

*Quantum computational chemical calculations to estimate the necessary energy
for hydrogen storage in the metal hydrides AlH_3ScH_3 and Al_2H_6*



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1. ABSTRACT

Hydrogen storage describes the methods of storing H_2 for subsequent use. Hydrogen storage is the main issue that needs to be solved before the technology can be implemented into key areas such as transport. The high energy density, good stability and reversibility of metal hydrides make them appealing as hydrogen storage materials. Metal hydrides have the potential for reversible on-board hydrogen storage and release at low temperatures and pressures.

The aim of this thesis is to describe, document and carry out the previous theoretical quantum chemical calculations by density functional theory (DFT) at B3LYP level of theory with 6-311++G(3df,3pd) basis set for aluminium and hydrogen, and a SDD pseudopotential for scandium in order to; first of all, optimize the molecular structures; secondly, predict the vibrational frequencies of the optimized structures and finally estimate the energies needed to absorb and release hydrogen from both metal hydrides AlH_3ScH_3 and Al_2H_6 .

Our calculated results show that the hydrogen absorption energy value for the formation of AlH_3ScH_3 (-47,479kcal/mol) is higher than the value for the formation of Al_2H_6 (-33,481 kcal/mol). These were not the expected results because the energy has been increased, and thus the operation temperatures are also higher. The transition metal scandium in the hydride does not decrease the hydrogenation energy due to cation matrix that seems to be the responsible for the thermal stability.



2. TABLE OF CONTENTS

1. ABSTRACT	2
2. TABLE OF CONTENTS	3
3. INTRODUCTION	4
3.1. HYDROGEN STORAGE	5
3.1.1. How is Hydrogen Stored?	5
3.1.2. Hydrogen Storage requirements and barriers.....	7
3.2. METAL HYDRIDES	8
3.2.1. Complexes	9
3.2.1.1. Transition Metal Hydrides.....	10
3.2.2. Alloys.....	12
3.2.2.1. Alloys with scandium and aluminum	12
3.3. THERMODYNAMICS OF HYDROGEN ABSORPTION	13
4. THESIS AIMS	16
5. THEORITICAL METHOD: DENSITY FUNCTIONAL THEORY CALCULATIONS	17
6. CALCULATIONS AND RESULTS.....	19
6.1. STRUCTURE OPTIMIZATION.....	19
6.2. FREQUENCY	21
6.3. ENERGY	22
7. CONCLUSIONS.....	24
8. AKNOWLEDGMENTS.....	25
9. BIBLIOGRAPHIC REFERENCES	26



3. INTRODUCTION

It is a known issue that the overuse and dependence of fossil fuels is leading to major environmental problems and exhaustion of fuel supplies [1]. The research and development of clean energy systems that involve renewable energy are very important due to the increasing demands of energy and the impending exhaustion of fossil fuel, the most widely used energy source [2, 3].

Hydrogen is one of the most interesting candidates to replace nonrenewable fuel sources used nowadays. Hydrogen is a renewable resource, environmentally friendly and in addition has the highest heating value per mass of all chemical fuels (The specific chemical energy of molecular hydrogen, 142 MJ/kg is approximately three times higher to other liquid hydrocarbons)[4]. Nevertheless, there are two main setbacks that prevent hydrogen to be the principle source of energy. On one hand, hydrogen is only an energy carrier. Despite the fact that hydrogen is the most abundant element in the universe, less than 1% is present as molecular H_2 . This implies the production of molecular hydrogen gas from water and hydrocarbons using clean and renewable energy sources, such as photoelectrolysis of water using solar light or electricity from a renewable source and catalysis or even using microorganisms in order to produce hydrogen under anaerobic conditions [5]. This production entails high costs; subsequently there is an economic problem. On the other hand, another obstacle is that hydrogen has a very low critical temperature (33K). Hydrogen's volumetric and gravimetric density is critical for mobile and stationary applications. For this reason, hydrogen storage is a big issue to be resolved. Hydrogen storage, for mobile and transport applications has to fulfill various industry demands concerning economy, security, light weight, and other aspects. Storage using pressurized tanks, either with hydrogen gas at ambient temperature or cryogenic hydrogen liquid do not fulfill these demands of safety and are deficient energy density [6]. For on-board hydrogen storage international organizations posed some criteria for efficient applications. The most important criteria for mobile applications are (Table 1): Useable energy density 1.5 kWh/L, storage weight percent 6 wt.% of H_2 , operating temperature -30/50°C, cycle life (> 1000 cycles), delivery pressure 2.5 bar, refueling time < 3 min (5 kg H_2). Nevertheless, there is still much research to do to achieve hydrides that satisfy these targets.



Property	Units	2010	2007	2006
		USA	Japan	IEA
System density (by weight)	wt.%H ₂	6	3	-
System density (by volumen)	kgH ₂ /m ²	45	-	-
System cost	US\$/kgH ₂	133	-	-
Refuelling time	Minutes	3	-	-
Medium density (by weight)	wt.%H ₂	-	5.5	5.0
H ₂ liberation temperature	°C	-	150	80

Table 1. Hydrogen storage system and media targets for on-board applications. (International Energy Agency, Hydrogen Implementation Agreement: Hydrogen Production and Storage, R&D Priorities and Gaps)

Alternative hydrogen storage systems have been studied, where hydrogen interacts chemically or physically with solid materials. The highest volumetric densities of hydrogen are found in metal hydrides. Many metals and alloys are capable of reversibly absorbing large amount of hydrogen.

This project mainly follows the work done by Xuefeng Wang and Lester Andrews and their paper published in Science [7], *The Infrared Spectrum of Al_2H_6 in Solid Hydrogen*. The main aim is to analyze the chemical quantum calculations in order to obtain the optimization of molecular structures, vibrational frequencies and global energies for the energy difference of the absorption and desorption of hydrogen for Al_3ScH_3 and Al_2H_6 molecules.

3.1. HYDROGEN STORAGE

3.1.1. How is Hydrogen Stored?

As mentioned before hydrogen storage has to meet several requirements in order for hydrogen to be a competitive fuel for vehicles. The hydrogen vehicle must be able to have the capacity to be able to travel a comparable distance to conventional liquid hydrocarbon energy fueled automobiles [8].



