CHAPTER 1

A BRIEF REVIEW OF THE SEMICONDUCTING COMPOUNDS AND INTRODUCTION TO THE THEORY OF ELASTICITY AND THERMAL EXPANSION

1.1 Introduction

Technological and theoretical interest in II–VI and III–V semiconductors and their alloys in zinc blende structure has been growing recently due to their appealing properties in electro-optical and electro-acoustical devices (1-4). ZnS, ZnSe and ZnTe are the prototype II–VI semiconductors and their cubic phases, which occur naturally as a mineral, have been the subject of intense investigation. Considerable efforts are made to realize a p-type material by doping or growing with impurities such as Li or Cl. When doped with Mn, the Zn based crystals form an interesting group of dilute magnetic semiconductors (5-7). Moreover, in recent years ZnSe has proved to be particularly interesting dilute magnetic semiconductor when doped with Mn (8-10). Efforts have also been made to fabricate a sustainable ZnSe blue laser. Very recent Molecular-Bean-Epitaxy (MBE) growth of BCC
Fe and Ni single crystals on ZnSe (11,12) has opened up the possibility of using such materials as micro electronic magnetic switches.

Zinc chalcogenides in the cubic sphalerite structure and direct-gap semiconductors with energy gap ranging from 2.3eV (ZnTe) to 3.7 eV (ZnS) exhibit increase in direct-gap energy, which is the behaviour usually observed in binary tetrahedral semiconductors (13-15). Recent interest in the high pressure behaviour of zinc chalcogenide has arisen in the context of high pressure investigations of strain effects in superlattices (16-19). By using diamond-anvil-cell techniques, the effect of pressure on the direct optical gaps of ZnSe (20) and ZnTe (21) has been investigated for pressure covering the full stability range of the tetrahedral phases. Phase transitions at high pressures (14,20,21,22) occur at about 9.5, 13.7 and 15 GPa in ZnTe, ZnSe and ZnS (14,22) respectively. In the case of ZnS and ZnSe these phases have been identified as rocksalt [B1] type (14,15). The 9.5 GPa phase transition in ZnTe leads to a lower-symmetry crystal structure (23) followed by phase transition (21,23) at a higher pressure (~11.94 Pa). The high pressure phases of zinc chalcogenides are found to be metallic (14,22) but for the first high-pressure phase of ZnTe this is not confirmed (21).

Photo emission spectra (1) show evidence of cation d bands and recent investigations (24,25) treating the cation d electron as valance electrons have indicated that the cation d electrons play a significant role in II-VI and III-V conduction mechanism. However, the ground state structural and cohesive
properties of these materials have not been widely investigated as has been done for other semiconductors. Therefore, it is meaningful to characterise theoretically the physical properties of cubic ZnS, ZnSe, ZnTe and GaAs crystals using the anharmonic effects.

The study of temperature dependence of acoustic attenuation in semiconductors in the Akhiezer regime has stimulated much interest among researchers in the last three decades (26-31). Lambade and Sahasrabudhe (26) suggested a method of calculation involving the non-linearity constant which is a function of second- and third-order elastic constants. Among the III-V semiconducting compounds, GaAs has been the most widely studied for its attenuating characteristics (32-36). However, the theoretical investigation on the temperature dependence of attenuation in GaAs has not been reported so far due to the lack of experimental data on temperature dependence of third-order elastic constant (TOEC). Recently, Joharapurkar et al. (37) have reported experimental determination of temperature dependence of the complete set of TOEC for GaAs in the range 77-300K. Lambade and Sahasrabudhe (26) have obtained the acoustic damping in GaAs. They also suggest new computational approach to determine the collective phonon-relaxation time in the range 80-300K. These relaxation times are used to estimate the temperature dependence of attenuation for the longitudinal waves along the [110] and [111] directions and for the shear waves along the [110] direction.
The method generally used to determine the elastic constant $C_{ij}$ of alloys usually consists in simple linear combination of those of the constituent components (38). This method has been employed for ternary halides whose elastic constants are used as input parameters for studying their hardness (39). Recently, Krieger and Sigg (40) using Brillouin light scattering in Al$_x$Ga$_{2}$As observed that the elastic constant tensor differs slightly from those calculated by linear interpolation of the binaries $C_{ij}$. From these results it can be seen that the method generally used for calculating the ternary alloy’s $C_{ij}$ by linear combination of its binary components could be inexact, because the requirement of linearity of the elastic constant behaviour is not fulfilled.

