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NMR Chemical Shifts of ^{11}B in Metal Borohydrides from First Principle Calculations.

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Abstract

The lightweight complex metal hydrides pose a challenge for experimental insight due to the lack of the long-range order in nanoconfined state or in intermediate phases. Understanding of the atomic scale properties might be the key to the utilization of complex hydrides in applications for versatile hydrogen storage. The first principle calculations support of Nuclear Magnetic Resonance methods applied to metal borohydrides is presented below. We show that boron NMR chemical shifts can be accurately calculated within Density Functional Theory approach, for a broad class of crystalline metal borohydrides. The calculated NMR parameters together with electronic and structural data provide detailed insight, on the atomic scale, to the properties of bulk and in particular of nano-sized structures. It is explained that for small nano-clusters of LiBH_4 the boron chemical shift is low frequency shifted due to lower coordination of ions compared to the bulk. The relation between Pauling electronegativity and boron chemical shift in metal borohydrides is proposed as a simple method for determining the stability of poorly crystalline materials.

Keywords: NMR parameters; Density Functional Theory; Hydrogen storage, metal tetrahydroborates; nanoconfinement

Introduction

The light complex metal hydrides have attracted significant research interest over the last decade as they are considered a potential storage media for hydrogen.¹ Among them metal borohydrides (with general formula $\text{M}(\text{BH}_4)_x$) are ones of the most important compounds due to their high gravimetric and volumetric hydrogen densities.^{2,3} They usually form ionic crystals with positively charged metal cation and the appropriate number of BH_4^- anions. Some metal borohydrides show ionic conductivity^{4,5} or the capability of tuning their properties via mixtures with amides or halides⁶ or eutectic mixtures within the compound family.⁷

Hydrogen release temperatures of metal borohydrides are far from optimal; their complex decomposition paths or problematic reversibility drive a variety of research oriented toward optimiz-

ing their physicochemical properties for the application as a novel hydrogen storage media. Some recent research directions aim for synthesis of multi-cation compositions or framework structures;⁸ analysis and modification of decomposition paths and intermediate products;^{7,9,10} detailed analysis of dynamics and diffusion on the atomic scale^{11,12} or establishing reliable methods for metal borohydrides thermodynamic destabilization via eutectic mixing or nanoconfinement^{8,13}

The decomposition paths or nanoconfinement of metal borohydrides are commonly studied by X-ray diffraction (XRD) or neutron scattering, infra red (IR) and Raman spectroscopy techniques. Due to poor crystallinity and structural complexity of intermediate products the scattering methods are sometimes non-applicable as they probe the average long range properties. The same concerns nanoconfined systems with reduced length-scales. Thus methods sensitive to the local atomic coordination are commonly used with ^{11}B nuclear magnetic resonance (NMR), being still most suitable one; even though the first NMR study of NaBH_4 was reported almost 60 years ago¹⁴ (3 years before ^{13}C NMR signal was observed). For example the NMR technique was used to confirm that decomposition products of Li-, Mg- borohydrides contain theoretically predicted $\text{B}_{12}\text{H}_{12}^{2-}$ anions by comparison of the ^{11}B chemical shift of products with these known for $\text{B}_{12}\text{H}_{12}^{2-}$ in solution experiments and reference system $\text{K}_2\text{B}_{12}\text{H}_{12}$.¹⁵ NMR was also used to study $\text{Ca}(\text{BH}_4)_2$ decomposition path and products;^{7,10,16} discovery of B_3H_8^- among decomposition species of $\text{Y}(\text{BH}_4)_3$;¹⁷ for studies of local dynamics within borohydrides, especially related to BH_4^- motion (rotation) or diffusion of the light elements.¹⁸

Theoretical methods are readily used within research of hydrogen storage materials, for predicting novel compositions/structures of materials or chemical transformation paths. Theoretical calculations serve also as a support for interpretation of the experimental data. IR and Raman spectroscopic data can be mentioned as examples of fruitful experimental - theoretical interplay.^{11,19,20} In fact, these methods were the first to indicate intermediate structures with $\text{B}_{12}\text{H}_{12}$ units⁹ upon decomposition of LiBH_4 . Structural studies of borohydrides frequently rely on the interplay between scattering techniques and theoretical predictions;^{21,22} neutron quasielastic scattering studies are supported by calculations.¹²

Among experimental methods commonly used for studies of metal borohydrides the nuclear magnetic resonance spectroscopy appears to be missing theoretical support. As the NMR method is becoming more routinely applied for local analysis of metal borohydrides and their derivatives in the present manuscript we show the capability of the state-of-the art Density Functional Theory (DFT) based methods to calculate accurately ^{11}B NMR chemical shifts and quadrupolar parameters for a broad class of metal borohydrides.

The paper is organized as follows: in the next section basic aspects of theoretical method are presented, followed by the results for metal borohydrides in the bulk and nanophases, intermediate decomposition products - boranes, and discussion of the relevance of the results.

Methods

Computational Details

The present calculations are based on density functional theory (DFT)²³ as implemented in the Quantum Espresso simulation package,²⁴ employing a plane-wave basis set with a maximum kinetic energy of 110 Ry to expand the one-electron wave functions of Kohn-Sham equations.²⁵ For electronic exchange and correlation effects the functional of Perdew, Burke, and Ernzerhof (PBE)²⁶ in the generalized gradient approximation (GGA) was used. The valence electrons core interactions were described using the projector-augmented-wave (PAW)²⁷ approach, combining ideas from Vanderbilt-type pseudopotential (PP) and all-electron LAPW (linearized augmented plane waves) methods. The PAW method allows to reproduce the exact all-electron potentials and charge densities in the core region (and hence avoids the need to use elaborate nonlinear core-corrections) and thus magnetic and optical properties are accurately described. The NMR parameters critically depend on the details of the all-electron wave functions at the nucleus, where the pseudo- and true wave functions differ. Pickard and Mauri developed a gauge including projector augmented waves (GIPAW)^{28,29} approach, extending Blochl's PAW approach to the *ab-initio* calculation of the NMR tensors through the reconstruction of the all-electron wave functions in

the core region. The GIPAW method can be applied to NMR parameters calculations with various types of pseudopotentials i.e. ultrasoft pseudopotentials (USPP),³⁰ the norm-conserving Troullier-Martins³¹ type PP, and PAW PP. We have generated and used PAW potentials with the following valance electron configurations $1s^1$ (H), $2s^2 2p^3$ (N), $1s^2 2s^1$ (Li), $2s^2 2p^1$ (B), $2s^2$ (Be), $2p^6 3s^1$ (Na), $3s^2 3p^6 4s^1$ (K), $3s^2$ (Mg), $3s^2 3p^6 4s^2$ (Ca), $3s^2 3p^1$ (Al), $3p^6 3d^1 4s^2$ (Sc), $4s^2 4p^6 4d^1 5s^2$ (Y), $3p^6 3d^2 4s^2$ (Ti), and $4s^2 4p^6 4d^2 5s^2$ (Zr). Additional calculations were performed with the norm-conserving Troullier-Martins³¹ type pseudopotentials for the accuracy comparison, further details concerning these potentials are provided in the Electronic Supplementary Information (ESI).

In the present approach the NMR parameters were calculated for a broad class of metal borohydrides represented as infinite solids using periodic boundary conditions. The calculations reported below used well converged Monkhorst-Pack³² Brillouin zone k-point sampling. The calculations of chemical shielding come down to the calculation of the induced magnetic field $\mathbf{B}_{in}$, at the nuclear positions $\mathbf{r}$ in response to an applied, uniform magnetic field $\mathbf{B}$, within a linear response framework,^{33,34}

$$\mathbf{B}_{in}(\mathbf{r}) = -\overleftrightarrow{\sigma}(\mathbf{r})\mathbf{B}. \quad (1)$$

NMR spectroscopy measures the isotropic shielding $\sigma(\mathbf{r})$, which is one-third of the trace of shielding tensor $\overleftrightarrow{\sigma}(\mathbf{r})$, and it is usually reported with respect to a reference material, σ_{ref} ,

$$\delta(\mathbf{r}) = -[\sigma(\mathbf{r}) - \sigma_{ref}], \quad (2)$$

where δ is the isotropic NMR chemical shift. The calculated ^{11}B isotropic shielding of BPO_4 ³⁵ at -3.60 ppm has been used as a reference in this study.

The ^{11}B quadrupolar coupling constant, C_q , and the asymmetry parameter, η , have been determined from the traceless electric field gradient (EFG) tensor taking into account the local electric field at the position $\mathbf{r}$, which can be obtained from the charge density, $n(\mathbf{r})$.³⁶ Labeling the eigenvalues of the EFG tensor as V_{xx} , V_{yy} and V_{zz} , and adopting the convention $|V_{zz}| > |V_{yy}| > |V_{xx}|$, one

can write

$$C_q = \frac{eQV_{zz}}{h}, \quad (3)$$

and

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}, \quad (4)$$

where e is the electron charge, h denotes the Planck constant, and Q is the ^{11}B nuclear quadrupole moment of 40.59 mb.

