Theory Focus Session on Hydrogen Storage Materials, 18 MAY 2006

Prediction of Novel Hydrogen Storage Reactions

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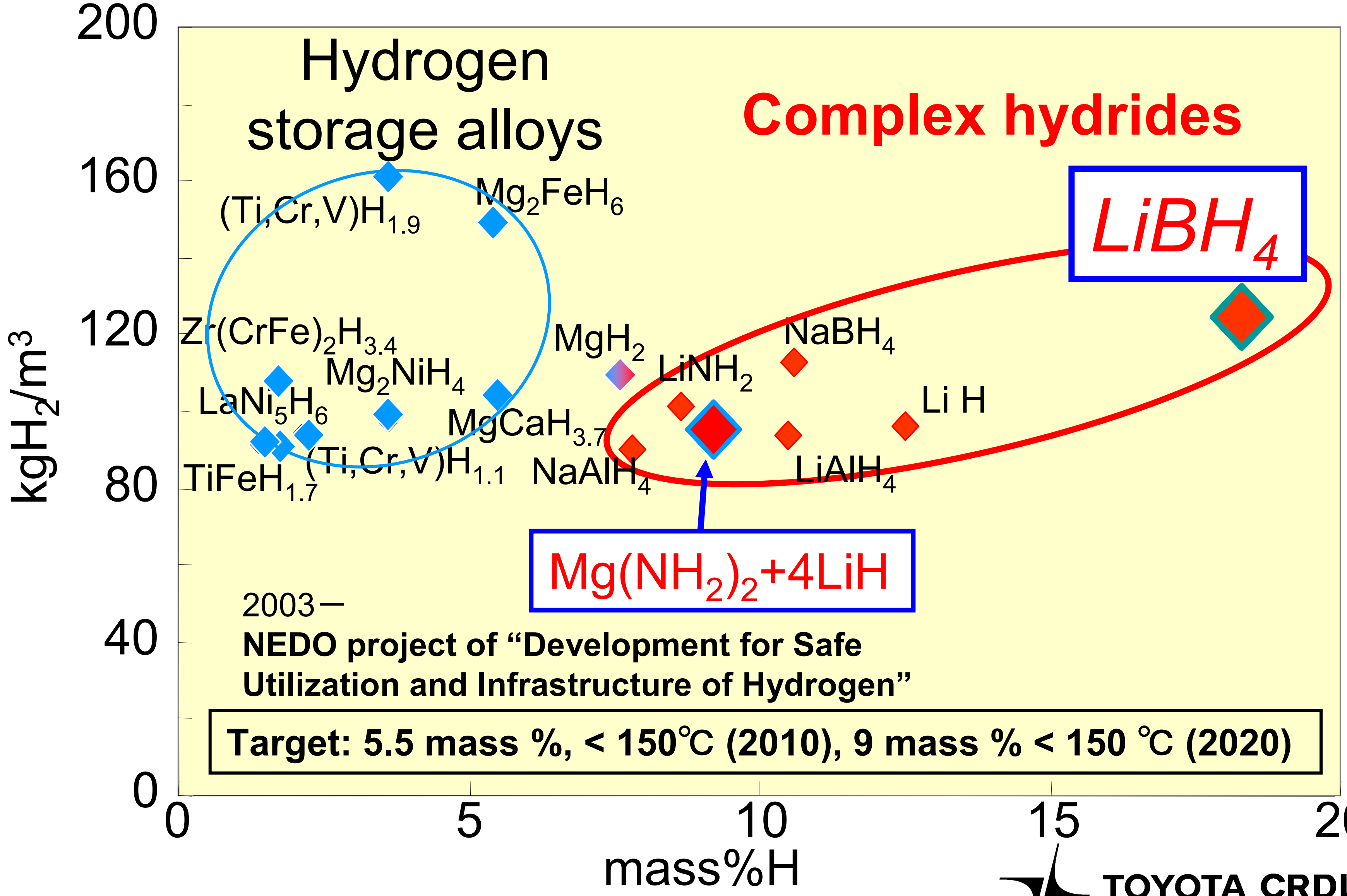
TOYOTA CRDL, INC.

Hydrogen Storage Materials



2003－

NEDO project of "Development for Safe Utilization and Infrastructure of Hydrogen"

Target: 5.5 mass %, < 150℃ (2010), 9 mass % < 150 ℃ (2020)

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Lithium Borohydride, $LiBH_4$

Advantages

☆ light weight

☆ high capacity of hydrogen storage (14 mass %)

Disadvantages

★ **thermodynamically too stability** (> 600 K)

★ poor reaction kinetics

1) Fundamental properties of $LiBH_4$

2) Thermodynamical stability of $M(BH_4)_n$

3) Intermediate compound of $LiBH_4$

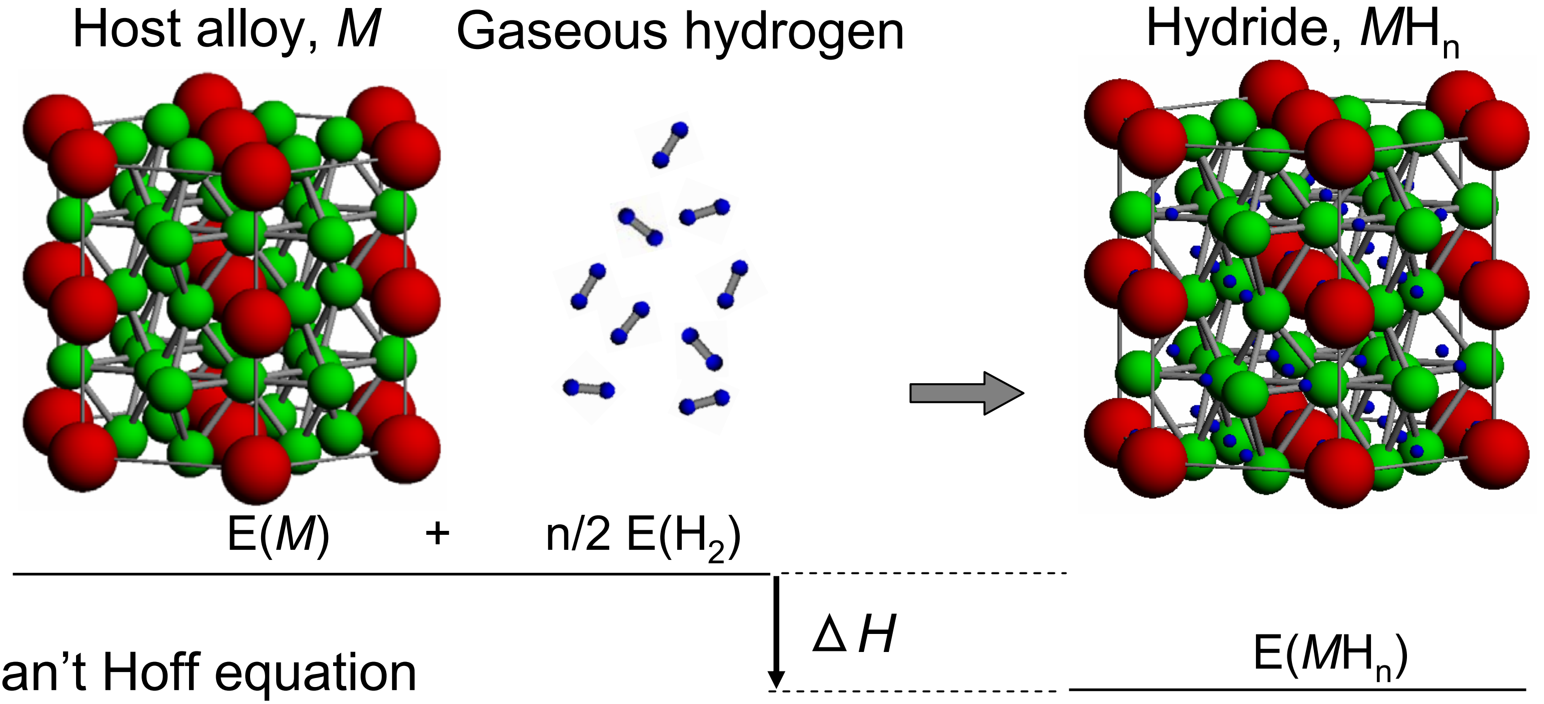
Methodology

- Density Functional Theory (Kohn-Sham energy functional)
- Exchange-correlation energy

