Hydrogen−Deuterium Exchange in Bulk $LiBH_4$

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Because of its apparent simplicity, diffusion of hydrogen in solids can be regarded as a general model system for diffusion. However, only rudimentary knowledge exists for the dynamics of hydrogen in complex hydrides. Insight into the specific diffusion process is given by hydrogen−deuterium exchange experiments. Thermogravimetry and Raman spectroscopy are used to measure the hydrogen−deuterium exchange during the decomposition of $LiBH_4$. At a temperature of 523 K the self-diffusion constant of deuterium in $LiBH_4$ is estimated to be $D \simeq 7 \cdot 10^{-14}$ m ^{2} s^{-1}. A careful analysis of the Raman spectra shows that hydrogen is statistically exchanged by deuterium in $LiBH_4$; i.e., the diffusing species is assumed to be the single hydrogen atom.

Introduction

Hydrogen storage in complex metal hydrides offers a safe alternative for transportation and storage of hydrogen.[1] Among those storage materials, $LiBH_4$ is a promising candidate, as it can store up to 18.4 mass % hydrogen.[2] Storage capacity, thermodynamic stability and sorption rate are the most important properties of hydrogen storage materials and are intensively studied, but in particular the slow sorption kinetics of complex hydrides is controversial.[3] Diffusion of hydrogen is one of the main mechanisms in hydrogen sorption. Insight into the specific diffusion processes could help to improve sorption kinetics. Although the diffusion of H in metals is relatively well understood, only rudimentary knowledge exists for the dynamics of hydrogen in complex hydrides. The reason for this originates from the different electronic structures of the hydrides. Hydrogen in most transition metals occupies interstitials. The covalent contribution to the hydrogen−metal bond is small,[5] and thus hydrogen can easily jump from interstitial to interstitial. Accordingly, the diffusion of hydrogen in transition metals is fast with small activation energies.[4] Hydrogen in complex hydrides, on the contrary, is covalently bound and arranged in subunits ("complexes").[3] It is not known, whether hydrogen can be removed from such a subunit without degradation of the whole compound, i.e., whether diffusion of hydrogen would then require the movement of the whole subunit and/or degradation of it.[6] Indeed, first quasi-inelastic neutron scattering measurements indicated a very slow diffusion of hydrogen in $NaAlH_4$.[7] Nuclear magnetic resonance measurements failed in determining the hopping rate of hydrogen, as most relaxation processes are associated with the molecular reorientation of the complex anion.[8] An alternative method to shed light onto the specific diffusion process is to label the diffusing atoms. This is experimentally realized by hydrogen−deuterium exchange during the decomposition of $LiBH_4$ followed by thermogravimetry and Raman spectroscopy. We measure the exchange rate quantitatively, which enables us to estimate the self-diffusion coefficient. Raman spectroscopy reveals that the hydrogen is partially exchanged in the $(BH_4)^-$ anion at temperatures below the melting point, evidence for classical diffusion mechanism via single hydrogen atoms in $LiBH_4$.

Experimental Methods

Thermogravimetry. $LiBH_4$ was purchased from Sigma-Aldrich Fine Chemicals, Switzerland (95%), and $LiBD_4$ from CatChem, Czech Republic (98%). The samples were handled solely in the argon glovebox. A magnetic suspension balance Rubotherm (Bochum, Germany) was used to measure thermodesorption kinetics in hydrogen and deuterium atmosphere, respectively, up to a temperature of 750 K. Because the data were obtained gravimetrically, it is necessary to account for buoyancy effects during the experiments. As the measurements were performed at constant pressure with a linear temperature ramp of 1 K/min, buoyancy contribution to the balance reading was calibrated using a dummy sample of similar volume.