The Born effective charge (BFC) tensor³⁷ $\mathbf{Z}_{\kappa,\alpha\beta}^*$ of atom k , define by the change in macroscopic polarization $\mathbf{P}_\alpha$ induced in direction β by the periodic displacement of atomic sublattice κ in direction α , $\tau_{\kappa,\alpha}$, has been calculated within density functional perturbation theory (DFPT)^{38,39} under a condition of zero macroscopic electric field. In this paper we report the isotropic component Z_κ^* of the BFC tensor, i.e. one-third of its trace. Partitioning of the ground-state electronic density into contributions attributed to the different atoms has been performed by means of Bader analysis.^{40–42}

In the present report we focus on magic angle spinning (MAS) ^{11}B NMR chemical shift for alkali metals (Li, Na, K), alkaline earth metals (Be, Mg, Ca) borohydrides complemented with borohydrides of Sc, Y, Zn, Zr, ammine borohydride and elemental boron in the α phase. Such choice of compounds shall unreveal intrinsic local properties that are common for more complex classes of materials, i.e. multiple cation or nanoconfine structures. For the latter small clusters of lithium borohydride with two to twelve formula units were considered in detail. For the decomposition intermediates chemical shifts for *closo* borane structures: $\text{Li}_2(\text{Ca})\text{B}_{12}\text{H}_{12}$, $\text{Li}_2\text{B}_{10}\text{H}_{10}$, $\text{Li}_2\text{B}_9\text{H}_9$, $\text{Li}_2\text{B}_8\text{H}_8$, $\text{Li}_2\text{B}_7\text{H}_7$, $\text{Li}_2\text{B}_6\text{H}_6$, $\text{Li}_2\text{B}_5\text{H}_5$, and $\text{Li}_2\text{B}_3\text{H}_8$ were considered.

For each compound we focus on the representative crystalline phases, and for the consistency of the present approach each system was optimized with respect to both lattice parameters and internal position of atoms within the unit cell. The symmetry of each phase was constrained for each calculations. The structural parameters of optimized structures are presented in Table S1 in the ESI. The test calculations for LiBH_4 indicate that the chemical shift calculated for the

experimentally reported lattice parameters differs by 1~2 ppm.

Experimental

Solid-state magic angle spinning nuclear magnetic resonance experiments were performed on a Bruker Avance-400 NMR spectrometer using a 4 mm CP-MAS probe. The ^{11}B NMR spectra were recorded at 128.38 MHz at 12 kHz sample rotation. Pulse lengths of $1.5\ \mu\text{s}$ ($\pi/12$ pulse) and $3.0\ \mu\text{s}$ were applied for the excitation and refocussing of the applied Hahn echo sequence, respectively. ^{11}B NMR chemical shifts are reported in parts per million (ppm) externally referenced to a 1M $\text{B}(\text{OH})_3$ aqueous solution at 19.6 ppm as external standard. Further details on the experimental method may be found in Ref. 7. The reference samples were obtained from Katchem (LiBH_4 , $\text{K}_2\text{B}_{10}\text{H}_{10}$, $\text{K}_2\text{B}_{12}\text{H}_{12}$), NaBH_4 , $\text{Mg}(\text{BH}_4)_2$ and $\text{Y}(\text{BH}_4)_3$ were prepared by gas solid reactions as described in.^{43,44} The measurements were done for LiBH_4 , NaBH_4 , $\text{Mg}(\text{BH}_4)_2$, $\text{Ca}(\text{BH}_4)_2$, $\text{Y}(\text{BH}_4)_3$.

Results

The calculated chemical shifts for a broad class of metal borohydrides are compared to the experimentally reported ones in Figure 1. The experimental data origin mostly from solid state measurements recently reported for the purpose of hydrogen storage; with the exception of $\text{Zr}(\text{BH}_4)_4$, $\text{Al}(\text{BH}_4)_3$, $\text{Be}(\text{BH}_4)_2$ that are determined from the solution NMR experiments performed in the second half of 20th century.^{45–47} The fitted slope of the correlation between experimental/calculated data in Fig. 1 is 1.08 and correlation coefficient equals 0.98. The agreement between the calculated and the experimentally determined ^{11}B chemical shifts is good (within a few ppm); however the calculations for single molecules in a solution can reach better accuracy.⁴⁸ The reason for a larger discrepancy than for the cluster calculations in solution may origin from errors in the actual crystalline structure description and the accuracy of electronic structure description related to the exchange-correlation functional. The solid state structures considered here possess crystalline

Figure 1: The correlation between experimental data and calculated chemical shifts $\delta^{11}\text{B}$ for metal borohydrides (filled circles) and metal boranes (open squares) in the solid state structures. Only the chemical symbol for a metal cation is given for borohydrides, AMB stands for ammine borohydride, $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$.

symmetries with a variety of chemical compositions and local coordination of cations around the boron atom. These features are accounted in the present calculations but they are not present in calculations for isolated clusters. Additionally the calculations of the Ref⁴⁸ were performed with Møller-Plesset second-order perturbation theory to account for electron correlations, while the gradient corrected exchange - correlation (PBE)²⁶ functional is used in the present studies. Analysis of the influence of exchange - correlation functional on the numerical values of the calculated

chemical shifts⁴⁹ deserve additional studies but is beyond the scope of this report. However, the accuracy of a few percent is similar to that achieved for accurate DFT calculations of IR or Raman spectra in crystalline structures.²⁰ The discrepancy with experimental data appears to be larger for more negative chemical shifts, which are related to larger shielding effects in light alkali metal borohydrides. Chemical shifts calculated with the norm conserving pseudopotentials (see Table S2 in ESI) have worse correlation with the experiment: the fitted slope is 1.22 and a correlation coefficient is 0.96. This is attributed to the inferior quality of description of BH_4^- anion.

Thus chemical shifts, in general, are more negative for borohydrides than those for crystalline boranes.^{47,50} This is attributed to a larger shielding introduced by hydrogen surrounding boron in sp^3 bond-like geometry. A complex bonding in boranes beside σ orbitals involve π -like orbitals with paramagnetic effects. For bare boron atoms the shielding related to B-H hybridization is absent and in the ^{11}B α - phase calculated chemical shifts: 0.8 and 1.1 ppm are still higher than in boranes. In borates the shielding of the boron nucleus is even lower and for these compounds DFT calculations have already contributed to elucidation of the important problem of $\delta^{11}\text{B}$ ordering with respect to coordination of boron atoms.^{50,51}

The chemical shifts for compounds containing BH_4^- units fall in the range from ~ -8 ppm to ~ -45 ppm.⁴⁷ The BH_4^- molecular group is very stable with temperature changes and boron – hydrogen bond lengths and angles do not vary significantly between different compounds or with temperature/pressure,⁵² therefore we will investigate the origin of differences in chemical shifts in more detail. In the following we will focus on chemical shifts in compounds containing BH_4^- anion both in the bulk and nano structures. This will be complemented by studies of borane containing intermediate products.

Metal Borohydrides

The NMR parameters calculated for selected alkali, alkaline earth, and transition metal borohydrides are presented in Table 1 (Table S2 of ESI shows these parameters calculated with norm conserving pseudopotentials). There is scarce literature data concerning quadrupolar coupling

Table 1: Calculated and measured chemical shifts $\delta^{11}\text{B}$, quadrupolar coupling $|C_q|$, and asymmetry parameters η for $\text{M}(\text{BH}_4)_n$ compounds in the crystalline state. The number of the space group for each compound is given in the last column, according to the International Tables for Crystallography;⁵³ for the space group symbol see Electronic Supplementary Information. Experimental data are from our measurements, unless noted with the literature reference.

