Structural Basis for Hydrogen Interaction in Selected Metal Hydrides

JONAS ÅNGSTRÖM
Dissertation presented at Uppsala University to be publicly examined in Häggsalen, Ångströmlaboratoriet Lägerhyddsvägen 1, Uppsala, Friday, 24 April 2015 at 09:15 for the degree of Doctor of Philosophy. The examination will be conducted in English. Faculty examiner: Fermin Cuevas (East Paris Institute of Chemistry and Materials Science, CNRS).

Abstract

Metal hydrides have existing and potential uses in many applications such as in batteries, for hydrogen storage and for heat storage. New metal hydrides and a better understanding of the behaviour of known metal hydrides may prove crucial in the realisation or further development of these applications. The aims of the work described in this thesis have been to characterise new metal hydrides, investigate how the properties of known metal hydrides can be improved and understand how their structure influences these properties. Metal hydrides, in most cases synthesised via high-temperature techniques, were structurally characterised using X-ray powder diffraction, X-ray single crystal diffraction and neutron powder diffraction and their thermodynamic and kinetic properties by *in-situ* X-ray powder diffraction, thermal desorption spectroscopy and pressure-composition-temperature measurements.

The investigations showed that: the storage capacity of the hexagonal Laves phase Sc(Al\textsubscript{1-x}Ni\textsubscript{x})\textsubscript{2} decreases with increasing Al content. There is a significant decrease in the stability of the hydrides and faster reaction kinetics when Zr content is increased in the cubic Laves phase Sc\textsubscript{1-x}Zr\textsubscript{x}(Co\textsubscript{1-x}Ni\textsubscript{x})\textsubscript{2}. Nb\textsubscript{0.9}M\textsubscript{1.1}Si\textsubscript{1.1} (M=Co, Ni) form very stable interstitial hydrides which have very slow sorption kinetics. MgH\textsubscript{2} mixed with 10 mol% ScH\textsubscript{2} reaches full activation after only one cycle at 673 K while it takes at least four cycles at 593 K. LnGa (Ln=Nd, Gd) absorb hydrogen in two steps, it is very likely that the first step is interstitial solution of hydride ions into Ln\textsubscript{4} tetrahedra and the second step places hydrogen atoms in Ln\textsubscript{3}Ga tetrahedra. The nature of the Ga-H bond is still unclear.

*Jonas Ångström, Department of Chemistry - Ångström, Box 523, Uppsala University, SE-75120 Uppsala, Sweden.*

© Jonas Ångström 2015

ISSN 1651-6214
ISBN 978-91-554-9187-1
urn:nbn:se:uu:diva-245046 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-245046)
“Jag känner mig däremot såsom transformist nästan förpliktigad antaga endast ett enkelt ämne, ur vilket de andra genom förtunning, förtätning, kopulation, korsning och så vidare uppståt, och detta utan att vilja nämna ur-ämnets namn, kanske inte en gång vid namnet väte.”

August Strindberg (Antibarbarus, 1905)
This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


Reprints were made with permission from the publishers.
The author also contributed to the following published and/or accepted scholarly works which are not included in this thesis:


My contributions to the papers

The authors contribution to the papers included in this thesis:

I I made some of the syntheses, took part in the conception of the project and did the \textit{in-situ} diffraction experiments together with the first author. I was involved in the writing and discussions about the manuscript. I approved the final proof of the paper.

II I planned the work together with the main author and did most of the experimental work except the structural refinements and PCT measurements. I wrote parts of the manuscript and was involved in all of the discussions. I approved the final proof of the paper.

III I planned and executed all the experimental work and the treatment and interpretation of the resulting data. The theoretical calculations were performed by the second author. I wrote most of the manuscript and was involved in all discussions. I approved the final proof of the paper.

IV I executed most of the \textit{in-situ} experiments, took part in the treatment in the data and wrote parts of the manuscript. I approved the final proof of the paper.

V I planned all and executed most of the experimental work and the treatment and interpretation of the resulting data. I wrote most of the manuscript and approved the final proof of the paper.

VI I planed and executed most of the experimental work. The theoretical calculations were performed by the second author. I did the majority of the treatment of the experimental data. I wrote most of the manuscript and approved the version appended to this thesis.
## Contents

1 Introduction .................................................................................................................. 13  
1.1 Examples of Metal Hydrides .................................................................................. 13  
1.1.1 Ionic Metal Hydrides ....................................................................................... 13  
1.1.2 Metallic Metal Hydrides .................................................................................. 15  
1.1.3 Covalent Metal Hydrides ................................................................................. 17  
1.1.4 Zintl Phase Hydrides ....................................................................................... 17  
1.2 Existing and Potential Applications of Metal Hydrides ............................................. 17  
1.2.1 Ni–MH Batteries ............................................................................................... 17  
1.2.2 Hydrogen storage ............................................................................................. 18  
1.2.3 Thermal Storage ............................................................................................... 19  
1.2.4 Other Applications and Effects of Hydrogen in Metals ..................................... 20  

2 Aims .................................................................................................................................. 21  

3 Methods ............................................................................................................................. 23  
3.1 Synthesis ....................................................................................................................... 23  
3.1.1 Arc Melting ......................................................................................................... 23  
3.1.2 Heat Treatment .................................................................................................... 23  
3.1.3 Hydrogenation/Deuteration ............................................................................... 24  
3.2 Diffraction .................................................................................................................... 24  
3.3 Characterisation by Diffraction Techniques ............................................................... 28  
3.3.1 X-ray Single Crystal Diffraction ....................................................................... 28  
3.3.2 X-ray Powder Diffraction .................................................................................. 28  
3.3.3 Neutron Powder Diffraction .............................................................................. 29  
3.3.4 Determination of Lattice Parameters ................................................................. 30  
3.3.5 Full Pattern Refinement Using the Rietveld Method ......................................... 30  
3.4 Thermodynamic and Kinetic Behaviour of Metal Hydrides ....................................... 31  
3.4.1 Thermodynamics of Metal Hydrides .................................................................. 31  
3.4.2 Kinetics ............................................................................................................. 33  
3.4.3 Density Functional Theory ................................................................................. 34  

4 Results and Discussion .................................................................................................... 37  
4.1 Laves Phases Containing Sc ..................................................................................... 38  
4.1.1 The Hexagonal Laves Phase Sc(Al$_{1-x}$Ni$_x$)$_2$ ............................................... 38  
4.1.2 The Cubic Laves Phase (Sc$_{1-x}$Zr$_x$)(Co$_{1-y}$Ni$_y$)$_2$ ...................................... 43  
4.2 Activation Effects in MgH$_2$ Mixed with ScH$_2$ ..................................................... 47  
4.3 Nb$_4$M$_{0.9}$Si$_{1.1}$ (M=Ni, Co) Hydrides ..................................................................... 49  
4.4 Hydrogen Absorption in LnGa (Ln=Gd, Nd) ............................................................ 54  
4.5 Ti–Zr–Ni–Co approximants ....................................................................................... 59
Abbreviations

A list of the abbreviations used in this thesis.

<table>
<thead>
<tr>
<th>abbreviation</th>
<th>meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCC</td>
<td>Body Centered Cubic</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
</tr>
<tr>
<td>CSP</td>
<td>Concentrated Solar Power</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>ICSD</td>
<td>Inorganic Crystal Structure Database</td>
</tr>
<tr>
<td>Ni–MH</td>
<td>Ni-Metal Hydride</td>
</tr>
<tr>
<td>NPD</td>
<td>Neutron Powder Diffraction</td>
</tr>
<tr>
<td>PCT</td>
<td>Pressure Composition Temperature</td>
</tr>
<tr>
<td>TDS</td>
<td>Thermal Desorption Spectroscopy</td>
</tr>
<tr>
<td>wt%</td>
<td>weight % of hydrogen</td>
</tr>
<tr>
<td>XRPD</td>
<td>X-Ray Powder Diffraction</td>
</tr>
<tr>
<td>XRSCD</td>
<td>X-Ray Single Crystal Diffraction</td>
</tr>
</tbody>
</table>
1. Introduction

Metals and hydrogen have a long and intimate history: hydrogen gas was arguably first observed by Robert Boyle, when he dissolved steel filings in acid in 1671.[1] Dissolution of iron in sulphuric acid was also used to fill the balloon Örnen, in the disastrous Arctic expedition in 1897 led by Salomon A. Andrée.[2] The interaction between metals and hydrogen is, however, far from limited to the production of hydrogen gas when metals are oxidised in acidic solutions; that metals absorb hydrogen has been known since the middle of the 19th century [3]. Since then, some kind of metal hydride has been reported for a majority of the metals; in these compounds hydrogen atoms form ionic, metallic or covalent bonds with the metal atoms (figure 1.1).

The existing and potential uses of metal hydrides are mainly energy related and include: as rechargeable batteries [5] anodes, as materials for a safer and more compact hydrogen storage [6] and as materials for thermal storage in concentrated solar power [7]. A deepened understanding of how the properties of known hydrides can be enhanced as well as the discovery of new metal hydrides could prove crucial for the realisation or improvement of these and other applications.

1.1 Examples of Metal Hydrides

1.1.1 Ionic Metal Hydrides

In some sense the ionic metal hydrides are the “true” metal hydrides since they actually contain the hydride ion. The hydrides of the stable group I elements are all ionic and can be seen as analogues of the halides; all crystallise in the NaCl-type structure (figure 1.2a); there is indirect evidence of a transition to the denser CsCl-structure for all but NaH and LiH under very high static pressure (figure 1.2b).[8]

Most hydrides of the stable group II elements are ionic, the exception is BeH₂ which has a BeH₄-network structure [9]; all but one of the ionic group II hydrides crystallise in the PbCl₂-type structure [10, 11, 12] while MgH₂ crystallises in the rutile-type structure [13] (figure 1.2c and d). Typical for group II ionic hydrides are that they are very stable (e.g. enthalpies of formation are 73 kJ mol⁻¹ for MgH₂ [14] and 174 mol⁻¹ for CaH₂ [15]).

1 The Inorganic Crystal Structure Database (ICSD) contains structures for binary metal hydrides (or deuterides) for 75% of the metallic elements (excluding the transuranic elements) [4].
Figure 1.1. Metal hydrides exhibits all three types of chemical bonding: ionic, metallic and covalent.

Figure 1.2. The crystal structures of the group I and II ionic hydrides. Metal ions are shown as blue spheres and hydride ions as red spheres. a) NaCl-type structure b) CsCl-type structure. c) PbCl$_2$-type structure d) Rutile-type structure.
\( \text{MgH}_2 \)

\( \text{MgH}_2 \) is arguably the most investigated hydride for hydrogen storage\(^2\) because of the high weight percent of hydrogen in the compound (7.66 wt%), low cost and the abundance of Mg in the earth’s crust. The aforementioned stability of \( \text{MgH}_2 \) and a tendency to oxidise to \( \text{MgO} \) are, however, large obstacles for some applications. Additionally, the kinetics of hydrogen desorption in the absence of additives combined with ball milling are rather sluggish.\(^{[16]}\)

1.1.2 Metallic Metal Hydrides

Binary metallic metal hydrides are mainly formed by the transition metals; however, there is a general (but not universal) trend of decreasing affinity for hydrogen with increasing group number for the transition metals in the periodic table. In these compounds H atoms are located in interstitial sites between the much larger metal atoms. In an interstitial hydride, where the M–H bond is metallic, the stoichiometry is not limited by requirements of charge neutrality or by the formation covalent bonds. This means that the composition can vary. When the affinity for hydrogen is “just right” hydrogen can easily and quickly be cycled in and out of a material at moderate pressures and temperatures. \( \text{PdH}_x \) \(^3\) is an example of such a Goldilocks hydride, but alloying a metal with high hydrogen affinity with one with low hydrogen affinity can achieve a similar result.

