An ideal crystal is a perfect crystal in which each atom has identical surroundings. Real crystals are not perfect. A real crystal always has a large number of imperfections in the lattice.

Since real crystals are of finite size, they have a surface to their boundary.

At the boundary, atomic bonds terminate and hence the surface itself is an imperfection.

One can reduce crystal defects considerably, but can never eliminate them entirely.
The basic classes of crystal defects are:

1. Point defects  
   (Zero-dimensional defects)

2. Line defects  
   (One-dimensional defects)

3. Surface defects  
   (Two-dimensional defects)

4. Volume defects  
   (Three-dimensional defects)
CLASSIFICATION OF DEFECTS BASED ON DIMENSIONALITY

0D  (Point defects)
- Vacancy
- Interstitial
- Frenkel defect
- Schottky defect

1D  (Line defects)
- Edge Dislocation
- Screw Dislocation

2D  (Surface / Interface)
- Grain boundary
- Twin boundary
- Stacking faults

3D  (Volume defects)
- Dispersant
- Precipitate
- Inclusion
- Voids / Cracks
POINT DEFECTS

Point defects, which are places where an atom is missing or irregularly placed in the lattice structure.

Point defects include lattice vacancies, self-interstitial atoms, substitution impurity atoms, and interstitial impurity atoms. There are three major types of point defect: Vacancies, Interstitials and Impurities.

- **Schottky defects** occur in ionic crystals where the size of anion is almost same with the size of the cation.

- **Frenkel Defect** is one type of point defect where an atom (better to say ion, especially cation) leaves its original lattice site and occupies an interstitial position on the same crystal.
Line **defect** weakens the structure along a one-dimensional space, and the **defects** type and density **affects** the **mechanical properties** of the solids. Thus, formation and study of dislocations are particularly important for structural **materials** such as metals.
Vacancy

Interstitial impurity
SCHOTTKY DEFECT

Fig. 1.26: Schottky defects

- Pair of anion and cation vacancies
- In order to maintain electrical neutrality, the number of missing cations and anions are equal
- It also decreases the density of crystal
- E.g., Alkali halides such as NaCl, KF, etc.
FRENKEL DEFECTS

- Cation (being smaller get displaced to interstitial voids)
- Combination of vacancy and interstitial atom
- No change in the density
- E.g. AgI, CaF₂
COLOR CENTERS

- **Color centers** are point defects or point defect clusters associated with trapped electrons or holes in normally transparent materials.

- These **centers** cause the solid to become **colored** when the electronic ground state of the defect is excited to higher energy states by the absorption of visible light.
The production of lattice defects thus results in the colouring of a crystal. A crystal can be coloured in a number of ways:

(a) by the introduction of chemical impurities,
(b) by introducing an excess of metal ion.

This can be achieved by heating the crystal in the vapour of alkali metal and then cooling it quickly. When NaCl crystal is heated in the presence of sodium vapour, it appears yellow.

(c) by X-rays, γ-ray, neutron and electron bombardment,
(d) by electrolysis.

**F-centre**: F-centre is an electron trapped at a negative ion vacancy.

If NaCl crystal is heated in an atmosphere of sodium vapour, excess alkali atoms are then added to the crystal. Each of excess sodium atoms absorbed from the vapour may then ionise into a positive ion (sodium ion) and an electron. Corresponding to the total number of sodium ions (positive ions), an equal number of negative ion vacancies will be created to keep the crystal neutral. The extra electrons from the ionised sodium atoms are injected into the conduction band where they do not remain for a long time and are soon captured by the
negative ion vacancies. Since the negative ion vacancy represents a net positive charge within the crystal, it attracts the electron to itself. **Thus negative ion vacancy captures an excess electron.** Because the dielectric constant is not large, the hydrogen like orbit of such a bound electron around the negative ion vacancy extends over few neighbouring ions surrounding the vacancy or in other words captured electron is shared by all the neighbouring positive ions which surround the vacant site (fig. 14). This vacancy with its trapped electron is called the **F-centre**.
Absorption band associated with $F$-centres in several alkali halides are shown in fig. and quantum energies as listed in the table 1.

