CHAPTER 2

UDRIATSEV'S THEORY
2.1 INTRODUCTORY REMARKS

Lattice energy of ionic crystals is an important parameter which is directly connected to the binding forces in ionic solids and hence to the elastic constants. There are various theories starting from the Born-Haber model to evaluate the lattice energies of ionic crystals apart from the experimental method based on Born-Haber cycle. The elastic constants and their pressure derivatives are valuable tools for investigating this model because they are strong indicators of the short-range contributions to the cohesive energy.

Kudriavtsev developed an expression relating the mean sound velocity to the lattice energy of ionic crystals. The mean sound velocity can be obtained from the experimental determination of the velocity of longitudinal and shear wave propagation in polycrystalline solids or from the elastic constants of single crystals.

A detailed discussion of the Kudriavtsev's theory employed in the present work to evaluate the lattice energies of ionic crystals is presented in the following section. The Voigt-Reuss-Hill approximation, employed to calculate the mean sound velocity in a polycrystal in terms of its single crystal elastic constants data, is detailed in Section 2.3.
2.2 KUDRIAVTSEV'S THEORY

Kudriavtsev\textsuperscript{43} developed an expression relating the mean sound velocity $u_m$ to the lattice energy $U_0$ of a substance, assuming the additivity of the internal energy and making use of the standard thermodynamic formulae. The derivation of the expression is detailed below closely following the treatment given by Kudriavtsev\textsuperscript{43}.

The internal energy $E$ of a system of volume $V$ at constant temperature $T$ and pressure $P$ is given by the thermodynamic relation

$$\left(\frac{\partial E}{\partial V}\right)_T = -P + T \left(\frac{\partial P}{\partial V}\right)_V$$ \hspace{1cm} (2.2.1)

Differentiating the above expression with respect to volume $V$ at constant temperature $T$ and making use of the relation

$$u^2 = -v^2 + \left(\frac{\partial P}{\partial V}\right)_T$$ \hspace{1cm} (2.2.2)

where $u$ represents the sound velocity and $\gamma$ represents the ratio of specific heats, we get

$$v^2 + \left(\frac{\partial P}{\partial V}\right)_T = u^2 - T(\frac{\partial u^2}{\partial T})_V$$ \hspace{1cm} (2.2.3)

The internal energy of any substance either solid or liquid consists of both kinetic energy and potential energy.
Since kinetic energy depends on the temperature and the equation 2.2.3 represents the derivatives at constant temperature, we can replace $E$ in the above equation by $\phi$, the potential energy. Hence equation 2.2.3 can be rewritten as

$$v^2 \frac{\partial^2 \phi}{\partial T^2} = u^2 - T \frac{\partial (\frac{1}{2}u^2)}{\partial T} \quad \ldots \quad (2.2.4)$$

The dependence of $U_0$ on $V$ is given by

$$\phi = \frac{A}{v^3} - \frac{B}{v^2} \quad \ldots \quad (2.2.5)$$

where $A$, $B$, $n$ and $m$ are constants. The first term is governed by the repelling forces and the second term is governed by the attracting forces. The constants $A$ and $B$ are functions of temperature, but at constant temperature they are constants characteristic of the specified substance.

Utilising equation 2.2.5, we may write

$$v^2 \frac{\partial^2 \phi}{\partial T^2} = mn^{-1} \phi_0 \quad \ldots \quad (2.2.6)$$

where $\phi_0$ represents the potential energy of the substance occupying an equilibrium volume at the specified temperature.

Substituting equation 2.2.6 in equation 2.2.4, we get

$$u^2 - T \frac{\partial (\frac{1}{2}u^2)}{\partial T} = mn^{-1} \phi_0 \quad \ldots \quad (2.2.7)$$
Assuming $n$, $m$, $\gamma$ as constants, by integrating the above equation, we get

$$u^2 = n m \gamma \phi_0 + f T + g(v) \quad \ldots \quad (2.2.8)$$

where $g(v)$ is a function of volume and $f$ is a constant.

