Structure and Properties of NaBH$_4$·2H$_2$O and NaBH$_4$

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NaBH$_4$·2H$_2$O and NaBH$_4$ were studied by single-crystal X-ray diffraction and vibrational spectroscopy. In NaBH$_4$·2H$_2$O, the BH$_4^-$ anion has a nearly ideal tetrahedral geometry and is bridged with two Na$^+$ ions through the tetrahedral edges. The structure does not contain classical hydrogen bonds, but reveals strong dihydrogen bonds of 1.77–1.95 Å. Crystal structures and vibrational spectra of NaBr·2H$_2$O and NaBH$_4$·2H$_2$O reveal many similarities. The unit cell volume of NaBH$_4$·2H$_2$O increases linearly with temperature between 200 and 313 K. At 313–315 K, the hydrate decomposes into NaBH$_4$ and H$_2$O, which react to release hydrogen.

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Introduction

Light-metal hydrides are considered as prospective energy carriers for future mobile applications. Hydrogen can be produced from metal hydrides by thermal decomposition (pyrolysis)[1] or in a reaction with water (hydrolysis).[2] Borohydrides of alkaline metals, such as LiBH$_4$ and NaBH$_4$, readily evolve hydrogen by hydrolysis, both upon direct reaction with water[3] and through a fuel cell.[4] Although the reactions with water are usually fast, the reaction kinetics under practical conditions is rather slow, thus suggesting the use of expensive catalysts.[5] Catalytically accelerated NaBH$_4$ hydrolysis for the generation of hydrogen has been studied since the 1950s,[6] and it is now under intensive investigation,[5] leading to a number of recent applications.[7] However, until now, there is no experimental structural information on intermediate phases or reaction pathways in the NaBH$_4$ + H$_2$O system.

The first report on a solid sodium borohydride dihydrate was published over 50 years ago.[8] Recently, the existence of short dihydrogen bonds has been reported for NaBH$_4$·2H$_2$O from neutron diffraction,[9] but a full account of the structural data has not been published until now. Hydrogen elimination from LiBH$_4$ and NaBH$_4$ complexes with less-reactive proton donors, such as alcohols, has been reported,[10] whereas the study of the NaBH$_4$ complex with water would be very important for hydrogen storage. This work is focused on the crystal structure of NaBH$_4$·2H$_2$O and its anhydrous counterpart and will contribute to a better understanding of the mechanism of borohydride hydrolysis.

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Results and Discussion

Although neutron powder diffraction is known as the main technique to study structure of metal hydrides,[11] as it reveals some of the most complex structures of transition metal hydrides,[12] neutron diffraction studies of metal borohydrides are hindered by the incoherent scattering by H and the high absorption of natural B isotopes. To overcome these drawbacks, isotopically labelled borohydride samples are prepared[13] and neutron and X-ray diffraction techniques are combined.[14] On the other hand, in light hydrides X-ray diffraction on its own was shown to be a powerful tool to locate hydrogen atoms and was applied to potential hydrogen storage materials.[15,16] In this work crystal structures, including hydrogen atoms' positions, of anhydrous and hydrated NaBH$_4$ were accurately determined from synchrotron diffraction on single crystals.

Anhydrous NaBH$_4$ at temperatures above ≈190 K[17] has a cubic structure isomorphous to NaCl, previously described either in $Fm\bar{3}m$[18] or $F\bar{4}3m$[19,20] space groups. The two models differ only by the absence of the inversion centre in $F\bar{4}3m$. Although the centrosymmetric structure is intrinsically disordered, showing two orientations of the BH$_4^-$ group, the noncentrosymmetric model allows the BH$_4^-$ anion to be fully ordered. A peak of heat capacity below ≈190 K[17] is consistent with an order–disorder transition[21] from cubic to tetragonal structure.[18] This thermodynamic data suggests that the high-temperature phase is disordered; therefore, the higher-symmetry space group $Fm\bar{3}m$ has to be assumed for its structure. We note that the fully disordered $F\bar{4}3m$ model assumed in ref.[20] is completely identical to the $Fm\bar{3}m$ model. It is important also to understand that the nonresonant single-crystal or any powder diffraction studies are not able to determine whether the BH$_4^-$ anion in cubic NaBH$_4$ is ordered or disordered. However, crystal-chemical analysis shows that the shortest, repulsive H···H interactions favour the disorder: a number of the shortest

H···H distances between BH_4^- anions in the disordered $Fm\bar{3}m$ structure is two times smaller than in a hypothetical ordered $F\bar{4}3m$ structure.[21] Thus, among the two possible models, the disordered $Fm\bar{3}m$ and the ordered $F\bar{4}3m$, only the first one agrees both with crystallographic and thermodynamic data.