<table>
<thead>
<tr>
<th>Alkali halides</th>
<th>Energy in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>3.3 eV</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.7 eV</td>
</tr>
<tr>
<td>KCl</td>
<td>2.3 eV</td>
</tr>
<tr>
<td>KBr</td>
<td>2.0 eV</td>
</tr>
<tr>
<td>RbCl</td>
<td>2.1 eV</td>
</tr>
<tr>
<td>CsCl</td>
<td>2.1 eV</td>
</tr>
</tbody>
</table>
Pohl investigated the following experimental properties of F-centre:

(a) It is noted that band in KCl is exactly the same whether the excess metal is added by heating the crystal in sodium or in potassium vapour. This implies that F absorption band is independent of the added metal and is the characteristic of the crystal.

Also the same band is formed when the stoichiometric crystals are irradiated with ultra violet, X-rays or other types of radiation which produce free electrons. Such free electrons are ultimately trapped at negative ion vacancies forming F-centres.
(b) It is noted that the density of crystal decreases when excess metal is introduced or in other words coloured crystals are less dense than uncoloured crystals. This is quite in agreement with the picture that the creation of vacancies lowers the density.

(c) F-absorption band is believed to be due to excitation of F-centre electron into an excited state close to the conduction band but not into the conduction band. It is also found that the width of F-band increases with temperature, the peak shifting at same time to lower energies.

Other centres in alkali halides:

F' centre: The F' centres are produced by irradiating at not too high temperatures an additively coloured crystal containing F centres. In this way a broad band appears at the long wavelength side of the F band which grows at the cost of F band and is called F' band. For example in fig. 16(a) curve A represents the absorption spectrum of KCl crystal containing $1.6 \times 10^{16}$ F centres per cm$^3$ measured at 38 K. After irradiating with a light with frequency corresponding to F absorption band at 173 K, the F band decreases and F' band appears (curve B). F' centres are stable only at low temperatures because at high temperatures they dissociate thermally and form F centres again. This happens simply
Fig. (a). The $F$ and the $F'$ bands in KCl. The $F'$ band was produced by irradiating the crystal with light lying in the center of the $F$ band.

Fig. (b). The $F$-band of KBr at different temperatures.

It is found that two $F$ centres are destroyed for each $F'$ centre formed. One of the two $F$ centres liberates electron due to irradiation and the liberated electron is subsequently captured by the second $F$ centre to form $F'$ centre consisting of an anion vacancy with two bound electrons.
F-CENTER

An F-center, Farbe center or color center is a type of crystallographic defect in which an anionic vacancy in a crystal lattice is occupied by one or more unpaired electrons. Electrons in such a vacancy tend to absorb light in the visible spectrum such that a material that is usually transparent becomes colored.
The anionic sites occupied by unpaired electrons are called F-centres (from the German word Farbenzenter for colour centre). Such defects also impart color to the crystals. The color results by excitation of these electrons when they absorb energy from the visible light falling on the crystals.
F-centers are often paramagnetic and can be studied by electron paramagnetic resonance techniques.

The greater the number of F-centers, the more intense the color of the compound.

One way of producing F-centers in a crystal artificially is to heat it in an atmosphere of the metal of which it is constituted, e.g., heating NaCl in a metallic Na atmosphere.

\[ \text{Na}^0 \rightarrow \text{Na}^+ + \text{e}^- \]
Na\(^+\) is incorporated into the NaCl crystal after giving up an electron. A Cl\(^-\) vacancy is generated to balance the excess Na\(^+\). The effective positive charge of the Cl\(^-\) vacancy traps the electron released by the Na atom. This trapping of the electrons by anion vacancies results in the formation of F-centers; that is, the electrons released in this process diffuse to the vacant sites where negatively charged ions (i.e., anions) normally reside. Ionizing radiation can also produce F-centers.
A grain boundary is the interface between two grains, or crystallites, in a polycrystalline material. Grain boundaries are 2D defects in the crystal structure, and tend to decrease the electrical and thermal conductivity of the material.
A **grain boundary** (GB) is the interface between two grains, or crystallites, in a polycrystalline material. Grain boundaries are defects in the crystal structure, and tend to decrease the electrical and thermal conductivity of the material.

