Microscopic indicator for thermodynamic stability of hydrogen storage materials provided by muon-spin spectroscopy

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Abstract. In search of a high-capacity hydrogen storage system, we have investigated the thermodynamic properties of borohydrides \([M(BH_4)_n]\). Using positive muon-spin rotation and relaxation (\(\mu^+\)SR), we have acquired experimental data for a wide range of different powder samples below ambient temperature. Zero-field \(\mu^+\)SR measurements indicate the formation of the H-\(\mu^+\)-H system in LiBH\(_4\), NaBH\(_4\), KBB\(_4\) and Ca(BH\(_4\))\(_2\), but not in Mg(BH\(_4\))\(_2\). It is also found that the amplitude of the H-\(\mu^+\)H signal (\(A_{H\mu^+H}\)) varies with the electronegativity (\(\chi_P\)) of \(M^n+\). This is because, when \(\chi_P\) of \(M^n+\) is small, [BH\(_4\)]\(^-\) should be more negative, resulting in an increase in the electron-density of H\(^-\) ions. Therefore, \(A_{H\mu^+H}\) increases with decreasing \(\chi_P\). Since the thermodynamic stability of \(M(BH_4)_n\) also depends on \(\chi_P\), \(A_{H\mu^+H}\) is thought to be a microscopic indicator for the stability of borohydrides.

1. Introduction

Vehicular applications of fuel cells face several huge barriers, among which the key component is still a safe, light, high-capacity hydrogen storage system, despite a long history of research into hydrogen storage materials [1]. All the alloys that are currently used, including the Ti-based compounds, have a disadvantage for practical applications due to their small gravimetric H\(_2\) density, which makes them too heavy to carry on automobiles. It is well recognized that complex borohydrides are possible candidates for future onboard hydrogen storage materials [2, 3]: however, their slow dehydrogenation kinetics and high operating temperature (for releasing H)— i.e., hydrogen desorption temperature (\(T_d\))—need to be drastically improved if they are to enable a practical hydrogen storage system. Furthermore, although the dehydrogenation and rehydrogenation are known to involve multi-process reactions, their mechanisms are still not fully understood [4, 5]. For instance, LiBH\(_4\), which exhibits the highest gravimetric H\(_2\) density (18.5 mass%), liberates three of four hydrogen atoms and decomposes into LiH and boron.
through four intermediate states [6]. However, only one intermediate state Li$_2$(B$_{12}$H$_{12}$) has been characterized [4, 7] so far.

The nature of the “hydrogen bond” between positive muons (µ$^+$) and anions has been extensively investigated by a positive muon-spin rotation and relaxation (µ$^+$SR) technique, since the discovery of the F$^-$µ$^+$F$^-$ (or “FµF") ion in metal fluoride crystals such as LiF, NaF, CaF$_2$ and BaF$_2$ [8]. The FµF system is easily identified via its characteristic muon spin oscillation signal in a zero magnetic field (ZF-) µ$^+$SR spectrum, due to a dipole-dipole coupling in the collinear $^{19}$F-µ$^+$.$^{19}$F spin system. The FµF system has also been found in organic polymers, e.g. Teflon [9] and Nafion [10], despite a lack of crystal symmetry in these polymers. The formation of the FµF system is thus a rather common phenomenon in compounds containing F$^-$ ions [11, 12]. Similar hydrogen bond systems with other anions e.g. “Hµ$^+$H” and/or “Hµ$^+$” have been reported in a Kagomé compound ZnCu$_3$(OH)$_6$Cl$_3$ [13], in a layered cobalt dioxide [Ca$_{0.85}$OH)$_{1.16}$[Co$_2$] [14] and in NaAlH$_4$ [15], the last of which was studied as a potential hydrogen storage material for fuel cells.

In NaAlH$_4$, the volume fraction of H$_2$H (V$_{H_2H}$) was proposed to be an indicator for the dehydrogenation kinetics via comparison of V$_{H_2H}$ between pure and Ti-doped NaAlH$_4$ [15, 16]. However, although the discovery of H$_2$H demonstrates that µ$^+$SR can contribute significantly to research in hydrogen storage materials, NaAlH$_4$ is unlikely to be a good solution for future onboard systems, due to its relatively small gravimetric H$_2$ density (compared to LiBH$_4$) and its insufficient rehydrogenation capacity. We have, therefore, performed a systematic µ$^+$SR investigation of all the five $M$(BH$_4$)$_n$ systems, for which pure powder samples are available. We have found that the H$_2$H system is a unique probe of both structural and dynamic/kinematic properties of H in these compounds.