  Generalized Gradient Approximation
  proposed by Perdew, Burke, and Ernzerhof
- Ultrasoft pseudopotential method
- Plane wave basis set
- Structural optimization (atomic forces and stress tensor)
- Linear response calculation (dielectric properties)

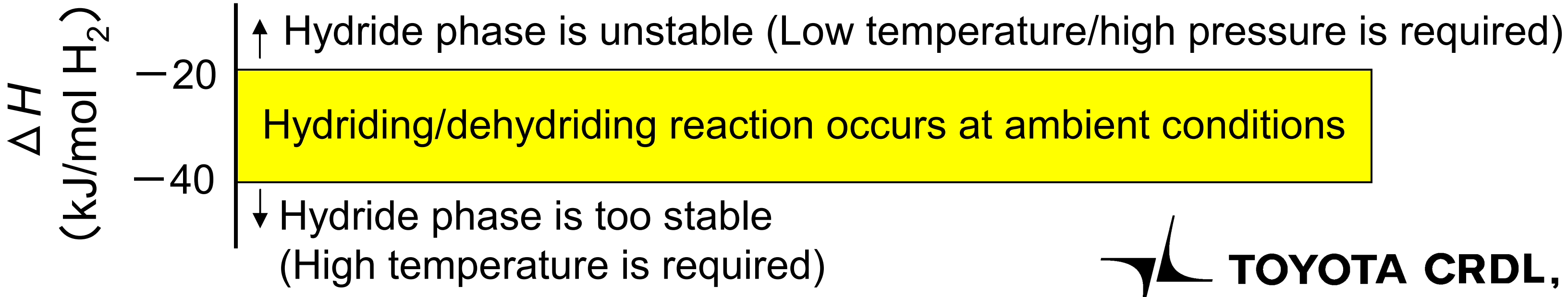
Heat of formation (hydrogenation)

$$M + n/2\ H_2 \rightarrow MH_n$$



van't Hoff equation

$$\log\left(\frac{p}{p_0}\right) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (\Delta S \simeq -120 \text{ J/mol } H_2 \cdot \text{K})$$



↑ Hydride phase is unstable (Low temperature/high pressure is required)

Hydriding/dehydriding reaction occurs at ambient conditions

↓ Hydride phase is too stable (High temperature is required)

Fundamental properties of $LiBH_4$

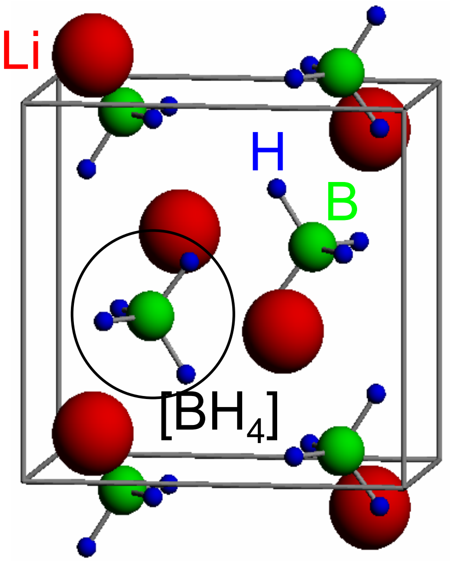
K. Miwa, N. Ohba, S. Towata, Y. Nakamori, and S. Orimo,
“First-principles study on lithium borohydrides $LiBH_4$,” Phys. Rev. B 69, 245120 (2004).

Structural parameters

$LiBH_4$ Orthorhombic, Space group *Pnma* (No.62)

Lattice constants			Geometry of BH_4 complexes		
a (Å)	*b* (Å)	*c* (Å)	bond lengths $d_{B\text{-}H}$ (Å)	bond angles $\theta_{H\text{-}B\text{-}H}$ (deg.)	
7.343	4.399	6.588	1.23～1.24	107～111	Present
7.179	4.437	6.803	1.04～1.28	85～120	XRD*
7.173	4.434	6.798	1.28～1.44		XRD**

*J-Ph. Soulié *et al.*,J. Alloys Comp. 346, 200 (2002) **A. Züttel *et al.*, J. Power Sources 118, 1 (2003)



Heat of formation

$LiH + B + 3/2\ H_2 \Leftrightarrow LiBH_4$ −56 kJ/mol H_2
(Expt. −69 kJ/mol H_2)

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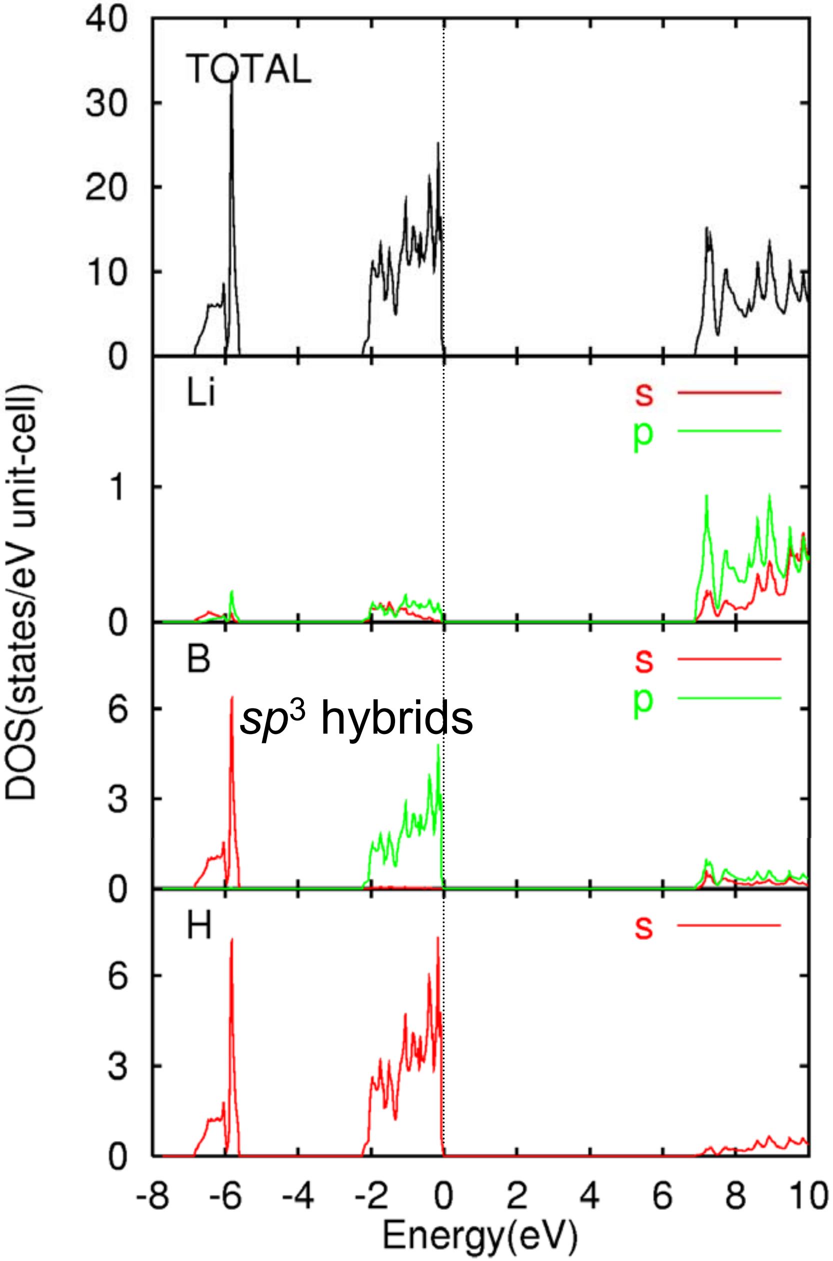
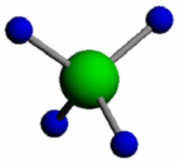
Density of states



Ionized as Li^+

$[BH_4]^-$



Internal bonding covalent-type

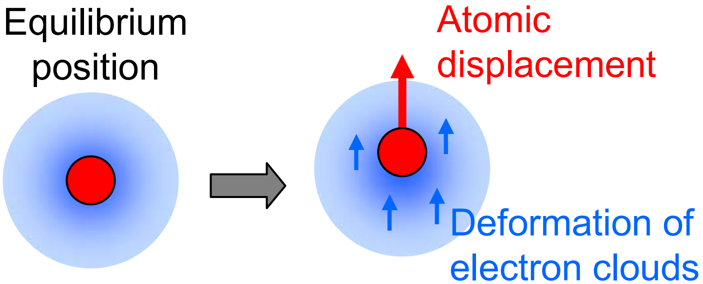
Born effective charge tensors

$$Z^*_{i,\alpha\beta} = V \frac{d P_\alpha}{d R_{i,\beta}}$$

P_α : macroscopic polarization

$R_{i,\beta}$: atomic position vector

V : unit cell volume



In the case of ideal Li⁺ cation

$$Z^*_{\mathrm{Li}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$Z^*_{\mathrm{Li}} = \begin{pmatrix} 0.98 & 0 & \pm 0.21 \\ 0 & 1.08 & 0 \\ \pm 0.15 & 0 & 1.02 \end{pmatrix}$$