A **grain boundary** is a general planar defect that separates regions of different crystalline orientation (such as grains) within a polycrystalline solid. Grain boundaries are usually the result of uneven growth when the solid is crystallizing. Grain sizes vary from 1 μm to 1 mm.
DISLOCATIONS

When the periodicity of atomic lattice is interrupted along certain directions in a crystal it is called a dislocation.

Two types of dislocations- edge dislocation and screw dislocation

An edge dislocation is a defect where an extra half-plane of atoms is introduced midway through the crystal, distorting nearby planes of atoms.

An edge dislocation therefore moves in the direction of the Burgers vector, whereas a screw dislocation moves in a direction perpendicular to the Burgers vector.
A dislocation is defined by its line and its displacement vector known as the Burgers vector.

Dislocation line is the boundary between the slipped and un-slipped areas.

The dislocation line is perpendicular to the Burgers vector in edge dislocations.
• When the incomplete plane starts from the top of the crystal, then it is called positive edge dislocation and is represented by “⊥” (see Fig. a)

• When the incomplete plane starts from the bottom of the crystal, then it is called negative edge dislocation and is represented by “⊥” (see Fig. b).
Positive Edge dislocation

Region of compression
Region of tension

Negative Edge dislocation
A **screw dislocation** is a topological defect of a crystal lattice. If one moves around the **dislocation**, the lattice plane shifts by one layer (or more layers), like a spiral staircase. The Burgers vector of a **screw dislocation** is parallel to the **dislocation** line.

It is produced by cutting the crystal partway and then shearing down one part relative to the other by one atomic spacing.
Screw dislocation

- A dislocation in the lattice structure of a crystal in which the atoms are arranged in a helical pattern that is normal to the direction of the stress
- The motion of screw dislocation is also a result of shear stress
- Motion is perpendicular to direction of stress
IONIC BONDING

- Ionic bonding is the complete transfer of valence electron(s) between atoms.
- It is a type of chemical bond that generates two oppositely charged ions.
- In ionic bonds, the metal loses electrons to become a positively charged cation, whereas the nonmetal accepts those electrons to become a negatively charged anion.
Ionic Bond

Transfer of electrons

Atom 1 (metal) → Atom 2 (nonmetal) → Ionic molecule
ionic bond

chemical reaction
Ionic Bond

Na: Metal atom
Cl: Non-metal

I have one extra electron, You can have it

I need one electron To Complete octet
Ionic bonding is a type of chemical bonding that involves the electrostatic attraction between oppositely charged ions, or between two atoms with sharply different electronegativities, and is the primary interaction occurring in ionic compounds.
Details of Madelung Constant for NaCl lattice

Madelung constant is a property of crystal structure. It depends on the lattice parameters and anion-cation distances.

Madelung constant represents the effect of a specific geometrical array of ions on the electrostatic potential energy.
Calculation of Madelung constant in a linear chain of ions

Taking middle two Na ions as reference. The relative distance of all ions are shown in fig.
The attractive Coulomb energy due to nearest two Cl ions is given by

\[-\frac{e^2}{4\pi \varepsilon_0 r_0} + \left( \frac{-e^2}{4\pi \varepsilon_0 r_0} \right) = -\frac{2e^2}{4\pi \varepsilon_0 r_0}\]

The repulsive energy due to two positive Na ions at a distance of \(2r_0\) on its both sides is given by

\[\frac{e^2}{4\pi \varepsilon_0 (2r_0)} + \frac{e^2}{4\pi \varepsilon_0 (2r_0)} = \frac{2e^2}{4\pi \varepsilon_0 (2r_0)}\]
Attractive Coulomb energy due to two next Cl ions on both sides at distances 3r_0 is given by

\[-\frac{e^2}{4\pi\varepsilon_0 (3r_0)} + \left(\frac{-e^2}{4\pi\varepsilon_0 (3r_0)}\right) = -\frac{2e^2}{4\pi\varepsilon_0 (3r_0)}\]