The crystal structure of $NaBH_4\cdot2H_2O$ contains sodium cations having a nearly octahedral coordination made up of four water molecules and two borohydride anions (Figure 1). The Na–O bonds are ≈2.4 Å long and the Na···B distances are around 3.0 Å (Table 1). The orientation of the BH_4^- tetrahedron is such that it is bridged with two Na^+ ions through the tetrahedral edges. The Na···μ_2-H_2B coordination is somewhat asymmetric, with one shorter and one longer Na–H distances of 2.46–2.67 Å (Table 1). The Na···B···Na angle is ≈96°. In anhydrous $NaBH_4$, the disordered BH_4^- anion symmetrically μ_2-coordinates Na atoms at Na–H distances of 2.59 Å. Although Na···B contacts in $NaBH_4\cdot2H_2O$ are only slightly shorter than in $NaBH_4$ [3.0654(1) Å], the Na···Na distances are considerably shortened from 4.34 to 3.61–3.80 Å. This is due to the fact that sodium atoms in $NaBH_4\cdot2H_2O$ do not form a close-packed substructure as in the anhydrous $NaBH_4$, but instead they form flat honeycomb layers in the *ab* plane.

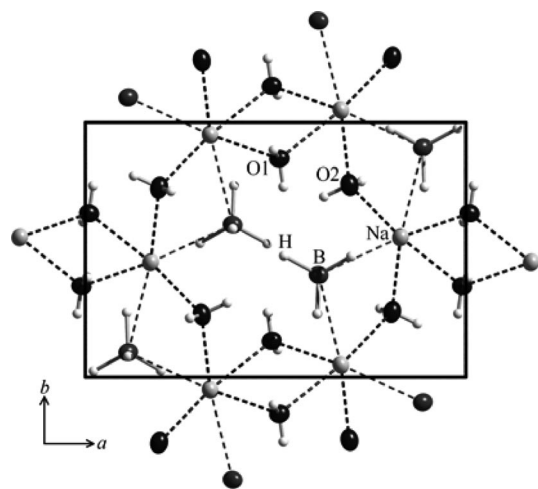Figure 1. Projection of the $NaBH_4\cdot2H_2O$ structure on the *ab* plane. Anisotropic thermal ellipsoids at 100 K are drawn at the 80% probability level. Coordination of sodium atoms (light-grey spheres) is highlighted by dashed lines.

As shown in Figure 1, Na atoms and one type of water molecules form centrosymmetric Na_2O_2 units, which are linked by the second type of water molecules into an infinite layer located in the *ab* plane. The Na–O1–Na and Na–O2–Na angles in the 12-membered Na_6O_6 rings are nearly the same, and are, respectively, 98.08(3) and 101.68(3)° at 100 K.

Very similar layers were observed in the monoclinic structures of $NaCl\cdot2H_2O$[22] and $NaBr\cdot2H_2O$.[23] The volume of the $NaX\cdot2H_2O$ formulae units ($V_{f.u.}$) shows that the BH_4^- anion ($V_{f.u.}$ = 106.7 Å^3 at 100 K, and 110.4 Å^3 at 295 K) is considerably larger than the Cl^- anion ($V_{f.u.}$ = 94.8 Å^3 at 105 K) and larger than the Br^- anion ($V_{f.u.}$ =

Table 1. Interatomic distances [Å] and angles [°] in $NaBH_4\cdot2H_2O$.

	100 K	150 K
Intramolecular contacts		
O–H (4×)	0.755(18)–0.792(16)	0.756(16)–0.814(17)
H–O–H (2×)	105.5(16)–105.9(15)	99.9(15)–100.4(17)
B–H (4×)	1.110(15)–1.134(13)	1.068(15)–1.123(16)
H–B–H (6×)	106.8(9)–112.4(10)	105.5(10)–112.5(11)
Coordination sphere of the sodium atom		
Na–O (4×)	2.3811(8)–2.4689(9)	2.3908(9)–2.4816(10)
Na···B (2×)	2.9533(12)–3.0059(13)	2.9635(13)–3.0100(14)
Na–H (4×)	2.455(12)–2.670(12)	2.464(12)–2.662(13)
O–Na–O (6×)	81.92(3)–169.45(3)	81.89(3)–169.19(4)
B–Na–O (8×)	86.39(3)–175.51(3)	86.75(4)–175.54(3)
B···Na···B	96.51(4)	96.42(4)

106.9 Å^3 at 295 K). The use of even larger iodine anion results in a different structure of $NaI\cdot2H_2O$ ($V_{f.u.}$ = 124.5 Å^3 at 295 K).[24] The unit cell volumes suggest that the size of anions change according to the sequence I^- > BH_4^- > Br^- > Cl^-. The final product of $NaBH_4$ hydrolysis, the isostoichiometric $Na[B(OH)_4]\cdot2H_2O$,[25] contains $Na_n(H_2O)_n$ chains linked by anions into layers, similar to those in $NaI\cdot2H_2O$.

