# Thermal and Elastic Properties of Solids and Geophysical Minerals at Elevated Temperatures and Pressures

A

Thesis

Submitted for the award of degree of

## Doctor of Philosophy

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*This Thesis is dedicated*

*to my inspiration*

*Late Prof. (Dr.) Sanjeev Kumar Srivastava*

# CERTIFICATE

This is to certify that the thesis entitled **"Thermal and Elastic Properties of Solids and Geophysical Minerals at Elevated Temperatures and Pressures"** which is being submitted by Sanjay Kumar in fulfillment of the requirements for the award of the degree of Doctor of Philosophy in the School of Physics and Materials Science, Thapar University, Patiala (Punjab), India is an exclusive record of candidate's own research work under our supervision. The thesis in part or in full has not been submitted in any other university or institute for the award of any degree. The thesis is fit to be considered for the award of degree of Doctor of Philosophy.


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# LIST OF PUBLICATIONS

## Research Publications

[1] S.K.Srivastava, **Sanjay Kumar** and O.P.Pandey, Relationship between Anderson-Grüneisen parameter and thermal expansivity, High Temperatures-High Pressures, 40 (2011) 161.

[2] **Sanjay Kumar,** S.K.Sharma and O.P.Pandey, Estimation of volume dependence of Grüneisen parameter for NaCl and $\varepsilon$–Fe, Ind. J. Pure and Applied Phys. 52 (2014) 541.

[3] **Sanjay Kumar,** S.K.Sharma and O.P.Pandey, Analysis of thermodynamic properties in the limit of infinite pressure, High Temperatures-High Pressures, (Accepted).

[4] **Sanjay Kumar,** S.K.Sharma and O.P.Pandey, Analysis of Volume dependence of Thermal Expansivity for NaCl, Canadian Journal of Physics. (communicated).

[5] **Sanjay Kumar,** O.P.Pandey and S.K.Sharma, Volume dependence of Isothermal Bulk Modulus and its higher pressure derivatives, Solid State Sciences (communicated).

[6] **Sanjay Kumar,** S.K.Sharma and O.P.Pandey, Volume dependence of Grüneisen parameter for solids under extreme compression, Pramana-Journal of Physics. (communicated).

# List of Papers presented in Conferences (International/National)

[1] **Sanjay Kumar,** S.K.Srivastava and O.P.Pandey, Thermal and Elastic properties of solids and geophysical minerals at elevated temperatures and pressures-A Review, 2nd International Conference on Emerging trends in Engineering and Technology (IETET-2011),20-22 October, 2011,G.I.M.T. Kanipla, Kurukshetra.

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# PREFACE

The present work deals with the thermal and elastic properties of solids and geophysical minerals at elevated temperatures and high pressures. The equation of state (EoS) for lower mantle and core regions of the Earth has also been discussed. The entire work has been divided into **six chapters**.

**Chapter 1** gives the introduction of the subject and information about the different models given by various researchers to study the thermal and elastic properties of the solids and geophysical minerals and review of the literature available. Also the background of the study is discussed. This chapter also focuses on the various terms involved in the study and their usefulness to study the behavior of solids at high temperatures and pressures. In the last section of this chapter, reason for selecting main objectives, methodology and the purpose of the present study is discussed which helps future researchers to carry out further research in the field of high temperatures and high pressures.

**Chapter 2** explains different theories of volume/pressure dependence of thermal expansivity. The Grüneisen theory represents the experimental data on thermal expansivity at atmospheric pressure to represent the temperature dependent thermal expansivity. Also, the Suzuki theory of thermal expansivity is discussed which yields good results with experimental data on thermal expansivity to wide temperature range for various geophysical minerals. In this section, Born and Huang method of thermal expansivity has also been described which is physically more fundamental and mathematically more convenient and is useful to predict the temperature dependence of volume of any crystal. In the last section of this chapter, a brief introduction about anharmonicity in thermal and elastic properties of solids is provided.

**Chapter 3** describes the details of two important dimensionless thermoelastic parameters i.e. isothermal and adiabatic Anderson-Grüneisen parameter which are having important role to study the thermal and elastic behavior of solids at high temperatures and high pressures and also the Grüneisen parameter- a very important thermodynamic quantity used to investigate the relationship between thermal and elastic properties of solids. The volume dependence of Grüneisen parameter and its higher order volume derivatives is also discussed following the expression based on thermodynamical constraints in the limit of infinite pressure.

**Chapter 4** deals with different forms of equations of state (EoS) for studying the high pressure behavior of solids using interatomic potentials which represents the relationship between pressure and volume. Keane equation of state is described which suggest that first pressure derivative of isothermal bulk modulus is a monotonically decreasing function with pressure and reaching a limiting value at infinite pressure. Keane EoS is useful for interpolation between shock wave data and lower pressure P-V data. In the last section of this chapter, more numerically simplified EoS given by Stacey has been described which follows the infinite pressure thermodynamics more accurately.

**Chapter 5** describes the various models developed in the present study and their formulations, results and discussions. An inter-relationship between the Anderson-Grüneisen parameter and thermal expansivity under adiabatic and isothermal compression has been developed for insulator materials. Further, a new empirical expression has been proposed to predict the values of volume dependence of Grüneisen parameter using two different models and higher order volume derivatives of Grüneisen parameter has also been discussed. In this chapter we have also analyzed the number of thermodynamic properties in the limit of infinite pressure. A reciprocal form model for the volume dependence of thermal expansivity has also been provided for different solids and geophysical minerals. In the last section of this chapter, a new $K$-prime equation of state (EoS) has been presented in the form of volume dependence of isothermal bulk modulus and its higher order pressure derivatives for lower mantle and core regions of the Earth. The temperature dependence of volume expansion ratio and its second order temperature derivative for NaCl and KCl has been proposed.

**Chapter 6** summarizes and concludes the results of the study on thermal and elastic properties of solids and geophysical minerals at high temperature and high pressure conditions. Relationship between Anderson-Grüneisen parameter and thermal expansivity show validation for lower mantle (an insulator) and for NaCl with experimental data reported in literature. NaCl and $\varepsilon$-Fe have been taken to check the reliability of the volume dependence of Grüneisen parameter model which gives a reasonably good agreement between calculated values and the values derived from experimental data on thermoelastic properties. Results of higher order volume derivatives of Grüneisen ratio is found consistent with Stacey and Davis relationship but the trend of third Grüneisen ratio has not been found satisfactory for NaCl and MgO. The results obtained for the analysis of thermodynamic properties in the infinite pressure limits are found consistent with the recent analysis of infinite pressure of thermoelastic properties and also based on the Stacey thermodynamics of solids at infinite pressure. Reciprocal form for volume dependence of thermal expansivity shows consistency with experimental data for NaCl and satisfies the thermodynamic constraints at infinite pressure on which it has been formulated. The newly developed EoS is found compatible to the Stacey $K$-prime EoS throughout the compression used. The better results for temperature dependence of volume expansion ratio and its higher order temperature derivative with the values obtained from basic thermodynamic relation exposes the validity of the expression. All the proposed models show close or better agreement with the experimental results and present a suitable model for further study to investigate the thermal and elastic properties of interior of the Earth.

# *CHAPTER 1*

# *Introduction*

## *Overview*

The present chapter gives the introduction of the subject and information about the different models given by various researchers to study the thermal and elastic properties of the solids with reference to geophysical minerals and review of the available literature. Also the background of the study is discussed. This chapter also focuses on the various terms involved in the work and their usefulness to study the behavior of solids at high temperatures and pressures. In the last section of this chapter, reason for selecting main objectives, methodology and the purpose of the present study is discussed.

## INTRODUCTION

The interior of the Earth is largely inaccessible and consequently our knowledge is primarily based on indirect inferences. In order to explore the understanding, one needs to know the average chemical composition of the solar system, chemical composition of rocks near the surface of the Earth, geophysical observations of the density of the Earth and laboratory study of the state and properties of materials at high temperatures and pressures.

## 1.1 THE COMPOSITION OF EARTH

The interior of the Earth exhibit an onion like structure with spherical layers. The Earth can be divided into three main parts: the crust, the mantle and the core (Fig. 1.1).

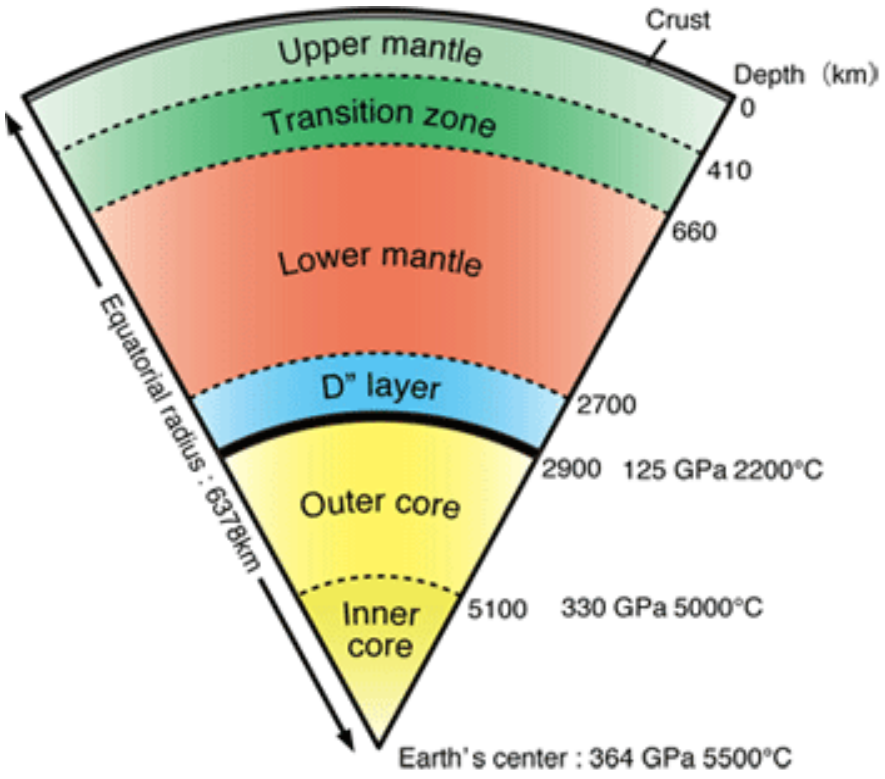


**Fig. 1.1** The interior of Earth

### 1.1.1 The Crust

It is the near surface layer (shell) with varying thickness (5-50 km). In the oceanic region, the crust is remarkably homogeneous (~ 6 km) and considerably thinner than the heterogeneous [1] continental crust (10-20 km) in the Basin and Range province in U.S.A; and (~ 50 km in Tibet). The crust in the oceanic region is mainly composite of sediments ($CaCO_3$ and $SiO_2$) and an underlying fine-grained rocks (basaltic layer) mainly composed of calcium-rich feldspar ($CaAl_2Si_2O_8$) and pyroxenes [$(Mg, Fe, Ca)SiO_3$]. The basaltic layer is created by the partial melting of upper mantle rocks at mid-oceanic ridges. The continental crust is further divided into two layers; the upper and the lower continental crusts. The upper continental crust is primarily made of silica–rich rocks such as granitites with major mineral constituents such as quartz ($SiO_2$), potassium or sodium-rich feldspars [$(K, Na)\ AlSi_3O_8$] and biotite [$K\ (Mg, Fe)_3(AlSi_3O_{10})\ (OH)_2$]. However, the lower crust consists of more mafic [MgO and FeO-rich] rocks such as basalt, gabbro or amphibolite with calcium-rich feldspar, pyroxenes, hornblende and amphibole [$(Mg, Fe, Ca, Na)_{2\text{-}3}\ (Mg, Fe, Al)_5\ (Si, Al)_8\ O_{22}\ (OH)_2$].

### 1.1.2 The Mantle

The crust mantle interface is generally referred to a Moho discontinuity. The mantle, in general, consists of three layers:

i) **The upper mantle:** The layer below the crust-mantle interface (Moho discontinuity) down to ~ 400 km is referred to as upper mantle. The major constituents of the upper mantle are olivine, pyroxenes and garnets [$(Mg, Fe, Ca)_3\ Al_2Si_3O_{12}$]. Olivine with highly anisotropic elastic properties is the most abundant mineral in this layer. The in homogeneity parameter [1] has low values in upper mantle and is an indicative of a temperature gradient much higher than the adiabatic gradient. The higher temperature gradient results in mechanical stratification of the upper mantle. The upper most cold part, called lithosphere, is characterized by low electrical conductivity and high creep strength; whereas a layer under the lithosphere, referred to as asthenosphere, generally represents high temperature (~ melting point). The interface between lithosphere and asthenosphere is defined by sharp changes in physical properties. The thickness of lithosphere varies from 50-100 km at the age of around 100 million years near the ocean ridges where new oceanic lithosphere is formed.

ii) **The transition zone:** Under high temperatures and pressures, the silicate minerals undergo various phase transformations [1] corresponding to the pressure and temperature conditions in the transition zone (400-670 km). For example, olivine [$(Mg, Fe)_2SiO_4$] with Fe or (Fe + Mg) transforms to the modified spinel structure at ~ 400 km and then to the spinel structure at ~ 500 km and ultimately to the perovskite [$(Mg, Fe)SiO_3$] + magnesiowustite [(Mg, Fe)O] at ~ 670 km. Pyroxenes [$(Mg, Fe)SiO_3$] transforms into garnet structure.

iii) **The lower mantle:** It is primarily composed of perovskite [(Mg, Fe) $SiO_3$] and magnesiowustite [(Mg, Fe) O]. Perovskite [(Mg, Fe) $SiO_3$] constitutes ~ 40-50% of the Earth. However, the amount of magnesiowustite [(Mg, Fe) O] ranges from 0% to 20% depends upon the model [1].

### 1.1.3 The Core

The core consists of two parts: the outer core and the inner core. The densities of the two layers are higher than those of silicates; and metallic iron is believed to be the major constituent of the core of the Earth. The mantle and the crust are significantly depleted in iron as compared to the solar abundance, which suggests the existence of an iron rich layer in the deep portion of the Earth. The absence of the propagation of shear wave in the outer core manifests the molten state of this portion. This metallic liquid is supposed to generate the geometric field by convection. The observed density [1] of the outer core signifies the low density of outer core compared to that of the molten iron. However, the shear waves pass through the inner core, which is an indicative of its solid state and its density close to the Earth appears to be composed of layers: a relatively pure solid inner core and a liquid outer core consisting of a significant amount of light elements. This indicates that the inner core might have been the result of solidification of outer layer as a consequence of secular cooling.

## 1.2 GEOPHYSICAL MINERALS

Geophysical minerals are the major constituents of the Earth's interior such as $MgSiO_3$, MgO, $Al_2O_3$, CaO and $Mg_2SiO_4$, NaCl, KCl etc. Periclase (MgO) is a simple oxide with cubic NaCl structure. Thermal and elastic properties of geophysical minerals are important to investigate the equations of state (EoS) of interior of the Earth. To describe the thermodynamic and elastic properties of solids and geophysical minerals, it is necessary to know the volume thermal expansion coefficient or thermal expansivity with the change in temperature and

pressure/volume. The thermal expansivity is one of the fundamental properties of solids. It results from the anharmonicity of the interatomic potential and is related to many thermodynamic and elastic quantities such as specific heat, elastic constant, Grüneisen ratio etc. Because of experimental difficulties at high temperatures, the reliable data on temperature dependence of thermal expansivity are not found. Therefore, an empirical, phenomenological or semi-phenomenological model of thermal expansivity is required to investigate high temperature behaviour of solids and minerals.

Jindal and Pathak [2] calculated the thermal expansion for sodium and potassium at all temperatures using realistic potentials, obtained from one-orthogonalized-plane-wave matrix elements and screening functions of Geldart and Taylor [3, 4] and of Vashishta and Singwi [5]. No significant difference between the results from these two potentials has been found. The agreement with experimental results of Schouten and Swenson [6] for potassium is found to be good. In the absence of appropriate experimental data for sodium, the theoretical results have been compared with the old data on polycrystalline sodium. These are found to be in qualitative agreement. A thermal-expansion contribution to the free energy and heat capacity of an anharmonic crystal has been estimated by Jindal and Pathak [7]. It has been found that the perturbation expansion for the free energy converges faster by taking into consideration the thermal-expansion contribution. Due to thermal expansion, the $T^2$ coefficient of the heat capacity at constant volume is reduced to about 50% of its explicit anharmonic contributions. Kushwah and Shanker [8] studied the thermal expansivity of MgO in the temperature range 300–1800 K, using various thermodynamic relationships. The volume-temperature relationship and thermal expansion coefficient as a function of temperature were predicted and compared with each other. It is found that among the various equations used, the Suzuki equation presents the best agreement with the experimental data. Thermal expansivity of MgO and $MgSiO_3$ perovskite are estimated by Chopelas [9] using the Maxwell's relationship. Cynn et al. [10] presented several thermodynamic properties for $Mg_2SiO_4$ (forsterite) as a function of volume and temperature, including: the entropy, $S$; the specific heat, $C_V$; the Grüneisen ratio, $\gamma$ in $V$, $T$ space. Kushwah et al. [11] used the Chopelas-Boehler approximation for the volume dependence of the Anderson-Grüneisen parameter and the Anderson's formula for the temperature dependence of thermal expansivity to study the pressure-volume-temperature relationship for LiF, NaF and CsCl

crystals up to a pressure of 90 kbar and in the temperature range 298–1073 K. The results obtained are found to present close agreement with the available experimental data.

The Grüneisen theory of thermal expansion as formulated by Born and Huang [12] has been modified by Shanker et al. [13] including higher-order terms for the change in volume in the expansion of potential energy. New expressions obtained for the thermal expansivity and bulk modulus were used to estimate these quantities for MgO and other minerals in the temperature range 300–1800 K. The results are found to be in close agreement with the experimental data. Kushwah et al. [14] calculated the variation of thermal expansivity ($\alpha$) with pressure for MgO at high temperature, using: (a) thermodynamic formulation developed by Guillermet [15] within the framework of Murnaghan's approximation [16], and (b) Anderson-Isaak [17] equation representing the variation of $\alpha$ with compression along an isotherm. The results obtained from the two methods are compared and the Anderson-Isaak equation is found to present an agreement to the experimental data. Shanker and Kushwah [18] have studied the volume-temperature relationship and thermal expansivity of NaCl and KCl crystals at high temperature. The results are in close agreement with the experimental data. Using the formulation for thermal expansivity of solids, Shanker and Kushwah [19] have calculated the volumes of $CaSiO_3$, $MgSiO_3$, $(Mg_{0.9}Fe_{0.1})SiO_3$ and $(Mg_{0.8}Fe_{0.2})SiO_3$ perovskites under high pressures and high temperatures. The results obtained are found to be in close agreement with the experimental *P*–*V*–*T* data for the solids. The temperature dependence of the volume thermal expansion and the interatomic separation are studied by Pandey [20] from a static lattice to melting temperature for NaCl crystal. A new semi-phenomenological isobaric EoS is derived and a good agreement between theory and experiment is found. Shanker and Kushwah [21] developed a method for determining volume expansion with temperature along isobars for NaCl crystal up to a pressure of 30 GPa and temperature up to 773 K, and also for $MgSiO_3$-perovskite up to a pressure of 160 GPa and temperature up to 3000 K. The results show close agreement with the data based on experimental studies for the temperature dependence of thermal expansivity at high pressure. Anderson [22] investigated the thermal pressure ($P_{TH}$) of solids and acquired the conditions under which it is independent of volume.

Jacobs and Oonk [23] proposed a linear relationship between molar volume and the logarithm of bulk modulus. This relation is also valid for oxide and silicate substances. From

the relationship, an equation of state has been developed and applied to the substance MgO. Singh and Chauhan [24] presented an analysis of the temperature dependence of thermal expansivity and isothermal bulk modulus in terms of the Anderson–Grüneisen parameter and the thermal pressure. The analysis is presented for ionic solids viz. NaCl, KCl, MgO and CaO in the temperature range starting from room temperature up to the temperature close to their melting temperatures. Deng and Yan [25] predicted the pressure–volume–temperature (*P*–*V*–*T*) relationships and the variations of $\alpha$ and $K_T$ with temperature and pressure for NaCl, CsCl, LiF, NaF crystals up to 30 GPa and in the temperature range 298–1073 K. It is found that these relationships are valid and are in good agreement with the available experimental data. Isaak and Anderson [26] determined the coefficient of thermal expansion ($\alpha$) for hexagonal close-packed (HCP) iron at simultaneous increment in pressure and temperature conditions.

A simple and straightforward method is developed by Singh and Gupta [27] for determining the volume thermal expansion coefficient in minerals (MgO, CaO) under the effect of temperature. The expressions for thermal expansion coefficient and the bulk modulus are obtained assuming that the Anderson parameter ($\delta_T$) varies with temperature. It shows close agreement with the data based on experimental studies of the temperature dependence of the thermal expansion and the bulk modulus at zero pressure.

A simple theoretical model was developed by Singh and Kumar [28] to investigate the temperature dependence of the bulk modulus and second order elastic constants. The method was based on the two different approaches, viz. (i) the theory of thermal expansivity formulated by Suzuki [29], based on the Mie–Grüneisen equation of state and (ii) the theory of high-pressure–high-temperature equation of state formulated by Kumar [30], based on thermodynamic analysis. It was concluded that the Kumar formulation is far better than the Suzuki theory of thermal expansivity. Vijay [31] showed an intimate relationship between the temperature dependence of elastic constants and volume expansion for MgO, CaO, $Al_2O_3$ and $Mg_2SiO_4$ for a wide range of temperature. Such a relationship can be represented by a power law as revealed by Murnaghan's approximation [16]. Values of elastic constants and bulk moduli have been predicted at higher temperatures using the volume expansion estimated from the Shanker equation [13] for thermal pressure. Singh et al. [32] reported a new relationship between $\alpha$ and $K_T$ for ionic solids such as NaCl, KCl, MgO and CaO. According to Singh et al.

[32], there exists a linear relationship between $\alpha$ and $K_{T,}$ for a wide range of temperature at 1 bar pressure. It is shown that this linear relationship describes the experimental data with better precision than the widely used approximation according to which the product $\alpha K_T$ is nearly independent of temperature at temperatures higher than Debye temperature. They have contrasted the new relationship with an existing relationship between the product $\alpha K_T$ and volume *V*. A critical analysis of the Suzuki [33], Shanker [13] and Kumar [30] formulations is presented by Kumar [34]. It is demonstrated that Suzuki formulation is not capable to yield compression behaviour of solids. Singh et al. [35] has studied the *P–V–T* relationship for MgO at high pressure and at high temperature. The results obtained in the study are found in good agreement with the available experimental data for predicting the pressure–volume relationship along different isotherms. Gaurav et al. [36] studied the thermoelastic behaviour of MgO for the temperature range (300–3000 K) under different compressions down to $V/V_0 = 0.3$. It has been shown that a comprehensive study of the thermoelastic properties of MgO can be made with the help of the Anderson–Isaak equation for thermal expansivity and the Vinet equation of state taken together. They estimated values of thermal expansivity α, isothermal bulk modulus $K_T$, their variations with pressure and temperature, the Anderson–Grüneisen parameter and the change in entropy with compression for MgO along isotherms at different temperatures. Srivastava [37] reported a new relationship for temperature dependence of thermal expansivity at high temperatures. The relation is acquired on the ground of high-temperature experimental data collected by Anderson for six geophysical minerals, viz. NaCl, KCl, MgO, CaO, $Mg_2SiO_4$ and Grossular Garnet. It is found that the thermal expansivity varies exponentially with temperature above the Debye temperature.

A new relation for predicting volume thermal expansion of alkali halides at high temperatures is derived by Fang [38] on the basis of the assumption that the two different diffusional driving force models presented by Sharma and Sharma [39] and Singh [40] are equivalent. The tests on NaCl and KCl crystals demonstrate that the agreement between the calculated results obtained by this relation and the corresponding experimental data is very good. Singh and Chandra [41] found that there exists a precise relationship showing exponential dependence of elastic moduli on isobaric volume expansion for some typical ionic solids such as NaCl, KCl, MgO and CaO at high temperatures up to the corresponding values of melting

temperatures. They predicted the values of elastic moduli $C_{11}$, $C_{44}$, $C_S$, $K_S$ and $K_T$ at different temperatures for the solids. The Anderson–Grüneisen parameter corresponding to each elastic modulus is determined and found to be directly proportional to the volume, with a variation in temperature under isobaric conditions. The temperature dependence of different parameters, i.e., density $\rho(T)$, bulk modulus $K_T(T)$, shear modulus $G_T(T)$ and thermal pressure $\Delta P_{th}$ for mantle minerals, i.e., $X_2SiO_4$ (X=Mg, Fe, Co, Mn) in high temperature range on the basis of semi-phenomenological isobaric equation of state has been studied by Pandey [42]. The calculated values of these parameters show good agreements with experimental value in case of each mantle mineral. A new relation has been found by Srivastava [43] for the experimental data on volume expansion ratio at 1 bar pressure and temperatures above the Debye temperature. The performed analysis is based on the thermodynamic and thermoelastic data reported in a compilation by Anderson [44]. The analysis is presented for ionic solids, viz. NaCl, KCl, MgO and CaO. The superiority over a number of models is shown by computing volume expansion ratio and isothermal bulk modulus as a function of temperature. The present approach may contribute to the understanding of the high-temperature behavior of ionic solids. A relationship between the isothermal bulk modulus and the isobaric volume expansion for MgO has been used by Sushil [45] to obtain values for the isothermal bulk modulus at different temperatures up to 3000 K along isobars at selected pressures up to 224 GPa. The volume dependence of the Anderson–Grüneisen parameter $\delta_T$, has also been taken into account under isobaric as well as isothermal conditions. The pressure dependence of thermal expansivity was also studied along selected isotherms up to 3000 K. The method predicted the thermal expansivity and isothermal bulk modulus in the pressure–temperature space, showing behaviour that is consistent with the available experimental data. Srivastava and Sharma [46] evaluated the thermal pressure for MgO from room temperature to 3000 K at atmospheric pressure. Various relationships between thermal pressure and volume expansion ratio were examined. Thermoelastic properties, viz., $C_{11}$, $C_{44}$, $C_S$, and $K_S$ are calculated at high temperatures for the solid MgO, with the help of Murnaghan and Tallon models [16, 47]. Predicted values of thermoelastic properties at higher temperatures can be used to understand the high-temperature behavior of MgO at 1 bar pressure. An empirical relationship for temperature dependence of volume expansion is reported by Srivastava [48] at atmosphere pressure for solids. The solids

MgO, CaO, $Al_2O_3$ and $Mg_2SiO_4$ are considered for the study. The newly developed relationship is based on the fact that isothermal bulk modulus decreases linearly with temperature. A close agreement between the theory and the experiment validates the work. Srivastava [49] analyzed the thermoelastic constants of ionic solids NaCl and KCl and the minerals MgO, CaO and $Mg_2SiO_4$ using the tabulated data compiled by Anderson and Isaak [17]. It is found that there exists a precise linear relationship between the thermoelastic constant the thermal pressure. This empirical relationship provides a method to estimate the thermoelastic properties outside the experimental data range. Srivastava and Sharma [50] studied various relationships belonging to the temperature dependence of elastic constants for NaCl at atmospheric pressure. Relationships are modified on the basis of the assumption that the Anderson–Grüneisen parameter remains unchanged with the change in temperature. It was found that the results obtained by modified relationships is in agreement with the available experimental data. Vinod et al. [51] proposed the empirical relationships for temperature dependence of thermal pressure at atmospheric pressure for NaCl and KCl solids. It was found that the thermal pressure is a complex function of temperature and deviates from linearity in the high-temperature region. The temperature dependence of volume expansion ratio is also established with the help of thermal pressure. A close agreement between theory and experiment is found.

A relationship between elastic constants and thermal expansivity for ionic solids, viz., NaCl, KCl, CaO and MgO has been obtained by Srivastava [52] in high temperature region at atmospheric pressure. The analysis is based on the experimental data tabulated by Anderson [44] and the extrapolated data reported by Singh and Chauhan [53]. Srivastava and Sharma [54] re-parametrized the thermodynamic and thermoelastic properties of NaCl at low compression and at high temperature. It is found that the thermal expansivity and isothermal bulk modulus both change linearly with the increase in temperature at compressions down to 0.90. It reveals that the thermal pressure is nearly independent of compression along an isotherm. Srivastava and Sharma [55] derived a new relationship to predict the temperature dependence of elastic constants. Proposed relationship is applied to study the elastic constants of NaCl and KCl. A linear relationship between thermal expansivity and elastic constants at high temperatures is exhibited for solids. The extrapolated data on elastic constants in very high temperature region, obtained in the study are useful to understand the thermoelastic properties of NaCl and KCl.

There is a close agreement between theory and experiment. Srivastava et al. [56] have modified the earlier calculations for the compression dependence of entropy of MgO using more accurate experimental data and more accurate equation of state. They estimated the thermal expansivity with the help of the Anderson–Isaak [57] equation at different compressions and at selected temperatures up to the melting temperature of the solid. *P–V* relationship and compression dependence of isothermal bulk modulus are computed with the help of the Stacey equation of state. The results are compared with those recommended by Cynn et al. [58]. It is found that the entropy decreases with increasing compression along an isotherm.

Fang [59] developed a simple and straightforward method for evaluating and predicting elastic moduli of ionic materials at high temperatures based on the approximation, as suggested first by Wang and Reeber [60]. It shows that the temperature derivative of the work done by thermal pressure approaches a constant at high temperature [47]. The tests on MgO and CaO demonstrated that the agreement between the calculated results and the corresponding experimental data is very good. A relationship between thermal pressure and volume expansion ratio for ionic solids at 1 bar pressure is disclosed by Sinha [61]. The ionic solids NaCl, KCl, MgO and CaO are considered for the analysis. The analysis is based on the experimental data tabulated by Anderson. A close agreement between theory and experiment is found.

Gupta [62] calculated the melting of geophysical minerals and isothermal bulk modulus ($K_T$) of MgO, CaO, $MgSiO_3$, $CaSiO_3$ and $Mg_3Al_2Si_3O_{12}$ perovskites at high pressure conditions, obtained from generalized Redberg EOS. The thermal effects at high temperature have been estimated using the formulation for thermal pressure. The results are consistent with the high-temperature and high-pressure experimental data. Sharma [63] proposed three relationships to predict the values of the mixed temperature and pressure derivative of isothermal bulk modulus ($\partial^2 K_T/\partial P\partial T$) at zero pressure based on different assumptions. It was found that ($\partial^2 K_T/\partial P\partial T$) changes linearly with increase in temperature above Debye temperature at zero pressure. The developed relationships are applied to MgO and the predicted values of ($\partial^2 K_T/\partial P\partial T$) and compare favorably with the experimental results. The compression dependence of $\alpha K_T$ was analyzed by Srivastava et al. [64] using Anderson–Isaak equation along with Stacey's equation of state for ionic solids such as NaCl and MgO. It was found that the value of $\alpha K_T$ decreases with increasing compression and attains a minimum, after which it increases with increasing value of

compression along an isotherm. It was also found that $\alpha K_T$ tends to infinity as $P \rightarrow \infty$ or $V \rightarrow 0$. The presented nature of $\alpha K_T$ is valuable to understand the thermoelastic and thermodynamic properties of MgO and NaCl at high compressions and at high temperatures. Srivastava et al. [65] proposed a suitable model to compute volume dependence of thermal expansivity, which is applicable up to infinite pressure or compression. The newly developed model satisfies the constraints of infinite pressure as suggested by high-pressure thermodynamics. The compression dependence of thermal expansivity for lower mantle of the Earth is evaluated with the help of the proposed model where close agreement between theory and the results, predicted with the seismic data is found. Srivastava and Sinha [66] developed a method to forecast thermal expansivity under adiabatic conditions with the change in density. The developed relationship is used to predict the density dependence of thermal expansivity for lower mantle region of the Earth. A good agreement between seismic data and theory reveals the validity of their approach. The predicted relationship is very useful to understand the interior of the Earth. Sinha et al. [67] developed new relationships to investigate temperature dependence of elastic constants and thermal pressure for ionic solids by using a formulation which is valid up to extreme compression limit. The ionic solids NaCl, KCl, MgO and CaO were considered for the study. Close agreement between theory and experiment shows the validity of result. Singh [68] studied the pressure P, bulk modulus $K_T$ and its first and second derivatives $K_T^{'}$ and $K_T^{''}$, and the Grüneisen parameter $\gamma$ and its volume derivative $q$ for NaCl crystal down to a compression 0.65. These properties have been calculated along different isotherms at selected temperatures in the range 300-1500 K using Holzapfel AP2 equation of state. The result obtained has been found to be in good agreement with the data reported in the literature.

Sharma et al. [69] have derived a relation for computing volume dependence of entropy at selected isotherms. This formula is based on the Al'tshuler et al. model [70] for volume dependence of Grüneisen parameter and used to determine entropy for MgO down to a volume ratio 0.50 at selected isotherms and also formulate a relationship between Debye temperature and entropy and it has been found that Debye temperature increases exponentially as entropy decreases. A new method for the determination of pressure–interatomic separation–temperature relationship has been investigated by Liu [71] and applied for some alkali halides by using the Mie–Grüneisen equation of state and the Anderson thermal pressure and an ionic model based on

Harrison's treatment of overlap repulsive potential which takes into account the interactions up to second neighbors. It has been found that the new method yields satisfactory results in agreement with the available experimental data.

Srivastava [72] have examined the various formulations for volume dependence of the Grüneisen ratio, $\gamma$. The thermodynamic constraints for $\gamma_\infty$, $q_\infty$ and $\lambda_\infty$ have been used to discuss the validity of various relationships. The volume dependence of $\gamma$ and its derivatives, reported by Stacey and Davis [73] are analyzed. The Al'tshuler et al. [70] relationship of $\gamma(V)$ widely used in recent literature has been found to be inadequate on the variation of $\lambda$ with compression. The estimates of $\gamma, q$ and $\lambda$ are obtained with the combination of generalized free volume theory and reciprocal *K*-prime equations of state for the Earth's interior. Further, Sinha et al. [74] introduced a new *K*-prime equation of state (EoS), which can be used to understand the interior of the Earth. The newly developed EoS has been found to yield similar results as given by Stacey *K*-prime EoS and Keane EoS, in reference to the seismological data. However, the zero pressure and infinite pressure extrapolation of higher pressure derivatives of bulk modulus are found different for different *K*-prime EoS.

Singh [75] have studied high derivative thermoelastic properties such as the pressure derivatives of bulk modulus and the volume dependence of the Grüneisen parameter in case of *MgO* for a wide range of pressures down to compression $V/V_0 = 0.6$, and temperatures up to 3,000 K approaching the melting temperature by using the isothermal pressure–volume equation of state (EoS) based on the adapted polynomial expansion of second order (AP2) due to Holzapfel [76]. The results for the P–V–T relationships and high derivative properties have been obtained using the Holzapfel AP2 EoS. The pressure derivatives of bulk modulus and volume derivatives of the Grüneisen parameter have been determined using the free volume theory. A relationship between the pressure derivative of bulk modulus and the ratio of pressure and bulk modulus has been found to hold good.

Shanker et al. [77] presented a direct method using the basic principles of calculus to derive the expression for the third-order Grüneisen parameter in terms of the pressure derivatives of bulk modulus at extreme compression. The derivation presented, does not depend on the assumptions regarding the values of free-volume parameter and its variation with pressure. On the basis of the free volume theory of Grüneisen parameter ($\gamma$) and using the calculus of

indeterminates, Singh [78] found that the second order Grüneisen parameter ($q$) and the second pressure derivative of bulk modulus ($K_T^{"}$) change in a similar manner in the limit of extreme compression. The ratio of $q$ and $K_T K_T^{"}$ becomes finite at infinite pressure. This finding has been used further to obtain a relationship for the third order Grüneisen parameter $\lambda$ in terms of pressure derivatives of bulk modulus up to the third order. The results are found to be consistent with the identities obtained recently by Shanker et al. [79] using the free volume theory.

A reciprocal equation for the volume dependence of Anderson–Grüneisen parameter has been proposed by Sharma [80]. This equation has been found to fit the seismic data for the lower mantle region of the Earth. Sharma [80] also developed a new expression for predicting the values of density (volume) dependence of volume thermal expansivity under adiabatic conditions based on the reciprocal equation for the volume dependence of Anderson–Grüneisen parameter. It has been found that the seismic data on thermal expansivity for lower mantle corresponding to a wide range of pressures (0–135.75GPa) and has been found consistent with the thermodynamic constraints. The extreme compression limits of thermal expansivity, isothermal bulk modulus, adiabatic bulk modulus and products of thermal expansivity and bulk modulus have been obtained by Shanker et al. [81] using the basic principles of calculus and some thermodynamic identities in terms of the Anderson-Grüneisen parameters and pressure derivatives of bulk modulus. The isothermal extrapolations are found to be different from the corresponding adiabatic extrapolations. The results have been obtained using the Stacey thermodynamics of materials at infinite pressure.

