CHAPTER IV

GRÜNEISEN AND ANDERSON-GRÜNEISEN PARAMETERS OF IONIC CRYSTALS

This Chapter is divided into two parts. In the first part, the volume-dependence of the vibrational frequencies of ionic crystals - the Grünisen parameter, $\gamma$, has been studied. Expressions are derived for computing the Grünisen $\gamma$ following Slater's theory and the Einstein single frequency model. The effect of cubic, quartic and fifth-order anharmonic terms has been considered while evaluating $\gamma$ at high temperatures and a new relation has been derived. This equation has been applied to the cases of LiF, MgO and KBr crystals and a satisfactory agreement between the $\gamma_{\text{calc.}}$ and $\gamma_{\text{exptl.}}$ has been found.

In the second part of this Chapter, the volume-dependence of the bulk-modulus-the Anderson-Grünisen parameter, $\delta$, has been studied. A general relation for $\delta$ has been developed including the volume-dependent
and other anharmonic contributions. It has been shown that all the earlier equations on $\delta$ derived by various workers are the special cases of our equation. The computation of $\delta$ in case of NaCl crystal on the basis of this new equation has shown a satisfactory agreement with $\delta_{\text{exptl.}}$, which results due to the inclusion of the substantial anharmonic contributions at high temperatures.
4.1 GRÜNEISEN PARAMETER

4.1.1. Introduction:

Since the publication of Grünisen's paper\(^1\) on the equation of state of solids, a large number of workers have tried to investigate both experimentally and theoretically the physical meaning of the Grünisen parameter, \(\gamma\), and its variation with temperature and volume.

Considering the thermodynamic relation

\[
p = -\left( \frac{\partial V}{\partial V} \right)_T
\]

in conjunction with the equation for free energy (eq. 3.3)

\[
F = \gamma_0 + \sum_j kT \log \left( 1 - e^{-\frac{\Delta V_j}{kT}} \right)
\]

the equation of state of a solid can be obtained as

\[
p = -\frac{\partial \gamma_0}{\partial V} + \frac{1}{V} \sum_j \gamma_j \frac{\Delta V_j}{(e^{\frac{\Delta V_j}{kT}} - 1)}
\]

where

\[
\gamma_j = -\frac{d(\log \gamma_j)}{d(\log V)}
\]

The eq. (4.3) defines the dimensionless quantity the Grünisen parameter for the \(j\)th mode of vibration. The Grünisen parameter for the crystal will be given by the sum of such \(\gamma_j\). The thermal average taken over all the nodes gave the relation\(^2\)

\[
\gamma = \frac{\alpha_y V}{\beta_T C_V} = \frac{\alpha_y V}{\beta_s C_p}
\]
where \( \beta_T \) and \( \beta_p \) are the isothermal and adiabatic compressibilities and \( C_v \) and \( C_p \) are the specific heats at constant volume and constant pressure, respectively. The average of all the \( \gamma_j \) over the Einstein specific heat function can be taken as

\[
\gamma = \sum_{j=1}^{3N} \left\{ \frac{\gamma_j \sigma_j e^\sigma_j}{\left(e^\sigma_j - 1\right)^2} \right\} / \sum_{j=1}^{3N} \frac{\sigma_j^2 e^\sigma_j}{\left(e^\sigma_j - 1\right)^2}
\]

in which \( \sigma_j = \hbar \gamma_j / kT \) and \( 3N \) is the total number of nodes. At low temperatures we have

\[
\gamma = \gamma_0 = -d \left( \log \theta \right) / d \left( \log \nu \right)
\]

(4.6)

and at high temperatures

\[
\gamma = \gamma_\infty = \bar{\gamma_j} = \sum_{j=1}^{3N} \gamma_j / 3N
\]

(4.7)

where \( \theta \) is the Debye temperature.

4.1.2 Slater's Derivation of the Grüneisen \( \gamma \)

A simple description of the equation of state of solids and of the Grüneisen's parameter have been given by Slater. He has considered two different types of relations between the pressure \( (p) \), volume \( (V) \) and temperature \( (T) \); one of which expresses \( V \) in terms of the ascending powers of \( p \) as

\[
V = V_0 \left[ 1 + a_0 (T) + a_1 (T) p + a_2 (T) p^2 + \ldots \right]
\]

(4.8)

where \( V_0 \) is the volume of the solid at zero pressure and absolute zero of temperature; the constants \( a_0, a_1, a_2, \ldots \) etc.
are functions of temperature. It has been shown by Slater that $a_0$ is related to $\alpha$ and $a_1$ is almost equal to $\beta_T$.

The other relation represents $p$ as a power series in proportionate change in volume.

$$p = p_0(T) + p_1(T) \left( \frac{V_0-V}{V_0} \right) + p_2(T) \left( \frac{V_0-V}{V_0} \right)^2 + \cdots \quad (4.9)$$

where $p_0(T), p_1(T), p_2(T), \ldots$ etc. are functions of temperature. $p_0(T)$ is the pressure that must be applied to the solid to reduce its volume to $V_0$. Obviously $p_0(T)$ goes to zero at absolute zero. At ordinary temperatures, while it represents a considerable pressure, still it is small compared to the quantity $p_1$ and $p_2$. $p_1$ is equal to the pressure to reduce the volume to zero and thus is approximately reciprocal of the compressibility. Obviously this is much greater than the pressure required to reduce the volume to $V_0$.

Neglecting the square and higher powers of $a_0$ and $p_0$, Slater then correlated the coefficients of equations (4.8) and (4.9) in the following way:

$$p_0 = (n_0/a_0)$$

$$p_1 = \left( \frac{1}{a_1} \right) \left[ 1 + \left( 2a_0 a_0/a_1^3 \right) \right] \quad (4.10)$$

and

$$p_2 = a_0/a_1^3$$

The energy of the solid at absolute zero, $\gamma_0$, is shown by Slater to be given by the following relation:

$$\gamma_0 = \gamma_{oc} + N V_0 \left[ \frac{9}{2} p_1^0 \left( \frac{r_0-r}{r_0} \right)^2 \right] - 9 \left( \frac{r_1^0 - r_2^0}{r_0} \right) \left( \frac{r_0 - r}{r_0} \right)^3 \quad (4.11)$$
Here $\eta_0$ is the value of $\eta$ at zero pressure and it can be identified with the Gibbs' free energy at zero temperature and pressure. $p^o$ and $p^o_0$ are values of $p_0$ and $p_a$ at absolute zero; $r_0$ is its equilibrium internuclear distance.

