CHAPTER - 7

Grüneisen Parameter of Ionic and Covalent Crystals for Low and High Temperatures – A Generalised approach.

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Abstract

Since the diffusion studies are always made at high temperatures, a study on thermal expansion and hence the anharmonicity becomes necessary. For example in CdTe, ZnTe, HgTe, GaAs and InP, the self and impurity diffusion takes place only at very high temperatures of the order of 700 - 1000°C. To work out a suitable model in the lattice dynamical environment, a study of anharmonicity is necessary on these systems.

Anharmonicity in crystals is viewed generally through Grüneisen parameter. A generalized theoretical approach for the study of anharmonicity is very sparse. NaCl type systems have been tried and reported for only one temperature of specific interest. Suitable modifications are made on the existing program so that it can be employed for a wide range of temperatures from 0 K to high temperatures. Similarly zinc blende type systems (covalent crystals) are also studied for a wide range of temperatures by developing another such package.
7.1 Introduction

The study of anharmonicity is not a new topic but it has aroused some interest in II-VI and III-V compounds, of late, for the reason that a lot of diffusion works in these systems have started coming [1]. Particularly CdTe, ZnTe, HgTe and GaAs and their mixed systems are very useful in the design of solar cells and infra-red detectors. Consequently the diffusion in these systems becomes important. It has been found experimentally [2], that the diffusion in these systems takes place only at very high temperatures of the order of 700 - 1000°C.

To work out a suitable model in the lattice dynamical environment, a simple harmonic approximation would not suffice to explore the diffusion mechanism and a study of anharmonicity becomes necessary in these systems. Theoretical models developed by Madhavan et al [3] for self-diffusion in CdTe, ZnTe and HgTe show consistently that it is due to single vacancy mechanism. Now, the interest is to study the effect of anharmonicity in these systems on the diffusion mechanism. With this motive, it is intended to work out the anharmonicity parameter (mode Grüneisen parameter) for some covalent systems like CdTe, ZnTe and some other ionic systems like NaCl, KCl from low to high temperatures.

It is known that the amplitude of vibration of the atoms will increase as the temperature increases and when this is appreciable to the lattice spacing,
the harmonic approximation fails. Thermal expansion, thermal conductivity, high temperature lattice specific heat, etc., of the crystals are some of the manifestations of this anharmonicity. The effect of anharmonicity on crystals is usually expressed in terms of a dimensionless Gruneisen parameter, \( \gamma \) or in other words \( \gamma \) is the measure of anharmonicity in the crystal.

Eventhough reports are available for the evaluation of this \( \gamma \) theoretically, starting from ionic crystals to molecular crystals [4-8], no generalised procedures have been reported in the literature. Similarly, the Gruneisen parameters for a variety of crystals have not been exhaustively investigated over a range of high temperatures.

Batana et al [9] have developed, a FORTRAN program to evaluate the Gruneisen parameter for NaCl for a temperature of 195 K, as the anharmonicity plays a significant role at this temperature in this system. They have evaluated \( \gamma \) from the elastic anisotropy of the system employing Daniel’s method [10] and the available anisotropy factor tables \( f(s,t) \) compiled by de Launay [11,12]. The program developed by Batana et al [9] is applicable for ionic systems only and that too for the low temperature regions.

In the present investigation, we present a simple generalized method to work out the Gruneisen parameters including elastic anisotropy and anharmonicity, in particular for NaCl and Zinc blende type systems for a wide range of temperatures. A modified FORTRAN program has been developed to
facilitate the computation of $\gamma$'s over a high temperature range, from 0 K to a temperatures up to 1000 K.

(i) This program calculates the Grüneisen parameter for covalent crystals like ZnTe, CdTe, etc., by employing an angular force model with 8 parameters using a Lennard-Jones (L-J) potential.

(ii) The program, also calculates the Grüneisen parameter for ionic crystals like NaCl, KCl, etc., by using the experimental values of the elastic stiffness constants, their pressure derivatives [10,11] and the de Launay's tables [12], which is a modified version of the program developed by Batana et al [9].

7.2 Theory

7.2.1 Phonon-Phonon interaction

Within the harmonic approximation, the phonons are independent quasi-particles. The validity of this picture depends on the number of phonons present and it breaks down at high temperatures, when this number is large. For the explanation of phenomena like thermal expansion, thermal conductivity of insulators, it is essential to include the anharmonic terms. The interactions between the phonons affect the phonon mean free path and the life time is then limited to finite values.

7.2.2 Thermal expansion

The important consequences of the harmonic approximation are that (a) there is no thermal expansion, (b) the adiabatic and isothermal elastic constants are
equal and are independent of temperature, (c) the specific heat becomes constant at high temperatures. But, contrary to the predictions of harmonic theory, (a) we do have thermal expansion, (b) the adiabatic and isothermal elastic constants are different and they do exhibit temperature dependence, (c) the specific heat also exhibits temperature dependence at high temperatures. All these explain the inadequacy of the harmonic theory in accounting for the properties of real crystals.

Timmesfeld and Elliot (TE) [13] treated the anharmonic terms in the potential energy expansion as a perturbation on the harmonic Hamiltonian. Almost a complete theory exists for the thermal expansion of pure crystals [14,15] and it is worth noting that TE's theory reduces to the one already given by Maradudin [14] in the absence of defects.