Compound	$\delta^{11}\text{B}$ (ppm)		$ C_q $ (kHz)	η	# Space group
	Calc.	Exp.			
LiBH ₄	-43.7	-41.3 -41.5 ^a	94	0.27	62
NaBH ₄	-44.6	-42.0	21	0.03	137
KBH ₄	-39.7	-38 ^e	1	0.06	137
Be(BH ₄) ₂	-33.5	-31.5 ^b	1641	0.81	110
	-41.3		219	0.07	
Mg(BH ₄) ₂	-42.7		284	0.40	70
Mg(BH ₄) ₂	-40.0	-40.6	328	0.25	141
Ca(BH ₄) ₂	-27.4	-29.8	217	0.89	70
Ca(BH ₄) ₂	-29.1	-32.2	142	0.45	84
Ca(BH ₄) ₂	-30.5		171	0.34	61
	-26.4		273	0.46	
Al(BH ₄) ₃	-39.2	-37.1 ^b	2025	0.50	33
Sc(BH ₄) ₃	-6.3		212	0.78	205
Y(BH ₄) ₃	-13.0	-17.8	161	0.67	205
		-17.3 ^c			
Zr(BH ₄) ₄	-8.0	-8.5 ^b	1584	0.00	148
AMB	-43.1	-38.1 ^d	110	0.00	165
	-40.4	-36.6 ^d	33	0.84	

(a) Ref. 54: $|C_q| = 105$ kHz; $\eta = 0.45$; Ref. 55: $\delta^{11}\text{B} = -41.2$ ppm, $|C_q| = 90$ kHz; $\eta = 0.94$;

(b) Ref. 46; (c) Ref. 55; $|C_q| = 77.4$ kHz; $\eta = 0.97$; (d) Ref. 6 (e) Ref. 56

$|C_q|$ and asymmetry parameters η for crystalline borohydrides. For LiBH₄ the calculated $|C_q|$ is in good agreement with the measured value of 90 kHz⁵⁵ or 105 kHz.⁵⁴ The discrepancy between the calculated and measured asymmetry parameters is larger; however there is also a significant discrepancy between experimental data, see Table 1. For Y(BH₄)₃ the calculated $|C_q|$ is two times larger than the experimental value (Table 1). In the $Fm\bar{3}c$ high symmetry Y(BH₄)₃ phase the calculated $|C_q| = 25$ kHz which indicates that the discrepancy might origin from orientational configuration of BH₄.

The calculated ^{11}B chemical shifts in the BH₄⁻ group span the range from -6.3 ppm (for Sc(BH₄)₃) to -44.6 ppm (for NaBH₄). Taking into account the variety of crystal structures and

atomic coordinations within crystals the agreement with available experimental data is good. For the calculations we have considered representative structures for metal borohydrides shown in Table 1. In particular for LiBH_4 the low temperature ordered phase was considered; for $\text{Mg}(\text{BH}_4)_2$ the low and high density structures, and for $\text{Ca}(\text{BH}_4)_2$ three most stable phases were accounted. Additionally, the chemical shift was calculated for ammine borohydride $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$ that can be perceived as a complex amine-borane structure, though it contains BH_4^- with geometry analogous to binary metal borohydrides.⁶ Within all structures the coordination of the metal cation varies from three to six.⁵⁷ The coordination of BH_4^- anion by the metal cations does not always correspond to the coordination of cations. For compounds with Be, Al and Zr each boron has only one nearest metal neighbor, thus they consist of $\text{M}(\text{BH}_4)_n$ molecular structures with metal cation in the center.⁵⁸ For this group of compounds the quadrupolar coupling is significantly larger ($|\text{C}_q| > 1500 \text{ kHz}$) than for all other borohydrides considered here. For borohydrides of Mg, Sc, and Y each boron has two cations in the nearest neighborhood (for these compounds $|\text{C}_q| > 170 \text{ kHz}$ has intermediated values). In $\text{Ca}(\text{BH}_4)_2$ there are three metal cations around each boron. In the alkali metal borohydrides the coordination of metal cation is the same as the coordination of anion, and the quadrupolar coupling is lower than 100 kHz. However, there is no correlation between the local coordination number for cations – anions and the chemical shift, for example for Zr borohydride with four BH_4^- neighbors $\delta^{11}\text{B} = -8 \text{ ppm}$ and for Mg-compound with the same number of neighbors $\delta^{11}\text{B} = -42.7 \text{ ppm}$. For anion – cation coordination such a correlation is also not observed (for example $\delta^{11}\text{B} = -39.2 \text{ ppm}$ for $\text{Al}(\text{BH}_4)_3$ and $\delta^{11}\text{B} = -8.0 \text{ ppm}$ for $\text{Zr}(\text{BH}_4)_4$ with one cation in the proximity of boron). Thus one shall expect the differences origin from the crystal field that modifies the properties of embedded complex BH_4^- anions. For this sp^3 - type of coordination, like in BH_4^- , it is well established that the shielding effects on the central atom are similar despite the replacement of hydrogen atoms by saturated organic groups.⁴⁶ Thus they cannot be responsible for deshielding over the range of 40 ppm. A substitution of hydrogen by halogen atoms usually results in a deshielding effect proportional to the electronegativity of halogen atom (combined with shielding related to the atomic number). The mixed substitution usually results

in chemical shifts that are linear intermediate between those of surrounding atoms separately.⁵⁹ Overall the variation of the chemical shifts as presented in Table 1 shall be related to interplay of local sp^3 hybridization and charge transfer from the surrounding cations.

Here, it is worth to mention that the relation between the chemical shifts and shielding of the electrons was studied already in 70-ties of 20th century. A relation between charge density around boron and $\delta^{11}\text{B}$ was reported with a fairly good linear correlations found (on the basis of CNDO, Complete Neglect of Differential Overlap, calculations) between ^{11}B chemical shifts and density matrix charges of diboranes, polyboranes, carboranes and selected organoboranes.⁶⁰ On the contrary more accurate *ab initio* calculations found no relationship between ^{11}B chemical shifts and atomic charges for boranes and carboranes.⁴⁸

In the present calculations we did not observe any correlation between the total charge on boron atoms and chemical shifts for compounds considered in Table 1, irrespective of whether atomic charges are calculated by Bader method or as effective charges in the linear response method, see Fig S1 in ESI. Therefore an analysis of the total charge on entire BH_4^- anion is more appropriate for borohydrides. This was performed via Bader charge analysis. The Bader charges were calculated in a separate calculation for each system with a dense grid for the charge density (spacing less than 0.02 Å). The results are summarized in Fig. 2. Indeed, this approach reveals some correlation between $\delta^{11}\text{B}$ and the total charge on the molecular units, i.e. the larger charge on BH_4^- (in the absolute number), the larger shielding (more negative chemical shift) that can be observed for most compounds in Fig. 2. This holds especially well for compounds with metals such as Li, Na, K, Ca, Be, Y, or Sc; while already for Al or Zr a deviation toward larger shielding can be observed. Interestingly, compounds that show the deviation from the linear correlation between Bader charge and ^{11}B chemical shift possess large quadrupolar coupling; moreover, their heat of formation is at less negative end of heats of formations observed for borohydrides and given by linear relation $\Delta H_{\text{boro}} = 248.7\chi_P - 390.8$, where χ_P is Pauling electronegativity.^{61,62} They also form more directional bonds between metal cation and BH_4^- , which is an indication of covalent features in the bonding and can be responsible for large $|\text{C}_q|$. Since the correlation between electronegativity and

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Figure 2: The ^{11}B chemical shift δ with respect to the Bader charge of BH_4 anion for selected metal borohydrides.

heat of formation of borohydrides is well established,^{61,62} we will discuss some further aspects of relation between atomic charges and $\delta^{11}\text{B}$ in the last section.

Tetrahedral coordination of hydrogen around boron is related to sp^3 hybridization. Visualization of the electronic density related to $2s$, $2p$ states of boron and $1s$ states of hydrogen reveals the origin of large differences in shielding between compounds. Analysis of the density of states indicates that boron $2p$ electrons are localized in the energy range from -6 to -2 eV below the Fermi level, while $2s$ states are deeper in the energy scale: -12 to -8 eV. The density of electronic states related to this energy range are depicted in Fig. 3 for LiBH_4 , $\text{Zr}(\text{BH}_4)_4$ and $\text{Al}(\text{BH}_4)_3$. For strongly ionic LiBH_4 the electronic cloud of s and p hybridization is symmetrically surrounding boron central atom, deeper states of s orbital are localized between boron and hydrogen. These σ orbitals have diamagnetic effect on ^{11}B nucleus, see Fig. 3(a). For $\text{Zr}(\text{BH}_4)_4$ the electron density

Figure 3: The charge density related to *s* (red haze) and *p*-orbitals (gray haze) of boron and *s*-orbitals of hydrogen for BH₄⁻ in LiBH₄ (a); Zr(BH₄)₄ (b) and Al(BH₄)₃ (c). Boron is represented by green spheres, hydrogen by small white ones, and metal cation by gray or blue. Electron density is plotted for the isosurface at 0.05 e/Å³ for *s*-*p* orbitals and at 0.04 e/Å³ for *s*-*s* orbitals.

related to *s* and *p* hybridization is symmetric, while the deeper states are strongly polarized due to interaction with zirconium *d* and *s* orbitals. In the tridentate orientation of BH₄⁻ in Zr(BH₄)₄ (see Fig. 3(b)) this appears as strong paramagnetic deshielding of boron and a qualitatively higher (less negative) chemical shift, see Table 1. Such electron distribution is also reflected in large quadrupolar coupling for Zr(BH₄)₄. In Al(BH₄)₃ three BH₄⁻ anions are in a bidentate orientation with respect to the central Al cation, see Fig. 3(c). For this compound *s* – *s* hybridization is also polarized, for two hydrogen atoms closest to the cation. The deshielding effect is smaller than for zirconium borohydride.

