A brief review of the subject
2.1 Introduction

The subject of ionic or electrolytic conductivity in solids was initially discussed by Hevesy and Le Claire and it was then only a descriptive study. The electrolytic conductivity of solid polar salts was first discussed from a theoretical point of view by Frenkel. It is not, therefore, surprising that the experimental work on ionic conduction inspired the idea of intrinsic lattice disorders or defects, following the laws of thermodynamics. It is clear, for example, that the diffusion of atoms from one part of a perfect crystal to another part is impossible so long as the heat motion of the atoms is visualized as being merely vibrations about fixed lattice points. Likewise the drift of ions through an ionic crystal under the action of an electric field is inconceivable if the crystal is perfect. Frenkel supposed that under the influence of thermal vibrations the ions sometimes received enough energy to leave their normal lattice positions, in effect being pushed into the interstices of the lattice. Under further thermal excitation such an interstitial ion jumped from one interstitial position to another, eventually to meet a vacant site and drop back into a new normal lattice position. Furthermore positive interstitial ions subject to an electric field will jump more frequently in the field direction than in the opposite direction (converse for -ve ions), so that an electric current flows and substance is an ionic conductor. Every ion will spend some fraction of its time in the interstitial state and the average number of vacant lattice sites and interstitial ions existing at any time may be calculated by the methods of statistical mechanics. A statistical mechanical description of
the mobility of vacant sites and interstitial atoms/ions can also be given, so that it is possible to set up a quantitative description of the model and of its diffusion and conduction properties. Frenkel's ideas were developed by Jost (4). According to Jost (4) in any polar lattice in thermal equilibrium at temp. T a number of ions will leave their proper positions and occupy interlattice positions. If \( E \) be the work required to remove an ion from a normal position to an infinite distance then these authors show that the proportion of the total number of ions, \( n \), of the lattice which are in interlattice positions is proportional to \( e^{-E/2kT} \). Both the holes-left by the displaced ions and the displaced ions themselves, will be mobile, and may be assumed to have a mobility \( \mu \) of the form

\[
\mu = \text{const} \ e^{-U/kT} \tag{2.1}
\]

\( U \) being, in the case of the ion in an interlattice position, the work required to move the ion half-way to its next metastable position. The conductivity \( \sigma \) will thus be

\[
\sigma = n e \mu = \text{const} \ e^{(\frac{E}{kT} + U)/kT} \tag{2.2}
\]

Schottky (5) proposed an alternative mechanism. According to him, in the alkali halide crystals, the work required to pack even the small metal ion into an interlattice space will be so great that at ordinary temperature the number of such ions will be insignificant. But even in this case it is possible to remove a positive and a negative ion from their lattice points, and to place them on the outside of the crystal. The work necessary for this process is

\[
V = V^+ + V^- - V_L \tag{2.3}
\]
where $U^+$ is the work required to remove a $+$ve ion out of the crystal, $W^-$
the work required to remove a $-$ve ion and $W_L$ the lattice energy of the
material per ion pair. Schottky showed that in a crystal in thermal equilibrium
at temperature $T$ the number of such pairs of vacant places was proportional
to $e^{-\frac{U}{kT}}$. The conductivity will be due to the motion of the vacant
lattice points through the crystal, a certain activation energy being again
necessary.

Schottky and Jost estimated the energies $F$, $U$, $V$ etc by treating the
vacant lattice points as holes in a medium of uniform dielectric constant, and
also by estimating the energy due to the exchange repulsive forces between the
ions. They showed on energetic grounds that for the alkali halides the conduc­
tivity will be mainly of the Schottky type, while for the silver halides it
will be of the Frenkel $\Gamma_3$ type, a conclusion which was supported by experi­
ments due to Wagner and Beyer $\Gamma_6$.

The classical theory of ionic crystals was founded by Madelung $\Gamma_7$ and by Born $\Gamma_3$, on the fundamental assumption that the essential constitu­
ents of an ionic crystal were the $+$vely and $-$vely charged ions situated at
points forming a regular crystal lattice in space. The system of ions was as­
sumed to be in equilibrium under the influence of two types of forces: an
attractive force, depending on the electrostatic interaction between the ions
and a repulsive force of a more complicated nature.

2.2 Different models of the interionic potentials of the ionic crystals.

Since the early stage, up to date, broadly three different models of
interionic potentials have been proposed:

(a) **Rigid Ion model**: It consists of a point coulombic attraction plus a short-range repulsion which arises from the overlap of the electron density on different ions. The ancient Born Model belongs to this model. This model fails for both static defect calculations and dynamical properties of ionic crystals because the coulombic field of one ion polarises the charge distribution on the other ions which is not taken care of in this model.

(b) **Point polarizable ion model (PPI)**: It is an extension of the rigid ion model by including a constant electronic polarizability. Each ion in the crystal lattice is given a dipole moment which is proportional to the effective field acting on it; the constant of proportionality being the polarizability of the ion. Faux and Lidiard reported that this class of model was unsuitable for defect calculation, because the polarization of each ion depended not only on the electrostatic forces but also on the short range forces; a point first suggested by Lyddane and Herzfeld. The omission of the latter consistently underestimates the Schottky defect formation energy by about 25% and leads to a static dielectric constant which overestimates the defect structures. Phenomenologically this situation has been improved either by adjusting the repulsive potential or adopting model polarizabilities to fit the static dielectric constant.

(c) **Polarizable ion model**: It extends the rigid ion model considering a short-range polarization produced by the short-range forces and then coupling together the electronic polarization with the short-range polarization. This model includes many-body forces and there exist two main types of this
model; the "shell model" introduced by Dick & Overhauser [14] and the
"deformation dipole model" introduced by Hardy [15]. The shell model as
used by Woods et al [16] is a simplified version of the original shell
model [14]. The basic idea is to regard the ion as being composed of a
central massive core that contains the nucleus and the inner valance elec-
trons and is attached by isotropic springs to an outer massless spherical
shell, taken to represent the valance electrons. Short-range interionic forces
are assumed to act between the shell, between the cores, and between the
shells and the cores. For the alkali halides, the short-range interionic
forces are often restricted to those acting between the shells alone. Later
the shell model was improved by many authors [16-18] and a number of attem-
pts [19,20] was made to give this model a formal quantum mechanical justifi-
cation. A significant improvement of simple shell model was carried out by
Schroder [21] who had proposed that one should allow for an additional
degree of freedom by allowing for a symmetric breathing distortion of the
shells (the shells are allowed to breath in and out). This leads to a "breath-
ing shell model". When the shell model is simplified with the dipolar approx-
imation, the deformation dipole model is obtained. This idea was originally
due to Saigeti [22] who pointed out that overlap caused a distortion of the
ionic charge distributions which could be described, to the lowest approxima-
tion, by deformation dipoles. With this idea Hardy [15] developed the deforma-
tion-dipole model. In this model, dipoles were assumed to arise from two
different sources - (1) dipoles generated by the electric fields acting on
the ions (known as electric dipoles) and (2) dipoles generated by the relative
movement of anions and cations which led to distortion of the electron distri-
2.3 Short-range interaction

Two main approaches have been developed to determine the short-range interactions between ions. One takes the crystal or molecular phenomena as its starting point and the other starts from an isolated ion pair applying a simple quantum mechanical approach based upon the electron density of the ions.