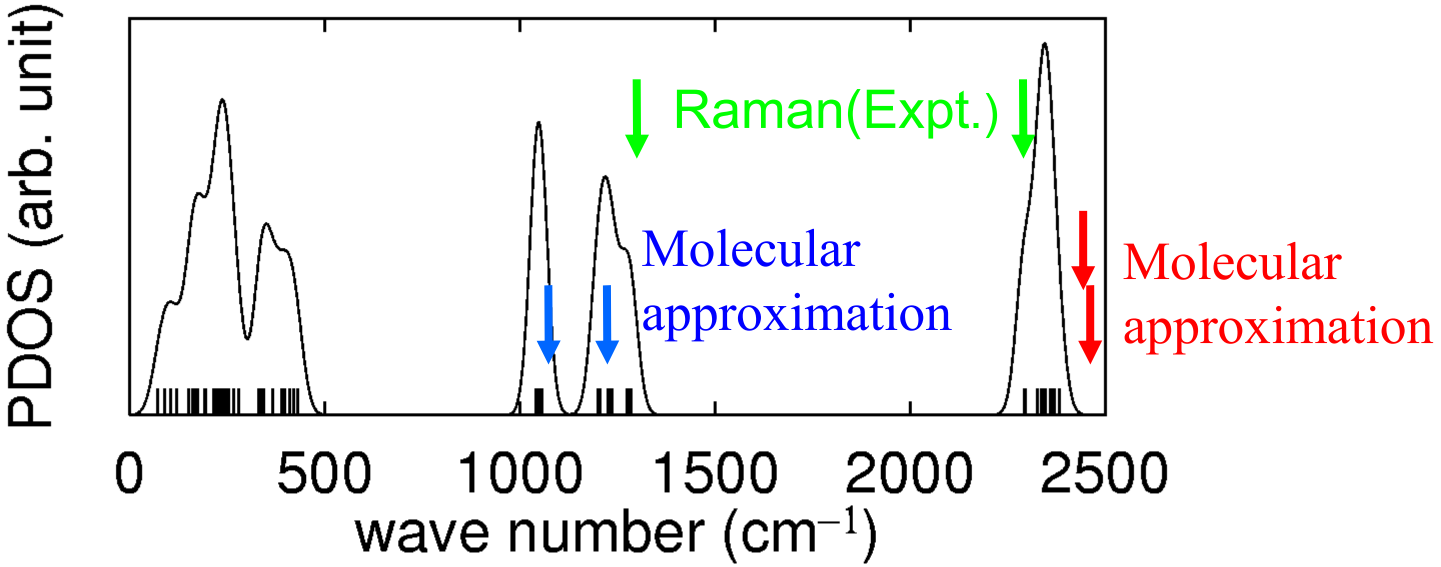
$$Z^*_{\mathrm{B}} = \begin{pmatrix} 0.10 & 0 & \pm 0.11 \\ 0 & 0.15 & 0 \\ \pm 0.12 & 0 & 0.06 \end{pmatrix}$$

$$Z^*_{\mathrm{H1}} = \begin{pmatrix} -0.28 & 0 & \pm 0.16 \\ 0 & -0.18 & 0 \\ \pm 0.17 & 0 & -0.33 \end{pmatrix}$$

$$Z^*_{\mathrm{H2}} = \begin{pmatrix} -0.32 & 0 & \pm 0.12 \\ 0 & -0.15 & 0 \\ \pm 0.12 & 0 & -0.41 \end{pmatrix}$$

$$Z^*_{\mathrm{H3}} = \begin{pmatrix} -0.24 & \pm 0.16 & \pm 0.01 \\ \pm 0.17 & -0.45 & \pm 0.05 \\ \pm 0.02 & \pm 0.03 & -0.18 \end{pmatrix}$$

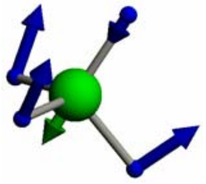
Γ-phonon frequencies



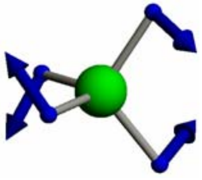
Normal mode frequencies of a free $[BH_4]^-$ anion

Bending modes

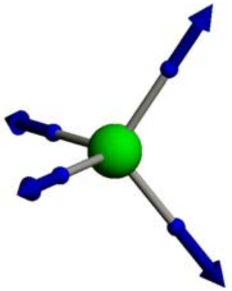
Stretching modes



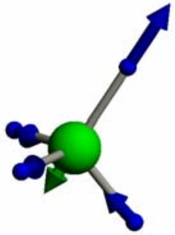
1081 cm^{-1} (T_2)



1228 cm^{-1} (E)



2426 cm^{-1} (A_1)

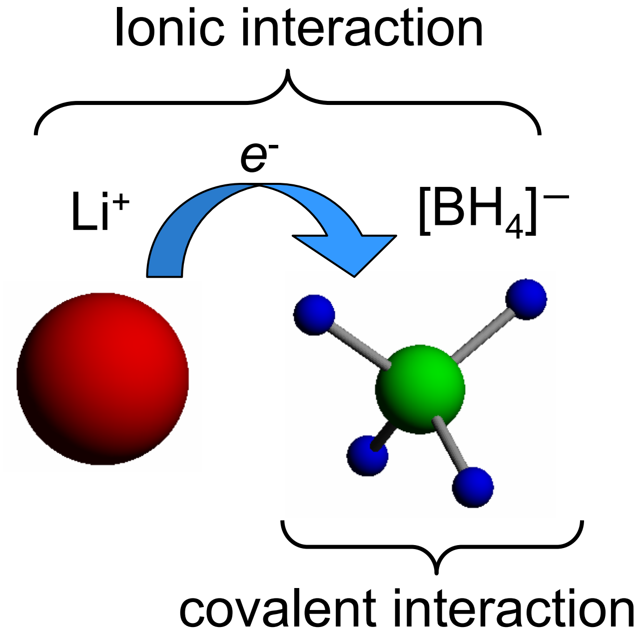


2459 cm^{-1} (T_2)

Bonding characters of $LiBH_4$

Fundamental properties of $LiBH_4$

- Structural property
- Electronic property
- Dielectric property
- Vibrational property



Charge transfer from Li^+ to $[BH_4]^-$ is a key feature

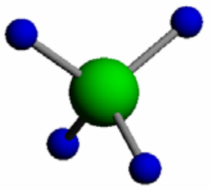
Cation electronegativity: a good measure for the stability of borohydrides?

Thermodynamical stability of $M(\mathrm{BH}_4)_n$

Y. Nakamori, K. Miwa, A. Ninomiya, H. Li, N. Ohba, S. Towata, A. Züttel, and S. Orimo,
“Correlation between thermodynamical stabilities of metal borohydrides and cation electronegativities: First-principles calculations and experiment,” Submitted to Phys. Rev. B

K. Miwa, N. Ohba, S. Towata, Y. Nakamori, and S. Orimo, J. Alloys Compd. 404-406, 140 (2005).

Borohydrides, $M(\mathrm{BH_4})_n$



M	K^+	Na^+	Li^+	Mg^{2+}	Sc^{3+}	Hf^{4+}	Zr^{4+}	Zn^{2+}	Cu^+
Pauling Electronegativity χ_P	0.8	0.9	1.0	1.2	1.3	1.3	1.4	1.6	1.9

$$\frac{1}{n}M + \mathrm{B} + 2\mathrm{H_2} \Leftrightarrow \frac{1}{n}M(\mathrm{BH_4})_n \qquad \Delta H\ (\mathrm{kJ/mol\ \ BH_4})$$

