

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

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In collaboration with

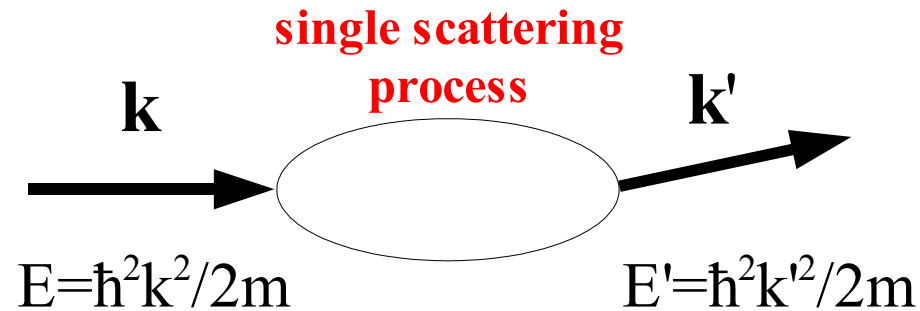
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[cond-mat/0401161](https://arxiv.org/abs/cond-mat/0401161)

Outline

- **Methods**
 - Neutron scattering by (multiple) phonons
 - First-principles calculations of vibrational properties
- **Structure and hydrogen dynamics of pure and Ti-doped NaAlH₄**

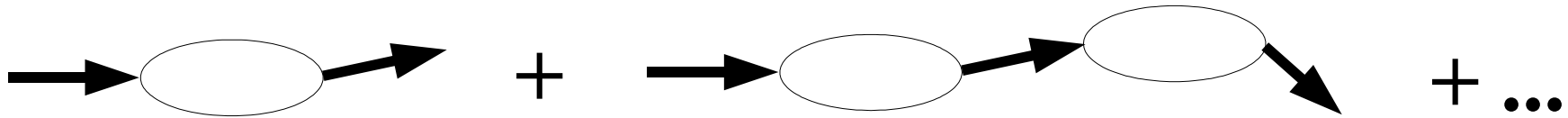
Scattering function $S(\mathbf{Q}, \omega)$



$$\frac{d^2\sigma}{d\Omega dE'} = \frac{\sigma}{4\pi} \frac{k'}{k} N S(\mathbf{Q}, \omega) = \text{elas} + 1\text{-ph} + 2\text{-ph} + \dots$$

