## Lecture 7: Defects in solids: Point defects and line defects
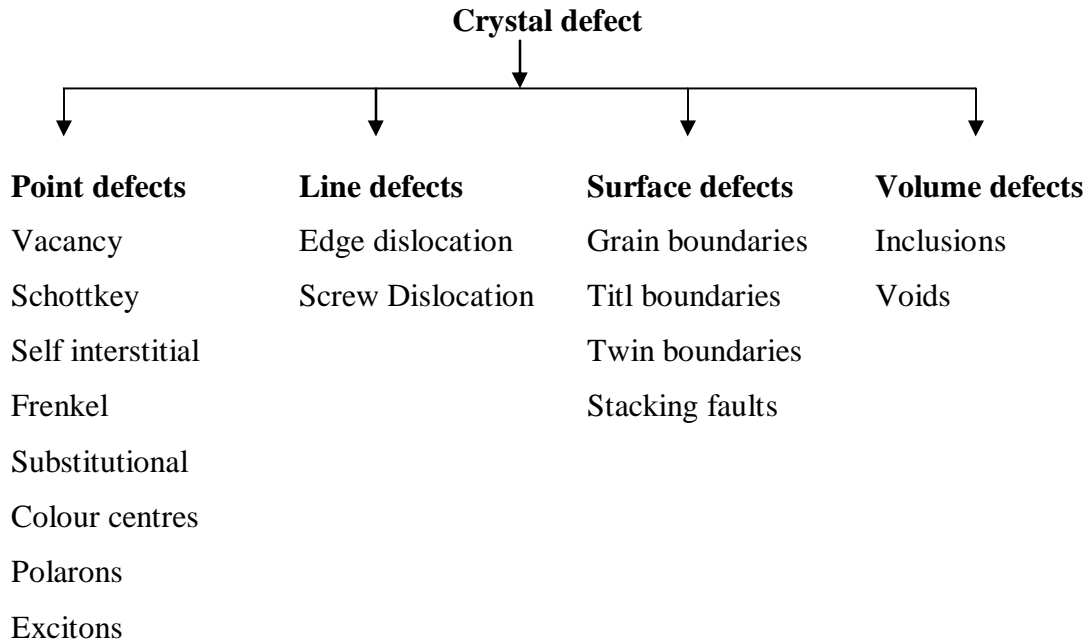
Imperfections or defects: Any deviation from the perfect atomic arrangement in a crystal is said to contain imperfections or defects. In fact, using the term "defect" is sort of a misnomer since these features are commonly intentionally used to manipulate the mechanical properties of a material. Adding alloying elements to a metal is one way of introducing a crystal defect. Crystal imperfections have strong influence upon many properties of crystals, such as strength, electrical conductivity and hysteresis loss of ferromagnets. Thus some important properties of crystals are controlled by as much as by imperfections and by the nature of the host crystals.

- The conductivity of some semiconductors is due entirely to trace amount of chemical impurities.
- Color, luminescence of many crystals arise from impurities and imperfections
- Atomic diffusion may be accelerated enormously by iumpurities or imperfections
- Mechnical and plastic properties are usually controlled by imperfections


Various Crystal Defects
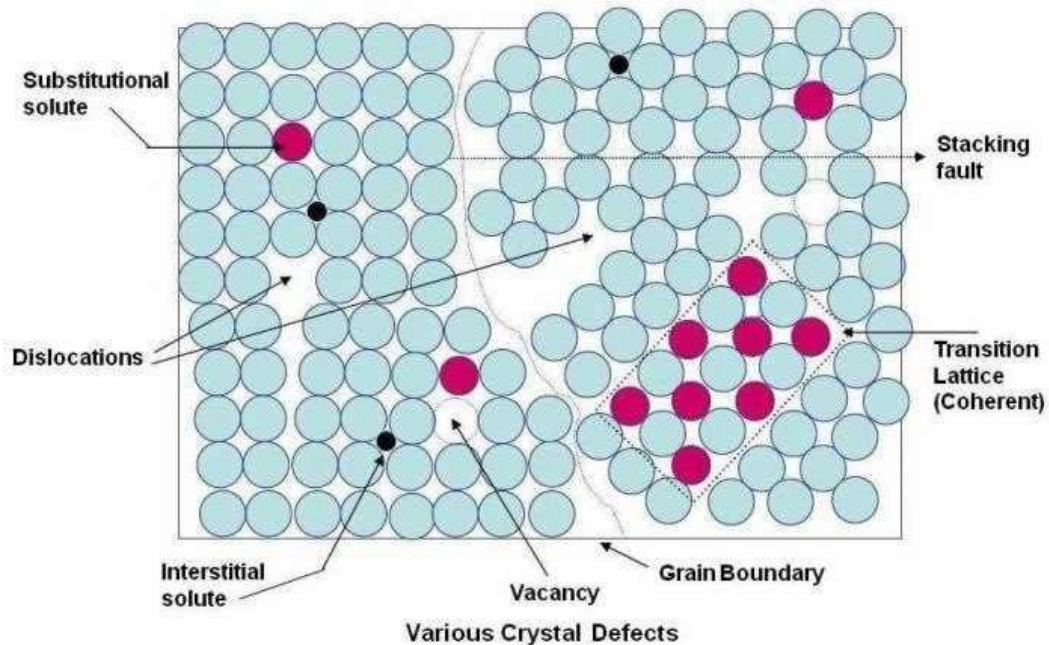
Imperfections in crystalline solids are normally classified according to their dimension as follows