Structural information is not available for *M* = Mg, Sc, Zn, Cu

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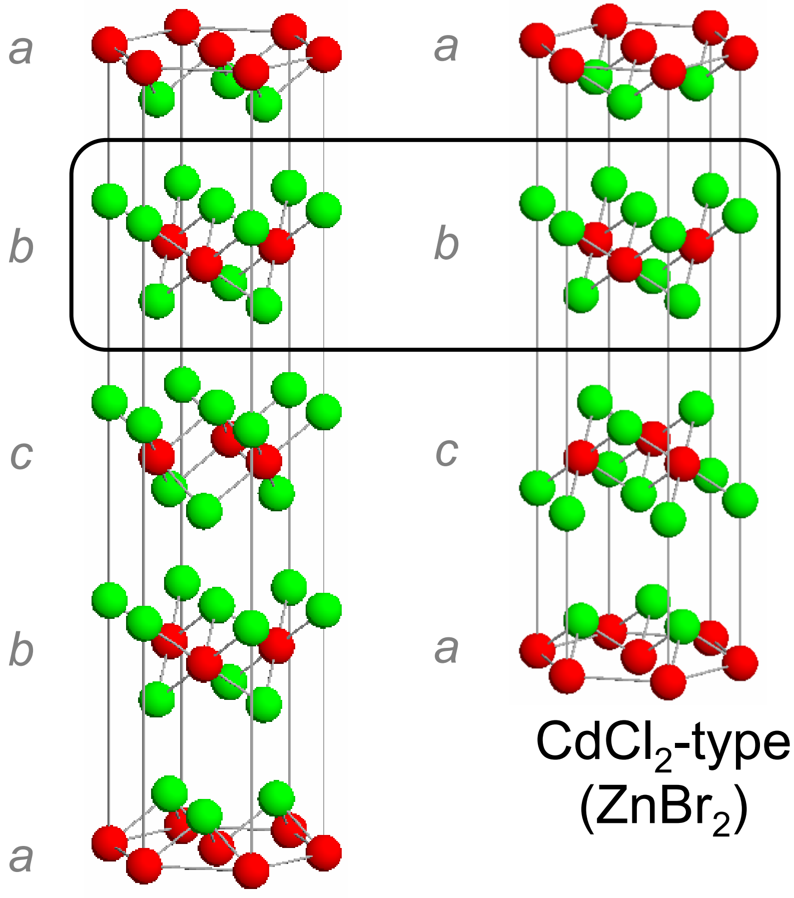
Structural survey for $M(BH_4)_2$, M = Mg, Zn

$[BH_4]^-$ effective ionic radius 2.03 Å, Br^- 1.96 Å, I^- 2.20 Å

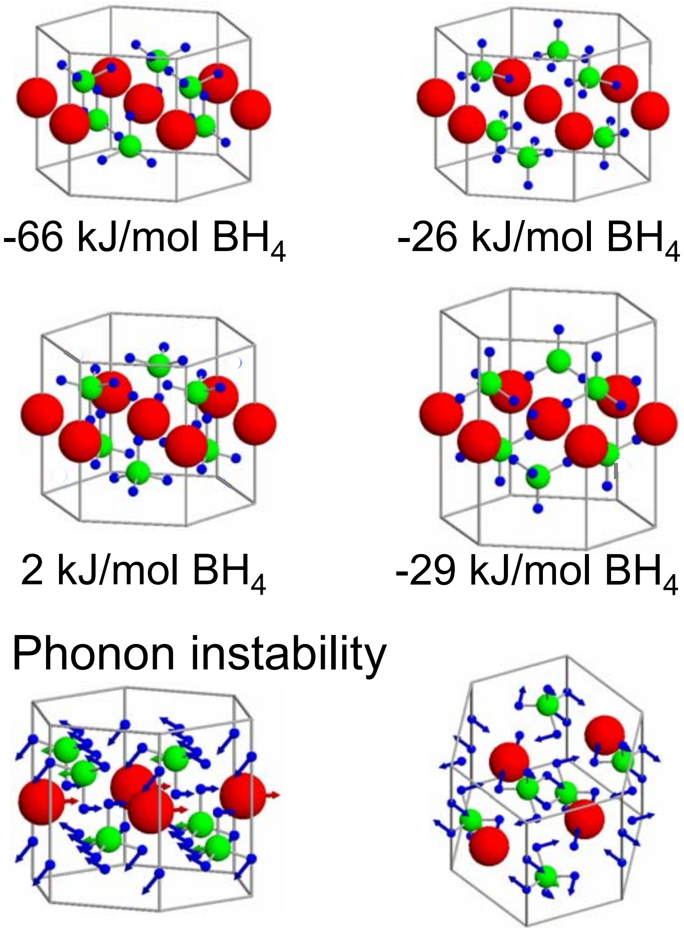
[Pistorius, Z. Phys. Chem. B 88, 253 (1974).]



CdI_2-type
($MgBr_2$, MgI_2)

$CdCl_2$-type
($ZnBr_2$)

$Mg(BH_4)_2$



-66 kJ/mol BH_4

-26 kJ/mol BH_4

2 kJ/mol BH_4

-29 kJ/mol BH_4

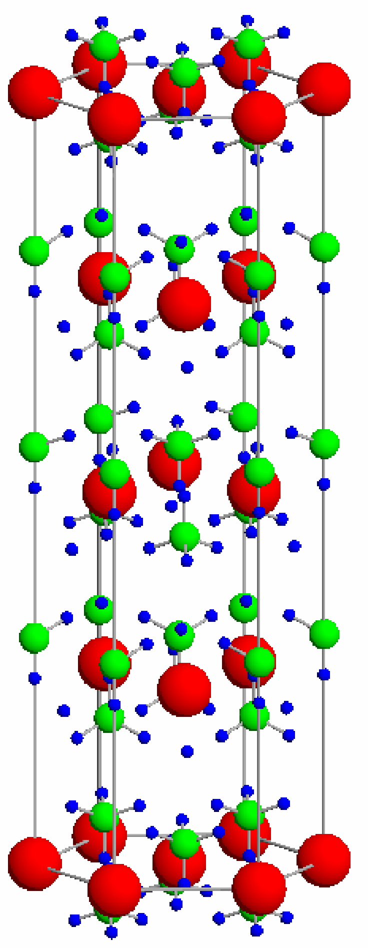
Phonon instability

127*i* cm^{-1}

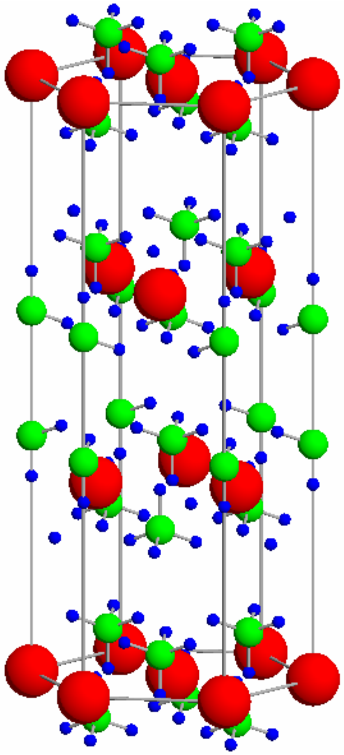
624*i* cm^{-1}

Heat of formation for $Mg(BH_4)_2$

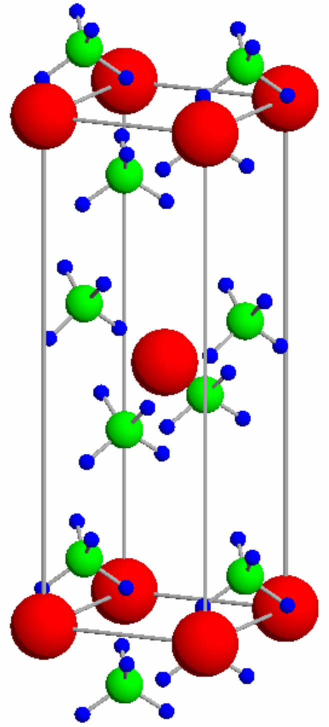
$$\frac{1}{2}Mg + B + 2H_2 \Leftrightarrow \frac{1}{2}Mg(BH_4)_2$$