LiBH₄ Clusters

The modification of thermodynamic and kinetic properties of metal borohydrides for hydrogen storage through nanoconfinement has been recently intensely studied.^{7,63} In nanoconfined systems nanostructured metal borohydride is encapsulated in small pores (up to several nm) of the host material. Nanoconfinement is responsible for superior reversibility and decomposition conditions with respect to the bulk.¹³ In nanoconfined LiBH₄ boron has higher shielding when compared to the bulk.^{63,64} We have calculated NMR parameters for the smallest nano-clusters of (LiBH₄)_N

($N = 2 - 12$) to gain an insight into the relation between the ^{11}B chemical shift and a deviation of the boron local surrounding and geometry from this observed in the solid state system. The results are presented in Table 2. The structures of clusters are based on Ref. 65, and they include

Table 2: Calculated chemical shifts $\delta^{11}\text{B}$, quadrupolar coupling $|C_q|$ and asymmetry parameters η for small $(\text{LiBH}_4)_N$, $N = 2, 3, 4, 5, 6, 8, 10, 12$, clusters. Number of boron neighbors of Li - $N(\text{Li})$, and BH_4 - $N(\text{BH}_4)$ separated by less than $4 \text{ \AA}$, are shown in the last column. In parentheses the change of $\delta^{11}\text{B}$ with respect to the bulk at -43.7 ppm is shown.

N	$\delta^{11}\text{B}$ (ppm)	$ C_q $ (kHz)	η	$N(\text{Li})$ $(N(\text{BH}_4))$
2	-40.4 (3.3)	890	0.33	2 (1)
3	-49.6 (-5.9)	398	0.59	2 (0)
4	-50.9 (-7.2)	190	0.69	2 (0)
5	-51.4 (-7.7)	141	0.63	2 (0)
6	-43.9 (-0.2)	462	0.02	3 (2)
8	-44.3 (-0.6)	466	0.25	3 (2)
10	-44.8 (-1.1)	462	0.43	3 (2)
12	-42.9 (0.8)	487	0.33	3 (1)

hypothetical dimer, the planar ring structures ($N = 3 - 5$), double ring structures with six, eight and ten molecular units, and icosahedral $(\text{LiBH}_4)_{12}$. When compared to the bulk LiBH_4 , (Table 2, $\delta^{11}\text{B} = -43.7 \text{ ppm}$) one can see that shielding is higher for the small clusters. For the ring structures with three to five LiBH_4 molecular units $\delta^{11}\text{B}$ is more negative for larger and more open rings, see Table 2. For double ring structures ($N = 6 - 10$) a similar trend of low frequency shift with the increasing size of the cluster can be observed.

The number of Li and B nearest neighbors around each boron atom and the equilibrium interatomic distance between ions depend on the cluster size: for the smallest cluster ($N = 2$) cations are separated from anions by $2.25 \text{ \AA}$, while anions are $3.69 \text{ \AA}$ apart each other. The anion cation distance drops to $\sim 2.10 \text{ \AA}$ for the ring structures; in this case anions are separated by $4.00 \text{ \AA}$ for $N = 3$ and this separation increases with the cluster size. For double ring structures the cation - anion distance is $2.30 \text{ \AA}$ and anions are separated by $\sim 3.60 \text{ \AA}$, this distance also increases with the cluster size. The number of neighbors for each cluster size is given in Table 2. These structural features indicate that the mutual proximity of anions lowers the shielding of boron in BH_4^- ($N = 2, 6, 12$),

while the proximity of lithium cation has the opposite effect on ^{11}B shielding ($N = 3, 4, 5$).

The above results indicate a shift of $\delta^{11}\text{B}$ in nanostructured LiBH_4 system toward more negative values, as long as it contains open rings or molecular fragments with the low coordination number of ions. An example of simulated NMR spectra for the system consisting of $(\text{LiBH}_4)_N$ ($N = 6 - 10$) clusters is presented in Fig. 4(a). The peak centered as -51 ppm originates from

Figure 4: Simulated MAS NMR spectrum for small nanoparticles of LiBH_4 (a), and for intermediate phases of Li- and Ca- borohydrides with $\text{B}_{12}\text{H}_{12}$ molecular units (b). The spectrum is simulated for the magnetic field of 7 T and the peak broadening of 150 Hz is applied.⁶⁶ Dashed blue line shows the NMR spectrum of LiBH_4 when the larger broadening is applied.

single ring nano-clusters, $(\text{LiBH}_4)_N$, ($N = 3 - 5$) for which only Li nearest neighbors are present around each BH_4^- . The peak at -45 ppm results from double ring structures. In the nanoconfined LiBH_4 the cluster size and geometry are not limited to the structures studied here; however, the observed peaks⁶³ consist of features depicted in Fig. 4(a).

Decomposition Intermediates: Boranes

The decomposition path for numerous light borohydrides usually includes undesirable intermediates that are stable and hamper hydrogen release in theoretical stoichiometric amounts. Intermedi-

ate phases include: stable metal hydrides (MH_n), that are usually unavoidable, or species containing boranes that might be considered as unwanted with respect to the reversibility.⁹ Such intermediate phases with $B_{12}H_{12}^{2-}$ are reported with cations such as Li^+ , Na^+ , K^+ , Ca^{2+} , Sc^{3+} .^{10,15,67,68} For magnesium or yttrium borohydride an intermediate with $B_3H_8^-$ was also reported.^{17,69} Identification of intermediates is of great importance for controlling hydrogen release and understanding of the decomposition process. The experimental observation of intermediates is difficult due to poor crystallinity under decomposition reaction conditions. Therefore, identification of intermediate boranes is usually performed by NMR methods.^{10,15,17,67–69}

The intermediate products of borohydrides decomposition were studied previously both experimentally^{10,15,67,68} and theoretically,^{70,71} with the main focus on identification of stable structures containing $B_{12}H_{12}^{2-}$ anions. Here, we report chemical shifts calculated for possible intermediate *closo* boranes $B_nH_n^{2-}$ with $n = 5..12$ and for $B_3H_8^-$ as decomposition products of $LiBH_4$; additionally, a crystalline structure of $CaB_{12}H_{12}$ is considered. Since in the gas phase the smallest *closo* boranes ($n = 5..9$) are unstable,⁷² the present calculations were done for solid state structures based on: Ref. 70 for compounds with $B_nH_n^{2-}$ ($n = 5..11$), Ref. 67 for $Li_2B_{12}H_{12}$; monoclinic structure from Ref. 68 was used for $CaB_{12}H_{12}$, and Ref. 73 provided a structure for $Li_2B_3H_8$. The calculated ^{11}B NMR parameters for possible intermediate boranes are presented in Table 3. (Table S3 of ESI shows these parameters calculated with norm-conserving pseudopotentials, for boranes the difference between two types of pseudopotentials is small, within a few ppm).

The symmetry of the ideal gas phase $B_nH_n^{2-}$ molecules (Ref. 77) is: $n = 5$: D_{3h} ; $n = 6$: O_h ; $n = 7$: D_{5h} ; $n = 8$: D_{2d} ; $n = 9$: D_{3h} ; $n = 10$: D_{4d} ; $n = 11$: C_{2v} ; $n = 12$: I_h . These high symmetries enforce that the majority of boron atoms are equivalent to each other. $B_nH_n^{2-}$ anions were intensively studied in the second half of the 20th century,^{45–48,74–76,78} and NMR was one of the most frequently used research methods. Thus a variety of NMR data exist for *closo* boranes in high symmetry as well with heavier atoms/groups substitution for hydrogen. These data are supported by variety of empirical rules relating the anion structure and ^{11}B chemical shifts.^{74,76} The results of the present calculations for the solid state structures are depicted in Table 3. They are in good

agreement with boron chemical shifts from solution experiments^{74–76} (within several ppm). The multiple degeneracy of the boron atoms positions in highly symmetric gas - phases $B_nH_n^{2-}$ is lifted in the solid state phase, where the number of symmetry inequivalent boron atoms (or the proximity of the cation) in the crystal structure is responsible for calculated distribution of $\delta^{11}B$. For $B_8H_8^{2-}$ the experimental results are unequivocal,⁷⁵ as the symmetry (thus chemical shifts) of this anion strongly depends on the solvent used in the NMR experiment.⁷⁹ For $B_{12}H_{12}^{2-}$ experimental ^{11}B chemical shift in solution equals -15.6 ppm⁷⁴ or as it was suggested this peak is located at -12 ppm in the solid state structure.¹⁵ The present $\delta^{11}B$ values are closer to the ^{11}B chemical shift for $B_{12}H_{12}^{2-}$ measured in the solution NMR experiment. The $B_3H_8^-$ anion is a fluxional molecule on the NMR time scale above ~ 140 K.⁸⁰ Two values of the calculated chemical shifts originate from the static structure and reasonably agree with reports for $Me_2AlB_3H_8$ (-45.6; -15.4 ppm⁸¹) with the average of $\delta^{11}B = -36.6$ ppm lower than experimental $\delta^{11}B$ of $Y(BH_4)_3$ decomposition products¹⁷ or previous calculations for the gas phase structure.⁸¹ The $B_{11}H_{11}^{2-}$ is also considered as a fluxional molecule with respect to BH exchange over all available sites, the calculated average ^{11}B chemical shift equals -17.0 ppm which is very close to experimental data.