1. Point imperfections (Zero dimensional defects)
2. Line imperfections (one dimensional defects)
3. Plane or surface imperfections (Two dimensional defects)
4. Volume imperfections (three dimensional defects)

Crystal defect

Point defects	Line defects	Surface defects	Volume defects
Vacancy	Edge dislocation	Grain boundaries	Inclusions
Schottkey	Screw Dislocation	Titl boundaries	Voids
Self interstitial		Twin boundaries	
Frenkel		Stacking faults	
Substitutional			
Colour centres			
Polarons			
Excitons			

Point Defects: Point defects are where an atom is missing or is in an irregular place in the lattice structure. Point defects include self interstitial atoms, interstitial impurity atoms, substitutional atoms and vacancies.

A **self interstitial** atom is an extra atom that has crowded its way into an interstitial void in the crystal structure. Self interstitial atoms occur only in low concentrations in metals because they distort and highly stress the tightly packed lattice structure. A **substitutional impurity** atom is an atom of a different type than the bulk atoms, which has replaced one of the bulk atoms in the lattice. Substitutional impurity atoms are usually close in size (within approximately 15%) to the bulk atom. An example of substitutional impurity atoms is the zinc atoms in brass. In brass, zinc atoms with a radius of 0.133 nm have replaced some of the copper atoms, which have a radius of 0.128 nm. **Interstitial** impurity atoms are much smaller than the atoms in the bulk matrix. Interstitial impurity atoms fit into the open space between the bulk atoms of the lattice structure.
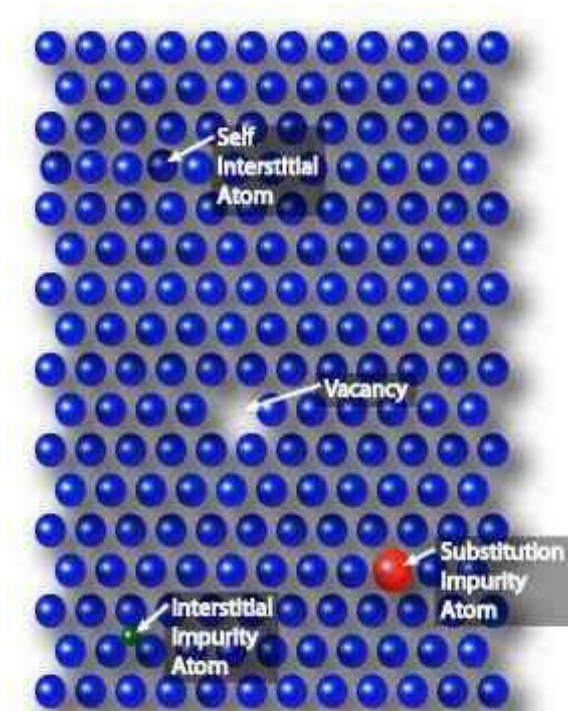
An example of interstitial impurity atoms is the carbon atoms that are added to iron to make steel. Carbon atoms, with a radius of 0.071 nm, fit nicely in the open spaces between the larger (0.124 nm) iron atoms. **Vacancies** are empty spaces where an atom should be, but is missing. They are common, especially at high temperatures when atoms are frequently and randomly change their positions leaving behind empty lattice sites. In most cases diffusion (mass transport by atomic motion) can only occur because of vacancies. **Schottkey imperfection** is a type of vacancy in which an atom being free from regular site, migrates through successive steps and eventually settles at the crystal surface. In a ionic crystal, however a vacancy on either a cation or anion site must be electrically balanced by some means. This may be achieved if there are an equal number of cation and anion vacancies, or if for every ionic crystal vacancy a similar charged interstitial appears.
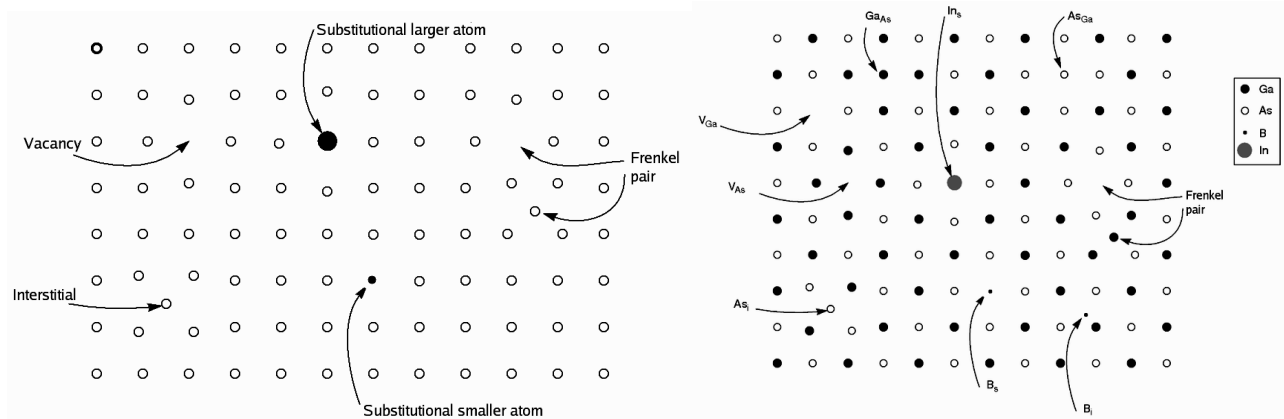