(a) Phenomenological Potentials

In this approach it has become a practice in many cases to fit the equilibrium condition of the static lattice to the lattice parameter. The one such condition is that the lattice energy of a crystal is minimum when the interionic separation assumes its equilibrium value $r_0$. This condition is given by

$$\frac{dU}{dr} \bigg|_{r = r_0} = 0 \quad \cdots \ (2.4)$$

where $U$ is the total energy of the crystal and is given by

$$U = -\frac{\alpha_M e^2}{r_0^2} + 6 \Phi_{+-}(r) \quad \cdots \ (2.5)$$

where $\Phi_{+-}(r)$ is the nearest neighbour repulsive potential energy of a pair of ions and $\alpha_M$ is the Madelung constant.

The second condition which is utilized is given by
\[
\frac{d^2V}{dv^2} \bigg|_{v=v_0} = \frac{1}{k_o v_0} \quad \ldots \quad (2.6)
\]

where \( k_o \) is the compressibility of the solid at absolute zero and \( v_0 \) is the volume at equilibrium condition (the condition \( V = v_0 \) is equivalent to the condition \( r = r_0 \)).

The potential of this repulsive force was first assumed by Born and Lande \([23]\) to have the form \( b/r^n \) where \( b \) and \( n \) were two constants which might be determined from two empirical data of the crystal and \( r \) was the distance between nearest unlike ions for a given crystal. From investigations of the interaction between two ions having electron shells, it was found by Unsöld \([24]\), Brück \([25]\), Pauling \([26]\) and Born and Mayer \([27]\) that the potential for the repulsive force was of an exponential type i.e.,

\[
\Phi_{ij} = A \exp \left( -\frac{r_{ij}}{\rho} \right) \quad \ldots \quad (2.7)
\]

where the constants \( A \) and \( \rho \) had to be determined from two empirical data of the crystal. The physical source of this repulsion is primarily the Pauli exclusion principle which effectively prevents the overlapping of the electron clouds of the outer shells of the colliding ions/atoms. The exponential form arises from the exponential tail in the electron density distribution about each ion/atom. In this expression (2.7) a small term \( -\frac{\mu^2}{\rho^6} \) corresponding to the van der Waals attraction was also added. This is the potential energy of coupling between the instantaneous dipoles on atoms/ions \([28]\). This potential constant was calculated accurately by Mayer \([29]\). More explicit form of the expression in (2.7), which can be used for the interac-
tion of the ions which are not nearest neighbours, was also given by Born and Mayer \([27]\) as below

\[
\Phi_{ij}(r_{ij}) = b \beta_{ij} \exp \left( \frac{R_1 + R_j - r_{ij}}{\rho} \right)
\]

... (2.8)

where \(R_1\) and \(R_j\) are the radii of the interacting ions. The factor \(\beta_{ij}\) depends on the charges and the electronic structures of the ions. Pauling \([26]\) gave an expression for this \(\beta_{ij}\) as below,

\[
\beta_{ij} = \frac{Z_i}{n_i} + \frac{Z_j}{n_j}
\]

... (2.9)

where \(Z_i\) and \(Z_j\) are the valencies of the two ions and \(n_i\) and \(n_j\) are the number of valence electrons in the outer shell of these ions. Born and Mayer \([27]\) computed the quantities \(\rho\) for all alkali halides from compressibility and thermal expansion data and found it to be roughly the same for all and gave the average value equal to 0.345 \(\text{Å}\). The value of \(b\) was taken to be equal to \(0.229 \times 10^{-12}\) erg which was the average of the two values obtained from the two thermodynamic equations adopting \(\rho = 0.345\).

Huggins and Mayer \([30]\) rejected the use of somewhat arbitrary Goldsmith ionic radii and calculated a consistent set of radii for alkali and halide ions from the observed lattice spacings of the alkali halides, with the same \(b\) values of Born and Mayer \([27]\). Huggins \([31]\) then recalculated constants in the Born-Mayer exponential expression for the repulsion between two ions in alkali halides, using more accurate values of compressibilities, coefficients of thermal expansion and van der Waals attraction constants and recalculated the ionic radii. They calculated the lattice
energies of the alkali halides with these new values of \( b \), \( R_+ \) and \( R_- \) and also with Hoggins and Mayer values of the same and expected that they obtained better values with new values of Born-Mayer repulsive parameters.

The Born-Mayer repulsive parameters (B-M RPs) were then recalculated by Cubissotti \cite{32} and Tosi and Fumi \cite{33,34}. Tosi and Fumi \cite{34} found that the crystal radii of the ions in the individual salts and the relative weights of the cation-cation, cation-anion and anion-anion contributions to the repulsive energy, were affected only very slightly by the uncertainties in the data. They obtained close agreement between the crystal radii of the ions in the individual NaCl type alkali halides with generalized Huggins-Mayer form and the crystal radii with the Huggins-Mayer \cite{30} and Pauling forms. They considered \( b \) determinable parameter as soon as the parameter \( \rho \) was considered not common to the entire family of salts. This point was overlooked by Cubissotti \cite{32} who allowed \( \rho \) to vary with the halogen ion but fixed \( b \) a priori as equal to \( 1 \times 10^{-12} \) erg/mole. Tosi-Fumi \cite{34} thus determined the complete set of B-M RPs \( b \) and \( \rho \) for each salt (in alkali halides) and the nine basic radii \( r_+ \) and \( r_- \) for the alkali and halogen ions using more accurate experimental crystal data than before. They also included van der Waals interactions estimated by Mayer. These B-M potential forms with Tosi-Fumi parameters gave excellent agreement with experimental values of interionic distance and cohesive energy while it failed to explain stability condition of potassium & rubidium halides in NaCl and CsCl structure and predicted poor values for the elastic constants over a range of temperature \cite{33,35,36}. Posvarva and Lidiard \cite{37} modified and adjus-
ted the parameters of B-M repulsive potential by neglecting van der Waals energy.

For the B-M form of repulsive potentials, the parameters were then again modified by Chaudhuri et al [38]. They determined these parameters for alkali halides from extrapolated 0°K values of the elastic constants. Lastly these parameters has been reevaluated for NaCl type alkali halides using more reliable recently published thermodynamic data and van der Waals coefficients by Boswarva [39]. As previously the model continues to give excellent agreement with experimental values of interionic distance and cohesive energy whilst earlier shortcomings in the failure of the stability condition and predicted elastic constants have been significantly reduced. The new parameters lead to short-range interaction with stronger van der Waals attractions and stiffer repulsions for the majority of salts in the family of NaCl type alkali halide.

Douglas [40,41] suggested that the B-M repulsive parameter $\rho$ was not constant for all types of interactions in a given crystal and took:

$$\rho_{aa} = a' \rho_{aa}$$

where $a' = \text{constant}$ and $a' \approx \sqrt{2}$. Rao [42,43] introduced four parameters in the B-M potential $(b_1 \rho_1, b_2 \rho_2)$ - two for the first neighbour interaction and another two were taken to account the next nearest neighbour interactions.

