

## CHAPTER 2

### SOLID STATE CHEMISTRY

Textbooks & Heaven only are Ideal

Solidity is an imperfect state.

Within the cracked and dislocated Real

Nonstoichiometric crystals dominate.

Stray Atoms sully and precipitate;

Strange holes, excitons, wander loose; because

of Dangling Bonds, a chemical Substrate

Corrodes and Catalyzes - surface Flaws

Help Epitaxial Growth to fix adsorptive claws (18).

What is solid - state chemistry ?

The importance of chemistry in solid - state science and technology is steadily growing, and it becomes increasingly apparent that there is a very great need for chemists to be more aware of the opportunities to give recognition to those in chemical education. Solid state chemistry is a very wide field of its own including many branches of science which are concerned with the physical properties of solids, particularly the special properties exhibited by atoms and molecules because of their association in the solid phase, especially diffusion in solid which causes the change that occur in solids or

solid reaction.

Chemists have a viewpoint that is so different from those of, say, physicists or metallurgists. The certain aspects of solid - state phenomena particularly interest the chemists are the chemistry of the solid state, which include the crystallography, the departure from ideal of the real crystal, in particular, it deals with the properties which resulted from ideal departure (19).

The term 'solid' used in this research refers to crystalline aggregation of atoms and molecules. Substances such as glasses that having no definite lattice structure is beyond the scope of this studied.

#### Crystalline, amorphous, polymorphism, allotropy (20)

Atoms and molecules in solids are binded together with the static forces which are almost entirely electrostatic in nature with only significant contributions from magnetic interactions. The compactness of atoms in solid give the structural unit which are exactly confined to the equilibrium positions within the crystal. These positions, which are the atoms may vibrate and most of them cannot readily leave.

Solid substances are frequently classified as either crystalline or amorphous entity. A crystalline solid is one in which the constituents of structural units are arranged in a definite configuration which can be characterized the substance. This configuration is

repetitive arrangement as finite and infinite with definite in dimensional periodicities and results a long - range order. These pattern can be instrumentally examined with X - ray crystallography.

Amorphous substances do not show under test an explicit configurational arrangement or order extending for any distance. But under certain conditions an amorphous substance may acquire crystalline characteristics.

Even many substances exist only in a single solid crystalline form. Quite frequently it is found that certain substances occur in more than one solid modification or undergo a change of crystalline form on heating or pressing under high pressure. The existence of more than one modification of substances is known as polymorphism. Polymorphism occurring in elements is more commonly referred to as allotropy.

The internal structure of the crystals is built up by repetition and extension in all directions of a fundamental structural unit known as a unit cell. Each unit cell, in turn, must be constitute of atoms, molecules, or ions, as the case may be, arranged to give the particular geometrical configuration of the crystal.

#### Unit cell

The basic periodicities inherent in crystalline solids can be pictured in three dimensions as a point lattice. Such a lattice can be constructed from the intersections of three sets of parallel planes. The spacing between each plane of a parallel set must be

constant, but it need not necessarily be equal to the spacings in the other two sets. An example of a point lattice is given in Fig 2.1

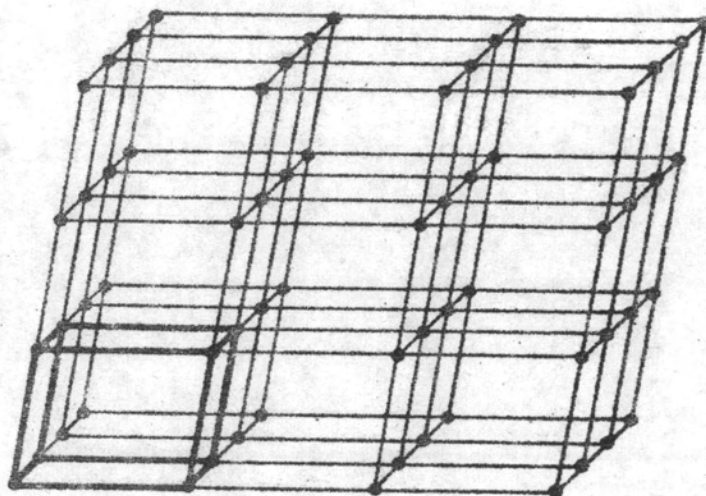


Fig 2.1 Example of a point lattice

It should be noted that each lattice point in the figure has an environment identical to that of every other point; i.e.; each point is surrounded by an equal number of points equidistant from it. The volume element enclosed by the heavier lines in the figure is the basic repeat volume unit of the lattice, i.e.; the unit cell. The size of this cell is determined by the magnitude of the spacing between the planes of each parallel set, while the shape of the cell is determined by the angles of intersection of the three sets of parallel planes.

The point lattice can be used to represent the geometry and periodicity of any crystalline substance. The basic arrangement of the atoms (molecules, or ions) is contained in the unit cell. Further, the basic periodicities which give rise to the long - range order in

solids are represented by the distances which separate lattice point, i.e., by the unit cell dimensions.

It should be emphasized that in general the lattice tells nothing about the actual and detailed arrangement of the structural elements composing the unit cell. Only in a limited number of cases do the atoms lie only on the lattice points. In all other instances the arrangement is more elaborate and requires determination by suitable means.

It might be imagined that a crystal which has certain facial symmetry may be cleaved along the planes until a solid is obtained which, if cleaved further, will not show the symmetry of the original crystal (21).

The two vectors are chosen to determine a point symmetry of the unit cell of three vectors,  $a_1$ ,  $a_2$ ,  $a_3$ . One vector is assumed to be the distance from A to C in Fig 2.2

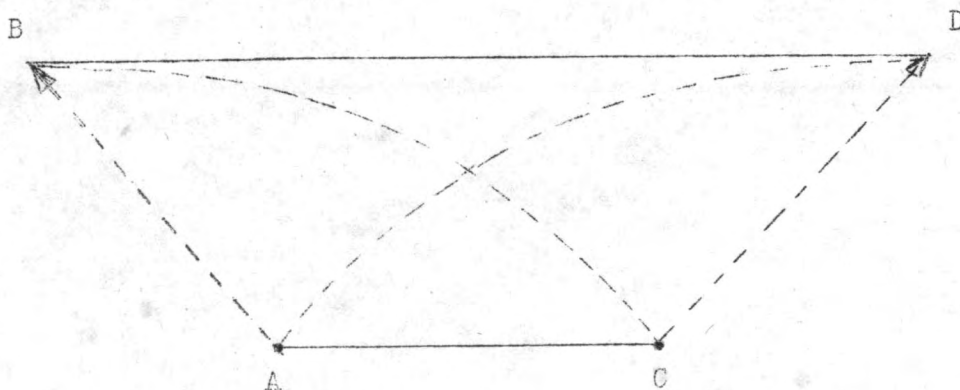


Fig 2.2 The effect of rotating about two equivalent  $n$ -fold points by  $+\frac{2\pi}{n}$  and  $-\frac{2\pi}{n}$  radians.

In addition, axes of  $n$  - fold symmetry is assumed to pass through point A and C where  $n$  is to be determined. When rotation about A by  $\frac{2\pi}{n}$  radians, point C is sent to point B and similarly point D occurs by rotation of  $-\frac{2\pi}{n}$  radians about C, points B and D may coincide. The distance  $\overline{BD}$  may be equal to the distance  $\overline{AC}$ , or else  $\overline{BD} > \overline{AC}$ . The requirement that the unit cell be the smallest unit plane which still has the proper symmetry forces the distance  $\overline{AC}$ , the length of the unit vector, to be equal to or less than any other distance to an axis of  $n$  - fold symmetry. If B and D coincide,  $n$  must be 6, and if  $\overline{BD} = \overline{AC}$ ,  $n = 4$ . For  $\overline{BD} = 2\overline{AC}$ ,  $n = 3$  but for any other length of  $\overline{BD} > \overline{AC}$ ,  $n = 2$ . Therefore the unit cells may have only 2-, 3-, 4-, or 6- fold symmetry. Any point in a given unit volume or unit cell has a corresponding point in another unit cell. It is convenient to use a two-dimensional lattice to obtain the number of ways that the three unit vectors be chosen. It could be guess that squares may be used as one unit cell since they may be repeated to fill a plane. The two repeated vectors,  $a_1$  and  $a_2$ , will determine the symmetry of the unit cell. The lengths of the two vectors are either equal or nonequal. If they are equal, then the unit cells are equilateral parallelograms, squares, or hexagons. If unequal vectors are used either a parallelepiped or rectangle is the unit cell. These unit cells in their lattices are illustrated in Fig 2.3. No other unit cells are possible for a plane. 005042

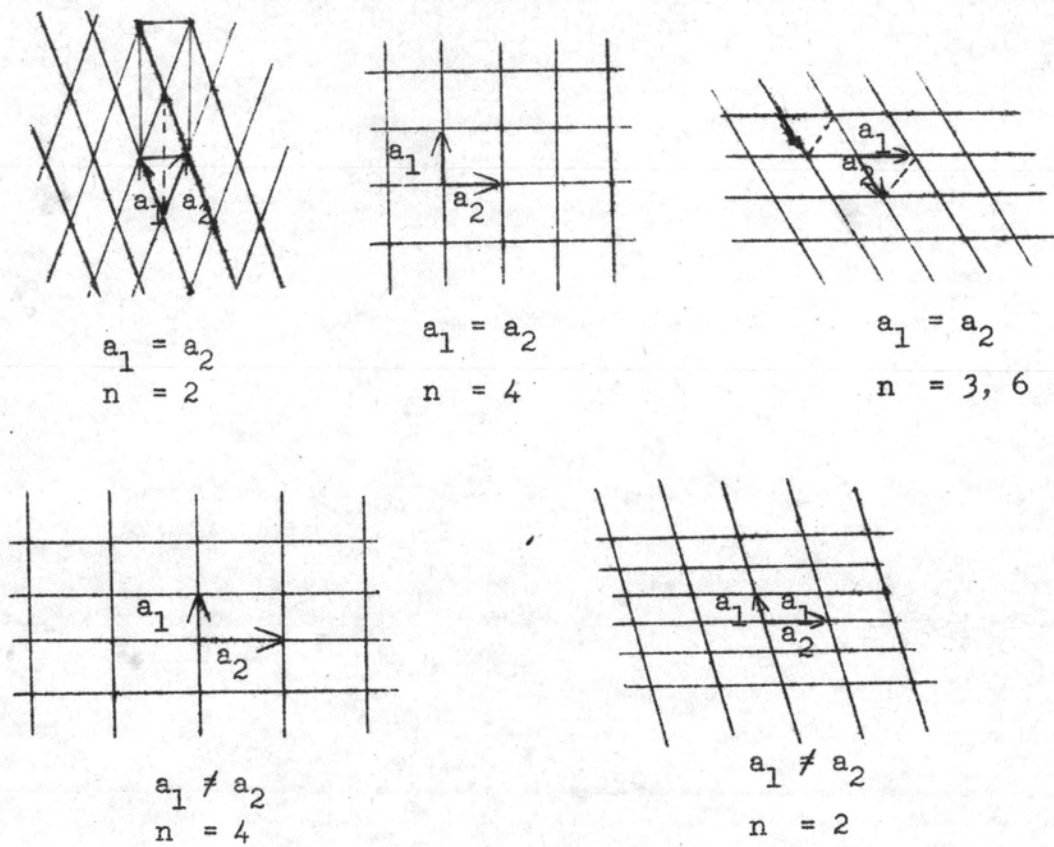


Fig. 2.3 The five possible two dimensional lattice.

