Formation of novel transition metal hydride complexes with ninefold hydrogen coordination

Shigeyuki Takagi, Yuki Iijima, Toyoto Sato, Hiroyuki Saitoh, Kazutaka Ikeda, Toshiya Otomo, Kazutoshi Miwa, Tamio Ikeshoji & Shin-ichi Orimo

Ninefold coordination of hydrogen is very rare, and has been observed in two different hydride complexes comprising rhenium and technetium. Herein, based on a theoretical/experimental approach, we present evidence for the formation of ninefold H-coordination hydride complexes of molybdenum ([MoH$_9^-$]), tungsten ([WH$_9^-$]), niobium ([NbH$_9^-$]) and tantalum ([TaH$_9^-$]) in novel complex transition-metal hydrides, Li$_5$MoH$_{11}$, Li$_5$WH$_{11}$, Li$_6$NbH$_{11}$ and Li$_6$TaH$_{11}$, respectively. All of the synthesized materials are insulated with band gaps of approximately 4 eV, but contain a sufficient amount of hydrogen to cause the H 1$s$-derived states to reach the Fermi level. Such hydrogen-rich materials might be of interest for high-critical-temperature superconductivity if the gaps close under compression. Furthermore, the hydride complexes exhibit significant rotational motions associated with anharmonic librations at room temperature, which are often discussed in relation to the translational diffusion of cations in alkali-metal dodecahydro-closo-dodecaborates and strongly point to the emergence of a fast lithium conduction even at room temperature.

Although exhibiting the simplest form, hydrogen has an exceptionally rich chemistry, forming various chemical bonds in materials. The flexibility of hydrogen is the source of many interesting functionalities in hydrides, such as hydrogen storage, superconductivity, fast ionic conductivity, magnetism and metal–insulator transition; thus, materials containing a large amount of hydrogen are promising candidates not only for improving material performance but also for the emergence of latent functionalities.

Complex transition metal hydrides represent a class of hydrogen-rich materials, wherein a number of H atoms covalently bind to a transition metal element (T) to form hydride complexes with a remarkably rich variety of H-coordination modes ranging from twofold to ninefold. These complexes are stabilized by charge transfer from electropositive counterions, such as alkali and alkaline earth metals, to form insulating hydrides. In general, the H-coordination number increases from right to left along a given period because of the trend of increasing atomic size, which allows more hydrogen binding. At the same time, despite research spanning the past several decades, the elements capable of forming hydride complexes are thought to be limited to those in Groups 7–12. This limitation has so far precluded further discovery of hydride complexes with high H-coordination.

For example, the presently known members with the ninefold H-coordination are limited to those comprising the Group 7 elements technetium ([TcH$_9^-$]) and rhenium ([ReH$_9^-$]). However, we recently reported the formation of the first Group 6 hydride complex [CrH$_7^-$] in Mg$_3$CrH$_8$, thereby demonstrating that there is no a priori reason for this limitation and paving the way for the discovery of higher H-coordination hydride complexes comprising unexplored elements to the left of Group 7.

To demonstrate the feasibility of this strategy, we have experimentally examined the formation of novel transition metal hydride complexes of Group 5 and Group 6 elements (Mo, W, Nb and Ta) based on a first-principles prediction. Lithium was selected as a counterion because of its low electronegativity, which is expected to thermodynamically stabilize the complex hydride phases. The crystal structures and electronic structures of the
obtained samples were investigated using a combination of experimental and \textit{ab initio} approaches. Finally, we discuss the prospects for the emergence of H-driven functionalities in the obtained materials.

Results

First-principles predictions. We first performed a ground-state structure search of Li–Mo–H and Li–Nb–H systems using first-principles calculations. Figure 1 shows the obtained most stable structures found with stoichiometries of Li$_5$MoH$_{11}$ and Li$_6$NbH$_{11}$. In Li$_5$MoH$_{11}$, nine H atoms (H1) form a tricapped trigonal prism around the Mo atoms sitting at the (0, 0, 0) and (0, 0, 1/2) coordinates of the hexagonal lattice and two isolated H atoms (H2) are located at the approximate centres of the trigonal prisms formed by the six Mo atoms. The four Li atoms coordinate to the H2 atoms, forming a two-dimensional network of corner-sharing tetrahedra between the layers of MoH$_9$ units. Li$_6$NbH$_{11}$ has a structure similar to that of Li$_5$MoH$_{11}$; however, it has an additional Li site between the NbH$_9$ tricapped trigonal prisms along the $c$-axis, which accommodates the 6:1 stoichiometry between Li and Nb.