$$\mathbf{Q} = \mathbf{k}' - \mathbf{k} \quad \hbar\omega = E - E'$$

Multiple scattering vs. multiple phonon



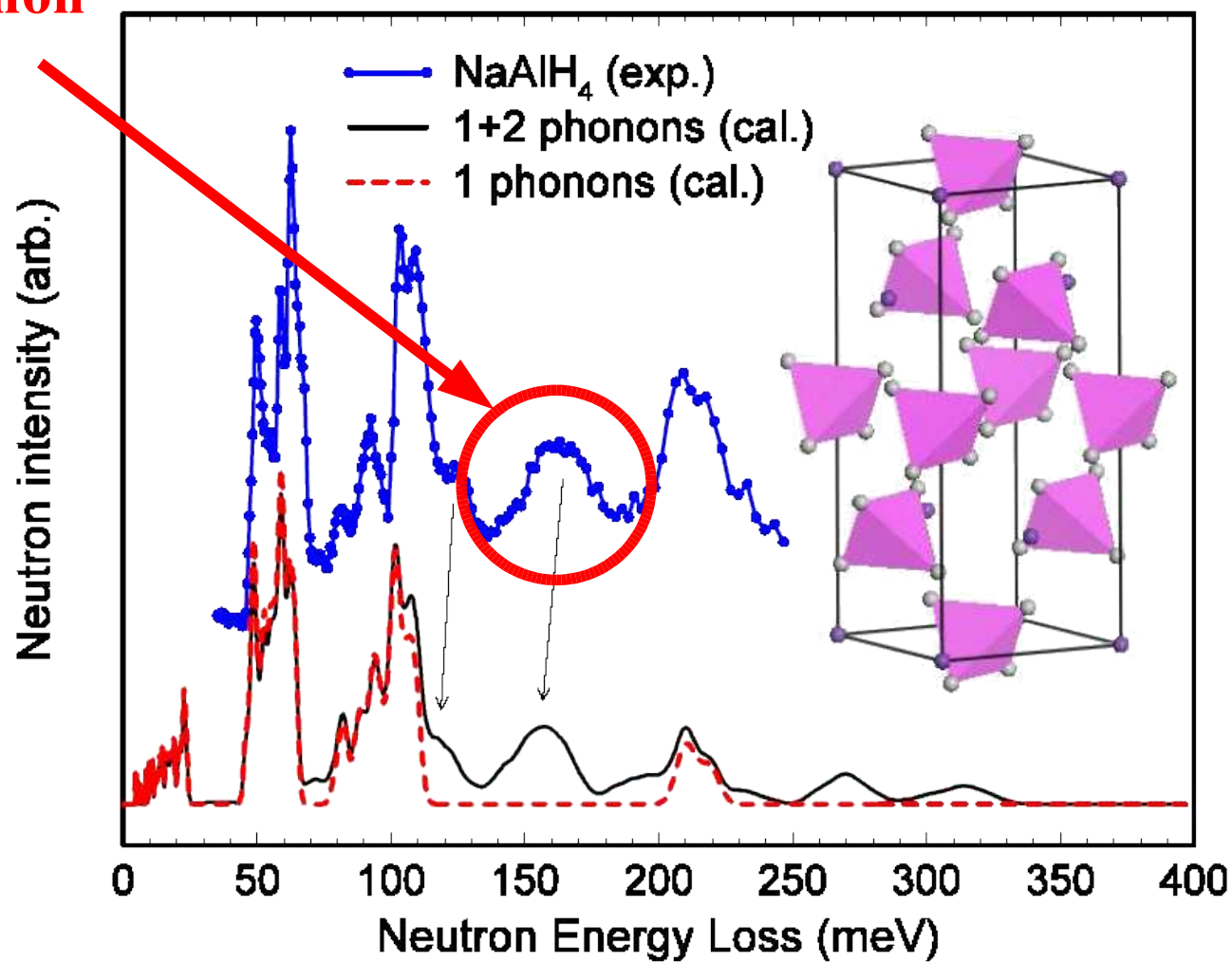
$$S^{\text{total}}(\mathbf{Q}, \omega) \simeq f_1 S(\mathbf{Q}, \omega) + f_2 \int d\omega' d\mathbf{Q}' S(\mathbf{Q}', \omega') S(\mathbf{Q} - \mathbf{Q}'; \omega - \omega') + \dots$$

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

NOTE $S(\mathbf{Q}, \omega)$ ← **multiple-phonon is always there!**

f_n 's If $f_1 \gg f_2, f_3, \dots$ we can neglect multiple-scattering

**Two-phonon
peak**



$S(\mathbf{Q}, \omega)$ for a non-Bravais system: the formulas

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

All we need from the *ab initio* calculations is

- Phonon frequencies $\{\omega_s\} \rightarrow g(\omega)$
- Phonon eigenvectors $\{\mathbf{e}_{ds}\}$

$$\begin{aligned} \left(\frac{d^2 \sigma}{d\Omega dE'} \right)_{\text{inc, +2}} &= \frac{1}{k} \frac{1}{\hbar} 9r^2 N \sum_d \{ \overline{b_d^2} - \overline{b_d}^2 \} \exp \{ -2W_d \} \frac{1}{(2M_d)^2} \\ &\times \omega^2 \int_0^\omega \frac{f_d(\hat{\mathbf{Q}}, \omega')}{\omega'} \frac{f_d(\hat{\mathbf{Q}}, \omega - \omega')}{\omega - \omega'} d\omega' \end{aligned}$$