So, the total energy due to all ions in the chain is

\[-\frac{2e^2}{4\pi\varepsilon_0 r_0} + \frac{2e^2}{4\pi\varepsilon_0 (2r_0)} - \frac{2e^2}{4\pi\varepsilon_0 (3r_0)}\]

\[-\frac{e^2}{4\pi\varepsilon_0 r_0} \left[2 - \frac{2}{2} + \frac{2}{3}\right] = \frac{-e^2}{4\pi\varepsilon_0 r_0} \left[2 \left(1 - \frac{1}{2} + \frac{1}{3}\right)\right] = \frac{-e^2}{4\pi\varepsilon_0 r_0} \left[\frac{1}{2}\right] = -\frac{e^2}{8\pi\varepsilon_0 r_0}\]
\[ i = -\frac{e^2}{4\pi\varepsilon_0 r_0} \left[ 2 \log e^2 \right] \]

\[ = -\frac{e^2}{4\pi\varepsilon_0 r_0} \alpha'_M \quad \text{where} \quad \alpha'_M = 2 \log_2 e^2 = 1.38 \]
Marcel-Lung constant in 3D for NaCl lattice.

In order to calculate the total Coulomb potential energy, we should take up the sum of all the attractive and repulsive energies between all ions.

Consider a single Na\(^+\) ion situated at the position A. This Na\(^+\) is surrounded by 6 Cl\(^-\) ions at a distance \(r_0\), 12 Na\(^+\) at \(\sqrt{2}r_0\), 8 Cl\(^-\) ions at \(\sqrt{3}r_0\), and 6 Na\(^+\) ions at a dist. \(2r_0\) and so on. There will be attractive potential energy between Na\(^+\) and Cl\(^-\) ion.
Attractive potential energy below. \( \text{Na}^+ \) ion & 6 Cl\(^-\) ions at a distance \( r_0 = \frac{6e^2}{4\pi\varepsilon_0 r_0} \)

Repulsive P. E. below. \( \text{Na}^+ \) ion and 12 \( \text{Na}^+ \) ions at a distance \( r_0 = \frac{12e^2}{4\pi\varepsilon_0 (r_0\sqrt{2})} \)

Attractive energy below. \( \text{Na}^+ \) ion and 8 Cl\(^-\) at a dist. \( \sqrt{3} r_0 = \frac{8e^2}{4\pi\varepsilon_0 (\sqrt{3} r_0)} \)

Repulsive P. E. below. \( \text{Na}^+ \) ion & 6 \( \text{Na}^+ \) ions at dist. \( 2r_0 \)

\[ = \frac{6e^2}{4\pi\varepsilon_0 (2r_0)} \]
The sum of all these energies for xenon is:

\[
U = -\frac{e^2}{4\pi\varepsilon_0} \left[ \frac{6 - 12'}{\sqrt{2}} + \frac{8}{\sqrt{3}} - 6 + \ldots \right]
\]

\[
= -\frac{e^2}{4\pi\varepsilon_0} \times \sigma M + \sigma M = \left[ 6 - \frac{12'}{\sqrt{2}} + \frac{8}{\sqrt{3}} - 6 + \ldots \right]
\]

Modelling constant for NaCl structure is \(1.75\)
The cohesive energy of an ionic crystal is the energy that would be liberated by the formation of the crystal from individual neutral atoms.

The principal contribution to the cohesive energy of an ionic crystal is the electrostatic potential energy $U_{\text{coulomb}}$ of the ions.
Expression for the cohesive energy of an ionic crystal

Let us consider an Na$^+$ ion in NaCl. Its nearest neighbours are six Cl$^-$ ions, each one the distance $r$ away.