The calculated standard heats of formation $\Delta H_f$ are $-510$ kJ/mol for Li$_5$MoH$_{11}$ and $-637$ kJ/mol for Li$_6$NbH$_{11}$, which are much lower than those of the conceivable decomposed products, 5LiH + Mo + 3H$_2$ and 6LiH + NbH$_{0.65}$ + 2.175H$_2$, respectively (note that the enthalpies of reaction are estimated to be $-105$ and $-91$ kJ/mol, respectively, using $-81$ kJ/mol for LiH and $-60$ kJ/mol for NbH$_{0.65}$). We observed that the isostructural 5d analogues Li$_5$WH$_{11}$ and Li$_6$TaH$_{11}$ also have higher thermodynamic stabilities of $-529$ and $-651$ kJ/mol with respect to the conceivable decomposition products 5LiH + W + 3H$_2$ and 6LiH + TaH$_{0.65}$ + 2.175H$_2$, respectively (note that the enthalpies of reaction are estimated to be $-128$ and $-117$ kJ/mol, respectively, using $-51$ kJ/mol for TaH$_{0.65}$). The results are summarized in Table 1.

Electronic structures. Based on the obtained structures, we discuss the electronic structures. Figure 2 shows the calculated electronic densities of states (DOSs) and the H $s$ and T spd projections. We checked for magnetic states and observed no magnetic ordering in any of the materials.

The most important feature of the electronic structures is that the 1$s$ states of the nine H1 atoms forming the $TH_4$ tricapped trigonal prisms reach the Fermi level ($E_F$) in all materials, as observed in the third panels from the top in Fig. 2a–d. These states strongly hybridize with the $Tspd$ states to form the $\sigma$-bonds, which is evident from the H1 $s$ and T spd characters of both the valence and conduction bands. These results are consistent with a previous electronic structure calculation by Singh et al.\textsuperscript{29} for BaReH$_4$, which contains the hydride complex ReH$_4$. Because all nine bonding states are fully occupied by 18 electrons per formula unit, the $TH_4$ units can be considered as the hydride complexes [MoH$_4$]$^{3-}$, [WH$_4$]$^{3-}$, [NbH$_4$]$^{4+}$ and [TaH$_4$]$^{5+}$. The 1$s$ states of the isolated H2 atoms

![Figure 1. Crystal structures. (a–d) Density functional theory (DFT) structures of Li$_5$MoH$_{11}$ (a,b) and Li$_6$NbH$_{11}$ (c,d) viewed along the [110] (a,c) and [001] (b,d) directions. Li$_5$WH$_{11}$ and Li$_6$TaH$_{11}$ have isostructures to Li$_5$MoH$_{11}$ and Li$_6$NbH$_{11}$, respectively.](image-url)
lie immediately below $E_F$ without noticeable hybridization with any other states, as observed in the second panels from the top in Fig. 2a–d. Thus, these atoms can be considered as $H^{-}$ ions. The electropositive Li states occur far above $E_F$ (not shown) and donate one electron per atom to the hydride complexes to become $Li^{+}$ cations. Thus, we conclude that the ionic configurations of the current materials are $[Li^{+}]_5[MoH_9]_3^{-}[H^{-}]_2$, $[Li^{+}]_5[WH_9]_3^{-}[H^{-}]_2$, $[Li^{+}]_6[NbH_9]_4^{-}[H^{-}]_2$ and $[Li^{+}]_6[TaH_9]_4^{-}[H^{-}]_2$. The band gaps are approximately 4 eV in all of the materials.

**Syntheses.** We experimentally examined the possibility of the formation of the theoretically predicted complex transition metal hydrides using a high-pressure and high-temperature technique. Powdered mixtures of LiH and Group 5 and Group 6 transition metals were hydrogenated under 5 GPa at 923–1023 K for 24–48 h. The colours of the samples recovered at ambient pressure and temperature were yellow for Li–Mo–H, greenish yellow for Li–W–H, light grey for Li–Nb–H and white for Li–Ta–H, implying the insulating character, as is typical with complex transition-metal hydrides.