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- Neutron scattering by (multiple) phonons

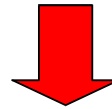
- **First-principles calculations of vibrational properties**

- **Structure and hydrogen dynamics of pure and Ti-doped NaAlH₄**

DENSITY FUNCTIONAL THEORY

INPUT:

Atomic numbers and positions



First-principles calculations
Kohn-Sham method

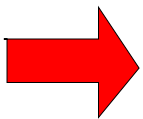
Original *unsolvable* problem
replaced by a *simple* one of
non-interacting electrons

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

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

$$V_{eff}(\mathbf{r}) = v_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{XC}(\mathbf{r})$$

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



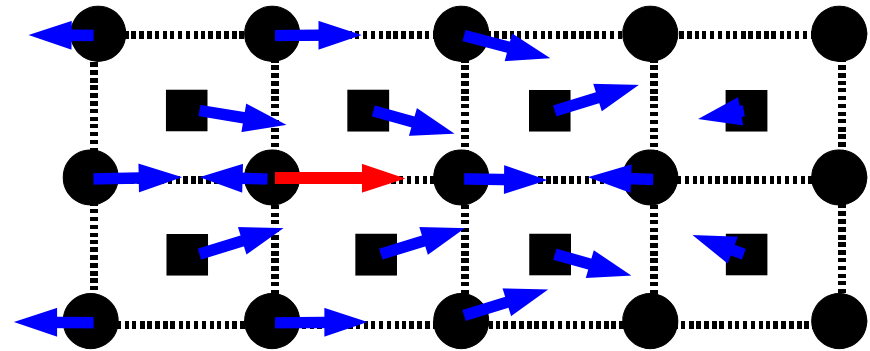
Energies and forces → structural and dynamical properties

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) → equilibrium (reference) structure

- Compute forces $f_{j\beta}$

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



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

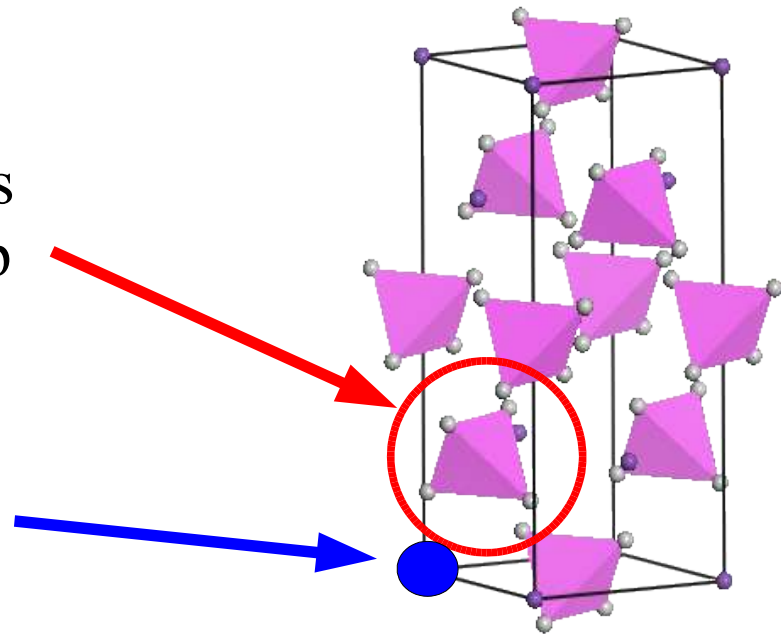
$$D_{i\alpha,j\beta} = \frac{1}{\sqrt{m_i m_j}} \Phi_{i\alpha,j\beta}$$

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 AlH_4 group

Substitute one Na atom by a dopant Ti atom and recompute the modes of the AlH_4 group



