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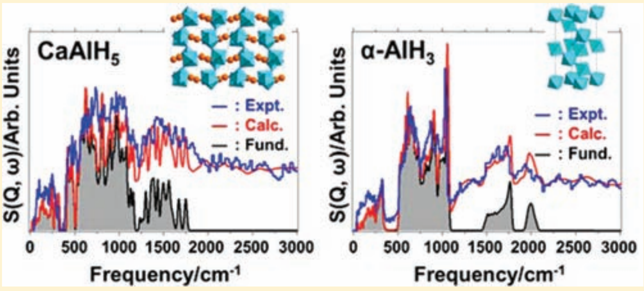
Vibrational Properties of $CaAlH_5$ and α-AlH_3 with Different AlH_6 Networks Studied by Inelastic Neutron Scattering

Toyoto Sato,*[†] A. J. (Timmy) Ramirez-Cuesta,[‡] Kazutaka Ikeda,[§] Shin-ichi Orimo,[∥] and Kazyoshi Yamada[†,∥]

[†]WPI Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
[‡]ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom
[§]Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan
[∥]Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

S Supporting Information



ABSTRACT: We performed a combined study using inelastic neutron scattering (INS) and first-principles calculations of the vibrational properties of $CaAlH_5$ and α-AlH_3 with different AlH_6 networks, a zigzag one-dimensional AlH_6 network for $CaAlH_5$, and a three-dimensional AlH_6 network for α-AlH_3. Both materials showed qualitatively similar INS spectra, in which $CaAlH_5$/α-AlH_3 was mainly divided into three regions: (i) the translational modes (318/316 cm^{-1}), (ii) the librational modes of the octahedral AlH_6 units (external molecular motion) in the lower frequency range and H—Al—H bond-bending modes (intra molecular motion) at a higher frequency (420—1157/513—1038 cm^{-1}), and (iii) the Al—H bond-stretching modes (1238—1750/1486—1942 cm^{-1}). In region ii, the appearance of both librational and bond-bending modes was determined by the networked nature of the octahedral AlH_6 units. In addition, the librational modes of AlH_6 on α-AlH_3 exhibit higher frequencies than $CaAlH_5$ due to the tighter bonding between the octahedral AlH_6 units. With regard to average frequencies for the Al—H, ω_S, bond-stretching modes, and average Al—H bond distances on the aluminum-based hydrides including $CaAlH_5$ and α-AlH_3, ω_S showed lower frequencies that correlate with lengthening of the Al—H bond distances.

1. INTRODUCTION

Hydrogen has been identified as an alternative clean energy carrier for mobile applications; efficient and safe hydrogen storage technologies are a necessity for the widespread use of hydrogen. As candidate materials for hydrogen storage, aluminum-based hydrides, so-called alanates and alanes, with high hydrogen gravimetric density (e.g., $LiAlH_4$, 10.5 wt %; AlH_3, 10.1 wt %) have been extensively studied both experimentally and theoretically, due to their high gravimetric hydrogen densities and hydrogen release at moderate temperatures and without impurity gases.[1−7]

The alanate system is characteristically represented as $M_m(AlH_x)_n$ with ionically bonded metal cations M^{n+} and complex anions $[AlH_x]^{m-}$ with Al—H covalent bonding (M, typically alkali or alkaline-earth n and m, valences of M and $[AlH_x]$). The values of x have been generally known as $x = 4-7$[5−7] (we here use tetra-hydride on $x = 4$, penta-hydride on $x = 5$, hexa-hydride on $x = 6$, and hepta-hydride on $x = 7$).