Isostoichiometric compounds containing tetrahedral anions other than BH_4^- reveal 3D framework structures where ligands display a different denticity. For example, the dihydrogenphosphate anion in $Na[H_2(PO_4)]\cdot2H_2O$ acts as a tridentate ligand, and moreover, one water molecule is bridging and the other is terminal.[26] In the group of compounds with a general formula $A(BO_4)\cdot2H_2O$ (A = Fe, Al, In, Ga; B = P, As), the anions act as tetradentate and water molecules as terminal ligands.[27]

$NaBH_4\cdot2H_2O$ is the first-known hydrated borohydride, but it is also the third-known structure containing borohydride anions and oxygen atoms. The other two compounds, $Na_8(GaSiO_4)_6(BH_4)_2$ and $Na_8(AlGeO_4)_6(BH_4)_2$, have been recently synthesized under mild hydrothermal conditions and studied by powder diffraction.[28] They were proposed as BH_4^--containing model compounds that could release hydrogen. However, the $NaBH_4/H_2O$ system has a higher H capacity and, at present, is the cheapest source of hydrogen. The $LiBH_4$–$LiNH_2$ system is an important alternative, as it can produce hydrogen under much milder conditions.[29]

In $NaBH_4\cdot2H_2O$, the BH_4^- anion has a nearly ideal tetrahedral geometry with an average B–H bond length of ≈1.12 Å (see Table 1). This value is completely consistent with recent single-crystal X-ray data on the BH_4^- anion in a light-metal hydride.[15] The O–H distances have an average value of 0.77 Å. The nearly ideal tetrahedral configuration of the BH_4 group and proper H–O–H angles in the H_2O molecules confirm that the hydrogen atoms are located from synchrotron data with a high accuracy. However, the observed O–H and B–H distances are systematically underestimated. Apart from a small effect of libration, this difference comes from a displacement of the electron cloud (seen by X-ray analysis) relative to an average nuclear position (seen by neutron diffraction and determined by DFT calcu-

lations). In order to evaluate better the geometry of the dihydrogen bonds, the apparent hydrogen atom positions at 100 K were corrected by "extending" the average O–H (0.77 Å) and B–H (1.12 Å) bond lengths to the ideal values of 0.96 and 1.22 Å.[20] Below we will discuss characteristics of the H···H bonds assuming corrected coordinates of the H atoms.

The structure of NaBH$_4$·2H$_2$O does not show classical hydrogen bonds, but reveals dihydrogen bonding. Their geometric characteristics, calculated for the 100 K data by using corrected positions of the H atoms, are listed in Table 2. The H···H distances are much shorter than twice the value of the van der Waals radius of a hydrogen atom (2.4 Å) and are very close to those preliminary reported for this compound from single-crystal neutron diffraction (1.79, 1.86 and 1.94 Å).[9] The latter shows that by assuming proper corrections, hydrogen atoms in light-metal hydrides can be determined from X-ray diffraction data with accuracy similar to the neutron diffraction study. It is remarkable that the three intermolecular O–H$^{\delta+}$···$^{\delta-}$H–B dihydrogen bonds are shorter than H···H distances within the BH$_4^-$ anion (≈2.0 Å). The interaction between neighbouring BH$_4^-$ anions is reduced to the minimum: the corresponding shortest H···H contact is 2.72(2) Å in length. The shortest dihydrogen bond of 1.77 Å connects the layers (Figure 1) along the c axis. The layers are associated only through dihydrogen bonds, and this is probably the reason why the crystals grow as thin plates.

Table 2. Geometric characteristics of dihydrogen bonds in NaBH$_4$·2H$_2$O (100 K data, corrected positions of H atoms).

Distance [Å]		Angle [°]	
Hw1···H3	1.77(2)	O1–Hw1···H3/B	170.1(14)/157.4(12)
Hw2···H3	1.90(2)	O1–Hw2···H3/B	151.1(18)/162.8(17)
Hw4···H3	1.95(2)	O2–Hw4···H3/B	156.8(13)/171.7(12)

Figure 2 shows the coordination environment for the BH$_4^-$ anion in NaBH$_4$·2H$_2$O. The three shortest dihydrogen bonds involve the same hydrogen atom (H3) of the BH$_4$ group. The H3 atom does not interact with sodium atoms, and the H1, H2 and H4 atoms are coordinated by sodium atoms through the edges of the BH$_4$ tetrahedra. The B–H3
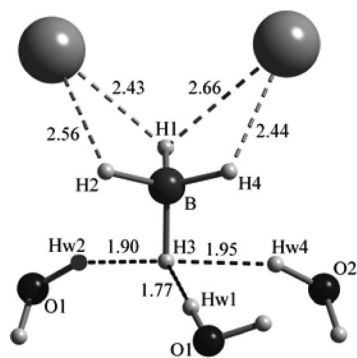

Figure 2. Coordination of the borohydride anion in NaBH$_4$·2H$_2$O by two sodium atoms and three water molecules. Interatomic distances are shown in Å for the corrected hydrogen atom positions at 100 K.

distance is longer than the average of the other three B–H distances by 0.02 Å, and the O1–Hw1 bond (forming the shortest dihydrogen bond of 1.77 Å) is longer than the other O–H distances by almost 0.04 Å. These differences are within the limits of two standard uncertainties. However, the lengthening of the B–H and O–H bonds in the B–H···H–O fragments was found in similar systems by ab initio calculations.[30]

