Synthesis and characterisation of Zintl hydrides

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Abstract

The synthesis, structural characterisation and the properties of the Zintl hydrides AeE_2H_2 and $AeAlSiH$ (Ae = Ba, Ca, Sr; E = Al, Ga, In, Si, Zn) are reported. The first hydride in this class of compounds is $SrAl_2H_2$ which was discovered under an experiment by Gingl, who hydrogenated $SrAl_2$ at various temperatures. (Gingl et al, Journal of Alloys and Compounds 306 (2000) 127-132). The intention was to form alanates, e.g. AlH_4^-, by terminating the three dimensional four connected aluminium network in $SrAl_2$. The new hydride, $SrAl_2H_2$, has a partially conserved aluminium network. The three dimensional anionic network in $SrAl_2$ is reduced to two dimensions in the hydride, with aluminium bonded to both aluminium and hydrogen. This type of bonding configuration has not been observed before.

The hydrogenation of $SrAl_2$ is straight forward, 190 ^{o}C and 50 bar, compared to the difficult synthesis of alanates and alane, AlH_3. The latter synthesises uses aluminium in its zero oxidation state in contrast to the synthesis of $SrAl_2H_2$ from $SrAl_2$. (In the $SrAl_2$-precursor aluminium is reduced by the electropositive metal to -I.) Thus, the discovery shows a different route to alanates by using precursors with aluminium in a reduced state. If $SrAl_2H_2$ is further hydrogenated at 250 ^{o}C the two dimensional network breaks and Sr_2AlH_7 forms.

We wanted to investigate if $SrAl_2H_2$ was a singularity or if other similar compounds exist. We wanted to study how hydrogenation of precursors similar to the aluminide result in 1) new routes to compounds with high hydrogen content, as alanates, 2) to investigate how the E-H bond is affected as function of the network composition among different ternary hydrides, in particular $BaAl_xSi_{2-x}H_x$, and choice of active metal.

$BaGa_2H_2$ and $SrGa_2H_2$, two hydrides isostructural with $SrAl_2H_2$, were synthesized from its precursors $BaGa_2$ and $SrGa_2$. In addition three ternary hydrides BaAlSiH, CaAlSiH and SrAlSiH were manufactured from their related AeAlSi precursors.

All powders were characterized by neutron and x-ray diffraction methods.

An increased stability towards water/moisture compared to ordinary saline hydrides was noticed, especially for the ternary hydrides. Heat stability was measured with DSC (differential scanning calorimetry). The hydrides $BaGa_2H_2$ and $SrGa_2H_2$ decompose around 300 ^{o}C at 1 atm. This is similar to isostructural $SrAl_2H_2$. The ternary hydrides BaAlSiH and SrAlSiH decompose at 600 ^{o}C, at 1 atm, which is the highest noticed temperature for compounds with Al-H bonds. Inelastic neutron scattering experiments showed that these hydrides Al-H and Sr-H bonds are really weak, even weaker then the Al-H interactions in alanates and alanes. These hydrides are probably stabilized be their lattices.

The electric properties among the ternary hydrides were measured with IR-spectroscopy (diffuse reflectance). The ternary hydrides, AeAlSiH, are indirect semi conductors. $BaGa_2H_2$ and $SrGa_2H_2$ are conductors. The ternary hydrides, $AeAl_xSi_{2-x}H_x$, may have adjustable band gaps, which we were not able to determine.

This work is leading into a new research area within the field of metal hydrides.

List of Papers

This thesis is based on the following papers:

I. **SrAlSiH: A polyanionic semiconductor hydride**
Thomas Björling, Dag Noréus, Kjell Jansson, Magnus Andersson, Ekaterina Leonova, Mattias Edén , Ulf Hålenius, and Ulrich Häussermann. *Angew Chemie*, 2005, 7269 – 7273

II. **Polyanionic Hydrides from Polar Intermetallics AeE_2 (Ae = Ca, Sr, Ba; E = Al, Ga, In)**
Thomas Björling, Dag Noréus, and Ulrich Häussermann, *J Am Chem Soc.* 2006 Jan 25;128(3):817-24.

III. **Vibrational Properties of Polyanionic Hydrides $SrAl_2H_2$ and SrAlSiH: New Insights into Al-H Bonding Interactions**
Myeong H. Lee, Otto F. Sankey, Thomas Björling, David Moser, Dag Noréus, Stewart F. Parker, and Ulrich Häussermann *Inorg. Chem. 2007,* 46 (17), 6987 -6991.

IV. **Characterisation of two new Zintl phase hydrides BaAlSiH and CaAlSiH**
Thomas Björling, Björn Hauback, Tomohiro Utsumi, David Moser, Dag Noréus, Ulrich Häussermann (Submitted)

V. **A series of Zintl phase hydrides; $BaAl_{2-x}Si_xH_{2-x}$ (0.4 < x < 1.6) with compositions and structures in between the electric conductors $BaSi_2$ and $BaAl_2H_2$**
Tomohiro Utsumi, Thomas Björling, David Moser, Dag Noréus, Ulrich Häussermann (In manuscript)

Contents

1. Introduction

The "oil crises" in the seventies came as a reminder that cheap oil is not an endless resource. During the following last 30 years the interest in alternative energy sources has been on the increase albeit with varying intensity. Lately this interest has accelerated with the awareness that the burning of fossil fuel also has a detrimental impact on our global climate. The rapidly growing economies in India and China with an accelerating use of energy have also brought the level of consumption of oil close to the maximum possible oil production capacity. In several of the non-opec producing countries like USA, Norway and England the oil production is declining, in spite of more efficient drilling and oil recovery technologies. Mayor oil field are now only remaining in the middle east, but it is not certain that even those can increase their production capacity to meet the growing demand. This is behind much of the political instability in world and also to oil prices escalating into the 100 U$ per barrel level. Developments of alternative energy resources are thus badly needed.

Alternative energy resources can be considered as "solar energy" in different forms such as hydropower, wind power, solar heat, solar electricity etc. These energy sources are rather extensive and the energy has to be collected and distributed to the consumers. The electric grid is good for this, but it needs to be complemented with some energy storage that ultimately also could be used as a fuel. Oil has several advantages as it can be energy source, energy storage and a fuel for the transportation sector. The latter two are still lacking in an alternative energy solution.

Hydrogen has been considered to be such an energy vector, to be used as a compliment to the electric grid for distributing alternative energy, as a fuel and for energy storage. Hydrogen can be burnt to water in conventional internal combustion engines, in turbines and also electrochemically in fuel cells with higher energy efficiency. Although hydrogen can be an energy efficient, as well as an environmentally friendly fuel it is still a voluminous gas at ambient condition, which needs to be stored in a denser form. The most challenging task for realizing a hydrogen based energy system is how to store hydrogen in sufficient amounts. For use in vehicles, the US Department of Energy together with mainly the US car industry have required 6 wt% of a systems total weight to be hydrogen. The system should be safe with respect to accidents and non-polluting. Such high storage densities leave very few alternatives for possible hydrogen storage solutions. Three possible hydrogen storage solutions have been discussed.

1) Compressed high pressure gas tubes.

This is the common storage today. With a conventional gas pressure of 200 bars and steel tubes, the stored hydrogen does not reach above 1 wt%. Development of high pressure tanks made of materials such as carbon fibre composites with an internal residue of aluminium to hinder hydrogen from reacting with the composite has increased the storage capacity up to 6 wt%. These containers can handle pressures up to 350 bar, maybe even higher [1]. However, the volume hydrogen density is still unsatisfactory (for example, to store 5 kg of hydrogen still requires 250L at 350bar) These systems have also not been tested in commerzial applications and it is still an open question if such high pressures will be accepted by the public in private cars.