The recovered samples were characterized by Raman spectroscopy, and the results are illustrated in Fig. 3a–d (black lines) along with the density functional theory (DFT) spectra (red lines) calculated using a method reported in the literature. Because the primitive cells of $Li_5MoH_{11}/Li_5WH_{11}$ and $Li_6NbH_{11}/Li_6TaH_{11}$ comprise 34 and 36 atoms, respectively, there are a total of 99 ($10A_1 + 6A_2 + 6B_1 + 11B_2 + 17E_1 + 16E_2$) and 105 ($11A_1 + 6A_2 + 12B_1 + 18E_1 + 17E_2$) zone-centre optical phonon modes, respectively, as represented by the tick marks in Fig. 3a–d. Among them, 76 modes ($10A_1 + 17E_1 + 16E_2$) of $Li_5MoH_{11}/Li_5WH_{11}$ and 81 modes ($11A_1 + 18E_1 + 17E_2$) of $Li_6NbH_{11}/Li_6TaH_{11}$ are Raman active. These modes provide an intense and asymmetric band at approximately 1660–1860 cm$^{-1}$ and a weak band at approximately 1000 cm$^{-1}$ in all the DFT spectra, which originate from the $T$–H stretching and $H$–$T$–$H$ bending vibrations, respectively. The experimental spectra exhibit very similar features to those obtained by the DFT calculations, strongly supporting the formation of the theoretically predicted ninefold $H$-coordination hydride complexes.

**Finite-temperature effects.** The DFT lattice parameters summarized in Table 2 are slightly smaller than those determined from the XRD profiles measured at room temperature (4–10% smaller in volume), implying

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**Figure 2.** Electronic structures. Total electronic density of states (DOS; top panels) and $H_2 1s$ (second panel from the top), $H_1 1s$ (third panel from the top), $T d$ (third panel from the bottom), $T p$ (second panel from the bottom) and $T s$ (bottom panels) projections for $Li_5MoH_{11}$ (a), $Li_5WH_{11}$ (b), $Li_6NbH_{11}$ (c) and $Li_6TaH_{11}$ (d). The energy zero is set at the valence-band maximum.
the presence of finite-temperature effects. As such, we examined the dynamics of the room-temperature phase of Li₅MoH₁₁ as an example using both first-principles molecular dynamics (FPMD) calculations in the isothermal–isobaric (NPT) ensemble at 298 K and neutron diffraction (ND) measurements at room temperature (strictly, ND measurements were performed on the deuteride analogue Li₅MoD₁₁).

In FPMD calculations, the two isolated H atoms (H₂) isotropically fluctuate around their original positions determined by DFT calculations at 0 K, whereas the nine H atoms in the MoH₉ units (H₁) rotate around the Mo atoms, generating spherical shell-like distribution, as illustrated in Fig. 4a. This type of rotational motion associated with anharmonic librations is acknowledged as leading to phase transitions in borohydrides and thus is expected to promote the volume expansion at room temperature. In fact, we observed a ~4% expansion (285 Å³) relative to the ground-state volume obtained by DFT calculations at 0 K (274 Å³), as shown in Fig. 4b. Additionally, the FPMD trajectory reasonably reproduces the experimental ND profile in Fig. 4c, as observed by the comparison of the simulated profile from the trajectory (red line in Fig. 4d) with the Rietveld refinement fit (black line in Fig. 4d), where the P₆₃mc structure (No. 185) with nine disordered D atoms surrounding the Mo atoms was employed, as shown in Fig. 4e, suggesting the adequacy of the current discussion. The experimentally determined structural parameters are summarized in Table 3.

Discussion

We have examined the possibility of the formation of novel transition metal hydride complexes with high H-coordination using a combined theoretical/experimental approach. All experimental data strongly point to the successful syntheses of a series of theoretically predicted complex transition metal hydrides Li₅MoH₁₁, Li₅WH₁₁, Li₆NbH₁₁, and Li₆TaH₁₁, containing ninefold H-coordination hydride complexes and two H⁻ anions. Our theoretical calculations reveal the σ-bonds of the nine H atoms forming the hydride complexes and the transition metals reach E_F in all synthesized materials.