As can be seen from Table 2, the O–H vectors are well directed towards the B and H3 atoms. However, they are not clearly pointed toward the middle of the B–H bond, as suggested.[9] The O–H vectors are even less directed with respect to the H–B bonds for a number of additional O–H···H–B contacts (not shown in Table 2), where the H···H distances are less than ≈2.4 Å. This suggests that the BH$_4^-$···H$^{\delta+}$(O) interaction is somewhat similar to the interaction of the BH$_4^-$ anion with a spherical cation, as, for instance, BH$_4^-$···Na$^+$ in the title compounds or BH$_4^-$···Li$^+$ in Li$_4$BN$_3$H$_{10}$.[15] The observed flexibility is in line with the conclusion that there is no sharp borderline between dihydrogen bonds and van der Waals interactions.[31]

In order to see whether short dihydrogen bonds enable hydrogen release directly from NaBH$_4$·2H$_2$O, we studied its thermal decomposition by in situ diffraction. To analyze the data collected upon heating the powder of NaBH$_4$·2H$_2$O, its single-crystal structure was used as an input for the sequential Rietveld refinement in Fullprof.[32] We found that within 196–313 K the unit cell volume (Å^3) of NaBH$_4$·2H$_2$O increases linearly with temperature (K): V = 825.3(1) + 0.1969(4) T. The unit cell parameters a and c also show a linear temperature dependence, whereas the b parameter can be approximated by a quadratic dependence:

$$a = 10.1427(7) + 1.080(3) \times 10^{-4}\ T$$

$$b = 6.8857(5) - 2.3(4) \times 10^{-4}\ T + 9.5(7) \times 10^{-7}\ T^2$$

$$c = 11.9308(9) + 1.040(4) \times 10^{-3}\ T$$

Under the experimental conditions (heating NaBH$_4$·2H$_2$O at 60 K per hour in a glass capillary), the structure decomposes at 313–315 K into NaBH$_4$ and H$_2$O. This is consistent with an earlier observation that NaBH$_4$·2H$_2$O, NaBH$_4$ and H$_2$O coexist in equilibrium at 1 bar and 35(1) °C.[8] Upon heating to higher temperatures above that required for NaBH$_4$·2H$_2$O decomposition, we observed that NaBH$_4$ and H$_2$O slowly react to release hydrogen. Thus, the hydrate NaBH$_4$·2H$_2$O does not directly release hydrogen, even upon thermal decomposition, but decomposes into anhydrous NaBH$_4$ and water. The latter react to produce hydrogen.

Figure 3 compares the IR spectra of NaBH$_4$ in solution with the spectra of the solid NaBH$_4$, NaBH$_4$·2H$_2$O and NaBr·2H$_2$O. The observed bands in the Raman and IR spectra at room temperature are collected in Table 3. These data confirm that NaBH$_4$ is stable in alkaline aqueous solution at room temperature. The spectra show that the BH$_4$ ions are unaltered, both in alkaline aqueous solution of NaBH$_4$ and in solid NaBH$_4$·2H$_2$O. The spectra show very

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Table 3. Vibrational frequencies in NaBr·2H$_2$O, NaBH$_4$·2H$_2$O, NaBH$_4$·2D$_2$O and NaBH$_4$. Raman bands above 2700 cm^{-1} could not be observed with our experimental setup.

NaBr·2H$_2$O		NaBH$_4$·2H$_2$O		NaBH$_4$·2D$_2$O		NaBH$_4$		Assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	
5156								3544+1612 ?
5051								3404+1635 ?
3544		3565		3554				O–H
3460		3502		3497				stretching
3404		3462		3479				
3374 (sh.)								
3234 (w)		3241						
				2648	2650			O–D
				2616	2615			stretching
				2586 (w)				
				2570 (w)				
				2554	2560			
				2540				
							2553	
		2380 (sh.)	2319	2346 (w, sh.)	2313		2416	B–H stretching
		2268	2299 (sh.)	2267	2300 (sh.)	2396	2340	
		2221	2233	2225	2233	2282	2321	
		2190 (sh.)	2170	2188 (sh.)	2178	2216	2231	
							2197	
1635	1650	1621	1642	1635				HOH bend
1612	1636	1613						
				1434				HOD bend
				1197	1210			DOD bend
				1190				
			1264		1265		1274	B–H def E
			1248 (sh.)		1245			
		1124	1133	1125	1132	1110	1124	B–H def F$_2$
		1097	1106	1097	1106			
620 (sh.)	630 (sh.)	616	595		458			libration
595	579	566	489		443			H$_2$O
	443		407		282			
	383		357					
	238 (w, sh.)							
	213							

similar absorption frequencies as in the anhydrous NaBH$_4$, a small splitting of the deformation bands suggests an almost tetrahedral symmetry of the borohydride group.

