Chapter 1

Introduction

Materials at high pressure occur at the center of planets and in stars and in both natural and man-made explosions. High pressure may also be applied to small laboratory samples in a controlled manner using devices such as the diamond anavil cell (DAC) [1-3]. The intense scientific and technological interest in the nature of materials under the extreme conditions has long been a subject of speculations and extrapolation due to the phenomena such as structural phase transformation [4-5], metallization [6], metal–semiconductor transitions, electronic transitions and high pressure phonon dynamics [7-8]. Over the last few years, study of materials under high pressure has become an extremely important subject displaying explosive growth. This is primarily due to both theoretical and experimental developments, which have at last facilitated such work. Experimentally high pressure studies suffer practical difficulties which finally complicates the measurements. The major developments towards phenomena such as structural phase transformations [4-5], metallization [6] , ms overcoming these difficulties are the Diamond Anvil Cell (DAC), in which the hardness of diamond is used to apply the pressure. With DAC it is possible to perform, a vast range of experimental measurements at high pressure. The static pressure applied in a DAC is a continuous variable parameter which can be used for systematic studies of the properties of solids as a function of the interatomic distances. These include x-ray and neutron diffraction, extended x-ray absorption fine structure (EXAFS) vibrational spectroscopy and optical measurements. Since the available pressure range is so high, in principle one may observe many new phenomenon such as shifts in the energy gap etc. However, Raman scattering still remains the most amenable method to study the effect of pressure on the lattice dynamics of III-V semiconductors up to their phase transition pressure.

In addition to these experimental advances, reliable computational methods for electronic structure and total energy calculation have made a substantial impact on high pressure physics. Algorithmic developments and rapid increase in computer power make reliable theoretical calculation of structural, electronic, and vibrational properties of materials almost routine. Implementation of new computational algorithms has been particularly important in dealing with complex structures containing several free internal parameters. The majorities of these calculations employ the density functional theory and use local approximations for the exchange and correlation contribution to the total energy. Pressure is a particularly attractive thermodynamic variable to exploit in such first principle calculations because it affords the possibility of studying the variation in the properties of solids as inter atomic distances are changed in a systematic way.

One of the interesting phenomenon that may occur under applied pressure is a sudden change in the arrangements of atoms, i.e. structural phase transition resulting into change in inter atomic distance and crystal structure. Thus a phase transition is said to have occurred if the change is continuous or discontinuous but with a change of crystal symmetry. The pressure at which such structural changes occur, known as phase transition pressure. The properties of the high pressure phases may be very different from those under normal conditions. However even though such a tremendous progress has been made in the field of high pressure research very few successful theoretical attempts have been made to investigate vibrational and allied properties of the III-V semiconductors at high pressure.

Thus during last decade physics of solids at high pressure has evolved as a fascinating and challenging area of research due to the development of several new techniques for the generation of high pressure. These techniques can be divided namely into the static and dynamic techniques. The high pressure techniques have not only been used to understand the physics of solids, but also in all branches of science. In some sense, high pressure mimics the phenomenon taking place during the cohesion of solids (e.g. pressure ionization, modification in electronic and phonon properties and phase changes etc.). The pressure induced changes in the properties of matter can all be traced to the simple fact that the constituent particles (molecules, ions, and atoms) are brought closer under pressure. The increased overlap of the electron cloud leads to a rearrangement of the band structure which is reflected in the changes in the optical, electrical and many other physical properties. The free energy of the system varies with pressure and at high pressure often assumes minimum for spatial arrangement of the particles different from the initial, resulting in a phase transition. The application of pressure stabilize the unusual valance states, hinders diffusion and dissociation, affects the kinetics of chemical reactions and phase transitions, provides new reaction paths, and modifies mechanical properties of engineering materials. It is not surprising that pressure as a thermodynamic variable has offered many opportunities for basic research in the various discipline of science, and also found numerous practical applications. Some of the phase changes under compressions lead to new synthesis of new materials. A shock wave creates a very high pressure on a metal could point the way to ultra hard metals for engineering in extreme environment, such as nuclear fusion reactors. In applied field like simulation of the reactor accidents, designing of a inertial confinement fusion schemes and for understanding rock mechanical effects of shock propagation in earth due to nuclear explosions, the pressure versus volume relation of condensed matter are a vital input.

