



# Effects of partial halide anion substitution on reorientational motion in NaBH<sub>4</sub>: A nuclear magnetic resonance study



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## ABSTRACT

To study the effects of partial halide anion substitution on the reorientational motion of [BH<sub>4</sub>]<sup>−</sup> anions in NaBH<sub>4</sub>, we have measured the <sup>1</sup>H and <sup>11</sup>B NMR spectra and spin–lattice relaxation rates in the cubic solid solutions Na(BH<sub>4</sub>)<sub>0.5</sub>Cl<sub>0.5</sub> and Na(BH<sub>4</sub>)<sub>0.5</sub>I<sub>0.5</sub> over broad ranges of temperature (8–324 K) and the resonance frequency (14–90 MHz). For both solid solutions, the measured <sup>1</sup>H spin–lattice relaxation rates are governed by reorientations of BH<sub>4</sub> groups, and the experimental data can be satisfactorily described by the model with a Gaussian distribution of the activation energies. The average values of the activation energies derived from the <sup>1</sup>H spin–lattice relaxation data are 192 ± 7 meV for Na(BH<sub>4</sub>)<sub>0.5</sub>Cl<sub>0.5</sub> and 120 ± 3 meV for Na(BH<sub>4</sub>)<sub>0.5</sub>I<sub>0.5</sub>. At a given temperature, the reorientational jump rates are found to increase in the order of Na(BH<sub>4</sub>)<sub>0.5</sub>Cl<sub>0.5</sub>–NaBH<sub>4</sub>–Na(BH<sub>4</sub>)<sub>0.5</sub>I<sub>0.5</sub>, in agreement with the quasielastic neutron scattering (QENS) results. This trend correlates with the lattice expansion reflecting the increase in the size of the corresponding anions (in the order of Cl<sup>−</sup>–[BH<sub>4</sub>]<sup>−</sup>–I<sup>−</sup>).

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## 1. Introduction

Light alkali-metal borohydrides, such as LiBH<sub>4</sub> and NaBH<sub>4</sub>, are considered as promising materials for hydrogen storage [1]. These compounds form ionic crystals consisting of metal cations and tetrahedral [BH<sub>4</sub>]<sup>−</sup> anions. Some of borohydrides and borohydride-based systems were also found to be superionic conductors [2,3]. The dynamical properties of borohydrides have received recent attention [4–6], since apart from translational diffusion of cations, they show very fast reorientational motion of [BH<sub>4</sub>]<sup>−</sup> anions. In some borohydride-based compounds, the jump rate of BH<sub>4</sub> reorientations exceeds 10<sup>8</sup> s<sup>−1</sup> even below 80 K [7,8].

Anion substitution is one of the approaches used in attempts to improve the hydrogen-storage and/or ion-conducting properties of borohydrides. For example, the partial halide (Cl<sup>−</sup>, Br<sup>−</sup>, I<sup>−</sup>) anion substitution for [BH<sub>4</sub>]<sup>−</sup> in LiBH<sub>4</sub> was found to suppress the hexagonal-to-orthorhombic phase transition in this compound, stabilizing the high-*T* hexagonal phase with rather high ionic conductivity [9] and extremely fast reorientational motion [7,10,11] down to low temperatures. In the present work, we investigate the effects of partial Cl<sup>−</sup> and I<sup>−</sup> substitution on the reorientational motion of