\( \text{AB}_x \) Interstitial Hydrides

Many interstitial hydrides are binary, or pseudo-binary, combinations of a metal (or metals) with a large metallic radius \( (r_m) \), A, and a metal (or metals) with a smaller \( r_m \), B. Typical combinations are \( \text{AB}_5 \), \( \text{AB}_2 \) and \( \text{AB} \). The high weight of transition-metal atoms in comparison to the H atom makes the gravimetric density of hydrogen rather low (<2 wt%); however, the storage capacity per volume is often high, \textit{e.g.} the volumetric density of hydrogen(deuterium) is higher in \( \text{LaNi}_5\text{D}_{6.7} \) \(^{[17]} \) than in \( \text{D(s)} \) \(^{[18]} \) or \( \text{H}_2(l) \) \(^{[19]} \). Additionally, the properties can be tuned to fit an application by changing the composition.

\( \text{AB} \) Interstitial Hydrides

\( \text{AB} \) or \( \text{BCC}^3 \)-type compounds crystallise in the W-type structure, or sometimes its more ordered cousin the CsCl-type structure\(^4\) (figure 1.2b). To form a substitution alloy with the W-type structure the atoms cannot differ much in size so these compounds are often made up of two (or more) 3d transition metals, where \( \text{TiFeH}_x \) \(^{[20]} \) is a classic example.

---

\(^2\) see applications on page 19

\(^3\) Body Centred Cubic

\(^4\) Which does not have BCC symmetry!
Figure 1.3. Laves phases and the Friauf polyhedron (green lines). The A atom is shown in a lighter shade of grey than the B atom. a) The Friauf polyhedron: one of the four AB$_3$ tetrahedra is shown in black. b) The tetrahedral A$_2$B$_2$-interstitial sites are shown in white on the hexagonal surfaces of the Friauf polyhedron. c) The cubic Laves phase MgCu$_2$ with Friauf polyhedron. d) The hexagonal Laves phase MgZn$_2$ with Friauf polyhedron.

$AB_2$ Interstitial Hydrides

The crystal structure of the $AB_2$-compounds (also known as Laves phases) can be constructed from Friauf-polyhedra stacked in different ways.[21] The polyhedron itself can be seen as four tetrahedra formed by the central A atom in the polyhedron and three B atoms (figure 1.3a). Interstitial hydrogen is often located in tetrahedral A$_2$B$_2$ voids on the faces of the Friauf-polyhedron (figure 1.3b). The two most common types of $AB_2$ compounds are the cubic MgCu$_2$-type (C15) and hexagonal MgZn$_2$-type (C14) (figure 1.3c and d). The difference in size of the A and B atoms are often larger than in the $AB_2$-hydrides. A typical example of an $AB_2$ hydride is Zr$_{(1-y)}$Ti$_y$(Cr$_{(1-x)}$Ni$_x$)$_2$H$_z$.[22]

$AB_5$ Interstitial Hydrides

The $AB_5$-type interstitial hydrides crystallise in the CaCu$_5$-type structure and can be formed by Y and a large number of lanthanides (A) combined with period four transition metals (B).[23] The structure can be rationalised as stacking of polyhedra built from $AB_3$ tetrahedra in a similar way as in the Laves phases. The archetypical examples of $AB_5$-hydrides are LaNi$_5$H$_x$ and its many variants.[24]
1.1.3 Covalent Metal Hydrides
Metals in the $p$-block form covalent hydrides that are typically unstable; one example is the methane analogue stannae (SnH$_4$).[25]

*Complex Hydrides*

Complex hydrides are formed by positive metal ions of group I or II elements and a negatively charged complex ion; these complex ions consist of one or many $p$-block atoms covalently bound to H atoms with structures resembling hydrocarbons. Much effort has gone into studying some of these hydrides [26] because of their high gravimetric hydrogen densities, e.g. NaAlH$_4$ with 7.5 wt% and LiBH$_4$ with 18.5 wt%. Complicated decomposition reactions and poor reversibility have, so far, made them unsuitable for most applications.

1.1.4 Zintl Phase Hydrides

Hydrides of Zintl phases are interesting since they are somewhere on the boarder between all the previously described metal hydrides. Zintl phases are formed by combining electropositive (also known as an active) alkali, alkaline earth, or rare-earth metals with electronegative $p$-block metals.[27] The crystal structures of these compounds can be rationalised as a cation of the active metal and a complex ion of the electronegative metal (where the complex ion is bound to fulfil the octet rule).

Hydrides of Zintl phases are often either hydridic or complex.[28] In hydridic hydrides, hydride ions (H$^-$) are located in interstitial sites coordinated by the active metal ions and, since the formal charge of the hydride ion is -1, this requires oxidation of the complex ion to preserve charge neutrality. In complex hydrides of Zintl phases, hydrogen atoms bind covalently to the complex ion, forming a complex hydride.

1.2 Existing and Potential Applications of Metal Hydrides

Metal hydrides are used in a number of niche and mainstream applications and have been suggested for use in a number of other applications (figure 1.2). A couple of examples are provided below.

1.2.1 Ni–MH Batteries

The main application of metal hydrides today is probably in Nickel-Metal Hydride (Ni–MH) batteries where they are used as anode materials (figure 1.2a).
In a typical battery, an interstitial metal hydride (often a pseudo-binary version of LaNi$_5$H$_x$) anode is combined with a NiOOH/Ni(OH)$_2$ cathode in a KOH solution. Ni–MH batteries have lost a large part of the mobile energy storage market to Li-ion batteries during the past decade; however, they are still used in a number of applications.

1.2.2 Hydrogen storage

H$_2$ is an attractive energy carrier because of its high gravimetric energy density and its complete lack of CO$_2$ emissions when it is oxidised in a combustion engine or fuel cell. An alternative storage technique to high pressure tanks has been sought to (depending on the application) improve safety, system gravimetric density and/or volumetric density.

Metal hydrides often require activation by a couple of hydrogenation/de-hydrogenation cycles or heating in H$_2$, before before they reach the reaction rates required for hydrogen storage applications. This process, the activation effect, is not well defined but probably involves changes in the microstructure of the hydride [29] and reduction or cracking of the surface oxide.

In applications where weight, and maybe also cost, is of lower importance hydrogen storage in interstitial metal hydrides is attractive because of their high volumetric storage capacity and safety. One example is submarines such as the Type 212 U-boats operated by the German and Italian navies that
uses GfE hydralloy C [26] (a commercial AB$_2$-type interstitial hydride material [30]) in combination with liquid oxygen storage to power the propulsions system during quiet operation (figure 1.2b).

**Light Mobile Applications**

Finding a metal hydride suitable for hydrogen storage in light mobile applications (*e.g.* cars) has long been the holy grail of metal hydride research (figure 1.2c).[6] Since light weight is paramount in such an application the main focus has been on light metal hydrides which contain more than one hydrogen per metal, such as Mg-based or complex metal hydrides. It should be noted, however, that no metal hydride currently surpasses carbon fibre reinforced high pressure tanks in all relevant aspects.[26]

The first commercially produced fuel-cell automobiles have recently entered, or will soon enter, the market. One example is Toyota Mirai [31] which will be launched in Japan, western Europe and the USA [32] this year. While these vehicles use the high pressure storage option, this may increase the interest in research into metal hydrides as a stand-alone storage alternative or in a combined high-pressure/metal-hydride storage solution.

Another example where metal hydrides are used for hydrogen production (in this case in a non-reversible way), is the portable charger POWERTREKK 2.0 by myFC. [33] This device uses a mixture of sodium silicide, NaBH$_4$ and Al which is mixed with water to produce H$_2$ for a small fuel cell.

1.2.3 Thermal Storage

The absorption of hydrogen in a metal is often a very exothermic process, especially for the ionic hydrides (see page 13); this can be exploited to store heat for Concentrated Solar Power (CSP) plants (figure 1.2d).[7] A possible set-up is that a very stable hydride, *e.g.* CaH$_2$, is heated by CSP during the day forming Ca and H$_2$. This increases the pressure enough so that a more labile hydride$^5$, *e.g.* FeTi, absorbs the H$_2$ and this absorption allows more hydrogen to be released from the stable hydride and so on:

$$\text{Day: CaH}_2 + \text{TiFe} + \text{heat} \rightarrow \text{Ca} + \text{TiFeH}_2$$ (1.1)

During the night the stable hydride is cooled down, causing it to absorb hydrogen which releases heat. The lowered pressure causes the labile hydride to release H$_2$ which the stable hydride absorbs and so on:

$$\text{Night: Ca} + \text{TiFeH}_2 \rightarrow \text{CaH}_2 + \text{TiFe} + \text{heat}$$ (1.2)

The heat released by the formation of the stable hydride can be used to produce electricity during the night.

$^5$which is not heated but in contact with the gas released from the stable hydride
1.2.4 Other Applications and Effects of Hydrogen in Metals

Here is a short list of additional applications/interesting properties of metal hydrides which will not be described in detail: production of high purity $\text{H}_2(\text{g})$ by diffusion through a metallic foil [34]; increased critical temperature for superconductors after hydrogenation [35] and using the difference in optical properties between a metal and its metal hydride to produce a switchable mirror.[36]
2. Aims

The aims of this thesis were to characterise new metal hydrides and to study how the properties of known metal hydrides can be improved by changing the chemical composition and crystal structure of these compounds via substitution for and addition of elements in the materials. Relating structural characteristics to properties was an important part of this process.

**Laves Phases Containing Sc**

AB$_2$ or Laves phase compounds can be used in hydrogen storage and in Ni–MH batteries. The aim in this projects was to chart the extension of hexagonal and cubic Laves phases in the Sc(Al$_{1-x}$Ni$_x$)$_2$ and (Sc$_{1-x}$Zr$_x$)(Co$_{1-y}$Zr$_y$)$_2$ systems and study how the composition and crystal structure affect the hydrogen sorption properties.

**Activation In MgH$_2$ Catalysed With ScH$_2$**

MgH$_2$, one of the most studied potential hydrogen storage materials is hampered by, among other things, slow kinetics. The aim of this project was to investigate the activation effect during cycling of a 90mol% MgH$_2$ mixed with 10mol% ScH$_2$, a possible catalyst.

**Nb$_4$MSi (M=Co, Ni) Hydrides**

Nb$_4$MSi (M=Co, Ni) have recently been shown to be superconductive and interstitial hydrogen has been known to increase the critical temperature of some superconductors. The aim of this project was to investigate hydrogen absorption/desorption of the Nb$_4$MSi (M=Co, Ni) hydrides and possible order between the M/Si sites to facilitate further studies of the superconductive properties of these hydrides.

**LnGa (Nd, Gd) Hydrides**

REGa compounds order magnetically at low temperatures and could potentially be used in magnetocaloric refrigeration; additionally, they are Zintl phases which can form different kinds of metal–hydrogen bonds. The aim of this project was to determine the crystal structure of the LnGa (Ln=Nd, Gd) hydrides and investigate how hydrogen is introduced into the structure as well as the nature of the metal-hydrogen bonds; this could facilitate the understanding of the magnetic properties of the REGa hydrides.
**Ti–Zr–Co–Ni Approximants**

Ti–Zr–Ni quasicrystals and their related approximants have been shown to absorb large amounts of hydrogen. The aim of this project was to synthesise Ti–Zr–Co–Ni approximants and hydrogenate them.