2) Liquefied hydrogen

Hydrogen condensates at 1 bar at -252 $^{\circ}$C and has a critical temperature of -241 $^{\circ}$C. The density of liquid hydrogen is low, 70.8 kg/m^3, and with modern cryostorage tanks hydrogen storage in excess of 20 wt% can be reached. A problem is, however, that an amount compared to ~1/3 of the energy stored in the system has to be used for liquefying the hydrogen. Boil off losses especially when filling the tanks can also be substantial. Cryogenic storage of liquid hydrogen is therefore only practical in special applications, as for example as rocket fuel in space applications.

3) Chemically bonded either as molecules (H_2) or atoms.

Molecular hydrogen, Van der Waals bonded to carbon nanotubes or other type of porous material has been a research topic [2]. These types of system only work satisfactory at liquid nitrogen temperature, -196 °C. But the idea to create a surface that could attract hydrogen with week Van der Waals forces has the advantage to avoid chemistry under hydrogenation/dehydrogenation.

Hydrogen can also be stored chemically, bonded to other elements and released by heat, a pressure decrease or formed from a chemical reaction. Compounds containing hydrogen are often called "hydrides". As familiar to chemists the nomenclature hydride indicates negatively charged hydrogen and real hydrides should therefore consist of positive and negative entities. Some of these compounds contain large amounts of hydrogen and some of them had been considered as potential hydrogen storage candidates:

Metal hydrides have earlier been explored as candidates for storage. Their volumetric densities are higher than for liquid hydrogen, this includes Mg_2NiH_4, $LaNi_5H_6$ etc. See table 1. [3].

Material	H-atoms per $cm^3 (x10^{22})$	H-density by volume (kg/m^3)	H-density by weight (%)
H_2 gas, 200 bar	0.99	16.4	100
H_2 liquid, 20K	4.2	69.7	100
H_2 solid, 4.2K	5.3	88	100
LiH	5.9	98.0	12.7
MgH_2	6.5	107.9	7.6
Mg_2NiH_4	5.9	98	3.6
$FeTiH_2$	6.0	99.6	1.89
$LaNi_5H6$	5.5	91.3	1.37

Table 1. Hydrogen content among different hydrogen storage systems.

It can be mention that hydrogen storage research on the latter system lead to the hydrogen storage alloys that are used in our present rechargeable NiMH batteries. These batteries are used in hybrid electric vehicles (HEV) such as Toyota´s Prius and Hondas Insight. One can say that results from hydrogen storage research are already today helping to reduce green house gas emissions by increasing the mileage of modern cars. These first generation metal hydrides have storage capacities in the order of 2 wt% but to reach above 6 wt% only the lightest elements in the periodic table can be used. Such are the first alkaline- and alkaline earth metal hydrides. Hydrides of magnesium and lithium are studied because of their high capacity of 12.5 % and 7.6 % respectively. These compounds are not perfectly ionic since the polarization ability related with the small positive ion is not negligible. These polar covalent hydrides are thus more easily decomposed by heat than their more ionic homologs, sodium- and calcium hydride. These systems can be described with the general formulas: $2A + H_2 \rightarrow 2AH$ and $Ae + H_2 \rightarrow AeH_2$, there A and Ae represent the s-block metals in valence order. Backward reactions are endothermic. Large efforts have been put into research how to weaken the metal-hydrogen bond to lower the decomposition temperature. This research is mainly contributed to substituting the s-block metal in the lattice with different transition state metals to decrease the lattice enthalpy.

Research in the nineties and beginning of this century was focused on storage systems based on aluminium, boron e.g. the second row in the periodic table. Especially hydrides based on boron and aluminium were in focus but also systems incorporating hydrogen bonded to nitrogen, e.g. ammonia or imides/amides. Among nitrogen based compounds the idea is to use substances as ammonia, NH_3, amide, $-NH_2^-$, as carrier for hydrogen. Hydrogen atoms are here affected by the electronegative nitrogen atom, thus they will be slightly positively polarized. Lithium hydride can react with a saline amide to form hydrogen, the hydride ion react with the more "acid" hydrogen bonded to the nitrogen in the amide. Actually this idea is old and is probably influenced by the reaction between potassium

and liquid ammonia, a reaction generating potassium amide and hydrogen gas, a process observed to be reversible [4]. Unfortunately this is not possible with the lighter alkali metals. Systems based on ammonia/amides have slow kinetics and are associated with to many problems too be practical for hydrogen storage. The ammonia release is for example detrimental to fuel cells.

Aluminium hydrides have been a strong candidate for storage. Aluminium hydrides are represented by the compounds alane, AlH_3 (10 wt%) and the alanates, AlH_4^-, AlH_6^{3-} with different electropositive counter ions. These compounds have satisfactory hydrogen content for storage but complications with kinetics and reversibility have made them slow to reach practical storage applications. My thesis aims at increasing the understanding of the aluminium-hydrogen bond in a new class of Zintl phase hydrides (as described below) and how this bond is influenced by different substitutions on neighbouring atomic sites. The results are not only interesting for the development of new light weight aluminium based hydrides but also for the understanding the interesting electron transport phenomena discovered in these new systems involving superconductivity and conductor-insulator transitions

1.1. A new class of hydrides and Zintl compounds

Attempts by Gingl et al to manufacture alanates with strontium aluminide, $SrAl_2$ as precursor lead to a new class of hydride compounds, described hereinafter [5]. $SrAl_2$ is a compound that obeys the so called Zintl concept [6]; Zintl phases have both ionic and covalent interactions. The negatively charged ions often form clusters, chains or a network imitating the structures represented by elements in the periodic table which the ion becomes isoelectronic to. The negatively charged atoms connect to each other through covalent bonds. To be a real Zintl compound the octet rule should be obeyed, otherwise the substance should be named "poly anionic". Zintl hydrides contain both –E-E- and –E-H bonds, in our case E represents a p-block element.

In $SrAl_2$ the aluminium atoms are arranged three dimensionally in a negatively charged net. When Gingl did an in situ x-ray measurement meanwhile heating a sample of strontium aluminide under hydrogen pressure he discovered a new type of hydride with most of the aluminium structure conserved. The three dimensional network had been reduced to a two dimensional one with hydrogen atoms attached in the vacant positions.

This lead us to speculate if other hydride compounds exists with a partially conserved network structure, and if so, what about their properties? How is the environment around aluminium affecting a hydrogen aluminium bond? We were also interested in if it was possible to form other type of hydrides via a similar process as the one done by Gingl. This work considers the homologs to the first Zintl hydride, $SrAl_2H_2$. If there exists a hydride of the aluminide why should there not exist one of the gallide, indide etc? Thus, we tried to hydrogenate a gallium substituted $SrAl_2$, e. g. $SrGa_2$, to discover a new hydride, isostructural to $SrAl_2H_2$ but with gallium as the network component instead of aluminium, $SrGa_2H_2$. Several new hydrides were discovered in this same way.