Raman Spectroscopy. Raman spectra were obtained in backscattering geometry using a Renishaw Ramascope 2000 (Renishaw plc, Gloucestershire, U.K.) with a spectral resolution of 1 cm^{-1}. The 633 nm line of the HeNe laser was focused on the sample through a 20 times magnifying objective of the microscope (beam diameter approximately 20 μm), the laser beam power on the sample being 2.8 mW. The spectrometer was equipped with a CCD camera detector and a second CCD camera to obtain the optical image of the sample, from which the crystal size is determined. Around 20 mg of $LiBH_4$/$LiBD_4$ were placed in a Linkam THMS600 cell (Linkam Scientific Instruments, U.K.) directly adapted to the microscope of the instrument; the cell allows the use of controlled atmosphere and temperature. The glass window of the cell is 0.1 mm thick. The sample was heated at 1 K/min rate in a flow of 100 cm^3/min deuterium and hydrogen flow, respectively, up to the final temperature. To increase the spatial resolution, the area on the CCD, which is used for analysis, is reduced to a width of 3 pixels. This corresponds to confocal optical setup of the spectrometer; however, the data noise is increased. The spatial resolution is around 10 μm. The spectrometer is also equipped with a CCD camera to take micrographs during desorption. The

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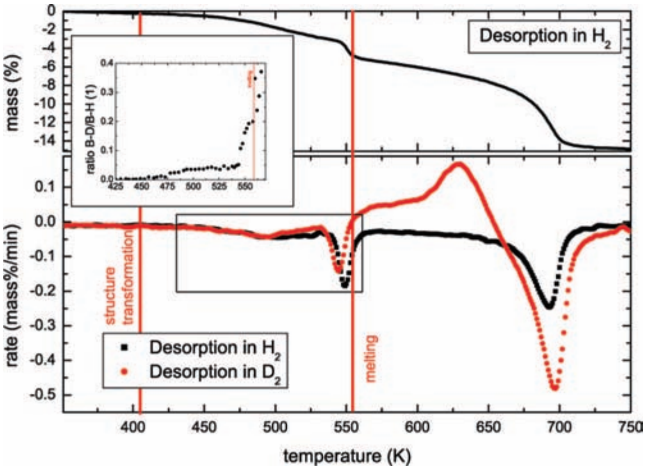

Figure 1. Top: thermodesorption spectra of $LiBH_4$ in 1.5 bar of hydrogen. The heating rate is 1 K/min and the mass is normalized to the amount of $LiBH_4$. Bottom: desorption rates r_H and r_D as obtained by differentiation of the corresponding thermodesorption spectra in 1.5 bar of hydrogen and deuterium, respectively. The inset shows the intensity ratio of the regions attributed to B−D vibrations and to B−H vibrations, respectively, measured by Raman spectroscopy during heating of $LiBH_4$ from 425 to 575 K in 1 bar deuterium.

area-averaged intensity of the micrographs is a measure of the optical absorbance.

Results

During heating in a hydrogen atmosphere of 1.5 bar, $LiBH_4$ decomposes into lithium hydride, elemental boron, gaseous diborane (or BH_3) and hydrogen according to

$$LiBH_4 \rightarrow LiH + (1-x)B + \frac{x}{2}B_2H_6 + \frac{3}{2}(1-x)H_2 \quad (1)$$

with $x \simeq 0.015$ (see Figure 1). The release x of the undesirable side product B_2H_6 is strongly pressure and temperature dependent and can be influenced by additives.[9] It is noted that additional intermediate states are observed during desorption from the liquid state.[3] Raman measurements suggest the formation of $Li_2B_{12}H_{12}$,[10] but there is controversy.[11] In this paper, we focus on the solid state. Here, a considerable desorption rate is observed for temperatures above 450 K. Additives like SiO_2 can increase the desorption rates in particular at these temperatures.[2,9] Just before reaching the melting point, the increased diffusion of hydrogen and probably also of the involved metals (Li and B) accelerates the desorption of hydrogen significantly. Interestingly, the desorption rate $r = dm/dt$ declines with melting and reaches a second maximum not until 700 K. This hints toward different desorption mechanisms of solid and liquid $LiBH_4$. To shed light onto the involved process, we label the hydrogen in $LiBH_4$; i.e., we follow the exchange of hydrogen by deuterium during the decomposition reaction. By measuring the weight change of $LiBH_4$ during annealing, we determined the mass change rates r_H and r_D of the decomposition in hydrogen and deuterium atmosphere, respectively (see Figure 1). At lower temperatures, no difference between the decomposition rates is observed, which is evidence for a negligible H/D exchange at these temperatures. Above 500 K, a significantly growing difference between r_H and r_D indicates the exchange of hydrogen by the heavier deuterium, in good agreement with literature data.[12,14] In the liquid state, the exchange rate $r_{ex} = r_H - r_D$ is approximately 5 times that of the decomposition rate, evidence for a high dissociation (recombination) and diffusion rate, while it much lower in solid state. The measured exchange rate is the lower estimate of a nonsurface limited diffusion rate. Thus the self-diffusion parameter D is estimated by calculating the deuterium diffusion rate into a sphere without considering further kinetic constraints. The total amount of diffusing substance entering a sphere of diameter a can be estimated by $m(t)/m_\infty = 6Dt/a^2$, where m_∞ is the maximum weight change (ref 15 p 91, estimation of eq 6.20 for $t \rightarrow 0$). The expression holds for small Dt/a^2 only, where the diffusion rate $d/dt(m/m_\infty) = 6D/a^2$ is constant. With $a = 250 \pm 50$ μm (typical crystal size as measured optically) and a D_2 diffusion rate of $d/dt(m/m_\infty) = r_{ex}/m_\infty \simeq 9.2 \times 10^{-6}$ s $^{-1}$, the self-diffusion parameter of deuterium in $LiBH_4$ is $D \geq (6 \pm 3) \times 10^{-14}$ m^2 s^{-1} at a temperature of 530 K. It should be noted that the self-diffusion can differ from the corresponding chemical diffusion coefficient as deduced, e.g., by transport measurements (refs 15, p 212, and 16, p 51).

