FIRST PRINCIPLES INVESTIGATION OF HYDROGEN STORAGE IN INTERMETALLIC SYSTEMS

A THESIS SUBMITTED TO THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES OF MIDDLE EAST TECHNICAL UNIVERSITY

BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN METALLURGICAL AND MATERIALS ENGINEERING

JULY 2007

Approval of the thesis:

"FIRST PRINCIPLES INVESTIGATION OF HYDROGEN STORAGE IN INTERMETALLIC SYSTEMS"

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ABSTRACT

FIRST PRINCIPLES INVESTIGATION OF HYDROGEN STORAGE IN INTERMETALLIC SYSTEMS

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July 2007, 89 pages

The design and production of efficient metal-hydrides for hydrogen storage is a long standing subject. Over the years, many different types of intermetallic hydride systems were studied and some of them came out to be operable. However, none of them meet all the storage criteria perfectly. In this study, total energies, hydrogen storage capacity and stability of AB (A = Al, Be, Cu, Fe, Ni, Sb, V and B = Ti) type intermetallics were investigated with the goal of spotting a potential hydrogen storage material. The relation between thermodynamic properties and the atomic and the electronic structure of hydrides are also pointed out. For this task, first principles pseudopotential method within the generalized gradient approximation (GGA) to density functional theory (DFT) was used. Calculations correctly predict experimentally determined structures except for CuTiH. Moreover, the atomic and cell parameter were found within the allowable error interval for DFT. In CuTi intermetallic, a structure having considerably lower formation energy than experimentally found mono-hydride was determined. This contradiction may be due to metastability of the experimental phase and high activation energy for the hydrogen movement in the system. It was found that AlTi and SbTi are not suitable candidates for hydrogen storage since their hydrides are too unstable. For the other intermetallic systems, the stability of the hydrides decreases in the order of VTi, CuTi, NiTi, BeTi, FeTi.

For VTi, FeTi and NiTi, a change in metallic coordination around hydrogen from octahedron to tetrahedron is predicted when tetra-hydride (MTiH₄) is formed. Additionally, at this composition, FeTi and NiTi have hydride structures with positive but near-zero formation energy which may be produced with appropriate alteration in chemical makeup or storage parameters. VTi is a promising intermetallic by means of storage capacity in that even VTiH₆ is found to have negative formation energy but the hydrides are too stable which can be a problem during hydrogen desorption.

Keywords: Intermetallic hydrides, Hydrogen Storage, First Principles, Density Functional Theory.

ÖΖ

ARAMETAL SİSTEMLERİNDE HİDROJEN DEPOLAMA ÖZELLİKLERİNİN TEMEL PRENSİPLERLE İNCELENMESİ

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Temmuz 2007, 89 sayfa

Metal-hidrürlerin verimli hidrojen depolama malzemeleri olarak üretimi ve tasarımı uzun zamandır devam etmekte olan bir araştırma konusudur. Yıllar içinde pek çok farklı metal-hidrür sistemi çalışılmış ve içlerinden bir kısmının hidrojen depolama amaçlı kullanılabileceği görülmüştür. Yine de bu malzemelerin hiçbiri gerekli depolama ölçütlerinin hepsini karşılayamamıştır. Bu çalışmada AB (A = Al, Be, Cu, Fe, Ni, Sb, V and B = Ti) tipi arametallerin, toplam energileri, hidrojen depolama kapasiteleri ve kararlılıkları olası bir depolma malzemesi bulmak amacıyla incelenmiştir. Ayrıca, araştırılan malzemelerin termodinamik özellikleri ve atomelektron yapıları arasındaki ilişkiler gösterilmiştir. Bu iş için bir temel prensipler psödopotansiyel yöntemi olan yoğunluk fonksiyonlu teori (DFT) ve bu teori kapsamındaki genelleştirilmiş değişim ölçüsü yaklaşımı (GGA) kullanılmıştır. Hesaplamalar, CuTiH dışında, deneyle gözlemlenen yapıları doğru olarak tahmin etmiş, atom ve hücre parametrelerini DFT için kabul edilen hata sınırları içinde bulmuştur. CuTi arametal sisteminde CuTiH yapısında deneysel olarak gözlemlenenden belirgin derecede düşük oluşum enerjisine sahip bir yapı belirlenmiştir. Bu çelişki, deneysel yapının yarı-kararlı ve hidrojenin yapı içindeki haraketi için gereken aktivasyon enerjisinin yüksek oluşundan kaynaklanıyor olabilir. Çalışma sonucunda AlTi ve SbTi arametallerinin, bu malzemelerin hidrürlerinin kararsız olması nedeniyle hidrojen depolamaya uygun olmadığı görülmüştür. Araştırılan diğer sistemlerde, hidrür kararlılığı VTi, CuTi, NiTi, BeTi, FeTi sırsıyla azalmaktadır. VTi, FeTi ve NiTi sistemlerinde dört-hidrür (MTiH₄) oluşumunda, hidrojen çevresindeki metal atomu düzeninde altı-kenarlıdan dört-kenarlıya geçiş öngörülmüştür. Bu kompozisyonda FeTi ve NiTi için belirlenen hidrürler kararlı değildir. Ancak oluşum enerjilerinin sıfıra yakınlığı nedeniyle kimyasal kompozisyonda veya depolama parametrelerinde yapılacak uygun bir değişiklik bu hidrürlerin oluşmasını sağlayabilir. VTi depolama kapasitesine bakıldığında VTiH₆'nın bile negatif oluşum enerjisine sahip olması nedeniyle umut vadetmektedir. Diğer yandan oluşan hidrürlerin kararlılığı genellikle yüksektir ve bu nedenle hidrojenin geri verilmesi güç olacaktır.

Anahtar Kelimeler: Arametal Hidrürler, Hidrojen Depolama, Temel Prensipler, Yoğunluk Fonksiyonlu Teori. To my family and friends

Acknowledgments

I would like to express my deepest gratitude to my supervisor Kadri Aydınol for his invaluable guidance and endless support during the study of this thesis.

I sincerely thank my laboratory comrade Fatih Gürçağ Şen for his friendship, encouragement and support during this thesis.

I specially thank to my friends Güher Kotan and Evren Tan for all the good times we had.

I am very grateful to my family, Nejla, Metin and Özlem Kınacı for their constant support and love.

Most of the numerical calculations reported in this study were carried out at the ULAKBİM High Performance Computing Center at the Turkish Scientific and Technical Research Council (TUBİTAK). I specially thank to Onur Temizsoylu for his continuous support during the usage of the computing facility.

I also thank to TUBİTAK-BİDEB (The Scientific and Technological Research Council of Turkey-The Department of Science Fellowships and Grant Programmes) for the National Scholarship Programme for M.Sc. Students.

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CHAPTER 1

INTRODUCTION

1.1 Hydrogen Era

The last two centuries of industrialization and technological development is achieved with continuously increasing demand for energy. Non-renewable sources i.e. fossil fuels, supplied the necessary energy during this period. However, this comes with the price of depletion of these energy sources. Thus, for the upcoming period, alternative energy sources must be the developed and used in order to build a sustainable energy economy. In this regard, studies intensify on non-polluting renewable sources of energy such as wind, solar, hydroelectric, geothermal, biomass, tidal etc.. This brings another important concern explicitly. What will be the means to carry energy efficiently!

Among possible answers, today, hydrogen is considered to be one of the most promising energy carrier that can store and deliver the energy in a usable form. Hydrogen is the simplest and most abundant element of the universe but it is rarely found by itself due to ease of combination with other elements. It is colorless, odorless and non-toxic in its gas form. Unlike the fossil fuels, hydrogen does not produce any polluting or green house gases or toxic chemicals but water when it is burned. Moreover, it has the highest energy content per mass. On a weight basis, hydrogen has more than two times the energy content of natural gas and nearly three times the energy content of gasoline (120 kJ/g for hydrogen versus 50 kJ/g natural gas and 44 kJ/g for gasoline) [1]. Due to these facts, hydrogen has been studied as an energy carrier for over five decades. Liquid hydrogen, hydrogen fuel cells and hydride batteries first came into use in late 1950s in space studies. However, the commercial usage of safe hydrogen energy systems such as in computers, cellular phones and cars are quite new.

What makes hydrogen so interesting is the storability of it in several media. Tanks can be used to store liquid and gaseous hydrogen physically and solid and liquid compounds can be used to store hydrogen chemically. Although the idea in physical storage in tanks is straight forward, technical difficulties and high costs in production of high specific strength containers for pressurized gas and proper insulation for cryogenic liquid make these types of storage less practical for daily usage [2, 3]. Regarding to storability and portability requirements of practical usage, chemical binding of hydrogen in various compounds became an important way of storing hydrogen [1, 4]. These chemical binders can be divided into two main groups according to their hydrogenation-dehydrogenation reactions as reversible and irreversible. The ones having irreversible reactions may offer high storage capacity however, the storage compound cannot be easily regenerated by applying an overpressure of hydrogen gas. High surface area sorbents (such as carbon based nanofibres, nanotubes etc.) and metal hydrides can be characterized as reversible storage media which can go easy charging and discharging of hydrogen with relatively low binding energy (less than $20 - 25 \ kJ/mol \ H_2$). Bercher et al. [5] stated in their review, studies until present did not pose a promising result on high surface area sorbents nevertheless these materials are still attractive because of their light weight.

The last important group of materials used in hydrogen storage is metal hydrides. In this method, a metallic phase is used to bind hydrogen by chemical bonding. Güther and Otto [6] explained the superiority of metal hydrides such that

- additional power supply is not required
- hydrogen loss in nearly zero
- hydrogen release can be attained at an optimum and constant pressure
- much more safer
- a high hydrogen density (may be higher than in liquid or solid hydrogen) can be obtained in some hydrides

Thus, metal and intermetallic hydrides are suitable candidates for commercial applications; however, for complete utilization some criteria must be met. Ivey and Northwood [7] proposed these criteria briefly as follows

• having high reversible storage capacity

- ease of hydrogenation and de-hydrogenation (at ambient temperature and pressure if possible)
- safety
- fast kinetics of hydrogen absorption and desorption
- little or no change in the temperature and pressure of absorption-desorption cycle during service life
- small hysteresis in isotherms of pressure vs. composition
- resistance to poisoning of O₂, H₂O, CO, CO₂
- low price

The chemical reaction between metallic species and hydrogen can be written as

$$M + \frac{x}{2}H_2 \rightleftharpoons MH_x \tag{1.1}$$

where M stands for the metallic species and H is hydrogen. The direction of the equation can be altered by varying reaction temperature and pressure of hydrogen gas (that also depends on temperature). Above equilibrium hydrogen pressure reaction advance to form the hydride and below the equilibrium pressure, hydride dissociates into hydrogen and metallic matrix. Hydrogenation-dehydrogenation behavior of the hydride is characterized by equilibrium pressure-temperature-composition curves (PTC or PCI pressure-composition-isotherms), Fig. (1.1). These curves are determined by keeping the sample at constant temperature while measuring hydrogen pressure. PCT diagram shows three distinct regions. At low pressure and hydrogen content a solid solution (α phase) appears. As the hydrogen content increases a two phase region (α and β phases) is obtained where the hydrogen pressure is constant that can be explained by Gibbs phase rule. β is the hydride phase. Finally, all α is transformed into hydride and further increase in hydrogen pressure produce solid solution of the hydride with insignificant hydrogen absorption. The reversible hydrogen capacity is defined as the plateau width however, most of metallic hosts that are used in practical applications do not show a flat plateau or have hysteresis between adsorption and desorption [8].

Complemental to PCT, van't Hoff equation, Eq. (1.2) and plot $(\ln P \text{ versus } 1/T)$, Fig. (1.1), are widely used for comparison between thermodynamic stabilities of hydrides.



Figure 1.1: At left PCT for a fictitious metal hydride and at right corresponding Van't Hoff plot [9]

$$\ln P = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{1.2}$$

where P, $\triangle H$, $\triangle S$ and T are pressure, enthalpy change of, entropy change and absolute temperature respectively in hydrogenation reaction, Eq. (1.1). R is the gas constant. Generally, the mid-point plateau hydrogen pressure in PCT is used in van't Hoff equation.

Andreasen [9] stated that it is be possible to make a reasonable estimate of $-130 \ J/mol \ K$ for entropy change, ΔS , at 1 bar H₂ pressure regardless of the host metal (i.e. ΔS is more or less the same when $\Delta H = T \Delta S$ is evaluated for different host metals). Moreover, it is pointed out that the formation of hydride should not be more exothermic than 48 kJ/mol in order to have desorption of hydrogen above 1 bar below 100 °C.

The literature is vast on the subject of spotting the right material for hydrogen storage. First logical attempt is to try pure metals as hydrogen absorber, unfortunately most of them do not have PCT properties convenient with 1-10 atm, 0-100 °C range of utility chosen for practical applications. Only vanadium, niobium and

palladium are around this range [8].

Ivey and Northwood [7], Sandrock [8] and Bououdina et al. [10] reviewed many binary metal alloy systems that have been studied so far including AB, AB₂, AB₅, AB₃ and A₂B₇. The properties of these binary systems can be summarized as follows: AB₅ intermetallics store 1.4-1.9 wt.% hydrogen, with fast reaction kinetics and the resulting hydrides are relatively stable. In AB₂ type, 1.5-2.0 wt.% hydrogen can be stored with fast kinetics producing stable hydrides. AB₃ and A₂B₇ type intermetallics can store 1.6 wt.% in stable hydrides. Mg based compounds can store up to 7 percent hydrogen by weight and the resulting hydrides are stable, however kinetic problems exist. AB type intermetallics can store 1.8% hydrogen by weight with medium kinetics and the stability of the hydrides varies.

Alanates and borohydrides are other promising material groups for hydrogen storage. They have a generic formula of ABH_4 with A is often representing an alkaline or alkaline earth metal and B is representing either aluminum or boron. Bogdanovic and co-workers [11, 12] showed that NaAlH₄ can be reversibly used in hydrogen storage with a multi step decomposition reaction occurring around 1 bar and 33-110 °C [13]. The theoretical reversible capacity is calculated to be 5.6 wt.% hydrogen. Main problems with this system are low volumetric capacity and slow hydrogen release rate. Among borohydrides, LiBH₄ is the most studied due to its high capacity with over 9 wt.% [14], however it suffers from (like other borohydrides) high decomposition temperature and unwanted by-products during reaction [2].

One final hydride that has received significant attention in recent years is lithium amide $(\text{LiNH}_2)/\text{imide}$ (Li_2NH) system. Chen et al. [15] showed that the system exhibit two-step absorption-desorption reaction at 1 atm pressure and have storage capacity up to 11.5 wt.%. On the other hand, the desorption reactions take place as high as 285 °C. It has been found that magnesium substitution destabilize LiNH₂ and lower the reaction temperature to 200 °C with a moderate reduction in hydrogen capacity [16, 17].

Presently, experimental effort continues intensely on many different aspects of hydrides in order to achieve H_2 release at or near ambient conditions. Modifying the matrix by alloying, mechanical, thermal and surface treatments, thin film production etc. can enhance properties of existing hydrides and new matrix alloys and compounds can offer higher limits in storage that are waiting to be explored.