Parish and Moore [82] present a rational foundation for the computation of equation of state (EoS) data for solids at high pressure and demonstrated a new method which makes use of an accurate relation expressing the Grüneisen parameter $\gamma$ (as a function of the specific volume V of the material) in terms of the specific inter-atomic potential energy $\phi(V)$. Existing expressions for $\gamma$ in the literature are usually approximations in terms of total pressure P. There is a variety of such "$(\gamma, P)$" formulas but has to be used selectively for particular application. The alternative "$(\gamma, \phi)$" relationship presented [82] are both unique and exact within the Debye and harmonic approximations and allows the individual terms of the EoS to be determined separately. It is rigorously derived and solved numerically, using experimental input data for aluminium, copper, lead and gold, to predict $\phi, d\phi/dV, \gamma, d\gamma/dV$ and EoS data for the four

metals. Comparison has been made with existing computations in the literature showing good agreement.

Brosh et al. [83] developed a new free energy formulation for calculations of thermophysical properties and high-pressure phase equilibria in Al, Si, MgO, Fe and the Al–Si binary alloy system specifically for inclusion of pressure effects in CALPHAD (CALculation of PHAse Diagrams) methodology. This formula is based on an interpolation between SGTE (Scientific Group Thermodata Europe) data at low pressures and the quasiharmonic lattice model at high pressures. The new formulation has been found constrained to physically credible predictions of the thermophysical properties, while preserving the simplicity of the CALPHAD method.

Although, various attempts have been made to study the variations of elastic moduli with temperature for ionic solids and geophysical minerals but a simple and accurate method for predicting high temperature elastic constants is still lacking. The present study will provide an anaytical method to understand the temperature dependent of elastic constants under isobaric conditions. Elastic properties of a solid are important because they relate to various fundamental solid-state properties such as interatomic potentials, equations of state, specific heat, thermal expansion, Debye temperature, melting point and the Grüneisen parameter. The elastic constant plays an important role in determining the strength of materials. Values of elastic constants provide valuable information about the bonding characteristics between adjacent atomic planes and anisotropic character of the bonding and structural stability. Grüneisen parameter is one of the important physics quantity that characterizes the anharmonic properties of solids. The thermoelastic properties are important to understand the thermodynamic and elastic behavior of solids at high temperatures and pressures.

The purpose of the present thesis is to develop a model for studying the thermal and elastic properties of solids and geophysical minerals. Such a study is useful for those who are engaged in research at high pressure and high temperature physics. The analysis of the temperature dependence of the thermoelastic parameters are of fundamental interest in studying the interior of the Earth. The data which will be obtained in the present work will be very useful for geophysicist.

# *CHAPTER 2*

# *Theory of Volume/Pressure Dependence of Thermal Expansivity*

## *Overview*

In this chapter, different theories of volume/pressure dependence of thermal expansivity have been discussed. The Grüneisen theory represents the experimental data on thermal expansivity at atmospheric pressure to represent the temperature dependent thermal expansivity. Also, the Suzuki theory of thermal expansivity is discussed which yields good results with experimental data on thermal expansivity to whole temperature range for various geophysical minerals. In this section, Born and Huang method of thermal expansivity has also been described which is physically more fundamental and mathematically more convenient and is useful to predict the temperature dependence of volume of any crystal. In the last section of this chapter, a brief introduction about anharmonicity in thermal and elastic properties of solids is provided.

## 2.1 THEORY OF VOLUME DEPENDENCE OF THERMAL EXPANSIVITY

Considering the regular lattice of atoms in a uniform solid material, there to be energy associated with the vibrations of these atoms. But they are tied together with bonds, so they can't vibrate independently. The vibrations take the form of collective modes which propagate through the material. Such propagating lattice vibrations can be considered to be sound waves and their propagation speed is the speed of sound in the material. Their vibrational energies are quantized and treated as quantum harmonic oscillators and these oscillators can accept or lose energy only in discrete units of energy $h\nu$, and these quanta of energy have been labeled "phonons". Physically, we can see why phonons scatter phonons. Wave-like motions propagate through a periodic lattice without scattering only if there are no distortions from periodicity. One phonon in a lattice distorts the lattice from periodicity and hence scatters another phonon. This view is a little oversimplified because it is essential to have anharmonic terms in the lattice potential in order for phonon–phonon scattering to occur. These cause the first phonon to modify the original periodicity in the elastic properties.

Without anharmonic terms, thermal expansion would not exist and the potential that each atom moved in would be symmetric. Anharmonic terms are responsible for small (linear in temperature) deviations from the classical specific heat at high temperature. We can understand this by assuming that there is some energy involved in the interaction process. If this is so, then there are ways (in addition to the energy of the phonons) that energy can be carried, and so the specific heat is raised. We have to consider that the anharmonic terms cause a temperature dependence of the phonon frequencies which can be understood by the temperature dependence of the phonon frequencies from the fact that they depend on interatomic spacing that changes with temperature (thermal expansion). Thus Grüneisen parameter $\gamma$ plays an important role in describing the pressure and temperature dependence of thermal properties of solids as it has both macroscopic and microscopic definition. The macroscopic definition is in terms of familiar thermodynamics properties while in microscopic definition, Grüneisen [84] defined a value of $\gamma_i$ for the volume derivative of each mode $\nu_i$ in the lattice. The investigation of the Grüneisen parameter and its volume dependence have been the subject of importance in understanding the macroscopic behaviour of solids.

The macroscopic formulation of the Grüneisen parameter is given by

$$\gamma = \frac{\alpha K_T V}{C_V} \tag{2.1}$$

where $\alpha$ is thermal expansivity, $K_T$ is isothermal bulk modulus, $V$ is molar volume and $C_V$, specific heat at constant volume. The microscopic definition originally proposed by Grüneisen [84] considered the volume dependences of the phonon frequencies $\nu_i$ of crystal vibrational modes and identified each mode $\nu_i$ with a value of $\gamma$ called the mode gamma $\gamma_i$, such that

$$\gamma_i = -\left(\frac{\partial \ln \nu_i}{\partial \ln V}\right)_T \tag{2.2}$$

We can write $\nu_i = v_i / \lambda_i$, where $v_i$ is the corresponding elastic wave speed and $\lambda_i$ is the wavelength. Since $i$ refers to a particular mode, $\lambda_i$ is a specified number of lattice spacing and its proportional to $V^{1/3}$, where V is specific volume.

## 2.2 GRÜNEISEN THEORY OF THERMAL EXPANSIVITY:

Various researchers used a number of Grüneisen theory to represent their experimental data on thermal expansivity ($\alpha(T)$) at atmospheric pressure i.e. $P = 0,$ which represents the temperature dependent thermal expansivity. If $L_i - L_0$ is the change in length and $L_0$ is the standard length, then

$$Y_i = \frac{L_i - L_0}{L_0} \tag{2.3}$$

and the change in volume is given by

$$Y = Y_1 * Y_2 * Y_3 \tag{2.4}$$

This theory involved using $Y = \Delta / V_0$, where $\Delta = V - V_0$

In this theory, Grüneisen [84] assumed the Mie-Grüneisen EoS, with its simplified expression for thermal energy

$$P = P_0(V) + \frac{\gamma_{mg} E_{TH}}{V} \tag{2.5}$$

where $\gamma_{mg}$ denotes to Mie-Grüneisen EoS and $E_{TH}$ is thermal energy.

Equation (2.5) is also written as

$$VP = VP_0(V) + \gamma_{mg} E_{TH} = G(V) \qquad (2.6)$$

Assuming infinitesimal elastisity, Grüneisen got rid of $P_0$ by taking $K_{T0}\Delta = P_0 V$. Grüneisen then expanded $G(V)$ as a Maclaurin's series to the second order in $\Delta$, which leads to a quadratic equation in $\Delta$, of the form

$$\Delta\left(1 - \frac{k}{V_0}\Delta\right) = \frac{\gamma_{mg} E_{TH}}{K_{T0}}, \text{ where } k = (1/2)(K_T' - 1) \qquad (2.7)$$

Grüneisen reduced equation (2.7) to a linear equation in $\Delta$ by reapplying the infinitesimal formula for $\Delta$ to the second term in the parentheses. This was justified because the thermally induced dilation is small. Therefore, equation (2.7) is replaced by

$$\Delta\left(1 - k\gamma_{mg}\frac{E_{TH}}{K_{T0}}\right) = \frac{\gamma_{mg} E_{TH}}{K_{T0}} \qquad (2.8)$$

For $\Delta$ versus $T$, the relationship is written as

$$Y = \frac{\Delta}{V_0} = \frac{E_{TH}(T, \theta_D)}{Q - kE_{TH}(T, 0)}, \text{ where } Q = \frac{K_{T0} V_0}{\gamma_{mg}} \qquad (2.9)$$

Differentiating equation (2.9) with respect to $T$, one can find the relationship for thermal expansivity by using the condition that $(\partial k / \partial T) = 0$ and $(\partial K_T' / \partial T) = 0$. These are not exactly zero, but nevertheless are small compared with $\partial E_{TH} / \partial T$. Thus, we have

$$\alpha = \left(\frac{\partial Y}{\partial T}\right)_P = \frac{\left(\frac{\partial E_{TH}}{\partial T}\right)_P}{Q\left(1 - \frac{kE_{TH}}{Q}\right)^2} \qquad (2.10)$$

Equation (2.9) or equation (2.10) is used semi empirically to fit the experimental data $Y$ versus $T$. Once the parameters are known, equation (2.10) is used to extrapolate or interpolate $\alpha$. It is usual to use a Debye function for $E_{TH}$, so that

$$E_{TH} = D\left(\frac{\theta_D}{T}\right) \qquad (2.11)$$

where $\theta_D$ is the Debye temperature. In the classical theory of a thermal solid, Debye approximated the phonon spectrum by assuming that all phonons are acoustic and the frequency

of the phonons is controlled by the sound velocities of an isotropic body. This theory led to good approximations of specific heat and entropy versus $T$ at high $T$ for metals by using the so-called Debye function $D(\theta_D/T)$ [44]. In his derivation, Debye defined the relationship between the Debye frequency $\omega_D$ and the mean sound velocity $v_m$. $\omega_D$ can be converted to a temperature (Debye temperature) by $\omega_D = (k/\hbar)\theta_D$, where $\hbar = h/2\pi$. By fitting measured $V-T$ data to the Grüneisen equation one will generate empirical values of $\theta_D$, $K_0^{'}$ and $\gamma_0$ for the minerals. If the values are reasonably close, the Grüneisen equation may be used with confidence to extrapolate for values of $\alpha$ at a temperature above the measurement range. If they do not agree, the resulting Grüneisen equation is unreliable for extrapolation purpose.

**2.3 SUZUKI'S THEORY OF THERMAL EXPANSIVITY:**

Suzuki [29] has found the drawback in the Grüneisen theory of thermal expansivity and reconsider equation (2.7) without the drastic assumption induced by going from equation (2.7) to equation (2.8), where equation (2.7) is a drastic equation in $\Delta$. By solving the real root of equation (2.7) which determines $\Delta$ at $T=0$. The thermal expansivity which is based on the volume at an arbitrary reference temperature is

$$Y = \frac{\left[1+2k-\left(1-\frac{4kE_{TH}}{Q}\right)^{1/2}\right]}{2ka_V} - 1 \qquad (2.12)$$

where $a_V$ is the ratio of volume at the reference temperature ($T_r$) and $T = 0K$. Above equation may be written as,

$$\eta = \frac{\left[1+2k-\left(1-\frac{4kE_{TH}}{Q}\right)^{1/2}\right]}{2ka_V} \text{ , where } \eta = (V/V_0) = 1+Y \qquad (2.13)$$

Above equation may also be written as

$$\frac{V}{V(T_0)} = \frac{\left[1+2k-\left(1-\frac{4kE_{TH}}{Q}\right)^{1/2}\right]\left(\frac{V}{V(T_0)}\right)}{2ka_V} \text{ , where } V/V(T_0) = (V/V_0)[V/V(T_0)] \qquad (2.14)$$

The analytical expression for $\alpha$ found by differentiation of equation (2.14) is quite complicated. Numerical differentiation of equation (2.14) is recommended for $\alpha(T)$. Equations (2.12), (2.13) and (2.14) are known as the Suzuki Equations. The Suzuki equations yield good agreement with experimental data on $\alpha$ corresponding to whole temperature range not only for $MgO$ [8] but also for other geophysical minerals [33, 85, 86].

## 2.4 BORN AND HUANG THEORY OF THERMAL EXPANSIVITY

The Suzuki equations are very complicated to obtain an analytical expression for thermal expansivity ($\alpha$) and therefore a numerical differentiation method has been used by earlier workers [44, 86]. Further, Born and Huang [12] adopted a method for formulating the Grüneisen theory of thermal expansivity. In this method the lattice potential energy is expanded in a power series of change in volume. On the other hand, Suzuki has expanded the quantity $G = PV$, where $P$ is the pressure and $V$ is the volume, following the work of Grüneisen. It is physically more fundamental and mathematically more convenient to use the expansion of lattice potential energy. By using this theory, it becomes possible to obtain an analytical expression not only for thermal expansion but also for bulk modulus. And this theory developed the method for predicting the temperature dependence of volume for any crystal. They obtained the following expressions

$$\frac{\nu - \nu_0}{\nu_0} = P_{TH} / K_0 \tag{2.15}$$

and

$$K_T - K_0 = \left\{ 2 + \frac{\nu_0 \left( d^3 u / d\nu^3 \right)_0}{\left( d^2 u / d\nu^2 \right)_0} \right\} P_{TH} - \frac{\gamma^2}{V} \left( TC_V - E_{TH} \right) \tag{2.16}$$

where $P_{TH} = \gamma E_{TH} / V$, $\gamma$ is the Grüneisen parameter and $E_{TH}$ is the vibrational or thermal energy. $K_T$ is the isothermal bulk modulus, $K_0$ its value at initial temperature, $\nu$ is the volume per mole and is equal to $N\nu$, where $N$ is the number of cells per mole, $C_V$ is the heat capacity at constant volume, $u$ is the lattice potential energy per unit cell, and its volume derivative are taken at $\nu = \nu_0$. Equations (2.15) and (2.16) are derived from two equations based on the EoS of Mie- Grüneisen is

$$P + \frac{du}{dv} = P_{TH} \tag{2.17}$$

and

$$K_T = \frac{du}{dv} + v\frac{d^2u}{dv^2} - \frac{\gamma^2}{V}\left(TC_V - E_{TH}\right) \tag{2.18}$$

Equation (2.18) is valid at atmospheric pressure i.e. $P = 0$. For obtaining equations (2.15) and (2.16), the potential energy $u(v)$ is expressed as a function of volume by Taylor expansion with respect to $(v - v_0)$ satisfying equilibrium condition

$$\left(\frac{du}{dv}\right)_{v_0} = 0 \tag{2.19}$$

If the change in volume $\Delta = (v - v_0)$ are assumed to be small i.e. the terms containing higher power of $\Delta$ are neglected, then equations (2.17) and (2.18) reduced to equations (2.15) and (2.16) respectively. Anderson [87] has investigated the thermodynamic behaviour of MgO and other minerals up to a sufficiently high temperature of nearly 2000 K. It was realized for the first time by Suzuki's et al. [29, 33] that at high temperature the term containing $\Delta^2$ becomes significant and can not be neglected. However, the method used in developing the Suzuki formulations is different from that adopted by Born and Huang [12]. This difference in two methods leads two different expressions for thermal expansivity. It is desirable to consider higher order terms in $\Delta$ in the expansion of potential energy to obtain an expression for thermal expansivity at high temperatures. Shanker et al. [13] considered the following expression for the potential energy

$$u = u_0 + u_0^{'}\Delta + u_0^{''}\frac{\Delta^2}{2} + u_0^{'''}\frac{\Delta^3}{6} \tag{2.20}$$

where $u_0^{'}$, $u_0^{''}$ and $u_0^{'''}$ are the first-, second- and third-order volume derivative of $u$ taken at $v = v_0$. In view of equilibrium condition, $u_0^{'} = 0$. Values of $u_0^{''}$ and $u_0^{'''}$ can be determined using the expression for $K_T$ and its pressure derivative at $P = 0$. These expressions are obtained as follows

$$u_0^{''} = \frac{K_0}{v_0} \tag{2.21}$$

and

$$u_0''' = -\frac{K_0\left(K_0' + 1\right)}{\nu_0^2} \tag{2.22}$$

where $K_0$ and $K_0'$ are the values of $K_T$ and $dK_T/dP$ at $P = 0$ respectively. Shanker et al. [13] have not considered the next higher order terms in equation (2.20) because such terms will contain fourth-and higher-order derivative of $u$ which can be determined only after knowing $K_0''$ and other higher-order pressure derivatives of $K_T$. At present, accurate and reliable data are available only for $K_0$ and $K_0'$. At $P = 0$, the Mie-Grüneisen equation of state (2.17) yields, with the help of equation (2.20), the following relationship:

$$\frac{du}{d\nu} = P_{TH} = u_0''\Delta + \frac{1}{2}u_0'''\Delta^2 \tag{2.23}$$

Substituting the values of $u_0''$ and $u_0'''$ from equation (2.21) and equation (2.22) in equation (2.23), we get

$$K_0\frac{\Delta}{\nu_0} - \frac{1}{2}\left(\frac{\Delta}{\nu_0}\right)^2 K_0\left(K_0' + 1\right) = P_{TH} \tag{2.24}$$

Equation (2.24) is quadratic in $\Delta/\nu_0$ and one of its solution is

$$\frac{\Delta}{\nu_0} = \frac{\nu}{\nu_0} - 1 = \frac{1 - \left[1 - 2\left(\frac{K_0' + 1}{K_0}\right)P_{TH}\right]^{1/2}}{\left(K_0' + 1\right)} \tag{2.25}$$

The result obtained with the above equation with negative sign was found close to the experimental data. On the other hand, if we use the other solution with positive sign before the square bracket in equation (2.25) we get the values of $\nu/\nu_0$, which are much higher than the experimental values. In the Suzuki formulation [29] also, the solution with negative sign only has been considered. In fact, the Suzuki equation, in the above notation can be expressed as

$$\frac{\nu}{\nu_0} - 1 = \frac{1 - \left[1 - 2\left(\frac{K_0' - 1}{K_0}\right)P_{TH}\right]^{1/2}}{\left(K_0' - 1\right)} \tag{2.26}$$

It is clear from above two equations (2.25) and (2.26) that in equation (2.26) $\left(K_0^{'}+1\right)$ is replaced by $\left(K_0^{'}-1\right)$. This difference arises due to the two different methods used in the derivatives of equation (2.25) and equation (2.26). Values of thermal pressure $P_{TH}$ for a number of minerals at different temperatures have been reported by Anderson [44]. These values make it possible to calculate $v/v_0$ as a function of temperature with the help of equation (2.25) and equation (2.26). After differentiating equation (2.24) with respect to $T$, at constant $P$, we get the following relationship for thermal expansivity:

$$\alpha = \frac{\left(\partial P_{TH}/\partial T\right)_P}{K_0\left(v/v_0\right)\left[1-\left(K_0^{'}+1\right)\left(v/v_0-1\right)\right]} \tag{2.27}$$

Thermal expansivity $\alpha$ may be defined as [44]

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{2.28}$$

Now, using the following thermodynamic identity

$$\alpha K_T \equiv \left(\frac{\partial P}{\partial T}\right)_V \tag{2.29}$$

and the relationship

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial P_{TH}}{\partial T}\right)_V \tag{2.30}$$

based on the condition suggested by Anderson [44] as follows

$$P(V,T) = P(V,T_0) + P_{TH} \tag{2.31}$$

we get

$$\left(\frac{\partial P_{TH}}{\partial T}\right)_V = \alpha K_T \tag{2.32}$$

From the calculus equation

$$\left(\frac{\partial X}{\partial T}\right)_V = \left(\frac{\partial X}{\partial T}\right)_P + \alpha K_T\left(\frac{\partial X}{\partial P}\right)_T \tag{2.33}$$

we get

$$\left(\frac{\partial P_{TH}}{\partial T}\right)_V = \left(\frac{\partial P_{TH}}{\partial T}\right)_P + \left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial P_{TH}}{\partial P}\right)_T \tag{2.34}$$

and using equation (2.30) we have

$$\left(\frac{\partial P_{TH}}{\partial T}\right)_V - \left(\frac{\partial P_{TH}}{\partial T}\right)_P = \alpha K_T \left(\frac{\partial P_{TH}}{\partial P}\right)_T \tag{2.35}$$

Now, if we assume that $\left(\partial P_{TH}/\partial P\right)_T$ is so small that the last term of equation (2.35) is negligible then with the help of equations (2.32) and (2.35) we have

$$\left(\frac{\partial P_{TH}}{\partial T}\right)_P = \alpha K_T \tag{2.36}$$

Using equation (2.36) in equation (2.27) we get

$$K_T(T) = K_0 \frac{\nu}{\nu_0}\left[1 - \left(K_0^{'} + 1\right)\left(\frac{\nu}{\nu_0} - 1\right)\right] \tag{2.37}$$

## 2.5 ANHARMONICITY IN THERMAL AND ELASTIC PROPERTIES

Positive thermal expansion and strongly pressure dependence bulk modulus require an asymmetrical potential function i.e. an anharmonic bond, but some properties notably high temperature specific heats of insulators, are reasonably explained by a purely parabolic minimum in $\phi$ i.e. harmonic bonding. The quasi harmonic approximation which accepts thermal expansion and pressure dependence elasticity but assumes no harmonic effect on specific heat or thermal pressure, can be understood as a restricted selection of derivatives of $\phi$ [88]. Writing $\phi$ as a Taylor expansion in the small departure, $x$, of $r$ from its equilibrium value, $a$, with primes to represent derivatives with respect to $r$,

$$\begin{aligned}\phi(r = a + x) = \phi(a) + \phi^{'}(a)x + \frac{1}{2!}\phi^{''}(a)x^2 + \frac{1}{3!}\phi^{'''}(a)x^3 \\ + \frac{1}{4!}\phi^{iv}(a)x^4 + \frac{1}{5!}\phi^{v}(a)x^5 + .....\end{aligned} \tag{2.38}$$

The harmonic approximation stops at $\phi^{''}$. As we demonstrate with a simple model, the quasi-harmonic approximation stops at $\phi^{'''}$ and can therefore be described as first-order anharmonicity. Anharmonic variation of specific heat with temperature requires $\phi^{iv}$ and is a second-order anharmonic effect, while the temperature dependence of $\alpha K_T$ requires non-zero $\phi^{v}$.

Some researchers [9, 87, 89-90] assume that the quasi-harmonicity suffices to explain their observations, but others [91-93] maintain that this is inadequate. Stacey and Isaak [88]

suggested that a general examination of the relative magnitudes of the terms in equation (2.38) presents a conclusion if the anharmonicity of any thermodynamic property can be identified with particular terms. Grüneisen parameter, $\gamma$, may be defined in terms of density $\rho$ as [44]

$$\gamma = \frac{\alpha K_T}{\rho C_V} \tag{2.39}$$

where $\alpha$ is thermal expansivity, $K_T$ is isothermal bulk modulus and $C_V$, specific heat at constant volume. Anharmonicity in $\gamma$ denotes to the amount by which $(\partial\gamma/\partial T)_V$ differs from zero. As the variation of thermal pressure with temperature is $(\partial P/\partial T)_V = \alpha K_T$ and the variation of thermal energy per unit volume, $E_{th}$ is $(\partial E_{th}/\partial T)_V = \rho C_V$ by equation (2.39),

$$\gamma = \left(\frac{\partial P}{\partial E_{th}}\right)_V \tag{2.40}$$

Now, the significance is that, anharmonicities of thermal pressure and thermal energy depend in assessable method on the derivatives of $\phi$ in equation (2.38) and Stacey and Isaak [88] used their ratio to examine the anharmonicity of $\gamma$.

The relationships for average bond energy

$$E = \phi^{"}(a)\frac{x^2}{2!} + \phi^{iv}(a)\frac{x^4}{4!} \tag{2.41}$$

and for average (thermal) bond force

$$\overline{F} = \phi^{'''}(a)\frac{\langle x^2\rangle}{2!} + \phi^{v}(a)\frac{\langle x^4\rangle}{4!} \tag{2.42}$$

Stacey and Isaak [88] found that the anharmonic departure of $(\partial\gamma/\partial T)_V$ from the quasi-harmonic condition, in which this derivative is zero, may have either sign, but that it is systematically smaller than the anharmonic variation of $C_V$, that is, the anharmonicity of $\gamma$ is small and negligible, therefore depends on an assessment of the anharmonicity of $C_V$, for which there have been several analyses and experiments. To understand this problem, one needs to distinguish between two kinds of crystal structure, those in which the bonds to each atom occur in opposite pairs and those that do not. The first of these, which include simple oxides, such as *MgO*, for which Anderson and Zou [94] showed that $C_V$ does not cross the Dulong-Petit limit

*3nRT*. Even at 2000 K, the suppression of higher-mode excitations is not completely eliminated, the Anderson and Zou [94] result is consistent with the numerical analysis of this symmetrical bonding situation by Stacey [95] who found that the anharmonic departure of $C_V$ from *3nRT* was small and negative, being typically -2.6% at 2000 K. Extensive studies of anharmonicity in oxides and silicates are reported by Gillet et al. [92, 96-99] and Guyot et al. [100], who found a systematically positive anharmonic contribution to $C_V$. Minerals used in these studies have crystal structures in which bonds do not occur in opposite pairs. By using the numerical analysis of Stacey [95] to the asymmetrical bonding and it has been confirmed that a positive contribution is characteristic of such structures. For $Ca_2GeO_4$ (a forsterite analogue) and $Mg_2SiO_4$ forsterite, Gillet et al. [96, 97] used the conventional thermodynamic method of estimating $C_V$ from $C_P$ by obtaining anharmomic increments of 8% and 5% at 2000 K, relative to the Dulong-Petit value.

$$C_V = C_P - T\alpha^2 V K_T, \tag{2.43}$$

An alternative approach was also taken by Gillet et al. [96, 97] by estimating the value of $a_i$ defined by

$$a_i = \left(\frac{\partial \nu_i}{\partial T}\right)_V = \alpha(\gamma_{i,T} - \gamma_{i,P}) \tag{2.44}$$

where

$$\gamma_{i,T} = \left(\frac{\partial \ln \nu_i}{\partial \ln V}\right)_T = K_T\left(\frac{\partial \ln \nu_i}{\partial P}\right)_T \tag{2.45}$$

$$\gamma_{i,P} = \left(\frac{\partial \ln \gamma_i}{\partial \ln V}\right)_P = -\frac{1}{\alpha}\left(\frac{\partial \ln \nu_i}{\partial T}\right)_P \tag{2.46}$$

By using observations of Raman modes that contribute significantly to $C_V$, Gillet et al. [96, 97] obtained estimates of anharmonicity consistent with anharmonicity calculated from equation (2.41). Liu [101], however, disputed the validity of these estimates on the grounds that the accuracy of estimates of input parameters, especially $\alpha$, was inadequate to discriminate between $\gamma_{i,T}$ and $\gamma_{i,P}$. If these $\gamma$'s are equal, as suggested by Liu [101], then variations in $\gamma_i$ are purely quasi-harmonic, that is, due to volume changes. Thus, the results of Gillet et al. [96, 97] has been found uncertain enough to be dismissed. Further study of Gillet et al. [92] avoided specific reference to $\alpha$ by writing $V$ as a polynomial in $T$ and obtained values of $a_i$ similar with

the earlier work. Since $\alpha$ is simply a coefficient in the expansion of $V(T)$, this was not really a change in methodology. There is also a paradoxical feature of the Gillet et al. [92] and that found $a_i$ for forsterite to be independent of pressure. This is contrary to normal expectations [90, 91, 102] that anharmonicity decreases with pressure, and is in conflict with Stacey and Isaak [88] numerical results for both symmetrical and asymmetrical bonding. For symmetrical bonding, as in forsterite, typically a three-fold decrease in $\Delta C_V$, the anharmonic contribution to $C_V$, for 30% volume compression at constant T was obtained. Another conflict with theory arises in the temperature variation of $C_V$. Gillet et al. [96] data indicate $\Delta C_V$ varying approximately as $T^2$ with no explanation. Numerical results of Stacey and Isaak [88] give $C_V$ almost precisely proportional to $T$ with an insignificant quadratic term. It has been observed by Gillet et al. [98, 99] on $MgSiO_3$- perovskite because of their relevance to the lower mantle. This do not quantify the estimated anharmonic effect on $C_V$ at 2000 K, but the value of $a_i$ used in their preferred model is only about 25% of that found in forsterite and found consistent with close-packed structure with reduced bond asymmetry, corresponding to $\Delta C_V \approx 2\%$ at 2000 K, with Stacey and Isaak [88] estimate, 0.7% under mid-lower mantle conditions. When combined with Stacey and Isaak [88], the anharmonicity of $\gamma$ is systematically less than that of $C_V$, Stacey and Isaak [88] understood the properties of lower mantle that has not reached a stage at which anharmonicity in $\gamma$ needs to be considered.

From Eq. (2.37) one can observe that the anharmonicity of the product $\alpha K_T$, has been represented by its temperature variation at constant *V*, must be identical to the anharmonicity of $\gamma C_V$ and is comparable to the anharmonicity of $C_V$ above. Separation of the effects on $\alpha$ and $K_T$ individually is not as straightforward. It would be attractive to apply the method of calculating $\alpha$ as given by Kittel [103], which estimates the average value of *x*, the length of an oscillating atomic bond versus *T*, by weighting each element *dx* of the range with its potential energy *E* according to a Boltzmann probability, exp(*-E/kT )dx*. However, this is not valid. The Boltzmann distribution applies to the relative occupation of independent states; it does not apply to the relative occupations of potential energy levels of an oscillating particle conserving total energy as it moves between states. A particle oscillating in a potential well moves more slowly at

higher potential energies and so spends more time at the higher potential energies, not less as the Boltzmann distribution suggests. A method of overcoming the problem was proposed by Dugdale and MacDonald [104], who showed that a correct treatment with a calculation of $\gamma$ not of $\alpha$. The calculation was repeated in three dimensions by Irvine and Stacey [105] with regard to the anharmonicity of $\alpha K_T$, or thermal pressure, and $C_V$, or thermal energy, as the primary calculated quantity, with $\gamma$ as the ratio of these two.

Using the thermodynamic identities

$$\left(\frac{\partial \ln(\alpha K_T)}{\partial T}\right)_V = \frac{1}{\gamma T}\left(\frac{\partial \ln C_V}{\partial \ln V}\right)_T \tag{2.47}$$

$$\left(\frac{\partial \ln K_T}{\partial T}\right)_V = \alpha\left[1 - q - \left(\frac{\partial \ln C_V}{\partial \ln V}\right)_T\right] \tag{2.48}$$

where $q = (\partial \ln \gamma / \partial \ln V)_T$, so that

$$\left(\frac{\partial \ln \alpha}{\partial T}\right)_V = \frac{1}{\gamma T}\left(\frac{\partial \ln C_V}{\partial \ln V}\right)_T - \alpha\left[1 - q - \left(\frac{\partial \ln C_V}{\partial \ln V}\right)_T\right] \tag{2.49}$$

It has been observed that without anharmonicity and in a hypothetical classical situation, with no deactivation of high-frequency modes at low temperature, the product $\alpha K_T$ would be independent of *T* at constant *V*, but equations (2.48) and (2.49) include terms that do not vanish with these assumptions. By taking, $\alpha$ and $K_T$ as separately the temperature-dependent by using the classical and quasi-harmonic assumptions, we found doubt in the significance of anharmonicity of $\alpha$ and $K_T$. The crucial measure of anharmonicity is the behavior of $\gamma$. By using the temperature dependences of $\alpha$ and $K_T$ under lower mantle conditions, for which we rely on theory, an examination of $(\partial \ln C_V / \partial \ln V)_T$ is necessary. Then, using the another identity,

$$\left(\frac{\partial \ln C_V}{\partial \ln V}\right)_T = \left(\frac{\partial \ln C_V}{\partial \ln V}\right)_S + \gamma\left(\frac{\partial \ln C_V}{\partial \ln T}\right)_V \tag{2.50}$$

The adiabatic derivative is small because the Debye temperature increases with pressure, as does the temperature on an adiabat because it is due to the reduction in amplitude of atomic vibrations. This reduction in amplitude of atomic vibrations increases the phonon frequency which results the rise in Debye temperature [106]. By Debye theory, this derivative vanishes

identically and then substitution for $(\partial \ln C_V / \partial \ln V)_T$ in equation (2.46) gives $(\partial \gamma / \partial T)_V = 0$, even at low temperatures. However, under lower mantle conditions, the $C_V$ derivative in equations (2.47) to (2.49) is not negligible in spite of the high temperature. One can estimate the approximate magnitude by applying Debye theory, by which for $T > \theta_D$ we have a polynomial expansion,

$$\left(\frac{\partial \ln C_V}{\partial \ln T}\right)_V = \frac{1}{10}\left(\frac{\theta_D}{T}\right)^2 - \frac{3}{1400}\left(\frac{\theta_D}{T}\right)^4 \qquad (2.51)$$

At 670-km depth, Stacey and Isaak [88] estimate $\theta_D$ = 1140 *K* and *T* = 1900 *K*, making $\theta_D / T$ = 0.6 and so $(\partial \ln C_V / \partial \ln T)_V \approx 0.06$. With $\gamma \approx 1.4$, $(\partial \ln C_V / \partial \ln V)_T \approx 0.084$. This value prevails over the whole depth of the lower mantle since $T/\theta_D \approx$ constant on an adiabat. Thus, when one discard the classical assumption, even the temperature independence of $\alpha K_T$ at constant *V* becomes a poor assumption. But $\gamma$ independent of *T* remains a good one. Applying equation (2.49) to the lower mantle, it has been found that the first term dominates. It turns out that $(\partial \ln \alpha / \partial \ln T)_V$ decreases with depth from 0.056 to 0.030. These values are much larger than the contribution by anharmonicity.

Stacey and Isaak [88] observed that thermal energy and thermal pressure as primary thermodynamic parameters from which anharmonicities of other parameters can be estimated. The Grüneisen parameter, $\gamma$, is of particular interest because of its wide use in geophysics and because it is a simple ratio of the two primary parameters. Stacey and Isaak [88] found a strong case for assuming the temperature dependence of $\gamma$ at constant *V* to be negligible, especially at high pressure and emphasized that it is restricted to high temperatures. At constant pressure, thermal dilation introduces temperature dependence by virtue of the volume dependence. The essence of anharmonicity of $\gamma$ is that Stacey and Isaak [88] do not attempt a direct calculation of the anharmonicity of $\gamma$, but only compare the anharmonicity of $\gamma$ with that of $C_V$ and found that these anharmonicities may have either the same or opposite signs, depending on fine details of the atomic potential function. Furthermore, the sign of the anharmonicity of $C_V$ depends on crystal structure and it is apparent that calculated anharmonicities are very much dependent and that a realistic fundamental calculation of the anharmonicity of $\gamma$ is still problematic. The

seriousness of the model dependence is confirmed by comparing a molecular dynamical calculation of $\gamma$ for perovskite [93] showing a decrease with *T*, with the increase inferred by Gillet et al. [99] from Raman spectra. But the model-independent, common features of all results are that anharmonicity of $\gamma$ is consistently weaker than that of $C_V$ and both decrease strongly with pressure. Thus, even without knowing its sign, it has been found that the anharmonicity of $\gamma$ in the deep mantle is unlikely to be more than about 0.7%. Thus, temperature variation of $\alpha$ under lower mantle conditions indicates that the anharmonic contribution is no bigger than the uncertainty in the quasiharmonic variation. So, a theoretical study of the effect of anharmonicity on $\alpha$ would not be rewarding. The effective indicator of anharmonicity is the behavior of $\gamma$, for which the temperature dependence, at constant *V*, is very small. It justifies a convenient simplification of some thermodynamic relationships used in studying the lower mantle. In addition to $\gamma$ itself, it implies that $q = \left(\partial \ln \gamma / \partial \ln V\right)_T$ is also effectively independent of *T* at constant *V*.

Using a thermodynamic identity,

$$\left(\frac{\partial \gamma}{\partial \ln T}\right)_V = \left(\frac{\partial \ln C_V}{\partial \ln V}\right)_S \qquad (2.52)$$

It has been found that Stacey and Isaak [88] conclusion is consistent with the common assumption [107] that $C_V$ is constant on an adiabat as is accurately given by Debye theory, even at low temperature.

# *CHAPTER 3*

# *Anderson-Grüneisen Parameter and Grüneisen Parameter*

## *Overview*

This chapter describes the details of two important dimensionless thermoelastic parameters i.e. isothermal and adiabatic Anderson-Grüneisen parameter which are having important role to study the thermal and elastic behavior of solids at high temperatures and high pressures and also the Grüneisen parameter- a very important thermodynamic quantity used to investigate the relationship between thermal and elastic properties of solids. The volume dependence of Grüneisen parameter and its higher order volume derivatives is also discussed following the expression based on thermodynamical constraints in the limit of infinite pressure.