For $Li_2B_{12}H_{12}$ and $CaB_{12}H_{12}$ intermediates the simulated spectra are presented in Fig. 4(b). The broad peak for calcium compound is a result of $B_{12}H_{12}^{2-}$ structural distortion. The gas phase ideal $B_{12}H_{12}^{2-}$ anion possesses icosahedral geometry (I_h), which is distorted in the solid state structure due to crystalline symmetry or, in other words, the proximity of Ca cations. For monoclinic $CaB_{12}H_{12}$ six symmetry inequivalent positions for boron atoms result in six chemical shifts (two are degenerated); $\delta^{11}B$ splitting span over 6 ppm. In cubic $Li_2B_{12}H_{12}$ intermediate boron is distributed between two symmetry inequivalent positions, and splitting between two peaks is below 1 ppm. Experimentally observed chemical shifts are broad for both compounds in the solid state.^{10,82} For other crystalline intermediates such as: $K_2B_{12}H_{12}$ $\delta^{11}B = -15.5$ ppm;⁶⁸ $MgB_{12}H_{12}$, $\delta^{11}B = -15$ ppm⁶⁸ the chemical shift compares within 3 ppm with calculated $\delta^{11}B$.

The calculated average quadrupolar coupling $|C_q| = 924$ kHz for $CaB_{12}H_{12}$ is larger than experimental report,⁶⁸ see Table 3. The NMR $|C_q|$ and η parameters for intermediate phases with

B_nH_n , $n = 5, 6, 7, 8, 9, 10$ are presented in Table 3 for completeness.

Discussion

We have shown in the present *ab initio* calculations that boron chemical shifts for a broad class of crystalline metal borohydrides can be calculated with an accuracy of a few ppm.

The analysis of the Bader charge on BH_4^- anion and chemical shift of $\delta^{11}B$ indicates that shielding of boron atom is correlated with a total charge on BH_4^- group. However, a deviation from such correlation for some cations indicates that the type of bonding/atomic arrangement within the solid phase is related to the electronic shielding of boron too. This is shown for $LiBH_4$, where ionic bonding between Li^+ and BH_4^- results in symmetric electron distribution on BH_4^- anion, while in $Zr(BH_4)_4$ or $Al(BH_4)_3$ the electron distribution is asymmetric due to polarization of $s-s$ orbital overlap in BH_4 . For the latter the quadrupolar coupling is an order of magnitude larger than for ionic systems.

For $(LiBH_4)_N$, ($N \leq 12$) nano-clusters a shift of $\delta^{11}B$ toward more negative values is predicted for clusters with less than 10 molecular units. The increase of boron shielding is related to the reduced coordination number of BH_4^- anions in $(LiBH_4)_N$ clusters compared to the bulk structure. The largest deviation from the bulk value of $\delta^{11}B$ is observed for the ring structures, where only Li neighbors are present around BH_4^- .

The linear relation between electronegativity of the metal cation and the heat of formation (or decomposition temperature) is well established for metal borohydrides.^{8,61,62} For bi-alkali metal borohydride $(LiK(BH_4)_2)$ the decomposition temperature is approximately the average of the decomposition temperature for the two constituting mono alkali borohydrides.⁸ By contrast, binary compositions of alkali and transition metal cations show only minor variations in the decomposition temperature with changes in alkali metal.⁸ In order to investigate whether this relation is reflected in chemical shifts of boron, the relation between the ^{11}B chemical shift and Pauling electronegativity of metal cation is presented in Fig. 5. Here, additional calculations were

performed for $\text{Ti}(\text{BH}_4)_{3,4}$ in hypothetical solid state structure⁵⁸ (for $\text{Ti}(\text{BH}_4)_3$ $\delta^{11}\text{B} = 7.1$ ppm; $|\text{C}_q| = 1778$ kHz; $\eta = 0.55$; for $\text{Ti}(\text{BH}_4)_4$ $\delta^{11}\text{B} = 3.1$ ppm; $|\text{C}_q| = 1448$ kHz; $\eta = 0.00$). No sin-

Figure 5: Relations between Pauling electronegativity and $\delta^{11}\text{B}$ for selected metal borohydrides. Lines are drawn to guide the eyes.

gle linear dependence can be distinguished. One can notice, however, two groups of compounds: one for which boron nucleus is deshielded with increasing electronegativity of the metal cation, and the second group where the chemical shifts only weakly depend on the electronegativity of the metal cation. The compounds from the second group consist of solids that are formed from $\text{M}(\text{BH}_4)_n$ molecular units that are arranged in chains (with Be and Al cations) and those with tetrahedral surrounding of the cation (Mg). Thermodynamic stability of these compounds is lower than ionic structures,⁶² and they decompose at low temperatures. Borohydrides of Zr and Ti also form molecular structures, and they follow the trend of lower shielding with increasing electronegativity of the metal. In these structures each boron atom has one cation in the neighborhood, and $\text{M}(\text{BH}_4)_4$ molecular units are arranged in a way that boron - boron distances are large (> 4.5 Å) for separate

units. The crystalline structure is formed due to Van der Waals interactions. For such compounds sublimations of the molecular anion-cation complexes are observed.⁸³ The relation presented in Fig. 5 suggests ^{11}B chemical shifts to be a simple probe of the stability of $\text{M}(\text{BH}_4)_n$ compounds where no molecular like entities are present. For the latter the quadrupolar coupling $|C_q|$ is large, and their heat of formation is low. The enhanced shielding with increasing quadrupolar coupling can be also observed (with a limited extent) for alkali metal borohydrides: these compounds form strongly ionic structures and $|C_q|$ is largest for lithium and smallest for potassium.

Conclusions

In the present manuscript we show that boron NMR chemical shifts can be accurately calculated within Density Functional Theory approach for a broad class of crystalline metal borohydrides. The shielding is larger for compounds with more negative charge on BH_4 anions, and it is argued that the symmetry of s -orbitals of boron is responsible for low shielding in $\text{Zr}(\text{BH}_4)_4$. These results motivate future studies of the influence of the exchange correlation functional on the calculated values of the chemical shifts in metal borohydrides. The calculated NMR parameters provide detailed insight, on the atomic scale, to the properties of nano-sized structures. It is explained that for small nano-clusters of LiBH_4 the boron chemical shift is low frequency shifted due to lower coordination of ions compared to the bulk. The chemical shifts calculated for a series of intermediate borane phases are in reasonable agreement with the experimental data. The relation between Pauling electronegativity and boron chemical shift in metal borohydrides is proposed as a simple method for determining the stability of poorly crystalline materials: the compounds with lower Pauling electronegativity (i.e. with larger decomposition temperature) have more negative ^{11}B chemical shifts with the exception of borohydrides of such metals as Mg, Be, and Al. This relation indicates that NMR experiments may serve as a simple indicator of the complex borohydrides stability; however, further studies are required to elucidate this relation and the origin of exceptions, especially in mixed borohydride compounds.