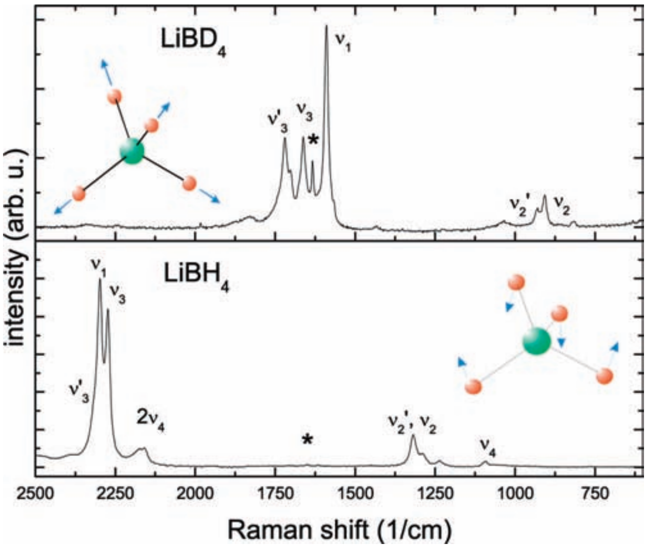

Figure 2. Raman spectra of $LiBH_4$ and $LiBD_4$ at room temperature. Main lines are $\nu_1^H = 2255$ cm^{-1}, $\nu_2^H = 1272$ cm^{-1}, $\nu_3^H = 2282$ cm^{-1}, $\nu 3'^H = 2300$ cm^{-1}, $\nu_4^H = 1091$ cm^{-1}, and $\nu_1^D = 1590$ cm^{-1}, $\nu_2^D = 909$ cm $^{-1}$, $\nu_3^D = 1662$ cm^{-1}, $\nu 3'^D = 1720$ cm^{-1}, for the hydrogenated and deuterided compound, respectively. $2\nu_4$ is an overtone of the ground vibration ν_4. The asterisks indicate impurity lines. For illustration, the real-space movements of atoms of the stretching mode vibration (ν_1, top left)) and of the bending mode (ν_2, bottom right) of the free BH $_4{}^-$ ion are sketched.

A gravimetric method does not give any answer to the question, in what material the hydrogen is exchanged. Vibrational spectroscopy, on the other hand, is sensitive to the mass of the vibrating species, and therefore Raman spectroscopy can be used to characterize the exchanging atoms. Figure 2 shows the Raman spectra of $LiBH_4$ and $LiBD_4$ at room temperature. $LiBH_4$ consists of covalently and thus strongly bound B and H forming $(BH_4)^-$ complexes, which are coupled via an attractive Coulomb potential to Li^+ ions.The corresponding vibrations can be well approximated by so-called "internal" and "external" vibrations,[19] where 'internal' refers to motions in which the center of mass of the ($BH_4{}^-$ ion does not move, and "external" refers to the motion of (BH $_4$) $^-$ as a rigid unit. The internal vibrations are of particular interest for this paper, as they show the largest isotope effect.

