

Hydrogen absorption and desorption reactions of hydrides studied by neutron diffraction and inelastic neutron scattering

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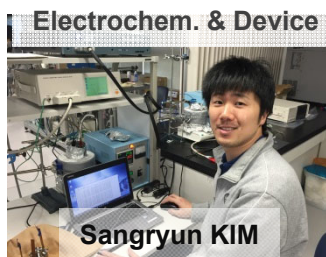
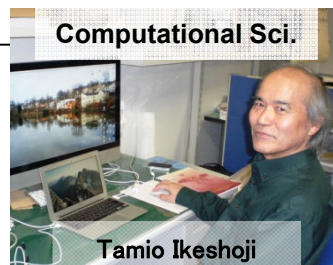
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Our research group

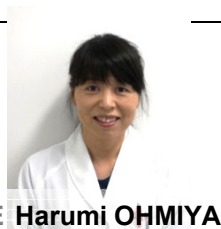
Head



Research Staff



Technical Staff



Students

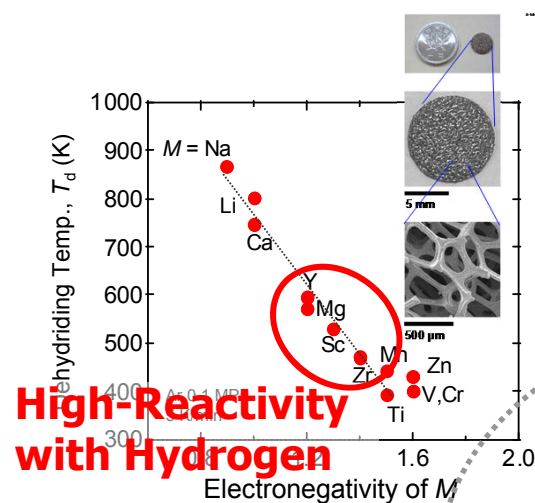
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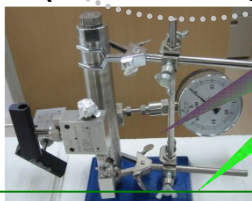
Our research activities

Hydrogen Energy Storage

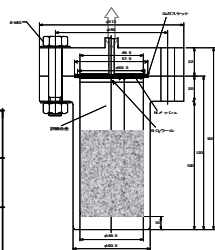


**High-Reactivity
with Hydrogen**

“Perovskite”
Hydride
(e.g. NaMgH_3)



**Fundamentals
(Synthesis and Characterization)**

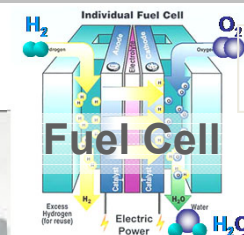
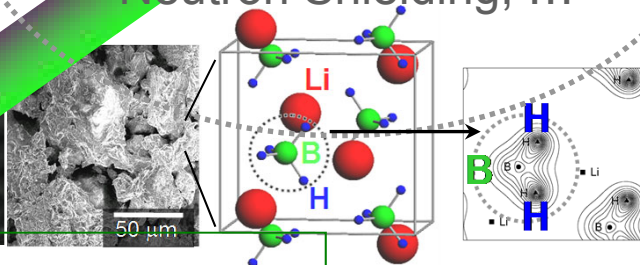


Elemental
Hydride
(e.g. AlH_3)



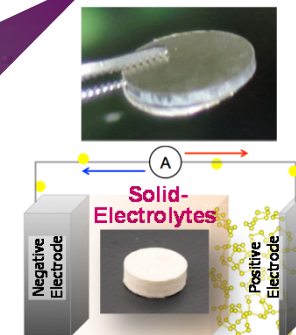
Complex Hydride
(e.g. $M(\text{BH}_4)_n$)

Ionic Conduction,
Microwave Absorption,
Neutron Shielding, ...

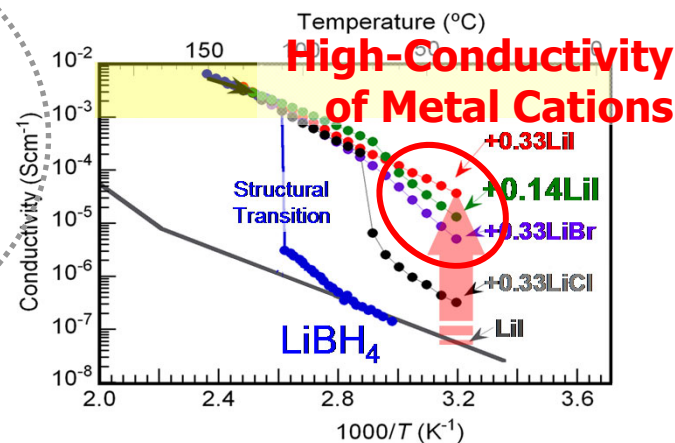


Metal Hydride
(e.g. LaNi_5H_6)
“Ni-MH” Reaction

Energy Devices



Li/Na/Mg-Ion Battery



**High-Conductivity
of Metal Cations**

**Electrochemical
Energy Storage**

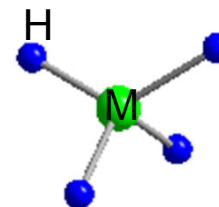
Summary

Complex hydrides as hydrogen storage materials

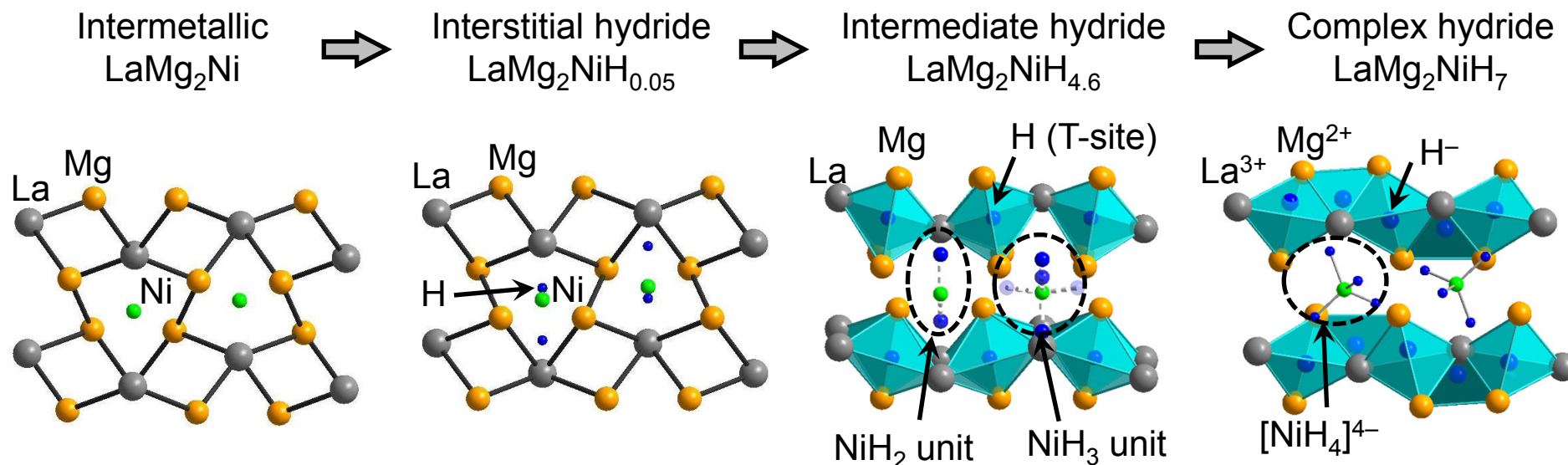
High gravimetric hydrogen density

Slow hydrogen absorption and desorption reaction kinetics

It is necessary to understand the reaction for improvement of the reaction.
 However, it had been **unclarified** yet...



In this presentation,
 we show **hydrogen absorption and desorption reaction of a complex hydride**
 $\text{LaMg}_2\text{NiH}_7$ viewed from **the crystal structure** and **the vibrational dynamics**



Outline

Introduction

- Hydrides for hydrogen storage materials
- General hydrogenation process of a complex hydride
- A complex hydride $\text{LaMg}_2\text{NiH}_7$

Methods

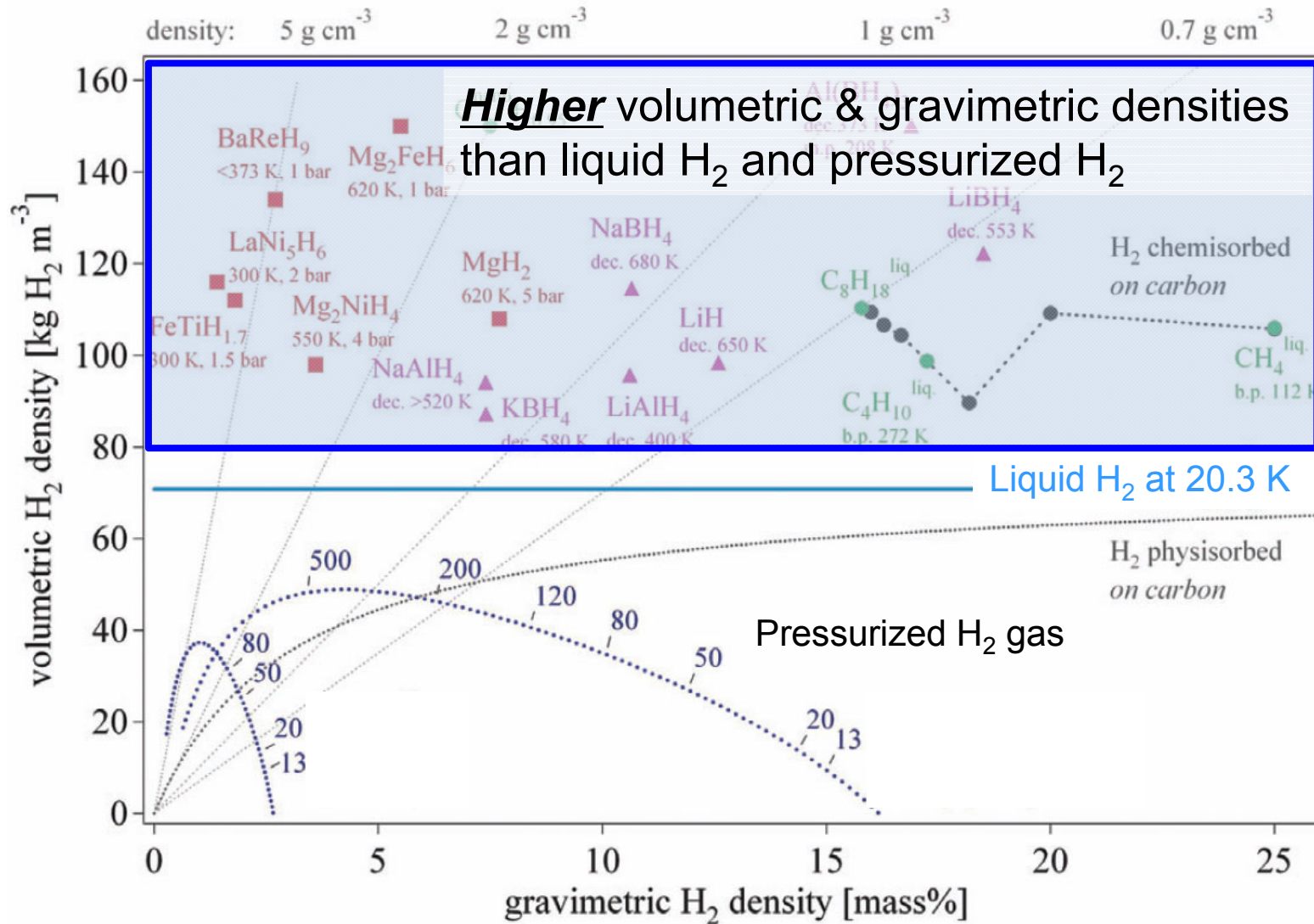
- Neutron diffraction and inelastic neutron scattering experiments