### 3.1 ISOTHERMAL AND ADIABATIC ANDERSON-GRÜNEISEN PARAMETER

Isothermal Anderson-Grüneisen parameter ($\delta_T$) and adiabatic Anderson-Grüneisen parameter ($\delta_S$) are the two important dimensionless thermoelastic parameters which are having important role for the study of thermal and elastic behaviour of solids at high temperatures and high pressures. These two parameters may be defined as following [57]

$$\delta_T = -\frac{1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_P \tag{3.1}$$

$$\delta_S = -\frac{1}{\alpha K_S}\left(\frac{\partial K_S}{\partial T}\right)_P = -\left(\frac{\partial \ln K_S}{\partial \ln V}\right)_P \tag{3.2}$$

where $\alpha, K_T, K_S$ are respectively thermal expansivity, isothermal bulk modulus and adiabatic bulk modulus and subscripts *S, T, P, V* represent entropy, temperature, pressure and volume respectively. The parameter $\delta_S$ were named the Anderson-Grüneisen parameter by Chang [108], due to derivation by Anderson [109], who was interested in the high temperature extrapolation of $K_S$.

Anderson [110] defined an equation in order to explain thermal expansivity at very high compression. Bassett et al. [111] who were scrupulous in indicating which variables were constant during partial differentiation, concluded that the values of $\delta_T$ and $\delta_S$ were distinctly different, and then presented a useful equation $\delta_T - \delta_S$. Barron [112] named both $\delta_T$ and $\delta_S$ the Anderson-Grüneisen function. Over the year the name has gradually reverted back to the Anderson-Grüneisen parameters. There was a series of papers in the 1960's and early 1970's [113-119], in which $\delta_S$ was derived from assumed atomic potentials and where the results are expressed in terms of $\delta_S$ as a function of

$$K_T^{'} = \left(\frac{\partial K_T}{\partial P}\right)_T \tag{3.3}$$

Srivastava et al. [120] presented a theory of incorporating anharmonicity in the term $K_T$, suggesting that $\delta_T$ and $\delta_S$ are increasing with temperature at high temperature. It was observed by him that $\delta_T$ does not increase with T at $\eta$=1, where $\eta = V/V_0$ (compression) and if $V = V_0$ then $\eta = 1$ even at T as high as $2\theta_D$ where $\theta_D$ is the Debye temperature. This

demonstrates that anharmonicity is not important to $\delta_T$ for *MgO* contrary to the expectations of Srivastava et al. [120]. The result was further explained by the report of Anderson et al. [121, 122] that anharmonic effects, which may be the evident in $C_V$, are not seen in the thermal pressure versus $T$ where $T > \theta_D$. When anharmonicity is absent in pressure, the themodynamic pressure is strictly linear in T, at high $T$ according to the quasiharmonic approximation. Strict linearilty has been observed between thermal pressures for many oxides and silicates [121, 122]. Since $K_T$ is a derivative of $P$, $(\partial K_T / \partial P)_T$ is insensitive to anharmonicity for $T > \theta_D$, unlike the prediction of Srivastava et al. [120]. Thus $\delta_T$ will be affected by anharmonicity only to the extent that $\alpha$ is affected by the anharmonic terms in the free energy. Anderson and Isaak [123] suggested that the coefficient of the term $T^2$ represent anharmonic contributions to the free energy and were insensitive to volume. However, when the volume derivative of the free energy was taken to define $P$, the anharmonic effects vanished.

The parameters $\delta_T$ and $\delta_S$ are dimensionless thermoelastic parameters in the same class as $\gamma$ and $K_T^{'}$. They arise in numerous thermodynamic derivations especially where $K_T(K_S)$ is differentiated with respect to $T$ at constant $P$, or differentiated with respect to $V$ at constant $P$. The values of $\delta_T$ are constrained to a narrow range of values from one material to another. The values of $\delta_S$ are similarly constrained, except that $\delta_T$ is always greater than $\delta_S$, in a solid by a number slightly larger than $\gamma$.

### 3.2 THEORY OF GRÜNEISEN PARAMETER

Grüneisen parameter $(\gamma)$ is a very important thermodynamic quantity used to investigate the relationship between thermal and elastic properties of a solids. Sometimes, $\gamma$ is called the thermal Grüneisen ratio. If the change in pressure is exactly proportional to the change in energy density, Grüneisen parameter $\gamma$ will be independent of pressure (P) and temperature (T). The Grüneisen parameter $(\gamma)$ is related to the thermal expansion coefficient $(\alpha)$, the bulk modulus $(K_T)$ and the frequency of lattice vibrations. Although the Grüneisen ratio tends to be nearly independent of T, especially at high temperatures, it generally decresases as the volume decreases [84]. Grüneisen defined a value of $\gamma_i$ for the volume derivative of each mode $\omega_i$ in

the lattice. Anderson [44] suggested that the Grüneisen ratio itself be of the similar form in its relation to volume. The investigation of the Grüneisen parameter and its volume dependence have been the subject of great interest in understanding the macroscopic behaviour of solids [108, 124-127]. The parameter $\gamma$ has become a quantity of central importance in describing the thermodynamic and thermoelastic behaviour of solids, because it is related to the volume dependence of the Debye temperature $(\theta_D)$, thermal expansion coefficient $(\alpha)$, bulk modulus $(K_T)$, specific heat $(C_V)$ and pressure (*P*). Earlier workers [108, 126-127] developed methods for calculating $\gamma$ of crystalline solids from the theory of elasticity.

The Grüneisen parameter may be defined as [44]

$$\gamma = \frac{\alpha K_T}{\rho C_V} = \frac{\alpha K_S}{\rho C_P} \tag{3.4}$$

where $\alpha$, $K_T$, $K_S$, $\rho$, $C_V$, $C_P$ are thermal expansivity, isothermal bulk modulus, adiabatic bulk modulus, density, specific heat at constant volume, specific heat at constant pressure respectively.

On the other hand, $\alpha$ is not subject to direct checks. However, it is central to much of our understanding of the deep Earth, in particular the adiabatic temperature gradient, convective power [128] and gravitational energy release by thermal contraction [129]. Using Eq. (3.4), knowledge of $\alpha$ is used not just as a hold on $\alpha$, but as a parameter, simplifying thermodynamic relationship such as

$$\left(\frac{\partial \ln T}{\partial \ln V}\right)_S = -\gamma \tag{3.5}$$

Conveniently, $\gamma$ varies with pressure less than does $\rho$ and much less than $\alpha$ or $K_T$ and its value is close to unity throughout the Earth. But the relevance of these considerations depends on the fact that $\gamma$ is related to elasticity and its pressure variation, which are available from seismological models. Given a theory of this relationship, seismology provides not only mechanical properties, but an essential input to thermal properties.

In Grüneisen theory [130], the thermodynamic definition of $\gamma$ (Eq. (3.4)) is a deduction, not a definition. Grüneisen considered the volume dependences of the frequencies $\nu_i$ of crystal vibrational modes and identified each mode $\nu_i$ with a value of $\gamma$ called the mode gamma $\gamma_i$,

such that

$$\gamma_i = -\left(\frac{\partial \ln \nu_i}{\partial \ln V}\right)_T \tag{3.6}$$

We can write $\nu_i = v_i / \lambda_i$, where $v_i$ is the corresponding elastic wave speed and $\lambda_i$ is the wavelength. Since $i$ refers to a particular mode, $\lambda_i$ is a specified number of lattice spacing and its proportional to $V^{1/3}$, where V is specific volume. Thus, Eq. (3.6) can be rewritten

$$\gamma_i = -\frac{1}{2}\frac{V}{X_i}\left(\frac{\partial X_i}{\partial V}\right)_T - \frac{1}{6} = \frac{1}{2}\frac{K_T}{X_i}\left(\frac{\partial X_i}{\partial P}\right)_T - \frac{1}{6} \tag{3.7}$$

where $K_T = -V(\partial P / \partial V)_T$ is the isothermal bulk modulus.

Eq. (3.7) is the starting point for the development of the acoustic formula for $\gamma$, which assumes that all of the modes of a material body contribute to the two seismologically observed elastic moduli, $X = (K_S + (4/3)\mu)$ and $\mu$ (isotropic material with a single rigidity modulus). Doubt about this prompted the study by Chopelas [9] of the pressure dependences of optic modes frequencies for lower mantle minerals, observed by Raman spectroscopy in a diamond anvil cell. Treating a lattice mode as an Einstein oscillator of frequency at temperature T, we can derive an expression for the relationship between thermal pressure $P_{th}$, caused by activation of the oscillator (with the material held at constant volume) and its average thermal energy $E_i$.

where $E_i = \dfrac{h\nu_i}{\exp(h\nu_i / kT) - 1}$ (3.8)

and ‘h’ and ‘k’ are the Planck’s and Boltzmann’s constants respectively. The corresponding specific heat at constant V is

$$C_i = \left(\frac{\partial E_i}{\partial T}\right)_V = \frac{k(h\nu_i / kT)^2 \exp(h\nu_i / kT)}{[\exp(h\nu_i / kT) - 1]^2} \tag{3.9}$$

if $\nu_i$ is independent of T at constant V. Differentiating Eq. (3.8) with respect to V at constant T, we note that $\nu_i$ varies as by Eq. (3.6)

$$\left(\frac{\partial E_i}{\partial V}\right)_T = \left(\frac{\partial \ln \nu_i}{\partial \ln V}\right)_T \left\{\frac{1}{V}\frac{h\nu_i}{\exp(h\nu_i / kT) - 1} - \frac{kT}{V}\frac{(h\nu_i / kT)^2 \exp(h\nu_i / kT)}{[\exp(h\nu_i / kT) - 1]^2}\right\} \tag{3.10}$$

Substituting for the two terms in Eq. (3.10) using Eqs. (3.8) and (3.9),

$$\left(\frac{\partial E_i}{\partial V}\right)_T = \left(\frac{\partial \ln \nu_i}{\partial \ln V}\right)_T \left[\frac{E_i}{V} - \frac{T}{V}\left(\frac{\partial E_i}{\partial T}\right)_V\right] - \left(\frac{\partial \ln \nu_i}{\partial \ln V}\right)_T \frac{T^2}{V}\left[\frac{\partial}{\partial T}\left(\frac{E_i}{T}\right)\right]_V \tag{3.11}$$

Since $E_i$ is the internal energy attributed to mode $i$, we can make use of a general thermodynamic identity for internal energy U

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V T - P = T^2\left[\frac{\partial}{\partial T}\left(\frac{P}{T}\right)\right]_V \tag{3.12}$$

and identifying this with Eq. (3.11), so that

$$\left[\frac{\partial}{\partial T}\left(\frac{P_{th}}{T}\right)\right]_V = -\frac{1}{V}\left(\frac{\partial \ln \nu_i}{\partial \ln V}\right)_T \left[\frac{\partial}{\partial T}\left(\frac{E_i}{T}\right)\right]_V \tag{3.13}$$

with the assumption that $\gamma_i = (\partial \ln \nu_i / \partial \ln V)_T$ is independent of T at constant V, because this is already assumed for $\nu_i$ by the Einstein theory, we can integrate Eq. (3.13) to give the Mie-Grüneisen equation for this mode

$$P_{th} = \frac{\gamma_i E_i}{V} \tag{3.14}$$

which is the integral form of a thermodynamic identity

$$\left(\frac{\partial P}{\partial T}\right)_v = \gamma \rho C_V \tag{3.15}$$

At very high temperatures, we can accept this as a satisfactory approximation encouraged by the fact that for the total $\gamma$, we have an identity

$$\left(\frac{\partial \gamma}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial \ln C_V}{\partial \ln V}\right)_S \tag{3.16}$$

Constancy of $C_V$ on an adiabatic is a particularly good approximation. Departures from this approximation arising from anharmonicity are discussed by Stacey and Isaak [88].

At high temperature, at which all modes are fully excited thermally. They are weighted equally, but at lower temperatures $\gamma$ is a weighted average according to the contributing heat capacities $C_i$ of the modes

$$C\gamma = \sum C_i \gamma_i \tag{3.17}$$

Derivation of the acoustic gamma assume that a solid body has two shear modes (S) for each compressional mode (P). Applying this assumption to Eq. (3.7) and weighting all modes equally because we are considering high temperatures where all modes are fully excited.

$$\gamma_A = \frac{1}{3}\gamma_P + \frac{2}{3}\gamma_S$$

$$\gamma_A = \frac{K_T}{6}\frac{(\partial K_S/\partial P)_T + (4/3)(\partial\mu/\partial P)_T}{K_S + (4/3)\mu} + \frac{K_T}{3}\frac{(\partial\mu/\partial P)_T}{\mu} - \frac{1}{6} \qquad (3.18)$$

Regarding the material as a classical continuum, there exists a wavelength $\lambda_C$ below which thermal diffusion becomes effective and a corresponding wave frequency $f_C$ above which the assumption of adiabatic compressions breaks down. Assuming classical thermal diffusion with diffusivity $\eta$, $\lambda_C = 2\pi\eta/v_P$ and $f_C = V_P^2/2\pi\eta$, where $v_P$ is the compressional wave speed using the zero pressure properties of silicate perovskite, as calculated by Oganov et al. [131].

The advantage of Eq. (3.18) from a geophysical perspective is that it makes maximum use of data available in a Earth model, at least over the depth ranges for which $\mu$ as well as $K_T$ can be obtained with reasonable accuracy. However, we need to recognize the several assumptions and approximations. Even in the case of monoatomic crystals, for which the only modes are acoustic, $\gamma$ is derived from only two moduli and an average shear modulus is prominent in the equation. The only crystals recognized to have just two independent moduli are those with diamond structures [132] where the pressure dependency of the different shear moduli are unequal. However, it creates doubt for the justification of an average modulus.

We refer to the other main class of formulae for $\gamma$ as the free volume type because, although there are several variants, the one most used was derived by Vashchenko and Zubarev [133] from free volume theory. They are all represented by a common formula

$$\gamma = \frac{(1/2)K_T' - (1/6) - (f/3)(1-(1/3)(P/K_T))}{1-(2/3)f(P/K_T)} \qquad (3.19)$$

with different values of $f$. The simplest of these is Slater's [134] equation, for which $f$ = 0. Slater's formula has a special role in high pressure equations of state because of its validity in the infinite pressure limit. But at finite pressure $\mu/K_T$ decreases with P and Slater's formula systematically overestimates $\gamma$. Dugdale and Mac Donald [104] introduced this approach by

pointing out that thermal expansion of solids is a consequence of the asymmetry of atomic potential functions. The Dugdale-Mac Donald [104] idea was that a hypothetical harmonic bond with bond energy proportional to the square of extension or compression symmetrical about equilibrium would give zero thermal expansion with this in mind they considered random one dimensional vibration of a lattice and obtained Eq. (3.19) with $f$ = 1.

The free volume formula (Eq. 3.19) with $f$ = 2. Here are three independent derivations with apparently quite different starting points. Leibfried and Ludwing [135] weighted the modes in the Grüneisen definition of $\gamma$ (Eq. 3.6) by equating the average logarithmic derivative of the average squared frequency. Their result was rewritten in terms of potential derivatives by Welch et al. [136] eq. (3.19) with $f$ = 2. The implicit assumptions in this derivation are not easy to see and it was generally neglected, so that the derivation of the same formula by Vashchenko and Zubarev [133], using free volume theory, is usually quoted. In turn, Irvine and Stacey [105] obtained the same equation by a three dimensional generalization of the Dugdale Mac Donald analysis.

The problem of non-random atomic motion by Barton and Stacey [137], who found that the correlation of x-directed motions of neighbouring atoms held together by an x- directed bond was typically $\delta_X = 0.3$, whereas the correlation of their y and z motions was $\delta_{y,Z} \cong 0.05$. Reworking the algebra of the Irvin and Stacey [105] derivation of $\gamma$ with these correlations gave Eq. (3.19) with

$$f = 1 + \frac{1-\delta_{y,z}}{1-\delta_X} \cong 2.35 \qquad (3.20)$$

for which the equation agreed with the molecular dynamical model. As confirmed by a lattice – dynamical calculation for a sum of modes with equal energies $\delta_x > \delta_{y,z}$ and $f > 2$.

Although $f$ varies slightly with pressure and with choice of potential function, the range is limited, giving $\gamma_0 \cong (1/2)K_0 - 0.95$ at zero pressure which is in agreement with lattice dynamics by Barron [138]. The free volume formula nominally assumes both $\delta_x$ and $\delta_{y,z} = 0$, but any value could be admitted if they were equal, and the Dugdale and Mac Donald formula is based on the assumption that $\delta_x = 0, \delta_{y,z} = 1$. The problem arising from the assumption that the

different bonds to an atom are independent was identified by Falzone and Stacey [139] as the "atomic Poision's ratio effect".

### 3.3 VOLUME DEPENDENCE OF THE GRÜNEISEN PARAMETER

The Grüneisen ratio $\gamma$ can be considered as the measure of the change of pressure resulting from the increase of energy at constant $\Delta V$. It is dimensionless, as $\Delta P$ and $\Delta u/V$ have the same units;

$$\gamma = V\left(\frac{\partial P}{\partial u}\right)_V \tag{3.21}$$

If the change in pressure were exactly proportional to the change in energy density, $\gamma$ would be independent of $P$ and $T$ by using Eq. (3.4) in another form as

$$\gamma = \frac{\alpha K_T V}{C_V} = \frac{\alpha K_S V}{C_P} \tag{3.22}$$

where

$$\left(\frac{\partial P}{\partial u}\right)_V = \frac{\alpha K_T}{C_V} \tag{3.23}$$

and

$$\left(\frac{\partial P}{\partial T}\right)_V = \alpha K_T \tag{3.24}$$

Although the Grüneisen ratio tends to be nearly independent of T, especially at high T, it generally decreases as the volume decreases. An approximation often used for solids is

$$\rho\gamma = \text{constant} \tag{3.25}$$

where $\rho$ is the density. Eq. (3.25) does not hold for low temperature $(T < \theta_D)$, but does hold for temperature in shock waves.

Grüneisen [84] defined a value for the volume derivative of each mode $\omega_i$ in the lattice $\gamma_i$ as given in Eq. (3.6). It is often called a mode gamma, but $\gamma$ itself is also a simple function of V at least approximately.

Anderson [44] suggested that the Grüneisen ratio itself be of a form similar to Eq. (3.26) in its relation to volume

$$\frac{\gamma}{\gamma_0} = \left(\frac{V}{V_0}\right)^q \tag{3.26}$$

where q is the second Grüneisen constant.

$$q = \left(\frac{d\ln\gamma}{d\ln V}\right)_T = \frac{V}{\gamma}\left(\frac{d\gamma}{dV}\right)_T \tag{3.27}$$

The most common method of averaging the mode gammas is to assume non-interacting oscillators and require that the energy, the pressure and the specific heat be thermodynamically consistent [126] and further that $\omega_i$ be independent of T but not on V.

We have the Mie-Grüneisen expression for $P_{th}$ as

$$P_{th} = \rho\gamma_{mg}E_{th} \tag{3.28}$$

It is well known [140] that under this approximation

$$\gamma = \frac{\sum C_i\gamma_i}{\sum C_i} \tag{3.29}$$

where $C_i$ is the Einstein specific heat capacity defined in terms of $\omega_i$ for each mode. The summation is taken over the 3nN modes of the lattice in the general case. Here N is Avogadro's number and n is the number of atoms in the vibrating cell.

Barron et al. [141] showed that in general, for the high temperature approximation of Eq. (3.29) approaches a limiting value and Eq. (3.28). Now

$$\gamma = \gamma^{ht} = \frac{1}{3nN}\sum_{j=1}^{3nN}\gamma_j \tag{3.30}$$

where $\gamma^{ht}$ be the Grüneisen constant at high temperature.

Barron et al. [141] showed that the acoustic modes Eq. (3.29) becomes

$$\gamma_i = \frac{1}{3} - \frac{V}{\nu_i}\left(\frac{\partial\nu_i}{\partial V}\right)_T = \frac{1}{3} + \frac{K_T}{\nu_i}\left(\frac{\partial\nu_i}{\partial P}\right)_T \tag{3.31}$$

where $\nu_i$ be the sound velocity.

The acoustic approximation to the Grüneisen ratio called $\gamma_{ac}$, thus

$$\gamma_{ac} = \frac{1}{2}\left(\frac{dK_T}{dP}\right) - \frac{1}{6} - \frac{4-5\sigma}{(1+\sigma)(1-\sigma)(1-2\sigma)}\left(\frac{K_T}{3}\right)\left(\frac{d\sigma}{dP}\right) \tag{3.32}$$

where $\sigma$ is the Poisson's ratio.

If $\left(\frac{d\sigma}{dP}\right)$ is assumed to be zero, Eq. (3.32) reduces to Slater [134]. Now, we have

$$\gamma_{se} = \left(\frac{1}{2}\right)\left(\frac{dK_T}{dP}\right) - \frac{1}{6} \tag{3.33}$$

The "free volume" expression for gamma was derived by at least two different method

$$\gamma_{VZ} = \frac{\frac{1}{2}K_T^{'} - \frac{5}{6} + \frac{2}{9}\frac{P}{K_T}}{1 - \frac{4}{3}\frac{P}{K_T}} \tag{3.34}$$

where subscript refers to Vaschenko's and Zubarev's [133] definition.

Stacey was dissatisfied with Eq. (3.34). Barton – Stacey [137] gave the following expression

$$\gamma_{ba-s} = \frac{\frac{1}{2}K_T^{'} - \frac{1}{6} - \frac{f}{3}\left[1 - \frac{1}{3}\frac{P}{K_T}\right]}{\left[1 - \frac{2}{3}f\frac{P}{K_T}\right]} \tag{3.35}$$

where f = 2.35 as in Eq. (3.34). At P = 0, Eq. (3.35) becomes

$$\gamma_{ba-s} = \frac{1}{2}K_0^{'} - 0.95 \tag{3.36}$$

According to the above equation, the Grüneisen constant is intimately connected with pressure derivative of the bulk modulus.

Under the quasiharmonic approximation at high temperature, the individual mode gammas are independent of temperature. At low temperature ($T < \theta_D$), $\gamma$ varies with *T*, sometimes dramatically as the individual mode gammas selectively take dominance. For alkali halides, $\gamma$ generally diminishes at low temperature T compares with $\gamma$ at $T = \theta_D$, but for oxides such as $Al_2O_3$ and $MgO, \gamma$ is high at T near zero and descends as T increases.

Chopelas and Boehler [142, 143] have allowed the determination of the pressure dependence of the optic modes

$$\gamma_i = \frac{K_T}{\omega_i}\frac{\partial\omega_i}{\partial P} \tag{3.37}$$

A number of optic modes and their pressure derivatives say $L$ may be used for finding the average $\gamma$, where it is seen that for the evaluation $\gamma$ at a particular $T$, the evaluation of each Einstein specific heat term for every model frequency $\omega_j$ is required for $L$ modes

$$\gamma_{opt} = \frac{\sum_{j=1}^{L} \gamma_j C_j}{\sum_{j=1}^{L} C_j} \tag{3.38}$$

### 3.4 VOLUME DEPENDENCE OF HIGHER ORDER GRÜNEISEN PARAMETER

The second order Grüneisen parameter ($q$) is defined in Eq. (3.27) and third-order Grüneisen parameter ($\lambda$) is defined as [144]

$$\lambda = \left(\frac{d\ln q}{d\ln V}\right)_T = \frac{V}{q}\left(\frac{dq}{dV}\right)_T \tag{3.39}$$

The parameters $\gamma, q,$ and $\lambda$ appear frequently in the thermodynamic identities for higher order thermoelastic properties of solids [144-146], and their knowledge is not only desirable, but also necessary.

Al'tshuler et al. [70] have presented the following relationship for the volume dependence of the Grüneisen parameter

$$\gamma = \gamma_\infty + (\gamma_0 - \gamma_\infty)\left(\frac{V}{V_0}\right)^m, \tag{3.40}$$

where $\gamma_0$ and $\gamma_\infty$ are the values of $\gamma$ at $V = V_0$ and $V \to 0$, respectively and $m$ is a constant. Eq. (3.40) has been used recently by many researchers [147-154]. Eq. (3.40) on differentiation with respect to $V$, yields the following expressions for higher order parameters

$$q = \frac{m}{\gamma}(\gamma - \gamma_\infty) \tag{3.41}$$

and

$$\lambda = m\frac{\gamma_\infty}{\gamma} \tag{3.42}$$

In the limit $V \to 0$ or $P \to \infty$, $\gamma \to \gamma_\infty$ and therefore $q \to 0$ (Eq. (3.41)), and from Eq. (3.42)

$$\lambda_\infty = m \tag{3.43}$$

and

$$\gamma\lambda = \gamma_\infty \lambda_\infty \tag{3.44}$$

Thus Eq. (3.40) satisfies the thermodynamic constraints viz. finite values of $\gamma_\infty$ and $\lambda_\infty$, and $q_\infty \to 0$. Eqs. (3.41) and (3.42) give the following relations also

$$q + \lambda = m \tag{3.45}$$

and

$$q_0 + \lambda_0 = q_\infty + \lambda_\infty = \lambda_\infty \tag{3.46}$$

Since γ and q both decrease with the increase in pressure, λ must increase with the increase in pressure according to Eq. (3.44) as well as Eq. (3.46). However, this finding is not supported by the seismic data for the lower mantle and the core region of the Earth [73]. It has been found [73, 144-146, 155] that λ decreases with the increase in pressure, and therefore Eq. (3.40), on which Eqs. (3.44) and (3.46) are based, is inadequate. Thermodynamic identities for higher derivative properties [144, 146] also reveal that λ decreases with the increase in pressure or compression. This shortcoming can be removed by using the model due to Stacey and Davis [73] who have used a linear relationship between λ and q supported by the seismic data. Eqs. (103)–(105) given in Ref. [73] yield the following relationships

$$\gamma_\infty = \gamma_0 \left( \frac{\lambda_0}{\lambda_\infty} \right)^{-\frac{q_0}{\lambda_0 - \lambda_\infty}} \tag{3.47}$$

and

$$\gamma = \gamma_\infty \left[ 1 - \frac{(\lambda_0 - \lambda_\infty)}{\lambda_0} \left( \frac{V}{V_0} \right)^{\lambda_\infty} \right]^{-\frac{q_0}{\lambda_0 - \lambda_\infty}} \tag{3.48}$$

One can use Eq. (3.48) to determine the values of Grüneisen parameter as a function of volume ratio $(V/V_0)$ for solids. The value of $\lambda_\infty$ can be determined with the following equation [155].

$$\lambda_\infty = \frac{K_\infty^{'2}}{K_0^{'}}, \tag{3.49}$$

where $K_0^{'}$ and $K_\infty^{'}$ are the values of $K_T^{'} = dK_T / dP$, pressure derivative of bulk modulus at $P = 0$ and $P \to \infty$, respectively. The important parameter $K_\infty^{'}$ can be determined with the following relationship [73, 144, 156]

$$\frac{K_{\infty}^{'}}{K_{0}^{'}} = \frac{3}{5}. \tag{3.50}$$

The value of $\gamma_{\infty}$ can be determined from the thermodynamic identity [73, 144]

$$\gamma_{\infty} = \frac{K_{\infty}^{'}}{2} - \frac{1}{6}. \tag{3.51}$$

Stacey and Davis [73] have written the following expression based on thermodynamical constraints in limit $P \to \infty$

$$\lambda = \lambda_{\infty} + (\lambda_0 - \lambda_{\infty})\frac{q}{q_0} \tag{3.52}$$

Integrating Eq. (3.52), we get

$$q = \frac{q_0}{1 + (\lambda_0 / \lambda_{\infty})[\{(V_0 / V)\}^{\lambda_{\infty}} - 1]} \tag{3.53}$$

and

$$\gamma = \gamma_0 \left[ \frac{\lambda_0}{\lambda_{\infty}} - \left( \frac{\lambda_0}{\lambda_{\infty}} - 1 \right) \left( \frac{V}{V_0} \right)^{\lambda_{\infty}} \right]^{-q_0 / \lambda_0 - \lambda_{\infty}} \tag{3.54}$$

Eq. (3.54) is another form of Eq. (3.48).

# *CHAPTER 4*

# *Equations of State*

## *Overview*

The present chapter explains different forms of equations of state (EoS) for studying the high pressure behavior of solids using interatomic potentials which represents the relationship between pressure and volume. Keane equation of state is described which suggest that first pressure derivative of isothermal bulk modulus is a monotonically decreasing function with pressure and reaching a limiting value at infinite pressure. Keane EoS is useful for interpolation between shock wave data and lower pressure P-V data. In the last section of this chapter, more numerically simplified EoS given by Stacey has been described which follows the infinite pressure thermodynamics more accurately.

## 4.1 INTERATOMIC FORCE CONSTANT

Different forms of the equation of state (EoS) for studying high pressure behaviour of solids have been developed by numerous investigators using interatomic potentials [157-161], as well as phenomenological approaches [16, 162, 163]. An EoS has also been derived from the finite strain theory by Birch [164, 165]. A common feature of the phenomenological equations is that they represent the relationship between pressure and volume which can be expressed analytically involving two quantities only viz., $K_0$, $K_0^{'}$ which are respectively, the isothermal bulk modulus and its first pressure derivative, both at zero pressure. This is not always the case for EoS derived from potentials using some specific function for the interatomic potential energy. The method adopted in the present study is based on the use of a simple relationship for the volume dependence of the interatomic force constant ($A$). The volume derivatives of $A$ have played a very significant role in the evaluation of higher-order elastic constants and dielectric properties for ionic solids [166-171] using the standard definition of the interatomic force constant as given by Born and Huang [12].

The EoS for a solid may be predicted accurately with the help of first-principles calculations. However, they are time-consuming because the calculations have to be done individually for a number of volumes. Values of isothermal bulk modulus $K_T$ and its pressure derivative $dK_T/dP$ can also be determined conveniently with the help of an isothermal phenomenological EoS. A phenomenological EoS for solids is universal if it is capable of predicting the pressure-volume-temperature $((P-V-T)$ data for all types of the bonding character [162, 172]. The Vinet EoS has been found to satisfy this criterion very well and therefore, it has been known as the universal EoS [173-176]. Recently, Hama and Suito [177] have presented a critical and comprehensive test for some recent universal equations of state [178-180] including the Vinet EoS and the Birch-Murnaghan (B-M) fourth order EoS [181].
Using the basic thermodynamic relationships [182]

$$P = -\frac{dW}{dV} \tag{4.1}$$

and

$$K_T = -V\left(\frac{dP}{dV}\right)_T = V\frac{d^2W}{dV^2} \tag{4.2}$$

where $K_T$ is the isothermal bulk modulus. The volume derivatives are taken at constant temperature. Here $W$ is the crystal lattice potential energy, Eqs. (4.1) and (4.2) are strictly valid for the static lattice i.e. at T=0K. At higher temperature the thermal pressure is significantly larger and its volume dependence plays an important role in the high temperature equation of state [183].

The crystal lattice potential energy ($W$) can be expressed as follows

$$W = -\frac{\alpha_m Z^2 e^2}{V^{1/3}} + \phi(V) \tag{4.3}$$

where the first term on the right represents the long range electrostatic Madelung potential energy and $\phi(V)$ is the overlap repulsive potential energy.

The derivatives of potential energy $W$ with respect to volume $V$ can be expressed in terms of the derivatives of $W$ with respect to the interatomic separation $r$ using the relationship

$$V = ar^3 \tag{4.4}$$

where $a$ is the geometrical factor depending on the type of structure of the solid. Thus one can write

$$\frac{dW}{dV} = \frac{dW}{dr}\frac{dr}{dV} = \frac{1}{3ar^2}\frac{dW}{dr} \tag{4.5}$$

and

$$V\frac{d^2W}{dV^2} = \frac{1}{9ar}\left[\frac{d^2W}{dr^2} - \frac{2}{r}\frac{dW}{dr}\right] \tag{4.6}$$

Eq. (4.6) can be rearranged in the following form:

$$V\frac{d^2W}{dV^2} = \frac{1}{9ar}\left[\frac{d^2W}{dr^2} + \frac{2}{r}\frac{dW}{dr}\right] + \frac{4}{3}P \tag{4.7}$$

The last term (4/3)P in Eq. (4.7) appears as a result of using Eqs. (4.1) and (4.5). The purpose of writing Eq. (4.7) in its present form is to introduce the force constant ($A$) in terms of Laplacian operator [12] as follows:

$$A = \frac{1}{3}\left[\frac{d^2W}{dr^2} + \frac{2}{r}\frac{dW}{dr}\right] \tag{4.8}$$

It has been found that A can be expressed as a function of volume and the volume derivatives of A have been used in the studies on pressure dependence of elastic and dielectric properties of solids [171, 184, 185]. Eq. (4.7) with the help of Eqs. (4.2), (4.4) and (4.8) can be written in the following form

$$K_T = \frac{A}{3a^{2/3}V^{1/3}} + \frac{4}{3}P \tag{4.9}$$

The pressure derivatives of $K_T$ represented by $K_T^{'} = dK_T/dP$ obtained from Eq. (4.9) is given below

$$K_T^{'} = \left(\frac{4}{3}\frac{P}{K_T} - 1\right)\left(\frac{V}{A}\frac{dA}{dV} - \frac{5}{3}\right) + \frac{16}{9}\frac{P}{K_T} \tag{4.10}$$

In order to determine the volume dependence of $A$, we take

$$A = A_0 f\left(\frac{V}{V_0}\right) \tag{4.11}$$

where $A_0$ is independent of volume and $f$ is a function of volume $V/V_0$. Now, at $P = 0, V = V_0$, we have from Eqs. (4.9) and (4.11)

$$\frac{A_0}{3a^{2/3}} = \frac{K_0 V_0^{1/3}}{f_0} \tag{4.12}$$

where $K_0$ is the value of the isothermal bulk modulus at $P = 0$ and $f_0$ is the value of $f$ at $V = V_0$. Using the definition of $K_T$ and inserting Eq. (4.12) in Eq. (4.9), we get

$$-V\left(\frac{dP}{dV}\right)_T = \frac{K_0}{f_0}\left(\frac{V}{V_0}\right)^{-1/3} f + \frac{4}{3}P \tag{4.13}$$

On integration Eq. (4.13), we obtain

$$P\left(\frac{V}{V_0}\right)^{4/3} = -\frac{K_0}{f_0 V_0}\int_{V_0}^{V} f dV \tag{4.14}$$

Eq. (4.14) is the basic equation which leads to the derivation of an EoS [186]. The formulation presented above is valid for different types of solids. It has been shown by Shanker et al. [186] that Eq. (4.14) yields the Born-Mie EoS [44, 187] and the Brennan-Stacey EoS [188], represented, when the function $f$ is represented by an inverse power dependence and by an

exponential dependence $V/V_0$. A new EoS has also been obtained [186] using the following form for $f$

$$f = (1 + y + y^2)\exp(ty) \tag{4.15}$$

where $y = 1 - V/V_0$ and $t$ is a constant. At $V = V_0$, $f = f_0 = 1$. Substituting Eq. (4.15) into Eq. (4.14), we get

$$P\left(\frac{V}{V_0}\right)^{4/3} = K_0 \int_0^y (1 + y + y^2)\exp(ty)dy \tag{4.16}$$

which yields the following equation known as the Shanker EoS [186]

$$P = \frac{K_0 (V/V_0)^{-4/3}}{t}\left[\left(1 - \frac{1}{t} + \frac{2}{t^2}\right)\{\exp(ty) - 1\} + y\left(1 + y - \frac{2}{t}\right)\exp(ty)\right] \tag{4.17}$$

The value of $t$ is determined from $K_0^{'}$, the zero pressure value of $dK_T/dP$. Using Eqs. (4.11) and (4.15), we find

$$\frac{V}{A}\frac{dA}{dV} = -\frac{V}{V_0}\left[t + \frac{(1+2y)}{1 + y + y^2}\right] \tag{4.18}$$

Substituting Eq. (4.18) into Eq. (4.10) and taking $V = V_0, y = 0, K_T^{'} = K_0^{'}$ at $P = 0$, we obtain

$$t = K_0^{'} - \frac{8}{3} \tag{4.19}$$

The expression for bulk modulus obtained from Eq. (4.17) is given below

$$K_T = K_0\left(\frac{V}{V_0}\right)^{-1/3}(1 + y + y^2)\exp(ty) + \frac{4}{3}P \tag{4.20}$$

Substituting Eq. (4.18) into Eq. (4.10), we get

$$K_T^{'} = \frac{4}{3} + \left(1 - \frac{4}{3}\frac{P}{K_T}\right)\left[\frac{1}{3} + x\left\{t + \frac{(1+2y)}{(1 + y + y^2}\right\}\right] \tag{4.21}$$

where $x = V/V_0, t = K_0^{'} - 8/3$ and $y = 1 - V/V_0$

An expression for the second-order pressure derivative of bulk modulus can be obtained by differentiating twice the first part of Eq. (4.2) with respect to pressure as

$$\frac{d^2K_T}{dP^2} = -\frac{1}{K_T}\left(\frac{dK_T}{dP}\right) - \frac{1}{K_T}\left(\frac{dK_T}{dP}\right)^2 + \frac{V^2 d^2K_T}{K_T^2 dV^2} \tag{4.22}$$

