
***In-situ* Neutron Diffraction Studies of Novel Hydrogen Storage Materials**

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Program Scope

Our work couples the unique capabilities of the University of Missouri Research Reactor (MURR) to conduct *in-situ* neutron diffraction experiments as a function of temperature and gas environment, with the wide range of capabilities of the Materials Research Center at the University of Missouri-Rolla (MRC) in the area of materials synthesis and characterization. In the first year of this project we intend to study the decomposition reactions of systems of the type AMH_4 where A is an alkali metal (Li, Na, K) and M is either Al or B, as well as to begin research on other chemical hydrides with potentially high reversible H capacity, such as $LiNH_2$ and $Mg(BH_4)_2$. Experiments will reveal the phases that form during these reactions and experiments will be conducted with and without catalysts, to determine if the catalysts participate in intermediate phase formation or are merely donating or accepting electrons in the reactions. Materials for study are being acquired both commercially and through synthesis at the MRC. In later years studies will be extended to the re-absorption of hydrogen and the reformation of the starting compounds to better understand the questions of reversibility.

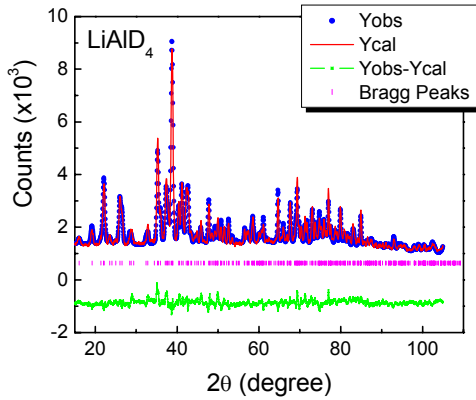
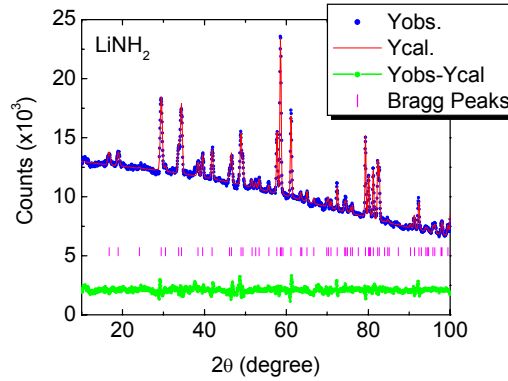
Recent Progress

(a) In-situ neutron diffraction measurements

Prior to the start of this project we had constructed a furnace for *in-situ* studies, which had been used to examine phenomena such as oxygen loss in perovskites, and hydrogen absorption/desorption in LiAl alloys. This furnace is less than optimum because its original (fragile) heater was replaced by a potted heater that attenuates roughly 40% of the incident neutrons, but we have continued to make use of it while constructing a new furnace with heaters above and below the sample region. This new design has the further advantage of having independent control of the two heaters, thereby allowing differences in heat loss above and below the sample to be compensated by different power levels. The thermal gradient across the sample thus can be minimized and in bench tests has been found to be of order 1°C at 200°C . Unfortunately, unexpected delays occurred because of late deliveries of some critical components and the necessity of making some design modifications. However the new furnace will probably be commissioned about the last week in April. Thus, measurements to date have been performed in the old furnace, and later work should be of still higher quality.

Subsequent to the submission of our proposal to the DOE, we discovered that researchers at the Norwegian research reactor JEEP-II had carried out a number of the studies we had proposed [1], especially on the alanates, where the neutron absorption by B is not a problem. We found this particularly ironic since the Norwegian reactor uses the same neutron detector technology we employ at MURR, and, in fact, they had purchased the system (developed by our former colleague Ron Berliner) from MURR several years ago. Despite

their head start, the higher power of MURR and its longer operating schedule than JEEP-II should allow us to catch up and surpass them in the near future. In the meantime, comparison of our data on LiAlD_4 (Fig. 1) has allowed us to confirm the reliability of our measurements. The two data sets (not shown) are virtually indistinguishable except for differences in wavelength, but the resolution of the MURR instrument at the highest q vectors is slightly superior to the JEEP-II data.