The combination of anion cation vacancies (in pairs) is called Schottkey imperfections. The combination of a vacancy and interstitial is called a Frankel imperfection.

Line Imperfections:

In **linear defects** groups of atoms are in irregular positions. Linear defects are commonly called dislocations. Any deviation from perfectly periodic arrangement of atoms along a line is called the line imperfection. In this case, the distortion is centered only along a line and therefore the imperfection can be considered as the boundary between two regions of a surface which are perfect themselves but are out of register with each other. 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.

To extreme types of dislocations are distinguish as

1. Edge dislocations and
2. Screw dislocations.

1
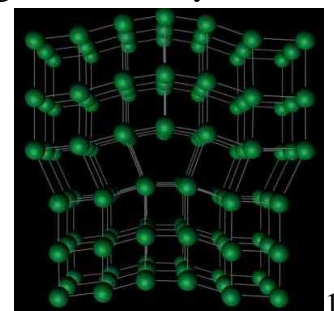
Edge Dislocations: The inter-atomic bonds are significantly distorted only in the immediate vicinity of the dislocation line. As shown in the set of images above, the dislocation moves similarly moves a small amount at a time. The dislocation in the top half of the crystal is slipping one plane at a 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.
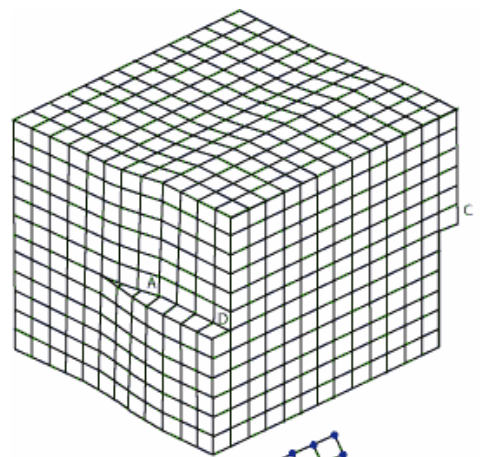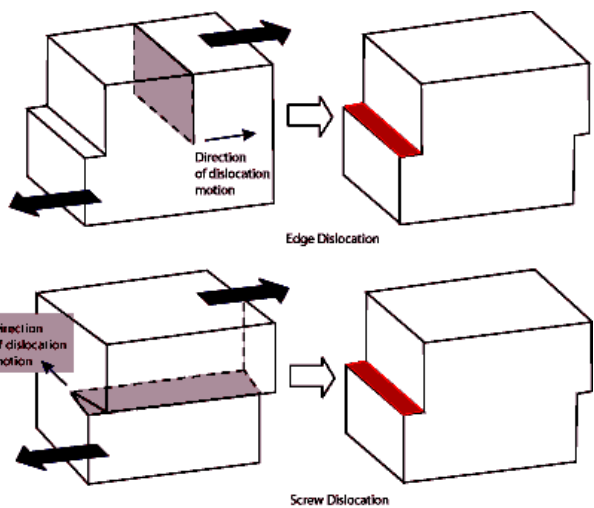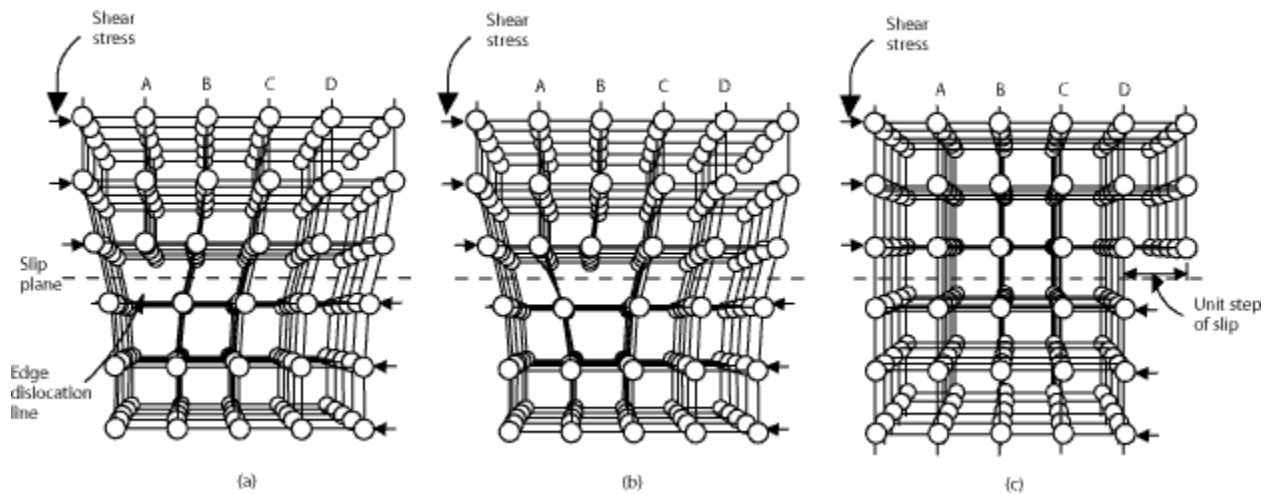
Screw Dislocations: The screw dislocation is slightly more difficult to visualize. The motion of a screw dislocation is also a result of shear stress, but the defect line movement is perpendicular to direction of the stress
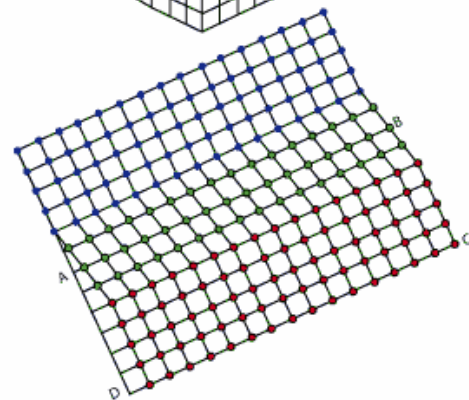
and the atom displacement, rather than parallel. To visualize a screw dislocation, imagine a block of metal with a shear stress applied across one end so that the metal begins to rip. This is shown in the upper right image. The lower right image shows the plane of atoms just above the rip. The atoms 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 broke 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 there 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.