2. Experimental

2.1. Starting materials and their synthesis

In a first study we tried to manufacture isostructural hydrides to $SrAl_2H_2$ from binary compounds AeE_2 there Ae = Ca, Sr, Ba and E = Si, Ga, Al, Zn and In. The binary compounds used in the study were $SrSi_2$, $SrAl_2$, $SrZn_2$, $CaGa_2$, $CaGa_{2+x}$ (x = 0.1 – 0.2), $SrGa_2$, $BaGa_2$, $SrIn_2$ and $BaIn_2$ [7-15]. The compounds were synthesised from the pure elements, the chemicals were at least 99 % pure and bought from Sigma-Aldrich, pressed into tablets, in stoichiometric ratios. For preparing $SrSi_2$ and $SrAl_2$ the samples were arc-melted. An alternate route to form $SrSi_2$ is to heat SrH_2, with Si to 800 ^{o}C for 12-24 h. Arc melting was also used to synthesise precursors, $AeAl_xSi_{2-x}$ [16], for different ternary hydrides $AeAl_xSi_{2-x}H_x$, there Ae = Ba, Ca and Sr. SrAlSi was sometimes made under vacuum from

tablets of SrH_2, heated to at least 900 °C for ca 3 h, mixed with silicon and aluminium. For preparing the zinkide, gallides or indides reactant mixtures were transferred into Ta or stainless steel ampoules, respectively, which were sealed and placed in a fused quartz Schlenk tube under reduced pressure. All samples were heated at 800 °C for 24 h except the one containing strontium and zink, it was held at 600 °C for a week.

All attempts to produce similar compounds from Mg ended in Mg_2Si [17].

2.2. Hydride synthesis

The methods used to form hydrides were first direct hydrogenation of the alloys, the reaction $AeE_2 + H_2$ and second the reaction $AeH_2 + 2E$ in a hydrogen atmosphere.

All samples were handled under argon atmosphere in a glove box with less than 1 ppm of O_2 and H_2O. The tablets were placed in Al_2O_3-tubes and reacted in sealed stainless steel autoclaves. The autoclaves were filled with hydrogen gas, at the conditions given in the tables below in the attempt to manufacture hydrides. (If no information is given the pressure was 50 bar)

2.3. Metal hydride synthesis conditions (Table 2.3.1-2.3.11)

2.3.1. $SrAl_2 + H_2$

Temp (°C)	Time	Comments:
150	5 days	Signs of $SrAl_4$
170	5 days	Signs of $SrAl_2H_2$. Amount of $SrAl_4$ did not increase.
190	2,5 days	$SrAl_2H_2$
240	5-7 days	$SrAl_2H_2$ drastically decreased. $SrAl_2$ reformed.
270	5-7 days	New hydrides and elemental Al.
320	5-7 days	Same as 270 °C synthesis.

2.3.2. $SrH_2 + Al$

Temp(°C)	Time	Comments
200-600		No products.

2.3.3. $SrSi_2 + H_2$

Temp(°C)	Time	Comments
500-800	1 day	No products.

2.3.4. $SrH_2 + Si$

Temp(°C)	Time	Comments
600	1 day	No products
800	1 day	$SrSi_2$

2.3.5. SrZn$_2$ + H$_2$

Temp(^{o}C)	Time	Comments
105	1 day	SrZn$_2$
125	1 day	SrZn$_2$ plus traces of amorphous SrZn$_{13}$.
154	1 day	Amorphous SrZn$_{13}$ formed. Not any SrZn$_2$ left.
200- 600	12 h	SrZn$_{13}$
750	6 h	SrH$_2$ + Zn

2.3.6. SrH$_2$ + Zn

Temp(^{o}C)	Time	Comments
200	2 days	No products.
300, 500	1 day	SrZn$_{13}$
600	3 days	SrZn$_{13}$ + SrH$_2$ and Zn.
750	1 day	SrH$_2$ + Zn

2.3.7. AeGa$_2$ + H$_2$ (Ae = Sr or Ba)

Temp(^{o}C)	Time	Comments
178	1.5 days	AeGa$_2$
200	4 days	AeGa$_2$H$_2$
230	1,5 days	AeGa$_2$H$_2$ and SrGa$_4$
250, 350	1 day	AeGa$_4$

2.3.8. AeH$_2$ + Ga (Ae = Sr or Ba)

Temp(^{o}C)	Time	Comments
50	5 days	AeH$_2$ + Ga
100, 200	5 days	AeH$_2$ + Ga + AeGa$_4$

2.3.9. CaGa$_2$ + H$_2$ and CaGa$_{2+x}$ + H$_2$

Temp(^{o}C)	Time	Comments
125	1 days	CaH$_2$ + CaGa$_4$

2.3.10. AeIn$_2$ + H$_2$ (Ae = Ca or Sr)

Temp(^{o}C)	Time	Comments
200,300	1.5 days	AeIn$_2$
400	1.5 days	AeIn$_2$ + AeH$_2$ + In

2.3.11. BaIn$_2$ + H$_2$

Temp(^{o}C)	Time	Comments
100	1.5 days	BaIn$_2$
200	1.5 days	BaH$_2$ + In

2.4. Ternary metal hydride synthesis conditions (Table 2.4.1-2.4.8)

2.4.1. BaAlSi + H_2 (H_2 pressure 70 bar)

Temp(^{o}C)	Time	Comments
200, 500	2 days	BaAlSi
600, 700	2 days	BaAlSiH

2.4.2. CaAlSi + H_2

CaAlSi + H_2		
Temp(^{o}C)	Time	Comments
250, 260	2 day	CaAlSi
270	2 day	$CaAl_2Si_2$, CaAlSi
450	2 day	CaAlSiH, $CaAl_2Si_2$
500	40 min	CaAlSiH

2.4.3. SrAlSi + H_2

Temp(^{o}C)	Time	Comments
200	2 days	SrAlSi
300	2 days	SrAlSi, trace of SrAlSiH
500, 600	2 days	SrAlSiH

2.4.4. 1) SrH_2 + Si + Al (vacuum) and 2) H_2 at 70 bar

Temp(^{o}C)	Time	Comments
1) 950	3 hours	SrAlSi
2) 700	2 days	SrAlSiH

2.4.5. $BaAl_{1.6}Si_{0.4}$ + H_2

Temp(^{o}C)	Time	Comments
300	2 days	$BaAl_{1.6}Si_{0.4}H_{1.6}$ + unknown phases.
700	2 days	BaAlSiH instead of $BaAl_{0.4}Si_{1.6}H_{0.4}$ + unknown phases.

2.4.6. $BaAl_{1.4}Si_{0.6}$ + H_2

Temp(^{o}C)	Time	Comments
300	2 days	$BaAl_{1.4}Si_{0.6}H_{1.4}$ + unknown phases.
550	2 days	$BaAl_{1.4}Si_{0.6}H_{1.4}$. BaAlSiH + unknown phases.
600	3 hours	$BaAl_{1.4}Si_{0.6}H_{1.4}$ + unknown phases.

2.4.7. $BaAl_{0.6}Si_{1.4}$ + H_2

Temp(^{o}C)	Time	Comments
300	2 days	No products.
550	3 hours	$BaAl_{0.6}Si_{1.4}H_{0.6}$, $BaSi_2$ + unknown phases.
600	12 hours	A phase close to $BaAl_{0.6}Si_{1.4}H_{0.6}$. $BaSi_2$ + unknown phases.

| 700 | 2 days | BaAlSiH instead of $BaAl_{0.6}Si_{1.4}H_{0.6}$. |
| | | $BaSi_2$ + unknown phases. |

2.4.8. $BaAl_{0.4}Si_{1.6}$ + H_2

Temp(^{o}C)	Time	Comments
300	2 days	$BaAl_{0.4}Si_{1.6}H_{0.4}$.
		Small peaks of $BaSi_2$ + unknown phases.
500	2 days	Formation of a phase closer to $BaAl_{0.6}Si_{1.4}H_{0.6}$.
		Strong peaks of $BaSi_2$, BaSi + unknown phases.
700	2 days	BaAlSiH instead of $BaAl_{0.4}Si_{1.6}H_{0.4}$.
		Strong peaks of $BaSi_2$, BaSi + unknown phases.