Compressed Gas and Cryogenic Liquid Storage

Hydrogen can be physically stored in tanks as gas or liquid. Compressed gas storage requires high-pressure tanks (35-70MPa tank pressure). Cryogenic liquid storage of hydrogen requires cryogenic temperatures because the boiling point of hydrogen at atmosphere pressure is -252.8 K and critical temperature of 33K (21 K cryogenic tanks).

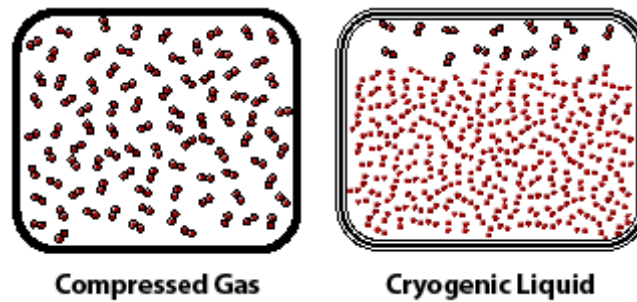


Figure 1. Image of two types of hydrogen storage: compressed gas and cryogenic liquid.

Materials-Based Hydrogen Storage

Furthermore, hydrogen can be stored by adsorption or by absorption.

- > *Adsorption*: hydrogen is stored on the surface of solids. Hydrogen is attached to the surface of a material either as hydrogen molecules or as hydrogen atoms.
- > *Absorption*: hydrogen is stored within the solids, hydrogen is dissociated into H-atoms, and then the hydrogen atoms are incorporated into the solid lattice framework. Storage in solid materials makes it possible to store larger amounts of hydrogen in lesser volumes at reasonable pressures and temperatures. Hydrogen can also strongly bound within molecular structures such as chemical compounds containing hydrogen atoms.

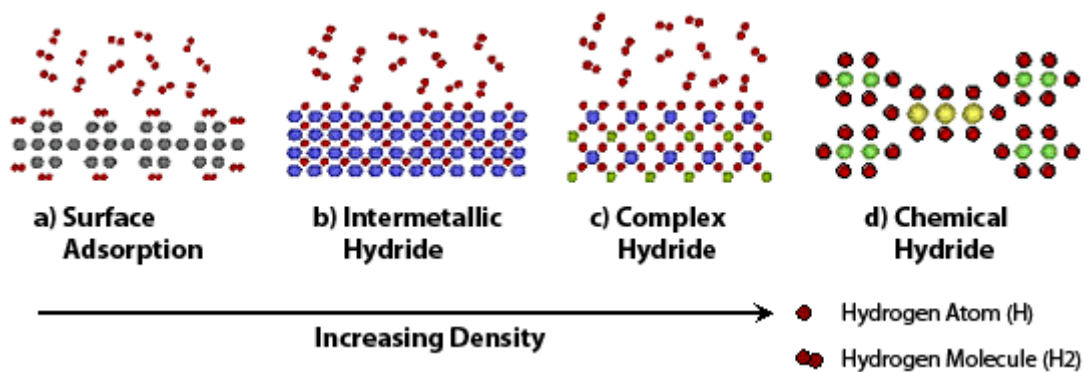


Figure 2. Comparison of hydrogen storage systems.

Hydrogen storage in solids may make it possible to store larger quantities of hydrogen in smaller volumes at low pressure and at temperatures close to room temperature. It is also possible to achieve volumetric storage densities greater than liquid hydrogen because the hydrogen molecule is dissociated into atomic hydrogen within the metal hydride lattice structure.

Finally, hydrogen can be stored through the reaction of hydrogen-containing materials with water (or other compounds such as alcohols). In this case, the hydrogen is effectively stored in both the material and in the water. The term "chemical hydrogen storage" or chemical hydrides is used to describe this form of hydrogen storage. It is also possible to store hydrogen in the chemical structures of liquids and solids.

3.1.2. Hydrogen Storage requirements and barriers.

It is still a challenge to store enough hydrogen required for transportation and to fulfill an independent driving range ($>500\text{Km}$) and vehicular limitations such as weight, volume, efficiency, acceptable refueling times, safety, and cost. Durability and lifetime of these must also be verified and validated.

Stationary hydrogen storage has less requirements than mobile application hydrogen storage systems. Nevertheless, volume and sustainability should be considered.

Some of the main hydrogen storage challenges are described below [9]:

- > *Weight and Volume.* The weight and volume of hydrogen storage systems are presently too high, resulting in inadequate vehicle range compared to conventional petroleum fueled vehicles. Materials and components are needed that allow compact, lightweight, hydrogen storage systems while enabling mile range greater than 300 miles in all light-duty vehicle platforms.
- > *Efficiency.* Energy efficiency is a challenge for all hydrogen storage approaches. The energy required to get hydrogen in and out is an issue for reversible solid-state materials. Life-cycle energy efficiency is a challenge for chemical hydride storage in which the byproduct is regenerated off-board. In addition, the energy associated with compression and liquefaction must be considered for compressed and liquid hydrogen technologies.
- > *Durability.* Durability of hydrogen storage systems is inadequate. Materials and



components are needed that allow hydrogen storage systems with a lifetime of 1500 cycles.

- > *Refueling Time.* Refueling times are too long. There is a need to develop hydrogen storage systems with refueling times of less than three minutes over the lifetime of the system.
- > *Cost.* The cost of on-board hydrogen storage systems is too high, particularly in comparison with conventional storage systems for petroleum fuels. Low-cost materials and components for hydrogen storage systems are needed, as well as low-cost, high-volume manufacturing methods.
- > *Codes and Standards.* Applicable codes and standards for hydrogen storage systems and interface technologies, which will facilitate implementation/commercialization and ensure safety and public acceptance, have not been established. Standardized hardware and operating procedures, and applicable codes and standards, are required.
- > *Life-Cycle and Efficiency Analyses.* There is a lack of analyses of the full life-cycle cost and efficiency for hydrogen storage systems.

3.2. METAL HYDRIDES

Metals, intermetallic compounds and alloys commonly react with hydrogen and form solid metal-hydrogen compounds. Metal hydrides have the potential for reversible on-board hydrogen storage and release at low temperatures and pressures. The discovery of palladium hydride in the nineteenth century (1866) by Thomas Graham was the first step of the study of hydrogen absorption of metal hydrides [10]. Later on, in 1969 with the discovery of the alloy $SmCo_5$ capable of reversibly absorb hydrogen at low temperatures [11] and $LaNi_5$ also a hydrogen storage alloy, was the starting point of extensive research of metal hydrides. These alloys (AB_5) are presently used in rechargeable batteries.