Besides these modifications of the usual B-M potential, a number of phenomenological potentials have been proposed and considered. Guccione [44] considered the potential as

$$\Phi = A + 5r^{-12}$$  \hspace{1cm} (2.10)
where the parameters A and B were determined by assuming that the repulsive energy of two ions of opposite sign interacting at an interionic distance \( r_0 \) had the same value and the same derivative as in the exponential D-M form.

This expression of the repulsive interaction was found important in the short distances and gave the value of barrier height for anion diffusion in NaCl and KCl in agreement with experiment. The short-range D-M RFs for alkali halide crystals derived from compressibility, static dielectric constant and transverse optic mode equation are critically discussed by Singh & Shankar [45].

A logarithmic potential of the form

\[
\Phi(r) = a \ln (1 + br^n)
\]

with \( n = 4 \) or \( n = 9 \) has been proposed by Prakash and Debari [46] and Thakur [47] in preference to D-M form. Prakash and Debari [46] have shown that cohesive energies of alkali halides calculated with this type of potential agree quite well with the experimental data. Recently Jha and Thakur [48] have proposed this type potential with \( a, b \) and also \( n \) treated as free parameters i.e., these values differ from crystal to crystal. But Gupta et al [49] have shown that these types of potentials with and without van der Waals term give cohesive energies with a deviation of 5% to 13% from experimental values.

A generalized repulsive term \( Ar^{-m} \exp (-b (r^n-1)) \) was suggested by Woodcock [50] and \( Ar^{-m} e^{-r/6} \) was suggested by Yadav [51]. According to Yadav, his repulsive potential \( \Phi \) satisfies the conditions,

1. When \( r \to 0, \Phi \to \infty \)
2. When \( r \to \infty, \Phi \to 0 \)
This form is generalized and dimensionally homogeneous while the first condition is not satisfied by both D-M form and logarithmic form. The generalized Woodcock potential is dimensionally inhomogeneous.

The repulsive energy contribution to the lattice energy per ion pair in an NaCl-type crystal is given by Romano et al \([52]\) in the following form

\[
U_L^{\text{rep}}(r) = 6 \frac{B}{\mu} \exp \left(-\alpha r\right)
+ 6 B_L \exp \left[-\sqrt{2} \alpha r\right]
+ 3 \frac{B}{\mu} \exp \left[-\sqrt{3} \alpha r\right]
+ 3 B_L \exp \left(-2 \alpha r\right)
+ 24 \frac{B}{\mu} \exp \left[-\sqrt{5} \alpha r\right] ...
\]  

(2.12)

where interactions up to fifth neighbours are included. The parameters \(B/\mu\), \(B_L\) and \(\alpha\) are determined, crystal by crystal, from data at atmospheric pressure and at temperatures in the range \(300^\circ-700^\circ\) K via the Hildebrand equation of state.

Besides the crystal dependent phenomenological repulsive potentials there are some empirical approaches which are being attempted to make the repulsive potential of ions in an ionic crystal structure independent and crystal independent so that once the repulsive parameters for an ion are evaluated in one compound, in one structure they could be used for that ion in any crystal \([53-56]\). The idea of single ion repulsive parameters was first introduced by Smith \([57]\) concerning the mutual distortion of the ions. Narayan and Ramaseshan \([54]\) propose for the repulsive potential per molecule in a binary ionic solid, the following specific form
\begin{align*}
W_{\text{rep}} (r, r_+, r_-) &= n_1(A_+ e^{-r+/\rho_+} + A_- e^{-r-/\rho_-}) \\
&\quad + n_2(A_+ e^{-br/2\rho_+} + A_- e^{-br/2\rho_-}) \quad \cdots (2.13)
\end{align*}

where \( A_+ \) and \( A_- \) are the pre-exponential factors for the two ions and \( \rho_+ \) and \( \rho_- \) are their hardness parameters and these are independent of the crystal.

\( b_1 \) and \( n_2 \) are the number of nearest and next nearest neighbours while \( r \) and \( br \) are the corresponding distances. The parameters for the various ions are determined through the Hildebrand equation of state and its volume derivative by a least square fit of crystal data on all the alkali halides at room temperature and at various pressures up to 45 Kbar (a range in which some of the salts undergo a phase transition from the NaCl to the CsCl structure). According to Baroni & Baldereschi \([53]\) this type of short range potential is unrealistic.

Very recently Hess \([56]\) used basically the same idea as Smith \([57]\) concerning the mutual distortion of the ions and combined this idea with Hardy & Karo's deformation-dipole model \([15]\). Hess \([56]\) assumed that the B-M repulsive interaction energy could be considered as the sum of the distortion energies of a cation and anion as follows:

\begin{align*}
P_{ij} (r_{ij}) &= b_i e^{-r_i/\rho_i} + b_j e^{-r_j/\rho_j} \quad \cdots (2.14)
\end{align*}

where \( b_i, \rho_i, b_j \) and \( \rho_j \) were single ion repulsion parameters and \( r_i \) and \( r_j \) were ionic radii. Equilibrium required that for any given \( r_{ij} \) the total distortion energy was minimal. From this equilibrium condition he obtained

\begin{align*}
b_i e^{-r_i/\rho_i} &= \frac{b_j e^{-r_j/\rho_j}}{\rho_i} = \frac{b_{ij} e^{-r_{ij}/\rho_{ij}}}{\rho_i} \quad \cdots (2.15)
\end{align*}
and assumed that the following combination rules derived earlier by Smith,

\[ \rho_{ij} = \rho_i + \rho_j \]  \hspace{1cm} (2.16)

\[ \left( \frac{b_{ij}}{\rho_{ij}} \right) \rho_{ij} = \left( \frac{b_i}{\rho_i} \right) \rho_i \left( \frac{b_j}{\rho_j} \right) \rho_j \]  \hspace{1cm} (2.17)

were valid for the D-M repulsion between any pair of ions which were first or second neighbours. He derived a set of ionic parameters based on the elastic and dielectric properties of sixteen alkali halides. The parameters completely determined the interactions between any pairs of the considered ions. He expected their model to be particularly useful in investigations of the behaviour of impurity systems. According to him their calculations of several off centre systems in alkali halides with their single ion parameters appeared to be highly successful while the model was only a crude one and it might not be expected to provide a very precise representation of the real interactions between ions in crystals. Recently various groups of authors [36,59-61] have tried to evaluate various phenomenological potentials for NaCl type alkali halides, combining Born model with models of deformable ions such as the shell models to attempt to reproduce simultaneously the elastic and the dielectric properties of the alkali halides.