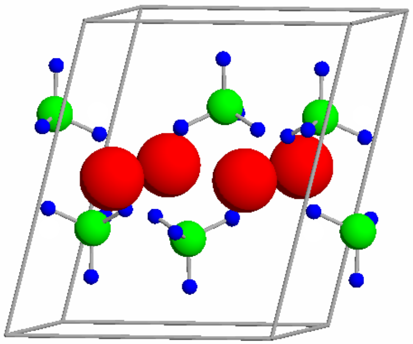
CdI_2-type
-66 kJ/mol BH_4



$CdCl_2$-type
-66 kJ/mol BH_4



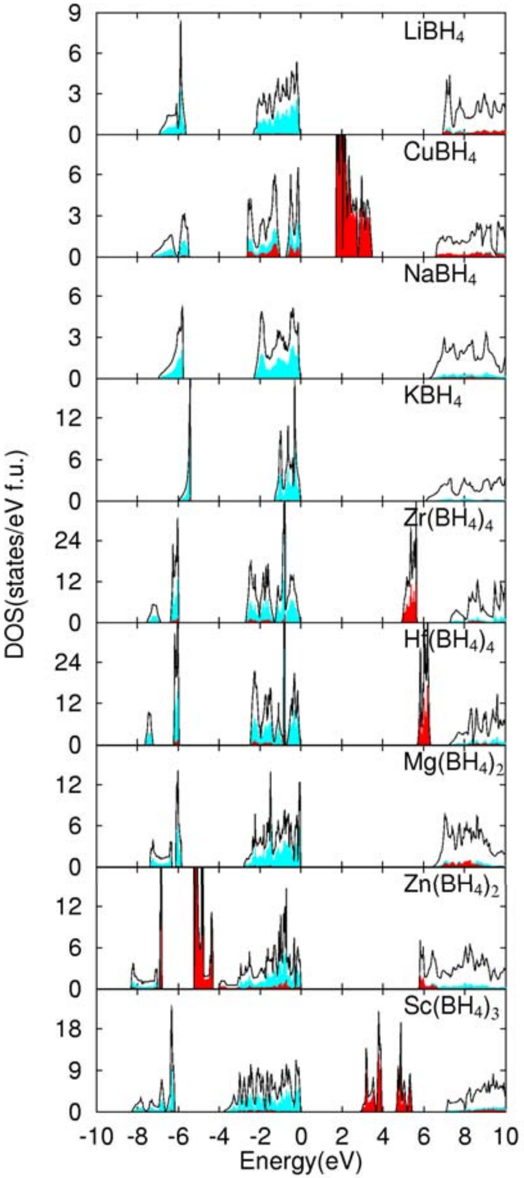
HgI_2-type
-61 kJ/mol BH_4

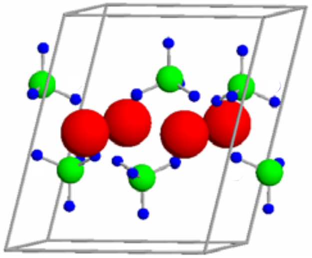


P2/c
-71 kJ/mol BH_4

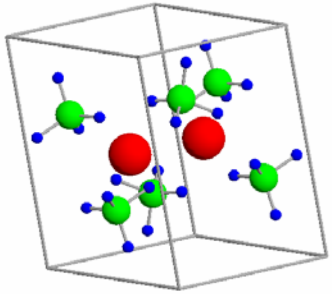
	Space Group	ΔH (kJ/mol BH_4)
$LiBH_4$	$Pnma$	−161
$CuBH_4$	$P2_12_12_1$	76
$NaBH_4$	$P4_2/nmc$	−155
KBH_4	$P4_2/nmc$	−201
$Zr(BH_4)_4$	$P\bar{4}3m$	−54
$Hf(BH_4)_4$	$P23$	−61
$Mg(BH_4)_2$	$P2/c$	−71
$Zn(BH_4)_2$	$P\bar{1}$	15
$Sc(BH_4)_3$	$R\bar{3}$	−72

DOS

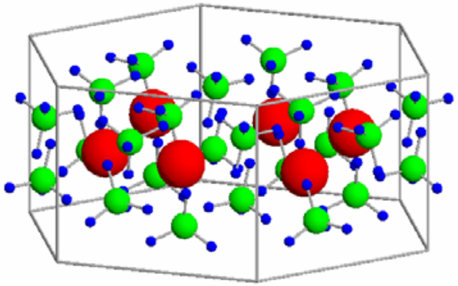




$Mg(BH_4)_2$



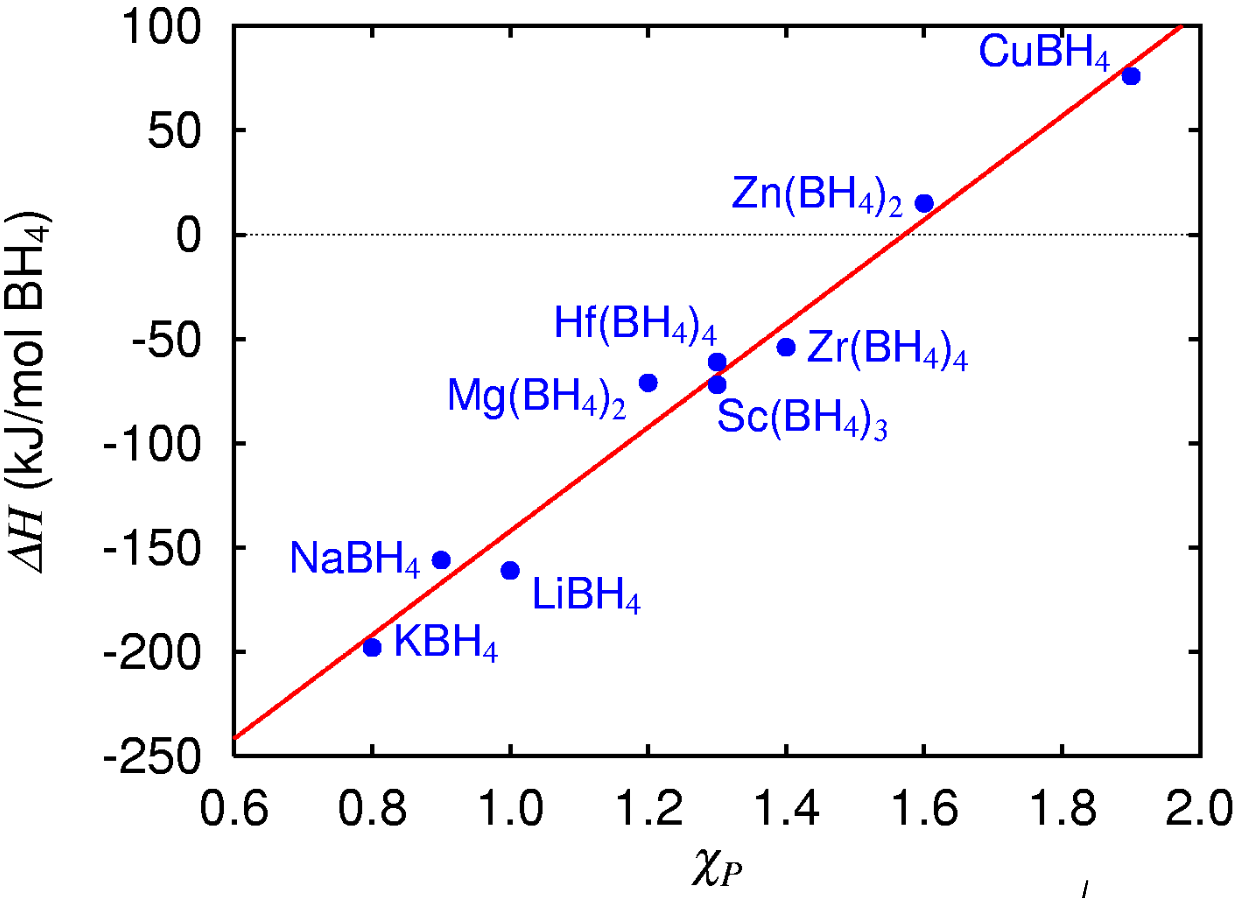
$Zn(BH_4)_2$



$Sc(BH_4)_3$

Relation between heats of formation ΔH and cation electronegativities χ_P

$$\frac{1}{n}M + \mathrm{B} + 2\mathrm{H}_2 \Leftrightarrow \frac{1}{n}M(\mathrm{BH}_4)_n$$