Planar defects, which are interfaces between homogeneous regions of the material. Planar defects include grain boundaries, stacking faults and external surfaces.

Stacking Faults and Twin Boundaries

A disruption of the long-range stacking sequence can produce two other common types of crystal defects: 1) a stacking fault and 2) a twin region. A change in the stacking sequence over a few atomic spacings produces a stacking fault whereas a change over many atomic spacings produces a twin region. A stacking fault is a one or two layer interruption in the stacking sequence of atom planes. Stacking faults occur in a number of crystal structures, but it is easiest to see how they occur in close packed structures. For example, it is know from a previous discussion that face centered cubic (fcc) structures differ from hexagonal close packed (hcp) structures only in their stacking order. For hcp and fcc structures, the first two layers arrange themselves identically, and are said to have an AB arrangement. If the third layer is placed so that its atoms are directly above those of the first (A) layer, the stacking will be ABA. This is the hcp structure, and it continues ABABABAB. However it is possible for the third layer atoms to arrange themselves so that they are in line with the first layer to produce an ABC arrangement which is that of the fcc structure. So, if the hcp structure is going along as ABABAB and suddenly switches to ABABABCABAB, there is a stacking fault present.

Alternately, in the fcc arrangement the pattern is ABCABCABC. A stacking fault in an fcc structure would appear as one of the C planes missing. In other words the pattern would become ABCABCAB_ABCABC. If a stacking fault does not corrects itself immediately but continues over some number of atomic spacings, it will produce a second stacking fault that is the twin of the first one. For example if the stacking pattern is ABABABAB but switches to ABCABCABC for a period of time before switching back to ABABABAB, a pair of twin stacking faults is produced. The red region in the stacking sequence that goes ABCABCACBACBABCABC is the twin plane and the twin boundaries are the A planes on each end of the highlighted region.

Grain Boundaries in Polycrystals

Another type of planer defect is the grain boundary. Up to this point, the discussion has focused on defects of single crystals. However, solids generally consist of a number of crystallites or grains. Grains can range in size from nanometers to millimeters across and their orientations are usually rotated with respect to neighboring grains. Where one grain stops and another begins is know as a grain boundary. Grain boundaries limit the lengths and motions of dislocations. Therefore, having smaller grains (more grain boundary surface area) strengthens a material. The size of the grains can be controlled by the cooling rate when the material cast or heat treated. Generally, rapid cooling produces smaller grains whereas slow cooling result in larger grains. For more information, refer to the discussion on solidification.

Volume or Bulk Defects

Bulk defects occur on a much bigger scale than the rest of the crystal defects discussed in this section. However, for the sake of completeness and since they do affect the movement of dislocations, a few of the more common bulk defects will be mentioned. **Voids** are regions where there are a large number of atoms missing from the lattice. The image to the right is a void in a piece of metal. The image was acquired using a Scanning Electron Microscope (SEM). Voids can occur for a number

of reasons. When voids occur due to air bubbles becoming trapped when a material solidifies, it is
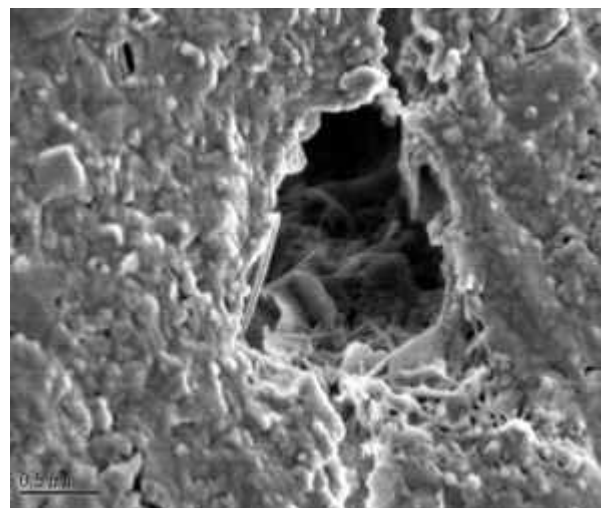
commonly called porosity. When a void occurs due to the shrinkage of a material as it solidifies, it is called cavitation.