The potential by Catlow et al [36] for the nearest neighbour interaction is given by

\[ \Phi_{+-}(r) = V_\infty \exp\left(-r/\rho_\infty\right) \]  \hspace{1cm} (2.18)

where they choose to reduce the number of parameters by assuming
with a common $b$ and $r_+ \& r_-$ as characteristic of the ions. They determined the second neighbour interactions from an "hybrid-Thomas-Fermi-Dirac model" like the Gordon and Kim model $[62]$. For this second neighbour interactions, in the set I, they assumed an exponential form, while in the set II, they used flexible potential forms (Polynomials with specified minima connected to the appropriate limiting forms). The parameters $A_{+-}$ and $\rho_{+-}$ were determined from the pertinent salt using the known second neighbour interactions by means of the equilibrium condition for the static crystal, and of the equation for the elastic constant $c_{11} - c_{12}$ of the static crystal, adopting low-temperature values for the pertinent quantities $[63]$. They then determined the shell model parameters, using both the set I & set II potentials, to describe the dielectric properties of the alkali halides.

For the overlap repulsion Sangster et al $[60]$ adopted the forms:

$$A_{+-} = b \exp \left( \frac{r_+ + r_-}{\rho_{+-}} \right)$$  \hspace{1cm} \ldots (2.19)

where $b$ and $r_+ \& r_-$ are assumed common to the entire family, while $\rho_{+-}$ is and

$$\Phi_{ij}^R (r) = b \exp \left[ \alpha (r_1 + r_j) - r \right]$$  \hspace{1cm} \ldots (2.20)

where $b$ and $\alpha$ were assumed to be characteristic of each salt and were determined salt by salt by means of the equilibrium equation for the static crystal.

$$\Phi_{ij}^R (r) = (b + B_i B_j) \exp \left[ \frac{t}{\sigma_i + r_j} + s_i s_j \right] x \left( \sigma_i + \sigma_j - r \right)$$  \hspace{1cm} \ldots (2.21)

where $b$ and $t$ were assumed common to the entire family, while $\sigma$'s and
$s$ and $S^2$ were assumed to be characteristic of the ions.

Hardy and Haro \cite{61} gave the nearest neighbour and next nearest neighbour interaction potentials as

$$
\phi_{12}(r) = \left(1-d\right) \lambda_{12} \exp \left(-r/\rho_{12}\right) + \phi^m_{12}/r^n \quad (0 < d < 1)
$$

$$
\phi_{22}(r) = \lambda_{22} \exp \left(-r/\rho_{22}\right) - c_{vdw}/r^6
$$

respectively. The determination of the potential parameters $\lambda_{12}$, $\rho_{12}$, $\lambda_{22}$, $\rho_{22}$, $\phi^m_{12}$, $c_{vdw}$ in each salt was a part of a broader treatment of the statistical thermodynamics of the crystal.

Murthi & Selvarajan \cite{62} modified the $s$-$S^2$ interaction potential form on taking into account the additional coupling between the repulsive overlap force and dispersion force. They determined the like ion parameters with the help of Thomas-Fermi electron gas model and fixed the unlike ion $RPs$ by the requirements of consistency with the equilibrium lattice constant as well as with the dielectric data as in the shell model.

Eggenhofer et al \cite{63} made a comparative study and Shanker et al \cite{64} made a critical test of phenomenological potentials for the NaCl-type alkali halides. They \cite{65} came to a conclusion that it was clearly difficult to say which, if any, of the new potentials was to be preferred over the others and that if the new potentials taken as a whole have not truly improved our knowledge of the effective short range interaction potentials in the alkali halides.
(b) Potentials based upon the electron density of the ions

Generally the model consists of a positive nucleus surrounded by a spherically symmetric negative charge distribution $\rho(x)$, $x$ being the distance to the centre of the distribution. No distortion of the separate electronic densities is allowed to occur as the two ions interact so the total density is the sum of the two ionic densities. The short range interaction energy is assumed, following Wedepohl \cite{66}, to be

$$
\Phi^{SR}(x) = \int_{V_{\text{overlap}}} \left[ F_{\text{kin}}(x) + F_{\text{ex}}(x) \right] \; \frac{1}{4 \pi}
$$

where

$$
F_{\text{kin}}(x) = \frac{3 \hbar^2}{10 m} \left( \frac{3}{\pi} \right)^{1/3} \int_{V_{\text{overlap}}} (\rho_1^5 + \rho_2^5)^{1/3} \; \rho_1 \rho_2 \; \frac{1}{\rho} \; \rho_1^{4/3} \rho_2^{4/3} \; dv
$$

and

$$
F_{\text{ex}}(x) = \frac{-3\varepsilon^2}{2} \left( \frac{3}{\pi} \right)^{1/3} \int_{V_{\text{overlap}}} (\rho_1^4 + \rho_2^4)^{1/3} \; (\rho_1^{4/3} + \rho_2^{4/3}) \; dv
$$

The integral is over the overlap volume for the kinetic energy and exchange energies. Wedepohl \cite{66} obtained better agreement with experiment with calculations based on the Thomas-Fermi-Dirac method (T-F-D). By this approach short-range potentials for an ionic solid is derived without any use of adjustable parameters fitted by employing experimental data.

The main improvement over earlier calculations is the substitution of accurate Hafner-Fock charge densities for the ions in preference to less valid T-F-D estimates. Gordon and Kim \cite{62} have calculated potentials for argon.
in this way that are in excellent agreement with gas-scattering results. The same method has already been applied to ionic systems with excellent effect. Kim & Gordon \cite{67} and Cohen & Gordon \cite{68} have calculated very satisfactory potentials for alkali halides. According to Catlow et al \cite{36} the method may be particularly suited for studying interactions between ions in regions where the crystal data are irrelevant, for example the overlap of like ions in alkali halides. They thus have used this semi-classical, electron gas potentials to use the crystal data to assess the attractive part of the next nearest neighbour interactions. Vedepohl \cite{69} has shown that better agreement with experimental results is obtained in NaCl and KCl using hybrid T-F-D (HFD) model of the atoms in the calculation of the interaction energies of the ions. Recently Rovarva & Murthy \cite{70} have studied systematically the interionic potentials in sixteen alkali halide crystals derived by using, firstly, the basic hybrid T-F-D statistical method and then incorporating some major modifications namely:

(1) the correction of the exchange energy term to exclude the self-exchange part \cite{70};

(2) scaling factors for the kinetic and exchange energy terms determined so as to produce correct values of the corresponding terms in an isolated form isoelectronic with the interaction of interest \cite{70}.

They, then, have assessed the success and limitation of the determined potential, just by comparison with three crystal properties: (a) lattice energy, (b) equilibrium nearest neighbour distance and (c) the Smith stiffness
parameter $\gamma^J$. According to them the ETPD method can often be successfully used to derive interionic potentials for alkali halide crystals. However, more flexible potential forms need to be developed for use over certain ranges.

