CHAPTER III

THERMAL EXPANSION OF IONIC CRYSTALS

Considering the cubic and quartic terms inharmonicity of the potential energy function, a new relation for the thermal expansion coefficient, $\alpha$, has been derived following the interaction potential approach for ionic solids. The equation has been tested for different crystal structures. Attempt has also been made to compute $\alpha$ at high temperatures in cases of NaF and AgO crystals and the satisfactory agreement between the computed and experimental values indicated that the temperature dependence of $\alpha$ of these solids can be explained very well on the basis of the present inharmonic theory.

Experimental investigations on the thermal expansion coefficient of NiO and AgO have also been done between 100-550 K and 150-550 K, respectively, using x-ray diffraction technique. These data of NiO have been used to explain the temperature dependence of the $q \approx 0$ TO mode of this solid (Chapter II).
3.1 EXPERIMENTAL STUDY

3.1.1 Introduction

All solid substances, when heated or cooled undergo a reversible change in dimensions, and often in shape, which is called thermal dilatation or, more commonly - thermal expansion. The magnitude of this change per unit change in temperature is expressed quantitatively by means of a coefficient which may take any one of several different forms and which may be based either on change in volume or on change in linear dimensions.

The basic principles governing the thermal dilatation of solids may be approached from several different points of view. One may be called the kinetic approach, that is, a consideration of the atomic mechanism of such expansion. Another is the thermodynamic approach based on general consideration of the energy changes involved without reference to any specific mechanism. A third is based upon structural chemistry and is concerned with the size of the atoms or ions, with their arrangement in the crystalline structure, and with the bonds which join them. None of these approaches has, as yet, provided a complete and satisfactory explanation for all the observations, yet each has led to significant contributions.
The thermal dilatation is a result of the thermal motion of the atoms, or groups of atoms, of which the matter is composed. In an ionic solid, as we have seen in Chapter I, the ions arrange themselves in certain regular patterns so that the potential energy of the system is at a minimum. They are not, however, fixed but vibrate about their respective equilibrium positions, with amplitudes that go on increasing with the rise of temperature. Thermal expansion of solids can be qualitatively explained as the result of displacement of the equilibrium positions of the ions due to increase of the amplitude of vibration 2).

In other words, it can be said that, the thermal expansion is due basically to the presence of anharmonic vibrations of the ions about their equilibrium position in the solid lattice. Moreover, because of zero-point vibrations the influence of anharmonicity does not disappear even at absolute zero. This is particularly large for small masses which have correspondingly large zero-point oscillations. The equilibrium positions therefore do not coincide with the minimum of the potential energy.

In view of the influence of ionic vibration on the thermal expansion of solids attempts were made by several workers to correlate this property with vibration characteristics of ions. A number of empirical relations correlating thermal expansion with certain other properties
such as melting point, specific heat and coordination number were also discussed. 2

Another approach to the problem can be the consideration of the free energy of the solid and the derivation of the appropriate expressions for the partition function, to give various thermodynamic properties based on a nearest neighbour central potential model. Wallace 3 has made extensive numerical calculations of thermodynamic properties using this approach, but his expressions involved lattice sums which were evaluated for a large number of points in the Brillouin zone as a function of volume. Since the evaluation of these sums for a specified interionic potential is generally very tedious, a simplification can be introduced for the purpose of obtaining macroscopic properties at moderate and high temperatures by assuming that all the oscillators oscillate with the same frequency (Einstein approximation). Expressions can now be derived to include the anharmonicity terms in a simple way 4). Using this simplification, a general expression for the linear thermal expansion coefficient, $\alpha$, for cubic ionic crystals has been derived. An attempt has been made to compute the magnitude of anharmonic terms for various structures on the basis of Born, Born-Mayer, and Born-Mayer with $\phi_{dd}$ and $\phi_{dy}$ terms, interatomic potentials. The results have been compared with the experimental values. The applicability of these
potentials to the present problem and the usefulness and the correctness of the derived relation for $\alpha$ are discussed.

3.1.2 General Expression for the Thermal Expansion Coefficients

From the knowledge of free energy and the partition function the equation for the thermal expansion coefficient can be derived as follows.

Let us start with Helmholtz free energy:

$$F = T - ES = -kT \log Z$$

(3.2)

where $E$ is the total energy, $S$ is the entropy and $Z$ is the partition function (sum over states). $Z$ is generally given as

$$Z = \sum_j \exp \left( -\epsilon_j / kT \right)$$

(3.3)

where $\epsilon_j$ are the eigenvalues of the energy operator. The complete free energy will then be given by

$$F = \psi_0 + \sum_j kT \log \left( 1 - e^{-\epsilon_j/kT} \right)$$

(3.3)

where $\psi_0$ is the cohesive energy at absolute zero, inclusive of zero-point energy and $\epsilon_j$ is the frequency of the $j^{th}$ mode of vibration.
Consider an atom executing its thermal motion along a straight line in an asymmetrical potential provided by another fixed atom at the origin. The total energy, \( E \), is expressed in terms of the momentum \( \tau \) and the displacement \( r \) from the equilibrium interatomic distance, \( r_0 \), by the equation,

\[
E = \frac{\tau^2}{2M} + ar^2 + br^3 + cr^4 + dr^5 + \ldots \quad (3.4)
\]

Here linear term in \( r \) vanishes, \( M \) is the mass of the atom, and \( a, b, c, d, \ldots \) etc., are coefficients which can be determined from the shape of the interatomic potential.

If the equilibrium position is altered by imposing an external force on the atom, it is important to note that these coefficients are altered, because the expansion of the interatomic potential into a power series must then be made about a different point of the potential curve.

For the above form of the energy, \( E \), the classical partition function has been derived by Wilson as

\[
Z = \int \int \exp \left( -\frac{E}{kT} \right) \, dr \, d\tau \quad (3.5)
\]

It is assumed that the effect of the third and subsequent terms of the above expansion for \( E \) is small, and \( Z \) is obtained in the form of a power series in \( kT \), of which only the first two terms are retained:

\[
Z = \frac{kT}{2} \left[ 1 + \frac{15}{16} \frac{b^2}{a^3} kT - \frac{3}{4} \frac{c}{a^2} kT \right] \quad (3.6)
\]
Here \( \nu \) is the frequency of vibrations of small amplitudes and is given by

\[
\nu = \left( \frac{1}{n} \right) \left( \frac{a}{2M} \right)^{1/2} \quad (3.7)
\]

A change in volume in terms of this model implies that the position of equilibrium has been shifted by an impressed force. If the distance from the new position of equilibrium is \( r \), and the impressed force has moved the position of equilibrium a distance \( dr \), the distance from the old position of equilibrium is \( r + dr \). The actual potential energy will be the same, whether expressed as a power series with old coefficients about the old position of equilibrium or with new coefficients about the new position of equilibrium. Hence

\[
a(r + dr)^2 + b(r + dr)^3 + c(r + dr)^4 + \ldots \]

\[
= (a + da) r^2 + (b + db) r^3 + (c + dc) r^4 + \ldots \quad (3.8)
\]

and, since this is true for all values of \( r \), we may equate the coefficient of powers of \( r \) to obtain

\[
d\nu/dr = 3b; \quad \frac{db}{dr} = 4c \ldots \text{etc.} \quad (3.9)
\]

