Experimental report

15/09/2023

Proposal: **7-05-515**

Council: 10/2019

Title: In-situ QENS investigation of Complex Hydrides

Research area: Materials

This proposal is a new proposal

Main proposer: **Neslihan ASLAN**

Experimental team: Neslihan ASLAN
Anastasiia KUZNETSOVA

Local contacts: Jean-Marc ZANOTTI

Samples: $Mg(NH_2)_2$-LiH-$LiBH_4$
$Mg(NH_2)_2$-LiH

Instrument	Requested days	Allocated days	From	To
IN6-SHARP	3	3		
IN5	3	0		
SHARP	3	3	06/09/2021	09/09/2021

Abstract:

Hydrides are in the focus of research for the application of energy storage and energy transportation. Complex hydrides has recently gained in importance because of good properties for reversible hydrogen storage. The composition $Mg(NH_2)_2$ + LiH has faster de- and rehydrogenation kintetics with the addition of $LiBH_4$. So far $Mg(NH_2)_2$ + LiH + $LiBH_4$ is a good candidate to be used for hydrogen storage with the high capacity (ca. 4 wt%) and good reversibility.
To understand the effect of the $LiBH_4$ additive on the kinetics, QENS experiments were applied at Heinz Maier-Leibnitz Zentrum (MLZ). At the TOFTOF instrument the Time-of-Flight spectroscopy of $Li_4BH_4(NH_2)_3$ was investigated, which is an intermediate of the dehydrogenated $Mg(NH_2)_2$ + LiH + $LiBH_4$-system. This product showed in the QENS measurement high degree of freedom for rotational and transversal motions below the melting temperature. The high mobility of the BH_4-tetrahedron can explain the fast absorption kinetics of $Mg(NH_2)_2$ + LiH + $LiBH_4$. To reinforce this consideration we want to measure in-situ QENS of $Mg(NH_2)_2$ + LiH + $LiBH_4$ in comparison to $Mg(NH_2)_2$ + LiH at the IN5 instrument.

Experimental Report

In-situ QENS investigation of Complex Hydrides (Experiment 7-05-515)

Measurement environment: Cryofurnace, 5.1 Å neutron wavelength, slit 20x30

Sample holder: sample stick for gas pressure, Al-cylinder sample holder with 1 mm wall thickness

Sample preparation: Samples were stored in the glovebox. Sample powder was filled in a pocket out of Al-foil and evenly distributed inside the pocket. The Al-foil pocket was wrapped to a tube to fit inside the cylindrical sample holder. The sample holder was loaded with the sample and attached to the sample stick inside the glove box.

Samples: $Li_4BH_4(ND_2)_3$, $Li_4BD_4(NH_2)_3$, 6 $Mg(NH_2)_2$ + 9 LiH + $LiBH_4$ (691)

1. Measurement: $Li_4BH_4(ND_2)_3$

$Li_4BH_4(ND_2)_3$ was measured in 1 bar He-gas atmosphere at 100 K, 300 K, 470 K and 505 K. Each temperature took 3 h to measure and during heating the sample was measured in 4 min time intervals.

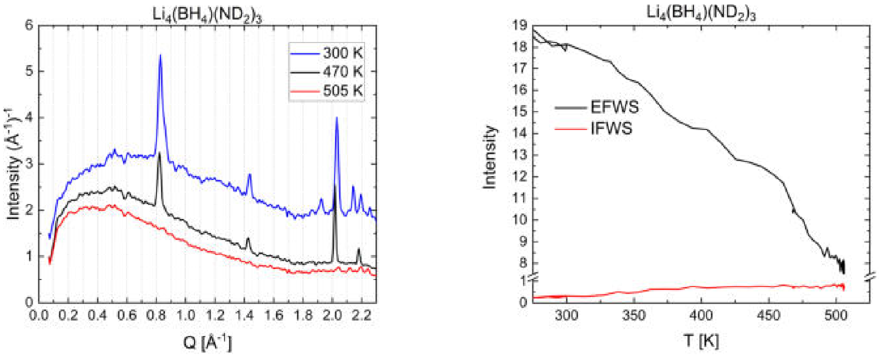

Figure 1 and 2: The diffraction patterns of $Li_4BH_4(ND_2)_3$ are shown at 300, 470 and 505 K on the left. On the right the elastic fixed window scan (EFWS) and the inelastic fixed window scan (IFWS) of $Li_4BH_4(ND_2)_3$ are shown.

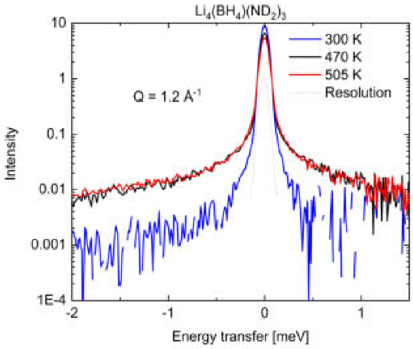

Figure 3: S(Q,ω) plots of $Li_4BH_4(ND_2)_3$ at 1.2 $Å^{-1}$ and at 300, 470 and 505 K.

