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First-Principles Studies of Complex Hydrides. Vidvuds Ozolins, Materials Science & Engineering, Univ. of California, Los Angeles, P.O. Box 951595, Los Angeles, CA 90095 USA.

The recent surge in research on complex hydrides has been motivated by Bogdanovic's discovery that sodium alanates ($NaAlH_4$ and $Na3AlH_6$) can reversibly store more than 4 wt.% hydrogen when doped with small amounts of Ti. Extending these methods to other compounds with higher hydrogen weight content has been challenging. The location of catalytically active Ti and the mechanism of enhanced hydrogen kinetics are also poorly understood. We will report on first-principles studies of the crystal bonding, thermophysical properties, lattice dynamics and energetics of lattice defects in sodium, lithium, and magnesium alanates. For $NaAlH_4$ and Na_3AlH_6, the formation nergies of all kinds of Ti impurities are found to be very high (>1 eV) and therefore unlikely to occur under normal experimental conditions. Effect of zero-point vibrations on the calculated lattice parameters of $NaAlH_4$ is found to be large (expansion by 1.2 and 1.5Å in the *a* and *c* parameters, respectively), as expected for a compound with many light elements.

We discuss the implications of the experimentally observed phonon mode softening for the kinetics of hydrogen release and hypothesize that breaking up the AlH_4 anions is the rate limiting step. The enhanced kinetics of absorption and desorption in Ti-doped $NaAlH_4$ powders is attributed to the effectiveness of Ti in promoting the break-up of the AlH4- anions.