Results

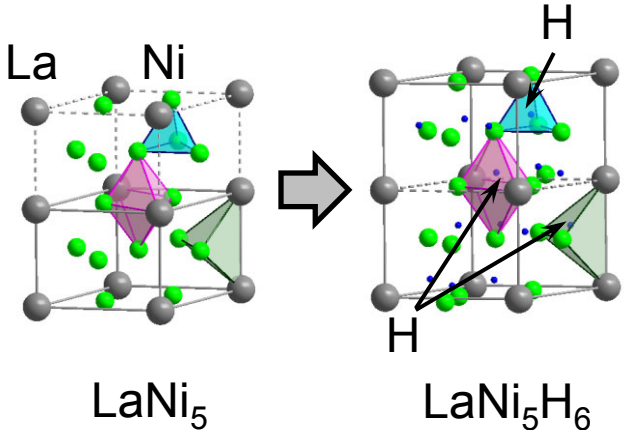
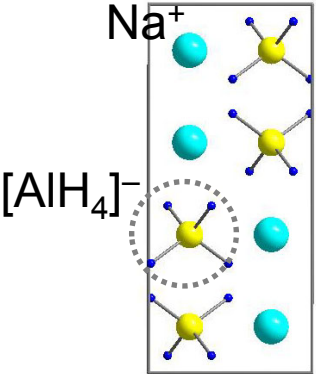
- Hydrogen absorption reaction of $\text{LaMg}_2\text{NiH}_7$
investigated by neutron diffraction and inelastic neutron scattering
- Hydrogen desorption reaction of $\text{LaMg}_2\text{NiH}_7$
investigated by neutron diffraction and inelastic neutron scattering

Conclusions

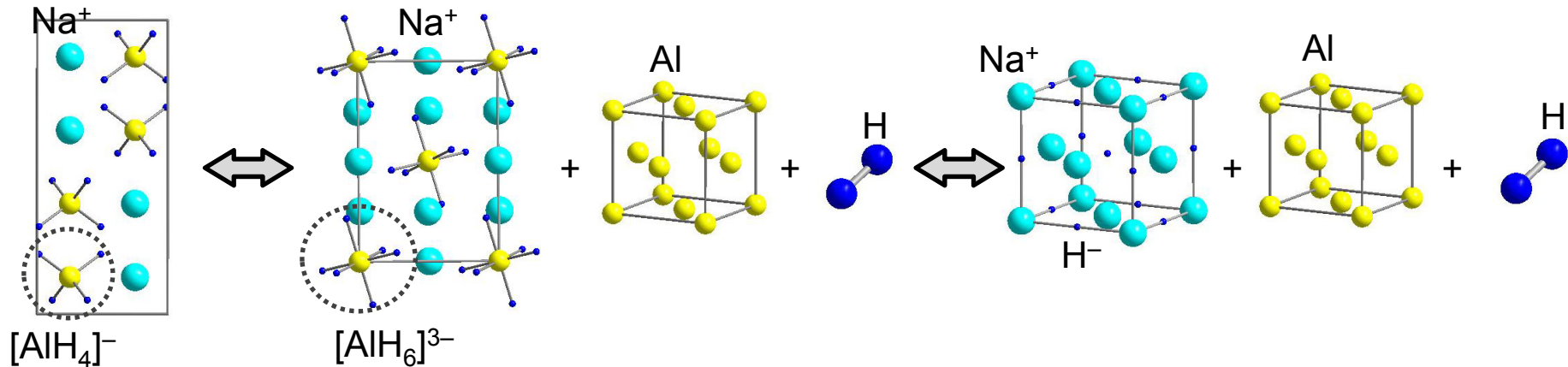
Volumetric & gravimetric hydrogen densities



Interstitial hydrides and complex hydrides

	Examples	Advantages	Disadvantages
<p>Interstitial hydride</p> <p>(hydrogen in interstitial sites)</p>	 <p>LaNi₅ → LaNi₅H₆</p>	<p><i>Fast</i> reaction kinetics</p>	<p><i>Low</i> hydrogen density</p> <p>LaNi₅H₆ : 1.4 mass%</p>
<p>Complex hydrides</p> <p>(covalently bonded hydrogen)</p>	 <p>NaAlH₄</p>	<p><i>High</i> hydrogen density</p> <p>NaAlH₄: 7.5 mass%</p>	<p><i>Slow</i> reaction kinetics</p>

General formation process of complex hydrides

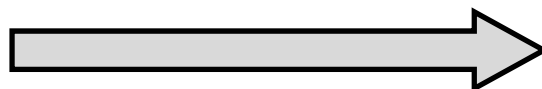


Large rearrangements of atomic positions (crystal structure)

⇒ It is difficult in understanding of formation process

Hydrogenation process of LaMg_2Ni

LaMg_2Ni (Metal)



$\text{LaMg}_2\text{NiH}_7$ (Insulator)

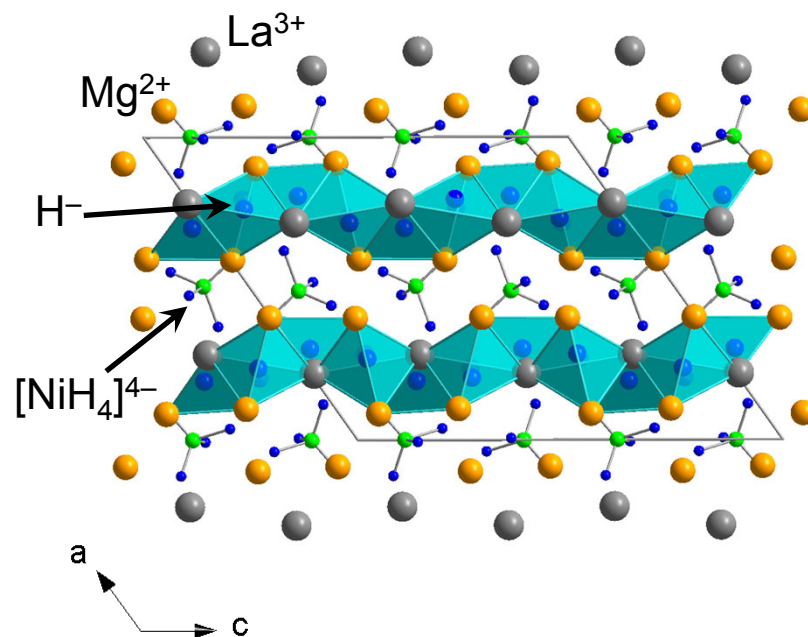
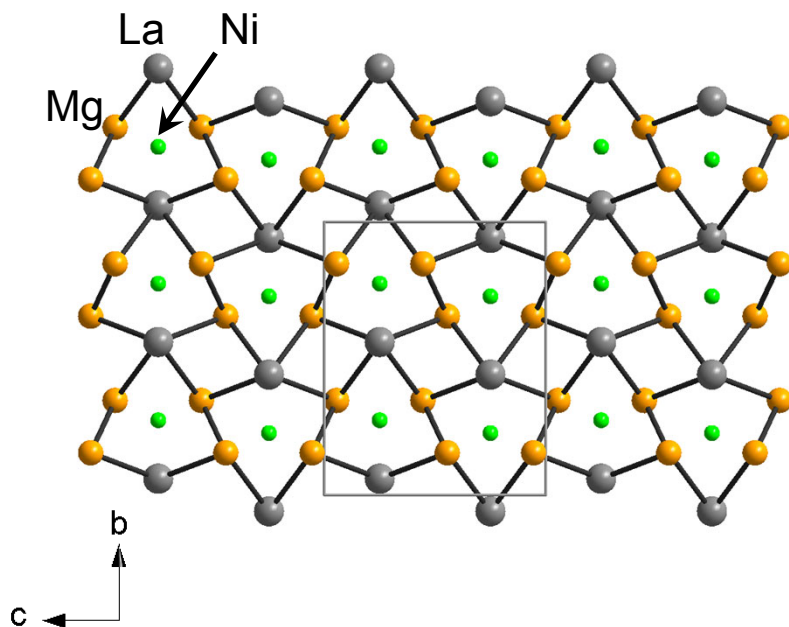
$(\text{La}^{3+}, \text{Mg}^{2+}, [\text{NiH}_4]^{4-}, 3 \times \text{H}^-)$

$\leq 200^\circ\text{C}$

$\leq 1.0 \text{ MPa of H}_2$

Orthorhombic
($a = 4.227 \text{ \AA}$, $b = 10.303 \text{ \AA}$,
 $c = 8.360 \text{ \AA}$)

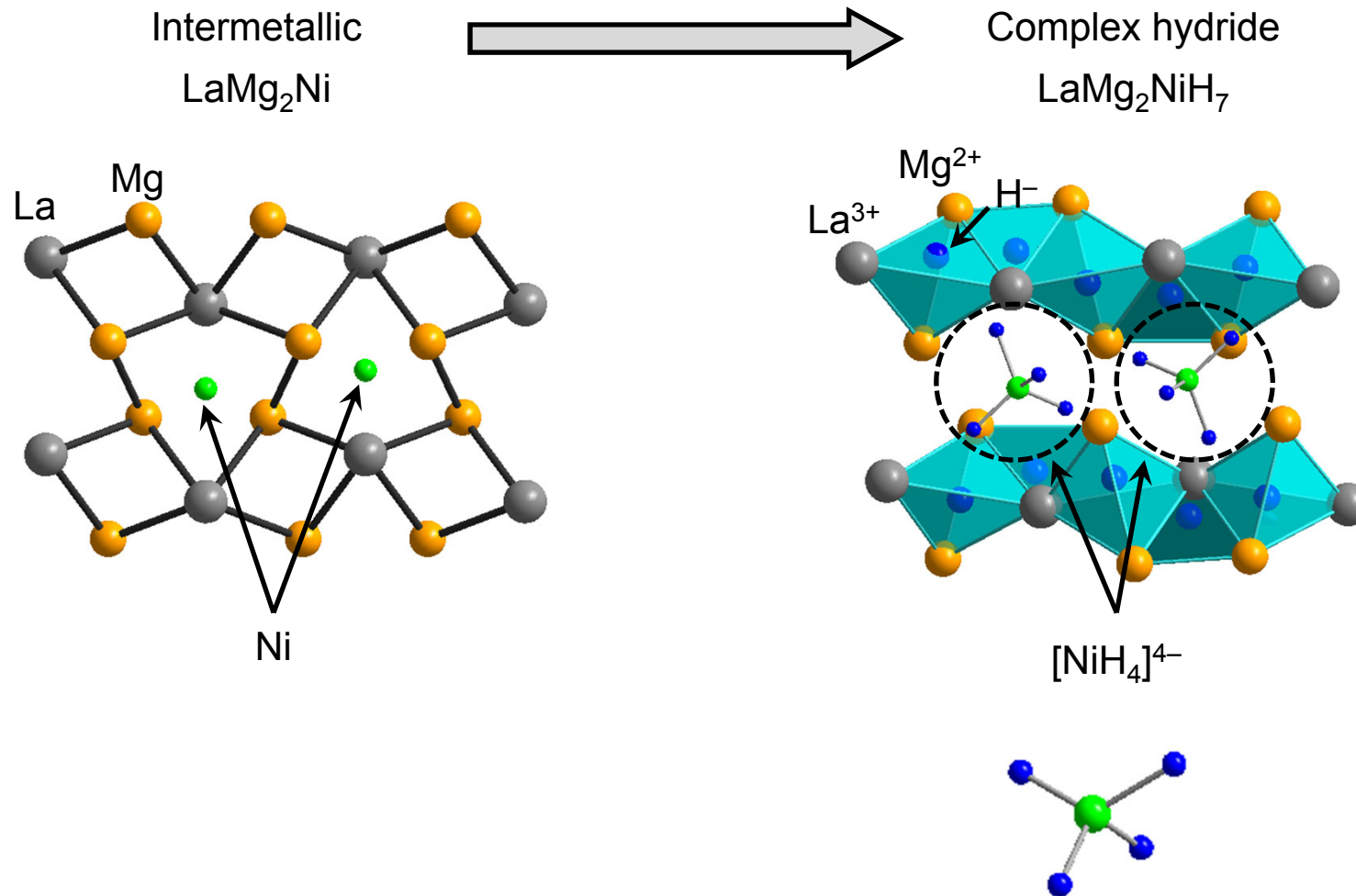
Monoclinic
($a = 13.979 \text{ \AA}$, $b = 4.703 \text{ \AA}$,
 $c = 16.025 \text{ \AA}$, $\beta = 125.240^\circ$)