Using the Born model (eq. 1.9) Slater obtained the relations

\[
\eta_0 = -\left(\frac{N M Z^2 e^2}{r_0}\right) \left(1 - \frac{1}{n}\right)
\]

\[
p^o_1 = \left(\frac{M Z^2 e^2}{18 r_0^4}\right) (n-1)
\]

and

\[
p^o_2 = \left(\frac{M}{108}\right) \left(\frac{Z^2 e^2}{r_0^4}\right) (n-1) (n+10)
\]

The Gruneisen parameter—then known as Gruneisen constant—can now be related under well defined approximations\(^4\) with $p_1$ and $p_a$ as

\[
y = -\frac{2}{3} + \frac{p_1}{p_a}
\]

as an approximation if we put $p_1 \approx p^o_1$ and $p_a \approx p^o_a$ at room temperature, we get

\[
y = \left(\frac{n}{6}\right) + 1
\]

for the simple Born model and

\[
y = \frac{1}{3} + \frac{\left[\frac{r_0^2}{6g^2} - 1\right]}{\left[r_0^2/p - 2\right]}
\]

for the Born-Mayer model (eq. 1.10).
Using eq. (4.14) Slater\(^3\) computed \(\gamma\) for various alkali halide crystals. Kochave and Sonnen\(^4\) repeated these calculations of Slater\(^3\) and also used eq. (4.15) for computations. For some alkali halides, metal oxides, fluorides and sulfides the values of \(\gamma\) obtained using these equations are given in Tables IV.1A, IV.1B and IV.2. When a comparison with experimental \(\gamma\) is made an appreciable deviation in the computed values is noted and it is found that the agreement is only of the order of magnitude. Evidently, the part of the discrepancy is due to the inappropriateness of a single term as used by these authors to describe the non-Coulombic interaction. Moreover, Slater's eq. (4.13) corresponded to a Debye solid and the logic of its derivation lay in the assumption of a functional relationship between \(\nu\) (Debye cut-off frequency), \(V\) and \(\beta_2\). This is not very correct and has been justified by Slater\(^3\) mostly in view of the crudity of the other approximations involved in the derivation. Therefore, from eq. (4.13) nothing but a qualitative agreement with the experimental value is expected.

Dugdale and MacDonald\(^5\) have also presented a discussion of Slater's eq. (4.13). According to them a more correct version of eq. (4.13) is

\[
\gamma = \theta - 1 - \frac{p_1}{p_2}
\]  
\[(4.26)\]
## Table IV.1A

Values of the Grimason Parameters obtained from eq. (4.18) using different models for alkali halides.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Static Lattice Conditions</th>
<th>Temperature-dependent Conditions</th>
<th>Exptl.</th>
<th>Theor.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>eq. (1.7)</td>
<td>eq. (1.11)</td>
<td>eq. (1.12)</td>
<td>eq. (1.13)</td>
</tr>
<tr>
<td>LiF</td>
<td>1.67</td>
<td>1.74</td>
<td>1.59</td>
<td>1.70</td>
</tr>
<tr>
<td>LiCl</td>
<td>2.20</td>
<td>2.36</td>
<td>1.88</td>
<td>1.89</td>
</tr>
<tr>
<td>LiBr</td>
<td>2.29</td>
<td>2.49</td>
<td>2.03</td>
<td>1.39</td>
</tr>
<tr>
<td>LiI</td>
<td>2.58</td>
<td>2.82</td>
<td>2.39</td>
<td>2.28</td>
</tr>
<tr>
<td>NaF</td>
<td>2.11</td>
<td>2.20</td>
<td>1.65</td>
<td>2.07</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.52</td>
<td>2.74</td>
<td>2.28</td>
<td>2.47</td>
</tr>
<tr>
<td>NaBr</td>
<td>2.51</td>
<td>2.74</td>
<td>2.28</td>
<td>2.61</td>
</tr>
<tr>
<td>NaI</td>
<td>2.66</td>
<td>2.87</td>
<td>2.42</td>
<td>2.45</td>
</tr>
<tr>
<td>KCl</td>
<td>2.59</td>
<td>2.60</td>
<td>2.32</td>
<td>2.43</td>
</tr>
<tr>
<td>KBr</td>
<td>2.69</td>
<td>2.69</td>
<td>2.44</td>
<td>1.92</td>
</tr>
<tr>
<td>KI</td>
<td>2.82</td>
<td>2.96</td>
<td>2.51</td>
<td>2.35</td>
</tr>
<tr>
<td>RbCl</td>
<td>2.74</td>
<td>2.95</td>
<td>2.49</td>
<td>2.84</td>
</tr>
<tr>
<td>RbBr</td>
<td>2.78</td>
<td>2.96</td>
<td>2.52</td>
<td>2.89</td>
</tr>
<tr>
<td>RbI</td>
<td>2.93</td>
<td>3.02</td>
<td>2.61</td>
<td>0.07</td>
</tr>
<tr>
<td>CsCl</td>
<td>2.99</td>
<td>3.13</td>
<td>2.74</td>
<td>1.41</td>
</tr>
<tr>
<td>CsBr</td>
<td>2.54</td>
<td>2.66</td>
<td>2.32</td>
<td>2.03</td>
</tr>
<tr>
<td>CsI</td>
<td>3.10</td>
<td>3.19</td>
<td>2.84</td>
<td>2.77</td>
</tr>
</tbody>
</table>
TABLE IV-1B

Values of the Gruneisen parameter for the H10 on the basis of various potential models at room temperature.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Potential parameters</th>
<th>$\gamma_E$ (eq. 4.10)</th>
<th>$\gamma$ (eq. 4.25)</th>
<th>$\gamma$ exp (eq. 4.6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Born</td>
<td>m: 3.94</td>
<td>1.32</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rho$: 24.42x10^{-12} (erg)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Born-Mayer</td>
<td>$\sigma$: 0.423x10^{-8} (cm)</td>
<td>1.35</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rho$: 21.64x10^{-10} (erg)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Leonard-Jones</td>
<td>$\chi$: 3.173x10^{-12} (erg)</td>
<td>0.38</td>
<td>0.39</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>$\rho$: 6.2x10^{-84} (erg)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Hasegawa</td>
<td>$\sigma$: 250.4x10^{-6} (erg)</td>
<td>0.45</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rho$: 6.265x10^{-8} (cm^{-1})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Versini-Shukla</td>
<td>$\chi$: 250.5x10^{-12} (erg)</td>
<td>0.66</td>
<td>0.66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rho$: 7.661x10^{-16} (cm^{-2})</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The potential parameters have been evaluated using the static lattice conditions (eqs. 1.20 and 1.21)*
It was later pointed out by Gilvenny\(^5\) that \(\gamma\) as given by eq. (4.16) does not apply to a Debye solid but corresponded to a model introduced by Drayvvestey and Mayering\(^7\). In this model each atom of a monatomic solid of simple cubic structure interacts only with the nearest neighbours and the bond between the two is connected by a non-linear spring. These oscillators are regarded as independent of each other. Thus, in view of the artificial nature of the Drayvvestey and Mayering\(^7\) model it is difficult to support the values of \(\gamma\) obtained from eq. (4.13) of Slater.