If we expand the total potential energy, \( \Psi \), into a Taylor series, we have

\[
\Psi = \Psi_0 + r_0 \left( \frac{d\Psi}{dr} \right)_{r=r_0} + \frac{r_0^2}{2!} \left( \frac{d^2\Psi}{dr^2} \right)_{r=r_0} + \ldots \quad (3.10)
\]

Comparing it with the equation (3.4) we get

\[
a = \frac{1}{2} \left( \frac{d^2\Psi}{dr^2} \right)_{r=r_0}; \quad b = \frac{1}{6} \left( \frac{d^3\Psi}{dr^3} \right) \ldots \text{etc.} \quad (3.11)
\]
With this two-atom model picture of Eastbrook\textsuperscript{4)} we now proceed to derive the relation for $\alpha$. The rate of change of $kT \log Z$ with interionic distance $r$ is

$$\Omega = kT \frac{d}{dr} (\log Z) \quad (3.12)$$

which from eqn. (3.6) on neglecting the higher order terms to a first approximation, becomes

$$\Omega = \frac{1}{(2a)^3} \left( \frac{d\alpha}{dr} \right)_{r=r_0} \left( \frac{-kT + \frac{15}{4} \frac{e^2}{a^2} k^2 T^2 - \frac{105}{16} \frac{b^2}{a^3} k^2 T^2}{1 - \frac{3}{4} \frac{e^2}{a^2} k T + \frac{15}{16} \frac{b^2}{a^3} k T} \right) \quad (3.13)$$

The coefficient of linear thermal expansion is defined as

$$\alpha = \left( \frac{1}{\eta_0} \right) \left( \frac{\partial x}{\partial T} \right) \quad (3.14)$$

where $x$ is the change in $r_0$ ($r_0 - r = x$) due to thermal expansion. Following Smyth\textsuperscript{7)} and considering that the main contribution is due to the quadratic term, we have

$$x = \left( \frac{\Omega}{2a} \right) \quad (3.15)$$

and

$$\alpha = \frac{1}{2a r_0} \left( \frac{\partial \Omega}{\partial T} \right) \quad (3.16)$$

By virtue of eqns. (3.7) and (3.13), the eqns. (3.14) for $\alpha$ becomes

$$\alpha = -\frac{1}{(2a r_0^2)} \left( \frac{1}{2} \right) \left( \frac{d\Omega}{dr} \right) \left[ C_v + \frac{75}{8} \frac{b^2}{a^3} k^2 T - \frac{9}{2} \frac{c^2}{a^2} k^2 T \right] \quad (3.17)$$
which is derived by the consideration of only one oscillator. In this equation \( C_v \) is the specific heat at constant volume given by

\[
C_v = k \left[ 1 + \left( \frac{15}{8} \frac{b^2}{a^3} - \frac{3}{2} \frac{c}{a^2} \right) kT \right]
\]

A solid containing \( n \) atoms is equivalent to a system of \( 3n \) oscillators of the same frequency \( \omega \) within Einstein’s approximation. In case of the type of ionic crystals that have been considered here there is a basis of two atoms and if one considers \( n \) ions of each kind present in the crystal, the system will be equivalent to \( 6n \) oscillators. Since the coefficients \( a, b, c, \ldots \) etc., can also be represented by eqn. (3.11), the equation for \( \alpha \) finally becomes,

\[
\alpha = -\left( \frac{C_v}{2\gamma_0} \right) \left( \frac{\psi'''}{\psi''^2} \right) - \left( \frac{450}{2\gamma_0} \right) \left( \frac{b^2 k^2 T}{\psi''^2} \right) \frac{\psi'''}{\psi''^3} + \left( \frac{108 c k^2 T}{2\gamma_0 \gamma''^2} \right) \left( \frac{\psi'''}{\psi''^3} \right)
\]  

(3.18)

with

\[
C_v = 6k \left[ 1 + \left( \frac{15}{8} \frac{b^2}{a^3} - \frac{3}{2} \frac{c}{a^2} \right) kT \right]
\]  

(3.19)

showing, therefore, that the specific heat will vary linearly with \( T \) above its classical value at high temperature due to anharmonicity.

The eqn (3.18) for \( \alpha \) derived for the first time on the basis of anharmonic considerations, has a few important features. It contains contributions from the third- and fourth-order anharmonicity terms, which are important at high temperatures. The first term of
eq. (3.18) is the same as has been derived by Smyth using a harmonic model and allowing the vibrational frequency to depend on volume (the quasi-harmonic approximation). This treatment was thus unable to explain the increase of the specific heat at constant volume, $C_v$, beyond its saturation value at high temperatures. As such, the present theory is more complete and adequate and eq. (3.18) explains the increase of $C_v$ at high temperatures due to the contributions of cubic and other higher-order anharmonicity terms.

3.1.3 Calculations of $\alpha$ using Born-Mayer Potential Function:

The eq. (3.18) in conjunction with the Born-Mayer interionic potential has been applied to various types of ionic solids to calculate the thermal expansion coefficient, $\alpha$. These applications can be discussed as follows:

(a) In case of isotopic lithium hydride crystals:

The values of $\alpha$ obtained using the eq. (3.18), on the basis of Born-Mayer interaction potential, for $\delta_{LiH}$, $\gamma_{LiH}$, $\delta_{LiD}$, and $\gamma_{LiD}$ are given in Table III-1. All the experimental data required for computations were taken from the sources compiled by Bowen (Table II-1).
Bouman\(^9\) has calculated the values of \(\alpha\) for these solids and his results have been compared with the present and experimental values\(^10\) in Table III-2.

(b) In case of alkali halide crystals:

The values of \(\alpha\) computed using eq (3.10) and the modified Born-Mayer potential (eq 1.11) for alkali halides are given in Table III-3. In this case, the experimental values of \(C_p\) used in the computation for \(\alpha\) were obtained from the experimental \(C_p\) values listed by Kussner\(^9\) and the standard thermodynamic relation

\[
C_p - C_v = \frac{(3\alpha)^2 V T}{\beta T}
\]

All the other data required for computations have already been given in Chapter II.

(c) In case of other ionic crystals:

The eq (3.10) has been tested in conjunction with Born-Mayer potential in case of a few more ionic crystals (Table III-4) which included metal fluorides, tellurium, silver, ammonium and copper halides and a few metal oxides and sulfides. The eq (3.10) has also been tried on SiC which is a semi-conductor.
The experimental data used in the computation for solids which have not been studied in Chapter II are listed in the Table III-4 itself.

