect generally occurs due to the missing cation from its lattice site and the presence of the cation having higher charge (e.g., +2 instead of +1) in the adjacent site.

*2.7.2 **Linear Defects***

Groups of atoms in irregular positions (e.g. screw and edge dislocations).

Line imperfections (one-dimensional defects) are also called Dislocations. They are abrupt changes in the regular ordering of atoms along a line (dislocation line) in the solid. They occur in high densities and strongly influence the mechanical properties of material. In linear defects groups of atoms are in irregular positions. Linear defects are commonly called dislocations. They are defects that produce distortion in the lattice situated around a line. Any deviation from a perfectly periodic arrangement of atoms along a line is called the line imperfection. These can be displaced in the interior of a crystal by applying relatively low forces and can produce a complete displacement over crystalline planes. The line imperfection acting as boundary between the slipped and un-slipped region, lies in the slip plane and is called a dislocation. Dislocations are generated and move when a stress is applied. The strength and ductility of metals are controlled by dislocations [3].

Line dislocations is of two types: -Screw dislocations -Edge dislocations

2.7.2.2 Burgers Vector

- Burgers vector represents the magnitude and direction of the lattice distortion resulting from a dislocation in a crystal lattice. In edge dislocation, Burgers vector is perpendicular to the dislocation line and in screw dislocation, Burgers vector is parallel to the dislocation line.

- For mobile dislocation, the direction of the vector is usually on one of the most packed crystallographic planes (slip planes) and always in the most packed crystallographic directions (slip directions). The slip plane is the plane that contains both the Burgers vector and the dislocation line.

- The slip planes + the slip directions call the slip systems and represent the planes and the directions in which plastic deformation can occur.

2.7.2.3 Edge Dislocations/Taylor-Orowan Dislocation:

This is characterized by a Burger's vector that is perpendicular to the dislocation line. It may be described as an edge of an extra plane of atoms within a crystal structure. Thus, regions of compression and tension are associated with an edge dislocation (Fig. 2.7). Because of the extra incomplete plane of atoms, the atoms above the dislocation line are squeezed together and are in a state of compression whereas atoms below are pulled apart and experience tensile stresses. Edge dislocation is considered positive when compressive stresses present above the dislocation line, and is represented by $\perp$. If the stress state is opposite i.e. compressive stresses exist below the dislocation line, it is considered as negative edge dislocation, and represented by ┬ (Fig.2.8) .

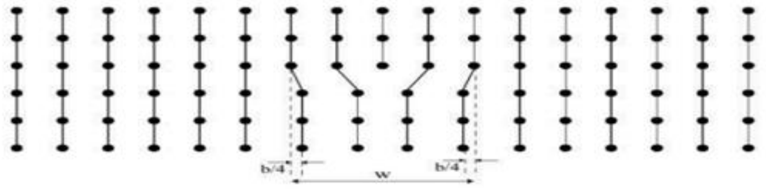


Fig. 2.7 Edge dislocation with shear and diatational stresses

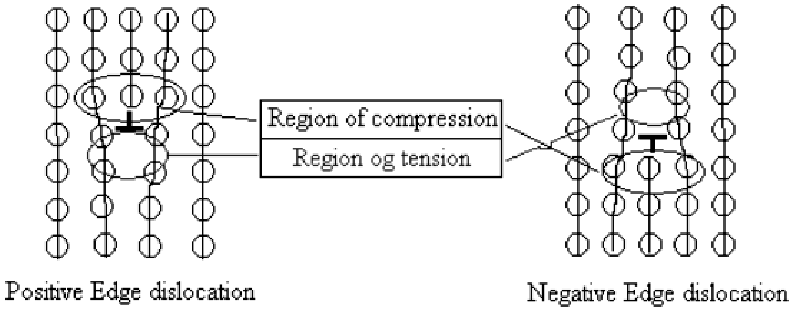


Fig. 2.8 Positive and Negative Edge Dislocations

The interatomic bonds are significantly distorted only in the immediate vicinity of the dislocation line. As shown in the set of images above, the dislocation moves similarly moves a small amount at a time. The dislocation in the top half of the crystal is slipping one plane at a time as it moves to the right from its position in image (a) to its position in image (b) and finally image (c). In the process of slipping one plane at a time the dislocation propagates across the crystal. The movement of the dislocation across the plane eventually causes the top half of the crystal to move with respect to the bottom half. However, only a small fraction of the bonds are broken at any given time. Movement in this manner requires a much smaller force than breaking all the bonds across the middle plane simultaneously.

2.7.2.3 Screw Dislocations/Burgers Dislocation

It has its dislocation line parallel to the Burger’s vector. A screw dislocation is like a spiral ramp with an imperfection line down its axis. Screw dislocations result when displacing planes relative to each other through shear (Fig. 2.9). Shear stresses are associated with the atoms adjacent to the screw dislocation; therefore, extra energy is involved as it is in the case of edge dislocations.

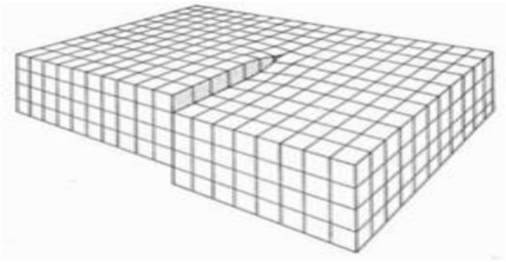


Fig. 2.9 Screw Dislocation with Pure Shear Stress

Screw dislocation is considered positive if Burger's vector and t-vector or parallel, and vice versa. (t-vector - a unit vector representing the direction of the dislocation line). A positive screw dislocation is represented by a dot surrounded by circular direction in clockwise direction", whereas the negative screw dislocation is represented by a dot surrounded by a circular direction in anticlockwise direction" (Fig.2.10).

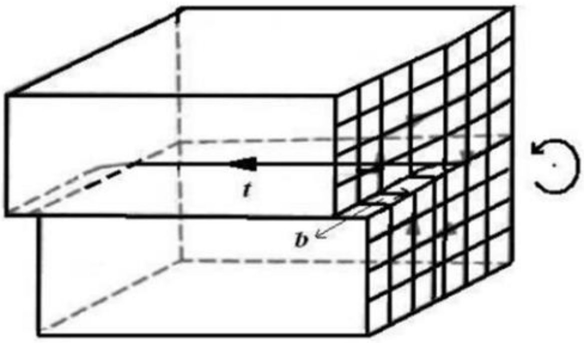


Fig. 2.10 Negative Screw Dislocation

The screw dislocation is slightly more difficult to visualize. The motion of a screw dislocation is also a result of shear stress, but the defect line movement is perpendicular to direction of the stress and the atom displacement, rather than parallel. To visualize a screw dislocation, imagine a block of metal with a shear stress applied across one end so that the metal begins to rip. This is shown in the upper right image. The lower right image shows the plane of atoms just above the rip. The atoms represented by the blue circles have not yet moved from their original position. The atoms represented by the red circles have moved to their new position in the lattice and have reestablished metallic bonds. The atoms represented by the green circles are in the process of moving. It can be seen that only a portion of the bonds are broken at any given time. As was the case with the edge dislocation, movement in this manner requires a much smaller force than breaking all the bonds across the middle plane simultaneously. If the shear force is increased, the atoms will continue to slip to the right. A row of the green atoms will find their way back into a proper spot in the lattice (and become red) and a row of the blue atoms will slip out of position (and become green).

In this way, the screw dislocation will move upward in the image, which is perpendicular to direction of the stress. A screw dislocation does not have a preferred slip plane, as an edge dislocation has, and thus the motion of a screw dislocation is less restricted than the motion of an Edge dislocation. As there is no preferred slip plane, screw dislocation can cross-slip on to another plane and can continue its glide under favorable stress conditions. However, screws cannot move by climb process, whereas edge dislocations cannot cross-slip**.**

*2.7.3 **Planar Defects***

The interfaces between homogeneous regions of the material (grain boundaries, stacking faults, external surfaces) [4].

A Planar Defect is a discontinuity of the perfect crystal structure across a plane. Planner defects can be categories as follows:

2.7.3.1 Grain Boundary

A Grain Boundary is a general planar defect that separates regions of different crystalline orientation (*i.e.* grains) within a polycrystalline solid. Across these boundaries crystal structure does not change. In the case of grain boundary, the orientation changes and the rotation type and crystal on one side of the boundary is rotated with respect to the crystal on the other side. Grain boundaries can further be classified in two ways, first low angle boundary. If the rotation angle is large, it is called high angle boundaries.

Sample has the same orientation of Crystal light true lol unit cells are parallel then it should be called a single button in this and if the bristles on one side is oriented only

2.7.3.2 Twin Boundary

It's a reflection boundary crystal on one side appears to be a reflected or mirror image of the Crystal on the other side. Twin boundary is a boundary that separates two domains of a crystal that are mirror images (Fig.2.12). The result is called a twinned crystal.

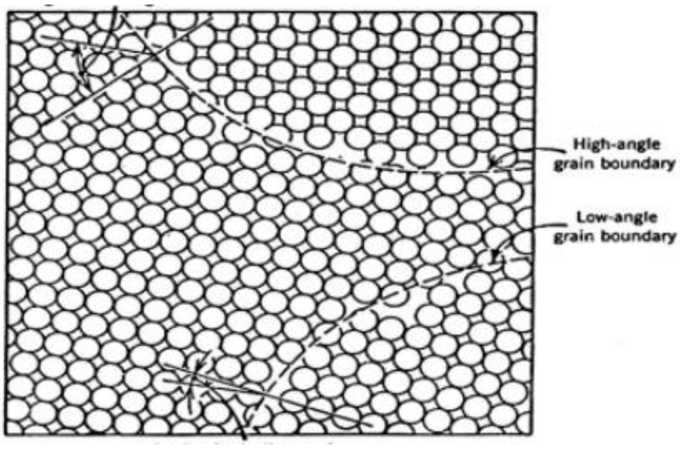


Fig. 2.11 Grain Boundaries

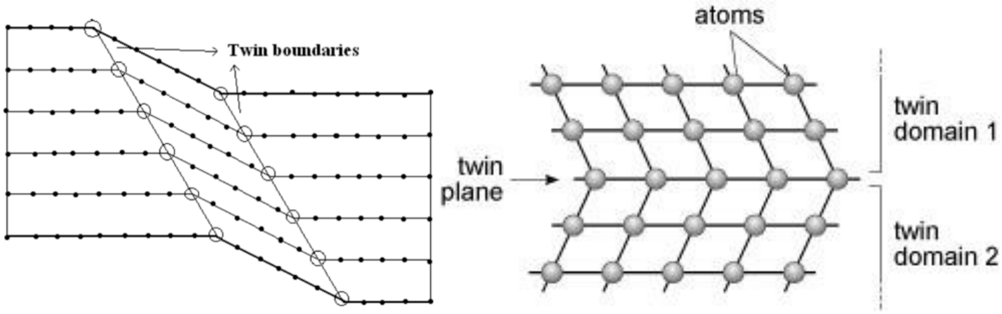


Fig. 2.12 Crystal twinning, in which a twin plane separates two regions of a single crystal that are mirror images. The two regions are referred to as twin domains.

Grain boundaries are different from twin boundaries because there is no orientation relationship between crystals on either side of the grain boundary. There are two distinct grains, with the same, or a different, mineral composition.

2.7.3.2 Stacking Fault

It is a translation boundary the orientation of the two crystals on either side of the stacking fault is the same but is still there not perfect matching because on one side the crystal is translated with respect to the other side so that causes that stacking mismatch or stacking fault.

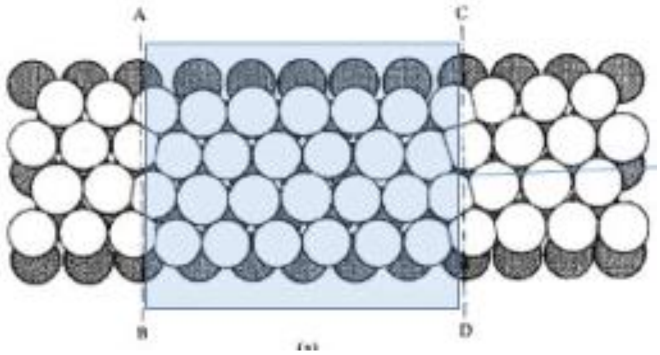


Fig. 2.13 Stacking Fault

The shifted portion of the partial dislocation is a “stacking fault “Atomic stacking order into the screen has changed was ABCA / BCABCABC …Now it is ABCA / CABCABC …

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2.9 QUESTIONS

1.Describe the advantages of solid-state reactions over solution phase.

2.Discuss the kinetics and give rate law’s expressions for solid state reactions.

3.What types of defects arise in solids?

4.How do defects affect material properties?

5. Describes boundaries defect.

UNIT 3 ORGANIC SOLIDS, FULLERENES, MOLECULAR DEVICES

CONTENTS

3.1 OBJECTIVES

- To impart advanced knowledge about the various aspects of organic solids
- To give understanding of electrical properties of conducting solids.
- Understanding of fullerenes and their properties.
- Describe the theory and functioning of optical storage devices and sensors.

3.2 INTRODUCTION

Electrical properties of solids are measured in terms of conductivity. Conductivity may be defined as the ease with which electric current can pass through a given substance. All solids do not conduct electricity in equal amounts. Some of them have high conductivity, whereas some of them do not conduct electricity at all. On the basis of conduction of electricity, solids can be broadly divided into three categories:

3.2.1 Conductors

Conductors are the solids that allow easy passage of electric current through them. Metals are generally good conductors of electricity. Electrical conductivity in metals is due to the presence of mobile electrons. The conductivity of metals is of the order of $10^{7}(\Omega\text{m})^{-1}$. There is no gap between the conduction band and the valence band. Thus, electrons can easily flow from the valence band to the conduction band under the influence of electric field, making them good conductors of electricity.

3.2.2 Semiconductors

The gap between the conduction band and the valence band is very less; therefore whenever sufficient energy is provided to the electrons in a semiconductor, electrons jump from the valence band to the conduction band. The conductivity of the semiconductors increases with an increase in temperature, for semiconductors, it lies in between 10^{-6} to $10^{-4}\,(\Omega\text{m})^{-1}$. There are two types of semiconductors:

3.2.2.1 Intrinsic Semiconductors

When heat is provided to the semiconductors, sometimes they eject electrons from their position leaving a positive hole behind them. The semiconductors can now conduct electricity because, on the application of electric field, electrons will now move in one direction and the holes in the opposite direction. These types of materials are known as undoped or intrinsic semiconductors. Example: Silicon, Germanium.

3.2.2.2 Extrinsic semiconductors

Silicon and germanium generally have a low conductivity in their pure state at room temperature. To increase the conductivity of the semiconductors small amount of impurity is added to the semiconductor (group 13 and group 15 elements). This process of adding the impurities to improve the conductivity of semiconductors is known as doping and the semiconductors are referred to as extrinsic semiconductors or doped semiconductors.

3.2.3 Insulators

These materials do not conduct electricity. The band gap between the valence band and conduction band is very large. Even if a large amount of energy is provided to these solids, they do not conduct electricity. Example: Wood, plastics etc.

Polymers have traditionally been considered good electrical insulators and a variety of their applications have relied on this property. Common polymers such as teflon and polystyrene have conductivity value about 10^{-18} S/cm. Due to the presence of partially filled energy bands, conductors have high electrical conductivity, in the same time energy bands of insulators and semiconductors, are either completely filled or completely empty and so they cannot be electrical conductors. The gap between the highest filled energy level (valence band) and lowest unfilled energy level (the conduction band) is called band gap (Eg). There is no band gap in metals *i.e.*, Eg=0 eV, large band gap in insulators and intermediate band gap in semiconductors. The different band gaps in metals, insulators and semiconductors are indicated in Fig 3.1. In a semiconductor there is a filled valence band and an empty conduction band at 0 K. Most conventional polymers as an example of insulators have full valence bands and empty conduction bands, which are separated from each other by wide energy gap [1].

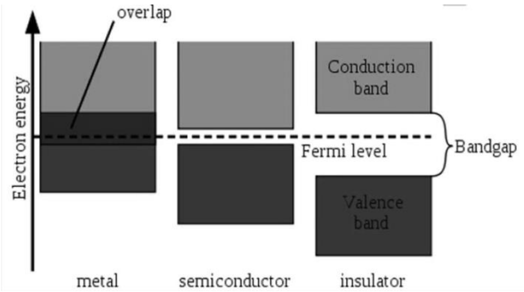


Fig. 3.1 Band gaps in metals, semiconductors and insulators.

Intrinsically conducting polymers are organic polymers that conduct electricity. During the last years, the electrically conducting polymers are called synthetic metals to signify their organic characteristic and metal-like properties. Due to combining the electrical properties of a semiconductor and metals as well as the advantages of conventional polymers such as easy synthesizing, preparation and fabrication, greater workability, light weight, resistance to corrosion and chemical attack, low cost and their properties can be tailored to the required applications. Conductive polymers firstly characterized by controllable conductivity and have special electrical and optical properties comparable to those of metals and inorganic semiconductors. The unique electronic structure is responsible for their high electron affinity and so there is no wonder that the conductive polymers are called the materials of the 21s century. Fig. 3.2 shows some of these polymers. There will be important to mention that being a multi-phase system in nature will result in homogeneity lacking and reproducibility has been an inherent weakness for conductively filled polymers. These polymers control the quality of dispersion to obtain homogeneous conducting polymer composites is critically important.

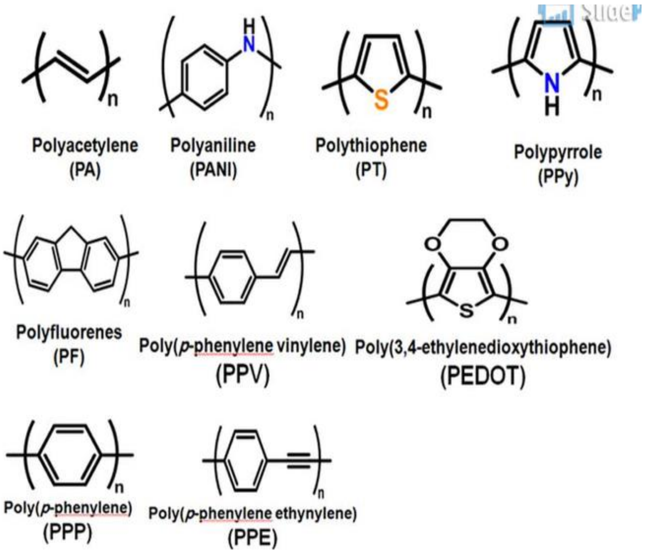


Fig. 3.2 Examples of some conducting polymers

Professor Alan J. Heeger at the University of California at Santa Barbara, USA Professor Alan G. MacDiarmid at the University of Pennsylvania, USA and Professor Hideki Shirakawa at the University of Tsukuba, Japan Awarded the Nobel Prize in Chemistry for 2000 “for the discovery and development of electrically conductive polymers”.

3.3 ELECTRICALLY CONDUCTING SOLIDS

Three simple carbon compounds are diamond, graphite and polyacetylene. They may be regarded, respectively, as three-, two- and one-dimensional forms of carbon materials. Diamond and graphite are modifications of pure carbon, while in polyacetylene one hydrogen atom is bound to each carbon atom. In many materials, macroscopic properties such as strength and optical and electrical properties generally depend on direction. They are said to be anisotropic. Diamond, which contains only σ bonds, is an insulator and its high symmetry gives it isotropic properties. Graphite and acetylene both have mobile π electrons and are, when doped, highly anisotropic conductors (Fig. 3.3). The conductivity is about one million times greater in the plane of the graphite rings than at right angles to this plane:σ (parallel)/σ(perpendicular) = 106. Correspondingly, the conductivity of stretch oriented polyacetylene is some 100 times higher in the stretch direction than perpendicular to it [2].

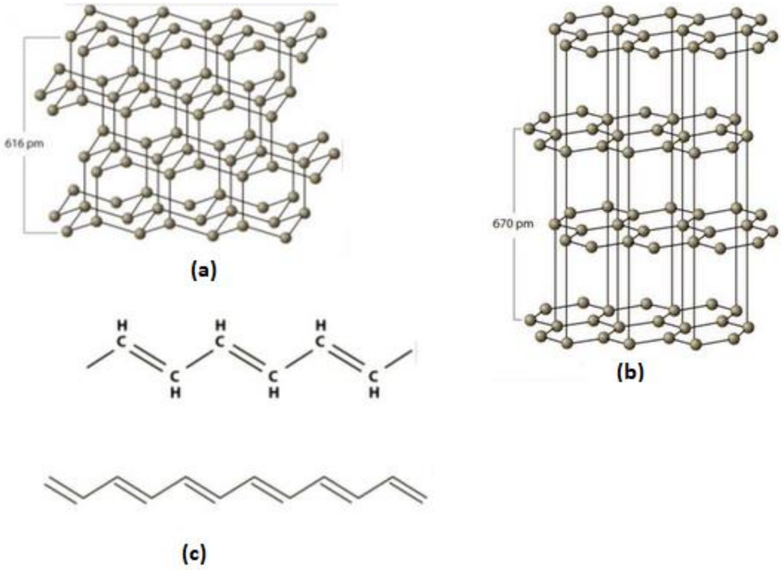


Fig 3.3 (a) Diamond lattice (b) Graphite lattice (c) Polyacetylene carbon polymers

In the early 1970s Shirakawa and co-workers made well-defined films of polyacetylene. They produced a copper-coloured film of all-cis-polyacetylene and also silvery all-trans-polyacetylene. Their conductivities were: cis-polyacetylene 10^{-8}-10^{-7} S.m^{-1} trans-polyacetylene 10^{-3}-10^{-2} S.m^{-1} (Fig. 3.4).

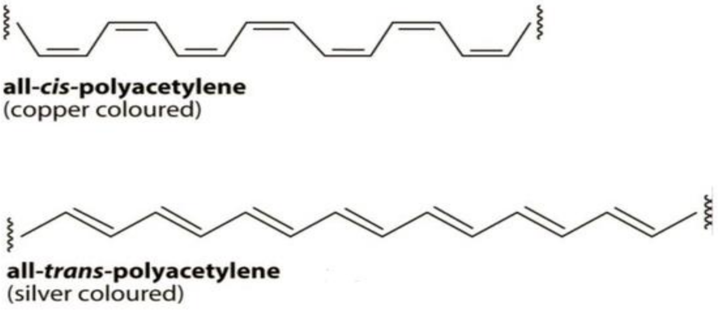


Fig. 3.4 Structure of cis and trans polyacetylene

In 1975 Professors Alan Heeger and Alan MacDiarmid collaborated to study the metallic properties of a covalent inorganic polymer. They shifted their attention to polyacetylene after MacDiarmid had met Shirakawa in Tokyo. MacDiarmid wanted to modify the polyacetylene by iodine treatment. Conductivity of 3000 $S.m^{-1}$ was measured for iodine-modified trans-polyacetylene, an increase of seven orders of magnitude over the undoped material. The seminal paper received for publication in 1977, had the title: Synthesis of electrically conducting organic polymers: Halogen derivatives of polyacetylene (CH)x. Doping cis-polyacetylene with AsF_5 resulted in an increase of conductivity by a factor of the high conductivity found by Heeger, MacDiarmid and Shirakawa clearly opened up the field of "plastic electronics". Polyacetylene remains the most crystalline conductive polymer but is not the first conductive polymer to be commercialized. This is because it is easily oxidized by the oxygen in air and is also sensitive to humidity. Polypyrrole and polythiophene differ from polyacetylene most notably in that they may be synthesized directly in the doped form and are very stable in air. Their conductivities are low, however: only around 10^4 $S.m^{-1}$, but this is enough for many practical purposes.

A key property of a conductive polymer is the presence of conjugated double bonds along the backbone of the polymer. In conjugation, the bonds between the carbon atoms are alternately single and double. The presence of C5 makes it impossible for the π electrons of the C6-C7 pi bond to join the conjugated system on the first four carbons (Fig. 3.5).

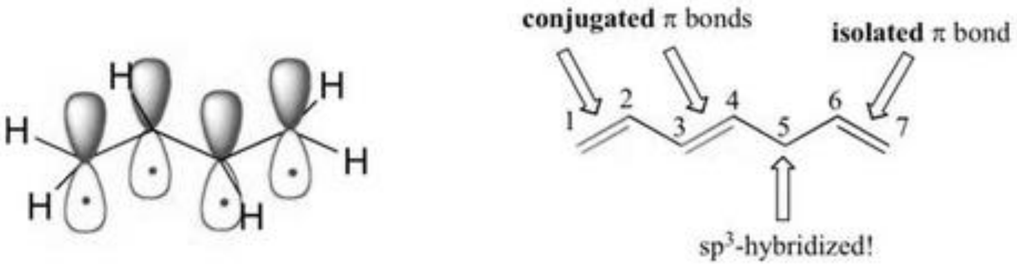


Fig. 3.5 C5 containing conjugated polymers

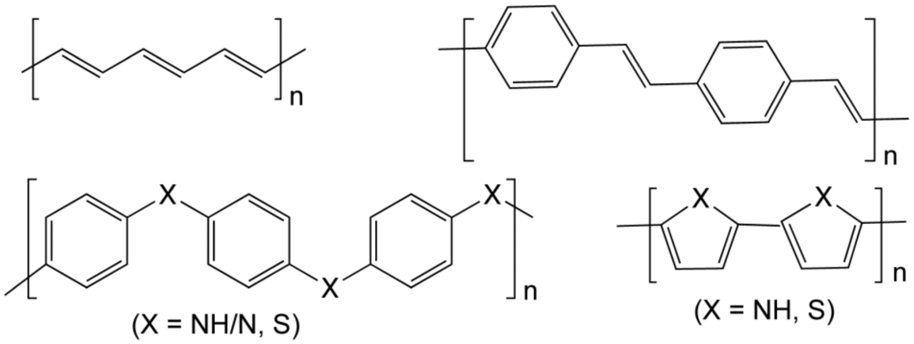


Fig. 3.6 Chemical structures of some conductive polymers. From top left clockwise: polyacetylene; polyphenylenevinylene; polypyrrole (X=NH) and polythiophene (X = S); and polyaniline (X = NH) and polyphenylene sulfide (X = S).

Conjugation is not enough to make the polymer material conductive (Fig.3.6). In addition – and this is what the dopant does – charge carriers in the form of extra electrons or "holes" have to be injected into the material. A hole is a position where an electron is missing. When such a hole is filled by an electron jumping in from a neighbouring position, a new hole is created and so on, allowing charge to migrate a long distance. The "doped" form of polyacetylene had a conductivity of 10^5 Siemens per meter, which was higher than that of any previously known polymer. As a comparison, teflon has a conductivity of 10^{-16} $S.m^{-1}$and silver and copper 10^8 $S.m^{-1}$.

The halogen doping that transforms polyacetylene to a good conductor of electricity is oxidation (or p-doping). Reductive doping (called n-doping) is also possible using, e.g., an alkali metal. The doped polymer is thus a salt. However, it is not the counter ions, I_3^- or Na^+, but the charges on the polymer that are the mobile charge carriers.

