



Nuclear magnetic resonance studies of atomic motion in borohydrides

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ABSTRACT

Two basic types of thermally activated atomic jump motion are known to exist in solid borohydrides: the fast reorientations of BH_4 groups and the slower translational diffusion of cations and anions. This paper reviews recent progress in nuclear magnetic resonance (NMR) studies of both these jump processes. It is shown that, for some borohydrides, NMR measurements of the nuclear spin-lattice relaxation can trace the changes in the reorientational jump rates over the range of eight orders of magnitude (10^4 to 10^{12} s^{-1}). Such a wide dynamic range leads to the high precision of the activation energies for BH_4 reorientations, as derived from the nuclear spin-lattice relaxation measurements.

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1. Introduction

The alkali and alkaline-earth borohydrides $\text{M}(\text{BH}_4)_n$ (where $n = 1$ or 2 for alkali or alkaline-earth M elements, respectively) are considered as promising materials for hydrogen storage [1,2]. These compounds form ionic crystals consisting of metal cations and tetrahedral $[\text{BH}_4]^-$ anions. While the volumetric and gravimetric hydrogen densities in these compounds are high, the stability of the borohydrides with respect to thermal decomposition and the slow sorption kinetics remain the major drawbacks for their practical use. A number of methods (such as mechanical alloying, nanoconfinement, and using catalytic additives) have been suggested [3–6] to destabilize the complex hydrides and make the kinetics of dehydrogenation and rehydrogenation more favorable. Elucidation of hydrogen dynamics in borohydrides may give a key to improving their hydrogen-storage properties. This work presents a brief review of the dynamical properties of alkali and alkaline-earth borohydrides. The emphasis is put on recent experimental results obtained using nuclear magnetic resonance (NMR) measurements. NMR appears to be especially effective for studies of atomic motion in borohydrides. In contrast to transition-metal hydrides, the measured nuclear spin-lattice relaxation rates in borohydrides do not contain any significant contributions not related to atomic motion (such as the conduction-electron contribution in metallic systems). This allows us to trace the atomic jump rates in borohydrides over the range of 8 orders of magnitude (10^4 to 10^{12} s^{-1}). Another important feature of NMR studies is that different nuclei (^1H , ^{11}B , ^7Li , ^{23}Na , ...) can serve as local probes of atomic motion, comple-

menting each other. The motional parameters derived from NMR measurements will be compared to those obtained by quasielastic neutron scattering (QENS).

2. The relation between nuclear spin-lattice relaxation rates and parameters of atomic jump motion

The measured nuclear spin-lattice relaxation rate R_1 characterizes the recovery of nuclear spin magnetization after deviations of a nuclear spin system from the equilibrium state. For most of the studied borohydrides, the dominant relaxation mechanism is due to the internuclear dipole–dipole interaction modulated by atomic jump motion. The motional contribution to $R_1(T)$ shows a maximum at the temperature at which the atomic jump rate τ^{-1} becomes nearly equal to the nuclear magnetic resonance frequency ω , i.e. when $\omega\tau \approx 1$. Typical values of ω are of the order of 10^8 to 10^9 s^{-1} . In the limit of slow motion ($\omega\tau \gg 1$), R_1 is proportional to $\omega^{-2}\tau^{-1}$, and in the limit of fast motion ($\omega\tau \ll 1$), R_1 is proportional to τ being frequency-independent. If the temperature dependence of τ follows the usual Arrhenius law,

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right), \quad (1)$$

the plot of $\ln R_1$ vs. T^{-1} should 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. Thus, the activation energy E_a for the atomic motion can be obtained directly from these slopes. Two basic types of atomic jump motion are known to exist in solid $\text{M}(\text{BH}_4)_n$ compounds: the reorientational motion of BH_4 groups and the translational diffusion of cations (M) or anions (BH_4). For the reorientational motion, the relation between R_1 and τ is available in the form of analytic expressions [7]. For the long-range diffusion, the corresponding analysis

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is usually based on the Bloembergen–Purcell–Pound (BPP) model [8]. It is known [9] that, in certain cases of the long-range diffusion, the BPP model may fail to yield absolute values of τ better than a factor of 2; however, the activation energies resulting from the BPP-type analysis are quite reliable.