4.1.3 Atomic Vibrations and the Gruneisen Parameter

The eq. (4.3) shows the volume dependence of lattice frequency over and above the anharmonic effect which are manifested through change of temperatures. Within the limits of a quasi-harmonic oscillator model, the Gruneisen parameter \(\gamma\) is expected to be constant. If we assume all \(\gamma\) to be equal, that means, there is only one frequency of oscillation \(\omega\) (single-frequency model). Such an assumption, known as Einstein approximation, if valid at all, will be applicable at high temperatures, at least above the Debye temperature of the solids.
On the basis of this assumption and special form of central force interaction, Born and his collaborators\(^2\) derived expressions for \(\gamma\) in terms of the parameters of the assumed potential. The definition of the Gruneisen \(\gamma\) can be rewritten as

\[
\gamma = - \frac{d(\log 2)}{d(\log V)}
\]

(4.17)

and using eqs. (3.4) and (3.11) can be solved as

\[
\gamma_E = - \frac{\gamma_0}{6} \left( \frac{d^3 \psi}{d V^3} \right)_{r=r_0} \left/ \left( \frac{d^2 \psi}{d V^2} \right)_{r=r_0} \right.
\]

(4.18)

This is the same equation which was obtained by Dugdale and MacDonald\(^5\) as

\[
\gamma_E = -1 - \frac{V}{2} \left( \frac{d^3 \psi}{d V^3} \right) \left/ \left( \frac{d^2 \psi}{d V^2} \right) \right.
\]

(4.19)

Assuming that Poisson's ratio is independent of volume, Slater's eq. (4.13) for an isotropic solid can be put into the form

\[
\gamma_s = - \frac{2}{3} - \frac{V}{2} \left( \frac{\partial^2 p}{\partial V^2} \right) \left/ \left( \frac{\partial p}{\partial V} \right) \right.
\]

(4.20)

It can be easily shown that eqs. (4.18) and (4.20) are related as

\[
\gamma_E = \gamma_s - \frac{1}{3}
\]

(4.21)
For the forms represented by eqns. (1.9), (1.10), (1.11), (1.12) and (1.13) the values of $\gamma$ calculated using eqns. (4.16) and (4.21) are listed in Tables IV-1 for alkali halide crystals. Using only the Born-Mayer potential the various values of $\gamma$ for some metal halides, sulfides, tellurides etc. have been also calculated and are reported in Table IV-2.

4.1.4 Anharmonicity and the Grüneisen $\gamma$

The contribution of the anharmonic cubic and higher-order terms to $\gamma$ can be calculated from the knowledge of the temperature-dependent part $kT \log Z$ of the free energy, $F$. The entropy $S$ and $C_V$ are related to $F$ as
\[ S = - \left( \frac{\partial F}{\partial T} \right)_V \]  
and
\[ C_V = T \left( \frac{\partial^2}{\partial T^2} (kT \log Z) \right) = T \left( \frac{\partial S}{\partial T} \right)_V \]  
which on simplification gives the eqn (3.19) for a diatomic solid. Relation (4.23) when combined with (4.17) gives
\[ C_V = 3 p' k\gamma_0 (1 + 2 \lambda' kT \Delta' / \Delta) \]  
where $p'$ is the number of ions per lattice cell, 
\[ \lambda' = \left( \frac{15}{16} \frac{b^2}{a^3} - \frac{3}{4} \frac{c}{a^2} \right) \]  
and \[ \Delta' = - \frac{d (\log \lambda')}{d (\log V)} \]  
Here $\gamma_0$ is the value of $\gamma$ obtained on the basis of quasi-harmonic model. The relation (4.24) was first derived
<table>
<thead>
<tr>
<th>Crystal</th>
<th>Potential parameters $\gamma_0$ $(10^{-3}$ cm$^{-1}$)</th>
<th>$A$ $(10^{-10}$ erg)</th>
<th>$\gamma_{\text{Slat}}$ (eq. 4.15)</th>
<th>$\gamma_E$ (eq. 4.18)</th>
<th>$\gamma$ (eq. 4.25)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl</td>
<td>0.303</td>
<td>47.10</td>
<td>1.90</td>
<td>1.56</td>
<td>1.58</td>
</tr>
<tr>
<td>CaBr</td>
<td>0.307</td>
<td>57.62</td>
<td>1.95</td>
<td>1.61</td>
<td>1.64</td>
</tr>
<tr>
<td>CaI</td>
<td>0.279</td>
<td>107.36</td>
<td>2.18</td>
<td>1.65</td>
<td>1.68</td>
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<tr>
<td>AgI</td>
<td>0.304</td>
<td>150.42</td>
<td>2.16</td>
<td>1.63</td>
<td>1.66</td>
</tr>
<tr>
<td>SnS</td>
<td>0.480</td>
<td>27.70</td>
<td>1.37</td>
<td>1.03</td>
<td>1.04</td>
</tr>
<tr>
<td>C=O</td>
<td>0.552</td>
<td>18.98</td>
<td>1.42</td>
<td>1.09</td>
<td>1.09</td>
</tr>
<tr>
<td>S=O</td>
<td>0.550</td>
<td>30.78</td>
<td>1.54</td>
<td>1.21</td>
<td>1.21</td>
</tr>
<tr>
<td>BaS</td>
<td>0.536</td>
<td>32.13</td>
<td>1.57</td>
<td>1.23</td>
<td>1.24</td>
</tr>
<tr>
<td>PbS</td>
<td>0.424</td>
<td>83.86</td>
<td>1.76</td>
<td>1.43</td>
<td>1.44</td>
</tr>
<tr>
<td>CdSe</td>
<td>0.530</td>
<td>20.06</td>
<td>1.48</td>
<td>1.11</td>
<td>1.12</td>
</tr>
<tr>
<td>IgSe</td>
<td>0.497</td>
<td>26.31</td>
<td>1.23</td>
<td>1.17</td>
<td>1.18</td>
</tr>
<tr>
<td>PbSe</td>
<td>0.474</td>
<td>65.53</td>
<td>1.73</td>
<td>1.40</td>
<td>1.42</td>
</tr>
<tr>
<td>AsSb</td>
<td>0.495</td>
<td>23.20</td>
<td>1.47</td>
<td>1.14</td>
<td>1.15</td>
</tr>
<tr>
<td>InSb</td>
<td>0.498</td>
<td>26.12</td>
<td>1.51</td>
<td>1.13</td>
<td>1.19</td>
</tr>
<tr>
<td>GeS</td>
<td>0.456</td>
<td>24.39</td>
<td>1.46</td>
<td>1.13</td>
<td>1.14</td>
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<tr>
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<td>0.441</td>
<td>79.56</td>
<td>1.76</td>
<td>1.43</td>
<td>1.43</td>
</tr>
</tbody>
</table>

* The sources of experimental data used for computations are listed in reference 30. Static lattice conditions (eqs. 1.20 and 1.21) have been used.*
by Rosebrock\textsuperscript{9}) to study the variation of the product $\gamma q_v$ with temperature in order to explain the variation of thermal expansion coefficient at high temperatures. Substituting eq. (3.19) for $q_v$ in eq. (4.24) and neglecting the square and other higher order terms in $kT$, since these are small, we get\textsuperscript{9})

$$\gamma = \gamma_0 + \gamma_0 \left( \frac{1}{2a} \right)^4 (116 abc - 75 b^3 - 40 a^2 d)^{kT}$$

The second term of relation (4.25) is thus an improvement over $\gamma_0$ when the effect of anharmonic terms of eq. (3.4) are also included. Using this relation the values of $\gamma$ above the Debye temperature have been calculated for the LiF and KBr crystals. The results obtained on the basis of modified Born-Mayer model, are listed in Tables IV-3A and IV-3B. In these Tables $\gamma_{\text{expbl}}$ are those values of $\gamma$ which have been obtained using eq. (4.4) using saturated values of $q_v$ or those obtained by including anharmonic contributions.