G. Renaudin et al., *J. Alloys Compd.* **350**, 145 (2003).

K. Yvon et al., *Phys Rev. Lett.* **94**, 066403 (2005).

Hydrogenation process of LaMg_2Ni



Maintaining of metal atomic frameworks

G. Renaudin et al., *J. Alloys Compd.* **350**, 145 (2003).

K. Yvon et al., *Phys Rev. Lett.* **94**, 066403 (2005).

Objective

Clarification of hydrogen absorption and desorption reactions of a complex hydride $\text{LaMg}_2\text{NiH}_7$ viewed from the crystal structure and vibrational dynamics

Crystal structure:

- Observation of crystal structure changes during hydrogen absorption and desorption processes of $\text{LaMg}_2\text{NiD}_7$ by neutron diffraction

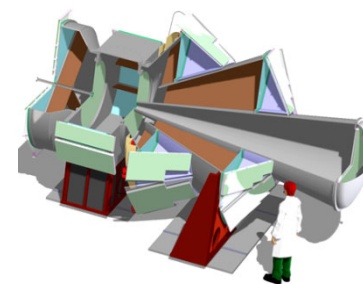
Vibrational dynamics:

- Observation of hydrogen vibration on an intermediate hydride $\text{LaMg}_2\text{NiH}_{4.6}$ and $\text{LaMg}_2\text{NiH}_7$ by inelastic neutron scattering

Methods

Neutron diffraction

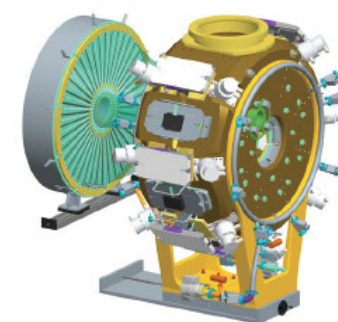
Sample	: LaMg_2Ni
Instrument	: High Intensity Total Diffractometer NOVA (MLF, J-PARC, Japan)
Condition	: < 450 K, < 5 MPa
Main analysis	: Rietveld method (GSAS)



NOVA

Inelastic neutron scattering (INS)

Sample	: $\text{LaMg}_2\text{NiH}_7$ $\text{LaMg}_2\text{NiH}_{4.6}$
Instrument	: Vibrational spectrometer VISION (SNS, Oak Ridge National Laboratory, USA)
Condition	: < 600 K under vacuum
Main analysis	: INS simulation (aCLIMAX)

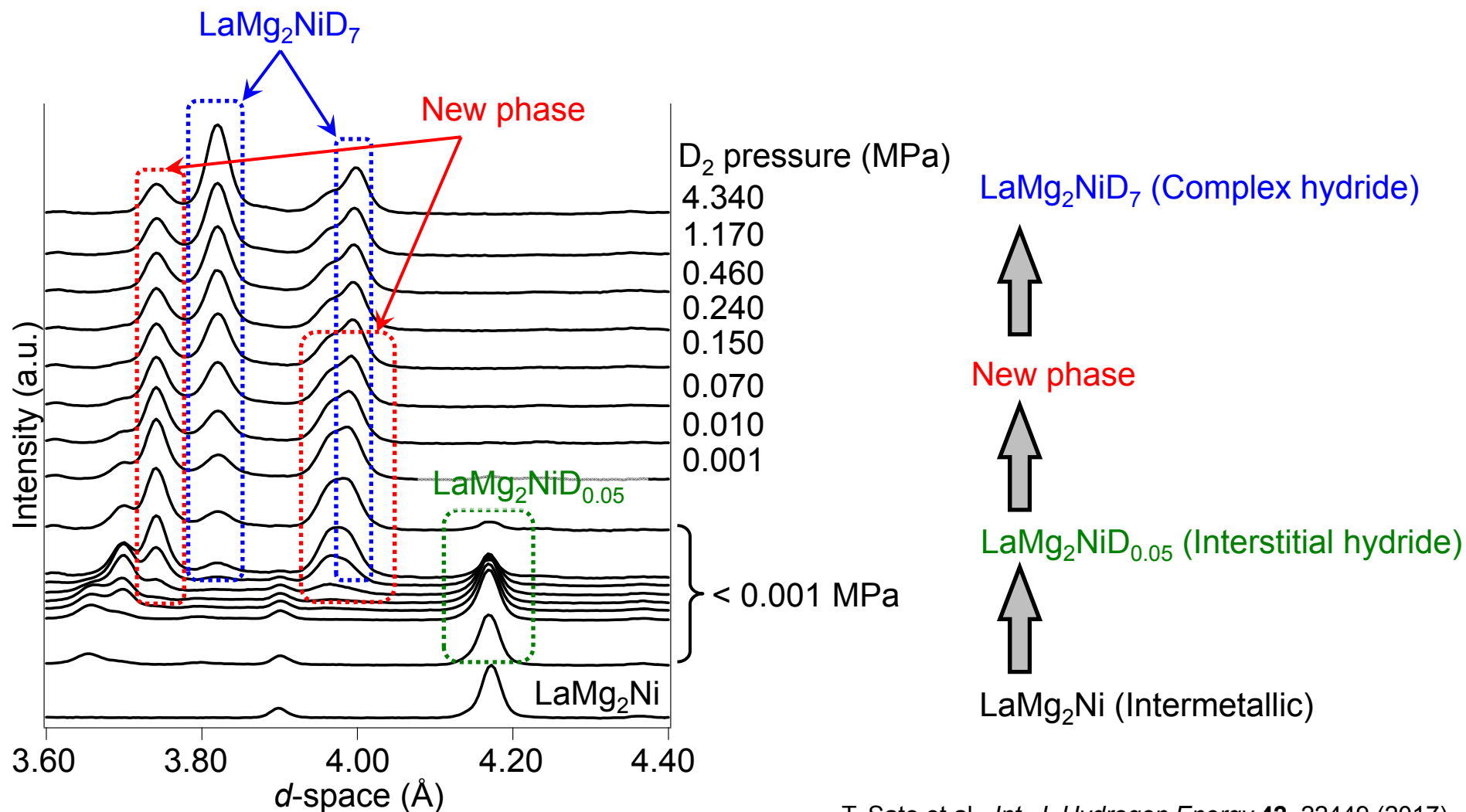


VISION

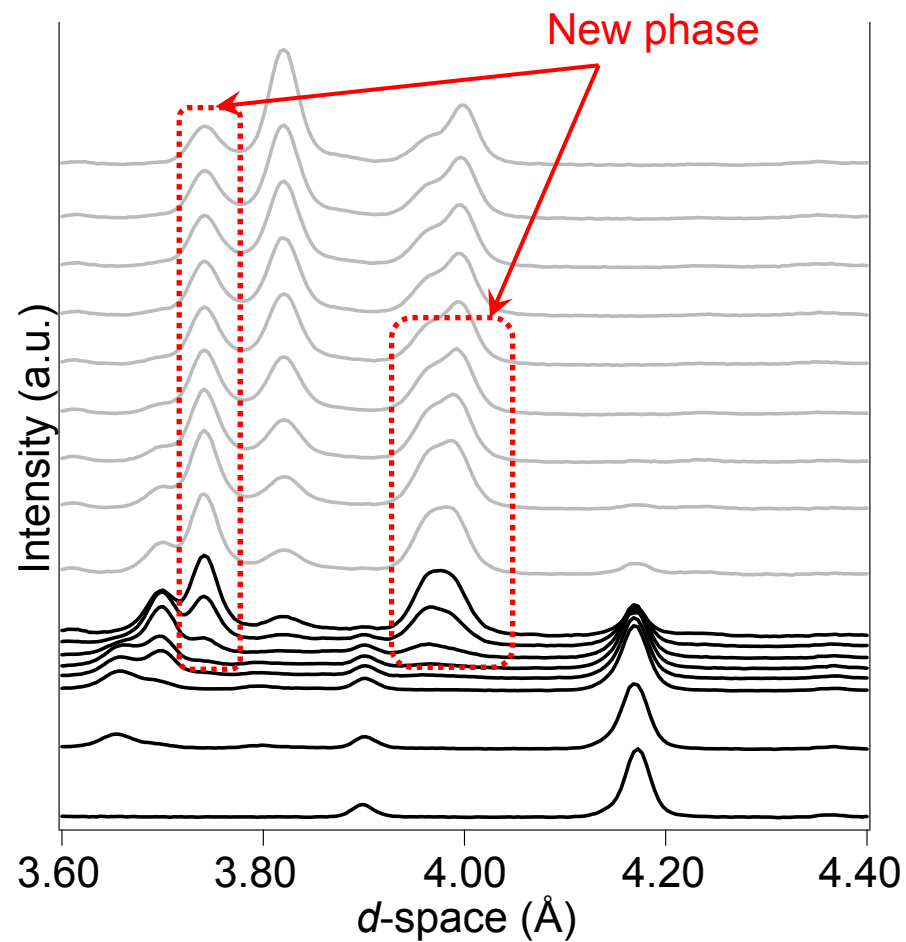


Hydrogen absorption process of $\text{LaMg}_2\text{NiH}_7$ studied by neutron diffraction

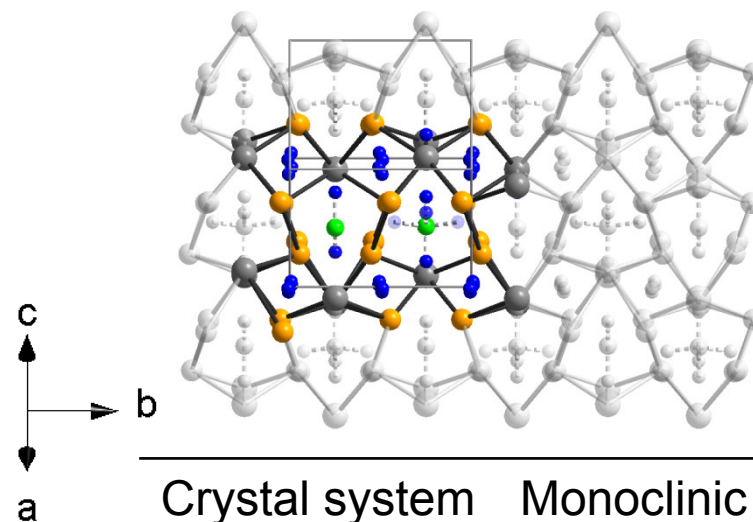
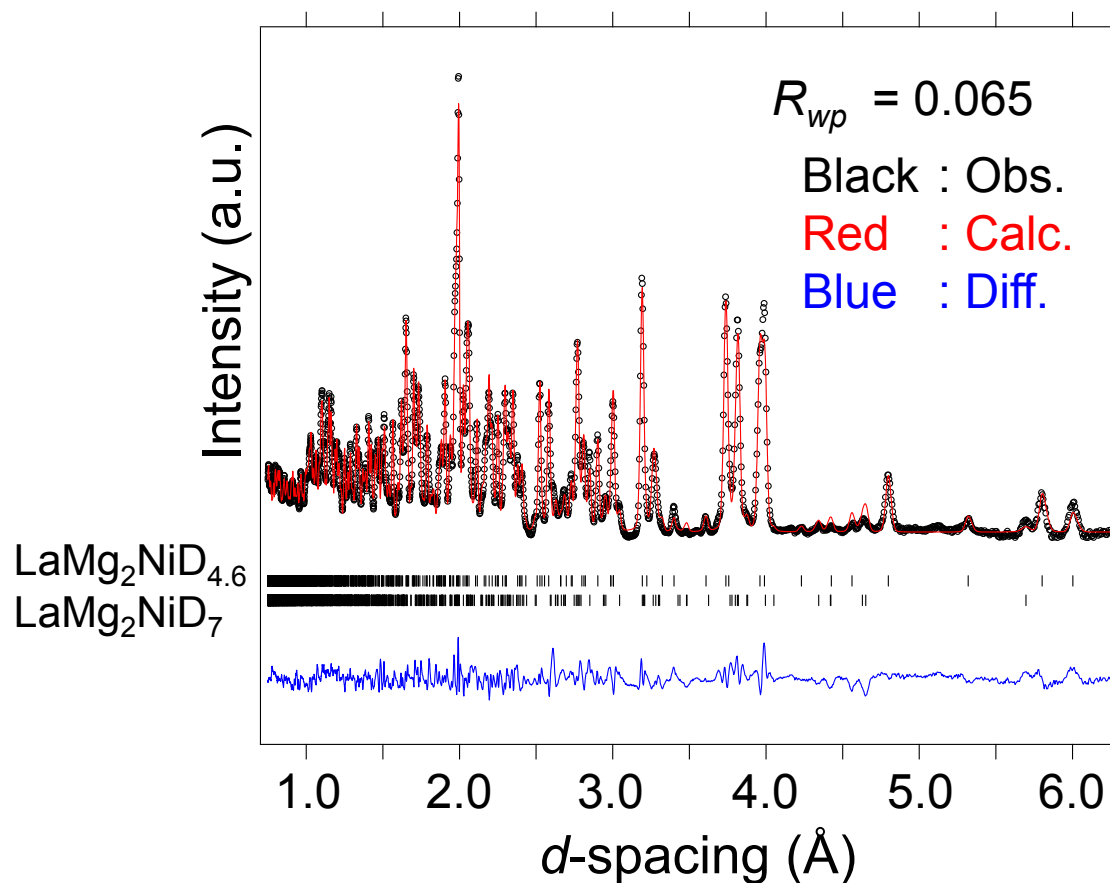
Neutron diffraction under D₂ pressure at RT