Transition metals and inner transition metals form a large variety of compounds with hydrogen, ranging from stoichiometric compounds to extremely complicated nonstoichiometric systems. Metallic hydrides essentially consist of protons and metal atoms in an electron sea [12].

Metal hydrides are formed by heating hydrogen gas with the metals or alloys. The most studied compounds are those of the most electropositive transition metals (scandium, titanium and vanadium families).



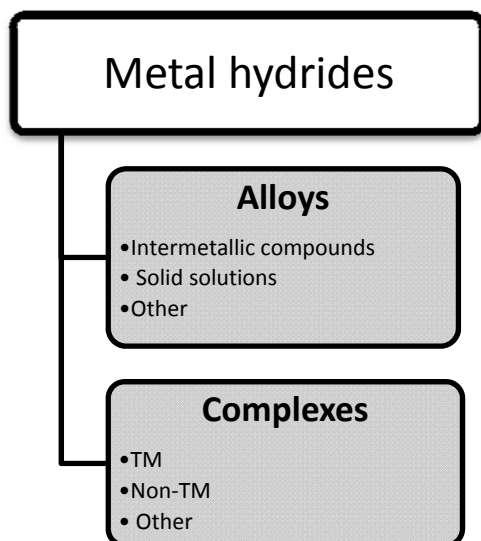


Figure 3. Classification of the different metal hydrides known by Gary Sandrock and Thomas [12].

3.2.1. Complexes

Complex metal hydrides are a subclass of metal hydrides. They are mixed covalent-ionic compounds. The origin of their name is the presence of discrete metal-hydrogen complexes in the crystal structure that are centered by d-elements or p-elements [14]. Generally, they have larger hydrogen capacity than alloys. However, they have a higher temperature of hydrogen desorption and difficult reversibility.

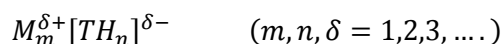
Issues with complex metal hydrides include low hydrogen capacity, slow uptake and release kinetics, and cost. One of the major issues with complex metal hydride materials, due to the reaction enthalpies involved, is thermal management during refueling. Depending on the amount of hydrogen stored and refueling times required, megawatts to half a gigawatt must be handled during recharging on-board vehicular systems with metal hydrides. Reversibility of these and new materials also needs to be demonstrated for over a thousand cycles.

The combination of transition metals (TM) with elements from group I or II in hydrogen, an anionic complex is formed and the cation corresponds to the element from groups I or II. Non-transition metal complex hydrides also are possible, for example aluminum.



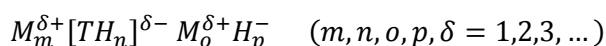
3.2.1.1. Transition Metal Hydrides

Hydrides containing transition metals can be divided in two main groups [14]. The first group is characterized by the hydrogen bonded to the T elements only. The general composition is as follows,



where $[TH_n]^{\delta-}$ are transition metal hydride complexes. The anion is stabilized by the charge transfer of the metal cation $M^{\delta+}$. M can be alkali, alkaline earth or divalent rare earth element. The connection between the elements is perfect.

The second family contains hydrogen bonded to T elements and hydrogen anions connected to metal cations $M^{\delta+}$ only. The general composition is as follows,



This complex hydride has special metal-hydrogen bonding in the same structure.

Various syntheses of these hydrides have been analyzed. However, the reaction of the element under high hydrogen pressure (~ 2 kbar) is the most used synthetic path. Surprisingly, most of hydrides obtained contain metals that do not form binary compounds themselves. Not many hydrides derive from stable binary metal compounds. Some examples are, magnesium and iron ($2Mg + Fe + 3H_2 \rightarrow Mg_2FeH_6$) or Mg_2NiH_4 ($Mg_2Ni + 2H_2$). Other production paths are ball milling (Mg_2FeH_6) or combustion (Mg_2NiH_4). Complex hydrides are generally insoluble, so solution is a uncommon method.

Transition metal hydride complexes can be characterized by the number of T-metal atoms, so mononuclear complexes, polynuclear complexes; intermetallic/interstitial hydrides can be described.

Bonding and ligand geometries of transition metal hydrides can be expressed as full charge transfer from the surrounding cation matrix and s-p-d hybridization schemes involving two-center-two-electron bonds.

T-metal hydrides complexes have interesting properties for hydrogen-storage. Table 1 contains the hydrogen weight, density and desorption temperature for some significant hydrides. Concerning thermal stability, regrettably, only a few complex metal hydrides decompose near room temperature. $BaReH_9$ and $Ba_7Cu_3H_{17}$ are able, but are quite heavy, expensive and not completely reversible. Generally, the other metal hydrides are more stable with decomposition temperatures above $300^\circ C$ and ΔH above $80 kJ/H_2$ and must be heated to recover



hydrogen, which is a drawback in energy. The cation matrix seems to be the responsible for the thermal stability, the high stability is directly dependable to the interaction between the metal cations and hydrogen of the complexes.

Formula	Hydrogen density		Desorption temperature (1bar) [°C]
	w.t.%	gL ⁻¹	
Mg ₃ MnH ₇	5.2	119	~280
BaRH ₉	2.7	134	<100
NaKReH ₉	3.5	117	<100
Mg ₂ FeH ₆	5.5	150	320
Ca ₄ Mg ₄ Fe ₃ H ₂₂	5.0	122	395
SrMg ₂ FeH ₈	4.0	115	440
LiMg ₂ RuH ₇	4.3	113	>400
LiMg ₄ Os ₂ H ₁₃	2.6	121	>400
BaMg ₂ RuH ₈	2.7	98	>400
Mg ₂ RuH ₄	2.6	95	>400
Mg ₂ CoH ₅	4.5	126	280
Mg ₆ Co ₂ H ₁₁	4.0	97	370
Ca ₄ Mg ₄ Co ₃ H ₁₉	4.2	106	>480
Mg ₆ Ir ₂ H ₁₁	2.0	89	<400
Mg ₂ NiH ₄	3.6	98	280
CaMgNiH ₄	3.2	87	405
LiSr ₂ PdH ₅	1.7	74	>400
Eu ₂ PdH ₄	1.0	68	<300
Ba ₇ Cu ₃ H ₁₇	1.5	63	20
K ₂ ZnH ₄	2.7	57	310
K ₃ ZnH ₅	2.7	56	360
α-MgH ₂	7.7	109	280
H ₂ (liquid)	100	71	~253

Table 2. Hydrogen storage properties of some complex T-metal hydride characterized in Geneva, Yvon (1998).