[BH<sub>4</sub>]<sup>−</sup> anions in the sodium borohydride NaBH<sub>4</sub>. At room temperature, NaBH<sub>4</sub> is a cubic compound (space group *Fm* $\bar{3}$ *m*) with disordered orientations of BH<sub>4</sub> tetrahedra [12,13]. Partial substitution of [BH<sub>4</sub>]<sup>−</sup> anions with Cl<sup>−</sup> or I<sup>−</sup> leads to the formation of cubic solid solutions Na(BH<sub>4</sub>)<sub>1−*x*</sub>Cl<sub>*x*</sub> or Na(BH<sub>4</sub>)<sub>1−*x*</sub>I<sub>*x*</sub> [14–16]. It should be noted that the ionic radius of [BH<sub>4</sub>]<sup>−</sup> (2.03 Å) [17] is larger than the ionic radius of Cl<sup>−</sup> (1.81 Å) [18], but smaller than the ionic radius of I<sup>−</sup> (2.20 Å) [18]. Therefore, the partial Cl<sup>−</sup> and I<sup>−</sup> substitutions are found to result in solid solutions with respectively smaller and larger lattice parameters than that for NaBH<sub>4</sub> [14–16]. Since the parameters of reorientational motion strongly depend on the local environment of BH<sub>4</sub> groups [19,20], one may expect significant changes in the reorientational jump rates for compounds with mixed anions. Recent quasielastic neutron scattering (QENS) measurements in Na(BH<sub>4</sub>)<sub>0.5</sub>Cl<sub>0.5</sub> and Na(BH<sub>4</sub>)<sub>0.5</sub>I<sub>0.5</sub> [21] have shown that the rates of BH<sub>4</sub> reorientations in the chlorine- and iodine-substituted compounds are respectively lower and higher than in NaBH<sub>4</sub>. In the present work, we study the reorientational motion of BH<sub>4</sub> groups in NaBH<sub>4</sub>–NaCl and NaBH<sub>4</sub>–NaI solid solutions using <sup>1</sup>H and <sup>11</sup>B nuclear magnetic resonance (NMR) measurements over wide ranges of temperature and the resonance frequency. NMR measurements of nuclear spin–lattice relaxation rates can probe the reorientational motion over the extremely broad dynamic range of jump rates (10<sup>4</sup>–10<sup>12</sup> s<sup>−1</sup>) [6]. This is

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expected to lead to a high precision in determination of activation energies for the reorientational motion. Furthermore, on the basis of nuclear spin–lattice relaxation measurements, it is possible to detect the presence of distributions of H jump rates [22], which may be of importance for disordered solid solutions.

## 2. Experimental details

The preparation of the  $\text{NaBH}_4\text{--NaX}$  ( $\text{X} = \text{Cl}, \text{I}$ ) solid solutions was analogous to that described in Ref. [21]. These solid solutions were synthesized by milling the 1:1 molar mixtures of  $\text{NaBH}_4$  and  $\text{NaX}$  in a helium atmosphere using a Fritsch Pulverisette No. 7 ball mill [23]. In order to avoid excessive sample heating, a repetitive two-step sequence was adopted, with periods of intensive milling (200 Hz) followed by periods with the mill off. For  $\text{NaBH}_4\text{--NaCl}$ , the 24 h total processing time consisted of cycles of 5 min milling with 2 min rest. For  $\text{NaBH}_4\text{--NaI}$ , the corresponding periods were 4 h, 2 min and 2 min. After milling, both samples were annealed for 4 days at 533 K in a helium atmosphere. According to X-ray diffraction analysis, the resulting  $\text{NaBH}_4\text{--NaX}$  samples were homogeneous solid solutions with the cubic NaCl-type structure and the lattice parameters  $a = 5.886 \text{ \AA}$  and  $6.319 \text{ \AA}$  for  $\text{X} = \text{Cl}$  and  $\text{I}$ , respectively. These values of  $a$  are in good agreement with the corresponding previous results [15,16] for the 1:1  $\text{NaBH}_4\text{--NaX}$  solid solutions. For NMR experiments, the samples were flame-sealed in glass tubes under vacuum.

NMR measurements were performed on a pulse spectrometer with quadrature phase detection at the frequencies  $\omega/2\pi = 14, 28$  and  $90 \text{ MHz}$  for  $^1\text{H}$  and  $28 \text{ MHz}$  for  $^{11}\text{B}$ . The magnetic field was provided by a 2.1 T iron-core Bruker magnet. A home-built multinuclear continuous-wave NMR magnetometer working in the range  $0.32\text{--}2.15 \text{ T}$  was used for field stabilization. For rf pulse generation, we used a home-built computer-controlled pulse programmer, a PTS frequency synthesizer (Programmed Test Sources, Inc.) and a 1 kW Kalmus wideband pulse amplifier. Typical values of the  $\pi/2$  pulse length were  $2\text{--}3 \mu\text{s}$  for both  $^1\text{H}$  and  $^{11}\text{B}$ . A probehead with the sample was placed into an Oxford Instruments CF1200 continuous-flow cryostat using nitrogen or helium as a cooling agent. The sample temperature monitored by a chromel – (Au–Fe) thermocouple was stable to  $\pm 0.1 \text{ K}$ . The nuclear spin–lattice relaxation rates were measured using the saturation – recovery method. NMR spectra were recorded by Fourier transforming the solid echo signals (pulse sequence  $\pi/2_x - t - \pi/2_y$ ).

