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Projekt

Destabilisation of metal hydride complexes and theoretical modelling

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Zusammenfassung

Catalysed desorption experiments on the iron based complex metal hydride Mg_2FeH_6 confirm the beneficial influence of catalysts such as $TiCl_3$ on its desorption kinetics but give less conclusive results on manganese based Mg_3MnH_7. The dynamics of metal hydride complexes has been investigated in lithium boro-hydride $LiBH_4$. This light-weight metal hydride (18.5 wt.% hydrogen) contains tetrahedral $[BH_4]^-$ complexes that decompose at 200°C in the presence of catalysts. Diffraction experiments and Raman spectroscopy in the absence of catalysts reveal an order-disorder transition at ~110°C and a considerable softening of the structure. The integrity of the tetrahedral $[BH_4]^-$ complexes, however, is maintained. Modelling of the conventional metal hydrides $LaNi_5$ and its derivatives $A(B,B')_5$ used in commercial nickel-metal hydride battery electrodes shows that these compounds occupy a rather well defined stability domain within the three-parameter space of valence electon concentration, electronegativity difference, and atomic radius ratio. Based on these modelling results four new intermetallic compounds of composition $LaNi_2Mn_3$, $LaMg_2Ni$, $LaMgNi_4$ and $NdMgNi_4$ were discovered and found to show interesting hydrogen sorption properties. They yield ternary and quaternary metal hydrides of composition $LaNi_2Mn_3H_4$, $LaMg_2NiH_7$, $LaMgNi_4H_4$ and $LaMgNi_4H_4$ that are reversible and have dissociation temperatures as low as 100°C at 1 bar hydrogen pressure and hydrogen capacities of up to 2.8 wt.%. Some are "interstitial" hydrides while others contain hydride complexes based on transition metals ($[NiH_4]^{4-}$, $[Ni_4H_4]^{5-}$) and thus constitute links between "interstitial" (usually metallic) and "complex" (usually non-metallic) metal hydrides. These results show the usefulness of the theoretical modelling approach for predicting new metal hydrides. Among the conventional hydrides $CeMn_{1.8}Al_{0.2}$ was found to absorb ~10% more hydrogen (~4.4 hydrogen per formula unit) than the previously investigated less manganese rich $CeMn_{1.5}Al_{0.5}$. The hydrogenation reaction occurs near ambient conditions and leads to a volume expansion of ~43 % that is the biggest known among reversible metal hydrides. The compound shows interesting hydrogenation properties and is cheap to fabricate but suffers from segregation if hydrogenated too rapidly.

Aim of the project

Compared to other reversible hydrogen storage media such as compressed gas cylinders metal hydrides have the advantage of higher volume efficiencies and greater safety [1]. Their hydrogen densities usually exceed that of liquid hydrogen while their risk of accidental ignition or explosion is minimal. Demonstration units are successfully used in the transportation sector (cars in Japan, USA and Germany), for energy storage (photovoltaic hydrogen production plants in USA, Italy, Spain, Germany and Switzerland) and for energy conversion (fuel cells). Drawbacks are their relatively high weights and costs of fabrication, and – at least for some of them - their high thermal stability and/or low desorption speed. Compounds belonging to the class of so-called "complex" metal hydrides are excellent candidates for hydrogen storage applications. Mg_2FeH_6 and Mg_3MnH_7, and $NaAlH_4$ and $LiBH_4$ are well known examples based on transition (*d*-) and main-group (*p*-) metals, respectively. They display high capacities (hydrogen/metal weight ratios >5wt.% for d-metal and >10% for p-metal complexes) and low fabrication costs (<20 Frs/kg), but suffer from high thermal stability (dissociation temperature T~300°C) and/or low desorption kinetics [2,3]. This project aims at the destabilisation of these type of metal hydrides. Three routes are chosen. The first (A) consists of testing suitable catalysts such as those used successfully for alanates [3]. Preliminary results on Mg_2FeH_6 obtained within the previous project (BEF No 31043) have shown that desorption in the presence of $TiCl_3$ starts already at 200°C as compared to 300°C without catalyst. The second route (B) attempts isomorphous replacement of elements such as magnesium and iron/manganese in Mg_2FeH_6 by divalent metals such as zinc. The third route (C) attempts to model the existence and thermodynamic stability of known metal hydrides by crystal chemistry arguments and to use the model for the search of novel metal hydrides.