**Techniques**

The tools used to meet these aims were: high temperature synthesis techniques to produce samples; XRPD, NPD and XRSCD for characterisation of crystal structures as well as phase analysis and *in-situ* XRPD, TDS and PCT measurements for characterisation of thermodynamic and kinetic properties.
3. Methods

3.1 Synthesis

Syntheses of samples for all but paper IV were done using the high temperature techniques described below (figure 3.1). The samples for paper IV were produced using ball milling.

3.1.1 Arc Melting

An electric arc is a continuous high voltage/low current discharge between two electrodes where the gas between them is broken down into ions (a plasma which carries the current). Reasonably conductive materials can be welded or melted using such an arc. Most of the samples in this thesis were produced using an arc furnace which consisted of a water-cooled Cu hearth (electrode one) on which the sample was placed and a W rod (electrode two) both encased in an airtight chamber (figure 3.1a). To minimise the partial pressure of $O_2$ and other reactive gases the chamber was flushed by high purity Ar and a Ti “getter” was melted prior to melting the sample. The samples were re-melted a number of times and flipped between each melting to improve homogeneity.

3.1.2 Heat Treatment

The poor temperature control and high cooling rate of arc melting often necessitated heat treatment to improve the crystallinity and phase homogeneity of the samples. For most samples the treatment was carried out in fused silica ampoules which were evacuated during at least 0.5 h using an oil-vacuum pump. The ampoules were then sealed and placed in a pit furnace and heated to the desired temperature (figure 3.1b). If higher temperatures than 1373 K were required\(^1\) a tube furnace with SiC heating elements was used (figure 3.1c); the samples were placed in an alumina boat and heated to the desired temperature under flowing high purity Ar.

\(^1\)Heat treatment in ampoules is limited by the crystallisation of the silica and the maximum temperature of the pit furnaces.
3.1.3 Hydrogenation/Deuteration

Powdered samples were hydrogenated or deuterated in an alumina “finger” crucible which in turn was placed in a steel autoclave (figure 3.1d). The autoclave was flushed three times with the reactive gas followed by an activation of the material by heating it in the reactive gas (H$_2$/$D_2$ pressures of >5 MPa). Finally the temperature was lowered down to room temperature (∼293-303 K).

3.2 Diffraction

Using the diffraction phenomenon is one of the most effective ways of determining the crystal structure of and identifying crystalline compounds. The techniques rely on finding some process that scatters incoming waves$^2$ elastically; if there is any kind of order in the material (short range or long range) the dispersed waves can interact in constructive and destructive ways and the patterns they form can be recorded. X-rays, which are easily produced in a laboratory, behave in this way and are therefore extensively used in diffraction experiments. Neutrons and electrons are also possible to use when accelerated to sufficient velocities, in part because of the wave/particle duality.

$^2$with wavelengths $\lambda$ close to length scale of what is to be studied
**Diffraction Conditions**

An ideal crystal has an infinite array of atoms which have long range order; this order can often be described using translational symmetry with a three dimensional unit cell repeated infinitely in all directions, but there are exceptions: e.g. quasi-crystals and incommensurate structures.

Crystals with translational symmetry can be described using an infinite lattice of points with identical surroundings and by defining a unit cell with the lattice vectors \( \mathbf{a}_1, \mathbf{a}_2 \) and \( \mathbf{a}_3 \) (equivalent to lattice parameters a, b, c, \( \alpha \), \( \beta \) and \( \gamma \)). It is convenient to convert these real-space vectors to reciprocal ones (\( \mathbf{b}_1 \), \( \mathbf{b}_2 \) and \( \mathbf{b}_3 \)), where \( \| \mathbf{b}_n \| = \| \mathbf{a}_n \|^{-1} \) and \( \mathbf{b}_n \) is orthogonal to the two \( \mathbf{a}_{\neq n} \) vectors.

The incident radiation is described by the vector \( \mathbf{k} \), where \( \| \mathbf{k} \|=1/\lambda \). If the incident wave is scattered elastically the vector describing the scattered wave vector \( \mathbf{k}_s \) must have the same length, i.e. \( \| \mathbf{k} \|=\| \mathbf{k}_s \|=1/\lambda \). For the scattered waves to interact constructively the difference between the two vectors must be a linear combination of integers (the indices \( h, k \) and \( l \)) times the reciprocal lattice vectors, i.e. \( \mathbf{k} - \mathbf{k}_s = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 \). This process is nicely illustrated by the Edwald’s sphere, see figure 3.2. In powder diffraction it is usually easier to think of these conditions as Bragg’s law where a reflection occurs at an angle \( \theta_{hkl} \) if:

\[
2\|h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3\|^{-1}\sin \theta_{hkl} = 2d \sin \theta_{hkl} = \lambda \tag{3.1}
\]

where \( d \) is the distance between crystallographic planes.
**The Structure Factor**

The intensity of a reflection is ideally proportional to the absolute value of the structure factor$^3$$^\text{3}$$^3$$^\text{3}$ $F_{hkl}$:

$$F_{hkl} = \sum_{j=1}^{n} g^j t^j \left( \frac{\sin \theta_{hkl}}{\lambda} \right) f^j \left( \frac{\sin \theta_{hkl}}{\lambda} \right) e^{2\pi i (hx^j + ky^j + lz^j)}$$  \hspace{1cm} (3.2)

where $n$ is the total number of atoms; $\theta_{hkl}$ and $\lambda$ are the angle and wavelength, respectively; $g^j$, $t^j \left( \frac{\sin \theta_{hkl}}{\lambda} \right)$ and $f^j \left( \frac{\sin \theta_{hkl}}{\lambda} \right)$ is the occupancy, the displacement and atomic scattering factor of the $j^{th}$ atom and $x^j$, $y^j$ and $z^j$ are the fractional coordinates of the $j^{th}$ atom. $f^j \left( \frac{\sin \theta_{hkl}}{\lambda} \right)$ is very dependent on what type of radiation is used in the experiment.

**Scattering of X-rays (Thompson Scattering)**

One way that X-rays can interact with matter is that the electrons start to undulate “on” the electro-magnetic wave. This makes each electron emit a spherical wave with the same wavelength as the incident radiation, a process called Thompson scattering. Thompson scattering relies on the very low weight of the electrons (which are also charged particles) do not scatter X-rays in this way. Since the electrons scatter X-rays the amount one atom scatters is proportional to the number of electrons. This makes it hard (but not impossible) to “see” the lightest atoms if they are surrounded by heavier atoms (such as in a metal hydride); it is also hard to distinguish between atoms or ions with equal, or close to equal, number of electrons (e.g. in NaF, figure 3.3a).

**Scattering of Neutrons**

Unlike X-rays, neutrons mainly interact with the nucleus of an atom rather than its electrons (figure 3.3b). When a neutron hits a nucleus the neutron can be: elastically scattered coherently (i.e. with the same phase as the other neutrons and is therefore interesting for diffraction experiments); elastically scattered in-coherently (i.e. not with the same phase as the other neutrons); scattered in-elastically by the nucleus (i.e. some energy is transferred to or from the nucleus) or absorbed by the nucleus. Unlike X-rays, with a linear relationship between elastically scattered photons and atomic number, the likelihood that isotopes scatter neutrons elastically and coherently follow an apparent random pattern; this makes it possible to distinguish some atoms with similar numbers of electrons, e.g. in the powder diffraction pattern of NaF (figure 3.3c). Additionally, since the neutron has a spin it is scattered by unpaired electrons and can thus be used to probe the magnetic ordering of a material.

$^3$In a real experiment this is complicated by a number of factors, see equation 3.3 on page 30.
Figure 3.3. The difference between the way NaF scatters X-rays and neutrons. a) What the X-ray “sees” (i.e. the electrons of the ions), b) What the neutron “sees” (i.e. the nuclei and their bound scattering lengths, b, in fm). c) Simulated X-ray and neutron powder diffraction patterns ($\lambda = 1.54056 \text{ Å}$).
3.3 Characterisation by Diffraction Techniques

“I suppose it is tempting, if the only tool you have is a hammer, to treat every problem as if it were a nail.”

Abraham Maslow (The Psychology of Science, 1966)

3.3.1 X-ray Single Crystal Diffraction
The X-ray Single Crystal Diffraction (XRSCD) experiment was performed on a single crystal mounted on a cactus spine with epoxy glue in a Bruker D8 single crystal diffractometer using MoK$_\alpha$ radiation and a Charged-Coupled Device (CCD) detector (figure 3.4a).

3.3.2 X-ray Powder Diffraction
Most X-ray Powder Diffraction (XRPD) experiments were performed on either of two Bruker D8 Advance diffractometers: one using monochromatic CuK$_\alpha_1$ radiation and a Vântec position sensitive detector and the other using CuK$_\alpha$ radiation and an energy dispersive Lynxeye XE detector; both diffractometers were in the Bragg-Brentano set-up$^4$ (figure 3.4c). Powdered samples were applied to a flat single-crystal silicon wafer$^5$ either by dusting powder trough a very fine sieve or by dispersing the powder in ethanol which was evaporated on the wafer.

In-situ X-ray Powder Diffraction
All in-situ Powder X-ray Diffraction (in-situ XRPD) experiments were performed at the I711 beam-line [37] on the MAXII synchrotron of the MAXIV laboratory in Lund, Sweden. The diffraction patterns were recorded in the Debye-Scherrer set-up$^6$ on a large area Titan or Mar165 CCD detector, using a sample cell designed to withstand high pressures and temperatures [38] (figure 3.4b). Sample–detector distances and wavelengths were determined using LaB$_6$ (in many cases NIST660b [39]).

The short wavelength ($\lambda \approx 1$ Å), large detector area and short sample–detector distance allowed measurements of rather short d-values without moving the detector; this combined with the high X-ray flux provided by the synchrotron allowed for very short exposure times (1-30 s) for each diffractogram. The recorded 2-dimensional images were reduced to 1-dimensional diffractograms by integrating the intensities in the Fit2D program[40].

$^4$ i.e. the incident angle and detector angle are identical.

$^5$ oriented in such a way as to produce no diffraction pattern

$^6$ i.e. transmission geometry.
Powdered samples were placed in fused silica capillaries\textsuperscript{7} with inner diameters of 0.5 mm. The capillaries were placed in single-crystal sapphire tubes\textsuperscript{8} which were mounted into the sample holder using graphite ferules. After flushing the system with Ar three times and leak checking, the samples were subjected to different H$_2$ pressures (<15 MPa) or dynamic vacuum at temperatures ranging from 303 to 823 K.

### 3.3.3 Neutron Powder Diffraction

The Neutron Powder Diffraction (NPD) experiments were performed using monochromatic neutron radiation on powdered samples in vanadium tubes on the MEREDIT instrument \textsuperscript{[41]} at the Nuclear Physics Institute in Rez, Czech Republic using $\lambda=1.46$ Å radiation or on the PUS diffractometer \textsuperscript{[42]} at the Institute for Energy technology in Kjeller, Norway using $\lambda=1.55$ Å radiation (figure 3.4d).

\textsuperscript{7}to reduce absorption

\textsuperscript{8}oriented in such a way as to produce no diffraction pattern
3.3.4 Determination of Lattice Parameters

The lattice parameters of a crystalline phase can be determined from a powder diffraction pattern if the Bravais lattice is known. This is done by a least squares fit of expected peak positions from Bragg’s law\(^9\) to the observed peak positions. The lattice parameters determined in this manner presented in this thesis were obtained using the UnitCell [43] and CHECKCELL [44] programs.

