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Inelastic neutron scattering spectra of $LiCa(AlH_4)_3$ upon heating and the local atomic structure around $[AlH_4]^-$

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Hydrogen release reactions of Al-based complex hydrides enhanced by vibrational dynamics and valences of metal cations

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Hydrogen release from Al-based complex hydrides composed of metal cation(s) and $[AIH_4]^-$ was investigated using inelastic neutron scattering viewed from vibrational dynamics. Hydrogen release followed the softening of translational and $[AIH_4]^-$ librational modes, which was enhanced by vibrational dynamics and the valence of the metal cation(s).

Complex hydrides, which are composed of metal cation(s), such as Li⁺ and Mg²⁺, and complex anion(s), such as $[AIH_4]^-$ and $[BH_4]^-$, with covalent bonding between the central atom and hydrogen, have attracted significant attention because of their potential use as high gravimetric and volumetric hydrogen storage materials and ionic conduction materials, among other useful applications.¹⁻⁴ For the reasons, numerous studies attempting to gain a fundamental understanding of such physical properties and functionalities have been reported.

Particularly, Ti doping on an Al-based complex hydride NaAlH₄ (sodium alanates), which is of interest in high gravimetric hydrogen storage applications, is acknowledged to enhance hydrogen release and uptake reaction kinetics of NaAlH₄.^{1a,1b} Owing to clarification of Ti effects, hydrogen dynamics has been studied.⁵ According to vibrational spectroscopic studies, Ti was proposed to be at Na⁺ site, on which vibrational modes were softened (shifted to lower frequencies) compared with a pure NaAlH₄.^{5a,5b,5d–f} Recently, we observed Intrinsic anharmonicity of librational modes of the complex anion [AlH₄]⁻ on LiAlH₄ before hydrogen release. Such phenomenon was also observed in a complex hydride, LiBH₄, with Li⁺ ionic conduction.⁷ Although the vibrational dynamics (librational modes of a complex anion) could be one

key issue to understand the functionality of complex hydrides, the relationship has not been elucidated properly yet.

Conventionally, Raman, infrared (IR) and inelastic neutron scattering (INS) spectroscopies are employed for the studies of vibrational dynamics. Although Raman and IR spectroscopies are convenient, they prevent the observation of all vibrational modes due to the selection rules. In contrast, INS provides access to all vibrational modes in materials because it provides information on the dynamics across the Brillouin zone and has no selection rules. Furthermore, hydrogen has larger incoherent neutron scattering cross-section (80.26 barns; 1 barn = $1 \times 10^{-24} \text{ cm}^2$)⁷ than most elements (less than 10 barns), which gives higher INS intensity. Then, hydrogen-contributed vibrational dynamics can be clearly observed using INS.^{6,7,9,10}

In this study, we therefore performed INS experiments on alanates with systematically different valences of metal cation(s); LiAlH₄, Ca(AlH₄)₂ and LiCa(AlH₄)₃ at 10–400 K with a broad frequency range and a high resolution to elucidate the relationship between vibrational dynamics and hydrogen release reaction kinetics viewed from dependences of valences of metal cation(s). LiCa(AlH₄)₃ is formally classified as a trivalent cation system, and adopts a mixed local atomic arrangement around $[AlH_4]^-$ of LiAlH₄ and Ca(AlH₄)₂ (Fig. 1).^{11,12} Although vibrational spectroscopic studies on LiAlH₄^{5,6,7d,9d} and Ca(AlH₄)₂¹³ were reported, our results firstly provide effects of different metal cation(s) on their vibrational dynamics and hydrogen release reaction kinetics using INS with broad frequency range and high resolution combined with theoretical calculations, which were not performed previously.

The INS experiments were performed using the VISION spectrometer¹⁴ (BL-16B) at the Spallation Neutron Source, Oak Ridge National Laboratory, USA. The detailed methods are described in the electronic supplementary information (ESI).

We assigned the vibrational modes of LiAlH₄, Ca(AlH₄)₂ and LiCa(AlH₄)₃ in the INS spectra (Fig. 1). These spectra can be mainly divided into three regions: the frequency ranges 0–550, 600–1100 and 1600–2000 cm⁻¹. Using the aCLIMAX program,¹⁵ the experimental INS spectra observed at 10 K were compared with the phonon density of states on LiAlH₄, Ca(AlH₄)₂ and

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Fig. 1 INS spectra of (top) LiAlH₄, (middle) Ca(AlH₄)₂ and (bottom) LiCa(AlH₄)₃ at 10 K. Inset figures are the local atomic structure around $[AlH_4]^-$ for each alanate. Red, purple, yellow and blue circles indicate Li, Ca, Al and H atoms, respectively. The external and internal motions of $[AlH_4]^-$ are observed at 0–550 and 600–2000 cm⁻¹, respectively.