2.5. Comments of Zintl hydride synthesis

To form $SrAl_2H_2$ a different approach was tried compared to the synthesis route applied by Gingl. We tried to manufacture the Zintl hydride from mixtures of SrH_2 and Al but these attempts failed because of difficulties to react aluminium at low temperature; actually at conditions there the Zintl hydride is stable. A reaction giving a lot of $SrAl_4$, hereinafter also called 1:4 phase, and hydrogen required more than 800 ^{o}C. (Close to strontium hydrides dissociation temperature)

Therefore gallium, a liquid near room temperature, was of more interest to study in a similar possible reaction path, e.g. AeH_2 and Ga, but these experiments did not result in any hydride, instead already around 100 ^{o}C, $AeGa_4$ was a result. To get $SrAl_2H_2$ and its homolog's a poly anionic network in the precursor was assumed to be required with the precursor on the form AeE_2. The compound $SrAl_2H_2$ forms in a good yield in a window of 190-200 ^{o}C, if the pressure is at least 50 bar, above 200 ^{o}C $SrAl_4$ and SrH_2 forms together with small amounts of different alanates as Sr_2AlH_7 [18]. The same synthesis condition as for $SrAl_2H_2$ appeared to be true for the gallide homologs and we were able to manufacture $SrGa_2H_2$ and $BaGa_2H_2$ from their $AeGa_2$ precursors in a similar way [19].

Hydrogenation of $AeIn_2$ resulted in indium instead of $AeIn_4$. The indides of Ca and Sr seemed inert to hydrogen up to 400 ^{o}C thereafter they decomposed into AeH_2 and In. For $BaIn_2$ this was observed already at 200 ^{o}C.

Hydrogenation experiments with different ternary phases, AeAlSi, resulted in the discovery of three new hydrides. AeAlSiH there Ae = Ba, Ca and Sr. The first successful hydrogenations were done with SrAlSi. Several such experiments with SrAlSi and hydrogen resulted in a compound with the composition SrAlSiH [20]. SrAlSiH forms at temperatures over 300 ^{o}C and at hydrogen pressures over 50 bar. Best hydrogenation results were obtained at 500-700 ^{o}C, with a hydrogen pressure of 50-70 bar. These conditions are also true for hydrogenation of BaAlSi, but on the other hand to produce CaAlSiH require a short hydrogenation time because of side reactions via an alternative reaction path to $CaAl_2Si_2$ and CaH_2 [21]. Hydrogenation of CaAlSi at pressures of 50-70 bar at 500 ^{o}C for 40-45 minutes gave best result.

Hydrogenation experiments with hexagonally $BaAl_xSi_{2-x}$, there x varied between 0.4 and 1.6 were performed [22]. When the 1:1:1 AeAlSi stoichiometry is abandoned the symmetry reduces and the hydrides destabilizes. To hydrogenate various stoichiometries of $BaAl_xSi_{2-x}$, x≠1, temperatures around 300 ^{o}C is preferred as formed hydrides decomposes at higher temperatures into $BaSi_2$ or $BaAl_4$. Dependent on the silicon/aluminium content also BaAlSiH and BaAlSi could be formed. Similar behaviour was observed in the calcium and strontium systems. Focus was on the barium system as it was the easiest to study due to fewer impurities.

3. Structural characterization

3.1. Details about the investigations with powder neutron and x-ray diffraction

To check quality of reactants and the general structure of the products powder x-ray diffraction was used. For more detailed information about atomic positions complementary studies with neutrons were performed.

Lattice constants of the compounds were obtained from least-squares refinement of measured and indexed lines of the corresponding Guinier powder diffractograms, using a Guinier-Hägg focusing camera of diameter 40 mm, with monochromatic $CuK_{\alpha 1}$ radiation ($\lambda = 1.5405980$ Å). The samples were mixed with silicon, as an internal standard, and placed into a sample holder on a tape and exposed for x-rays. The obtained data was recorded on a photographic film; this method requires very small amounts of powder. The developed films were measured in an LS 18 film scanner [23] and the program SCANPI [24] was used to determine d-values and intensities recorded in the photographs. The programs TREOR [25] and PIRUM [26] were used to index the patterns and to refine the unit cell parameters. Obtained data was then compared with calculated powder patterns of known phases in the systems (program Powdercell [27]). By this we could follow the formation of the reaction products as a function of synthesis temperature, or to check if the reactants were pure.

Atomic positions were determined from Rietveld refinements of the obtained neutron powder diffraction data [28] measured at Studsvik Neutron Research Laboratory, Sweden or Kjeller, Institute for Energy technology (IFE), Norway [29].

## 3.2. X-ray single crystal diffraction

Single crystals of $SrSi_2$ and $SrAl_2$ were used for X-ray structure investigations. Intensity data of the single crystals were collected at room temperature on a STOE IPDS system using monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). Data reduction and numerical absorption correction were made with the programs X-red [30] and X-shape [31], respectively. The obtained data were refined with the program SHELXL97 [32].

3.3. Structures of the precursors and there resulting hydrides (Paper I, II, IV and V)

3.3.1. $SrAl_2$, $SrZn_2$ and $BaIn_2$

Orthorhombic $SrAl_2$, $SrZn_2$ and $BaIn_2$ crystallises in the space group *Imma* ($CeCu_2$ structure type). Their structure consists of puckered hexagon layers of E atoms, which are stacked on top of each other. The E atoms have a distorted tetrahedral environment: they are linked to three neighbours within a puckered layer and to a fourth one in the adjacent layer either above or below, thus forming a three-dimensional polymer Zintl anion. The E-E atom distances within a layer are considerably shorter than the one linking layers. The difference is about 0.1 Å for $SrAl_2$ and $BaIn_2$ and about 0.2 Å for $SrZn_2$. The positive ions are located between the nets, slightly displaced from the centres of the hexagons. According to the Zintl concept E atoms are formally reduced by electropositive Sr. In- and Al- is isolectronic to Si and, thus, the formation of a poly anionic three-dimensional four-connected network in these compounds is reasonable. However, the Al-Al distances in $SrAl_2$ are rather large (2.78 and 2.88Å) and much closer to the Al-Al nearest neighbour distance in fcc-Al (2.86Å) than to the distance expected for a pair of two-electron two-centre bonded Al atoms (around 2.6 Å). In $BaIn_2$ these distances are close to 3 Å. In $SrZn_2$ the poly anionic Zn network is electron-deficient: Zn- has three electrons to form four nearest neighbour bonds. The elongation of the interlayer distance in $SrZn_2$ compared to $SrAl_2$ might be connected to that. As mentioned above $SrAl_2$ can be hydrogenated to the compound $SrAl_2H_2$. The indide does not form any hydrides.

Isostructural $SrZn_2$ does not form any hydride at the conditions applied by us. Hydrogenation of $SrZn_2$ may have possibility to success in forming a hydride of the same reasons as mentioned for CaAlSiH.
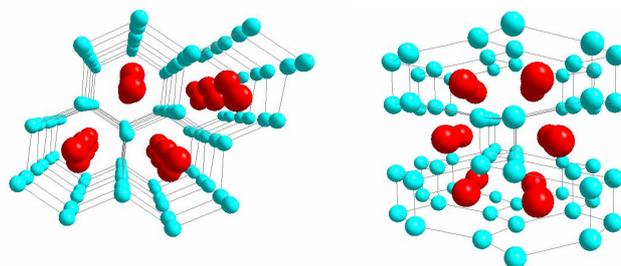
Ae=red and E=blue. Ae = Alkaline earth metal. E = d or p-block element.