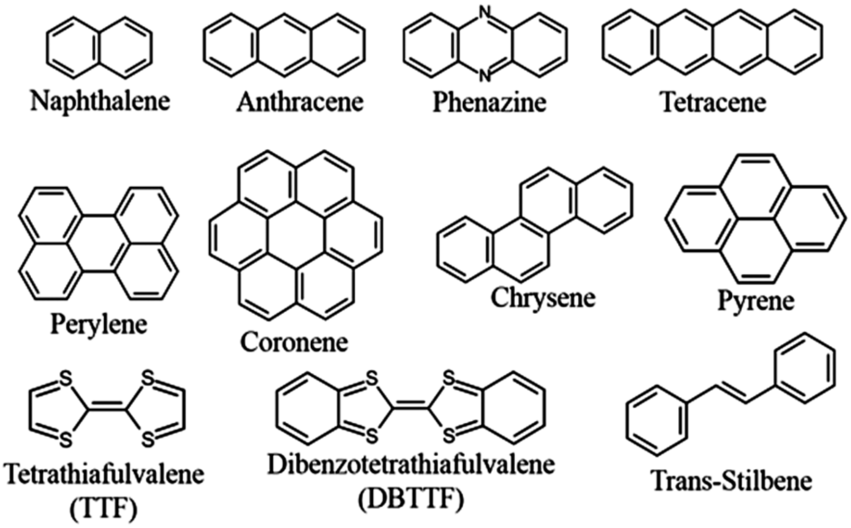
3.4 ORGANIC CHARGE TRANSFER COMPLEXES

A charge-transfer complex (CT complex) or electron-donor-acceptor complex is an association of two or more molecules, in which a fraction of electronic charge is transferred between the molecular entities. The resulting electrostatic attraction provides a stabilizing force for the molecular complex. Conductive polymers or, more precisely, intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors like insulating polymers, they are organic materials [3].

Charge-transfer complexes are combinations of charge donating (D) and charge-accepting (A) materials. While the parent compounds tend to be unipolar semiconductors, the CT complex can have entirely different properties; it can be an ambipolar semiconductor, a metal, or even a superconductor. The choice of donor and acceptor and their organization within the CT crystal are arguably the most important factors in determining its electronic properties. The electronic coupling between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor molecules yields a partial degree of charge transfer ρ between the two, which results in a ground state characterized by a partial ionicity, $D^{\rho+}A^{\rho-}$, where ρ is the degree of charge transfer. The ionization potential of the donor (ID) and the electron affinity of the acceptor (EA) dictate the magnitude of ρ, which in turn is responsible for the observed transport properties. A neutral or quasi-neutral CT, characterized by $\rho < 0.5$, is derived from a D: A combination with $I_D - E_A >> E_M$, where E_M is the electrostatic Madelung energy of the crystal.

On the contrary, when D–A combinations for which $I_D - E_A << E_M$ are employed, the resulting ρ is much greater and a quasi-ionic (D^+A^-), or ionic CT is obtained. The most common ration of D: A are 1:1 while other more complex ratios, such as 2: 1, 3: 1, and 3: 2, have been crystallized and studied, although Herbstein's count in 2005 suggested that the 1: 2 and 2: 1 ratio make up roughly 5% of all known CT compounds, while other ratios are even less common (Fg 3.7).

a) Examples of Donors



b) Examples of Acceptors

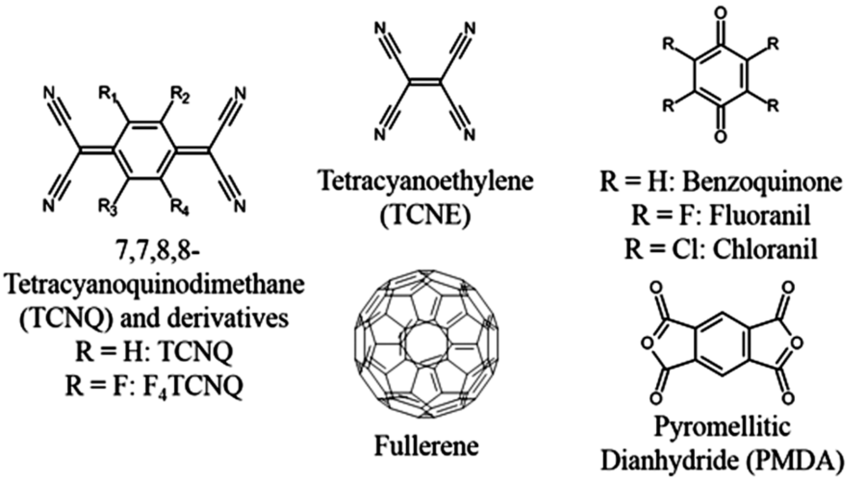


Fig: 3.7 Examples of some donors and acceptors in organic CT complexes

The first highly conductive organic compounds were the charge transfer complexes. In the 1950s, researchers reported that polycyclic aromatic compounds formed semi-conducting charge-transfer complex salts with halogens. In 1954, researchers at Bell Labs and elsewhere reported organic charge transfer complexes with resistivities as low as 8 ohms-cm. In the early 1970s, researchers demonstrated salts of tetrathiafulvalene show almost metallic conductivity, while superconductivity was demonstrated in 1980. Broad research on charge transfer salts continues today. While these compounds were technically not polymers, this indicated that organic compounds could carry current. While organic conductors were previously intermittently discussed, the field was particularly energized by the prediction of superconductivity following the discovery of BCS theory. In 1963 Australians B.A. Bolto, D.E. Weiss, and coworkers reported derivatives of polypyrrole with resistivities as low as 1 ohm·cm. There are multiple reports of similar high-conductivity oxidized polyacetylenes. With the notable exception of charge transfer complexes (some of which are even superconductors), organic molecules were previously considered insulators or at best weakly conducting semiconductors. Subsequently, DeSurville and coworkers reported high conductivity in a polyaniline. Likewise, in 1980, Diaz and Logan reported films of polyaniline that can serve as electrodes.

3.5 NEW SUPER CONDUCTORS

An organic superconductor is a synthetic organic compound that exhibits superconductivity at low temperatures. As of 2007 the highest achieved critical temperature for an organic superconductor at standard pressure is 33 kelvins, observed in the alkali-doped fullerene $RbCs_2C_{60}$. In 1979 Klaus Bechgaard synthesized the first organic superconductor $(TMTSF)_2PF_6$. Although superconductivity in organic conductors has been first stabilized under pressure, more detailed investigations of this phenomenon have been conducted in $(TMTSF)_2ClO_4$, the only compound of the 1D-Bechgaard salts series exhibiting superconductivity at ambient pressure below 1.2 K. Evidence for superconductivity in $(TMTSF)_2ClO_4$ came out from transport, specific heat measurements and Meissner flux expulsion [4].

Many materials may be characterized as organic superconductors. These include the Bechgaard salts and Fabre salts which are both quasi-one-dimensional, and quasi-two-dimensional materials such as k-BEDT-TTF_2X charge-transfer complex, λ-$BETS_2X$ compounds, graphite intercalation compounds and three-dimensional materials such as the alkali-doped fullerenes. Organic superconductors are of special interest not only for scientists, looking for room-temperature superconductivity and for model systems explaining the origin of superconductivity but also for daily life issues as organic compounds are mainly built of carbon and hydrogen which belong to the most common elements on earth in contrast to copper or osmium.

With the phase transition to a fully gapped density wave state occurring only at TSDW 12 K in $(TMTSF)_2PF_6$, the uniaxially-oriented SDW is suppressed with only modest pressure by worsening the nesting conditions. Superconductivity is stabilized at pressures greater than Pc ≈ 0:6 GPa. Antiferromagnetic spin fluctuations (SF) nevertheless persist to much greater pressures, and consequently, the Bechgaard salts are among the first known examples where superconducting pairing is often linked to magnetic interactions. Temperature/pressure phase diagram for $(TMTSF)_2PF_6$, showing the suppression of the spin density wave ground state with pressure, and the emergence of a superconducting state. The ground states of $(TMTSF)_2AsF_6$ evolve with pressure similarly (Fig.3.7).

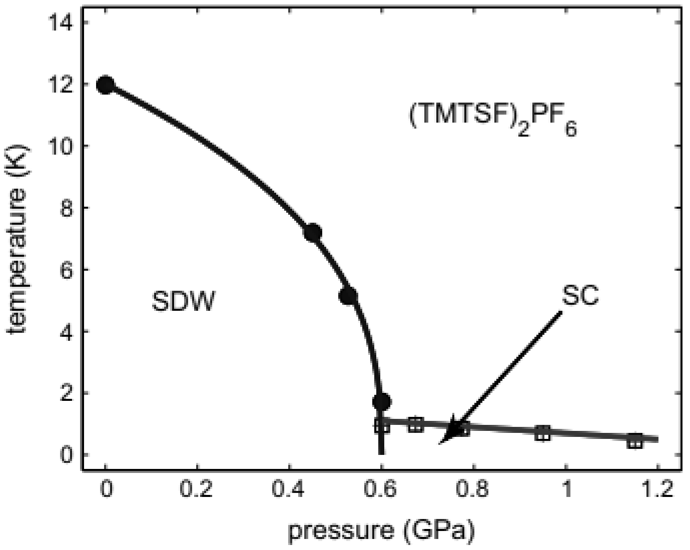


Fig. 3.7. The temperature/pressure phase diagram for $(TMTSF)_2PF_6$.

3.6 ORGANIC METALS

Understanding how organic compounds conduct electricity at all is the first step in appreciating the varied properties of organic superconductors. The charge-transfer salts are by far the largest and most diverse class of organic conductors or "organic metals." Organic conductors are graphite and its intercalation compounds and certain doped polymers. Charge-transfer salts are substances in which a donor molecule such as TTF transfers electrons to an acceptor molecule such as TCNQ to form a charge-transfer compound, TTF-TCNQ. Figure 3.8 shows these and other examples of donor (cation) molecules that combine with acceptor (anion) molecules to produce organic metals [5].

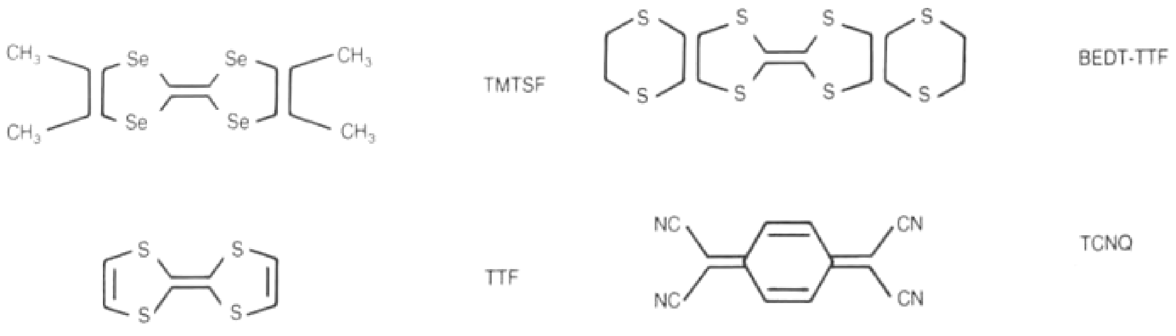


Fig 3.8 Donor-acceptor compounds tetramethyltetraselenafulvalene (TMTSF), tetrathiafulvalene (TTF) and bis(ethylenedithiolo)tetrathiafulvalene (BEDT-TTF), which are donors, and tetracyanoquinodimethane (TCNQ), which is an acceptor.

The large planar molecules of the charge-transfer compound can stack on top of one another like pancakes, allowing the transferred charge to move easily along the separate donor and acceptor stacks. In charge-transfer compounds made from sulfur- or selenium-based molecules. A conduction band forms due to the overlap of electron wave functions in the sulfur or selenium atoms that are made neighbors by the stacking. The partial filling of this band with electrons by charge transfer from donor to acceptor leads to the observed metallic conduction levels. The pancake-like stacking suggests that the charge-transfer salts are quasi one-dimensional. The overlap of orbitals, and hence the electron hopping rate, is greater along the stacks of molecules than it is between them, making the conductivity greater along the stack than in other directions. The best organic conductors have conductivity on the order of 2000 $\Omega^{-1}cm^{-1}$ at room temperature, or about three of magnitude smaller than that of copper. Below room temperature, the metallic conduction is usually interrupted by a transition to a semiconducting or insulating state. This transition, as we shall see, is intimately connected with the one-dimensional character of the materials.

The dark material in the photograph is a single crystal of the organic metal $(TMTSF)_2CIO_4$ (Fig.3.9). The four gold wires attached with gold paste are for electrical-conductivity measurements along the direction of highest conductivity. This typical crystal is 4 mm long, 0.2 mm wide and 0.05 mm thick. The crystals are prepared by electrochemical growth in solution, yielding very small single crystals that are perfect but quite brittle. The photo above shows crystals grown on a platinum electrode from a solution (highly diluted for the photo) of BEDTTFF with triiodide anions. The largest crystal is β-$(BEDT\text{-}TTF)_2$, I_3. The black color is a result of the strong absorption of visible light in the crystalline state.

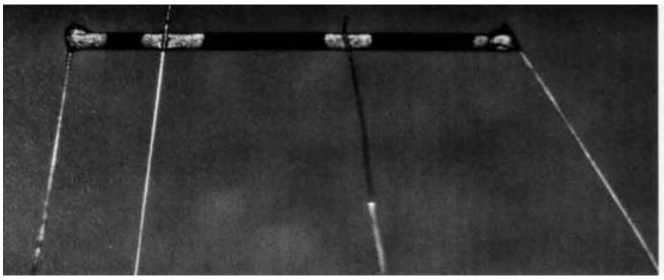


Fig. 3.9 A single crystal of the organic metal $(TMTSF)_2CIO_4$

3.7 MAGNETISM IN ORGANIC MATERIALS

TDAE-C_{60}: a compound comprising spherical carbon cages attached to an organic molecule known as tetrakis-dimethylamino-ethylene (Fig. 3.10). Since its identification in 1991, many theoretical and experimental studies have provided some insight into the mechanism driving this unexpected ferromagnetism, but the explanation was not definitive. A full understanding would help materials scientists to develop more advanced magnetic materials in the future.

“A precise model for organic magnetism could aid the design of high-density recording materials for use in next-generation memories,”

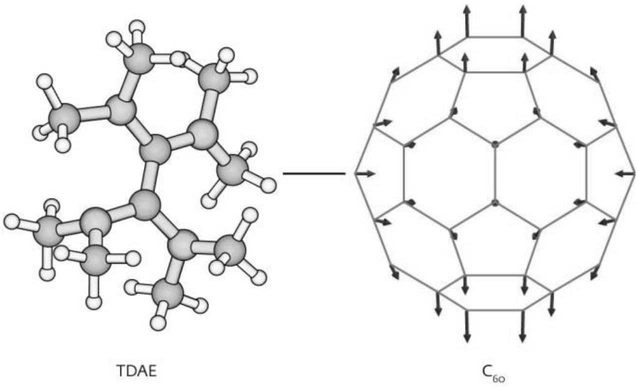


Fig.3.10 A compound comprising C60 (right), a spherical molecule of carbon atoms, and TDAE (left), tetrakis-dimethylamino-ethylene, is unusual because it can display magnetic behavior at low temperatures.

3.8 FULLERENES

Fullerene is a spherical carbon compound and is an allotrope of carbon such as diamond, graphite and carbon nanotubes. Fullerenes of C_{60}, C_{70} and C_{84} are well known (Fig.3.11). They are isolable carbon compounds in a sole molecular species. A fullerene is a pure carbon molecule C20 being the smallest one. Fullerenes are closed hollow cages consisting of carbon atoms interconnected in pentagonal and hexagonal rings. Among them, the C_{60} is a representative species, it is most famous fullerene and known as bucky ball. The shape of C60 resembles the geodesic dome structure based on hexagons and pentagons designed by Fuller in1960's FULLERENE C60 [6].

In 1996 Curl, Kroto and Smalley was awarded the Nobel Prize in chemistry to for their discovery of fullerenes. C60 was named buckminsterfullerene in honour of Buckminster Fuller. The shortened name ‘fullerene is used to refer to the family of fullerenes. The structure of fullerene was suggested to be like a soccer ball: a spherical shape that can be made using 12 pentagons and 20 hexagons 1985 British chemist Sir Harold W. Kroto and the colleagues Richard E. Smalley and Robert F. Curl, Jr., discovered fullerene by using pulsed laser to vaporize graphite rods in an atmosphere of helium gas.

The fullerene hybridization is not fixed but has variable characteristics depending on the number of carbon atoms in the molecule (Fig.3.12). Each carbon is part of one pentagon and two hexagons, each has two single bonds and one double bond for the traditional carbon valence of four. C60 contains 60 vertices for the carbon atoms and 90 covalent bonds between them, 60 single bonds and 30 double bonds. It contains 12 pentagons surrounded by 20 hexagons. C60 contains two types of bond lengths: 0.140 +/- 0.0015 nm for the bond between the six-membered rings and 0.145 +/-0.0015 nm for the bonds between five- and six-membered rings. The pentagonal rings contain only single bonds; double bonds have a shorter bond length and lead to instability in the pentagonal ring. A. Top portion (1 pentagon, 5 hexagons) B. Midpotion (10 hexagons, 10 pentagons) C. Bottom portion (1 pentagon, 5 hexagons)

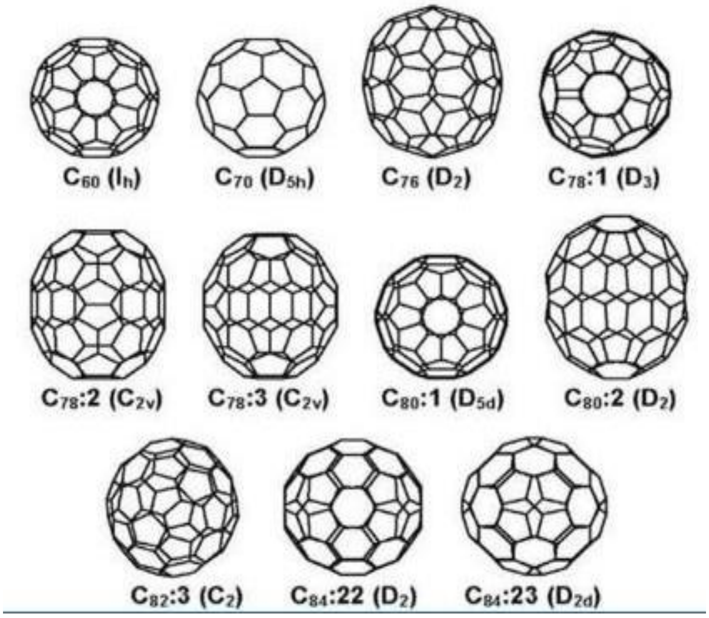
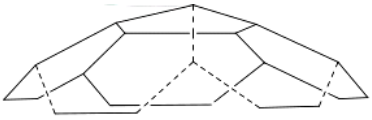


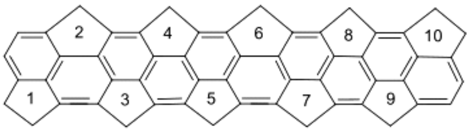
Fig.3.11 Structure of some common Fullerene

3.8.1 Properties of Fullerenes:

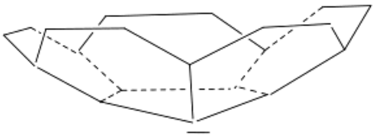
- Can be compressed to lose 30% of its
- Exists as a discrete molecule unlike the other two allotropes of carbon (graphite and diamond)
- Very tough and thermally stable
- Forms deep magenta solution in benzene
- A black powdery material



A. Top portion (1 pentagon, 5 hexagons)



B. Midpotion (10 hexagons, 10 pentagons)



C. Bottom portion(1 pentagon, 5 hexagons)

Fig. 3.12 Detailed structure of C60

- The most specific feature of fullerene is that it is an excellent electron acceptor. Any fullerenes are n-type semiconductors, which are suitable for organic electronic materials with electron carriers.

- Rubidium- and cesium-doped fullerenes can be superconductors with electron carriers. These superconducting transitions occur at more than 30 K.

3.8.2 Applications of Fullerenes

- Researchers have found that water-soluble derivatives of fullerenes inhibit the HIV-1 protease (enzyme responsible for the development of the virus) and are therefore useful in fighting the HIV virus that leads to AIDS

- Used in electronic, microelectronic and non-linear optical devices

- Used as a soft ferromagnet (TDAE C60)

- As a superconductor when mixed with alkali metals

- As a lubricant due to its spherical structure -the buckyballs act as a molecular ball bearing

3.9 DOPED FULLERENES AS SUPERCONDUCTORS

Doping is used to modify the electronic properties of the fullerene molecule and bulk crystals. Doped fullerene crystals are also known as fullerides. A new kind of molecule-based superconductor was initiated by the discovery of superconductivity in alkali-metal-doped fullerene with low transition temperatures. Fullerene superconductors exhibit a number of features that are also exhibited by organic superconductors. The similarity between these superconductors is derived from the fact that the principal conducting carriers are pie electrons. In both cases, big molecules each with a large number of freedoms are assembled, forming relatively narrow bands with a low electron density. The unique structure of the C_{60} molecule and crystal allow the possibility of doping in, at least, four different ways [7].

3.9.1 Intercalation

Dopants are located between the C_{60} molecules in the interstitial positions of the host crystal structure. Intercalated fullerides may be produced by the simultaneous vacuum evaporation of C_{60} molecules and dopant atoms or diffusion of dopant atoms into pristine C_{60} crystal. Impurity diffusion may occur as a spontaneous process or it can be induced by an external stimulus, like vapor pressure or an electric field applied to the sample. There has been a considerable research effort to study M_3C_{60} compounds (where M is an alkali or alkali-earth metal) since the discovery of superconductivity in these compounds. Several stable crystalline phases for C_{60} intercalated with alkaline or alkaline-earth metals have been reported. The resultant solid may retain the *fcc* structure of the pristine crystal or transform into *bct, bcc* or *sc* structure. However, charge transfer from the dopant to the C_{60} host is observed only in vacuum conditions because of the fast oxidation of the system. Intercalation of C_{60} fullerite by metals, other than alkaline or alkaline-earth, nonmetal elements (S, Te, halogens), inorganic (H_2, N_2, H_2O, CO, $SbCl_5$, ASF_5, $InCl_3$) and even organic (cationic dye “pyronin B (PyB)”) molecules have been also reported.

3.9.2 Endohedral Doping

The dopant goes inside a fullerene molecule (Fig. 3.13a). Since initial discovery in 1985 that La atoms might be trapped inside the molecule to form endohedral $La_2@C_{60}$ and $La@C_{60}$, the synthesis of many endofullerenes has been reported (e.g., $M@C_{60}$, where M = Ca, Y, Ba, Ce, Pr, Nd, Gd, Er, Eu, Dy; $R@C_{60}$, where R = N, P; $X@C_{60}$, where X = He, Ne, Ar, Kr, Xe). In the most of techniques endofullerenes are produced at the technological step of the molecule formation. Another approach which is developed by Cambell et al. suggests endofullerene synthesis by low energy ion implantation of C_{60}. Growth of thin films of $Li@C_{60}$ produced by this technique have been already demonstrated. In Sections 5 and 6.3, we will briefly discuss growth, crystalline structure and semiconductor properties of thin films of some endofullerenes which could be used in photovoltaic solar cells, for example, $Dy@C_{82}$ (see

Section 10.2). Here we would like to note only those properties of endoffulelrenes could be strongly affected by the dopant atom position with respect to a fullerene cage.

3.9.3 Substitutional Doping

Noncarbon atom replaces one (Fig. 3.13b) or more of the carbon atom on the surface of the molecule. This kind of doping is common for Group IV semiconductors, such as Si or Ge. Already in 1991 Smalley's group reported on the preparation and mass spectroscopy identification of *heterofullerene* $C_{59}N$ and $C_{59}B$ molecules. Shortly thereafter, the electronic structure for these compounds was calculated. An electronic behavior similar to that of deep donor and acceptor levels in doped semiconductors was predicted. The publication on a method for the production of $C_{59}N$ in bulk quantities provided a possibility to grow thin films and investigate the electronic structure and properties of the material. Unfortunately, such a study concluded that a dimer formation which prevents donation of an extra electron is observed in the solid state. However, recently such novel heterofullerenes as $C_{48}N_{12}$ and $C_{50}Cl_{10}$ were synthesized in large quantities. It was demonstrated that the HOMO–LUMO band gap for $C_{48}N_{12}$ is of 1 eV and *fcc* solid of $C_{48}N_{12}$ is an n-type semiconductor material. Since $C_{48}N_{12}$ is a good electron donor, it was suggested that a molecular rectifier can be formed in contact with an acceptor $C_{48}B_{12}$. Photovoltaic cell with a heterojunction $C_{48}N_{12}/C_{48}B_{12}$ was also theoretically suggested.

3.9.4 Adductive or Exohedral

Bonding to the outside of the C_{60} molecule is demonstrated to produce the exohedral complexes of C_{60} with metals and an extremely wide variety of organic molecules and can be considered as the fourth type of doping.

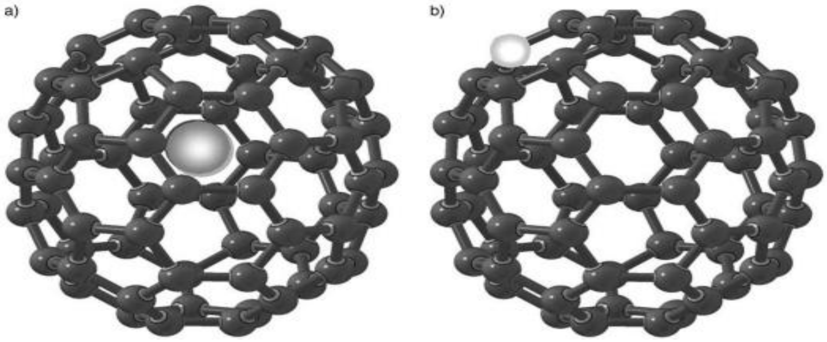


Fig. 3.13 Endohedral (a) and substitutional, (b) doping of C_{60} molecule

The one molecule composed of 3 alkalines for one fullerene is superconducting. For instance, Rb_3C_{60} has a critical temperature Tc of 27 K (-246°C). If a strong pressure is applied to the compound Cs_3C_{60}, the Tc can even increase to 40 K. The molecular structure of this compound gives it significant superconducting properties. Now it is accepted that the interaction responsible for the electron pairing is located on the ball and was caused by the vibration modes of the ball. In order to try and increase the Tc, attempts to insert Cs (the biggest alkaline ion) were made, but it was only in 2008 that the synthesis of Cs_3C_{60} compounds was achieved. The most surprising part was that the space between C_{60} was so big that the electrons were pinned to the balls and prevented them from relocating. At atmospheric pressure, the Cs_3C_{60} compound was hence both insulating and magnetic (Fig. 3.14). However, under a stronger pressure, the compound becomes a superconducting metal with a maximum Tc of 35 K (-238°C). This transition from an insulator to a metal (Mott transition) reminds of what happens in cuprates, pnictides, and heavy fermion compounds. When pressure is applied to the fullerene, the intermolecular distance is shortened, the electrons start moving, and the fullerene is transformed into a metal and exhibits superconductivity. The superconductivity of this fullerene with a high Tc is related to its electrical properties, which enable its transformation from an insulator to a metal (Fig. 3.15). Hole doped fullerenes exhibit higher critical temperature than electron doped fullerenes. A hole doped C_{60} superconducting system $C_{60}/CHBr_3$, this exhibited very high critical temperature Tc = 117K at ambient pressure. It is the greatest Tc for an organic superconductor with a buckyball doped with holes and intercalated with $CHBr_3$.

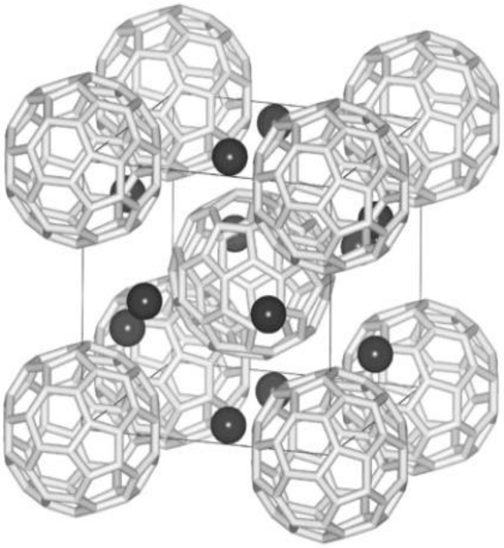


Fig. 3.14 Structure of Cs doped fullerene compound Cs_3C_{60}. [The grey spheres in the shape of a soccer ball indicate fullerene molecules. The black spheres indicate cesium atoms].

