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

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In search of a high-capacity hydrogen storage system, we have investigated the thermodynamic properties of borohydrides $[M(BH_4)_2]$. Using positive muon-spin rotation and relaxation (μ^+SR), we have acquired data for five different powder samples below ambient temperature. Zero-field μ^+SR measurements indicate the formation of the H-μ^+-H system in $LiBH_4$, $NaBH_4$, KBH_4, and $Ca(BH_4)_2$ but not in $Mg(BH_4)_2$. It is also found that the amplitude of the HμH signal ($A_{H\mu H}$) varies with the electronegativity (χ_P) of M^{n+}. Since the thermodynamic stability of $M(BH_4)_n$ also depends on χ_P, $A_{H\mu H}$ is thought to be a microscopic indicator for the stability of $M(BH_4)_n$.

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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 multiprocess 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 $F^-\mu^+F^-$ (or "$F\mu F$") ion in metal fluoride crystals such as LiF, NaF, CaF_2, and BaF_2.[8] The $F\mu F$ 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 $F\mu F$ 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 $F\mu F$ system is thus a rather common phenomenon in compounds containing F^- ions.[11,12] Similar hydrogen bond systems with other anions, e.g., "$H\mu^+H$" and/or "$H\mu^+$" have been reported in a Kagomé compound $ZnCu_3(OH)_6Cl_2$ (Ref. 13) in a layered cobalt dioxide $[Ca_{0.85}OH]_{1.16}[CoO_2]$ (Ref.

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 $H\mu H(V_{H\mu H})$ was found to decrease by the Ti doping via a comparative μ^+SR study on pure and Ti-doped $NaAlH_4$.[15] Since T_d also decreases with the Ti doping,[16] $V_{H\mu H}$ was proposed as an indicator for the dehydrogenation kinetics of hydrogen storage materials.[15] However, only one doped sample was examined and its T_d was not reported in Ref. 15. It is, thus, difficult to know the quantitative relationship between $V_{H\mu H}$ and the thermodynamic stability for $NaAlH_4$. Furthermore, although the discovery of $H\mu H$ 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 $H\mu H$ system is a unique probe of both structural and dynamic/kinematic properties of H in these compounds.

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 beamline at TRIUMF, using an experimental setup and techniques described elsewhere.[17]

Figure 1(a) shows the temperature (T) variation in 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 $H\mu H$ system in $LiBH_4$. In fact, the ZF spectrum is well fitted by a combination of the $H\mu H$ signal, a static Gaussian Kubo-Toyabe (G_{KT}) signal (from other muon sites experiencing
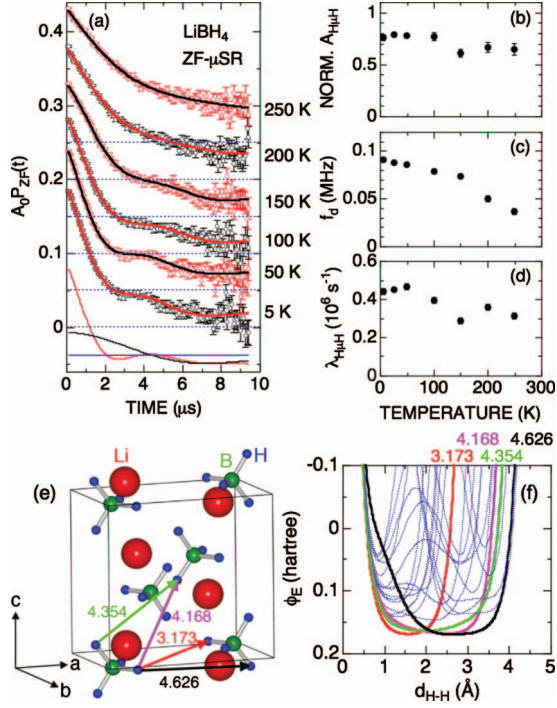
FIG. 1. (Color) Temperature dependence of (a) the ZF-μ^+SR time spectrum for LiBH$_4$, (b) the normalized $A_{H\mu H}$, (c) f_d, (d) $\lambda_{H\mu H}$, crystal structure of (e) orthorhombic LiBH$_4$ below $\sim$381 K, and (f) the calculated electrostatic potential (ϕ_E) along the H-H bond in the distance 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 μ^+SR parameters in (b)–(d) were obtained by fitting the ZF-μ^+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 hydrogen atoms, at the center of which μ^+ locates, based on the prediction from the ϕ_E calculations. In (f), the lowest 4 ϕ_E's are represented by a bold line while the rest 17 by a narrow (blue) dotted line.

disordered magnetic fields due to nuclear moments), and a background (BG) signal from the powder cell (which is made of high-purity aluminum),

