Multi-phonon scattering and Ti-induced hydrogen dynamics in sodium alanate

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Outline

• Methods
  • Neutron scattering by (multiple) phonons
  • First-principles calculations of vibrational properties

• Structure and hydrogen dynamics of pure and Ti-doped NaAlH$_4$
Scattering function \( S(Q, \omega) \)

\[
\frac{d^2 \sigma}{d \Omega d E'} = \frac{\sigma}{4\pi} \frac{k'}{k} N S(Q, \omega) = \text{elast} + 1\text{-ph} + 2\text{-ph} + \ldots
\]

\[
Q = k' - k \quad \hbar \omega = E - E'
\]
Multiple scattering vs. multiple phonon

\[ S_{\text{total}}(Q, \omega) \approx f_1 S(Q, \omega) + f_2 \int d\omega' dQ' S(Q', \omega') S(Q-Q'; \omega-\omega') + \ldots \]

\( f_n \) : ratio of processes in which the neutron scatters \( n \) times before leaving the sample

**NOTE**

\( S(Q, \omega) \) ← multiple-phonon is always there!

\( f_n 's \) If \( f_1 \gg f_2, f_3, \ldots \) we can neglect multiple-scattering
Two-phonon peak
$S(Q,\omega)$ for a non-Bravais system: the formulas

\[
\left( \frac{d^2 \sigma}{d\Omega dE'} \right)_{\text{inc, el}} = \frac{k'}{k} \frac{N}{2\pi \hbar} \sum_d \{b_d^2 - \overline{b_d}^2\} \exp \{-2W_d\} 2\pi \delta(\omega)
\]

All we need from the \textit{ab initio} calculations is

- Phonon frequencies \{\omega_s\} \rightarrow g(\omega)
- Phonon eigenvectors \{e_{ds}\}

\[
\left( \frac{d\Omega dE'}{d\Omega dE'} \right)_{\text{inc, } +2} = \frac{9r^2 N}{k \hbar} \sum_d \{b_d^2 - \overline{b_d}^2\} \exp \{-2W_d\} \frac{(2M_d)^2}{(2M_d)^2}
\]

\[
\times \omega^2 \int_0^\omega \frac{f_d(\hat{Q}, \omega')}{\omega'} \frac{f_d(\hat{Q}, \omega - \omega')}{\omega - \omega'} d\omega'
\]
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DENSITY FUNCTIONAL THEORY

INPUT:
Atomic numbers and positions

First-principles calculations
Kohn-Sham method
Original unsolvable problem replaced by a simple one of non-interacting electrons

\[
\left( -\frac{1}{2} \nabla^2 + V_{\text{eff}}(r) \right) \psi_i(r) = \varepsilon_i \psi_i(r)
\]

\[
n(r) = \sum_i |\psi_i(r)|^2
\]

\[
V_{\text{eff}}(r) = \varepsilon_{\text{ext}}(r) + \int \frac{n(r')}{|r - r'|} d\mathbf{r}' + V_{XC}(r)
\]

\[
V_{XC}(r) = \frac{\delta E_{XC}[n]}{\delta n}
\]

Energies and forces → structural and dynamical properties
Computing phonons from first-principles
(finite differences approach)

• Start from best available guess of the structure

• Relax structure until forces on atoms and stresses are zero
  (i.e., negligibly small) $\rightarrow$ equilibrium (reference) structure

• Compute forces $f_{j\beta}$

  Then: $\Phi_{i\alpha,j\beta} = -f_{j\beta} / u_{i\alpha}$

$$E(\{u_{i\alpha}\}) = E_{eq} + \frac{1}{2} \sum_{i\alpha,j\beta} \frac{\partial^2 E}{\partial u_{i\alpha} \partial u_{j\beta}} u_{i\alpha} u_{j\beta} + ...$$

$$D_{i\alpha,j\beta} = \frac{1}{\sqrt{m_i m_j}} \Phi_{i\alpha,j\beta}$$
Using these ideas you can...