3. Reorientational motion of BH_4 groups

At low temperatures (80–400 K), the measured nuclear spin-lattice relaxation rates in borohydrides are usually governed by the reorientational motion of BH_4 groups. In alkali borohydrides this motion is fast enough to give rise to the $R_1(T)$ maxima in the range 120–190 K. The results of the first ^1H and ^{11}B relaxation rate measurements for LiBH_4 , NaBH_4 and KBH_4 have been reported by Tsang and Farrar [10]. These results are consistent with the Arrhenius behavior of the jump rate $\tau^{-1}(T)$ for the reorientational motion, typical values of the activation energy being in the range of 110–210 meV. Subsequent NMR studies of the reorientational motion in alkali borohydrides [11–16] have extended the temperature and frequency ranges of the measurements and addressed the deuterium-substituted borohydrides and borohydrides of Rb and Cs. Recent studies [14,16,17] have emphasized the importance of probing the frequency dependence of R_1 , in particular, in cases when a certain distribution of the jump rates τ^{-1} can be expected.

In the following, we shall discuss the results of NMR studies of the reorientational motion in borohydrides in the order of increasing complexity of the R_1 data. Fig. 1 shows the ^1H spin-lattice relaxation rates measured at three resonance frequencies $\omega/2\pi$ as functions of the inverse temperature for RbBH_4 . These results provide a textbook example of the behavior of R_1 governed by a single thermally activated jump process. Our analysis is based on the standard expression [7] for the relaxation rate due to the dipole–dipole interaction modulated by atomic motion,

$$R_1^H = A_{HB} \left[\frac{\tau}{1 + (\omega_H - \omega_B)^2 \tau^2} + \frac{3\tau}{1 + \omega_H^2 \tau^2} + \frac{6\tau}{1 + (\omega_H + \omega_B)^2 \tau^2} \right] + A_{HH} \left[\frac{\tau}{4 + \omega_H^2 \tau^2} + \frac{\tau}{1 + \omega_H^2 \tau^2} \right], \quad (2)$$

where ω_H and ω_B are the resonance frequencies of ^1H and ^{11}B , respectively, and the amplitude parameters A_{HB} and A_{HH} are proportional to the fluctuating parts of the dipolar second moment due to ^1H – ^{11}B and ^1H – ^1H interactions (the dipolar ^1H – $^{85,87}\text{Rb}$ con-