The potential energy of the Na$^+$ ion due to the 6 Cl$^-$ ions
\[
U_1 = -\frac{6e^2}{4\pi\varepsilon_0 r}
\]

The next nearest neighbours are 12 Na$^+$ ions, each one the distance $\sqrt{2}r$ away.

The potential energy of the Na$^+$ ion due to the 12 Na$^+$ ions
\[
U_2 = +\frac{12e^2}{4\pi\varepsilon_0 \sqrt{2}r}
\]

Then there are 8 Cl$^-$ ions at $\sqrt{3}r$ distance, 6 Na$^+$ ions at $2r$ distance and so on. When the summation is continued over all the + and – ions in a crystal of infinite size, the result is

\[
U_{\text{coulomb}} = -\frac{6e^2}{4\pi\varepsilon_0 r} + \frac{12e^2}{4\pi\varepsilon_0 \sqrt{2}r} - \frac{8e^2}{4\pi\varepsilon_0 \sqrt{3}r} + \frac{6e^2}{4\pi\varepsilon_0 2r} + \ldots
\]

\[
= -\frac{e^2}{4\pi\varepsilon_0 r} \left( \frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \ldots \right)
\]
\[ U_{\text{coulomb}} = -1.748 \frac{e^2}{4\pi\varepsilon_0 r} \]

or in general, \[ U_{\text{coulomb}} = -\alpha \frac{e^2}{4\pi\varepsilon_0 r} \] \(\ldots(1)\)

This result holds for the potential energy of a Cl\(^-\) ion also. \(\alpha\) is called the Madelung constant of the crystal. It has the same value for all crystals of the same structure. For simple crystal structures \(\alpha\) lies between 1.6 and 1.8.

Two ions cannot continuously approach each other under coulomb attraction on account of the exclusion principle. When they are at a certain small distance apart, they begin to repel each other with a force which increases rapidly with decreasing internuclear distance \(r\). The potential energy contribution of the short-range repulsive forces can be expressed approximately in the form

\[ U_{\text{repulsive}} = \frac{B}{r^n} \] \(\ldots(2)\)

where \(B\) is a constant and \(n\) is a number \((n \approx 9)\).
Therefore, the total potential energy $U$ of each ion due to its interactions with all the other ions is

$$U = U_{\text{Coulomb}} + U_{\text{repulsive}} = -\frac{\alpha e^2}{4\pi \varepsilon_0 r} + \frac{B}{r^n} \quad \cdots (3)$$

We must now evaluate the constant $B$. At the equilibrium separation $r_0$ of the ions, $U$ is a minimum. So $(dU/dr) = 0$ when $r = r_0$.

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

\[ B = \frac{\alpha e^2}{4\pi \varepsilon_0 n} r_0^{n-1} \]...

(4)

The total potential energy at the equilibrium separation is

\[ U = -\frac{\alpha e^2}{4\pi \varepsilon_0 r_0} + \frac{\alpha e^2}{4\pi \varepsilon_0 n r_0^n} \]

\[ \therefore \]

\[ U = -\frac{\alpha e^2}{4\pi \varepsilon_0 r_0} \left( 1 - \frac{1}{n} \right) \]...

(5)

This is the magnitude of the energy needed to separate an ionic crystal into individual ions (not into atoms).
In an NaCl crystal, the equilibrium distance $r_0$ between ions is $2.81 \times 10^{-10}$ m, $\alpha = 1.748$ and $n \approx 9$, $1/4\pi\varepsilon_0 = 9 \times 10^9$ Nm$^{-2}$ C$^{-2}$.