Since a three - dimensional lattice is a simple extension of a two - dimensional lattice, the same rotational restrictions must hold. However, the number of possible unit cells increases to six because of the combinations of rotational symmetry about different axes. The three spacing or axes of the unit cell are designated by the letters,  $a_1$ ,  $a_2$  and  $a_3$ . Again, the angle between  $a_2$  and  $a_3$  is  $\alpha_1$  that between  $a_1$  and  $a_3$  is  $\alpha_2$ , while that between  $a_1$  and  $a_2$  is  $\alpha_3$  and all the possible polyhydra may be constructed. The six solids so constructed are shown in Fig 2.4.

For each figure, the angle between each pair of vectors is given as well as the vectors. All known crystals may be classified according to the particular unit cell which makes up the crystal. These classifications are called the six crystal systems.

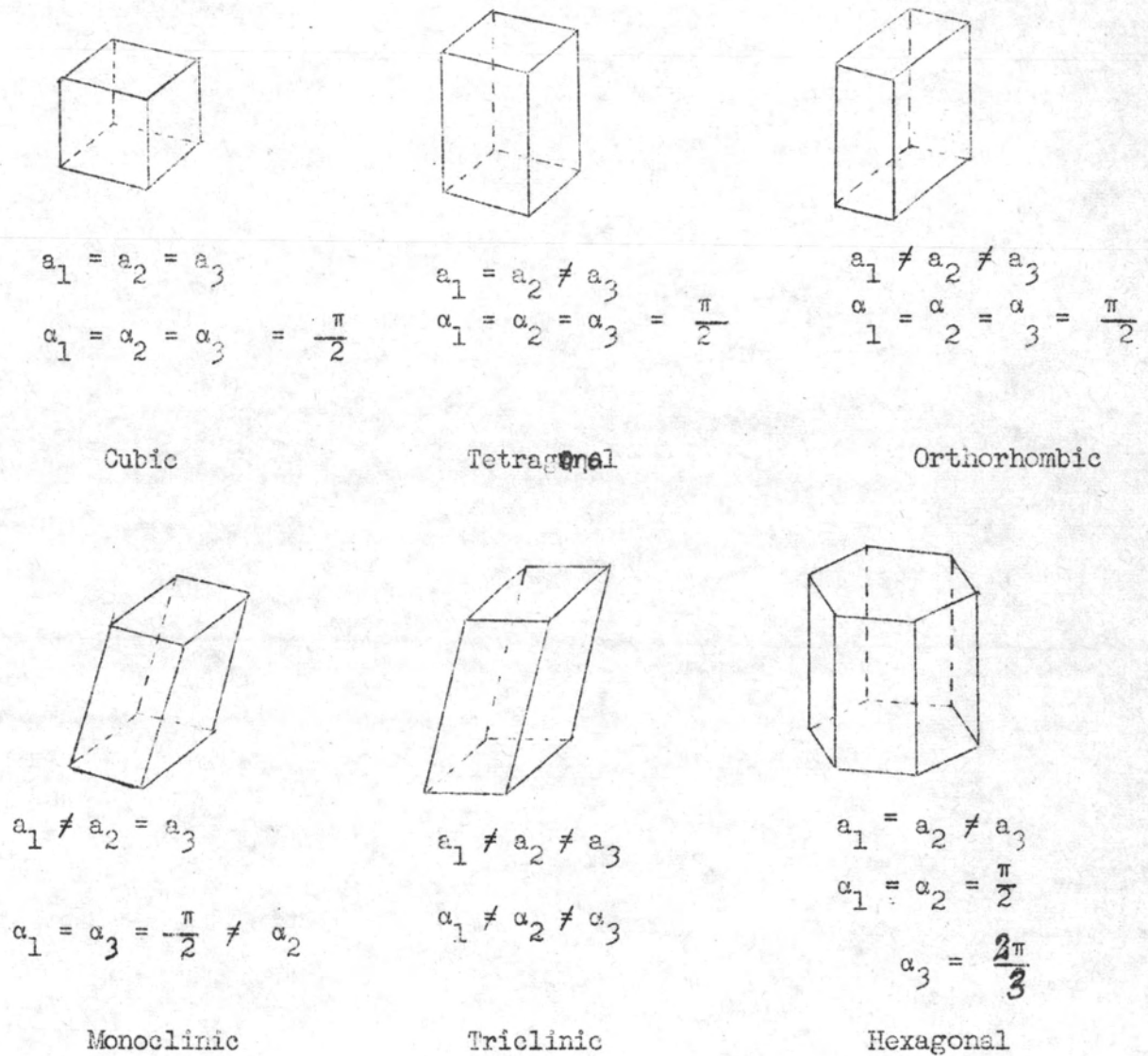


Fig. 2.4. The six crystal systems.

It may be argued that there is, in addition to these figures, the possibility of  $a_1 = a_2 = a_3$  and  $\alpha_1 = \alpha_2 = \alpha_3 \neq \frac{\pi}{2}$ . However, the rhombohedron so formed can be placed in the hexagonal system.



The unit cell volume,  $V$ , possesses the symmetry of the crystal and by stacking  $n$  units together a crystal of volume  $nV$  is obtained. The unit volume may be described by three vectors,  $a_1, a_2, a_3$ , whose volume is the scalar triple product,  $(a_1 \cdot (a_2 \times a_3))$ . The displacement vector or distance vector from one unit cell to another is given by

$$L = n_1 a_1 + n_2 a_2 + n_3 a_3$$

Where  $n_1, n_2$  and  $n_3$  are integers. Thus any point in a given unit cell represented by a vector  $R$  has a corresponding point in another cell given by the vector  $L + R$ .

There are 230 crystal forms possible, and practically all have been observed. On the basis of their symmetry these 230 crystal forms may be grouped into 32 classes, and these in turn may be referred to six or seven crystal systems.

### Crystal systems (22)

According to the set of axes used to represent their faces, crystals may be divided into seven systems, summarized in Table 2.1. They range from the completely general set of three unequal axes ( $a_1, a_2, a_3$ ) at three unequal angles ( $\alpha_1, \alpha_2, \alpha_3$ ) of the triclinic system to the highly symmetrical set of three equal axes at right angles of the cubic system.

Table 2.1 The seven crystal systems

System	Axes	Angles	Example
Cubic	$a_1 = a_2 = a_3$	$\alpha_1 = \alpha_2 = \alpha_3 = 90^\circ$	Rock salt
Tetragonal	$a_1 = a_2, a_3$	$\alpha_1 = \alpha_2 = \alpha_3 = 90^\circ$	White tin
Orthorhombic	$a_1; a_2; a_3$	$\alpha_1 = \alpha_2 = \alpha_3 = 90^\circ$	Rhombic sulfur
Monoclinic	$a_1; a_2; a_3$	$\alpha_1 = \alpha_3 = 90^\circ; \alpha_2$	Monoclinic sulfur
Rhombohedral	$a_1 = a_2 = a_3$	$\alpha_1 = \alpha_2 = \alpha_3$	Calcite
Hexagonal	$a_1 = a_2; a_3$	$\alpha_1 = \alpha_2 = 90^\circ;$ $\alpha_3 = 120^\circ$	Graphite
Triclinic	$a_1; a_2; a_3$	$\alpha_1; \alpha_2; \alpha_3$	Potassium dichromate

Generally, it was assumed implicitly that each solid crystal consisted of a perfectly regular repeating array of atoms (ions or molecules) as described by the definition of a lattice. One exception to this perfect pattern, which has been mentioned, is that each atom

within the lattice is not held rigidly at the lattice point. These are expected as a consequence of thermal agitation. Thermal vibration leads to oscillation about the idealized location, the latter point being defined with reference to the average position of other lattice units. At  $0^{\circ}\text{K}$  crystal would be expected to be ideal and at room temperature, temperature above  $0^{\circ}\text{K}$ , it would be real crystal so that order of crystal depend on temperature. In a real solid, however, several types of deviation from the perfect behaviour can, and do, occur. This is called imperfections or defect (23). The kinds of imperfections need to be described and classify as they are the key to most of the chemical properties of solids as well as to many of the physical properties. These may be classified in the following main divisions:

1. Distortion of the lattice through departures from perfect alignment of repetitive units. This type of imperfection is termed a dislocation or line defect and the effect is embodied in the relative positioning of many lattice units with respect to each other and to adjoining regions of perfect lattice.

2. A lattice position may be unoccupied and/or a component unit of the lattice may be located within the solid at a position in the repetitive array other than that at which the greater proportion of such units are accommodated. The imperfection which is resulted from the absent or misplaced atom (or ion) is known as a point defect.

3. The solid may contain impurity atoms (ions or molecules), two types of impurity systems are possible;

3.1 excess of one of the constituent units of a binary (or ternary, etc.) substance resulting in deviation from the exact stoichiometric composition of the compound - Nonstoichiometry.

3.2 excess of atoms (ions or molecules) which are not a constituent of the pure substance - Foreign Atoms.

### Dislocation or Line Defects ( 21 )

It is a deviation of perfect crystal along lines and surfaces. It need not be straight lines but may exhibit jogs or kinks. Two basic types can be distinguished, edge and screw dislocation. One type is the edge dislocation in which an extra half plane of atoms is inserted into the crystal lattice as shown in fig. 2.5.