In all these Tables III-1 to III-4, $\lambda_{eh}$ is the values of $\lambda$ obtained using the first term and $\lambda_{anh}$ is the contribution due to second and third terms of anharmonicity, of the right hand side of Eq. (3.16)

3.1.4 Discussion of the results obtained using Eq. (3.16):

For the case of isotopic lithium hydride crystals (Tables III-1 and III-2), Bowser\textsuperscript{8} has recently calculated the thermal expansion coefficient $\alpha$ using the Born-Mayer interaction potential (Eq. 1.10) in an attempt to study the isotopic effect on $\alpha$. Using the equation for $\alpha$ derived by Smyth\textsuperscript{7} and Kumar\textsuperscript{9} under the quasi-harmonic approximation (Eq. 3.16 after dropping the second and third terms on the right hand side), Bowser found his results to be more reliable than the earlier Nordman and Lipson's values\textsuperscript{11} predicted from the quasi-theoretical calculations. However, the calculated values of $\alpha$ for these isotopic crystals by Bowser\textsuperscript{8} were found to be smaller than the corresponding experimental values in every case.
TABLE III-1

Values of the thermal expansion coefficient, $\alpha \ (10^{-6}/\text{deg})$, calculated using eq. (3.18) for isotopic lithium hydride crystals at room temperature.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$\lambda _\text{ch} \ (\text{Bowman})$</th>
<th>$\lambda _\text{NH}$</th>
<th>$\lambda \ (\text{ch}+\text{NH})$</th>
<th>$\lambda \ _\text{expt.}$</th>
<th>Red mass (M proton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{6}\text{LiH}$</td>
<td>32.4</td>
<td>1.87</td>
<td>33.27</td>
<td>$34.4\times10^6$</td>
<td>0.863</td>
</tr>
<tr>
<td>$^{6}\text{LiD}$</td>
<td>36.4</td>
<td>1.85</td>
<td>38.25</td>
<td>$38.4\times10^6$, $39.5\times10^6$, $39.1\times10^6$</td>
<td>1.810</td>
</tr>
<tr>
<td>$^{7}\text{LiH}$</td>
<td>32.9</td>
<td>1.86</td>
<td>33.76</td>
<td>$37.4\times10^6$, $35.2\times10^6$, $40.1\times10^6$, $34.7\times10^6$</td>
<td>0.862</td>
</tr>
<tr>
<td>$^{7}\text{LiD}$</td>
<td>37.2</td>
<td>1.84</td>
<td>39.04</td>
<td>$42.9\times10^6$, $41.2\times10^6$, $3.965$, $41.4\times10^6$, $40.8\times10^6$</td>
<td></td>
</tr>
</tbody>
</table>

Ref. 10a) : $\alpha$ between 25 and 160°C
Ref. 10b) : $\alpha$ at 25°C from Fig. 3
Ref. 10c) : $\alpha$ at 25°C
Ref. 10d) : $\alpha$ at 20°C for $^{6}\text{Li}$
Ref. 10e) : $\alpha$ between 8-69°C for $^{6}\text{Li}$
### TABLE III-2

**Ratio of $\alpha$ to $\beta$ for isotopic lithium hydride crystal**

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Dushman</th>
<th>Present Investigation</th>
<th>Experimental$^{10)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{\alpha}{\beta}$ for $^7\text{Li}$</td>
<td>0.656, 0.66$^{11)}$</td>
<td>0.663</td>
<td>0.672$^{10a)}$, 0.665$^{10d)}$, 0.660$^{10e)}$</td>
</tr>
<tr>
<td>$\frac{\alpha}{\beta}$ for $^6\text{Li}$</td>
<td>0.643</td>
<td>0.970</td>
<td>0.996$^{10a)}$</td>
</tr>
<tr>
<td>$\frac{\alpha}{\beta}$ for $^9\text{Li}$</td>
<td>0.984</td>
<td>0.985</td>
<td>0.926$^{10a)}$</td>
</tr>
<tr>
<td>$\frac{\alpha}{\beta}$ for $^7\text{Li}$</td>
<td>0.978</td>
<td>0.980</td>
<td>0.995$^{10a)}$, 0.980$^{10b)}$</td>
</tr>
</tbody>
</table>
On a comparison of the calculated values of \( \alpha \) with those obtained experimentally\(^9,10\), it can be seen from Table XIII-2 that the present calculated values of \( \alpha \) are in a more satisfactory agreement in every case which resulted after the addition of considerable anharmonic contributions to Bowan's values. The ratio of \( \alpha \)'s for different isotopes are given in Table XIII-2, along with Bowan's and experimental values. The agreement between the present and the experimental values is found to be considerably improved over those obtained by Bowan\(^5\).

The values of \( \alpha \) computed for alkali halides are listed in Table XIII-3. It is seen from this table that the eq. (3.16) yields values of \( \alpha \) which are in satisfactory agreement with those obtained experimentally\(^13\) for the cases of lithium, sodium and cesium halides. For the cases of potassium and rubidium halides, the agreements are, however, not so satisfactory. For these alkali halides it can be noted that as we move down the Table, that is towards the higher reduced mass of the solid, the disagreement is becoming more and more conspicuous. The anharmonic contribution to \( \alpha \) has also been found to increase with the reduced mass and lie between 5 to 10\% of the value of \( \alpha \). The increase in the anharmonic contribution with the reduced mass may be explained to be due to the increase in ionic radii of cations, increasing
<table>
<thead>
<tr>
<th>Crystal</th>
<th>$\alpha$ (cm$^2$/cm)</th>
<th>$\alpha$ (cm$^2$/cm)</th>
<th>($\alpha_{\text{ch}} + \alpha_{\text{arh}}$)</th>
<th>$\alpha$ (cm$^2$/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>29.98</td>
<td>0.76</td>
<td>30.74</td>
<td>34.0</td>
</tr>
<tr>
<td>LiCl</td>
<td>39.38</td>
<td>1.33</td>
<td>40.61</td>
<td>44.0</td>
</tr>
<tr>
<td>LiBr</td>
<td>45.05</td>
<td>1.32</td>
<td>46.37</td>
<td>50.0</td>
</tr>
<tr>
<td>LiI</td>
<td>52.07</td>
<td>1.55</td>
<td>53.62</td>
<td>59.0</td>
</tr>
<tr>
<td>NaF</td>
<td>37.14</td>
<td>0.96</td>
<td>38.10</td>
<td>36.0</td>
</tr>
<tr>
<td>NaCl</td>
<td>40.12</td>
<td>1.33</td>
<td>41.45</td>
<td>40.0</td>
</tr>
<tr>
<td>NaBr</td>
<td>43.44</td>
<td>1.56</td>
<td>45.00</td>
<td>43.0</td>
</tr>
<tr>
<td>NaI</td>
<td>48.19</td>
<td>1.82</td>
<td>47.91</td>
<td>48.3</td>
</tr>
<tr>
<td>KCl</td>
<td>45.14</td>
<td>1.70</td>
<td>46.84</td>
<td>38.3</td>
</tr>
<tr>
<td>KBr</td>
<td>47.66</td>
<td>1.82</td>
<td>49.48</td>
<td>40.0</td>
</tr>
<tr>
<td>KI</td>
<td>51.10</td>
<td>2.12</td>
<td>53.22</td>
<td>45.0</td>
</tr>
<tr>
<td>RbCl</td>
<td>47.27</td>
<td>1.96</td>
<td>49.22</td>
<td>36.0</td>
</tr>
<tr>
<td>RbBr</td>
<td>48.69</td>
<td>2.12</td>
<td>50.81</td>
<td>38.0</td>
</tr>
<tr>
<td>RbI</td>
<td>49.31</td>
<td>2.22</td>
<td>51.53</td>
<td>43.0</td>
</tr>
<tr>
<td>CsCl</td>
<td>47.33</td>
<td>4.01</td>
<td>52.34</td>
<td>56.0</td>
</tr>
<tr>
<td>CsBr</td>
<td>49.46</td>
<td>5.57</td>
<td>55.03</td>
<td>47-52.25</td>
</tr>
<tr>
<td>CsI</td>
<td>52.68</td>
<td>6.35</td>
<td>59.03</td>
<td>47-54.25</td>
</tr>
</tbody>
</table>
thereby the overlapping of the electron clouds of the ions and giving therefore more anharmonicity in the potential energy function. Such a trend is also obvious from the last column of Table III-1 for the isotopic lithium hydride crystals.

