

Hydrogen Release from Sodium Alanate Observed by Time-resolved Neutron Backscattering

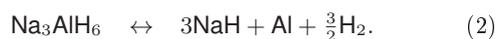
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Time-resolved quasielastic measurements on the backscattering spectrometer SPHERES were used to monitor the decomposition kinetics of sodium alanate, $\text{NaAlH}_4 \rightarrow \text{Na}_3\text{AlH}_6 \rightarrow \text{NaH}$. Both reaction steps were found to be accelerated by autocatalysis, most likely at the surfaces of Na_3AlH_6 and NaH crystallites.

Sodium alanate NaAlH_4 is widely studied as a model system for hydrogen storage. Hydrogen release through the reaction steps



is very slow and irreversible in undoped bulk material, but the desorption and absorption kinetics can be improved decisively by doping [1] and nanostructuring [2]. Further improvement requires a detailed understanding of the reaction mechanism.

Neutron scattering offers promising ways to observe structural changes in situ while the hydrogen is being released. In this project, we use intermolecular dynamics, probed by quasielastic scattering, as a very sensitive proxy for structural changes. So far, we have completed a series of measurements on hydrogen release from pure bulk alanate [3].

To obtain reasonable statistics within short time slices we choose an energy window of $\pm 8.6 \mu\text{eV}$ out of the full energy range of SPHERES of $\pm 31 \mu\text{eV}$. Within our window, NaAlH_4 and NaH only show elastic scattering. Therefore, the intermediate reaction product Na_3AlH_6 can be clearly identified from its strong quasielastic scattering, fitted in Fig. 1 by two Lorentzians.

In a good first approximation, the Lorentzians have temperature-independent amplitudes $a(q)$ and wavenumber-independent linewidths $\Gamma(T)$, which is the signature of localized processes. We see no scattering by long-ranged diffusion: Most probably, diffusion of H_2 is too fast and diffusion of heavier species is too slow to be observed within the dynamic window of SPHERES.

The temperature dependence of the $\Gamma(T)$ is compatible with an Arrhenius law, and at least for one of the

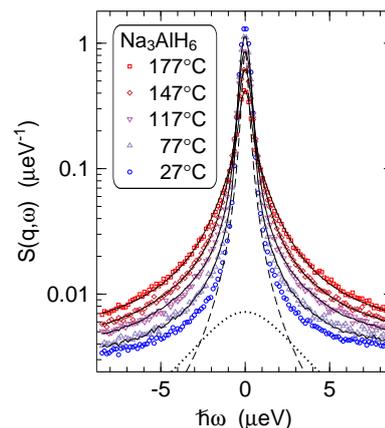


FIG. 1: Neutron scattering spectra of Na_3AlH_6 . The 27°C data represent the resolution function. The other data are fitted with a delta line and two Lorentzians, convoluted with the measured resolution. The dashed and the dotted line show the two Lorentzians for 117°C separately and in unconvoluted form.

two Lorentzians it is consistent with NMR observations of thermally activated rotational jumps of AlH_6 octahedra around C_4 axes in Na_3AlH_6 below room temperature (Fig. 2). On this base, the amplitude of the dominant Lorentzian can be used as a well understood measure of the amount of Na_3AlH_6 present in a transforming sample.

Time-resolved measurements were performed with four fresh NaAlH_4 samples. After measuring the resolution at room temperature, the sample was quickly heated to 170, 180, or 185°C , and kept there at constant temperature for 2 days or more. Initially, no quasielastic scattering is observed. It takes several hours before a quasielastic signal appears above the wings of the resolution function. The signal continues to grow, until a maximum is reached about 30 h after the start of the measurement. Then, the quasielastic intensity decreases and about 65 h after the start of the measurement we are left with purely elastic scattering, which however is only half as strong as in the beginning.

The time-resolved spectral data are binned in time slots covering 20 minutes each, and fitted with a delta line plus a Lorentzian with a fixed linewidths obtained for each experimental temperature from the Arrhe-

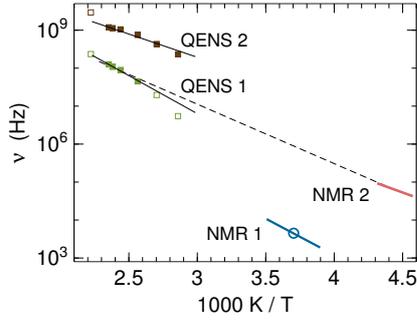


FIG. 2: Rotation frequencies in Na_3AlH_6 as determined by quasielastic neutron scattering (QENS) and by nuclear magnetic resonance (NMR) [4, 5]. The dashed line suggests that NMR 2 and QENS 1 are one and the same process.

nius law of Fig. 2, yielding the amplitudes shown in Fig. 3. Solid lines are fits with a quantitative kinetic model.