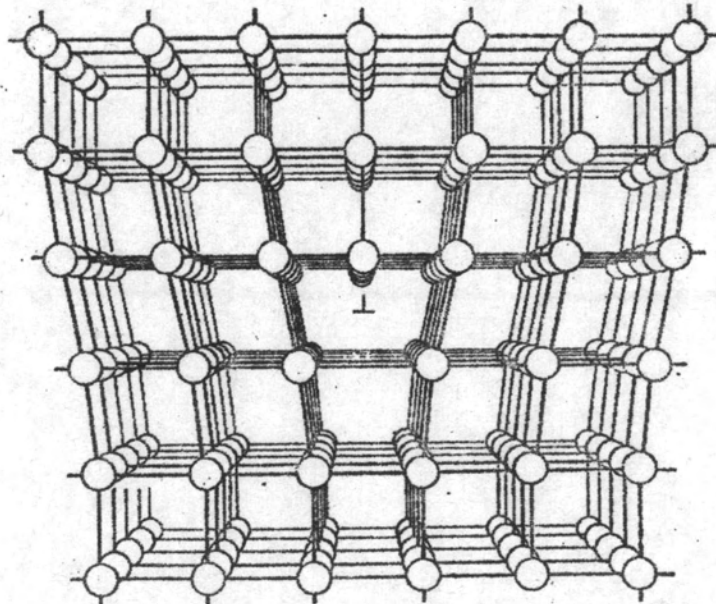


Fig 2.5 Edge dislocation

This can be introduced by accidents occurring during the growth of the crystal and can move through a crystal. This movement results in slip when the atoms are displaced over the slip plane and results in climb when the direction is perpendicular to its slip plane as in Fig 2.6 and Fig 2.7. The net result of this motion is the generation of vacancies or interstitials.

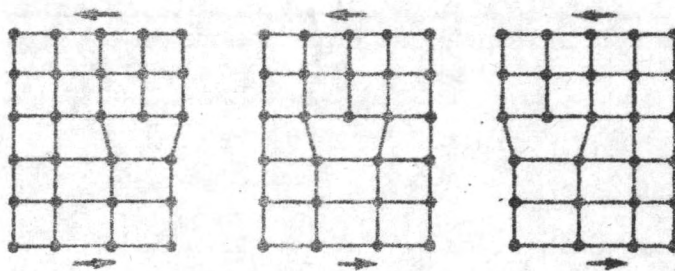


Fig 2.6 Motion of an edge dislocation under shear,  
leading to slip.

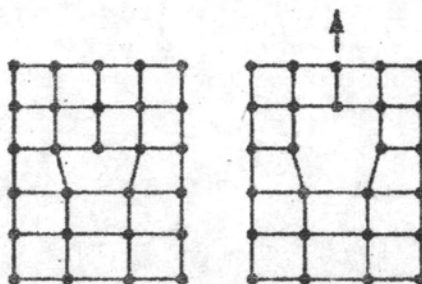


Fig 2.7 Production of interstitials or annihilation of vacancies by dislocation climb; motion in the opposite sense produces vacancies and annihilates interstitials.

The other type is screw dislocation, shown in Fig 2.8

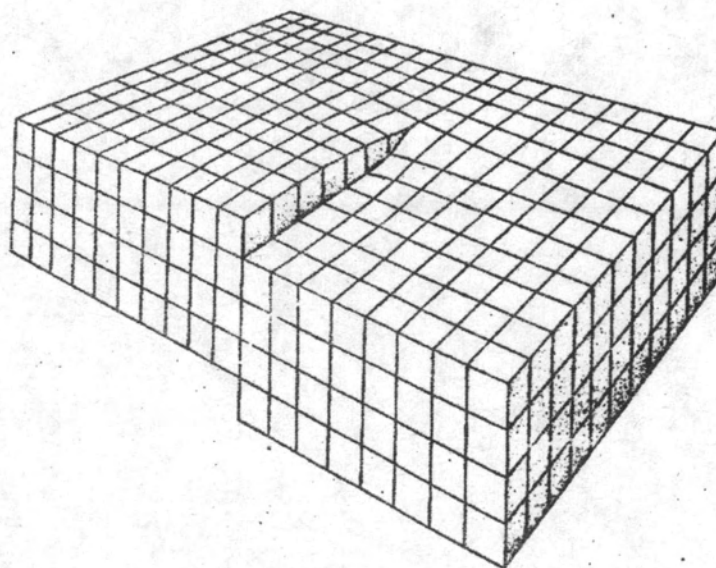


Fig 2.8 Screw dislocation.

this results from a displacement of the atoms in one part of a crystal relative to the rest of the crystal, forming a spiral ramp around the dislocation line.

Dislocation generation is a high energy process and may occur as a result of kinetic factors operating during crystal growth or from the application of stress to solid.

#### Point Defect (Structural atomic imperfections)

The term defect is used to describe both missing and misplaced atoms from positions in the ideal crystal lattice (also combinations of these). The simplest structural atomic imperfections are of two kinds, interstitial atom and lattice vacancy. The interstitial atom occupies a position in the crystal lattice not normally occupied, as shown in Fig 2.9

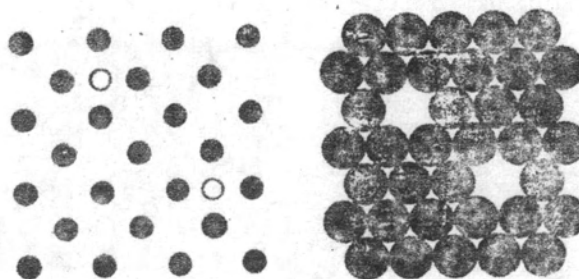


Fig 2.9 Interstitials and vacancies.



The lattice vacancy results from missing of an atom from a normally occupied lattice site. The combination of anion and cation vacancies is a Schottky defect, and the combination of a vacancy and interstitial is a Frenkel defect.

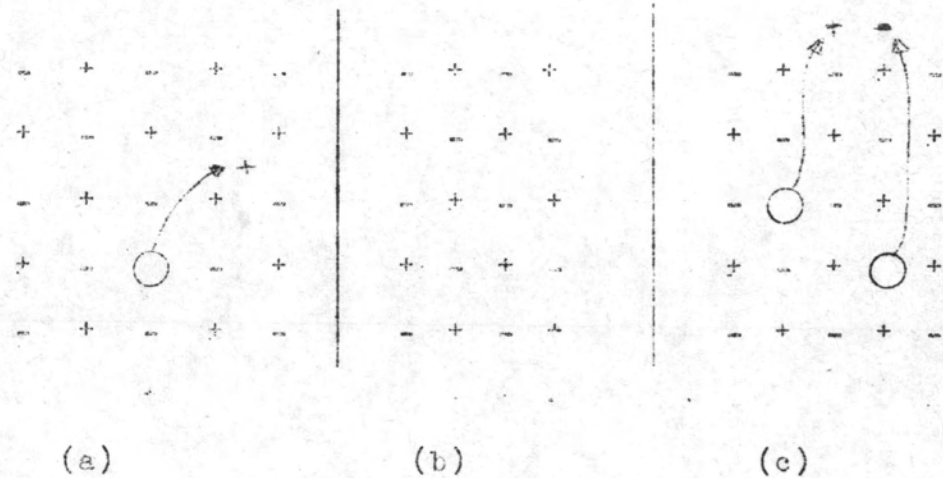


Fig 2.10 (a) Crystal with Frenkel defects

(b) ideal crystal

(c) crystal with Schottky defects.

Another kind is antistructure disorder with the occasional interchange of positions from their normal sites. There may also be hybrid types of disorder, for example, a combination of Schottky and antistructure disorder.

Frenkel and Schottky defects are called *intrinsic thermodynamic* defects. They do not alter the exact stoichiometry of the crystal, but they provide a facile mechanism by which atoms can move within the crystal. It is much easier for an atom to move from an occupied site into a vacancy than for two atoms in occupied site to change places



directly.

The formation of defects, Schottky and Frenkel types, requires very much less energy since the distorted region is limited to a small number of lattice units and does not extend any appreciable distance through the lattice.

The presence of defects results in an increase in crystal entropy, due to the large number of possible combinations of defect location which are possible for the relatively small proportion of such vacancies in the solid.

#### Nonstoichiometry and Foreign atoms (Chemical atomic imperfection)

Two general types of impurity system may be recognized:

1. Nonstoichiometry (20) : This is the slight variation of the proportions of the constituent elements of a compound, usually between fairly narrow limits, without the introduction of species other than those present in the ideal solid. Many compounds show a strong tendency to nonstoichiometry. This can greatly enhance its conductivity. Nonstoichiometry can arise in any of several possible ways in a binary compound. Group II - group VI compounds, like CdS and ZnO, are notable examples of this. Zinc oxide, ZnO, usually contains more Zn than O, whereas nickel oxide, NiO, usually contains more O than Ni. Such nonstoichiometry may be due to the incorporation of extra atoms into the crystal at interstitial sites, or to vacancies caused by the absence of atoms from normal sites. Evidence suggests that the excess zinc in ZnO is largely interstitial Zn, whereas the

excess oxygen in NiO is largely due to vacant  $\text{Ni}^{2+}$  sites. The electrical and spectral properties may be significantly altered by such composition variation.

2. Impurity or Foreign atoms: Foreign atoms, that is, species other than those present in the ideal compound. Foreign atoms in the crystal can occupy either interstitial sites or normal lattice sites by substitution atoms of the host crystal. Size considerations are usually important for the formation of interstitial impurity solutions, and the electronic structure of the foreign atom is usually important for the substitutional case. The substitution occur more readily for impurities of the same or adjacent groups of the periodic table.

By additions of selected impurities, vacancies or changed-valence sites can be introduced into crystals. Because the requirement that the crystal must be electrically neutral with equal numbers of positive and negative charges. Vacancies can result from the addition of a foreign atom with a valence different from that of the corresponding host crystal atoms. An  $\text{AgCl} - \text{CdCl}_2$  mixed crystal, with only a small amount of  $\text{CdCl}_2$  present, is shown in Fig 2.11, the  $\text{Cd}^{2+}$  ions occupy normal cation sites, but for every  $\text{Cd}^{2+}$  in the crystal there must be incorporated also a cation vacancy (omission of an  $\text{Ag}^+$ ), to maintain charge neutrality in the crystal as a whole. In principle, at least, interstitials can be produced in an entirely analogous method.



Fig 2.11 Production of cation vacancies in AgCl by the addition of a divalent impurity.