From Table III-4 we note that the agreement between the calculated and the experimental value of \( \lambda \) are quite satisfactory. These agreements are better even than those observed in cases of lithium, sodium and cesium halides. For CsF, SrF, and BaF, like the earlier case of reiteration frequency computation, the Verschuyl-Shukla model has been found to yield better results in comparison to Born-Mayer model.

From a close observation of Tables III-3 and III-4 it is seen that the theoretical values of \( \lambda \), calculated using eq.(3.18), are showing a trend that \( \lambda \) is increasing when both the anion and cation of higher ionic radii are substituted. In the experimental measurements\(^{13}\) this trend is found to be less pronounced, particularly when an anion of higher ionic radius is substituted. In case of fluorides of lithium, sodium, potassium and rubidium, for example, the experimental values of \( \lambda \) have been found nearly to be the same, while in case of chlorides of these alkali metals, only slightly decreasing trend has been noticed. These trends thus suggest that the thermal expansion coefficient is not that sensitive to the substitution
<table>
<thead>
<tr>
<th>Crystal</th>
<th>$\alpha_{\text{qh}}$</th>
<th>$\alpha_{\text{anh}}$</th>
<th>$(\alpha_{\text{qh}} + \alpha_{\text{anh}})$</th>
<th>$\alpha_{\text{exp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeF₆</td>
<td>39.76 (25.66)</td>
<td>0.86 (0.22)</td>
<td>40.62 (15.88)</td>
<td>20.3</td>
</tr>
<tr>
<td>SnF₆</td>
<td>44.27 (17.29)</td>
<td>1.12 (0.27)</td>
<td>45.39 (17.56)</td>
<td>15.12</td>
</tr>
<tr>
<td>BaF₂</td>
<td>47.43 (10.72)</td>
<td>3.12 (1.10)</td>
<td>50.55 (19.82)</td>
<td>20.3</td>
</tr>
<tr>
<td>CuCl</td>
<td>20.36</td>
<td>2.37</td>
<td>22.63</td>
<td>22.8</td>
</tr>
<tr>
<td>CuBr</td>
<td>21.23</td>
<td>2.61</td>
<td>23.84</td>
<td>20.7</td>
</tr>
<tr>
<td>TiCl₄</td>
<td>49.29</td>
<td>4.34</td>
<td>53.59</td>
<td>56.0</td>
</tr>
<tr>
<td>Ni₄Cl₂</td>
<td>47.69</td>
<td>4.31</td>
<td>52.20</td>
<td>47.3</td>
</tr>
<tr>
<td>Ni₄Br₂</td>
<td>48.30</td>
<td>4.66</td>
<td>53.16</td>
<td>53.9</td>
</tr>
<tr>
<td>MgO</td>
<td>7.66</td>
<td>1.19</td>
<td>9.05</td>
<td>18.0²⁵</td>
</tr>
<tr>
<td>CaO</td>
<td>10.53</td>
<td>1.12</td>
<td>11.67</td>
<td>12.5</td>
</tr>
<tr>
<td>SrO</td>
<td>11.15</td>
<td>0.92</td>
<td>12.07</td>
<td>13.72</td>
</tr>
<tr>
<td>BaO</td>
<td>10.74**</td>
<td>0.06</td>
<td>10.62</td>
<td>13.16</td>
</tr>
<tr>
<td>ZnS</td>
<td>6.92</td>
<td>0.17</td>
<td>7.09</td>
<td>6.3</td>
</tr>
<tr>
<td>SiC</td>
<td>4.67</td>
<td>0.06</td>
<td>4.73</td>
<td>4.0 ± 0.3</td>
</tr>
</tbody>
</table>

* In parentheses are given the $\alpha$ values calculated using the Vereshchagin-Shchelina (eq. 1.16) model. The value of $G_v = 11.62 \times 10^{-16} \text{erg}$
deg for GeF₆ has been used for SnF₆ and BaF₂ as well.

** at 473°C; $G_v = 12 \text{cal/mole}$ has been used.
of anions. Our theoretical equation however shows a
increasing trend in $\alpha$ with substitution of anions having
higher ionic radii. The trend observed with the
substitution of cation matches satisfactorily with that
obtained from theory. These differences might be due to
the simplified two-atom model picture assumed in the
derivation of eq. (3.18). The smaller the ratio of the
ionic radii of anion and cation, the larger the difference
between the theoretical and experimental values of $\alpha$ have
been found.

The present theory is deficient in the sense that
the contributions due to the polarization, which has an
effect on the amplitude of atomic vibrations, have not
been taken into account. Since, these contributions
increase with the decrease in the ratio of the ionic
radii; as we move from lithium halides to rubidium
halides in Table III-3, the calculated values of $\alpha$
becoming more and more approximate. This is also the
reason that due to the low polarizability of the ions of
the solids of Table III-4, the values of $\alpha$ calculated
in this case using the simple Born-Mayer model (eq. 1.10)
are in better agreement with the experimental values than
those obtained in case of alkali halides using even the
more realistic modified Born-Mayer (eq. 1.11) potential.
A third short-coming of the theory, although minor in nature, is that to avoid the computational difficulties, the contributions beyond first nearest neighbours have not been considered. Since these contributions have been shown to be very small\(^{15}\), lying well within the experimental errors of the various input data used, their contributions to the calculated values of \(\alpha\) are negligible.

Due to these reasons, Liner\(^9\) in his original equation for \(\alpha\), derived under the quasi-harmonic approximation (\(\alpha_{\text{qh}}\) term of present work), made arbitrary modifications to include the contributions due to some of the above factors. It is also interesting to note that because of these modifications Liner\(^9\) obtained satisfactory results even with such a simple potential as that due to inverse power law for the repulsive forces (eq.1.9) which has been shown\(^{15}\) to yield invariably poor results in comparison to the Born-Mayer potential, and also without including the contributions of the Van der Waal's and anharmonic cubic and higher order terms.

