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## Crystal and electronic structures of LiNH<sub>2</sub> and related compounds

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Recently, Li-N-H has attracted much attention as a hydrogen storage material.<sup>1</sup> The crystal structure of LiNH<sub>2</sub> was first determined using x-ray diffraction by R. Juza and K. Opp in 1951,<sup>2</sup> and reinvestigated with neutron diffraction in 1972.<sup>3</sup> Its structure appears to be peculiar because the reported distance between the nearest nitrogen and hydrogen atoms,  $d_{\text{N-H}}$  is only 0.70 Å, which is much shorter than  $d_{\text{N-H}} = 1.022$  Å for monomeric, unsolvated LiNH<sub>2</sub><sup>4</sup> and  $d_{\text{N-H}} = 0.82$  Å in Li<sub>2</sub>NH.<sup>5</sup> The main problem in the x-ray structural analysis for compounds such as light metal hydrides, with low atomic numbers, is their poor scattering power of hydrogen for the incident x-rays. The intensity of coherently diffracted x-rays is proportional to the square of the atomic number and falls dramatically with the decrease of this value. In contrast, neutron scattering from the hydrogen proton (or alternatively, the deuteron) gives a reliable measurement of the hydrogen location and occupation. Hydrogen possesses a large incoherent cross section (related to processes in which the neutron and hydrogen atom spins flip during the interaction). These processes lead to a large, featureless background in the diffraction pattern, reducing the statistical accuracy of the final result. Thus, deuterium, with a much smaller incoherent scattering cross section, has been employed for many studies. The replacement of the hydrogen with deuterium will improve the statistical accuracy of the measurement, but might not be able to provide information relevant to hydrogen storage in the hydrides, such as chemical bonding and interactions, because the factor of two difference in mass between H and D may affect many properties. Knowledge of the fundamental properties of LiNH<sub>2</sub>, especially the accurate location of the hydrogen atoms, is critical to an understanding of, and improvement in, the hydrogen absorption and desorption in the Li-N-H system. In addition, it may (or may not) be difficult to obtain deuterated samples of some of the interesting hydrides, but it is obviously easier and less costly to use protonated material for mixed hydrides and for cycling studies. Thus it is useful to determine the limits for which high quality neutron data can be obtained with protonated samples. In this presentation, we report the revised crystal structure for LiNH<sub>2</sub> and show data for LiNH<sub>2</sub>-LiBH<sub>4</sub> compounds, using neutron powder diffraction with high sensitivity. We also report a calculation of the electronic structures of LiNH<sub>2</sub> based on the resulting structural parameters.

The crystal structures of LiNH<sub>2</sub> and LiNH<sub>2</sub>-LiBH<sub>4</sub> system were reinvestigated using powder neutron diffraction with high sensitivity ( Fig. 1 and Fig. 2) The LiNH<sub>2</sub> compound crystallizes in the tetragonal space group  $I\bar{4}$  with lattice parameters  $a=b=5.03442(24)$  Å,  $c=10.25558(52)$  Å. It is found that H atoms occupy  $8g_1(0.2429, 0.1285, 0.1910)$  and  $8g_2(0.3840, 0.3512, 0.1278)$  sites. The bond lengths between the nearest nitrogen and hydrogen atoms are 0.986 and 0.942 Å, respectively. The bond angle between H-N-H is about 99.97°. These results are significantly different from those of previous experiments. The results confirm our ability to use such a sample with as much as 50% hydrogen (atomic concentration). The electronic structure was calculated ac-

ording to the revised structural data using the Wien2k code. The full potential linearized augmented plane wave method was employed using the density function theory within the generalized-gradient approximation (GGA) with the exchange correction potential of Perdew-Burke-Ernzerhof-96. The calculated density of states and charge density distribution show strong ionic characteristics between the ionic  $\text{Li}^+$  cation and the covalent bonded  $[\text{NH}_2]^-$  anion ( Fig. 3). Room temperature neutron diffraction data have also been collected on milled mixtures of  $\text{LiNH}_2$  and  $\text{LiBH}_4$  with different ratios. The samples appear to be nearly single phase<sup>6,7</sup>, but the peaks appear to be broadened, probably due to the small crystallite size of the milled mixtures. It will be interesting to follow the peak shapes as a function of temperature. Nevertheless, we expect that detailed structures will be determined by refinement of neutron diffraction data. The structures and hydrogen desorption from  $\text{LiNH}_2$  and  $\text{LiNH}_2\text{-LiBH}_4$  system are being studied at elevated temperature with and without the addition of catalysts, in an effort to determine the role of the catalyst in forming intermediate phases.

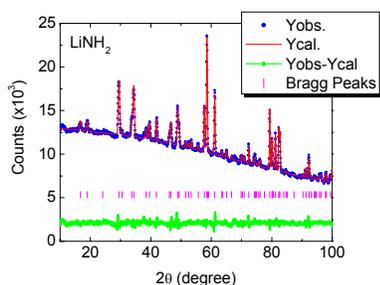


Fig. 1: Neutron diffraction pattern of  $\text{LiNH}_2$  at RT.

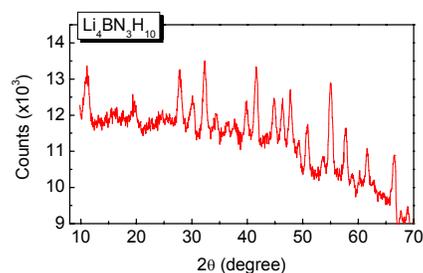


Fig. 2: Neutron diffraction pattern of  $\text{Li}_4\text{BN}_3\text{H}_{10}$  at RT

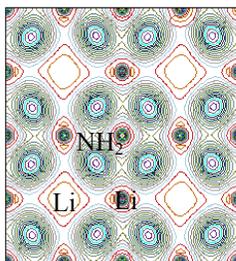


Fig. 3: Valence electron density contours of  $\text{LiNH}_2$  in the a-b plane. The contour spacing is  $0.01 e/\text{\AA}^3$ .

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## Acknowledgements

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