The peak positions in Figure 2 are attributed to internal vibrations labeled ν_i ($i = 1, 2, 3, 4$) (taken from refs 19 and 20), and show the expected isotope shift of about $2^{1/2}$ in good agreement with literature data (for a more detailed analysis of the spectra, see refs 20 and 21). External vibrations occur at

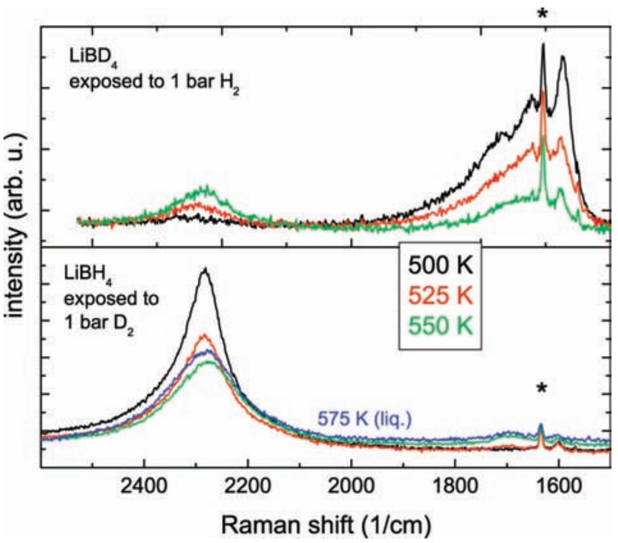

Figure 3. Representative Raman spectra of $LiBD_4$ and $LiBH_4$ during heating in 1 bar hydrogen and deuterium, respectively. Heating rate is 1 K/min. The asterisks indicate impurity lines.

lower energies, which are not shown here. Due to the strong B−H bond and lightweight of hydrogen, anharmonic effects play an important role in the interpretation of the vibrational spectra, as several peaks originate from higher harmonics. E.g., $2\nu_4$ refers to the first overtone of the ν_4 mode. These additional excitations become more prominent at lower temperature. The advantage of the measurement of the vibrations of "quasi-free" vibrating molecular units is that the modes are rather insensitive to the exact arrangement of the units; i.e., the effects of the structure transformation of $LiBH_4$ at 493 K as well as its melting at 553 K on the vibrational spectra are relatively small (broadening and intensity loss[20]). This makes Raman spectroscopy the perfect method to study complex hydrides and H/D exchange in them in particular. The robustness of the measurements is exemplarily demonstrated in Figure 3, where the exchange of hydrogen by deuterium and vice versa in $LiBH_4$ and in $LiBD_4$, respectively, is followed by Raman spectroscopy.

The spectra of $LiBD_4$ and $LiBH_4$ are taken during heating in a hydrogen and deuterium atmosphere, respectively, at various temperatures. As discussed above, the excitations loose intensity and broaden with temperature, and thus we only discuss the intensity averaged over approximately 100 cm^{-1} around 2270 cm^{-1} (B−H vibrations) and 1660 cm^{-1} (B−D vibrations). The ratio is a measure of the exchanged hydrogen by deuterium in the compound $LiBH_4$, and is plotted as a function of temperature in the inset of Figure 1. The temperature dependence of the exchange rate in $LiBH_4$ measured by Raman spectroscopy resembles the exchanged rate measured gravimetrically, evidencing a fast H−D exchange in $LiBH_4$.

Furthermore, Raman spectroscopy provides us with the information, which species is diffusing: single H (D) or BH_4^- (BD_4^-). At room temperature, the point group symmetry of the free BH_4^- ion is T_d. Partial exchange of H by D will result in lower symmetries: $(BH_3D)^- = C_{3v}$, $(BH_2D_2)^- = C_{2v}$, etc. Accordingly, a splitting of the lines is expected for a partial isotope exchange, while a complete exchange does not change the symmetry. The Raman spectra of solids are, however, restricted to those vibrations, which are in the same phase in the lattice and are determined by the factor group. Here the site symmetry of the "lattice-confined" BH_4^- ion becomes C_5, which causes the splitting of some lines (e.g., ν_3, ν_3').[20,21] A partial exchange of single hydrogen atoms by deuterium in a crystalline solid will then not lead to a line splitting, but to an intensity decrease and broadening (the Q-factor of the resonance decreases).