The vibrational spectra of NaBH$_4$ in alkaline D$_2$O solution (Figure 4) show that the hydrogen atoms of the borohydride ion and the water molecules do not exchange
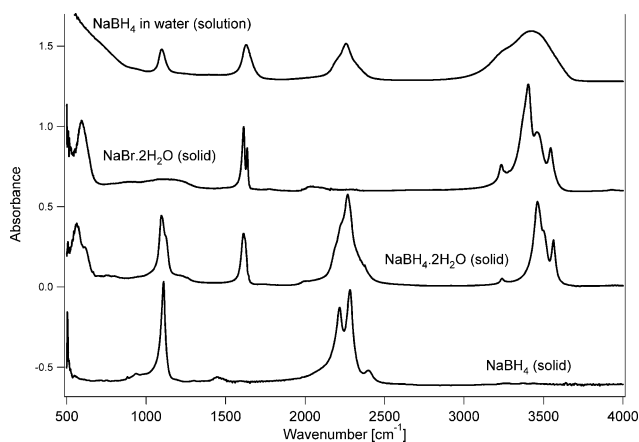

Figure 3. Room-temperature IR spectra of solid NaBH$_4$, solid NaBH$_4$·2H$_2$O, solid NaBr·2H$_2$O and alkaline (pH > 13) 8.8 M aqueous solution of NaBH$_4$.
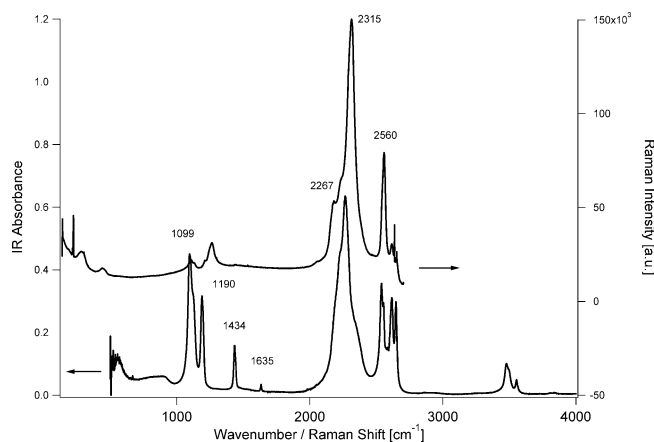

Figure 4. IR and Raman spectra of NaBH$_4$·2D$_2$O (95% D isotope purity) at room temperature.

significantly at 20 °C. This agrees with the recent observation made in a detailed kinetic NMR spectroscopic study of Pd-catalyzed hydrolysis of NaBH$_4$.[33]

The O–H stretching in NaBH$_4$·2H$_2$O reveals a sharp band at 3553 cm^{-1} and a strong band at 3478 cm^{-1} with a shoulder at 3490 cm^{-1}. This is consistent with the presence of the strong dihydrogen bonds for three O–H groups and the absence of the dihydrogen bonding for the fourth one (O2–Hw3). In comparison, the spectra for NaBr·2H$_2$O are spread over a wider range (3404–3544 cm^{-1}), but show a similar intensity pattern (see Figure 3). The librational modes of the water molecules in NaBr·2H$_2$O and NaBH$_4$·2H$_2$O are found at around 600 cm^{-1} and below.

The F$_2$ deformation band of BH$_4$ ($\approx$1100 cm^{-1}, shoulder at higher energy), and the F$_2$ stretching band together with other bands arising from Fermi resonances (2300 cm^{-1}) appear at similar positions as in NaBH$_4$.[34,35] The positions of the totally symmetrical stretching mode at 2340 cm^{-1} in NaBH$_4$ and 2319 cm^{-1} in NaBH$_4$·2H$_2$O are similar, suggesting a similar B–H bond length in the hydrated and the anhydrous form. Under the experimental conditions of the diffraction experiments, the B–H bond lengths in hydrated and anhydrous NaBH$_4$ are similar: the average length of the B–H bonds in NaBH$_4$·2H$_2$O at 100 K is 1.12(1) Å, whereas in anhydrous NaBH$_4$ at 200 K the B–H bond length is 1.09(2) Å. The B–D distance determined in NaBD$_4$ from neutron powder diffraction at room temperature is $\approx$1.17 Å.[20] If we assume for NaBH$_4$ the same 0.10 Å difference between the centre of an electron cloud and an average nuclear position of an H atom, as in the case of NaBH$_4$·2H$_2$O, the effect of the libration would be responsible for a sensible 0.02 Å decrease in the apparent B–H distance from 200 K (1.09 + 0.10 = 1.19 Å) to room temperature (1.17 Å). Thus, the 0.10-Å correction for the positions of the H atoms as determined by X-ray diffraction appears to be practical and may be applied to structures of other borohydrides.