Recently, quantum mechanical potentials also have been developed to replace classical B—M potential. Harrison $\gamma^J$ has developed on the basis of his tight binding theory an expression for the potential energy of interaction between closed shell atoms. The author has adopted electron gas method of Wadepohl $\gamma^G$ and considered the electron density on the basis of quantum mechanical calculation. According to him the normalised charge density is given by

$$n(r) = 6\mu^3 e^{-2\gamma^j/M/\pi}$$ \hspace{1cm} (2.25)

where $\mu$ is related to the valence $\phi$ state energy given by

$$E = \frac{\hbar^2}{2m}$$ \hspace{1cm} (2.27)

The author has assumed that the total overlap interaction is of the form of the kinetic energy term and has written the following analytical form for the cation-anion repulsion.

$$\phi_{-+} = \frac{6n_0 \hbar^2}{2m} e^{-5/\mu r_0/3} \mu^3 r_0$$ \hspace{1cm} (2.28)

$\mu$ is the arithmetic average of $\mu_1$ and $\mu_2$ for cation & anion respectively and $r_0$ is the scaling parameter in order to fit the experimental data on interionic distance.
In the Harrison's overlap potential the empirical B-M parameters are interpreted in terms of the fundamental quantities like energy term values $\mu_1$ and $\mu_2$ for individual ions. This is in agreement with recent efforts to derive the ion dependent B-M parameters [53 - 56]. Narayan et al [73] demonstrate the validity of Harrison’s overlap repulsive potential along with the Madelung energy to alkali halides.

2.4 Defect Calculation

Any deviation in a crystal from a perfect periodic lattice or structure is due to an imperfection or a defect. The common point defects in alkali halide crystals are vacant lattice sites and chemical impurities.

The intrinsic defects in alkali halides are of Schottky type, namely cation and anion vacancies. A large number of attempts have been made by many workers to calculate the Schottky defect formation energies and the energies of migration and activation of the host ions and energies of substitution, migration and activation and solution enthalpies of isovalent and divalent defects in the alkali halides adopting different models and different forms of short range repulsive potentials.

Earlier important attempts to deal theoretically with point imperfections in alkali halides are due to Jost [4] and Schottky [5].

The formation energy $E_F$ as given by Jost and Schottky is

$$E_F = \frac{v^2}{2} \left( 1 - \frac{1}{N} \right) \left( \frac{1}{r_a} + \frac{1}{r_o} \right)$$

... (2.29)
where $r_a$ and $r_0$ are the radii of anion and cation vacancies, $U_L$ is the lattice energy which is necessary to form a Schottky defect in a rigid non-polarizable lattice and \( \frac{e^2}{2} \left( 1 - \frac{1}{K} \right) \left( \frac{1}{r_a} + \frac{1}{r_0} \right) \) is the polarization of the lattice estimated as the difference in energy at the electric fields surrounding a spherical charge when the charge is in a medium of dielectric constant $K$ and in vacuum.

The important step forward in making the estimate of $\Delta H_2$ quantitatively was taken by Mott and Littleton \[74\] and consisted mainly in a better treatment of the polarization energy. Fumi and Toci \[75\] made a criticism of the Mott-Littleton approach as it neglected the elastic distortion of the crystal around the defect and that it did not consider explicitly the repulsive interaction between non-nearest neighbours. Breuer \[76\] had shown that the elastic distortion of the crystal around the defect can be included in Mott-Littleton treatment. Similarly, the repulsion between non-nearest neighbours can be easily included in Mott-Littleton treatment \[77\]. Bassani & Fumi \[77\] calculated the Schottky energies employing better physical constants. Fumi and Toci \[75\] recalculated the Schottky defect formation energies. Nowadays most of the calculations of the lattice energies are based on extended Mott-Littleton approach i.e., dividing the crystal into two regions I & II. In the atomistic region I (in the vicinity of the defect) the displace-
ment of the ions are independently and freely varied, whilst in the region II the displacements of ions are prescribed according to the microscopic theory. Boswarva & Lidiard [37] studied the contribution of region I and region II and their interaction carefully. However their region I contained only the six nearest neighbours around the vacancy and it was not large enough. On the other hand Scholz [78] considered a large region I containing 256 ions around the vacancy. However his study neglected the influence of region II and obtained the Schottky formation energies of alkali halides nearly 5 eV higher than the experimental values. Scholz again calculated Schottky energies of alkali halides by taking into account region II and obtained values which were in agreement with the values of Boswarva and Lidiard [37]. These were roughly 0.5 eV lower than the experimental values. Boswarva and Lidiard [37] reformulated the method so that the problem was reduced to the minimization of the energy function whereas Mott-Mottleton approach was a force balance.

Now-a-days using several sets of interionic potentials for the alkali halides and using different models, many workers calculated the vacancy formation energies and Schottky defect formation energies.

Another type of intrinsic defect energy which is very useful is the migration energy of the host ion in alkali halide crystals. Jost [4] tried to estimate the migration energy of a +ve ion vacancy as the difference in coulombic and repulsive energies between the saddle point and equilibrium configurations. When they allowed the two immediate neighbouring ions to relax, they found that the relaxation energy was sufficient to cancel entirely the
migration barrier. Nott and Littleton calculated the migration energies for the positive ion and the negative ion vacancy in NaCl including the effect of polarization energy and obtained 0.51 eV for the +ve ion and 0.56 eV for -ve ion. The values were too small and far too close to each other. Thus it failed so far \cite{75,76} to account for the height of the vacancy migration barriers of ions and also failed to explain the difference between the energies of vacancy migration for cations and anions as indicated by the existing experimental evidence for most of these salts \cite{80}.

It was suggested that in calculating migration barrier in alkali halides, the use of the equilibrium repulsive interaction potential in treating repulsive interaction between ions at distance considerably smaller than the equilibrium interionic distance in the crystal may appreciably affect the result \cite{75,30}. Gaccione et al \cite{44} calculated the barrier heights for migration of both positive ion vacancy and negative ion vacancy in NaCl and KCl crystals adopting two different repulsive potentials: (1) Born-Mayer \cite{27} repulsive potential & (2) Born-Mayer-Worsey potential \cite{79} of the form $A + Br^{-2}$ where $A$ and $B$ were constants. They also considered the next nearest neighbour repulsive interaction energies. Their theoretical values of the vacancy migration barrier obtained with the B-M repulsive potential were considerably lower than the experimental values while the values computed with the harder repulsive potential \cite{B-N-W potential} for the immediate neighbourhood of the saddle point lay in the range of the experimental values. Tosi and Doyama \cite{30} however showed that with a set of ionic radii and Born parameters of Tosi and Porsi \cite{34} reliable migration energies could be
obtained even with the experimental form of the overlap potential \[ V_{\text{overlap}} \] for the alkali chlorides. Later the migration energies of the host ions in alkali chlorides were also calculated by Rao and Rao \[ 31 \] and Pitas et al \[ 32 \] with their modified D3 potential \[ 42,43 \]. Their calculated values were in better agreement with experimental values in the respect that they obtained higher values for migration energies of anion than that of cation. Beniars et al \[ 33 \] calculated the migration energies of both cation and anion in NaCl crystal with both polarizable point ion model and shell model and showed that the values with shell model agreed well with their experimental values. Catlow et al \[ 34 \] calculated migration and activation energies of all alkali halides, with their \[ 36 \] both set I and set II potentials, considering different possible types of jumps of the migrating ion. Their results were also in agreement with experiments. Rowell and Sangster \[ 35 \] recently calculated successfully migration energies of all alkali halides based on the polarizable ion potentials of Sangster and Atwood \[ 36 \].