Fig. 1: Neutron diffraction pattern of LiAlD_4 Fig. 2: Neutron diffraction pattern of LiNH_2

In addition to the room temperature work on LiAlD_4 , we have studied LiNH_2 at RT [2]. In mixtures with 2LiH , it can reversibly yield 5.5% H under practical conditions. Early x-ray and neutron diffraction studies of the material gave anomalously short N-H bonds (0.70\AA). Our study was carried out with H (and not D) and we found (Fig. 2) that despite the large incoherent scattering cross section of H, excellent data could be collected and refined. This is possible because the MURR samples are small, and coherently scattered neutrons have only a small chance of being rescattered (and their information lost). Thus, the information content is maximized. Rietveld refinement shows that the N-H bonds are actually 0.986\AA and 0.942\AA long, in much better agreement with other results, and indicative of normal bond strength, as expected from the decomposition. We have also carried out a theoretical study of the electronic density of states and charge density distribution in this material [2].

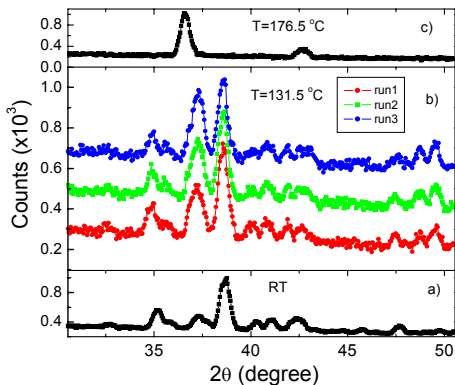


Fig. 3: Data for LiAlD_4 as a function of temperature and time. Each spectrum is measured in 30 minutes and spans 20° (2θ). The lower panel shows the data at room temperature; the middle panel shows 3 successive scans at 131.5°C and shows the coexistence of LiAlD_4 , Li_3AlD_6 and Al. The upper panel shows data at 176.5°C , and consists of diffraction from LiD and Al.

Preliminary work at elevated temperature has been carried out on LiAlD_4 . It shows the expected decomposition steps, resulting finally in Al + LiH (Fig.3). The detector geometry allows for data collection over a 20° (2θ) range

simultaneously, and good quality data was obtained in only a few minutes. The intensity gains associated with the new furnace will improve this further. Unfortunately, these first data sets (which also confirm the Norwegian results), were compromised by a large (10°C) gradient across the sample. The furnace has been since improved and can be better used, but, as mentioned above, the new design will reduce the gradient to less than 1°C.

As this report is being written we are collecting data on NaBD₄ as a function of temperature. Once again, the instrument geometry is very helpful; a conventional diffractometer would show negligible intensity due to the B absorption, unless the separated ¹¹B isotope was employed. We will know in the next few days whether the quality of these data is sufficient for detailed analysis, but preliminary data indicate that the first decomposition is at a higher temperature than previously reported.

(b) Sample synthesis

Although many of the materials of interest to this project can be obtained commercially, the special needs of neutron diffraction in (sometimes) demanding deuterium or isotopically separated B, and the desire to study the effects of various catalysts makes synthesis an essential component of the work. While the scientists at the MRC have extensive experience in solid state synthesis methods, the special environmental requirements (dry, preferably inert, atmosphere) have led us to procure new tools for this program. These include a high quality dry box with airlock and high energy mills with controlled environment and temperature. Efforts have begun to synthesize some novel compounds through high energy milling of metal hydrides with B metal, followed by high temperature-high pressure treatment in hydrogen (deuterium) gas to complete the reaction.