The last term in Eq. (4.22) can be determined by taking the second-order volume derivative of Eq. (4.9) which yields

$$V^2\frac{d^2K_T}{dV^2} = \left(K_T - \frac{4}{3P}\right)\left[\frac{V^2}{A}\frac{d^2A}{dV^2} - 2\frac{V}{A}\frac{dA}{dV} + 4\right] + \frac{112}{27}P \tag{4.23}$$

Eqs. (4.9), (4.10), (4.22) and (4.23) can be used to predict the isothermal bulk modulus $K_T$ and its pressure derivatives $dK_T/dP$ and $d^2K_T/dP^2$ as a function of pressure involved provided we know the interatomic force constant $A$ and its volume derivatives $dA/dV$ and $d^2A/dV^2$ at different pressures. Values of $A$ and its volume derivatives determined by Shanker et al. [167-169] from the data on higher-order elastic constants and pressure derivatives of dielectric constants for ionic crystals reveals the existence of a direct relationship between the interatomic force constant and volume. Shanker et al. [167-169] consider an inverse square form as well as an exponential form for the function of appearing in Eq. (4.11). Thus, we take

$$f\left(\frac{V}{V_0}\right) = \left(\frac{V}{V_0}\right)^{-m} \tag{4.24}$$

and

$$f\left(\frac{V}{V_0}\right) = \exp\left\{-k\left(\frac{V}{V_0}\right)\right\} \tag{4.25}$$

Here $A_0$, $m$ and $k$ are constants independent of volume and pressure. The inverse power form (Eqs. 4.11 and 4.24 ) yields

$$\frac{V}{A}\frac{dA}{dV} = -m \tag{4.26}$$

and

$$\frac{V^2}{A}\frac{d^2A}{dV^2} = m(m+1) \tag{4.27}$$

whereas the exponential form, Eqs. (4.11) and (4.25), yields

$$\frac{V}{A}\frac{dA}{dV} = -k\frac{V}{V_0} \tag{4.28}$$

and

$$\frac{V^2}{A}\frac{d^2A}{dV^2} = k^2\left(\frac{V}{V_0}\right)^2 \tag{4.29}$$

The constants $m$ and $k$ are determined by substituting Eq. (4.26) or (4.28) in Eq. (4.10) and applying the condition that $dK_T / dP = K_0^{'}$ at $P = 0$ and $V = V_0$. Values of both $m$ and $k$ are found to be equal to $K_0^{'} - (5/3)$. The constant $A_0$ is determined by substituting Eq. (4.11) for $A$ in Eq. (4.10) and taking $K_T = K_0$ at $P = 0$ and $V = V_0$. Substituting the values of $A_0$, $m$ and $k$ thus determined and obtain the following expressions with the help of Eqs. (4.9), (4.10), (4.22) and (4.23) using the relations (4.26) and (4.27) based on the inverse power form

$$K_T = K_0\left(\frac{V}{V_0}\right)^{-m-1/3} + \frac{4}{3}P \tag{4.30}$$

$$\frac{dK_T}{dP} = \left(1 - \frac{4}{3}\frac{P}{K_T}\right)K_0^{'} + \frac{16}{9}\frac{P}{K_T} \tag{4.31}$$

$$\begin{aligned}\frac{d^2K_T}{dP^2} = &-\frac{1}{K_T}\frac{dK_T}{dP} - \frac{1}{K_T}\left(\frac{dK_T}{dP}\right)^2 \\ &+ (m^2 + 3m + 4)\left(\frac{1}{K_T} - \frac{4}{3}\frac{P}{K_T^2}\right) + \frac{112}{27}\frac{P}{K_T^2}\end{aligned} \tag{4.32}$$

Similarly, using the relations (Eqs. (4.28) and (4.29)) based on the exponential form in Eqs. (4.9), (4.10), (4.22) and (4.23), we can get

$$K_T = K_0\left(\frac{V}{V_0}\right)^{-1/3}\exp\left\{\left(K_0^{'} - \frac{5}{3}\right)\left(1 - \frac{V}{V_0}\right)\right\} + \frac{4}{3}P \tag{4.33}$$

$$K_T^{'} = \left(1 - \frac{4}{3}\frac{P}{K_T}\right)\left(k\frac{V}{V_0} + \frac{5}{3}\right) + \frac{16}{9}\frac{P}{K_T} \tag{4.34}$$

$$K_T^{''} = -\frac{1}{K_T}\frac{dK_T}{dP} - \frac{1}{K_T}\left(\frac{dK_T}{dP}\right)^2 + \left(\frac{1}{K_T} - \frac{4}{3}\frac{P}{K_T^2}\right) \left[k^2\left(\frac{V}{V_0}\right)^2 + 2k\left(\frac{V}{V_0}\right) + 4\right] + \frac{112}{27}\frac{P}{K_T^2} \tag{4.35}$$

The main limitation of the exponential form such as that given by Eq. (4.25), is that the interatomic force remains finite in the limit of extremely large compressions (i.e. $V/V_0 \to 0$). On the other hand, the inverse power form given by Eq. (4.24) yields an infinitely large interatomic force as $V/V_0 \to 0$. In order to fulfill this criterion, we take the following function for the interatomic force constant as:

$$f\left(\frac{V}{V_0}\right) = \frac{1}{V}\exp\left\{-t\left(\frac{V}{V_0}\right)\right\} \tag{4.36}$$

where $t$ is a constant. Using Eq. (4.36) in Eq. (4.11), we get

$$A = \frac{A_0}{V}\exp\left\{-t\left(\frac{V}{V_0}\right)\right\} \tag{4.37}$$

so that

$$\frac{V}{A}\frac{dA}{dV} = -\left(1 + t\frac{V}{V_0}\right) \tag{4.38}$$

and

$$\frac{V^2}{A}\frac{d^2A}{dV^2} = \left[1 + \left(1 + t\frac{V}{V_0}\right)^2\right] \tag{4.39}$$

Substituting Eq. (4.38) in Eq. (4.10) and applying the condition that at $P = 0$ and $V = V_0$, we get $t = K_0^{'} - 8/3$. Using Eq. (4.37-4.39) in Eqs. (4.9), (4.10), (4.22) and (4.23), we get the following expressions for isothermal bulk modulus and its pressure derivatives

$$K_T = K_0\left(\frac{V}{V_0}\right)^{-4/3}\exp\left\{\left(K_0^{'} - \frac{8}{3}\right)\left(1 - \frac{V}{V_0}\right)\right\} + \frac{4}{3}P \tag{4.40}$$

$$K_T^{'} = \left(1-\frac{4}{3}\frac{P}{K_T}\right)\left(\left(K_0^{'}-\frac{8}{3}\right)\frac{V}{V_0}+\frac{8}{3}\right)+\frac{16}{9}\frac{P}{K_T} \tag{4.41}$$

$$K_T^{''} = -\frac{1}{K_T}\frac{dK_T}{dP}-\frac{1}{K_T}\left(\frac{dK_T}{dP}\right)^2+\left(\frac{1}{K_T}-\frac{4}{3}\frac{P}{K_T^2}\right) \left[\left\{2+\left(K_0^{'}-\frac{8}{3}\right)\frac{V}{V_0}\right\}^2+4\right]+\frac{112}{27}\frac{P}{K_T^2} \tag{4.42}$$

Differentiating Eq. (4.21) with respect to $P$, we get

$$K_T K_T^{''} = \left(\frac{4}{3}\frac{P}{K_T}-1\right)x\left\{t+\left(\frac{1+2y}{1+y+y^2}\right)-x\left(\frac{1-2y-2y^2}{1+y+y^2}\right)\right\} -\frac{4}{3}\left(1-\frac{PK_T^{'}}{K_T}\right)\left\{\frac{1}{3}+x\left(t+\frac{1+2y}{1+y+y^2}\right)\right\} \tag{4.43}$$

At, $x=0, K_T^{'} = K_T/P = K_\infty^{'} = 4/3$, therefore $K_T K_T^{''} = 0$

## 4.2 KEANE EQUATION OF STATE

Keane [189] suggested that $K_T^{'} = dK_T/dP$ is a monotonically decreasing function with pressure, ultimately reaching a limiting value of $K_\infty^{'} = (\partial K_T/\partial P)_T$ as $P \to \infty$. $K_\infty^{'}$ can be considered as a floating parameter. The Keane EoS is useful for interpolation between shock wave data and lower pressure *P-V* data. He had good idea of the range of values and realized that it is not a universal constant. He argued that $K_\infty^{'}$ was tightly bounded

$$\frac{K_0^{'}}{2} < K_\infty^{'} < K_0^{'}-1 \tag{4.44}$$

The simplest of Mie-potential is

$$\phi = -A\left(\frac{a}{r}\right)^m + B\left(\frac{a}{r}\right)^n \tag{4.45}$$

and zero and infinite pressure conditions of bulk modulus $K_T$ are respectively

$$K_0^{'} = 2+\frac{1}{3}m+\frac{1}{3}n \tag{4.46}$$

$$K_\infty^{'} = 1 + \frac{1}{3}n \tag{4.47}$$

Although Eq. (4.44) was derived rather simplistically from Eq. (4.45), that is, by applying Eqs. (4.46) and (4.47) and Keane concluded by proposing a finite strain equation different from Eq. (4.45). By making the assumption that pressure can be written as a truncated polynomial in Birch strain [181]

$$P = P_0 + A_1 \in + A_2 \in^2 \tag{4.48}$$

with coefficients $A_1$ and $A_2$ linearly related.

The importance of $K_\infty^{'}$ was first recognized by Keane [189] with the relationship that we refer to as Keane's equation

$$K_T^{'} = K_\infty^{'} + (K_0^{'} - K_\infty^{'})\frac{K_0}{K_T} \tag{4.49}$$

To obtain expressions for $K_T / K_0$ and $P / K_0$ as a function of $x = V / V_0$, multiply Eq. (4.49) by $K_T$ and note that $K_T = -x(dP/dx)$, so that

$K_T K_T^{'} = -x(dP/dx)(dK_T/dP) = -x(dK_T/dx)$. Then

$$\int_{K_0}^{K_T} \frac{dK_T}{K_\infty^{'} K_T + (K_0^{'} - K_\infty^{'})K_0} = \int_1^x \frac{dx}{x} \tag{4.50}$$

which gives

$$\frac{K_T}{K_0} = \frac{K_0^{'}}{K_\infty^{'}}\left(x^{-K_\infty^{'}} - 1\right) + 1 \tag{4.51}$$

Now integrating Eq. (4.49) with respect to pressure, noting that $dP / K_T = dx / x$

$$K_T - K_0 = K_\infty^{'} P - (K_0^{'} - K_\infty^{'})K_0 \ln x \tag{4.52}$$

Then use Eq. (4.51) to eliminate $K_T$, giving

$$\frac{P}{K_0} = \frac{K_0^{'}}{K_\infty^{'2}}\left(x^{-K_\infty^{'}} - 1\right) + \left(\frac{K_0^{'}}{K_\infty^{'}} - 1\right)\ln x \tag{4.53}$$

By differentiating Eq. (4.49) , we get

$$K_0 K_0^{''} = -K_0^{'}\left(K_0^{'} - K_\infty^{'}\right) \tag{4.54}$$

By Keane's rule, this means

$$K_0^{'} < -K_0^{'}K_0^{''} < \frac{1}{2}K_\infty^{'} \tag{4.55}$$

But there is an inconsistency,

$$K_0 K_0^{''} = -(1+\frac{1}{3}m)(1+\frac{1}{3}n) \tag{4.56}$$

Eqs. (4.46) , (4.47) and (4.56), which Keane [189] used to derive his rule, give

$$K_0 K_0^{''} = -K_\infty^{'}(K_0^{'} - K_\infty^{'}) \tag{4.57}$$

in place of Eq. (4.54). Use of Eq. (4.57) to give smaller values to ($K_0 K_0^{''}$) would allow reconsideration of Eq. (4.45) and

$$P = \frac{3K_0}{(n-m)}\left[\left(\frac{1}{x}\right)^{1+n/3} - \left(\frac{1}{x}\right)^{1+m/3}\right] \tag{4.58}$$

## 4.3 STACEY EQUATION OF STATE

After finding some numerical difficulties in Keane [189] EoS, a different $K$-prime approach is prompted by equation

$$\left(\frac{P}{K_T}\right)_\infty = \frac{1}{K_\infty^{'}} \tag{4.59}$$

To make use of this equation we need to represent $K_T^{'}$ in terms of $P/K_T$. We believe that the first suggestion of an equation of this form was by Stevenson [190], whose study of the physics of liquid metal at high pressure, directed to an understanding of the core. Stacey [191] first tried a quadratic $K_T^{'}$ versus $P/K_T$ equation and subsequently an exponential one [192] but these were seen to be unsatisfactory when the thermodynamic limit on $K_T$ by following equation

$$\frac{P}{K_T} = \frac{-Ax^{5/3} + Bx^{7/3} - Cx^3 + Dx^{11/3}}{\left(-A\left(\frac{5}{3}\right)x^{5/3} + B\left(\frac{7}{3}\right)x^{7/3} - C3x^3 + D\left(\frac{11}{3}\right)x^{11/3}\right)} \tag{4.60}$$

was recognized [46] requiring curvature of reciprocal form,

$$\frac{1}{K_T^{'}} = \frac{1}{K_0^{'}}\left(1 - \frac{K_\infty^{'}}{K_0^{'}}\right)\frac{P}{K_T} \tag{4.61}$$

By considering this as the reciprocal *K*-primed equation, differentiation yields Eq. (4.54), so it is evident that Eqs. (4.49) and (4.61) are very similar although having apparently quite different forms. Eq. (4.61) does not integrate to analytical expressions for $P/K_0$ and $K_T/K_0$ as functions of $V/V_0$, which are standard for finite strain theories, but gives $K_T/K_0$ and $V/V_0$ as functions of $P/K_T$. The use of $P/K_T$ as the independent variable is a significant advantage in fitting Earth model tabulations, which list both *P* and $K_T$, because an equation relating $V/V_0$ to $P/K_T$ can be fitted without needing a value of $K_0$.

To integrate Eq. (4.61) first multiply $K_T^{'}/K_T$, so that

$$\frac{1}{K_T}=\frac{1}{K_0^{'}}\frac{K_T^{'}}{K_T}+\left(1-\frac{K_\infty^{'}}{K_0^{'}}\right)K_T^{'}\frac{P}{K_T^2} \tag{4.62}$$

There are two ways of integrating this, using the derivative

$$\frac{d}{dP}\left(\frac{P}{K_T}\right)=\frac{1}{K_T}-K_T^{'}\frac{P}{K_T^2} \tag{4.63}$$

First, rearrange the terms in Eq. (4.62) so that the left-hand side is the same as the right-hand side of Eq. (4.63) and substitute for it

$$\frac{d}{dP}\left(\frac{P}{K_T}\right)=\frac{1}{K_0^{'}}\frac{K_T^{'}}{K_T}\left(1-K_\infty^{'}\frac{P}{K_T}\right) \tag{4.64}$$

This separates into two standard integrals

$$\int_0^{P/K_T}\frac{d(P/K_T)}{1-K_\infty^{'}P/K_T}=\frac{1}{K_\infty^{'}}\int_{K_0}^{K_T}\frac{dK_T}{K_T} \tag{4.65}$$

from which we obtain one of the required solutions

$$\frac{K_T}{K_0}=\left(1-K_\infty^{'}\frac{P}{K_T}\right)^{-K_0^{'}/K_\infty^{'}} \tag{4.66}$$

For the second integration substitute for $K_T^{'}P/K_T^2$ in Eq. (4.62) by Eq. (4.63), with cancellation of the $1/K_T$ terms that appear on both sides

$$0=\frac{1}{K_0^{'}}\frac{K_T^{'}}{K_T}-\frac{1}{K_0^{'}}\frac{K_\infty^{'}}{K_T}-\left(1-\frac{K_\infty^{'}}{K_0^{'}}\right)\frac{d}{dP}\left(\frac{P}{K_T}\right) \tag{4.67}$$

And integrate with respect to *P*, we get

$$0 = \frac{1}{K_0'}\int_{K_0}^{K_T}\frac{dK}{K_T} - \frac{K_\infty'}{K_0'}\int_0^P \frac{dP}{P} - \left(1-\frac{K_\infty'}{K_0'}\right)\int_0^{P/K} d\left(\frac{P}{K_T}\right)$$

$$= \frac{1}{K_0'}\ln\left(\frac{K_T}{K_0}\right) - \frac{K_\infty'}{K_0'}\ln\left(\frac{V}{V_0}\right) - \left(1-\frac{K_\infty'}{K_0'}\right)\frac{P}{K_T} \qquad (4.68)$$

so that the substitution for $K_T / K_0$ from Eq. (4.66) gives

$$\ln\left(\frac{V}{V_0}\right) = \frac{K_0'}{K_\infty'^2}\ln\left(1-K_\infty'\frac{P}{K_T}\right) + \left(\frac{K_0'}{K_\infty'}-1\right)\frac{P}{K_T} \qquad (4.69)$$

Eqs. (4.66), (4.69) have $K_0'$ and $K_\infty'$ as fitting parameters with either $K_0$ or $V_0$ but not both. The choice between the Keane and reciprocal K-primed equations must be made on the basis of convenience in application. Generally, this means that if zero pressure properties $K_0$ or $V_0$ are known, then the Keane equation is easier to apply but for deep Earth data the reciprocal K-primed equation is better. By differentiating Eq. (4.61) we can express the next two derivatives at arbitrary compression, in terms of $K_T', K_0'$ and $K_\infty'$ with convenient simplicity

$$K_T K_T'' = -\frac{K_T'^2}{K_0'}(K_T' - K_\infty') \qquad (4.70)$$

Which reduces to Eq. (4.54) at *P=0* and

$$K_T^2 K_T''' = \frac{K_T'^3}{K_0'^2}(K_T' - K_\infty')(3K_T' - 2K_\infty' + K_0') \qquad (4.71)$$

# *CHAPTER 5*

# *Formulations, Results and Discussions*

## *Overview*

This chapter deals with the various models developed in the present study and their formulations, results and discussions. An inter-relationship between the Anderson-Grüneisen parameter and thermal expansivity under adiabatic and isothermal compression has been developed for insulator materials. Further, a new empirical expression has been proposed to predict the values of volume dependence of Grüneisen parameter using two different models and higher order volume derivatives of Grüneisen parameter has also been discussed. In this chapter we have also analysed the number of thermodynamic properties in the limit of infinite pressure. A reciprocal form model for the volume dependence of thermal expansivity has also been provided for different solids and geophysical minerals. In the last section of this chapter, a new $K$-prime equation of state (EoS) has been presented in the form of volume dependence of isothermal bulk modulus and its higher order pressure derivatives for lower mantle and core regions of the Earth. The temperature dependence of volume expansion ratio and its second order temperature derivative for NaCl and KCl has been proposed.

## 5.1 RELATIONSHIP BETWEEN ANDERSON-GRÜNEISEN PARAMETER AND THERMAL EXPANSIVITY

Thermal expansivity is an important physical parameter to understand many problems of thermodynamics. It is the parameter by which many other thermal properties can directly be derived. The thermal expansivity is essential to understand the deep earth, such as the adiabatic temperature gradient, convective power, interpretation of tomographically observed seismic velocity anomalies and gravitational energy release by thermal contraction [73, 144]. It is emphasized that many serious problems in thermodynamic functions arise due to uncertainty in thermal expansivity; therefore, many attempts [57, 65, 66, 193-195] have been made to understand the knowledge of thermal expansivity along an isotherm as well as along an adiabat. Mathematically, thermal expansivity or volume thermal expansion coefficient is defined as follows;

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{5.1}$$

where P, V, T have their usual meanings.

The variation of thermal expansivity with volume or compression is already recognized. It is found [57] that thermal expansivity decreases with increasing compression. The other important parameter, which connects thermal and elastic properties of a solid, is termed as the Anderson-Grüneisen parameter. The thermodynamic approach shows that it is an explicit function of two dimensionless parameters; one is $K_T^{'} = (\partial K_T / \partial T)_P$ and the other, known as the Grüneisen ratio ($\gamma$). The dimensionless Anderson-Grüneisen parameters can be obtained either at constant temperature ($\delta_T$) or at constant entropy ($\delta_S$). In the present study, we have made an attempt to find a relevant inter-relationship between the Anderson-Grüneisen parameter and thermal expansivity under adiabatic and isothermal compression for insulators.

The high pressure thermodynamics, formulated by Stacey and Davis [73, 144], results in two important findings. That is the Anderson-Grüneisen parameter, which relates thermal and elastic properties, ($\delta$) tends to a positive finite value, and thermal expansivity tends to zero at infinite pressure ($P \to \infty$) or zero volume ($V \to 0$). These constraints have very important role in thermodynamics of solids in the limit of infinite pressure. In view of these constraints, we can

write following relationship between thermal expansivity and the isentropic Anderson-Grüneisen parameter;

$$\delta_S = \delta_{S\infty} + (\delta_{S0} - \delta_{S\infty})\left(\frac{\alpha}{\alpha_0}\right) \tag{5.2}$$

Here subscript "$S$" refers to the adiabatic condition. Stacey and Davis [73] reported the values of $\delta_T$ and $\alpha$ for lower mantle (an insulator) region of the Earth. We used these data to check the validity linear relationship between $\delta_T$ and $\alpha$. Figure-5.1 shows a precise linear relationship as expressed by eq. (5.2). The linear relationship between $\delta_S$ and $\alpha$ can be expressed as follows for the lower mantle region of the Earth,

$$\delta_S = 0.27 + (3.18 - 0.27)\frac{\alpha}{34.918} \tag{5.3}$$

Comparing eq. (5.3) to eq. (5.2), we get $\delta_S^0$ =3.18, $\delta_{S\infty}$ = 0.27 for lower mantle region of the Earth. The value of $\delta_S^0$ for lower mantle is exactly the same as reported in literature [73]. Thus these value of $\delta_S^0$ and $\delta_{S\infty}$ can be used to investigate the thermal and elastic properties of the Earth. Here, we again assume that the relationship (5.2) is also applicable along an isotherm. Therefore, we write

$$\delta_T = \delta_{T\infty} + (\delta_{T0} - \delta_{T\infty})\left(\frac{\alpha}{\alpha_0}\right) \tag{5.4}$$

Here subscript "$T$" refers for the isothermal condition. Using the following thermodynamic relationship

$$\delta_T = \frac{V}{\alpha}\left(\frac{\partial \alpha}{\partial V}\right)_T \tag{5.5}$$

in eq. (5.4), we obtain the following expression

$$\alpha = \frac{\alpha_0}{\left[1 + \frac{\delta_T^0}{\delta_{T\infty}}\left\{\left(\frac{V}{V_0}\right)^{-\delta_{T\infty}} - 1\right\}\right]} \tag{5.6}$$

Further, following the constraints made by high-pressure thermodynamics [73, 144], we propose following expressions to inter-relate the Anderson-Grüneisen parameter and thermal expansivity;

$$\alpha\delta_T = \alpha_0\delta_T^0\left(\frac{V}{V_0}\right)^m \tag{5.7}$$

$$\frac{\alpha}{\delta_T} = \frac{\alpha_0}{\delta_T^0}\left(\frac{V}{V_0}\right)^n \tag{5.8}$$

where *m* and *n* are material dependent constants. With the help of eqs. (5.5) and (5.7), we get

$$\alpha = \alpha_0\left[1+\frac{\delta_T^0}{m}\left\{\left(\frac{V}{V_0}\right)^m - 1\right\}\right] \tag{5.9}$$

The corresponding value of volume dependence of $\delta_T$ from eqs. (5.7) and (5.9) is

$$\delta_T = \frac{\delta_T^0\left(\frac{V}{V_0}\right)^m}{\left[\left(1-\frac{\delta_T^0}{m}\right)+\frac{\delta_T^0}{m}\left(\frac{V}{V_0}\right)^m\right]} \tag{5.10}$$

If we put, $V \to 0 (P \to \infty)$ in eqs. (5.9) and (5.10), we observe that expression (5.9) gives a finite value for $\alpha$ while eq. (5.10) yields a zero value for $\delta_T$. These conditions are not consistent with the high-pressure thermodynamics [73, 144]. However, if $m = \delta_T^0$ then eqs. (5.9) and (5.10) will follow the constraints imposed by high-pressure thermodynamics. Under this condition $\delta_T$ remains unchanged with the change in compression, and eq. (5.9) is reduced as follows;

$$\frac{\alpha}{\alpha_0} = \left(\frac{V}{V_0}\right)^{\delta_T} \tag{5.11}$$

Relationship (5.11) can also be obtained from eq. (5.7) under the condition $m = \delta_T^0$. It is known [44] that relationship (5.11) is applicable only in high temperature and low compression region because in low compression region, $\{(V/V_0) < 0.90\}$, the value of $\delta_T$ approximately remains constant. Experimentally and theoretically it is confirmed [44] that $\delta_T$ decreases with

increasing compression. Hence, we need another expression for compression dependence of thermal expansivity, which can be applied up to extreme compression. Now, the combination of eqs. (5.5) and (5.8) yields the next relationship for volume dependence of thermal expansivity;

$$\alpha = \frac{\alpha_0}{\left[1+\frac{\delta_T^0}{n}\left\{\left(\frac{V}{V_0}\right)^{-n}-1\right\}\right]} \tag{5.12}$$

and from eqs. (5.8) and (5.12), we get

$$\delta_T = \frac{\delta_T^0}{\left[\left(1-\frac{\delta_T^0}{n}\right)\left(\frac{V}{V_0}\right)^{n}+\frac{\delta_T^0}{n}\right]} \tag{5.13}$$

Applying the infinite pressure boundary condition i.e. at $V \to 0$, $\delta_T \to \delta_{T\infty}$, we get form eq. (5.13)

$$n = \delta_{T\infty} \tag{5.14}$$

Thus, eqs. (5.6) and (5.12) are identical. It is clear that eqs. (5.12) and (5.13) satisfy the constraints provided by high pressure thermodynamics [73, 144]. Thus, these expressions may apply up to extreme compression and eq. (5.8) may be considered to be more appropriate than eq. (5.7). Further, a direct relationship between $\delta_T$ and $\alpha$ can be obtained from eq. (5.12). Eq. (5.12) can be written in following manner, with the help of eq. (5.14),

$$\frac{\delta_T^0}{\alpha_0}\left(\frac{V}{V_0}\right)^{-\delta_{T\infty}} = \frac{\delta_{T\infty}}{\alpha}+\left(\frac{\delta_T^0-\delta_{T\infty}}{\alpha_0}\right) \tag{5.15}$$

Equation (5.15) and eq. (5.8) directly yield eq. (5.4). Equation (5.6) provides a way to compute volume dependence of thermal expansivity, under isothermal condition. To validate Eq. (5.6), we require experimental data on $\alpha$ ($V$). Currently, we have experimental data for HCP iron and for solid NaCl. The thermal expansivity data of HCP iron (metal) are reported in references [196, 197]. However, the values of references [196, 197] are seriously wrong. If one estimates the zero

pressure value of thermal expansivity from the Grüneisen parameter $\gamma \approx 1.8$ to 2.0, with $K$ about 170 GPa, $\rho$ =8352 kgm$^{-3}$ and $Cv \approx 470\ JKg^{-1}K^{-1}$ [7], one gets $\alpha \approx 44 \times 10^{-6}K^{-1}$, not $78 \times 10^{-7}K^{-1}$ [196, 197]. Of course HCP iron does not exist at zero pressure, but the extrapolation is close enough and if one compares high pressure values with the data for the Earth's core in reference [73], it is clear that the reference [196, 197] values are too much high. In fact, the so called experimental data [196, 197] are not experimental at all (there are no direct observations of $\alpha$ for HCP iron) but are very indirect empirical fits to the theories. The other experimental data on volume dependence of thermal expansivity are reported by Birch [165] for solid NaCl (insulator). Birch [165] combined the several kinds of experimental data viz. ultrasonic, volumetric and shock compression, to produce a set of isotherms of NaCl on the temperature-pressure region between 25ºC and 500ºC and 0-30 GPa. These results of pressure-volume relationship and thermo elastic properties of NaCl have been considered to be reliable and used by Anderson [44] in further analysis of the volume dependence of the Anderson-Grüneisen parameter ($\delta_T$) and thermal expansivity ($\alpha$) of NaCl. Therefore, these data are considered significant and are used to validate our approach. The computed values of $\alpha(V)$ from eq. (5.10) for solid NaCl are compared with available experimental data in Figure-5.2. A close agreement between theory and experiment is found, which in turn reveals the validity of our approach. Thus, in the present study, we disclosed the relationship between Anderson-Grüneisen parameter and thermal expansivity for insulators. The predicted relationship is validated under the adiabatic as well as isothermal conditions. For adiabatic temperature profile, we used the data reported by Stacey and Davis [73] based on the seismic values for lower mantle (an insulator) region of the Earth. The isothermal data reported by Birch [165] for solid NaCl is used for validation. A linear relationship between the Anderson-Grüneisen parameter and thermal expansivity is observed. Such relationship is useful to investigate the thermal and elastic properties of insulator materials.

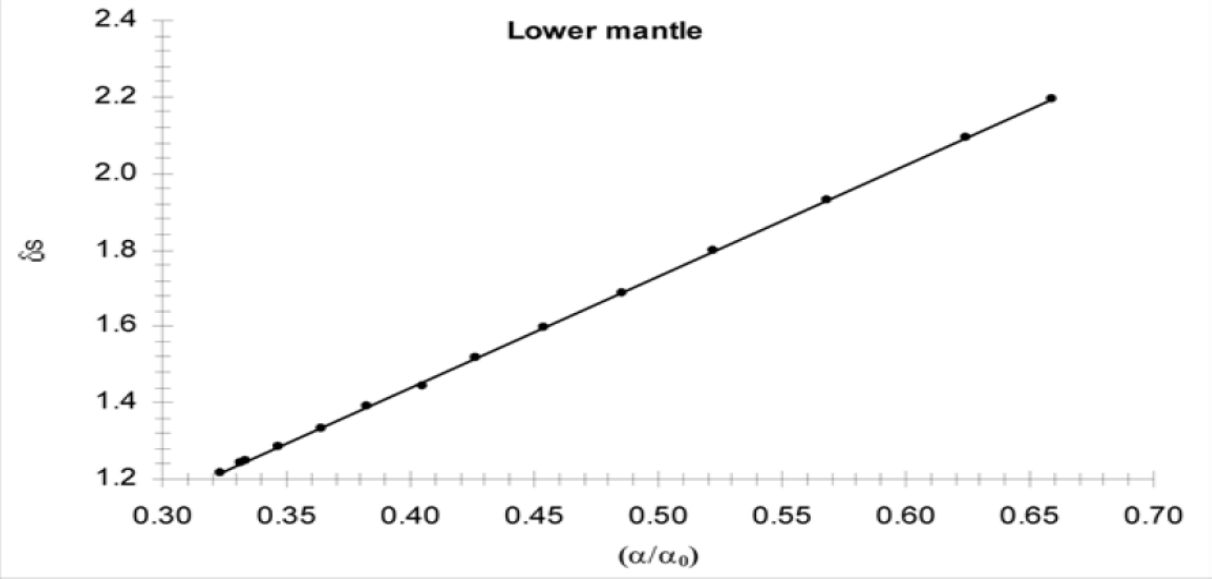


**Fig. 5.1** Plot between the Anderson-Grüneisen parameter and thermal expansivity for lower mantle region of the Earth. The data points are extracted from reference [73]

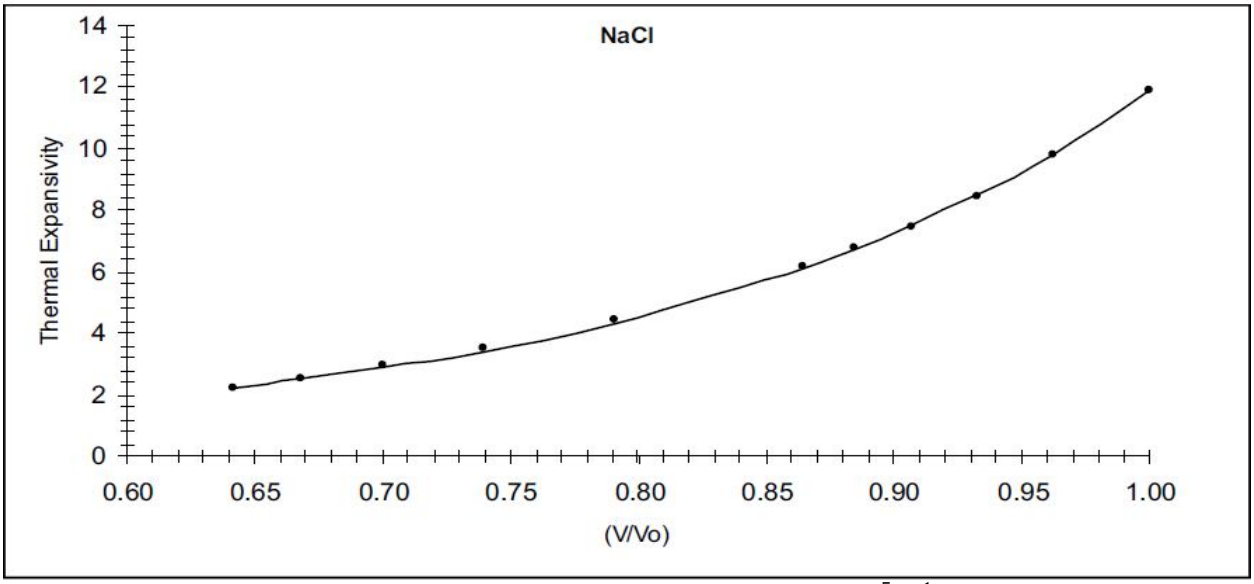


**Fig. 5.2** Volume dependence of thermal expansivity ($10^{-5}K^{-1}$) of solid NaCl. The experimental values [165] are represented by points and calculated values with the help of Eq. (5.6), are represented by lines. At compression higher than 0.85, the data points are found by extrapolation, under the approximation that the product of thermal expansivity and isothermal bulk modulus remains unchanged with the change in compression. Here $\delta_T^0 = 5.3$ [165] and $\delta_{T\infty} = 2.5$

## 5.2 VOLUME DEPENDENCE OF GRÜNEISEN PARAMETER

### 5.2.1 Estimation of volume dependence of Grüneisen parameter for NaCl and $\varepsilon$-Fe

The Grüneisen parameter ($\gamma$) is an important physical quantity in geophysics as it often appears in equations which describe the thermoelastic behaviour and the anharmonic properties of materials at high pressure and temperature. The Grüneisen parameter can be considered as the measure of the change of pressure resulting from the increase of energy density at constant volume [44]. Due to lack of suitable theory and enough experimental data, it is interesting to estimate a simple method for evaluating the pressure or volume dependence of the Grüneisen parameter ($\gamma$). Many attempts [193, 198-206] have been made to study the volume dependence of Grüneisen parameter. The Grüneisen parameter is useful to calculate the values of Debye temperature ($\theta_D$) with the help of basic definition of Debye-Grüneisen model.

$$\gamma = -\left(\frac{d\ln\theta_D}{d\ln V}\right)_T \tag{5.16}$$

and the thermal pressure can be evaluated with the following relationship

$$P_{th} = \frac{\gamma E_{th}}{V} \tag{5.17}$$

In the present study, we propose a new empirical relationship for volume or pressure dependence of the Grüneisen parameter ($\gamma$). We check the validity of present formulation to NaCl and $\varepsilon$-Fe. We compare the results obtained from present model with those values of $\gamma$ [165, 196] derived from the experimental data on thermoelastic properties.

Sharma and Sharma [207] used the following relationship for volume dependence of Anderson-Grüneisen parameter ($\delta_T$) as

$$\delta_T = \delta_T^{\infty} + (\delta_T^0 - \delta_T^{\infty})\left(\frac{V}{V_0}\right)^m \tag{5.18}$$

where $\delta_T^0$ and $\delta_T^{\infty}$ are respectively the values of $\delta_T$ at $P = 0$ or $V \to V_0$ and $P \to \infty$ or $V \to 0$ and $m$ is an adjustable parameter.