When calculating the lattice energies of crystals doped with solvent or alicyclic foreign ion, one requires the short-range interaction parameters for the foreign ion-host ion interaction along with the host ion-host ion interaction parameters. According to Brauer \[ 76 \] interaction between foreign ion and its neighbouring ions may be different from that of the host ions i.e., the parameters \( b \) and \( \rho \) for the interactions of the foreign ion with host ions, will have to be determined from experimental data on the corresponding pure compound of the perturbing ion. But this is actually an approximation.
With the help of the earlier Born method (i.e., with short range repulsive potentials in the form $1/r^3$) Grimm and Hersfeld [36] and Tobolsky [37] computed lattice energies of ionic crystals and crystalline solutions and had obtained expressions for estimating heat of formation ($\Delta H_f$) for alkali halide solid solutions from the observed lattice spacings and interaction potentials of the pure salts. Fineman and Wallace [38] pointed out that attempts to calculate heat of formation from lattice energies imposed severe demands upon the model used. Using the more refined treatment of ionic lattice due to Born and Mayer [27] and Mayer [29] and employing interaction parameters characteristic of the pure compounds, Wallace [39] calculated the heat of formation for binary systems of alkali halides and compared them with experimental data. In all theoretical treatments of Grimm and Hersfeld [36], Tobolsky [37] and Wallace [39], the relaxations of the neighbouring lattice ions of the defect were neglected, resulting in poor agreement with experiment.

Dick and Das [40] first took into account the relaxation of these neighbouring ions and calculated heats of formation of solid solutions of alkali halides (NaCl-Br, NaBr-Cl, KBr-Na and NaBr-K) using Born model. They used both Born-Mayer and Huggins-Mayer values for the constants in the repulsive interaction, the host ion-defect ion parameters taking equal to host ion-host ion parameters of the crystal of impurity ion and obtained poor agreement with experiment. Douglas [41] calculated heats of dilute solid solution among the alkali halides (other than cesium salts) using their own repulsive potential form [40] and taking defect ion-host ion repulsive parameters to
be the same as those of host ion-host ion parameters.

Tosi and Doyama [30] calculated energy of substitution, energy of solution, energy of migration and energy of activation for substitutional alkali impurities in alkali halide crystals. They took P-H repulsive interaction potential and Tosi-Fumi [34] repulsive parameters and used for the alkali impurities the values of parameters $\rho$ to be the same as in their br.31dos. They found very good agreement between theory and experiment for the formation energy of Schottky defects and for the migration energy of vacancies in alkali halides whereas for substitutional defects, discrepancies up to 50° and 100° occurred. Fancher and Barash [91] successfully calculated heat of formation of alkali halide solid solutions developing a statistical theory on the basis of the substitutional impurity model of Dick and Bas. They took the repulsive energy due to an anion-cation interaction in the pure host crystal to be of the form $A \exp (-r/\rho)$ and due to impurity ion and its neighbour to be of the form $B \exp (-r/\sigma)$, when the two ions were separated by a distance $r$. According to them the superiority of their work over the previous theoretical attempts of Nasastjernas [92], Novi [93] and Durham and Hawkins [94], was due to the fact that the displacements around the defect were considered approximately. Deniere et al [33] calculated defect formation energies for NaCl of (i) an isolated vacancy at cation or anion site (ii) a substitutional alkali or halogen impurity (iii) saddle points for the motion of both a positive and a negative host ion and (iv) a substitutional alkali and halogen impurity into a vacancy. They considered the two models separately-polarisable point ion model (PPT) and shell model. In the calculation of PPT model they took $b = 0.295 \times 10^{-22}$ erg $\cdot$ $\rho = 0.3 \AA$ in host ion-host ion interaction as
well as in defect ion-host ion interaction and obtained results which was in
disagreement with experiment. In the shell model they took for the cation-
anion interaction the impurity-lattice ion potential from the appropriate
perfect lattice potential (e.g. for $K^+ - Cl^-$ potential with $K^+$ as a dopant
in NaCl, the first neighbour potential parameters were derived from KCl). But
for cation-cation and anion-anion potentials, no such procedure was possible.
So they estimated such potentials using the geometric mean rule i.e.

$$
\Lambda_{ij} = (\Lambda_{ii} \Lambda_{jj})^{\frac{1}{2}} \quad \ldots \quad (2.30)
$$

and

$$
\rho_{ij}^{-1} = \frac{1}{2} (\rho_{ii}^{-1} + \rho_{jj}^{-1}) \quad \ldots \quad (2.31)
$$

the repulsive potential being in the form as below

$$
V_{ij} = \Lambda_{ij} \exp \left( \frac{-r}{\rho_{ij}} \right) \quad \ldots \quad (2.32)
$$

They showed that this shell model calculations however agreed well with expe-
riment. Corish et al. [95] calculated association and migration energies for
seven cation and six anion univalent impurity-host systems and for twelve
univalent anion impurity systems obtained by incorporating $F^-, Br^- \& I^-$ in
the alkali metal chlorides LiCl, NaCl, KCl & RbCl [96]. For the potential
describing impurity-host ion interaction, they took same RPs as for the cor-
responding pure crystal. They determined the second neighbour interaction
parameters either using the electron gas approximation or by geometric mean
approximation.

Though reasonable values for solution enthalpies have been obtained
for monovalent impurities, however, corresponding calculations for divalent cation impurities were unsuccessful for long time \[76,93,99\]. Tosi obtained negative values for the solution enthalpies of divalent defects in alkali halides whereas the experimental values were positive i.e. process is endothermic. The failure of those calculations has been attributed \[75\] to the use of experimental lattice energies for the divalent metal halides while using theoretical parameters in the remaining calculations. Bowman \[93,99\] following a modified Mott-Littleton procedure, in which the impurity-host interaction parameters were determined from experimental lattice energies of corresponding impurity halides and host-host interaction parameters were taken from Boswarva-Lidiard values \[37\], calculated heat of formation of some divalent defects (Ca\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\), Cd\(^{2+}\) & Pb\(^{2+}\)) in some alkali fluorides and those of Sr\(^{2+}\) and Ba\(^{2+}\) in some alkali chlorides. These values agreed reasonably well with available experimental results. But their method cannot be used for general divalent cations whose halides do not possess cubic crystal structure for inadequacy of the Born theory. Detailed theoretical study of alkaline earth cations in crystalline sodium chloride, potassium chloride and potassium bromide was done by Catlow et al \[100\]. They calculated energies for (i) the divalent defect ion on a substitutional site (ii) the substitutional divalent ion with an associated vacancy in the (110) nearest neighbour position, in the (111), (200) and (211) positions and finally saddle point configuration for the possible jump of the divalent ion into the vacancies. They then evaluated the binding energies of the vacancy impurity complexes and the activation energies for the four jumps. In their calculations they used electron gas method to obtain short-range dopant cation and
dopant anion interaction parameters and their results agreed well with experimental values though the electron gas method was not favourably applicable to the case of crystalline solids to evaluate the short range potentials. This is because there is a significant difference in the electronic charge distribution in the free molecule and in the crystal.

