 CHAPTER 1

 INTRODUCTION
1.1 IMPORTANCE OF LATTICE ENERGY

The study of cohesion in solids is of fundamental importance to understand the nature of interionic forces and their effects on elastic, thermal and anharmonic properties. Lattice energy of ionic crystals is an important parameter which is directly related to the binding forces in ionic solids and hence to the elastic constants. For this reason, there have been various theoretical methods starting with the Born-Mayer model to evaluate the lattice energy of ionic crystals apart from the experimental method based on the Born-Haber cycle. The lattice energy determined based on the Born-Haber cycle is an experimental lattice energy and is not dependent upon the nature of assumptions made about the bonding in the crystal. The classical theoretical calculations are based on the assumptions of the ionic nature of the bonding in the lattice.

Ionic crystals are made up of positive and negative ions. The ions arrange themselves, when the crystal is formed, with the coulomb attraction between ions of opposite sign being stronger than the coulomb repulsion between the ions of the same sign. The ionic bond is thus the bond resulting from the electrostatic interaction of oppositely
charged ions. Two common crystal structures found for ionic crystal are the sodium chloride structure and the cesium chloride structure.

The elastic constants and their pressure derivatives are valuable tools for investigating Born model because they are strong indicators of the short-range contributions to the cohesive energy. This model has been found to be very much successful in predicting the binding energies and moderately successful in explaining elastic properties. Hence elastic constant data can be utilised for the evaluation of lattice energies in ionic crystals.

A brief review of the different theories for the evaluation of lattice energies of ionic crystals is presented in the following section.
1.2 A BRIEF REVIEW OF THE DIFFERENT THEORIES EMPLOYED FOR THE EVALUATION OF LATTICE ENERGIES OF IONIC CRYSTALS

The basic assumption in the theory of the cohesive energy of ionic crystals is that the solid may be considered as a system of positive and negative ions. Born\textsuperscript{1} devised formulae which permit the calculations of the lattice energy of an ionic crystal. The lattice energy of such a crystal may be defined as the increase in internal energy at absolute zero accompanying the separation of the constituent ions, to positions where they are infinitely removed from one another. In order to account for the stability of crystals known to be composed of ions it is necessary to introduce forces between the ions that are non-coulombic, for, no stable equilibrium is possible in an electrostatic system of charges unless other forces are present.

In Born's\textsuperscript{1} theory of the lattice energy of ionic crystals, it is assumed that the charge distribution in the positive and negative ions is spherically symmetric and hence the force between two such ions depends only on their distance apart and is independent of direction. Considering a lattice of the NaCl type structure, as an illustrative case,
a given sodium ion is surrounded by 6 Cl⁻ ions at a distance
r, 12 Na⁺ ions at a distance \( r \sqrt{2} \), 8 Cl⁻ ions at a distance
\( r \sqrt{3} \) etc., where \( r \) represents the shortest interionic
distance. The coulomb energy of the sodium ion in the
field of all other ions is given by

\[
\varepsilon_c = -\frac{e^2}{r} \left[ \frac{6}{2} + \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} + \frac{6}{\sqrt{4}} + \cdots \right]
\]  

... (1.2.1)

where \( e \) is the charge per ion.

The coefficient of \( \frac{e^2}{r} \) is a pure number determined only
by the crystal structure. For the NaCl type structure, the
result is

\[
\varepsilon_c = -\frac{4e^2}{3r}
\]  

... (1.2.2)

with \( \lambda = 1.74798 \)

The constant \( \lambda \) is called the Madelung constant. For
other crystal structures composed of positive and negative
ions of the same valency, the values of the Madelung
constant are different.

