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HYDROGEN STORAGE IN NEW COMPLEX HYDRIDES (COMPHY)

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ABSTRACT

Complex hydrides i.e. alanates (e.g. $Na[AlH_4]$) as reversible hydrogen storage materials were first described by Boris Bogdanovic in 1996 at the MH96 conference in Les Diablerets, Switzerland. In 2001 Züttel and coworkers have started to investigate related complexes the borohydrides (e.g. $Li[BH_4]$) as hydrogen storage materials. The borohydrides offer a much greater gravimetric hydrogen density as compared to the alanates. The hydrogen absorption and desorption mechanism as well as the role of the catalyst are still not known. Furthermore, the structure of the complex ion e.g. $[BH4]^-$ during the hydrogen desorption is investigated and the hydrogen dynamics in the lattice is modelled. These measurements are supplemented by UV-vis spectroscopy and isotope exchange experiments (hydrogen-deuterium). The final goal of the project is to describe the mechanism of the hydrogen sorption reaction in great detail together with the physical properties of the compounds as a function of the hydrogen concentration. This work represents also the contribution to the IEA Task 22.

Projektziele

Workpackage 1: Local environment of the catalyst

Titanium is used in $Na[AlH_4]$ as a catalytic active additive for the thermal desorption of hydrogen at temperatures far below the melting temperature. However, since the discovery of the catalyst in 1996 and despite an extensive research activity the role of the catalyst is still not known. It is not even known in what chemical state the catalyst acts. Therefore, a local probe like EXAFS allows investigating the chemical state and the local environment of the catalyst in-situ and the results lead to a better understanding of the mechanism. EXAFS experiments at the synchrotron (SLS, PSI) on model complexes like $Na[AlH_4]$ during the hydrogen desorption will be carried out and the chemical state as well as the local environment will be described during the hydrogen desorption reaction.

Workpackage 2: Local structure of $[BH_4]^-$

The stability of the $[BH_4]^-$ strongly depends on the localisation of the electron on the boron atom. Therefore, the structure of the $[BH_4]^-$ is crucial for the desorption mechanism. Raman spectroscopy allows us investigating the relevant vibrational modes of hydrogen and deuterium. These vibrational modes are analyzed and semi-empirical models are developed for the stability of the complex hydrides.

Workpackage 3: Hydrogen diffusion

Hydrogen in the solid appears always in atomic form. However, during desorption a hydrogen molecule is formed. For metallic hydrides with a well defined lattice and surface the hydrogen diffuses through the lattice of the host metal to the surface and recombines at the surface to form a molecule. However, in a complex hydride the hydrogen diffusion is not understood nor is the surface in the multiphase system upon desorption defined. Therefore, the hydrogen diffusion is investigated by quasi-elastic neutron scattering and the diffusion sites as well as the hoping frequency are measured and related to the activation energy.

Workpackage 4: Vibrations and excitations

The distribution of the electrons between the constant atoms in the complex hydrides is defining the physical properties of the materials. By means of in-situ UV-vis-IR spectroscopy the electronic properties of the complexes is probed as well as the vibrational excitations. Therefore, it is possible to investigate the materials during the desorption process independent of the crystal structure, i.e. also in the molten state. This leads to a completely new understanding of the relevant processes during hydrogen desorption.

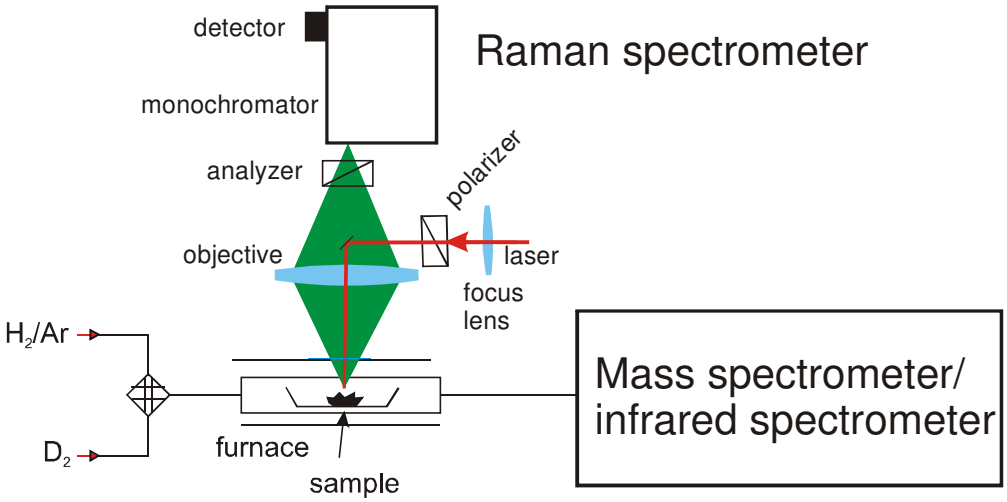
Workpackage 5: Mobility of the hydrogen in the lattice

The local hydrogen mobility does not necessarily allow a transport of the hydrogen atoms through the lattice. Only the isotope exchange experiments where the hydrogen is replaced by deuterium is a true measure of the mobility of hydrogen in the host lattice. The exchange of deuterium with hydrogen and vice versa allows the investigation of the global mobility of hydrogen and an empirical description of the diffusion process.