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

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

$$P_{H\mu H}(t) = \frac{1}{2} + \frac{1}{6}\cos(\sqrt{3}\omega_d t) + \frac{1 + 1/\sqrt{3}}{6}\cos\left(\frac{3 + \sqrt{3}}{2}\omega_d t\right)$$
$$+ \frac{1 - 1/\sqrt{3}}{6}\cos\left(\frac{3 - \sqrt{3}}{2}\omega_d t\right),$$
(2)

where ω_d is the muon precession frequency due to the nuclear dipole field of the proton in the H-μ^+ bond. From ω_d, it is possible to calculate the distance r between the μ^+ and the nucleus according to Ref. 8,

$$\omega_d \equiv 2\pi \cdot f_d = \mu_0 \hbar \frac{\gamma_\mu \gamma_N}{4\pi r^3}.$$
(3)

Here, γ_μ is the gyromagnetic ratio of μ^+ and γ_N is the nuclear gyromagnetic ratio of ^{1}H. Finally, G_{KT} is given by $G_{KT}(t) = \frac{1}{3} + \frac{2}{3}(1 - \Delta^2 t^2)\exp(-\frac{\Delta^2 t^2}{2})$, where Δ is the field distribution width at the muon site.[17]

Figures 1(b)–1(d) show the T dependences of the μ^+SR parameters for LiBH$_4$. The normalized $A_{H\mu H}[N_{A_{H\mu H}} = A_{H\mu H}/(A_{H\mu H}+A_{KT}) = V_{H\mu H}]$ 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 (ϕ_E) calculations using a first-principles calculation based on density-functional theory with generalized gradient approximation method,[18] there are four stable μ^+ sites for the HμH system; namely, the center between the neighboring hydrogen atoms with the distance $d_{H\text{-}H} = 3.173$, 4.168, 4.354, 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 μ^+ at the center of the four $d_{H\text{-}H}$ with T. Particularly, since $2r = 3.16$ Å at 5 K, μ^+ locates at the center of the shortest $d_{H\text{-}H}$ among four stable sites in the ground state. The monotonic decrease in $\lambda_{H\mu H}$ with T implies an increase in homogeneity of the local (nuclear magnetic) environment caused by thermal fluctuation/vibration. This is consistent with the T dependences of $N_{A_{H\mu H}}$ and f_d. It should be noted that μ^+ 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 μ^+ motion from the HμH signal.

In order to learn the nature of the Hμ^+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 HμH unit. Note that $A_0 \sim 0.24$ for the present experimental setup. This means that some muons form a muonium ($\mu^+ e^-$) state, which reduces A_0, as in the case for NaAlH$_4$.[15] This is because all the borohydrides are a dielectric ionic crystal. The results of fits to the ZF spectra obtained at 5 K are summarized in Table I. In contrast to LiBH$_4$, there are mainly two muon sites for the HμH system in the tetrahedral NaBH$_4$ lattice. The estimated r suggests that the μ^+ is located at the center of the second-nearest-neighboring hydrogen atoms [3.367 Å away, Fig. 3(d)].

Furthermore, we found a dynamic change in the HμH 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$_4$
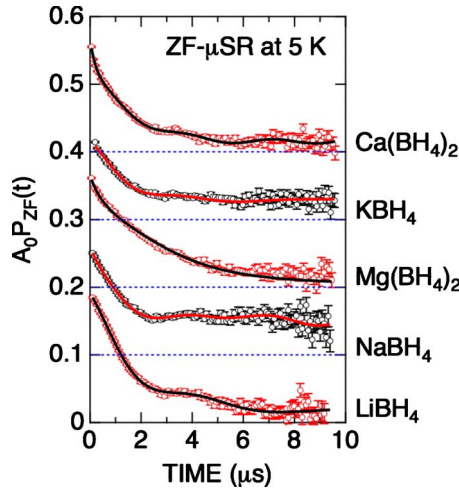
FIG. 2. (Color online) ZF-μ^+SR time spectra for LiBH$_4$, NaBH$_4$, Mg(BH$_4$)$_2$, KBH$_4$, and Ca(BH$_4$)$_2$ at 5 K. Solid lines represent the fitting result using Eq. (1). Each spectrum is offset by 0.1 for clarity of display.
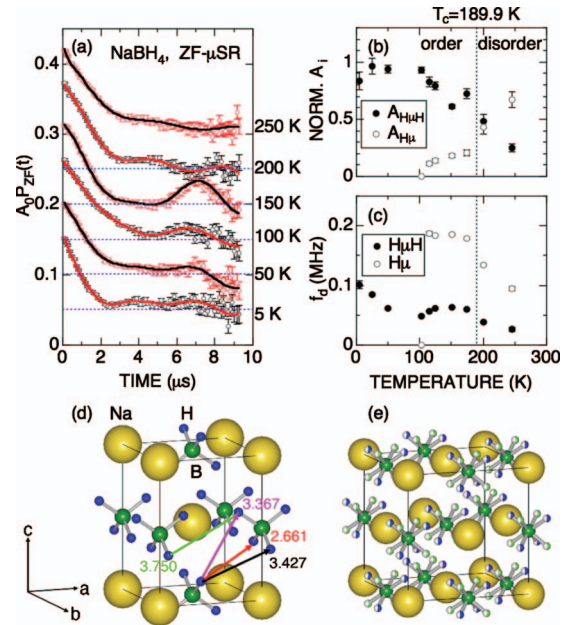