With the help of eq. (4.25) values of $\gamma$ have also been calculated for some metal fluorides at room temperature using the modified Born-Mayer model (eq. 1.10) the Rittner model (eq.1.14), the Veselova model (eq. 1.15) and the Vereshchagin-Shukla model (eq. 1.16). The values obtained on the basis of modified Born-Mayer model and the Vereshchagin-Shukla model are listed in Table IV-4.
<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Potential Parameters</th>
<th>( \gamma )</th>
<th>Anharmonic contribution ( \gamma_{an} )</th>
<th>( \gamma )</th>
<th>( \gamma_{exp} ) (eq. 4.4)</th>
<th>( \gamma_{from \ eq. \ 3.19} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>0.241 ( (10^{-6} \ \text{cm}) )</td>
<td>1028</td>
<td>1.78</td>
<td>1.86</td>
<td>2.06</td>
<td>2.02</td>
</tr>
<tr>
<td>500</td>
<td>0.236 ( (10^{-6} \ \text{cm}) )</td>
<td>1130</td>
<td>1.63</td>
<td>1.93</td>
<td>2.14</td>
<td>2.09</td>
</tr>
<tr>
<td>550</td>
<td>0.230 ( (10^{-6} \ \text{cm}) )</td>
<td>1454</td>
<td>1.90</td>
<td>2.02</td>
<td>2.22</td>
<td>2.17</td>
</tr>
<tr>
<td>600</td>
<td>0.224 ( (10^{-6} \ \text{cm}) )</td>
<td>1763</td>
<td>1.97</td>
<td>2.11</td>
<td>2.30</td>
<td>2.23</td>
</tr>
<tr>
<td>650</td>
<td>0.217 ( (10^{-6} \ \text{cm}) )</td>
<td>2255</td>
<td>2.05</td>
<td>2.22</td>
<td>2.38</td>
<td>2.30</td>
</tr>
<tr>
<td>700</td>
<td>0.210 ( (10^{-6} \ \text{cm}) )</td>
<td>3004</td>
<td>2.13</td>
<td>2.34</td>
<td>2.46</td>
<td>2.36</td>
</tr>
<tr>
<td>T (°K)</td>
<td>ψ (10^-6 a.u.)</td>
<td>a (10^-12 erg)</td>
<td>γ₀ (quasi-harmonic)</td>
<td>γ_a (eq.4.25)</td>
<td>γ (eq.4.25)</td>
<td>10^γ (Reuss Dynamic)</td>
</tr>
<tr>
<td>--------</td>
<td>---------------</td>
<td>----------------</td>
<td>---------------------</td>
<td>---------------</td>
<td>-------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>300</td>
<td>0.469</td>
<td>322.6</td>
<td>2.05</td>
<td>0.06</td>
<td>2.10</td>
<td>1.83</td>
</tr>
<tr>
<td>350</td>
<td>0.471</td>
<td>315.2</td>
<td>2.06</td>
<td>0.07</td>
<td>2.13</td>
<td>1.84</td>
</tr>
<tr>
<td>400</td>
<td>0.474</td>
<td>302.3</td>
<td>2.07</td>
<td>0.08</td>
<td>2.15</td>
<td>1.86</td>
</tr>
<tr>
<td>450</td>
<td>0.477</td>
<td>293.4</td>
<td>2.08</td>
<td>0.11</td>
<td>2.19</td>
<td>1.88</td>
</tr>
<tr>
<td>500</td>
<td>0.481</td>
<td>282.3</td>
<td>2.10</td>
<td>0.13</td>
<td>2.23</td>
<td>1.89</td>
</tr>
</tbody>
</table>
TABLE IV-4A

Values of Gr"uneisen parameter at room temperature of some metal fluorides calculated by using the eq.(4.29) on the basis of modified Born-Mayer model.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$\alpha 10^{-4}$</th>
<th>$\beta 10^{-12}$</th>
<th>$\gamma 10^{-20}$</th>
<th>$\delta 10^{-28}$</th>
<th>$\gamma$</th>
<th>$\gamma_{	ext{sh}}$ (eq.4.29)</th>
<th>$\gamma_{	ext{exp}}$ (eq.4.4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF$_2$</td>
<td>27.44</td>
<td>-61.24</td>
<td>222.2</td>
<td>-623.4</td>
<td>3.50</td>
<td>0.01</td>
<td>3.51</td>
</tr>
<tr>
<td>SrF$_2$</td>
<td>22.00</td>
<td>-61.64</td>
<td>158.1</td>
<td>-415.5</td>
<td>3.51</td>
<td>0.02</td>
<td>3.53</td>
</tr>
<tr>
<td>BaF$_2$</td>
<td>19.13</td>
<td>-49.00</td>
<td>116.5</td>
<td>-209.7</td>
<td>3.51</td>
<td>0.02</td>
<td>3.53</td>
</tr>
</tbody>
</table>

TABLE IV-4B

On the basis of Vershni-Shklis model.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$\alpha 10^{-4}$</th>
<th>$\beta 10^{-12}$</th>
<th>$\gamma 10^{-20}$</th>
<th>$\delta 10^{-28}$</th>
<th>$\gamma$</th>
<th>$\gamma_{	ext{sh}}$ (eq.4.29)</th>
<th>$\gamma_{	ext{exp}}$ (eq.4.4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF$_2$</td>
<td>27.44</td>
<td>-32.00</td>
<td>18.13</td>
<td>-3.33</td>
<td>1.38</td>
<td>0.01</td>
<td>1.39</td>
</tr>
<tr>
<td>SrF$_2$</td>
<td>22.00</td>
<td>-24.09</td>
<td>12.66</td>
<td>-2.06</td>
<td>1.37</td>
<td>0.02</td>
<td>1.38</td>
</tr>
<tr>
<td>BaF$_2$</td>
<td>19.13</td>
<td>-19.00</td>
<td>9.66</td>
<td>-1.70</td>
<td>1.40</td>
<td>0.01</td>
<td>1.41</td>
</tr>
</tbody>
</table>

* Value of $C_p$ for CaF$_2$ is taken as $11.62 \times 10^{-16}$ erg/deg. The same value has been assumed for the other two crystals as well.
4.1.5 Evaluation of $\gamma$ from the Individual Normal Modes:

Attempts\textsuperscript{10-15} have been made to evaluate $\gamma$ from the individual normal modes as well. For the $\pi \simeq \sigma$ mode, Mitter\textsuperscript{10,12} have derived relations to compute the values of $\gamma_{20}$ and $\gamma_{10}$ from the transverse optic and the longitudinal-optic modes, using the Kellerman\textsuperscript{16} rigid-ion model. For a polarizable ion, Mitter\textsuperscript{10} modified the relations for $\gamma$ obtained using Kellerman approximations. New equations for this case have also been derived by Mitter\textsuperscript{11} using Salgot's equations.