The present investigation thus presents a clearer picture on the study of \(\alpha\) of ionic crystals in which the effect of Van der Waal's terms and the anharmonic effects have been explicitly considered and all the arbitrary modifications of Liner\(^9\) have been removed. Moreover, unlike Liner's equation\(^9\), our eq. (3.18) for \(\alpha\) is general and can be used with any interatomic potential and also at any temperature.
3.1.5 On the Applicability of Various Potential Energy Functions for the Calculation of $\alpha$ of Ionic Solids

Uptil now, our discussions for $\alpha$ have been confined to the Born-Mayer interatomic potential except the case of CaF$_2$, BaF$_2$, and SrF$_2$. Quantitative calculations of anharmonic effects on various properties have been extensively carried out for various models with short-range central forces in case of rare gas solids. Since the ions of the alkali halides and a few metal oxide crystals studied here have the electronic configurations of inert gas atoms it is interesting to compare the results obtained in the two cases. Calculations of crystal properties in case of rare gas solids at low temperatures$^{16}$ indicate that the anharmonic effects are dominated by the nearest neighbour interaction and therefore depend primarily on the shape of the pair potential $\phi$ in the neighbourhood of its minimum at $r = r_0$, and, in particular, on the ratios $r_0$, $\phi''/\phi'$ and $r_0^3$, $\phi'''/\phi''$. If it is found that the calculations agree for a particular model with the available experimental data, we shall then have a model which can be used to evaluate other anharmonic effects which are not known experimentally. On the other hand, a disagreement will suggest that the shape of the pair potential at $r_0$ is not given even approximately by this potential. Unfortunately, neither theory nor experiment is at present sufficiently established to make a reliable comparison.
Using the other forms of the repulsive energy - the Lennard-Jones (6-12) form, the Morse form and the inverse power law form - the values of $4''/4''$ and $4''/4''$ were calculated and it had been found that these values were very low in cases of all the crystals studied here. Consequently, the values of $\alpha$ were also found to be very low when compared to the experimental values. It was, therefore, concluded that the simple exponential form of Born-Meyer represented the repulsive energy most satisfactorily than any other form.

3.1.6 High Temperature Dependence of the Thermal Expansion Coefficient of Ionic Solids:

A few attempts\textsuperscript{17-19) have been made to explain the temperature-dependence of $\alpha$ of ionic solids at high temperatures, up to near their melting point. All these workers\textsuperscript{17-19) have tried to explain the rapid rise of thermal expansion coefficient at high temperatures as due to the creation of vacancies. However, Eastabrook\textsuperscript{4) has discarded the theory of vacancies generation for the explanation of the increase in $\alpha$ at high temperature and indicated that the temperature-dependence of $\alpha$ at high temperatures could be satisfactorily explained by taking into account the contributions of cubic and higher-order anharmonicity terms of the potential energy function. More recently, Shah\textsuperscript{20) has shown that the large variation of $\alpha$ at high temperatures is almost certainly an anharmonic effect
and it is probably a higher-order anharmonic effect because the change in $\alpha$ could not be explained in terms of quasi-harmonic theory, even if allowance is made for the volume change of the crystal with temperature. He also explicitly evaluated the magnitude of the higher-order anharmonic contributions over and above the volume-dependent contribution.

Using eq. (3.16) the temperature dependence of $\alpha$ of LiF and MgO crystals at high temperatures have been studied. Following the procedure adopted in the earlier sections, the values of $\alpha$ for LiF and MgO crystals at high temperatures have been calculated using the Born-Mayer potential and are reported in Tables III.5 and III.6, respectively. Besides the values of $\alpha$ calculated using the experimental $C_V$ values $^{9,21,22}$, the values of $C_V$ from eq. (3.19) have also been computed and the values of $\alpha$ thus obtained are listed in these Tables.

From Tables III.5 and III.6 it is thus seen that the general theoretical behaviour of the coefficient of thermal expansion agrees fairly well with the observed experimentally $^{23-26}$. The anharmonic contributions are increasing with the rise in temperature and at higher temperatures their magnitudes are considerable $^{27}$. A comparison for the case of LiF and MgO crystals shows that for lighter ions (LiF) the magnitude of anharmonic contributions are larger than for crystals having heavier ions (MgO). A similar conclusion has been drawn by Barron et al. $^{28}$ in their studies on the heat capacities of ionic solids.
### Table III.5

Study of the thermal expansion coefficient, $\lambda$ ($10^{-6}$/deg), of LiF at high temperatures on the basis of eq (3.16)

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$G_v$ (cal/mol deg) (Calc. using eq 3.19)</th>
<th>$\lambda$</th>
<th>$\lambda$ (eqn 3.19)</th>
<th>$\lambda$ (eqn 3.19)</th>
<th>exp$\mu$</th>
<th>ref 23</th>
<th>ref 24</th>
<th>ref 26</th>
</tr>
</thead>
<tbody>
<tr>
<td>673</td>
<td>12.29</td>
<td>45.41</td>
<td>64.42</td>
<td>50.02</td>
<td>49.80</td>
<td>49.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>723</td>
<td>12.23</td>
<td>46.01</td>
<td>7.66</td>
<td>53.63</td>
<td>52.24</td>
<td>52.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>773</td>
<td>12.27</td>
<td>47.69</td>
<td>8.95</td>
<td>56.52</td>
<td>54.42</td>
<td>56.24</td>
<td>54.55</td>
<td></td>
</tr>
<tr>
<td>823</td>
<td>12.31</td>
<td>49.51</td>
<td>10.35</td>
<td>60.06</td>
<td>56.44</td>
<td>59.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>873</td>
<td>12.37</td>
<td>51.36</td>
<td>12.47</td>
<td>64.03</td>
<td>58.49</td>
<td>63.68</td>
<td>60.26</td>
<td></td>
</tr>
<tr>
<td>923</td>
<td>12.44</td>
<td>53.93</td>
<td>14.06</td>
<td>68.79</td>
<td>60.67</td>
<td>67.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>973</td>
<td>12.50</td>
<td>56.46</td>
<td>17.72</td>
<td>74.18</td>
<td>62.56</td>
<td>72.06</td>
<td>66.46</td>
<td></td>
</tr>
</tbody>
</table>

* Calculated using experimental $G_v$ values."
## Table III-6

Study of the thermal expansion coefficient, \( \alpha \times 10^{-6} / \text{deg} \), of MgO crystal at high temperatures on the basis of eq. (3.19)

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>( \varphi_0 ) (cal/deg)</th>
<th>( \varphi_0 ) (cal/deg) using eq. (3.19)</th>
<th>using expl. c. val.</th>
<th>( \alpha ) ( \text{(eq. (3.19))} )</th>
<th>( \alpha ) ( \text{calc.} )</th>
<th>c, val. PG</th>
<th>ref. 23</th>
<th>ref. 24</th>
<th>ref. 25</th>
</tr>
</thead>
<tbody>
<tr>
<td>1073</td>
<td>12.00</td>
<td>14.35</td>
<td>14.30</td>
<td>0.58</td>
<td>14.93</td>
<td>14.88</td>
<td>16.14</td>
<td>16.34</td>
<td>15.30</td>
</tr>
<tr>
<td>1173</td>
<td>12.02</td>
<td>14.76</td>
<td>14.67</td>
<td>0.66</td>
<td>15.42</td>
<td>15.53</td>
<td>16.76</td>
<td>17.10</td>
<td>15.60</td>
</tr>
<tr>
<td>1273</td>
<td>12.02</td>
<td>15.13</td>
<td>15.03</td>
<td>0.74</td>
<td>15.87</td>
<td>15.17</td>
<td>17.38</td>
<td>17.66</td>
<td>15.80</td>
</tr>
<tr>
<td>1373</td>
<td>12.04</td>
<td>15.79</td>
<td>16.03</td>
<td>0.90</td>
<td>16.69</td>
<td>17.33</td>
<td>19.66</td>
<td>19.50</td>
<td>16.30</td>
</tr>
<tr>
<td>1473</td>
<td>12.06</td>
<td>16.49</td>
<td>17.40</td>
<td>1.09</td>
<td>17.52</td>
<td>18.49</td>
<td>19.68</td>
<td>21.20</td>
<td>16.80</td>
</tr>
<tr>
<td>1673</td>
<td>12.06</td>
<td>17.50</td>
<td>18.73</td>
<td>1.30</td>
<td>18.88</td>
<td>20.11</td>
<td>20.49</td>
<td>22.08</td>
<td>17.20</td>
</tr>
</tbody>
</table>

* extrapolated at these temperatures from the experiment-1 data.
This investigation thus confirms the conclusions of Bestebroer\(^4\) and Shah\(^20\) that increase in the thermal expansion coefficient of solids at high temperatures are due to the anharmonicity in the lattice vibrations, which is more pronounced at high temperatures, in a quantitative way\(^27\).