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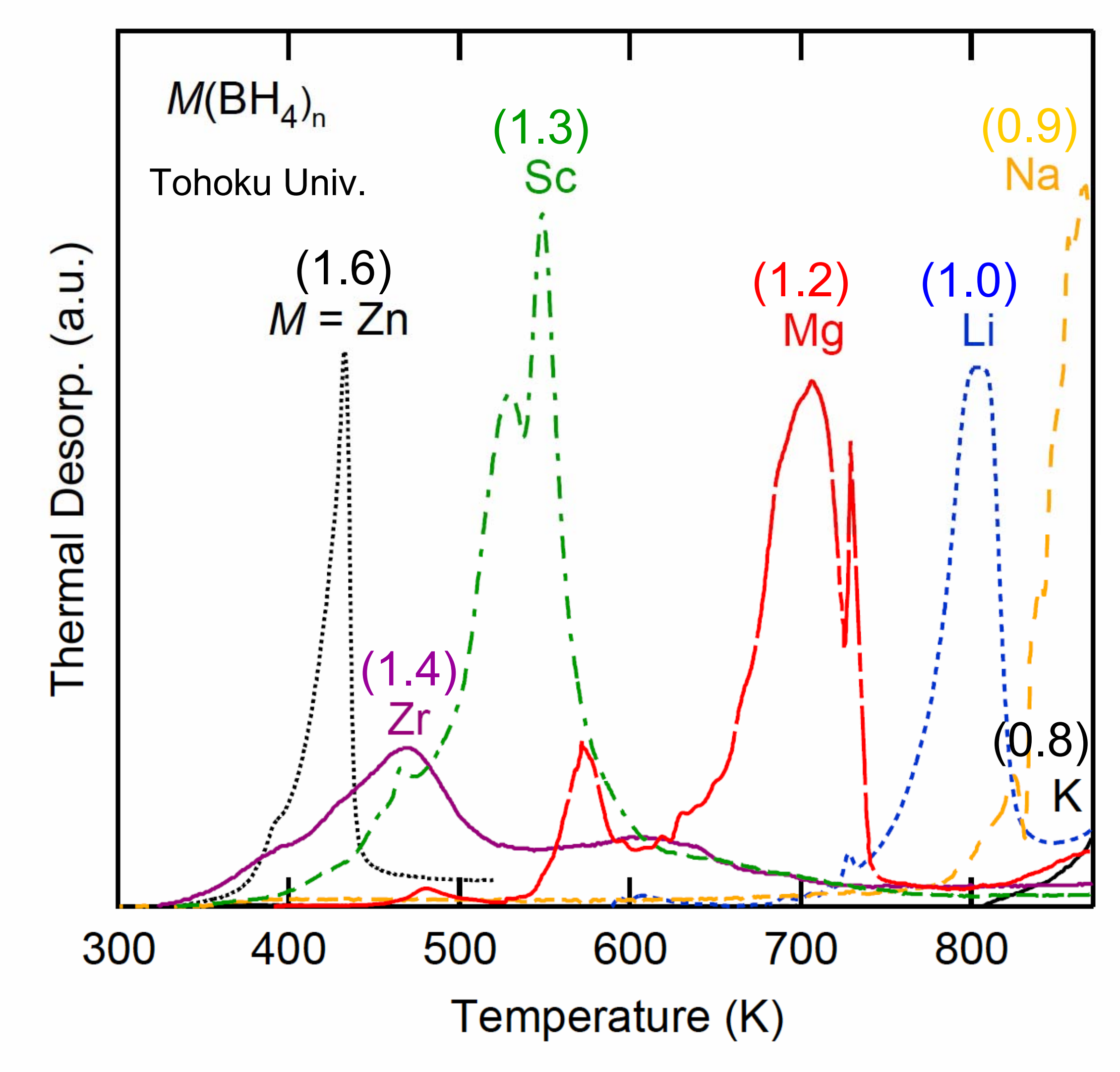
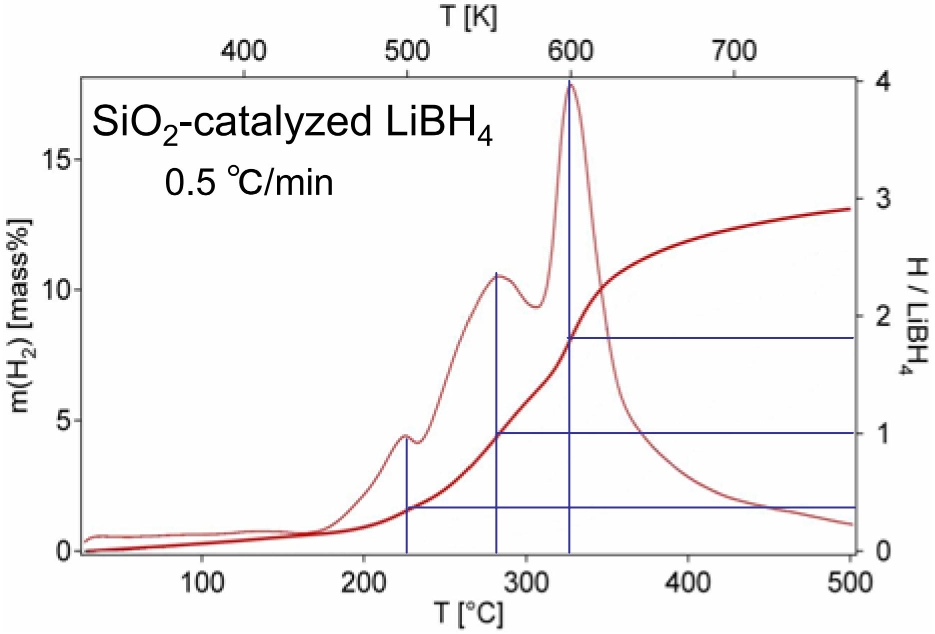
Experimental examination



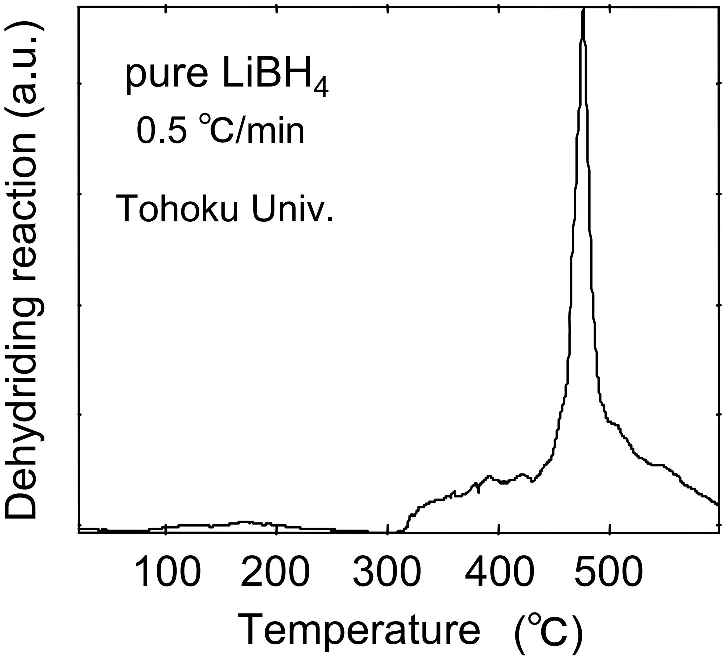
Intermediate compound of $LiBH_4$

N. Ohba, K. Miwa, M. Aoki, N. Noritake, S. Towata, Y. Nakamori, S. Orimo, and A. Züttel,
“First-principles study on intermediate compound of $LiBH_4$,”
Submitted to Phys. Rev. B

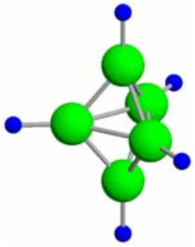
Hydrogen desorption reaction of $LiBH_4$



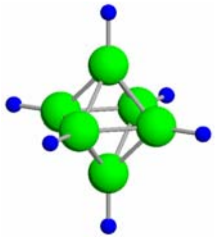
Züttel *et al*., J. Power Sources 118, 1 (2003).