3.2.2. Alloys

Hydride alloys are characterized to be metals or alloys that absorb hydrogen and form stable hydrides. Typically they are a combination of a metal that forms stable binary hydrides and another that facilitate the dissociation of hydrogen from the compound.

Figure 4 describes the two steps of hydrogen absorption by alloys [15, 16]. The first phase corresponds to a solid solution called α -phase, a small quantity of hydrogen is absorbed by the metal matrix. The β -phase is the second stage formed by a higher amount of hydrogen that interacts with the metal. The reaction with hydrogen is reversible, and the two phases coexist in equilibrium conditions, until the alloy completely turns into a β -phase hydride.

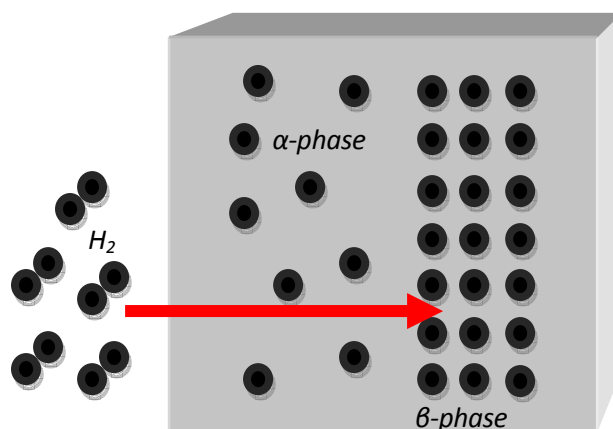


Figure 4. Representation of hydrogen absorption in a metal alloy.

3.2.2.1. Alloys with scandium and aluminum

Different studies about scandium-aluminum alloys as hydrogen storage materials have been analyzed with different conclusions. In *Interaction of hydrogen with the intermetallic compounds Sc_2Al and Sc_2Ni* by Burkhanov et al. demonstrated that Sc_2Al tends to decompose into ScH_2 and Al during the reaction with hydrogen instead of forming the single phase hydride. The reason is that the heat of formation of Sc_2Al is lower than ScH_2 [17]. The reaction was not reversible at temperatures below $1200^\circ C$, reason that they claim that prevents this compound to be used for hydrogen storage. Conversely, Antonova et al. in *Resistance to Hydrogen of Al-Sc Alloys* have demonstrated that all binary phases in the Sc-Al system are able to absorb hydrogen and form single phase hydrides [18].

Scandium is a transition metal characterized for being highly capable of accommodating hydrogen. It is able to form ScH_2 , or as a component in intermetallic compounds such as ScFe_2 (ScFe_2H_2) and Sc_2Ni (Sc_2NiH_5) [17, 19, 20]. On the other hand, elemental aluminum doesn't accommodate hydrogen. Nevertheless, AlH_3 can be obtained by the reaction between LiAlH_4 and AlCl_3 [21]. Also the reaction of laser-ablated aluminum atoms with hydrogen during codeposition at 3.5 kelvin, followed by ultraviolet irradiation and increasing the temperature to 6.5K allows the dimerization of the intermediate AlH_3 photolysis product to form Al_2H_6 [7]. Aluminum is beneficial as a component in component in intermetallic compounds with high hydrogen affinity [22].

The hydride ScAlNi was studied and was crystallized in a MgZn_2 -type structure. This compound can absorb hydrogen by two different mechanisms at different temperature regions [120-500°C]. The reversibility of the reaction and destabilization effects reduced the decomposition temperature of ScH_2 by 460°C [23].

3.3. THERMODYNAMICS OF HYDROGEN ABSORPTION

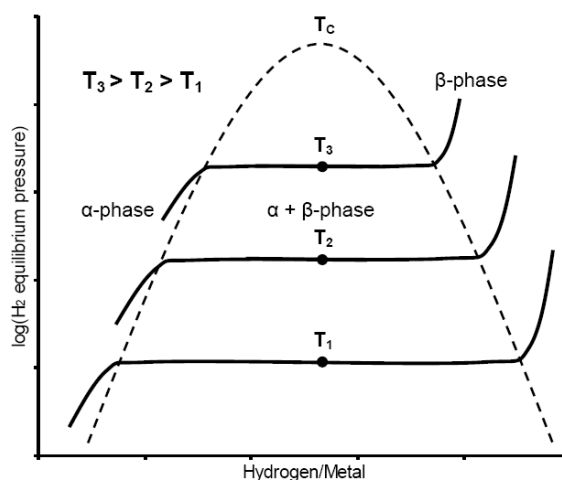
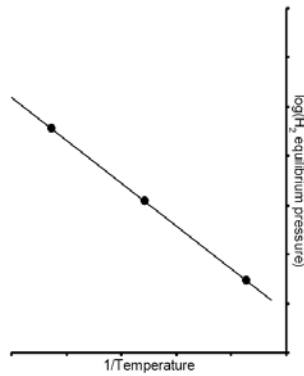


Figure 5. Representation of pressure-composition isotherms.

Figure 5 represents the pressure-concentration-temperature thermodynamic process of how the absorption is related to the hydrogen pressure at constant temperature conditions, so called pressure-composition isotherms. The single phase regions are characterized to need large pressure changes in order to increase the hydrogen concentration. At a specific pressure, p_{eq} , hydrogen equilibrium pressure, there is an equilibrium state between α and β phases,

where a large amount of hydrogen is absorbed with small pressure variations. According to Van't Hoff equation pressure equilibrium, p_{eq} , is dependent of the temperature, T.



$$\ln \left(\frac{P_{eq}}{P_0} \right) = \frac{\Delta H}{(RT)} - \frac{\Delta S}{R} \quad (1)$$

Figure 6. Van't Hoff equation and plot.