Assuming the velocity of sound at the critical temperature or above the critical temperature is the same as the velocity of sound in the gas and also assuming that the velocity to be independent of pressure (volume) we find $g(v) = 0$ and $f = \frac{L}{R}$ where $R$ represents the gas constant and $M$ the molecular weight. Hence the velocity of sound is given by

$$u^2 = n m \gamma \phi_0 + \frac{L}{R} \quad \ldots \quad (2.2.9)$$

The above equation applies to both liquids and solids.

In the case of electrolytes, $\phi_0$ can be replaced by lattice energy of the crystal $U$, given by

$$U = \frac{a_e}{2} - \frac{b e^2}{r} \quad \ldots \quad (2.2.10)$$

where $r$ represents the distance between the ions in the lattice, $e$ is the electronic charge and $a$, $b$ and $n_1$ are constants. Since the distance $r$ between the ions in the lattice is associated with the molecular volume of the crystal in a single-valued manner, equation 2.2.10 can be
written as

\[ u = -\frac{\gamma_n^2}{n^2} + \frac{\gamma_n^2}{n^2} \] ... (2.2.11)

From equations 2.2.9 and 2.2.11, we can write

\[ u^2 = \frac{\gamma n}{a} u + \frac{\gamma_n}{n} \] ... (2.2.12)

At ordinary temperatures, the contribution of the term \( \frac{\gamma_n}{n} \) is small compared with other terms. Hence equation 2.2.12 can be simplified as

\[ u^2 = \frac{\gamma n}{a} u \] ... (2.2.13)

For solids \( \gamma \) may be taken to be equal to 1. In calculating the lattice energies of crystalline lattices, for ions with a different electron structure, values of \( n_1 \) that may be used are equal to 3, 5, 7, 9 and 10. Taking \( n_1 = 5 \), \( \gamma = 1 \) and expressing \( U \) in J mole\(^{-1}\), equation 2.2.13 can be written as

\[ u^2 = 2.32 \times 10^7 U \] ... (2.2.14)
The theory was extended to electrolytic solutions, and sound velocities in electrolytic solutions were evaluated. Andriievtsiev applied his theory to calculate sound velocities in aqueous solutions of alkali nitrates, sodium and magnesium sulphates and sodium and potassium halides employing the experimentally determined lattice energy data and velocity in pure water. The expression used to calculate the sound velocity in aqueous electrolytic solutions is

\[ u_{\text{sal}}^2 = (1 - x) u_0^2 + x (2.32 \times 10^7 v) \ldots (2.2.15) \]

where \( x \) represents the concentration of the electrolyte by weight (weight fraction of the solute) and \( u_0 \) represents the velocity of sound in pure water. The calculated velocities in the solutions are in good agreement with the experimental data. Recently. The theory has also been successfully applied to aqueous electrolytic solutions. These results indicate that one can employ equation 2.2.14 to evaluate the lattice energies of electrolytes via sound velocity data, and hence the author has taken up the problem of testing the applicability of the Andriievtsiev's theory to evaluate the lattice energies of ionic crystals.

It is clear from equation 2.2.14 that ultrasonic velocity data in the electrolyte is necessary to calculate the
lattice energy. Since the electrolytes in the present study are cubic in nature, we have three velocities - one longitudinal and two transverse wave velocities. There is no specific reason to prefer any one of the above velocities. Hence the mean velocity \( u_m \), which actually represents the sum of the contributions from each type of sound wave, averaged over all directions, is employed to calculate the lattice energy \( U \) using equation 2.2.14. The reason for preferring \( u_m \) to obtain \( U \) is that the Debye characteristic temperature \( \Theta_D \) evaluated using \( u_m \) agrees well with the calorimetric data for isotropic crystals, for which the longitudinal and transverse wave velocities \( u_L \) and \( u_T \) are invariant with direction. The mean sound velocity \( u_m \) is given by the expression

\[
    u_m = \left[ \frac{1}{2} \left( \frac{1}{u_L^2} + \frac{2}{u_T^2} \right) \right]^{-1/3} \quad \ldots \quad (2.2.16)
\]

Hence the final expression used to evaluate lattice energy of ionic crystals is given by

\[
    U = \frac{u_m^2 N}{2.32 \times 10^7} \quad \ldots \quad (2.2.17)
\]
for \( n_2 = 3 \), where \( M \) represents the molecular weight of the crystal. The constant in the denominator of the above equation changes depending upon the value of \( n_2 \) say 3, 7, 9 and 10.