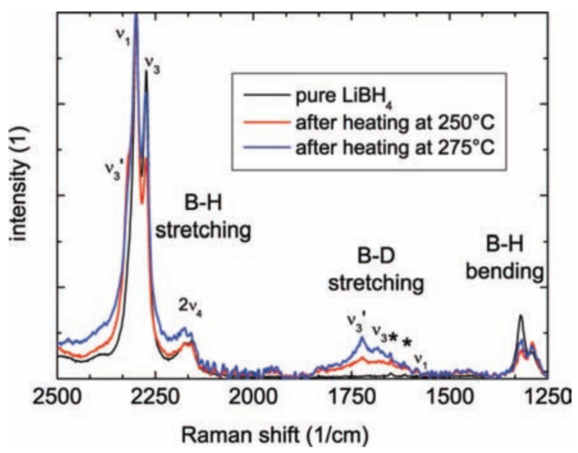

Figure 4. Raman spectra of $LiBH_4$ and $LiBH_4$ exposed to 1 bar D_2 at 250 and 275 °C, respectively, for 30 min. All spectra have measured at room temperature and normalized to the ν_1 peak.

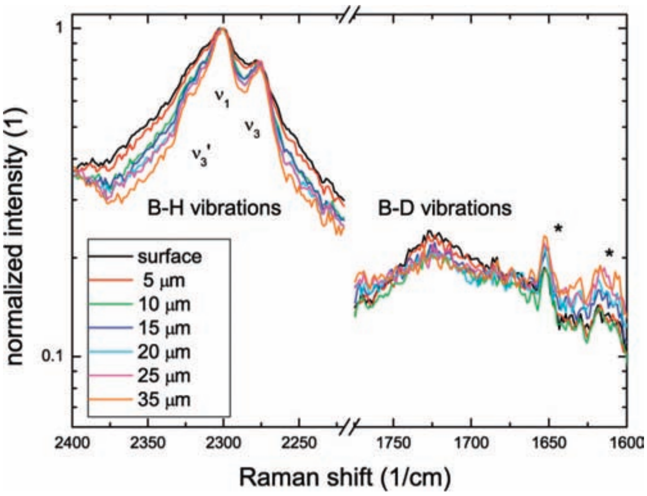

Figure 5. Spatially resolved Raman spectra of $LiBH_4$ after heating in 1 bar deuterium at 250 °C measured at various depths. All spectra have been measured at room temperature and normalized to the ν_1 peak.

Figure 4 shows the spectra of $LiBH_{4-\delta}D_\delta$ with two different deuterium contents δ, as obtained by exposing $LiBH_4$ to 1 bar D_2 at 250 and 275 °C, respectively, for 30 min. Both spectra are measured at room temperature and normalized to the ν_1^H peak. The ν_1^D vibrations of B−D are hardly visible but develop with higher deuterium content (after exposure to D_2 at 275 °C). All lines originating from hydrogen broaden with increasing deuterium content, while B−D vibrations sharpen. This result is evidence that hydrogen is partially exchanged in $LiBH_4$, i.e., that the spectra in Figure 5 resemble $LiBH_{4-\delta}D_\delta$, in good agreement with NMR data.[13] From the gravimetric analysis it appears that diffusion is only possible in the high temperature phase or in the liquid. In the liquid state $LiBH_4$ decomposes into free Li^+ and BH_4^- ions,[22] and $LiBH_4$ is known to be a good ion conductor. Thus, the enhanced exchange might originate from the high mobility of ions, i.e., from transport of the subunit BH_4^-. Though this mechanism can explain the fast exchange in the liquid state, it fails in explaining the statistical distribution of hydrogen and deuterium, in particular in the solid state. The diffusing species in the solid complex hydride $LiBH_4$ is thus expected to be the single hydrogen atom.