Work performed and results obtained

A. Destabilisation of metal hydride complexes by catalysts: Following our encouraging results on Mg_2FeH_6 (see previous progress report) we have extended the catalysed desorption experiments to Mg_3MnH_7 in collaboration with K.Gross (Sandia Nat. Labs., U.S.A.). While first attempts showed signs for improvement no conclusive results have been obtained so far. On the other hand, we have investigated hydrides containing *p*-metal complexes that were originally not included in the project. Among these the light-weight lithium boro-hydride $LiBH_4$ (18.5 wt.% hydrogen) was of particular interest because it was found to decompose at 200°C in the presence of "catalysts" such as SiO_2 (A. Züttel, private communication). We have characterized this compound for the first time with respect to crystal structure [4] and Raman spectra [5]. At room temperature its structure is orthorhombic and contains tetrahedral $[BH_4]^-$ anions that are strongly distorted (point symmetry *m*) and aligned along two orthogonal directions. As the temperature is increased the structure becomes hexagonal. The $[BH_4]^-$ tetrahedrons align along *c* and become more symmetric (symmetry 3*m*). The Raman data [5] support these features on a local level. As the temperature is increased, the sudden disappearance of mode splitting points to the onset of a structural phase transition. The transition occurs at ~110°C, is of first-order and has a hysteresis of about 8°C. A strong and discontinuous broadening of bands remaining after the transition suggests that the $[BH_4]^-$ tetrahedrons continue to vibrate at increasing amplitudes (see Fig. 1). However, up to 150°C there is no evidence for a possible decomposition of these complexes. These results are of importance from a kinetics point of view because they suggest that in the absence of catalysts the compound - like the related alanates - undergoes a significant softening of its structure while the integrity of its tetrahedral $[BH_4]^-$ complexes is maintained.

B. Destabilisation of metal hydride complexes by substitution: Following our attempts to destabilize the $[FeH_6]^{4-}$ complexes in Mg_2FeH_6 by substituting Mg and/or Fe by Zn (see previous progress report) we have re-investigated the solid solution series $Ce(Mn_{1-x}Al_x)_2$. The compounds form "interstitial" rather than "complex" hydrides. One member has been studied before by our colleges at the University Fribourg [6] at the composition $CeMn_{1.5}Al_{0.5}$ (x=0.25) and found to absorb up to ~4 deuterium atoms per formula unit (f.u.) at room temperature and 25 bar pressure, thereby undergoing a lattice expansion of ~34%. Our work [7] on the more manganese rich composition $CeMn_{1.8}Al_{0.2}$ (x=0.1) shows that it absorbs ~10% more hydrogen (~4.4 H/f.u.) already at lower pressure (~10 bar) and undergoes a volume expansion of ~43 % that is the biggest known among reversible metal hydrides. Furthermore, the compound shows for the first time a hydrogenation induced metal atom exchange at/or below room temperature. While the Mn/Al distribution in the alloy is partially ordered it is disordered in the hydride, even after slow hydrogenation. Only very slow hydrogenation while cooling the sample to low temperature (-70°C) is capable of maintaining the partial Mn/Al order in the structure. The exceptional mobility of the metal substructure during hydrogenation together with its very large volume expansion is attributed to a valence change of cerium ($Ce^{IV} \rightarrow Ce^{III}$). Magnetic susceptibility measurements confirm this hypothesis and show that the valency change is partly reversible at low temperature. This result is encouraging because it shows that already low concentrations of substituting elements (Al) lead to a significant increase of both hydrogen capacity and mobility of the metal substructure and thus improve the hydrogenation properties. However, while $CeMn_{1.8}Al_{0.2}$ has good absorption properties and is relatively cheap to fabricate it suffers from the requirement to keep hydrogenation speeds low in order to prevent (irreversible) precipitation of binary CeH_{2+x}.

