Chapter 1

Introduction

![Graph showing Raman shift vs. pressure](image)

- Raman shift (cm\(^{-1}\)) vs. Pressure (GPa)
  - Data points and trend lines indicate changes in Raman shift with increasing pressure.
The field of many body problems to explain the behavior of electrons in condensed materials was discovered more than seven decades ago is still vibrating and interesting. As Dirac observed it is unlikely that research in this area will ever be complete since the many body problem all ensure that a complete description of the electrons in any non trivial system will never be practically possible. However, the field has witnessed remarkable progress since then. This is primarily due to the large scale adoption of integrated circuits and the quest for semiconductor with better properties than silicon. The material scientists are now able to synthesize extremely high quality single crystals of many materials. Similarly, the numerical approximations of the ground state many-electrons wave function have improved dramatically and quantum mechanical theories are now reliable methods to predict new materials and explain their properties [1]. The quantum theory applications have progressed slowly for solids than molecules. However, with the discovery of density functional theory (DFT) [2] and rapid increase in computing power, the computational ability has reached the point where it can be claimed that any crystalline material in which the electrons can be considered reasonably independent of each other is well understood. To understand and describe accurately the physical properties of a material governed by the behavior of complex many body ensembles of the order of $10^{23}$ strongly interacting particles (tiny almost mass less electron), it is important to develop a valid quantum mechanical description. In this quantum mechanical model it is necessary to solve the Schrödinger equation,

$$H\Psi = E\Psi (\vec{r}_1, \ldots, \vec{r}_N)$$  \hspace{1cm} (1.1)

where, H is Hamiltonian acting on the N-particle wavefunction $\Psi$. The exact solution of the equation for a single atom is easy but usually very difficult for a solid with $10^{23}$ strongly interacting particles. Thus, it is unavoidable to introduce
methods that approximate and reduce the size of the computational problem. Out of many modern theoretical quantum approaches [2, 3], one of the most popular approach involves pseudopotentials (which are generated in various schemes starting from atomic wave function calculations) and assumes that the core electron of an atom remain unchanged during the formation of solid structure [2]. The Schrödinger \( \text{equation} \) is solved in density functional theory (DFT) to determine the pseudo wave function. Different type of pseudopotentials exists but in the present study we use local density approximation (LDA), generalized gradient approximation (GGA) and Hartwigsen, Goedecker, Hutter (HGH) [1]. Further details will be provided in next chapter. As a result recent interest has moved to strongly correlated materials and hard materials, systems without possible ignorance of electron-electron interactions. This shift on focus depended on the convergence of a number of independent factors. Firstly, the experimental growth of novel materials and secondly the strongly correlated materials and hard materials, which require a relaxation of the independent electron approximation and perhaps the correct “final frontier” in crystalline condensed matter physics. Superconducting magnetic materials belong to strongly correlated materials with significant economic potentials [4]. The latter are used in rapidly developing field of spintronics (spin-electronics) [4] in which the electron spin and charge both are utilized. The present thesis focuses on two different class of materials, transition metal and rare-earth nitrides which are not only useful, interesting and complex in themselves but also interrelated in terms of applications and involved science. Despite the fact that these rare-earth metal nitrides may often be seen as only the combination of the transition metals and nitrogen, some of them show interesting chemical and properties which are not notable in the metals and nitrogen alone. While the rare-earth nitrides are mainly emphasized due to its promising spintronics behavior
the transition metal nitrides are focused due to its applications in hard coating, catalysis and optoelectronics [5].

It has been quest for scientist from the field of physics, material science and chemistry to design new low compressible materials with hardness similar or even larger than that of diamond [6-9]. These materials generally called ultrahard materials are of considerable practical importance in the wide range of applications such as cutting tools, hard coatings, in oil drilling, surgical knives and potential novel semiconductors.

A material is called ultrahard if it satisfies three conditions: shorter bond length, higher bond density or electronic density and a greater degree of covalent bandings [9]. The ultrahard materials are classified in three groups:

(1) The ionic-covalent and covalent compound formed by the addition of light elements from period II and III of the periodic table. The Al₂O₃ (corundum) and high pressure phase of SiO₂ stishovite are few old examples of this class of ultrahard materials. These oxides have the capability of forming of three dimensional rigid lattice with shortest covalent bonds [7].

(2) The second class is the specific covalent compounds which includes various crystalline and disorder carbon allotropes. These carbon allotropes are regarded as special due to the existence of different types of chemical bond such as sp³ and sp² respectively between the carbon atoms in the case of diamond, carbon, fullerene and grapheme etc. Graphite crystallizes in a hexagonal crystal structure in trigonal co-ordinates as a result of the sp² hybridization of carbon atoms. The weak Van der Waals interaction despite a shorter and stronger carbon bonds hold them together. Diamond which occurs naturally as gemstone and has been synthesized under high pressure and temperature having strong covalent bond with sp³ hybridization of carbon atoms is still the hardest material to date.
(3) The third and final class of material includes the transition metals with light elements such as carbon (C), boron (B), oxygen (O) and nitrogen (N) the partially covalent compounds. The present thesis considers the transition metals with one of these light elements, nitrogen N.

