Experimental report

11/05/2017

Proposal:	**7-03-150**	**Council:**	4/2016

Title: Hydrogen dynamics in novel solid-state Li conductors

Research area: Materials

This proposal is a new proposal

Main proposer: **Arndt REMHOF**

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Samples:
$Li_4BN_3H_{10}$
Li_2BNH_6

Instrument	Requested days	Allocated days	From	To
IN16B	6	4	21/11/2016	25/11/2016

Abstract:

We propose to use high resolution neutron spectroscopy to investigate the hydrogen dynamics in lithium amide-borohydrides, which are novel superionic Li^+ conductors for all solid-state Li-ion batteries. Recently, unprecedented Li superionic conductivity near room temperature was discovered in lithium amide-borohydrides ($Li_{1+x}(BH_4)(NH_2)_x$). Representative examples including $Li_3BH_4(NH_2)_2$ (cubic, I213) and $Li_2(BH_4)(NH_2)$ (trigonal, R3) respectively, showing Li^+ conductivity of 6 and 8 mS cm^{-1} at 40 °C, comparable to the existing liquid electrolyte.

Based on DFT and molecular dynamic calculations, we attribute the high conductivity to the presence of a network of vacant tetrahedral sites, acting as conduction channels. The diffusion of Li^+ in the conduction channel is thereby a collective motion, supported by the localized motion of the anions, especially of the $[NH_2]^-$ ions. We therefore propose to investigate the hydrogen dynamics in the anions of lithium amide-borohydrides by IFWS and quasielastic scans. The goal is to understand the role of the $[BH_4]^-$ and $[NH_2]^-$ anions in the conduction mechanism.

Hydrogen dynamics in novel solid-state Li conductors

Proposal No.: 7-03-150

Experimental team: Léo Duchêne, Tatsiana Burankova, Arndt Remhof
Instrument: IN16b (21.11.2016–25.11.2016)
Local contact: Bernhard Frick

The samples used in the present study are lithium amide-borohydrides with a general formula $Li_{1+x}[BH_4][NH_2]_x$. To separate the quasielastic contributions of the two species, BH_4 and NH_2, two samples were synthesized for each of the studied compositions with x = 2 and x = 3. In the first case, the samples were protiated, whereas the second pair of the samples contained deuterated NH_2 groups. Assuming that the studied compounds scatter mainly incoherently and that the BH_4 and NH_2 motions are not correlated, the dynamic structure factor of the protiated and deuterated sample can be expresses in the following way:

$$S_{\mathrm{prot}}(Q,E) = \frac{4\sigma_{\mathrm{H}} S_{\mathrm{BH4}}(Q,E) + 2x\sigma_{\mathrm{H}} S_{\mathrm{NH2}}(Q,E)}{4\sigma_{\mathrm{H}} + 2x\sigma_{\mathrm{H}}} \tag{1a}$$

$$S_{\mathrm{deut}}(Q,E) = \frac{4\sigma_{\mathrm{H}} S_{\mathrm{BH4}}(Q,E) + 2x\sigma_{\mathrm{D}} S_{\mathrm{NH2}}(Q,E)}{4\sigma_{\mathrm{H}} + 2x\sigma_{\mathrm{D}}} \tag{1b}$$

where $S_{BH4}(Q,E)$ and $S_{NH2}(Q,E)$ stand for the BH_4 and NH_2 contributions, σ_H and σ_D are the neutron incoherent scattering cross sections of hydrogen and deuterium, respectively. Eq 1 is basically a system of two linear equations, which can be solved in the whole scanned temperature range (Figure 1). Apparently, all main characteristic step-like features of the EFWS in the mixed compounds originate from the BH_4 units. The decrease of the NH_2 elastic intensity is mostly due to vibrational and librational motions.

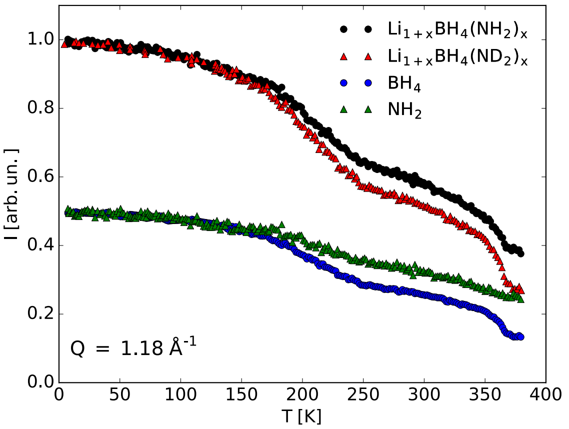

Figure 1. EFWS of the protiated and partially deuterated samples (x = 2). The BH_4 and NH_2 contributions are the solutions of eq 1 and scaled to 0.5 at low temperature for clarity

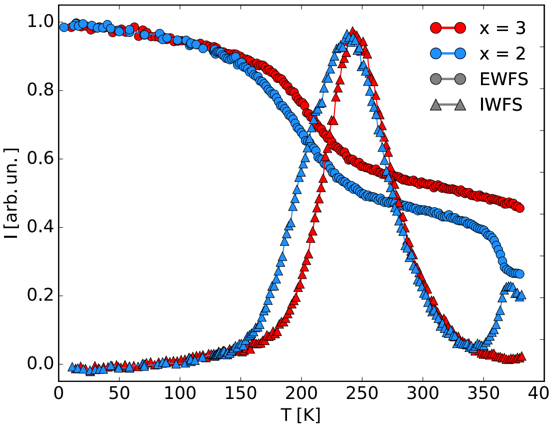

Figure 2. EFWS (circles) and IFWS (triangles) of the partially deuterated samples $Li_{1+x}[BH_4][ND_2]_x$ with x = 3 (red) and x = 2 (blue) averaged over the studied Q-range