3.3.2. Cell parameters of $SrAl_2$, $SrZn_2$ and $BaIn_2$

	$SrAl_2$	$SrZn_2$	$BaIn_2$ [values from reference, 17]
a (Å)	4.7954(6)	4.801(2)	5.2204(19)
b (Å)	7.8956(9)	7.798(2)	8.504(3)
c (Å)	7.953(1)	7.826(4)	8.520(3)
V (Å^3)	301.12	293.02	378.24
Z	4	4	4

3.3.3. Atomic positions obtained from single crystal measurement

$SrAl_2$

Atom	Wyck	x	y	z	Uiso
Sr	4e	0	1/4	0.05047(4)	0.0113(1)
Al	8h	0	0.93253(9)	0.33882(9)	0.0111(2)

R = 1.84 & R_w =3.30

3.3.4. Distance table $SrAl_2$ of and $SrZn_2$

		$SrAl_2$	$SrZn_2$	$BaIn_2$
Ae-E	4x	3.270	3.28	3.524
	2x	3.404	3.28	3.655
	2x	3.422	3.37	3.661
	4x	3.584	3.52	3.876
E-E	1x	2.784	2.75	2.975
	2x	2.787	2.73	3.020
	1x	2.285	2.95	3.096

3.4. $SrSi_2$

$SrSi_2$ is cubic, the reported space group is *P $4_3$32,* (no. 212). Si$^-$, which is isoelectronic to P, is expected to form either two- or three-dimensional three-connected polyanions. In $SrSi_2$ the silicon network is three-dimensional and chiral. The Si-Si distance is 2.39 Å and compares well with that in elemental Si (2.35 Å). The refinement of our investigated crystal resulted in the enantiomorphous space group P4$_1$32 (213). The R-value decreased from 0.023 to 0.012 when using the correct handedness. As is usually the case for solid state compounds, it can be expected that our $SrSi_2$ sample contains crystals of both space groups, *P4$_1$32* and *P4$_3$32*, in equal amounts. The hydrogenation of $SrSi_2$ did not yield a hydride compound at the conditions applied by us.
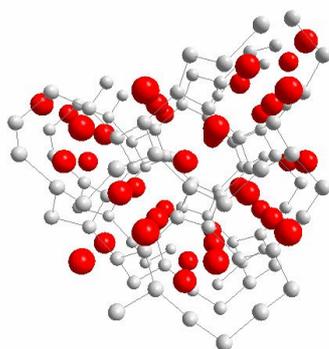
SrSi₂, Sr=red and Si=grey

3.4.1. Cell parameter of SrSi₂

	SrSi₂
a (Å)	6.5373(3)
V (Å³)	279.38
Z	4

3.4.2. Atomic positions from single crystal measurement

SrSi₂

Atom	Wyck	x	y	z	Uiso
Sr	4a	0.37500	0.37500	0.37500	0.0096(1)
Si	8c	0.67243(6)	0.67243(6)	0.67243(6)	0.0071(2)

R = 2.31 & R_w =7.17

3.4.3. Distance table SrSi₂

		Distance
Sr-Si	6x	3.256
	2x	3.368
	8x	3.828
Si-Si	3x	2.393

3.5. SrGa₂, BaGa₂, AeAlSi and CaGa₂₊ₓ (x = 0.1-0.2) (Paper I, II, IV and V)

SrGa₂ and BaGa₂, (Ae = Sr and Ba) are representatives of the widely adopted hexagonal AlB₂ structure type (space group *P6/mmm*, no 191). Graphitic layers of Ga atoms are stacked on top of each other; the Sr atoms are located in between and sandwiched by two Ga hexagon rings. Contrary to Al⁻ in SrAl₂, Ga⁻ in AeGa₂ adopts two-dimensional three-connected plane layers. This is also a solution to an electron count of four because of possible π-bonding (compare with the carbon polymorphs graphite and diamond). When Ba/SrGa₂ is hydrogenated AeGa₂H₂compounds forms.
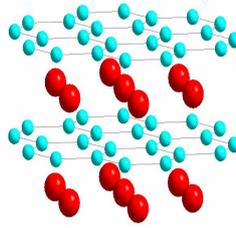
Ae=red and E=blue. Ae = Alkaline earth metal. E = d or p-block element.

3.5.1. Cell parameters of SrGa$_2$, BaGa$_2$ and CaGa$_{2+x}$

	SrGa$_2$	BaGa$_2$	CaGa$_{2+x}$ (x = 0.1-0.2) [values taken from reference, 13]
a (Å)	4.3488(6)	4.4323(3)	4.319(1)
c (Å)	4.742(1)	5.0823(8)	4.329(2)
V (Å^3)	77.66	86.47	69.93
Z	1	1	1

3.5.2. Distance table

		SrGa$_2$	*BaGa$_2$*	*CaGa$_{2+x}$*
Ae-Ga	12x	3.454	3.606	3.302
Ga-Ga	3x	2.511	2.559	2.494

AeAlSi is reported to be isostructural with the gallides. The SrAlSi alloy was investigated with the polaris spectrometer at ISIS research centre in Rutherford England. The aim was to study if the Al/Si network was ordered or not. This was not possible to verify but the R_f value for the refinement of the structure decreased from 8 to 6 % for a slightly puckered Al/Si, in space group P-6m2, compared to a flat as described in P6/mmm. Akimtsu et al found that CaAlSi has an ordered Al/Si network maybe this is also true for the BaAlSi and SrAlSi [33]. The increased amounts of electrons introduced with the silicon turns AeAlSi into poly anionic compounds as the number of electrons are too many to satisfy the octet rule.

3.5.3. Cell parameters of CaAlSi, SrAlSi and BaAlSi

	CaAlSi	SrAlSi	BaAlSi
a (Å)	4.1902(4)	4.2367(7)	4.2989(6)
c (Å)	4.3994(6)	4.7442(9)	5.1437(7)
V (Å^3)	66.89	73.89	82.32
Z	1	1	1

Among AeAlSi the network distances, E-E, is similar. This is expected and also observed for above mentioned gallides with AlB$_2$ structure. The Ae-E distance varies more and this is related with the different size of the alkaline earth metal ions.

3.5.4. Distance table of CaAlSi, SrAlSi and BaAlSi

	CaAlSi	SrAlSi	BaAlSi
Ae-E 12x	3.27	3.407	3.574
E-E 3x	2.419	2.446	2.482

3.5.5. Different composition $BaAl_xSi_{2-x}$ (0.4 < x < 1.6)

Different composition precursors in the $BaAl_xSi_{2-x}$ system, (0.4 < x < 1.6) were synthesised to be used as precursors for new hydrides

The a-axis and cell volume is linearly decreasing with increasing x-value. This is reasonable as Al atoms are replaced by smaller Si atoms as x increases. The c-axis is rather independent on x.
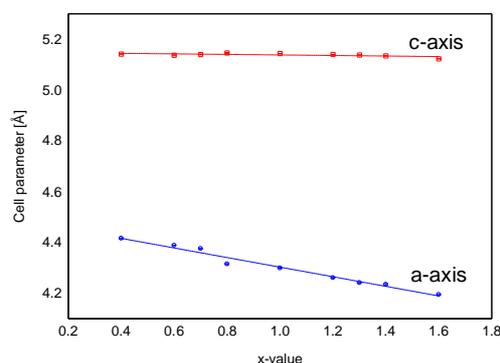
Cell parameters obtained from powder diffractograms of $BaAl_{2-x}Si_x$ as a function of x.