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Supporting Information Available

The lattice parameters for $M(BH_4)_n$ compounds and $\delta^{11}B$ chemical shift with respect to the Born effective charge $Z_{BH_4}^*$ are given in ESI. Chemical shifts $\delta^{11}B$, quadrupolar coupling $|C_q|$ and asymmetry parameters η for $M(BH_4)_n$ compounds in the crystalline state; for intermediate boranes calculated with norm conserving Troullier - Martins pseudopotentials are available free of charge via the Internet at <http://pubs.acs.org>. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

References

- (1) Schlapbach, L.; Züttel, A. Hydrogen-Storage Materials for Mobile Applications. *Nature* **2001**, *414*, 353.
- (2) Orimo, S.-i.; Nakamori, Y.; Eliseo, J. R.; Züttel, A.; Jensen, C. M. Complex Hydrides For Hydrogen Storage. *Chem. Rev.* **2007**, *107*, 4111–4132.
- (3) Züttel, A.; Borgschulte, A.; Orimo, S.-I. Tetrahydroborates As New Hydrogen Storage Materials. *Scr. Mater.* **2007**, *56*, 823–828.
- (4) Matsuo, M.; Orimo, S.-i. Lithium Fast-Ionic Conduction in Complex Hydrides: Review and Prospects. *Adv. Ener. Mat.* **2011**, *1*, 161–172.
- (5) Ikeshoji, T.; Tsuchida, E.; Morishita, T.; Ikeda, K.; Matsuo, M.; Kawazoe, Y.; Orimo, S.-i. Fast-Ionic Conductivity of Li^+ in $LiBH_4$. *Phys. Rev. B* **2011**, *83*, 144301.
- (6) Guo, Y.; Wu, H.; Zhou, W.; Yu, X. Dehydrogenation Tuning of Ammine Borohydrides Using Double-Metal Cations. *J. Am. Chem. Soc.* **2011**, *133*, 4690–4693.

- (7) Yan, Y.; Remhof, A.; Mauron, P.; Rentsch, D.; Łodziana, Z.; Lee, Y.-S.; Lee, H.-S.; Cho, Y. W.; Züttel, A. Controlling the Dehydrogenation Reaction Toward Reversibility of the $\text{LiBH}_4\text{Ca}(\text{BH}_4)_2$ Eutectic System. *J. Phys. Chem. C* **2013**, *117*, 8878–8886.
- (8) Rude, L. H.; Nielsen, T. K.; Ravnsbæk, D. B.; Bösenberg, U.; Ley, M. B.; Richter, B.; Arnbjerg, L. M.; Dornheim, M.; Filinchuk, Y.; Besenbacher, F. et al. Tailoring Properties of Borohydrides For Hydrogen Storage: A Review. *phys. stat. sol. (a)* **2011**, *208*, 1754–1773.
- (9) Orimo, S. I.; Nakamori, Y.; Ohba, N.; Miwa, K.; Aoki, M.; Towata, S. I.; Züttel, A. Experimental Studies On Intermediate Compound of LiBH_4 . *Appl. Phys. Lett.* **2006**, *89*, 021920.
- (10) Bonatto Minella, C.; Garroni, S.; Olid, D.; Teixidor, F.; Pistidda, C.; Lindemann, I.; Gutfleisch, O.; Baro, M. D.; Bormann, R.; Klassen, T. et al. Experimental Evidence of $\text{Ca}[\text{B}_{12}\text{H}_{12}]$ Formation During Decomposition of a $\text{Ca}(\text{BH}_4)_2 + \text{MgH}_2$ Based Reactive Hydride Composite. *J. Phys. Chem. C* **2011**, *115*, 18010–18014.
- (11) Gremaud, R.; Łodziana, Z.; Hug, P.; Willenberg, B.; Racu, A.-M.; Schoenes, J.; Ramirez-Cuesta, A. J.; S. J. Clark,; Refson, K.; Züttel, A. et al. Evidence for Hydrogen Transport in Deuterated LiBH_4 From Low-Temperature Raman-Scattering Measurements and First-Principles Calculations. *Phys. Rev. B* **2009**, *80*, 100301.
- (12) Remhof, A.; Łodziana, Z.; Martelli, P.; Friedrichs, O.; Züttel, A.; Skripov, A. V.; Embs, J. P.; Strässle, T. Rotational Motion of BH_4 Units in MBH_4 ($M = \text{Li}, \text{Na}, \text{K}$) from Quasielastic Neutron Scattering and Density Functional Calculations. *Phys. Rev. B* **2010**, *81*, 214304.
- (13) Remhof, A.; Mauron, P.; Züttel, A.; Embs, J. P.; Łodziana, Z.; Ramirez-Cuesta, A. J.; Ngene, P.; de Jongh, P. Hydrogen Dynamics in Nanoconfined Lithiumborohydride. *J. Phys. Chem. C* **2013**, *117*, 3789–3798.
- (14) Ogg, R. A. Nuclear Magnetic Resonance Spectra and Structure of Borohydride Ion and Diborane. *J. Chem. Phys.* **1954**, *22*, 1933–1935.

- (15) Hwang, S.-J.; Bowman, R. C.; Reiter, J. W.; Rijssenbeek, G. L.; Zhao, J.-C.; Kabbour, H.; Ahn, C. C. NMR Confirmation for Formation of $[\text{B}_{12}\text{H}_{12}]_2^-$ Complexes During Hydrogen Desorption from Metal Borohydrides. *J. Phys. Chem. C* **2008**, *112*, 3164–3169.
- (16) Bonatto Minella, C.; Garroni, S.; Pistidda, C.; Gosalawit-Utke, R.; Barkhordarian, G.; Rongeat, C.; Lindemann, I.; Gutfleisch, O.; Jensen, T. R.; Cerenius, Y. et al. Effect of Transition Metal Fluorides on the Sorption Properties and Reversible Formation of $\text{Ca}(\text{BH}_4)_2$. *J. Phys. Chem. C* **2011**, *115*, 2497–2504.
- (17) Yan, Y.; Remhof, A.; Rentsch, D.; Lee, Y.-S.; Whan Cho, Y.; Züttel, A. Is $\text{Y}_2(\text{B}_{12}\text{H}_{12})_3$ the Main Intermediate in The Decomposition Process of $\text{Y}(\text{BH}_4)_3$? *Chem. Commun.* **2013**, *49*, 5234–5236.
- (18) Borgschulte, A.; Jain, A.; Ramirez-Cuesta, A. J.; Martelli, P.; Remhof, A.; Friedrichs, O.; Gremaud, R.; Züttel, A. Mobility and Dynamics in The Complex Hydrides LiAlH_4 and LiBH_4 . *Faraday Discuss.* **2011**, *151*, 213–230.
- (19) Zavorotynska, O.; Corno, M.; Damin, A.; Spoto, G.; Ugliengo, P.; Baricco, M. Vibrational Properties of MBH_4 and MBF_4 Crystals ($\text{M} = \text{Li}, \text{Na}, \text{K}$): A Combined DFT, Infrared, and Raman Study. *J. Phys. Chem. C* **2011**, *115*, 18890–18900.
- (20) Racu, A.-M.; Schoenes, J.; Łodziana, Z.; Borgschulte, A.; Züttel, A. High-Resolution Raman Spectroscopy Study of Phonon Modes in LiBH_4 and LiBD_4 . *J. Phys. Chem. A* **2008**, *112*, 9716–9722.
- (21) Buchter, F.; Łodziana, Z.; Remhof, A.; Friedrichs, O.; Borgschulte, A.; Ph. Maun, P.; Züttel, A.; Sheptyakov, D.; Barkhordarian, G.; Bormann, R. et al. Structure of $\text{Ca}(\text{BD}_4)_2$ Beta-Phase From Combined Neutron and Synchrotron X-ray Powder Diffraction Data and Density Functional Calculations. *J. Phys. Chem. B* **2008**, *112*, 8042.
- (22) Buchter, F.; Łodziana, Z.; Remhof, A.; Friedrichs, O.; Borgschulte, A.; Maun, P.; Züttel, A.;

- Sheptyakov, D.; Palatinus, L.; Chłopek, K. et al. Structure of the Orthorhombic gamma-Phase and Phase Transitions of $\text{Ca}(\text{BD}_4)_2$. *J. Phys. Chem. C* **2009**, *113*, 17223–17230.
- (23) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136*, B864.
- (24) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I. et al. QUANTUM ESPRESSO: A Modular and Open-Source Software Project For Quantum Simulations of Materials. *J. Phys.: Condens. Matter* **2009**, *21*, 395502.
- (25) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133.
- (26) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (27) Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50*, 17953.
- (28) Pickard, C. J.; Mauri, F. All-electron Magnetic Response With Pseudopotentials: NMR Chemical Shifts. *Phys. Rev. B* **2001**, *63*, 245101.
- (29) Bonhomme, C.; Gervais, C.; Babonneau, F.; Coelho, C.; Pourpoint, F.; Azas, T.; Ashbrook, S. E.; Griffin, J. M.; Yates, J. R.; Mauri, F. et al. First-Principles Calculation of NMR Parameters Using the Gauge Including Projector Augmented Wave Method: A Chemists Point of View. *Chem. Rev.* **2012**, *112*, 5733–5779.
- (30) Yates, J. R.; Pickard, C. J.; Mauri, F. Calculation of NMR Chemical Shifts For Extended Systems Using Ultrasoft Pseudopotentials. *Phys. Rev. B* **2007**, *76*, 024401.
- (31) Troullier, N.; Martins, J. A Straightforward Method For Generating Soft Transferable Pseudopotentials. *Solid State Commun.* **1990**, *74*, 613616.
- (32) Monkhorst, H. J.; Pack, J. D. Special Points For Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, *13*, 5188.