7.2.3 Grüneisen parameter

The measure of anharmonicity is expressed in terms of the Grüneisen parameter involving bulk properties as,

\[
\gamma = \frac{\beta V}{\chi C_v} \tag{7.1}
\]

where \( \beta \) is the coefficient of volume expansion, \( V \) is the crystal volume, \( \chi \), the isothermal compressibility and \( C_v \) is the heat capacity at constant volume [16].

The effect of anharmonicity is defined in terms of a microscopic quantity namely the mode Grüneisen parameter [17]
which is a measure of the volume dependence of the frequency $\omega_{qj}$ of the vibrational $qj$ mode [18], where $q$ is the wave vector, $j$ is the number of mode and $V$ is the unit cell volume. The negative sign indicates that the frequency decreases as the volume increases. The mode Grüneisen parameter is usually evaluated by using the pressure derivatives.

$$\gamma_{qj} = -\left( \frac{\partial \ln \omega_{qj}}{\partial \ln V} \right)_T$$

(7.2)

In Grüneisen theory [19], $\gamma$ is assumed to be temperature independent constant. Grüneisen's theory of constant $\gamma$ means, all values of $\gamma_{qj}$, corresponding to a particular $j$ and wave vector $q$, are same. But, theoretical [20-23] and experimental [24-26] observations have provided a strong evidence that $\gamma$ changes drastically with temperature, according to the character of bond between the atomic lattice points and for some lattice
modes, it may assume even a negative value [16] in the low temperature region. The temperature dependence on $\gamma$ is obtained from $C_{q_j}$, the Einstein's specific heat function (contribution of the corresponding mode to the heat capacity at constant volume)[18].

i.e.,

$$\gamma(T) = \sum_{q_j} \gamma_{q_j} \frac{C_{q_j}}{C_v}$$  \hspace{1cm} \text{(7.4)}$$

where $C_{q_j}$ is the contribution of the corresponding mode to the heat capacity at constant volume $C_v$, which is given by

$$C_v = \sum_{q_j} C_{q_j}$$  \hspace{1cm} \text{(7.5)}$$

where,

$$C_{q_j} = N k_B E(x)$$  \hspace{1cm} \text{(7.6)}$$

and

$$E(x) = \frac{x^2 e^x}{(e^x - 1)^2} \quad \text{with} \quad x = \frac{\hbar \omega_{q_j}}{k_B T}$$  \hspace{1cm} \text{(7.7)}$$

$k_B$ - Boltzmann's constant

$T$ - Temperature.

Therefore,

$$\gamma(T) = \frac{\sum_{q_j} \gamma_{q_j} C_{q_j}}{\sum_{q_j} C_{q_j}}$$  \hspace{1cm} \text{(7.8)}$$

$$\gamma(T) = \frac{\sum_{q_j} \gamma_{q_j} \left(\frac{\hbar \omega_{q_j}}{k_B T}\right)}{\sum_{q_j} \left(\frac{\hbar \omega_{q_j}}{k_B T}\right)}$$  \hspace{1cm} \text{(7.9)}$$
With the introduction of volume dependent frequencies in the above equations the theory moves from harmonic to quasi-harmonic approximation for the lattice i.e., the atom may move to some nearby site, where it would undergo harmonic vibrations. It is evident from the above equations that at high temperatures, \( \gamma \) is simply the arithmetic mean of \( \gamma_q \) but at low temperatures, \( \gamma_q \) from lower frequencies contribute much to the average value, so that the parameter \( \gamma \) in general becomes a temperature dependent factor.

At fairly high temperatures, the Einstein specific heat theory is quite adequate and it will lead to the Dulong Petit’s limit and Debye’s theory is needed only for extremely low temperatures. So, for any studies involving the anharmonicity Einstein’s specific heat function will be enough, as this will be dominant at high temperatures. But here in the software, developed in the present investigation option exists to replace the Einstein’s function with any other related specific heat function.

Previously Soma et al [18] had worked out the Gruneisen parameter using thermal expansion as the input parameter for some of the covalent systems and demonstrated that Einstein’s specific heat function is enough for such calculations. Similarly Soma et al [27] had again shown that Einstein’s specific heat function is adequate to work out the defect mode contribution to the specific heat even at 50 K for Al-Si and Al-Ge alloys. This is the reason
for the choice of Einstein's specific heat function in the present program. This
type of calculations is performed only to isotropic crystals.

7.3 Method

7.3.1 Covalent systems

In the absence of pressure derivatives of elastic constants, one can look into
the anharmonicity through thermal expansion i.e., through the lattice constant
at different temperatures. A Lennard-Jones potential (LJ potential) is used for
the evaluation of the force constants $A$ and $B$ in terms of the Kellerman's
parameters.

$$\phi(R) = \frac{P}{R^{12}} - \frac{Q}{R^6}$$

where $P$ and $Q$ are some constants and $R$ is half of the lattice parameter
(nearest neighbour distance in NaCl structures). For the evaluation of the
phonon frequencies, we use a rigid ion model with angular forces. In the
concept of angular forces, it is assumed that a change in angle is related to a
change in potential energy by a Hook's law force constant for the non-central
forces. If $V_A$ is the potential energy and $\delta \theta$ a change in angle, then

$$V_A = \frac{1}{2} \sigma (\delta \theta)^2$$

where $\sigma$ is the angular force constant. In this treatment two types of angles are
considered. Let $\sigma_1$ be the force constant associated with the first neighbours
subtending an angle $\theta_1$ and $\sigma_2$ that of second neighbours subtending an angle $\theta_2$.