The elastic properties of semiconductors ZnS, ZnSe, ZnTe and GaAs are of interest both for technology and basic research (41-45). Anisotropy in elasticity is a fundamental property of the semiconducting crystals. We investigate primarily on II-VI and III-V semiconducting compounds. We briefly review here the status of the experimental and theoretical work (46-52) on the elastic properties, which give additional insight into the basic microscopic mechanism underlying the condensed state of these materials.

1.2 Zinc Sulphide (ZnS)

Although less studied than III-V compound superlattices, wide-gap semiconductors ZnS and its alloys are interesting in connection with opto-electronic application in the blue-light wavelength regime. They may be tuned by means of built-in strains produced by epitaxial growth of hetero structures
under controlled conditions. Analysis of such effects requires the knowledge of elastic constants. Casali and Christensen (53) study the effects of external pressure on the elastic moduli. Such calculations of structural and electronic properties performed directly for heterojunctions or strained-layer superlattices under pressure (54-56).

The elastic constants of ZnS have been determined by Berlincourt et al. using a piezo resonance technique (57). Casali and Christensen (53) calculated the inter strain parameter as a function of pressure which defines the relative displacement of the anion and cation sublattices under a trigonal strain. In addition, they find the transverse optical phonon frequency at the zone center as well as its pressure variations. Further, the deformation potentials of the states at the valence-band maximum related to tetragonal and trigonal strains have been estimated as a function of pressure. Benkabou et al. (1) predict the behaviour of solid ZnS under temperature and pressure effect. These potential parameters are used to calculate the elastic constants, equilibrium lattice parameters, bulk modulus, pressure derivatives and cohesive energies in the cubic phase of ZnS. They also use these parameters to obtain the thermal expansion coefficient and specific heat.

Lugueva et al. (58) measure the thermal conductivity of poly crystalline zinc sulfide under hydrostatic pressure upto 0.35 GPa in the temperature range 273-420K. It gives an increase in the pressure leading to an increase in the thermal conductivity coefficient of ZnS. Thermal atomic vibrations in ZnS, ZnSe
and ZnTe crystals are studied by precise X-ray structure analysis in the temperature range 300-800K by Rabadanov et al. (59).

ZnS has an FCC cubic zinc blende structure with \( \bar{4}3m \) point group (60) and its lattice parameter is \( a = 0.541 \text{nm} \) with the co-ordinates of Zn atoms are \((0,0,0), (0,\frac{1}{2},\frac{1}{2}), (\frac{1}{2},0,\frac{1}{2}), (\frac{1}{2},\frac{1}{2},0)\) and those of atom S are \((\frac{1}{4},\frac{1}{4},\frac{1}{4}), (\frac{1}{4},\frac{3}{4},\frac{1}{4}), (\frac{3}{4},\frac{1}{4},\frac{1}{4}), (\frac{3}{4},\frac{3}{4},\frac{1}{4})\). ZnS structure can be viewed as two interpenetrating FCC lattices with one composed entirely of Zn atoms, the other entirely of S atoms. These FCC lattices are displaced from each other by one-quarter of a body diagonal. Each atom in this semiconducting crystal has four atoms as first nearest neighbours and twelve atoms as second nearest neighbours.