The potential energy of an ion of either sign is

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

$$= -\frac{(9 \times 10^9 \text{ Nm}^{-2} \text{ C}^{-2}) (1.748) (1.60 \times 10^{-19} \text{ C})^2}{2.81 \times 10^{-10} \text{ m}} \left(1 - \frac{1}{9}\right)$$

$$= -1.27 \times 10^{-18} \text{ J} = -7.96 \text{ eV}.$$  

Because we may not count each ion more than once, only half this potential energy, or $-3.98$ eV, represents the contribution per ion to the cohesive energy of the crystal.
Some energy is needed to transfer an electron from a Na atom to a Cl atom to form a Na$^+$ – Cl$^-$ ion pair. This electron transfer energy is the difference between the +5.14 eV ionization energy of Na and the –3.61 eV electron affinity of Cl, or +1.53 eV. Each atom thus contributes +0.77 eV to the cohesive energy.

:: the total cohesive energy per atom in the NaCl crystal is

$$E_{\text{cohesive}} = (-3.98 + 0.77) \text{ eV/atom} = -3.21 \text{ eV/atom}.$$
Calculation of Repulsive exponent $n$:

The compressibility $K$ of a solid is given by:

$$K = -\frac{1}{\nu} \left( \frac{\partial V}{\partial p} \right) = \frac{1}{\beta}$$

where $\beta$ is bulk modulus.

According to the law of thermodynamics:

$$d\rho = d\nu + d\omega$$

$$d\nu = d\omega - d\rho$$

$$d\rho = d\omega - pd\nu$$

$$d\omega = d\rho$$

As $d\omega = c_v dt$ and at absolute zero, $c_v$ is negligibly small:

$$d\nu = -pd\nu$$

$$\frac{d^2\nu}{d\nu^2} = \frac{dp}{d\nu}$$

\text{(2)}
Using (1) and (2), the compressibility at absolute zero is given by

\[ \frac{1}{k_0} = \frac{d^2u}{dv^2} \quad (3) \]

For NaCl, \( v = 2N\pi^2 \), where \( N \) is the total no. of molecules and \( r \) is the nearest neighbour distance.

\[ \frac{du}{dv} = \left( \frac{du}{dr} \right) \left( \frac{dr}{dv} \right) \]

\[ \frac{d^2u}{dv^2} = \left( \frac{du}{dr} \right) \frac{d^2r}{dv^2} + \frac{dr}{dv} \frac{d}{dr} \left( \frac{du}{dr} \right) \frac{dr}{dv} \]

\[ \frac{d^2u}{dv^2} = \left( \frac{du}{dr} \right) \frac{d^2r}{dv^2} + \frac{dr}{dv} \frac{d}{dr} \left( \frac{du}{dr} \right) \frac{dr}{dv} \]

\[ \frac{d^2u}{dv^2} = \frac{du}{dr} \frac{d^2r}{dv^2} + \frac{dr}{dv} \frac{d}{dr} \left( \frac{du}{dr} \right) \frac{dr}{dv} \]

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\[ \frac{d^2u}{dv^2} = \frac{du}{dr} \frac{d^2r}{dv^2} + \frac{dr}{dv} \frac{d}{dr} \left( \frac{du}{dr} \right) \frac{dr}{dv} \]
At equilibrium separation $r = r_0$, $\frac{dU}{dr} = 0$.

$$\left( \frac{d^2U}{dr^2} \right)_{r = r_0} = \left( \frac{d^2U}{dr^2} \right)_{r = r_0}$$  \hspace{1cm} (4)

The values of $\frac{dr}{dV}$ and $\left( \frac{dr}{dV} \right)^2$ can be obtained using the following relation:

$$V = 2N\tau^3$$

Differentiating $V$, $1 = 6N\tau^2 \left( \frac{dr}{dV} \right)$.

$$\left( \frac{dr}{dV} \right) = \frac{1}{6N\tau^2}$$

$$\left( \frac{dr}{dV} \right)^2 = \frac{1}{36N^2\tau^4}$$ \hspace{1cm} (5)
Sub. the value of \( \frac{d^2U}{dV^2} \) from eqn. (4) in (3) we have

\[
\frac{1}{k_0} = V_0 \left( \frac{d^2U}{dV^2} \right)_{r=r_0} = V_0 \left( \frac{d^2U}{dr^2} \right)_{r=r_0} \left( \frac{dr}{dV} \right)_{r=r_0}^2
\]  \hspace{1cm} (6)