3.3.5 Full Pattern Refinement Using the Rietveld Method

Full pattern refinement is a powerful technique to determine the crystal structure of a crystalline material that is approximately known or the phase content of a sample from powder data. In this technique a calculated pattern is refined to fit the experimental diffractogram by changing structural and profile parameters using the least squares method. The technique was developed and first used by H. M. Rietveld [45] and is commonly called Rietveld refinement.

Ideally, diffraction peaks should be located at angles \(2\theta\) determined by Bragg’s law\(^9\); however, this angle is affected by a number of instrumental imperfections such as absorption and sample displacement. The integrated intensity \((I_{hkl})\) of a peak depends on the structure factor\(^{10}\) \((F_{hkl})\), but also a number of other parameters and is calculated as:

\[
I_{hkl} = K p_{hkl} L_\theta P_\theta A_\theta T_{hkl} E_{hkl} |F_{hkl}|^2
\]

where \(K\) is a constant known as the scale factor which roughly accounts for the amount of compound, measurement time and incident radiation flux; \(p_{hkl}\) is the multiplicity of the specific reflection; \(L_\theta, P_\theta\) and \(A_\theta\) are multipliers which take the geometry of the experiment, partial polarisation of the electromagnetic wave and absorption of incidence and diffracted beam as well as porosity into account; \(T_{hkl}\) is the preferred orientation factor and \(E_{hkl}\) in an extinction multiplier (which is usually not important for small crystals).

The peak shape is often calculated as a linear interpolation of a Gaussian and Lorentzian peak function, called a pseudo Voigt peak function, where the Full Width at Half Maximum (FWHM) depends on \(\theta\):

\[
FWHM = \sqrt{U tan^2 \theta + V tan \theta + W}
\]

where \(U, V\) and \(W\) are constants.

The structural determinations and phase analyses done in the work presented in this thesis were performed with the FullProf [46] or JANA2006 [47] programs. Interstitial D atoms were located by combining NPD and XRPD data using Fourier difference maps in JANA2006. Standard deviations are given in parenthesis after all determined values.

\(^9\) equation 3.1, page 25
\(^{10}\) equation 3.2, page 26
3.4 Thermodynamic and Kinetic Behaviour of Metal Hydrides

The thermodynamic and kinetic properties of a metal hydride are crucial for most applications. Methods for determining the heat of formation and activation energies of hydrogen desorption are described below.

3.4.1 Thermodynamics of Metal Hydrides

In a first order phase transition where hydrogen dissociates from a metal hydride:

\[
\frac{1}{x}MH_x(s) \rightleftharpoons \frac{1}{x}M(s) + \frac{1}{2}H_2(g)
\]  

(3.5)

the equilibrium constant is calculated as\(^\text{11}\):

\[
K = \frac{\{M(s)\}^{\frac{x}{2}} \{H_2(g)\}^{\frac{1}{2}}}{\{MH(s)\}^{\frac{1}{2}}} \approx \frac{\frac{1}{2} \cdot (P_{H_2\text{dis}}/P^\circ)^{\frac{1}{2}}}{1^{\frac{x}{2}}} = (P_{H_2\text{dis}}/P^\circ)^{\frac{1}{2}}
\]  

(3.6)

where \(P^\circ=1\) bar=0.1 MPa. If \(K\) is inserted into the van ’t Hoff equation a relationship between the heat of formation, \(\Delta H^\circ\) and the equilibrium pressure is obtained:

\[
\ln K = \frac{1}{2} \ln(P_{H_2\text{dis}}/P^\circ) = \frac{\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R}
\]  

(3.7)

where \(R\) is the ideal gas constant and \(T\) is the temperature. The entropy of formation \(\Delta S^\circ\) is almost constant for all metal hydrides and depends mostly of the entropy loss in the transition from gas to solid phase. Equation 3.7 predicts that the phase transition will take place at a specific pressure for each temperature. In a solid solution of hydrogen in metal on the other hand, the metal hydride is not a pure solid and its activity is not equal to unity; therefore, the pressure at which a certain amount of hydrogen is desorbed is dependent on both hydrogen concentration and temperature.

In a real metal hydride both behaviours are often observed. When the partial \(H_2\) pressure is increased at a fixed temperature, hydrogen is first dissolved in the metal (called the \(\alpha\) phase) where the concentration will be a function of pressure; at some pressure a phase transition to a more ordered hydride phase (the \(\beta\) phase) occurs which leads to a large increase in hydrogen concentration without a large change in pressure, \(i.e.\) a plateau (figure 3.5). Just as in the \(\alpha\) phase more hydrogen can be dissolved in the \(\beta\) phase, and the concentration will be a function of pressure. If a continual phase transition from \(\alpha\) to \(\beta\) phase is structurally possible a first order phase transition may occur above a critical temperature (\(T_c\)).

\(^{11}\) Using the definition that the activity of a pure solid is unity and assuming that hydrogen is an ideal gas.
**Figure 3.5.** Pressure-Composition-Temperature (PCT) diagram for a system containing the solid solution $\alpha$ phase and ordered hydride $\beta$ phase. $T_1<T_2<T_3<T_c$.

**Pressure Composition Temperature Measurements**

By measuring a series of Pressure Composition Temperature (PCT) curves at different temperatures, $\Delta H^\circ$ of a hydride can be determined by plotting equilibrium pressures of the plateaus against the temperatures in a van ‘t Hoff plot (equation 3.7). This value is not only important to solid gas applications but also for electrochemical systems, *e.g.* batteries, since the standard potential depends on $\Delta H^\circ$.

The PCT curves presented in this thesis were measured using a Setaram PCTPro–2000 automatic Sieverts apparatus (figure 3.6a). The sample was placed in a stainless steel autoclave and heated to a fixed temperature and the $H_2(g)$ pressure was stepwise increased by filling a large or small reservoir and then opening a set of valves to the sample. After equilibration the amount of hydrogen absorbed was calculated by the drop in pressure and the equilibrium pressure was noted. The samples were activated by cycling a number of times before the PCT curves were recorded.

**Predicting the Stability of a Hydride**

A number of factors have been suggested to correlate with and/or determine the stabilities of metal hydrides [48]: the size of interstitial voids [49], the unit cell volume [24], the difference between $\Delta H$ of the inter-metallic compound and the binary hydrides of the metals that it consists of [50] and the difference between the Fermi energy and the centre of the lowest band of the host metal [51]. It should be noted that the number of valence electrons, hydrogen affinity and atomic radii are correlated. With the ever increasing computational power available, and therefore decreasing cost of calculations, computational methods such as Density Functional Theory (DFT) are more and more viable and seems to yield reasonable predictions for a number of hydrides [52].
3.4.2 Kinetics

The Kissinger equation [53], originally developed for differential thermal analysis, can be used to determine the activation energy ($E_a$) of a reaction. It is obtained from the Arrhenius equation and the rate equation:

\[
k(T) = Ae^{-E_a/RT} \text{ and } \frac{dx}{dt} = k(t)f(x)
\]  

(3.8)

where $k(T)$ is the rate constant, $A$ the pre-exponent factor, $R$ the ideal gas constant, $T$ the temperature, $t$ time and $f(x)$ a function of the amount of reactant $x$ (which describes the kinetic model). The combination of the two equations yields the general rate equation:

\[
\frac{dx}{dt} = Af(x)e^{-E_a/RT} \text{ or } f(x) = \frac{dx}{dt}A^{-1}e^{E_a/RT}
\]  

(3.9)

differentiating the function by time yields:

\[
\frac{d^2x}{dt^2} = e^{-E_a/RT} \left( \frac{df(x)}{dx} \frac{dx}{dt} + f(x) \frac{E}{RT^2} \frac{dT}{dt} \right)
\]  

(3.10)

inserting $f(x)$ from equation 3.9 yields:

\[
\frac{d^2x}{dt^2} = e^{-E_a/RT} \frac{dx}{dt} \left( \frac{df(x)}{dx} + e^{E_a/RT} \frac{E}{ART^2} \frac{dT}{dt} \right)
\]  

(3.11)
If the temperature is increased linearly ($\frac{dT}{dt} = \beta$) then, at some temperature $T_{\text{max}}$, the maximum reaction rate will be reached, which implies $\frac{dx}{dt} = 0$:

$$0 = \frac{df(x_{\text{max}})}{dx} + e^{E_a/RT_{\text{max}} \frac{\beta}{AR T_{\text{max}}^2}}$$

Finally taking the natural logarithm of the result yields the general Kissinger equation\[54]\:

$$\ln\left(\frac{\beta}{T_{\text{max}}^2}\right) = \ln\left(\frac{df(x_{\text{max}})}{dx}\right) + \ln\left(\frac{AR}{E_a}\right) - E_a \cdot (RT_{\text{max}})^{-1}$$

If $\ln\left(\frac{df(x_{\text{max}})}{dx}\right)$ is assumed to be independent of $(RT_{\text{max}})^{-1}$ (or rather $\beta$), which is a good approximation in many cases\[12\], $E_a$ can be obtained by determining the $T_{\text{max}}$ at a number of $\beta$ and doing a linear regression of $\ln\left(\frac{\beta}{T_{\text{max}}^2}\right)$ and $-(RT_{\text{max}})^{-1}$.

Thermal Desorption Spectroscopy (TDS) is a method used to study the desorption of a volatile compound from a material during heating where the partial pressure of the desorbed species is monitored by a mass-spectrometer. If the sample is heated linearly and the maximum partial pressure is assumed to indicate the maximal reaction rate a series of TDS measurements may be used to determine $E_a$ via the Kissinger equation.

The TDS data presented in this thesis were obtained by linear heating samples placed in a stainless steel sample holder in high vacuum (figure 3.6a). The sample temperature was monitored by a thermocouple in close proximity to the sample holder and the partial pressure of H$_2$ (or D$_2$) was monitored using a Microvision Plus residual gas analyser/mass spectrometer.

### 3.4.3 Density Functional Theory

Density Functional Theory (DFT) is a theoretical method that can be used to calculate properties of a material using quantum physics, independent of experimental results. These properties could be obtained by solving the many electron time independent Shrödinger equation directly; however, every electron added to the system adds four dimensions to the problem, so a system with many atoms is very computationally expensive. In DFT the electrons are replaced by an electron density dependent on three coordinates, the location in physical space.

DFT in this pure form approximates the nuclear–electron interactions well but is not as good at, for example, approximating electron–electron interactions; a number of corrections are used to compensate for these shortcomings. The DFT data presented in this thesis were calculated using The Vienna

\[12\] but not for e.g. Avrami-Erofev and diffusion kinetics[54]
Ab initio Simulation Package [55] and the Perdew–Burke–Ernzerhof approach [56] was used to compensate for the approximations.
4. Results and Discussion

“Chemists are always right, but for the wrong reasons.”

Olle Eriksson

The results presented in this thesis are divided into four parts: hydrides of Laves phases containing Sc (papers I, II and III), MgH$_2$ mixed with ScH$_2$ (paper IV), Nb$_4$MSi (M=Ni, Co) hydrides (paper V) and NdGa and GdGa hydrides (paper VI) (figure 4.1). In addition there is a fifth part dealing with the attempted synthesises of Ti–Zr–Ni–Co quasicrystal approximants.