1.3 Zinc Selenide (ZnSe)

Large band gap materials including ZnSe have recently gained increasing interest because they are excellent candidates for the blue emitting laser diodes (61). In the first ZnSe based laser diode, a ZnSe waveguide with a ternary \( \text{Cd}_x \text{Zn}_y \text{Se} \) single quantum well was used for the device emitting in the blue-green spectral range at 77K (62). Later, considerable improvement towards higher temperature and shorter wavelength was achieved by use of quaternary layers on GaAs substrates (63-67). Most of the layers are considerably stressed due to lattice mismatch and different thermal expansion coefficients (68). In order to analyse the crystal properties in composite devices, it is important to understand the elastic and electronic properties of crystals under biaxial strain (68,69). Sörgel and Scherz (70) performed the
first principle calculation based on density functional theory using local density approximation (71,72) for cubic ZnSe under uniaxial and biaxial strains. They used separable norm conserving ab initio pseudopotentials (73-75) for the calculation with 3d valence states for Zn, they used Troullier-Martins pseudopotentials (76). Rockwell et al. (77) measured the splitting of the heavy hole and light hole states in ZnSe epilayers grown on GaAs substrates by means of photo modulated spectroscopy under external pressure. Since the substrate and the epilayer material have different elastic properties, the nominal lattice mismatch between the constituents varies when pressure is applied, and consequently tuning varies. Casali and Christensen (53) compared the results with ab initio theoretical calculations of the elastic properties and they investigated the effects of external pressures on the elastic moduli. The elastic constants of ZnSe have been determined by Berlincourt et al. (57) using a piezo resonance technique, and by Lee (68) using ultrasonic echo technique. The dependence of the crystal lattice constant on isotopic substitution of atomic masses is investigated in ZnSe using perturbation theory in a density functional framework by Alberto Debernardi and Cardona (78). Migal et al. (79) report the first observation of piezo electric textures formed in poly crystalline ZnSe during the growth of the crystals. ZnSe bulk crystals often suffer from severe electrical compensation. Some theoretical calculations suggest that the formation energy of native defects would be too high to make them a source of any significant compensation in ZnSe (80,81). Other calculations yielded low formation energies for vacancy-dopant complexes in p- and n- type ZnSe.
Gebauer et al. (84) show that the vacancies in n-ZnSe can directly be identified to be $V_{zn}$ monovacancies forming complexes with the donors, in accordance with Electron Paramagnetic Resonance (EPR). Dai et al. (85) have measured the temperature dependence of the energy $E_0 (T)$ and broadening parameter $T_0 (T)$ of the direct gaps of ZnSe using contactless electroreflectance in the temperature range $25K<T<400K$. Vinogradov et al. (86) obtained the results of the first measurements of the lattice reflection IR spectra from ZnSe/Zn$_{1-x}$Cd$_x$Se ($x = 0.2, 0.4, 0.47$) superlattices. Guan et al. (87) made the Brillouin scattering spectra for ZnSe-ZnSe$_{1-x}$S$_x$ [001] obtained superlattices with the composition $x = 0.2$.

Vodopyanov et al. (88) studied the IR reflectivity and Raman scattering for the single constituent layers of ZnSe/ZnCdSe superlattice grown on GaAs substrate by Molecular Beam Epitaxy. Vodopyanov has reported the measurements of lattice vibrations in ZnSe/ZnCdSe/GaAs superlattices using far infrared reflection spectroscopy. According to Plekhanov (89) the isotopic composition of a crystal lattice exerts some influence on the thermal, elastic and vibrational properties of crystals. These effects are large and can be readily measured by ultrasound, Brillouin, Raman and the neutron scattering. Mosca et al. (90) have studied chemical and structural evolution of thick pseudomorphic ZnSe epilayers grown by Molecular Beam Epitaxy (MBE) on GaAs [001] substrates. ZnSe structure consists of two interpenetrating FCC lattices displaced from each other by one-quarter of a body diagonal. About
each atom, there are four equally distant atoms of opposite kind arranged at the corners of a regular tetrahedron. ZnSe possesses a \( \overline{4} 3m \) point group symmetry and the lattice parameter is \( a = 0.567 \text{nm} \).

### 1.4 Zinc Telluride (ZnTe)

Zinc telluride at ambient condition is a semiconductor with zinc blende crystal structure and a fundamental direct energy gap in the visible spectral range (2.3eV at 300K). Similar to other tetrahedral semiconductors (91) the effect of pressure on the physical properties of ZnTe has been the subject of numerous experimental and theoretical investigations. ZnTe and its solid solutions are widely used in infrared and laser techniques, in nuclear radiation detectors, solar cells and in semiconductor electronics. Sörgel and Scherz (70) have calculated the second-and third-order elastic constants under uniaxial strain. They have used first-principle density-functional theory applied to super cells with the plane wave method and energy cutoffs at 30-40 Ry. Here, the 3d state of Zn is treated as a core state but a non-linear core correction is used for the exchange and correlation energy. They determine internal strain parameter, the density of states and the change of deformation density of ZnTe due to biaxial strain. Camacho et al. (92) have calculated the phonon densities of states, mode Grüneisen parameters and thermal expansion coefficients as a function of pressure for ZnTe using the rigid-ion model. Kurilo et al. (93) made an investigation of some mechanical properties of ZnTe crystal grown by the Bridgman method, by sublimation and by chemical
transport reaction methods. Schall et al. (94) measure the absorption and dispersion spectra of ZnTe below 3THz, in the temperature range between 10K and 300K to show the importance of interaction between long wavelength photons and vibrational modes of the crystal lattice in the interpretation of the spectra.

ZnTe crystallises in zinc blende form. There are eight atoms per unit cell. The lattice parameter of ZnTe is $a = 0.61\text{nm}$ and it possesses a $\overline{4}3m$ point group symmetry.