Outline

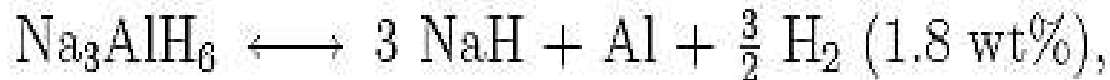
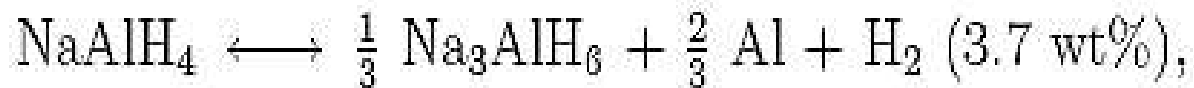
- **Methods**

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

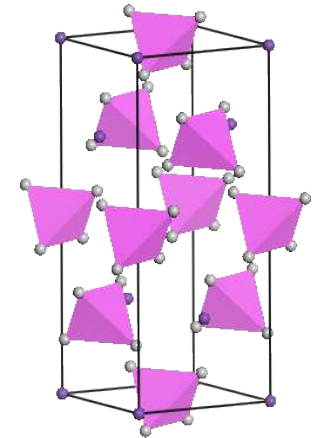
- **Structure and hydrogen dynamics of pure and Ti-doped NaAlH₄**

NaAlH₄: A good candidate for reversible hydrogen storage

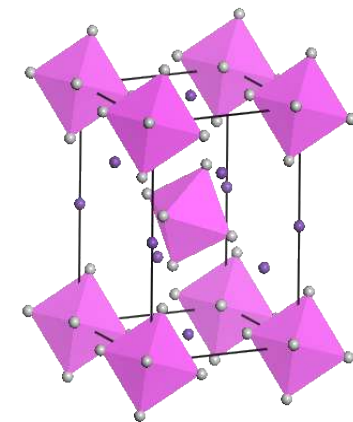
Two-step **reversible** solid-state reaction



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



NaAlH₄



Na₃AlH₆

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

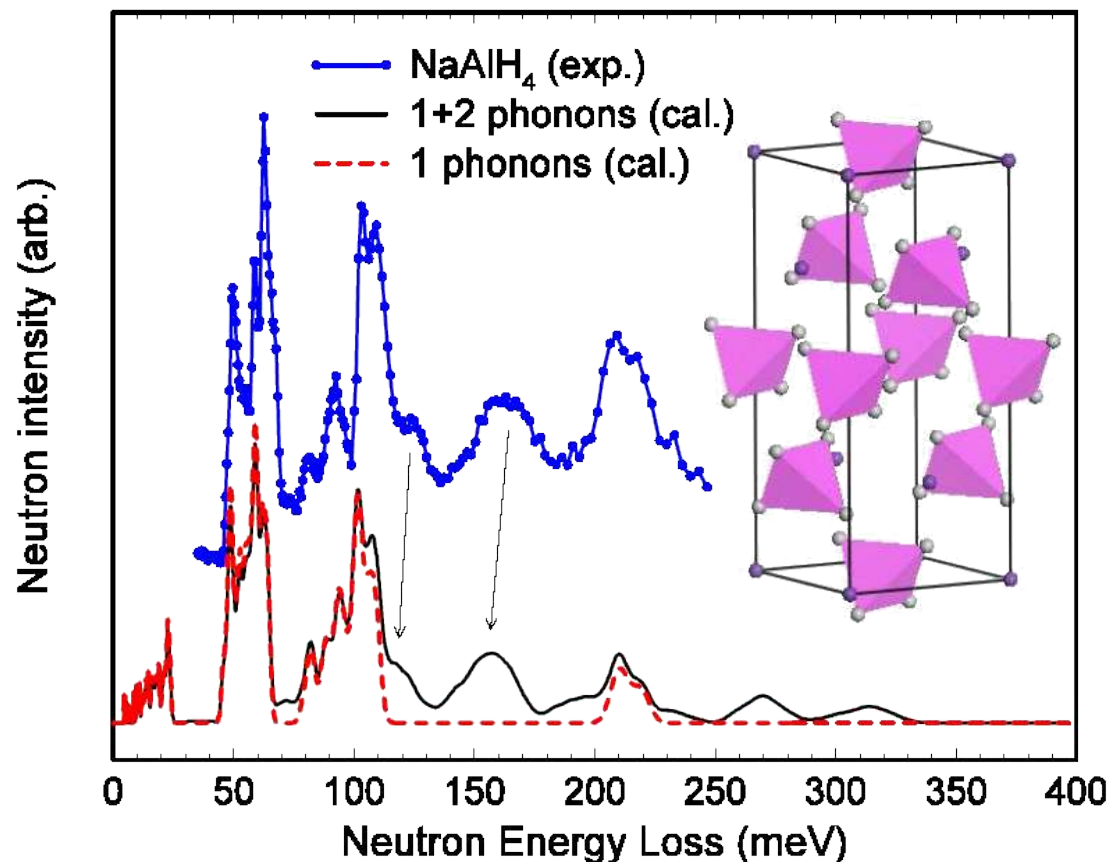
Very difficult for theory too!