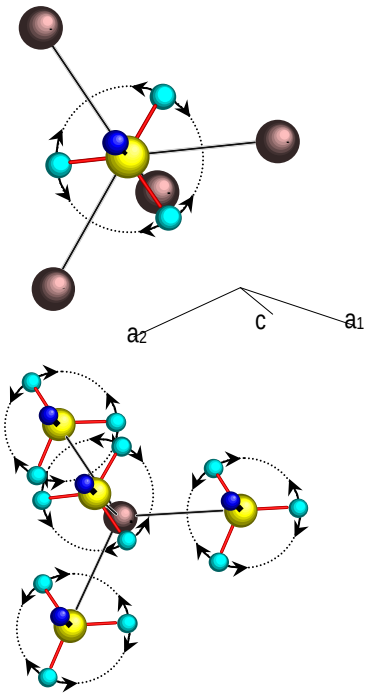
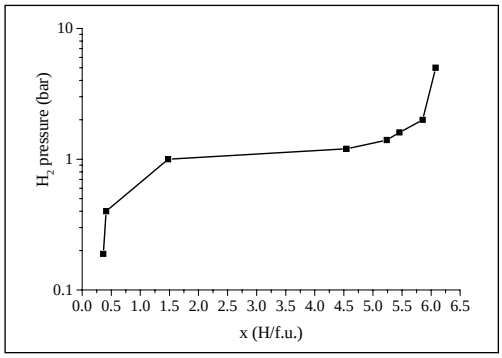


Fig. 1: Librations of the tetrahedral $[BH_4]^-$ complexes in hexagonal $LiBH_4$ about their trigonal axis at 408 K (see arrows). Lithium surrounding $[BH_4]^-$ (top) and $[BH_4]^-$ surrounding lithium (bottom).

C. Structure modelling and search for new metal hydrides: The structural stability of AB_5 compounds (A=lanthanide, alkaline earth, transition element; B=*d*- and/or *p*-block element) has been modelled in terms of atomic properties and represented in the form of structure stability maps [8,9]. The results on some 520 known binary and ternary known representatives show that the various structure types form rather well defined stability domains in three-dimensional space spanned by valence electron concentration (VEC), electronegativity difference ($\Delta\chi$), and radius ratio (R_A/R_B). Hexagonal $CaCu_5$ type compounds, for example, occur within the intervals $5.5<VEC<9.5$, $-0.3<\Delta\chi<0.1$ and $1.3<R_A/R_B<1.5$. Clearly, such maps are of interest for the search of new hydrogen storage materials, in particular those containing light and inexpensive 3*d* transition metals (Fe, Mn *etc*) and electropositive alkali/alkaline earth metals (Li, Na, Mg, Ca), or light rare earth elements (La, Ce, Mischmetall). The predictive power of these maps has been demonstrated by the discovery of the following new hydrogen absorbing compounds.

$LaNi_2Mn_3$: The compound has been synthesized by induction melting and found [10] to crystallise with the hexagonal YNi_2Al_3 type structure that is distinctly different from the $CaCu_5$ type structure of the classical hydrogen storage material $LaNi_5$ and its substitution derivatives. It absorbs reversibly up to 5.6 hydrogen atoms per formula unit near ambient conditions (60°C), i.e. its capacity exceeds that of the end member of the $LaNi_{5-x}Mn_x$ ($CaCu_5$ type) series ($LaNi_3Mn_2$: 4.8 H/f.u. at 60°C). The structure of the hydride remains hexagonal and contains "interstitial" hydrogen that is disordered. As shown in Fig. 2 (left) the hydrogen absorption plateau (~1 bar at 60°C) is relatively well developed and in a more useful pressure range than that of $LaNi_3Mn_2$ (~10^{-5} bar at 60°C). Its kinetics (Fig. 2 right) is relatively slow at the beginning of the hydrogenation reaction but becomes rather fast once the reaction has started, which indicates that it can be improved by activation.