Such an addition can also produce changes in valence for a controlled number of ions of the host crystal, when the chemical nature of the host crystal is such that at least two valence states are possible. This is often the case with transition metal compounds, and the example used, NiO, illustrates the point. If a small amount of  $\text{Li}_2\text{O}$  is incorporated into the solid, the  $\text{Li}^+$  occupies normal cation sites, as shown in Fig 2.12.

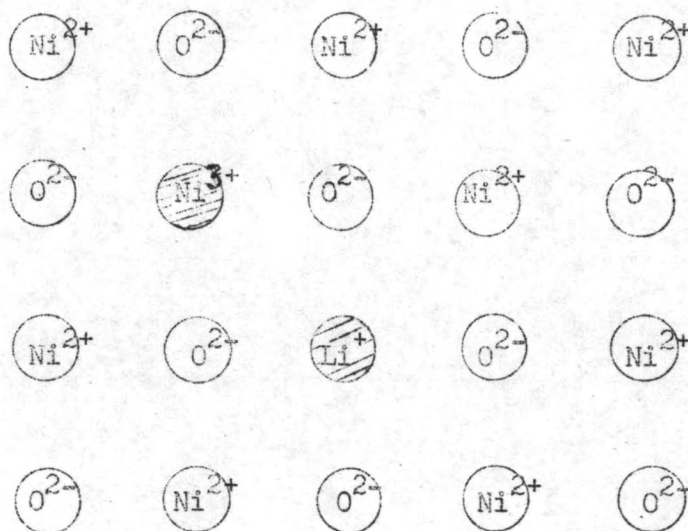


Fig 2.12 Effect of addition of a monovalent impurity  
on NiO (controlled valency)

The over-all charge neutrality of the crystal would be preserved, in one conceivable structure, if a concentration of anion vacancies equal to one-half the lithium concentration were present, the actual result is a change in the valence of an equal number of divalent nickel ions to a trivalent state.

These impurities may sometimes be incorporated in the solid with little more than local perturbation of the band structure of the crystal. Though in different systems the presence of such defects may cause significant changes in the electrical and spectral properties of the crystal.

The presence of imperfections, or defects, in the real solid result many of the interesting physical properties of solids (24).

In particular, many properties depend upon deviations from the ideal structure. These include electrical, optical, magnetic, thermal, mechanical properties and etc.

1. Electrical properties such as electrical conductivity was distinguished between electronic conductivity which conduct through motion of electrons and holes, and ionic conductivity which conduct through motion of ion. If the unbound electron and hole concentrations are exceedingly small by comparison with ion concentrations, these solids such as alkali halide, there are appreciable ionic mobilities. Chemical impurities or lattice defects are not effect the conductivity of metal but usually determine the electrical conductivity of semi-conductors and this increases rapidly with temperature over certain ranges. The conductivity of metal depends on temperature but the resistivity does not fall to zero at  $0^{\circ}\text{K}$ . The reason is explained according to the role of imperfect crystal or departure from ideal crystal. For this reason the resistance ratio, the ratio of the resistivities at room and liquid helium temperatures is used as a simple measure of the purity and perfection of a metal crystal. Impurities in semiconductors act as acceptors and donors. Lattice vacancies can be electrically active. The energy required to remove an electron from a donor, or to add one to an acceptor, is the ionization energy of the impurity or defect. If impurity acts as donor this

leads to n-type semiconductivity, i.e. normal electron conduction mechanism, such as the excessive Zn in ZnO. In NiO, the Ni<sup>2+</sup> vacancies, each associated with two Ni<sup>3+</sup> to preserve electrical neutrality, provide typical acceptor levels leading to p - type semiconductivity, i.e. positive hole conduction mechanism, because of the formation of cation vacancies and positive holes. The nomenclature of type is alter negative holes or positive holes. It is distinguished between a vacancy and a hole. A vacancy is the absence of an atom from a normal structural site and a hole is the absence of an electron from a normal band or band orbital.

The electrical conductivity of molecular crystals is generally very low, because of low carrier mobilities and low carrier concentrations.

Dielectric phenomena is bulk properties of the crystal, for the most part, and the role of imperfections in minor. Dipoles in insulators are induced by a local shift in the charges, or polarization, by which the centers of the positive and negative charges being displaced slightly in opposite directions. Some crystals spontaneously polarize to produce a dipole moment even in the absence of an electric field this results from spontaneous displacements in the ionic structure. Ordinary dielectrics show a linear dependence of the polarization on the applied field.

The ionic shifts contribute up to infrared frequencies, the electronic shifts contribute up into the ultraviolet and the orientation of permanent dipoles contributes to the polarizability only at low

frequencies (up to ultrahigh or microwave frequencies). Some crystals show asymmetric displacements of negative and positive ions, by mechanical stress, and become polarized, it is called piezoelectric.

2. Many optical properties of solid are bulk properties, some are related to imperfections. Optical absorption results from transitions of the host atoms or electrons of a solid by a quantum of electromagnetic energy. Imperfections can be responsible for optical absorption example are the alkali halide colour centers or F centre. Pure, perfect alkali halides are transparent through out the visible region of the spectrum, but defect centers absorb in the visible and produce a deep colouration. The identification of the observed absorption bands can shows specific models for imperfections. Absorption due to atomic motions can also be used to obtain information about imperfections in solids. As an example, infrared absorption shows that oxygen dissolved in silicon lies in an interstitial position, bonded to two adjacent silicon atoms at an included angle of  $\sim 110$  deg. The configuration was deduced from an analysis of the infrared absorptions corresponding to stretching and bending modes of the Si-O bonds.

Photoconductivity in insulators are closely related to absorption which leads to dissociation of an electron from its normal bound state when radiated. The released electron can conduct and it is more convenient to measure electrical conductivity than absorption.

Luminescence, fluorescence or phosphorescence is the emission of radiation when electron return to a lower-lying state. The light emission of material which is bombarded with electrons, cathodoluminescent materials or phosphors, is depended directly upon the presence of impurities. Impurities are called activators, coactivators, killers or poisons, depending upon the role they play. The solid - state laser is a luminescent solid in which certain special conditions have been achieved. This falls into two main groups. Firstly, an active ion, such as rare - earth or transition metal, is present in an inactive host crystal, and the excitation and decay to the ground state of this ion constitute the emission process. The second includes semiconductors in which a nonequilibrium concentration of carriers is produced and the excess conduction electrons and holes recombine through impurity centers.

3. The magnetic moments of the host crystal ions are considered as bulk magnetic properties which can effect by impurities.

Interstitial impurities such as C, S, O and N can reduce the susceptibility of ordinary iron, even a few parts per million of impurities can have marked effects. Materials are divided into general classes according to their response to magnetic fields, diamagnetic and paramagnetic, corresponding to negative and positive magnetic susceptibility. Magnetic susceptibility is the proportionality constant between the magnetization and an applied magnetic field, if the magnetic moments line up parallel or antiparallel to



an applied field the susceptibility is positive. Paramagnetic materials also have a permanent magnetic dipole which occurs with atom or molecules with unpaired electron.

Magnetic resonance especially nuclear magnetic resonance (NMR) is used to study solids and spectra are so broad for solids because of internuclear magnetic interaction but molecular rotation often causes partial narrowing of a broad resonance. NMR spectra can be used to interpret for crystallographic information and also been used to study of diffusion process in solids. Electron spin resonance (ESR) spectra can provide important information about the nature of an imperfection especially colour center which is point defects in alkali halides. ESR offers a unique method for identifying the atomic nature of semiconductors for both simple and complex centers, precise electronic structure of a center is an example.

4. Thermal properties such as specific heat and thermal conductivity are contributed from electron and imperfections as characteristic lattice vibrations. The specific heat are contributed from the absorption of heat as vibration energy of a lattice atom and the conduction of electrons as electronic specific heat. Lattice vibration of solid shows that the vibrational mode are quantized and thermal expansion may also be treated quantitatively as the temperature increases, oscillation of the atoms about the equilibrium separation distance increase too. The effect of imperfection depends

intimately upon the details of the interatomic forces and the crystal structure.

5. Many of the mechanical properties of solids can not be understood in a fundamental way. Deviations of real solids from the ideal model change these properties by orders of magnitude. Chemical purity and crystalline perfection need to be isolated and identified all the effect of individual imperfections to mechanical properties of solids. The ability to control the chemistry, both with respect to chemical purity and to crystalline defects, is very important for advance technology.

The strength of a real crystal which falls orders of magnitudes short of that expected for an ideal crystal because of slip in terms of dislocation. Most ordinary solids contain dislocations at concentrations of  $10^6/\text{cm}^2$  or more. It has been possible under special circumstances to obtain crystals entirely free of dislocations, called whiskers. The presence of dislocations or simple slip can yield plastically instead of decreasing of strength. The hardness of ordinary solids depend upon the detail of the heat treatment and its chemical purity. At high temperature, the vicinity of dislocations occur as expanded crystal lattice, impurities can solute in this vicinity and hence movement of dislocation. As the crystal cools, the solute atoms are frozen and the dislocation can move and leave the solute atoms behind. This movement is called pinning. Impurities pinning of dislocations can

improve ductility of solids.

### Band theory (24)(25)

The band theory seeks to explain the properties determined by the overall electrons within the complete crystal which were treated theoretically in two ways, in terms of nearly free electrons which results from the interaction of free electron waves localized within the lattice, and in the tight-binding approximation with small overlaps of atomic wave function to give molecular waves embracing the whole lattice.

When the number of atoms brought together increases, the spacing between the atoms resulting from the interaction of atoms in a linear array decrease and the atomic levels begin to split, as shown in Fig 2.13 into bands of allowed levels.

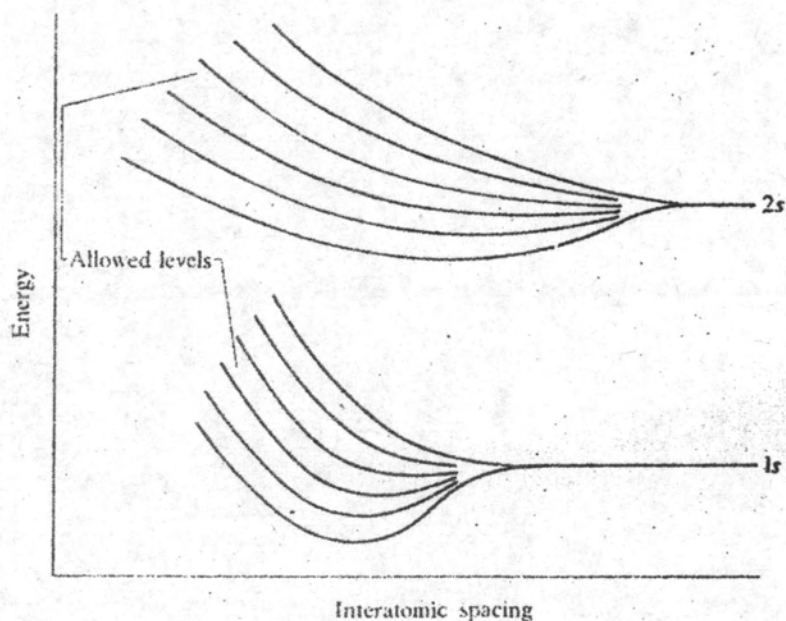


Fig 2.13 Energy as a function of spacing, for a linear array of six atoms.