The isotropic velocities \( u_1 \) and \( u_6 \) used in equation 2.2.16, to obtain \( u_\alpha \) generally refer to polycrystalline aggregates of the substances. Due to paucity of data available on polycrystalline aggregates, \( u_1 \) and \( u_6 \) have been calculated from single crystal elastic constants data by an averaging method, known as the Voigt-Reuss-Hill approximation. The details of the VRH approximation are presented in the following section.
2.3 THE VOIGT–REUSS–HILL APPROXIMATION

Due to the paucity of elastic constants data on polycrystalline aggregates of the ionic crystals under consideration, the isotropic velocities $u_1$ and $u_2$ are evaluated from the single crystal elastic constants. The Young's modulus and the rigidity modulus evaluated using single crystal elastic constants data agree well with the experimental data on polycrystalline samples after accounting for the porosity of the samples. For cubic crystals Voigt has obtained the following relations for the Young's modulus and rigidity modulus of a polycrystal in terms of the single crystal elastic moduli by assuming that the strain is uniform throughout the grain.

\[ E_Y = \frac{(C_{11} - C_{12} + 3C_{44})(C_{11} + 2C_{12})}{2C_{11} + 3C_{12} + C_{44}} \]

... (2.3.1)

and

\[ G_Y = \frac{C_{11} - C_{12} + 3C_{44}}{3} \]

... (2.3.2)

Assuming that each grain is subjected to a constant stress, Reuss had arrived at the following expressions for the Young's modulus and the rigidity modulus.
$$E_R = \frac{5 \, c_{44} \, (c_{11} - c_{12}) \, (c_{11} + 2 \, c_{12})}{c_{44} \, (3 \, c_{11} + 2 \, c_{12}) + (c_{11} - c_{12}) \, (c_{11} + 2 \, c_{12})}$$

... (2.3.3)

and

$$q_R = \frac{5 \, c_{44} \, (c_{11} + c_{12})}{4 \, c_{44} + 3 \, (c_{11} - c_{12})}$$

.... (2.3.4)

where $c_{11}$, $c_{12}$ and $c_{44}$ are the elastic constants of the single crystal. Hill\textsuperscript{49} observed that the two classical approaches\textsuperscript{47,48} have certain limitations and suggested that either the arithmetic mean or the geometric mean of the two approximations can be used for evaluating the polycrystalline constants from the single crystal data. Hill\textsuperscript{49} pointed out that the values of Young's modulus and rigidity modulus evaluated using the arithmetic mean agree well with the experimental data for aluminium, copper, silver and a-iron. In the present work, the arithmetic mean of $E_Y$ and $E_R$ and $q_Y$ and $q_R$ are used to obtain Young's modulus $E$ and the rigidity modulus $G$ in the polycrystalline aggregates. Hence

$$E = \frac{E_Y + E_R}{2}$$

... (2.3.5)

and

$$G = \frac{q_Y + q_R}{2}$$

... (2.3.6)
The isotropic velocities \( u_1 \) and \( u_2 \) are obtained using the relations

\[
\begin{align*}
\mathbf{\nu} &= \sqrt{\frac{2}{\rho} \left( \frac{g}{g - h} \right)}^{1/2} & \quad \text{(2.3.7)}
\end{align*}
\]

and

\[
\begin{align*}
\mathbf{\nu} &= \left[ \frac{2}{\rho} \right]^{1/2} & \quad \text{(2.3.8)}
\end{align*}
\]

where \( \rho \) is the density of the crystal at the given temperature. The mean velocity \( \mu_\text{m} \) is calculated using the relation (2.2.15) from the values of \( u_1 \) and \( u_2 \) obtained using the above relations.