Srivastava and Sinha [208] formulated the following expression for first pressure derivative of isothermal bulk modulus

$$K_T^{'} = K_{\infty}^{'} + \left(K_0^{'} - K_{\infty}^{'}\right)\left(\frac{V}{V_0}\right)^{K_0^{'}} \tag{5.19}$$

where $K_0^{'}$ and $K_\infty^{'}$ are respectively the values of first order pressure derivative of isothermal bulk modulus ($K_T$) at atmospheric pressure and at infinite pressure $P \to \infty$ or $V \to 0$. Recently, Sharma et al. [209] have also used Eqs. (5.18, 5.19) to formulate the expression to evaluate the values of volume dependence of thermal pressure for aluminium and found the good agreement with the available data for a wide range of pressures and temperatures. Thus we have chosen these Eqs. (5.18, 5.19) in the present study to establish the relationship to predict the values of volume dependence of Grüneisen parameter.

Anderson [44] has established the following fundamental thermodynamic identity

$$q = \delta_T - K_T^{'} + 1, \tag{5.20}$$

and $q$ is the second Grüneisen parameter

$$q = \left(\frac{d\ln\gamma}{d\ln V}\right)_T \tag{5.21}$$

$\delta_T$ is the Anderson-Grüneisen parameter

$$\delta_T = -\frac{1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_P \tag{5.22}$$

$K_T^{'}$ is the first pressure derivative of isothermal bulk modulus ($K_T$)

$$K_T^{'} = \left(\frac{\partial K_T}{\partial P}\right)_T \tag{5.23}$$

Eq. (5.20) is frequently used by many researchers [183, 205, 210, 211]. Now using Eqs. (5.18), (5.19) and (5.21) in Eq. (5.20), we get

$$\left(\frac{\partial\ln\gamma}{\partial\ln V}\right)_T = \delta_T^{\infty} + (\delta_T^0 - \delta_T^{\infty})\left(\frac{V}{V_0}\right)^m - K_\infty^{'} - (K_0^{'} - K_\infty^{'})\left(\frac{V}{V_0}\right)^{K_0^{'}} + 1 \tag{5.24}$$

On Integration of Eq. (5.24), we get

$$\frac{\gamma}{\gamma_0} = \left(\frac{V}{V_0}\right)^{\delta_T^{\infty} - K_\infty^{'} + 1} \times \exp\left\{\left(\frac{\delta_T^0 - \delta_T^{\infty}}{m}\right)\left[\left(\frac{V}{V_0}\right)^m - 1\right] - \left(\frac{K_0^{'} - K_\infty^{'}}{K_0^{'}}\right)\left[\left(\frac{V}{V_0}\right)^{K_0^{'}} - 1\right]\right\} \tag{5.25}$$

Stacey [144] has listed the following basic thermodynamic identity

$$\left(\frac{d\ln\alpha K_T}{d\ln V}\right)_T = \delta_T - K_T^{'} \tag{5.26}$$

where

$$\delta_T = \left(\frac{d\ln\alpha}{d\ln V}\right)_T \tag{5.27}$$

and

$$K_T^{'} = -\left(\frac{d\ln K_T}{d\ln V}\right)_T \tag{5.28}$$

Eq. (5.26) has been used by various researchers [36, 64, 183, 207, 211, 212] to discuss the nature of variation of $\alpha K_T$ with compression. At $P \to \infty$ or $V \to 0$, $\alpha K_T \to \infty$ only when $\delta_T - K_T^{'}$ is negative quantity which suggests that $\delta_T^{\infty}$ must be less than $K_{\infty}^{'}$.Thus the value of $\delta_T^{\infty}$ should be constrained according to the following relationship [213]

$$0 < \delta_T^{\infty} < K_{\infty}^{'} \tag{5.29}$$

At $P \to \infty$ or$V \to 0$, Eq. (5.20) becomes

$$q_{\infty} = \delta_T^{\infty} - K_{\infty}^{'} + 1 \tag{5.30}$$

Since $q_{\infty} \to 0$ [73, 144], now Eq. (5.30) becomes

$$\delta_T^{\infty} = K_{\infty}^{'} - 1 \tag{5.31}$$

Following the Stacey–Davis model [73] i.e., $K_{\infty}^{'} = 0.6K_0^{'}$, where $K_0^{'}$ is the value of isothermal bulk modulus at $P = 0$ and room temperature i.e., $T_0 = 300K$. The values of $\delta_T^{\infty}$ obtained from Eq. (5.31) for both solids under consideration are enlisted in Table 5.1 and the calculated values satisfy the constrained (Eq. (5.29)).

Using Eq. (5.31) in Eq. (5.25), we get

$$\frac{\gamma}{\gamma_0} = \exp\left\{\left(\frac{\delta_T^0 - \delta_T^{\infty}}{m}\right)\left[\left(\frac{V}{V_0}\right)^m - 1\right] - \left(\frac{K_0^{'} - K_{\infty}^{'}}{K_0^{'}}\right)\left[\left(\frac{V}{V_0}\right)^{K_0^{'}} - 1\right]\right\} \tag{5.32}$$

where all symbols are having their usual meanings.

The values of input parameters [17, 196, 203, 214, 215] are enlisted in Table 5.1. We have calculated the values of Grüneisen parameter through Eq. (5.32) for NaCl and $\varepsilon$-Fe for pressure ranges 0-30GPa for NaCl and 0-359.5GPa for $\varepsilon$-Fe because NaCl has a stable rocksalt structure (B1) up to a pressure of about 30GPa and the high pressure/ low temperature stable phase of iron is hcp (often called the $\varepsilon$ phase). It is the most likely stable phase at Earth's core conditions up

to a pressure of about 360 GPa. The results obtained through Eq. (5.32) are compared with the values of $\gamma$ [165, 196] derived from the experimental data on thermoelastic properties in Tables 5.2 and 5.3 for NaCl and $\varepsilon$-Fe respectively. For direct vision we have also plotted the graphs for Grüneisen parameter versus volume alongwith those values of $\gamma$ derived from the experimental data on thermoelastic properties in Figs. 5.3 and 5.4 for NaCl and $\varepsilon$-Fe respectively. Figures 5.3 and 5.4 reflect that as the volume decreases the value of Grüneisen parameter is decreased and the good agreement with those values of $\gamma$ [165, 196] derived from the experimental data on thermoelastic properties thus supports the validity of the present model.

In conclusion, we have thus proposed a new simple and straightforward empirical relationship to calculate the values of Grüneisen parameter $\gamma$ for NaCl and $\varepsilon$-Fe under wide range of pressure. It is found that the results obtained through Eq. (5.32) are compatible with those values of $\gamma$ [165, 196] derived from the experimental data on thermoelastic properties throughout the wide range of pressure for both solids under consideration. The results obtained through Eq. (5.32) are consistent with those values of $\gamma$ [165, 196] derived from the experimental data on thermoelastic properties.

**Table 5.1** Input parameters [17, 196, 203, 214, 215] used in calculations

| Solids | $\gamma_0$ | $K_0^{'}$ | $K_\infty^{'}$ | $\delta_{T0}$ | $\delta_{T\infty}$ | $m$ |
|---|---|---|---|---|---|---|
| NaCl | 1.6275 | 5.11 | 3.066 | 5.2 | 2.066 | 2.74 |
| $\varepsilon-$Fe | 1.71 | 5.47 | 3.282 | 5.02 | 2.282 | 3 |

**Table 5.2** The values of volume dependence of Grüneisen parameter ($\gamma$) for NaCl calculated through (a) Eq. (5.32); and (b) experimental data [165].

| | | $\gamma$ | |
|---|---|---|---|
| $P$ (GPa) | $V/V_0$ (Ref. 165) | (a) | (b) |
| 0 | 1.0000 | 1.6275 | 1.62 |
| 1 | 0.9627 | 1.56 | 1.55 |
| 2 | 0.9324 | 1.50 | 1.51 |
| 3 | 0.9067 | 1.46 | 1.46 |
| 4 | 0.8845 | 1.41 | 1.43 |
| 5 | 0.8649 | 1.38 | 1.40 |
| 10 | 0.7910 | 1.25 | 1.27 |
| 15 | 0.7397 | 1.17 | 1.19 |
| 20 | 0.7004 | 1.12 | 1.12 |
| 25 | 0.6685 | 1.07 | 1.07 |
| 30 | 0.6416 | 1.04 | 1.03 |

**Table 5.3** The values of volume dependence of Grüneisen parameter ($\gamma$) for $\varepsilon-$Fe calculated through (a) Eq. (5.32); and (b) experimental data [196].

| | | $\gamma$ | |
|---|---|---|---|
| $P$ (GPa) | $V/V_0$ (Ref. 196) | (a) | (b) |
| 0.00 | 1.000 | 1.71 | 1.71 |
| 29.96 | 0.877 | 1.56 | 1.59 |
| 35.56 | 0.862 | 1.54 | 1.57 |
| 41.75 | 0.847 | 1.52 | 1.55 |
| 48.62 | 0.832 | 1.50 | 1.53 |
| 56.22 | 0.817 | 1.48 | 1.51 |
| 64.64 | 0.802 | 1.45 | 1.49 |
| 73.99 | 0.788 | 1.44 | 1.47 |
| 84.38 | 0.773 | 1.42 | 1.45 |
| 95.92 | 0.758 | 1.40 | 1.43 |
| 108.76 | 0.743 | 1.38 | 1.41 |
| 123.05 | 0.728 | 1.36 | 1.39 |
| 139.00 | 0.713 | 1.34 | 1.37 |
| 156.80 | 0.698 | 1.32 | 1.35 |
| 176.71 | 0.684 | 1.30 | 1.32 |
| 198.99 | 0.669 | 1.29 | 1.30 |
| 223.98 | 0.654 | 1.27 | 1.28 |
| 252.06 | 0.639 | 1.26 | 1.25 |
| 283.65 | 0.624 | 1.24 | 1.23 |
| 319.26 | 0.609 | 1.23 | 1.20 |
| 359.50 | 0.594 | 1.21 | 1.18 |

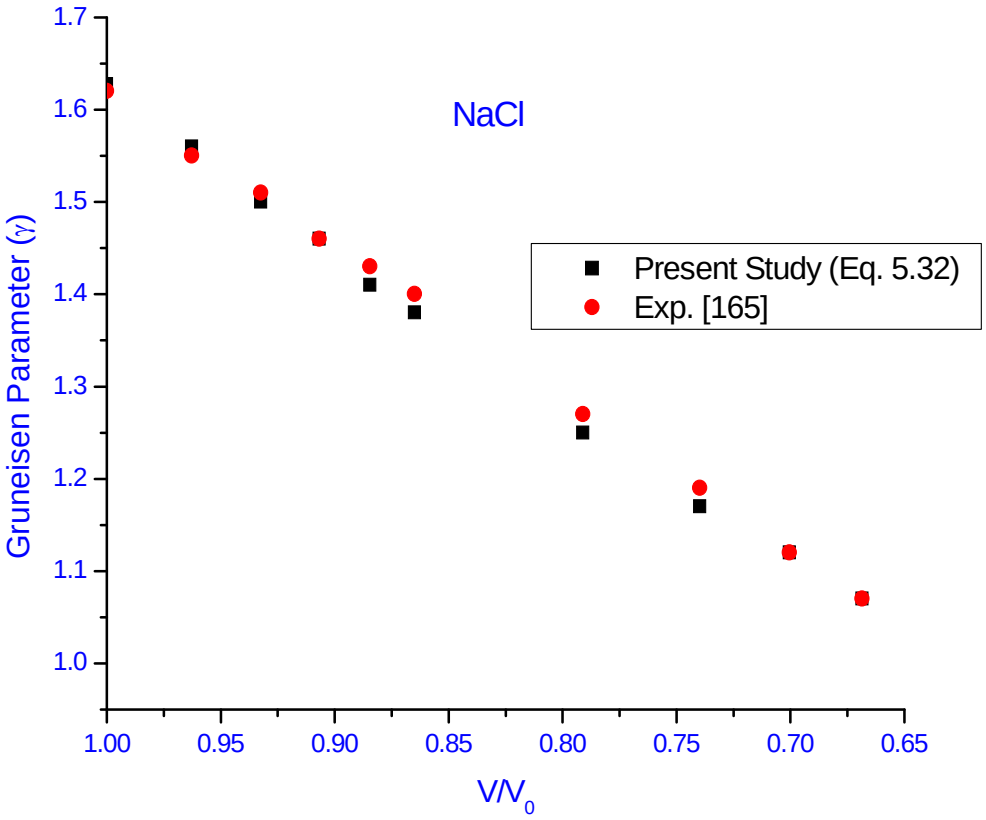


**Fig. 5.3** Volume dependence of Grüneisen parameter for NaCl. The values of Grüneisen parameter is decreased as the volume decreases and show good agreement between calculated values through Eq. (5.32) and those values of $\gamma$ [165] derived from experimental data on thermoelastic properties.

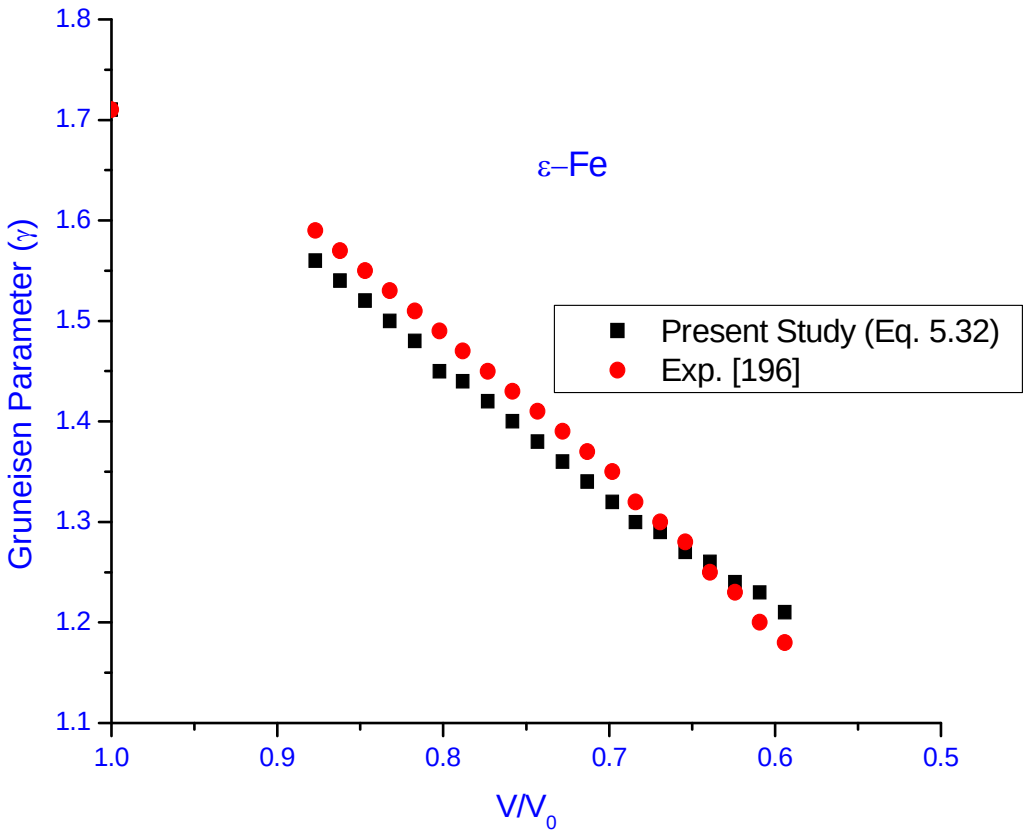


**Fig. 5.4** Volume dependence of Grüneisen parameter for $\varepsilon$-Fe. The values of $\gamma$ is decreased as volume decreases. The calculated values through Eq. (5.32) are compatible with those values of $\gamma$ [196] derived from the experimental data on thermoelastic properties.

### 5.2.2 Volume dependence of Grüneisen parameter for solids under extreme compression

Grüneisen parameter $(\gamma)$ is an important parameter to study thermal and elastic properties of solids. It is related to explain the anharmonic properties of solids in condensed matter Physics and geophysics. Grüneisen parameter is useful to predict the Debye temperatures $(\theta_D)$ for solids and minerals. The knowledge of Grüneisen parameter is also required for investigating the melting curves from Lindemann-Gilvarry criterion [216, 217]. One common experimental research of Grüneisen parameter in its macroscopic definition has been done by Birch [165] based on experimental measurement of thermodynamic properties at high temperatures and high pressures. The experimental determination of the Grüneisen parameter defined in the microscopic definition is extremely difficult, as it requires a detailed knowledge of the phonon dispersion spectrum of a solid [218]. There is a long history of attempts to study Grüneisen parameter [219] by the following relationship

$$\gamma = \frac{\frac{1}{2}K_T^{'} - \frac{1}{6} - \frac{f}{3}\left(1 - \frac{P}{3K_T}\right)}{1 - \frac{2}{3} f \frac{P}{K_T}} \tag{5.33}$$

where $P$, $K_T$ and $K_T^{'}$ are respectively the pressure, isothermal bulk modulus and the first order pressure derivative of isothermal bulk modulus, and $f$ is the parameter which takes different values of different derivations of $\gamma$, based on different approximations. Hence $f = 0$ for Slater's formula [134], $f = 1$ for Dugdale and Mac Donald formula [104], $f = 2$ for free volume formula [133], and $f = 2.35$ resulted in a molecular dynamical calculation by Barton and Stacey [137].

At $P = 0$, Eq. (5.33) becomes

$$\gamma_0 = \frac{1}{2}K_0^{'} - \frac{1}{6} - \frac{f}{3} \tag{5.34}$$

If the values of $\gamma_0$ and $K_0^{'}$ for given solids are known then the value of $f$ is adjusted [73]. Many expressions [198-205, 211, 220, 221] have been made for estimating the volume or pressure dependence of Grüneisen parameter.

According to Jeanloz [206] assumption the second order Gruneisen parameter $(q)$ varies with pressure or volume as

$$q = q_0 \left( \frac{V}{V_0} \right)^{\lambda} \tag{5.35}$$

where $q_0$ is the second Gruneisen parameter at zero pressure and $\lambda$ is a material dependent fitting parameter. $q$ is defined in Eq. (3.27).

One can get subsequent expression for volume dependence of the Grüneisen parameter as given below

$$\gamma = \gamma_0 \exp\left[ \left( \frac{q_0}{\lambda} \right) \left\{ \left( \frac{V}{V_0} \right)^{\lambda} - 1 \right\} \right] \tag{5.36}$$

where $\gamma_0$ is value of $\gamma$ at zero pressure. Similar expression is used by Hui and Bao [201] to study the volume dependence of Grüneisen parameter for Lithium, Sodium and Potassium at $298K$.

In the present study, a new simple and straightforward relationship for volume dependence of Grüneisen parameter is produced. This expression is applied on NaCl and $\varepsilon$-Fe for which experimental data are available.

Peng et al. [222] have shown that Eq. (5.36) gives better results than others [199, 202] and Srivastava and Sinha [220] also preferred this expression to give the modified form. At infinite pressure, Eq. (5.36) gives [73]

$$\gamma_{\infty} = \gamma_0 \exp\left( -\frac{q_0}{\lambda} \right) \tag{5.37}$$

and at infinite pressure Eq. (5.33) becomes

$$\gamma_{\infty} = \frac{1}{2} K_{\infty}^{'} - \frac{1}{6} \tag{5.38}$$

where $K_{\infty}^{'}$ is an important parameter i.e., first order pressure derivative of isothermal bulk modulus $\left(K_T\right)$ at infinite pressure limit. This parameter remains constant under the variation of temperature for a material of interest.

After rearranging Eq. (5.37) we get

$$\frac{q_0}{\lambda} = \ln\left( \frac{\gamma_0}{\gamma_{\infty}} \right) \tag{5.39}$$

Following Thomas-Fermi model i.e., $K_{\infty}^{'} = 5/3$ [223-226], we find the value of $\gamma_{\infty} = 2/3$ from Eq. (5.38) which is consistent with earlier workers [153, 227, 228].

Now using Eqs. (5.36, 5.38, 5.39) we get

$$\gamma = \gamma_0 \exp\left[ \ln(1.5\gamma_0)\left\{\left(\frac{V}{V_0}\right)^{\lambda} - 1\right\}\right] \tag{5.40}$$

The modified expression Eq. (5.40) is established for predicting the values of volume dependence of Grüneisen parameter along an isotherm at high compression. NaCl and $\varepsilon$-Fe under different compression or pressure ranges have been employed to test the suitability of the present expression (Eq. (5.40)). The values of fitted parameter $\lambda$ are found to be 1.413 and 0.81 for NaCl and $\varepsilon$-Fe respectively which are computed with the help of experimental values of volume dependence of Grüneisen parameter using relationship (Eq. (5.40)). And the values of $\gamma_0$ for NaCl and $\varepsilon$-Fe are 1.6275 [196] and 1.71 [214] respectively. The experimental values of $\gamma(V)$ for NaCl and $\varepsilon$-Fe are available in literature [165, 196]. The results obtained through Eq. (5.40) are given in Table 5.4 & 5.5 and plotted in Figs. 5.5 & 5.6, along with available experimental data [165, 196] for the sake of comparison. It is evident from figures that results obtained from Eq. (5.40) throughout the pressure ranges are more consistent with experimental data.

The fitted value of parameter $\lambda$ discloses a method to compute the value of $q_0$ with the help of Eq. (5.39); we get $q_0 = 1.26$ for in case of NaCl. Cui and Yu [205] and Xing et al. [229] estimated $q_0 = 1.5$ and 1.1 respectively. Many researchers [44, 211, 220] suggested a value of $q_0 = 1.2$ for NaCl. Our results for $q_0 = 1.26$ which is very near to other [44, 205, 211, 220, 229]. We get $q_0 = 0.76$ for $\varepsilon$-Fe. Our result for $q_0 = 0.76$ is consistent with experimental data. This value of $q_0$ for $\varepsilon$-Fe is near to those obtained by many researchers [203, 220, 230]. This analysis also validates our relationship (Eq. (5.40)).

In the present study, we have demonstrated the reliability of the proposed new empirical relationship to find out the values of volume dependence of Grüneisen parameter based on the assumption that $K_{\infty}^{'} = 5/3$ [223-226]. We have estimated $\gamma(V)$ through Eq. (5.40) of solids under study. It is found that the results obtained from Eq. (5.40) are consistent with experimental data

throughout the compression or pressure ranges for both solids under consideration. Consistency between calculated and experimental values exposes the accuracy of present formulation.

**Table 5.4** The values of volume dependence of Grüneisen parameter ($\gamma$) for NaCl calculated through (a) Eq. (5.40); and (b) experimental data [165].

| | | $\gamma$ | |
|---|---|---|---|
| $P$ (GPa) | $V/V_0$ (Ref. 165) | (a) | (b) |
| 0 | 1.0000 | 1.63 | 1.62 |
| 1 | 0.9627 | 1.55 | 1.55 |
| 2 | 0.9324 | 1.50 | 1.51 |
| 3 | 0.9067 | 1.45 | 1.46 |
| 4 | 0.8845 | 1.41 | 1.43 |
| 5 | 0.8649 | 1.38 | 1.40 |
| 10 | 0.7910 | 1.27 | 1.27 |
| 15 | 0.7397 | 1.19 | 1.19 |
| 20 | 0.7004 | 1.14 | 1.12 |
| 25 | 0.6685 | 1.10 | 1.07 |
| 30 | 0.6416 | 1.07 | 1.03 |

**Table 5.5** The values of volume dependence of Grüneisen parameter ($\gamma$) for $\varepsilon-$Fe calculated through (a) Eq. (5.40); and (b) experimental data [196].

| | | $\gamma$ | |
|---|---|---|---|
| $P$ (GPa) | $V/V_0$ (Ref. 196) | (a) | (b) |
| 0.00 | 1.000 | 1.71 | 1.71 |
| 29.96 | 0.877 | 1.56 | 1.59 |
| 35.56 | 0.862 | 1.54 | 1.57 |
| 41.75 | 0.847 | 1.52 | 1.55 |
| 48.62 | 0.832 | 1.50 | 1.53 |
| 56.22 | 0.817 | 1.48 | 1.51 |
| 64.64 | 0.802 | 1.47 | 1.49 |
| 73.99 | 0.788 | 1.45 | 1.47 |
| 84.38 | 0.773 | 1.43 | 1.45 |
| 95.92 | 0.758 | 1.42 | 1.43 |
| 108.76 | 0.743 | 1.40 | 1.41 |
| 123.05 | 0.728 | 1.38 | 1.39 |
| 139.00 | 0.713 | 1.36 | 1.37 |
| 156.80 | 0.698 | 1.35 | 1.35 |
| 176.71 | 0.684 | 1.33 | 1.32 |
| 198.99 | 0.669 | 1.32 | 1.30 |
| 223.98 | 0.654 | 1.30 | 1.28 |
| 252.06 | 0.639 | 1.28 | 1.25 |
| 283.65 | 0.624 | 1.27 | 1.23 |
| 319.26 | 0.609 | 1.25 | 1.20 |
| 359.50 | 0.594 | 1.24 | 1.18 |

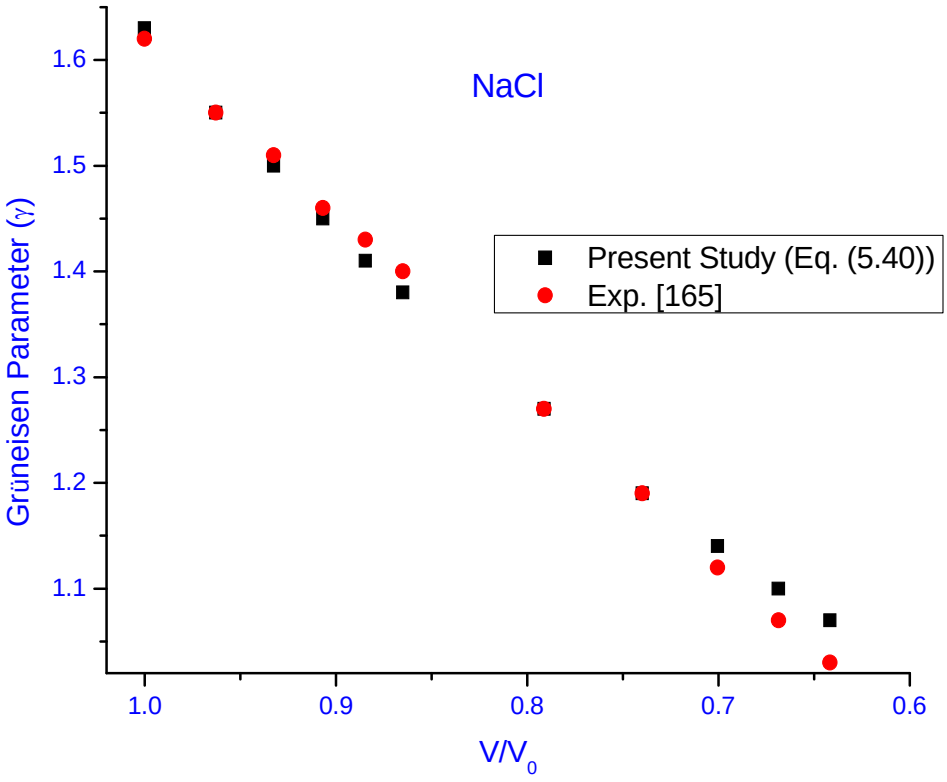


**Fig. 5.5** Volume dependence of Grüneisen parameter predicted through Eq. (5.40) alongwith experimental data for NaCl. It is evident from Fig. that results obtained from Eq. (5.40) are more consistent with experimental data throughout the pressure ranges.

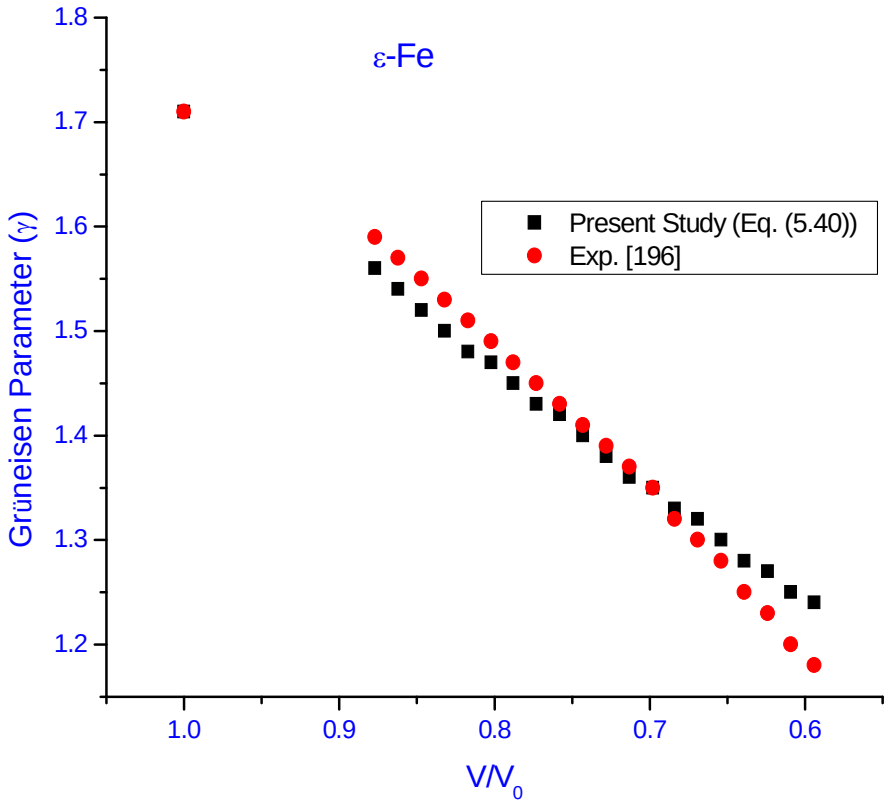


**Fig. 5.6** Volume dependence of Grüneisen parameter predicted through Eq. (5.40) alongwith experimental data for $\varepsilon$ – Fe. It is found that the results obtained from Eq. (5.40) are consistent with experimental data throughout the compression or pressure ranges.

### 5.2.3 Higher order Volume derivatives of Grüneisen parameter

For understanding the high pressure–high temperature behaviour of solids, it is necessary to have a reliable knowledge of pressure *P*-volume *V*-temperature *T* relationships [44]. For this purpose an equation of state (EoS) can be used with the help of different approaches. First, we can use an isothermal EoS to determine *P*-*V* relationships along different isotherms at selected temperatures using input parameters corresponding to each temperature [231, 232]. The other approach is based on the Mie–Grüneisen–Debye (MGD) model for evaluating the thermal effects in order to determine *P*-*V* relationships at high temperatures [147-152]. Thus, we need to have an accurate knowledge of the volume dependence of the Grüneisen parameter, $\gamma(V)$ [147].

We use the relationship for volume dependence of the Grüneisen parameter, $\gamma(V)$, given by Srivastava et al. [228] in reciprocal form and its higher order volume derivatives. The results have been obtained and reported for the volume dependences of γ and higher-order derivatives in the case of MgO and NaCl.

The Grüneisen parameter $\gamma$ is an important thermoelastic property related to other thermal and elastic properties as follows [44]

$$\gamma = \frac{\alpha K_T V}{C_V} = \frac{\alpha K_S V}{C_P} \tag{5.41}$$

where $\alpha$ is the thermal expansivity, $V$ the volume, $K_T$ ($K_S$) the isothermal (adiabatic) bulk modulus, and $C_V$ ($C_P$) the constant volume (pressure) specific heat. The second order ($q$) and third-order Grüneisen parameters ($\lambda$) are defined in Eq. (3.27) and Eq. (3.39) respectively.

The parameters $\gamma, q,$ and $\lambda$ appear frequently in the thermodynamic identities for higher order thermoelastic properties of solids [144-146], and their knowledge is not only desirable, but also necessary.

Srivastava et al. [228] have used the following relationship for volume dependence of the Grüneisen parameter

$$\frac{1}{\gamma} = \frac{1}{\gamma_\infty} + \left(\frac{1}{\gamma_0} - \frac{1}{\gamma_\infty}\right)\left(\frac{V}{V_0}\right)^m \tag{5.42}$$

where $\gamma_0$ and $\gamma_\infty$ are the values of $\gamma$ at $V = V_0$ and $V \to 0$, respectively and $m$ is a constant.

The corresponding value of second and third Grüneisen parameter are obtained with the help of eq. (5.42) as

$$q = q_0\left(\frac{\gamma_\infty}{\gamma_0-\gamma_\infty}\right)\left[\frac{\gamma_0}{\gamma_0-(\gamma_0-\gamma_\infty)\left(\frac{V}{V_0}\right)^m}-1\right] \tag{5.43}$$

$$\lambda = \frac{q_0\gamma_\infty}{(\gamma_0-\gamma_\infty)\left[1-\left(\frac{\gamma_0-\gamma_\infty}{\gamma_0}\right)\left(\frac{V}{V_0}\right)^m\right]} \tag{5.44}$$

where $m = \frac{q_0\gamma_\infty}{(\gamma_0-\gamma_\infty)} = \lambda_\infty$ (5.45)

Stacey and Davis [73] have written the following expression based on thermodynamical constraints in limit $P \to \infty$

$$\lambda = \lambda_\infty + (\lambda_0-\lambda_\infty)\frac{q}{q_0} \tag{5.46}$$

Integrating Eq. (5.46), we get

$$q = \frac{q_0}{1+(\lambda_0/\lambda_\infty)[\{(V_0/V)\}^{\lambda_\infty}-1]} \tag{5.47}$$

and

$$\gamma = \gamma_0\left[\frac{\lambda_0}{\lambda_\infty}-\left(\frac{\lambda_0}{\lambda_\infty}-1\right)\left(\frac{V}{V_0}\right)^{\lambda_\infty}\right]^{-q_0/\lambda_0-\lambda_\infty} \tag{5.48}$$

The values of input parameters are listed in Table 5.6. We analyse the volume dependence of Grüneisen ratio $\gamma$ and its higher order derivatives $q$ and $\lambda$ for *MgO* and *NaCl*. We use a reciprocal form of equation for Grüneisen ratio given by Srivastava et al. [228] and its higher order volume derivatives. The results of *MgO* and *NaCl* are shown in Table 5.7-5.9. For direct vision, the results are plotted in Figs. 5.7-5.9 and Figs. 5.10-5.12 for MgO and NaCl respectively. It has been observed that the trend of $\gamma$ and $q$ is found to be consistent with the Stacey and Davis relationship [73] but the trend of third Grüneisen ratio $\lambda$ has not been found satisfactory. Thus, one can rectify this equation for further study.