Each band contains the number of levels following the number of atoms in the array. The width of the band depends upon the extent of the interaction. As the number of interacting atoms increases, the number of sublevels increases in exactly the same way, but without a corresponding increase in the width of the band at a given interatomic separation. Thus the levels become more and more closely spaced within a band, although they always remain discrete. The number of electrons which can be accommodated in the band is exactly twice the number of sublevels, because of the Pauli exclusion principle and the two spin directions for each level. In real solids, where the number of atoms is of the order of  $10^{23}/\text{cm}^3$ , the number of levels within the band becomes of this order and their spacing is extremely close; the spacing between the allowed bands is preserved, however. In a solid, the discrete separate energy levels of atoms and molecules are replaced by energy band, each containing very large numbers of discrete levels, but which the possibility of large separations in energy between the bands.

This is a qualitative description of the 'tight-binding approximation' for electronic energy states in solid; it starts from atomic wave functions and considers them to be somewhat overlapping. It is a better approximation for the inner cores of electrons than it is for the outer, valence shell, which 'free - electron approximation' is suitable.

Drude, Lorentz, and others considered the valence electrons as free to move throughout the volume of the solid, with the metal ion cores embedded in a sea of electrons. The free electron concept explains such properties as electrical conductivity and light absorption but it failed to explain specific heat, magnetic susceptibility, and the occurrence of insulating materials, until it was modified by Sommerfeld by the introduction of quantum mechanics. The solution to the Schrödinger equation for free electrons is a travelling wave, the energy of a free electron is related to the wave number by the de Broglie relationship. The detailed mathematical development is outside the scope of the present chapter.

The number of allowed states as a function of energy is shown in Fig 2.14. The filling of these states by electrons is shown by the hatched area

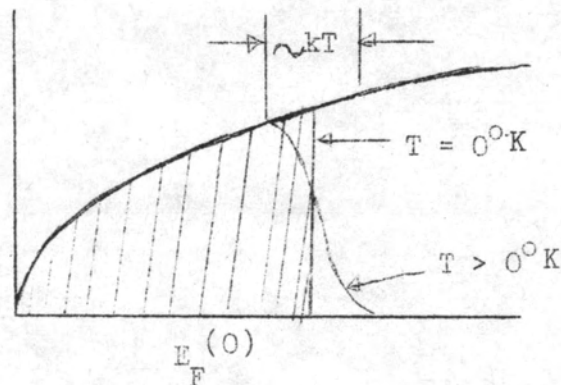


Fig 2.14 Number of states as a function of energy, for the free electron model. Hatched area shows filling at  $T = 0^\circ\text{K}$ ; at higher temperatures the filling curve is rounded, as shown.

The filling is described by a characteristic energy called the Fermi level (or Fermi energy). At absolute zero the cutoff in the filling of states is sharp, at the Fermi level; higher-lying states are empty and lower-lying states are filled. At high temperatures thermal agitation empties some of the states just below the Fermi level and fills a corresponding number above it, as shown by the rounded-off gray line; this produces a small shift in the Fermi level with temperature. This quantum - mechanical modification of the free-electron theory gives a much improved value for the important physical properties, which deduce that only the uppermost electron level are significant and affected by ordinary electrical and magnetic field or by the action of heat, electronic specific heat.

The modern theory of the electronic structure of solids follows in a more exact way from the Schrödinger equation with a periodic potential arising from the lattice atoms. The energy of such electrons distributed after Maxwell-Boltzmann distribution law. The electrons possess a characteristic wave motion and a crystal can be considered to be a periodic potential field in which a wave - motion is accommodated. Solutions of Schrödinger wave equation for electrons were derived by Bloch,

$$\psi_{\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{X}} u_{\mathbf{k}}(\mathbf{x})$$

Where  $k$  is the wave number and,  $\mu_k(\chi)$  is a periodic function with the same periodicity as the potential, that is, its period is the lattice constant  $a$ . The solutions are the energy level in which an electron may be present within the solid. The results of calculations using this equation show that electrons in the solid may be accommodated only in bands between limiting permitted energy level. The energy separation between successive level, within each permitted band of a crystallite of appreciable size, is very small so that the assemblage of closely spaced levels can be regarded as a band of permitted levels. The positions and widths of permitted energy bands are a property of lattice and constituent components of a particular solid. A solid may possess several such permitted energy bands separated by forbidden regions within which no electron may be accommodated.

The quadratic dependence of energy on wave number obtained in the free electron approach is shown in Fig 2.15 (a) The energy dependence for electrons in a periodic (one - dimensional) lattice is shown in (b). At values of  $k$  equal to  $\frac{\pi}{a}$ ,  $\frac{2\pi}{a}$ ,  $\frac{3\pi}{a}$ , etc., discontinuities in the energy appear. Thus there are allowed and forbidden ranges of the energy; these correspond to the energy bands and forbidden regions (also called energy gaps).

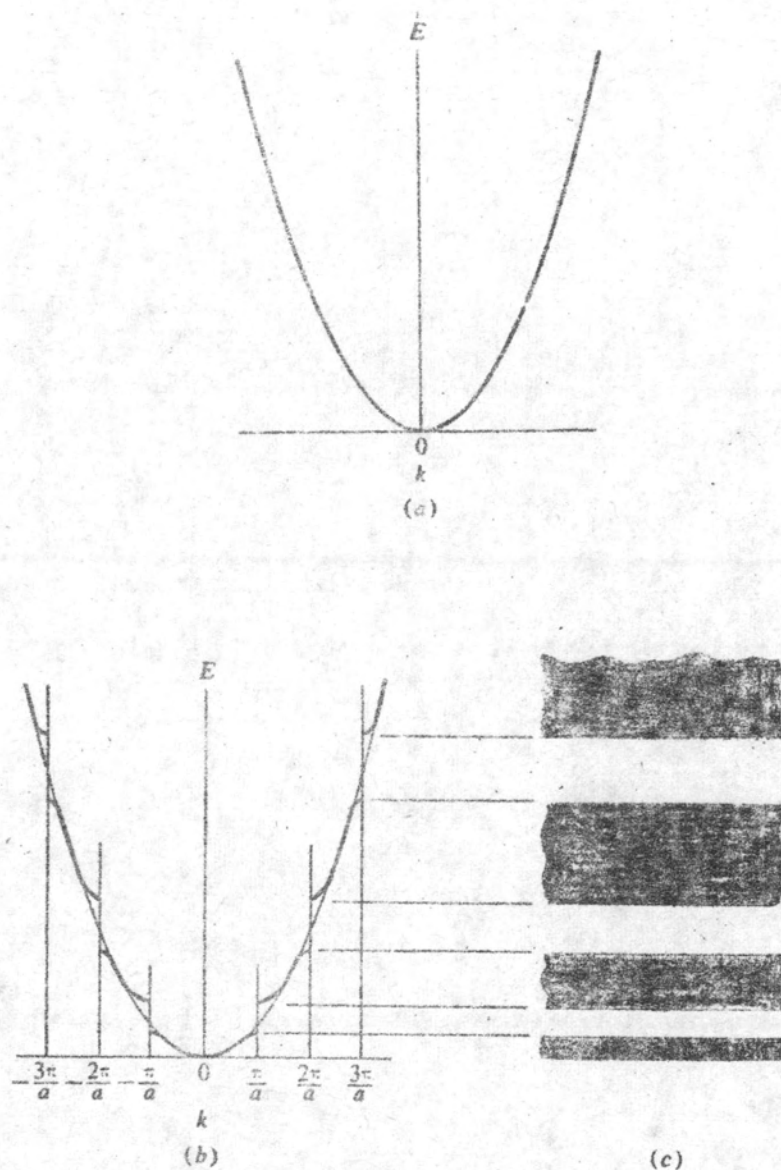


Fig. 2.15 Electron energies as a function of wave number, for (a) free electrons, and (b) electrons moving in a periodic potential. The allowed energy bands (as a function of distance through the crystal) are shown in (c).



In Fig 2.16 the bands in sodium and in diamond are shown that band theory of solids relates to the tight - binding approximation