The EFWS and IFWS of the samples with x = 2 and x = 3 are similar in the temperature range of 10–340 K (Figure 2). These dynamics correspond to the rotational motion of the BH_4 groups around C3-axes with different jump rates, $1/\tau$ (around one selected C3-axis) and $1/\tau_0$ (around the other three axes)

$$\begin{aligned} S_{\mathrm{rot\_120}}(Q,E) =& \frac{1}{4}\left(1 + 3j_0\left(Qr_0\sqrt{3}\right)\right)\delta(E) + \\ &+ \frac{1}{4}\left(1 - j_0\left(Qr_0\sqrt{3}\right)\right)\mathcal{L}(\Gamma_1,E) + \frac{1}{2}\left(1 - j_0\left(Qr_0\sqrt{3}\right)\right)\mathcal{L}(\Gamma_2,E) \end{aligned} \tag{2a}$$

$$\Gamma_1 = \frac{4\hbar}{\tau_0};\;\; \Gamma_2 = \frac{\hbar}{2}\left(\frac{3}{\tau} + \frac{5}{\tau_0}\right) \tag{2b}$$

where r_0 is related to the B-H bond length $r_{B\text{-}H}$ as $r_0 = \frac{2\sqrt{2}}{3} r_{B-H}$. From the fits of the QENS spectra measured at 220, 250 and 300 K we estimated the residence times. The slowest component (τ_0) appeared to be resolved only at 300 K and is of the order of 20 ns for all the samples. The faster residence times (τ) corresponding to the uniaxial rotation are summarized in Table 1.

Table 1. Residence time τ (in ps) of the uniaxial C_3-rotation as obtained from the fits of the QENS spectra.

$Li_{1+x}[BH_4][Y]_x$	Y	T = 220 K	T = 250 K	T = 300 K
x = 2.0	NH_2	1120(50)	460(20)	55(4)
x = 2.0	ND_2	1160(50)	370(12)	54(2)
x = 3.0	NH_2	1230(50)	516(30)	77(4)
x = 3.0	ND_2	1620(50)	501(15)	73(2)

Table 2. Parameters of the best fit IFWS curves obtained for the uniaxial C_3-rotation model with a Gaussian distribution of activation energies

$Li_{1+x}[BH_4][Y]_x$	Y	$\tilde{\tau}$, fs	E_A, kJ/mol	ΔE_A, kJ/mol
x = 2.0	NH_2	1.22(0.12)	25.2(0.2)	2.64(0.04)
x = 2.0	ND_2	2.57(0.18)	23.3(0.2)	2.59(0.04)
x = 3.0	NH_2	2.87(0.19)	24.3(0.2)	1.30(0.04)
x = 3.0	ND_2	1.62(0.11)	25.5(0.2)	1.66(0.05)

The shape of the IFWS curves can be analyzed in terms of the same model assuming a Gaussian distribution of activation energies (Figure 3). The sample with the BH_4:NH_2 ratio of 1:2 exhibits a broader range of the activation energies than the 1:3 composition (Table 2).

The second characteristic feature of the IFWS/EFWS (Figure 2) can be seen only in the highly conducting sample with x = 2 above ~355 K, which can be related to a pronounced endothermic event at 313 K on heating. The possible origin this feature in IFWS/EFWS could be a diffusion-like motion for a certain fraction of the particles in the system. The Chudley-Elliott model yields the jump vector of 4.4±0.6 Å and the residence time of 0.62±0.06 ns (Figure 4).

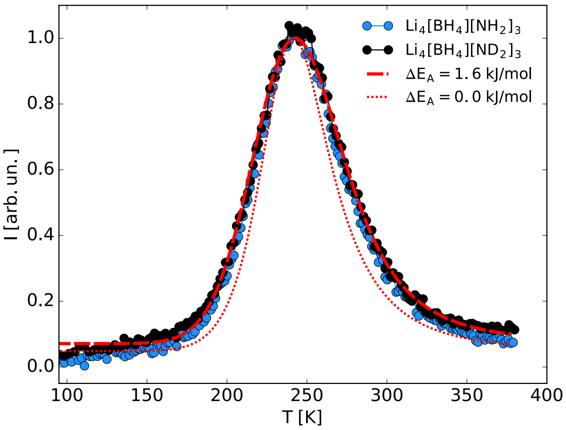

Figure 3. IFWS of the protiated (blue circles) and partially deuterated (black circles) samples with the BH_4:NH_2 ratio of 1:3 at Q = 1.18 Å^{-1}. The red lines are the model IFWS curves taking into account the uniaxial C3-reorientations with a single activation energy (dotted line) and a Gaussian distribution of energies (dashed line)

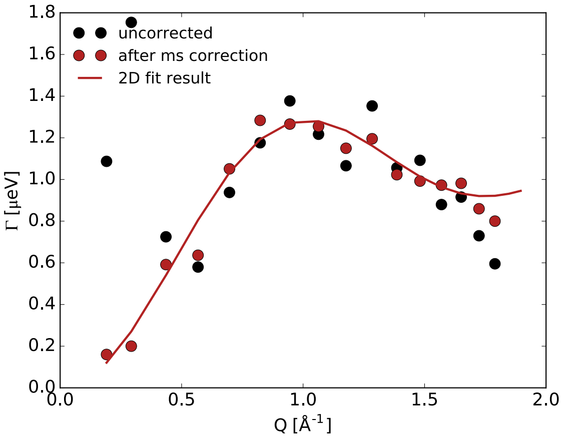

Figure 4. Quasielastic linewidths as obtained from the model independent fit (black circles: raw data, red circles: after multiple scattering procedure) and the result of the surface fit with the Chudley-Elliott model