Nuclear magnetic resonance studies of atomic motion in borohydride-based materials: Fast anion reorientations and cation diffusion

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ABSTRACT

Two basic types of thermally activated atomic jump motion are known to exist in solid borohydrides and the related systems: the reorientations of complex anions ($[BH_4]^-$, $[B_{12}H_{12}]^{2-}$) and the translational diffusion of metal cations or complex anions. This paper reviews recent progress in nuclear magnetic resonance (NMR) studies of these jump processes in complex hydrides, such as solid solutions of halide anions in borohydrides, bimetallic borohydrides and borohydride–chlorides, borohydride–amides, and $B_{12}H_{12}$-based compounds. The emphasis is put on the systems showing fast-ion conductivity. For these systems, we discuss a possible relation between the reorientational motion of complex anions and the translational motion of metal cations.

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1. Introduction

Metal tetrahydroborates (borohydrides) have received recent attention as promising materials for hydrogen storage [1]. These compounds form ionic crystals consisting of metal cations and tetrahedral $[BH_4]^-$ anions. While the volumetric and gravimetric hydrogen densities in these compounds are generally quite high, practical use of the alkali and alkaline-earth borohydrides is hindered by their high stability with respect to thermal decomposition and the slow hydrogen sorption kinetics. In attempts to destabilize borohydrides and make the kinetics of dehydrogenation and rehydrogenation more favorable, a large number of borohydride-based systems with mixed cations and/or anions have been synthesized recently. It is interesting to note that some of borohydrides and borohydride-based systems were also shown to exhibit fast ionic conduction. For example, in lithium borohydride LiBH$_4$ the first-order phase transition from the low-T orthorhombic phase to the high-T hexagonal phase near 380 K is accompanied by the three-orders-of-magnitude increase in Li-ion conductivity, so that the conductivity exceeds 10^{-3} S/cm above 390 K [2].

Alkali-metal dodecahydro-*closo*-dodecaborates $A_2B_{12}H_{12}$ are ionically-bonded salts consisting of alkali-metal A^+ cations and icosahedral $[B_{12}H_{12}]^{2-}$ anions. These salts have attracted recent attention, since they appear to be energetically favorable intermediate compounds in the decomposition of the corresponding borohydrides ABH$_4$. The formation of these highly stable compounds is believed to be partly responsible for the poor hydrogen cycling performance of the borohydrides. The relatively large anion/cation size ratios and the rotational mobility of the anions lead to interesting physical properties of $A_2B_{12}H_{12}$, including high-temperature order–disorder phase transitions [3,4].

Understanding the hydrogen dynamics and cation mobility in borohydrides and the related systems may give a key to improving their hydrogen-storage and ion-conducting properties. Nuclear magnetic resonance (NMR) has proved to be an effective technique for studies of atomic motion in solids at the microscopic level. This technique was widely applied to investigate both the reorientational motion of anions and the diffusive motion of cations in alkali-metal borohydrides [2,5–12] and alkaline-earth borohydrides [13–16]. However, systematic studies of atomic motion in more complex systems, such as mixed BH$_4$-based and B$_{12}$H$_{12}$-based compounds have just begun. This work presents a brief review of the dynamical properties of mixed BH$_4$-based compounds, B$_{12}$H$_{12}$-based compounds and the related systems. The emphasis is put on the systems showing extremely fast reorientational motion down to low temperatures and fast cation diffusion. For these systems, we will discuss recent experimental results obtained using NMR measurements. The motional parameters derived from NMR measurements will be compared to those obtained by quasielastic neutron scattering (QENS).

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## 2. NMR approach to studies 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 borohydride-based systems, the dominant relaxation mechanism of ^{1}H nuclei is due to the internuclear dipole–dipole interaction modulated by atomic jump motion. For nuclei with the spin $I > 1/2$ (such as ^{11}B, ^{7}Li, ^{23}Na), the electric quadrupole interaction modulated by atomic motion may also be important. The motional contribution to $R_1(T)$ exhibits 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 $\omega\tau \approx 1$ [17]. Typical values of ω are of the order of 10^8–10^9 s^{-1}. The amplitude of the $R_1(T)$ peak is determined by the strength of dipole–dipole and/or quadrupole interactions that are caused to fluctuate due to atomic motion; in addition, this amplitude is inversely proportional to ω. 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, $\tau = \tau_0 \exp(E_a/k_BT)$, 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. For simple types of reorientational motion, the relation between R_1 and τ is available in the form of analytic expressions [17]. For the long-range diffusion, the corresponding analysis is usually based on the Bloembergen–Purcell–Pound (BPP) model [18]. In favorable cases, spin–lattice relaxation measurements allow one to trace the changes of τ^{-1} over the dynamic range of 8 orders of magnitude (10^4–10^{12} s^{-1}) [8]. If considerable distributions of τ^{-1} values are present, the observed low-T slope of the $R_1(T)$ peak becomes less steep than the high-T one, and the frequency dependence of R_1 at the low-T slope becomes weaker than ω^{-2} [19]. Thus, measurements of R_1 over wide ranges of temperature and the resonance frequency give an opportunity to reveal the presence of jump rate distributions.