- Realistic *ab initio* MD simulations? Pretty much impossible to do
- Force-field models? Do not work here

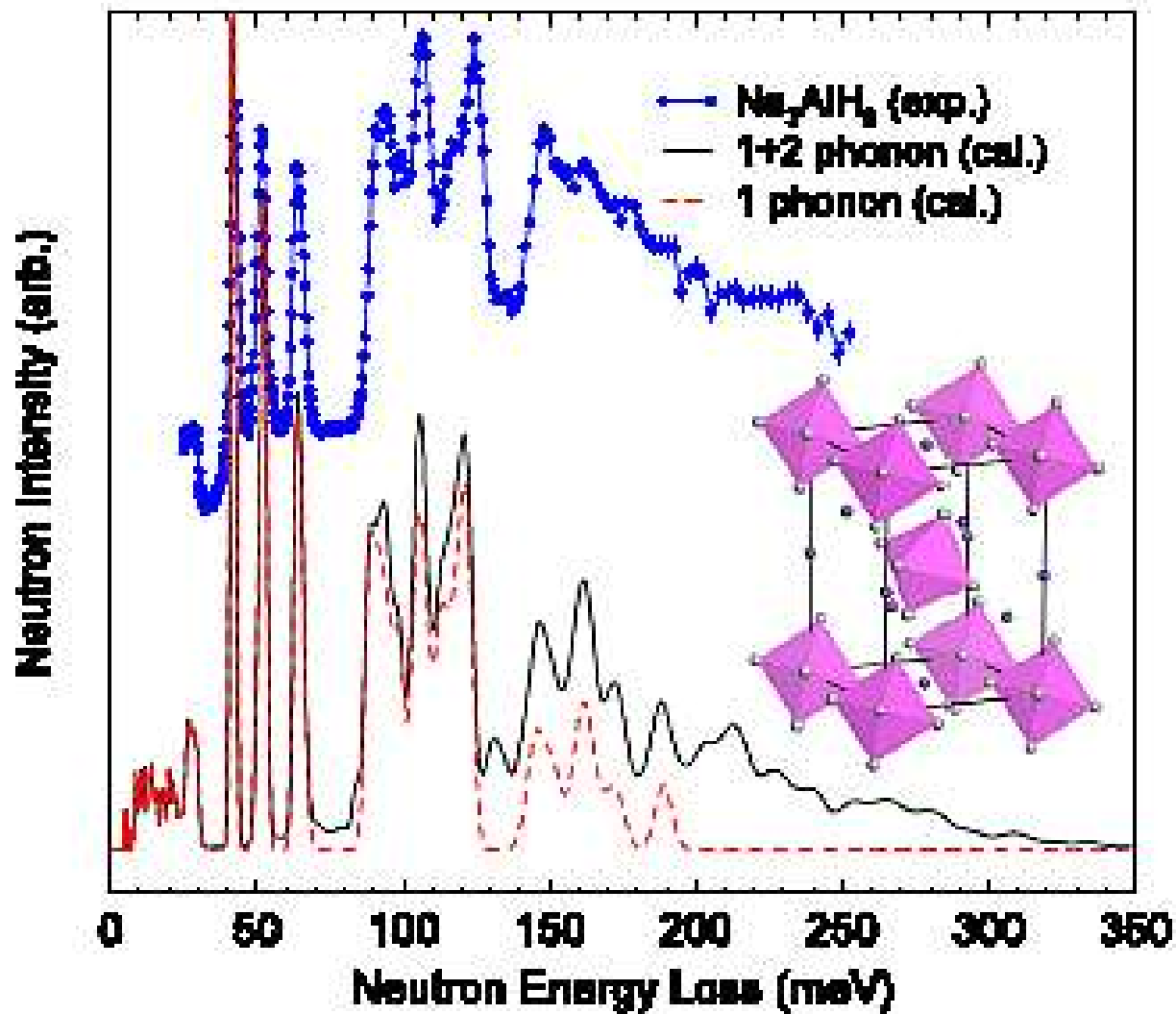
Our approach

- Neutron study of the phonon DOS of pure and Ti-doped NaAlH₄