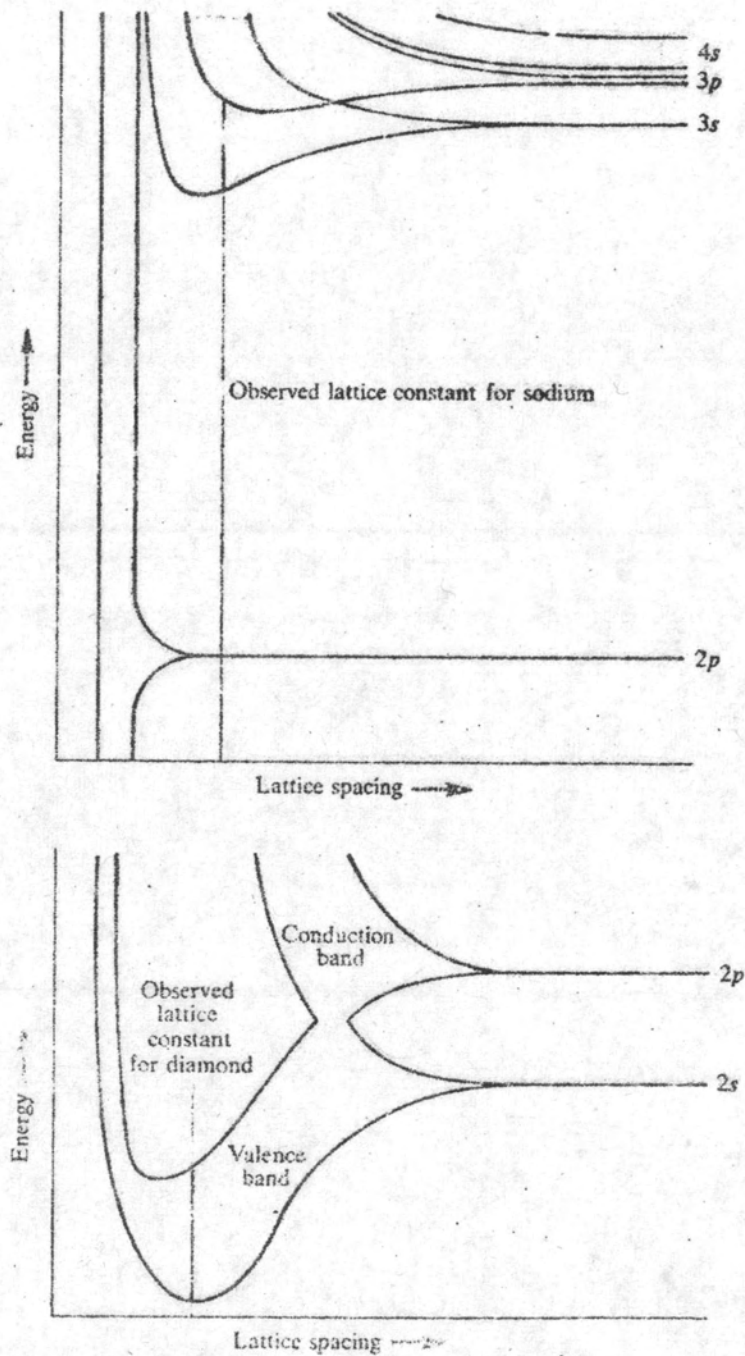


Figure 2.16 Some of the energy bands in sodium and in diamond.

At the equilibrium internuclear separation the lower - energy bands are separated, and are narrow in energy range. The higher - energy bands are broader, and finally begin to overlap.

The band theory when applied to continuous solids such as metals or salts there are bands of electron - energy levels or states. Each band consists of an almost continuous series of levels rather than a series of discontinuous widely - separated levels such as those in the theories of atoms and small molecules. In some cases the band overlap but in others there are several permitted energy band, separated from one another by considerable energy gaps.

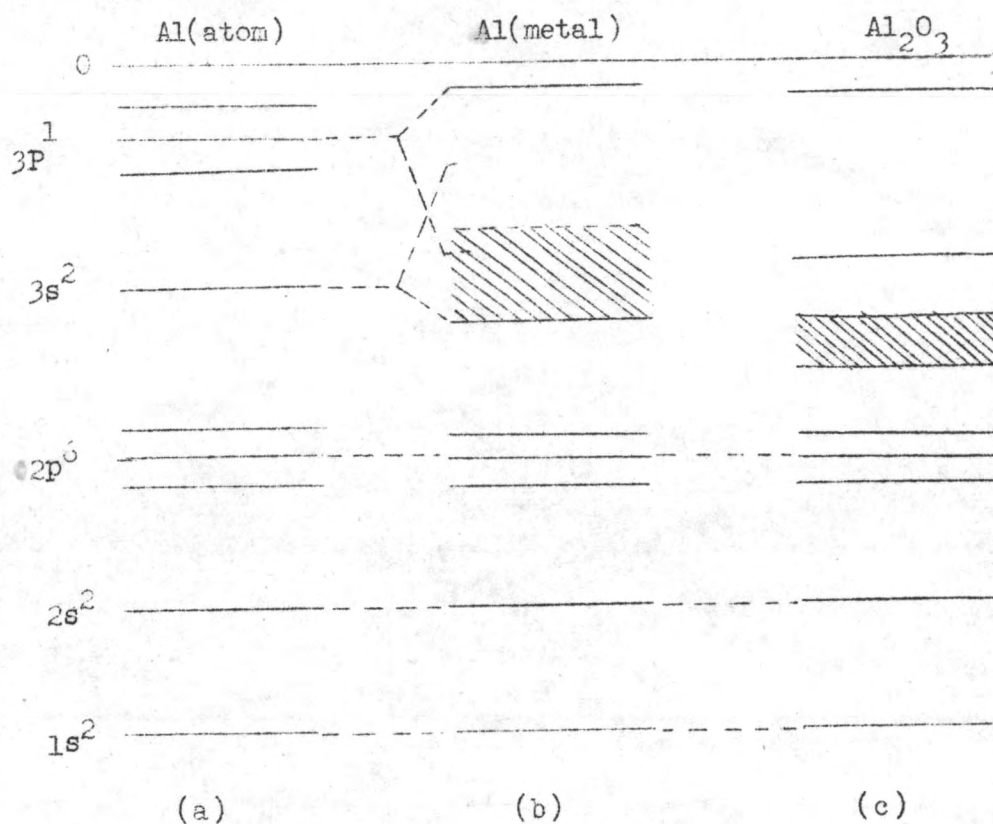


Fig 2.17 The relative distribution of energy level for  
(a) the Al atom, (b) Al metal, (c) Al<sub>2</sub>O<sub>3</sub>

Occupied levels in the Al metal and Al<sub>2</sub>O<sub>3</sub> energy bands are hatched.

As the energy levels in the proposed band are levels of electrons, the valence electrons which are grossly affected by the fields are non-localized and the core electrons which are hardly influenced may be regarded as occupying individual atomic orbitals. The valence electrons can under go very different energy changes from the emission of very large X - ray quanta to the absorption of very small thermal quanta.

An electron is excited from a low lying occupied energy level to a higher - energy unoccupied level by absorption the electromagnetic radiation.

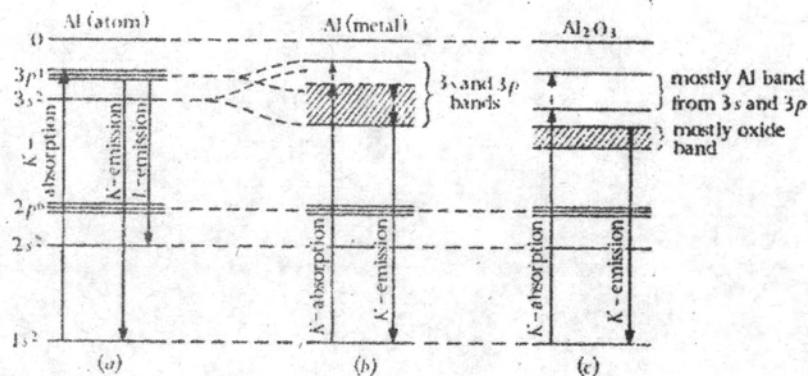


Fig. 2.13. The relative distribution of energy levels for (a) the Al atom, (b) Al metal, and (c) Al<sub>2</sub>O<sub>3</sub>. Occupied levels in the Al metal and Al<sub>2</sub>O<sub>3</sub> energy bands are hatched.

The transitions of electrons give rise to the emission spectrum. In atoms the absorption or emission of radiation by the valence electrons leads to sharp line spectra. In solids absorption or emission band spectra are usually observed. The energies at which these band spectra appear allow us to associate them with transitions of electrons from certain energy levels to others. For example there are corresponding absorption and emission K - band spectra of metallic aluminium as in Fig 2.19.

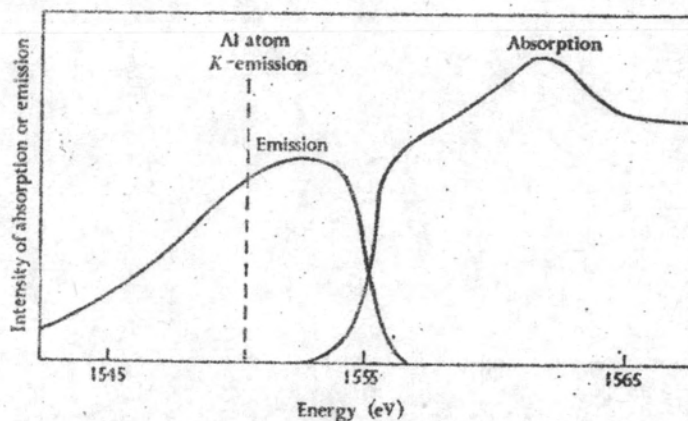


Fig 2.19 X-ray K-emission and K-absorption spectra of aluminium metal compared with the K-emission line of the aluminium atom.

It would be of great value to determine the number ( $N(E)$ ) of available levels per energy increment (i.e. between  $E$  and  $E+dE$ ) close to the energy of the valence electrons and so to be able to plot a graph of this number of energy levels,  $N(E)$ , against this energy,  $E$ . This plot would then be available for comparison with theories of energy levels in solids. The plot of metallic aluminium for emission spectra is Fig 2.20 and for emission - absorption spectra is Fig 2.21.

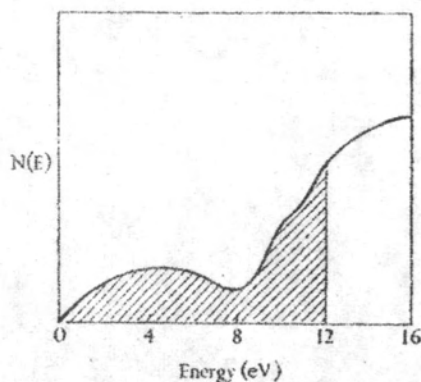


Fig 2.20 Calculated distribution  $N(E)$  of energy levels for the valence band of aluminium metal. The zero of the scale is the bottom of the band. Occupied levels are hatched.

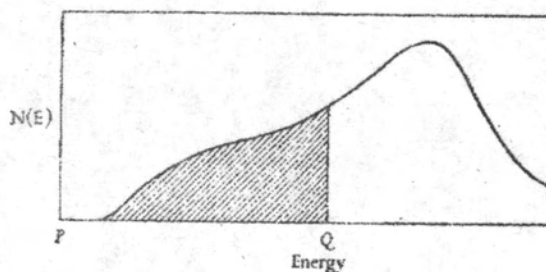


Fig. 2.21 A typical metal  $N(E)$  against  $E$  plot such as would give rise to the X-ray spectra found for aluminium metal, Fig. 2.19. Occupied levels are hatched.

By the same manner, the emission and absorption curves of aluminium oxide which is non-metallic compound is shown in Fig. 2.22.