Durchgeführte Arbeiten und erreichte Ergebnisse

Workpackage 1: Local environment of the catalyst

Since the discovery of the catalyst in 1996 and despite an extensive research activity the role of the catalyst is still not known. The following scenario is currently discussed: the Ti-catalyst facilitates H_2 dissociation and favours the transport of metal atoms to the alanate. On the other hand, the experiments could not explain why additives with a much higher dissociation activity (e.g. Pd) have a smaller effect on sorption kinetics than Ti-compounds.[1] We could show by hydrogen-deuterium exchange experiments that NaH can also serve as an atomic hydrogen source [1]. Thus, Ti seems to facilitate yet another process. Apart from the case-study, the results demonstrate the performance of the developed methods to probe the hydrogen exchange mechanisms on the surface and in the bulk.



Sketch of the equipment developed within this project to measure the hydrogen exchange rates on surface and bulk of complex hydrides.

Recent X-ray absorption near-edge structure measurements it was proposed that 30% of the Ti resides in the Al surface and 70% is located in an interstitial place in the $NaAlH_4$ lattice, possibly forming trimeric, triangular Ti entities.[2] Our theoretical studies confirm that neutral titanium atoms are the most stable on the surface, but when incorporated into the bulk of $NaAlH_4$ interstitial Ti^{4+} cations are energetically favourable [2]. The studies explain why high oxidation states of Ti are crucial for its catalytic activity and point out that charge transfer effects are important in description of Ti in $NaAlH_4$.

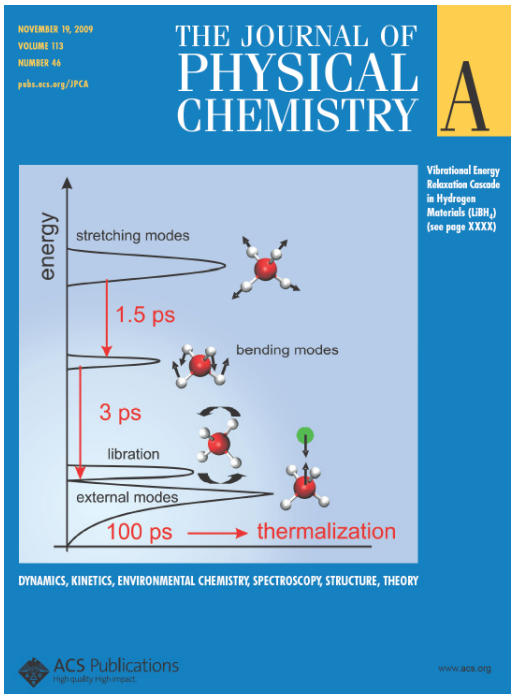
However, the additive might play an additional role than described by the electronic effect. We synthesized a catalyst for $NaAlH_4$, TiN nanopowder, through a novel method using a mechanochemical reaction. The synthesized TiN nanopowder consisted of single-crystal particles of an average particle size of 6 nm. We attempted to use it with NaAlH4 as a catalyst for hydrogen sorption reactions.[3] In comparison with $TiCl_3$ and TiB_2 nanopowder catalysts, $NaAlH_4$ with TiN nanopowder show improved hydrogen desorption rates and enhanced hydrogen capacity close to the theoretical capacity of pure NaAlH4. In contrast to the nanopowders, micron-sized TiN- and TiB_2 powders hardly exhibit the catalytic effects on the hydrogen desorption of $NaAlH_4$. In-situ XRD and Raman spectroscopy studies re-

[1] D. L. Anton, J. Alloys Compd., 2004, 356, 400–404.
[2] C. P. Baldé, H. A. Stil, A. M. J. van der Eerden, K. P. de Jong and J. H. Bitter, J. Phys. Chem. C, 2007, 111, 2797–2802.

vealed that the TiN nanopowder remains stable during the milling and dehydrogenation processes, which might help maintaining its catalytic effect during hydrogen sorption cycles.

Workpackage 2: Local structure of $[BH_4]^-$

To improve the rather slow kinetics of hydrogen evolution in $LiBH_4$ and possibly lower the decomposition/formation temperature, it is mandatory to understand the mechanism involved in the structure changes, formation, and decomposition of the compound. In particular, insight into dynamical properties, which depend on the local structure of the pseudo-atom $[BH_4]^-$, are not well understood.



Cover of the Journal of Physical Chemistry C showing the vibrational energy relaxation cascade mechanism and time-scale in $LiBH_4$. (volume 113, issue 46)

We have established the time scales of the fastest possible dynamics in metal hydrides using femtosecond IR-pump-probe and 2D-IR measurements.[4] This, together with our measurements of anharmonicities and our establishing that the vibrational bands are purely homogenously broadened represent new insights into the nature of the B-H (B-D) bond.

In addition, we have investigated the subsequent vibrational energy redistribution and thermalization process. We propose a model which includes three types of modes: the BH or BD stretching modes, which are the ones we excite in the experiment, the low frequency external modes (librational and translational), and the BH or BD bending modes in between. Finally, we completed the assignment of the stretching vibrations for all five different isotopically different $BH_{4-x}D_x$ units, aided by temperature-difference FTIR and 2D-IR spectra, and *ab initio* infrared intensity calculations. A consistent analysis is made possible by the *ab initio* calculation of intensities and the comparison of the FTIR spectra of different $BH_{4-x}D_x$ units. This led to the revision of the assignment of certain modes. The symmetry breaking induced by H/D exchange within the BH_4 unit enhances the intensity of the symmetric stretching modes significantly and enables a direct comparison with Raman spectra, where these modes are always very active. The detailed understanding of the B-D stretching modes makes it possible to study the orientational relaxation of the BH_2D_2 isotopomer by IR pump-probe polarization-dependent measurements. We find that the BH_2D_2 tetrahedral unit does not rotate within 5 ps after excitation by the pump pulse in the LT phase at room temperature. We plan to extend our measurements to the HT phase, where reorientations and thermal effects play a major role.