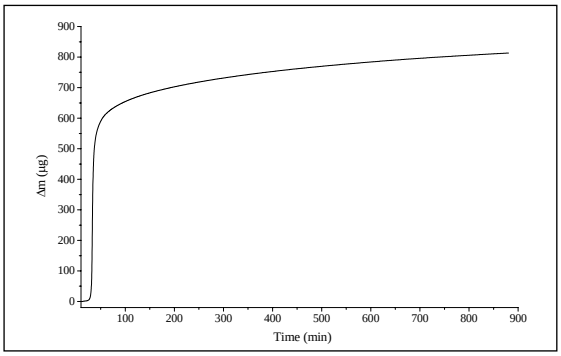


Fig. 2: Pressure-composition isotherm of $La_{1.07}Ni_2Mn_3$ at T=60°C (**left**) and mass increase versus time at 60°C and 1.5 bar hydrogen pressure (**right**) as measured on a microbalance

The calculated hydrogen densities of $LaNi_2Mn_3H_5$ are 1.42 wt.% and 82.5 $g.H_2.l^{-1}$. Thus the hydrogenation properties of $LaNi_2Mn_3$ are distinctly different from those of $LaNi_3Mn_2$ having similar composition. The relatively abrupt changes of hydrogenation properties as a function of Ni/Mn ratio are attributed to the structural differences between the alloys that lead to different hydrogen environments and thus different metal-hydrogen interactions in the hydrides. The new compound $LaNi_2Mn_3$ has relatively good hydrogen storage properties and may be useful for applications. Its discovery underlines the usefulness of modelling the structural stability of intermetallic compounds for the search of new hydrogen storage materials.

LaMg2Ni: The compound has been prepared by induction melting and found [11] to crystallize with the orthorhombic $MgAl_2Cu$ type structure. It absorbs hydrogen near ambient conditions (<200°C, <8 bar) thereby forming a quaternary metal hydride of composition $LaMg_2NiH_7$. The calculated hydrogen storage efficiencies are 2.8 wt.% and 109.5 $g.l^{-1}$. The interstices of the monoclinic distorted metal substructure are filled by hydrogen atoms that are nearly ordered. Interestingly, the H atom distribution can also be described in terms of two symmetry independent tetrahedral $[NiH_4]^{4-}$ complexes and six H^- anions in tetrahedral metal configurations, as shown by the limiting ionic formula $La^{3+}Mg^{+2}{}_2.[NiH_4]^{4-}.3H^-$. Thus the compound should be considered as a link between "complex" and "interstitial" metal hydrides. Similar compounds are likely to exist in other systems and may open the door for new classes of metal hydrides.

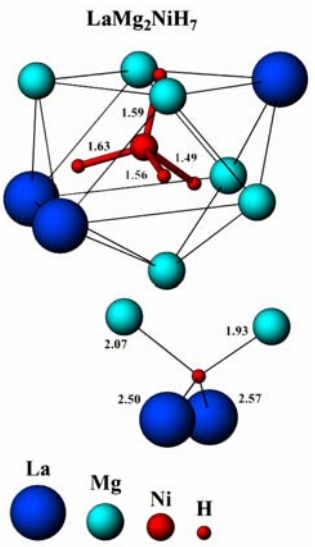


Fig. 3: Metal hydride complex $[NiH_4]^{4-}$ and hydride anion H^- in monoclinic $LaMg_2NiH_7$; metal-hydrogen distances (Å) refer to the deuteride.