This potential $\phi_1(R)$, between the first nearest neighbours, is purely central, which can be represented in Kellerman' notation as $B = \frac{d\phi_1(R)}{dR}$ and $A = \frac{d^2\phi_1(R)}{dR^2}$ and it is a common experience from other solids that $|B| < |A|$. There is one more potential $\phi_2$, which is due to the change in bond angle. This will be represented by a force constant $\sigma_1$. Similarly $A_1$ and $\sigma_2$ can be shown to be that for second neighbours. It is also assumed that $\sigma_1 + \sigma_2 = 2A_1$. By assuming a potential like L-J potential one can evaluate the first neighbour force constant $A$. The other force constants $A_1$, $\sigma_1$ and $\sigma_2$ are taken from reference [1] and are given in Table 7.1.

The expressions used for finding out the lattice parameter at any given temperature $T$ for ZnTe and CdTe are\[D. P. Singh and B. P. Dayal, Acta euyd. A 26 (Pt. 3), 363 (1970)]

\[
a_T = 6.1016 + 54.63 \times 10^{-6} T + 6.82 \times 10^{-9} T^2 + 5.28 \times 10^{-12} T^3 \tag{7.12}
\]

and

\[
a_T = 6.4802 + 31.94 \times 10^{-6} T + 7.55 \times 10^{-9} T^2 + 9.25 \times 10^{-12} T^3 \tag{7.13}
\]

respectively. With the help of these equations the lattice parameters at various temperatures are evaluated. The L-J potential is then used to evaluate the force constants $A$ and $B$. The values of the constants $P$ and $Q$ are evaluated first using the known values of $A$, $B$, $e$ and $V$ at room temperature, ($A$ values are
Table 7.1(a). Force Constants (in units of $e^2/V$).

<table>
<thead>
<tr>
<th>System</th>
<th>$A$</th>
<th>$A_1$</th>
<th>$\sigma_1$</th>
<th>$\sigma_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTe</td>
<td>47.699</td>
<td>-0.729</td>
<td>6.009</td>
<td>-7.469</td>
</tr>
<tr>
<td>CdTe</td>
<td>63.415</td>
<td>-1.235</td>
<td>6.436</td>
<td>-8.9077</td>
</tr>
</tbody>
</table>

Table 7.1(b). The physical parameters of ZnTe and CdTe used for the evaluation of phonons.

<table>
<thead>
<tr>
<th>System</th>
<th>$a_0$ (Å)</th>
<th>$m_1$ (g)</th>
<th>$m_2$ (g)</th>
<th>$\alpha_m$</th>
<th>$Z$ (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTe</td>
<td>6.1016</td>
<td>65.37</td>
<td>127.6</td>
<td>1.6381</td>
<td>0.724</td>
</tr>
<tr>
<td>CdTe</td>
<td>6.4802</td>
<td>112.4</td>
<td>127.6</td>
<td>1.6381</td>
<td>0.847</td>
</tr>
</tbody>
</table>
taken from Table 7.1). $e$ is the electronic charge, $V$ is the volume of unit cell,

$$V = 2r_0^3$$ and $r_0 = a/2$, where $a$ is the lattice parameter.

The value of $B$ is found by using the relation

$$B = -\frac{2}{3} \alpha_m Z^2$$ (7.14)

where $\alpha_m$ is the Madelung constant [28], which is given as 1.6381 for Zinc blende structure and $Z$ is the effective charge.

Two nearby temperatures, $T_1$ and $T_2$, are chosen. Due to thermal expansion the volume gets changed and the phonon frequencies also change accordingly. Since, the temperatures $T_1$ and $T_2$ are very close, it may be assumed that the whole procedure is carried out at the constant temperature $T = (T_1 + T_2)/2$. The phonons and the volume of the unit cell are evaluated for the two temperatures $T_1$ and $T_2$ on a simple rigid ion model. Now, the mode Grüneisen parameter is evaluated using the relation, $\gamma_q = -\left( \frac{\partial \ln \omega_q}{\partial \ln V} \right)_T$.

### 7.3.2 Ionic systems

When the system is anisotropic, the procedure adopted by Batana et al [9] is followed i.e., the Daniel’s method [10], which uses the de Launay’s anisotropy table [11]. {Table 7.2(a) & (b)}.