3.1.7 Application of Eq. (3.18) in case of some molecular crystals

An interesting and important application of eq. (3.18) has been recently made to the case of organic molecular crystals of some globular hydrocarbons\(^29\). The solids of naphtha (C\(_4\)H\(_8\)), neopentane (C\(_5\)H\(_{12}\)), bicycle [2,2,2] octane (C\(_6\)H\(_{14}\)) and adamantane (C\(_6\)H\(_{14}\)) fall into such a category since they retain their molecular symmetry in the solid state also. Since this study does not form the basis of the present thesis, the results will be discussed in brief only.

In Table XIII-7 are listed the calculated values of \(\beta\) for bicycle [2,2,2] octane and adamantane using the Leonard-Jones (6-12), modified Buckingham, the 6-6 (modified Born model) and the Morse potential functions. The data for computations were taken from the compilation of Breitling et al\(^{29}\).

From this Table it is seen that, like the case of ionic crystals, the contributions due to the anharmonicity
### Table III-7

Application of eq. (3.18) to the molecular crystal of bicyclo[2.2.2]octane and adamantane

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Lennard-Jones (6-12)</th>
<th>H-6 Function</th>
<th>Modified Buckingham Function</th>
<th>Morse Function</th>
<th>29) exp1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>qh</td>
<td>mnh</td>
<td>(10(^{-4}) deg.)</td>
<td>qh</td>
<td>mnh</td>
</tr>
<tr>
<td>Bicyclo[2.2.2]</td>
<td>0.87</td>
<td>0.24</td>
<td>1.47</td>
<td>3.35</td>
<td>0.33</td>
</tr>
<tr>
<td>adamantane</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.77</td>
<td>0.70</td>
</tr>
</tbody>
</table>
terms to $\alpha$ are significant for those molecular crystals as well. For adamantane and bicyclo [2.2.2] octane, the $8-6$ potential function, where both attractive and repulsive forces are represented by inverse power law, has been found to be suitable for such calculations. The agreement between the theoretical and experimental values of $\alpha$ further demonstrates that our eq. (3,18) is successful for computing $\alpha$ for these solids as well.
3.2 EXPERIMENTAL STUDY

3.2.1 Different Methods for the Measurement of $\alpha$

The different methods for the measurement of the thermal expansion coefficient can be broadly classified under two categories:

(i) Macromolecular expansion measurements and
(ii) Lattice expansion measurements.

The following methods are included in the macromolecular expansion measurements:

(a) Pycnometer and dilatometer methods:

The volume expansion coefficient of a solid is determined by the volume of the liquid or gas it displaces\(^{30}\). These methods do not yield the anisotropy in the expansion coefficient of crystals.

(b) Comparator method:

The change in length of a long rod of the solid is measured with the aid of a comparator or a similar apparatus. This method has been of very little use in studying the expansion of crystals, since long specimens of many crystals are difficult to obtain.

(c) Mirror and optic lever methods:

The change in length of the specimen causes a tilt of a mirror or optic lever arrangement and this is determined with the aid of a scale and telescope. This method is capable of great accuracy.
(d) Heterodyne beat method:

The capacity of a condenser in an oscillatory circuit is altered by the expansion of the specimen. The change in the frequency of the oscillator can be detected by the heterodyne beat method and can be compensated for by altering the capacity of a standard condenser. The change in capacity needed for compensation is a direct measure of the expansion of the specimen.

(e) Interference methods:

The principle of all the methods coming under this heading is the same. The expansion of the specimen causes an alteration in the optical path of two interfering light beams thereby causing a shift in the interference pattern produced by the light beams. The method was originally applied by Fizeau and has been discussed by Kerrit \(^{31}\) in detail. The designed features of the apparatus includes a furnace, a temperature measuring device and the interferometer. The visual method has been employed by counting the fringes and the time of transit of the fringes at different temperatures were measured. No correction due to air film between the interferometric plates should also be applied for the accurate value of \(\alpha\).
The modification of Peters\textsuperscript{32}) is best suited for the measurement of expansion of crystals obtainable in the form of small specimens. In this apparatus three small pyramids of the crystal cut in the required direction are used as spacers between two interferometer plates of fused quartz. Provided the heights of the specimens are equal to within $1/2000^{\text{th}}$ cm., interference fringes of the wedge type are formed when a beam of monochromatic light is made to fall on the interferometer plates by a suitable optical arrangement. The crystal pyramids and the interferometer plates are enclosed in a furnace and the transit of the fringes across a reference mark as the specimens are heated is either noted visually or recorded by a photomultiplier tube arrangement.

The interference methods have the following advantages: (i) small specimens can be employed; (ii) measurements are absolute; (iii) anisotropies in thermal expansion can be studied even with crystals available in small sizes; and (iv) dynamic measurements are possible.

In case of the lattice expansion measurements methods, the alteration in the distance between the atomic planes, or the lattice spacing, consequent to the expansion of the specimen, is determined by the change in glancing angle for a given reflection of an X-ray beam of known wavelength from the planes. Two principal methods are in vogue: (a) The single crystal Bragg reflection method and (b) the powder and rotation photograph method.
In the first method the glancing angle of reflection of an x-ray beam at a single crystal is measured as a function of temperature. Several modifications\textsuperscript{33)} of this method has been used by various workers.

In the second method the shifts in the position of the lines in powder photographs or spots in rotation photographs are measured as a function of temperature. Special cameras have been designed for this purpose\textsuperscript{34)}.

The asymmetric powder photograph method evolved by Streunnic\textsuperscript{33)} yields accurate measurements up to 70\(^\circ\)C of the lattice expansion coefficient of substances over small temperature intervals. Numerous corrections have been applied to these methods\textsuperscript{36)}.