The NMR line width is also sensitive to atomic jump motion. At low temperatures, the ^{1}H NMR line width $\Delta\omega_R$ is usually determined by static dipole–dipole interactions between nuclear spins. With increasing temperature, this 'rigid lattice' line width starts to decrease when the H jump rate τ^{-1} becomes nearly equal to $\Delta\omega_R$ [17]. For typical hydrides, this narrowing occurs at the temperature, at which τ^{-1} reaches about 10^5 s^{-1}. Although NMR line width measurements can trace changes in τ^{-1} over a rather narrow dynamic range (usually not exceeding two orders of magnitude), they may help to distinguish between the translational diffusion and localized atomic motion. For the translational (long-range) diffusion, the internuclear dipole–dipole interaction is completely averaged out when $\tau^{-1} \gg \Delta\omega_R$, so that at high temperatures the line width becomes very small (being determined by the magnetic field inhomogeneity). Localized atomic motion (such as reorientations of complex anions) leads to only partial averaging of the dipole–dipole interactions in the limit $\tau^{-1} \gg \Delta\omega_R$, so that at high temperatures the ^{1}H NMR line width exhibits a plateau with the value corresponding to a substantial fraction of $\Delta\omega_R$. Similar qualitative features of NMR line width behavior are also expected for other nuclei participating in the motion.

3. Mixed BH$_4$-based compounds

First, we shall discuss the dynamical properties of LiBH$_4$–LiI solid solutions. It has been found [20] that the structure of the high-T (hexagonal) phase of LiBH$_4$ can be stabilized down to low temperatures by a partial halide ion substitution of [BH$_4$]$^-$ anions.

Since the high-T phase of LiBH$_4$ exhibits high Li-ion conductivity (see Section 1), this may give a chance to retain rather high conductivity down to room temperature. The temperature dependence of the ^{1}H spin–lattice relaxation rate R_1^H in solid solutions Li(BH$_4$)$_{1-y}$I$_y$ (y = 0.33, 0.5, 0.67) exhibits two frequency-dependent peaks [21]. As an example of the data, Fig. 1 shows the behavior of R_1^H for Li(BH$_4$)$_{0.67}$I$_{0.33}$ at three resonance frequencies $\omega/2\pi$. The low-T peak of R_1^H attributed to reorientational motion of BH$_4$ groups indicates that in solid solutions Li(BH$_4$)$_{1-y}$I$_y$ this motion remains extremely fast down to low temperatures. In fact, the position of the $R_1^H(T)$ maximum for y = 0.33 shows that the H jump rate τ^{-1} reaches $\sim 10^8$ s^{-1} already at 55 K. With increasing iodine content y, the relaxation rate maximum shifts to lower temperatures [21]; this means that the reorientational motion becomes even faster. These observations are consistent with the results of QENS measurements for Li(BH$_4$)$_{1-y}$I$_y$ (y = 0.2, 0.33, 0.5) at $T \geqslant 200$ K [22]. Note that such fast BH$_4$ reorientations down to low temperatures have not been observed for regular alkali- and alkaline-earth borohydrides [15,23]. It is reasonable to assume that the fast low-T reorientational motion in Li(BH$_4$)$_{1-y}$I$_y$ is related to stabilization of the hexagonal phase retaining the BH$_4$ environment favorable for easy uniaxial rotation. The closer inspection of the low-temperature R_1^H data as functions of the inverse temperature (see the inset of Fig. 1) shows that the data should be described in terms of at least two jump processes with different motional parameters. Moreover, the weak frequency dependence of R_1^H at the low-T slope indicates the presence of a broad distribution of H jump rates. Such a distribution may be expected for disordered solid solutions where the local environment of a BH$_4$ group changes from one group to another. The solid lines in the inset of Fig. 1 show the *simultaneous* fit of the model with a two-Gaussian distribution of the activation energies to the data at three resonance frequencies. The corresponding average E_a values for the two jump processes are included in Table 1 that summarizes experimental data for activation energies of reorientational motion in the mixed BH$_4$-based and B$_{12}$H$_{12}$-based compounds. It can be seen that, for both jump processes in Li(BH$_4$)$_{1-y}$I$_y$, the average E_a values decrease with increasing iodine content. The nature of the two jump processes was clarified by recent QENS measurements for Li(BH$_4$)$_{0.5}$I$_{0.5}$ [24]. It has been found that the faster jump process corresponds to BH$_4$ reorientations around the c-directed 3-fold symmetry axis, and the slower process is associated with the jump
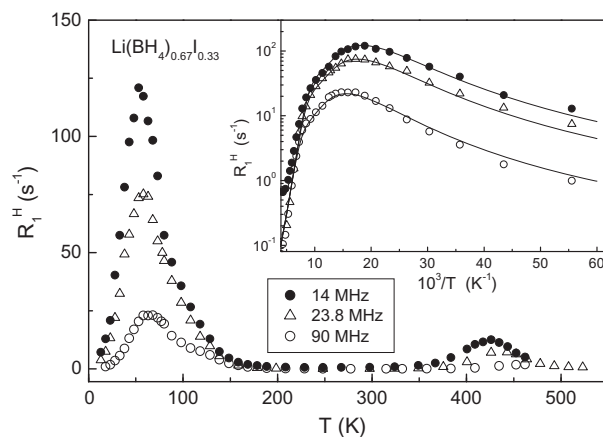
Fig. 1. Temperature dependences of the ^{1}H spin–lattice relaxation rates measured at the resonance frequencies $\omega/2\pi$ = 14, 23.8 and 90 MHz for Li(BH$_4$)$_{0.67}$I$_{0.33}$. Inset: the ^{1}H spin–lattice relaxation rates for Li(BH$_4$)$_{0.67}$I$_{0.33}$ in the region of the low-T peak as functions of the inverse temperature. The solid lines show the simultaneous fit of the model with a two-Gaussian distribution of activation energies to the data.