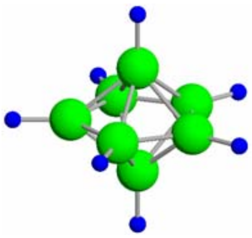
closo Dianionic Boranes, $[B_nH_n]^{2-}$



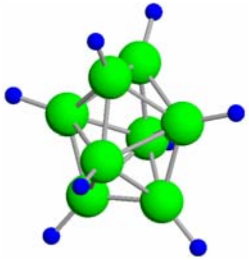
$n = 5$



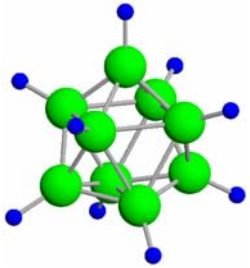
$n = 6$



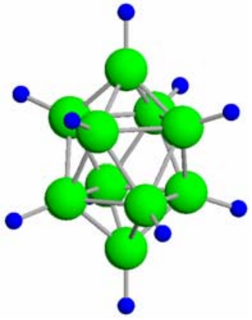
$n = 7$



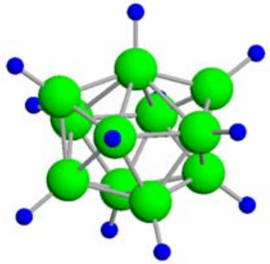
$n = 8$



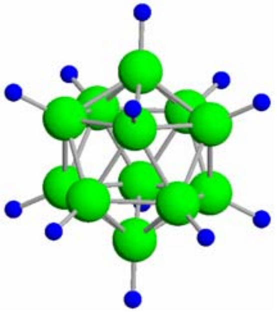
$n = 9$



$n = 10$

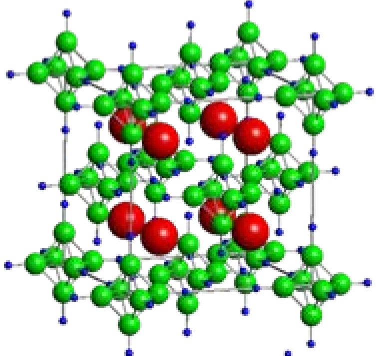


$n = 11$

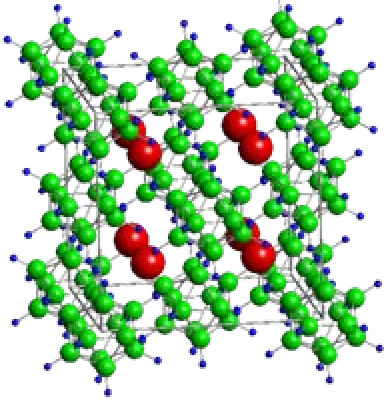


$n = 12$

【Existing Materials】



$K_2B_6H_6$



$K_2B_{12}H_{12}$

Prediction for stabilities of $Li_2B_nH_n$

Intermediate compound ?

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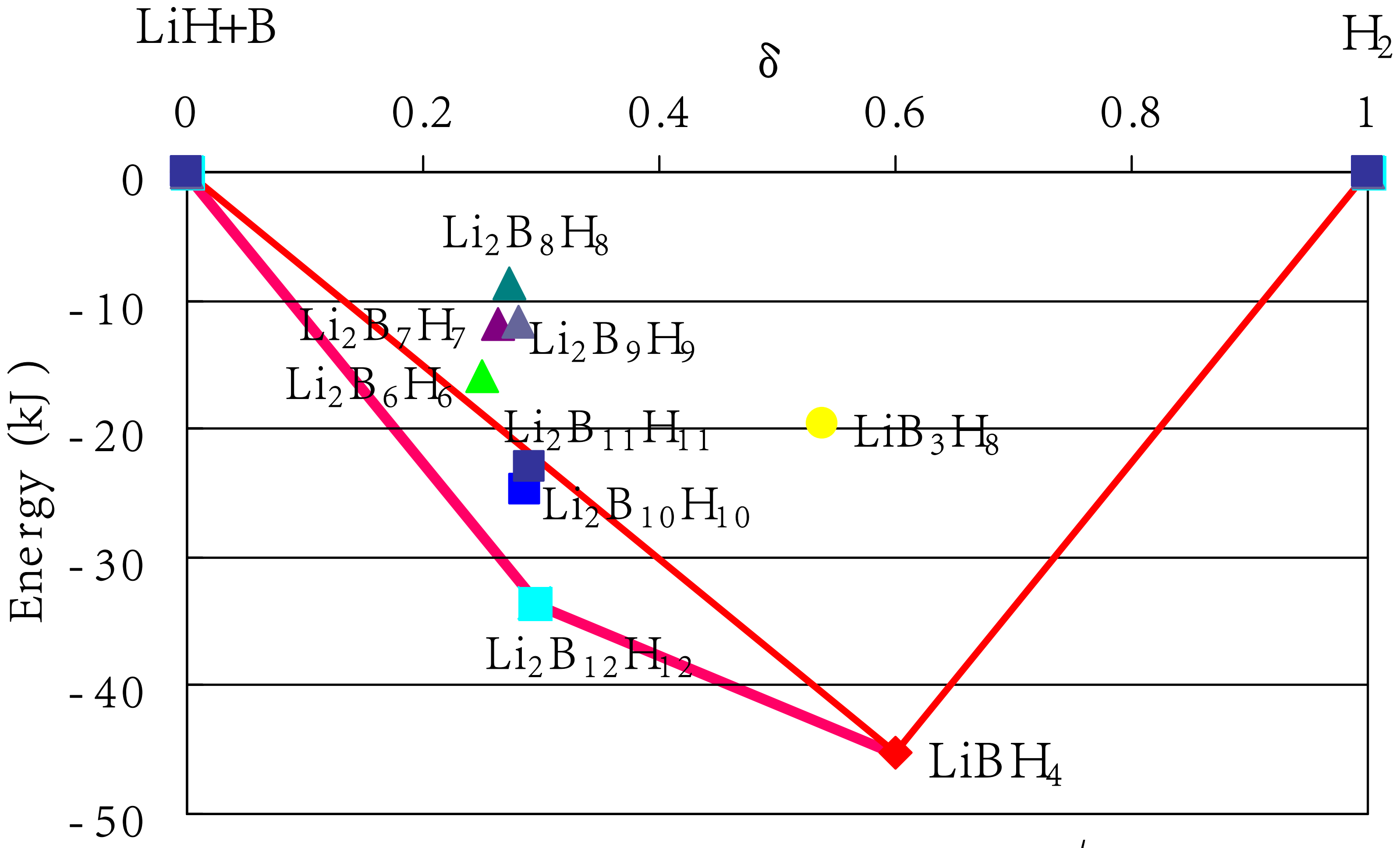
Possibility of intermediate compound

$$(1-\delta)[LiH+B]+\delta H_2 \rightarrow \frac{(1-\delta)}{x} LiB_xH_y + \frac{(1-\delta)(x-1)}{x} LiH$$



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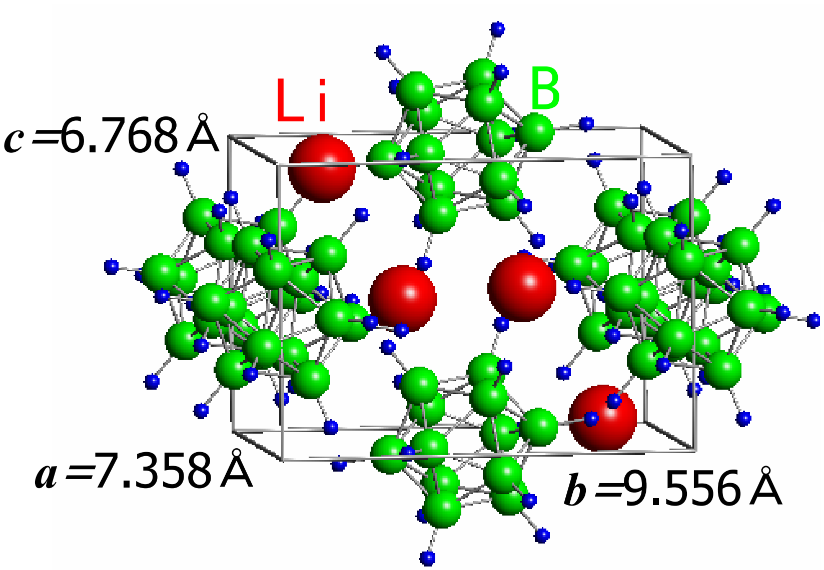
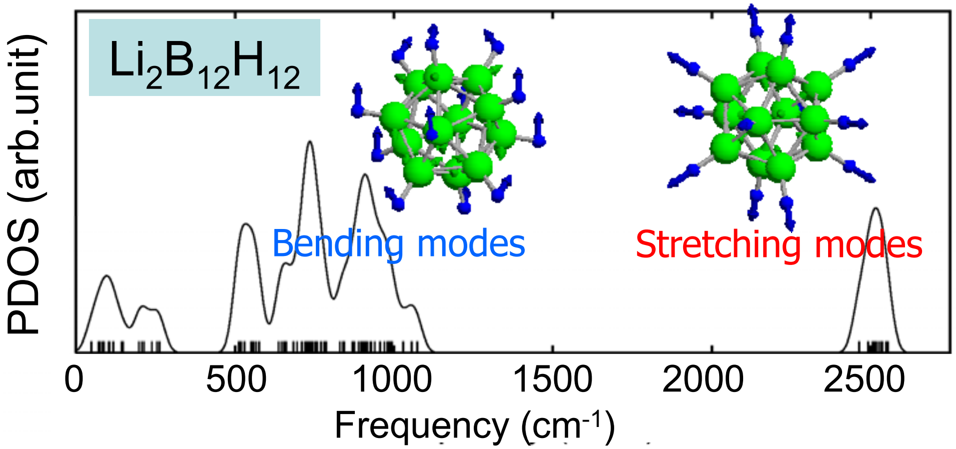
Intermediate compound, $Li_2B_{12}H_{12}$