1.2 Ab-Initio Methods

In the last few decades, the advent of computational capabilities has triggered a new field of research that combine classical materials science, materials physics, physical chemistry, mechanics, computer science and mathematics in analysis and prediction of material behavior formally known as computational materials science. Within this very short time, material models and simulation prove themselves as companions to experiment in explaining many phenomena in physics, chemistry, biology and engineering. Today, simulations can link atomic behavior to macroscopic properties of materials. This multiscale approach (on length and time), Fig. (1.2), helps scientists and engineers to understand fundamental materials theory then predict the possible material property and use these in macro-world applications [18]. Another advantage of computational methods is that they provide a fast and cheap means of explaining the system under consideration. These techniques can even be applied to phenomena where practice is impossible, as long as the sufficient theoretical information is present. Moreover, a full control on the system variables can be achieved and thus effects of the parameters on the results can easily be determined.



Figure 1.2: Length versus time scale in materials modeling

One distinct group in materials simulation is ab-initio methods (or equally First Principles) which means *from the beginning*. Originating from quantum theory, ab-initio methods can estimate the properties of the solid state in connection with the electronic structure and determine free energies of the systems based on statistical mechanical formulation. They require only specification of ions with their atomic numbers in the system and no other experimental input.

First principles Density Functional Theory (DFT) [19–21] is one of the most successful theoretical tool in materials modeling that Nobel Prize in chemistry was awarded in 1998 for its theorist Walter Kohn. Variety of models were implemented in DFT after its formulation. Among all implementations, total-energy pseudopotential method [22–27] is still a widely held method in simulations. The calculations in this method involve prediction of the electronic and ionic structure (involving the geometry) of the system by calculating the quantum mechanical total energy of the system and minimizing it with respect to position of electrons and ions using electronic density as the main parameter. Then, many physical properties can be related to the total energy or to differences between total energies of different states of the system.

The predictions of DFT has provided fundamental understanding for a wide variety of situations. For instance, Ceder et al. [28] searched replacement materials for cathode materials in lithium batteries via ab initio ultra-soft pseudopotential method and predicted and verified experimentally the aluminum substitution to LiCoO_2 cathode raises the cell voltage with a decrease in cathode density and cost. In another case, Vaithyanathan et al. [29] used a multiscale method including ab initio ultra-soft pseudopotential, cluster expansion and phase field approaches to evaluate Al_2Cu precipitate microstructure in aluminum. Their technique correctly predict the shape of precipitates but there is a discrepancy for temperature due to omission of vibrational entropy.

1.3 Ab-Initio Modeling of Hydrides

As in many other scientific and engineering subject, first principles studies assisted extensively in understanding of hydrides, their design and development. Many properties of hydrides from hydrogen diffusion to electronic and band structure along with the energy for hydride formation have been studied with ab-initio methods.

In order to be more representative about the capabilities of ab-initio modeling of

hydrides, some selective studies in this subject should be pointed out.

Min and Ho [30] studied hydrogen diffusion in yttrium and calculated formation and activation energy for diffusion. They also show the consistency of their results with the experimental data.

Yu and Lam [31] calculated cell and electronic structures of MgH₂ using DFT-LDA (local density approximation) pseudopotential method. Equilibrium cell parameters are predicted with 2.2 % error at most. MgH₂ was found to be an insulator with a band gap of 3.06 eV which is quite lower than experimentally determined value of 5.16 eV. Moreover, their results on cohesive energy varied between 11.2 to 13.5 eVthat corresponds to formation enthalpy in the range of -38.4 to -72 kJ/mol H₂. Experimental value for cohesive energy and formation enthalpy of MgH₂ was given by Andreasen [9] as 13.56 eV and -75 kJ/mol H₂ respectively.

A more recent study on MgH₂ was carried out by Vegge et al. [32]. Formation energies of MgMH₃ (M = first row transition metals) were investigated using DFT ultrasoft pseudopotential approach. The authors used a body centered tetragonal unit cell for MgM and perovskite structure for the hydride. Mg(Sc, Ti, V, Cr, Mn, Fe)H₃ have found to have negative formation energies with a gradual increase in stability from Sc to Fe. A rapid decrease in stability is observed after iron with MgCuH₃ and MgZnH₃ having positive formation energies. The authors concluded that the structural and stoichiometric construction of the intermetallics and their hydride do not represent the experiment, nevertheless trends are found to be similar to experimental formation energy data in this study.

Smithson et al. [33] presented the study on the stability and electronic structure of alkali, earth-alkali and transition metal hydrides. The electronic structures and formation energies of the hydrides are calculated by considering various crystal structures. The hydriding energy was considered to have three contributions. First is the energy to convert metal crystal structure to the structure formed by metals in the hydride phase. Second is the change in cohesive energy when metal structure transform into hydride. The third contribution is the chemical bonding between metal atoms and hydrogen. The study [33] showed that the early transition metals have higher tendencies for hydride formation and this tendency was systematically decreased to the right of the periodic table.

In different studies, Nagasako et al. [34] investigated C14 type Laves phase Ti-Mn hydrides and Miwa and Fukumoto [35] investigated 3d transition metal hydrides with DFT. Similar conclusions were drawn in these studies regarding to formation energies as Smithson et al. [33]. In addition, Nagasako et al. [34] stated that the equilibrium volume and the bulk modulus of the metal are two important parameters in the determination of the formation energy of the hydride.

Wolverton et al. [36] examined the hydrogen behavior (i.e site preference, heat of solution, diffusivity and vacancy binding) in aluminum. The authors tested DFT-GGA (generalized gradient approximation) and LDA ultrasoft pseudopotential approaches on many metal hydrides. They included zero point energies and vibrational properties so as to obtain room temperature formation energies. Their results very well agreed with experimental formation energies of hydrides.

Dompablo and Ceder [37] studied thermodynamic stability of AMH_4 and A_3MH_6 (A= Li, Na, K M=B, Al, Ga) type alanate hydrides. It is shown that the overall stability of the hydride and as a consequence temperature and pressure variables of the storage process can be altered by substations on Na and Al sites. As a result, more hydrogen release may be obtained in a narrower range of temperature and pressure.

Hong and Fu [38] investigated the effect of hydrogen on electronic and magnetic properties of ZrX_2 (X= V, Cr, Mn, Fe, Co, Ni) Laves phase compounds. The stabilities of the hydrogen at different crystal sites are compared. In a parallel study, Huang et al. [39] inspected the electronic structure and stability of ZrV_2 hydrides of different composition.

The crystal and electronic structures of all alkali-aluminum and alkali-gallium tetra-hydrides ABH_4 (A = Li, Na, K, Rb, Cs; B = Al, Ga) were studied by Vajeeston et al. [40] via projected augmented plane-wave method. It is claimed that BH_4 is like a sub-unit in A matrix and an ionic interaction exists between A and BH4 units. Also the strongest bond in the system was defined as B-H bond.

Morinaga and friends [41–44] used DV-X α cluster method in the modeling of several types of binary hydrogen storage alloys including MTi intermetallics. According to Nambu et al. [42], considering two different hydrogen centered octahedron, the interaction between (Fe,Co,Ni)-H is stronger than Ti-H in MTiH₂ hydrides. It was also noted that the distortion of lattice during hydrogenation mostly arose among Ti atoms due to relatively weak Ti-Ti bonds.

DFT is also used in evaluation of lithium amide/imide system. Orimo et al. [45] and Miwa et al. [46] calculated electronic structure of amide and concluded that

 $[NH_2]^-$ anion has strong internal covalent bonds and deficient electron is compensated with Li⁺ cation. Moreover, Orimo et al. [45] predicted that partial substitution of Li by Mg destabilize LiNH₂ due to its higher electronegativity. In another study, Mueller and Ceder [47] tried to resolve the structure of imide (Li₂NH) by using DFT and cluster expansion methods. In addition, they proposed a ground state crystal structure which has the lowest energy of any known structure calculated by DFT.

In this current study, hydrogen storage capacity, stability and thermodynamic properties of Metal-Ti (AB type) intermetallics is modeled using first principles pseudopotential total energy method (i.e. density functional theory in this study) with the goal of spotting a potential hydrogen storage system with a hydride having high capacity and low stability. In presenting this work the subsequent organization is followed: In Chapter 2, a brief discussion of DFT is given and in Chapter 3 methodology is explained. Finally, in Chapter 4 results of calculations and discussions are presented.

CHAPTER 2

DENSITY FUNCTIONAL THEORY

The evolution of quantum theory have led to drastic changes in understanding of solid state. Quatum mechanics made it possible to describe the elementary particles (i.e. atom nuclei and electrons) and statistical mechanics connects basic quantum knowledge to observed thermodynamic behavior of the solid. Although elementary principles of classical statistical mechanics were already available by significant contributions of Boltzmann, Maxwell and Gibbs, the quantum revolution was about to start in the beginning of twentieth century. Ideas of Planck in quantization of energy and deBroglie in momentum-wavelength relation became the corner stones in conception of wave-particle duality. The fundamentals of quantum mechanics was nearly completed by the year 1930 by major involvements of Einstein, Rutherford, Bohr, Geiger, Hertz, Compton, Millikan, Bose, Pauli, Schrödinger, Heisenberg, Born, Fermi, Dirac and Oppenheimer.

A solid can be described by determining the lowest energy configuration of electrons and ions via solving time independent many-body Schrödinger Equation [48], Eq. (2.1).

$$\hat{H}(\mathbf{r}, \mathbf{R})\psi(\mathbf{r}, \mathbf{R}) = E\psi(\mathbf{r}, \mathbf{R})$$
(2.1)

 \hat{H} is the Hamiltonian operator (hat denotes the operator), ψ is the many body wavefunction and E is the energy of the system. The notation **R** and **r** denote the position of all nuclei and position of all electrons respectively. With a non-relativistic derivation from kinetic (\hat{T}) and potential (\hat{U}) operators, the Hamiltonian can be written as

$$\hat{H}(\mathbf{r}, \mathbf{R}) = \hat{T}_i(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{U}_{ii}(\mathbf{R}) + \hat{U}_{ee}(\mathbf{r}) + \hat{U}_{ie}(\mathbf{r}, \mathbf{R})$$
(2.2)

where

$$\hat{T}_i(\mathbf{R}) = -\sum_I \frac{\hbar^2}{2M} \nabla_{\mathbf{R}_I}^2$$
(2.3)

$$\hat{T}_e(\mathbf{r}) = -\sum_i \frac{\hbar^2}{2m} \nabla_{\mathbf{r}_i}^2$$
(2.4)

$$\hat{U}_{ii}(\mathbf{R}) = +\frac{1}{2} \sum_{I,J(J \neq I)} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$
(2.5)

$$\hat{U}_{ee}(\mathbf{r}) = +\frac{1}{2} \sum_{i,j(j\neq i)} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$
(2.6)

$$\hat{U}_{ie}(\mathbf{r}, \mathbf{R}) = -\sum_{i,I} \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}_i|}$$
(2.7)

On right hand side of Eq. (2.2), first two terms are the kinetic energy operators for ions having mass M and electrons having mass m. \hbar is the Planck's constat divided by 2π . Remaining terms are potentials defining ion-ion repulsion, electron-electron repulsion and ion-electron attraction. Z denotes the valence charge of the ion.

Exact solution of Schrödinger equation can be obtained for the hydrogen atom. Above that, solving the equation become a formidable task. Thus, Eq. (2.2) need serious simplifications in order to determine eigenfunction (wavefunction) ψ and eigenvalue (total energy) E. As a first approximation, also known as Born-Oppenheimer approximation, electronic and ionic freedoms can be separated by considering mass difference between electrons and ions. Electrons respond any ionic movement instantaneously and adiabatically (to note that in quantum mechanical sense, adiabatic process is an infinitely slow change in the Hamiltonian of a system and not related to no-heat exchange condition in thermodynamics [49]). They position themselves in their lowest energy state (i.e. ground state) for the corresponding ionic arrangement. Thus, instead of using a quantum mechanical kinetic energy term, Eq. (2.3), a classical contribution can be taken into account (i.e. a Hamiltonian with fixed ionic position). Secondly ionic repulsive potential, Eq. (2.5) can be taken as a constant from the point of electronic contribution. For a fixed set of ionic positions, it can be calculated, leaving the energy of the electrons in the presence of ions, Eq. (2.8). This energy is composed of kinetic energy of electrons, electron-electron and electron-ion interaction potential.

$$E_{electron}(\mathbf{R}) = K_e(\mathbf{R}) + E_{ee}(\mathbf{R}) + E_{ie}(\mathbf{R})$$
(2.8)

The equation for the electronic problem gives eigenvalue of the energy $E_{electron}(\mathbf{R})$ that depend parametrically on the coordinates of the nuclei. Once found, it enters into the nuclear equation which describes the motion of nuclei. The Hamiltonian for the remaining problem can be written as

$$\hat{H}(\mathbf{r}) = -\sum_{i} \frac{\hbar^2}{2m} \nabla_{\mathbf{r}_i}^2 + \frac{1}{2} \sum_{i,j(j \neq i)} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i} V_{ion}(\mathbf{r}_i)$$
(2.9)

where

$$V_{ion}(\mathbf{r}) = -\sum_{I} \frac{Z_{I} e^{2}}{|\mathbf{R}_{I} - \mathbf{r}|}$$
(2.10)

From this point on, further simplifications are concentrated on expressing the many-body problem as a single particle picture. There are basically two popular approaches to this problem, Hartree Fock (HF) and Density Functional (DFT) methods for which extensive reviews can be found in [50–54].