Attempts to compute $\gamma$ for the crystal by evaluating contributions of various normal modes to it have been done by Arenstein et al.\textsuperscript{13}, Barron et al.\textsuperscript{14}, and Cowley and Cowley\textsuperscript{15}. While Arenstein et al.\textsuperscript{13} have used the perturbation method to study the Grünisen $\gamma$, Barron et al.\textsuperscript{14} have applied the method of 'frequency moments'. Cowley and Cowley's\textsuperscript{15} calculations are based upon the shell model. By using the technique of thermodynamic Green's function these authors solved the phonon equations for the Grünisen parameter and found that $\gamma$ for the individual modes varied widely in magnitude and can have different signs.

Recently we have applied the lattice theory as has been developed by Raman\textsuperscript{17} to calculate $\gamma$ from the individual modes for KBr crystal\textsuperscript{18}. From this investigation we have found the main conclusions of Cowley and Cowley\textsuperscript{15} to be
valid in that (i) different normal modes have widely different values of \( \gamma \) both in magnitude and sign and (ii) the average value of \( \gamma \), obtained from the individual \( \gamma_j^0 \), is found to increase with temperature. The average values of \( \gamma, \bar{\gamma} \), at different temperatures have been included in Table IV.3B (last column).

4.1.6 Discussion of the Results:

We now discuss the various values of \( \gamma \) obtained in the present work. From Tables IV.1A and IV.1B it is seen that there is a definite dependence of \( \gamma \) on the form of the interionic potential. None of the potentials used here is entirely suitable to give a definite and precise conclusion about its superiority. However, the modified Born-Mayer model (eq. 1.11) yields fairly good results and is preferable. In view of the simple theory developed on the basis of single frequency model of Einstein, the results presented in these tables for the Born-Mayer potential when compared with those obtained experimentally, may be said to be satisfactory. It is also interesting to note that while one potential function may be suitable for describing a few of the crystal properties, it may not be able to give results for other properties for which another potential is found to be more acceptable and appropriate. In the present case the Grüneisen parameter computed on the basis of modified Born-Mayer model (eq 1.11)
in better than those obtained on the basis of Morse potential, while the latter is found to be more suitable for computing the infrared absorption frequencies (Chapter II Section 2). The elementary properties such as the cohesive energy etc., seem to be relatively insensitive to the form of the potential model, where a satisfactory agreement with the experimental values can be obtained even with a relatively simple potential form such as the Born model (eq. 1.9). Arensstein et al. 13) have also indicated a similar trend and have accordingly used two sets of potential parameters, one of which gave good results for the cohesive energy and the other gave better values for the resonance frequencies. The choice of different parameters for describing different properties of the same crystal is to a certain extent equivalent to using different potential models. However, it is felt that for all halides and H2O the Born-Mayer model, in general, is successful in explaining almost all the crystal properties.

The Born-Mayer potential for other types of ionic crystals have also been applied and the results are presented in Table IV-2. In Tables 3A, 3B, and 4A we have reported the values of \( \gamma \) calculated on the basis of Born-Mayer model (eq. 1.10) using our eq. (4.25) in which contributions due to cubic, quartic and fifth-order harmonic terms have also been included. From Table 3A, we note that, at high temperatures, \( \gamma \) calculated is in more satisfactory agreement with \( \gamma_{\text{expt.}} \). The differences in the \( \gamma_{\text{calc.}} \) (eq. 4.25) and
\( \gamma_{\text{expt}} \) are, however, large at lower temperatures. But as the temperature is increased the anharmonic contribution become more pronounced; and further, as the melting point of the solid is approached, the anharmonic contributions are appreciably large, giving a better agreement of \( \gamma_{\text{calc}} \) with its experimental values.

A similar trend has been observed in case of KBr as well (Table IV-3b). However, in this case, besides using the Einstein single frequency model, we have also used the lattice theory as has been developed by Raman\(^{17} \) to study the temperature-dependence of \( \gamma \). \(^{16} \) Values of the Grüneisen parameter for different normal modes were calculated using the modified Born-Mayer potential (eq.1.11) on the basis of Raman's theory and a weighted average were taken on the basis of Einstein specific heat function\(^{16} \) to obtain \( \overline{\gamma} \) (Table IV-3b, last column). On a comparison of the \( \gamma \) values at room temperature calculated in the present work and also with those obtained by other workers\(^{5,7} \) we find that \( \overline{\gamma} \) value obtained using Raman theory is in better agreement with the \( \gamma_{\text{expt}} \)\(^{\text{expt}} \) (\( = 1.52 \)). The value of \( \gamma \) obtained by Slater\(^{3} \) on the basis of Born-Mayer model (eq.4.15) is 2.05 and that obtained by Dugdale and MacDonald\(^{5} \) on the basis of eq. (4.16) is 1.72. Due to the hypothetical nature of the Drury-Devyn and Meyer's model\(^{7} \) as has been used by Dugdale and MacDonald\(^{5} \), the latter value cannot be relied upon.
Coulery and Coulery\textsuperscript{15)} have also calculated the Grüneisen parameter from the individual mode on the basis of shell model using the technique of thermodynamic Green's function in case of KBr crystal. These authors have shown that the average value of $\gamma$ increases with temperature at high temperatures and the effect of anharmonicity is pronounced. These facts can be verified from the present investigation as well. The average value of $\gamma$ calculated by Coulery and Coulery\textsuperscript{15)} for KBr crystal is also matching satisfactorily with $\bar{\gamma}$ of the present investigation.

On a comparison of the $\bar{\gamma}$ values with those obtained on the basis of Einstein's single frequency model for KBr crystal (Table IV-3B, last two columns), we find that the former values are more close to the experimental values than the latter values are. Nevertheless, the single frequency model still appears as a good approximation at high temperatures.