The anisotropy factor $f(s,t)$ is evaluated by using the de Launay’s table,

where

$$s = \frac{(C_{11} - C_{44})}{(C_{12} + C_{44})} \quad \text{and} \quad t = \frac{(C_{12} - C_{44})}{C_{44}}$$ (7.15)
Table 7.2(a). THE ANISOTROPY FACTOR $F(S \geq 1, T \geq 0)$

<table>
<thead>
<tr>
<th>S/T</th>
<th>.0</th>
<th>.2</th>
<th>.4</th>
<th>.6</th>
<th>.8</th>
<th>1.0</th>
<th>1.2</th>
<th>1.4</th>
<th>1.6</th>
<th>1.8</th>
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<td>1.026</td>
<td>1.031</td>
<td>1.036</td>
<td>1.039</td>
<td>1.043</td>
<td>1.046</td>
<td>1.049</td>
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<td>1.5</td>
<td>1.264</td>
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<td>1.358</td>
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<td>1.416</td>
<td>1.443</td>
<td>1.470</td>
<td>1.497</td>
<td>1.522</td>
<td>1.547</td>
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<td>1.577</td>
<td>1.623</td>
<td>1.667</td>
<td>1.710</td>
<td>1.752</td>
<td>1.793</td>
<td>1.833</td>
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<td>1.787</td>
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<td>1.901</td>
<td>1.955</td>
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<td>2.059</td>
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<td>2.159</td>
<td>2.206</td>
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<td>1.903</td>
<td>1.973</td>
<td>2.041</td>
<td>2.105</td>
<td>2.169</td>
<td>2.229</td>
<td>2.289</td>
<td>2.348</td>
<td>2.405</td>
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<td>1.980</td>
<td>2.062</td>
<td>2.142</td>
<td>2.215</td>
<td>2.289</td>
<td>2.359</td>
<td>2.428</td>
<td>2.496</td>
<td>2.560</td>
<td>2.624</td>
<td>2.686</td>
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<td>2.207</td>
<td>2.293</td>
<td>2.377</td>
<td>2.457</td>
<td>2.535</td>
<td>2.610</td>
<td>2.683</td>
<td>2.755</td>
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<td>2.613</td>
<td>2.697</td>
<td>2.779</td>
<td>2.858</td>
<td>2.935</td>
<td>3.010</td>
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<td>2.571</td>
<td>2.667</td>
<td>2.761</td>
<td>2.849</td>
<td>2.937</td>
<td>3.021</td>
<td>3.104</td>
<td>3.184</td>
<td>3.262</td>
</tr>
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</table>
Table 7.2(b). THE ANISOTROPY FACTOR \( F(S > 1, T < 0) \)

<table>
<thead>
<tr>
<th>S/T</th>
<th>-1.0</th>
<th>-0.9</th>
<th>-0.8</th>
<th>-0.7</th>
<th>-0.6</th>
<th>-0.5</th>
<th>-0.4</th>
<th>-0.3</th>
<th>-0.2</th>
<th>-0.1</th>
</tr>
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<td>1.0</td>
<td>0.9315</td>
<td>0.9415</td>
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<td>0.9588</td>
<td>0.9663</td>
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<td>0.9794</td>
<td>0.9852</td>
<td>0.9905</td>
<td>0.9954</td>
</tr>
<tr>
<td>1.5</td>
<td>1.0715</td>
<td>1.0942</td>
<td>1.1158</td>
<td>1.1366</td>
<td>1.1567</td>
<td>1.1760</td>
<td>1.1948</td>
<td>1.2130</td>
<td>1.2307</td>
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</tr>
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<td>1.2278</td>
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<td>1.3191</td>
<td>1.3477</td>
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<td>1.4292</td>
<td>1.4551</td>
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<td>1.4255</td>
<td>1.4626</td>
<td>1.4986</td>
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</tr>
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<td>1.6113</td>
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<tr>
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<td>2.0383</td>
<td>2.0923</td>
<td>2.1449</td>
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<td>5.0</td>
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<td>1.9608</td>
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<td>2.0852</td>
<td>2.1446</td>
<td>2.2025</td>
<td>2.2588</td>
<td>2.3138</td>
</tr>
</tbody>
</table>
\( C_{11}, C_{12} \) and \( C_{44} \) are elastic stiffness constants (Table 7.3).

The elastic Grüneisen parameter is then evaluated as follows [9]

\[
\gamma = -\frac{1}{6} + \left[ \frac{1}{2 \chi_t C_{44}} \right] + \left[ \frac{1}{3 f \chi_t} \left( \frac{\partial f}{\partial s} \frac{\partial s}{\partial p} + \frac{\partial f}{\partial t} \frac{\partial t}{\partial p} \right) \right]
\]  

(7.16)

where \( \frac{\partial C_{44}}{\partial p}, \frac{\partial s}{\partial p}, \frac{\partial t}{\partial p} \) are the pressure derivatives, \( f \) is the anisotropy factor (a function of the independent variables \( s \) and \( t \)), \( \frac{\partial f}{\partial s} \) and \( \frac{\partial f}{\partial t} \) are the partial derivatives of \( f \) with respect to \( s \) and \( t \), respectively [29] and \( \chi_t \) is the isothermal compressibility.