Focused on those crystal structures, with the exception of the tetra-hydride, they commonly adopt octahedral AlH_6 units; in which Al is octahedrally coordinated by six H atoms. So far, $CaAlH_5$,[8,9] $BaAlH_5$,[6] Li_3AlH_6,[6] Na_3AlH_6,[6] Sr_2AlH_7,[6] and Ba_2AlH_7[6] with octahedral AlH_6 units have been experimentally identified from neutron diffraction studies. Interestingly, they have different networks of the octahedral AlH_6 unit: the hexa- and hepta-hydrides have an isolated regular octahedral AlH_6 unit with Al—H bond distances in the range of 1.73—1.77 Å and H—Al—H angles of ~90° (the shape in hepta-hydrides is distorted);[6] the ones in the penta-hydrides are one-dimensional zigzag chains (zigzag one-dimensional AlH_6 network) and have a distorted shape with Al—H bond distances in the range of 1.69—1.85 Å and H—Al—H angles in the range of 75.6—103.7°.[6,8,9] (Crystal structures of Na_3AlH_6[10] and $CaAlH_5$[9] are illustrated in Figure 1.)

On the other hand, alane (AlH_3) is a binary compound of Al and H, which has been reported with different polymorphic crystal structures (α, α', β, and γ).[6] Though the alane does not have metal cations, their Al—H bonding natures have been reported to be similar to Al—H covalent bonding in the alanates.[11,12] Indeed, the crystal structures of the alanes also have octahedral

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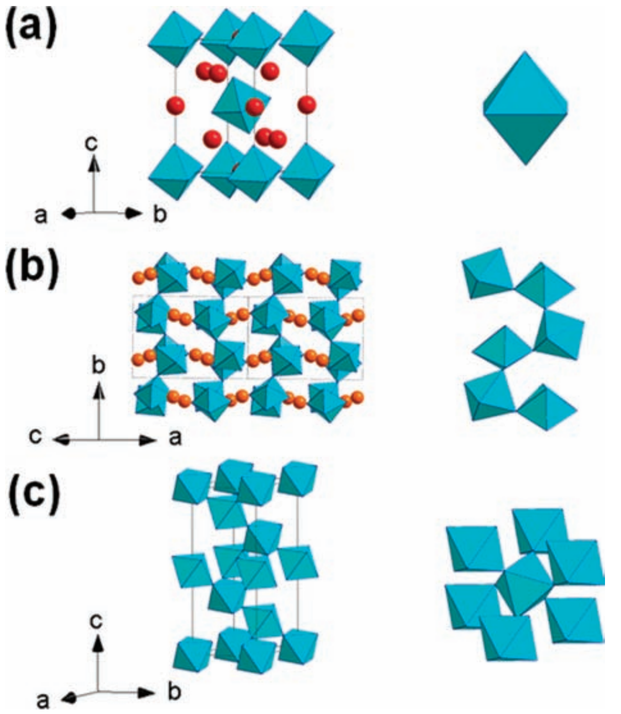

Figure 1. Crystal structures (left) and AlH_6 networks (right) of (a) Na_3AlH_6,[10] (b) $CaAlH_5$,[9] and (c) α-AlH_3.[13] Na and Ca atoms and octahedral AlH_6 units are displayed as red and orange circles and sky blue octahedra, respectively.

AlH_6 units with Al−H bond distances of 1.68−1.76 Å and H−Al−H angles of ~90°, similar to the alanates.[6] The AlH_6 networks are vertex- or edge-sharing (α-AlH_3 with all vertex sharing (three-dimensional AlH_6 network)[13] is illustrated in Figure 1).

With regard to the AlH_6 networks, in addition to the information on their crystal structures (static information), it is important to investigate the vibrational properties (dynamic information) in order to gain further insight into its implications in the fundamental understanding of the crystal structures and the vibrational properties in the aluminum-based hydrides and, ideally, to understand the hydrogen storage properties of such materials.

Raman, infrared (IR), and inelastic neutron scattering (INS) spectroscopies are usually employed in the investigation of vibrational properties. Whereas Raman and IR spectroscopies are convenient instruments, not all vibrational modes are allowed. INS can, however, obtain all vibratinal modes because INS conveys information on the dynamics across the Brillouin zone, and it has no selection rules. The INS intensities $S(Q, n\omega_i)$ are given by[14−16]

$$S(Q, n\omega_i) \propto \frac{(QU_i)^{2n}}{n!}\exp(-(QU_{Tot})^2)\sigma \qquad (1)$$

Q is the momentum transfer; ω_i is the ith mode at wavenumber ω; $n = 1, 2, 3$, etc. is the order of the vibrational transition (1 for fundamental transitions, 2 for first overtones and combinations, and so forth); U_i is the root-mean-square displacement of the atoms in the mode; U_{Tot} is the total root-mean-square displacement of all of the atoms in all of the modes; and σ is the inelastic scattering cross-section of the atom (a total of coherent and incoherent scattering cross-sections).