In the case of Calcium, Strontium and Barium fluorides, the calculated values of $\gamma$ using the Born-Mayer potential are higher than the experimental values (Table IV-4A). This is also the case with the Rittner and the Wasastjerna models. For these solids, the Varshni-Shukla model (eq. 1.16) nevertheless seems to yield better results (Table IV-4B).
4.2 \textbf{Anderson-Grübler Parameter}

4.2.1 \textit{Introduction:}

In 1961, Wechtman et al.\cite{footnote} measured the Young modulus for several inorganic compounds as a function of temperature. They found that the modulus data can be adequately represented by the equation of the form

\[ Y = Y_\infty - b_1 T \exp \left( -\frac{T_0}{T} \right) \quad (4.26) \]

where \( Y \) and \( Y_\infty \) are the Young's moduli at any temperature \( T \) and absolute zero temperature, respectively, and \( b_1 \) and \( T_0 \) are two empirical parameters characteristic of a solid. According to this equation, \( Y \) approaches \( Y_\infty \) at absolute zero with a zero slope as required by the third law of thermodynamics. At high temperatures, the term \( \frac{1}{\exp(-T_0/T)} \) approaches unity and the Young modulus thus decreases linearly with temperature. Although no theoretical interpretation was given for the success of eq. (4.26) in describing the temperature dependence of the Young modulus of several inorganic oxide compounds, Wechtman et al.\cite{footnote} did point out that \( T_0 \) should in some way correlate with the Debye temperature while \( b_1 \) correlates with the Grüneisen parameter.

Since the bulk modulus \( B \) is related to the Young's modulus \( Y \) by the equation

\[ B = \frac{Y}{3} \left( 1 - 2\nu \right) \quad (4.27) \]
and since the Poisson's ratio \( \sigma \) changes slowly with temperature, it was anticipated that the temperature dependence of the bulk modulus can also be described by an equation of the similar form as eq. (4.26), i.e.,

\[
B_s = B_{\infty} - b T \exp \left( - \frac{T}{T_0} \right) \quad (4.28)
\]

where \( B_s \) and \( B_{\infty} \) are the adiabatic bulk moduli at any temperature \( T \) and the absolute zero, respectively, and \( b \) is a parameter, similar to \( b_1 \), characteristic of a solid. More recently, from theoretical considerations Anderson\(^2c\) has derived a relationship, which relates the temperature dependence of the bulk modulus as a function of the specific heat and atomic volume, as follows:

\[
\frac{dB_s}{dT} = - 8 \gamma \left( \frac{C_P}{V} \right) \quad (4.29)
\]

where \( C_P \) is the specific heat at constant pressure, \( V \) is the atomic volume, and \( \gamma \) is the Grüneisen parameter. The dimensionless parameter, \( \delta \), which is a fundamental parameter of a solid similar to the Grüneisen \( \gamma \), is known as the Anderson-Grüneisen parameter. This parameter has been defined by Anderson\(^2c\) as

\[
\delta = - \left( \frac{1}{3b} \right) \left( \frac{d \ln B_s}{dT} \right) = - \left( \frac{d \ln B_s}{d \ln V} \right) \quad (4.30)
\]
and is similar to the Grüneisen $\gamma$ defined by the relation (4.17).

Eq. (4.30) was first derived by Grüneisen\(^1\) and more recently by Anderson\(^2\) based on the Hie-Grüneisen equation of state and Hie's formula to represent the potential energy of a solid.

From eqs. (4.29), Anderson\(^2\) showed that

$$b = \frac{3k \varepsilon_y}{V_0} \quad (4.31)$$

and

$$T_0 = \frac{\varepsilon_y}{2} \quad (4.32)$$

where $R$ is the universal gas constant, $V_0$ is the atomic volume at absolute zero and $\varepsilon_y$ is the characteristic Debye temperature. Using the recent modulus data of MgO reported by Soga\(^2\) and Anderson\(^2\) and other necessary thermal data, Anderson\(^2\) studied the temperature dependence of the bulk modulus of this solid by computing the Anderson-Grüneisen parameter $\delta$.

4.2.2 Anderson-Grüneisen Parameter of Ionic Solids:

Since Anderson published his paper in 1966, a number of investigations have been made to understand the physical meaning of the Anderson-Grüneisen parameter. Chang\(^2\) in his studies on $\delta$ of some oxide compounds correlated $\delta$ with other thermodynamical quantities and recalculated $\delta$ for
On the basis of Born-Mayer interaction potential and derived relation for $\varphi$ and applied it to the case of alkali halides. The temperature dependence of the bulk modulus of these solids in terms of Anderson-Grunisen parameter has been studied by Mudan using the modified Born-Mayer potential function (eq.1.11). Mudan has also computed $\varphi$ for some of these alkali halides from the long wavelength optic mode frequencies. More recently, Shears and Cowburn have elaborated some of these approaches and made attempts to correlate $\varphi$ with $\gamma$. The last authors have also tried to study the temperature dependence of $\varphi$ by removing the approximation in Cheng's equation, but without discussing the physical reasons for the temperature variation of $\varphi$.

Born and Huang have shown that at elevated temperatures there is a significant contribution to the bulk modulus from volume and anharmonicity terms and have shown that these are responsible for the temperature dependence of bulk modulus of solids. Since, according to eq. (4.39), the temperature dependence of bulk modulus is intimately connected with $\varphi$, it was thought desirable to study the effects of volume and higher-order anharmonicity terms on the Anderson-Grunisen parameter.
4.2.3 Equations for the Andersen-Grüneisen Parameter

From thermodynamics, it can be seen that the temperature dependence of the isothermal compressibility is related to the pressure dependence of the volume coefficient of expansion as

\[
\left( \frac{\partial B_T}{\partial T} \right)_P = - \left( \frac{\partial \alpha_Y}{\partial P} \right)_T
\]  

(4.33)

Since the bulk modulus is the reciprocal of the compressibility, one obtains

\[
\left( \frac{\partial B_S}{\partial T} \right)_P = - \frac{C_P}{V} \left[ \left( \frac{\partial B_T}{\partial P} \right)_T \right]^{-1}
\]  

(4.34)

From eqs. (4.33) and (4.34) we have

\[
\left( \frac{\partial B_T}{\partial T} \right)_P = B_T^2 \left( \frac{\partial \alpha_Y}{\partial P} \right)_T
\]  

(4.35)

Considering the Grüneisen equation of state for solids in the form

\[
\alpha_Y = \frac{\gamma C_V}{B_T V} = \frac{\gamma C_P}{B_S V}
\]  

(4.36)

derived under the quasi-harmonic approximation, \( \left( \frac{\partial \alpha_Y}{\partial P} \right)_T \) can be calculated. All the quantities \( B_T, V, C_V \), and \( \gamma \) appearing in the right hand side of the above equation are pressure-dependent, but the variation of \( C_V \) and \( \gamma \) with pressure and relatively small\textsuperscript{2,3}, in comparison to the other quantities. With these assumptions we get

\[
\left( \frac{\partial \alpha_Y}{\partial P} \right)_T = - \frac{C_V \gamma}{V B_T^2} \left[ \left( \frac{\partial B_T}{\partial P} \right)_T \right]^{-1}
\]  

(4.37)

Combining eqs. (4.35) and (4.37) we have

\[
\left( \frac{\partial B_T}{\partial T} \right)_P = - \frac{\gamma C_V}{V} \left[ \left( \frac{\partial B_T}{\partial P} \right)_T \right]^{-1}
\]  

(4.38)
since

$$R_2 = R_S \left( \frac{C_v}{C_p} \right) \quad (4.39)$$

$$\left( \frac{\partial B_S}{\partial T} \right)_P = -\frac{C_p \gamma}{V} \left[ \left( \frac{\partial B_T}{\partial P} \right)_V - 1 \right] \quad (4.40)$$

can be evaluated for the determination of $\delta$.