A small part of the 0.10-Å correction originates from a geometric effect caused by libration of the BH$_4$ unit. An extent of the BH$_4^-$ libration is not only temperature-dependent (at higher temperature the motion of the BH$_4^-$ groups is more pronounced) but also specific to each crystal structure. However, a larger part of the 0.10-Å correction comes from the well-known displacement of the electron cloud relative to an average nuclear position, and it is temperature independent. Thus, the 0.10 Å increment can be used as an empirical correction for the B–H distances, which brings H atom positions determined from X-ray diffraction in borohydrides to a direct comparison with those derived from neutron diffraction. Such estimates are known for systems containing N–H or O–H bonds,[36] but not for those containing B–H bonds. Correction of systematic errors for H positions determined from X-ray diffraction leads to an increased accuracy of this technique being applied to low-Z hydride systems. Nonoverlapped three-dimensional information uncovered by the scattering of X-rays on single crystals gives an advantage over the neutron powder diffraction, which gives one-dimensional projec-

tions. This sets new standards for experimental studies of light hydrides and opens new routes to characterize them, such as single-crystal X-ray diffraction at multiple temperatures and inelastic X-ray scattering on single crystals. Such experiments on NaBH$_4$ are in progress.

Conclusions

In this work, the positions of hydrogen atoms were unambiguously determined from synchrotron diffraction on single crystals of anhydrous and hydrated NaBH$_4$, which are potential hydrogen storage materials. In NaBH$_4$·2H$_2$O, the BH$_4^-$ anion has a nearly ideal tetrahedral geometry and is bridged with two Na$^+$ ions through the tetrahedral edges. The structure does not contain classical hydrogen bonds, but reveals strong dihydrogen bonds of 1.77–1.95 Å. The crystal structures and vibrational spectra of NaBr·2H$_2$O and NaBH$_4$·2H$_2$O show many similarities. It appears that the BH$_4^-$ ion is rather robust in alkaline aqueous solutions, as no isotopic exchange was observed in D$_2$O at a pH value of ca. 11. The unit-cell volume of NaBH$_4$·2H$_2$O increases linearly with temperature between 200 and 313 K. At 313–315 K, NaBH$_4$·2H$_2$O decomposes into NaBH$_4$ and H$_2$O, which react to release hydrogen.

Experimental Section

Crystal growth: Single crystals of NaBH$_4$ were obtained by slow evaporation of a saturated solution in isopropylamine under nitrogen flow by varying slightly the crystal growth procedure described earlier.[8] Single crystals of NaBH$_4$·2H$_2$O were obtained by recrystallization of NaBH$_4$ from an aqueous solution of NaOH. The crystals can be kept at 0 °C in a closed container. In open air they take up water from the atmosphere and dissolve.

Single-Crystal Diffraction: One crystal of NaBH$_4$·2H$_2$O was measured at 100 K by using synchrotron radiation and MAR345 image plate detector, and the other at 150 K on a Stoe IPDS diffractometer equipped with an image plate detector and Mo X-ray tube. Diffraction intensities were indexed and integrated[37,38] in an orthorhombic cell. A single crystal of NaBH$_4$ was measured at 200 K by using a KM-6 goniometer, Onyx CCD detector and synchrotron radiation. The data were corrected for Lorentz factor and polarization effects. Absorption correction was not applied. The structures were solved by direct methods,[39] hydrogen atoms were located from difference Fourier maps. A full least-squares refinement on F^2 was performed on positional and thermal parameters for all atoms (anisotropic for Na, O and B) by using SHELXL-97.[39] Neutral atom scattering factors were used, yielding refined occupancies that were very close to 100%. Crystal data and details of data collection and structure refinement are given in Table 4. Further details of the crystal-structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number(s) CSD-419040, -419045, -419041 and -419039.

In Situ Powder Diffraction: Single crystals of NaBH$_4$·2H$_2$O were rapidly ground in air and sealed in a glass capillary of 0.3-mm diameter. Capillary was heated from 196 to 336 K at a 60 K per hour heating rate, and synchrotron powder diffraction data were collected in situ. The temperature was controlled with an Oxford

Table 4. Crystal data, details of data collection and structure refinement for NaBH$_4$·2H$_2$O and NaBH$_4$.

	NaBH$_4$·2H$_2$O	NaBH$_4$·2H$_2$O	NaBH$_4$
ICSD No.	419045	419041	419039
Radiation	synchrotron	X-ray, Mo-K_α	synchrotron
λ [Å]	0.71053	0.71073	0.71700
Detector	MAR345 IP	STOE IPDS	Onyx CCD
T [K]	100	150	200
Fw	73.86	73.86	37.83
Space group	$Pbca$	$Pbca$	$Fm\bar{3}m$
a [Å]	10.2870(9)	10.3390(16)	6.13080(10)
b [Å]	6.8759(7)	6.8894(12)	
c [Å]	12.0651(12)	12.1434(18)	
V [Å^3]	853.39(14)	865.0(2)	230.437(7)
Z, $D_{calcd.}$ [g cm^{-3}]	8, 1.150	8, 1.134	4, 1.090
$2\theta_{max}$ [°], completeness [%]	51.3, 99.8	56.0, 98.9	79.7, 98.2
R_{int}, R_σ	0.0264, 0.0095	0.0523, 0.0447	0.036, 0.011
Reflections collected, unique	5607, 813	4441, 1028	996, 55
Data, restraints, parameters	813, 0, 69	1028, 0, 69	55, 0, 6
Final R indices	$R_1 = 0.0212$	$R_1 = 0.0242$	$R_1 = 0.0158$
[$I > 2\sigma(I)$]	w$R_2 = 0.0397$	w$R_2 = 0.0460$	w$R_2 = 0.0176$
R indices (all data)	$R_1 = 0.0263$	$R_1 = 0.0442$	$R_1 = 0.0350$
	w$R_2 = 0.0456$	w$R_2 = 0.0489$	w$R_2 = 0.0358$
GOF on F^2	1.177	0.845	1.282
$(\Delta/\sigma)_{max}$	0.000	0.001	0.000
Largest Fourier diff. [e Å^{-3}]	0.18(4), –0.16(4)	0.14(4), –0.15(4)	0.06(2), –0.06(2)