## 3. Results and discussion

The proton spin–lattice relaxation rates  $R_1^H$  measured at different resonance frequencies for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  and  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  are shown in Fig. 1 as functions of the inverse temperature. For both solid solutions, the temperature dependence of  $R_1^H$  exhibits the frequency-dependent peak that is typical of the mechanism of nuclear dipole–dipole interaction modulated by atomic motion [24]. For this mechanism, the relaxation rate maximum should occur at the temperature at which the atomic jump rate  $\tau^{-1}$  becomes nearly equal to the nuclear magnetic resonance frequency  $\omega$ , i.e. when  $\omega\tau \approx 1$  [24]. Thus, the position of the  $R_1^H(T)$  peak may

serve as an indicator of H mobility in different systems. For systems with higher H jump rates, the  $R_1^H(T)$  peak should occur at lower temperatures. As in the case of pure  $\text{NaBH}_4$  [25], the motion probed by our proton spin–lattice relaxation measurements corresponds to reorientations of the  $\text{BH}_4$  tetrahedra. For comparison with the results for the  $\text{NaBH}_4\text{--NaX}$  solid solutions, we have included in Fig. 1 the fit to the  $R_1^H(T)$  data for  $\text{NaBH}_4$  at  $\omega/2\pi = 14 \text{ MHz}$  from Ref. [25]. It can be seen that for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  the  $R_1^H(T)$  peak is observed at a higher temperature than that for  $\text{NaBH}_4$ , whereas for  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  the peak is observed at a lower temperature than that for  $\text{NaBH}_4$ . Therefore, the reorientational mobility of  $\text{BH}_4$  groups increases in the order of  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$ – $\text{NaBH}_4$ – $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$ . This is in qualitative agreement with recent quasielastic neutron scattering results for  $\text{NaBH}_4\text{--NaX}$  solid solutions [21]. Furthermore, this behavior correlates with the changes in the anion ( $\text{Cl}^-$ ,  $[\text{BH}_4]^-$ ,  $\text{I}^-$ ) radius: the reorientational mobility of  $\text{BH}_4$  groups increases with increasing anion radius (and with increasing lattice parameter).

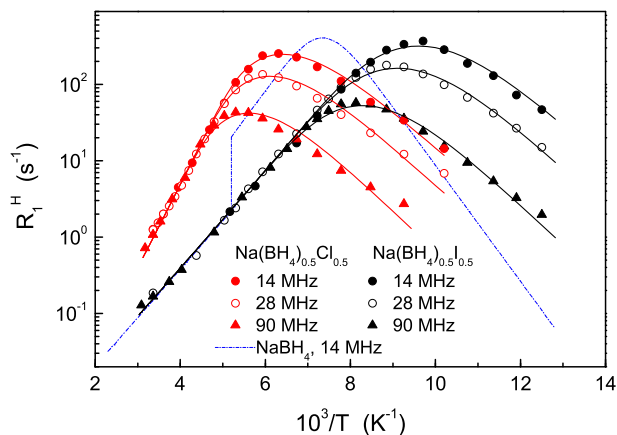
It should be noted that near  $190 \text{ K}$  pure  $\text{NaBH}_4$  undergoes the first-order transition from the high- $T$  cubic phase with orientationally-disordered  $[\text{BH}_4]^-$  anions to the low- $T$  tetragonal phase with ordered  $[\text{BH}_4]^-$  anions [26]. This phase transition is accompanied by an order-of-magnitude decrease in the reorientational jump rate [5,25]. For  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  and  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  solid solutions, such a phase transition is suppressed [27]. Similar behavior was found for  $\text{Li}(\text{BH}_4)_{1-x}\text{I}_x$  solid solutions, where the iodine substitution corresponding to  $x \geq 0.33$  suppresses the structural phase transition, stabilizing the high- $T$  hexagonal phase down to low temperatures [7]. Strictly speaking, only the dynamical properties of the high- $T$  cubic phase of  $\text{NaBH}_4$  can be directly compared to those of  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  and  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$ . For pure  $\text{NaBH}_4$ , the detailed comparison of the  $^1\text{H}$  and  $^{11}\text{B}$  spin–lattice relaxation rates with calculated second moments of NMR lines [28] suggests isotropic reorientations of  $\text{BH}_4$  groups around B site. This is consistent with QENS results [5] which were discussed in terms of H jumps between eight corners of a cube formed by hydrogen positions of half occupancy.