Enthalpy, ΔH , is a very important factor that indicates the stability of the metal-hydrogen bond. It is an important factor to be considered when a specific hydride is studied for hydrogen storage [4]. Enthalpies of hydride formation, ΔH , can be determined from the pressure-composition isotherms as measured on Sievert's apparatus or on a thermobalance. Generally, the reaction of hydrogen with metals is exothermic, and thus the equilibrium pressure increases with temperature. Absorption capacity of metals is reduced when the temperature increases and reaches a critical temperature T_c where both α and β phase become homogeneous. Current research is looking for hydrides stable enough to be formed, but sufficient unstable in order to allow the release of hydrogen at moderate conditions.

To obtain storage materials which are interesting for on-board hydrogen storage, the compound must have lower operating temperatures (the right hand side of Figure 7) and lower enthalpy of formation

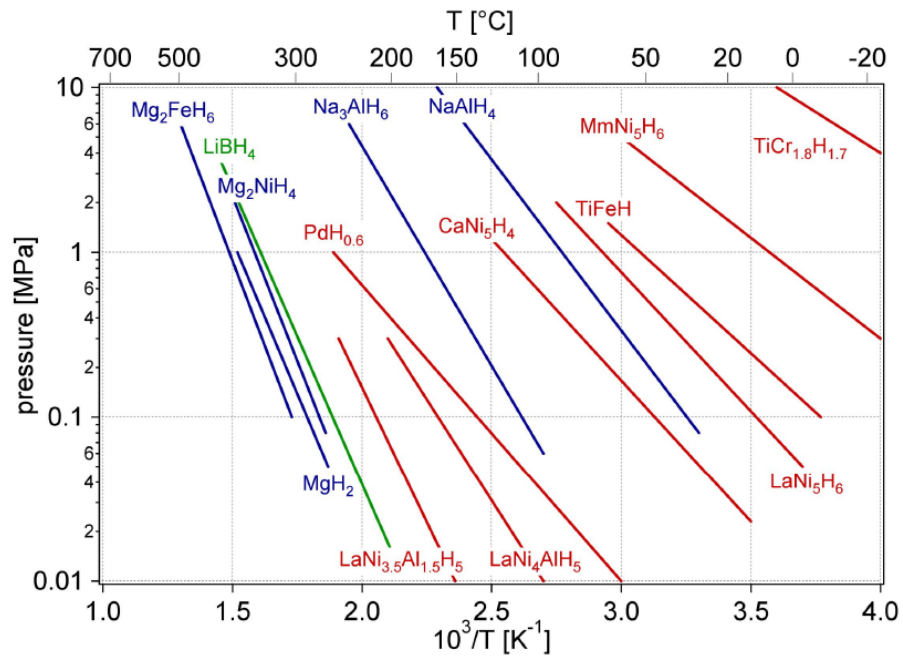


Figure 7. Van't Hoff equation plots for selected metal hydrides. (Züttel,2003a).



4. THESIS AIMS

The scope of this project is to investigate and analyze the calculations for obtaining the optimization of molecular structures, vibrational frequencies and global energies for the absorption and release hydrogen from the metal hydrides AlH_3SCH_3 and Al_2H_6 .

This project mainly follows the work done by Xuefeng Wang and Lester Andrews and their paper published in Science [7], *The Infrared Spectrum of Al_2H_6 in Solid Hydrogen*. They obtained Al_2H_6 through the use of pure hydrogen as the matrix, allowing the dimerization of the intermediate AlH_3 . The dibridged molecule Al_2H_6 is recognized by seven new infrared absorptions, which were predicted by quantum chemical calculations. Now the goal is to study the introduction of a transition metal like scandium to decrease the hydrogenation energy and temperature. It is significant to point out the importance of the quantum computational chemical calculations. These calculations are necessary, and are the previous step to the experimental synthesis of the metal hydrides. The results of the density functional theory calculations are very close to experimental results and they are very helpful to determine the viability of the experimental stage.



5. THEORETICAL METHOD: DENSITY FUNCTIONAL THEORY CALCULATIONS

In order to obtain comparable results for the studied molecules, a basis set was selected: Density Functional Theory (DFT) Method.

Density Functional Theory (DFT) is a computational method that derives properties of the molecule based on a determination of the *electron density* of the molecule. Unlike the wavefunction, which is not a physical reality but a mathematical construct, electron density is a physical characteristic of all molecules. In this method, the following energy functional is minimized with respect to the density, ρ .

$$E[\rho(r)] = T - \sum_K Z \int \frac{\rho(r)}{r} dr + \frac{1}{2} \iint \frac{\rho(r_i)\rho(r_j)}{|r_i-r_j|} dr_i dr_j + \xi_{xc}[\rho] \quad (2)$$

Hybrid methods, attempt to incorporate some of the more useful features from *ab initio* methods (Hartree-Fock methods) with some of the improvements of DFT mathematics.

The first terms represent the kinetic energy, the electron-nucleus attraction, and the electron-electron repulsion. The last idiom is a general functional for the exchange and correlation energy, not present in the Hartree-Fock method.

Hybrid methods such as the three-parameter B3LYP functional currently tend to be the most commonly used methods for good predictions compared with experimental results and give more accurate geometries. The B3LYP functional is based on an exchange-correlation functional developed by Becke in 1993 and modified by Stevens in 1994 by introduction of the Lee-Yang-Parr 1988 correlation functional [24]. The success of the method have often been attributed to inclusion of the exact Hartree-Fock exchange and gradient corrections for exchange and correlation.

The *ab initio* calculations presented in this thesis are based on DFT method B3LYP/6-311++G(3df,3pd) level of theory with the Gaussian 98 program system [25]. It is considered to be standard model chemistry for many applications and has been proved to give comparable results. There are several references that have proved the accuracy and viability of this method [26]. However, this method has its limitations, but for transition-metal complexes, it gives unexpectedly reliable results for ground state properties and can be applied to



large sized systems that cannot be computed by more accurate methods. It includes correlation and is much less basis set dependent than correlated wave function based methods.

Concerning the molecules containing scandium, a pseudopotential method was used as it is appropriate for transition metals and decreases the computation costs of calculation involving heavy elements. The procedure was using an all-electron basis set for hydrogen and aluminum and a SDD pseudopotential for scandium. Assuming the validity of the Born-Oppenheimer approximation, the task is to evaluate what happens if the core electrons are separated from the valence electrons. In this case, the valence electrons can be treated as if they were moving in an effective potential, generated by the core electrons (and the nuclei). The pseudopotential method employs the fact that only valence electrons take part in chemical bond formation. With this assumption, calculations can be done using the valence basis set only. The cores (inner-shell electrons and the atomic nucleus) of the individual atoms are approximated through a nonlocal effective potential, the pseudopotential.



