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# Hydrogen dynamics in the low temperature phase of $LiBH_4$ probed by quasielastic neutron scattering

Arndt Remhof [a,*], Andreas Züttel [a], Timmy (A.J.) Ramirez-Cuesta [b], Victoria García-Sakai [b], Bernhard Frick [c]

[a] Empa, Swiss Federal Institute for Materials Science and Technology, Hydrogen and Energy, CH-8600 Dübendorf, Switzerland
[b] ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, United Kingdom
[c] Institut Laue-Langevin, F-38002 Grenoble, France

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ABSTRACT

$LiBH_4$ contains 18.5 wt% hydrogen and undergoes a structural phase transition (orthorhombic → hexagonal) at 381 K which is associated with a large increase in hydrogen and lithium solid-state mobility. We investigated the hydrogen dynamics in the low temperature phase of $LiBH_4$ by quasielastic neutron scattering, including a new kind of inelastic fixed window scan (IFWS). In the temperature range from 175 to 380 K the H-dynamics is dominated by thermally activated rotational jumps of the $[BH_4]^-$ anion around the *c*3 axis with an activation energy of about 162 meV. In agreement with earlier NMR data, a second type of thermally activated motion with an activation energy of about 232 meV could be identified using the IFWS. The present study of hydrogen dynamics in $LiBH_4$ illustrates the feasibility of using IFWS on neutron backscattering spectrometers as a probe of localised motion.



## 1. Introduction

Lithium borohydride ($LiBH_4$) is a well explored model system for the investigation of localised hydrogen dynamics. $LiBH_4$ forms ionic crystals consisting of negatively charged $[BH_4]^-$ ions and positively charged $[Li]^+$ ions [1]. Within the $[BH_4]^-$ unit the hydrogen atoms surround the boron in a tetrahedral configuration. $LiBH_4$ undergoes a solid–solid structural phase transition from an orthorhombic low-temperature structure (Pnma) to a hexagonal high-temperature structure ($P6_3mc$) at $T_c = 381$ K [2,3]. The high-temperature phase is associated with dynamical disorder, high $[Li]^+$ translational mobility, rotational jumps of the $[BH_4]^-$ anions in the terahertz range, and strong lattice anharmonicities [4,5]. Due to its high hydrogen content of 18.5 wt%, $LiBH_4$ is currently discussed as a light weight hydrogen storage material [6]. In addition, owing to its high lithium ion conductivity of $\sigma = 1 * 10^{-3}$ S/cm in the hexagonal phase at 393 K, $LiBH_4$ is considered as a potential solid-state electrolyte for lithium-ion batteries and fuel cells [7]. In many cases, the rotational motion of the anion seems to be a prerequisite for the fast cation mobility and thereby for the superionic conductivity.

The anion dynamics of $LiBH_4$ have been investigated by quasielastic neutron scattering (QENS) [8,9] and by nuclear magnetic resonance spectroscopy (NMR) [10,11]. The QENS measurements so far focussed on the hexagonal high temperature (HT) phase of $LiBH_4$. In the low temperature (LT) phase of $LiBH_4$, two types of rotational motion are observed by NMR. The two different kind of motion were attributed to two types of jump rotational motion with different jump rates. Skripov et al. measured activation energies of 182 and 251 meV, respectively. For both types of motions the jump rates reach values in the order of $10^{11}$ $s^{-1}$close to $T_c$ [10]. Jimura et al. measures similar values of 183 and 238 meV [11]. They attribute the motion with the lower barrier to rotational jumps around the *c*3 axis. Previous QENS studies also support the *c*3 axis rotation [8].

Here we present QENS spectra and Fixed Window Scans on the LT phase of $LiBH_4$. Different spectrometers with different energy resolutions and thereby with different time-windows have been used to follow the quasielastic signal from 175 K up to $T_c$. $LiBH_4$ can be used as a model system to demonstrate the feasibility to investigate Inelastic Fixed Window Scans (IFWS) [12], which represent an alternative way to quickly scan the thermal behaviour of a sample in a backscattering spectrometer.

