Synopsis

Recently, there has been a spurt in the study of the nonlinear elastic properties of semiconducting crystals. This is due to the fact that, by altering the epitaxial strain on the crystal, the crystal structure is altered. This structural freedom provides an opportunity for making more efficient and reliable electronic devices by choosing appropriate polyptism. The understanding of the pressure dependence on the elastic constants is essential in the device fabrication and the third order elastic constants provide a better understanding of the pressure dependence of the elastic constants. The elastic constants of the semiconducting crystals are essential in predicting and understanding the material response, strength, mechanical stability and phase transitions in them.

In parallel with the experimental and phenomenological studies, theoretical investigations have been made from the thermodynamical and lattice dynamical points of view regarding the elastic and thermal properties. Elastic properties link thermodynamically with specific heat, thermal expansion, Debye temperature and Grüneisen parameters. In engineering design, elastic constants enter many practical applications: load deflection, thermoelastic stress, internal strain, sound velocities and fracture toughness.

A theoretical treatment of the elasticity in uniaxial crystals is difficult when realising that the strains needed to calculate them give rise to a geometry with low symmetry. The use of pseudopotential models for solids of low symmetry and for many electron solids which yield physically acceptable results is cumbersome. Phenomenological models which attempt to study the elastic and thermal properties would carry a large number of force constants. Thus the theoretical modelling to explain the anharmonic properties of solids is quite an involved problem.

The wurtzite structure has a hexagonal unit cell with two lattice parameters a and c with the ideal ratio c/a =1.633 and belongs to the space group $P6_3mc$. Each of the two interpenetrating hexagonal close packed sublattices, consists of one type of atom

displaced with respect to each other along the threefold c-axis. The basal plane lattice parameter is universally represented by a; the axial lattice parameter, perpendicular to the basal plane, is described by c. Each sublattice contains four atoms per unit cell, and every atom of one kind is surrounded by four atoms of the other kind, or vice versa, which are coordinated at the edges of a tetrahedron. There are six second order elastic constants and ten third order elastic constants for such system of crystals. In uniaxial crystals there are two principal linear thermal expansion coefficients, one parallel to the unique axis and the other perpendicular to the unique axis. The symmetry of the crystal brings about some simplifying features in the characteristics of the elastic wave propagation in it.

The thesis represents a modest attempt on the difficult problem of working out the complete sets of non-vanishing second order elastic constants and third order elastic constants of the hexagonal wurtzite cadmium sulphide (CdS), cadmium selenide (CdSe), cadmium telluride (CdTe), aluminium nitride (AlN), gallium nitride (GaN), indium nitride (InN) and silicon carbide (SiC). The strain energy has been derived using finite strain elasticity theory by considering interactions upto four nearest neighbours of each atom in the unit cell. This is then compared with the strain dependent lattice energy density obtained from the continuum model approximation to obtain the expressions for the second and third order elastic coefficients.

We have determined the properties quantifying the anharmonic behaviour of the materials, such as the pressure derivatives of the second order elastic constants and the low temperature lattice thermal expansion by expressing their relationship with the higher order elastic constants. The II-VI, III-V and IV-IV groups of semicondctors are technologically important and the nonlinear effects are particularly significant. The knowledge of the third order elastic constants will definitely improve the design and fabrication of more efficient electro mechanical devices.

The present study has four objectives.

1. Determination of the second order elastic constants of the semiconductor crystals.

2. Determination of third order elastic constants of the semiconductor crystals.

3. Determination of the first order pressure derivatives of the second order elastic constants of the semiconductor crystals.

4. Determination of the low temperature limits of the lattice thermal expansion of these crystals.

The thesis is divided into six chapters. The following are the results of the work reported in the thesis:

Chapter 1 gives a brief review of the II-VI, III-V and IV-IV semiconducting crystals. A literature survey is conducted on CdS, CdSe, CdTe, AlN, GaN, InN and SiC with a focus on their structural and mechanical properties. Basic poperties of these materials are also discussed .

