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On the effect of thermal treatment and hydrogen vibrational dynamics in sodium alanates: An inelastic neutron scattering study

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ABSTRACT

We have measured inelastic neutron scattering (INS) spectra from Ti-doped polycrystalline alanates ($NaAlH_4$ and Na_3AlH_6), at low temperature, in the energy transfer range 3–500 meV, both for thermally treated and untreated samples. From the spectral range corresponding to the fundamental vibrational bands of these aluminohydrides, accurate one-phonon spectra and hydrogen-projected densities of phonon states have been extracted and analyzed using *ab initio* lattice dynamics calculations. Satisfactory agreement has been found for the untreated samples. In the case of thermally treated samples, due to thermal decomposition, different ionic species are present and the sample composition could be quantitatively evaluated. No evidence for the existence of intermediate species such as AlH_3 or AlH_5^{2-} has been found.

1. Introduction

The possibility of using hydrogen as an environmentally friendly and efficient fuel is very actively investigated [1,2], but an efficient way of storing hydrogen is still an unsolved problem. In fact, applications such as on-board storage for automotive uses or hydrogen fuelled portable electronics will require new materials that can store large amounts of hydrogen (more than 5 wt.%, H_2) at ambient, or close to ambient, temperature and relatively low pressures with small volume, low weight, and fast kinetics for charging/discharging. Metal hydrides [3] carbon-based nanomaterials (such as metal-doped carbon nanotubes) and MOFs have been studied [4], but there are still many problems associated with their practical implementation, including cost, low specific uptake, unfavorable thermodynamics and/or kinetics etc. Binary ionic hydrides of the elements of groups 1, 2 and 13 such as $M(EH_4)_x$, (M = Li, Na, K, Mg or Ca, and E = Al or B) have been studied as promising materials. In particular, sodium alanates (*i.e.* $NaAlH_4$ and Na_3AlH_6) have attracted a great deal of interest since Bogdanović and Schwickardi [5] have shown that the hydrogenation reaction can be kinetically enhanced and rendered reversible, under mild conditions, after doping with transition metal halides such as MX_3 (M = Ti, Zr, Co, Ni, or Fe; X = F, Cl, or I). The relevant reversible reactions involved in the process are:

$$3NaAlH_4 \leftrightarrows Na_3AlH_6 + 2Al + 3H_2(3.7\,wt.\%) \quad (I)$$

$$Na_3AlH_6 \leftrightarrows 3NaH + Al + 3/2H_2(1.8\,wt.\%) \quad (II)$$

These reactions occur at moderate pressures ($p < 100$ bar) and temperatures ($T < 438$ K), so the doped $NaAlH_4$-plus-Na_3AlH_6 system exhibits characteristics not too far from those required for practical applications. However, much work is still necessary to improve the storage properties of the alanates, and to this aim a detailed understanding of the H_2 absorption/desorption process is crucial. A microscopic mechanism of the catalytic processes in Ti-doped $NaAlH_4$ has been recently suggested [6–8], but not yet experimentally validated. Moreover, recent "anelastic relaxation" measurements [9] have shown that after thermal activation (at temperatures in the range 370–436 K) a new species appears in Ti-doped sodium alanates (and to a very much less extent also in those undoped). This species gives rise to a thermally activated relaxation at $T \approx 70$ K and $\nu = 1$ kHz, with an activation energy of $E = 0.126$ eV, and a pre-exponential factor of $\tau = 7 \times 10^{-14}$ s, typical values for a point-defect relaxation. This reactive species shows a fast dynamics and, according to the deuterium isotopic effect found, involves hydrogen. These observations are consistent with the formation, upon thermal treatment, of a distorted octahedral defect of type AlH_x^{n-} ($x < 6$), causing a local vacancy dynamics. The formation of such defects appears to be catalyzed by the presence of the Ti dopant [9].

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Table 1
Sample description, including doping amount, thermal treatment temperature, experimental temperature T, Integrated Proton Current (IPC), and mass. One hour of counting time corresponds approximately to 150 μA h IPC.

#	Sample	Ti doping (mol.%)	Thermal treat. (K)	T (K)	IPC (μA h)	Mass (mg)
1	$NaAlH_4$	4	–	16 (2)	543.7	762
2	$NaAlH_4$	4	435	16 (2)	453.1	698
3	Na_3AlH_6	4	–	16 (2)	818.8	725
4	Na_3AlH_6	4	435	16 (2)	1146.3	811

The present work aims at extending the microscopic investigation of the effect of the thermal treatment on the proton dynamics in doped $NaAlH_4$ and Na_3AlH_6, (before and after thermal treatment) by using high-resolution inelastic neutron scattering (INS). Compared to Raman and infrared spectroscopy, INS allows, more easily and reliably, the separation of the various contributions stemming from different atoms. Moreover, neutron vibrational mode intensities can be accurately reproduced by lattice dynamics simulations [10].

Previously, inelastic neutron scattering studies have been performed on $NaAlH_4$ (pure and 2% Ti-doped) and on Na_3AlH_6 [11], with an energy resolution of 2–4.5% in the energy transfer range (50–250) meV; an INS study on $NaAlH_4$ was also carried out by Fu et al. [12], using a larger energy transfer range (3 meV < E < 500 meV) and greater energy resolution (1.5–3%). While the former work has been aimed at providing some microscopic understanding of the role of the Ti-additive in $NaAlH_4$ and its specific occurrence in the material, the latter work has been mainly focused on the spectral modifications of doped samples after several H_2 charging/discharging cycles of $NaAlH_4$ only. In contrast, our work is focused on the search for spectral evidences for the H-containing extra-species or defect structures responsible for the observations by "anelastic relaxation" experiments [9] after thermal treatment of both $NaAlH_4$ and Na_3AlH_6. Additionally, some essential improvements of the instrumentation used regarding resolution, background levels and sensitivity have been achieved since the previous work [12].