Cheng\(^{22}\) and Hadam\(^{25}\) have discussed that at low
temperatures, $C_v/C_p$ approaches to unity, while at high
temperatures $C_v/C_p$ nearly approaches a constant value.
At intermediate temperatures, however, $C_v/C_p$ varies with
temperature. Assuming that $C_v/C_p$ is independent of
temperature, Cheng\(^{22}\) derived the relation

$$\left( \frac{\partial B_S}{\partial T} \right)_P = -\frac{C_p \gamma}{V} \left[ \left( \frac{\partial B_T}{\partial P} \right)_V - 1 \right]$$

which on a comparison with eq. \((4.39)\) yields

$$\delta = \left( \frac{d B_T}{d P} - 1 \right) \approx \left( \frac{d B_S}{d P} - 1 \right) \quad (4.41)$$

Slater\(^3\) and Bagdale and MacDowall\(^8\) have given
relationships between the Grünisen parameter $\gamma$ and the
change of the compressibility with the volume of a solid.
Based upon these relations, and using eq. \((4.41)\), Cheng\(^{22}\) obtained the relations for $\delta$ as

$$\delta = 2 \gamma - \frac{2}{3}$$

and

$$\delta = 2 \gamma$$

respectively.
Haden solved the eq. (4.41) in terms of potential energy function and derived relation for $\delta$ in terms of the Born-Mayer interaction potential.

Using the Grimsehl's equation of state for solids, Mathur and Singh and Mathur et al. have also derived a general relation for $\delta$ in terms of potential energy function and specialized it for the Born-Mayer interionic potential. The equation in terms of Born-Mayer potential as obtained by these authors can be written as

$$\delta = -y + 2 + \left( \frac{r_0}{3g} \right) - \frac{\left( \frac{r_0}{3g} \right)}{\left( \frac{r_0}{g} \right)^2} \quad (4.43)$$

Haji Cheng applied his eqs. (4.41) and (4.42) to the case of $\text{H}_2\text{O}$ and Haden and Mathur and coworkers used their eqs. to the case of alkali halides. In the present work as an illustration eqs. (4.41) to (4.43) have been used to study $\delta$ in the case of some metal oxides of $\text{H}_2\text{O}$, $\text{CaO}$, and $\text{SrO}$ (Table IV) for which various experimental data for computations are available.

Sharma and Gupta instead of assuming $c_v / c_p$ to be independent of temperature, as had been done by earlier workers, derived a general relation for $\delta$ as

$$\delta = \delta_T - \left( \frac{1}{\alpha_v} \right) \left( \frac{\partial \ln (c_p/c_v)}{\partial T} \right)_P \quad (4.44)$$

where

$$\delta_T = -\frac{V}{\gamma c_p} \left( \frac{\partial B_T}{\partial T} \right)_P \quad (4.45)$$
<table>
<thead>
<tr>
<th>Crystal</th>
<th>(10^{-8} \text{ cm}^3)</th>
<th>(5 \times 10^{-8} \text{ cm}^3)</th>
<th>(\delta) (eq. 4.41)</th>
<th>(\delta) (eq. 4.43)</th>
<th>(\delta) (\text{expt}) (eq. 4.36)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>2.10</td>
<td>0.370</td>
<td>2.20</td>
<td>1.98</td>
<td>3.12</td>
</tr>
<tr>
<td>CaO</td>
<td>2.57</td>
<td>0.374</td>
<td>3.59</td>
<td>2.55</td>
<td>4.53</td>
</tr>
<tr>
<td>SrO</td>
<td>2.40</td>
<td>0.367</td>
<td>3.46</td>
<td>1.85</td>
<td>1.94</td>
</tr>
</tbody>
</table>
In a more useful form eq. (4.44) can be put as

$$\delta = \left[ \left( \frac{\partial B_T}{\partial P} \right) - 1 \right] - \frac{B_T V}{C_p \gamma} \frac{\partial}{\partial T} \left( 1 - \frac{C_v}{C_p} \right)$$

(4.46)

Eq. (4.46) has been applied to the case of NaCl crystal\(^2\).

It is obvious that eq. (4.46) is equivalent to eq. (4.42)

when \(\gamma C_v / C_p\) is assumed to be temperature independent.

Implicit in these derivations is the idea of anharmonicity

which has been found to affect both \(C_v\) and \(C_p\) at elevated

temperatures.

4.2.4 Effect of Anharmonicity on the Anderson-Grüneisen Parameter

The effect of anharmonicity on the Anderson-Grüneisen parameter can also be explicitly considered.

Born and Huang\(^2\) have shown that at elevated temperatures there is a significant contribution from volume and other anharmonic effects to the bulk modulus and the relation

for \(B_T\) including these contributions can be written as

$$B_T = B_0 + \left[ 2 + V_0 \left( \frac{d^2 \psi}{d V^2} \right)/\left( \frac{d^2 \psi}{d V^2} \right) \right] \frac{V}{V} E_{vib}$$

$$- \frac{V^2}{V} (T C_v - E_{vib})$$

(4.47)

where \(B_0\) and \(V_0\) are the bulk modulus and the volume at

\(0^\circ\) \(\psi\) is the potential energy including the zero-point
vibration, $E_{\text{vib}}$, is the vibrational part of the total energy and $\frac{d^2\gamma}{dV^2}$ and $\frac{d^3\gamma}{dV^3}$ are the second and the third-order derivatives of $\gamma$ with respect to $V$ at static equilibrium. Substituting eqs. (4.47) in eqs. (4.29) we get

$$
\delta = \delta_0 - \left( \frac{\delta_0}{B_0} \right) \left[ \frac{\gamma}{V} \frac{E_{\text{vib}}}{V} \left( 2 + V \frac{\gamma''}{\gamma'^2} \right) - \frac{\gamma^2}{V} (T C_V - E_{\text{vib}}) \right] \\
+ \left( \frac{E_{\text{vib}}}{C_V} \right) \left[ 2 \alpha + \gamma \alpha - V^2 \alpha \left( \frac{\gamma'}{\gamma''} - \frac{\gamma'''}{\gamma''^2} \right) \right] \left( 2 + V T \alpha + V \frac{\gamma'''}{\gamma''^2} \right) \\
+ \gamma T \frac{\delta}{\partial T} \frac{3}{2} \ln (C_T/C_V) - \left( \frac{1}{3\alpha} \right) \frac{\delta}{\partial T} \left[ \ln (C_T/C_V) \right] \tag{4.48}
$$

where $\delta_0$ is the value of $\delta$ at $0$ K and $\gamma''$, $\gamma'''$, etc., have been used for $\frac{d^2\gamma}{dV^2}$, $\frac{d^3\gamma}{dV^3}$, etc. The eq. (4.48) shows that, on the assumption that $\delta$ is independent of temperature and volume and $B_0 = B_0$, $\delta = \delta_0$, which is Guggenheim's equation (eq. 4.41). Agrad. $\delta_0$, assuming that the volume and other anharmonic effects on $B_0$ are negligible and $B_0 = B_0$, we get Norden's equation (eq. 4.44).