1.5 Gallium Arsenide (GaAs)

Among the III–V semiconducting compounds, GaAs has been the most widely studied for its elastic properties (95). As a sensor material, GaAs possesses many interesting properties. These include properties such as direct band gap transition and high mobility of electrons. GaAs also has piezoelectric properties comparable with those of quartz, and it exhibits a strong photoelastic effect leading to birefringence and consequently the opto-mechanical polarization effect. Moreover, various physical effects give higher piezo resistive values. GaAs is also considered to be a good material for high temperature electronics due to its large band gap.

The measured elastic stiffness constants $C_{11}$, $C_{12}$ and $C_{44}$ exhibit random variations covering as much wider range in the quoted experimental values. Stefano de Gironcoli et al. (96) calculated the piezo electric constant from...
the stress induced by an applied electric field at vanishing macroscopic strain.

The linear response to the applied perturbation is obtained by a recently introduced self-consistant Green's function method (97). Lambade and Sahasrabudhe (26) suggest a new computational approach to determine the collective phonon-relaxation time for GaAs. The approach is based on the work of Llisavskii and Sternin (98). These calculations are performed in the temperature range 80–300K. Using these relaxation times, they estimated the temperature dependence of attenuation for longitudinal wave along the [110] and [111] directions for shear waves along the [110] direction. Gehrsitz et al. (99) measured the elastic constants and relaxed lattice parameter of the technologically important Al$_x$Ga$_{1-x}$As/GaAs systems by near infrared Brillouin scattering and high resolution X-ray diffraction. The composition of layers is specified by inductively coupled plasma atomic emission spectroscopy, photoluminescence and Raman spectroscopy. There is a significant and unexplained drop in the band gap pressure coefficients of III-V ternary semiconductor alloys grown as strained layers compared with the bulk binary values.

Kubacki et al. (69) introduced the deformation potentials in strained layer heterostructure by measuring the piezoflectance of biaxially strained ZnSe/GaAs layers under additional application of an external uniaxial stress along the [100] axis. Sawada et al. (100) develop the thermo elastic analysis for predictions of slip defect generation on [001] GaAs wafers by means of
the finite element method by considering the anisotropic structure and slip system of dislocation. De Caro et al. (101) introduce a new procedure for the determination of the Poisson’s ratio, the elastic stiffness constant ratios and the lattice parameters of epitaxial films based on the strain tensor determination by high-resolution X-ray diffraction using epitaxial layers simultaneously grow on three different substrate orientation and different alloy compositions. A de Bernabe et al.(38) determine the elastic tensors of thin layers of In$_x$Ga$_{1-x}$As and In$_x$Ga$_{1-x}$P with composition around $x = 0.5$ using surface acoustic waves measured by Brillouin light scattering. Constantino et al. (102) report the stress effects on GaAs at the ZnSe–GaAs hetero interface using the samples with the structures ZnSe/GaAs/GaAs. Glazov and Pashinkin (103) measure the thermal expansion of GaAs and InAs in the temperature ranges 396-1149K and 441-1206K respectively and calculated the thermal expansion coefficient, Debye temperature and root mean square atomic displacements.

Xu et al. (104) reported that a strikingly well defined square two dimensional lattice of InGaAs dots are formed on the GaAs [311] B surface. This remarkable self-organization behaviour is explained by the special ordering mechanism originating from the high elastic anisotropy of the GaAs. According to Dowens et al. (105) there is a significant drop in the band gap pressure coefficients of II–V ternary semiconductor alloys grown as strained layers compared with the bulk binary values. Miyazaki et al. (106) develop a computer code for simulation of dislocation density in a bulk single crystal.
In the computer code they have taken into account the effects of crystal anisotropy such as elastic constants and slip direction by averaging the Young’s modulus, the Poisson’s ratio and resolved shear stress along the azimuthal direction. Using high contrast Brillouin spectroscopy Zuk et al. (107) investigated the acoustic waves in supported layers formed on GaAs substrates. Miyazaki et al. (108) develop a computer code for dislocation density evaluation of a single crystal ingot during annealing process. In this the temperature in a single crystal ingot is used as input data, which are obtained from a transient heat conduction analysis. Flannery et al. (109) have investigated both experimentally and theoretically, the Surface Acoustic Wave (SAW) velocity behaviour on [001], [111], and [311] surfaces for GaAs. Several different acoustic modes can be measured on each surface. Fil (110) has considered the piezo electric mechanism for the orientation of stripes in two dimensional electron systems in GaAs–AlGaAs heterostructures. When the anisotropy of the elastic constants and the influence of the boundary of the sample are taken into account, the theory gives orientations of the stripes along [110] direction, which is in agreement with the experimental data.