tributions to R_1^H in this system can be neglected). The solid lines in Fig. 1 show the simultaneous fit of Eqs. (2) and (1) to the data at three resonance frequencies. The motional parameters resulting from the fit are $\tau_0 = (9 \pm 2) \times 10^{-15}$ s and $E_a = 138 \pm 4$ meV. Note that in the studied temperature range of 78–400 K, RbBH_4 does not exhibit any phase transitions, and the $R_1^H(T)$ data correspond to its cubic phase (space group $Fm\bar{3}m$). Similar behavior of $R_1^H(T)$ at different resonance frequencies have been found for the isomorphous cubic phase of KBH_4 [16] in the T range of 82–424 K. Although KBH_4 is known to exhibit the phase transition to the ordered tetragonal phase [18], the transition temperature ($T_0 \approx 70$ K) is outside our experimental T range. For NaBH_4 , the transition temperature is considerably higher ($T_0 \approx 190$ K), so that the $R_1^H(T)$ maximum is observed in the ordered tetragonal phase. The first-order transition from the low- T tetragonal to the high- T cubic phase of NaBH_4 is accompanied by the sharp change in R_1^H (corresponding to nearly an order of magnitude increase in the jump rate τ^{-1}) and by the decrease in the activation energy. The temperature dependences of the jump rates resulting from our fits for NaBH_4 [16], KBH_4 [16], and RbBH_4 are shown in Fig. 2 in the form of Arrhenius plots. The temperature ranges of the lines in this figure correspond to the actual ranges of our proton $R_1(T)$ data. As can be seen from Fig. 2, the proton spin-lattice relaxation measurements allow us to trace the changes in the jump rate of reorientations over the range of eight orders of magnitude. This unique feature of the spin-lattice relaxation measurements leads to high precision of the E_a values derived from the $R_1(T)$ data. For comparison, the ranges of τ^{-1} values traced by recent QENS experiments [19–22] for NaBH_4 and KBH_4 do not exceed two [19,20,22] or three [21] orders of magnitude. The main mechanism of the ^{11}B spin-lattice relaxation in alkali borohydrides is the ^{11}B – ^1H dipole–dipole interaction modulated by reorientational motion of BH_4 groups, and the results of the ^{11}B relaxation measurements at different resonance frequencies [14,16] yield practically the same motional parameters as the ^1H relaxation measurements. The activation energies for BH_4 reorientations obtained from NMR and QENS measurements in $\text{M}(\text{BH}_4)_n$ are presented in Table 1. As can be seen from this table, for NaBH_4 , KBH_4 , and RbBH_4 , the values of E_a derived by different groups are in reasonable agreement. The agreement is especially good in the case of the low- T phase of NaBH_4 . It should be noted, however, that on the basis of the $R_1(T)$ data it is difficult to obtain unambiguous information on the type of BH_4 reorientations. In fact, the reorientational motion of a regular BH_4 tetrahedron can be represented by rotations around three 2-fold axes and four 3-fold axes; only some

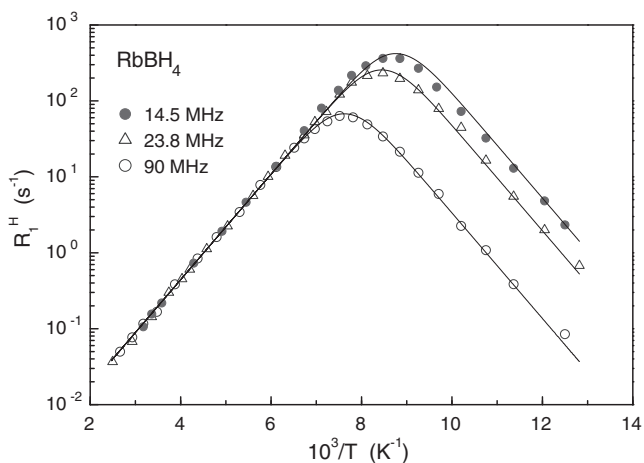


Fig. 1. Proton spin-lattice relaxation rates measured at 14.5, 23.8 and 90 MHz for RbBH_4 as functions of the inverse temperature. The solid lines show the simultaneous fit of the standard theory (Eqs. (2) and (1)) to the data.

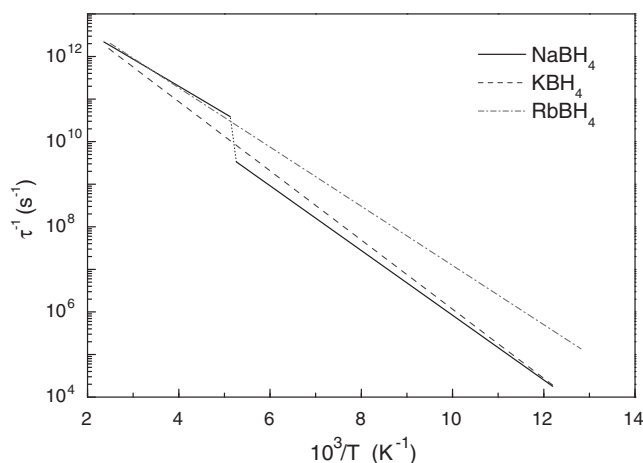


Fig. 2. Temperature dependences of the jump rates of BH_4 group reorientations, as derived from the fits to the proton spin-lattice relaxation data for NaBH_4 , KBH_4 and RbBH_4 .

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