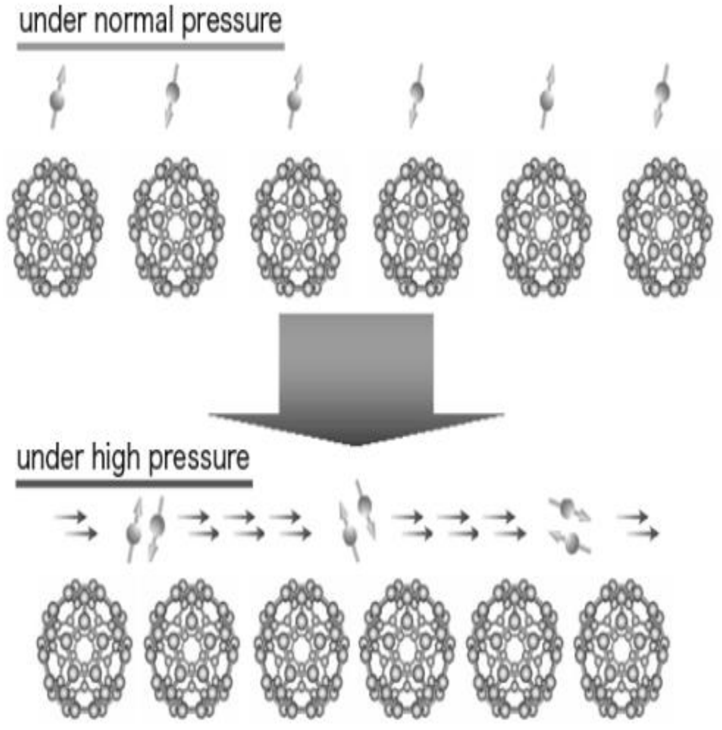


Fig 3.15: Change in electronic state of Cs3C60 with respect to pressure clarified in this experiment

3.10 MOLECULAR RECTIFIERS AND TRANSISTORS

Many organic solids are semiconductors, just think of phthalocyanines, the photoconductive properties of which are the basis for our copy machines and laser printers. A large impact on the field of molecular electronics emerged from organic charge transfer salts like TTF-TCNQ. The compound TTF (tetrathiafulvalene) is an organic donor and TCNQ (tetracyanoquinodimethane) an acceptor. Crystals of TTF-TCNQ are composed of alternating stacks of TTF and TCNQ, and electrons are transferred from the donor to the acceptor moiety. Because of this charge transfer there are partially filled bands for both of the stacks and the material behaves as an organic metal. Fig. 3.16 presents a didactic route from TTF-TCNQ crystals to rectifying molecules: the mixed crystal with sequence DADADADA is metallic. If we could arrange all donors on one side and all acceptors on the other side, with sequence DDDAAA, we would have the analog to a semiconductor pn junction. Of course, for a rectifying device we do not need the bulk crystal, a bilayer DA will do, and if we link donor and acceptor by a covalent bridge, we have a ‘rectifying molecule’ [7].

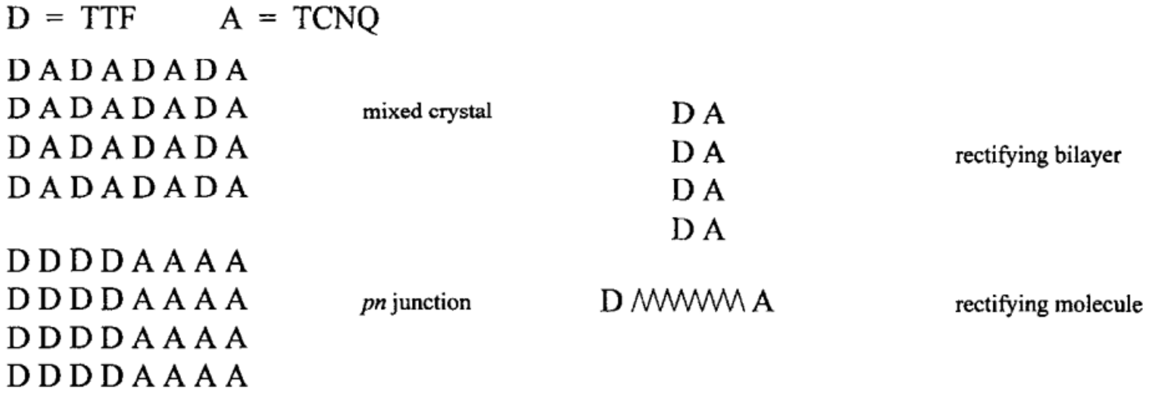


Fig. 3.16 Didactic route from bulk TTF-TCNQ crystal to rectifying molecule.

Three types of rectifying molecules have been reported:

3.10.1 D-σ-A molecules

These are molecules with a 'sigma' bridge between donor and acceptor, as in the Aviram-Ratner proposal. A u bridge is a bridge with saturated bonds. Such molecules have two separated IT systems: one at the donor, the other at the acceptor moiety (Fig. 3.17).

3.10.2 D-π-A molecules

Here the bridge is also a n conjugated system (unsaturated bonds, regular alternation of single and double bonds) and the donor and acceptor n systems are strongly coupled. There is electron transfer from donor to acceptor, both moieties are ionized, the molecule is called 'zwitterionic' (Fig. 3.18).

3.10.3 Only π system rectifier

Molecules with only one π system, which must be asymmetrically placed between the two external electrodes (Fig. 3.19).

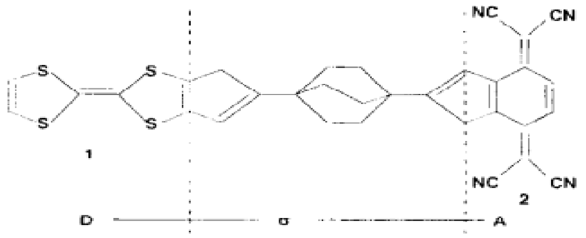


Fig. 3.17 D-σ-A rectifying molecules

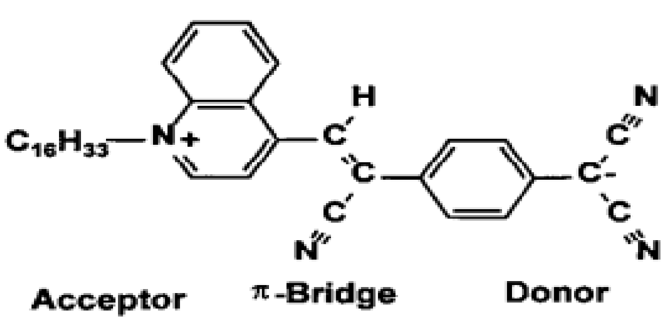
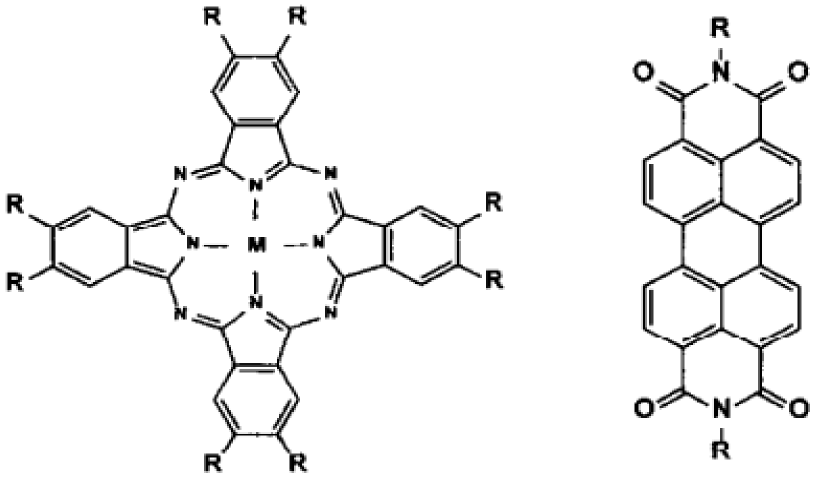


Fig. 3.18 D-π-A rectifying molecules



PcPd: M=Pd, R=OC_5H_{11}

PTCDI-OEt: R=CH_2-CH(OEt)$_2$
PTCDI-SPent: R=CH_2-CH(SPent)$_2$

Fig. 3.19 Only π system rectifier

Transistors are that in which current-voltage characteristics can be modulated by bringing a gate electrode close to the ‘active’ molecule and changing the potential there. Fig. 3.20 shows such a set-up in which carborane is incorporated as ‘cluster molecules’ into a Langmuir-Blodgett film. Electrons tunnel from the STM tip through the molecular orbitals of carborane into the graphite substrate. A gold layer near the tip acts as gate electrode. The oscillations in trace (1) demonstrate how the tunneling current is modulated by changing the gate potential. Trace (2) corresponds to a blind experiment when the STM tip is over an inert part of the film and when only noise is observed. Another ‘molecular transistor’ has been investigated. Carbon nanotubes were deposited over a Si/SiO, substrate with a lithographic array of Pt electrodes on a sub-micrometer scale. One of the nanotubes came to lie over two platinum electrodes so that tunneling experiments Pt-nanotube-Pt could be carried out.

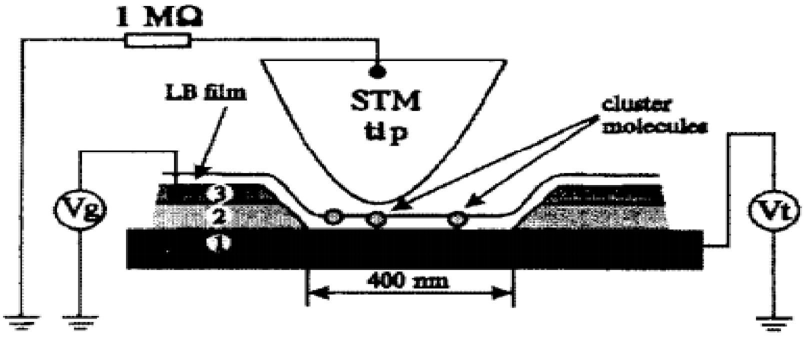


Fig. 3.20 Molecular transistor' based on the cluster molecule carborane. The STM tip acts as source, the graphite substrate (1) as drain, and the gold layer (3) as gate. Layer (2) is an insulating SiO_2, film.

3.11 ARTIFICIAL PHOTOSYNTHETIC DEVICES

Artificial photosynthesis is a chemical process that biomimics the natural process of photosynthesis to convert sunlight, water, and carbon dioxide into carbohydrates and oxygen. The term artificial photosynthesis is commonly used to refer to any scheme for capturing and storing the energy from sunlight in the chemical bonds of a fuel (a solar fuel). Artificial photosynthesis was first anticipated by the Italian chemist Giacomo Ciamician during 1912 [8].

Global energy needs are expected to double over the next 40 years and to account for this rise in global energy usage and renewable energy utilization, initiatives focused on finding cost-effective, carbon-neutral, geo-politically favorable energy sources are critically important. The most important renewable energy resource is the sun and the conversion of only a small fraction of this available solar energy to a usable fuel source would dramatically change the inherent energy infrastructure, while helping to reduce emission of greenhouse gases associated with fossil fuel consumption. Solar fuels are storable fuels produced using solar energy that can indirectly generate usable fuels through biomass. Alternatively, the direct conversion of solar energy into fuels through a fully integrated system is known as artificial photosynthesis. Artificial photosynthesis applies the principles that govern natural photosynthesis to develop a man-made technology. It strives to be a viable fuel source based on the consumption of abundant resources: solar energy, water, and carbon dioxide. Artificial photosynthesis takes advantage of the efficient primary solar energy conversion steps of photosynthesis, but does not use energy to sustain life as does the natural process, nor does it necessarily require the land usage associated with biomass production.

Artificial photosynthesis produces fuel *via* two main pathways: carbon dioxide reduction to ultimately yield hydrocarbons and water oxidation to generate hydrogen. At pH = 0, water splitting can be described by the following overall equation:

$$2H_2O \leftrightarrow 2H_2 + O_2 \qquad E° = 1.23\ \text{V vs. NHE}\ (1)$$

In (artificial) photosynthesis, sunlight provides the required energy (kinetic and thermodynamic) to drive the reaction in the forward direction and split water into hydrogen and oxygen. Expansion of equation 1 demonstrates that it is the summation of two underlying half-reactions:

$$2H_2O \leftrightarrow O_2 + 4H+ + 4e- \qquad E_{ox} = 1.23\ \text{V vs. NHE}\ (2)$$

$$2H+ + 2e- \leftrightarrow H_2 \qquad E_{red} = 0.00\ \text{V vs. NHE}\ (3)$$

These reactions show that converting water to hydrogen and oxygen is a multi-step, multielectron process that not only needs energy to perform redox chemistry, but also requires different redox catalysts. These catalysts facilitate each of the above multi-electron half-reactions, where one catalyst evolves molecular oxygen by oxidizing water (equation 2) and a second catalyst generates hydrogen (equation 3) by reducing protons. Similar to natural photosynthesis, artificial photosynthesis uses light absorbing molecules and/or materials to capture light and produce a charge separation. Then, through a series of inter-/intramolecular charge transfer reactions these charges are transported to catalytic sites to provide the requisite oxidizing/reducing energy to evolve oxygen or hydrogen. Fig. 3.21 illustrates a proposed, fully-integrated model device architecture. When high energy blue light is absorbed by a photoanode material, charge separation occurs that drives water splitting to generate protons and molecular oxygen. The remaining low energy red light then passes through the photoanode to reach a second molecular interface that selectively absorbs this light and serves to pump protons through a semi-permeable membrane. In the second compartment, a proton reduction catalyst reduces these protons to generate molecular hydrogen fuel. This example device architecture illustrates the complexity of integrating light capture, charge separation, and catalysis in a compartmentalized integrated artificial photosynthetic device that optimizes both efficiency and cost to increase the commercial viability of the technology.

The artificial photosynthesis system includes an enzyme bed reactor to fix CO_2 in the air and CO_2 recovered directly from the atmosphere to achieve a fully closed CO_2 cycle, as observed in photosynthesis. Integrated photodriven CO_2 capture and reduction systems capable of removing and using CO_2 directly from the atmosphere need to be developed to achieve solar fuels formation.

3.12 OPTICAL STORAGE MEMORY AND SWITCHES

Optical digital data storage, for example CD or DVD, is extensively used in the recordings of music, movies, and others. Jn three-dimensional high resolution, the use of two-photon absorbing photochromic molecules is preferred. as there are several photochromic molecules having good properties for memory. The continuously increasing amount of data to be stored digital optical data storage is a promising method, where recording of information is carried out by the use of light. One of the most important challenges in this field is the development of materials and techniques to place as much data as possible on the least amount of material. The ultimate goal would be to achieve information storage at the molecular or even at the atomic level,' whereas processing of data should occur at close to the speed of light by the use of all optical switching devices.

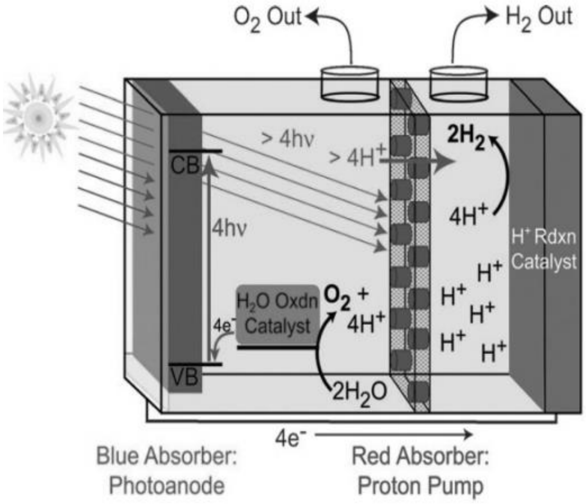


Fig. 3.21 Model artificial photosynthetic water splitter.

The most widely investigated materials at present, for these purposes, are based on alloys of rare earth elements and transition metals as the recording substrate thereby combining the magnetic and optical recording techniques. Although some problems still remain to be solved, and future developments will aim at further increasing the rates of data storage and storage densities. During recent years the design and synthesis of organic compounds for applications as useful synthetic building blocks in optical devices. Some typical features of organic materials are: the ease of fabrication, the possibility to shape organic compounds into the desired structures make it suitable candidates for optical storage memory and switches.

3.13 MOLECULAR SWITCHES

For the development of a molecular switching or optical data storage device it involves the design and synthesis of molecules, followed by incorporating these compounds into supramolecular assemblies, in order to obtain ordered molecular systems. The synthesis of molecular switches and molecular storage elements can give answers to fundamental questions on the level of molecular and nanoscale dimensions and leads to further developments of model concepts with respect to possible modes of operation of molecular memories. The basic requirement for a switch is bistability, i.e., the occurrence of two different forms of a molecule, which can be interconverted by means of an external source. Any material or device that has two stable states which can be reversibly switched from one state to another and which states at any instant can be identified, can in principle be used as a memory element in a digital computer using binary logic. This is illustrated A and B represent the two different forms of a bistable system, whereby S1 and S, refer to different stimuli to affect the reversible switching behavior.

$$\mathbf{A} \underset{S_2}{\overset{S_1}{\rightleftharpoons}} \mathbf{B}$$

The bistability might be based on various properties of molecules like electron transfer, isomerization, differences in complexation behavior and photocyclixations, whereas light, heat, pressure, magnetic or electric fields, chemical reactions etc. can be used to achieve the change in the bistable state. The most important requirements for the use of photochromic compounds as molecular switches are:

- photochemical switching between the two forms should be possible.
- no thermal interconversion of the isomers should occur in a large temperature range, allowing storage of information almost infinitely.
- the isomers should be fatigue resistant, with the possibility to perform the write/erase cycle many times, and no thermal or photochemical degradation to any side products should occur. both forms should be readily detectable.
- a non-destructive read-out procedure should be available; this read-out method should not interfere with or erase the written data. high quantum yields should be achieved, allowing an efficient switching process and avoiding the necessity of long irradiation times.
- fast response times should be reached, leading to fast switching cycles. retention of all the properties is necessary when the switchable compound becomes part of a macromolecular structure.

Typical examples of reversible photochromic processes are cis-harts isomerizations like in olefinic compounds, stiblenes, azobenzenes and photocyclization reactions like in photochromic valance tautomerisim, Fulgides, diarylakenes, azulenes, Spiropyrans etc (Fig.3.22).

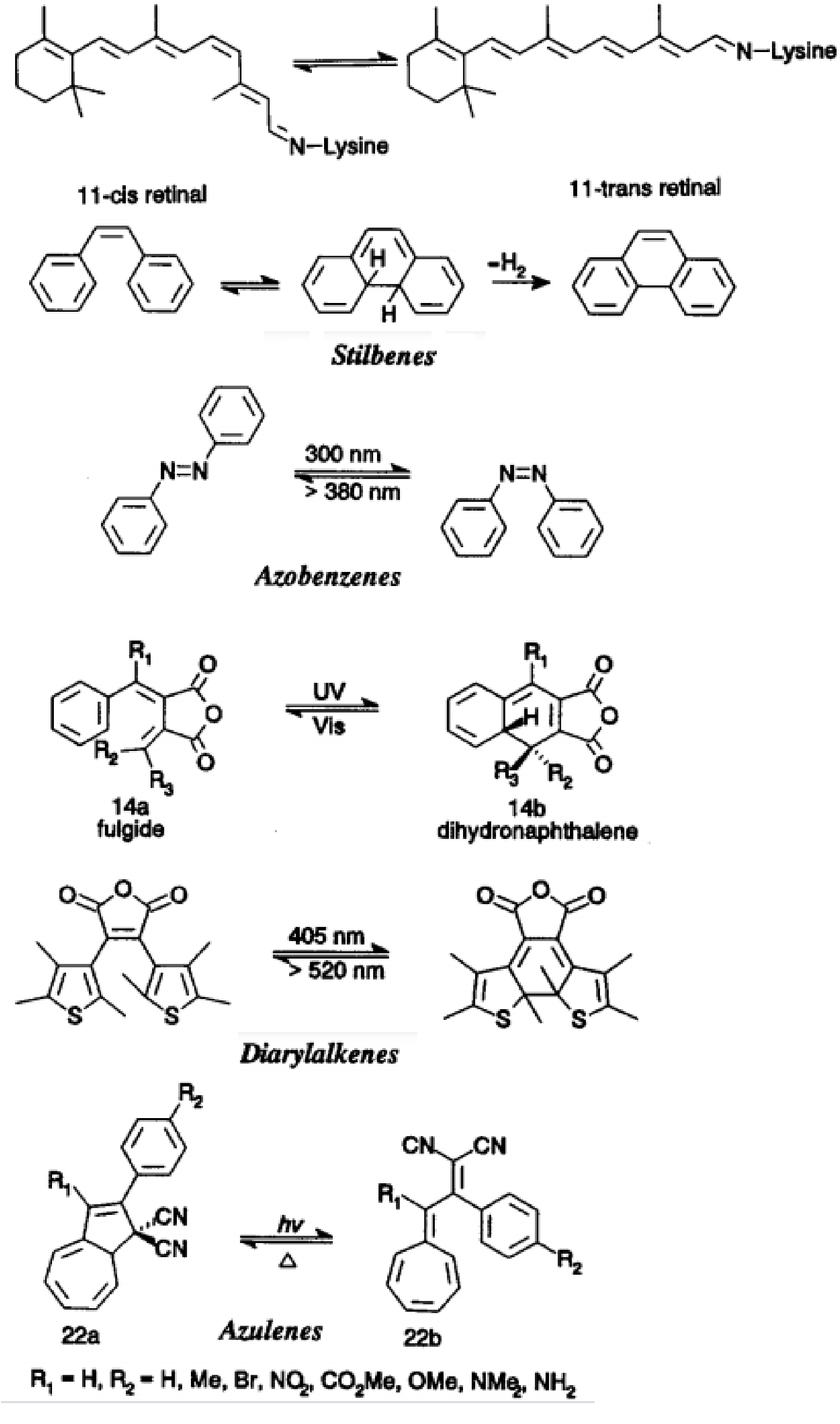


Fig. 3.22 Structures of some important reversible photochromic processes

3.14 SENSORS

A sensor is a device that responds to any change in physical phenomena or environmental variables like heat, pressure, humidity, movement etc. This change affects the physical, chemical or electromagnetic properties of the sensors which is further processed to a more usable and readable form. Sensor is the heart of a measurement system. It is the first element that comes in contact with environmental variables to generate an output. The temperature sensitivity of electrical resistance in a variety of materials was noted in the early 1800s and was applied by Wilhelm von Siemens in 1860 to develop a temperature sensor based on a copper resistor [9].

“A sensor is a device that receives a signal or stimulus and responds with an electric signal”

Sensors measurement system is composed of an input device, which senses the environment or surrounding to generate an output and, a signal processing block which processes the signal from input device and an output device which presents the signal to human or machine operator in a more readable and usable form.

Fig. 3.23 Block diagram of input/output device

Sensors are used to measure a particular characteristic of any object or device. The signal produced by the sensor is equivalent to the quantity to be measured. For example, a thermocouple will sense heat energy (temperature) at one of its junctions and produce equivalent output voltage which can be measured by a voltage read by the voltmeter (Fig.3.23).

All sensors need to be calibrated with respect to some reference value or standard for accurate measurement (Fig.3.24).

Analogue sensors tend to produce output signals that are changing smoothly and continuously over time. These signals tend to be very small in value from a few mico-volts (uV) to several milli-volts (mV), so some form of amplification is required. Then circuits which measure analogue signals can be easily converted into digital type signals for use in micro-controller systems by the use of analogue-to-digital converters, or ADC’s.

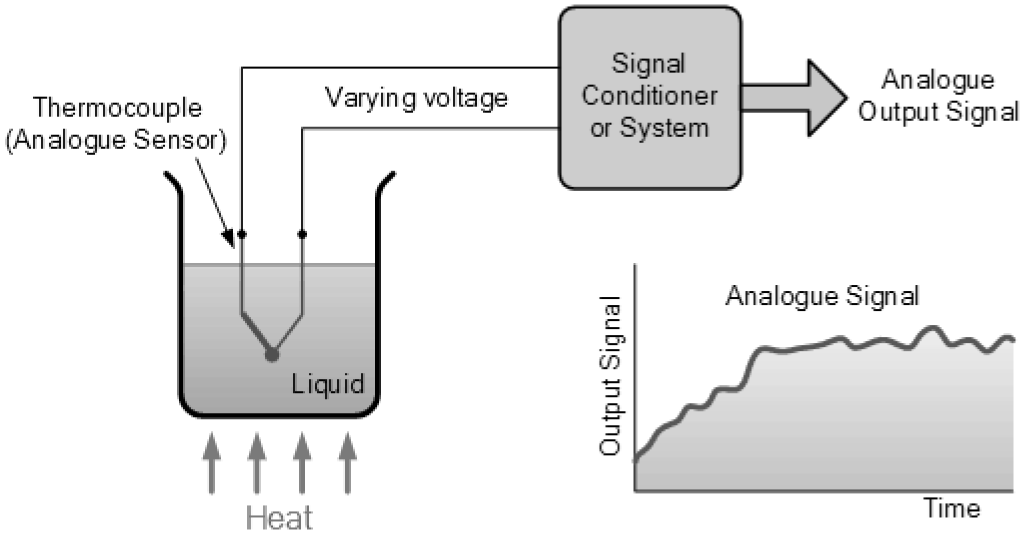


Fig. 3.24 Thermocouple (Analogue Sensor)

3.14.1 Characteristics of Sensors

A good sensor should have the following characteristics

1. High Sensitivity: Sensitivity indicates how much the output of the device changes with unit change in input (quantity to be measured). For example, the voltage of a temperature sensor changes by 1mV for every 1oC change in temperature than the sensitivity of the sensor is said to be 1mV/oC.
2. Linearity: The output should change linearly with the input.
3. High Resolution: Resolution is the smallest change in the input that the device can detect.
4. Less Noise and Disturbance.
5. Less power consumption.

3.14.2 Types of Sensors

Sensors are classified based on the nature of the quantity they measure. Following are the **types of sensors** with few examples.

Sensor classification

Based on the quantity being measured

- Temperature: Resistance Temperature Detector (RTD), Thermistor, Thermocouple
- Pressure: Bourdon tube, manometer, diaphragms, pressure gauge
- Force/ torque: Strain gauge, load cell
- Speed/ position: Tachometer, encoder, LVDT
- Light: Photo-diode, Light dependent resistor

3.14.3 Active and passive sensors

Based on power requirement sensors can be classified as active and passive. Active sensors are those which do not require external power source for their functioning. They generate power within themselves to operate and hence called as self-generating type. The energy for functioning is derived from the quantity being measured. For example, piezoelectric crystal generates electrical output (charge) when subjected to acceleration. Passive sensors require external power source for their functioning. Most of the resistive, inductive and capacitive sensors are passive (just as resistors, inductors and capacitors are called passive devices).

3.14.4 Analog and digital sensor

An analog sensor converts the physical quantity being measured to analog form (continuous in time). Thermocouple, RTD, Strain gauge are called analog sensors. A digital sensor produces output in the form of pulse. Encoders are example of digital sensors (Fig.3.25).