Sub. the value of \( \left( \frac{dr}{dV} \right)^2 \) from eqn. (5) in eqn. (6), we have

\[
\frac{1}{k_0} = V_0 \left( \frac{d^2U}{dr^2} \right)_{r=r_0} \times \frac{1}{36N^2r_0^4}
\]  \hspace{1cm} (7)
The value of \( \frac{d^2U}{dr^2} \) can be obtained as follows:

(Acc. to eqn (3), in Cohesive energy) The total potential energy \( U_T = U \) for \( N \) molecules is given by

\[
U = U_T = -\frac{\alpha M N e^2}{4\pi \varepsilon_0 r} + \frac{NB}{\gamma^n}
\]

\[
\frac{dU}{dr} = \frac{\alpha M N e^2}{4\pi \varepsilon_0 r^2} - n \frac{NB}{\gamma^{n+1}}
\]

\[
\left( \frac{d^2U}{dr^2} \right)_{r=r_0} = -\frac{2\alpha M N e^2}{4\pi \varepsilon_0 r_0^3} + n(n+1) \frac{NB}{\gamma^{n+2}}
\]

where \( B = \frac{\alpha N e^2}{4\pi \varepsilon_0 r_0^{n-1}} \) and \( \gamma \) is a constant.
\[
\left( \frac{d^2U}{dy^2} \right)_{r=r_0} = - \frac{2 \alpha_M N e^2}{4 \pi \varepsilon_0 r_0^3} + \frac{\mu (n+1) N \alpha_M e^2 r_0^{n-1}}{4 \pi \varepsilon_0 n r_0^{n+2}}
\]
\[
= \frac{\alpha_M N e^2}{4 \pi \varepsilon_0 r_0^3} \left[ (n+1) - 2 \right] = \frac{\alpha_M N e^2}{4 \pi \varepsilon_0 r_0^3} \left[ (n-1) \right]
\]

Sub. the value of \( \left( \frac{d^2U}{dy^2} \right)_{r=r_0} \) from eqn.8 in eqn.7, we get

\[
\frac{1}{K_0} = \left( \frac{2 N r_0^3}{(2N)^3} \right) \times \frac{\alpha_M N e^2 (n-1)}{4 \pi \varepsilon_0 r_0^3} \times \frac{1}{36 N^2 r_0^4}
\]
\[
= \frac{\alpha_M e^2 (n-1)}{72 \pi \varepsilon_0 r_0^4}
\]

\[
K_0 \alpha_M e^2 (n-1) = 72 \pi \varepsilon_0 r_0^4
\]

\[
h = 1 + \frac{72 \pi \varepsilon_0 r_0^4}{K_0 \alpha_M e^2}
\]

For sodium chloride, the value of \( h = 9.4 \)
**Born-Haber Cycle**

**Lattice energy:** The lattice energy is defined as the energy released in the process when the constituent ions are placed in their respective positions in the crystal lattice or this is the amount of energy which is spent to separate the solid ionic crystal into its constituent ions.

An experimental check on the calculated values of the lattice energies may be obtained from Born-Haber cycle. The Born-Haber cycle for NaCl is represented as follows:

Here

\[ S = \text{Heat of sublimation}, \quad D = \text{Dissociation energy} \]
\[ I = \text{Ionisation energy}, \quad E = \text{Electron affinity} \]
\[ \Delta H = \text{Heat of dissociation}, \quad U = \text{Lattice energy} \]

The cycle can be explained as follows:

(i) Initially we start with solid sodium and chlorine molecule. The solid sodium is subjected to the sublimation energy \( S \) and it is vaporised. To the chlorine molecule, *dissociation energy* \( D \) is supplied and as a result it is dissociated into its constituent atoms. Here \( \frac{D}{2} \) is the dissociation energy per chlorine atom.