According to the standard theory of nuclear spin relaxation due to motionally-modulated dipole–dipole interaction [24], in the limit of slow motion ( $\omega\tau \gg 1$ ),  $R_1^H$  should be proportional to  $\omega^{-2}\tau^{-1}$ , and in the limit of fast motion ( $\omega\tau \ll 1$ ),  $R_1^H$  should be proportional to  $\tau$  being frequency-independent. If the temperature dependence of  $\tau$  follows the Arrhenius law with the activation energy  $E_a$ ,

$$\tau = \tau_0 \exp(E_a/k_B T), \quad (1)$$

the plot of  $\ln R_1^H$  versus  $T^{-1}$  is expected to be linear in the limits of both slow and fast motion with the slopes of  $-E_a/k_B$  and  $E_a/k_B$ , respectively. As can be seen from Fig. 1, the experimental  $R_1^H(T)$  data for both  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  and  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  exhibit strong deviations from this expected behavior. First, the high- $T$  slopes of the  $\log R_1^H$  versus  $T^{-1}$  plots appear to be considerably steeper than the corresponding low- $T$  slopes. Second, the frequency dependence of  $R_1^H$  at the low- $T$  slope appears to be weaker than the expected  $\omega^{-2}$  dependence. These are the typical signs indicating the presence of a distribution of H jump rates [22]. It should be noted that a certain distribution of H jump rates in disordered solid solutions can be expected, since the local environment of  $\text{BH}_4$  groups changes from one group to another. The simplest model allowing one to take such a distribution into account is based on using a Gaussian distribution of the activation energies [22]. For this model, the measured proton spin–lattice relaxation rate is expressed as

$$R_1^H = \int R_1^H(E_a) G(E_a, \bar{E}_a, \Delta E_a) dE_a, \quad (2)$$



**Fig. 1.** Proton spin–lattice relaxation rates measured at the resonance frequencies  $\omega/2\pi = 14, 28$  and  $90 \text{ MHz}$  for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  and  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  as functions of the inverse temperature. The solid lines show the simultaneous fits of the model with a Gaussian distribution of activation energies to the data. The dash-dotted line shows the fit to the  $R_1^H(T)$  data at  $14 \text{ MHz}$  for  $\text{NaBH}_4$  from Ref. [25].

where  $G(E_a, \bar{E}_a, \Delta E_a)$  is a Gaussian distribution function centered at  $\bar{E}_a$  with the dispersion  $\Delta E_a$ , and  $R_1^H(E_a)$  is determined by combining the standard expression that relates  $R_1^H$  and  $\tau$  (see, for example, Eq. (1) in Ref. [25]) and the Arrhenius law (Eq. (1)). The parameters of this model are the average activation energy  $\bar{E}_a$ , the dispersion  $\Delta E_a$ , the pre-exponential factor  $\tau_0$  and the amplitude factor determined by the strength of the fluctuating part of dipole–dipole interaction. These parameters have been varied to find the best fit of the model  $R_1^H(T)$  to the experimental data at three resonance frequencies simultaneously. The results of such simultaneous fits for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  and  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  are shown by the solid curves in Fig. 1. The motional parameters resulting from the fits are listed in Table 1. Included in Table 1 are also the motional parameters for the cubic and tetragonal phases of pure  $\text{NaBH}_4$  from Ref. [25]. The value of  $\bar{E}_a$  for  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  appears to be close to  $E_a$  for the cubic phase of  $\text{NaBH}_4$ , while the value of  $\bar{E}_a$  for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  is considerably higher. It should also be noted that the width of the activation energy distribution for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  is quite substantial.

The temperature dependences of the most probable values of H jump rates resulting from these fits for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  and  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  are shown by the solid lines in Fig. 2. The shaded areas in this figure correspond to H jump rates described by the activation energies between  $\bar{E}_a - \Delta E_a$  and  $\bar{E}_a + \Delta E_a$ , i.e., within the dispersion of the Gaussian distribution. For pure  $\text{NaBH}_4$ , no signs of a distribution of H jump rates have been found [25]. The temperature dependences of  $\tau^{-1}$  for the cubic and tetragonal phases of  $\text{NaBH}_4$  are included in Fig. 2 for comparison. The temperature ranges of the lines in this figure correspond to the actual ranges of the  $R_1^H(T)$  data. Fig. 2 clearly shows that the effects of partial anion substitution on  $\text{BH}_4$  reorientations are very strong. For example, at  $T = 100$  K the most probable values of the jump rates  $\tau^{-1}$  for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  and  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  differ by three orders of magnitude. These results support the idea [29] that the parameters of the reorientational motion are extremely sensitive to subtle details of local environment of  $\text{BH}_4$  groups.