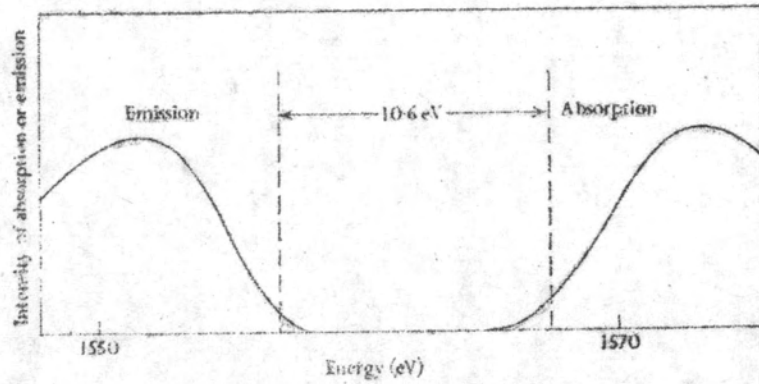


Fig 2.22 X-ray K-emission and K-absorption spectra of aluminium oxide.

The absorption and emission bands for non-metallic have a gap of energies between them, these characteristics may be related to a permitted band of energy levels as in Fig 2.23.

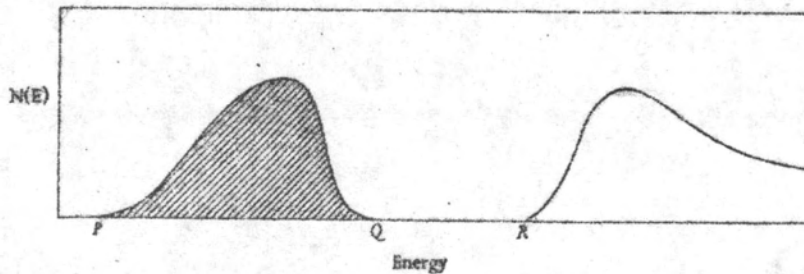


Fig. 2.23 A typical non-metal  $N(E)$  against  $E$  plot such as would give rise to the X-ray spectra found for  $Al_2O_3$  (Fig. 2.22); occupied levels are hatched.

The plots of  $N(E)$  against  $E$  are made for free electrons in a box, in a separated band (with energy gap), and in a continuum of energy levels. These plots are compared with the plots of energy against wavelength for a three - dimensional of the same kind of electrons.

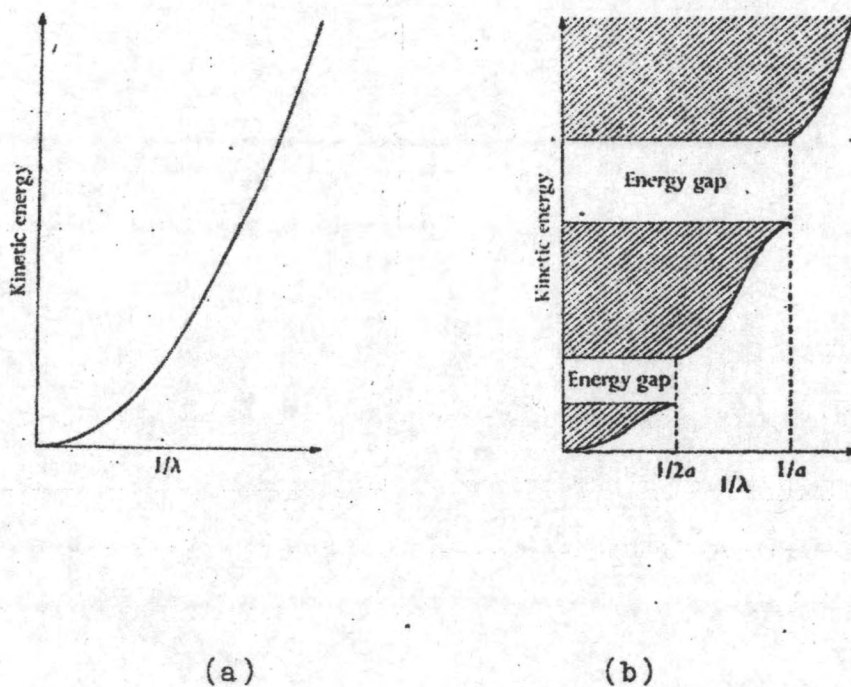


Fig. 2.24 The relationship between kinetic energy and reciprocal wavelength for (a) a free electron in a potential energy box (b) Bloch waves (Schematic)



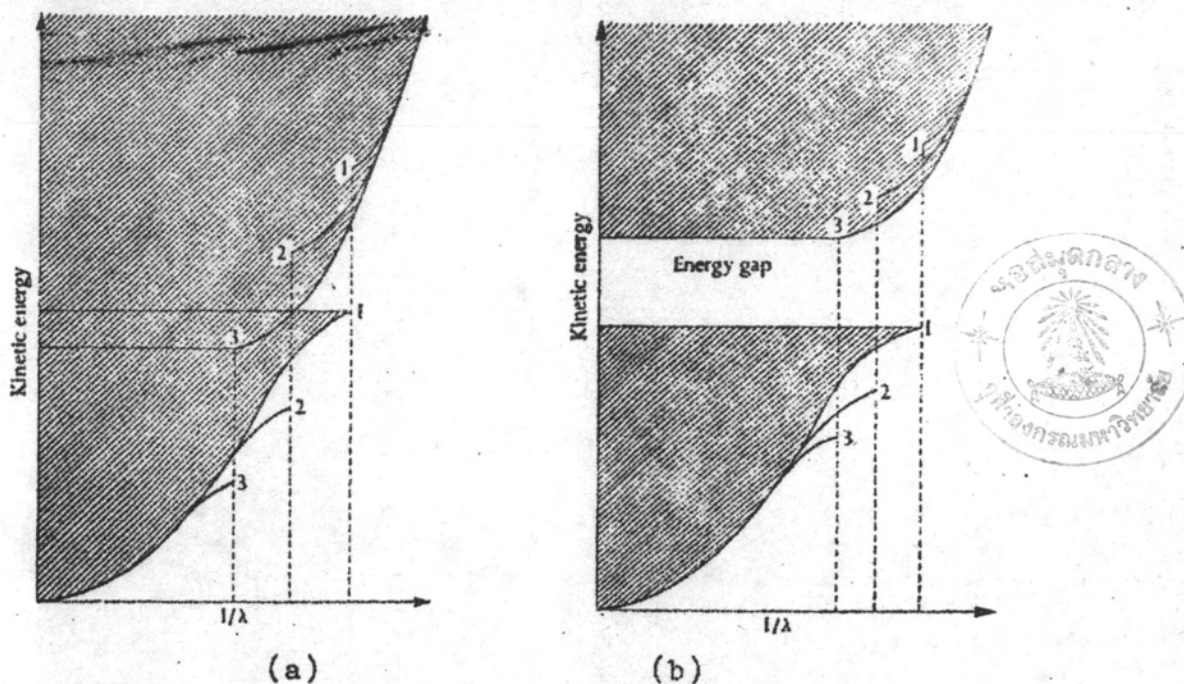


Fig. 2.25 The relationship between kinetic energy and wavelength for a three dimensional lattice where the repeat distance  $a$  is different in three directions. In case (a) there is a continuum of energy levels. (b) there is a band gap.

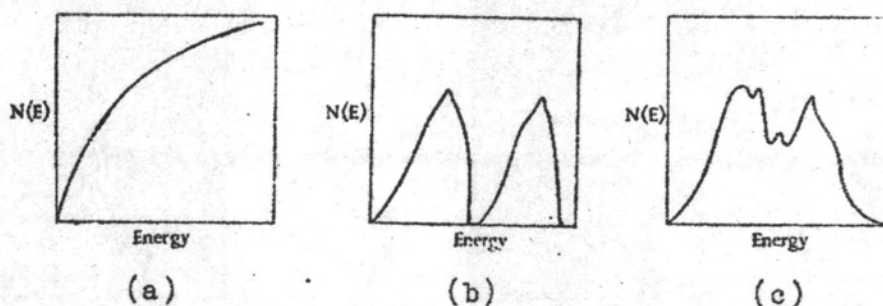


Fig. 2.26 The distribution of energy levels (a) for a free electrons in a box as pictured in Fig.2.24 (a), (b) discontinuities energy level as pictured in Fig.2.24 (b), 2.25(b) (c) discontinuities energy level as pictured in Fig.2.25(a).

The particular interest is the effect on the electrons of an applied electric field, for it is the electrical conductivity which is often used to define the difference between a conducting solid and insulated solid. In a conducting solid the electron levels may be divided into those corresponding to waves travelling to the right and those corresponding to wave travelling to the left as in Fig 2.27 (a)