Future directions for this work could be to initiate the phase transition between *e.g.* the LT and the HT phases or the hydride decomposition by a temperature jump within a few 10's of picoseconds, and study its structural transition in great detail.

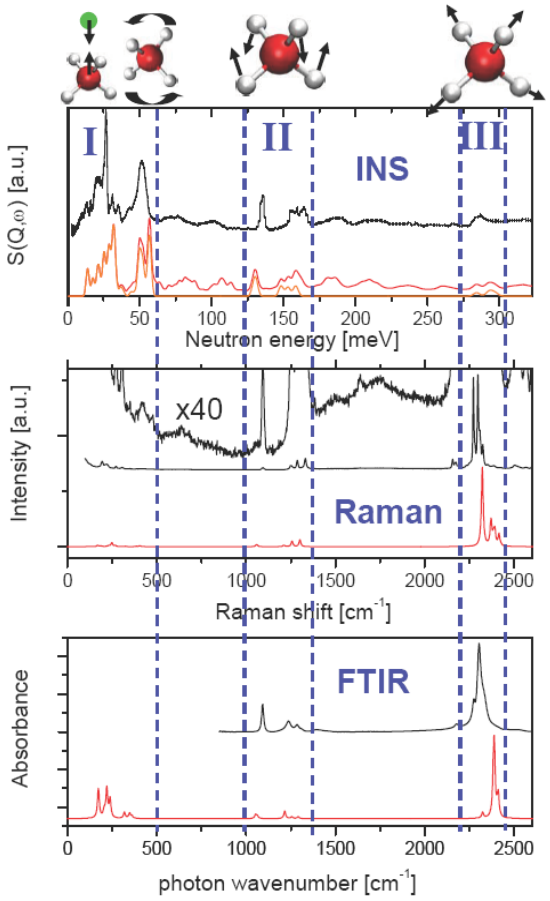
Workpackage 3: Hydrogen diffusion

The starting materials in the $NaAlH_4$ sorption cycle are NaH and Al. Surprisingly, the diffusion parameters of hydrogen in NaH are still unknown, as are the underlying mechanisms. We report on hydrogen-deuterium-exchange experiments on NaH probed by thermogravimetry.[5] From the measurements a diffusion parameter of deuterium in NaH of $D = 1.1 \cdot 10^{-17}$ $m^2/\tilde{s}$ s at 523 K is derived. The activation

energy of tracer diffusion of D in NaH is found to be 1.0 eV. The results are hints for a diffusion process mediated by neutral hydrogen vacancies. We have demonstrated the use of HD exchange experiments to derive the diffusion parameters of deuterium in NaH. The measurements confirm recent DFT calculations and thereby the hypothesis of hydrogen diffusion mediated by charge neutral hydrogen vacancies in NaH.

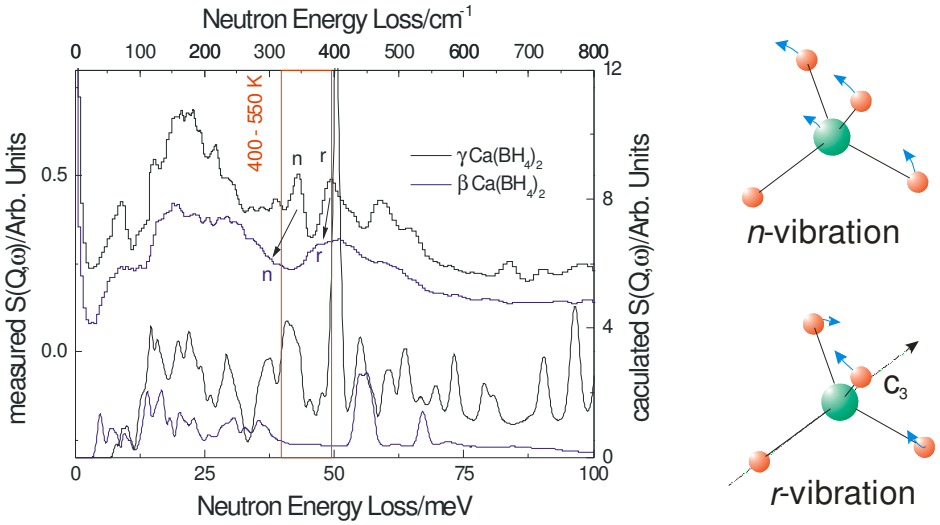
Workpackage 4: Vibrations and excitations

The vibrational properties of the complex hydrides $LiBH_4$, $Ca(BH_4)_2$ (α, β and γ phases), $Li_2Zn(BH_4)_5$, $NaZn(BH_4)_3$ and $KZnBH_4Cl_2$ have been were measured by infra-red [4] and Raman spectroscopy [6] in-house and inelastic neutron scattering (INS) at the ISIS Facility, Rutherford Appleton Laboratory (RAL), UK [7,8]. The sample preparation was possible through collaborations with the groups of M. Fichtner (Karlsruhe) and T. Jensen (Aarhus). The infrared, Raman and INS spectra have been calculated in collaboration with T. Ramirez-Cuesta (RAL). The $Ca(BH_4)_2$ INS spectra reflect the peculiarity of the local bonding in complex hydrides, making it possible to use a molecular description of vibrations in a solid. Li, Na and K-borohydrides show an increasing stiffness of the lattice with increasing weight of the cation and new vibrational modes possibly associated to a BH_4-BH_4 chain polymerisation.