6. CALCULATIONS AND RESULTS

As mentioned before the calculations have been executed using the density functional theory DFT method B3LYP/6-311++G(3df,3pd) level of theory with the Gaussian 98 computational system. The procedure for the compounds containing scandium was using an all-electron basis set for hydrogen and aluminum and a SDD pseudopotential for scandium.

The results of these calculations are presented below. The first step in order to achieve the energy and frequency calculations is to optimize the compound's structure. The optimized structure is helpful to visualize the subsequent vibrational modes. The second step corresponds to the analysis of the computed vibrational modes. The last point is the energy calculations and comparison for the hydrogenation process for the dialane hydride and the scandium-aluminium hydride.

6.1. STRUCTURE OPTIMIZATION

The first step in order to achieve the energy and frequency calculations is to optimize the compound structure. The optimized structure is helpful to visualize the subsequent vibrational modes.

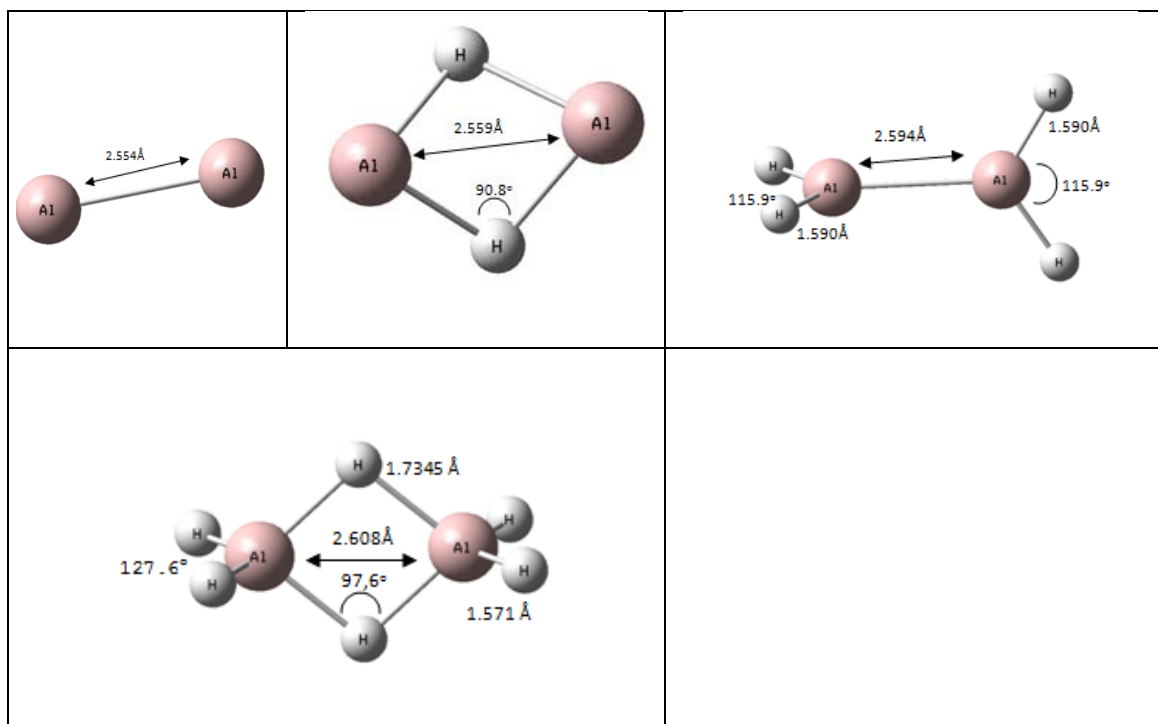


Table 3. Structure representations calculated for Al_2H_6 with the B3LYP/6-311++G(3DF,3PD) method

The optimized structure for Al_2H_6 corresponds with previous reports [7]. As represented in Table 3, the Al_2H_6 structure is a planar dibridged $\text{Al-H}_2\text{-Al}$ structure and the terminal metal-hydrogens are on a perpendicular plane. The total dipole moment for the Al_2H_6 is 0 Debye.

Table 4 contains the optimized structures for the aluminium-scandium hydride and the intermediate structures.

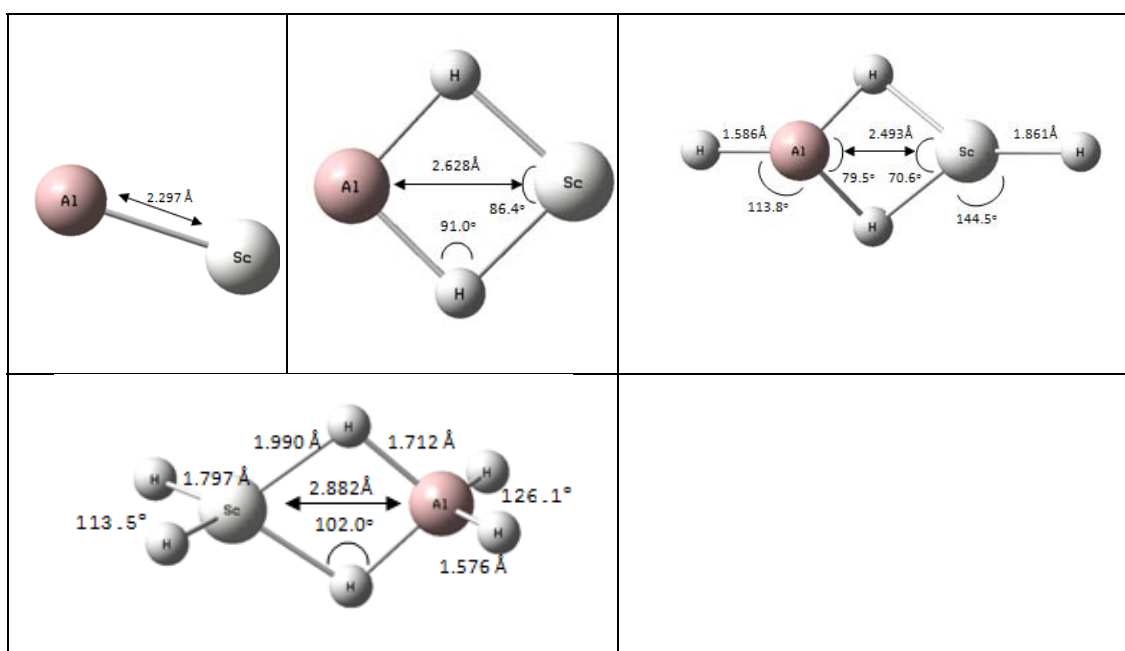


Table 4. Structure representations calculated for the metal hydrides AlH_3ScH_3 with the B3LYP/6-311++G(3DF,3PD) method.