3.6. CaGa₂, CaIn₂, and SrIn₂

The $CaIn_2$ (*P6₃/mmc, no 194*) and $CeCu_2$ structures have three dimensional four connected E atom networks and are easily derived from the AlB_2 type. In the $CaIn_2$ –type, E atom hexagon layers are corrugated as in grey As and connected as in hexagonal diamond. (In the $CeCu_2$ type E atom hexagon layers are corrugated as in black P, which yields a smoother corrugation compared to $CaIn_2$, and connected to give a ladder of four-membered rings.) We did not success in producing hydrides from these precursors.
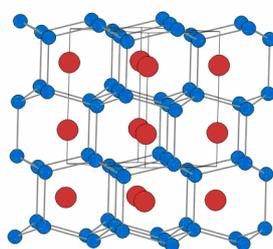

Picture of CeCu₂-type structure. Red and blue circles denote Ae and E atoms, respectively.

3.7. Zintl hydrides AeE_2H_2, Ae = Sr or Ba, E = Ga or Al. (Paper II)

In the trigonal structure of AeE_2H_2 (space group *P-3₂/m1*, no 164) E atoms form slightly puckered graphitic layers. Additionally each E atom is coordinated to one hydrogen atom. The relationship to

SrAl$_2$ is easily seen. The puckered E hexagon layers are present in both structures. In SrAl$_2$ they are connected by long Al-Al interlayer bonds, which are cut in SrAl$_2$H$_2$ and terminated by hydrogen atoms. This yields a two-dimensional polyanion [Al$_2$H$_2$]$^{2-}$ which formally is electron precise. The occurrence of polyanions with both, Al-Al and Al-H bonds has not been observed earlier. Instead, main group Al-hydrides feature isolated tetrahedral or octahedral complexes [AlH$_4$]$^-$ and [AlH$_6$]^3
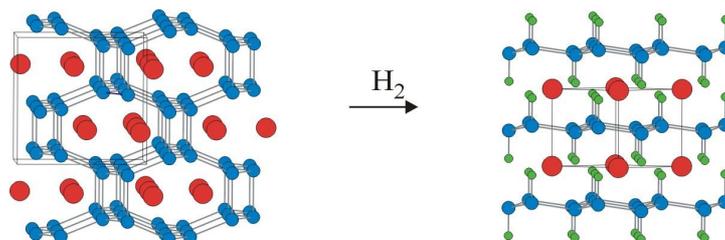
Reaction of SrAl$_2$ reacting with H$_2$ (left) to form SrAl$_2$H$_2$ (right) viewed along [110].
Red, blue, and green circles denote Sr, Al, and H atoms, respectively.

Among the gallides and the ternary alloys hydrogen adds directly to the network to form hydrides isostructural to SrAl$_2$H$_2$. How the hydrogenation reactions proceed in detail is unknown.
The compound SrGa$_2$H$_2$ was not easy to detect in the powder diffractogram. This is explained by very similar cell parameters between the hydride and alloy. However the peak intensities show some differences. Peaks that especially distinguish the hydride from the alloy are marked with arrows in 3.7.1.

3.7.1. Calculated intensity data for SrGa$_2$ and SrGa$_2$H$_2$ with the same cell parameters

H	K	L	2Theta/deg	d/Å	SrGa$_2$ I/rel.		SrGa$_2$H$_2$ I/rel
0	0	1	18.749	4.72910	7.53		5.93
1	0	0	23.270	3.81952	0.82		0.63
1	0	1	30.050	2.97140	100.00		100
0	0	2	38.024	2.36455	18.33		16.56
1	1	0	40.890	2.20520	44.72		45.94
1	0	2	45.057	2.01047	0.27	←	3.77
1	1	1	45.340	1.99859	4.12		3.44
2	0	0	47.575	1.90976	0.11		0.10
2	0	1	51.570	1.77082	21.67		21.79
1	1	2	57.063	1.61271	34.28		30.85
0	0	3	58.504	1.57637	0.33		0.08
2	0	2	62.460	1.48570	0.11		1.53
1	0	3	63.827	1.45714	11.95		12.71
2	1	0	64.495	1.44364	0.11		0.10
2	1	1	67.820	1.38074	20.50		20.66
1	1	3	73.835	1.28241	1.02		0.24
3	0	0	74.461	1.27317	8.73		8.06
2	1	2	77.389	1.23215	0.17	←	1.90
3	0	1	77.594	1.22940	0.90		0.77
2	0	3	78.635	1.21571	7.53		7.95
0	0	4	81.316	1.18228	2.49		1.54
1	0	4	86.006	1.12941	0.09	←	2.75
3	0	2	86.810	1.12100	13.88		12.48
2	2	0	88.633	1.10260	6.84		6.93

The Al-Al distance in $SrAl_2H_2$ is considerably reduced (2.64 Å) compared to the interlayer distances in $SrAl_2$ and corresponds much closer to what is considered an Al-Al single bonded distance.

3.7.2. Cell parameters and atomic positions of $SrAl_2D_2$, $SrGa_2H_2/D_2$ and $BaGa_2H_2/D_2$

Compound	$SrAl_2D_2$[5]	$SrGa_2H_2/D_2$	$BaGa_2H_2/D_2$
Z	1	1	1
a, Å	4.5253(1)	4.4010(4)/4.3932(8)	4.5334(6)/4.5286(5)
c, Å	4.7214(2)	4.7109(4)/4.699(1)	4.9069(9)/4.8991(9)
V, Å^3	83.73	79.02/78.54	87.33/87.01
T, K		295	295
R_{Bragg}		4.73	4.51
R_p		11.9	10.4
R_{wp}		12.0	11.5
Ae(0, 0, 0)			
Ae/B_{eq}	0.0148(6)	0.45(10)	0.61(7)
E(1/3, 2/3, z)	0.4589(7)	0.4656(7)	0.4680(4)
E/B_{eq}	0.0106(4)	0.17(6)	0.78(4)
D(1/3, 2/3, z)	0.0976 (4)	0.1067(8)	0.1232(4)
D/B_{eq}	0.0275(5)	2.03(8)	1.75(5)

Refinement results for $AeGa_2H_2/D_2$ (cell parameters obtained from X-ray data)

3.7.3. Interatomic distances (Å) and angles (º) in AeE_2D_2 ($SrAl_2D_2$ values are taken from ref. [7]).

The Ga-Ga distances in $SrGa_2$ are 2.52 and 2.57 Å for $BaGa_2$ respectively. In $AeGa_2H_2$ they are widened to 2.56 and 2.63 Å. This is in accord with the idea that the stronger bonded Ga-Ga bonded π-system is destroyed in the precursor upon hydrogenation and that the Ga atoms become four-coordinated in the hydride.

	$SrAl_2D_2$	$SrGa_2D_2$	$BaGa_2D_2$
Ae-D 6x	2.653(1)	2.586(1)	2.683(1)
Ae-E 6x	3.394(2)	3.350(2)	3.477(1)
Ae-E 6x	3.654(2)	3.569(2)	3.692(2)
E-D 1x	1.706(4)	1.687(5)	1.689(3)
E-E 3x	2.641(1)	2.557(1)	2.6334)
D-E 1x	1.706(4)	1.687(5)	1.689(3)
D-Ae 3x	2.653(1)	2.586(1)	2.683(1)
D-D 3x	2.770(1)	2.727(3)	2.880(2)
E-E-E	117.88(2)	118.42(6)	118.60(4)
E-E-D	98.5(2)	97.3(1)	96.8(1)

3.8. Ternary hydrides AeAlSiH, there Ae = Ba, Ca and Sr (Paper I, IV and V)

AeAlSiH has got a similar structure, (space group *P3m1,* no 156), to previous gallides and aluminide but with the half hydrogen content. The aluminium-hydrogen bond is slightly polarized due to the electro negativity difference between the elements. Silicon does not bond to hydrogen instead it

coordinates an electron lone pair. These hydrides have a strictly ordered network with alternating –Al-H and –Si- entities.
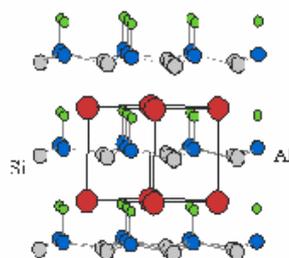
Crystal structure of AeAlSiH) viewed along [110]. Red, blue, and green circles denote Ae, Al, Si, and H atoms, respectively.