2. Experimental

Powder samples of LiBH$_4$, NaBH$_4$, KBH$_4$, and Ca(BH$_4$)$_2$ were purchased from Aldrich Co. LTD, and Mg(BH$_4$)$_2$ from FZK (Forschungszentrum Karlsruhe). Since the samples are unstable in air, they were packed in an In- or Au-sealed aluminum powder cell in an Ar-filled glove box. The µ$^+$SR experiments were performed on the M20 surface muon beam line at TRIUMF, using an experimental setup and techniques described elsewhere [17].

3. Results and Discussion

Figure 1(a) shows the temperature (T) variation of the ZF-µ$^+$SR time spectrum for LiBH$_4$ in the $T$ range between 5 and 250 K. One can clearly see a damped oscillation, particularly below 150 K. Since there are no magnetic moments in LiBH$_4$, such oscillation indicates the formation of the H$_2$H system in LiBH$_4$. In fact, the ZF- spectrum is well fitted by a combination of the H$_2$H signal, a static Gaussian Kubo-Toyabe ($G_{KT}$) signal (from other muon sites experiencing disordered magnetic fields due to nuclear moments), and a background (BG) signal from the powder cell (which is made of high-purity aluminum):

$$A_0 \ P_{ZF}(t) = A_{H_2H}P_{H_2H}(t) \exp(-\lambda_{H_2H} t) + A_{KT}G_{KT} + A_{BG} \ .$$  (1)

Here $A_0$ is the initial ($t = 0$) asymmetry, $P_{ZF}(t)$ is the muon spin polarization function in ZF, $A_{H_2H}$, $A_{KT}$ and $A_{BG}$ are the asymmetries of the three signals, $\lambda_{H_2H}$ is the exponential relaxation rate of the precessing signal, and $\sigma_G$ is the Gaussian relaxation rate. Here $P_{H_2H}(t)$ is the muon spin relaxation function caused by a collinear three spin 1/2 system, given in [8]:

$$P_{H_2H}(t) = \frac{1}{2} + \frac{1}{6} \cos(\sqrt{3} \omega_d t) + \frac{1 + \sqrt{3}}{6} \cos(\frac{3 + \sqrt{3}}{2} \omega_d t) + \frac{1 - \sqrt{3}}{6} \cos(\frac{3 - \sqrt{3}}{2} \omega_d t) \ .$$  (2)
Figure 1. Temperature dependence of (a) the ZF-$\mu^+$SR time spectrum for LiBH$_4$; (b) the normalized $A_{\mu\mu\mu}$; (c) $f_d$; and (d) $\lambda_{\mu\mu\mu}$, crystal structure of (e) orthorhombic LiBH$_4$ below $\sim$ 381 K, and (f) the calculated electrostatic potential ($\phi_E$) along the H-H bond in the distance range between 2.45 and 4.69 Å, in which 21 combinations are included. Bold solid lines in (a) represent the fitting result using Eq. (1) and the bottom three solid lines show the three components in Eq. (1). Each spectrum is offset by 0.05 for clarity of display. The $\mu^+$SR parameters in (b)-(d) were obtained by fitting the ZF-$\mu^+$SR time spectra using Eq. (1). Error bars in (c) are comparable to or below the size of solid circles. Arrows and numbers in (e) represent the distance to the neighboring hydrogens, at the center of which $\mu^+$ locates, based on the prediction from the $\phi_E$ calculations. In (f), the lowest 4 $\phi_E$s are represented by a bold line, while the rest 17 by a narrow (blue) dotted line.
where $\omega_d$ is the muon precession frequency due to the nuclear dipole field of the proton in the H-$\mu^+$ bond. From $\omega_d$, it is possible to calculate the distance $r$ between the $\mu^+$ and the nucleus according to [8]:

$$\omega_d = 2\pi \cdot f_d = \mu_0 \gamma \frac{\gamma_N}{4\pi r^3},$$

Here $\gamma$ is the gyromagnetic ratio of $\mu^+$ and $\gamma_N$ is the nuclear gyromagnetic ratio of $^1\text{H}$.