FIG. 3. (Color) Temperature dependences of (a) the ZF-μ^+SR time spectrum for NaBH$_4$, (b) $N_{A_{H\mu H}}$ and $N_{A_{H\mu}}$, and (c) f_d, and the crystal structure (d) below and (e) above T_c=189.9 K. In (a), the solid lines represent the fitting result using Eq. (1) plus an additional Hμ signal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

tetrahedra [Figs. 3(d) and 3(e)].[19–21] The HμH system is stable in the ordered state but would be unstable in the disordered state due to the rotation of the [BH$_4$]$^-$ group (Fig. 3). We, therefore, fitted the ZF spectrum using Eq. (1) plus an additional Hμ signal $[A_{H\mu}P_{H\mu}(t)\exp(-\lambda_{H\mu}t)]$.[9,22] This means that μ^+ forms a "H$^+$[BH$_4$]$^-$"-like μBH$_4$ molecule at high T instead. In addition, despite the fact that the transition is thought to be second order, the present μ^+SR result suggests the presence of the μ[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 HμH 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, Ca, Mg, Zn, and Sc), the stability of M(BH$_4$)$_n$ is likely to show a good correlation with the electronegativity (χ_P) of cations M^{n+} [Fig. 4(a)],[23] that is, larger χ_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.[23]

As already proposed by Kadono *et al.*,[15] protonlike hydrogen atoms would be generated during the desorption reaction of M(BH$_4$)$_2$. In order to accelerate this reaction, the generated hydrogen atoms 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

TABLE I. μ^+SR parameters obtained by fitting the ZF spectra at 5 K using Eqs. (1)–(3). For Mg(BH$_4$)$_2$, since f_d=0, $N_{A_{H\mu H}}$=0. However, for such case, the first term of Eq. (1) is equivalent to $A_e \exp(-\lambda_e t)$, as indexed by * and **.

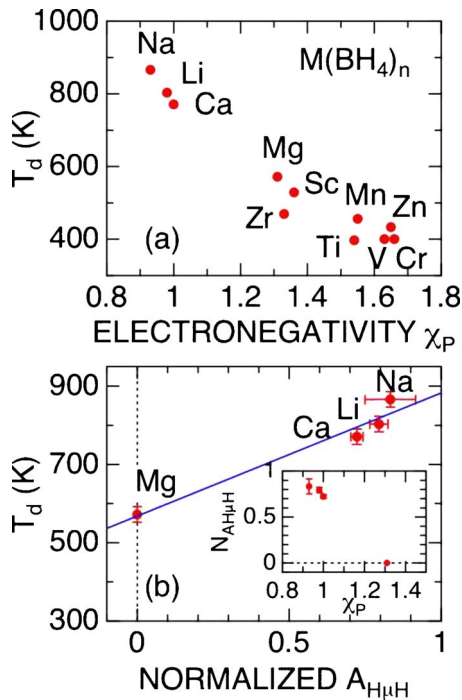| M for M^{n+}(BH$_4$)$_n$	$N_{A_{H\mu H}}$	f_d (MHz)	$2r$ (Å)	$\lambda_{H\mu H}$ (10^6 s^{-1})	$N_{A_{KT}}$	Δ (10^6 s^{-1})
Li	0.79(4)	0.095(5)	3.19(6)	0.44(2)	0.21(4)	0.29(5)
Na	0.83(8)	0.101(7)	3.12(7)	0.45(5)	0.17(8)	0.50(2)
Mg	0, [N_{A_e}=0.72(17)]*	0	∞	[λ_e=0.58(3)]**	0.28(15)	0.26(7)
K	0.74(2)	0.107(3)	3.07(3)	0.44(2)	0.26(2)	0.36(2)
Ca	0.72(2)	0.094(12)	3.20(13)	0.52(11)	0.28(2)	0.24(4)

FIG. 4. (Color online) The relationship between (a) hydrogen desorption temperature (T_d) and electronegativity (χ_P) (Ref. 23) and (b) T_d and $N_{A_{H\mu H}}$. The inset of (b) shows the relationship between $N_{A_{H\mu H}}$ and χ_P. Note that T_d for KBH$_4$ was not reported in Ref. 23.

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). Furthermore, such relationship is consistent with the result that the Ti doping reduces both $N_{A_{H\mu H}}$ and T_d for NaAlH$_4$.[15] This also demonstrates that μ^+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 χ_P was found empirically for $M(BH_4)_n$ [Fig. 4(a)], the underlying mechanism has been successfully clarified by the present μ^+SR experiment. In fact, there was no experimental evidence regarding which parameters were predominant for determining T_d. μ^+SR is, therefore, a unique tool to investigate the thermal stability of $M(BH_4)_n$ and related compounds.

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