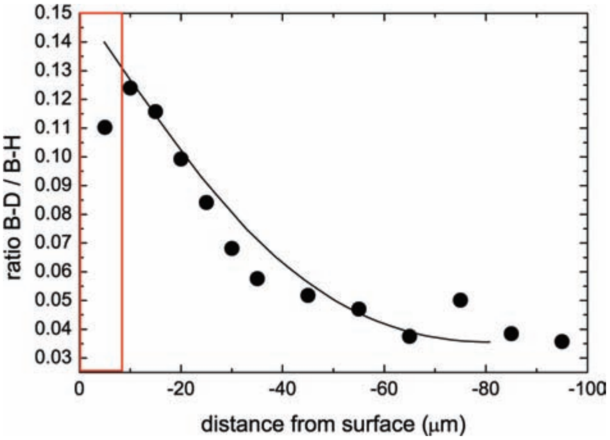

Figure 6. Depth hydrogen profiling: deuterium distribution in $LiBH_4$ after heating in 1 bar deuterium at 250 °C for 45 min. The box indicates the spatial resolution. The line is a guide to the eyes.

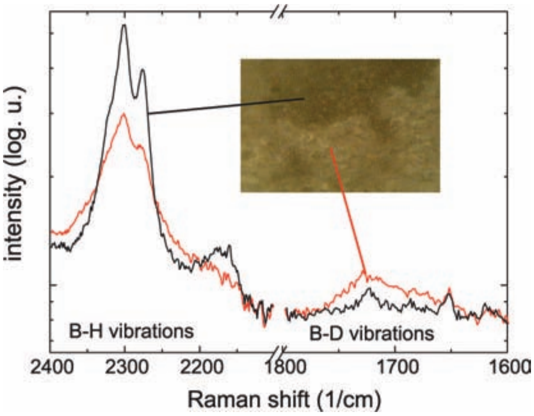

Figure 7. Raman spectra of $LiBH_4$ and $LiBH_4$ exposed to 1 bar D_2 at 250 and 260 °C, respectively, for 30 min. All spectra have measured at room temperature and normalized to the ν_1 peak.

Diffusion is driven by concentration gradient, and its measurement offers an alternative determination of the self-diffusion coefficient. It is measured by moving the focal point of the Raman microscope from the surface area into the bulk of $LiBH_4$ exposed to 1 bar D_2 at 250 °C for 30 min. Figure 5 shows the corresponding Raman spectra. With increasing depth the B−H lines sharpen, while the B−D lines vanish, confirming the hypothesis of single hydrogen diffusion. The intensity ratio of B−D to B−H lines as a function of the depth of the focal point is used to estimate the depth profile of the deuterium concentration in $LiBH_4$ (Figure 6). The concentration declines as expected from diffusion theory (ref 15, p 92). From the averaged diffusion depth of deuterium in $LiBH_4$, $\langle x^2\rangle \simeq (20\ \mu\mathrm{m})^2$, we estimate a diffusion coefficient of

$$\langle x^2 \rangle = 2Dt \Rightarrow D = 7 \times 10^{-14}\ \mathrm{m^2\,s^{-1}} \qquad (2)$$

in good agreement with the value derived from thermogravimetry measurements. The determination of the diffusion coefficient via the measurement of the deuterium distribution in the bulk has the advantage that surface constraints do no play an important role. Indeed, the low surface concentration of exchanged deuterium indicates the existence of a surface barrier (ref 15, compare p 92 with p 98). During measurement it was observed that the optical appearance of the $LiBH_4$ crystal changes (Figure 7). These changes are accompanied with different H/D exchange rates. The nature of the surface changes has to be clarified by further research; its effect on the H/D exchange highlights the relevance of surface processes also in complex hydrides. The diffusion coefficient is relatively high compared to the desorption rate at the same conditions. Diffusion seems thus not to be the rate-limiting step of desorption of $LiBH_4$. This is in good agreement with kinetic data on the desorption process. The pressure dependence of the decomposition kinetics of complex hydrides is found to be $\propto \ln(p_{\mathrm{appl}}/p_{\mathrm{eq}})$ with the applied pressure p_{appl} and equilibrium pressure p_{eq},[25] very similar to that of $NaAlH_4$.[17] This relation is expected for a slow interfacial reaction,[18] probably at the surface of the grains.