![Figure 4.1. The crystal structures of the hydrides or hydride forming compounds studied in this thesis. First row: A hexagonal Laves phase and a cubic Laves phase. Second row: MgH$_2$, Nb$_4$MSi and NdGaD$_{1.51}$.](image-url)
4.1 Laves Phases Containing Sc

Papers I, II and III concern Laves phases containing Sc. Laves phase, or AB$_2$-type, compounds can be used in Ni–MH batteries and as hydrogen storage materials. Paper I and II deals with the hexagonal Laves phase formed in the Sc(Al$_{1-x}$Ni$_x$)$_2$ system and Paper III concerns the cubic Laves phase (Sc$_{1-x}$Zr$_x$(Co$_{1-y}$Ni$_y$)$_2$) system. Both of these systems are pseudo binary, where Sc and Zr act as the larger A atom and Co, Ni and Al act as the smaller B atom. Although Sc may not be a viable raw material for most applications (because of its high cost) it is interesting from a fundamental point of view, since it is the lightest d-block metal as well as the lightest and smallest rare earth metal. The structural relationship between the hexagonal and cubic Laves phases is discussed in the introduction on page 16.

4.1.1 The Hexagonal Laves Phase Sc(Al$_{1-x}$Ni$_x$)$_2$

**Phase Analysis and Structure Determination**

A hexagonal Laves phase with the MgZn$_2$-type structure was observed in as cast Sc(Al$_{1-x}$Ni$_x$)$_2$ samples while $0.25 \leq x \leq 0.75$ and single phase samples were obtained when $0.36 \leq x \leq 0.65$ (figure 4.2 and 4.3a). At the extremes $x=0.00$ and $0.90 \leq x \leq 1.00$ the samples contained only a cubic Laves phase.

A linear decrease in lattice parameters was observed as a function of $x$ (*i.e.* Ni content) which is not surprising since the Al atom is much larger than the Ni atom[19] (table 4.1 and figure 4.3b and c); the fact that lattice parameters kept changing even at compositions where multiphase samples were obtained suggested that the hexagonal Laves phase had a larger homogeneity area at elevated temperatures. Structure determination using XRSCD and NPD confirmed that Sc(Al$_{0.50}$Ni$_{0.50}$)$_2$ crystallises in the MgZn$_2$-type structure where Ni and Al are close to randomly distributed between the two B sites available in the structure.

**Interstitial Hydrogen Absorption**

Lattice expansion was seen when samples with $0.36 \leq x \leq 0.67$ were hydrogenated at 573 K under 2 MPa H$_2$ pressure and the change in lattice parameters was larger the higher the Ni content (table 4.1). Piesl [57] found that the expansion of the unit cell volume as a function of hydrogen content was surprisingly constant for many metals (∼2.9 Å$^3$/H atom). Using this relationship the stoichiometry of the interstitial hydrides was approximated to vary from Sc(Al$_{0.64}$Ni$_{0.36}$)$_2$H$_0$ to Sc(Al$_{0.33}$Ni$_{0.67}$)$_2$H$_{0.76}$ (table 4.1).

Determination of the structure of Sc(Al$_{0.33}$Ni$_{0.67}$)$_2$D$_{0.39}$ from NPD data revealed that the compound absorbs deuterium into interstitial tetrahedral A$_2$B$_2$ sites (*i.e.* coordinated by two Sc and two Ni/Al atoms). A series of PCT measurements determined that the maximal storage capacity of Sc(Al$_{0.33}$Ni$_{0.67}$)$_2$ was 1.95 H/(form. unit) at 353 K.
Figure 4.2. XRPD patterns of as-cast Sc(Al$_{x-1}$Ni$_x$)$_2$-samples. Expected peak positions of the hexagonal Laves phase is marked with vertical bars.
Table 4.1. Lattice parameters of the hexagonal Laves phase of the Sc(Al$_{1-x}$Ni$_x$)$_2$ system and their interstitial hydrides with hydrogen content approximated from unit cell volume expansion.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a/Å</th>
<th>c/Å</th>
<th>a$_{hyd}$/Å</th>
<th>c$_{hyd}$/Å</th>
<th>H/form. unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(Al$<em>{0.25}$Ni$</em>{0.75}$)$_2$</td>
<td>5.0809(3)</td>
<td>7.8605(7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sc(Al$<em>{0.30}$Ni$</em>{0.70}$)$_2$</td>
<td>5.0728(2)</td>
<td>8.0268(5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sc(Al$<em>{0.33}$Ni$</em>{0.67}$)$_2$</td>
<td>5.0838(2)</td>
<td>8.0032(7)</td>
<td>5.1613(5)</td>
<td>8.1471(7)</td>
<td>0.76</td>
</tr>
<tr>
<td>Sc(Al$<em>{0.35}$Ni$</em>{0.65}$)$_2$</td>
<td>5.0943(2)</td>
<td>8.0288(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sc(Al$<em>{0.40}$Ni$</em>{0.60}$)$_2$</td>
<td>5.1171(5)</td>
<td>8.067(1)</td>
<td>5.1487(2)</td>
<td>8.1679(4)</td>
<td>0.4</td>
</tr>
<tr>
<td>Sc(Al$<em>{0.50}$Ni$</em>{0.50}$)$_2$</td>
<td>5.1434(1)</td>
<td>8.1821(2)</td>
<td>5.1695(2)</td>
<td>8.3000(6)</td>
<td>0.4</td>
</tr>
<tr>
<td>Sc(Al$<em>{0.60}$Ni$</em>{0.40}$)$_2$</td>
<td>5.1749(3)</td>
<td>8.309(1)</td>
<td>5.1783(3)</td>
<td>8.3459(5)</td>
<td>0.1</td>
</tr>
<tr>
<td>Sc(Al$<em>{0.64}$Ni$</em>{0.36}$)$_2$</td>
<td>5.1908(9)</td>
<td>8.3629(1)</td>
<td>5.1859(4)</td>
<td>8.3558(6)</td>
<td>(-0.05)</td>
</tr>
<tr>
<td>Sc(Al$<em>{0.69}$Ni$</em>{0.31}$)$_2$</td>
<td>5.2051(4)</td>
<td>8.4039(9)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sc(Al$<em>{0.75}$Ni$</em>{0.25}$)$_2$</td>
<td>5.2324(3)</td>
<td>8.5262(8)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Structural Reason for Maximal Interstitial Storage Capacity

The decreasing amount of hydrogen absorbed as a function of Al content is probably caused by Al blocking interstitial sites, since H atoms avoid occupying voids in close proximity to p-block elements [58]. Supposing a random Al/Ni distribution the likelihood that none of the B sites is occupied by an Al atom decreases with Al content in a given A$_2$B$_2$ site, e.g. it is 42% when x=0.65, 25% at x=0.5, and 13% at x=0.65.

Interstitial Hydrogen Cycling and Desorption

In-situ XRPD experiments showed that there was a continuous unit cell volume expansion and contraction when Sc(Al$_{0.50}$Ni$_{0.50}$)$_2$ was cycled between dynamic vacuum and 50 MPa H$_2$(g) at 453 K; the hydrogenation/dehydrogenation process was reversible over multiple cycles. The gradual change of the unit cell volume suggests that a solid solution rather than a second order phase transition occurs.

Desorption curves obtained from TDS of the interstitial Sc(Al$_{0.33}$Ni$_{0.67}$)$_2$H$_x$ show one distinct bell-shaped peak (figure 4.4a). Kissinger analysis (figure 4.4b) of the desorption data gives $E_a = 51.7$ kJ mol$^{-1}$ which is close to that of other interstitial hydrides such as LaNi$_5$ which has $E_a = 40$ kJ mol$^{-1}$ [59].

Decomposition to ScH$_2$ and NiAl

Both ex- and in-situ PXRD experiments showed that Sc(Al$_{0.50}$Ni$_{0.50}$)$_2$ decomposes according to:

$$
Sc(Al_{0.50}Ni_{0.50})_2 + H_2 \rightleftharpoons ScH_2 + NiAl
$$

1 or any other type of void since there are no interstitial sites surrounded by only A atoms in the Laves phase structures.

2 $E_a$ is incorrectly calculated as 4.6 kJ mol$^{-1}$ in paper II.
Figure 4.3. a) Composition map for Sc–Al–Ni with reported phases marked as large open circles, synthesised single phase samples marked with filled circles and multi-phase samples marked as half-filled circles. b) Lattice parameter $a$ of the hexagonal Laves phase as a function of composition. c) Lattice parameter $c$ of the hexagonal Laves phase as a function of composition.
Figure 4.4. Result of TDS of Sc(Al_{0.33}Ni_{0.67})_2H_x. a) Partial pressure of H_2 as a function of temperature for a number of ramp rates (β). Peaks are shifted towards higher temperature with higher β. b) E_a calculated using the Kissinger equation.

when heated to 823 K under 5 MPa H_2 pressure (figure 4.5). The peaks of the ScH_2 and NiAl phases (with CaF_2-type and CsCl-type structure respectively) were much broader than those of the mother compound (indicating a much smaller average size of, and/or strain in, the crystals); TDS of the resulting ScH_2+NiAl sample showed one large and one small bell-shaped peak; Kissinger analysis of the larger peak gave an activation energy of 182 kJ mol^{-1}. Sc(Al_{0.50}Ni_{0.50})_2 was reformed indicating that this reaction may be reversible over multiple cycles.

Figure 4.5. Densitometric view of diffractograms recorded in situ during heating of Sc(Al_{0.50}Ni_{0.50})_2 under 5 MPa H_2 pressure. The white line at ~scan 120 is caused by missing scans.
4.1.2 The Cubic Laves Phase \((\text{Sc}_{1-x}\text{Zr}_x)(\text{Co}_{1-y}\text{Ni}_y)_2\)

**Phase analysis**

All \((\text{Sc}_{1-x}\text{Zr}_x)(\text{Co}_{1-y}\text{Ni}_y)_2\) samples contained a cubic Laves phase and most samples were single phase (figure 4.6). The two samples, \(\text{Sc}_{0.75}\text{Zr}_{0.25}\text{CoNi}\) and \(\text{ScNi}_2\), which were not completely phase pure, contained small amounts of a phase with the CsCl-type structure. Lattice parameters increased with increasing Zr content while the samples without Zr had very similarly sized unit cells (table 4.2 and figure 4.7); these lattice parameters were in good agreement the ones reported in the literature [60, 61].

**Absorption and Desorption of Interstitial Hydrogen**

Multiple cycles of interstitial hydrogen absorption and desorption were observed for all samples with a Zr content equal to or less than \(\text{Sc}_{0.50}\text{Zr}_{0.50}\text{CoNi}\), when cycled at 303 or 333 K under 15 MPa \(\text{H}_2\)/dynamic vacuum monitored using *in-situ* XRPD (figure 4.8a). A gradual shift of peak positions of the pristine materials, followed by a decrease in peak intensities at the expense of a growing hydride phase during hydrogen absorption indicated a solid solution of hydrogen in the \(\alpha\)-phase followed by a phase transition to the \(\beta\) phase. During desorption this process was reversed.

