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Physical properties of Ti-doped sodium alانات: First-principles studies and experiments

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The recent surge in research on sodium alانات, NaAlH_4 and Na_3AlH_6 , has been motivated by Bogdanovic's discovery that, when doped with small amounts of Ti, these compounds can reversibly store more than 4 wt.% hydrogen. The location of catalytically active Ti and the mechanisms of enhanced H_2 sorption kinetics are still poorly understood. We will report on combined first-principles and experimental studies of structural, thermophysical and lattice dynamical properties of bulk alانات. Polarized Raman scattering on single crystals of NaAlH_4 has been used to determine the frequencies of the Raman-active vibrational modes between 300 and 425 K, i.e., up to the melting point T_m . Significant softening (by up to 6 %) is observed in the modes involving rigid translations of Na^+ cations and translations and librations of AlH_4^- tetrahedra. Surprisingly, less than 1.5 % softening is seen for the Al-H stretching and Al-H bending modes, indicating that the AlH_4^- anion remains a stable structural entity even near T_m . The phonon mode Grüneisen parameters, calculated using the quasiharmonic approximation, are found to be significantly higher for the translational and librational modes than for the Al-H bending and stretching modes, but cannot account quantitatively for the dramatic softening observed near T_m , suggesting an essentially anharmonic mechanism. The calculated lattice expansion due to zero-point vibrations is found to be large (1.2 and 1.5% for the a and c parameters, respectively), as expected for a compound with many light elements. The formation energies of Ti impurities in bulk alانات are found to be high (> 1 eV), indicating that bulk substitution should not occur under normal conditions. We discuss the implications of these results for the kinetics of hydrogen release and hypothesize that breaking up the AlH_4^- anions is the rate limiting step. The enhanced kinetics in Ti-doped NaAlH_4 powders is attributed to the effectiveness of Ti in promoting the break-up of the AlH_4^- anions at the interface between NaAlH_4 and Na_3AlH_6 .