Comparing to the dialane hydride Al_2H_6 , the aluminium-scandium hydride represents some structural and bonding differences. It is obvious that the hydrogen-scandium bond differs to the aluminium-hydrogen terminal and bridge bond. The structure is also a planar metal-hydrogen dibridged structure attached to the terminal hydrogen perpendicularly. Both terminal and bridge bond for scandium-hydrogen is a bit longer than the aluminium-hydrogen. The distance between is also a bit longer, 2.882 Å for the AlH_3ScH_3 in comparison to the 2.608 Å for Al_2H_6 . The total dipole moment for the AlH_3ScH_3 is 0.072 Debye.

6.2. FREQUENCY

In order to visualize the vibrational modes, the frequencies have been computed also using the B3LYP/6-311++G(3df,3pd) level of theory. Regarding the calculated frequencies, the predictions for the dialane Al_2H_6 are detailed in Table 5. These calculations are accurate, as the observed experimental values by Xuefeng Wang and Lester Andrews [7] were found to be very similar.

Mode	Sym	Frequency [cm^{-1}]	Infrared intensity [$\text{km} \cdot \text{mol}^{-1}$]
6	b_{1u}	631	252
11		1285	307
1	b_{2u}	221	15
10		853	193
18		1985	392
7	b_{3u}	717	615
13		1478	1054
15		1965	129

Table 5. Calculated IR active frequencies (cm^{-1}) and IR intensities ($\text{km} \cdot \text{mol}^{-1}$) for dibridged Al_2H_6 (Sym, D_{2h} point group)

The terminal metal-hydrogen stretch mode Al-H_2 corresponds to the 1985 and 1965 cm^{-1} absorptions that are antisymmetric b_{2u} and b_{3u} . The 1478 and 1285 cm^{-1} bands are antisymmetric b_{3u} and b_{1u} stretching modes of the bridged $\text{Al-H}_2\text{-Al}$. The AlH_2 wag, rock is responsible of the lower frequencies absorptions [27].

The following Table 6 indicates the frequencies and infrared intensities calculated for the aluminium-scandium compound AlH_3ScH_3 .



Mode	Sym	Frequency [cm^{-1}]	Infrared intensity [$\text{km} \cdot \text{mol}^{-1}$]
4	A_1	302	1.02
7		590	102
9		737	325
12		1267	666
14		1550	998
16		1654	104
17		1946	55
2	B_1	284	381
6		558	110
11		1132	341
13		1391	100
1	B_2	147	25
5		314	10
10		823	146
15		1591	652
18		1954	204

Table 6. Calculated IR active frequencies (cm^{-1}) and IR intensities ($\text{km} \cdot \text{mol}^{-1}$) for AlH_3ScH_3 (Sym, C_{2v} point group)

Concerning the results for the frequency and IR intensity for AlH_3ScH_3 , the strongest IR active modes are selected. The terminal metal-hydrogen stretch mode Al-H_2 corresponds to 1954cm^{-1} absorption. The terminal stretch mode for Sc-H_2 matches the 1591cm^{-1} absorption. The 823 and 1550cm^{-1} bands are antisymmetric and are the stretching modes of the bridged $\text{Al-H}_2\text{-Sc}$.

6.3. ENERGY

Energy calculations are very important in order to study compounds for hydrogen storage systems. Hydrogen storage materials which are interesting for on-board hydrogen storage, the compound must have lower operating temperatures, especially low desorption temperature, and lower enthalpy of formation. The hydrogenation energy is a very important factor that indicates the stability of the metal-hydrogen bond.

The energy values can be considered accurate because they correspond to the zero-point energy that is the lowest energy, (global minimum of the system) which has been corrected with the zero-point correction. So these results can be considered reliable as they have been corrected.

Table 7 and 8 show the calculated values for hydrogen absorption energies (Kcal/mol) for the global process of obtaining Al_2H_6 and AlH_3ScH_3 from the initial metal Al-Al and Al-Sc . As expected all the reactions of hydrogen with metals are exothermic.



Reactions	ΔZ (Kcal/mol)
$Al_2 + H_2 \rightarrow Al_2H_2$	-35,9336754
$Al_2H_2 + H_2 \rightarrow Al_2H_4$	-35,8131936
$Al_2H_4 + H_2 \rightarrow Al_2H_6$	-33,4807427

Table 7. Calculated hydrogen absorption energies for Al_2H_6 with the B3LYP/6-311++G(3df,3pd) method

Reactions	ΔZ (Kcal/mol)
$AlSc + H_2 \rightarrow AlHScH$	-54,57194769
$AlHScH + H_2 \rightarrow AlH_2ScH_2$	-41,31958512
$AlH_2ScH_2 + H_2 \rightarrow AlH_3ScH_3$	-47,47858596

Table 8. Calculated hydrogen absorption energies for AlH_3ScH_3 , with the B3LYP/6-311++G(3df,3pd) method

The results do not match the anticipated hypothesis, the hydrogen absorption energy value for the formation of AlH_3ScH_3 (-47,479kcal/mol) is higher than the value for the formation of Al_2H_6 (-33,481 kcal/mol). Technically this is not a good result because the energy has been increased, and consequently the operation temperatures are also higher.

The comparison between Al_2H_6 and AlH_3ScH_3 has shown that the introduction of the transition metal scandium does not decrease the hydrogenation energy due to cation matrix that seems to be the responsible for the thermal stability. The high stability is directly dependable to the interaction between the transition metal cations and hydrogen of the complexes.



7. CONCLUSIONS

As an overall conclusion, it is important to point out that the past years there has been a lot of investigation and research on the subject of hydrogen storage as a substitute of fossil fuel energy source. A large success has been achieved in the reversible storage of hydrogen in complex metal hydrides. High-pressure hydrogen or cryogenic liquid is one of the most studied techniques. However, there is a large energy loss involved in the compression and liquefaction. For this reason, hydrogen, solids such as metal hydrides are very interesting as hydrogen storage material.