A theoretical study of variation in exciton binding energy with quantum dot size and dot in plane and perpendicular separation for periodic arrays of self organized InGaAs/GaAs quantum dots was conducted by Andreev and O’reilly (111). Pletal et al. (112) present a complete first-principle study of trends in the lattice dynamics of tetrahedral semiconductors.
in the zinc blende or diamond structure, using the plane-wave pseudopotential method within density-functional perturbation theory. They also present phonon-dispersion curves, eigen vector phases and the results of the calculation of some linear and non-linear elastic constants.

Sorokin et al. (113) modified the simplified phenomenological theory based on a conception of finite strains, which appear in a solid during thermal expansion and the propagation of small amplitude bulk acoustic waves under such conditions. Thus the temperature dependence of the second-order elastic constants is calculated for a series of cubic crystals with various type of predominant chemical bonding. To make a deeper understanding of the physio-chemical nature of melts of these compounds, Glazov and Shchelikov (114) conducted a detailed study of the temperature dependence of the specific volume of their melts. The composition dependence of the elastic constants and the related properties for quaternary semiconductor alloy \( \text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{Sb}_{1-y}/\text{InAs} \) are reported by Bouarissa and Bachiri (115). Applying lithographic and Focused Ion Beam (FIB) techniques for \( \text{InAs}/\text{GaAs} \) heterostructures on [111] surface, Yamaguchi et al. (116) have successfully fabricated and characterized several Free Standing (FS) structure with InAs thickness ranging from 50 to 300nm.

Sörgel and Scherz (70) have made ab initio calculations for the higher order elastic constants, internal strain parameters and relative deformation potentials of GaAs. Detlef Conrad and Kurt Scheerschmidt (117) proposed a
parameter set for GaAs, yielding elastic constants and surface defect properties. GaAs exists in zinc blende structure, which can be considered as a special form of diamond structure. Unlike in diamond structure, the two interpenetrating FCC sublattices are of different atoms—one composed entirely of Ga atoms, the other entirely of As atoms. The four nearest neighbours of an atom are of the opposite kind and disposed tetrahedrally.

1.6 Finite Strain Theory of Elasticity

Consider an elastic medium where the co-ordinates of any point can be denoted as \((a_1, a_2, a_3)\). Choose a set of orthonormal vectors \(e_1, e_2, e_3\) as the basis vectors for the co-ordinate system and denote the \(k^{th}\) component of the stress acting on the plane \(e_i = 0\) by \(\sigma_{ik}\) where \(i\) and \(k\) are the component indices. Consider the equilibrium of a small element centered at the point \(a_i\) and bounded by the plane \(a_i + \frac{1}{2} da_i\). Let \(u_i\) denote the elastic displacement of the point \(a_i\) of the body and \(\rho\) the density of this point. The equation of volume element can be derived by considering the total force acting on the volume element. If we ignore the body forces, the equations of motion for an elastic solid can be written as (the convention that repeated indices indicate summation over the indices will be followed here).

\[
\rho \ddot{u}_i = \frac{\partial \sigma_{ik}}{\partial a_k}
\]  

(1.1)

where the stress tensor \(\sigma_{ik}\) is given by

\[
\sigma_{ik} = \frac{\partial \phi}{\partial e_{ik}}
\]  

(1.2)

where \(\phi\) is the crystal potential and \(e_{ik}\) are the components of the strain tensor given by
\[ \varepsilon_{ik} = \frac{1}{2} \left( \frac{\partial u_k}{\partial a_i} + \frac{\partial u_i}{\partial a_k} \right) \]  

(1.3)

\[ \sigma_{ik} \text{ and } \varepsilon_{ik} \text{ are symmetric tensors of second rank. According to Hook’s law} \]

\[ \sigma_{ik} = C_{iklm} \varepsilon_{lm} \]  

(1.4)

The constants \( C_{iklm} \) form a fourth rank tensor with 81 components.

