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NEUTRON SCATTERING STUDIES ON DOPED AND UNDOPED SODIUM ALANATES

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Sodium alanate, $NaAlH_4$, may be a good candidate[1,2] as a hydrogen-storage material, based on the reversible (after Ti doping) decomposition reaction:

$$NaAlH_4 \rightleftharpoons \frac{1}{3} Na_3AlH_6 + \frac{2}{3} Al + H_2 \qquad Na_3AlH_6 \rightleftharpoons 3\,NaH + Al + \frac{3}{2} H_2$$

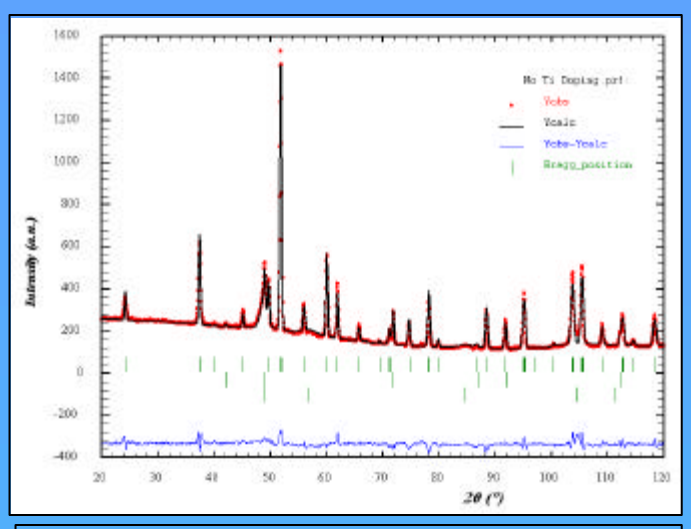
There is much disagreement on the issue of the location of the Ti dopant[3,4] and we have carried out elastic (powder diffraction) and incoherent inelastic neutron scattering experiments to look for differences between doped and undoped alanate samples (both for $NaAlH_4$ and Na_2AlH_6)

Neutron Powder Diffraction Data

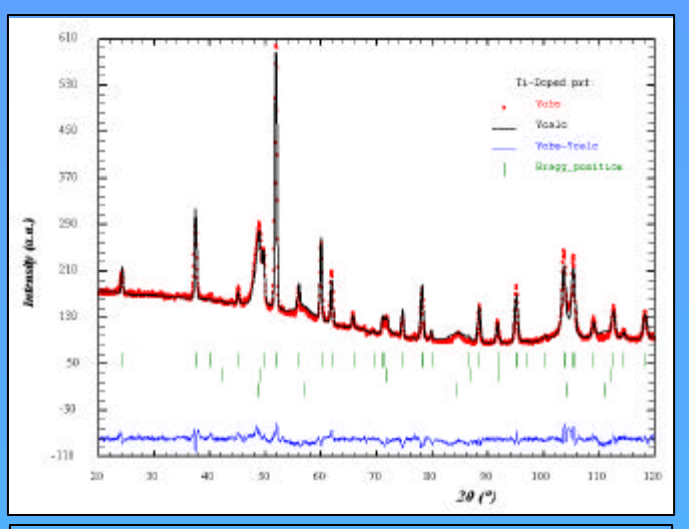
Collected on D1A (ILL, France)
***T* = 5K**

Undoped $NaAlD_4$
2 mol % $TiCl_3$-Doped $NaAlD_4$
Peak Shape Profile: Pseudo-Voigt
Spherical Harmonics Particle Size and Anisotropic Strain Broadening Parameters Refined

2 mol % Ti Added in a General Position
All Refinements Fail or Give Nonsensical Parameter Values



$NaAlD_4$ Bragg R-Factor = 11.1
a = 4.9712 (9) Å, c = 11.1354 (4) Å
B_{iso} / Å² : Na = 0.60, Al = 0.57, D = 1.87