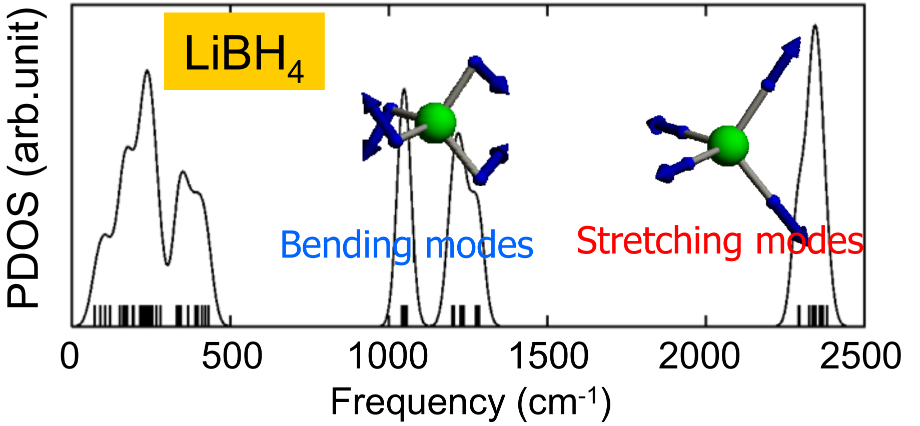


$Li_2B_{12}H_{12}$	
Interatomic distance	
Li-Li	3.52
Li-B	2.45～2.76
Li-H	1.90～2.34
B-B	1.78～1.81
B-H	1.20～1.21
H-H	2.11～2.68

(Reference structure: $K_2B_{12}(OH)_{12}$)

Γ-phonon frequencies





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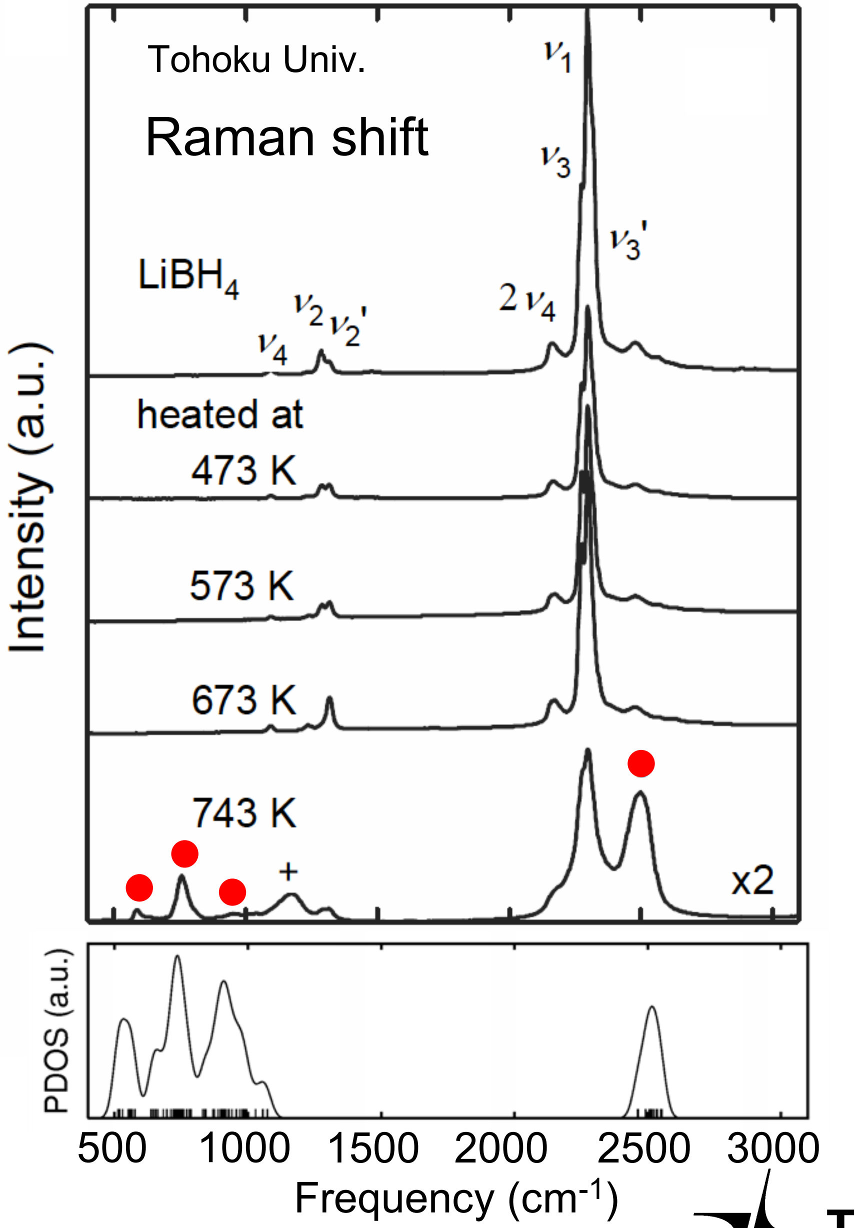
Experimental examination



S. Orimo *et al*.,
"Experimental studies on intermediate compound of LiBH4,"
submitted to Appl. Phys. Lett.

Experiment

Calculation

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Dehydriding process via Intermediate phase

56 kJ/mol H_2, 14 mass % (Expt. 69 kJ/mol H_2)

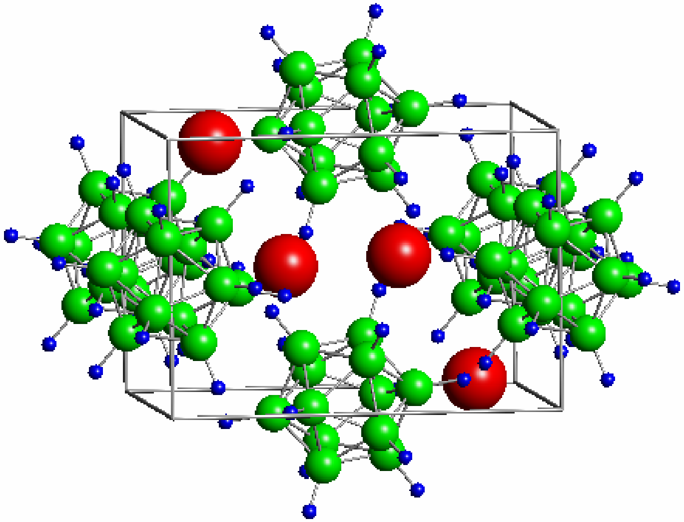
$$LiBH_4 \longrightarrow LiH + B + \frac{3}{2}H_2$$

39 kJ/mol H_2
10 mass %

$$\frac{1}{12}Li_2B_{12}H_{12} + \frac{5}{6}LiH + \frac{13}{12}H_2$$

101 kJ/mol H_2
4 mass %

$Li_2B_{12}H_{12}$ is predicted to be a stable intermediate phase.



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Summary

- ☆ **Fundamental properties of $LiBH_4$**

  The charge transfer from Li^+ to $[BH4]^-$ is a key feature for the stability of $LiBH_4$.

- ☆ **Thermodynamical stability of $M(BH_4)_n$**

  The cation electronegativity is a good indicator to control the stability of borohydrides, $M(BH4)_n$.

- ☆ **Intermediate compound of $LiBH_4$**

  $Li_2B_{12}H_{12}$ is predicted to be a stable intermediate phase for the desorption reaction of $LiBH_4$.

Acknowledgements

TCRDL	N. Ohba S. Towata, T. Noritake, M. Aoki
Tohoku Univ.	S. Orimo, Y. Nakamori, H. Li, A. Ninomiya (Present affiliation HONDA)
Univ. of Fribourg	A. Züttel, F. Buchter, T. Matsunaga

NEDO “Development for Safe Utilization and Infrastructure of Hydrogen” Project