2.1 Hartree-Fock Method

In this method [55, 56], one tries to construct an approximate many-electron wave function from one electron wavefunctions determined in some appropriate effective potential. It is important to note that the single-electron wavefunctions mentioned here and in the following content have both spatial coordinate and spin degrees of freedom and they can explicitly be introduced by considering electrons with up and down spins at position \mathbf{r} . A simplest way is to assume electrons as non-interacting entities and write the many-body wavefunction as

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\dots\phi_N(\mathbf{r}_N)$$
(2.11)

This is known as Hartree approximation (or Hartree product). In order to be more realistic (Hartree-Fock approximation), fermionic nature of electrons is incorporated such that

$$\psi(\mathbf{r}_1, ..., \mathbf{r}_i, ..., \mathbf{r}_j ..., \mathbf{r}_N) = -\psi(\mathbf{r}_1, ..., \mathbf{r}_j, ..., \mathbf{r}_i ..., \mathbf{r}_N)$$
(2.12)

$$\psi(\mathbf{r}_1, ..., \mathbf{r}_i, ..., \mathbf{r}_i ..., \mathbf{r}_N) = 0$$
(2.13)

Slater [57] suggested a determinant form, Eq. (2.14), constructed from an orthonormal set of one-electron wavefunctions (or orbitals) for the N electron wavefunction which is antisymmetric (interchanging of any two columns produces a sign change) as in Eq. (2.12) and goes to zero if any two electrons are in same state (two identical rows in Slater determinant) as in Eq. (2.13). In fact the determinant is a linear combination of antisymmetrized Hartree products which satisfies the Pauli exclusion principle. $1/\sqrt{N!}$ is the normalization factor for the amplitude (and probability) of the ψ .

$$\psi(\mathbf{r}_{1}, \mathbf{r}_{2}, ..., \mathbf{r}_{N}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{1}(\mathbf{r}_{1}) & \phi_{1}(\mathbf{r}_{2}) & ... & \phi_{1}(\mathbf{r}_{N}) \\ \phi_{2}(\mathbf{r}_{1}) & \phi_{2}(\mathbf{r}_{2}) & ... & \phi_{2}(\mathbf{r}_{N}) \\ \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{N}(\mathbf{r}_{1}) & \phi_{N}(\mathbf{r}_{2}) & ... & \phi_{N}(\mathbf{r}_{N}) \end{vmatrix}$$
(2.14)

The expectation value of energy is calculated via Eq. (2.15) then single-particle Schrödinger equation for the Hartree-Fock approximation Eq. (2.16) is obtained by variational calculation.

$$E = \langle \psi | H | \psi \rangle$$

$$= \sum_{i} \langle \phi_{i} | -\frac{\hbar^{2}}{2m} \nabla_{r}^{2} + V_{ion}(\mathbf{r}) | \phi_{i} \rangle$$

$$+ \frac{e^{2}}{2} \sum_{i,j(j\neq i)} \langle \phi_{i}\phi_{j} | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \phi_{i}\phi_{j} \rangle$$

$$- \frac{e^{2}}{2} \sum_{i,j(j\neq i)} \langle \phi_{i}\phi_{j} | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \phi_{j}\phi_{i} \rangle \qquad (2.15)$$

$$\left[-\frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + V_{ion}(\mathbf{r}) + V_i^H(\mathbf{r})\right]\phi_i(\mathbf{r}) - e^2 \sum_{j\neq i} \langle \phi_j | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \phi_i \rangle \phi_j(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad (2.16)$$

In Eq. (2.16), V^H is the Hartree potential which defines only Coulomb repulsion between an electron in certain state and the field created by all other electrons. In reality, only Coulomb repulsion is not enough to describe electronic interaction. The motion of electrons is correlated so the interaction between them depends on the position of particles. Electrons with parallel spins avoid each other following Pauli exclusion principle. Electrons with anti-parallel spins avoid each other to lower their mutual Coulomb repulsion. Former leads exchange and the latter leads correlation energy. Because of these, the electron density in the vicinity of an electron is depleted and the electron density away from an electron is increased. So in brief it can be said that an electron at **r** reduces the probability of finding another electron at **r**'.

Last term on the left hand side of Eq. (2.16) represents the exchange term. This exchange term has opposite sign with the Hartree potential and decreases overestimated Hartree potential. Although including electronic exchange, Hartree-Fock equations totally neglects correlation effects. As a result, the electrons are a little further apart than estimated by the HF-method.

Hartree-Fock method involves solving an eigenvalue equation for all one electron quantum states within a mean field effective potential. As the mean field has to be known to solve the eigenvalue problem, and the eigenstates have to be known to calculate the mean field potential, the equations are solved in practical calculations by using an iterative procedure. An initial guess is made for the single particle states and this is used to calculate the mean field potential. Then the mean field potential is used to calculate better one particle states. This iteration procedure is continued until the input and output potential and states are self-consistent within some small error. Such a method is called a Self Consistent Field (SCF) cycle.

2.2 Density Functional Theory

Another attempt to reduce the many-body problem to single particle equations have come from Hohenberg, Kohn and Sham [19, 20] turned out to be one of the most successful methods in calculating materials properties. Instead of finding the manybody wavefunction of the system, Density Functional Theory (DFT) [21] considers the electronic density, $n(\mathbf{r})$, as the basic variable of the problem. So the problem is reduced from $3 \times N_{electrons}$ (which is needed in description of quantum mechanical wavefunction) to 3 spatial variables (which is needed for the description of density). This idea of adopting electron density in search of system properties was first introduced by Thomas-Fermi model [58, 59]. However, this model has almost no use in describing valence electrons and thus atomic bonding.

For a given Hamiltonian of the form Eq. (2.9) where ionic potential can be assumed as an external potential $v_{ext}(\mathbf{r})$,

$$\hat{H} = \hat{T}_e + \hat{U}_{ee} + v_{ext}(\mathbf{r}) \tag{2.17}$$

Hohenberg and Kohn [19] proved (by the use of variational principle) that there are no two different external potentials, $v_{ext}(\mathbf{r})$, differing by more than a costant, which give the same electron density, $n(\mathbf{r})$, for the ground state of the system. So they rephrase their basic lemma as 'The ground state electron density of the many electron system determines the external potential within the limits of a constant'. Additionally, $n(\mathbf{r})$ gives total number of electrons N via

$$N = \int n(\mathbf{r}) \ d^3\mathbf{r} \tag{2.18}$$

By determining N and H, $n(\mathbf{r})$ specifies implicitly all properties derivable from H through the solution of the time-independent (or time-dependent) Schrödinger equation. The original formulation of Hohenberg and Kohn led to an energy functional (function of a function i.e. $n(\mathbf{r})$) given below.

$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int v_{ext}(\mathbf{r}) \ n(\mathbf{r}) \ d^3(\mathbf{r})$$
(2.19)

From the variational principle it is concluded that energy functional $E[n(\mathbf{r})]$ has its minimum for ground state electron density hence the total energy functional needs to be minimized in order to find the true ground state. However, the true form of functional $F[n(\mathbf{r})]$ is unknown. It can be rewritten as

$$F[n(\mathbf{r})] = T[n(\mathbf{r})] + E^{H}[n(\mathbf{r})] + E^{XC}[n(\mathbf{r})]$$
(2.20)

In Eq. (2.20), $E^{H}[n(\mathbf{r})]$ is the Hartree energy (Coulombic electron-electron repulsion). $T[n(\mathbf{r})]$ (kinetic energy of electrons) and $E^{XC}[n(\mathbf{r})]$ (exchange and correlation energy) are the unknown parts of the functional $F[n(\mathbf{r})]$. Practical implementation of minimizing the energy functional in Eq. (2.19) in order to find the ground state of a many electron system is the subject of Kohn and Sham's study [20]. In this work, a system of non-interacting particles moving in an external potential v_s was introduced as a reference. In addition, it is assumed that the ground state electron density of non-interacting system equals to the one in interacting system. Then, the many body ground state wavefunction is obtained as Slater determinant orbitals as discussed in Hartree-Fock method. In this assumption, Schrödinger equality, Eq. (2.21) for single orbitals and electron density, Eq. (2.22), are found as follows

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$$
 (2.21)

$$\left[-\frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + v_s(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$
(2.22)

From this assumption non-interacting electron kinetic and total energy functional $T_s[n(\mathbf{r})]$ and can be given respectively as Eq. (2.23) and Eq. (2.24).

$$T_{s}[n(\mathbf{r})] = \sum_{i=1}^{N} \langle \phi_{i} | -\frac{\hbar^{2}}{2m} \nabla_{\mathbf{r}}^{2} | \phi_{i} \rangle$$
$$= \sum_{i=1}^{N} \int \phi_{i}^{*}(\mathbf{r}) \left(-\frac{\hbar^{2}}{2m} \nabla_{\mathbf{r}}^{2} \right) \phi_{i}(\mathbf{r}) d^{3}\mathbf{r}$$
(2.23)

$$E_s[n(\mathbf{r})] = T_s[n(\mathbf{r})] + \int v_s(\mathbf{r}) \ n(\mathbf{r}) \ d^3(\mathbf{r})$$
(2.24)

In order to use this approximate kinetic energy, the difference between exact kinetic energy $T[n(\mathbf{r})]$ and approximation $T_s[n(\mathbf{r})]$ should be treated in the exchange-correlation functional as in Eq. (2.25).

$$E^{XC}[n(\mathbf{r})] = T[n(\mathbf{r})] - T_s[n(\mathbf{r})] + U^{XC}[n(\mathbf{r})]$$
(2.25)

where $U^{XC}[n(\mathbf{r})]$ is the potential functional due to interaction of the electrons with their own exchange-correlation hole. Basicly this hole, surrounding an electron, is a mutual exclusion zone (or a hole from which other electrons are banned) due to exchange and correlation effects. Every electron is surrounded by this hole in the electron density of equal and opposite charge to itself.

The variational formalisms for exact and non-interacting systems show that in order to have the same ground state electron density in these two systems, the given constraint should be met

$$v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$$
(2.26)

where

$$v_H(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}'$$
(2.27)

$$v_{xc}(\mathbf{r}) = \frac{\delta E^{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$
(2.28)

Once an exchange and correlation energy is approximated, the Kohn-Sham equations can be solved with an iterative process such that

- 1) Guess an initial density
- 2) Compute effective potential, v_s via Eq. (2.26)
- 3) Find the N lowest eigenvalues of the Eq. (2.22)

4) Calculate the electron density from Eq. (2.21). Use an efficient mixing scheme for input and output density

5) Construct a new functional by minimization by methods based on molecular dynamics [60], steepest descent or conjugate gradient algorithms [61–64]

- (6) Go back to (2) and repeat until a self consistent solution is obtained
- 7) Calculate total energy

2.2.1 Implementations in DFT

On principal grounds, DFT shows a way for reformulation and solution of Schrödinger equation. Yet, obtaining total energies and related properties of materials still require assumptions, approximations and approaches for system variables and computational methods. In this section, the essential concepts that should be introduced into computations will be presented. A detailed comparison of different implementations can be found in Mattsson and friends' review [65]. In Fig. (2.1) some of the important implementations on the terms of the single particle Kohn-Sham equation can be seen.



Figure 2.1: Different implementations for the terms in singe-electron Kohn-Sham equation

Exchange-Correlation Functional

The exact form of exchange-correlation hole is unknown except for the one calculated for homogenous electron gas [66, 67]. Hohenberg, Kohn and Sham [20] replaced the exact exchange-correlation energy per electron at a point r in the electron gas, ε^{XC} , with the exchange-correlation energy per electron in a homogeneous electron gas that has the same density as the electron gas at point r. This is called local density approximation (LDA). From this assumption E^{XC} can be written as

$$E^{XC}[n(\mathbf{r})] = \int \varepsilon_{hom}^{XC}[n(\mathbf{r})] \ n(\mathbf{r}) \ d^3\mathbf{r}$$
(2.29)

This formulation of LDA ignores near-by inhomogeneities in the electron density. An alternative technique is to use a semi-local approximation which includes both electron density and its gradient (or higher order gradient expansion) at point **r**. These gradient corrected or formally known GGA (generalized gradient approximation)It is important to note that the single-electron wavefunctions mentioned in here and in the following content have also spin degrees of freedom and they can explicitly be introduced by considering electrons with up and down spins at position \mathbf{r} functionals [68–73] can be written in the form

$$E_{GGA}^{XC}[n(\mathbf{r})] = \int \varepsilon_{GGA}^{XC}[n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r})] \ n(\mathbf{r}) \ d^3\mathbf{r}$$
(2.30)

Other functionals like Meta-GGA [74] (that depends on the kinetic energy density of the Kohn-Sham orbitals), Hyper-GGA [75] (in which Kohn-Sham one-electron wavefunctions are used to calculate Hartree-Fock exchange) and Hybrids [76–78] (which mix Hartree-Fock exchange and DFT exchange) are progressive steps in prediction power of DFT.

LDA and GGA are the most common exchange-correlation functionals in DFT calculations. Moreover, they both have spin-degenerate, Eq.'s (2.29, 2.30), and spin-polarized forms [79]. For a spin-polarized calculation $(n_{\uparrow}(\mathbf{r}) \neq n_{\downarrow}(\mathbf{r}), n = n_{\uparrow} + n_{\downarrow})$, local spin density (LSD) can be implemented in LDA and GGA respectively as

$$E_{LDA}^{XC}[n(\mathbf{r})] = \int \varepsilon^{XC}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})] \ n(\mathbf{r}) \ d^{3}\mathbf{r}$$
(2.31)

$$E_{GGA}^{XC}[n(\mathbf{r})] = \int \varepsilon^{XC}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}), \nabla n_{\uparrow}(\mathbf{r}), \nabla n_{\downarrow}(\mathbf{r}), ...] n(\mathbf{r}) d^{3}\mathbf{r} \qquad (2.32)$$

Periodicity and k-point Sampling

Effective single-particle formalism is a great simplification in DFT. However, it is still necessary to evaluate a huge number of these non-interacting electrons with the backround of an effective potential created by another huge number of nuclei. Luckily, the periodicity makes calculations easier in DFT. The ionic potential have the periodicity of the underlying ionic arrangement such as in a crystal. If v_{ext} is the ionic potential acting on an electron, then for all real-space Bravais lattice vectors **T**,

$$v_{ext}(\mathbf{r} + \mathbf{T}) = v_{ext}(\mathbf{r}) \tag{2.33}$$

This invariance under lattice translation \mathbf{T} helps the entire solution to be made in some reduced part of the system and the solution will repeat itself with the translational symmetry of the system.

The Bloch's theorem [80] states that in a periodic potential eigenstate ψ of one-

electron Hamiltonian, Eq. (2.22) can be written as the product of a wave-like part and a periodic part. Thus for a periodic system

$$\psi_i(\mathbf{r}) = e^{ik \cdot r} f_i(\mathbf{r}) \tag{2.34}$$

$$f_i(\mathbf{r} + \mathbf{T}) = f_i(\mathbf{r}) \tag{2.35}$$

$$\psi_i(\mathbf{r} + \mathbf{T}) = e^{ik \cdot \mathbf{T}} \psi_i(\mathbf{r})$$
(2.36)

Bloch formulation replaces the problem of solving a massive number of electronic wavefunctions to problem of introducing sampling k points (or wave vectors in reciprocal lattice) in the Brillouin zone having feasible number of wavefunctions to be solved. In addition to the translation symmetry, periodic systems may also obey other symmetry operations like rotations, inversions etc.. which transform one wave vector into another wave vector. So, complete symmetry definition reduces the problem to smallest possible zone so called irreducible Brillouin zone. In theory an infinite number of k points should be considered in the calculations but fortunately electronic wavefunctions at closely spaced k points vary a little from each other. Consequently, a single k point can be enough to describe a region in reciprocal space.

Several methods [81–85] have been developed to sample out the k points in order to obtain an accurate definition of the electronic structure however a computational error is introduced in DFT due to small number of k points used in calculations. The magnitude of the this error must be checked and reduced by increasing the size of kpoint mesh in order to keep it out of the energy resolution of DFT i.e. on the order of 1 meV.

Basis Sets and Electron-Ion interactions

In chemistry, basis set is a set of functions used to create the molecular orbitals that are expanded as a linear combination of such functions with the weights or coefficients to be determined. In accordance with this, basis set is the type of expanded function in defining Kohn-Sham single-electron wavefunction in Eq. (2.22).

The type of basis functions can vary in connection with the external potential of ions. There are several approaches in describing ionic potential and corresponding basis function. One of the most commonly used approach is the pseudopotential method [86, 87] with plane wave type basis. The basic idea of the pseudopotential theory is that the core electrons are chemically inactive and valence electrons determine the chemical properties of atoms and solids. So valence states are described by smooth wavefunctions (and a weaker potential) as in Fig. (2.2). There are several ab initio schemes for generating pseudopotentials such as Kerker [88], Bachelet-Hamann-Schlüter (BHS) [89], Hamann-Schlüter-Chiang (HSC) [90, 91], Rabe-Rappe-Kaxiras-Joannopoulos (RRKJ) [92], Troullier-Martins (TM) [93], Vanderbilt (US-PP) [94] and Fritz-Haber Institute (FHI) [95].