The QENS measurement of $Li_4BH_4(ND_2)_3$ detects the stochastic motions of $(BH_4)^-$ anions. The diffraction patterns in **Figure 1** show that the sample is crystalline up to 470 K and melted at 505 K. The elastic fixed window scan (EFWS) in **Figure 2** shows the high mobility of the $(BH_4)^-$ anions increasing with increased temperature. Finally, the S(Q,ω) plots in **Figure 3** show that the $(BH_4)^-$ anions have at 470 K, when the sample is crystalline, similar motion as at 505 K, when the sample is melted. The broad width of S(Q,ω) at 470 and 505 K indicate a long range motion of the $(BH_4)^-$ anions.

2. Measurement: $Li_4BD_4(NH_2)_3$

$Li_4BD_4(NH_2)_3$ was measured under 1 bar He at 300 K, 440 K, 470 K and 510 K. Each temperature was measured for 3 h and during heating the sample was continuously measured in 4 min intervals.

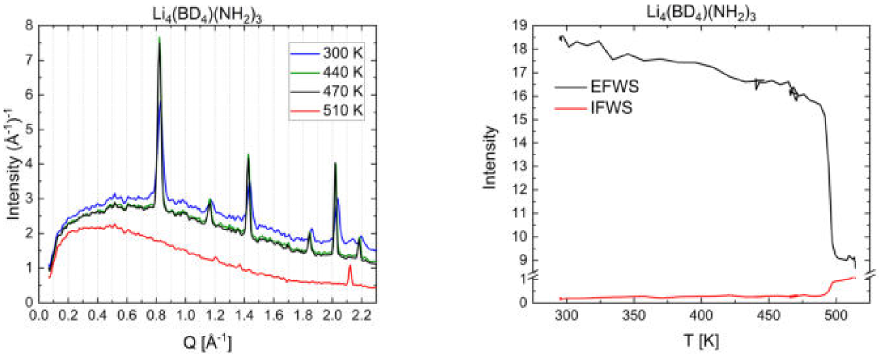

Figure 4 and 5: The diffraction patterns of $Li_4BD_4(NH_2)_3$ are shown at 300, 440, 470 and 510 K on the left. On the right the EFWS and the IFWS of $Li_4BD_4(NH_2)_3$ are shown.

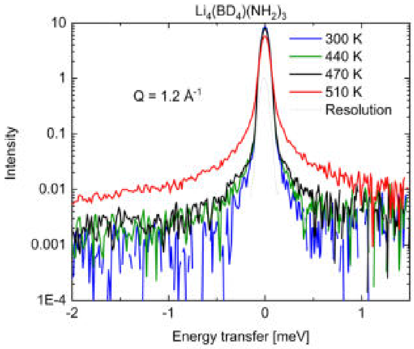

Figure 6: S(Q,ω) plots of $Li_4BD_4(NH_2)_3$ at 1.2 $Å^{-1}$ and at 300, 440, 470 and 510 K.

The QENS measurement of $Li_4BD_4(NH_2)_3$ detects the stochastic motions of $(NH_2)^-$ anions. The diffraction patterns in **Figure 4** show that the sample is crystalline up to 470 K and melted at 510 K. EFWS in **Figure 5** shows that the $(NH_2)^-$ anions have a low mobility when the sample is in solid phase up to 470 K. When the temperature increases to 500 K the EFWS rapidly declines, indicating the fast mobility of the $(NH_2)^-$ anions when the sample melts. Also the S(Q,ω) plots in **Figure 6** support this observations. The S(Q,ω) of $Li_4BD_4(NH_2)_3$ at temperatures up to 470 K have a narrow width, which shows a significant broadening at 510 K. In other words, up to 470 K the $(NH_2)^-$ anions have slow, localized motions and at 510 K they undergo long-range motion.

In conclusion, the $(BH_4)^-$ and $(NH_2)^-$ anions have different mobility in $Li_4BH_4(NH_2)_3$. $(BH_4)^-$ anions have a higher mobility and show a long-range mobility in solid and melted sample. $(NH_2)^-$ anions have lower mobility than $(BH_4)^-$ anions. $(NH_2)^-$ anions undergo long-range motion only when the sample $Li_4BH_4(NH_2)_3$ is melted.

3. Measurement: 6 $Mg(NH_2)_2$ + 9 LiH + $LiBH_4$ (691)

6 $Mg(NH_2)_2$ + 9 LiH + $LiBH_4$ (691) was measured under 80 bar H_2. It was measured at 300 K, 448 K, 490 K and again at 300 K after cooling down for 3 h at each temperature. During heating and cooling measurements of 4 min intervals were taken continuously.

