Chapter 7

Summary

The high pressure research is currently a very active area of research the world over. During the past few years, there has been impressive progress in the experimental as well as theoretical techniques in handling the effect of pressure as a thermodynamic variable on materials. In the experimental field, advances in the diamond anavil cell technology coupled with the laser heating technique have facilitated the understanding of the behavior of materials under the high pressure and high temperature conditions existing in earth and other planetary interiors. Also the developments of microscopic techniques, spectroscopic and flash X-ray diffraction, have made it possible to probe with nano second resolution the changes occurring in the shocked condensed state. In the theoretical field, with the advent of the supercomputing speeds and availability of newer algorithms, the computational methods have acquired new predictive capabilities. With these developments, there has been an intense and exciting interplay between experiment and theory.

Under normal conditions, solids exhibit a particular crystal structure for which the total energy is minimum. However, on application of pressure the atomic arrangement in solid changes resulting into change in interatomic distance and crystal structure. The pressure at which such structural changes occurs is called phase transition pressure. In the absence of the phase transition the phonon frequencies are expected to increase with the application of the hydrostatic pressure. This is because the atoms are brought closer to each other under compression and hence they sit in steeper potential wells. This is termed as normal behavior of phonon under pressure. However, often one encounters a few phonons, which shows the opposite behavior i.e. the frequency of some phonon decreases with increasing pressure. A decrease in frequency implies a reduction in corresponding force constant, which in turn is connected to elastic constants. The phonon, which exhibit decrease in frequency with increasing pressure, is called a soft phonon as it leads to softening of the lattice. This also points towards instability of the crystal structure against certain atomic vibrations and displacements and often leads to structural phase transition. This may result in (a) discrete change in the phonon energies (b) disappearance or appearance of the new modes or (c) splitting of degenerate modes or a combination of these. Similarly, the study of microscopic atomic dynamics in the condensed matter at the high densities, i.e. the study of the relative motion among particles under pressure, can give the information on issues such as inter atomic force constants, departure from two body potential approximations, Anharmonicity of crystal potential and the mechanism responsible for the phase transition.

The use of diamond anavil cell for optical absorption and reflectivity measurements, inelastic light scattering (Raman and Brillouin) and x-ray diffraction techniques have stimulated considerable interest in the high pressure studies for the electrical and the vibrational properties of materials. Since the available pressure range is so high (~ 500 GPa). One may, in principle observe many new phenomenon concerning the behavior of solids. For example, the shifts in the energy gap with pressure have been reported in the recent year using optical absorption and luminescence measurements.

For extracting the information regarding the vibrational properties at high pressure, from among the available techniques, Raman scattering is probably the most amenable method. Cardona and his co-workers have recently used Raman spectroscopy to observe the effect of pressure on the lattice dynamics of III-V compounds upto their phase transition pressure. With the recent developments in high pressure and neutron diffraction techniques, the interest in Raman studies has significantly increased in recent years. When a material undergoes a phase transition, the phonon mode may undergo changes, some mode can disappear, some new modes can appear, and the intensity of the modes in the daughter phase ca become drastically different from the initial phase. All these can be picked up during Raman scattering measurements.

Despite the wealth of information about the pressure dependent vibrational properties, very few realistic attempts have been made to understand the existing experimental data. To extract the knowledge on the interatomic binding forces in the semiconducting compounds under compression and to relate the information to effects on phonons and structural instabilities, the existing experimental results provide us a good testing ground for theoretical studies.

A comprehensive study for the pressure induced vibrational properties of III-nitrides, phosphides and antimonide is reported using a realistic dynamical models. In this macroscopic approach, once the pressure dependence of the model parameters in a solid is accurately established, nearly all of its all vibrational properties at $P \neq 0$ can be predicated with reasonable success. In conclusion we have calculated pressure dependence of the phonon dispersion curves, phonon density of states, mode Grüneisen parameters and specific heat at constant volume for nitrides (InN, GaN, AlN and BN), III-phosphides (InP, GaP and BP) and III-antimonide (GaSb) by using rigid ion and deformation bond approximation model. It is observed that the energies of the optical phonons as well as longitudinal acoustic phonons increase with pressure. The important observation of the dispersion curves can be summarized as follows:

(1) The energies of zone boundary and near zone boundary TA phonons from the lowest branch decrease or soften with pressure. The shifts of the TA(X) and TA (L) phonons are typical of effect seen in other large $\vec{q}$ phonons from this branch.