3.2.2 Measurement of the Thermal Expansion Coefficient of Ionic Crystals

A number of attempts have been made to measure the thermal expansion coefficient of ionic crystals, mostly alkali halides. Since a majority of ionic crystals crystallize in the cubic system, only one independent constant defines the thermal expansion coefficient. Sharma\textsuperscript{34)} has used a modified form of the interferometric method to measure the thermal expansion coefficient of sodium chloride, sodium bromate, magnetite, fluorite, ammonium chloride, ammonium bromide, silver bromide, lithium fluoride, and magnesium oxide crystals. Sreenivasan\textsuperscript{37)} has also measured
the thermal expansion coefficients of a few ionic crystals, which were not included in the study of Sharan.\textsuperscript{24}

Another method, using the X-ray photograph of the powdered sample obtained with a Debye-Scherrer camera, has been used to measure the lattice parameter and hence the thermal expansion coefficient by Deshpande and Co-workers\textsuperscript{25}. The results of the thermal expansion coefficient measurements of the earlier workers have already been summarized in the American Institute of Physics - Handbook.\textsuperscript{26}

In the measurement of \( \alpha \) using the X-ray powder photograph technique, it is not possible to measure the specimen temperature directly; the lattice constant of some standard sample is used as an indicator of temperature. Further, the X-ray photographic technique usually takes too much time for the measurements of the lattice parameters at various temperatures for a particular sample. Moreover, measurements at low temperatures are also not possible.

With the advent of X-ray diffractometers, now commercially available, these difficulties and limitations of the photographic technique have been overcome and the lattice parameter can now be measured with a precision of \( \pm 0.0001 \) Å.

Using the O.K. XRD diffractometer Arivastava and Herchand\textsuperscript{27} have recently remeasured the thermal expansion coefficients of alkali halides from room temperature to near their melting points and bridged the gap which were existing between the various earlier measurements. In the present study we have used this method to measure the thermal...
expansion coefficient of ionic crystals of HIO and 
Ag₂O - both of which are used as oxidation catalysts 
in petroleum and chemical industries from liquid nitrogen 
temperatures to about 650°C. The high temperature 
measurements have been done using a 'Zen-Pres' research 
furnace designed to provide a spherical zone of uniform 
temperature. The low temperature measurements have been 
done using a low temperature attachment designed and 
constructed for this purpose in our laboratory.

3.2.3 Instrumentation:

1) The General Electric XRD-6 Diffractometer:

The essential features of these diffractometers 
are shown in Fig 3.1. A powder specimen C, in the 
form of a flat plate, is supported on a table H, which 
can be rotated about an axis G perpendicular to 
the plane of the drawing. The x-ray source is S, 
the line focal spot on the target F of the x-ray 
tube; G is also normal to the plane of the drawing 
and therefore parallel to the diffractometer axis 0. 
X-rays diverge from this source and are diffracted 
by the specimen to form a convergent diffracted beam 
which comes to a focus at the slit F and then 
enters the counter G (a proportional counter). A 
and B are special slits which define and collimate 
the incident and diffracted beams.
FIG. 3-1 X-RAY DIFFRACTOMETER (SCHEMATIC)

C: Powder Specimen.
H: Supports.
O: Diffractometer Axis
A, B, F: Slits.
S: X-Ray Source.
T: Target of the X-Ray Tube.
G: Counter
E: Carriage
K: Graduated Scale.
The receiving slits and counter are supported on the carriage \( \text{c} \), which may be rotated about the axis \( 0 \) and whose angular position \( 29 \) may read on the graduated scale \( \text{g} \). The supports \( \text{e} \) and \( \text{h} \) are mechanically coupled so that a rotation of the counter through \( 2\pi \) degrees is automatically accompanied by rotation of the specimen through \( \pi \) degrees. This coupling ensures that the angles of incidence on, and reflection from, the flat specimen will always be equal to one another and equal to half the total angle of diffraction, an arrangement necessary to preserve focusing conditions. The counter may be power driven at a constant angular velocity about the diffractometer axis or moved by hand to any desired angular position.

The way in which a diffractometer is used to measure a diffraction pattern depends on the kind of circuit used to measure the rate of production of pulses in the counter. The pulse rate may be measured in two different ways: (a) the succession of current pulses is converted into a steady current, which is measured in the counting-rate meter, calibrated in such units as counts (pulses) per second. Such a circuit gives a continuous indication of x-ray intensity. (b) The pulses of current are counted electronically in a circuit called a scaler, and the average counting rate is obtained simply by dividing the number of pulses counted by the time spent in counting. This operation is essentially discontinuous because of the
time spent in counting and a scaling circuit cannot be used to follow continuous changes in x-ray intensity but it yields more precise measurements of intensity.

A diffractometer may be used for measurements at high or low temperatures by surrounding the specimen with the appropriate heating or cooling unit.

(12) *Zon-Prep* High Temperature-X-Ray Diffractometer Furnace, Model 30:

This furnace unit (Fig 3-2) consists of two hemispherical chambers internally wound with platinum-alloy heating elements designed for use in air or controlled atmospheres at temperature up to 1850°C. The sample holder assembly is mounted on a refractory pedestal which locates the sample in the geometric center of the heating chamber and effectively isolates it from the furnace exterior. Provision for critical alignment is made through three independent motions—translation, rotation and tilt—which are completely independent of the furnace proper. X-ray passes in and out of the furnace through an opening at value of 20 slightly greater than 180° which is covered with a thermal radiation shield.

Precise temperature control is made possible with the thermocouple-activated magnetic amplifier system.
FIG. 3-2 HIGH TEMPERATURE X-RAY DIFFRACTOMETER FURNACE
provided, and the continuously proportioning, saturable-core reactor unit permits smooth, stepless control. This is achieved by using a sensitive galvanometer and "buckling" the thermocouple (Pt = 40% Pt-20% Rh, 1200°C) with a precision voltage divider. The heating chamber produces a zone of uniform temperature such that the sample face is maintained with temperature variation of less than ±2°C at 500°C and less than ±3°C at 1400°C. Since the furnace design and precise temperature control have essentially eliminated thermal gradients and the sample temperature is measured at the sample, the inherent difficulty of comparing thermocouple and sample temperature encountered in film units is overcome.

The furnace is efficiently cooled externally by maintaining a moderate flow of air through an air-cooling ring located at the base of the unit, and by three water-cooled jackets.

(iii) The Low Temperature Attachment

The low-temperature attachment consisted of a brass chamber in which the sample is suspended through a brass rod. The chamber can be evacuated and the inside pressure can be brought down to the order of 10⁻⁶ mm of mercury. Such a high order of vacuum provided a good temperature stability over a fairly long period. A semi-circular beryllium window
is provided in the chamber for the entry and exit of X-rays. The upper portion of the brass rod (the lower portion of which is holding the sample in vacuum) is attached to a concentric hollow cylinder (having the same diameter as that of the chamber and fits over it tightly) which is filled with liquid nitrogen. The sample temperature is measured by using a copper-constantan thermocouple, one junction of which is attached to the sample, which is mounted in a metallic turret, and the other to the potentiometer. A set of heating wires are also wound on the brass rod near the sample to obtain temperatures between liquid nitrogen and room temperature.