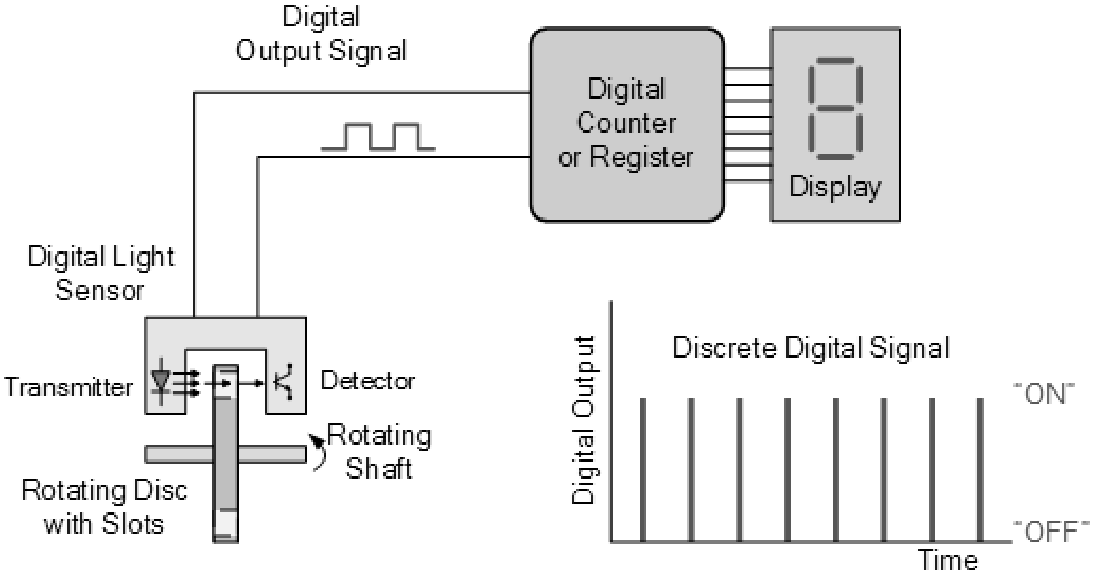


Fig. 3.25 Digital Sensors

3.14.5 Inverse Sensors

There are some sensors which are capable of sensing a physical quantity to convert it to other form and also sense the output signal form to get back the quantity in original form. For example, a piezoelectric crystal when subjected to vibration generates voltage. At the same time when a piezo crystal is subjected to varying voltage they begin to vibrate. This property makes them suitable to use in microphone and speakers.

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3.16 QUESTIONS

1. Describe the properties of electrically conducting organic polymers.

2. Draw the chemical structures of some conductive polymers.

3. Discuss the choice of donor and acceptor and their organization in charge transfer complexes.

4. Discuss Magnetism in Organic Materials.

5 Describe variable characteristics of fullerenes and structures of some common fullerens.

6. What are Molecular Rectifiers and Transistors, discuss there theories with suitable examples.

7. Discuss the process of artificial photosynthesis scheme for capturing and storing the energy.

UNIT 4 DIFFRACTION TECHNIQUES

CONTENTS

4.1 OBJECTIVES

Students will become familiar with the types of information that x-ray diffraction can provide on the structure of a wide variety of samples.

Students will learn to interpret real data and extract structural information.

Learning of structure of simple lattices andits relation with X-ray intensities.

Understanding of solid-state matter in terms of crystallinity and bonding

4.2 INTRODUCTION

In November 1895, Wilhelm Röntgen discovered X-rays while working at the University of Wurzburg, Germany. Röntgen was investigating cathode rays in different types of evacuated glass tubes and trying to determine their range in air. He noticed that while the rays were being produced, a screen coated in fluorescent barium platinocyanide would glow. He was intrigued because the screen was too far from the tube to be affected by the cathode rays. He assumed unknown rays, X-rays, were being emitted from the walls of the tube while the cathode ray tube was running. To his amazement, Röntgen found that the rays could pass straight through his hand and cast shadows of his bones on the fluorescent screen. X-radiation (composed of X-rays) is a form of electromagnetic radiation. Most X-rays have a wavelength in the range of 0.01 to 10 nm, corresponding to frequencies in the range 30 petahertz to 30 exahertz (3×1016 Hz to 3×1019 Hz) and energies in the range 100 eV to 100 kEV.

X-ray diffraction analysis (XRD) is a technique used in materials science to determine the crystallographic structure of a material. XRD works by irradiating a material with incident X-rays and then measuring the intensities and scattering angles of the X-rays that leave the material. XRD technique finds out the nature of the materials as crystalline or amorphous. It will define the quantification of cementitious materials. The XRD analysis is done with an X-ray source of Cu Kα radiation ($\lambda = 1.5406$ Å). It will analyse and identify the unknown crystalline compounds by Brag Brentano method. The different parameters such as scan step size, collection time, range, X-ray tube voltage and current should be fixed based on the specimen's requirement analysis. The standard database (JCPDS database) for XRD pattern is used for phase identification for a large variety of crystalline phases in the concrete specimens [1].

XRD is used for assessment of phase purity and crystallinity of inorganic material and to evaluate the crystalline structure, the ratio of crystalline to non-crystalline (amorphous) regions, crystal size, the arrangement pattern of crystals and the distance between the planes of the crystal. This means that structural changes induced in a crystalline material by blending with other materials can be monitored using the XRD technique [2].

When a high voltage with several tens of kV is applied between two electrodes, the high-speed electrons with sufficient kinetic energy, drawn out from the cathode, collide with the anode (metallic target). The electrons rapidly slow down and lose kinetic energy. Since the slowing down patterns (method of loosing kinetic energy) vary with electrons, continuous X-rays with various wavelengths are generated. When an electron loses all its energy in a single collision, the generated X-ray has the maximum energy (or the shortest wavelength D SWL). The value of the shortest wavelength limit can be estimated from the accelerating voltage V between electrodes.

$$\mathrm{e}V \equiv h\nu_{\max}$$

$$\lambda_{\mathrm{SWL}} = \frac{c}{\nu_{\max}} = \frac{hc}{\mathrm{e}V}$$

4.3 LAUE METHOD

In crystallography, the Laue equations relate the incoming waves to the outgoing waves in the process of diffraction by a crystal lattice. They are named after physicist Max von Laue (1879–1960). In the Laue method the incident radiation covers a wide band of wavelengths. Correspondingly, all Ewald spheres with radii within the appropriate range of incident wave vectors are to be drawn in the reciprocal lattice; whenever the Ewald spheres intercept points of the reciprocal lattice, elastic diffractions become possible. The Laue method is mainly used to determine the orientation of large single crystals. White radiation is reflected from, or transmitted through, a fixed crystal. Each set of planes picks out and diffracts the particular wavelength from the white radiation that satisfies the Bragg law for the values of d and q involved [3].

The Max von Laue (1879-1960) equations relate the incoming waves to the outgoing waves in the process of diffraction by a crystal lattice. They can be derived in a somewhat less formal mode than made by the author, but intuitively and in a simple way. It is enough to to consider a row of atoms separated at regular distances, as shown in the figure on the left, and to consider the hypothesis that a wave front (OP), incident on the line of atoms, scatters cooperatively (diffracts) and produces another wavefront (QR) on the other side of the line whose direction of propagation will have changed (Fig. 4.1 to 4.3).

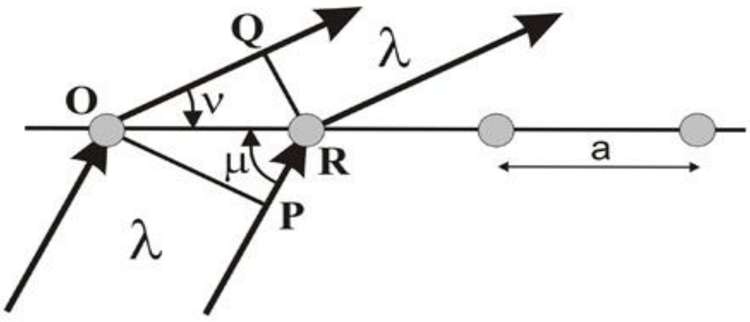


Fig. 4.1 Scatters cooperatively

Therefore, if the wavefront QR is observed (that is, if a cooperative scattering occurs), it is because the two component beams that define that front are in phase. In other words, the difference of paths followed by the beams OQ and PR is an integer number (m) of wavelengths (λ), ie:

$OQ - PR = m\lambda$ and as:

$\cos \nu = OQ / a$

$\cos \mu = PR / a$

it becomes: $a(\cos \nu - \cos \mu) = m\lambda$

If we look carefully at this equation, it is easy to realize that:

No fractional cooperative dispersion orders can occur, since m is an integer number.

If the incident angle μ is maintained constant, the last equation will also be valid for any scattered beam that maintains the same angle of scattering (ν) shown in the Fig. 4.2, and therefore all scattered beams around the row of atoms (with the same ν) will fulfill that equation and will form a conical surface coaxial with the row of atoms.

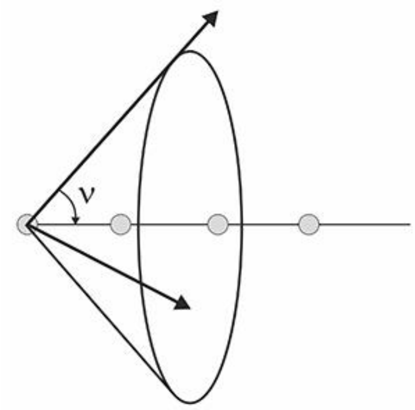


Fig. 4.2 Scattering from a row of atoms separated at regular distances

In the two-dimensional case, i.e. if we consider two rows of atoms, such as those shown with the letters a and b (Fig. 4.3), each one will scatter the X-rays in the same manner as described above, that is in the form of cones coaxial with those atoms rows. But if both dispersions have to be cooperative (diffraction) they will have to perform simultaneously two equations equivalent to the one shown above, i.e.:

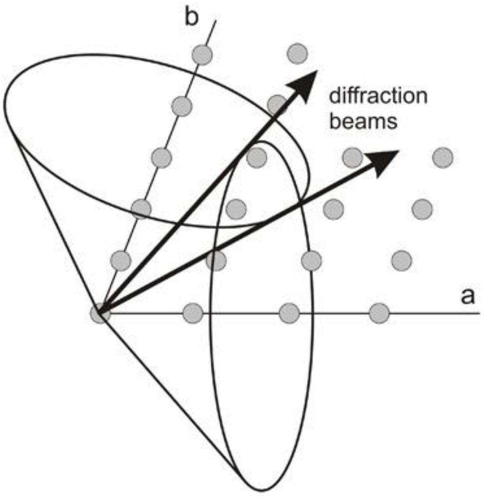


Fig. 4.3 Cooperative scattering (diffraction) from two rows of atoms regularly spaced

$a (\cos \nu 1 - \cos \mu 1) = m\lambda$

$b (\cos \nu 2 - \cos \mu 2) = n\lambda$

The fact that these two equations are fulfilled simultaneously is equivalent as to consider graphically as valid only the common points of both cones, ie their intersections, which are two straight lines (shown as arrows). In other words, cooperative scattering (diffraction) from two non-parallel rows of atoms (and in general from a plane of atoms) is reduced to discrete diffraction lines only.

Generalizing to any ordered three-dimensional distribution of atoms, we must consider that three equations of the type shown above must be fulfilled simultaneously:

$a (\cos \nu 1 - \cos \mu 1) = m \lambda$

$b (\cos \nu 2 - \cos \mu 2) = n \lambda$

$c (\cos \nu 3 - \cos \mu 3) = p \lambda$

Where m, n, prepresent three integer numbers. These are the so called Laue equations.

4.4 BRAGG METHOD

William Henry and William Lawrence Bragg (father and son) found a simple interpretation of von Laue’s experiment. They assume that each crystal plane reflects radiation as a mirror and analyze this situation for cases of constructive and destructive interference. Bragg's law is the result of experiments derived by physicist Sir William Lawrence Bragg in 1912 and first presented on the same year to the Cambridge Philosophical Society. William Lawrence Bragg and his father, Sir William Henry Bragg, were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS, and diamond.

Bragg's law, a special case of Laue diffraction, gives the angles for coherent and incoherent scattering from a crystal lattice. When X-rays are incident on an atom, they make the electronic cloud move, as does any electromagnetic wave. The movement of these charges re-radiates waves with the same frequency, blurred slightly due to a variety of effects; this phenomenon is known as Rayleigh scattering (or elastic scattering). The scattered waves can themselves be scattered but this secondary scattering is assumed to be negligible [4].

A similar process occurs upon scattering neutron waves from the nuclei or by a coherent spin interaction with an unpaired electron. These re-emitted wave fields interfere with each other either constructively or destructively (overlapping waves either add up together to produce stronger peaks or are subtracted from each other to some degree), producing a diffraction pattern on a detector or film. The resulting wave interference pattern is the basis of diffraction analysis. This analysis is called Bragg diffraction. Bragg diffraction occurs when radiation, with a wavelength comparable to atomic spacings, is scattered in a specular fashion by the atoms of a crystalline system, and undergoes constructive interference. For a crystalline solid, the waves are scattered from lattice planes separated by the interplanar distance d. When the scattered waves interfere constructively, they remain in phase since the difference between the path lengths of the two waves is equal to an integer multiple of the wavelength. The path difference between two waves undergoing interference is given by 2dsin θ, where θ is the glancing angle this differs from the convention in Snell's law where θ is measured from the surface normal. The effect of the constructive or destructive interference intensifies because of the cumulative effect of reflection. Electrons will be diffracted when the angle of incidence, θ on a crystal plane satisfies the Bragg Equation:

$n\lambda = 2\ d \sin \theta$

Where λ is the wavelength of the electrons d is the spacing of the crystal planes and n is an integer.

A simple way to derive the Bragg equation is as follows. The path difference between electrons scattered from adjacent crystal planes is 2d sin θ. For constructive interference between the two scattered beams the difference must be an integer multiple of electron wavelengths, nλ which gives the Bragg equation.

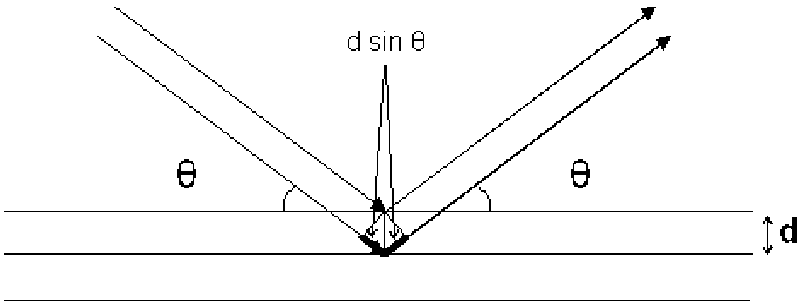


Fig.4.4 Braggs diffraction patter

4.5 DEBYE SCHERRER METHOD

It is a method for studying the structure of finely crystalline substances using X-ray diffraction (powdered-crystal method). It was named after P. Debye and the German physicist P. Scherrer, who proposed this method in 1916. A narrow parallel beam of monochromatic X rays, upon falling onto a polycrystalline sample and being reflected by the crystallites that make up the sample, produces a number of coaxial, that is, having one common axis, diffraction cones (Fig. 4.5).

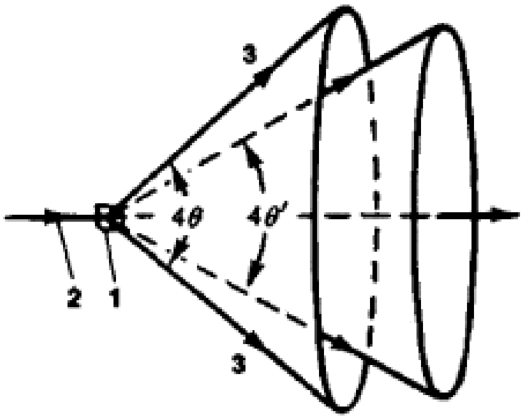


Fig. 4.5. Formation ot coaxial diffraction cones: (1) crystal, (2) monochromatic X rays incident on crystal, and (3) diffracted rays; 40 and 40 are apex angles of diffraction cones

The direction of the primary X ray serves as the axis of the cones. Their vertices lie within the object under study, and the apex angles are determined according to the Bragg-Vul'f condition $n \lambda = 2d \sin \theta$ (where n is a positive integer, λ is the wavelength of the X rays, d is the distance between the parallel planes of the points of the space crystal lattice, and θ is the angle between the reflecting plane and the incident beam). The cone's apex angle is equal to four times the value of the angle of reflection ø. The intensity and position of the diffraction cones is recorded on a photographic film or by one of the ionization methods . The interaction of the diffracted beams with the photographic film leaves a trace in the form of a series of diffraction lines, the shape of which depends on the geometry of X-ray photographing—namely, the mutual position of the sample, photographic film, and incident X-ray beam. The film in some cameras that are used for making roentgenograms of polycrystals is placed on the surface of a cylinder, the axis of which is at right angles to the incident X-ray beam, and the sample is placed on the cylinder's axis.

In other cameras the flat film is placed at right angles to the incident X-ray beam so that the beam, which passes through the sample without diffraction, falls onto the center of the film. This method records the full Debye ring, that is, the curve of intersection of the diffraction cone with the photographic film. Powder patterns of this type are usually used for determining the texture (the predominant orientation of crystallites) [5].

Measurement of the apex angles of the cone makes it possible to determine the interplanar distance d using the Bragg equation. In some cases, these data, together with the measurements of the X-ray intensities in each diffraction cone, are sufficient for the complete determination of the crystal lattice structure.

The Debye-Scherrer method is of particular importance for the solution of various technical problems. For example, it may be used for the study of structural changes arising during various treatments of metals and alloys. In the case of plastically deformed crystals, this method makes it possible to determine the presence of the texture in the sample and during heat treatment to observe phase transitions. The Debye-Scherrer method is also widely used in mineralogy and chemistry for the identification of various minerals and chemical compounds.

4.6 Identification of unit cells from systematic absences in diffraction pattern

Systematic absences is that part of lattice, where the structure factor is zero, either due to the centering of the lattice or to the presence of glide or screw symmetry elements. Conversely, the conditions for a reflection to exist and not to be systematically absent, are called reflection conditions.

Symmetry elements, or in certain lattice types, the arrangement and spacing of lattice planes produces diffractions from certain classes of planes in the structure which are always exactly 180° out of phase producing a phenomenon called systematic extinction. In these cases, certain types of reflections from valid lattice planes (recognizable by simple rules in their hkl indices) will produce no visible diffraction spots.

Systematic absences (or systematic extintions) in hkl reflections arise when symmetry elements containing translational components are present, such as in the following cases:

lattice centering (translational operations derived from the lattice type)

screw axes (symmetry axes that imply rotation and an additional translation)

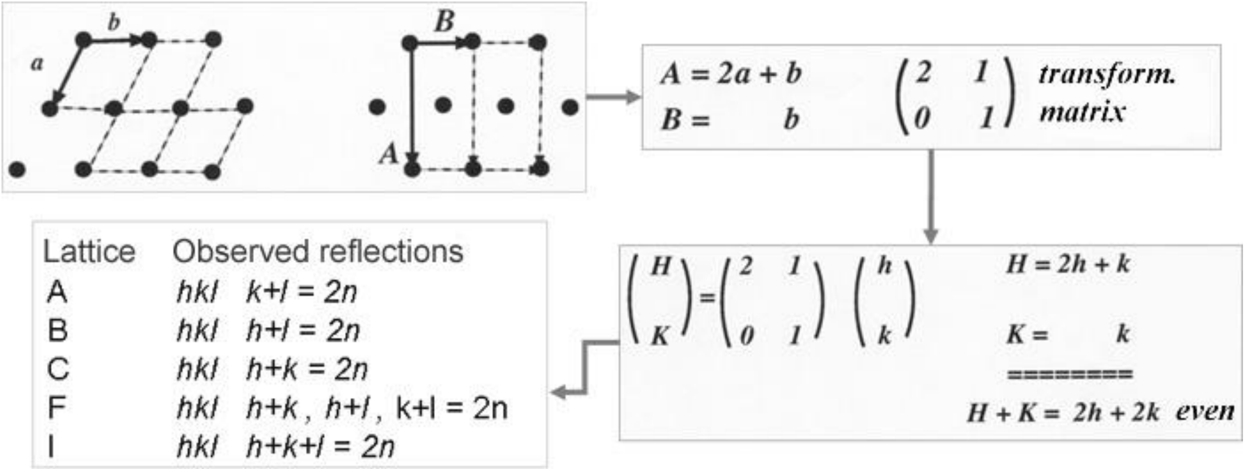
glide planes (mirror planes that imply reflection and an additional translation)

4.6.1 Centered lattices

Consider a crystal lattice (shown in 2-dimensions), such as the one shown in the figure below (left) 4.6, with axes a and b. This lattice is called primitive because it contains one lattice node inside the unit cell (actually in terms of 4 quarters of a point).

If for some reason we have interpreted this lattice in terms of another unit cell, with axes A and B (figure 4.6 on the right), the lattice will become what we call a centered lattice (non primitive) because it contains more than one lattice point inside the unit cell (in this case 2 points: 1/4 in each corner + 1 in the center).

The transformation of axes inherent to this change of unit cell is given at the upper right part of the figure 4.6. The new A axis is a vector obtained by adding two times the old a axis and the old b axis (2a + b), and the new B axis is identical to b. This transformation (from one cell to the other) can be represented by the matrix shown above (obtained with the coefficients of the terms of the second member of the equations) [6].



Lattice	Observed reflections
A	*hkl* *k+l* = 2*n*
B	*hkl* *h+l* = 2*n*
C	*hkl* *h+k* = 2*n*
F	*hkl* *h+k* , *h+l* , k+l = 2n
I	*hkl* *h+k+l* = 2*n*

Fig. 4.6 Crystal lattice

It can be demonstrated that this cell-to-cell transformation matrix can also be applied to the hkl indices of the original lattice to obtain the new HKL indices that, according to the new unit cell, interpret the lattice. If we do this in this example (as is shown in the lower right corner of the figure) we will obtain the equations which relate old and new Miller indices. After adding both equations we will discover that the new Miller indices (HK) are such that its sum (H+K) is always an even number. In other words, if we interpret a diffraction pattern in terms of a reciprocal cell and we only see intensity at those points given by H+K=2n, we can be sure that the crystal lattice is centered (in this particular case a C-centered lattice). Other systematic absences, which also apply to all hkl reciprocal points, are indicated in the above figure 4.6.

4.6.2 Screw axes

Two-fold screw axes, such as the one shown in the figure 4.7 on the left (a screw axis parallel to c), also leave their footprints in the diffraction pattern.

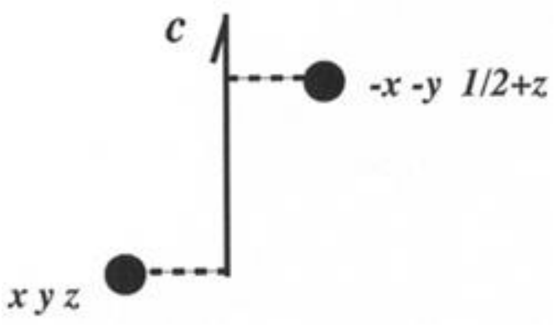


Fig. 4.7 A screw axis parallel to c

The reason why such a symmetry operator cancels certain intensities is very simple to deduce if we look at the structure factors that would result from the cooperative scattering of these two atoms:

$$F = f \cos 2\pi (hx + ky + lz) + f \cos 2\pi (- hx - ky + l [(1/2) + z])$$

However, taking into account the well-known relation:

$$\cos a + \cos b = 2 \ [\cos (a+b)/2] [\cos (a-b)/2]$$

The formula above can be rewritten as:

$$F = 2 f[\cos \pi (2 l z + l/2)] [\cos \pi (2hx + 2ky - l/2)]$$

This expression vanishes ($F=0$) for those hkl reflections with $h=0$, $k=0$ and $l=2n+1$. Therefore, diffraction patterns showing systematic absences of this type, or in other words, showing intensity only for reflections of type 00l with $l=2n$, indicate the existence of a screw axis parallel to the c axis.

Generalizing for other two-fold screw axes, and depending of their direction, the corresponding rules for systematic absences are:

Two-fold screw axis parallel to:	Existing reflections
a	h00 h=2n
b	0k0 h=2n
c	00l h=2n

For systematic absences produced by other screw axis types are presented in table 4.1.

4.6.3 Glide planes

Glide planes, which are mirror planes which contain an additional translation (see the figure 4.8 on the left), are also responsible for some systematic extinctions in the reciprocal lattice as seen in the table below:

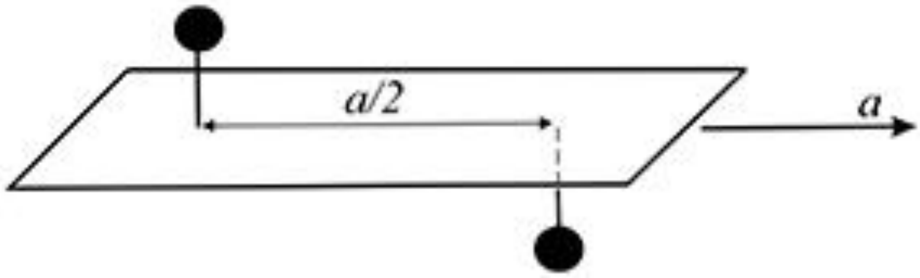


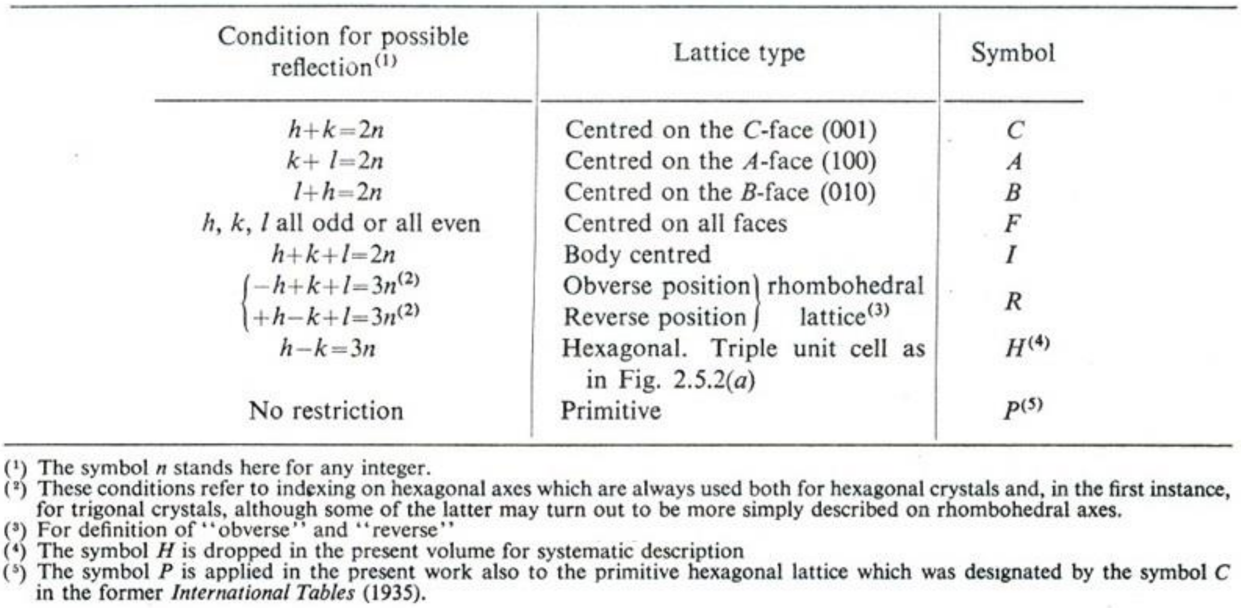
Fig. 4.8 Glide planes

Glide plane parallel to:	Translation:	Existing reflections:
a	b/2	0kl k = 2n
a	c/2	0kl l = 2n

By observation of systematic extinction rules, such as those shown above, one can confirm the presence of different lattice types (centered lattices) or symmetry elements such as screw axes and glide planes, which provide a very valuable tool for determining the space group (the symmetry) of the crystal.

In order to solve the internal structure of a crystal it is necessary to know its approximate chemical composition, the dimensions of the unit cell, the diffraction intensities, and the symmetry of the crystal. It seems reasonable to assume that the internal symmetry of a crystal (the space group) could hardly be inferred from observing its external habit. The crystal symmetry can only be deduced from the diffraction pattern itself, since certain crystal symmetry operations leave some type of trace in the diffraction pattern, systematically canceling certain intensities that follow the rules that are shown below in table 4.1 and 4.2.