- (33) Mauri, F.; Pfrommer, B. G.; Louie, S. G. Ab Initio Theory of NMR Chemical Shifts in Solids and Liquids. *Phys. Rev. Lett.* **1996**, *77*, 5300.
- (34) Sebastiani, D.; Parrinello, M. A New ab-Initio Approach for NMR Chemical Shifts in Periodic Systems. *J. Phys. Chem. A* **2001**, *105*, 1951.
- (35) Hayashi, S.; Hayamizu, K. Shift References in High-Resolution Solid-State NMR. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2429.
- (36) Profeta, M.; Mauri, F.; Pickard, C. J. Accurate First Principles Prediction of ^{17}O NMR Parameters in SiO_2 : Assignment of the Zeolite Ferrierite Spectrum. *J. Am. Chem. Soc.* **2003**, *125*, 541548.
- (37) Born, M.; Huang, K. *Dynamical Theory of Crystal Lattices*; Oxford University Press, Oxford, 1954.
- (38) Giannozzi, P.; de Gironcoli, S.; Pavone, P.; Baroni, S. Ab Initio Calculation of Phonon Dispersions in Semiconductors. *Phys. Rev. B* **1991**, *43*, 72317242.
- (39) Baroni, S.; de Gironcoli, S.; Dal Corso, A.; Giannozzi, P. Phonons and Related Crystal Properties From Density-Functional Perturbation Theory. *Rev. Mod. Phys.* **2001**, *73*, 515562.
- (40) Bader, R. *Atoms in Molecules: A Quantum Theory*; Oxford University Press, New York, 1990.
- (41) Henkelman, G.; Arnaldsson, A.; Jónsson, H. A Fast and Robust Algorithm For Bader Decomposition of Charge Density. *Comput. Mater. Sci.* **2006**, *36*, 254–360.
- (42) Sanville, E.; Kenny, S. D.; Smith, R.; Henkelman, G. An Improved Grid-Based Algorithm For Bader Charge Allocation. *J. Comp. Chem.* **2007**, *28*, 899–908.
- (43) Friedrichs, O.; Remhof, A.; Borgschulte, A.; Buchter, F.; Orimo, S. I.; Züttel, A. Breaking the Passivation-The Road To a Solvent Free Borohydride Synthesis. *Phys. Chem. Chem. Phys.* **2010**, *12*, 10919–10922.

- (44) Remhof, A.; Borgschulte, A.; Friedrichs, O.; Mauron, P.; Yan, Y.; Züttel, A. Solvent-Free Synthesis and Decomposition of $\text{Y}(\text{BH}_4)_3$. *Scripta Materialia* **2012**, *66*, 280 – 283.
- (45) Lipscomb, W.; Eaton, G. *NMR Studies of Boron Hydrides and Related Compounds*; Benjamin, New York, 1969.
- (46) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag, Berlin, 1978.
- (47) Mason, J., Ed. *Multinuclear NMR*; Plenum Press, New York, 1987.
- (48) Buehl, M.; Schleyer, P. v. R. Application and Evaluation of Ab Initio Chemical Shift Calculations For Boranes and Carboranes. How Reliable Are "Accurate" Experimental Structures? *J. Am. Chem. Soc.* **1992**, *114*, 477–491.
- (49) Laskowski, R.; Blaha, P.; Tran, F. Assessment of DFT functionals with NMR Chemical Shifts. *Phys. Rev. B* **2013**, *87*, 195130.
- (50) Sen, S. Density Functional Theory Calculations of ^{11}B NMR Parameters in Crystalline Borates. *Mol. Sim.* **2008**, *34*, 1115–1120.
- (51) Ferlat, G.; Charpentier, T.; Seitsonen, A. P.; Takada, A.; Lazzeri, M.; Cormier, L.; Calas, G.; Mauri, F. Boroxol Rings in Liquid and Vitreous B_2O_3 from First Principles. *Phys. Rev. Lett.* **2008**, *101*, 065504.
- (52) Farrell, D. E.; Wolverton, C. Structure and Diffusion in Liquid Complex Hydrides Via *Ab Initio* Molecular Dynamics. *Phys. Rev. B* **2012**, *86*, 174203.
- (53) Hahn, T., Ed. *International Tables for Crystallography*; Springer, Dordrecht, The Netherlands, 2005; Vol. A: Space-Group Symmetry.
- (54) Soloveichik, G. L.; Gao, Y.; Rijssenbeek, J.; Andrus, M.; Kniajanski, S.; Bowman Jr., R. C.; Hwang, S.-J.; Zhao, J.-C. Magnesium Borohydride As a Hydrogen Storage Material: Proper-

- ties and Dehydrogenation Pathway of Unsolvated $\text{Mg}(\text{BH}_4)_2$. *Int. J. Hydrogen Energy* **2009**, *34*, 916–928.
- (55) Ravnsbæk, D. B.; Filinchuk, Y.; Černý, R.; Ley, M. B.; Haase, D.; Jakobsen, H. J.; Skibsted, J.; Jensen, T. R. Thermal Polymorphism and Decomposition of $\text{Y}(\text{BH}_4)_3$. *Inorg. Chem.* **2010**, *49*, 3801–3809.
- (56) Heyn, R. H.; Saldan, I.; Sorby, M. H.; Frommen, C.; Arstad, B.; Bougza, A. M.; Fjellvag, H.; Hauback, B. C. Structural and Spectroscopic Characterization of Potassium Fluoroborohydrides. *Phys. Chem. Chem. Phys.* **2013**, *15*, 11226–11230.
- (57) Łodziana, Z.; van Setten, M. J. Binding in Alkali and Alkaline-Earth Tetrahydroborates: Special Position of Magnesium Tetrahydroborate. *Phys. Rev. B* **2010**, *81*, 024117.
- (58) Łodziana, Z. Multivalent Metal Tetrahydroborides of Al, Sc, Y, Ti, and Zr. *Phys. Rev. B* **2010**, *81*, 144108.
- (59) Spielvogel, B. F.; Purser, J. M. Correlations Between Carbon-13 and Boron-11 Chemical Shifts. III. Pairwise Interaction Parameters. *J. Am. Chem. Soc.* **1971**, *93*, 4418–4426.
- (60) Kroner, J.; Wrackmeyer, B. ^{11}B -Chemical Shifts of Diboranes, Polyboranes, Carboranes and Coupling Constants $1J(^{11}\text{B}1\text{H})$, $1J(^{11}\text{B}^{11}\text{B})$. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 2283–2290.
- (61) Nakamori, Y.; Miwa, K.; Ninomiya, A.; Li, H.; Ohba, N.; Towata, S.-i.; Züttel, A.; Orimo, S.-i. Correlation Between Thermodynamical Stabilities of Metal Borohydrides and Cation Electronegativities: First-Principles Calculations and Experiments. *Phys. Rev. B* **2006**, *74*, 045126.
- (62) Nakamori, Y.; Li, H.-W.; Kikuchi, K.; Aoki, M.; Miwa, K.; Towata, S.; Orimo, S. Thermodynamical Stabilities of Metal-Borohydrides. *J. Alloys Compounds* **2007**, *446–447*, 296–300.