In the cases of interstitial defect calculation, Hatcher & Dienes [101] and Norgott & Lidiard [102] used $b$ & $\beta$ for the interaction of a neutral defect (Cl$^-$ atom)-host ion to be the same as those of host ion-host ion interaction. Abrahamson [103] proposed various other potentials for these types of interactions.

Keeping the idea in mind that the repulsion between the ions originates from the overlap of their charge clouds, Feb and Ghosh [104] case forward with a plan of investigating the relationship between the B-N parameters of a solid and some individual parameters of the interacting ions of the solid. They considered this relation through the overlap of the electronic charge densities of the interacting ions. They plotted the charge densities of the interacting ions at the ends of the interionic equilibrium separation of the solid, $r_0$, and defined two parameters $h$ & $s$ relating to the height and spread of the overlap region (Fig. 2.1). The overlap height ($h$) was defined to be the charge density at the point where the charge density plots for the constituent ions cross each other. The overlap spread parameter ($s$) was defined to be the distance between the points where the charge densities of the constituent ions fall to a value equal to $h/e$. They then actually
Fig. 2.1 - Schematic of the plot for estimating overlap parameters, $S$ and $h$ (A, B being the positions of the centre of ions) for nearest neighbour interaction of two host ions in an alkali halide crystal.
obtained empirical correlations between B-M parameters and $h$ and $a$ for alkali chlorides and bromides.

When a defect ion occupies a substitutional position in an ionic solid, the charge density distribution of this ion overlaps the core of the nearest neighbour host ions.

Hoegy and Deb [105] suggested a method to find the repulsive parameters for the interstitial defect (foreign) atoms or substitutional defect ions in alkali halides from the charge density overlap parameters between the defect ions/atoms and the host ions with the help of these previously obtained empirical correlations and referred these parameters as the repulsive parameters of the defect ion in an ionic solid. They thus found $b$ and $\rho$ for different interstitial defects like hydrogen atom, chlorine atom and inert gas atoms in sodium chloride lattice and utilised these RPs to calculate the activation energies of interstitial atom diffusion in sodium chloride lattice. Their results explained satisfactorily the experimental activation energies. Hoegy and Deb [106] in another work expressed the repulsive energy of interaction between the atoms in the crystalline state of the inert gases (except helium) in the B-M form and then showed that even for the inert gas crystals there exist empirical correlations between repulsive parameters and overlap parameters. The authors [107] suggested that there should exist separate correlations (one between $b$ and $h$ and another between $\rho$ and $a$) for each separate class of solids for which the repulsive energy can be expressed in the B-M form and obtained two empirical correlations between B-M repulsion parameters and corresponding overlap parameters of all NaCl-type alkali halides. With the
help of these correlations, and the charge density overlap parameters of isovalent impurities (alkali ions & halogen ions) with nearest neighbour host ions. Neogy & Deb [102] determined the defect ion RPs and calculated solution enthalpies of those isovalent impurities in alkali halide crystals. Their theoretical data agreed quite well with experimental data.

In the following Chapter 3 of this thesis, the charge density overlap method of obtaining the B-M RPs has been extended to find the RPs for the interaction of the defect ion with the next nearest neighbour host ion in alkali halide crystals. Later, in Chapter 6 this method has been extended to find the RPs of isovalent defects in alkali halides (divalent and trivalent ion in alkali halides) from the charge density overlap of the divalent and trivalent defects with the host ions. These RPs for the defect ion-host ion interactions also have been utilised to calculate the defect energies for the imperfect crystals where the imperfections are due to the presence of isovalent ions (Chapter 3, 4 & 5) and also due to the presence of isovalent ions (Chapter 6, 7 & 8).

2.5 Experimental determination of defect energies from the conductivity measurements.

The defect energies, like Schottky defect formation energies of the host ion and the defect ion and solution-enthalpies of the defect ion in alkali halide crystals have been experimentally determined from the conductivity and diffusion measurements of pure and doped alkali halide crystals.

The ionic conductivity of alkali halide crystals of the NaCl type
occurs predominantly through the motion of vacancies [97]. Measurements of mass transport during conduction have further established that, except near the melting point, the current is carried almost entirely by the motion of the cations [97]. Accordingly, the cation vacancy is regarded as the mobile charge carrier. The electrical conductivity is given by the following expression [97]

$$\sigma = n_0 \mu = \frac{4 e^2 \alpha^2 \nu_0}{kT} n \exp \left(-\frac{E_a}{kT}\right)$$ \hspace{1cm} (2.33)

where $n$ is the concentration of cation vacancy, $\mu$ is the mobility of the vacancy, $\alpha$ is the distance between the nearest neighbour cation and anion, $E_a$ is the activation energy for the motion of a cation vacancy, $\nu_0$ is a frequency factor and $e$ and $kT$ have their usual meanings. The expression for mobility is derived from the fact that the mean time $\tau$ between vacancy jumps is given by

$$\tau^{-1} = 12 \nu_0 \exp \left(\frac{E_a}{kT}\right)$$ \hspace{1cm} (2.34)

Here the factor 12 appears because of the 12 nearest neighbour sites into which the vacancy may jump.

When data for conductivity, as a function of temperature, are plotted as $\log \sigma \tau$ vs $T^{-1}$, the scheme is called the conductivity plot. If the slope of such a plot is set equal to $-\tau/2.303 k$, the quantity $\tau$ which represents an effective activation energy is equal to $E_a$ plus an energy associated with the temperature dependence of $n$. Generally conductivity plots of ionic solids show three regions [Fig. 2.2].
Fig. 2.2 - Schematic conductivity plot (\(\log(\sigma T)\) Vs \(1/T\)) showing region I (intrinsic, region II (extrinsic, dissociated) and III (extrinsic, associated).
In region I which is known as the intrinsic region, \( n \) is the equilibrium concentration of Schottky defects in the lattice and is given by \( \frac{n}{u} \propto \exp \left( -\frac{E_g}{2kT} \right) \) ...

(2.35)

where \( E_g \) is the energy of formation of a Schottky pair and \( u \) is the concentration of cation lattice sites. Combining eqns. \( 2.33 \) and eqns. \( 2.35 \), it is seen that the effective activation energy for region I is given by

\[ E_{II} = E_m + \frac{1}{2} E_g \]

(2.36)

For crystals of ordinary purity, the cation vacancies below about 400°C have a different origin. Those are the vacancies which accompany divalent metallic impurity ions (M\(^{2+}\)) so as to maintain the electrical neutrality of the crystal. When the number of vacancies introduced by divalent cation impurities exceeds the number produced thermally, the conductivity breaks into region II (Fig. 2.2). In this region the concentration of cation vacancies is constant and equal to the total concentration of divalent metallic impurity present i.e.

\[ n = u_M^\circ = \text{constant} \]

\[ E_{II} = E_m \]

(2.37)

The region II fails to continue at very low temperature due to - (1) tendency of the M\(^{2+}\) ion and the cation vacancy to associate to form a neutral complex and (2) the precipitation of M\(^{2+}\) ions at temperature where their concentration in solution begins to exceed the solubility limit. Both these
effects result in a decrease in $n$ below the value $\eta^0_\mu$ and therefore can account for the onset of region III (Fig. 2.2). The association reaction may be expressed in the form

$$M + V = MV$$

where $M$ and $V$ represent the metallic impurity and the cation vacancy respectively and $MV$, the associated complex. Application of elementary statistical mechanics to this reaction gives

$$\frac{\eta_{MV}^n}{n^*} = k_1^{-1} \sum_l Z_l \exp \left( \frac{E_l}{kT} \right)$$

where $\eta_{MV}$ is the concentration of $MV$ complexes, $\eta^*_M$ is the concentration of isolated impurity ions, the subscript $l$ refers to the various bound states in which the pair may be found (e.g., $n.n., n.n.n.$ etc.), while $Z_l$ and $E_l$ are the number of possible configuration and the binding energy respectively, for state $l$.