Interestingly, the σ of hydrogen (82.02 barns) is approximately 10 times as large as those of most other elements (less than 12 barns).[17] For this reason, E−H (E: elements) vibrational modes mainly dominate in INS spectra, and a lot of vibrational property on hydrides have been elucidated.[15,16,18−25]

To the best of our knowledge, vibrational properties of penta-hydrides studied by INS have not been reported previously. Therefore, the purpose of this study is first the elucidation of the vibrational properties of the penta-hydride, of which $CaAlH_5$ has been selected, by INS combined with first-principles calculations. Second, the INS spectrum of $CaAlH_5$ with a zigzag one-dimensional AlH_6 network is compared with α-AlH_3 possessing a three-dimensional AlH_6 network, and their differences are discussed. Further, those networked AlH_6 units are compared with Al−H vibrational modes, and a correlation map can be drawn between crystal structure and vibrational properties. In addition, this study also shows the identity of networked AlH_6 units which are believed to form during the hydrogen release reaction from tetra-hydrides into hexa-hydrides (e.g., $NaAlH_4 \rightarrow 1/3Na_3AlH_6 + 2/3Al + H_2(g)$).[20,26]

2. EXPERIMENTAL AND COMPUTATIONAL DETAILS

$CaAlH_5$ was synthesized by mechanochemical milling of CaH_2 (Sigma-Aldrich, 99.99%) and α-AlH_3 in a molar ratios of 1:1. α-AlH_3 as the starting material was synthesized in ether according to the chemical reaction of $LiAlH_4$ and $AlCl_3$.[27,28] The mixture was milled at 400 rpm under a hydrogen gas pressure of 0.35 MPa by using a planetary ball mill (Fritsch PULVERRISETTE 7). The effective milling time to obtain $CaAlH_5$ was 5.5 h. Milling times of 5 min were alternated with pauses of 5 min duration, and the details are described in refs 9 and 29 (the X-ray diffraction pattern of $CaAlH_5$ measured by a conventional X-ray diffractometer is shown in Figure S1 in the Supporting Information).

The INS spectra of $CaAlH_5$ and α-AlH_3 were obtained at 25 K with a data collection time of 6−12 h from those powder samples (less than 1.5 g) sealed in an airtight Al container on the high resolution time-of-flight INS spectrometer, TOSCA, at the pulsed neutron spallation source ISIS in the U.K. TOSCA is an inverted geometry inelastic neutron scattering spectrometer with access to an energy transfer from 0 to 4000 cm^{-1}, with a resolution of 1.5% $\Delta E/E$.[14] As mentioned above, INS can strongly detect hydrogen vibrational modes or features. In order to prevent thermal broadening and signal reduction due to the Debye−Waller factor effect from hydrogen on the spectra, all INS spectra were obtained at 25 K.

For the structural computation, optimization of $CaAlH_5$ and α-AlH_3 structures using as a starting point the crystal structure models of $CaAlD_5$[9] and α-AlD_3[13] was performed in the framework of the frozen core all-electron projected augmented wave method (PAW)[30] as implemented in the Vienna ab initio simulation package (VASP)[31] installed in Materials Design MedeA, version 2.4. The energy cutoff was set to 500 eV. Exchange and correction effects were treated by the generalized gradient approximation (GGA) functional of Perdew et al.[32,33] The phonon calculations of $CaAlH_5$ and α-AlH_3 were performed using the CASTEP program[34] and making use of the interpolation algorithm.[35] The periodic calculation containing a sampling of the reciprocal unit cells of the 6 × 6 × 5 point for $CaAlH_5$ and the 11 × 11 × 11 point for α-AlH_3 were performed. The resulting eigenvalues and eigenvectors, in the interpolated Brilloiun zone, were used to calculate the INS spectrum on TOSCA by the aCLIMAX program.[36]