Another type of bulk defect occurs when impurity atoms cluster together to form small regions of a different phase. The term 'phase' refers to that region of space occupied by a physically homogeneous material. These regions are often called precipitates or **inclusions**.
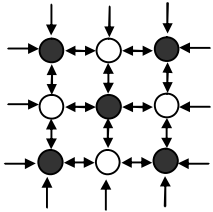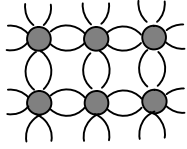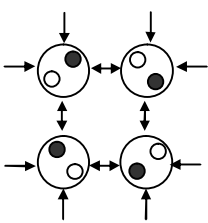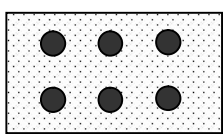
Effect of point defect:
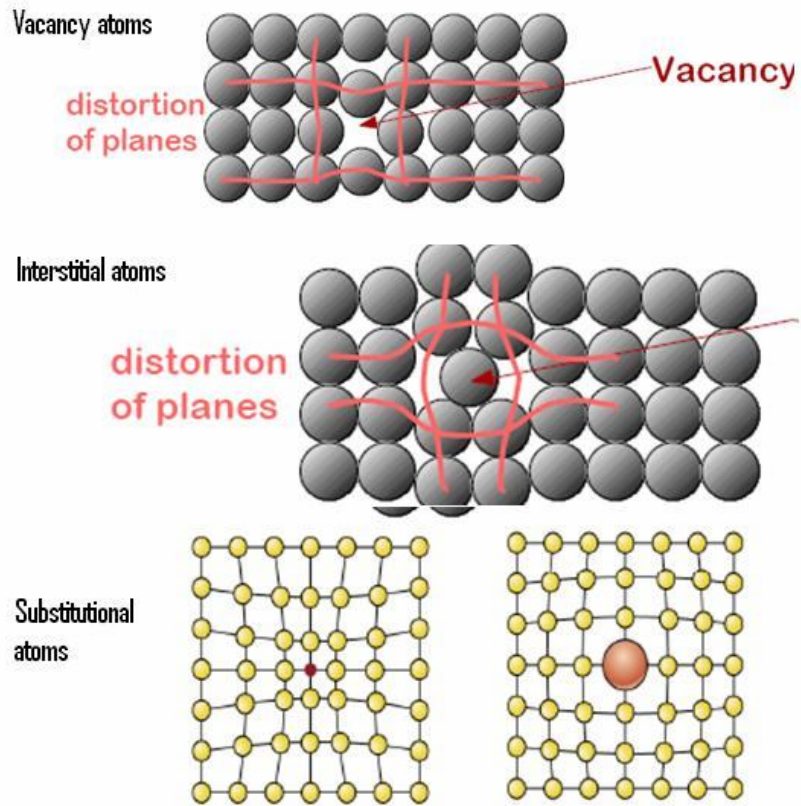
Lecture 10: **Bonds in solid**

A solid consists of atoms, ions, or molecules packed cosly together and forces that hold them in place give rise to the distinctive properties of the various kind of solids. The covalent bonds that can link a fixed number of atoms to forms a certain molecule can also link an unlimited number of molecules to form a solid. I addition ionic, Van der Waals, and metallic bonds provide the cohesive forces in solids. Whose structural elements afre respectively ion, molecules, and metal atoms.

Types of Crytalline solids on the basis of bonding types:

Types	Lattice	Bond	Properties	Example
Ionic		Electron attraction	• Hard • Melting point high • Solube in polar liquids • Elelctrical insulators (Conductors in solution)	Alkali Halides, Alkaline oxides (Na_2O), etc.
Covalent		Shared Electrons	• Very hard • High melting points • Insoluble in nearly all liquids • Semiconductors (Except diamond)	Diamond, C, Etc.
Molecular		Van der Waals forces	• Soft • Low melting and boiling points • Soluble in covalent liquids • Electrical insulators	Methane (CH_4)
Metallic		Electron gas	• Ductile • Metallic luster • High electrical and thermal conductivity	Sodium (Na)

Thus on the basis of bonding type, we have following five categories of solids:

1. Ionic solids (NaCl, NaOH, etc.)
2. Covalent solids (Diamond, Silicon)
3. Metallic solids (various metals and alloys)
4. Van der waals bonded solids/ molecules (O_2, H_2, Solid He, Kr, Xe)
5. Hydrogen bonded solids (Ice, Some fluorides)

- The reason of condensation is due to van der Waals bonding.