(ii) Next ionisation energy \( I \) is supplied. The outer electron of Na gaseous atom is removed. This electron is added to Cl atom. As the Cl atom has the electron affinity \( E \), an energy \( E \) is given out.
(iii) The two ions \( (\text{Na}^+ \text{ and Cl}^-) \) are arranged in the lattice and hence the lattice energy \( U \) is released.

(iv) We again reach the starting point by supplying an energy \( (\Delta H) \) known as heat of dissociation.

Now

\[
S + \frac{D}{2} + I - E - U + \Delta H = 0
\]

\[
\therefore \quad U = S + \frac{D}{2} + I - E + \Delta H
\]

All quantities excepting \( U \) are experimentally determinable. Hence the lattice energy \( U \) can be calculated.
CHARACTERISTICS OF IONIC BOND

• Ionic bond is strong
• Due to their high binding energies Ionic crystals have high melting points and boiling point.
• They are transparent for all frequencies up to the point called absorption frequency. Above this frequency, they are opaque.
• Ionic crystals crystallize in close packed structure.
• Ionic compounds are hard and brittle.
• Ionic crystals are soluble in ionizing solvents such as water, dissociate into ions when dissolved in water.
• Solutions of ionic crystals and melted ionic compounds **conduct electricity**, but solid materials do not. The electrical conductivity is much lower than that of metals and increases with increase in temperature.
• Due to spherical charge distribution ionic bond is nondirectional.
• They are compounds formed from metals and non-metals.
In the case of NaCl, Na after losing one electron becomes Na+ and Cl after gaining becomes Cl-. Now, since they are point charges, they have spherical symmetry of their electric fields which means they can attract oppositely charged ions from any direction in space.
For example, consider you have placed a magnet on a table. Then you have distributed small iron pieces around it within its range. As you know, it's going to attract all the iron pieces around it, no matter what will be the direction of force.

So, these forces are non-directional forces, as it doesn't act in a specific direction and hence the ionic bond so formed between Na+ and Cl- is a non-directional bond.
Covalent compounds have bonds where electrons are shared between atoms.

Due to the sharing of electrons, they exhibit characteristic physical properties that include lower melting points and electrical conductivity compared to ionic compounds.

A covalent bond is formed between two similar electronegative non-metals.
Elements having very high ionisation energies are incapable of transferring electrons and elements having very low electron affinity cannot take up electrons.

The atoms of such elements tend to share their electrons with the atoms of other elements or with other atoms of the same element in a way that both the atoms obtain octet configuration in their respective valence shell and thus achieve stability.

Such association through sharing of electron pairs among different or same kinds is known as Covalent Bond.
COVALENT BOND
# CHARACTERISTICS OF COVALENT BOND

<table>
<thead>
<tr>
<th>Property</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting and Boiling points</td>
<td>Similar to the ionic bond, the covalent bond is also very strong and it requires a large amount of thermal energy to separate the ions so that the melting and boiling points are very high.</td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>Poor conductors because electrons are held tightly within the atoms and cannot move through the lattice.</td>
</tr>
<tr>
<td>Hardness</td>
<td>Covalent solids are hard because the atoms are strongly bound in the lattice.</td>
</tr>
<tr>
<td>Brittleness</td>
<td>When sufficient force is applied to a crystal, covalent bonds are broken as the lattice is distorted and shattering occurs.</td>
</tr>
</tbody>
</table>
CHARACTERISTICS OF COVALENT BOND

• Covalent crystals are transparent to long wavelength radiation but opaque to shorter wavelengths.
• Due to bond formation dipole moment exists in covalent crystals.
• They are strongly directional in character.
For the formation of HCl, H atom shares its 1 electron with Cl atom and same is done by Cl atom. So the covalent bond, that hold together these atoms, is due to the two electrons which they are sharing. Now, these shared electrons are continuously roaming in the direction of the line joining the centers of the two atoms binding the two atoms with each other (this can be a way to imagine that covalent bond). Hence, the net force in this case is specified in one direction i.e. in the direction of line joining the centers of the atoms. So, that's why a covalent bond is also called a directional bond.