To obtain storage materials which are interesting for on-board hydrogen storage, the compound must have lower operating temperatures, especially low desorption temperature, and lower enthalpy of formation. The studied materials have to meet these criteria, as well as a competitive production. Some hydrides are relatively inexpensive to fabricate but thermally too stable for room-temperature applications, whereas others are sufficiently unstable but too expensive for large-scale applications.

The comparison between Al_2H_6 and AlH_3ScH_3 has shown that the introduction of the transition metal scandium increases the hydrogenation energy due to cation matrix that seems to be the responsible for the thermal stability. The high stability is directly dependable to the interaction between the transition metal cations and hydrogen of the complexes.

A challenge for future work is to perform experiments in order to obtain the Al-Sc hydride and to confirm the results obtained in this project. The hydrogen absorption and desorption process and preparation of the metal hydride will play a very important role in the success of the AlH_3ScH_3 storage system. The subsequent experiments will be able to indicate if this compound is able to meet all the international criteria for hydrogen-storage systems.

The following work should head to study larger aluminum-scandium metal hydrides, such as, Al_4H_{12} , Al_3H_9 , $\text{Al}_3\text{ScH}_{12}$, Al_2ScH_9 , etc. in order to find the appropriate compound where the hydrogen desorption energy and temperature is reduced. These metal hydrides should also be characterized by low hydrogen absorption/desorption temperature/pressure, high amount of cycles possible, high volume storage capacity, good hydrogenation kinetics and low gravimetric storage capacity.



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9. BIBLIOGRAPHIC REFERENCES

- [1] International Energy Agency (IEA)- Key World Statistics, **2009**
- [2] European Commission, EUR 20719 EN- Hydrogen Energy and Fuel Cells – A vision of our future, **2003**
- [3] Chalk,S.G.; Miller, J.F. *Journal of Power Sources* **2006**,159,73.
- [4] L. Schlapbach; A. Zuttel, *Hydrogen-storage materials for mobile applications*, Nature 414 **2001** 553-558
- [5] Ghiardi, M.L.; Zhang,L.; Lee, J.W.;Flynn,T.; Seibert, M.; Greenbaum, E.; Melis, A. *Trends in Biotechnology* **2000**, 18-506.
- [6] D.Mori; K. Hirose, *Recent challenges of hydrogen storage technologies for fuel cell vehicles*, International Journal of Hydrogen Energy, 34, **2009** 4569-4574
- [7] L. Andrews, X.Wang, *Science* **2003**, 299, 2049 – 2052.
- [8] U.S. Department of Energy; *Program's Multi-Year Research, Development, and Demonstration -Energy Efficiency and Renewable Energy-Fuel Cell Technologies Program – Hydrogen Storage* **2011**
- [9] U.S. Department of Energy; *Program's Multi-Year Research, Development, and Demonstration -Energy Efficiency and Renewable Energy-Fuel Cell Technologies Program – Hydrogen Storage Challenges* **2011**
- [10]Graham, T. *Journal of the Chemical Society* **1867** 20-235.
- [11] Van Vucht, J.H.N.; Kujipers, F.A.; Bruning, H.C.A.M.; *Reversible room temperature absorption of large quantities of hydrogen by intermetallic compounds*, Philips Res. Repts. **1970** 133-140.
- [12] Encyclopædia Britannica. Encyclopædia Britanica Online; “hydride”. Encyclopædia Britanica, **2011**. Web 10 Jun. 2011.
- [13] Sandrock,G. *Journal of Alloys and Compounds* **1999**, 293-295,877.
- [14] Yvon K. *Metal hydrides: Transition Metal Hydrides Complexes* **2004** 1-9
- [15] Sobkowiak,A. *Hydrogen absorption properties of scandium and aluminium based compounds*, Uppsala Universitet, **2010**
- [16] Sahlbreg, M. *Light-Metal Hydrides for Hydrogen Storage* , Uppsala Universitet, **2009**
- [17] Burkhanov, G.S.; Kol’chugina, N.B.; Chistyakov, O.D.; Verbetsky, V.N.; Salamova, E.; Andreeva,E.Y.; Volkova, E.S.; *Interaction with hydrogen with intermetallic compounds $ScAl_2$ and Sc_2Ni* , Inorganic materials 42 **2006** 491-495.



- [18] Antonova, M.M.; Chernogorenko, V.B, Resistance to hydrogen of Al-Sc alloys, Russian J. Appl. Chem. **2001** 369-399
- [19] Sandrock, G.; Thomas, G.; *The IEA/DOE/SNL on-line hydride databases*, Appl. Phys. **2001** 153-155
- [20] Aleksanyan, A.G.; Dolukhanyan, S.K.; Shekhtman, V.Sh.; Harutyunyan, Kh.S.; Abrahamyan, A.; Mnatsakanyan, N.L.; *The thermal radiation process in the Sc-H system*, J.Alloys and Compounds **2003** 562-565
- [21] Brower, F.M.; Matzek, N.E.; Reigler, P.F.; Rinn, H.W.; Roberts, C.B.; Schmidt, D.L.; Snover, J.A.; Terada, K.; *Preparation and properties of aluminum hydride*, J.Am.Chem.Soc. **1976** 2450-2453
- [22] Kolomiets, A.V.; Havela, L.; Yartys, A., Andreev, A.V.; *Hydrogen absorption-desorption, crystal structure and magnesium in ReNiAl intermetallic compounds and their hydrides*, Journal of Alloys and Compounds, 253-254 **1997** 343-346
- [23] Sobkowiak, A. *Hydrogen absorption properties of scandium and aluminum based compounds*, Uppsala Universitet **2010**
- [24] Stephens, P. J.; Devlin, F. J. ; Chabrowski, C. F. and M. Frisch, J. *Phys.Chem.* **1994**, 98, 11623, and refs therein.
- [25] Gaussian98 (Revision A.7) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**, and references therein.
- [26] Ricca and Bauschlicher, C. W. *Theor. Chim. Acta*, 92, **1995** 123-131.
- [27] Enderby, J.E.; Ansell, S.; Krishnan, S.; Price, D.L.; Saboungi, M.-L.; *Appl. Phys. Lett.* **1997** 71, 116