Cryostream 700+. The data were collected by using MAR345 image plate detector at the BM01A line of SNBL (ESRF). The data were measured at a sample-to-detector distance of 150 mm by using the radiation with λ = 0.718320 Å. Data collection time: 60 s per image, readout ≈83 s per image. 64 images were collected in total. The data were integrated by using Fit2D program[40] and a calibration measurement of a NIST LaB$_6$ standard sample. Uncertainties of the integrated intensities $\sigma(I)$ were calculated at each 2θ-point applying Poisson statistics to the intensity data, considering geometry of the detector.

Spectroscopy: IR spectra were obtained at room temperature by using a Perkin–Elmer Spectrum One instrument in conjunction with a Golden Gate ATR setup with a nominal resolution of 2 cm^{-1}. Solid NaBH$_4$, NaBH$_4$·2H$_2$O and alkaline solutions of NaBH$_4$ in H$_2$O and D$_2$O were studied at room temperature. Raman spectra were measured by using ca. 70 mW 488 nm irradiation, with a Kaiser Optical Holospec Monochromator in conjunction with a liquid nitrogen-cooled CCD camera.

Acknowledgments

[1] W. Grochala, P. P. Edwards, *Chem. Rev.* **2004**, *104*, 1283–1315.
[2] a) D. K. Ross, *Vacuum* **2006**, *80*, 1084–1089; b) E. Fakioglu, Y. Yürüm, T. N. Veziroglu, *Int. J. Hydrogen Energy* **2004**, *29*, 1371–1376; c) Ł. Maj, W. Grochala, *Adv. Funct. Mater.* **2006**, *16*, 2061–2076.
[3] Y. Kojima, Y. Kawai, M. Kimbara, H. Nakanishi, S. Matsumoto, *Int. J. Hydrogen Energy* **2004**, *29*, 1213–1217.
[4] Z. P. Li, B. H. Liu, K. Arai, N. Morigazaki, S. Suda, *J. Alloys Compd.* **2003**, *356–357*, 469–474.
[5] a) S. C. Amendola, S. L. Sharp-Goldman, M. S. Janjua, M. T. Kelly, P. J. Petillo, M. Binder, *J. Power Sources* **2000**, *85*, 186–

189; b) Y. Kojima, K. Suzuki, K. Fukumoto, M. Sasaki, T. Yamamoto, Y. Kawai, H. Hayashi, *Int. J. Hydrogen Energy* **2002**, *27*, 1029–1034; c) Y. Kojima, K. Suzuki, K. Fukumoto, Y. Kawai, M. Kimbara, H. Nakanishi, S. Matsumoto, *J. Power Sources* **2004**, *125*, 22–26; d) Y. Kojima, Y. Kawai, H. Nakanishi, S. Matsumoto, *J. Power Sources* **2004**, *135*, 36–41; e) V. I. Simagina, P. A. Storozhenko, O. V. Netskina, O. V. Komova, G. V. Odegova, T. Yu. Samoilenko, A. G. Gentsler, *Kinet. Catal.* **2007**, *48*, 168–175.
[6] H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra, E. K. Hyde, *J. Am. Chem. Soc.* **1953**, *75*, 215–219.
[7] a) D. Gervasio, S. Tasic, F. Zenhausern, *J. Power Sources* **2005**, *149*, 15–21; b) S. W. Jorgensen, U. S. Patent 6,866,836, **2005**.
[8] W. H. Stockmayer, D. W. Rice, C. C. Stephenson, *J. Am. Chem. Soc.* **1955**, *77*, 1980–1983.
[9] R. Custelcean, J. E. Jackson, *Chem. Rev.* **2001**, *101*, 1963–1980.
[10] a) O. A. Filippov, A. M. Filin, V. N. Tsupreva, N. V. Belkova, A. Lledos, G. Ujaque, L. M. Epstein, E. S. Shubina, *Inorg. Chem.* **2006**, *45*, 3086–3096; b) R. Custelcean, J. E. Jackson, *J. Am. Chem. Soc.* **1998**, *120*, 12935–12941; c) R. Custelcean, J. E. Jackson, *J. Am. Chem. Soc.* **2000**, *122*, 5251–5257; d) R. Custelcean, M. Vlassa, J. E. Jackson, *Angew. Chem. Int. Ed.* **2000**, *39*, 3299–3302.
[11] K. Yvon, *Z. Kristallogr.* **2003**, *218*, 108–116.
[12] J.-N. Chotard, Y. Filinchuk, B. Revaz, K. Yvon, *Angew. Chem. Int. Ed.* **2006**, *45*, 7770–7773.
[13] M. R. Hartman, J. J. Rush, T. J. Udovic, R. C. Bowman Jr, S.-J. Hwang, *J. Solid State Chem.* **2007**, *180*, 1298–1305.
[14] R. Cerný, Y. Filinchuk, H. Hagemann, K. Yvon, *Angew. Chem. Int. Ed.* **2007**, *46*, 5765–5767.
[15] Y. E. Filinchuk, K. Yvon, G. P. Meisner, F. E. Pinkerton, M. P. Balogh, *Inorg. Chem.* **2006**, *45*, 1433–1435.
[16] a) Y. Filinchuk, A. Talyzin, D. Chernyshov, V. Dmitriev, *Phys. Rev. B* **2007**, *76*, 092104; b) Y. Filinchuk, D. Chernyshov, A. Nevidomskyy, V. Dmitriev, *Angew. Chem. Int. Ed.* **2008**, *47*, 529–532.
[17] L. Johnston, N. C. Hallett, *J. Am. Chem. Soc.* **1953**, *75*, 1467–1468.
[18] S. C. Abrahams, J. Kalnajs, *J. Chem. Phys.* **1954**, *22*, 434–436.
[19] R. L. Davis, C. H. L. Kennard, *J. Solid State Chem.* **1985**, *59*, 393–396.