3. RESULTS AND DISCUSSION

The observed and calculated INS spectra of $CaAlH_5$, including phonon dispersion curves along the high symmetry directions, are shown in Figure 2. In order to obtain the calculated spectra,

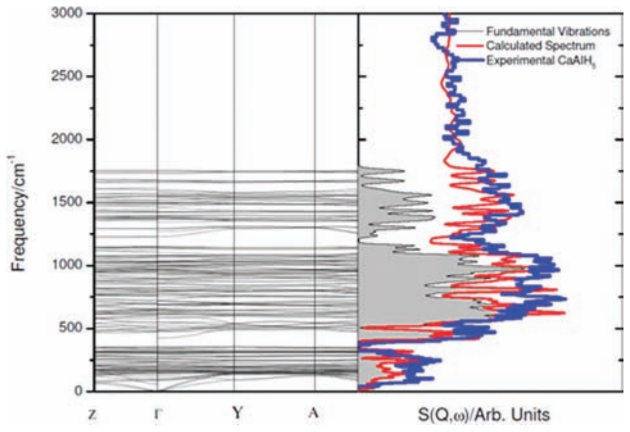

Figure 2. The experimental (blue line) and total calculated (red line) INS spectra of $CaAlH_5$ (right side) with the calculated phonon dispersion curves (left side). The shaded gray color represents the contribution from the fundamental vibrations.

Table 1. Vibrational Properties for $CaAlH_5$ and α-AlH_3[a]

	translational	librational and H—Al—H bond-bending	Al—H bond-stretching
$CaAlH_5$	0—318	420—1157	1238—1750
α-AlH_3	0—316	513—1038	1403—1942

[a] The frequencies (in cm^{-1}) were obtained the maximum intensity positions from the calculated fundamental INS spectrum generated by aCLIMAX.

the phonon density of states and dispersions for $CaAlH_5$ were calculated by the CASTEP program using an initial optimized structure model of $CaAlH_5$ by the VASP program. Using the aCLIMAX program, the phonon calculation results were used to calculate the INS spectra and compared with the experimental data. The plot of the calculated spectra with the phonon dispersion result shows the very good agreement between theory and experiment. The calculated INS spectrum with shaded gray color is the contribution to the INS signal from the fundamental vibrations ($n = 1$ in eq 1), excluding the contributions from the overtones and the combinations.[14,36,37] In order to interpret the spectra, we will use the standard separations of molecular modes into external and internal motions; a vibrational mode in a molecular solid will have an external character when the internal coordinates of the molecule in question do not change and the main motion is the motion of the molecule as a whole, for example, translation and libration. Internal motions, on the other hand, are modes that involve the distortion of the molecule itself, for example, bond-bending and stretching modes.

The INS spectrum of $CaAlH_5$ can be mainly divided into three regions located in the following frequency ranges 0—318, 420—1157, and 1238—1750 cm^{-1} (Table 1). The first region shows translational modes that Ca, Al, and H atoms are slightly displaced from the equilibrium positions. In the second region, two different modes exist, which are librational modes of the octahedral AlH_6 units classified into external molecular motions in the lower frequency part of the range and H—Al—H bond-bending modes classified into intramolecular motions in the higher frequency part (external molecular motions, between octahedral AlH_6 units; intramolecular motions, inside of octahedral AlH_6 unit). A narrow gap on the calculated INS spectra appears at around 500 cm^{-1}. Although it might be a gap between them, it is difficult to distinguish because the zigzag one-dimensional AlH_6 network makes complicated motions. As mentioned above, Na_3AlH_6 has an isolated AlH_6 unit. Na_3AlH_6 shows a much different INS spectrum from $CaAlH_5$, on which the librational modes and bond-bending modes are obviously separated (see Figure S2 in Supporting Information). The appearance of both librational and bond-bending modes on the region is, therefore, caused by the networking of the octahedral AlH_6 unit. On the third region, the Al—H bond-stretching modes appear. The Al—H bond-stretching modes are not simple bond-stretching modes as Na_3AlH_6 with the isolated AlH_6 unit[19] because of the zigzag one-dimensional AlH_6 network, theses modes are mixed with translational and librational motions, but the main characteristic feature is bond-stretching of the A—H bond.