Right: INS, Raman and infrared spectra of $LiBH_4$.[6] Black, experiments, Red, density functional theory calculations. Types of hydrogen vibrations can be categorized into lattice vibration (Region I) and internal vibration of the BH_4 (Region II: B-H bending, Region III: B-H stretching).

Furthermore, we show that the vibrational properties of $Ca(BH_4)_2$ depend on the specific phase and hitherto determine their stability [10]. The observed changes in the INS spectra are attributed to librational vibrations (n-, r- vibrations as sketched in the figure). Librational modes depend sensitively on the environment of the tetrahedrons in a gear-like fashion. Thus their energy depends on the orientation of the tetrahedrons, i.e. on the crystal structure. In a simplified picture, at high temperatures, the BH_4 –units vibrate in a way to minimize the free energy of the system by intending a crystal structure with minimum influence of the librational modes. The effect has consequences on the anticipation of novel hydrogen storage materials. The energy differences from vibrational entropy are of the order of 16 meV/H_2, which is not negligible when compared to the optimum heat of formation of 420 meV/H_2 required for application. Consequently, the impact of vibrational entropy should be carefully taken into account for the calculation of complex hydrides.



Comparison of the INS spectra of the β-and γ-phases, respectively, as measured (top curves) and as calculated (bottom curves). The opening of the gap between the two characteristic librational modes n and r is indicated.

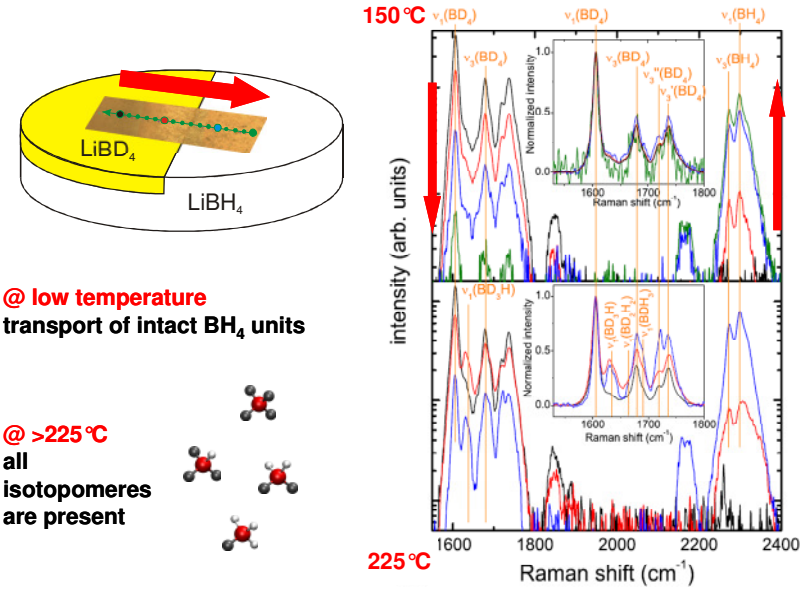
Workpackage 5: Mobility of the hydrogen in the lattice

BH_4 diffusion

First indication of a high mobility of hydrogen was found by gas hydrogen-deuterium exchange experiments.[9] The estimate of the hydrogen diffusion coefficient was further evaluated by the measurement of the hydrogen tracer diffusion in $LiBH_4$ by spatially resolved Raman spectroscopy [11]. The measurements give direct evidence of a macroscopic diffusion of BH_4 ions as well as atomic exchange of hydrogen between the anions. At low temperatures, diffusion of intact BH_4-unitsis dominating, while direct H-exchange is visible at high temperatures only (see Figure). An *effective* tracer diffusion coefficient of deuterium in $LiBH_4$ of $D = 7*10^{14}$ m^2/s at 473 K is derived. The direct exchange rate of hydrogen between BH_4 units is 10 orders of magnitude slower, i.e. the relatively fast effective hydrogen diffusion has its origin in the fast diffusion of BH_4 units [11]. These results solve a controversy originating from inconsistencies between NMR measurements[3] and DFT-calculations[4].

In liquid $LiBH_4$, diffusion of hydrogen was measured using quasi-elastic neutron scattering (QENS). The measured diffusion coefficients are in the $10^{-5}cm^2/s$ range at temperatures around 700 K, which is in the same order of magnitude as the self-diffusion of liquid lithium or the diffusion of ions in molten alkali halides [12]. The temperature dependence of the diffusion coefficient shows an Arrhenius behaviour, with an activation energy of E_a = 88 meV and a prefactor of D_0 = 3.1 × 10-4cm^2/s.

[3] D. T. Shane, R. C. Bowman, Jr. and M. S. Conradi, J. Phys. Chem. C, 2009, 113, 5039.
[4] M. Ramzan and R. Ahuja, Appl. Phys. Lett., 2009, 94, 141903.