From equations (1.2) and (1.4), we have

\[ C_{iklm} = \frac{\partial \sigma_{ik}}{\partial \varepsilon_{lm}} = \frac{\partial^2 \phi}{\partial \varepsilon_{lm} \partial \varepsilon_{ik}} = \frac{\partial^2 \phi}{\partial \varepsilon_{ik} \partial \varepsilon_{lm}} = C_{lm,ik} \]  

(1.5)

Hence the elastic constants \( C_{iklm} \) are multiple strain derivatives of the state functions and since the strains \( \varepsilon_{lm} \) are symmetric, the elastic constants possess complete Voigt symmetry. Thus,

\[ C_{iklm} = C_{klm} = C_{ikml} = C_{lmik} \]  

(1.6)

These quantities are symmetric with respect to interchange of the subscripts. It will be convenient to abbreviate the double subscript notation to the single subscript Voigt notation running from 1 to 6, according to the following scheme:

11→1; 22→2; 33→3; 23→4; 13→5 and 12→6.

Hence the matrix of elastic constants \( C_{iklm} \) would contain a 6 \times 6 array of 36 independent quantities in the most general case. This number is, however, reduced to 21 by the requirements that the matrices be symmetric on interchange of double indices. The number of independent elastic constants will be further reduced by the symmetry operations of the respective crystal classes. The cubic compounds have three independent elastic constants (118). The elastic constant matrix for this class of compounds is given by
In the equation of motion for an elastic medium, the forces on an element of volume are given by the divergence of the stress field.

Using equations (1.3) and (1.4), the equation (1.1) can be written as

\[
\rho \ddot{u}_i = \frac{\partial}{\partial a_j} \left[ C_{ijkl} \left( \frac{\partial u_k}{\partial a_i} + \frac{\partial u_l}{\partial a_k} \right) \right]
\]  

(1.8)

For an elastic plane wave, we have

\[
u_k = A_k \exp(i(\omega t - \mathbf{k} \cdot \mathbf{r})
\]

(1.9)

where \(A_k\) are the components of the amplitude of vibration, \(\omega\) is the angular frequency and \(\mathbf{k}\) is the wave vector corresponding to the wavelength \(\lambda = 2\pi/k\).

The resulting equations of motion from equation (1.8) are

\[
(\rho \omega^2 \delta_{im} - C_{ijkl} k_j k_l) u_m = 0
\]

(1.10)

Substituting \(k = \mathbf{k} \hat{n}\), where \(\hat{n}\) is the unit vector, we get

\[
(T_{ijm} n_j n_l - \nu^2 \delta_{im}) u_m = 0
\]

(1.11)
where \( T_{ijkl} = C_{ijkl}/\rho \) are the reduced elastic constants and \( v \) is the phase velocity given by \( v = \omega/k \). The components of second rank tensor \( \Lambda \) are given by

\[
\Lambda_{ij} = T_{ijkl} n_j n_l
\]  
(1.12)

Hence equation (1.11) can be written as

\[
(\Lambda - v^2)u = 0
\]  
(1.13)

This shows that \( u \) is the eigen vector of tensor \( \Lambda \) where eigen value is \( v^2 \). Hence \( v^2 \) is the root of the equation

\[
|\Lambda - v^2| = 0
\]  
(1.14)

The theory of elastic waves generally reduces to find \( u \) and \( v \) for all plane waves propagating in an arbitrary direction for crystals possessing different symmetries. In this situation, all terms in equation (1.11) that involves differentiation with respect to co-ordinates other than that along the propagation direction drop out.

A more fundamental significance to the elastic constants is implied by their appearance as the second derivatives of elastic energy with respect to strains. It should be noted here that the stored elastic energy is only a part of the complete thermodynamic potential of the crystal, since it depends on many other variables. Also, one can introduce elastic constants as a constitutive, local relation between stress and strain for materials in which long-range atomic forces are unimportant.

Let the position co-ordinates of a material particle in the unstrained state be \( a_i \) \((i = 1, 2, 3)\). Let the co-ordinates of the material particle in the strained state be \( x_i \). Consider two material particles located at \( a_i \) and \( a_i + da_i \).
Let their co-ordinates in the deformed state be $x_i$ and $x_i + dx_i$. The elements $dx_i$ are related to $da_i$ by the equation

$$dx_i = \frac{\partial x_i}{\partial a_i} da_i$$

$$= \sum_{j=1}^{3} (\delta_{ij} + \varepsilon_{ij}) da_i$$  \hspace{1cm} (1.15)