In the present thesis, we aim to give a coherent presentation of the theoretical results, together with comparison with experiment about the effects of high pressure on the vibrational properties of some zinc blende compound semiconductors (e.g. III-V nitrides, phosphides and antimonide) and high pressure behavior, elastic and mechanical properties of diluted magnetic semiconductors leading to general conclusions of the high pressure behavior of these materials. All of these materials have an average of four valance electrons per atom and they show some similarities in the structures they adopt both under normal conditions and under applied pressure. The pressure driven transitions undergone by these materials are normally associated with an abrupt change in their resistivity. They therefore form a group of related compounds, and it is helpful to consider them altogether. The results of the available previous theoretical and experimental work suggest that in these materials, the valance and conduction band overlap at high pressure. However, direct measurements of the lattice dynamical properties under high static pressure have not been carried out. The literature reveals that extensive theoretical and experimental efforts have been made to understand structural phase transition for the above class of solids by using several model theories and *ab intio* calculations [9-25], but no serious efforts have been made to investigate the vibrational mode and allied properties at high pressures [26-32]. In order to investigate the properties of the above class of solids, we have used the lattice dynamical theory framed for the tetrahedrally bonded semiconductors. This has been achieved by writing the crystal potential in terms of different interactions such as responsible for atomic cohesion in solids. We incorporate coulomb interactions and short range overlap along with the energy due to bond strength and deformation energies.

Chapter I deals with the introduction of the present thesis followed by **chapter II**, which is devoted to the various experimental techniques currently being used for high pressure generation and measurements. In **chapter III**, we discuss the approximation and geometry of the tetrahedrally bonded semiconductors and the underlying theories of lattice vibrations. The review attempted in this chapter is exhaustive and however further details can be found elsewhere. In this chapter we have also discussed the present lattice dynamical model theories used for the investigation of vibrational modes and allied properties. The detailed account of the lattice dynamical theories such as Rigid Ion Model (RIM) and Deformation Bond Approximation Model (DBA) is presented in this chapter.

In **chapter IV**, we discuss the lattice dynamics of technologically important III-V nitride compound semiconductors at ambient pressure as well as at high pressure by using the rigid ion model with proper account of bond strength. The variation of vibrational modes in high symmetry directions with pressure has been analyzed. The present chapter also analyzes the softening and hardening of phonon modes and calculates the mode Grüneisen parameters in all high symmetry directions. The pressure variation of phonon density of states close to the phase transition value has been reported. Specific heat at constant volume with pressure has also been reported.

Chapter V is the report of lattice vibrational properties of some III-V phosphides and GaSb by using the Rigid Ion (RIM) and Deformation Bond Approximation Model (DBA). We report the phonon dispersion curves and phonon density of states at ambient and at high pressures. We also report the mode Grüneisen parameters. The results obtained have been compared with the available neutron and

Raman scattering data. The pressure variation of phonon density of states is also reported.

Chapter VI deals with the study of mechanical, anharmonic and thermal properties of some diluted magnetic semiconductors (DMSs). These properties have been studied with the variation of concentration of the magnetic ion i.e. by creating the chemical pressure for $Zn_{1-x}M_xSe$ (M= Fe, cd, Mn) and $Zn_{1-x}Cr_xTe$. The chapter also reports the effect of extremely applied mechanical pressure on the mechanical properties and vibrational properties for $Zn_{1-x}M_xSe$ (M= Fe, cd, Mn) and $Zn_{1-x}Cr_xTe$. The high pressure behavior of structural and elastic properties is reported. The Debye temperature has also been calculated and the effect of pressure is seen on the Debye temperature to analyze the structural properties of considered DMSs.

In **chapter VII**, the detailed discussion on the various results presented in the thesis is summarized. We have reported our calculations for the phonon dispersions through out the Brillouin zone (BZ), both at ambient and high pressure. The knowledge of phonon frequencies and Eigen vectors enables us to calculate a number of important vibrational properties and to check reliability of our phenomenological lattice dynamical model. The effect of high pressure on phonon dispersion curves are shown to lead to a softening in the transverse acoustics modes. The calculated results of the mode Grüneisen parameters which is indirectly related to the relative frequency shifts have also been discussed in the present chapter. Numerical results for phonon properties discussed in the present thesis are shown to be in reasonably good agreement with the existing experimental data.