The amount of absorbed hydrogen, approximated from unit cell expansion using Peisl’s relationship [57], increased as a function of the Co and Sc content (table 4.2). For the samples without Zr this is in good agreement with the results of Yoshida and Akiba [62] who reported a maximum storage capacity of 1.03 H/M for \(\text{ScCo}_2\) (\(\Delta H=30\) kJ mol\(^{-1}\)) and 0.65 H/M for \(\text{ScNi}_2\) (\(\Delta H=16\) kJ mol\(^{-1}\)) under 4MPa \(\text{H}_2\) pressure at 313 K. There is, to my knowledge, no literature data to compare the Zr containing samples to; however, hydrogen only forms a solid solution up to 0.4 H/M with \(\text{ZrCo}_2\) even under the extreme \(\text{H}_2\) pressure of 80 MPa at 298 K![63] It is reasonable to assume that the hy-

**Table 4.2.** Lattice parameters determined from *ex- and in-situ* PXRD and ab-initio calculations of the \((\text{Sc}_{1-x}\text{Zr}_x)(\text{Co}_{1-y}\text{Ni}_y)_2\) cubic Laves phases and their hydrides. Hydrogen content per metal atom was approximated using Peisl’s relationship [57] and, in parenthesis, estimated expansion from DFT.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(a_{\text{ex-in situ}}/\text{Å})</th>
<th>(a_{\text{calc.}}/\text{Å})</th>
<th>(a_{\text{in situ}}/\text{Å})</th>
<th>(a_{\text{hyd in situ}}/\text{Å})</th>
<th>H/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{ZrCoNi})</td>
<td>6.9550(1)</td>
<td>6.90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Sc}<em>{0.25}\text{Zr}</em>{0.75}\text{CoNi})</td>
<td>6.9479(5)</td>
<td>6.89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Sc}<em>{0.50}\text{Zr}</em>{0.50}\text{CoNi})</td>
<td>6.9400(3)</td>
<td>6.88</td>
<td>6.9388(2)</td>
<td>7.1983(4)</td>
<td>0.56 (0.60)</td>
</tr>
<tr>
<td>(\text{Sc}<em>{0.75}\text{Zr}</em>{0.25}\text{CoNi})</td>
<td>6.9364(3)</td>
<td>6.87</td>
<td>6.9371(3)</td>
<td>7.2795(4)</td>
<td>0.75 (0.80)</td>
</tr>
<tr>
<td>(\text{ScNi}_2)</td>
<td>6.9213(2)</td>
<td>6.88</td>
<td>6.9185(7)</td>
<td>7.2660(6)</td>
<td>0.75 (0.93)</td>
</tr>
<tr>
<td>(\text{ScCoNi})</td>
<td>6.9263(2)</td>
<td>6.86</td>
<td>6.9257(4)</td>
<td>7.3036(4)</td>
<td>0.82 (1.01)</td>
</tr>
<tr>
<td>(\text{ScCo}_2)</td>
<td>6.9276(2)</td>
<td>6.82</td>
<td>6.9260(5)</td>
<td>7.378(1)</td>
<td>1.00 (1.23)</td>
</tr>
</tbody>
</table>
Figure 4.6. Experimental (red dots) and calculated (black lines) diffraction patterns of the (Sc$_{1-x}$Zr$_x$)(Co$_{1-y}$Ni$_y$)$_2$-samples and their corresponding difference curves (blue lines). Expected peak positions are indicated as vertical bars.
Figure 4.7. Values for lattice parameter a in \((\text{Sc}_{1-x} \text{Zr}_x)(\text{Co}_{1-y} \text{Ni}_y)\) as a function composition, determined from XRPD (red squares) and calculated using DFT (black dots). Lines are added as aid to the eye. a) As a function of x (i.e amount of Zr). b) As a function of y (i.e amount of Ni).

Figure 4.8. a) Densitometric view diffraction patterns recorded in situ as hydrogen is cycled in and out of \(\text{Sc}_{0.50} \text{Zr}_{0.50} \text{CoNi}\). The change in \(\text{H}_2\) pressure from 15 MPa to dynamic vacuum, or vice-versa, caused an almost instant shift of the peaks indicating hydrogen absorption/desorption. b) wt% of the \(\alpha\) (green line) and \(\beta\) phase (black line) obtained from sequential refinement of the in-situ diffractograms.
dride of ZrCoNi is very unstable\textsuperscript{3}. A gradual decrease in hydride stabilities from ScCoNi to ZrCoNi is a plausible explanation for the reduction in hydrogen absorption between the two compositions.

Sequential refinement made it possible to follow the amount of the $\alpha$ and $\beta$ phases as a function of time (figure 4.8b); even though no kinetic parameters were extracted from these data it was clear that the samples containing Zr had much higher reaction rates\textsuperscript{4}, especially during desorption. A possible explanation for this is that Zr has lower affinity for hydrogen than Sc [64] which could lead to faster diffusion.

*Comparison with Ab-initio Calculations*

The *ab-initio* calculations slightly underestimated the size of the unit cell (table 4.2 and figure 4.7); the difference was close to the thermal expansion from 0 to 300 K expected for Laves phases based on the linear expansion parameters calculated by Mayer et. al [65]. Additionally, the *ab-initio* calculations predicted that the unit cell volume would expand by $\sim$2.72 Å\textsuperscript{3}/H atom introduced into the unit cell for the compounds containing Zr and by $\sim$2.36 Å\textsuperscript{3}/H atom for the ones without. Using these expansions to calculate the amount of absorbed hydrogen yielded the same trends as using the 2.9 Å\textsuperscript{3}/H atom expansion (table 4.2).

\textsuperscript{3}If it behaves like the ScCo\textsubscript{2}/ScNi\textsubscript{2} system it is probably even slightly less stable than ZrCo\textsubscript{2}.

\textsuperscript{4}This is the reason why the samples without Zr were cycled at 333 K rather than 303 K.
4.2 Activation Effects in MgH₂ Mixed with ScH₂

As mentioned in the introduction (page 15) the low cost and high wt% of hydrogen in MgH₂ have made it very interesting for some applications, especially hydrogen storage. However, its thermodynamic stability, sensitivity to oxygen and slow kinetics present major obstacles to its use in these applications. One way to improve the kinetics is to add a catalyst to the material, another way is to reduce the grain size (e.g. by ball-milling the material); these methods are often combined. Paper IV concerns the activation effect during cycling of MgH₂ ball-milled together with the possible catalyst ScH₂ investigated by in-situ XRPD.

Phase Analysis
A sample prepared via ball-milling of MgH₂ and ScCl₃ formed MgCl₂ and ScH₂, while the ball-milled MgH₂ (90 mol%) and ScH₂ (10 mol%) showed no sign of reaction between the hydrides after milling. For this reason, the second ball milled mixture was selected for in-situ experiments.

In-situ Cycling
Multiple transitions between Mg and MgH₂ were observed using in-situ XRPD when three different MgH₂/ ScH₂ samples were cycled at 593 K, 673 K and 723 K between 10 MPa or 15 MPa H₂ and dynamic vacuum (figure 4.9a, b and c). No side reactions were observed except for formation of MgO.

Reaction Rates and Activation Effect
Sequential refinements using the Rietveld method yielded the wt% of the constituent phases which made it possible to follow the reactions as a function of scan number (or time). As expected the reaction rates (the slope at 50% conversion) increased with increasing temperature and cycle number; however, at 723 K the reactions were as fast as or faster than the exposure time of one diffractogram, this meant that the reaction rates could not be determined for this temperature. The activation effect was seen as a linear increase in relative reaction rate as a function of cycle number in the 593 K experiment, while the increase was only observed from the first to second cycle in the 673 K experiment (figure 4.9d). The results suggest that activation of the material takes multiple cycles at 593 K and 10 MPa but only one cycle at 673 K and 15 MPa.

Since the publication of Paper IV a thorough study by Luo et al. [16] on the effect of ScH₂ addition to MgH₂ has shown that these mixtures have a reduced activation energy compared to pure MgH₂. The best ball-milled ScH₂/MgH₂ mixture had a $E_a$ of dehydrogenation to just above half that of pure untreated MgH₂.
Figure 4.9. Densitometric view of the diffractograms recorded during hydrogenation/de-hydrogenation cycling of MgH$_2$ (90 mol%) and ScH$_2$ (10 mol%), between a high and a low H$_2$ pressure at isothermal conditions, and the relative reaction rates for each dehydrogenation. a) Cycling at 593 K with high pressure 10 MPa. b) Cycling at 673 K with high pressure 15 MPa. c) Cycling at 723 K with high pressure 15 MPa. d) Relative reaction rate $r/r_1$ compared to the first cycle for the desorption for at 593 K and 673 K as a function of cycle number.
4.3 $\text{Nb}_4\text{M}_{0.9}\text{Si}_{1.1}$ (M=Ni, Co) Hydrides

The structures of $\text{Nb}_4\text{MSi}$ (M=Fe, Ni or Co) were first reported by Gladuchevsky and Ku'zma [66] in 1965 and the deuterides of the Co and Ni variants by Vennström and Andersson [67] in 2004. Both studies agree on the structure type of the materials (Al$_2$Cu, figure 4.10) and on the location of the Nb atom (in the Al site); however, while the earlier study suggested that the M and Si atoms were ordered into two different sites, the latter found them randomly distributed between the two sites. The more recent study also found that H(D) atoms are located in two types of $\text{Nb}_4$-tetrahedral voids in the $\text{Nb}_4\text{MSi}$ deuterides. Paper V concerns the hydrides of $\text{Nb}_4\text{M}_{0.9}\text{Si}_{1.1}$ (M=Ni, Co).

Recently Ryu et al. [68] found that $\text{Nb}_4\text{MSi}$ (M=Fe, Ni or Co) are all superconducting below 6 K. In this paper it was also claimed that their samples consisted of two phases with ordered and disordered M/Si sites and that only the ordered phase was superconductive.

**Analysis of Hydride (Deuteride) Structure**

If the metal atoms are removed from the $\text{Nb}_4\text{MSiD}_x$ structure perpendicular hexagon “chains” of partially occupied D-atom sites appear (figure 4.10b); each hexagon is made up of five H sites: four sites of its own and two that connects it to (and shares with) the two adjacent hexagons. These sites are only partially occupied (about 1.3/5) with a much higher occupation of the interconnecting sites than the four other sites in the chain. Westlake[69, 48] found that a minimum hole radius of 0.4 Å and H–H distance of 2.1 Å can be used to predict site occupancy and maximum storage capacity in many interstitial metal hydrides. The shortest inter “chain” distance is 2.6 Å, so only distances in the “chains” need to be considered. Filling the two sites closest to one of the two linking sites in each hexagon (in the same direction) yields a shortest H–H distance of 2.3 Å and a stoichiometry of $\text{Nb}_4\text{MSiH}_4$. Filling the four sites surrounding every second linking site and every other linking site yields a shortest H–H distance of 2.1 Å and a stoichiometry of $\text{Nb}_4\text{MSiH}_6$. The hole radii, calculated as the shortest Nb-hole distance minus the shortest Nb-Nb distance, is at least 0.48Å for both types of sites.

As previously mentioned hydrogen avoids sites close to $p$-block elements in interstitial hydrides.[58] The interconnecting H site in the hexagons is surrounded by four equidistant M/Si sites. The non-interconnecting H sites have two M/Si sites at about the same distance as the interconnecting H site but two M/Si sites $\sim 0.5$ Å closer than that (figure 4.10c and d). The blocking effect of the $p$-block elements would mean that none of the non-interconnecting sites could be occupied if the M/Si sites were ordered, since one of the two closest M/Si sites would always be occupied by a Si atom. Assuming a random distribution of M and Si atoms between the two sites 25% of these sites would be available for hydrogen occupation.
Figure 4.10. The structure of Nb$_4$MSi and some structural details. Nb is shown as light grey spheres and M/Si as dark grey spheres. D atom sites are shown as white spheres with the interconnecting sites marked with an x. a) The Nb$_4$MSi with the coordination polyhedra of the two D sites shown with green lines. b) “Chains” of D atom sites filled with blue D atoms in two ways. c) The four closest M/Si sites to the interconnecting site d) The four closest M/Si sites to the non-interconnecting sites in the hexagons.
Phase Analysis

The Nb4Ni0.9Si1.1 and Nb4Co0.9Si1.1 samples contained a majority phase with the CuAl2-type structure and disordered M/Si sites after heat-treatment (figure 4.11). No phase with ordered M/Si positions was observed in any of the samples produced, even though a number of compositions, heat treatment temperatures and times, with and without quenching, were performed. Further investigation of the superconductivity of the hydrides of Nb4MSi suggest that some Nb4MSi samples were composed of two Nb4MSi phases but both had disordered M/Si sites.[70]

In addition to the aforementioned Nb4MSi phase a few faint peaks were found in the sample indicating the presence of other phases. The strongest extra peaks in the Nb4Ni0.9Si1.1 sample could be explained by a phase with W-type structure. The unit cell volume was slightly smaller than that of pure Nb suggesting that it was a Nb-rich alloy with Si and/or Ni.