In equation (1.2.2), \( e \) represents in general the
electronic charge times the valency of the ions under
consideration. The minus sign in eqn. (1.2.2) indicates
that the average influence of all other ions on the one
under consideration is of an attractive nature. To prevent
the lattice from collapsing there must also be repulsive forces between the ions. These repulsive forces become noticeable when the electron shells of neighbouring ions begin to overlap, and they increase strongly in this region with decreasing values of \( r \). These forces, like other types overlap forces, can best be understood on the basis of wave mechanics, because they are of a non-classical nature. Born\(^1\) has simply assumed that the repulsive energy between two ions as a function of their separation could be expressed by a power law of the type \( B^r / r^n \) where \( B^r \) and \( n \) are as yet undetermined constants characteristic of the ions under consideration. Thus the repulsive energy of one ion due to the presence of all other ions may be written as

\[
\varepsilon_{rep} = \frac{B^r}{r^n} \quad \ldots \quad (1.2.5)
\]

where \( B \) is related to \( B^r \) by a numerical factor. Because of the fact that the repulsive forces depend so strongly on the distance between the ions, the repulsive energy given by eqn. (1.2.3) is mainly determined by the nearest neighbours of the central ion. The total energy of one ion due to the presence of all other ions is obtained by adding the equations (1.2.2) and (1.2.3)
\[ s = - \frac{e^2}{r} + \frac{1}{r^k} \quad \ldots \quad (1.2.4) \]

Assuming that the two types of forces just discussed are the only ones that have to be taken into account and neglecting surface effects, the total binding energy of a crystal containing \( N \) positive and \( N \) negative ions can be given as

\[ U = E(r) = N \left( - \frac{e^2}{r} + \frac{1}{r^k} \right) \quad \ldots \quad (1.2.5) \]

The variation of \( U \) with \( r \) is shown in Fig. 1.2.1.

Considering the crystal at absolute zero, the equilibrium conditions require \( U \) to be a minimum. This will be the case for the equilibrium value of \( r = r_o \) as shown in Fig. 1.2.1 where \( r_o \) represents the smallest interionic distance in the crystal at \( T = 0 \). For this minimum

\[ \left( \frac{\partial U}{\partial r} \right)_{r=r_o} = 0 \quad \ldots \quad (1.2.6) \]

From equations (1.2.5) and (1.2.6) the relation between the two unknown parameters \( a \) and \( n \) can be written as

\[ B = \left( \frac{e^2}{a} \right) r_o^{n-1} \quad \ldots \quad (1.2.7) \]
Fig. 1.1.2 - Variation of $U$ with interionic distance $r$.

Curve $a \rightarrow$ attraction as a function of $r$

Curve $b \rightarrow$ repulsion as a function of $r$

Resultant of $a$ and $b$ exhibits a minimum at $r = r_o$ at absolute zero.
Substituting equation (1.2.7) into equation (1.2.9) we obtain the following expression for the lattice energy \( U_L \)

\[
U_L = U(r_o) = -\Delta A \frac{2}{2} \left( 1 - \frac{1}{n} \right) \quad \ldots \quad (1.2.8)
\]

where \( U_L = U(r_o) \). The interionic distance can be obtained from X-ray diffraction data, the charge per ion is known, and thus the lattice energy can be calculated if the repulsive exponent \( n \) is known. Born obtained the value of \( n \) from measurements on the compressibility of the crystals and using the following expression

\[
n = 1 + \frac{9C}{K_0} \frac{r_o^2}{\sigma^2} \quad \ldots \quad (1.2.9)
\]

where \( C \) is a constant determined by the type of lattice, \( K_0 \) is the compressibility at absolute zero and the other terms have their usual meaning.

According to equation (1.2.9) and in view of the relatively large value of \( n \) which varies from crystal to crystal most of the lattice energy is due to the coulomb interaction, and the repulsion contributes only a relatively small fraction. On the other hand, the repulsive and attractive forces acting on any one ion just balance for \( r = r_o \) and thus are equal in magnitude.
The development of the theory of lattice energies is largely on account of the development of the ideas about the non-spherical forces between the ions. Born and Lande$^2$ represented these forces as varying as the inverse $n$th power of the distance and treated the potential energy of the crystal as the sum of the two terms, given by the expression

$$U_0 = \frac{N A Z_1 Z_2 e^2}{r} - \frac{B}{r^n} \quad \ldots \quad (1.2.10)$$

where $N$, $A$, $Z_1$, $Z_2$, $e$ and $r$ represent the Avagadro number, Madelung constant, valencies of the ions, charge on the electron, distance between unlike ions respectively. $B$ is a constant. The value of $n$ is usually determined empirically from the compressibility.