- Hydrogen bonding is a special type of van der Waals bonding containing Hydrogen atoms.

Ioninc bonds come into being when atoms that have low ionization energies, and hence loss electron readily interect with other atoms that tend to aquire excess electrons. The formar atoms give up electrons to the later, and they thereupon become positive and negative ions respectively. In ionic crystals this ions assemble themselves in an equilibrium configuration in which the attaractive forces between the positive and negative ions balance the repulsive forces between ions.

Electron affinity: It is the energy, ralesed when an electron si addede to an atm of an given elements:; the greater the electro, the more such atoms tends to becobe negative ions. Sodium, wit an ionization energy of 5.14 eV, tends to form Na^+, and Chlorine atom wioth an electron affinity, tends to form Cl^- ions.

The bond energy and Medulung constant for NaCl Crystal

The cohesive energy is the work needed to remove an atom (or molecule) fro the crystal and so indicates the strength of the bond holding it in palce. Part of the cohesive energy is the electrical potential energy $U_{coloumb}$ of ions. Let us consider an Na^+ ion in crystal NaCl in which Na_+ has six nearest neighbours Cl^- ions, each one are in r distance away. The potential energy of the Na^+ ion due to this six Cl^- ion is therefore
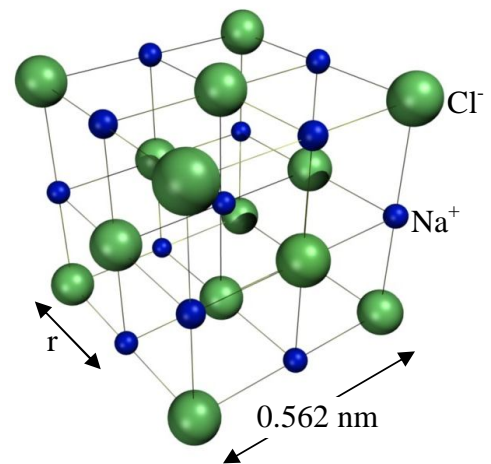
$$U_1 = -\frac{6e^2}{4\pi\varepsilon_0 r} \dots\dots\dots(1)$$

The next nearest neighbors are twewlve Na^+ ions, each on the distance $\sqrt{2}r$ away since the diagonal of a square r long on a side is $\sqrt{2}r$.

The potential energy of the Na$^+$ ion due to the Na$^+$ ions each

$$U_2 = +\frac{12e^2}{4\pi\varepsilon_0\sqrt{2}r} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(2)$$
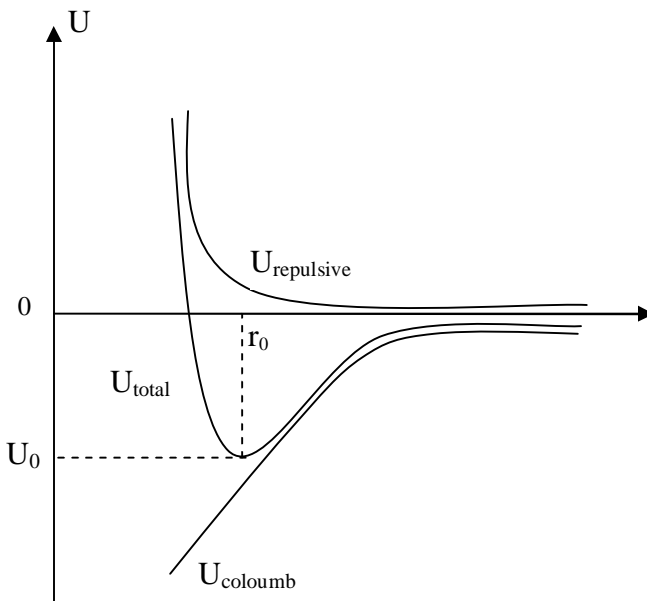
When the summation is continued over all the positive and negative ions in a crystal of infinite size, the result is

$$U_{Co\,lub\,m} = -\frac{6e^2}{4\pi\varepsilon_0 r}(6 - \frac{12}{\sqrt{2}} + \cdots\cdots) = -1.748\frac{e^2}{4\pi\varepsilon_0 r}$$

In general,

$$U_{Co\,lub\,m} = -\alpha\frac{e^2}{4\pi\varepsilon_0 r} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(3)$$

This result holds the potential energy of a Cl$^-$ ion as well, of course.