Kinetics

TDS showed two distinct desorption peaks for some ramp rates (β) for the Nb4Ni0.9Si1.1Hx sample and all β for the Nb4Co0.9Si1.1Hx sample (figure 4.12a). The rather noisy signal complicated the Kissinger analysis, which had low R^2 values, which gave E_a=79 kJ mol\(^{-1}\) for Nb4Ni0.9Si1.1Hx and 94 and 170 kJ mol\(^{-1}\) for Nb4Co0.9Si1.1Hx (figure 4.12b).

Slow diffusion caused by the high affinity for hydrogen of Nb and the “chains” of available H sites may explain the slow kinetics in both samples. However, the assumption that the kinetic model can be ignored in Kissinger analysis does not work well for diffusion kinetics [54] and the apparent E_a...
Figure 4.12.  a) TDS curves for desorption of Nb₄Ni₀.₉Si₁.₁Hₓ (black squares) and Nb₄Co₀.₉Si₁.₁Hₓ (white circles) β ≈ 0.04 K s⁻¹. b) Kissinger analysis to determine activation energies.

Figure 4.13. PCT curves for Nb₄M₀.₉Si₁.₁ (M=Co, Ni) samples.
may be underestimated. The overlapping nature and “noisyness” of the peaks made it impossible to determine the correct kinetic model for this system.

*Thermodynamics*

Regardless of the correct values of $E_a$, absorption and desorption of hydrogen in the $\text{Nb}_4\text{M}_{0.9}\text{Si}_{1.1}$ samples were very slow which complicated the PCT-measurements (figure 4.13). Even after a few cycles the equilibration at each point was very slow; the equilibration time was fixed to 10 h so the curves were only reliable at elevated temperatures. Even though $\Delta H$ could not be extracted from this data it was clear that the hydrides were very stable and the close to linear appearance of the PCT curves at 573 K suggest that this temperature is above $T_c$. 
4.4 Hydrogen Absorption in LnGa (Ln=Gd, Nd)

Most REGa-compounds (where RE is a rare earth element) form typical Zintl phases with the CrB-type structure.[71, 72] The active metals are present as tetrahedra of RE$^{3+}$ ions and the more electronegative Ga forms poly-anionic chains of Ga$^{3-}$-species (figure 4.14a). Hydrogen could potentially be introduced into this structure in two ways (page 17) [28]: either as interstitial hydride ions (H$^{-}$) in RE$^{3+}$ tetrahedra causing the oxidation of the poly-anion or by covalent bonding to the Ga chains, forming a new poly-anion.

The REGa compounds order magnetically at low temperatures and could potentially be used in magnetic refrigeration.[73] The magnetic properties of their hydrides have not been investigated and knowing the structure and the nature of M–H bonds in these compounds could help in understanding their magnetic properties. Paper VI concerns the structures and hydrogen sorption properties of the hydrides of LnGa (Ln=Gd, Nd), especially the nature of the M–H bonds.

**Determination of the Structure of a NdGa Deuteride**

The structure of NdGaD$_{1.51}^5$ was determined from PXRD and PND patterns of a deuterated NdGa-sample (figure 4.14b, figure 4.15 and table 4.3). D atoms were found in two tetrahedral sites: one fully occupied Nd$_4$ site and one just off the centre of a $\sim$1/4 occupied-Nd$_3$Ga site, with a Ga–D distance of 1.80 Å. The fractional coordinates of the metal atoms were about the same as in the non-deuterated material and the unit cell volume was also almost unaffected; however the a axis was significantly shortened and the c axis significantly elongated. In addition to the main NdGaD$_{1.51}$ phase the sample contained weak peaks identified as small amounts of the GaNd$_3$, GaNd$_2$ and NdD$_2$ phases.

**Desorption of D$_2$ from NdGaD$_{1.51}$**

TDS curves of the NdGaD$_{1.51}$ sample used in the structure determination showed two clear peaks indicating that hydrogen(deuterium) is desorbed in two discrete steps (figure 4.16a). Kissinger analysis gave E$_a$ of 115 kJ mol$^{-1}$ and

---

$^5$GdGaD$_x$ cannot be studied in this way because of the extreme neutron absorption of Gd.

**Table 4.3. Crystallographic data for NdGaD$_{1.51}$ at $\sim$298 K.**

<table>
<thead>
<tr>
<th>Space Group</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>V/Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cmcm</td>
<td>4.1093(3)</td>
<td>12.2531(9)</td>
<td>4.1644(3)</td>
<td>209.70(3)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wykoff pos.</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B/Å$^2$</th>
<th>occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>4c</td>
<td>0</td>
<td>0.0581(4)</td>
<td>1/4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Nd</td>
<td>4c</td>
<td>0</td>
<td>0.3465(2)</td>
<td>1/4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>D1</td>
<td>4c</td>
<td>1/2</td>
<td>0.2484(6)</td>
<td>1/4</td>
<td>2.3(1)</td>
<td>1</td>
</tr>
<tr>
<td>D2</td>
<td>8g</td>
<td>0.434(3)</td>
<td>0.041(1)</td>
<td>1/4</td>
<td>0.84(4)</td>
<td>0.26(1)</td>
</tr>
</tbody>
</table>
Figure 4.14. The structure of REGa and a REGa deuteride. a) REGa: RE ion are shown as blue spheres and Ga species as red spheres. The Ga chains are shown by black lines. b) NdGaD$_{1.51}$: deuteride ions are shown as large red spheres and the deuterium atoms as small white spheres.

156 kJ mol$^{-1}$ for the first and second peak respectively (figure 4.16b). Post-mortem PXRD showed that the NdGa phase had reformed after desorption suggesting that the compound can be cycled multiple times.

**Hydrogen Absorption of GdGa**

Two significant peak position shifts were observed using *in-situ* XRPD when GdGa was heated linearly to and cooled from 773 K under 2 MPa H$_2$ pressure (figure 4.17a); sequential refinement revealed that these shifts, the first (larger one) during heating and the second (smaller one) during cooling, were caused by contraction of the a axis and elongation of the c axis (figure 4.17a). Just as in the structure of NdGaD$_{1.51}$ the b axis and the unit cell volume were almost unaffected.

**Comparison with Results from DFT**

The inter-atomic distances of NdGaH and NdGaH$_2$ calculated using DFT were in good agreement with the experimental values for NdGaD$_{1.51}$. Hydrogen occupation of the tetrahedral Nd$_4$ voids was energetically favourable compared to the site closer to the Ga chain in NdGaH. The calculated NdGaH$_2$ structure was a slightly distorted version of the NdGaD$_{1.51}$ structure with all of the Nd$_3$Ga voids filled on one side of the Ga chain. Filling the tetrahedral Gd$_4$ void first and then the sites adjacent to the Ga chain to the composition GdGaH$_{1.66}$ reproduced the experimental results remarkably well (figure 4.17).
**Figure 4.15.** Diffractograms used to determine the structure of NdGaD$_{1.51}$. Experimental data are shown as red rings, the calculated pattern as a black line, the difference curve as a blue line and expected peak positions of identified phases vertical bars. 

a) XRPD pattern. b) NPD pattern.

**Figure 4.16.** a) TDS curves of NdGaD$_{1.51}$ for a number of ramp rates ($\beta$). Increasing $\beta$ shifted peaks to higher temperatures. b) Kissinger analysis of the two peaks.
Figure 4.17. a) Densitometric view of the in-situ PXRD patterns recorded during heating and cooling of a GdGa sample under 2 MPa H$_2$ pressure. b) Relative change in lattice parameters as a function of time is shown as red lines. Calculated changes from first filling the Gd$_4$-tetrahedral site and then the site adjacent to the Ga chains is shown as dashed lines.
Analysis of the Structure of and Bonding in LnGaH$_x$

Results for both GdGa and NdGa indicate that hydrogen will first occupy the Ln$_4$ site and then the Ln$_3$Ga site. The first step can easily be explained by the current understanding of Zintl-phase hydrides. Hydride ions go into the Ln$_4$ voids, their formal charge requires that the Ga chain is oxidised from Ga$^{3-}$ to Ga$^{2-}$ to keep charge neutrality; this could be accomplished by the formation of a $\pi$-bond along the chain. A possible second step would be the formation of a covalent bond to the H atom in the Ln$_3$Ga site, the Ga–D distance (1.80 Å) in NdGaD$_{1.51}$ is a bit longer than the covalent Nd–D bonds reported in the literature [74, 75]. The value of the electronic localisation function obtained from DFT between Ga and H in NdGaH$_2$ was $\sim$0.37 suggesting a weak covalent interaction. The nature of Ga–H interaction in the second step of hydrogenation is thus not yet known and requires further investigations.
4.5 Ti–Zr–Ni–Co approximants

The quasicrystals and approximants in the Ti–Zr–Ni system have been shown to absorb and desorb large amounts of hydrogen interstitially.\cite{76, 77} These compounds have local structures very similar to those of the Laves phases and, as seen in the results presented in this thesis, it has been possible to substitute Co for Ni because of their almost identical metallic radius.

A number of samples with compositions $\text{Ti}_{50}\text{Zr}_{35}(\text{Ni}_{1-x}\text{Co}_x)_{15}$ ($x=0, 0.17, 0.5, 0.83, 1$) were produced. A $\text{Ti}_{50}\text{Zr}_{35}\text{Ni}_{12.5}\text{Fe}_{2.5}$ sample was also produced. While the $\text{Ti}_{50}\text{Zr}_{35}\text{Ni}_{15}$ approximant was easily reproduced no sign of an approximant phase was found in any of the other samples even though a number of heat treatment regimes were performed.

A quasicrystal phase with composition $\text{Ti}_{53}\text{Zr}_{27}\text{Co}_{20}$ synthesised via melt-spinning has been reported \cite{78}; it is possible that fast cooling rates, such as in melt-spinning or suction-casting can produce $\text{Ti}_{50}\text{Zr}_{35}(\text{Ni}_{1-x}\text{Co}_x)_{15}$ approximants.
5. Conclusions and Outlook

Sc-Based Laves-Phase Hydrides
As cast Sc(Al\textsubscript{1-x}Ni\textsubscript{x})\textsubscript{2} samples only contained the hexagonal MgZn\textsubscript{2}-type Laves phase when 0.36 ≤ x ≤ 0.65. Ni and Al were randomly distributed between the B sites in the x=0.5 sample. Hydrogenation either lead to interstitial solution in tetrahedral A\textsubscript{2}B\textsubscript{2} sites or decomposition into ScH\textsubscript{2} and NiAl. Both reactions were reversible. The amount of interstitial hydrogen that could be stored in the material was inversely correlated with the Al content; this is probably caused by Al proximity to available interstitial sites as H atoms often avoid interstitial sites close to p-block elements.