Recent time has witnessed tremendous research in the field of transition metal nitrides after the first successful synthesis of nitride platinum nitride at high pressure \([10-11]\). This is mainly due to high bulk modulus and synthesis of nitride. The platinum nitride due to controversy on its structure itself and many technological applications in the area of hard coatings for cutting tools, magnetic storage devices, thermoelectricity, catalysis etc paved the road for other transition metal nitrides \([12-20]\).

Recently, due to the development of the high pressure experimental technique, our knowledge of materials at high pressure is considerably improved. Further, in contrast to experiments, where every minor increase in the maximum achievable pressure is considered as major technical achievements, atomistic and simulations at high pressure require confining the same number of particles in a smaller simulation box, with periodic boundary conditions to achieve arbitrary high pressure. This is due to the fact that the enormous improvement in computational power and development and a number of new ab-initio packages mainly based on DFT considerably expanded our ability to predict new phases and understand the mechanism of pressure properties relation even in complex systems. The strongly correlated materials, system in which electron-electron interaction can no longer be ignored are another class of materials which finds attention of the material and condensed matter scientists. This shift is in attention and interest due to the convergence of a number of independent features. Superconductors and magnetic crystals are both belong to strongly correlated materials with significant potential. The magnetic materials are tremendously used in the rapidly
developing field of spintronics in which the electron spin and charge are both utilized. The development of impressive electronics device, magnetic read head has been benefited from the discovery of giant magneto resistance [21-22]. However, the spintronics devices that have been mass produced to date are based on typical magnetic materials like iron (Fe) or cobalt (Co) combined with magnesium oxide but the requirement of materials with strong-spin electron (charge) coupling is in fore front, due to applications. In particular magnetic semiconductors which are half-metal would be extremely useful. Though, the diluted magnetic semiconductors (DMS) [23], semiconductors that have been doped with magnetic materials, another class of intrinsic magnetic semiconductors are the rare-earth nitrides (ReNs). Modern band structure calculations suggesting that the series contains both half-metals and semiconductors appeared at roughly the same time as the increased interest in novel spintronics materials. Rare-earth elements are defined by their partially filled 4f shell, which increases occupancy across the series. When bonding with nitrogen with rare-earth atoms each contribute with three valence electrons, and the electrons remaining in the unfilled 4f shell are relatively atomic like in nature. This implies that the ReN series tends to exhibits very consistent chemical properties, but widely varying magnetic behavior proving a number of candidates for use as base or a dopant in spintronics devices [24]. Furthermore, these materials are very close to the characteristic mainly hardness, bulk modulus, mechanical and electronic properties of transition metals nitrides. This thesis is therefore combined study of two different classes of materials whose many characteristic are similar despite same basic differences.

Following the fact that the structural, the relative stability and the phonon properties of materials are being predicted, electronic structure studies have since become prominent
in this field of research. It provides valuable information about the formation of alloys, their relative stability and various physical and chemical properties, quantitatively. The availability of high performance computing has given researchers and edge to elucidate the following unclear questions relating to; what atomic structure of material is composed of, its electronic properties and how the bond between atoms that constitute the material can be modified in order to create a novel hard material. Attempts are still in progress in applying first principle calculations employing DFT to the problem of understating the structural behavior, mechanical, vibrational and electronic properties of material [25].

In this work, we employed the use of ab-initio quantum mechanical dynamic simulation using the plane wave pseudopotential method implemented in ABINIT [26] and Quantum-Espresso [27] simulation packages. The ab-initio calculations used are based on the formalism on density functional theory with the local density (LDA) and generalized gradient approximations (GGA). The functional were used in the treatment of the electron-electron interaction. In the following, we briefly describe the motivations of present work.

1. The mixed valence state is a common feature of the metal nitrides and rare-earth compounds, a systematic prediction of the possibilities of NaCl to CsCl or ZBS to NaCl transition in some transition and rare earth compounds at high and low pressure will be useful to define the correct structures. For the sake of completeness electronic band structure and equation of states will also be performed using first principle method.

2. The study of the extent of interactions of the valence electrons with the lattice phonons and their pressure dependence will be carried out in details. This fact will
reveal mode-softening phenomena observed so far in some metal nitride and rare-earth compounds.

3. To investigate structural properties of metal nitride and rare-earth compounds from model calculation and ab-initio density functional theory and to interpret with the experimental results. The contributions of intra atomic and short range exchange interactions to 5d band polarizations will also calculated in rare-earth compounds.

4. The present study will include dynamical, elastic (e.g. harmonic elastic constants), thermodynamic (e.g. thermal expansion, specific heat, Poisson’s ratio and anisotropic factor) and optical (dielectric constants) properties of these series of compounds.

5. The present study will be first of its kind to understand the role of valence electrons (d- or f- band) on the structural, dynamical and magnetic properties of rock-salt structural transition and rare-earth compounds.

6. Information about phonon spectra and Eigen vectors will be used to calculate 1\textsuperscript{st} order and 2\textsuperscript{nd} order Raman spectra to compare the results with existing Experimental observations. This will testify the results predicted from the present investigations on several other properties of the class of materials.
References


[26] The present results have been obtained through the use of the ABINIT code, a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors (URL http://www.abinit.org)

[27] P. Giannozzi et al., http://www.quantum-espresso.org