Here the quantity α is callded the Madulung constant of the crystal, and it has the same value of the same sturcure. Now the potential energy contribution opf the exclusion principle has approximate form

$$U_{repulsive} = \frac{B}{r^n} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(4)$$

The sign of $U_{repulsive}$ is +ve, which corresponds to repulsion. The dependence on r $^{-n}$ implies a short range force that increases as the interatomic distance r decreases. The total potential energy of each ion due to its interactions with all the other ions is therefore,

$$U_{total} = U_{repulsive} + U_{Co\,lub\,m} = -\alpha\frac{e^2}{4\pi\varepsilon_0 r} + \frac{B}{r^n} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots\ldots\ldots.(5)$$

At equilibrium separation, r = r$_0$, of the ions, U is a minimum by defeniation, and so $\frac{dU}{dr} = 0$, when

r = r$_0$. Hence,

$$\left(\frac{dU}{dr}\right)_{r=r_0} = \frac{\alpha e^2}{4\pi\varepsilon_0 r_0^2} - \frac{nB}{r_0^{n+1}} = 0$$

$$B = \frac{\alpha e^2}{4\pi\varepsilon_0 n} r_0^{n-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

The total potential energy at the equilibrium separation is therefore, (from Equations 5 and 6)

$$U_0 = -\frac{\alpha e^2}{4\pi\varepsilon_0 r_0}(1-\frac{1}{n}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

We must add this amount of **energy per ion pair** to separate an ioninc crystal into indivisual ions. The exponent n can be found from the observed compressibilities of ionic crystals. The average result is $n \approx 9$. which means that the repulsive force varies sharply with r. Figure shows the variation of potential energy in an ionic crystal with ionic separation. The minimum value of U_{total} is U_0 occurs at an equilibrium separation of r_0. Thus

Cohesive energy = Atom separation energy = Ion separation energy + Electron transfer energy.

Problem: In an NaCl crystal, the equilibrium distance r_0 between ions is 0.281 nm. Find the cohesive energy in NaCl. Provided that ionization energy for Na is +5.14 eV and electron affinity of Cl is -3.61 eV.

Solution: Since $\alpha = 1.748$ and $n = 9$, the potential energy per ion is

$$U_0 = -\frac{\alpha e^2}{4\pi\varepsilon_0 r_0}(1-\frac{1}{n})$$

$$= -\frac{(9\times10^9 N.m^2C^{-2})(1.748)(1.6\times10^{-19}C)^2}{2.81\times10^{-10}m}(1-\frac{1}{9})$$

$$= 1.27\times10^{-18}J = -7.96eV$$

$\therefore$ The contribution to the cohesive energy per ion of the crystal $= \frac{1}{2}\times(-7.96eV) = -3.98eV$

Now, electron transfer energy = Ionization energy of Na + Electron affinity of Cl

$$= (+5.14 \text{ eV}) + (-3.61 \text{ eV})$$

$$= 1.53 \text{ eV}$$

Each atom therefore contributes ½(1.53) or 0.77 eV to the cohesive energy from this source. The total cohesive energy per atom is thus

$$E_{cohesive} = (-3.98 + 0.77) \text{ eV} = -3.21 \text{ eV}.$$

Which is not far from the experimental value of -3.28 eV.

Lecture 11: Introduction to Band Theory-Metals, Semiconductors and Insulators

There are many energy levels ($\sim 10^{23}$) in a given band. A given atom in a solid has a fixed number of nearest neighbors, but many distant neighbors as shown in Fig. 1.

If we consider just a single plane and an arbitrary atom, there may be four nearest neighbors as in Fig. 1(a). Isolated from others, this system should give rise to four split energy levels. With the widest energy separations; the interaction occurs between neighbors.
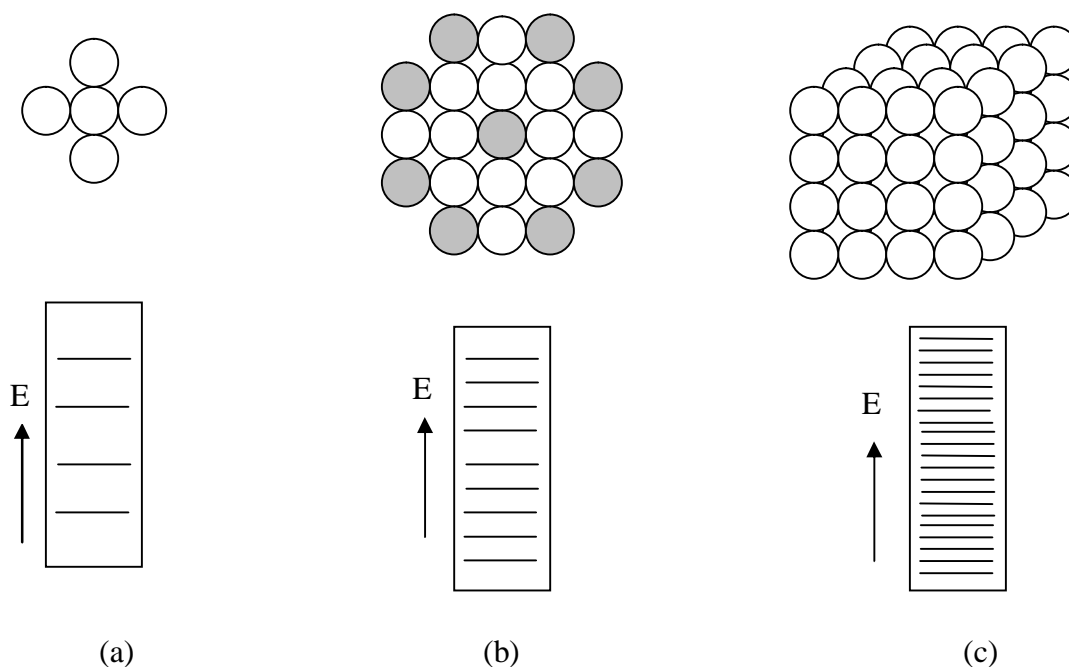