New phase



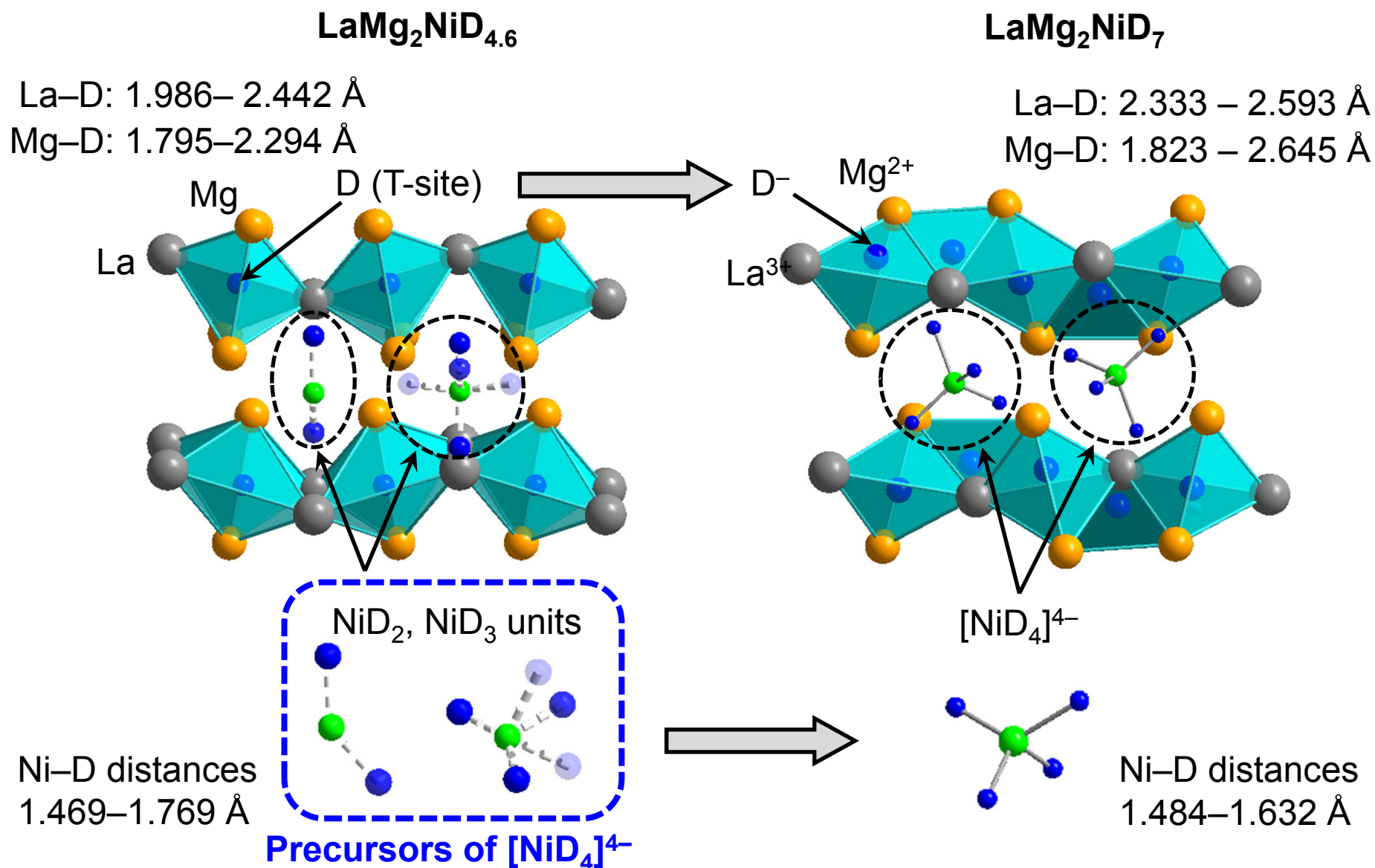
New phase ($\text{LaMg}_2\text{NiD}_{4.6}$)



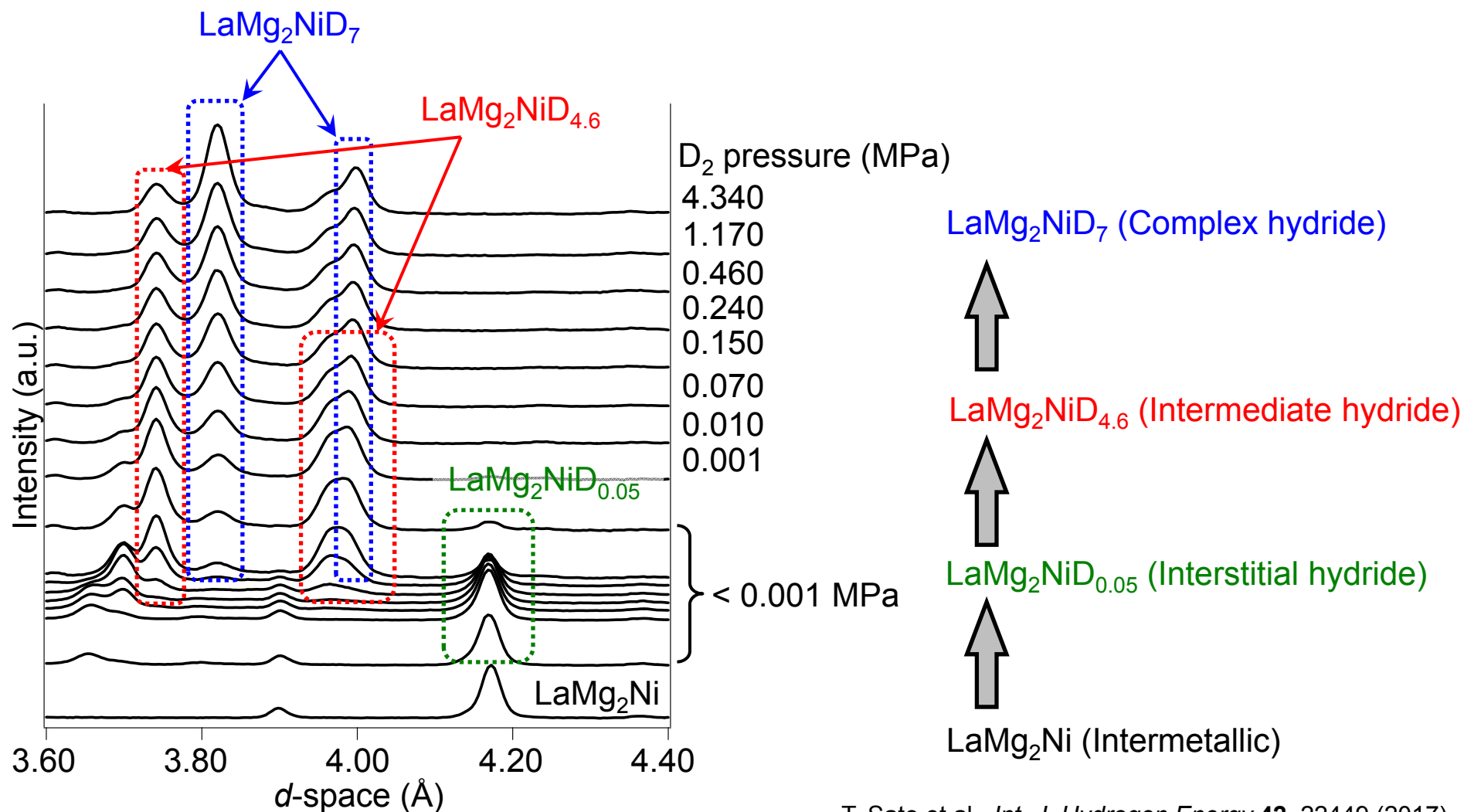
Crystal system	Monoclinic
Space group	$P2_1/m$
a (Å)	8.59236(6)
b (Å)	7.99549(4)
c (Å)	6.09887(4)
β (°)	99.3178(6)
V (Å ³)	413.46
Z	4

Intermediate hydride: $\text{LaMg}_2\text{NiD}_{4.6}$
 with a monoclinic unit cell

New phase ($\text{LaMg}_2\text{NiD}_{4.6}$)



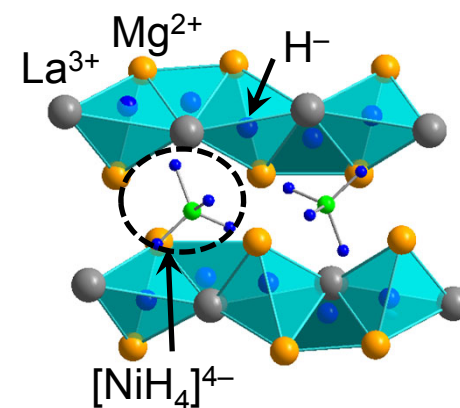
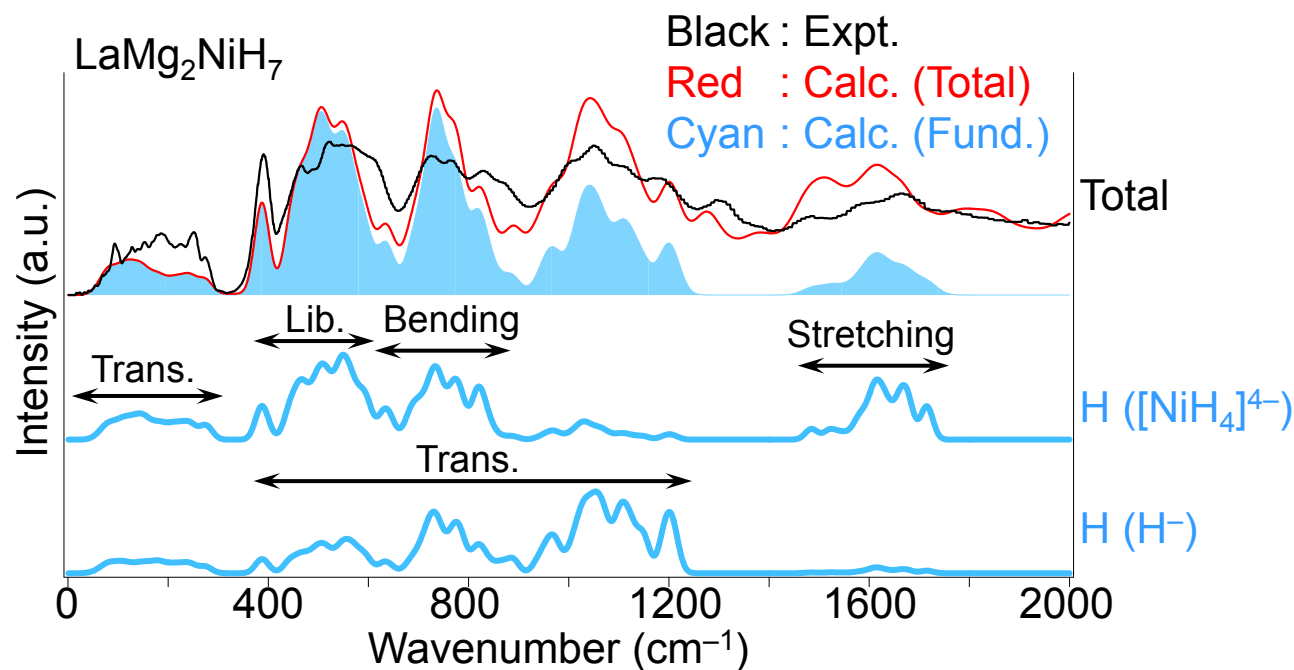
Formation process of $\text{LaMg}_2\text{NiH}_7$ (crystal structure)