- *Ab initio* calculations of the phonon DOS of pure NaAlH₄
- **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?)

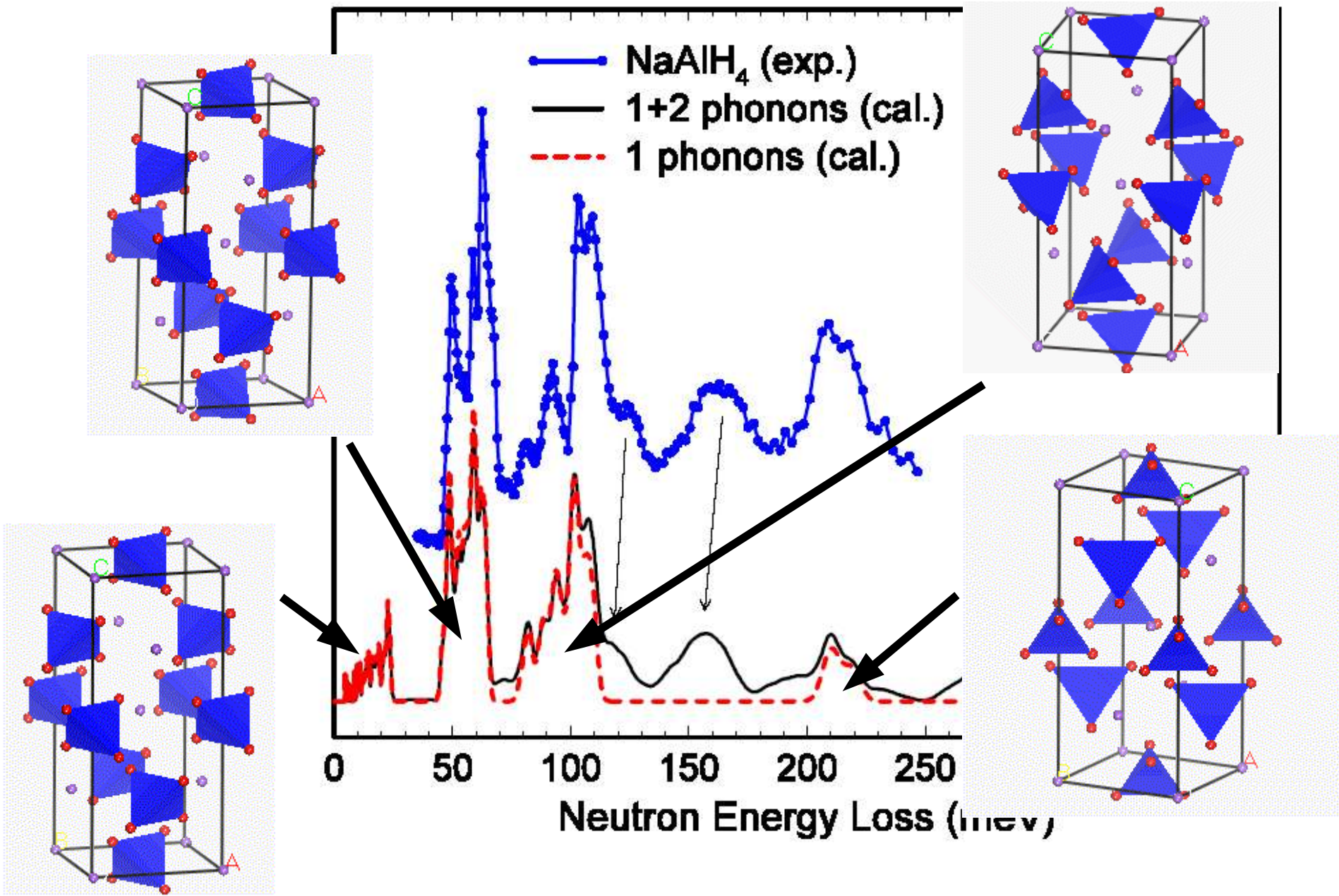
Measured (top) and calculated (bottom) NIS spectra of NaAlH₄. The calculated 1 and 1+2 phonon contributions are shown.