- Compute the entire phonon spectrum of a crystal
- Play tricks, e.g., to compute the vibrational modes of an atom cluster embedded in a solid

We can compute the modes associated with a single AlH₄ group

Substitute one Na atom by a dopant Ti atom and recompute the modes of the AlH₄ group

NaAlH₄
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- **Structure and hydrogen dynamics of pure and Ti-doped NaAlH$_4$**
NaAlH$_4$: A good candidate for reversible hydrogen storage

Two-step reversible solid-state reaction

\[
\text{NaAlH}_4 \leftrightarrow \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2 \ (3.7 \text{ wt\%}),
\]

\[
\text{Na}_3\text{AlH}_6 \leftrightarrow 3 \text{NaH} + \text{Al} + \frac{3}{2} \text{H}_2 \ (1.8 \text{ wt\%}),
\]

- Total of 5.6 wt\% reversible hydrogen storage
- Reactions occur at $\sim$ 100°C, and are relatively slow
- With small Ti doping ($\sim$ 1 mol.\%) reaction rates increase dramatically!
Current status

• Despite extensive investigation, role of Ti is still unknown
• Even the location of the Ti atoms remains unclear!
• Very small amount of Ti involved
  → Very difficult to track experimentally

Very difficult for theory too!

• Realistic \textit{ab initio} MD simulations? Pretty much impossible to do
• Force-field models? Do not work here
Our approach

- Neutron study of the phonon DOS of pure and Ti-doped NaAlH$_4$
- \textit{Ab initio} calculations of the phonon DOS of pure NaAlH$_4$
- Assume the Ti dopant is in the bulk and study:
  - where it is located
  - how it affects the dynamics of neighboring H atoms (to be compared with experiment)
  - induced atomic rearrangements (can Ti break bonds?)
Excellent agreement between theory and experiment

Thanks to calculations, unusually sharp two-phonon scattering identified

Measured (top) and calculated (bottom) NIS spectra of NaAlH₄. The calculated 1 and 1+2 phonon contributions are shown.
Measured (top) and calculated (bottom) NIS spectra of Na$_3$AlH$_6$. The calculated 1 and 1+2 phonon contributions are shown.
Calculated one-phonon NIS spectrum for (a) NaAlH$_4$ and for a single MH$_4$ tetrahedron embedded in the lattice for various cases: (b) pure alanate, (c) Ti → Na, and (d) Ti → Al.
Where does Ti go?

1. It is energetically favorable for Ti to go into the bulk of NaAlH₄

2. Ti prefers to substitute for Na rather than for Al

3. When substituting for Na, Ti drags neighboring H atoms and breaks the corresponding H--Al bonds!

4. It is energetically favorable for Ti to drag extra H atoms into the system

→ Idea: Try to produce a new material, sodium-titanium alanate, that might exhibit better H-storage capabilities
Summary

- First-principles & NIS study of pure and Ti-doped sodium alanate

- Pure alanate: good agreement between theory and experiment for the phonon spectrum; unusually sharp two-phonon features

- Doped alanate: neutrons do not see the changes in the H dynamics that the calculations predict
  → try high resolution spectroscopic techniques
  → maybe Ti is not in the bulk of the system?

- Energetically possible for Ti to go into the bulk of the system
  → Ti prefers to substitute for Na
  → Powerful hydrogen attractor; breaks H--Al bonds
  → Energetically favorable for Ti to drag extra H's into the system
What's next?

- First-principles molecular dynamics of the doping process
  → consider NaAlH$_4$ surface in the presence of Ti dopant

- Popular doping technique: “dry” ball milling with TiCl$_3$
  → Cl and Na form NaCl
  → H$_2$ is released
  → solid Al is deposited
  → part of the NaAlH$_4$ transforms into Na$_3$AlH$_6$
  → Formation of a TiAl alloy ??

No way we can simulate that in a computer !!!!
If the real thing is impossible, go for something easier

• Simplified doping models → surface in the presence of: TiCl₃ molecule, Ti atom (w/ and w/o Na vacancies), ...

• Ask easy questions:
  → Does the Ti atom stay on the surface or get into the bulk?
  → Surface melts at about 100°C: compare pure vs. doped
  → Does the dopant lower the temperature at which H₂ is released? What is the mechanism?