LaNi4Mg and NdNi4Mg: The compounds have been prepared by induction melting and found [12] to crystallise with the cubic $MgCu_4Sn$ type structure. They absorb reversibly up to 4 hydrogen atoms per formula unit at 7-8 bar and ~50°C while undergoing an orthorhombic lattice distortion. The hydrogen storage efficiencies of the neodymium compound ($NdNi_4MgH_4$) are 0.99 wt.% and 65.05 $g.H_2.l^{-1}$. Hydrogen occupies almost fully three deuterium sites of which two are coordinated by a trigonal metal bipyramid ($[A_2B_3]$ apices: A=2Nd, base: B=2Ni,Mg) and one is coordinated by a metal tetrahedron ($[AB_3]$ A=Nd, B=3Ni). However, as shown in Fig. 4 the hydrogen distribution can also be interpreted in terms of tetrahedron shaped $[Ni_4H_4]^{5-}$ moieties that are reminiscent of metal hydride complexes in complex metal hydrides.

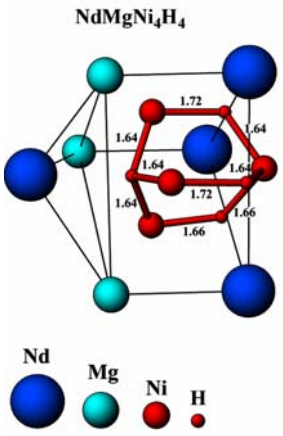


Fig. 4: Metal hydride complex $[Ni_4H_4]^{5-}$ in orthorhombic $NdMgNi_4H_4$; metal-hydrogen distances (Å) in refer to the deuteride

Thus the compound constitutes a further link between "interstitial" and "complex" metal hydrides. The hydride is stable at room temperature under 1 bar hydrogen pressure and desorbs rapidly at 80°C under vacuum. Interestingly, it decomposes under air by catalytic water formation. The practical relevance of this discovery is subject of current investigations.

In conclusion, structure modelling has lead to the discovery of four novel metal hydrides that are reversible and have dissociation temperatures as low as <100°C at 1 bar hydrogen pressure and hydrogen capacities up to 2.8 wt.%. While some are "interstitial" hydrides others contain transition metal hydride complexes and thus can be considered as links between "interstitial" (usually metallic) and "complex" (usually non-metallic) metal hydrides (for a recent review on such "links" see [13]). Altogether the results show the usefulness of the theoretical modelling approach for predicting new metal hydrides.

National collaboration

The project has benefited from collaborations with the *University of Fribourg* in the field of boro-hydrides (group of Professor Schlapbach) and with the *Paul-Scherrer Institute* (Villigen) in the fields of applications of metal hydrides (catalytic burner) and scattering experiments (*SINQ, SLS*). The collaborations were extremely fruitful und essential for the project. Funding by the *Swiss National Science Foundation* and the *University of Geneva* has allowed the manpower to be raised to the level necessary for the project.

International collaboration

The project is integrated into the *International Energy Agency* (IEA) agreement on the production and utilisation of hydrogen; *Task 17* : '*Solid und Liquid State Hydrogen Storage Materials*' (operating agent : Gary Sandrock, Ph.D.). The task target is the identification of a formulation technique for a material that is capable of 5 wt.% hydrogen capacity (target A) with a dehydriding temperature of less than 80°C at 1 bar hydrogen pressure (target B). The collaborations resulting from this international effort allowed us to interact with researchers across the world, such as with Dr. K.Gross (Sandia National Laboratories, U.S.A.) whose contribution to the catalysed desorption work of the present project was essential.

Assessment of the year 2002 and outlook for 2003

Among the various routes tested to destabilize known metal hydrides and to find new metal hydrides that of modelling (route C) was clearly the most successful. During the year 2002 new compounds were found/investigated that meet either target A or target B of task 17 of the IEA. Unfortunately, compounds meeting both targets simultaneously have not been found as yet. Thus the primary aim of the work during the year 2003 will be to search for such compounds. There is hope for success, in particular by following the modelling approach. The results obtained during the year 2002 in the frame of this project have lead to 8 scientific publications (see No 4, 5, 7, 9, 10, 11, 12, 13 in the list below). The situation concerning possible patent applications for the novel compounds $LaNi_2Mn_3$, $LaNi_4Mg$ and $NdNi_4Mg$ is currently examined.

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