Generally, the electronic structures of complex transition-metal hydrides can be viewed as comprising low-lying H 1s- and high-lying T spd-derived states, as schematically depicted in Fig. 5. The ligand field induced by the H-coordination divides the T spd states into the nonbonding and antibonding states (σ*-bands), and E_F falls in the ligand-field gap to accommodate the so-called 18-electron rule. Therefore, the valence bands around E_F are normally dominated by the Tspd-derived nonbonding states (strictly, the Td-derived nonbonding states); however, we emphasize here that the contribution from the H 1s-derived σ-bands in the valence bands increases with increasing H-coordination number, pushing the Tspd-derived states out of the valence bands and reaching E_F at ninefold coordination (Fig. 5). This is a novel strategy for obtaining solid-state covalently bonded hydrides with the H 1s-derived states reaching E_F.
As is well known, it is indispensable to have \( \sigma \)-bands of light elements at \( E_F \) to achieve high-critical-temperature (high-\( T_c \)) superconductivity within the Bardeen–Cooper–Schrieffer (BCS) theory. For example, the relatively high \( T_c \) observed in \( \text{MgB}_2 \) is primarily attributed to the high-lying two-dimensional \( \sigma \)-bands derived from the in-plane \( \text{B–B} \) bonds, the holes of which strongly couple with the bond stretch phonons. Conversely, in all of the materials synthesized in this study, nine of the lightest \( \text{H} \) atoms form strong \( \sigma \)-bonds with transition metal elements, providing a DOS just below \( E_F \). In this context, the occurrence of stronger electron–phonon coupling may be expected if the band gaps close under compression. From our preliminary calculations, we observed that there is at least one stable metallic phase of \( \text{Li}_5\text{MoH}_{11} \) above 94 GPa (see Supplementary information).

Besides the electronic feature, these materials have a characteristic phonon property such that the ninefold hydride complexes exhibit rotational motions associated with anharmonic librations at room temperature. This type of motion has never been observed in the complex transition metal hydrides, but has often been discussed in relation to the occurrence of fast ion conduction in alkali metal dodecahydro-\( \text{closo}-\text{dodecaborates} \) such as \( \text{Na}_2\text{B}_{12}\text{H}_{12} \). In this material, the first-order phase transition from the low-temperature monoclinic to the

### Table 3. Structural parameters of \( \text{Li}_5\text{MoH}_{11} \) determined by neutron diffraction (ND) measurements at room temperature.

| Element  | Wyckoff notation | \( x \)  | \( y \)  | \( z \)  | occupancy | \( 100 \times U_{iso} \) (Å) |
|----------|------------------|---------|---------|---------|-----------|------------------|
| \( \text{Mo1} \) | 2\( a \) | 0 | 0 | −0.018(3) | 1.0 | 4.0 |
| \( \text{Li1} \) | 4\( b \) | 1/3 | 2/3 | 0.0780 | 1.0 | 1.0 |
| \( \text{Li2} \) | 6\( c \) | 1/2 | 0 | 0.2943 | 1.0 | 1.0 |
| \( \text{D1} \) | 12\( d \) | 0.3011(11) | 0.0000(11) | −0.018(3) | 0.3 | 3.77(27) |
| \( \text{D2} \) | 12\( d \) | 0.1819(11) | 0.3546(9) | 0.0234(30) | 0.3 | 3.77(27) |
| \( \text{D3} \) | 12\( d \) | 0.1915(15) | 0.0004(18) | 0.1066(30) | 0.3 | 3.77(27) |
| \( \text{D4} \) | 12\( d \) | 0.1819(11) | 0.3546(9) | 0.441(4) | 0.3 | 3.77(27) |
| \( \text{D5} \) | 12\( d \) | 0.1915(15) | 0.0004(18) | 0.3569(30) | 0.3 | 3.77(27) |
| \( \text{D6} \) | 4\( b \) | 1/3 | 2/3 | 0.2324(7) | 0.3 | 2.62(28) |

As is well known, it is indispensable to have ‘\( \sigma \)-bands’ of light elements at \( E_F \) to achieve high-critical-temperature (high-\( T_c \)) superconductivity within the Bardeen–Cooper–Schrieffer (BCS) theory. For example, the relatively high \( T_c \) observed in \( \text{MgB}_2 \) is primarily attributed to the high-lying two-dimensional \( \sigma \)-bands derived from the in-plane \( \text{B–B} \) bonds, the holes of which strongly couple with the bond stretch phonons. Conversely, in all of the materials synthesized in this study, nine of the lightest \( \text{H} \) atoms form strong \( \sigma \)-bands with transition metal elements, providing a DOS just below \( E_F \). In this context, the occurrence of stronger electron–phonon coupling may be expected if the band gaps close under compression. From our preliminary calculations, we observed that there is at least one stable metallic phase of \( \text{Li}_5\text{MoH}_{11} \) above 94 GPa (see Supplementary information).

