

MAR11-2010-000973

Abstract for an Invited Paper
for the MAR11 Meeting of
the American Physical Society

Point-defect-mediated dehydrogenation of alane¹

LARS ISMER, University of California, Santa Barbara

For the engineering of better hydrogen storage materials a systematic understanding of their hydrogen sorption kinetics is crucial. Theoretical studies on metal hydrides have indicated that in many cases point defects control mass transport and hence hydrogen uptake and release. Manipulating point-defect concentrations thus allows control over hydrogen sorption kinetics, opening up new engineering strategies. However, in some cases the relevance of kinetic limitations due to point defects is still under debate; kinetic inhibition of hydrogen sorption has also been attributed to surface effects, e.g. oxide layers or low recombination rates. We present a systematic analysis of the dehydrogenation kinetics of alane (AlH₃), one of the prime candidate materials for hydrogen storage. Using hybrid-density functional calculations we determine the concentrations and mobilities of point defects and their complexes. Kinetic Monte Carlo simulations are used to describe the full dehydrogenation reaction. We show that under dehydrogenation conditions charged hydrogen vacancy defects form in the crystal, which have a strong tendency towards clustering. The vacancy clusters denote local nuclei of Al phase, and the growth of these nuclei eventually drives the AlH₃/Al transformation. However, the low concentration of vacancy defects limits the transport of hydrogen across the bulk, and hence acts as the rate-limiting part of the process. The dehydrogenation is therefore essentially inactive at room temperature, explaining why AlH₃ is metastable for years, even though it is thermodynamically unstable. Our derived activation energy and dehydrogenation curves are in excellent agreement with the experimental data, providing evidence for the relevance of bulk point-defect kinetics.

¹Work performed in collaboration with A. Janotti and C. G. Van de Walle, and supported by DOE.