All the samples in the cubic Laves phase (Sc\textsubscript{1-x}Zr\textsubscript{x})(Co\textsubscript{1-y}Ni\textsubscript{y})\textsubscript{2} system that have been studied were single, or close to single, phase. An inverse correlation between hydrogen absorption and the content of Zr was observed when hydrogenation/de-hydrogenation cycles were performed. This was attributed to a decreased stability of the hydride affecting the plateau pressure. Zr content improved hydrogen sorption kinetics that may be caused by faster hydrogen diffusion.

Activation in MgH\textsubscript{2} with ScH\textsubscript{2}
Activation of MgH\textsubscript{2} mixed with 10mol % ScH\textsubscript{2} was observed during hydrogenation/de-hydrogenation cycling. No reaction between the two hydrides could be observed. A plateau of desorption rate seems to have been reached after the second cycle at 673 K while the rate was still increasing significantly between the third and fourth cycle at 593 K.

Nb\textsubscript{4}MSi (M=Co, Ni) Hydrides
The hydrides of Nb\textsubscript{4}MSi (M=Co, Ni) were shown to be very stable and have very slow hydrogen sorption kinetics. Stoichiometry of the hydrides where probably limited by the proximity of most of the available interstitial sites to M/Si sites which may be occupied by Si (a p-block element). No phase with ordered M/Si sites was observed.

LnGa (Ln=Nd, Gd) Hydrides
Hydrogen was absorbed/desorbed by LnGa (Ln=Nd, Gd) in two steps. After the second step H(D) atoms were located in fully occupied Nd\textsubscript{4} tetrahedra and ∼1/4 occupied Nd\textsubscript{3}Ga tetrahedra in the NdGaD\textsubscript{1.51} phase. Occupation of the Ln\textsubscript{4} tetrahedra was probably the first step, this required an oxidation of the Ga chains present in the structure possibly by a formation of a π bond. The nature of the Gd–D bond formed in the second step is still unclear.
Ti–Zr–Ni–Co Approximants
No approximant phases were observed in the Ti\textsubscript{50}Zr\textsubscript{35}(Ni\textsubscript{1−x}Co\textsubscript{x})\textsubscript{15} system unless x=0.

Future Outlook
Measurements of the superconductivity of the Nb\textsubscript{4}MSi (M=Co, Ni) hydrides were beyond the scope of this thesis but will be presented soon; the same goes for the magnetic properties of the LnGa (Ln=Nd, Gd) hydrides. In the latter case there are still many unanswered questions regarding the nature of the second hydrogenation step that will hopefully be explained in the not to distant future.
Produktion och lagring av förnybar energi ställer stora krav på utvecklingen av nya material. Metallhydriderna är en stor grupp av föreningar med väldigt varierande egenskaper som används, eller skulle kunna användas, i ett flertal energirelaterade tillämpningar, såsom: uppladdningsbara batterier, vätelagring och värmelagring för termisk solkraft (se figur 6.1). Metallhydriderna kan delas in i tre grupper utifrån vilken typ av kemisk bindning som dominerar i dem: metalliska-, joniska- och kovalenta metallhydrider (se figur 6.2).

I de joniska metallhydriderna bildar negativa hydridjoner (H\(^-\)) och positiva metalljoner (M\(^{n+}\)) mycket stabila salter som strukturellt liknar halidernas\(^1\) salter med samma metaller. MgH\(_2\) är en jonisk hydrid med en mycket hög viktandel väte (7.66%), vilket gör den intressant som vätelagringssalter för lättanvända delar som vätgasdrivna bilar (figur 6.1a). Två mycket stora problem för användningen av denna hydrid är att den är för stabil för att avge väte vid rumstemperatur och att absorptionen och avgivandet av väte sker mycket långsamt.

I den här avhandlingen visas att blandningen nio delar MgH\(_2\) och en del ScH\(_2\) uppnår maximal reaktionshastighet efter en absorption/desoptionscykel vid 673 K.

De metalliska metallhydriderna, där väteatomerna sitter i hålt av de mycket större metaller, har en relativt låg viktandel väte (≈2%). Trots detta är de de metallhydrider som används i störst utsträckning, till exempel i batterier och i vätelagring i ubåtar (figur 6.1b och c). De metalliska metallhydridernas styrkor är den extrema volymetiska tätheten av väte (i vis- sa fall högre än i fast och flytande väte) och att deras stabilitet, reaktionshastighet och elektrokemiska egenskaper är relativt lätt att kontrollera genom att ändra den kemiska sammansättningen. Kombinationen av en stabil jonisk metallh-ydrid och en instabil metallisk metallhydrid skulle kunna användas för att lagra värmé i termisk solkraft (figur 6.1d).

I den här avhandlingen visas att ökad aluminiumhalt i Sc(Al\(_{1-x}\)Ni\(_x\))\(_2\) minskar mängden väte som vill lösa sig i föreningen och att ökad mängd zirkonium i (Sc\(_{1-x}\)Zr\(_x\))(Co\(_{1-y}\)Ni\(_y\))\(_2\) destabiliserar metallhydriden, vilket gör att extremt tryck krävs för väteabsorption. Dessutom visas att föreningarna Nb\(_4\)MSi (M=Co, Ni) bildar mycket stabila interstitiella hydriden med mycket långsamt reaktionshastighet.

\(^1\)F, Cl, Br och I

62

Figur 6.3. a) Två enhetsceller av NdGa där neodymjoner (Nd$^{3+}$) kan ses som blå sfärer och galliummolekyljonkedjorna av Ga$^{3-}$ som röda sfärer bundna med svarta streck. b) En enhetscell av NdGaD$_{1.51}$: hydridjoner (egentligen deuteridjoner) ses som stora röda sfärer mellan de blå neodymjonerna och väteatomer (deuteriumatomer) som små vita sfärer.

Zintlfaser ligger i gränslandet mellan föreningarna med kovalent-, jonisk- och metallbidning. Deras strukturer kan beskrivas som positiva metallkatjoner av en aktiv metall $\text{Ma}^{n+}$ och molekylanjoner av en elektronegativ metall $\text{Mp}^{m-}$, där Mp försöker få åtta elektroner i sitt yttersta elektronskal genom sin jonladdning och sina kovalenta bindningar. Väte kan absorberas på två sätt i strukturen: antingen en hydridjon (H$^-$) i hålrum mellan de positiva metallkatjoner (Ma$^{n+}$) eller kovalent bundna till molekylkatjonen (Mp$^{m-}$).

I den här avhandlingen visas att LnGa (Ln=Gd, Nd), som byggs upp av Ln$^{3+}$-joner och Ga$^{3-}$-kedjor (figur 6.3a), absorberar väte i två steg: först absorberas väte i hål mellan Ln$^{3+}$-jonerna vilket kräver att Ga$^{3-}$ kedjorna oxide-ras till Ga$^{2-}$ för att laddningsbalansen ska behållas. Detta kräver att det bildas en extra binding i Ga-kedjan för att Ga fortfarande har åtta elektroner i sitt yt-tersta elektronskal. I det andra steget absorberas väte i hålrum nära Ga-kedjan. Bindningen mellan Ga och H är fortfarande oklar.
7. Acknowledgements

“Don’t worry, everybody gets paid.”

Leif Hammarström

First of all I would like to thank all my supervisors for your support and your guidance during my time as a PhD student. I am extra thankful to Martin Sahlberg for always introducing me to new people and instigating collaborations, Yvonne Andersson for the meticulous proofreading and Björgvin Hjörvarsson for always asking the (for a chemist) surprising questions.

Secondly I would like to thank the troglodytes: First of all I would like to say I am sorry, and you are welcome, to Viktor “Abobo” Höglin for my backseat refinement. I am also thankful to Girma Gebresenbut for teaching me about quasicrystals and Ethiopian beer brands. I would also like to thank Johan Cedervall, Ocean Fang and Pedro Berastegui for livening up the basement. Cesar Pay Gómez deserves a special thanks for all his help with crystallography. I would also like to acknowledge the very talented summer and degree project workers Tom Faske, Maciek Kaplan and Petter Tammela for their all their help.

I am also very grateful to Adrian Renne for proof-reading parts of the thesis on very short notice.

The collaborators outside the UU department of chemistry who helped make this thesis possible are also acknowledged: first of all the group of Torben Jensen at Aarhus University (Morten Ley, Line Holdt Rude, Dmytro Korablov, Thomas Kollin Nielsen, Flemming Besenbacher et al.) for helping me to get started with in-situ diffraction. I am also hugely indebted to Claudia Zlotea and Michel Latroche at CNRS for your help with PCT-measurements and for the opportunity to work in your lab. I am also thankful to, the ever enthusiastic, materials theory group at UU (Olle Eriksson, Rajeev Ahuja and Ralph Scheicher with a special shout-out to my beard + plaid shirt + glasses brother Robert Johansson). I am grateful to Ulrich Häussermann at Stockholms University for handing me a GdGa sample to measure at MAX-lab which started the very interesting LnGa project. Finally I would like to thank the beam line scientists and other personnel at MAX-lab, the nuclear physics institute in the Czech republic and institute for energy technology in Norway (Yngve Cerenius, Cartsten Gunlach, Olivier Balmes, Dörthe Haase, Premysl Beran, Magnus Sørby et al.) for all their help.

I am very thankful to all current and former members of the department of chemistry at Ångström for making it a great place to work, but a number
of people deserves special mention: Rolf Berger for teaching me why lattice energy is unfortunately named. Adam “kanske” Sobkowiak, Viktor “Eazy-E” Renman and Rickard “Sheldon” Eriksson who I like to remind to always remember, newer forget I711. Ulf Jansson for directing my application for summer work to Yvonne and Martin which, eventually, led to this thesis. Brewing partners Mats Tydén and Gabriel Oltean in Rackarbergets Bathroom Brewery. Mikael Ottosson for discussion about beer and help with diffraction. Fang Mao for being the best possible office-mate. Crossword wizards Sara Munktell and Jill Sundberg. Linus von Fiandt and Tim Nordh for coffee from their coffee machine. Fredrik “Mannen på bilden” Lindgren for having the vegetarian blood discussion with me three times. Tomas Edvinsson for elevating the lunch-room discussions to philosophy from time to time. Mats Boman and Erik Lewin for introducing me the secrets of Glögg-making. Leif Hammarström for providing the quote above at the end of a meeting describing the Byzantine economy of the department. The administrative and technical staff: especially Katarina “Tatti” Israelsson and Eva Larsson for help with many administrative problems, Anders Lund for building and fixing innumerable things remarkably fast. I would like to apologise to Leif Nyholm for all the where/were and plural/singular errors...

A very special thanks goes to David Rehnlund for always having my back, you are a true friend!

I thank my family for your support, especially my parents for inspiring me to pursue a scientific career.

Last but not least I would like to thank my wife Sara Frykstrand Ångström for your love and support, especially during these last few weeks before handing in the thesis.
Bibliography


[22] M. Bououdina, H. Enoki, and E. Akiba. “The investigation of the Zr_{1-y}Ti_y (Cr_{1-x}Ni_x)_{2-y}H_2 system 0.0\leq y\leq1.0 and 0.0\leq x\leq1.0 Phase composition analysis and thermodynamic properties”. In: *Journal of Alloys and Compounds* 281.2 (1998), pp. 290 –300. DOI: 10.1016/S0925-8388(98)00792-0.


Acta Universitatis Upsaliensis

Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology 1234

Editor: The Dean of the Faculty of Science and Technology

A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)