One important parameter in using plane waves as the basis set is the kinetic energy of the waves. Higher this kinetic energy, higher the number of plane waves in the wavefunction expansion which adds to computation time. Like in the k point case, the convergence in the energy must be controlled. So it is necessary to select an optimum cut-off energy considering both accuracy and computation time.

Over the years, modifications and new approximations have been made in potential and corresponding basis set definitions. One technique is to include core electrons in the calculations (all electron methods). These methods require modified basis sets such as full potential (no shape approximations for the potential field) linearized augmented plane waves (FPLAPW) or linearized muffin tin orbitals (LMTO). These adaptations are achieved by dividing the unit cell into two regions of non-overlapping atomic spheres (centered at the atomic sites) and an interstitial region in which different types of basis sets are used. Another very popular method is the Projector Augmented Wave method (PAW) which combine the traditions of augmented wave methods and the pseudopotential approach into a unified electronic structure method.

Dynamics of Ionic System

In the previous sections, the relaxation of the electronic configuration to its ground state was discussed on the backround of fixed ionic positions, cell shape and size. These ionic and lattice wise degrees of freedom can also be included in the calculations as comprehensively discussed in reviews of Payne et al. [22] and Kresse and Furthmüller [23, 24].

The equations of motion for the positions of ions, Eq. (2.37) and the coordinates of the unit cell, Eq. (2.38) can be given as follows



Figure 2.2: Schematic illustration of all-electron (solid lines) and pseudo-electron approximation of potential and wavefunction. r_C is the core boundary above which where all-electron and pseudoelectron potentials are equal [22]

$$M_I \ddot{\mathbf{R}}_I = -\frac{\partial E}{\partial \mathbf{R}_I} \tag{2.37}$$

$$\beta \ddot{\alpha}_v = -\frac{\partial E}{\partial \alpha_v} \tag{2.38}$$

where M_I is the mass of ion I and β is a fictious mass related with the dynamics of the unit cell coordinates (α). Hellmann-Feynman Theorem [96] states that partial derivative of the Kohn-Sham energy with respect to ionic position gives the real physical force on the ion when the electronic wavefunction is the eigenstate of the Kohn-Sham Hamiltonian (i.e. the electronic configuration at ground state or very near). Than, the relation can easily be written as in Eq. (2.39). Moreover, the ration holds for any derivative of the total energy which in turn also simplifies the calculation of stresses on the unit cell.

$$\mathbf{f}_I = -\frac{dE}{d\mathbf{R}_I} \tag{2.39}$$

In calculation of Kohn-Sham ground state, two methods can be distinguished. First is the simultaneous solution of equations of motion and update of parameters for electrons, ions and cell. This method has been pioneered by Car and Parinello [60]. The second is the iterative or formally known self consistent cycle methods in which iterative improvement of charge density and potential is involved. As the ground state for electrons is obtained, Hellmann-Feynman forces can be calculated and ionic and cell wise parameters can be updated. Decreasing the forces at each step reduces the kinetic energy in the system and the system moves through a local minimum. In calculations ionic and cellular motions may or may not be constrained depending on the conservation or destroying the crystal symmetry.

In all methods the aim is to reach the global minimum, however there is no quarantee that the global energy minimum is located. Instead, a local one might be obtained. Thus, in calculations involving structural optimization, many different starting points for the atomic and cellular arrangements are needed to predict the global energy minimum of the chemical system correctly. This problem somewhat reduced in metallic, ceramic and semiconductor systems because of the limited number of underlying lattices (such as face centered cubic, body centered cubic, hexagonal closed packed etc.).

CHAPTER 3

METHODOLOGY

In this study, thermodynamic stability, hydrogen storage capacity, equilibrium crystal and electronic structures of AB type (A = Al, Be, Cu, Fe, Ni, Sb, V and B = Ti) binary intermetallic hydrides were systematically investigated at ground state. For this task, ABINIT [97, 98] software package was used. The code relies on an efficient Fast Fourier Transform algorithm [99] for the conversion of wavefunctions between real and reciprocal space, on the adaptation to a fixed potential of the bandby-band conjugate gradient method [22] and on a potential-based conjugate-gradient algorithm for the determination of the self-consistent potential [100]. Generalized gradient approximation (GGA) was performed and Fritz-Haber-Institute GGA pseudopotentials [95] were used to represent atomic cores.

The main code takes the description of the unit cell and atomic positions as input. Then, it assembles a crystal potential from the input atomic pseudopotentials and generates an initial charge density and screening potential by using either an input wavefunction or simple gaussians. The planewave coefficients are adjusted through an iterative self-consistent algorithm until sufficient energy convergence is reached. Consequently, the code allows one to find the electronic structure (or equally the set of eigenvalues and wavefunctions that gives the lowest (DFT) energy possible for given basis set -the number of planewaves specified by energy cutoff-) for a fixed set of atomic positions within a periodic unit cell.

The code is also capable of determining the derivatives of the energy with respect to atomic positions and unit cell primitive translations analytically which yield atomic forces and the stress tensor respectively. Subsequently, atomic forces and lattice stresses can be minimized until equilibrium by adjusting ionic positions and cell parameters.
3.1 Computational Tools

Within the capabilities of ABINIT, the equilibrium structures, total energies, electronic density and electronic occupations at energy levels (i.e. density of states -DOS-) can be determined by letting the systems relax electronically, ionically and lattice wise to ground state. At this point, it is important to note that ground states are the structures that are stable in the limit temperature of zero Kelvin. Thus, the calculations do not involve temperature excitations. On the other hand, many of the electronic properties of a metal hardly differ from their values at zero Kelvin, even at room temperature because room temperature indeed a very low temperature for the electron gas at metallic densities [80].

Electronic analysis can also be employed since chemical bonds and their type (i.e ionic, covalent, metallic etc.) are results of electronic structures and electronic interactions. Simply to say, chemical bonds are the redistribution of valence electrons of chemical species in order to reduce the energy of the system. Accordingly, keeping track of electronic evolution can provide valuable information about the bonds that form during chemical reactions. As a result, physical properties can be deduced since they are consequences of chemical bonding between constituent atoms. Because of these facts, several methods in conjunction with electronic structure such as charge density, differential charge density, density of states and Hirshfeld charge analyses can be performed. The points stated above are illustrated below for Al, NaCl and Si which are typical examples for metallic, ionic and covalent materials.

3.1.1 Charge Density

Electronic density is the main variable in DFT. It shows the distribution of valence charge in real space. A plot of charge density in real space coordinates can display main features of the type of bonding. In Fig. (3.1) calculated electron densities of Al, NaCl and Si are given. It is seen that electronic charge is homogeneously distributed in the lattice around ions (i.e. metallic bonding) for Al. For the ionic compound NaCl, the charge is accumulated around Cl and Na has almost no valence electron showing electron transfer from electropositive to electronegative species. Finally, in Si, charge is collected on a line connecting neigbor silicons that implies electron sharing for covalent bonding.

Yet, it is important to realize that as the system gets complicated, bond identification become more of a problem. So other means of characterization are needed.



Figure 3.1: Valance electron density plot for (a) Al FCC-(111), (b) NaCl (100) and (c)Si diamond-(110)

3.1.2 Density of States

Density of states is simply the distribution of electrons on energy levels. From this data, one can deduce whether the material is metallic, semiconductor or insulator depending on the position of Fermi Energy and the width of the band gap. However, it should always be kept in mind that DFT underestimates band gap width when compared to experimental data.

Thanks to ABINIT, it is also possible to obtain density of states specific to each constituent atom separately with angular momentum (s,p,d,f) components. This partial DOS analysis can be used to observe contribution of states to bonding from different atoms. Moreover, hybridization of valence orbitals can be predicted.

In Fig. (3.2, 3.3, 3.4), DOS for Al, NaCl and Si are given along with their with angular momentum components. The Fermi energy is shifted to zero and will be so for the rest of the DOS plots. The distribution of electrons on energy levels in aluminum indicates a metallic character since there are available empty conduction states next to Fermi energy. In NaCl a wide band gap is observed indicating an insulating material. It is an indication of highest filled state. Cl has very sharp and definite 3s and 3p (i.e. valence electron orbitals) states just like an inert gas. When compared to Cl, Na has almost no electrons around itself. Again, for silicon 3s and 3p states are dominant. A small band gap of about 0.65 eV is seen which is lower than experimentally determined band gap of 1.11 eV for Si. This underestimation of the band gap is an example of DFT band-gap problem.



Figure 3.2: Total DOS and its angular momentum components for Al



Figure 3.3: Total DOS and its angular momentum components for NaCl



Figure 3.4: Total DOS and its angular momentum components for Si

3.1.3 Hirshfeld Charge

As discussed earlier, charge transfer is an important concept in discussion of chemical bonds. Several methods including Mulliken, Bader, Hirshfeld, Weinhold and Voronoi Deformation Density are compared in Guerra et al.'s study [101]. Among these, Hirshfeld charge analysis [102] is based on the electron density as a function of real space coordinates. In this method a promolecule is created from ground state atomic densities of constituent atoms. Then, it is assumed that the contribution of atom A to real electronic density have the same ratio as atomic density of A contributing in the promolecule, Eq. (3.1).

$$n(\mathbf{r})_{A}^{molecule} = \frac{n(\mathbf{r})_{A}^{atomic}}{n(\mathbf{r})^{promolecule}} \ n(\mathbf{r})^{molecule}$$
(3.1)

Then, Hirshfeld charge is obtained by Eq. (3.2) where Z_A is the nuclear charge.

$$Q_A^{Hirshfeld} = Z_A - \int n(\mathbf{r})_A^{molecule} d\mathbf{r}$$
(3.2)

From the formulation it is seen that the atomic radius and charge distribution to this radius accounts heavily in the calculated charge.

Hirshfeld charge calculations are given in Table (3.1) for Al, NaCl and Si. Here, Hirshfeld charge is the charge associated with the corresponding atom in the compound. The net charge is the difference between valence charge of free atom and the charge associated with the atom in the compound. Negative and positive net charge means charge taken and given respectively. Since Hirshfeld analysis is a quantitative tool and Al and Si are pure, no data can be obtained for these. On the other hand, a charge transfer is seen from Na to Cl in NaCl. Atomic Cl has seven valence electrons but in the compound this value is increased by an amount indicated as net charge. Conversely, Na lost electrons by the same amount.

Table 3.1: Hirshfeld and net charges of Al, NaCl and Si

Atom	Z-ion	Hirshfeld Charge	Net Charge
Al	3.0	-2.999992	8.422096×10^{-6}
Na	1.0	$-8.551319 imes 10^{-1}$	1.448681×10^{-1}
Cl	7.0	-7.144850	-1.448502×10^{-1}
Si	4.0	-3.999990	9.557732×10^{-6}

3.1.4 Differential Charge Density

Charge density of the final product displays the chemical bonds in that system. It does not say anything about the chemical reaction (or electronic changes). So, in order to have a better picture of changes following hydrogen insertion to the system, charge densities of the initial and final compounds can be compared. To do so, charge density difference can be investigated, Eq. (3.3).

$$\Delta n(\mathbf{r}) = n(\mathbf{r})^*_{compound} - n(\mathbf{r})^*_{metal}$$
(3.3)

The (*) means that the electron density is obtained from the same cell structure (i.e. the structure of fully relaxed corresponding hydride) for both hydride and intermetallic. The second term on the left hand side of the Eq. (3.3) is calculated by removing hydrogen from hydride structure and relaxing the remaining electronically. Then charge density of this structure is subtracted from the charge density of hydride point by point in space.

3.2 Computational Details

The studied systems AlTi, BeTi, CuTi, FeTi, NiTi, SbTi, VTi and their hydrides with various hydrogen compositions are modeled with an accuracy such that the total energy convergence for the k-point mesh and cut-off kinetic energy for plane waves are on the order of 1 meV for all systems. According to this, the selected parameters are given in Table (3.2). The structures were fully relaxed (electronic, ionic and cell wise) in order to obtain the minimum total energy. The electronic relaxation is stopped when the energy difference between two consequtive steps drops below 5.0×10^{-9} Hartree. Ionic and cell wise iterations are stopped when maximal absolute force tolerance reaches 5.0×10^{-5} Hartree/Bohr. Spin polarization was taken into account for FeTi and NiTi because of the magentic nature of Fe and Ni. Moreover, calculated cell parameters were compared with experimental data so as to check the validity of calculations.

3.2.1 Thermodynamic Evaluation of Hydrides

The formation reaction for the AB-hydride can simply be written as in Eq. (3.4) and with the calculated total energies of the intermetallic (AB), its hydride (ABH_x) and

System	Cut-off (Hartree)	Space group	k-point mesh
AlTi	35	17, 47, 65, 83,	$8 \times 8 \times 8$
		89, 99, 111, 115,	
		123	
BeTi	35	17,65,166	$8 \times 8 \times 8$
		123, 200, 215,	$10\times10\times10$
		221	
CuTi	75	17, 59, 65, 67,	$6 \times 6 \times 6$
		85, 90, 99, 113,	
		115, 129	
FeTi	60	17,65	$8 \times 8 \times 8$
		123, 200, 215,	$12\times12\times12$
		221	
		166	$10\times10\times10$
NiTi	70	17,65,166	$8 \times 8 \times 8$
		123, 200, 215,	$12\times12\times12$
		221	
SbTi	45	63, 164, 176,	$6 \times 6 \times 6$
		186, 187, 190,	
		194	
VTi	45	17, 123, 166,	$10\times10\times10$
		200, 215, 221	
		65	$6 \times 6 \times 6$

Table 3.2: Energy cut-off and k-point mesh for all systems and their corresponding space groups

hydrogen molecule (H₂), formation energy Eq. (3.5) of the hydride can simply be determined.

$$\frac{2}{n}AB + H_2 \to \frac{2}{n}ABH_n \tag{3.4}$$

$$\Delta E_{form} = (\frac{2}{n}) E_{ABH_n} - (\frac{2}{n}) E_{AB} - E_{H_2}$$
(3.5)

The coefficients of the reaction are normalized to define the formation energies per one molecule of H_2 so as to simplify the comparison. H_2 gas contains an important entropy term, however it is not included in first principles calculations. Thus the energy of H_2 is approximated to the energy of an H_2 molecule in vacuum at zero Kelvin. Moreover, even at a temperature of absolute zero, the atoms in any material must have a non-zero vibrational energy, which is called the zero-point energy. Due to low mass of hydrogen this contribution can be significant in hydrides. It is also true for hydrogen gas in vacuum at zero Kelvin. The determined formation energies, therefore, do not represent the absolute values of real formation energies. Instead, relative energy differences can provide a good means of comparison of systems. Although formation energy is a useful parameter in determination of relative stability among hydrides with same hydrogen composition, it is more convenient to use mixing energy for stability comparison between hydrides with different hydrogen composition. Mixing energy can be described as the energy of the reaction, Eq. (3.6), between two compounds which determines either these compounds mix to form a tertiary compound or phase separation occurs.

$$(1 - \frac{n}{m})AB + \frac{n}{m}ABH_m \to ABH_n \tag{3.6}$$

$$\triangle E_{mix} = E_{ABH_n} - \left(\frac{n}{m}\right) E_{AB_m} - \left(1 - \frac{n}{m}\right) E_{AB} \tag{3.7}$$

Again, the coefficients are normalized to describe mixing energies per mole of the formed hydride. For all hydrides, formation energies and mixing energies were calculated. In addition, 2-dimensional convex hulls are constructed on mixing energy plots (via Qhull [103]) which form the smallest convex around the points, trace the lowest energy path between phases. These in turn visualize a simple phase distribution diagram.