The constant $B$ can be eliminated by utilising the fact that at the equilibrium separation of the ions in the crystal may at $r = r_0$, $\left(\frac{\partial U}{\partial r}\right)_r = r_0 = 0$, so that

$$U_0 = \frac{N A Z_1 Z_2 e^2}{r_0} \left[1 - \frac{1}{n}\right] \quad \ldots \quad (1.2.11)$$

The development of wave mechanics led to the realisation that ions with completed subgroups are spherically symmetrical and that, for the outermost shell, the electron density falls off exponentially with distance.
Born and Mayer\(^3\), utilising this fast and considering only the coulombic and repulsive forces, obtained the following expression for the lattice energy

\[
U_0 = \frac{N a Z_1 Z_2 e^2}{r} - N B^* e^{-r/R^*} \quad \ldots \quad (1.2.12)
\]

In the above expression, \(B^*\) is another constant and has the dimensions of length. Utilising the condition that \((\partial U / \partial r)_r = r_0 = 0\), we get

\[
U_0 = \frac{N a Z_1 Z_2 e^2}{r_0} \left[1 - \frac{r}{r_0}\right] \quad \ldots \quad (1.2.15)
\]

These two expressions are called the simple Born-Mayer expressions for the lattice energy of an ionic crystal.

The simple Born-Mayer equation was further modified and terms are introduced to allow for the induced dipole-dipole and dipole-quadrupole interactions in the lattice and for the zero point energy of the lattice. The extended form of the Born-Mayer equation is given below

\[
U_0 = \frac{N a Z_1 Z_2 e^2}{r} - N B^* e^{-r/R^*} + \frac{64 \pi Q G}{r_0^3} + \frac{2}{5} N n h c \max \quad \ldots \quad (1.2.14)
\]
where \( h \) is Planck's constant and \( \nu_{max} \) is the Debye maximum frequency.

Huggins, later recalculated the lattice energies using the values of 'basic radii'. These 'basic radii', determined using the condition \( \left( \frac{\partial V}{\partial r} \right)_r = r_0 = 0 \) produced the equilibrium internuclear distance when put into the equation for the lattice energy. His treatment is similar to the extended Born-Mayer equation except that adjusted crystal 'basic radii' are used to obtain \( B' \) and optical data on the crystal itself to obtain \( C \).

Because of the difficulty of assigning basic radii in many salts Ladd and Lee have extended the simple Born-Mayer equation eliminating \( B' \) and hence the basic radii and including dispersion energy terms. Employing the condition \( \left( \frac{\partial V}{\partial r} \right)_r = r_0 = 0 \), an expression for the lattice energy was obtained which is given below

\[
U_o = \frac{N A Z_1 Z_2 e^2}{r_0} \left[ 1 - \frac{r}{r_0} \right] - \frac{4 \pi \varepsilon_0 Z_1^2}{r_0} \left[ 1 - \frac{r^2}{r_0^2} \right] - \frac{4 \pi \varepsilon_0 Z_2^2}{r_0} \left[ 1 - \frac{r^2}{r_0^2} \right] + \frac{8 \pi \varepsilon_0 N h ^2 \nu_{max}}{r_0} \]

\( \ldots \) (1.2.15)

If we consider the expression for the lattice energy to contain basically the first two terms namely attractive and
repulsive, then by adopting either an inverse power law or an exponential law for the repulsive term, \( U_0 \) may be written as either

\[
U_0 = \frac{N A Z_1 Z_2 e^2}{P_0} [1 - \frac{1}{A}] \quad \ldots \quad (1.2.11)
\]

or

\[
U_0 = \frac{N A Z_1 Z_2 e^2}{P_0} [1 - \frac{\rho}{P_0}] \quad \ldots \quad (1.2.13)
\]