## 2. Experiment

To avoid the strong neutron absorption by the $^{10}B$ isotope in natural boron, $^{11}B$ enriched (99.5%) $Li^{11}BH_4$ (chemical purity > 98%), purchased from Katchem, was used. The material was handled solely under inert gas conditions in purified Ar or He.

Quasielastic neutron scattering (QENS) measurements were carried out using the neutron spectrometer IRIS at the ISIS facility of the Rutherford Appleton Laboratory in Didcot, UK [13] and the

* Corresponding author. Tel.: +41 587654369; fax: +41 587654022.
*E-mail address:* arndt.remhof@empa.ch (A. Remhof).

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spectrometer IN16 at the Institut Max von Laue – Paul Langevin in Grenoble, France [14]. IRIS is a time of flight spectrometer in inverted geometry. Neutrons scattered by the sample are energy analysed by means of Bragg scattering from large-area PG (002) crystal analyser array. The incident neutron flux at the sample position is approximately $5.0 \times 10^7$ neutrons $cm^{-2}\,s^{-1}$ (white beam at full ISIS intensity). IN16 is a focussing backscattering spectrometer [14]. First, the desired wavelength is selected by a graphite (002) deflector, preparing a beam which is directed by a graphite (002) chopper to a spherically shaped monochromator mounted on a Doppler drive. Highly monochromatic neutrons are selected by Si-(1 1 1) monochromator crystals in exact backscattering geometry. As the monochromator undergoes a periodic sinusoidal motion, the exact wavelength (energy) selected is effectively scanned by the Doppler effect. These monochromatic neutrons are focussed onto the sample and the scattered neutrons are analysed again by Si (1 1 1) analysers in perfect backscattering. Both type of spectrometers are connected to the cold source of their respective neutron sources. The spectrometers are complementary with respect to their energy resolution. In the settings used, IRIS has a resolution of 17 μeV, while IN16 has a resolution of less than one μeV. Together with the data measured earlier at the TOF spectrometer FOCUS [8,15], which was operated at a resolution of 60 μeV, we could follow the quasielastic broadening in the low temperature phase of $LiBH_4$ from 175 K up to the transition temperature, over a wide energy range.

Two different kinds of scans were performed. First, so called "fixed window scans" (FWS) were taken to define the temperatures for subsequent inelastic spectra were recorded. In these measurements the incident and the final wave vector (and thereby the energy transfer ΔE) is fixed. A FWS in which $\Delta E = \hbar\omega_{off} = 0$ is called an elastic FWS (EFWS) or just an "elastic scan". In case of $\Delta E = \hbar\omega_{off} \neq 0$, this type of scan is called "inelastic FWS" (IFWS). IFWS are very sensitive to observe a broadening of the elastic line. As soon as the broadening of the elastic line reaches the pre-set value, the intensity rises above the background level. In the case of a quasielastic bradening caused by a thermally activated jump motion, Grapengeter at al. calculated the temperature dependent IFW intensity $I(T)$ for a temperature independent elastic incoherent scattering factor $A(Q)$ to be [16]

$$L(T) \propto [1 - A(Q)]\frac{\tau(T)}{1 + \omega_{off}^2 \tau(T)^2} \quad (1)$$

where $\tau(T) = \tau_0 \exp(E_a/kT)$ is the residence time, $E_a$ the activation energy, $k$ the Boltzmann constant and $\tau_0$ the high temperature limit of the residence time. The benefits of IFWS and their interpretation have recently been discussed by Frick et al. [12].

At IRIS a neutron wavelength of $\lambda$ = 6.66 Å was chosen. The sample was filled into an annular sample container with a wall thickness of 0.5 mm and a diameter of 24 mm. The spectra were recorded in a range of scattering vectors of $0.45 < Q < 1.85$ $Å^{-1}$ and binned into 17 different $Q$-groups. Energy transfers of up to ±400 μeV were recorded. A typical scan was recorded within 2 h. The data reduction was carried out by using the data analysis and visualisation environment "DAVE" [17].