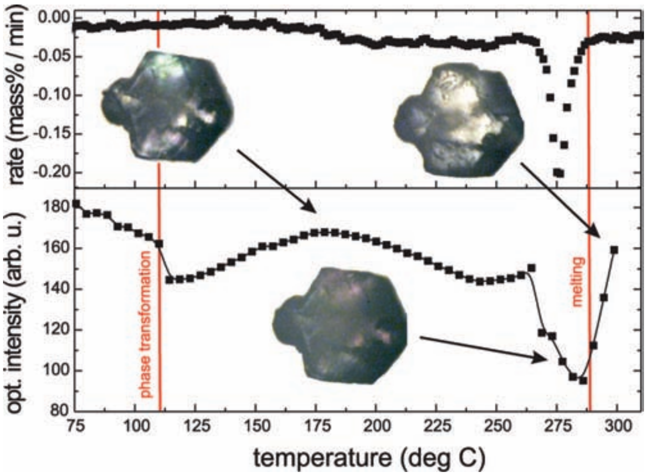

Figure 8. Micrographs and desorption rate during heating of a $LiBH_4$ crystal in inert atmosphere at 1 °C/min. The area-averaged intensity of the micrographs is a measure of the optical absorbance. The size of the crystallite is 260 μm.

An important outcome of this study is evidence for an exchange of single hydrogen (deuterium) in $LiBH_4$. This is in contradiction to the idea of rigid molecular BH_4^- subunits (complexes) and raises the question on the exchange (diffusion) mechanism. One possible pathways of atoms might be vacancies formed by diffusion of the highly mobile Li^+ ion[23] and exchange via nearly free rotating $(BH_4)^-$ ions.[24] However, $NaBH_4$ exchanges hydrogen by deuterium similar to $LiBH_4$.[13] The fast exchange process is thus not a peculiarity induced by Li. Similar observations have been made on the related compound $NaAlH_4$.[26,27] Recent theoretical work explains the decomposition reaction of $NaAlH_4$ via an interface reaction mediated by AlH_3 vacancies.[29] Interestingly, color centers were observed upon X-ray exposure on borohydrides.[28] Color centers are vacancies, which are occupied by electrons, which can excite light in the visible energy range. It is thus likely that vacancies exists in $LiBH_4$. To give evidence for the existence of vacancies and to link them with the desorption of hydrogen, we followed the optical absorbance of a $LiBH_4$ crystallite during heating in inert atmosphere at 1 °C/min. The optical absorbance shown in Figures 7 and 8 is in first order the transmission through the crystal, the measurement of the corresponding optical properties is under way.

At 110 °C, a sharp intensity change is observed, which is attributed to the change of the optical properties due to the crystal transformation from orthorombic (*Pnma*) to hexagonal ($P6_3mc$) structure.[24] This transformation is not associated with hydrogen desorption. Hydrogen desorption starts at around 200 °C, and with it the optical intensity decreases first slowly and then rapidly just before the melting point. The intensity change is coupled to a color change. The molten crystal becomes transparent, which is a hint that the optical changes are associated with defects of the crystalline solid. The exact nature of these defects is not known yet and requires further research. However, following the idea of Gunaydin et al.,[29] we propose that these defects consists of BH_3 vacancies, i.e., BH_4^- vacancies, which have been refilled with H^-. (Di)borane desorption has been observed in particular at temperatures below melting (see ref 9), explaining the formation of these BH_3 vacancies. The single hydrogen anion is assumed to be easily exchanged by deuterium, and subsequently the deuterium is exchanged with one hydrogen of the neighbored BH_4^- anion. This mechanism agrees perfectly with the observed behavior of the hydrogen−deuterium exchange, which is coupled to the desorption process (see Figure 1), and can explain the desorption reaction of hydrogen (B_2H_6) from solid $LiBH_4$.

Conclusions

To conclude, we have demonstrated the exchange of single hydrogen atoms in the solid complex hydride $LiBH_4$ and estimated the self-diffusion coefficient of deuterium in $LiBH_4$, $D \simeq 7 \times 10^{-14}$ m^2 s^{-1} at a temperature of 523 K. $LiBH_4$ is the archetypical example of a lightweight complex metal hydride. With Raman spectroscopy on bulk hydrides we were able to shed light on the tracer diffusion mechanism in the bulk material, similar to "hydrogenography", i.e., optical spectroscopy on thin films.[30] Thus we think that the principles of this bulk study can be transferred to analogous materials.

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