1) Borohydrides

Attempts to synthesize the borohydrides of Li and Mg have been made using the high energy mill and either the pure metal precursors or hydrides (LiH, MgH₂) followed by heat treatment under hydrogen (deuterium) atmosphere at pressures up to 500 psi and temperatures up to 310° C (the limit of our current “bomb”). Since MgB₂ is commercially available, it was also used as a precursor for potential hydrogenation. After six hours of milling, x-ray diffraction showed that all samples became amorphous. However, the subsequent attempts at hydrogenation did not lead to the formation of the borohydrides. We believe that the heat treatment conditions are too mild to allow this reaction to proceed. Thus we are procuring a new PARR pressure cell that will allow the application of 1800 psi at temperatures up to 700°C.

In addition to these solid state reaction pathways, we will attempt to prepare these borohydrides by means of a liquid state reaction using LiH (MgH₂) and B₂H₆ liquid and ether under D₂ atmosphere. One important question we will attempt to answer is the rate of exchange of H and D under these conditions and whether treatment in the appropriate deuterated solvent can result in highly deuterated products.

2) LiNH₂–LiBH₄ mixtures[3]

Mixtures of LiNH₂–LiBH₄ in ratios of 3:1, 2:1 and 1:1 were prepared by ball milling of the precursors. The results of the milling appear to be nearly single phase materials with stoichiometry Li₄N₃BH₁₀, Li₃N₂BH₈ and Li₂NBH₆, respectively. In each case a small impurity phase was observed and will be characterized. We plan to run high resolution neutron diffraction at room temperature on these samples to determine their crystal structures as well as to perform *in-situ* temperature dependent studies. Based on our results on the

LiNH₂ system, which yielded perfectly useful data with 50% hydrogen, and examination of the LiAlH₄ system which was unsatisfactory with 67% hydrogen, we hope that the first two of these compounds will be accessible for study without deuteration, while the last may well exceed the limits of our method. Based on research by other groups, it seems likely that these compounds can be made to yield a large quantity of hydrogen, but that reformation of the compounds after hydrogen desorption may be quite difficult.

3) *LiNH₂–LiAlH₄ mixtures*

Mixtures of LiNH₂–LiAlH₄ in the same ratios as was examined in 2) above, i.e. 3:1, 2:1 and 1:1, were processed by ball milling. Unlike the previous case, amorphous products were formed (based on x-ray diffraction). These samples will be heat treated in the new PARR apparatus, with the same products expected as above with Al substituted for B. Assuming success in the synthesis, the same studies will be carried out using room temperature and high temperature neutron diffraction.

4) *Catalyzed LiAlD₄*

Attempts to prepare LiAlD₄ mixed with catalysts such as TiCl₃ or TiCl₄, using high energy ball milling have thus far been unsuccessful due to decomposition induced by the high energy process. These samples will be remade using low energy milling (or perhaps very brief high energy milling), and the resulting products characterized by neutron diffraction.

5) *Other studies*

We will be studying the low temperature exchange of H and D in both the alanates and borohydrides by soaking the hydrogenated systems in D₂ gas at temperatures below the first decomposition reactions. Because the neutron diffraction measurements are very sensitive to the H-D ratio it will be easy to determine the degree of exchange. Samples prepared in this way may be a lower cost alternative to acquisition of deuterated materials, and could be used in the preparation of catalyzed samples for further studies.

Future Plans

Our early results have given us confidence that the program we originally outlined in our proposal is feasible and can be accomplished in the time period outlined (more or less). While the first year's studies are focused on the decomposition reactions, work in later years will also focus on reformation reactions *in-situ*. These will require the construction of a small volume pressure cell that can be inserted into the neutron diffraction furnace and operated at the same temperatures and pressures as the PARR cell. Studies will be conducted as a function of both parameters; temperature and pressure to establish the smallest energy input needed to achieve the desired result. Still later work will build on all of the earlier results to characterize material that is undergoing multiple cycles of decomposition and reformation. In these we hope to uncover any undesirable side reactions and search for methods to ameliorate them.

References:

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