3.2.4 Thermal Expansion Coefficient of NiO and Ag$_2$O

Both NiO and Ag$_2$O crystallize in the cubic system. The measurement of the thermal expansion coefficients of these solids have not yet been done, particularly in case of Ag$_2$O, which decomposes at about 300°C. In case of NiO, the earlier work of Nielsen and Leipold\(^{39}\) reported the measurement of the mean coefficient of thermal expansion between 473 K and 293 K, using a automatic recording dilatometer. No attempt however, seems to have been made to measure its thermal expansion below room temperature.
The x-ray diffraction patterns of various temperatures of these solids were recorded with Cu-K$_x$ radiation on a G.E. XRD-6 diffractometer equipped with 'TemP-Lens' furnace and the low-temperature attachment. The lattice parameter of NiO has been measured using four reflections 111, 200, 220 and 420 and that of Ag$_2$O using 200, 220 and 222. The values of Bragg's angle, 2$\theta$, across these planes have been precisely measured by using the point-count technique in place of strip-chart recording method$^{40}$. The accurate measurement of the lattice parameter from the diffractometer data was done using the Hilsen and Riley function$^{40}$. 

Under the experimental conditions the accuracy in the measurement of lattice parameters of NiO and Ag$_2$O was $\pm 0.002$ Å. A maximum change 2°K in temperature measurement was observed at low temperature and of 4°K in the high temperature range, in both the cases.

The values of the lattice parameter, $a_T$, of NiO and Ag$_2$O at different temperatures are given in Tables III-6 and III-9 and are plotted in Figs. 3.3 and 3.4, respectively. An orthogonal polynomial of second order with least square error approximation was fitted to the lattice parameter versus temperature data. The orthogonal nature of polynomials averted solving the simultaneous equations which builds up large round off errors. The final relationship between the lattice parameter $a_T$ and the absolute temperature $T$ was obtained in the form

$$ a_T = a_0 + a_1 T + a_2 T^2 $$

(3.20)
Table IX-8

Experimental values of the lattice parameter, \( a_\parallel (10^{-3} \text{ cm}) \), and the linear thermal expansion coefficient, \( \alpha (10^{-6}/\text{deg}) \), of HgO at various temperatures.

<table>
<thead>
<tr>
<th>( T (^\circ \text{C}) )</th>
<th>( a_\parallel )</th>
<th>( \alpha ) (eq. 3.21)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Calculated (eq. (3.20))</td>
</tr>
<tr>
<td>105</td>
<td>4.1689</td>
<td>4.169</td>
</tr>
<tr>
<td>205</td>
<td>4.1733</td>
<td>4.174</td>
</tr>
<tr>
<td>254</td>
<td>4.1769</td>
<td>4.176</td>
</tr>
<tr>
<td>305</td>
<td>4.1788</td>
<td>4.179</td>
</tr>
<tr>
<td>373</td>
<td>4.1831</td>
<td>4.183</td>
</tr>
<tr>
<td>473</td>
<td>4.1982</td>
<td>4.188</td>
</tr>
<tr>
<td>700</td>
<td>4.2013</td>
<td>4.201</td>
</tr>
<tr>
<td>813</td>
<td>4.2078</td>
<td>4.208</td>
</tr>
</tbody>
</table>
TABLE III-9

Experimental values of the lattice parameter, \(a_2\left(10^{-6}\text{cm}\right)\), and the average linear thermal expansion coefficient, \(\alpha\left(10^{-6}/\text{deg}\right)\), of Ag,9 at various temperatures.

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>(a_2) (measured)</th>
<th>T(°K)</th>
<th>(\alpha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>4.716</td>
<td></td>
<td></td>
</tr>
<tr>
<td>235</td>
<td>4.726</td>
<td></td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>4.735</td>
<td>150-298</td>
<td>31.97</td>
</tr>
<tr>
<td>390</td>
<td>4.753</td>
<td>300-620</td>
<td>116.02</td>
</tr>
<tr>
<td>435</td>
<td>4.761</td>
<td></td>
<td></td>
</tr>
<tr>
<td>520</td>
<td>4.826</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
where \( a_1 \), \( a_2 \) and \( a_3 \) are the characteristic parameters of the solid. The values of these parameters for \( \text{MIO} \) have been determined to be: \( a_1 = 4.1644 \ \AA \), \( a_2 = 0.04444 \times 10^{-6} \ \AA^2 \ K \) and \( a_3 = 0.1132 \times 10^{-7} \ \AA^2 \ K^{-2} \). With these values of the characteristic parameters, the values of \( a_T \), calculated for \( \text{MIO} \) using eq. (3.20), are given in column (3) of the Table III-8.

The thermal expansion coefficient, \( \alpha \), at each temperature was obtained as:

\[
\alpha = \left( \frac{1}{a_T} \right) \left( \frac{da_T}{dT} \right) = \left( \frac{1}{a_T} \right) (a_2 + 2a_3 T) \tag{3.21}
\]

These values of \( \alpha \) are given in the last column of Table III-8.

For \( \text{Ag}_2\text{O} \), average values of \( \alpha \) have been determined in the different temperature ranges and are given in Table III-9.

3.2.5 Discussion of the Results:

On a comparison of the present values of \( \alpha \), with the mean value of the expansion coefficient by Nelson and Leipold\(^{39}\) for \( \text{MIO} \) (obtained by using an automatic recording dilatometer) in the overlapping temperature region, we find that our values are slightly higher than those obtained by these workers. Though there are instances in literature\(^{41}\)
Fig. 3.3 Temperature-dependance of $a_t$ and $a$ of NiO
when slightly different results have been found by using a
different sampling or experimental technique, it is difficult
to comment on the possible reasons for the difference
observed in the present case, because the accuracy of the
measurement of \( \lambda \) has not been reported by Neisen and
Leipold\(^\text{39}\).

Using our theoretical equation for \( \lambda \), the value
of \( \lambda \) for \( \text{MgO} \) at room temperature has already been calculated
(Table XII-4). Keeping in view the approximate nature
of the theory and uncertainties in the various data used
in the calculation, the agreement between the theoretical
and experimental values of \( \lambda \) may be said to be fairly
satisfactory. The validity of the theoretical equation for
\( \lambda \) has been further demonstrated from the fact that by yielding
a very small contribution towards the temperature-dependent
term it shows a small temperature-dependence of \( \lambda \) for \( \text{MgO} \);
which is in agreement with the experimental measurements\(^\text{42}\).

In case of \( \text{Ag}_2\text{O} \)-unlike that of \( \text{MgO} \)-a larger dependence of
the lattice parameter on temperature has been observed\(^\text{43}\). A
possible reason for this is the fact that the temperature of
dissociation of \( \text{Ag}_2\text{O} \) is very low (\( \sim 300^\circ \text{C} \)) in comparison with
temperature of melting of \( \text{MgO} \) (\( \sim 1800^\circ \text{C} \)). A sharp increase
in the value of \( a_2 \) with temperature above about 350\(^\circ \text{K} \) has been
observed (Fig. 3,4) in case of \( \text{Ag}_2\text{O} \). Although much is not known
about the behaviour of \( a_2 \) near the melting points of solids, the
curve of Fig 3,4 for \( \text{Ag}_2\text{O} \) shows the trend which is in agreement
with the behaviour of alkali halides observed by Srivastava
\(^\text{13}\) and Merchant near the melting temperatures.
REFERENCES


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22. T. H. E. Barron, W. T. Berg and J. A. Morrison:


    40 (1934) 624.


30. For example, H. Klein: Z. Elekt. Chem. 34 (1929) 923.