It is interesting to compare the activation energies derived from NMR experiments with those obtained from QENS measurements. For the cubic and tetragonal phases of  $\text{NaBH}_4$ , the  $E_a$  values found from QENS measurements [5] are 123(5) meV and 139(8) meV, respectively. These values are in reasonable agreement with the corresponding NMR results (see Table 1). For the solid solutions, the  $E_a$  values found from QENS measurements [21] are 114(4) meV for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  and 121(3) meV for  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$ . While for  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  the agreement between the QENS and NMR results is excellent, for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  the  $E_a$  value derived from QENS is considerably lower than the  $\bar{E}_a$  value found from NMR (see Table 1). The most probable reason for such a discrepancy is the presence of a broad distribution of H jump rates in the chlorine-substituted compound. As noted above, the proton spin–lattice relaxation measurements over wide ranges of temperature and the resonance frequency allow one to detect the presence of a jump rate distribution; moreover, the effects of this

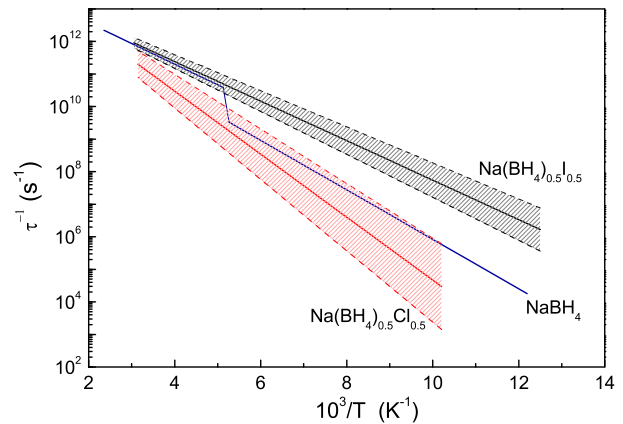


Fig. 2. Temperature dependences of the most probable H jump rates resulting from the fits for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$ ,  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$ , and  $\text{NaBH}_4$  [25]. For the solid solutions, the shaded areas correspond to H jump rates described by the activation energies between  $\bar{E}_a - \Delta E_a$  and  $\bar{E}_a + \Delta E_a$ . For pure  $\text{NaBH}_4$ , no signs of a distribution of H jump rates have been found [25].

distribution can be easily parameterized [22]. On the other hand, it is very difficult to detect the presence of a jump rate distribution from the shape of QENS spectra. If a broad distribution is present, the standard analysis of QENS spectra is expected to underestimate the changes in the quasielastic line width with temperature. Indeed, the faster part of the H jump rate distribution may be outside the frequency ‘window’ of the neutron spectrometer (contributing only to the flat background of QENS spectra), while the slower part of this distribution may be below the spectrometer resolution (contributing only to the elastic line of QENS spectra). At different temperatures, different parts of the H jump rate distribution may appear within the frequency ‘window’ of the neutron spectrometer; this tends to smear the actual temperature dependence of the most probable  $\tau^{-1}$  value.

Fig. 3 shows the temperature dependences of the width  $\Delta\nu$  (full width at half-maximum) of the  $^1\text{H}$  NMR spectra for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  and  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$ . For  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$ , the behavior of  $\Delta\nu(T)$  is typical of that for borohydrides with reorientational motion of  $\text{BH}_4$  groups [20,29]. At low temperatures,  $\Delta\nu$  is determined by dipole–dipole interactions between static nuclear spins; this is the ‘rigid lattice’ line width  $\Delta\nu_R$ . With increasing temperature,  $\Delta\nu$  starts to decrease when the H jump rate  $\tau^{-1}$  becomes nearly equal to  $2\pi\Delta\nu_R$  [24]. For typical borohydrides, such a motional narrowing occurs at the temperature, at which  $\tau^{-1}$  reaches the values of the

