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**Atomic Motions in Ionic Hydrides: MgH<sub>2</sub>, NaMg<sub>3</sub>H<sub>3</sub>, and LiBH<sub>4</sub>**

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In hydrogen storage, rapid hydrogen diffusion is a key component for rapid reaction rates of dehydriding and rehydriding. In metallic systems, the light interstitial H atoms typically do display rapid diffusion. However, recent interest has focused on ionic and complex hydrides of light metal-atoms because of their high weight fractions of reversible hydrogen. These ionic complex hydrides generally reveal slow hydrogen diffusion and resultingly slow reaction kinetics. We report here studies of H diffusion using NMR in several such hydrides. In MgH<sub>2</sub>, the rate  $\omega_H$  of H hopping remains too slow to narrow the H NMR up to 400 °C.  $T_{1D}$  measurements, however, can detect the motion and find an activation energy of 1.72 eV, the first reported direct measurement of diffusion in MgH<sub>2</sub>. In ball-milled (bm) material with Nb<sub>2</sub>O<sub>5</sub> catalyst additive, a fraction of the resonance intensity is narrowed starting at 50 °C, with the narrow fraction growing to 30% by 400 °C. A model for continuous growth of the narrow line, based on a wide distribution of motion rates, is presented. Ball-milling also greatly increases the laboratory-frame relaxation rates,  $T_1^{-1}$ , from paramagnetic defects created by the mechanical process. In bm NaMgH<sub>3</sub>, an even larger fraction of the resonance is motionally-narrowed, growing to nearly 100% by 300 °C. Clearly, ball-milling has a much more profound effect on ionic hydrides than the simple reduction of grain sizes and diffusion distances. In coarse-grain LiBH<sub>4</sub> (with 13.8 weight% reversible hydrogen), an orientationally disordered solid phase occurs above 110 °C. Above the transition, the rate of Li ion diffusion increases remarkably. H diffusion starts to narrow the H NMR line around 170 °C, continuing to narrow up to the melt near 280 °C. To distinguish diffusion of (already rapidly rotating) BH<sub>4</sub> units from H exchange between neighboring BH<sub>4</sub>, the <sup>11</sup>B resonance was studied. The boron line central transition becomes much narrower (400 Hz) than the width (1500 Hz) expected from Van Vleck  $M_2$  for the case of static boron spins (with rapid Li and H diffusion). Thus, intact BH<sub>4</sub> units are the diffusing species. Even in molten LiBH<sub>4</sub>, the BH<sub>4</sub> lifetime is found to be at least 2 seconds from observations of the B-H J-coupling pattern, so it is probably much larger in the solid.