3.2.2 Structures of Hydrides

The crystal structures of the studied intermetallics can be obtained from literature but most the important aspect of this study is to devise a route for hydrogen insertion to these intermetallics and predict the resulting structural changes. To illustrate the approach used in this work, the question 'what may happen to an AB-type intermetallic in CsCl structure (say FeTi, see Fig. (3.5)) during hydride formation?' can be raised.

First of all, hydrogen intercalation may not change the crystal structure and symmetry. The size of the cell can alter but the space group does not change, see Fig. (3.6). Another possibility is that the A-B coordination (cubic in this case) and symmetry is conserved but the crystal symmetry is reduced due to inserted hydrogens. This time cubic subgroups of the starting space group are produced, for example Fig. (3.7).

Secondly, A-B coordination can be conserved but A-B metallic symmetry may break down along with crystal symmetry due to distortions caused by hydrogen. This situation can be handled with non-cubic (tetragonal, orthorhombic, monoclinic



Figure 3.5: Unit cell for FeTi in CsCl (space group no. 221) structure where Fe and Ti sit 1a and 1b Wyckoff positions respectively.



Figure 3.6: A sample unit cell for $FeTiH_3$ in s.g. no. 221 (cubic) where Fe, Ti and H sit 1a, 1b and 3c Wyckoff positions respectively.



Figure 3.7: A sample unit cell for FeTiH_4 in s.g. no. 215 (cubic) where Fe, Ti and H sit 1a, 1b and 4e Wyckoff positions respectively.

etc.) subgroups of CsCl, for example Fig. (3.8, 3.9).

Finally, crystal symmetry, A-B symmetry and coordination are all lost for which the number of systems to be considered in the phase space can be infinite in order to predict the ground state correctly. There is not much to do in such a circumstance.

Taking these conditions in consideration, CsCl (s.g. no. 221), its subgroups (s.g. no. 215, 200, 166, 123), subgroups of the subgroups (s.g. no. 17, 65 i.e. experimentally determined crystal structures of FeTiH and FeTiH₂) where A-B atomic coordination is similar to original AB were taken into account. In doing so, it is assumed that upon hydrogenation, the eight-fold CsCl metallic coordination does not change. Nevertheless, restrictions imposed by symmetry are decreased gradually as going through lower subgroups. As a result, the relaxation freedom is increased either in lattice parameters or in atomic positions. Then the procedure defined above is employed to create sampling phase space and hydrogen atoms are placed in available Wyckoff positions in these structures to construct ABH_x (x=1,2,...,n) compounds. Lastly, all of these structures are fully relaxed by using ABINIT.

In addition, experimentally determined crystal structures for the given hydrides were also considered and in the reassessment of these structures, the constituent atoms were placed in Wyckoff positions with the highest site occupancy.



Figure 3.8: A sample unit cell for $FeTiH_2$ in s.g. no. 123 (tetragonal) where Fe and Ti sit 1a and 1d. Wyckoff positions respectively. H is positioned in 1b and 1c site.



Figure 3.9: A sample unit cell for FeTiH in s.g. no. 17 (orthorhombic) where Fe, Ti and H sit 2c, 2d and 2a Wyckoff positions

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Formation Energies of Hydrides

4.1.1 BeTi

The crystal structure of BeTi was given by Tanner and Giessen [104] as CsCl and described as a metasable phase. Experimentally determined cell parameter is 2.940 Å. Be is in 1a (x = 0 y = 0 z = 0) and Ti is in 1b (x = 1/2 y = 1/2 z = 1/2) sites. This structure is calculated to have a lattice parameter of 2.956 Å. According to this the error in calculation is 0.54 %. There are no specific data about the hydride of this phase in literature possibly because of poisinious nature of beryllium.

In Table (4.1), the trial hydride systems with corresponding crystal structures and atomic positions are given. The calculated formation energies versus hydrogen content for the given structures are presented in Fig. (4.1). Hydrides with negative formation energies are spotted at three different compositions $BeTiH_{0.5}$, BeTiH and $BeTiH_2$. These structures are summarized in Table (4.2).

Space group	Be	Ti	H/BeTi						
			0.5	1.0	2.0	3.0	4.0	6.0	7.0
17	2c	2d		2a					
65	2a	2c		2b, 2d	2b+2d, 4e,	2b+4e, 2b+4f,	4g+4i, 4g+4j,		
					4f, 4g, 4h, 4i,	2d+4e, 2d+4f	4h+4i, 8m, 8n,		
					4j, 4k, 4l		80		
65	4i	4h	2a, 2b,	4e, 4f, 4g, 4j,	2a+2c+4e,				
			2c, 2d	4k	$8\mathrm{m}$				
123	1a	1d		1b, 1c	1b+1c, $2e$,	1b+2e, 1b+2f,	1b+1c+2g,		
					2f, 2g, 2h	1b+2h, 1c+2e,	2e+2f, $2e+2g$,		
						1c+2f, $1c+2g$,	2e+2h, $2f+2g$,		
						1c+2h	2f+2h, $2g+2h$,		
							4i, 4j, 4k, 4l,		
	_						4m, 4n, 4o		
166	1a	1b			2c	3d, 3e			
200	1a	1b						6f, 6g	
215	1a	1b				_	4e	_	3c+4e
221	1a	1b				3c, 3d		3c+3d,	
								6e, 6f	

Table 4.1: The definition of the structures for BeTi-hydrides giving the space groups and Wyckoff positions of the atoms with in the unit cells. Total number of structures calculated is 73



Figure 4.1: Formation energies of calculated BeTi-hydride systems

The eight-fold cubic coordination of Be around Ti and vice versa, is distorted upon hydrogen entry during formation of $BeTiH_{0.5}$. In this composition hydrogen is placed in an octahedral interstitial postion. The Ti-Ti interatomic distances lie between 2.871-3.161 Å. On the other hand, Be-Be distance shows a range between 2.907-3.414 Å. Be-Ti distance varies a little between 2.535-2.667 Å. The hydrogen placed in a 2Be-4Ti octahedra which separates Be-Be atoms mainly. This indicates a weaker bond strength among Be-Be atoms. In this octahedra, Be-H and Ti-H distances are 1.707 Å and 2.048 Å that means the beryllium and hydrogen react more strongly in the system. Further increase in hydrogen content does not change the metal coordination around H. New coming hydrogen sits in the same octahedral position. Ti-H and Be-H distances change very slightly. This is also true for Be-Ti distance. However, the Be-Ti coordination is changed to an eight-fold tetragonal with distances 2.845 Å and 3.467 Å. BeTiH₂ forms with a significant increase in formation energy through positive values. Metallic eight-fold coordination is again distorted with Ti-Ti and Be-Be distances between 2.765-4.203 Å and 2.765-3.729 Å respectively. Be-Ti distance is increased to 2.751-2.779 Å. There are three types of octahedral sites exist that hydrogen is inside. Two 2Be-4Ti octahedra with different

hydrogen-metal distances and one 4Be-2Ti octahedron.

	s.g.	Cell	param.	Be		Ti		Η	
BeTi	221	a = 2.956	$\alpha = 90$	1a	x = 0.0	1b	x = 0.5		
		b = 2.956	$\beta = 90$		y = 0.0		y = 0.5		
		c = 2.956	$\gamma = 90$		z = 0.0		z = 0.5		
$BeTiH_{0.5}$	65	a = 5.824	$\alpha = 90$	4i	x = 0.0	4h	x = 0.246	2a	x = 0.0
		b = 6.321	$\beta = 90$		y = 0.270		y = 0.0		y = 0.0
		c = 2.922	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.0
BeTiH	65	a = 4.023	$\alpha = 90$	2a	x = 0.0	2c	x = 0.5	2d	x = 0.0
		b = 4.023	$\beta = 90$		y = 0.0		y = 0.0		y = 0.0
		c = 3.467	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.5
$BeTiH_2$	65	a = 7.315	$\alpha = 90$	4i	x = 0.0	4h	x = 0.213	2a	x = 0.0
		b = 5.911	$\beta = 90$		y = 0.312		y = 0.0		y = 0.0
		c = 2.765	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.0
								2c	x = 0.5
									y = 0.0
									z = 0.5
								4 e	x = 0.25
									y = 0.25
									z = 0.0

Table 4.2: Optimized structural parameters for the stable phases in BeTi system

4.1.2 AlTi

A tetragonal unit cell with space group no. 123 is given for AlTi [105]. The lattice parameter a is equal to 4.001 Å and c is equal to 4.071 Å. Aluminum atoms are placed in 1a ($x = 0.0 \ y = 0.0 \ z = 0.0$) and 1c ($x = 0.5 \ y = 0.5 \ z = 0.0$) sites and titanium atoms are placed in 2e site ($x = 0.0 \ y = 0.5 \ z = 0.5$). The calculations yield a as 4.040 Å and c as 4.134 Å. The maximum error is about 1.6 % in c parameter. The calculated hydride structures are given in Table (4.3). In this table some of the Wyckoff positions are written twice (or more) side by side for hydrogen. This is due to the fact that different coordinates were used for hydrogen at the same Wyckoff position. In all other trial structure definition tables the same logic is valid.

The formation energies of AlTi-hydrides are all positive except $AlTiH_{\sim 0.5}$, see Fig. (4.2). This phase is barely stable since it has a negative formation energy with an absolute value very close to zero. AlTiH is also taken into consideration because of its small positive formation energy. These structures are summerized in Table (4.4).

Space group	Al	Ti	H/AlTi						
			0.5	1.0	1.5	2.0	2.5	3.0	4.0
17	2c	2d		2a					
47	1a+1f	1d+1g	1b, 1c,	2i, 2j, 2k, 2l,		4u, 4v, 4w			
			1e, 1h	2m, 2n, 2o,					
				2p, 2q, 2r,					
				2s, 2t					
65	2a+2b	4f	2c, 2d	4g, 4h, 4i, 4j,	2a + 2c + 4e,				
				4k, 4l	$8\mathrm{m}$				
65	4i	4h			2a+2c+4e				
83	1a+1c	2f				4j, 4k			81
89	1a+1c	2f							$8\mathrm{p}$
99	1a+1b	2c				4d, 4d, 4e, 4f			4d+4d
111	1a+1d	2f				4n			80
115	1a+1b	$2\mathrm{g}$	1c, 1d	1c+1d, $2e$,	1c+2e,	2e+2f, 4i, 4j, 4k	1c+4i, 1c+4j,	2f+4i	4i+4j,
				2f, 2g, 2g	1c+2g,		1c+4k, 1d+4i,		4i+4k
					1d+2f		1d+4j, 1d+4k		
123	1a+1c	2e	1b, 1d	1b+1d, $2f$,	1b+2f,	1b+1d+2f,			8r, 8s, 8t
				2g, 2h	1b+2h,	2f+2h, 2g+2h,			
					1d+2f	4i, 4k, 4l, 4m,			
						4n			

Table 4.3: The definition of the structures for AlTi-hydrides giving the space groups and Wyckoff positions of the atoms with in the unit cells. Total number of structures calculated is 85



Figure 4.2: Formation energies of calculated AlTi-hydride systems

In AlTiH_{~0.5}, hydrogen is placed inside a 2Al-4Ti octahedral interstitial site. Only aluminum at 1c Wyckoff position is included in this octahedron. The eight-fold tetragonal Al (Ti) coordination around Ti (Al) is conserved for both AlTiH_{~0.5} and AlTiH. Only the longer edge in this tetragonal expand with hydrogen insetion from 4.134 Å (for AlTi) to 4.233 Å (for AlTiH_{~0.5}) and 4.431 Å (for AlTiH). Increasing hydrogen content increases Al-H distance and decreases Ti-H bond length very slightly.

4.1.3 VTi

The crystal structure of VTi is a disordered body centered cubic with space group no. 229 [105]. The lattice parameter is 3.140 Å and the metals are placed in 2a $(x = 0.0 \ y = 0.0 \ z = 0.0)$ Wyckoff position. To model this structure, a CsCl-type cell (space group no. 221) is used. V and Ti atoms are placed in 1a $(x = 0.0 \ y =$ $0.0 \ z = 0.0)$ and 1b $(x = 0.5 \ y = 0.5 \ z = 0.5)$ sites respectively. The calculated lattice parameter for this CsCl-type cell is 3.194 Å so the error for this approximation is about 1.7 %.

Nowak and Minier [106] reported $VTiH_{\sim 4}$ with a cubic unit cell (space group

	s.g.	Cell	param.	Al		Ti		Η	
AlTi	123	a = 4.040	$\alpha = 90$	1a	x = 0.0	2e	x = 0.0		
		b = 4.040	$\beta = 90$		y = 0.0		y = 0.5		
		c = 4.134	$\gamma = 90$		z = 0.0		z = 0.5		
				1c	x = 0.5				
					y = 0.5				
					z = 0.0				
$AlTiH_{0.5}$	123	a = 4.052	$\alpha = 90$	1a	x = 0.0	2e	x = 0.0	1d	x = 0.5
		b = 4.052	$\beta = 90$		y = 0.0		y = 0.5		y = 0.5
		c = 4.233	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.5
				2b	x = 0.5				
					y = 0.0				
					z = 0.0				
AlTiH	65	a = 8.861	$\alpha = 90$	2a	x = 0.0	4f	x = 0.25	4g	x = 0.251
		b = 5.693	$\beta = 90$		y = 0.0		y = 0.25		y = 0.0
		c = 2.846	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.0
				2b	x = 0.5				
					y = 0.0				
					z = 0.0				

Table 4.4: Optimized structural parameters for the stable phases in AlTi system

no. 225) in which V and Ti have a disordered occupancy at 4a site ($x = 0.0 \ y = 0.0 \ z = 0.0$) and hydrogen occupies 8c site ($x = 0.25 \ y = 0.25 \ z = 0.25$). The lattice parameter is 4.355 Å. The calculated hydride structures and predicted stable structures are given in Table (4.5) and Table (4.6).