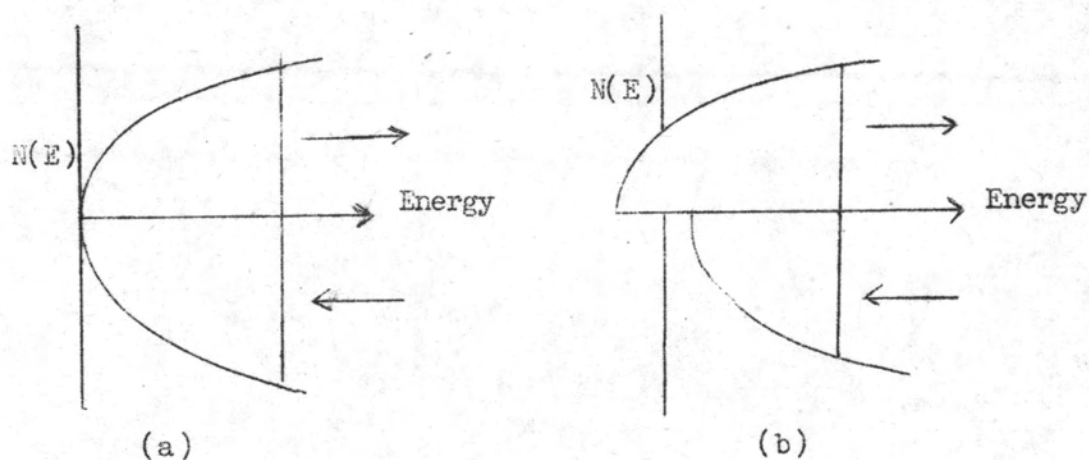


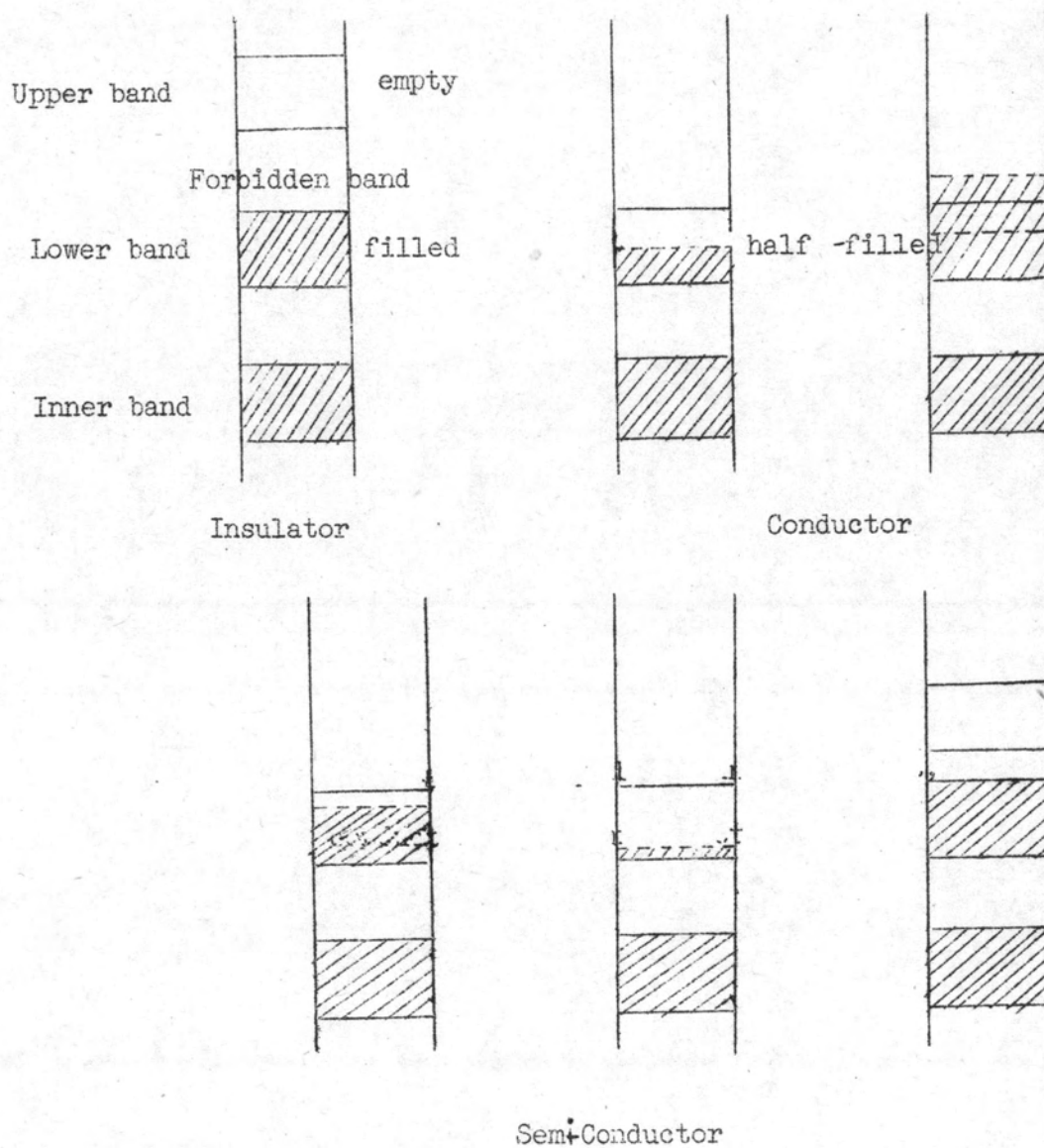
Fig. 2.27 The effect of an electric field on the energy of the electrons travelling in opposite directions: (a) no field,  
(b) field applied

For a given wavelength and in the absence of an applied electric field, the energy of the electron will not differ in the two cases. However, if a positive electrode is placed on the right

and a negative electrode on the left, the electrons moving to the right will all be lowered in energy, while the electrons moving to the left will all be raised. A redistribution of electrons then takes place as envisaged in Fig 2.27 (b) so that there is a net flow of electrons through the conducting solid.

Types of solids can be distinguished by using the energy band structure and the distribution of electrons in these bands. The inner electrons are associated with particular nuclei and would require appreciable energy to surmount the barrier to transfer to a neighbour. The outermost electrons are accommodated within the band and are used to distinguish types of solids.

If all the bands which contain electrons are completely filled, the material is an insulator. If, on the other hand, the highest-lying occupied or outermost band is half - filled band, the solid is a conductor. Finally, if this highest occupied band contains only a very small concentration of occupied or empty states, otherwise in any event which cause the reduction of energy or band gap between occupied band and conduction band then the material is a semiconductor. These situations are shown in Fig 2.28



Figs. 2.28 Filling of energy bands in insulators conductors and semiconductors.

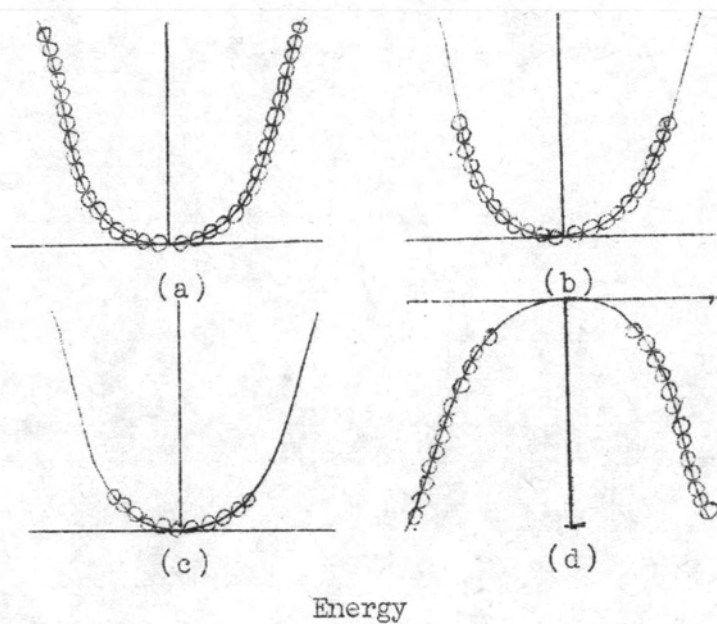


Fig 2. 29 Energy vs. wave number in

- (a) a complete filled band (insulator)
- (b) a half - filled band (conductor)
- (c) a band with only a few electrons (n-type semiconductor)
- (d) a nearly full band (p-type semiconductor)

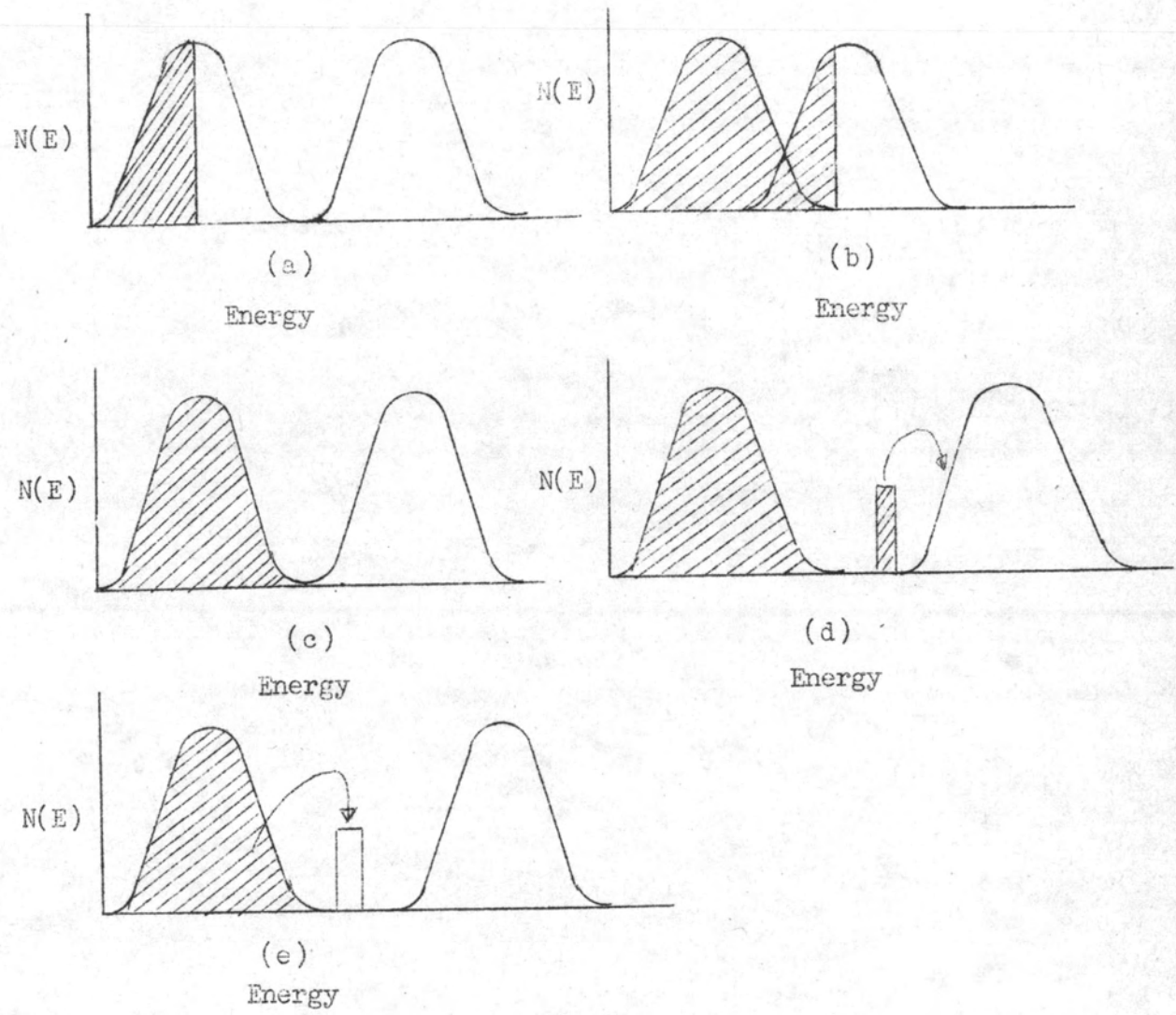


Fig. 3.30 The distribution of energy levels for (a), (b) conductor, (c) insulator and (d), (e) semi-conductor.

The filled band is termed the valence band, since these electrons contribute towards the bonding of the solid; the empty band is the conduction band. The ability of singly outermost electrons to migrate throughout the solid can be used to measure the conductivity of solid.