The sample holder was not tight and the 80 bar H_2 decreased during measurement to 1 bar. With 80 bar H_2, QENS was anyway not possible to measure as the incoherent background of the S(Q,ω) curves was too high. At 1 bar H_2 the incoherent background is low enough to analyse the QENS signal.

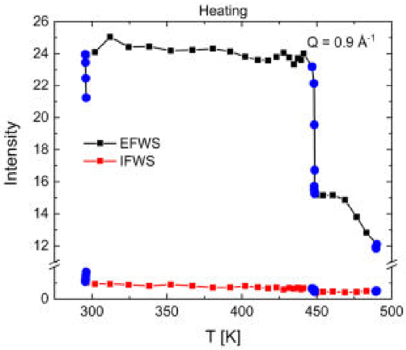

Figure 7: EFWS and IFWS of 691 during heating.

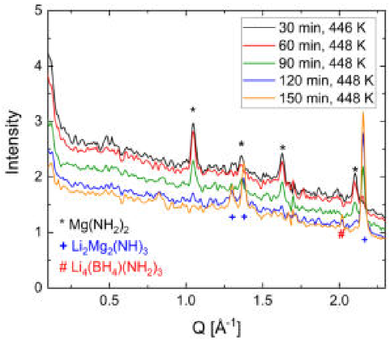

Figure 8: In-situ diffraction patterns of 691 at 448 K.

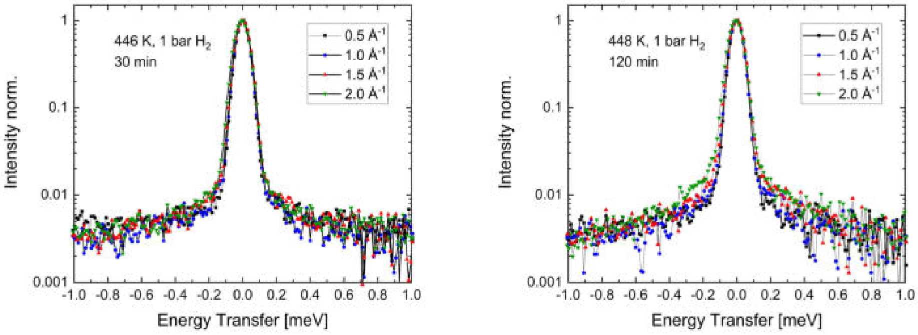

Figure 9 and 10: S(Q,ω) of 691 at 446-448 K for different Q. In the left plot the sample was measured the first 30 min when the temperature reached 446 K. On the right the temperature was at 446-448 for 120 min and the data was collected for the last 30 min.

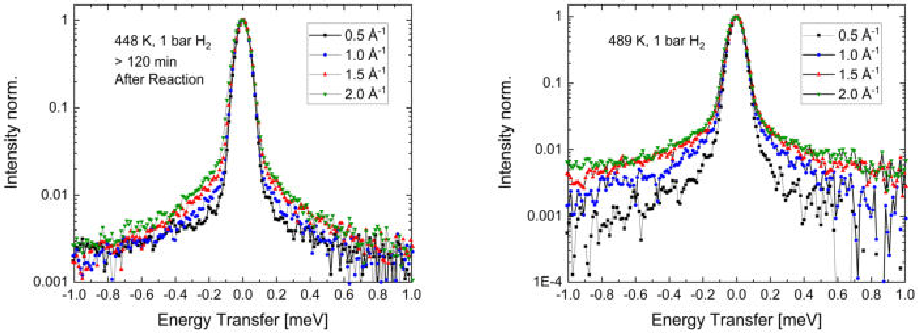

Figure 11 and 12: S(Q,ω) of 691 at 448 and 489 K for different Q. In the left plot the sample was measured after it was 120 min at 446-448 K. In the right plot the sample was at 489 K.

The QENS measurement of 691 is a complex signal of different hydrogen containing compounds. At temperatures lower than 446 K there was hardly a QENS broadening detected in the S(Q,ω) curves, which is shown in **Figure 9**. The in-situ QENS measurement at 446-448 K showed S(Q,ω) curves changing with time (**Figure 9-11**). Also the EFWS in **Figure 7** shows the change in the QENS signal at these temperatures. The diffraction patterns in **Figure 8** show what happens to the sample: The sample reacts to $Li_2Mg_2(NH)_3$ and $Li_4BH_4(NH_2)_3$. At 1 bar H_2 the sample 691 desorbs hydrogen and the QENS signal at 446-448 K origins from this chemical reaction. At 489 K the S(Q,ω) plots have a broader width than at 448 K shown in **Figure 12**. This high mobility origins presumably from $Li_4BH_4(NH_2)_3$, which has high mobility as detected in the previous measurements.