**Table 5.6** Input parameters [73, 156, 200, 202, 205, 222, 233] used in calculations

| Solids | $\gamma_0$ | $\gamma_\infty$ | $K_0^{'}$ | $K_\infty^{'}$ | $\lambda_0$ | $\lambda_\infty$ | $q_0$ |
|---|---|---|---|---|---|---|---|
| MgO | 1.52 | 1.08 | 4.15 | 2.49 | 8.84 | 1.49 | 1.41 |
| NaCl | 1.63 | 1.39 | 5.2 | 3.12 | 10.5 | 1.87 | 0.8 |

**Table 5.7** Volume dependence of Grüneisen parameter $\gamma$ for MgO and NaCl.

| $\left(\frac{V}{V_0}\right)$ | *MgO* $\gamma$ | | $\left(\frac{V}{V_0}\right)$ | *NaCl* $\gamma$ | |
|---|---|---|---|---|---|
| | From Eq. (5.42) | From Eq. (5.48) | | From Eq. (5.42) | From Eq. (5.48) |
| 1.00 | 1.52 | 1.52 | 1.000 | 1.63 | 1.63 |
| 0.95 | 1.48 | 1.43 | 0.963 | 1.61 | 1.59 |
| 0.90 | 1.44 | 1.37 | 0.932 | 1.60 | 1.56 |
| 0.85 | 1.40 | 1.32 | 0.907 | 1.58 | 1.55 |
| 0.80 | 1.36 | 1.29 | 0.885 | 1.57 | 1.53 |
| 0.75 | 1.33 | 1.25 | 0.865 | 1.57 | 1.52 |
| 0.70 | 1.30 | 1.23 | 0.791 | 1.54 | 1.49 |
| 0.65 | 1.27 | 1.21 | 0.740 | 1.52 | 1.47 |
| 0.60 | 1.25 | 1.19 | 0.700 | 1.50 | 1.46 |
| 0.55 | 1.23 | 1.17 | 0.669 | 1.49 | 1.45 |
| 0.50 | 1.20 | 1.16 | 0.642 | 1.49 | 1.44 |
| 0.45 | 1.18 | 1.14 | | | |
| 0.40 | 1.17 | 1.13 | | | |
| 0.35 | 1.15 | 1.12 | | | |
| 0.30 | 1.13 | 1.11 | | | |
| 0.25 | 1.12 | 1.10 | | | |
| 0.20 | 1.11 | 1.10 | | | |
| 0.15 | 1.10 | 1.09 | | | |
| 0.10 | 1.09 | 1.09 | | | |
| 0.05 | 1.08 | 1.08 | | | |
| 0.00 | 1.08 | 1.08 | | | |

**Table 5.8** Volume dependence of second order Grüneisen parameter $q$ for MgO and NaCl.

| $\left(\frac{V}{V_0}\right)$ | *MgO* $q$ | | $\left(\frac{V}{V_0}\right)$ | *NaCl* $q$ | |
|---|---|---|---|---|---|
| | From Eq. (5.43) | From Eq. (5.47) | | From Eq. (5.43) | From Eq. (5.47) |
| 1.00 | 1.41 | 1.41 | 1.000 | 0.800 | 0.800 |
| 0.95 | 1.27 | 0.96 | 0.963 | 0.736 | 0.566 |
| 0.90 | 1.14 | 0.70 | 0.932 | 0.687 | 0.448 |
| 0.85 | 1.02 | 0.54 | 0.907 | 0.647 | 0.376 |
| 0.80 | 0.91 | 0.42 | 0.885 | 0.614 | 0.327 |
| 0.75 | 0.80 | 0.34 | 0.865 | 0.586 | 0.291 |
| 0.70 | 0.71 | 0.27 | 0.791 | 0.486 | 0.196 |
| 0.65 | 0.62 | 0.22 | 0.740 | 0.424 | 0.152 |
| 0.60 | 0.54 | 0.18 | 0.700 | 0.379 | 0.127 |
| 0.55 | 0.47 | 0.15 | 0.669 | 0.345 | 0.109 |
| 0.50 | 0.40 | 0.12 | 0.642 | 0.318 | 0.097 |
| 0.45 | 0.33 | 0.10 | | | |
| 0.40 | 0.28 | 0.08 | | | |
| 0.35 | 0.22 | 0.06 | | | |
| 0.30 | 0.18 | 0.05 | | | |
| 0.25 | 0.13 | 0.03 | | | |
| 0.20 | 0.09 | 0.02 | | | |
| 0.15 | 0.06 | 0.01 | | | |
| 0.10 | 0.03 | 0.01 | | | |
| 0.05 | 0.01 | 0.00 | | | |
| 0.00 | 0.00 | | | | |

**Table 5.9** Volume dependence of third order Grüneisen parameter $\lambda$ for MgO and NaCl.

| $\left(\frac{V}{V_0}\right)$ | *MgO* $\lambda$ | | $\left(\frac{V}{V_0}\right)$ | *NaCl* $\lambda$ | |
|---|---|---|---|---|---|
| | From Eq. (5.44) | From Eq. (5.46) | | From Eq. (5.44) | From Eq. (5.46) |
| 1.00 | 4.87 | 8.84 | 1.000 | 5.43 | 10.50 |
| 0.95 | 4.73 | 6.49 | 0.963 | 5.37 | 7.97 |
| 0.90 | 4.60 | 5.15 | 0.932 | 5.32 | 6.70 |
| 0.85 | 4.48 | 4.29 | 0.907 | 5.28 | 5.92 |
| 0.80 | 4.37 | 3.69 | 0.885 | 5.25 | 5.39 |
| 0.75 | 4.27 | 3.25 | 0.865 | 5.22 | 5.01 |
| 0.70 | 4.17 | 2.91 | 0.791 | 5.12 | 3.98 |
| 0.65 | 4.08 | 2.65 | 0.740 | 5.06 | 3.51 |
| 0.60 | 4.00 | 2.44 | 0.700 | 5.01 | 3.24 |
| 0.55 | 3.93 | 2.26 | 0.669 | 4.98 | 3.05 |
| 0.50 | 3.86 | 2.12 | 0.642 | 4.95 | 2.91 |
| 0.45 | 3.80 | 1.99 | | | |
| 0.40 | 3.74 | 1.89 | | | |
| 0.35 | 3.68 | 1.80 | | | |
| 0.30 | 3.64 | 1.73 | | | |
| 0.25 | 3.59 | 1.67 | | | |
| 0.20 | 3.55 | 1.61 | | | |
| 0.15 | 3.52 | 1.57 | | | |
| 0.10 | 3.49 | 1.53 | | | |
| 0.05 | 3.47 | 1.50 | | | |
| 0.00 | 3.46 | | | | |

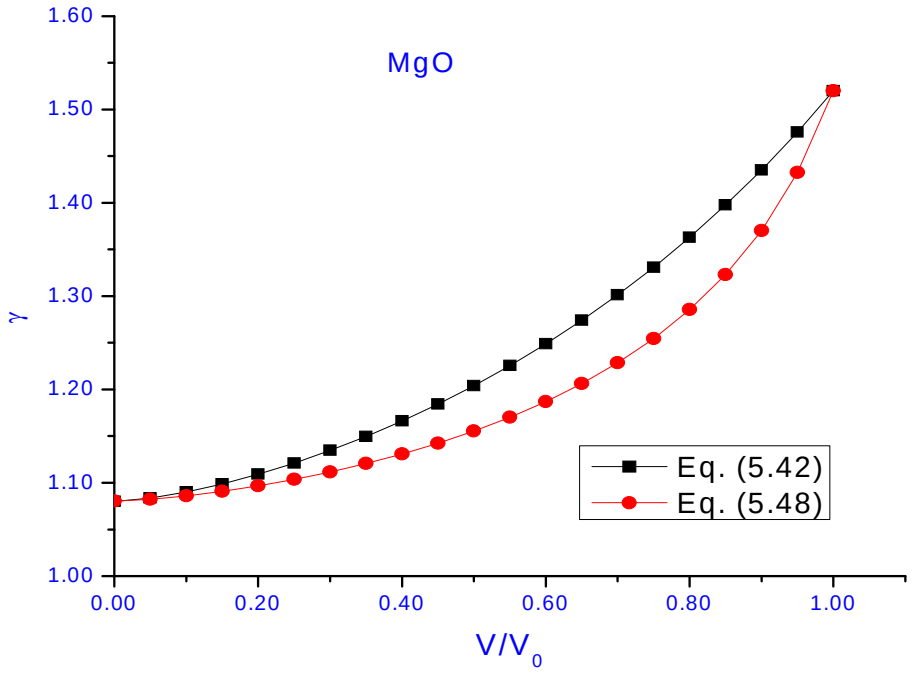


**Fig. 5.7** Volume dependence of Grüneisen parameter $\gamma$ for MgO. It has been observed that trend of $\gamma$ is found consistent with Stacey and Davis relationship (Eq. 5.48).

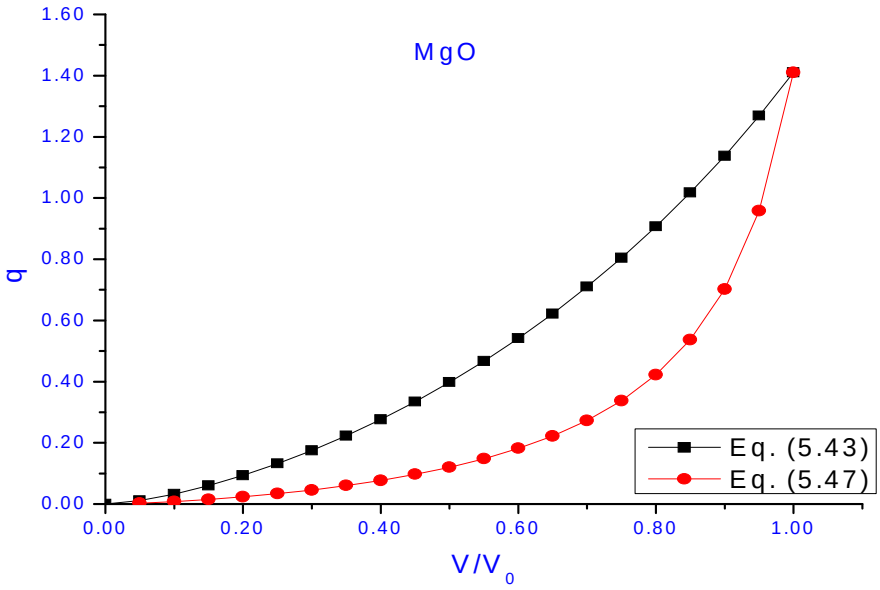


**Fig. 5.8** Volume dependence of second order Grüneisen parameter $q$ for MgO. Fig. shows that trend of $q$ is found consistent with Stacey and Davis formulation (Eq. 5.47).

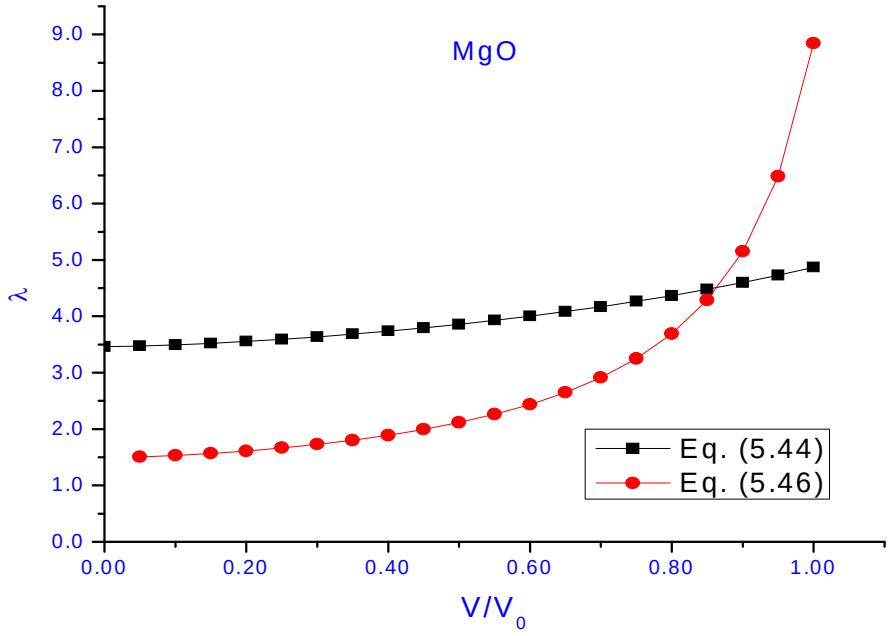


**Fig. 5.9** Volume dependence of third order Grüneisen parameter $\lambda$ for MgO. Fig. shows that trend of $\lambda$ has not found satisfactory.

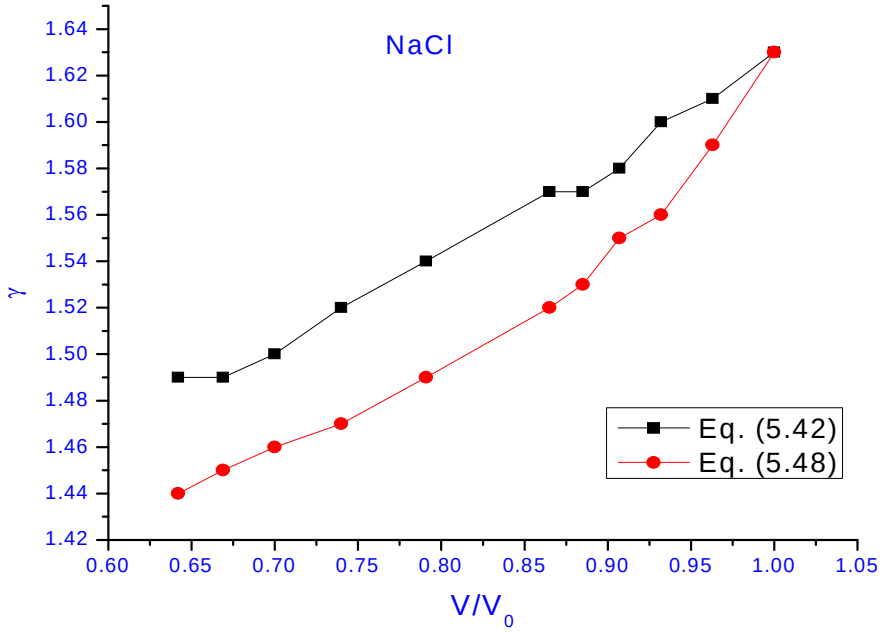


**Fig. 5.10** Volume dependence of Grüneisen parameter $\gamma$ for NaCl. Fig. shows that trend of $\gamma$ is found to be consistent with Stacey and Davis relationship (Eq. 5.48).

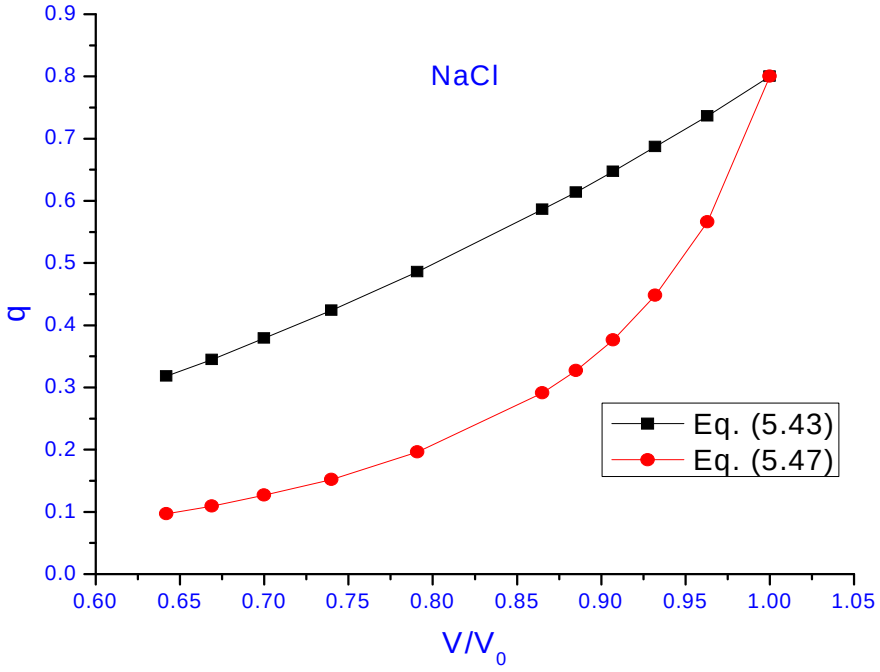


**Fig. 5.11** Volume dependence of second order Grüneisen parameter $q$ for NaCl. It has been observed that trend of $q$ is found to be consistent with Stacey and Davis formulation (Eq. 5.47).

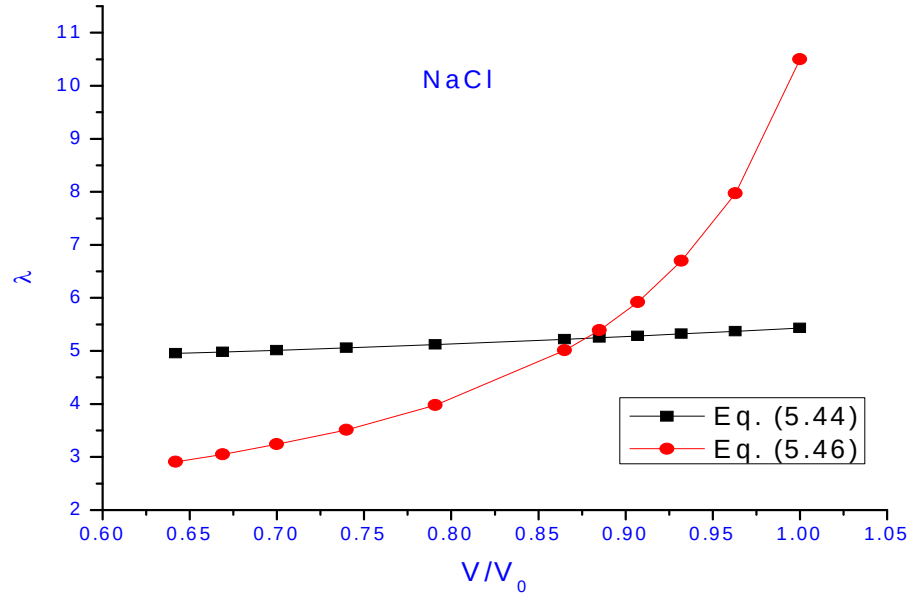


**Fig. 5.12** Volume dependence of third order Grüneisen parameter $\lambda$ for NaCl. From fig. it has been observed that trend of $\lambda$ has not found satisfactory.

## 5.3 ANALYSIS OF THERMODYNAMIC PROPERTIES IN THE LIMIT OF INFINITE PRESSURE

Grüneisen parameter is an important parameter to interpret any thermodynamic and thermoelastic quantity. Many researchers [73, 77, 79, 144, 154, 220, 226] gave the theory of infinite pressure behaviour of Grüneisen parameter and its higher order volume derivatives. Earliar workers [64-66, 73, 144, 195, 207, 213] proved that volume thermal expansivity $(\alpha)$ becomes zero at infinite pressure. And the product of volume thermal expansivity $(\alpha)$ and isothermal bulk modulus $(K_T)$ or adiabatic bulk modulus $(K_S)$ becomes infinite at infinite pressure [64-66, 73, 144, 195, 207, 213].

In the present study, we have made an attempt to analyse the thermodynamic properties in the limit of infinite pressure. Some new results have been disclosed based on the demonstration of product $\gamma\alpha T$ in the limit of infinite pressure.

The following thermodynamic identity is taken from [Eq. (A.1) of ref.73]

$$K_S = K_T(1+\gamma\alpha T) \tag{5.49}$$

where $K_S$ is adiabatic bulk modulus which is defined as

$$K_S = -V\left(\frac{\partial P}{\partial V}\right)_S \tag{5.50}$$

$K_T$ is isothermal bulk modulus which is defined as

$$K_T = -V\left(\frac{\partial P}{\partial V}\right)_T \tag{5.51}$$

$\gamma$ and $\alpha$ is the Grüneisen parameter and volume thermal expansivity which is defined in Eq. (5.16) and Eq. (5.1) respectively and $T$ is the temperature.

At infinite pressure i.e., $P \to \infty$ or $V \to 0$, Eq.(5.49) takes the form

$$(K_S)_\infty = (K_T)_\infty(1+\gamma\alpha T)_\infty \tag{5.52}$$

The following thermodynamic identity is taken from [Eq. (B3) of ref.144]

$$K_S' = K_T'(1+\gamma\alpha T) - \gamma\alpha T(\delta_S + \delta_T + q) \tag{5.53}$$

where $K_S'$ is the first order pressure derivative of adiabatic bulk modulus which is defined as

$$K_S' = \left(\frac{\partial K_S}{\partial P}\right)_S \tag{5.54}$$

$K_T^{'}$ is the first order pressure derivative of isothermal bulk modulus $(K_T)$ which is defined as

$$K_T^{'} = \left(\frac{\partial K_T}{\partial P}\right)_T \tag{5.55}$$

$\delta_T$ is the isothermal Anderson- Grüneisen parameter which is defined as

$$\delta_T = -\frac{1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_P \tag{5.56}$$

$\delta_S$ is the adiabatic Anderson- Grüneisen parameter which is defined as

$$\delta_S = -\frac{1}{\alpha K_S}\left(\frac{\partial K_S}{\partial T}\right)_P \tag{5.57}$$

$q$ is the second Grüneisen parameter which is defined in Eq. (3.27) and other parameters are having their usual meanings.

Rearranging the Eq. (5.53) we have

$$(\gamma\alpha T) = \frac{(K_S^{'} - K_T^{'})}{\left(K_T^{'} - (\delta_S + \delta_T + q)\right)} \tag{5.58}$$

The following thermodynamic identity are taken from [Eq. (B4) and (B5) of ref.144]

$$\delta_S = K_S^{'} - 1 + q - \gamma - C_S^{'} \tag{5.59}$$

and

$$\delta_T = K_T^{'} - 1 + q + C_T^{'} \tag{5.60}$$

Introducing Eqs. (5.59, 5.60) in Eq. (5.58) we get

$$(\gamma\alpha T) = \frac{(K_S^{'} - K_T^{'})}{\left(2 - K_S^{'} - 3q + \gamma + C_S^{'} - C_T^{'}\right)} \tag{5.61}$$

At $P \to \infty$ or $V \to 0$ Eq. (5.61) becomes

$$(\gamma\alpha T)_\infty = \frac{(K_{S\infty}^{'} - K_{\infty T}^{'})}{\left(2 - K_{S\infty}^{'} - 3q_\infty + \gamma_\infty + C_{S\infty}^{'} - C_{T\infty}^{'}\right)} \tag{5.62}$$

The following thermodynamic identity is taken from [Eq.(B2) of ref.144]

$$K_T^{'} = K_S^{'}(1 + \gamma\alpha T) + \gamma\alpha T\left[3q - 2 - \gamma + \gamma\left(\frac{\partial \ln C_V}{\partial \ln T}\right)_V\right] \tag{5.63}$$

where $C_V$ is the heat capacity at constant volume which is defined as

$$C_V = \frac{T}{m}\left(\frac{\partial S}{\partial T}\right)_V \tag{5.64}$$

where $m$ is the mass of material.

And the following thermodynamic identity is taken from [Eq. (B6) of ref.144]

$$C_S^{'} = C_T^{'} - \gamma\left(\frac{\partial \ln C_V}{\partial \ln T}\right)_V \tag{5.65}$$

And the following thermodynamic identity is taken from [Eq. (B8) of ref.144]

$$q_S = q - C_S^{'} \tag{5.66}$$

where $q_S$ is

$$q_S = \left(\frac{\partial \ln \gamma}{\partial \ln V}\right)_S \tag{5.67}$$

Inserting Eqs. (5.65, 5.66) in Eq. (5.63) we have

$$K_T^{'} = K_S^{'}(1+\gamma\alpha T) + \gamma\alpha T\left[2q - 2 - \gamma + C_T^{'} + q_S\right] \tag{5.68}$$

Rearranging the above equation, we get

$$\gamma\alpha T = \frac{\left(K_T^{'} - K_S^{'}\right)}{\left[K_S^{'} + 2q - 2 - \gamma + C_T^{'} + q_S\right]} \tag{5.69}$$

At $P \to \infty$ or $V \to 0$ above equation takes the form

$$(\gamma\alpha T)_\infty = \frac{\left(K_{T_\infty}^{'} - K_{S_\infty}^{'}\right)}{\left[K_{S_\infty}^{'} + 2q_\infty - 2 - \gamma_\infty + C_{T_\infty}^{'} + q_{S_\infty}\right]} \tag{5.70}$$

The following thermodynamic identity is taken from [Eq. (B5) of ref.144]

$$\delta_T = \left(\delta_S + C_T^{'}\right)(1+\gamma\alpha T) + \gamma + C_S^{'} + \gamma\alpha T(2q-1) \tag{5.71}$$

where all the parameters are having their usual meanings

Rearranging the above equation we have

$$\gamma\alpha T = \frac{\left[\delta_T - \left(\delta_S + C_T^{'} + \gamma + C_S^{'}\right)\right]}{\left(\delta_S + C_T^{'} + 2q - 1\right)} \tag{5.72}$$

Introducing Eqs. (5.59, 5.60) in Eq. (5.72) we get

$$\gamma\alpha T = \frac{\left(K_T^{'} - K_S^{'}\right)}{\left[K_S^{'} + 3q - 2 - \gamma - C_S^{'}\right]} \tag{5.73}$$

At $P \to \infty$ or $V \to 0$ above equation takes the form

$$(\gamma\alpha T)_{\infty} = \frac{\left(K'_{T\infty} - K'_{S\infty}\right)}{\left[K'_{S\infty} + 3q_{\infty} - 2 - \gamma_{\infty} - C'_{S\infty}\right]} \tag{5.74}$$

There are so many thermal and elastic parameters that are introduced in Eqs. (5.52, 5.62, 5.67, 5.70) at $P \to \infty$ or $V \to 0$. It has been found [73, 144] that $K_{S\infty} = K_{T\infty}$, $K'_{S\infty} = K'_{T\infty}$, $\gamma_{\infty} \to finite$, $q_{\infty} \to 0$, $q_{S\infty} \to 0$, $C'_{T\infty} \to 0$ and $\delta_{S\infty}$ remain finite [73, 144, 195, 213]. Now inserting these values in Eqs. (5.52, 5.62, 5.67, 5.70) in the following manner

Now Eq. (5.52) becomes

$$\left(\gamma\alpha T\right)_{\infty} = \frac{K_{T\infty}}{K_{T\infty}} - 1 \tag{5.75}$$

which gives $(\gamma\alpha T)_{\infty} = 0$

Now Eq. (5.62) becomes

$$\left(\gamma\alpha T\right)_{\infty} = \frac{(K'_{T\infty} - K'_{\infty T})}{\left(2 - K'_{S\infty} + \gamma_{\infty}\right)} = \frac{0}{finite} \tag{5.76}$$

which gives $(\gamma\alpha T)_{\infty} = 0$

Now Eq. (5.70) becomes

$$(\gamma\alpha T)_{\infty} = \frac{\left(K'_{T_{\infty}} - K'_{T_{\infty}}\right)}{\left[K'_{S_{\infty}} - 2 - \gamma_{\infty}\right]} = \frac{0}{finite} \tag{5.77}$$

which gives $(\gamma\alpha T)_{\infty} = 0$

Now Eq. (5.74) becomes

$$(\gamma\alpha T)_{\infty} = \frac{\left(K'_{T\infty} - K'_{T\infty}\right)}{\left[K'_{S\infty} - 2 - \gamma_{\infty}\right]} = \frac{0}{finite} \tag{5.78}$$

which gives $(\gamma\alpha T)_{\infty} = 0$

Hence Eqs. (5.75-5.78) lead to results where the product of $\gamma\alpha T$ becomes zero in the limit of infinite pressure since $\gamma_{\infty}$ remains positive finite [144] however, $\alpha_{\infty}$ becomes zero for both isothermal as well as adiabatic extrapolations. The decrease in $\alpha$ is more fast than the increase in $T$ which gives $\left(\alpha T\right)_{T_{\infty}} = 0$, even on an adiabat. Thus $(\gamma\alpha T)_{\infty} = 0$ [73, 144].

The following thermodynamic identity is taken from [Eq. (B13) of ref.144]

$$\left(\frac{d\ln(\gamma\alpha T)}{d\ln V}\right)_T = \delta_T + q \tag{5.79}$$

At $P \to \infty$ or $V \to 0$, Eq.(5.79) becomes

$$\left[\left(\frac{d\ln(\gamma\alpha T)}{d\ln V}\right)_T\right]_\infty = \delta_{T_\infty} + q_\infty \tag{5.80}$$

The values of $\delta_{T_\infty}$ has positive finite value while $q_\infty$ becomes zero [73, 144]. Thus we get the right hand side of Eq. (5.80) is positive finite. i.e.,

$$\left[\left(\frac{d\ln(\gamma\alpha T)}{d\ln V}\right)_T\right]_\infty = \text{Positive finite} \tag{5.81}$$

The following thermodynamic identity is taken from [Eq. (B14) of ref.144]

$$\left(\frac{d\ln(\gamma\alpha T)}{d\ln V}\right)_S = (1+\gamma\alpha T)(\delta_S + q) \tag{5.82}$$

At $P \to \infty$ or $V \to 0$, Eq.(5.82) becomes

$$\left[\left(\frac{d\ln(\gamma\alpha T)}{d\ln V}\right)_S\right]_\infty = (1+\gamma\alpha T)_\infty\left(\delta_{S_\infty} + q_\infty\right) \tag{5.83}$$

The values of $\delta_{S_\infty}$ has positive finite value while $q_\infty$ becomes zero $(\gamma\alpha T)_\infty = 0$ [73, 144]. Thus we get the right hand side of Eq. (5.80) is positive finite. i.e.,

$$\left[\left(\frac{d\ln(\gamma\alpha T)}{d\ln V}\right)_S\right]_\infty = \text{Positive finite} \tag{5.84}$$

Three possibilities for thermoelastic properties, to become zero, remain finite or become infinitely large can be understood on the basis of the calculus [77, 234]. If y is a function of x such that y becomes zero in the limit x tends zero [81], then:

$$\left(\frac{d\ln y}{d\ln x}\right)_{x\to 0} = \text{Positive finite} \tag{5.85}$$

If the logarithmic volume derivatives of $(\gamma\alpha T)$ is positive finite which is proved from Eqs. (5.81, 5.84) henceforth $(\gamma\alpha T)_\infty$ must be zero which satisfies the calculus condition given in Eq. (5.85).

Shanker et al. [81] have concluded that

$$\left(\alpha K_T V\right)_{T_\infty} = 0 \tag{5.86}$$

$$\left(\alpha K_T V\right)_{S_\infty} = \text{+ve finite} \tag{5.87}$$

$$\left(\alpha K_S V\right)_{T_\infty} = 0 \tag{5.88}$$

$$\left(\alpha K_S V\right)_{S_\infty} = \text{+ve finite} \tag{5.89}$$

As Knopoff [224] pointed out that $P$ is the function of $x$, where $x = V_0/V$, is represented as an arbitrary power series in $x$, with the highest exponent being $K'_\infty$. As $P \to \infty$ this term becomes dominant and $P$ can be expressed as

$$P \propto V^{-K'_\infty} \tag{5.90}$$

Using Eqs. (5.51) and (5.90) we get the following relationship

$$K_T \propto V^{-K'_\infty} \tag{5.91}$$

or

$$K_T V = C(V^{-K'_\infty + 1}) \tag{5.92}$$

where C is a constant quantity.

Using Eqs. (5.86-5.89) and Eq. (5.92) we get

$$\left(\alpha\right)_{T_\infty} = \frac{0}{C\left(V^{-K'_\infty + 1}\right)} \tag{5.93}$$

or

$$\left(\alpha\right)_{T_\infty} = 0 \times V^{K'_\infty - 1} \tag{5.94}$$

Since $K'_\infty \rangle 1$ [73], which gives $\left(\alpha\right)_{T_\infty} = 0$ , in similar way one can get $\left(\alpha\right)_{S_\infty} = 0$.

$\gamma_\infty$ remains positive finite [144] however, $\alpha_\infty$ becomes zero for both isothermal as well as adiabatic extrapolations. The decrease in $\alpha$ is more fast than the increase in $T$ which gives $\left(\alpha T\right)_{T_\infty} = 0$, even on an adiabat. Thus $(\gamma \alpha T)_\infty = 0$ [73, 144].

Now the heat capacity required for thermodynamic calculations in the $P-T$ region, is the isobaric heat capacity ($C_P$), which is always greater than isochoric heat capacity ($C_V$) by the following fundamental thermodynamic identity [Eq. (B1) of ref.144]

$$C_P = C_V(1+\gamma\alpha T) \tag{5.95}$$

It is known that the difference between $C_P$ and $C_V$ becomes negligible at low temperatures. Both the Grüneisen parameter $(\gamma)$ [73, 199-203, 211, 221] and volume thermal expansivity $(\alpha)$ [26, 73, 196, 197, 207, 212] decrease as the compression or pressure increase.

At $P \to \infty$ or $V \to 0$, Eq.(5.95) becomes

$$(C_P)_\infty = (C_V)_\infty (1+\gamma\alpha T)_\infty \tag{5.96}$$

which gives

$$(C_P)_\infty = (C_V)_\infty$$

It means that the isobaric heat capacity converges to the isochoric heat capacity i.e., the ratio $C_P/C_V$ remains unity in the limit of infinite pressure.

Now let us turn our attention to the relations between the adiabatic-isothermal derivatives of $K_S$ and $K_T$.

The following thermodynamic identity is taken from [Eq.(A.10) of ref.73]

$$\left(\frac{\partial K_S}{\partial P}\right)_T = \left(\frac{\partial K_S}{\partial P}\right)_S + \delta_S \gamma\alpha T \tag{5.97}$$

At $P \to \infty$ or $V \to 0$, Eq. (5.97) becomes

$$\left(\frac{\partial K_S}{\partial P}\right)_{T\infty} = \left(\frac{\partial K_S}{\partial P}\right)_{S\infty} + \delta_{S\infty}(\gamma\alpha T)_\infty \tag{5.98}$$

which gives

$$\left(\frac{\partial K_S}{\partial P}\right)_{T\infty} = \left(\frac{\partial K_S}{\partial P}\right)_{S\infty} \tag{5.99}$$

It reveals that in the infinite pressure extrapolation isothermal and adiabatic properties become indistinguishable [235].

From the definition of Grüneisen parameter $\gamma$ [236] given in Eq. (5.41), it has been found [64, 195] that the products $\alpha K_T$ and $\alpha K_S$ become infinite in the limit of extreme compression ($V \to 0$). This is also revealed from Eq. (5.41) since $\gamma$ and $C_P(C_V)$ remain finite in the limit of infinite pressure. The rate of change of $\alpha$ with volume $(\partial\alpha/\partial V)$ is faster than the rate of change of $K_T$ with volume $(\partial K_T/\partial V)$ at low pressures [26, 44, 183]. As Pressure

increases the quantity $(\partial\alpha/\partial V)$ decreases, while the quantity $(\partial K_T/\partial V)$ increases. At a particular pressure both quantities become equal and result in the minima of the product $\alpha K_T$. After a point where $(\partial\alpha/\partial V)$ = $(\partial K_T/\partial V)$ [44, 78, 237, 238], the rate of increase in $K_T$ becomes faster than the rate of decrease in $\alpha$ with respect to pressure or compression. It means that at higher pressure $K_T$ dominates over $\alpha$ [64].

Sharma and Sharma [207] found that

$$\left(\frac{\partial K_T}{\partial T}\right)_P = -\infty \tag{5.100}$$

and

$$\left(\frac{\partial K_S}{\partial T}\right)_P = -\infty \tag{5.101}$$

Using Eqs. (5.56, 5.57, 5.100, 5.101) and $\alpha K_T \to \infty$ and $\alpha K_S \to \infty$ at $P \to \infty$ or $V \to 0$, we get

$$\frac{\delta_T}{\delta_S} = \textit{finite} \tag{5.102}$$

It is apparent from Eq. (5.102) that the isothermal and adiabatic Anderson- Grüneisen parameters become identical.

The following thermodynamic identity is taken from [Eq. (A.11) of ref.73]

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \left(\frac{\partial \mu}{\partial P}\right)_S + \gamma\alpha T\varepsilon\frac{\mu}{K_S} \tag{5.103}$$

where $\mu$ is the rigidity modulus and $\varepsilon$ is

$$\varepsilon = -\frac{1}{\alpha\mu}\left(\frac{\partial \mu}{\partial T}\right)_P \tag{5.104}$$

At $P \to \infty$ or $V \to 0$, Eq.(5.103) becomes

$$\left(\frac{\partial \mu}{\partial P}\right)_{T\infty} = \left(\frac{\partial \mu}{\partial P}\right)_{S\infty} + (\gamma\alpha T)_\infty \varepsilon_\infty \left(\frac{\mu}{K_S}\right)_\infty \tag{5.105}$$

which gives

$$\left(\frac{\partial \mu}{\partial P}\right)_{T\infty} = \left(\frac{\partial \mu}{\partial P}\right)_{S\infty}$$

Above result is only possible when $(\mu/K_S)_\infty \rightarrow finite$ [73, 144] and $\varepsilon_\infty \rightarrow finite$. Anderson-Grüneisen parameters become finite in the limit of infinite pressure. It means that $\mu$ remains same under isothermal and adiabatic conditions at $P \rightarrow \infty$ or $V \rightarrow 0$.

We have analysed the thermodynamic properties in the limit of infinite pressure. A number of thermodynamic properties in the infinite pressure limits have been used to establish that the isothermal and adiabatic properties become identical. The results obtained in the present study are consistent with the recent analysis of infinite pressure of thermoelastic properties recently presented by Shanker et al. [81]. Isobaric heat capacity $(C_P)$ and isochoric heat capacity $(C_V)$ remains same at $P \rightarrow \infty$ or $V \rightarrow 0$. $(\partial K_S/\partial P)_T$ becomes $(\partial K_S/\partial P)_S$ at infinite pressure. $\mu$ remains same under both conditions i.e., isotherm and adiabatic conditions in the limit of infinite pressure. It has also been found that $(\partial\mu/\partial P)_T$ equals to $(\partial\mu/\partial P)_S$. The ratio $\delta_T/\delta_S$ remains finite in the limit of infinite pressure. The results obtained in the present study are based on the Stacey thermodynamics of solids at infinite pressure.