2. Experiment description

The neutron scattering measurements were carried out on the TOSCA-II inelastic spectrometer at the ISIS neutron source. TOSCA-II is a crystal-analyzer inverse-geometry spectrometer [13] spanning a broad energy range transfers ($E = E_0 - E_1$, 3 meV < E < 500 meV), with an energy resolution $\Delta E/E_0 \cong 1.5$–3%.

Special care was taken to prevent possible wetting and decomposition of the alanates, during the sample loading, in a flat Al scattering-cell that was performed in a glove box under He atmosphere. Four samples were used for the data collections:

(1) $NaAlH_4$, recrystallized from tetrahydrofuran, and doped with 4 mol.% TiF_3 by ball milling (30 min at 350 rpm) [14].
(2) $NaAlH_4$, recrystallized from tetrahydrofuran, doped with 4 mol.% TiF_3 by ball milling (30 min at 350 rpm), and thermally treated (1 h at T = 435 K).
(3) Na_3AlH_6, produced and purified via the standard Huot et al. method [15], and doped with 4 mol.% TiF_3 by ball milling (30 min at 350 rpm).
(4) Na_3AlH_6, produced and purified via the standard Huot et al. method [15], doped with 4 mol.% TiF_3 by ball milling (30 min at 350 rpm), and thermally treated (1 h at T = 435 K).

The most important experimental details are given in Table 1; further details on the synthesis, purification and treatment can be found in Ref. [14]; the phase purity of all untreated samples was checked by X-ray powder diffraction using part of each sample batch. Before the neutron data collection, the empty cell was cooled down to the temperature of the experiment: (16 ± 2 K). The INS spectra of the four samples were then measured in the same conditions. The experimental time-of-flight spectra were transformed into energy transfer data by using the standard TOSCA-II data reduction routines. Further details are given in Appendix A.

The resulting INS spectra, proportional to $S(Q,E)$, are reported in Fig. 1.

3. Computational details

Periodic density functional theory calculations were carried out using a plane wave basis-set and pseudopotentials as implemented in the CASTEP code [16–18] The PBE [19] version of the localized density approximation within DFT was used in conjunction with optimized norm-conserving pseudopotentials. The Brillouin zone sampling for the electronic calculations used a 3 × 3 × 2 grid of k-points generated using the Monkhorst–Pack method. A full geometry optimization (with a plane-wave cut-off energy of 770 eV) of the internal atomic co-ordinates was performed to reduce the residual atomic forces to less than 1.5 meV/Å. This procedure converged to the following lattice cell parameters: a = 5.038 Å, c = 11.300 Å for $NaAlH_4$ and a = 5.413 Å, b = 5.546 Å, c = 7.765 Å, β = 89.87° for Na_3AlH_6. These values are in agreement with those obtained by powder diffraction [20] for tetragonal $NaAlH_4$ (a = 5.02508(6) Å, c = 11.3571(2) Å) and for monoclinic Na_3AlH_6 (a = 5.4145(3) Å, b = 5.5402(3) Å, c = 7.7620(4) Å, β = 89.871(4)°).

Phonon modes were calculated using density functional perturbation-theory [16,21] on a 5 × 5 × 3 grid to calculate the dynamical matrix; the Brillouin zone was sampled on a 9 × 9 × 6 grid, using the interpolation algorithm included in CASTEP to obtain a smooth density of phonon states and calculated spectra as described in [10]. The INS spectrum was generated using the program ACLIMAX [22]. Calculations were performed on the complete unit cell using the experimentally determined structural data as input [20]. The corresponding calculated INS spectra are shown together with their experimental counterparts in Fig. 2. The excellent agreement between theory and experiment further confirms the phase purity of the untreated samples.

4. Discussion

The neutron spectra from Ti-doped $NaAlH_4$ and Na_3AlH_6 (see Fig. 1, spectra #1 and #3) may be compared with the results reported in the energy transfer range 35 meV < E < 250 meV in Ref. [11]. Despite an evident similarity in the band positions and intensities, some care is needed in comparing the spectra, since the two

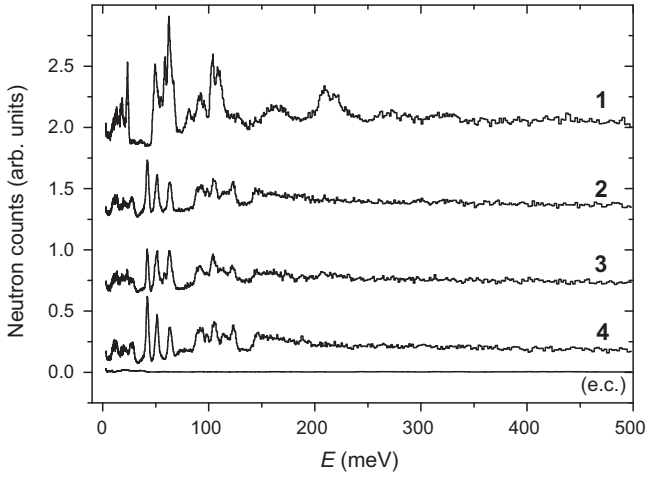

Fig. 1. Examples of raw neutron spectra from samples #1, #2, #3 and #4 as from Table 1 plus the empty cell (e.c.), all recorded in backscattering at T = 16 K. Spectra have been vertically shifted.