The values of \( \frac{\partial s}{\partial p} \) and \( \frac{\partial t}{\partial p} \) are obtained from the relations [9]

\[
\frac{\partial s}{\partial p} = \frac{\left( C_{12} + C_{44} \right) \left( \frac{\partial C_{11}}{\partial p} - \frac{\partial C_{44}}{\partial p} \right) - \left( C_{11} - C_{44} \right) \left( \frac{\partial C_{12}}{\partial p} + \frac{\partial C_{44}}{\partial p} \right)}{(C_{12} + C_{44})^2}
\]  

(7.17)

\[
\frac{\partial t}{\partial p} = \frac{C_{44} \left( \frac{\partial C_{12}}{\partial p} - \frac{\partial C_{44}}{\partial p} \right) - \left( C_{12} - C_{44} \right) \left( \frac{\partial C_{44}}{\partial p} \right)}{C_{44}^2}
\]  

(7.18)

From ref. [30] and [31]

\( \chi_t = 3.3 \times 10^{-12} \text{ cm}^2\text{dyne}^{-1} \) for NaCl

\( \chi_t = 4.8 \times 10^{-12} \text{ cm}^2\text{dyne}^{-1} \) for KCl  

(7.19)

It is known that there are two types of contributions to the Grüneisen parameter. The first is from the elastic stiffness constants or thermal expansion
Table 7.3. (CDATA) Elastic Constants in units of $10^{12}$ dyne/cm$^2$

<table>
<thead>
<tr>
<th>System</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{44}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.4940</td>
<td>0.1240</td>
<td>0.1280</td>
</tr>
<tr>
<td>KCl</td>
<td>0.4050</td>
<td>0.0690</td>
<td>0.0627</td>
</tr>
<tr>
<td>ZnTe</td>
<td>0.7150</td>
<td>0.4080</td>
<td>0.3110</td>
</tr>
<tr>
<td>CdTe</td>
<td>0.5350</td>
<td>0.3690</td>
<td>0.2020</td>
</tr>
</tbody>
</table>
i.e., \( \gamma_1 = \frac{1}{2 \chi \chi C_{44}} \frac{\partial C_{44}}{\partial p} \) and the second from the anisotropy of the system

i.e., \( \gamma_2 = \frac{1}{3 f \chi t} \left( \frac{\partial f}{\partial s} \cdot \frac{\partial s}{\partial p} + \frac{\partial f}{\partial t} \cdot \frac{\partial t}{\partial p} \right) \).

When the system is highly anisotropic, the anisotropic contribution will dominate and compared to this, the contribution from thermal expansion would be negligible. Therefore, for such systems \( \gamma_2 \) alone should be considered. But in other cases where the thermal expansion contribution is appreciable, all the terms in Eqn.(7.16) are to be considered.

### 7.4 Description of the program

A generalized program is developed for the evaluation of \( \gamma \) and the source code for the evaluation of the Grüneisen parameter both for the isotropic and anisotropic cases is in FORTRAN 77. The program is developed to evaluate the Grüneisen parameter of a system at various temperatures from 0 K to a high temperature up to 1000 K.

The program consists of a main program and eleven subroutines. It is pictorially represented in Fig. 7.1. Among them two are major subroutines SLTONE and SGTONE. Only one of these is used at a time depending on the system. Selection of any one of these two is made by fixing the value of the parameter s,
The elastic stiffness constants $C_{11}, C_{12}$ and $C_{44}$ [32,33] are given in the CDATA file (Table 7.3) and the data generating subroutines like FCZNT, FCCDTE, etc., in the case of systems with $s < 1$ are included, which would generate the data (force constants) and store them in file FC.OUT. Whereas, in the case of systems with $s > 1$, a file like *PAR.INP similar to NACLPAR.INP (Table 7.4) or KCLPAR.INP (Table 7.5) with values of elastic stiffness constants $C_{ij}$, pressure coefficients $PC_{ij}$ and temperature coefficients $TC_{ij}$ [32,33] are to be given as data. The subroutine PARAM(LL) reads these data and generates the data (FC.OUT) for the second major subroutine SGTONE. The names of the chosen systems are properly entered in the main program, subroutines SLTONE, PRINTB and PARAM(LL). The flow of the main program and the subroutines is explained in detail.

(a) Main program:

A number is allotted for each system in the main program. During the execution, the number corresponding to the system, for which the $\gamma$ values are required, is typed out, for NaCl; NO=1, KCl; NO=2, ZnTe; NO=3, CdTe; NO=4, etc. Once the number is entered, the program reads the corresponding $C_{ij}$ values from the CDATA file and calculates the $s$ value. Based on this $s$
Table 7.4. (NACLPAR.INP) Elastic Constants and their pressure and temperature coefficients of NaCl.

<table>
<thead>
<tr>
<th>$C_{ij}$</th>
<th>$PC_{ij}$</th>
<th>$TC_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>in units of $10^{12}$ dyne/cm$^2$</td>
<td>in units of $10^{-12}$ cm$^2$/dyne</td>
<td>in units of $10^{-4}$ K$^{-1}$</td>
</tr>
<tr>
<td>0.494</td>
<td>23.0</td>
<td>-7.8</td>
</tr>
<tr>
<td>0.124</td>
<td>22.0</td>
<td>4.7</td>
</tr>
<tr>
<td>0.128</td>
<td>2.8</td>
<td>-2.2</td>
</tr>
</tbody>
</table>
Table 7.5. (KCLPAR.INP) Elastic Constants and their pressure and temperature coefficients of KCl.