3.8.1. Cell parameters of the ternary hydrides CaAlSiH, SrAlSiH and BaAlSiH

|	CaAlSiH	SrAlSiH	BaAlSiH
a (Å)	4.1278(7)	4.2139(3)	4.3186(4)
c (Å)	4.7618(9)	4.9550(6)	5.2080(9)
V (Å^3)	70.27	76.20	84.12
Z	1	1	1

The neutron powder diffractograms of SrAlSiD and BaAlSiD were straight forward to refine, a larger challenge was to refine the spectrum of CaAlSiD. The fast synthesis of CaAlSiD resulted in a not well defined micro structure. Poorer crystallinity among c-direction was manifested by anisotropic broadening of the 00l reflection peaks. These were twice as broad as the (hk0) reflections and (hkl) reflections were in between. Intercalation of hydrogen along c-axis is probably the reason for this trend in broadening of the reflections.

3.8.2. Distance table of the AeAlSiH hydrides (Ae= Ca, Sr and Ba)

	CaAlSiD	SrAlSiD	BaAlSiD
Ae-H	2.420(4)	2.478(1)	2.581(1)
E-E	2.420(4)	2.498(2)	2.528(3)
E-H	1.75(3)	1.768(9)	1.73(2)

3.8.3. Different composition BaAl$_{2-x}$Si$_x$H$_{2-x}$, (0.4 < x < 1.6)

We wanted to study how changes in the Al/Si composition among BaAlSiH affected the structure. It was assumed that hydrogen sticks to aluminium as this was observed for all the AeAlSiH compounds. Hypothetical BaAl$_2$H$_2$ and BaSi$_2$ constitute the end points in a theoretically full range solid solution of the BaAl$_x$Si$_{2-x}$H$_x$ network. However the practical solid solution range is narrower, 0.4 < x < 1.6. The structure of BaAlSiH closely relates to the high pressure trigonal BaSi$_2$
The c-axis expands as the (Al-H)$^-$ entities are substituted by an increasing number of repulsive (Si)$^-$-lone pairs indicating that these need more space than the (Al-H)$^-$ entities, making the silicon rich compounds more puckered.
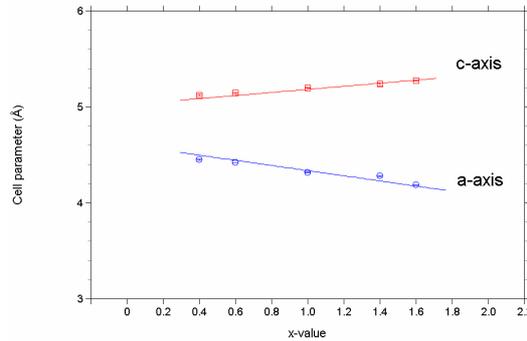
Cell parameters from powder diffractograms of BaAl$_{2-x}$Si$_x$H$_{2-x,}$ (0.4 < x < 1.6)


4.   Properties of the different hydrides (Papers I-V)

4.1. Diffuse reflectance measurements (Paper I and IV)

Optical diffuse reflectance measurements were made on the finely grounded ternary hydrides at room temperature. The spectrum was recorded in the region 3200 – 10500 cm^{-1} with a Bruker Equinox 55 FT-IR spectrometer equipped with a diffuse reflectance accessory (Harrick). The measurement of diffuse reflectivity can be used to determine band gaps. For this, absorption data were extracted from the reflectance data by using the Kubelka-Munk function *; that allows the optical absorbance of a sample to be approximated from its reflectance, R [34]:

$$* F(R) = (1-R)^2/2R$$

A Tauc Plot there *(F(R).hv)^n* is plotted vs *hv* can be obtained from measured data. If n is ½ the compound is a direct semi conductor. If a better line could be fitted to the absorption edge when n is 2 an indirect gap is measured.

[35]
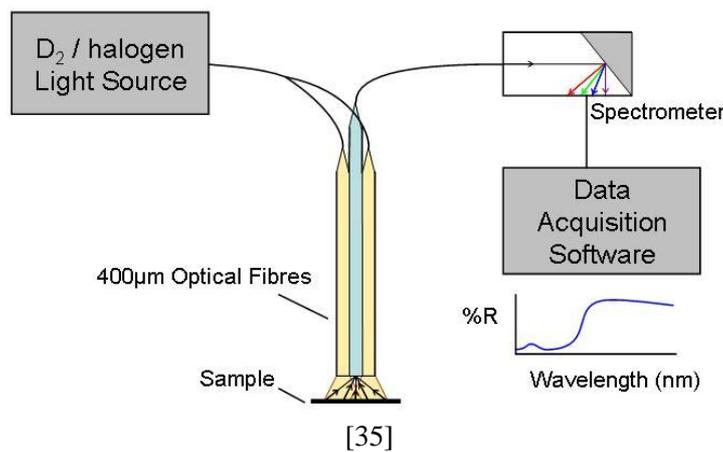
All three hydrides, BaAlSiH, CaAlSiH and SrAlSiH were measured with this method. It should be kept in mind, however, that small band gaps are difficult to measure correctly. Errors in the fit procedure as well as uncertainties in hydrogen content and possible topological disorder add to these difficulties. The measured values are 0.47 eV, 0.74 eV and 0.63 eV respectively and the AeAlSiH satisfies n=2 in the Tauc plot. Thus these compounds are indirect semi conductors. Attempts to measure band gaps among the different compositional hydrides in the system BaAl$_{2-x}$Si$_x$H$_{2-x}$ failed

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because of impure samples. A new study with pure samples may have a possibility to determine if the band gap is tunable with the composition.

4.2. Inelastic neutron scattering (Paper III and IV)

The INS measurements were carried out using TOSCA [36], a crystal-analyzer inverse-geometry spectrometer operating at the ISIS pulsed neutron spallation source (Rutherford Appleton Laboratory, UK), accessing an energy transfer from 0 to 4000 cm^{-1}, providing an excellent energy resolution, ΔE, (delta E/E=1.5-3%). Special care was taken to prevent possible alkaline earth hydroxide formation by working in an inert-gas glove box. The powders were loaded into flat aluminum cells and mounted into the TOSCA closed-cycle refrigerator at 20 K. The low temperature is used to decrease the thermal vibrations. INS is a good method to study hydrogen bonds because of hydrogen's high incoherent cross section for neutrons, in addition, all modes are possible to observe.