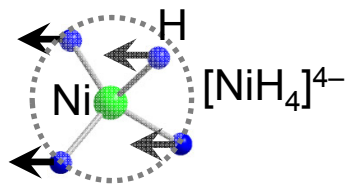


Hydrogen absorption reaction of $\text{LaMg}_2\text{NiH}_7$ studied by inelastic neutron scattering

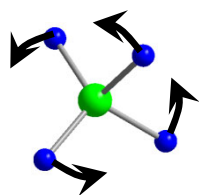
Inelastic neutron scattering spectrum of $\text{LaMg}_2\text{NiH}_7$



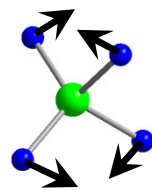
Translational mode



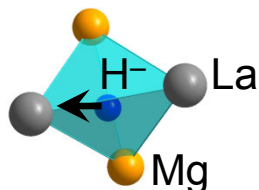
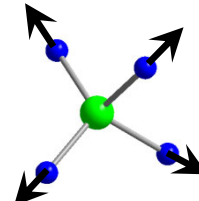
Libration mode



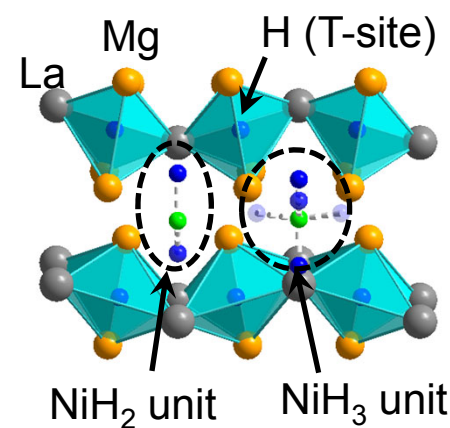
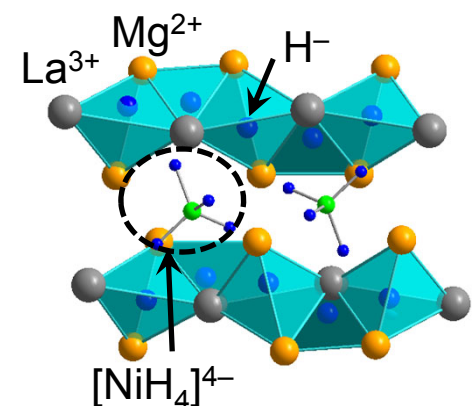
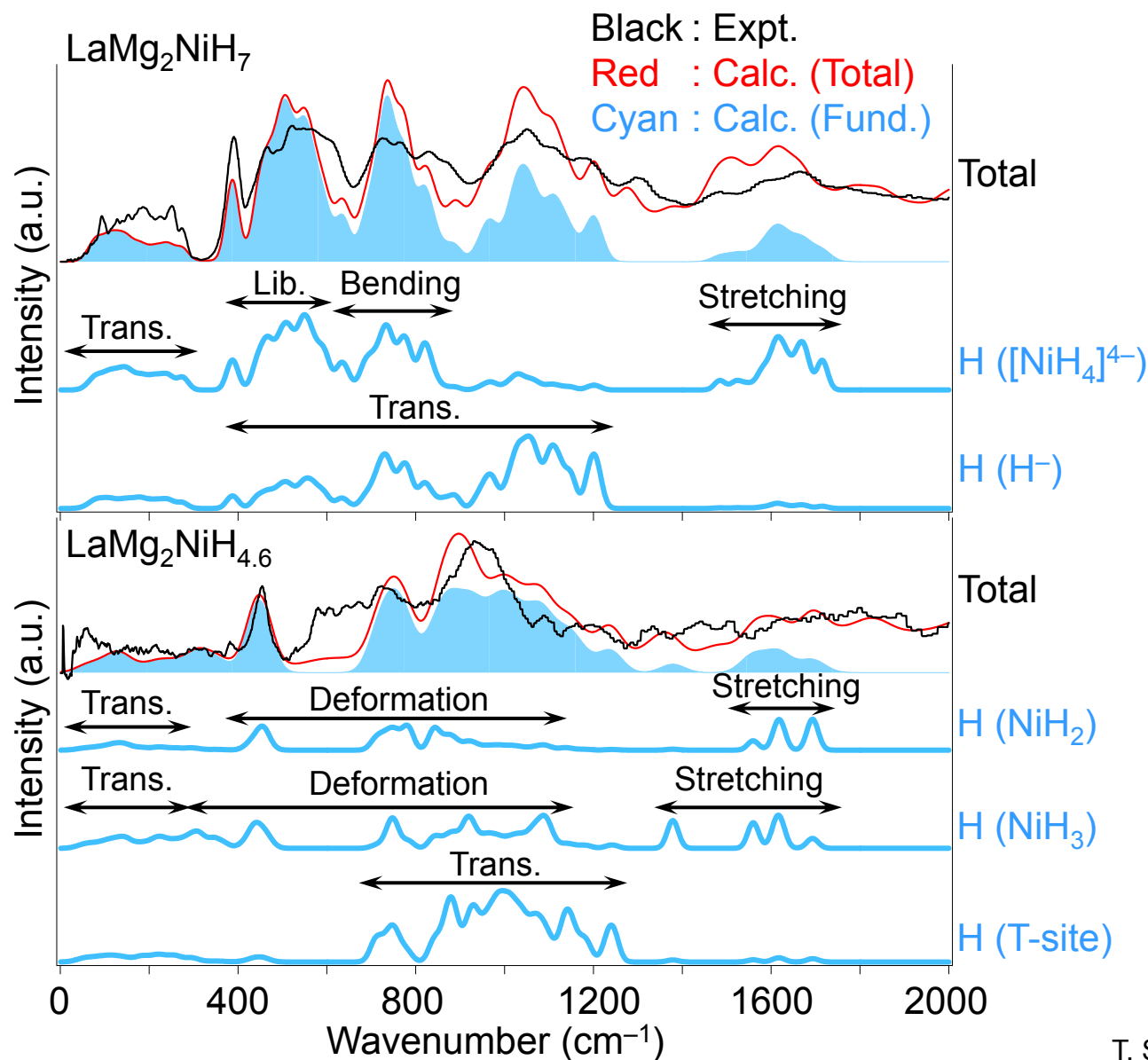
Bending mode



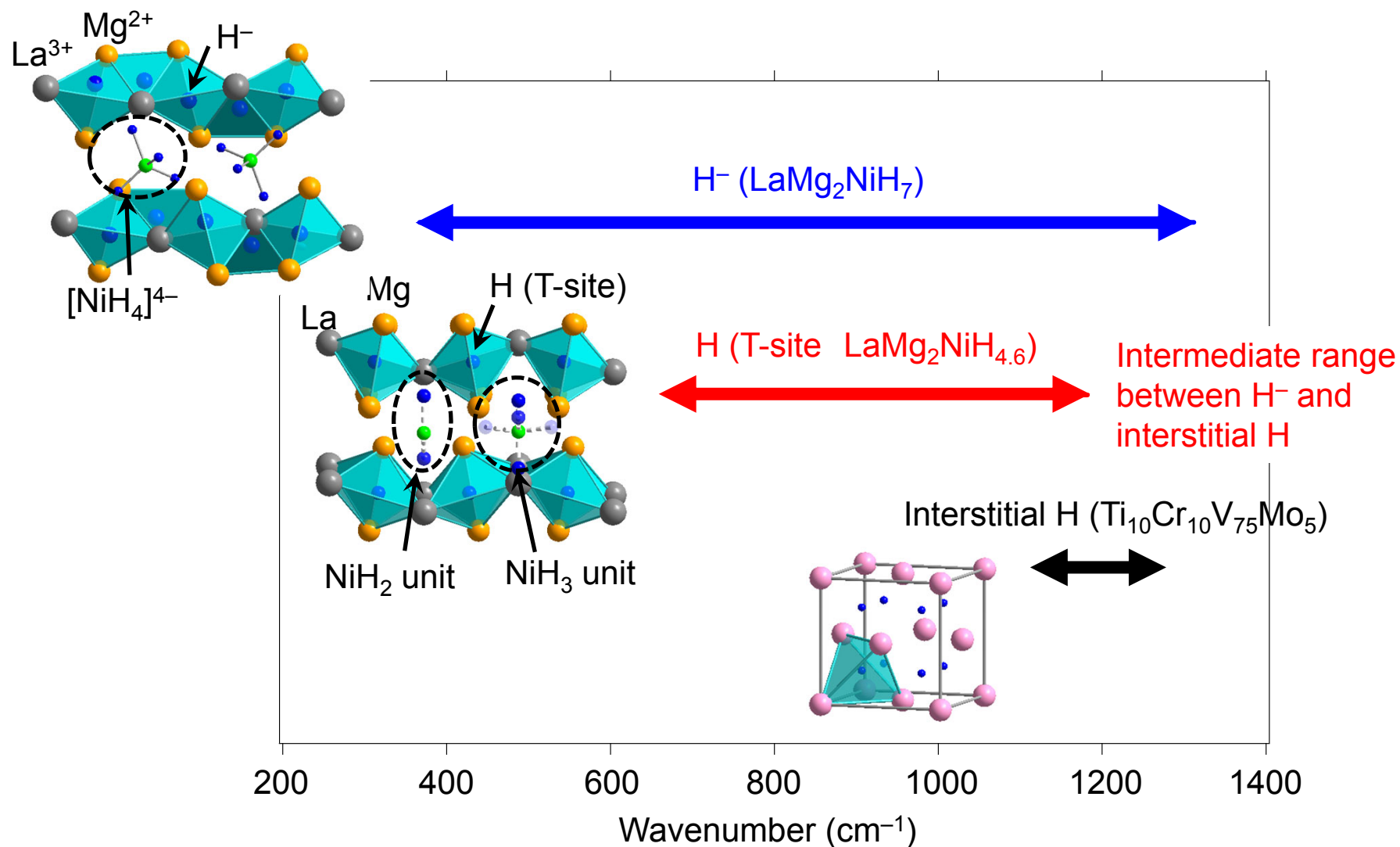
Stretching mode



Inelastic neutron scattering spectrum of $\text{LaMg}_2\text{NiH}_{4.6}$



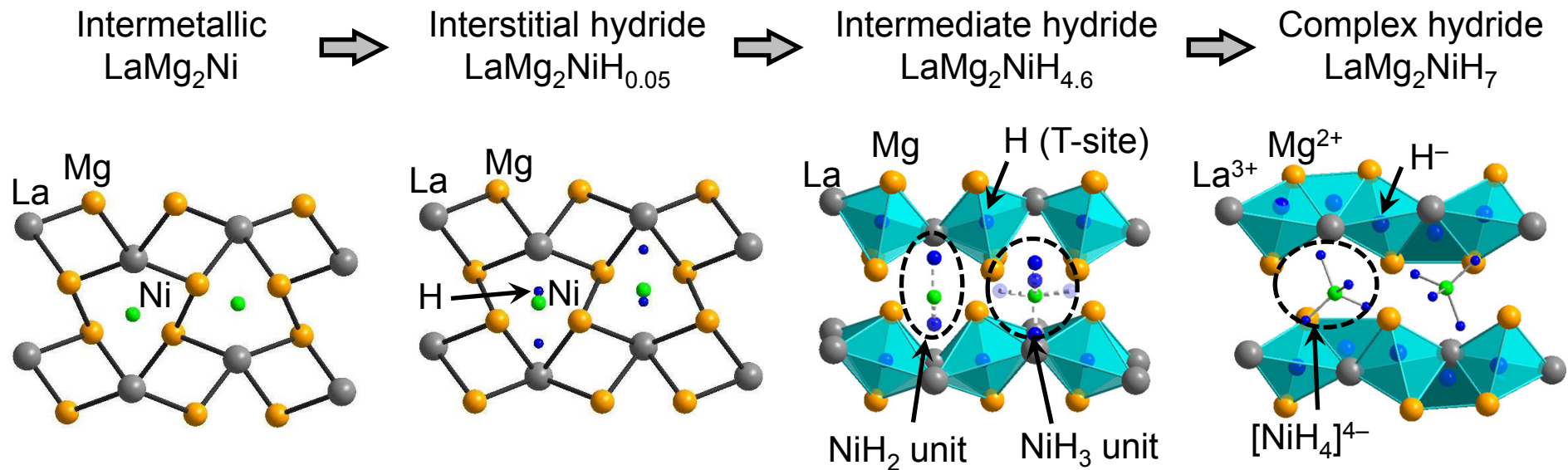
Wavenumber range for H in T-site in $\text{LaMg}_2\text{NiH}_{4.6}$