<table>
<thead>
<tr>
<th></th>
<th>$C_{ij}$</th>
<th>$P_{ij}$</th>
<th>$T_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in units of $10^{12}$ dyne/cm$^2$</td>
<td>in units of $10^{-12}$ cm$^2$/dyne</td>
<td>in units of $10^{-4}$ K$^{-1}$</td>
</tr>
<tr>
<td>0.4050</td>
<td>29.2</td>
<td>-8.3</td>
<td></td>
</tr>
<tr>
<td>0.0690</td>
<td>24.5</td>
<td>-3.6</td>
<td></td>
</tr>
<tr>
<td>0.0627</td>
<td>-6.5</td>
<td>-2.1</td>
<td></td>
</tr>
</tbody>
</table>
value, it then chooses one of the major subroutines SLTONE or SGTONE and evaluates the $\gamma$ values for different temperatures.

---

**Fig. 7.1.** Block diagram of the Program

(b) Subroutine **SLTONE**: (S Less Than ONE)

The main program calls the first major subroutine SLTONE for systems with $s$ values less than one. Two sample cases are tested here, i.e., ZnTe and CdTe. This subroutine

(i) reads the data from the file FC.OUT.

(ii) reads the data from the file WV.DAT. – the wave vector values, the weighing factors, etc.,

(iii) evaluates the phonons.

(iv) calculates the mode Grüneisen parameter $\gamma_{qj}$ and the Grüneisen constant $\gamma$

(v) repeats the execution for various temperatures from 0 to 1000 K.
(vi) makes the results available in file GAMA.QU.

(i) Subroutine FCZNT and FCCDTE:

These programs generate the eight required parameters for the angular force model along with the volume of the unit cell. These parameters are repeatedly generated for various temperatures. Eqns. (7.12) and (7.13) are used for finding out the lattice parameter at any given temperature T for ZnTe and CdTe.

The force constants involved in the model are $A, A_1, \sigma_1, \sigma_2$ and the effective charge $Z$. $A$ and $A_1$ are the central force constants for the first and second neighbours; $\sigma_1$ and $\sigma_2$ are the angular force (non-central) constants for the first and second neighbours, which would take care of the anisotropy also. In short these subroutines generate the required data for the evaluation of the phonons at different temperatures and make them available in a file FC.OUT. This data is then read by the subroutine SLTONE.

(ii) Subroutine HIDJAG:

This program is used to diagonalize a real symmetric matrix of any order by Jacobian method, to find the eigen values and the eigen displacements.

(c) Subroutine SGTONE: (S Greater Than ONE)

The main program calls the second major subroutine SGTONE for systems with $s>1$. Again two samples are considered i.e., NaCl and KCl. For
such systems, the method developed by Batana et al. [9] is followed with some modifications. This subroutine

(i) reads anisotropy values from file ANITAB.DAT.

(ii) writes anisotropy tables.

(iii) reads the temp, \( C_{ij} \), \( \frac{\partial C_{ij}}{\partial p} \), \( \chi_i \) and number from a file PAR.OUT.

(iv) evaluates Grüneisen parameter for different temperatures.

(v) makes the results available in file ANICON.OUT.

(In the present package, (iii), (iv) and (v) are the new modifications introduced in the program of by Batana et al[9])

(i) Subroutine SETTBL: (SET TaBLE)

This part of the program reads the anisotropy values corresponding to various values of \( s \) and \( t \) from the file ANITAB.DAT.

(ii) Subroutine PRINTB: (PRINt TaBLE)

This part of the program prints two tables of the anisotropy factors pertaining to the values of \( s > 1 \) & \( t > 0 \) and \( s > 1 \) & \( t < 0 \) separately. These tables are then used to calculate the value of anisotropy factor \( f(s,t) \) and its partial derivative at a given point of \( s \) and \( t \), obtained from the \( C_{ij} \) values of the chosen system.

(iii) Subroutine PARAM(LLL):

This subroutine reads the values of elastic stiffness constants \( C_{ij} \), pressure coefficients \( PC_{ij} \) and temperature coefficients \( TC_{ij} \) [27,28] at the
room temperature from the input files NACLPAR.INP or KCLPAR.INP and generates the elastic stiffness constants $C_{ij}$, and their pressure derivatives $\frac{\partial C_{ij}}{\partial p}$ downwards from 300 K upto 0 K in steps of 25 K (i.e., the temperature difference, TD is -25) from the first set of data (below 300 K) and upwards upto 1000 K in steps of 50 K (TD=+50) from the second set of data (above 300 K). These values along with the compressibility value are written in its output file PAR.OUT. This file is the input data for the subroutine SGTONE. Such data for any system can thus be generated by this subroutine.

(iv) Subroutine GACAL: (GAmma CALculation)

A modification in [9] is made so that this subroutine can be employed for various temperatures. In the program developed by Batana et al [9], this subroutine executes only once for a single temperature. This subroutine calculates the $s$ and $t$ values, calls the subroutines FANDDR and METHD and writes the temperature and its corresponding $\gamma_1$ (contribution to the Grüneisen parameter from thermal expansion), $\gamma_2$ (contribution to the Grüneisen parameter from anisotropy) and $\gamma$ (the total value of the Grüneisen parameter) values in the output file ANICON.OUT. Now, in the present program, this file ANICON.OUT will contain the values of $\gamma_1$, $\gamma_2$ and $\gamma$ for all temperatures.