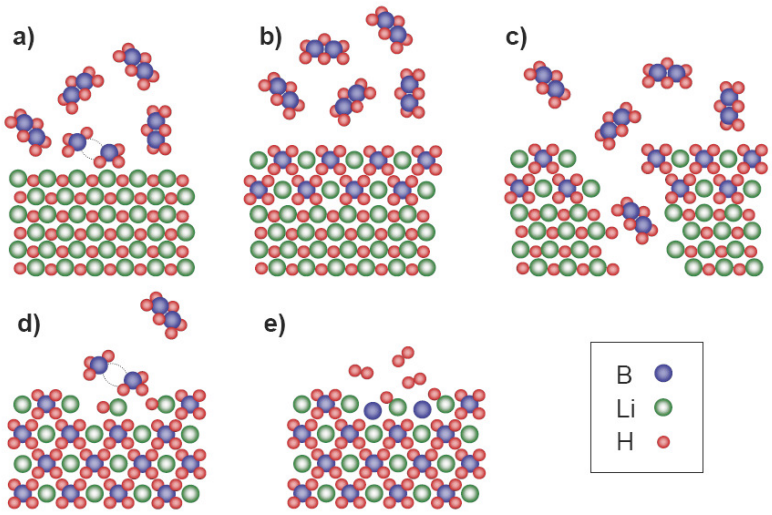
Right: Selected Raman spectra at various distances from the $LiBH_4/LiBD_4$ interface; (top) after annealing at 150°C for 240 h, (bottom) after annealing at 225°C for 26 h. Insets show spectra on linear scale normalized to the $v_1(BD_4)$-peak. Black, red and blue curves correspond to spectra measured at different locations on the sample.

Atomic hydrogen diffusion

Raman measurements give hints for a similar mechanism in the iso-electronic hydride $LiBH_4$. By hydrogen/deuterium experiments on $LiBH_4$, we managed to detect partially exchanged $B(H_{4-n}D_n)_4$ units (n=1…4) in low-temperature Raman spectra of H/D exchanged $LiBD_4$. These measurements show that the $B(H_{4-n}D_n)_4$ units are statistically distributed in the compound, an evidence that the single hydrogen atom is the diffusing species in $LiBH_4$.[13] The very similar desorption mechanisms of both $NaAlH_4$ and $LiBH_4$ raise hope that also for $LiBH_4$ an efficient dopant might be found – being a breakthrough in hydrogen storage.

Borohydride synthesis mechanism

We have synthesized $LiBH_4$ by a solid–gas reaction between LiH and borane at 120°C and ambient pressures.[14] This is the first time that a gas–solid formation of $LiBH_4$ has been realized below the melting point of LiBH4, in contrast to the report by Schlesinger et al. in 1952, who claimed that LiH does not react with borane in the absence of a liquid medium. In addition to the new way of synthesizing $LiBH_4$, the presented process also provides new insights into the formation mechanism. The reaction is clearly taking place not only on the surface of LiH but also in the bulk, which shows that diffusion is not the main problem in the formation process. It indicates that the formation of the B-H bond is the rate-limiting step in the $LiBH_4$ formation. With a suitable catalyst supporting the formation of this bond, the formation of borohydrides, in general, might be facilitated. On the one hand this catalyst should promote the formation of the B-H bond during the formation process, and, on the other hand, it should promote the splitting during desorption. The splitting is a major issue, because tetrahydroborates in general tend to emit diborane during desorption at lower temperatures. This is probably due to the high decomposition temperature of diborane (300°C). Accordingly, the new synthesis method is applicable for other promising tetrahydroborate systems, in which, for example, LiH is replaced by a different metal hydride such as CaH_2 or MgH_2 [15].



Schematic presentation of the formation and decomposition mechanism in borohydrides. For the formation process, the figure shows: a) diborane splitting at the surface of the metal hydride, b) the passivation layer of borohydride forming on the surface of the metal hydride and c) the breakdown of the passivation layer, enabling further formation of borohydride. For the desorption process, two cases are depicted: d) diborane emission by combination of BH_3 molecules on the surface and e) BH_3 decomposition, with boron remaining in the material and hydrogen atoms combining to form H_2.

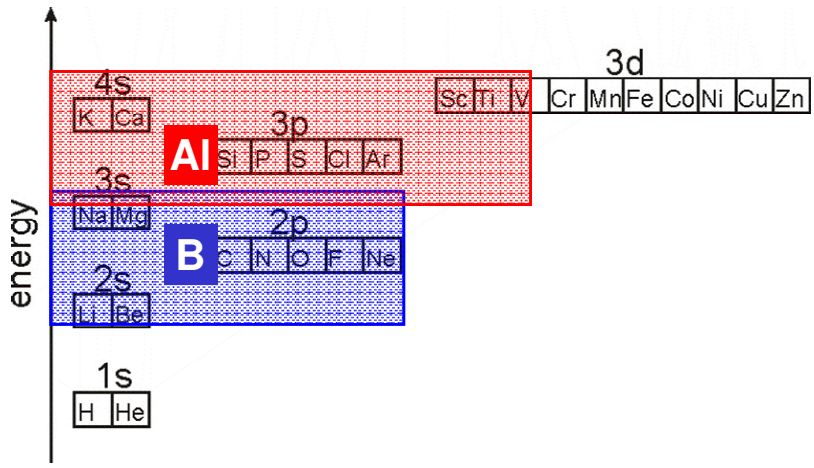
Discussion

Research on complex hydrides as hydrogen storage materials may be divided into empirical investigations such as the measurement of sorption kinetics and the effect of catalysts on it and on basic research focusing on the underlying microscopic phenomena (e.g. diffusion etc.). Within this project, both attempts were followed with the aim of the understanding of the mechanism of hydrogen sorption in complex hydrides.