**Table 5.10** Thermodynamic identities used in the present study

| **Thermodynamic identity ( Eq. no. in the present study)** | **References with original Eq. no.** | **Thermodynamic identity in the infinite pressure limit (Eq. No. in the present study)** | **Thermodynamic notation in the limit of infinite pressure** |
|---|---|---|---|
| $K_S = K_T(1+\gamma\alpha T)$ (Eq.(5.49)) | [Eq.(A.1) of ref.73] | $(K_S)_\infty = (K_T)_\infty(1+\gamma\alpha T)_\infty$ (Eq.(5.52)) | $K'_{S\infty} = K'_{T\infty}$ [73,144], $\gamma_\infty \to$ *finite* [73,144] $q_\infty \to 0$ [73,144] $q_{S\infty} \to 0$ [73,144] , $C'_{T\infty} \to 0$ [73,144] $\delta_{S\infty}$ remain finite. [73,144,195,213,226]. and $(\gamma\alpha T)_\infty = 0$ [73,144] $(\mu/K_S)_\infty \to$ *finite* [73,144] and $\varepsilon_\infty \to$ *finite* . |
| $K'_S = K'_T(1+\gamma\alpha T) - \gamma\alpha T(\delta_S + \delta_T + q)$ (Eq.(5.53)) | [Eq.(B3) of ref.144] | $(\gamma\alpha T)_\infty = \dfrac{(K'_{S\infty} - K'_{\infty T})}{(2 - K'_{S\infty} - 3q_\infty + \gamma_\infty + C'_{S\infty} + C'_{T\infty})}$ (Eq.(5.62)) | |
| $K'_T = K'_S(1+\gamma\alpha T) + \gamma\alpha T\left[3q - 2 - \gamma + \gamma\left(\dfrac{\partial \ln C_V}{\partial \ln T}\right)_V\right]$ (Eq.(5.63)) | [Eq.(B2) of ref.144] | $(\gamma\alpha T)_\infty = \dfrac{\left(K'_{T_\infty} - K'_{S_\infty}\right)}{\left[K'_{S_\infty} + 2q_\infty - 2 - \gamma_\infty + C'_{T_\infty} + q_{S_\infty}\right]}$ (Eq.(5.70)) | |
| $\delta_T = (\delta_S + C'_T)(1+\gamma\alpha T) + \gamma + C'_S + \gamma\alpha T(2q-1)$ (Eq.(5.71)) | [Eq.(B5) of ref.144] | $(\gamma\alpha T)_\infty = \dfrac{\left(K'_{S\infty} - K'_{T\infty}\right)}{\left[K'_{S\infty} + 3q_\infty - 2 - \gamma_\infty - C'_{S\infty}\right]}$ (Eq.(5.74)) | |
| $C_P = C_V(1+\gamma\alpha T)$ (Eq.(5.95)) | [Eq.(B1) of ref.144] | $(C_P)_\infty = (C_V)_\infty(1+\gamma\alpha T)_\infty$ (Eq.(5.96)) | |
| $\left(\dfrac{\partial K_S}{\partial P}\right)_T = \left(\dfrac{\partial K_S}{\partial P}\right)_S + \delta_S\gamma\alpha T$ (Eq.(5.97)) | [Eq.(A.10) of ref.73] | $\left(\dfrac{\partial K_S}{\partial P}\right)_{T\infty} = \left(\dfrac{\partial K_S}{\partial P}\right)_{S\infty} + \delta_{S\infty}(\gamma\alpha T)_\infty$ (Eq.(5.98)) | |
| $\left(\dfrac{\partial \mu}{\partial P}\right)_T = \left(\dfrac{\partial \mu}{\partial P}\right)_S + \gamma\alpha T\varepsilon\dfrac{\mu}{K_S}$ (Eq.(5.103)) | [Eq.(A.11) of ref.73] | $\left(\dfrac{\partial \mu}{\partial P}\right)_{T\infty} = \left(\dfrac{\partial \mu}{\partial P}\right)_{S\infty} + (\gamma\alpha T)_\infty\varepsilon_\infty\left(\dfrac{\mu}{K_S}\right)_\infty$ (Eq.(5.105)) | |

## 5.4 VOLUME DEPENDENCE OF THERMAL EXPANSIVITY

Volume thermal expansivity ($\alpha$) is very important thermodynamic parameter for modeling the equation of state of the Earth's interior at high temperatures and high pressures. It is a necessary parameter for solving many materials science problems and is useful for understanding the nature of stress in materials. Volume thermal expansivity has been related to other thermodynamic parameters through Grüneisen rules. It is an important factor in the equations interpreting many important properties of solids i.e., thermodynamic and thermoelastic behaviours of solids, because it has been emphasized [239] that most of the serious errors in the calculations of thermodynamic functions arise due to uncertainty of volume thermal expansivity, so various attempts [30, 47, 57, 193-195, 213, 240] have been made to find the high temperatures and pressures data of volume thermal expansivity for solids.

The isothermal Anderson- Grüneisen parameter $\delta_T$ is defined as [44]

$$\delta_T = -\frac{1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_P \tag{5.106}$$

where $\alpha$ is volume thermal expansivity which is defined in Eq. (5.1) and $K_T$ is isothermal bulk modulus which is given by

$$K_T = -V\left(\frac{\partial P}{\partial V}\right)_T \tag{5.107}$$

In addition, for describing the temperature dependence of the isothermal bulk modulus, ($\delta_T$) has been used for the discussion of pressure dependence of volume thermal expansivity. We can understand the pressure dependence of $\alpha$ through Maxwell's relation as

$$\left(\frac{\partial \alpha}{\partial P}\right)_T = \frac{1}{K_T^2}\left(\frac{\partial K_T}{\partial T}\right)_P \tag{5.108}$$

Using this thermodynamic identity Eq. (5.108) in Eq. (5.106), we get

$$\delta_T = \frac{V}{\alpha}\left(\frac{\partial \alpha}{\partial V}\right)_T \tag{5.109}$$

We choose NaCl which is one of the most studied inorganic crystal and a typical ionic solid for study because of the necessity to understand its high temperatures and high pressures properties. This solid has been used as a pressure gauge in laboratory measurements of compression data by many researchers [241, 242]. NaCl has a stable B1 (rocksalt) structure up to a pressure of about

30 GPa, and its melting temperature is nearly 1074 K. This may explain the stability of rocksalt NaCl under normal temperature and pressure. Besides, NaCl exhibit phase transition under high pressure because B1 phase becomes less stable with decreased cell volume. Thus we have a wide range of pressures and temperatures for studying the equation of state and thermoelastic properties of NaCl.

In the present study, we have made an attempt to derive a new relationship for volume dependence of volume thermal expansivity on the basis of the volume dependence of the isothermal Anderson-Grüneisen parameter in reciprocal form. NaCl is used to check the validity of the formulated relationship.

Al'tshuler et al. [70] have given the following expression for Grüneisen parameter

$$\gamma = \gamma_\infty + (\gamma_0 - \gamma_\infty)\left(\frac{V}{V_0}\right)^\beta \tag{5.110}$$

where $\gamma_0$ and $\gamma_\infty$ are Grüneisen parameter at $P = 0$ or $V \to V_0$ and $P \to \infty$ or $V \to 0$ respectively and $\beta$ is an adjustable parameter.

Many researchers [47, 195] pointed out the similarity for the volume dependence of $\gamma$ and $\delta_T$.

$$\delta_T = \delta_T^\infty + (\delta_T^0 - \delta_T^\infty)\left(\frac{V}{V_0}\right)^n \tag{5.111}$$

where $\delta_T^0$ and $\delta_T^\infty$ are respectively the values of $\delta_T$ at $P = 0$ or $V \to V_0$ and $P \to \infty$ or $V \to 0$ and $n$ is an adjustable parameter.

Thus we can write a simple choice of isothermal Anderson-Grüneisen parameter ($\delta_T$) in reciprocal form as

$$\frac{1}{\delta_T} = \frac{1}{\delta_T^\infty} + \left(\frac{1}{\delta_T^0} - \frac{1}{\delta_T^\infty}\right)\left(\frac{V}{V_0}\right)^m \tag{5.112}$$

where $m$ is a dimensionless fitting parameter.

Using Eq. (5.112) with Eq. (5.109) one can get the following eqn.

$$\frac{\alpha}{\alpha_0} = \left(\frac{V}{V_0}\right)^{\delta_T^\infty}\left(\frac{\delta_T}{\delta_T^0}\right)^{\delta_T^\infty / m} \tag{5.113}$$

Chopelas-Boehler [193], Anderson-Isaak [57] and Srivastava et al. [243] have used the following expressions to evaluate the volume dependence of volume thermal expansivity respectively.

$$\frac{\alpha}{\alpha_0} = \left(\frac{V}{V_0}\right)^{-1} \exp\left[-\left(\delta_T^0 + 1\right)\left(1 - \frac{V}{V_0}\right)\right] \tag{5.114}$$

where $\alpha_0$ is the volume thermal expansivity at $P = 0$.

$$\frac{\alpha}{\alpha_0} = \exp\left\{-\frac{\delta_T^0}{k}\left[1 - \left(\frac{V}{V_0}\right)^k\right]\right\} \tag{5.115}$$

$$\frac{\alpha}{\alpha_0} = \frac{1}{\left[1 + \frac{\delta_T^0}{\delta_T^\infty}\left\{\left(\frac{V}{V_0}\right)^{-\delta_T^\infty} - 1\right\}\right]} \tag{5.116}$$

The value of $\delta_T^\infty$ is calculated by using the well known thermodynamic identity [144]

$$\delta_T = K_T^{'} + q - 1 + C_T^{'} \tag{5.117}$$

where $K_T^{'}$ is the first-order pressure derivative of isothermal bulk modulus ( $K_T$ ) which is defined as

$$K_T^{'} = \left(\frac{\partial K_T}{\partial P}\right)_T \tag{5.118}$$

The last term in Eq. (5.117) is

$$C_T^{'} = \left(\frac{\partial \ln C_V}{\partial \ln V}\right)_T \tag{5.119}$$

$q$, the second Grüneisen parameter as explained in Eq. (3.27) and $C_V$ is the specific heat at constant volume as follows

$$C_V = \left(\frac{dU}{dT}\right)_V \tag{5.120}$$

At infinite pressure ( $P \to \infty$ ) or $V \to 0$, Eq. (5.117) becomes

$$\delta_T^\infty = K_T^{\infty'} + q_\infty - 1 + C_T^{\infty'} \tag{5.121}$$

Since at $P \to \infty$ or $V \to 0, q \to 0$ [73]. In high temperature and high pressure region,

$C_T^{\infty'} \to 0$ at $P \to \infty$ or $V \to 0$ [56], Now Eq. (5.121) becomes

$$\delta_T^{\infty} = K_T^{\infty'} - 1 \tag{5.122}$$

To discuss $\delta_T^{\infty}$, we must keep in our mind the following thermodynamic identities [144]

$$\left[\frac{\partial \ln(\alpha K_T)}{\partial \ln V}\right]_T = \delta_T - K_T' \tag{5.123}$$

and

$$\left[\frac{\partial \ln(\alpha K_T)}{\partial \ln V}\right]_S = q - 1 \tag{5.124}$$

Eq. (5.123) has been used by many researchers [36, 64, 183, 207, 211-213] to discuss the nature of variation in product $\alpha K_T$ with volume. From Eq. (5.123), $\alpha K_T \to \infty$ only when $\delta_T - K_T'$ is negative at $P \to \infty$ which gives that $\delta_T^{\infty}$ must be less than $K_{\infty}'$. Thus the value of $\delta_T^{\infty}$ should be constrained by the relationship [213]

$$0 < \delta_T^{\infty} < K_{\infty}' \tag{5.125}$$

Following Stacey-Davis model [73] i.e. $K_{\infty}' = \frac{3}{5}K_0'$ where $K_0'$ is the value of isothermal bulk modulus at $P = 0$ and room temperature i.e. $T_0 = 300K$. The values of $\delta_T^{\infty}$ obtained from Eq. (5.122) for solid under consideration and the calculated values satisfy the constrained Eq. (5.125).

We have estimated the values of volume thermal expansivity through Eq. (5.113) using input parameter cited in Table 5.11 and calculated results are shown in Table 5.12 and these values are plotted in Fig. 5.13 along with experimental data [165]. It is clear that the values of $\alpha$ through Eq. (5.113) are much better than those values extracted through Eqs. (5.114-5.116). It is emphasized here that the better competency of proposed relationship as evident from Fig. 5.13 that reveals the support of the present model and also satisfy the thermodynamic constraints i.e. $\alpha \to 0$ at $P \to \infty$ or $V \to 0$ [73, 235].

A reciprocal form for the volume dependence of volume thermal expansivity has been proposed. We have estimated the values of $\alpha$ through Eq. (5.113) and it is found that the results obtained through Eq. (5.113) shows the consistency with those values given by Birch [165] for NaCl. Volume thermal expansivity decreases as volume decrease i.e. $\alpha \to 0$ at $P \to \infty$ or $V \to 0$ [73, 144, 195, 207, 213]. Thus, Eq. (5.112) satisfies the thermodynamic constraint i.e.

$\delta_T \to \delta_T^{\infty}$ [73, 195]. This is the basic thermodynamic background on which Eq. (5.113) has been formulated. At last, we can say that one can use the reciprocal form of Anderson- Grüneisen parameter; the most remarkable is the Stacey reciprocal K-primed Equations of State (EoS) [235].

**Table 5.11** Input parameters used in calculations

| Solid | $K_0^{'}$ | $\delta_{T0}$ | $\delta_{T\infty}$ | $m$ | $\alpha_0$ ($10^{-5}K^{-1}$) |
|---|---|---|---|---|---|
| NaCl | 5.5 [165] | 5.3 [165] | 2.3 | 1.856 | 11.9 [165] |

**Table 5.12** The values of volume dependence of thermal expansivity ( $\alpha$ ) ($10^{-5}K^{-1}$) for NaCl calculated through (a) This study Eq. (5.113); (b) Eq. (5.116); (c) Eq. (5.114); (d) Eq. (5.115); and (e) experimental data [165].

| | | $\alpha$ | | | | |
|---|---|---|---|---|---|---|
| $P$ (GPa) | $V/V_0$ (Ref. 165) | (a) | (b) | (c) | (d) | (e) |
| 0 | 1.0000 | 11.9 | 11.9 | 11.9 | 11.9 | 11.9 |
| 1 | 0.9627 | 9.8 | 9.8 | 9.8 | 9.8 | 9.8 |
| 2 | 0.9324 | 8.4 | 8.5 | 8.3 | 8.4 | 8.5 |
| 3 | 0.9067 | 7.4 | 7.5 | 7.3 | 7.3 | 7.5 |
| 4 | 0.8845 | 6.7 | 6.8 | 6.5 | 6.5 | 6.7 |
| 5 | 0.8649 | 6.1 | 6.2 | 5.9 | 5.9 | 6.1 |
| 10 | 0.7910 | 4.3 | 4.5 | 4.0 | 4.1 | 4.3 |
| 15 | 0.7397 | 3.4 | 3.6 | 3.1 | 3.2 | 3.4 |
| 20 | 0.7004 | 2.9 | 3.0 | 2.6 | 2.7 | 2.9 |
| 25 | 0.6685 | 2.5 | 2.6 | 2.2 | 2.3 | 2.5 |
| 30 | 0.6416 | 2.2 | 2.3 | 1.9 | 2.1 | 2.2 |

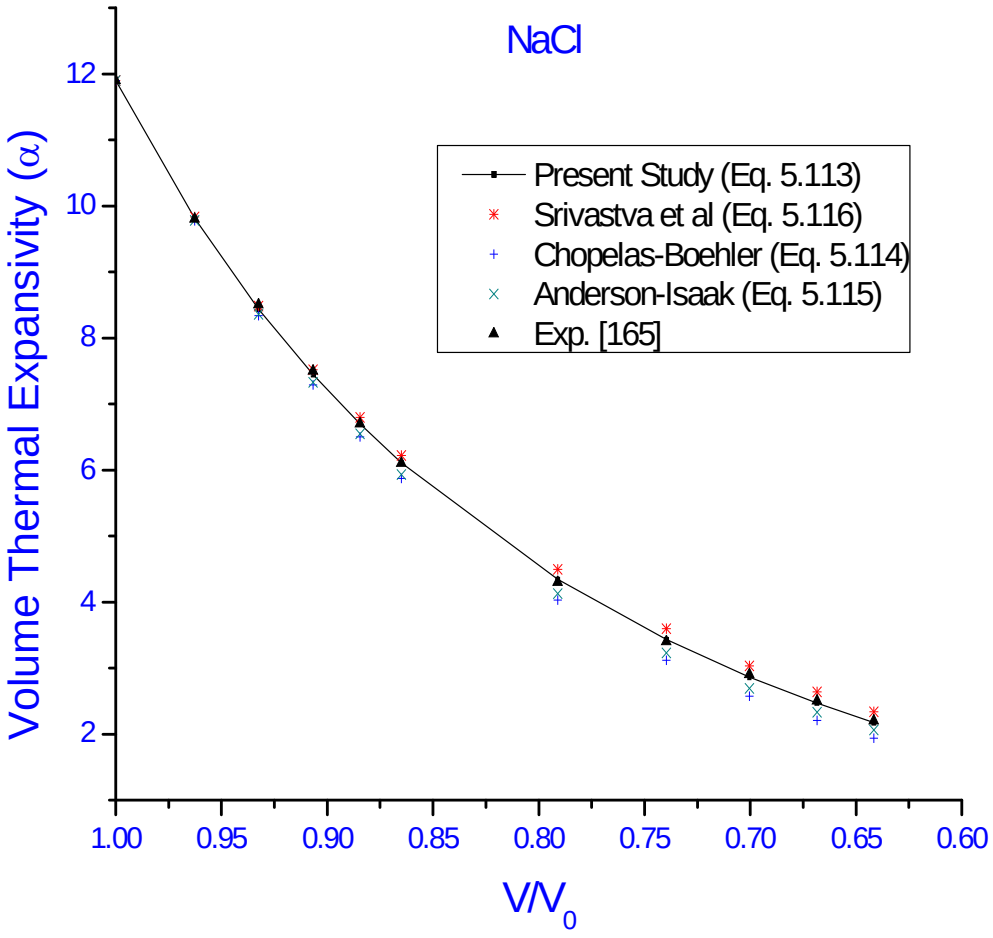


**Fig. 5.13** Comparison of volume dependence of volume thermal expansivity ($10^{-5}K^{-1}$) of solid NaCl calculated with various equations along with available data [165]. The caluculated values with the help of Eq. (5.113) are represented by line. Volume thermal expansivity decreases as volume decrease i.e. $\alpha \to 0$ at $P \to \infty$ or $V \to 0$. The values of $\alpha$ through Eq. (5.113) are much better than those values extracted through Eqs. (5.114-5.116). It emphasized the better competency of proposed relationship and also satisfy the thermodynamic constraints i.e. $\alpha \to 0$ at $P \to \infty$ or $V \to 0$ [73, 235].

## 5.5 VOLUME DEPENDENCE OF ISOTHERMAL BULK MODULUS AND ITS HIGHER PRESSURE DERIVATIVES

The equation of state (EoS) is having very important role for studying thermal and elastic properties of any solids under high temperatures and high pressures [44, 73]. Equation of state provides pressure-volume-temperature relationship for solids. The first pressure derivative of bulk modulus [isothermal bulk modulus ($K_T$), adiabatic bulk modulus ($K_S$)], is an important parameter for developing various equations of state. This concept was used by different researchers [74, 189, 235]. Stacey and Davis [73] have found that the seismic data based on geophysical model such as the Preliminary Reference Earth Model (PREM) [244] are more accurate than the laboratory data [245] because laboratory data involve uncertainty due the pressure calibration. The $K$-prime EoS is very convenient to investigate higher pressure derivatives of bulk modulus along with other elastic properties up to extreme compression [154]. It is found that lower mantle region lies nearly between 23 GPa to 136 GPa. However, the core region from 136 to 360 GPa.

The present study introduces a new $K$-prime equation of state by using the concept of dimensionless thermoelastic parameter kappa $(k)$. Results obtained by the formulated equation of state are compared with those obtained by the Stacey reciprocal $K$-prime equation of state [235]. Sharma [211] used to study the volume dependence of the Gruneisen parameter $(\gamma)$ with the following expression

$$K_T^{'} = K_\infty^{'} + \left(K_0^{'} - K_\infty^{'}\right)\left(\frac{V}{V_0}\right)^k \tag{5.126}$$

where $K_\infty^{'}$ is an important parameter [73, 235] in the field of equation of state at extreme compression or pressure. All equations of state for which $K_\infty^{'}$ is greater than zero satisfies the following relationship

$$\left(\frac{P}{K}\right)_\infty = \frac{1}{K_\infty^{'}} \tag{5.127}$$

$K_0^{'}$ is the first pressure derivative of isothermal bulk modulus $(K_T)$ at zero pressure and kappa $(k)$ is known as dimensionless thermoelastic parameter which has been used by many researchers [36, 57, 64, 123, 213] to solve thermoelastic properties for solids.

$K_T^{'}$ is defined as

$$K_T^{'} = -\frac{V}{K_T}\left(\frac{dK_T}{dV}\right) \tag{5.128}$$

where $V$ is the volume and $K_T$ is the isothermal bulk modulus

Using Eq. (5.126) with Eq. (5.128), we get the following relationship for volume dependence of bulk modulus

$$\left(\frac{K_T}{K_0}\right) = \left(\frac{V}{V_0}\right)^{-K_\infty^{'}} \exp\left[\left(\frac{K_0^{'} - K_\infty^{'}}{k}\right)\left\{1-\left(\frac{V}{V_0}\right)^{k}\right\}\right] \tag{5.129}$$

The pressure-volume relationship cannot be obtained directly through Eq. (5.126) but an approximate value, which is near to real, can be obtained by the following way. The term inside the square bracket of Eq. (5.129) can be expanded up to second order as higher order terms are not very significant. Therefore, Eq. (5.129) can be expressed as follows:

$$\left(\frac{K_T}{K_0}\right) = \left(\frac{V}{V_0}\right)^{-K_\infty^{'}}\left[1+m\left\{1-\left(\frac{V}{V_0}\right)^{k}\right\}+\frac{m^2}{2}\left\{1-\left(\frac{V}{V_0}\right)^{k}\right\}^2\right] \tag{5.130}$$

where

$$m = \left(\frac{K_0^{'} - K_\infty^{'}}{k}\right) \tag{5.131}$$

Using the basic definition of isothermal bulk modulus $K_T$ as given in Eq. (5.51) with Eq. (5.130), we obtain the following expression for Pressure

$$P = K_0\left[\left(\frac{1+m+m^2/2}{K_\infty^{'}}\right)\left\{\left(\frac{V}{V_0}\right)^{-K_\infty^{'}}-1\right\}+\frac{m(m+1)}{(k-K_\infty^{'})}\left\{\left(\frac{V}{V_0}\right)^{k-K_\infty^{'}}-1\right\}-\frac{m^2}{2(2k-K_\infty^{'})}\left\{\left(\frac{V}{V_0}\right)^{2k-K_\infty^{'}}-1\right\}\right] \tag{5.132}$$

The reciprocal $K$-prime EoS due to Stacey [235] is expressed as follows

$$\frac{1}{K_T^{'}} = \frac{1}{K_0^{'}} + \left(\frac{1}{K_\infty^{'}} - \frac{1}{K_0^{'}}\right)K_\infty^{'}\frac{P}{K_T} \tag{5.133}$$

Integration of Eq. (5.133) gives

$$\frac{K_T}{K_0} = \left(1 - K_\infty^{'} \frac{P}{K_T}\right)^{-K_0^{'}/K_\infty^{'}} \tag{5.134}$$

and

$$\ln\left(\frac{V}{V_0}\right) = \left(\frac{K_0^{'}}{K_\infty^{'2}}\right)\ln\left(1 - K_\infty^{'} \frac{P}{K_T}\right) + \left(\frac{K_0^{'}}{K_\infty^{'}} - 1\right)\frac{P}{K_T} \tag{5.135}$$

We estimated the values of volume dependence of $K_T$ and $K_T^{'}$ for lower mantle and outer core regions of the Earth through Eqs. (5.129) and (5.126) respectively. Computed data through Eqs. (5.129) and (5.126) are compared with those predicted values with the help of Stacey Equations of State (5.134) and (5.133) respectively in Table 5.14. For direct vision, calculated values of $K_T$ and $K_T^{'}$ are compared in Figs. 5.14 & 5.15 and Figs. 5.17 & 5.18 for lower mantle and outer core of the Earth respectively. It is apparent from Figs. 5.14-5.15 and 5.17-5.18 that the predicted values are found to be in good agreement with data predicted by Stacey Equation of state. Our equation of state shows the compatibility with the more stable EoS (Stacey EoS). The input data used in the present study are shown in Table 5.13. The calculated pressure-volume relationship for lower mantle and outer core is shown in Table 5.15 along with the data obtained from Stacey EoS. An excellent agreement between our data and data extracted through Stacey EoS reveals the validity of pressure-volume relationship obtained with the help of Eq. (5.126) in the form of Eq. (5.132). Computed values of pressure-volume data through Eqs. (5.132) and (5.135) are compared in Figs. 5.16 and 5.19 for lower mantle and outer core respectively. It is clear from Figs. 5.16 and 5.19 that the data in the present study are compatible with the Stacey EoS throughout the compression used.

Now, differentiating Eq. (5.126) with respect to pressure, we obtain

$$K_T K_T^{''} = -k\left(K_T^{'} - K_\infty^{'}\right) \tag{5.136}$$

Again differentiating Eq. (5.136) with respect to pressure, we obtain

$$K_T^2 K_T^{'''} = k\left(K_T^{'} - K_\infty^{'}\right)\left(K_T^{'} + k\right) \tag{5.137}$$

And the ratio $\left(\frac{K_T^2 K_T^{'''}}{K_T K_T^{''}}\right)$ for $K$-prime EOS is given below by using Eqs. (5.136) and (5.137)

$$\left(\frac{K_T^2 K_T^{'''}}{K_T K_T^{''}}\right) = -\left(K_T^{'} + k\right) \tag{5.138}$$

One can easily find out the values of $K_T K_T^{''}$ and $K_T^2 K_T^{'''}$ through Eqs. (5.136) and (5.137).

In the present study, we introduced a new $K$-prime Equation of state. It is concluded that the newly developed EoS is compatible to the Stacey $K$-Prime EoS. The EoS is useful to understand the interior properties of the Earth.

**Table 5.13** Input parameters used in the present study

| **Parameters** | $K_0$ | $K_0^{'}$ | $K_\infty^{'}$ | $k$ |
|---|---|---|---|---|
| **Lower mantle** | 206.06[73] | 4.2[73] | 2.41[73] | 3.153 |
| **Outer core** | 124.553[73] | 4.9599[73] | 3.0 [73] | 3.095 |

**Table 5.14** Computed values of volume dependence of $K_T$ (GPa) and $K_T^{'}$ from (a) Stacey EoS (Eq. 5.134 and 5.133) and (b) present study (Eq. 5.129 and 5.126) for lower mantle and outer core.

| $\left(\frac{V}{V_0}\right)$ | **Lower mantle** | | | | $\left(\frac{V}{V_0}\right)$ | **Outer core** | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $K_T$ (GPa) | | $K_T^{'}$ | | | $K_T$ (GPa) | | $K_T^{'}$ | |
| | (a) | (b) | (a) | (b) | | (a) | (b) | (a) | (b) |
| 0.7144 | 667.17 | 671.68 | 3.0790 | 3.0299 | 0.5396 | 1301.35 | 1359.58 | 3.3171 | 3.2904 |
| 0.7221 | 645.43 | 650.14 | 3.0955 | 3.0512 | 0.5438 | 1267.81 | 1325.30 | 3.3227 | 3.2975 |
| 0.7240 | 640.04 | 644.94 | 3.0997 | 3.0566 | 0.5494 | 1225.90 | 1281.21 | 3.3300 | 3.3070 |
| 0.7353 | 610.11 | 614.97 | 3.1246 | 3.0889 | 0.5558 | 1179.46 | 1232.99 | 3.3387 | 3.3182 |
| 0.7490 | 575.69 | 580.67 | 3.1563 | 3.1296 | 0.5583 | 1128.70 | 1214.75 | 3.3489 | 3.3227 |
| 0.7634 | 541.96 | 546.84 | 3.1911 | 3.1741 | 0.5715 | 1073.81 | 1123.68 | 3.3609 | 3.3469 |
| 0.7786 | 508.80 | 513.43 | 3.2297 | 3.2231 | 0.5812 | 1015.11 | 1061.97 | 3.3749 | 3.3654 |
| 0.7946 | 476.06 | 480.58 | 3.2730 | 3.2770 | 0.5921 | 952.87 | 997.40 | 3.3914 | 3.3871 |
| 0.8118 | 443.62 | 447.73 | 3.3221 | 3.3376 | 0.6046 | 887.40 | 929.01 | 3.4110 | 3.4129 |
| 0.8303 | 411.40 | 414.97 | 3.3786 | 3.4059 | 0.6190 | 818.09 | 856.99 | 3.4344 | 3.4441 |
| 0.8503 | 379.31 | 382.31 | 3.4446 | 3.4835 | 0.6354 | 748.33 | 782.80 | 3.4625 | 3.4816 |
| 0.8721 | 347.27 | 349.65 | 3.5231 | 3.5727 | 0.6544 | 675.51 | 706.01 | 3.4970 | 3.5276 |
| 0.8962 | 315.14 | 316.76 | 3.6187 | 3.6770 | 0.6628 | 645.93 | 674.86 | 3.5129 | 3.5488 |
| 0.9093 | 298.88 | 300.17 | 3.6756 | 3.7363 | | | | | |

**Table 5.15** Computed values of volume dependence of pressure $P$ (GPa) from (a) Stacey EoS (Eq. 5.135) and (b) present study (Eq. 5.132) for lower mantle and outer core.

| $\left(\frac{V}{V_0}\right)$ | **Lower Mantle** | | $\left(\frac{V}{V_0}\right)$ | **Outer core** | |
|---|---|---|---|---|---|
| | (a) | (b) | | (a) | (b) |
| 0.7144 | 135.75 | 136.29 | 0.5396 | 328.85 | 337.98 |
| 0.7221 | 128.71 | 129.25 | 0.5438 | 318.75 | 327.76 |
| 0.7240 | 126.97 | 127.55 | 0.5494 | 306.15 | 314.64 |
| 0.7353 | 117.35 | 117.86 | 0.5558 | 292.22 | 300.33 |
| 0.7490 | 106.39 | 106.88 | 0.5583 | 277.04 | 294.93 |
| 0.7634 | 95.76 | 96.20 | 0.5715 | 260.68 | 268.06 |
| 0.7786 | 85.43 | 85.80 | 0.5812 | 243.25 | 249.96 |
| 0.7946 | 75.36 | 75.73 | 0.5921 | 224.85 | 231.13 |
| 0.8118 | 65.52 | 65.82 | 0.6046 | 205.60 | 211.31 |
| 0.8303 | 55.90 | 56.13 | 0.6190 | 185.64 | 190.60 |
| 0.8503 | 46.46 | 46.66 | 0.6354 | 165.12 | 169.45 |
| 0.8721 | 37.29 | 37.41 | 0.6544 | 144.19 | 147.80 |
| 0.8962 | 28.29 | 28.34 | 0.6628 | 135.75 | 139.10 |
| 0.9093 | 23.83 | 23.87 | | | |

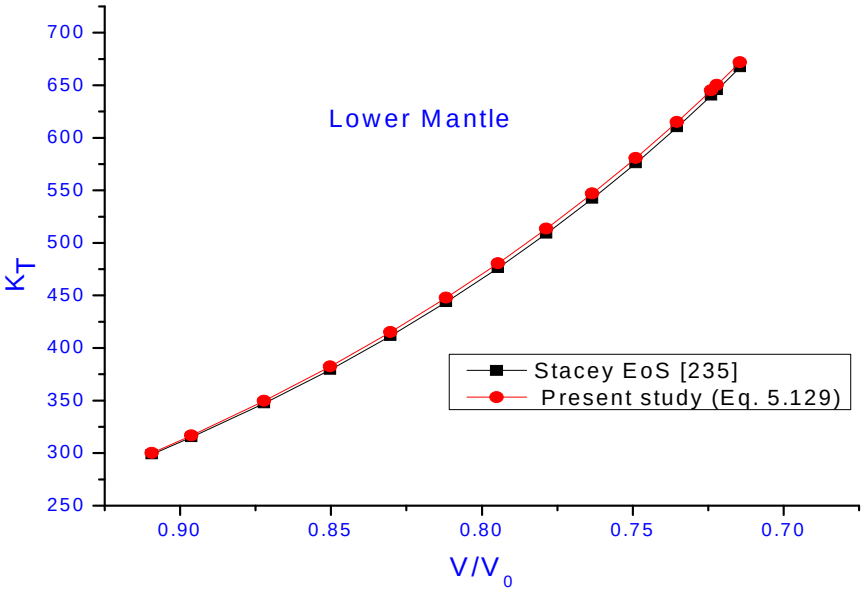


**Fig. 5.14** Volume dependence of $K_T$ calculated through Eq. (5.129) along with experimental data [235]. As volume decreases, $K_T$ increases which is compatible with more stable EoS [235].

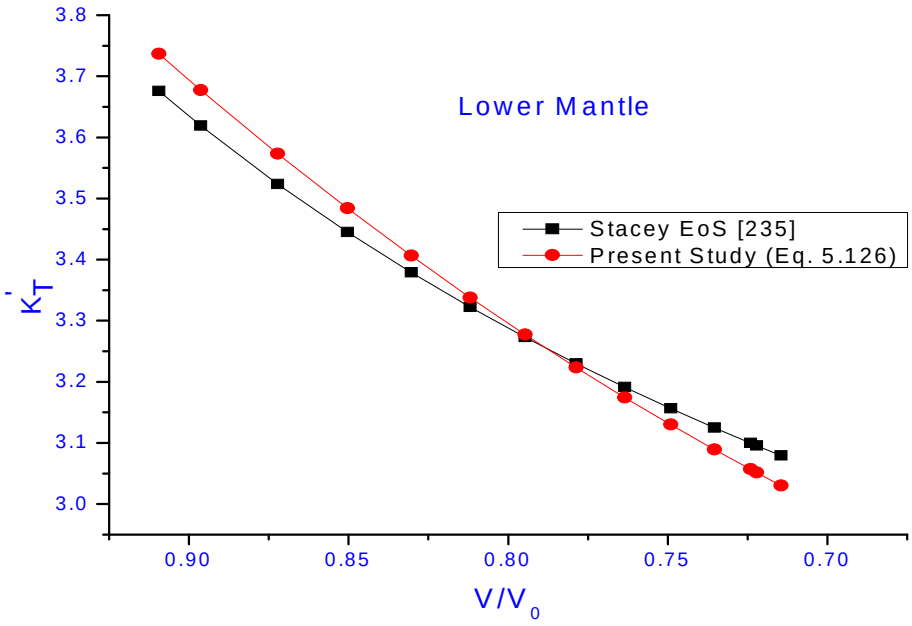


**Fig. 5.15** Volume dependence of $K_T'$ calculated through Eq. (5.126) along with experimental data [235]. $K_T'$ decreases with decrease in volume which Shows consistency with Stacey EoS [235].

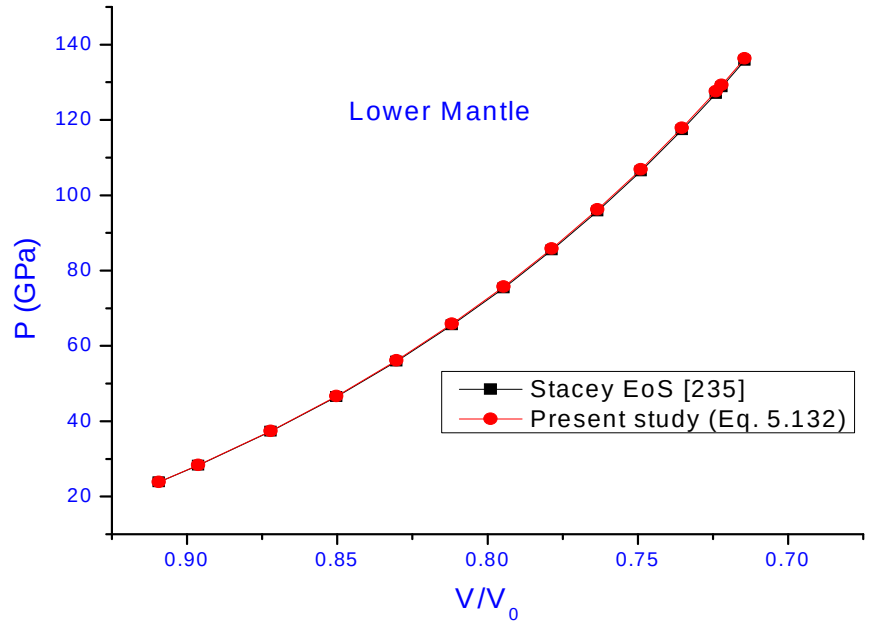


**Fig. 5.16** Comparison of pressure-volume data calculated through Eq. (5.132) and Stacey EoS [235]. Volume is decreased with the increased in pressure. The presented pressure-volume data shows compatibility with Stacey EoS throughout the compression used.