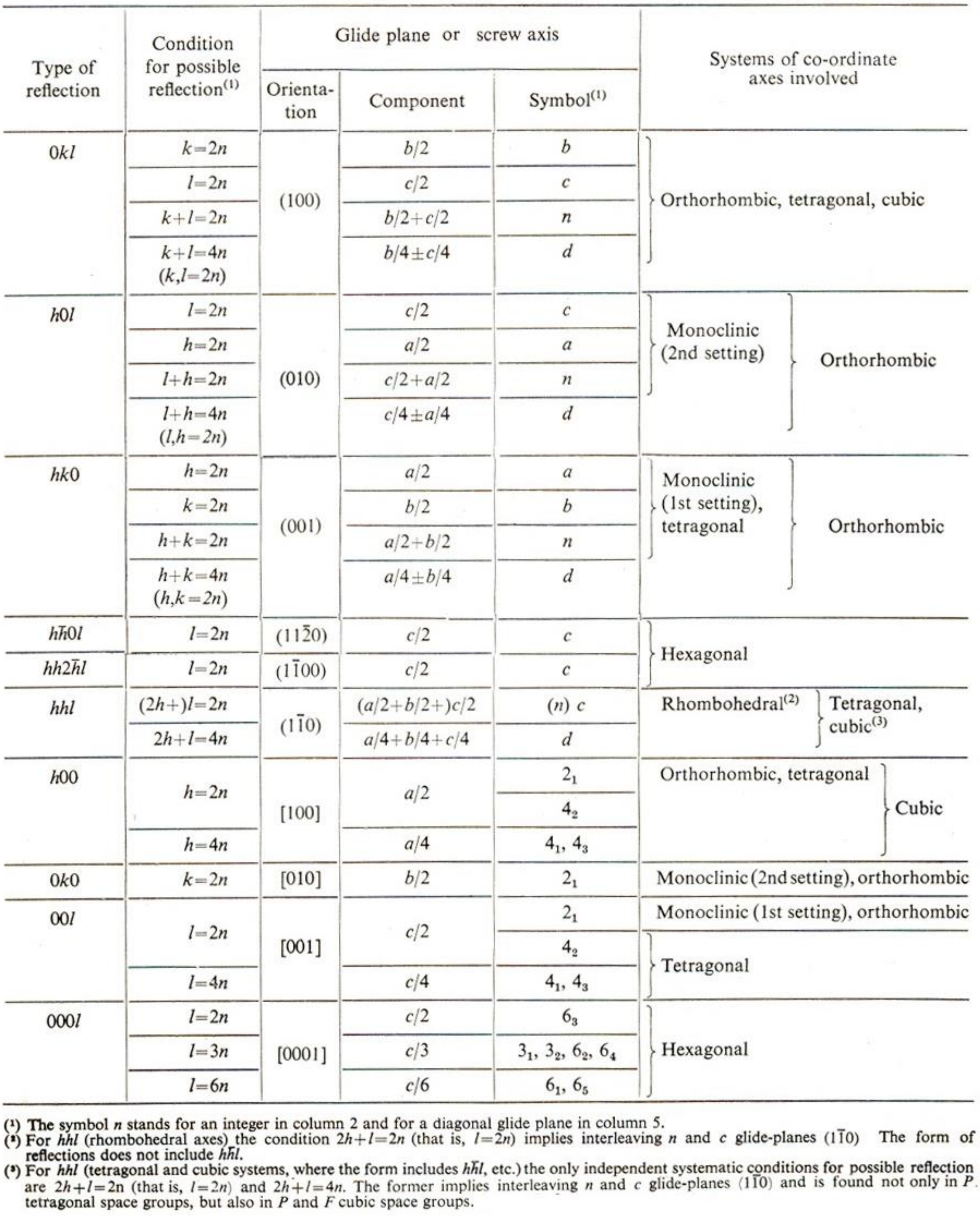
Table 4.1 Determination of lattice sites with general reflections hkl.



Condition for possible reflection(1)	Lattice type	Symbol
$h+k=2n$	Centred on the *C*-face (001)	*C*
$k+l=2n$	Centred on the *A*-face (100)	*A*
$l+h=2n$	Centred on the *B*-face (010)	*B*
h, *k*, *l* all odd or all even	Centred on all faces	*F*
$h+k+l=2n$	Body centred	*I*
$-h+k+l=3n$(2) $+h-k+l=3n$(2)	Obverse position Reverse position } rhombohedral lattice(3)	*R*
$h-k=3n$	Hexagonal. Triple unit cell as in Fig. 2.5.2(*a*)	*H*(4)
No restriction	Primitive	*P*(5)

(1) The symbol *n* stands here for any integer.
(2) These conditions refer to indexing on hexagonal axes which are always used both for hexagonal crystals and, in the first instance, for trigonal crystals, although some of the latter may turn out to be more simply described on rhombohedral axes.
(3) For definition of "obverse" and "reverse"
(4) The symbol *H* is dropped in the present volume for systematic description
(5) The symbol *P* is applied in the present work also to the primitive hexagonal lattice which was designated by the symbol *C* in the former *International Tables* (1935).

Table 4.2 Determination of translation elements of symmetry from special refections



Type of reflection	Condition for possible reflection(1)	Glide plane or screw axis			Systems of co-ordinate axes involved
		Orientation	Component	Symbol(1)	
$0kl$	$k=2n$	(100)	$b/2$	b	Orthorhombic, tetragonal, cubic
	$l=2n$		$c/2$	c	
	$k+l=2n$		$b/2+c/2$	n	
	$k+l=4n$ $(k,l=2n)$		$b/4 \pm c/4$	d	
$h0l$	$l=2n$	(010)	$c/2$	c	Monoclinic (2nd setting) Orthorhombic
	$h=2n$		$a/2$	a	
	$l+h=2n$		$c/2+a/2$	n	
	$l+h=4n$ $(l,h=2n)$		$c/4 \pm a/4$	d	
$hk0$	$h=2n$	(001)	$a/2$	a	Monoclinic (1st setting), tetragonal Orthorhombic
	$k=2n$		$b/2$	b	
	$h+k=2n$		$a/2+b/2$	n	
	$h+k=4n$ $(h,k=2n)$		$a/4 \pm b/4$	d	
$h\bar{h}0l$	$l=2n$	$(11\bar{2}0)$	$c/2$	c	Hexagonal
$hh2\bar{h}l$	$l=2n$	$(1\bar{1}00)$	$c/2$	c	
hhl	$(2h+)l=2n$	$(1\bar{1}0)$	$(a/2+b/2+)c/2$	$(n)\ c$	Rhombohedral(2) Tetragonal, cubic(3)
	$2h+l=4n$		$a/4+b/4+c/4$	d	
$h00$	$h=2n$	$[100]$	$a/2$	2_1	Orthorhombic, tetragonal Cubic
				4_2	
	$h=4n$		$a/4$	4_1, 4_3	
$0k0$	$k=2n$	$[010]$	$b/2$	2_1	Monoclinic (2nd setting), orthorhombic
$00l$	$l=2n$	$[001]$	$c/2$	2_1	Monoclinic (1st setting), orthorhombic
				4_2	Tetragonal
	$l=4n$		$c/4$	4_1, 4_3	
$000l$	$l=2n$	$[0001]$	$c/2$	6_3	Hexagonal
	$l=3n$		$c/3$	3_1, 3_2, 6_2, 6_4	
	$l=6n$		$c/6$	6_1, 6_5	

(1) The symbol n stands for an integer in column 2 and for a diagonal glide plane in column 5.

(2) For hhl (rhombohedral axes) the condition $2h+l=2n$ (that is, $l=2n$) implies interleaving n and c glide-planes $(1\bar{1}0)$ The form of reflections does not include $h\bar{h}l$.

(3) For hhl (tetragonal and cubic systems, where the form includes $h\bar{h}l$, etc.) the only independent systematic conditions for possible reflection are $2h+l=2n$ (that is, $l=2n$) and $2h+l=4n$. The former implies interleaving n and c glide-planes $(1\bar{1}0)$ and is found not only in P tetragonal space groups, but also in P and F cubic space groups.

4.7 A Brief Introduction to Miller Indices

•The Miller indices (hkl) define the reciprocal axial intercepts of a plane of atoms with the unit cell (Fig. 4.9)

–The (hkl) plane of atoms intercepts the unit cell at a/*h*, □/□, and □/□

–The (220) plane drawn to the right intercepts the unit cell at ½a, ½b, and does not intercept the c-axis.

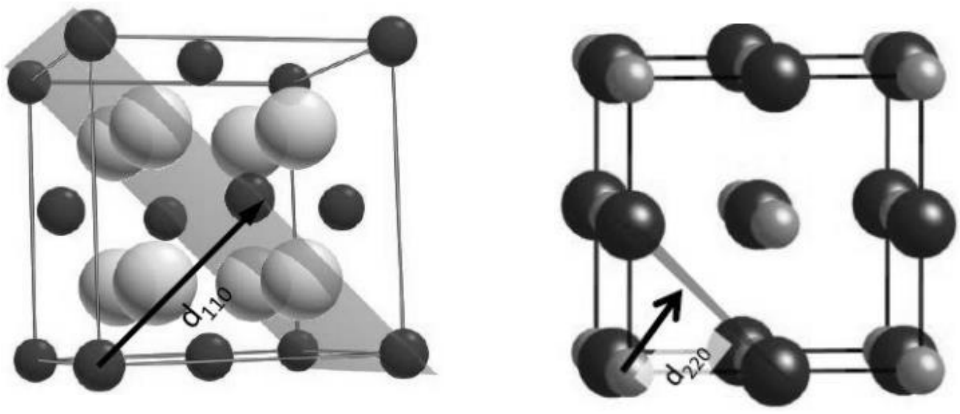


Fig. 4.9 Representation of hkl values

•When a plane is parallel to an axis, it is assumed to intercept at ∞; therefore its reciprocal is 0

•The vector dhkl is drawn from the origin of the unit cell to intersect the crystallographic plane (hkl) at a 90° angle.

–The direction of dhkl is the crystallographic direction.

–The crystallographic direction is expressed using [] brackets, such as [220]

The diffraction peak position is a product of interplanar spacing, as calculated by Bragg's law:

Bragg's law relates the $\lambda = 2d_{hkl} \sin\theta$ diffraction angle, 2θ, to dhkl

– In most diffractometers, the X-ray wavelength λ is fixed.

– Consequently, a family of planes produces a diffraction peak only at a specific angle 2θ.

• dhkl is a geometric function of the size and shape of the unit cell

– dhkl is the vector drawn from the origin to the plane (hkl) at a 90° angle.

– dhkl , the vector magnitude, is the distance between parallel planes of atoms in the family (hkl)

– Therefore, we often consider that the position of the diffraction peaks are determined by the distance between parallel planes of atoms (Fig. 4.10).

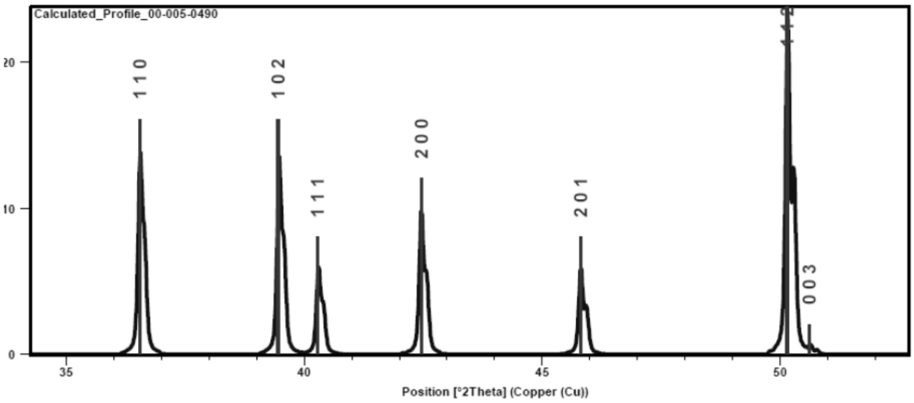


Fig. 4.10 Diffraction pattern calculations treat a crystal as a collection of planes of atoms

•Each diffraction peak is attributed to the scattering from a specific set of parallel planes of atoms.

•Miller indices (hkl) are used to identify the different planes of atoms •Observed diffraction peaks can be related to planes of atoms to assist in analyzing the atomic structure and microstructure of a sample

4.8 STRUCTURE FACTOR

Structure factor is a mathematical description to understand how a material scatters incident radiation. The structure factor is a critical tool in the interpretation of scattering or interference patterns, obtained in X-ray, electron and neutron diffraction experiments. There are two different mathematical expressions in use, both called 'structure factor'. One is usually written S(q); it is more generally valid, and relates the observed diffracted intensity per atom to that produced by a single scattering unit. Second is written as F_{hkl} and is valid for systems with long-range positional order-crystals. This expression relates the amplitude and phase of the beam diffracted by the (hkl) planes of the crystal (hkl, are the Miller indices of the planes) to that produced by a single scattering unit at the vertices of the primitive unit cell. S(q); that gives the scattering intensity, but F_{hkl} gives the amplitude and the squared modulus $/F_{hkl}/^2$ also gives the scattering intensity. F_{hkl} is defined for a perfect crystal, and is

$$I_{hkl} \propto |F_{hkl}|^2$$

$$F_{hkl} = \sum_{j=1}^{m} N_j f_j \exp\left[2\pi i\left(hx_j + ky_j + lz_j\right)\right]$$

used in crystallography, while S(q) is most useful for disordered systems. The diffraction peak intensity is determined by the arrangement of atoms in the entire crystal and it can be represented as follows [7]:

The structure factor F_{hkl} sums the result of scattering from all of the atoms in the unit cell to form a diffraction peak from the (hkl) planes of atoms.

The amplitude of scattered light is determined by:

– where the atoms are on the atomic planes

  • this is expressed by the fractional coordinates xj yj zj

– what atoms are on the atomic planes

  • the scattering factor f j quantifies the efficiency of X-ray scattering at any angle by the group of electrons in each atom

– The scattering factor is equal to the number of electrons around the atom at 0° θ, the drops off as θ increases

  • Nj is the fraction of every equivalent position that is occupied by atom j

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4.10 QUESTIONS

1. How does Bragg's law relate to X-ray diffraction?

2. How Bragg description of diffraction is different from Laue?

3. Discuss the process showing the equivalence of von Laue and Bragg diffraction?

4. Why is it important to vary angle and/or wavelength of X-rays when investigating diffraction peaks?

5. What acceleration potential V must be applied to electrons to cause electron diffraction on {220} planes of gold (Au) at $\theta = 5°$?

UNIT 5 LIQUID CRYSTALS

CONTENTS

5.1 OBJECTIVE

To understand soft materials.

Understanding of orientation and ordering in soft materials

To have a deep knowledge of liquid crystals and its various form

To describe the various forms of liquid crystals and with their advantages and disadvantages

5.2 INTRODUCTION

The discovery of an intermediate, liquid crystalline, state of matter is credited to Friedrich Reinitzer. In 1888, during the experiments on a cholesterol-based substance trying to figure out the correct formula and molecular weight of cholesterol, he was struck by the fact that this substance seemed to have two melting points. At 145.5oC the solid crystal melted into a cloudy liquid which existed until 178.5oC where the cloudiness suddenly disappeared, giving way to a clear transparent liquid. Later this cloudy liquid was named as Liquid Crystal (LC) by Otto Lehman [1].

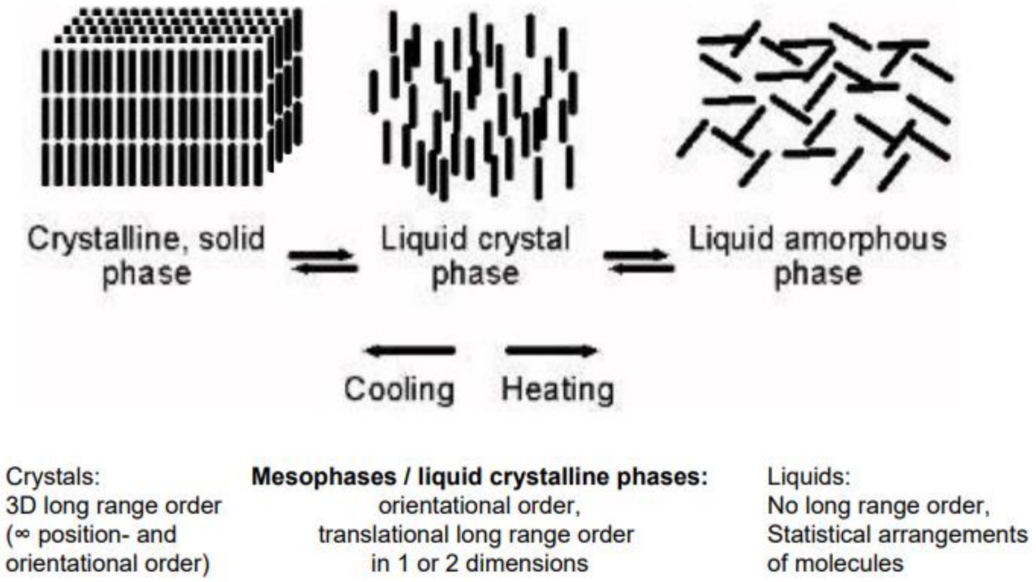


Fig. 5.1 LC or mesophase representation

5.3 LIQUID CRYSTALS

LC phases or mesophases (mesomorphic phases) (meso (gr.): middle; morphe: shape): long range (but not perfect) order in respect to the position and/or orientation of molecules;

anisotropic (like crystals) but fluid properties (like liquids). Mesophase represents a unique state of matter characterized by both mobility and order on a molecular and at the supramolecular levels. This behavior appears under given conditions, when phases with a characteristic order intermediate to that of a three dimensionally ordered solid and a completely disordered liquid are formed. Molecules in the crystalline state possess orientational and three-dimensional positional orders. Thus, LC has been defined as "orientationally ordered liquids" or "positionally disordered crystals" that combine the properties of both the crystalline (optical and electrical anisotropy) and the liquid (molecular mobility and fluidity) states [2]. LC flows on the surface like a liquid and possesses optical properties like crystals. Therefore, such substances of thermotropic or lyotropic varieties are neither fully crystalline nor fully liquid (Fig.5.1). LC phases (*mesophases*) have found wide applications in the manufacturing of displays, spatial light modulators, optical connectors and switches, molecular sensors and detectors, and in many other topics. A broad classification of LC is presented in Fig. 5.2.

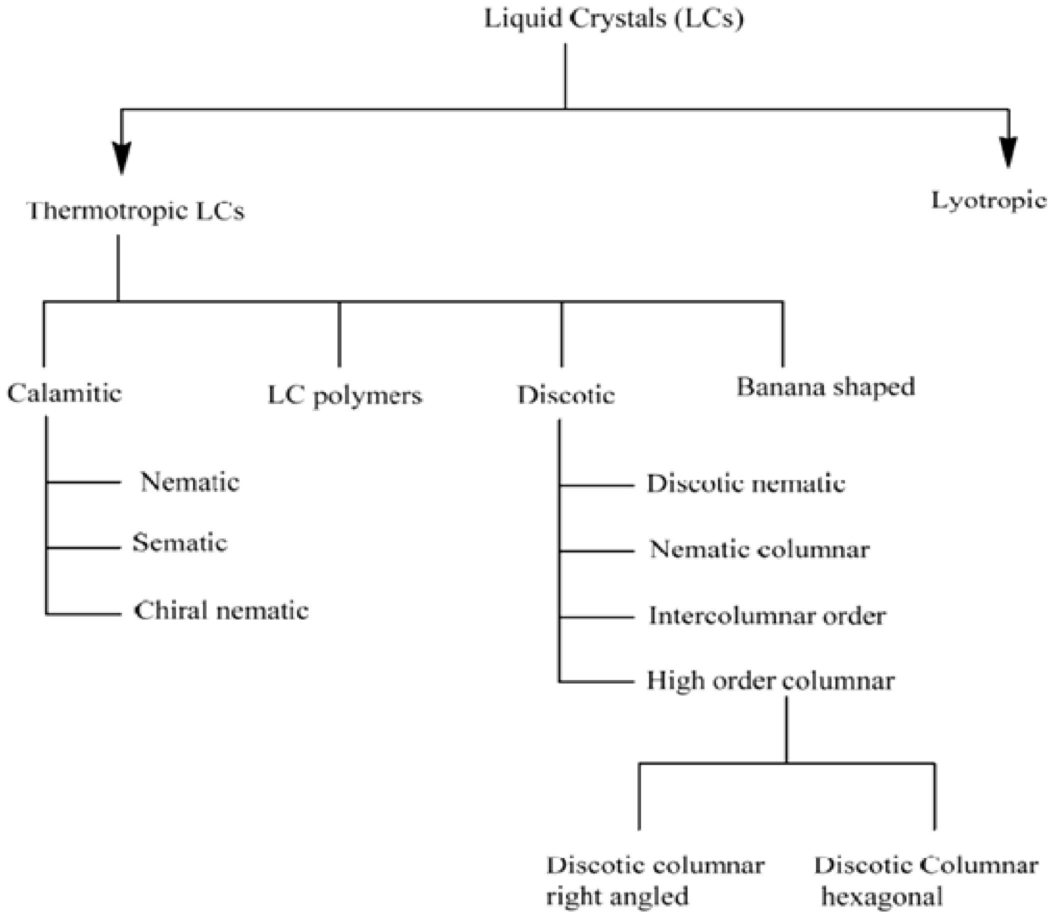


Fig. 5.2 Classification of Liquid Crystals

5.4 THERMOTROPIC MESOPHASE

It is formed by heating a solid or cooling an isotropic liquid (or another mesophase). Thermotropic LCs are temperature induced formation of the LC phases (Fig. 5.3) [3].

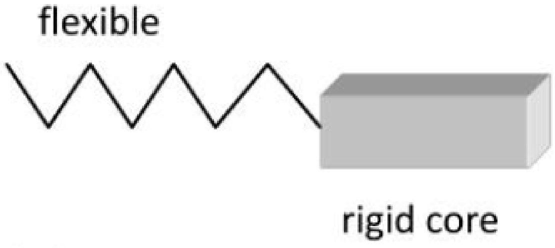


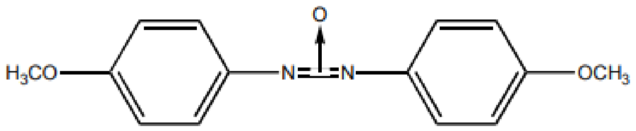
Fig. 5.3 Representation of thermomorphic mesophaase

In thermotropic phase transition depends on temperature, and it can further be classified in the following categories.

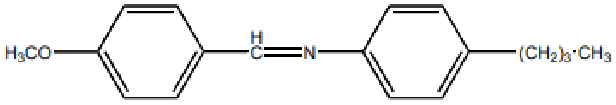
5.4.1 Nematic

Nematics (from the Greek: nematon- thread-like) are uniaxial liquid crystals in which the average direction of the long axes of the molecules defines the direction N.These are thread like Liquid crystals. They posses no translational order, but how ever posses a significant degree of long range orientational order. These on heating generally transformed into the isotropic liquids. They are mobile in three directions and can rotate about one axis (Fig.5.4).

Fig. 5.4 Representation of Nematic phase



PAA: p-azoxyanisole



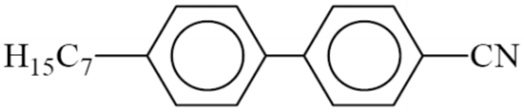
MBBA: n-(p-methoxybenzyidene)-
p-butylaniline

Fig. 5.5 Examples of nematic system compounds

The energy required to deform the nematic phase is so small that even dust particle can distort the structure considerably. Two examples are cyanobiphenyls and another with rigid and mantle group in the system (Fig. 5.5) [4].

5.4.2 Smectic

The word Smectic is derived from Greek for soap. The molecules show a degree of translational order not shown in nematics. The molecules maintain general orientation order of nematics but align themselves in layers or planes. There are eight smectic structures labeled from A to H. Out of which three A, C and C* are important (Fig. 5.6).



Increasing the length of the alkyl tail increases the order (CH2)x
x = 3-7 nematic , 7-11 smectic, >12 crystalline

Fig. 5.6 Smectic structures

Molecules in this phase show a degree of translational order not present in the nematic. In the smectic state, the molecules maintain the general orientational order of nematics, but also tend to align themselves in layers or planes. Motion is restricted to within these planes, and separate planes are observed to flow past each other. The increased order means that the smectic state is more "solid-like" than the nematic

5.4.3 Cholesteric

It is equivalent to nematic, which has been twisted periodically about an axis perpendicular to the director chiral nematic (Fig. 5.7). Cholesteric is the nematic state superimposed with a natural twist between layers including the long axis of the molecules induced by the incorporation of the chiral group to give helical twist to the orientation of the director. It formed from chiral mesogenic molecules or after doping of a nematic phase with a chiral molecule. Structure of first identified mesophase from Cholesterol benzoate is represented in Fig. 5.8.

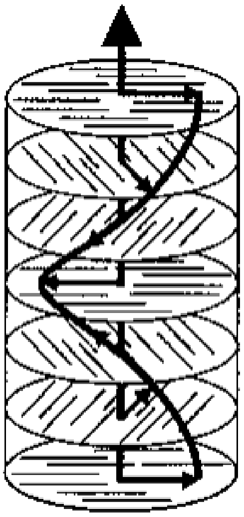


Fig. 5.7 Representation of Chiral Nematic (Cholesteric)

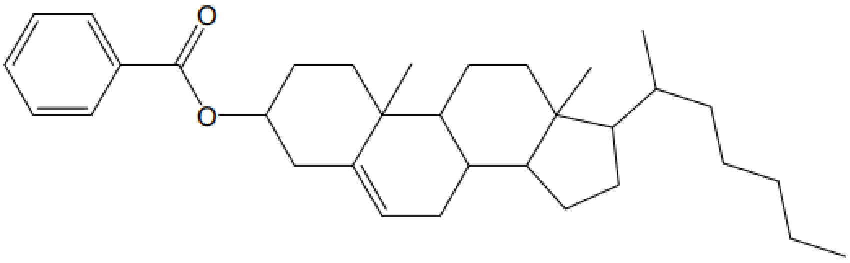


Fig. 5.8 Structure of from Cholesterol benzoate

5.5 LYOTROPIC MESOPHASES

When two different substances are mixed together, the mixture can exhibit different phases not only as the temperature is changed, but also as the concentration of one component of the mixture is varied. They are prepared by dissolving an amphiphilic mesogen (a compound that displays liquid crystalline behavior) in suitable solvents, under appropriate conditions of concentration and temperature. Lyotropic LC are the formation of LC phases upon salvation [5].

Example: a molecule that has end groups with different properties (one is hydrophobic and the other is hydrophilic. Compounds forming lyotropic mesophases usually consist of a flexible lipophilic chain (the tail) and a polar (ionic or non-ionic) head group (Fig. 5.9 and 5.10).