LiCa(AlH₄)₃ calculated using the CASTEP program.¹⁶ The calculated INS spectra are in reasonably good agreement with the experimental INS spectra (Figs. S6–S8 in the ESI). Combining the experimental and calculated results, we refer to the motions at 0–550 cm⁻¹ as the external motion of [AlH₄]⁻, namely, the translational and [AlH₄]⁻ librational modes, and the motion above 600 cm⁻¹ as the internal motion of [AlH₄]⁻, namely, the Al–H bending and stretching modes in [AlH₄]⁻.

It is difficult to experimentally separate the translational and [AlH₄]⁻ librational modes, although there is separation between the modes, similar to [AlH₄]⁻ in NaAlH₄.¹⁷ To resolve these modes in the experimentally obtained INS spectra, the INS spectra calculated from the partial phonon density of states and the area fractions for the external motions of $[A|H_4]^-$ are compared with the experimental spectra (Fig. 2). Increasing H contribution and decreasing Al contribution to the area fractions with increasing frequency suggest the weight shifting from translational mode to [AlH₄]⁻ librational modes (marked arrows in Fig. 2). This is consistent with vibrational motions calculated using the CASTEP. Therefore, the [AIH₄]⁻ librational modes in LiAlH₄, Ca(AlH₄)₂ and LiCa(AlH₄)₃ are observed around approximately 200, 250 and 100 cm⁻¹, respectively. Although a more highly charged cation(s) allows easier libration of the complex anions (lower peak frequency),¹⁸ the [AIH₄]⁻ librational modes in LiAlH₄ are observed at lower frequencies than those for $Ca(AIH_4)_2$. This originates from the coupling between the translational modes of light mass of Li⁺ and librational modes of [AlH₄]⁻. The coupling can be found that the Li⁺ contribution in the area fraction of $LiAlH_4$ or $LiCa(AlH_4)_3$ is synchronized with the increase in H contribution to the [AlH₄]⁻ librational modes as shown in Fig. 2. Such coupling and softening (discussed later) of translational and complex anion librational modes have been previously observed in complex hydrides with ionic conduction (e.g. LiBH₄).^{7,19} In LiAlH₄, the mobility of Li⁺ is much lower than that of $LiBH_4$.²⁰ This is hypothesized to be due to the lack of an order-disorder transition of Li⁺ during the



Fig. 2 INS spectra of (left) LiAlH₄, (middle) Ca(AlH₄)₂ and (right) LiCa(AlH₄)₃ at the frequency region of 0–600 cm⁻¹ with partial phonon density of states generated from aCLIMAX. The area fractions obtained from each partial phonon density of states are superimposed on the INS spectra. Black, red, purple, yellow and blue lines indicates experimentally obtained INS spectrum and partial phonon density of states for Li, Ca, Al and H, respectively. Arrows indicate the weight shifting from translational mode to [AlH₄]⁻ librational modes.

exhibiting of Li⁺ ionic conduction.

The internal motion of [AIH₄]⁻ comprises the Al-H bending modes (600–1100 cm⁻¹) and the Al–H stretching modes (1600– 2000 cm⁻¹). In particular, the Al–H stretching modes are often used for the identification of [AlH₄]⁻ because they are one of the most characteristic and simplest motions of [AIH₄]⁻. An evaluation of the local atomic structure around [AIH₄]⁻ (see Fig. 1) shows that H coordinated to two cations (Li⁺) results in a lower frequency of Al-H stretching modes and longer Al-H distances than H coordinated to one cation (Fig. 3 and Table 1). The higher frequency of the Al-H stretching modes reflects a shorter interatomic distance between Al and H, since motion involving shorter interatomic distances requires more energy.^{10e,21} Therefore, the larger number of cations around H might attract H atoms farther away from Al, inducing longer Al-H distances. This increased bond length in turn leads to lower frequency Al–H stretching modes.

We now describe the hydrogen release reactions in terms of the temperature dependence of the INS spectra. Upon heating,



Fig. 3 INS spectra of (left) LiAlH₄, (middle) Ca(AlH₄)₂ and (right) LiCa(AlH₄)₃ in the 1400–2200 cm⁻¹ frequency region. The blue and green spectra, which are generated from aCLIMAX, indicate the contributions from H atoms with one and two cation(s) around H, respectively.

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	Averaged Al–H	Peak frequency of	Al-H
	distance (Å)	stretching modes (cm ⁻¹)	
LiAlH ₄	1.61 (one Li)	1794	
	1.63 (two Li)	1651	
$Ca(AIH_4)_2$	1.61	1798	
$LiCa(AIH_4)_3$	1.62 (one Ca)	1830	
	1.66 (two Li)	1660	
	1.66 (two Li)	1660	