Conclusion (Hydrogen absorption reaction)

H₂ absorption reaction of a complex hydride LaMg₂NiH₇

Crystal structure:



Vibrational dynamics:

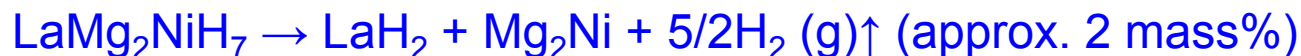
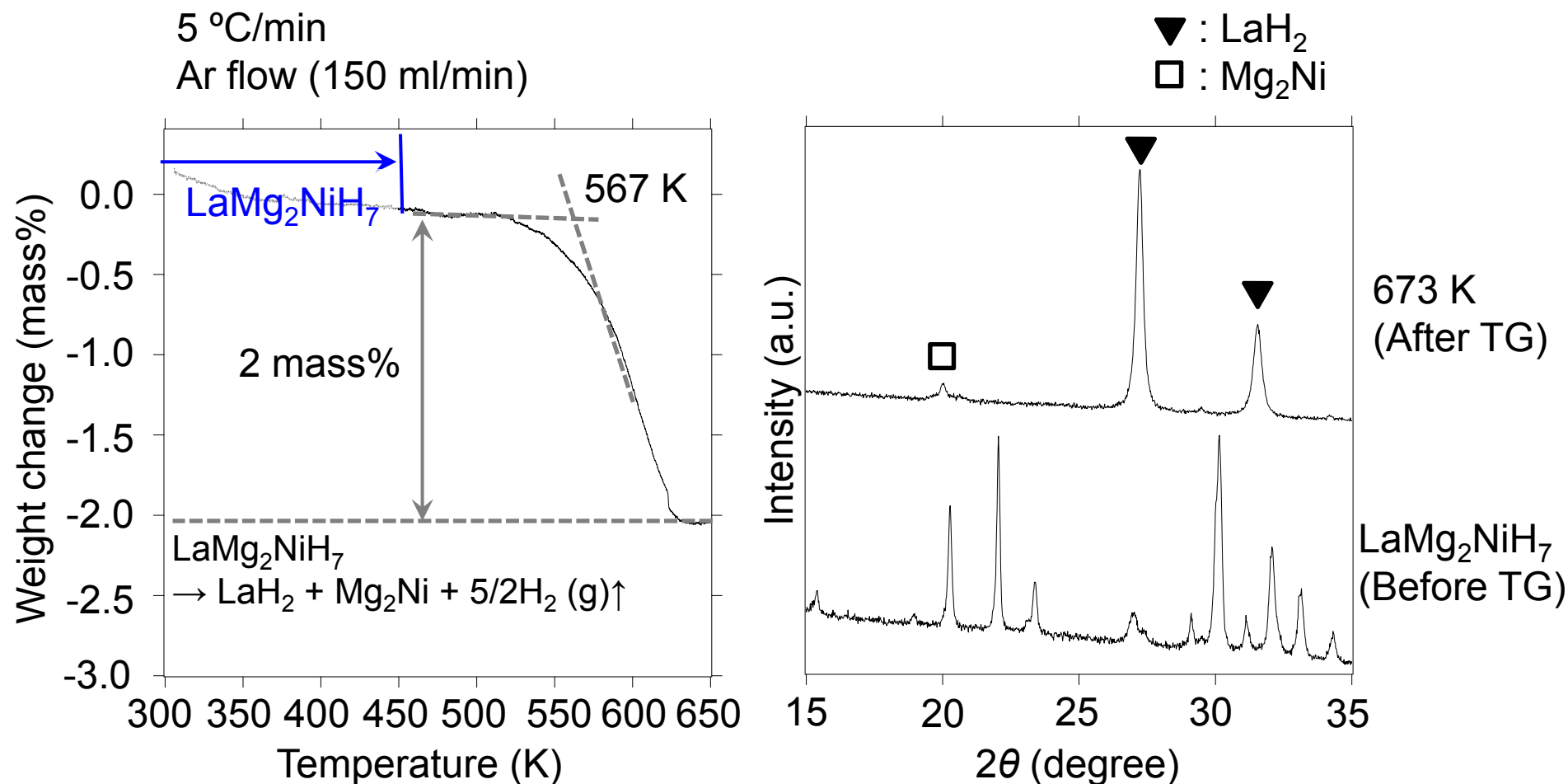
- NiH₂ and NiH₃ units : lack of librational modes
- H in T-site in LaMg₂NiH_{4.6} : Intermediate wavenumber range between H⁻ in LaMg₂NiH₇ and hydrogen in interstitial hydrides

\Rightarrow H in LaMg₂NiH_{4.6} exhibited intermediate states between H in complex hydrides and interstitial hydrides

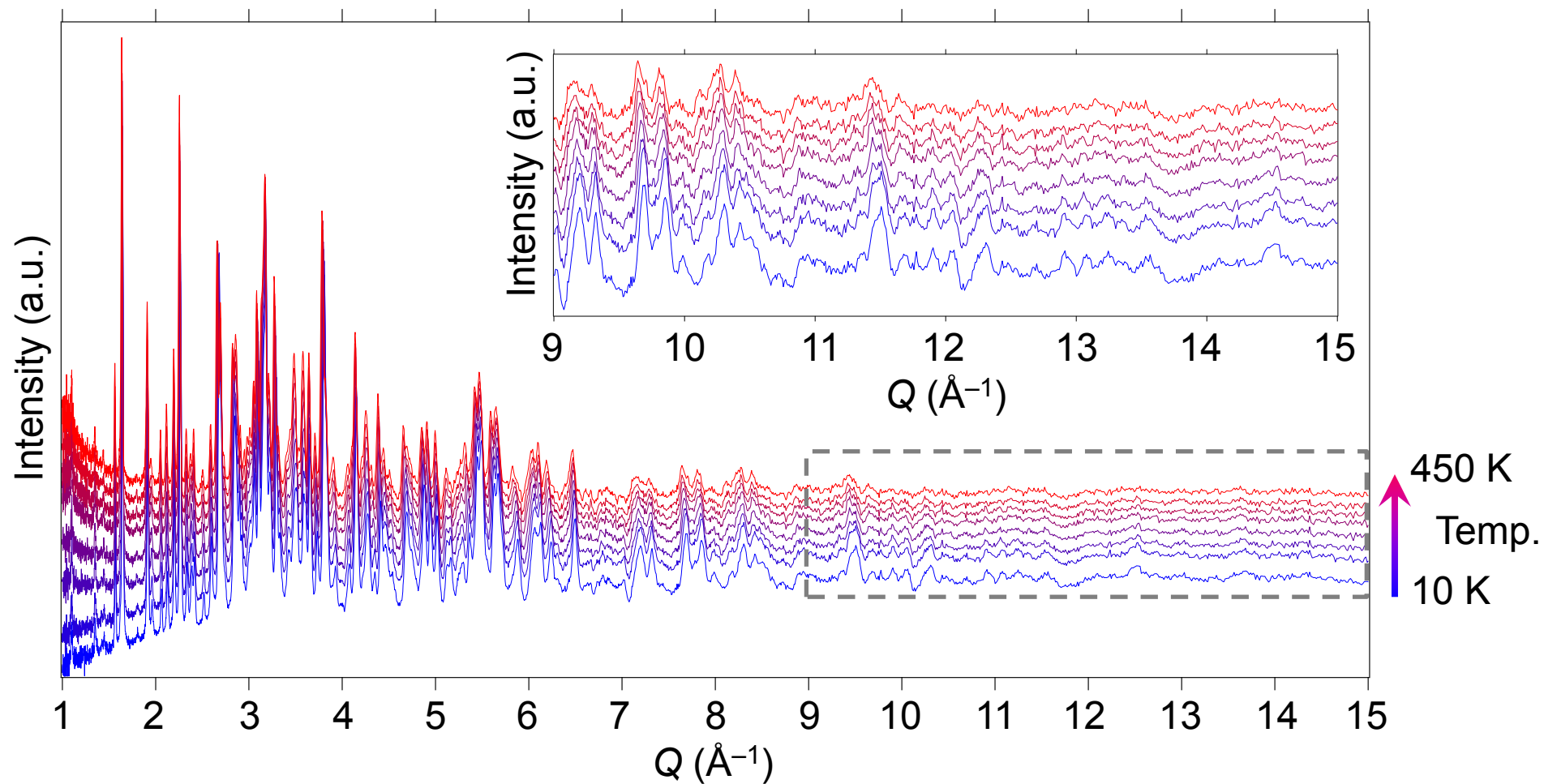


Hydrogen desorption reaction of $\text{LaMg}_2\text{NiH}_7$ studied by neutron diffraction

Hydrogen desorption reaction of $\text{LaMg}_2\text{NiH}_7$



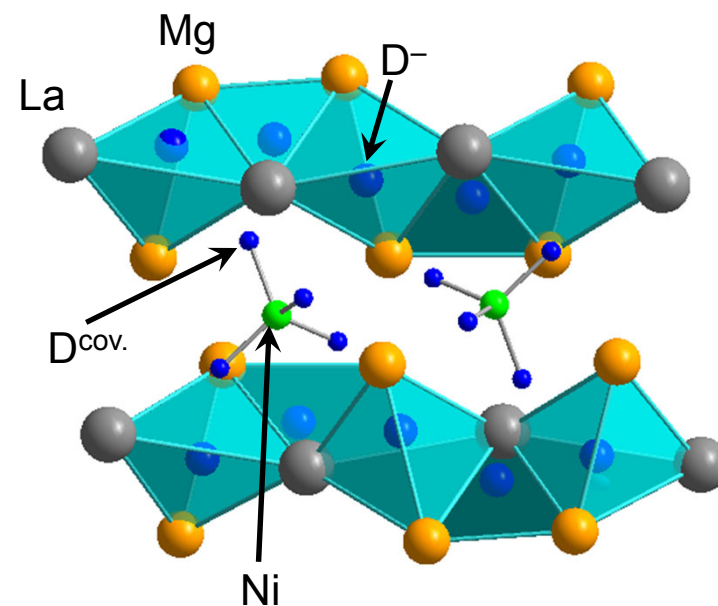
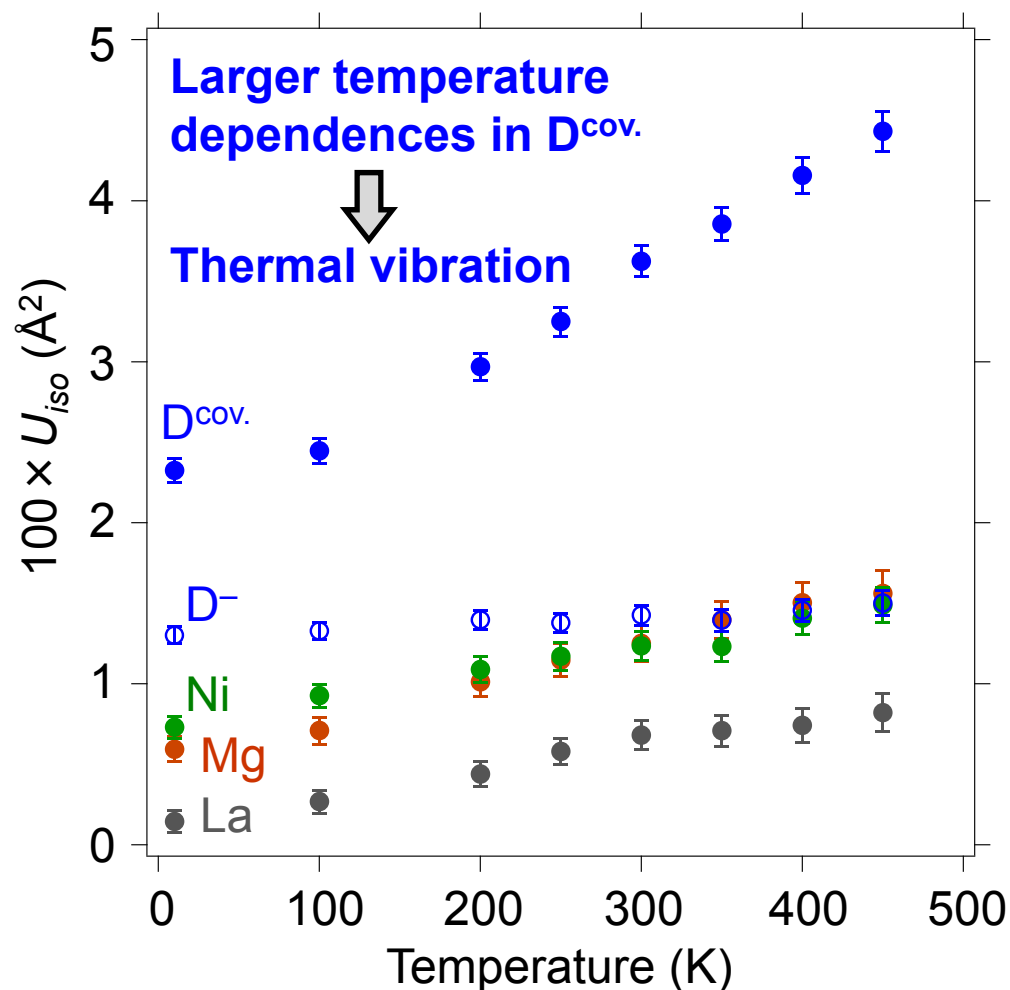
Neutron diffraction of $\text{LaMg}_2\text{NiH}_7$ (10–450 K)