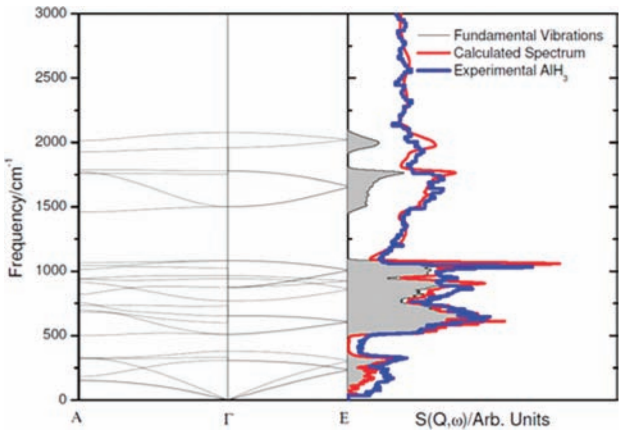

Figure 3. The experimental (blue line) and total calculated (red line) INS spectra of α-AlH_3 (right side) with the calculated phonon dispersions (left side). The shaded gray color represents the contribution from the fundamental vibrations.

The observed and calculated INS spectra of α-AlH_3 with the calculated phonon dispersions are shown in Figure 3. Using the same calculation procedures as used with $CaAlH_5$, the result also shows good agreement between theory and experiment. The experimental and calculation results are consistent with the INS results for α-AlH_3 previously reported by Kolesnikov et al.[18]

The INS spectrum of α-AlH_3, qualitatively similar to that of $CaAlH_5$, can be mainly divided into three regions, namely, 0—316, 513—1038, and 1486—1942 cm^{-1} (Table 1). On the INS spectrum, the first region shows the translational modes where Al and H atoms are slightly displaced from the equilibrium positions. In the second region, both librational modes of the octahedral AlH_6 unit (external molecular motions) in the lower frequency part and H—Al—H bond-bending modes (intra molecular motions) in the higher frequency part exist as well as $CaAlH_5$. It should be noted that the lower frequency part (the librational modes region) on α-AlH_3 starts at higher frequencies than $CaAlH_5$. This is originated from the tightened bonding between the octahedral AlH_6 units, which are α-AlH_3 with all vertexes sharing and $CaAlH_5$ with two vertexes sharing in six, because tight bonding needs higher excitation energy for the motion. This is consistent in Na_3AlH_6 where the AlH_6 units isolated are isolated (see Figure S2 in Supporting Information). In the third region, the Al—H bond-stretching modes appear. The Al—H bond-stretching modes are not simple bond-stretching

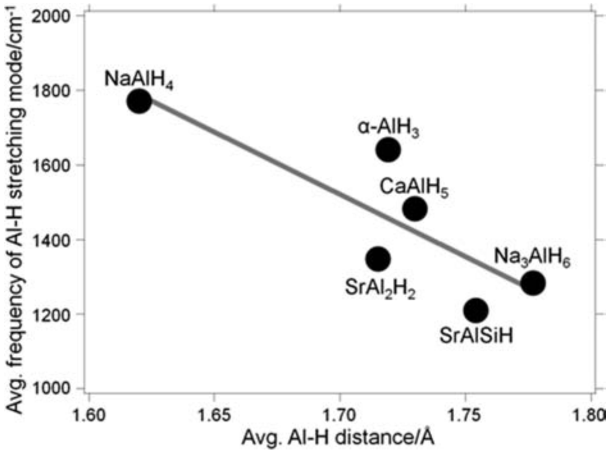

Figure 4. Correlation between the averaged frequencies ω_S (Al−H bond-stretching modes) and averaged Al−H bond distances. The averaged Al−H bond distances were referred from the deuterides[6,9,10,13,39,40] instead of the hydrides. The gray line is obtained from the linear regression of all plots.

modes such as in Na_3AlH_6[19] because of the three-dimensional AlH_6 network, as is the case for $CaAlH_5$, see above.