(2) The transverse optical phonons [TO (Γ)] is found to shift faster than the [LO (Γ)]. So that the splitting [ω_{LO}- ω_{TO}] at Γ point decrease with pressure.

Phonon density of state calculated at high pressure corresponding solid show pronounced shift in the frequency spectrum with pressure. The mode Grüneisen parameters indicates that TA phonon modes have negative values and responsible for the lattice softening. Specific heat at constant volume, Cv increases with pressure for all considered compounds. The calculated results are in general good agreement with the available experimental data.

The static properties of $Zn_{1-x} M_xSe$ diluted magnetic semiconductor (DMS) and mechanical, elastic and anharmonic properties of Zn1-xCrxTe DMS have also been reported by using phenomenological model based on the charge transfer effects due to deformation of the electronic shell of overlapping ions. The obtained results agree reasonably well with the experimental data. The decrease in Debye temperature with increase in Cr concentration in Zn1-xCrxTe suggests that the lattice gets soften with the increase in Cr concentration. As for a high pressure behavior of zn1-xMnxSe is concerned there is systematic trend, identical to that observed in other compound of zinc blende structure family. The Born and relative stability criteria have been predicated successfully.

A comprehensive study for the pressure induced vibrational properties of III-nitrides is reported using a realistic dynamical model in chapter 4. In this macroscopic approach, once the pressure dependence of the model parameters in a solid is accurately established, nearly all of its vibrational properties at $P \neq 0$ can be predicated with reasonable success. In conclusion, we have calculated the pressure dependence of the phonon dispersion curves, phonon density of states, mode Grüneisen parameters, and specific heat at constant volume for III- nitrides namely InN, GaN, AlN and BN by using rigid ion model. It is observed that the energies of the optical phonons (both longitudinal and transverse) as well as longitudinal acoustic phonons increase with pressure. Phonon density of states calculated at high pressure of corresponding solid, show pronounced shift in the frequency spectra with pressure. The mode Grüneisen parameter indicates that the TA phonon modes have negative values and responsible for the lattice softening. Specific heat at constant volume, C_v increases with pressure for all compounds

In the chapter 5, a comprehensive lattice dynamical study of InP, GaP, BP and GaSb under pressure is reported by using two lattice dynamical model theories namely rigid ion and deformation bond approximation models. It is observed that the energies of the optical phonons and longitudinal acoustic phonons increase with pressure, while the transverse acoustic phonon frequency decreases for all considered compounds. The phonon density of states show pronounced shift in the frequency spectra with pressure.

The gap in the phonon spectra at both ambient and high pressure decreases as the mass ratio decreases. The mode Grüneisen parameter indicates that the TA phonon modes have negative values and responsible for the lattice softening . The lattice specific heat at constant volume, C_V increases with pressure all compounds.

The chapter 6 reports the systematic investigations of the structural phase transition, high pressure behavior and anharmonic properties of ZnSe compound doped with Cd, Fe and Mn ions by using a theoretical approach which considers the effect of charge transfer due to the overlap of neighboring ions in the crystal energy. The results obtained for $Zn_{0.9}Cd_{0.1}Se$, $Zn_{0.84}Fe_{0.16}Se$ and $Zn_{0.76}Mn_{0.24}Se$ are in general good agreement with the available experimental data. It reflects that the pressure which causes the reduction in the interatomic distance in these compounds has been properly included in the potential. It seems that the potentials potential which takes account of charge transfer is successful in describing the investigated properties as the charge transfer increases with the increase of pressure. However, the deviation in agreements might be due to the exclusion of the effect of covalency in these compound semiconductors. We have seen that the stability criterion has been satisfied for these compounds. The calculations show that the zinc blende structure is more stable for all these three compounds.

The results obtained on the mechanical, elastic and anharmonic properties of $Zn_{1-x}Cr_xTe$ ($0\leq x\leq 1$) agree fairly well with the available experimental data. The elastic constants decrease with the increase of Cr concentration. Debye temperature which has been calculated by using the value of elastic constants decreases with increase in concentration of Cr at room temperature. Obtained value of anisotropy predicts that material will be anisotropic in elastic behavior. The decrease of Debye temperature with the Cr concentration suggests that these compounds get soften with the increase of Cr concentration. Overall results are in good agreement with experimental values, which indicates success of our approach.