At high Q region, broadening of the Bragg peaks

T. Sato et al., *ChemPhysChem* **20**, 1392 (2019) .

Temperature dependences of U_{iso} for each element



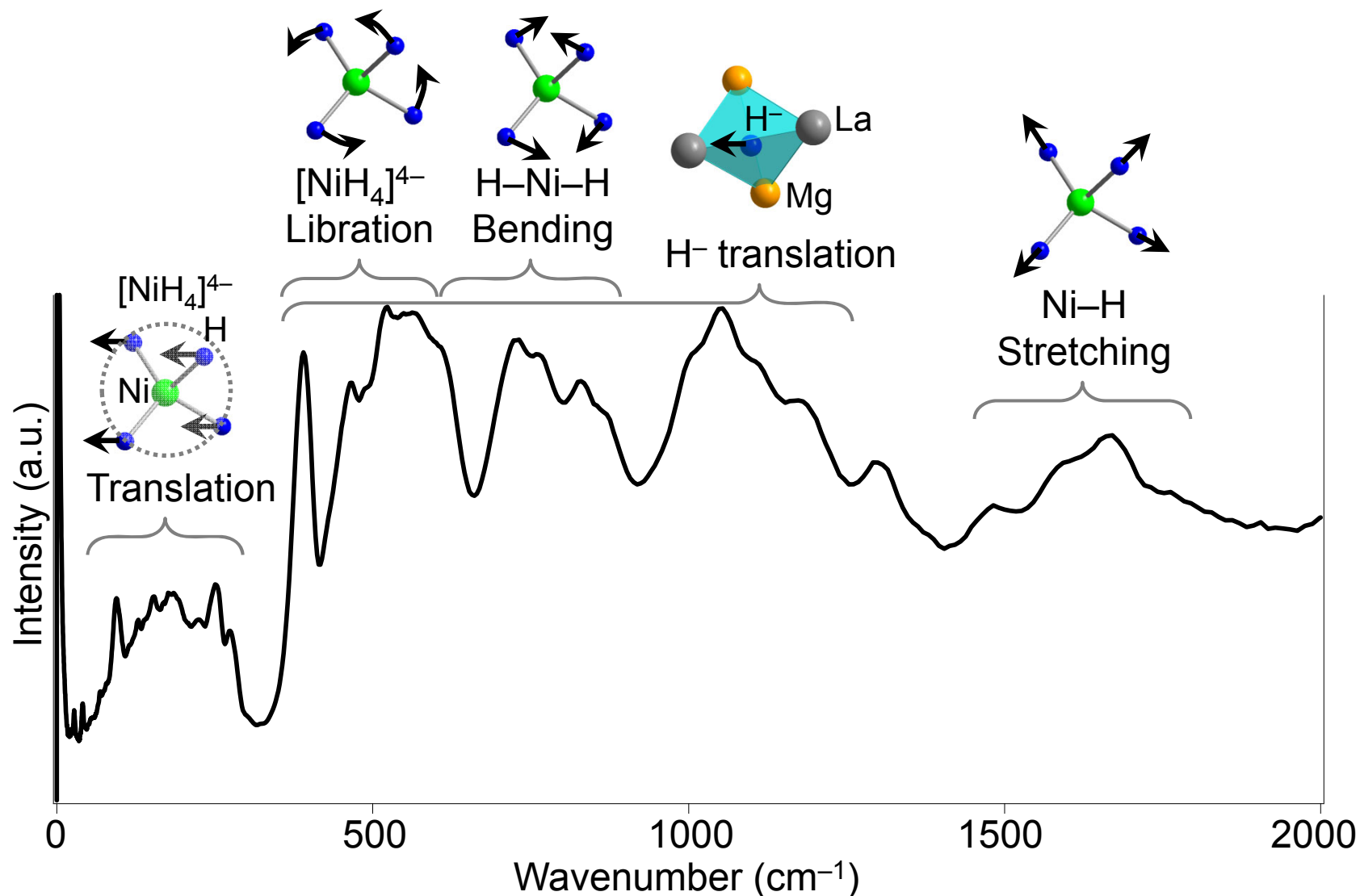
Local atomic arrangements around $[NiD_4]^{4-}$ and D^-

Temperature dependences of U_{iso} for each element

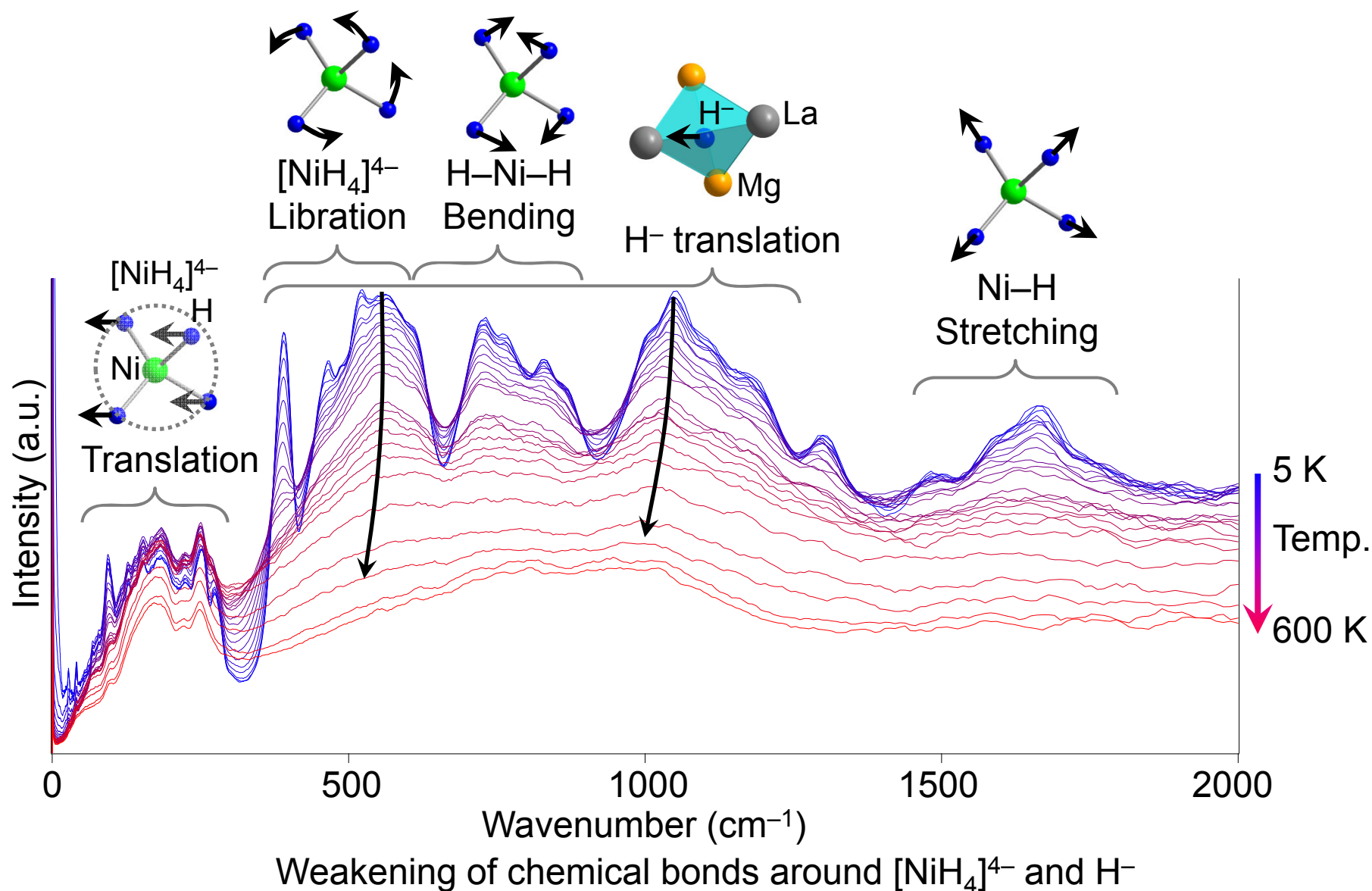


Hydrogen desorption reaction of $\text{LaMg}_2\text{NiH}_7$ studied by inelastic neutron scattering