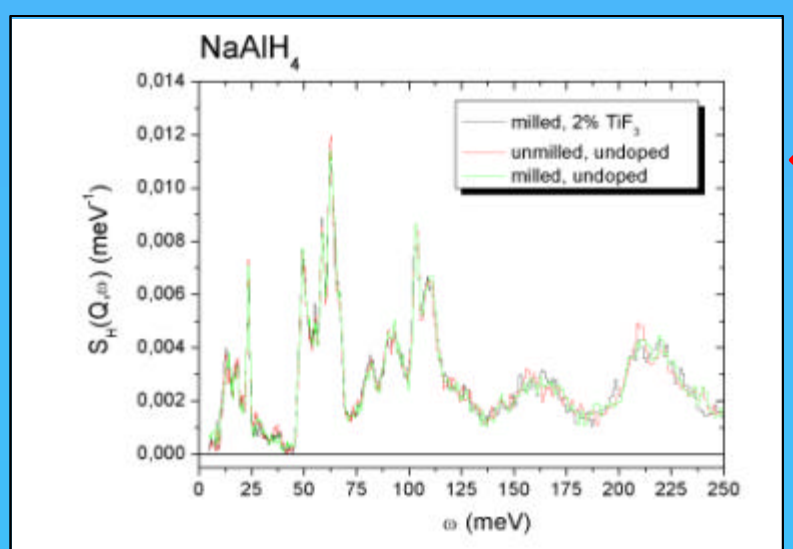
$NaAlD_4$ Bragg R-Factor = 10.8
a = 4.9729 (1) Å, c = 11.1337 (6) Å
B_{iso} / Å² : Na = 0.37, Al = -0.1, D = 1.97

Conclusions

No evidence for titanium atoms being located in a general position
Experimental data slightly favor Ti in the Al position

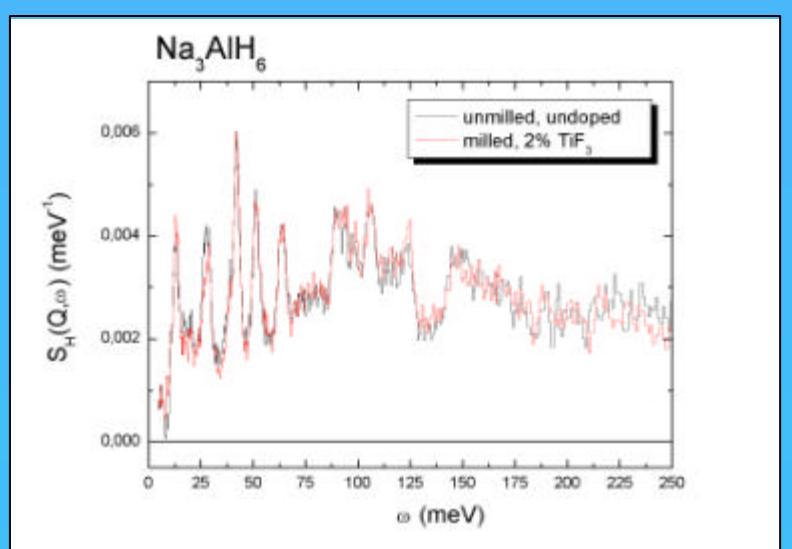
Incoherent Inelastic Neutron Scattering

Collected on TOSCA (ISIS, UK)
***T* = 20 K**



Undoped $NaAlH_4$
2 mol % TiF_3-doped $NaAlH_4$

Undoped Na_3AlH_6
2 mol % TiF_3-doped Na_3AlH_6



Conclusions

The measured IINS spectra are characterized by a very high resolution and quality. No evidence of significant band shifts and distortions, upon doping or milling, is observed. This finding may be compatible with recent *ab-initio* results[5] predicting Ti to stay preferentially on the surface. Further data analysis and dynamical simulations are in progress.

[1] J. Íñiguez, T. Yildirim, T. J. Udovic, M. Sulic & C. M. Jensen (2004). Phys. Rev. B 70, 060101-1.
[2] B. Bogdanovic & M. Schwickardi (1997). J. Alloys Compd. 253, 1.
[3] H. W. Brinks, C. M. Jensen, S. S. Srinivasan, B. C. Hauback, D. Blanchard & K. Murphy (2004). J. Alloys Compd. 376, 215 and references therein.
[4] D. L. Sun, T. Kiyobayashi, H. T. Takeshita, N. Kuriyama & C. M. Jensen (2002). J. Alloys Compd. 337, L8.
[5] J. Íñiguez, T. Yildirim, (2005). Appl. Phys. Lett. 86, 103109.