Focused on Al−H bond-stretching modes on not only $CaAlH_5$ and α-AlH_3 but also aluminum-based hydrides, Lee et al. and Yukawa et al. reported an interesting correlation between frequencies for the Al−H bond-stretching modes and Al−H distances.[21,38] So far, vibrational properties of aluminum-based hydrides, which are SrAlSiH,[21] $SrAl_2H_2$,[21] $NaAlH_4$,[20] and Na_3AlH_6,[19] were revealed from INS studies combined with the first-principles calculations. Including the present study, the calculated average frequencies ω_s for the Al−H bond-stretching modes and the averaged optimized Al−H bond distances on SrAlSiH (1215 cm^{-1} and 1.75 Å), $SrAl_2H_2$ (1343 cm^{-1} and 1.72 Å), α-AlH_3 (1635 cm^{-1} and 1.72 Å), $NaAlH_4$ (1771 cm^{-1} and 1.72 Å), $CaAlH_5$ (1485 cm^{-1} and 1.73 Å), and Na_3AlH_6 (1287 cm^{-1} and 1.78 Å) are plotted in Figure 4. It follows that the ω_s showed lower frequencies with lengthening Al−H bond distances because shorter Al−H distance means stronger bonds and therefore needs higher excitation energy.

The considered correlations between vibrational and material properties (i.e., hydrogen release temperatures) are difficult to deal with directly because the INS spectra were obtained at 25 K, which was much lower than those hydrogen release temperatures.[29] On the other hand, networked AlH_6 units have been reported to form during the hydrogen release reaction from tetrahydrides into hexa-hydrides (e.g., $NaAlH_4 \rightarrow 1/3Na_3AlH_6 + 2/3Al + H_2(g)$).[20,26] In spite of many studies on such aluminum-based hydrides in order to clarify the hydrogen release mechanism, the networked AlH_6 units and the mechanism have not yet been well understood because of chemically unstable and amorphous phases. In this study, the vibrational modes on the well-characterized $CaAlH_5$ and α-AlH_3 with different AlH_6 networks have been assigned and discussed on those differences compared with Na_3AlH_6 with isolated AlH_6 units. Therefore, the results of this study can strongly support the identity of the networked AlH_6 phases during the hydrogen release reaction from tetra-hydrides into hexa-hydrides and a clarification of the hydrogen release mechanism on these aluminum-based hydrides.

4. CONCLUSIONS

The vibrational properties of $CaAlH_5$ and α-AlH_3 with different AlH_6 networks, in which $CaAlH_5$ and α-AlH_3 have a zigzag one- and three-dimensional AlH_6 network, respectively, were studied using inelastic neutron scattering (INS) combined with first-principles calculations. $CaAlH_5$/α-AlH_3 quantitatively showed similar INS spectra, which were mainly divided by three regions where there were (i) translational modes at 0−318/0−316 cm^{-1}, (ii) librational modes of the octahedral AlH_6 units (external molecular motions) in the lower frequency part and H−Al−H bond-bending modes (intra molecular motions) in the higher frequency part at 420−1157/513−1038 cm^{-1}, and (iii) Al−H bond-stretching modes at 1238−1750/1486−1942 cm^{-1}, respectively. In region ii, the appearance of both librational and bond-bending modes is due to the network of the octahedral AlH_6 units. Considered in the librational modes in the lower frequency part in region ii, α-AlH_3 starts at slightly higher frequencies than $CaAlH_5$. It was concluded to originate from tightness bonding between the octahedral AlH_6 units. With regard to the average bond-stretching frequencies ω_S for the Al−H bond-stretching modes and the average Al−H bond distances, the ω_S showed a correlation between lower frequencies and the lengthening Al−H bond distances.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** X-ray diffraction pattern of $CaAlH_5$ (Figure S1) and INS spectrum of Na_3AlH_6 observed by TOSCA at ISIS in UK (Figure S2). The material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Telephone: +81-22-215-2039. Fax: +81-22-215-2036. E-mail: toyoto@imr.tohoku.ac.jp.

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