[20] P. Fischer, A. Züttel, *Mater. Sci. Forum* **2004**, *443–444*, 287–290.

[21] W. H. Stockmayer, C. C. Stephenson, *J. Chem. Phys.* **1953**, *21*, 1311–1312.

[22] B. Klewe, B. Pedersen, *Acta Crystallogr., Sect. B* **1974**, *30*, 2363–2371.

[23] J. Tegenfeldt, R. Tellgren, B. Pedersen, I. Olovsson, *Acta Crystallogr., Sect. B* **1979**, *35*, 1679–1682.

[24] J. Verbist, P. Piret, M. van Meerssche, *Bull. Soc. Fr. Min. Crist.* **1970**, *93*, 509–514.

[25] S. Block, A. Perloff, *Acta Crystallogr.* **1963**, *16*, 1233–1238.

[26] H. Bartl, M. Catti, G. Ferraris, *Acta Crystallogr., Sect. B* **1976**, *32*, 987–994.

[27] Y. Song, P. Yu. Zavalij, M. Suzuki, M. S. Whittingham, *Inorg. Chem.* **2002**, *41*, 5778–5786.

[28] J.-C. Buhl, T. M. Gesing, T. Höfs, C. H. Rüscher, *J. Solid State Chem.* **2006**, *179*, 3877–3882.

[29] a) F. E. Pinkerton, G. P. Meisner, M. S. Meyer, M. P. Balogh, M. D. Kundrat, *J. Phys. Chem. B* **2005**, *109*, 6–8; b) G. P. Meisner, M. L. Scullin, M. P. Balogh, F. E. Pinkerton, M. S. Meyer, *J. Phys. Chem. B* **2006**, *110*, 4186–4192; c) F. E. Pinkerton, M. S. Meyer, G. P. Meisner, M. P. Balogh, *J. Phys. Chem. B* **2006**, *110*, 7967–7974.

[30] L. M. Epstein, E. S. Shubina, E. V. Bakhmutova, L. N. Saitkulova, V. I. Bakhmutov, A. L. Chistyakov, I. V. Stankevich, *Inorg. Chem.* **1998**, *37*, 3013–3017.

[31] S. J. Grabowski, W. A. Sokalski, J. Leszczynski, *J. Phys. Chem. A* **2004**, *108*, 5823–5830.

[32] J. Rodriguez-Carvajal, *FULLPROF SUITE*, LLB Sacley & LCSIM Rennes, France, **2003**.

[33] G. Guella, C. Zanchetta, B. Patton, A. Miotello, *J. Phys. Chem. B* **2006**, *110*, 17024–17033.

[34] P. Carbonnière, H. Hagemann, *J. Phys. Chem. A* **2006**, *110*, 9927–9933.

[35] G. Renaudin, S. Gomes, H. Hagemann, L. Keller, K. Yvon, *J. Alloys Compd.* **2004**, *375*, 98–106.

[36] R. Taylor, O. Kennard, *Acta Crystallogr., Sect. B* **1983**, *39*, 133–138.

[37] *X-RED and X-Area Software.* Stoe & Cie, Darmstadt, Germany, **1999**.

[38] Oxford Diffraction, *CrysAlis Software Package*, Oxfordshire, UK, **2006**.

[39] G. M. Sheldrick, *SHELXS97 and SHELXL97: Programs for the Solution and Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

[40] A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch, D. Häusermann, *High Pressure Res.* **1996**, *14*, 235–248.