References

1. S Schilling and R N Shelton, *Physics of solids under Pressure* (North-Holland, Newyork, 1981), A Jayraman, W Kelment Jr. and G C Kennedy, *Phys. Rev.* **B30**, 2277 (1963).
2. Y K Vohra, S T Weir and A L Ruoff, *Phys. Rev.* **B31**, 7344 (1985).
3. A L Ruoff and M A Babulitz, *J. Appl. Phys.* **53**, 6179 (1982).
4. A Jayaraman, *Rev. Mod. Phys.* **55**, 65 (1983).
5. A K Singh, *Rev. Sci. Instrum.* **60**, 253 (1989).
6. H Hirano, S Uehara, A Mori, A Onodera, K Takemura, O Shimonura, Y Akahama and H Kawamura, *J. of Phys. and Chem. of Solids* **62**, 941 (2001).
7. I Galit, R Glovanni, R Hearne, E Sterer and M P Pasternak, *Phys. Rev.* **B51**, 3195 (1995); P Cervoutes and Q Williams, *Phys. Rev.* **B58**, 9793 (1998).
8. A R Goni, H Siege, K Syssen, C Thomsen, J M Wagner, *Phys. Rev.* B64, 035205(2001).
9. M Ueno, A Ondera, O Shimomura and K Takemura, *Phys. Rev.* **B45**, 10123 (1992).
10. Q Xia, H Xia and A L Ruoff, *J. Appl. Phys.* **73**, 8198 (1993).
11. N E Christensen and I Gorczyca, *Phys. Rev.* **B47**, 4307 (1993).
12. J Serrano, A Rubio, E hernandez, A Munoz and A Mujica, *Phys. Rev.* **B62**, 16612 (2000).
13. R G Greene, H Luo and A L Ruoff, *J. Appl. Phys.* **76**, 7296 (1994).
14. A Mujica, P Rodriguez-Hernandez, S Radescu, R J Needs and A Munoz, *Phys. Stat. Sol. (b)* **211**, 39 (1999).
15. R G Greene, H Luo, T Li and A L Ruoff, *Phys. Rev. Lett.* **72**, 2045 (1994).
16. G C Liu, Z W Lu and M Klein, *Phys. Rev.* **B51**, 5678 (1995).
17. R J Nelmes, M I McMahon and S A Belmonte, *Phys. Rev. Lett.* **79**,3668 (1997).
18. H S Hirano, A Uehara, A Mori, A Ondera, K Takemura, O Shimomura, Y Akahama and H Kawamura, *J. Phys. Chem. Solids* **62**, 941 (2001).
19. Q Xia, H Xia and A L Ruoff, *Phys.Rev.* **B47**, 12925 (1993).

20. M Ueno, M Yoshida, A Ondera, O Shimomura and K Takemura *Phys. Rev.* **B49**,14 (1994).

21. N E Christensen and I Gorczyca, *Phys. Rev.* **B50**, 4397 (1994).

22. A Mujica and R J Needs, *Phys. Rev.* **B55**, 9659; **56**, 12653 **(E)** (1997).

23. M I Mcmahon and R J Nelmes, *Phys. Rev. Lett.* **78**, 3697 (1997).

24. M I Mcmahon, R J Nelmes, D R Allan, S A Belmonte and T Bovornratanaraks, *Phys. Rev. Lett.* **80**, 5564 (1998).

25. A Mujica, R J Needs and A Munoz, *Phys. Rev.* **B52**, 8881 (1995); **57**, 1344 (1998).

26. J Camacho, I Loa, A Cantarero and K Syassen, *J. Phys. Condens. Matter* **14** , 739-757 (2002).

27. S S Mitra, O Brafmann, W B Daniels and R K Crawford, *Phys. Rev.* **186**, 942 (1969).

28. R J Thomas, M S Boley, H R Chandrashekhar, M Chandrashekhar, C Parks, A K Ramdas, J Han, m Kobayashi and R L Gunshor, *Phys. Rev.* **B49**, 2181 (1994).

29. M D frogley, D J Dunstan and W Palsoz, *Solid State Commun.* **107**, 537 (1998).

30. M J Herrera-Cabrera, P Rodriguez-Hernandez and A Munoz, *Phys. Stat. Sol. (b)* **223**, 411 (2001).

31. P Kocinski and M Zbroszczyk, *Semicond. Sci. Technol.* **10**, 1452 (1995).

32. A Polian and M Grimsditch, *Phys. Rev.* **B60**, 1408 (1999).