Besides the electronic feature, these materials have a characteristic phonon property such that the ninefold hydride complexes exhibit rotational motions associated with anharmonic librations at room temperature. This type of motion has never been observed in the complex transition metal hydrides, but has often been discussed in relation to the occurrence of fast ion conduction in alkali metal dodecahydro-\( \text{closo}-\text{dodecaborates} \) such as \( \text{Na}_2\text{B}_{12}\text{H}_{12} \). In this material, the first-order phase transition from the low-temperature monoclinic to the
high-temperature cubic phase occurs near 520 K, which is accompanied by an increase of two orders of magnitude in the rate of reorientational jumps of the icosahedral [B\textsubscript{12}H\textsubscript{12}]\textsuperscript{2−} anions with the fast translational diffusion of Na\textsuperscript{+} ions\textsuperscript{35}. Although we observed no obvious translational diffusion of Li\textsuperscript{+} ions in our FPMD calculations because of the limited simulation time (12 ps) and the unit cell size (136 atoms), the significant rotational motions of [MoH\textsubscript{9}]\textsuperscript{3−} ions, as observed in Fig. 4a, suggest the potential fast lithium ion conduction even at room temperature. It should be noted that given the quantum mechanical tunnelling of the H atoms, the rotational motions of hydride complexes may be sustained at extremely low temperature at which thermal diffusion is suppressed.

Although the hydride complexes with ninefold H-coordination were discovered in 1964\textsuperscript{18}, they are very rare and their properties have not been fully clarified. Therefore, our findings will facilitate the discovery of latent functionalities, such as those described in this study and will lead to renewed interest in complex transition metal hydrides.

Methods

DFT calculations. The ground-state crystal structures of the Li–Mo–H, Li–W–H, Li–Nb–H and Li–Ta–H systems were explored using the structures of existing compounds as references. This exploration was performed using first-principles DFT calculations as implemented in the Vienna ab initio simulation package (VASP)\textsuperscript{36,37}. We used a plane-wave basis and the projector augmented wave method\textsuperscript{38,39} within the generalized gradient approximation with the Perdew–Burke–Ernzerhof exchange-correlation functional\textsuperscript{40}. For Li\textsubscript{5}MoH\textsubscript{11}, we assumed that the structure has a metal framework similar to that of CaNi\textsubscript{5} because of the similarity in their metal stoichiometries (Ca and Ni were replaced by Mo and Li, respectively, in the doubled CaNi\textsubscript{5} structure along the \(c\)-axis). We used nine H atoms (18 H atoms per formula unit) to coordinate the Mo atoms in the fashion of a tricapped trigonal prism, and placed two H atoms (four H atoms per formula unit) in the largest tetragonal site comprising four Li atoms. For Li\textsubscript{6}NbH\textsubscript{11}, an additional Li atom (two Li atoms per formula unit) was placed at the centre of the largest trigonal antiprism comprising six H atoms in Li\textsubscript{5}MoH\textsubscript{11} to accommodate the 6:1 stoichiometry between the Li and transition metals. We assumed that Li\textsubscript{5}WH\textsubscript{11} and Li\textsubscript{6}TaH\textsubscript{11} have isostructures to Li\textsubscript{5}MoH\textsubscript{11} and Li\textsubscript{6}NbH\textsubscript{11}, respectively. Next, full structure relaxations, including those for the lattice parameters, shapes and internal coordinates, were performed. Subsequently, phonon calculations were performed to verify that the relaxed structures were at the true minimum. When imaginary phonon frequencies were observed, we slightly displaced the atoms along the directions of the eigenvectors of the imaginary modes and further relaxed the structures to eliminate them. This procedure was performed until the ground state was reached. This was done using well-converged plane-wave basis sets with a cut-off energy of 800 eV. An 8 × 8 × 4 grid was used for the \(k\)-point sampling of the Brillouin zone.

FPMD calculations. The room-temperature phase of Li\textsubscript{5}MoH\textsubscript{11} was examined using FPMD calculations in the NPT ensemble at 298 K with a 2 × 2 × 1 supercell (136 atoms) of the primitive cell. We employed a well-converged cut-off energy of 600 eV with \(k\)-point sampling at the \(\Gamma\)-point. The simulation temperature was set to 298 K, which was controlled by a Langevin thermostat\textsuperscript{41} with a friction coefficient of 10 ps\textsuperscript{−1} for all atoms. The simulation pressure was controlled by a Parrinello–Rahman barostat\textsuperscript{42,43}, where a friction coefficient of 10 ps\textsuperscript{−1} were used for the lattice degrees of freedom. The total simulation time was 12 ps with a timestep of 0.5 fs.