From a materials' point of view, the focus was laid on the borohydrides, because the alanates had been already extensively investigated in the past. Here we would like to highlight links between the two systems. The extremely low direct H–D exchange is an indication of the strong B–H bond. The bonding strength was first postulated from DFT-calculations. We determined the local B–H bond strength experimentally with the help of non-linear spectroscopy (workpackage 2). The anharmonicity of the stretching vibration energy is related to the depth of the potential well $E_{B–H}$, i.e. the sum of all vibrational energy levels up to zero binding energy gives the potential well depth. An estimate gives 0.75 eV < $E_{B–H}$ < 5 eV, akin to the bond dissociation energy in diatomic B–H (3.5 eV). For direct H–D exchange, the strong B–H bond has to be broken, explaining the extremely low atomic hydrogen hopping, which eventually causes the slow sorption kinetics in borohydrides rate. These finding may be compared to Ti-doped $NaAlH_4$, which has been shown to exhibit excellent hydrogen sorption kinetics. The mobility in $NaAlH_4$ is generally very low. Significant mobility of AlH_4 ions as found in $LiBH_4$ has not been observed. This might be related to the larger ionic radius of AlH_4 compared to that of BH_4 (r(Al–H) = 160 pm, r(B–H) = 120 pm). The low atomic H mobility in $NaAlH_4$ might be due to the same reason as proposed for $LiBH_4$: the bond dissociation energy in diatomic Al–H is 3 eV, and thus only slightly lower than in B–H. However, although alanates exhibit a slightly slower H-mobility than the borohydrides, the sorption kinetics is faster in alanates.

The marked differences in sorption kinetics between may thus be explained by the electronic structure of the transition states. During the breaking of bonds, energetically higher, but unoccupied states are transitionally occupied. The figure depicts the energy levels in aluminium and boron compounds. In aluminium compounds, the (empty) 3d states are energetically near enough to contribute to the transition states, possibly supported by 3d-transition metal catalysts (e.g. Ti). In boron compounds, these

states are energetically too far away resulting in high activation energies for B-H bond breaking. Here, novel concepts have to be developed. An interesting approach might be the combination of borohydrides and imides, i.e. the combination of electrophile (BH_3) and nucleophile (NH_3) reagents. Apart from lowering of the desorption temperatures, some compounds are liquid at low temperatures opening the possibility of using complex hydrides as liquid energy carriers.[5] Further possibilities are the syntheses of complex hydrides, where the anion is partially exchanged by e.g. halides, such as $Li(BH_4)_{1-x}Cl_x$ [6] and $NaAlH_{4-x}F_x$,[7] In our group, the proof of principle of this idea was recently demonstrated on the example $Ca(BH_4)_{2-x}Cl_x$ [20].



Schematic presentation of the energy levels relevant for alanates and borohydrides.

Summary and Outlook

Particular during the first two years (2007/2008), main activities were the development and testing of new methods and concepts. This resulted in several papers on alanate systems on one hand, and on the evaluation of the methods on the other. While vibrational spectroscopy proved to be a very useful tool to shed light on complex hydrides, UV-Vis spectrometry on complex hydrides is a difficult task. This is originated from the difficult handling of the materials and on the circumstance that in most cases the interesting energy range (band gap) exceeds the possibility of the equipment. With running equipment, a multitude of new and interesting results were obtained, resulting in more than 20 papers.

2009/10 have been fruitful years in term of collaborations and new research directions, with the successful collaboration on infrared pump-probe spectroscopy with the group of Peter Hamm at the University of Zürich and the INS measurements and calculations made possible by Timmy Ramirez-Cuesta (RAL, UK), Max Fichtner (Karlrsuhe Institute of Technology) and Torben Jensen (Aarhus University). These collaborations will be intensified and new collaborations will be started with D. Chandra (University of Nevada) for heat capacity measurements and T. Elsaesser (Max-Born Institute, Berlin) for UV-pump-XRD-probe measurements. Prof. Elsaesser developed this novel time-resolved method to follow bond-breaking in the NH_4 molecular unit of ammonium sulphate in real time and the subsequent displacement of the freed proton. This is a potentially very interesting possibility to see the hydrogen hopping in the BH_4 unit of borohydrides as well. These measurements will be performed within new projects.

[5] Paul A. Anderson, Philip A. Chater, William I. F. David, Ian C. Evans and Alexandra L. Kersting, *New B,N-hydrides: Characterization and Chemistry*, Mater. Res. Soc. Symp. Proc. Vol. 1216-W09-05 (2010) Materials Research Society.
[6] L. M. Arnbjerg, D. B. Ravnsbæk, Y. Filinchuk, R. T. Vang, Y. Cerenius, F. Besenbacher, J.-E. Jørgensen, H. J. Jakobsen and T. R. Jensen, Chem. Mater., 2009, 21, 5772.
[7] H.W. Brinks, A. Fossdal, B.C. Hauback, J. Phys. Chem. C, 112 (2008) 5658.