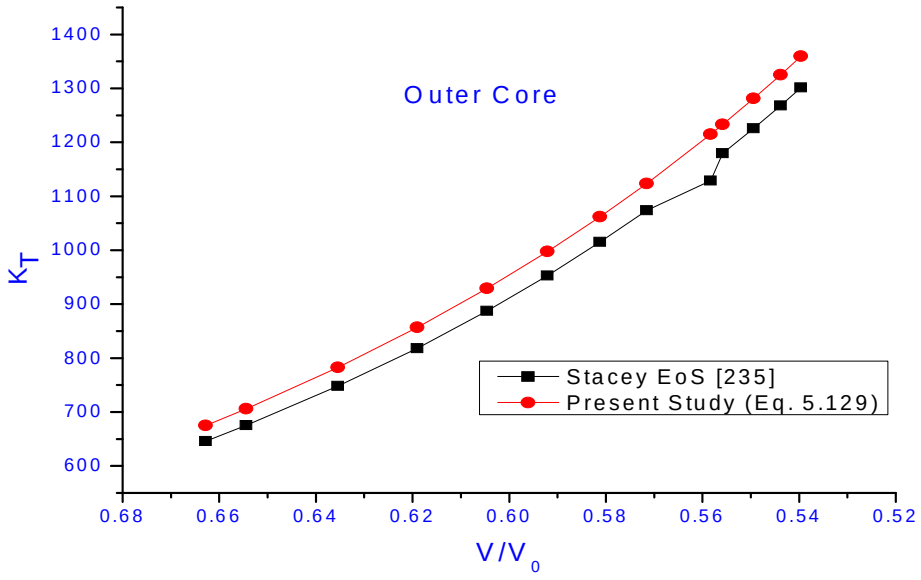


**Fig. 5.17** Volume dependence of $K_T$ calculated through Eq. (5.129) along with experimental data [235]. Fig. reflects that as the volume decreases, the values of $K_T$ is increased and show good agreement with Stacey EoS [235].

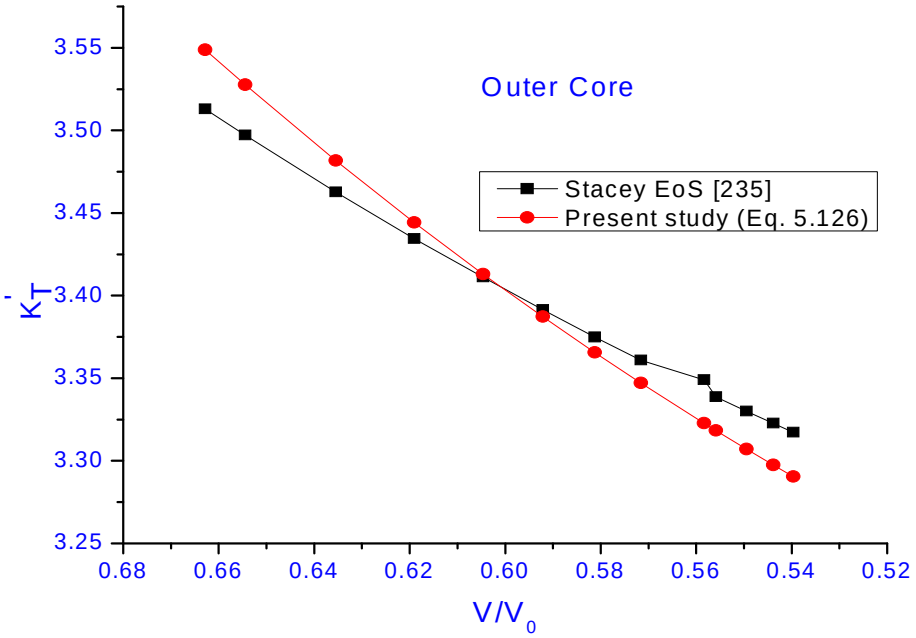


**Fig. 5.18** Volume dependence of $K_T^{'}$ calculated through Eq. (5.126) along with experimental data [235]. With decrease in volume, $K_T^{'}$ decreases. At higher and lower volume range, there is some deviation but volume around 0.60, it shows best compatibility with Stacey EoS.

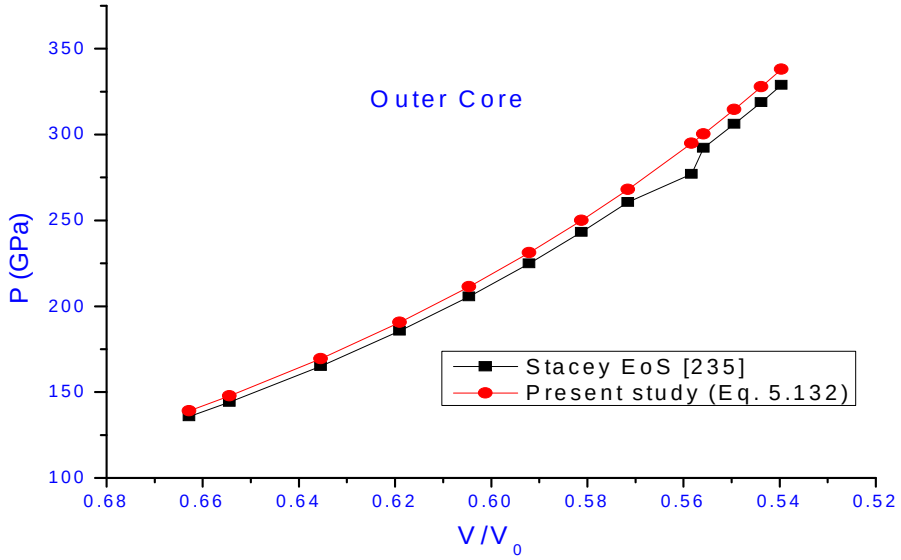


**Fig. 5.19** Comparison of pressure-volume data calculated through Eq. (5.132) and Stacey EoS [235]. The calculated data presented here shows best consistency with more stable EoS (Stacey EoS) throughout the compression used.

## 5.6 ANALYSIS OF SECOND ORDER TEMPERATURE DERIVATIVE OF VOLUME EXPANSION

The volume-temperature relationship and volume thermal expansivity data are required for investigating the Equation of State (EoS) and predicting the compression data for solids at high temperatures [241, 242]. The sufficient knowledge of temperature dependence of volume expansion is necessary to understand the high temperature behavior of solids. Various attempts [242, 246-248] have been made to predict volume expansion in pressure-temperature space. The reliable experimental data on temperature dependence of volume expansion for many solids corresponding to temperatures much higher than Debye temperatures are available [44, 86].

Here, temperature dependence of volume expansion of NaCl and KCl are considered. For these solids the data are available in the temperature range 300-750 and 300-850 K, respectively. However, this available temperature dependence of volume expansion data is still lower than the corresponding melting temperatures. In the present study, we have studied the temperature dependence of volume expansion ratio and its second order temperature derivative for NaCl and KCl. A close agreement between calculated and values based on thermodynamic identity reveals the validity of present work.

Srivastava [48] proposed a relationship for temperature dependence of volume expansion ratio

$$\left(\frac{V}{V_0}\right)=1-\frac{1}{B}\ln\left[1-d\alpha_0\delta_T^0(T-T_0)\right] \tag{5.139}$$

It is found that equation (5.139) is identical in nature to the relations given by previous workers [38, 249]. The identical relation is proposed by Fang [38], which can be written as

$$\left(\frac{V}{V_0}\right)=1-\frac{1}{\delta_T^0}\ln\left[1-\alpha_0\delta_T^0(T-T_0)\right] \tag{5.140}$$

Sharma [250], formulated the following expression

$$\left(\frac{V}{V_0}\right)=\left[1-d\alpha_0\delta_T^0(T-T_0)\right]^{-1/d\delta_{T0}}. \tag{5.141}$$

The volume thermal expansivity may be defined as [44]

$$\alpha=\frac{1}{V}\left(\frac{dV}{dT}\right)_P \tag{5.142}$$

On differentiation equations (5.139) and (5.140) w.r.t $T$, we get

$$\frac{1}{V_0}\left(\frac{dV}{dT}\right)=\frac{d\alpha_0\delta_T^0}{B}\left[1-d\alpha_0\delta_T^0(T-T_0)\right]^{-1} \tag{5.143}$$

and

$$\frac{1}{V_0}\left(\frac{dV}{dT}\right)=\alpha_0\left[1-\alpha_0\delta_T^0(T-T_0)\right]^{-1} \tag{5.144}$$

Using eqs. (5.142-5.144) we have

$$\alpha=\frac{d\alpha_0\delta_T^0}{\left\{1-d\alpha_0\delta_T^0(T-T_0)\right\}\left[B-\ln\left\{1-d\alpha_0\delta_T^0(T-T_0)\right\}\right]} \tag{5.145}$$

$$\alpha=\frac{\alpha_0\delta_T^0}{\left\{1-\alpha_0\delta_T^0(T-T_0)\right\}\left[\delta_T^0-\ln\left\{1-\alpha_0\delta_T^0(T-T_0)\right\}\right]} \tag{5.146}$$

Sharma [250] used the following relation for volume thermal expansivity ($\alpha$)

$$\alpha=\frac{\alpha_0}{\left\{1-d\alpha_0\delta_T^0(T-T_0)\right\}} \tag{5.147}$$

On differentiation eqns. (5.143-5.144) w.r.t.$T$, we get the following expression for finding the second order temperature derivative of volume expansion

$$\frac{1}{V}\left(\frac{d^2V}{dT^2}\right)=\alpha^2\left[B-\ln\left\{1-d\alpha_0\delta_T^0(T-T_0)\right\}\right] \tag{5.148}$$

$$\frac{1}{V}\left(\frac{d^2V}{dT^2}\right)=\alpha^2\left[\delta_T^0-\ln\left\{1-\alpha_0\delta_T^0(T-T_0)\right\}\right] \tag{5.149}$$

Also double differentiating equation (5.141) w.r.t. *T*, we get

$$\frac{1}{V}\left(\frac{d^2V}{dT^2}\right)=\alpha^2\left[1+d\delta_{T0}\right] \tag{5.150}$$

Input parameters [44] used in calculations are given in Table 5.16. The empirical constants $B$ and $d$ are extracted from the methods suggested by Srivastava [251] and Singh and Chauhan [24] respectively. The calculated values of volume expansion ratio with the help of equations (5.139-5.141) are shown in Figs. 5.20 and 5.21 for NaCl and KCl respectively, along with the experimental data. It has shown that Sharma equation is more compatible with the experimental data than other equations (5.139, 5.140).

In the present study, we have estimated the values of second order temperature derivatives of volume expansion using equations (5.139-5.142) & (5.145-5.147). We have also

evaluated the values of $1/V\left(d^2V/dT^2\right)$ from the following basic thermodynamics

$$\frac{1}{V}\left(\frac{d^2V}{dT^2}\right)=\alpha^2(1+\delta_T) \qquad (5.151)$$

The calculated values of $1/V\left(d^2V/dT^2\right)$ versus $T$ are shown in Figs. 5.22 and 5.23 for NaCl and KCl respectively. From Figs. 5.22 and 5.23, which reflect that the values predicted from equation (5.150) shows close agreement with those values calculated through equation (5.151). However, for volume expansion equations (5.139, 5.140 and 5.141) give almost identical results.

A method for analysis of second order temperature derivative of volume expansion based on different assumptions for ionic solids i.e., NaCl and KCl is presented. The relationship developed by Srivastava [48] is based on the fact that isothermal bulk modulus $(K_T)$ decreases linearly with temperature. This relationship has shown the close agreement for temperature dependence of volume expansion between theory and experimental data. Fang [38] assumed that two different diffusional driving force models are equivalent i.e. $\alpha K_T = \frac{C_0}{V}$ *or* $\alpha K_T V = const.$ where $C_0 = 2CK_B/3$ for establishing the relationship (Eq. 5.142). But Sharma [250] gave simple method for temperature dependence of volume thermal expansivity based on the assumption that $\alpha K_T$ remains constant for NaCl and KCl at high temperatures and zero pressure which extend the expression for higher order temperature derivative of volume expansion. Out of these assumptions, Sharma [250] equation (5.150) gives better results for higher order temperature derivative of volume expansion ratio which shows the close agreement with the values those obtained from basic thermodynamic relation equation (5.151) and supports the validity of present work. From Figs. 5.22 and 5.23, it is evident that above 500 K varies linearity with temperature because of anharmonic effects become significant at high temperatures.

**Table 5.16** Input parameters used in calculations

| Solids | $\alpha_0\,(10^{-5}K^{-1})$ | $\delta_T^0$ | $B$ | $d$ |
|---|---|---|---|---|
| NaCl | 11.8 [44] | 5.56 [44] | 5.7051 [251] | 1.06 [24] |
| KCl | 11.0 [44] | 5.84 [44] | 5.7517 [251] | 1.02 [24] |

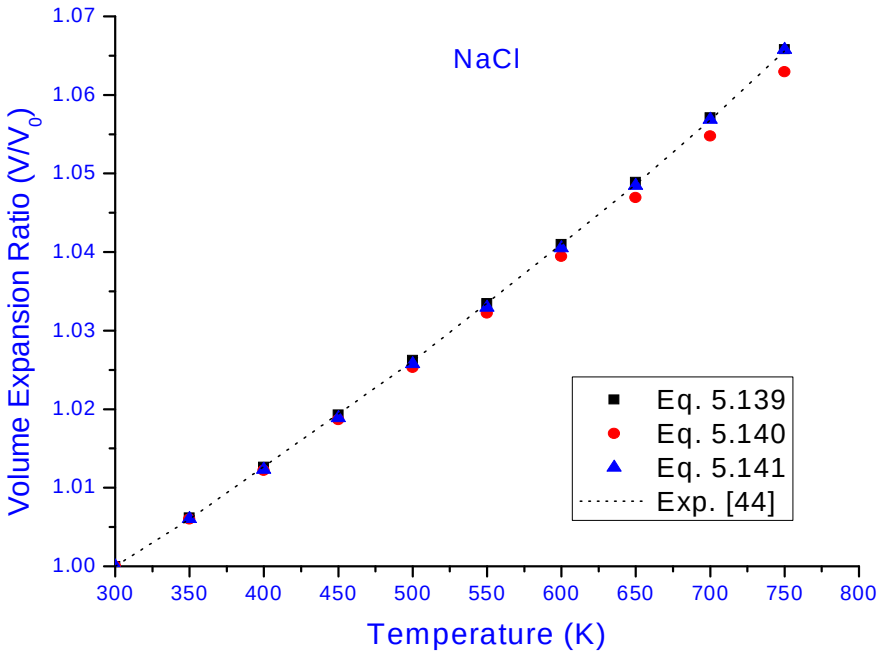


**Fig. 5.20** Volume expansion ratio versus temperature (K) for NaCl. Volume expansion ratio increases with increase in temperature. It has shown that Sharma Eq. (5.141) is more consistent with experimental data [44] than other equations used.

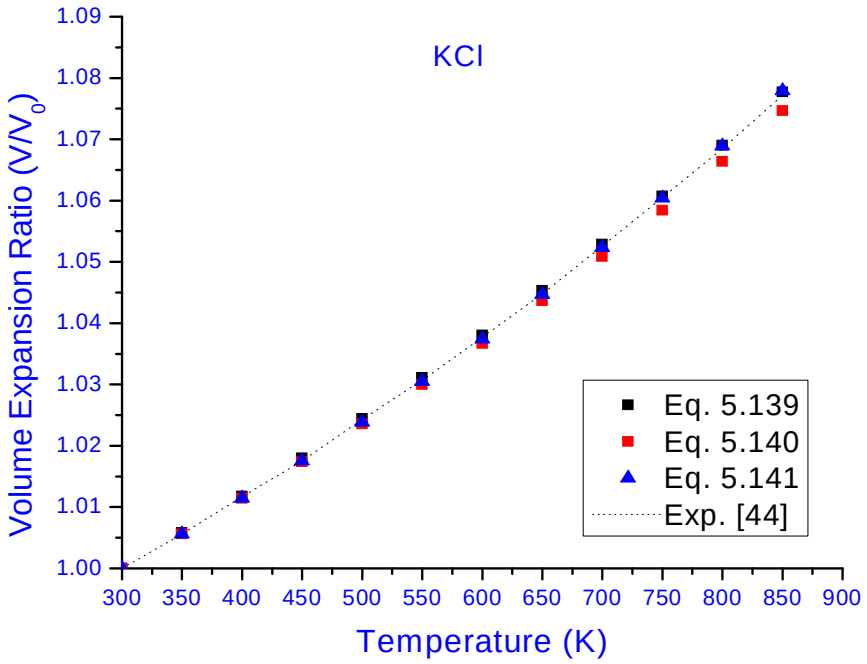


**Fig. 5.21** Volume expansion ratio versus temperature (K) for KCl. With increase in temperature, volume expansion ratio increases and Sharma Eq. (5.141) is more compatible with experimental data [44] than other equations used.

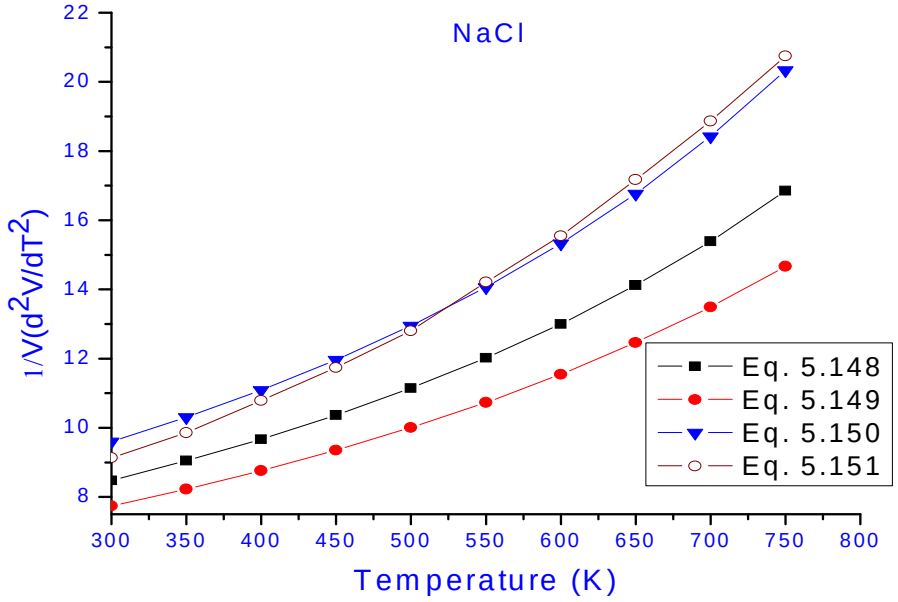


**Fig. 5.22** $\frac{1}{V}\left(\frac{d^2V}{dT^2}\right)\left(K^{-2}\right)$ versus temperature (K) for NaCl. Fig. reflect that values calculated through Eq. (5.150) shows close agreement with the values obtained from basic thermodynamic relation (Eq. (5.151)).

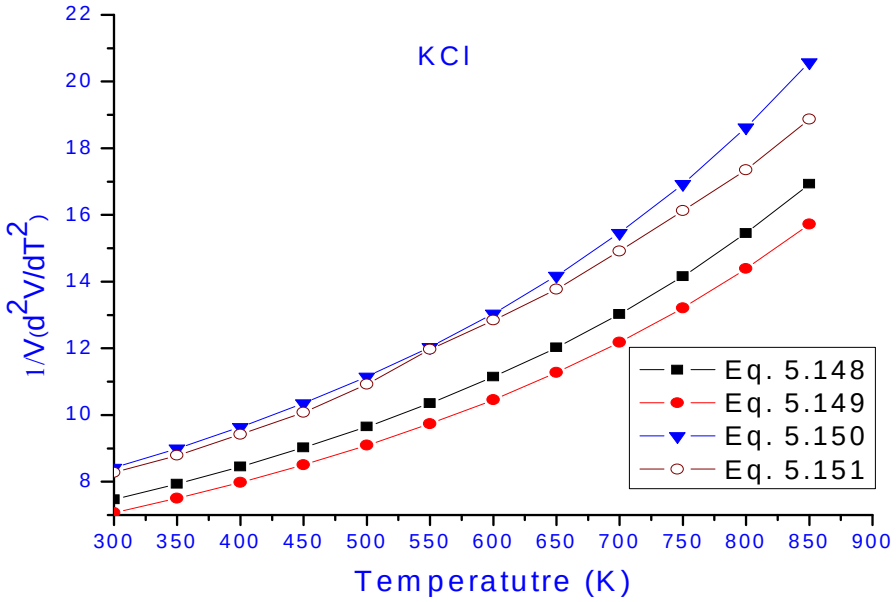


**Fig. 5.23** $\frac{1}{V}\left(\frac{d^2V}{dT^2}\right)\left(K^{-2}\right)$ versus temperature (K) for KCl. It is evident from Fig. that Sharma Eq. (5.150) gives better results for higher order temperature derivative of volume expansion ratio with values obtained from basic thermodynamic relation (Eq. (5.151)).

# CHAPTER 6

# Summary and Conclusions

## Overview

The present chapter summarizes and concludes the results of the study on thermal and elastic properties of solids and geophysical minerals at high temperatures and high pressures conditions. Relationship between Anderson-Grüneisen parameter and thermal expansivity show validation for lower mantle (an insulator) and for NaCl with experimental data reported in literature. NaCl and $\varepsilon$-Fe have been taken to check the reliability of the volume dependence of Grüneisen parameter model which gives a reasonably good agreement between calculated values and the values derived from experimental data on thermoelastic properties. Results of higher order volume derivatives of Grüneisen ratio is found consistent with Stacey and Davis relationship but the trend of third Grüneisen ratio has not been found satisfactory for NaCl and MgO. The results obtained for the analysis of thermodynamic properties in the infinite pressure limits are found to be consistent with the recent analysis of infinite pressure of thermoelastic properties and also based on the Stacey thermodynamics of solids at infinite pressure. Reciprocal form for volume dependence of thermal expansivity shows consistency with experimental data for NaCl and satisfies the thermodynamic constraints at infinite pressure on which it has been formulated. The newly developed EoS is found to be compatible to the Stacey $K$-prime EoS throughout the compression used. The better results for temperature dependence of volume expansion ratio and its higher order temperature derivative with the values obtained from basic thermodynamic relation exposes the validity of the expression. All the proposed models show close or better agreement with the experimental results and present a suitable model for further study to investigate the thermal and elastic properties of interior of the Earth.

## 6.1 SUMMARY AND CONCLUSIONS

Thermal and elastic properties of solids and geophysical minerals are important to investigate the equations of state (EoS) for interior of the Earth. It is necessary to know the volume thermal expansion coefficient or thermal expansivity with the change in temperature and pressure/volume to describe the thermodynamic and elastic properties of solids and geophysical minerals. It is one of the fundamental properties of solids. It results from the anharmonicity of the interatomic potential and is related to many thermodynamic and elastic quantities such as specific heat, elastic constant, Grüneisen ratio etc. It is an important physical parameter and is essential to understand the deep earth such as the adiabatic temperature gradient, convective power, interpretation of tomographically observed seismic velocity anomalies and gravitational energy release by thermal contraction [73, 144]. It is emphasized that many serious problems in thermodynamic functions arise due to uncertainty in thermal expansivity. Therefore, many attempts [57, 65, 66, 193-195] have been made to understand the knowledge of thermal expansivity along an isotherm as well as along an adiabat. The variation of thermal expansivity with volume or compression is already recognized. It is found [57] that thermal expansivity decreases with increasing compression. The other important parameter, which connects thermal and elastic properties of a solid, is termed as the Anderson-Grüneisen parameter. The thermodynamic approach shows that it is an explicit function of two dimensionless parameters; one is $K_T^{'} = \left(\partial K_T / \partial T\right)_P$ and the other is known as the Grüneisen ratio ($\gamma$). The dimensionless Anderson- Grüneisen parameter can be obtained either at constant temperature ($\delta_T$) or at constant entropy ($\delta_S$).

Various attempts have been made to study the variations of elastic moduli with temperature for ionic solids and geophysical minerals but a simple and accurate method for predicting high temperature elastic constants is still lacking. Due to experimental difficulties at high temperatures, the reliable data on temperature dependence of thermal expansivity are not found. Therefore, an empirical, phenomenological or semi-phenomenological model of thermal expansivity is required to investigate high temperature behaviour of solids and minerals. We try to provide an analytical method to understand the temperature dependency of elastic constants under isobaric conditions. Elastic properties of a solid are important because they relate to various fundamental solid-state properties such as equations of state, Debye temperature and

melting point and it plays an important role in determining the strength of materials. Values of elastic constants provide valuable information about the bonding characteristics between adjacent atomic planes and anisotropic character of the bonding and structural stability. Grüneisen parameter $(\gamma)$ is one of the important physics quanta that characterize the anharmonic properties of solids. It is used to study thermal and elastic properties of solids at high temperatures and pressures and explain the anharmonic properties of solids in condensed matter Physics and geophysics. Grüneisen parameter is useful to predict the Debye temperatures $(\theta_D)$ for solids and minerals. The knowledge of Grüneisen parameter is also required for investigating the melting curves from Lindemann-Gilvarry criterion [216, 217]. One common experimental research of Grüneisen parameter in its macroscopic definition has been done by Birch [165] based on experimental measurement of thermodynamic properties at high temperatures and high pressures. The experimental determination of the Grüneisen parameter defined in the microscopic definition is extremely difficult, as it requires a detailed knowledge of the phonon dispersion spectrum of a solid [218]. There is a long history of attempts to study Grüneisen parameter [219].

We also use the high pressure thermodynamic proposed by Stacey and Davis [73] to predict the thermal and elastic properties of materials in the region of high temperature and high pressure. The infinite pressure constraints imposed by extreme pressure thermodynamics along with recently developed models have been used to investigate the properties of materials. Basic thermodynamic identities and relationships derived by the Maxwell is also included in our study. They are frequently used in mineral physics to review the legitimacy of approximations and assumptions about mineral properties at high temperatures and pressures. For example, the relationship between the pressure dependence of thermal expansivity $\alpha$, and the temperature dependence of bulk modulus $K_T$. However, for geophysics applications, we are more interested in the variations in properties on an adiabat. For this an equations of state (EoS) or thermodynamic formulation is required which must satisfy the boundary conditions at zero pressure and also at infinite pressure. Analyses of the behavior of materials at zero and at extreme compression have been very useful to derive some thermodynamic constraints which provide a critical test of different theories. The infinite pressure parameters determined through extrapolation by considering a material to remain in the same phase when compressed to extreme

limit $(V \to 0 \text{ or } P \to \infty)$ are equally important as the zero-pressure parameters, for predicting the properties of materials in the observed range of finite pressure with the help of EoS. This is true that no material can exist at extreme compression $(V \to 0 \text{ or } P \to \infty)$, and some material with a particular phase do not exist even at zero pressure or atmospheric pressure. They exist only for a given range of finite pressure. But the extrapolated values of parameters in the limit of infinite pressure provide a fine and powerful control on the properties to be determined in the observed range of pressure. This point has been discussed in detail by Stacey and Davis [73] and the infinite pressure parameters such as $K_\infty^{'}$ and $\gamma_\infty$ are used in the same manner as the zero pressure parameter $K_0^{'}$ and $\gamma_0$. Here $K_T^{'}$ and $\gamma$ are identified as the first pressure derivative of bulk modulus ($K_T$) and the Grüneisen ratio ($\gamma$) respectively. The subscripts "0" and "$\infty$" are used to indicate the values of concern parameter at zero pressure ($P \to 0$) and infinite pressure ($P \to \infty$) respectively. In the limit of extreme pressure many of these relationships simplify and the simplified forms impose constraints that equations of state must satisfy. This means that we are considering the extrapolation of equations to $P \to \infty / V \to 0$ and need to be careful about the implications of the extrapolation. We emphasize this point because, in the analysis, we make use of the principle that an equation of state must satisfy basic physical laws, in particular thermodynamic relationships, even outside the pressure ranges over which the materials that it describes can exist. We are imposing constraints on parameters of equations of state, in particular $K_\infty^{'}$. The practical significance of this constraint is emphasized by pointing out that in the core and the lower half of the lower mantle $K^{'}$ is nearer to $K_\infty^{'}$ than it is to $K_0^{'}$. This applies quite generally to derivative properties, including the Grüneisen parameter, $\gamma$. Deep in the Earth they are all much closer to their infinite pressure extrapolations than to zero pressure values.

In the present study, we have disclosed the relationship between Anderson- Grüneisen parameter and thermal expansivity for insulators. The predicted relationship is validated under the adiabatic as well as isothermal conditions. The presented relationship follows the constraints made by high pressure thermodynamics [73]. For adiabatic temperature profile, we used the data reported by Stacey and Davis [73] based on the seismic values for lower mantle (an insulator) region of the Earth. The isothermal data reported by Birch [165] for solid NaCl is used for validation because Birch [165] combined the several kinds of experimental data viz. ultrasonic,

volumetric and shock compression, to produce a set of isotherms of NaCl on the temperature – pressure region between 25ºC and 500ºC and 0-30 GPa. These results of pressure – volume relationship and thermoelastic properties of NaCl have been considered to be reliable and used by Anderson [44] in further analysis of the volume dependence of the Anderson-Grüneisen parameter ($\delta_T$) and thermal expansivity ($\alpha$) of NaCl. Therefore, these data are considered significant and are used to validate our approach. The computed values of $\alpha(V)$ for solid NaCl are compared with available experimental data. A close agreement between theory and experiment is found, which in turn reveals the validity of our approach. Further, a linear relationship between the Anderson-Grüneisen parameter and thermal expansivity is observed. Such relationship is useful to investigate the thermal and elastic properties of insulator materials.

A simple and straightforward empirical relationship is also studied to calculate the values of volume dependence of Grüneisen parameter $\gamma$ for NaCl and $\varepsilon-$Fe under wide range of pressure because Grüneisen parameter is an important physical quantity in geophysics which describes the thermoelastic behaviour and anharmonic properties of materials at high pressure and high temperature. $\varepsilon-$Fe is taken for the study because it is available in the Earth core region for wide range of pressures (0-360 GPa) and it is found that as volume decreases the value of Grüneisen parameter is decreased and the results obtained for Grüneisen parameter are compatible with the values derived from the experimental data [165, 196] on thermoelastic properties throughout the wide range of pressure thus supports the validity of the present model. We also have developed a new empirical relationship to find out the values of volume dependence of Grüneisen parameter based on the assumption that $K_\infty^{'}=5/3$ [223-226]. We have estimated $\gamma(V)$ values for NaCl and $\varepsilon-$Fe under different compression or pressure ranges to test the suitability of the expression. It is found that the results obtained are consistent with experimental data throughout the compression or pressure ranges for both solids under consideration. Consistency between calculated and experimental values [165, 196] exposes the accuracy of present formulation. Further, we analyse the volume dependence of Grüneisen ratio $\gamma$ and its higher order derivatives $q$ and $\lambda$ for $MgO$ and NaCl. We used a reciprocal form of equation for Grüneisen ratio given by Srivastava et al. [228] and its higher order volume derivatives. It has been observed that the trend of $\gamma$ and $q$ is found to be consistent with the

Stacey and Davis relationship [73] but the trend of third Grüneisen ratio $\lambda$ has not been found satisfactory. Thus, one can rectify this equation for further study.

We have also analysed the thermodynamic properties in the limit of infinite pressure. A number of thermodynamic properties in the infinite pressure limits have been used to establish the isothermal and adiabatic properties. The results obtained in the present study are consistent with the recent analysis of infinite pressure of thermoelastic properties recently presented by Shanker et al. [81]. Isobaric heat capacity $(C_P)$ and isochoric heat capacity $(C_V)$ remains same at $P \to \infty$ or $V \to 0$. $(\partial K_S/\partial P)_T$ becomes $(\partial K_S/\partial P)_S$ at infinite pressure. $\mu$ remains same under both conditions i.e., isotherm and adiabatic conditions in the limit of infinite pressure. It has also been found that $(\partial \mu/\partial P)_T$ equals to $(\partial \mu/\partial P)_S$. The ratio $\delta_T/\delta_S$ remains finite in the limit of infinite pressure. The results obtained in the present study are based on the Stacey thermodynamics of solids at infinite pressure [73]. Considering the product $(\gamma \alpha T)$, which relate adiabatic and isothermal bulk moduli and their pressure derivatives is a small quantity for solids, even at temperatures of the Earth's interior, and it decreases with pressure and it vanishes identically at $P \to \infty$. Here $\alpha$ decreases more strongly than $T$ increases, making the product $\alpha T$ to vanish at $V \to 0$. In the limit of infinite pressure $(P \to \infty or\ V \to 0)$, $K_{S\infty} = K_{T\infty}$ and $K'_{S\infty} = K'_{T\infty} = K'_{\infty}$. Therefore, at extreme compression, in the limit of zero volume, not only the adiabatic and isothermal bulk modulus become identical but also their first pressure derivatives become equal. In other words, both properties become indistinguishable. This fact reveals some constraints to high pressure thermodynamics, which should be followed by all relationship at extreme compression. Another important fact regarding the infinite pressure value of the Grüneisen ratio is obtained by high pressure thermodynamics. Accordingly the extreme pressure thermodynamics, the Slater formula [134] of the Grüneisen ratio becomes an identity in the limit of infinite pressure. Thus, $\gamma_\infty = \frac{1}{2}K'_\infty - \frac{1}{6}$ which provides a constraint for second Grüneisen ratio at $V \to 0$, i.e. $q_\infty = 0$. These constraints have provided a solid background to our calculations for thermal and elastic properties of materials at high pressures and high temperatures. It has also been found [64, 195] that the products $\alpha K_T$ and $\alpha K_S$ become infinite in the limit of extreme compression $(V \to 0)$. Thus, $\gamma$ and $C_P(C_V)$ remain finite in the limit of

infinite pressure. The rate of change of $\alpha$ with volume $(\partial\alpha/\partial V)$ is faster than the rate of change of $K_T$ with volume $(\partial K_T/\partial V)$ at low pressures [26, 44, 183]. As pressure increases the quantity $(\partial\alpha/\partial V)$ decreases, while the quantity $(\partial K_T/\partial V)$ increases. At a particular pressure both quantities become equal and result in the minima of the product $\alpha K_T$. After a point where $(\partial\alpha/\partial V) = (\partial K_T/\partial V)$ [44, 78, 183, 238], the rate of increase in $K_T$ becomes faster than the rate of decrease in $\alpha$ with respect to pressure or compression. It means that at higher pressure $K_T$ dominates over $\alpha$ [64]. Stacey [235] pointed out that isothermal (adiabatic) properties become identical at extreme compression. It has also studied that $\delta_T$ becomes $\delta_S$ at infinite pressure and in turn the ratio of $\delta_T/\delta_S$ becomes finite at infinite pressure.

A relationship for the volume dependence of thermal expansivity ($\alpha$) by using a simple choice of isothermal Anderson-Grüneisen parameter in reciprocal form has been presented and from the estimated values of $\alpha$, it is found that the results obtained show the consistency with those values given by Birch [165] for NaCl. Thermal expansivity decreases as volume decrease and it tends to zero at infinite pressure i.e. $\alpha \to 0$ at $P \to \infty$ or $V \to 0$ [73, 144, 195, 207, 213]. The presented relationship also satisfies the thermodynamic constraints which is the base of this formulation. So, we can say that one can use the reciprocal form of Anderson-Grüneisen parameter.

A new $K$-prime Equation of state is also introduced in the present work and concluded that the newly developed EoS is compatible to the Stacey $K$-Prime EoS. The EoS is useful to understand the interior properties of the Earth. We estimated the values of volume dependence of $K_T$ and $K_T^{'}$ for lower mantle and outer core regions of the Earth. Computed data are compared with those of the predicted values with the help of Stacey Equations of State. It is apparent that the predicted values are found to be in good agreement with data predicted by Stacey Equation of state [73]. Our equation of state shows the compatibility with the more stable EoS (Stacey EoS). Further, it has been found that the pressure-volume relationship for lower mantle and outer core regions of the Earth gives an excellent agreement with those obtained through Stacey EoS, and it is also found that our EoS is compatible with Stacey EoS throughout the compression range used.

A method for analysis of second order temperature derivative of volume expansion based on different assumptions for ionic solids i.e., NaCl and KCl is presented. The relationship is based on the work of Srivastava [48] where isothermal bulk modulus ($K_T$) decreases linearly with temperature. This relationship has shown the close agreement for temperature dependence of volume expansion between theory and experimental data. However, for volume expansion we obtain almost identical results compared with the previous models [38, 249].

The study presented in this thesis is highly informative to the researchers. It is felt that the present work will be of basic understanding to the thermal and elastic properties of solids and geophysical minerals at high temperatures and high pressures. It is further expected that the studies of thermal and elastic properties would release a new outlook of thermoelastic properties at extreme compression or infinite pressure for the solids and geophysical minerals and also for the lower mantle and core regions of the Earth.

## 6.2 SUGGESTION FOR FUTURE WORK

On the basis of work presented in this thesis, above mentioned conclusion have been drawn. However, there and some areas which requires further investigation. These are:

(1) One can establish the different models to study the anharmonicity in thermal and elastic properties of solids by using presented models in the present study.

(2) One may formulate the relationship for thermal conductivity with the help of different models developed for solid materials.

(3) One can study the melting temperature of solids by using the reciprocal Grüneisen parameter with the help of presented models in this work.

(4) One may also apply this study to know the temperature dependency of elastic constants for analyzing the bonding and structural stability of solids.

(5) We may further study the mineralogical composition of each layer and physical properties of each phase of lower mantle and core regions of the Earth by using the present study.

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