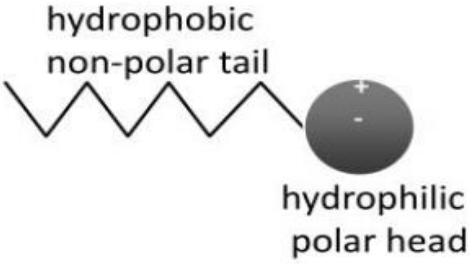
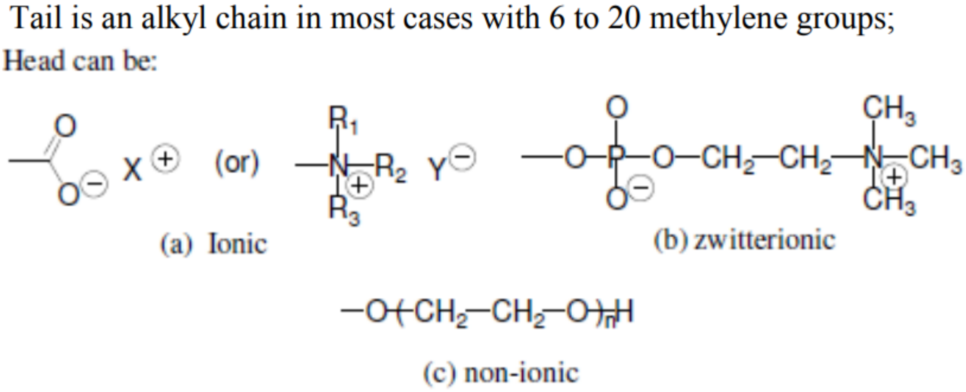


Fig. 5.9 Lyotropic mesophases


Tail is an alkyl chain in most cases with 6 to 20 methylene groups;

Head can be:

(a) Ionic

(b) zwitterionic

(c) non-ionic

Fig. 5.10 Examples for amphiphilic molecules composed of polar hydrophilic head group and a hydrophobic tail.

Liquid crystals, which are obtained by melting a crystalline solid, are called thermotropic. Liquid crystalline behavior is also found in certain colloidal solutions, such as aqueous solutions of tobacco mosaic virus and certain polymers. This class of liquid crystals is called lyotropic. For lyotropic liquid crystals the important controllable parameter is the concentration, rather than temperature or pressure. Most of the theories presented below are equally valid for thermotropic and lyotropic liquid crystals.

5.6 ORDER PARAMETER

It is sometimes difficult to determine whether a material is in a crystal or liquid crystal state. Crystalline materials demonstrate long range periodic order in three dimensions. By definition, an isotropic liquid has no orientational order. Substances that aren't as ordered as a solid, yet have some degree of alignment are properly called liquid crystals [6].

The following parameters describe the liquid crystalline structure:

- Positional Order

- Orientational Order

- Bond Orientational Order

Each of these parameters describes the extent to which the liquid crystal sample is ordered. Positional order refers to the extent to which an average molecule or group of molecules shows translational symmetry (as crystalline material shows). Orientational order, as discussed above, represents a measure of the tendency of the molecules to align along the director on a long-range basis. Bond Orientational Order describes a line joining the centers of nearest-neighbor molecules without requiring a regular spacing along that line. Thus, a relatively long-range order with respect to the line of centers but only short range positional order along that line (Fig. 5.11).

Most liquid crystal compounds exhibit polymorphism, or a condition where more than one phase is observed in the liquid crystalline state. The term mesophase is used to describe the "subphases" of liquid crystal materials. Mesophases are formed by changing the amount of order in the sample, either by imposing order in only one or two dimensions, or by allowing the molecules to have a degree of translational motion. The following section describes the mesophases of liquid crystals in greater detail.

To quantify just how much order is present in a material, an order parameter (S) is defined. Theta is the angle between the director and the long axis of each molecule The brackets denote an average over all of the molecules in the sample. In an isotropic liquid, the average of the cosine terms is zero, and therefore the order parameter is equal to zero. For a perfect crystal, the order parameter evaluates to one Typical values for the order parameter of a liquid crystal range between 0.3 and 0.9, with the exact value a function of temperature, as a result of kinetic molecular motion. Traditionally, the order parameter is given in Fig. 5.11.

As an LC is heated, a transparent isotropic liquid result at the nematic-isotropic phase transition temperature *T*NI. This transition is a first-order phase transition. In the vicinity of *T*NI-and unlike ordinary liquids-LCs maintain according to Landau-de Gennes theory regularity over short distances. As depicted in Figure 5.12, the square of the molecular correlation length ξ follows in the isotropic phase $1/(T - T^*)$, where T^* is a fictitious second-order phase transition temperature, with $(T\text{NI} - T^*) < 1$K (Fig. 5.12).

The tendency of the liquid crystal molecules to point along the director leads to a condition known as anisotropy. This term means that the properties of a material depend on the direction in which they are measured. For example, it is easier to cut a piece of wood along the grain than against it. The anisotropic nature of liquid crystals is responsible for the unique optical properties exploited by scientists and engineers in a variety of applications.

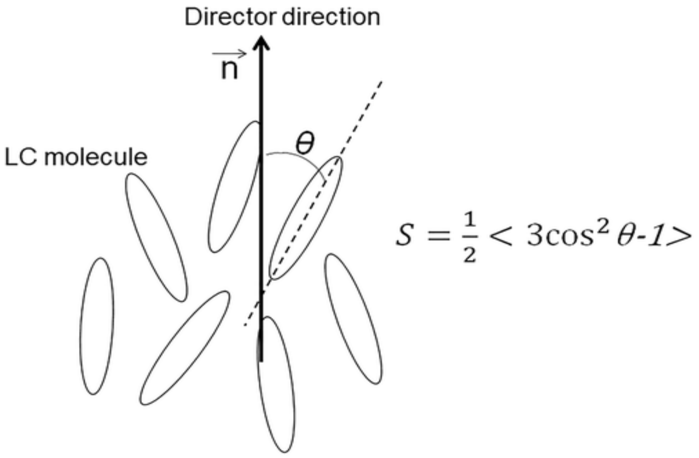


Fig 5.11 Order parameter

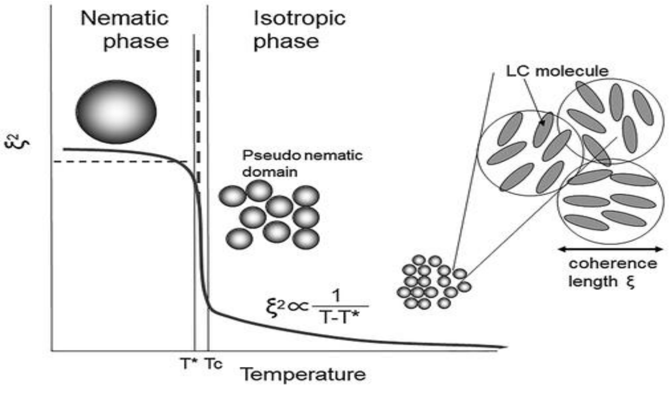


Fig. 5.12 Temperature dependence of the coherent length in nematic liquid crystals

5.7 MOLECULAR REARRANGEMENT IN SMECTIC A AND SMECTIC C PHASES

Smectic A (SmA) and chiral SmA phases the director lies along the layer normal. The molecular packing within the layers is liquid-like and has no long-range positional correlation. Likewise, there is no correlation between the lateral positions of the molecules in successive layers. Because of the disorder within the layers, the layers are not well defined and in formal terms the SmA phase can be described as a one-dimensional mass density wave. The idealized picture of the SmA phase is shown in Fig. 5.13 in which the sub-phases of SmA such as SmA2 (a bilayer phase), SmAd (a partially-bilayer phase) and SmÃ (a modulated phase) are also known. Like biaxial nematic phase, SmA can also possess biaxial symmetry that has been termed biaxial smectic A (SmAb) phase wherein the molecules are along the layer normal but have an additional director in the plane of the layers. Though the chiral version of the smectic A phase (observed with optically active molecules) is structurally the same as that of achiral SmA, owing to molecular chirality the symmetry is reduced from Dh to D. As a consequence, in the SmA phase (Fig. 13a), when an electric field is applied orthogonal to the layer normal direction there will be a coupling of the electroclinic susceptibility to the field and the long molecular axes of the molecules will tilt with respect to the layer planes (Fig. 13b) for relatively low applied fields, the tilt angle varies linearly with the field. This linear electrooptic phenomenon is called electroclinic effect. Both SmA and chiral SmA phases exhibit characteristic focal-conic texture in slides treated for planar orientation and a dark field of view in slides treated for homeotropic orientation.

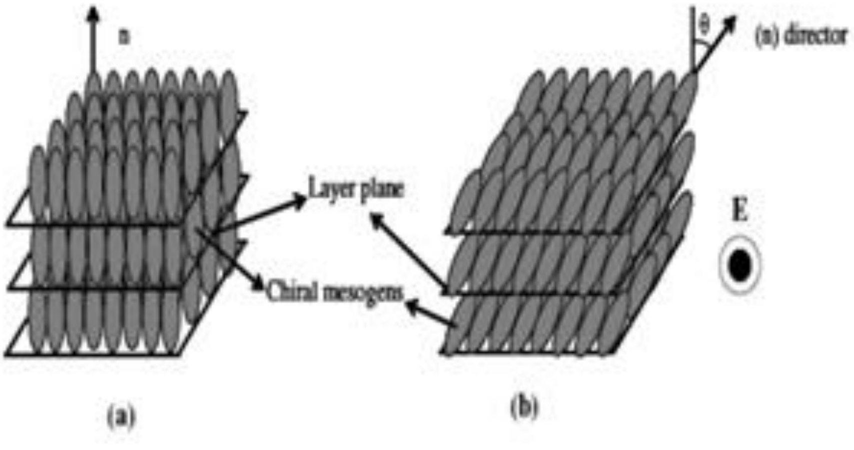


Fig. 5.13 Schematic representation of the SmA phase formed by chiral rod-like anisometric molecules: (a) orthogonal layered geometry; (b) tilted layered structure (electroclinic effect) obtained by the application of electric field along the layer planes of geometry (a)

5.8 SMECTIC C (SMC) AND CHIRAL SMECTIC C (SMC) PHASES*

They differ from the SmA phase in that the director of each layer is inclined at an angle to the layer normal and this angle being identical for all layers (Fig. 5.14a). While the SmA phase is generally optically uniaxial, the SmC phase is optically biaxial. The tilt angle in this phase has been shown to vary with temperature and it often increases monotonically with decreasing temperature. X-ray studies indicate that the layer thickness in this phase is considerably less than the molecular length. The symmetry elements of this phase correspond to the point group C2h (Fig. 5.14a). In the chiral smectic C (SmC*) phase, formed by optically active molecules a macroscopic molecule exists. The helix occurs as a result of a gradual change in molecular tilt direction (n) from layer to layer, about an axis perpendicular to the layer planes (Fig. 5.14b). Due to the presence of chiral molecules, the SmC* phase has reduced C2 symmetry (Fig. 5.14b) which creates in equivalence in the dipole moment along the C2 axis normal to the tilt direction , resulting in spontaneous polarization (Ps) in each layer.

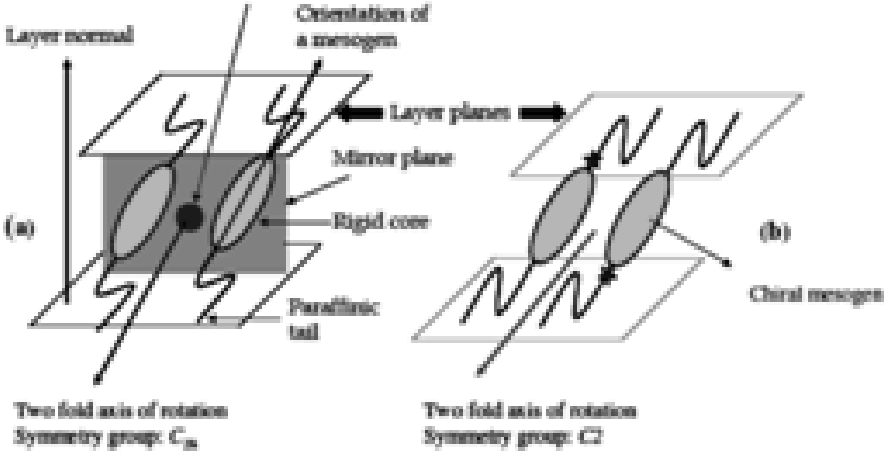


Figure 5.14. Symmetry in the (a) SmC and (b) SmC* mesophases

5.9 SMECTIC-NEMATIC TRANSITION

Liquid crystals are anisotropic liquids or partially ordered fluids, combining order and mobility, and are often referred to as the 4th state of matter. And indeed, the liquid crystalline phases are separated from the isotropic liquid and the crystalline solid through thermodynamic phase transitions, while their phase diagram can schematically be summarized as in Fig. 5.15 [7].

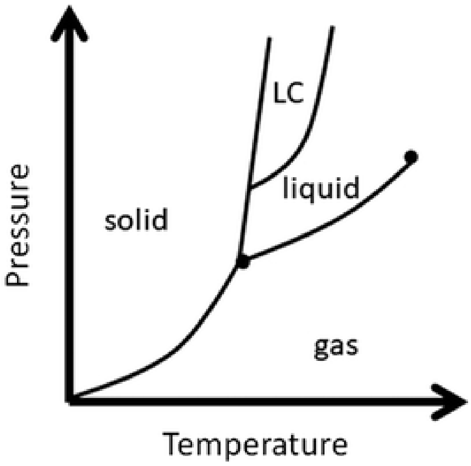


Fig. 5.15 Thermodynamic phase diagram with the inclusion of the liquid crystalline state, beside the three well-known states of matter, gases, liquids and solids.

Common liquid crystal phases, shown in Fig. 5.15, include the Nematic phase, Smectic A phase, and Smectic C phase, as well as isotropic, which is another name for the liquid phase, and crystalline, which is the same as the solid phase. The Nematic phase occurs when the molecules are simply orientationally ordered, and are free to move in all directions (Fig. 5.16). The Smectic A phase occurs when the molecules form discrete layers and the molecules orient on average normal to the layer plane, but can still move fluidly within the layer. The Smectic C phase is similar to the Smectic A phase, but the molecules orient at an angle to the layer-plane normal. This orientation causes defects to form in the film, which can alter the hydrodynamics of objects close to them. Similar to the way most materials transition from solids at lower temperatures to liquids or gasses at higher temperatures, liquid crystals can undergo transitions between different liquid crystal phases with changing temperature (Fig. 5.17).

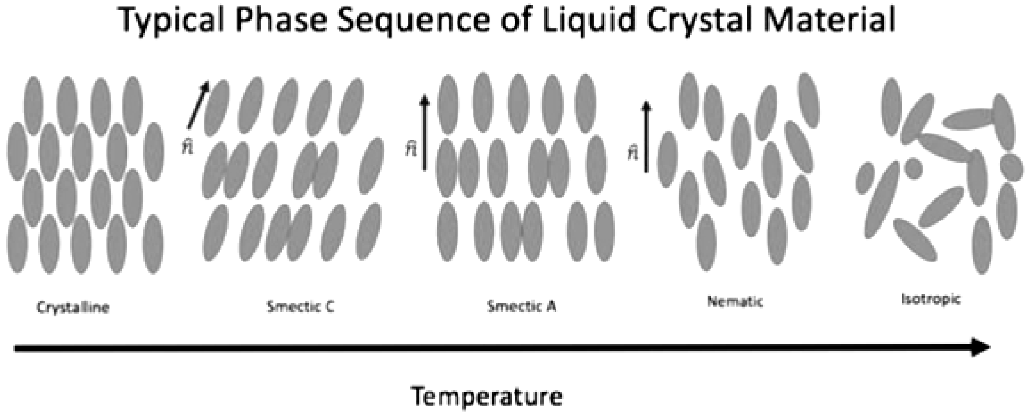


Fig. 5.16 In the Smectic A, Smectic C, and Nematic phases, indicates the average orientation of the molecules.

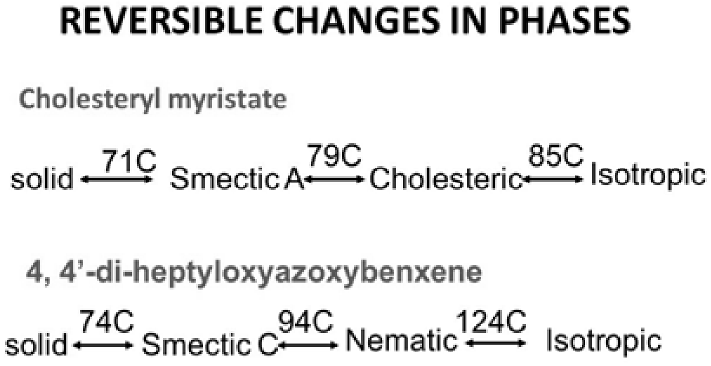


Fig. 5.17 Common liquid crystal phases ordered according to temperature dependence.

5.10 HOMEOTROPIC, PLANAR AND SCHLIEREN TEXTURES

The natural texture of a liquid-crystalline phase is the texture that would be inherently formed on cooling the isotropic liquid into the mesomorphic state. Subsequent cooling may produce transitions to other phases, which generally will exhibit paramorphotic textures based on the defects of the preceding natural texture. Typically, defects can be characterized *via* two forms of alignment or orientations of the molecules; these orientations are called homogeneous and homeotropic sample preparations. Studying the defects formed in combinations of these two sample orientations is again a powerful way in which to achieve phase classification. For phase identification, using polarized light microscopy, the liquid crystal material is usually sandwiched between a glass slide and coverslip. For calamitic (rod-like) liquid crystals, a homeotropic sample preparation is obtained when the long axes of the molecules are found to be on average perpendicular to the surface of the glass plate, whereas homogeneous alignment is obtained where the molecules have their long axes lying parallel or at an angle to the surface of the glass (Fig.5.18).

Homeotropic (or vertical) alignment can be achieved in a number of different ways and then the long axes of the molecules are on average parallel to the glass substrates, this orientation is said to be ‘‘planar’’ alignment. Thus, when dealing with phase characterization and classification two distinct experimental observations can be made based on phase sequence (paramorphosis) and on sample orientation. The combination of these observations produces a powerful method of phase classification.

Schlieren textures were once considered to be exclusively associated with the nematic phase until it was found that they were also exhibited by tilted smectic phases. The schlieren texture observed in the polarizing microscope is produced either by a continuous, but sharp, change of molecular orientation within the sample, or by a change in molecular orientation about a point or line singularity. Between crossed polars characteristic dark brushes (lines of extinction) appear when the molecules are aligned with one or other of the two polarizers of the microscope. When the polarizer and the analyzer of the microscope are rotated simultaneously, the black brushes are seen to rotate across the area being viewed, while the origin or point source of the brushes remains in a fixed position. At the center of the schlieren a point or a line singularity is found; in the case of the line singularity it runs perpendicular to the viewing direction (Fig. 5.19).

5.11 OPTICAL PROP

Chirality is a fascinating aspect of geometry in its widest sense, and can be encountered in all aspects of physics, chemistry, biology, or mathematics, to name just a few of the subjects that it affects. Chirality manifests itself through the lack of mirror symmetry. It is an inherent property of many systems in nature like the helical macromolecules of DNA or polypeptides, shells, snails and plants, growing in a helical fashion and is also seen in the well-known molecular asymmetry of many molecules, known as stereochemistry. Probably one of the best-known examples is that of limonene, where the R-enantiomer exhibits a pronounced smell of orange, while the S-enantiomer smells of turpentine with a lemon note. They exhibit identical scalar physical properties, such as the melting points, but their chiral properties, like the optical rotation due to optical activity, have equal modulus, but with opposite sign [8].

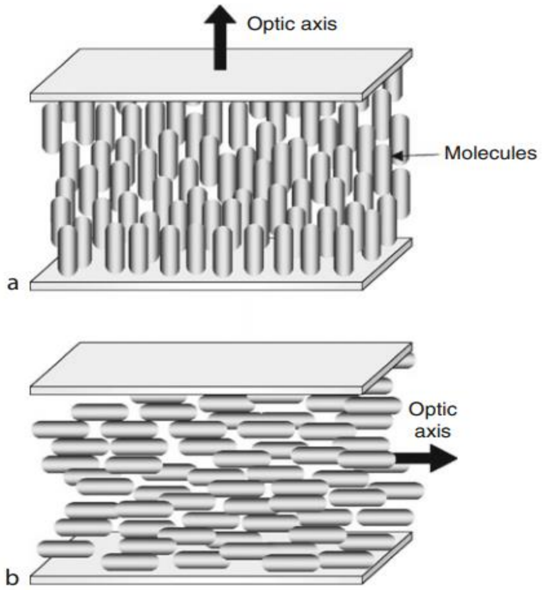


Fig.5.18 Homeotropic (a) and rubbed homogeneous (b) sample preparations for a nematic phase ***ERTIES OF LIQUID CRYSTALS***

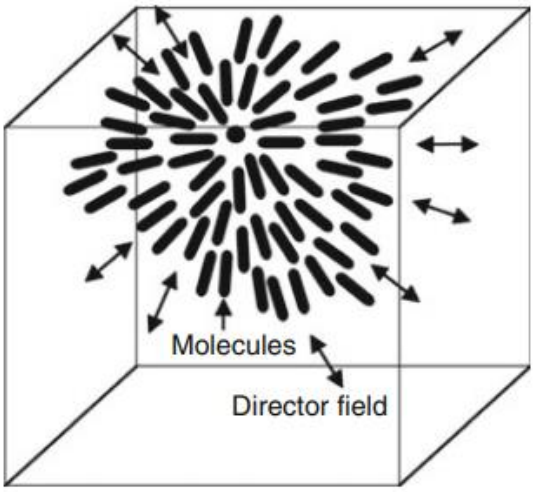


Fig. 5.19 The director field about a singularity in a nematic phase

Perhaps the most remarkable features of liquid crystals, crucial for their applications, are their anisotropic optical properties. A uniaxial liquid crystal is birefringent, meaning that it possesses two different indices of refraction. One index of refraction corresponds to light polarized along the director of the liquid crystal, and the other is for light polarized perpendicular to the director. Light propagating along a certain direction has electric and magnetic field vectors perpendicular to that direction. Supposing that the director lies perpendicular to the direction of propagation of the light, we can think of each field vector as being made up of two components, one parallel to the director of the liquid crystal and one perpendicular. Essentially, what this birefringence property amounts to is that these two components of either the electric or the magnetic field will propagate through the liquid crystal at different speeds and, therefore, can be out of phase when they exit the crystal. As the temperature increases, the birefringence of the sample decreases and is zero at the nema tic-isotropic transition. The orientational order and hence the birefringence can be manipulated easily, for example, with the help of rather weak magnetic, electric or optical fields, leading to huge magnetooptical, electro-optical and opto-optical effects. The most successful application of liquid crystals namely displays in wrist watches, pocket calculators or flat screens of laptop computers, take advantage of electro-optical effects. More recently, it has been shown that the orientational order can be also affected by optical fields, leading to rather sensitive opto-optical effects and nonlinear optical properties which are important for optical switching and other photonic devices in future optical information technologies.

Special cases of nematic and smectic phases are sometimes formed by molecules that display chirality-that is, they can exist in either left- or right-handed forms that cannot be superposed on each other. In the resulting chiral phase, successive molecules positioned along the long axis are rotated around this axis, giving rise to a periodicity that repeats itself at distances corresponding to a complete rotation. These twisted phases are able to rotate the plane of polarized light that passes along the axis (Fig. 12. If the molecules are polar, this twisting can be turned off by imposing an external electric field at either end of the long axis. Besides the very important application of this property (known as *ferroelectricity*) to liquid crystal displays, these materials can be used to make electrooptic shutters which can be switched open and closed in microseconds.

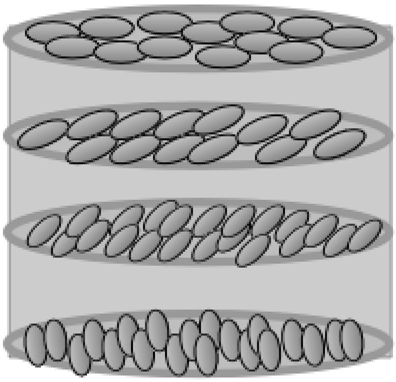


Fig. 5.20 Chirality in Cholesteric

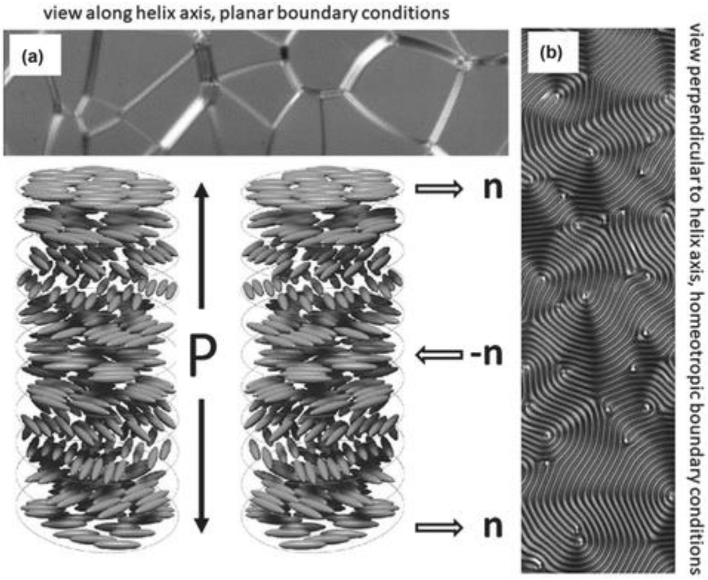


Fig. 5.21 The chiral nematic or cholesteric phase can exhibit a right- or a left-handed helical superstructure, depending on the configuration of the chiral centre(s) or that of the chiral dopant. (a) When viewed along the helical axis, which is generally achieved by planar boundary conditions, an oily-streak texture is often observed. (b) For homeotropic boundary conditions, the helix axis oriented perpendicular to the direction of light propagation, and a typical fingerprint texture is shown. Note that the periodicity of the cholesteric phase is P/2, due to the head-tail symmetry of the director n=−n.

In liquid crystals, the introduction of chirality either through chiral elements directly within the mesogens (in most cases chiral centres), or through chiral dopants, leads to a multitude of novel structures, phases and effects. In the chiral nematic, N*, and the chiral SmC* phase, one observes for example the spontaneous formation of helical superstructures, which can be left- or right-handed, depending on the handedness, and thus configuration, of the chiral centre or dopant. This is schematically illustrated in Fig. 5.20 and 5.21. Nevertheless, it should be mentioned that at this time no prediction of the helical handedness in relation to that of the chiral centre or dopant can be made [9].

5.12 DIELECTRIC SUSCEPTIBILITY AND DIELECTRIC CONSTANTS

A dielectric material is an insulator that can be polarized by the application of an electric field. Here, the electrons are bound to the nucleus and have limited movement and when an external field is applied, the nucleus of the atoms are attracted to the negative terminal and the electrons are pulled towards the positive terminal and tend to align in equilibrium position. These charges separated by a small distance constitute a 'dipole' and the process is known as 'polarization' (P). The term 'dielectric' is often used to indicate the energy storing capacity of the material and dielectrics are an efficient supporter of electrostatic fields. The extent to which a substance concentrates the electrostatic lines of flux can be quantified by "Dielectric constant" or in other words, the response of charge-free sample to an applied electric field. 1 In corollary, all dielectrics are insulators but not all insulators are dielectrics. The polarizability and structural arrangement dictates the behavior of dielectrics (Fig. 5.22). The built-up polarization in dielectrics takes a certain finite time (τ) before reaching its maximum value. This time-dependent dynamics is characteristic to each material and is termed as 'dielectric relaxation'.