If the number of ions in the chemical molecule is \( X \), the number in a mole is \( N X \). The above equations may then be written as

\[
U_0 = \frac{N X \alpha}{P_0} \left[ \frac{Z_1 Z_2 e^2}{P_0} \right] [1 - \frac{1}{A}] \quad \ldots \quad (1.2.16)
\]

\[
U_0 = \frac{N X \alpha}{P_0} \left[ \frac{Z_1 Z_2 e^2}{P_0} \right] [1 - \frac{\rho}{P_0}] \quad \ldots \quad (1.2.17)
\]

where \( \alpha = \frac{Z A}{X} \) is a constant. Apustinskii\(^{6,7} \) found empirically that in passing from one lattice type to another, the change in the constant \( \alpha \) was proportional to the change in the interatomic distance. Apustinskii's\(^{6,7} \) equation for the lattice energy is given as
where \( r_C + r_A \) is the sum of the ionic radii for the coordination number 6 and taking \( \rho = 0.345 \, \text{Å}, \beta = 1.745 \) and \( \text{Ne}^2 = 329.7 \, \text{Kcal/Å} \).

Kapustinskii's formula gives approximate lattice energies, especially in those cases where the structure is unknown. The values for the lattice energies given by the Kapustinskii equation fall on the low side of the correct lattice energy.

Hylleraas applied a general quantum mechanical treatment to the calculation of the lattice energies. He used one-electron wave functions of the hydrogenic type with nuclear screening so that the entire computation could be performed analytically. The wave functions were

\[
\psi = \exp\left(-\frac{Z - \frac{5}{16}}{r/a_b}\right) \quad \quad \text{(1.2.19)}
\]

where \( a_b \) is the Bohr unit distance (0.53 Å).

In addition to the potential functions already discussed above, recent workers, have suggested three new potential functions which give improved potential energy and force curves for the ionic crystals. These new potential energy functions are
\[ U = \frac{N A Z_1 Z_2 e^2}{F} - P \log \left( 1 + \frac{Z_2}{F} \right) \quad \ldots \quad (1.2.20) \]

\[ U = \frac{N A Z_1 Z_2 e^2}{F} - Q \log \left( 2 + \frac{Z_2}{F} \right) \quad \ldots \quad (1.2.21) \]

\[ U = \frac{N A Z_1 Z_2 e^2}{F} - D \log \left( 4 + \frac{d}{F} \right) \quad \ldots \quad (1.2.22) \]

where \( P, Q, Q, D \) and \( d \) are constants and the other terms have their usual significance.

The lattice energies of alkali metal halides have been calculated theoretically by a large number of workers. The principal calculations by the classical ionic theory have been made by Mayer and Helmolts, Verwey and de Boer, and by Hoggins. Ladd and Lee have used a method to evaluate lattice energies, eliminating the need for basic radii. Kapustinii has also calculated the lattice energies although his values are rather low. In recent times the lattice energies of the alkali halides have been calculated by Sinha and Thakur, Thakur et al., Singh and Shankar, Shankar et al., Jha and Thakur. Apart from these Landshoff calculated the lattice energies of NaCl by the general quantum mechanical model developed by Hylleraas.
The same method was adopted by Löwdin\textsuperscript{20,21} for calculating the cohesive energies of LiCl, NaCl, KCl and NaF.

The lattice energies of alkali metal hydrides have been calculated by the quantum mechanical calculations by Moller\textsuperscript{8} who had evaluated the lattice energy of LiH. Lindquist\textsuperscript{23} has also calculated the lattice energy of LiH basing on the quantum mechanical model. Richencks\textsuperscript{24} and Rossini\textsuperscript{24} derived the lattice energy of LiH using a Born-Lande expression. Waddington\textsuperscript{25} has obtained values for the lattice energies of all the alkali metal hydrides using a simple Born-Mayer expression and ignoring van der Waals terms. Sinha and Thakur\textsuperscript{14} have also evaluated the lattice energies of alkali hydride crystals.