Theoretical ND profile. The integrated time-of-flight (TOF) ND peak intensity \(I(K_n)\) at the FPMD step \(n\) was calculated from the FPMD trajectory using the following equation:

\[
I(K_n) = L(K_n) \left| \sum_j b_j \exp(iK_n \cdot r_{j,n}) \right|^2,
\]
where $\mathbf{K}_n$ is the reciprocal lattice vector, $L(\mathbf{K}_n)$ is the Lorentz factor, $b_j$ is the neutron-scattering length of atom $j$, and $r_{j,n}$ is the position of atom $j$. The ND profile was obtained by integrating the discrete ND peaks broadened by a Gaussian function with a width of 0.02 Å over a range from 0.8 fs to 12 ps, where the unit cell volume is well converged (see Fig. 4b).

### Syntheses.

High-purity metal powders of Mo (99.99%, Sigma-Alrich), W (99.99%, Sigma-Alrich), Nb (99.9%, Mitsuwa Chemicals Co., Ltd.) and Ta (99.9%, Mitsuwa Chemicals Co., Ltd.) were mixed with LiH (95%, Sigma-Aldrich) at molar ratios of 1:6 (Li–Mo–H and Li–W–H) and 1:8 (Li–Nb–H and Li–Ta–H) by mechanical milling at 400 rpm for 4 h under a 0.1-MPa Ar atmosphere. The mixtures were compacted into pellets (diameter and thickness = 1.0 mm) and encapsulated in sample capsules comprising pyrolytic boron nitride. The capsules were loaded together with a hydrogen source (AlH$_3$) into NaCl capsules, which were used to seal the hydrogen fluid that evolved from AlH$_3$. The NaCl capsules were pressurized to 5 GPa at room temperature using a multi-anvil high-pressure apparatus, followed by subsequent heating at 923 K (Li–Nb–H) and 1023 K (Li–W–H and Li–Ta–H) for 24 h (Li–W–H and Li–Ta–H) and 48 h (Li–Mo–H and Li–Nb–H). A similar procedure was used to synthesize the deuteride analogue Li$_5$MoD$_{11}$, where LiD and AlD$_3$ were used in place of LiH and AlH$_3$.

### ND.

Neutron scattering experiments of Li$_5$MoD$_{11}$ (41 mg) were performed for an exposure time of 8 h at room temperature under He on the NOVA high-intensity total diffractometer installed at the 500 kW spallation neutron source at the Materials and Life Science Experimental Facility (MLF) Japan Proton Accelerator Research Complex (J-PARC). The sample was filled in a cylindrical sample container with an external diameter of 3.0 mm and thickness of 0.1 mm. Rietveld analysis was performed using the General Structure Analysis System (GSAS) software and the graphical interface EXPGUI (version 1.80) on the ND data, with $d = 0.25$ Å–6.16 Å obtained at room temperature from detectors of medium resolution ($\Delta d/d = 0.6\%$) at the scattering angle $2\theta = 72°–108°$. The profile function developed by Von Dreele et al. was used for performing Rietveld analysis. The background was modeled using the 10-terms Chebyshev polynomial function model in GSAS. The distances of Mo–D in the complex anion [MoD$_9$]$^3^-$ and Li–D in the tetrahedral site in Li$_5$MoD$_{11}$ were soft constrained to 1.75 Å. The constraints were weighted such that they imposed only a minor deterioration of the fit to the experimental data. ND peaks of an unknown phase were indexed by a monoclinic unit cell with $a \approx 9.79$ Å, $b \approx 7.03$ Å, $c \approx 5.55$ Å and $\beta \approx 105.7°$ using the indexing programs TREVOR$^7$ and PIRUM$^7$. Based on $hk\bar{\ell}$ extinction rules, the space group for the unknown phase was predicted to be $P2_1/m$ (No. 11). It was not possible to determine the atomic positions in the unknown phase, Le Bail fitting was simultaneously performed for the unknown phase in Rietveld analysis.

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Author Contributions
S.T. conceived this study, performed the theoretical calculations, analysed the data and wrote the manuscript. Y.I. prepared the samples with immense help from H.S. and performed the XRD and Raman measurements. T.S. analysed the XRD data and prepared AlH$_3$. K.I. and T.O. performed the ND measurements. T.I. provided significant help in analysing the data. K.M. calculated the theoretical Raman spectra. S.O. designed and conducted the project. All authors commented on the final manuscript and conclusions of this work.

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