(v) Subroutine FANDDR:
It calculates the values of the anisotropy factor $f(s,t)$ and its partial derivative at a given point $(s,t)$ using an interpolating polynomial $P(x,y)$ [24]. It generates the values of $f(s,t), \frac{\partial f}{\partial s}$ and $\frac{\partial f}{\partial t}$, ie., $(FST, FDS$ and $FDT)$ to be used by the subroutine METHD.

(vi) Subroutine METHD:

This subroutine calculates the values of $\frac{\partial s}{\partial p}$ and $\frac{\partial t}{\partial p}$ by using the eqns. (7.17) and (7.18) [9]. It separately evaluates the contribution of the different terms of the eqn. (7.16), the contribution from the elastic constants, $\gamma_1$ and the contribution from the anisotropy factor $f(s,t)$, $\gamma_2$ and finally the Grüneisen parameter $\gamma$.

Input:

The different variables, used in the different programs, are given below in brief.

First case, (cases with $s < 1$):

JMAX $\rightarrow$ number of temperatures for which $\gamma$ is calculated

TEMP $\rightarrow$ initial temperature in Celsius

$DD(1,J) \rightarrow \frac{e^2}{V}$,  $e$ – charge & $V$ – volume.

$DD(2,J) \rightarrow M_1$ $\rightarrow$ mass of the cation
DD(3,J) → $M_2$ → mass of the anion

DD(4,J) → $A_0$ → first neighbour central force constant

DD(5,J) → $A_1$ → second neighbour central force constant

DD(6,J) → $\sigma_1$ → first neighbour angular force constant

DD(7,J) → $\sigma_2$ → second neighbour angular force constant

DD(8,J) → Z → effective charge

DD(9,J) → V → volume

DD(10,J) → T → temperature in Kelvin

Second case, (cases with $s > 1$):

TD → temperature difference for which $\gamma$ is calculated

N → number of temperatures for which $\gamma$ is calculated.

TK → temperature in Kelvin.

$C_{ij}$ → elastic stiffness constants.

$PC_{ij}$ → pressure coefficients.

$TC_{ij}$ → temperature coefficients.

Output:

When the program is executed for any system, the results will be seen at the output as follows.

First case, (cases with $s < 1$):
The name of the system (For example: ZnTe or CdTe) will appear first and then the Grüneisen Parameter along with the corresponding temperature will appear next.

Second case, (cases with \( s > 1 \)):

The name of the system (For example: NaCl or KCl) will appear first, the Anisotropy table for \( s \geq 1 \) and \( t \geq 0 \), and the Anisotropy table for \( s \geq 1 \) and \( t < 0 \), will appear next, and finally the \( \gamma_1 \), \( \gamma_2 \) and \( \gamma \) values along with the corresponding temperature.

On the P-III, 800 MHz machine, 50 runs (50 different temperatures) take less than 1 sec. for the cases of \( s > 1 \) and 30 runs (30 different temperatures) take 30 sec. for \( s < 1 \).

### 7.5 Results and discussions

The Grüneisen parameter, at high temperatures, is essential to understand the transport phenomena at these temperatures. Similarly the origin of low temperature anharmonicity in certain systems had been investigated in the past and such reports are available in literature [34-37]. As several independent investigations on low and high temperature anharmonicity are reported, there is no attempt to present a unified approach to workout the Grüneisen parameter for any system and for any temperature till Batana et al [9] have reported a small section of the above idea in their program. That is, the low temperature anharmonicity alone has been considered their program.
Batana et al. [9] have presented a program to evaluate the Grüneisen parameter of some ionic crystals for a temperature of 195 K, as the anharmonicity plays its role even at low temperatures in those systems where low temperature anharmonicity is dominant. They visualized this through the anisotropic nature of the system; i.e., this program could handle only the systems with $s$ greater than one (greater anisotropy). But the systems having $s < 1$ (lower anisotropy) cannot be studied using this program. Since there is the need for a generalized program to work out the Grüneisen parameter including anisotropy and anharmonicity, the present program is developed after suitable modifications on the program of Batana et al. [9] with extensions to other type of systems. This becomes essential as the role of anharmonicity in different systems are different and once such a software is available, it will be simpler to study a specific system with this software for anharmonicity immediately. However, the program has been developed only for cubic systems, irrespective of the nature of anharmonicity.

This modified program computes the value of $\gamma$ for different temperatures from $\sim 0$ K to any high temperature (1000 K). The low and high temperatures are determined from the Debye temperatures of the systems. The results of the modified program are compared with the available experimental results reported by Born et al. [31], Sheard [38], and recently by Chuan-Hui Nie [39]. Appreciable agreement is observed between the calculated and the experimental results, as can be seen in Tables 7.6 and 7.7.
Table 7.6. Grüneisen Parameter for NaCl and KCl. (Systems with $s > 1$)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>NaCl Our Calculation</th>
<th>NaCl Experiment $[31,39]$</th>
<th>NaCl Experiment $[38]$</th>
<th>KCl Our Calculation</th>
<th>KCl Experiment $[31,38]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.44</td>
<td>1.43</td>
<td>1.36</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>1.45</td>
<td></td>
<td>1.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>1.46</td>
<td></td>
<td>1.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>1.47</td>
<td></td>
<td>1.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>1.64</td>
<td>1.63</td>
<td>1.60</td>
<td>1.47</td>
<td>1.48</td>
</tr>
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<td>400</td>
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<td></td>
<td>1.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>1.65</td>
<td></td>
<td>1.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>550</td>
<td>1.66</td>
<td>1.69</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>1.68</td>
<td></td>
<td>1.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>1.70</td>
<td></td>
<td>1.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>1.73</td>
<td>1.76</td>
<td>1.68</td>
<td></td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>1.77</td>
<td></td>
<td>1.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>1.79</td>
<td></td>
<td>1.80</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 7.7. Grüneisen Parameter For ZnTe and CdTe (Systems with S < 1)