Figures 1(b)-1(d) show the $T$ dependences of the $\mu^+$SR parameters for LiBH$_4$. The normalized $A_{H\mu H}$ [$N_{A_{H\mu H}} = A_{H\mu H}/(A_{H\mu H} + A_{KT})$] reaches $\sim 0.8$ at 5 K and decreases monotonically with increasing $T$. However, even at 250 K, $N_{A_{H\mu H}} \sim 0.6$. As $T$ increases from 5 K, $f_d$ also decreases monotonically up to 280 K, which means that the increase in $r$ with $T$ is probably connected to thermal fluctuations/vibrations of the BH$_4$ anions. Using Eq (3), $2r$ is estimated to be 3.16-4.42 Å. According to electrostatic potential ($\phi_E$) calculations using a first-principles DFT+GGA method [18], there are four stable $\mu^+$ sites for the H$_2\mu$H system; namely, the center between the neighboring hydrogens with the distance $d_{H-H} = 3.173, 4.168, 4.354, \text{and } 4.626$ Å [Figs. 1(e) and 1(f)]. These values are in good agreement with $2r$ estimated from $f_d$, indicating the change in occupancy of $\mu^+$ at the center of the four $d_{H-H}$ with $T$. Particularly, since $2r = 3.16$ Å at 5 K, $\mu^+$ locates at the center of the shortest $d_{H-H}$ among four stable sites in the ground state. The monotonic decrease in $A_{H\mu H}$ with $T$ implies an increase in homogeneity of the local (nuclear magnetic) environment caused by thermal fluctuation/vibration. That is, the local variation of “distance” for the H-$\mu$ bond in the H$_2\mu$H system may be averaged out by local motion, while the atomic membership of H$_2\mu$H itself is maintained. This is consistent with the $T$ dependences of $N_{A_{H\mu H}}$ and $f_d$. It should be noted that $\mu^+$ starts to diffuse at high $T$, at which its thermal energy is comparable to the barrier energy between the potential minima. In order to clarify such diffusive behavior, we need to measure ZF-spectra above 250 K together with longitudinal field spectra to distinguish the $\mu^+$ motion from the H$_2\mu$H signal.

In order to learn the nature of the H$_2\mu$H system in other borohydrides, Fig. 2 shows the ZF-spectrum for LiBH$_4$, NaBH$_4$, MgBH$_4$, KBH$_4$ and CaBH$_4$ at 5 K. Except for MgBH$_4$, all the ZF-spectra exhibit oscillations, indicating formation of an H$_2\mu$H unit. The results of fits to the ZF-spectra obtained at 5 K are summarized in Table 1. In contrast to LiBH$_4$, there are mainly two muon sites for the H$_2\mu$H system in the tetrahedral NaBH$_4$ lattice. The estimated $r$ suggests that the $\mu^+$ is located at the center of the second nearest neighboring hydrogens [3.427 Å away, Fig. 3(d)].

### Table 1. H$_2\mu$H parameters obtained by fitting the ZF-spectra at 5 K using Eqs. (2)-(3).

| $M$ for $M$(BH$_4$)$_2$ | $f_d$ (MHz) | $2r$ (Å) | $N_{A_{H\mu H}}$ |
|------------------------|-------------|----------|-----------------|
| Li                     | 0.0974(2)   | 3.16(2)  | 0.82(4)         |
| Na                     | 0.0854(1)   | 3.30(1)  | 0.99(1)         |
| Mg                     | 0           | $\infty$ | -               |
| K                      | 0.106(3)    | 3.07(3)  | 0.7399(1)       |
| Ca                     | 0.119(2)    | 2.96(2)  | 0.34(8)         |

Furthermore, we found a dynamic change in the H$_2\mu$H signal accompanying a structural phase transition of NaBH$_4$ at $T_c = 189.9$ K from a low-$T$ tetragonal phase to a high-$T$ cubic phase due to an order-disorder transition of the BH$_4$ tetrahedra [Figs. 3(d) and 3(e)] [19–21]. The H$_2\mu$H system is stable in the ordered state, but would be unstable in the disordered state due to the
Figure 2. ZF-µSR time spectra for LiBH$_4$, NaBH$_4$, Mg(BH$_4$)$_2$, KBH$_4$ and Ca(BH$_4$)$_2$ at 5 K. Solid lines represent the fitting result using Eq. (1). Each spectrum is offset by 0.1 for clarity of display.