peak frequencies below 550 cm⁻¹, corresponding to the external motion of [AlH₄], clearly shift to lower frequencies, termed the softening of the external motion of [AIH₄]⁻ in all alanates (Fig. 4). Although prominent softening is confirmed in [AlH₄]⁻ librational modes as observed in LiAlH₄,⁶ a shift in the translational modes to lower frequencies are also observed (see Fig. 4) in this study because of the high resolution of INS spectroscopy. The softening of the external motion suggests appearing an intrinsic anharmonicity of the translational and the librational modes upon heating that would be related to hydrogen release reaction.⁶ In contrast, no such shift is observed above 600 cm⁻¹, corresponding to the internal motion of [AlH₄]⁻. Note that the peak intensities and widths are clearly decreased and broadened (Figs. S9-S11 in the ESI). This is due to the fact that chemical bonding of Al–H in [AlH₄][–] is rigidly maintained though thermal motions of H atom are increased. This is consistent with our previous results on local atomic structural analysis of LiAlH₄.²¹ In addition to the softening on the three alanates, spectroscopic studies on Ti doped NaAlH₄ have been shown the softening of the external motions correlated with the improvement of hydrogen release reaction kinetics.^{1a,1b,5} Therefore, the softening of the external motion of $[AIH_4]^-$ observed above 150 K, which is equivalent to weakening of chemical bonding between the metal cation(s) and [AlH₄]⁻, could be observed as an initial stage phenomenon to enhancing hydrogen release reaction kinetics of alanates. Such phenomena would be observed in complex hydrides (e.g. LiBH₄) since softening of [BH₄]⁻ librational modes in LiBH₄ observed during the exhibiting of Li⁺ ionic conduction.⁷ Although softening of vibrational modes on complex transition metal hydrides (e.g. Mg₂NiH₄) have not been reported, they would be a similar with complex hydrides with [AlH₄]⁻ and [BH₄]⁻ because of similarities of their vibrational dynamics.^{5d}

At 400 K, the background of the INS spectra decreases in 3 h owing to hydrogen release (Figs. S12–14 in the ESI). LiCa(AIH₄)₃ particularly exhibited the fastest hydrogen release reaction kinetics among the three alanates. Focusing on the peak frequencies of the $[AIH_4]^-$ librational modes because of obvious metal cation(s) and temperature dependences of the external motion of $[AIH_4]^-$, interestingly, LiCa(AIH₄)₃ with faster hydrogen release reaction kinetics shows lower $[AIH_4]^-$ librational mode peak frequencies than LiAIH₄ and Ca(AIH₄)₂ due to the coupling of Li⁺ translational modes and the valences of the metal cation(s). Such relationship has been also



Fig. 4 INS spectra of (top) LiAlH₄, (middle) Ca(AlH₄)₂ and (bottom) LiCa(AlH₄)₃ at 10–400 K. The intensity was divided by the Bose factor, $B(E, T) = 1 + 1/[\exp\{E/k_{\rm B}T\} - 1]$.^{5c} *E*: energy transfer in meV (= 8.066 × in cm⁻¹), *T*: temperature in kelvin and $k_{\rm B}$: the Boltzmann constant in J/K. The maxima of the [AlH₄]⁻ librational modes at 10 K are denoted and connected with curve at each temperature.

reported in water in ionic exchanged smectite clay minerals by different cations with different valences, in which their hydration enthalpies were depended on frequencies of water molecules librational modes with a trend of metal cations.²² Therefore, the hydrogen release reaction kinetics on alanates was speculated to be enhanced by the vibrational dynamics and the valences of the metal cation(s) because they affected for peak shifting to lower frequencies of $[AIH_4]^-$ librational modes. Thus, frequency of $[AIH_4]^-$ librational modes would imply a relevant to their hydrogen release reaction kinetics.

In summary, we investigated vibrational dynamics on LiAlH₄, Ca(AlH₄)₂ and LiCa(AlH₄)₃ with systematically different metal cation(s) and a [AlH₄]⁻ complex anion by inelastic neutron scattering (INS) spectroscopy to elucidate the relationships between their vibrational dynamics and hydrogen release reaction kinetics viewed from dependences of valences of metal cation(s). The INS spectra were divided into two regions corresponding to two different types of motion, external (<550 cm⁻¹) and internal motion (>600 cm⁻¹) of [AlH₄]⁻. In the external motion of [AlH₄]⁻ librational modes, the [AlH₄]⁻ librational and [AlH₄]⁻ librational modes, the [AlH₄]⁻ librational modes appeared at lower peak frequencies because of vibrational dynamics and the valence of the metal cation(s). In addition, the INS experiments upon heating revealed that the external motion of [AlH₄]⁻ was softened equivalent to

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weakening of the chemical bonding between the metal cations and $[AlH_4]^-$ above 150 K before hydrogen release reaction at 400 K, while the internal motion of $[AlH_4]^-$ is maintained. Such phenomena were also observed on Ti doped NaAlH₄. Those facts indicated that the softening of the external motion of $[AlH_4]^-$ was observed as an initial stage phenomenon for the hydrogen release. In addition, isothermal INS experiment at 400 K suggested that hydrogen release reaction kinetics showed to be faster with lower frequency of $[AlH_4]^-$ librational modes originated from the vibrational dynamics and the valences of the metal cation(s). Such phenomena were shown in water molecule in smectite clay minerals. Therefore, hydrogen release reaction kinetics could be enhanced by vibrational dynamics and the valences of the metal cation(s).

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