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Our Calculation</th>
<th>Theoretical (Using Pressure Derivatives) [18]</th>
<th>Expt. [18]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZnTe</td>
<td></td>
<td>CdTe</td>
</tr>
<tr>
<td>0</td>
<td>0.760</td>
<td>0.100</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>-0.043</td>
<td>-0.050</td>
<td>0.443</td>
</tr>
<tr>
<td>10</td>
<td>0.677</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>75</td>
<td>0.749</td>
<td>0.600</td>
<td>125</td>
</tr>
<tr>
<td>125</td>
<td>0.758</td>
<td>0.750</td>
<td>0.784</td>
</tr>
<tr>
<td>225</td>
<td>0.777</td>
<td>0.870</td>
<td>0.799</td>
</tr>
<tr>
<td>325</td>
<td>0.796</td>
<td>0.900</td>
<td>0.817</td>
</tr>
<tr>
<td>425</td>
<td>0.819</td>
<td></td>
<td>575</td>
</tr>
<tr>
<td>675</td>
<td>0.840</td>
<td></td>
<td>0.846</td>
</tr>
<tr>
<td>775</td>
<td>0.940</td>
<td></td>
<td>675</td>
</tr>
<tr>
<td>875</td>
<td>0.987</td>
<td></td>
<td>0.863</td>
</tr>
<tr>
<td>1025</td>
<td>1.060</td>
<td></td>
<td>0.882</td>
</tr>
</tbody>
</table>

T(K) | Our Calculation |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.443</td>
</tr>
<tr>
<td>10</td>
<td>-0.461</td>
</tr>
<tr>
<td>75</td>
<td>0.784</td>
</tr>
<tr>
<td>125</td>
<td>0.789</td>
</tr>
<tr>
<td>225</td>
<td>0.799</td>
</tr>
<tr>
<td>375</td>
<td>0.817</td>
</tr>
<tr>
<td>575</td>
<td>0.846</td>
</tr>
<tr>
<td>675</td>
<td>0.863</td>
</tr>
<tr>
<td>775</td>
<td>0.882</td>
</tr>
<tr>
<td>825</td>
<td>0.894</td>
</tr>
<tr>
<td>975</td>
<td>0.877</td>
</tr>
<tr>
<td>1025</td>
<td>0.949</td>
</tr>
</tbody>
</table>
From the term \( \frac{1}{2\chi_4 C_{44}} \frac{\partial C_{44}}{\partial p} \), it is obvious that \( C_{44}, PC_{44}, \) and \( TC_{44} \) play an important role in deciding the contribution from thermal expansion to the Grüneisen parameter. The negative value of \( PC_{44} \) (for KCl) takes the \( \gamma_1 \) value below zero. That is, \( \gamma_1 \) becomes negligible when compared to the anisotropic contribution \( \gamma_2 \). Therefore \( \gamma_1 \) is neglected in such cases where the anisotropy is very high and the Grüneisen parameter is calculated by taking into account the anisotropic contribution, \( \gamma_2 \), alone.

The evaluation of thermal expansion or Grüneisen parameter for systems like ZnTe, CdTe, etc., where the anisotropy and the low temperature anharmonicity are not very high could not be carried out with the program of Batana et al [9], or the modified program of Batana et al [9], as we developed earlier.

Hence, another program is developed (i.e., Subroutine SLTONE, which uses the FC.OUT –force constants and WV.DAT – wave vector, files as data files) for the evaluation of \( \gamma \) for such systems for different temperatures. The results computed by this method for systems with \( s < 1 \), give a very satisfying agreement compared to the available experimental values reported by Soma et al [18] and Talwar et al [40]. This method is capable of predicting the negative values of \( \gamma \), which is due to the negative thermal expansion of
such solids. This particular fact could not be visualized explicitly from the program of Batana et al [9].

The present software has two different procedures. The first procedure gives a clear idea about the role of anisotropy on the Grüneisen parameter and the second procedure takes care of the anisotropy and the thermal expansion by way of actual lattice dynamics. The program has been tested on many of the NaCl type systems and Zinc blende type systems. Even though Batana et al [9] have studied the Grüneisen parameter at low temperature, particularly at 195 K, where the anisotropy is larger (as they are interested in the role of anisotropy in the low temperature region), the same program cannot be extended to any other temperatures as such. The program is therefore modified in such a way that Grüneisen parameter can be worked out for temperatures even up to 1000 K for the same NaCl type systems.

Such works for systems other than cubic systems can also be developed in the future, as this will be a very useful study before venturing into other thermal properties.
7.6 References.