Sherman\textsuperscript{26} used the simple Born formula for the evaluation of lattice energies of alkaline earth oxides. Mayer and Maltbie\textsuperscript{27} used the Born-Mayer expression for the lattice energies, calculating the London dispersion energies from the polarizabilities of the free ions. Later de Boer and Verwey\textsuperscript{28} recalculated the lattice energies of the oxides because the Mayer and Maltbie\textsuperscript{27} calculations of the interatomic distances differed significantly from those obtained from the X-ray data. Kupertinskii and Yatsimirskii\textsuperscript{29} have recalculated the lattice energies
for a large number of crystals. Huggins and Sakamoto have recalculated the lattice energies of all the alkaline earth chalcogenides. Recently the lattice energies of some alkaline earth chalcogenides have been calculated by Sasmu et al. Later, Son and Bertals have applied a simple Born model considering repulsion between nearest neighbours only for the cohesive energy of MgO, CaO and SrO and found it less satisfactory. They have also considered the addition of next nearest neighbour repulsion and considered the ionic charge to be varying between two values. Neither approach significantly improved theory-experiment agreement. Recently Thakur has employed three new logarithmic potentials and calculated the cohesive energies of BeO, MgO, CaO, SrO and BaO. Using a modified Born-Mayer equation, Thakur et al. have evaluated the lattice energies of all the alkaline earth chalcogenides, and alkali metal chalcogenides.

Sharma obtained the lattice energies of the argentous, the thallous and the cuprous halides. The lattice energies of the above ionic crystals were recalculated by Mayer and by Mayer and Levy. Later, Ladd and Lee have recalculated the lattice energies of the silver and thallous halides by a method avoiding the
use of Huggins' basic radii which are difficult to fix for these salts. Recently, Saxena et al.\textsuperscript{31} have evaluated the lattice energies of these heavy metal halides. Uma Rani Pant\textsuperscript{36}, using different interaction potentials including the logarithmic potentials has evaluated the lattice energies. Bakshi et al.\textsuperscript{37} calculated the cohesive energies of copper, silver and thallium halides by considering van der Waals dipole-dipole and dipole-quadrupole interaction energies. Thankur\textsuperscript{38} and Sharma et al.\textsuperscript{39} have also calculated the lattice energies of these crystals. Recently Thankur et al.\textsuperscript{15} have calculated the cohesive energies of these heavy metal halides and also ammonium halides from a modified form of the Born-Mayer equation.

The lattice energies of the divalent metal halides have been presented by Sherman\textsuperscript{26} on the basis of the Born-Lande equation. Morris\textsuperscript{40} has extended the theoretical calculation, again using the Born-Lande equation and has recalculated the thermochemical data. Later, the cohesive energies of CaF\textsubscript{2}, SrF\textsubscript{2} and BaF\textsubscript{2} have been calculated by Benson and Dempsey\textsuperscript{41} and more recently by Shanker et al.\textsuperscript{42}

Sherman\textsuperscript{26} has calculated the lattice energies of the chalcogenides of the monovalent metals other than alkali
metals and obtained values which differed significantly from the experimental values. The lattice energies of Al$_2$O$_3$ and Cr$_2$O$_3$ have also been calculated by Sherman.

An examination of the review presented above indicates the usefulness of the Born theory of the lattice energy of ionic crystals. It can also be inferred that a large number of workers have applied this theory considering some modifications to the Born-Mayer equation in the repulsive term and also incorporating terms that involve the van der Waals energy, the dispersion energy, the zero-point energy and different forms of the potential energy. An exhaustive survey of the literature indicates that the lattice energies of ionic crystals have been calculated only from theories based on the Born's theory and its refinements. The present work deals with the evaluation of lattice energy of ionic crystals based on Medriatsev's theory which relates the lattice energy with sound velocity. This approach to evaluate lattice energies is altogether a new one which has not been attempted earlier. The details of this theory are given in Chapter 2. The results on the calculations of the lattice energies of ionic crystals and discussion of the results are presented in Chapter 3 of the thesis.