rotation of the [BH$_4$]$^-$ group [Fig. 3]. We, therefore, fitted the ZF-spectrum using Eq. (1) plus an additional Hµ signal $[A_{H\mu}P_{H\mu}(t)\exp(-\lambda_{H\mu}t)]$, where $P_{H\mu}(t)$ is given by [9].

$$P_{H\mu}(t) = \frac{1}{6} + \frac{1}{6} \cos(\omega_\mu t) + \frac{1}{3} \cos\left(\frac{1}{2}\omega_\mu t\right) + \frac{1}{3} \cos\left(\frac{3}{2}\omega_\mu t\right).$$ (4)

This means that $\mu^+$ forms a “H$^+\[BH_4\]^-”-like $\mu$BH$_4$ molecule at high $T$ instead. In addition, despite the fact that the transition is thought to be second-order, the present $\mu$SR result suggests the presence of the $\mu[\BH_4]$ state even below $T_c$, probably due to microscopic vibration/rotation of the BH$_4$ tetrahedra.

Although structural considerations are likely to explain the magnitude of $N_{A_{H\mu}H}$ for LiBH$_4$, NaBH$_4$, and KBH$_4$, they offer no acceptable reasons for the absence of the Hµ signal in Mg(BH$_4$)$_2$ and the rather small $N_{A_{H\mu}H}$ in Ca(BH$_4$)$_2$. We, therefore, wish to discuss the stability of $N_{A_{H\mu}H}$ from another viewpoint. According to theoretical and experimental work on the thermodynamic stability of $M$(BH$_4$)$_n$ ($M$ = Li, Na, K, Ca, Mg, Zn and Sc), the stability of $M$(BH$_4$)$_n$ is likely to show a good correlation with the electronegativity ($\chi_P$) of cations $M^{n^+}$ [Fig. 4(a)] [22]; that is, larger $\chi_P$, implies less thermodynamic stability. This indicates that, although the bonding between $M^{n^+}$ and $n[\BH_4]$ is basically ionic, the charge transfer from $[\BH_4]$ to $M^{n^+}$ is a key feature for the stability of $M$(BH$_4$)$_n$. This situation is thus expected to be drastically changed if the liberated H ions are coupled with the neighboring [BH$_4$]$^-$ anions. In other words, the stability of the Hµ$^+H$ system in $M$(BH$_4$)$_n$ should also be a good indicator for their performance of dehydrogenation. In fact, one can clearly see a good correlation between $T_d$ and $N_{A_{H\mu}H}$ [Fig. 4(b)], where $T_d$ was determined by thermal desorption spectroscopy measurements using gas chromatography [22].
As already proposed by Kadono and coworkers [15], proton-like hydrogens would be generated during the desorption reaction of $M$(BH$_4$)$_2$. In order to accelerate this reaction, the generated hydrogens should be removed from the materials through a solid state diffusion process. The presence of a stable HµH (and/or Hµ) system indicates the formation of a [BH$_4$]$^-$-H$^+$-[BH$_4$]$^-$ (and/or H$^+$-[BH$_4$]$^-$) bond in $M$(BH$_4$)$_2$ during the desorption reaction. Since such a bond clearly reduces the reaction rate, it is expected that additional thermal energy is necessary to decompose the $M$(BH$_4$)$_2$ with high $N_{A_{H\mu H}}$ compared with that for the materials with low $N_{A_{H\mu H}}$. This is a reasonable explanation for the linear relationship in Fig. 4(b). This also demonstrates that $\mu^+$SR is a unique tool for investigating the nature of LiBH$_4$ and related hydrogen storage materials via the HµH signal. Finally, we wish to emphasize that, although the relationship between $T_d$ and $\chi_P$ was found empirically for $M$(BH$_4$)$_n$ [Fig. 4(a)], the underlying mechanism has been successfully clarified by the present $\mu^+$SR experiment. In fact, there was no experimental evidence regarding which parameters were predominant for determining $T_d$. $\mu^+$SR is, therefore, a unique tool to

Figure 3. Temperature dependences of (a) the ZF-$\mu^+$SR time spectrum for NaBH$_4$; (b) $N_{A_{H\mu H}}$ and $N_{A_{H\mu}}$; and (c) $f_d$, and the crystal structure (d) below and (e) above $T_c = 189.9$ K. In (a), the solid lines represent the fitting result using Eq. (1) plus an additional Hµ signal [9]. Each spectrum in (a) is offset by 0.05 for clarity of display.
investigate the thermal stability of $M(BH_4)_n$ and related compounds.

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