In most cases the values of $E_l$ for one or two of the closest bound states are distinctly larger than that for the higher states, so that the summation is reasonably replaced by a single term,

$$\sum_l Z_l \exp \left( \frac{E_l}{kT} \right) = Z_0 \exp \left( \frac{E_0}{kT} \right)$$

Now charge neutrality condition gives

$$n = \eta^*_M$$

(2.39)

From the conservation of added impurity one can write

$$\eta^*_M + \eta_{MV}^n = \eta_{MV}$$

(2.40)

From eqns. (2.38), (2.39) and (2.40) one can write for the lower temp where association is almost complete (i.e. $n << \eta^0_\mu$)
When the region III is due to this association reaction, then combining eqn. (2.41) with eqn. (2.33), the effective activation energy of that region is obtained as

$$E_{III} = E_m + \frac{1}{2} E_a$$  \hfill (2.42)

In particular, extensive evidence for precipitation in this region is experimentally observed \([110,111]\). The precipitation region is referred to as region IV.

It has been suggested that the substitution of isovalent impurities in alkali halides causes strain in the crystal lattice, and that this strain could be relieved by the creation of vacancies \([112]\). Further at high temperature, the strain effects are reduced. Actually the effect of isovalent substitution in alkali halides, still now is unclear. Very interesting phenomena is obtained when divalent ion is doped in an alkali halide crystal. The cation vacancy concentration is increased by the creation of excess concentration of cation vacancies. Since the crystal must be electrically neutral, it is assumed that each divalent impurity ion replaces two host cation in an alkali halide crystal with the result that the excess concentration of positive ion vacancies is equal to the concentration of impurity ion, introduced in the crystal. A pure crystal contains equal concentrations of positive and negative ion vacancies. The effect of the vacancies which are introduced into the crystal by the divalent impurity is to shift the equilibrium existing
between positive and negative ion vacancies, promoting their combination. As a result, the equilibrium concentration of cation vacancies in the impure crystal is less than the sum of the original concentration in the pure crystal and the concentration of the divalent impurity ion. Stasiev and Teltow pointed out a second reaction, between divalent impurity ions and positive ion vacancies. Because of its double charge, a positive divalent ion attracts a positive ion vacancy, which has an effective negative charge. The fraction of positive ion vacancies, which are nearest neighbours of a positive divalent ion, exceeds that accepted on the basis of chance and a vacancy tends to remain a nearest neighbour of a divalent ion for a time greater than the normal jump time of a vacancy. Such an association between a vacancy and a divalent ion are called a complex.

Etzel and Maurer had analyzed experimentally the influence of known additions of cadmium and calcium halides on electrolytic conductivity of NaCl. Wagner and Hantelmann and Selting and Wilt had made similar measurements on specimens of KCl containing additions of calcium, strontium and barium chlorides. Brown and Hoodless measured the ionic conductivities of Mg$^{2+}$, Mn$^{2+}$, Ca$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ and Sr$^{2+}$ doped NaCl crystals. They also determined enthalpy of solution from the variation of free impurity solubility with temperature as this variation was given by

$$C = \exp \left(-\frac{\gamma}{2kT}\right)$$

$$= \exp \left(-\frac{\eta V}{2kT}\right) \exp \left(-\frac{\Delta F}{2kT}\right) \quad (2.43)$$
where $F$, $S$, and $H$ were respectively the free energy, the entropy and the enthalpy of solution and the effect of the precipitation or the dissolution of the impurity was easily recognised in the conductivity plot by a sharp change in the slope. The enthalpies of solution were also obtained from the difference in activation energies in conduction region IV and V \[97\]. The conductivity of Sr\(^{2+}\) doped NaCl crystal was also measured by Larodo Dartygo \[119\] and by Varzovhava et al \[122\]. Later author also calculated the solution enthalpies of the defects.

The conductivities of quenched and slowly cooled sodium chloride crystals doped with different concentration of Na\(^{2+}\) as well as of Ca\(^{2+}\), Cd\(^{2+}\) and Ba\(^{2+}\) impurities were measured by Jain and Pahade \[121\]. They studied in details about the extents of different regions of the conductivity with the concentration of the impurity added. The conductivity of cobalt-doped sodium chloride crystals had been measured by Jain and Narasimha \[122\].

On the other hand, there are very few data about the influence of trivalent cations in alkali halides. Al\(^{3+}\) & Fe\(^{3+}\) are very common trivalent defects to be present in ordinary pure crystals. Lidard \[97\] suggested from a physical concept that Al could enter into the NaCl crystal as Al\(^{2+}\) ions, while, it had been suggested that Al\(^{3+}\) and Fe\(^{3+}\) impurities could be responsible for the anomalous self-diffusion of the cation in the extrinsic range of the undoped sample \[115\].

Existence of both Sb\(^{2+}\) and Sb\(^{3+}\) in NaCl has been shown from the diffusion of antimony in NaCl by Radhakrishna & Saruppiakar \[123\] from the
measurement of ionic conductivity and colour centre absorption. Low temperature conductivity measurements of NaCl doped with Cr$^{3+}$ has been reported by Hartmanova et al \cite{124}.

Beniere and Rokhani \cite{125} doped Y$^{3+}$ in NaCl and analysed experimentally the influence of the presence of known concentration of Yttrium in NaCl from electrolytic conductivity as well as diffusion coefficient. According to them, each Y$^{3+}$ ion introduced two vacancies in the NaCl lattice which satisfied the charge neutrality condition for a trivalent defect ion in an alkali halide crystal. They obtained for Y$^{3+}$ doped NaCl crystal the conductivity in the extrinsic range (region II) to be twice as that obtained for same concentration of divalent impurity doped NaCl crystal. They obtained the enthalpy of association of the Y$^{3+}$ cation vacancy complex to be about twice the value of the divalent cations and enthalpy of solubility per molecule of YCl$_2$ to be more than that of divalent cations.

Recently Beniere and Reddy \cite{126} and Sistor and Stefanescu \cite{127} have been able to dope Fe$^{3+}$ in NaCl. The former investigators measured the diffusion profiles and the latter investigators measured the electron spin resonance.

In this thesis in Chapter 9 ionic conductivity measurements have been done with pure NaCl, divalent (Mg$^{2+}$) impurity doped NaCl and different concentration of aluminium doped NaCl. From the different conductivity plots different defect energies have been calculated.