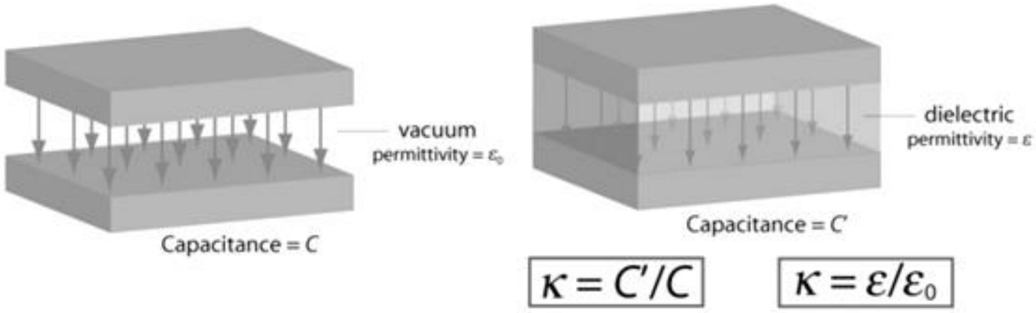


Fig. 5.22 Dielectric properties

5.13 ADVANTAGE OF LIQUID CRYSTAL POLYMER:

High heat resistance

Flame retardant

Chemical resistance

Dimensional stability

Mold ability

Heat aging resistance

Adhesion Low viscosity

Wieldable

Low cost

In Soap and Conducting foams

Heat Sensitive cameras,

Liquid crystal screens that respond to heat

Surface Thermometry

Thermochromic behavior of chiral nematic phase

Switchable Light Panels (windows)

Liquid crystal droplets dispersed in a polymer film, whose optical properties change under the action of an electric field

5.14 DISADVANTAGE OF LCP

Form weak weld lines

Highly anisotropic properties

Drying required before processing

High Z-axis thermal expansion coefficient

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5.16 QUESTIONS

1. Describe optical properties of liquid crystals.

2. Define liquid crystal and give its classification.

3. Define Molecular rearrangement in smectic A and smectic C phases.

4. describes the extent to which the liquid crystal sample is ordered.

5. Give advantages and disadvantages of liquid crystals.

UNIT 6 SURFACE ACTIVE AGENTS

CONTENTS

6.1 OBJECTIVE

- Know about surfactants and their behavior in the solution.
- Learn about formation of surfactants and their solubility behaviour in different phases.
- Classify the surfactants by their process of formation
- Know about the various applications of surfactant in different fields.

To understand catalytic activity at surfaces

6.2 INTRODUCTION

Surface active agents (surfactants) are amphiphilic compounds with two opposing portions, one part is hydrophilic and the other is hydrophobic. They reduce the free energy of the system by replacing the bulk molecules of higher energy at an interface. By reducing the interfacial tension and forming micelles, surfactants or biosurfactants have shown many environmental applications including enhanced oil recovery, removal of heavy metals from contaminated soil and remediation of hydrophobic organic compounds from soil. They are used in environmental applications to enhance solubility of organic or inorganic components for soil washing or flushing. Typical desirable properties include solubility enhancement, surface tension reduction and low critical micelle concentrations (CMC).

6.3 CLASSIFICATION OF SURFACE ACTIVE AGENTS

The term surfactant is a blend of surface active agent. A molecule that contains a polar portion and a non polar portion is called surface active agent. A surfactant can interact with both polar and non polar molecules. Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). Surfactants can be classified according to its polar head groups [1]. Non-ionic surfactants have no charged groups on their heads. The head of the ionic surfactant carries a net positive or negative charge, and if the charge is negative, the surfactant is more specifically called an anion; if the charge is positive, it is called a cation. If the surfactant contains a head with two oppositely charged groups, it is called a zwitterion. Surfactants are generally divided into the following categories:

6.3.1 Nonionic surfactants

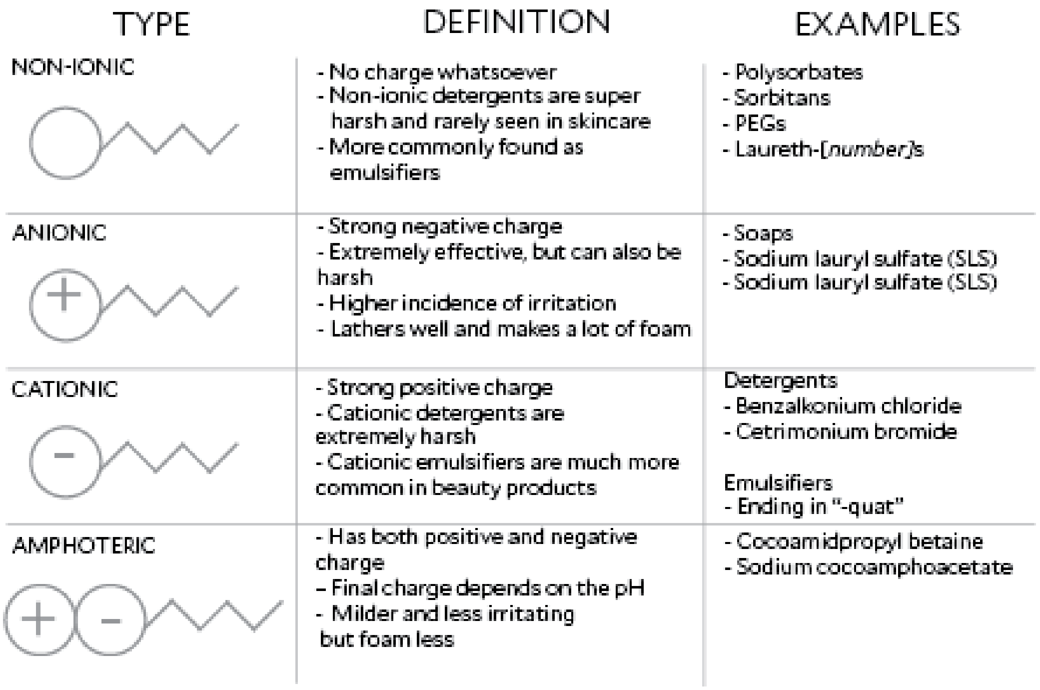
A non-ionic surfactant has no charge groups in its head. The head of an ionic surfactant carries a net charge. They derive their polarity from having an oxygen–rich portion of the molecule at one end and a large organic molecule at the other end. The oxygen component is usually derived from short polymers of ethylene oxide or propylene oxide. Just as in water chemistry, the oxygen is a dense electron-rich atom that gives the entire molecule a partial net-negative charge which makes the whole molecule polar and able to participate in hydrogen bonding with water. Non-ionic detergents are super harsh and rarely seen in skincare. More commonly found as emulsifiers. Many long chain alcohols exhibit some surfactant properties [2]. Some examples of nonionic surfactants are alcohol ethoxylates, nonylphenoxy polyethylenoxy alcohols and ethylene oxide/propylene oxide block copolymers, Nonoxynol-9 (Polyoxyethylene glycol alkylphenol ethers: C9H19–(C6H4)–(O-C2H4)1–25–OH), Polysorbate (Polyoxyethylene glycol sorbitan alkyl esters). (Fig. 6.1)

6.3.2 Anionic surfactants

These have a negatively charged end of the molecule that gives it the hydrophilic part of the molecule [3]. These negatively charged parts of the molecules are usually sulfonates, sulfates, or carboxylates that are usually neutralized by positively charged metal cations such as sodium or potassium. Examples include sodium alkylbenzene sulfonates, sodium stearate (a soap), and potassium alcohol sulfates. Mixture of sodium alkyl sulphates, the chief of which is sodium dodecyl sulfate. It is very soluble in water at room temperature, and is used pharmaceutically as a preoperative skin cleaner, having bacteriostatic action against gram- positive bacteria, and also in medicated shampoos. Anionic surfactants are ionic and are Anionic surfactants made up of two ions positively charged, usually metal, ion and a negatively charged organic ion (Fig. 6.2).

It fall into four categories: Sulfonates, Alkyl Sulfates, carboxylates, and phosphates. Anionic surfactants have good decontamination, foaming, dispersing, emulsifying, and wetting properties and that’s why they are widely used as detergents, foaming agents, wetting agents, emulsifiers, and dispersants. The production of anionic surfactants tops the list of surfactants. Anionic surfactants cannot be used with cationic surfactants, as they will precipitate in aqueous solutions and lose their effectiveness. It is stable in alkali, dilute acid and hard water, and the decomposition temperature is 240°C. It has a good stability in a wide range of pH.

Alkyl Sulfates (RO-SO3-M) Typical of such active agents are fatty alcohol polyoxyethylene ether sulfates(AES) and sodium lauryl sulfate. Fatty alcohol polyoxyethylene ether sulfate is easily soluble in water, and its appearance is light yellow viscous liquid (translucent) with 70% of active content, and its stability is inferior to that of normal sulfonate. It hydrolyzes quickly below pH 4 but is stable in alkaline conditions. Sodium dodecyl sulfate is synonymous with AS, K12, sodium lauryl sulfate. It dissolves in water and dissolves in water and its water solubility is inferior to AES. It is insensitive to alkalis and hard water, but is less stable than normal sulfonates in acidic conditions. Fatty acid soap ((RCOO$^-$)nM) stearate, oleic acid, and lauric acid are common fatty acid hydrocarbons. According to the different substances represented by M, they can be divided into alkali metal soap, alkaline earth metal soap and organic amine soap. They all have good emulsifying properties and the ability to disperse oil, but they can be easily decomposed.



TYPE	DEFINITION	EXAMPLES
NON-IONIC	- No charge whatsoever - Non-ionic detergents are super harsh and rarely seen in skincare - More commonly found as emulsifiers	- Polysorbates - Sorbitans - PEGs - Laureth-[*number*]s
ANIONIC	- Strong negative charge - Extremely effective, but can also be harsh - Higher incidence of irritation - Lathers well and makes a lot of foam	- Soaps - Sodium lauryl sulfate (SLS) - Sodium lauryl sulfate (SLS)
CATIONIC	- Strong positive charge - Cationic detergents are extremely harsh - Cationic emulsifiers are much more common in beauty products	Detergents - Benzalkonium chloride - Cetrimonium bromide Emulsifiers - Ending in "-quat"
AMPHOTERIC	- Has both positive and negative charge – Final charge depends on the pH - Milder and less irritating but foam less	- Cocoamidpropyl betaine - Sodium cocoamphoacetate

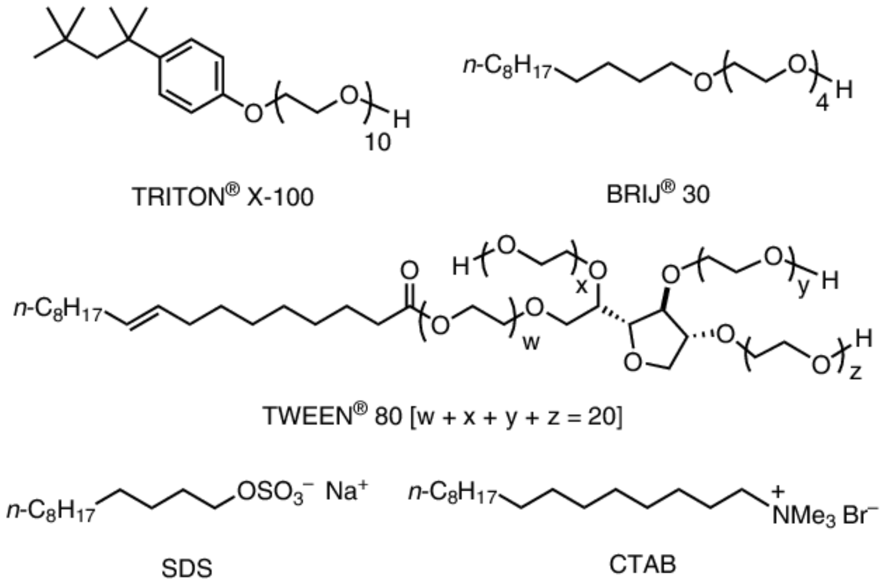


Fig. 6.1 Examples of nonionic surfactants

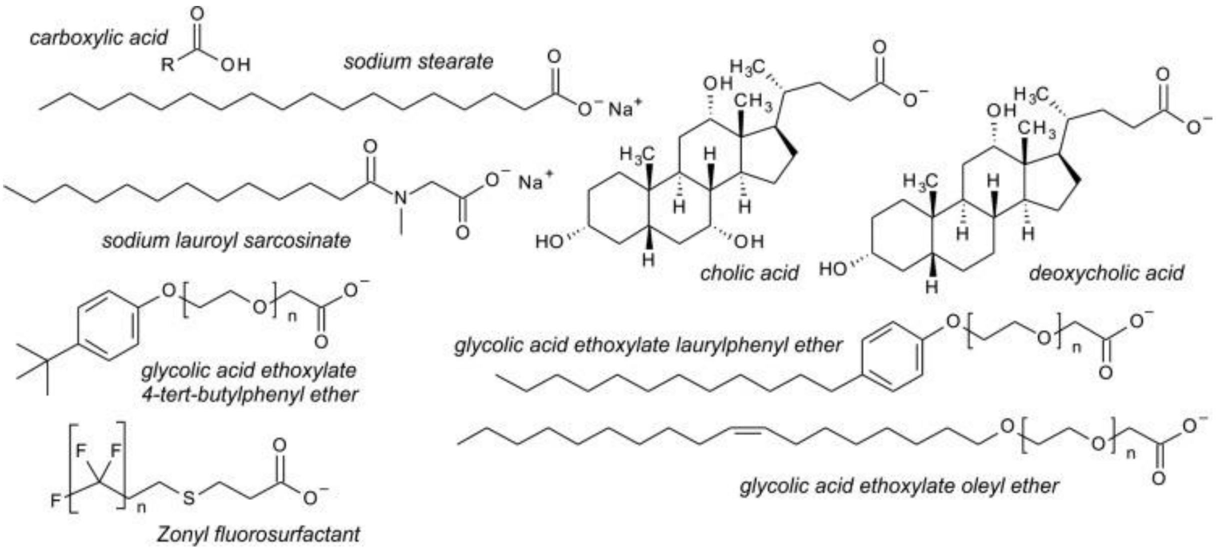


Fig. 6.12 Examples of anionic surfactants

The alkali metal soap can also be decomposed by calcium and magnesium salts, and the electrolyte can also salt it out. Different fatty acid salts have different properties. As a surfactant, the fatty acid salt is soluble in water, but its solubility and surface activity are affected by pH, gold urine ions such as calcium and magnesium, and temperature factors. It is easily hydrolyzed under acidic conditions and loses its surface activity while its water solubility is reduced. At lower temperatures, the water-solubility of fatty acid salts is reduced and can easily become a solid gel. Phosphate salt (RO-PO_3-M) Phosphate surfactant is the representative of phosphorus-containing surfactants. This is a widely-used surfactant with high performance. It has excellent properties such as wetting, washing, solubilizing, emulsifying, antistatic, corrosion inhibition and rust resistance, and it is easily biodegradable. Its thermal stability, alkali resistance, electrolyte resistance and antistatic properties are all superior to those of general anionic surfactants. It is widely used in the fields of chemical fibers, textiles, plastics, paper-making, leather and household chemicals. The main varieties of phosphate ester surfactants are alkyl(aryl) phosphates(salts), alkyl alcohol amide phosphates (salts), imidazolines Phosphates (salts), high molecular polyphosphates (salts), and siloxane phosphates. Alkyl (aryl)phosphates are an important class of anionic surfactants,

6.3.3 Cationic surfactants

These are positively charged molecules usually derived from nitrogen compounds. They are not commonly used as cleaning agents in hard-surface cleaners because of the tendency of the cationic positively charged molecule to be attracted to hard surfaces. Many cationic surfactants have bacteriacidal or other sanitizing properties that are useful in creating disinfectants that leave a cationic disinfectant film on the surface. Cationic surfactants are usually incompatible with anionic surfactants, because they will react with the negatively charged anionic surfactant to form an insoluble or ineffective compound. They may be used on the skin, especially in the cleaning of wounds [4].

Cationic surfactant is a pentavalent nitrogen atom, it is also referred to as a quaternary ammonium compound. Its characteristics are water-soluble, stable in acidic and alkaline solutions, and has a good surface activity and bactericidal effect. Common types of cationic surfactants are cetyldimethylammonium chloride, octadecyltrimethylammonium chloride, cationic guar gum, cationic panthenol. Cationic surfactants, unlike other surfactants, have poor detergency and foaming properties and tend to have some irritation and lower toxicity. Cationic surfactants are used in liquid detergents as a co-surfactant and as a formulation component with a small amount of formulation, and they are generally used for higher end products such as shampoos. Cationic surfactants are not directly compatible with anionic surfactants, although the combination of cations and anions may have good results, the risk of precipitation (crystallization) is greater. Cationic surfactants have a small share of surfactant production and are often more expensive than other surfactants. Compared with other surfactants, cationic surfactants have the most outstanding adjustment effect and the strongest bactericidal effect. Despite the disadvantages of poor detergency, poor foaming, poor compatibility, irritation, and high cost, as a regulator ingredient in detergents and shampoos, cationic surfactants cannot be replaced by any other types of surfactants (Fig. 6.3).

6.3.4 Amphoteric Surfactants

Amphoteric surfactants refer to surfactants that have both anionic and cationic hydrophilic groups. This surfactant is cationic in acidic solutions, anionic in alkaline solutions, and has non-ionic properties in neutral solutions. Those surfactants that change their charge with pH. Usually, any one amphoteric can be any two of the three charge states. Examples- Amino acids, Betaines and lecithin. Amphoteric surfactants are easily soluble in water, soluble in concentrated acid and alkali solutions, and even dissolved in concentrated solutions of inorganic salts. They have good resistance to hard water, little irritation to the skin, good fabric softness, antistatic properties and good bactericidal effect. This type of surfactants can be used in a wide range of pH, but their performance under acidic and neutral conditions should be better than under alkaline conditions. Important amphoteric surfactants are lauryl dimethyl betaine and carboxylate imidazoline. Compared to anionic surfactants, nonionic surfactants have more comprehensive properties and fewer defects. Amphoteric surfactants have better foaming capabilities than nonionic surfactants. Therefore, amphoteric surfactants are mainly used in shampoos, shower cleaners and other skin cleaners (Fig.6.4).

6.4 Micellization

A micelle is an aggregate of surfactant molecules dispersed in a liquid colloid [5]. A typical micelle in aqueous solution forms an aggregate with the hydrophilic head region in contact with surrounding solvent, sequestering the hydrophobic tail regions in the micelle centre. This type of micelle is known as normal phase micelle. Micelle is a self-assembled structure of amphiphilic molecules and consists of core and shell. The process of forming micelle is known as micellization (Fig. 6.5). Most micelles are spherical and contain between 60 and 100 surfactant molecules. Driving force for the formation of micelles is the increase of entropy that occurs when the hydrophobic regions of the surfactant are removed from water and the ordered structure of the water molecules around this region of the molecule is lost. Reason for micelle formation is the attainment of a minimum free energy state. Concentration of surfactant at which micelles first appear in solution is called as CMC Self-association of the amphiphile into small aggregates called micelles. As concentration of surfactant increased there is alteration in physical properties of solution (Fig. 6.6).

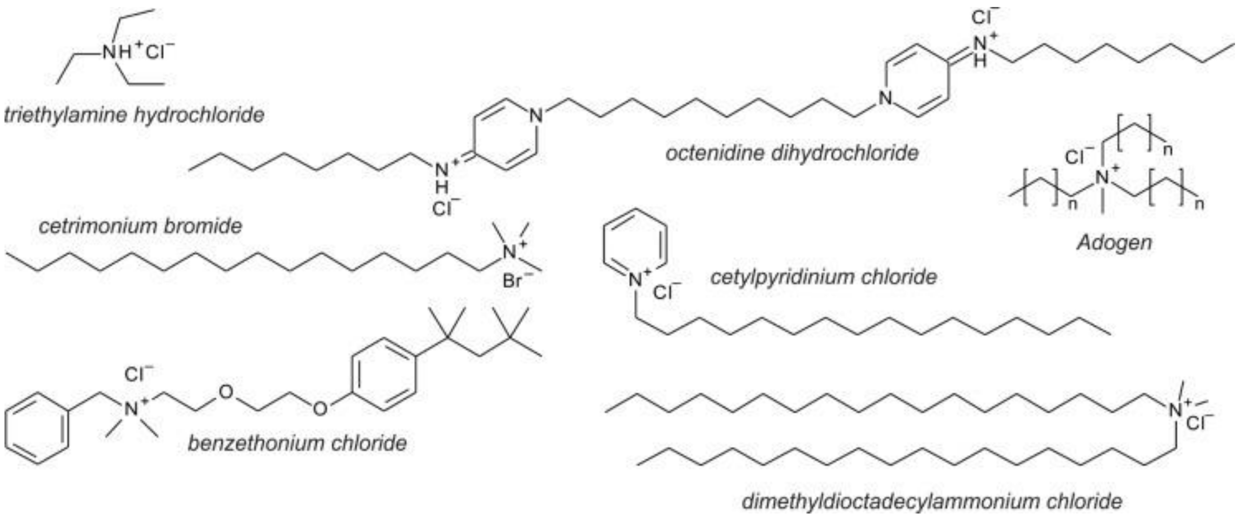
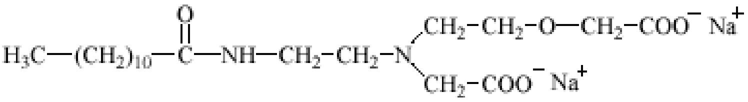


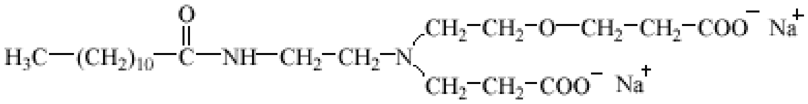
Fig. 6.3 Examples of cationic surfactants

Alkylamphodiacetate
(Disodium Lauroamphodiacetate)



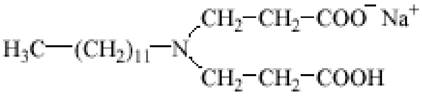
$$H_3C-(CH_2)_{10}-\overset{\overset{O}{\|}}{C}-NH-CH_2-CH_2-N\begin{array}{l} CH_2-CH_2-O-CH_2-COO^- \ Na^+ \\ CH_2-COO^- \ Na^+ \end{array}$$

Alkylamphodipropionate
(Disodium Lauroamphodipropionate)



$$H_3C-(CH_2)_{10}-\overset{\overset{O}{\|}}{C}-NH-CH_2-CH_2-N\begin{array}{l} CH_2-CH_2-O-CH_2-CH_2-COO^- \ Na^+ \\ CH_2-CH_2-COO^- \ Na^+ \end{array}$$

Alkyliminodipropionate
(Sodium Lauriminodipropionate)



$$H_3C-(CH_2)_{11}-N\begin{array}{l} CH_2-CH_2-COO^- \ Na^+ \\ CH_2-CH_2-COOH \end{array}$$

Fig. 6.4 Examples of amphoteric surfactants

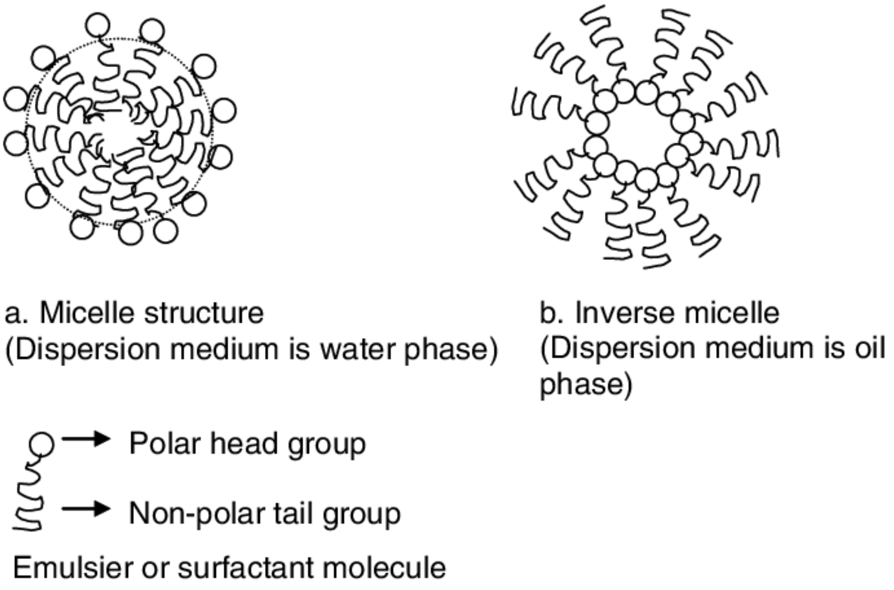


Fig. 6.5 Micelle structures

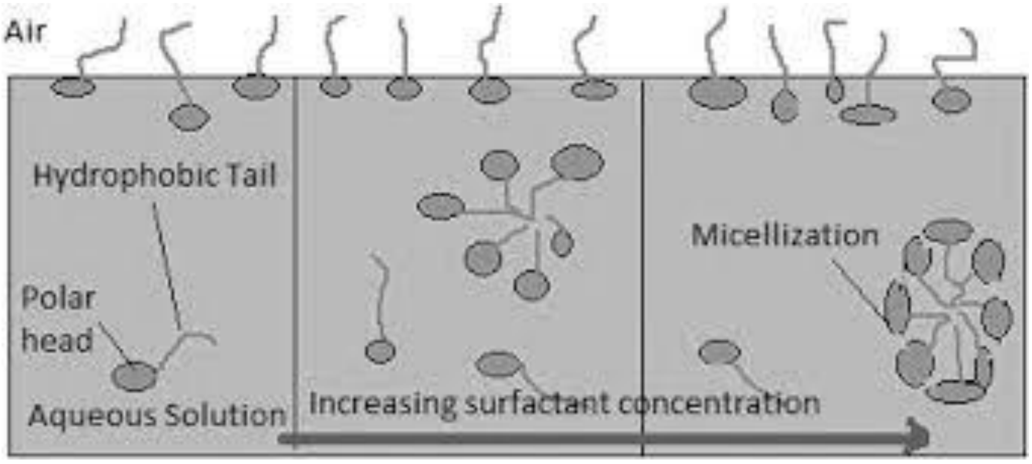


Fig. 6.6 Process of micelle formation

6.5 CRITICAL MICELLE CONCENTRATION (CMC)

The lowest concentration at which micelles first appear is called the critical concentration for micelle formation [6]. The critical micelle concentration is the point at which surfactant molecules aggregate together in the liquid to form groups known as micelles. The critical micelle concentration of a surfactant indicates the point at which surface active properties are at an optimum and performance is maximised. The CMC is the concentration above surfactant when micelles will form spontaneously. Increase in concentration of surfactant beyond CMC change number size or shape but not provide increase in concentration of monomeric species. The CMC is an important characteristic of a surfactant. Before reaching the CMC (Fig. 6.7), the surface tension changes strongly with the concentration of the surfactant. The value of the CMC for a given dispersant in a given medium depends on temperature, pressure, and (sometimes strongly) on the presence and concentration of other surface active substances and electrolytes. Micelles only form above critical micelle temperature. For example, the value of CMC for sodium dodecyl sulfate in water at 25°C, atmospheric pressure, is 8×10^{-3} mol/L. The critical micelle concentration of a surfactant is decreased by other components in a detergent, in particular, electrolytes such as inorganic builders and alkalis [7,8].

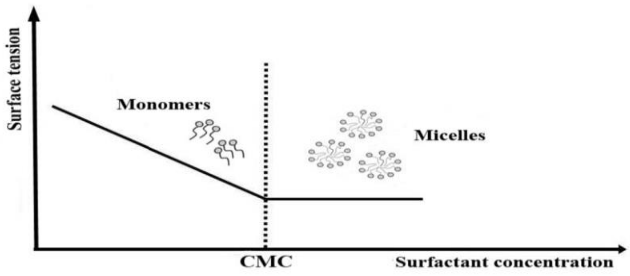


Fig. 6.7 CMC development

6.5.1 Hydrophobic Interactions

Hydrophobic interactions describe the relations between water and hydrophobes (low watersoluble molecules). Hydrophobes are nonpolar molecules and usually have a long chain ofcarbons that do not interact with water molecules. The mixing of fat and water is a good example of this particular interaction. The common misconception is that water and fat doesn't mix because the Van der Waals forces that are acting upon both water and fat molecules are too weak. However, this is not the case. The behavior of a fat droplet in water has more to do with the enthalpy and entropy of the reaction than its intermolecular forces.