Figure 1: Splitting of valence band

As we move away from an atom, there are more and more neighbors. For example, an atom may have eight 4th neighbors in one plane as shown in Fig. 1(b). In isolation from the rest, the energy would have split into nine narrowly separated levels, since the atoms are further isolated. In a crystal, there are hundreds and thousands of distant neighbors, so the number of narrowly-split energy level will correspondingly be very large. The outermost energy band that is completely or partially filled is called the valence band in solids. The band that is above the valence band and is empty at 0 K, is called the conduction band.

According to the nature of band occupation by electrons, all solids can be classified broadly into two groups.

Firstly, the group in which there is partially filled band immediately above the uppermost filled valence band. This is possible in two ways. One - the balance band is only partially filled. Second- A completely filled valence band overlaps the partially filled conduction band as shown in Fig. 2.
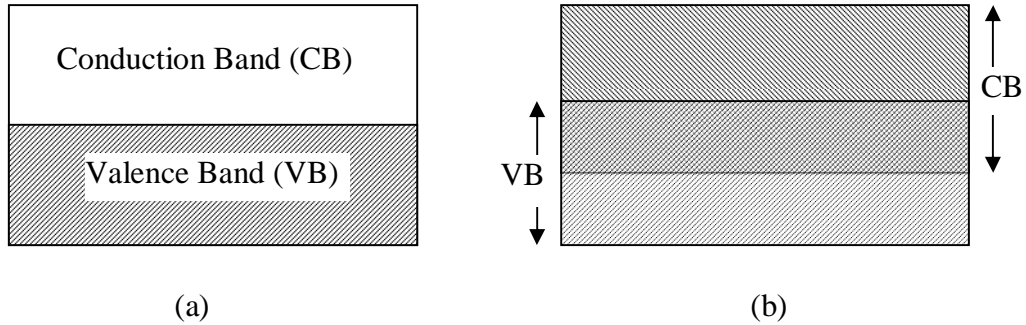
(a)   (b)

Fig. 2: Metals have partially filled or overlapping bands.

Secondly, the groups which include empty bands lying above completely filled band levels. The solids of this group conveniently subdivided into insulators (dielectrics) and semiconductors depending on the width of the forbidden band.

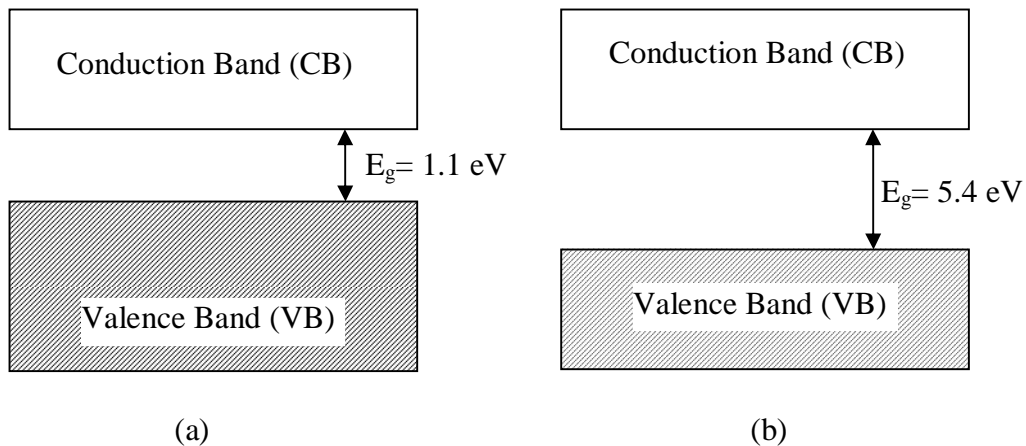(a)   (b)

Fig. 3: The difference between a semiconductor and an insulator in terms of energy gap.

Insulators include solids with relatively wide forbidden bands. For typical insulators the band gap, $E_g > 3$ eV. (Diamond: 5.4 eV, BN: 4.6 eV, Al_2O_3: 7 eV).

On the other hand, semiconductors include solids with relatively narrow forbidden bands. For typical semiconductors, $E_g \leq 1$ eV. (Ge: 0.7 eV, Si: 1.12 eV, InSb: 0.17 eV, GaAs: 1.43 eV)

According to Pauli's exclusion principle, each energy level must be occupied by no more than two electrons. Thus, Monovalent metals such as Cu, Ag, and Au have one electron in the outermost shell and hence the corresponding energy band is only half filled. On the other hand, the divalent metals such as Be, Mg, Ca, etc. have overlapping valence and conduction bands. The trivalent metals Al, Ga, etc. have similar band structure as monovalent metals.

The tetravalent nonmetals such as C, Si, etc. have even number of electrons in the outermost (4 electrons in each case) shell like divalent atoms. The corresponding valence band is full but unlike the divalent metals there is no overlapping of the VB with the CB in this case.