Papers:

[1] A. Borgschulte, A. Züttel, P. Hug, G. Barkhordarian, N. Eigen, M. Dornheim, R. Bormann and A. J. Ramirez-Cuesta, *Hydrogen–deuterium exchange experiments to probe the decomposition reaction of sodium alanate,* Phys. Chem. Chem. Phys., 2008, **10**, 4045 – 4055.

[2] Z. Łodziana and A. Züttel, *Ti cations in sodium alanate*, Journal of Alloys and Compounds 471 (2009) L29 (2008).

[3] J. W. Kim, J-H. Shimb, S. C. Kim, A. Remhof, A. Borgschulte, O. Friedrichs, R. Gremaud, F. Pendolino, A. Züttel, Y. W. Chob and K. H. Oh, *Catalytic effect of TiN nanopowder on hydrogen desorption properties of $NaAlH_4$ and its stability in $NaAlH_4$*, J. Pow. Sour. 192, 582 (2009).

[4] E. R. Andresen, R. Gremaud, A. Borgschulte, P. Hamm, *Vibrational dynamics of $LiBH_4$*, J. Phys. Chem. A 113, 12838 (2009).

[5] A. Borgschulte, F. Pendolino, R. Gremaud, A. Züttel, *Hydrogen diffusion in NaH as derived from isotope exchange experiments,* Appl. Phys. Lett. 94, 111907 (2009).

[6] A.-M. Racu, J. Schoenes, Z. Lodziana, A. Borgschulte, and A. Züttel, *High-Resolution Raman Spectroscopy Study of Phonon Modes in $LiBH_4$ and $LiBD_4$*, J. Phys. Chem. A 2008, 112, 9716–9722.

[7] F. Buchter, Z. Lodziana, Ph. Mauron, A. Remhof, O. Friedrichs, A. Borgschulte, A. Züttel, D. Sheptyakov, Th. Strässle, and A. J. Ramirez-Cuesta, *Dynamical properties and temperature induced molecular disordering of $LiBH_4$ and $LiBD_4$*, Phys. Rev. B 78, 094302 (2008).

[8] A. Remhof, R. Gremaud, F. Buchter, Z. Lodziana, J. P. Ebs, A. J. Ramirez-Cuesta, A. Borgschulte and A. Zütttel, *Hydrogen dynamics in lightweight tetrahydroborates*, Zeitschrift für physikalische Chemie, 224, 263 (2010).

[9] A. Borgschulte, A. Züttel, P. Hug, A.-M. Racu, and J. Schoenes, *Hydrogen-deuterium exchange in bulk $LiBH_4$*, J. Phys. Chem. A **112**, 4749–4753 (2008).

[10] A. Borgschulte, R. Gremaud, Z. Lodziana, and A. Züttel, *Hydrogen tracer diffusion in $LiBH_4$ measured by spatially resolved Raman spectroscopy*, Phys. Chem. Chem. Phys. **12**, 5061 - 5066 (2010).

[11] A. Borgschulte, R. Gremaud, A. Züttel, P. Martelli, A. Remhof, A. J. Ramirez-Cuesta, K. Refson, E. G. Bardaji, W. Lohstroh, M. Fichtner, H. Hagemann, and M. Ernst, *Experimental evidence of librational vibrations determining the stability of calcium borohydride*, submitted (2010).

[12] P. Martelli, A. Remhof, A. Borgschulte, P. Mauron, D. Wallacher, E. Kemner, M. Russina, F. Pendolino, and Andreas Züttel, *BH_4^- Self-Diffusion in Liquid $LiBH_4$*, J. Phys. Chem. A 2010, 114, 10117–10121.

[13] R. Gremaud, Z. Lodziana, P. Hug, B. Willenberg, A.-M. Racu, J. Schoenes, A. J. Ramirez-Cuesta, S. J. Clark, K. Refson, A. Züttel, and A. Borgschulte, *Evidence for hydrogen transport in deuterated $LiBH_4$ from low-temperature Raman-scattering measurements and first-principles calculations*, Phys. Rev. B 80, 100301(R) (2009).

[14] O. Friedrichs, A. Borgschulte, S. Kato, F. Buchter, R. Gremaud, A. Remhof, A. Züttel, *Low temperature synthesis of $LiBH_4$ by gas-solid reaction*, Chemistry - A European Journal 15, 5531 (2009).

[15] O. Friedrichs, A. Remhof, A. Borgschulte, F. Buchter, S. I. Orimo and A. Züttel, *Breaking the passivation - the road to a solvent free borohydride synthesis,* Phys. Chem. Chem. Phys., 2010, 12, 10919.

[16] R. Gremaud, J. L. M. van Mechelen, H. Schreuders, M. Slaman, B. Dam, and R. Griessen, Int. J. Hydrogen Energy 34, 8951 (2009)

[17] R. Gremaud, M. Gonzalez-Silveira, Y. Pivak, S. de Man, M. Slaman, H. Schreuders, B. Dam and R. Griessen, Acta Mater. 57, 1209 (2009).

[18] A. Borgschulte, R. Gremaud, S. Kato, N. P. Stadie, A. Remhof, A. Züttel, M. Matsuo, and S.-I. Orimo, *Anharmonicity in $LiBH_4$–LiI induced by anion exchange and temperature*, Appl. Phys. Lett. 97, 031916 (2010).

[19] S. Kato, M. Bielmann, A. Borgschulte, V. Zakaznova-Herzog, A. Remhof, S.-i. Orimo and A. Züttel, *Effect of the surface oxidation of $LiBH_4$ on the hydrogen desorption mechanism,* Phys. Chem. Chem. Phys., 2010, 12, 10950.