6.5.2 Kraft Temprature

The Krafft temperature (Krafft point) is the minimum temperature at which ionic surfactants, such as sodium lauryl sulphate (a component of household detergents), form micells. It depends on the nature of hydrophobic groups and ionic composition of the detergent. On the contrary, the solubility of nonionic surfactants decreases with increasing temperature. They are characterised by the cloud point, i.e. the maximum temperature at which nonionic surfactants form micelles and above which the mixture starts to phase separately in the surfactant- solvent , thus changes in its optical properties occur.

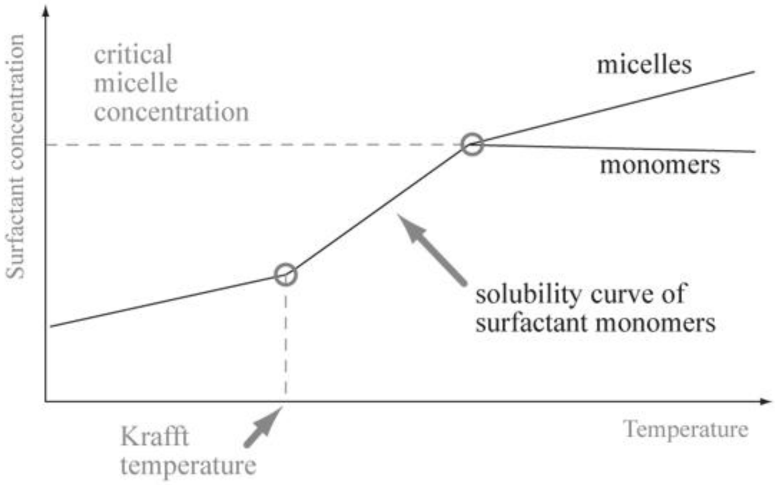


Fig. 6.8 Kraft temprature

6.5.3 Factors affecting the Critical Micelle Concentration

After the formation of micelles in the solution, the properties of the solution significantly change and therefore it is critical to study the factors that can affect the CMC [9].

(1) Structure of the amphiphiles: In general CMC decrease as the hydrophobic character of the surfactant increases.

(2) Ionic surfactants: in general surfactants with ionic headgroups have a higher CMC in aqueous solution than surfactants with non-ionic headgroups.

(3) Bulky hydrophobic/hydrophilic groups: Due to the difficulty in incorporating bulky groups in the interior of the micelle, the bulkiness of the surfactants increases the CMC.

(4) Presence of Additives: Electrolyte: High ionic strength solution lowers the repulsion between the head groups due to the presence of counter ions surrounding the groups, therefore the CMC decreases; Organic: Organic compounds (impurities) can either penetrate the micellar regions or modify the interaction between solvent-

micelles. For example Urea, formaldehyde are believed to increase the CMC by disrupting the H-bonding network.

(5) Experimental conditions: Temperature: High temperature causes a decrease in hydration of the hydrophilic groups and thus it favors micellization (low CMC). High temperature may cause disruption in structured water around head groups and CMC increases. Micelles (CMC) pH: CMC will be high at a pH value where head group is charged for example: Low pH for –COOH head group and high pH for –NH2 group will increase the CMC for both cases.

(6) Effect of Additives :In non ionic surfactants lower alcohols causes increase in the cmc (weakening of hydrophobic bond) and higher alcohols causes increase. Linear relationship between cmc and the number of carbon atom in the alcohol molecule was established in a series of potassium soaps . Addition of lower alcohols to ionic surfactant causes a decrease in the cmc which becomes more pronounced with increase in hydrophobicity of added alcohol [10]. Alcohols θ Inorganic additives have appreciable effect on cloud point of non ionic surfactants. Two categories of additives are identified that make change to cloud point. (a)urea and salts with anion known to break the water structure such as iodides, thiocynates etc (b)salts with cations . Inorganic Electrolytes θ Micellar size increases for a particular cationic surfactant as the counter ion is changed according to the series Cl−. In ionic surfactants the change of the counter ion to one of greater polarizability or valence leads to decrease in cmc and corresponding increase in aggregation number.

(7) Effect of Temperature : Increase in temperature results in a decreased micellar size. At temperatures up to the cloud point there is an increase in micellar size and a corresponding decrease in CMC. Aqueous solutions of many non-ionic surfactants become turbid at a characteristic temperature called the cloud point. Dissociation of monomers is observed at low pressure while association at high pressure. This can be due to solidification of the micellar interior or change in the dielectric constant of water at high pressure [11].

6.5.4 Thermodynamics of micellization:

The formation of micelle can be understood using thermodynamics: micelles can form spontaneously because of balance between entropy and enthalphy. A surfactant, when present at low concentrations in a system, adsorbs onto surfaces or interfaces significantly changing the surface free energy. Primary reason of micelle formation is attainment of minimal free energy [12].

6.5.5 Solubilization

Micelle can be used to increase the solubility of material that are normally insoluble or poorly soluble in dispersed medium phenomenon called as solubilization. Because the interior of micelles in aqueous solution is essentially hydrophobic, water-insoluble compounds are able to dissolve in it is known as solubilization [13]. The solubility of the added compound increases markedly at concentration of amphipath above the CMC. E.g. Digestion of fats by animals.

6.6 REVERSED MICELLE

In Reversed micelle at middle able to hold relatively large amounts of water in their interior. In that way, a "pocket" is formed which is particularly suited for the dissolution and transportation of polar solutes through a non polar solvent. Reverse micelles are taxicabs that are a transport oily substance in a polar solvent. They are self-organized molecular collections of surfactants in a polar media. Also, their polar heads are in the interior and their hydrophobic chains are in the exterior. Moreover, it gives polar substances a ride through an oily medium. Furthermore, they depict the polarity in the opposite way of micelles Moreover,the extraction of proteins happens by the interaction among the proteins surface and the reverse micelles. In addition, the extraction control of the protein in the usualreversemicellar system is approved by using a modification of the surface characteristics ofproteinsand the size of the reverse micelles that are affected by the pH and salt concentration.Also, proteins suffer from denaturation, and the efficiency of proteins division using it decreases drastically when the interface between proteins and micelles is too powerful. Besides, it’s probable to significantly alter the distinctiveness and structure of reverse micelles by means of external stimulation; it will be probable to raise a more efficient division process of proteins [14]. Besides, some studies reported on the control of the formation of reverse micelles by pH, temperature, and pressure (Fig. 6.9). They are water droplets that we obtain from the action of sulfates when it disperses in water. Moreover, its size is nanometer. Also, surfactant atoms create with the polar part to the internal side ready to solubilize water and the polar part in contact with the natural dissolvable. The use of reverse micelles is a possible means to help separate proteins and other biological products of interest. The aggregation of incorrectly refolded proteins is due to the interactions of the hydrophobic patches exposed on the polypeptide chains. Presumed that if the polypeptide chains could be isolated from each other, this would assist in the recovery of activity of these proteins. They suggested isolating these polypeptide chains in reverse micelles. The reverse micelles are water droplets stabilized by bis-(2-ethylhexyl)sodium sulfosuccinate (AOT) (surfactant) in isooctane [15]. Each reverse micelle contains a single protein (albeit not completely folded). Briefly, the following steps were involved:

(1) the denatured protein solubilized in guanidine hydrochloride is transferred into the reverse micelles by the phase transfer method.

(2) the denaturant concentration is reduced gradually in the reverse micelles.

(3) the disulfide bonds in the denatured protein are reoxidized by the addition of a redox agent, and the protein attains its active conformation.

(4) the protein is extracted from the reverse micelles into an aqueous solution.

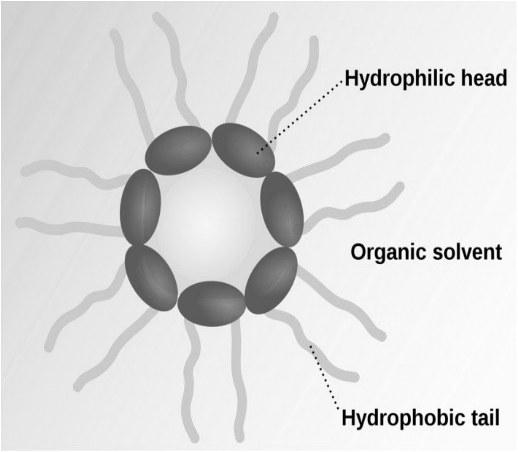


Fig. 6.9 Reverse micelle

6.6.1 Formation of Reverse Micelles

6.7 MICROEMULSION

Microemulsion (ME) refer to monophasic, optically isotropic, thermodynamically stable, and clear dispersions formulated from oil, water, surfactant, and a cosurfactant. The term microemulsion, which was first used in 1943 by Hoar and Schulman, is ambiguous because it is not clear from the term that several phases and structures can be present. Water or oily droplets and bicontinuous structures can form even within the microemulsion domains.

Microemulsions are effective drug delivery vehicles since they are simple to prepare (an external energy source is not required) and are thermodynamically stable (ME phases do not easily separate over time and a majority of microemulsions are stable for many years). Compared to regular emulsions, microemulsions form spontaneously following the mixing of the correct amounts of the constituents, with no need for a supplementary source of mechanical energy. Another difference is that microemulsions are clear or translucent with droplet size in nanometers, while emulsions are coarse, milky dispersions with droplet size usually measured in micrometers. The use of microemulsions for the transdermal delivery of specific therapeutic agents is also described. Microemulsions may be used as the carrier for protein and peptide delivery to the GI tract [16]. With all types of microemulsions, water–oil–water type microemulsion offers unique advantages, including these:

Degradation of proteins is effectively reduced due to the use of relatively mild conditions during the formulation process of microemulsions.
Use of protein-compatible ingredients such as surfactants, water, and oils.
These excipients are used in pharmaceutical formulations and generally recognized as safe. Their toxicities and metabolic profiles are well-known.
Microemulsions are stable for relatively long periods. Microemulsions are recognized as a thermodynamically stable system.
Microemulsion-based formulations are prepared in liquid forms, which are preferable for patients with difficulties in swallowing solid.

Permeation studies of microemulsion using mouse skin showed a steady increase in drug flux for 24 h, which indicated that the microemulsions were able to provide a prolonged release of triptolide. A microemulsion comprised of oleic acid (6%), Tween 80 (20%), propylene glycol (10%), and menthol (1%) in water (62.97%) was found to be the most efficient for the delivery of triptolide. The microemulsion was non-irritant, ensured adequate protection from drug degradation, provided prolonged release, and was found to be suitable for long-term use.

6.8 CATALYTIC ACTIVITY AT SURFACES

A catalyst accelerates a chemical reaction. It does so by forming bonds with the reacting molecules, and by allowing these to react to a product, which detaches from the catalyst, and leaves it unaltered such that it is available for the next reaction. In fact, we can describe the catalytic reaction as a cyclic event in which the catalyst participates and is recovered in its original form at the end of the cycle.

A heterogeneous catalytic reaction involves adsorption of reactants from a fluid phase onto a solid surface, surface reaction of adsorbed species, and desorption of products into the fluid phase. The presence of a catalyst provides an alternative sequence of elementary steps to accomplish the desired chemical reaction from that in its absence. If the energy barriers of the catalytic path are much lower than the barrier(s) of the noncatalytic path, significant enhancements in the reaction rate can be realized by use of a catalyst.

The platinum-catalyzed oxidation of carbon monoxide according to the overall $CO + \frac{1}{2} O_2 \Rightarrow CO_2$ reaction , The first step in the profile represents the adsorption of carbon monoxide and dioxygen onto the catalyst. In this case, adsorption of dioxygen involves dissociation into individual oxygen atoms on the Pt surface. The product is formed by addition of an adsorbed oxygen atom (Oads) to an adsorbed carbon monoxide molecule (COads)' The final step in the catalytic reaction is desorption of adsorbed carbon dioxide (CO_2ads) into the gas phase. The Pt catalyst facilitates the reaction by providing a low energy path to dissociate dioxygen and form the product. The noncatalytic route depicted in Fig.6.10 is extremely slow at normal temperatures due to the stability of dioxygen molecules.

The potential energy diagram for the chemisorption of hydrogen atoms on nickel is schematically depicted in Fig.6.11. As molecular hydrogen approaches the surface, it is trapped in a shallow potential energy well associated with the physisorbed state having an enthalpy of physisorption ΔHp. The deeper well found closer to the surface with enthalpy ΔHc is associated with the hydrogen atoms chemisorbed on nickel. There can be an activation barrier to chemisorption, E, which must be overcome to reach a chemisorbed state from the physisorbed molecule. Since molecular hydrogen (dihydrogen) is dissociated to form chemisorbed hydrogen atoms, this phenomenon is known as dissociative chemisorption. Because rates of heterogeneous catalytic reactions depend on the amounts of chemisorbed molecules, it is necessary to relate the fluid phase concentrations of reactants to their respective coverages on a solid surface.

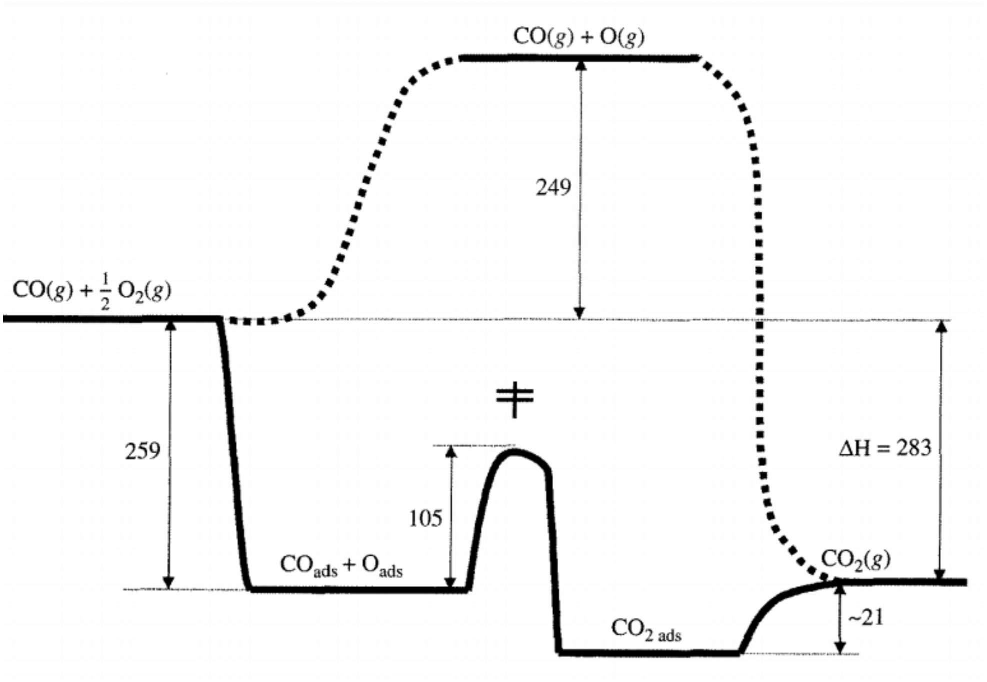


Fig. 6.10 Energy dif for the catalytic oxidation of CO over Pt.

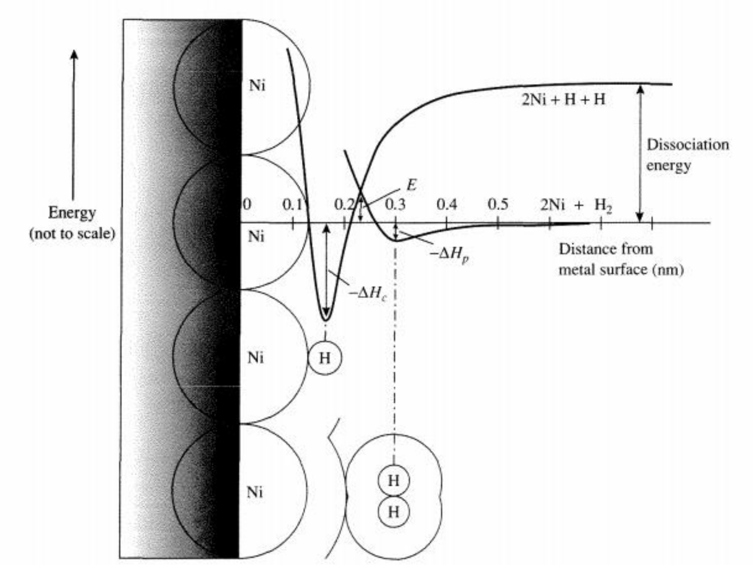


Fig. 6.11 Potential energy diagram for the chemisorption of hydrogen on nickel

6.9 ELECTRODE/ELECTROLYTE INTERFACE

An electrolytic cell has three component parts: an electrolyte and two electrodes (a cathode and an anode). The electrolyte is usually a solution of water or other solvents in which ions are dissolved. Molten salts such as sodium chloride are also electrolytes. Electrode–electrolyte interfaces in Li-ion batteries are usually thermodynamically unstable and are stabilized by surface (solid electrolyte interface, SEI) layers. SEI layers are therefore essential for the performance and stability of Li-ion batteries [17]. SEI layers are naturally formed in contact with the electrolyte or are artificially produced by coating processes. The most important function of the SEI on the positive electrode (cathode) is to minimize electrolyte oxidation at high electrode potentials.

The naturally formed cathodic SEI is a several nanometer thick, multi-component organic–inorganic film, which effectively suppresses electron transfer and allows for easy Li-ion transfer. The formation, composition, and properties of the SEI have been extensively investigated on composite electrodes by surface analysis and/or electrochemical methods, and have been subject of several review articles. Typical inorganic compounds found in the cathodic SEI are lithium carbonates, lithium oxides, and lithiumfluoride, which are partly embedded in a matrix of polymeric species formed from the electrolyte. This organic–inorganic top layer covers the electrode which itself is chemically and structurally altered in the surface region due to corrosion processes. SEI formation and electrolyte degradation are complex processes that take place by numerous, partially interrelated reaction pathways,such as solvent reduction and formation of semi-carbonates, or solvent oxidation with subsequent polymerization.

The oxidation potential of organic compounds is determined in electrochemical cells using inert electrodes, and can be related to the energetic conditions of the removal of one electron from the compound. In the field of Li-ion batteries, experimentally determined (practical) oxidation potentials and electrolyte stability are commonly discussed using qualitative energy level diagrams. A more in-depth evaluation requires the knowledge of the real electronic interface structure and must consider the influence of ionic effects and reaction product formation [18]. Suitable approaches to investigate these issues are theoretical calculations and experimental investigations using surface science methods. More recently, several theoretical research papers have been published that investigate the energetic conditions of electrolyte oxidation, demonstrating the relevance of solvation effects and salt anion-solvent molecule interactions. On the other hand, the chemical and electronic structure of model cathode surfaces and cathode–solvent interfaces was experimentally explored by us and others, which showed inter alia high electronic energy level offsets precluding electrolyte oxidation until very high positive potentials are reached.

Changes at the electrode/electrolyte interface due to reactions of the negative electrode with the electrolyte are considered to be the major source for aging of/at the negative electrode. It is well known that carbonaceous negative electrodes in lithium-ion batteries operate at a potential outside the electrochemical stability window of the electrolyte components.

Reductive electrolyte decomposition accompanied by irreversible consumption of lithium ions takes place at the electrode/electrolyte interface when the electrode is in the charged state (i.e., polarized to low potentials) [19]. The decomposition products build up ‘protective layers’ that cover the electrode’s surface. This process occurs mainly (but not exclusively) at the beginning of cycling, especially during the first cycle. The protective layers act as a so-called SEI (solid electrolyte interphase). They are permeable to lithium cations but rather impermeable to other electrolyte components and electrons. Thus, normally the SEI reasonably protects (1) the electrolyte compounds from further reduction and (2) the charged electrode from corrosion (Fig. 6.12).

6.9.1 The Electrical Double Layer

The model which gave rise to the term 'electrical double layer' was first put forward in the 1850's by Helmholtz. In this model he assumed that no electron transfer reactions occur at the electrode and the solution is composed only of electrolyte. The interactions between the ions in solution and the electrode surface were asssumed to be electrostatic in nature and resulted from the fact that the electrode holds a charge density (qm) which arises from either an excess or deficiency of electrons at the electrode surface. In order for the interface to remain neutral the charge held on the electrode is balanced by the redistribution of ions close to the electrode surface [20]. Helmholtz's view of this region is shown in the figure below (Fig. 6.12).

The attracted ions are assumed to approach the electrode surface and form a layer balancing the electrode charge, the distance of approach is assumed to be limited to the radius of the ion and a single sphere of solvation round each ion. The overall result is two layers of charge (the double layer) and a potential drop which is confined to only this region (termed the outer Helmholtz Plane, OHP) in solution. The result is absolutely analogous to an electrical capacitor which has two plates of charge separated by some distance (d) ith the potential drop occurring in a linear manner between the two plates. It is perhaps no surprise that when impedance analysis is performed on electrochemical systems the response due to the electrolyte redistribution is modelled in terms of capacitative elements.

The model of Helmholtz while providing a basis for rationalising the behaviour of this region does not account for many factors such as, diffusion/mixing in solution, the possibility of absorption on to the surface and the interaction between solvent dipole moments and the electrode. A later model put forward by Stern begins to address some of these limitationsnow the ions are assumed to be able to move in solution and so the electrostatic interactions are in competition with Brownian motion. The result is still a region close to the electrode surface (100×10^{-10} m) containing an excess of one type of ion but now the potential drop occurs over the region called the diffuse layer (Fig.6.13).

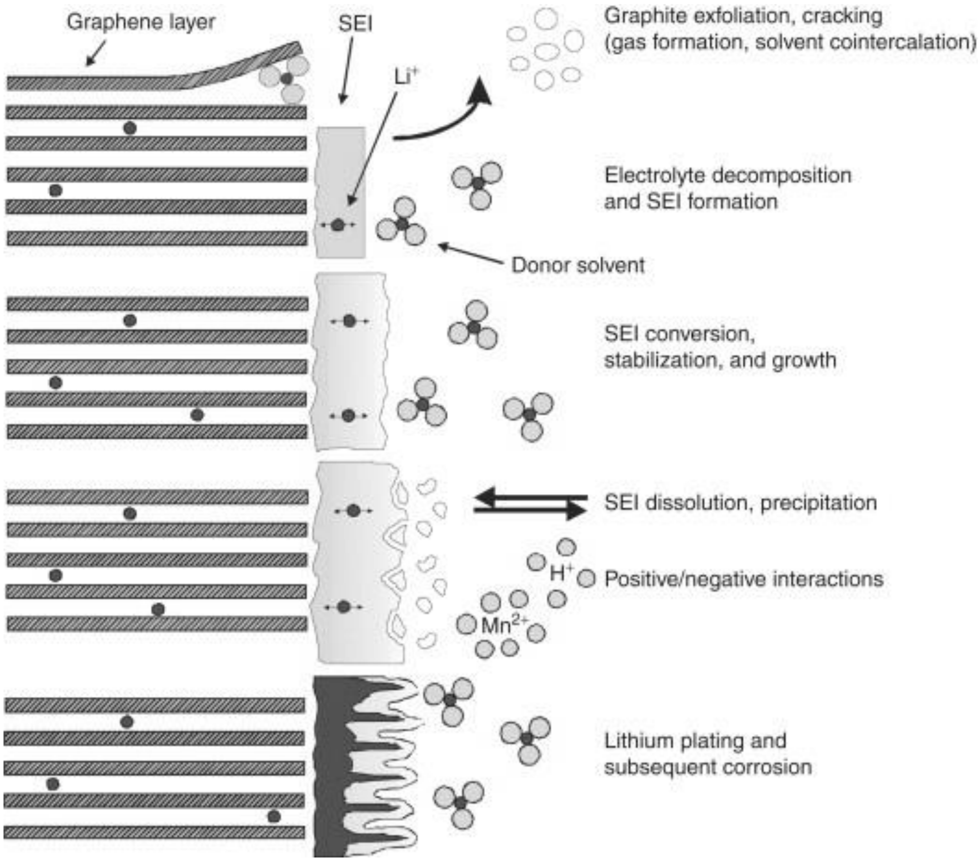


Fig. 6.12 Electrode interface

Many modifications and improvements have been made to these early models with the latest approaches using numerical modelling to follow the redistribution effects as the electrode potential is varied.

6.10 APPLICATIONS OF SURFACTANTS

The surfactant plays an important role in cleaning, wetting, dispersing, emulsifying, foaming and anti-foaming agents with many practical applications and products, including a wide variety of consumer products like Shampoos, Dish detergents, Laundry detergents, Conditioners, Fabric softeners, Diapers Contact, lens cleaners, Cosmetics, Toothpastes, Biocides (sanitizers), Fabric softeners. Surfactants are also widely used in the industries of Emulsions, Paints, Adhesives, Recycled, papers deinking, in flotation, washing and enzymatic processes, Heavy and tertiary oil recovery, Ore flotation, Dry cleaning, Pesticide and herbicide applications, Water repellency.

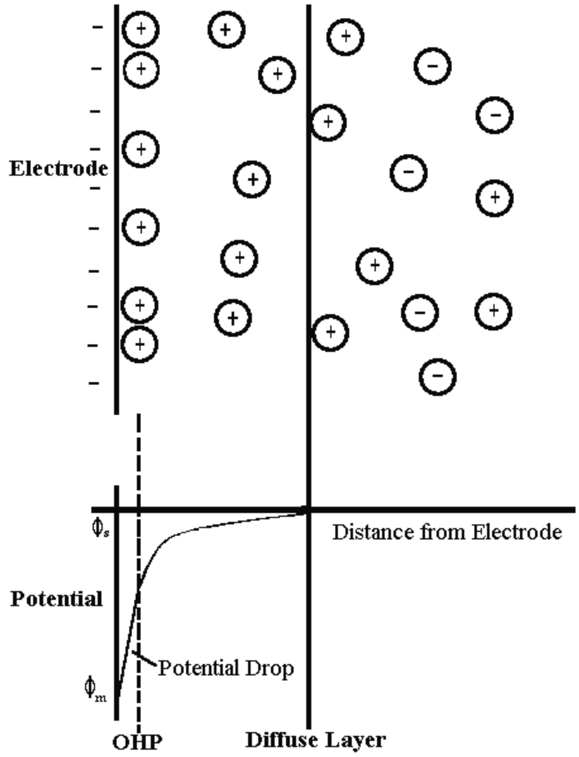


Fig 6.13 Helmholtz's view of of electrode double layer

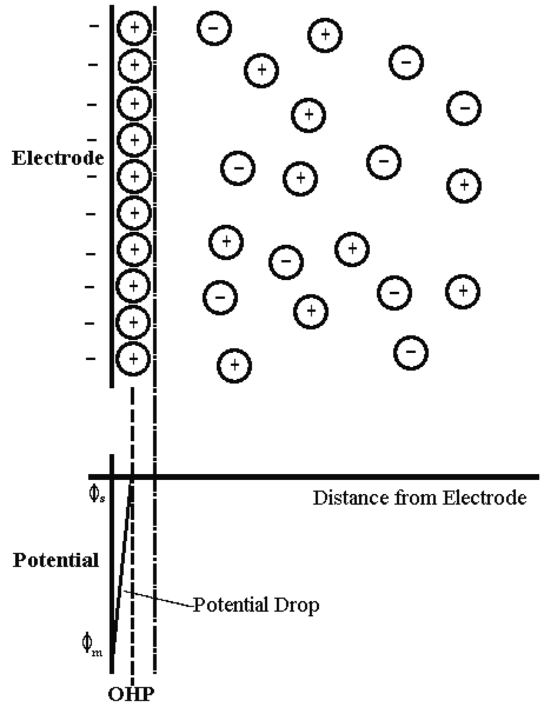


Fig. 6.14 Second electrode double layer model

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6.12 QUESTIONS

1. What are surface active agents and how it can be classified.

2. Discuss the various factors affecting the critical micelle concentration.

3. What is micelle, reverse micelle and critical micelle concentrations.

4. Discuss the thermodyanamics of micellization.

5. Draw the structure of cationic and anioic surfactant molecules.

6. Describe the important applications of surfactants.