- (63) Verkuijlen, M. H. W.; Ngene, P.; de Kort, D. W.; Barre, C.; Nale, A.; van Eck, E. R. H.; van Bentum, P. J. M.; de Jongh, P. E.; Kentgens, A. P. M. Nanoconfine LiBH_4 and Enhanced Mobility of Li^+ and BH_4 Studied by Solid-State NMR. *J. Phys. Chem. C* **2012**, *116*, 22169–22178.
- (64) Liu, X.; Majzoub, E. H.; Stavila, V.; Bhakta, R. K.; Allendorf, M. D.; Shane, D. T.; Conradi, M. S.; Verdal, N.; Udovic, T. J.; Hwang, S.-J. Probing the Unusual Anion Mobility of LiBH_4 Confine in Highly Ordered Nanoporous Carbon Frameworks Via Solid State NMR and Quasielastic Neutron Scattering. *J. Mater. Chem. A* **2013**, *1*, 9935–9941.
- (65) Hazrati, E.; Brocks, G.; de Wijs, G. A. First-Principles Study of LiBH_4 Nanoclusters and Their Hydrogen Storage Properties. *J. Phys. Chem. C* **2012**, *116*, 18038–18047.
- (66) Kemp, T.; Smith, M. QuadFit A New Cross-Platform Computer Program For Simulation of {NMR} Line Shapes From Solids With Distributions of Interaction Parameters. *Solid State Nuclear Magnetic Resonance* **2009**, *35*, 243 – 252.
- (67) Her, J.-H.; Yousufuddin, M.; Zhou, W.; Jalisatgi, S. S.; Kulleck, J. G.; Zan, J. A.; Hwang, S.-J.; Bowman, R. C.; Udovic, T. J. Crystal Structure of $\text{Li}_2\text{B}_{12}\text{H}_{12}$: a Possible Intermediate Species in the Decomposition of LiBH_4 . *Inorg. Chem.* **2008**, *47*, 9757–9759.
- (68) Stavila, V.; Her, J.-H.; Zhou, W.; Hwang, S.-J.; Kim, C.; Ottley, L. A. M.; Udovic, T. J. Probing the Structure, Stability and Hydrogen Storage Properties of Calcium Dodecahydro-Closo-Dodecaborate. *J. Solid State Chem.* **2010**, *183*, 1133 – 1140.
- (69) Chong, M.; Karkamkar, A.; Autrey, T.; Orimo, S.-i.; Jalisatgi, S.; Jensen, C. M. Reversible Dehydrogenation of Magnesium Borohydride To Magnesium Triborane in The Solid State Under Moderate Conditions. *Chem. Commun.* **2011**, *47*, 1330–1332.
- (70) Ohba, N.; Miwa, K.; Aoki, M.; Noritake, T.; Towata, S.-i.; Nakamori, Y.; Orimo, S.-i.; Züttel, A. First-Principles Study On The Stability of Intermediate Compounds of LiBH_4 . *Phys. Rev. B* **2006**, *74*, 075110.

- (71) Ozolins, V.; Majzoub, E. H.; Wolverton, C. First-Principles Prediction of Thermodynamically Reversible Hydrogen Storage Reactions in the Li-Mg-Ca-B-H System. *J. Am. Chem. Soc.* **2009**, *131*, 230–237.
- (72) Nguyen, M. T.; Matus, M. H.; Dixon, D. A. Heats of Formation of Boron Hydride Anions and Dianions and Their Ammonium Salts $[B_nH_mY^-][NH_4^+]_y$ with $y = 1-2$. *Inorg. Chem.* **2007**, *46*, 7561–7570.
- (73) Deiseroth, H. J.; Sommer, O.; Binder, H.; Wolfer, K.; Frei, B. CsB_3H_8 : Kristallstruktur und Optimierung der Synthese. *Zeitschrift Anorg. allgemeine Chemie* **1989**, *571*, 21–28.
- (74) Heřmánek, S. NMR as a Tool For Elucidation of Structures and Estimation of Electron Distribution in Boranes and Their Derivatives. *Inorg. Chim. Acta* **1999**, *289*, 20 – 44.
- (75) Heřmánek, S. Boron-11 NMR Spectra of Boranes, Main-Group Heteroboranes, and Substituted Derivatives. Factors Influencing Chemical Shifts of Skeletal Atoms. *Chem. Rev.* **1992**, *92*, 325–362.
- (76) Teixidor, F.; Vinas, C.; Rudolph, R. W. Rules For Predicting The Boron-11 NMR Spectra of Closo-Boranes and Closo-Heteroboranes. *Inorg. Chem.* **1986**, *25*, 3339–3345.
- (77) McKee, M. L.; Wang, Z.-X.; Schleyer, P. v. R. Ab Initio Study of the Hypercloso Boron Hydrides B_nH_n and B_nH_{n-1} . Exceptional Stability of Neutral $B_{13}H_{13}$. *J. Am. Chem. Soc.* **2000**, *122*, 4781–4793.
- (78) Buehl, M.; Schleyer, P. v. R.; Havlas, Z.; Hnyk, D.; Hermanek, S. On the Origin of The Antipodal Effect in Closo-Heteroboranes. *Inorg. Chem.* **1991**, *30*, 3107–3111.
- (79) Muetterties, E. L.; Wiersema, R. J.; Hawthorne, M. F. Detection of Polytopal Isomers in The Solution State. I. Eight-Atom Family. *J. Am. Chem. Soc.* **1973**, *95*, 7520–7522.
- (80) McKee, M. L.; Lipscomb, W. N. Ab Initio Study of the Transient Boron Hydrides B_3H_7 , B_3H_9 , B_4H_8 , and B_4H_{12} and the Fluxional Anion $B_3H_8^-$. *Inorg. Chem.* **1982**, *21*, 2846–2850.

- (81) Wrackmeyer, B. Indirect Nuclear Spin-Spin Coupling Constants $nJ(^{11}\text{B}, ^1\text{H})$ and $nJ(^{11}\text{B}, ^{11}\text{B})$ in Some Boron Hydrides - Density Functional Theory (DFT) Calculations. *Z. Naturforsch.* **2004**, *59b*, 1192–1199.
- (82) Yan, Y.; Remhof, A.; Hwang, S.-J.; Li, H.-W.; Mauron, P.; Orimo, S.-i.; Züttel, A. Pressure and Temperature Dependence of The Decomposition Pathway of LiBH_4 . *Phys. Chem. Chem. Phys.* **2012**, *14*, 6514–6519.
- (83) Callini, E.; Borgschulte, A.; Ramirez-Cuesta, A. J.; Züttel, A. Diborane Release and Structure Distortion in Borohydrides. *Dalton Trans.* **2013**, *42*, 719–725.

Table 3: Calculated chemical shifts $\delta^{11}\text{B}$, quadrupolar coupling $|C_q|$, asymmetry parameters η , and relative intensity I for intermediate boranes. Data for solution measurements of $\text{B}_n\text{H}_n^{2-}$ are given for comparison, unless solid state measurements (SS; Ref. 68) are available. The average of calculated values is given in *italics* for structures with inequivalent born atoms in the symmetric anion.

Compound	$\delta^{11}\text{B}$ (ppm)		$ C_q $ (kHz)	η	I
	Calc.	Exp.			
$\text{Li}_2\text{B}_3\text{H}_8$	-49.0		959	0.60	0.67
	-11.8		2520	0.77	0.33
	-36.7	-30.8 ^a	1474	0.66	
$\text{Li}_2\text{B}_5\text{H}_5$	-43.9		1982	0.76	0.60
	-11.7		797	0.00	0.20
	19.8		1047	0.00	0.20
	-24.7		1559	0.46	
$\text{Li}_2\text{B}_6\text{H}_6$	-12.4	-13.6 ^b	1310	0.00	1.00
$\text{Li}_2\text{B}_7\text{H}_7$	-22.4	-22.6 ^b	1082	0.49	0.29
	-5.8		1585	0.56	0.29
	-1.0		2226	0.20	0.13
	1.2		1951	0.39	0.29
$\text{Li}_2\text{B}_8\text{H}_8$	-2.2	-0.2 ^b	1315	0.30	
	-8.8	-6.8 ^c	1821	0.57	0.50
	6.1		1889	0.78	0.50
$\text{Li}_2\text{B}_9\text{H}_9$	-23.8		1882	0.14	0.33
	-21.8	-20.5 ^b	1679	0.17	0.33
	2.2	-2.9 ^b	1220	0.02	0.33
$\text{Li}_2\text{B}_{10}\text{H}_{10}$	-29.3	-30.9 ^b , -28 ^d	1172	0.48	0.80
	-2.1	0.9 ^b , -1 ^d	1232	0.00	0.20
$\text{Li}_2\text{B}_{11}\text{H}_{11}$	-31.8		2070	0.32	0.10
	-27.5		1039	0.88	0.18
	-19.5		1244	0.61	0.18
	-17.7		1395	0.78	0.18
	-16.4		1197	0.19	0.18
	4.5		1698	0.16	0.18
$\text{Li}_2\text{B}_{12}\text{H}_{12}$	-17.0	-16.9 ^a	1390	0.50	
	-14.8	-15.6 ^b	906	0.20	0.50
	-14.2	-16.9 ^d	981	0.13	0.50
	-14.5		944	0.16	
$\text{CaB}_{12}\text{H}_{12}$	-14.9	-14.5 ^e	1186	0.07	0.17
	-12.8		686	0.05	0.32
	-12.3		771	0.10	0.17
	-11.0		1359	0.08	0.17
	-9.1		829	0.34	0.17
	-12.1		924	0.12	

(a) Ref. 17, data for $\text{Y}(\text{B}_3\text{H}_8)_3$; (b) Ref. 74; (c) Ref. 75 D_{4d} symmetry, for C_{2v} structure $\delta^{11}\text{B}$ = -22.2, -3.6, 9.5 ppm; (d) Ref. 76; (e) SS; Ref. 68; $|C_q|$ = 600 kHz; η = 0.25