[20] C. Rongeat, V. D'Anna, H. Hagemann, A. Borgschulte, A. Züttel, L. Schultz, and O. Gutfleisch, *Effect of additives on the synthesis and reversibility of $Ca(BH4)_2$,* J. All. Comp. 493 (2010) 281–287.

[21] C. Rongeat, I. Lindemann, A. Borgschulte, L. Schultz, O. Gutfleisch, *Effect of the presence of chlorides on the synthesis and decomposition of $Ca(BH_4)_2$*, International Journal of Hydrogen Energy (2010), in press.

Präsentationen:

A. Borgschulte, Optics and spectroscopy on complex hydrides, invited lecture at the Summer School on Materials for the hydrogen economy, Reykjavik, Iceland (2008)

A. Borgschulte Seeing Hydrogen talk DPG Frühjahrstagung des Arbeitskreises Festkörperphysik, Berlin (2008).

R. Gremaud, Short-range order in Mg-Ti-H thin films: an accident of Nature?, Poster at the Metal-Hydrogen systems conference, Reykjavik, Iceland (2008)

R. Gremaud, Vibration and diffusion of hydrogen in complex hydrides, talk at the 2nd Swiss-Korean workshop, Dübendorf, Switzerland (2008)

R. Gremaud, Raman spectroscopy on H/D exchanged LiBH4, talk at the FZK meeting, Dübendorf, Switzerland (2008)

R. Gremaud, *Vibrations and diffusion of hydrogen in complex hydrides: Raman spectroscopy on H/D exchanged $LiBH_4$* talk at the ,3rd international symposium on Hydrogen & Energy, 25-30 January 2009, Braunwald, Switzerland.

R. Gremaud, *Vibrational spectroscopy on H/D exchanged $LiBH_4$:Hydrogen dynamics and diffusion mechanism*, talk at HYPOTHESIS VIII, April 1-4 2009, Lisbon, Portugal.

R. Gremaud, invited lecture on Nanocomposites *for hydrogen storage: from synthesis to catalysis*, 11th International conference on advanced materials, 20-25 September 2009, Rio de Janeiro, Brazil.

R. Gremaud, *Stability and reversibility of borohydrides for hydrogen storage***,** progress report talk at the IEA HIA TASK 22 Meeting October 12-15, 2009 Paris, France.

R. Gremaud, *Vibrational dynamics of the hydrogen storage material $LiBH_4$ by infrared pump-probe spectroscopy*, talk at the MRS Fall meeting, 30.11-4-12 2009, Boston (MA), USA.

R. Gremaud, Time and frequency resolved dynamics in deuterated $LiBH_4$, poster at the MRS Fall meeting, 30.11-4-12 2009, Boston (MA), USA.

A. Borgschulte, Seeing Hydrogen in Materials, invited talk, Physikalische-Chemisches Institut der Universität Zürich, 08.10.2009

A. Borgschulte; *Diffusion of Hydrogen*, invited lecture, 6th COSY Tranining Workshop, 3.11.2009, Grenoble, France

A. Borgschulte; *Das Potenzial für erneuerbare Energien in der Schweiz: Wasserstoff, der erneuerbare Energieträger*; invited talk, Empa Akademie Dübendorf, 09.11.2009

A. Borgschulte, *Technologien für die Energiespeicherung von morgen*, Enaw-Fachtagung 2009, Kongresszentrum Basel, 12.11.2009

A. Borgschulte, *Hydrogen the renewable energy carrier*, invited talk, Energy Delta Convention Groningen 2009, Groningen, The Netherlands, 18.11.2009

A. Borgschulte, *Molecular vibrations as the origin of solid state effects in borohydrides*, talk at the MRS Fall meeting, 30.11-4-12 2009, Boston (MA), USA.

A. Borgschulte, *Hydrogen sorption kinetics, reaction dynamics, and spectroscopy*, talk at the First International Conference on Materials for Energy, ENMAT2010, Karlsruhe, Germany, 04. - 08.07.2010

Nationale Zusammenarbeit

- Prof. Peter Hamm, Physical chemistry Institute, Universität Zürich (Ultrafast pump-probe measurements)
- Dr. Paul Hug, Solid State Chemistry, Empa.
- Dr. Hans Hagemann, Inorganic Chemistry, University of Geneva.

Internationale Zusammenarbeit

- Prof. J. Schoenes, Institute of Condensed Matter Physics, Technical University Braunschweig, Germany
- Prof. Gerd Ganteför, Fachbereich Physik Universität Konstanz D-78434 Konstanz, Germany
- Dr. A. J. Ramirez-Cuesta, Dr. Keith Refson, ISIS Facility, Rutherford Appleton Laboratory, Chilton, United Kingdom
- Prof. R. Griessen, Condensed Matter Physics, VU University Amsterdam, The Netherlands
- Prof. Bernard Dam, Materials for Energy Conversion and Storage (MECS) DelftChemTech, Faculty of Applied Science Delft University of Technology, Delft, The Netherlands
- K. Refson, CASTEP developer group, Rutherford Appleton Laboratory, United Kingdom.
- Prof. T. Jensen, Aarhus University, Denmark.
- Dr. M. Fichtner, Institute of Nanotechnology, Karlsruhe Institute of Technology, Germany.