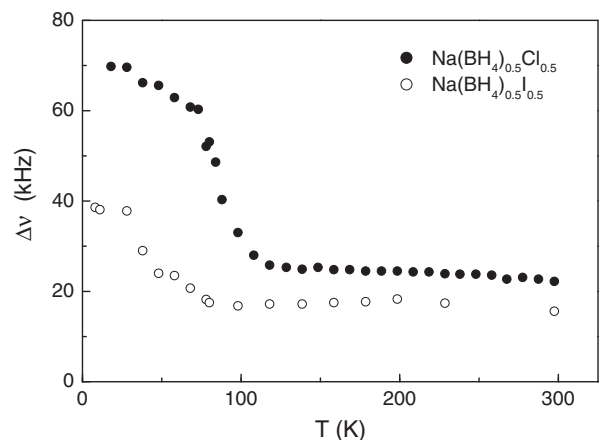


Fig. 3. Temperature dependences of the width (full width at half-maximum) of the  $^1\text{H}$  NMR spectra measured for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  and  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  at 28 MHz.

Table 1

Parameters of  $\text{BH}_4$  reorientations resulting from simultaneous fits to the proton spin–lattice relaxation data in  $\text{NaBH}_4\text{--NaX}$ . Uncertainties in the last digit of  $E_a$  are given in parentheses.

Compound	Phase	$\bar{E}_a$ or $E_a$ (meV)	$\Delta E_a$ (meV)	$\tau_0$ (s)
$\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$	Cubic	192 (7)	26 (4)	$4.5(9) \times 10^{-15}$
$\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$	Cubic	120 (3)	11 (2)	$1.5(6) \times 10^{-14}$
$\text{NaBH}_4^a$	Cubic	126 (3)	–	$1.4(2) \times 10^{-14}$
$\text{NaBH}_4^a$	Tetragonal	151 (2)	–	$3.0(1) \times 10^{-14}$

<sup>a</sup> From Ref. [25].

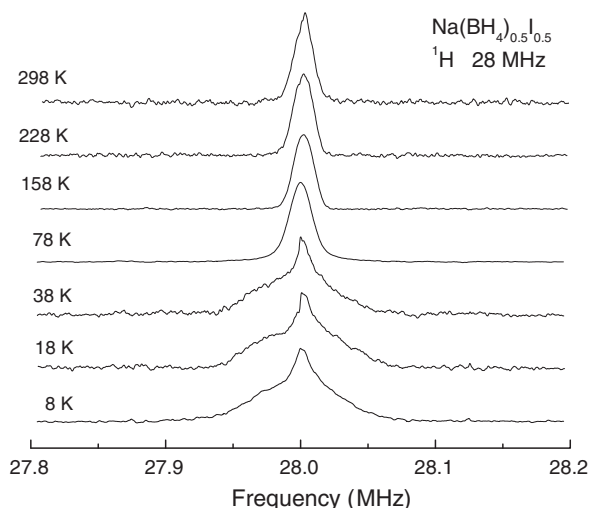


Fig. 4. Evolution of the proton NMR spectrum for  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  with temperature.

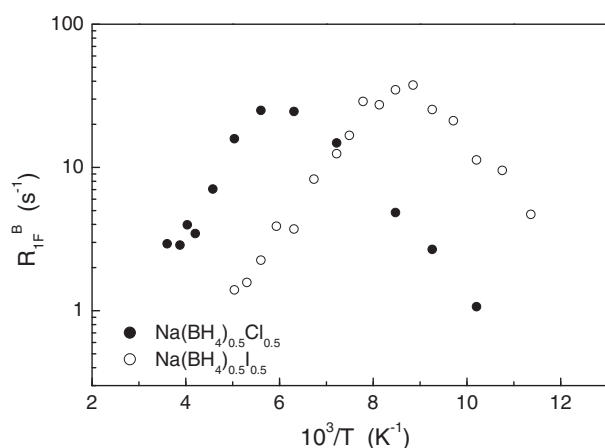


Fig. 5. Fast components of the  $^{11}\text{B}$  spin-lattice relaxation rates measured at 28 MHz for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  and  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  as functions of the inverse temperature.