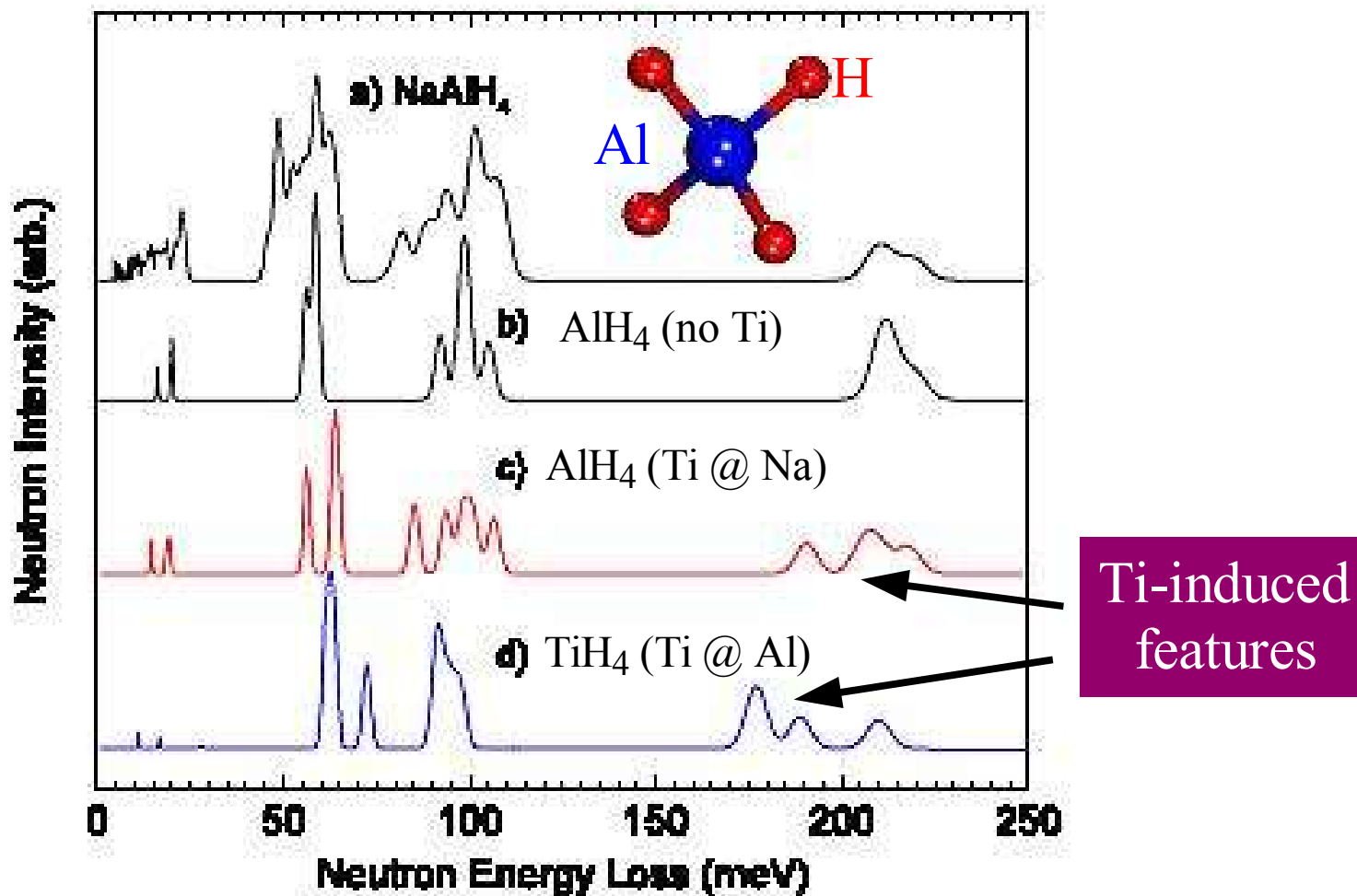


- Excellent agreement between theory and experiment
- Thanks to calculations, unusually sharp two-phonon scattering identified



Measured (top) and calculated (bottom) NIS spectra of Na_3AlH_6 . The calculated 1 and 1+2 phonon contributions are shown.





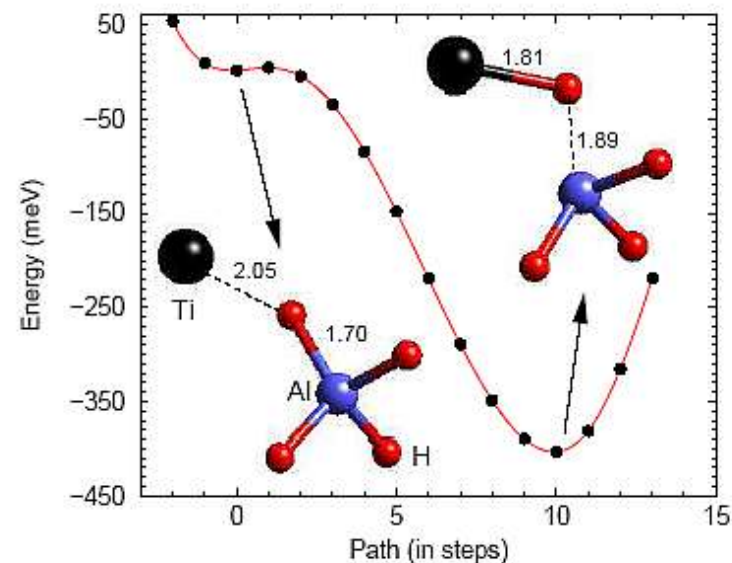
Calculated one-phonon NIS spectrum for (a) NaAlH₄ and for a single MH₄ tetrahedron embedded in the lattice for various cases: (b) pure alunate, (c) Ti → Na, and (d) Ti → Al.

Where does Ti go?

1. It is energetically favorable for Ti to go into the bulk of NaAlH_4
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_3AlH_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?