Space group	V	Ti	H/VTi					
			0.5	1.0	2.0	3.0	4.0	6.0
17	2c	2d		2a				
65	2a	2c		2b, 2d	2b+2d, 4e,	2b+4e, 2b+4f,	4g+4i, 4g+4j,	
					4f, 4g, 4h, 4i,	2d+4e, 2d+4f	4h+4i, 8m, 8n,	
					4j, 4k		80	
65	4i	4h	2a, 2b,	4e, 4f, 4j, 4k,	2a+2c+4e			
			2c, 2d	41				
123	1a	1d		1b, 1c	1b+1c, 2e,	1b+2e, 1b+2f,	1b+1c+2e,	
					2f, 2g, 2h	1b+2h, 1c+2e,	1b+1c+2f,	
						1c+2f, $1c+2g$,	1b+1c+2g,	
						1c+2h	2e+2f, $2e+2g$,	
							2e+2h, $2t+2g$,	
							2g+2h, 4i, 4j,	
							4k, 4l, 4m, 4n,	
100	1	11			0	01.0	40	
100	$_{1a}$	1D			2c	3a, 3e		<u> </u>
200	1a 1	1b					4	61, 6g
215	1a 1	1D				0 01	4e	
221	la	Tp				3c, 3d		

Table 4.5: The definition of the structures for VTi-hydrides giving the space groups and Wyckoff positions of the atoms with in the unit cells. Total number of structures calculated is 68



Figure 4.3: Formation energies of calculated VTi-hydride systems

As seen in Fig. (4.3) at all hydrogen compositions, hydrides with negative formation energies are obtained. Hydrogen insertion into the system transforms eight-fold cubic metal-metal coordination to a distorted tetragonal arrangement. Hydrogen is inside a octahedron made up by two vanadium and four titanium atoms with V-H and Ti-H distances 1.940 Å and 2.137 Å respectively. When hydrogen content is increased and mono-hydride is obtained, the distortion is almost ceased in tetragonal metalmetal arrangement with very minor changes in Ti-Ti, V-V and V-Ti distances. New coming hydrogen atoms also placed in a 2V-4Ti octahedron and the V-H and Ti-H bond lengths are 1.913 Å and 2.143 Å. Further increase in hydrogen content produce a perfect tetragonal metallic coordination. This time however, there are two types of octahedra of equal edge lengths but one is 2V-4Ti and the other is 4V-2Ti that is V and Ti atoms switch sites. $VTiH_3$ is like an intermediate structure since some hydrogen atoms do not have proper metallic cages around them. The tetra-hydride is different from the previous hydrides by means of hydrogen-metal arrangement. Although the metallic coordination is still eight-fold tetragonal, hydrogen is inside a tetrahedron made up of two vanadium and two titanium atoms. V-H (1.923 Å) and Ti-H (1.955 Å) bond lengths are quite near. Close inspection of this structure revealed that it is equivalent to experimentally determined tetra-hydride [106] with maximum difference of 0.07 Å in bond lengths. In VTiH₆, hydrogen atoms are again in 2V-2Ti tetrahedra with V-H and Ti-H bond lengths 2.011 Å and 2.017 Å. There is a huge rise in formation energy after VTiH₄ and VTiH₆ is slightly stable as seen in Fig. (4.3). So it may be possible for VTi to store higher amount of hydrogen than four moles per formula. On the other hand, over six moles hydrogen per formula seems unlikely.

	s.g.	Cell	param.	V		Ti		Н	
VTi	221	a = 3.194	$\alpha = 90$	1a	x = 0.0	1b	x = 0.5		
		b = 3.194	$\beta = 90$		y = 0.0		y = 0.5		
		c = 3.194	$\gamma = 90$		z = 0.0		z = 0.5		
VTiH _{0.5}	65	a = 5.984	$\alpha = 90$	4i	x = 0.0	4h	x = 0.256	2a	x = 0.0
		b = 7.620	$\beta = 90$		y = 0.255		y = 0.0		y = 0.0
		c = 2.982	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.0
VTiH	65	a = 7.652	$\alpha = 90$	4i	x = 0.0	4h	x = 0.250	4e	x = 0.25
		b = 6.064	$\beta = 90$		y = 0.250		y = 0.0		y = 0.25
		c = 3.028	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.0
$VTiH_2$	123	a = 3.033	$\alpha = 90$	1a	x = 0.0	1d	x = 0.5	1b	x = 0.0
		b = 3.033	$\beta = 90$		y = 0.0		y = 0.5		y = 0.0
		c = 3.940	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.5
								1c	x = 0.5
									y = 0.5
									z = 0.0
$VTiH_3$	123	a = 2.749	$\alpha = 90$	1a	x = 0.0	1d	x = 0.5	1c	x = 0.5
		b = 2.749	$\beta = 90$		y = 0.0		y = 0.5		y = 0.5
		c = 5.345	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.0
								2g	x = 0.0
									y = 0.0
									z = 0.340
$VTiH_4$	65	a = 4.602	$\alpha = 90$	2a	x = 0.0	2c	x = 0.5	$8\mathrm{m}$	x = 0.25
		b = 4.622	$\beta = 90$		y = 0.0		y = 0.0		y = 0.25
		c = 4.197	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.243
$VTiH_6$	200	a = 3.604	$\alpha = 90$	1a	x = 0.0	1b	x = 0.5	6g	x = 0.248
		b = 3.604	$\beta = 90$		y = 0.0		y = 0.5		y = 0.5
		c = 3.604	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.0

Table 4.6: Optimized structural parameters for the stable phases in VTi system

4.1.4 FeTi

Among AB intermetallics, one of the most studied system is FeTi due to its moderate kinetics with relatively high equilibrium hydrogen pressure ($\approx 4 - 5$ atm) at room temperature. However, low storage capacity (1.8-1.9 wt%) and O₂, H₂O, CO poisoning problems could not be resolved fully in order to use in practical applications.

FeTi has CsCl-type structure which corresponds to $Pm\bar{3}m$ space group (no. 221) with a lattice parameter of 2.9789 Å [107]. Reilly and Wishwall [108] observed that FeTi reacts readily with hydrogen to form FeTiH_{~1} (β phase) and FeTiH_{~2} (γ phase) according to reactions:

$$2.13FeTiH_{0.1}(\alpha) + H_2 \to 2.13FeTiH_{1.04}(\beta)$$
(4.1)

followed by:

$$2.20FeTiH_{1.04}(\beta) + H_2 \to 2.20FeTiH_{1.95}(\gamma)$$
(4.2)

Reidinger et al. [109] claimed that phases present in a given FeTiH_x sample depends on the method of preparation and the sample history thus producing a hysteresis effect. They suggested that β_1 (FeTiH_{~1}) phase coexists with α phase during hydrogen desorption. On the other hand β_2 (FeTiH_{~1.4}) phase coexists with α phase during hydrogen absorption. Thompson et al. [110–112], in their consecutive studies, provided the possible crystal structures and atomic positions for the solid solution of FeTi-H (α phase) and the two known hydrides FeTiH_{~1}(β phase) and FeTiH_{~2} (γ phase). Fischer et al. [113] investigated FeTiD_{~2} assuming an orthorhombic symmetry for the crystal structure. They identified 4Ti-2Fe and 2Ti-4Fe octahedral sites for deuterium. 4Ti-2Fe sites are 100 % and 2Ti-4Fe sites are 91 % occupied by deuterium. The proposed crystallographic parameters for the FeTiH_{~1} and FeTiH_{~2} phases were summarized in Table (4.1.4).

Hydride	Reference	Structure	Cell parameters	Space group
$FeTiH_{\sim 1}$	Reilly and Wishwall [108]	Tetragonal	a = 3.18 Å	
(β)			$c=8.73~{\rm \AA}$	
	Thompson et al. $[110]$	Orthorhombic	a = 2.956 Å	No. 62, No. 26
			$b=4.543~{\rm \AA}$	No. 17, No. 28
			$c=4.388~{\rm \AA}$	
	Fischer et al. [114]	Orthorhombic	a=2.996 Å	No. 17
			b = 4.522 Å	
			$c=4.370~{\rm \AA}$	
$FeTiH_{\sim 2}$	Reilly and Wishwall [108]	Cubic	a = 6.61 Å	
(γ)		Monoclinic	$a=c=4.7044~{\rm \AA}$	No. 10
			$b = 2.8301 \text{\AA}$	
			$\beta = 96.97$	
	Thompson et al. [111]	Orthorhombic	a = 7.041 Å	No. 65
			b = 6.234 Å	
			$c=2.828~{\rm \AA}$	
	Fischer et al. $[113]$	Orthorhombic	a = 7.029 Å	No. 65
			b = 6.233 Å	
			c = 2.835 Å	

Table 4.7: Experimental data available for FeTi-hydrides

Space group	Fe	Ti	H/FeTi					
			0.5	1.0	2.0	3.0	4.0	6.0
17	2c	2d		2a				
65	2a	2c		2b, 2d	2b+2d, 4e, 4f, 4g, 4h, 4i, 4j, 4k, 4l	2b+4e, 2b+4f, 2d+4e, 2d+4f	4g+4i, 4g+4j, 4h+4i, 8m, 8n, 80	
65	4i	4h	2a, 2b, 2c, 2d	4e, 4f, 4g, 4j, 4k	2a+2c+4e, 8m			
123	1a	1d		1b, 1c	1b+1c, 2e, 2f, 2g, 2h	$\begin{array}{ll} 1b+2e, & 1b+2f, \\ 1b+2h, & 1c+2e, \\ 1c+2f, & 1c+2g, \\ 1c+2h \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
166	1a	1b			2c	3d, 3e		
200	1a	1b						6f, 6g
215	1a	1b					$4\mathrm{e}$	
221	1a	1b				3c, 3d		3c+3d

Table 4.8: The definition of the structures for FeTi-hydrides giving the space groups and Wyckoff positions of the atoms with in the unit cells. Total number of structures calculated is 69



Figure 4.4: Formation energies of calculated FeTi-hydride systems

When only the hydrogen compositions are considered, the calculations indicate that only half, mono and di-hydrides are stable among other trail hydrides, see Table (4.8), since only for these chemistries negative formation energies were obtained as in Fig. (4.4). In addition, for the tetra-hydride chemistry a nearly stable structure was identified. When the crystal structures are considered, experimentally determined structures for FeTiH [110, 114] and FeTiH₂ [111, 113] are found to have the most negative formation energy among their own composition groups. The computed lattice parameters for FeTi and hydrides came out to be very close to the experimental values, see Table (4.9), errors being in the order of 1-1.8 % which is acceptable for the DFT approximation.

Hydrogen is located inside an octahedral site surrounded with four titanium and two iron atoms in both FeTiH_{0.5} and FeTiH, see Fig. (4.5). However, in di-hydride, there are three kinds of octahedral hydrogen sites two having a similar coordination with FeTiH but different edge lengths from each other and one caged by four iron and two titanium atoms as in Fig. (4.6). Crystal systems having negative formation energies other than these, have also hydrogen at octahedral interstitial sites. All Structures, containing 2Fe-4Ti octahedra, have bond lengths of Fe-H 1.66-1.8 Å, Ti-H



Figure 4.5: Metal arrangement around hydrogen atom in FeTiH

2.14-2.20 Å. In 4Fe-2Ti octahedral cage, Fe-H (1.933 Å) and Ti-H (1.968 Å) distances almost same. As a general trend, systems having Fe-H bond length smaller than that of Ti-H have relatively lower energies. Smaller bond length indicates stronger interaction between iron and hydrogen in the structure. If Fe-Ti arrangement is inspected, FeTiH_{0.5}, FeTiH and FeTiH₂ have all distorted eight-fold tetragonals which can be seen in Fig. (4.7). The amount of distortion increases with increasing hydrogen content.

At FeTiH₄ composition the calculated lowest energy structure has a different metallic coordination around hydrogen. Rather than having an octahedral cage as in previously discussed stable structures, hydrogen has a tetrahedral coordination of two iron and two titanium atoms with Fe-H and Ti-H bond lengths of 1.756 Å and 1.967 Å, see Fig. (4.8) The calculations also showed that for the FeTiH₃, structures with H in octahedral cages are not the lowest energy states. The octahedral framework of FeTiH₀.5 and FeTiH is conserved when FeTiH₂ is produced. New hydrogen atoms are positioned at the other octahedral site of the structure without altering the previous one. Due to this structure preservation, the transformation reaction from mono to di-hydride has an energy bonus. On the other hand, the octahedral framework is destroyed when FeTiH₄ is formed. This in turn necessitates extra energy. The increase in the formation energy for FeTiH₄ can easily be correlated to this condition. The Fe-Ti coordination also changes from a distorted eight-fold arrangement to a tetragonal. Positive formation energy of this compound indicates that it is unstable. However, the magnitude is very small (~3.5 kJ/mol H₂). A minor



Figure 4.6: Metal arrangement around hydrogen atom in FeTiH₂

decrease, therefore, can favor the formation of this compound. Moreover, a small negative formation energy is advantageous when desorption is considered. So, with appropriate alterations in the composition of the intermetallic phase or temperature and pressure of the storage system, the tetra-hydride may be obtained.

4.1.5 NiTi

Intermetallic NiTi has been studied as a basic industrial shape memory alloy. It displays the martensitic transformation from the cubic (CsCl-type structure) to the monoclinic structure (space group no.11) upon cooling, proceeded by the premartensitic phenomena with transformation temperature near room temperature (TM = 333 K) [115]. CsCl-type structure has a lattice parameter of 3.007 Å [116]. NiTiH_{~1} and NiTiH_{~1.4} hydrides were reported to be experimentally obtained [117]. Experimentally found $H/M \approx 0.7$ ratio gives a 1.3 wt % which is low for practical usage. For this system, the trial hydrides and their formation energies are given in Table (4.10) and Fig. (4.9). The predicted stable structures are provided in Table (4.11).

In order to control the results of computations, the experimental NiTi cell parameters are compared with the computed ones. The cell parameter for the CsCl structure is found to be 3.075 Å. The error is on the order of 2 % which is acceptable for the DFT approximation.



Figure 4.7: Iron arrangement around titanium atom in FeTiH



Figure 4.8: Metal arrangement around hydrogen atom in $\rm FeTiH_4$

	s.g.	Cell	param.	Fe		Ti		Η	
FeTi	221	a = 3.004	$\alpha = 90$	1a	x = 0.0	1b	x = 0.5		
		b = 3.004	$\beta = 90$		y = 0.0		y = 0.5		
		c = 3.004	$\gamma = 90$		z = 0.0		z = 0.5		
$FeTiH_{0.5}$	65	a = 6.179	$\alpha = 90$	4i	x = 0.0	4h	x = 0.248	2b	x = 0.5
		b = 6.182	$\beta = 90$		y = 0.232		y = 0.0		y = 0.0
		c = 3.016	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.0
FeTiH	17	a = 2.986	$\alpha = 90$	2c	x = 0.0	2d	x = 0.5	2a	$x \simeq 0.0$
		b = 4.594	$\beta = 90$		y = 0.295		y = 0.747		y = 0.0
		c = 4.376	$\gamma = 90$		z = 0.25		z = 0.25		z = 0.0
$FeTiH_2$	65	a = 7.155	$\alpha = 90$	4i	x = 0.0	4h	x = 0.225	2a	x = 0.0
		b = 6.251	$\beta = 90$		y = 0.289		y = 0.0		y = 0.0
		c = 2.829	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.0
								2c	x = 0.5
									y = 0.0
									z = 0.5
								4 e	x = 0.25
									y = 0.25
									z = 0.0
$FeTiH_4$	123	a = 2.957	$\alpha = 90$	1a	x = 0.0	1d	x = 0.5	4i	x = 0.0
		b = 2.957	$\beta = 90$		y = 0.0		y = 0.5		y = 0.5
		c = 4.489	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.211

Table 4.9: Optimized structural parameters for the stable phases in FeTi system

Space group	Ni	Ti	H/NiTi					
			0.5	1.0	2.0	3.0	4.0	6.0
17	2c	2d		2a				
65	2a	2c		2b, 2d	2b+2d, 4e, 4f, 4g, 4h, 4i, 4j, 4k	2b+4e, 2b+4f, 2d+4e, 2d+4f	$\begin{array}{ll} 4g+4i, & 4g+4j, \\ 4h+4i, 8m \end{array}$	
65	4i	4h	2a, 2b, 2c, 2d	4e, 4f, 4j, 4k	2a+2c+4e, 8m			
123	1a	1d		1b, 1c	1b+1c, 2e, 2f, 2g, 2h	1b+2e, 1b+2f, 1b+2h, 1c+2e, 1c+2f, 1c+2g, 1c+2h	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
166	1a	1b			2c	3d, 3e		
200	1a	1b						6f, 6g
215	1a	1b					$4\mathrm{e}$	
221	1a	1b				3c, 3d		6e, 6f

Table 4.10: The definition of the structures for NiTi-hydrides giving the space groups and Wyckoff positions of the atoms with in the unit cells. Total number of structures calculated is 66



Figure 4.9: Formation energies of calculated NiTi-hydride systems

Unlike FeTi case, hydrogen is located inside an octahedral site surrounded with four titanium and two iron atoms up to NiTiH₄. Ni-H and Ti-H bond lengths in these octahedra are 1.729-1.809 Å and 2.071-2.349 Å. Previously proposed experimental structures for NiTiH_{~1} and NiTiH_{~1.4} [117] in space group no. 139, have Ni-H bond lengths of 1.70-1.80 Å and Ti-H 2.10-2.25 Å when highest occupancy atoms were considered.

