



Effects of partial halide anion substitution on reorientational motion in NaBH₄: A nuclear magnetic resonance study



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ABSTRACT

To study the effects of partial halide anion substitution on the reorientational motion of [BH₄][−] anions in NaBH₄, we have measured the ¹H and ¹¹B NMR spectra and spin–lattice relaxation rates in the cubic solid solutions Na(BH₄)_{0.5}Cl_{0.5} and Na(BH₄)_{0.5}I_{0.5} over broad ranges of temperature (8–324 K) and the resonance frequency (14–90 MHz). For both solid solutions, the measured ¹H spin–lattice relaxation rates are governed by reorientations of BH₄ 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 ¹H spin–lattice relaxation data are 192 ± 7 meV for Na(BH₄)_{0.5}Cl_{0.5} and 120 ± 3 meV for Na(BH₄)_{0.5}I_{0.5}. At a given temperature, the reorientational jump rates are found to increase in the order of Na(BH₄)_{0.5}Cl_{0.5}–NaBH₄–Na(BH₄)_{0.5}I_{0.5}, 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[−]–[BH₄][−]–I[−]).

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1. Introduction

Light alkali-metal borohydrides, such as LiBH₄ and NaBH₄, are considered as promising materials for hydrogen storage [1]. These compounds form ionic crystals consisting of metal cations and tetrahedral [BH₄][−] 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 [BH₄][−] anions. In some borohydride-based compounds, the jump rate of BH₄ reorientations exceeds 10⁸ s^{−1} 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[−], Br[−], I[−]) anion substitution for [BH₄][−] in LiBH₄ 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[−] and I[−] substitution on the reorientational motion of

[BH₄][−] anions in the sodium borohydride NaBH₄. At room temperature, NaBH₄ is a cubic compound (space group *Fm* $\bar{3}$ *m*) with disordered orientations of BH₄ tetrahedra [12,13]. Partial substitution of [BH₄][−] anions with Cl[−] or I[−] leads to the formation of cubic solid solutions Na(BH₄)_{1−*x*}Cl_{*x*} or Na(BH₄)_{1−*x*}I_{*x*} [14–16]. It should be noted that the ionic radius of [BH₄][−] (2.03 Å) [17] is larger than the ionic radius of Cl[−] (1.81 Å) [18], but smaller than the ionic radius of I[−] (2.20 Å) [18]. Therefore, the partial Cl[−] and I[−] substitutions are found to result in solid solutions with respectively smaller and larger lattice parameters than that for NaBH₄ [14–16]. Since the parameters of reorientational motion strongly depend on the local environment of BH₄ 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(BH₄)_{0.5}Cl_{0.5} and Na(BH₄)_{0.5}I_{0.5} [21] have shown that the rates of BH₄ reorientations in the chlorine- and iodine-substituted compounds are respectively lower and higher than in NaBH₄. In the present work, we study the reorientational motion of BH₄ groups in NaBH₄–NaCl and NaBH₄–NaI solid solutions using ¹H and ¹¹B 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 (10⁴–10¹² s^{−1}) [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 $\text{NaBH}_4\text{-NaX}$ ($X = \text{Cl}, \text{I}$) solid solutions was analogous to that described in Ref. [21]. These solid solutions were synthesized by milling the 1:1 molar mixtures of NaBH_4 and 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 \AA for $X = \text{Cl}$ and 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 MHz for ^1H and 28 MHz for ^{11}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 ^1H and ^{11}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 τ^{-1} becomes nearly equal to the nuclear magnetic resonance frequency ω , 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 NaBH_4 [25], the motion probed by our proton spin–lattice relaxation measurements corresponds to reorientations of the 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 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 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 NaBH_4 . Therefore, the reorientational mobility of 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 (Cl^- , $[\text{BH}_4]^-$, I^-) radius: the reorientational mobility of BH_4 groups increases with increasing anion radius (and with increasing lattice parameter).

It should be noted that near 190 K pure 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 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 NaBH_4 , the detailed comparison of the ^1H and ^{11}B spin–lattice relaxation rates with calculated second moments of NMR lines [28] suggests isotropic reorientations of 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 τ being frequency-independent. If the temperature dependence of τ 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 ω^{-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 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

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

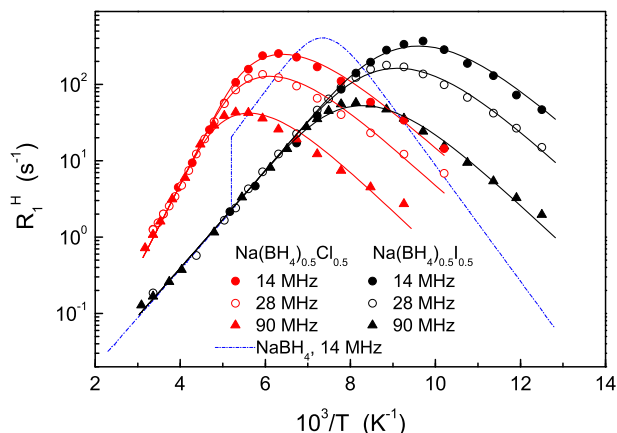


Fig. 1. Proton spin–lattice relaxation rates measured at the resonance frequencies $\omega/2\pi = 14, 28$ and 90 MHz for $\text{Na}(\text{BH}_4)_{0.5}\text{Cl}_{0.5}$ and $\text{Na}(\text{BH}_4)_{0.5}\text{I}_{0.5}$ as functions of the inverse temperature. The solid lines show the simultaneous fits of 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 MHz for NaBH_4 from Ref. [25].

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