The convention that repeated indices indicate summation over the indices will be followed here. $\delta_{ij}$ is the Kronecker delta and $\varepsilon_{ij}$ are the deformation parameters. The Jacobian of the transformation

$$J = \text{Det}\left(\frac{\partial x_i}{\partial a_i}\right)$$  \hspace{1cm} (1.16)

is taken to be positive for all real transformations. If $dV_a$ is a volume element in the natural state and $dV_x$ its volume after deformation

$$\frac{dV_x}{dV_a} = \frac{\rho_0}{\rho} = J$$  \hspace{1cm} (1.17)

where $\rho_0$ and $\rho$ are the densities in the natural and strained states respectively. Let the square of the length of arc from $a_i$ to $a_i + da_i$ be $dl_0^2$ in the unstrained state and $dl^2$ in the strained state. Then

$$dl^2 = dx_i dx_i - da_i da_i$$

$$= \left(\frac{dx_i}{da_i} \frac{dx_j}{da_j} - \delta_{ik}\right) da_i da_k$$

$$= 2\eta_{ik} da_i da_k$$  \hspace{1cm} (1.18)

where $\eta_{ik}$ are the Lagrangian strain components which are symmetric with respect to the interchange of the indices $j$ and $k$. In terms of $\varepsilon_{ik}$,

$$\eta_{ik} = \frac{1}{2} \left( \varepsilon_{ik} + \varepsilon_{ki} + \sum_j \varepsilon_{ij} \varepsilon_{jk} \right)$$  \hspace{1cm} (1.19)
The internal energy function $U(S, \eta_{jk})$ for the material is a function of the entropy $S$ and Lagrangian strain components. $U$ can be expanded in powers of the strain parameters about the unstrained state as

$$U = U_0 + \frac{1}{2!} \left[ \frac{\partial^2 U}{\partial \eta_{ij} \partial \eta_{kl}} \right]_{0,S} \eta_{ij} \eta_{kl} + \frac{1}{3!} \left[ \frac{\partial^3 U}{\partial \eta_{ij} \partial \eta_{kl} \partial \eta_{mn}} \right]_{0,S} \eta_{ij} \eta_{kl} \eta_{mn} + \ldots$$

(1.20)

The linear term in strain is absent because the unstrained state is one where $U$ is minimum. We shall define the elastic constants of different orders referred to the unstrained state as

$$C_{ij,kl}^S = \left[ \frac{\partial^2 U}{\partial \eta_{ij} \partial \eta_{kl}} \right]_{0,S}$$

and

$$C_{ij,kl,mm}^S = \left[ \frac{\partial^3 U}{\partial \eta_{ij} \partial \eta_{kl} \partial \eta_{mn}} \right]_{0,S}$$

(1.21) (1.22)

Here the derivatives are to be evaluated at equilibrium configuration and constant entropy. $C_{ij,kl}^S$ and $C_{ij,kl,mm}^S$ are the adiabatic elastic constants of second- and third-orders respectively. They are tensors of fourth and sixth ranks. The number of independent second- and third-order elastic constants for different crystal classes are tabulated by Bhagavantam (118).

1.7 Quasi-harmonic Theory of Thermal Expansion

In the harmonic approximation, the atoms in a solid are assumed to oscillate symmetrically about their equilibrium positions, which remain unaltered irrespective of the temperature. The thermal expansion of a solid, therefore, is a property arising strictly due to the anharmonicity of the lattice. In the quasi-harmonic approximation, the oscillations are still assumed to be harmonic in nature but the frequencies are taken to be functions of the strain...
components in the lattice. The strained state of the lattice is specified fully by the six strain components \( \eta_{rs} \) (\( r, s = 1, 2, 3; \eta_{rs} = \eta_{sr} \)).

A normal mode with frequency \( \omega(q,j) \) makes a contribution \( F(q,j) \) to the total vibrational free energy \( F_{vib} \), given by

\[
F(q,j) = K_B T \left[ \frac{1}{2} X + \log(1 - e^{-X}) \right] \tag{1.23}
\]

where \( X = \frac{\hbar \omega(q,j)}{K_B T} \), \( \hbar = h/2\pi \), \( h \) being the Plank’s constant, \( K_B \) is the Boltzmann’s constant, \( T \) is the absolute temperature and \( q \) is the wave vector of the \( j^{th} \) acoustic mode. The total vibrational free energy is, therefore

\[
F_{vib} = \sum_{q,j} F(q,j)
= K_B T \sum_{q,j} \left[ \frac{1}{2} X + \log(1 - e^{-X}) \right] \tag{1.24}
\]