In Chapter 2, an introduction to the finite strain elasticity theory of Murnaghan is presented. The theory behind the method of calculating the full sets of second order elastic constants and third order elastic constants is presented. The expressions for the effective second order elastic constants of hexagonal systems based on the finite strain elasticity theory in the natural state and deformed state are given. The basic importance of these expressions is that they enable one to fix up the anharmonic parameters in the potential energy of the crystal in the lattice dynamical model which are used to study the anharmonic properties such as thermal expansion. Expressions for the pressure derivatives of the second order elastic constants using the finite strain elasticity theory are also presented in this chapter.

A procedure to obtain the mode Grüneisen parameters and also the low temperature limits of the thermal expansion from the quasi-harmonic theory of thermal expansion is described in detail for uniaxial crystals. The low temperature behaviour of the lattice

thermal expansion depends on the generalized Grüneisen parameters for the elastic modes propagating in the crystal. These Grüneisen parameter can be calculated (and hence the low temperature limits of the Grüneisen parameters $\bar{\gamma}_{\perp}$ and $\bar{\gamma}_{\parallel}$) from a knowledge of the third order elastic constants.

Chapter 3 describes the second order elastic constants and third order elastic constants for II-VI group semiconductors - CdS, CdSe and CdTe. Interatomic interactions extending upto four neighbours are worked out such that the potential is automatically invariant towards rigid rotations and translation. The five independent second order elastic constants and ten third order elastic constants are derived. From the analysis of the results obtained from second order elastic constants for CdS, CdSe and CdTe, it is observed that the contribution from the longitudinal modes is greater than that from the shear counterparts.

Atomistic study of the wurtzite phase of group III-nitrides is presented in chapter 4. From the study of second order elastic constants of AlN, GaN and InN, it is observed that for all the three semiconductor materials C_{33} is greater than C_{11}, consequently the in-plane bonding is weaker than the out of plane bonding. It is also found that for all the three materials C_{44} and C_{66} are smaller than their longitudinal counterparts. The third order elastic constants of AlN, GaN and InN are negative, indicating an increase of the vibrational frequencies under stress. The absolute values of all the third order elastic constants are large. This means that the wurtzite phase of AlN, GaN and InN observed is considerably anharmonic. The second order elastic constants and third order elastic constants are used to investigate the pressure derivatives of the second order elastic constants and there by study the behaviour of longitudinal and shear moduli under pressure. The obtained results confirm the previous experimental works in which GaN and InN becomes softer in shear-type acoustic vibrations. The pressure derivatives of C_{11} and C_{33} for all the three materials increase linearly with pressure, but show negative dependence with pressure for C_{44} and C_{66}. From the study of the Grüneisen parameter

of the three semiconductor crystals, it is observed that the transverse acoustic branch γ_1', anisotropy is large in all the three materials. Anisotropy in γ_1' reduces when the applied strain is parallel to the hexagonal axis. For all these three semiconductors the values of the Grüneisen parameter γ' and γ'' are small.

Chapter 5 gives the second order elastic constants, third order elastic constants and the pressure derivatives of the second order elastic constants of SiC together with the polycrystalline aggregate elastic moduli and its pressure derivatives. The layers close up substantially under hydrostatic pressure while the change in interatomic distance in a layer is much smaller. The results on the pressure derivative along the c-axis and the pressure derivative of the elastic constant in the ab-plane establish the above characteristics. Third order elastic constants of SiC are all negative indicating an increase in vibrational frequencies under stress, giving rise to an increase in the strain energy. The pressure derivatives of pure shear single-crystal elastic constants are negative, corroborates the results obtained in polycrystalline elastic moduli where pressure derivative of the shear modulus is negative. The softening of the shear modulus predicts the first order structural phase transition induced by pressure in SiC. The ten third order elastic constants of the hexagonal silicon carbide have been determined.