The Zintl hydrides Al-H stretching modes correspond to the lowest energies observed for aluminium hydrogen bonds, the lowest value was measured for SrAlSiH. This was already indicated from the Al-H bond distance, which is larger in SrAlSiH, 1.77 Å, compared to $SrAl_2H_2$, 1.71, indicating a stronger covalent bond in $SrAl_2H_2$. However these compounds are stabilized by their ionic lattices making them more stable then the alanes.
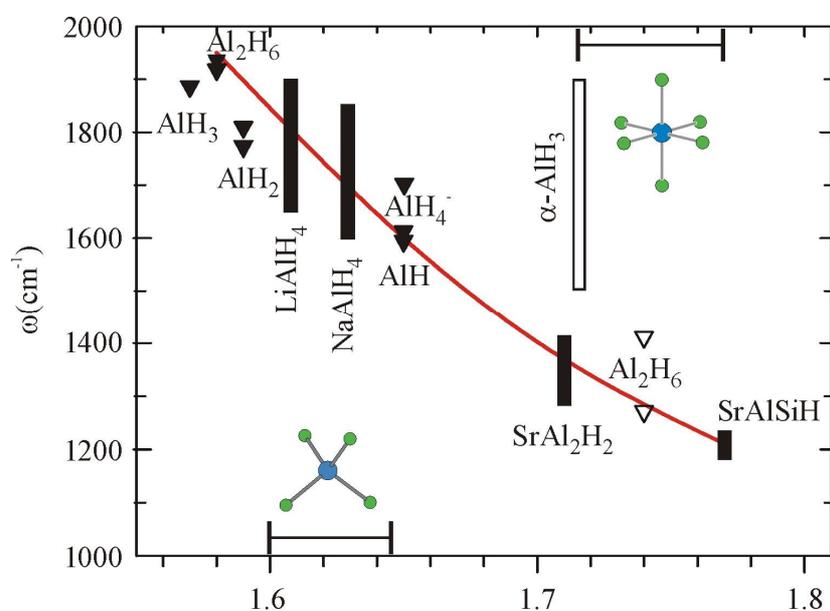
Compilation of experimentally obtained Al-H stretching frequencies over Al-H distances in various systems: triangles represent molecular compounds and extended bars (dispersed) solid state systems. Open symbols indicate Al-H-Al bridging units, solid symbols terminal Al-H bonds. Two markers show the range of Al-H distances in tetrahedral [AlH$_4$] and octahedral [AlH$_6$] ensembles in solid state hydrides. The red line is a guide to the eye.

4.3. Thermal investigation setup (Paper I, II and IV)

The thermal behaviour of powdered samples was investigated by differential thermal analysis (DTA-TG 1600, Labsys^{TM}). The aluminide and gallide hydrides were placed in a steel container which was sealed with a gold foil to prevent exposure to air and moisture and temperature was raised from 40 to 400 ^{o}C. The AeAlSiH hydrides were placed in corundum crucibles which were heated from 40 to 800 ^{o}C under a continuous flow of dry Ar. For all runs the temperature increase rate was 5 K/min. We also investigated the AeAlSiH compounds by heating them, in an evacuated reactor, to record the

temperature when the pressure first increased. A very qualitative method as the heating rate was uncontrolled.

4.4. Stability of the Zintl hydrides

Comparing $SrAl_2H_2$ to the two gallide hydrides, $SrGa_2H_2$ and $BaGa_2H_2$, the later were observed to decompose at 300 ^oC, forming mixtures of AeH_2 and $SrAl_4$ or $AeGa_4$.

The 1:1:1 composition ternary hydrides have an increased thermal stability. The observed dissociation temperature for SrAlSiH and BaAlSiH is 600 ^oC at one atmosphere, or 500 ^oC in vacuum. CaAlSiH was observed to decompose at lower temperature, 400 ^oC in vacuum. For CaAlSiH its corresponding stable 1:4 phase and AeH_2 easily tend to form. When hydriding CaAlSi the formation of CaAlSiH competes with $CaAl_2Si_2$ and CaH_2 as hydrogenation products. The latter route is thermodynamically preferable. $CaAl_2Si_2$ forms under CaAlSiH synthesis, together with amorphous CaH_2. If an evacuated reactor with an intimate mixture of $CaSi_2Al_2$ and CaH_2 is heated to 600 ^oC CaAlSi forms. The reaction to CaAlSi probably takes place at lower temperatures but at a slow rate.

However, no definite conclusions concerning decomposition temperatures among these compounds should be drawn without performing proper equilibrium measurements of pressure versus temperature.
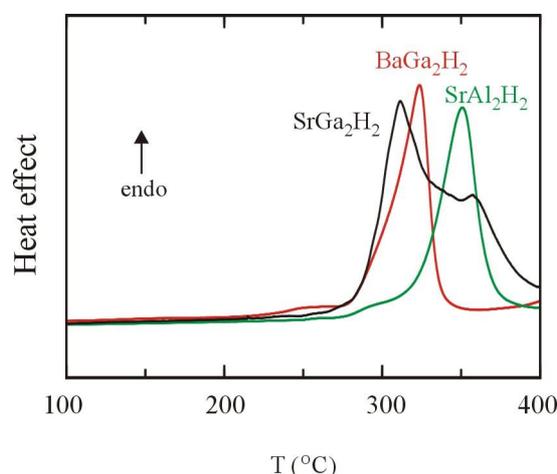
DTA heating curves for SrAl₂H₂, SrGa₂H₂, and BaGa₂H₂

$SrAl_2H_2$ is sensitive to humidity and decomposes in air after a short time. We exposed a small amount of $SrAl_2H_2$ to air (295 K and normal humidity) and recorded an x-ray powder film of the sample. After five hours in air the diffraction lines of $SrAl_2H_2$ disappeared completely. Remarkably SrAlSiH was stable to neutral water and air. Storage of the hydride under water for a week did not affect the hydride; no changes were possible to observe with x-ray investigation. Over a long time probably SrAlSiH is protonated the by water to form hydrogen gas, amorphous strontium hydroxide, alane and silane gas similar to the carbides and their reactions with water giving unsaturated hydrogen carbons as result.

5. Summary

The synthesised Zintl hydrides $SrGa_2H_2$, $BaGa_2H_2$, BaAlSiH, CaAlSiH and SrAlSiH represents with earlier discovered $SrAl_2H_2$ a new class of compounds. Their sensitivity to moisture and oxygen is lower compared to saline hydrides as AeH_2. This is expected since the negative charge is distributed on the poly anionic part in the Zintl hydrides compared to only on hydrogen, as in AeH_2, resulting in less basic characteristics for the poly anionic hydrides. These novel hydrides are also remarkable heat

stable compared to other hydrides containing a bor-group element. Especially stable are the one to one stoichiometric silicon containing hydrides. The Al-H bond is weaker in these Zintl hydrides compared to the Al-H bonds in alane, probably the ionic interactions in the Zintl hydrides stabilizes them. Hydrogenation of aluminium and gallium to form E-H bonds, e.g. EH_3, require an extremely high hydrogen pressure [37]. If instead alkaline metal alanates are synthesised from their elements these form already at 100-200 bars, but the process requires catalysis to proceed at a measurable rate [38]. Even better is if the E-element already is in a reduced state, as in our precursors, then the reaction with hydrogen takes place at rather mild conditions (see the experimental part.) To synthesise Zintl hydrides as $SrAl_2H_2$, $SrGa_2H_2$ and $BaGa_2H_2$ the precursor must have a poly anionic structure which is very close to the final hydride structure. Therefore compounds as $Ba_{21}Al_{40}$ and $CaAl_2$ with Laves structure and synthesis reactions like $AeH_2 + 2Ga$, which in principle allow low reaction temperatures, do not result in AeE_2H_2 hydrides. On the other hand the ternary compounds BaAlSiH and SrAlSiH can be made from AeH2, Al and Si, probably this is possible because of their stable AeAlSi precursors.

It is not clear whether Zintl hydrides with entities E-H (there E is not a group 13 element) exist and how hydride formation depends on the choice and especially the concentration of the cation (e.g. the stoichiometry and the oxidation state on the anionic component). This opens up opportunities to manufacture several similar compounds and to explore new properties and behaviours among these types of novel hydrides.

6.   Acknowledgements

7.   References

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