### 4.2.5 Calculation of the Effect of Anharmonicity on $\delta$

in case of NaCl Crystal:

Eq (4.48) has been applied to the case of NaCl (31) for which crystal data for computations are available. At high temperatures such that $kT \gg h^2$, we have $E_{\text{vib}} = 6kT$ under this condition eq. (4.48) reduces to

$$
\delta = \delta_0 - \epsilon_1 T + \epsilon_2 T + \gamma T \frac{\delta}{\partial T} \left[ \ln (C_T/C_V) \right] - \delta_C F \tag{4.49}
$$

where

$$
\epsilon_1 = \left( \frac{\delta}{B_0} \right) \left( 2 + V \frac{\gamma''}{\gamma''^2} \right) \left( \frac{\gamma'}{\gamma''} \right) (6k) \tag{4.50}
$$
\[ \epsilon_2 = \left[ 2\alpha + \gamma \alpha - \nu^2 \alpha \left( \frac{\nu^{IV}}{\nu''} - \frac{\nu''''}{\nu''^2} \right) \right] - \frac{1}{T} \left[ 2 + \gamma T \alpha + \nu \frac{\nu''''}{\nu''} \right] \]

(4.51)

and

\[ \delta_{CF} = \frac{1}{3 \alpha} \frac{\partial}{\partial T} \left[ \ln \left( \frac{C_F}{C_V} \right) \right] \]

(4.52)

The values of \( \delta \) at various temperatures above the Debye temperature of NaCl crystal calculated using eq. (4.49) are given in Table IV.6. The various volume derivatives of \( \nu \) were calculated on the basis of the modified Born-Mayer potential (eq. 1.11). The sources of various data used in this computation are listed in the work of Sharma and Gupta(29).

4.2.6 Discussion of the Results:

The values of \( \delta \) using eqs. (4.30), (4.41) and (4.42) have earlier been calculated by Chang(22) for the MgO crystal. All these equations were found to yield values of \( \delta \) for this solid which were in essential agreement with each other. In the present work these equations have been tested in cases of CaO and SrO as well and the eq. (4.43) derived by Nathan and Coworkers(23,24) on the basis of Born-Mayer model, has also been applied (Table IV.5). It is seen from Table IV.5 that the values of \( \delta \) calculated for MgO, CaO and SrO using eqs. (4.43) are much lower than those obtained using eqs. (4.41) and (4.30). Chang's relation
**Table IV-6**

Values of Anderson-Günther parameter \( \delta \), for the rock-salt crystal at high temperatures.

<table>
<thead>
<tr>
<th>( T(°K) )</th>
<th>( \varepsilon_1^T ) (eq. 4.50)</th>
<th>( \varepsilon_2^T ) (eq. 4.51)</th>
<th>( \chi_T^2 ) (Ind.)</th>
<th>( \chi_T^2 ) (eq. 4.52)</th>
<th>( \delta_{\text{CF}} ) (eq. 4.52)</th>
<th>( \delta ) (eq. 4.49)</th>
</tr>
</thead>
<tbody>
<tr>
<td>553</td>
<td>-0.241</td>
<td>2.981</td>
<td>0.637</td>
<td>6.931</td>
<td>2.011</td>
<td>4.920</td>
</tr>
<tr>
<td>653</td>
<td>-0.262</td>
<td>2.680</td>
<td>0.668</td>
<td>6.302</td>
<td>1.961</td>
<td>4.940</td>
</tr>
<tr>
<td>753</td>
<td>-0.327</td>
<td>2.504</td>
<td>0.706</td>
<td>6.708</td>
<td>1.925</td>
<td>4.793</td>
</tr>
<tr>
<td>853</td>
<td>-0.372</td>
<td>2.332</td>
<td>0.753</td>
<td>6.429</td>
<td>1.888</td>
<td>4.774</td>
</tr>
<tr>
<td>953</td>
<td>-0.419</td>
<td>2.206</td>
<td>0.808</td>
<td>6.605</td>
<td>1.799</td>
<td>4.687</td>
</tr>
</tbody>
</table>

\( \delta_{\text{anh}} = -\varepsilon_1^T + \varepsilon_2^T + \chi_T^2 \left( \ln \xi_T \right) \) which includes both the volume and the cubic and higher-order anharmonic contributions.
(eq 4.41) yields values of $S$ for MgO and CaO crystals which are in better agreement with those obtained by eqs. (4.39). For SrO there is a striking disagreement. It is difficult to say which one of these equations is more correct, since all these equations have been derived based upon various assumptions. As such, one cannot say any single one of these relationships is intrinsically better based on theoretical ground. It is hoped, with the availability of a large number of experimental data on many substances, it can be possible to make certain which one of these equations are the best one for calculating the Anderson-Criminon parameter, $S$, as far as describing the correct temperature dependence of the bulk modulus of solids is concerned.

All these equations for $S$ derived by earlier workers, including Chang (22), Nathan and coworkers (23, 24), lovely (25) and Sharpe and coworkers (26, 27) are based on the quasi-harmonic approximation. As such these are not valid for any solid having strong anharmonic effect or at high temperatures, we have derived the general eqs. (4.49) for the purpose where all the approximations of the earlier workers have been removed. This equation has been applied to the case of NaCl crystal (Table IV-6).
From Table IV.5 we see that the anharmonic contributions to $S$, which has been neglected in all the previous studies, are quite significant. At elevated temperatures, the contribution due to the correction factor $\delta_{CF}$ for converting $B_1$ into $B_S$ is also quite large which has been neglected in the work of Cheng\textsuperscript{22)} and Sharma and Co-workers\textsuperscript{26-28)}. The Anderson-Grimvall parameter, $\delta$, has been found to increase with temperature and it is in satisfactory agreement with the experimental values reported by Sharma and Gupta\textsuperscript{29)}. The present results thus exhibit marked improvement over those calculated by Cheng\textsuperscript{22)}, Madsen\textsuperscript{25)} and Sharma and Co-workers\textsuperscript{26-27)}, which is due to the more generalized form for the equation for $S$ used in the present study.

The eq. (4.48) thus is a more satisfactory equation for $S$ where all the approximations of the earlier workers have been removed and is applicable to a wider temperature range and also to any types of crystals.

For molecular crystal of acetaminol, the eq. (4.48) has also been tried\textsuperscript{32)} and has been found to be quite successful in the determination of $S$.
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