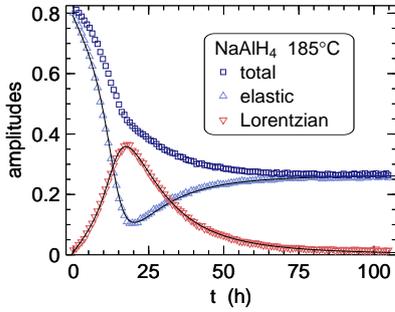


FIG. 3: Transformation of NaAlH_4 at 185°C : Total backscattering intensity I , fitted elastic amplitude a_δ , and fitted Lorentzian amplitude a_1 versus time. Solid lines are fits with a kinetic model described in the text.

We now abbreviate the two-step reaction (1), (2) as $A \rightarrow B \rightarrow C$, where A stands for NaAlH_4 , B for $1/3 \text{Na}_3\text{AlH}_6$, and C for NaH , ignoring side products that do not significantly contribute to the observed spectra. Writing concentrations as dimensionless mol/mol fractions, normalized to a pure NaAlH_4 sample, the initial composition is $[A] = 1$, $[B] = [C] = 0$. Since our scattering signal is almost exclusively due to bound hydrogen, we set

$$a_1(t) = \frac{1}{2}[B]f_B, \quad (3)$$

$$a_\delta(t) = [A]f_A + \frac{1}{4}[C]f_C, \quad (4)$$

where the f are Lamb-Mössbauer factors.

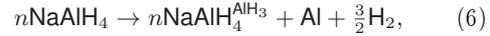
On this base, we searched for rate equations that reproduce the observed time series $a_1(t)$ and $a_\delta(t)$. It turned out that the relatively sharp peak in $a_1(t)$ can only be reproduced if some autocatalysis is assumed. To improve the agreement with the experimental $a_\delta(t)$ and $a_1(t)$, we admitted concentration dependences with fractional exponents. In this heuristic way, we found that the following simple ki-

netic model to be compatible with the measured amplitudes $a_\delta(t)$ and $a_1(t)$:

$$\begin{aligned} d[A]/dt &= -k_{00}[A] - k_{01}[A][B]^2, \\ d[B]/dt &= -d[A]/dt - d[C]/dt, \\ d[C]/dt &= k_{10}[B]^{4/3} + k_{11}[B]^{4/3}[C]^{2/3}, \end{aligned} \quad (5)$$

The exponents, multiples of $2/3$, are suggestive of an autocatalytic reaction at a surface; that k_{j0} stands for nucleation and k_{j1} for crystallite growth.

Our model is perfectly compatible with the reaction pathways proposed in a density-functional study [6]. Based on first-principles calculations, the migrating species were suggested to be AlH_3 and NaH vacancies. The lowest activation energy was found for AlH_3 vacancies, leading to the following pathway for reaction (1):



where the superscript denotes one vacancy, and n indicates an arbitrary amount of bulk material. The proposed diffusion mechanism also involves an AlH_5^{2-} ion. Anyway, the vacancy ultimately reaches a NaAlH_4 - Na_3AlH_6 boundary, where it annihilates, releasing an excess Na^+ that aggregates with the growing Na_3AlH_6 phase.

An alternate pathway starts with the unassisted release of Na^+ and H^- at the boundary of the growing Na_3AlH_6 according to



The two ionic vacancies migrate together to the Al - NaAlH_4 boundary, where hydrogen is released:



Using positron annihilation, it was confirmed experimentally that vacancies are formed in NaAlH_4 during dehydrogenation [7].

In these pathways, hydrogen release is limited by processes at boundaries: The NaAlH_4 - Na_3AlH_6 boundary as a sink for AlH_3 vacancies and as a source for NaH vacancies, and the Al - NaAlH_4 boundary as a sink for NaH vacancies and as the location of H_2 release. This is in accordance with the autocatalytic terms of our kinetic model.

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- [1] Bogdanović B and Schwickardi M (1997) *J. Alloys Comp.* **253**–254 71.
 - [2] Zaluski L, Zaluska A and Ström-Olsen J O (1999) *J. Alloys Comp.* **290** 71.
 - [3] Léon A and Wuttke J (2011) *J. Phys. Condensed Matt.* **23** 254214.
 - [4] Senegas J, Villepastour A M and Bonnetot B (1981) *J. Phys. Chem. Solids* **42** 1061.
 - [5] Verkuijlen M H W, van Bentum P J M, van Eck E R H, Lohstroh W, Fichtner M and Kentgens A P M (2009) *J. Phys. Chem. C* **113** 15467.
 - [6] Gunaydin H, Houk K N and Ozoliņš V (2008) *Proc. Natl. Acad. Sci. USA* **105** 3673.
 - [7] Sakaki K, Nakamura Y, Akiba E, Kuba M T and Jensen C M (2010) *J. Phys. Chem. C* **114** 6869.