order of  $10^5 \text{ s}^{-1}$ . As can be seen from Fig. 3, for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  the significant line narrowing is observed near 90 K. It should be noted that for  $\text{BH}_4$  reorientations the line narrowing is not complete, since such a localized H motion leads to only partial averaging of the dipole-dipole interactions in the limit  $\tau^{-1} \gg 2\pi\Delta\nu_R$ . Thus, at high temperatures the  $^1\text{H}$  NMR line width exhibits a plateau, the height of which is determined mostly by ‘intermolecular’ dipole-dipole interactions (between nuclear spins at different  $\text{BH}_4$  groups). For  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$ , the significant line narrowing is observed at much lower temperatures than for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  (see Fig. 3). This is consistent with faster reorientational motion in the iodine-substituted compound. Furthermore, even at  $T = 8 \text{ K}$  the value of  $\Delta\nu$  for  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  appears to be lower than the ‘rigid lattice’ limit. Such a behavior may be related to the presence of a distribution of H jump rates. Indeed, at low temperatures the  $^1\text{H}$  NMR spectra for  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  (Fig. 4) look like superpositions of two components with different widths. This means that, even at the lowest temperatures of our study, a part of protons remain mobile at the scale of  $\sim 10^5 \text{ s}^{-1}$ , and these protons are responsible for the narrower component of the low- $T$  spectra. At  $T > 70 \text{ K}$ , practically all protons are mobile at the scale of  $10^5 \text{ s}^{-1}$ , and the spectra contain only the narrower component (Fig. 4). It is interesting to note that the high-temperature plateau value of  $\Delta\nu$  for  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  is lower than for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  (Fig. 3). Since

the plateau value of  $\Delta\nu$  is determined by ‘intermolecular’ dipole-dipole interactions, this is consistent with the larger lattice parameter of the iodine-substituted compound.

Although boron atoms do not participate in the reorientational motion of  $\text{BH}_4$  groups,  $^{11}\text{B}$  NMR measurements can probe the reorientations via the fluctuating  $^{11}\text{B}$ – $^1\text{H}$  dipole-dipole and quadrupole interactions. For both  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  and  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  the recovery of the  $^{11}\text{B}$  is found to deviate from the single-exponential behavior. In the studied temperature range, the  $^{11}\text{B}$  recovery curves can be reasonably approximated by a sum of two exponential functions. The two-exponential  $^{11}\text{B}$  relaxation was also observed in some other borohydrides [8,30,31]; such a behavior may be related [24] to the non-zero electric quadrupole moment of  $^{11}\text{B}$ . The faster components of the  $^{11}\text{B}$  spin-lattice relaxation rate,  $R_{1F}^B$ , measured at 28 MHz for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  and  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  are shown in Fig. 5 as functions of the inverse temperature. The considerable scatter of the data points in this figure can be attributed to a certain instability of the two-exponential description of the recovery curves. Comparison of Figs. 5 and 1 shows that for each of the halide-substituted compounds, the  $R_{1F}^B(T)$  maximum is observed at nearly the same temperature as the corresponding  $R_1^H(T)$  maximum. Thus, the results of the  $^{11}\text{B}$  relaxation measurements support the conclusions made on the basis of the  $R_1^H(T)$  data.

#### 4. Conclusions

The analysis of the temperature and frequency dependences of the measured  $^1\text{H}$  spin-lattice relaxation rates for the cubic solid solutions  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  and  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$  has shown that a partial halide anion substitution in  $\text{NaBH}_4$  strongly affects the parameters of the reorientational motion of tetrahedral  $\text{BH}_4$  groups. The partial substitution of  $[\text{BH}_4]^-$  with the smaller  $\text{Cl}^-$  anion is found to lead to the considerable decrease in the reorientational rate  $\tau^{-1}$ , whereas the substitution with the larger  $\text{I}^-$  anion results in the increase in  $\tau^{-1}$ . It should be noted that while for pure  $\text{NaBH}_4$  no signs of a distribution of  $\tau^{-1}$  values have been detected [25], for both  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  and  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$ , our spin-lattice relaxation data indicate the presence of significant distributions of the reorientational jump rates. The behavior of the  $^1\text{H}$  spin-lattice relaxation rates in both solid solutions can be satisfactorily described by the model with a Gaussian distribution of the activation energies. The average values of the activation energies derived from the data are  $192 \pm 7 \text{ meV}$  for  $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$  and  $120 \pm 3 \text{ meV}$  for  $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$ , and the distribution widths (dispersions) are  $26 \pm 4 \text{ meV}$  and  $11 \pm 2 \text{ meV}$ , respectively. Our results show that the parameters of reorientational motion are very sensitive to details of the local environment of  $\text{BH}_4$  tetrahedra in borohydrides.

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