The thermal coefficients \( \alpha_{lm} \) of the crystal are obtained as

\[
\nu \alpha_{lm} = \left[ \frac{\partial}{\partial \sigma_{lm}} \left( \frac{1}{2} F_{vib} \right) \right]_{(\sigma^{'}, \sigma)}
= \sum_{q,j} S_{lm,rs} \gamma_{rs}(q,j) \frac{1}{K_B \sigma}[\omega(q,j), T] \tag{1.25}
\]

Here, \( \alpha_{lm} = \left( \frac{\partial \eta_{lm}}{\partial T} \right)_{\sigma} \)

\( \sigma_{lm} \) are the components of the stress tensor, \( S_{lm,rs} \) are the compliance coefficients relating \( \eta_{rs} \) and \( \sigma_{lm} \) and

\[
\gamma_{rs}(q,j) = \left[ \frac{\partial}{\partial \eta_{rs}} \log \omega(q,j) \right] \tag{1.26}
\]

Here, \( \gamma_{rs} \) are the generalised Grüneisen parameters (Gps) of the normal mode frequencies. In equation (1.25), the subscript \( \sigma' \) means that all other \( \sigma_{ik} \) are to be held constant while differentiating with respect to \( \sigma_{lm} \) and subscript \( \sigma \) means that all \( \sigma_{lm} \) are held constant. \( \sigma[\omega(q,j), T] = X^2 e^{-X}/(1-e^{-X})^2 \) is the
Einstein specific heat function. In the quasi-harmonic approximation, the Gps are assumed to be constants independent of temperature.

It is more advantageous to choose such strains that do not alter the crystal symmetry, instead of choosing any arbitrary strain, while defining Gps. For ZnS, ZnSe, ZnTe and GaAs, there is only one principal thermal expansion coefficient namely \( \alpha \). Here, it is convenient to use the following strains for the determination of the thermal expansion.

(i) A uniform areal strain \( \varepsilon \) in the basal plane

(ii) Then \( \eta_{11} = \eta_{22} = \eta_{33} = \varepsilon/3 \). All other \( \eta_{ij} \) vanish.

\[
\gamma'(q, j) = -\frac{\partial \log \omega(q, j)}{\partial \log \lambda} \quad (1.27)
\]

From equation (1.25), we now obtain

\[
\nu \alpha = \sum_{q, j} [2S_{12} \gamma(q, j) + S_{11} \gamma(q, j)] K_B \sigma(\omega(q, j)) \quad (1.28)
\]

The effective Grüneisen parameters are defined as

\[
\gamma_\ell(T) = \left( \left( C_{11}^S + 2C_{12}^S \right) \alpha \right) V / C_p \quad (1.29)
\]

The \( C_{ij}^S \) are the adiabatic elastic constants, \( C_p \) is the specific heat at constant pressure and \( V \) is the volume of the crystal.

Comparing equations (1.29) with (1.28), we get

\[
\gamma_j(T) = \frac{\sum_{q, j} \gamma(q, j) \sigma[\omega(q, j), T]}{\sum_{q, j} \sigma[\omega(q, j), T]} \quad (1.30)
\]

The expression (1.30) gives the temperature dependence of effective Grüneisen parameter.
In the low temperature limit, only the low frequency acoustic modes make a contribution to the specific heat. The number of such normal modes in the \( j \)th acoustic branch is proportional to \( v_j^{-3}(\theta,\phi) \), where \( v_j(\theta,\phi) \) is the velocity of the \( j \)th acoustic mode travelling in the direction \((\theta,\phi)\). The GP \( \gamma(q,j) \) depends only on the branch index \( j \) and the direction \((\theta,\phi)\). It is independent of the magnitude of the wave vector \( q \). The effective lattice Grüneisen parameters \( \gamma_j \) approach the limits defined below, at low temperatures.

\[
\lim_{T \to 0} \gamma(T) = \gamma(0) = \frac{\int \sum_{j=1}^{3} \gamma_j(\theta,\phi) v_j^{-3}(\theta,\phi) d\Omega}{\int \sum_{j=1}^{3} v_j^{-3}(\theta,\phi) d\Omega}
\]

where \( \gamma(0,\phi) \) are the GPs for the acoustic modes propagating in the direction \((\theta,\phi)\). Calculation of the low temperature limit of \( \gamma(T) \) is possible knowing the pressure derivatives of the second-order elastic constants (SOEC) or the third-order elastic constants (TOEC) of the crystal. The evaluation of the low temperature limits \( \gamma(0) \) for ZnS, ZnSe, ZnTe and GaAs is given in Chapter 6 of this thesis.
References


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