At IN16 a neutron wavelength of $\lambda$ = 6.271 Å was chosen. The Doppler drive allows varying the incident energy by ±15 μeV. The momentum transfer ranges from 0.2 to 1.9 $Å^{-1}$. The samples were measured in a flat sample holder (width × height × thickness = 30 × 40 × 1 $mm^3$) placed at a sample angle of 45° and measuring times were 4–6 h per temperature.

The resulting QENS spectra were also analysed using DAVE. For both instruments, the QENS spectra were analysed by using the general purpose curve fitting utility "PAN", which is included in the DAVE distribution. The QENS spectra were modelled by using three components: First, a resolution limited elastic peak using a Gaussian line shape of full width at half maximum $\Gamma_{el}$ and an integrated area $I_{el}$, and second, a quasielastic broadened component arising from the reorientational motion of the $BH_4$ units using a Lorentzian line shape of width $\Gamma_{qe}$ and integrated intensity $I_{qe}$. The third component is a linear background. In all fits, the peak centres of the elastic and the quasielastic peaks were constrained to be the same. The width of the elastic line was fixed to the width of the measured elastic line of a vanadium standard sample.

## 3. Results and discussion

Fig. 1 displays the EFWS, summed over the whole $Q$-range. The scans recorded at IN16 are represented by red squares; the ones recorded at IRIS are represented by blue circles. At low temperatures, the intensity decreases with temperature due to an effective Debye Waller factor which includes angular libration of the hydrogen. The different initial slopes for the different instruments are determined by the different energy width of the elastic line, i.e. by the different energy resolution. The hydrogen dynamics match roughly the instrument's time window between 170 and 240 K for IN16 and between 240 and 360 K for IRIS. At lower temperatures, the energy resolution exceeds the quasielastic broadening, so the scattered quasielastic intensity cannot be distinguished from the elastic line. At higher temperatures, the broadening of the quasielastic line is too large to be distinguishable from a flat background. The step at 380 K corresponds to the structural phase transition.

Fig. 2 displays the IFWS (symbols) together with a model curve. We will first compare the experimental IFWS (Fig 2) with the EFWS measured at IN16 (Fig. 1). At low temperatures, the IFWS displays a constant background, while the EFWS drops with increasing temperature. Around 150 K, a redistribution of intensity away from the elastic line to the inelastic part of the spectrum occurs, the elastic line broadens and the intensity of the IFWS rises. Note that the deviation from the background is noticeable around 130 K in the IFWS, while the onset of the increased loss of elastic intensity is observed from 150 K onwards, showing the higher sensitivity of the IFWS as compared to the elastic scan. The IFWS reaches is maximum around 215 K. At this temperature the EFWS almost levelled out to its equilibrium value. The IFWS is slightly asymmetric, showing a shoulder on the descending flank. The IFWS reaches the background level again above room temperature. The background level at high temperatures is lower than at low temperatures as the IFWS is carried out close to the elastic line and is

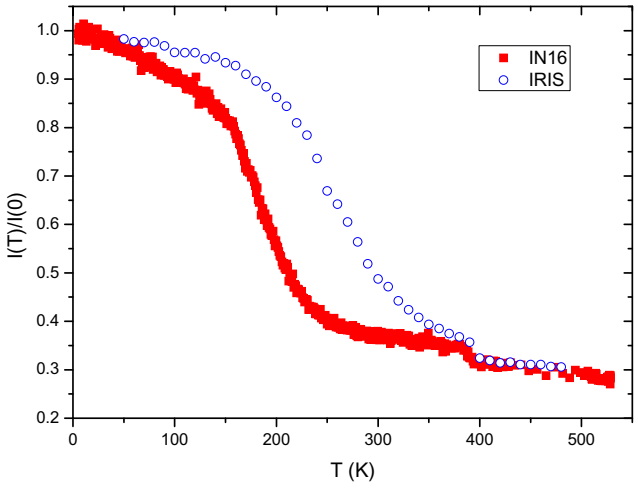


**Fig. 1.** Elastic fixed window scans recorded at IN16 (red, bold symbols) and at IRIS (blue, open symbols). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)