As in VTi and FeTi, the tetra-hydride has a different metallic coordination around hydrogen. Instead of having an octahedral cage as in lower hydrogen bearing hydrides, hydrogen has a tetrahedral coordination of two nickel and two titanium atoms. The Ni-H bond length is 1.795 Å and Ti-H bond length is 1.964 Å. The calculations also show that this coordination change is between NiTiH₃ and NiTiH₄ since structures with octahedral sites are the lowest energy states in NiTiH₃. When metal-metal coordination is explored, except NiTiH_{0.5}, all structures have eight-fold tetragonal Ni-Ti arrangement. In NiTiH_{0.5}, some distortion can be observed in this eight-fold orientation.

	s.g.	Cell	param.	Ni		Ti		Η	
NiTi	221	a = 3.075	$\alpha = 90$	1a	x = 0.0	1b	x = 0.5		
		b = 3.075	$\beta = 90$		y = 0.0		y = 0.5		
		c = 3.075	$\gamma = 90$		z = 0.0		z = 0.5		
$NiTiH_{0.5}$	65	a = 6.127	$\alpha = 90$	4i	x = 0.0	4h	x = 0.245	2a	x = 0.0
		b = 6.513	$\beta = 90$		y = 0.275		y = 0.0		y = 0.0
		c = 2.995	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.0
NiTiH	65	a = 7.184	$\alpha = 90$	4i	x = 0.0	4h	x = 0.250	$4 \mathrm{e}$	x = 0.25
		b = 5.861	$\beta = 90$		y = 0.250		y = 0.0		y = 0.25
		c = 2.928	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.0
$NiTiH_2$	65	a = 4.890	$\alpha = 90$	2a	x = 0.0	2c	x = 0.5	4 e	x = 0.25
		b = 4.889	$\beta = 90$		y = 0.0		y = 0.0		y = 0.25
		c = 2.792	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.0
$NiTiH_3$	65	a = 4.381	$\alpha = 90$	2a	x = 0.0	2c	x = 0.5	2d	x = 0.0
		b = 4.697	$\beta = 90$		y = 0.0		y = 0.0		y = 0.0
		c = 3.618	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.5
								4 e	x = 0.25
									y = 0.25
									z = 0.0
$NiTiH_4$	123	a = 3.039	$\alpha = 90$	1a	x = 0.0	1d	x = 0.5	4i	x = 0.0
		b = 3.039	$\beta = 90$		y = 0.0		y = 0.5		y = 0.5
		c = 4.400	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.217

Table 4.11: Optimized structural parameters for the stable phases in NiTi system

4.1.6 CuTi

The crystal structure for CuTi intermetallic is primitive tetragonal with space group no. 129 [105]. The lattice parameters are a = 3.107 Å and c = 5.919 Å. Copper and titanium atoms are both placed in 2c sites with Cu at $(x = 0.0 \ y = 0.5 \ z = 0.10)$ and Ti at $(x = 0.0 \ y = 0.5 \ z = 0.65)$ positions. In another study, a hydride phase with compostion CuTiH_{~1} was determined by Santoro et al. [118]. This structure is also in space group no. 129 with lattice parameters 3.020 Å and 6.873 Å. The constituent atoms Cu, Ti and H are in 2c $(x = 0.0 \ y = 0.5 \ z = 0.0933)$, 2c $(x = 0.0 \ y = 0.5 \ z = 0.6751)$ and 2b $(x = 0.0 \ y = 0.0 \ z = 0.5)$ sites respectively. According to experimental structure of CuTi, structures in Table (4.12) are constructed.

In order to control the computations, the experimental CuTi and CuTiH cell parameters are compared with the computed ones. For copper-titanium and its hydride, maximum errors are in c parameter and they are about 3.6 %. and 1.8 % respectively.

Space group	Cu	Ti	H/CuTi						
			0.5	1.0	2.0	3.0	4.0		
17	2c	2d		2a					
59	2b	2b		2a, 2a, 2b		2a+2a+2a			
65	4i	4h			2a+2c+4e				
67	4g	4g		4a, 4b, 4c, 4d, 4f					
85	2c	2c			4f		8g		
90	2c	2c			4e, 4f		4e+4f		
99	1a+1b	1b+1b		2c, 2c	4d, 4d, 4e		$4\mathrm{e}$		
113	2c	2c			$4\mathrm{e}$				
115	2g	2g	1a, 1b, 1c, 1d	1a+1c, 2e, 2f	4h, 4i, 4j				
129	2c	2c		2a, 2b, 2c	2a+2b, 4d, 4e, 4f, 4f, 4f	$\begin{array}{ll} 2a+4d, & 2a+4e, \\ 2a+4f, & 2b+4d, \\ 2b+4f, & 2c+4f \end{array}$	8g, 8i, 8j		

Table 4.12: The definition of the structures for CuTi-hydrides giving the space groups and Wyckoff positions of the atoms with in the unit cells. Total number of structures calculated is 51



Figure 4.10: Formation energies of calculated CuTi-hydride systems

Except tetra-hydrides, negative formation energies are spotted at every composition which can be seen in Fig. (4.10). The calculated formation energy for experimentally determined CuTiH is $-88.4 \ kj/mole \ H_2$. Below that, another structure with same composition is found to have formation energy of $-120.4 \ kj/mole \ H_2$ that is given in Table (4.1.6). It belongs to space group no. 59. Although this space group is orthorhombic, two of the cell parameters (*a* and *b*) came out to be equal. Thus, it can also be realized as a tetragonal structure (space group no. 129).

The metal-metal coordination is a lot more different in CuTi. In previous systems, an eight-fold arrangement is observed, however in copper-titanium intermetallic a highly distorted six-fold arrangement present. Structures having this orientation came out to have lowest energy among their composition group except the di-hydride (which is the experimentally determined structure of FeTi having an eight-fold metal-metal coordination). So it is very unlikely for the compound to change crystal structure from mono to di-hydride then change back to original orientation at tri-hydride. Thus, most probably, CuTiH₂ will not appear in the phase diagram.

For $\text{CuTiH}_{0.5}$, the hydrogen atom is in a tetrahedron with titanium at the corners. Ti-H bond length in this tetrahedron is 1.868 Å. The nearest Cu atom is 2.938 Å

	s.g.	Cell	param.	Cu		Ti		Η	
CuTi	129	a = 3.137	$\alpha = 90$	2c	x = 0.0	2c	x = 0.0		
		b = 3.137	$\beta = 90$		y = 0.5		y = 0.5		
		c = 6.130	$\gamma = 90$		z = 0.108		z = 0.644		
$CuTiH_{0.5}$	115	a = 3.195	$\alpha = 90$	2g	x = 0.0	2g	x = 0.0	1d	x = 0.0
		b = 3.195	$\beta = 90$		y = 0.5		y = 0.5		y = 0.0
		c = 6.216	$\gamma = 90$		z = 0.103		z = 0.656		z = 0.5
CuTiH	129	a = 2.857	$\alpha = 90$	2c	x = 0.0	2c	x = 0.0	2c	x = 0.0
		b = 2.857	$\beta = 90$		y = 0.5		y = 0.5		y = 0.5
		c = 7.891	$\gamma = 90$		z = 0.096		z = 0.652		z = 0.395
CuTiH	129	a = 3.063	$\alpha = 90$	2c	x = 0.0	2c	x = 0.0	2b	x = 0.0
		b = 3.063	$\beta = 90$		y = 0.5		y = 0.5		y = 0.0
		c = 6.963	$\gamma = 90$		z = 0.090		z = 0.674		z = 0.5
$CuTiH_2$	65	a = 7.775	$\alpha = 90$	4i	x = 0.0	4h	x = 0.226	2a	x = 0.0
		b = 6.235	$\beta = 90$		y = 0.291		y = 0.0		y = 0.0
		c = 2.852	$\gamma = 90$		z = 0.0		z = 0.5		z = 0.0
								2c	x = 0.5
									y = 0.0
									z = 0.5
								4 e	x = 0.25
									y = 0.25
									z = 0.0
$CuTiH_3$	129	a = 3.087	$\alpha = 90$	2c	x = 0.0	2c	x = 0.0	2b	x = 0.0
		b = 3.087	$\beta = 90$		y = 0.5		y = 0.5		y = 0.0
		c = 8.241	$\gamma = 90$		z = 0.101		z = 0.647		z = 0.5
								4f	x = 0.0
									y = 0.0
									z = 0.788

Table 4.13: Optimized structural parameters for the stable phases in CuTi system

away from a hydrogen. Thus interaction between hydrogen and copper seems to be very limited. Experimentally proposed CuTiH [118] has also hydrogen in a four Ti tetrahedron with Ti-H and Cu-H distances 1.953 Å and 3.237 Å. On the other hand, the calculated lowest energy CuTiH have its hydrogen atoms in a deformed octahedral with five titanium and one copper at the corners. The H-Ti distances are 2.055 and 2.023 Å and H-Cu distance is 2.359 Å. Hydrogen is still close to titanium but hydrogen copper distance is much smaller than case where hydrogen is inside the tetrahedron. The contradiction between theoretically and experimentally determined structures might be due to the experimentally proposed one being a metastable phase. It can be said that the first-coming hydrogen atoms occupy tetrahedral positions forming CuTiH_{0.5} leaving the only available sites as tetrahedrons for the forthcoming hydrogen atoms. In spite of the driving force, if the activation energy is high for hydrogen motion from tetrahedral position to octahedral position, the kinetics of
this transformation will be too slow to observe any substantial change. Theoretically predicted structure can be obtained by thermally activating the system. However, the temperature should not be higher than 200 $^{\circ}$ C otherwise titanium hydride might precipitate as reported in Santoro and friends study [118].

In lowest energy structure of $CuTiH_3$ composition, there are two different hydrogen positions with different tetrahedral metal coordinations around. One is built from four titanium atoms at the corners. The Ti-H bond length is calculated as 1.962 Å. Two titanium and two copper atoms cage the hydrogen is the other tetrahedron. The bond lengths are 1.931 Å and 1.795 Å respectively for Ti-H and Cu-H.

4.1.7 SbTi

The crystal structure for SbTi is reported to be an HCP (space group no. 194) with lattice parameters a = 4.115 Å and c = 6.264 Å [105]. Sb and Ti atoms are located in 2a sites ($x = 0.0 \ y = 0.0 \ z = 0.0$) and 2c sites ($x = 1/3 \ y = 2/3 \ z = 1/4$) respectively Calculated lattice parameters for this system are a = 4.203 Å and c = 6.105 having a maximum error of 2.5 %.

Space group	Ti	Sb	H/SbTi						
			0.5	1.0	1.5	2.0	3.0	4.0	
63	4a	4e		4b		8e, 8f			
164	1a+1b	2d		2c	3e, 3f		6g, 6h, 6i, 6i		
176	2b	2c					$6\mathrm{h}$		
186	2a	2b					6c, 6c		
187	2g	1d+1e	1a, 1b,	2h, 2i, 2j, 2j, 2j,			6n,6n,6n,6n		
190	2a	2c	10, 11	2K, 2K			$6\mathrm{h}$		
194	2a	2c		2b, 2d		2b+2d, 4e, 4f	2b+4f, 2d+4e, 2d+4f, 6g, 6h	2b+6g, 2b+6h, 2d+6g, 2d+6h, 4e+4f	

Table 4.14: The definition of the structures for SbTi-hydrides giving the space groups and Wyckoff positions of the atoms with in the unit cells. Total number of structures calculated is 43



Figure 4.11: Formation energies of calculated SbTi-hydride systems

The calculated systems and corresponding formation energies can be seen in Table (4.14) and Fig. (4.11) respectively. Formation energies are positive for all trial hydrides. This means that the hydrogenetation is unlikely. This may be due to close packing of the structure where hydrogen atoms could not find the interstitial opening having enough space to fit in.

4.1.8 Trends in Formation Energy

The formation energies of hydrides as a function of hydrogen content is plotted for all systems in Fig. (4.12). sp valence metals Al and Sb in their compound with titanium did not give promising results in sense of hydrogenetion. Be, as an s valence metal has hydrides with negative formation energies. There is a sharp increase in formation energy after mono-hydride and the di-hydride is barely stable. In the first row transition metal series (V, Fe, Ni, Cu) it can be seen that the absolute values of negative formation energies are very high at the beginning of the row then fall through minimum at the middle and rise again through the end.

Stability trends between different chemistries (i.e. between different M-Ti) can be explained better by two main contributions. First is the energy necessary to



Figure 4.12: Calculated formation energies for the minimum energy hydride structures in all studied systems

change the shape-size of the cell and move metal ions. Bulk modulus (for perfect crystal) of the system is the main concern here. As the strength of the metallic bonding increases, the intermetallic become more stable and relaxation of the cell and ions needs more energy so the corresponding hydride is less stable. Second contribution to stability is the chemical energy gain by hydrogen insertion. The competition between these two contributions mostly define the overall stability. In Fig (4.13), the energy needed to convert the starting intermetallic structure into hydride structure without hydrogen versus hydrogen content is plotted for systems in consideration. Whereas in Fig. (4.14), the energy difference between intermetallic (in mono-hydride structure) and its hydrated structure versus M (Al, Be, Cu, Fe, Ni, V) is plotted. In Fig (4.13), it is seen that in transition series VTi has the lowest and FeTi has the highest cohesive energies. NiTi and CuTi are in between VTi-FeTi and have comparable cohesive energies. On the other hand, if hydrogen affinity is considered, VTi and CuTi has similar hydrogen affinities. FeTi and NiTi has also similar hydrogen affinities but their affinities are smaller compared to VTi or CuTi. With this outcome, VTi, CuTi, NiTi and FeTi hydrides are arranged in a decreasing order of stability. BeTi has comparable cohesive energy with NiTi and

CuTi and it has similar affinity for hydrogen with FeTi and NiTi. This puts BeTi near NiTi by means of overall stability (at least for mono-hydride). Finally, AlTi has somewhat lower cohesive energy than NiTi but it has considerably low affinity for hydrogen compared to other intermetalics. So the most unstable hydrides belong to AlTi. Nevertheless, for a better understanding this trend, electronic evaluation is necessary.