The wave velocities and the Grüneisen parameters for the elastic waves propagating at different angles θ to the c-axis in silicon carbide are reported. The plots of the variation of the Grüneisen parameters γ' and γ'', for the three acoustic branches as a function of the angle which the direction of propagation makes with the hexagonal axis are studied. The anisotropy in the γ_1' branch is more pronounced than that in the γ_2' branch. The low temperature limit of the volume Grüneisen function for silicon carbide is obtained.

In Chapter 6, the results of the present work are summarised. It is observed that SiC has the highest value for the second order elastic constants. This is due to the smaller bond length associated with SiC structure. It is also observed that the distance between nearest neighbours is smallest for SiC compared with the other crystals. The third order

elastic constants which quantify the coefficients of the cubic term in the expansion of strain energy density of CdS, CdSe, CdTe, AlN, GaN, InN and SiC are also given.

In the semiconducting compounds under study, the pressure induced variations in pure shear modes are negative, while a linear positive dependence in pressure is observed for longitudinal coefficients. Softening of transverse acoustic phonons is known to be an important precursor to structural transformation and this phenomenon has been widely used to explain first order phase transition induced by temperature or pressure. The low temperature limits of the volume Grüneisen functions γ_L obtained in the present work for the semiconducting materials are presented. The future scope of work is also indicated.

Most of the work presented in this thesis have either been published or presented in conferences or are in the process of publication. A list of such publications is given below:

Publications

1. Non-linear elastic characterization of hexagonal cadmium selenide.
   Sindu Jones and C.S. Menon, Physica B, 437: 82 (2014)

2. Non-linear elastic behaviour of hexagonal cadmium sulfide single crystals.
   Sindu Jones and C.S. Menon, Eur. Phys. J. B 87: 85 (2014)

3. Non-linear elastic effects in hexagonal silicon carbide single crystal.
   Sindu Jones and C.S. Menon, Phys. Status Solidi B 251: 1186 (2014)

4. Higher Order Elastic Constants Of Hexagonal Silicon Carbide.
   Sindu Jones and C.S. Menon, National Seminar on Nanoscience & Engineering, 22-23 Jan 2013.

5. Non-Linear Elastic Behavior Of Hexagonal Aluminium Nitride And Gallium Nitride.
   Sindu Jones, 25^{th} Kerala Science Congress, 27-29 Jan, 2013.

6. Low Temperature Thermal Expansion Of Hexagonal Crystals-Aluminium Nitride And Gallium Nitride.
   Sindu Jones, 25^{th} Kerala Science Congress, 27-29 Jan, 2013.

7. Acoustic Vibrations In Wurtzite Cadmium Sulfide Single Crystals.
   Sindu Jones and C. S. Menon, 4^{th} International conference for perspective vibrational spectroscopy (ICOPVS), 6-9 Aug, 2013.

8. Non-Linear Elastic Constants Of Hexagonal Cadmium Selenide.
   Sindu Jones and C. S. Menon, 23^{rd} Swadeshi Science Congress, 6-8 Nov, 2013.

9. Non-Linear Elastic Coefficients In Wurtzite Cadmium Telluride Single Crystals Under Pressure.
   Sindu Jones, C. S. Menon and S. P. Kuruvilla, 23^{rd} Swadeshi Science Congress, 6-8 Nov, 2013.

10. Acoustic Vibrations In Hexagonal Silicon Carbide Single Crystals.
    Sindu Jones and C. S. Menon, 23^{rd} Swadeshi Science Congress, 6-8 Nov, 2013.

11. Pressure derivatives of the elastic moduli of polycrystalline aggregate of hexagonal wurtzite phase of CdX (X= S, Se) semiconductors from elastic constants of single crystal pressure derivatives.
    Sindu Jones and C. S. Menon, 26^{th} Kerala Science Congress, 28-31 Jan, 2014.

12. Non-linear elastic coefficients in wurtzite aluminium nitride single crystals under pressure.
    Sindu Jones and C.S. Menon, (communicated to Solid State Communications)