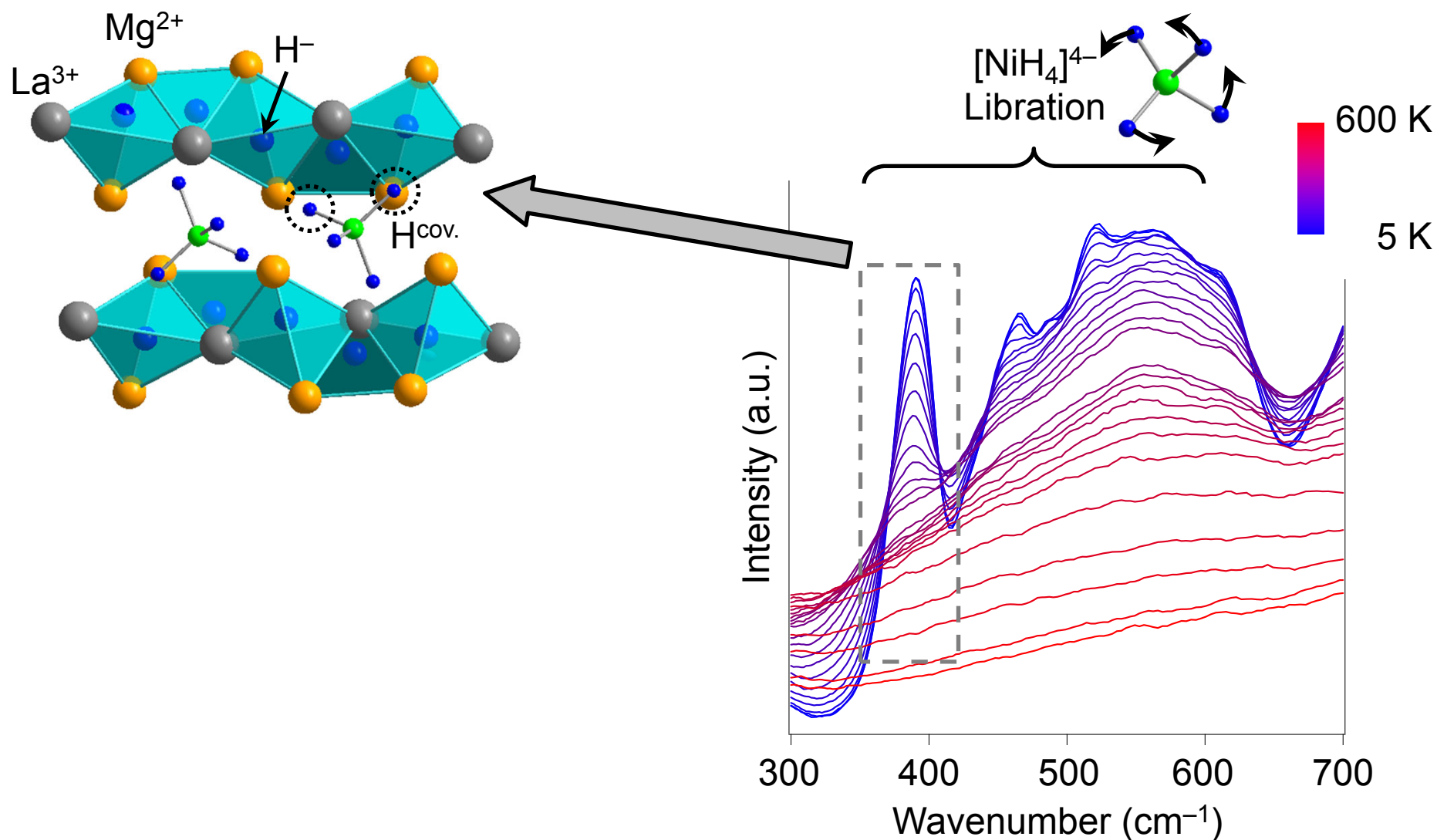
Inelastic neutron scattering of $\text{LaMg}_2\text{NiH}_7$ (5 K)



Inelastic neutron scattering of $\text{LaMg}_2\text{NiH}_7$ (5–600 K)

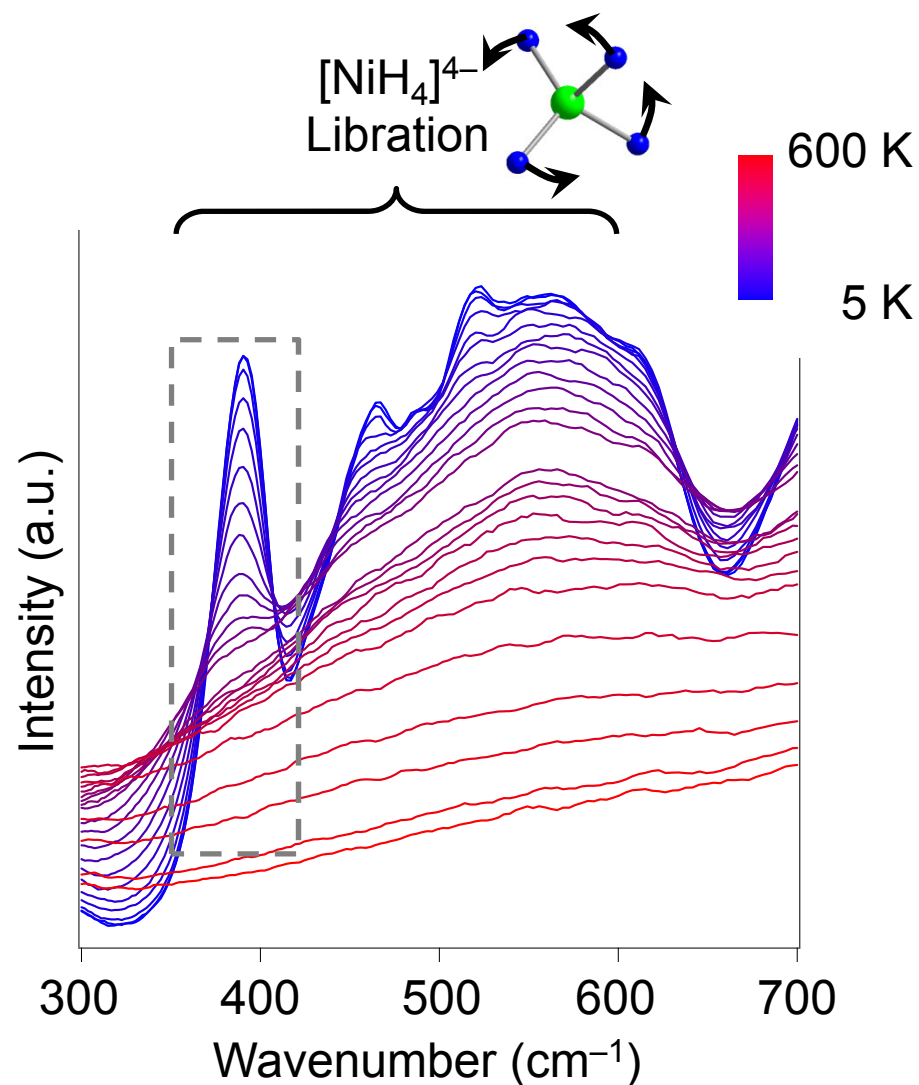
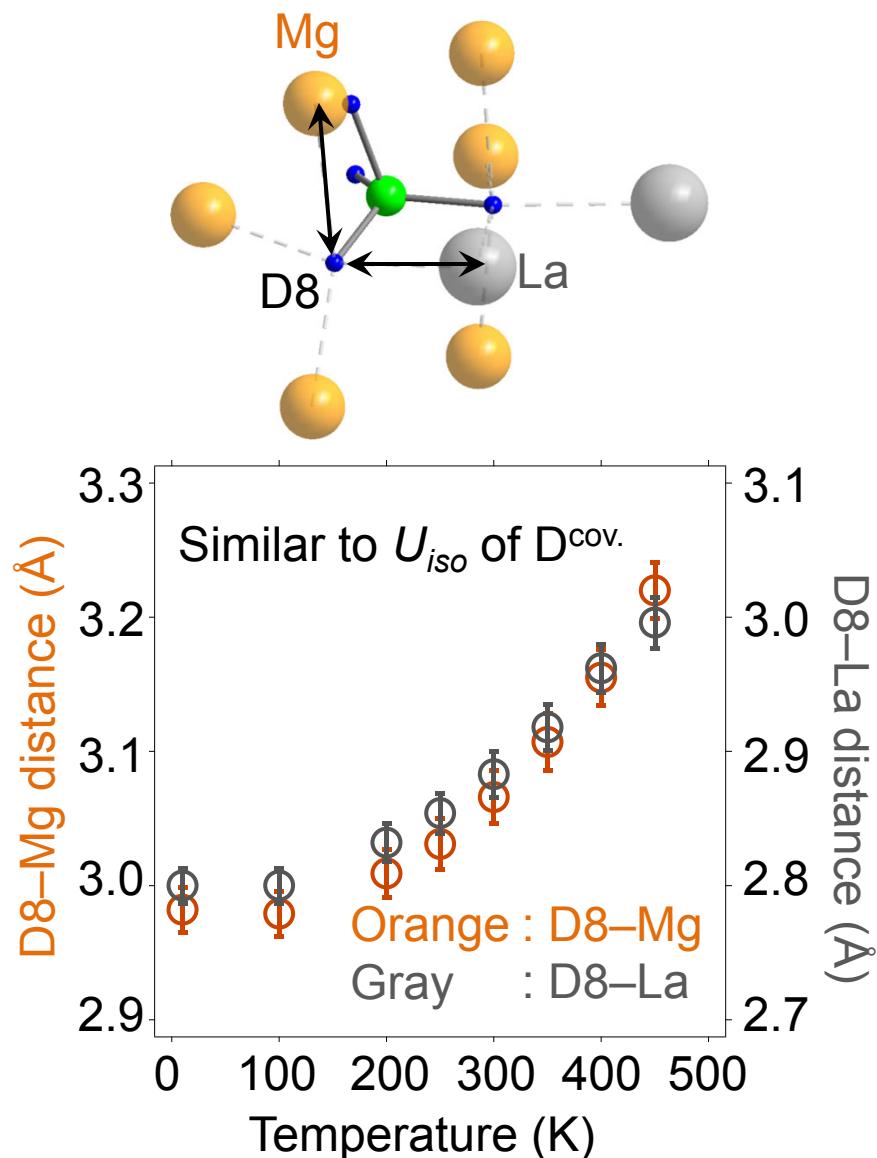


Inelastic neutron scattering of $\text{LaMg}_2\text{NiH}_7$ (5–600 K)



Larger $\text{D}^{\text{cov.}}$ vibration leads to hydrogen release reaction

Inelastic neutron scattering of $\text{LaMg}_2\text{NiH}_7$ (5–600 K)



Conclusion (Hydrogen desorption reaction)

H₂ desorption reaction of a complex hydride LaMg₂NiH₇

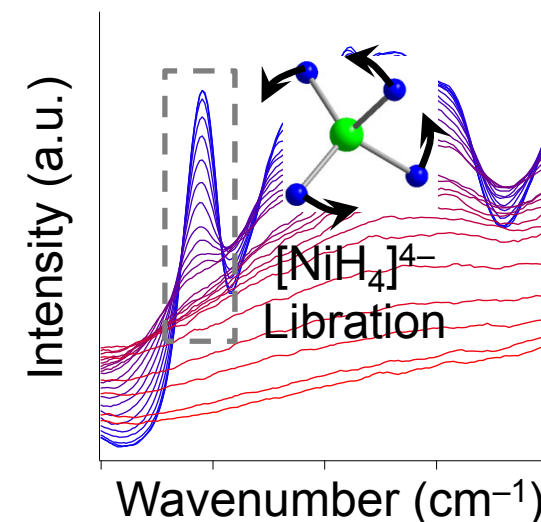
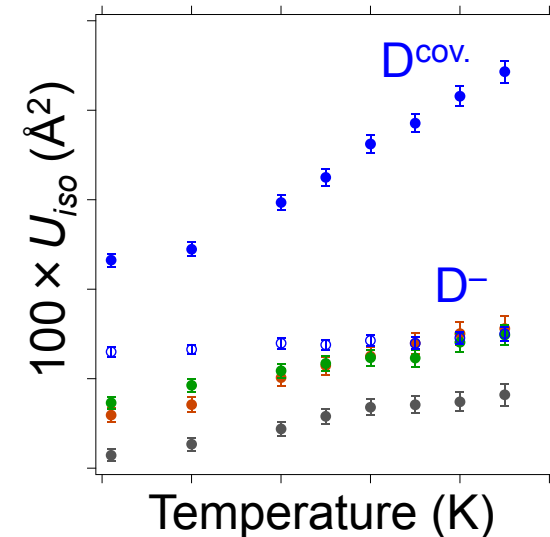
Crystal structure:

- Atomic displacement U_{iso} of H^{cov.} is larger than that of H⁻.
- Interatomic distances of La–H^{cov.} and Mg–H^{cov.} were elongated related with U_{iso} of H^{cov.}.

Vibrational dynamics:

- Libration mode of [NiH₄]⁴⁻ at approx. 400 cm⁻¹ was clearly softened.
- The softening of Libration mode of [NiH₄]⁴⁻ was related with large changes of U_{iso} and interatomic distances related with H^{cov.}.

➡ Weakening of chemical bonds around H^{cov.} is trigger for the H₂ desorption reaction of LaMg₂NiH₇.



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Integrated Project of ICC-IMR of Tohoku University,
Collaborative Research Center on Energy Materials in IMR (E-IMR), Tohoku University.  **Hydrogenomics**

Neutron diffraction and inelastic neutron scattering experiments were performed by
the NOVA at MLF, J-PARC in Japan (Proposal No. 2014A0200) and
the VISION at ORNL's Spallation Neutron Source in U.S.A (Proposal No. IPTS-16527).