VTi seems to be the most promising intermetallic by means of storage capacity then again the formed hydrides are too stable. If hydrogenation up to six hydrides per formula is achieved without disproportinating, this hydride is going to store 5.7 % hydrogen by weight and the desorption reaction would be easy due to its nearzero negative formation energy. The stability of the FeTi-hydrides are the lowest (except AlTi-hydrides which can be taken out of the picture because of being too unstable) so the dissociation reactions are easier (occur at lower temperatures) in thermodynamics point of view. But the problem is the low capacity of FeTiH₂. If FeTiH₄ to be produced the hydrogen storage capacity will be doubled.



Figure 4.13: Change in internal energy during structure alteration from intermetallic to hydride structure (having no hydrogen)



Figure 4.14: Change in internal energy of systems during insertion of hydrogen to dehydrogenated mono-hydride structure

4.2 Formation Sequence of Hydrides

In the previous section, for each different chemical make-up, hydrides with negative formation energies were spotted at various hydrogen compositions. Having this information, it is possible to determine a phase formation sequence as hydrogen compostion increases in the metallic matrix at zero Kelvin. However, in this sequence, all spotted hydrides may not be seen. Instead, a solid solution of a neighbor or a mixture of two neighbors may be observed. In order to determine the formation sequence, mixing energies are calculated. The end members in composition range are metal-Ti intermetallic and the hydride with highest hydrogen content having negative formation energy (hydrides with positive formation energies are also used in some cases where the value of the formation energy is close to zero).

In BeTi system, according to calculated energies, the formation sequence follows the order $BeTiH_{0.5}$, $BeTiH_{1.0}$ and $BeTiH_{2.0}$, see Fig. (4.15).

In AlTi system, although $AlTiH_{1.0}$ is not found to have a negative formation energy, it is included in the convex hull plot because of its small positive formation energy, see Fig. (4.16).



Figure 4.15: Mixing energies of hydrides with respect to BeTi and $BeTiH_{2.0}$

According to calculations the VTiH_{0.5}, VTiH_{1.0}, VTiH_{2.0} VTiH_{4.0} and even VTiH_{6.0} may be observed in the zero Kelvin phase formation sequence, see Fig. (4.17).

In FeTi system, except tri-hydride, all trial compositions with given minimum formation energies are on the convex hull, see Fig. (4.18).

In Fig. (4.19), mono, di and tetra-hydride phases are local minima of the mixing energy plot for NiTi system.

Mono and tri-hydrides came out to be structures with minimum mixing energies in CuTi system, see Fig. (4.20).

4.3 Experimental Point of View

Pressure-composition isotherms as given in Fig. (1.1) are practical tools when the key properties such as plateau pressure, reversible hydrogen capacity, van't Hoff variables etc. of metal hydrides are considered. Thus, PCT plots are quite important by means of comparing hydride properties from application point of view. The calculated ground state formation energies versus hydrogen content as in Fig. (4.12) can be



Figure 4.16: Mixing energies of hydrides with respect to AlTi and AlTi $H_{1,0}$

thought as a zero Kelvin isotherm since formation energy and hydrogen pressure are related through reaction free energy change concept. The PCT for hydrogen absorption of FeTi at zero Celsius degree was given by Reilly and Wiswall [108]. FeTiH_{~1} and FeTiH_{~2} formations are observed at plateau pressures that are very close to each other. In addition, no plateau corresponding to a different hydride is observed after FeTiH_{~2}. These findings agree well with the present calculations in that the formation energy difference between mono and di-hydride is very small. Moreover, a stable hydride having a higher hydrogen content than FeTiH₂ could not be determined.

The sharp decrease in formation energy from NiTiH_{0.5} to NiTiH and CuTiH_{0.5} to CuTiH are somewhat strange considering the expected isotherm behavior. This may be due to inadequate sampling of the phase space at NiTiH_{0.5} and CuTiH_{0.5} compositions in the study. In such a case, however, there must be experimental evidence showing that at these concentrations such phases exit, since the systems were studied previously. Yet, there is no such finding. Although these structures found to have negative formation energies, it is not possible for them to be formed due to phase diagram. Actually this is so, as evident from Fig. (4.19, 4.20) that at



Figure 4.17: Mixing energies of hydrides with respect to VTi and $VTiH_{6.0}$

these concentrations mentioned phases do not lie on the convex hull.

4.4 Investigation of Electronic Structure

In order to explain cohesive energies of the intermetallics (the elastic contributions to hydride formation energy), band structure of the metals can be used, see Fig. (4.21). In transition series, the low cohesive energy of VTi is due to fewer number of d electrons in the bonding states. Moving to the right, nuclear charge increases for the complementary atom (M) pulling its d states more and more to lower energies in addition to contracting them. Thus the energy degeneracy and the overlap of the d bands of M and Ti decreases. On the other hand d band filling increases. The calculations show, the energy degeneracy and overlapping is still considerable for FeTi but disintegrate very rapidly through Ni and Cu. So bonding strength is high for FeTi but reduce while going to NiTi and CuTi. AlTi and BeTi has also elastic modulus values near NiTi and CuTi. It is found that an spd hybridization is primary for both BeTi and AlTi. Although the number of filling electrons is higher for AlTi, the extend of s-d overlapping is very limited compared to BeTi so the cohesion is



Figure 4.18: Mixing energies of hydrides with respect to FeTi and $FeTiH_{4,0}$

somewhat higher for BeTi.

Total and partial densities of states for all stable hydride structures are also calculated in the studied systems. Total DOS for all mono-hydrides are given in Fig. (4.22). Low energy states in all DOS plots are hydrogen 1s, metal s or p states (i.e. Be-2s2p and Al-3s3p). All analyzed structures are metallic since there are neighboring states on both side of Fermi level without a gap.

Other than AlTi-hydrides which do not have gaps between hydrogen and metal states, in all systems, as hydrogen content increases, the separation between H-1s states and high energy metallic states decreases. A continuous s, p, d hybridization is evident for AlTi-hydrides. In BeTi-hydrides, Be states split into two in the hydride producing a gap. Lower energy s-p states hybridized with hydrogen s. In contrast, higher energy s-p part hybridized with titanium d bands.

In first transition metal row, two trends can be observed. First is the energy wise separation of 3d states of Ti and complementary metal while moving from right to left on the row. Vanadium has almost complete degenerate states with titanium on both below Fermi energy (filled bands) and above Fermi energy (empty bands). On



Figure 4.19: Mixing energies of hydrides with respect to NiTi and NiTi $H_{4,0}$

the other hand, Cu and Ti 3d states are almost separated and all Cu-3d states are in bonding side and all empty states belong to Ti. Second trend can be seen during change in hydrogen composition. Increasing hydrogen content spreads titanium states below Fermi energy coupled with decreasing the intensity. The empty states of titanium on the other, are not affected considerably.

Smithson et al. [33] claimed that variation of chemical energy part of the total formation energy is mostly determined by the location of Fermi surface. In this sense, VTi has has relatively lower number of electrons thus the Fermi surface is at relatively lower energies. Moreover, some amount of ionicity can be expected due to large difference in electronegativity between H and VTi. Going to right in the row higher energy orbitals fill so the position of Fermi level shifted away from hydrogen. But again this behavior is counterbalanced with contraction and lowering of d band energies due to increasing nuclear attraction. In the case of FeTi and NiTi destabilizing effect of d band filling is dominant. If it was not titanium in the compound, the position of the Fermi level will be at the end of the Cu states due to high number of valence electron of Cu. Relatively lower energy empty titanium states hinder this picture and stabilization due to core attraction is affective. Instability of AlTi-



Figure 4.20: Mixing energies of hydrides with respect to CuTi and $CuTiH_{3.0}$

hydrides can be explained by strong hybridization and stability of s,p and d states of AlTi intermetallic. As the stability of the parent intermetallic increases, stability of the hydride decreases. BeTi-hydrides also have s-p-d hybridization. However, in this case, the states are energetically more flexible as demonstrated in state splitting due to hydrogen insertion.

Density difference plots shows regions of positive and negative charge difference around metals (except Be, Al and Cu) meaning loss or gain in 3d state occupation. In all systems, electronic charge is accumulated at orbitals pointing away from hydrogen and depleted at orbitals pointing hydrogen for titanium which can be seen in Fig. (4.23-4.24). The changes around Be, Al and Cu upon hydrogenation are insignificant compared to titanium. On the other hand, around V, Fe and Ni observable changes occur. Charge transfer behavior around vanadium is much like titanium. Moreover, this behavior does not change with increasing hydrogen content so determination of metallic coordination change from octahedron to tetrahedron around hydrogen cannot be understood with charge difference plot. But when partial density of states is investigated, up to di-hydride, it is seen that there is a small difference between Ti and V corresponding to shape and intensity of empty and filled bands.



Figure 4.21: Density of states for the studied intermetallic systems. In all plots, Fermi energy is at zero.

Beginning with tetra-hydride this small difference is disappeared and vanadium DOS looks much like titanium states in the hydride. For iron and nickel an opposite situation is occurred when compared to titanium. Electron accumulation takes place at bands aligned through hydrogen and depletion takes place at non-aligned bands, see Fig. (4.23). This picture is reversed for Fe and Ni and looks more like titanium with metallic coordination change around hydrogen during formation of tetra-hydride as in Fig. (4.24).

It is a little bit harder to explain the outcome of the Hirshfeld charge analysis, see Table (4.15). First, almost in all cases hydrogen has taken a very little charge suggesting a very slight ionic character. However, the net gained charge is generally too small indicating a dominant metallic bond. The charge sharing in intermetallics is confusing because titanium seem to gain electrons although it has lower electronegativity. This result is due to the fact that Hirshfeld analysis accounts the dispersed charged in favor of Ti since the electronic density of the isolated Ti becomes higher than the counterpart atom at distant points. The charge transfer between the metal atoms in the hydrides does not show a specific trend which is again a result of metallic bonding.



Figure 4.22: Density of states for all mono-hydrides.



Figure 4.23: Electronic density difference for FeTiH



Figure 4.24: Electronic density difference for $FeTiH_4$

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Systems	s.g.	Μ	Hirshfeld charge	Ti	Hirshfeld charge	Η	Hirshfeld charge
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	BeTi	221	1a	-1.968	1b	-4.032		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$BeTiH_{0.5}$	65	4i	-1.952	4h	-4.045	2a	-1.006
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	BeTiH	65	2a	-1.931	2c	-4.062	2d	-1.007
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$BeTiH_2$	65	4i	-1.917	4h	-4.077	2a	-1.001
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $							2c	-1.005
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$							4e	-1.003
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	AlTi	123	1a	-2.912	2e	-4.088		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			1c	-2.912				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$AlTiH_{0.5}$	123	1a	-2.917	2e	-4.101	1d	-1.024
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			1c	-2.857				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	AlTiH	65	2a	-2.865	4f	-4.109	4g	-1.027
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			2b	-2.864				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	VTi	221	1a	-4.983	1b	-4.017		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$VTiH_{0.5}$	65	4i	-4.990	4h	-4.004	2a	-1.011
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	VTiH	65	4i	-4.994	4h	-3.992	4 e	-1.014
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$VTiH_2$	123	1a	-4.968	1d	-4.011	1b	-1.011
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$							1c	-1.010
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$VTiH_4$	65	2a	-4.959	2c	-3.942	$8\mathrm{m}$	-1.025
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$VTiH_6$	200	1a	-4.944	1b	-3.999	6g	-1.009
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	FeTi	221	1a	-7.989	1b	-4.011		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$FeTiH_{0.5}$	65	4i	-8.006	4h	-3.990	2b	-1.007
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	FeTiH	17	2c	-8.018	2d	-3.977	2a	-1.005
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$FeTiH_2$	65	4i	-8.010	4h	-3.990	2a	-1.001
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$							2c	-0.994
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$							4e	-1.002
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$FeTiH_4$	123	1a	-7.997	1d	-3.976	4i	-1.007
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	NiTi	221	1a	-10.036	1b	-3.964		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	NiTiH	65	4i	-10.002	4h	-3.986	4 e	-1.011
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$NiTiH_2$	65	2a	-10.003	2c	-3.956	4 e	-1.009
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$NiTiH_4$	123	1a	-9.957	1d	-4.002	4i	-1.010
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	CuTi	129	2c	-10.855	2c	-4.145		
CuTiH ₃ 129 2c -10.791 2c -4.046 2b -1.027 4f -1.070	CuTiH	129	2c	-10.892	2c	-4.083	2c	-1.025
4f -1.070	CuTiH_3	129	2c	-10.791	2c	-4.046	2b	-1.027
							4f	-1.070

Table 4.15: Hirshfeld charges for the constituent atoms in stable structures for the studied systems. Number of valence electrons for M = Al, Be, Cu, Fe, H, Ni, Ti and V are 3, 2, 11, 8, 1, 10, 4 and 5.

CHAPTER 5

CONCLUSION

In this study, AB type intermetallic alloys with A = Al, Be, Cu, Fe, Ni, Sb, V and B = Ti was investigated in order to find a potential medium having high hydrogen storage capacity and forming a hydride with low stability for the ease of hydrogen desorption. For this goal, the mentioned intermetallics are modeled using density functional theory with generalized gradient approximation. In each system, hydrogen content was increased until the resulting hydride became unstable. As a result, following conclusions can be stated.

First of all, the results were compared with the experimentally determined cell structures whenever the data is available. A good agreement is obtained in the sense of crystal structure and relative stabilities except CuTiH where the experimentally determined phase might be metastable phase.

The calculations show that the formation energies of the hydrides can be divided into two parts. Elastic contribution is the energy necessary to change the shape of the cell structure and move the ions of the intermetallic in order to obtain the hydride structure. This energy is related to the stability of the intermetallic. Chemical part is the affinity of given chemistries to hydrogen which is closely related with metalhydrogen bonding. The combination of these two result in a decreasing overall hydride stability in the order of VTi, CuTi, NiTi, BeTi, FeTi, AlTi, SbTi. The hydrides of AlTi and SbTi are too unstable. Thus, these systems do not offer a suitable media for hydrogen storage. VTi seems to reach high storage capacities, however hydrides up to VTiH₆ have very negative formation energies so the desorption will be at high temperatures. FeTi, on the other hand, is a well known intermetallic due to its ambient temperature desorption thermodynamics but its capacity is low. The structure at FeTiH₄ has a very small positive formation energy. So, if it is to be produced with some kind of chemical alteration, the storage capacity will be doubled.

In CsCl type transition metal compounds, octahedral metal organization around H has changed to tetrahedral framework at $MTiH_4$ where the electronic behavior of the complementary intermetallic begin to look like the behavior of Ti.

Finally, in experimental point of view, formation energy versus hydrogen content can be thought as a zero-Kelvin PCT curve. For example, the absorption PCT at 0 °C is given by Reilly and Wiswall [108]. Two plateau-like can be identified as FeTiH and FeTiH₂ but the pressure difference between them is so small. After FeTiH₂ no other hydride is determined. In present calculations, the formation energy difference between FeTiH and FeTiH₂ is again very small. Moreover, a hydride with negative formation energy cannot be determined after FeTiH₂.

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